### Accepted Manuscript

Bi-anchoring organic sensitizers of type  $D(\pi-A)_2$  comprising thiophene-2-acetonitrile as  $\pi$ -spacer and malonic acid as electron acceptor for dye sensitized solar cell applications

Gachumale Saritha Reddy, Sekar Ramkumar, Abdullah M. Asiri, Sambandam Anandan

PII:	\$1386-1425(15)00328-5
DOI:	http://dx.doi.org/10.1016/j.saa.2015.03.032
Reference:	SAA 13446
To appear in:	Spectrochimica Acta Part A: Molecular and Biomo lecular Spectroscopy
Received Date:	7 November 2014
Revised Date:	29 January 2015
Accepted Date:	1 March 2015



Please cite this article as: G.S. Reddy, S. Ramkumar, A.M. Asiri, S. Anandan, Bi-anchoring organic sensitizers of type  $D(\pi-A)_2$  comprising thiophene-2-acetonitrile as  $\pi$ -spacer and malonic acid as electron acceptor for dye sensitized solar cell applications, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015), doi: http://dx.doi.org/10.1016/j.saa.2015.03.032

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Bi-anchoring organic sensitizers of type $D-(\pi-A)_2$ comprising thiophene-2-acetonitrile as $\pi$ -spacer and malonic acid as electron acceptor for dye sensitized solar cell applications

Gachumale Saritha Reddy<sup>[a]</sup>, Sekar Ramkumar<sup>[a]</sup>, Abdullah M. Asiri<sup>[b]</sup> and

### Sambandam Anandan<sup>\*[a]</sup>

<sup>[a]</sup>Nanomaterials and Solar Energy Conversion Laboratory, Department of Chemistry, National

Institute of Technology, Trichy-620 015, India.

<sup>[b]</sup>The Center of Excellence for Advanced Materials Research, King Abdulaziz University,

Jeddah 21413, P.O. Box 80203, Saudi Arabia.

\* Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133.

E-mail addresses: sanand@nitt.edu, sanand99@yahoo.com (S. Anandan).

#### ABSTRACT

Two new bi-anchoring organic sensitizers of type D- $(\pi$ -A)<sub>2</sub> comprising the identical  $\pi$ -spacer (thiophene-2-acetonitrile) and electron acceptor (malonic acid) but different aryl amine as electron donors (diphenylamine and carbazole) were synthesized, characterized and fabricated metal free dye-sensitized solar cell devices. The intra molecular charge transfer property and electrochemical property of these dyes were investigated by molecular absorption, emission, cyclic voltammetric experiments and in addition, quantum chemical calculation studies were performed to provide sufficient driving force for the electron injection into the conduction band of TiO<sub>2</sub> which leads to efficient charge collection. Among the fabricated devices, carbazole based device exhibits high current conversion efficiency ( $\eta$ = 4.7 %) with a short circuit current density ( $J_{SC}$ ) 15.3 mA/cm<sup>2</sup>, an open circuit photo voltage ( $V_{OC}$ ) of 0.59 V and a fill factor of 0.44 under AM 1.5 illumination (85 mW/cm<sup>2</sup>) compared to diphenylamine based device.

Keywords: DSSCs, malonic acid, binding strength, planar nature, electron lifetime.

#### 1. Introduction

Dye-sensitized solar cells (DSSCs) have become one of the most promising alternatives to silicon-based photovoltaic devices [1] due to its remarkable performances in converting solar energy to electricity at low cost fabrications after the pioneering research work published by O'Regan and Gratzel in 1991 [2]. There are four main factors: anode [3], cathode [4], electrolyte [5] and sensitizer [6], that plays a major role in the DSSCs performance improvement. As a key part of DSSCs, the dye (metal-based and metal free) sensitizers take the function of light absorption and generation of the electric charges [7]. Apart from precious metal-based sensitizers (ruthenium sensitizers shows power conversion efficiency ( $\eta$ ) > 10%) [8], the metal free organic dyes have also achieved up to 10% efficiency under AM 1.5 G sunlight intensity [9]. In order to gain effective photo induced intramolecular charge transfer characteristics, most of the efficient organic sensitizers are modelled as donor- $\pi$ -spaceracceptor/anchoring (D- $\pi$ -A) architecture [10] and it provides grand flexibility of molecular tailoring, simple preparation process of low cost, high molar extinction coefficients, high purity and less environment issues. In general, TiO<sub>2</sub> semiconductor act as a photocatalyst for dye degradation and organic transformation processes [11-14], whereas in DSSC charge regeneration takes place by bonding dye molecules towards  $TiO_2$  surface. However, to design and syntheses of such more efficient organic dyes are still a challenge [15]. The main reason for the low conversion efficiency of metal free DSSCs is its lower  $V_{oc}$  [16], sharp absorption band in the visible region [17], lower binding strength of dye on the TiO<sub>2</sub> surface [18] and lower stability [19]. To rectify these problems researchers tailoring the D-π-A core structure by substituting appropriate functional groups. Further, the presence of only one anchoring functionality per molecule raise a serious constraint in organic dyes with respect to Ru (II) sensitizers (N3 dye); where upon, minimum 4 anchoring groups are readily available for tuneable interfacial electron transfer processes [20]. Recently, many groups reported bi-branched bi-anchoring dyes  $[D-(\pi-A)_2]$  due to their extended  $\pi$ -conjugation, double binding abilities, higher photocurrent and increased efficiencies over the mono anchoring counterparts [21,22]. Hence, it is beneficial to synthesis the metal free sensitizers with more -COOH groups which will improve the binding strength and also induces the efficient charge injection from dye to semiconductor surface similar to metal based sensitizers.

A series of bi-branched bi-anchoring dyes based on cyanoacrylic acid and rodhanine-3-acetic acid as acceptor have been reported by us earlier [23-25], and in continuation introduced here malonic acid as an acceptor in bi-anchoring dyes which may further increase the interfacial electron injection by providing four anchoring – COOH groups and also increase the absorption maximum values. The reason for choosing malonic acid as an electron acceptor is: (1) it act as a better electron withdrawing group compared to cyano acetic acid and rodhanine-3-acetic acid, and (2) it also provide better anchoring groups to nanocrystalline  $TiO_2$  [26,27]. With these designed features, two new metal free organic dyes 2,2'-((5,5'-((1E,1'E)-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl))bis(thiophene-5,2-diyl))bis (methanylylidene))dimalonic acid (Car-th-Ma) and 2,2'-((5,5'-((1E,1'E)-((hexylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene -2,1-diyl))bis(thiophene-5,2-diyl))bis(methanylylidene))di



malonic acid (Dpa-th-Ma) Fig. 1, was synthesized based on carbazole or diphenylamine as donor, cyanovinylthiophene as  $\pi$ -linker and malonic acid as acceptor.

