Dyes and Pigments 97 (2013) 397-404

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis of bianchored metal free organic dyes for dye sensitized solar cells

Sekar Ramkumar, Sambandam Anandan*

Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Tiruchirappalli-620 015, India

ARTICLE INFO

Article history: Received 21 November 2012 Received in revised form 12 January 2013 Accepted 16 January 2013 Available online 25 January 2013

Keywords: DSSC Bi-anchoring molecules Carbazole Diphenylamine Planarity Impedance

ABSTRACT

Two bianchored metal free organic dyes (Car-th-CN and Dpa-th-CN) were designed and synthesized for DSSC application, in which carbazole or diphenylamine moieties were used as the donor, cyano vinyl thiophene unit as the π -bridge and cyanoacrylic acid group as the electron acceptor. The structures of the synthesized dyes were confirmed by NMR, HR-Mass and elemental analysis. The optical, electrochemical, theoretical and photovoltaic properties of the synthesized dyes were investigated. Fabricated photovoltaic devices based on carbazole unit as a donor (Car-th-CN) showed a maximum current conversion efficiency of 4.04% under AM 1.5 illumination (85 mW cm⁻²) and monochromatic incident photon to current efficiency (IPCE) of 38.1%. The reason for the higher efficiency of Car-th-CN is due to the planar nature of carbazole moiety and hence increases the capability of adsorbed dye amount and electron lifetime in TiO₂ surface.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

After the first revelation of a dve sensitized solar cell (DSSC) in 1991 by Gratzel and O'Regan [1-3], numerous metal dyes and metal free organic molecules that exhibit conversion of light into electricity have been found by many researchers. Among the metal and metal free dyes, the metal free dyes have attracted a great deal of interest nowadays, due to their high molar extinction coefficient, simple synthesis procedure, and environmental friendliness, even though their efficiencies are relatively low [4–7]. In general, the efficiency of a metal free DSSC strongly depends on the choice of functional groups and on the design of the device structure. That is, the D- π -A (Donor, π -conjugated unit/linker and acceptor) ambipolar system is the basic aspect for most metal free organic dyes [8]. Recently, bi-anchoring dyes have aroused considerable interests in the area of DSSCs because they can provide more dye adsorption, increases the light absorption efficiency and the photoinduced intramolecular charge transfer (ICT) processes and thus enhances the electron injection from dye to TiO_2 nanoparticle [9–13]. We have also reported a series of bi-anchoring metal free dyes based on donor (carbazole and diphenylamine), π -linker (cyano vinyl biphenyl) and acceptor (cyanoacrylic acid and rodanine-3-acetic acid) with better efficiencies [14].

The absorption wavelengths of organic dyes, the rate of internal charge recombination and the electron injection to the TiO₂ surface will depends upon the π -conjugated unit which bridged the donor and acceptor moieties [15]. Hence the modification in π -conjugated unit plays a critical parameter for designing the organic dyes for DSSCs [16-18]. That is, lowering of delocalization energy occurs due to increase in the π -conjugation, leads to lowering of the HOMO and LUMO energy level band gap and thereby shift the absorption band to the visible region which helps to increase the solar cell performance [19]. Hence in this manuscript, we report the synthesis of two novel organic dyes [Car-th-CN ((2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2, 1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid)), and Dpath-CN ((2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(4,4'-(hexylazanediyl)bis(4, 1-phenylene))bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl)) bis(2-cyanoacrylic acid))] (Scheme 1) based on donor (carbazole and diphenylamine), π -linker (double bridged cyano vinyl thiophene) and bi electron acceptor (cyanoacrylic acid). The reason for choosing thiophene attached cyano vinyl as π -linker in this organic dyes instead of our earlier published work with biphenyl attached cyano vinyl as π -linker is due to the (i) effective conjugation (ii) lower resonance stabilization energy (thiophene, 29 kcal/mol; benzene, 36 kcal/mol) [20], (iii) increasing the





^{*} Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133. *E-mail addresses*: sanand@nitt.edu, sanand99@yahoo.com (S. Anandan).

^{0143-7208/\$ –} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2013.01.014



absorption wavelength towards visible [21] and (iv) negatively decreases the LUMO levels [22]. Thus, synthesized dyes have been well characterized by experimental and theoretical approach and studied their photoelectrochemical and photovoltaic performance by fabricating DSSC devices.

