Supporting Information

Organic sensitizers with a rigid dithienobenzotriazole-based spacer for high performance 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, 2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2",3":5,6]benzo[1,2-*d*][1,2,3]triazole (DTBZ),[1] (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tri-*n*-butylstannane,[2] (5-(1,3-dioxolan-2-yl)-4-*n*-hexylthiophen-2-yl)tri-*n*-butylstannane,[3] *N*,*N*-diphenyl-4-(tri-*n*-butylstannyl)aniline (TPA-Sn^nBu_3),[4] 9-(2-ethylhexyl)-3-(tri-*n*-butylstannyl)-9*H*-carbazole (CBZ-Sn^nBu_3)[5] and 4-(2-ethylhexyl)-2-(tri-*n*-butylstannyl)-4*H*-thieno[3,2-*b*]indole (TID-Sn^nBu_3)[6] were prepared according to the published procedures. TiO_2 paste was purchased from Solaronix S. A., Switzerland.

Characterization. ^{1}H 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 to 10 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.

Fabrications 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 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 0.6 × 0.6 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) and differential pulse voltammetry (DPV) 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 (−1.09 to −1.22 V vs. NHE) is more negative than the conduction band edge of TiO_2 (−0.5 V vs. NHE). Dye regeneration should also be energetically favored as the first oxidation potentials of the dyes (1.21 to 1.26 V vs. NHE) are more positive than that of the I^-/I_3^- redox couple (0.4 V vs. NHE).

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 using time-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. In some cases underestimation of the excitation energies was seen. 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.

Synthesis of 5,8-dibromo-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3] triazole (Br-DTBZ-Br). DTBZ (0.82 g, 2.39 mmol) was dissolved in DMF (2 mL), and NBS (0.89 g, 5.02 mmol) dissolved in DMF (2 mL) was added slowly in the ice-bath. 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 give a yellow oil in 86.7% yield (1.04 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 2H), 4.62 (d, J = 7.2 Hz, 2H), 2.25−2.19 (m, 1H), 1.37−1.24 (m, 8H), 0.91 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.45, 132.84, 126.78, 124.77, 122.60, 59.63, 40.62, 30.65, 28.63, 24.05, 23.12, 14.24, 10.71. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{18}H_{19}Br_2N_3S_2$, 501.30; found, 498.9377; 500.9334; 502.9311.

Synthesis of 4-(8-bromo-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)-*N*,*N*-diphenylaniline (1a). Br-DTBZ-Br (1.04 g, 2.07 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.10 mmol) and *N*,*N*-diphenyl-4-(tri-*n*-butylstannyl)aniline (1.11 g, 2.07mmol) were dissolved in 4 mL of dry DMF and stirred at 80 °C for 16 h. 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 (1/3, v/v) as the eluent to afford an yellow oil in 17.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.87 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.28 (dd, J = 8.0, 7.6 Hz, 4H), 7.14−7.04 (m, 8H), 4.64 (d, J = 7.2 Hz, 2H), 2.27−2.22 (m, 1H), 1.37−1.25 (m, 8H), 0.92 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H).

Synthesis of 5-bromo-2-(2-ethylhexyl)-8-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazole (1b). Yield of 32.3% (0.7 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.85 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.47 (dd, J = 7.2, 7.6 Hz, 1H), 7.39−7.36 (m, 2H), 7.26 (dd, J = 7.6, 6.4 Hz, 1H), 4.64 (d, J = 6.8 Hz, 2H), 4.13 (d, J = 6.8 Hz, 2H), 2.29−2.26 (m, 1H), 2.06−2.04 (m, 1H), 1.39−1.24 (m, 16H), 0.96−0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.77, 141.64, 141.02, 139.37, 138.66, 133.75, 129.91, 128.18, 126.31, 126.03, 125.62, 124.92, 124.21, 123.51, 123.04, 120.73, 119.50, 118.01, 116.33, 112.52, 109.48, 60.02, 47.66, 40.92, 39.76, 32.40, 32.06, 31.41, 30.94, 30.18, 29.85, 29.21, 28.92, 24.82, 24.30, 23.50, 23.40, 23.17, 14.57, 14.48, 11.30, 10.91. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{38}H_{43}BrN_4S_2$, 698.2107; found, 698.2093.

