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Carbazole based A- π -D- π -A dyes with double electron acceptor for dye-sensitized solar cell



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ARTICLE INFO

Article history: Received 26 July 2013 Received in revised form 4 November 2013 Accepted 4 November 2013 Available online 22 November 2013

Keywords: Dye sensitized solar cells Double acceptor dye A- π -D- π -A structure Anchoring stability Carbazole Linker

ABSTRACT

Three novel carbazole-based A- π -D- π -A-featured dyes (**CSG1–CSG3**) have been designed, synthesized for applications in dye-sensitized solar cells and fully characterized with NMR, MS, IR, UV–vis and electrochemical measurements. These dyes share the same donor (N-hexylcarbazole) and acceptor/anchoring group (cyanoacrylic acid), but differs in conjugated linkers incorporated, such as benzene, furan or thiophene, to configure the novel A- π -D- π -A framework for effective electron flow. The power conversion efficiencies were observed to be sensitive to the π -bridging linker moiety. The photovoltaic experiments showed that dye with a benzene linker exhibited a higher open-circuit voltage (0.699 V) compared to thiophene and furan linker. Among all dyes, **CSG2** containing a thiophene linker exhibited the maximum overall conversion efficiency of 3.8% (J_{SC} = 8.90 mA cm⁻², V_{OC} = 584 mV, *FF* = 0.74) under standard global AM 1.5 G solar condition. Under similar fabrication conditions, champion dye **N719** exhibited the maximum overall conversion efficiency of 6.4% (J_{SC} = 14.74 mA cm⁻², V_{OC} = 606 mV, *FF* = 0.716).

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1. Introduction

Dye-sensitized solar cells (DSSCs), one of the most promising alternatives to crystalline silicon-based photovoltaics for converting clean, inexhaustible sunlight to electricity have received significant research interest due to their low fabrication cost and relatively high power conversion efficiency (η), since the seminal work was reported in 1991 by O'Regan and Graetzel [1–10]. In the past 5 years, such solar cells have witnessed tremendous progress. For example, a power conversion efficiency (η) of 11.9% has been reached with bipyridyl-based ruthenium sensitizer [11] and particularly a certified record η of 11.4% has also been achieved very recently for terpyridine based dyes

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using a simple co-adsorbent developed by our group [12] under standard AM 1.5 solar light irradiation. Record efficiencies of 12.3% under AM 1.5 conditions have been achieved by using Zn(II)-porphyrin dyes and cobalt poly pyridyl redox electrolyte [13]. Recently, organic-inorganic hybrid perovskites have attracted attention as lightharvesting materials for mesoscopic solar cells [14-18]. Moreover, solar cells based on these hybrids exhibited a highest power conversion efficiency of 15.0% under standard AM 1.5 conditions [18]. Although metal based dyes have high efficiency and long-term stability, they have encountered problems such as relatively low molar extinction coefficient, limited resources, morphological variations, challenging synthesis and tedious purification which might retard future large scale power production based on DSSCs [4].

On the other hand, metal-free organic dyes have been developed for DSSCs. Their advantages are due to their

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high molar absorption coefficients, inexpensive syntheses by using well-established synthetic methodologies and they present optical, electronic, and electrochemical properties that can be modulated through appropriate molecular design [19–23]. Moreover, organic dyes normally possess higher molar extinction coefficients than Ru dyes $(<20,000 \text{ M}^{-1} \text{ cm}^{-1})$, which make them ideal for solid state DSSCs, utilizing thinner TiO₂ layers. In particular, encouraging efficiency up to 10.3% has been reported by Wang et al. using metal free organic dyes [22]. Among metal-free organic dyes, a common strategy in the design of highly efficient sensitizers for DSSCs is linking the electron donor (D) and acceptor (A) systems (D–A) through the π -conjugated linkers with TiO₂ surface anchoring groups (e.g., carboxylate) integrated onto the acceptor moiety [24]. Variation of the π -conjugated linker seriously affects the efficiency of the intramolecular charge transfer, and partially determines the DSSC performance of the corresponding cells [25]. However, the low conversion efficiency and low stability are important issues still to be resolved [26]. Another crucial factor is the binding strength of dye on the TiO₂ surface, which affects the conversion efficiency and stability of DSSC device. Strong binding of the dye on TiO₂ not only improves adsorption but also induces efficient charge injection. One of the drawbacks of most of the organic dye molecules is the presence of single anchoring functionality which can be a serious constraint for inferior performance as compared to Ru(II) sensitizers, where 1-4 anchoring groups are present [27]. Thus, several di/ multi anchoring organic dyes have been synthesized for use in DSSCs, and have demonstrated better cell performance than single D- π -A sensitizers with an improved photoresponse, photocurrent and stability [28–33].