2. Experimental section

2.1. Material and methods

¹H and ¹³C NMR spectra were obtained on Bruker 300 MHz and 400 MHz NMR spectrometer using tetramethylsilane as internal standard. Mass spectra HR-MS (ITS + ESI Scan 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 AUTOLAB-potentiostat/galvanostat with a conventional 3-electrode system such as platinum working electrode, Ag/AgNO₃ reference electrode and glassy carbon counter electrode at room temperature. The potentials are reported vs ferrocene as standard using a scan rate of 0.1 Vs⁻¹ and 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. Argon was bubbled for 10 min before each measurement. The IPCE spectra were recorded using Oriel 300 W Xe Arc lamp in combination with an Oriel Cornerstone 2601/4 monochromator. The number of incident photons was calculated for each wavelength using a calibrated monocrystalline silicon diode as reference. All reactions were monitored using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh) and neutral alumina powder.

2.2. Synthesis

2.2.1. Synthesis of 9-hexyl-9-H-carbazole (1a)

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 Na₂SO₄. 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).

¹H NMR (CDCl₃, ppm): δ 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). ¹³C NMR (CDCl₃, 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)

Freshly distilled POCl₃ (23.1 ml, 25eq) was added drop wise to DMF (17.6 ml, 23eq) under an atmosphere of N₂ 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%).

¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, ppm): δ 191.43, 144.73, 129.61, 127.79, 124.19, 123.12, 109.72, 43.78, 31.39, 28.85, 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)

Freshly distilled methanol (100 ml) was taken in a 250 ml single neck round bottom flask. The compound 1b (3 g, 1eq) and thiophene-2-acetonitrile (2.65 g, 2.2eq) were added to the methanol. A catalytic amount of potassium tert-butoxide was added into this mixture at room temperature. 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%).

¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, ppm): δ 142.22, 140.77, 140.08, 128.21, 127.42, 126.47, 125.63, 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)

DMF (7 ml, 23eq) was taken in a 100 ml 3 neck round bottom flask. To this freshly distilled POCl₃ (9 ml, 25eq) was added drop wise under an atmosphere of N₂ 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 mixture was poured into a beaker containing ice-cube, and basified with 4 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%).

¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(9-hexyl-9H-carbazole-3,6-diyl)bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (1e)

A chloroform solution of 1d (0.5 g, 0.8714 mmol) and cyano acetic acid (0.3 g, 3.49 mmol) was refluxed in the presence of piperidine (0.181 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 CHCl₃:CH₃OH (10:1, v:v) mixed as the eluent to give the dye as red colour solid (0.27 g, yield = 43.8%).

¹H NMR (CDCl₃, ppm): δ 7.81–7.78 (m, 4H), 7.25 (d, 2H, J = 4.2 Hz), 7.14 (d, 2H, J = 6.0 Hz), 7.09–7.02 (m, 4H), 7.00 (d, 2H, J = 4 Hz), 3.80 (t, 2H, J = 8 Hz), 1.71–1.68 (m, 2H), 1.37–1.25 (m, 6H), 0.90–0.88 (m, 3H). ¹³C NMR (CDCl₃, ppm): δ 163.56, 140.43, 139.86, 138.27, 135.58, 133.80, 129.73, 129.29, 128.90, 127.98, 126.01, 118.39, 118.08, 107.03, 90.50, 50.23, 32.90, 27.99, 27.91, 24.18, 15.50. Anal. Calcd for C₄₀H₂₉N₅O₄S₂: C, 67.87; H, 4.13; N, 9.89. Found: C, 68.26; H, 3.81; N, 9.82. HR-MS (ITS + ESI Scan spectra) Anal. Calcd. for C₄₀H₂₉N₅O₄S₂: 707.16. Found: 708.1 [M + H]⁺.

2.2.6. Synthesis of N-hexyl-N-phenylaniline (2a)

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

¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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)

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

¹H NMR (CDCl₃, 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 = 8.0 Hz), 1.67 (d, 4H, J = 8.4 Hz), 1.33–1.26 (m, 6H), 0.85 (t, 3H, J = 6.4 Hz). ¹³C NMR (CDCl₃, 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)

It was synthesized according to the procedure of 1c. The product obtained was red colour solid (Yield = 68.5%).

¹H NMR (CDCl₃, 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 Hz), 1.72–1.66 (m, 2H), 1.38–1.25 (m, 6H), 0.91–0.87 (m, 3H). ¹³C NMR (CDCl₃, 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'-(4,4'-(hexylazanediyl)bis(4,1-phenylene))bis(2-(5-formylthiophen-2-yl)acrylonitrile) (2d)

It was synthesized according to the procedure of 1d. The product obtained was red colour solid (Yield = 39%).

