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Fluorene-based organic dyes containing acetylene linkage for dye-sensitized solar cells

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ABSTRACT

New organic dyes based on diphenylaminofluorene donors, cyanoacrylic acid acceptors and either ethynylbenzene or ethynylthiophene π -spacers have been synthesized and characterized as sensitizers for dye-sensitized solar cells. The dye with thiophene in the conjugation pathway exhibited longer wavelength absorption due to the significant lowering of the LUMO level when compared to the phenyl analog. However, the dye with the phenylacetylene linker displayed promising DSSC characteristics such as short circuit current, open circuit voltage and fill factor indicative of efficient charge generation and injection. The solvatochromic behavior of the dyes were examined in solvents of different polarity and found to exhibit negative solvatochromism of the fluorescence emission suggestive of a nonpolar solvent stabilized excited state with a significant structural reorganization. The TDDFT computations were used to explain the optical properties of the dyes.

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1. Introduction

There is a growing interest for the development of metal free organic dyes displaying broad spectral response and efficient charge separation due to their potential application as sensitizers in the nanocrystalline anatase TiO2 based dye-sensitized solar cells (DSSCs) [1] and donors in bulk-heterojunction solar cells [2]. The DSSCs based on organic or organometallic dyes have exhibited several advantages such as easy fabrication process, cost reduction and easy functional alternations by chemical modification over the conventional silicon-based solar cells. Grätzel and co-workers have developed several ruthenium complexes [3,4] based on polypyridyl ligands and found to perform as efficient sensitizers in DSSCs. Despite the superiority of the ruthenium-based dyes, there is rapid progress in the development of metal free organic dyes [1]. Several attempts have been devoted to optimize the functional properties such as absorption, intramolecular charge transfer and redox stability by simple molecular engineering. The molecular configuration of the organic sensitizers suitable for dye sensitized solar cells can be divided into three components: donor, π -linker and acceptor. Most of the organic dyes possessed a substituted triphenylamine [5–7], carbazole [8,9], phenothiazine [10,11], coumarin [12,13], indoline [14,15], oligothiophene substituted polyaromatic hydrocarbons [16–18] or imidazoles [19–21], as the electron donor. Dyes with the triphenylamine segment as the electron-donor have shown long-lived charge-separated state and good hole-transporting ability. In addition, trigonal geometry of triarylamine prevents the formation of aggregates at the semiconductor surface. An ideal π conjugated linker should promote the absorption of light over a wide wavelength region and at the same time facilitate intramolecular charge transfer from donor to acceptor. Spacer units also play a crucial role to hinder the rate of internal charge recombination. A slight tilt from planarity in the conjugation bridge has been found to be beneficial for charge collection despite displaying blueshifted absorption [22]. Various conjugated segments such as carbazole [23,24], fluorene [25-27], spirobifluorene [28], phenoxazine [29], oligothiophene [30], dithienothiophene [31], and thienothiophene [32] have been used as the π -bridge between the electron donor and electron acceptor for tuning the absorption parameters and photovoltaic performance. Incorporation of an acetylene segment is an interesting approach to increase the π conjugation in dyes that provide enhanced photovoltaic properties and ensure an efficient intramolecular charge separation with high photocurrent generation and slow recombination [33].

Fluorene-based triarylamines have been widely used as donors in the construction of efficient organic dyes for DSSCs



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[34,35]. However, fluorene-based organic dyes possessing acetylene linkers have not been explored. In continuation of our efforts to develop organic dyes suitable for application in dyesensitized solar cells [36,37], we report in this paper metal free organic dyes featuring *N*,*N'*-diphenylfluoreneamine donor, thienylacetylene or phenylacetylene conjugation pathway and cyanoacrylic acid or dicyanovinyl acceptor as potential materials for the fabrication of photovoltaic devices. We suppose that elongation of the conjugation pathway by aryl/heteroaryl acetylene would benefit the absorption characteristics and intramolecular charge separation. We have demonstrated the use of the new cyanoacrylic acid derivatives as sensitizers in the conventional Grätzel DSSCs and found to exhibit efficiency up to 3.0% (vide supra).

2. Experimental details

2.1. Materials and methods

All reactions and manipulations were carried out under N₂ with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (100-200 mesh, Rankem) as the stationary phase in a column of 30 cm long and 2.0 cm diameter. The ¹H and ¹³C NMR spectra were measured by using Bruker AV 500 FT-NMR spectrometer. Cyclic voltammetric experiments were performed with a CH Instruments electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a nonaqueous Ag/AgNO3 reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and $E_{\rm p}^{\rm c}$ are the anodic and cathodic peak potentials, respectively. The potentials are quoted against the ferrocene internal standard. The solvent in all experiments was dichloromethane $(1 \times 10^{-4} \text{ M})$ solutions) and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. Electronic absorption spectra were obtained on a UV-1800 Shimadzu UV-Visible spectrophotometer using 1×10^{-5} M solutions. The HRMS was done on Agilent 1200 series system equipped with an Agilent 6210 Time-Of-Flight (TOF) mass detector. 9,9-Diethyl-7-ethynyl-N,N-diphenyl-9H-fluoren-2amine was prepared by following the literature procedure [38].

2.2. 4-(2-(7-(Diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl) benzaldehyde (**2a**)

To a mixture of (1.0 g, 2.42 mmol) 9,9-diethyl-7-ethynyl-N,N-diphenyl-9H-fluoren-2-amine, (0.45 g, 2.42 mmol) 4bromobenzaldehyde, (17 mg) Pd(PPh₃)₂Cl₂, (13 mg) PPh₃ were added successively (5 mg) CuI and Et₃N (25 mL) under N₂ atmosphere. The reaction mixture was refluxed at 95 °C for 24 h. The resulting reaction mixture was poured in water and extracted with dichloromethane and further purified by chromatography on silica gel with CH₂Cl₂:hexane (2:1) to give compound 2a as yellow solid. Yield 80%. Mp 181 °C. ¹H NMR (CDCl₃, 500.13 MHz) δ 0.34–0.37 (m, 6H), 1.87-1.99 (m, 4H), 7.01-7.04 (m, 3H), 7.10-7.13 (m, 5H), 7.25–7.28 (m, 4H), 7.48 (s, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz 2H), 10.01 (s, 1H). ¹³C NMR (CDCl₃, 125.75 MHz) δ 182.62, 142.85, 141.11, 139.03, 138.96, 133.57, 126.60, 126.29, 123.58, 123.10, 122.18, 122.12, 121.05, 120.77, 120.37, 117.19, 115.19, 115.08, 114.48, 113.89, 111.97, 111.74, 110.74, 110.20, 109.94, 91.08, 86.09, 79.67, 47.29, 23.73, 13.79. GC/TOF HRMS-EI (*m*/*z*): [M + H]⁺ calcd for C₃₈H₃₂NO 518.2484; found, 518.2482.

2.3. 5-(2-(7-(Diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl) thiophene-2-carbaldehyde (**2b**)

This was synthesized from 9,9-diethyl-7-ethynyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine and 5-bromothiophene-2-carbaldehyde by following the procedure described above for **2a**. Yellow solid. Yield: 75%. Mp 204–206 °C. ¹H NMR (CDCl₃, 500.13 MHz): 0.35–0.38 (m, 6H), 1.88–2.00 (m, 4H), 7.03–7.06 (m, 3H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.13–7.15 (m, 4H), 7.26–7.29 (m, 4H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.48 (m, 1H), 7.51–7.53 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 4.0 Hz, 1H), 9.88 (s, 1H). ¹³C NMR (CDCl₃, 125.75 MHz) δ 182.47, 151.81, 150.05, 148.07, 147.83, 143.57, 142.86, 136.31, 135.33, 133.43, 132.20, 131.00, 129.28, 125.94, 124.15, 123.32, 122.85, 120.96, 119.13, 118.97, 118.73, 99.99, 99.56, 82.02, 56.23, 32.61 8.55. GC/TOF HRMS-EI (*m*/*z*): [M + H]⁺ calcd for C₃₆H₃₀NOS 524.2048; found, 524.2041.

