

Structurally Engineered Unsymmetrical Squaraine Dyes for Dye-Sensitized Solar Cells: Importance of Side Chain, Position of Acceptor Unit and Extension of Conjugation within the Polymethine Framework

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Under the supervision of
Dr. Jayaraj Nithyanandhan



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Certificate

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Date: 30/10/2023



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Date: 30/10/2023

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I, Amrita Singh, a Ph.D. student of the Academy of Scientific and Innovative Research (AcSIR) with Registration No. 10CC17A26019 hereby undertake that, the thesis entitled “Structurally Engineered Unsymmetrical Squaraine Dyes for Dye-Sensitized Solar Cells: Importance of Side Chain, Position of Acceptor Unit and Extension of Conjugation within the Polymethine Framework” has been prepared by me and that the document reports original work carried out by me and is free of any plagiarism in compliance with the UGC Regulations on “*Promotion of Academic Integrity and Prevention of Plagiarism in Higher Educational Institutions (2018)*” and the CSIR Guidelines for “*Ethics in Research and in Governance (2020)*”.



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Date: 30/10/2023

Place: Pune

Dedicated to My Beloved Father

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Abstract of indexing

List of Publications and patent

List of Poster, Oral Presentation and Conferences Attended

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Erratum

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Abbreviation	Expansion
AcOH	Acetic acid
AM	Air mass
BTD	Benzo(1,2,5)thiadiazole
n-BuOH	Butanol-1
CDCA	Chenodeoxycholic acid (3 α ,7 α -dihydroxy-5 β -cholic acid)
CPDT	Cyclopentadithiophene
CIGS	Copper indium gallium diselenide
CV	Cyclic voltammetry
CH ₃ CN	Acetonitrile
CDCl ₃	Chloroform- <i>d</i>
DFT	Density functional theory
DSSCs	Dye-sensitized solar cells
DCM	Dichloromethane
DMSO- <i>d</i> ₆	Dimethyl sulfoxide- <i>d</i> ₆
EIS	Electrochemical impedance spectroscopy
EDOT	3,4-Ethylenedioxythiophene
EtOAc	Ethyl acetate
FMO	Frontier molecular orbital
FTO	Fluorine-doped-tin oxide
HOMO	Highest occupied molecular orbital
HR-MS	High resolution mass spectrometry
IPCE	Incident photon-to-current conversion efficiency
IR	Infrared
I ⁻ /I ₃ ⁻	Iodide/triiodide
ITO	Indium-doped-tin oxide
NIR	Near-Infrared
<i>J</i> - <i>V</i>	Current-Voltage
LHE	Light harvesting efficiency
LUMO	Lowest unoccupied molecular orbital
OPV	Organic photovoltaic
PCEs	Power conversion efficiencies
PV	Photovoltaic
PCC	Pyridiniumchlorochromate
PEDOT	Poly(3,4-ethylenedioxythiophene)
QDs	Quantum dots
UV-vis	Ultraviolet-visible
NMR	Nuclear magnetic resonance
REN21	Renewable Energy Policy Network for the 21st Century
SQ	Squaraine

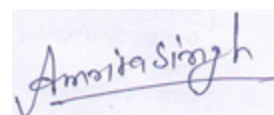
THF	Tetrahydrofuran
TBAClO ₄	Tetrabutylammonium perchlorate
UV-vis	Ultraviolet-visible
MeOH- <i>d</i> ₄	Methanol- <i>d</i> ₄
<i>E_g</i>	Energy band gap
<i>E_{CB}</i>	Conduction band edge
<i>ff</i>	Fill factor
<i>J_{SC}</i>	Short-circuit photocurrent
<i>V_{OC}</i>	Open-circuit photovoltage
<i>R_{ct}</i>	Charge recombination transfer/ resistance
<i>R_s</i>	Series resistance
<i>R_{sh}</i>	Shunt resistance
<i>C_μ</i>	Chemical capacitance
<i>η</i>	Solar cell efficiency
<i>η_{inj}</i>	Charge injection efficiency
<i>η_{coll}</i>	Charge collection efficiency
<i>τ</i>	Electron lifetime
<i>ε</i>	Extinction coefficient
<i>s</i>	Singlet
<i>d</i>	Doublet
<i>t</i>	Triplet
<i>m</i>	Multiplet
<i>M⁺</i>	Molecular ion
mmol	Millimole
MHz	Megahertz
ppm	Parts per million
Å	Angstrom
<i>λ</i>	Wavelength
eV	Electron volt
°C	Degree celsius
min	Minute(s)
h	Hour (s)
g	Gram
mg	Miligram
mL	Mililitre
kW	Kilowatt
GW	Gigawatt
TW	Terawatt

Synopsis

	Synopsis of the Thesis to be submitted to the Academy of Scientific and Innovative Research for Award of the Degree of Doctor of Philosophy in Chemical Sciences/Engineering
Name of the Candidate	Ms. Amrita Singh
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Title of the Thesis	"Structurally Engineered Unsymmetrical Squaraine Dyes for Dye-Sensitized Solar Cells: Importance of Side Chain, Position of Acceptor Unit and Extension of Conjugation within the Polymethine Framework"
Research Supervisor	Dr. Jayaraj Nithyanandhan

Chapter 1. Introduction:**Dye-Sensitized Solar Cells – An Overview**

Dye-sensitized solar cells (DSSCs), a third generation solar cells, is an attractive photovoltaic technology due to its features of tunable properties of the various components (anode, dye, electrolyte and cathode materials), low-cost device fabrication methods, fabrication of flexible photovoltaic devices and working under the indoor light condition. Light harvesting dyes, sensitizers, used for the DSSC device needs to satisfy the requirements of (i) good light absorbing property with high extinction coefficient, (ii) LUMO and HOMO energy levels are well aligned with conduction band position of TiO_2 and Nernst potential of the electrolyte with sufficient over potentials for charge injection and dye regeneration processes, respectively. Further, features that help avoiding the aggregation of dyes, and enhancing the dye regeneration process boost the DSSC device performance.¹⁻⁴ Sensitizers are classified into two major category namely, metal-, and metal-free organic dyes. Metal-free organic dyes have the several advantages, such as, tunable spectral properties by design and synthesis, high extinction coefficient, high synthetic yield, high photovoltaic efficiency, etc. To date maximum photovoltaic efficiency of 13.6% achieved by metal-free Donor- π -Acceptor- π -Anchoring group (D- π -A- π -An) based organic dye,⁵ 15.2% by co-sensitizing with optically complementary dyes with copper electrolyte,⁶ and 37.07% under ambient light condition (6000 lux).⁷ Among the metal-free organic dyes, squaraine dyes with the Donor-Acceptor-Donor (D-A-D) architecture is very impressive because of a very sharp electronic transition with high extinction coefficient in the far-red region of the solar spectrum ($\geq 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).⁸⁻¹⁰ To date maximum photovoltaic efficiency of achieved by the visible light active D-A-D based unsymmetrical squaraine

dye is 7.93% which used the feature of wrapping the dye with alkyl group to reduce the dye-dye interaction on the TiO_2 surface and passivate the surface effectively to reduce the charge recombination process.¹¹ Squaraine dyes possess low device V_{OC} due to its zwitterionic nature compared to the D- π -A based sensitizers. Hence, more structural design strategy required to enhance the light harvesting property and high V_{OC} for D-A-D based squaraine with enhanced DSSC device efficiency.

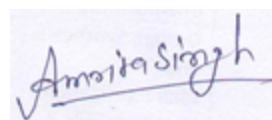
2. Statement of Problem:

Three generations of solar cell technology are widely known with their materials specificity and device efficiency, where first- and second-generation solar cell technology are still running with the cost's limitation, and poor device efficiency in the cloudy or diffused light conditions. Dye-sensitized solar cells (DSSCs), makes third generation solar cells, attractive due to its features of tunable properties of the various components (anode, dye, electrolyte and cathode materials), low-cost device fabrication methods and working under the indoor light condition. To achieve high DSSC efficiency it is necessary to control the dye-aggregation, enhance broad-light absorption, and reduce charge recombination processes. Therefore, sensitizer with in-built features that can control the dye-aggregation, enhance panchromatic light absorption and reduce charge recombination process is still challenging that need to be solved to enhance high DSSC device performance.

3. Objectives: Squaraine dyes are found to be a potential sensitizers that have high extinction coefficient in the visible, far-red and NIR-regions of the solar spectrum. The objectives of this thesis pertaining to the structural engineering of squaraine based dyes are given in **Figure 1**.

1. Effect of N-functionalization at the aniline donor of visible light active squaraine dyes on DSSC device performance

- ❖ To design and synthesize a set of aniline and indoline donors based visible light active squaraine dyes with N-alkylated and N-arylated aniline based donor units
- ❖ To study the photophysical, electrochemical, and photovoltaic properties by fabrication DSSC devices



2. Effect of position of the acceptor unit within the polymethine framework in visible active squaraine dyes for DSSCs

- ❖ To design and synthesize the aniline and indoline donors based visible light active dyes in which the position of squaric acid acceptor unit has changed systematically
- ❖ To study the importance of position of alkyl groups on the visible active squaraine dyes as well as the effect of dipole moments of dyes on the open-circuit potential (V_{OC}) and short-circuit current (J_{SC}) of the DSSC device

3. Extension in conjugation within the polymethine framework in squaraine dyes for DSSCs

- ❖ To design and synthesize the squaraine dyes with extended π -conjugation within polymethine framework
- ❖ Photophysical, electrochemical characterization of synthesized dyes
- ❖ To study the effect of conjugation on the V_{OC} , J_{SC} and DSSC device efficiency

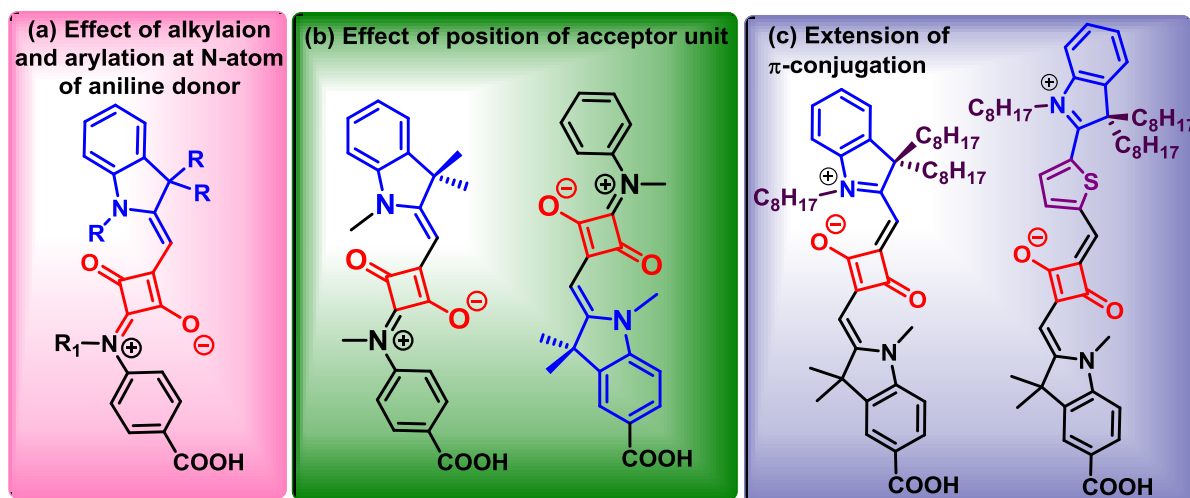


Figure 1. Structural engineering of D-A-D based squaraine dyes for dye-sensitized solar cells (DSSCs).

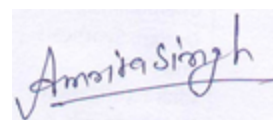
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4. Methodology:

Chapter 2: Effect of alkylation and arylation at N-atom of aniline donor on dye-sensitized solar cell performance

Developing organic sensitizers with high extinction coefficient in the visible region of the solar spectrum, and controlling the aggregation of dyes on the TiO_2 surface has been a challenging task to enhance the dye-sensitized solar cell device efficiency. Further, dihedral angles between the donor and acceptor units and dipole moment of the dyes anchored on the TiO_2 surface play an important role to enhance the device efficiency by enhancing the J_{SC} and V_{OC} , respectively. Furthermore, developing sensitizers which is compatible with various electrolytes and achieving the high DSSC device V_{OC} and efficiency for the squaraine (zwitterionic) dyes is still challenging. Hence in order to develop a sensitizer that compatible with the various electrolytes and inbuilt character for controlling the aggregation on TiO_2 surface, here series of aniline and indoline donor based unsymmetrical visible-light active squaraine dyes (**AM1**, **AM2**, and **AM3**) have designed (**Figure 2**), synthesized and characterized for solar cell applications by fabricating the DSSC device. In the present work, one of the donor units (indoline) wrapped with alkyl groups and other donor unit (aniline) has been functionalized with the -hexyl, -ethylhexyl, and phenyl groups for controlling the aggregation, charge recombination, and to modulate the dihedral angles (between the aniline donor and squaric acid unit) and dipole moments of the dyes. **AM** dyes E_{HOMO} energy levels lies in-between the 1.03-1.13 V, which opens an opportunity to select the different electrolytes to gains better device V_{OC} , and efficiency. A systematic structure-property relationship studies have been performed for the **AM** dyes with I^-/I_3^- and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes. DSSC device fabricated with the **AM1** and **AM2** dyes showed good DSSC efficiency of 7.44% and 7.22%, respectively with I^-/I_3^- electrolyte without CDCA (chenodeoxycholic acid) compared to the **AM3** dye 5.41%. Chenodeoxycholic acid (CDCA), an optically transparent co-adsorbent helps avoiding the aggregation of dyes due to the competitive binding of the dyes and co-adsorbent on TiO_2 surface. Further, CDCA also passivate the TiO_2 surface which reduces the charge recombination process. Use of $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte along with the PEDOT showed an impressive V_{OC} values of 1030, 1025, 1001, and 1009 mV, and DSSC efficiency of 8.05%, 7.96%, 5.84% and 7.98%, respectively for **AM1**, **AM2**, **AM3**, and model **AK4** in the absence of CDCA. Here, **AM1** dye showed the highest achieved DSSC device efficiency of 8.05%, and V_{OC} of 1030 mV for D-A-D based unsymmetrical squaraine dyes with Cu(I/II) electrolyte (**Figure 3**). This is the first time where any squaraine dyes achieved more than 1 V of V_{OC} .



Introduction of alkyl- and aryl-group at N-atom of aniline donor modulates the dihedral angle

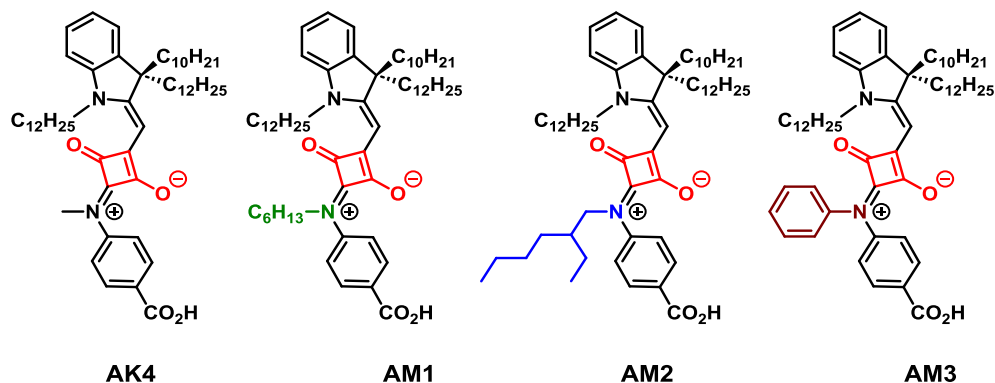


Figure 2. Structures of visible light active unsymmetrical squaraine dyes (AM1-AM3) along with AK4 dye.

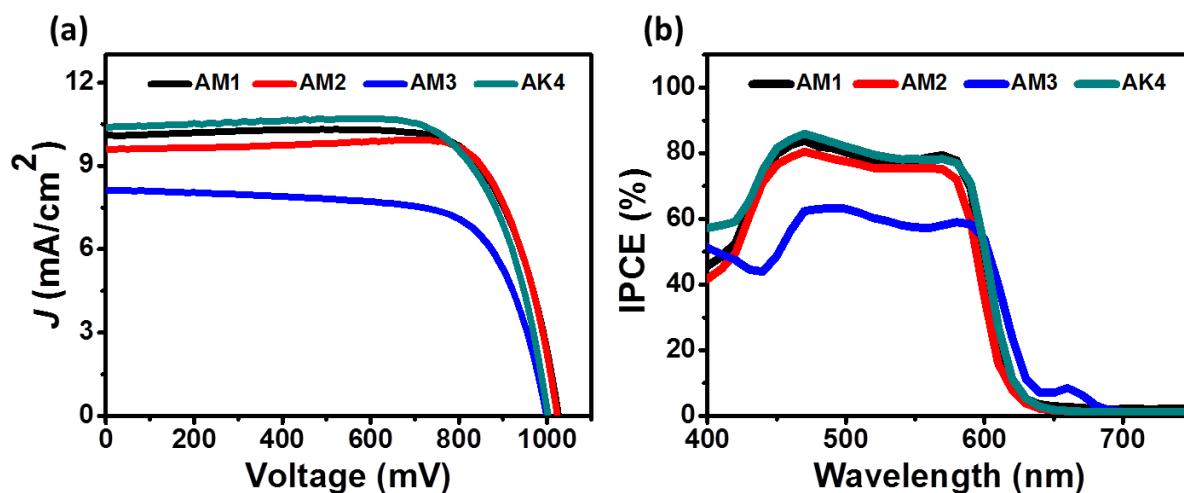


Figure 3. (a) I-V, and (b) IPCE curves for AM and AK4 dyes in the absence of CDCA with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte.

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Chapter 3: Squaraine Dyes for Dye-Sensitized Solar Cells: Effect of Position of Acceptor Unit in Visible Light Active Squaraine Dyes

Position of acceptor unit plays an important role in enhancing the DSSC device efficiency besides, controlling the dye-aggregation and modulating the electronic properties of dye molecules. In the present work, dyes **AS1-AS5** have been designed and synthesized by varying the position of squaric acid (acceptor) unit in a set of Aniline-Squaric acid-Indoline based visible active dyes. Further, to control the aggregation of dyes, N-atoms of the aniline and indoline donors are alkylated with either linear or branched alkyl groups (**Figure 4**). Photophysical and electrochemical properties have been carried out. Dyes with indoline units on the top **AS2**, and **AS5** showed 18 nm and 30 nm bathochromic shift compared to the **AS1**, **AS3** and **AS4**. All the **AS** dyes possess similar HOMO energy levels ~ 1.0 V (vs NHE). DFT studies exhibited that all the **AS** dyes possess different dipole moments, as introduction of alkyl groups modulate the structural planarity of the dyes, and such parameters helps modulating the photovoltaic parameters. The E_{HOMO} and E_{LUMO} energy levels for the **AS** dyes are well aligning with redox level of I^-/I_3^- electrolyte and TiO_2 conduction band for dye regeneration and charge injection processes, respectively.

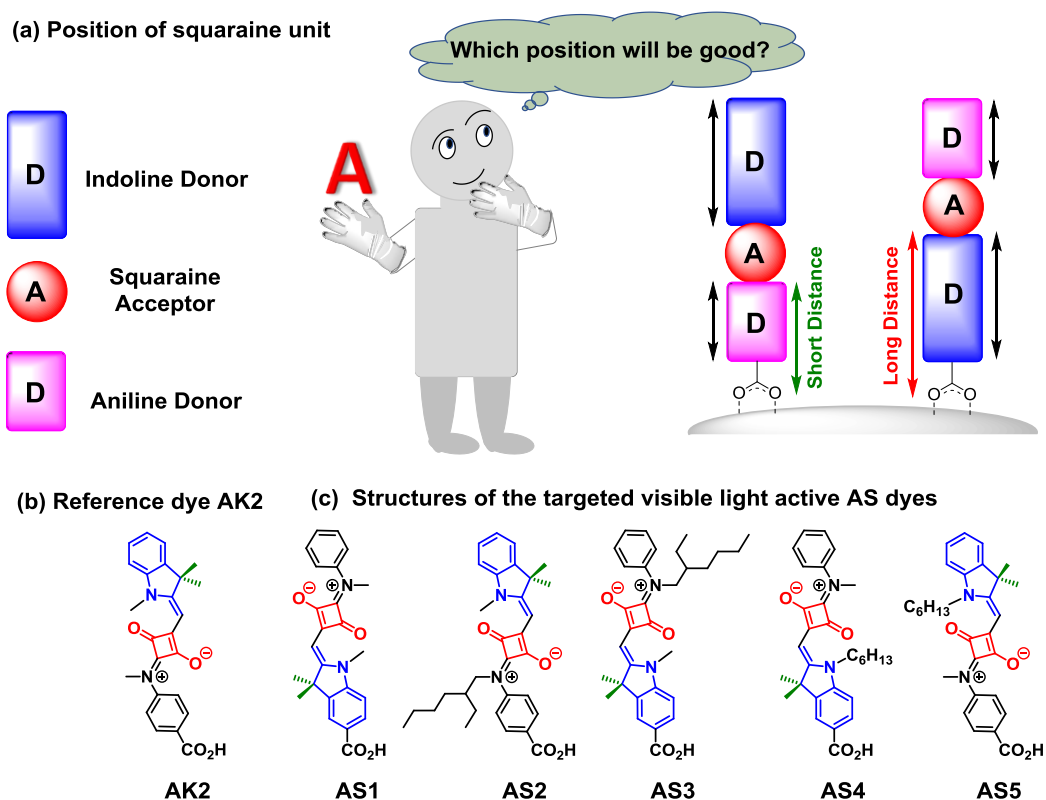


Figure 4. Structures of visible light active unsymmetrical squaraine dyes (**AS1-AS5**).

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The DSSC device characterizations have been performed where 5.49, 6.34, 6.16, 5.57 and 7.06% have been achieved by **AS1**, **AS2**, **AS3**, **AS4** and **AS5** dyes, respectively in the absence of CDCA. To reduces the aggregation of dyes on TiO_2 sruface and the fabricated with CDCA as co-adsorbent and CDCA passivate the TiO_2 surface that reduced the rate of charge recombination process, **AS1**, **AS2**, **AS3** and **AS4** dyes showed little changes in efficiency with CDCA **Figure 5 and Table 1**. The **AS5** dye achieved highest efficiency of 8.01% due to alkyl group at top helps to reduced the charge recombination and increase the dye loading on the TiO_2 surfaces compared to the having alkyl group at down near to the anchoring group. Furthre the alkyl groups away from TiO_2 surface helps more loading of dyes results the increased J_{SC} value (**AS3** and **AS5** dyes) compared to the dyes with alkyl group near to the surface (**AS2** and **AS4** dye). The photovoltaic results obtained from the DSSC studies revealed that, the dyes with aniline donor near to TiO_2 surface performs better than that of dyes with indoline donor nar to the TiO_2 surface in the given set of AS dyes. Changing the position of acceptor unit modulates the V_{OC} of the DSSC device due to the change in the dipole moment of the dyes which causes the shift in the position of E_{CB} .¹²

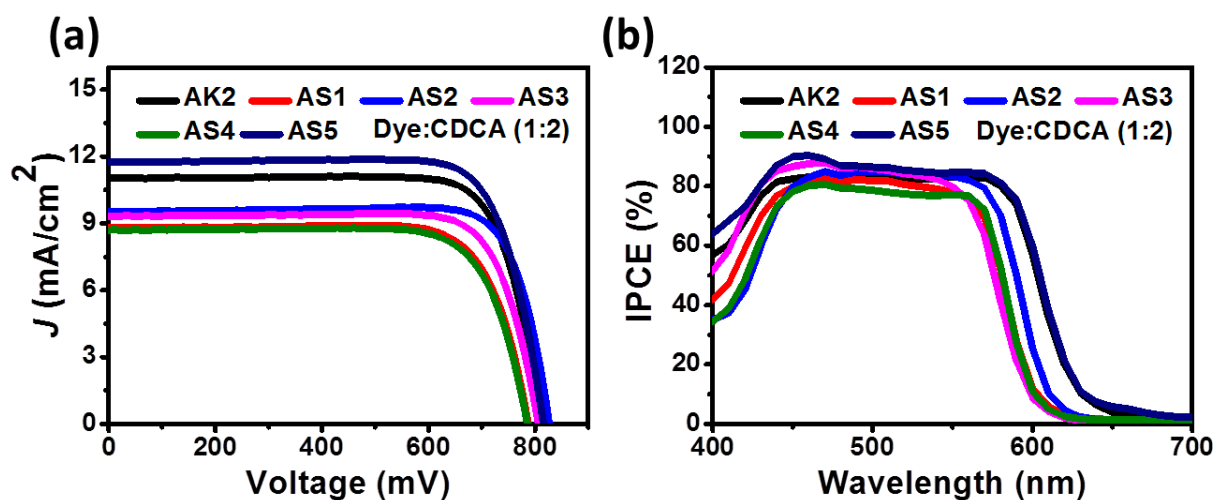


Figure 5. (a) I - V , and (b) IPCE curves for **AK2** and **AS** dyes with CDCA in I^-/I_3^- electrolyte.

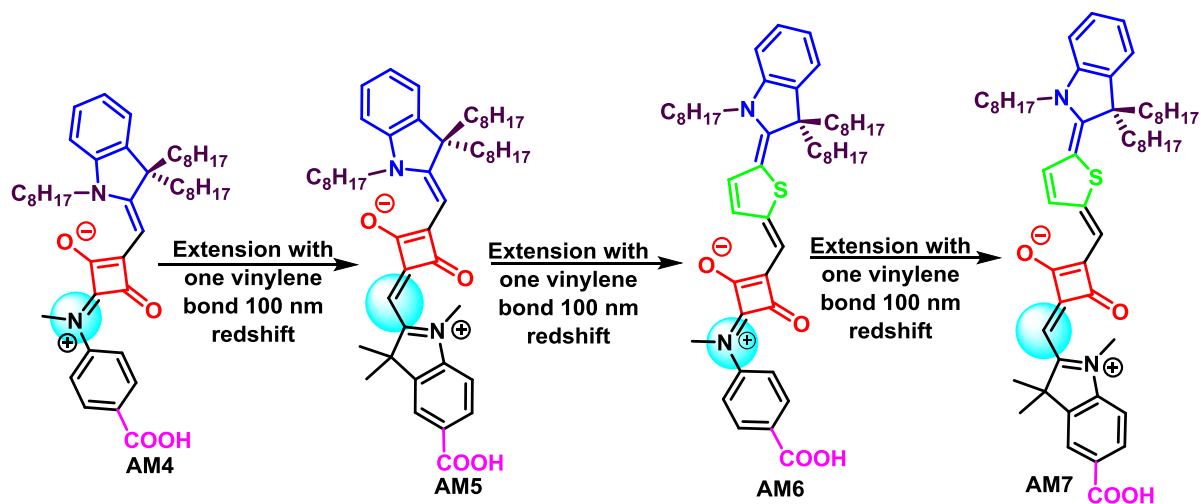
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Table 1. Photovoltaic performance of **AS** and **AK2** dyes with I^-/I_3^- electrolyte.

Dyes	CDCA	V_{oc} (mV)	J_{sc} (mA/cm ²)	ff (%)	η (%)	Dye Loading (10 ⁻⁷ mol/cm ²)
AK2	2	812 ± 1	11.03 ± 0.27	80 ± 0.95	7.17 ± 0.27	0.816
AS1	2	787 ± 4	8.80 ± 0.18	78 ± 0.67	5.40 ± 0.19	0.721
AS2	2	827 ± 2	9.53 ± 0.19	82 ± 0.83	6.46 ± 0.21	0.587
AS3	2	807 ± 3	9.32 ± 0.21	79 ± 0.78	5.94 ± 0.22	0.675
AS4	2	805 ± 2	8.70 ± 0.10	78 ± 0.64	5.46 ± 0.13	0.500
AS5	2	816 ± 3	11.74 ± 0.24	81 ± 0.56	7.76 ± 0.25	0.808

Chapter 4: Synthesis of Visible, Far-red and NIR Active Squaraine Dyes for Dye-Sensitized Solar Cells: π -Extension conjugation within the Polymethine Framework

**Figure 6.** Structures of π -conjugated unsymmetrical squaraine dyes (**AM4-AM7**).

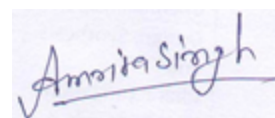
J. Nithyanandh

Amrita Singh

Enhancing the DSSC device J_{SC} is very important parameter to enhance the device efficiency. Besides panchromatic absorption and co-sensitization, light harvesting in the NIR region is needed to enhance the device J_{SC} . By extending the π -conjugation between the π -framework leads to 15-20 nm red-shift for D-A, D- π -A dyes, but dyes belongs to polymethine family showed 100 nm red shift by incorporating each vinyline double bond. By considering the design principle of polymethine dyes by extension of conjugation, a series of visible-NIR light active dyes (**AM4-AM7**, **Figure 6**) have been designed, synthesized and tested for DSSC applications. The photophysical and electrochemical properties have been systematically tuned by incorporation of thiophene unit within the polymethine framework. Here, each conjugated double bond provided ~ 100 nm red-shifts in absorbance, and enhanced the light harvesting efficiency (LHE) of the dyes, where, **AM7** dye showed maximum LHE of ($\Delta\lambda$ 386) nm at 60% compared to other **AM** dyes. Further, extension of conjugation lead to the change the HOMO energy levels (vs NHE) of the AM dyes systematically and the enegy levels are 1.01 V, 0.78 V, 0.53 V and 0.47 V for **AM4**, **AM5**, **AM6** and **AM7** dyes, respectively. DSSC devices have been fabricated and the photovoltaic parameters is provided in **Table 2**. DSSC devices have been fabricated with the I^-/I_3^- electrolyte (0.4 V vs NHE). Extension of conjugation in the **AM6** and **AM7** leads to less positive HOMO energy level and the reduced device performance compared to **AM4** and **AM5** are may be due to the less efficient dye regeneration process which leads to the DSSC device performance of 0.079% (**AM6**) and 0.05% (**AM7**). Hence the maximum DSSC device efficiency of 7.62% has been achieved by **AM4** dye and the **AM5** dye showed the efficiency 5.18% with the I^-/I_3^- electrolyte.

Table 2. Photovoltaic performance of **AM4-AM7** dyes with the I^-/I_3^- electrolyte.

Dyes	$V_{oc}(mV)$	$J_{sc}(mA/cm^2)$	ff (%)	η (%)
AM4	823	11.30	79	7.35
AM5	702	9.59	77	5.18
AM6	480	0.26	63	0.079
AM7	448	0.22	51	0.050

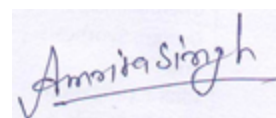



5. Summary:

This thesis summarizes the understanding the importance of side chain engineering, position of acceptor unit and extension of π -conjugation within the polymethine framework in dye-sensitized solar cells (DSSCs). N-functionalization on aniline donor with hexyl-, ethylhexyl-, and phenyl-groups demonstrated for decreased J_{SC} and DSSC efficiency with I^-/I_3^- electrolyte compared to N-methylation due to low dye-loading. Whereas, N-functionalization on aniline donor with hexyl-, ethylhexyl- groups demonstrated for enhanced V_{OC} and DSSC efficiency with Cu(I/II) electrolyte compared to N-methylation due to better surface passivation, where, **AM1** dye showed maximum V_{OC} of 1030 mV and efficiency of 8.05% in the absence of CDCA. Further, changed in the position of acceptor unit, showed the varied photophysical, electrochemical, and photovoltaic properties, where, **AS5** dye showed maximum of 8.01% efficiency with I^-/I_3^- electrolyte in the presence of CDCA. Hence having indoline donor and alkyl groups away from the TiO_2 surface helps enhancing the DSSC device performance. Further, extension in conjugation within the polymethine framework showed excellent photophysical, LHE properties with the DSSC device performance of 7.35% and 5.18% for **AM4** and **AM5** with I^-/I_3^- electrolyte. Though the extension of conjugation helps enhancing the light harvesting property of the sensitizers **AM6** and **AM7**, and it is observed that the HOMO energy levels of the dye is less positive than **AM4** dye which makes the dye-regeneration process less effective and hence the device efficiency 0.08% and 0.05% are obtained for **AM6** and **AM7** with I^-/I_3^- electrolyte.

6. Future Direction:

As there were only few far-red and NIR active chromophores such as porphyrin and phthalocyanine, developing polymethine based sensitisers for DSSC device is important. The research work carried out in this thesis will provide the guidelines for designing new dye molecules belongs to polymethine family which will be useful for dye-sensitized solar cell applications. It was observed that extending the conjugation within the polymethine framework lead to shift the absorption bathochromically ~ 100 nm/vinylene unit. However the HOMO energy levels of the dyes are also changed in such a way that the dye-regeneration process is less effective. In this regard, cobalt and copper based redox shuttle with less positive Nernst potential will help enhancing the DSSC devices sensitized with squaraine dyes.



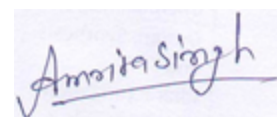
7. Publications:

List of Publications and Patents:

- 1) **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kumar Vanka, Kothandam Krishnamoorthy and Jayaraj Nithyanandhan. Visible-Light-Active Unsymmetrical Squaraine Dyes with 1 V of Open-Circuit Voltage for Dye-Sensitized Solar Cells. *ChemPhotoChem*, **2023**, e202200328 (1-10), <https://doi.org/10.1002/cptc.202200328>.
- 2) **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kumar Vanka, Kothandam Krishnamoorthy and Jayaraj Nithyanandhan. Effect of Position of Acceptor Unit on Dye-Sensitized Solar Cell Performance: Indoline-Aniline Donors Based Visible-Light Responsive Squaraine Dyes performance (Manuscript submitted).
- 3) **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kumar Vanka, Kothandam Krishnamoorthy and Jayaraj Nithyanandhan. Visible and NIR-Light Active Unsymmetrical Squaraine Dyes: effect of conjugation within polymethine framework on dye sensitized solar cell performance (Manuscript is under preparation).
- 4) Unsymmetrical squaraine dyes and applications thereof, J Nithyanandhan, AK Singh, **Amrita Singh**, US Patent App. 17/697,511, 2022.

8. References:

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- (7) C. Chen, V. S. Nguyen, H. Chiu, Y. Chen, T. Wei and C. Yeh, *Adv. Energy Mater.*, **2022**, 12, 2104051.
- (8) Singh, A. K ; Mele Kavungathodi, M. F.; Nithyanandhan, J. *ACS Appl. Mater. Interfaces*, **2020**, 12, 2555.
- (9) Alagumalai, A. Munavvar, M. F.; Vellimalai, P. Sil, M. C.; Nithyanandhan, J. *ACS Appl. Mater. Interfaces*, **2016**, 8, 35353.
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Chapter 1

Introduction

1.1 Energy

Energy is the one of indispensable needs for running the things smoothly present from the small houses to the large industries and life as well. As the world population has been increasing rapidly day by day that will increase the energy needs and increase the numbers of industries worldwide. Therefore, energy is a great task that should be solved for the bright future for new generation of our society and world. In this respect one of the major contributors to producing the energy in the form of electricity on our planet is non-renewable energy resources (fossil fuels, nuclear fuels) but they are limited and will not keep up long future with the growth rate of the world population.¹ Besides resources limitations (replenishing takes ~10 million years), combustion of fossil fuels is not friendly with our health and environment, because huge quantities of poisonous gases (such as, oxides of carbon, nitrogen, and sulfur) have been released in the air every year as a side product during the production of energy which cause global warming, serious diseases in human, acid-rain, etc. Researchers around the world came up with method of generation electricity from natural resources and are categories as renewable energy resources.² In this category sunlight, water, wind, bioenergy, and geothermal heat resources have been commonly used to generate electricity (**Figure 1**). The electricity production from renewable resources is environmentally and societal friendly and are good alternatives to non-renewable resources, but contribution of these resources in electricity production is very low. Electricity generation from the renewable resources have the potential to satisfy the future demands of energy, for that researchers and scientists need to pay much more attention towards the new inventions that produce more energy from the renewable resources and enhance their contribution in electricity production.

One of the leading resources of electricity in renewable energy is hydropower energy (15%). The second leading resource of electricity in renewable energy is wind power energy (2%),⁴ however, wind availability will not be same respect to the time and places. Coastal areas are the best place to harvest the energy from the wind due to wind continuity, however source to destination transportation through grid connection is very expensive. Apart from two major energy resources belonging to renewable energy bioenergy and geothermal energy are also contributing together 3% of electricity in the respected categories, respectively. Biological feedstocks like biomass,

biofuel and biogas are coming to categories of bioenergy and emitted carbon dioxides while energy production by these resources can be fixed by higher plants through photosynthesis. It required excess land density, and their efficiency is poor compared to non-renewable energy resources.³ In geothermal water stream is used to rotate a turbine which is the product of high internal heat of the earth. Resources risk and huge drilling costs are the major concern of geothermal energy.

The third and most reliable resource of renewable energy is solar energy which contributes 8% of total energy in this category. Solar energy is one of the most abundant, promising, eco-friendly, and cost-free resources of energy in the renewable energy category which can generate electricity through photovoltaic effect by solar cell (solar PV).⁴ Although, intensity of the solar light varies at the different parts of the globe, still it has the tendency to satisfy the future energy demand with no emission of gases, because 1 hour of sunshine fulfils the energy need for one year for the entire world if can be fully harvested. Energy distribution of solar light onto the surface of earth (with density of $1.0\text{--}2.5 \times 10^2 \text{ W m}^{-2}$ annually) and top of atmosphere is provided in **Figure 2**. However, significant investments in infrastructure, research and development are needed to meet the energy demand for the future.

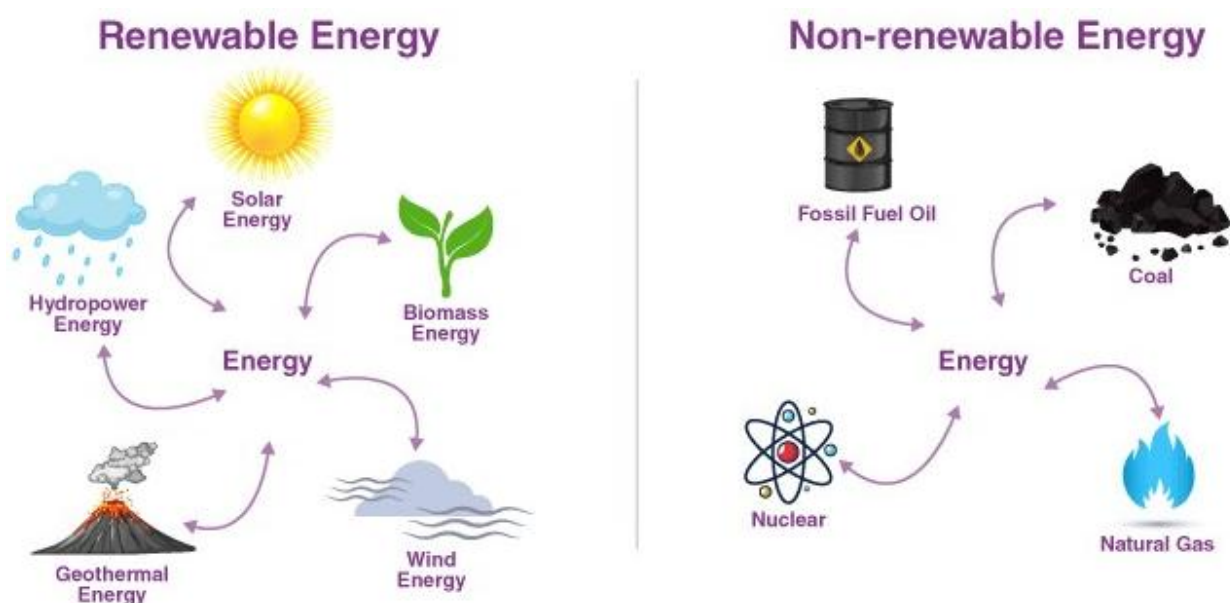


Figure 1. Renewable and non-renewable sources of energy (adapted from <https://byjus.com/physics/natural-sources-of-energy/>).

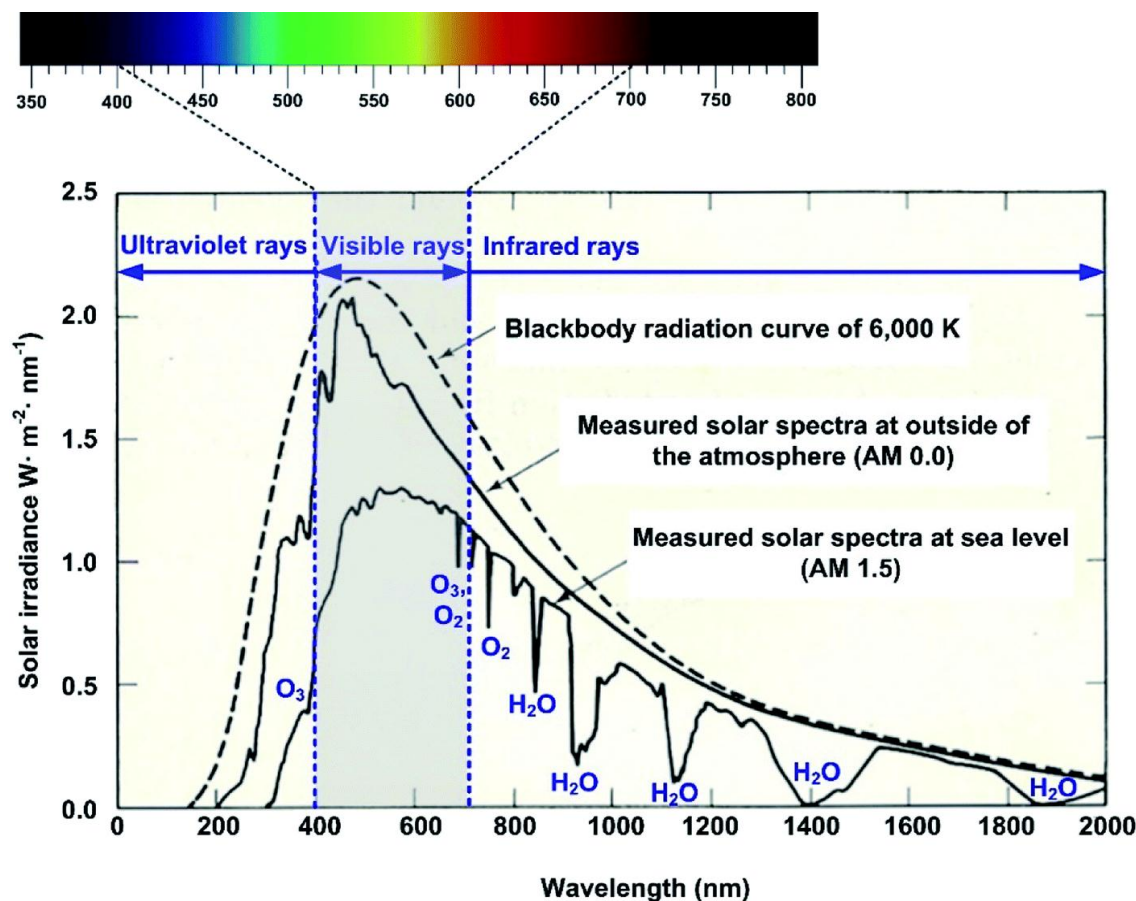


Figure 2. Solar irradiance onto earth and on the top of the atmosphere (adapted from https://pubs.rsc.org/image/article/2019/ra/c9ra03442k/c9ra03442k-f2_hi-res.gif).

1.2 Photovoltaics (PV) or Solar Cell

In 1839, the term of the photovoltaic effect and photovoltaic solar cell working principle was used by Becquerel, where materials which was semiconducting nature (in general semiconducting silicon wafer) generates electricity by shining the solar light.^{5,6} Bell laboratory reports the first practical application of solar cell device that was made from silicon in 1950.⁷ Afterwards, a lot of solar devices were invented and few of them have been used by space-agencies to power the satellites in the world. Solar cells are available around the world in the form of solar panels to generate electricity for residential and commercial use. The best solar cells efficiency output from the entire world is graphically represented by National Renewable Energy Laboratory (NREL) (**Figure 3**).

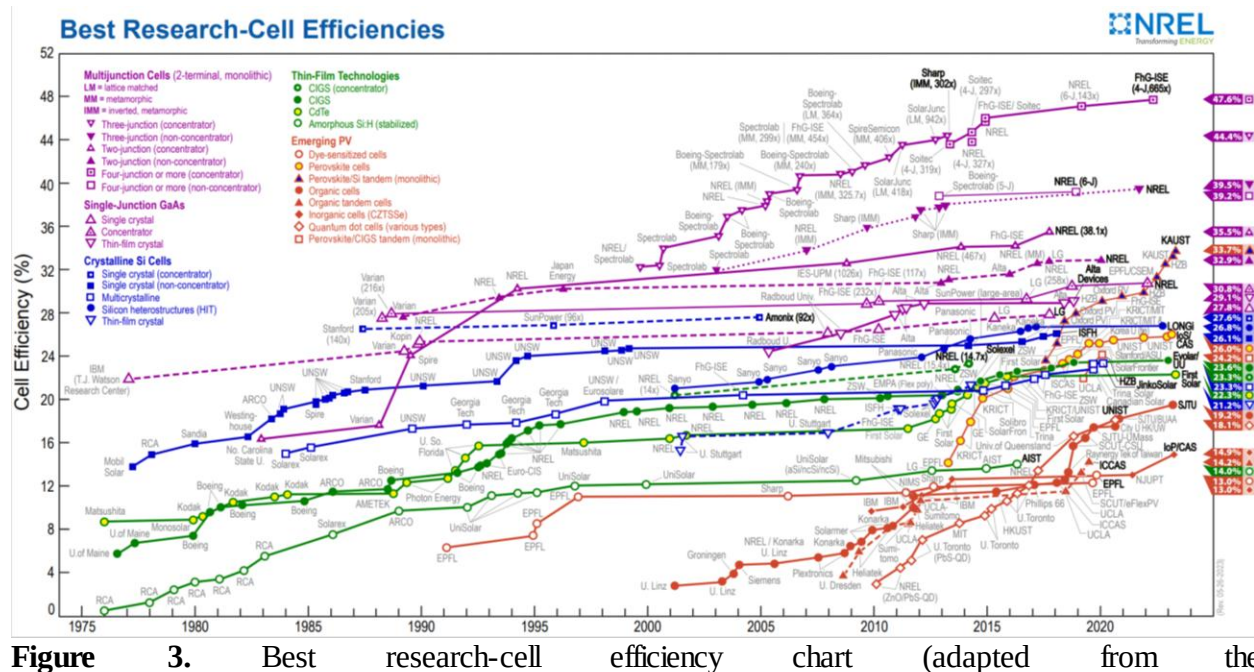


Figure 3. Best research-cell efficiency chart (adapted from the <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.pdf>).

Based on the materials used for the solar cell fabrication solar cells are broadly categorized in three main categories, namely first-, second-, and third-generation solar cells.

1.2.1 First Generation Solar Cells

Solar cells belonging to this generation are commonly used solar cells for electric production and available as mono- and poly-crystalline in the market around the world. They are made from the highly pure crystalline silicon wafer with the thickness between 150 to 250 μm , where wafers are doped with the element of group third and fifth to create a junction called p-n junction. Sunshine on this depletion zone of the p-n junction leads to movement of electrons and holes on the opposite side and generates electricity. Multi- and single-crystalline wafer-based silicon solar cells are known, where due to crystal-defects multi-crystalline solar cells giving low photovoltaic efficiency (23.3%) compared to single-crystalline (26.8%). However, 33.7% is the theoretical photovoltaic Schokley-Quessier efficiency limits for photovoltaic device made from silicon (1.1 eV of band gap) with 1.5 air mass.⁸ Wafer based silicon solar cells are expensive to make due to their high fabrication and processing costs, therefore researchers paid their attention to making thin film solar cells to reduce the fabrication and processing costs.

1.2.2 Second Generation Solar Cells

Solar cells belonging to this generation are light weight, low cost and which are made from amorphous silicon,⁹ cadmium telluride, and copper indium gallium selenide with the thickness between 2 to 10 μm on the glass or polymer sheets and 1.7-1.0 eV of band gap to achieve more V_{OC} . Here, photovoltaic efficiency of 14.0%,^{10,11} 22.3%,^{12,13} and 23.6%^{14,15} have been achieved by amorphous silicon, cadmium telluride, and copper indium gallium selenide, respectively. Although solar cells belong to this generation are cost-effective but low efficiency, low lifetime, indium abundance, and chemical hazard (CdTe)¹⁶ they did not replace first-generation solar cells.

Further, solar cells belonging to first- and second- generations have poor-device efficiency in cloudy days or diffused light conditions and latitude dependent, therefore emerging photovoltaics have been developed.

1.2.3 Third Generation Solar Cells

Solar cells belonging to this generation are light weight, tunable band gap, and they are made from cheap polymeric, organic, and inorganic semiconducting materials with the nanomaterial thickness between 2 to 10 μm on the glass or polymer sheets and have the 10 years outdoor lifetime.¹⁷ Photovoltaic cells coming to this category also known as emerging photovoltaic due to diversity of semiconducting materials. Emerging photovoltaics working in cloudy days or diffused light conditions with high photovoltaic efficiency. This thin thickness on the polymer substrate gives an accessibility to make the device very light weight and flexible which will be easy to carry them and make bags, umbrella etc. which is fully powered with photovoltaic devices to harvest the solar energy.¹⁸ Perovskite, quantum dot, organic, and dye-sensitized solar cells belong to this generation solar cells. Emerging photovoltaics have not been commercialized yet because they are still in a phase of research and development.

1.2.3.1 Perovskite Solar Cells

Perovskite attracted the great attention of researchers across the world from 2013 due to its light harvesting and charge carrier ability, however perovskite was discovered in 1839 as calcium titanate (an inorganic oxide perovskite).¹⁹⁻²³ Perovskites used for the solar cells by researchers

are hybrid with the general formula of AMX_3 , where “A” represent organic cations ($CH_3NH_3^+$), “M” represent metal ions (Pb^{2+} , Sn^{2+} , Bi^{3+} , Cu^{2+} , etc.), and “X” represent halogens (Cl^- , Br^- , I^- , etc.). The optical and electrical properties can be tuned by varying the thickness of the inorganic layers (layered halide perovskites) or by the halogen atom substitution. Solar cells made from hybrid perovskite interlayer form with SnO_2 electrode achieved 26.0% photovoltaic efficiency based on the data provided by National Renewable Energy Laboratory (NREL).^{24, 25}

1.2.3.2 Dye-Sensitized Solar Cells (DSSCs)

In dye-sensitized solar cell (DSSC), researchers are using dye as sensitizer and is a key material that absorbs solar light and generates electricity. The diversity of sensitizers, freedom to use different electrolytes, counter electrodes attracted great attention of researchers towards the dedicate their research on DSSC to achieve best device efficiency.²⁶⁻²⁹ Solar cells made dyes (SM315) achieved 13.0% photovoltaic efficiency.^{25, 30} Further, device fabrication of solar cell devices in the ambient fabricating condition (in air) other than dye-sensitized solar cells is difficult for third generation solar cells.

1.2.3.3 Quantum Dot Solar Cells

Quantum dots (QDs) are nano-crystal materials with different sizes and excellent optical properties and can harvest solar energy with a wide range and convert them into electricity. “Sb” and “As” based QDs have been commonly used to make QDs solar cells, where oxidation states (III) of the QDs play an important role in solar light harvesting.³¹⁻³³ The working principle of the QDs and dye cells are similar, here QDs are used as sensitizer to absorb solar light. Quantum dot solar cells with caesium and formamidinium lead triiodide perovskite system ($CsFAPbI_3$) have reached maximum 16.6% device efficiency.³⁴ Solar cells made from QDs achieved 18.1% photovoltaic efficiency.²⁵

1.2.3.4 Organic Solar Cells

Organic solar cells are made from semiconducting materials with n-type small organic and p-type polymeric materials to harvest solar light. Polymer solar cells V_{OC} , J_{SC} , and efficiency can

synergistically enhance by modulating the donor and acceptor ability of organic materials.³⁵⁻³⁷ Modulation in organic materials proving the accessibility to tune the bandgap, avoid the energy loss, efficient charge separation and transport. Solar cells made from organic and polymer materials (PM6:D18-Cl:L8-BO) achieved 19.2% photovoltaic efficiency.^{25,38}

1.3 Dye-Sensitized Solar Cells (DSSCs)

Since the first report on the importance of colloidal TiO_2 (1991) for the DSSC applications,³⁴ researchers are attracted and dedicated their research on DSSC, due to modular spectral behavior, production costs, weight, flexibility, scalability, and working in the diffused or reflected light conditions. And lots of effort have been made by researchers across the world to commercialize the DSSCs, where maximum efficiency of 15.2%³⁹ and 10.0%⁴⁰ were reported at the laboratory scale and based on small modules (64 cell modules of size $10 \times 10 \text{ cm}^2$), respectively. The general working principle of dye-sensitized solar cells is displayed in **Figure 4**. There are two major classes of the dyes namely organic and metal-containing dyes (ruthenium complexes, porphyrin dyes)^{41,29} has been commonly used in the DSSC application.

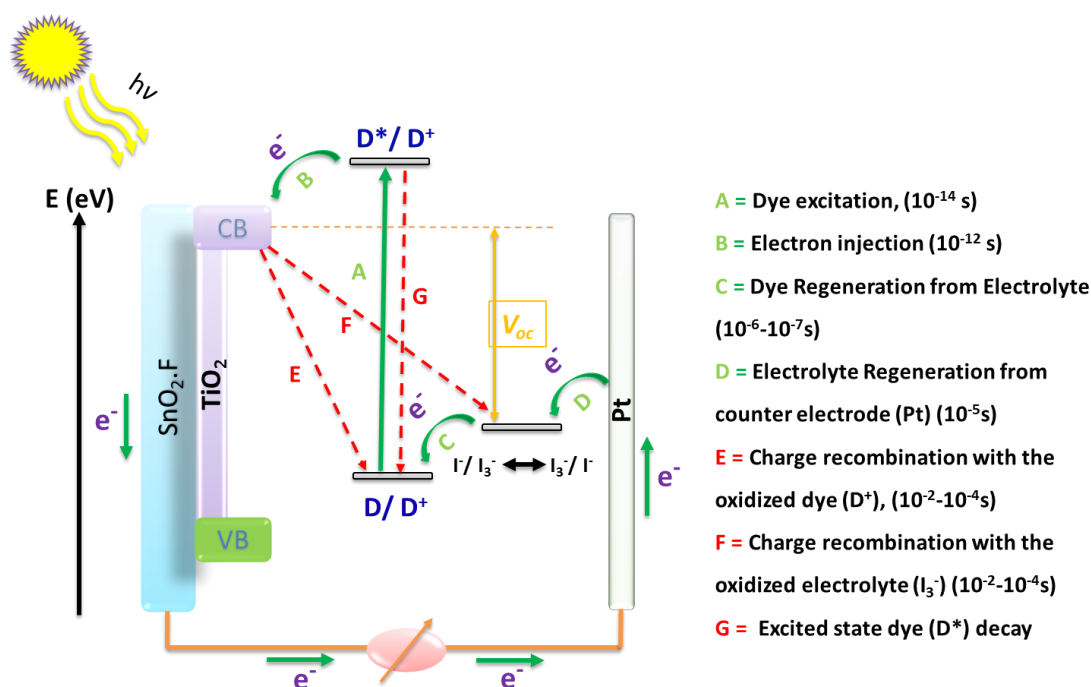


Figure 4. The general working principle of dye-sensitized solar cells.

1.3.1 General Working Principle of the Dye-Sensitized Solar cells

As displayed in **Figure 4**, dye absorbs photon from the sun and inject one electron in the conduction band (CB) of the semiconducting metal oxide TiO_2 within 10^{-12} s from the LUMO (B), oxidized dye will be regenerated by electrolytes between 10^{-6} to 10^{-7} s (C), and electron injected in CB of TiO_2 will arrived to counter electrode between 10^{-3} to 10^{-4} s through load and regenerate the electrolytes that oxidized by dye within 10^{-5} S (D), and is required processes for completing the circuit of solar cell devices. In between the time of completion of circuit, interfacial charge recombination E and F) between 10^{-2} to 10^{-4} s, and excited state dye (G) within 10^{-9} s (if charge is not being injected) kills the photovoltaic performances of DSSC devices.

1.3.2 Components of the Dye-Sensitized Solar cells

1.3.2.1 Dyes or Sensitizers

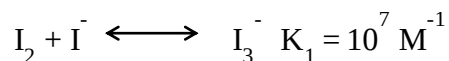
The principal component of the DSSC is dye (made with donor, acceptor, and spacer) which will sensitize on the surface of metal-oxides (i.e., TiO_2 , ZnO , etc.) with the help of an anchoring group (i.e., $-\text{COOH}$, $-\text{H}_2\text{PO}_3$, $-\text{SO}_3\text{H}$, etc.) and harvest the solar energy from the visible to far-red regions and converts them into electrical currents.

1.3.2.2 Electrolyte or Redox-Couple

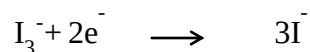
After electron injection from the LUMO of the dye upon photoexcitation, electrolyte regenerate the oxidized dye and promote the circuit to complete. Diversity in the dye electronic levels allow us to use the electrolyte that well aligning with dye HOMO for efficient dye-regeneration process. Electrolyte based on iodide (I^-/I_3^-), cobalt Co(II/III) and copper Cu(I/II) are common electrolytic systems generally used for DSSC application. These electrolytes have their different redox levels with the various overpotentials required for the dye-regeneration process. There are few limitations of the electrolyte made with iodide, iodide electrolyte generally gives low photovoltaic V_{OC} due to large overpotentials (≥ 500 mV) associated with dye-regeneration process, and corrosive towards sealing kit.^{42,43} Whereas electrolyte made with cobalt and copper gives up to 1 V, which is an important parameter to enhance DSSC efficiency.^{29,44-47} However,

electrolyte made with iodide and copper are commonly used electrolytes for the DSSC application because of their costs of preparation.

In Solution, Iodine binds with iodide and form a triiodide in equilibrium.



Excess iodine concentration used during preparation of electrolyte formed polyiodide species such as I_5^- , I_7^- and I_9^- . In DSSC, transport of electrolyte between the electrodes (photoanode and cathode) determines the regeneration or reduction of electrolytic species I_3^- and is expressed as follows.



The two-electron process of I^-/I_3^- electrolyte possesses huge loss in the internal potential for dye regeneration process. However, the cobalt complex required large internal reorganization energy between d^7 and d^6 state for dye regeneration is the major disadvantage of cobalt based redox couple. The copper based redox couple act as an alternative hole transport material in DSSC, and less inner sphere reorganization energy required for the dye regeneration.⁴⁸ The electronic configuration of Cu(I) is d^{10} having tetrahedral geometry with the ligands, while Cu(II) having tetragonal geometry. The coordination sphere may expand from four to six during the energy minimization of electronic configuration. Due to the change in geometry from the Cu(I) to the Cu(II) retard its electron-transfer rate required for the large reorganization energy. The versatile ligand with substituents can prohibited the conformational change between the Cu(I) to Cu(II) geometry.⁴⁹

1.3.2.3 Photo anode

Photo anode made with the combination of several sub-components, such as glass or plastic substrate on that a thin layer of conducting (FTO) and mesoporous semiconducting metal-oxides (TiO_2 or ZnO , 2-10 μm) coated through doctor-blade or deposition techniques.^{25,50} Sensitization of dyes takes place on the metal-oxide surface with the help of anchoring group to keep the

sensitizer near to the TiO_2 surface for an efficient charge injection process. The anatase titanium oxide (101) facet contains 5-coordinated Ti (5c-Ti) and 6-coordinated Ti (6c-Ti) atoms. The dye molecule binds on the 5-coordinated Ti on the TiO_2 surface (101 plane). Here, after electron injection in metal-oxide conduction band electron moves toward the counter electrode through load in DSSC. Dyes were bridged with TiO_2 surface predominantly with bi-dentate bridging mode (Figure 5c).^{51,52}

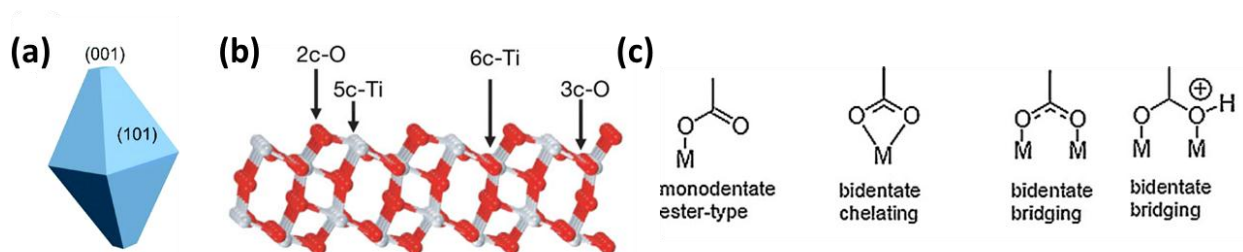


Figure 5: (a) TiO_2 nanocrystal, (b) mesoporous TiO_2 (101 facet), and (c) binding mode of TiO_2 .

1.3.2.4 Counter electrode

A counter electrode is the site where charge collection and electrolyte regeneration take place simultaneously. Pt-foil, Pt-nanoparticle on FTO,⁵³ graphite,^{54,55} carbon-black,⁵⁶ PEDOT (poly(3,4-ethylenedioxythiophene))^{57,58} etc. are the counter electrodes that have been used for DSSC due to their excellent electro-catalytic behaviors.

1.3.3 Parameters of the Dye-Sensitized Solar cells

1.3.3.1 Short-Circuit Photocurrent (J_{SC})

Maximum photocurrent achieved when there is no load termed as short-circuit photocurrent (J_{SC}), and is the collective output of (i) range of photons being absorbed by a dye, termed as light harvesting efficiency (LHE), (ii) how efficiently charges being injected (η_{inj}), termed as charge injection efficiency, (iii) how efficiently charges getting regenerated (η_{reg}), termed as charge regeneration efficiency, and (iv) how efficiently charges are being collected (η_{coll}), termed as

charge collection efficiency.⁵⁹⁻⁶² To achieve the better photocurrent response in DSSC, we must play around these parameters which can be controlled by the ability of donor-acceptor (D-A), π -conjugation between D-A, planarity between D-A, dye-density, orientation of dyes on metal-oxide surface, controlling the aggregation, alkyl- or non-communicable aromatic groups wrapping with donor unit, co-sensitization.

1.3.3.2 Open-Circuit Photovoltage (V_{OC})

Redox function of electrolyte and TiO_2 conduction band (CB) Fermi-level potential difference or maximum photovoltage achieved at zero current termed as open-circuit photovoltage (V_{OC}) and is the collective output of redox level of electrolyte, dipole moment of the dye at the interface of TiO_2 , dye-density, charge recombination and lifetime of electron.⁵⁹⁻⁶² To achieve the better photovoltage response in DSSC, we must play around these parameters which can be controlled by using the different electrolyte, donor unit wrapping with alkyl groups, addition of additives (i.e., 4-*tert*-Butylpyridine) and sensitizing solution pH. A schematic representation of interfacial dipole moment and use of various electrolytes in photovoltage modulation are provided in Figure 6.

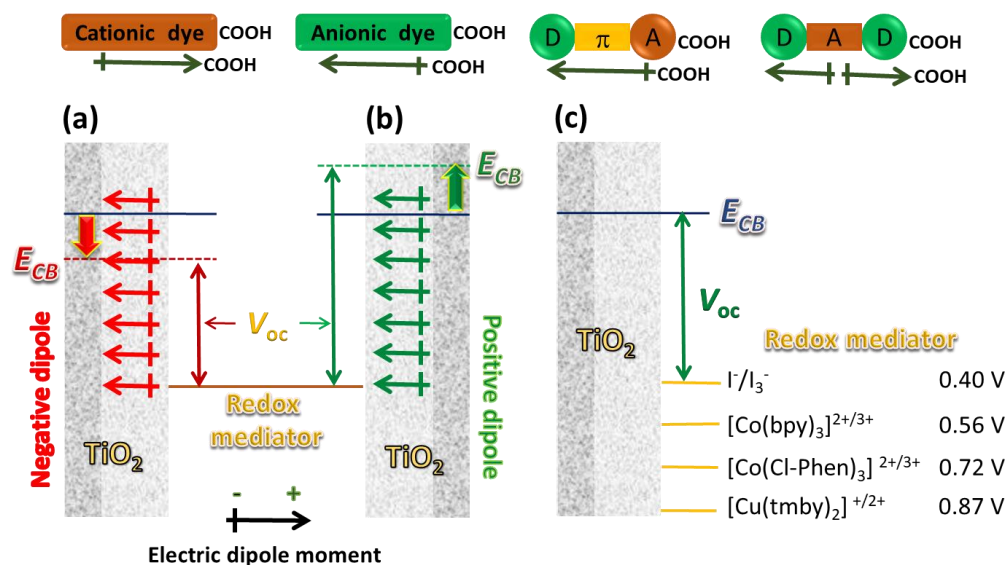


Figure 6. (a) and (b) Effect of interfacial dipole moment of dyes on the conduction band of TiO_2 , (c) effect of various electrolytes on V_{OC} .

1.3.3.3 Fill factor (*ff*)

The fill factor is the area of *I-V* curve with the maximum V_{OC} and J_{SC} of devices, and a highly important parameter that determines the DSSC device performance.⁶¹ The fill factor of DSSC device can be enhanced by integrating proper interfacial contact between the semiconducting materials and metal (reduced series resistance (R_s), which is zero for an ideal solar cell device), and by avoiding the damages in device during fabrication (enhanced shunt resistance (R_s), which is infinite for an ideal solar cell device). Solar cell J_{SC} and V_{OC} are highly affected and decreased by series (high) and shunt (very low) resistance. (**Figure 7**)

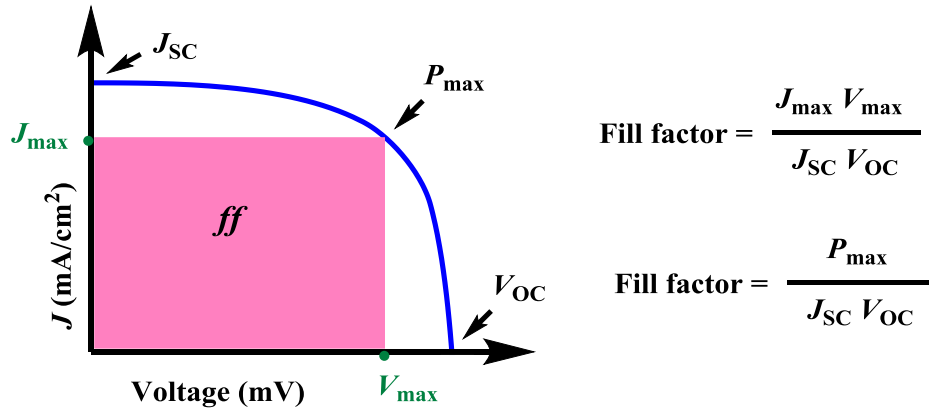


Figure 7. Schematic representation of device fill factor.

1.3.3.4 Power Conversion Efficiency (η)

The power conversion efficiency of the solar cell device is determined by the open circuit voltage, short circuit current, fill factor and incident light power (P_{in}) under at 1.5 G AM sun intensity.⁶²

$$\eta (\%) = \frac{V_{OC} \times J_{SC} \times ff}{P_{in}} \times 100$$

Therefore, high V_{OC} , J_{SC} , and ff values are required to enhance the device efficiency.

1.4 Challenges at Dye-TiO₂ Interfaces

There are two major challenges of DSSC: (1) dye aggregation and (2) charge recombination.

1.4.1 Dye aggregation

Dye-aggregation is a common phenomenon where the dye molecule is attracted by several dye molecules or dyes attracted by one to another and forming a self-assembled aggregated structures or clusters in solution and on the metal-oxide surface.⁶³ Dye-aggregation is the product of strong intermolecular attraction between the dye molecules. Dyes such as porphyrin, merocyanine, cyanine, perylene and squaraine are forming aggregation due to their dipole moment. Aggregated structures absorb differently compared monomeric structure,⁶⁴ either they absorb towards the high energetic/ lower wavelength region known as H-aggregate (face to face alignment) or absorb towards low energetic/ high wavelength region known as J-aggregate (edge to edge alignment)^{65,66} (Figure 8).

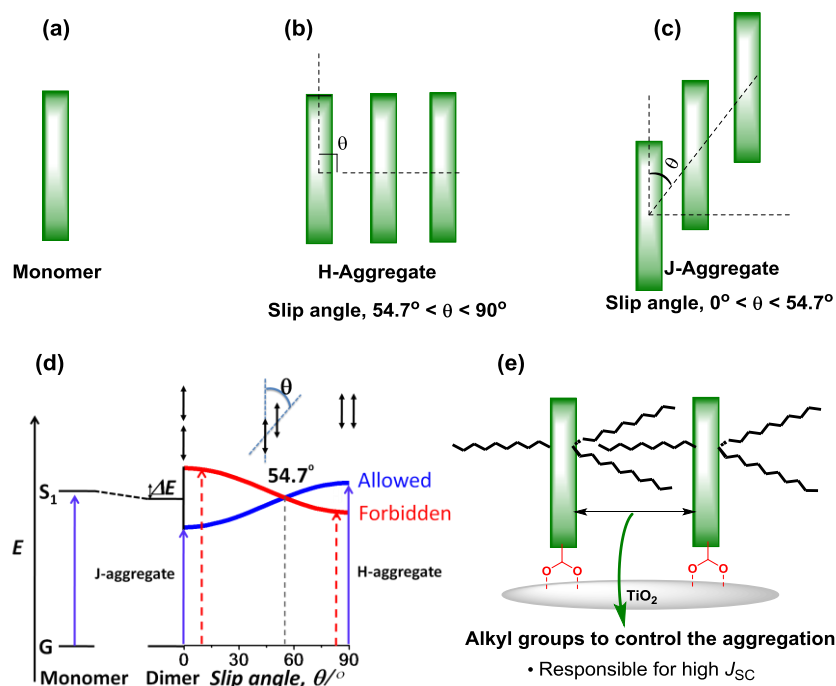


Figure 8. (a), (b) and (c) are representation of monomer, H- and J-aggregates, (d) H- and J-aggregates energy levels with their slip angles, (e) controlled aggregation by alkyl groups.

S. E. Sheppard first observed and use the term dye-aggregation in the isocyanine with water in 1909, afterward Jelly found and reported the first J-aggregation in the cyanine dye with water.^{67,68} However, in DSSC, dye-aggregation plays a detrimental role on the device efficiency by self-hopping of photoexcited dyes with non-photoexcited dyes. Introduction of linear or branched alky-chains or bulky substituents into the dye-backbone or use of co-adsorbent such as chenodeoxycholic acid (CDCA) are the efficient approaches to control the dye-aggregation and enhance DSSC device performance.⁶⁹

1.4.2 Charge recombination

The charge recombination is the most critical and challenging factor that affects the electron transport between the interfaces of TiO_2 /dye/electrolyte in DSSC and responsible in lowering the device efficiency.^{70,71} There are two paths of charge recombination of the electron injected to the TiO_2 conduction band upon photoexcitation; (i) inner-path recombination which decrease device current and associated with recombination with oxidized dyes, (ii) outer-path recombination which decrease device voltage and associated with oxidized species of electrolyte, respectively (Figure 9).

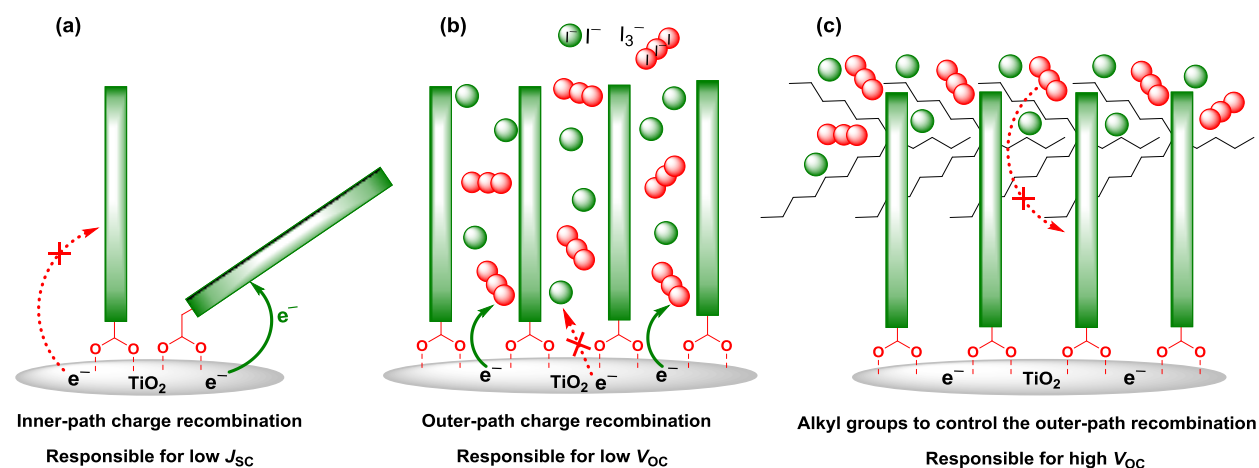


Figure 9. (a) and (b) Inner- and outer-path charge recombination and their effect on device parameters, and (c) controlled outer-path charge recombination by non-polar alkyl groups.

Inner-path recombination can be controlled by molecular design and orientation on the surface, whereas outer-path recombination can be controlled by introducing the alkyl-groups in dye-backbone (by passivating the TiO_2 surface).⁷²⁻⁷⁴ Further, alkyl-group incorporation is also important in enhancing the current of DSSC devices by increasing the electron-lifetime in TiO_2 .⁷⁵

1.5 Recent Advantage of DSSC

1.5.1 Indoor Photovoltaic and Internet of Things

Besides 10 years of outdoor device stability, dye-sensitized solar cells (DSSCs) showed their potential in harvesting indoor or artificial light with high device efficiency from last few years and known as indoor photovoltaics (IPVs).^{76,77} DSSC provides an opportunity to decorate houses with different colors and design due to diversity in the dye color. IPVs gave the prospect to make our buildings smart and independent portable devices that provided effective energy sources that can be developed for use in ambient (indoor) conditions. Further to address the important issue, the IPVs were developed to power autonomous IoT devices, that allows the device implementation of artificial intelligence and capable machine learning. Internet of Things (IoT) is a low power device that is equipped with actuators, sensors, and Internet connectivity. The internet of thing is technology which covers the whole engineering and scientific fields besides internet technology. The IoT is a portable device due to its small size, power efficient, hence shown battlefields operating capability, transportation, healthcare, and roof top event monitoring. The communication mode can be wireless or wired, based on users' requirements, but wireless is preferable mode.⁷⁸ The easy mobility of wireless mode provides the data hand to hand to the users. The wireless IoT devices are equipped with several connection facilities like IEEE 802.15.4 (Zigbee), IEEE 802.15 (Bluetooth) and IEEE 802.11 (Wireless fidelity) protocols. These protocols provide the data from the desire's location and in many cases, it collects the data from cloud interfaced.⁷⁹ However, numerous challenges such as storage and device power exist; communication and data collection make this technology attractive for practical applications.

1.6 Dyes or Sensitizers

Dye or sensitizer is a light harvesting component of dye sensitized solar cells (DSSCs), that converts incident photon into the photocurrent. Ideal sensitizers have fulfilled the indispensable design criteria to achieve high DSSC efficiency; (i) sensitizers should have broad absorption in visible and NIR regions with high molar extinction coefficient, (ii) sensitizers should have appropriate energy alignment for efficient dye-regeneration and electron-injection processes, the LUMO energy level should be $\sim 250\text{--}300$ mV more negative than TiO_2 conduction band, and the HOMO energy level should have more positive potential than redox potential of the electrolyte, (iii) sensitizers should have an anchoring group to binding with TiO_2 , and (iv) sensitizer should be electrochemically and thermally stable in their ground and excited state.⁵⁹ There are two types of sensitizers or dyes used in DSSCs: metallic and metal-free sensitizers.

Ruthenium,^{80,81} and zinc-porphyrin⁸²⁻⁸⁵ are the dyes which contain transition metal as a central metal atom. From the beginning ruthenium metal containing dyes have received interest due to their broad absorption from visible to NIR-region, tunable HOMO and LUMO energy levels by changing the ligand and high photovoltaic efficiency. Ruthenium-based sensitizer has achieved maximum of 11.7% of cell efficiency under standard illumination (AM 1.5G).⁴¹ Few of the ruthenium-based dyes with their DSSC efficiency are provided in **Figure 10**.

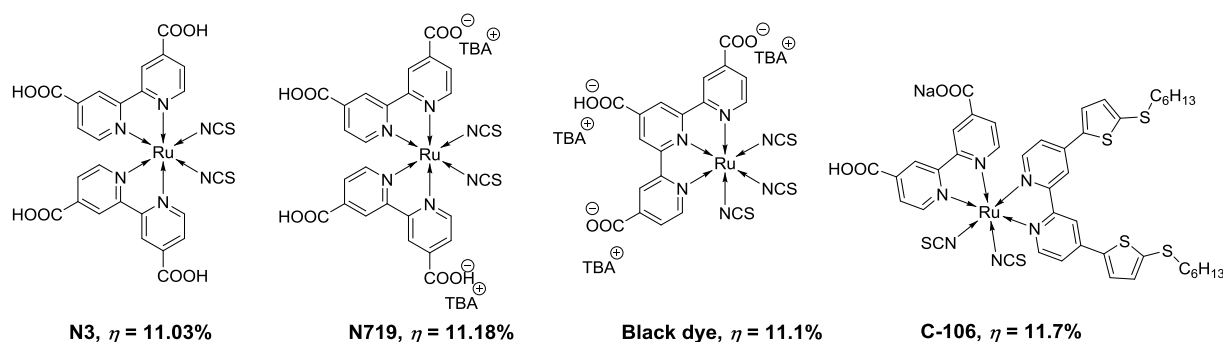


Figure 10. Structures of highly efficient ruthenium-based dyes used in DSSC.