¹H NMR (CDCl₃, ppm): δ 9.87 (s, 2H), 7.88 (d, 4H, *J* = 8.8 Hz), 7.71 (d, 2H, *J* = 4 Hz), 7.47 (s, 2H), 7.41 (d, 2H, *J* = 4 Hz), 7.15–7.13 (m, 4H), 3.84 (t, 2H, *J* = 8 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). ¹³C NMR (CDCl₃, 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 (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(4,4'-(hexylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl) bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (2e)

It was synthesized according to the procedure of 1e. The product obtained was dark red colour solid (Yield = 32%).

¹H NMR (CDCl₃, ppm):δ 8.93 (m, 2H), 8.60 (m, 2H), 8.20 (m, 2H), 8.10 (d, 2H, J = 8.2 Hz), 7.96 (m, 2H), 7.79 (m, 2H), 7.70 (d, 2H, J = 8.1 Hz), 7.48 (m, 2H), 4.36 (s, 2H), 1.74–1.54 (m, 4H), 1.24 (m, 4H), 0.78 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 160.01, 151.81, 140.27, 139.16, 132.28, 129.54, 128.67, 128.34, 127.85, 126.03, 121.43, 121.19, 120.13, 117.70, 108.21, 55.33, 31.39, 29.63, 23.31, 22.49, 13.90. Anal. Calcd for C₄₀H₃₁N₅O₄S₂: C, 67.68; H, 4.4; N, 9.87. Found: C, 67.29; H, 4.51; N, 9.92. HR-MS (ITS + ESI Scan spectra) Anal. Calcd. for C₄₀H₃₁N₅O₄S₂: 709.18. Found: 710.3 [M + H]⁺.

3. Results and discussion

3.1. Synthesis of bi-anchoring dyes

The synthetic pathways of organic dyes Car-th-CN and Dpa-th-CN were depicted in Scheme 1. Alkylation of amine compounds (carbazole (1), diphenylamine (2)) using 1-bromohexane in dimethysulfoxide afforded alkylated carbazole (1a) and diphenylamine (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 thiophene-2acetonitrile and cyano acetic acid were condensed by Knoevenagel Condensation to gave different products (1c, 2c; and 1e, 2e) respectively. Synthesized compounds were well confirmed by various analytical tools (See Supporting information).

3.2. Absorbance and photoluminescence properties

The UV-vis spectra of the synthesized dyes in DMF solution $(3 \times 10^{-4} \text{ M})$ exhibit two intense peaks, one in the ultraviolet region and the other in the visible region as illustrated in Fig. 1. The higher energy peaks 338 nm for Car-th-CN and 363 nm for Dpa-th-CN are associated with a $\pi - \pi^*$ transition localized in aromatic portion of the molecules and the lower energy peaks 438 nm for Car-th-CN and 458 nm for Dpa-th-CN are associated with the intramolecular charge transfer (ICT) from the donor to the acceptor due to the orbital mixing between the donor and acceptor fragments. However, the end absorption of Dpa-th-CN was red shifted by approximately 20 nm and its molar extinction coefficients were 3000 times greater than the Car-th-CN. This is mainly due to the (i) planar nature of carbazole decreases the conjugation between the two aryl segments (i.e., in general two types of electronic transitions $(\pi - \pi^* \text{ and } n - \pi^*)$ are possible in aromatic amines, of which the $n-\pi^*$ transition is comparatively less in carbazole (C_{2v} symmetry) moeity compared to diphenylamine (C_2 symmetry) moiety because of its planar nature) [23,24] and (ii) ionization potential of carbazole moiety is comparatively higher than diphenylamine moiety [25]. Further upon comparing the thiophene attached cyano vinyl as π -linker and biphenyl attached cyano vinyl as π -linker [14], an anticipated bathochromic and hyperchromic shift was observed by introduction of a thiophene bridging unit, due to the planar nature of the thiophene group [26]. Fig. 2 shows the absorption spectra of the dye loaded TiO₂ films after 12 h adsorption which



Fig. 1. Absorption and emission spectra of Car-th-CN and Dpa-th-CN dyes recorded in DMF.

shows the maxima absorption peak at 433 and 446 nm for Car-th-CN and Dpa-th-CN. Both spectra are and blue shifted upon comparing with the absorption spectra of the corresponding dyes in solution due to the strong interaction between the dyes and the semiconductor surface; and as well as the formation of H-aggregate (deprotonation of carboxylic acid) on the TiO₂ electrode respectively leads to efficient electron injection from the excited dye to the TiO₂ conduction bands [27,28]. The fluorescence spectra recorded upon their excitation of absorption maxima value of Carth-CN and Dpa-th-CN exhibits strong luminescence maxima at 558 nm ($\lambda_{ex} = 442$ nm) and 582 nm ($\lambda_{ex} = 462$ nm) respectively.

