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Graphical Abstract

Bibridged bianchoring metal free dyes based on Phenoxazine and Triphenyl amine as donors for dye sensitized solar cell applications

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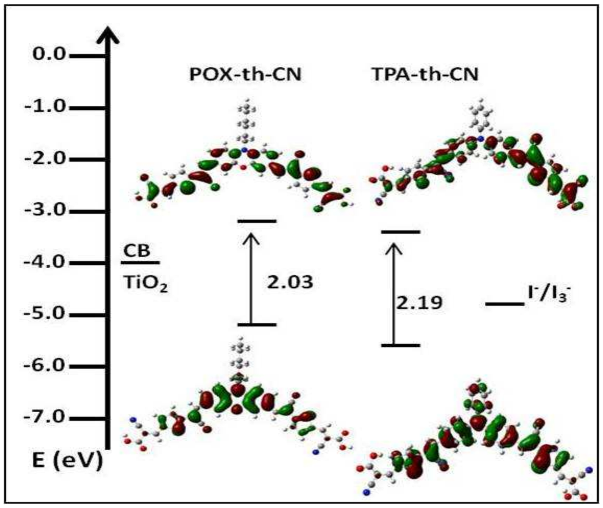
Designed and synthesized two new metal free bibridged bianchoring ambipolar dyes (D-(π-A)$_2$) by linking electron donating triphenyl amine/phenoxazine and electron-accepting cyanoacetic acid through a cyanovinyl thiophene π-bridge for fabrication of metal free dye-sensitized solar cells (DSSC).



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Bibridged bianchoring metal free dyes based on Phenoxazine and Triphenyl amine as donors for dye sensitized solar cell applications

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Designed and synthesized two new metal free bibridged bianchoring ambipolar dyes ($\text{D-}(\pi\text{-A})_2$) by linking electron donating triphenyl amine/phenoxazine and electron-accepting cyanoacetic acid through a cyanovinyl thiophene π-bridge for fabrication of metal free dye-sensitized solar cells (DSSC). The structures of the synthesized dyes were confirmed by NMR, mass and elemental analysis. The experimental and theoretical (DFT) approaches revealed that phenoxazine (POX-th-CN) dye exhibits lowered band gap (2.03 eV) compared to triphenyl amine (TPA-th-CN) dye (2.19 eV). Due to such lowered band gap electronic absorption of phenoxazine dye get red shifted and in addition the fabricated dye sensitized solar cell device based on phenoxazine dye shows higher current conversion efficiencies (□= 1.78%) compared to TPA-th-CN dye.

Introduction

Research on dye sensitized solar cells (DSSCs) has been intensively progressing in recent years due to their low cost, lightweight and flexible power production applications compared to conventional p-n junction solar cells.[1] Alternative generation of new type of sensitizers based on metal and metal free dyes have been continuously under progress to meet the improvements particularly in terms of efficiency and stability compared to the early works on DSSCs.[2-5] In particular, research on metal free dyes which has the general structure donor-π-bridge-acceptor (D-π-A) have attracted a great deal of interest nowadays, due to their high molar extinction coefficient, simple synthesis procedure, and environmental friendliness.[6-8] Upon illumination, D-π-A dye absorbs light, then intramolecular charge transfer (ICT) occurs from D to A through the π-bridge and from the acceptor moiety electrons are injected to the semiconductor nano particles which are chemisorbed by the acceptors.[9] The absorption, ICT properties and efficiencies of the dyes can be tuned through chemical and structural modification by altering the donor, π-bridge and acceptor moieties.

Generally, triphenylamine, phenoxazine, phenothiazine, carbazole, diphenylamine, coumarin, indoline, and tetrahydroquinoline[10,11] are the promising electron donor moieties for DSSC. Recently, considerable attention has been paid toward the exploration of triphenylamine[12,13] and phenoxazine[14] based chromophores for DSSC due to their potential electron-donating ability and their hole-transport properties. In addition, fabricated DSSC with triphenylamine[15] and phenoxazine[16] donors show efficiency of about 5.5% and 4.4%. Besides the use of triphenylamine and phenoxazine as a donor for sensitizer, many research groups synthesized bi-anchoring organic materials with double π-bridge ($\text{D-}(\pi\text{-A})_2$) charge transporting character for the development of highly efficient DSSCs.[15-17] Such materials can provide extended π-conjugation which increases the ICT properties, multilinking abilities, enhanced stability and efficiency of devices compare to monoanchoring counterparts.[15,20,21] Furthermore, in the recent years a series of bi-anchoring metal free dyes based on donor (carbazole and diphenylamine), π- linker (cyano vinyl thiophene and cyano vinyl biphenyl) and acceptor (cyanoacetic acid and rhodanine-3-acetic acid) were synthesized to fabricate DSSC which shows efficiencies in the range 0.56 - 4.04%.[22,23] In continuation, replacement of carbazole and diphenylamine donors with triphenyl amine and phenoxazine particularly to alter the HOMO energy levels and to shift their absorption behavior to the red region which play a crucial role in determining the overall conversion efficiency.[24,25] Hence, bi-bridged bi-anchoring metal free dyes namely (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl)bis (thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (TPA-th-CN) and (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (POX-th-CN) (Scheme 1) based on triphenylamine or phenoxazine as donor, cyanovinylthiophene as π–linker and cyanoacrylic acid as acceptor were synthesized and characterized by ^{1}H, ^{13}C-NMR, mass and elemental analysis. The electronic and structural properties of the synthesized dyes were investigated by UV-vis and fluorescence spectroscopy. The HOMO and LUMO energy levels were calculated using cyclic voltammetry and Density Functional Theory (DFT). Finally, the synthesized dyes are used for the fabrication of DSSCs.