Fig. 1. Molecular structures of the new (Car-th-Ma) and (Dpa-th-Ma) sensitizers.

The synthesized dyes were characterized by <sup>1</sup>H, <sup>13</sup>C-NMR, FTIR and mass; and their photophysical, electrochemical properties were investigated. The photophysical properties of the new dyes in solution and in thin films were investigated by absorption spectroscopy and solution mode photoluminescence (PL) spectroscopy. The redox properties of the new dyes were investigated by cyclic voltammetry and density functional theory (DFT) calculations. The synthesized dyes were used as a sensitizer in TiO<sub>2</sub> based DSSCs.

#### 2. Experimental Section

#### 2.1. Materials

All reagents and chemicals were purchased from Alfa Aesar and Sigma-Aldrich and used without further purification unless specified otherwise. All solvents were dried by refluxing for at least 24 h over CaH<sub>2</sub> and freshly distilled prior to use. All column chromatographic separations were carried out on Merck silica gel (60-120 mesh). FTO glass plates (sheet resistance  $10\Omega/\Box$ ) were purchased from BHEL, INDIA. The photoanode was prepared by the following procedure as follows: [28] Glacial acetic acid (5 mL), 7.5 mL of tetra isopropyl titanate (C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti) and one drop of Triton X-100 were mixed with 15 mL of 2-propanol. Water (5 mL) was added to the above solution drop wise while vigorously stirring the solution. The resulting semi colloidal suspension was dispersed on fluorine doped tin oxide (FTO) conducting glass plate by doctor blade technique. Loose crust of particles on the TiO<sub>2</sub> film was removed by wiping smoothly using cotton wool. The thickness of the TiO<sub>2</sub> film was successively controlled, by repeating the above coating procedure. Then it was sintered at 450 °C for 1 h for removing the binder, solvent and getting an electrically-connected network of TiO<sub>2</sub> particles by burning under tubular furnace. After the sintering process, when the temperature of the plate drops to 50 °C to 70 °C, it was immersed into the dye solution and leave for 24 h. Excess non-adsorbed dye were washed with anhydrous ethanol. The Platinum catalyst counter electrode

was prepared by deposition of  $H_2PtCl_6.6H_2O$  solution (0.005 mol/dm<sup>3</sup> in isopropanol) onto FTO glass and then sintering at 400 °C for 20 min [29,47]. The DSSC device was fabricated by the following method: the photo cathode was placed on top of the photo anode and was tightly clipped together. Then, liquid electrolyte 0.05 M  $I_2/0.1$  M LiI/0.5 M 4-tert-butyl pyridine (TBP) in 3-methoxypropionitrile was injected in-between the two electrodes.

#### 2.2. Instruments

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were realized on a 300/400 MHz BRUKER spectrometer in deuterated chloroform or dimethylsulfoxide solution at 298 K. Chemical shifts (& values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. The molecular weights of the dyes were determined by Micromass QUATTRO 11 ESI-MS spectrometer coupled to a Hewlett Packard series 1100 degasser. ATR-FTIR spectra were measured with a thermo spectrophotometer system equipped with a ZnSe prism. Absorption and fluorescence spectra were measured in DMF solution on a Specord S 600 diode-array UV-Vis spectrophotometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively. Electrochemical measurements were performed on a Metrohm Autolab PGSTAT potentiostat/galvanostat-84610. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum disc working electrode, a glassy carbon (GC) auxiliary electrode, and an Ag/AgCl (aq) was used as the reference electrode. The potentials were reported vs ferrocene as standard using a scan rate of  $0.1 \text{ Vs}^{-1}$  and the sample solutions contained  $3 \times 10^{-4} \text{ M}$ sample and 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous DMF as a supporting electrolyte under Argon atmosphere. Electrochemical impedance spectroscopy (EIS) measurements were done under 85 mW/cm<sup>2</sup> light illumination by using an Autolab PGSTAT potentiostat/galvanostat-84610. The impedance spectra were recorded with a frequency ranging between 10 kHz to 1 Hz at their open circuit potential (OCP). The IPCE spectra were recorded using Oriel 300W Xe Arc lamp in combination with an Oriel Cornerstone 260<sup>1</sup>/<sub>4</sub> monochromator. The number of incident photons was calculated for each wavelength using a calibrated monocrystalline silicon diode as reference.

#### 2.3. Synthesis

### 2.3.1. Synthesis of 9-hexyl-9H-carbazole (1a) [30]

1-Bromohexane (5 g, 1.7 eq), carbazole (3 g, 1 eq) and sodium hydroxide (6 g, 8.4 eq) were added to dimethylsulfoxide (DMSO) (45 mL), followed by heating at 110 °C for 12 h. After cooling to room temperature the resulting mixture was extracted with Ethyl acetate (EA)/water and then dried with  $Na_2SO_4$ . The solvent was evaporated and the resulting crude was purified by column chromatography on silica gel (60-120 mesh) by using hexane as solvent to give white solid with yield 88.22% (3.97 g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 8.18 (d, 2H, J=7.6Hz), 7.56-7.54 (m, 2H), 7.52-7.46 (m, 2H), 7.31 (t, 2H, J=7.2Hz), 4.33 (t, 2H, J=7.2Hz), 1.96-1.89 (m, 2H), 1.54-1.37 (m, 6H), 0.96 (d, 3H, J=6.8Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 140.35, 125.48, 122.75, 120.25, 118.61, 108.57, 42.90, 31.51, 28.84, 26.89, 22.48, 13.97.

#### 2.2.2. Synthesis of 9-hexyl-9H-carbazole-3, 6-dicarbaldehyde (1b) [31]

Freshly distilled POCl<sub>3</sub> (36 mL, 25 eq) was added drop wise to DMF (27 mL, 23 eq) under N<sub>2</sub> atmosphere at 0 °C, and then it was stirred for 1 h. Compound 1a (3.89 g, 0.015 mol) was added to the above solution, and then resulting mixture was stirred for 4 h at 95 °C. After cooling to room temperature, the mixture was poured into a beaker containing ice-cube, and basified with 6 M NaOH. Filtered the solid and dried. The solid crude product was purified by column chromatography on silica gel (60-120 mesh) by using Ethyl acetate/Hexane (1:4), to give a white solid (2.94 g, yield = 63.46%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 10.13 (s, 2H), 8.67 (d, 2H, J=1.5 Hz), 8.10-8.08 (m, 2H), 7.55 (d, 2H, J =8.5 Hz), 4.39 (t, 2H, J =7.5 Hz), 1.94-1.88 (m, 2H), 1.41 (d, 2H, J =7 Hz), 1.38-1.30 (m, 4H), 0.86 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 191.43, 144.73, 129.61, 127.79, 124.19, 123.12, 109.72, 43.78, 31.39, 28.89, 26.81, 22.42, 13.90.

