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Impact of the different electron-releasing subunits on the dye-

sensitized solar cell performance of new triphenylamine-

benzimidazole based molecules

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ABSTRACT

New triphenylamine-benzimidazole type small molecules with different electron-releasing groups were designed and synthesized to investigate their photovoltaic performances in dye sensitized solar cells (DSSCs). Their good visible absorptions covering the 400-535 nm in addition to suitable lowest unoccupied molecular orbital (LUMO) energy levels between -3.03 and -3.11 eV make good candidates them for DSSC devices. Fluorescence quenching studies of the dyes with pristine titania support the good electron injection to conduction band of TiO₂. Time resolved measurements of the dyes in solutions indicate the occurence of charge generation during the excited state. One of the used dyes in DSSC devices, **TPA5a**, carrying a methoxy group in triphenylamine part of the structure, gave much higher power conversion efficiency (PCE) value of 4.31% as compared to the other derivatives. Device fabricated from **TPA5a** dye gives good external quantum efficiency (EQE) value above 70%

at 460 nm. Also, electron impedance spectroscopy (EIS) analysis of the devices gives a good explanation of the understanding of the cell performances.

Keywords: Triphenylamine, Benzimidazole; Time resolved emission spectra, Charge transfer, Dye sensitized solar cells, Electron impedance analysis

Introduction

Most of the devices/techniques used in the conversion of solar energy into the electricity could not give satisfactory efficiencies for marketing purposes. Dye-sensitized solar cells (DSSCs) present good opportunities to the dealers in order to gain much cheaper solar cells and relatively much higher cell performances as compared to the silicon solar cells. Nowadays, high conversion efficiency value of 12.7% obtained from a D- π -A porphyrin dye [1] under incident intensity of AM1.5 solar light for DSSCs allows us to look with hopefully for the future in ensuring energy demands. In this context, it is necessary to design novel materials for DSSCs such as D- π -A structures enabling to control an efficient electron transfer from dye to the TiO₂ surface in the working mechanism.

Triphenylamine (TPA) group is chosen as a core group in most of efficient molecular architectures for DSSCs. Both its good solution-processability arising from three dimensional structure of benzene rings [2] and also efficient hole-transporting property [3, 4] enable it an efficient chromophore for DSSC devices. Bäuerle et al. reviewed the metal-free organic dyes used in DSSCs and reported that the power conversion efficiencies for different type TPA molecules have been varied between the values of 1.7% and 9.1% [5]. The number of TPA groups is also important in cell performances. Efficiency was reached to 5.06% when the bis-TPA substituted dye was used instead of the corresponding mono-TPA substituted dye [6]. In the literature survey, it is reported a wide variety of substituted groups attached to TPA core in order to increase cell efficiencies. Researchers have used different TPA motifs which are

incorporated into the special subunits including thiophene [7-9], rhodanine-3-acetic acid [10], diketopyrrolopyrrole [11], thieno[3,4-c]pyrrole-4,6-dione [12], benzothiadiazole [13], carbazole [14], quinoxaline [15], triazine [16] and phenoxazine [17] groups. Wang et al. reported much higher cell efficiency of 6.6% with a thiophene bridged double D- π -A dye as compared to its monobranched analogue. Wang also emphasized that the cross shape of the double D- π -A branched dyes can inhibit charge recombination [18].

Also, hole transporting property of the sensitizer should be more effective than the charge recombination in dye regenaration. Hsu et al. synthesized 1H-phenanthro[9,10-d]imidazole dyes as the sensitizers for DSSCs and obtained good efficiencies, ranging from 2.95% to 4.68%. They reported that incorporation of benzimidazole into TPA structure delays charge recombination of the electrons in the conduction band of TiO₂ with the oxidized dyes in DSSCs [19]. Among the limited number of studies for DSSCs using TPA-benzimidazole conjugates, Jia and co-workers synthesized two novel TPA- and benzimidazole-based chromophores and obtained good efficiencies around 2.5% under full sunlight of AM 1.5G. They also reported that the introduction of benzimidazole group into the TPA increases the molar extinction coefficients and λ_{max} values [20].

In our study, novel D-A type **TPA5a-b** and **TPA4c** organic dyes (Fig. 1a-b) which contain TPA-benzimidazole hybrid donor and 2-cyanoacetic acid acceptor have been synthesized and used in DSSCs. Ground state optical properties both in solution and on thin films and excited state behaviours in two different solvents of polarities have been investigated in detail. The impact of the electron releasing subunits on the device performance has been also investigated.

Fig. 1a [21]

Fig. 1b [22], [20], [23], [24, 25]

Experimental section

General procedures

¹H NMR and ¹³C NMR were measured on a Bruker 400 MHz spectrometer. FT-IR spectra were recorded on a Perkin Elmer-Spectrum BX spectrophotometer preparing KBr pellets. The UV–vis spectra were recorded with a Perkin Elmer Lambda 950 spectrometer in solutions and on thin films. FLSP 920 Edinburg fluorescence phosphorescence spectrophotometer was used to determine the fluorescence decay kinetics of the dyes in solution. The Edinburgh Instruments F900 exponential tail fit method [26] was used for the calculation of decay times after the single photon timing analysis of the compounds were completed at the excitation wavelength of 368 nm. Fluorescence decay histograms were recorded in 10000 data channels. The fitted decay curve was settled by the fitting parameters such as χ^2 <1.2 goodness of fit [27].