Synthesis of 5-(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)thiophene-2-carbaldehyde (2a). Compound **1a** (0.24 g, 0.36 mmol), $Pd(PPh_3)_2Cl_2$ (0.013 g, 0.018 mmol) and (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tri-*n*-butylstannane (0.18 g, 0.4 mmol) were dissolved in 1 mL of dry DMF and stirred at 80 °C for 16 h. The solvent was removed under vacuum, and HCl (4N, 10 mL) and DCM (25 mL) were added. After further stirred for 2 h, the solution was 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 oil in 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 8.06 (s, 1H), 7.94 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 4.0 Hz, 1H), 7.29 (dd, J = 8.0, 7.6 Hz, 4H), 7.14 (d, J = 7.6 Hz, 4H), 7.10−7.05 (m, 4H), 4.64 (d, J = 7.2 Hz, 2H), 2.28−2.25 (m, 1H), 1.39−1.28 (m, 8H), 0.93 (t, J = 7.6 Hz, 3H), 0.86 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.28, 147.24, 146.65, 144.81, 142.34, 139.37, 137.15, 134.32, 132.99, 130.36, 129.43, 128.85, 127.12, 126.99, 126.89, 124.96, 123.57, 122.97, 120.99, 116.81, 59.85, 53.38, 40.54, 30.49, 28.46, 27.83, 26.81, 23.87, 22.88, 17.51, 13.97, 13.56, 10.47. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{41}H_{36}N_4OS_3$, 696.2046; found, 696.2043.

Synthesis of 5-(2-(2-ethylhexyl)-8-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-2*H*-dithieno[3',2':3,4;2'', 3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)thiophene-2-carbaldehyde (2b). Yield of 21% (93 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 8.41 (s, 1H), 8.12 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 3.6 Hz, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 4.0 Hz, 1H), 7.48 (dd, J = 7.6, 7.2 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 3.6 Hz, 1H), 7.26 (dd, J = 7.6, 9.2 Hz, 1H), 4.65 (d, J = 7.2 Hz, 2H), 4.14 (d, J = 4.4 Hz, 2H), 2.30−2.27 (m, 1H), 2.07−2.05 (m, 1H), 1.40−1.27 (m, 16H), 0.96−0.84 (m, 12H). ^{13}C NMR (100 MHz，d_8−THF): δ 182.67, 147.20, 146.76, 142.49, 141.87, 141.36, 139.77, 139.52, 134.43, 133.47, 130.45, 129.31, 126.98, 126.58, 125.15, 124.98, 124.44, 123.75, 123.13, 121.33, 120.89, 119.75, 118.35, 116.73, 109.74, 60.29, 47.97, 41.02, 39.91, 32.41, 31.50, 31.00, 30.18, 29.84, 29.28, 28.97, 24.89, 24.36, 23.53, 23.41, 23.17, 14.58, 14.50, 11.38, 10.96. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{43}H_{46}N_4OS_3$, 730.2828; found, 730.2822.