### 2.2.3. Synthesis of (2E, 2'E)-3, 3'-(9-hexyl-9H-carbazole-3, 6-diyl) bis (2-(thiophen-2-yl) acrylonitrile) (1c) [23]

Freshly distilled methanol (100 mL) was taken in a 250 mL single neck round bottom flask. The compound 1b (3 g, 1 eq) and thiophene-2-acetonitrile (2.65 g, 2.2 eq) were added to the methanol. A catalytic amount of potassium tert-butoxide was added into this mixture at room temperature. Then the reaction mixture was stirred for 12 h at 50 °C. It was monitored by TLC. A bright yellow solid was filtered after 12 h. It was recrystallized in dichloromethane and methanol to give the product 2.6 g (yield = 52%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 8.60-8.50 (m, 2H), 8.12-8.09 (m, 2H), 7.51-7.45 (m, 2H), 7.42-7.38 (m, 2H), 7.26 (s, 2H), 7.13-7.10 (m, 2H), 7.04-7.00 (m, 2H), 4.32 (t, 2H, J=7.2 Hz), 1.93-1.55 (m,2H), 1.39-1.25 (m, 6H), 0.89-0.87 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 142.22, 140.77, 140.08, 128.21, 127.42, 126.47, 125.60, 123.32, 122.93, 117.91, 109.87, 103.17, 43.79, 31.64, 29.14, 27.05, 22.66, 14.13.

# 2.2.4. Synthesis of (2E,2'E)-3,3'-(9-hexyl-9H-carbazole-3,6-diyl)bis(2-(5-formylthiophen-2-yl)acrylonitrile) (1d) [31]

DMF (7 mL, 23 eq) was taken in a 100 mL 3 neck round bottom flask. To this freshly distilled POCl<sub>3</sub> (9 mL, 25 eq) was added drop wise under an atmosphere of  $N_2$  at 0 °C, and then it was stirred for 1 h. 2 g of compound 1c was added to the above solution, and the resulting mixture was stirred for 4 h at 95 °C. It was monitored by TLC. After the completion of the reaction, it was cooled to RT, and then the reaction mixture was poured into a beaker containing ice-cubes, and basified with 6 M NaOH. It was extracted with dichloromethane/brine. After evaporating the organic solvent the crude product was purified by column chromatography on silica using a mixture of Ethyl acetate/Hexane (1:4, v/v), to give an orange colour solid 1.04 g (yield = 47%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 10.14 (s, 2H), 8.15-8.17 (m, 2H), 7.57 (s, 2H), 7.47 (d, 2H,J=8.8 Hz), 7.39 (s, 2H), 7.39-7.29 (m, 2H), 7.26 (s, 2H), 7.10-7.08 (m, 2H), 4.33 (t,2H, J=7.2 Hz), 1.92-1.88 (m, 2H), 1.55-1.25 (m, 6H), 1.38-1.25 (m, 4H), 0.89-0.86 (m,3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 180.94, 147.37, 144.52, 140.54, 125.67, 122.92, 120.44, 118.79, 113.02, 108.76, 107.19, 90.92, 43.15, 31.71, 29.04, 27.09, 22.67, 14.15.

2.2.5. Synthesis of 2,2'-((5,5'-((1E,1'E)-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl))bis(thiophene-5,2-diyl))bis(methanylylidene))dimalonic acid (1e)

Freshly distilled acetonitrile (30 mL) was taken in a 100 mL 2 neck round bottom flask. 1 g of compound 1d was added to the above solvent and maintains the reaction at 60 °C and piperidine (0.482 mL, 2.8 eq), malonic acid (0.430 mg, 2.4 eq) was added to the above solution, and then refluxed it for overnight. It was monitored by TLC. After completion of the reaction, cooled to room temperature (RT) and then distillate the solvent by using rotovac evaporator, then the solid compound was washed with 1:1 ratio of CHCl<sub>3</sub>:CH<sub>3</sub>OH mixture. Filter the dark red colour solid compound about 47 mg (yield = 36.5%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 8.59 (s, 1H), 8.27 (s, 1H), 8.00 (s, 2H), 7.83 (s, 2H), 7.79 (m, 2H), 7.74 (m, 2H), 7.64 (d, 1H, J=8.4 Hz), 7.52 (m, 1H), 7.31 (d, 1H, J=8 Hz), 7.26 (s, 1H), 4.30-4.21 (m, 2H), 1.84 (m, 2H), 1.65 (m, 2H), 1.41-1.25 (m, 4H), 0.84 (s, 3H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, ppm): δ 166.18, 156.34, 153.15, 146.47, 143.12, 141.42, 132.10, 126.73, 125.54, 124.86, 115.07, 105.10, 45.21, 31.45, 26.54, 22.17, 14.81. ESI-MS Anal. Calcd. for  $C_{40}H_{31}N_{3}O_8S_2$ : 745.82. Found: 746.

### 2.2.6. Synthesis of N-hexyl-N-phenylaniline (2a) [30]

It was synthesized according to the procedure of 1a whereas diphenylamine is used as starting compound instead of carbazole. The product obtained was colourless liquid (yield = 81.7%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.27-7.23 (m, 4H), 6.98-6.96 (m, 4H), 6.94-6.91 (m, 2H), 3.67 (t, 2H, J=8Hz), 1.66-1.62 (m, 2H), 1.35-1.26 (m, 6H), 0.88-0.85 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 148.05, 129.15, 120.95, 120.82, 52.28, 31.59, 27.36, 26.71, 22.62, 13.99.

#### 2.2.7. Synthesis of 4, 4'-(hexylazanediyl) dibenzaldehyde (2b) [31]

It was synthesized according to the procedure of 1b by using compound 2a. The product is brown colour liquid (yield = 94%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 9.85 (s, 2H), 7.78 (d, 4H, J=8.4 Hz), 7.13 (d, 4H, J=8.4 Hz), 3.82 (t, 2H, J=8.0Hz), 1.67 (d, 4H, J=8.4 Hz), 1.33-1.26 (m, 6H), 0.85 (t, 3H, J=6.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 190.25, 148.89, 129.92, 121.95, 121.69, 52.31, 31.69, 27.42, 26.90, 22.69, 13.87.

