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### Synthesis of D-( $\pi$ -A)<sub>2</sub> organic chromophores for dye-sensitized solar cells

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn the attention of many researchers due to their ability of converting sunlight to electricity at a low cost fabrication technique with moderate efficiencies compared to conventional p-n junction solar cells [1-3]. A typical DSSC is constructed with dye-adsorbed wide band gap oxide semiconductor electrode (TiO<sub>2</sub>), electrolyte containing  $I^-/I_3^$ redox couples, and a platinum counter electrode [4]. In the DSSCs system, electrons are injected into the conduction band (CB) of the TiO<sub>2</sub> from the excited dye molecules under light illumination, while the ground state of the dye is regenerated by the electrolyte to give efficient charge separation [5]. For this, the photosensitizers (dyes) namely metal-organic complexes and metal-free organic dye molecules, is one of the critical components in DSSC to improve the solar energy-to-electricity conversion efficiency [6]. Even though the metal-organic complexes (Ru dyes such as N3 and N719) have been used to achieve high power conversion efficiencies above 11% under AM 1.5 irradiation [7,8], the metal-free organic dyes have recently become noticeable due to their many advantages such as high molar extinction coefficient, simple synthesis procedure, and environmental friendliness, despite to their slightly lower efficiencies in the range of 6-9% [9-11]. The photoconversion efficiencies of DSSCs fabricated using metal-free organic dye molecules

### ABSTRACT

New bi-anchoring donor- $\pi$ -acceptor (D- $\pi$ -A) metal-free organic dyes based on diphenylamine, carbazole as donor, cyano vinyl biphenyl as a  $\pi$ -linker and cyanoacrylic acid, rhodanine-3-acetic acid as acceptor/ anchor are synthesized, characterized and used for the dye-sensitized solar cell (DSSC) applications. Among the fabricated DSSCs, device based on the carbazole as donor, cyano vinyl biphenyl as a  $\pi$ -linker and cyanoacrylic acid as acceptor exhibits a high power conversion efficiency of 2.37% with a short-circuit current density of 5.18 mAcm<sup>-2</sup>, an open-circuit photo voltage of 0.766 V and a fill factor of 50.8% under AM1.5 illumination (85 mWcm<sup>-2</sup>) compared to other devices.

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deeply depend on the molecular structures (i.e.) donor (D) and acceptor (A) groups of the organic molecules and the amount of adsorbed molecules on the TiO<sub>2</sub> surface [12]. The D- $\pi$ -A ambipolar system is the basic feature for most metal-free organic dyes due to the effective photoinduced intramolecular charge transfer property [13–15], and these dyes are firmly grafted on to the semiconductor oxide surface through anchoring groups such as carboxylate or phosphonate. Among the various types of metal-free organic dye molecules, in which most of the organic dyes contain only one anchoring group [16], however organic dyes containing bianchoring groups [17–21] has been received much attention from the researchers and industrialists to design as an efficient photo sensitizer for DSSCs. The reason for much attention has been paid to these materials is due to (i) increasing the photoinduced intramolecular charge transfer (ICT) from donor to acceptor [22] (ii) enhancing the electron injection from the LUMO level of the dye molecule to conduction band (CB) of TiO2 surface [23] and (iii) enhancing the optical density and absorbing the maximum solar spectrum due to extended  $\pi$ -conjugated framework.

Hence, we report the synthesis, exhaustive structural characterization, and investigation of the electrochemical, photophysical and photovoltaic properties of a series of four novel organic dyes [Car-CN ((2E,2'E)-3,3'-(4',4''-(1Z,1'Z)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl)bis(biphenyl-4',4-diyl))bis(2cyano acrylic acid)), Car-Rh (2,2'-(5E,5'E)-5,5'-(4',4''-(1Z,1'Z)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl)bis (biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid), Dpa-CN ((2E,2'E)-3,3'-





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(4',4"-(1Z,1'Z)-2,2'-(4,4'-(hexylazanediyl)bis(4,1-phenylene))bis (1-cyanoethene-2,1-diyl)bis(biphenyl-4',4-diyl))bis(2-cyanoacrylic acid)) and Dpa-Rh (2,2'-(5E,5'E)-5,5'-(4',4"-(1Z,1'Z)-2,2'-(4,4'-(hexylazanediyl)bis(4,1-phenylene)) bis(1-cyanoethene-2,1-diyl) bis(biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid)] (Fig. 1) based on amine (carbazole and diphenylamine) framework as donor containing bi electron acceptor (either cyano acrylic acid or rhodanine-3-acetic acid) and the bridging cyanovinyl biphenyl unit to provide conjugation between the donor amine and the anchoring acid group (acceptor). In order to reduce the aggregation and enhance the solubility of the sensitizer, the hydrophobic hexyl groups [24,25] are attached to the donor group.