3,6-Functionalized carbazole is a nonplanar compound which can improve the hole transporting ability of the materials and prevent the formation of dye aggregates [34]. Due to its unique optical, electrical, and chemical properties, carbazole has been used widely as a functional building block or substituent in the construction of organic molecules for use as light-emitting and hole-transporting layers in OLED devices [35–42], as host materials for electrophosphorescent applications [43], and as active components in solar cells [44,45]. Moreover, upon introduction of a carbazole unit into the structure, the thermal stability and glassy state durability of the organic molecules improves significantly [46,47].

Furthermore, alkyl-functionalized carbazole dyes have been designed and used in DSSCs to improve both performance and stability. Kohjiro Hara et al. showed that the presence of hexyl substituents increased the electron lifetime and consequently open circuit voltage [48–53]. We and others reported that the substitution of alkyl chains on dye peripheral can inhibit the recombination losses in DSSC [48,54–57]. As mentioned above, the introduction of π -linker moieties were expected to allow red-shift of the spectrum, and broaden the spectral region of absorption. Based on the above consideration, and our experience on metal free organic sensitizers and carbazole substituted ruthenium [58–60], we have designed and synthesized three new efficient organic carbazole-based double electron acceptor dyes (**CSG1–CSG3** shown in Fig. 1) with



Fig. 1. Chemical structures of organic dyes CSG1-CSG3.

cyanoacrylic acid moiety acting as the anchoring group and variation of π -conjugated linkers. Finally, the three new sensitizers have been applied successfully to the sensitization of nanocrystalline TiO₂-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented.

2. Experimental

2.1. Materials and instruments

All reactions were carried out under nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. ¹H and ¹³C NMR spectra were recorded on Avance 300 or 500 MHz spectrometer. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in CDCl₃. Low resolution mass spectrometer (Thermo Fisher, Sanjose, CA, USA) equipped with an ESI source. IR spectra were recorded on a Perkin– Elmer 1800 series FTIR spectrometer and samples were analyzed as thin films on KBr pellets.

The optical spectra of dyes in solution were recorded with a UV–vis spectrophotometer (Shimadzu) while their emission measurements were performed using a Fluorolog 3, JY Horiba fluorescence spectrometer. Electrochemical data were recorded using Autolab potentiostat/ Galvano-stat PGSTAT30. The cyclic voltammogram curves were obtained from a three electrode cell in 0.1 M Bu₄NPF₆ *N*,*N*-dimethylformamide solution at a scan rate of 100 mV s⁻¹, Pt wire as a counter electrode and an Ag/AgCl reference electrode and calibrated with ferrocene.

2.1.1. Synthesis of 3,6-dibromo-9 hexyl-9H carbazole(3)

To a solution of 3,6-dibromo-9H-carbazole (0.200 g, 0.615 mmol) in dry *N*,*N*-dimethylformamide was added KOH (0.105 g, 1.845 mmol) and allowed to stir for 30 min. To this, 1-bromo hexane (0.962 mL, 0.799 mmol) dissolved in dry *N*,*N*-dimethylformamide was added drop wise and allowed to room temperature with stirring for 12 h. After complete consumption of the dibromocarbazole (TLC), crushed ice was added and stirred well. The

precipitate formed filtered and dried. Then, the obtained crude solid was subjected to silica gel chromatography using a mixture of ethyl acetate and n-hexane as an eluent to obtain pure product **3** (83%). ¹H NMR (CDCl₃, 300 MHz) δ 8.13 (s, 2H), 7.55–7.52 (m, 2H), 7.25–7.27 (m, 2H), 4.24–4.22 (t, 2H, *J* = 6.929 Hz), 1.79–1.84 (m, 2H), 1.24–1.35 (m, 6H), 0.873–0.87(m, 3H). ¹³C NMR (CDCl₃, 300 MHz) δ 139.2, 128.9, 123.3, 123.1, 111.8, 110.3, 43.2, 31.4, 28.7, 26.8, 22.4, 13.9. MS (ESI) *m/z*: 411 (M+2)⁺.