2.2.8. Synthesis of (2E, 2'E)-3, 3'-(4, 4'-(hexylazanediyl) bis (4, 1-phenylene)) bis (2-(thiophen-2-yl) acrylonitrile) (2c) [23]

It was synthesized according to the procedure of 1c by using compound 2b. The product obtained was red colour solid (yield = 68.5%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.79 (d, 2H, J=10.4 Hz), 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.26-7.22 (m, 2H), 7.12-7.04 (m, 4H), 6.97-6.95 (m, 2H), 3.80 (t, 2H, J=8.0 Hz), 1.72-1.66 (m, 2H), 1.38-1.25 (m, 6H), 0.91-0.87 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 148.82 139.91, 139.26, 130.89, 128.22, 126.98, 126.54, 125.67, 120.93, 117.61, 103.21, 52.49, 31.69, 27.68, 26.82, 22.76, 14.14.

2.2.9. Synthesis of (2E,2'E)-3,3'-((hexylazanediyl)bis(4,1-phenylene))bis(2-(5-formylthiophen-2-yl)acrylonitrile) (2d) [31]

It was synthesized from compound 2c according to the similar procedure of 1d. The product was red colour solid (yield = 39%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 9.87 (s, 2H), 7.88 (d, 4H, J=8.8 Hz), 7.71 (d, 2H, J= 4Hz), 7.47 (s, 2H), 7.41 (d,2H, J=4 Hz) 7.15-7.13 (m, 4H), 3.84 (t, 2H, J=8.0 Hz), 1.73 -1.62 (m, 2H), 1.38-1.34 (m, 2H), 1.32-1.25 (m, 4H), 0.90-0.87 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 182.56, 149.53, 149.01, 142.67, 142.45, 137.11, 131.74, 126.94, 126.48, 121.07, 116.80, 102.18, 52.57, 31.63, 27.72, 26.76, 22.72, 14.11.

2.2.10. Synthesis of 2,2'-((5,5'-((1E,1'E)-((hexylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene-2,1diyl))bis(thiophene-5,2-diyl))bis(methanylylidene))dimalonic acid (2e)

It was synthesized according to the procedure of 1e by using compound 2d. The product was dark red colour solid (yield = 37.9%).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): 8.31 (s, 2H), 8.16 (s, 2H), 7.91 (d, 2H, J=8.7 Hz), 7.85-7.82 (m, 2H), 7.73-7.60 (m, 4H), 7.56-7.32 (m, 2H), 7.22-7.01 (m, 2H), 2.97 (s, 2H), 1.57 (m, 2H), 1.33 (m, 2H), 1.21 (m, 4H), 0.84 (m, 3H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, ppm): δ 165.87, 159.28, 157.16, 149.24, 140.72, 134.86, 130.61, 120.54, 120.12, 119.67, 114.17, 107.24, 50.64, 30.95, 29.15, 26.95, 22.54, 13.71. ESI-MS Anal. Calcd. for  $C_{40}H_{33}N_3O_8S_2$ : 747.84. Found: 747.

#### 3. Results and Discussion

### 3.1 Synthesis of organic dyes

The synthetic pathways of organic dyes Car-th-Ma and Dpa-th-Ma were depicted in scheme 1. The electron-donor part, N-hexyl diphenylamine and N-hexyl carbazole are synthesized by hexylation of diphenylamine and carbazole in basic DMSO medium and then coupled with cyanovinylthiophene  $\pi$ -linker via Vilsmeier-Haack formylation reaction followed by Knoevenagel condensation. Then the product is coupled with anchoring malonic acid group through Vilsmeier-Haack formylation reaction followed by Knoevenagel condensation. All the intermediates and target products were purified by column chromatography and the new compounds were well confirmed by various analytical tools (See Supporting information).



Scheme 1. Synthetic pathway of the organic dyes. (i) 1- Bromohexane, NaOH, DMSO, 110 °C . (ii) POCl<sub>3</sub>, DMF, 95 °C. (iii) 2-(thiophene-2-yl)-acetonitrile, t-BuOK, CH<sub>3</sub>OH, refluxed. (iv) POCl<sub>3</sub>, DMF, 95 °C. (v) Malonic acid, piperidine, acetonitrile, refluxed.

### 3.2 Photophysical properties

The UV-Vis spectra of the synthesized organic dyes in DMF solution  $(6 \times 10^{-5} \text{ M})$  and adsorbed on TiO<sub>2</sub> film are presented in Fig. 2 and 3, respectively and the detailed parameters are collated in Table 1. As can be seen in Fig. 2, Car-th-Ma and Dpa-th-Ma exhibit obvious maximum absorption peaks at two distinct regions. The higher energy peaks at 299 nm ( $\varepsilon$ =27,971 M<sup>-1</sup> cm<sup>-1</sup>) for Car-th-Ma and at 273 nm ( $\varepsilon$ =38,426 M<sup>-1</sup> cm<sup>-1</sup>) for Dpa-th-Ma dyes can be ascribed to a  $\pi$ - $\pi$ \* transition of the conjugated aromatic rings and the lower energy peaks at 537 nm ( $\varepsilon$ =43,411 M<sup>-1</sup> cm<sup>-1</sup>) for Car-th-Ma and at 465 nm ( $\varepsilon$ =35,080 M<sup>-1</sup> cm<sup>-1</sup>) for Dpa-th-Ma can be attributed to the

intramolecular charge transfer (ICT) between the arylamine donating unit and malonic acid acceptor/anchoring moiety, thereby producing an efficient charge separated state [32].



Fig. 2. Absorption and emission spectra of Car-th-Ma and Dpa-th-Ma dyes recorded in DMF.

In that spectra, the Car-th-Ma dye red shifted by 72 nm and its molar extinction coefficients were 8,331 times greater than the Dpa-th-Ma which is reasoned out with the help of DFT calculations, that the former (Car-th-Ma) has the dihedral angles of the corresponding ring units R1-R2 is  $0.25^{\circ}$  and R1-R3 is  $-179.1^{\circ}$ , supports more planar configuration and hence more delocalization over entire conjugate system upon compared to Dpa-th-Ma [33]. Fig. 3 shows the absorption spectra of the dye loaded TiO<sub>2</sub> films after 24 h immersion of TiO<sub>2</sub> films in dye solution. The maximal absorption peaks for Car-th-Ma and Dpa-th-Ma are at 513 nm and 478 nm respectively. Upon comparing with the absorption spectra of the corresponding dyes in solution Car-th-Ma shows blue shifted by 24 nm may be due to the H-aggregation, i.e., the aggregation of the dyes on the surface of TiO<sub>2</sub> nanoparticles due to strong interactions between the dyes and semiconductor surface [34] and such phenomenon has been found in other organic dyes reported earlier [35-37].