Porphyrin ring is the common chemical structure of the chlorophyll derivatives which having 4 meso-position and 8 β -positions for substitution.⁸² In 1993 Gratzel et al, first reported 2.6%

energy conversion efficiency under simulated sunlight illumination for the β -substituted copper-chlorophyll derivative.⁸⁶ Subsequently they investigated in 2004, the Zn-1a, porphyrin sensitizer with 4.8% efficiency.⁸⁷ Further in 2007, Gratzel and co-workers reported with little modification in GD2 sensitizer having two anchoring group have achieved 7.1% efficiency.⁸⁸ Porphyrin sensitizers showed aggregation behavior, to reduce the aggregation of the porphyrin sensitizers bulky substituent have been incorporated at the meso-position. In 2009, Imahori and co-workers reported meso-substituted Zn-porphyrin sensitizers with 3.7% efficiency.⁸⁹ In 2009, Yeh, Diao and co-workers introduce 3,5-di-tert-butylphenyl at meso-position and acetylene group in the YD0 sensitizer has achieved the 2.4% efficiency.⁹⁰ In 2010 Yeh, Diao et al. reported first time more than 10% efficiency by engineering of the porphyrin molecule by introducing the auxiliary donor at meso-position have achieved 11% efficiency, substitution with electron donating group increases the photo stability.⁹¹⁻⁹³ The highly efficient BTD-functionalized porphyrin sensitizer SM315 has been reported by Gratzel et al. in 2014 with 13% efficiency, and was the highest efficiency reported in porphyrin family (**Figure 11**).²⁹

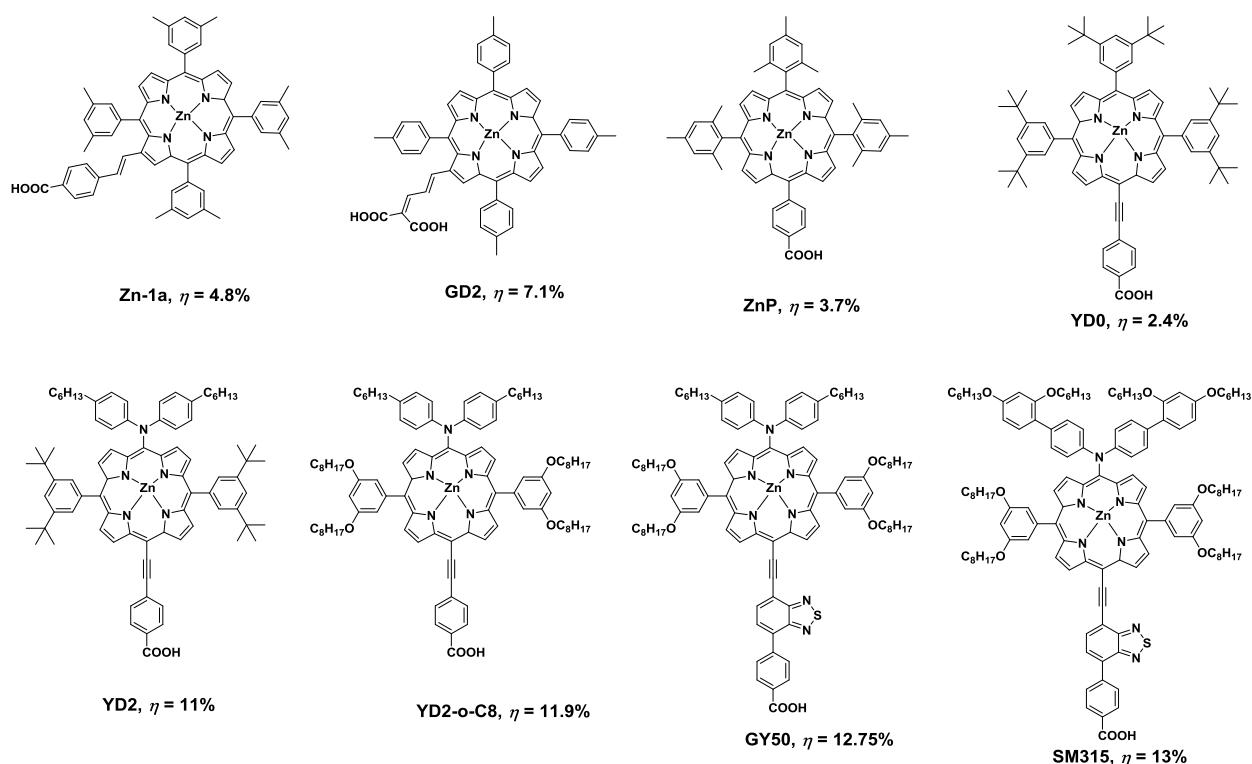


Figure 11. Structures and efficiency of zinc-porphyrin based dyes used in DSSC.

Although, metal-containing ruthenium-polypyridyl and porphyrin-based sensitizers have achieved more than 10% of DSSC efficiency, but high synthetic costs, low synthetic yield, low molar extinction coefficient attracted the researcher's attention toward the metal-free organic dyes. Based on the position of the donor, acceptor, and π -spacer (optional) within the dye molecules, sensitizers are categorized as donor-acceptor (D-A), donor- π -acceptor (D- π -A), donor-acceptor- π -acceptor (D-A- π -A), donor-donor- π -acceptor (D-D- π -A) and donor-acceptor-donor (D-A-D) (**Figure 12**).²⁹

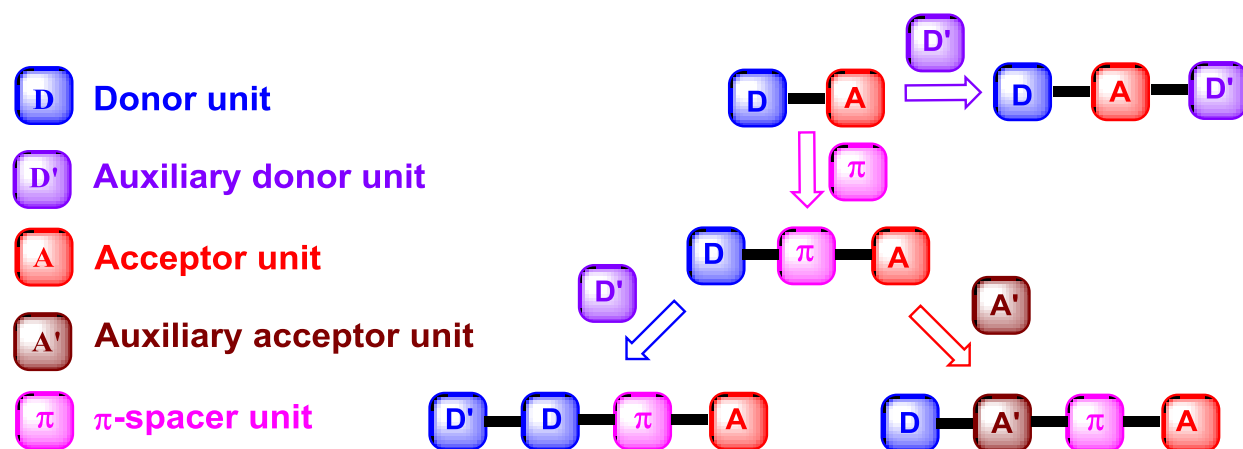


Figure 12. Schematic representation of different architecture of metal-free organic dyes.

1.6.1 Donor-Acceptor (D-A) dyes

Metal-free D-A dyes are known for the high DSSC efficient dyes that contains polyaromatic and fused aromatic moiety-based amine donor attached with the acceptor. Such bulkiness and planar π -conjugated moiety within the molecule helps to harvest the visible light and facile electronic communication between donor and acceptor units in the molecule. Due to the planarity, these dyes forming the aggregated structures while dye-sensitization process on the metal-oxide surface. Introduction of normal or branched alkyl-groups or addition of co-adsorbents (CDCA) during the sensitization process helps to control and suppress the unfavorable dye aggregation. Wang and co-workers reported a C272 sensitizer functionalized with N-annulated perylene (PNP) donor and cyanoacrylic acid, ethynylbenzothiazole-benzoic acid (EBTBA) acceptor-based D-A C272 dye with 10.4% efficiency,⁹⁴ where branched alkyl-group at N-atom control the self-

assembly of the dyes on the TiO_2 surface. Further same group reported C275 sensitized function with N-annulated indeno[2,1-b]-perylene as donor with 12.5% efficiency.²⁷ Notably, the introduction of donor leads to the absorption red shift by 24 nm and improvement in extinction coefficient in C275 dye compared to the C272 dye. Yao *et al* reported C281 dye with the efficiency of 13.0%,⁹⁵ where they rigidified the donor unit along with the peripherally alkylation. Zhang *et al* reported triazatruxene donor and BTD acceptor based ZL003 dye with the efficiency of 13.6% efficiency (**Figure 13**).⁹⁶

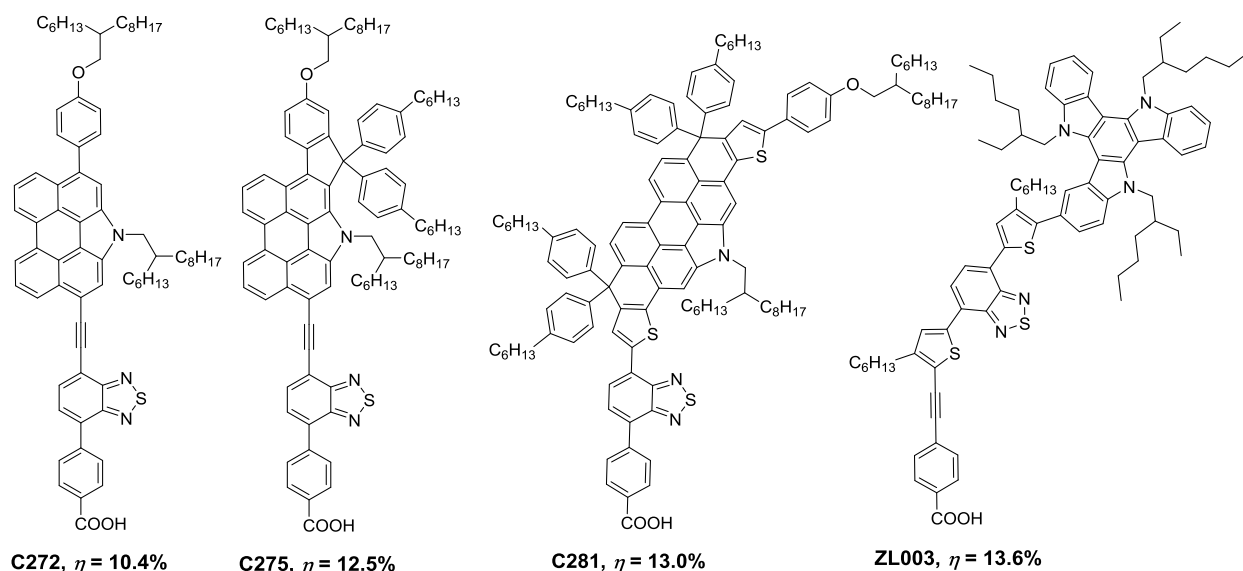


Figure 13. Structures of highly efficient metal-free D-A dyes.

1.6.2 Donor- π -Acceptor (D- π -A) dyes

D- π -A dyes known for its divers' number of π -spacer and acceptor moieties through them the optical, electrochemical, and photovoltaic properties can be tuned systematically. These dyes containing amine-based donor unit such as diarylamine, triarylamine, indoline, phenothiazine etc, cyanoacrylic acid or BTB along with alkyl-group acceptor and variety of π -spacer such as monothiophene, bithiophene, tri thiophene, fused-thiophene, tetrathienoacene, cyclopentadithiophene (CPDT), thienobenzothiophene, peripheral-alkylation based fused-anthracenethiophene etc. Triphenylamine and tetrathienoacene donor and π -spacer based TPA-TTAR-T-A dye achieved 10.1% DSSC efficiency,⁹⁷ whereas thienobenzothiophene and CPDT

π -spacer along with bulky-triarylamine based SGT-121 and Y-123 dyes achieved 8.2% and 9.5% of DSSC efficiency, respectively.⁹⁸ Further, indoline donor, bithiophene spacer, and cyanoacrylic acid based AKT2 dye has achieved 4.7% of DSSC efficiency.⁹⁹ The maximum DSSC device efficiency achieved by D- π -A based organic dyes was 12.6% by R6 dye,¹⁰⁰ where fused-anthracene-thiophene with peripheral-alkylation used as a π -spacer, BTD as an acceptor and diarylamine was used as a donor (**Figure 14**).

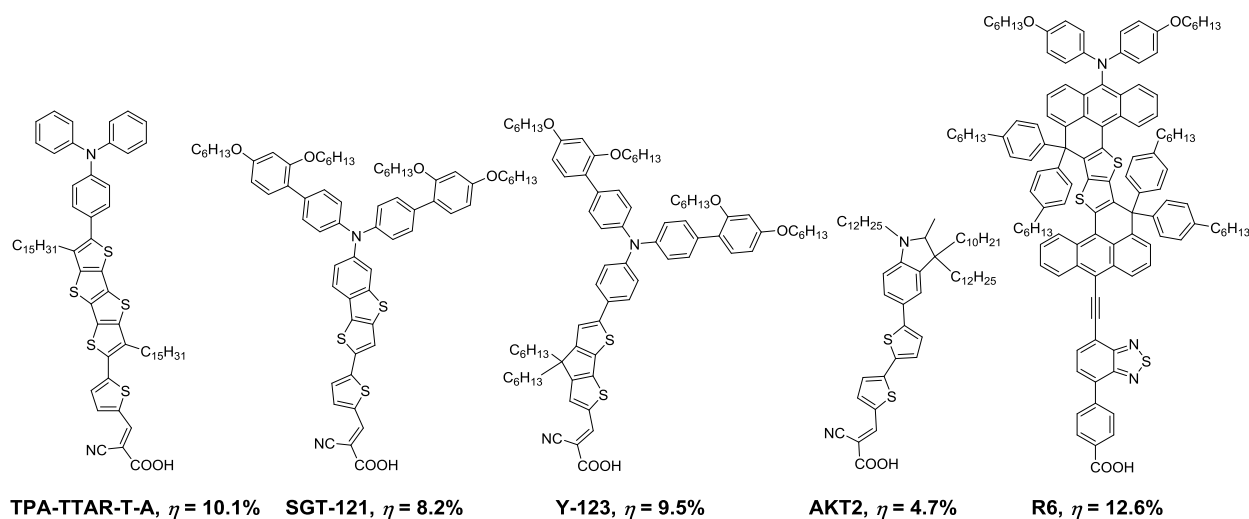


Figure 14. Structures of highly efficient metal-free D- π -A dyes.

1.6.3 Donor-Acceptor- π -Acceptor (D-A- π -A) Dyes

D-A- π -A dyes made with an additional acceptor incorporated between the donor and π -spacer moieties of a regular D- π -A dye, and such acceptor named as auxiliary acceptor. BTD, diphenylpyridopyrazine, and diphenylthienopyrazine are commonly used as an auxiliary acceptor in D-A- π -A dyes **Figure 15**. Indoline donor, branched silolodithiophene spacer, and BTD auxiliary acceptor-based dye B-87 achieved 10.0% DSSC efficiency, and replacement of silolodithiophene spacer by CPDT spacer for dye WS-51 showed 10.1% DSSC efficiency.¹⁰¹ That means there are no significant changes found while substitution of spacer unit for B-87 and WS-51 dyes.¹⁰² However, substitution of BTD of B-87 dye by diphenylpyridopyrazine showed DSSC efficiency of 9.4% for Q-85 dye.¹⁰¹ Whereas the maximum DSSC efficiency of 7.1% has been achieved by the NL6 dye with the triphenylamine donor, and diphenylthienopyrazine auxiliary acceptor.¹⁰³

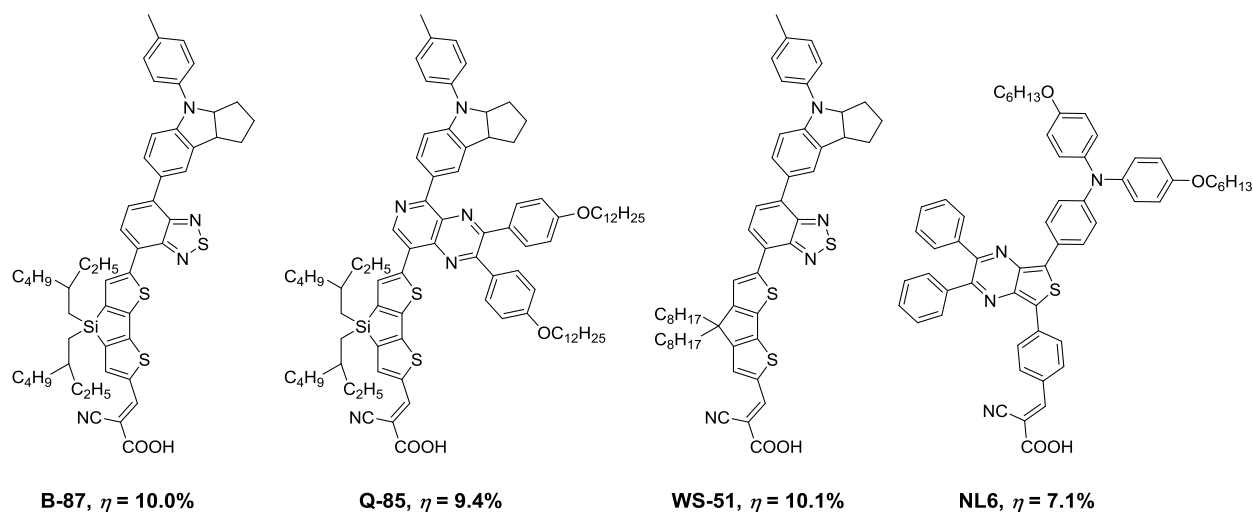


Figure 15. Structures of highly efficient metal-free D-A- π -A dyes.

1.6.4 Donor-Donor- π -Acceptor (D-D- π -A) Dyes

There are few numbers of D-D- π -A skeleton based-dyes were synthesized and utilized for DSSC, where donor unit appended with bulky substituents and auxiliary donor have been found commonly in most of the structures.^{104,105} The maximum DSSC efficiency achieved by this family was 9.8% for M60 dye.¹⁰⁵ A few of the dyes along with their DSSC efficiency are provided in **Figure 16**.

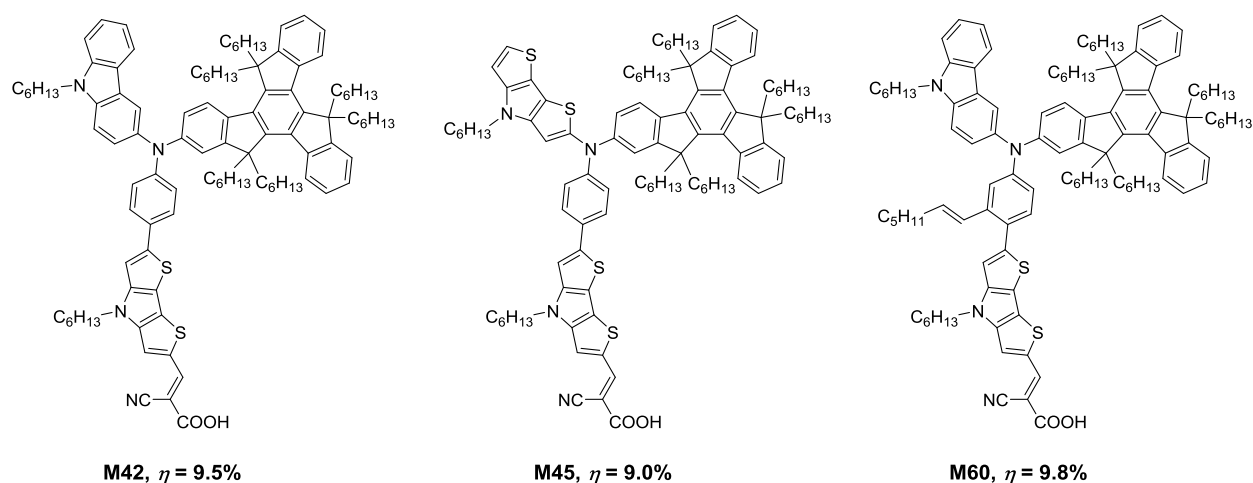


Figure 16. Structures of highly efficient metal-free D-D- π -A dyes.

1.6.5 Donor-Acceptor-Donor (D-A-D) Dyes

D-A-D architecture is one of the basic skeletal structures of most of the squaraine dyes, whether they are symmetric or unsymmetric. Few of the D-A-D architecture based squaraine dyes with their DSSC efficiency are provided in **Figure 17**. Squaraine chromophore-based dyes are very attractive due to their tunable photophysical and electrochemical properties, high molar coefficient, and used in protein labeling, photodynamic therapy, fluorescence probe, organic solar cells application besides DSSC.¹⁰⁶⁻¹¹² Maximum DSSC efficiency of 7.93% have been achieved by visible-light active unsymmetrical squaraine dye AK4, and 9.36% of co-sensitized efficiency has been achieved by co-sensitization of optically opposite dye AK4:SQS4 (1:1) without co-absorbent due to their controlled aggregation on the TiO₂ surface by alkyl-group wrapping.¹¹³

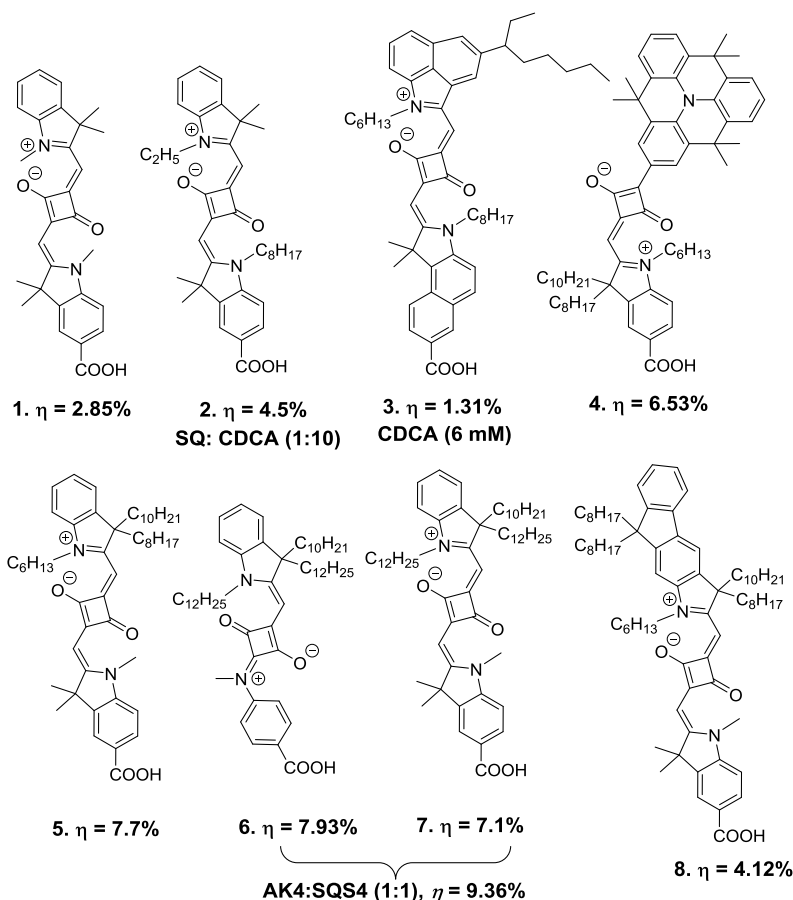


Figure 17. Structures of D-A-D based unsymmetrical squaraine dyes with their efficiency.

In 1993 Kamat and coworkers used squaraine dye as a sensitizer for first time and found the IPCE response of the dye with low intensity.¹¹⁴ Afterward researchers started to use squaraine dyes as a sensitizer for DSSC, where Zhao and co-workers found 2.16% of DSSC efficiency by using symmetrical squaraine dyes.¹¹⁵ Then after, Yum *et al.* achieved 4.5% DSSC efficiency with CDCA for unsymmetrical squaraine dye, where they used indoline as donor moiety.¹¹⁶

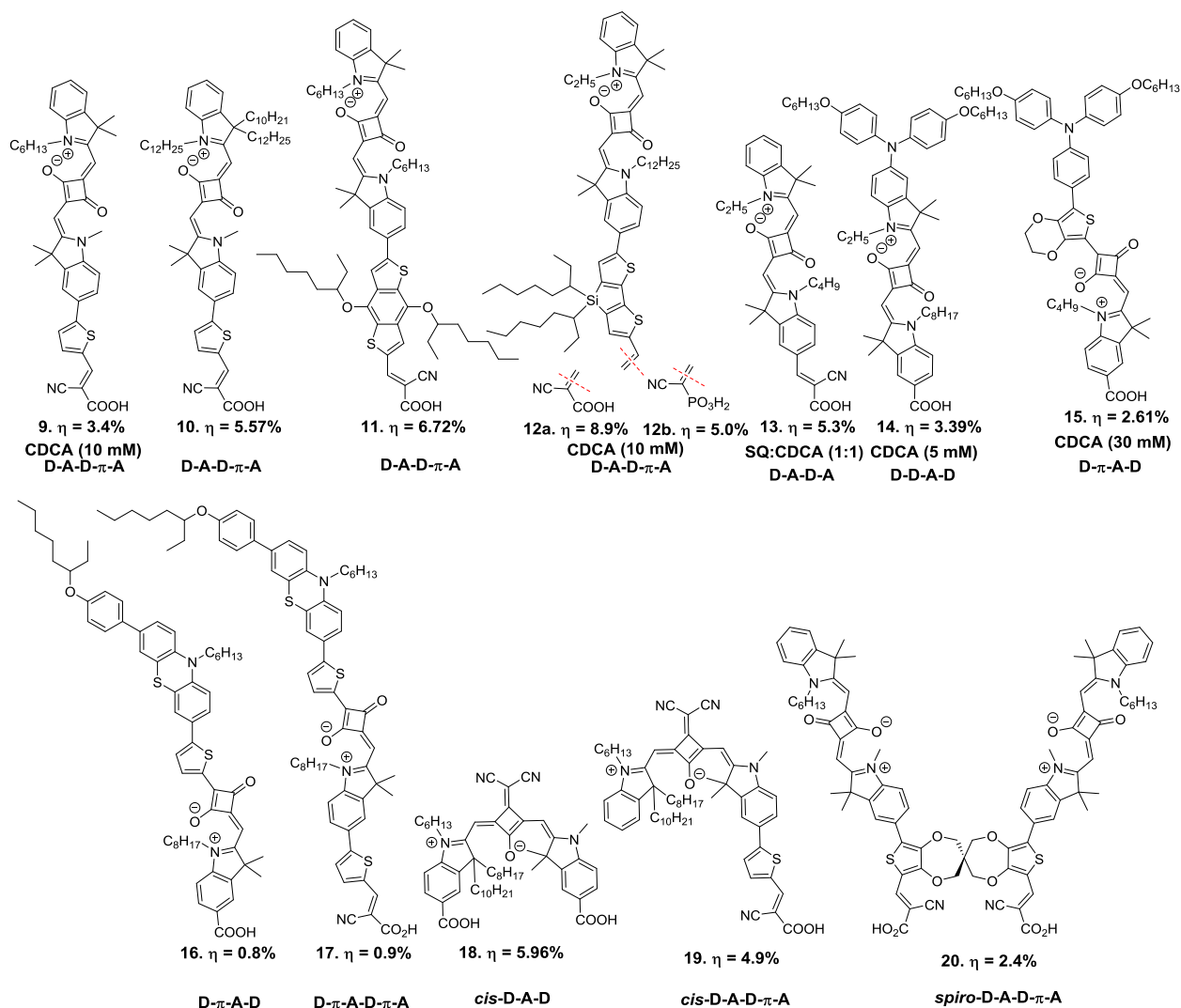


Figure 18. Structures of different types unsymmetrical squaraine dyes with their efficiency

Huge modulations have been done by researchers around the world to achieve high DSSC efficiency, however only a few of the dyes have achieved more than 7.0% DSSC efficiency without any co-adsorbent. No significant changes have been found while addition of auxiliary-donor or auxiliary-acceptor or π -spacer or substitution of anchoring group (**Figure 18**). And,

obtained DSSC efficiency from the different squaraine based dyes it has been clear that the dyes with D-A-D and D-A-D- π -A architectures responsible for high DSSC efficiency, where 7.93% achieved by D-A-D based aniline-indoline (AK4) dye without CDCA,¹¹³ and 8.9% achieved by D-A-D- π -A based (DTS-CA) dye with 10 mM of CDCA.¹¹⁷

1.7 Objectives of Thesis and Sensitizer Engineering.

Tunable photophysical and electrochemical properties, and high molar coefficient made squaraine dyes as a potential sensitizer to be used for DSSC applications. Dihedral angle between the donor-acceptor moieties, extension in conjugation, and position of acceptor moiety play an important role in DSSC device efficiency, which have been done with few D-A, D- π -A dyes and needs to be done for the unsymmetrical squaraine dyes. And engineering a few new series of unsymmetrical squaraine dyes that can be used for DSSC is the objective of my thesis.

1. Effect of alkylation and arylation at N-atom of aniline donor on dye-sensitized solar cell performance

- To design and synthesize a series of alkyl-group-wrapped visible-light active dyes with changed in N-functionalization at aniline unit for DSSC,
- To study the photophysical, electrochemical, aggregation properties of the dyes, and
- To study the open circuit voltage (V_{OC}), short-circuit current (J_{SC}) and DSSC device efficiency (η)

2. Extension in conjugation within the polymethine framework and their effect on photophysical, electrochemical and photovoltaic properties

- To design and synthesise a series of Visible and NIR-light active dyes by introducing of thiophene unit within the polymethine framework, and
- To study the effect of conjugation toward V_{OC} , J_{SC} , and device efficiency

3. Position of acceptor unit within the polymethine framework and their effect on dye-sensitized solar cell performance

- To synthesize a series of visible-light active dyes with changed in the position of acceptor unit, and
- To study their effect toward the photophysical, electrochemical, dipole moment, V_{OC} , J_{SC} , and DSSC device efficiency

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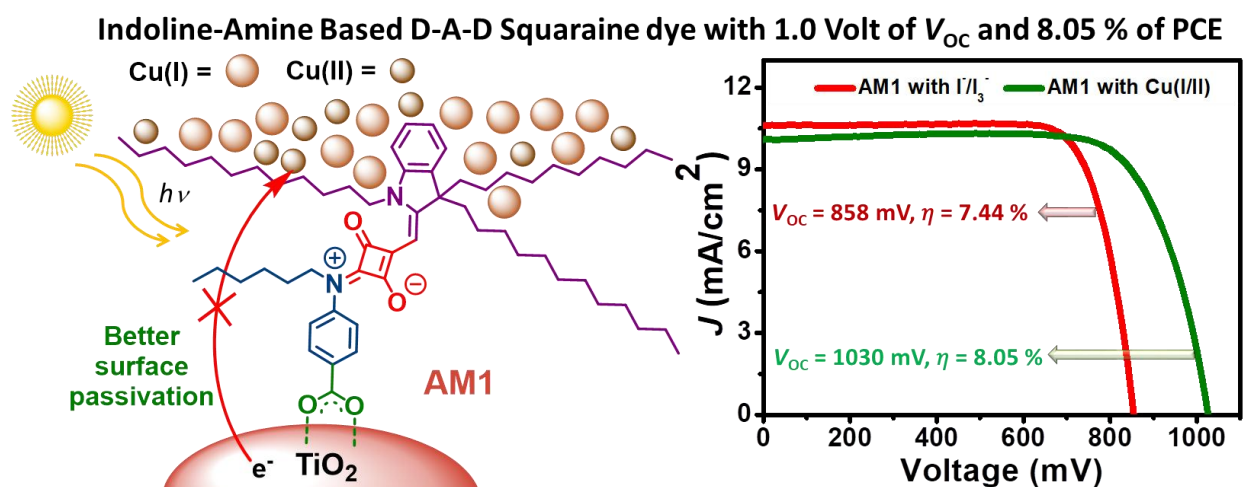
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Chapter 2

Effect of N-functionalization at the Aniline Donor of Visible Light Active Squaraine Dyes on DSSC Device Performance



This chapter is published as a research article:

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2.1 INTRODUCTION

The potential of sensitizers to harvest light and convert it into the electricity with high device performance in dye-sensitized solar cells (DSSCs) makes this third generation solar technology more attractive.^{1,2} Tunable spectral properties of light harvesting materials, low-cost device fabrication and working in the diffused light conditions are the salient features of the dye-sensitized solar cells (DSSC) compared to the first two generation solar cells.^{3,4} In DSSCs, both organic and inorganic sensitizers have the potential to generate high device efficiency by harvesting the photons in visible and near-IR regions.^{3,5} Several highly efficient ruthenium polypyridine^{6,7} and Zinc-porphyrin^{3,8-14} complexes based dyes came up with the judicious structural design in which both steric and electronic factors were integrated to achieve high DSSC efficiency. Compared to the transition metal complex-based dyes, metal-free organic dyes are very promising, because of tunable photophysical, electrochemical and photovoltaic properties by modulating the structural components of the sensitizers such as donor, acceptor and π -spacer units.¹⁵⁻²⁰ There are several metal-free organic dyes that achieved >10% efficiency with I^-/I_3^- ¹⁵⁻¹⁷ and Co(II/III) ^{3,18,19} electrolytes by structural modulations. Fast electron injection and low energy loss in triazatruxene (TAT) based metal-free organic dye showed highest efficiency of 13.6% with Co(II/III) electrolyte.²¹ Dyes wrapped with the auxiliary donor²² and acceptor²³ moieties have been utilized for DSSC which gave good device efficiency by broadening the spectral responses associated with the visible and NIR regions^{24,25} due to the intramolecular charge transfer between the donor and acceptor moieties. Further, structural modulation in the donor and acceptor opens the opportunity for tuning the HOMO and LUMO electronic levels, which facilitate to use the other electrolytes to maximize the photovoltaic parameters such as V_{OC} and J_{SC} ^{15,26} beside side chain engineering.²⁷⁻³⁰ The HOMO energy level of the dyes based on the D-A, D- π -A, and D-A- π -A with more positive potential vs NHE have been used with the Cu(I/II) electrolytes which exhibited excellent V_{OC} and DSSC device efficiencies.³¹⁻³⁸ Further, it has been observed that most of the sensitizers used for the DSSC device fabrication which showed more than 1 V of V_{OC} with the Cu(I/II) electrolytes were based on the alkyl group functionalized bulky arylamine based Hagfeldt-donor with judicious structural modulations in the acceptors, π -spacers, and change in the ligand properties in the electrolyte itself.^{31,39} Benztricarbazole (BTC) electron donor based dyes showed more than 1 V of V_{OC} with Cu(I/II) electrolyte⁴⁰ (**Figure 1**).

D-A, D- π -A, D-A- π -A, D-A- π -A and D-A-D based sensitizers which exhibit more than 1 V of V_{OC} with DSSC device with $[Cu(tmby)_2]^{2+/+}$ electrolyte

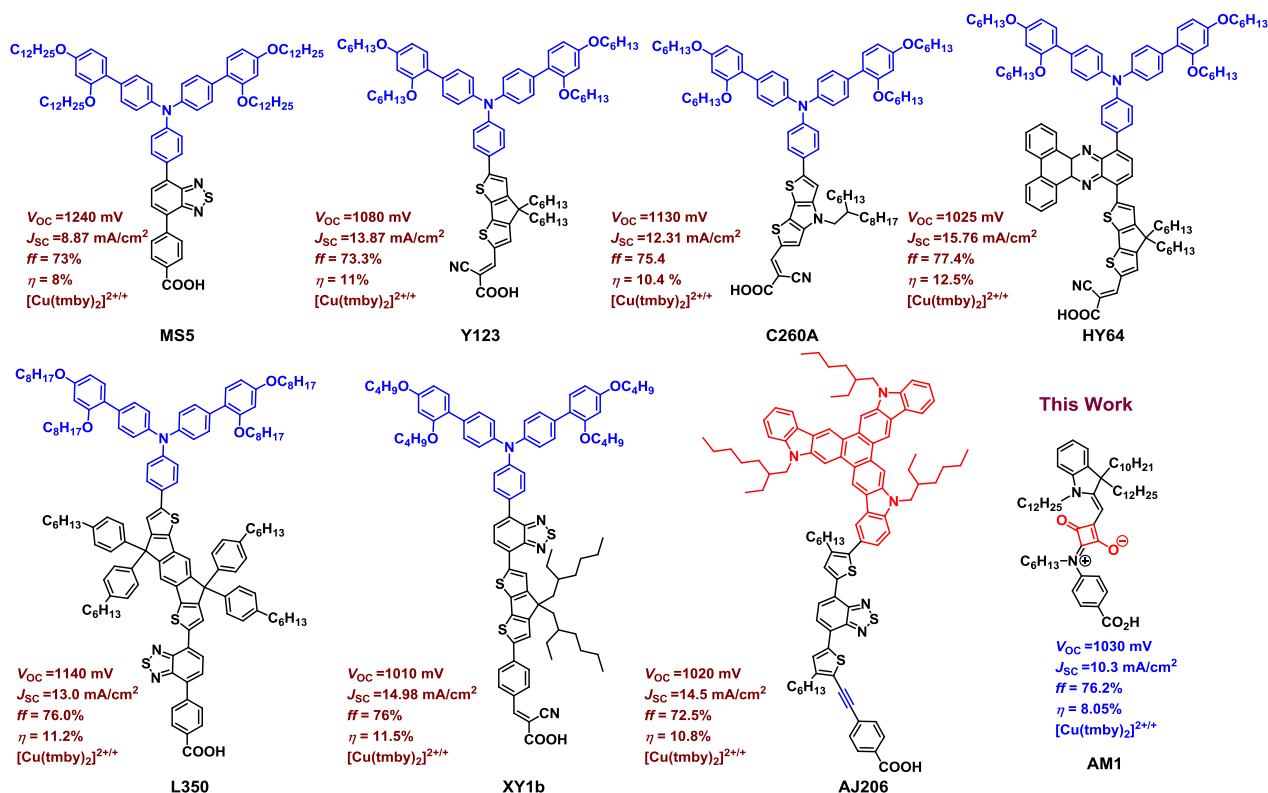


Figure 1. Structures of the metal-free organic dyes with more than 1 V of open-circuit potential (V_{OC}) with Cu (I/II) electrolyte.

Further, DSSC device performance more than 30% under low light condition open avenues for utilizing this technology in building integrated photovoltaic (BIPV) and internet of things (IoT) applications.⁴¹ Besides the other sensitizer, D-A-D based squaraine dyes are very attractive because these chromophores possess high extinction coefficient in the order of $10^5 M^{-1} cm^{-1}$ and forms aggregated structures on the semiconducting metal oxide surface.⁴²⁻⁴⁶ Aggregation of dyes on the surface enhance the light harvesting properties by broadening the absorption spectrum of the sensitizer and such self-assembled structure formed in solution and in bulk have been explored in wide range of applications.⁴⁷⁻⁵⁰ Further, the photo-physical and electrochemical properties of the D-A-D based unsymmetrical squaraine dyes can be modulated by extending the conjugation between the donor and acceptor moieties. All the above characteristics of squaraine dyes make it as a potential sensitizer for the DSSC device fabrication with both I^-/I_3^- electrolyte and $Co(II/III)^{26,51}$ electrolytes. Recently, by modulating the conjugation, structural optimization for indoline and aniline donors based visible active squaraine dye was reported for DSSC device

with I^-/I_3^- electrolyte. Structural features such as alkyl group wrapping around indoline donor and the N-methyl group at the aniline N-atom were important for achieving good DSSC device performance.⁴³ In this work we have designed and synthesized alkyl groups wrapped indoline and aniline donors based unsymmetrical squaraine dyes where the N-atom of aniline donor functionalized with a linear n-hexyl (AM1), branched 2-ethylhexyl (AM2) and an aromatic phenyl (AM3) groups (Figure 2) to understand the (i) correlation between the dihedral angle around the aniline donor and squaric acid unit for the observed device performance, (ii) extent of surface passivation/shielding for reducing the charge recombination process besides having the alkyl groups at the sp^3 -C and N-atoms of indoline unit. As cationic and zwitterionic dyes having low V_{OC} , and this set of dyes possess deep positive HOMO level and hence compatibility with $[Cu(tmby)_2]^{+/2+}$ electrolyte was tested to enhance the open-circuit potential besides establishing the structure property relationship with iodolyte electrolytes.^{45,52}

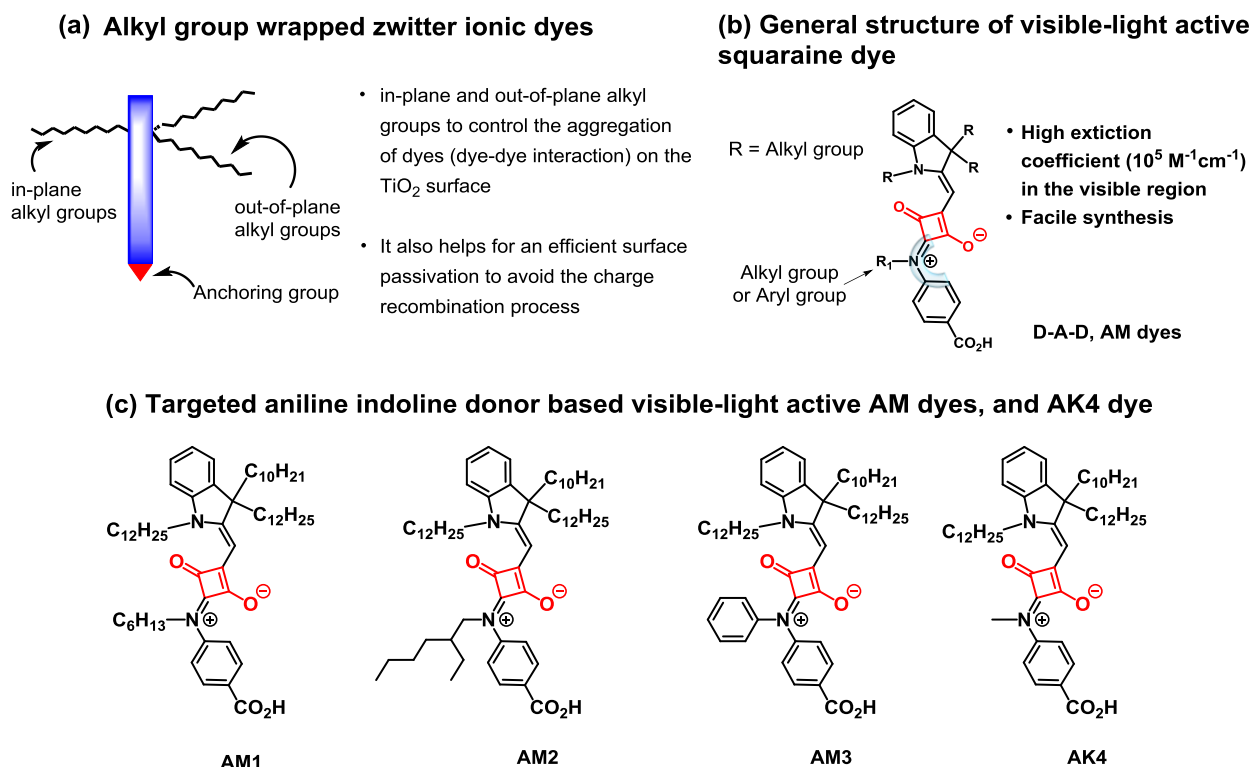
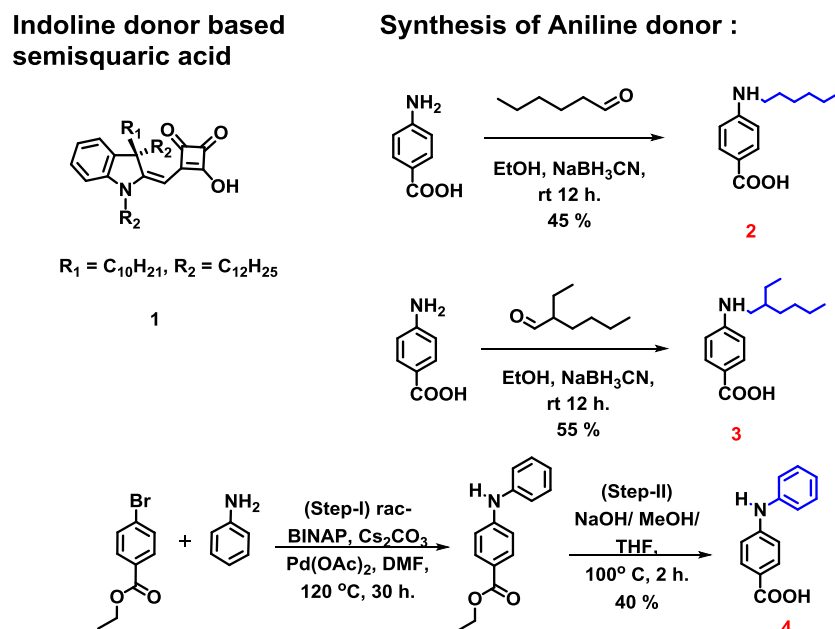


Figure 2. (a) Design of alkyl group wrapped metal free organic dye (b) general structure of visible active unsymmetrical squaraine dyes (AM dyes), and (c) targeted D-A-D based unsymmetrical squaraine dyes.

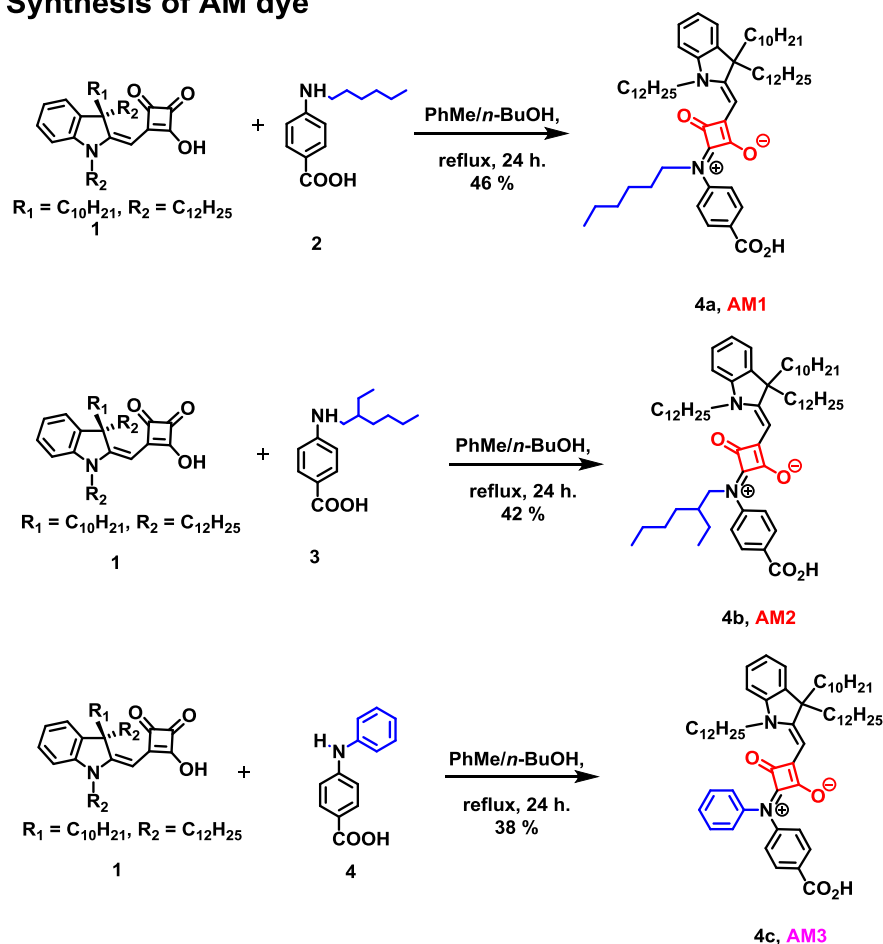
2.2 RESULTS AND DISCUSSION

2.2.1 Synthesis of aniline and indoline-based donor-acceptor-donor (AM) dyes. Synthesis of unsymmetrical squaraine dyes requires a semi-squaric acid and Fischer's base (indolium). Fischer's base derived squaraine dye exhibit absorption at 640 nm, however reducing the conjugation by a vinylene unit by means of utilizing a Fischer's base and aniline donor units provide the dye that absorbs at 520 nm with the high extinction coefficient in the order of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The Alky group present in the Fisher's base and aniline donors control the aggregation of dyes on the TiO_2 photoanode and passivate the surface effectively to reduce the charge recombination process. Here, 4-aminobenzoic acid reacted with hexanal or 2-ethylhexanal under reductive amination reaction conditions to afford the N-alkylated-4-amino benzoic acid derivatives 4-(hexylamino) benzoic acid (2), and 4-((2-ethylhexyl)amino) benzoic acid (3).⁵³ Whereas Pd^{2+} catalyzed coupling of ethyl-4-bromobenzoate with aniline provided 4-(phenylamino)benzoic acid (4).⁵⁴ **AM** dyes were synthesized by condensation reaction between the N-alkylated or N-arylated aniline derivatives and alkyl group wrapped semisquaric acid, **1**, by employing the Dean-Stark apparatus for the azeotropic removal of water to afford the red color dyes in moderate yields (**Scheme 1** and 2). All the dyes have been characterized by NMRs (^1H -NMR and ^{13}C -NMR), and IR spectroscopic and mass spectrometric techniques.



Scheme 1. Synthetic scheme of aniline donors.

Synthesis of AM dye



Scheme 2. Synthesis of aniline and indoline donors-based AM dyes.

2.2.2 Photophysical properties. The UV-vis absorption spectra of **AM1-AM3** dyes and reference **AK4** dye have been carried out in CH_2Cl_2 solution which exhibited intense absorbance peak between 528-546 nm with the extinction coefficients of $1.44\text{-}1.68 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ (Figure 3, and Table 1). Incorporation of the hexyl and 2-ethylhexyl alkyl unit at the N-atom of aniline donor unit showed 9 and 12 nm of blue shift in λ_{max} for the **AM1** and **AM2** dyes respectively, whereas incorporation of the phenyl group at the N-atom of aniline donor unit showed 9 nm of red shift in λ_{max} for the **AM3** dye compared to reference dye **AK4**. Emission studies of the **AM** dyes exhibited the peak between 571-597 nm and showed longer Stoke's shift between 48-52 nm in CH_2Cl_2 compared to the **AK4** dye (34 nm) upon exciting at the 500 nm. Hence, effect of the N-alkylation and N-arylation at the aniline donor led to larger. Stoke's shift than **AK4** dye that indicates the

more change in dipole moment for the **AM1**, **AM2** and **AM3** dyes in the excited state. To understand the self-assembly of **AM** dyes on the TiO_2 , absorption of **AM** dyes has been carried out on the TiO_2 surface with different sensitization time (**Figure 3d**). As the **AM** dyes were wrapped with alkyl groups, shorter dipping time leads to observe broadening of the peaks and additional peaks were observed when the electrodes dipped for more than 60 minutes due to the formation of H- and J- type aggregates on the TiO_2 surface (**Figure 3b**) for **AM1** and **AM2** dyes. For the dye **AM3**, spectral profile was broadened without any additional peaks which indicates the N-substitution at the aniline donor modulates the self-assembly of dyes.

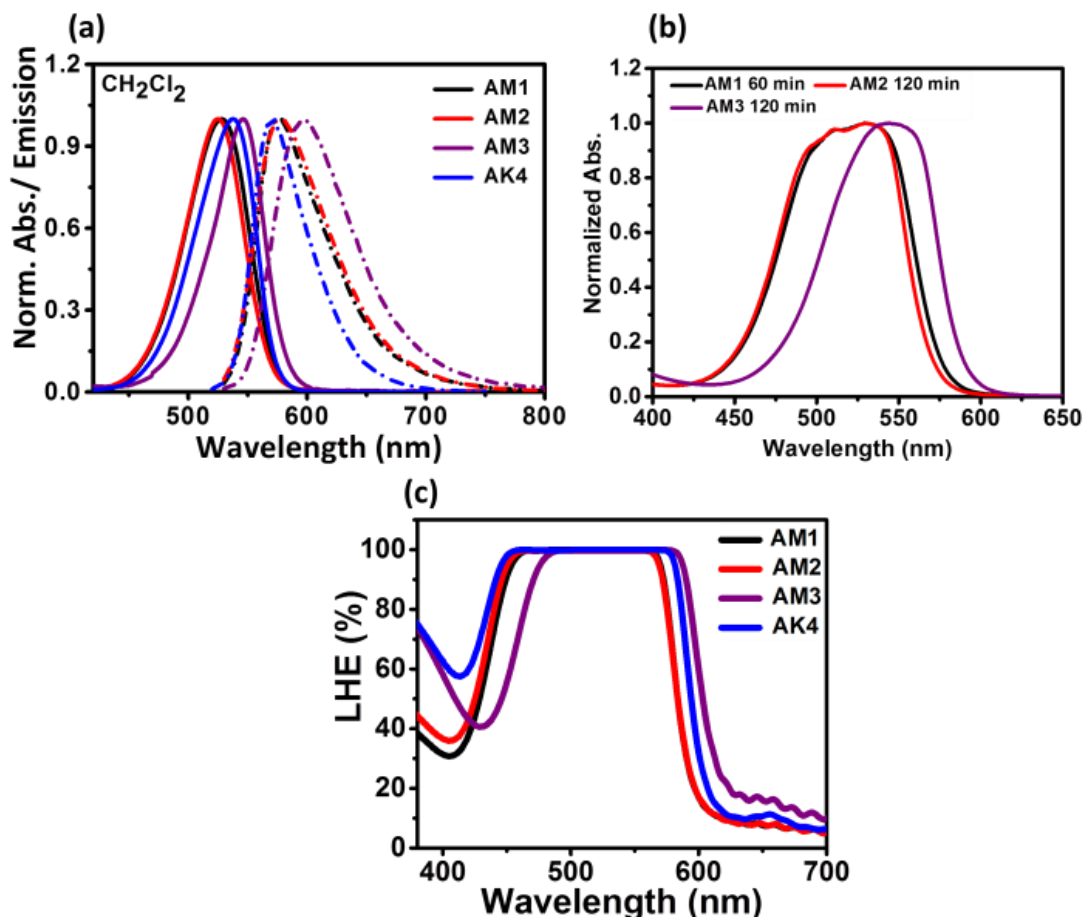


Figure 3. (a) Normalized UV-vis (solid) and fluorescence (dotted) spectra of the **AM** and **AK4** dyes in CH_2Cl_2 solution, (b) UV-vis spectra of the **AM** dyes on TiO_2 (TiO_2 electrode thickness was 6 μm , dipping time: 60 min for **AM1**; 120 min for **AM2** and **AM3** dyes) and (c) LHE ($=1-10^{-A}$) profiles of **AM** and **AK4** dyes on TiO_2 electrodes (dipping time 12 h).

Incorporation of hexyl and ethyl-hexyl group on the aniline donor for the **AM1** and **AM2** dyes narrowed the LHE of 18, and 16 nm, whereas aryl group incorporation for **AM3** dye lead 22 nm narrowed LHE performances compared to **AK4** dye. Such reduction in the LHE performance for **AM** dyes compared to **AK4** dye probably due to more hindrance near to the TiO_2 surface between the dye molecules by alkyl and aryl group incorporation, which reduced the aggregation of dyes on the TiO_2 surface (**Figure 3c**). Further, charge injection efficiency of **AM** dyes has been calculated from the steady state emission quenching experiment by utilizing dye coated TiO_2 and ZrO_2 films (procedure is provided in the general methods, **Figure 4**). The integrated charge injection efficiency ($\text{CIE} = 1 - I_{\text{Titania}}/I_{\text{Zirconia}} \times 100\%$) of 90.3, 95.5, and 92.7% have been achieved for **AM1**, **AM2**, and **AM3** dyes, respectively.

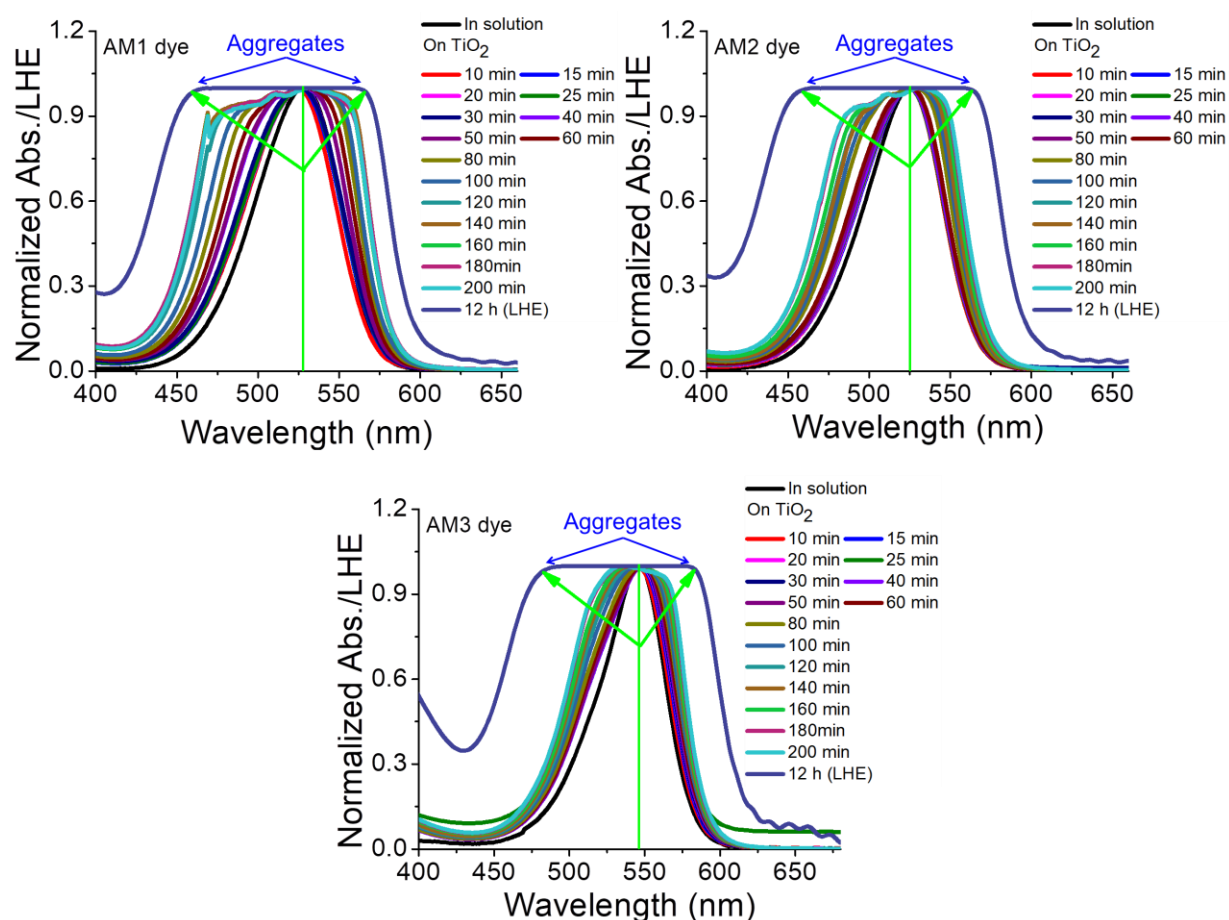


Figure 3d. Normalized absorbance (with the various dipping time) and LHE of **AM** dyes on the TiO_2 .

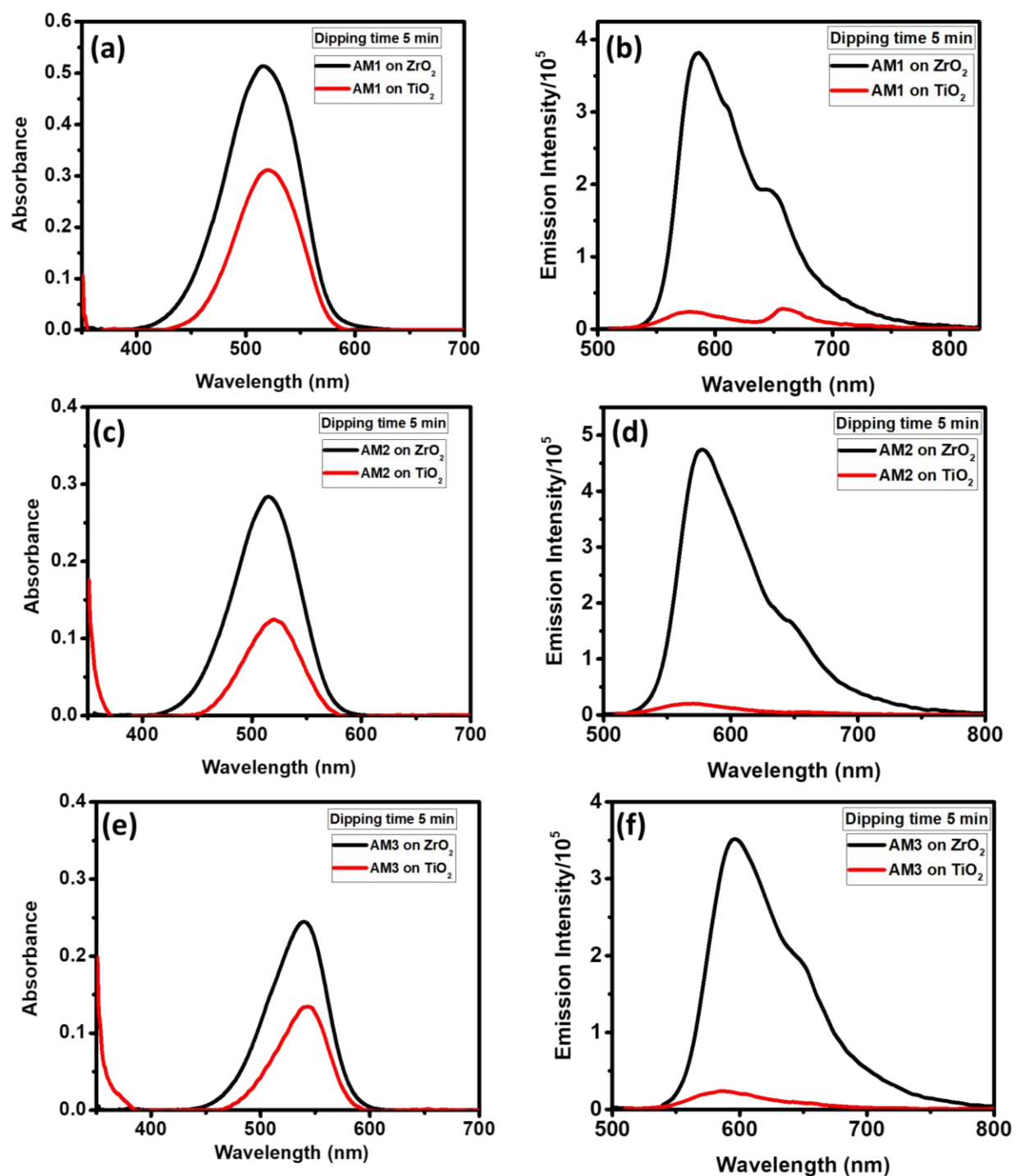


Figure 4. Absorbance and emission spectra of AM dyes on the TiO₂ and ZrO₂, where dipping time was 5 min in dye stock solution (0.1 mM in CH₃CN). The excitation wavelength for dyes anchored on the TiO₂ was 495 nm, whereas 470, 473, and 485 nm was the excitation wavelength for AM1, AM2, and AM3 dyes on ZrO₂, respectively.

2.2.3 Electrochemical properties. Differential pulse voltammetry and cyclic voltammograms experiments have been carried out in CH_2Cl_2 to find the energy levels of the **AM** dyes (**Figure 5**). The HOMO energy levels of the **AM** dyes were calculated from the first oxidation potential of the differential pulse voltammograms and the LUMO energy levels were calculated by subtracting the HOMO values from the optical energy gap of the dyes. The HOMO energy levels of **AM** dyes showed between 1.03 and 1.13 V, and LUMO obtained between the -1.21 and -1.06 V vs NHE (**Figure 5a**, **Table 1**). The HOMO energy levels of **AM** dyes possesses enough positive potentials for the efficient dye regeneration through I^-/I_3^- and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes, and LUMO possesses enough negative potentials for the efficient charge injection to the TiO_2 conduction band upon photoexcitation.

Table 1. Photophysical and electrochemical properties of the **AM** and **AK4** dyes at room temperature.

Dyes	^a λ_{max} (nm)	^b λ_{max} (nm)	^c λ_{max} (nm) On TiO_2	^a ϵ (10^5 $\text{M}^{-1} \text{cm}^{-1}$)	LHE $\Delta\lambda$ at 80 % (nm)	^d E_{ox} (V vs Ag/Ag+)	E_{HOM} E_{O} (V vs NHE)	E_{LUMO} (V vs NHE)	^e E_{g} (eV)
AM1	528	576	529,510	1.55	133	0.490	1.03	-1.20	2.23
AM2	525	577	530,511	1.64	135	0.493	1.04	-1.28	2.25
AM3	546	597	545	1.68	129	0.589	1.13	-1.06	2.19
AK4	537	571	526	1.44	151	0.507	1.05	-1.18	2.23

^aabsorption, ^bemission of **AM** and **AK4** dyes in dichloromethane, ^con TiO_2 , thickness 6 μm , dipping time was 60 min for **AM1**; 120 min for **AM2**, **AM3** and 10 min **AK4** dyes (MeCN), ^doxidation potentials were measured in CH_2Cl_2 , where tetrabutylammonium perchlorate (TBAClO_4) used as a supporting electrolyte, Fc/Fc^+ used as an internal standard and converted to NHE by addition of 0.7 V, ^e E_{g} optical energy gap (from the intersection point of absorption and fluorescence spectra, $1240/\lambda$).

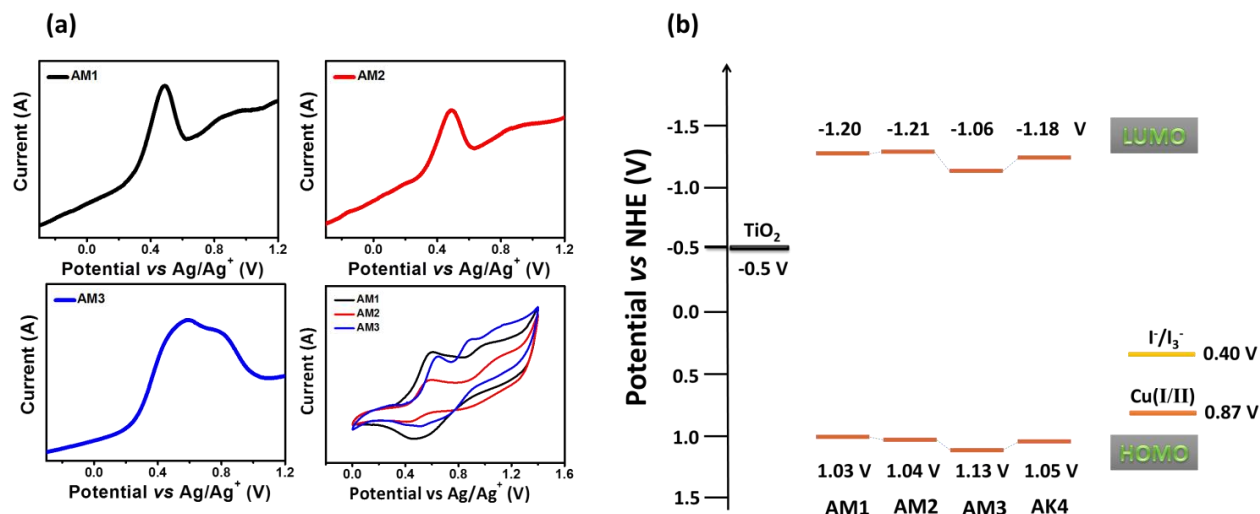


Figure 5. (a) Differential pulse and cyclic voltammograms of the **AM** dyes in CH₂Cl₂, and (b) energy level diagram of the **AM** and **AK4** dyes with DSSC components.

2.2.4 Dye-desorption studies. The desorbed dyes UV-spectrum were recorded on SPECORD[®] 210/ PLUS, Analytikjena UV–Visible spectrophotometer at room temperature (**Figure 6** and **Table 2**). Area of photo anode was 0.23 cm² (8 μm thickness), dipping for 12 h at room temperature in 0.1 mM of dye solution, 1 M HCl ethanolic solution (2 mL) have been used to desorb the adsorbed dyes and path length of cuvette was 0.01 cm² for dye desorption studies of **AK4** and **AM** dyes.

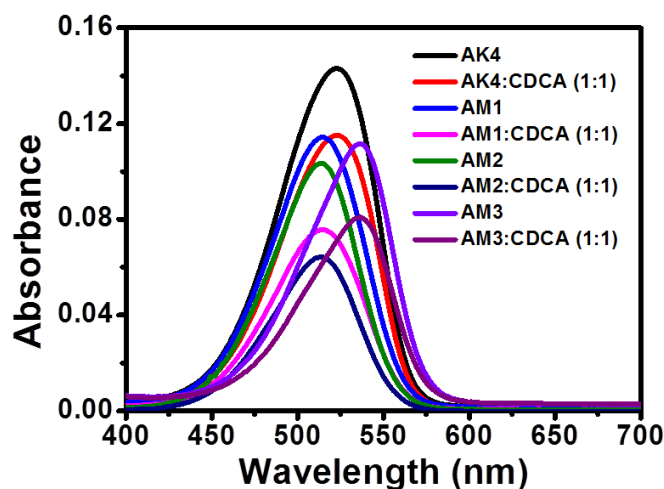


Figure 6. UV-vis spectra of desorbed dyes from the TiO₂ surface in 1 N HCl (in EtOH).

Table 2. Amount of dye desorbed from the TiO₂ surface in 1 N HCl (in EtOH).

Cell	CDCA (mM)	$\lambda_{\max}$	ϵ ($10^5 \text{ M}^{-1} \text{ cm}^{-1}$)	Dye Loading on TiO ₂ (10^{-7} mol/cm^2)
AK4	0	0.1429	1.44	0.862
AK4	0.1	0.1152	-	0.695
AM1	0	0.1143	1.55	0.641
AM1	0.1	0.0756	-	0.424
AM2	0	0.1032	1.64	0.547
AM2	0.1	0.0642	-	0.340
AM3	0	0.1116	1.68	0.577
AM3	0.1	0.0808	-	0.418

2.2.5 Computational Studies. Density functional theory (DFT) calculations for the N-functionalized aniline donor based **AM1**, **AM2** and **AM3** dyes (indoline donor without branching) were performed at B3LYP, 6-311G (++) level.⁵⁵⁻⁵⁹ The electronic distributions at the different electronic states (where the, isodensity surface value was fixed at 0.03) are provided in **Figure 7**. The electron density was localised on the squaraine unit in HOMO-1, whereas in the HOMO, the electron density was localised on the π -framework between the N-atom of both donor units. The electron density in LUMO was located on the D-A-D units, and in **AM1** and **AM2** dyes, the LUMO+1 was located on the aniline donor unit that was near to the carboxylic acid anchoring group, whereas in **AM3**, the LUMO+1 was localised over the aniline donor, as well as over the phenyl unit.

Dihedral angles between the donor and acceptor units are seen to play an important role in efficient charge injection process by facile electronic communication. The D-A, D- π -A dyes with high planarity, and low dihedral angles between the donor and acceptor units, show better DSSCs performance due to dense packing of dyes on the TiO₂.^{60,61} It has been found that the dihedral angles between the aniline donor and acceptor moieties of D-A-D based squaraine dye **AK2** (34.5°) compared to **AK1** dye (0.05°) play an important role in modulating the

photophysical as well as DSSCs performance.⁴³ The calculated dihedral angle values for **AM** dyes from the simulated geometry between the squaraine and aniline donor units was -36.63° , -41.26° and 37.98° for the **AM1**, **AM2** and **AM3** dyes, respectively (**Figure 8**).

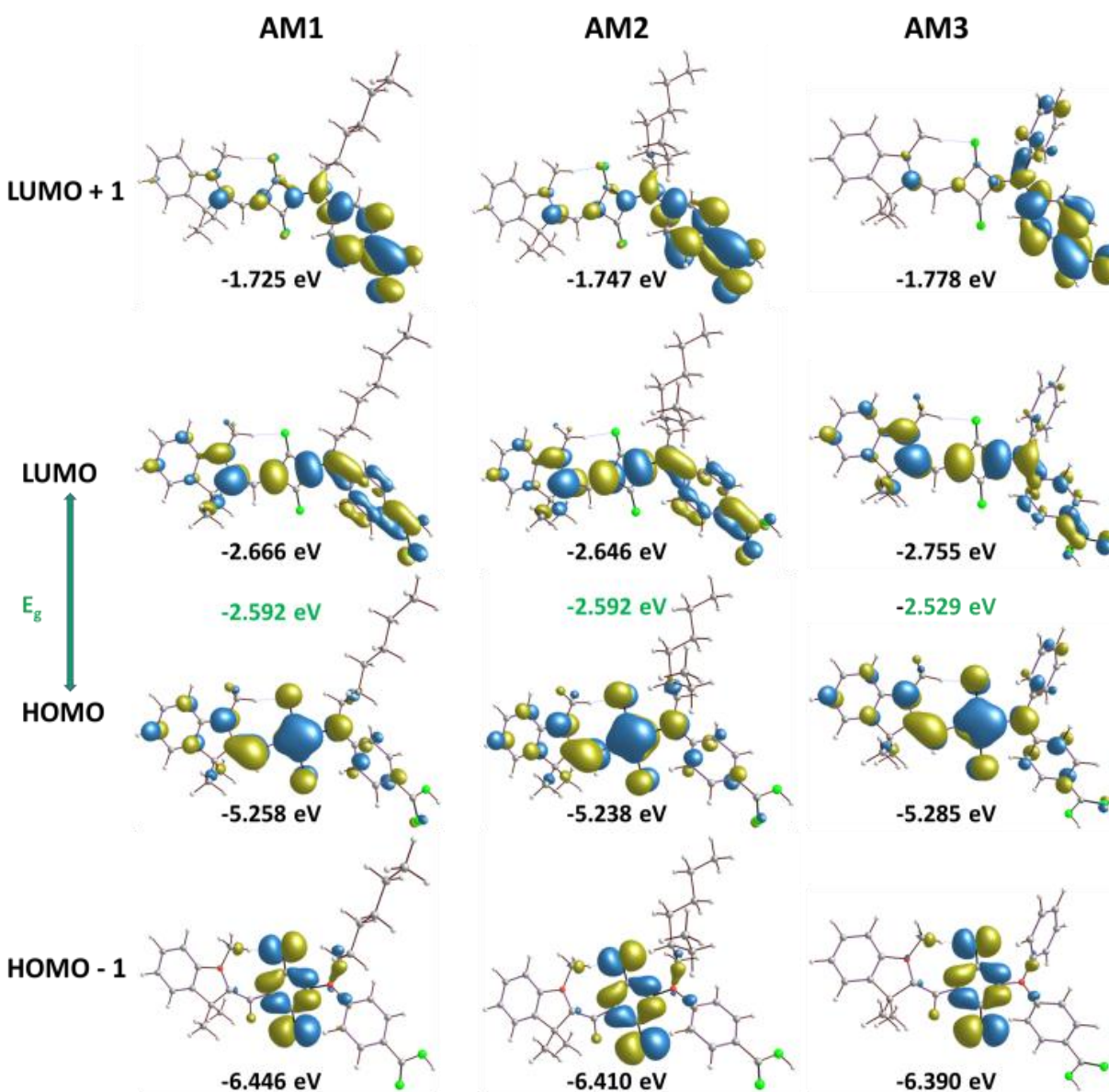


Figure 7. The frontier molecular orbital diagram of D-A-D based **AM1**, **AM2** and **AM3** dyes (alkyl groups at the indoline donor unit have not included for calculation).