2.1.2. Synthesis of 4,4'-(9-hexyl-9H-carbazole-3,6diyl)dibenzaldehyde (**4**)

4-Formylphenylboronic acid (0.92 g, 0.583 mmol), 3,6dibromo-9 hexyl-9H carbazole (0.100 g, 0.243 mmol) and $Pd(PPh_3)_4$ (0.056 g, 20 mol%) in dimethoxyethane (5 mL) and a 2 M Na₂CO₃ aqueous solution (2 mL) was degassed with nitrogen. Then, the reaction mixture was refluxed for 36 h under nitrogen atmosphere. After cooling the mixture down to room temperature, filtered through Celite, extracted with ethyl acetate. The extracts were combined and dried with anhydrous Na₂SO₄, and then filtered. The solvent was completely removed by rotary evaporation. The solid residue was purified by column chromatography using ethyl acetate-hexane as the eluent to get 4 (41%). ¹H NMR (CDCl₃, 300 MHz) δ 10.08 (s, 2H), 8.44–8.46 (m, 2H), 7.98-8.02 (m, 2H), 7.89-7.93 (m, 4H), 7.79-7.83 (m, 2H), 7.52-7.55 (m, 4H), 4.38 (t, 2H, J = 6.798 Hz), 1.89-1.96 (m, 2H), 1.26–1.30 (m, 6H), 0.85–0.91(m, 3H). ¹³C NMR (CDCl₃, 300 MHz) δ 191.9, 147.9, 141, 134.5, 130.3, 127.5, 125.6, 123.5, 119.3, 109.5, 43.4, 31.5, 28.9, 26.9, 22.5, 13.9. MS (ESI) m/z: 460 (M+1)⁺.

2.1.3. Synthesis of 5,5'-(9-hexyl-9H-carbazole-3,6diyl)dithiophene-2-carbaldehyde (5)

A mixture of 5-formylthiophen-2-ylboronic acid (0.91 g, 0.583 mmol), 3,6-dibromo-9 hexyl-9H carbazole (0.100 g, 0.243 mmol) and Pd(PPh₃)₄ (0.056 g, 20 mol%) in dimethoxyethane (5 mL) and a 2 M Na₂CO₃ aqueous solution (2 mL) was degassed with nitrogen. Then, the reaction mixture was refluxed for 36 h under nitrogen atmosphere. After cooling the mixture down to room temperature, filtered through Celite, extracted with ethyl acetate. The extracts were combined and dried with anhydrous Na₂SO₄, and then filtered. The solvent was completely removed by rotary evaporation. The solid residue was purified by column chromatography using ethyl acetate-hexane as the eluent to get 5 (45%). ¹H NMR (CDCl₃, 300 MHz) δ 9.89 (s, 2H), 8.40-8.42 (m, 2H),7.77-7.82 (m, 2H), 7.42-7.48 (m, 4H), 6.86–6.88 (m, 2H), 4.31 (t, 2H, J = 6.78 Hz), 1.84-1.94 (m, 2H), 1.27-1.32 (m, 6H), 0.87-0.90 (m, 3H). ¹³C NMR (CDCl₃, 300 MHz) δ 182.5, 155.5, 141.2, 137.8, 124.8, 124.5, 122.9, 118.4, 109.5, 43.3, 31.3, 29.5, 26.7, 22.4, 13.9. MS (ESI) m/z: 472 (M+1)⁺.

2.1.4. Synthesis of 5,5'-(9-hexyl-9H-carbazole-3,6diyl)difuran-2-carbaldehyde (**6**)

5-Formylfuran-2-ylboronic acid (0.82 g, 0.583 mmol), 3,6-dibromo-9 hexyl-9H carbazole (0.100 g, 0.243 mmol) and Pd(PPh₃)₄ (0.056 g, 20 mol%) in dimethoxyethane (5 mL) and a 2 M Na₂CO₃ aqueous solution (2 mL) was degassed with nitrogen. Then, the reaction mixture was refluxed for 36 h under nitrogen atmosphere. After cooling the mixture down to room temperature, filtered through Celite, extracted with ethyl acetate. The extracts were combined and dried with anhydrous Na₂SO₄, and then filtered. The solvent was completely removed by rotary evaporation. The solid residue was purified by column chromatography using ethyl acetate-hexane as the eluent to get **6** (40%). ¹H NMR (CDCl₃, 300 MHz) δ 9.64 (s, 2H), 8.56–8.58 (m, 2H), 7.90–7.93 (m, 2H), 7.36–7.42 (m, 4H), 6.86–6.88 (m, 2H), 4.27 (t, 2H, *J* = 6.789 Hz), 1.83–1.89 (m, 2H), 1.27–1.34 (m, 6H), 0.86–0.90 (m, 3H). ¹³C NMR (CDCl₃, 300 MHz) δ 176.7, 160.7, 151.5, 141.5, 123.8, 123.1, 120.7, 118, 109.4, 43.4, 31.8, 29.6, 26.8, 22.6, 14.1. MS (ESI) *m/z*: 440 (M+1)⁺.