3.3. Electrochemical properties

The cyclic voltammograms (CV) of synthesized organic dyes in DMF are shown in Fig. 3 and their data are summarized in Table 1. The voltammogram of dyes, Car-th-CN and Dpa-th-CN exhibits single oxidation peaks with onset of 1.04, 0.85 V respectively with respect to Ag/AgCl reference electrode which corresponds to the



Fig. 2. Absorption spectra of bare TiO_2 film, Car-th-CN and Dpa-th-CN dyes adsorbed on nanocrystalline TiO_2 films.



Fig. 3. Cyclic volammogram of dyes were measured in DMF solutions with TBAP (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⁻¹.

highest occupied molecular orbital (HOMO) energy level of the organic dyes, were determined from the intersection of two tangents drawn at the rising current and background charging current of a cyclic voltammogram [29]. The oxidation potential of Car-th-CN is more positive than that of Dpa-th-CN is due to the weaker electron donating nature of Carbazole segment (high ionization potential) [30]. 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 [31] and 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 the absorption and emission spectra [32]. The introduction of thiophene π -bridge will negatively increases the LUMO energy levels of the dyes [22] and in turn enhances the electron injection to the TiO₂ conduction band compared to previous reported dyes containing cyano vinyl biphenyl as π -linker [14]. For better electron injection, this LUMO level should lie above the conduction band (CB) of the TiO₂ semiconductor (-4.0 eV vs vacuum) and for effective dye regeneration the HOMO energy level should lie below the I^-/I_3^- redox electrolyte (-4.6 eV vs vacuum) which is further improved negatively about 0.3 V by adding additives such as 4-tert-butyl pyridine (TBP) to the I^{-}/I_{3}^{-} redox electrolyte [33]. Hence, the energy levels of the synthesized dyes are suitable for electron injection and dye regeneration thermodynamically [34].

3.4. Exploring the electronic structure of dyes using computational methods

The optimized electronic structures of the synthesized dyes are calculated by density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods using B3LYP/6-31 G (d) level in gas phase with Gaussian 09 program. Calculated HOMO and LUMO energies of the compounds are listed in Table 1. The optimized structure of dyes and their HOMO, LUMO characters are shown in Fig. 4. According to the optimized molecular geometry of the Dpa-th-CN, the dihedral angle in $\angle C$ –N–C–C is \pm 90.98°, whereas in Car-th-CN it is 0° or 180°. As a result, the HOMO of the bi branched Dpa-th-CN is mainly on the one side of the central electron donating amine and thiophene moieties and LUMO is localized on the another side of the dye mainly on the electron withdrawing

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

Dye	$\lambda_{abs}/nm~(\epsilon/M^{-1}~cm^{-1})^a$	$\lambda_{em}/nm^{a,b}$	E ^{opt} (eV) ^c	E _{ox} /V (vs. Fc)	E _{HOMO} (eV) ^d	$E_{LUMO}(eV)^d$	HOMO ^e	LUMO ^e
Car-th-CN	438 (35,526)	558	2.54	1.04	5.39	2.85	-5.69	-3.54
Dpa-th-CN	458 (38,578)	582	2.36	0.85	5.20	2.84	-5.33	-3.94

 $^a\,$ Absorption and emission spectra were recorded in DMF solution (3 \times 10 $^{-4}\,$ M) at room temperature.

^b Dyes were excited at their absorption maximum value (for Car-th-CN, $\lambda_{ex} = 442$ nm and for Dpa-th-CN, $\lambda_{ex} = 462$ nm).

^c Optical band gap calculated from intersection between the absorption and emission spectra.

^d 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 intersection between the absorption and emission spectra of the sensitizers.