Whereas, Dpa-th-Ma dye shows red shifted by 13 nm may be due to the J-aggregation [38] occurred by increased delocalization of the  $\pi^*$  orbital of the conjugated framework caused by the interaction between the carboxylate group and Ti<sup>4+</sup> ions that directly decreases the energy of the  $\pi^*$  level [39] respectively. The absorption spectra of the dyes became broadened after adsorption on the TiO<sub>2</sub> surface, which should favor the light harvesting of the solar cells [40]. Further, the introduction of malonic acid electron acceptor shifts the absorption bands of the both dyes to red region compare to cyano acetic acid electron acceptor [23]. The fluorescence spectra recorded upon

their excitation of absorption maxima value of Car-th-Ma and Dpa-th-Ma exhibit strong luminescence maxima at 661 nm ( $\lambda_{ex} = 577$  nm) and 578 nm ( $\lambda_{ex} = 483$  nm) respectively.



Fig. 3. Absorption spectra of Car-th-Ma and Dpa-th-Ma dyes adsorbed on nanocrystalline TiO<sub>2</sub> films.

#### 3.3 Electrochemical properties

The estimation of the energy levels, the effect of arylamine donors on the energy level of the synthesized dyes and the electron transfer from the excited dye molecule to conductive band ( $E_{cb}$ ) of TiO<sub>2</sub> were measured by cyclic voltammetry (Fig. 4) and their data are summarized in Table 1. The onset oxidation potentials  $E_{onset}^{ox}$  are observed at 0.72 V and 1.07 V were determined from the intersection of two tangents drawn at the rising current and background charging current of a cyclic voltammograms [41] for Car-th-Ma and Dpa-th-Ma dyes respectively. The HOMO energy levels were calculated based on the relationship of HOMO (eV) = -e ( $E_{onset}^{ox}$  V (vs Fc/Fc<sup>+</sup>) + 4.8 V) by assuming the ferrocene (Fc) energy level to be -4.8 eV below the vacuum level [42], these HOMO values are positive than I7I<sub>3</sub><sup>-</sup> redox couple (-4.6 eV vs vacuum) which may further improved negatively about 0.3 V by adding additives such as 4-*tert*-butylpyridine (TBP) to the  $\Gamma/I_3^-$  redox electrolyte [43]. The LUMO levels of the dyes were calculated by ( $E_{onset}^{ox}$ ) -  $E_{0.0}$ , where  $E_{0.0}$  is the zero-zero energy of the dyes estimated from the intersection between absorption and emission spectra [44,45]. Probably, the LUMO energy values are negative than of conduction band (Fig. 5), provides sufficient driving force for the electron injection into the conduction band of TiO<sub>2</sub> which leads to efficient charge collection [46]. Further, the HOMO and LUMO energy levels of the synthesized dyes are very suitable for the electron regeneration from the electrolyte  $\Gamma/I_3^-$  and electron injection to the conduction band of TiO<sub>2</sub> respectively.



Fig. 4. Cyclic voltammograms of dyes were measured in DMF solution with Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as an electrolyte. Working electrode: Pt; reference electrode: Ag/AgCl (aq); counter electrode: Glassy carbon; calibrated with Fc/Fc<sup>+</sup> as a standard reference; scan rate: 0.1 Vs<sup>-1</sup>.

#### Table 1

Optical, electrochemical data and HOMO, LUMO energy levels of Car-th-Ma and Dpa-th-Ma dyes.

Dye	λ <sub>abs</sub> /nm (ε(M <sup>-1</sup> cm <sup>-1</sup> )) <sup>a</sup>	λ <sub>em</sub> /nm <sup>a,b</sup>	$E_g^{opt}(eV)^c$	E <sub>ox</sub> /V(vs, Fc)	Е <sub>номо</sub> (eV) <sup>d</sup>	E <sub>LUMO</sub> (eV) <sup>d</sup>	HOMO <sup>e</sup>	LUMO <sup>e</sup>
Car-th-Ma	537 (43,411)	661	1.99	0.72	5.07	3.08	-5.70	-2.88
Dpa-th-Ma	465 (35,080)	578	2.30	1.07	5.42	3.12	-5.47	-3.08
<sup>a</sup> Absorption and emission spectra were recorded in DMF solution ( $6 \times 10^{-5}$ M) at room temperature.								
<sup>b</sup> Dyes were excited at their absorption maximum value (for Car-th-Ma, $\lambda_{ex}$ = 577 nm and for Dpa-th-Ma, $\lambda_{ex}$ = 483								

nm).

<sup>c</sup> Optical band gap calculated from intersection between the absorption and emission spectra.

<sup>d</sup> The values of  $E_{HOMO}$  and  $E_{LUMO}$  were calculated with the following: HOMO (eV)= -e ( $E_{onset}^{ox}$  V (vs Fc/Fc<sup>+</sup>) + 4.8 V); LUMO (eV)= ( $E_{onset}^{ox}$ ) -  $E_{0-0}$ , where  $E_{0-0}$  is the intersection between the absorption and emission spectra of the sensitizers.

<sup>e</sup> B3LYP/6-31G(d) calculated values.



Fig. 5. Energy level diagrams of Car-th-Ma and Dpa-th-Ma dyes from electrochemical data.

#### 3.4. Computational analysis

To get an insight into the molecular structure and electron distribution of the synthesized organic dyes, their geometries have been optimized by density functional theory (DFT) calculations using B3LYP/6-31 G (d) level in gas phase with Gaussian 09 program. The electron distribution of HOMO and LUMO of the dyes with optimized structures were shown in Fig. 6 and the calculated HOMO and LUMO energies of the dyes were listed in Table 1. The dihedral angle in  $\angle$ C-N-C-C (R2-R3) is -142.6° and in  $\angle$ C-N-C-C (R3-R2) is -155.5° for Dpa-th-Ma, and the dihedral angle in  $\angle$ C-N-C-C (R1-R2) 0.25° and in  $\angle$ C-N-C-C (R1-R3) -179.1° for Car-th-Ma dye. However in Car-th-Ma and Dpa-th-Ma, the electron density is mainly localized at the electron donors as well as thiophene moieties at both sides in HOMO, whereas in LUMO electron density is localized only at the thiophene and electron withdrawing malonic acid moieties. This indicates that in both dyes the intra molecular charge transfer (ICT) takes place from donor moiety to withdrawing group through the  $\pi$ -bridge. Therefore, the expected spatial orientation of HOMO and LUMO levels for the dyes is suitable for DSSCs, which can facilitate the interfacial electron injection from the excited dye to the conduction band of TiO<sub>2</sub>.