### 2. Experimental section

### 2.1. Material and methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Bruker 400 MHz and 500 MHz NMR Spectrometer using tetramethylsilane as internal standard. Mass spectra (ESI-MS) were recorded on a Micromass QUATTRO 11 spectrometer coupled to a Hewlett Packard series 1100 degasser. UV-vis and fluorescence spectra were recorded on a T90+ UV/VIS spectrometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively. The cyclic voltammograms reported here were recorded with a computer controlled AUTOLABpotentiostat/galvanostat with a conventional 3-electrode system such as platinum working electrode, Ag/AgNO<sub>3</sub> reference electrode and glassy carbon counter electrode in deoxygenated and anhydrous DMF at room temperature. The potentials are reported vs ferrocene as standard using a scan rate of 0.1 Vs<sup>-1</sup> and the sample solutions contained 3.0  $\times$  10^{-4} M sample and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Argon was bubbled for 10 min before each measurement. All reactions were monitored using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh).

#### 2.2. Synthesis

### 2.2.1. Synthesis of 9-hexyl-9H-carbazole (1a) [26]

1-Bromohexane (3.356 g, 0.02033 mol), carbazole (2.0 g, 0.01196 mol) and sodium hydroxide (4.0 g, 0.10046 mol) were added in dimethylsulfoxide (DMSO) (30 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<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the resulting crude solid was purified by column chromatography on neutral alumina by using hexane as solvent to give white solid with yield 90.4% (3.1 g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  8.18 (d, 2H, *J* = 7.6 Hz), 7.56–7.54 (m, 2H), 7.52–7.46 (m, 2H), 7.31 (t, 2H, *J* = 7.2 Hz), 4.33 (t, 2H, *J* = 7.2 Hz), 1.96–1.89 (m, 2H), 1.54–1.37 (m, 6H), 0.96 (d, 3H, *J* = 6.8 Hz).

### 2.2.2. Synthesis of 9-hexyl-9H-carbazole-3,6-dicarbaldehyde (1b) [26,27]

Freshly distilled POCl<sub>3</sub> (23.1 ml, 25 eq) was added drop wise to DMF (17.6 ml, 23 eq) under an atmosphere of N<sub>2</sub> at 0 °C, and then it was stirred for 1 h. Compound **1a** (2.5 g, 9.9 m mol) was added to the above solution, and the 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 4 M NaOH. Filtered the solid and extracted with EA/brine. After evaporating the organic solvent the crude product was purified by column chromatography on neutral alumina using a mixture of ethyl acetate/hexane (1:4, v/v), to give a white solid (1.5 g, yield = 49%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  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).

### 2.2.3. Synthesis of (2Z,2'Z)-3,3'-(9-hexyl-9H-carbazole-3,6-diyl) bis(2-(4-bromophenyl) acrylonitrile) (1c) [26]

The obtained compound **1b** (1.0 g, 3.25 mmol), 4bromophenylacetonitrile (2.55 g, 13.01 mmol), were dissolved in dried methanol (34 mL). A catalytic amount of potassium *tert*-



Fig. 1. Molecular structures of the synthesized dyes.

butoxide was added into this mixture at room temperature. A bright yellow solid was filtered after 12 h reflection. It was recrystallized in methylene chloride and methanol to give the product 1.3 g (yield = 60.2%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  8.65 (d, 2H, J = 1.5 Hz), 8.18–8.2 (m, 2H), 7.72 (s, 2H), 7.57 (d, 8H, J = 19 Hz), 7.53 (d, 2H, J = 9 Hz), 4.35 (t, 2H, J = 7.5 Hz), 1.89–1.92 (m, 2H), 1.40 (d, 2H), 1.29–1.35 (m, 4H), 0.89 (m, 3H).