^e B3LYP/6-31G(d) calculated values.

cyano acetic acid and thiophene moieties. But, in Car-th-CN the HOMO lobes are localized both in amine and thiophene moieties and LUMO lobes are also localized in both cyano acetic acid and thiophene moieties. The LUMO of the thiophene moiety in Car-th-CN is similar to the HOMO of Car-th-CN, but the lobes do not align. This strategy appears more like an anti-bonding orbital which indicates that the intramolecular charge transfer induced electron movement from the donor site to the acceptor moiety through the thiophene π -bridge. In addition, the theoretical absorbance spectra calculated using TDDFT shows higher absorption maxima (λ_{max}) and molar extinction coefficient (ε) for Dpa-th-CN when compared to Car-th-CN similar to experimental absorbance spectra (Fig. 5). However, the theoretical λ_{max} values are highly red shifted compared to experimental values due to the error in TDDFT for charge transfer (CT) excited states and in addition the end absorption peak of Dpa-th-CN is blue shifted compared to Car-th-CN. The reasons for such blue shift in Dpa-th-CN is due to the planes are aligned perpendicular in diphenylamine which prevents the orbital overlapping and in turn reduces the ICT band [35].

3.5. Fabrication and characterization of DSSCs

TiO₂ nanoparticles were prepared according to the literature [36] and it was coated on a FTO glass substrate in the area of 1 cm². This plate was immersed in a DMF solution containing 3×10^{-4} M



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

dye sensitizers for 24 h. The photo cathode was prepared by H₂PtCl₆ solution (50 mM in isopropyl alcohol) which is deposited on the FTO glass by drop casting method and heated at 400 °C for 15 min [37,38]. The device was fabricated by the following method: the photo cathode was placed on top of the photo anode and was tightly clipped together. Then, 0.05 M I₂/0.5 M KI/0.5 M 4-tert-butyl pyridine (TBP) in 2-methoxypropionitrile electrolyte was injected in-between the two electrodes. Fig. 6 shows the photovoltaic properties of the fabricated devices under illumination in simulated AM 1.5 irradiation (85 mW cm⁻²). The short-circuit photocurrent density (J_{SC}), open circuit photovoltage (V_{OC}), and fill factor (FF) of Car-th-CN and Dpa-th-CN were tabulated (see Table 2). Upon comparing the photovoltaic properties of Car-th-CN and Dpath-CN, Car-th-CN based device shows better efficiency even though Dpa-th-CN have the better absorbance in the visible region [8]. This is because; according to DFT calculation the optimized structure of Car-th-CN is more planar than the Dpa-th-CN which helps to enhance the dyes adsorption and increases the high number of injected electrons through bi-anchoring -COOH groups. This is further confirmed by calculating the adsorbed amount (Γ) of dyes on TiO₂ surface by desorption of the dye from the TiO₂ surface using 0.1M NaOH in DMF/H₂O (1:1) mixture [39]. From the results, it is found that Car-th-CN adsorbs comparatively more than Dpath-CN dye may be due to the controlled aggregation of planar Car-th-CN dye on TiO₂ surface [40]. The spectra of incident photon to current conversion efficiency (IPCE) for DSSC based on Car-th-CN and Dpa-th-CN are shown in Fig. 7 and their data are summarized in Table 2 also supports the above facts. That is, the IPCE spectra of both dyes show the broader response between 350 nm and 600 nm with a maximum efficiency of about 38.1% for Car-th-CN and 26.6% for Dpa-th-CN at its wavelength maximum but the



Fig. 5. The TDDFT absorbance spectra of dyes calculated with B3LYP/6-31G (d) level.



Fig. 6. Current density-voltage characteristics for Car-th-CN and Dpa-th-CN based devices for DSSCs under illumination of simulated solar light (AM 1.5, 85 mW cm⁻²).

later have red shifted about 15 nm which is consistent with the absorption spectra of dye. Further comparing the IPCE spectra of the fabricated devices (Fig. 7) with the absorption spectra of dye loaded TiO₂ film (Fig. 2), both the spectra resembles same which led to efficient electron injection from the excited dye to the TiO₂ conduction band.

Further to understand the correlation between the improved cell performance and the internal resistances of the fabricated DSSCs the Electrochemical impedance spectroscopy (EIS) analysis [41] was performed at their open circuit potential (OCP) over a frequency range of 10^0-10^4 Hz under AM 1.5. The observed Nyquist plots (Fig. 8) for the DSSCs fabricated using the both dyes shows two semicircles; a small arc at high frequencies corresponds to the impedance of the Pt/electrolyte interface and a large arc at the low frequency regime corresponds to the impedance at the TiO₂/electrolyte interface [42]. The calculated radius of the semicircle in the low frequency regime indicates that the charge transport resistance is high for Dpa-th-CN based DSSC [43].Further, Bode phase plots were plotted in order to calculate the effective lifetime (τ_{eff}) of electrons in TiO₂ conduction band using the following equation [44].

