SUPPLEMENTARY INFORMATION

Organic Dyes with Fused Segment Comprising Benzotriazole and Benzotriazole Entities as the Conjugated Spacer for Dye-Sensitized Solar Cells

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Materials and Reagents. All chemicals were obtained from Acros, Aldrich, Alfa Lancaster, and Matrix scientific. The solvents were dried over sodium or CaH_2 and distilled before use. The starting materials, 4,7-Dibromo-2-(2-ethylhexyl)-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole,[1] 4-bromo-*N*,*N*-diphenylaniline (**TPA-Br**), and 3-bromo-9-(2-ethylhexyl)-9*H*-carbazole (**Cbz-Br**) were prepared according to the published procedures. TiO_2 paste was purchased from Solaronix S. A., Switzerland.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Absorption spectra were recorded on a Dynamica DB-20 probe UV-vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. Cyclic voltammetry experiments were performed with a CHI-621A electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, an auxiliary electrode and a non-aqueous $Ag/AgNO_3$ reference electrode. The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class AAA solar simulator (Oriel 94043 A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100 mW/cm^2 calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100, Newport Corp.) at short circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW/cm^2. Electrochemical impedance spectra (EIS) were recorded for DSSCs under illumination at open-circuit voltage (V_{oc}) or dark at −0.65 V potential at room temperature. The frequencies explored ranged from 10 mHz to 100 kHz. Intensity-modulated photovoltage spectroscopy (IMVS) was

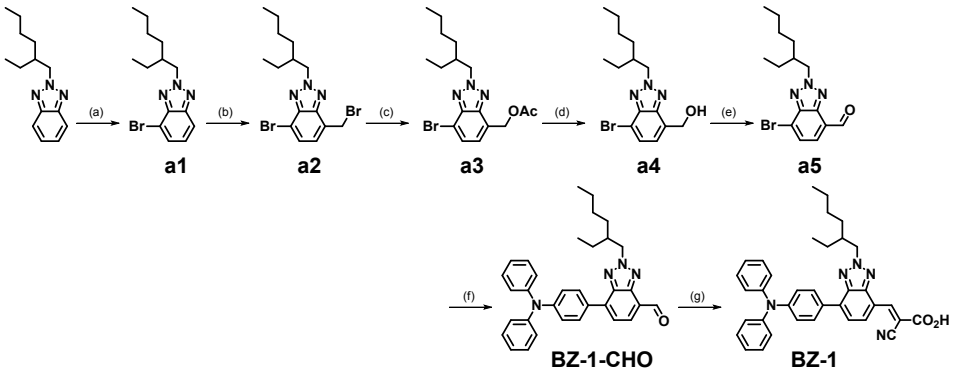
carried out on the electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (10 to 300 W m^{-2}) white light emitting diode driven by a Zahner (0982wlr02) source supply. The frequency range was set from 100 kHz to 10 mHz.

Assembly and characterization of DSSCs. The photoanode used was the TiO_2 thin film (12 μm of 20 nm particles as the absorbing layer and 6 μm of 100 nm particles as the scattering layer) coated on FTO glass substrate with a dimension of 0.4 × 0.4 cm^2, and the film thickness measurement by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). The TiO_2 thin film was dipped into the mixture solution of ethanol and chloroform (v/v, 1/1) containing 0.3 mM dye sensitizers for at least 12 hours. For the coadsorbed solar cell, chenodeoxycholic acid (CDCA) was added into the dye solutions at a concentration of 1 or 5 mM. After rinsing with acetonitrile, the photoanode adhered with a polyimide tape of 30 μm in thickness and with a square aperture of 0.36 cm^2 was placed on top of the counter electrode and tightly clipping them together to form a cell. A 0.5 × 0.5 cm^2 of cardboard mask was clipped onto the device to constrain the illumination area. Electrolyte was then injected into the seam between two electrodes. The electrolyte was composed of 0.8 M 1-methyl-3-propyl imidazolium iodide (PMII), 0.1 M lithium iodide (LiI), 0.05 M iodine (I_2), and 0.5 M 4-*tert*-butylpyridine dissolved in acetonitrile.

Electrochemical measurements: The electrochemical properties of the organic dyes were measured by cyclic voltammetry (CV) in THF solutions at a concentration of 1 mM with ferrocene/ferrocenium as the internal reference. This first oxidation potential (E_{ox}) together with the zero-zero excitation energy ($E_{0\text{-}0}$) can be used to deduce the excited state potential ($E_{0\text{-}0}$*) of the sensitizer, i.e., $E_{0\text{-}0}^* = E_{ox} - E_{0\text{-}0}$. Electron injection from the excited dye to the TiO_2 is energetically favored as the $E_{0\text{-}0}$* value of the dye (−1.20 to −1.24 V vs. NHE) is more negative than the conduction band edge of TiO_2 (−0.5 V vs. NHE).[2] Dye regeneration should also be energetically favored as the first oxidation potentials of the dyes (0.98 to 1.30 V vs. NHE) are more positive than that of the I^-/I_3^- redox couple (0.4 V vs. NHE).[3]

Quantum chemistry computation: The computations were performed with Q-Chem4.0 software.[4] Geometry optimization of the molecules was performed using hybrid B3LYP functional and 6-31G* basis set. For each molecule, a number of possible conformations were examined and the one with the lowest energy was used. The same functional was also applied for the calculation of excited states usingtime-dependent density functional theory (TD–DFT). There exist a number of previous works that employed TD–DFT to characterize excited states with charge-transfer character.[5,6] In some cases underestimation of the excitation energies was seen.[7]

Therefore, in the present work, we use TD–DFT to visualize the extent of transition moments as well as their charge-transfer characters, and avoid drawing conclusions from the excitation energy.



(a) HBr, NBS; (b) trioxane, HBr, H_2SO_4, AcOH; 120 ^oC, 1 d; (c) KOAc, MeOH; reflux, 2 h; (d) K_2CO_3, MeOH; reflux, 2 h; (e) PCC, EtOH; r.t., 2 h; (f) TPA-Sn^{n}Bu$_3$, Pd(PPh$_3$)$_2$Cl$_2$, DMF; 80 ^oC, 1 d; (g) Cyanoacetic acid, piperidine, ACN; 100 ^oC, 1 d.

Scheme S1. Synthetic routes of **BZ-1**.

Synthesis of 4-bromo-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazole (a1). A mixture of 2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazole (8.51 g, 36.8 mmol) in aq. HBr (48%, 15 mL) as heated to reflux with stirring, while Br_2 (2.8 mL, 110 mmol) was added slowly within 1 h. Towards the end of the addition, the mixture became a suspension. To facilitate stirring aq. HBr (48%, 10 mL) was added, and the mixture was heated to reflux for 2 h after completion of the Br_2 addition. The mixture was filtered while hot, cooled, filtered again, and washed well with H_2O. The organic layers were dried with $MgSO_4$ and purified with flash column chromatography on silica gel using CH_2Cl_2/hexanes (v/v, 1/4) as the eluent to afford the white oil in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 7.2 Hz, 2H), 2.30−2.25 (m, 1H), 1.33−1.24 (m, 8H), 0.91−0.84 (m, 6H).

Synthesis of 4-bromo-7-(bromomethyl)-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazole (a2). Compound **a1** (2.55 g, 8.23 mmol) was dissolved in a mixture of hydrobromic acid (33 wt% in AcOH, 8.53 mL) and glacial acetic acid (8 mL) and then trioxane (1.5 g, 16.46 mmol) and H_2SO_4 (1 mL) were added. The mixture was stirred and refluxed overnight. After cooling, the mixture was poured into ice-water, and extracted with CH_2Cl_2 and deionized water. The combined organic layers were dried over anhydrous $MgSO_4$, evaporated to yield the crude compound **a2** and used without further purification (2.50 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 4.83 (s, 2H), 4.67 (d, J = 7.2 Hz, 2H),

2.35−2.29 (m, 1H), 1.33−1.24 (m, 8H), 0.91−0.84 (m, 6H).