Synthesis of 5-(2-(2-ethylhexyl)-8-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-2*H*-dithieno[3',2':3,4;2'', 3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)thiophene-2-carbaldehyde (2c). Yield of 10% (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 8.31 (s, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.95 (s, 1H), 7.93 (s, 1H), 7.72 (dd, J = 2.0, 1.6 Hz, 1H), 7.45 (dd, J = 7.6, 7.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.07 (s, 1H), 4.59 (d, J = 7.2 Hz, 2H), 4.07 (d, J = 6.8 Hz, 2H), 2.83 (t, J = 7.6 Hz, 2H), 2.30−2.24 (m, 1H), 2.04−2.00 (m, 1H), 1.70−1.65 (m, 2H), 1.38−1.27 (m, 22H), 0.96−0.83 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.80, 146.66, 146.08, 141.85, 141.33, 139.76, 139.53, 136.67, 134.72, 133.32, 130.52, 129.24, 127.46, 126.98, 126.56, 125.01, 124.45, 123.73, 123.12, 121.17, 120.88, 119.73, 118.32, 116.76, 109.76, 109.72, 60.27, 47.95, 41.23, 41.01, 39.90, 32.42, 32.06, 31.73, 31.49, 30.99, 30.53, 30.20, 30.16, 29.86, 29.54, 29.28, 29.00, 28.97, 24.88, 24.34, 23.54, 23.42, 23.18, 23.06, 14.59, 14.51, 11.37, 10.95. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{49}H_{58}N_4OS_3$, 797.2886; found, 797.2892.

Synthesis of 5-bromo-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazole (DTBZ-Br). DTBZ (1.01 g, 2.94 mmol) was dissolved in DCM (6 mL), and NBS (0.52 g, 2.94 mmol) dissolved in AcOH (6 mL) was added slowly in the ice-bath. 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 give a yellow oil in 97% yield (1.2 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 4.0 Hz, 1H), 7.86 (s, 1H), 7.51 (d, J = 4.0 Hz, 1H), 4.64 (d, J = 6.8 Hz, 2H), 2.26−2.23 (m, 1H), 1.38−1.24 (m, 8H), 0.92 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.36, 139.17, 137.96, 133.40, 132.00, 131.42, 126.81, 126.70, 126.36, 126.30, 125.25, 125.12, 124.98, 124.68, 122.57, 122.47, 113.34, 112.94, 59.67, 53.73, 40.64, 30.70, 29.99, 28.70, 24.09, 23.18, 14.32, 10.77. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{18}H_{20}BrN_3S_2$, 422.41; found, 421.0288; 421.0258.

Synthesis of 5-(2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)-3-hexylthiophene-2-carbaldehyde (3). DTBZ-Br (1.70 g, 4.02 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol) and (5-(1,3-dioxolan-2-yl)-3-hexylthiophen-2-yl)tributylstannane (3.2 g, 6.04 mmol) were dissolved in 4 mL of dry DMF and stirred at 80 °C for 16 h. The solvent was removed under vacuum, and HCl (4N, 10 mL) and DCM (25 mL) were added. After further stirred for 2 h, the solution was 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 (2/1, v/v) as the eluent to afford an orange solid in 21% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.88 (s, 1H), 7.74 (d, J = 5.2 Hz, 1H), 7.42 (d, J = 5.2 Hz, 1H), 7.00 (s, 1H), 4.57 (d, J = 7.2 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 2.25−2.21 (m, 1H), 1.64−1.58 (m, 2H), 1.35−1.20 (m, 14H), 0.95−0.91 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.08, 145.71, 139.85, 139.33, 136.88, 135.25, 133.24, 132.32, 128.06, 127.63, 127.49, 126.06, 125.49, 123.02, 121.03, 119.63, 60.15, 40.93, 32.36, 32.13, 31.99, 31.66, 30.90, 30.13, 29.45, 28.94, 28.88, 24.28, 23.35, 22.99, 14.49, 14.44, 10.91. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{29}H_{35}N_3OS_3$, 537.80; found, 537.1942.

Synthesis of 5-(8-bromo-2-(2-ethylhexyl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3] triazol-5-yl)-3-hexylthiophene-2-carbaldehyde (4). Compound **3** (0.45 g, 0.84 mmol) was dissolved in DCM (4 mL), and NBS (0.16 g, 0.92 mmol) dissolved in AcOH (1.5 mL) was added slowly in the ice-bath. 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 give a deep-yellow oil in 97% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.61 (s, 1H), 7.49 (s, 1H), 6.85 (s, 1H), 4.51 (d, J = 7.2 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 1.58−1.52 (m, 1H), 1.64−1.58 (m, 2H), 1.28−1.18 (m, 14H), 0.89−0.85 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.79, 145.15, 138.90, 138.45, 136.78, 135.36, 132.66, 131.42, 127.40, 125.56, 120.45, 119.19, 114.17, 40.84, 31.93, 31.54, 30.86, 30.07, 29.45, 28.84, 24.22, 23.31, 22.96, 14.46, 10.86. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{29}H_{34}BrN_3OS_3$, 616.70; found, 615.1057; 617.1052.