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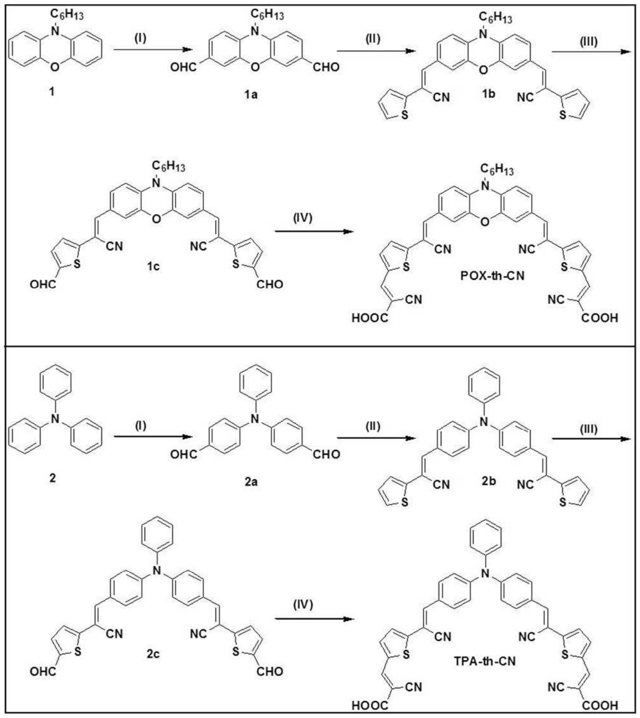

Scheme 1. Synthetic pathway of the organic dyes: (i) POCl$_3$, DMF, 95°C, 4h stirring (Yield: 54% for 1a and 59% for 2a). (ii) 2-(thiophen-2-yl)-acetonitrile, 6 M NaOH, ethanol, 2h refluxed (Yield: 60% for 1b and 80% for 2b). (iii) POCl$_3$, DMF, 95°C, 4h stirring (Yield: 32% for 1c and 30% for 2c). (iv) Cyanoacetic acid, piperidine, acetonitrile, 12-24 h refluxed (Yield: 20% for POX-th-CN and 18% for TPA-th-CN).

Synthesis and characterization of materials

The synthetic pathways of organic dyes POX-th-CN and TPA-th-CN were depicted in Scheme 1. The Vilsmeier-Haack formylation of hexylated phenoxazine (1) and triphenylamine (2) gave aldehyde compounds 10-hexyl-10H-phenoxazine-3,7-dicarbaldehyde (1a) and 4,4'-diformaltriphenylamine (2a) respectively. The synthesized aldehydes (1a and 2a) were coupled with active methylene compound thiophene-2-acetonitrile by Knoevenagel condensation to yield (2E,2'E)-3,3'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(2-(thiophen-2-yl)acrylonitrile) (1b) and (2E,2'E)-3,3'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(2-(thiophen-2-yl)acrylonitrile) (2b) respectively which on then undergo Vilsmeier-Haack formylation reaction followed by Knoevenagel condensation with cyanoacetic acid gave different products (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (POX-th-CN) and (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (TPA-th-CN) respectively. The synthesized dyes were characterized by ^{1}H, ^{13}C NMR, Mass and elemental analysis. ^{1}H NMR spectrum of the synthesized dye POX-th-CN in DMSO-d$_6$ solvent shows the chemical shift (δ) of hexyl chain protons at 0.92–1.98 ppm and the methylamine protons (-CH$_2$N-) in hexyl chain shows triplet at 4.32 ppm. Further, the aromatic phenyl protons, thiophene ring protons and vinyl protons adjacent to the phenyl, thiophene rings are appear at 7.26-8.47 ppm. ^{13}C NMR spectrum of the POX-th-CN in DMSO-d$_6$ solvent shows the chemical shift (δ) of hexyl chain carbons at 14.11–31.59 ppm and the methylamine carbon (-CH$_2$N-) in hexyl chain at 44.86 ppm. Further, the aromatic phenyl carbons, thiophene ring carbons and vinyl carbons adjacent to the phenyl, thiophene rings are appear at 91.93-145.07 ppm. The carboxylic acid carbons in cyanoacrylic acid groups (-COOH) appear at 160.74 ppm. Similarly, the ^{1}H NMR specrum of the synthesized TPA-th-CN dye in DMSO-d$_6$ solvent shows the chemical shift (δ) of the aromatic phenyl protons, thiophene ring protons and vinyl protons adjacent to the phenyl, thiophene rings at 7.19-8.16 ppm and ^{13}C NMR spectrum of the TPA-th-CN dye in DMSO-d$_6$ solvent shows the chemical shift (δ) of aromatic phenyl carbons, thiophene ring carbons and vinyl carbons adjacent to the phenyl, thiophene rings are appear at 108.09-146.92 ppm. The carboxylic acid carbons in cyanoacrylic acid groups (-COOH) appear at 159.53 ppm. Thus from the ^{1}H NMR and ^{13}C NMR spectral data described in the experimental section, the assigned peaks are found consistent with the proposed structure.

Optical Characteristics

The absorption and emission spectra of the synthesized dyes TPA-th-CN and POX-th-CN in DMF solution (3 × 10^{-4} M) are shown in Fig. 1 and their data are depicted in Table 1. TPA-th-CN and POX-th-CN shows two absorbance bands in solution (a high energy peak at 354 nm and 378 nm followed by a low energy peak at 485 nm and 518 nm) likely arising from the π-π* transition and intra molecular charge transfer (ICT) transition from donor amine to cyano acrylic acid acceptor, respectively. To confirm the ICT property, the absorption behaviour of the preliminary compounds 1c and 2c have been done and compared with POX-th-CN and TPA-th-CN compounds respectively [26] (Fig. S1).

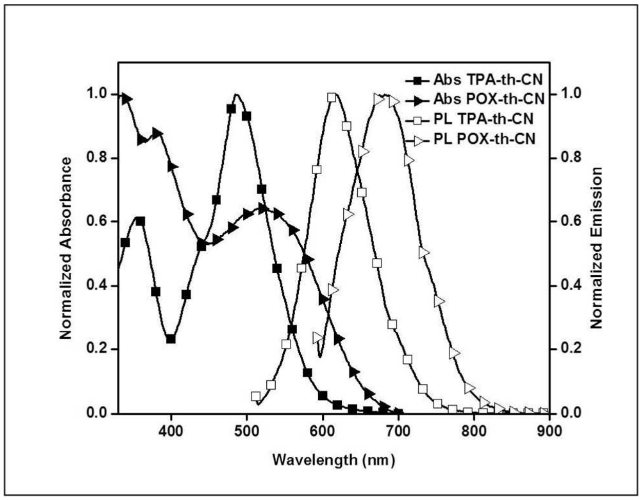

Fig.1 Normalized absorption and fluorescent spectra of Tpa-th-CN and POX-th-CN dyes recorded in DMF.