Electrochemical characterization of the sensitizers were performed using a CH instruments-Electrochemical Workstation with a standard three-electrode electrochemical compartment in 100 mM [TBA][PF6] solution in Me-CN as the supporting electrolyte. Ag and Pt wires were preferred as reference and counter electrodes, respectively. A polished glassy carbon was used as working electrode in the measurements at the scan rate of 100 mV/s. Oxidation potential of ferrocene-ferrocenium (Fe/Fe⁺) couple was detected at +0.72 V for the calculation of the onset values of E_{red} . HOMO and LUMO energy levels of **TPA5a-b** and **TPA4c** dyes were calculated by the formulas:

 $E_{HOMO} = -(4.8 + E_{ox}^{onset}), E_{ox}^{onset} = E_{ox}^{0} - E_{ox}^{0} - E_{ox}^{0} + E_{LUMO} = E_{HOMO} + E_{gap}[28]$

Molecular geometries of **TPA5a-b** and **TPA4c** dyes were optimized by MM+ force field using Hyperchem Package Version 8.0 computational software. Semiempirical calculations

were performed using ZINDO/S (Single Point/CI) method to illustrate the possible electron distribution on HOMO and LUMO energy levels of the structures.

Materials

Chloroform, acetonitrile, tetrahydrofuran, sodium borohydride, piperidine, silica gel, *tetrakis*(triphenylphosphine)palladium(0), hydrogen bromide solution (47%), triphenylamine, N-bromosuccinimide, phosphoryl chloride were purchased from Merck Company. Benzene, sodium carbonate, bromine were purchased from Carlo Erba. 2,1,3-benzothiadiazole, magnesium sulfate, 3-(*N*,*N*-dimethylamino)-phenylboronic acid and cyanoacetic acid were purchased from Sigma-Aldrich. 3-methoxybenzeneboronic acid, CoCl₂·6H₂O (Alfa Aesar) and methanol (Riedel-de-Haën) were used as received. Other organic solvents were analytical grade and used without further purification.

4,7-dibromo-2,1,3-benzothiadiazole (**BT1**) and 4,7-bis(3-methoxyphenyl)-2,1,3benzothiadiazole (**BT2**) were synthesized according to the reference [29]. (4-Bromophenyl)diphenylamine (**TPA1**) precursor was synthesized to the well-known procedure [30].

DSSC fabrication and characterization

DSSCs were fabricated by coating of the TiO_2 nanocrystalline paste onto transparent conducting oxide coated glass electrode (TCO, Pilkington TEC15, •15_/sq resistance) using Doctor Blading technique.

The paste is prepared by sol-gel method by hydrolysis of titanium tetraisopropoxide [31]. Ethyl cellulose was added to the paste as a binder and α -terpineol was used as a surfactant. In order to get good electrical contact between the TiO₂ nanoparticles, the photo-anodes were

first sintered at 450 °C for 1 h and then, immersed in 0.04M TiCl₄ solution for 30 min at 70 °C and finally, electrodes were calcinated at 500 °C for 30 min. The thickness of the resulting layer was measured as 10 μ m. The resulting electrodes were cooled down slowly to 100 °C and then, the electrodes were immersed to 0.3 mM solutions of the photosensitizers in chloroform for 4 h to obtain a monolayer dye coated mesoporous titania electrode. Electrodes were rinsed with the same solvent to get rid-off the non-adsorbed dye from the titania surface.

Alumina, Al_2O_3 , was used as control layer with much higher band gap energy than that of TiO_2 layers in fluorescence quenching studies. It was prepared by the hydrolysis of aluminium tri-sec-butoxide [Al(OC₄H₉)₃, 0.25 mol] in the solutions of water (25 mol) and HCl (0.01 mol). Then, polyethylene glycol (PEG 400) was added to this solution giving the desired particles in 70% porosity and 7 nm in dimensions. TCO (Pilkington TEC15, •15_/sq resistance) was coated with Al_2O_3 nanocrystalline paste using Doctor Blading technique. Al_2O_3 coated TCO electrodes were sintered at 450 °C for 1 h.

Platinum catalyst layer on the counter electrode was coated onto the TCO electrode by thermal reduction of hexachloroplatinic acid to the metallic platinum. DSSC device was fabricated by placing the counter electrode and dye sensitized TiO₂ electrode in sandwich geometry and sealing with a thermoplastic frame (Surlyn 50 μ m thick). DSSC device was completed after the redox electrolyte [0.6M BMII, 0.1M LiI (99.9%), 0.05M I₂ (99.9%) and 0.5M tBP in 3-methoxypropionitrile] was injected into the space between electrode by using the pre-drilled hole on the counter electrode that was sealed afterwards.

The light-to-electric energy conversion efficiency measurements for the devices with 0.25 cm² working area were performed by a solar simulator equipped with a 750W metal halide lamp and AM 1.5G filter. The light intensity was calibrated to 100 mW/cm² using reference Si solar cell (Frunhofer ISE Calab). External quantum efficiency (EQE) and electrochemical impedance spectroscopy (EIS) measurements were used to characterize the DSSC devices.

