

Co-sensitization of Ru (II) Complex with Terthiophene-based D- π - π -A Metal-free Organic Dyes for Highly Efficient Dye-sensitized Solar Cells: Influence of Anchoring Group on Molecular Geometry and Photovoltaic Performance

Mohamed R. Elmorsy^{a,b}, Rui Su^a, Ahmed A. Fadda^b, H.A. Etman^b, Eman H. Tawfik^b, Ahmed El-Shafei^{a,*}.

*a*Polymer and Color Chemistry Program, North Carolina State University, Raleigh, NC, 27695, United States.

*b*Department of Chemistry, Faculty of Science, Mansoura University, El-Gomhoria Street, 35516 Mansoura, Egypt.

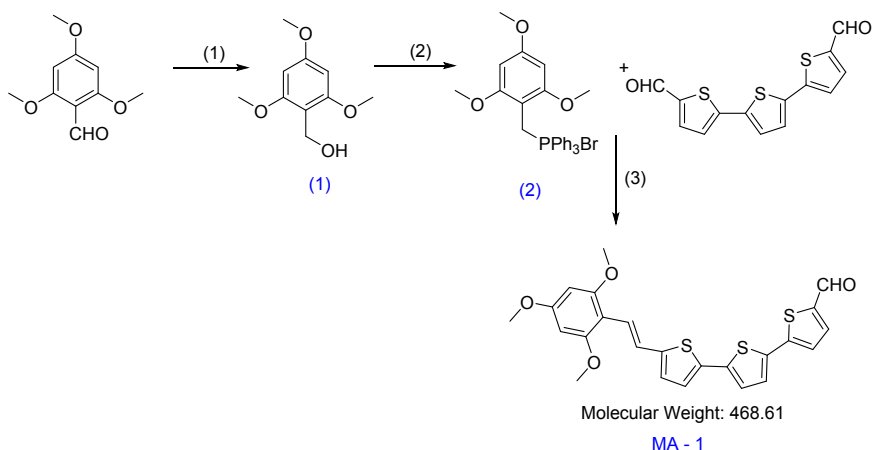
* Corresponding author: E-mail: Ahmed_El-Shafei@ncsu.edu

1. Experimental Section

1.1. Materials and Equipment's

The solvents and chemicals were purchased from Sigma-Aldrich, Fisher Scientific, TCI-America or Ark Pharm and used as received. Sephadex LH-20 was purchased from Fisher Scientific. The mass spectrometry analysis was carried out on a high-resolution mass spectrometer, the Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan Orbitraps mass spectrometer using heated electrospray ionization (HESI). Samples were dissolved in methanol and sonicated for 15 min. They were then diluted 1:1 with 20 mM ammonium acetate and analyzed via syringe injection into the mass spectrometer at a flow rate of 10 μ L/min. The mass spectrometer was operated in positive ion mode. Fourier transform infrared spectroscopy (FT-IR) (ATR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Scientific, USA) and UV-visible spectra were measured by using Cary 300 spectrophotometer. ¹H NMR spectra were recorded using a Varian 400 MHz spectrometer.

1.2. Synthesis



(1) NaBH₄, CH₂Cl₂, MeOH, rt. (2) PPh₃HBr, CHCl₃, reflux. (3) DMF/18-Crown-6, K₂CO₃, 70°C.

Scheme 1: Synthesis of MA-1

1.2.1. Synthesis of (2,4,6-trimethoxyphenyl)methanol (1):

To a solution of NaBH₄ (160 mg, 4.2 mmol) in 30 ml dry dichloromethane and 10 ml anhydrous ethanol, 2,4,6-trimethoxybenzaldehyde (0.82 g, 4.2 mmol) was added rapidly and the bath was stirred at room temperature for 2h. The solution was poured into 50 ml water under vigorous stirring, and then extracted with dichloromethane (15 ml). The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated to remove the solvent and recrystallized using hexanes, to give **1** as a yellow solid.

¹H NMR: (400 MHz, DMSO- *d*₆) δ 6.24 (s, 2H), 4.80 (s, 2H), 3.82 (s, 6H), 3.75 (s, 3H). FT-IR: 3440.43 cm⁻¹ (–OH stretch); 2940.77, 2839.12 cm⁻¹ (–CH₃ stretch). ESI mass spectrum: C₁₀H₁₂O₃ [M+H]⁺ Theo. M/Z = 181.086 [M+H]⁺, Found. M/Z 181.086, Error = 0.0145 ppm.

1.2.2. Synthesis of bromotriphenyl(2,4,6-trimethoxybenzyl)-15-phosphane (2)

Compound (1) (0.75 g, 3.8 mmol) and PPh₃.HBr (1.37 g, 4 mmol) were dissolved in 20 ml chloroform and refluxed for 2h. After removing the solvent, the residue was solidified with ether and filtrated to obtain a white solid.

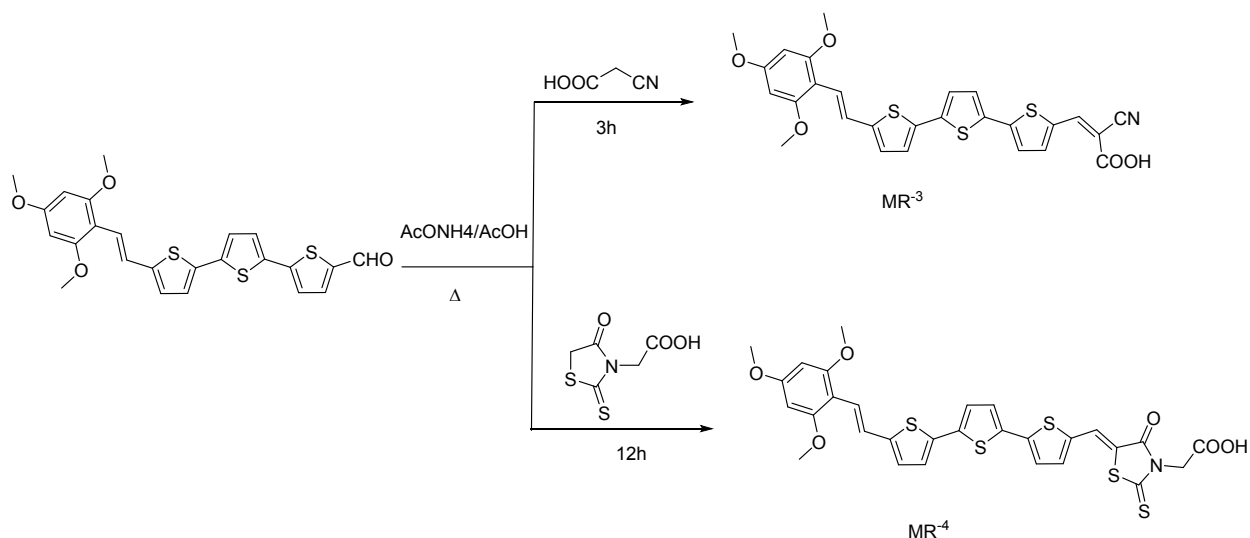
¹H NMR: (400 MHz, DMSO-*d*₆) δ 7.46(dd, 6H), 7.35 (m, 9H), 6.13 (s, 2H), 3.82 (s, 6H), 3.78 (s, 3H), 2.60 (s, 2H). FT-IR: 2986.85, 2936.54 cm⁻¹ (-CH₃ stretch). ESI mass spectrum: C₂₈H₂₈O₃P[M⁺] Theo. M/Z = 443.177 [M⁺], Found. M/Z 443.178, Error = 0.305 ppm.