Synthesis of (7-bromo-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)methyl acetate (a3). To a 50 mL round bottom flask was added compound **a2** (2.49 g, 6.17 mmol), DMF (12 mL), and potassium acetate (KOAc, 3.60 g, 37.0 mmol). The mixture was then heated to 100 °C with stirring overnight. Upon completion, the product was extracted with CH_2Cl_2 and deionized water. The organic layers were dried with $MgSO_4$ and purified with column chromatography on silica gel using CH_2Cl_2 and 2% MeOH/CH_2Cl_2 (v/v) as the eluent to afford a yellow solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.47 (s, 2H), 4.65 (d, J = 7.2 Hz, 2H), 2.35−2.29 (m, 1H), 1.33−1.24 (m, 8H), 0.91−0.84 (m, 6H).

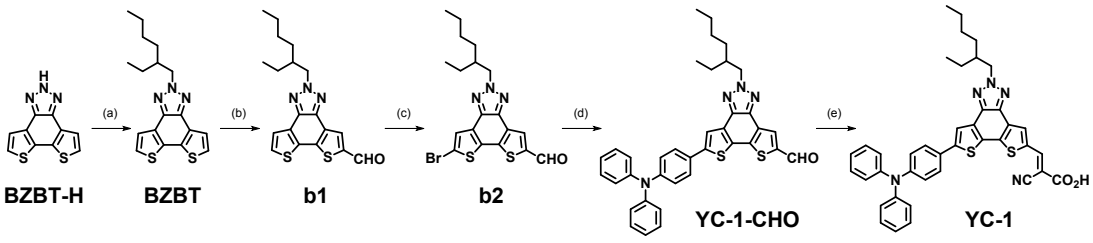
Synthesis of (7-bromo-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)methanol (a4). Compound **a3** (2.24 g, 5.86 mmol) was added MeOH (12 mL) and saturated aqueous solution of potassium carbonate (aq. K_2CO_3, 12 mL). The mixture was stirred and heated to 60 °C overnight. The reaction was cooled to room temperature and extracted with CH_2Cl_2 and deionized water. The organic layers were dried over $MgSO_4$, concentrated and used without further purification (76% yield, 1.51 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 5.04 (s, 2H), 4.64 (d, J = 7.2 Hz, 2H), 2.45 (br, 1H), 2.35−2.29 (m, 1H), 1.33−1.24 (m, 8H), 0.91−0.84 (m, 6H).

Synthesis of 7-bromo-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazole-4-carbaldehyde (a5). Pyridinium chlorochromate (PCC, 1.10 g, 5.33 mmol) was added into the mixture solution of compound **a4** (1.51 g, 4.44 mmol) and CH_2Cl_2 (44 mL), and then stirred for 2 h. After completed, the precipitate was filtered off, and the solution was extracted with CH_2Cl_2 and deionized water. The organic layers were dried with $MgSO_4$ and purified with column chromatography on silica gel using 5% EA/hexanes (v/v) as the eluent to afford a yellow solid in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.46 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 4.74 (d, J = 7.2 Hz, 2H), 2.35−2.29 (m, 1H), 1.33−1.24 (m, 8H), 0.91 (t, 3H), 0.85 (t, 3H).

Synthesis of 7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazole-4-carbaldehyde (BZ-1-CHO). Compound **a5** (0.58 g, 1.72 mmol), $Pd(PPh_3)_2Cl_2$ (72 mg, 3 mmol%) and *N*,*N*-diphenyl-4-(tri-*n*-butylstannyl)aniline (TPA-$SnBu_3$, 1.80 g, 3.44 mmol) were dissolved in 4 mL of dry DMF and stirred at 80 °C overnight. The solvent was removed under vacuum, and then extracted with

CH_2Cl_2 and deionized water. The combined organic layers were dried over anhydrous $MgSO_4$, evaporated and the residue was purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/2, v/v) as the eluent to afford a yellow solid in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1H), 8.05 (m, 2H), 8.00 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.31−7.27 (m, 4H), 7.18−7.16 (m, 6H), 7.09−7.06 (m, 2H), 4.74 (d, J = 7.1 Hz, 2H), 2.33−2.30 (m, 1H), 1.39−1.27 (m, 8H), 0.92 (t, 3H), 0.84 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.38, 148.96, 147.05, 143.22, 142.52, 137.55, 132.21, 129.87, 129.39, 129.22, 128.99, 125.20, 124.11, 123.69, 123.69, 122.16, 122.11, 122.10, 60.30, 40.22, 30.26, 28.23, 23.67, 22.88, 13.99, 10.35. MS-HR-EI (*m/z*): $[M]^+$ calcd for $C_{33}H_{34}N_4O$, 502.2733; found, 502.2703.

Synthesis of *(E)*-2-cyano-3-(7-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2*H*-benzo[*d*][1,2,3]triazol-4-yl)acrylic acid (BZ-1). Compound **BZ-1-CHO** (0.55 g, 1.10 mmol), cyanoacetic acid (0.47 g, 5.50 mmol), piperidine (0.05 mL, 0.55 mmol) were dissolved in 11 mL of acetonitrile. The reaction mixture was then vigorously stirred at 100 °C for 20 h. The solvent was removed under vacuum, washed with deionized water, dried under vacuum, and purified with column chromatography on silica gel using acetic acid/ethyl acetate (1/100, v/v) as the eluent to give a light-red solid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.05 (s, 1H), 7.71 (m, 2H), 7.26 (m, 1H), 7.22−7.18 (m, 4H), 7.11 (br, 1H), 7.06−7.04 (m, 4H), 7.02 (m, 2H), 6.98−6.95 (m, 2H), 4.54 (m, 2H), 2.15−2.12 (m, 1H), 1.18 (m, 8H), 0.77 (m, 3H), 0.69 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.91, 148.41, 147.09, 146.49, 144.31, 141.81, 134.63, 129.50, 129.36, 129.03, 127.14, 124.30, 123.97, 123.54, 122.84, 122.46, 121.94, 119.71, 117.58, 105.43, 60.18, 40.17, 30.22, 28.23, 23.59, 22.84, 13.97, 10.34.MS-HR-EI (*m/z*): $[M]^+$ calcd for $C_{36}H_{35}N_5O_2$, 569.2791; found, 569.2758. Anal. calcd for $C_{36}H_{35}N_5O_2$: C, 75.90; H, 6.19; N, 12.29; found: C, 75.83; H, 6.18; N, 12.27. Melting point (Mp): 177.4 °C.



(a) ^{t}BuOK, THF; reflux, 1 h; 2-ethylhexyl bromide; reflux, 14 h; (b) $POCl_3$, DMF; 0 ^{o}C, 0.5 h; 100 ^{o}C, 16 h; (c) NBS, DCM/AcOH; r.t., 15 h; (d) TPA-Br, $Pd(PPh_3)_2Cl_2$, DMF; 80 ^{o}C, 1 d; (e) Cyanoacetic acid, NH_4OAc, AcOH; 110 ^{o}C, 20 h.

Scheme S2. Synthetic routes of **YC-1**.

Synthesis of 2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3] triazole (BZBT). BZBT-H (1.00 g, 4.32 mmol) and potassium *t*-butoxide (^{t}BuOK, 0.58 g, 5.18 mmol) were dissolved in the 10 mL of THF. After reflux for 1 hour, 2-ethylhexyl bromide (0.93 mL, 5.18 mmol) was added and further refluxed for 14 hours. After completion, the solvent was removed under vacuum and extracted with CH_2Cl_2 and H_2O. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/6, v/v) as the eluent to give a yellow oil in 50% yield (0.74 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 5.2 Hz, 2H), 7.50 (d, J = 5.2 Hz, 2H), 4.65 (d, J = 7.2 Hz, 2H), 2.30−2.24 (m, 1H), 1.39−1.27 (m, 9H), 0.92 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H).