EIS measurements were carried out under reverse bias of V_{oc} condition at -0.65 V in dark with frequencies in the range of between 0.1 Hz to 1 MHz.

Synthesis

Synthesis of 3,3"-dimethoxy-1,1':4',1"-terphenyl-2',3'-diamine (PDA)

BT2 (0.1 g, 0.287 mmol) was dissolved in 4 mL of EtOH:THF (3:1) solvent mixture and then, NaBH₄ (0.027 g, 0.7175 mmol) and CoCl₂.6H₂O (6.8 mg, 0.0287 mmol) were slowly added to this solution. Black solid Co₂B was formed instantly and H₂S evolution was noted in a few minutes. The mixture was refluxed under an argon atmosphere for 4 h, then cooled to room temperature and then filtered to separate the black solid. The solvent was evaporated and then, 50 mL of water was added to the solution. The organic product was extracted with Et₂O (3×30 mL). The combined organic extracts were dried over MgSO₄ and the solvent was removed. The resulted bisamine product was very air-unstable so that it would be used immediately in the next step. Yield 93%.

Synthesis of 4,4'-[(4-bromophenyl)imino]dibenzaldehyde (TPA2)

Phosphoryl chloride (0.691 g, 4.45 mmol) was slowly added to 7 mL of DMF in an ice bath. After the mixture was slowly cooled to room temperature, Vilsmeier reagent is ready to use. **TPA1** (0.580 g, 1.78 mmol) was added to this solution and the mixture was refluxed at 95 °C for 20 h. The reaction mixture was poured into an ice-water and then, neutralized with 2 N NaOH. Mono- and bis-aldehydes precipitated together. The crude mixture was filtered and then, purified by column chromatography on silica gel using dichloromethane:*n*-hexane (3:1) as eluent. Yield 55%. FT–IR (KBr pellet, cm⁻¹): 2928 and 2871 (aromatic v_{c-H}), 1743, 1693 (aldehyde $v_{c=0}$), 1588 (aromatic $v_{c=C}$), 1505, 1489, 1319, 1274, 1166, 1007, 827, 520

cm⁻¹. ¹H NMR (400 MHz, CDCl₃ δ 7.27 ppm): δ = 9.90 (2H, s), 7.79 (4H, d, J = 8.7 Hz), 7.50 (2H, d, J = 8.7 Hz), 7.19 (4H, d, J = 8.7 Hz), 7.06 (2H, d, J = 8.7 Hz) ppm. ¹³C NMR [100 MHz, CDCl₃ δ 77.2 (3 peaks)]: δ = 190.5, 151.7, 144.8, 133.4, 131.8, 131.5, 128.4, 123.2, 119.4 ppm.

Synthesis of 4-[{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}(4bromophenyl)amino]benzaldehyde (**TPA3**)

TPA2 (0.059 g, 0.156 mmol) was added to the 15 mL of methanol solution of **PDA** (0.050 g, 0.156 mmol) and then, the mixture was refluxed for 5 h under an argon atmosphere. Yellow solids appeared in the reaction medium. After the reaction was completed, the reaction mixture was evaporated in vacuo to dryness and then, the crude product was purified by column chromatography on silica gel using dichloromethane:ethyl acetate (5:0.5) as eluent. Yield 45%. FT–IR (KBr pellet, cm⁻¹): 2928 and 2832 (aromatic v_{c-H}), 1690 (aldehyde $v_{c=0}$), 1593 (aromatic $v_{c=c}$), 1483, 1363, 1317, 1282, 1225, 1162, 1042, 832, 782, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃ δ 7.27 ppm): δ = 9.83 (s, 1H), 8.01 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.45 (t, J = 5.2 Hz, 9H), 7.19 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.96 (dd, J = 8.7, 2.5 Hz, 4H), 3.89 (s, 6H) ppm. ¹³C NMR [100 MHz, CDCl₃ δ 77.2 (3 peaks)]: δ = 191.7, 161.1, 153.3, 152.1, 148.6, 146.0, 140.7, 133.9, 132.3, 131.4, 130.8, 129.2, 128.6, 126.8, 126.0, 123.6, 122.1, 121.8, 119.2, 115.3, 113.9, 55.9 ppm.

Synthesis of 4-[{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}(3'methoxybiphenyl-4-yl)amino]benzaldehyde (**TPA4a**)