The ICT absorption spectrum of the phenoxazine compound is red shifted about 38 nm and broadened compared to triphenyl amine dye due to the high electron donating ability of phenoxazine which induces the electronic transition probability in

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conjugated dipolar systems.[27,28]

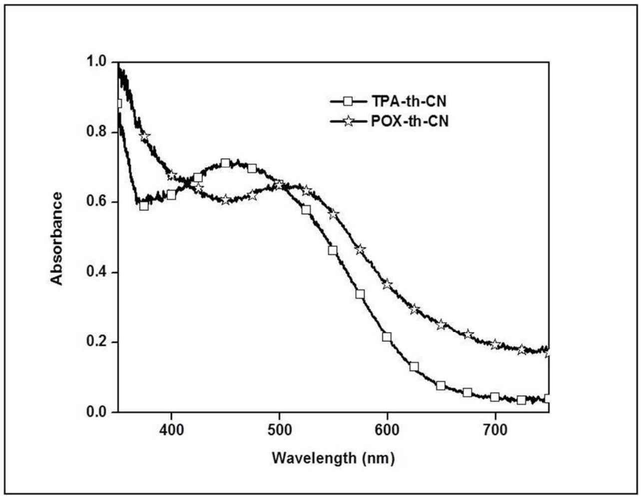

Fig.2 Absorption spectra of Tpa-th-CN and POX-th-CN dyes adsorbed on nanocrystalline TiO_2 films.

However the absorption spectrum of the dyes on TiO_2 surface (Fig. 2) shows blue shifted wavelength maximum and broadened longer wavelength compared to solution spectra due to the H-aggregation of dyes on TiO_2 surface and dye-dye or dye-TiO_2 interactions respectively.[29,30] Further, this donors (triphenyl amine (TPA) and phenoxazine (POX)) act as a good light absorber compared to the donors (carbazole (Car) and diphenyl amine (Dpa)).[22,23] The fluorescence emission spectra of triphenylamine and phenoxazine derivatives in DMF solution were recorded at their excitation wavelength shows emission wavelength at 617 nm (λ_{ex}= 510 nm), 682 nm (λ_{ex}= 590 nm) respectively.

Electrochemical Characteristics

The electron injection from the excited dye to conduction band (CB) of the semiconductor nano particles and the dye regeneration through the electrolytes are mainly depends on the LUMO energy level relative to reduction potential and HOMO energy level relative to oxidation potential of the dyes respectively. The conduction band energy level of TiO_2 (−4.0 eV vs vacuum) is generally lower than the LUMO level of the dye for electron injection while the redox potential of electrolyte (I^-/I_3^- is −4.6 eV vs vacuum) generally higher than the HOMO level of the dye for regeneration of the oxidized dye molecule by iodide ion (I^-) and avoiding the charge recombination between the oxidized dye molecules and photo-injected electrons in the nanocrystalline TiO_2 film.[10] The oxidation peak potentials of Tpa-th-CN and POX-th-CN dyes are determined by cyclic voltammogram by comparison with ferrocene (Fc; 4.8 eV)[31] in DMF medium (Fig. 3) and the corresponding data were shown in Table 1. Cyclic Voltammogram of both dyes (Fig. 3) showed one quasi-reversible oxidation peak due to the electron donating ability of triphenyl amine (1.10 V) and phenoxazine (0.79 V) groups and one irreversible reduction peak due to the electron withdrawing ability of cyanoacrylic acid group (-0.02 V in TPA-th-CN and -0.01V in POX-th-CN). The oxidation potential of TPA-th-CN and POX-th-CN are 1.10 V and 0.79 V vs $Ag/AgCl_{(aq)}$ which were determined from the intersection of two tangents drawn at the rising current and background charging current of a cyclic voltammogram, may be due to the electron donating ability of triphenyl amine and phenoxazine. The lower the oxidation potential of phenoxazine based dye indicated that phenoxazine is a good electron donor compared to triphenyl amine.[32] The HOMO and LUMO energy levels of the synthesized dyes were calculated based on the relationship mentioned in supporting information.[33] The lower HOMO energy levels of POX-th-CN (-5.14 eV) compared to TPA-th-CN (-5.45 eV) indicates the effective regeneration of dyes from redox electrolyte which in turn may responsible to improve the device efficiency.[34] The LUMO level of dyes was calculated to be -3.26 eV for TPA-th-CN and -3.11 eV for POX-th-CN by subtracting the band gap which was estimated by the intersection between the absorption and emission spectra, from the HOMO level.[33]

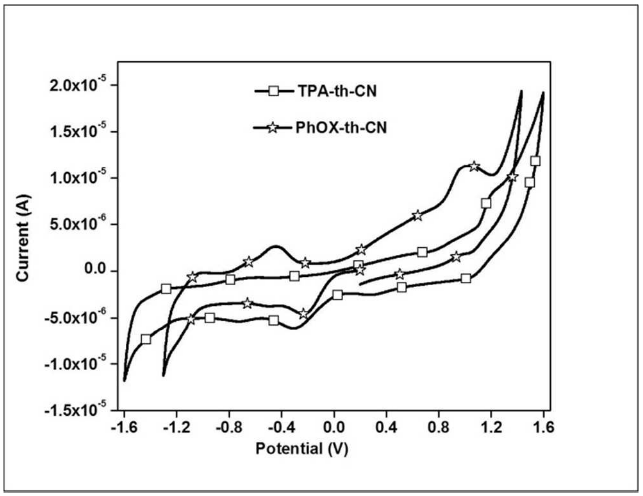

Fig.3 Cyclic voltammogram measured in DMF (3× 10^{-4} M) of POX-th-CN and TPA-th-CN at a Pt working electrode, glassy carbon counter electrode and Ag/Ag^+ reference electrode. (0.1 M TBAP as an electrolyte; scan rate 0.1V/s).