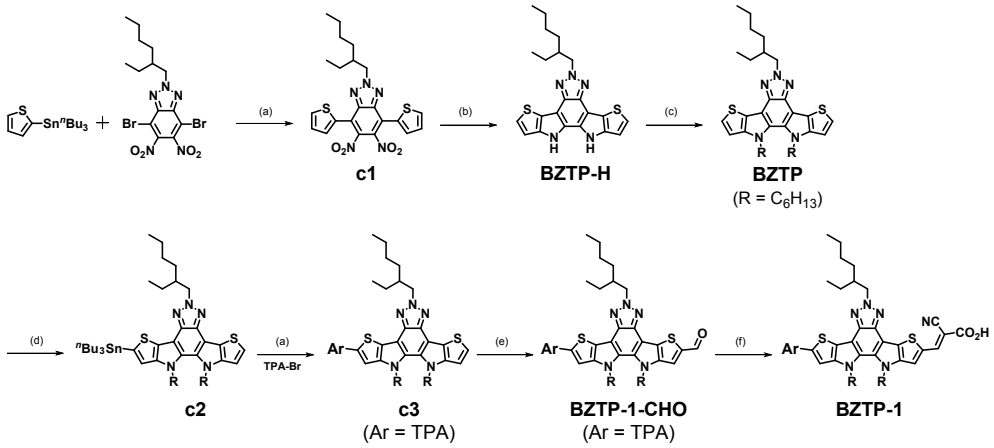
Synthesis of 2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3] triazole-5-carbaldehyde (b1). BZBT (0.87g, 2.53 mmol) was dissolved in the 4 mL of dry DMF, and phosphoryl chloride ($POCl_3$, 0.25 mL, 2.78 mmol) was added dropwise in the ice-bath. After stirred for 30 min at 0 °C, the reaction was heated to 100 °C. After heated for 16 h, the aqueous solution of ammonium chloride (aq. NH_4Cl) was added at 0 °C and stirred for 30 min at the same temperature. The reaction mixture was extracted with CH_2Cl_2 and H_2O. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/1, v/v) as the eluent to give a yellow oil in 11% yield (0.1 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.43 (s, 1H), 7.85 (d, J = 5.2 Hz, 1H), 7.61 (d, J = 5.2 Hz, 1H), 4.63 (d, J = 7.2 Hz, 2H), 2.25−2.22 (m, 1H), 1.39−1.22 (m, 9H), 0.92 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H).

Synthesis of 8-bromo-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo [1,2-*d*][1,2,3]triazole-5-carbaldehyde (b2). Compound **b1** (0.28 g, 0.75 mmol) was dissolved in the mixture solution of CH_2Cl_2 and AcOH (3 mL, v/v, 1/1), and NBS (0.16 g, 0.9 mmol) was added slowly. After stirred for 15 h at the room temperature, the reaction mixture was extracted with CH_2Cl_2 and H_2O. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/1, v/v) as the eluent to give a yellow oil in 76% yield (0.28 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.34 (s, 1H), 7.82 (s, 1H), 4.65 (d, J = 7.2 Hz, 2H), 2.23−2.17 (m, 1H), 1.39−1.22 (m, 9H), 0.92 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H).

Synthesis of 8-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2*H*-dithieno [3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazole-5-carbaldehyde (YC-1-CHO). Compound **b2** (0.28 g, 0.62 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 5 mmol%) and *N*,*N*-

diphenyl-4-(tri-*n*-butylstannyl)aniline (0.36 g, 0.68 mmol) were dissolved in 3 mL of dry DMF and stirred at 80 °C overnight. The solvent was removed under vacuum, and then extracted with CH_2Cl_2 and deionized water. The combined organic layers were dried over anhydrous $MgSO_4$, evaporated and the residue was purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/1, v/v) as the eluent to afford an orange solid in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.52 (s, 1H), 8.00 (s, 1H), 7.61 (m, 2H), 7.29 (m, 4H), 7.14 (m, 4H), 7.11−7.06 (m, 4H), 2.29−2.25 (m, 1H), 1.41−1.26 (m, 9H), 0.94 (t, J = 7.6 Hz, 3H), 0.86 (t, J = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.44, 147.14, 147.04, 141.44, 139.69, 139.35, 138.33, 132.17, 132.04, 131.95, 130.96, 130.42, 129.47, 129.27, 127.90, 127.21, 126.68, 126.01,125.07, 123.71, 122.86, 122.78, 116.84, 59.83, 40.53, 30.45, 28.43, 27.83, 27.74, 26.83, 23.84, 22.87, 17.51, 13.98, 13.59, 10.47. MS-HR-EI (*m/z*): $[M]^+$ calcd for $C_{37}H_{34}N_4OS_2$, 614.2174; found, 614.2178.

Synthesis of *(E)*-2-cyano-3-(8-(4-(diphenylamino)phenyl)-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)acrylic acid (YC-1). YC-1-CHO (0.12 g, 0.2 mmol), cyanoacetic acid (0.05 g, 0.6 mmol), ammonium acetate (NH_4OAc, 5 mg) were dissolved in 2 mL of acetic acid. The reaction mixture was then vigorously stirred at 110 °C for 20 h. The solvent was removed under vacuum, washed with deionized water, dried under vacuum, and purified with column chromatography on silica gel using acetic acid/ethyl acetate (1/100, v/v) as the eluent to give a light-red solid in 32% yield. ^{1}H NMR (400 MHz, d_8−THF): δ 8.62 (s, 1H), 8.59 (s, 1H), 8.18 (s ,1H), 7.78 (m, 2H), 7.30 (m, 4H), 7.14 (m, 4H), 7.09−7.05 (m, 4H), 4.55 (d, J = 6.8 Hz, 2H), 2.26−2.25 (m, 1H), 1.40−1.30 (m, 9H), 0.97 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, d_8−THF): δ 149.92, 148.47, 140.50, 140.26, 138.32, 133.72, 132.16, 130.73, 130.43, 128.19, 128.02, 127.21, 126.08, 124.67, 123.88, 118.14, 67.35, 67.13, 60.22, 41.78, 33.00, 31.69, 30.77, 29.64, 28.17, 25.87, 25.67, 25.47, 25.27, 25.07, 23.89, 14.46, 11.06. MS-HR-FAB (*m/z*): $[M]^+$ calcd for $C_{40}H_{35}N_5O_2S_2$, 681.2232; found, 681.2219. Anal. calcd for $C_{40}H_{35}N_5O_2S_2$: C, 70.46; H, 5.17; N, 10.27; found: C, 70.54; H, 5.22; N, 10.23. Melting point (Mp): 273.2 °C.



(a) $Pd(PPh_3)_2Cl_2$, DMF; 80 °C, 1 d; (b) PPh_3, o-DCB; 180 °C, 1 d; (c) K_2CO_3, KI, $C_6H_{13}Br$, DMF; 90 °C, 1 d; (d) ^{n}BuLi, TMEDA, THF; -78 °C, 0.5 h; 0 °C, 0.5 h; ^{n}Bu$_3$SnCl; rt, 2 h; (e) ^{n}BuLi, TMEDA, THF; -78 °C, 0.5 h; 0 °C, 0.5 h; DMF; rt, 2 h; (f) Cyanoacetic acid, piperidine, ACN; 100 °C, 20 h.

Scheme S3. Synthetic routes of **BZTP-1**.