A solution of **TPA3** (0.030 g, 0.0482 mmol) in benzene (7 mL) and aqueous 2 M Na_2CO_3 (3 mL) were added at 60 °C under an argon atmosphere to a mixture of 3-methoxybenzeneboronic acid (0.010 g, 0.0578 mmol) and *tetrakis*(triphenylphosphine)palladium(0) (catalytic level, \approx 3 mg) in ethanol (1 mL). After the

mixture was refluxed at 85 °C for 4 h under an argon atmosphere, the reaction mixture was poured into 50 mL of water and then, extracted with chloroform (3×50 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was separated by column chromatography on silica gel (dichloromethane:ethanol 5:0.5 (v/v)). Yield 60%. FT–IR (KBr pellet, cm⁻¹): 3288, 2925 and 2832 (aromatic v_{c-n}), 1686 (aldehyde $v_{c=0}$), 1590 (aromatic $v_{c=c}$), 1482, 1436, 1361, 1320, 1293, 1222, 1162, 1048, 831, 780, 696 cm⁻¹. ¹H NMR (400 MHz, CDCl₃ δ 7.27 ppm): δ = 9.85 (s, 1H), 8.02 (d, J = 8.6 Hz, 2H), 7.74 (t, J = 8.2 Hz, 4H), 7.58 (t, J = 8.2 Hz, 4H), 7.47-7.35 (m, 6H), 7.28-7.14 (m, 8H), 6.94 (dd, J = 8.6, 2.5 Hz, 2H), 3.91 (s, 6H), 3.89 (s, 3H) ppm. ¹³C NMR [100 MHz, CDCl₃ δ 77.2 (3 peaks)]: δ = 191.7, 161.5, 153.6, 152.1, 148.9, 146.1, 143.3, 140.9, 140.5, 139.1, 134.0, 132.3, 131.3, 130.7, 130.2, 129.4, 129.0, 127.3, 126.6, 126.0, 125.4, 123.9, 123.1, 122.5, 122.1, 120.9, 120.3, 115.6, 114.7, 114.1, 113.9, 113.6, 55.8 ppm.

Synthesis of 4-{{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}[3'-(dimethylamino)biphenyl-4-yl]amino}benzaldehyde (**TPA4b**)

A solution of **TPA3** (0.040 g, 0.0588 mmol) in benzene (8 mL) and aqueous 2 M Na₂CO₃ (4 mL) were added to a mixture of 3-(*N*,*N*-dimethylamino)-phenylboronic acid (0.015 g, 0.088 mmol) and *tetrakis*(triphenylphosphine)palladium(0) (catalytic level, \approx 4 mg) in ethanol (2 mL) at 60 °C under an argon atmosphere. After the mixture was refluxed at 85 °C for 2 h under an argon atmosphere, the reaction mixture was poured into 50 mL of water and then, extracted with chloroform (3×50 ml). The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to dryness. The residue was separated by column chromatography on silica gel (dichloromethane:*n*-hexane 5:1 (v/v)). Yield 65%. FT–IR (KBr pellet, cm⁻¹): 3056, 2926 and 2853 (aromatic v_{c-H}), 1693 (aldehyde $v_{c=0}$), 1592 (aromatic $v_{c=c}$), 1485, 1359, 1294, 1227, 1163, 1119, 1048, 839, 778, 736, 696 cm⁻¹. ¹H NMR (400 MHz,

CDCl₃ δ 7.27 ppm): δ = 9.84 (s, 1H), 8.05 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.65 – 7.54 (m, 6H), 7.49 – 7.41 (m, 6H), 7.27 – 7.13 (m, 8H), 6.95 (d, J = 8.5 Hz, 2H), 3.89 (s, 6H), 3.02 (s, 6H) ppm. ¹³C NMR [100 MHz, CDCl₃ δ 77.2 (3 peaks)]: δ = 191.5, 161.1, 153.4, 152.1, 151.8, 148.6, 140.1, 133.5, 132.8, 132.7, 132.6, 132.5, 132.0, 130.7, 130.6, 130.2, 129.9, 129.3, 129.2, 129.1, 128.9, 127.2, 127.1, 125.8, 121.6, 121.4, 116.7, 116.1, 112.5, 112.4, 112.1, 111.7, 55.6, 40.9 ppm.

Synthesis of (2E)-3-{4-[{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}(3'methoxybiphenyl-4-yl)amino]phenyl}-2-isocyanoacrylic acid (**TPA5a**)

A mixture of compound **TPA4a** (0.0270 g, 0.0381 mmol), cyanoacetic acid (0.004 g, 0.0490 mmol) and piperidine (10 μ L, 0.11 mmol) was refluxed in 4 mL of MeCN at 80 °C for 4 h under argon atmosphere. The reaction progress was controlled by TLC. After completion, the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane:ethanol (4:1) as eluent. Yield 55%. FT–IR (KBr pellet, cm⁻¹): 3436 (O–H stretching), 2936 (aliphatic v_{c-H}), 2214 (nitrile v_{c-N}), 1593 (carboxylic acid v_{c-60}), 1506, 1483, 1390, 1363, 1323, 1295, 1183, 1047, 834, 785, 696 cm⁻¹. ¹H NMR (400 MHz, DMSO δ 2.49 ppm): δ = 12.65 (s, 1H), 8.31 (d, J = 8.5 Hz, 2H), 7.99 (s, 1H), 7.90 (d, J = 8.5 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.54 – 7.35 (m, 4H), 7.31 – 7.21 (m, 10H), 7.12 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.94 (t, J = 8.5 Hz, 2H), 3.85 (s, 6H), 3.82 (s, 3H) ppm. ¹³C NMR [100 MHz, DMSO-d6 δ 40.2 ppm (7 peaks)]: δ = 160.7, 153.4, 151.3, 148.6, 148.5, 146.3, 143.3, 140.7, 140.5, 134.8, 132.8, 132.8, 131.1, 131.1, 130.4, 130.4, 130.1, 129.4, 127.0, 126.9, 126.3, 125.7, 125.7, 124.1, 122.6, 122.2, 122.0, 121.7, 119.8, 115.7, 114.8, 114.6, 113.7, 113.0, 112.9, 55.8 ppm.