1.2.3. (E)-5''-(2,4,6-trimethoxystyryl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (MA-1)

The mixture of [2, 2':5',2''-terthiophene]-5,5''-dicarbaldehyde (0.304g, 1 mmol), 18-crown-6 (15 mg, 0.05 mmol), K₂CO₃ (276 mg, 2 mmol) was charged sequentially in a three-necked flask and then dried in vacuo for 30 min. A mixture of adduct (2b) (0.523 g, 1.00 mmol) in dried DMF (30 mL) was added dropwise to the mixture of over 3h at 70 °C under N₂ atmosphere. The reaction mixture was stirred for a further 5h at 70 °C, then was quenched with water and extracted with CH₂Cl₂. The organic layer was dried with anhydrous MgSO₄. Silica gel chromatography with CH₂Cl₂: hexane (1: 5) gave aldehyde (MA-1).

¹H NMR: (400 MHz, DMSO- *d*₆) δ 9.75 (s, 1H), 7.12-7.86 (m, 6H), 6.13 (s, 2H), 7.12 (d, 1H), 6.69 (d, 1H), 6.34 (s, 2H), 3.91 (s, 6H), 3.84 (s, 3H). FT-IR: 2940.56, 2840.13 cm⁻¹ (-CH₃

stretch), 1661.85 cm^{-1} ($-\text{CHO}$ stretch); ESI mass spectrum: $\text{C}_{24}\text{H}_{20}\text{O}_4\text{S}_3$ $[\text{M}+\text{H}]^+$ Theo. $\text{M}/\text{Z} = 469.059$ $[\text{M}+\text{H}]^+$, Found. M/Z 459.060, Error = 1.398 ppm.



Scheme 2: Synthesis of MR-3 and MR-4.

1.2.4. (Z)-2-cyano-3-(5'-((E)-2, 4,6-trimethoxystyryl)-[2,2':5',2''-terthiophen]-5-yl)acrylic acid (MR-3)

A mixture of aldehyde (MA-1) (1.2g, 2.69mmol), cyanoacetic acid (0.265g, 3.12 mmol), ammonium acetate (2.2g, 2.85mmol), and glacial acetic acid (50 mL) was heated at 118 $^{\circ}\text{C}$ for 3h under N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and then was quenched with water and extracted with CH_2Cl_2 . The organic layer was washed with water and dried with anhydrous MgSO_4 and purified by silica gel chromatography with CH_2Cl_2 : CH_3OH (10:1) to yield MR-3 as an orange colored solid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) $\delta = 12.05$ (s, 1H), 8.50 (s, 1H), 7.99 (d, 1H), 7.61 (d, 1H), 7.13-7.52 (m, 6H), 6.30 (s, 2H), 3.88 (s, 6H), 3.83 (s, 3H) ; FT-IR: 2942.38, 2838.19 cm^{-1} ($-\text{CH}_3$ stretch), 2220 cm^{-1} ($-\text{CN}$ stretch), 1684(-

conjugated C=O stretch of -COOH); ESI-FTMS for $C_{27}H_{21}NO_5S_3$ [M+H]⁺ Theo. M/Z = 536.065 [M+H]⁺, Found. M/Z 536.064, Error = -1.823 ppm.

1.2.5 2-((Z)-4-oxo-2-thioxo-5-((5'-(E)-2,4,6-trimethoxystyryl)-[2,2':5',2''-terthiophen]-5-yl)methylene)thiazolidin-3-yl) acetic acid (MR-4)

A mixture of aldehyde (MA-1) (1.2g, 2.69mmol), rhodanine-3-acetic acid (0.59 g, 3.12 mmol), and NH₄OAc (2.2g, 2.85mmol), dissolved in 50 mL of glacial acetic acid . The mixture was refluxed for 12 h under argon atmosphere. The progress of the reaction was monitored by TLC technique. After completion of the reaction, the content was cooled to room temperature, then it was poured into 100 g of crushed ice and obtained red solid was filtered and dried. The product was purified by column chromatography using silica gel and CHCl₃: CH₃OH (10:1) as mobile phase to yield **MR-4** as Red colored solid

¹H NMR (400 MHz, DMSO-*d*₆) δ = 13.03 (s, 1H), 8.14 (s, 1H), 7.04 (d, 1H), 7.15 (d, 1H), 7.79-7.33 (m, 6H), 6.29 (s, 2H), 4.66 (s, 1H), 3.85 (s, 6H), 3.80 (s, 3H) ; FT-IR: 2938.92, 2836.56 cm⁻¹ (-CH₃ stretch), 1712.90(C=O stretch) cm⁻¹ , 1762.97 (conjugated C=O stretch of -COOH); ESI-FTMS for $C_{26}H_{23}NO_6S_5$ [M+H]⁺ Theo. M/Z = 641.012 [M+H]⁺, Found. M/Z 641.011, Error = -1.445 ppm.

2. Analytical Measurements

2.1. Infra-Red Spectroscopy

Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR/FT-IR) spectra were recorded on a Thermo Nicolet, Nexus 470 FTIR Spectrophotometer with Omnic 7.2 software. An average of 32 scans was used at a resolution of 4cm⁻¹.

Compound 1: 3440.43 cm⁻¹ (-OH stretch); 2940.77, 2839.12 cm⁻¹ (-CH₃ stretch).