### 2.2.4. Synthesis of (2Z,2'Z)-3,3'-(9-hexyl-9H-carbazole-3,6-diyl) bis(2-(4'-formylbiphenyl-4-yl)acrylonitrile) (**1d**)

A mixture of compound **1c** (0.500 g, 0.7536 mmol), 4-Formylphenylboronic acid (0.26 g, 2.3 eq), 0.05 eq.  $Pd(OAc)_2$ (0.0195 g, 0.0866 mmol) and 0.1 eq.  $P(O-tolyl)_3$  (0.053 g, 0.1733 mmol) were dissolved in a distilled, degassed THF (45 ml) at N<sub>2</sub> atmosphere. To this K<sub>2</sub>CO<sub>3</sub> (0.59 g, 2.5 eq) was added and refluxed for 12 h. After cooling to room temperature, distilled out the solvent under vacuum. The resulting solid was purified by column chromatography using hexane:ethyl acetate as the eluent, to generate the sandal color solid which was dried in vacuum. The resulting product yield was 41% (0.22 g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 10.07 (s, 2H), 8.67 (d, 2H, *J* = 1.6 Hz), 8.21 (dd, 2H, *J* = 8.4 Hz), 7.99–7.92 (m, 4H), 7.84–7.79 (m, 6H), 7.78–7.69 (m, 4H), 7.60–7.58 (m, 2H), 7.57–7.48 (m, 2H), 7.26 (s, 2H), 4.33 (s, 2H), 1.62–1.92 (m, 3H), 1.34–1.28 (m, 4H), 1.27–1.25 (m, 2H), 0.9–0.85 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) δ 191.96, 146.05, 143.28, 142.35, 139.89, 135.59, 135.26, 130.5, 130.44, 129.83, 128.32, 128.04, 127.84, 127.66, 126.44, 126.39, 125.8, 123.3, 123.13, 118.94, 109.86, 107.55, 52.35, 31.62, 29.07, 27.04, 22.65, 14.13. Anal. Calcd for C<sub>50</sub>H<sub>39</sub>N<sub>3</sub>O<sub>2</sub>: C, 84.12; H, 5.51; N, 5.89. Found: C, 84.26; H, 5.47; N, 5.79. *m/z* (ESI) Anal. Calcd. for C<sub>50</sub>H<sub>39</sub>N<sub>3</sub>O<sub>2</sub>: 713.86. Found: 714.39 [M + H] <sup>+</sup>, 731.42 [M + NH<sub>4</sub>] <sup>+</sup>.

## 2.2.5. Synthesis of (2E,2'E)-3,3'-(4',4"-(1Z,1'Z)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl)bis(biphenyl-4',4-diyl))bis(2-cyanoacrylic acid) (**1e**)

A chloroform solution of **1d** (0.25 g, 0.3502 mmol) and cyanoacetic acid (0.12 g, 1.4 mmol) was refluxed in the presence of piperidine (0.083 ml) for 12 h. After cooling to room temperature, the solvent was removed by distillation. The residue was purified by column chromatography using silica gel and CHCl<sub>3</sub>:CH<sub>3</sub>OH (v:v, 10:1) mixed as the eluent to give the dye as Dark sandal color solid (0.147 g, yield = 49.5%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 9.30–9.25 (bs, 2H), 8.70 (s, 2H), 8.17 (d, 4H, *J* = 4.5 Hz), 8.04 (d, 6H, *J* = 7.8 Hz), 7.82–7.84 (m, 12H), 7.62 (d, 2H, *J* = 8.1 Hz), 4.41 (s, 2H), 1.87–1.64 (m, 4H), 1.32 (m, 4H), 0.86 (m, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub>, ppm) δ 166.20, 150.23, 142.28, 141.66, 138.70, 134.28, 131.45, 130.62, 127.16, 126.85, 125.89, 125.36, 122.36, 106.20, 43.65, 30.95, 26.18, 22.19, 22.00, 13.71. Anal. Calcd for C<sub>56</sub>H<sub>41</sub>N<sub>5</sub>O<sub>4</sub>: C, 79.32; H, 4.87; N, 8.26. Found: C, 79.26; H, 4.81; N, 8.38. *m*/*z* (ESI) Anal. Calcd. for C<sub>56</sub>H<sub>41</sub>N<sub>5</sub>O<sub>4</sub>: 847.32. Found: 865.35 [M + NH<sub>4</sub>] <sup>+</sup>.