Synthesis of (2E)-3-(4-{{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}[3'-(dimethylamino)biphenyl-4-yl]amino}phenyl)-2-isocyanoacrylic acid (TPA5b)

A mixture of compound **TPA4b** (0.040 g, 0.055 mmol), cyanoacetic acid (0.006 g, 0.071 mmol) and piperidine (10 μ L, 0.11 mmol) was refluxed in 7 mL of MeCN at 80 °C for 2 h under argon atmosphere. The reaction progress was controlled by TLC. After completion, the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane:ethanol (4:1) as eluent. Yield 70%. FT–IR (KBr pellet, cm⁻¹): 3429 (O–H stretching), 2924, 2852 (aliphatic v_{c-H}), 2214 (nitrile v_{cN}), 1598 (carboxylic acid v_{c-o}), 1505, 1485, 1385, 1360, 1322, 1293, 1227, 1183, 1047, 834, 784, 696 cm⁻¹. ¹H NMR (400 MHz, DMSO δ 2.49 ppm): δ = 12.65 (s, 1H), 8.31 (d, J = 8.7 Hz, 2H), 7.96 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.54 – 7.41 (m, 4H), 7.28 – 7.22 (m, 10H), 7.11 (d, J = 8.7 Hz, 2H), 7.01 (s, 1H), 6.93 (t, J = 8.3 Hz, 2H), 6.72 (d, J = 8.3 Hz, 1H), 3.84 (s, 6H), 2.94 (s, 6H) ppm. ¹³C NMR [100 MHz, DMSO-d6 δ 40.3 ppm (7 peaks)]: δ = 160.4, 153.3, 152.1, 150.3, 148.6, 146.0, 145.9, 141.3, 140.7, 140.5, 138.8, 135.6, 134.8, 134.7, 133.0, 132.3, 131.1, 130.6, 130.4, 130.0, 129.3, 127.7, 127.0, 126.6, 126.3, 125.3, 122.8, 122.0, 121.7, 119.2, 115.7, 115.6, 114.7, 113.7, 111.4, 55.7 ppm.

Synthesis of (2E)-3-{4-[{4-[4,7-bis(3-methoxyphenyl)-1H-benzimidazole-2-yl]phenyl}(4-bromophenyl)amino]phenyl}-2-isocyanoacrylic acid (**TPA4c**)

A mixture of compound **TPA3** (0.050 g, 0.0735 mmol), cyanoacetic acid (0.008 g, 0.0945 mmol) and piperidine (10 μ l, 0.11 mmol) was refluxed in 3 mL of MeCN at 80 °C for 3 h under argon atmosphere. The reaction progress was controlled by TLC. After completion, the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane:ethanol (4:1) as eluent. Yield 60%. FT–IR (KBr pellet, cm⁻¹): 3429 (O–H stretching), 2923, 2852 (aliphatic v_{C-H}), 2218 (nitrile v_{C-N}), 1588 (carboxylic acid $v_{C=0}$), 1484, 1436, 1323, 1293, 1182, 1119, 1047, 833, 696 cm⁻¹. ¹H NMR (400 MHz, DMSO δ 2.49 ppm): δ = 12.67 (s, 1H), 8.30 (dd, J = 13.8, 8.7 Hz, 2H), 7.90 (dd, J = 13.8, 8.7 Hz, 4H), 7.69 – 7.53 (m, 8H), 7.52 – 7.39 (m, 2H), 7.32 – 7.17 (m, 5H), 7.02 (t, J = 9.8 Hz, 1H), 6.95 (d, J =

8.2 Hz, 1H), 3.85 (s, 6H) ppm. ¹³C NMR [100 MHz, DMSO-d6 δ 39.9 ppm (7 peaks)]: δ = 159.9, 159.5, 139.9, 139.7, 133.7, 132.4, 131.9, 131.8, 130.4, 130.3, 129.6, 129.2, 129.1, 126.5, 125.9, 125.6, 123.8, 123.5, 121.4, 121.1, 115.0, 114.2, 113.9, 113.1, 55.4 ppm.