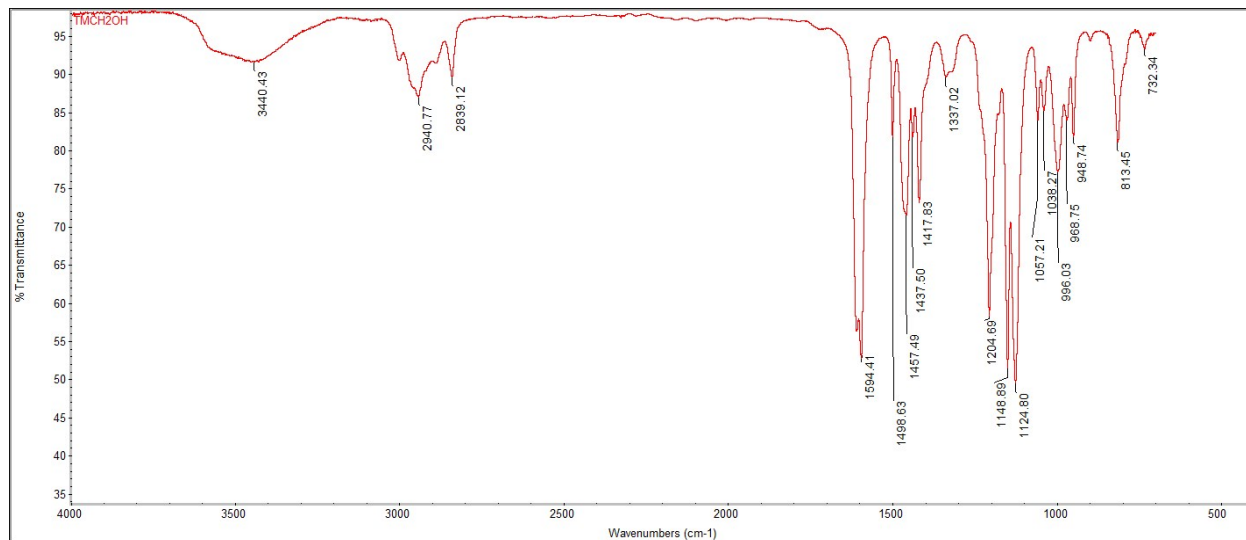


Fig. S1: ATR/FT-IR of 1

Compound 2: 2986.85, 2936.54 cm⁻¹ (-CH₃ stretch).

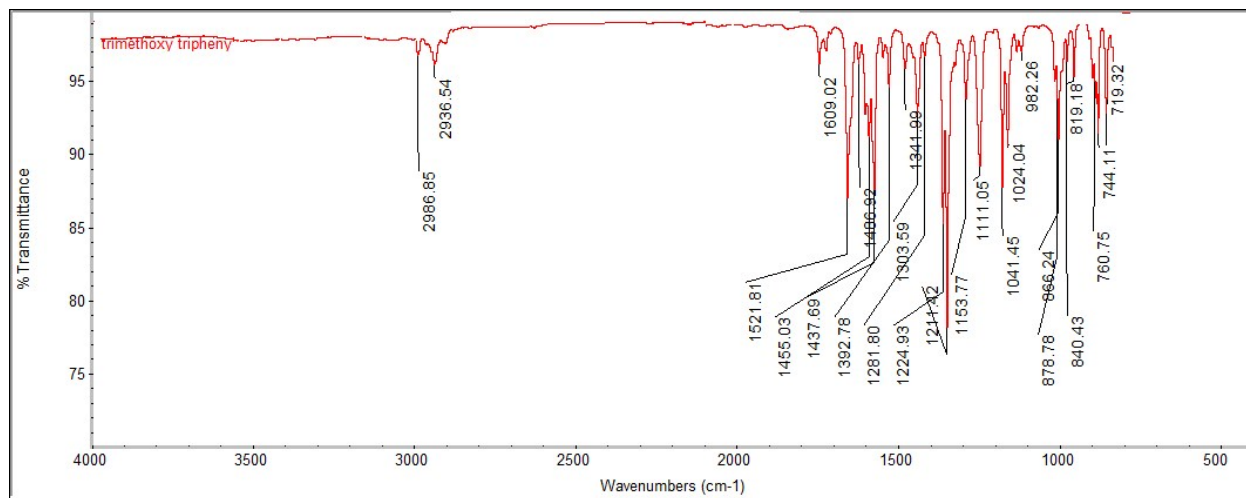


Fig. S2: ATR/FT-IR of 2

MA-1: 2940.56, 2840.13 cm^{-1} (-CH₃ stretch), 1661.85 cm^{-1} (-CHO stretch).

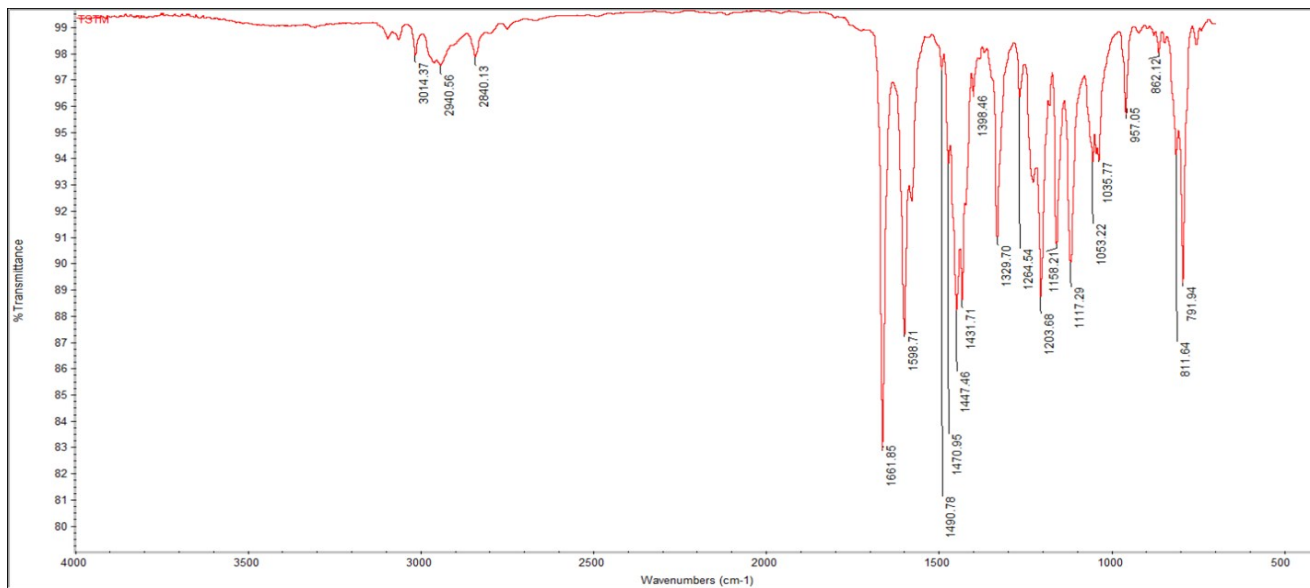


Fig. S3: ATR/FT-IR of MA-1

MR-3: 2942.38, 2838.19 cm^{-1} (-CH₃ stretch), 2220 cm^{-1} (-CN stretch), 1684(-conjugated C=O stretch of -COOH).