Fig. 6. The frontier HOMO and LUMO orbitals of Car-th-ma and Dpa-th-ma dyes.

#### 3.5. Photovoltaic performance of the DSSCs

TiO<sub>2</sub> nanoparticles were prepared according to the literature [28] and it was coated on a FTO glass substrate with an effective area of 0.49 cm<sup>2</sup>. This plate was immersed in a DMF solution containing  $3 \times 10^{-4}$  M dye sensitizers for 24 h. The photo cathode was prepared by H<sub>2</sub>PtCl<sub>6</sub> (50 mM in isopropyl alcohol) solution which is deposited on the FTO glass by drop casting and heated at 400 °C for 20 min [29,47]. The device was fabricated as follows: the photo cathode was placed on top of the photo anode and was tightly clipped together. Then, 0.05 M I<sub>2</sub>/0.1 M LiI/0.5 M 4-*tert*- butyl pyridine (TBP) in 3-methoxypropionitrile electrolyte was injected in-between the two electrodes.

The current-voltage (*I-V*) curves of the fabricated DSSCs sensitized by the Car-th-Ma and Dpa-th-Ma dyes are shown in Fig. 7 and the performance statistics were tabulated in Table 2. Among the two dyes, Car-th-Ma dye showed high efficiency due to high  $J_{SC}$  and  $V_{OC}$ , mainly high  $J_{SC}$  contributed by longer wavelength absorption with high molar extinction coefficient in the series. Probably, the low band gap value of Car-th-Ma suggest an increase in  $J_{SC}$  values, which may leads to further increase in device efficiency. Further, the planar nature of carbazole moiety facilitates the good adsorption on TiO<sub>2</sub> surface which may be reason for the higher efficiency of Car-th-Ma.

The spectra of incident photon to current conversion efficiency (IPCE) (Fig. 8) almost covers the entire visible region, similar to the absorption spectrum of the dye adsorbed thin  $TiO_2$  layer, facilitating the DSSCs to efficiently convert solar light to electricity. The IPCE spectra of Car-th-Ma showed 24% in the range of 444 - 508 nm. In contrast, the IPCE of Dpa-th-Ma gives relatively low values (15%) at the wavelength maximum (478 nm), which might be due to the poor injection efficiency arising from the unfavourable binding at the  $TiO_2$  surface [48].



Fig. 7. Current density-voltage characteristics for Car-th-Ma and Dpa-th-Ma based devices for DSSCs under illumination of simulated solar light (AM 1.5, 85 mW/cm<sup>2</sup>).



Fig. 8. IPCE spectra of the fabricated devices based on Car-th-Ma and Dpa-th-Ma dyes.



Fig. 9. Nyquist plots of DSSCs based on Car-th-Ma and Dpa-th-Ma dyes under illumination of simulated solar light (AM 1.5, 85 mW/cm<sup>2</sup>).

This is further confirmed by calculating the adsorbed amounts ( $\Gamma$ ) of dyes on TiO<sub>2</sub> surface by desorption of the dye from the TiO<sub>2</sub> surface using 0.1 M NaOH in DMF/H<sub>2</sub>O (1:1) mixture [34]. From these results, Car-th-Ma adsorbs comparatively more than Dpa-th-Ma dye may be due to the planar nature of Car-th-Ma dye on TiO<sub>2</sub> surface, probably this may augment the device efficiency.

The electrochemical impedance spectroscopy (EIS) analysis [49] was performed to understand the correlation between the improved cell performance and internal resistance, and to confirm relation between  $V_{OC}$  and the charge recombination rate of the fabricated DSSCs over a frequency range of  $10^{0}$ - $10^{4}$  Hz under AM 1.5. The Nyquist plot displayed in Fig. 9 looks like a semicircle which corresponds to the charge transfer resistance at the counter electrode and TiO<sub>2</sub>/dye/electrolyte interface. The diameter of the bigger semicircle in the order of Dpa-th-Ma $\angle$  Car-th-Ma, which means that the electron recombination resistance is high for Car-th-Ma dye on the TiO<sub>2</sub>/electrolyte interface, and it is in accordance with the  $V_{OC}$  value of the device [10,50]. The electron lifetime for Car-th-Ma (7.16 ms) is high compare to Dpa-th-Ma (2.79 ms), which can be measured from bode plot Fig. 10. Probably, the lower electron recombination and longer electron lifetime of Car-th-Ma further induce the device efficiency [51]. Malonic acid based device [23], which may be the reason for higher efficiency of malonic acid based device.





(AM 1.5, 85 mW/cm<sup>2</sup>).

#### Table 2

DSSC performance parameters of the fabricated devices.

Dye	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)	FF	η (%) <sup>ª</sup>	Electron	Surface			
					lifetime	concentration			
					(τ <sub>eff</sub> ) (ms)	Γ(mol/cm²)			
Car-th-Ma	15.3	590	0.44	4.7	7.16	4.0 x 10 <sup>-5</sup>			
Dpa-th-Ma	13.3	558	0.47	4.1	2.79	1.0 x 10 <sup>-5</sup>			
<sup>a</sup> Illumination: 85 mW/cm <sup>2</sup> simulated AM 1.5 G solar light; electrolyte containing: 0.05 M I <sub>2</sub> /0.1 M Lil/0.5 M 4- <i>tert</i> -butyl pyridine in 3-methoxypropionitrile.									

### 3.6. Adsorption of Dyes on the TiO<sub>2</sub> surface: ATR-FTIR Studies

Fourier-transform infrared (FTIR) spectra of the Car-th-Ma (Fig. 11a) dye shows most prominent bands for C=O stretching at 1674 cm<sup>-1</sup>, -C=N stretching at 2210 cm<sup>-1</sup>, and asymmetric and symmetric stretching modes of the aliphatic –CH<sub>2</sub> groups at 2931 and 2858 cm<sup>-1</sup> respectively. And the Dpa-th-Ma dye (Fig. 12a) shows prominent bands for C=O stretching at 1672 cm<sup>-1</sup>, -C=N stretching at 2210 cm<sup>-1</sup>, and asymmetric and symmetric stretching modes of the aliphatic –CH<sub>2</sub> groups at 2921 and 2856 cm<sup>-1</sup> respectively. An attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy has been shown to be a powerful tool to extract structural information about the dye adsorbed onto the TiO<sub>2</sub> surface [52]. The spectrum of Car-th-Ma dye (Fig. 11b) anchored on TiO<sub>2</sub> shows bands at 1627 and 1389 cm<sup>-1</sup> for the asymmetric and symmetric stretching modes of the carboxylate group and complete disappearance of C=O stretching peak at 1674 cm<sup>-1</sup>.