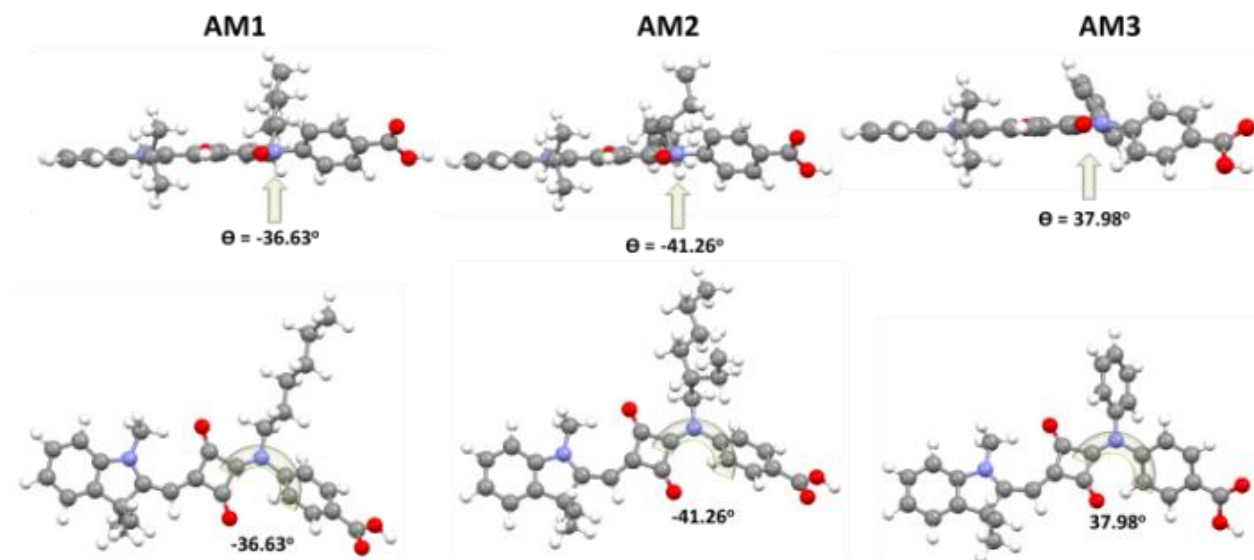


Figure 8. The dihedral angle for the **AM1**, **AM2** and **AM3** dyes.

2.2.6 Photovoltaic performance. The DSSC device fabrication and photovoltaic characterization of N-functionalized aniline donor-based **AM** dyes and **AK4** dye have been carried out with the I^-/I_3^- electrolyte, and the optimized device performance is provided in **Figure 9** and **Table 3**. Incorporation of the alkyl groups in the **AM1** and **AM2** dyes showed positive and phenyl group in **AM3** dye showed negative impact on the V_{OC} of the device compared to the **AK4** dye (which possess –methyl group at the aniline donor) respectively. N-functionalization in **AM** dyes showed negative impact on the J_{SC} , and efficiency of the device compared to the **AK4** dye due to the low dye-loading on the TiO_2 surface (**Figure 6** and **Table 2**). The maximum power conversion efficiency of 7.44, 7.22, 5.41, and 7.99% have been achieved for the **AM1**, **AM2**, **AM3** and **AK4** dyes in the absence of chenodeoxycholic acid (CDCA), respectively. Addition of CDCA helps to (i) fill the vacancy of the dye adsorbed TiO_2 film so that the back current (from the charge recombination of the electron in TiO_2 film to the electrolyte) is reduced and (ii) reduces the dye aggregation, on the TiO_2 surface. It was observed that increased CDCA concentration reduces the dye loading and J_{SC} also reduced, and hence we have utilized dye: CDCA ratio of 1:1 in the present studies. V_{OC} , J_{SC} and efficiency of the DSSC device decreased when the devices were fabricated with 0.1 mM of CDCA (1 equiv. with respect to dyes) for all the dyes. Further, N-hexyl, and branched N-ethyl-hexyl on the aniline unit for the **AM1** and

AM2 dyes showed improved V_{OC} due to better surface passivation and reduced J_{SC} due to low dye loading compared to **AK4** dye. Similarly, branched alkyl group for **AM2** dye near to the TiO_2 passivate the surface more effectively compared to the hexyl group of **AM1** dye and reduce the binding sites to the dye-anchoring, therefore, **AM2** dye showed improved V_{OC} and reduced J_{SC} compared to **AM1** dye. Further, the N-phenyl group on the aniline unit for the **AM3** dye showed reduced V_{OC} due to less passivated surface that promotes charge recombination and reduced J_{SC} due to low dye loading compared to **AM1** and **AK4** dyes. The observed V_{OC} for **AM** dyes and **AK4** were in the range of 806-865 mV such high values with iodide electrolyte have arisen from the avoided charge recombination process. Here, **AM2** dye with 2-ethylhexyl group on the N-atom of aniline donor gave the highest V_{OC} of 865 mV in AM dye series.

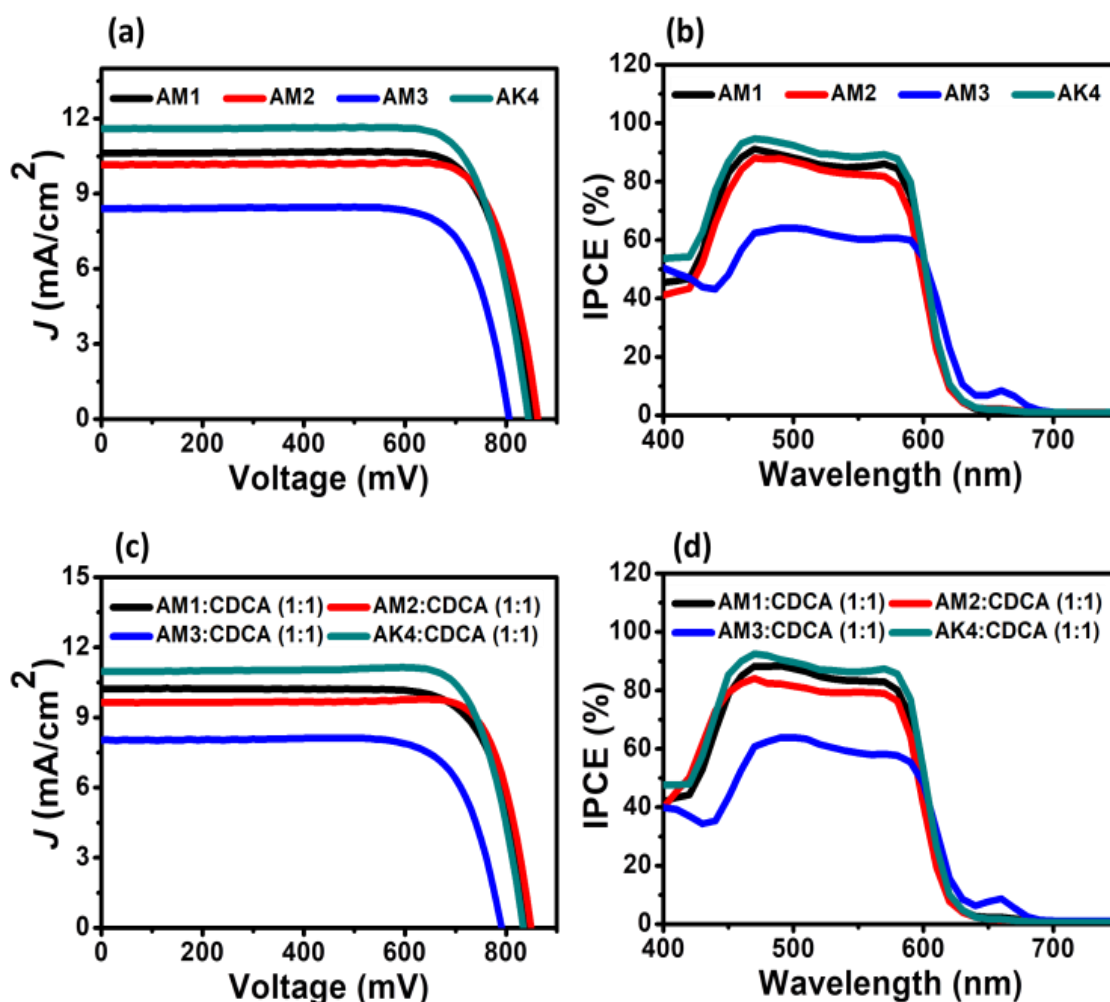


Figure 9. (a) I - V , and (b) IPCE curves for **AM** and **AK4** dyes without CDCA, (c) I - V , and (d) IPCE curves for **AM** and **AK4** dyes with CDCA in I^-/I_3^- electrolyte.

Table 3. Optimized DSSC performances of **AM** and **AK4** dyes with and without co-adsorbent (CDCA) in I^-/I_3^- electrolyte.

Dyes	CDCA (equiv.)	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AM1	0	855 ± 3	10.61 ± 0.23	79 ± 1.06	7.17 ± 0.27
AM1	1	844 ± 2	10.23 ± 0.17	77 ± 1.18	6.65 ± 0.22
AM2	0	863 ± 2	10.15 ± 0.20	80 ± 0.69	7.08 ± 0.14
AM2	1	849 ± 1	9.65 ± 0.25	83 ± 1.07	6.80 ± 0.27
AM3	0	806 ± 2	8.41 ± 0.16	77 ± 1.13	5.22 ± 0.19
AM3	1	790 ± 2	8.02 ± 0.22	76 ± 1.61	4.82 ± 0.24
AK4	0	844 ± 3	11.60 ± 0.18	79 ± 1.05	7.73 ± 0.26
AK4	1	833 ± 3	10.98 ± 0.13	80 ± 0.43	7.32 ± 0.15

Concentration of dyes 0.1 mM in $CH_3CN:CHCl_3$ (95:5), active area was 0.23 cm².

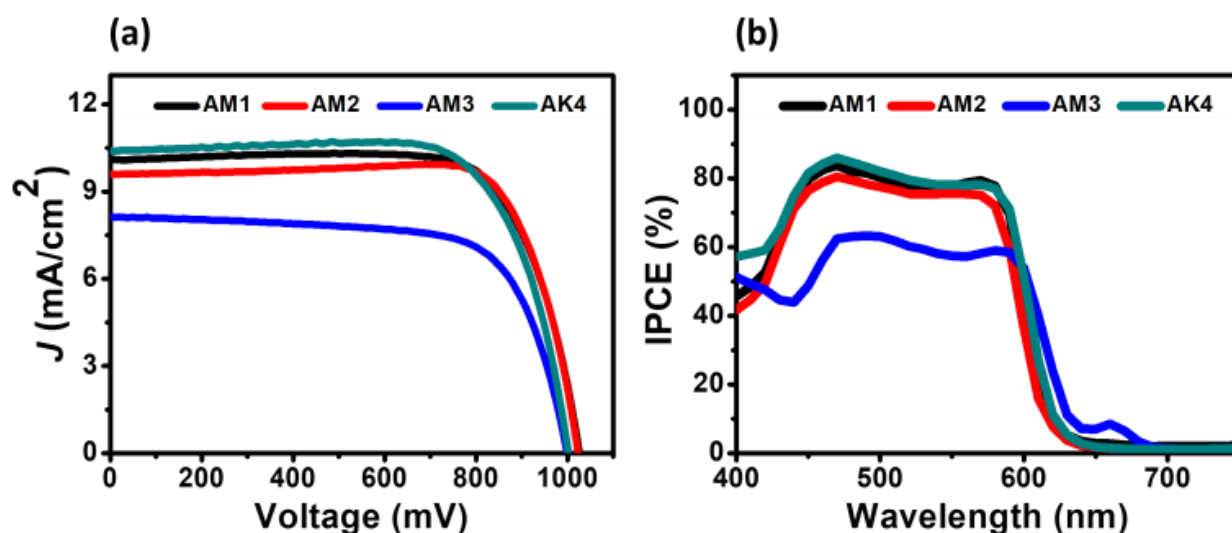


Figure 10. (a) I - V , and (b) IPCE curves for **AM** and **AK4** dyes in the absence of CDCA with $[Cu(tmby)_2]^{+/2+}$ electrolyte.

The V_{OC} of the DSSC devices by employing I^-/I_3^- redox shuttle were found to be limited to 0.8–0.86 V due to the large overpotential associated with the dye regeneration process. To overcome this limitation, Co and Cu, complexes have attracted attention due to the small overpotentials required for the dye regeneration process, weak visible light absorption, and stability compared to the iodine based redox shuttle.⁶² However, it also requires the HOMO energy levels

of the dyes need to possess more positive, and the present set of dyes fulfil such requirements (Figure 5b).

Hence, the DSSC devices have been fabricated for **AM** and **AK4** dyes with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte and PEDOT counter electrode, and the optimized device performance is provided in **Figure 10** and **Table 4**. Similar to the I^-/I_3^- electrolyte, $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte also showed same impact of N-functionalization in **AM** dyes on the V_{OC} and J_{SC} of the DSSC devices. The maximum power conversion efficiency of 8.05, 7.96, 5.84, and 7.98%, and V_{OC} of 1030, 1025, 1001, and 1009 mV have been achieved for the **AM1**, **AM2**, **AM3**, and **AK4** dyes in the absence of CDCA, respectively. Although, variations in V_{OC} and J_{SC} of the device have been observed by N-alkylation on the aniline donor for **AM1**, **AM2**, and **AK4** dyes, however, power conversion efficiencies have not changed much. Here, **AM1** dye showed the highest DSSC device efficiency of 8.05%, and V_{OC} of 1030 mV for D-A-D based unsymmetrical squaraine dyes for the first time. IPCE response of the **AM** and **AK4** dyes showed the maximum participation from the aggregated structures in the generation of photocurrents, and the highest IPCE response has been observed for the **AK4** dye with both I^-/I_3^- and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes and reason for the high photocurrent. The IPCE responses were decreased when DSSC devices were sensitized with 0.1 mM of CDCA compared to without CDCA in I^-/I_3^- electrolyte. Further, dye desorption studies showed that reduced dye loading in the presence of CDCA was the reason for the decreased J_{SC} and efficiency for **AM** and **AK4** dyes in I^-/I_3^- electrolyte (**Figure 6** and **Table 2**). Hence, the alkyl group wrapped dyes (**AM1-AM3**) structures were inherently optimized for better monolayer formation and for enhanced photocurrent generation.

Table 4. Optimized DSSC performances of **AM** and **AK4** dyes in the absence of CDCA with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte. Concentration of dyes 0.1 mM in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (95:5), active area was 0.23 cm^2 .

Dyes	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff (%)	η (%)
AM1	1026 ± 4	10.10 ± 0.15	75 ± 1.22	7.77 ± 0.28
AM2	1023 ± 2	9.61 ± 0.06	79 ± 1.31	7.76 ± 0.20
AM3	999 ± 2	8.12 ± 0.11	70 ± 0.92	5.67 ± 0.17
AK4	1002 ± 7	10.40 ± 0.13	74 ± 1.14	7.71 ± 0.27

The **AK4** dye gave less V_{OC} with cobalt electrolyte than iodide electrolyte, due to interaction between dye and cobalt electrolyte. The highest value of V_{OC} (1009 mV) was achieved with Cu(I/II) electrolyte which was investigated for the first time (**Figure 11** and **Table 5**).

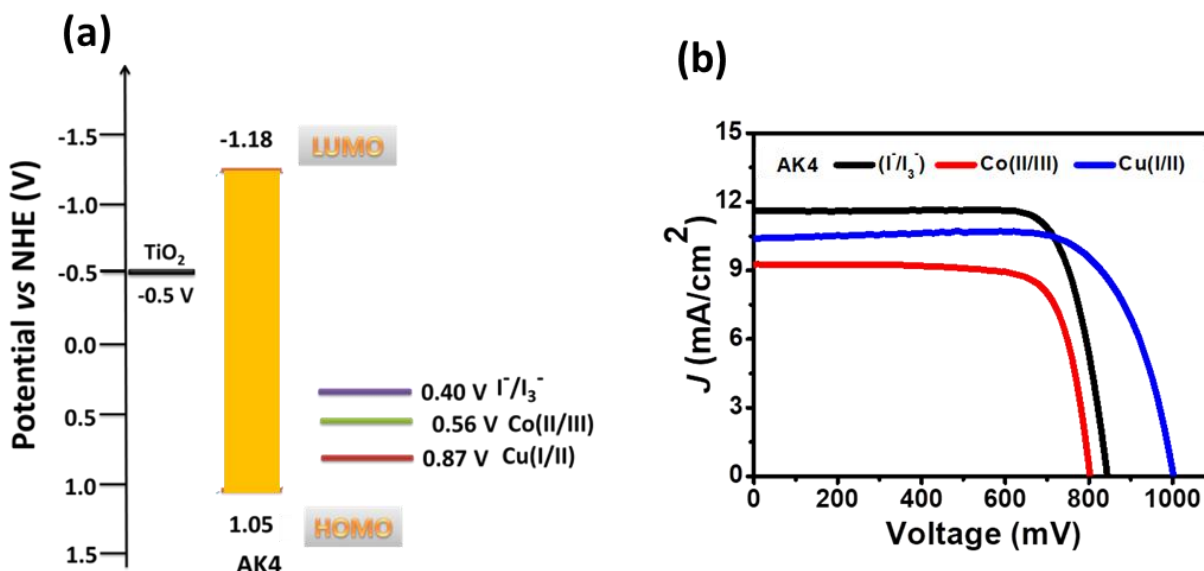


Figure 11. (a) Energy level diagram of the **AK4** and redox level of various electrolytes, (b) I - V curve of **AK4** dye with I^-/I_3^- , $[Co(bpy)_3]^{2+/3+}$, and $[Cu(tmby)_2]^{+/2+}$ electrolytes.

Table 5. DSSC device performance of **AK4** dye with various electrolytes.

Dyes	Electrolyte	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AK4	I^-/I_3^-	844 ± 3	11.60 ± 0.18	79 ± 1.05	7.73 ± 0.26
AK4	Co (II/ III)	802 ± 2	9.27 ± 0.10	78 ± 0.95	5.80 ± 0.15
AK4	Cu (I/II)	1002 ± 7	10.40 ± 0.13	74 ± 1.14	7.71 ± 0.27

2.2.7 Electrochemical Impedance Spectroscopy (EIS). The EIS characterization for N-functionalized aniline donor based **AM** dyes and **AK4** dye have been carried out with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ and I^-/I_3^- electrolytes in dark experimental condition with the different applied potentials (Figure 12, 13, 14, 15 and Table 6, 7).⁶³

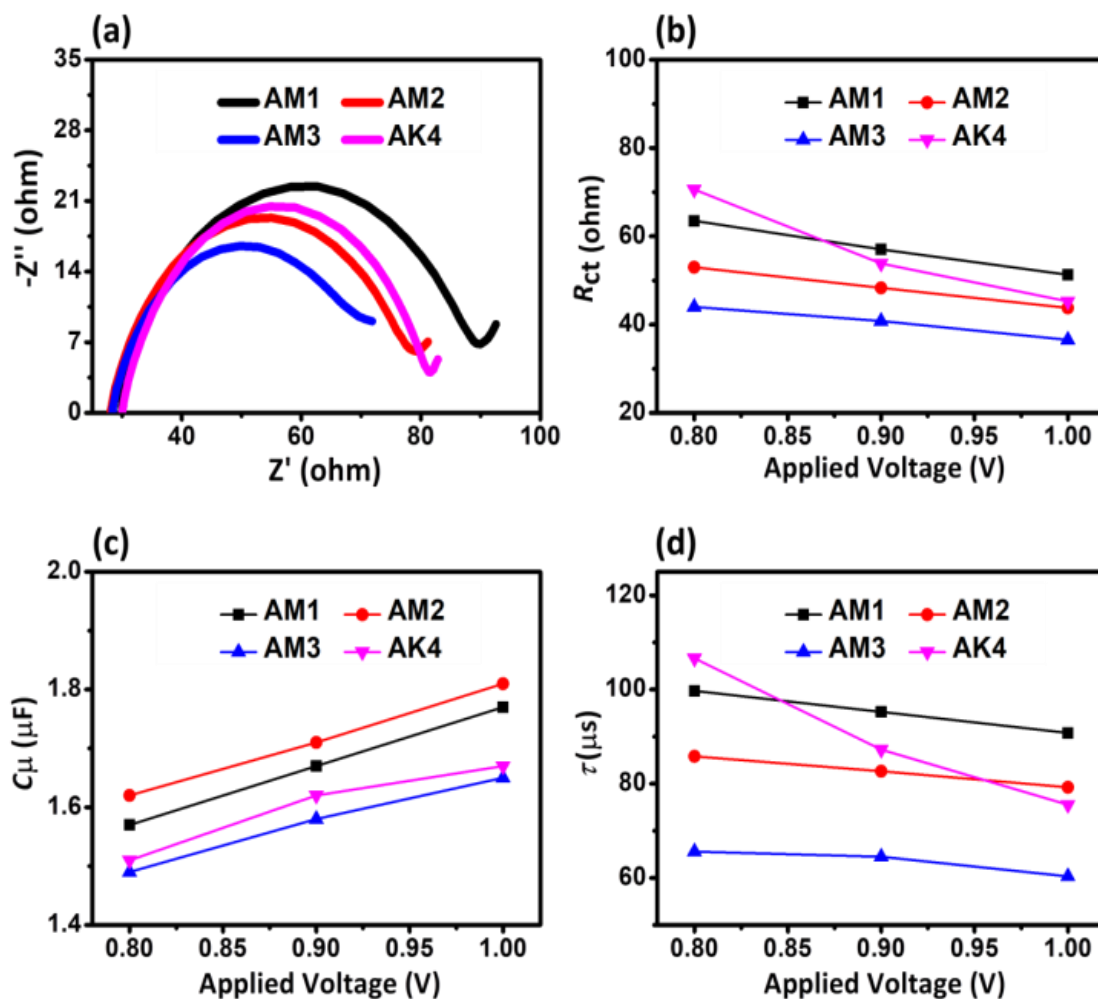


Figure 12. (a) Nyquist plot (at 1.0 V applied potential), (b) charge recombination resistance, (c) chemical capacitance, and (d) electron lifetime of **AM** and **AK4** dyes with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte, as a function of applied potential without CDCA.

Semicircle corresponds to charge transfer resistance between the counter-electrode and electrolytes have not been found for all the dyes in the Nyquist plots for copper electrolyte. **AM1** dye showed relatively high charge recombination resistance (R_{ct}) with increased applied potential compared to the other dyes, which is the result of better surface passivation. **AM2** dye showed

better chemical capacitance (C_{μ}) values at different applied potentials compared to other dyes and following the order of **AM2** (1.81 μF)>**AM1** (1.77 μF)>**AK4** (1.67 μF)>**AM3** (1.65 μF). Electron lifetime (τ) has been calculated by multiplying the R_{ct} and C_{μ} , and the highest electron lifetime of 90.80 μs have been found for **AM1** dye. Further, the maximum R_{ct} values have been obtained without CDCA for all the dyes and follow the order of **AK4** (25.25 ohm) >**AM1** (19.43 ohm) >**AM2** (15.80 ohm) >**AM3** (11.26 ohm) with I^-/I_3^- electrolyte. Further chemical capacitance (C_{μ}) and electron lifetime (τ) are other parameters that affect the device performance by the extent of surface passivation as the dipole moments of the dyes were almost similar for **AM1** and **AM3**. Here, C_{μ} and τ are following the same trend of **AK4**> **AM1**> **AM2**> **AM3** as R_{ct} for all the dyes. The maximum C_{μ} have been observed for the **AK4** dye with I^-/I_3^- electrolyte. The lifetime of electrons in TiO_2 were estimated to be 25.25 ms for **AK4** dye, 19.43 ms for **AM1** dye, 15.80 ms for **AM2** dye and 11.26 ms for **AM3** dye. The highest R_{ct} and electron lifetime values obtained for the **AK4** dye may be the reason for the high J_{SC} and efficiency compared to the **AM** dyes with I^-/I_3^- electrolyte.

Table 6. EIS parameters of **AM** and **AK4** dyes with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte at 1.0 V applied potential (with PEDOT counter electrode).

Dye	R_{ct} (ohm)	C_{μ} (mF)	τ (ms)
AM1	51.30	1.77	90.80
AM2	43.78	1.81	79.24
AM3	36.55	1.65	60.31
AK4	45.24	1.67	75.55

$$\tau = R_{ct} \times C_{\mu}$$

Further, EIS characterization of **AM** and **AK4** dyes in dark with I^-/I_3^- and in real operating conditions with both electrolytes have been carried out and provided in **Figure 16** and **Table 8**. Significant differences have been noted in the EIS parameters (R_{ct} , C_{μ} , and τ) with copper electrolyte compared to I^-/I_3^- electrolyte, which due to change in the interfacial contacts. The N-functionalization of aniline with linear, branched alkyl and aryl groups make significant impact on the charge recombination resistance R_{ct} (**Table 6**) which led to observed difference in the

photovoltaic parameters for **AM1-3** and **AK4** dyes. Though the dihedral angle for the **AK4** (34.5°), **AM1** (-36.63°), and **AM3** (37.98°) are almost similar, having phenyl group at the N-atom of aniline showed the decreased DSSC device performance (also dye loading of **AM3** is comparable with **AM1**). Hence the reduced device performance of **AM3** is due to the charge transfer kinetics at the Dye-TiO₂ interface, EIS capture such event, for example the R_{ct} for the device fabricated with **AM3** dye is low at a particular bias potential compared to the devices sensitized with other dyes (in both iodide and copper-based electrolyte).

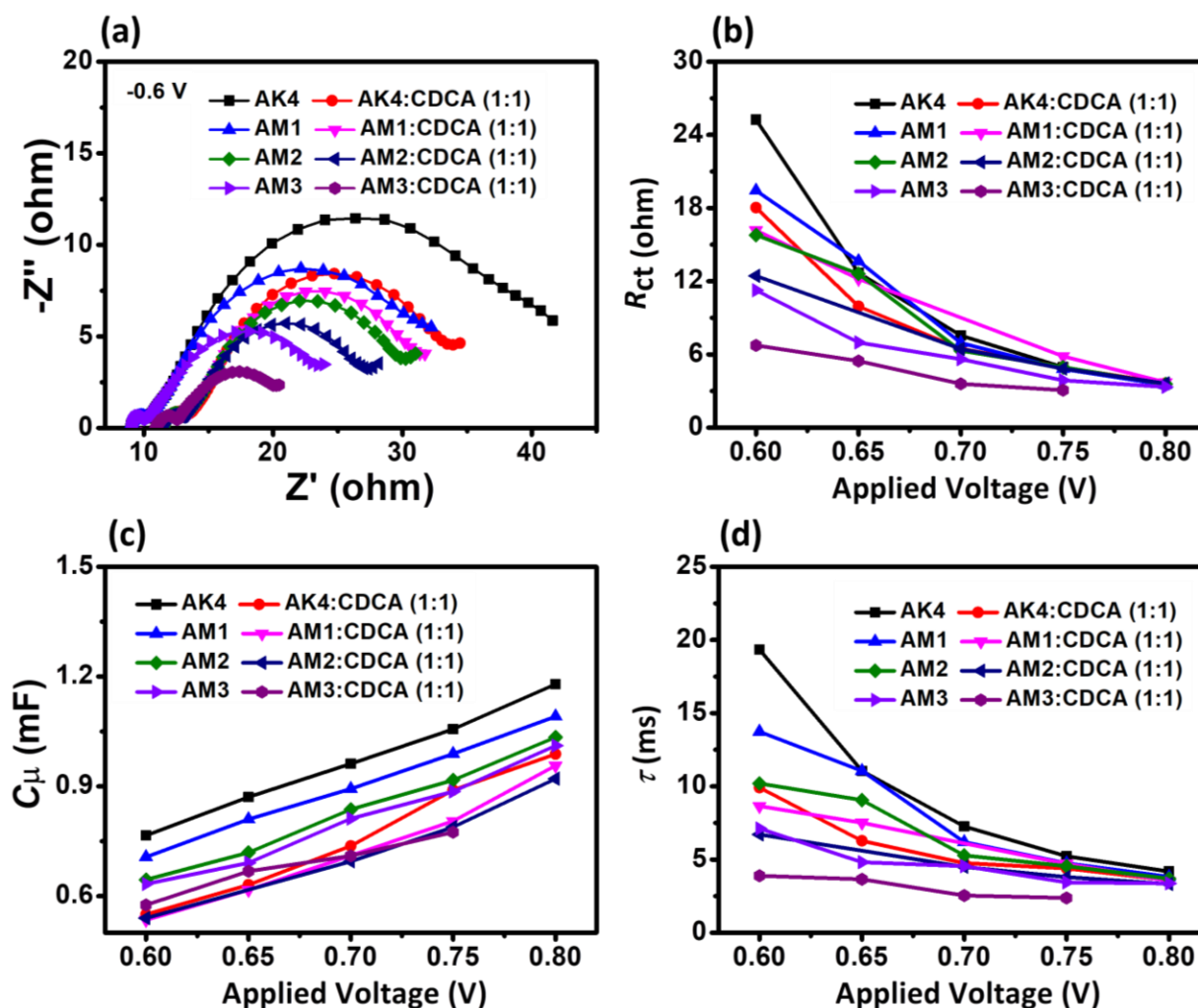


Figure 13. (a) Nyquist plot, (b) charge recombination resistance, (c) chemical capacitance and (d) lifetime of electron of **AM** and **AK4** dyes with and without CDCA with (I^-/I_3^-) electrolyte.

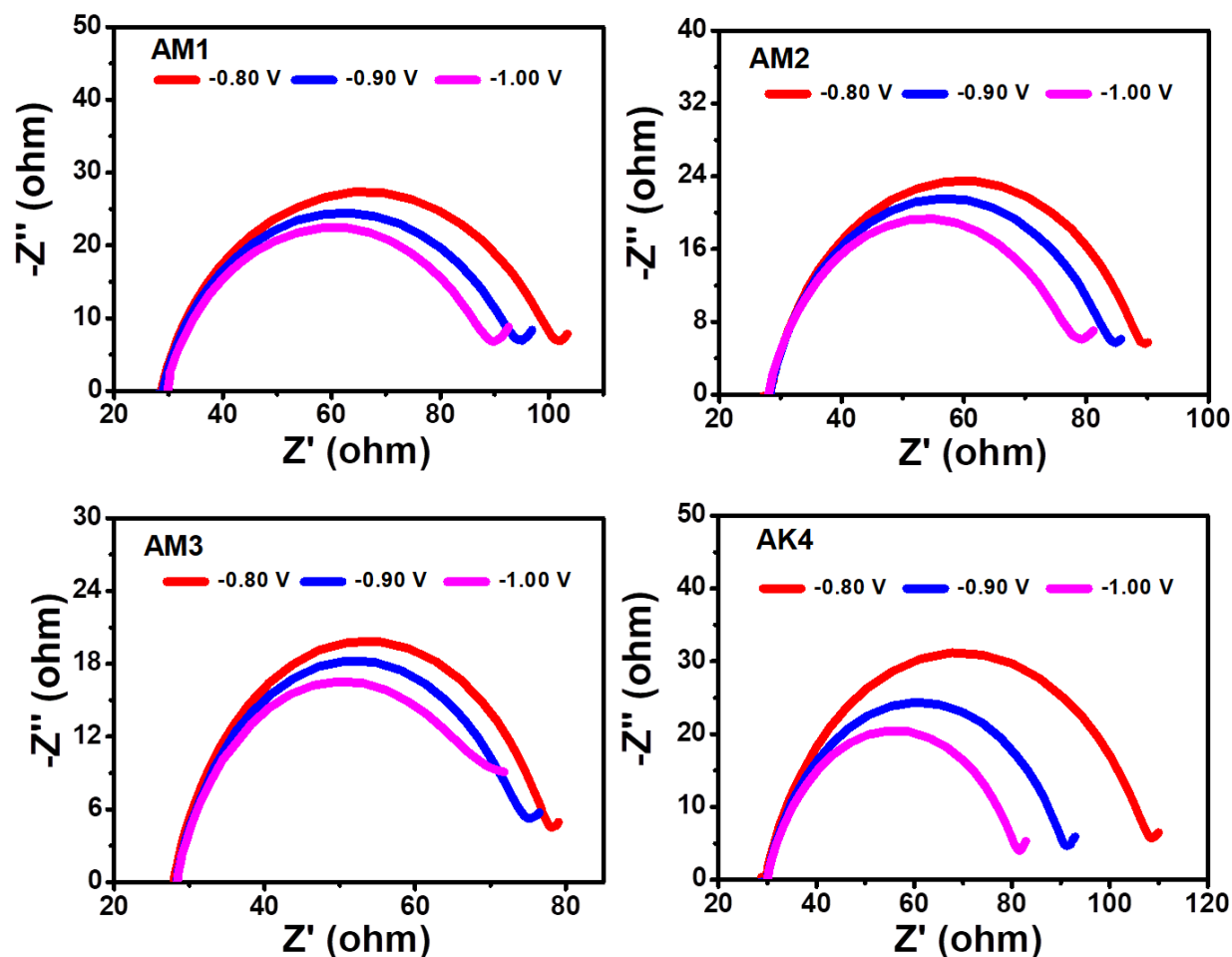


Figure 14. Nyquist plot of **AK4** and **AM** dyes vs applied bias with Cu(I/II) electrolyte in the absence of CDCA.

Table 7. EIS parameters of DSSC device made with the **AM** and **AK4** dyes in dark with the applied potential of 0.60 V.

Dye	R_{ct} (ohm)	C_{μ} (mF)	τ (ms)
AM1	19.43	0.707	13.74
AM1:CDCA (1:1)	16.18	0.535	8.66
AM2	15.80	0.645	10.19
AM2:CDCA (1:1)	12.44	0.540	6.72
AM3	11.26	0.633	7.13
AM3:CDCA (1:1)	6.75	0.576	3.89
AK4	25.25	0.766	19.34
AK4:CDCA (1:1)	18.04	0.550	9.93

$$\tau = R_{ct} \times C_{\mu}.$$

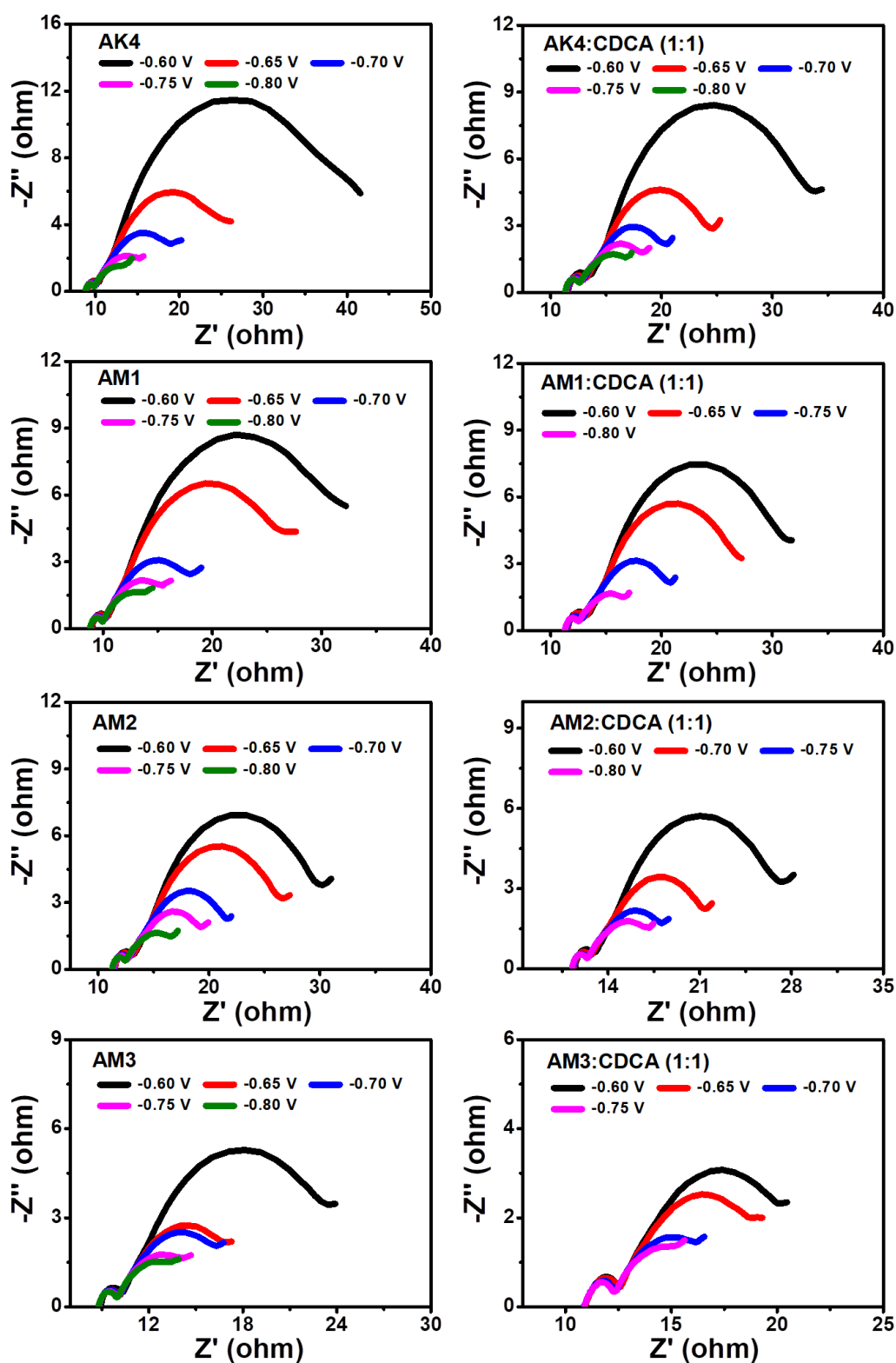


Figure 15. Nyquist plot of AK4 and AM dyes vs applied potential with (Γ/I_3^-) electrolyte, with and without CDCA.

Hence having phenyl group at the aniline donor site enhances the charge recombination. Further, despite having similar steric factors on the indoline based donors, having a linear and branched alkyl groups such as n-hexyl (**AM1**) and 2-ethylhexyl (**AM2**) groups at the aniline donor site modulate the dye loading capabilities compared to **AK4** on TiO_2 . We believe that the alkyl groups at the aniline may block/shield the dye anchoring site which in turn reduce the charge recombination process, and it can be explained based on enhanced V_{OC} obtained for **AM1** and **AM2** (in both iodide and copper electrolytes) compared to **AK4**.

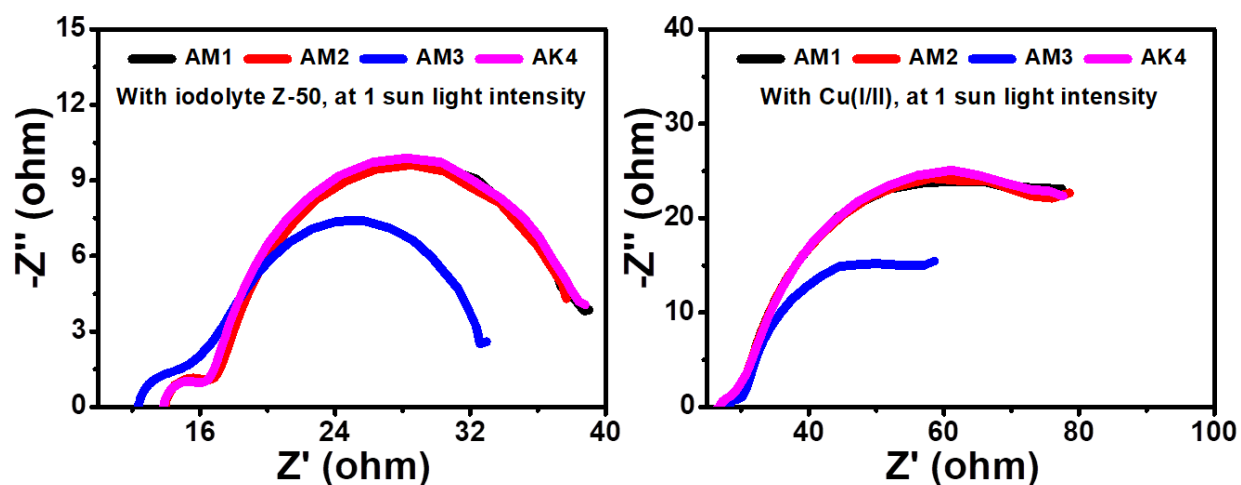


Figure 16. Nyquist plot of **AK4** and **AM** dyes at 1 sun light intensity without CDCA.

Table 8. EIS parameters of **AM** and **AK4** dyes in the real operating conditions (1 Sun).

Dye	R_{ct} (ohm)		C_{μ} (mF)		τ (ms)	
	$\bar{I}/\bar{I}_3$	Cu(I/II)	$\bar{I}/\bar{I}_3$	Cu(I/II)	$\bar{I}/\bar{I}_3$	Cu(I/II)
AM1	20.54	49.98	0.215	0.139	4.42	6.94
AM2	20.13	50.76	0.216	0.140	4.35	7.10
AM3	15.48	30.57	0.166	0.117	2.57	3.58
AK4	20.91	51.38	0.213	0.124	4.46	6.37

$$\tau = R_{\text{ct}} \times C_{\mu}.$$

2.3 CONCLUSION

In summary, donor-acceptor-donor (D-A-D) based visible-light active squaraine sensitizers **AM1**, **AM2** and **AM3** with N-functionalized aniline donor have been designed and synthesized. These dyes possess a high extinction coefficient in the visible region of the solar spectrum. A systematic structure-property relationship studies have been performed for **AM** dyes and model dye **AK4** with I^-/I_3^- and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes. Here, aniline unit functionalized with the -hexyl and -ethylhexyl for **AM1** and **AM2** dyes showed enhanced V_{OC} , and decreased J_{SC} and efficiencies compared to the aniline unit functionalized with the -methyl for **AK4** dye with I^-/I_3^- electrolyte in the absence of CDCA due to low dye loading, respectively. The photovoltaic parameters decreased upon the addition of CDCA for **AM** and **AK4** dyes. Whereas, device fabricated with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte showed an enhanced device efficiency of 8.05, 7.96, 5.84, and 7.98% for **AM1**, **AM2**, **AM3**, and **AK4** dyes in the absence of CDCA, respectively. Further, aniline donor functionalized with the methyl or alkyl groups showed their importance to improve the photovoltaic parameters of dyes over the aryl functionalization. Here, all the **AM** dyes and **AK4** dye were proved their excellent compatibility with I^-/I_3^- and $\text{Cu}^+/\text{Cu}^{2+}$ electrolytes which is rare especially for zwitterionic dyes. Where, normal-alkyl group functionalized D-A-D based unsymmetrical squaraine dye **AM1** has achieved the maximum DSSC device efficiency of 8.05%, and V_{OC} of 1030 mV for the first time with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte along with the PEDOT as a cathode material.

2.4 EXPERIMENTAL SECTION

Semisquaric acid with the alkyl group wrapped indoline unit, compound 1, and 2-ethylhexanal were synthesized by following the procedure reported in the literature,^{43,53,54} and 4-aminobenzoic acid, hexanal, aniline and ethyl-4-bromobenzoate are commercially available. The dyes **AM1**, **AM2** and **AM3** were synthesized by condensing the alkyl group wrapped semisquaric acid with the aniline carboxylic acid derivatives under azeotropic removal of water.⁴⁵

2.4.1 General methods

Chemicals and reagents required for the synthesis of **AM** dyes were purchased from commercial sources, and standard procedures are used for drying PhMe. ¹H and ¹³C NMR were recorded on Bruker NMR spectrometers AV 200 MHz, AV 400 MHz, and AV-500 MHz, in CDCl₃. The Bruker FT-IR spectrometer has been used for IR studies. MALDI-TOF-MS was recorded on ABSciex 5800 MALDI TOF mass spectrometer. 4-hydroxy-3-5-dimethoxycinnamic acid (Sinapic acid) has been used for matrix preparation. All the quantum mechanical calculations were conducted by using the Gaussian 09 software. The optimization of the ground-state geometry was carried out at the Density Functional Theory (DFT) level, using the B3LYP hybrid functional and the 6-311G(++) atomic basis set.

Absorption spectra of **AM** dyes were recorded on SPECORD[®] 210/ PLUS, Analytikjena UV-Visible spectrophotometer at room temperature. Emissions of **AM** dyes were recorded on Edinburgh spectrofluorometer FS5 at room temperature. For the light-harvesting efficiency (LHE) calculation, 6 μm thin film of TiO₂ coated on the transparent glass slide was dipped in 0.1 mM **AM** dye solution for 12 h at room temperature, and absorption spectra are converted into light-harvesting efficiency profile ($LHE = 1 - 10^{-A}$). To calculate the charge injection efficiency (CIE) of the squaraine dyes, a steady state emission experiment has been carried out at the metal-oxide surface (TiO₂ and ZrO₂) with the sensitization time of 5 min in 0.1 mM dye solution in CH₃CN. Here, metal-oxide coated on glass substrate was first dipped in the 2 mM CDCA solution prepared in CH₃CN for 12 h to saturate the surface with CDCA, and then dipped in the squaraine dye stock-solution prepared in CH₃CN for 5 min at room temperature.

Differential pulse voltammetry (DPV) and cyclic voltametric (CV) studies of **AM** dyes were performed on BioLogic SP300 potentiostat in anhydrous CH₂Cl₂ solvent, at 25 °C under an inert

atmosphere, where platinum wire as a working electrode, platinum foil as a counter electrode, non-aqueous Ag/Ag^+ (0.01M) as a reference electrode, TBAClO_4 (0.05 M) as supporting electrolyte, and Ferrocene/Ferrocene⁺ as the internal-standard, scan rate of 100 and 50 mV s⁻¹ for DPV, and CV respectively.

Electrochemical impedance measurements (EIS) were performed using a BioLogic SP300 potentiostat equipped with a frequency response analyzer. EIS studies were carried out in the dark with various applied potential and frequency ranges from 3 MHz to 10 mHz with sinus amplitude of 10 mV. For *I-V* characteristics of the cells were measured by using PHOTO EMISSION TECH (PET, CT200AAA, USA) solar-simulator, and IPCE measurements were carried out with a Newport QE measurement kit. $[\text{Cu}(\text{tmby})_2]^{+/2+}$ based redox couple were prepared from 0.20 M bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(I) bis(trifluoromethanesulfonyl)imide (procured from Dyenamo), 0.04 M bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(II) bis[bis(trifluoromethanesulfonyl)imide] (procured from Dyenamo), 0.10 M Bis(trifluoromethylsulfonyl)amine lithium salt, and 0.60 M 4-*tert*-butylpyridine in acetonitrile (electrolyte composition was made in glove-box)

Cleaned fluorine-doped SnO_2 glass (FTO glass; 8- 10 Ω /sq; Pilkington TEC 7) with 2 % mucasol in water, de-ionized water, and isopropanol were treated for 30 min with 50 mM aqueous TiCl_4 solution where the temperature was 70 °C. The substrate washed with de-ionized water and ethanol, dried at 110 °C for 10 min on hot plate. On the conducting side of the FTO a paste of TiO_2 nanocrystal (< 20 nm, Ti-Nanoxide T/SP, Solaronix) was coated by using the doctor-blade technique, kept for 10 min in air and then annealed at 125 °C in air for 20 min. Scattering layer TiO_2 paste (WER2-O, Dyesol) were coated with the same technique then annealed for 10 min at 125 °C in air. Resultant substrates were sintered with the heating rate of 5 °C per min in air at 325, 375, 450, and 500 °C for 5, 5, 15, and 15 min, respectively. Once substrate temperature reached between 30-35 °C, again treated for 30 min with 50 mM aqueous TiCl_4 solution at 70 °C followed by washing with de-ionized water and ethanol and sintering at 500 °C for 30 min. Once substrate temperature reached between 30-35 °C, cells were immersed in 0.1 mM dye solution of **AM** dyes for 12 h. Iodolyte Z-50 (Solaronix) and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ (Dyenamo) have been used as an electrolyte, 0.23 cm² was the active area and 0.36 cm² was the area of black mask.

Electropolymerization of EDOT onto the FTO was performed on BioLogic SP300 potentiostat at 25 °C, where cleaned FTO have been used as a working electrode, platinum foil as a counter electrode, non-aqueous Ag/Ag^+ (0.01 M) as a reference electrode. Solution for electropolymerization were prepared from a mixture of 0.01 M of 3,4-ethylenedioxythiophene (EDOT) and 0.1 M of lithium perchlorate (LiClO_4) in anhydrous acetonitrile by sonicating for 5 min. Electropolymerization were performed under in potentiostatic mode of chronoamperometry with 2.0 V voltage for 120 seconds, deposited films onto the FTO were washed with acetonitrile and dried.

2.4.2 Synthesis.

4-(Hexylamino) benzoic acid (2): 4-Amino benzoic acid (1.0 g, 10.0 mmol) was dissolved in 20 mL of EtOH and cooled to 0 °C in an ice-bath and further hexanal (1.3 g, 10.0 mmol) was added. Sodium cyanotrihydroborate (0.63 g, 10.0 mmol) was dissolved in 10 mL of EtOH and added to the above reaction mixture drop-wise and stirred for 1 h at 0 °C, which was further stirred for 12 h at room temperature. Solvents was removed under reduced pressure and obtained white solid was treated with 1 N aqueous HCl and stirred for 15 min. White precipitate was filtered and washed with water until the filtrate become neutral. Compound 2 has been recrystallized with EtOH: H_2O (4: 1) and dried under reduced pressure.⁵³ Yield: 1.0 g, 45%. ^1H NMR (200 MHz, CDCl_3): δ 7.93 (d, J = 8.82 Hz, 2H), 6.56 (d, J = 8.82 Hz, 2H), 3.18 (t, J = 7.06 Hz, 2H), 1.54–1.80 (m, 2H), 1.25–1.49 (m, 6H), 0.91 (t, J = 6.91 Hz, 3H).

4-((2-Ethylhexyl)amino) benzoic acid (3): 4-Amino benzoic acid (1.0 g, 10.0 mmol) was dissolved in 20 mL of EtOH and cooled to 0 °C and 2-ethylhexanal (1.15 g, 8.75 mmol) was added. Sodium cyanotrihydroborate (0.46 g, 7.29 mmol) was dissolved in 10 mL of EtOH and added to the above reaction mixture drop-wise and stirred for 1 h at 0 °C, which was further stirred for 12 h at room temperature. Solvents was removed under reduced pressure and obtained white solid was treated with 1 N aqueous HCl and stirred for 15 min. White precipitate was filtered and washed with water until the filtrate become neutral. Organic layers were separated with CH_2Cl_2 (30 mL $\times$ 3), dried over Na_2SO_4 . Column chromatography has been subjected with pet ether and EtOAc to obtain compound 3.52 Yield: 1.0 g, 55%. ^1H NMR (400 MHz, DMSO-

d₆): δ 11.95 (br. s., 1H), 7.66 (m, J = 8.71 Hz, 2H), 6.57 (m, J = 8.82 Hz, 2H), 6.39 (t, J = 5.35 Hz, 1H), 2.96 (t, J = 5.84 Hz, 2H), 1.47-1.64 (m, 1H), 1.20–1.39 (m, 8H), 0.81–0.91 (m, 6H).

4-(Phenylamino)benzoic acid (4): Compound 4 has been synthesized by following the procedure provided in literature.⁵⁴ Ethyl-4-bromobenzoate was coupled with aniline by Pd catalysed Buchwald-Hartwig amination reaction conditions, and the resulted ester derivative was hydrolysed by NaOH.

Step 1: Ethyl-4-bromobenzoate (0.5 g, 2.2 mmol), aniline (0.254 g, 2.72 mmol), CS₂CO₃ (1.06 g, 3.27 mmol), rac-BINAP (0.1 g, 0.16 mmol), Pd(OAc)₂ (0.04 g, 0.178 mmol) were dissolved in 10 mL of DMF and heated at 120 °C for 30 h. The reaction mixture was cooled, and solvents were removed under reduced pressure. Thin layer chromatography of the reaction mixture showed only one major product and the crude mixture has been used for next step without purification.

Step 2: Crude mixture (0.4 g) was dissolved in THF: MeOH (1:1) 80 mL and added 4 M NaOH (20% w/w in water, 20 mL), and heated to 40 °C for 4 h, then checked TLC that indicate the completely hydrolysis of the ester group. The reaction mixture was cooled to 0 °C and carefully neutralized with 1 M HCl solution (1 mL) then organic layer was separated with using diethyl ether (30 mL $\times$ 3) and dried over Na₂SO₄ and solvent removed under reduced pressure and purified with column using pet ether and EtoAc. Yield: 0.23 g, 40%. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.70 Hz, 2H), 7.37 (t, J = 8.70 Hz, 2H), 7.21 (d, J = 8.24 Hz, 2H), 7.11 (d, J = 7.33 Hz, 1H), 7.01 (d, J = 8.70 Hz, 2H), 6.11 (br. s., 1H).

General synthetic procedure for the AM dyes:

AM dyes have been synthesized by the condensation reaction between the semisquaric acid, **1**, and the respective aniline donors (**2**, **3** and **4**) in PhMe and *n*-BuOH under reflux reaction conditions. The water formed during the reaction was continuously removed by utilizing Dean-Stark distillation apparatus. The reaction mixture was purified by column chromatography (SiO₂, 100-200 mesh, MeOH and CH₂Cl₂) to obtain the required dye.^{43,46}

4-((4-Carboxyphenyl)(hexyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-ylidene)methyl)-3-

oxocyclobut-1-en-1-olate (AM1): Compound **1** (0.2 g, 0.28 mmol), 4-(hexylamino)benzoic acid (0.062 g, 0.28 mmol) (SiO₂, 100-200 mesh, 2.5% MeOH and 97.5% CH₂Cl₂). Yield: 0.12 g, 46%. Mp: 128 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 8.24 Hz, 2H), 7.37 (d, *J* = 8.70 Hz, 2H), 7.31 (t, *J* = 7.78 Hz, 1H), 7.16 (t, *J* = 7.33 Hz, 1H), 6.96 (d, *J* = 7.78 Hz, 1H), 6.84 (d, *J* = 8.70 Hz, 1 H), 5.98 (s, 1H), 4.47 (t, *J* = 6.87 Hz, 2H), 4.12 (t, *J* = 5.06 Hz, 1H), 3.96 (t, *J* = 6.18 Hz, 2H), 3.85 (t, *J* = 4.81 Hz, 1H), 3.59–3.78 (m, 6H), 2.79–3.00 (m, 2H), 1.87–2.06 (m, 2H), 1.72–1.82 (m, 2H), 1.61–1.72 (m, 3H), 1.33–1.44 (m, 6H), 1.24–1.27 (m, 19H), 1.20 (d, *J* = 4.58 Hz, 10H), 1.07 (br. s., 12H), 0.84–0.88 (m, 12H), 0.67–0.81 (m, 4H), 0.46 (t, *J* = 7.55 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 13.94, 14.09, 22.46, 22.62, 22.65, 23.97, 25.87, 27.10, 27.19, 28.93, 29.28, 29.31, 29.41, 29.49, 29.60, 29.68, 31.33, 31.84, 31.87, 40.10, 43.58, 58.46, 61.62, 69.77, 70.20, 70.51, 70.71, 72.52, 86.31, 109.01, 113.60, 113.71, 113.78, 122.20, 123.38, 123.64, 126.96, 127.62, 131.11, 138.63, 142.73, 144.11, 169.12, 175.22, 180.72; IR (cm⁻¹): 2954, 2919, 2851, 1750, 1704, 1589, 1562, 1488, 1469, 1433, 1410, 1354, 1310, 1269, 1243, 1208, 1187, 1176, 1130, 1104, 1078, 1014, 963, 939; MALDI-TOF(*m/z*): [M+H]⁺ calculated for C₆₀H₉₅N₂O₄, 907.7214; found, 907.5406.

4-((4-Carboxyphenyl)(2-ethylhexyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-

ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AM2): Compound **1** (0.2 g, 0.277 mmol), 4-((2-ethylhexyl) amino)benzoic acid (0.069 g, 0.277 mmol), column chromatography (SiO₂, 100-200 mesh, 2.5% MeOH and 97.5% CH₂Cl₂). Yield: 0.110 g, 42%, Mp: 108 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 8.24 Hz, 2H), 7.36 (d, *J* = 8.70 Hz, 2H), 7.31 (t, *J* = 8.24 Hz, 1H), 7.15 (t, *J* = 7.56 Hz, 2H), 6.95 (d, *J* = 7.79 Hz, 1H), 6.84 (d, *J* = 8.70 Hz, 1H), 5.96 (s, 1H), 4.36–4.56 (m, 2H), 4.12 (t, *J* = 4.81 Hz, 1H), 3.95 (t, *J* = 6.87 Hz, 2H), 3.85 (t, *J* = 4.81 Hz, 1H), 3.70–3.77 (m, 2 H), 3.59–3.70 (m, 7H), 2.89 (t, *J* = 11.22 Hz, 2H), 1.89–2.03 (m, 2 H), 1.70–1.83 (m, 2H), 1.49–1.55 (m, 1H), 1.37–1.43 (m, 4H), 1.21–1.29 (m, 30H), 1.16–1.20 (m, 10H), 1.07 (br. s., 12H), 0.84–0.88 (m, 14H), 0.63–0.79 (m, 4H), 0.47 (t, *J* = 6.41 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 10.52, 13.98, 14.10, 22.66, 22.91, 23.29, 24.00, 27.08, 27.21, 28.35, 29.32, 29.42, 29.52, 29.60, 29.89, 31.88, 37.24, 40.21, 43.53, 58.39, 61.66, 67.15, 69.79, 70.26, 70.52, 70.57, 70.74, 72.44, 86.16, 108.93, 113.60, 113.71, 113.78, 122.18, 123.54, 123.76, 127.59, 129.18, 131.08, 138.59, 142.20, 144.18, 168.83, 175.83, 180.48; IR (cm⁻¹): 2956, 2921, 2852, 1752,

1705, 1589, 1563, 1470, 1433, 1412, 1378, 1352, 1309, 1273, 1260, 1217, 1203, 1176, 1134, 1118, 1102, 1064, 1015, 965, 938; MALDI-TOF(m/z): $[M+H]^+$ calculated for $C_{62}H_{99}N_2O_4$, 935.7527; found, 935.5762.

4-((4-Carboxyphenyl)(phenyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AM3): Compound **1** (0.25 g, 0.347 mmol), 4-(phenylamino)benzoic acid (0.074 g, 0.347 mmol), column chromatography (SiO_2 , 100-200 mesh, 2.5% MeOH and 97.5% CH_2Cl_2). Yield: 0.12 g, 38%, Mp: 108 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.39 Hz, 2H), 7.46 (d, J = 8.39 Hz, 2H), 7.38 (t, J = 7.44 Hz, 3H), 7.33 (d, J = 7.25 Hz, 1H), 7.29 (d, J = 3.43 Hz, 2H), 7.23–7.27 (m, 3H), 7.07 (d, J = 8.01 Hz, 1H), 6.17 (br. s., 1H), 4.07 (br. s., 2H), 2.97 (br. s., 2H), 1.98 (td, J = 11.07, 4.01 Hz, 2H), 1.82 (quin, J = 7.34 Hz, 2H), 1.42–1.47 (m, 2H), 1.35–1.39 (m, 2H), 1.28 (d, J = 5.72 Hz, 21H), 1.20–1.25 (m, 12H), 1.11 (d, J = 9.92 Hz, 12H), 0.86–0.92 (m, 11H), 0.71–0.80 (m, 2H), 0.43–0.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.08, 22.65, 24.01, 27.18, 27.37, 29.30, 29.38, 29.59, 31.88, 40.02, 44.07, 59.29, 87.84, 106.95, 109.75, 120.70, 122.35, 124.54, 124.60, 125.56, 127.58, 127.82, 128.51, 129.01, 129.48, 131.11, 132.18, 139.14, 140.23, 144.45, 168.13, 171.44, 186.35; IR (cm^{-1}): 2953, 2922, 2852, 1760, 1706, 1605, 1559, 1488, 1465, 1425, 1406, 1352, 1294, 1235, 1207, 1172, 1138, 1104, 1185, 1016, 1004, 960, 920; MALDI-TOF(m/z): $[M+H]^+$ calculated for $C_{60}H_{87}N_2O_4$, 899.6588; found, 899.5042.

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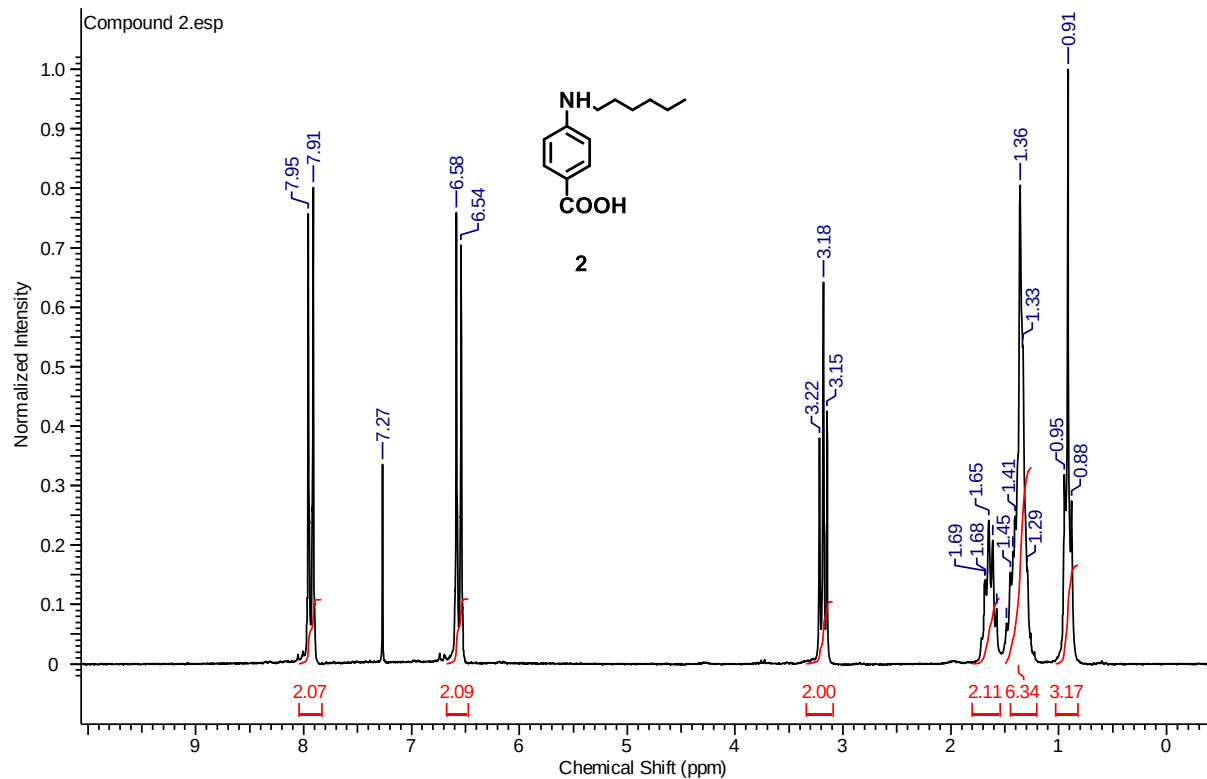
^1H -NMR, ^{13}C -NMR, and IR

Figure 17. ^1H -NMR spectrum of compound 2 in CDCl_3 .

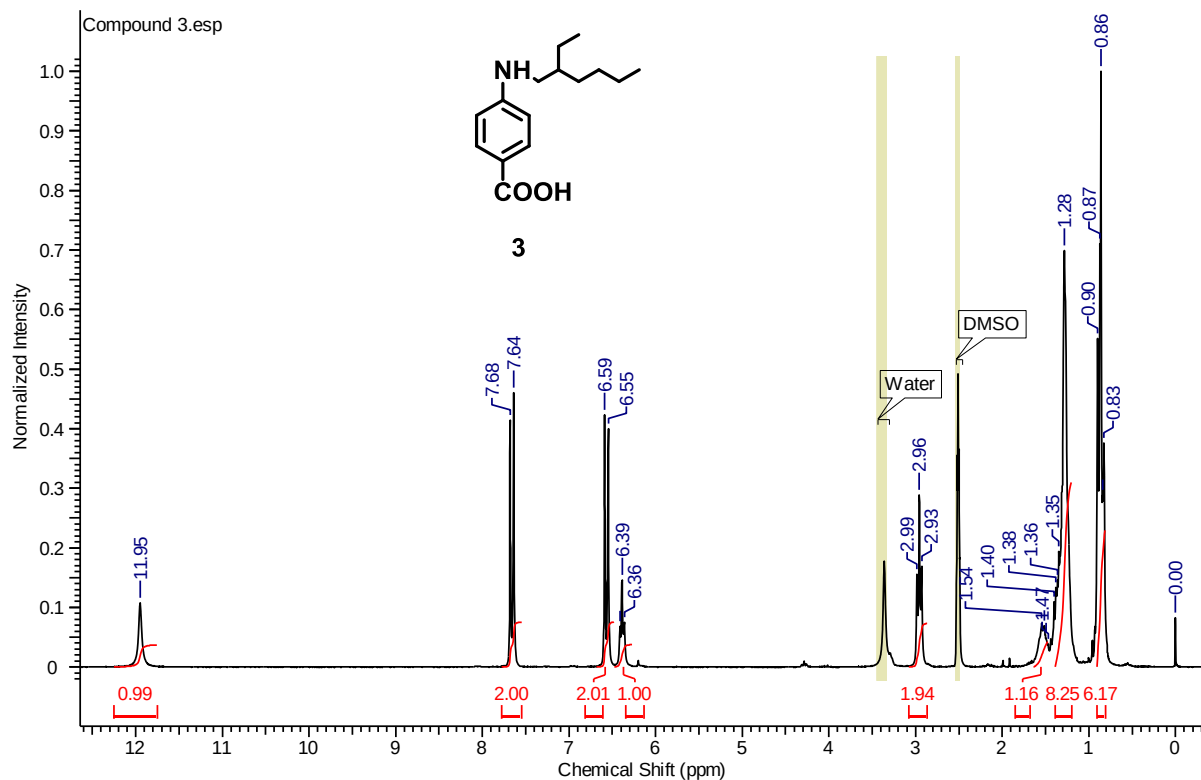


Figure 18. ^1H -NMR spectrum of compound 3 in DMSO-d_6 .

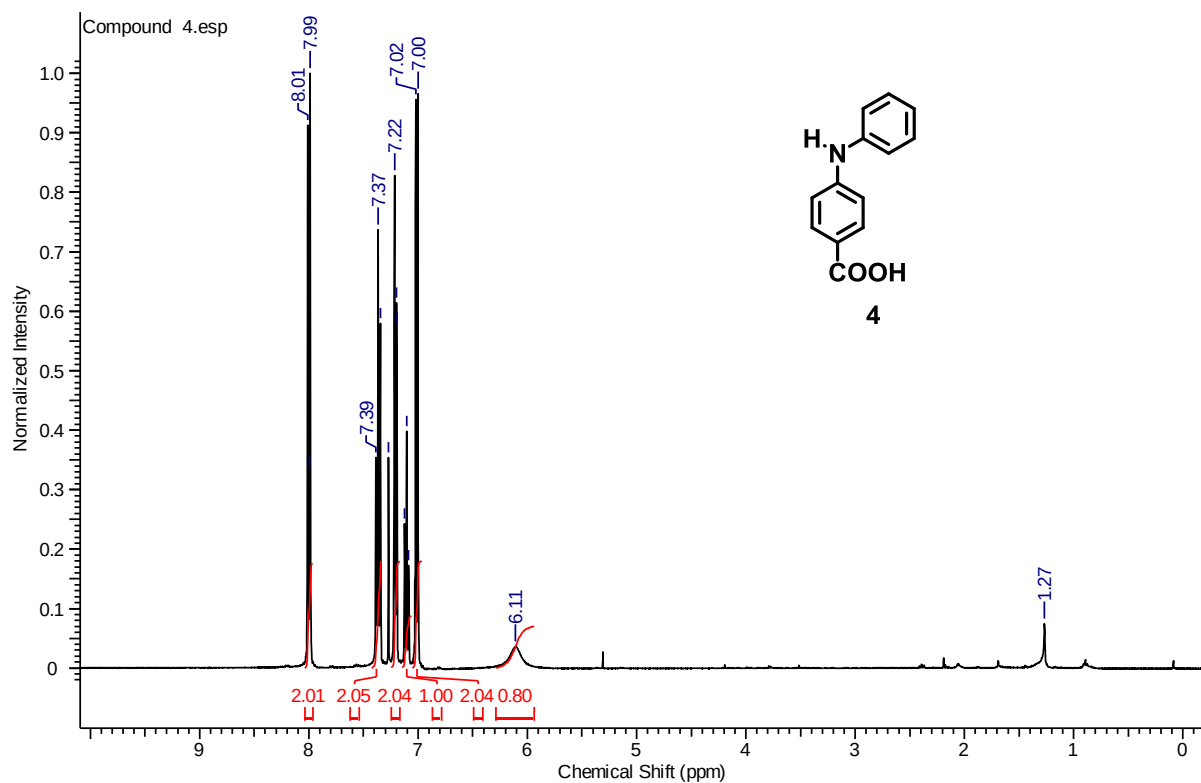


Figure 19. ^1H -NMR spectrum of compound 4 in CDCl_3 .

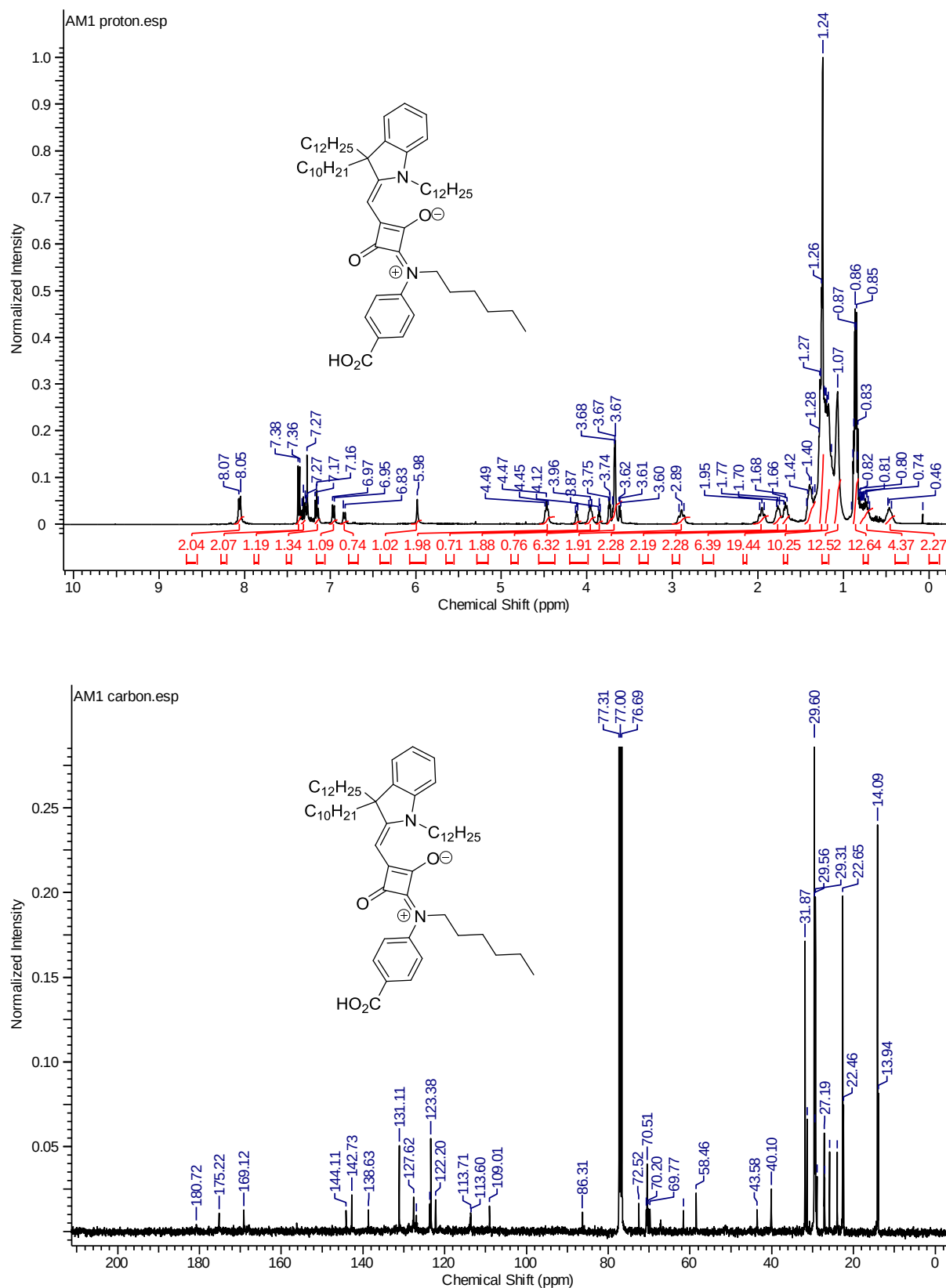


Figure 20. ¹H-NMR and ¹³C-NMR spectra of AM1 dye in CDCl₃.

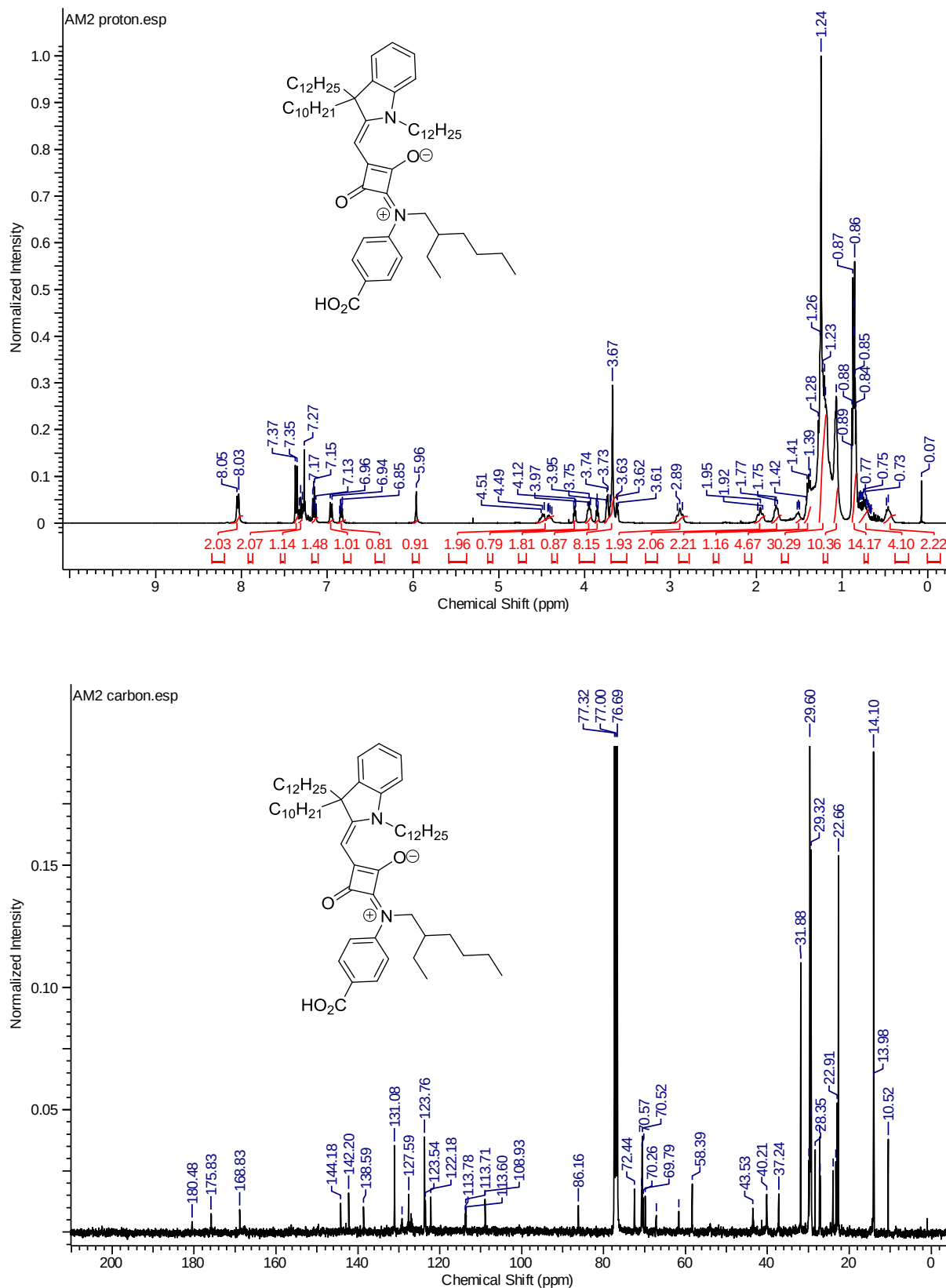


Figure 21. ^1H -NMR and ^{13}C -NMR spectra of **AM2** dye in CDCl_3 .