2.1.5. Synthesis of 3,3'-(4,4'-(9-hexyl-9H-carbazole-3,6diyl)bis(4,1-phenylene))bis(2-cyanoacrylic acid) (**CSG1**)

Compound 4, 4,4'-(9-hexyl-9H-carbazole-3,6-diyl) dibenzaldehyde (0.100 g, 0.217 mmol), dissolved in acetic acid was condensed with cyanoaceticacid (0.055 g, 0.651 mmol) in the presence of ammonium acetate (5 mol%). Then, the reaction mixture was refluxed well for 12 h under N₂. After cooling to room temperature, the reaction mixture was poured into a crushed ice and solid obtained was washed thoroughly with water to remove excess of acetic acid and cyanoacetic acid. Finally, washed with pentane, hexane and 3% ethyl acetate in hexane to afford a fine yellow colored solid **CSG1** (80%). ¹H NMR (CDCl₃, 300 MHz) & 8.51 (s, 2H),8.28 (s, 2H), 8.09-8.14 (d, 4H), 7.89-7.94 (m, 4H), 7.81-7.86 (d, 2H), 7.54-7.59 (m, 2H), 4.35-4.42 (m, 2H), 1.87-1.95 (m, 2H), 1.28-1.43 (m, 6H), 0.83–0.89 (m, 3H). ^{13}C NMR (CDCl₃ + DMSO, 300 MHz) δ 161.6, 151.8, 143.5, 138.8, 129.5, 127.6, 124.9, 123.1, 121.2, 114.4, 108.1, 100.3, 40.7, 29.1, 26.6, 24.2, 20.1, 11.9. IR (KBr, cm⁻¹) 3437.15, 2926.63, 2222.89, 1697.04, 1571.09, 1482.98, 1425.39, 1271.44, 1186.64, 802.87, 705.08. MS (ESI-) m/z: 572 (M-1)⁺. MS (ESI-) m/z: 592 $(M-1)^{+}$.

2.1.6. Synthesis of 3,3'-(5,5'-(9-hexyl-9H-carbazole-3,6-

divl)bis(thiophene-5,2-divl))bis(2-cyanoacrylic acid) (CSG2) Compound 5, 5,5'-(9-hexyl-9H-carbazole-3,6-diyl) dithiophene-2-carbaldehyde (0.100 g, 0.212 mmol), dissolved in acetic acid was condensed with cyanoacetic acid (0.054 g, 0.636 mmol) in the presence of ammonium acetate (5 mol%). Then, the reaction mixture was refluxed well for 12 h under N₂. After cooling to room temperature, the reaction mixture was poured into a crushed ice and solid obtained was washed thoroughly with water to remove excess of acetic acid and cyanoacetic acid. Finally, washed with pentane, hexane and 3% ethyl acetate in hexane to afford a fine red colored solid **CSG2** (85%). ¹H NMR (CDCl₃, 300 MHz) δ 8.69 (s, 2H), 8.36-8.39 (m, 2H), 7.84-7.93 (m, 4H), 7.69-7.71 (m, 2H), 7.58-7.62 (m, 2H), 4.38-4.44 (m, 2H), 1.82-1.88 (m, 2H), 1.23-1.36 (m, 6H), 0.83-0.88 (m, 3H). ¹³C NMR (CDCl₃ + DMSO, 300 MHz) δ 162, 153.1, 144.4, 139, 131.6, 122.2,121.8, 120.9, 116.9, 114.6, 93.7,40.93, 29.2, 27.3, 24.4, 20.2, 12.1. IR (KBr, cm⁻¹) 3441.84, 2923.68, 2210.32, 1684.30, 1567.97, 1413.42, 1258.66, 1214.40, 1181.26, 1069.26, 786.74. MS (ESI-) m/ $z: 604 (M-1)^+$.

2.1.7. Synthesis of 3,3'-(5,5'-(9-hexyl-9H-carbazole-3,6diyl)bis(furan-5,2-diyl))bis(2-cyanoacrylic acid)(**CSG3**)

Compound 6, 5,5'-(9-hexyl-9H-carbazole-3,6-diyl)difuran-2-carbaldehvde (0.100 g, 0.227 mmol), dissolved in acetic acid was condensed with cyanoaceticacid (0.058 g, 0.681 mmol) in the presence of ammonium acetate (5 mol%). Then, the reaction mixture was refluxed well for 12 h under N₂. After cooling to room temperature, the reaction mixture was poured into a crushed ice and solid obtained was washed thoroughly with water to remove excess of acetic acid and cyanoacetic acid. Finally, washed with pentane, hexane and 3% ethyl acetate in hexane to afford a fine red colored solid **CSG3** (84%). ¹H NMR (CDCl₃, 300 MHz) δ 8.71 (s, 2H), 8.05-8.11 (m, 4H), 7.78-7.83 (d, 2H), 7.60-7.64 (d, 2H), 7.29-7.32(d,2H), 4.42-4.49 (m, 2H), 1.76-1.84 (m, 2H), 1.23-1.32 (m, 6H), 0.76-0.84 (m, 3H). ¹³C NMR (DMSO, 300 MHz) δ 164, 160.1, 146.9, 141.2, 137.4, 122.3, 120, 117.7, 116.7, 110.5, 108.3, 42.5, 30.7, 28.3, 25.9, 21.9, 13.7. IR (KBr, cm⁻¹)3434.65, 2925.3, 2213.17, 1688.43, 1589.92, 1528.92, 1460.66, 1417.66, 1263.42, 1234.49, 1191.4, 1037.3, 708.19. MS (ESI-) m/z: 572 $(M-1)^+$.