 $\tau_{\rm eff} = 1/2\pi f$

Table 2

where the frequency (*f*) corresponding to peak in Bode phase plot for Car-th-CN and Dpa-th-CN is 35.56 Hz and 130.84 Hz and their electron lifetime (τ_{eff}) calculated from the above equation is 4.47 ms and 1.21 ms respectively. Comparing Car-th-CN and Dpa-th-CN dye based device, Car-th-CN dye based device exhibits longer electron lifetime (τ_{eff}) in TiO₂ conduction band because the generated radical cation of the sensitizer by photo excitation, is stabilized well in carbazole dye by the delocalization of the π - electrons compared

Tuble 2				
DSSC performance	parameters	of the	fabricated	devices.

Dye	Jsc (mA cm ⁻²)	Voc (mV)	FF	η (%) ^a	IPCE (%)	Surface concentration Γ (mol/cm ²)	Electron lifetime (τ_{eff}) (ms)
Car-th-CN	7.64	656	0.6848	4.04	38.1	2.84×10^{-7}	4.47
Dpa-th-CN	7.01	612	0.6270	3.16	26.6	2.12×10^{-7}	1.21

^a Illumination: 85 mW cm⁻² 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. 7. IPCE spectra of the fabricated devices based on Car-th-CN and Dpa-th-CN dyes.



Fig. 8. Electrochemical impedance spectra of DSSCs measured at V_{OC} , 85 mW cm⁻². (a) Nyquist plots. (b) Bode phase plots.



Fig. 9. Schematic representation for enhancement of electron lifetime (τ_{eff}) in TiO₂ conduction band while the donor of dye is changed from diphenylamine to carbazole.

to diphenylamine dye [40]. The longer electron lifetime observed with Car-th-CN sensitized cells indicates the inhibition of recombination of the injected electrons with the electrolyte $(I_3^- + 2e_{cb}^-(TiO_2) \rightarrow 3I^-)$ and that may be the cause for improve in the photocurrent and photovoltage, and in turn yielding to large extent enhanced device efficiency. This result suggests that planarity make a bigger role in designing of metal free organic dyes which enhance the adsorbed amount of dyes on TiO_2 surface and increases the electron lifetime in the TiO_2 photoelectrode (Fig. 9).

4. Conclusion

Novel dyes based on carbazole and diphenylamine (donors) combined with cyano vinyl thiophene π linkers and cyanoacrylic acid (acceptors) were designed and synthesized which opens up a new way for DSSCs. The photophysical, electrochemical and photovoltaic properties of the dyes were extensively studied. Both dyes have similar architecture but the carbazole based device exhibit a maximum solar energy to electricity conversion efficiency of 4.04% (Jsc = 7.684 mA cm⁻², Voc = 656 mV, ff = 0.68) under simulated AM 1.5 solar light irradiation. The result suggests that planarity make a bigger role in designing of metal free organic dyes which enhance the adsorbed amount of dyes on TiO₂ surface and increases the electron lifetime in the TiO₂ photoelectrode.

Acknowledgements

Authors thank DST, New Delhi (SR/S1/PC-49/2009) for sanctioning major research project and India-Spain Joint Collaborative project (DST/INT/Spain/P-37/11).

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.dyepig.2013.01.014.

References

- Regan BO, Gratzel M. A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ films. Nature 1991;353:737–40.
- Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chem Rev 2010;110:6595–663.
- [3] Gratzel M. Solar energy conversion by dye-sensitized photovoltaic cells. Inorg Chem 2005;44:6841-51.
- [4] Li SL, Jiang KJ, Shao KF, Yang LM. Novel organic dyes for efficient dyesensitized solar cells. Chem Commun 2006:2792–4.
- [5] Koumura N, Wang ZS, Mori S, Miyashita M, Suzuki E, Hara K. Alkyl-functionalized organic dyes for efficient molecular photovoltaics. J Am Chem Soc 2006;128:14256–7.
- [6] Horiuchi T, Miura H, Sumioka K, Uchida S. High efficiency of dye-sensitized solar cells based on metal-free indoline dyes. J Am Chem Soc 2004;126: 12218–9.