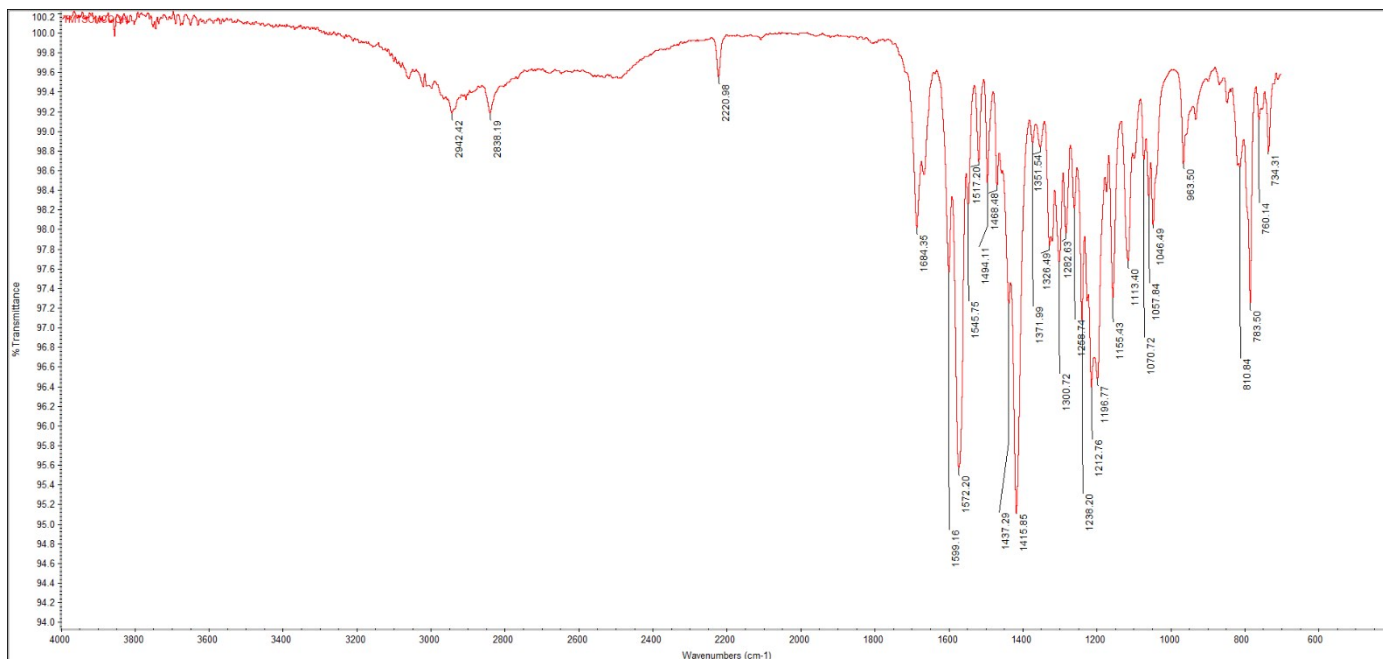


Fig. S4: ATR/FT-IR of compound (1a)

MR-4: 2938.92, 2836.56 cm^{-1} (-CH₃ stretch), 1712.90(C=O stretch) cm^{-1} , 1762.97 (conjugated C=O stretch of -COOH)

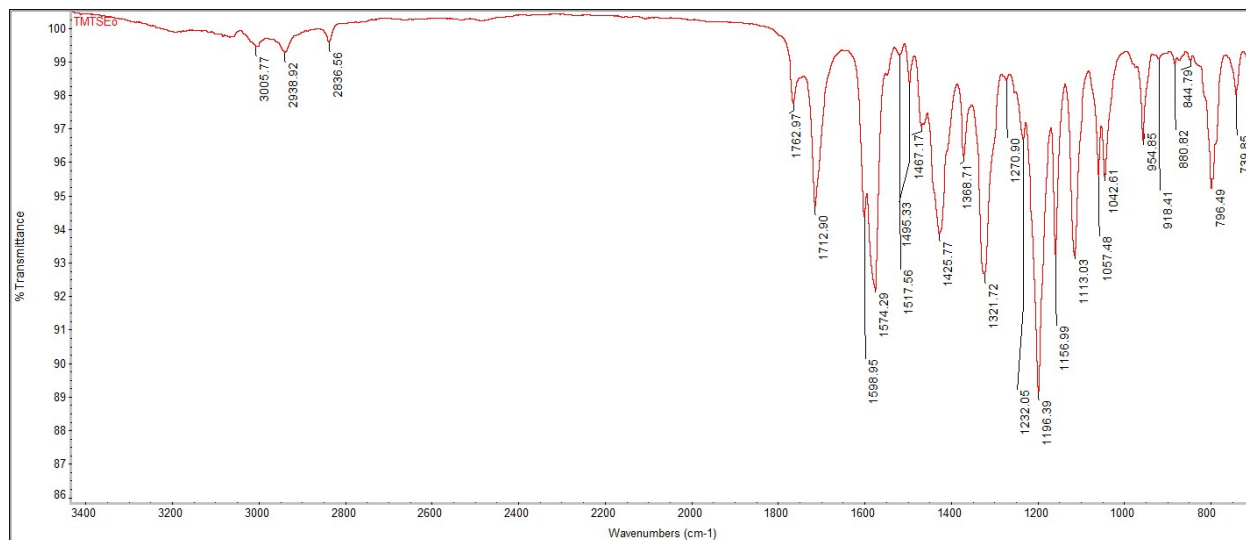


Fig. S5: ATR/FT-IR of compound MR-4

2.2. High Resolution Mass spectrometry

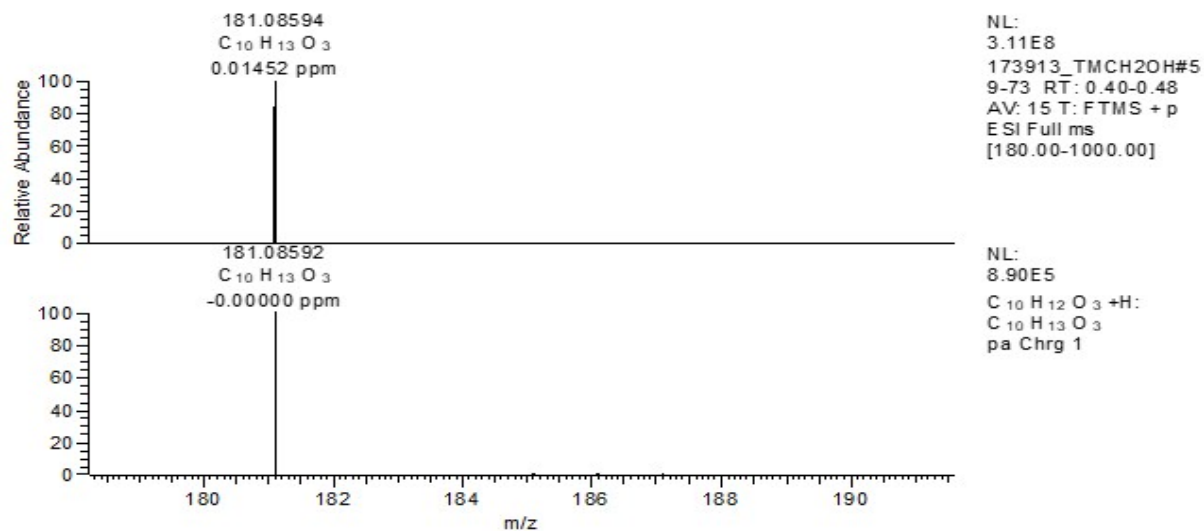


Fig. S6: ESI mass spectrum of **1**, [M+H]⁺; Theo. M/Z = 181.086 [M+H]⁺, Found. M/Z 181.086, Error = 0.0145ppm.