Fig. 11. ATR-FTIR spectra of the Car-th-Ma dye obtained using a solid sample and adsorbed on a nanocrystalline TiO<sub>2</sub> film.

Similarly, Dpa-th-Ma dye (Fig. 12b) also shows bands at 1630 and 1390 cm<sup>-1</sup> for the asymmetric and symmetric stretching modes of the carboxylate group and complete disappearance of C=O stretching peak at 1672 cm<sup>-1</sup>. From these ATR-FTIR data, it can be inferred that the dye is anchored on the surface through the carboxylate groups via a bidentate chelation or a bridging of surface titanium ions rather than an ester type linkage [53]. In addition, the peaks observed for Car-th-Ma dye (at 2952, 2856 cm<sup>-1</sup>) and for Dpa-th-Ma dye (at 2926, 2857 cm<sup>-1</sup>) are corresponds to the asymmetric and symmetric stretching modes of the aliphatic  $-CH_2$  groups, while peaks for  $-C\equiv N$  group stretching for Car-th-Ma (at 2221 cm<sup>-1</sup>) and for Dpa-th-Ma (2211 cm<sup>-1</sup>), and finally the observed large and broad absorption band centered at 3423 cm<sup>-1</sup> may be due to adsorbed moisture presumably from the dye solution since the TiO<sub>2</sub> film is heated prior to staining.



Fig. 12. ATR-FTIR spectra of the Dpa-th-Ma dye obtained using a solid sample and adsorbed on a nanocrystalline TiO<sub>2</sub> film.

### 4. Conclusion

In summary, two metal free organic dyes Dpa-th-Ma and Car-th-Ma featuring thiophene-2-acetonitrile as the  $\pi$ -spacer and malonic acid as the electron acceptor with different arylamine (diphenylamine and carbazole) as electron donors were designed and synthesized. The photophysical, electrochemical, photovoltaic and ATR-FTIR properties of the dyes were extensively studied illustrates such metal free organic dyes may be suitable for DSSCs. Among the fabricated devices, the device based on Car-th-Ma dye showed higher efficiency ( $\eta$ ) compared to Dpath-Ma dye based device. This is due to the higher  $J_{SC}$  and  $V_{OC}$ , mainly the higher  $J_{SC}$  values contributed by high absorption and high molar extinction coefficient values of Car-th-Ma as well as the low band gap energy level, the energy levels of Car-th-Ma provides sufficient driving force for the electron injection and dye regeneration. In addition to this the high electron recombination resistance and longer electron life time augment the device efficiency. From this conclusion the malonic acid provide stronger binding ability to TiO<sub>2</sub> film.

#### Acknowledgment

Author SA thank SERI-DST, New Delhi (Ref. No. DST/TM/SERI/2k12/109(C)) and DST-FIST, New Delhi (SR/FT/CSI-190/2008 dated 16th Mar 2008) for the sanction of research fund towards development of new facilities. Author GSR thanks MHRD, New Delhi for the junior research fellowship position.

#### References

[1] [1] G. Li, K.J. Jiang, Y.F. Li, S.L. Li, L.M. Yang, J. Phys. Chem. C 112 (2008) 11591–11599.

[2] B. O'Regan, M. Grätzel, Nature 353 (1991) 737-740.

- [3] N.G. Park, J. Van de Lagemaat, A.J. Frank, J. Phys. Chem. B 104 (2000) 8989-8994.
- [4] A. Hauch, Electrochimi. Acta 46 (2001) 3457–3466.
- [5] Q.B. Meng, K. Takahashi, X.T. Zhang, I. Sutanto, T.N. Rao, O. Sato, A. Fujishima, Langmuir 19 (2003) 3572-3574.
- [6] N. Robertson, Angew. Chem. Int. Ed. 45 (2006) 2338-2345.

[7] M. Katono, T. Bessho, M. Wielopolski, M. Marszalek, J.E. Moser, R.H. Baker, S.M. Zakeeruddin, M. Gratzel, J. Phys. Chem. C 116 (2012) 16876–16884.

- [8] K.J. Jiang, J.B. Xia, N. Masaki, S. Noda, S. Yanagida, Inorganica Chimi. Acta 361 (2008) 783-785.
- [9] L. Zhou, C. Jia, Z. Wana, X. Chen, X. Yao, Org. Electron. 14 (2013) 1755-1762.
- [10] M. Cheng, X. Yang, F. Zhang, J. Zhao, L. Sun, J. Phys. Chem. C 117 (2013) 9076-9083.
- [11] K. Muthu, K. Selvam, B. Krishnakumar, M. Swaminathan, Appl. Catal. A 358 (2009) 259-263.
- [12] B. Krishnakumar, R. Velmurugan, S. Jothivel, M. Swaminathan, Catal. Commun. 11 (2010) 997–1002.
- [13] B. Krishnakumar, M. Swaminathan, J. Mol. Catal. A Chemical 334 (2011) 98-102.
- [14] R. Velmurugan, B. Krishnakumar, Rajendra Kumar, M. Swaminathan, Arabian J. Chem. 5 (2012) 447-452.
- [15] A. Mishra, M.K.R. Fischer, P. Buerle, Angew. Chem. Int. Ed. 48 (2009) 2474 2499.

[16] F. Zhang, Y.H. Luo, J.S. Song, X.Z. Guo, W.L. Liu, C.P. Ma, Y. Huang, M.F. Ge, Z. Bo, Q.B. Meng, Dyes Pigm. 81 (2009) 224–230.

[17] K. Sayama, M. Sugino, H. Sugihara, Y. Abe, H. Arakawa, Chem. Lett. (1998) 753-754.

[18] K.S.V. Gupta, T. Suresh, S.P. Singh, A. Islam, L. Han, M. Chandrasekharam, Org. Electron. 15 (2014) 266–275.

- [19] H. Choia, J.K. Leea, K. Songb, S.O. Kanga, Mation, A Ko, Tetrahedron 63 (2007) 3115–3121.
- [20] R. Sirohi, D.H. Kim, S.C. Yu, S.H. Lee, Dyes Pigm. 92 (2012) 1132-1137.
- [21] K.D. Seo, B.S. You, I.T. Choi, M.J. Ju, M. You, H.S. Kang, H.K. Kim, ChemSusChem 6 (2013) 2069-2073.
- [22] A. Baheti, K.R. Justin Thomas, C.P. Lee, K.C. Ho, Org. Electron. 14 (2013) 3267–3276.
- [23] S. Ramkumar, S. Anandan, Dyes Pigm. 97 (2013) 397-404.