2.4. 3-(2-(7-(Diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl) benzaldehyde (**2c**)

This was synthesized from 9,9-diethyl-7-ethynyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine and 3-bromobenzaldehyde by following the procedure described above for **2a**. Yellow solid. Yield: 70%. Mp 175 °C. ¹H NMR (CDCl₃, 500.13 MHz): 0.48–0.51 (m, 6H), 2.01–2.10 (m, 4H), 7.15–7.17 (m, 3H), 7.21–7.25 (m, 5H), 7.36–7.39 (m, 4H), 7.59 (s, 1H), 7.62–7.73 (m, 4H), 7.90–7.92 (m, 1H), 7.95–7.97 (m, 1H), 8.17–8.18 (m, 1H), 10.16 (s, 1H). ¹³C NMR (CDCl₃, 125.75 MHz) δ 191.69, 151.73, 150.00, 147.90, 147.85, 142.19, 137.02, 136.53, 135.62, 132.99, 130.92, 129.26, 129.15, 128.69, 126.02, 124.83, 124.07, 123.43, 122.75, 120.81, 119.86, 119.07, 118.94, 92.28, 87.77, 56.18, 32.63, 8.56. GC/TOF HRMS-EI (*m*/*z*): [M + H]⁺ calcd for C₃₈H₃₂NO 518.2484; found, 518.2477.

2.5. (E)-2-Cyano-3-(4-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl)phenyl)acrylic acid (**3a**)

A mixture of the aldehyde **2a** (1.0 g, 1.93 mmol), 2-cyanoacetic acid (0.18 g, 2.32 mmol), ammonium acetate (20 mg) and acetic acid (5 mL) was refluxed for 12 h. The resulting dark yellow solution was poured into water. The solid separated was filtered and thoroughly washed with water and dried. Red solid. Yield: 68%. Mp 220–222 °C. ¹H NMR (DMSO, 500.13 MHz) δ 0.24–0.27 (m, 6H), 1.86–1.88 (m, 2H), 1.97–1.99 (m, 2H), 6.95–6.97 (m, 1H), 7.02–7.07 (m, 8H), 7.29–7.32 (m, 4H), 7.53–7.55 (m, 1H), 7.61 (s, 1H), 7.65–7.67 (d, *J* = 8.5 Hz, 2H), 7.76–7.78 (m, 2H), 7.92–7.95 (m, 3H). ¹³C NMR (DMSO, 125.75 MHz) δ 163.48, 151.76, 150.24, 147.85, 147.76, 146.86, 142.12, 135.67, 132.15, 131.39, 130.09, 129.99, 126.24, 125.15, 124.03, 123.63, 123.44, 121.97, 120.03, 119.95, 119.45, 119.01, 56.24, 44.41, 32.11, 23.12, 22.49, 8.84. GC/TOF HRMS-EI (*m/z*): [M + H]⁺ calcd for C₄₁H₃₃N₂O₂, 585.2542; found, 585.2541.

2.6. (E)-2-Cyano-3-(5-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl)thiophen-2-yl)acrylic acid (**3b**)

This was synthesized in 67% yield from **2b** as described above for **3a**.Orange solid. Mp 240–242 °C. ¹H NMR (DMSO, 500.13 MHz) δ 0.33–0.39 (m, 6H), 1.71 (s, 2H), 1.90–2.02 (m, 2H), 7.03–7.06 (m, 3H), 7.10 (s, 1H), 7.13–7.15 (d, *J* = 7.5 Hz, 4H), 7.26–7.29 (m, 5H), 7.46 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.57–7.62 (m, 3H), 8.17 (s, 1H). ¹³C NMR (DMSO, 125.75 MHz) δ 151.82, 150.02, 147.95, 147.86, 142.53, 137.67, 135.47, 134.76, 131.89, 130.80, 130.15, 129.26, 125.89, 124.11, 123.36, 122.79, 120.89, 119.39, 119.11, 118.81, 56.19, 44.42, 32.60, 22.72, 22.56, 8.55. GC/TOF HRMS-EI (*m*/*z*): [M + H]⁺ calcd for C₃₉H₃₁N₂O₂S 591.2106; found, 591.2101.

2.7. (E)-2-Cyano-3-(3-(2-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)ethynyl)phenyl)acrylic acid (**3c**)

This was synthesized from **2c** in 79% yield as described above for **3a**. Red solid. Mp 208–212 °C. ¹H NMR (DMSO, 500.13 MHz) δ 0.24–0.27 (m, 6H), 1.84–1.91 (m, 2H), 1.96–2.03 (m, 2H), 6.96 (dd, J = 8.5, 4.0 Hz, 1H), 7.00–7.08 (m, 7H), 7.28–7.32 (m, 4H), 7.53 (dd, J = 8.0, 1.0 Hz, 1H), 7.62–7.65 (m, 2H), 7.77–7.79 (m, 3H), 8.03 (d, J = 7.5 Hz, 1H), 8.16 (s, 1H), 8.31 (d, J = 3.5 Hz, 1H). ¹³C NMR (DMSO, 125.75 MHz) δ 151.75, 150.26, 147.85, 147.77, 142.14, 135.69, 135.40, 133.19, 132.92, 131.36, 130.54, 130.23, 130.00, 126.22, 124.02, 123.71, 123.41, 122.06, 120.06, 119.82, 119.10, 92.06, 88.64, 79.62, 56.26, 32.10, 8.87. GC/TOF HRMS-EI (m/z): $[M + H]^+$ calcd for C₄₁H₃₃N₂O₂, 585.2542; found, 585.2540.

2.8. 2-((4-(2-(7-(Diphenylamino)-9,9-diethyl-9H-fluoren-2-yl) ethynyl)phenyl)methylene)malononitrile (**4a**)

A mixture of the aldehyde **2a** (1.0 g, 1.93 mmol), malononitrile (0.19 g, 2.89 mmol), piperidine (catalytic amount) and ethanol (10 mL) was refluxed for 12 h. The resulting dark red precipitate was filtered and thoroughly washed with ethanol and dried. Red solid. Yield: 69%. Mp 235–237 °C. ¹H NMR (CDCl₃, 500.13 MHz) δ 0.35–0.38 (m, 6H), 1.86–2.01 (m, 4H), 7.02–7.05 (m, 3H), 7.09 (d, *J* = 1.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 4H), 7.25 (m, 1H), 7.26–7.27 (m, 2H), 7.48 (s, 1H), 7.51–7.54 (m, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.60–7.62 (m, 1H), 7.65–7.70 (m, 2H), 7.74 (s, 1H), 7.87–7.92 (m, 2H). ¹³C NMR (CDCl₃, 125.75 MHz) 158.59, 148.08, 147.84, 132.32, 131.25, 130.77, 129.96, 129.27, 126.19, 124.15, 124.10, 123.31, 122.85, 120.93, 119.12, 118.74, 76.78, 56.20, 32.61, 8.54. GC/TOF HRMS-EI (*m/z*): [M + H]⁺ calcd for C₄₁H₃₂N₃ 566.2596; found, 566.2587.