Synthesis of 5-(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)-3-*n*-hexylthiophene-2-carbaldehyde (5a). Compound **4** (0.32 g，0.47 mmol), $Pd(PPh_3)_2Cl_2$ (0.01 g，0.02 mmol) and *N*,*N*-diphenyl-4-(tri-*n*-butylstannyl)aniline (0.28 g，0.52 mmol) were dissolved in 1 mL of dry DMF and stirred at 80 °C for 16 h. The solvent was removed under vacuum, and 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 (2/1, v/v) as the eluent to afford a red oil in 20% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.98 (s, 1H), 7.90 (s, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.27 (t, J = 7.5 Hz 4H), 7.19−7.11 (m, 4H), 7.08−7.04 (m, 4H), 7.04 (s, 1H), 4.61 (d, 2H), 2.89 (t, J = 8.0 Hz, 2H), 2.28−2.23 (m, 1H), 1.70−1.67 (m, 2H), 1.39−1.28 (m, 14H), 0.94−0.84 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.91, 154.27, 148.68, 147.71, 145.96, 145.11, 139.79, 139.59, 136.89, 135.05, 133.25, 130.84, 129.91, 129.18, 127.70, 127.60, 127.43, 127.31, 125.42, 124.03, 123.42, 121.24, 117.25, 60.28, 41.00, 32.04, 31.75, 30.94, 29.50, 29.05, 28.93, 24.31, 23.38, 23.03, 14.54, 14.49, 10.96. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{47}H_{48}N_4OS_3$, 780.2990; found, 780.2988.

Synthesis of 5-(2-(2-ethylhexyl)-8-(4-(2-ethylhexyl)-4*H*-thieno[3,2-b]indol-2-yl)-2*H*-dithieno [3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)-3-hexylthiophene-2-carbaldehyde (5b). Yield of 29%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.89 (s, 1H), 7.76 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.25 (s, 1H), 7.14 (dd, J = 6.4, 6.0 Hz, 1H), 7.07−7.05 (m, 2H), 4.57 (d, J = 7.2 Hz, 2H), 3.90 (d, J = 6.4 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.28−2.22 (m, 1H), 1.96−1.93 (m, 1H), 1.70−1.63 (m, 2H), 1.38−1.25 (m, 22H), 0.95−0.86 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.17, 145.74, 141.99, 139.44, 139.30, 137.77, 136.78, 135.23, 132.69, 130.41, 128.63, 127.54, 123.32, 121.91, 121.06, 119.76, 119.40, 117.91, 116.27, 110.55, 108.32, 60.28, 49.62, 40.98, 40.35, 32.03, 31.70, 31.28, 30.97, 29.51, 29.15, 28.94, 24.70, 24.32, 23.53, 23.39, 23.04 , 14.53, 14.48, 11.26, 10.92. MS-HR-FAB (m/z): $[M+H]^+$ calcd for $C_{47}H_{56}N_4OS_4$, 821.2337; found, 821.3414.