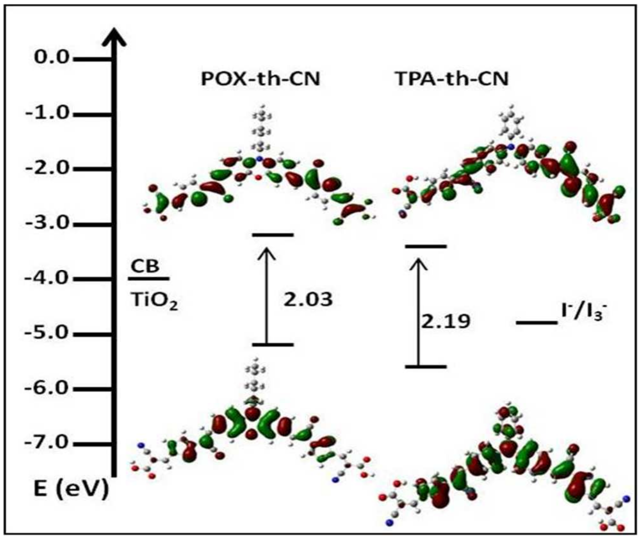

Fig.4 Schematic experimental energy levels of the dyes with frontier molecular orbital of HOMO and LUMO at the B3LYP/6-31G (d).

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Table 1: Photophysical, electrochemical and theoretical data of synthesized dyes.

Dye	λ_{abs}/nm(ε/M^{-1}cm^{-1})[a]	λ_{em} /nm[a,b]	E_g^{opt} (eV)[c]	E_{ox}/V (vs. Fc)	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[d]	E_{HOMO} (eV)[e]	E_{LUMO} (eV)[e]
POX-th-CN	378 (34876) 518 (26219)	682	2.03	0.79	-5.14	-3.11	-5.56	-3.30
TPA-th-CN	354 (25736) 484 (41702)	617	2.19	1.10	-5.45	-3.26	-5.93	-3.51

[a]Absorption and emission spectra were recorded in DMF solution (3×10^{-4} M) at room temperature. [b]Dyes were excited at their absorption maximum value (for POX-th-CN, λ_{ex} = 590 nm and for TPA-th-CN, λ_{ex} = 510 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)= $E_{0\text{-}0}$ (eV) + E_{HOMO}(eV), where $E_{0\text{-}0}$ is the intersection between the absorption and emission spectra of the sensitizers. [e]B3LYP/6-31G (d) calculated values.

Table 2: Photovoltaic performance data of the fabricated devices based on synthesized dyes.

Dye	J_{SC} (mAcm^{-2})	V_{OC} (mV)	FF	□ (%)[a]	IPCE (%)	Surface concentration Γ (mol/cm^2)	Electron lifetime (τ_{eff}) (ms)
POX-th-CN	7.4	631	0.32	1.78	57.5	2.92×10^{-7}	9.10
TPA-th-CN	4.7	500	0.48	1.32	48.0	2.76×10^{-7}	2.21

[a]Illumination: 85 mW cm^{-2} simulated AM 1.5 G solar light; electrolyte containing: 0.05 M I_2/0.5 M KI/0.5 M 4-*tert*-butyl pyridine in 3-methoxypropionitrile.

The band gap of the POX-th-CN is smaller than the TPA-th-CN; this lowers the HOMO–LUMO energy bandgap which inturn shifts the absorption region towards longer wavelength of the solar spectrum.[35] Thus, HOMO and LUMO values are in good agreement with the energy level of TiO_2 conduction band and electrolyte redox potential respectively as shown in Figure 4.

Theoritical Characteristics using DFT calculation

The optimized electronic structures and frontier molecular orbital diagrams of the synthesized dyes were determined using density functional theory (DFT) (B3LYP/6-31G (d) basis set with the Gaussian 09 program package) and it is shown in Figure 5. In both TPA-th-CN and POX-th-CN, the HOMO is mainly populated over the amine and cyano vinyl thiophene blocks with considerable contribution from the former, whereas LUMO is delocalized through the cyano vinyl thiophene and cyanoacrylic acid fragments with sizable contribution from the latter. The LUMO of the π-bridge is similar to the HOMO of the dyes, but the lobes do not align. This spatial separation in HOMO and LUMO orbitals through π-bridge is an important characteristic for D-π-A organic dyes in DSSCs because this structural strategy will induce the intramolecular charge transfer (ICT) from the donor to acceptor groups under illumination and increases the interfacial electron injection from organic dye to semiconductor nano particles.[36] Thus the theoretically calculated HOMO, LUMO and band gap energy levels are in good agreement with the experimental values (see Table 1).

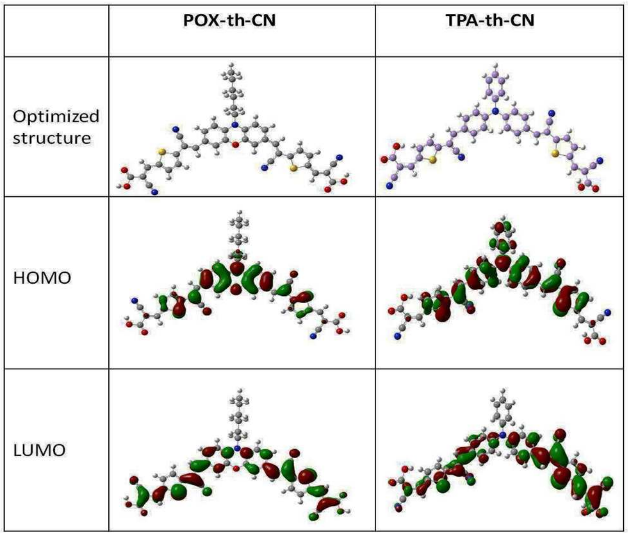

Fig.5 The optimized structure and frontier orbitals of the POX-th-CN and TPA-th-CN dyes calculated with B3LYP/6-31G (d) level.

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Photovoltaic Characteristics