Synthesis of 2-(2-ethylhexyl)-5,6-dinitro-4,7-di(thiophen-2-yl)-2*H*-benzo[*d*][1,2,3] triazole (c1). 4,7-Dibromo-2-(2-ethylhexyl)-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole[1] (10 g, 26.0 mmol), tri-*n*-butyl(thiophen-2-yl)stannane (23.3 g, 62.5 mmol) and $Pd(PPh_3)_2Cl_2$ (1.1 g, 6 mmol%) were dissolved in 30 mL of dry DMF and stirred at 80 °C overnight. The solvent was removed under vacuum, and then extracted with CH_2Cl_2 and deionized water. The combined organic layers were dried over anhydrous $MgSO_4$, evaporated and the residue was purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/2, v/v) as the eluent to afford a light-yellow solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 4.6 Hz, 2H), 7.53 (d, J = 3.9 Hz, 2H), 7.20−7.18 (m, 2H), 4.74 (d, J = 6.8 Hz, 2H), 2.25−2.20 (m, 1H), 1.39−1.27 (m, 8H), 0.94 (t, 3H), 0.87 (t, 3H).

Synthesis of 5-(2-ethylhexyl)-10,11-dihydro-5*H*-thieno[2',3':4,5]pyrrolo[3,2-*g*] thieno[3,2-b][1,2,3]triazolo[4,5-*e*]indole (BZTP-H). Compound **c1** (3.0 g, 6.2 mmol) and triphenylphosphine (PPh_3, 16.0 g, 61.8 mmol) were dissolved in the *o*-dichlorobenzene (*o*-DCB, 15 mL). After being heated at 180 °C overnight, the solution was removed under vacuum and extracted with EA and H_2O. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using EA/hexanes (1/3, v/v) as the eluent to give a light-yellow solid in 45% yield (1.17 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, 2H), 7.14 (d, J = 5.2 Hz, 2H), 6.77 (d, J = 5.2 Hz, 2H), 4.64 (d, J = 7.2 Hz, 2H), 2.26−2.23 (m, 1H), 1.29−1.27 (m, 8H), 0.80−0.72 (m, 6H).

Synthesis of 5-(2-ethylhexyl)-10,11-di-*n*-hexyl-10,11-dihydro-5*H*-thieno[2',3':4,5] pyrrolo[3,2-*g*]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole (BZTP). **BZTP-H**[1] (1.0 g, 1.85 mmol), 1-bromohexane (1.31 mL, 9.27 mmol), potassium iodide (0.1 g, 0.74

mmol) and potassium hydroxide (1.05 g, 18.53 mmol) were dissolved in the *N*,*N*-dimethylmethanamide (DMF, 10 mL). After being heated at 90 °C overnight, the solution was removed under vacuum and extracted with CH_2Cl_2 and H_2O. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using CH_2Cl_2/hexanes (3/7, v/v) as the eluent to give a light-yellow solid in 98% yield (1.07 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 5.3 Hz, 2H), 7.18 (d, J = 5.2 Hz, 2H), 4.71 (d, J = 7.1 Hz, 2H), 4.44 (t, J = 7.7 Hz, 4H), 2.33 (m, 1H), 1.77−1.69 (m, 4H), 1.42−1.29 (m, 8H), 1.17−1.07 (m, 12H), 0.94 (t, 3H), 0.87 (t, 3H), 0.74 (t, 6H).

Synthesis of 5-(2-ethylhexyl)-10,11-di-*n*-hexyl-2-(tri-*n*-butyl-stannyl)-10,11-dihydro-5*H*-thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole (c2). Compound **BZTP** (1 g, 1.70 mmol) and tetramethylethylene-diamine (TMEDA, 0.4 mL, 2.54 mmol) dissolved in dry THF (3 mL) was cooled to −78 °C under nitrogen atmosphere. *n*-Butyllithium (^{n}BuLi, 1.1 mL, 1.6 M in hexane, 1.78 mmol) was added dropwise with vigorous stirring. After stirred at the same temperature for 0.5 hour additionally, it was brought to 0 °C during 0.5 h. The mixture was cooled to −78 °C and tri-*n*-butyl tinchloride (0.51 mL, 1.78 mmol) was added at once. The solution was brought to room temperature and stirred overnight. The reaction was quenched by $NH_4Cl_{(aq)}$ and extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to yield the crude compound **c2** and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 5.3 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H), 7.14 (s, 1H), 4.70 (d, J = 7.2 Hz, 2H), 4.46−4.41 (m, 4H), 2.34 (m, 1H), 1.78−1.70 (m, 4H), 1.67-1.59 (m, 6H), 1.42−1.24 (m, 16H), 1.20−1.08 (m, 16H), 0.95−0.85 (m, 15H), 0.75 (t, 6H).

Synthesis of 4-(5-(2-ethylhexyl)-10,11-di-*n*-hexyl-10,11-dihydro-5*H*-thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indol-2-yl)-*N*,*N*-diphenylaniline (c3). Compound **c2** (1.00 g, 1.32 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 4 mmol%) and **TPA-Br** (0.45 g, 1.39 mmol) were dissolved in 3 mL of dry DMF and stirred at 80 °C overnight. The solvent was removed under vacuum, and then extracted with CH_2Cl_2 and deionized water. The combined organic layers were dried over anhydrous $MgSO_4$, evaporated and the residue was purified with column chromatography on silica gel using CH_2Cl_2/hexanes (1/2, v/v) as the eluent to afford a yellow solid in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 2H), 7.38 (d, J = 5.2 Hz, 1H), 7.32 (s, 1H), 7.29−7.26 (m, 4H), 7.18 (d, J = 5.1 Hz, 1H), 7.15−7.10 (m, 5H), 7.04 (m, 3H), 4.72 (d, J = 7.2 Hz, 2H), 4.46−4.43 (m, 4H), 2.34 (m, 1H), 1.79−1.70 (m, 4H), 1.44−1.26 (m, 8H), 1.20−1.07 (m, 12H), 0.95 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 0.75 (m, 6H). MS-FAB (*m/z*): $[M]^+$ calcd for $C_{52}H_{60}N_6S_2$, 832.4; found,

832.4.

Synthesis of 8-(4-(diphenylamino)phenyl)-5-(2-ethylhexyl)-10,11-di-*n*-hexyl-10,11-dihydro-5*H*-thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2-carbalde-hyde (BZTP-1-CHO). Compound **c3** (0.20 g, 0.24 mmol) and TMEDA (0.05 mL, 0.36 mmol) dissolved in dry THF (3 mL) was cooled to −78 °C under nitrogen atmosphere. ^{n}BuLi (0.23 mL, 1.6 M in hexane, 0.36 mmol) was added dropwise with vigorous stirring. After stirred at the same temperature for 0.5 hour additionally, it was brought to 0 °C during 0.5 h. The mixture was cooled to −78 °C and dry DMF (0.04 mL, 0.48 mmol) was added at once. The solution was brought to room temperature and stirred overnight. The reaction was quenched by $NH_4Cl_{(aq)}$ and extracted with CH_2Cl_2. The organics were combined and dried over $MgSO_4$, filtered, and purified with column chromatography on silica gel using CH_2Cl_2/hexanes (3/1, v/v) as the eluent to give an orange solid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.80 (s, 1H), 7.60 (m, 2H), 7.31−7.26 (m, 4H), 7.15−7.09 (m, 6H), 7.06−7.03 (m, 3H), 4.71 (d, J = 7.1 Hz, 2H), 4.50−4.44 (tt, 4H), 2.32 (m, 1H), 1.81−1.71 (m, 4H), 1.40−1.25 (m, 8H), 1.16−1.08 (m, 12H), 0.96 (t, 3H), 0.87 (m, 3H), 0.77−0.72 (m, 6H). MS-HR-FAB (*m/z*): $[M]^+$ calcd for $C_{53}H_{60}N_6OS_2$, 860.4270; found, 860.4249.