2.9. 2-((5-(2-(7-(Diphenylamino)-9,9-diethyl-9H-fluoren-2-yl) ethynyl)thiophen-2-yl)methylene)malononitrile (**4b**)

This was prepared from **2b** by following the procedure similar to that described above for **4a**. Red solid. Yield: 70%. Mp 258–260 °C. ¹H NMR (CDCl₃, 500.13 MHz) δ 0.35–0.37 (m, 6H), 1.88–1.98 (m, 4H), 7.02–7.05 (m, 3H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.0 Hz, 4H), 7.25–7.26 (m, 1H), 7.26–7.27 (m, 1H), 7.27–7.28 (m, 2H), 7.32 (d, *J* = 4.5 Hz, 1H), 7.46 (d, *J* = 1.0 Hz, 1H), 7.50–7.52 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.77 (s, 1H). ¹³C NMR (CDCl₃, 125.75 MHz) δ 152.72, 151.95, 150.38, 148.17, 147.72, 143.11, 141.47, 136.29, 135.36, 133.85, 133.25, 131.58, 130.01, 126.48, 124.16, 123.53, 122.23, 120.16, 118.85, 118.62, 114.19, 101.66, 82.57, 77.05, 56.32, 32.03, 8.85. GC/TOF HRMS-EI (*m/z*): [M + H]⁺ calcd for C₃₉H₃₀N₃S 572.2160; found, 572.2156.

2.10. Computational methods

For theoretical dipole moment and electronic vertical transition calculations, the structures of the dyes were optimized by applying DFT with the hybrid B3LYP [39] functional and 6-31G (d,p) basis set. With the optimized structures, the ground state dipole moments were calculated with the DFT (B3LYP) models (vacuum) and CAM-B3LYP [40] (Coulomb-attenuating method) (vacuum and in THF) as an exchange-correlation functional and the 6-31G (d,p) basis set. The electronic transitions were calculated using time-dependent DFT (B3LYP) theory and the 6-31G (d,p) basis set. Even though the time-dependent DFT method less accurately describes the states with charge-transfer nature, the qualitative trends in the TDDFT results can still offer correct physical insight. At least 20 excited states were calculated for each molecule. For all the dyes, the first excited states were highly optically active as indicated by the larger oscillator strengths.

2.11. DSSC fabrication and characterization

A fluorine-doped SnO₂ conducting glass (FTO, 7 Ω sq⁻¹, transmittance ~80%, NSG America, Inc., New Jersey, USA) was first cleaned with a neutral cleaner, and then washed with deionized water, acetone, and isopropyl alcohol, sequentially. The conducting surface of the FTO was treated with a solution of titanium tetraisopropoxide (1 g) in 2-methoxyethanol (3 g) for obtaining a good mechanical contact between the conducting glass and TiO₂ film, as well as to isolate the conducting glass surface from the electrolyte. TiO₂ paste was coated onto the treated conducting glass by rolling a metal strip over it (doctor blade technique). After coating each TiO₂ layer, the dried TiO₂ film was gradually heated to 450 °C in an oxygen atmosphere, and subsequently sintered at that temperature for 30 min. The TiO₂ photo-anodes of the DSSCs employed in the experiments were composed of a 14 μ m thick transparent TiO₂ layer with a scattering layer of 4.5 µm thickness. After sintering at 450 °C and cooling to 80 °C, the TiO₂ film was immersed in a 3 \times 10⁻⁴ M solution of dye at room temperature for 24 h. N719 (Solaronix S.A., Aubonne, Switzerland) was dissolved in acetonitrile (ACN) and tert-butyl alcohol (volume ratio of 1:1) and used as a standard dye solution for device optimization. The solutions of the dyes were prepared in a mixing solvent containing ACN, tertbutyl alcohol and dimethyl sulfoxide (DMSO) (volume ratio of 1:1:3). Then the photoanode (FTO/TiO₂/dye) was placed on a platinum-sputtered conducting glass electrode (ITO, 7 Ω sq⁻¹, Ritek Corporation, Hsinchu, Taiwan), keeping the two electrodes separated by a 25 µm-thick Surlyn[®] (SX1170-25, Solaronix S.A., Aubonne, Switzerland). The two electrodes were then sealed by heating. A mixture of 0.1 M LiI, 0.6 M 1-propyl-2,3dimethylimidazolium iodide (DMPII), 0.05 M I₂, and 0.5 M tertbutylpyridine (TBP) in 3-methoxypropionitrile (MPN)/ACN (volume ratio of 1:1) was used as the electrolyte. The electrolyte was injected into the gap between the electrodes by capillarity; the electrolyte-injecting hole was previously made in the counter electrode with a drilling machine, and the hole was sealed with hot-melt glue after the injection of the electrolyte.

Surface of the DSSC was covered by a mask with a lightilluminated area of 0.16 cm² and then illuminated by a class-A quality solar simulator (XES-301S, AM 1.5 G, San-Ei Electric Co., Ltd.). Incident light intensity (100 mW cm⁻²) was calibrated with a standard Si Cell (PECSI01, Peccell Technologies, Inc.). Photocurrent-voltage curves of the DSSCs were obtained with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, The Netherlands). The thickness of the TiO₂ film was judged by scanning electron microscopic images (SEM, NanoSEM 230, Novat). For UV-absorption spectra, dye molecules were coated on the TiO₂ films and the corresponding spectra were obtained using an UV-visible spectrophotometer (V-570, Jasco, Japan) equipped with a total integrating sphere. Electrochemical impedance spectra (EIS) were obtained by the above-mentioned potentiostat/galvanostat, equipped with an FRA2 module, under a constant light illumination of 100 mW cm⁻². The frequency range explored was 10 mHz-65 kHz. The applied bias voltage was set at the opencircuit voltage of the DSSC, between the ITO-Pt counter electrode and the FTO-TiO₂-dye working electrode, starting from the shortcircuit conditions; the corresponding AC amplitude was 10 mV. The impedance spectra were analyzed using an equivalent circuit model. Incident photo-to-current conversion efficiency (IPCE) curves were obtained under short-circuit conditions. The light source was a class A quality solar simulator (PEC-L11, AM 1.5 G, Peccell Technologies, Inc.); light was focused through a monochromator (Oriel Instrument, model 74100) onto the photo-voltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by IPCE (λ) = 1240 (J_{SC} /

 $\lambda\varphi$), where λ is the wavelength, J_{SC} is short-circuit photocurrent density (mA cm⁻²) recorded with a potentiostat/galvanostat, and φ is the incident radiative flux (W m⁻²) measured with an optical detector (Oriel Instrument, model 71580) and a power meter (Oriel Instrument, model 70310).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route for the new dipolar dyes containing fluorene-based triarylamine donor, aryl (phenyl/thienyl) acetylene π -linkers and cyanoacrylic acid or dicyanovinyl acceptor is depicted in Scheme 1. The aldehydes (2a-2c) required were first assembled from the terminal acetylene, 1 and the corresponding bromosubstituted aryl aldehydes by utilizing a palladium-catalyzed Sonogashira coupling reaction [41]. They were later converted to the desired dyes (3 and 4) in good yields by Knoevenagel condensation [42] with either cyanoacetic acid or malononitrile in the presence of appropriate catalyst (ammonium acetate/piperidine). The meta-substituted derivative (3c) and the dicvanovinvl derivatives (4a and 4b) were synthesized to study the influence of acceptor on the optical and electrochemical properties. The dyes were thoroughly characterized by ¹H, ¹³C and mass spectral methods and the spectral data are consistent with the formulated structures. The dyes are yellow to red in color and reasonably soluble in common organic solvents such as toluene, dichloromethane, acetonitrile and methanol.