173835_TMSALT #57-72 RT: 0.32-0.39 AV: 16 NL: 3.22E9
T: FTMS + p ESI Full ms [200.00-1000.00]

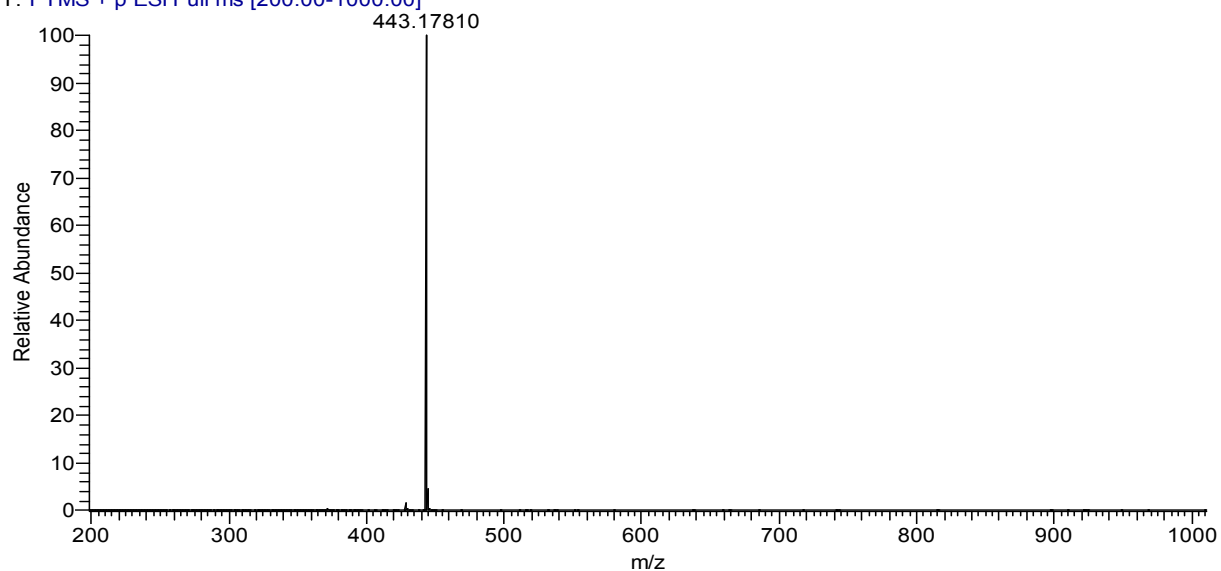


Fig. S7: ESI mass spectrum of **2**, $[M]^+$; $M/Z = 443.177 [M^+]$, Found. $M/Z 443.178$, Error = 0.305 ppm..

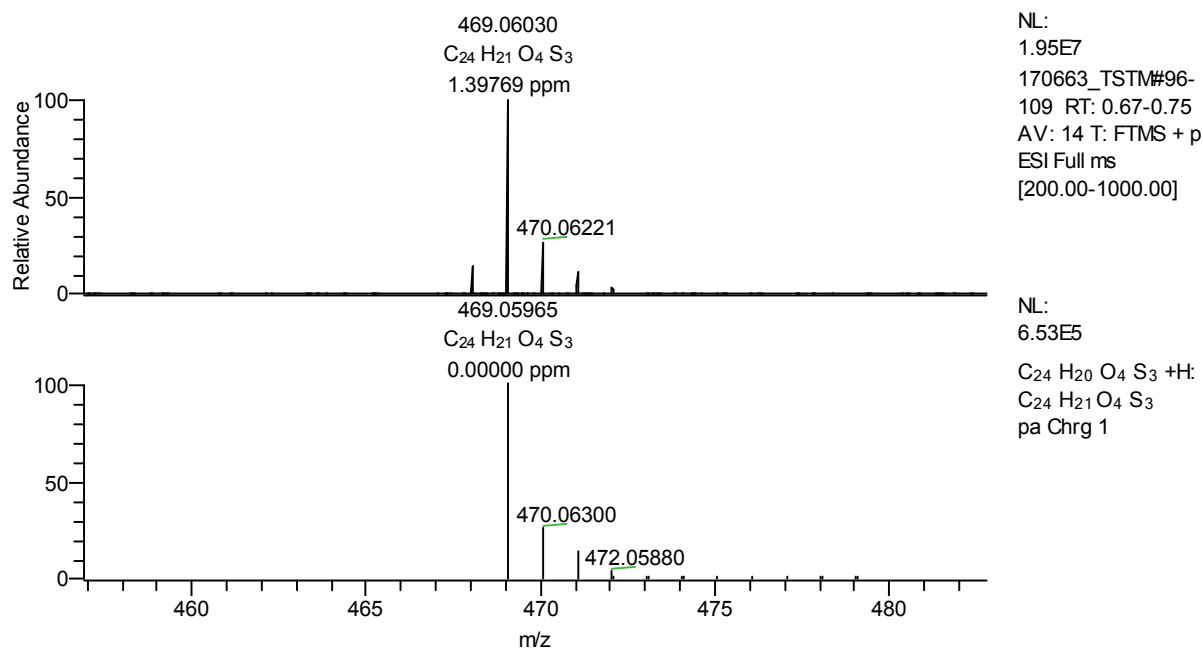


Fig. S8: ESI mass spectrum of **MA-1**, $[M+H]^+$; Theo. $M/Z = 469.059 [M+H]^+$, Found. $M/Z 459.060$, Error = 1.398ppm.

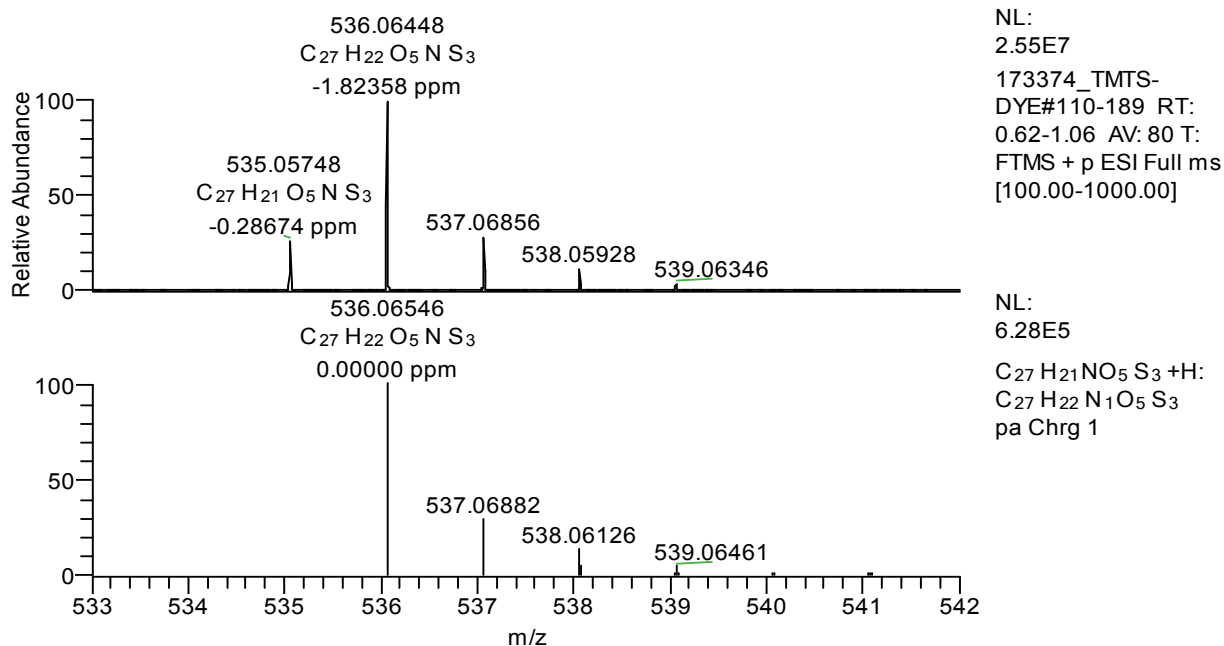


Fig.S9: ESI mass spectrum of **MR-3**, [M+H]⁺ + Theo. M/Z = 536.065 [M+H]⁺, Found. M/Z 536.064, Error = -1.823 ppm.