The current-voltage characteristics of fabricated DSSCs using synthesized organic dyes (TPA-th-CN and POX-th-CN) as sensitizers of type (FTO/TiO_2/dye/liquid electrolyte/Pt/FTO) were measured under simulated AM 1.5 irradiation (85 mW/cm^2) and the calculated data such as short-circuit photocurrent density (J_{SC}), open circuit photovoltage (V_{OC}), and fill factor (FF) were determined from Fig. 6 and it is summarized in Table 2. The fabricated device based on POX-th-CN dye exhibits a short circuit current density (J_{SC}) of 7.4 mA cm^{-2}, open circuit photo voltage (V_{OC}) of 631 mV and a fill factor (FF) of 0.32%. Similarly the device based on TPA-th-CN dye exhibits a short circuit current density (J_{SC}) of 4.7 mA cm^{-2}, open circuit photo voltage (V_{OC}) of 500 mV and a fill factor (FF) of 0.48%. The efficiency (□) of POX-th-CN is 1.78% and TPA-th-CN is 1.32% which was calculated using the following equation: □= J_{SC}×V_{OC}×FF/light intensity. The reason for the lower efficiency of these dyes based devices are due to their lower fill factor.[37] The efficiency of phenoxazine dye is higher than the triphenyl amine dye may be due to the absorption red shift and as well as low band gap property of the phenoxazine dye.[28] The incident photon-to-current conversion efficiencies (IPCE) as a function of wavelength for POX-th-CN and TPA-th-CN are presented in Fig. 7. Fabricated solar cell based on both the dyes exhibited a broad IPCE spectrum from 350 to 700 nm. POX-th-CN showed the IPCE value of 57.5% at 440 nm and 32% at 535 nm whereas TPA-th-CN showed the IPCE value of 48.0 % at 475 nm. Compared to triphenyl amine based device, phenoxazine based devices exhibited broader wavelength IPCE spectra resemble with the absorption spectra on dye adsorbed TiO_2 film (Fig. 2). Thus the longer wavelength absorption region favors the light harvesting ability and increases the photocurrent response on the POX-th-CN DSSC device. The adsorbed dye amount (Γ) on TiO_2 surface was calculated for correlating the efficiency of the devices by desorbing the dye from the TiO_2 surface using 0.1M NaOH in DMF/H_2O (1:1) mixture[38] indicates that the phenoxazine based dyes are adsorbed comparatively higher than the triphenyl amine based dyes due to the presence of hexyl substituent in POX-th-CN which induces the controlled aggregation of dyes on TiO_2 surface.[39]

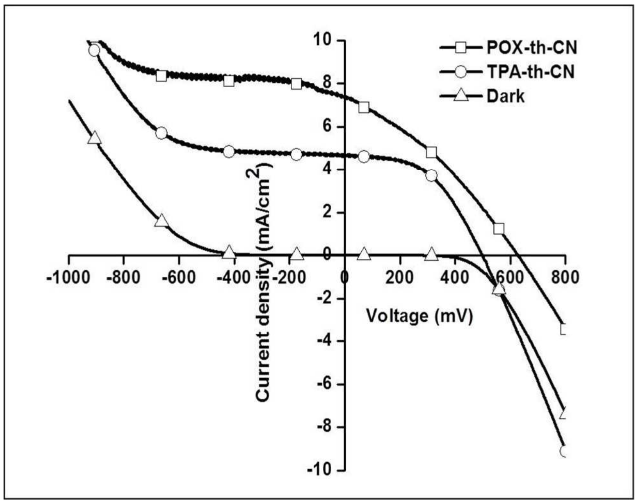

Fig. 6 Current density-voltage characteristics for POX-th-CN and TPA-th-CN based devices for DSSCs under illumination of simulated solar light (AM 1.5, 85 mW/cm^2).

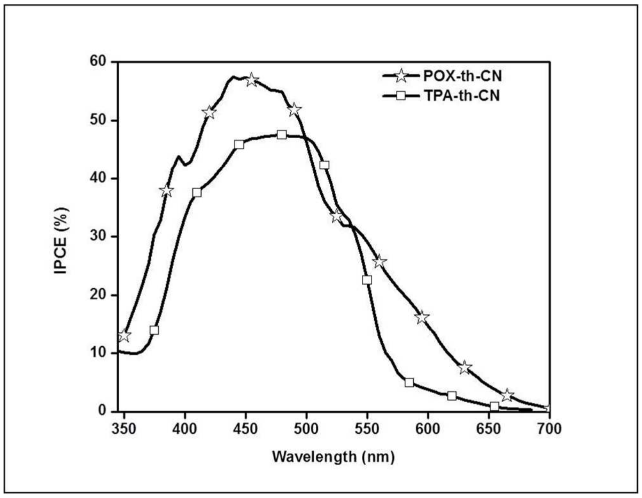

Fig. 7 IPCE spectra of the fabricated devices based on POX-th-CN and TPA-th-CN dyes.

Electrochemical Impedance Characteristics

To further understand the internal resistances for the charge transfer processes such as the charge recombination at the

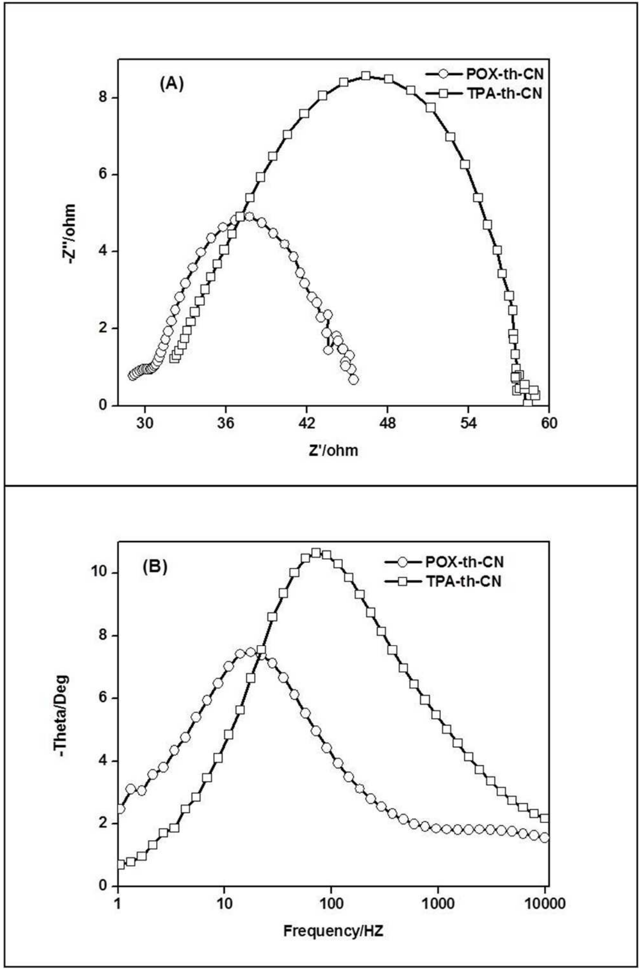

Fig. 8 EIS spectra of DSSCs based on POX-th-CN and TPA-th-CN dyes measured at V_{OC}, 85 mW/cm^2. (A) Nyquist plots. (B) Bode phase plots.