3.2. Photophysical properties

The absorption spectra of the dyes recorded in dichloromethane (DCM) are displayed in Fig. 1, and the data summarized in Table 1. All the dyes with the exception of **3a** exhibited two major absorption bands covering the wavelength region from 350 nm to 600 nm. The dye **3a** displayed a single band peaking at 391 nm. The shorter wavelength absorption appearing at ca. 360 nm is assigned to a $\pi - \pi^*$ transition while the band appearing at lower energy (>400 nm) may originate from an electronic excitation resulting in charge transfer from the amine donor to the cyanoacrylic acid acceptor. Absence of any such absorption in **3c** supports this assignment. In **3c**, the acceptor group is delinked from the donor by *meta*-disposition and may not exhibit a donor–acceptor



Fig. 1. Absorption spectra of the dyes **3a–3c**, **4a** and **4b** recorded in dichloromethane solutions.

interaction. Within a group, the thiophene containing dye (**3b** or **4b**) exhibits red-shifted absorption when compared to the corresponding phenylene derivative (**3a** or **4a**). It is attributed to the enhanced electronic communication between the donor and acceptor entities in **3b** and **4b** due to thiophene which can provide more efficient conjugation than a benzenoid moiety and lower the energy of the charge transfer in conjugated dipolar molecules. Similarly, the dicyanovinyl derivatives (**4a** and **4b**) show a redshifted absorption profile when compared to the corresponding cyanoacrylic acid derivatives (**3a** and **3b**) illustrating the pronounced electron withdrawing ability of the dicyanovinyl unit.

It is interesting to compare the absorption parameters of the dyes with that of the closely related compounds known in the literature [36,44]. The effect of the ethynylthiophene linkage becomes clear by comparing the photophysical properties of dye **3b** with the previously reported dye (*E*)-2-cyano-3-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)acrylic acid [36]. The absorption spectra of the dye **3b** (462 nm) is significantly red-shifted (>35 nm) when compared to the dyes (*E*)-2-cyano-3-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)acrylic acid (424 nm) and (*E*)-2-cyano-3-(5-(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-



Scheme 1. Synthesis of the dyes.

Table 1Absorption data of the dyes in different solvents.

Dyes	λ_{\max} , nm (ε_{\max} , \times 10 ³ M ⁻¹ cm ⁻¹)									
	TOL	TOL + TEA	TOL + TFA	DCM	DCM + TEA	DCM + TFA	THF	ACN	MeOH	
3a	391 (40.2),	388 (50.2),	426 (27.4),	390 (30.5),	390 (29.9),	433 (21.8),	384 (29.8)	382 (30.5),	387 (40.1),	
	314 (34.2)	312 (38.4)	366 (41.7), 313 (28.6)	315 (21.6)	315 (25.2)	368 (35.3), 313 (25.1)		309 (21.6)	312 (30.9)	
3b	453 (26.20),	410 (43.6),	467 (25.9),	462 (38.9),	401 (69.9),	462 (43.4),	396 (19.2)	425 (29.1),	415 (37.1),	
	368 (26.1),	312 (22.7)	370 (38.6), 306 (18.4)	368 (38.8),	310 (47.1)	371 (56.9), 306 (42.7)		304 (16.5)	307 (18.8)	
	307 (17.2)			307 (24.7)						
3c	378 (41.8),	377 (42.9),	379 (44.2),	373 (43.1),	373 (37.0),	379 (39.2),	375 (42.77),	373 (37.8),	373 (43.1),	
	306 (38.7)	301 (38.2)	308 (40.6),	298 (40.5)	299 (35.4)	308 (40.4)	304 (28.0)	300 (38.2)	298 (40.5)	
4a	442 (23.7),	_	_	443 (20.7),	_	_	413 (22.4),	406 (27.3),	365 (13.2)	
	367 (40.0)			367 (34.6)			364 (32.23),	361 (32.8)		
4b	453 (25.0),	_	_	479 (34.5),	_	_	463 (14.46),	455 (32.4),	458 (21.1),	
	368 (24.9),			371 (36.1),			392 (26.0),	365 (28.4),	365 (19.8),	
	308 (16.4)			306 (22.7)			368 (29.23)	302 (18.4)	302 (12.9)	

yl)thiophen-2-yl)acrylic acid (427 nm) [44] which supports the elongation of conjugation due to the ethynyl bridge. Similarly, conjugation extension by ethynylbenzene in **3a** is expected to result in a red-shift in absorption when compared to (*E*)-2-cyano-3-(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)acrylic acid. But the shorter wavelength absorption realized for **3a** is against this expectation. It is probably the twisted conjugation effects. Similarly, the dicyanovinyl derivatives (**4a** and **4b**) also displayed blue-shifted absorption when compared to the known dyes 2-((7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)methylene)malononitrile (479 nm) and 2-((5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl) amino)-9*H*-fluoren-2-yl)thiophen-2-yl)methylene)malononitrile (492 nm) [43] suggesting a poor donor–acceptor interaction in **4a** and **4b** attributable to the acetylene linkage.

The cyanoacrylic acid derivatives (**3a** and **3b**) showed alternations in the absorption maxima due to solvent polarity while the dicyanovinyl derivatives (**4**) were found to be less sensitive to the nature of the solvent (Fig. 2). Particularly, they displayed a blueshifted absorption in the polar solvents such as tetrahydrofuran (THF), acetonitrile (ACN) and methanol (MeOH) as compared to the absorption peak realized in toluene (TOL) and DCM. The variation of the absorption peak did not correlate well with the solvent parameters such as orientation polarizability and the solvent polarity parameter of solvents introduced by Dimroth and Reichardt [45], $E_T(30)$ suggesting a specific interaction of the dyes with the polar solvents (see below). It appears that the polar solvents effectively solvate the dyes in the ground state probably due to the presence of more quantities of deprotonated species. The shift of acid—base equilibrium toward the deprotonated form is facilitated by the solvents capable of coordinating with the carboxylic acid unit which led to the deprotonation. Such a deprotonation may diminish the electron-accepting ability of the acceptor moiety, which in turn will cause a reduction in donor acceptor interaction in the dye and a consequent blue shift in absorption [36]. This hypothesis is further supported by the fact that addition of a base such as triethylamine to the TOL/DCM solution of the dyes 3a and **3b** (see Fig. 3 and Table 1) blue shifted the absorption peak and that addition of an acid (trifluoroacetic acid) to the TOL/DCM solution of the dye led to a red shift. These observations suggest the presence of a protonation-deprotonation equilibrium for the dyes in solution. It is speculated that in TOL/DCM solution, the dyes are predominantly in the protonated form (DH). However, addition of triethylamine deprotonated the dye and shifted the equilibrium to the deprotonated form (D⁻) side, while the addition of trifluoroacetic acid reversed the equilibrium and increased the amount of protonated form in the solution.

Though the dyes **3a**–**3c**, **4a** and **4b** exhibited weak fluorescence, their emission properties were examined in solvents of different polarity to qualitatively ascertain their behavior in the excited state. The emission spectra recorded for the dyes in toluene are presented in Fig. 4, representative examples of solvatochromic behavior of the dyes **3b** and **4b** are illustrated in Fig. 5 and relevant data compiled in Table 2. The emission peak wavelength decreases as the solvent polarity increases. A clear negative solvatochromism observed for the dyes in fluorescence further corroborates the presence of an intramolecular charge transfer transition from the donor to acceptor within the D– π spacer-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



Fig. 2. Absorption spectra of the dyes (a) 3b and (b) 4b recorded in different solvents.



Fig. 3. Absorption spectra of the dye 3b recorded in dichloromethane and in the presence of TEA or TFA.



Fig. 4. Emission spectra of the dyes (3 & 4) recorded in toluene.

shift observed for the emission spectra recorded for polar solvents such as methanol and acetonitrile when compared to that measure for toluene solution is interesting and indicate a less polar excited state. The large Stokes shifts observed for the dyes reveal significant structural reorganization on excitation.

Table 2						
Emission	data	of the	dyes	in	different	solvents.