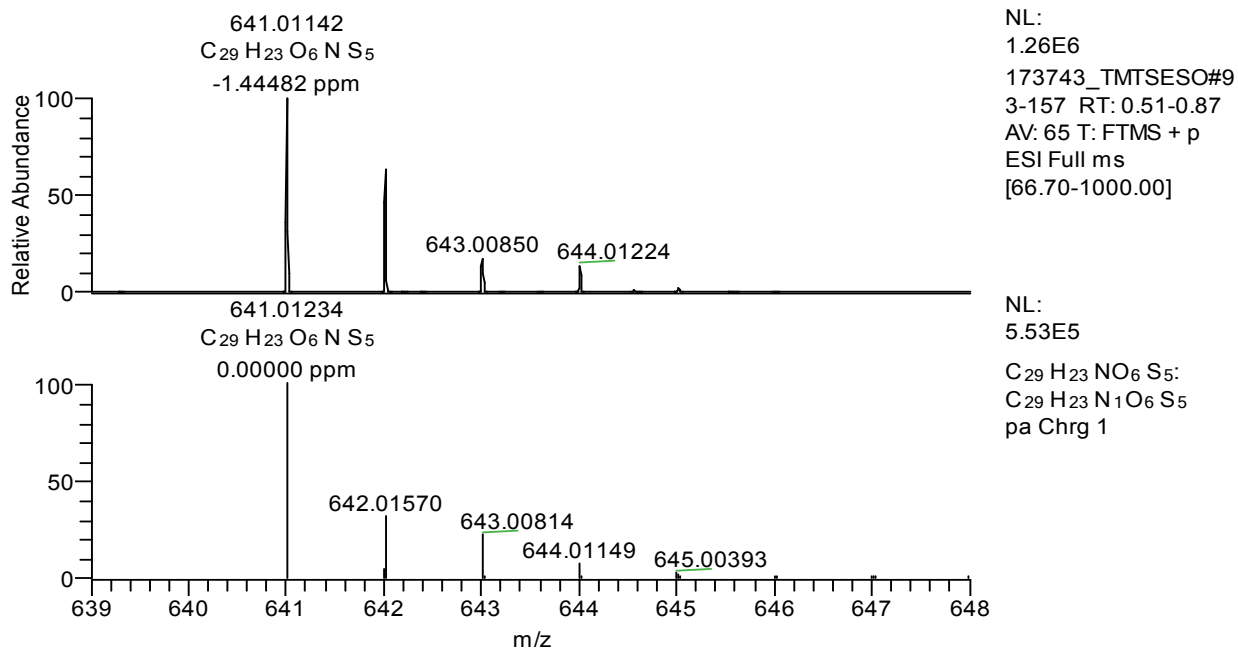


Fig. S10: ESI mass spectrum of **MR-4**, [M+H]⁺; Theo. M/Z = 641.012, Found. M/Z 641.011, Error = -1.44 ppm.