Synthesis of *(E)*-2-cyano-3-(8-(4-(diphenylamino)phenyl)-5-(2-ethylhexyl)-10,11-di-*n*-hexyl-10,11-dihydro-5H-thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*][1,2,3] triazolo[4,5-*e*] indol-2-yl)acrylic acid (BZTP-1). Compound **BZTP-1-CHO** (0.20 g, 0.23 mmol), cyanoacetic acid (0.10 g, 1.16 mmol), piperidine (0.12 mL, 1.16 mmol) were dissolved in 5 mL of acetonitrile. The reaction mixture was then vigorously stirred at 100 °C for 20 h. The solvent was removed under vacuum, washed with deionized water, dried under vacuum, and purified with column chromatography on silica gel using acetic acid/ethyl acetate (1/100, v/v) as the eluent to give a deep-red solid in 20% yield. ^{1}H NMR (400 MHz, d_8−THF): δ 8.56 (s, 1H), 7.67 (m, 2H), 7.56 (s, 1H), 7.28−7.24 (m, 4H), 7.12−7.08 (m, 7H), 7.04−7.01 (m, 2H), 4.70 (m, 2H), 4.54 (m, 4H), 2.58 (m, 1H), 1.80 (m, 4H), 1.40−1.16 (m, 20H), 0.89−0.86 (m, 6H), 0.73 (m, 6H). MS-HR-FAB (*m/z*): $[M]^+$ calcd for $C_{56}H_{61}N_7O_2S_2$, 927.4328; found, 927.4344. Anal. calcd for $C_{56}H_{61}N_7O_2S_2$: C, 72.46; H, 6.62; N, 10.56; found: C, 72.56; H, 6.67; N, 10.37. Melting point (Mp): 227.8 °C.

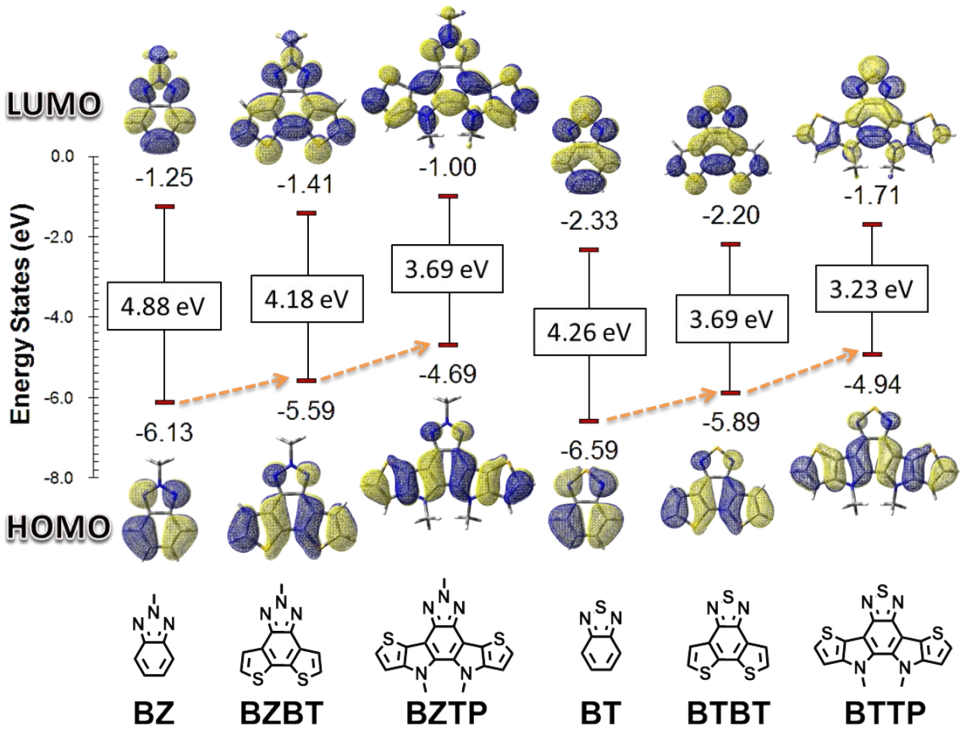


Fig. S1 The calculated electronic structures and frontier orbitals of the rigid spacers in the gas-phase. (**BZ**: benzo[*d*][1,2,3]triazole, **BZBT**: dithienobenzotriazole, **BZTP**: dithieno[3,2-*b*]pyrrolobenzotriazole, **BT**: benzo[*c*][1,2,5]thiadiazole, **BTBT**: dithienobenzothiadiazole and **BTTP**: dithieno[3,2-*b*]pyrrolobenzothiadiazole.)

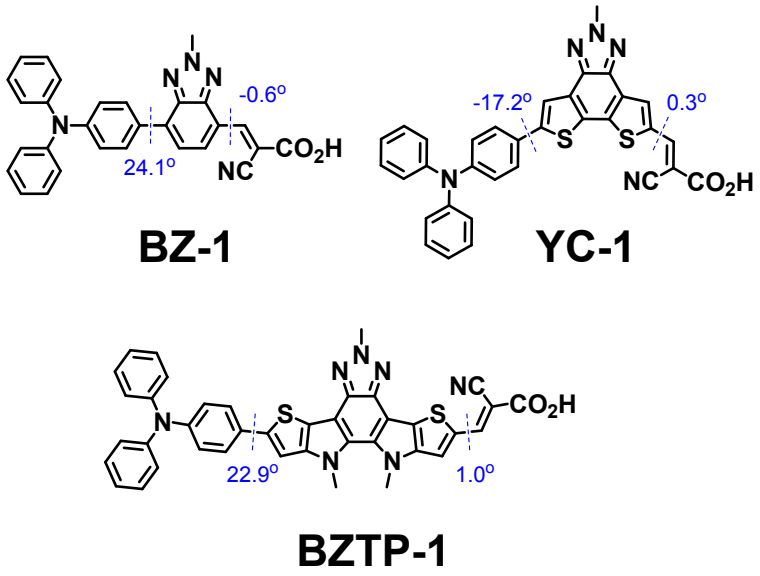
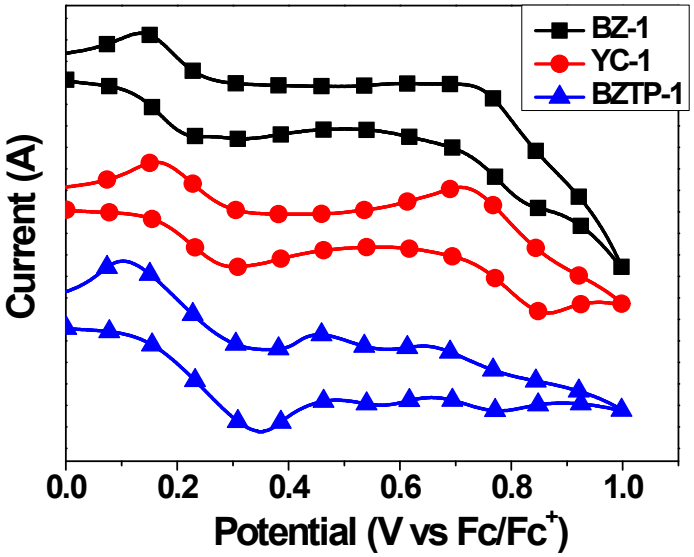


Fig. S2 Schematic division and dihedral angles of the molecules.

(a)



(b)

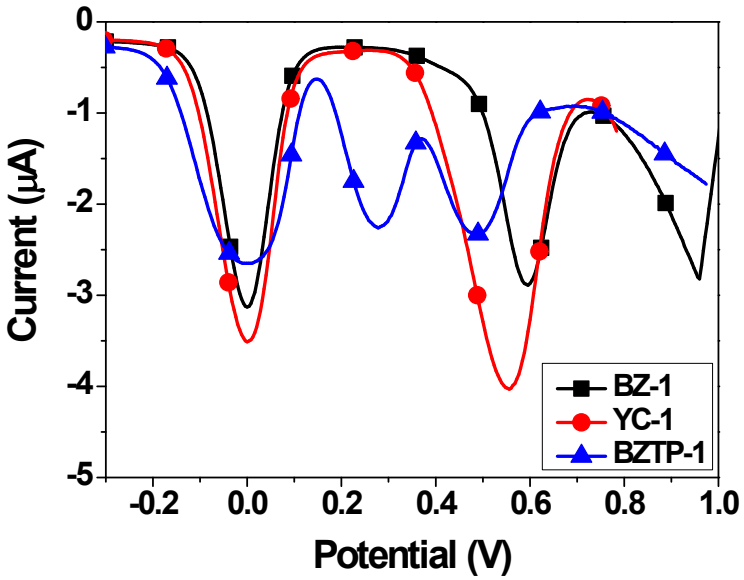


Fig. S3 (a) Cyclic and (b) differential pulse voltammograms of dye in THF (1 mM).