Dyes	$\lambda_{\rm em}$, nm					Stokes shift, cm ⁻¹				
	Toluene	DCM	ACN	THF	MeOH	Toluene	DCM	ACN	THF	MeOH
3a	568	455	467	449	452	7970	3663	4765	3770	3716
3b	555	473	468	509	454	4057	503	2162	5606	2070
3c	535	456	460	501	455	7763	4880	5017	6707	4832
4a	569	511	494	502	483	5050	3004	4388	4293	6693
4b	577	512	510	546	468	4744	1346	2370	3283	467

3.3. Electrochemical properties

In order to identify the feasibility of electron injection from the dye into the conduction band of TiO₂ and regeneration of the dye by the conducting electrolyte, we have performed electrochemical measurements for the dyes using cyclic voltammetry (CV) in dichloromethane solution with 0.1 M tetrabutylammonium perchlorate as the electrolyte at a scan rate 100 mV/s. The cyclic voltammograms recorded for the selected dyes are shown in Fig. 6. All the dyes displayed a quasireversible one electron oxidation process at potentials higher than that observed for internal ferrocene/ferrocenium couple. It is attributed to the removal of electron from the arylamine unit. The oxidation potential for the dyes shift to lower values on changing the spacer from thienylacetylene (3b and **4b**) to phenylacetylene (**3a** to **4a**) or decreasing the strength of the acceptor moiety (compare **3a/3b** against **4a/4b**). The high oxidation potentials observed for **3b** and **4b** when compared to **3a** and **4a** respectively is attributed to the stronger electronic communication between the donor and acceptor via the thienylacetylene linker. Similarly, the difficulty in oxidation observed for the dicyanovinyl derivatives (4a and 4b) when compared to the corresponding cyanoacrylic acid derivatives (**3a** and **3b**) is assigned to the stronger electron-accepting ability of dicyanovinyl moiety [46] which delocalizes the electron-density from the amine segment toward the acceptor segment and makes it less prone for oxidation. The dyes 3a and 4a have undergone more facile oxidation when compared to the dyes without a phenylacetylene linkage [36,37] which further supports the identification of relatively weaker interaction between the donor and acceptor units in the present dyes caused by the extension of conjugation pathway.

The HOMO and LUMO energy levels for the dyes were from the optical and electrochemical parameters (Table 3) in an attempt to understand the interfacial charge transport thermodynamics. The excited-state oxidation potential (E_{ox}^*) of the sensitizers (**3a–3c**), estimated [47] from their first oxidation potential (E_{ox}) at the ground-state and the zero–zero excitation energy (E_{0-0}), is more negative (Fig. 7) than the conduction band-edge energy level of



Fig. 5. Emission spectra of the dye (a) 3b and (b) 4b recorded in different solvents.



Fig. 6. Cyclic voltammograms recorded for the dyes (3 and 4) in dichloromethane.

TiO₂ (-0.5 V vs NHE) [48] and suggests that the electron injection process from the excited dye molecules to the conduction band of TiO₂ is energetically feasible and all dyes can complete the process of electron flow from dye to TiO₂. The oxidation potential of the dyes are more positive (Fig. 7) than that of the electrolyte redox couple I^-/I_3^- (ca.~0.4 V vs NHE) [49]. This is favorable for the regeneration of the oxidized dyes by the electrolyte. While the HOMO energies remain largely unaltered for the dyes, the LUMO showed significant alternations attributable to the nature of the π -linker and electron acceptor. The presence of thienylacetylene π -spacer and dicyanovinyl acceptor dramatically lowered the LUMO of the dyes. However, the dyes without the phenylacetylene/thienylacetylene bridges have possessed higher HOMO and LUMO levels [27,36] attributable to the stronger donor–acceptor interactions.

3.4. Thermal properties

The thermal properties of dyes were determined by thermogravimetric analysis (TGA) (Table 3). The dyes displayed high decomposition temperatures (>450 °C) and the thiophene containing dyes (**3c** and **4b**) possess higher decomposition temperatures than the phenyl analogs (**3a** and **4a**). In general, the dicyanovinyl derivatives (**4**) display greater thermal robustness than the cyanoacrylic acid derivatives (**3**). Also the metasubstituted derivative (**3c**) showed poor thermal stability. All these observations indicate the importance of dipolar character in

Table 3			
Redox and thermal	properties	of the	dyes.



Fig. 7. Energy levels of the dyes and other materials used for DSSC fabrication.

enhancing the thermal stability for the materials. Thienyl conjugation and dicyanovinyl acceptor have been identified to render effective donor—acceptor interaction in the dyes from optical and electrochemical measurements (vide supra). The dicyanovinyl dyes exhibit improved stability than the dyes without acetylene linkages reported earlier [43]. The rigid rod-like configurations resulting due to the presence of acetylene linkages is beneficial for the thermal stability of the compounds.

3.5. Theoretical interpretations

To understand the optical and electrochemical properties of the dyes we have modeled the electronic structure by density functional theory calculations. We have used B3LYP [39] or CAM-B3LYP [40] exchange correlation functional in conjunction with 6-31G** basis set to simulate the molecular orbital characteristics and the vertical transitions. The electronic distributions in the frontier molecular orbitals of the selected dves are displayed in Fig. 8. Typically, the highest occupied molecular orbitals (HOMO) of the dves are generally contributed by the diphenylaminofluorene unit and the lowest unoccupied molecular orbitals (LUMO) by the acceptor unit (cyanoacrylic acid or dicyanovinyl) and spread up to the acetylene linkage toward the amine segment. From this it is evident that the electronic excitation from HOMO to LUMO would result in the migration of charge from amino segment to the acceptor end. In case of the meta-substituted derivative, the longer wavelength absorption originated from the HOMO to LUMO + 1

Dye	$\lambda_{max} \ nm \ (\epsilon_{max}, \ M^{-1} \ cm^{-1} imes 10^3)$	$E_{\rm ox}$, mV, $(\Delta E_{\rm p})^{\rm a}$	HOMO, eV ^b	E_{0-0} , eV ^c	LUMO, eV ^d	$E_{\rm ox}^*$, V ^e	$T_{\text{onset}}, \circ C^{f}$	$T_{\mathbf{d}}, \circ \mathbf{C}^{\mathbf{f}}$
3a	390 (30.5), 315 (21.6)	416 (53)	5.216	2.495	2.721	-1.31	467	539
3b	462 (38.9), 368 (38.8), 307 (24.7)	431 (65)	5.231	2.214	3.017	-1.01	505	585
3c	373 (43.1), 298 (40.5)	421 (60)	5.221	2.924	2.297	-1.73	491	535
4a	443 (20.7), 367 (34.6)	430 (69)	5.230	2.366	2.864	-1.17	519	601
4b	479 (34.5), 371 (36.1), 306 (22.7)	438 (68)	5.238	2.130	3.108	-0.92	657	696

^a Obtained from cyclic voltammograms recorded using tetrabutylammonium perchlorate (TBAPC) as supporting electrolyte at a scan rate of 100 mV/s in dichloromethane solution and the potentials are quoted with reference to the ferrocene which was used as potential marker.

^b Deduced from the equations HOMO = E_{ox} + 4.8 [47].

^c Derived from the optical edge.

^d Deduced from the equations $LUMO = HOMO - E_{0-0}$.

^e Excited state oxidation potential vs NHE.

^f Measured under a flow of nitrogen at a heating rate of 10 °C/min.



Fig. 8. Electronic distributions observed in the selected molecular orbitals of the dyes 3a and 3b.

Table 4

Excitation wavelengths, oscillator strength, assignment and orbital energies of the dyes in vacuum computed using B3LYP.