2.2. Preparation of TiO2 electrode

Nanocrystalline TiO2 photoelectrodes of about 20 µm thickness (area: 0.25 cm²) were prepared using a variation of a method reported by Graetzel and co-workers [61]. Fluorine-doped tin oxide coated (FTO) glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8–10 ohm m^{-2} and an optical transmission of >80% in the visible range were used. Anatase TiO₂ colloids (particle size ~13 nm) were obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). The nanocrystalline TiO₂ thin films of approximately 20 µm thickness were deposited onto the conducting glass by screen-printing. The film was then sintered at 500 °C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co., Ltd.). The electrodes were impregnated with a 50 mM titanium tetrachloride solution and sintered at 500 °C. The dye solutions $(2 \times 10^{-4} \text{ M})$ were prepared in 1:1 acetonitrile and tert-butyl alcohol solvents. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 h to adsorb the dye onto the TiO₂ surface.

2.3. Fabrication of dye-sensitized solar cell

Photovoltaic measurements were performed in a twoelectrode sandwich cell configuration. The dye-deposited TiO₂ film was used as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were separated by a surlyn spacer (40 μ m thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M I₂, 0.5 M TBP and 0.1 M LiI in acetonitrile and is introduced into the device by vacuum filling method through the predrilled hole on the counter electrode.

2.4. Photovoltaic characterization

The current–voltage characteristics were measured using the previously reported method with a solar simulator (AM-1.5, 100 mW cm⁻², WXS-155S-10: Wacom Denso Co., Japan) [62]. Monochromatic incident photon-tocurrent conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co., Ltd.).

3. Results and discussion

3.1. Synthesis

The photosensitive dyes in this study are depicted in Fig. 1. Synthetic routes to the as synthesized organic dyes are illustrated in Scheme 1. Carbazole (1) was used as starting material. The dibromocarbazole derivative 2 was synthesized according to previously published procedure in 90% yield [63]. This dibromocarbazole (2) was N-alkylated using n-hexylbromide and KOH as base in DMF medium at room temperature for 12 h to give compound 3 in 83% yield. In the next step, Suzuki coupling reaction of 3 with (4-formylphenyl)-, (5-formylthiophen-2-yl)-, or (5-formylfuran-2-yl)-boronic acid afforded corresponding Knoevenagel precursors 4-6 in quantitative yields (40-45%). These reactions were carried out in DME medium by using $Pd(PPh_3)_4$ as catalyst under reflux conditions for 48 h. Finally, these aldehyde intermediates were converted into corresponding dyes through Knoevenagel reaction by treating with cyanoacetic acid using piperdine as base affording 80%, 85% and 84% yields for CSG1, CSG2 and CSG3 respectively. These target dyes were fully characterized by NMR spectroscopy and mass spectrometry. All the compounds found to be consistent with the proposed structures.

3.2. Photophysical properties

The UV-vis absorption spectra of CSG1, CSG2 and CSG3 in DMF solution are depicted in Fig. 2 and the corresponding data are summarized in Table 1. The band located at shorter wavelength is attributed to the $\pi - \pi^*$ electron transition of the chromophore. The absorption band at 369–293 nm can be ascribed to localized aromatic π – π transitions. The absorption band at around 359-427 nm can be ascribed to an intramolecular charge transfer (ICT) between the carbazole donor and the cyanoacetic acceptor [64], the absorption maximum wavelength (λ_{max}) of **CSG1**, CSG2 and CSG3 was at 362, 415, and 427 nm respectively, and the corresponding molar extinction coefficients were 3.43×10^4 , 3.27×10^4 and $3.92 \times 10^4 M^{-1} cm^{-1}$, respectively (i.e., increasing in the order CSG2 < CSG1 < **CSG3**). The λ_{max} of **CSG3** with the furan linker was red-shifted 3 nm compared to that of CSG2 with the thiophene linker, while the λ_{max} of **CSG2** was red-shifted 38 nm compared to that of dye CSG1 with the benzene linker. This is due to the better delocalization of electrons over the π -conjugated molecules when furan



Scheme 1. Synthetic route for organic dyes CSG1–CSG3. Reagents and conditions: (i) NBS in DMF, toluene, 0 °C, 2 h; (ii) 1-bromohexane, KOH, DMF, RT, 12 h; (iii) (OH)₂B-Ar-CHO, Na₂CO₃, DME, reflux, 48 h; (iv) cyanoaceticacid, CH₃COONH₄, CH₃COOH, reflux, 6 h.

and thiophene were used as linkers in this A- π -D- π -A framework.