- [7] Zhu W, Wu Y, Wang S, Li W, Li X, Chen J, et al. Organic D-A-π-A solar cell sensitizers with improved stability and spectral response. Adv Funct Mater 2011;21:756–63.
- [8] Tang J, Hua J, Wu W, Li J, Jin Z, Long Y, et al. New starburst sensitizer with carbazole antennas for efficient and stable dye-sensitized solar cells. Energy Environ Sci 2010;3:1736–45.
- [9] Park SS, Won YS, Choi YC, Kim JH. Molecular design of organic dyes with double electron acceptor for dye-sensitized solar cell. Energy Fuels 2009;23: 3732-6.
- [10] Won YS, Yang Y, Kim JH, Ryu JH, Kim KK, Park SS. Organic photosensitizers based on terthiophene with alkyl chain and double acceptors for application in dye-sensitized solar cells. Energy Fuels 2010;24:3676–81.
- [11] Sahu D, Padhy H, Patra D, Yin JF, Hsu YC, Lin JT, et al. Synthesis and applications of novel acceptoredonoreacceptor organic dyes with dithienopyrrole- and fluorene-cores for dye-sensitized solar cells. Tetrahedron 2011;67:303–11.
- [12] Abbotto A, Manfredi N, Marinzi C, Angelis FD, Mosconi E, Yum JH, et al. Dibranched di-anchoring organic dyes for dye-sensitized solar cells. Energy Environ Sci 2009;2:1094–101.
- [13] Sirohi R, Kim DH, Yu S, Lee SH. Novel di-anchoring dye for DSSC by bridging of two mono anchoring dye molecules: a conformational approach to reduce aggregation. Dyes Pigm 2012;92:1132–7.
- [14] Ramkumar S, Manoharan S, Anandan S. Synthesis of D-(π-A)₂ organic chromophores for dye-sensitized solar cells. Dyes Pigm 2012;94:503-11.
- [15] Xu J, Zhu L, Fang D, Chen B, Liu L, Wang L, et al. Substituent effect on the π linkers in triphenylamine dyes for sensitized solar cells: a DFT/TDDFT study. ChemPhysChem 2012;13:3320–9.
- [16] Zhang L, Liu Y, Wang Z, Liang M, Sun Z, Xue S. Synthesis of sensitizers containing donor cascade of triarylamine and dimethylarylamine moieties for dye-sensitized solar cells. Tetrahedron 2010;66:3318–25.
- [17] Shen P, Liu Y, Huang X, Zhao B, Xiang N, Fei J, et al. Efficient triphenylamine dyes for solar cells: effects of alkyl-substituents and π -conjugated thiophene unit. Dyes Pigm 2009;83:187–97.
- [18] Hara K, Sato T, Katoh R, Furube A, Ohga Y, Shinpo A, et al. Molecular design of coumarin dyes for efficient dye-sensitized solar cells. J Phys Chem B 2003; 107:597–606.
- [19] Qin P, Yang X, Chen R, Sun L, Marinado T, Edvinsson T, et al. Influence of π -conjugation units in organic dyes for dye-sensitized solar cells. J Phys Chem C 2007;111:1853–60.
- [20] Wu IY, Lin JT, Luo J, Li CS, Tsai C, Wen YS, et al. Syntheses and second-order optical nonlinearity of ruthenium σ-acetylides with an end-capping organic electron acceptor and thienyl entity in the conjugation chain. Organometallics 1998;17:2188–98.
- [21] Zhao GJ, Chen RK, Sun MT, Liu JY, Li GY, Gao YL, et al. Photoinduced intramolecular charge transfer and S2 fluorescence in thiophene-π-conjugated donor-acceptor systems: experimental and TDDFT studies. Chem Eur J 2008; 14:6935–47.
- [22] Hara K, Kurashige M, Dan-oh Y, Kasada C, Shinpo A, Suga S, et al. Design of new coumarin dyes having thiophene moieties for highly efficient organicdye-sensitized solar cells. New J Chem 2003;27:783–5.
- [23] Huang T-H, Lin JT, Tao Y-T, Chuen C-H. Benzo[a]aceanthrylene derivatives for red-emitting electroluminescent materials. Chem Mater 2003;15:4854–62.
- [24] Elaine Adams J, Mantulin WW, Robert Huber J. Effect of molecular geometry on spin-orbit coupling of aromatic amines in solution. Diphenylamine, iminobibenzyl, acridan, and carbazole. J Am Chem Soc 1973;17:5477–81.
- [25] Winget P, Bredas JL. Ground-state electronic structure in charge-transfer complexes based on carbazole and diarylamine donors. J Phys Chem C 2011;115:10823–35.
- [26] Chang YJ, Chow TJ. Dye-sensitized solar cell utilizing organic dyads containing triarylene conjugates. Tetrahedron 2009;65:4726–34.
- [27] Wu Y, Marszalek M, Zakeeruddin SM, Zhang Q, He Tian, Gratzel M, et al. Highconversion-efficiency organic dye-sensitized solar cells: molecular engineering on D–A–π-A featured organic indoline dyes. Energy Environ Sci 2012;5: 8261–72.
- [28] Mao J, He N, Ning Z, Zhang Q, Guo F, Chen L, et al. Stable dyes containing double acceptors without COOH as anchors for highly efficient dye-sensitized solar cells. Angew Chem Int Ed 2012;51:1–5.
- [29] Agrawal AK, Jenekhe SA. Electrochemical properties and electronic structures of conjugated polyquinolines and polyanthrazolines. Chem Mater 1996;8: 579–89.
- [30] Chen BC-H, Huang W-S, Lai M-Y, Tsao W-C, Lin JT, Wu Y-H, et al. Versatile, benzimidazole/amine-based ambipolar compounds for electroluminescent applications: single-layer, blue, fluorescent OLEDs, hosts for single-layer, phosphorescent OLEDs. Adv Funct Mater 2009;19:2661–70.
- [31] Pomrnerehne BJ, Vestweber H, Gun W, Muhrt RF, Bassler H, Porsch M, et al. Efficient two layer leds on a polymer blend basis. Adv Mater 1995;7:551-4.
- [32] Tian H, Yang X, Cong J, Chen R, Liu J, Hao Y, et al. Tuning of phenoxazine chromophores for efficient organic dye-sensitized solar cells. Chem Commun 2009:6288–90.
- [33] Boschloo G, Ha1ggman L, Hagfeldt A. Quantification of the effect of 4-tertbutylpyryidine addition to I⁻/I₃ redox electrolytes in dye-sensitized nanostructured TiO₂ solar cells. J Phys Chem B 2006;110:13144–50.
- [34] Justin Thomas KR, Hsu YC, Lin JT, Lee KM, Ho KC, Lai CH, et al. 2,3-Disubstituted thiophene-based organic dyes for solar cells. Chem Mater 2008;20: 1830–40.