Dyes	λ_{max}	f	Assignment	μ_{g} (debye)	НОМО	LUMO
	(nm)				(eV)	(eV)
3a	583.0	0.5693	HOMO \rightarrow LUMO (100%)	8.06	-5.01	-2.61
	417.8	1.2807	Homo-1 \rightarrow Lumo (92%)			
3b	595.5	0.6547	HOMO \rightarrow LUMO (100%)	9.14	-5.02	-2.74
	433.3	1.1620	HOMO-1 \rightarrow LUMO (94%)			
3c	418.1	1.0252	Homo \rightarrow Lumo + 1 (84%)	8.36	-4.98	-2.60
	325.0	1.0296	$HOMO-1 \rightarrow LUMO + 1 (74\%)$			
4a	626.4	0.5232	HOMO \rightarrow LUMO (100%)	10.73	-5.07	-2.91
	431.8	1.2384	HOMO-1 \rightarrow LUMO (93%)			
4b	632.3	0.6096	HOMO \rightarrow LUMO (100%)	11.87	-5.10	-2.95
	444.0	1.1816	HOMO-1 \rightarrow LUMO (94%)			

excitation which is a diphenylaminofluorenylacetylene localized $\pi-\pi^*$ transition.

The computed vertical energies and their orbital contributions are listed in Tables 4 and 5. The qualitative trends in the absorption peak positions (3c < 3a < 3b; 4a < 4b) and intensities (3c > 3b > 3a; 4b > 4a) corresponding to the charge transfer transitions matched well with the first prominent vertical

transition arising from the HOMO to LUMO excitation. TDDFT computations using B3LYP gave significantly red-shifted absorption peaks while CAM-B3LYP model resulted in slightly blue-shifted absorption than the observed values. Overestimation of charge transfer transitions in dipolar compounds at the B3LYP level is quite expected.

3.6. DSSC characteristics

The dye-sensitized solar cells (DSSCs) based on nanocrystalline anatase TiO₂ were constructed by using the dyes (3a-3c) as the sensitizer. The DSSCs with an effective area of 0.16 cm² were fabricated with an electrolyte composed of 0.05 M I₂/0.5 M Lil/0.5 M *tert*-butylpyridine in 3-methoxypropionitrile/acetonitrile (1:1) solution. The device performance statistics were obtained under AM 1.5 solar irradiation and collected in Table 6. The current–voltage curves of the DSSCs sensitized by the dyes are shown in Fig. 9(a). Among the dyes **3a** showed better efficiency contributed by the high values of photocurrent density, opencircuit voltage and fill factor. The higher photoconversion efficiency observed for **3a** was interesting as it possess shorter wavelength absorption with smaller molar extinction coefficient in the

Table 5

Excitation wavelengths, oscillator strength, assignment and orbital energies of the dyes in vacuum and in THF computed using CAM-B3LYP.

Dyes	Medium	$\lambda_{max} \left(nm \right)$	f	Assignment	μ_{g} (debye)	HOMO (eV)	LUMO (eV)
3a	Vacuum	377.6	1.9987	Homo \rightarrow Lumo (52%), Homo-1 \rightarrow Lumo (27%), Homo \rightarrow Lumo + 1 (14%)	6.86	-6.19	-1.56
	THF	388.2	2.1582	Homo \rightarrow Lumo (52%), Homo-1 \rightarrow Lumo (30%), Homo \rightarrow Lumo + 1 (12%)	8.15	-6.20	-1.62
3b	Vacuum	401.6	1.8294	Homo \rightarrow Lumo (51%), Homo-1 \rightarrow Lumo (36%), Homo \rightarrow Lumo + 1 (7%)	7.88	-6.19	-1.64
	THF	419.3	1.9332	Homo \rightarrow Lumo (48%), Homo-1 \rightarrow Lumo (39%), Homo \rightarrow Lumo + 1 (6%)	9.84	-6.20	-1.75
3c	Vacuum	341.7	1.2484	Homo \rightarrow Lumo + 1 (40%), Homo \rightarrow Lumo (30%), Homo-1 \rightarrow Lumo (12%),	7.70	-6.19	-1.38
				$HOMO \rightarrow LUMO + 2 (6\%)$			
4a	Vacuum	389.3	1.8807	Homo \rightarrow Lumo (56%), Homo-1 \rightarrow Lumo (26%), Homo \rightarrow Lumo + 1 (11%)	9.05	-6.25	-1.81
	THF	399.6	2.0735	Homo \rightarrow Lumo (50%), Homo-1 \rightarrow Lumo (30%), Homo \rightarrow Lumo + 1 (10%)	10.07	-6.22	-1.80
4b	Vacuum	412.9	1.7710	Homo \rightarrow Lumo (53%), Homo-1 \rightarrow Lumo (35%), Homo \rightarrow Lumo + 1 (7%)	10.06	-6.26	-1.89
	THF	431.4	1.9022	Homo \rightarrow Lumo (50%), Homo-1 \rightarrow Lumo (39%), Homo \rightarrow Lumo + 1 (6%)	11.78	-6.22	-1.91

 Table 6

 Performance parameters of the DSSC device using the cyanoacrylic acid dyes 3a-3c.

Dye	$J_{\rm SC}$, mA cm ⁻²	V _{OC} , mV	ff	η, %	R _{ct2} , ohm	Electron lifetime, τ_{e} , ms
3a	7.36	587	0.69	3.00	21.52	18.61
3b	5.45	541	0.67	1.99	24.58	0.95
3c	1.92	498	0.63	0.61	63.51	1.72
N719	18.6	665	0.70	8.62	-	-



Fig. 9. (a) *I–V* characteristics and (b) IPCE plots observed for the DSSCs fabricated using the dyes.

series. Probably, the more negative LUMO observed for **3a** (Fig. 7) provides sufficient driving force for the electron injection into the conduction band of TiO_2 and leads to efficient charge collection. The dye **3b** exhibited slightly higher power conversion efficiencies (IPCE) at longer wavelength incident light when compared to the dye **3a** (Fig. 9(b)). But >75% IPCE was realized for **3a** in the shorter wavelength region which is in accordance with the shorter wavelength absorption maximum realized for this dye. This clearly supports poor charge collection efficiency for **3b** despite possessing longer wavelength absorption with high molar extinction coefficient. It is speculated that the more planar conjugation in **3b** probably facilitates the intramolecular charge recombination [37b].

The Nyquist plot displayed in Fig. 10(a) shows semicircles corresponding to the charge transfer resistances at the at the counter electrode and TiO₂/dye/electrolyte interface. The radius of the bigger semicircle for the dye **3c** is significantly larger than the other dyes (**3a** and **3b**) and suggest a huge charge transfer resistance for this dye. The smallest charge transfer resistance is observed for **3a** which is in agreement with the larger V_{oc} observed for the corresponding DSSC. In the Bode phase plot (Fig. 10(b)), the prominent lower frequency peak of the dye **3a** is shifted to lower frequency when compared to those of other dyes (**3b** and **3c**). This

corresponds to an increase in the electron lifetime for the 3a sensitized DSSCs. The electron lifetime can be extracted from the angular frequency (ω_{\min}) [50] at the mid-frequency peak in the Bode phase plot using $\tau_e = 1/\omega_{min}$. The electron lifetime measured for the dyes **3a**, **3b**, and **3c** are 18.61, 0.95 and 1.72 ms, respectively, and follows the trend, 3a > 3c > 3b. This trend is reverse of that observed for the ground state oxidation potentials of the dyes (3a < 3c < 3b). Dye 3a exhibited the lowest redox potential and highest electron lifetime. This indicates that the position of the HOMO of the dye relative to the redox potential of electrolyte is crucial to suppress the dark current. The increase in electron lifetime for **3a** leads to more effective suppression of the back reaction of the injected electrons with the I_3 in the electrolyte and contributes to the improvement in the photocurrent and photovoltage and to the substantial enhancement of the device efficiency. The high-frequency peak observed in the Bode plot corresponds to charge transfer at the counter electrode. The position of this peak for the devices remained unaltered. This suggests the absence of significant reaction at the counter electrode/electrolyte interface.