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TiO_2/dye/electrolyte interface, electron transport in the TiO_2 electrode, electron transfer at the Pt counter electrode and I^-/I_3^- transport at the electrolyte were measured using electrochemical impedance spectra (EIS)[40] at V_{OC} under AM 1.5 with a frequency range of 10^0-10^4 Hz. As shown in Nyquist plots (Fig. 8A) the radius of the middle semicircle is in the order of POX-th-CN < TPA-th-CN indicating the electron transport is in the order of TPA-th-CN < POX-th-CN which reflected in the efficiency of devices.[41] The electron lifetime (τ_{eff}) in TiO_2 conduction band were calculated from the Bode phase plots (Fig. 8B) using the following equation:[42] $\tau_{eff} = 1/2\pi f$, where, f is the frequency peak in Bode phase plot. The electron lifetime was calculated for POX-th-CN device (9.10 ms) and TPA-th-CN device (2.21 ms) from the corresponding frequency peak maxima in Bode phase plot respectively. Thus, the higher electron life time in TiO_2 conduction band for POX-th-CN device indicates the inhibition of the electron recombination to the I_3^- ions and thus enhances the device efficiency compare to TPA-th-CN device.[23]

FT-IR Characteristics

To understand the adsorption behavior of synthesized dyes (POX-th-CN and TPA-th-CN) on the TiO_2 nanoparticles for interfacial electron injection, Fourier Transform Infrared (FT-IR) spectroscopy was performed in ATR mode (Fig. S2 (A) & (B)). The ATR-FT-IR spectrum of both dye molecules shows the characteristic peaks of the -C≡N and –C=O of carboxylic acid group at 2210 cm^{-1}, 1738 cm^{-1} for POX-th-CN and 2209 cm^{-1}, 1732 cm^{-1} for TPA-th-CN respectively. The large broad peak above 3000 cm^{-1} is due to the adsorbed moisture and –OH stretching of carboxylic acid group. Whereas for the dye adsorbed TiO_2 films, the –C=O stretching band around 1730 cm^{-1} are disappeared and a new band appeared in 1583 cm^{-1} indicates the nature of dye binding on TiO_2 surface via the bidendate carboxylate (-O-C-O-) due to the deprotonation of –COOH group.[43] In addition, observed peak broadening also supports that the dye-TiO_2 interactions have occurred.[44]

Experimental Section

Materials

All reagents and chemicals were purchased from Alfa Aesar and Sigma-Aldrich and used without further purification unless specified otherwise. All solvents were dried by refluxing for at least 24 h over CaH_2 and freshly distilled prior to use. All column chromatographic separations were carried out on Merck silica gel (60-120 mesh). FTO glass plates (sheet resistance 10Ω/□) were purchased from BHEL, INDIA**.** The photoanode was prepared by the following the procedure as follows[45]: The glacial acetic acid (5 ml), 7.5 ml of tetraisopropyl titanate ($C_{12}H_{28}O_4Ti$) and one drop of Triton X-100 were mixed with 15 ml of 2-propanol. Water (5 ml) was added to the above solution drop wise while vigorously stirring the solution. The resulting semi colloidal suspension was dispersed on a fluorine doped tin oxide (FTO) glass plate by glass rod using doctor blade technique. Loose crust on TiO_2 film was removed by wiping smoothly by cotton wool. The thickness of the TiO_2 film was successively controlled, by repeating the above coating procedure. Then it was sintered at 450°C for 1 h for removing the binder, solvent and giving an electrically-connected network of TiO_2 particles under tubular furnace. After the sintering process, when the temperature of the plate drops to 50° to 70°C, it was immerse into the dye solution and leave for 24 h. Excess non-adsorbed dye were washed with anhydrous ethanol. And the Platinum catalyst counter electrode was prepared by deposition of $H_2PtCl_6.6H_2O$ solution (0.005 mol dm^{-3} in isopropanol) onto FTO glass and then sintering at 400^{o}C for 20 min.[46] The DSSC device was fabricated by the following method: the photo cathode was placed on top of the photo anode and was tightly clipped together. Then, liquid electrolyte 0.05MI_2/0.5MKI/0.5M 4-*tert*-butyl pyridine (TBP) in 3-methoxypropionitrile was injected in-between the two electrodes.

Instruments

^{1}H- and ^{13}C-NMR spectra was realized on a 300/400 MHz BRUKER spectrometer in deuterated chloroform or dimethylsulfoxide solution at 298K. Chemical shifts (δ values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. The molecular weight of the dyes were determined by Micromass QUATTRO 11 ESI-MS spectrometer coupled to a Hewlett Packard series 1100 degasser. Elemental analyses were performed on a Vario EL III elemental analyzer. Absorption and fluorescence spectra were measured in DMF solution on a T90+ UV-vis spectrometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively. Electrochemical measurements were performed on a Metrohm Autolab PGSTAT potentiostat/galvanostat-84610. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum disc working electrode, a glassy carbon (GC) auxiliary electrode, and a Ag/AgCl(aq) was used as the reference electrode. The potentials were reported vs ferrocene as standard using a scan rate of 0.1 Vs^{-1} and the sample solutions contained 3×10^{-4} M sample and 0.1 M tetrabutylammonium perchlorate (TBAP) in anhydrous DMF as a supporting electrolyte under Argon atmosphere. Electrochemical impedance spectroscopy (EIS) measurements were done under 85 $mWcm^{-2}$ light illumination by using an Autolab PGSTAT potentiostat/galvanostat-84610. The impedance spectra were recorded with a frequency ranging between 10 kHz to 1Hz at their open circuit potential (OCP). The IPCE spectra were recorded using Oriel 300W Xe Arc lamp in combination with an Oriel Cornerstone 260¼ monochromator. The number of incident photons was calculated for each wavelength using a calibrated monocrystalline silicon diode as reference. ATR-FT-IR spectra were measured with a Thermo spectrophotometer system equipped with a ZnSe prism.

Synthesis

Synthesis of 10-hexyl-10H-phenoxazine (1)

1-Bromohexane (2.2 g, 0.01308 mol), phenoxazine (2.0 g, 0.0109 mol) and potassium hydroxide (0.734 g, 0.01308 mol) were added to 26 mL of dimethylsulfoxide (DMSO) and stirred the reaction mixture for 4 h at RT. After identifying the completion of reaction by TLC, the resulting mixture was extracted with dichloro methane (DCM)/water and then dried the organic portion with Na_2SO_4. The solvent was evaporated and the resulting dark brown liquid was purified by column chromatography on silica by using hexane as solvent to give

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colorless liquid (Yield: 63.4%; 1.85 g). ^{1}H NMR ($CDCl_3$, ppm): δ 6.80-6.76 (m, 2H), 6.63-6.60 (m, 4H), 6.46 (d, 2H, J=8Hz), 3.46 (t, 2H, J=8Hz), 1.68-1.56 (m, 2H), 1.43-1.34 (m, 6H), 0.92 (t, 3H, J=7.2Hz).