# 2.2.6. Synthesis of 2,2'-(5E,5'E)-5,5'-(4',4"-(1Z,1'Z)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl)bis(biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid (**1f**)

The compound **1d** (0.17 g, 0.2381 mmol), rhodanine-3-acetic acid (0.273 g, 1.4288 mmol), ammonium acetate (0.46 g), and glacial acetic acid (10 mL) were mixed together and refluxed for 12 h. The clear red solution was cooled to room temperature to yield a red colored precipitate. It was filtered and washed with cooled acetic acid and water mixture. The obtained solid was further purified by crystallization from the dichloromethane/ hexane mixture to give saffron color solid (0.133 g, yield = 53%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 8.75–8.69 (m, 2H), 8.31–8.27 (m, 2H), 8.21–8.15 (m, 2H), 8.0–7.82 (m, 14H), 7.76–7.72 (m, 6H), 4.71 (s, 4H), 4.48 (s, 2H), 1.82 (s, 2H), 1.3–1.24 (m, 6H), 0.83–0.81 (m, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub>, ppm) δ 192.38, 167.52, 165.43, 147.42, 145.73, 144.59, 143.95, 131.48, 131.00, 127.39, 125.97, 121.61, 120.42, 108.19, 106.48, 53.44, 47.63, 28.02, 27.72, 26.35, 22.05, 13.83. Anal. Calcd for C<sub>60</sub>H<sub>45</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: C, 67.97; H, 4.28; N, 6.61. Found: C, 67.91; H, 4.39; N, 6.66. *m/z* (ESI) Anal. Calcd. for C<sub>60</sub>H<sub>45</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: 1059.23. Found: 1077.23 [M + NH<sub>4</sub>] <sup>+</sup>.

### 2.2.7. Synthesis of N-hexyl-N-phenylaniline (2a) [26]

It was synthesized according to the procedure of **1a**. The product obtained was colorless liquid (Yield = 80.2%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.27–7.23 (m, 4H), 6.98–6.96 (m, 4H), 6.94–6.91 (m, 2H), 3.67 (t, 2H, J = 8 Hz), 1.66–1.62 (m, 2H), 1.35–1.26 (m, 6H), 0.88–0.85 (m, 3H).

### 2.2.8. Synthesis of 4, 4'-(hexylazanediyl)dibenzaldehyde (2b) [26,27]

It was synthesized according to the procedure of **1b**. The product is Brown color liquid (Yield = 94%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  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* = 8.0 Hz), 1.67 (d, 4H, *J* = 8.4 Hz), 1.33–1.26 (m, 6H), 0.85 (t, 3H, *J* = 6.4 Hz).

### 2.2.9. Synthesis of (2Z,2'Z)-3,3'-(4,4'-(hexylazanediyl)bis(4,1-

phenylene))bis(2-(4-bromophenyl) acrylonitrile) (**2c**) [26]

The compound **2c** (Dark yellow solid) was prepared from **2b** by following the procedure similar to **1c**. (Yield = 44%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.86 (d, 4H, J = 8.8 Hz), 7.82–7.50 (m, 8H), 7.43 (s, 2H), 7.32–7.30 (m, 2H), 7.13–7.05 (m, 2H), 3.81 (t, 2H, J = 7.6 Hz), 1.74–1.64 (m, 2H), 1.38–1.29 (m, 6H), 0.89 (t, 3H, J = 6.8 Hz).

### 2.2.10. Synthesis of (2Z,2'Z)-3,3'-(4,4'-(hexylazanediyl)bis(4,1-phenylene))bis(2-(4'-formyl biphenyl-4-yl)acrylonitrile) (2d)

It was synthesized according to the procedure of **1d**. The final product is light red color solid (Yield = 42%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 10.06 (s, 2H), 7.99–7.96 (m, 4H), 7.92–7.85 (m, 4H), 7.80–7.77 (m, 4H), 7.75–7.67 (m, 4H), 7.58–7.50 (m, 4H), 7.26–7.06 (m, 4H), 6.92 (d, 2H, J = 8.8 Hz), 3.81 (t, 2H, J = 7.6 Hz), 1.60 (m, 2H), 1.34–1.28 (m, 6H), 0.90–0.85 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 191.94, 149.02, 146.06, 144.08, 141.86, 141.77, 140.44, 139.99, 135.67, 135.61, 135.16, 132.29, 131.69, 131.26, 131.19, 130.51, 128.17, 128.04, 127.77, 127.68, 127.35, 127.23, 126.45, 126.42, 120.93, 52.41, 31.65, 27.64, 26.81, 22.76, 14.15. Anal. Calcd. for C<sub>50</sub>H<sub>41</sub>N<sub>3</sub>O<sub>2</sub>: C, 83.89; H, 5.77; N, 5.87. Found: C, 83.78; H, 5.81; N, 5.94. m/z (ESI) Anal. Calcd. for C<sub>50</sub>H<sub>41</sub>N<sub>3</sub>O<sub>2</sub>: 715.86. 716.91 [M + H] +.