2.3. ^1H NMR spectra

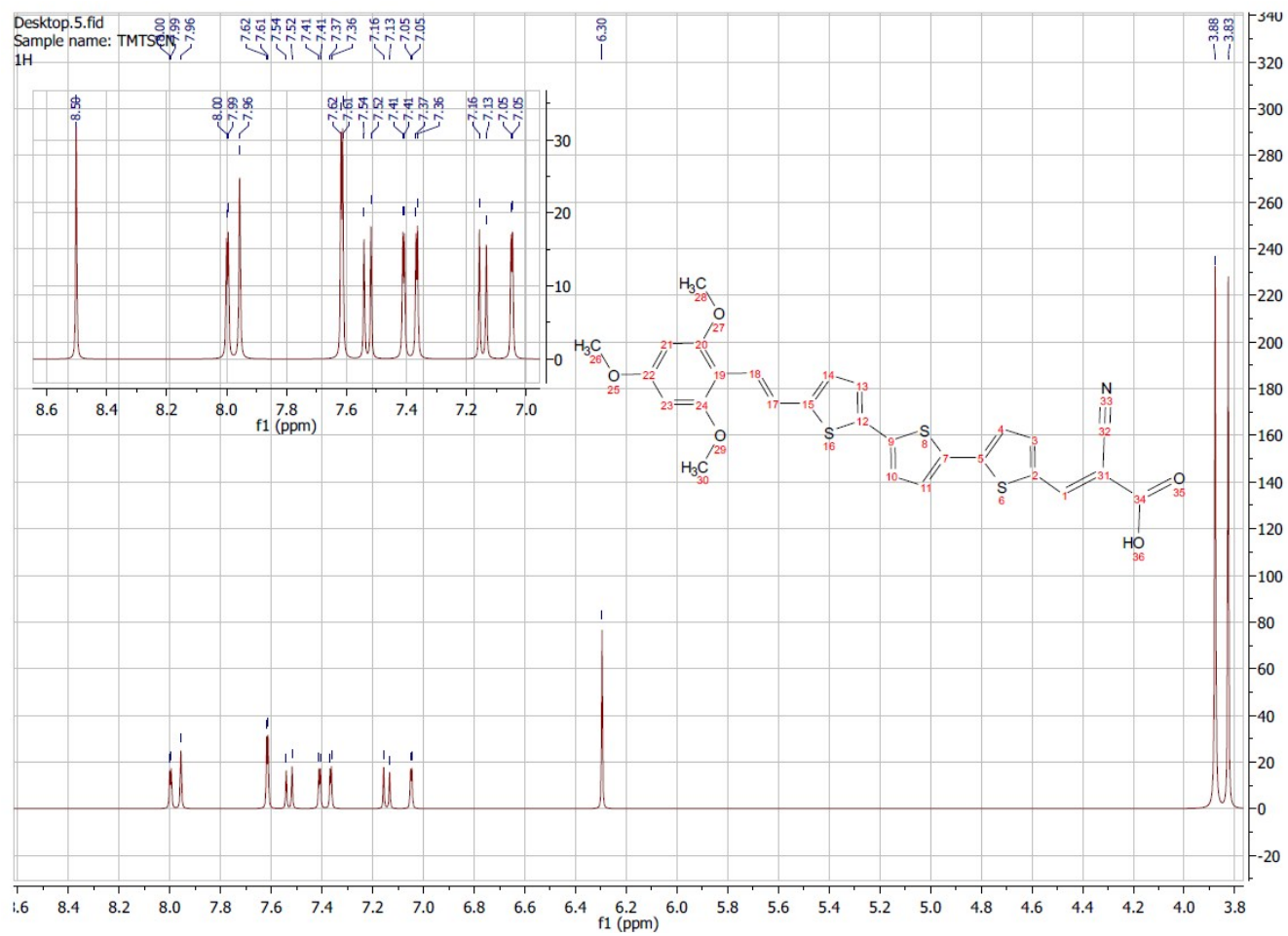


Fig. S11: ^1H NMR spectra of compound MR-3

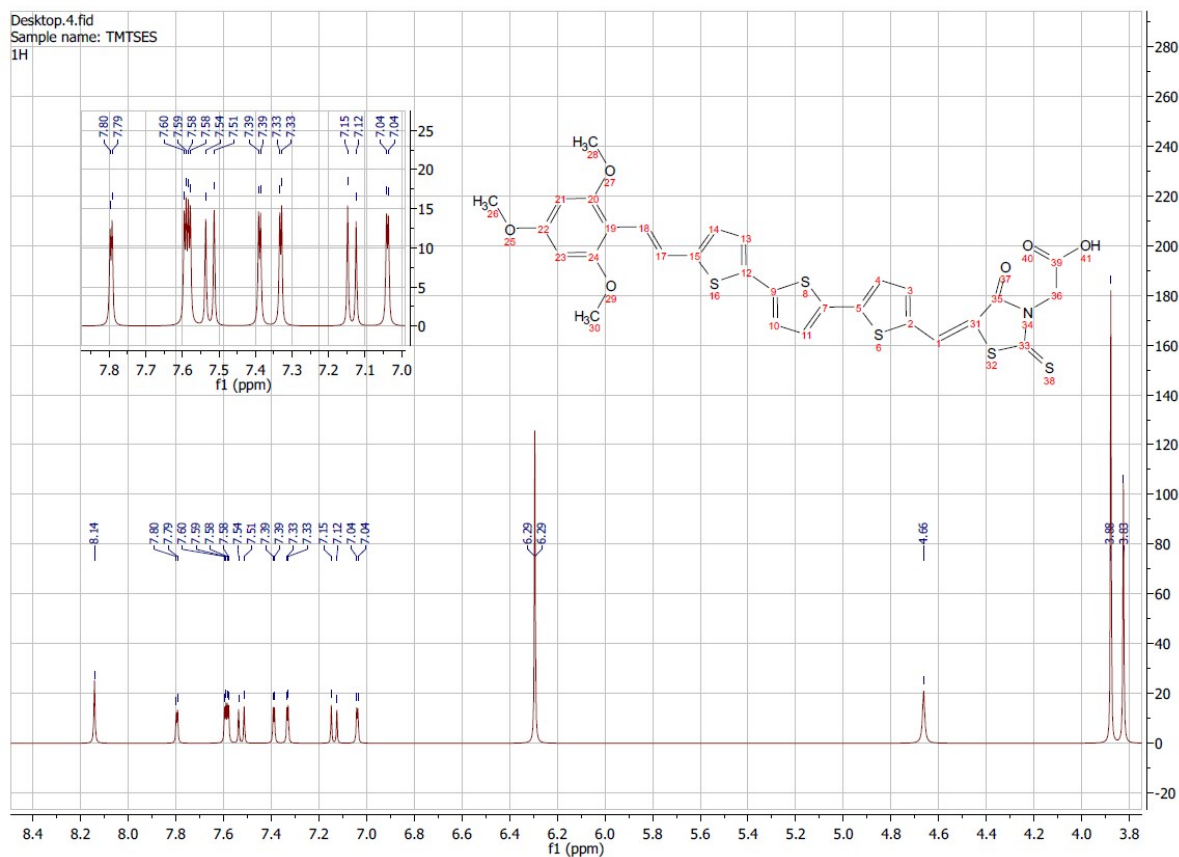


Fig. S12: HNMR spectra of compound MR-4

3. Cell Preparations and Photovoltaic Characterizations

3.1. TiO_2 Electrode Preparation

A double-layer TiO_2 photoelectrode ($10 + 5$) μm in thickness with a $10 \mu\text{m}$ thick nanoporous layer and a $5 \mu\text{m}$ thick scattering layer (area: 0.25 cm^2) was prepared using a reported method. Fluorine-doped tin oxide (FTO) coated glasses (Nippon Sheet Glass Co., Japan) with a sheet resistance of $8\text{-}10 \text{ ohm-}2$ and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO_2 colloids (particle size $\sim 13 \text{ nm}$) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO_2 thin films were deposited onto the conducting glass by screen-printing, which was then sintered at 500° C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500° C . The films were further treated with 0.1 M HCl(aq) before examination.

The dye solutions of the main sensitizer NCSU-10 (0.2 mM) were prepared in 1:1:1 mixture of acetonitrile, tert-butyl alcohol and dimethyl sulfoxide (DMSO). Deoxycholic acid was added to the dye solution as a coadsorbent at a concentration of 20 mM. 0.2 mM of cosensitizer (MR-3 & MR-4), were prepared. A mixture of 1:1 acetonitrile, tert-butyl alcohol was used as a solvent. Deoxycholic acid was added to the dye solution as a coadsorbent at a concentration of 10 mM. For cosensitization, of MR-3 with NCSU-10 (0.2mM MR-3 + 0.2mM NCSu-10) were dissolved in 1:1:1 mixtures of the same solvent used later. Deoxycholic acid was added to the dye solution as a coadsorbent at a concentration of 20 mM. The same way for MR-4 cosensitized with NCSU-10. The electrodes were immersed in the dye solutions and then kept at 25 ° C for 20 h to adsorb the dye onto the TiO₂ surface.

For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1M HCl in EtOH, and sonication in acetone bath for 10 min. These washed TCO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 min.

3.2. Fabrication of Dye-Sensitized Solar Cell

Photovoltaic and incident photon-to-current efficiency (IPCE) measurements were made on sandwich cells, which were prepared using TiO₂ coated working electrodes and platinum coated counter electrodes and were sealed using a 40 μm Syrlyn spacer through heating of the polymer frame. The redox electrolyte (Solaronix, Iodolyte HI-30) consisted of a solution of 0.6 M DMPII, 0.05 M I₂, 0.1 M LiI and 0.5 M TBP in acetonitrile.

3.3. Photovoltaic Measurements

Photovoltaic measurements of sealed cells were made by illuminating the cell through the conducting glass from the anode side with a solar simulator (WXS-155S-10) at AM 1.5 illuminations (light intensity: 100 mW cm⁻²).