The present dyes exhibited lesser efficiency [**3a** (3.00%), **3b** (1.99%) and **3c** (0.61%)] than the dye, (*E*)-2-cyano-3-(7-



Fig. 10. (a) Nyquist and (b) Bode phase plots measured for the DSSCs fabricated using the dyes.

(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)acrylic acid (5.23%) earlier reported by us [36]. It is probably due to the presence of elongated conjugation pathway in the new dyes, which minimizes the donor—acceptor interaction and produces a higher energy optical excitation (vide supra).

4. Conclusions

In summary, we have synthesized new dyes containing an N.Ndiphenvlaminofluorene donor, cvanoacrvlic acid/dicvanovinvl acceptor and phenylacetylene or thienvlacetylene π -linkers. It has been found that the presence of acetylene unit in the conjugation pathway was found to be detrimental to the transmission of conjugating effects. Consequently the present dyes exhibited reduced donor-acceptor interactions which manifested in the photophysical and electrochemical properties and provided a method to fine tune the electronic properties. Thienylacetylene served as an efficient π -linker when compared to phenylacetylene unit and resulted in a red-shifted absorption in the dyes originating from the lowered LUMO. The cyanoacrylic acid derivatives have been demonstrated as successful sensitizers in the dye-sensitized solar cells based on nanocrystalline TiO₂. Favorable LUMO in the phenylacetylene-based dye led to efficient electron injection into TiO₂ layer and generated high photocurrent in DSSCs and low-lying HOMO reduced the dark current.

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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.dyepig.2012.06. 004.

References

- (a) Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chem Rev 2010;110:6595–663;
- (b) Mishra A, Bäuerle P. Small molecule organic semiconductors on the move: promises for future solar energy technology. Angew Chem Int Ed 2012;51: 2020–67.
- [2] Walker B, Kim C, Nguyen TQ. Small molecule solution-processed bulk heterojunction solar cells. Chem Mater 2011;23:470–82.
- [3] O'Regan B, Grätzel M. A low-cost high-efficiency solar-cell based on dye sensitized colloidal TiO₂ films. Nature 1991;253:737-40.
- [4] Grätzel M. Recent advances in sensitized mesoscopic solar cells. Acc Chem Res 2009;42:1788–98.
- [5] Ning Z, Tian H. Triarylamine: a promising core unit for efficient photovoltaic materials. Chem Commun 2009:5483–95.
- [6] (a) Han H, Liang M, Tang K, Cheng X, Zong X, Sun Z, et al. Molecular design of triarylamine dyes incorporating phenylene spacer and the influence of alkoxy substituent on the performance of dye-sensitized solar cells. J Photochem Photobiol A-Chem 2011;225:8–16;
 (b) Zhang MD, Pan H, Ju XH, Ji YJ, Qin L, Zheng HG, et al. Improvement of dye-sensitized solar cells' performance through introducing suitable heterocyclic groups to triarylamine dyes. Phys Chem Chem Phys 2012;14:2809–15.
- [7] Ning Z, Zhang Q, Wu W, Pei H, Liu B, Tian H. Starburst triarylamine based dyes for efficient dye sensitized solar cells. J Org Chem 2008;73:3791-7.
- [8] Lee W, Cho N, Kwon J, Ko J, Hong JI. New organic dye based on a 3,6disubstituted carbazole donor for efficient dye-sensitized solar cells. Chem Asian J 2012;7:343–50.
- [9] (a) 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;

(b) Koumura N, Wang ZS, Miyashita M, Uemura Y, Sekiguchi H, Cui Y, et al. Substituted carbazole dyes for efficient molecular photovoltaics: long electron

lifetime and high open circuit voltage performance. J Mater Chem 2009;12: 4829–36.

- [10] Marszalek M, Nagane S, Ichake A, Humphry-Baker R, Paul V, Zakeeruddin SM, et al. Tuning spectral properties of phenothiazine based donor-π-acceptor dyes forefficient dye-sensitized solar cells. J Mater Chem 2012;22:889–94.
- [11] Cao D, Peng J, Hong Y, Fang X, Wang L, Meier H. Enhanced performance of the dye-sensitized solar cells with phenothiazine-based dyes containing double D-A branches. Org Lett 2011;13:1610–3.
- [12] Wang ZS, Cui Y, Dan-Oh Y, Kasada C, Shinpo A, Hara K. Molecular design of coumarin dyes for stable and efficient organic dye-sensitized solar cells. J Phys Chem C 2008;112:17011-7.
- [13] 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.
- [14] Ito S, Miura H, Uchida S, Takata M, Sumioka K, Liska P, et al. High-conversionefficiency organic dye-sensitized solar cells with a novel indoline dye. Chem Commun 2008:5194–6.
- [15] Higashijima S, Inoue Y, Miura H, Kubota Y, Funabiki K, Yoshida T, et al. Organic dyes containing fluorene-substituted indoline core for zinc oxide dyesensitized solar cell. RSC Adv 2012;2:2721–4.
- [16] (a) Thomas KRJ, 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; (b) Zhang XH, Wang ZS, Cui Y, Koumura N, Furube A, Hara K. Organic sensitizers based on hexylthiophene-functionalized indolo[3,2-b]carbazole for efficient dye-sensitized solar cells. J Phys Chem C 2009;113:13409–15.
- [17] (a) Wang ZS, Koumura N, Cui Y, Takahashi M, Sekiguchi H, Mori A, et al. Hexylthiophene-functionalized carbazole dyes for efficient molecular photovoltaics: tuning of solar-cell performance by structural modification. Chem Mater 2008;20:3993–4003;
 (b) Baheti A, Lee CP, Thomas KRJ, Ho KC. Pyrene-based organic dyes with thiophene containing π-linkers for dye-sensitized solar cells: optical, electrochemical and theoretical investigations. Phys Chem Chem Phys 2011;13: 17210–21
- [18] Zhang XH, Cui Y, Katoh R, Koumura N, Hara K. Organic dyes containing thieno [3,2-b]indole donor for efficient dye-sensitized solar cells. J Phys Chem C 2010:114:18283–90
- [19] Mao M, Wang JB, Xiao ZF, Dai SY, Song QH. New 2,6-modified BODIPY sensitizers for dye-sensitized solar cells. Dyes Pigm 2012;94:224–32.
- [20] Erten S, Eren E, Icli S. Dye sensitized solar cell based on 1,8-naphthalene benzimidazole comprising carboxyl group. Eur Phys J App Phys 2007;38: 227–30.
- [21] Kumar D, Thomas KRJ, Lee CP, Ho KC. Novel pyrenoimidazole-based organic dyes for dye-sensitized solar cells. Org Lett 2011;13:2622–5.
- [22] (a) Wu YZ, Zhnag X, Li WQ, Wang ZS, Tian H, Zhu WH. Hexylthiophene-featured D-A-π-A structural indoline chromophores for coadsorbent-free and panchromatic dye-sensitized solar cells. Adv Energy Mater 2012;2:149–56; (b) Kim JJ, Choi H, Lee JW, Kang MS, Song K, Kang SO, et al. A polymer gel electrolyte to achieve ≥6% power conversion efficiency with a novel organic dye incorporating a low-band-gap chromophore. J Mater Chem 2008;18: 5223–9.
- [23] (a) Lai H, Hong J, Liu P, Yuan C, Li Y, Fang Q. Multi-carbazole derivatives: new dyes for highly efficient dye-sensitized solar cells. RSC Adv 2012;2:2427–32; (b) Ooyama Y, Inoue S, Nagano T, Kushimoto K, Ohshita J, Imae I, et al. Dye-sensitized solar cells based on donor–acceptor π-conjugated fluorescent dyes with a pyridine ring as an electron-withdrawing anchoring group. Angew Chem Int Ed 2011;50:7429–33.
- [24] Panthi K, Adhikari RM, Kinstle TH. Carbazole donor-carbazole linker-based compounds: preparation, photophysical properties, and formation of fluorescent nanoparticles. J Phys Chem A 2010;114:4550–7.
- [25] (a) Li W, Wu Y, Li X, Xie Y, Zhu W. Absorption and photovoltaic properties of organic solar cell sensitizers containing fluorene unit as conjunction bridge. Energy Environ Sci 2011;4:1830–7;
 (b) Thomas KRJ, Lin JT, Hsu YC, Ho KC. Organic dyes containing thienyl-fluorene conjugation for solar cells. Chem Commun 2005:4098–100.
- [26] Zhou H, Xue P, Zhang Y, Zhao X, Jia J, Zhang X, et al. Fluorenylvinylenes bridged triphenylamine-based dyes with enhanced performance in dyesensitized solar cells. Tetrahedron 2011;67:8477–83.
- [27] (a) Shen P, Tang Y, Jiang S, Chen H, Zheng X, Wang X, et al. Efficient triphenylamine-based dyes featuring dual-role carbazole, fluorene and spirobifluorene moieties. Org Electronics 2011;12:125–35;
 (b) Bai Y, Zhang J, Zhou D, Wang Y, Zhang M, Wang P. Engineering organic sensitizers for iodine-free dye-sensitized solar cells: red-shifted current response concomitant with attenuated charge recombination. J Am Chem Soc 2011;133:11442–5.
- [28] Schmidt-Mende L, Bach U, Humphry-Baker R, Horiuchi T, Miura H, Ito S, et al. Organic dye for highly efficient solid-state dye-sensitized solar cells. Adv Mater 2005;17:813–5.
- [29] Tian H, Bora I, Jiang X, Gabrielsson E, Karlsson KM, Hagfeldt A, et al. Modifying organic phenoxazine dyes for efficient dye-sensitized solar cells. J Mater Chem 2011;21:12462–72.
- [30] (a) Mishra A, Fischer MKR, Bäuerle P. Metal-free organic dyes for dyesensitized solar cells: from structure: property relationships to design rules. Angew Chem Int Ed 2009;48:2474–99;