Synthesis of *(Z)*-2-cyano-3-(5-(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)thiophen-2-yl)acrylic acid (YC-2). Compound **2a** (0.12 g, 0.176 mmol), cyanoacetic acid (0.15 g, 1.76 mmol), NH_4OAc (5 mg) were dissolved in 2 mL of AcOH. 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 deep-purple solid in 24.6% yield (32 mg). ^1H NMR (400 MHz, d_8−THF): δ 8.39 (s, 1H), 8.29 (s, 1H), 8.14 (s, 1H), 7.88 (d, J = 3.9 Hz, 1H), 7.75 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 3.8 Hz, 1H), 7.29 (dd, J = 7.8, 7.7 Hz, 4H), 7.14 (d, J = 8.6 Hz, 6H), 7.08−7.04 (m, 2H), 4.72 (d, J = 6.6 Hz, 2H), 2.28−2.25 (m, 1H), 1.40−1.32 (m, 8H), 0.97 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, d_8−THF): δ 148.57, 146.29, 140.07, 130.42, 128.60, 128.09, 126.65, 125.97, 124.55, 124.11, 122.13, 118.14, 60.26, 41.86, 31.77, 30.50, 29.74, 25.88, 25.68, 25.48, 25.29, 25.09, 23.91, 14.50, 11.10. MS-HR-EI (m/z): $[M]^+$ calcd for $C_{44}H_{37}N_5O_2S_3$, 763.2104; found, 763.2114. Anal. calcd for $C_{44}H_{37}N_5O_2S_3$: C, 69.17; H, 4.88; N, 9.17; found: C, 69.32; H, 4.76; N, 9.15.

Synthesis of *(Z)*-2-cyano-3-(5-(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)-3-*n*-hexylthiophen-2-yl)acrylic acid (YC-3). Yield of 98% (75 mg). ^{1}H NMR (400 MHz, d_8−THF): δ 8.42 (s, 1H), 8.26 (s, 1H), 8.13 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 4H), 7.15−7.04 (m, 8H), 4.72 (d, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.27−2.26 (m, 1H), 1.42−1.29 (m, 16H), 0.99−0.85 (m, 9H). ^{13}C NMR (125 MHz, d_8−THF): δ 165.78, 164.50, 156.39, 149.58, 148.54, 145.97, 145.07, 143.58, 140.55, 140.33, 135.67, 133.57, 131.17, 131.06, 130.42, 128.57, 128.40, 128.24, 128.07, 125.95, 124.54, 124.09, 122.16, 118.13, 116.89, 114.84, 60.22, 41.84, 35.64, 32.21, 31.75, 30.07, 29.83, 29.74, 24.36, 23.92, 23.62, 14.58, 14.52, 11.10. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{47}H_{48}N_4OS_3$, 847.3048; found, 847.3053. Anal. calcd for $C_{47}H_{48}N_4OS_3$: C, 70.81; H, 5.82; N, 8.26; found: C, 70.73; H, 5.91; N, 8.56.

Synthesis of *(Z)*-2-cyano-3-(5-(2-(2-ethylhexyl)-8-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)thiophen-2-yl)acrylic acid (YC-4). Yield of 29% (30 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.38 (s, 1H), 8.28 (s, 1H), 8.25 (s, 1H), 8.20 (d, *J* = 3.6 Hz, 1H),7.79 (d, *J* = 6.8 Hz, 1H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.62 (s, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.50 (d, *J* = 6.4 Hz, 1H), 7.45 (t, *J* = 6.0 Hz, 1H), 7.23 (dd, *J* = 6.0, 5.6 Hz, 1H), 4.73 (d, *J* = 5.6 Hz, 2H), 4.30 (d, *J* = 6.0 Hz, 2H), 2.29−2.27 (m, 1H), 2.15−2.13 (m, 1H), 1.47−1.26 (m, 16H), 1.01−0.95 (m, 12H). ^{13}C NMR (125 MHz, d_8−THF): δ 147.80, 146.71, 146.33, 142.68, 142.26, 140.61, 140.34, 140.17, 136.75, 135.33, 133.70, 130.80, 130.56, 128.31, 127.09, 126.58, 125.75, 125.15, 124.66, 123.96, 122.18, 121.51, 120.28, 119.09, 117.68, 116.72, 110.73, 110.43, 100.65, 48.20, 41.87, 40.54, 32.03, 31.78, 30.80, 29.84, 29.76 , 24.96, 24.12, 23.92, 23.72, 14.52, 11.34, 11.12. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{46}H_{47}N_5O_2S_3$, 797.2886; found, 797.2892. Anal. calcd for $C_{46}H_{47}N_5O_2S_3$: C, 69.23; H, 5.94; N, 8.78; found: C, 69.73; H, 5.68; N, 8.86.