Synthesis of 10-hexyl-10H-phenoxazine-3,7-dicarbaldehyde (1a)

Freshly distilled $POCl_3$ (17.4 ml, 25eq) was added drop wise to DMF (13.3 ml, 23eq) under N_2 atmosphere at 0° C, and then the solution was stirred for 1 h. Compound 1 (2 g, 7.48 m.mol) was added to the above solution, and the resulting mixture was stirred for 4 h at 95^{o}C. After cooling to room temperature, the mixture was poured into a beaker containing ice-cube, and basified with 4M NaOH. Filtered the solid and extracted with ethylacetate (EA)/brine. After evaporating the organic solvent the crude product was purified by column chromatography on silica using a mixture of EA/Hexane (1:6, v/v), to give a greenish yellow solid (Yield: 54%; 1.31 g). ^{1}H NMR ($CDCl_3$, ppm): δ 9.69 (s, 2H), 7.34-7.32 (m, 2H), 7.25 (s, 2H), 6.59 (d, 2H, J=8Hz), 3.56 (t, 2H, J=8 Hz), 1.71-1.63 (m, 2H), 1.45-1.36 (m, 6H), 0.92 (t, 3H, J=7.2Hz).

Synthesis of (2E,2'E)-3,3'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(2-(thiophen-2-yl)acrylonitrile) (1b)

Freshly distilled ethanol (24ml) was taken in a 100 ml single neck round bottom flask. The compound 1a (1g, 1eq) and thiophene-2-acetonitrile (0.84g, 2.2eq) were added to 100 ml single neck round bottom flask containing 24ml freshly distilled ethanol. Then, 6M NaOH (0.7 ml) was added to this reaction mixture at room temperature after that the reaction mixture was refluxed for 2 h. A dark red color solid was formed. It was filtered and recrystallized in chloroform and methanol to give the product (Yield: 60%; 1.0 g). ^{1}H NMR ($CDCl_3$, ppm): δ 7.36 (d, 2H, J=8.4 Hz), 7.31 (d, 2H, J=3.2 Hz), 7.25 (d, 2H, J=3.6 Hz), 7.15-7.09 (m, 2H), 7.05-7.03 (m, 4H), 6.55-6.50 (m, 2H),3.52 (t, 2H,J=8 Hz), 1.67 (d, 2H, J=6 Hz),1.43-1.38 (m, 6H), 0.95-0.93 (m, 3H).^{13}C NMR ($CDCl_3$, ppm): δ 139.11, 138.55, 136.95, 134.20, 132.44, 128.37, 127.97, 127.54, 126.63, 116.73, 105.73, 44.23, 31.55, 27.05, 26.64, 22.81, 14.13.

Synthesis of (2E,2'E)-3,3'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(2-(5-formylthiophen-2-yl)acrylonitrile) (1c)

DMF (3.3 ml, 23eq) was taken in a 3 neck 50 ml round bottom flask. To this freshly distilled $POCl_3$ (4.4 ml, 25eq) was added drop wise under N_2 atmosphere at 0° C, and then it was stirred for 1 h. 1g of compound 1b 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 room temperature and then the mixture was poured into a beaker containing ice-cube, and basified with 4M 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 a dark red color solid (Yield: 32%; 0.35 g). ^{1}H NMR ($CDCl_3$, ppm): 9.81 (s, 2H), 8.37 (d, 4H, J=9 Hz), 8.26 (s, 2H), 7.51 (d, 2H, J=9 Hz), 7.40 (s, 2H), 7.33-7.25 (m, 2H), 7.10-7.08 (m, 2H), 4.27 (t, 2H,J=8.1 Hz), 1.99-1.97 (m, 2H), 1.59-1.58 (m, 2H), 1.56-1.43 (m, 4H), 0.98-0.94 (m, 3H). ^{13}C NMR ($CDCl_3$, ppm) δ 189.28, 141.69, 135.16, 133.05, 131.94, 131.32, 125.01, 123.42, 117.03, 116.44, 116.35, 49.40, 31.46, 26.67, 26.58, 22.71, 14.07. HR-MS Waters (Micromass): Q-Tof micro (YA-105) (TOF MS ES+) Anal. Calcd. for $C_{34}H_{27}N_3O_3S_2$: 589.1494. Found: 590.1412 $[M+H]^+$.

Synthesis of (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(10-hexyl-10H-phenoxazine-3,7-diyl)bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (POX-th-CN)

0.4g (0.6312 mmol) of compound 1c, 0.21 g (2.89 mmol) of cyanoacetic acid was added to 50 ml of freshly distilled acetonitrile. 0.181 ml of piperidine was added to this mixture and refluxed the reaction for 12 h. After cooling to room temperature, the solvent was removed by distillation. The residue was purified by column chromatography using silica gel and $CHCl_3$:CH_3OH (10:1, v:v) mixed solvent as the eluent to give the dye as red colour solid (Yield: 20%; 0.15 g). ^{1}H NMR (DMSO-d_6, ppm): 8.47-8.42 (m, 2H), 8.20-8.17 (m, 2H), 8.14-8.11 (m, 2H), 7.99-7.96 (m, 2H), 7.68 (m, 2H), 7.60-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.35-7.26 (m, 2H), 4.32 (t, 2H,J=8.1 Hz), 1.98-1.96 (m, 2H), 1.59-1.53 (m, 2H), 1.44-1.38 (m, 4H), 0.93 (t, 3H,J=6.9 Hz).^{13}C NMR (DMSO-d_6, ppm): δ 160.74, 145.07, 137.56, 131.33, 128.48, 124.28, 121.97, 114.92, 111.70, 109.85, 100.78, 91.93, 44.86, 31.59, 26.59, 25.17, 22.75, 14.11. ATR-FT-IR: 2210 cm^{-1}, 1738 cm^{-1}.Anal. Calcd. for $C_{40}H_{29}N_5O_5S_2$: C, 66.37; H, 4.04; N, 9.68. Found: C, 66.21; H, 4.14; N, 9.84. m/z (ESI) Anal. Calcd. for $C_{40}H_{29}N_5O_5S_2$: 723.161. Found: 723.24 $[M]^+$.