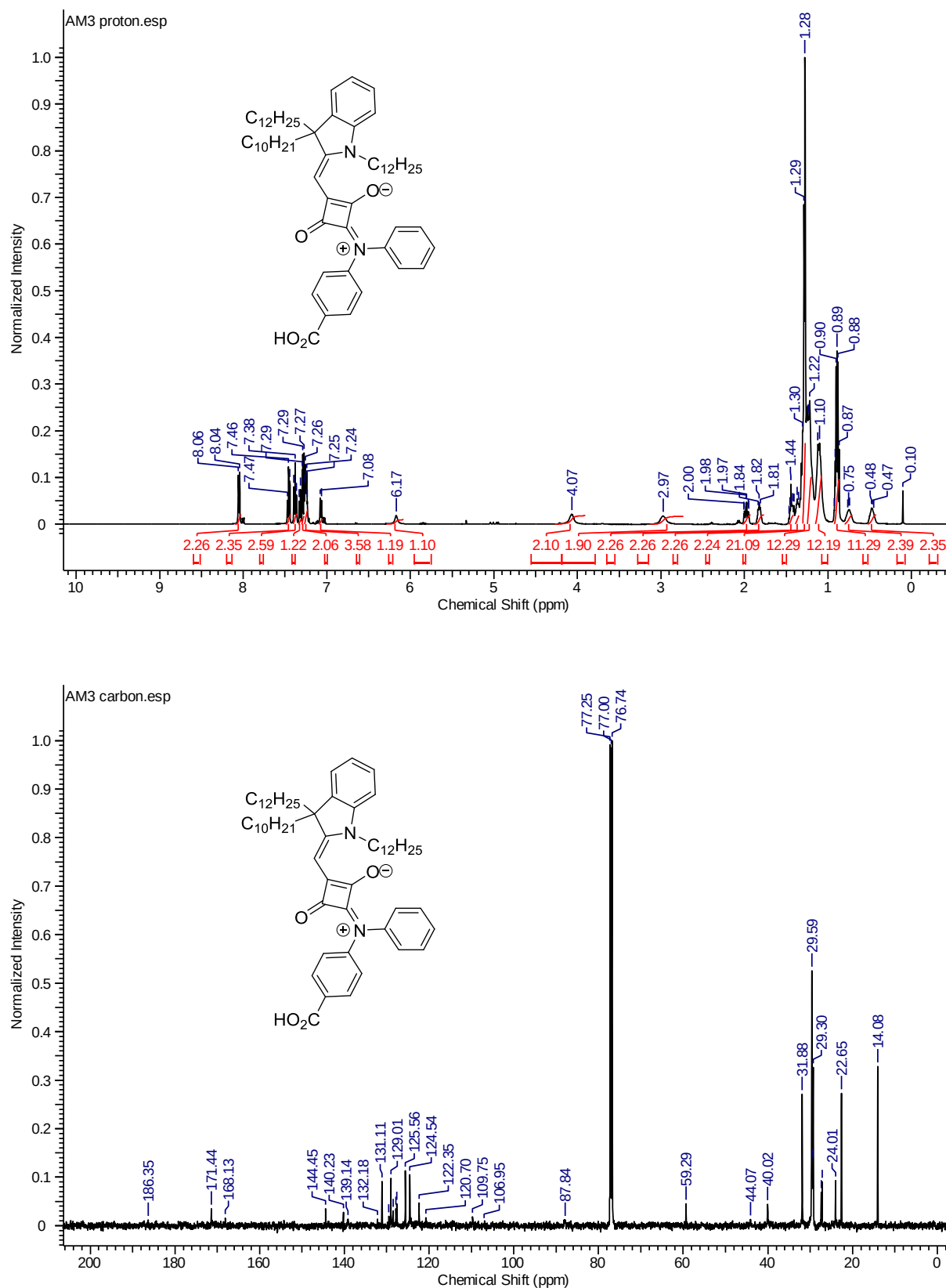


Figure 22. ^1H -NMR and ^{13}C -NMR spectra of AM3 dye in CDCl_3 .



Figure 23. MALDI-TOF-MS spectrum of **AM1** dye.

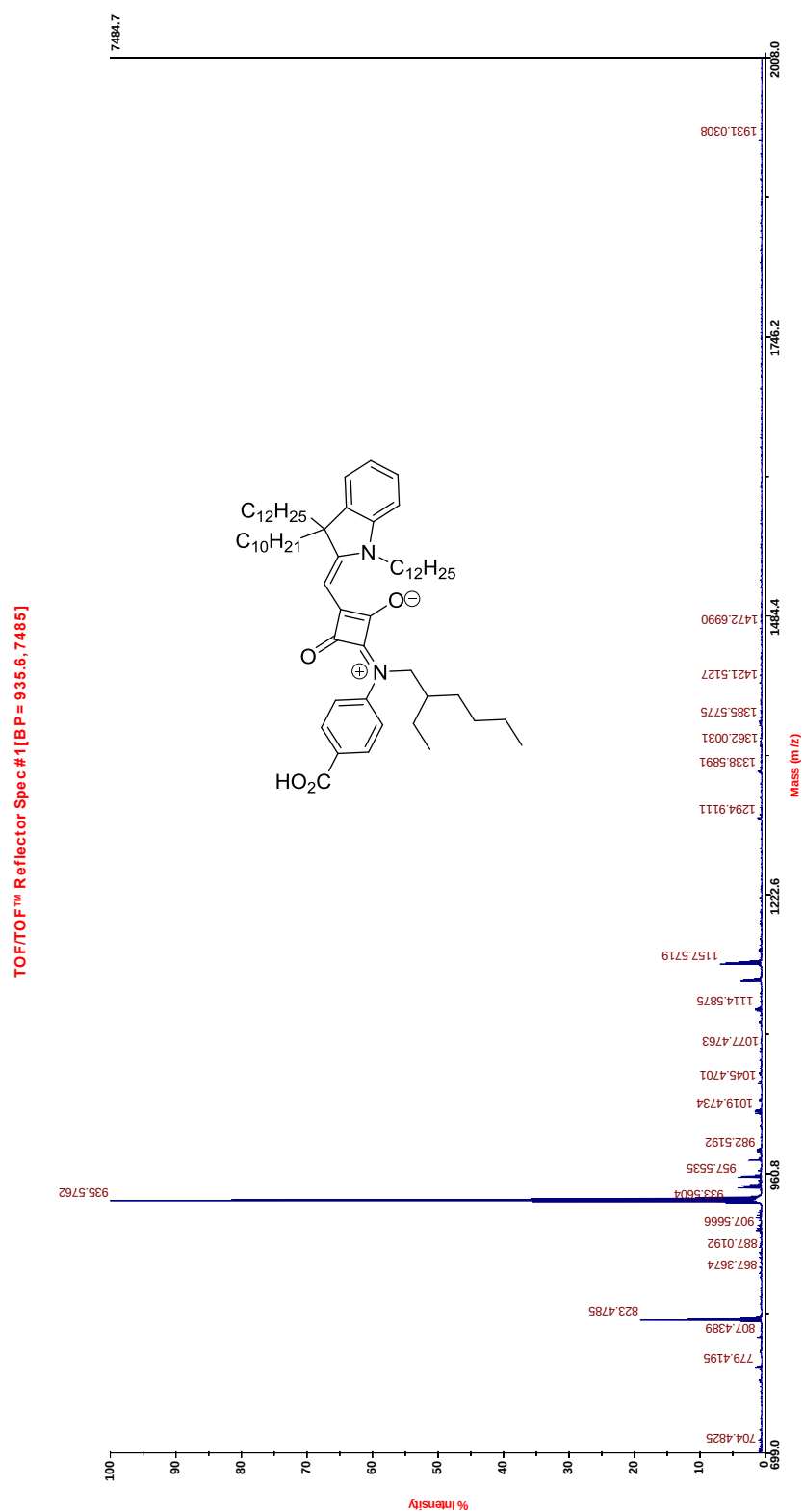


Figure 24. MALDI-TOF-MS spectrum of AM2 dye.

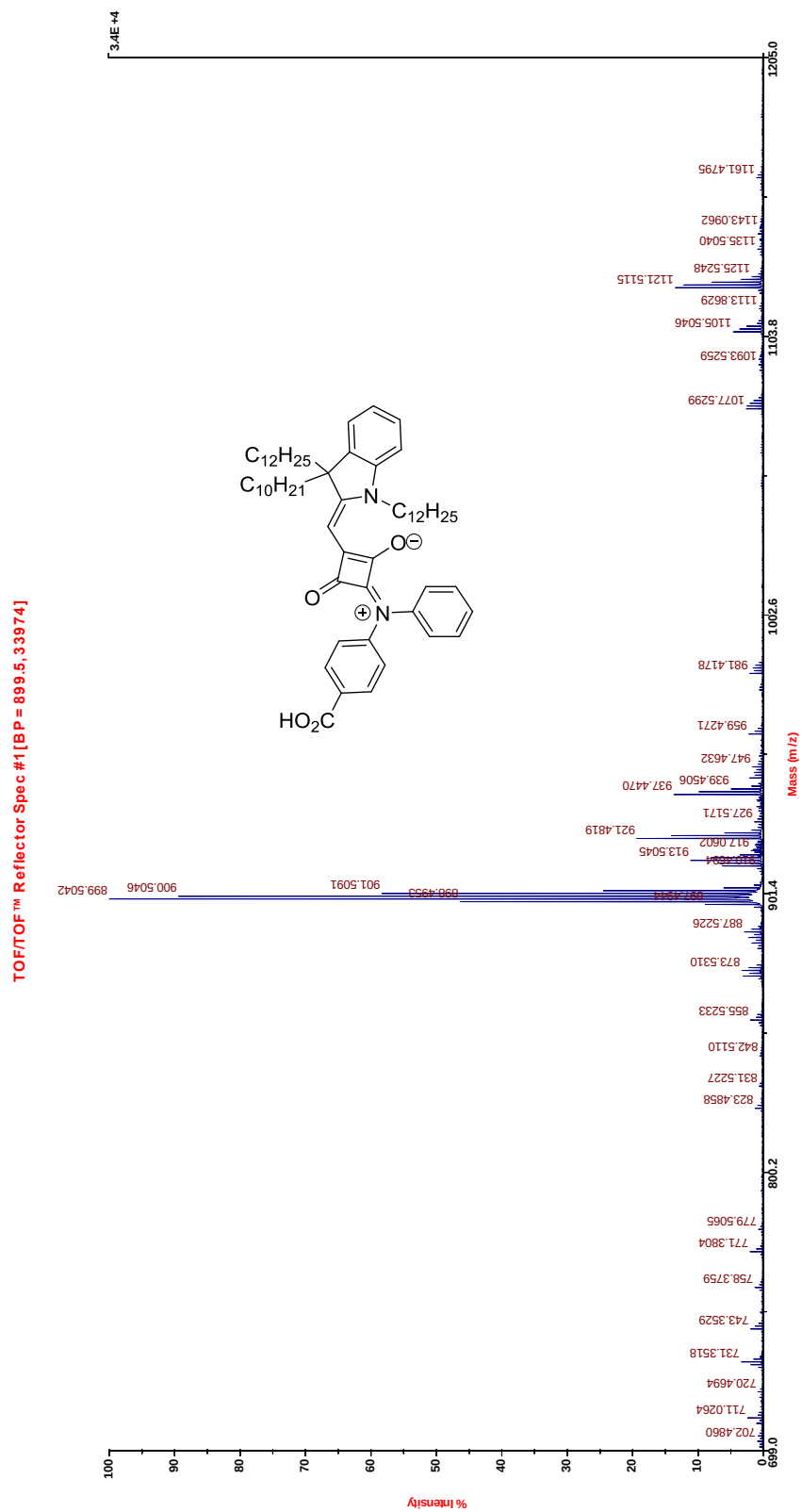


Figure 25. MALDI-TOF-MS spectrum of AM3 dye.

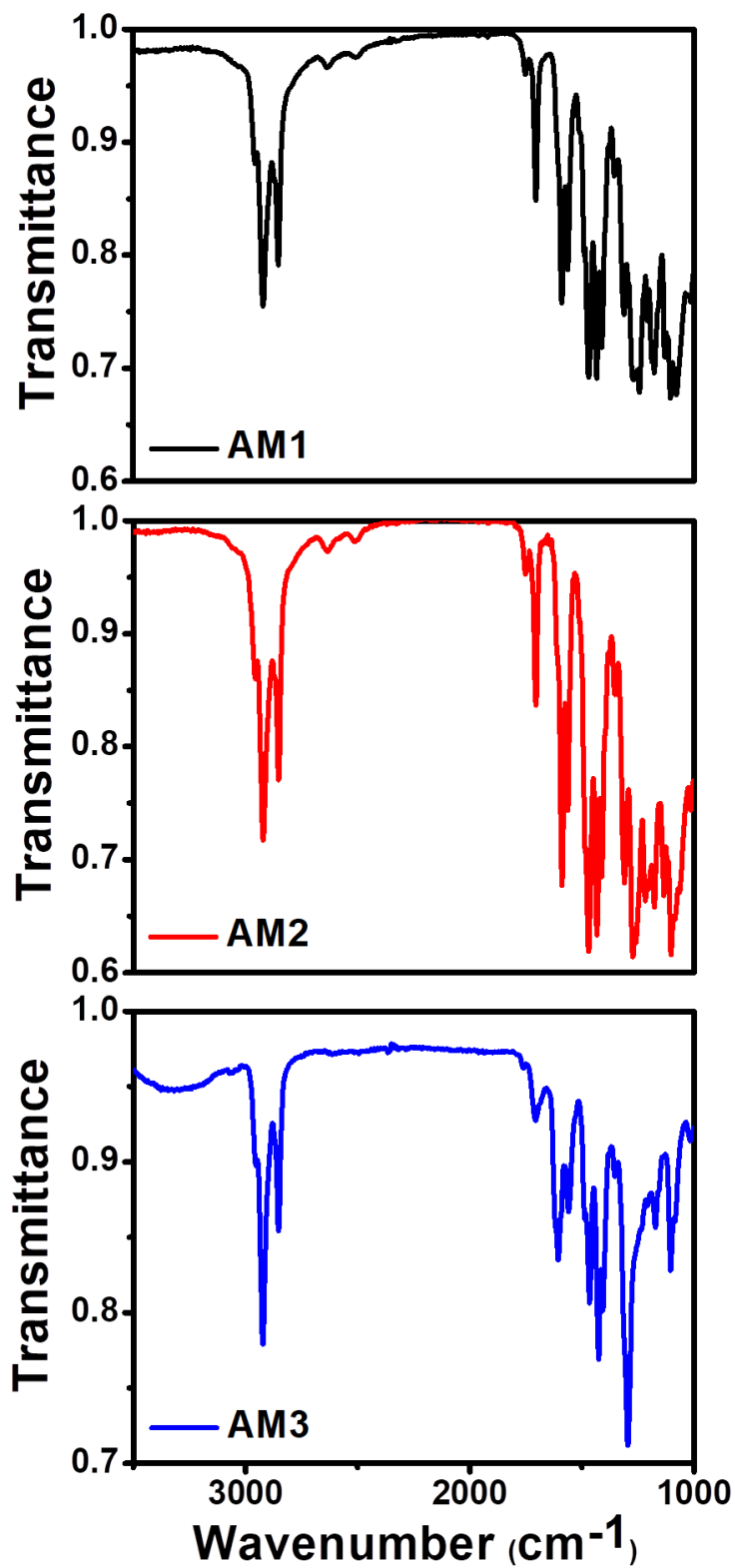
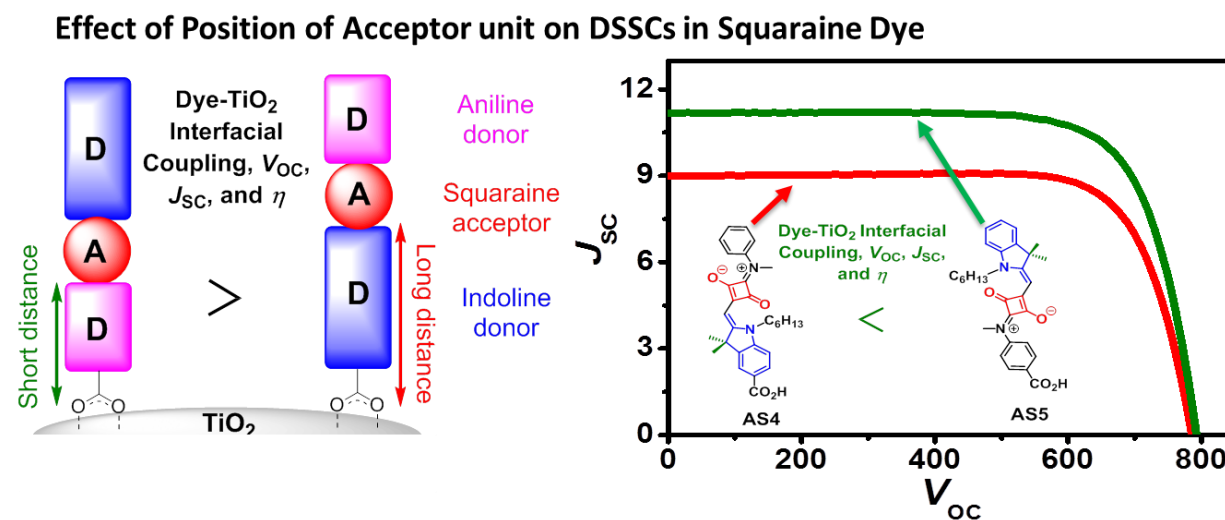


Figure 26. IR spectra (neat) of AM dyes.

Chapter 3

Squaraine Dyes for Dye-Sensitized Solar Cells: Effect of Position of Acceptor Unit in Visible Light Active Squaraine Dyes



3.1 INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been considered as an alternative source of clean energy for the future due to their advantages over the first- and second-generation solar cells in the terms of production costs, weight, flexibility, scalability, and works in the diffused or reflected light conditions.¹⁻⁸ The operational performance under the artificial light conditions with the high device efficiency output makes DSSC as a potential and promising technology for harvesting the indoor lights over the silicon solar cells.⁹⁻¹² A multidisciplinary and concerted research performed from the last two decades for commercializing the DSSC devices. Dye-anchored on the mesoporous TiO_2 surface is the main component which determine the overall device performance and stability¹³, therefore designing the new sensitizers that can efficiently absorb the solar light from the various solar regions and convert them into electricity is one of the major research topics in DSSC.^{4,14} Since 1991, metal-containing dyes (ruthenium complexes, porphyrin dyes) and organic dyes are commonly used sensitizers in dye sensitized solar cells,^{15,16} structurally engineering metallic dye have achieved efficiency 13.0% for porphyrin dye¹⁷ and 11.7% for ruthenium dye.¹⁸ whereas metal-free organic dye achieved 13.6%¹⁹ photovoltaic efficiency and co-sensitizing with other optically opposite dyes reached 15.2%²⁰ device efficiency and 37%²¹ device efficiency reached under the dim light condition reported at the laboratory scale and 10.0% for the small modules.^{22,23} Among of them, organic sensitizers attracted the great attention of the researchers due to diversity in the tuning of donor, acceptor and π -spacer moieties that absorb solar light from visible to near-Infrared (NIR) regions.²⁴⁻²⁵ Organic sensitizers with the numerous architectures of donor-acceptor (D-A), donor- π -acceptor (D- π -A), donor-acceptor- π -acceptor (D-A- π -A), and donor-donor- π -acceptor (D-D- π -A) with changed in the position and ability of donor, acceptor and π -spacer moieties have been well explored in DSSC.²⁴⁻²⁹ Further, charge-injection and dye-regeneration processes of a DSSC device are strongly affected by the distance and interactions between the anchoring group and acceptor unit of the dyes.³⁰⁻³³ Variation in alkyl-group-wrapped donor group have been studied for the D-A-D based unsymmetrical squaraine dyes, but position of donors and acceptors within the framework are yet to be studied to achieve better DSSC efficiency.³⁴⁻³⁸ Squaraine dyes falls in the family of polymethine and are very attractive due to its aggregation behaviour in both solution and on the metal-oxide surface among the other dyes belongs to this family.^{39,40} The

self-assembled structures of the squaraine dyes have the variety of applications, such as in organic photovoltaic, sensors, and DSSC.^{41,42}

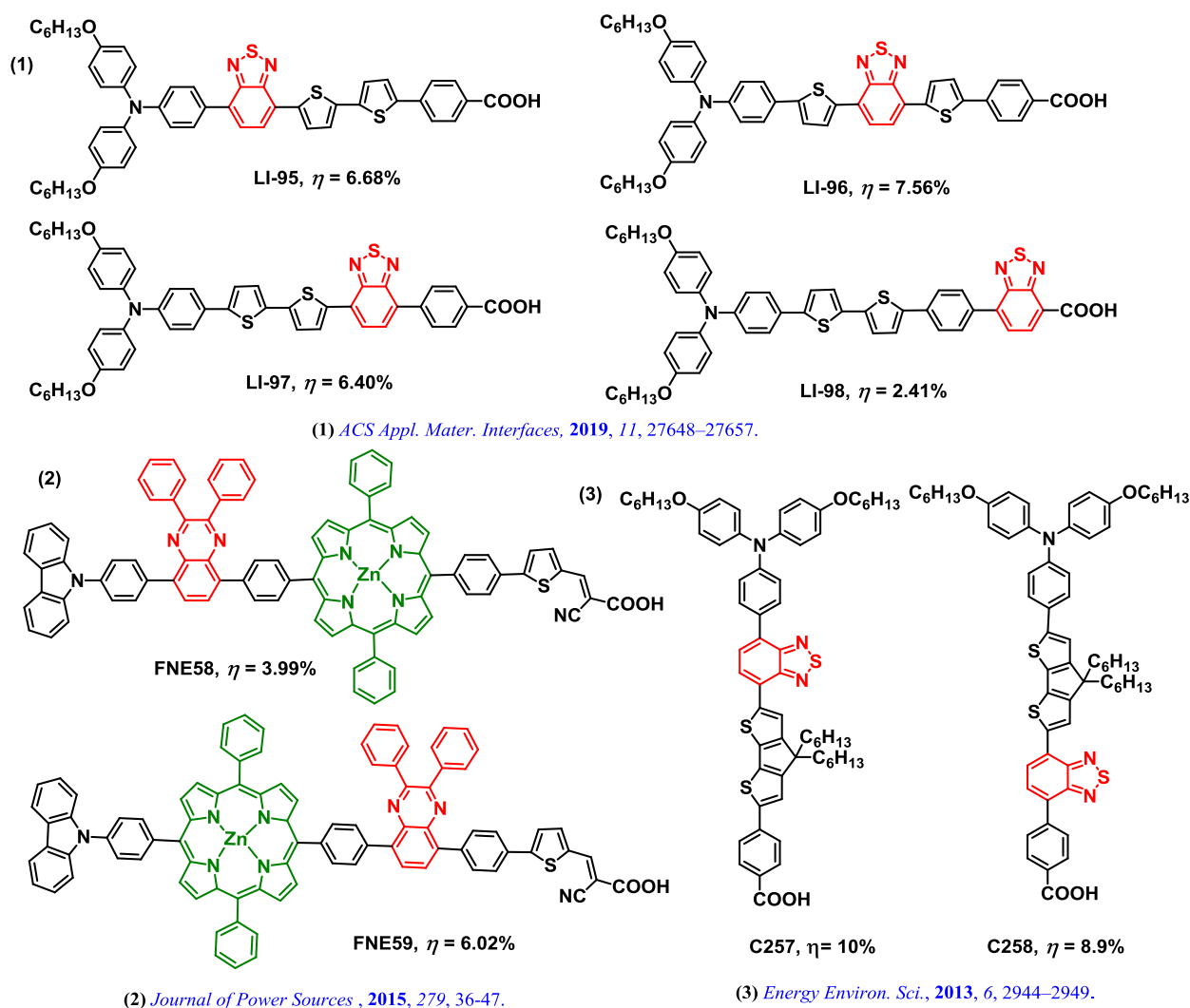
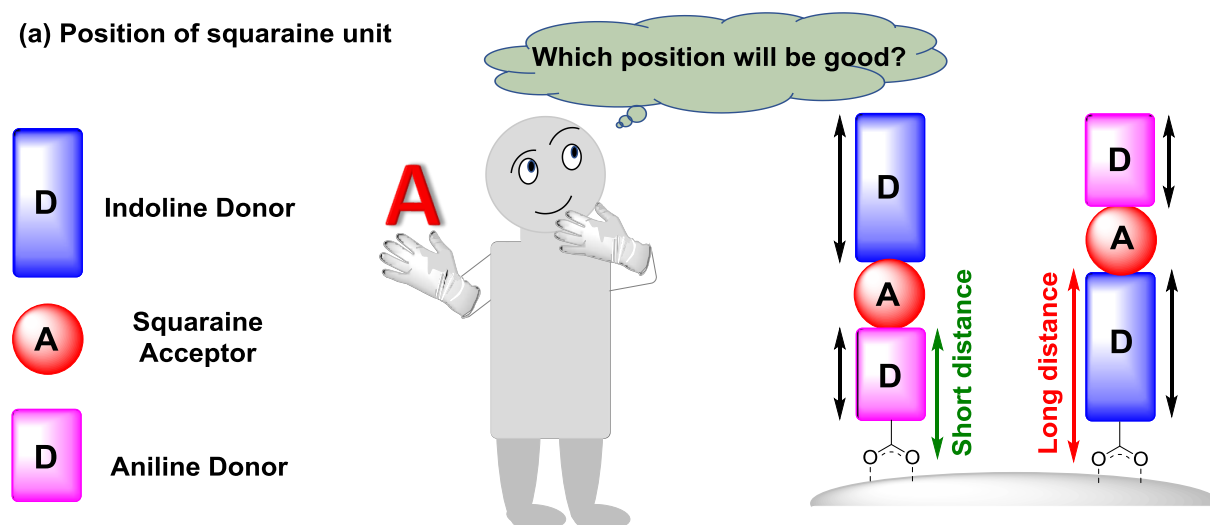


Figure 1. Structures of sensitizers with variation in the acceptor unit position.

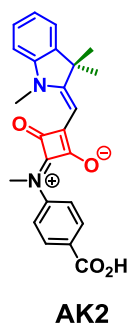
Further, squaraine dyes absorbed visible and NIR light with high molar extinction coefficient, which is an important quality to make DSSC device flexible. In our previous work, we have systematically studied the effect of alkyl-group-wrapping, position of anchoring group, best sensitizing solvents/ electrolyte, and effect of changing the donor moieties for unsymmetrical squaraine on the DSSC performance.^{35–37, 43–48} Recently, it has been observed that the alkyl group wrapped visible light active squaraine dye AK4 ($\eta = 7.73\%$) and dye with methyl groups (AK2, $\eta = 7.34\%$) showed little difference in the photovoltaic parameters, and position of acceptor unit

within such type of D-A-D' framework has not been studied.³⁵ Therefore, here we have used visible active squaraine dye with methyl groups **AK2** as a reference dye and designed the D-A-D' based squaraine dyes with the variation in the position of acceptor unit along with incorporation of alkyl group at the N-atoms of indoline and aniline donor units. In this study, we have changed the electronic structures of the D-A-D based squaraine dyes by keeping the short and large distance between acceptor-anchoring group to evaluate their effect on DSSC device performance. A series of visible-light responsive squaraine **AS** dyes with changed in the position of acceptor unit (where small linear and branched alkyl-groups placed systematically at the N-atoms of aniline and indoline donors) have been designed, synthesized for DSSC. Change in the anchoring group position changed the position of acceptor as well as donor units (**Figure 2**).

(a) Position of squaraine unit



(b) Reference dye **AK2**



(c) Structures of the targeted visible light active **AS** dyes

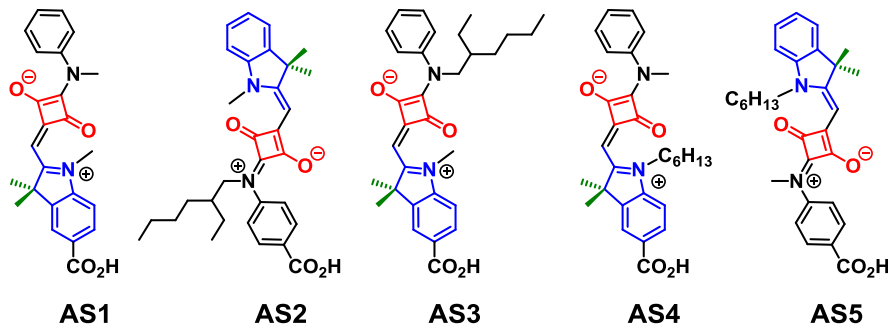
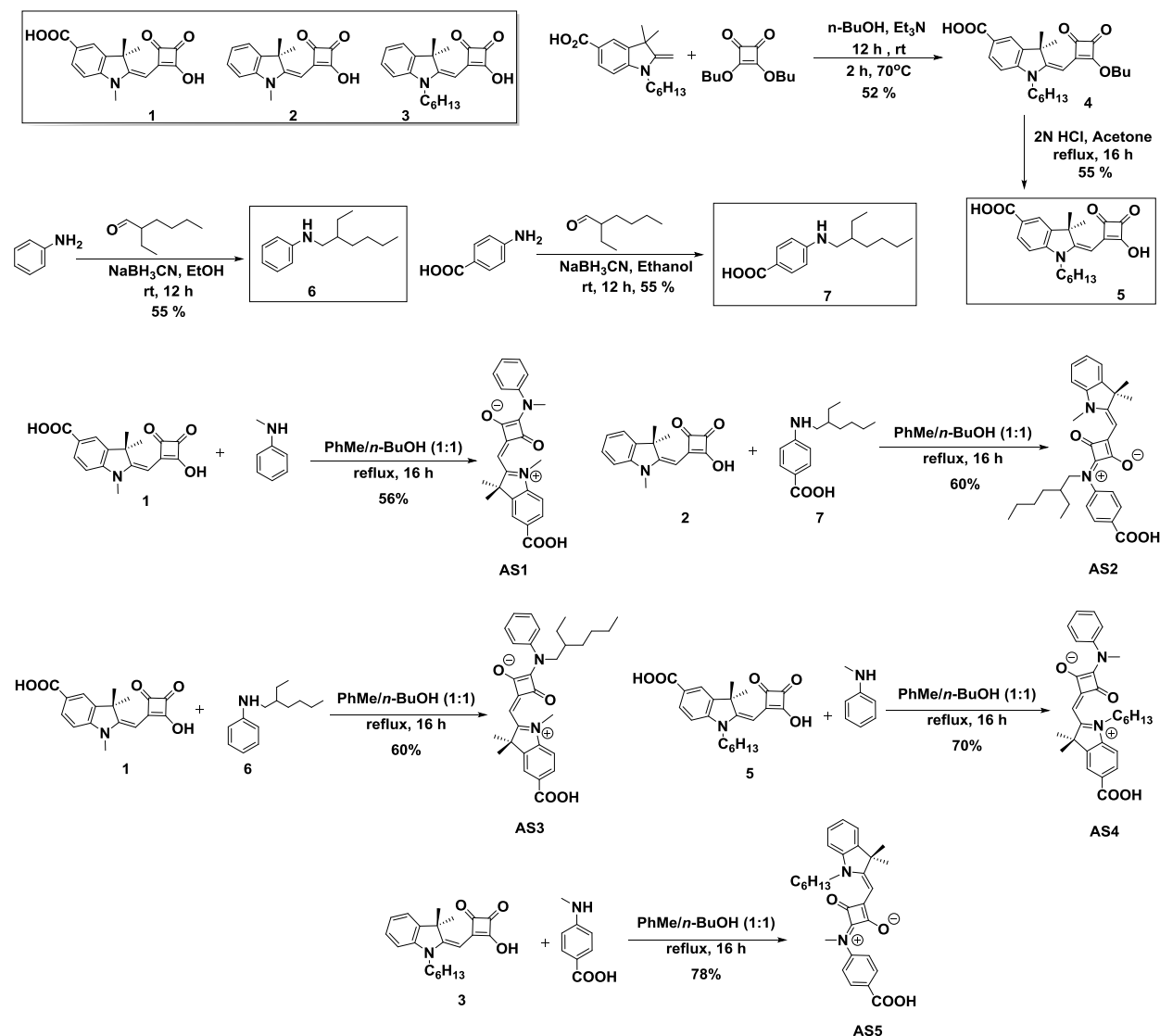


Figure 2. (a) Design idea for the acceptor unit position variation within the same D-A-D based squaraine dye, (b) Structures of visible light active **AK2** (reference dye) and targeted **AS** dyes.

3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis of indoline-aniline based AS dyes.

Synthesis of D-A-D based visible active unsymmetrical squaraine dyes with changed in the position of acceptor unit comprised a condensation reaction between the semisquaric acid derivatives and corresponding aniline derivatives.



Scheme 1. Synthesis of aniline and indoline donors based visible light active AS dyes.

To obtain the required semisquaric acid derivatives, **1**, **2**, **3**, and **5**, we have followed the reported procedures which involve Fischer indole reaction, alkylation with alkyl-iodide, formation of semi-squaraines and substitution followed by deprotection transformation. N-methyl aniline, 4-

amino-benzoic acid, and 4-N-methylamino-benzoic acid are commercially available derivatives of aniline, whereas derivatives **6**, and **7** were synthesized by condensation of corresponding amine with 2-ethylhexanal followed by the reduction reaction with NaBH_3CN . And finally, semisquaric acid derivatives condensed with the aniline derivatives (1 equiv.) in anhydrous toluene and *n*-BuOH (1:1) to obtain the required **AS** dyes (**Scheme 1**).

3.2.2 Photophysical properties.

The UV-vis measurement for the **AS1-5**, dyes have been carried out in CH_2Cl_2 solution as well as on the TiO_2 surface (with short dipping time) to evaluate the absorbance properties of the dyes in solution and on metal-oxide surface. The UV-vis spectra for **AS** dyes along with the reference dye **AK2** are provided in **Figure 3** and **Table 1**. In CH_2Cl_2 solution the absorbance maxima for the **AS** dyes have been found between 501-535 nm and showed its molar extinction coefficients between $1.46\text{-}1.61 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ (**Figure 3** and **Table 1**). Here, **AS** dyes with the short acceptor-anchoring group distance (In-SQ-An-Anchoring group) showed 12 nm blue shift for **AS2** dye and 5 nm red shift for **AS5** dye, whereas, **AS** dyes with the large acceptor-anchoring group distance **AS1**, **AS3** and **AS4** (An-SQ-In-Anchoring group) showed 21-29 nm blue shift compared to reference dye **AK2** in CH_2Cl_2 solution, respectively. Obtained 25 nm of blue shift for the **AS1** in CH_2Cl_2 solution is due to change in the distance between acceptor-anchoring group, whereas 12 nm blue shift for **AS2** dye and 5 nm red shift for **AS5** dye is due to the interactions between solvent-alkyl groups compared to the reference dye **AK2**, respectively. Similarly, obtained differences in the absorbance maxima for **AS3** and **AS4** dyes is due to large acceptor-anchoring group distance and interactions between solvent-alkyl groups compared to reference dye **AK2**. Further, **AS** dyes with the 10 minutes sensitization time on the TiO_2 surface showed the absorbance maxima between 490-535 nm, where absorbance maxima for the **AS5** dyes showed like the solution, and **AS1** and **AS3** dyes showed broad absorbance compared to other **AS** dyes. Dyes belongs to **AS** series showed the emission maxima between 560-572 nm with the onset of $>700 \text{ nm}$. **AS** dyes with the small acceptor-anchoring group distance showed similar emission maxima (572 nm) like reference dye **AK2**, whereas dyes with large acceptor-anchoring group distance showed different emission maxima. The light harvesting efficiency (LHE) of the **AS** dyes have been calculated ($\text{LHE} = 1 - 10^{-A}$) at 80% and showed different LHE properties due to the changed acceptor unit position and alkyl group incorporation (**Figure 3c**

and **Table 1**). Here, **AS2** dye showed relatively narrowed LHE due to more hindrance near to anchoring group compared to other **AS** dyes.

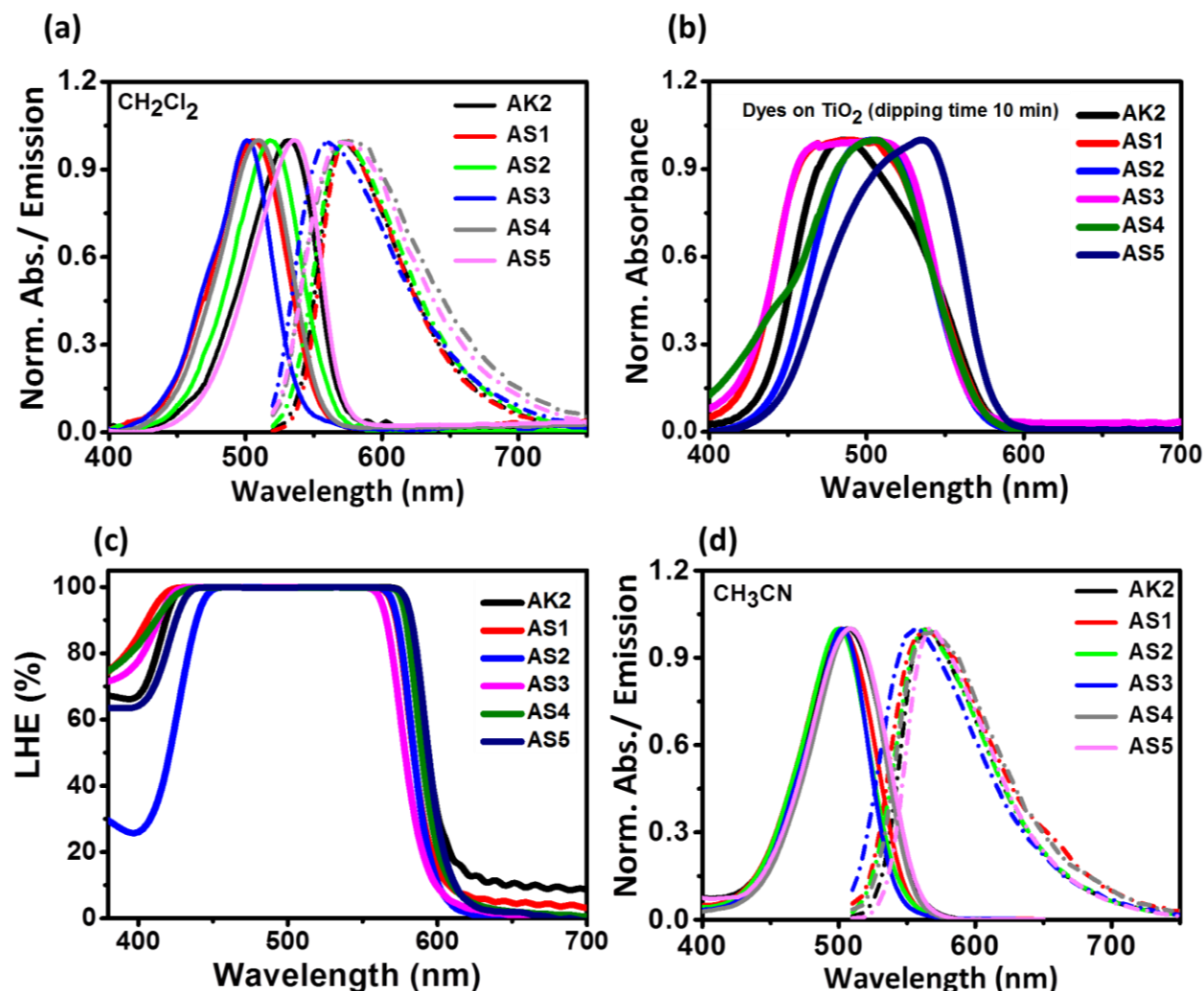


Figure 3. (a) Normalized UV-vis (solid) and fluorescence (dotted) spectra of **AS** and **AK2** dyes in CH_2Cl_2 solution, (b) UV-vis spectra of **AS** and **AK2** dyes on TiO_2 (thickness of the TiO_2 electrode 6 μm , dipping time was 10 min), (c) LHE ($=1-10^{-A}$) profiles of **AS** and **AK2** dyes on TiO_2 electrodes (thickness 6 μm , dipping time was 12 h), (d) Normalized UV-vis (solid) and fluorescence (dotted) spectra of **AS** and **AK2** dyes in CH_3CN solution,.

3.2.3 Electrochemical properties. The differential pulse voltammetry (DPV) experiment was performed in anhydrous CH_2Cl_2 solution (**Figure 4a**). **AS** dyes showed two oxidation peaks, where dye with small acceptor-anchoring group distance oxidized little faster compared to the

dyes with large acceptor-anchoring group distance. First oxidation potential obtained from the DPV experiment for the **AS** dyes have been used to calculate the highest molecular occupied orbital (HOMO) energy level, where oxidation potential converted into the NHE by addition of 0.7 V. Intersection point of absorbance and emission spectra have been used to calculate optical bandgap of the **AS** dyes by using the formula of $E_g = 1240/\lambda_{\text{intersection}}$. Further, the lowest unoccupied molecular orbital (LUMO) energy levels were calculated by subtracting the bandgap from the HOMO of the dyes. The HOMO energy levels were estimated to be 1.06, 1.03, 1.07, 1.08 and 1.05 eV (vs NHE) for **AS1-AS5**, respectively and the LUMO of the dyes were found to be -1.21, -1.24, -1.27, -1.20 and -1.27 eV (vs NHE) for **AS1-AS5**, respectively. The HOMO of **AS** dyes has the sufficient over potential in the range of 0.63 V to 0.68 V to I^-/I_3^- electrolyte for the dye regeneration processes, and LUMO have the sufficient negative potential in the range of -0.70 V to -0.77 V compared to TiO_2 conduction band level (-0.5 V vs NHE) for the electron injection processes, respectively.

Table 1. Photophysical and electrochemical properties of **AS1-5** dyes along with reference dye **AK2** at room temperature.

Dyes	^a λ_{max} (nm) $\text{CH}_2\text{Cl}_2/$ CH_3CN	^b λ_{max} (nm) $\text{CH}_2\text{Cl}_2/$ CH_3CN	ϵ (10^5 M^{-1} cm^{-1})	^c λ_{max} (nm) on TiO_2	LHE $\Delta\lambda$ at 80%(nm)	^d E_{ox} (V vs Ag/Ag^+)	E_{HOMO} (V vs NHE)	E_{LUMO} (V vs NHE)	^e E_g (eV)
AK2	530/507	572/564	1.84	485	174	0.439	0.98	-1.27	2.25
AS1	505/502	573/563	1.46	490	185	0.525	1.06	-1.21	2.27
AS2	518/500	572/565	1.61	502	143	0.487	1.03	-1.24	2.27
AS3	501/503	560/557	1.54	506	166	0.532	1.07	-1.27	2.34
AS4	509/509	576/566	1.53	505	188	0.545	1.08	-1.22	2.30
AS5	535/509	572/568	1.52	535	168	0.508	1.05	-1.20	2.25

^aabsorption, ^bemission of **AK2** and **AS1-5** dyes in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, ^con TiO_2 (thickness 6 μm , dipping time 10 min) ^doxidation potentials were measured in CH_2Cl_2 , where tetrabutylammonium perchlorate (TBAClO_4) used as a supporting electrolyte, Fc/Fc^+ used as an internal standard and converted to NHE by addition of 0.7 V, ^e E_g optical band gap.

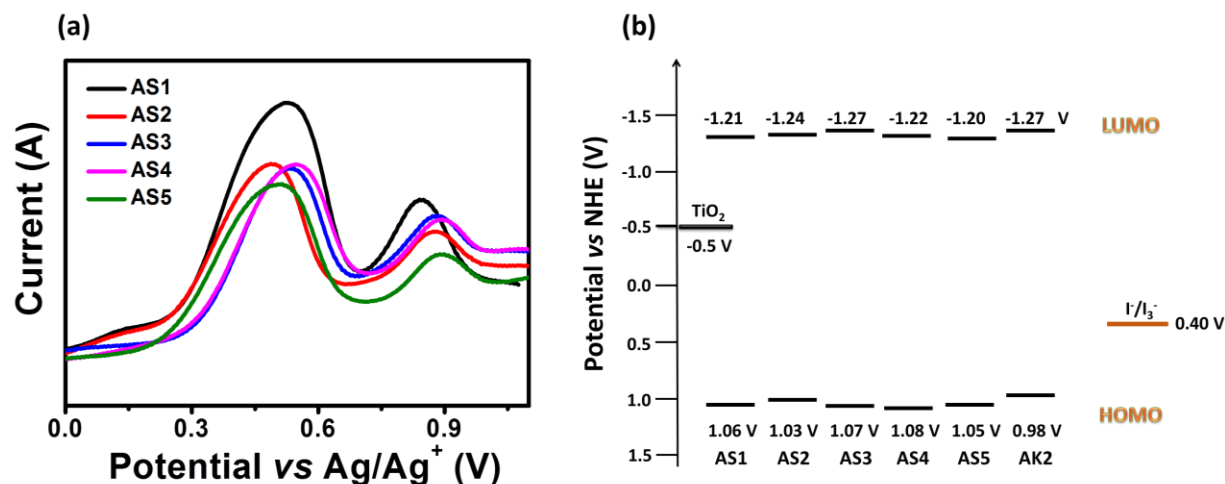


Figure 4. (a) Differential voltammograms of AS dyes in CH₂Cl₂ solution, and (b) energy level diagram of AS1-5 dyes along with reference dye AK2.

3.2.4 Dye-desorption studies. The dye desorption UV-spectrum of AK2 and AS dyes was recorded at room temperature. Area of photo anode was 0.23 cm² (8 μm thickness), dipping for 12 h at room temperature in 0.1 mM of dye solution, 1 M HCl ethanolic solution (2 mL) have been used to desorb the adsorbed dyes and path length of cuvette was 0.01 cm² for dye desorption studies of AK2 and AS dyes (**Figure 5** and **Table 2**).

Table 2. Amount of dye desorbed from the TiO₂ surface in 1 N HCl (in EtOH).

Cell	CDCA (mM)	$\lambda_{\max}$	ϵ (10 ⁵ M ⁻¹ cm ⁻¹)	Dye Loading on TiO ₂ (10 ⁻⁷ mol/cm ²)
AK2	0.0	0.2458	1.8	1.161
AK2	0.2	0.1727	-	0.816
AS1	0.0	0.2373	1.46	1.413
AS1	0.2	0.1211	-	0.721
AS2	0.0	0.1707	1.61	0.921
AS2	0.2	0.1087	-	0.587
AS3	0.0	0.2374	1.54	1.339
AS3	0.2	0.1197	-	0.675
AS4	0.0	0.1836	1.53	1.043
AS4	0.2	0.0880	-	0.500
AS5	0.0	0.2212	1.52	1.265
AS5	0.2	0.1413	-	0.808

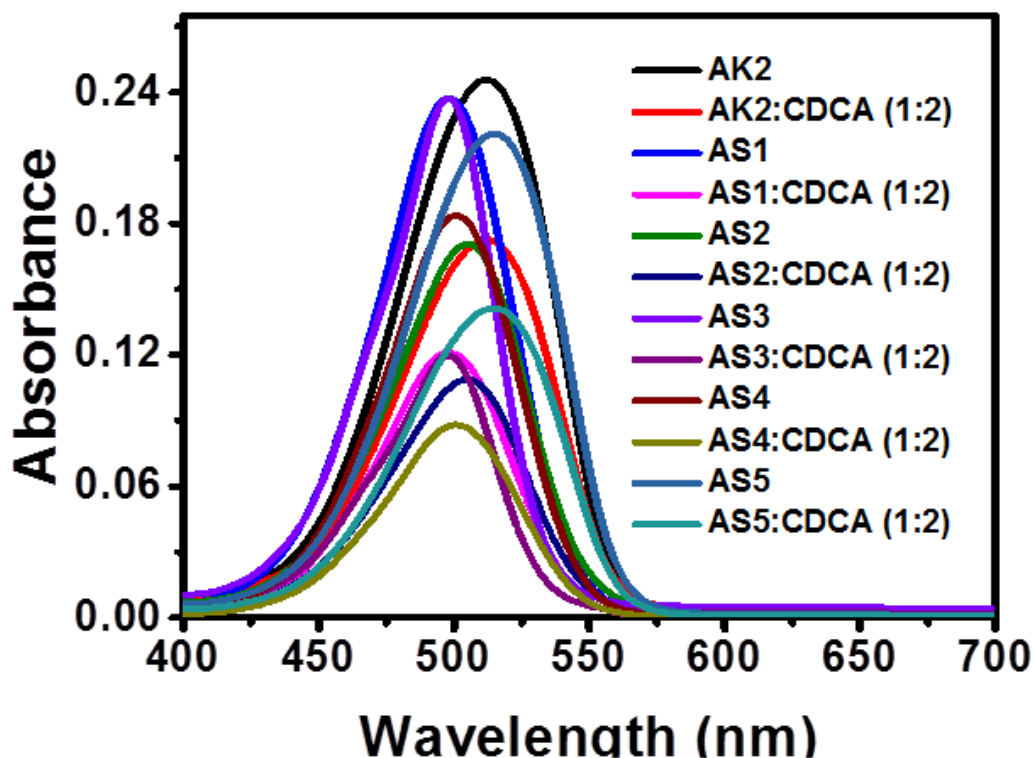


Figure 5. UV-vis spectra of desorbed dyes from the TiO_2 surface in 1 N HCl (in EtOH).

3.2.5 Computational Studies.

All the DFT calculations were performed by employing Gaussian09 software⁴⁹ for **AS** dyes with changes in the position of the acceptor unit, using the B3LYP, 6-311G (++) level of theory, to assess the effect of acceptor unit position on electronic distributions in different electronic states. The isodensity surface value was fixed at 0.03 (**Figure 6**). For all dyes, the HOMO electronic level showed the maximum electron density on the acceptor unit, while in the LUMO level exhibited electronic distribution in D-A-D units with slight variations. Here, **AS1**, **AS3** and **AS4** dyes with similar π -backbone (long distance) showed similar electronic distributions in the different electronic levels, but the dihedral angle changed in **AS3** dye by incorporating the ethyl-hexyl chain at aniline donor. The **AS2** and **AS5** dyes with similar π -backbone (short distance) showed slight variations in electronic distributions for the different electronic levels and the dihedral angle of **AS2** dye changed due to incorporating the ethyl-hexyl chain at aniline donor. It

has been observed that the branched N-alkylation of aniline and indoline donors disturbed the planarity of the molecule compared to the normal N-alkylation.

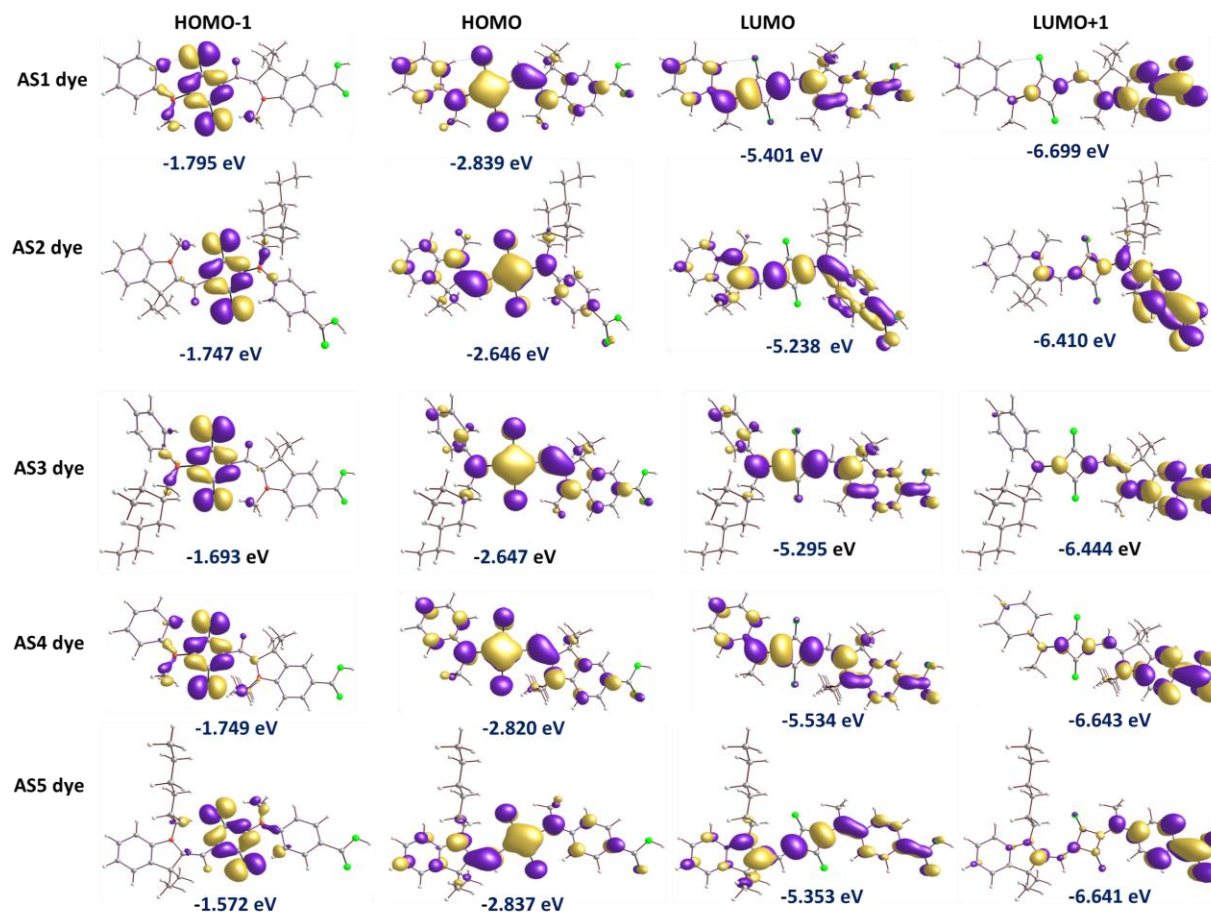


Figure 6. Energy minimized frontier molecular orbital diagram of D-A-D based **AS1**, **AS2**, **AS3**, **AS4** and **AS5** dyes with their electronic levels.

Further, the dipole moment obtained from the energy optimized structures for the large acceptor-anchoring group distance based **AS1**, **AS3** and **AS4** dyes was relatively low (1.96D, 3.23 D, and 2.14 D, respectively), compared to small acceptor-anchoring group distance based **AS2** (5.40 D), **AS5** (6.77 D) and **AK2** (6.728 D) dyes. The dipole moment of the dyes increased with an aniline donor attach to the anchoring group (short distance) compared to the non-anchoring indoline donor unit due to change in the electronic structures. The distance between the N-atom of indoline, aniline donor and carbonyl C-atom of carboxylic acid, acceptor unit was calculated from the minimized energy structure of molecules by DFT (**Figure 7**). The average lengths of visible light active **AS** dyes range from 15.5 Å to 16.6 Å, and depending on the anchoring group

position on donor units. Anchoring group attached to the aniline donor promote the molecule to slightly twisted, resulting in a decreased length compared to anchoring group attached to the indoline donor. The distance between the both carbonyl-C of acceptor unit and carboxylic acid C=O of the anchoring group was greater for **AS1** (10.4-11.0 Å), **AS3** (10.39 - 11.01 Å) and **AS4** (10.34 - 11.0 Å) dyes compared to **AS2** (7.13 - 8.62 Å) and **AS5** (7.32 - 8.70 Å) dyes. The dihedral angles between the aniline unit and acceptor unit in-plane were 0.81° , -41.26° , -46.42° , 0.85° and -1.16° for the **AS1**, **AS2**, **AS3**, **AS4** and **AS5** dyes respectively, indicating that branching at the aniline donor distorted the geometry of molecule.

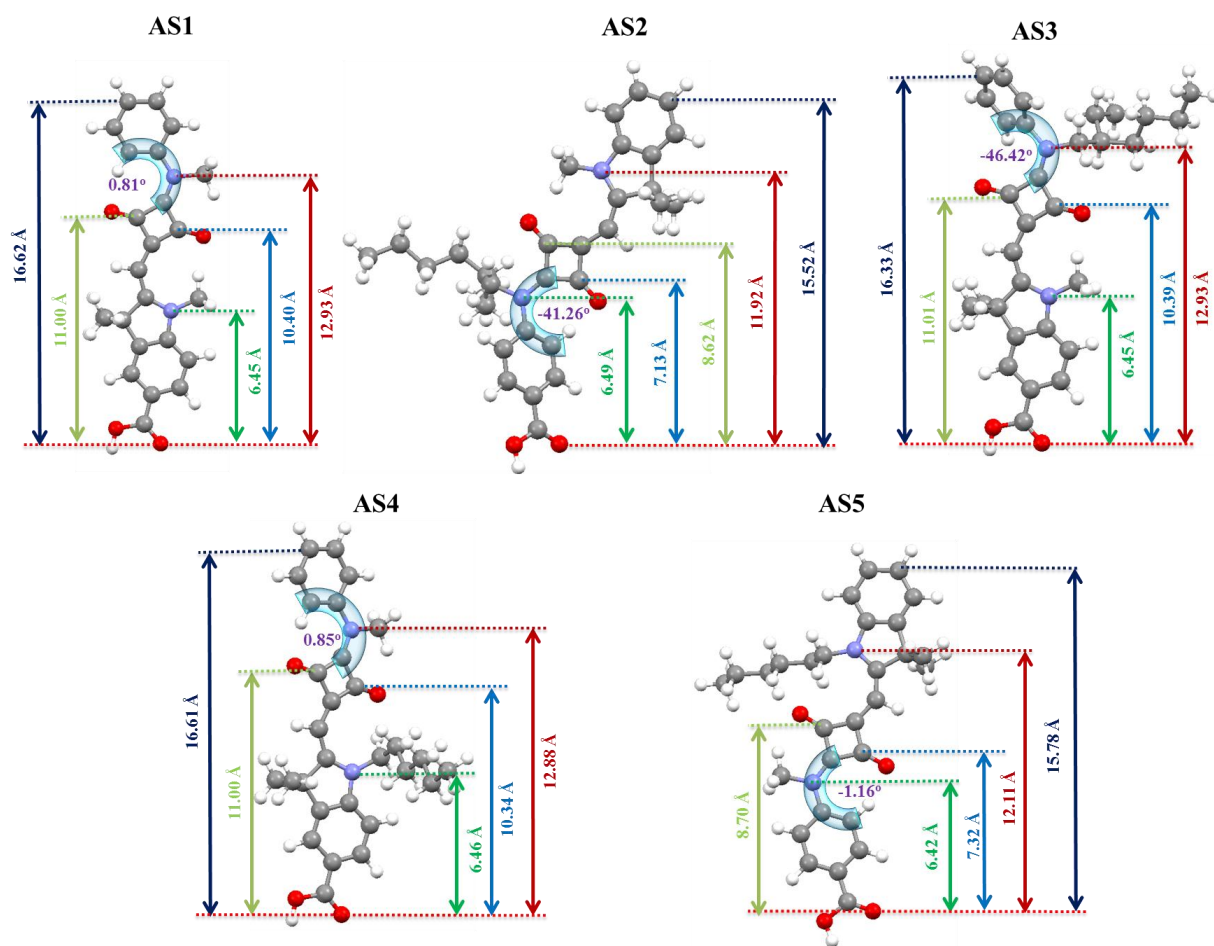


Figure 7. Energy minimized structures of **AS1–AS5** dyes with the distance (between carboxylic acid C=O of anchoring group to N-atom of donors and carbonyl-C of acceptor) and dihedral angles between aniline donor and acceptor units.

3.2.6 Photovoltaic performance.

The DSSC device characterizations of photoanode made from the **AS** dyes and **AK2** dye with I^-/I_3^- electrolyte have been carried out and optimized DSSC results have been provided in **Figure 8** and **Table 3**. The DSSC device performance for **AS2**, **AS5** and **AK2** dyes (with small acceptor-anchoring group distance) were obtained high compared to the **AS1**, **AS3** and **AS4** dyes (with large acceptor-anchoring group distance). **AS1** dye with large acceptor-anchoring group distance gave the V_{OC} of 768 mV, J_{SC} of 9.46 mAcm^{-2} and efficiency of 5.49%, whereas **AK2** dye (which is only differ in respect to the acceptor position) gave the maximum V_{OC} of 802 mV, J_{SC} of 11.90 mAcm^{-2} and efficiency of 7.51% in the absence of CDCA. Similarly, device performance patterns have been observed between **AS3/AS2**, and **AS4/AS5** dyes, respectively in the absence of CDCA that indicates the charge injection enhanced with the small acceptor-anchoring group distance without steric hindrance. Incorporation of ethyl-hexyl alkyl group into aniline unit near to TiO_2 surface for **AS2** dye enhanced the V_{OC} by passivating the TiO_2 surface and reduced the J_{SC} (dye loading on TiO_2) and DSSC efficiency compared to **AK2** dye. Fabrication of DSSC devices of **AS** dyes with the 2 equivalents of CDCA enhanced the V_{OC} of all the dyes due to better TiO_2 passivation from the oxidized electrolytes (by minimizing the charge recombination between oxidized electrolytes and electrons present into conduction band of TiO_2). However, J_{SC} of **AS** dyes (except **AS5** dye) decreased when the dyes were sensitized with CDCA. Meanwhile the J_{SC} was found high for short distance acceptor unit dyes **AS5** and **AK2** but decreased in case of **AS2** due to branched alkyl group near to TiO_2 leads low dye-loading without CDCA. Whereas dyes with long distance acceptor unit **AS1**, **AS3** and **AS4** showed little difference in J_{SC} value, but the **AS1** dye has high dye loading showed low J_{SC} value due to aggregation and charge recombination (**Figure 5**, **Table 2**). Here, **AS5** dye sensitized with the 2 equivalents of CDCA showed maximum DSSC device efficiency of 8.01% with the V_{OC} of 819 mV and J_{SC} of 11.98 mAcm^{-2} compared to reference **AK2** and other **AS** dyes. Here, visible light-responsive D-A-D based unsymmetrical squaraine dyes **AS** with the N-hexylation on the indoline moiety which is away from the TiO_2 surface showed significant effect on the DSSC device performance compared to N-alkylation on the aniline moiety that near or away from the TiO_2 surface. **AS** dyes with the small acceptor-anchoring group distance showed better IPCE response over the dyes with the large acceptor-anchoring group distance. Incorporation of N-ethylhexyl alkyl group in

the aniline moiety of the **AS2** dye showed decreased IPCE response, whereas N-hexylation on the indoline moiety for **AS5** dye showed enhanced IPCE response which was further enhanced by CDCA addition compared to **AS2** dye. The value of V_{OC} of the dye changed due to shifts in the conduction band of TiO_2 due to dipole moment of dyes.^{50,51} It is observed that the V_{OC} for the DSSC devices sensitized with the dyes with An-SQ-In-Anchoring group (long distance between SQ unit and the anchoring group) were lower than its other counterpart (In-SQ-An-Anchoring group), and it may be due to the reduced dipole moments of the earlier set of dyes. Further, the presence of alkyl group away from TiO_2 surface helps more loading of dyes compared to the dyes with alkyl group which is near to the surface.

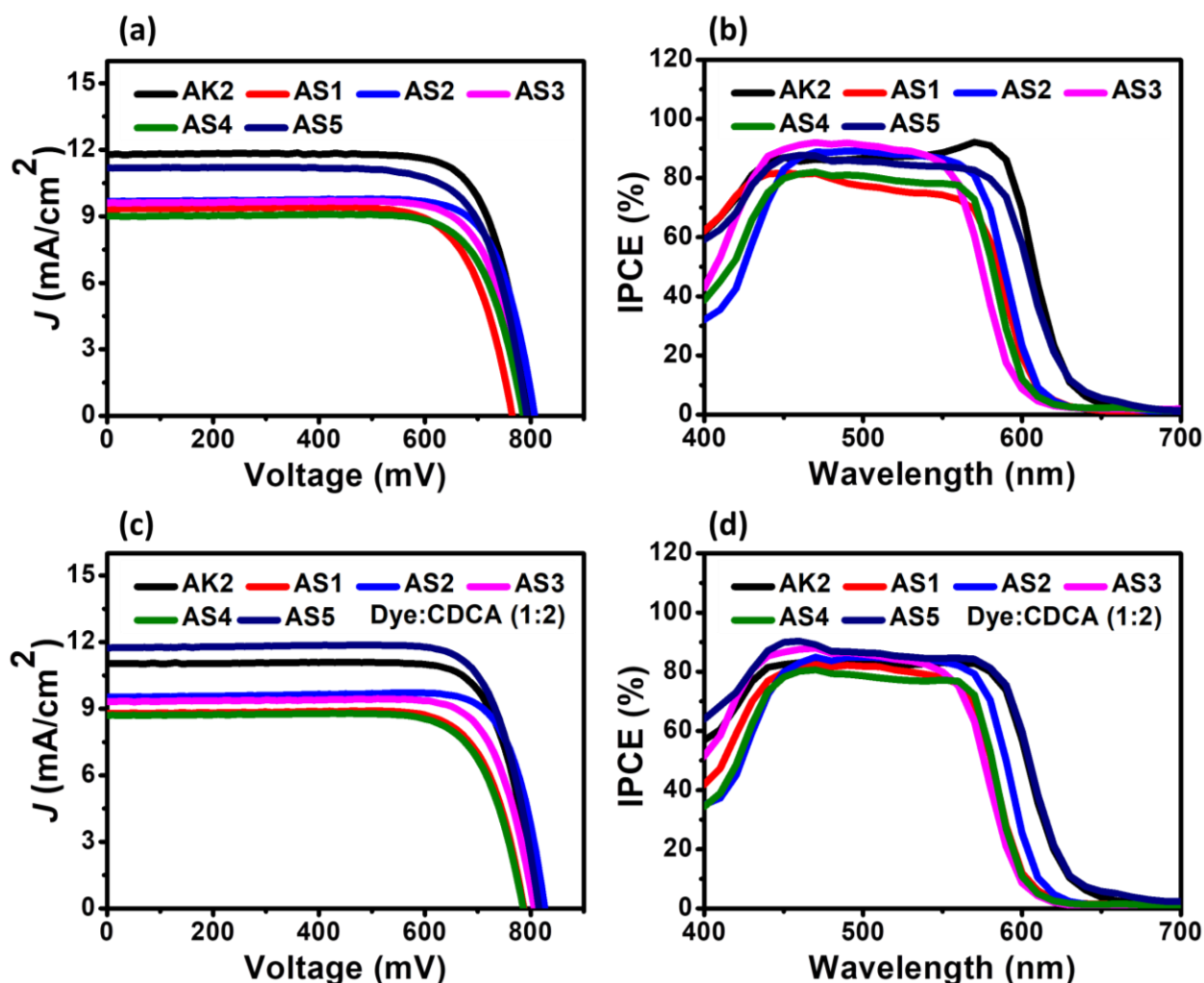


Figure 8. (a) I - V , and (b) IPCE curves for **AK2** and **AS** dyes without CDCA) (c) I - V , and (d) IPCE curves for **AK2** and **AS** dyes with CDCA in I^-/I_3^- electrolyte.

Table 3. Optimized DSSC performances of AS and AK2 dyes with and without co-adsorbent (CDCA) in I^-/I_3^- electrolyte.

Dyes	CDCA (Equiv.)	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AK2	0	800 $\pm$ 2	11.76 $\pm$ 0.14	78 $\pm$ 0.68	7.34 $\pm$ 0.17
AK2	2	812 $\pm$ 1	11.03 $\pm$ 0.27	80 $\pm$ 0.95	7.17 $\pm$ 0.27
AS1	0	765 $\pm$ 3	9.34 $\pm$ 0.12	75 $\pm$ 0.59	5.36 $\pm$ 0.13
AS1	2	787 $\pm$ 4	8.80 $\pm$ 0.18	78 $\pm$ 0.67	5.40 $\pm$ 0.19
AS2	0	808 $\pm$ 2	9.69 $\pm$ 0.16	79 $\pm$ 0.43	6.19 $\pm$ 0.15
AS2	2	827 $\pm$ 2	9.53 $\pm$ 0.19	82 $\pm$ 0.83	6.46 $\pm$ 0.21
AS3	0	791 $\pm$ 4	9.59 $\pm$ 0.23	78 $\pm$ 0.82	5.92 $\pm$ 0.24
AS3	2	807 $\pm$ 3	9.32 $\pm$ 0.21	79 $\pm$ 0.78	5.94 $\pm$ 0.22
AS4	0	786 $\pm$ 3	9.01 $\pm$ 0.17	76 $\pm$ 0.94	5.38 $\pm$ 0.19
AS4	2	805 $\pm$ 2	8.70 $\pm$ 0.10	78 $\pm$ 0.64	5.46 $\pm$ 0.13
AS5	0	793 $\pm$ 3	11.19 $\pm$ 0.25	77 $\pm$ 0.61	6.83 $\pm$ 0.23
AS5	2	816 $\pm$ 3	11.74 $\pm$ 0.24	81 $\pm$ 0.56	7.76 $\pm$ 0.25

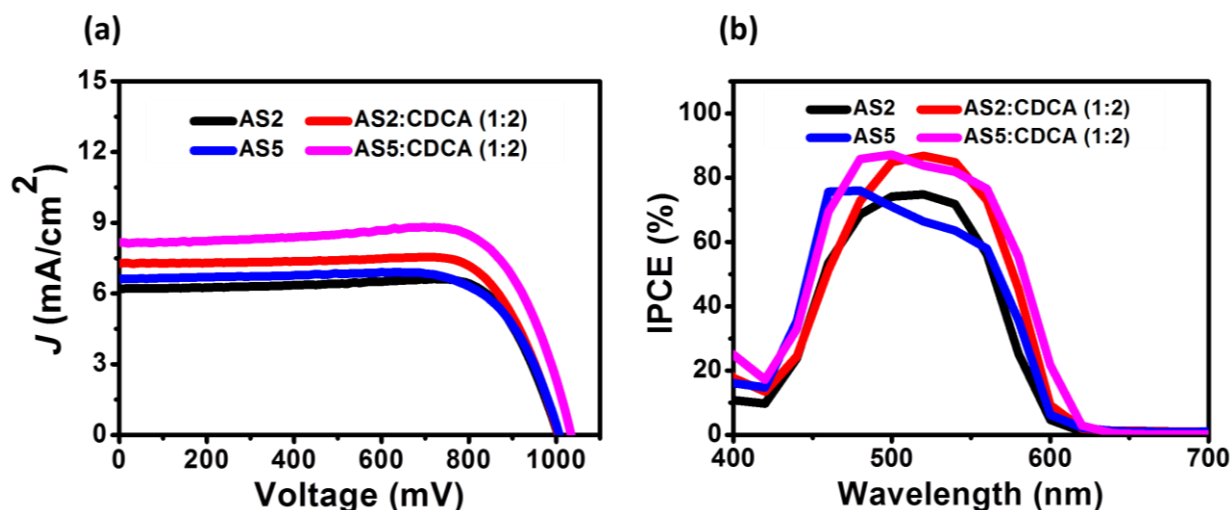


Figure 9. (a) I - V , and (b) IPCE curves for AS2 and AS5 dyes without co-adsorbent (CDCA) with Cu (I/II) electrolyte.

Furthermore, the HOMO energy level of the highly efficient **AS2** and **AS5** dyes was more positive, therefore have been tested with the copper electrolyte. The DSSC device characterizations of photoanode made from **AS2** and **AS5** dye in Cu(I/II) electrolyte with and without CDCA have been carried out and optimized DSSC results have been provided in **Figure 9** and **Table 4**. Here, **AS5** dye gave the highest V_{OC} of 1036 mV, J_{SC} of 8.36 mAcm^{-2} and efficiency of 7.08%, whereas **AS2** dye gave V_{OC} of 1007 mV, J_{SC} of 7.38 mAcm^{-2} and efficiency of 5.95% with 2 equivalents of CDCA. The V_{OC} of 1010 mV, J_{SC} of 6.78 mAcm^{-2} and efficiency of 5.34% has been achieved by **AS5** dye, whereas 1006 mV of V_{OC} , 6.30 mAcm^{-2} of J_{SC} and 5.25% efficiency has been achieved by **AS2** dye in the absence of CDCA. Further, the integrated J_{SC} value obtained from IPCE are well aligning with the J_{SC} value obtained from the I - V characterization with the I^-/I_3^- electrolyte and Cu (I/II) electrolyte for **AS** dyes (**Table 5** and **Table 6**).

Table 4. Optimized DSSC performances of **AS2** and **AS5** dyes with and without co-adsorbent (CDCA) with Cu(I/II) electrolyte.

Dyes	Electrolyte	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff (%)	η (%)
AS2	Cu(I/II)	1004 ± 2	6.21 ± 0.09	82 ± 0.88	5.11 ± 0.14
AS2:CDCA (1:2)	Cu(I/II)	1005 ± 2	7.27 ± 0.11	79 ± 1.03	5.77 ± 0.18
AS5	Cu(I/II)	1007 ± 3	6.63 ± 0.15	77 ± 0.93	5.14 ± 0.20
AS5:CDCA (1:2)	Cu(I/II)	1034 ± 2	8.16 ± 0.20	81 ± 0.72	6.84 ± 0.24

Table 5. Integrated value of J_{SC} from IPCE of **AK2** and **AS** dyes with I^-/I_3^- electrolyte.

Dyes	CDCA (Equiv.)	J_{sc} (mA/cm^2)	J_{sc} (mA/cm^2) from IPCE	Error (%)
AK2	0	11.76	11.28	4.08
AS1	0	9.34	8.92	4.49
AS2	0	9.69	9.40	2.99

AS3	0	9.59	9.22	3.85
AS4	0	9.01	8.62	4.32
AS5	0	11.19	10.75	3.93
AK2	2	11.03	10.44	5.34
AS1	2	8.80	8.61	2.16
AS2	2	9.53	9.15	3.98
AS3	2	9.32	8.87	4.82
AS4	2	8.70	8.30	4.59
AS5	2	11.74	11.05	5.87

Table 6. Integrated value of J_{SC} from IPCE of AS2 and AS5 dye with Cu(I/II) electrolyte.

Dyes	CDCA (Equiv.)	$J_{sc} \text{ (mA/cm}^2\text{)}$	$J_{sc} \text{ (mA/cm}^2\text{)}$ from IPCE	Error (%)
AS2	0	6.21	5.93	4.50
AS2	2	7.27	7.14	1.79
AS5	0	6.63	6.44	2.86
AS5	2	8.16	7.92	2.94

The mass transport limitations were determined by the photocurrent transient experiment. Here, we have selected the highly efficient dye AS5 along with AS2 dye for the transient experiment with I^-/I_3^- and Cu(I/II) electrolytes. The current values increase along with the light illumination intensity of 0.8 Sun to 1.0 Sun. Here, AS2 and AS5 dyes with the Cu(I/II) electrolyte showed relatively low current compared to I^-/I_3^- electrolyte, and supports the current obtained from I - V characterization. Further, regeneration efficiency of the AS2 and AS5 dyes were calculated which showed more than 90% with both electrolytes. Where, AS5 dye with CDCA showed highest regeneration efficiency in I^-/I_3^- over without CDCA and Cu(I/II) electrolyte.

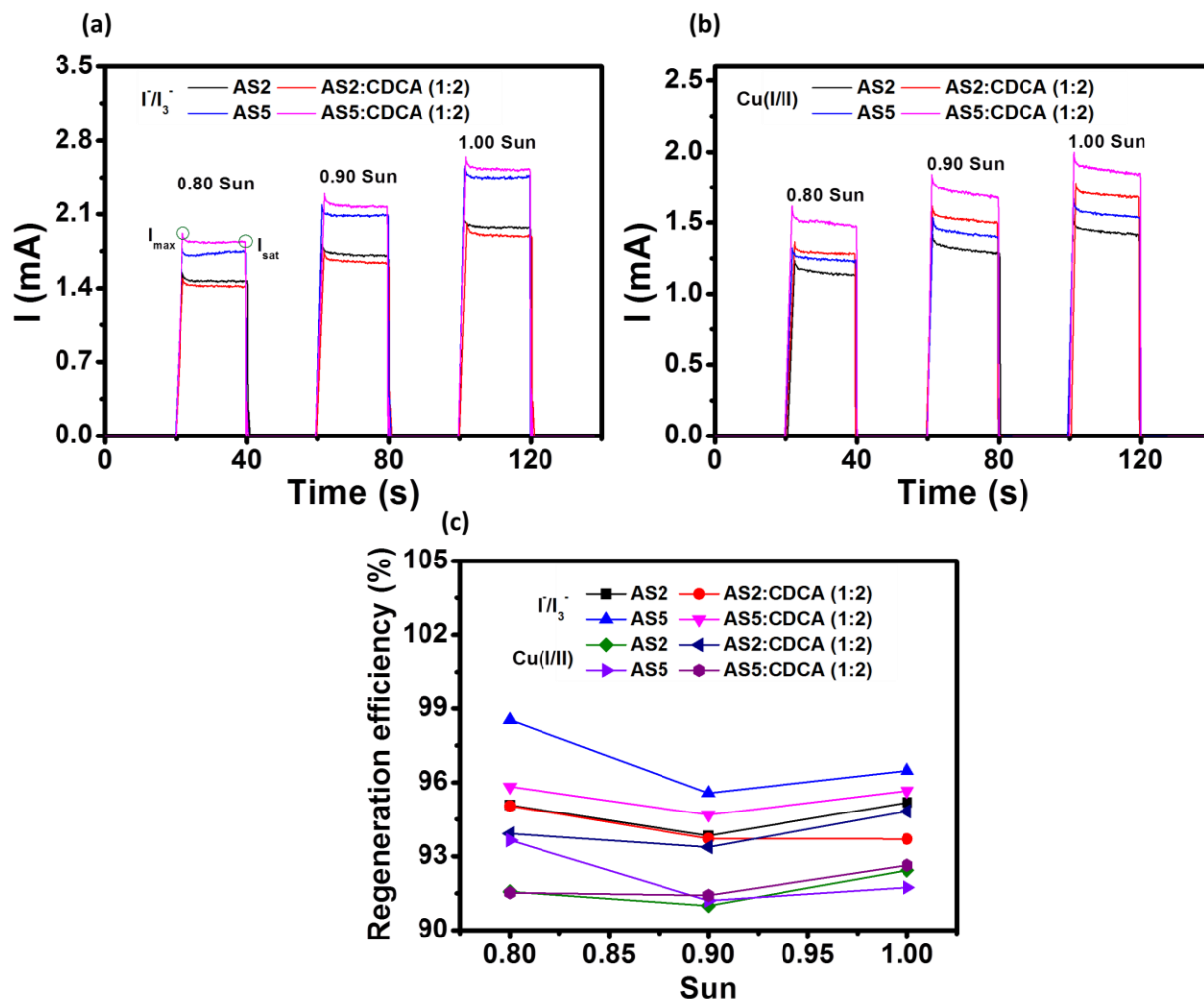


Figure 10. Current transient profile of AS2 and AS5 dyes (a) with I^-/I_3^- electrolyte, (b) with Cu (I/II) electrolyte, and (c) regeneration efficiency of AS2 and AS5 dye with I^-/I_3^- and Cu (I/II) electrolytes at different sun intensities.