Synthesis of *(Z)*-2-cyano-3-(5-(2-(2-ethylhexyl)-8-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)-3-*n*-hexylthiophen-2-yl)acrylic acid (YC-5). Yield of 45% (40 mg). ^{1}H NMR (500 MHz, d_8−THF): δ 8.66 (s, 1H), 8.43 (s, 1H), 8.26−8.23 (m, 3H), 7.95 (d, *J*= 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.23 (dd, *J* = 7.6, 7.0 Hz, 1H), 4.73 (d, *J* = 6.0 Hz, 2H), 4.30 (d, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.30−2.27 (m, 1H), 2.15−2.13 (m, 1H), 1.49−1.33 (m, 24H), 0.99−0.86 (m, 15H). ^{13}C NMR (125 MHz, d_8−THF): δ 156.06, 147.73, 143.20, 142.66, 142.23, 140.55, 140.30, 135.48, 131.21, 130.83, 128.25, 128.15, 127.09, 125.72, 125.15, 124.62, 123.92, 122.03, 121.50, 120.26, 119.05, 117.67, 110.73, 110.42, 41.84, 40.52, 33.01, 32.71, 32.22, 32.00, 31.75, 30.77, 30.55, 30.44, 30.05, 29.82, 29.73, 24.10, 23.90, 23.70, 23.60, 14.57, 14.51, 11.37, 11.11. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{52}H_{59}N_5O_2S_3$, 881.3831; found, 881.3850. Anal. calcd for $C_{52}H_{59}N_5O_2S_3$: C, 70.79; H, 6.74; N, 7.94; found: C, 70.63; H, 6.56; N, 7.96.

Synthesis of *(Z)*-2-cyano-3-(5-(2-(2-ethylhexyl)-8-(4-(2-ethylhexyl)-4*H*-thieno[3,2-b]indol-2-yl)-2*H*-dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-*d*][1,2,3]triazol-5-yl)-3-*n*-hexylthiophen-2-yl)acrylic acid (YC-6). Yield of 82% (90 mg). ^{1}H NMR (400 MHz, d_8−THF): δ 8.37 (s, 1H), 8.18 (s, 1H), 7.98 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.55 (s, 1H), 7.48 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 7.2 Hz, 1H), 4.71 (d, *J* = 6.4 Hz, 2H), 4.20 (d, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.28−2.25 (m, 1H), 2.09−2.02 (m, 1H), 1.40−1.32 (m, 24H), 1.00−0.85 (m, 15H). ^{13}C NMR (125 MHz, d_8−THF): δ 164.74, 156.17, 146.68, 144.85, 143.39, 142.92, 140.29, 140.26, 138.05, 135.95, 133.09, 131.20, 130.80, 130.70, 129.83, 129.14, 128.79, 128.11, 123.94, 122.64, 122.01, 120.31, 119.82, 118.61, 117.03, 116.94, 111.30, 109.85, 99.29, 60.28, 50.01, 41.83, 40.98, 38.21, 33.92, 33.04, 32.72, 32.15, 31.82, 31.77, 31.13, 30.80, 30.47, 30.12, 29.82, 29.75, 29.68, 28.18, 23.94, 23.72, 23.64, 14.59, 14.55, 11.25, 11.10. MS-HR-FAB (m/z): $[M]^+$ calcd for $C_{46}H_{47}N_5O_2S_3$, 888.28; found, 887.3391. Anal. calcd for $C_{50}H_{57}N_5O_2S_4$: C, 67.61; H, 6.47; N, 7.88; found: C, 67.67; H, 6.40; N, 7.65.