2.2.11. Synthesis of (2E,2'E)-3,3'-(4',4"-(1Z,1'Z)-2,2'-(4,4'-

(hexylazanediyl)bis(4,1-phenylene))bis (1-cyanoethene-2,1-diyl)

bis(biphenyl-4',4-diyl))bis(2-cyanoacrylic acid) (**2e**)

It was synthesized according to the procedure of 1e. The product is orange red color solid (Yield = 39%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 8.78–8.73 (m, 4H), 8.33 (s, 2H), 8.23 (d, 4H, *J* = 8.5 Hz), 8.18 (s, 4H), 7.95–7.91 (m, 12H), 7.85 (d, 2H, *J* = 8.5 Hz), 4.49 (s, 2H), 1.65–1.63 (m, 2H), 1.56–1.55 (m, 2H), 1.32–1.22 (m, 4H), 0.84–0.83 (m, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub>, ppm) δ 161.26, 148.96, 141.87, 133.93, 132.53, 132.23, 131.15, 131.12, 127.28, 127.01, 125.89, 122.89, 120.84, 118.38, 107.25, 52.43, 52.35, 31.63, 27.62, 26.75, 26.71, 22.72, 14.12. Anal. Calcd. for C<sub>56</sub>H<sub>43</sub>N<sub>5</sub>O<sub>4</sub>: C, 79.13; H, 5.10; N, 8.24. Found: C, 79.21; H, 5.14; N, 8.94. *m*/*z* (ESI) Anal. Calcd. for C<sub>56</sub>H<sub>43</sub>N<sub>5</sub>O<sub>4</sub>: 849.32. Found: 850.34 [M + H]+.



Scheme 1. Synthetic procedure of the organic dyes. (i) 1-Bromohexane, NaOH, DMSO, 110 °C. (ii) PoCl<sub>3</sub>, DMF, 95 °C. (iii) 4-bromophenyl acetonitrile, t-BuOK, CH<sub>3</sub>OH, refluxed. (iv) 4-Formylphenylboronic acid, Pd(OAc)<sub>2</sub>, P(O-tolyl)<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, THF, refluxed. (v) Cyanoaceticacid, piperidine, CHCl<sub>3</sub>, refluxed. (vi) Rhodanine-3-acetic acid, ammonium acetate, glacial CH<sub>3</sub>COOH, refluxed.

2.2.12. Synthesis of 2,2'-(5E,5'E)-5,5'-(4',4"-(1Z,1'Z)-2,2'-(4,4'-(hexylazanediyl)bis(4,1-phenylene)) bis(1-cyanoethene-2,1-diyl) bis(biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)bis(4-oxo-2-thioxothiazolidin-3-yl-5-ylidene)diacetic acid (**2f**)

The compound **2f** (Dark red solid) was prepared from **2d** by following the procedure similar to synthesis of **1f** (Yield = 44%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 7.98 (s, 2H), 7.95–7.90 (m, 10H), 7.87 (d, 4H, *J* = 8 Hz), 7.81 (d, 4H, *J* = 8.4 Hz), 7.74 (d, 4H, *J* = 8 Hz), 7.20 (m, 4H) 4.73 (s, 2H), 3.85 (s, 4H), 1.61 (s, 2H), 1.33–1.25 (m, 6H), 0.86–0.82 (m, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub>, ppm) δ 190.57, 161.39, 160.79, 157.69, 151.99, 144.52, 143.34, 141.39, 131.65, 130.64, 120.79, 118.34, 111.95, 110.64, 98.36, 52.61, 43.51, 31.54, 30.98, 27.52, 26.65, 22.63, 14.03. Anal. Calcd. for C<sub>60</sub>H<sub>47</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: C, 67.84; H, 4.46; N, 6.59. Found: C, 67.91; H, 4.34; N, 6.64. *m/z* (ESI) Anal. Calcd. for C<sub>60</sub>H<sub>47</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: 1061.24. Found: 1079.24[M + NH]<sup>+</sup>.