Synthesis of 4,4'-Diformaltriphenylamine (2a)

Freshly distilled $POCl_3$ (28.4 ml, 25eq) was added drop wise to DMF (21.7 ml, 23eq) under an atmosphere of N_2 at 0° C, and then it was stirred for 1 h. Compound 2 (3 g, 12.24 m.mol) was added to the above solution, and the resulting mixture was stirred for 4 h at 95^{o}C. After cooling to room temperature, the mixture was poured into a beaker containing ice-cube, and basified with 4M NaOH. Filtered the solid and extracted with ethylacetate (EA)/brine. After evaporating the organic solvent the crude product was purified by column chromatography on silica using a mixture of EA/Hexane (1:6, v/v), to give a yellow solid (Yield: 59%; 2.2 g). ^{1}H NMR ($CDCl_3$, ppm): δ 9.95 (s, 2H), 7.85-7.82 (m, 4H), 7.48-7.44 (m, 2H), 7.34-7.32 (m, 1H), 7.26-7.22 (m, 6H).

Synthesis of (2E,2'E)-3,3'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(2-(thiophen-2-yl)acrylonitrile) (2b)

The compound 2a (1.5g, 1eq) and thiophene-2-acetonitrile (1.35g, 2.2eq) were added to 100 ml single neck round bottom flask containing 45 ml freshly distilled ethanol. Then, 6M NaOH (0.1 ml) was added to this reaction mixture at room temperature after that the reaction mixture was refluxed for 2 h. It was monitored by TLC. An orange color solid was formed. It was filtered and recrystallized in dichloromethane and methanol to give the product (Yield: 80%; 2.26 g). ^{1}H NMR ($CDCl_3$, ppm): δ 7.77 (d, 4H, J=8Hz), 7.38-7.34 (m, 4H), 7.29-7.25 (m, 4H), 7.21-7.12(m, 7H), 7.07-7.05 (m, 2H).^{13}C NMR ($CDCl_3$, ppm): δ 148.82, 146.00, 139.76, 138.99, 130.65, 130.03, 128.23, 127.96, 126.75, 126.62, 125.85, 125.58, 123.2, 117.43, 103.82.

Synthesis of (2E,2'E)-3,3'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(2-(5-formylthiophen-2-yl)acrylonitrile) (2c)

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DMF (3.5 ml, 23eq) was taken in a 3 neck 50 ml round bottom flask. To this freshly distilled $POCl_3$ (4.5 ml, 25eq) was added drop wise under N_2 atmosphere at 0° C, and then it was stirred for 1 h. 1g of compound 2b 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 room temperature and then the mixture was poured into a beaker containing ice-cube, and basified with 4M 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 $CHCl_3$:CH_3OH (20:1, v/v), to give a dark red color solid (Yield: 30%; 0.33 g). ^1H NMR ($CDCl_3$, ppm): δ 10.00 (s, 2H), 7.82 (d, 4H, J=8.7 Hz), 7.55-7.51 (m, 8H), 7.44-7.37 (m, 1H), 7.35-7.26 (m, 2H), 7.20-7.14 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 190.66, 153.39, 152.15, 145.64, 140.94, 131.44, 130.29, 127.20, 126.40, 122.90, 108.54, 104.24. HR-MS Waters (Micromass): Q-Tof micro (YA-105) (TOF MS ES+) Anal. Calcd. for $C_{34}H_{21}N_3O_2S_2$: 567.1075. Found: 568.1062 $[M+H]^+$.

Synthesis of (2E,2'E)-3,3'-(5,5'-(1E,1'E)-2,2'-(4,4'-(phenylazanediyl)bis(4,1-phenylene))bis(1-cyanoethene-2,1-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (TPA-th-CN)

0.5g (0.8808 mmol) of compound 2c, 0.3 g (3.52 mmol) of cyanoacetic acid was added to 50 ml of freshly distilled acetonitrile. 0.261 ml of piperidine was added to this mixture and refluxed the reaction for 24 h. After cooling to room temperature, the solvent was removed by distillation. The residue was purified by column chromatography using silica gel and $CHCl_3$:CH_3OH (10:1, v:v) mixed solvent as the eluent to give the dye as red colour solid (Yield: 18%; 0.12 g). ^1H NMR (DMSO-d_6, ppm): 8.16-8.13 (m, 2H), 8.01-7.98 (m, 4H), 7.90-7.79 (m, 4H), 7.75-7.69 (m, 4H), 7.55-7.50 (m, 2H), 7.40-7.38 (m, 4H), 7.27-7.19 (m, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 159.53, 146.92, 140.16, 134.23, 134.16, 132.41, 132.31, 132.05, 131.50, 131.44, 127.39, 127.35, 126.01, 122.42, 119.10, 118.83, 116.77, 116.19, 109.53, 108.09. ATR-FT-IR: 2209 cm^{-1}, 1732 cm^{-1}.Anal. Calcd. for $C_{40}H_{23}N_5O_4S_2$: C, 68.46; H, 3.30; N, 9.98. Found: C, 68.38; H, 3.36; N, 9.82. m/z (ESI) Anal. Calcd. for $C_{40}H_{23}N_5O_4S_2$: 701.1191. Found: 701.17 $[M]^+$.

Conclusion

In conclusion, designed and synthesized here two new bi-bridged bi-anchoring metal free dyes based on phenoxazine and triphenyl amine as donor, cyanovinylthiophene as π–linker and cyanoacrylic acid as acceptor for DSSC applications. Among the two dyes (POX-th-CN and TPA-th-CN), phenoxazine based dye exhibits higher power conversion efficiency due to the higher electron donating ability of phenoxazine compared to triphenyl amine because the former has electron rich nitrogen and oxygen atoms while the latter have only nitrogen atom. In addition, such property is responsible for the decrease in the band gap and as well as increases the light harvesting property to red region; brings the HOMO energy level near to redox potential of electrolytes for effective dye regeneration and the increases electron life time in TiO_2 conduction band. The lower the efficiency of these devices compared to literally available devices may be due to their lower fill factor which will be rectified by adding appropriate electrolytes.

Notes and references

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