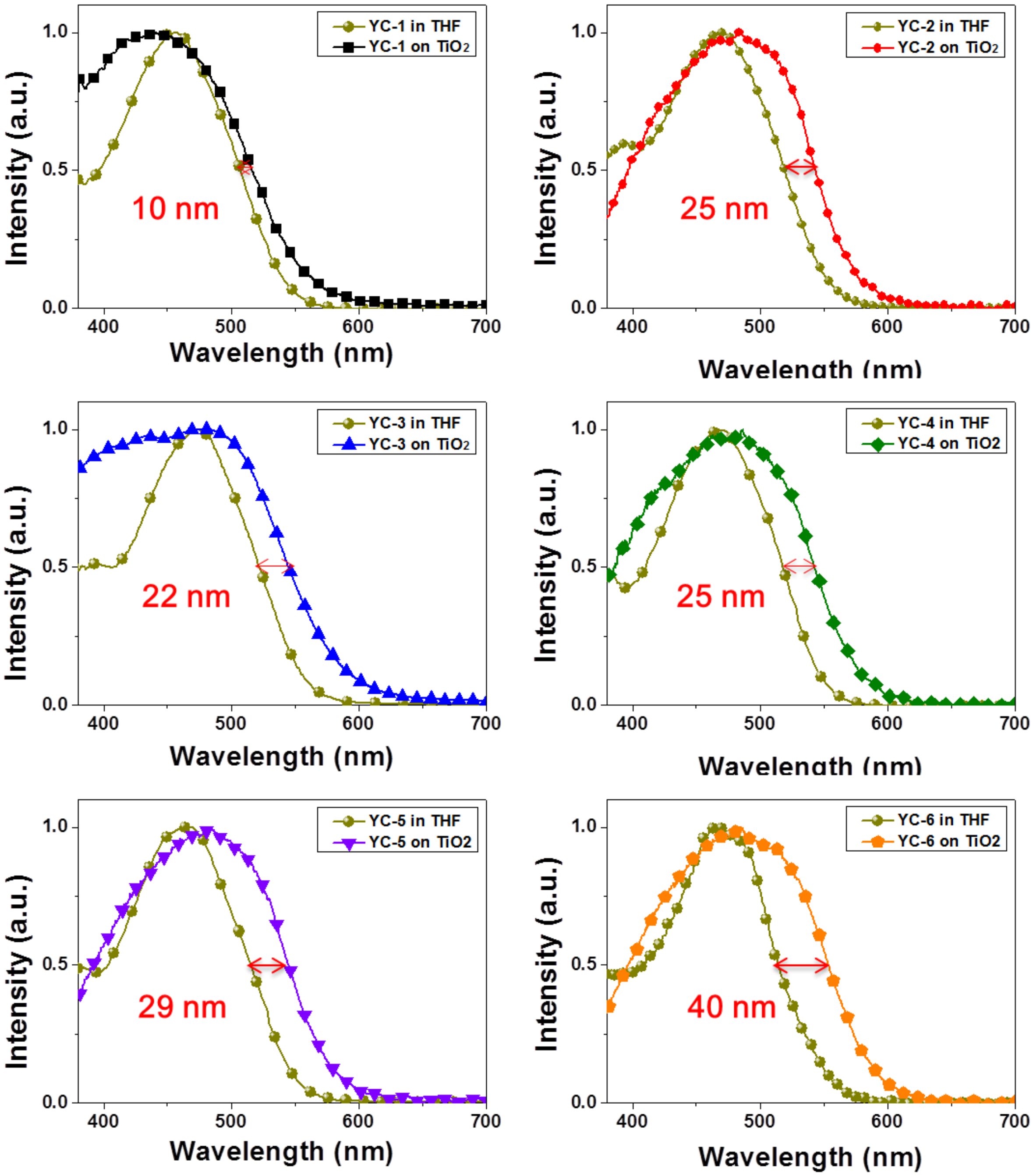


Fig. S1 Absorption spectra of **YC** dyes in THF (10 μM) and on the TiO_2 film.