### 3. Results and discussion

### 3.1. Synthesis of bi-anchoring dyes

The synthetic pathways of organic dyes Car-CN, Car-Rh, Dpa-CN and Dpa-Rh were depicted in Scheme 1. Alkylation of amine compounds using 1-bromohexane in dimethylsulfoxide afforded compounds **1a** and **2a**. The Vilsmeier—Haack formylation in alkylated carbazole and diphenylamine gave compounds **1b** and **2b**. The aldehydes (**1b**, **2b** and **1d**, **2d**) and active methylene compounds such as 4-bromophenylacetonitrile, cyano acetic acid and rhodanine-3-acetic acid were condensed by Knoevenagel Condensation to gave different products (**1c**, **2c**; **1e**, **2e**; and **1f**, **2f**) respectively. Suzuki coupling of dibromo compounds (**1c**, **2c**) with 4-formylphenylboronicacid in the presence of Pd(OAc)<sub>2</sub> gave compounds **1d** and **2d**. Synthesized compounds were well confirmed by various analytical tools (See Supplementary data).

#### 3.2. Optical properties

The UV-vis absorption and normalized emission spectra of all dyes in DMF solution are depicted in Fig. 2a and b respectively and the corresponding data are summarized in Table 1. Two major absorption features were observed in the spectra of all the molecules: one relatively weak band in the near-UV region (330–400 nm) corresponding to the  $\pi$ – $\pi$ \* electron transition, and the other strong absorption in the visible region (415-460 nm) that can be assigned to an intramolecular charge transfer (ICT) between the donor unit and the acceptor end group [28]. For the similar structural architecture, the rhodanine acetic acid acceptor compounds (Dpa-Rh and Car-Rh) display red-shifted and induced intramolecular charge transfer absorption band when compared to the cyano acetic acid analogs (Dpa-CN and Car-CN) due to the stronger electron-withdrawing nature of rhodanine acetic acid substituents [17,29]. However, their molar extinction coefficients are lower than the latter. Upon comparing all the compounds, Dpa-CN and Dpa-Rh shows red-shifted absorption peaks, due to low ionization potential of diphenylamine [30]. Whereas in the case of carbazole derivative conjugation is disallowed between the two aryl segments may be due to its planar nature and hence it exhibits shorter wavelength maxima  $(\lambda_{max})$  [31]. The fluorescence emission spectra of all the dyes exhibited strong luminescence maxima in the wavelength region 490-550 nm recorded upon their excitation of absorption maximum value.

### 3.3. Electrochemical measurements

To understand the electronic structures of the bi anchoring D- $(\pi$ -A)<sub>2</sub> molecules, we performed cyclic voltammetry measurements



Fig. 2. Absorption (a) and normalized emission (b) spectra of dyes recorded in DMF.

of all compounds in DMF (Fig. 3), and their data are summarized in Table 1. We find that all the dyes which have electron donating/ withdrawing groups show one quasi-reversible peak arising from the oxidation potential which were determined from the intersection of two tangents drawn at the rising current and background charging current of a cyclic voltammogram [32] at around 0.60-1.19 V and two irreversible peaks arising from reduction potential at around -0.22 to -0.95 V and are very close to each other. This was attributed due to the sp<sup>3</sup>-type donor nitrogen center [33] and electron withdrawing group contained aromatic linker, acceptor groups. The HOMO energy levels were calculated based on the relationship of HOMO (eV) =  $-e(E_{onset}^{OX} V(vs Fc/$  $Fc^+$ ) + 4.8 V) by assuming the Ferrocene (Fc) energy level to be -4.8 eV below the vacuum level [34] and the LUMO levels of the dyes were calculated by  $E_{\text{onset}}^{\text{ox}} - E_{0-0}$ , where  $E_{0-0}$  is the zero-zero energy of the dyes estimated from the solution absorption edge [35,36]. In our work, the potential of Fc was measured to be 0.45 V against Ag electrode. The oxidation onset potentials of Car-CN, Car-Rh, Dpa-CN and Dpa-Rh were unequivocally determined to be 0.90, 0.63, 0.67 and 0.75 V respectively. The reason for high oxidation potential of Car-CN compared to other dyes may be due to the weaker electron donating nature of Carbazole moiety [37]. The HOMO and LUMO energy levels of all the dyes (Table 1), compared to the levels of the conduction band of TiO<sub>2</sub> (-4.0 eV vs vacuum) and the  $I^-/I_3^-$  redox electrolyte (-4.6 eV vs vacuum), are suitable for