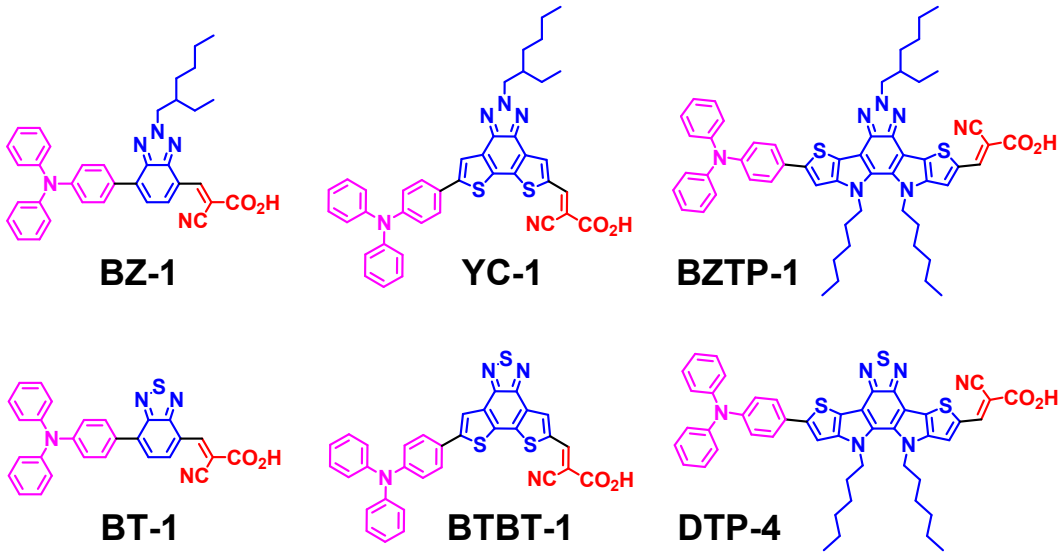


Fig. S4 The structure of the dyes.

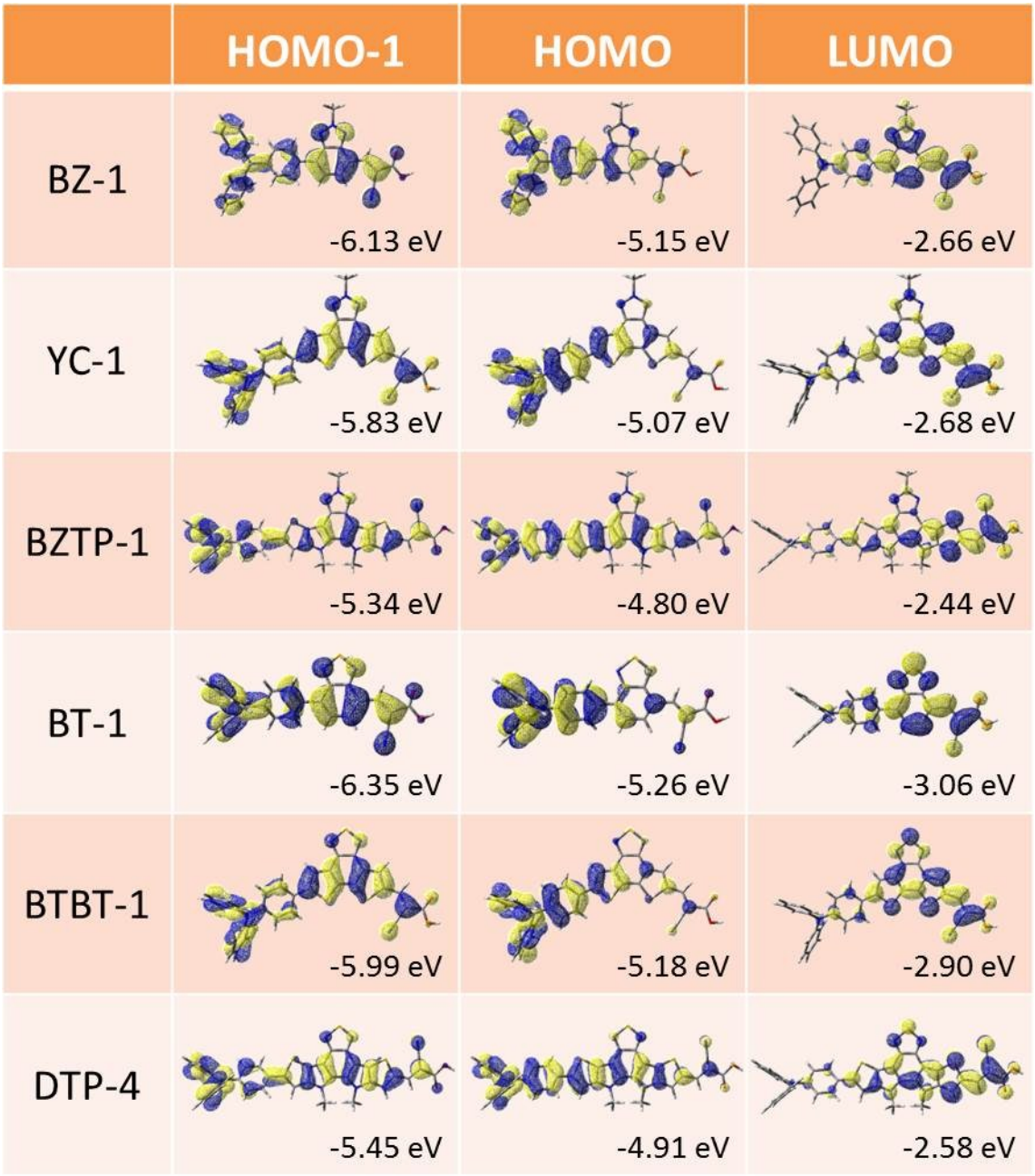


Fig. S5 Frontier orbitals of the dyes.

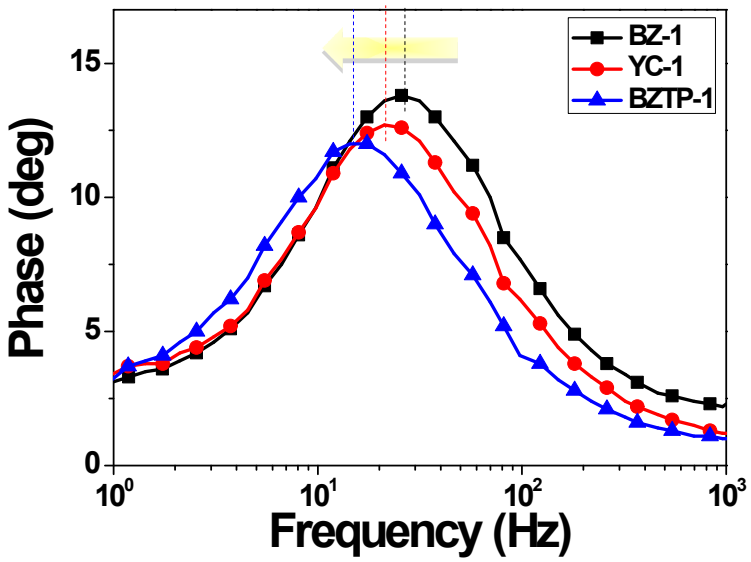


Fig. S6 Bode plots of the DSSCs of dyes under 100 mW/cm^2 illumination.