3.4. Incident Photon to Current Efficiency (IPCE) Conversion

IPCE measurements were made on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each wavelength was calculated using Equation 1, where ISC is the short-circuit photocurrent density

(mA cm⁻²) under monochromatic irradiation, q is the elementary charge, λ is the wavelength of incident radiation in nm and P_0 is the incident radiative flux in W/m².

$$IPCE(\lambda) = 1240 \left(\frac{I_{sc}}{q\lambda P_0} \right) \quad (1)$$

3.5. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz to 200 kHz at room temperature. The applied bias voltage was set at the VOC of the DSCs, with AC amplitude set at 10 mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

3.6. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed in DMF with the electrolyte 0.1 M [TBA][PF₆] at a scan rate of 50 mV s⁻¹. The working electrode used is the Glassy carbon, Pt wire represented the counter electrode and the reference electrode is Ag/Ag⁺ in ACN. Fc/Fc⁺ was introduced as internal reference.

4. Molecular Modeling

Equilibrium molecular geometries of MR-3 and MR-4 were calculated using the Becke's three parameter hybrid functional, Lee–Yang–Parr's gradient corrected correlation functional (B3LYP) and (6-31g(d,p)) [1, 2, 3]. The geometry optimization calculations were followed by energy calculations using time-dependent density functional theory (TD-DFT) utilizing the energy functional B3lyp and the basis set 6-31g(d,p). The solvent (DMF) effect was accounted for by using the conductor-like polarizable continuum model (C-PCM), implemented in Gaussian 09, and the ground and excited states oxidation potentials were calculated. All DFT and TD-DFT jobs were submitted remotely at North Carolina State University's Supercomputer Jasta via HPC

linkage. Tables 1S and 2S show the coordinates of the optimized molecular geometries of MR-3 and MR-4, respectively.

Table 1S Cartesian coordinates for the optimized geometry of MR-3.

Atom	Cartesian Coordinates		
C	-2.10294	0.676471	0
C	-0.70778	0.676471	0
C	-0.01024	1.884222	0
C	-0.7079	3.092731	-0.0012
C	-2.10272	3.092653	-0.00168
C	-2.80032	1.884447	-0.00068
H	-0.15827	-0.27604	0.001315
H	-3.89993	1.88463	-0.00086
O	1.419757	1.884326	0.000824
O	-2.81788	-0.56198	0.000585
O	-2.81804	4.330887	-0.00292
C	-3.41499	-0.76784	1.283542
H	-4.28781	-0.15541	1.373133
H	-3.68899	-1.79683	1.38845
H	-2.71497	-0.50532	2.049015
C	-3.0562	4.743225	-1.35131
H	-3.64946	4.005703	-1.85031
H	-3.57554	5.678738	-1.35175
H	-2.1218	4.853767	-1.8608
C	1.897878	1.882664	-1.34688
H	1.637788	2.807112	-1.81873
H	2.961794	1.768729	-1.34774
H	1.451806	1.070909	-1.88258
C	0.062607	4.426119	-0.00128
C	-0.54475	5.604749	-0.00239
H	1.155895	4.321703	-0.00037
H	-1.63804	5.709165	-0.0033
C	0.225754	6.938137	-0.0025
C	-0.341	8.193343	-0.00362
S	1.89601	7.018062	-0.00113
C	0.657036	9.220423	-0.00262
H	-1.41221	8.402722	-0.00484
C	1.927977	8.689981	-0.0016
H	0.417021	10.2852	-0.00268
C	3.238784	9.498302	-0.00103
C	4.509686	8.96768	-1.5E-05
S	3.27091	11.17016	-0.00171

C	5.507803	9.994677	-0.0005
H	4.749613	7.902894	0.000783
C	4.941231	11.24993	-0.00105
H	6.579008	9.785212	-0.00043
C	5.711735	12.58332	-0.001
C	5.144983	13.83852	-0.00155
S	7.381991	12.66324	-0.00013
C	6.143016	14.8656	-0.00054
H	4.073772	14.0479	-0.00236
C	7.413958	14.33516	-9.4E-05
H	5.903002	15.93038	-0.0002
C	8.724765	15.14348	0.000304
C	9.920283	14.57008	0.000732
H	8.589125	16.23334	0.000227
C	10.11048	13.04187	0.000835
N	10.25374	11.89075	0.000912
C	11.23109	15.3784	0.001157
O	12.39937	14.99279	0.00157
O	11.01026	16.7173	0.001108
H	11.85154	17.20249	0.001387

Table 2S Cartesian coordinates for the optimized geometry of MR-4.

Atom	Cartesian Coordinates		
C	-2.10294	0.676471	0
C	-0.70778	0.676471	0
C	-0.01024	1.884222	0
C	-0.7079	3.092731	-0.0012
C	-2.10272	3.092653	-0.00168
C	-2.80032	1.884447	-0.00068
H	-0.15827	-0.27604	0.001315
H	-3.89993	1.88463	-0.00086
O	1.419757	1.884326	0.000824
O	-2.81788	-0.56198	0.000585
O	-2.81804	4.330887	-0.00292
C	-3.41499	-0.76784	1.283542
H	-4.28781	-0.15541	1.373133
H	-3.68899	-1.79683	1.38845
H	-2.71497	-0.50532	2.049015
C	-3.0562	4.743225	-1.35131
H	-3.64946	4.005703	-1.85031
H	-3.57554	5.678738	-1.35175
H	-2.1218	4.853767	-1.8608

C	1.897878	1.882664	-1.34688
H	1.637788	2.807112	-1.81873
H	2.961794	1.768729	-1.34774
H	1.451806	1.070909	-1.88258
C	0.062607	4.426119	-0.00128
C	-0.54475	5.604749	-0.00239
H	1.155895	4.321703	-0.00037
H	-1.63804	5.709165	-0.0033
C	0.225754	6.938137	-0.0025
C	-0.341	8.193343	-0.00362
S	1.89601	7.018062	-0.00113
C	0.657036	9.220423	-0.00262
H	-1.41221	8.402722	-0.00484
C	1.927977	8.689981	-0.0016
H	0.417021	10.2852	-0.00268
C	3.238784	9.498302	-0.00103
C	4.509686	8.96768	-1.5E-05
S	3.27091	11.17016	-0.00171
C	5.507803	9.994677	-0.0005
H	4.749613	7.902894	0.000783
C	4.941231	11.24993	-0.00105
H	6.579008	9.785212	-0.00043
C	5.711735	12.58332	-0.001
C	5.144983	13.83852	-0.00155
S	7.381991	12.66324	-0.00013
C	6.143016	14.8656	-0.00054
H	4.073772	14.0479	-0.00236
C	7.413958	14.33516	-9.4E-05
H	5.903002	15.93038	-0.0002
C	8.724765	15.14348	0.000304
H	8.589125	16.23334	0.000227
C	9.946687	14.55742	0.000742
S	10.12467	13.69482	1.242191
N	11.95818	15.33696	1.186127
C	11.04382	15.6121	0.00109
O	11.16915	16.52373	-0.81102
C	11.35167	14.19604	1.990402
S	11.89459	13.63625	3.348892
C	13.2945	14.95617	0.7064
H	13.30119	15.03698	-0.4078
H	13.47176	13.88757	0.979672
C	14.37427	15.86332	1.325093
O	14.26335	16.93591	1.917381

O	15.62374	15.35834	1.166295
H	16.28414	15.94857	1.564609

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