3.2.5 Electrochemical Impedance Spectroscopy (EIS).

Charge recombination resistance (R_{ct}), chemical capacitance (C_{μ}) and lifetime of electron (τ) in the TiO_2 are the important parameters to study the dye- TiO_2 /electrolyte interface in a DSSC device and determines the device performance, and high values of these parameters directly reflect the DSSC device efficiency. All the above parameters can be captured by doing the EIS experiment. To scrutinize the device efficiency indoline-aniline donor-based AS and AK2 dyes with I^-/I_3^- electrolyte, EIS characterizations were carried out in dark conditions by applying the

different potentials (Figure 12, 13, and 14).⁵³ The Nyquist plots for AS dyes along with reference dye AK2 without CDCA at 0.5 V applied potentials are shown in Figure 11a.

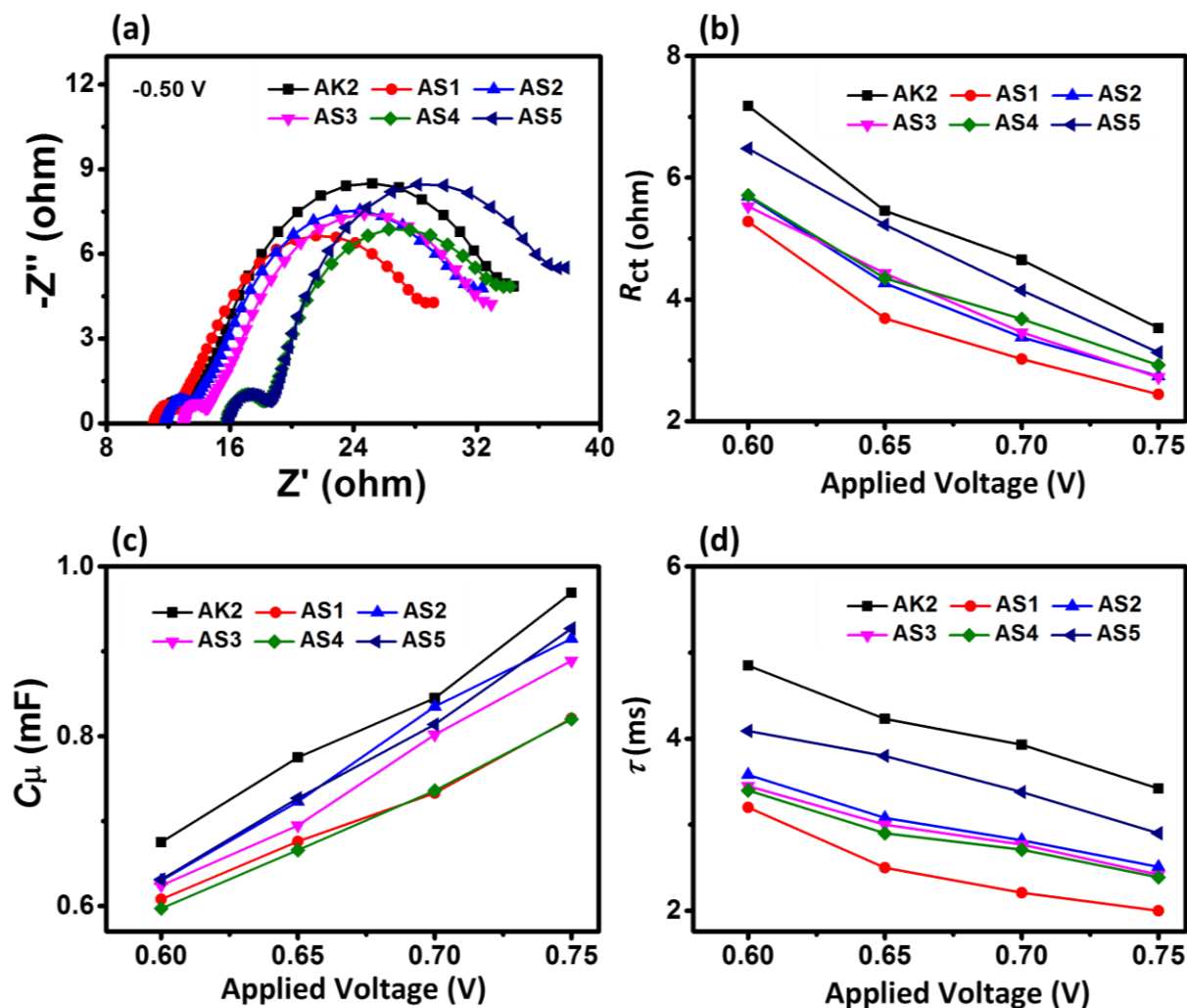


Figure 11. (a) Nyquist plot, (b) charge recombination resistance, (c) chemical capacitance and (d) lifetime of electron of AK2 and AS dyes without CDCA.

The R_{ct} and C_{μ} values have been obtained by fitting the Nyquist plot, and multiplication of these two parameters gave the τ value. The order of R_{ct} values without CDCA are 5.28Ω (AS1) < 5.53Ω (AS3) < 5.70Ω (AS2) < 5.71Ω (AS4) < 6.48Ω (AS5) < 7.18Ω (AK2) which were further changed in order of 5.49Ω (AS1) < 5.59Ω (AS2) < 5.69Ω (AS3) < 5.95Ω (AS4) < 6.38Ω (AK2) < 8.86Ω (AS5) with CDCA by sensitizing the dyes with CDCA. The R_{ct} value showed low for long distance acceptor unit compared to short distance acceptor without CDCA but the

R_{ct} of **AS2** dye decreased due to branched alkyl group position at down. Low R_{ct} for **AS5** dye without CDCA compared to the **AK2** dye is due to the unwanted vacant spaces between the anchored **AS5** dyes which arises due to steric hindrance on the TiO_2 . The spaces between the **AS5** dyes were filled by CDCA molecules, which passivated the TiO_2 surface from the oxidized electrolyte and enhanced the R_{ct} compared to the **AK2** (increased competition between dye-CDCA anchoring).

Table 7. EIS parameters of DSSC device made with the reference dye **AK2** and **AS** dyes in dark with the applied potential of 0.60 V.

Dye	R_{ct} (ohm)	C_{μ} (mF)	τ (ms)
AK2	7.18	0.675	4.85
AK2:CDCA (1:2)	6.38	0.648	4.13
AS1	5.28	0.608	3.20
AS1:CDCA (1:2)	5.49	0.617	3.38
AS2	5.70	0.630	3.58
AS2:CDCA (1:2)	5.59	0.628	3.50
AS3	5.53	0.624	3.45
AS3:CDCA (1:2)	5.69	0.606	3.44
AS4	5.71	0.597	3.40
AS4:CDCA (1:2)	5.95	0.618	3.67
AS5	6.48	0.631	4.09
AS5:CDCA (1:2)	8.86	0.734	6.50

Further it has been observed that the branched alkyl groups at up and down position showed poor response over the normal alkyl groups with or without CDCA. Whereas the short distance acceptor unit depicted the good response due to increase the interfacial electron process with TiO_2 . Similarly, chemical capacitance (C_{μ}) and lifetime (τ) values were obtained high for **AK2** (6.728 D) without and for **AS5** (6.77 D) with CDCA and supports the achieved efficiency for the respective dyes (**Table 7**). Obtained high C_{μ} values for the **AK2** and **AS5** due to change in dipole moment and revealed the importance of small acceptor-anchoring group distance over the

large distance, whereas value revealed the high achieved current and voltage for the respective dyes. The conduction band E_{CB} depends on the dipole moment (μ) of the dye (equation 1). The E_{CB} is directly proportional to the dipole moment so when the dipole moment of the sensitizer will increase the E_{CB} upshift resultant the V_{OC} also increased.⁵⁰

Equation 1

$$\Delta E_{CB} = - \frac{q\mu\gamma}{\epsilon_0\epsilon}$$

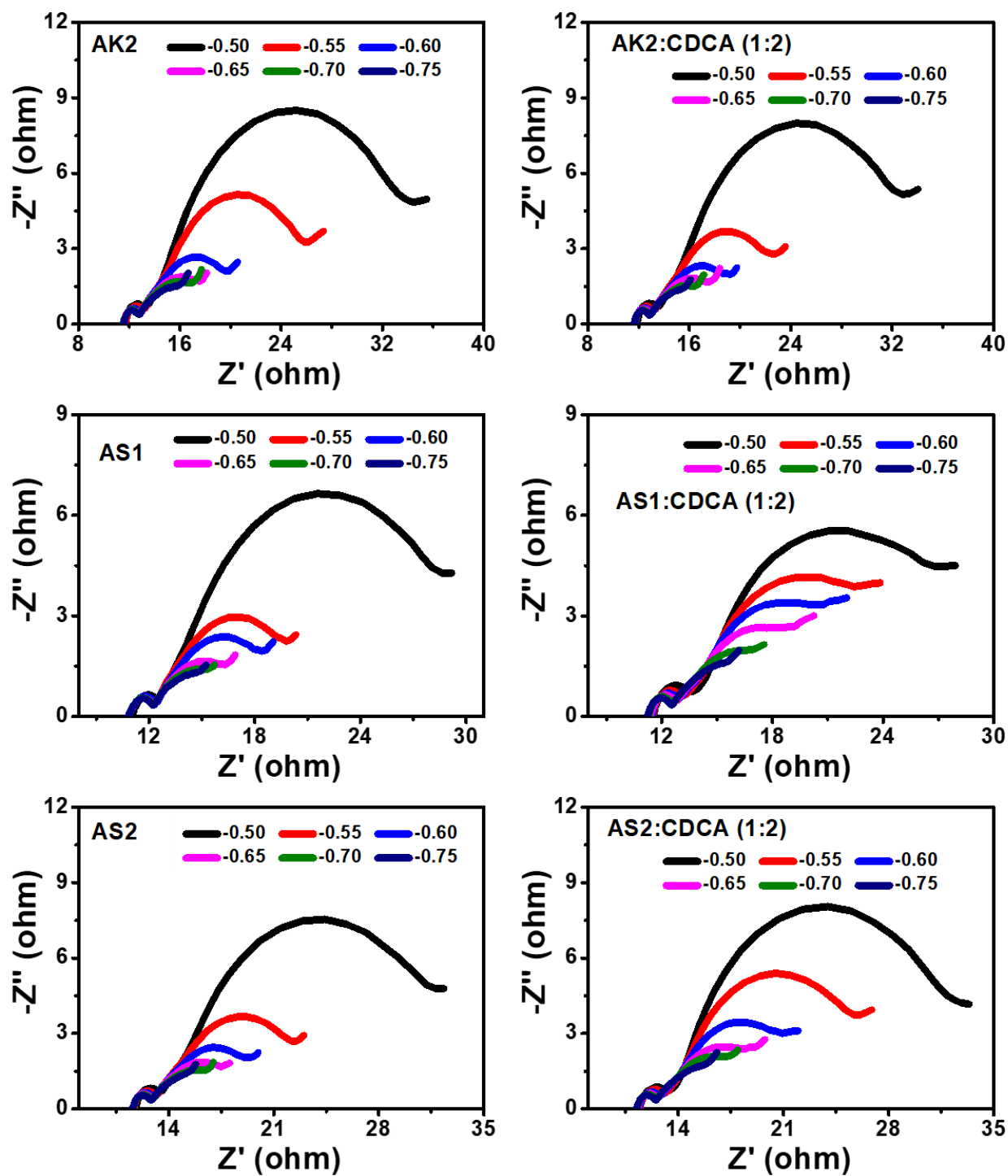


Figure 12. EIS studies of AK2, AS1, and AS2 dyes vs applied bias with and without CDCA.

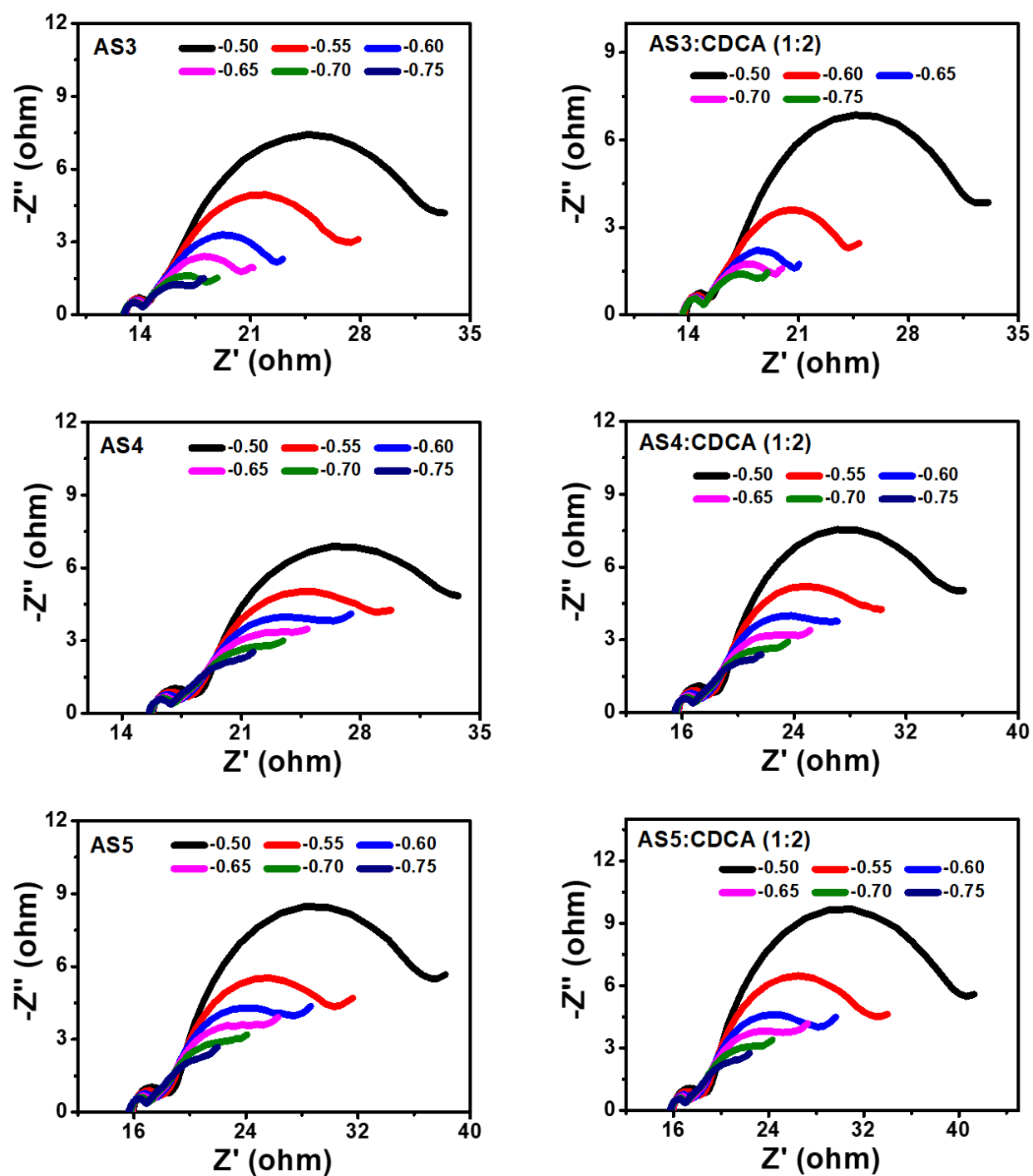


Figure 13. EIS studies of AS3, AS4, and AS5 dyes vs applied bias with and without CDCA.

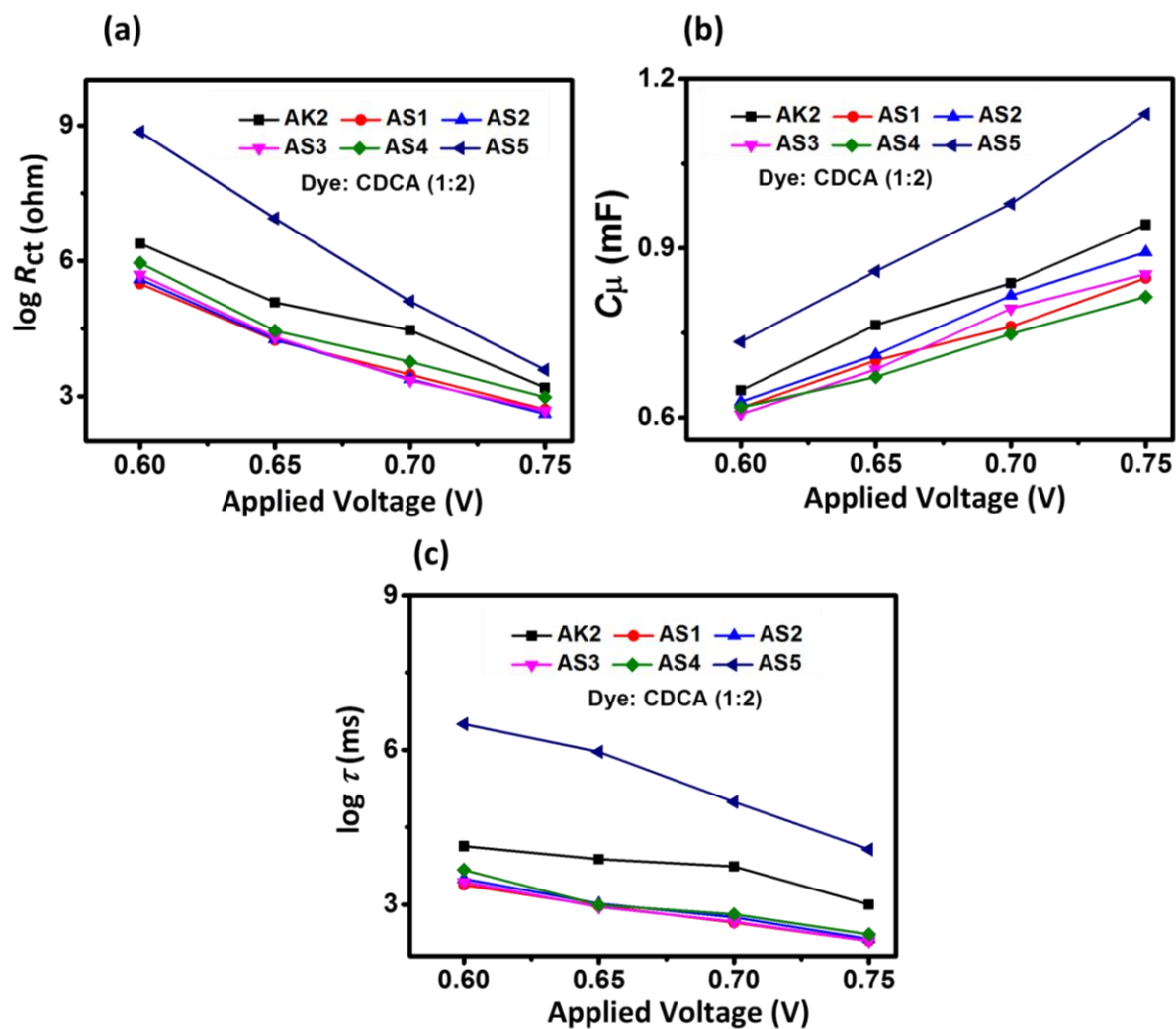


Figure 14. EIS studies of AK2 and AS dyes vs applied bias with CDCA.

3.3 CONCLUSION

In summary, a series of indoline-aniline donor-based D-A-D sensitizers **AS1-AS5** with change the position of acceptor unit and along with less hindered alkyl group have been design and synthesized for DSSC. Here our objective was to study the effect of acceptor unit position on the DSSC device performance for D-A-D based squaraine dyes. Synthesized **AS** dyes showed different absorption properties due to change in the position of acceptor unit and alkyl group. The absorption of long acceptor-anchoring group distance **AS1**, **AS3** and **AS4** dyes showed blue shift compared to short acceptor-anchoring group distance for the **AS2** and **AS5** dye in CH_2Cl_2 . The dihedral angle between the aniline unit and squaraine unit in-plane was high for -41.26°/**AS2**, -46.42°/**AS3** dye, due to branching at aniline donor compared to the normal alkyl chain 0.85°/**AS4** and -1.16°/**AS5** dyes. The DSSC device performance for the **AS** dyes showed the importance of short acceptor-anchoring groups over large distance. The maximum DSSC device efficiency of 8.01% has been achieved for **AS5** dye with CDCA in I^-/I_3^- electrolyte. Further, **AS5** dye sensitized with CDCA gave the highest V_{OC} of 1036 mV, J_{SC} of 8.36 mAcm^{-2} and efficiency of 7.08% with Cu(I/II) electrolyte. The obtained results from these sets of dyes revealed the importance of acceptor-anchoring group distance on photovoltaic performance and will be useful for further designing the new and better D-A-D based dyes for DSSC.

3.4 EXPERIMENTAL SECTION

Compounds 1,³⁵ 2,⁴³ 1-hexyl-2,3,3-trimethylindoline-5-carboxylic acid,⁴⁴ 4⁴⁴ and 7³⁶ were synthesized using the procedure provided in literature, aniline, N-methylaniline, and 4-(methylamino)benzoic acid, 3,4-dibutoxycyclobut-3-ene-1,2-dione were procured from the commercial sources.

3.4.1 General methods.

Refer section 2.4.1 for general methods utilized and DSSC device fabrication procedure (Chapter 2, Page No: Page No: 66-68). High-resolution mass spectrometric (HRMS) measurements were recorded on SYNAPT G2 HDM in MeOH as a solvent.

3.4.2 Synthesis of AS dyes.

2-((2-butoxy-3,4-dioxocyclobut-1-en-1-yl)methylene)-1-hexyl-3,3-dimethylindoline-5-

carboxylic acid (4): Compound 1-hexyl-2,3,3-trimethylindoline-5-carboxylic acid (0.9 g, 2.16 mmol) and compound 3,4-dibutoxycyclobut-3-ene-1,2-dione (0.49 g, 2.16 mmol) were dissolved in n-BuOH 20 mL in round bottom flask (100 mL) then added triethylamine (0.55 g, 5.4 mmol) stirred at room temperature for 12 h then reaction was heated for 2 h at 70 °C. The reaction mixture was cooled to room temperature and solvents were removed under reduced pressure and purified with column chromatography (SiO₂, 100-200 mesh) with using MeOH and CH₂Cl₂. Yield: 500 mg, 52%. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (dd, *J*=8.38, 1.63 Hz, 1H), 7.98 (d, *J*=2 Hz, 1H), 6.90 (d, *J*=8 Hz, 1H), 5.51 (s, 1H), 4.88 (t, *J*=6.63 Hz, 2H), 3.84 (t, *J*=7.50 Hz, 2H), 1.83–1.95 (m, 2H), 1.76 (t, *J*=7.00 Hz, 2H), 1.49–1.58 (m, 2H), 1.31–1.47 (m, 6H), 1.02 (t, *J*=7.44 Hz, 3H), 0.87–0.95 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 13.6, 13.9, 18.7, 22.4, 26.2, 26.6, 27.0, 31.3, 32.1, 43.1, 47.3, 74.1, 83.2, 107.7, 122.9, 123.87, 131.5, 140.8, 147.5, 167.3, 171.1, 173.4, 188.5, 188.8, 192.3.

2-((2-Butoxy-3,4-dioxocyclobut-1-en-1-yl)methylene)-1-hexyl-3,3-dimethylindoline-5-

carboxylic acid (5): Compound 4 (0.45 g, 1.02 mmol) was dissolved in 10 mL acetone, 2 N aqueous HCL (3 mL) was added to the above mixture and refluxed for 12 h. The reaction mixture was cooled to room temperature and solvents were removed under reduced pressure and dried with high vacuum pump. Yield: 0.25 g, 55%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.88 (s,

1H), 7.86 (d, $J=4$ Hz, 1H), 7.14 (d, $J=8.39$ Hz, 1H), 5.59 (s, 1H), 3.87 (t, $J=7.25$ Hz, 2H), 1.59–1.67 (m, 2H), 1.56 (s, 6H), 1.24–1.39 (m, 6H), 0.83 (t, $J=7.25$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6): 14.2, 22.4, 26.2, 26.2, 27.2, 31.3, 46.8, 83.7, 108.4, 123.3, 124, 130.8, 140.5, 147.3, 164.8, 167.7, 174.5, 193.

N-(2-Ethylhexyl)aniline (6): Aniline (0.7 g, 7.51 mmol) and 2-ethylhexanal (1.15 g, 9.01 mmol) were dissolved in 20 mL of anhydrous CH_2Cl_2 and added 1 mL of acetic acid in a 100 mL round bottom flask and stirred at rt for 1 h, added $\text{NaBH}(\text{OAc})_3$ (3.18 g, 15.03 mmol) in reaction flask stirred at room temperature for 12 h after that reaction mixture quenched with NaHCO_3 aqueous solution, organic layer was extracted with CH_2Cl_2 (3×30 mL), dried over Na_2SO_4 , concentrated and purified with 97.5% pet ether and 2.5% EtOAc. Yield: 0.85 g, 55%. ^1H NMR (500 MHz, DMSO- d_6): δ 7.00–7.07 (m, 2H), 6.52–6.57 (m, 2H), 6.44–6.50 (m, 1H), 5.46 (t, $J=5.63$ Hz, 1H), 2.88 (t, $J=6.07$ Hz, 2H), 1.47–1.58 (m, 1H), 1.29–1.41 (m, 4H), 1.24–1.28 (m, 4H), 0.79–0.93 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3): 15.9, 19.2, 27.8, 29.0, 33.6, 35.8, 43.2, 51.3, 116.9, 120.3, 134.0, 154.4.

General procedure for the synthesis of AS dyes: Semisquaric acid derivative (1 equiv.) and corresponding aniline derivative (1 equiv.) were dissolved in anhydrous toluene and n -BuOH (1:1, 10 mL of each) in a 50 mL of round bottomed flask and charged with the Dean-Stark distillation apparatus. The reaction mixture was refluxed for 16 h under an inert atmosphere. After completion of reaction, solvents were removed and purified by either simple filtration or column chromatography (SiO_2 , 100–200 mesh, MeOH and CH_2Cl_2) to obtain the required dyes.

2-((-5-Carboxy-1,3,3-trimethylindolin-2-ylidene)methyl)-4-(methyl(phenyl)iminio)-3-

oxocyclobut-1-en-1-olate (AS1): Compound **1** (0.2 g, 0.63 mmol) and N-methylaniline (0.068 mg, 0.63 mmol), orange colour solid were filtered and dried under reduced pressure. Yield: 150 mg, 56%. Mp: 248 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.09 (dd, $J = 8.39, 1.53$ Hz, 1H), 8.00 (d, $J = 1.53$ Hz, 1H), 7.41–7.54 (m, 4H), 7.31–7.41 (m, 1H), 6.96 (d, $J = 8.39$ Hz, 1H), 5.88 (s, 1H), 4.06 (s, 3H), 3.48 (s, 3H), 1.75 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): 27.4, 30.4, 39.3, 46.0, 48.0, 86.7, 107.9, 122.8, 123.8, 127.8, 129.0, 131.2, 140.3, 141.4, 147.4, 169.1, 170.6, 174.5, 180.2. HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4\text{N}_2$: 402.1580; found: $[\text{M}+\text{H}]^+$ 403.1653.

4-((4-Carboxyphenyl)(2-ethylhexyl)iminio)-3-oxo-2-((1,3,3-trimethylindolin-2-ylidene)

methyl)cyclobut-1-en-1-olate (AS2): Compound **2** (0.2 g, 0.74 mmol) and 4-((2-ethylhexyl)amino)benzoic acid **7** (0.184 g, 0.74 mmol), orange colour solid were filtered and dried. Yield: 230 mg, 60%. Mp: 250 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J=8.63$ Hz, 2H), 7.29–7.42 (m, 4H), 7.14 (t, $J=7.50$ Hz, 1H), 7.00 (d, $J=7.88$ Hz, 1H), 5.85 (br. s., 1H), 4.30–4.59 (m, 2H), 3.51 (br. s., 3H), 1.75 (br. s., 5H), 1.46–1.58 (m, 1H), 1.15–1.45 (m, 9H), 0.80–0.93 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): 10.5, 13.9, 22.8, 23.3, 27.2, 28.3, 29.8, 37.2, 48.9, 54.4, 85.5, 109.0, 122.1, 123.6, 124.0, 127.8, 129.4, 131.1, 142.0, 167.5, 171.2, 177.0, 180.6. HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{31}\text{H}_{36}\text{O}_4\text{N}_2$: 500.2675; found: $[\text{M}+\text{H}]^+$ 501.2748.

2-((5-Carboxy-1,3,3-trimethylindolin-2-ylidene)methyl)-4-((2-ethylhexyl)(phenyl)iminio)-3-

oxocyclobut-1-en-1-olate (AS3): Compound **1** (0.2 g, 0.63 mmol) and N-(2-ethylhexyl)aniline (**6**) (0.13 g, 0.63 mmol), orange colour solid were filtered and dried at high vacuum pressure pump. Yield: 200 mg, 60%. Mp: 210 °C. ^1H NMR (500 MHz, CDCl_3): δ 8.08 (dd, $J=8.20$, 1.72 Hz, 1H), 7.98 (d, $J=1.53$ Hz, 1H), 7.48 (t, $J=7.82$ Hz, 2H), 7.32–7.43 (m, 3H), 6.93 (d, $J=8.39$ Hz, 1H), 5.84 (s, 1H), 4.45–4.52 (m, 1H), 4.36–4.44 (m, 1H), 3.45 (s, 3H), 1.74 (s, 6H), 1.48–1.56 (m, 1H), 1.38–1.44 (m, 2H), 1.29–1.37 (m, 2H), 1.18–1.27 (m, 5H), 0.82–0.88 (m, 6H); ^{13}C NMR (126 MHz, CDCl_3): 10.4, 13.9, 22.8, 23.2, 27.5, 28.0, 28.3, 29.8, 30.2, 37.1, 47.8, 55.1, 86.6, 107.7, 123.6, 123.8, 124.4, 128.2, 129.0, 131.2, 137.9, 141.3, 147.5, 168.4, 170.7, 174.5, 176.7, 179.5, 182.3. HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{31}\text{H}_{36}\text{O}_4\text{N}_2$: 500.2675; found: $[\text{M}+\text{H}]^+$ 501.2748.

2-((-5-Carboxy-1-hexyl-3,3-dimethylindolin-2-ylidene)methyl)-4-(methyl(phenyl)iminio)-3-

oxocyclobut-1-en-1-olate (AS4): Compound **5** (0.2 g, 0.589 mmol) and N-methylaniline (0.089 g, 0.589 mmol), orange colour solid were filtered and dried under reduced pressure. Yield: 200 mg, 70%. Mp: 180 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.09 (d, $J=8.75$ Hz, 2H), 7.45 (d, $J=8.88$ Hz, 2H), 7.30–7.39 (m, 2H), 7.15–7.22 (m, 1H), 7.02 (d, $J=8.00$ Hz, 1H), 5.95 (s, 1H), 4.03 (s, 3H), 3.93–4.02 (m, 2H), 1.77–1.87 (m, 2H), 1.76 (s, 6H), 1.38–1.49 (m, 2H), 1.28–1.38 (m, 4H), 0.84–0.93 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3): 13.9, 22.4, 26.6, 26.9, 27.1, 31.4, 43.7, 49.4, 85.8, 109.6, 121.8, 122.2, 124.1, 127.8, 127.8, 131.1, 142.0, 142.1, 144.5, 168.4, 171.6, 175.3, 181.8. HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_2$: 472.2360; found: $[\text{M}+\text{H}]^+$ 473.2435.

4-((4-Carboxyphenyl)(methyl)iminio)-2-((1-hexyl-3,3-dimethylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AS5): Compound **3** (0.15 g, 0.39 mmol) and 4-(methylanino) benzoic acid (0.042 g, 0.391 mmol), orange colour solid were filtered and dried at high vacuum pressure pump. Yield: 150 mg, 78%. Mp: 228 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.09 (dd, $J=8.32, 1.69$ Hz, 1H), 8.01 (d, $J=1.50$ Hz, 1H), 7.41–7.51 (m, 4H), 7.33–7.39 (m, 1H), 6.95 (d, $J=8.38$ Hz, 1H), 5.92 (s, 1H), 4.06 (s, 3H), 3.92 (t, $J=7.57$ Hz, 2H), 1.81 (br. s., 2H), 1.75 (s, 6H), 1.36–1.46 (m, 2H), 1.21–1.34 (m, 4H), 0.87 (m, $J=7.06$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): 13.9, 22.4, 26.6, 26.6 27.4, 31.4, 39.2, 43.4, 48.1, 86.6, 108.2, 122.8, 123.6, 123.9, 127.7, 129.1, 131.2, 140.3, 141.5, 147.1, 168.6, 170.7, 180.2, 180.7. HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{28}\text{H}_{32}\text{O}_4\text{N}_2$: 472.2360; found: $[\text{M}+\text{H}]^+$ 473.2435.

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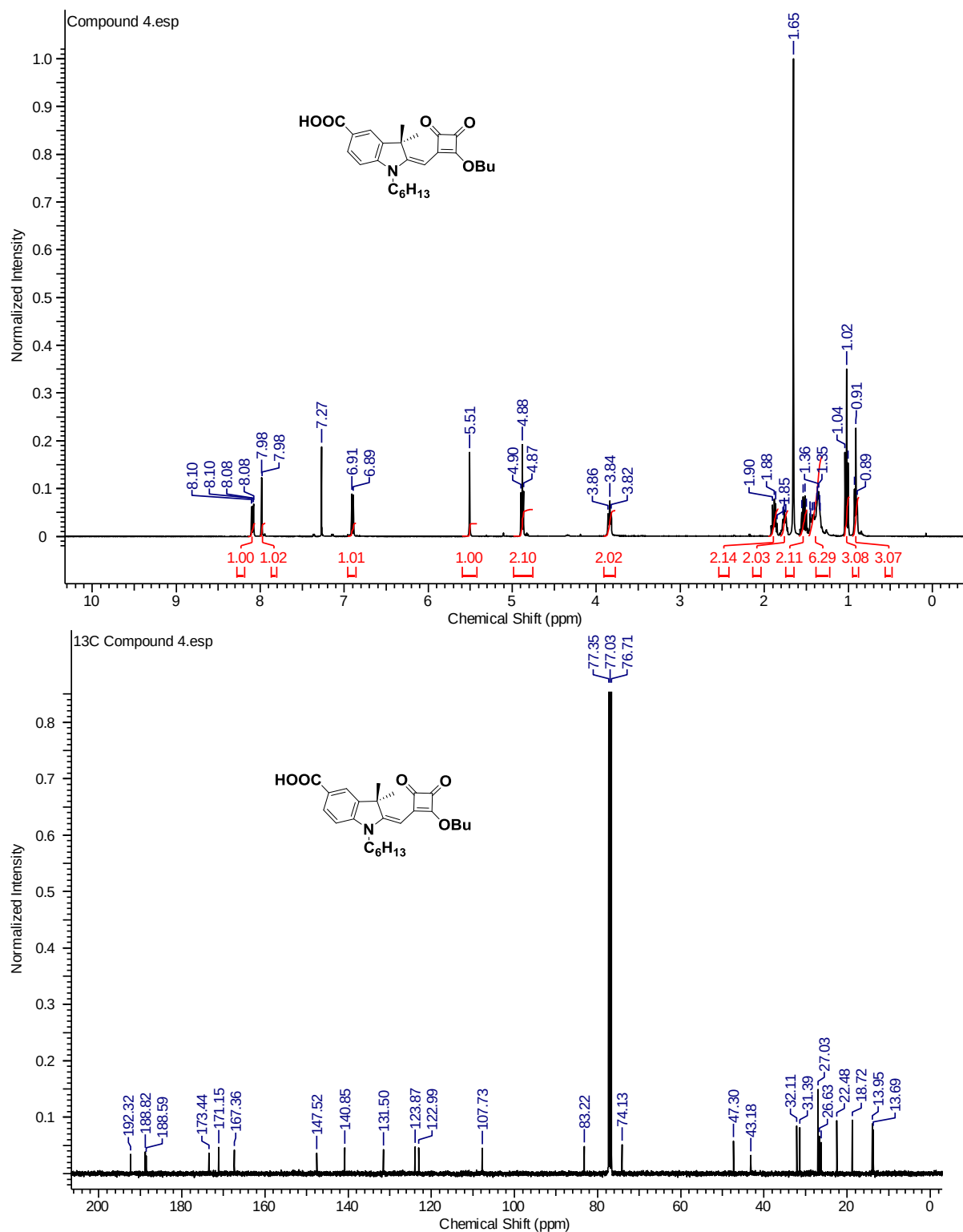
^1H -NMR, ^{13}C -NMR, and HRMS

Figure 15. ^1H - and ^{13}C - NMR spectra of **Compound 4** in CDCl_3 .

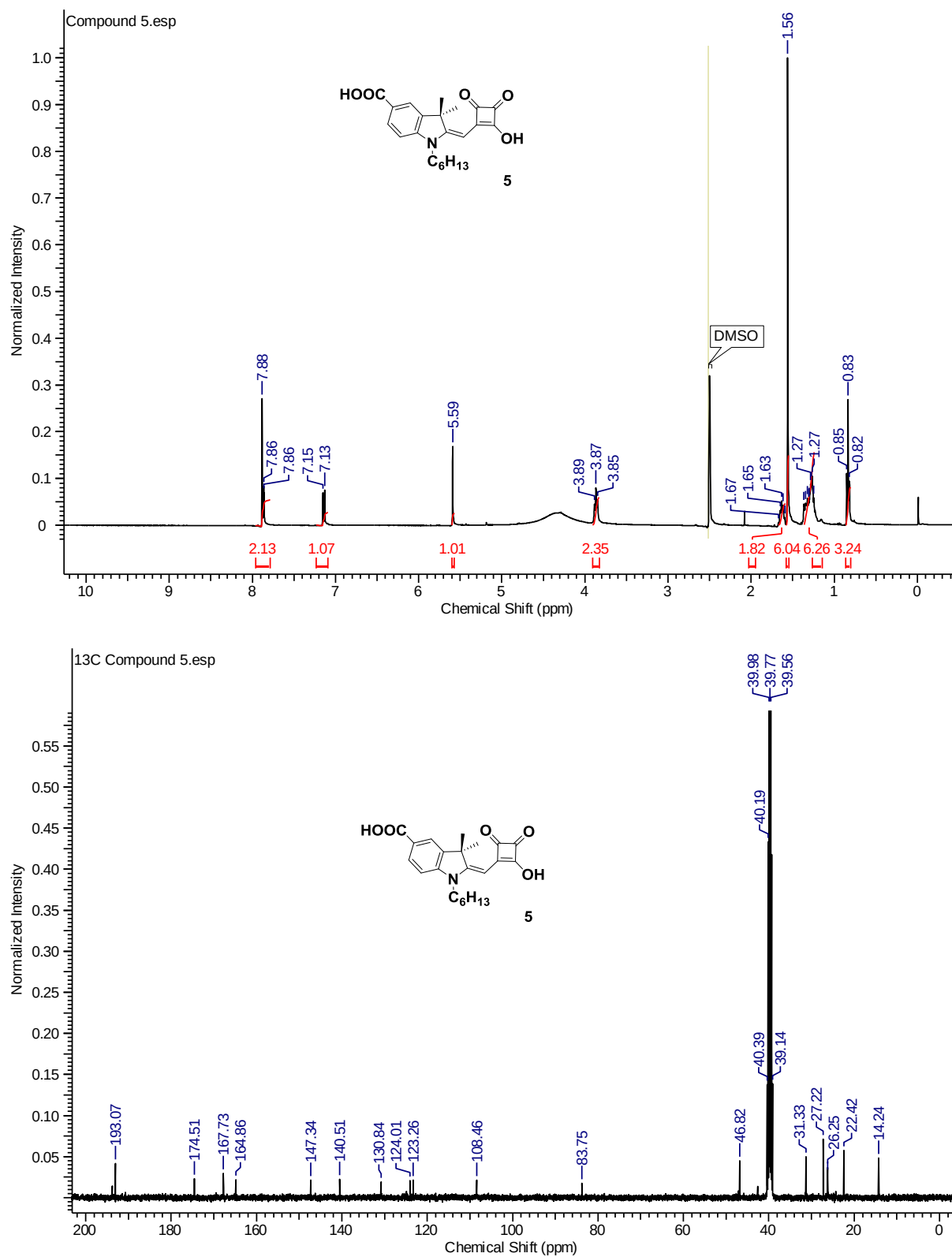


Figure 16. ¹H- and ¹³C- NMR spectra of **Compound 5** in DMSO-d₆.

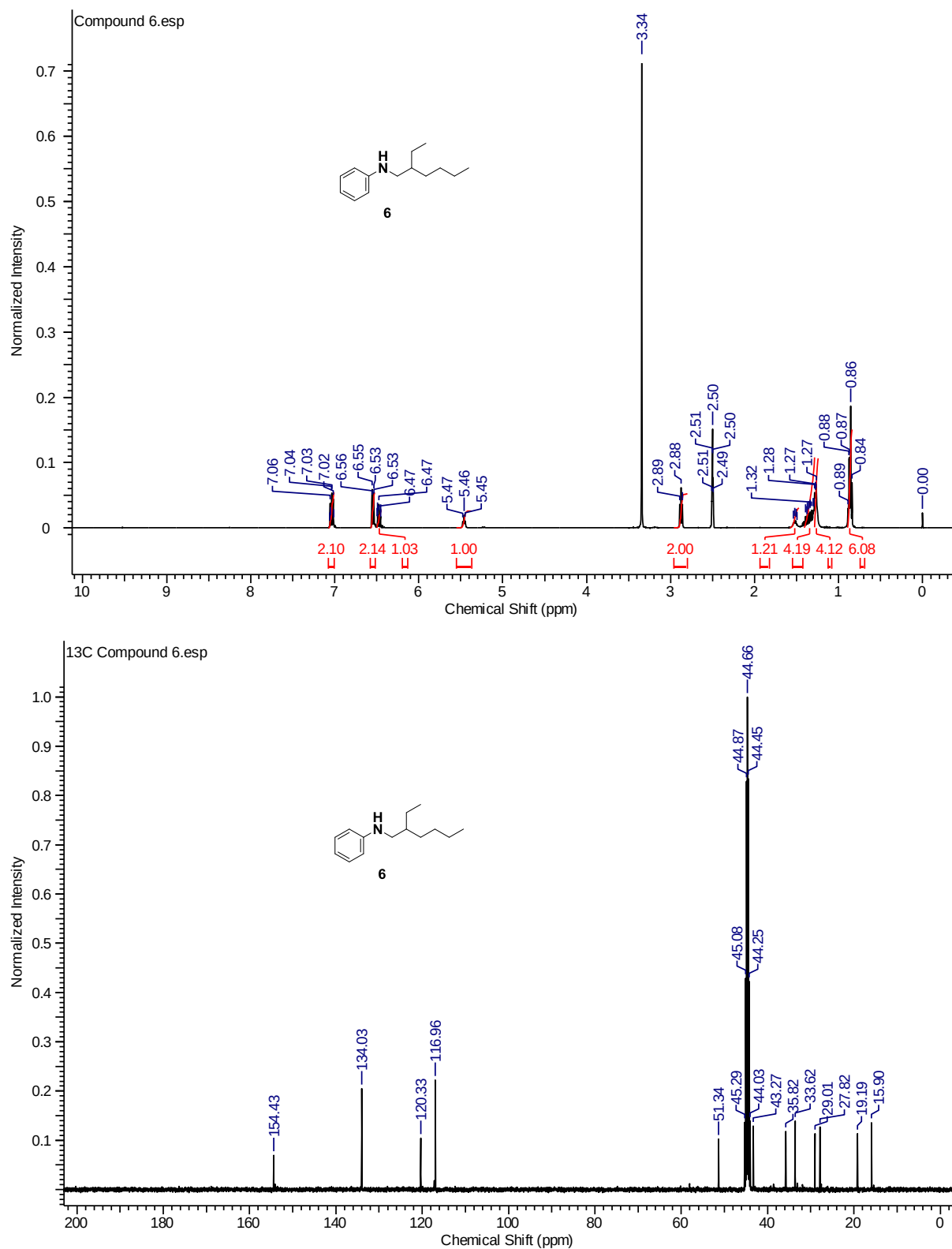


Figure 17. ¹H- and ¹³C- NMR spectra of Compound 6 in DMSO-d₆.

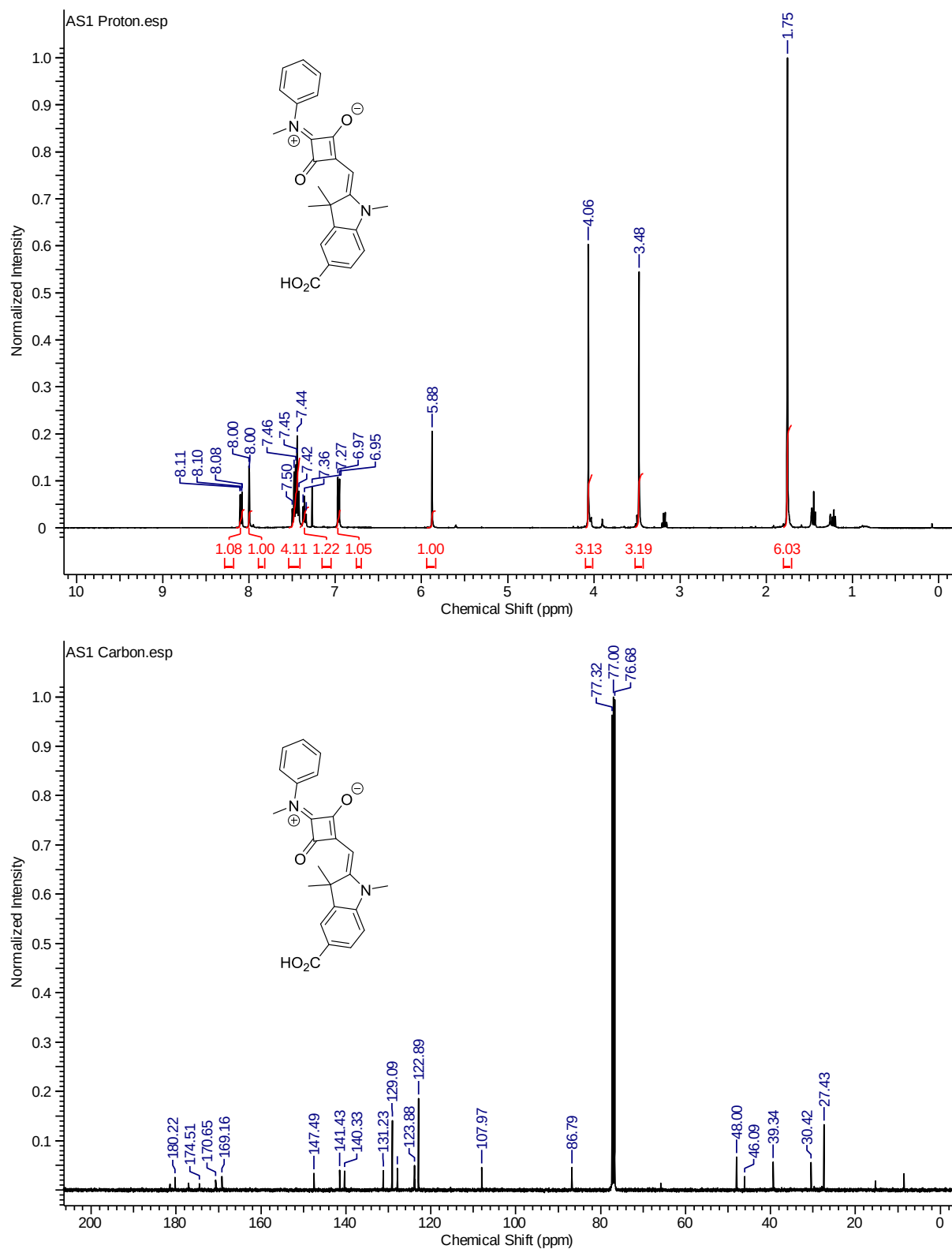


Figure 18. ^1H - and ^{13}C - NMR spectra of AS1 dye in CDCl_3 .

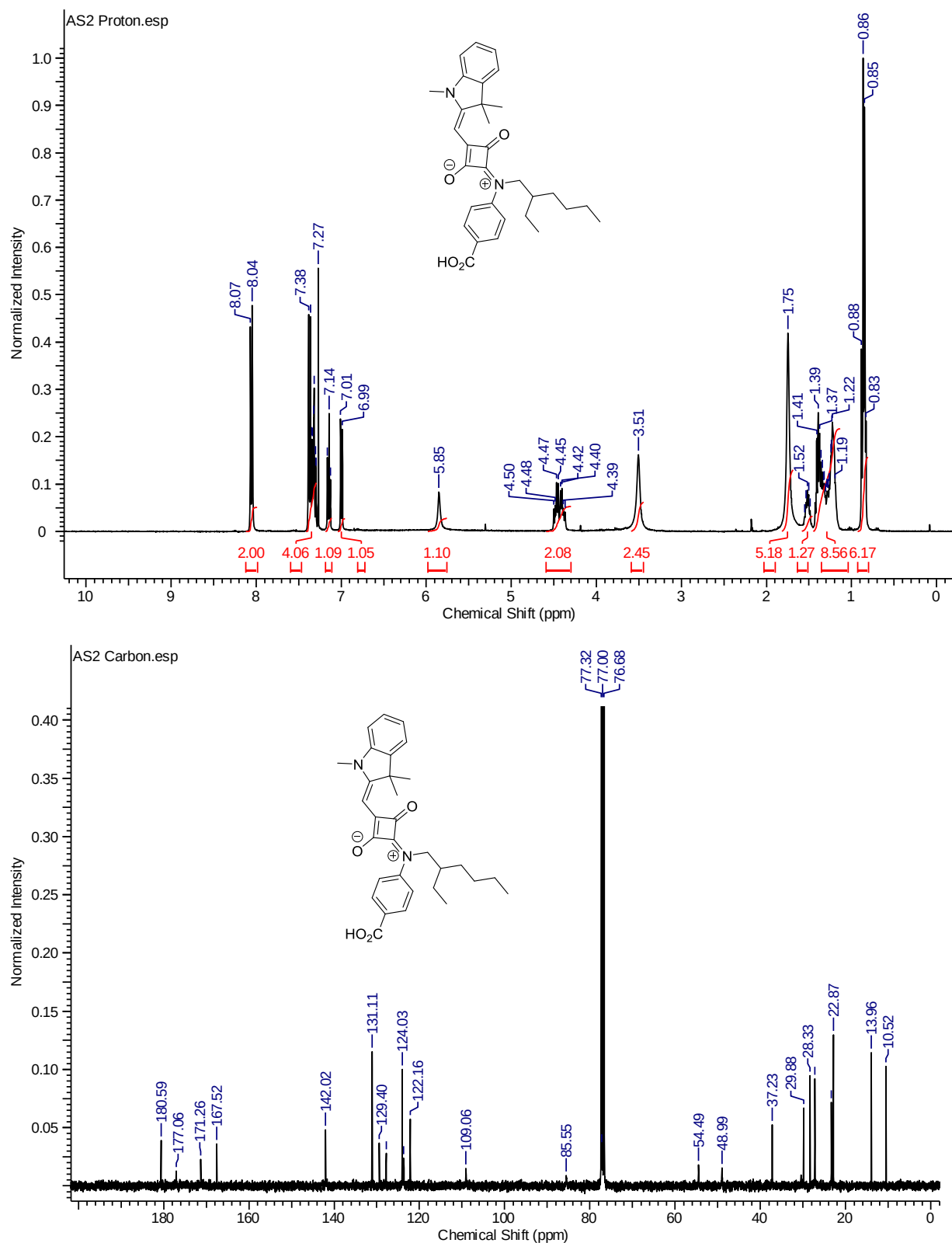


Figure 19. ^1H - and ^{13}C - NMR spectra of AS2 dye CDCl_3 .

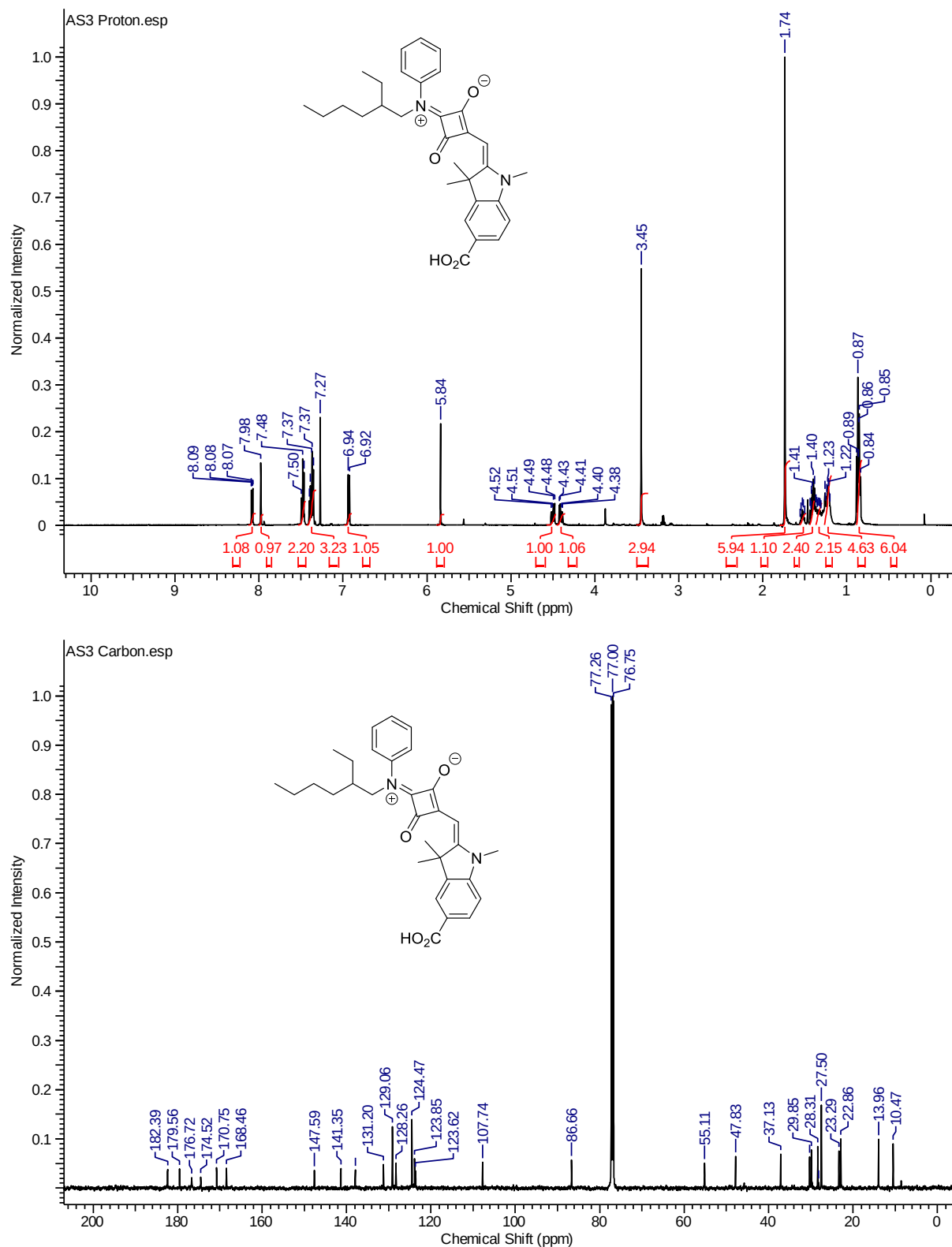


Figure 20. ¹H-NMR and ¹³C-NMR spectra of AS3 dye CDCl₃.

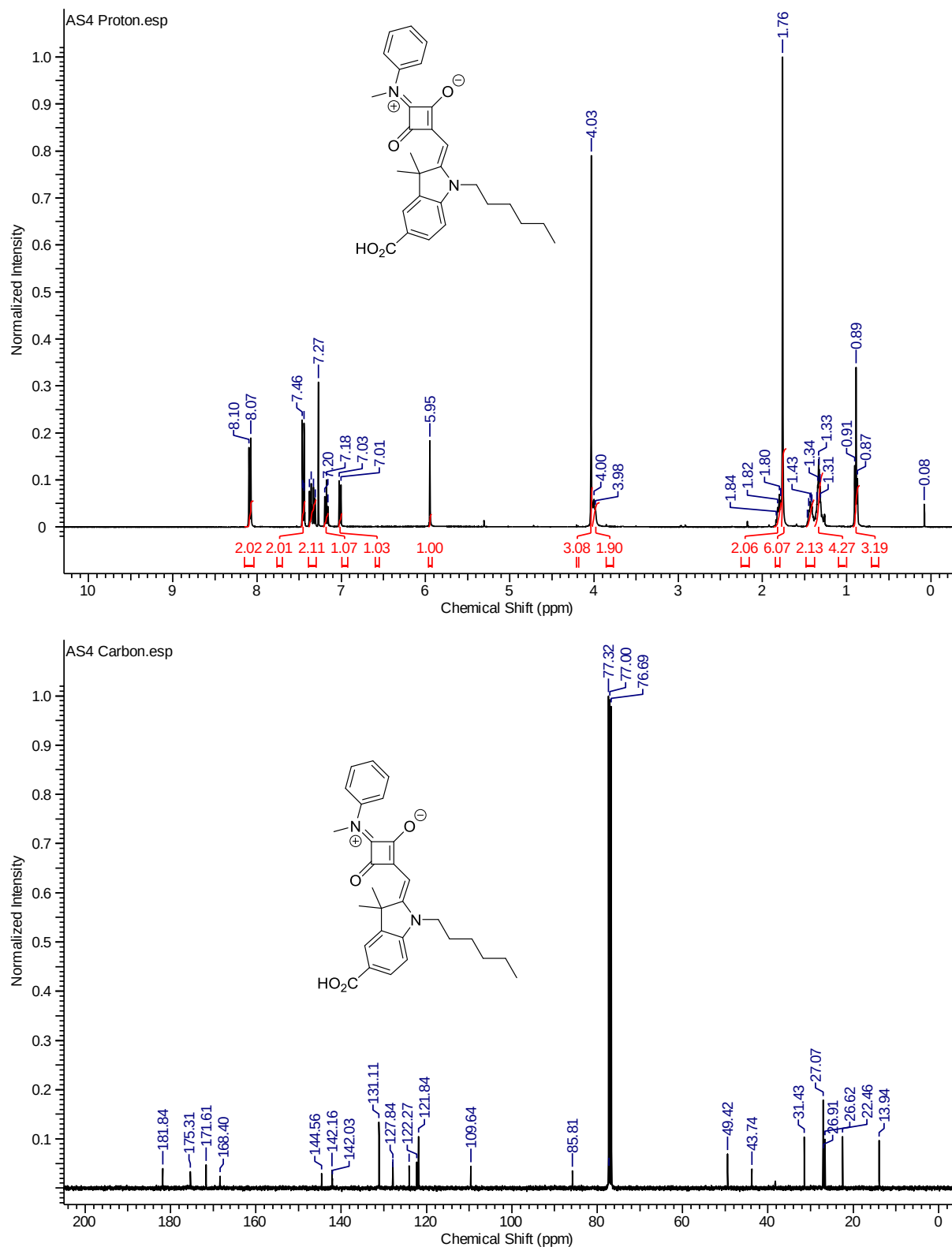


Figure 21. ^1H -NMR and ^{13}C -NMR spectra of AS4 dye in CDCl_3 .

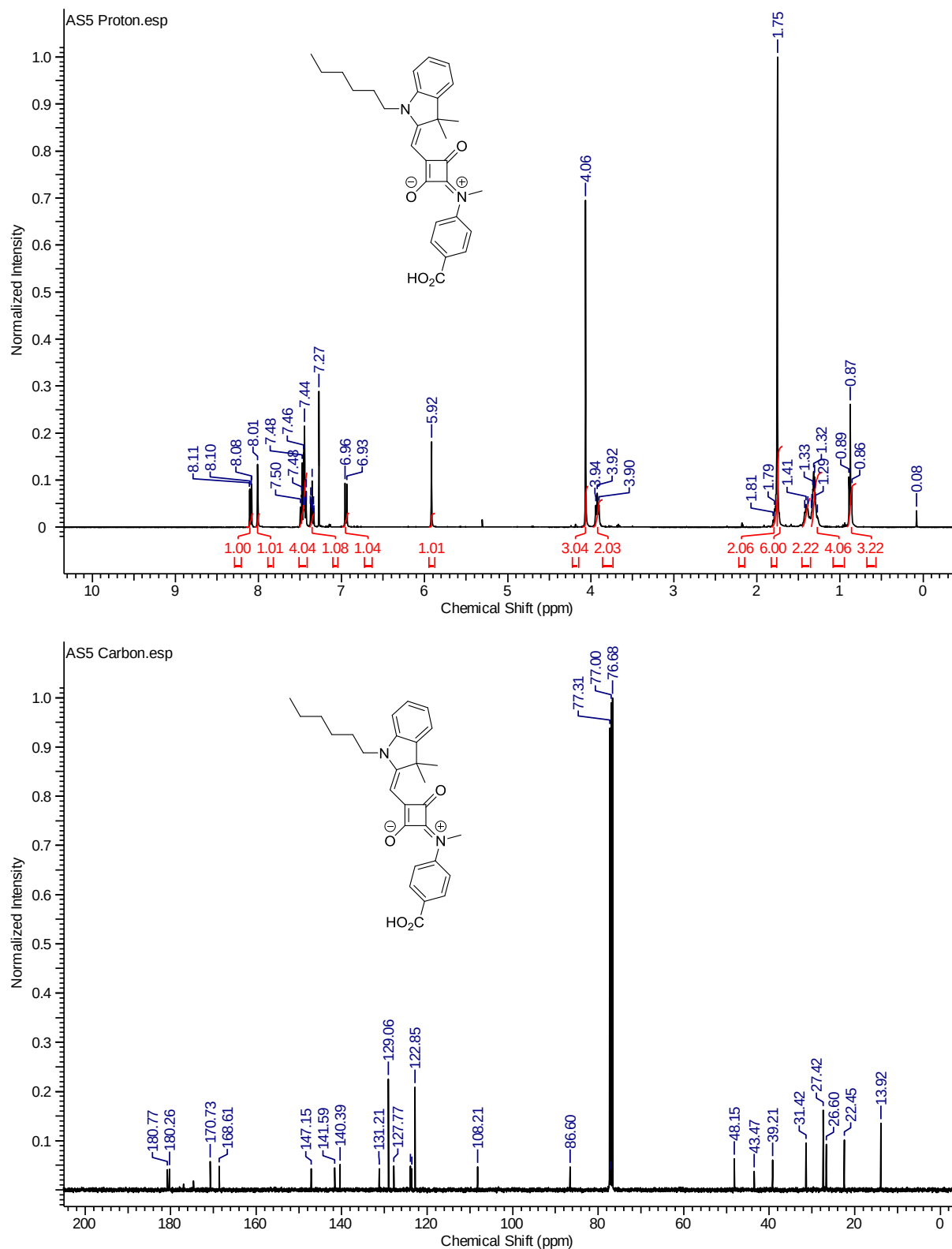


Figure 22. ¹H-NMR and ¹³C-NMR spectra of AS5 dye in CDCl₃.

AS-1 #268 RT: 1.48 AV: 1 NL: 1.64E8
T: FTMS + p ESI Full ms [100.0000-1500.0000]

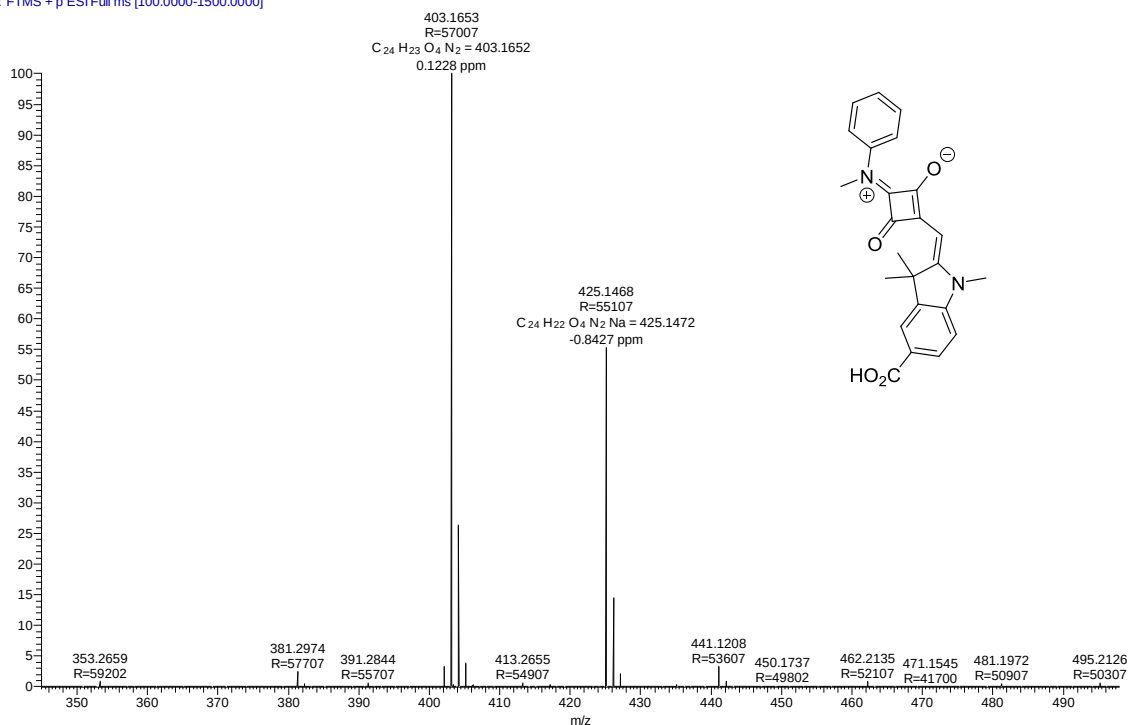


Figure 23. HRMS spectrum of AS1 dye

AS-2 #336 RT: 1.85 AV: 1 NL: 7.51E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]

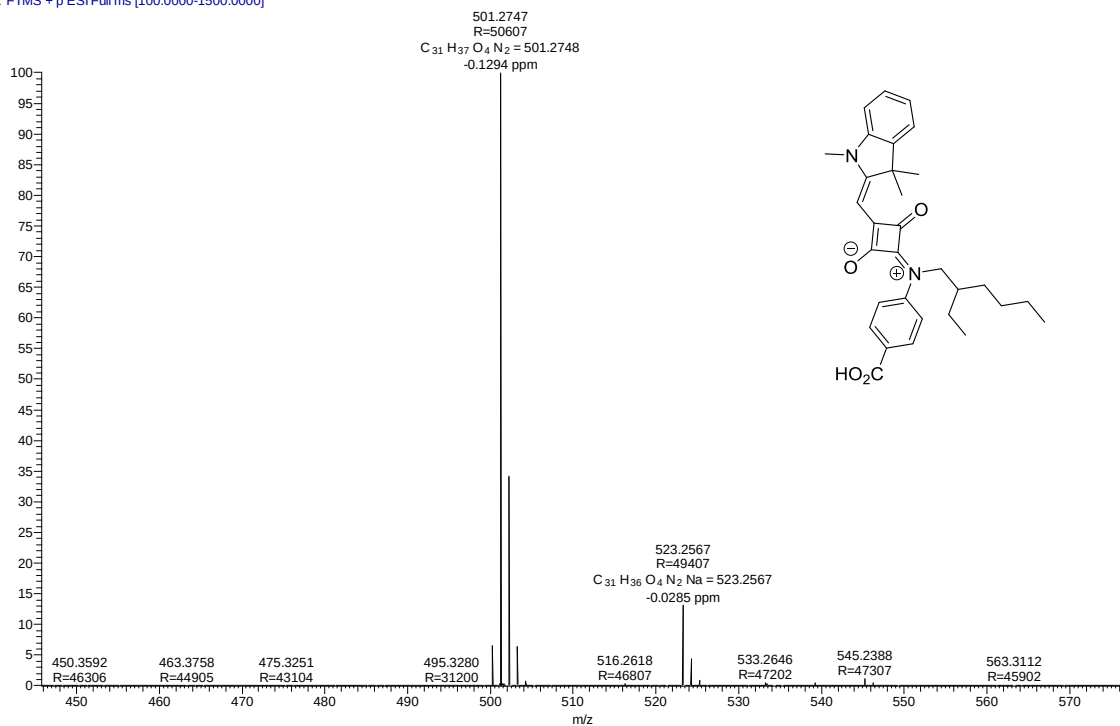


Figure 24. HRMS spectrum of AS2 dye.

AS-3 #332 RT: 1.83 AV: 1 NL: 8.13E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]

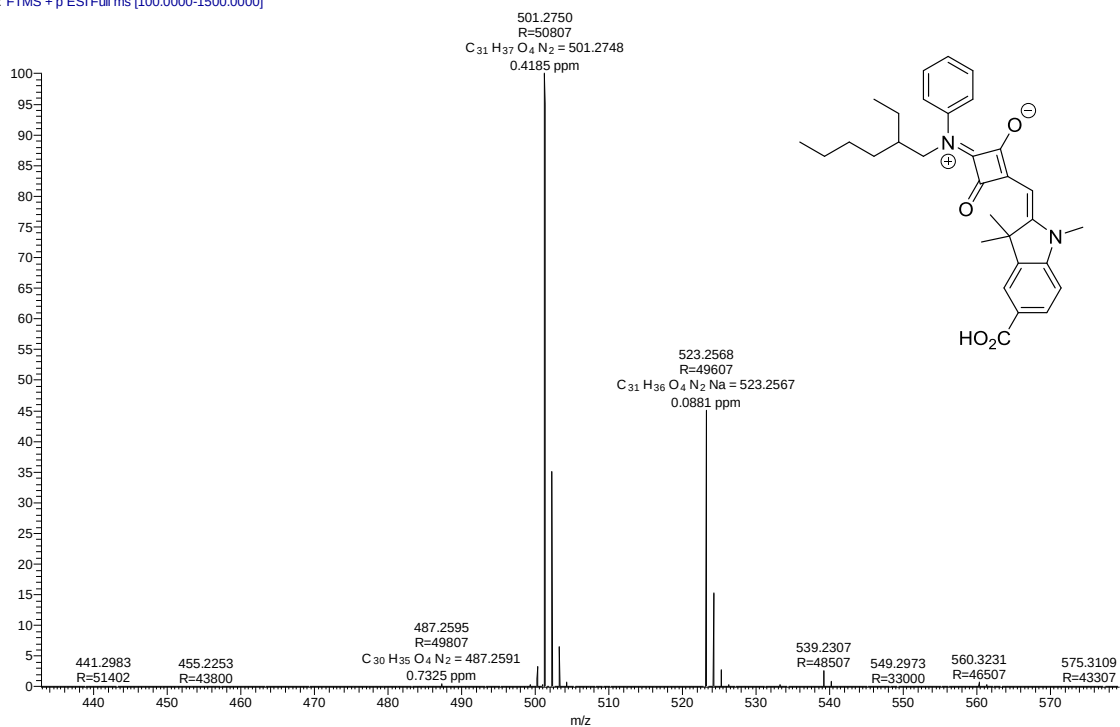


Figure 25. HRMS spectrum of AS3 dye.

AS-4 #308 RT: 1.70 AV: 1 NL: 2.29E8
T: FTMS + p ESI Full ms [100.0000-1500.0000]

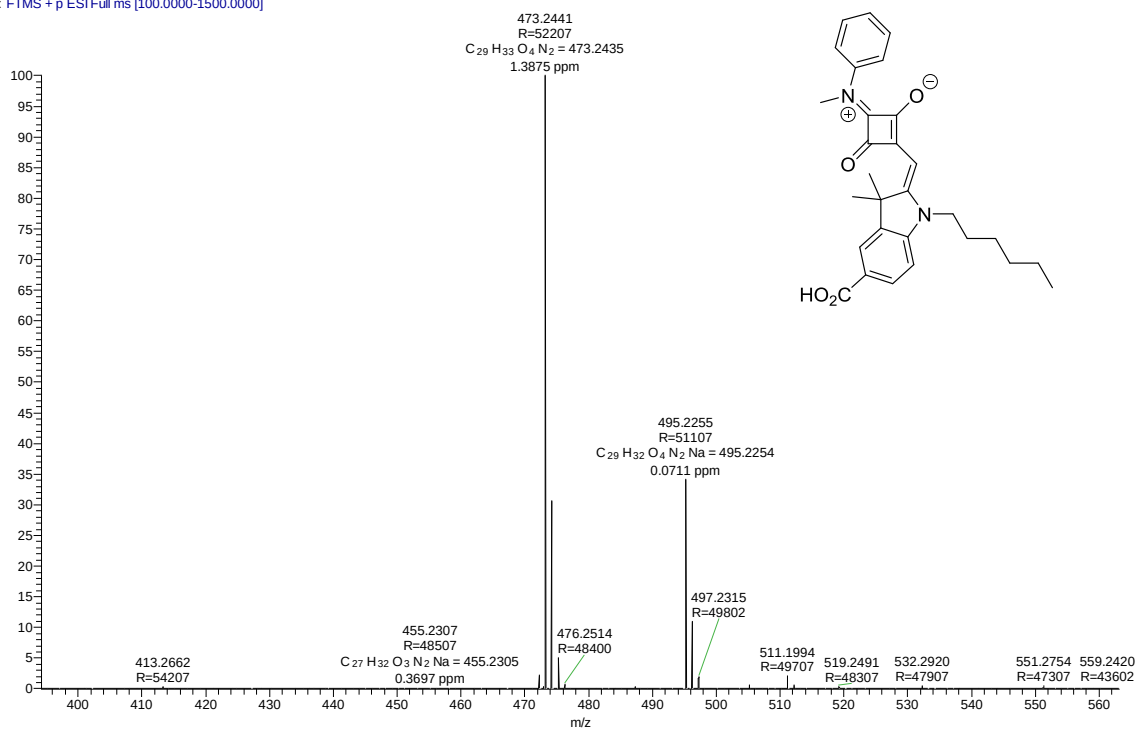


Figure 26. HRMS spectrum of AS4 dye.

AS-5 #324 RT: 1.79 AV: 1 NL: 5.64E7
T: FTMS + p ESI Full ms [100.0000-1500.0000]

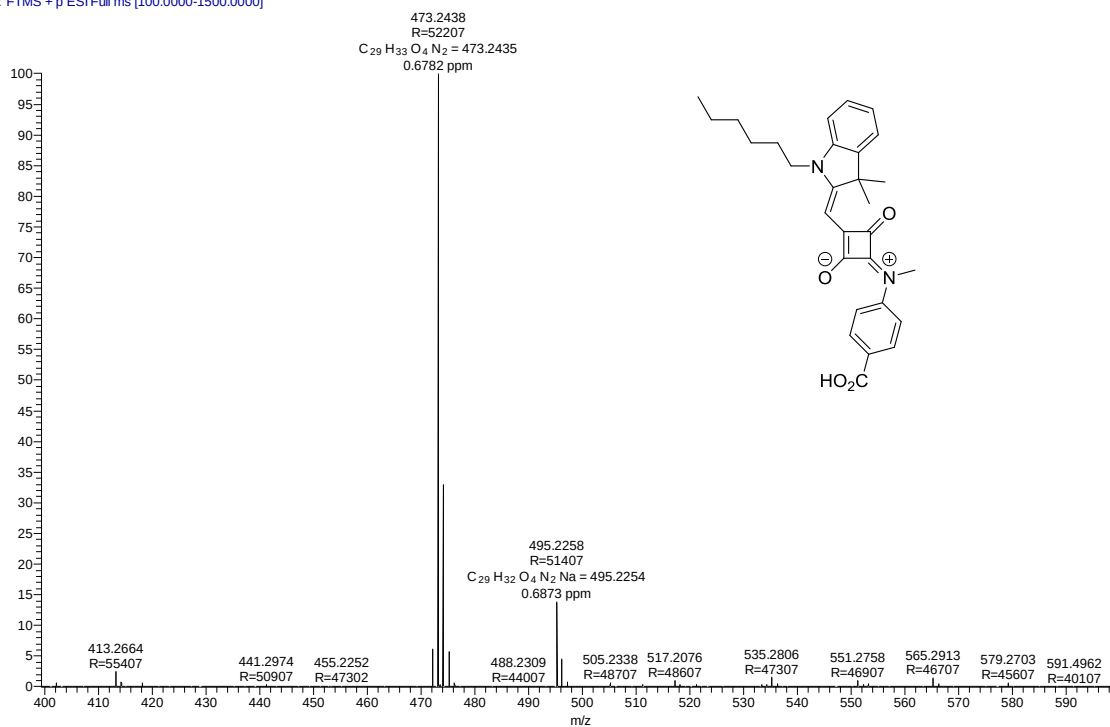
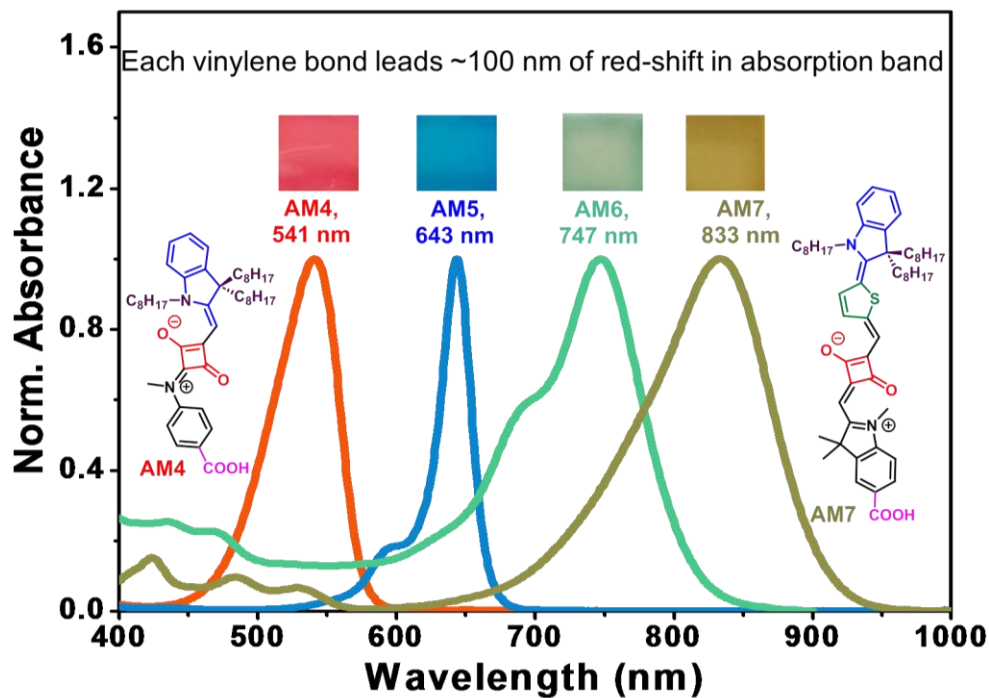


Figure 27. HRMS spectrum of AS5 dye.