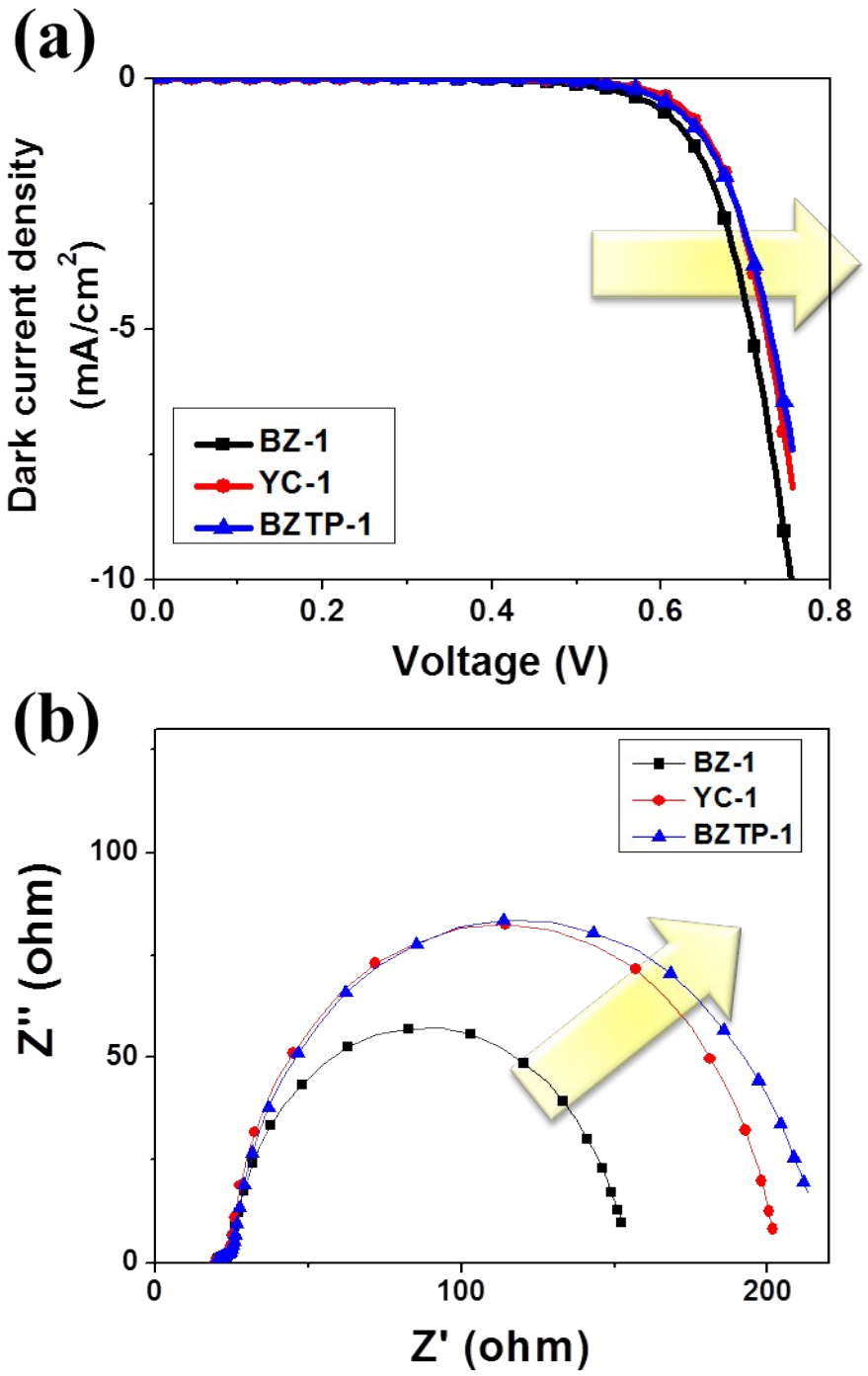


Fig. S7 (a) *J*−*V* and (b) Nyquist plots of the DSSCs with the dyes in the dark.

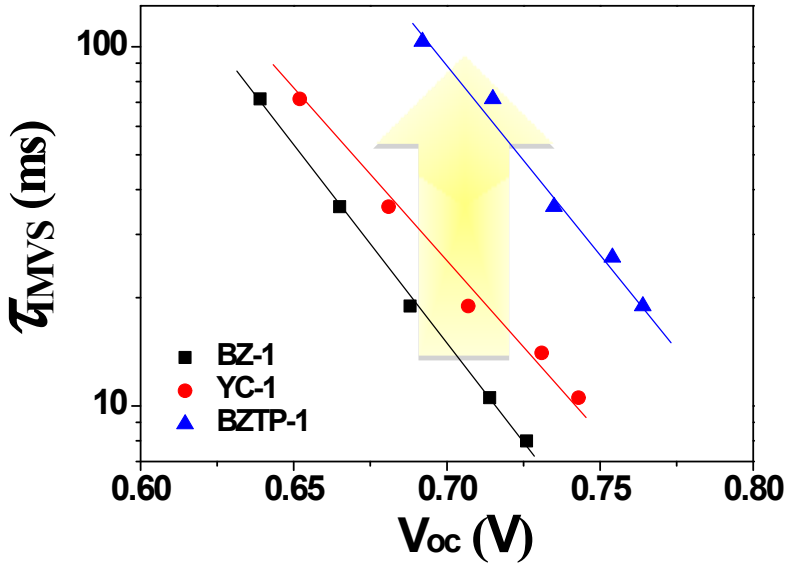


Fig. S8 Electron lifetime vs. photovoltage of DSSCs based on IMVS measurement.

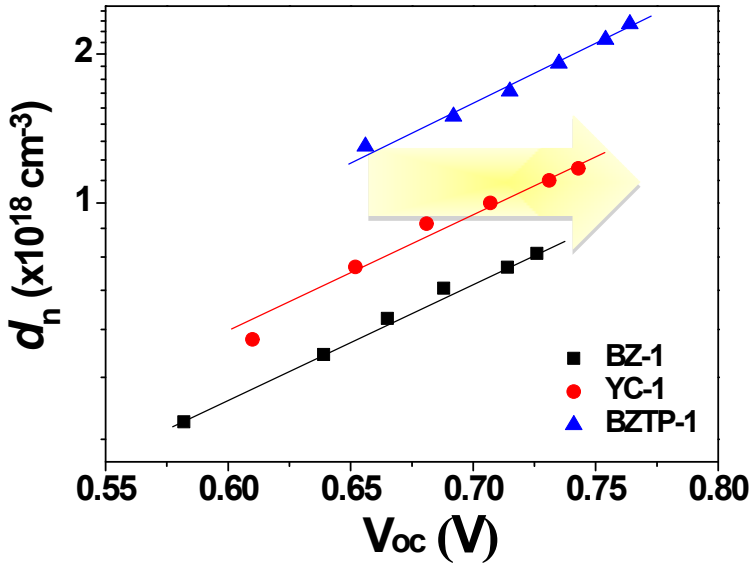
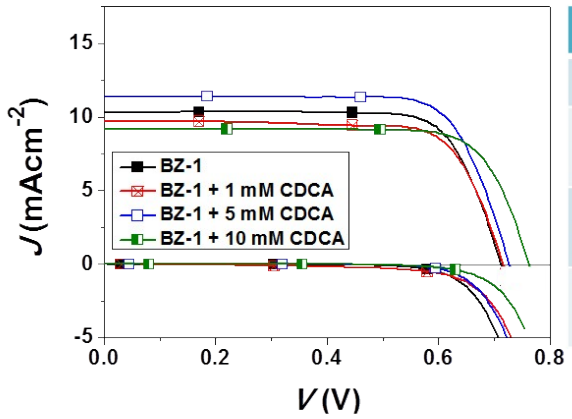
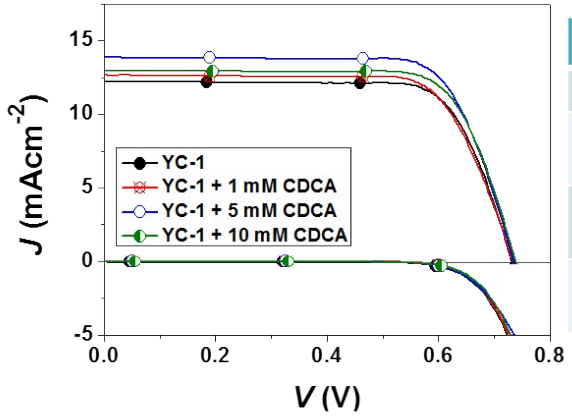