- [24] S. Ramkumar, S. Manoharan, S. Anandan, Dyes Pigm. 94 (2012) 503-511.
- [25] S. Ramkumar and S. Anandan, RSC Adv. 3 (2013) 21535-21543.
- [26] N.W. Duffy, K.D. Dobson, K.C. Gordon, B.H. Robinson, A.J. McQuillan, Chem. Phys. Lett. 266 (1997) 451-455.
- [27] L. Giribabu, M. Chandrasekheram, M. Lakshrni Kanthamn, V. Gopal Reddy, D. Satyanarayana, O.S. Rao, P. Yella eddy, Indian J. Chem. 45A (2006) 629-634.
- [28] P.M. Sirimanne, H. Tributsch, J. Solid State Chem. 177 (2004) 1789-1795.
- [29] J. He, W. Wu, J. Hua, Y. Jiang, S. Qu, J. Li, Y. Long, H. Tian, J. Mater. Chem. 21 (2011) 6054-6062.
- [30] J.H. Park, N.S. Cho, Y.K. Jung, H.J. Cho, H.K. Shim, H. Kim, Org. Electron 8 (2007) 272-285.
- [31] T. Mallegol, S. Gmouh, M.A.A. Meziane, M.B. Desce, O. Mongin, Synthesis 11 (2005) 1771-1774.
- [32] Z. Ci, X. Yu, M. Bao, C. Wang, T. Ma, Dyes Pigm. 96 (2013) 619-625.
- [33] W. Wu, J. Yang, J. Hua, J. Tang, L. Zhang, Y. Long, H. Tian, J. Mater. Chem. 20 (2010) 1772-1779.
- [34] H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt, L. Sun, J. Phys. Chem. C 112 (2008) 11023-11033.
- [35] K. Hara, Z.S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, et al, J. Phys. Chem. B 109 (2005) 15476-15482.
- [36] H.N. Tian, X.C. Yang, R.K. Chen, Y.Z. Pan, L Li, A Hagfeldt, et al, Chem. Commun. (2007) 3741-3743.
- [37] M.K.R. Fischer, S. Wenger, M.K. Wang, A. Mishra, S.M. Zakeeruddin, M. Grätzel, et al, Chem. Mater. 22 (2010) 1836-1845.
- [38] M. Guo, P. Diao, Y.J. Ren, F. Meng, H. Tian, S.M. Cai, Sol. Energy Mater. Sol. Cells 88 (2005) 23-35.
- [39] Y. Ooyama, Y. Harima, Eur. J. Org. Chem. (2009) 2903-2934.
- [40] J. Shi, Z. Chai, C. Zhong, W. Wu, J. Hua, Y. Dong, J. Qin, Q. Li, Z. Li, Dyes Pigm. 95 (2012) 244-251.
- [41] A.K. Agrawal, S.A. Jenekhe, Chem. Mater. 8 (1996) 579-589.
- [42] B.J. Pomrnerehne, H. Vestweber, W. Gun, R.F. Muhrt, H. Bassler, M. Porsch, et al, Adv. Mater. 7 (1995) 551-554.
- [43] G. Boschloo, L. Ha1ggman, A. Hagfeldt, J. Phys. Chem. B 110 (2006) 13144-13150.

[44] S.T. Huang, Y.C. Hsu, Y.S. Yen, H.H. Chou, J.T. Lin, C.W. Chang, C.P. Hsu, C.T sai, D.J. Yin, J. Phys. Chem. C 112 (2008) 19739-19747.

[45] H. Tian, X. Yang, J. Cong, R. Chen, J. Liu, Y. Hao, et al, Chem. Commun. (2009) 6288-6290.

[46] P. Singh, A. Baheti, K.R. Justin Thomas, C.P. Lee, K.C. Ho, Dyes Pigm. 95 (2012) 523-533.

[47] W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, J. Phys. Chem. C 112 (2008) 874-880.

[48] D.P. Hagberg, T. Marinado, K.M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun. J. Org. Chem. 72 (2007) 9550-9556.

[49] R. Kern, R. Sastrawan, J. Ferber, R. Stangl, J. Luther, Electrochim. Acta 47 (2002) 4213-4225.

[50] J. Zhao, X. Yang, M. Cheng, S. Li, L. Sun, J. Phys. Chem. C 117 (2013) 12936-12941.

[51] K.W. Ko, M. Lee, S.S. Sekhon, S. K. Balasingam, C.H. Han and Y. Jun, ChemSusChem 6 (2013) 2117–2123.

[52] C. Klein, Md.K. Nazeeruddin, D. Di Censo, P. Liska, M. Gratzel, Inorg. Chem. 14 (2004) 4216-4226.

[53] V. Shklover, Y.E. Ovehinnikov, L. S. Braginsk, S.M. Zakeeruddin, M. Gratzel, Chem. Mater. 10 (1998) 2533-2541.

# Bi-anchoring organic sensitizers of type $D-(\pi-A)_2$ comprising thiophene-2-acetonitrile as $\pi$ -spacer and malonic acid as electron acceptor for dye sensitized solar cell applications

Gachumale Saritha Reddy<sup>[a]</sup>, Sekar Ramkumar<sup>[a]</sup>, Abdullah M. Asiri<sup>[b]</sup> and

Sambandam Anandan\*<sup>[a]</sup>

<sup>[a]</sup>Nanomaterials and Solar Energy Conversion Laboratory, Department of Chemistry, National

Institute of Technology, Trichy-620 015, India.

<sup>[b]</sup>The Center of Excellence for Advanced Materials Research, King Abdulaziz University,

Jeddah 21413, P.O. Box 80203, Saudi Arabia.

\* Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133.

E-mail addresses: sanand@nitt.edu, sanand99@yahoo.com (S. Anandan).

GRAPHICAL ABSTRACT

23

Two new bi-anchoring organic sensitizers of type  $D(\pi-A)_2$  comprising the identical  $\pi$ -spacer as thiophene-2-acetonitrile, electron acceptor as malonic acid but different aryl amine as electron donors (diphenylamine and carbazole) were synthesized for dye sensitized solar cell fabrication. Among two dyes, carbazole based device exhibits high current conversion efficiency ( $\eta$ = 4.7%) under AM 1.5 illumination (85 mW cm<sup>-2</sup>) compared to Diphenylamine based device.



24

### Highlights

- Two new bi-anchoring organic sensitizers of type  $D-(\pi-A)_2$  were synthesized and characterized
- Carbazole based device exhibits high current conversion efficiency (η= 4.7%) under AM
  1.5 illumination
- More negative LUMO energy levels provides sufficient driving force for the electron injection into TiO<sub>2</sub>

M