Chapter 4

Synthesis of Visible, Far-red and NIR Active Squaraine Dyes for Dye-Sensitized Solar Cells: π -Extension Conjugation within the Polymethine Framework

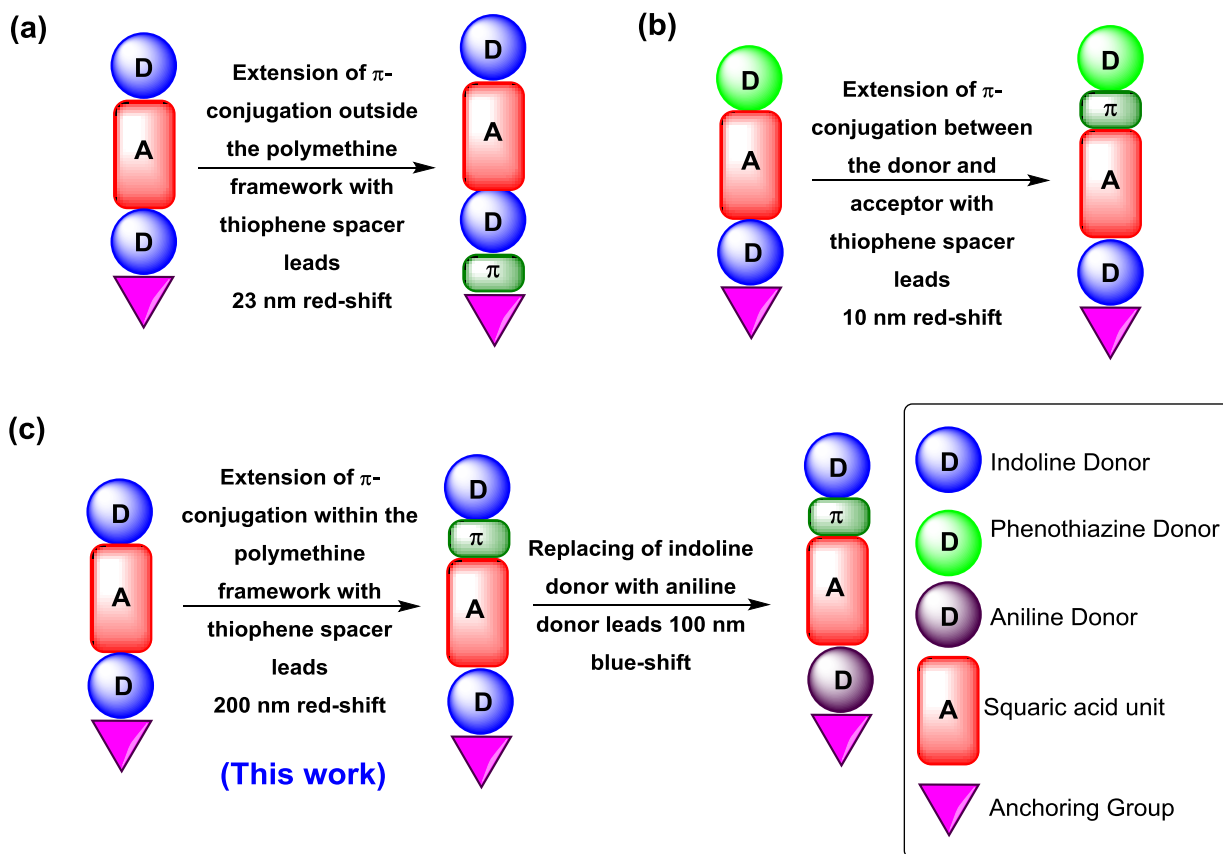
Effect of π -extension within polymethine framework of squaraine dye



4.1 INTRODUCTION

Modular nature of the various components of dye-sensitized solar cells (DSSCs) and low cost device fabrication makes third generation photovoltaic technology very attractive solar energy harvesting devices.¹⁻³ Light harvesting sensitizers play an important role in DSSC device, and features that enhance the charge injection from LUMO of the photo-excited dye to the conduction band of TiO_2 , regeneration of photo-oxidized dye by electrolyte and reduce the charge recombination of electrons in the TiO_2 with the oxidized electrolyte species at the TiO_2 -dye/electrolyte interface helped designing efficient sensitizers with high device performance. Transition metal-containing ruthenium-based dyes have ability to harvest the solar light from visible to NIR-regions, and DSSC efficiency 11.7%⁴ have been achieved. Porphyrin chromophores are one of the most popular dyes used in DSSC due to its unique photophysical behavior (Soret band in visible and Q- bands in NIR-regions).^{5,6} Further, meso-position of the porphyrin ring has been utilized to functionalize with different donors, π -spacers, and acceptors moieties to modulate the photophysical, electrochemical properties of the dyes.⁷ Porphyrin dye (SM315) has achieved maximum of 13.0% DSSC efficiency.⁸ Further, metal-free organic dyes have the several advantages over the metal-containing dyes, such as, tunable spectral properties, high extinction coefficient, high photovoltaic efficiency, selection of donors, acceptors, and π -spacers etc.⁹ To date maximum photovoltaic efficiency of 13.6%,¹⁰ achieved by metal-free organic dye, 14.2%¹¹ and 15.2%¹² by co-sensitizing with optically complementary dyes and 37.07%¹³ device efficiency under the ambient light condition. Further, polymethine dyes such as cyanine,¹⁴ hemicyanine (ionic dyes)¹⁵ squaraine,¹⁶ and croconaine dyes¹⁷ (zwitterionic) absorb visible, far-red and NIR light with high extinction coefficients. Among the polymethine dyes, squaraine dyes are very impressive because of its sharp absorption in visible and far-red region with high extinction coefficient, high DSSC performance.^{18,19} Suitably functionalized squaraine dyes have been explored in the area of sensor,²⁰ DSSC,^{9,21,22} photodynamic-therapy,²³ protein-labelling²⁴ and fluorescent-probe.^{25,26} Further these chromophore forms H- and J- type aggregates in solution as well as on thin film and such feature has been utilized in DSSC and OPV.²⁷⁻³⁰ To date maximum photovoltaic efficiency of achieved by the unsymmetrical squaraine dye is 7.93%³¹ with I^-/I_3^- redox shuttle and 8.05%³² with Cu(I/II) electrolytes have been achieved in the absence of CDCA.

Effect of extension in conjugation for unsymmetrical squaraine dye



(d) Structure of targeted dyes (AM4-AM7)

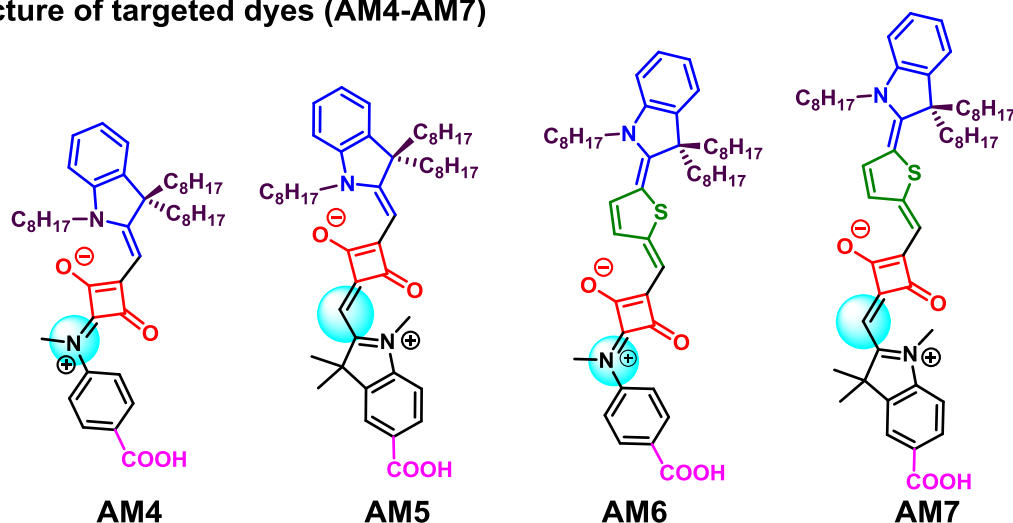


Figure 1. Effect of extension in conjugation (a) outside of polymethine framework, (b) between the donor and acceptor moieties (c) within the polymethine framework, and (d) structures of targeted dye molecules.

Enhancing the DSSC device J_{SC} is an important parameter to enhance the device efficiency by maintaining the V_{oc} . Besides panchromatic absorption³³⁻³⁵ and co-sensitization,^{11,36,37} NIR-light absorption is highly needed to enhance the device J_{SC} .^{20,38} Sensitizers with extended π -conjugation (with π -spacer, and electron deficient acceptor units) has been found as an important strategy to harvest the photons in the far-red and NIR regions.³⁹⁻⁴³ In general, by extending the conjugation between the π -framework for D-A, D- π -A dyes and outside the polymethine framework of squaraine dyes leads 15-20 nm red-shift in the absorption profile.⁴⁴

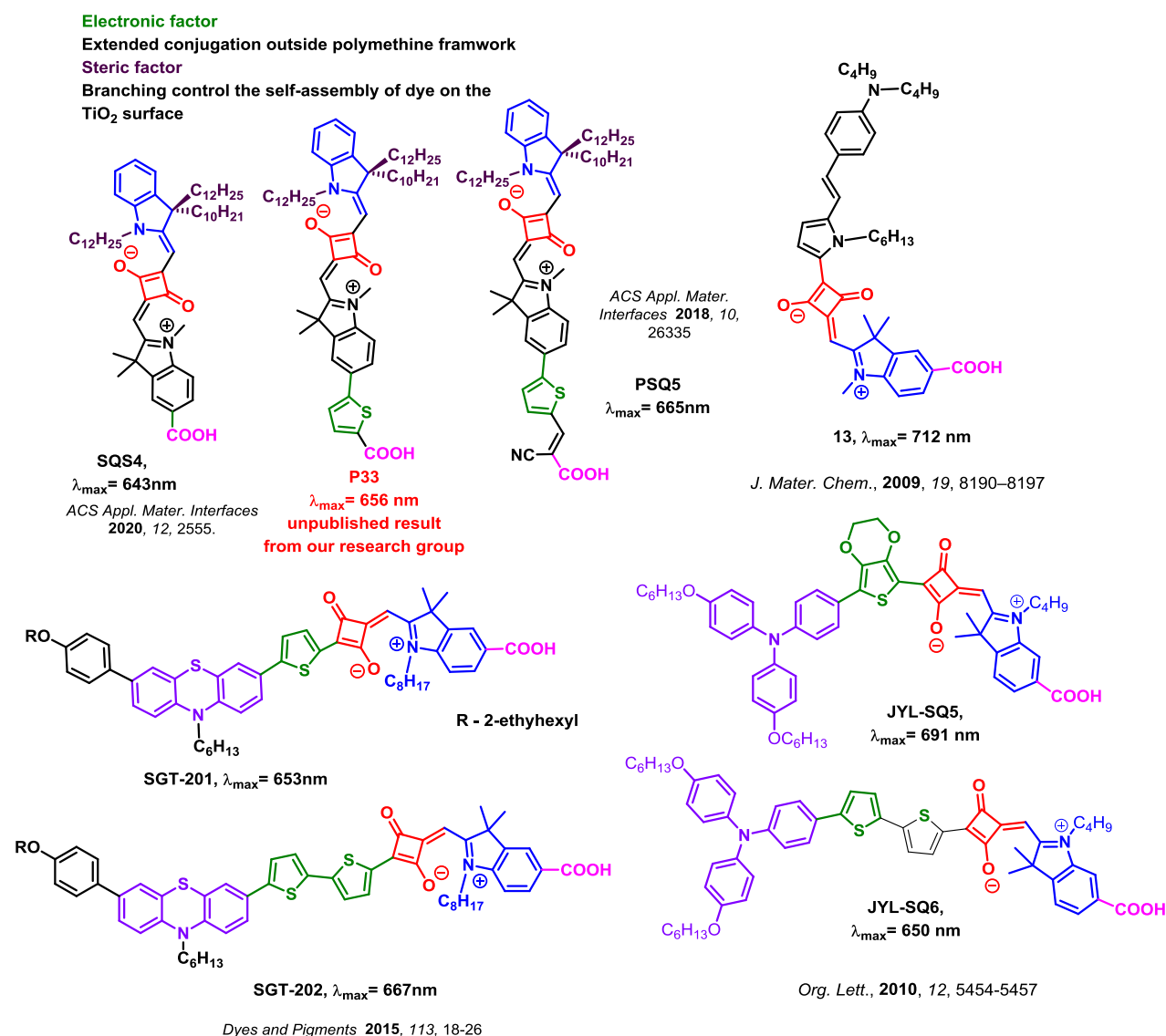


Figure 2. Effect of extension in conjugation for unsymmetrical squaraine dyes

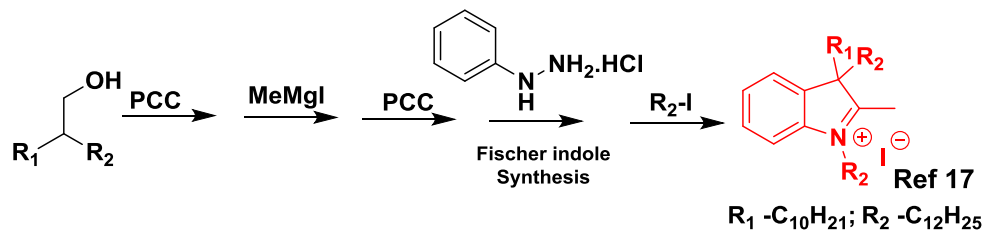
However extending the conjugation within the polymethine framework in cyanine dyes exhibited 100 nm red shifted transition per $-C=C-$ bond extension.⁴⁵ In the case of squaraine dyes, the red-shift in the transition by extending the π -conjugation is depends on the donor units (**Figure 1**, and **Figure 2**),⁴⁶⁻⁴⁸ such as phenothiazine donor based squaraine dyes, lead 15 nm red shift upon introducing thiophene spacer.⁴⁶ In the present studies, extending the conjugation of squaraine dyes within polymethine π -framework showed 100 nm red shift by incorporation of each double bond (~ 190 nm for thiophene spacer). Further, selection of proper electrolyte and electrolytic compositions is a very important aspect to enhance the DSSC efficiency for ionic and zwitterionic dyes. The photovoltaic parameters of DSSC devices such as J_{SC} , V_{OC} and ff can be effectively controlled and modulated by addition of lithium salts (Li^+),⁴⁹⁻⁵¹ 4-*t*-butylpyridine (TBP) and ionic liquids.⁵²⁻⁵⁴ Such additives responsible to change the E_{CB} position of the TiO_2 , which modulate DSSC parameters directly. Variation in the concentrations of LiI modulates the Coulombic interaction of Li-ions with the metal oxide TiO_2 surface which changes the flat band potential and affects the J_{SC} .^{50,51,55} Squaraine dyes showed high DSSC efficiency with I^-/I_3^- redox electrolyte by achieving the high V_{OC} and J_{SC} of DSSC devices in the visible and far-red regions.^{15,56,57} By considering the controlled aggregation of dyes on TiO_2 , and extending the conjugation of polymethine dyes, a series of visible to NIR light active dyes (**AM4-AM7**, **Figure 1d**) have been designed, synthesized, and tested for the DSSC applications. To control the aggregation of dyes on the TiO_2 surface, one of the indoline moieties of this dye series is wrapped with symmetrical alkyl groups.

4.2 RESULTS AND DISCUSSION

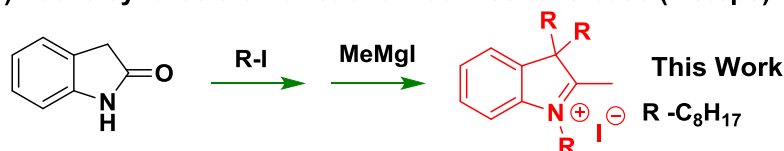
4.2.1 Synthesis of AM dyes.

Synthesis of D-A-D and D- π -A-D based visible and NIR active unsymmetrical squaraine dyes with increased π -conjugation within the polymethine framework comprised a condensation reaction between the semisquaric acid derivatives and corresponding Fischer base or aniline. Generally, synthesis of alkyl group wrapped Fischer base (indolium salt) requires five synthetic steps¹⁷ that has been minimized into two steps for branched-indolium and three steps for branched-indolium with thiophene spacer (**Scheme 1**).

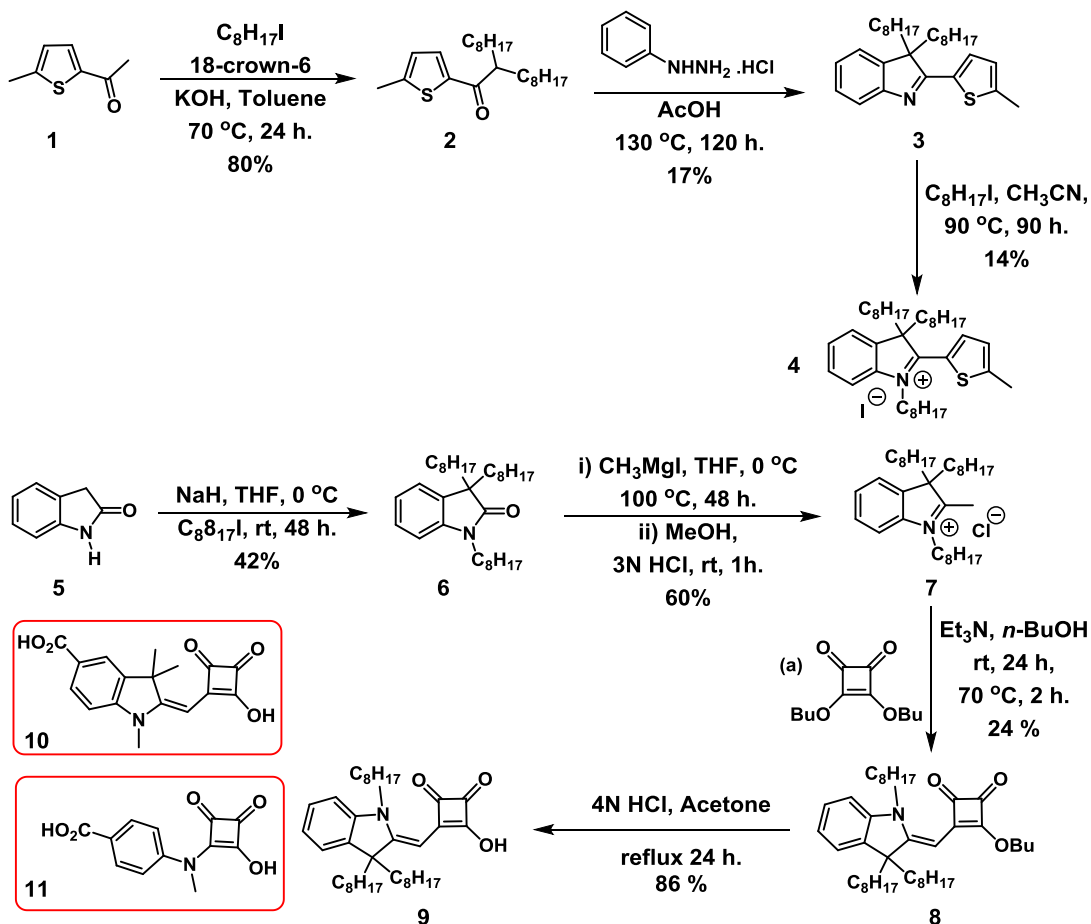
(a) Previously reported route for functionalized Fischer's base (5 steps)

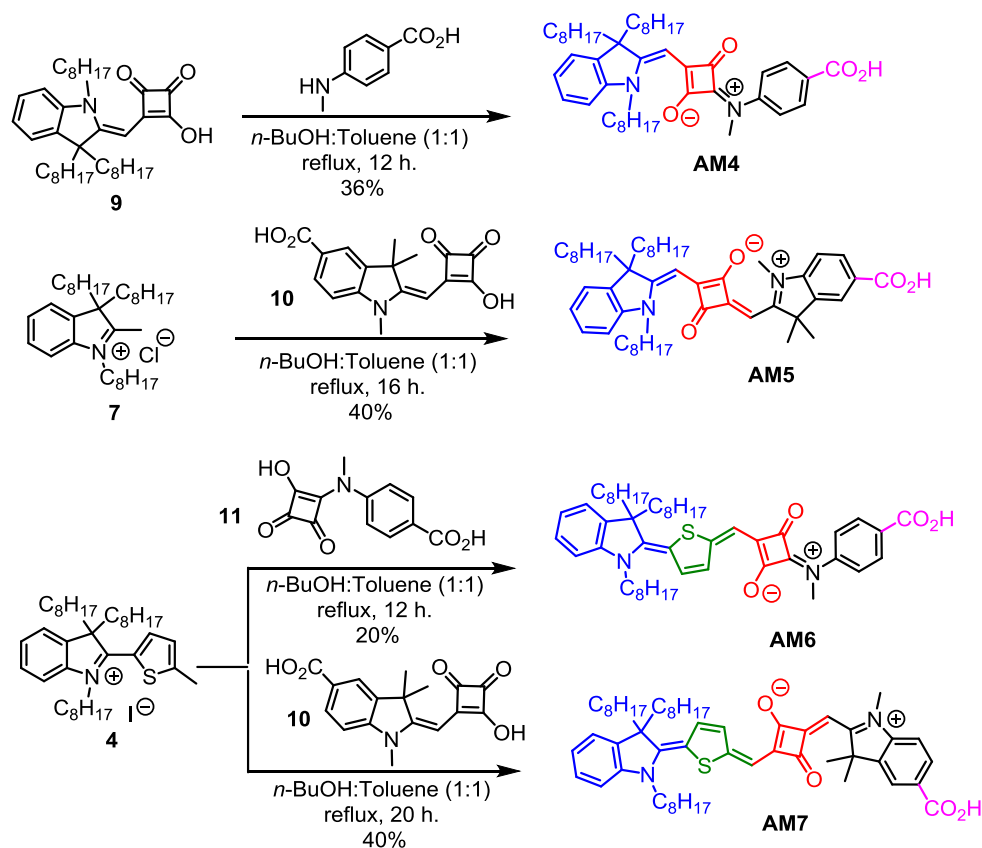


(b) Facile synthesis of functionalized Fischer's base (2 steps)

**Scheme 1.** Synthetic routes for the functionalized Fischer's base.

(a) Synthesis of functionalized Fischer's base 4, 7 and branched semisquaric acid, 9

**Scheme 2.** Synthetic scheme for the Fischer's base and semisquaric acid.



Scheme 3. Synthetic scheme for the unsymmetrical squaraine based **AM** dyes.

To obtain the functionalized Fischer base, **4**, alkylation of 2-acetyl-5-methylthiophene with 1-iodooctane in the presence of KOH and catalytic amount of 18-C-6 has been carried out followed by Fischer indole reaction with phenylhydrazine hydrochloride afforded the thiophene-based indoline derivative **3**. Further, N-alkylation with 1-iodooctane afforded the required indolium salt **4**. On the other hand, Fischer base, **7** was achieved in two steps starting from oxindole.⁵⁹ Both N- and C-alkylation of oxindole with 1-iodooctane provided the cyclic-amide which was further reacted with MeMgI to afford the required alkyl group wrapped Fischer's base in moderate yields. Branched semisquaric acid, **9** has been synthesised by the reaction between dibutylsquarate with Fischer base, **7** followed by the deprotection of butyl groups with aqueous HCl in the presence of acetone. Indoline and aniline based semi-squaric acids with carboxylic acid groups, **10**¹⁷ and **11**⁵⁸ were synthesized by following the procedure reported in the literature. Finally, Fischer base derivatives (1 equiv.) condensed with the semisquaric acid derivatives (1 equiv.) in anhydrous toluene and *n*-BuOH (1:1) to obtain the required **AM4-AM7** dyes (Scheme 2, and 3).

4.2.2 Photophysical properties.

The UV-vis characterization of the π -extended unsymmetrical squaraine dyes **AM4**, **AM5**, **AM6**, and **AM7** have been carried out in anhydrous dichloromethane and results have been displayed in **Figure 3** and corresponding data have been tabulated in the **Table 1**.

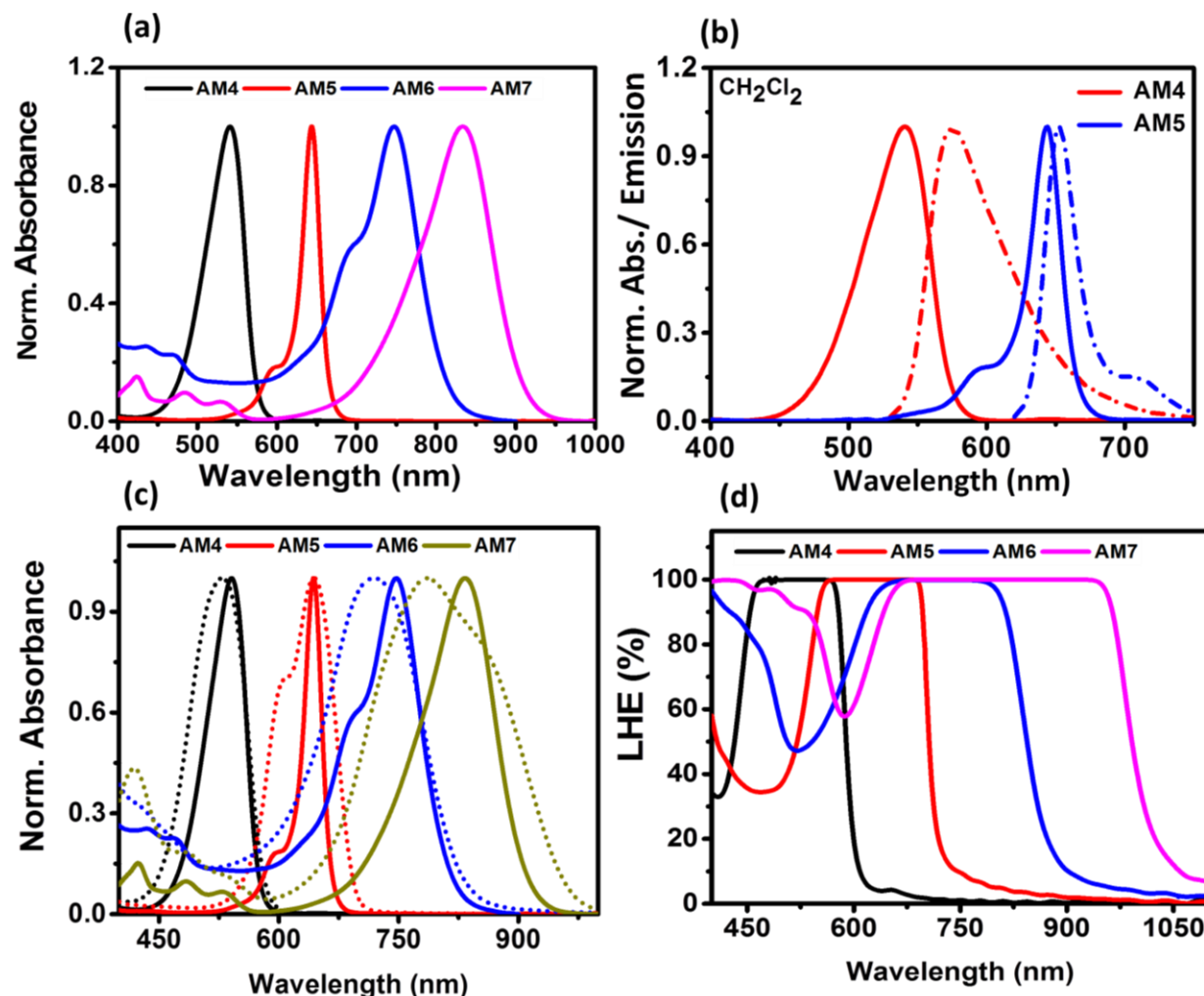


Figure 3. (a) Normalized UV-vis spectra of **AM4-AM7** dyes in CH_2Cl_2 solution, (b) Normalized absorption and emission spectra of **AM4** and **AM5** dyes in solution (c) Normalized UV-vis spectra of **AM4-AM7** dyes in solution (solid line) and on TiO_2 (dotted line, thickness of the TiO_2 electrode was 6 μm , dipping time was 10 min), and (d) LHE ($=1-10^{-A}$) profiles of **AM4-AM7** dyes on TiO_2 electrodes (thickness was 6 μm , dipping time was 12h).

The absorption maxima of 541 nm, 643 nm, 747 nm, and 833 nm have been found for the **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. It has been found that each conjugated --C=C-- double bond gave ~ 100 nm red shifts in the absorbance bands when moved from **AM4** to **AM7** dyes. Absorption band for **AM5** dye has been found to be sharper than **AM4**, **AM6**, and **AM7** dyes which are due to its dye symmetry compared to other **AM** dyes.^{47,60,61} Molar extinction coefficients of 1.28 , 3.62 , 1.54 , and $1.86 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ were found for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively.

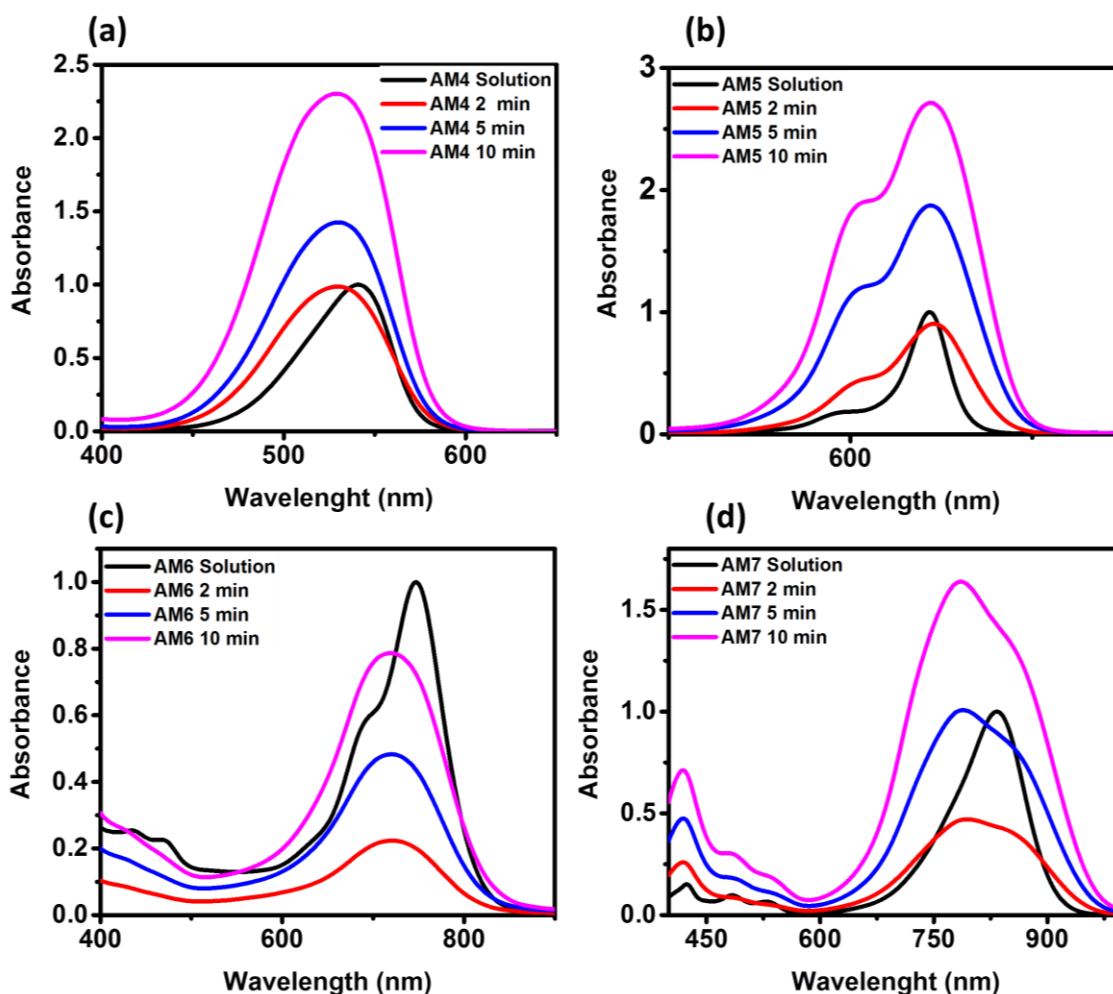


Figure 4 UV spectra of **AM4-AM7** dyes in solution (CH_2Cl_2) and on TiO_2 with dipping time (thickness of the TiO_2 electrode was $6 \mu\text{m}$).

The UV-vis studies of **AM** dyes on the TiO_2 surface (10 min sensitization) showed the absorption maxima of 528, 644, 718, and 847 for **AM4**, **AM5**, **AM6**, and **AM7** dyes,

respectively. **AM4** dyes on TiO_2 surface with short dipping time (10 min) showed broadening of the peak on TiO_2 surface towards blue shift that showed the H-aggregation, however **AM5** dye showed the broadening as well as an additional peak at 600 nm toward the blue shift due to H-aggregation. Further **AM7** and **AM6** dyes showed more broadening along with the blue shift in short dipping time (10 min) on TiO_2 surface due to the formation of aggregation **Figure 3c** and **4**. Emission maxima of were found to be 575 and 652 for **AM4** and **AM5** dyes, respectively (**Figure 3b**). Emission of **AM5** dye was found sharper as absorption band with little stokes shift than **AM4** dye. Further, light harvesting efficiency (LHE) of the dyes highlight the regions which can be useful for the current conversion by the anchored dye molecules on the semiconducting metal-oxide surface. LHE of 149, 175, 269, and 386 nm have been found at 60% of the spectrum height for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. Positive impact on the LHE of the dyes have been noticed by the extension in conjugation within polymethine framework, where **AM7** dye with the highly extended structure has been achieved maximum LHE of 386 nm broad at 60%. Hence, extension of conjugation within the polymethine framework is not only important to shift the absorption band toward the NIR light region side, but also is important to enhance the LHE property of the dyes.

4.2.3 Electrochemical properties.

To calculate the HOMO of the **AM** dyes cyclic voltammetry has been carried out in anhydrous dichloromethane (**Figure 5a**), where HOMO of the dyes was calculated from the first oxidation onset value that converted into the NHE by the addition of 0.7 V (by using Ferrocene as an internal standard).⁶² UV-vis and emission intersection point of the **AM4** and **AM5** dyes were used to calculate optical energy-gap by using the formula of $E_g = 1240/\lambda_{\text{intersection value}}$ (whereas, absorption onset was used for **AM6** and **AM7** dyes), and LUMO of the dyes obtained by subtracting the band-gap from the HOMO value. The HOMO energy levels of 1.01, 0.79, 0.53, and 0.47 eV have been found for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. Whereas the LUMO energy levels of -1.21, -1.25, -0.98, and -0.89 eV have been found for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. **AM4**, **AM5**, **AM6** and **AM7** dyes showed their potential to use as a sensitizer for DSSC with I^-/I_3^- electrolyte, because its electronic energy levels are well aligning with the charge injection and dye-regeneration processes, respectively (**Figure 5b**, and **Table 1**).

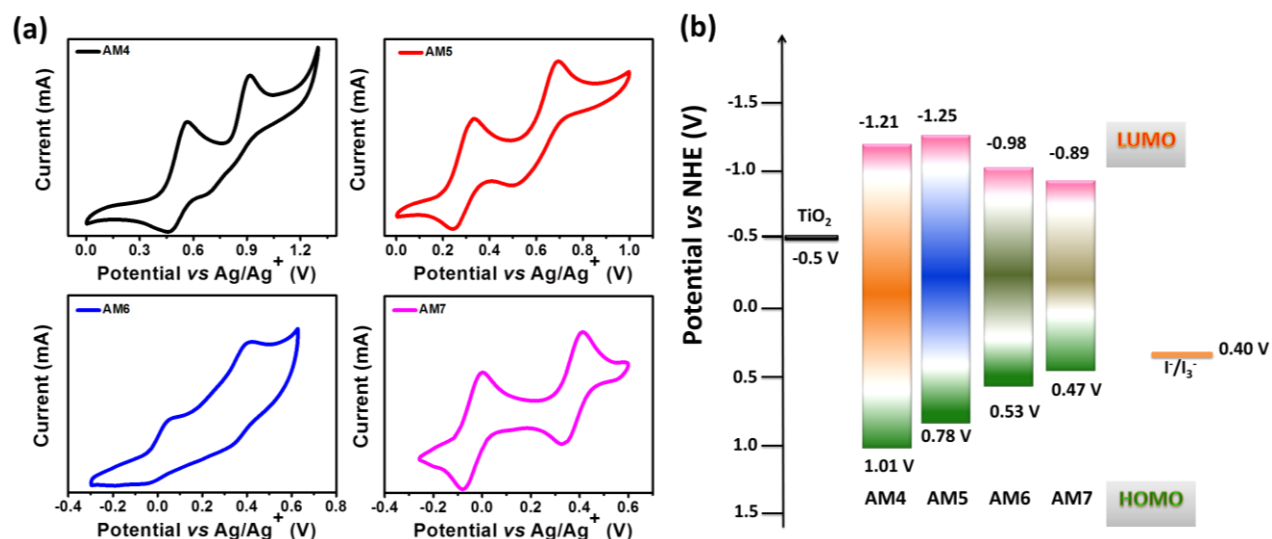


Figure 5. (a) Cyclic voltammograms of **AM4-AM7** dyes in CH₂Cl₂ solution, and (b) energy level diagram of **AM** dyes along with the redox function of iodine electrolyte.

Table 1. Photophysical and electrochemical properties of unsymmetrical squaraine based **AM** dyes at room temperature.

Dyes	^a $\lambda_{\max}$ (nm)	ϵ (10 ⁵ M ⁻¹ cm ⁻¹)	^b $\lambda_{\max}$ (nm) on TiO ₂	LHE $\Delta\lambda$ at 60%(n m)	^c E_{ox} (V vs Ag/A g ⁺)	E_{HOMO} (V vs NHE)	E_{LUMO} (V vs NHE)	^d E_g (eV)	^e $-\Delta G_{\text{inj}}$ (V)	^f $-\Delta G_{\text{reg}}$ (V)
AM4	541	1.28	528	149	0.442	1.01	-1.21	2.22	0.71	0.61
AM5	643	3.62	644	175	0.220	0.79	-1.25	1.91	0.75	0.38
AM6	747	1.54	718	269	-0.034	0.53	-0.98	1.52	0.48	0.13
AM7	833	1.86	847	386	-0.097	0.47	-0.89	1.36	0.39	0.07

^aabsorption in CH₂Cl₂, ^babsorption on TiO₂ (thickness 6 μm , dipping time 10 min) ^coxidation onset of **AM** dyes measured in CH₂Cl₂, where tetrabutylammonium perchlorate (TBAClO₄) used as a supporting electrolyte, Fc/Fc⁺ used as an external standard and converted to NHE by addition of 0.7 V, ^d E_g optical band gap, ^e $-\Delta G_{\text{inj}}$ is the energy difference between E_{LUMO} and E_{CB} , ^f $-\Delta G_{\text{reg}}$ is the energy difference between E_{redox} and E_{HOMO} .

The free energy change ($-\Delta G_{inj}$) is the rate and efficiency of the charge injection Φ_{inj} from the excited state of the dye to the TiO_2 conduction band. Thus $-\Delta G_{inj}$ must be positive ($>0.2\text{eV}$) for charge injection process for a high efficiency. $-\Delta G_{inj}$ is represented as follow:

$$-\Delta G_{inj} = E_{CB/TiO_2} - E_{LUMO}$$

The charge injection driving force of dye is 0.71 V, 0.75 V, 0.48 V and 0.39 V for **AM4**, **AM5**, **AM6** and **AM7 dye** respectively (**Table 1**). These values are greater than the 0.2 eV that is sufficient for a feasible electron injection from LUMO of the photoexcited dye to the conduction band of TiO_2 . The photocurrent of the DSSC i.e., determined by the dye regeneration efficiency (η_{reg}), which is directly related to the driving force of regeneration $-\Delta G_{reg}$ is represented as follow:

$$-\Delta G_{reg} = E_{redox} (I^- / I_3^-) - E_{HOMO}$$

The regeneration driving forces ($-\Delta G_{reg}$) of **AM4-AM7 dye** is **AM4/0.61 V** and **AM5/0.38 V** is higher than the thiophene unit containing dyes **AM6/0.13 V** and **AM7/0.07 V** respectively (**Table 1**). Dye regeneration process suggest that the required driving force for regeneration of dye ($\approx 0.35\text{ V}$ versus NHE) for DSSC with I^- / I_3^- redox electrolyte.⁶³ The value of **AM4** and **AM5** dyes are approximate same to required overpotential that is sufficient for dye regeneration from the redox couple. Despite the value of **AM6** and **AM7 dye** are possess less overpotential for dye regeneration that will affect the device performance. Hence, the photophysical and electrochemical properties can be systematically tuned by incorporating the vinylene or thiophene unit within the polymethine framework of the squaraine dyes.

4.2.4 Computational Studies.

DFT calculations for the π -extension based **AM4**, **AM5**, **AM6** and **AM7** dyes were performed at B3LYP, 6-31G (d) level.⁶⁴ Obtained electronic distribution within the HOMO-1, HOMO, LUMO and LUMO+1 for all dyes based on π -extension are provided **Figure 6** (where, isodensity surface value was fixed at 0.03). A clear effect of π -extension on the electronic distribution at different energy states has been found for the **AM** dyes. The HOMO-1 electronic

state of all the dyes showed nearly similar electronic distribution and situated on the acceptor moiety. A uniform electronic distribution has been found within the polymethine framework (between the two donors) in HOMO energy state for all the dyes, however LUMO showed a dispersed electronic distribution over acceptor/donors (and π -spacer if thiophene) moieties.

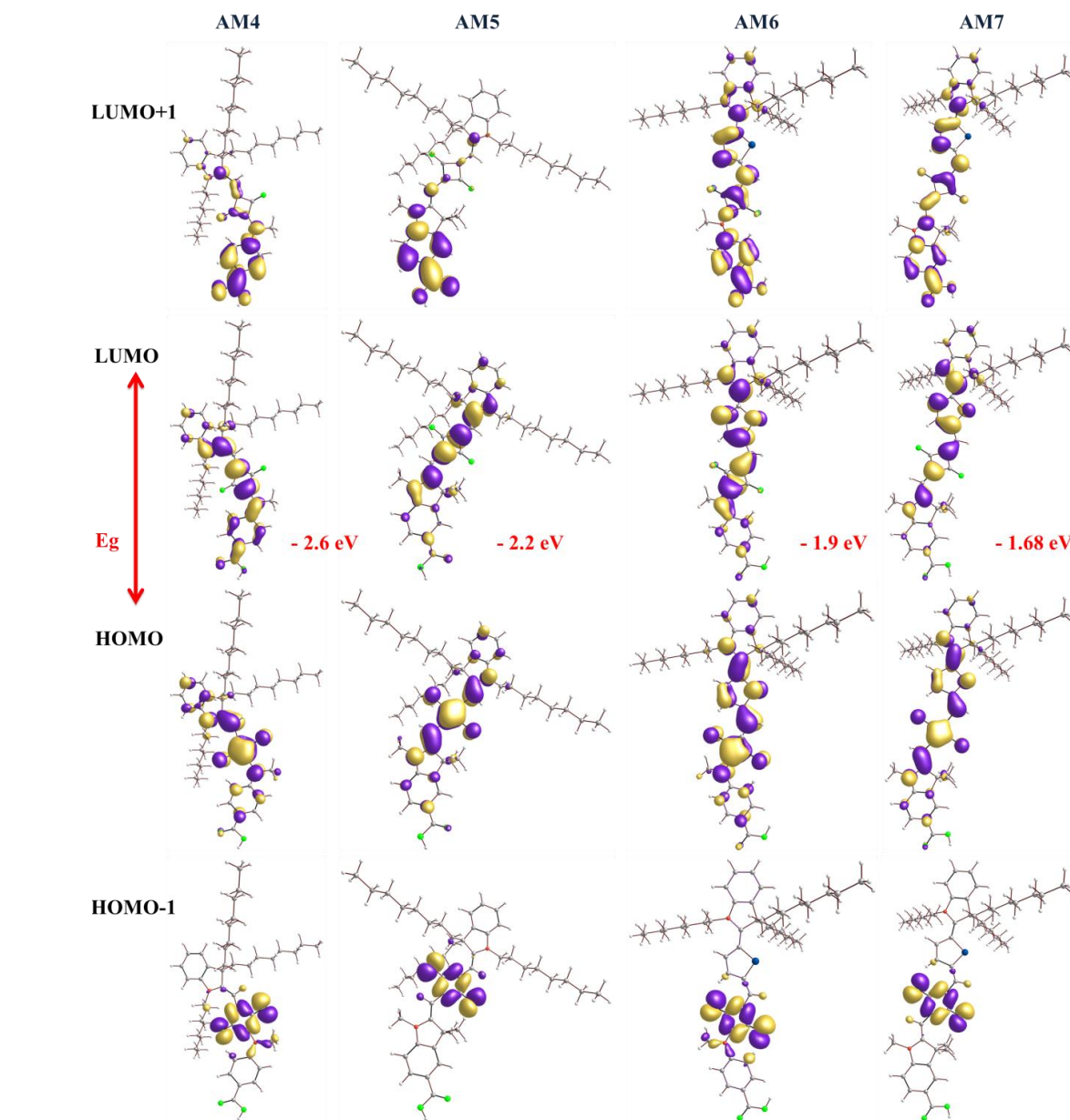


Figure 6. Energy minimized frontier molecular orbital diagram of π -extension based AM4, AM5, AM6 and AM7 dyes with their band gap.

Further, LUMO+1 for the **AM4** and **AM5** dyes showed movement of electrons mostly on the anchoring group along with the connected donor moiety, whereas the electron density for **AM6** and **AM7** dyes spread over the donor/spacer/acceptor/donor/ and anchoring group. Meanwhile, incorporation of thiophene as a π -spacer disturbed the electronic distribution in the LUMO+1 for **AM6** and **AM7** dyes and may affect the DSSC performance. Further, energy minimized structure have been used to get the height and dihedral angles of the dye molecules (**Figure 7**).

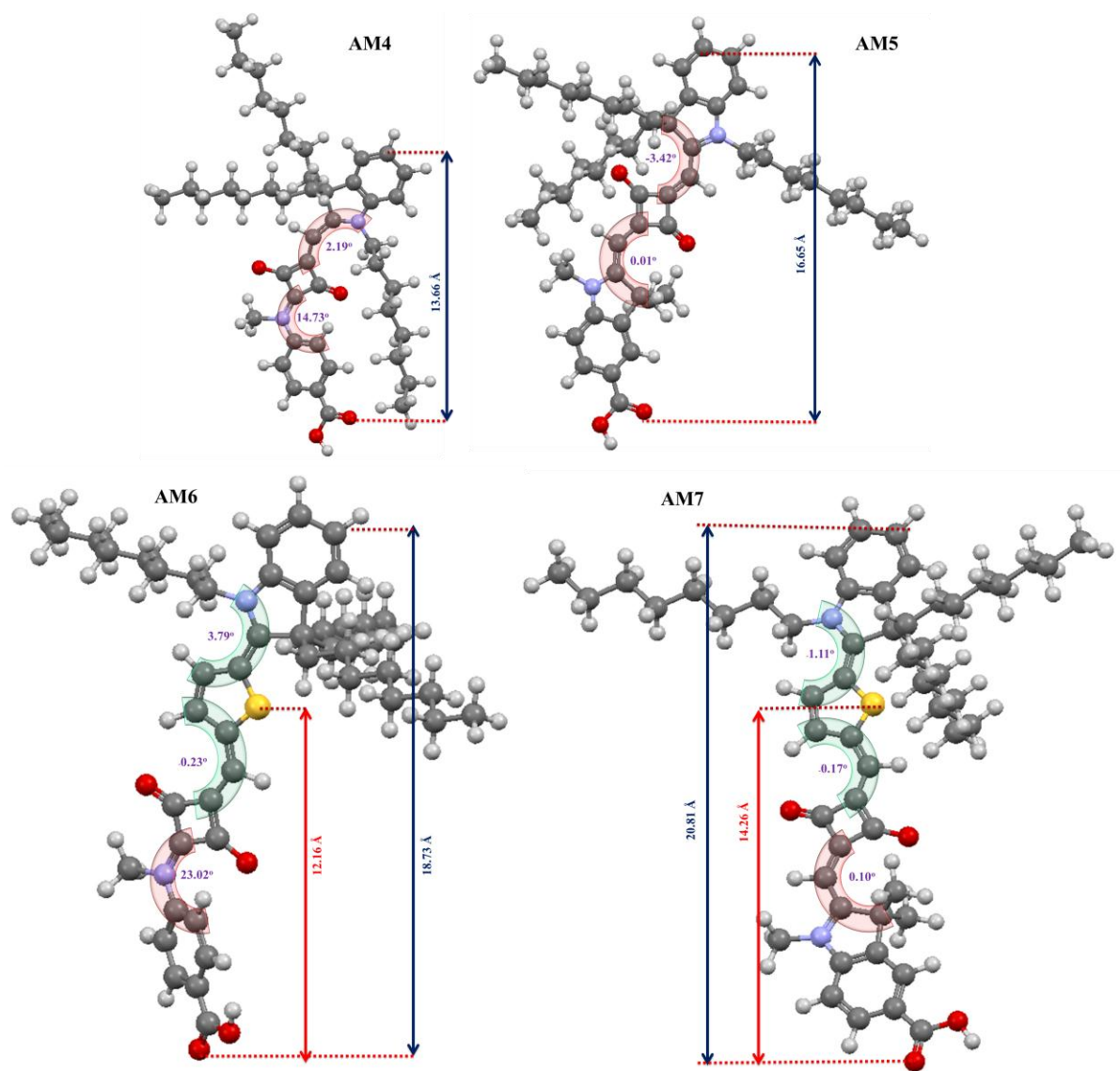


Figure 7. Energy minimized structures of **AM4-AM7** dyes with the distance (between carboxylic acid C=O of anchoring group to C-atom of non-anchoring donor and thiophene-C) and dihedral angles between donor, acceptor, and π -spacer units.

The height of the dye molecules from the O-atom of anchoring group ($-\text{CO}_2\text{H}$ group) to sp^2 -C-atom of the phenyl unit of the donor (non-anchoring side) have been calculated and were in between 13.66 Å - 20.81 Å for the **AM** dye series. Systematic changes in the dye height with π -extension have been found (**AM4** 13.66 Å, **AM5** 16.65 Å **AM6** 18.73 Å, and **AM7** 20.81 Å). A significant torsional strain has been found in the dyes with aniline donor (between aniline and acceptor moieties), further π -extension by introducing thiophene spacer has not altered the dihedral angles between indoline and acceptor moieties.

4.2.5 Photovoltaic performance.

DSSC devices of **AM4-AM7** dyes have been fabricated with (i) commercial I^-/I_3^- electrolyte (Z-50 from Solaronix), and (ii) iodide/triiodide electrolyte with different concentrations of LiI.⁵¹ Electrolyte composition has been made by mixing LiI (0.25 M, 0.50 M, and 1.0 M), with DMII (1 M), I_2 (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v. The concentrations of LiI has been varied to enhance the photocurrent because coulombic attraction of Li-ions with the metal oxide TiO_2 surface increases the flat band potential.^{49,50,65-67} Further, acetonitrile has been used as a sensitizing solvent for all the **AM** dyes, as utilization of chlorinated solvents for sensitization of alkyl wrapped squaraine dyes lead to good solvation of dyes, which reduced the dye loading and showed poor DSSC performance.⁶⁸ As the **AM** dyes were not completely soluble in the acetonitrile, therefore a small amount of chloroform has been used to dissolve the dyes, where the ratio of acetonitrile and chloroform was 97.5: 2.5 was used as dye sensitizing solvent. An optimized photovoltaic performance with the above fabrication conditions is provided in (Table 2 and 4), and corresponding J-V and IPCE profiles are provided in Figure 8, respectively. The highest DSSC efficiency of 7.35, 5.18, 0.08, and 0.05% have been achieved with I^-/I_3^- electrolyte (Z-50) for the **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. Whereas the highest of 6.17% (LiI 0.0 M), 4.28% (LiI 1.0 M), 0.43% (LiI 1.0 M), and 0.28% (LiI 1.0 M), of DSSC efficiency have been achieved with different concentrations of the LiI in I^-/I_3^- electrolyte for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. LiI 0.0 M concentration means electrolyte made with DMII (1.0 M), I_2 (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI. The J_{SC} of the device for all dyes increases with increased LiI concentrations in the I^-/I_3^- electrolyte, whereas V_{OC} of the device varied with increased concentrations of LiI compared to without LiI and commercial I^-/I_3^- electrolyte (Z-50), respectively. **AM4** dye showed

minor changes and other **AM** dyes showed significant changes in the device J_{SC} with increased LiI concentrations in electrolytes (**Figure 8, Table 4**).

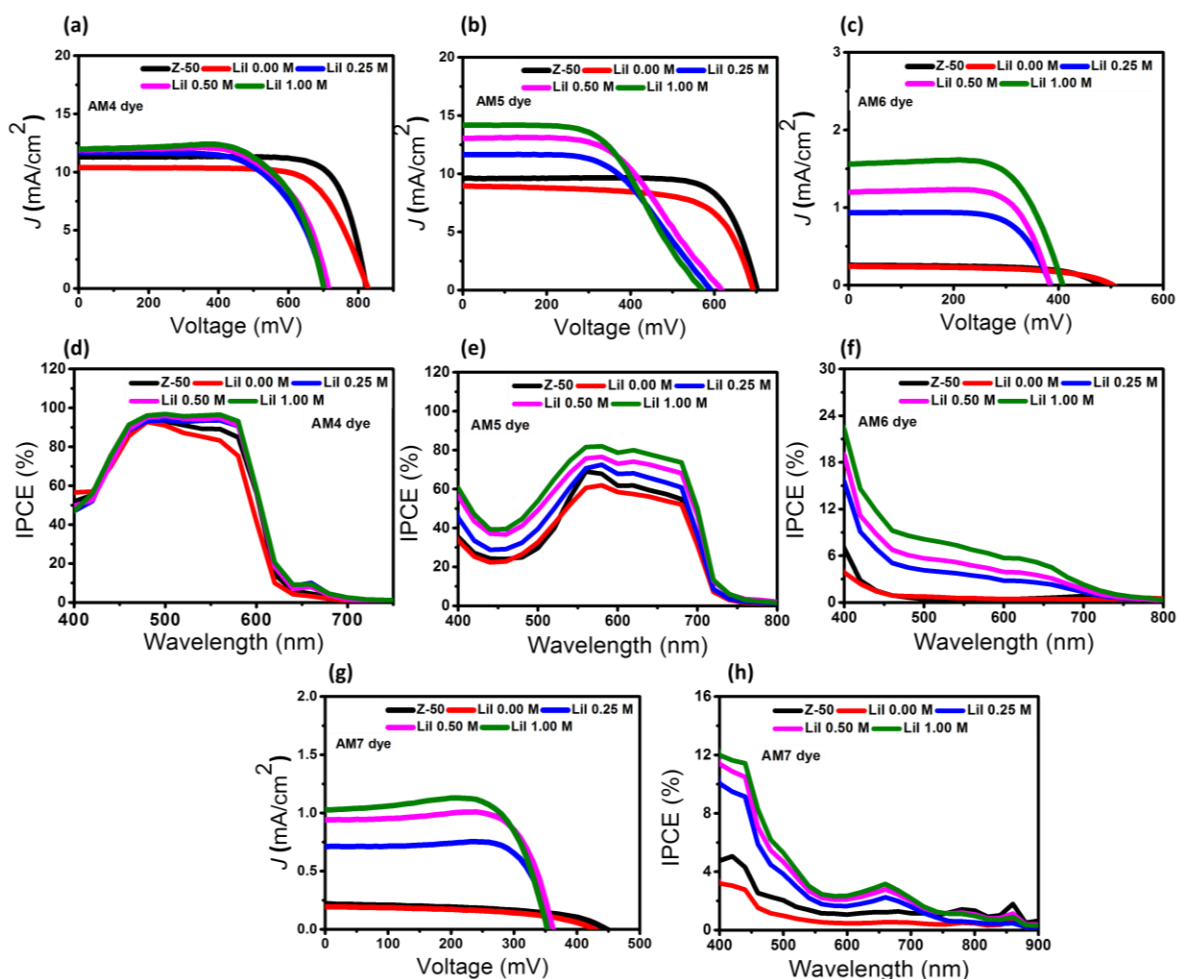


Figure 8. (a-c and g) I - V , and (d-f and h) IPCE curves for **AM** dyes. LiI 0.0 M concentration means electrolyte made with DMII (1 M), I_2 (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI.

Further, varied LiI concentrations in electrolytes also affect the fill factor of the DSSC device which plays an important role in enhancing DSSC efficiency. The difference of 3-20 mV in V_{OC} have been found between the commercial I^-/I_3^- electrolyte (Z-50) and electrolyte made without LiI, whereas these differences have been increased from 67-120 mV between the electrolyte made with 0.25 M LiI and without LiI, respectively for the **AM** dyes (**Table 4**). Meanwhile, 0.25 M concentrations of LiI showed 67-120 mV low V_{OC} compared to electrolyte made without LiI

for **AM** dyes. Further, commercial I^-/I_3^- electrolyte (Z-50) showed 0.02-0.92 mAcm^{-2} and electrolyte with 0.25 M concentrations of LiI showed 0.52-2.68 mAcm^{-2} higher J_{SC} compared to electrolyte made without LiI, respectively (**Table 4**). LiI with 1.0 M concentrations showed the maximum device J_{SC} for **AM** dyes over other LiI concentrations, which can be easily understood from the IPCE profiles where systematic enhancement has been found with increased LiI concentrations (**Figure 8**). Here, **AM6** and **AM7** dyes showed DSSC efficiency more than five times with 1.0 M concentrations of LiI compared to the LiI with 0.00 M concentrations and commercial I^-/I_3^- electrolyte (Z-50). The IPCE profile for all the dyes has been enhanced systematically by tuning the different concentrations of LiI. After careful optimization of devices, it has been found that the dyes with highly extended structures showed poor DSSC device performance. Meanwhile, absorption shifts from visible to NIR regions by extending the conjugation within the polymethine framework drastically decreases DSSC performance. Extension in conjugation showed the negative effect on the V_{OC} , J_{SC} , and efficiency of the dyes when moved from low- to highly conjugated structures. The efficient dye regeneration needs approximate 0.35 V versus NHE over potential with I^-/I_3^- electrolyte,⁶³ **AM4** and **AM5** dyes possesses sufficient regeneration over potential that increase the device efficiency whereas the **AM6** and **AM7** dyes having low over-potential for dye regeneration. Due to poor compatibility with I^-/I_3^- electrolyte π -extended dyes **AM6** and **AM7** are showed the low photovoltaic response.

Table 2. Optimized DSSC device performance of **AM** dyes.

Dyes	Electrolytes	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff (%)	η (%)
AM4	Z-50	823 ± 3	11.30 ± 0.11	79 ± 0.56	7.35 ± 0.15
AM4	LiI (1.00 M)	701 ± 2	11.97 ± 0.17	67 ± 1.14	5.62 ± 0.19
AM5	Z-50	702 ± 2	9.59 ± 0.10	77 ± 0.91	5.18 ± 0.13
AM5	LiI (1.00 M)	570 ± 3	14.16 ± 0.09	53 ± 2.07	4.28 ± 0.21
AM6	Z-50	480 ± 5	0.26 ± 0.01	63 ± 0.84	0.079 ± 0.004
AM6	LiI (1.00 M)	408 ± 4	1.56 ± 0.03	68 ± 0.74	0.433 ± 0.017
AM7	Z-50	448 ± 2	0.22 ± 0.01	51 ± 2.50	0.050 ± 0.005
AM7	LiI (1.00 M)	353 ± 6	1.02 ± 0.02	77 ± 0.93	0.277 ± 0.006

Further, **AM** dyes with different absorption properties have been co-sensitized, optimized, and provided in **Figure 9** and **Table 3** and **Table 5**. Co-sensitization of **AM4** with **AM5** dye showed enhanced device efficiency due to enhanced J_{SC} , whereas co-sensitization of **AM4** with **AM5** and **AM6** decreases the device efficiency dramatically due to decreased V_{OC} and J_{SC} . Co-sensitization of **AM4** with **AM5**, **AM6** and **AM7** dyes showed poor device performance. The maximum co-sensitized device efficiency of 8.12% has been achieved by **AM4** and **AM5** dyes (1:1 ratio) with I^-/I_3^- electrolyte (Z-50). Like non-co-sensitized devices J_{SC} and IPCE response of co-sensitized devices increases with increased concentrations of the LiI in electrolyte. IPCE profile of co-sensitized devices revealed the maximum participation of **AM4** and **AM5** dyes into current conversion with different current intensities for all the compositions. Here, **AM4:AM5** dyes compositions showed impressive IPCE responses which further decreases drastically for **AM4:AM5:AM6** and **AM4:AM5:AM6:AM7** compositions, respectively. Meanwhile, use of **AM6** and **AM7** dyes kills the co-sensitized solar cell performance.

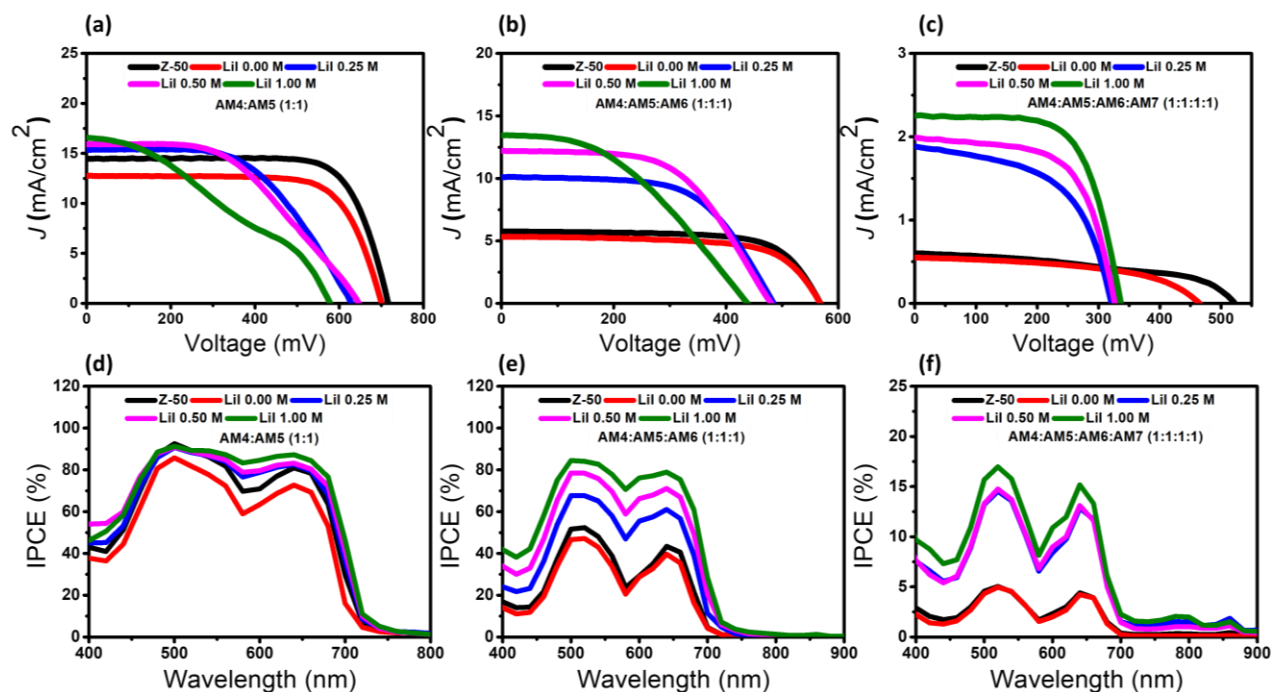


Figure 9. (a-c) I - V , and (d-f) IPCE curves for co-sensitized device made from **AM** dyes. LiI 0.0 M concentration means electrolyte made with DMII (1 M), I_2 (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI.

Table 3. Optimized DSSC device performance of co-sensitized AM dyes.

Dyes	Electrolytes	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AM4:AM5	Z-50	716 ± 2	14.45 ± 0.26	76 ± 0.87	7.86 ± 0.26
AM4:AM5	LiI (1.00 M)	578 ± 5	16.57 ± 0.24	33 ± 1.13	3.16 ± 0.18
AM4:AM5:AM6	Z-50	568 ± 3	5.76 ± 0.18	69 ± 1.09	2.26 ± 0.12
AM4:AM5:AM6	LiI (1.00 M)	438 ± 5	13.44 ± 0.22	41 ± 0.68	2.41 ± 0.11
AM4:AM5:AM6: AM 7	Z-50	522 ± 3	0.60 ± 0.02	47 ± 1.48	0.147 ± 0.011
AM4:AM5:AM6: AM 7	LiI (1.00 M)	336 ± 7	2.25 ± 0.04	66 ± 0.84	0.499 ± 0.026

Table 4. Optimized DSSC performances of AM4-AM7 dyes with I^-/I_3^- electrolyte.

Dyes	Electrolytes	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AM4	Z-50	823	11.30	79	7.35
AM4	0.00 M	826	10.38	72	6.17
AM4	0.25 M	706	11.69	63	5.20
AM4	0.50 M	714	11.90	65	5.52
AM4	1.00 M	701	11.97	67	5.62
AM5	Z-50	702	9.59	77	5.18
AM5	0.00 M	692	8.95	68	4.21
AM5	0.25 M	591	11.63	54	3.71
AM5	0.50 M	618	13.04	53	4.27
AM5	1.00 M	570	14.16	53	4.28
AM6	Z-50	480	0.26	63	0.079
AM6	0.00 M	504	0.24	58	0.070
AM6	0.25 M	385	0.93	69	0.247
AM6	0.50 M	384	1.19	72	0.329

AM6	1.00 M	408	1.56	68	0.433
AM7	Z-50	448	0.22	51	0.050
AM7	0.00 M	428	0.19	51	0.041
AM7	0.25 M	361	0.71	79	0.203
AM7	0.50 M	362	0.94	78	0.265
AM7	1.00 M	353	1.02	77	0.277

LiI 0.00 M concentration means electrolyte made with DMII (1 M), I₂ (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI.

Table 5. Optimized DSSC performances of co-sensitized devices made from **AM** dyes.

Dyes	LiI	V_{OC} (mV)	J_{SC} (mA/cm²)	ff (%)	η (%)
AM4:5	Z-50	716	14.45	76	7.86
AM4:5	0.00 M	700	12.75	72	6.43
AM4:5	0.25 M	629	15.37	55	5.32
AM4:5	0.50 M	646	15.92	49	5.04
AM4:5	1.00 M	578	16.57	33	3.16
AM4:5:6	Z-50	568	5.76	69	2.26
AM4:5:6	0.00 M	568	5.33	66	1.99
AM4:5:6	0.25 M	484	10.09	61	2.98
AM4:5:6	0.50 M	479	12.21	56	3.28
AM4:5:6	1.00 M	438	13.44	41	2.41
AM4:5:6:7	Z-50	522	0.60	47	0.147
AM4:5:6:7	0.00 M	464	0.55	51	0.130
AM4:5:6:7	0.25 M	322	1.88	54	0.327
AM4:5:6:7	0.50 M	328	1.98	62	0.403
AM4:5:6:7	1.00 M	336	2.25	66	0.499

LiI 0.00 M concentration means electrolyte made with DMII (1 M), I₂ (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI.

Table 6. Integrated current J_{SC} (mA/cm²) from IPCE.

Dyes	Z-50	LiI 0.00 M	LiI 0.25 M	LiI 0.50 M	LiI 1.00 M
AM4	10.91	10.15	11.25	11.29	11.66
AM5	9.78	9.33	11.13	12.72	13.72
AM6	0.25	0.21	0.87	1.14	1.57
AM7	0.47	0.24	0.76	0.93	1.02
AM4:AM5	14.64	12.88	15.24	15.76	16.20
AM4:AM5:AM6	6.52	5.80	9.91	12.12	13.95
AM4:AM5:AM6:AM7	0.62	0.56	1.94	1.93	2.35

LiI 0.00 M concentration means electrolyte made with DMII (1 M), I₂ (0.03 M) in acetonitrile/valeronitrile solvent mixture 85/15 v/v in the absence of LiI.

4.2.6 Electrochemical Impedance Spectroscopy (EIS).

Electrochemical impedance spectroscopy (EIS) characterization of **AM4**, **AM5**, **AM6**, and **AM7** dyes as such and co-sensitized solar cell has been carried out with commercial I⁻/I₃⁻ electrolyte (Z-50).⁶⁹ EIS characterization was carried out in dark conditions by applying the various potentials and obtained Nyquist plot (**Figure 11**) from this experiment were fitted to get the charge recombination resistance (R_{ct}) and chemical capacitance (C_{μ}) values. Multiplication of these two (R_{ct} and C_{μ}) gave the electron lifetime (τ) into TiO₂. As the V_{OC} of the **AM** dyes are different respect to each other, therefore EIS characterization has been done near to V_{OC} and lower applied potentials for the respective dyes (**Figure 10**, **Table 7**, **Table 8**, and **Table 9**). High recombination resistance, chemical capacitance and electron lifetime have been noticed for **AM4**, **AM5** dyes, and co-sensitized **AM4:AM5** dyes and they support the obtained enhanced V_{OC} and J_{SC} of them compared to other dyes or co-sensitized compositions. **AM6** and **AM7** dyes as such and their co-sensitization with other dyes showed poor chemical capacitive and electron lifetime values and is the reason for poor V_{OC} and J_{SC} of the corresponding devices. Here, **AM** dye with low conjugated vinylene bond between the polymethine framework showed its better device ability over **AM** dye with high conjugation.

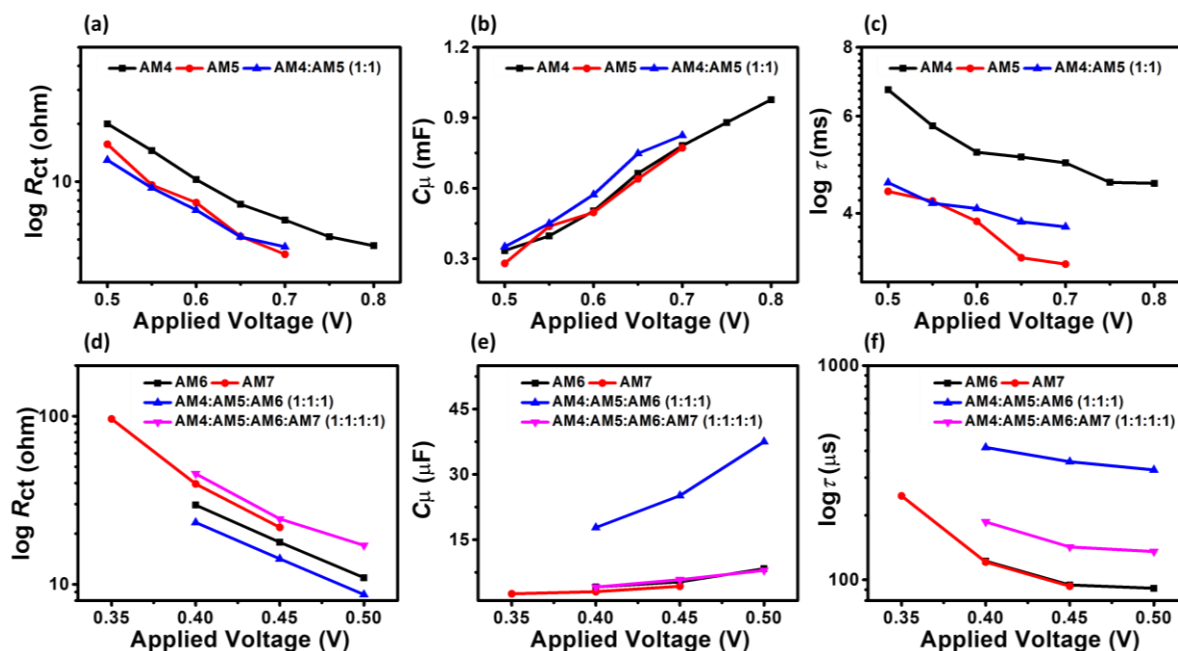


Figure 10. (a, d) Charge recombination resistance, (b, e) chemical capacitance, and (c, f) lifetime of electron by devices made from **AM** dyes and co-sensitized devices at various applied potentials in dark.

Table 7. EIS parameters of **AM** dyes and co-sensitized dyes with Γ/I_3^- electrolyte (Z-50) at applied potential of $^a0.45/^b0.55$ V.

Dyes	R_{ct} (Ω)	C_{μ} (mF/ μ F)	τ (ms/ μ s)
b AM4	14.51	0.397 mF	5.76 ms
b AM5	9.61	0.438 mF	4.21 ms
a AM6	17.78	5.32 μ F	94.59 μ s
a AM7	21.81	4.28 μ F	93.35 μ s
b AM4:AM5	9.27	0.45 mF	4.17 ms
a AM4:AM5:AM6	14.17	25.11 μ F	355.8 μ s
a AM4:AM5:AM6:AM7	24.5	5.81 μ F	142.34 μ s

The dipole moment was found to be 3.68 D/**AM4**, 2.58 D/**AM5**, 15.77 D/**AM6** dye and 10.59 D/**AM7** dyes. The dipole moment of the dyes shifted the position of TiO_2 conduction band. In

ionic dyes dipole moment are directional, in cationic dye the energy gap narrowed is negative dipole, conversely in anionic dye the energy gap increased is positive dipole, whereas zwitterionic dye possess the dipole moment in both direction positive dipole and negative dipole. Introduction of squaryl unit in dye backbone can improve the interfacial properties of the dye and charge distribution which is reason of the higher open circuit voltage of squaraine dyes compared to the ionic dyes.⁵⁰ Further the huge change has been observed in the dipole moment of π -extended squaraine dyes **AM6** and **AM7** due to narrowed energy gap compared to the **AM4** and **AM5** dyes. The charge recombination resistance values are high for **AM6**/17.78 Ω and **AM7**/21.81 Ω compared to the **AM4**/14.51 Ω and **AM5**/9.61 Ω dye due to changes in the interfacial properties and dipole moment of the dyes.

Table 8. EIS parameters of DSSC device made with **AM4**, **AM5** dyes and co-sensitized dyes in dark at the different applied potentials.