Dye	$\lambda abs/nm~(\epsilon/M^{-1}cm^{-1})^a$	$\lambda_{em}/nm^{a,b}$	$E_g^{opt} (eV)^c$	$E_{\rm ox}/V$ (vs. Fc)	$E_{\rm HOMO}~({\rm eV})^{\rm d}$	$E_{LUMO}(eV)^d$	HOMO <sup>e</sup>	LUMO <sup>e</sup>	Eg <sup>e</sup>
Car-CN	419 (25000)	487	2.68	0.90	5.25	2.57	-5.72	-2.77	2.95
Dpa-CN	446 (32579)	536	2.46	0.67	5.02	2.56	-5.46	-2.73	2.73
Car-Rh	421 (22313)	506	2.61	0.63	4.98	2.37	-5.55	-2.81	2.74
Dpa-Rh	458 (28617)	544	2.41	0.75	5.1	2.69	-5.44	-2.84	2.56

Table 1		
Optical, electrochemical data and HOMO	, LUMO energy levels of Car-CN, Dpa-CN, Car-Rh and Dpa-	-Rh

 $^a\,$  Absorption and emission spectra were recorded in DMF solution (3.8  $\times$  10  $^{-5}$  M) at room temperature.

<sup>b</sup> Dyes were excited at their absorption maximum value.

<sup>c</sup> Optical band gap calculated from absorption edge.

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

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

electron injection and dye regeneration thermodynamically [19,38]. However the potential is further improved negatively about 0.3 V by adding additives such as 4-*tert*-butylpyridine (TBP) to the  $I^-/I_3^-$  redox electrolyte [39].

### 3.4. Ab initio molecular orbital (MO) calculations

To gain more insight into the electronic structures of dyes, density functional theory (DFT) calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization. As shown in Fig. 4, the HOMO levels of Car-CN and Dpa-CN dyes are mainly delocalized on the central electron donating amine moieties, the neighboring cyano vinyl phenyl groups with considerable contribution to the former, whereas LUMO levels are delocalized through the aromatic bridge and cyanoacrylic acid fragments however sizable contribution from the latter. According to Franck Condon

principle, the overlapping of both HOMO and LUMO levels by the  $\pi$ bridged cyano vinyl biphenyl units enhance the electronic transition dipole moments between vibrational energy levels [40]. This suggests that such strong intramolecular charge transfer (ICT) nature of Car-CN and Dpa-CN dyes upon illumination results the electron injection from the excited dyes to TiO<sub>2</sub> conduction band [41]. Nevertheless, in Car-Rh and Dpa-Rh dves, the HOMO levels were entirely populated on anchoring Rhodanine moiety especially on the sulfur and thiocarbonyl group and LUMO levels are also delocalized on the anchoring units as well as on the  $\pi$ -bridged biphenyl units. Hence, the encumbrances in the electronic transitions between the HOMO to LUMO energy levels had been anticipated in Car-Rh and Dpa-Rh dyes. These results indicate that dyes with rhodanine-acetic acid units cannot give effective and fast electron injection from LUMO level to TiO<sub>2</sub> conduction band while comparing to the dyes with cyanoacrylic acid units [29].



Fig. 3. Cyclic volammogram of dyes were measured in DMF solutions with TBAPF6 (0.1 M) as the electrolyte (working electrode: Pt; reference electrode: Ag/Ag+; counter electrode: glassy carbon; calibrated with Fc/Fc+ as a standard reference; scan rate: 0.1 Vs<sup>-1</sup>).