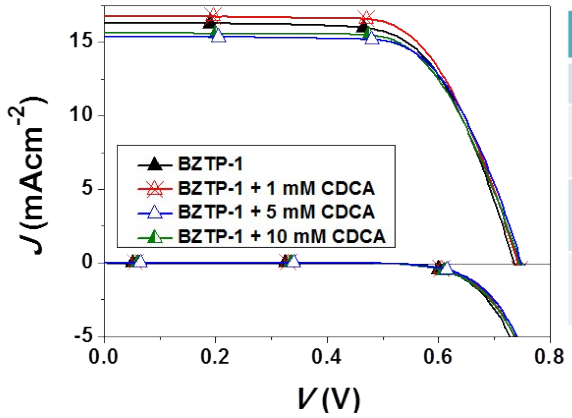
Fig. S9 Electron density vs. photovoltage of DSSCs based on charge extraction measurement.



	Voc	Jsc	ff	PCE
BZ-1	0.711	10.36	0.76	5.63
BZ-1 + 1 mM CDCA	0.715	9.76	0.75	5.22
BZ-1 + 5 mM CDCA	0.727	11.40	0.76	6.29
BZ-1 + 10 mM CDCA	0.762	9.18	0.77	5.41



	Voc	Jsc	ff	PCE
YC-1	0.731	12.26	0.75	6.81
YC-1 + 1 mM CDCA	0.733	12.68	0.74	6.85
YC-1 + 5 mM CDCA	0.735	13.89	0.75	7.62
YC-1 + 10 mM CDCA	0.738	12.98	0.75	7.21



	Voc	Jsc	ff	PCE
BZTP-1	0.739	16.33	0.68	8.15
BZTP-1 + 1 mM CDCA	0.743	16.76	0.68	8.48
BZTP-1 + 5 mM CDCA	0.749	15.36	0.69	7.97
BZTP-1 + 10 mM CDCA	0.745	15.63	0.68	7.96

Fig. S10 *J*−*V* curves of the DSSCs with the dyes at the different concentrations of CDCA under 100 mWcm^{-2} of illumination.

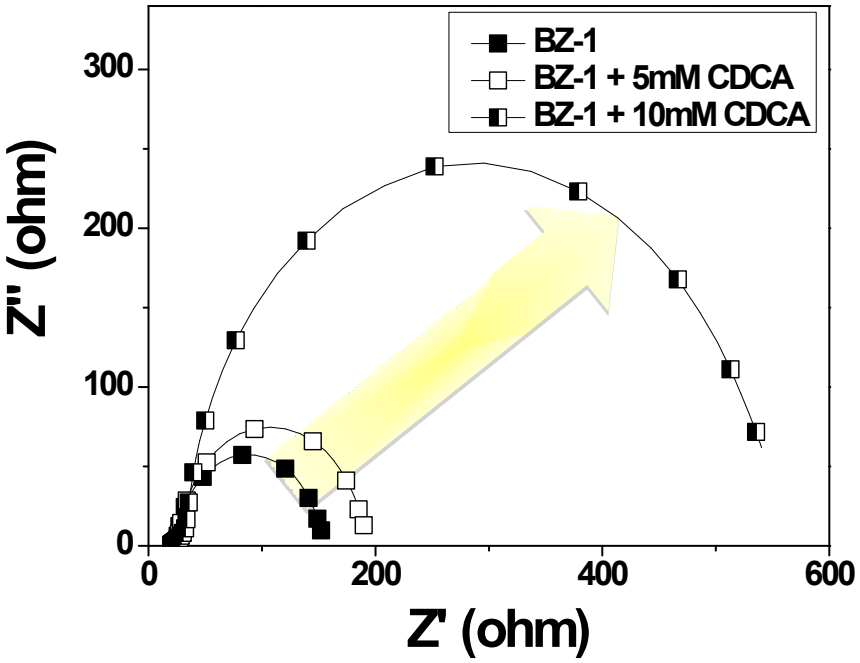


Fig. S11 Nyquist plots of the DSSCs with the **BZ-1** at the different concentrations of CDCA in the dark.

Table S1. Calculated lower-lying transitions of the dyes.[a]

dye	State	Excitation[a]	λ_{cal} (eV)[b]	f[c]	Δ(Mulliken charge), (e)[d]	$f \times \Delta q$[e]
BZ-1	S_1	H → L (99%)	2.27	0.71	TPA: 0.75, Btz: -0.38, Ac: -0.37	-0.26
	S_2	H1 → L (94%)	3.27	0.52	TPA: 0.18, Btz: 0.04, Ac: -0.22	-0.11
	S_3	H → L1 (90%)	3.70	0.02	TPA: 0.70, Btz: -0.42, Ac: -0.28	-0.004
YC-1	S_1	H → L (99%)	2.17	0.64	TPA: 0.72, BZBT: -0.34, Ac: -0.39	-0.25
	S_2	H1 → L (92%) , H → L1 (7%)	2.96	0.66	TPA: 0.24, BZBT: 0.02, Ac: -0.26	-0.17
	S_3	H2 → L (98%)	3.22	0.05	TPA: -0.03, BZBT: 0.49, Ac: -0.45	-0.02
BZTP-1	S_1	H → L (98%)	2.23	1.29	TPA: 0.47, BZTP: -0.10, Ac: -0.37	-0.47
	S_2	H1 → L (92%)	2.76	0.65	TPA: 0.41, BZTP: -0.08, Ac: -0.32	-0.21
	S_3	H2 → L (96%)	2.85	0.06	TPA: -0.01, BZTP: 0.46, Ac: -0.45	-0.03
BT-1	S_1	H → L (100%)	1.94	0.47	TPA: 0.80, Btda: -0.61, Ac: -0.19	-0.09
	S_2	H1 → L (41%), H → L1 (57%)	2.92	0.005	TPA: 0.57, Btda: -0.39, Ac: -0.18	-0.001
	S_3	H1 → L (56%), H → L1 (42%)	3.09	0.53	TPA: 0.50, Btda: -0.33, Ac: -0.17	-0.09
BTBT-1	S_1	H → L (99%)	2.04	0.56	TPA: 0.74, BTBT: -0.47, Ac: -0.28	-0.16
	S_2	H1 → L (10%), H → L1 (88%)	2.67	0.001	TPA: 0.64, BTBT: -0.48, Ac: -0.16	-2E-4
	S_3	H1 → L (85%), H → L1 (10%)	2.90	0.57	TPA: 0.31, BTBT: -0.16, Ac: -0.15	-0.09
DTP-4	S_1	H → L (98%)	2.16	1.11	TPA: 0.53, DTP: -0.23, Ac: -0.30	-0.33
	S_2	H1 → L (45%), H → L1 (50%)	2.64	0.21	TPA: 0.36, DTP: -0.25, Ac: -0.12	-0.02
	S_3	H1 → L (51%), H → L1 (43%)	2.77	0.42	TPA: 0.37, DTP: -0.15, Ac: -0.23	-0.09

[a] Results are based on gas-phase TD−DFT calculation.

[b] H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO–1, H2 = HOMO–2, L1 = LUMO+1, L2 = LUMO+2. In parentheses is the population of a pair of MO excitations.

[c] Oscillator strength, *f*.

[d] The difference of the Mulliken charge between the ground state and excited state, Δ(M.C.).

[e] The Δ(M.C.) of the anchor group (Ac), Δq.

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