EIS	App Vol (V)	AM4	AM5	AM4:5
R_{ct} (ohm)	-0.80	4.64	-	-
	-0.75	5.17	-	-
	-0.70	6.32	4.19	4.58
	-0.65	7.63	5.19	5.16
	-0.60	10.26	7.78	7.12
	-0.55	14.51	9.61	9.27
	-0.50	20.0	15.65	12.95
	-0.80	0.977	-	-
$C\mu$ (mF)	-0.75	0.880	-	-
	-0.70	0.781	0.772	0.825
	-0.65	0.663	0.64	0.748
	-0.60	0.503	0.497	0.573
	-0.55	0.397	0.438	0.45
	-0.50	0.335	0.28	0.351
	-0.80	4.53	-	-
	-0.75	4.55	-	-
τ (ms)	-0.70	4.93	3.23	3.78
	-0.65	5.06	3.32	3.86
	-0.60	5.16	3.86	4.08
	-0.55	5.76	4.20	4.17
	-0.50	6.7	4.38	4.54

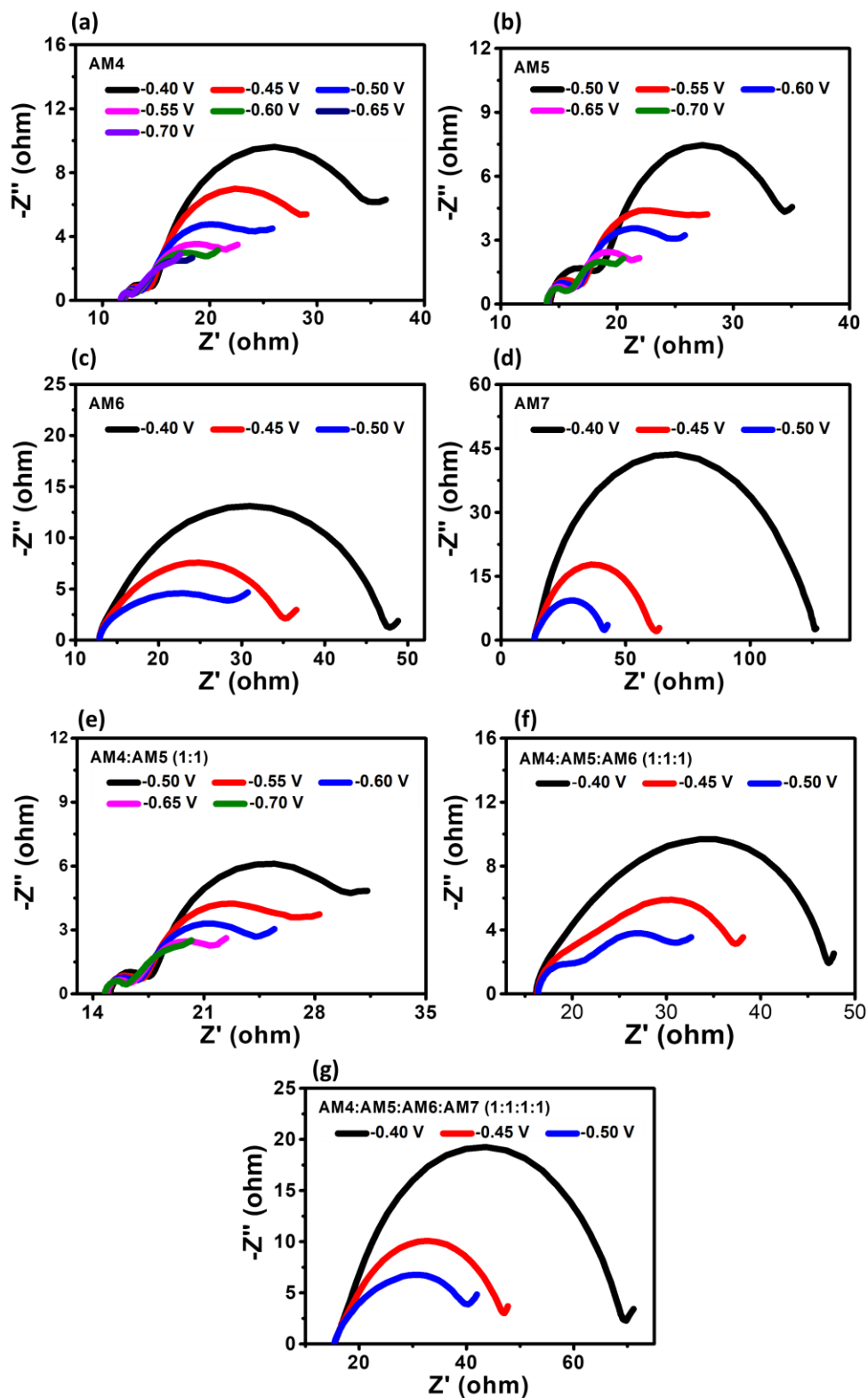


Figure 11. Nyquist Plot of AM4-AM7 dyes at different applied potentials in dark.

Table 9. EIS parameters of DSSC device made with **AM6**, **AM7** dyes and co-sensitized dyes in dark at the different applied potentials.

EIS	App Vol (V)	AM6	AM7	4:5:6	4:5:6:7
R_{ct} (ohm)	-0.55	-	-	-	10.98
	-0.50	10.95	-	8.69	17.05
	-0.45	17.78	21.81	14.17	24.5
	-0.40	29.6	39.55	23.33	45.45
	-0.35	-	96.24	-	-
$C\mu$ (μF)	-0.55	-	-	-	11.74
	-0.50	8.34	-	37.5	7.95
	-0.45	5.32	4.28	25.11	5.81
	-0.40	4.13	3.06	17.79	4.1
	-0.35	-	2.56	-	-
τ (μs)	-0.55	-	-	-	128.90
	-0.50	91.32	-	325.87	135.55
	-0.45	94.59	93.35	355.81	142.34
	-0.40	122.25	121.02	415.04	186.34
	-0.35	-	246.37	-	-

4.3 CONCLUSION

In order to extend the absorption property of unsymmetrical squaraine dye from visible to NIR regions and enhancing the light harvesting property, a series of extended π -conjugated unsymmetrical squaraine dye (**AM4-AM7**) with symmetrical alkyl-group wrapping have been designed and synthesized. The absorption wavelength showed 100 nm red shifts with each vinylene bond for these dyes **AM4**/541nm, **AM5**/643nm, **AM6**/747nm and **AM7**/833nm respectively. The light harvesting property (LHE) of the dyes also enhanced along with the absorption maxima and found that **AM7** dye exhibited the maximum of 386 nm broad LHE at 60% of the spectrum height. The HOMO energy level of dyes shifted towards negative potential and LUMO shifted towards positive potential (for **AM4**, **AM6**, and **AM7**) along with the π -extension. Photovoltaic characterizations of AM dyes have been carried out with commercial I^-/I_3^- electrolyte (Z-50) and electrolytes containing different concentrations of LiI. Here, extension in conjugation showed negative effect on the device performance, and huge variation in the V_{OC} , J_{SC} , and device efficiency has been noted from low- to highly conjugated dye structures. **AM4** and **AM5** dyes showed maximum of 7.35 and 5.18% of DSSC efficiency with I^-/I_3^- electrolyte (Z-50) DSSC. Whereas **AM6** and **AM7** dyes showed maximum of 0.43 and 0.28% of DSSC efficiency with electrolyte containing 1.0 M concentration of LiI, due to enhanced J_{SC} . Co-sensitization of **AM4** dye with **AM5**, **AM6**, and **AM7** dyes showed different device efficiency, and co-sensitization of **AM4** with **AM5** achieved highest efficiency of 8.12% with I^-/I_3^- electrolyte (Z-50) compared to other co-sensitization and electrolyte compositions. Present study on the π -extension within the polymethine framework for the unsymmetrical squaraine dye will be helpful to designing the polymethine dyes with enhanced photophysical, electrochemical, and photovoltaic properties.

4.4 EXPERIMENTAL SECTION

Compounds **10**¹⁷ and **11**⁵⁸ were synthesized by using the procedure provided in the literature.

4.4.1 General methods

Refer section 2.2.1 for general methods utilized and DSSC device fabrication procedure (Chapter 2, Page No: 66-68). The optimization of the ground-state geometry was carried out at the Density Functional Theory (DFT) level using the B3LYP hybrid functional and the 6-31G (d) atomic basis set.

Procedure for dye-sensitized solar cell fabrication: The cells (area of TiO₂ is 0.23 cm²) immersed in 0.1 mM **AM** dye for 12 h, and for co-sensitization concentration of dyes was **AM4:AM5** (0.05 mM each), **AM4:AM5:AM6** (0.05 mM each), and **AM4:AM5:AM6:AM7** (0.05 mM each) for 12 h, at room temperature. Electro-platinised platinum foil used as a cathode iodolyte Z-50 (Solaronix) and LiI with various concentrations were used as electrolyte and 25 μ m spacer and area of black mask was 0.36 cm². The device performance of **AM4-AM7** and co-sensitized dyes was measured under standard simulator condition (AM 1.5 G 100 mW/cm²).

4.4.2 Synthesis of AM4-AM7 dyes.

Synthesis of 2-methyl-1-(5-methylthiophen-2-yl)propan-1-one (2): Freshly grinded KOH (12 g, 214 mmol) was added to the 100 mL round bottomed flask that contain 20 mL PhMe, then compound **1** (1.5 g, 10.7 mmol) was added and stirred at room temperature 10 min. 18-C-6 (0.1 g) was added to the above reaction mixture and stirred for additional 10 min. 1-Iodooctane (24 g, 100 mmol) was added drop wise to the reaction mixture and heated at 70 °C for 36 h. The reaction mixture was filtered through Whatman (No 1) filter paper and solvents were evaporated, and reaction mixture was purified by column chromatography using EtOAc and pet-ether (2:98). Yield: 1.4 g, 36%. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J*=3.75 Hz, 1H), 6.80 (dd, *J*=3.75, 0.88 Hz, 1H), 3.06–3.19 (m, 1H), 2.53 (s, 3H), 1.67–1.81 (m, 2H), 1.39–1.55 (m, 2H), 1.23–1.32 (m, 10H), 1.22 (br. s., 14H), 0.86 (t, *J*=6.94 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 197.4, 149.6, 143.5, 132.0, 126.8, 48.1, 33.1, 31.8, 29.8, 29.4, 29.3, 27.7, 22.6, 16.1, 14.1.

Synthesis of 2-(5-methylthiophen-2-yl)-3,3-dioctyl-3H-indole (3): Dissolved the compound 2 (0.5 g, 1.37 mmol) and phenylhydrazine hydrochloride (0.2 g, 1.37 mmol) in 10 mL of acetic acid in a 50 mL pressure tube and heated at 130 °C for 120 h. Solvents were evaporated and reaction mixture was purified by column chromatography using EtOAc and pet-ether (3:97). Yield: 0.1 g, 17%. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J*=7.63 Hz, 1H), 7.50 (d, *J*=3.63 Hz, 1H), 7.31–7.35 (m, 1H) 7.19–7.24 (m, 2H), 6.81–6.86 (m, 1H), 2.56 (s, 3H), 1.98–2.15 (m, 4H), 1.16–1.24 (m, 4H), 1.01–1.14 (m, 16H), 0.85–0.92 (m, 1H), 0.82 (t, *J*=7.13 Hz, 6H), 0.72–0.79 (m, 1H), 0.43–0.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 155.2, 144.8, 143.7, 136.1, 128.7, 127.7, 126.6, 125.1, 121.0, 120.1, 62.7, 39.4, 31.8, 29.7, 29.1, 29.0, 23.5, 22.6, 15.7, 14.1.

Synthesis of 2-(5-methylthiophen-2-yl)-1,3,3-trioctyl-3H-indol-1-ium (4): Dissolved the compound 3 (0.32 g, 0.73 mmol) and C₈H₁₇I (0.36 g, 1.09 mmol) in 10 mL of MeCN in a 20 mL glass pressure tube and heated at 90 °C for 90 h. Solvents were evaporated and reaction mixture was dissolved in CHCl₃ (1 mL) and washed with *n*-pentane (5 mL × 5), dried and use for next step without further purification. Yield: 0.07 g, 14%. ¹H NMR (200 MHz, CDCl₃) δ 8.39 (d, *J*=4.17 Hz, 1H), 7.84 (d, *J*=7.45 Hz, 1H), 7.61–7.77 (m, 2H), 7.42–7.58 (m, 2H), 4.93 (t, *J*=7.83 Hz, 2H), 2.83 (s, 3H), 2.19–2.53 (m, 4H), 1.92–2.12 (m, 2H), 1.66 (br. s., 4H), 1.27 (br. s., 10H), 1.06 (br. s., 13H), 0.70–0.93 (m, 12H), 0.39–0.64 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 176.5, 159, 142.6, 141, 139.2, 130.9, 130.2, 129.9, 123.7, 122.7, 115.4, 64.5, 50.5, 41.3, 31.7, 31.6, 29.3, 29.1, 28.9, 28.8, 28.3, 26.9, 23.8, 22.6, 22.6, 16.8, 14.1, 14.0.

Synthesis of 1,3,3-trihexylindolin-2-one (6): Dissolved the compound 5 (1.0 g, 7.5 mmol) in 100 mL of anhydrous THF in a 500 mL size of double neck round bottom flask, NaH (0.72 g, 30.04 mmol, 60% suspension in paraffins oil) was added at 0 °C and stirred for 30 min, after 30 min octyl iodide (6.3 g, 26.3 mmol) was added to the reaction flask at 0 °C. Reaction mixture was stirred at room temperature for 48 h. Aqueous solution of NH₄Cl was added to the reaction mixture and the organic layer was extracted with EtOAc (50 mL × 2), dried over Na₂SO₄, solvents were evaporated under reduced pressure and purified by column chromatography using EtOAc and pet-ether (7 : 93). Yield: 1.5 g 42 %. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (t, *J*=7.69 Hz, 1H), 7.13 (d, *J*=7.25 Hz, 1H), 7.05 (t, *J*=7.38 Hz, 1H), 6.83 (d, *J*=7.75 Hz, 1H), 3.69 (t, *J*=7.32 Hz, 2H), 1.80–1.92 (m, 2H), 1.63–1.77 (m, 4H), 1.33 (br. s., 4H), 1.20–1.30 (m, 10 H), 1.05–1.19 (m, 16H), 0.91–1.03 (m, 2H), 0.81–0.90 (m, 9H), 0.66–0.81 (m, 2H). ¹³C NMR (101

MHz, CDCl_3) δ 180.1, 143.6, 132.9, 127.3, 122.7, 121.9, 107.9, 52.9, 39.8, 38.2, 31.8, 31.8, 29.8, 29.3, 29.3, 29.2, 27.6, 27.1, 24.1, 22.6, 22.6, 14.1.

Synthesis of 2-methyl-1,3,3-trioctyl-3H-indolium (7): Dissolved the compound 6 (1.0 g, 2.13 mmol) in 20 mL of anhydrous THF and cooled to 0 °C, MeMgI (3 M solution in di-ethyl ether, 4.13 mL, 12.78 mmol) was added drop wise. Resultant reaction mixture was warmed to room temperature and then at 100 °C for 60 h. Reaction flask cooled to 0 °C and 5 mL of MeOH was added drop-wise to the reaction mixture and solvents were evaporated, further 10 mL of 3N HCl solution in MeOH was added and stirred the reaction at room temperature for 1 h. Organic layer was extracted with dichloromethane (30 mL $\times$ 2), dried over Na_2SO_4 and solvents were evaporated. Reaction mixture was dissolved in 1 mL of chloroform and washed with *n*-pentane (5 mL $\times$ 3), to get required product. Yield = 0.65 g, 61%. ^1H NMR (200 MHz, CDCl_3) δ 7.68–7.81 (m, 1H), 7.58–7.68 (m, 2H), 7.44–7.57 (m, 1H), 4.88 (t, $J=7.45$ Hz, 2H), 3.14 (s, 3H), 2.00–2.28 (m, 4H), 1.82–1.99 (m, 2H), 1.42–1.58 (m, 2H), 1.31–1.41 (m, 2H), 1.24 (br. s., 10H), 1.13 (br. s., 15H), 0.78–0.86 (m, 9H), 0.50–0.71 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.7, 142.3, 138.9, 130.1, 129.8, 123.7, 115.4, 63.8, 50.6, 37.4, 31.8, 31.7, 31.6, 29.4, 29.2, 29.1, 28.9, 28.7, 26.9, 24.1, 22.6, 17.4, 14.

Synthesis of 3-butoxy-4-((1,3,3-trioctylindolin-2-ylidene)methyl)cyclobut-3-ene-12-dione (8): Dissolved the compound 7 (0.5 g, 0.99 mmol) in 6 mL of *n*-BuOH in a 100 mL round bottomed flask, Et_3N (0.15 g, 1.48 mmol) and compound (a) dibutylsquarate (0.23 g, 0.99 mmol) were added to the reaction flask and stirred at room temperature for 24 h, and then heated at 70 °C for 2 h. Solvents were evaporated and reaction mixture was purified by column chromatography by using EtOAc and pet-ether (3:97). Yield: 0.15 g, 24%. ^1H NMR (400 MHz, CDCl_3) δ 7.24–7.30 (m, 1H), 7.17–7.22 (m, 1H), 7.04–7.11 (m, 1H), 6.85 (d, $J=7.88$ Hz, 1H), 5.51 (s, 1H), 4.87 (t, $J=6.63$ Hz, 2H), 3.82 (t, $J=7.44$ Hz, 2H), 2.43–2.55 (m, 2H), 1.80–1.93 (m, 4H), 1.69–1.76 (m, 2H), 1.49–1.57 (m, 2H), 1.33–1.46 (m, 4H), 1.24–1.32 (m, 6H), 1.17–1.24 (m, 4H), 1.04–1.15 (m, 15H), 0.99–1.03 (m, 3H), 0.85–0.91 (m, 3H), 0.79–0.85 (m, 6H), 0.69–0.79 (m, 2H), 0.46–0.58 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.8, 187.4, 186.9, 173.1, 166.3, 144.5, 137.3, 127.6, 122.6, 122.1, 108.0, 81.7, 57.1, 43.0, 39.6, 32.2, 31.8, 29.6, 29.3, 29.2, 29.1, 29.1, 27.2, 26.5, 23.9, 22.6, 18.8, 14.1, 13.7.

Synthesis of 3-hydroxy-4-((1,3,3-trioctylindolin-2-ylidene)methyl)cyclobut-3-ene-12-dione (9): Dissolved the compound 8 (0.32 g 0.52 mmol) in 10 mL of acetone in a 100 mL round bottomed flask. 10 mL of 4 N HCl in water was added to the reaction flask and refluxed for 20 h. Solvents were evaporated and purified by column chromatography using MeOH and CH₂Cl₂ (3:97). Yield: 0.25 g, 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.13–7.26 (m, 2H), 7.01 (d, *J*=7.19 Hz, 1H), 6.79 (d, *J*=7.75 Hz, 1H), 5.81 (s, 1H), 3.84 (br. s., 2H), 2.51–3.05 (m, 2H), 1.80–1.95 (m, 2H), 1.52–1.80 (m, 3H), 1.24–1.38 (m, 7H), 0.97–1.24 (m, 25H), 0.70–0.92 (m, 14H), 0.31–0.58 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.2, 179.7, 166.7, 163.9, 145.1, 137.9, 127.2, 122.0, 121.7, 107.5, 84.4, 56.9, 42.8, 40.1, 31.9, 31.8, 31.7, 31.7, 29.7, 29.5, 29.3, 29.3, 29.1, 28.9, 27.4, 26.9, 26.7, 24.1, 23.9, 22.6, 14.2, 14.1.

General synthetic procedure of AM4-AM7 dyes: Semi-squaric acid (1 equiv.) and donor aniline or Fischer's base (1 equiv.) were dissolved in anhydrous PhMe and *n*-BuOH (1:1, 10 mL of each) in a 50 mL round bottomed flask and refluxed in the Dean-Stark apparatus for 12-20 h under an inert atmosphere. The reaction mixture was purified by column chromatography (SiO₂ 100-200 mesh MeOH and CH₂Cl₂) to afford the required dye.

AM4 dye: Compound 9 (0.2 g 0.4 mmol), and 4-(methylanino)benzoic acid (0.1 g, 0.4 mmol) for 12 h. Column chromatography (SiO₂ 100-200 mesh, MeOH and CH₂Cl₂). Yield: 0.1 g, 36%. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J*=8.24 Hz, 2H), 7.44 (d, *J*=8.54 Hz, 2H), 7.28–7.36 (m, 2H), 7.16–7.22 (m, 1H), 7.00 (d, *J*=7.93 Hz, 1H), 6.04 (br. s., 1H), 4.02 (s, 3H), 3.94–4.02 (m, 2H), 2.91 (br. s., 2H), 1.93–2.03 (m, 2H), 1.72–1.82 (m, 2H), 1.37–1.46 (m, 2H), 1.31–1.37 (m, 2H), 1.24–1.28 (m, 5H), 1.17–1.22 (m, 4H), 1.03–1.15 (m, 17H), 0.87 (t, *J*=7.02 Hz, 3H), 0.81 (t, *J*=7.17 Hz, 6H), 0.69–0.78 (m, 2H), 0.41–0.52 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 181.7, 174.6, 169.9, 168.6, 144.7, 144, 138.8, 131.1, 127.7, 124, 122.3, 121.6, 109.3, 86.7, 58.8, 43.8, 40.1, 38.1, 31.8, 31.7, 29.6, 29.4, 29.2, 29.1, 29.1, 27.2, 23.9, 22.6, 14.1. MALDI-TOF(*m/z*): [M]⁺ calculated for C₄₆H₆₄N₂O₄, 696.4866; found, 696.4089.

AM5 Dye: The compound 7 (0.2 g 0.4 mmol) and compound 10 (0.13 g, 0.4 mmol) for 16 h. Column chromatography (SiO₂ 100-200 mesh, MeOH and CH₂Cl₂). Yield = 0.12 g, 40%, ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J*=8.26 Hz, 1H), 8.06 (s, 1H), 7.30–7.40 (m, 2H), 7.23 (t, *J*=7.32 Hz, 1H), 7.06 (d, *J*=7.63 Hz, 1H), 6.97 (d, *J*=8.38 Hz, 1H), 6.19 (br. s., 1H), 6.00 (s, 1H),

4.11 (br. s., 2H), 3.51 (s, 3H), 3.00 (br. s., 2H), 1.95–2.11 (m, 2H), 1.85 (s, 6H), 1.81 (br. s., 2H), 1.39–1.46 (m, 3H), 1.33 (br. s., 4H), 1.21 (br. s., 4H), 1.14–1.20 (m, 4H), 1.05 (br. s., 14H), 0.86 (t, $J=6.57$ Hz, 4H), 0.79 (t, $J=7.00$ Hz, 9H), 0.47 (br. s., 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 182.4, 176.2, 171.3, 170.5, 168.4, 147.5, 143.9, 141.8, 131.2, 127.9, 124.7, 124.1, 123.9, 122.5, 109.9, 107.9, 88.1, 59.4, 48.2, 39.9, 31.9, 31.8, 31.8, 30.4, 29.7, 29.6, 29.4, 29.2, 29.1, 27.5, 27.3, 27.2, 24.0, 22.7, 22.6, 14.1. MALDI-TOF(m/z): $[\text{M}]^+$ calculated for $\text{C}_{50}\text{H}_{70}\text{N}_2\text{O}_4$, 762.5336; found, 762.4372.

AM6 dye: The compound **4** (0.15 g, 0.221 mmol) and compound **11** (0.054 g, 0.221 mmol) 12 h. Column chromatography (SiO_2 100-200 mesh, MeOH and CH_2Cl_2). Yield = 0.035 g, 20%. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J=8.50$ Hz, 1H), 8.04 (d, $J=8.63$ Hz, 2H), 7.82 (d, $J=5.13$ Hz, 1H), 7.41–7.51 (m, 2H), 7.38 (d, $J=8.88$ Hz, 2H), 7.20 (d, $J=8.63$ Hz, 1H), 7.05 (d, $J=8.13$ Hz, 1H), 6.35 (s, 1H), 4.25 (t, $J=8.13$ Hz, 2H), 3.89 (s, 3H), 2.20–2.26 (m, 2 H), 2.02–2.07 (m, 2 H), 1.50–1.57 (m, 3 H), 1.30 (br. s., 5H), 1.17–1.19 (m, 6 H), 1.06 (br. s., 19H), 0.81 (s, 11 H), 0.47–0.54 (m, 2 H). ^{13}C NMR (101 MHz, CDCl_3) δ 185, 176.6, 171, 169.6, 165.6, 153.5, 146.8, 144.4, 142.9, 139.7, 137.6, 132.2, 131, 130.7, 122.0, 119.7, 118.3, 117, 111.1, 110.0, 88.9, 70.6, 60.8, 42.6, 36.9, 35.9, 31.7, 30.5, 30.1, 29.7, 29.4, 29.3, 29.2, 29, 27.9, 26.9, 26.8, 23.9, 22.6, 14.0. MALDI-TOF(m/z): $[\text{M}]^+$ calculated for $\text{C}_{49}\text{H}_{66}\text{N}_2\text{O}_4\text{S}$, 778.4743; found, 779.3304.

AM7 dye: The compound **4** (0.10 g, 0.147 mmol) and **10** (0.47 g, 0.147 mmol) for 24 h. Column chromatography (SiO_2 100-200 mesh, MeOH and CH_2Cl_2). Yield = 0.05 g, 40%. ^1H NMR (400 MHz, CDCl_3) δ 8.48–8.75 (m, 1H), 8.06 (d, $J=8.38$ Hz, 1H), 7.99 (s, 1H), 7.90 (d, $J=5.13$ Hz, 1H), 7.39–7.49 (m, 1H), 7.29–7.36 (m, 2H), 7.12 (d, $J=8.13$ Hz, 1H), 6.82 (d, $J=8.50$ Hz, 1H), 6.45 (br. s., 1H), 5.84 (br. s., 1H), 4.23–4.41 (m, 2H), 3.40 (br. s., 3H), 2.21–2.36 (m, 2H), 2.03–2.14 (m, 2H), 1.87–1.99 (m, 2H), 1.81 (s, 6H), 1.52–1.62 (m, 2H), 1.39–1.46 (m, 2H), 1.31 (br. s., 6H), 1.15–1.21 (m, 4H), 1.04–1.11 (m, 14H), 0.85–0.93 (m, 4H), 0.81 (t, $J=7.13$ Hz, 9H), 0.44–0.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 184.3, 183.3, 175.6, 170.8, 164.6, 164.1, 163.2, 163.1, 148.3, 144.1, 141.4, 139.8, 137.9, 131.2, 130.9, 128.9, 125.7, 123.8, 122.5, 122.1, 110.4, 106.8, 99.1, 88.7, 61.2, 47.1, 46.9, 42.6, 31.8, 31.7, 30.1, 29.4, 29.3, 29.2, 29.0, 28.9, 27.8, 27.5, 26.9, 23.8, 22.6, 22.6, 14.1, 14.0. MALDI-TOF(m/z): $[\text{M}]^+$ calculated for $\text{C}_{54}\text{H}_{72}\text{N}_2\text{O}_4\text{S}$, 844.5213; found, 844.4163.

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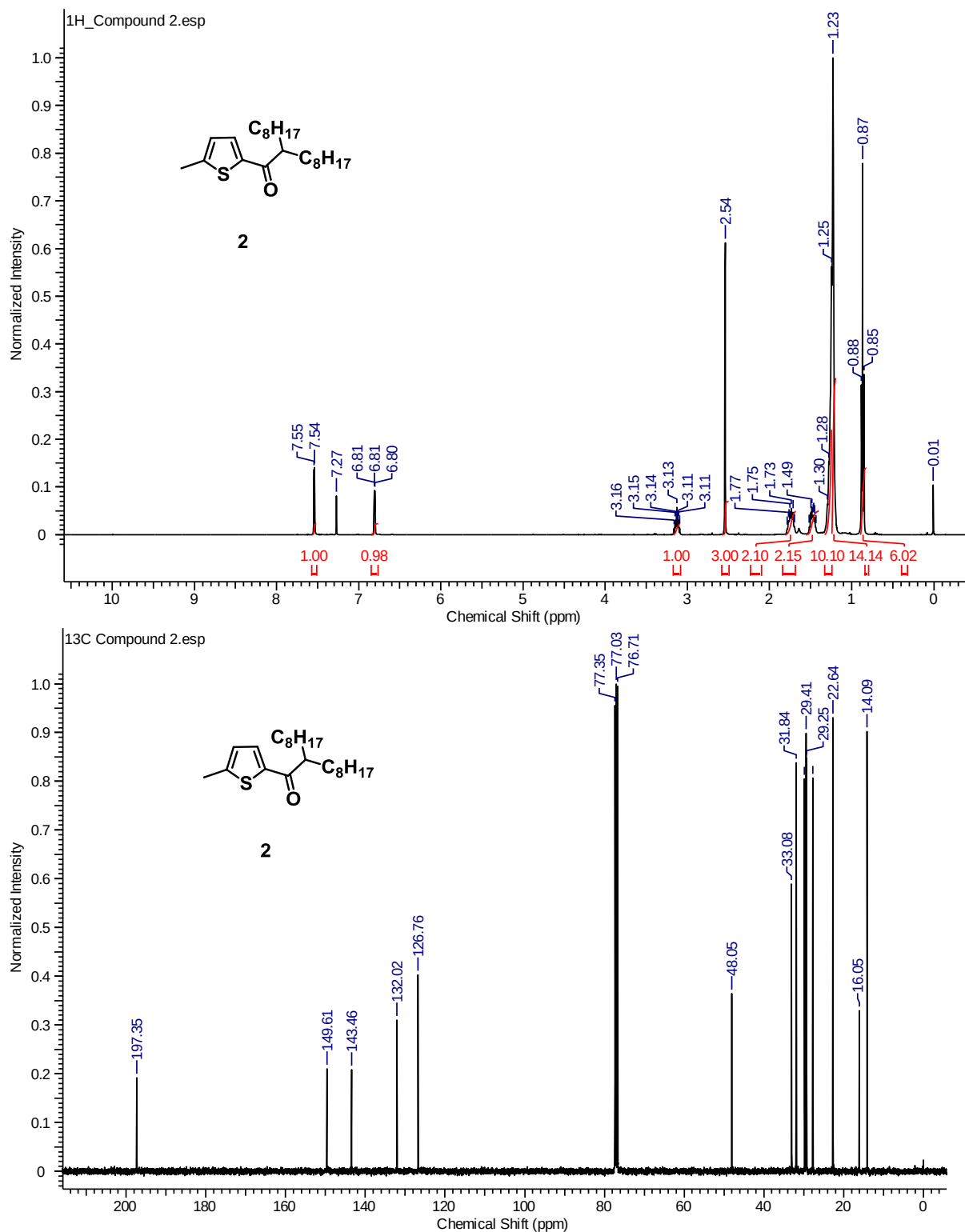
^1H -NMR, ^{13}C -NMR, and MALDI-TOF

Figure 12. ^1H -NMR (400 MHz) and ^{13}C -NMR (101 MHz) spectra of **Compound 2** in CDCl_3 .

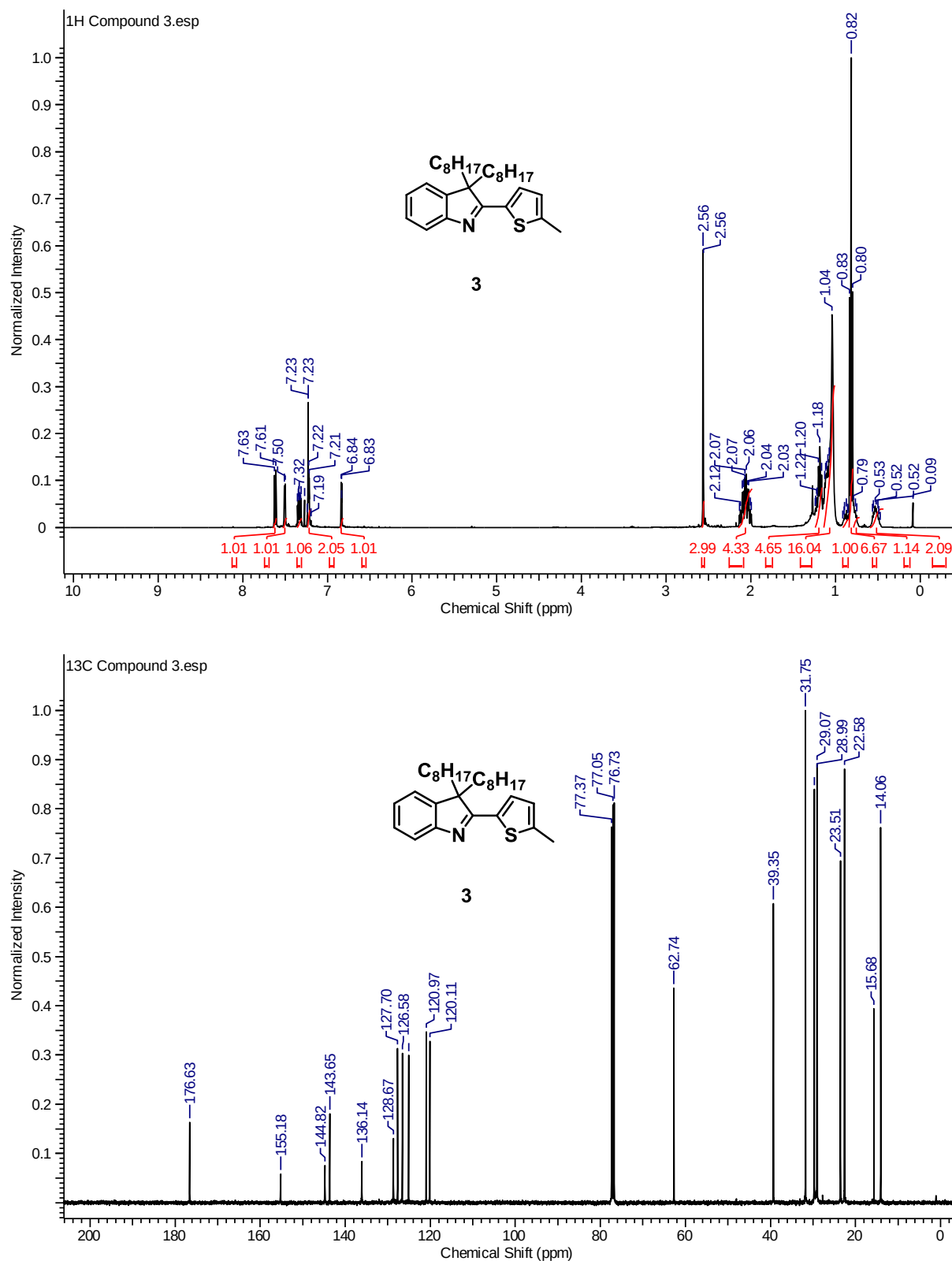


Figure 13. ¹H-NMR (400 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 3** in CDCl₃.

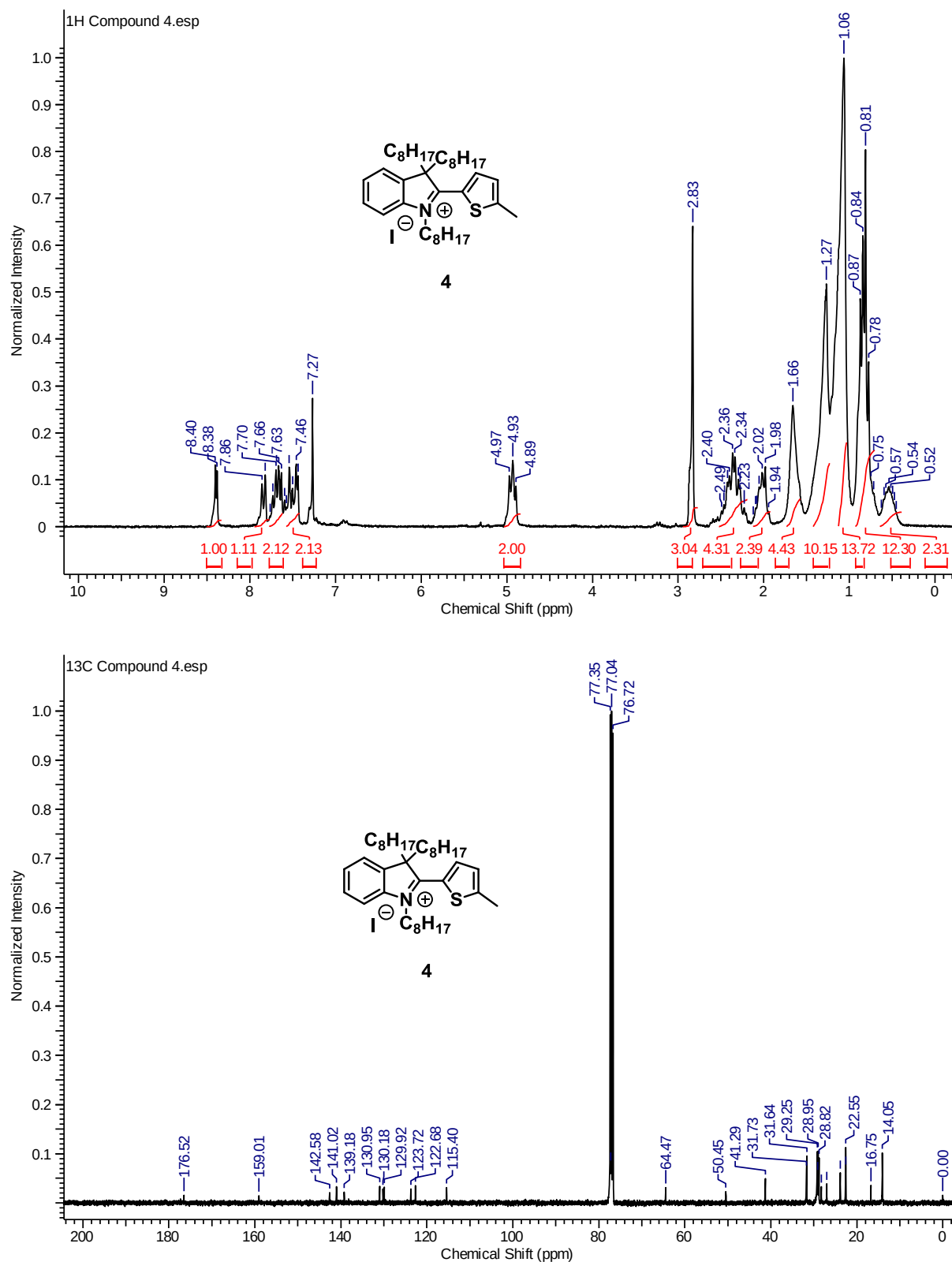


Figure 14. ¹H-NMR (200 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 4** in CDCl₃.

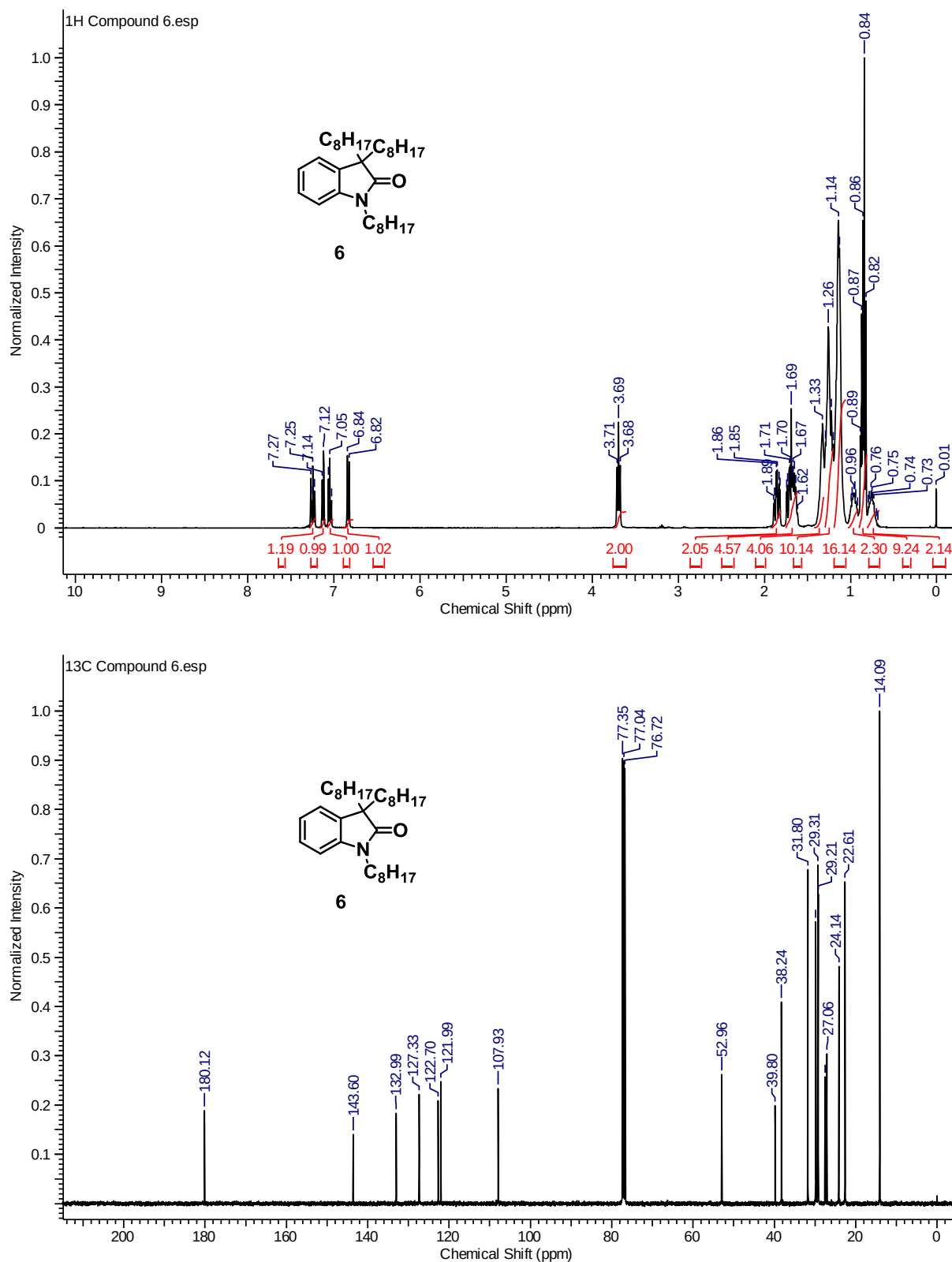


Figure 15. ¹H-NMR (400 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 6** in CDCl₃.

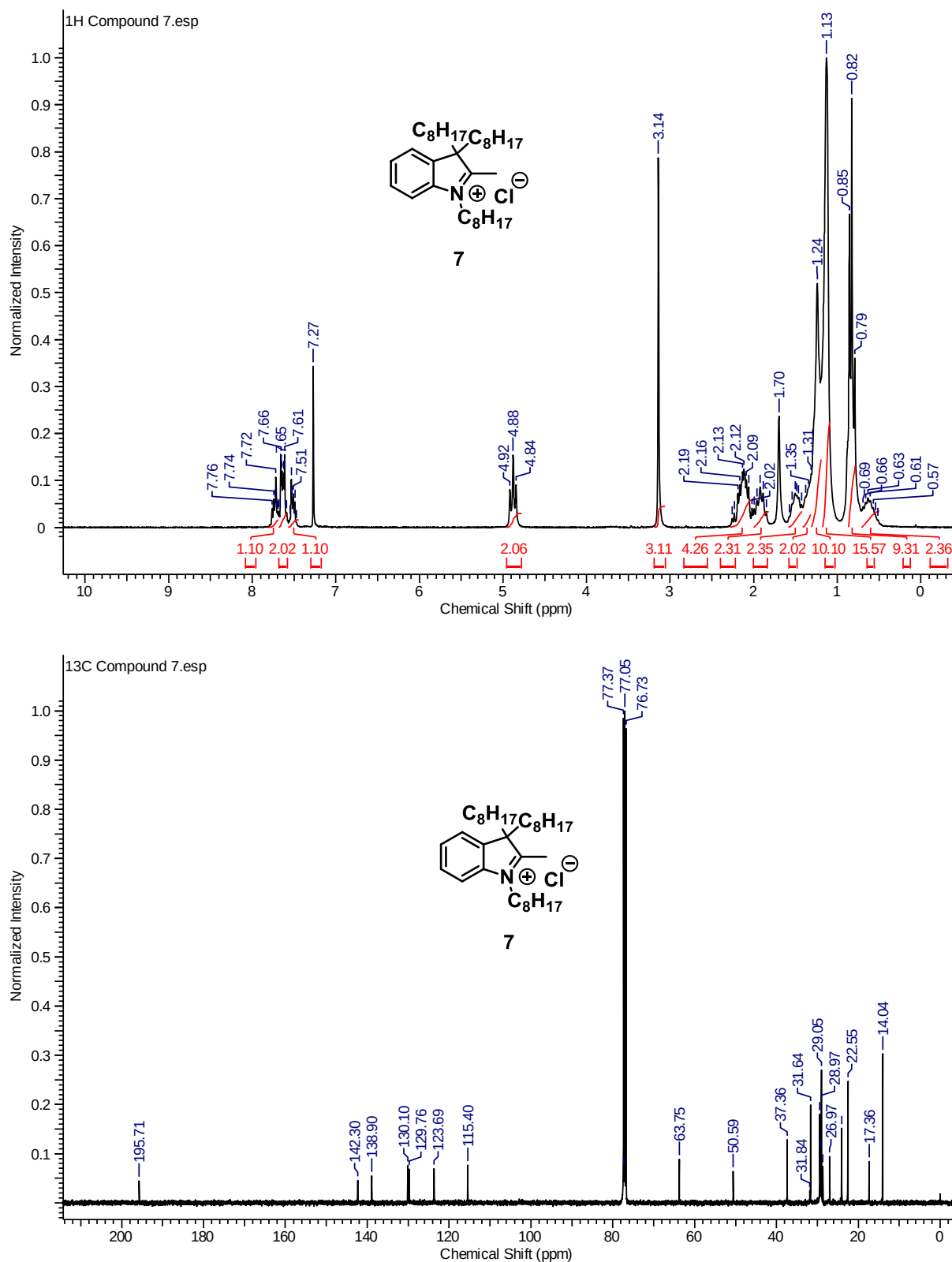


Figure 16. ¹H-NMR (200 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 7** in CDCl₃.

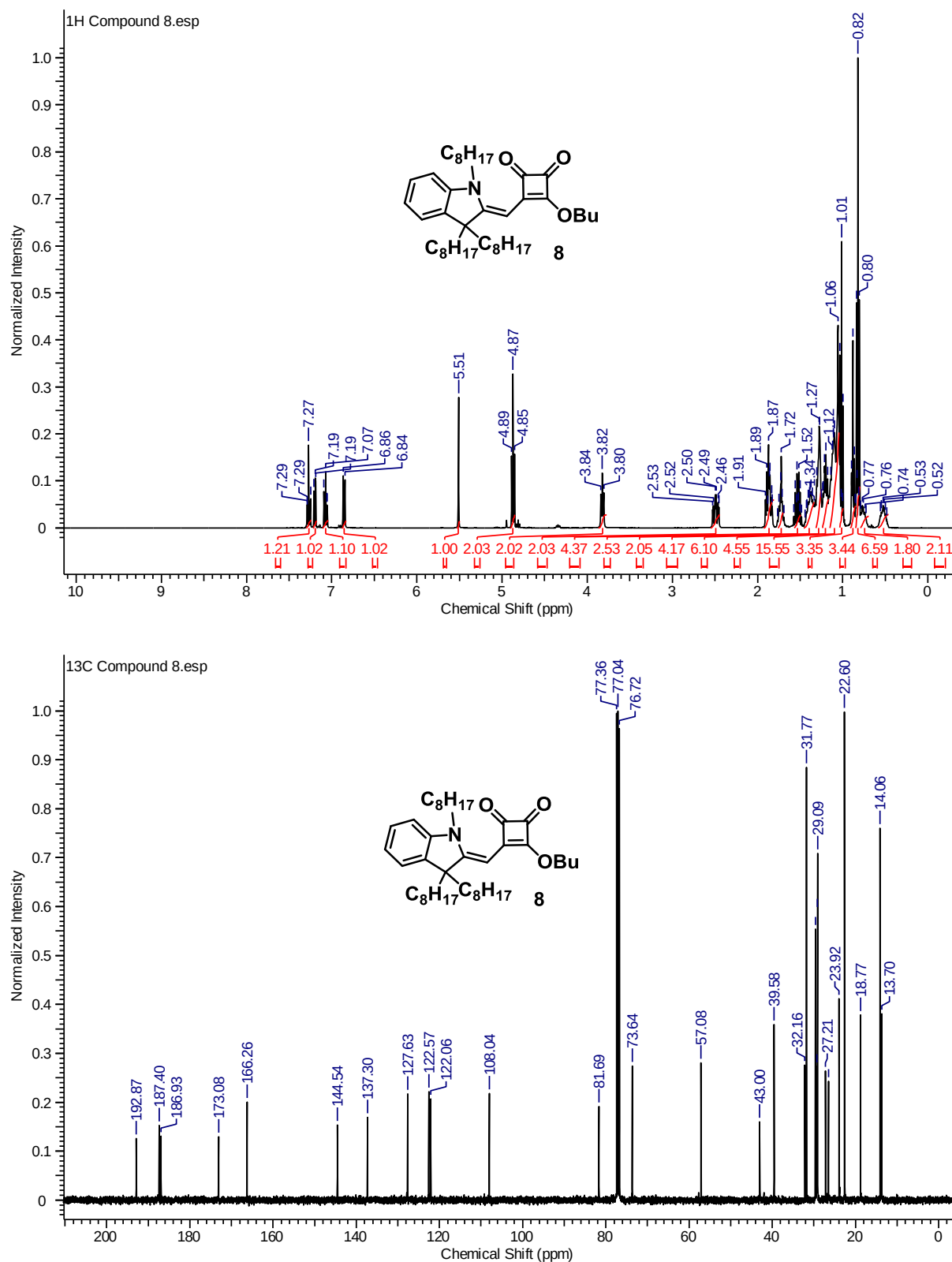


Figure 17. ¹H-NMR (400 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 8** in CDCl₃.

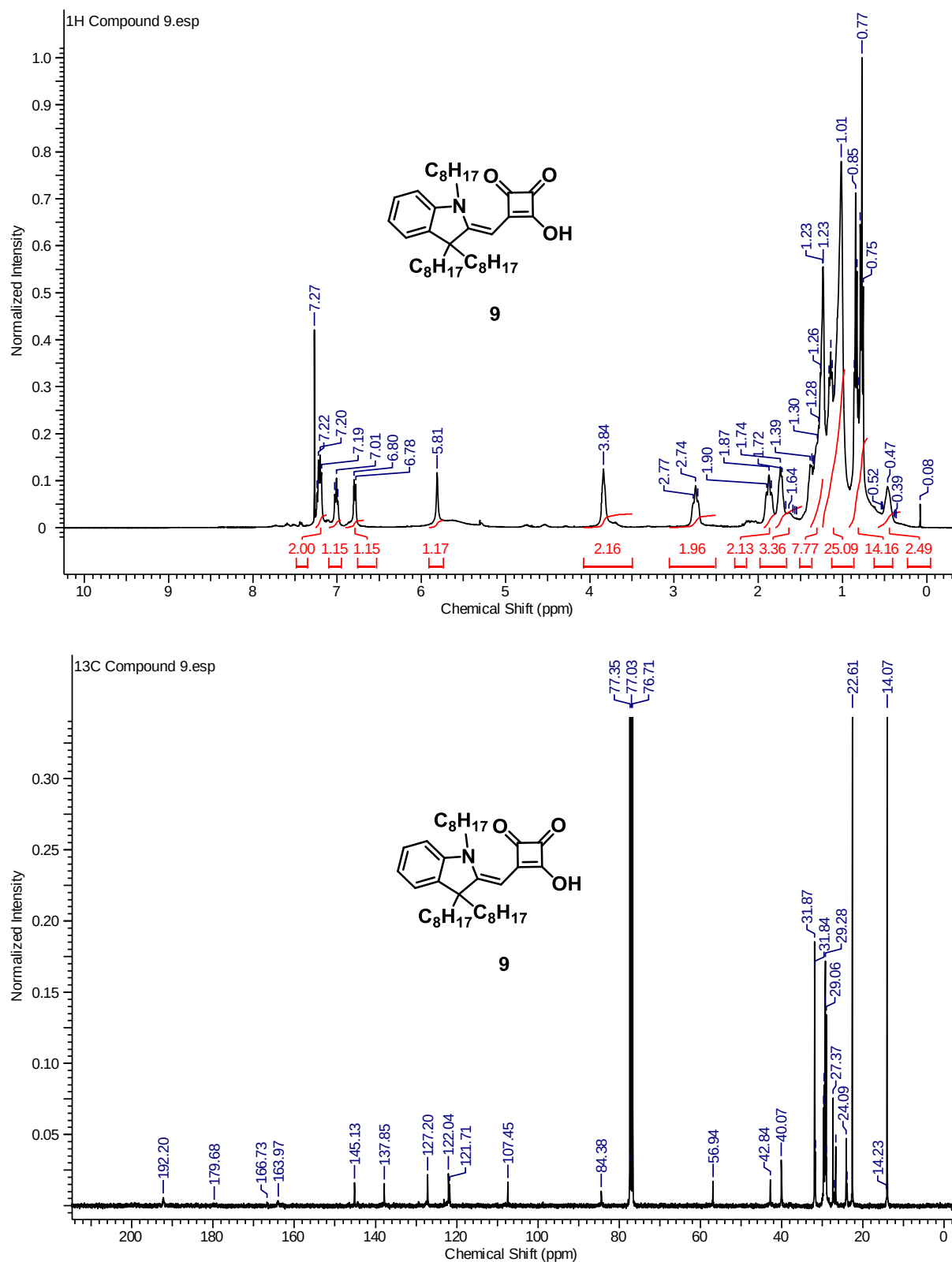


Figure 18. ¹H- NMR (400 MHz) and ¹³C- NMR (101 MHz) spectra of **Compound 9** in CDCl₃.

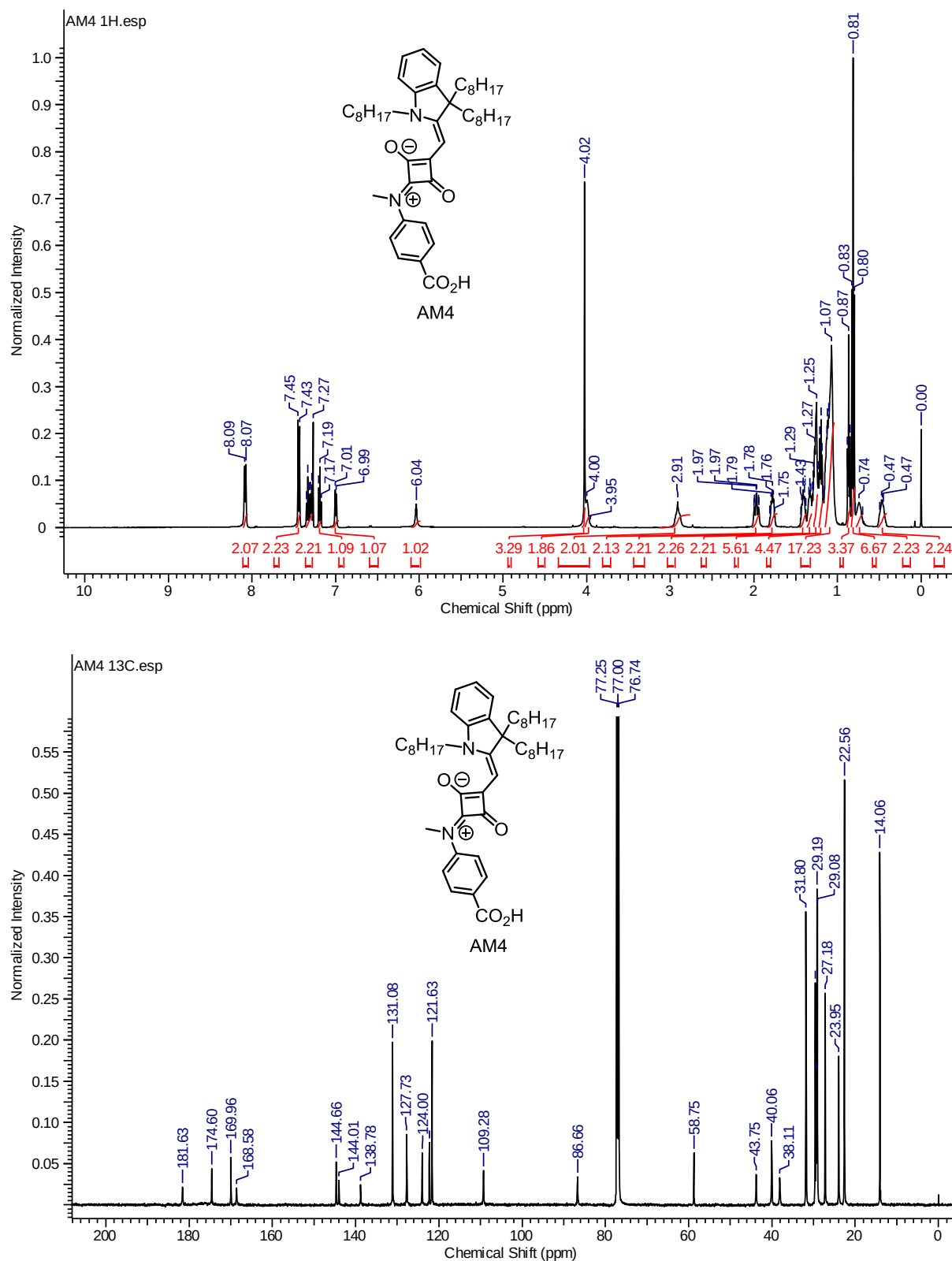


Figure 19. ¹H-NMR (400 MHz) and ¹³C-NMR (126 MHz) spectra of **AM4** dye in CDCl₃.

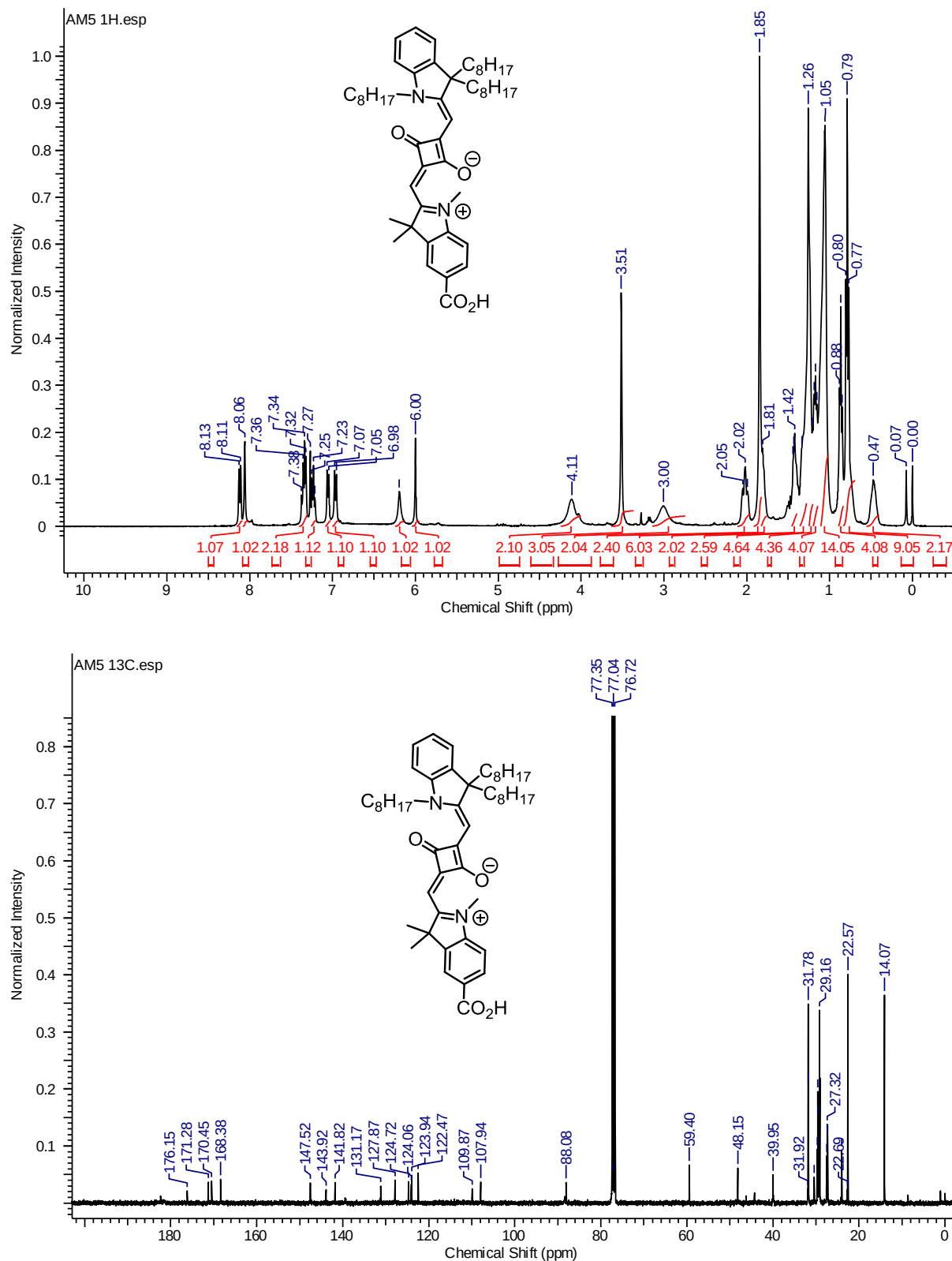


Figure 20. ¹H-NMR (400 MHz) and ¹³C- NMR (101 MHz) spectra of AM5 dye in CDCl₃.

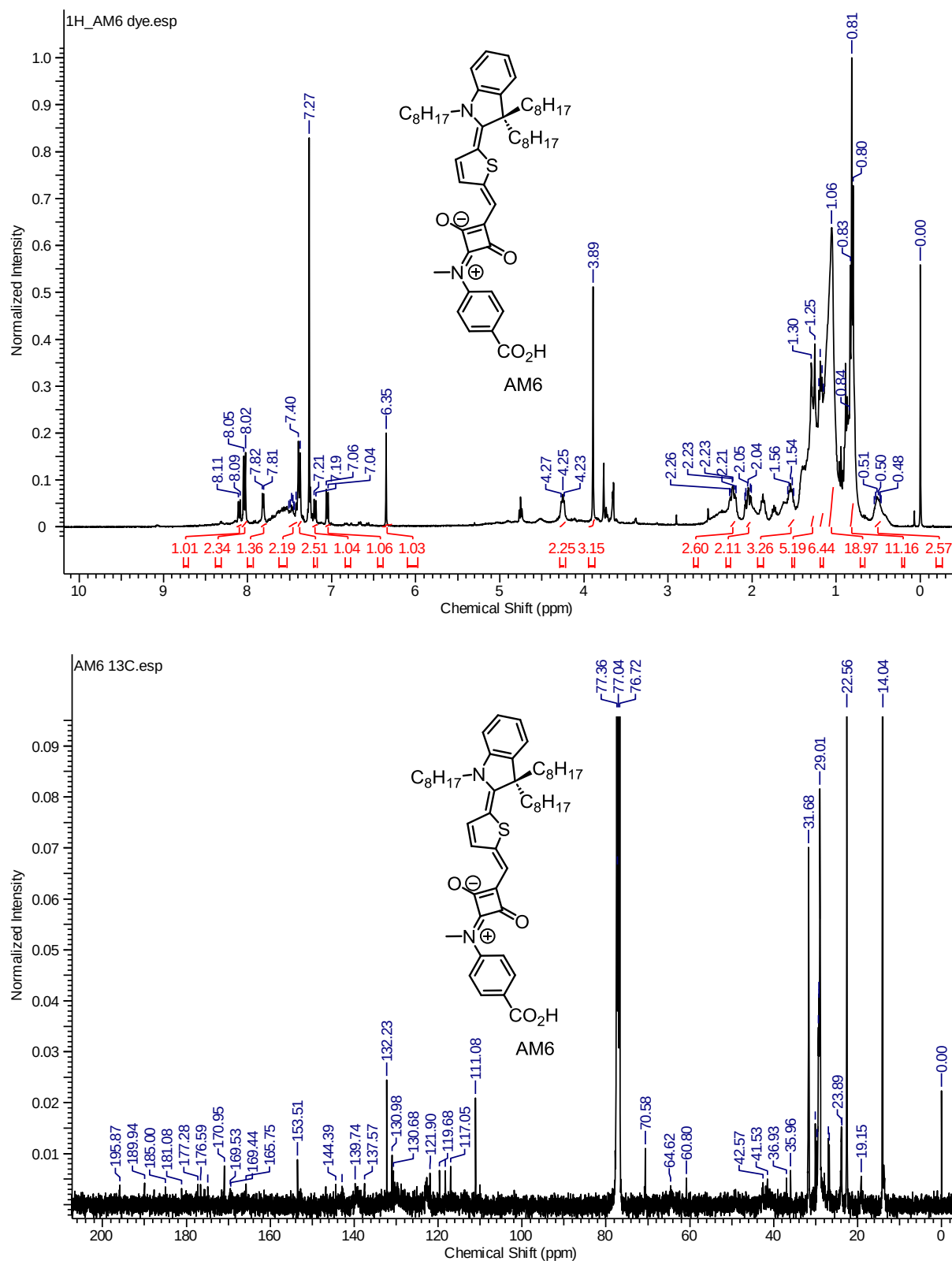


Figure 21. ¹H-NMR (400 MHz) and ¹³C-NMR (101 MHz) Spectra of AM6 dye in CDCl₃.

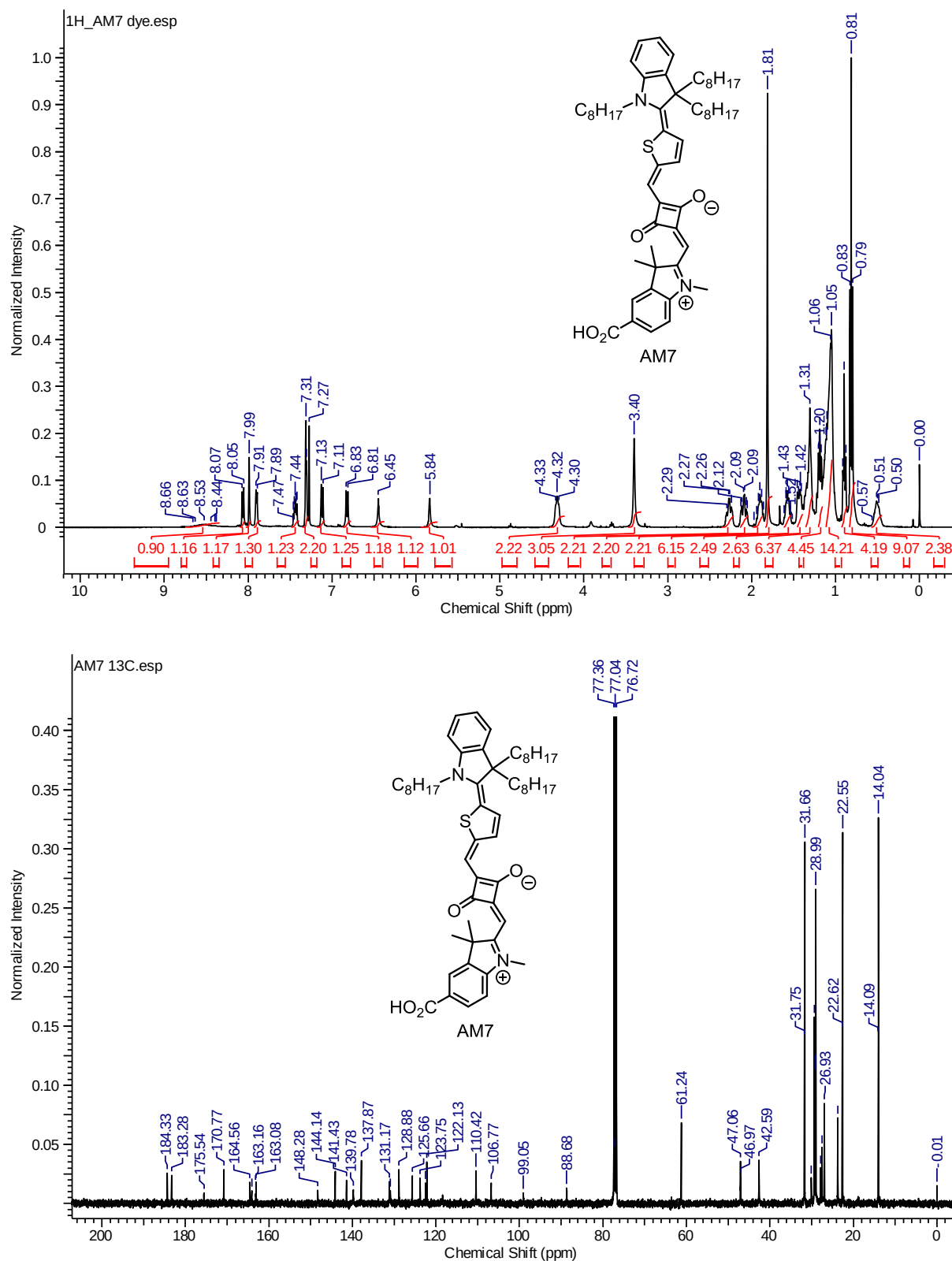


Figure 22. ¹H-NMR (400 MHz) and ¹³C- NMR (101 MHz) Spectra of AM7 dye in CDCl₃.

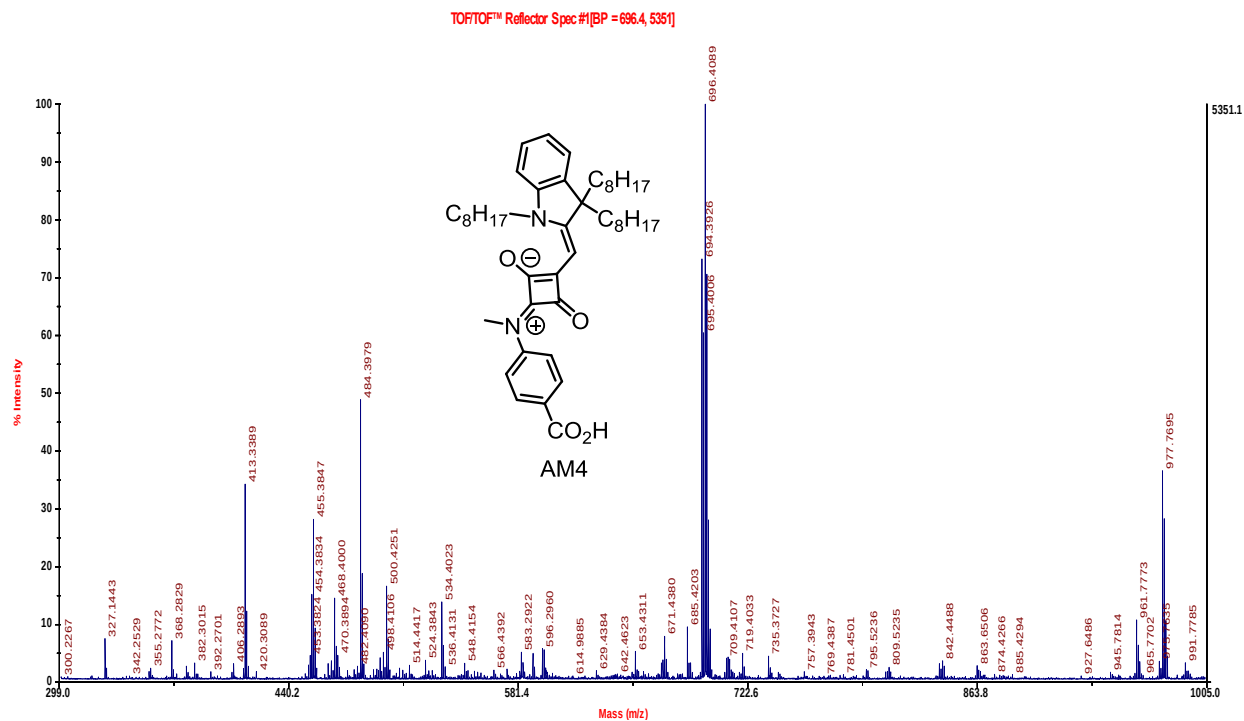


Figure 23. MALDI-TOF spectrum of AM4 dye ($C_{46}H_{64}N_2O_4$, m/z calcd 696.4866).

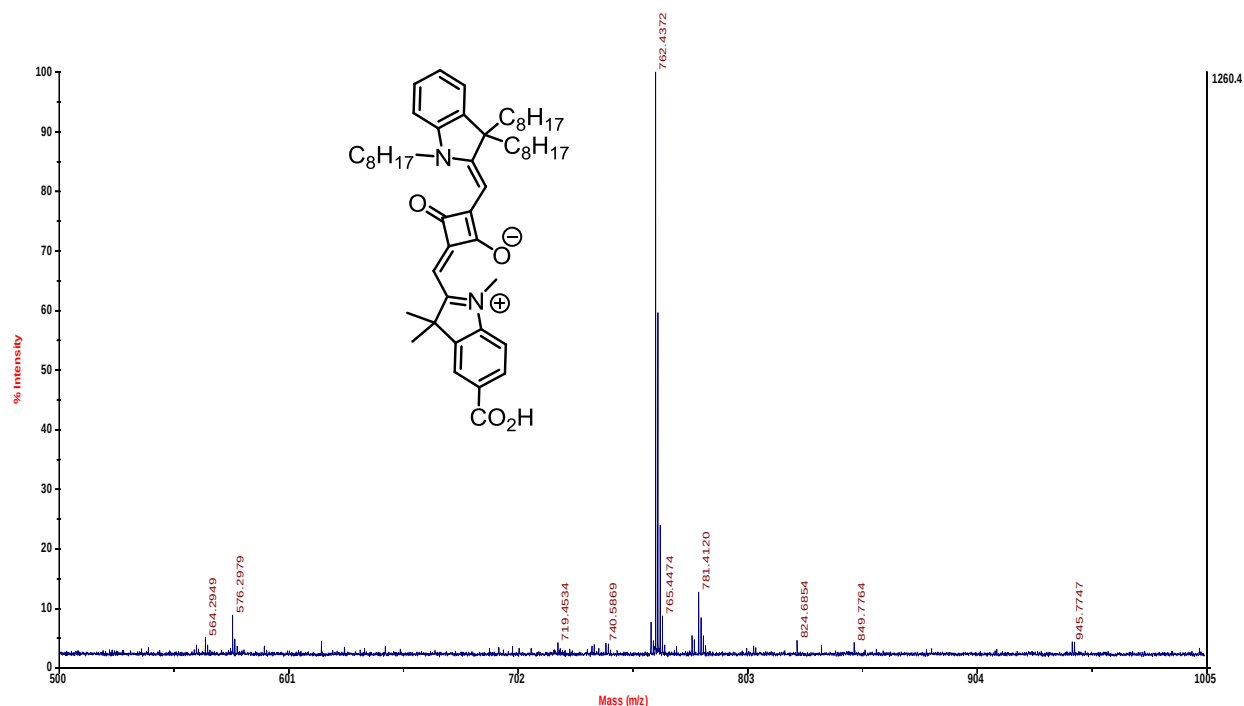


Figure 24. MALDI-TOF spectrum of AM5 dye ($C_{50}H_{70}N_2O_4$, m/z calcd 762.5336).

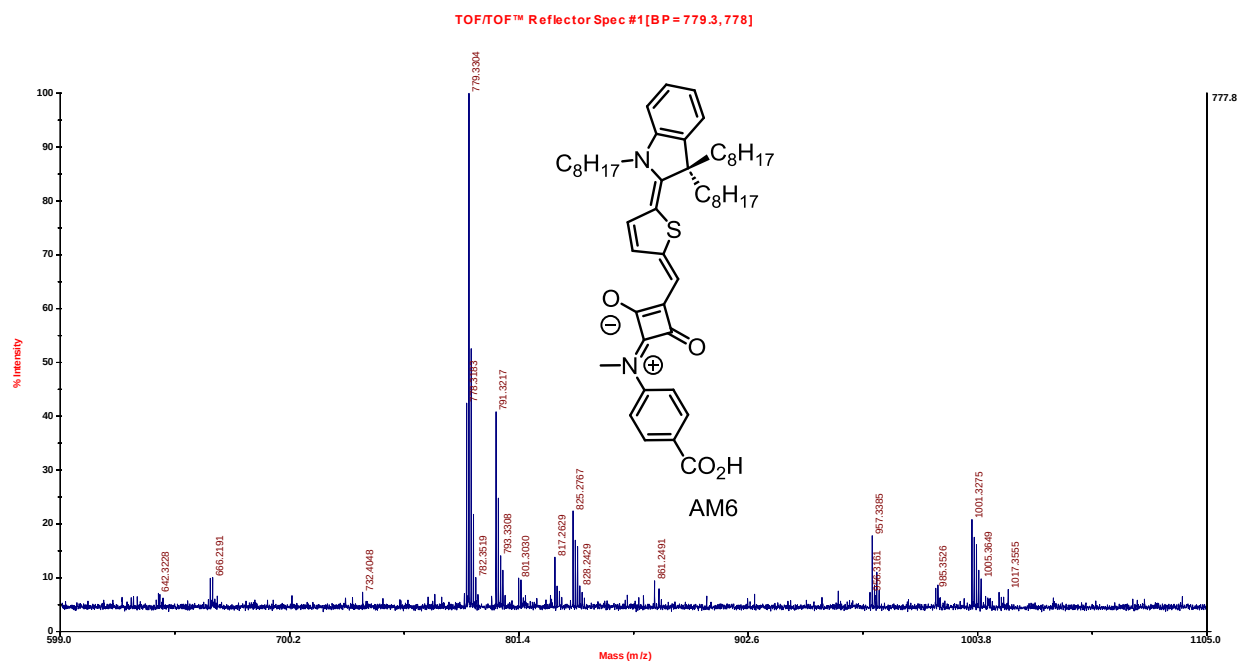


Figure 25. MALDI-TOF spectrum of AM6 dye ($C_{49}H_{66}N_2O_4S$, m/z calcd 778.4743).