Results and discussion

Excited state properties of the dyes in solutions and on thin films

Normalized UV-vis absorption spectra of TPA5a-b and TPA4c dyes in chloroform and on thin films are shown in Fig. 2a and Fig. 2b, respectively. The spectroscopic parameters are also summarized in Table 1. The absorption spectra of the dyes in chloroform display two distinct absorption peaks around 359 and 428 nm. The narrow absorption bands around 359 nm can be attributed to the $\pi - \pi^*$ electronic transition and the other broad bands with shoulder extending up 520 nm region are assigned to the intramolecular charge transfer (ICT) between the TPA donor and the cyanoacrylic acid acceptor [9, 32-34]. When the dyes are adsorbed onto the TiO, films, the absorption spectra give a broad band at maximum wavelength of 428 nm. This observation may be related to the aggregation of the dyes on the semiconductor surface [22]. When TiO₂ cover is replaced by the alumina (Al₂O₃) coating, the absorption spectra of the dyes are shifted to the blue region as compared to those on TiO₂ surface because of the formation of H-type aggregates [35]. Visible absorption maximum of **TPA4c** dye gives a blue shift of 10 nm in chloroform as compared to that of in toluene solution. This behaviour can be explained by the increase in band gap energy resulted from the interaction between the bromine group of **TPA4c** dye and the chloride atoms of the solvent. While **TPA4c** dye shows higher molar extinction coefficients than that of the others in chloroform solution, this value for TPA5a dye is higher than that of other coated dyes on TiO, surface. This means that the

strongest solar light harvesting capacity could be expected from **TPA5a** dye causing the much higher cell efficiency than that of the others in DSSC device which will be fabricated later.

Fig. 2a

Fig. 2b

When the dyes are excited at 365 nm in solutions, they exhibit emission maxima between 547 and 557 nm in chloroform (Fig. 3a). In toluene, **TPA5a** dye gives a red shift of 18 nm with respect to the chloroform solution. Fig. 3b shows the fluorescence emission spectra of the dyes adsorbed onto the TiO_2 surface. All of the bands were red-shifted and broadened as compared to those of the dyes in solutions. Studied dyes give large Stoke's shift values which can be attributed to the delocalization of the excited energy along TPA-benzimidazole conjugate then forming ICT state. In order to understand electronic interaction between the dyes and TiO_2 -coated substrates, we examined the fluorescence quenching measurements on thin film. Fig. 3c illustrates the fluorescence emission change of **TPA5a** dye when adsorbed on alumina- or TiO_2 -coated glass substrates at the excitation wavelength of 400 nm. Significant energy losses in its emission intensity can be attributed to the good electron transfer from LUMO level of dye to the conduction band of TiO_2 . However, no quenching behaviour was observed when TiO_2 coating was replaced by alumina possesing a high band gap value of $\approx 9eV$, which is beyond the possible electron transfer limits from the dye to the alumina.

Fig. 3a Fig. 3b Fig. 3c Table 1

The fluorescence lifetimes of the dyes were measured using time-correlated single-photoncounting system at the collected emission wavelength of 570 nm in solutions as shown in Fig. 4 and summarized in Table 2. In toluene, the time profile shows biexponential decay

consisting of a major contribution (66%) at around 3.78 ns and a minor contribution (34%) of the long decay component at around 8.06 ns for **TPA5a** dye. Similar contributions were detected for **TPA5b** and **TPA4c** dyes in both solvents. The shortest decay components define the decay profile of excited state fluorescence of benzimidazole subunits mixed with TPA main cores. Time constants for similar TPA structures are within the range of 2-3 ns in the literature [36-38]. Such large shifts of the emission spectra to longer wavelengths in less polar toluene solutions could not be explained by only solvatochromic effect. This result supports the formation of charge-separated (CS) state in solutions. The longest decay profiles can be attributed to the CS process via the donor and acceptor sites of the molecules. Fluorescence quantum yields of **TPA5a-b** dyes are higher than that of **TPA4c** in toluene. **TPA4c** dye gains its highest yield value in more polar chloroform solution. It can be understood from Table 2 that changes in fluorescence quantum yields are consistent with the relative amplitude values for the generation of ICT complex in the studied solvents. Higher percentage of contribution (α_2) for **TPA5a-b** and **TPA4c** dyes in the studied solvents, the more increase in the corresponding fluorescence quantum yields of the sensitizers.

Fig. 4

Table 2 [39]

CV measurements and molecular orbital calculations

Fig. 5 gives the CV graphs of **TPA5a-b** and **TPA4c** dyes and Table 3 summarizes the redox potentials with band gaps of the studied dyes. **TPA5a**, **TPA5b** and **TPA4c** dyes exhibit only one oxidation potentials at $E_{ox}^{\circ} = 1.38$, 1.30 and 1.32 eV, respectively. The easier oxidation of **TPA5b** dye is assigned to the presence of aniline group having more electron releasing capacity than that of other substituents. LUMO energy levels of **TPA5a**, **TPA5b** and **TPA4c** dyes are calculated from the reduction onset values and found to be about -3.11,

-3.03 and -3.06 eV for, respectively. These values are fairly suitable level for injecting electron from LUMO excited level of dye to the CB band of TiO₂ surface.

Fig. 5

Table 3

Fig. 6 shows the electronic distribution on HOMO and LUMO orbitals for the geometrically optimized structure of the sensitizers. Electronic distribution of HOMO level of the compounds is densily localized on the benzimidazole side. In the first excited state, electronic cloud moves from benzimidazole to the acceptor acrylic acid side through TPA group. This pathway is good hint for an efficient electron transfer from LUMO level of the dyes to the CB of titania.