The fluorescence emission spectra of all the dyes exhibited strong luminescence maxima in the wavelength region 486–502 nm recorded in DMF medium (Fig. 3) upon their excitation of absorption maximum value. To find out their excited state behavior, the fluorescence emission properties for **CSG1-CSG3** were examined in solvents of different polarity. The examples of solvatochromic behavior of the dyes **CSG1-CSG3** are illustrated in Fig. 4 and corresponding data presented in Table 2. The emission peak wavelength decreases as the solvent polarity increases. A clear negative solvatochromism observed for the dyes in fluorescence further supports the presence of an intramolecular charge transfer transition from the donor to acceptor within the A- π -D- π -A framework. Since the dyes are dipolar in nature, polar solvents are expected to stabilize them in the ground and excited states equally. However a significant blue shift observed for the emission spectra recorded for polar solvents such as DMF and THF when compared to that measured in CHCl₃ solution is interesting and indicate a less polar excited state [65].

The absorption spectra of **CSG1**, **CSG2** and **CSG3** on TiO_2 films are shown in Fig. 5. The maximum absorption peaks for **CSG1**, **CSG2** and **CSG3** on TiO_2 films are at 391, 427, and 396 nm, respectively. Compared with the solution spectra, the absorption bands of the **CSG1** and **CSG2** dyes on the TiO_2 films are red shifted by 29 and 12 nm, respectively.



Fig. 2. UV-vis absorption spectra of three organic dyes in DMF.

Table 1

Optical and redox parameters of CSG1-CSG3.

Dye	$\lambda_{abs}^{a} (nm)$ ($\epsilon/M^{-1} cm^{-1}$)	λ_{em}^{b} (nm)	E _{OX} ^c (V vs. SCE)	E_{0-0}^{d} (V)	E _{LUMO} ^e (V vs. SCE)
CSG1	362(34,300)	494	1.15	2.77	-1.62
CSG2	415(32,700)	502	1.07	2.66	-1.59
CSG3	427(39,200)	486	1.05	2.66	-1.61

^a Absorption spectra.

^b Emission spectra.

^c E_{ox} is oxidation potential.

 $^{\rm d}~E_{\rm 0-0}$ is voltage of intersection point between absorption and emission pectra.

 E_{LUMO} was calculated by $E_{\text{ox}} - E_{0-0}$.



Fig. 3. Emission spectra of the dye CSG1-CSG3 recorded in DMF.

This red shift can be explained by the formation of J-aggregates of the dye on TiO₂ [66]. Whereas the absorption band of the **CSG3** on the TiO₂ film is blue shifted by 31 nm, which is attributed to the formation of H-type aggregates or deprotonation of the carboxylic acid units. Similar phenomena have been observed for several other organic dyes [67–70]. Results of previous research indicated that the smaller λ_{max} shifts associated with dyes from solution *vs.* the solid state suggest a smaller tendency to

form dye aggregates on the semiconductor surface. This phenomenon leads to higher photo-current densities [64,71]. Based on this assumption, **CSG2**, showing the smallest change of absorption spectrum on TiO_2 , seemed to be more efficient in suppressing the formation of dye aggregates on the TiO_2 surface.

To explain the anchoring mode of **CSG1–CSG3** on TiO₂, FTIR spectra of pristine **CSG1–CSG3** powders and that of dyes adsorbed on TiO₂ have been measured (Fig. 6). The IR spectra of the sensitized films display two characteristic bands centered at ~1592 and ~1355 cm⁻¹, respectively, are associated with the COO⁻ antisymmetric and symmetric stretching vibrations of carboxylate groups coordinated with surface titanium atoms. The FT-IR spectra reveal that bands observed at ~1685 cm⁻¹ assigned to the free carboxylic acid groups of powdered **CSG1– CSG3** dyes completely disappeared indicating that **CSG1–CSG3** dyes are absorbed on the TiO₂ surface with both of the anchors [33].

3.3. Electrochemical properties

To evaluate the thermodynamically allowed electron transfer processes from the excited dye molecule to the conduction band of TiO_2 , cyclic voltammetry (CV) measurements were performed. The ground and excited state oxidation potentials of the three dyes were measured and the results summarized in Table 1.