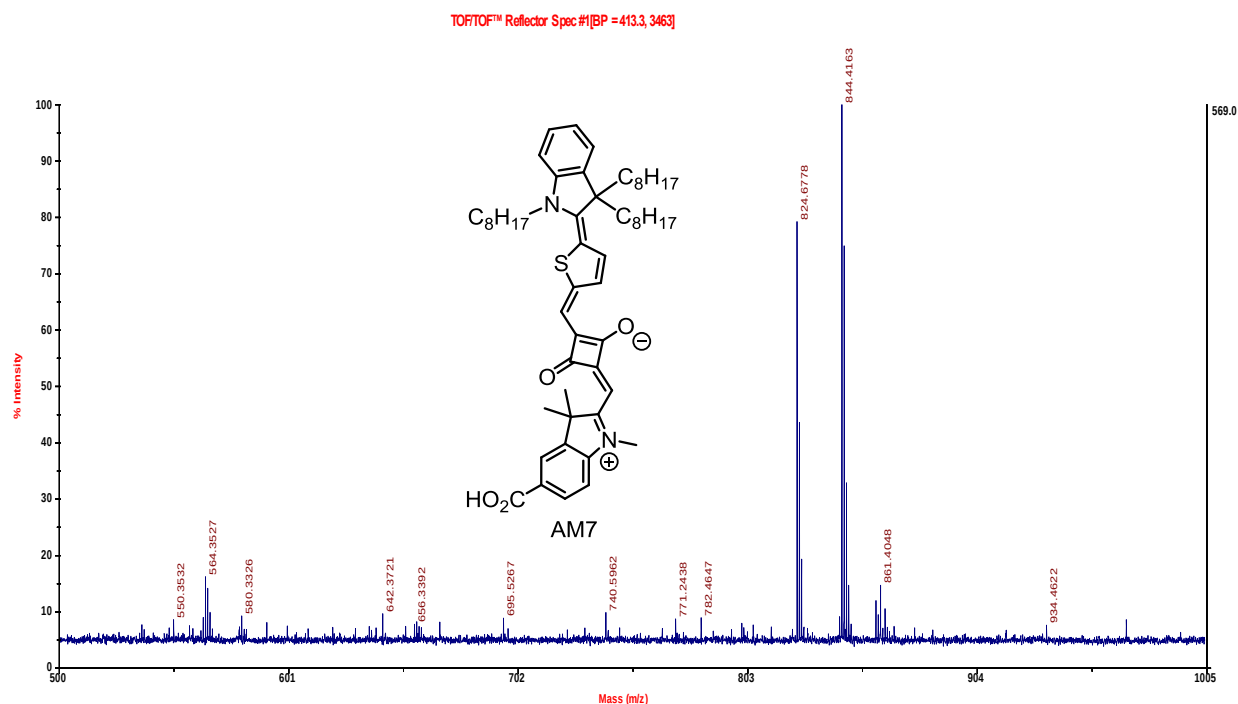
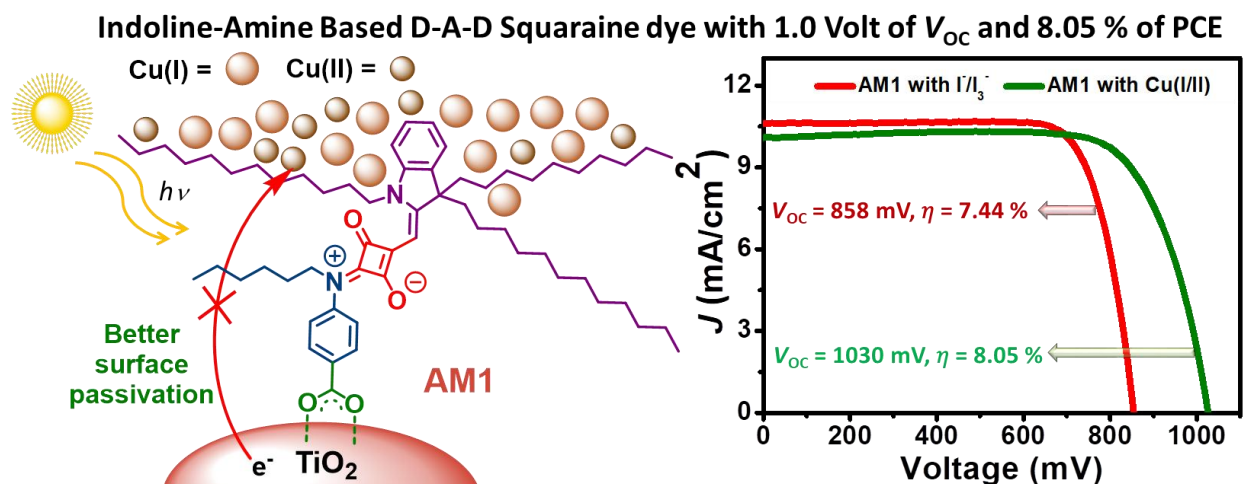


Figure 26. MALDI-TOF spectrum of AM7 dye ($C_{54}H_{72}N_2O_4S$, m/z calcd 844.5213).

Chapter 5

Summary

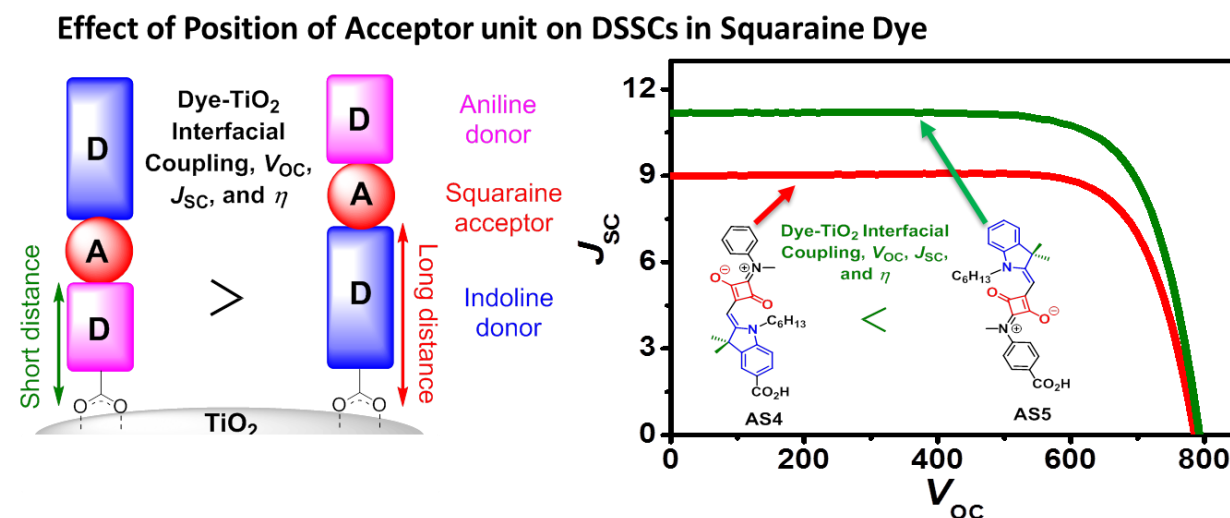
Chapter 2: Effect of Alkylation and Arylation at N-atom of Aniline Donor on Dye-Sensitized Solar Cell Performance



Unsymmetrical squaraine dyes are promising sensitizers for dye-sensitized solar cell (DSSC) applications due to its high molar extinction coefficient with tunable photophysical from visible to NIR regions. Achieving high V_{OC} and efficiency for the squaraine dyes is still challenging with the various electrolytes due to the zwitterionic nature of this class of chromophores. Hence in order to develop squaraine dye that is compatible with various electrolytes and with the inbuilt features for controlling the aggregation on TiO_2 surface, a series of aniline and indoline donors based unsymmetrical visible-light active squaraine dyes (**AM1**, **AM2**, and **AM3**) have been designed, synthesized and utilized in DSSC applications. In the present work one of the donor unit, indoline, is wrapped with the alkyl groups and other donor unit, aniline, is functionalized with the -hexyl, -ethylhexyl, and phenyl groups for controlling the aggregation of dyes on TiO_2 , avoiding the charge recombination, to modulate the dihedral angles between donors/ acceptor and dipole moments of the dyes. The E_{HOMO} energy level of **AM** dyes and model dye **AK4** were situated between 1.03-1.13 V, which opens an opportunity to use the different electrolytes for the better device V_{OC} , and efficiency. The photovoltaic studies were carried out by fabricating the DSSC device with I^-/I_3^- and $[Cu(tmby)_2]^{+/2+}$ electrolytes. DSSC device sensitized with the **AM1** and **AM2** dyes showed relatively high power conversion efficiency 7.44% (V_{OC} 858 mV, J_{SC} 10.84 mAcm⁻², ff 80.06%) and 7.22% (V_{OC} 865 mV, J_{SC} 10.35 mAcm⁻², ff 80.69%), respectively

with I^-/I_3^- in the absence of chenodeoxycholic acid (CDCA) compared to the **AM3** dye which exhibited the device efficiency of 5.41% (V_{OC} 808 mV, J_{SC} 8.57 mA cm^{-2} , ff 78.13%). Whereas, use of $[Cu(tmby)_2]^{+/2+}$ electrolyte along with the PEDOT as cathode showed enhanced V_{OC} of 1030, 1025, 1001, and 1009 mV with enhanced DSSC efficiency of 8.05%, 7.96%, 5.84% and 7.98%, respectively for the **AM1**, **AM2**, **AM3**, and **AK4** dyes in the absence of CDCA. Here, **AM1** dye exhibited maximum power conversion efficiency of 8.05% and V_{OC} of 1030 mV which was the highest obtained efficiency and V_{OC} , for visible-light active D-A-D based unsymmetrical squaraine dyes with copper-based electrolyte.

Chapter 3: Squaraine Dyes for Dye-Sensitized Solar Cells: Effect of Position of Acceptor Unit in Visible Light Active Squaraine Dyes

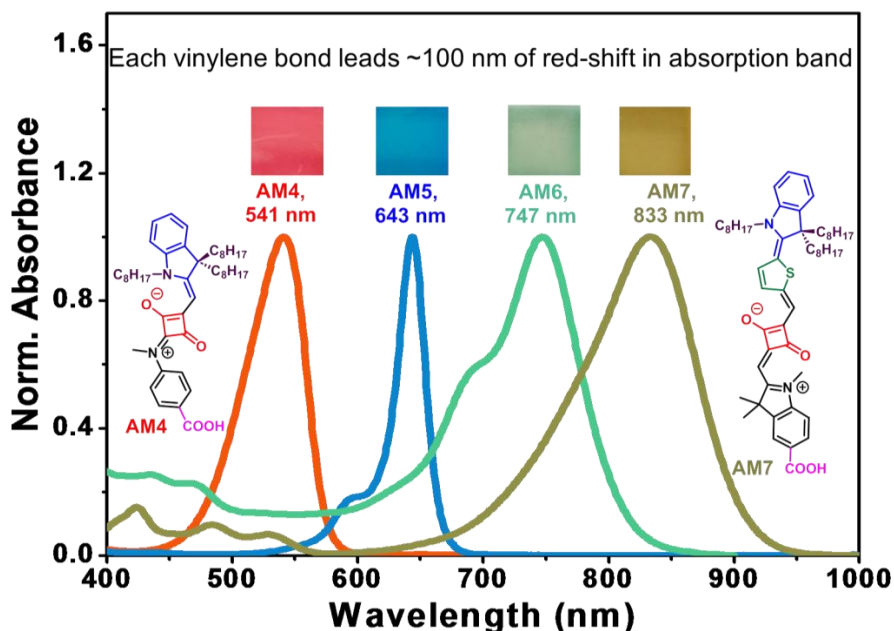


Indoline-aniline donor-based D-A-D squaraine sensitizers (**AS1-AS5**) have been synthesized for dye-sensitized solar cells (DSSCs), where the position of acceptor unit has been changed with respect to anchoring group (carboxylic acid). Here, **AS2** and **AS5** dyes represent short, whereas **AS1**, **AS3** and **AS4** dyes represent long acceptor-anchoring group distance, respectively. **AS** dyes showed an absorption band between 501-535 nm with the extinction coefficients of $1.46 - 1.61 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Change in the position of acceptor unit showed red shift in the absorbance properties for the **AS2** and **AS5** compared to the **AS1**, **AS3** and **AS4** dyes. The DSSC device was fabricated with the iodolyte (I^-/I_3^-) electrolyte because electronic levels of the **AS** dyes have been

found favorable for the electron injection and dye-regeneration processes. The DSSC device fabricated with the dyes contains short acceptor-anchoring group distance (**AS2** and **AS5**) showed high photovoltaic performances compared to the long distance (**AS1**, **AS3** and **AS4**). The DSSC device efficiency of 5.49, 6.34, 6.16 and 5.57% have been achieved for **AS1**, **AS2**, **AS3** and **AS4** dyes, respectively in the absence of chenodeoxycholic acid (CDCA) which again showed little changes in efficiency with CDCA. Significant changes have been found in the DSSC parameters (V_{OC} , J_{SC} , ff and efficiency) for **AS5** dye while sensitized with the CDCA and showed highest 8.01% of DSSC efficiency in the **AS** dye series. This study revealed the potential of shorter acceptor-anchoring group distance over the longer on the overall DSSC device performance for squaraine dyes.

Chapter 4: Synthesis of Visible, Far-red and NIR Active Squaraine Dyes for Dye-Sensitized Solar Cells: π -Extension Conjugation within the Polymethine Framework

Effect of π -extension within polymethine framework of squaraine dye



Unsymmetrical squaraine dye series with low to highly extended structures (**AM4-AM7**) and wrapped with symmetrical alkyl-groups have been designed, synthesized, and characterized for

the dye-sensitized solar cells (DSSCs). Here, to extend the conjugation within the polymethine framework vinylene and thiophene group have been incorporated. UV-vis studies revealed each conjugated vinylene double bond gave ~ 100 nm red shifts in the absorbance bands and showed an absorption maximum of 541, 643, 747, and 833 nm for **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. Extension in conjugation within polymethine framework showed a positive response on the light harvesting efficiency (LHE), where highly extended **AM7** dye showed LHE of 386 nm broad at 60% of spectrum height. Electrochemical studies of **AM** dyes revealed their well align electronic levels for electron injection and dye-regeneration processes. However, extension in conjugation within the polymethine framework showed dramatic effect on V_{OC} , J_{SC} , and device efficiency for the dyes when move from low- to highly conjugated structures. The highest DSSC efficiency of 7.35, 5.18, 0.08, and 0.05% have been achieved with I^-/I_3^- electrolyte (Z-50) for the **AM4**, **AM5**, **AM6**, and **AM7** dyes, respectively. Further, **AM4** dye has been co-sensitized with **AM5**, **AM6**, and **AM7** dyes, where **AM4:AM5** (1:1) composition achieved maximum efficiency of 8.0% with I^-/I_3^- electrolyte (Z-50) compared to other compositions.

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Title of the thesis: “Structurally Engineered Unsymmetrical Squaraine Dyes for Dye-Sensitized Solar Cells: Importance of Side Chain, Position of Acceptor Unit and Extension of Conjugation within the Polymethine Framework.”

Sensitizers engineering with respect to dihedral-angles, position of acceptor unit, and extension in conjugation are important aspects to achieve high DSSC device efficiency by enhancing the device J_{SC} , V_{OC} . Such types of designed principle have been applied and tested for different types of sensitizers and showed their potential contribution in achieving high DSSC efficiency. In this respect, three series of dyes have been designed, synthesized, and tested for DSSC application. Chapter 2 deals with the synthesis of N-functionalized visible light active squaraine dyes, **AM1-AM3** with alkyl and phenyl group functionalization on the N-atom of aniline donor. Where, aniline functionalization with aryl showed a negative effect on DSSC performance than alkyl groups, and **AM1** dye showed maximum of 8.05% DSSC device efficiency with $[Cu(tmby)_2]^{+/2+}$ electrolyte. Chapter 3 deals with the synthesis of visible light active squaraine dyes **AS1-AS5** with systematic change in the position of acceptor unit. Photophysical and electrochemical properties varied with changed in the acceptor position within the framework. **AS** dyes with the small acceptor-anchoring group distance showed better photovoltaic performance over the dyes with the long acceptor-anchoring group distance. Maximum DSSC device efficiency of 8.01% and 7.08% have been achieved for **AS5** dye in the presence of CDCA with I^-/I_3^- and Cu(I/II) electrolyte. Chapter 4 deals with the synthesis of visible, far-red and NIR light active dyes with π -extended conjugation within the polymethine framework, **AM4-AM7**. Extending the π -conjugation in squaraine dyes leads in shifting the charge transfer transition bathochromically by 15-20 nm per $-C=C-$ bond, however, in the present investigation it has been found that, introducing the π -conjugation within the polymethine framework of squaraine dyes, showed ~ 100 nm shift by per vinylene unit. **AM6** and **AM7** dyes showed broad absorbance and light harvesting efficiency (LHE). **AM4** dye showed 7.35% of DSSC device efficiency with iodide electrolyte. Dyes with high number of conjugations showed poor DSSC device efficiency, even decreases the device efficiency when they co-sensitized with other optically different dyes.

List of Publications and Patent Emanating from the Thesis Work

- 1) Visible-Light-Active Unsymmetrical Squaraine Dyes with 1 V of Open-Circuit Voltage for Dye-Sensitized Solar Cells. *ChemPhotoChem*, **2023**, 7, e202200328 (1-10). **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kuamr Vanka, Kothandam Krishnamoorthy, Jayaraj Nithyanandhan.
- 2) Unsymmetrical Squaraine Dyes and Applications Thereof. **2022** (US 2022/0227999 A1). Jayaraj Nithyanandhan, Ambarish Kumar Singh, **Amrita Singh**.

List of Publications not Emanating from the Thesis Work

- 1) Effect of Position of Acceptor Unit on Dye-Sensitized Solar Cell Performance: Indoline-Aniline Donors Based Visible-Light Responsive Squaraine Dyes. **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kuamr Vanka, Kothandam Krishnamoorthy, Jayaraj Nithyanandhan. (**Manuscript under review**).
- 2) Visible, Far-red and NIR Active Unsymmetrical Squaraine Dyes based on Extended Conjugation within the Polymethine Framework for Dye-sensitized Solar Cells. **Amrita Singh**, Ambarish Kumar Singh, Ruchi Dixit, Kuamr Vanka, Kothandam Krishnamoorthy, Jayaraj Nithyanandhan. (**Manuscript under review**).

List of Publications not Emanating Apart from the Thesis Work

- 1) Synthesis and Photochemical Study of Visible and NIR-Light active Phototriggers. **Amrita Singh**, Jayaraj Nithyanandhan. (**Manuscript under preparation**)

Details of the abstract presented (oral/poster) at national/international conferences/seminars

- 1) Poster Presentation at “NCL-Research Foundation & CSIR-NCL Annual Students Conference” 2022 held on 29th and 30th November 2022, CSIR-National Chemical Laboratory, Pune, India. **(Best Poster Presentation Award).**
- 2) Poster Presentation at “International Conference on Chemistry and Applications of Soft Materials (CASM 2022)” held on 25-27 July 2022, CSIR-NIIST, Thiruvananthapuram, India.
- 3) Oral Presentation at “NCL-Research Foundation & CSIR-NCL Annual Students Conference” 2022 held on 29th and 30th November 2021, CSIR-National Chemical Laboratory, Pune, India
- 4) Participation at International Conference on “Recent Advances and Innovation in Solar energy (Raise 2021)” held on 2-4 December 2021, IIT Madras, India.
- 5) Participation at International Workshop on “Supporting Chemistry Research with Modern DFT (Density Functional Theory): Software, Techniques and Application” 2021, held on 5-16 February 2021, Sankalchand Patel university India.
- 6) Poster Presentation at “National Science Day” 2020 held on 26th and 27th February 2020, CSIR-National Chemical Laboratory, Pune, India.
- 7) Participation at “NCL-Research Foundation & CSIR-NCL Annual Students Conference” 2019 held on 29th and 30th November 2019, CSIR-National Chemical Laboratory, Pune, India.
- 8) Participation at “NCL-Research Foundation & CSIR-NCL Annual Students Conference” 2018 held on 29th and 30th November 2018, CSIR-National Chemical Laboratory, Pune, India.

Visible-Light-Active Unsymmetrical Squaraine Dyes with 1 V of Open-Circuit Voltage for Dye-Sensitized Solar Cells

Amrita Singh,^[a, c] Ambarish Kumar Singh,^[a, c] Ruchi Dixit,^[a, c] Kumar Vanka,^[a, c]
Kothandam Krishnamoorthy,^{*[b, c]} and Jayaraj Nithyanandhan^{*[a, c]}

A series of alkyl-group-functionalized, aniline- and indoline-donor-based, unsymmetrical visible-light-active squaraine dyes, **AM1-3**, were designed and synthesized. Dye-sensitized solar cell (DSSC) devices were fabricated with both I^-/I_3^- and $[Cu(tmby)_2]^{+/2+}$ electrolytes. DSSC devices sensitized with the **AM1** and **AM2** dyes showed relatively high-power conversion efficiency of 7.44% and 7.22%, respectively with I^-/I_3^- in the absence of chenodeoxycholic acid (CDCA) than those of the **AM3** dye (5.41%). The $[Cu(tmby)_2]^{+/2+}$ electrolyte along with

poly(3,4-ethylenedioxythiophene) (PEDOT) as cathode material showed excellent open-circuit potentials (V_{OC}) of 1030, 1025, and 1001 mV with the DSSC efficiency of 8.05%, 7.96%, and 5.84%, respectively, for the **AM1**, **AM2**, and **AM3** dyes in the absence of CDCA. Here, the **AM1** dye exhibited the maximum DSSC efficiency of 8.05% and V_{OC} of 1030 mV, which is the highest obtained efficiency and V_{OC} for the visible-light active zwitterionic unsymmetrical-squaraine dye with copper-based electrolyte.

Introduction

The potential of sensitizers to harvest light and convert it into the electricity with high device performance in dye-sensitized solar cells (DSSCs) makes this third generation solar technology more attractive.^[1,2] Tunable spectral properties of light harvesting materials, low-cost device fabrication and working in the diffused light conditions are the salient features of the DSSCs compared to the first two generation solar cells.^[3,4] In DSSCs, both organic and inorganic sensitizers have the potential to generate high device efficiency by harvesting the photons in visible and near-IR regions.^[3,5] Several highly efficient ruthenium polypyridine^[6,7] and Zinc-porphyrin^[8–14] complexes based dyes came up with the judicious structural design in which both steric and electronic factors were integrated to achieve high DSSC efficiency. Compared to the transition metal complex-based dyes, metal-free organic dyes are very promising, because of tunable photophysical, electrochemical and photo-

voltaic properties by modulating the structural components of the sensitizers such as donor, acceptor and π -spacer units.^[15–20] There are several metal-free organic dyes that achieved >10% efficiency with I^-/I_3^- ^[15–17] and $Co(II/III)$ ^[3,18,19] electrolytes by structural modulations. Fast electron injection and low energy loss in triazatruxene (TAT) based metal-free organic dye showed highest efficiency of 13.6% with $Co(II/III)$ electrolyte.^[21] Dyes wrapped with the auxiliary donor^[22] and acceptor^[23] moieties have been utilized for DSSC which gave good device efficiency by broadening the spectral responses associated with the visible and NIR regions^[24,25] due to the intramolecular charge transfer between the donor and acceptor moieties. Further, structural modulations in the donor and acceptor opens the opportunity for tuning the HOMO and LUMO electronic levels, which facilitate to use the other electrolytes to maximize the photovoltaic parameters such as V_{OC} and J_{SC} ^[15,26] beside side chain engineering.^[27–30] The HOMO energy level of the dyes based on the D–A, D– π –A, and D–A– π –A with more positive potential vs NHE have been used with the $Cu(I/II)$ electrolytes which exhibited excellent V_{OC} and DSSC device efficiencies.^[31–38] Further, it has been observed that most of the sensitizers used for the DSSC device fabrication which showed more than 1 V of V_{OC} with the $Cu(I/II)$ electrolytes were based on the alkyl group functionalized bulky arylamine based Hagfeldt-donor with judicious structural modulations in the acceptors, π -spacers, and change in the ligand properties in electrolyte itself.^[31,39] Benztricarbazole (BTC) electron donor based dyes showed more than 1 V of V_{OC} with the $Cu(I/II)$ electrolyte^[40] (Figure 1). Further, DSSC device performance more than 30% under low light condition open avenues for utilizing this technology in building integrated photovoltaic (BIPV) and internet of things (IoT) applications.^[41] Besides the other sensitizers, D–A–D based squaraine dyes are very attractive because these chromophores possess high extinction

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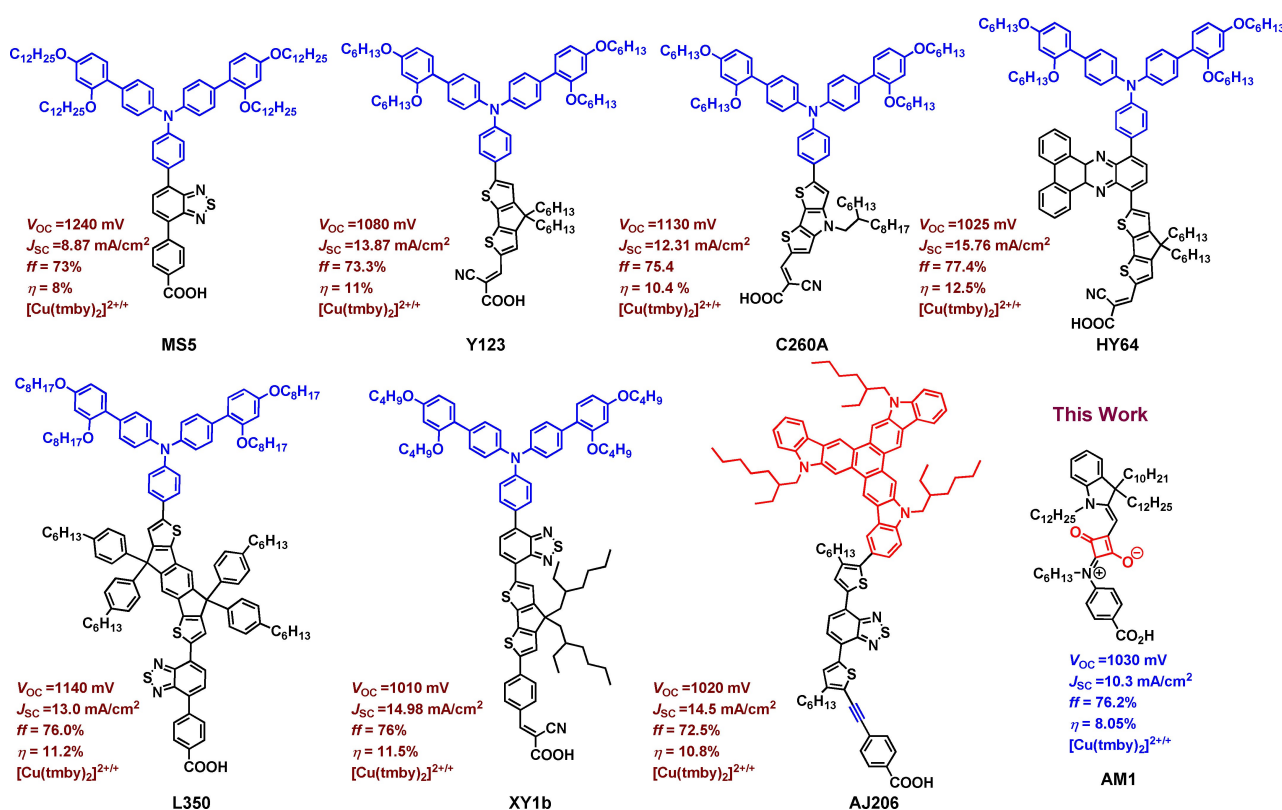
D-A, D- π -A, D-A- π -A and D-A-D based sensitizers which exhibit more than 1 V of DSSC device V_{OC} with $[Cu(tmby)_2]^{2+/+}$ electrolyte

Figure 1. Structures of the metal-free organic dyes with more than 1 V of open-circuit potential (V_{OC}) with Cu (I/II) electrolyte.

coefficient in the order of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and forms aggregated structures on the semiconducting metal oxide surface.^[42–46]

Aggregation of dyes on the surface enhance the light harvesting properties by broadening the absorption spectrum of the sensitizer and such self-assembled structure formed in solution and in bulk have been explored in wide range of applications.^[47–50] Further, the photo-physical and electrochemical properties of the D–A–D based unsymmetrical squaraine dyes can be modulated by extending the conjugation between the donor and acceptor moieties. All the above characteristics of squaraine dyes make it as a potential sensitizer for the DSSC device fabrication with both I^-/I_3^- electrolyte and $Co(II/III)$ ^[26,51] electrolytes. Recently, by modulating the conjugation, structural optimization for indoline and aniline donors based visible active squaraine dye was reported for DSSC device with I^-/I_3^- electrolyte. Structural features such as alkyl group wrapping around indoline donor and the N-methyl group at the aniline N-atom are important for achieving good DSSC device performance.^[43] In this work we have designed and synthesized alkyl groups wrapped indoline and aniline donors based unsymmetrical squaraine dyes where the N-atom of aniline donor functionalized with a linear *n*-hexyl (AM1), branched N-ethyl-hexyl (AM2) and an aromatic phenyl (AM3) groups (Figure 2) to understand the (i) correlation between the dihedral angle around the aniline donor and squaric acid unit for the observed device performance, (ii) extent of surface

passivation/shielding for reducing the charge recombination process besides having the alkyl groups at the sp^3 -C and N-atoms of indoline unit. As this set of dyes possess deep positive HOMO level and hence compatibility with $[Cu(tmby)_2]^{+/2+}$ electrolyte was tested to enhance the open-circuit potential besides establishing the structure property relationship with iodolyte electrolytes.^[45,52]

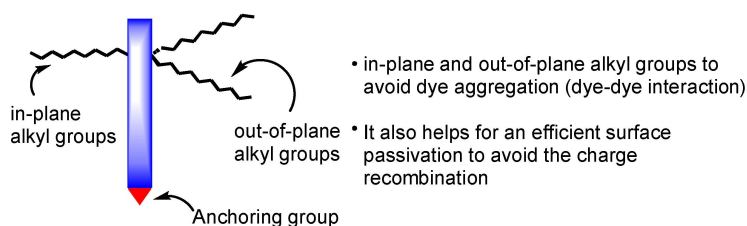
Results and Discussion

Synthesis of aniline and indoline-based donor-acceptor-donor (AM) dyes

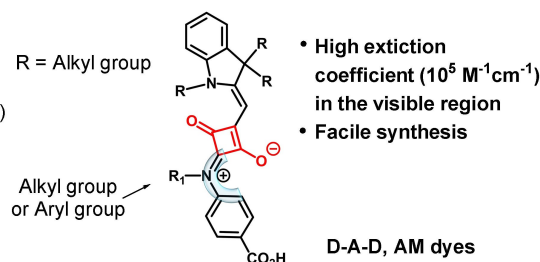
Synthesis of unsymmetrical squaraine dyes requires a semi-squaric acid and a Fischer's base (indolium). Fischer's base derived squaraine dye exhibit absorption at 640 nm, however reducing the conjugation by a vinylene unit by means of utilizing a Fischer's base and aniline donor units provide the dye that absorbs at 520 nm with the high extinction coefficient in the order of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Alkyl group present in the Fischer's base and aniline donors control the aggregation of dyes on the TiO_2 photoanode and passivate the surface effectively to reduce the charge recombination process.

Here, 4-aminobenzoic acid reacted with hexanal or 2-ethylhexanal under reductive amination reaction conditions to

(a) Alkyl group wrapped zwitter ionic dye



(b) General structure of visible-light active squaraine dye



(c) Targeted aniline indoline donor based visible-light active AM dyes, and AK4 dye

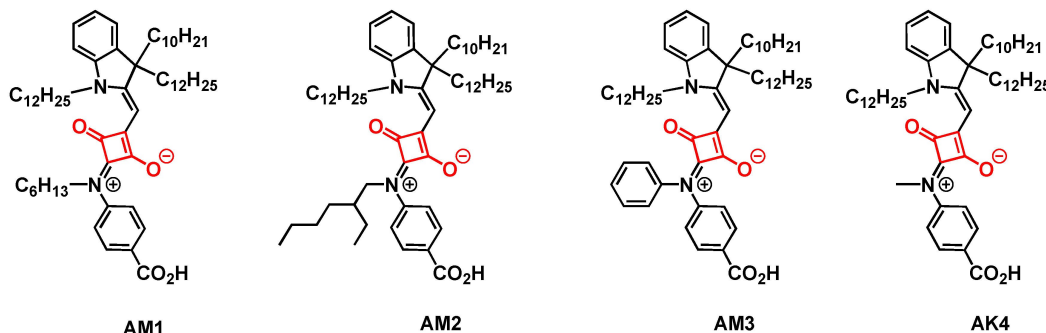


Figure 2. (a) Design of alkyl group wrapped zwitterionic dye (b) general structure of visible active unsymmetrical squaraine (AM) dyes, and (c) targeted D-A-D based unsymmetrical squaraine dyes.

afford the N-alkylated-4-amino benzoic acid derivatives 4-(hexylamino) benzoic acid (2), and 4-((2-ethylhexyl)amino) benzoic acid (3).^[53] Whereas Pd^{2+} catalyzed coupling of ethyl-4-bromobenzoate with aniline provided 4-(phenylamino)benzoic acid (4).^[54] AM dyes were synthesized by condensation reaction between the N-alkylated or N-arylated aniline derivatives and alkyl group wrapped semisquaric acid, 1, by employing the Dean-Stark apparatus for the azeotropic removal of water to afford the red color dyes in moderate yields (Scheme 1 and 2).

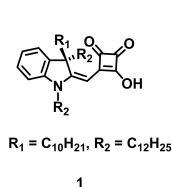
All the dyes have been characterized by NMRs (^1H -NMR and ^{13}C -NMR), IR spectroscopic and mass spectrometric techniques.

Photophysical and electrochemical properties

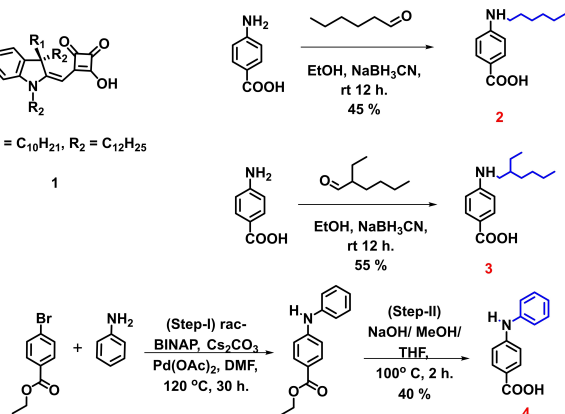
The UV-vis absorption spectra of AM1–AM3 dyes and reference AK4 dye have been carried out in CH_2Cl_2 solution which exhibited an intense absorbance peak between 528–546 nm with the extinction coefficients of $1.44\text{--}1.68 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 3, and Table 1). Incorporation of the hexyl and N-ethyl-hexyl alkyl unit at the aniline donor unit showed 9 and 12 nm of blue shift in λ_{max} for the AM1 and AM2 dyes respectively, whereas incorporation of the phenyl group at the N-atom of aniline donor unit showed 9 nm of red shift in λ_{max} for the AM3 dye compared to the reference dye AK4. Emission studies of the AM dyes exhibited the peak between 571–597 nm and showed longer Stoke's shift between $1565\text{--}1717 \text{ cm}^{-1}$ in CH_2Cl_2 compared to the AK4 dye (1109 cm^{-1}) upon exciting at the 500 nm. Hence, effect of the N-alkylation and N-arylation at the aniline donor led to larger Stoke's shift than AK4 dye that indicates the more change in dipole moment for the AM1, AM2 and AM3 dyes in the excited state.

To understand the self-assembly of AM dyes on the TiO_2 , absorption of AM dyes have been carried out on the TiO_2 surface with different sensitization time (Figure S11). As the AM dyes were wrapped with alkyl groups, shorter dipping time leads to observe broadening of the peaks and additional peaks were observed when the electrodes dipped for more than

Indoline donor based semisquaric acid

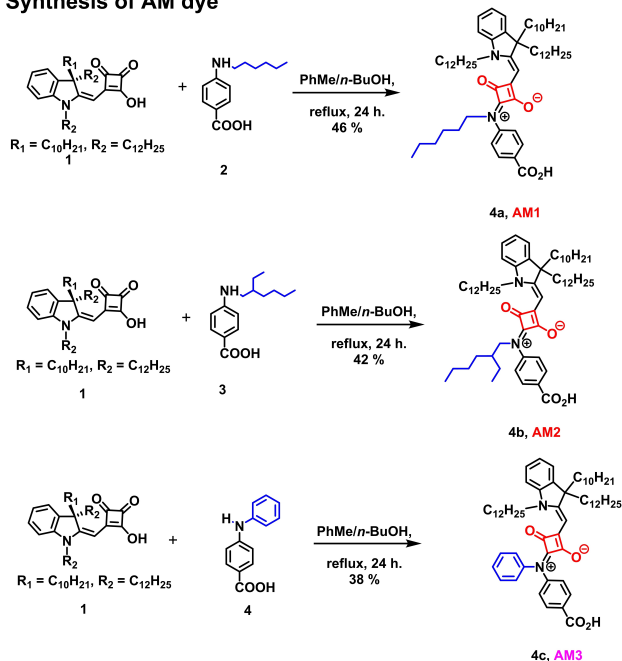


Synthesis of Aniline donor :



Scheme 1. Synthesis of aniline donors.

Synthesis of AM dye



Scheme 2. Synthesis of aniline and indoline donors based AM dyes.

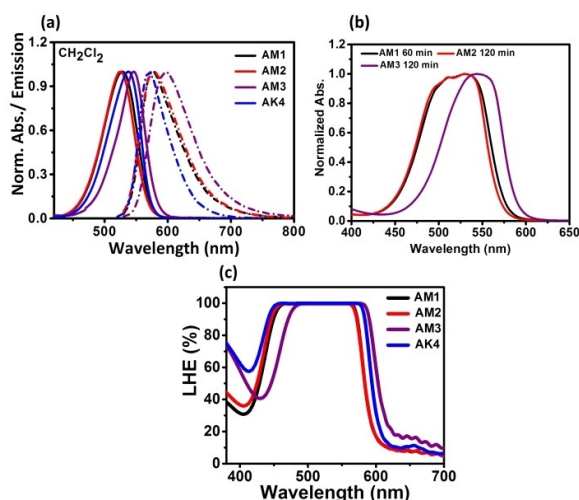


Figure 3. (a) Normalized UV-vis (solid) and fluorescence (dotted) spectra of the AM and AK4 dyes in CH_2Cl_2 solution, (b) UV-vis spectra of the AM dyes on TiO_2 (thickness of the TiO_2 electrode was 6 μm , dipping time: 60 min for AM1; 120 min for AM2 and AM3 dyes) and (c) LHE ($= 1 - 10^{-A}$) profiles of AM and AK4 dyes on TiO_2 electrodes (thickness 6 μm , dipping time 12 h).

60 minutes due to the formation of H- and J- type aggregates on the TiO_2 surface (Figure 3b) for AM1 and AM2 dyes. For the dye AM3, spectral profile was broadened without any additional peaks which indicates the N-substitution at the aniline donor modulates the self-assembly of dyes. Incorporation of hexyl and ethyl-hexyl group on the aniline donor for the AM1 and AM2 dyes narrowed the LHE of 18, and 16 nm, whereas aryl group incorporation for AM3 dye lead 22 nm narrowed LHE performances compared to AK4 dye (width at 80% of LHE). Such reduction in the LHE performance for AM dyes

compared to AK4 dye probably due to more hindrance near to the TiO_2 surface between the dye molecules by alkyl and aryl group incorporation, which reduced the aggregation of dyes on the TiO_2 surface (Figure 3c). Further, charge injection efficiency of AM dyes have been calculated from the steady state emission quenching experiment by utilizing dye coated TiO_2 and ZrO_2 films (procedure is provided in the general methods of supporting information, Figure S12).

The integrated charge injection efficiency ($\text{CIE} = 1 - I_{\text{TiO}_2}/I_{\text{Zirconia}} \times 100\%$) of 90.3, 95.5, and 92.7% have been achieved for AM1, AM2, and AM3 dyes, respectively. Differential pulse voltammetry and cyclic voltammograms experiments have been carried out in CH_2Cl_2 to find the energy levels of the AM dyes (Figure 4). The HOMO energy levels of the AM dyes were calculated from the first oxidation potential of the differential pulse voltammograms and the LUMO energy levels were calculated by subtracting the HOMO values from the optical energy gap of the dyes. The HOMO energy levels of AM dyes showed between 1.03 and 1.13 V, and LUMO obtained between the -1.21 and -1.06 V vs NHE (Figure 4b, Table 1). The HOMO energy levels of AM dyes possesses enough positive potentials for the efficient dye regeneration through I^-/I_3^- and $[\text{Cu}(\text{tmb})_2]^{+2/+}$ electrolytes, and LUMO possesses enough negative potentials for the efficient charge injection to the TiO_2 conduction band upon photoexcitation.

Computational studies

Density functional theory (DFT) calculations for the N-functionalized aniline donor based AM1, AM2 and AM3 dyes (indoline donor without branching) were performed at B3LYP, 6-311G (+ +) level.^[55–59] The electronic distributions at the different electronic states (where, the isodensity surface value was fixed at 0.03) are provided in Figure 5 and Table S7.

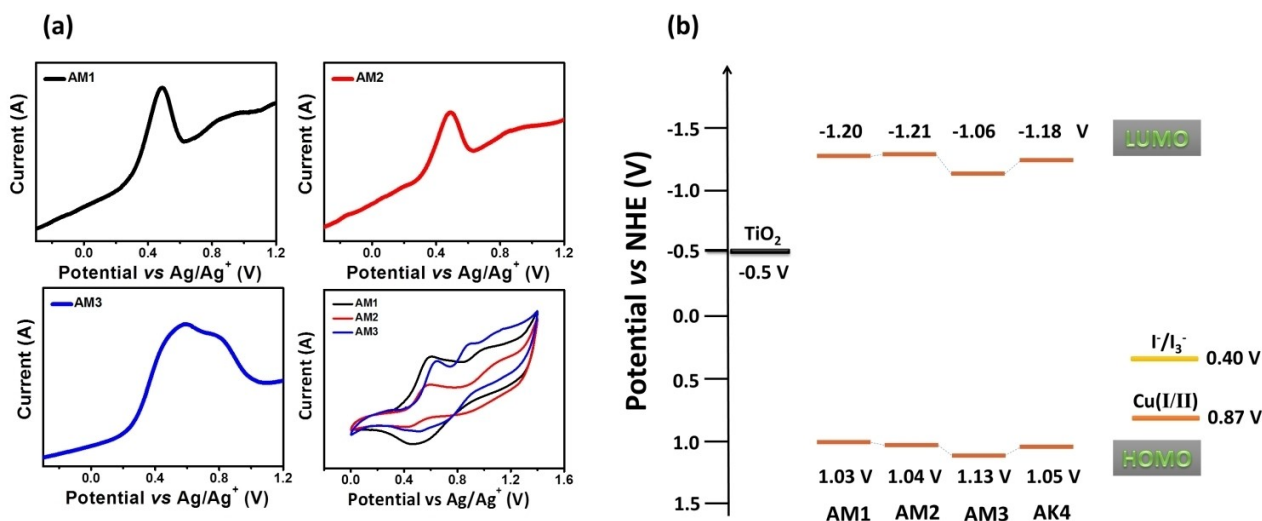
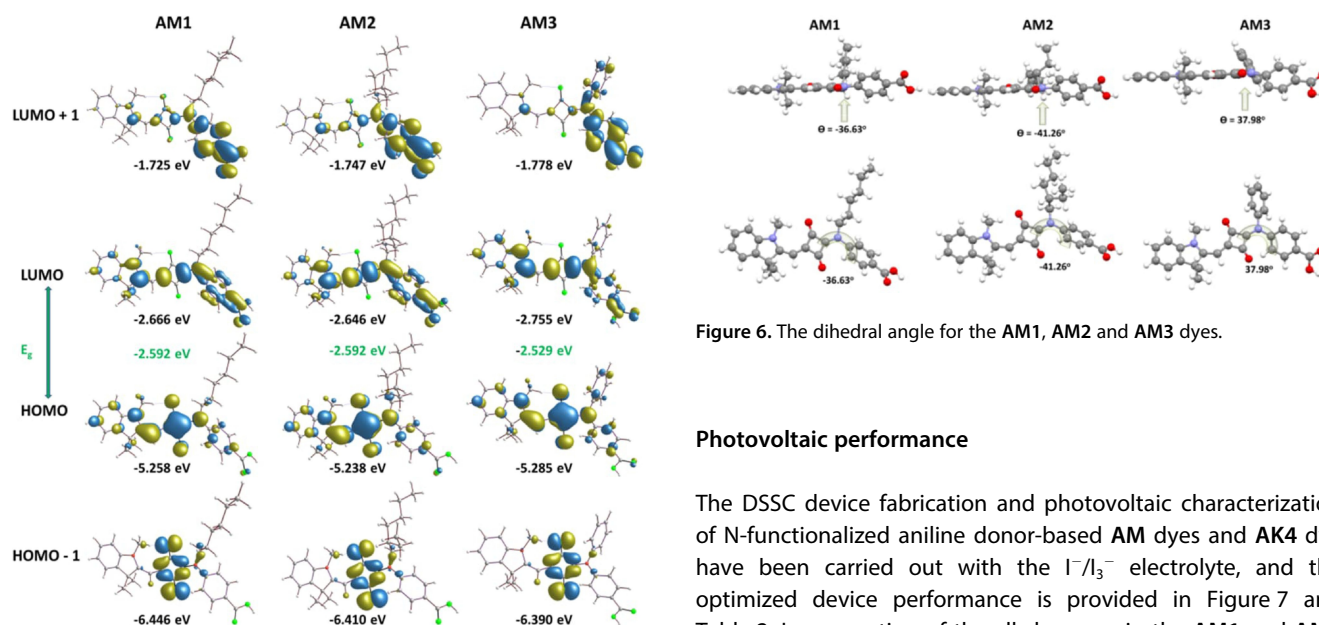
The electron density was localized on the squaraine unit in HOMO-1, whereas in the HOMO, the electron density was localized on the π -framework between the N-atom of both donor units. The electron density in LUMO was located on the D–A–D units, and in AM1 and AM2 dyes, the LUMO + 1 was located on the aniline donor unit, whereas in AM3, the LUMO + 1 was localized over the aniline donor, as well as over the phenyl unit.

Dihedral angles between the donor and acceptor units are seen to play an important role in efficient charge injection process by facile electronic communication. The D–A, D– π –A dyes with high planarity, and low dihedral angles between the donor and acceptor units, show better DSSCs performance due to dense packing of dyes on the TiO_2 .^[60,61] It has been found that the dihedral angles between the aniline donor and acceptor moieties of D–A–D based squaraine dye AK2 (34.5°) compared to AK1 dye (0.05°) play an important role in modulating the photophysical as well as DSSCs performance.^[43] The calculated dihedral angle values for AM dyes from the simulated geometry between the squaraine and aniline donor units was -36.63° , -41.26° and 37.98° for the AM1, AM2 and AM3 dyes, respectively (Figure 6).

Table 1. Photophysical and electrochemical properties of the **AM** and **AK4** dyes at room temperature.

Dyes	λ_{max} [nm] ^[a]	λ_{max} [nm] ^[b]	λ_{max} [nm] On TiO ₂ ^[c]	ϵ [10 ⁵ M ⁻¹ cm ⁻¹] ^[a]	LHE $\Delta\lambda$ at 80 % [nm]	E_{ox} (V vs Ag/Ag ⁺) ^[d]	E_{HOMO} (V vs NHE)	E_{LUMO} (V vs NHE)	E_g [eV] ^[e]
AM1	528	576	529,510	1.55	133	0.490	1.03	-1.20	2.23
AM2	525	577	530,511	1.64	135	0.493	1.04	-1.28	2.25
AM3	546	597	545	1.68	129	0.589	1.13	-1.06	2.19
AK4	537	571	526	1.44	151	0.507	1.05	-1.18	2.23

[a] absorption, [b] emission of **AM** and **AK4** dyes in dichloromethane, [c] on TiO₂, thickness 6 μm , dipping time was 60 min for **AM1**; 120 min for **AM2**, **AM3** and 10 min **AK4** dyes (MeCN), [d] oxidation potentials were measured in CH₂Cl₂, where tetrabutylammonium perchlorate (TBAClO₄) used as a supporting electrolyte, Fc/Fc⁺ used as an internal standard and converted to NHE by addition of 0.7 V, [e] E_g optical energy gap (from the intersection point of absorption and fluorescence spectra, 1240/ λ).

**Figure 4.** (a) Differential pulse and cyclic voltammograms of the **AM** dyes in CH₂Cl₂, and (b) energy level diagram of the **AM** and **AK4** dyes with DSSC components.**Figure 5.** The frontier molecular orbital diagram of D–A–D based **AM1**, **AM2** and **AM3** dyes (alkyl groups at the indoline donor unit have not included for calculation).**Figure 6.** The dihedral angle for the **AM1**, **AM2** and **AM3** dyes.

Photovoltaic performance

The DSSC device fabrication and photovoltaic characterization of N-functionalized aniline donor-based **AM** dyes and **AK4** dye have been carried out with the I⁻/I₃⁻ electrolyte, and the optimized device performance is provided in Figure 7 and Table 2. Incorporation of the alkyl groups in the **AM1** and **AM2** dyes showed positive and phenyl group in **AM3** dye showed negative impact on the V_{OC} of the device compared to the **AK4** dye (contain methyl group at the aniline donor) respectively. N-functionalization in **AM** dyes showed negative impact on the J_{SC} and efficiency of the device compared to the **AK4** dye due

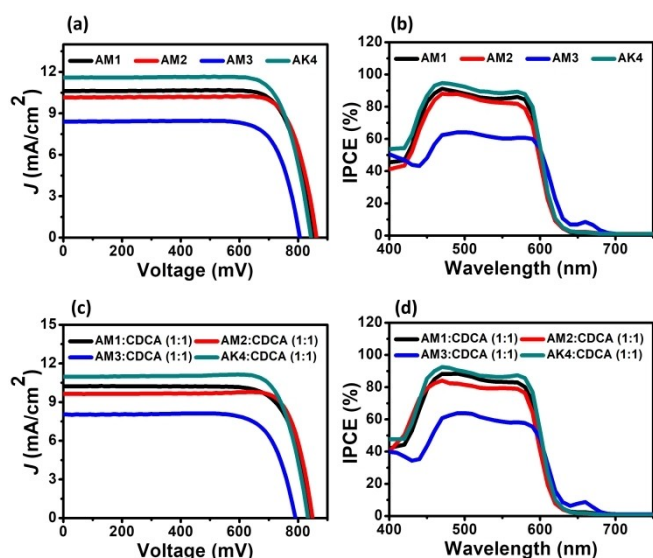


Figure 7. (a) I - V , and (b) IPCE curves for AM and AK4 dyes without CDCA, (c) I - V , and (d) IPCE curves for AM and AK4 dyes with CDCA in I^-/I_3^- electrolyte.

to the low dye-loading on the TiO_2 surface (Figure S13 and Table S1). The maximum power conversion efficiency of 7.44, 7.22, 5.41, and 7.99% have been achieved for the AM1, AM2, AM3 and AK4 dyes in the absence of chenodeoxycholic acid (CDCA), respectively. Addition of CDCA helps to (i) fill the vacancy between the dye adsorbed TiO_2 film so that the back current (charge recombination of the electron in TiO_2 film to the electrolyte) can be reduced and (ii) reduces the dye aggregation on the TiO_2 surface. Further functionalizing the dye with alkyl groups which shield the surface of TiO_2 from the electrolyte results reducing the charge recombination process. As AM1-3 dyes were wrapped with long alkyl chains, it was observed that sensitization of TiO_2 electrode with 1:1 dye:CDCA solution reduces the dye loading as well as J_{SC} , and hence the dye:CDCA ratio was not increased more than that of 1:1 in the present investigation. V_{OC} , J_{SC} and efficiency of the DSSC device decreased when the devices were fabricated with 0.1 mM of CDCA (1 equiv. with respect to dyes) for all the dyes. Further, N-hexyl, and branched N-ethyl-hexyl on the aniline unit for the AM1 and AM2 dyes showed improved V_{OC} due to better surface passivation and reduced J_{SC} due to low dye loading compared to AK4 dye. Similarly, branched alkyl group for AM2 dye near to the TiO_2 passivate the surface more

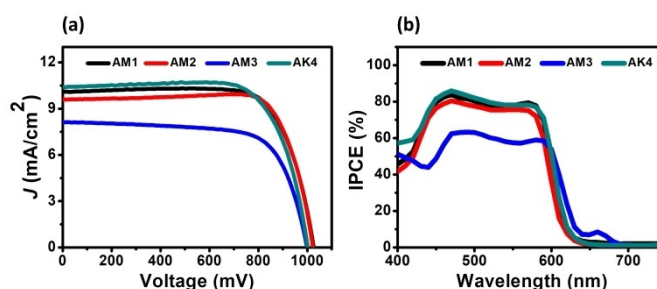


Figure 8. (a) I - V , and (b) IPCE curves for AM and AK4 dyes in the absence of CDCA with $[Cu(tmby)_2]^{+2+}$ electrolyte.

effectively compared to the hexyl group of AM1 dye, and also reduce the binding sites for the dye-anchoring, therefore, AM2 dye showed improved V_{OC} and reduced J_{SC} compared to AM1 dye. Further, N-phenyl group on the aniline unit for the AM3 dye showed reduced V_{OC} due to less passivated surface that promotes charge recombination and reduced J_{SC} due to low dye loading compared to AM1 and AK4 dyes. The V_{OC} for AM dyes and AK4 were observed in the range of 806–865 mV such high values with iodide electrolyte have arisen from the avoided charge recombination process. Here, AM2 dye with N-ethyl-hexyl on the aniline donor gave the highest V_{OC} of 865 mV in AM dye series.

The V_{OC} of the DSSC devices by employing I^-/I_3^- redox shuttle were found to be limited to 0.8–0.87 V due to the large overpotential associated with the dye regeneration process. To overcome this limitation, Co and Cu, complexes have attracted attention due to the small over potentials required for the dye regeneration process, weak visible light absorption, and stability compared to the iodine based redox shuttle.^[62] However, it also requires the HOMO energy levels of the dyes need to have more positive potential, and the present set of dyes fulfil such requirements (Figure 4b).

Hence, the DSSC devices have been fabricated for AM and AK4 dyes with $[Cu(tmby)_2]^{+2+}$ electrolyte and PEDOT counter electrode, and the optimized device performance is provided in Figure 8 and Table 3. Similar to the I^-/I_3^- electrolyte, $[Cu(tmby)_2]^{+2+}$ electrolyte also showed same impact of N-functionalization in AM dyes on the V_{OC} and J_{SC} of the DSSC devices. The maximum power conversion efficiency of 8.05, 7.96, 5.84, and 7.98%, and V_{OC} of 1030, 1025, 1001, and 1009 mV have been achieved for the AM1, AM2, AM3, and AK4

Table 2. Optimized DSSC performances of AM and AK4 dyes with and without co-adsorbent (CDCA) in I^-/I_3^- electrolyte.^[a]

Dyes	CDCA (equiv.)	V_{OC} [mV]	J_{SC} [mA/cm ²]	ff [%]	η [%]	Dye loading on TiO_2 [10^{-7} mol/cm ²]
AM1	0	855 ± 3	10.61 ± 0.23	79 ± 1.06	7.17 ± 0.27	0.641
AM1	1	844 ± 2	10.23 ± 0.17	77 ± 1.18	6.65 ± 0.22	0.424
AM2	0	863 ± 2	10.15 ± 0.20	80 ± 0.69	7.08 ± 0.14	0.547
AM2	1	849 ± 1	9.65 ± 0.25	83 ± 1.07	6.80 ± 0.27	0.340
AM3	0	806 ± 2	8.41 ± 0.16	77 ± 1.13	5.22 ± 0.19	0.577
AM3	1	790 ± 2	8.02 ± 0.22	76 ± 1.61	4.82 ± 0.24	0.418
AK4	0	844 ± 3	11.60 ± 0.18	79 ± 1.05	7.73 ± 0.26	0.862
AK4	1	833 ± 3	10.98 ± 0.13	80 ± 0.43	7.32 ± 0.15	0.695

[a] Concentration of dyes 0.1 mM in $CH_3CN:CHCl_3$ (95:5), active area was 0.23 cm².

Table 3. Optimized DSSC performances of AM and AK4 dyes in the absence of CDCA with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte. Concentration of dyes 0.1 mM in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (95:5), active area was 0.23 cm^2 .

Dyes	V_{OC} (mV)	J_{SC} (mA/cm ²)	ff (%)	η (%)
AM1	1026 ± 4	10.10 ± 0.15	75 ± 1.22	7.77 ± 0.28
AM2	1023 ± 2	9.61 ± 0.06	79 ± 1.31	7.76 ± 0.20
AM3	999 ± 2	8.12 ± 0.11	70 ± 0.92	5.67 ± 0.17
AK4	1002 ± 7	10.40 ± 0.13	74 ± 1.14	7.71 ± 0.27

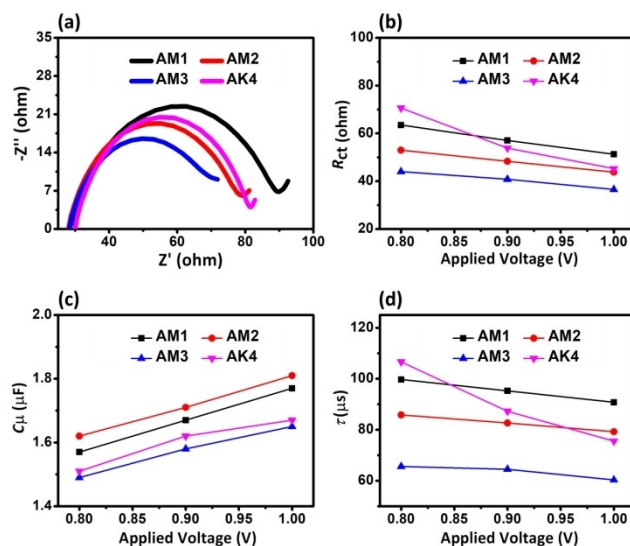
dyes in the absence of CDCA, respectively. Although, variations in V_{OC} and J_{SC} of the device have been observed by N-alkylation on the aniline donor for AM1, AM2, and AK4 dyes, but power conversion efficiencies not changed much. Here, AM1 dye showed the highest DSSC device efficiency of 8.05 %, and V_{OC} of 1030 mV for D–A–D based unsymmetrical squaraine dyes for the first time. IPCE response of the AM and AK4 dyes showed the maximum participation from the aggregated structures in the generation of photocurrents, and the highest IPCE response has been observed for the AK4 dye with both I^-/I_3^- and $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes and reason for the high photocurrent. The IPCE responses were decreased when DSSC devices were sensitized with 0.1 mM of CDCA compared to without CDCA in I^-/I_3^- electrolyte. Further, dye desorption studies showed that reduced dye loading in the presence of CDCA was the reason for the decreased J_{SC} and efficiency for AM and AK4 dyes in I^-/I_3^- electrolyte (Table 2, and Figure S13 and Table S1 in the supporting information). Hence, the alkyl group wrapped dyes (AM1–AM3) structures were inherently optimized for better monolayer formation and for enhanced photocurrent generation. The integrated photocurrent from IPCE profile matched well with the J_{SC} obtained from I - V characteristics of the DSSC device (Table S2 in the supporting information).

Electrochemical impedance spectroscopy (EIS)

The EIS characterization for N-functionalized aniline donor based AM dyes and AK4 dye have been carried out with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolytes in dark (Figures 9, S14 and Table 4) with the different applied potentials and under 1 sun (Figure S17, Table S4 in the supporting information).^[63]

Here, semicircle corresponds to charge transfer resistance between the counter-electrode and electrolytes have not been found for all the dyes in the Nyquist plots. AM1 dye showed relatively high charge recombination resistance (R_{ct}) with increased applied potential compared to the other dyes, which is the result of better surface passivation. AM2 dye showed better chemical capacitance (C_{μ}) values at different applied potentials compared to other dyes and following the order of AM2 (1.81 μF) > AM1 (1.77 μF) > AK4 (1.67 μF) > AM3 (1.65 μF). Electron lifetime (τ) has been calculated by multiplying the R_{ct} and C_{μ} , and the highest electron lifetime of 90.80 μs have been found for AM1 dye.

Further, EIS characterization of AM and AK4 dyes in dark with I^-/I_3^- and in real operating conditions with both electro-

**Figure 9.** (a) Nyquist plot (at 1.0 V applied potential), (b) charge recombination resistance, (c) chemical capacitance, and (d) electron lifetime of AM and AK4 dyes with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte, as a function of applied potential without CDCA.**Table 4.** EIS parameters of AM and AK4 dyes with $[\text{Cu}(\text{tmby})_2]^{+/2+}$ electrolyte at 1.0 V applied potential (with PEDOT counter electrode).

Dyes	R_{ct} [ohm]	C_{μ} [μF]	τ [μs] ^[a]
AM1	51.30	1.77	90.80
AM2	43.78	1.81	79.24
AM3	36.55	1.65	60.31
AK4	45.24	1.67	75.55

[a] $\tau = R_{\text{ct}} \times C_{\mu}$.

lytes have been carried out and provided in supporting information (Figures S15–S17 and Table S3, S4). Significant differences have been noted in the EIS parameters (R_{ct} , C_{μ} and τ) with copper electrolyte compared to I^-/I_3^- electrolyte (Figure S16, Table S3–S4), which due to change in the interfacial contacts. The N-functionalization of aniline with linear, branched alkyl and aryl groups make significant impact on the charge recombination resistance R_{ct} (Table 4) which led to observed difference in the photovoltaic parameters for AM1–3 and AK4 dyes. Though the dihedral angle for the AK4 (34.5°), AM1 (–36.63°), and AM3 (37.98°) are almost similar, having phenyl group at the N-atom of aniline showed the decreased DSSC device performance (also dye loading of AM3 is comparable with AM1). Hence the reduced device performance of AM3 is due to the charge transfer kinetics at the Dye- TiO_2 interface, EIS capture such event, for example the R_{ct} for the device fabricated with AM3 dye is low at a particular bias potential compared to the devices sensitized with other dyes (in both iodide and copper-based electrolyte). Hence having phenyl group at the aniline donor site enhances the charge recombination. Further, despite having similar steric factors on the indoline based donor, having a linear and branched alkyl groups such as N-hexyl (AM1) and N-ethyl-hexyl (AM2) groups at the aniline donor site modulate the dye loading capabilities

compared to **AK4** on TiO₂. Hence the alkyl groups at the aniline may block/shield the dye anchoring site which in turn reduce the charge recombination process, and it can be explained on the basis of enhanced V_{OC} obtained for **AM1** and **AM2** (in both iodide and copper electrolytes) compared to **AK4**.

Conclusion

In summary, donor-acceptor-donor (D–A–D)-based, visible-light-active, squaraine sensitizers **AM1**, **AM2** and **AM3** with N-functionalized aniline donor have been designed and synthesized. These dyes possess high extinction coefficients in the visible region of the solar-light spectrum. A systematic study of the structure-property relationship has been performed for the **AM** dyes and the model dye **AK4** with I^-/I_3^- and $[Cu(tmby)_2]^{+/2+}$ electrolytes. Here, the aniline unit functionalized with -hexyl and 2-ethylhexyl for **AM1** and **AM2** dyes showed enhanced V_{OC} and decreased J_{SC} and efficiencies compared to the aniline unit functionalized with the -methyl for **AK4** dye with I^-/I_3^- electrolyte in the absence of CDCA due to low dye loading. The photovoltaic parameters decreased upon addition of CDCA for **AM** and **AK4** dyes. Whereas, the device fabricated with the $[Cu(tmby)_2]^{+/2+}$ electrolyte showed an enhanced device efficiency of 8.05, 7.96, 5.84, and 7.98% for **AM1**, **AM2**, **AM3**, and **AK4** dyes, respectively, in the absence of CDCA. Further, aniline donor functionalized with methyl or alkyl groups showed improved photovoltaic parameters of the dyes compared with aryl functionalization. Here, all the **AM** dyes and **AK4** dye proved their excellent compatibility with I^-/I_3^- and Cu^+/Cu^{2+} electrolytes, which is rare, especially for zwitterionic dyes. Alkyl-group-functionalized D–A–D-based unsymmetrical squaraine dye **AM1** achieved the maximum DSSC device efficiency of 8.05%, and V_{OC} of 1030 mV for the first time with the $[Cu(tmby)_2]^{+/2+}$ electrolyte along with PEDOT as a cathode material. Though the dihedral angle around the aniline donor and squaric acid unit was systematically changed in these **AM** dyes, passivation of the TiO₂ surface by N-alkyl/N-aryl groups is important for improving the device performance. Considering the high extinction coefficient of the **AM** dyes in the visible region, the compatibility with a copper electrolyte, and its facile synthesis, developing highly efficient zwitterionic dyes with synergistically enhanced V_{OC} and J_{SC} can be extended beyond triarylamine-based donors (Figure S19 and Table S8).

Experimental Section

Semisquaric acid with the alkyl group wrapped indoline unit, compound 1, and 2-ethylhexanal were synthesized by following the procedure reported in the literature,^[43,53,54] and 4-aminobenzoic acid, hexanal, aniline and ethyl-4-bromobenzoate are commercially available. The dyes **AM1**, **AM2** and **AM3** were synthesized by condensing the alkyl group wrapped semisquaric acid with the aniline carboxylic acid derivatives under azeotropic removal of water.^[45]

Synthesis

4-(Hexylamino) benzoic acid (2): 4-Amino benzoic acid (1.0 g, 10.0 mmol) was dissolved in 20 mL of EtOH and cooled to 0 °C in an ice-bath and further hexanal (1.3 g, 10.0 mmol) was added. Sodium cyanotrihydroborate (0.63 g, 10.0 mmol) was dissolved in 10 mL of EtOH and added to the above reaction mixture drop-wise and stirred for 1 h at 0 °C, which was further stirred for 12 h at room temperature. Solvents were removed under reduced pressure and obtained white solid was treated with 1 N aqueous HCl and stirred for 15 min. White precipitate was filtered and washed with water until the filtrate become neutral. Compound 2 has been recrystallized with EtOH: H₂O (4: 1) and dried under reduced pressure.^[53] Yield: 1.0 g, 45%. ¹H NMR (200 MHz, CDCl₃): δ 7.93 (d, J = 8.82 Hz, 2H), 6.56 (d, J = 8.82 Hz, 2H), 3.18 (t, J = 7.06 Hz, 2H), 1.54–1.80 (m, 2H), 1.25–1.49 (m, 6H), 0.91 (t, J = 6.91 Hz, 3H).

4-((2-Ethylhexyl)amino) benzoic acid (3): 4-Amino benzoic acid (1.0 g, 10.0 mmol) was dissolved in 20 mL of EtOH and cooled to 0 °C and 2-ethylhexanal (1.15 g, 8.75 mmol) was added. Sodium cyanotrihydroborate (0.46 g, 7.29 mmol) was dissolved in 10 mL of EtOH and added to the above reaction mixture drop-wise and stirred for 1 h at 0 °C, which was further stirred for 12 h at room temperature. Solvents were removed under reduced pressure and obtained white solid was treated with 1 N aqueous HCl and stirred for 15 min. White precipitate was filtered and washed with water until the filtrate become neutral. Organic layer were separated with CH₂Cl₂ (30 mL $\times$ 3), dried over Na₂SO₄. Column chromatography has been subjected with pet ether and EtOAc to obtain compound 3. Yield: 1.0 g, 55%.

¹H NMR (400 MHz, DMSO-*d*₆): δ 11.95 (br. s., 1H), 7.66 (m, J = 8.71 Hz, 2H), 6.57 (m, J = 8.82 Hz, 2H), 6.39 (t, J = 5.35 Hz, 1H), 2.96 (t, J = 5.84 Hz, 2H), 1.47–1.64 (m, 1H), 1.20–1.39 (m, 8H), 0.81–0.91 (m, 6H).

4-(Phenylamino)benzoic acid (4): Compound 4 has been synthesized by following the procedure provided in literature.^[54] Ethyl-4-bromobenzoate was coupled with aniline by Pd catalyzed Buchwald-Hartwig amination reaction conditions, and the resulted ester derivative was hydrolyzed by NaOH.

Step 1: Ethyl-4-bromobenzoate (0.5 g, 2.2 mmol), aniline (0.254 g, 2.72 mmol), CS₂CO₃ (1.06 g, 3.27 mmol), *rac*-BINAP (0.1 g, 0.16 mmol), Pd(OAc)₂ (0.04 g, 0.178 mmol) were dissolved in 10 mL of DMF and heated at 120 °C for 30 h. The reaction mixture was cooled and solvents were removed under reduced pressure. Thin layer chromatography of the reaction mixture showed only one major product and the crude mixture has been used for next step without purification.

Step 2: Crude mixture (0.4 g) was dissolved in THF: MeOH (1:1) 80 mL, and added 4 M NaOH (20% w/w in water, 20 mL), and heated to 40 °C for 4 h, then checked TLC that indicate the completely hydrolysis of the ester group. The reaction mixture was cooled to 0 °C and carefully neutralized with 1 M HCl solution (1 mL) then organic layer was separated with using diethyl ether (30 mL $\times$ 3), and dried over Na₂SO₄ and solvent removed under reduced pressure and purified with column using pet ether and EtOAc. Yield: 0.23 g, 40%.

¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.70 Hz, 2H), 7.37 (t, J = 8.70 Hz, 2H), 7.21 (d, J = 8.24 Hz, 2H), 7.11 (d, J = 7.33 Hz, 1H), 7.01 (d, J = 8.70 Hz, 2H), 6.11 (br. s., 1H).

General synthetic procedure for the AM dyes

AM dyes have been synthesized by the condensation reaction between the semisquaric acid, 1, and the respective aniline donors

(2, 3 and 4) in PhMe and *n*-BuOH under reflux reaction conditions. The water formed during the reaction was continuously removed by utilizing Dean-Stark distillation apparatus. The reaction mixture were purified by column chromatography (SiO_2 , 100–200 mesh, MeOH and CH_2Cl_2) to obtain the required dye.^[43,46]

4-((4-Carboxyphenyl)(hexyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AM1): Compound 1 (0.2 g, 0.28 mmol), 4-(hexylamino)benzoic acid (0.062 g, 0.28 mmol) (SiO_2 , 100–200 mesh, 2.5% MeOH and 97.5% CH_2Cl_2). Yield: 0.12 g, 46%. Mp: 128 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J=8.24$ Hz, 2H), 7.37 (d, $J=8.70$ Hz, 2H), 7.31 (t, $J=7.78$ Hz, 1H), 7.16 (t, $J=7.33$ Hz, 1H), 6.96 (d, $J=7.78$ Hz, 1H), 6.84 (d, $J=8.70$ Hz, 1H), 5.98 (s, 1H), 4.47 (t, $J=6.87$ Hz, 2H), 4.12 (t, $J=5.06$ Hz, 1H), 3.96 (t, $J=6.18$ Hz, 2H), 3.85 (t, $J=4.81$ Hz, 1H), 3.59–3.78 (m, 6H), 2.79–3.00 (m, 2H), 1.87–2.06 (m, 2H), 1.72–1.82 (m, 2H), 1.61–1.72 (m, 3H), 1.33–1.44 (m, 6H), 1.24–1.27 (m, 19H), 1.20 (d, $J=4.58$ Hz, 10H), 1.07 (br. s., 12H), 0.84–0.88 (m, 12H), 0.67–0.81 (m, 4H), 0.46 (t, $J=7.55$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 13.94, 14.09, 22.46, 22.62, 22.65, 23.97, 25.87, 27.10, 27.19, 28.93, 29.28, 29.31, 29.41, 29.49, 29.60, 29.68, 31.33, 31.84, 31.87, 40.10, 43.58, 58.46, 61.62, 69.77, 70.20, 70.51, 70.71, 72.52, 86.31, 109.01, 113.60, 113.71, 113.78, 122.20, 123.38, 123.64, 126.96, 127.62, 131.11, 138.63, 142.73, 144.11, 169.12, 175.22, 180.72; IR (cm^{-1}): 2954, 2919, 2851, 1750, 1704, 1589, 1562, 1488, 1469, 1433, 1410, 1354, 1310, 1269, 1243, 1208, 1187, 1176, 1130, 1104, 1078, 1014, 963, 939; MALDI-TOF(m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{60}\text{H}_{95}\text{N}_2\text{O}_4$, 907.7214; found, 907.5406.

4-((4-Carboxyphenyl)(2-ethylhexyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AM2): Compound 1 (0.2 g, 0.277 mmol), 4-((2-ethylhexyl)amino)benzoic acid (0.069 g, 0.277 mmol), column chromatography (SiO_2 , 100–200 mesh, 2.5% MeOH and 97.5% CH_2Cl_2). Yield: 0.110 g, 42%, Mp: 108 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, $J=8.24$ Hz, 2H), 7.36 (d, $J=8.70$ Hz, 2H), 7.31 (t, $J=8.24$ Hz, 1H), 7.15 (t, $J=7.56$ Hz, 2H), 6.95 (d, $J=7.79$ Hz, 1H), 6.84 (d, $J=8.70$ Hz, 1H), 5.96 (s, 1H), 4.36–4.56 (m, 2H), 4.12 (t, $J=4.81$ Hz, 1H), 3.95 (t, $J=6.87$ Hz, 2H), 3.85 (t, $J=4.81$ Hz, 1H), 3.70–3.77 (m, 2 H), 3.59–3.70 (m, 7H), 2.89 (t, $J=11.22$ Hz, 2H), 1.89–2.03 (m, 2 H), 1.70–1.83 (m, 2H), 1.49–1.55 (m, 1H), 1.37–1.43 (m, 4H), 1.21–1.29 (m, 30H), 1.16–1.20 (m, 10H), 1.07 (br. s., 12H), 0.84–0.88 (m, 14H), 0.63–0.79 (m, 4H), 0.47 (t, $J=6.41$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 10.52, 13.98, 14.10, 22.66, 22.91, 23.29, 24.00, 27.08, 27.21, 28.35, 29.32, 29.42, 29.52, 29.60, 29.89, 31.88, 37.24, 40.21, 43.53, 58.39, 61.66, 67.15, 69.79, 70.26, 70.52, 70.57, 70.74, 72.44, 86.16, 108.93, 113.60, 113.71, 113.78, 122.18, 123.54, 123.76, 127.59, 129.18, 131.08, 138.59, 142.20, 144.18, 168.83, 175.83, 180.48; IR (cm^{-1}): 2956, 2921, 2852, 1752, 1705, 1589, 1563, 1470, 1433, 1412, 1378, 1352, 1309, 1273, 1260, 1217, 1203, 1176, 1134, 1118, 1102, 1064, 1015, 965, 938; MALDI-TOF(m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{62}\text{H}_{99}\text{N}_2\text{O}_4$, 935.7527; found, 935.5762.

4-((4-Carboxyphenyl)(phenyl)iminio)-2-((-3-decyl-1,3-didodecylindolin-2-ylidene)methyl)-3-oxocyclobut-1-en-1-olate (AM3): Compound 1 (0.25 g, 0.347 mmol), 4-(phenylamino)benzoic acid (0.074 g, 0.347 mmol), column chromatography (SiO_2 , 100–200 mesh, 2.5% MeOH and 97.5% CH_2Cl_2). Yield: 0.12 g, 38%, Mp: 108 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, $J=8.39$ Hz, 2H), 7.46 (d, $J=8.39$ Hz, 2H), 7.38 (t, $J=7.44$ Hz, 3H), 7.33 (d, $J=7.25$ Hz, 1H), 7.29 (d, $J=3.43$ Hz, 2H), 7.23–7.27 (m, 3H), 7.07 (d, $J=8.01$ Hz, 1H), 6.17 (br. s., 1H), 4.07 (br. s., 2H), 2.97 (br. s., 2H), 1.98 (td, $J=11.07$, 4.01 Hz, 2H), 1.82 (quin, $J=7.34$ Hz, 2H), 1.42–1.47 (m, 2H), 1.35–1.39 (m, 2H), 1.28 (d, $J=5.72$ Hz, 21H), 1.20–1.25 (m, 12H), 1.11 (d, $J=9.92$ Hz, 12H), 0.86–0.92 (m, 11H), 0.71–0.80 (m, 2H), 0.43–0.53 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 14.08, 22.65, 24.01, 27.18, 27.37, 29.30, 29.38, 29.59, 31.88, 40.02, 44.07, 59.29, 87.84, 106.95, 109.75, 120.70, 122.35, 124.54, 124.60, 125.56, 127.58, 127.82,

128.51, 129.01, 129.48, 131.11, 132.18, 139.14, 140.23, 144.45, 168.13, 171.44, 186.35; IR (cm^{-1}): 2953, 2922, 2852, 1760, 1706, 1605, 1559, 1488, 1465, 1425, 1406, 1352, 1294, 1235, 1207, 1172, 1138, 1104, 1185, 1016, 1004, 960, 920; MALDI-TOF(m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{60}\text{H}_{87}\text{N}_2\text{O}_4$, 899.6588; found, 899.5042.

General Methods and Instrumentation: General methods, characterization techniques have been provided in the supporting information.

Dye-Sensitized Solar Cell Fabrication: To fabricate the DSSC device we have followed our previous report.^[26] Cells were immersed in 0.1 mM dye solution of AM dyes for 12 h. Iodolyte Z-50 (Solaronix) and $[\text{Cu}(\text{tmbpy})_2]^{+2+}$ (Dyename) have been used as an electrolyte, 0.23 cm^2 was the active area and 0.36 cm^2 was the area of black mask.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: squaraine dyes • dihedral angle • Cu electrolytes • open circuit voltage • dye-sensitized solar cells

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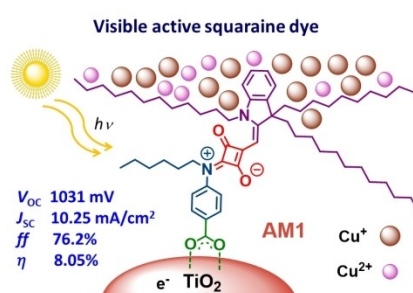
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RESEARCH ARTICLES

Aniline- and indoline-donor-based, zwitterionic, visible-light-active, squaraine sensitizer **AM1** exhibited 1 V of open-circuit voltage (V_{OC}) and 8% of dye-sensitized solar cell efficiency with a copper electrolyte.



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Visible-Light-Active Unsymmetrical Squaraine Dyes with 1 V of Open-Circuit Voltage for Dye-Sensitized Solar Cells



Erratum