#### 3.5. Fabrication of DSSCs and photovoltaic measurements

The nanocrystalline TiO<sub>2</sub> [42] and Pt counter electrode [43,44] were prepared by the known method reported in the literature for fabrication of dye-sensitized solar cells. The prepared titania paste was deposited onto an F-doped tin oxide (FTO) coated conducting glass by doctor blade technique (around 1 cm<sup>2</sup> area) and it was immersed in the dye solution ( $3 \times 10^{-4}$  M in DMF) for 24 h at room temperature. 0.05 M I<sub>2</sub>/0.5 M KI/0.5 M 4-*tert*-butyl pyridine (TBP) in 2-methoxypropionitrile was used as an electrolyte. The photovoltaic properties of the solar cells fabricated from the prepared electrodes under simulated AM 1.5 irradiation (85 mW cm<sup>-2</sup>) are shown in Fig. 5. The measured open-circuit

photovoltage (V<sub>OC</sub>), short-circuit photocurrent density (J<sub>SC</sub>), fill factor (FF), and solar-to-electric conversion efficiencies ( $\eta$ ) are listed in Table 2. It is clear from Fig. 5 that the efficiency of the fabricated device decrease in the order Car-CN > Car-Rh > Dpa-CN > Dpa-Rh. This indicates that carbazole moiety may act as a good light harvester due to its planar nature [45] and in addition its lowered HOMO level allows efficient regeneration of the oxidized dye and as well as minimize the charge recombination [46]. The observed V<sub>OC</sub> values of Car-Rh and Dpa-Rh were much lower than that of the other two dyes, showing rhodanine–acetic acid has the low tendency to inject electrons from the LUMO to TiO<sub>2</sub> conduction band due to the presence of the –CH<sub>2</sub>– group [47]. The incident photon to current conversion efficiency (IPCE) as



Fig. 4. The frontier molecular orbitals of the HOMO and LUMO levels calculated with B3LYP/6-31G (d) of synthesized dyes.



Fig. 5. Current density–voltage characteristics for (A) Car-CN, Car-Rh, and (B) Dpa-CN Dpa-Rh based devices for DSSCs under illumination of simulated solar light (AM 1.5, 85 mW cm<sup>-2</sup>).

a function of wavelength was measured for all the fabricated device (Fig. 6) with an Oriel 300 W 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. The IPCE (%) of fabricated devices shows a broader response between 400 and 600 nm with a maximum efficiency of about 33.4% for Car-CN followed by DPA-CN (20.0%), Car-RH (16.6%) and DPA-RH (16.5%) at its wavelength maximum. In order to identify whether surface adsorbed dye may play any vital role in the device fabrication, desorption of the dye from the TiO<sub>2</sub> surface was done using 0.1 M NaOH in DMF/

### Table 2

DSSC performance parameters of the dyes.

Dye	J <sub>sc</sub> /mAcm <sup>-2</sup>	V <sub>oc</sub> /mV	FF	η (%) <sup>a</sup>	IPCE (%)	Surface concentration $\Gamma$ (mol/cm <sup>2</sup> )
Car-CN	5.18	766	0.5081	2.37	33.4	$2.23 \times 10^{-7}$
Dpa-CN	1.67	832	0.6220	1.02	20.0	$1.92 \times 10^{-7}$
Car-Rh	5.56	709	0.4676	2.17	16.6	$1.34 \times 10^{-7}$
Dpa-Rh	2.15	545	0.4093	0.56	16.5	$0.97  imes 10^{-7}$

<sup>a</sup> Illumination: 85 mW cm<sup>-2</sup> simulated AM 1.5 G solar light; electrolyte containing:  $0.05 \text{ M } I_2/0.5 \text{ M } \text{Kl}/0.5 \text{ M } 4$ -tert-butyl pyridine in 2-methoxypropionitrile.



Fig. 6. IPCE spectra of Car-CN, Car-Rh, Dpa-CN and Dpa-Rh.

 $H_2O$  (1:1) mixture [29]. The surface concentration ( $\Gamma$ ) of the dyes was spectrophotometrically measured [48] (see Table 2) indicates that cyano acetic acid analogs have adsorbed better on TiO<sub>2</sub> surface compared to rhodanine acetic acid analogs which also supports the observed IPCE (%) order of the fabricated devices.

### 4. Conclusion

In this study, we have synthesized a series of new bi-anchoring metal-free organic dyes for dye-sensitized solar cell applications. It was found that both the absorption and emission peaks of diphenylamine with rhodanine moieties are red-shifted compared to the carbazole with cyanoacrylic acid moieties. However, their DSSC performances are lower than the latter due to the bad LUMO overlap with the conduction band of TiO<sub>2</sub>. Car-CN based device exhibits a power conversion efficiency of 2.37%. This result indicates that compared to diphenylamine and rhodanine-3-acetic acid, carbazole and cyanoacetic acid based device open up a new way for researchers toward DSSCs.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2012.02.016.

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