Fig. 7 shows a schematic energy diagram of three dyes based on absorption and electrochemical data. The ground-state oxidation potentials Eox of CSG1, CSG2 and CSG3, corresponding to the highest occupied molecular orbital (HOMO) level of dyes, range from 1.05 to 1.15 V vs. SCE. These values are more positive than the I_2^-/I^- redox potential (0.42 V vs. SCE) [72-75], indicating that the oxidized dye formed after electron injection into the conduction band of TiO₂ and thermodynamically accepted electrons from I^- ions from the electrolyte [76,77]. The excited-state oxidation potentials E_{0x}^* , which reflect the lowest occupied molecular orbital (LUMO) level of the sensitizers, play an important role in the electron injection process. The excited-state oxidation potential E_{0x}^* was calculated using: $E_{OX}^* = E_{OX} - E_{0-0}$ where E_{0-0} is the zerothzeroth transition value obtained from the intersection of the normalized lowest energy absorption peak and highest energy fluorescence peak. The LUMO levels of these dyes are in the range of -1.59 to -1.62 V vs. SCE, which are more negative than the conduction band edge of TiO₂ (-0.5 V vs. SCE) [78-80]. The driving force is sufficient for efficient charge injection, provided that an energy gap between dye LUMO and TiO₂ conduction band (CB) is >0.2 eV [81,82]. Thus, the electron injection process from the excited dye molecule to the TiO₂ conduction band and the subsequent dye regeneration are energetically permitted. Such electronic structures thus ensure a favorable exothermic flow of charges throughout the photo-electric conversion. Further, the LUMO level of CSG1 (-1.62 V vs. NHE) is more negative than that of CSG2 and CSG3 (-1.59 and -1.61 V vs. NHE, respectively), indicating that **CSG1** dye has more efficient electron injection.



Fig. 4. Emission spectra of the dye (a) CSG1 (b) CSG2 and (c) CSG3 recorded in different solvents.

Table 2Emission data of the CSG1-CSG3 in different solvents.

Dye	$\lambda_{\rm em}$ (nm)			
	CHCl ₃	THF	DMF	DMSO
CSG1	544	520	494	524
CSG2	540	502	502	525
CSG3	527	495	486	512



Fig. 5. Absorption spectra of the three dyes absorbed onto ${\rm TiO}_2$ film electrodes.

3.4. Photovoltaic performance in dye-sensitized solar cells

Fig. 8 shows the incident photon-to-current conversion efficiency (IPCE) as a function of incident wavelength for DSSCs based on CSG1, CSG2 and CSG3. The dye-coated TiO₂ film was used as the working electrode, platinized FTO glass as the counter electrode, and 0.5 M 1,2-dimethyl-3-propylimidazole iodide (DMPII), 0.05 M I₂, 0.1 m LiI, and 0.5 M 4-tert butylpyridine (TBP) in acetonitrile as the redox electrolyte. In comparison to CSG1, the onset wavelengths for CSG2 and CSG3 were shifted to longer wavelength. The onset wavelengths for CSG2 and CSG3 were around 700 nm while that with CSG1 was around 625 nm, suggesting the increased donor ability of CSG2 and CSG3. Excellent IPCE performance was observed from 350 to 550 nm, CSG1 with a maximum of 82% at 420-490 nm, CSG2 with a maximum of 72% at 365-545 nm and CSG3 with a maximum of 66% at 360-525 nm.



Fig. 6. FT-IR spectra of CSG1-CSG3 in KBr and adsorbed on TiO₂ film.



Fig. 7. The schematic energy levels of CSG1-CSG3 based on absorption and electrochemical data.

On the other hand, the IPCE of **CSG1** is higher than that of **CSG3** in the region of 330–510 nm, although the IPCE value of **CSG1** is significantly lower than **CSG3** in the remaining visible region (see Fig. 8), which suggests that **CSG1** has a higher cell performance. Despite of highest absorption wavelength, the decreased IPCE values observed for **CSG3** can be attributed to the increase of dye aggregation on TiO₂ surface [21,83]. The sensitizer **CSG2** has broader action spectra compared to **CSG1** which means that it can generate greater conversion efficiency. In addition,



Fig. 8. Action spectra of monochromatic incident photo-to-current conversion efficiency (IPCE) of the three dye-sensitized solar cells.

although the IPCE of **CSG2** are lower than those of **CSG1** in the region 370–495 nm, the IPCE values of **CSG2** are higher and broader than those of **CSG1** in the remaining region, which indicates that the **CSG2**-sensitized TiO₂ electrode would generate the highest conversion yield among the three dyes. In the whole region, the IPCE values of **CSG2** are more or less similar in intensity and broader than those of **CSG1** and **CSG3** in the remaining region, which indicates that the **CSG2**-sensitized TiO₂ electrode that the **CSG2**-sensitized that the three dyes.