- [35] Dreuw A, Head-Gordon M. Failure of time-dependent density functional theory for long-range charge-transfer excited states: the zincbacteriochlorinbacteriochlorin and bacteriochlorophyll-spheroidene complexes. J Am Chem Soc 2004;126:4007–16.
- [36] Sirimanne PM, Tributsch H. Parameters determining efficiency and degradation of TiO_2 |dye|Cul solar cells. J Solid State Chem 2004;177: 1789–95.
- [37] Xu W, Peng B, Chen J, Liang M, Cai F. New triphenylamine-based dyes for dyesensitized solar cells. J Phys Chem C 2008;112:874–80.
- [38] He J, Wu W, Hua J, Jiang Y, Qu S, Li J, et al. Bithiazole-bridged dyes for dyesensitized solar cells with high open circuit voltage performance. J Mater Chem 2011;21:6054–62.
- [39] Tian H, Yang X, Chen R, Zhang R, Hagfeldt A, Sun L. Effect of different dye baths and dye-structures on the performance of dye-sensitized solar cells based on triphenylamine dyes. J Phys Chem C 2008;112:11023–33.

- [40] Do K, Kim D, Cho N, Paek S, Song K, Ko J. New type of organic sensitizers with a planar amine unit for efficient dye-sensitized solar cells. Org Lett 2012;14:222–5.
- [41] Kern R, Sastrawan R, Ferber J, Stangl R, Luther J. Modeling and interpretation of electrical impedance spectra of dye solar cells operated under open-circuit conditions. Electrochim Acta 2002;47:4213–25.
- [42] Lee CP, Chen PY, Vittala R, Ho KC. Iodine-free high efficient quasi solid-state dye-sensitized solar cell containing ionic liquid and polyaniline-loaded carbon black. J Mater Chem 2010;20:2356–61.
- [43] Wu W, Yang J, Hua J, Tang J, Zhang L, Long Y, et al. Efficient and stable dyesensitized solar cells based on phenothiazine sensitizers with thiophene units. J Mater Chem 2010;20:1772–9.
- [44] Naveen Kumar E, Jose R, Archana PS, Vijila C, Yusoff MM, Ramakrishna S. High performance dye-sensitized solar cells with record open circuit voltage using tin oxide nano flowers developed by electrospinning. Energy Environ Sci 2012;5:5401–7.