Fig. 6

Photovoltaic properties of DSSCs and electrochemical impedance spectroscopy analysis

Fig. 7 shows the current-voltage (J-V) characteristics of DSSCs based on **TPA5a-b** and **TPA4c** dyes adsorbed on TiO₂ and Table 4 gives the photovoltaic parameters of the devices. In DSSC devices **TPA5a**, **TPA5b** and **TPA4c** dyes exhibited cell efficiencies of 4.31%, 2.65% and 2.57%, respectively. DSSC based on organic dye **TPA5a** yielded a short-circuit current (J_{se}) of 9.03 mA cm⁻², an open-circuit voltage (V_{oc}) of 740 mV, and a fill factor (*ff*) of 0.64. The methoxy groups attached to the TPA can enhance the electron delocalization and therefore optimize the electron donation ability of the sensitizer. Also, Fig. 8 compares the EQE spectra of the devices fabricated with the synthesized dyes. DSSC based on **TPA5a** dye yields the highest and broadest EQE curve in the graph with the value of 71% at 460 nm among the devices using the other sensitizers.

Fig. 7

Table 4

Fig. 8

Fig. 9 shows the Nyquist plots for DSSCs based on **TPA5a-b** and **TPA4c** dyes which were measured under reversed bias of V_{oc} condition at -0.65 V in dark with frequency of 0.1 Hz to 1 MHz. Electrochemical impedance spectroscopy (EIS) dedicates the interfacial charge recombination kinetics of the DSSCs. Generally, DSSCs exhibit three semi-circles in a Nyquist plot. The high frequency semi-circle which is related to charge transfer resistance arises from the double layer of electrolyte/TCO electrodes. The low frequency semi-circle is related to diffusion resistance of the redox species in the electrolyte which is called Warburg Impedance. Finally, the larger middle semi-circle is related to the charge recombination resistance (R_{rec}) of TiO₂/Dye/Electrolyte interface arising from charge recombination from TiO₂ CB to the dye HOMO and redox couple oxidation potential. Larger R_{rec} indicates much slower charge recombination which increases J_{sc} and V_{oc} .

Since the semicircle for Nernst diffusion within the electrolyte was overlapped by the intermediate frequency large semicircle, only two semicircles are observed in the Nyquist plots of the presented work. Nyquist plots offer the enhancement of recombination resistance (R_{rec}) in the order of **TPA4c**<**TPA5b**<**TPA5a**, as well-correlated with increasing efficiencies.

Fig. 9

Fig. 10 proposes a suitable electron injection pathway from the excited sensitizer to the CB band of titania from donor TPA main core.

Fig. 10

Conclusion

In summary, we have synthesized a series of new metal-free DSSC sensitizers carrying triphenylamine-benzimidazole group as donor and cyanoacrylic acid acceptor bridged with a methine linker. The formation of CT complex could be estimated by means of time resolved

measurements and steady-state optical studies. Computational and experimental results support that the electron transfer from rich π -system of the donor group to the acceptor side could give good spectral responses and cell efficiencies in DSSC devices. In particular, the highest power conversion efficiency obtained for **TPA5a** dye with 4.31% remarks the significant contribution of methoxy group to electron delocalization for whole structure.

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Figure Legends

r molecule ^{*} tebr Fig. 1. Synthetic pathways of the (a) primary molecule PDA: (i) 2,1,3-benzothiadiazole, Br₂/HBr, 120 °C, 95%; (ii) 3-methoxybenzeneboronic acid, 2M Na₂CO₃, Pd(PPh₃)₄, EtOH/benzene, 85 °C, 85%; (iii) NaBH₄/CoCl₂·6H₂O, Et-OH/THF, 80 °C [21], 93% and, (b) the target molecules: (i) NBS, DMF, 25 °C, 16 h, 79%; (ii) POCl₃, DMF, 100 °C [22], 20 h, 55%; (iii) PDA, MeOH, reflux, [20] 45%; (iv) 3-methoxybenzeneboronic acid, 2M Na₂CO₃, Pd(PPh₃)₄, Et-OH/benzene, 85 °C, 16 h, 60% for TPA4a; 3-(N,N-dimethylamino)phenylboronic acid, 2M Na₂CO₃, Pd(PPh₃)₄, Et-OH/benzene, 85 °C, 16 h, 65% for TPA4b [23]; (v) cyanoacetic acid, piperidine, Me-CN, 80 °C, [24, 25] 60%; (vi) cyanoacetic acid, piperidine, Me-CN, 80 °C [24, 25], 55-70%.

Fig. 2. (a) Normalized UV-vis absorption spectra of TPA5a-b and TPA4c dyes in chloroform solution, and (b) UV-vis absorption spectra of TPA5a-b and TPA4c dyes on alumina or TiO₂-coated glass substrates.

Fig. 3. Normalized fluorescence emission spectra of **TPA5a-b** and **TPA4c** dyes in chloroform solution ($\lambda_{exc} = 365 \text{ nm}$), and (b) fluorescence emission spectra of **TPA5a-b** and **TPA4c** dyes on TiO₂-coated glass substrates. (c) Fluorescence emission change of **TPA5a** dye when adsorbed on alumina- or TiO₂-coated glass substrates ($\lambda_{exc} = 400 \text{ nm}$).