The photocurrent density-photovoltage (I-V) curves of the DSSCs based on CSG1-CSG3 are shown in Fig. 9, and key parameters including short-circuit current density (I_{SC}) , open-circuit voltage (V_{OC}) , fill factor (FF) and overall power conversion efficiency (η) are summarized in Table 3. For the three dyes, the CSG2-sensitized cell exhibited a maximum η of 3.8% (I_{SC} = 8.90 mA cm⁻², V_{OC} = 584 mV, FF = 0.74). Under the same conditions, the cells sensitized with **CSG1** and **CSG3** gave J_{SC} of 6.36 and 7.61 mA cm⁻², V_{OC} of 699 and 579 mV and FF of 0.75 and 0.73, corresponding to η of 3.4% and 3.2%, respectively. Under similar fabrication conditions, champion dye N719 exhibited the maximum overall conversion efficiency of 6.4% $(J_{SC} = 14.74 \text{ mA cm}^{-2}, V_{OC} = 606 \text{ mV}, FF = 0.716)$. Among the three organic dyes, CSG2 sensitized cell has the highest η resulting from its relatively higher J_{SC} , which can be attributed to its broader absorption and enhanced molar extinction coefficient in the visible region. The short-circuit current (J_{SC}) is related to the molar extinction coefficient of the dye molecule, a higher molar extinction coefficient showing good light-harvesting ability and yielding a higher short-circuit current. The relative lower plateau from CSG3 despite a high driving force for electron injection might arise from dye aggregation behavior on the TiO₂ surface, decreasing electron injection yield. This assumption is consistent with the absorption curve for a **CSG3** loaded TiO₂ film, which showed the largest spectral shift relative to that in solution. On the other hand, the device constructed from CSG1 resulted in the highest plateau. This finding further supports aggregation behavior as a factor affecting IPCE plateaus. Nonetheless, CSG1 based device did not give the highest current density, due to solar



Fig. 9. Photocurrent–voltage characteristics of the three dye-sensitized solar cells under illumination of simulated solar light (AM 1.5, 100 mW cm^{-2}).

Table 3	
DSSC performance parameters of CSG1-CSG3 and standard	N719.

J_{SC}^{a} (mA cm ⁻²)	$V_{OC}^{b}(V)$	FF ^c	η^{d} (%)
6.36	0.699	0.757	3.4
8.90	0.584	0.740	3.8
7.61	0.579	0.732	3.2
14.74	0.606	0.716	6.4
	<i>J_{SC}^a</i> (mA cm ⁻²) 6.36 8.90 7.61 14.74	$\begin{array}{c c} J_{Sc}{}^{a} (mA cm^{-2}) & V_{Oc}{}^{b} (V) \\ \hline 6.36 & 0.699 \\ 8.90 & 0.584 \\ 7.61 & 0.579 \\ 14.74 & 0.606 \end{array}$	$\begin{array}{c c} J_{Sc}{}^{a} (mA cm^{-2}) & V_{Oc}{}^{b} (V) & FF^{c} \\ \hline 6.36 & 0.699 & 0.757 \\ 8.90 & 0.584 & 0.740 \\ 7.61 & 0.579 & 0.732 \\ 14.74 & 0.606 & 0.716 \end{array}$

^a J_{SC}: short photocurrent density.

^b V_{OC} : open-circuit photovoltage.

^c ff: fill factor.

^d η : power conversion efficiency.

energy capture in a narrower region of the solar spectrum than the **CSG2** and **CSG3** based devices.

Under illumination, V_{OC} of the device is the potential difference between the quasi-Fermi level of the electrons in the conduction band (CB) of TiO₂ film and redox potential of the electrolyte (I^-/I_3^-) . The pronounced rate of electron recombination between the injected electron onto the CB of TiO₂ and the I_3^- or oxidized sensitizer could reduce the V_{OC} . In addition, the band-edge shift occurring due to the interaction of the sensitizer with TiO₂ will also alter the V_{OC} . However, a strong dipole present at the TiO₂/sensitizer interface will contribute to a more negative shift in the Fermi level of the TiO₂ conduction band. The highest V_{OC} observed for the devices fabricated using the sensitizer CSG1 may be attributed to the stronger interaction between the TiO_2 and the sensitizer while the lowest V_{OC} exhibited by CSG2 and CSG3 may be probably due to poor interaction between the sensitizer and TiO₂ [75].

4. Conclusions

Three metal-free organic dyes (**CSG1–CSG3**) comprising a carbazole moiety and cyanoacrylic acid as the common electron donorand anchoring group with different linker moieties such as benzene, thiophene, or furan were designed and synthesized for application in dye-sensitized solar cells (DSSCs). The results based on photovoltaic experiments show that dye with a benzene linker exhibit a higher open-circuit voltage (0.699 V) compared to thiophene and furan linker. The power conversion efficiency was shown to be sensitive to the π -bridging linker employed. Among the three dyes, DSSCs based on **CSG2** exhibited the best overall light-to-electricity conversion efficiency of 3.8% (J_{SC} = 8.90 mA cm⁻², V_{OC} = 0.584 V, *FF* = 0.73) under AM 1.5 irradiation (100 mW cm⁻²). The results reveal that these metal-free organic carbazole based dianchoring dyes are promising in the development of DSSCs and the optimization of their chemical structure and the device is in progress to further improve their energy conversion efficiency.

Acknowledgements

KSVG thanks UGC and TS thanks CSIR, New Delhi for Senior Research Fellowship.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2013.11.020.

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