(b) Liu J, Li R, Si X, Zhou D, Shi Y, Wang Y, et al. Oligothiophene dye-sensitized solar cells. Energy Environ Sci 2010;3:1924–8.

- [31] Kwon TH, Armel V, Nattestad A, MacFarlane DR, Bach U, Lind SJ, et al. Dithienothiophene (DTT)-based dyes for dye-sensitized solar cells: synthesis of 2,6-dibromo-DTT. J Org Chem 2011;76:4088–93.
- [32] (a) Paek S, Choi H, Choi H, Lee CW, Kang MS, Song K, et al. Molecular engineering of efficient organic sensitizers incorporating a binary π-conjugated linker unit for dye-sensitized solar cells. J Phys Chem C 2010;114:14646–53; (b) Chen YC, Chou HH, Tsai MC, Chen SY, Lin JT, Yao CF, et al. Thieno[3,4-b] thiophene-based organic dyes for dye-sensitized solar cells. Chem Eur J 2012; 18:5430–7.
- [33] (a) Song J, Zhang F, Li C, Liu W, Li B, Huang Y, et al. Phenylethyne-bridged dyes for dye-sensitized solar cells. J Phys Chem C 2009;113:13391-7;
 (b) Teng C, Yang XC, Yang C, Li SF, Cheng M, Hagfeldt A, et al. Molecular design of anthracene-bridged metal-free organic dyes for efficient dye-sensitized solar cells. J Phys Chem C 2010:114:9101-10.
- [34] Kim S, Lee JK, Kang SO, Ko J, Yum JH, Fantacci S, et al. Molecular engineering of organic sensitizers for solar cell applications. J Am Chem Soc 2008;128: 16701–7.
- [35] Choi H, Baik C, Kang SO, Ko J, Kang MS, Nazeeruddin MK, et al. Highly efficient and thermally stable organic sensitizers for solvent-free dye-sensitized solar cells. Angew Chem Int Ed 2008;47:327–30.
- [36] Baheti A, Tyagi P, Thomas KRJ, Hsu YC, Lin JT. Simple triarylamine-based dyes containing fluorene and biphenyl linkers for efficient dye-sensitized solar cells. J Phys Chem C 2009;113:8541–7.
- [37] (a) Baheti A, Singh P, Lee CP, Thomas KRJ, Ho KC. 2,7-Diaminofluorene-based organic dyes for dye-sensitized solar cells: effect of auxiliary donor on optical and electrochemical properties. J Org Chem 2011;76:4910–20;
 (b) Thomas KRJ, Kapoor N, Lee CP, Ho KC. Organic dyes containing
- pyrenylamine-based cascade donor system with different aromatic π-linkers for dye-sensitized solar cells: optical, electrochemical and device characteristics. Chem Asian J 2012;7:738–50.
 38] Andrade CD, Yanez CO, Rodriguez L, Belfield KD. A series of fluorene-based
- [38] Andrade CD, Yanez CO, Rodriguez L, Belfield KD. A series of fluorene-based two-photon absorbing molecules: synthesis, linear and nonlinear characterization, and bioimaging. J Org Chem 2010;75:3975–82.

- [39] Becke AD. A new mixing of Hartree-Fock and local density-functional theories. Chem Phys 1993;98:1372-7.
- [40] Yanai T, Tew DP, Handy NC. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). Chem Phys Lett 2004; 393:51-7.
- [41] Sonogashira K, Tohda Y, Hagihara N. A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. Tetrahedron Lett 1975;16:4467–70.
- [42] Knoevenagel E. Chem Ber 1896;29:172.
- [43] Baheti A, Singh P, Thomas KRJ. The synthesis and spectral characterization of red dyes containing biphenyl or fluorene conjugation and dicyanovinyl acceptors. Dyes Pigm 2011;88:195–203.
- [44] Chen CH, Hsu YC, Chou HH, Thomas KRJ, Lin JT, Hsu CP. Dipolar compounds containing fluorene and a heteroaromatic ring as the conjugating bridge for high-performance dye-sensitized solar cells. Chem Eur | 2010;16:3184–93.
- [45] Reichardt C. Solvatochromic dyes as solvent polarity indicator. Chem Rev 1994;94:2319-58.
- [46] Ko HM, Choi H, Paek S, Kim K, Song K, Lee JK, et al. Molecular engineering of push—pull chromophore for efficient bulkheterojunction morphology in solution processed small molecule organic photovoltaics. J Mater Chem 2011; 21:7248–53.
- [47] Cardona CM, Li W, Kaifer AE, Stockdale D, Bazan GC. Electrochemical considerations for determining absolute frontier orbital energy levels of conjugated polymers for solar cell applications. Adv Mater 2011;23:2367–71.
- [48] Wang P, Zakeeruddin SM, Moser JE, Grätzel M. A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells. J Phys Chem B 2003;107:13280–5.
- [49] Grätzel M. Photoelectrochemical cells. Nature 2001;414:338–44.
- [50] van de Lagemaat J, Park NG, Frank AJ. Influence of electrical potential distribution, charge transport, and recombination on the photopotential and photocurrent conversion efficiency of dye-sensitized nanocrystalline TiO₂ solar cells: a study by electrical impedance and optical modulation techniques. J Phys Chem B 2000;104:2044–52.