Fig. 4. Fluorescence decays of **TPA5a** dye in toluene and chloroform solutions ($\lambda_{detection} = 570$ nm, time increments in toluene and chloroform are about 8.2 and 5.2 ps, respectively).

Fig. 5. Comparison of cyclic voltammograms of TPA5a-b and TPA4c dyes on glassy carbon

working electrode in 0.1 M [TBA][PF6]/Me-CN (Scan rate: 100 mV s⁻¹).

Fig. 6. Illustration of theoretically calculated electron distribution on HOMO and LUMO energy levels of optimized structure for **TPA5a-b** and **TPA4c** dyes.

Fig. 7. Current-voltage (J-V) characteristics of DSSCs based on TPA5a-b and TPA4c dyes adsorbed on TiO₂.

Fig. 8. EQE spectra of DSSCs based on TPA5a-b and TPA4c dyes.

Fig. 9. EIS Nyquist plots for DSSCs based on TPA5a-b and TPA4c dyes.

Fig. 10. Schematic explanation of possible electron transfer from the sensitized **TPA5a** dye to the titania surface in DSSC device.

Table Legends

Table 1

Optical properties of **TPA5a-b** and **TPA4c** dyes in toluene and chloroform solutions, and on TiO₂-coated glass substrates ($\lambda_{exc} = 365$ nm for solutions and 400 nm for thin films).

^{*} also indicates the long-wavelength absorptions of the dyes.

Table 2

Fluorescence decay times ($\tau_{\rm f}$ (ns)), associated relative amplitudes ($\alpha_{\rm i}$ (%)) and fluorescence quantum yields^{*a*} of **TPA5a-b** and **TPA4c** dyes in toluene and chloroform solutions ($\lambda_{\rm exc} = 365$ nm was used for quantum calculations).

^{*a*} Fluorescence quantum yields have been determined using quinine sulfate dihydrate ($\lambda_{exc} = 365$ nm, $\Phi_F = 0.546$,

0.1 N H₂SO₄) [39].

Table 3

Cyclic voltammetry data and molecular orbital energies of TPA5a-b and TPA4c dyes with respect to the vacuum level.

, ctra att ^a E₀₋₀ transitions were estimated from the intersection of the absorption and emission spectra attached to a

nanocrystalline TiO₂ film.

Table 4

Photovoltaic data of DSSCs based on TPA5a-b and TPA4c dyes.





















	So	olvents				•									
Dvos	Тс	oluene				C	hlorofo	rm				TiO ₂	2		
Dyes	λ	λ	λ		$(\overline{V}_{A} - \overline{V})$	λ	λ	λ	($(\overline{V}_A - \overline{V}$		λ_{m}		λ	$(\overline{V}_A - \overline{V}$
	long	max	em			long	max	em			* ax		em		
TPA5	4	3	5		1477	4	2	5	1	1997		42		6	7051
а	28	10	72	6		28	63	54	2		8		13		
TPA5	4	3	5		1017	4	2	5	2	2236		42		6	6698
b	28	60	68	2		28	48	57	9		8		00		
TPA4	4	3	5		9412	4	3	5	9	9574		42		5	6717
С	33	65	56			23	59	47			1		87		

				~	-	01	Φ
Solvents /	Dyes	2 X	l	ά	L (2)	α	Ψ
	ΤΡΔ	1	t(1) 3	1 6	f(2)	2 3	F 0
Toluene	5a	.12	.78	6.1	.06	3.9	120
	ТРА	1	3	6	7	3	0.
	5b	.19	.29	1.7	.08	8.3	141
	ТРА	1	2	7	9	2	0.
	4c	.13	.95	6.8	.04	3.2	065
	TPA	1	2	8	5	1	0.
Chlorofo	5a	.02	.19	5.6	.16	4.4	051
rm	TPA	0	1	6	4	3	0.
	5b	.94	.64	7.9	.28	2.1	055
	TPA	1	2	5	5	4	0.
	4c	.20	.54	1.3	.93	8.7	097
						5	P
						5	P
		2					P
		2					
		2					
		2					
		2					
		2					

Dyes	E ⁰ _{ox} (V	LUM O (eV)	HOM O (eV)	E ₀₋ o ^a (eV) (abs/em)		
TPA5 a) 1. 38	-3.11	-5.46	2.35		
TPA5 b	1. 30	-3.03	-5.38	2.35		
TPA4 c	1. 32	-3.06	-5.40	2.34		2-
		R				

Dyes	J _{sc}	V _{oc}	F	PCE				
TPA5 a TPA5	(mA/cm ⁻) 9.03 7.20	(V) 0.7 4 0.6	F 0 .64 0	(%) 4.31 2.65				~
b TPA4 c	6.45	4 0.6 8	.58 0 .59	2.57				
						5	5	
							5	
					P		5	
				4	P		5	
					R		5	
							5	
							5	

Research Highlights

- CT complex forms between the TPA donor and the cyanoacrylic acid acceptor. 1.
- Contribution of methoxy group to electron delocalization was determined. 2.
- TPA5a dye gives excellent external quantum efficiency value above 70% at 460 nm. 3.
- TPA5a dye gives cell efficiency of 4.31% under solar simulator and AM 1.5G filter. 4.

Graphical abstract