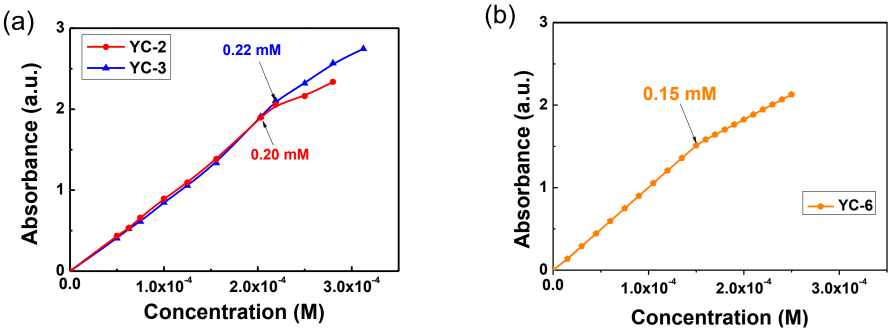


Fig. S2 Absorbance vs. concentration plots for (a) **YC-2**, **YC-3**, and (b) **YC-6** dyes in THF.

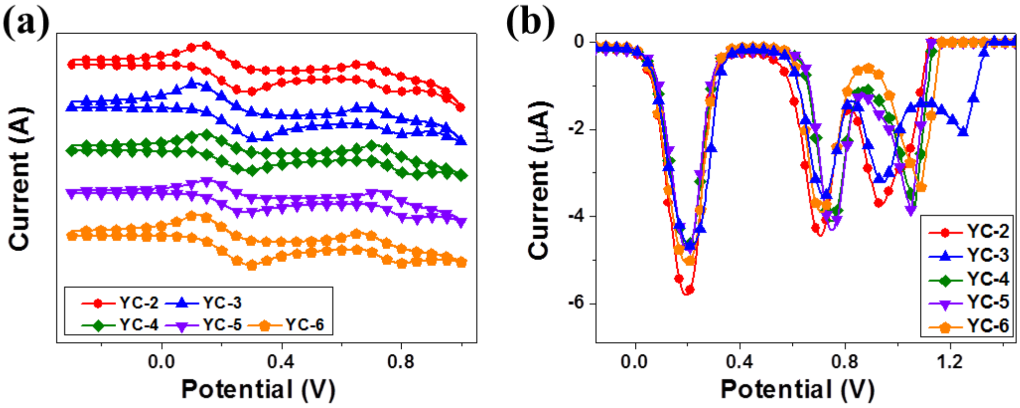


Fig. S3 (a) Cyclic voltammograms and (b) differential pulse voltammograms of dyes in THF (1 mM).

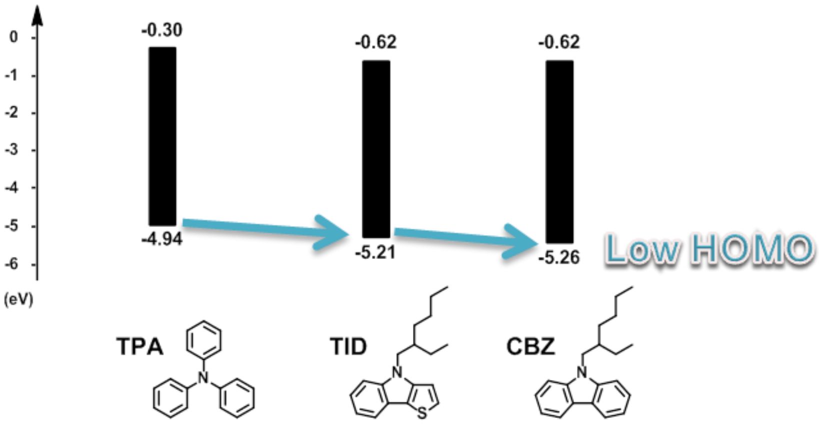


Fig. S4 Energy level diagram in the gas-phase for donors.

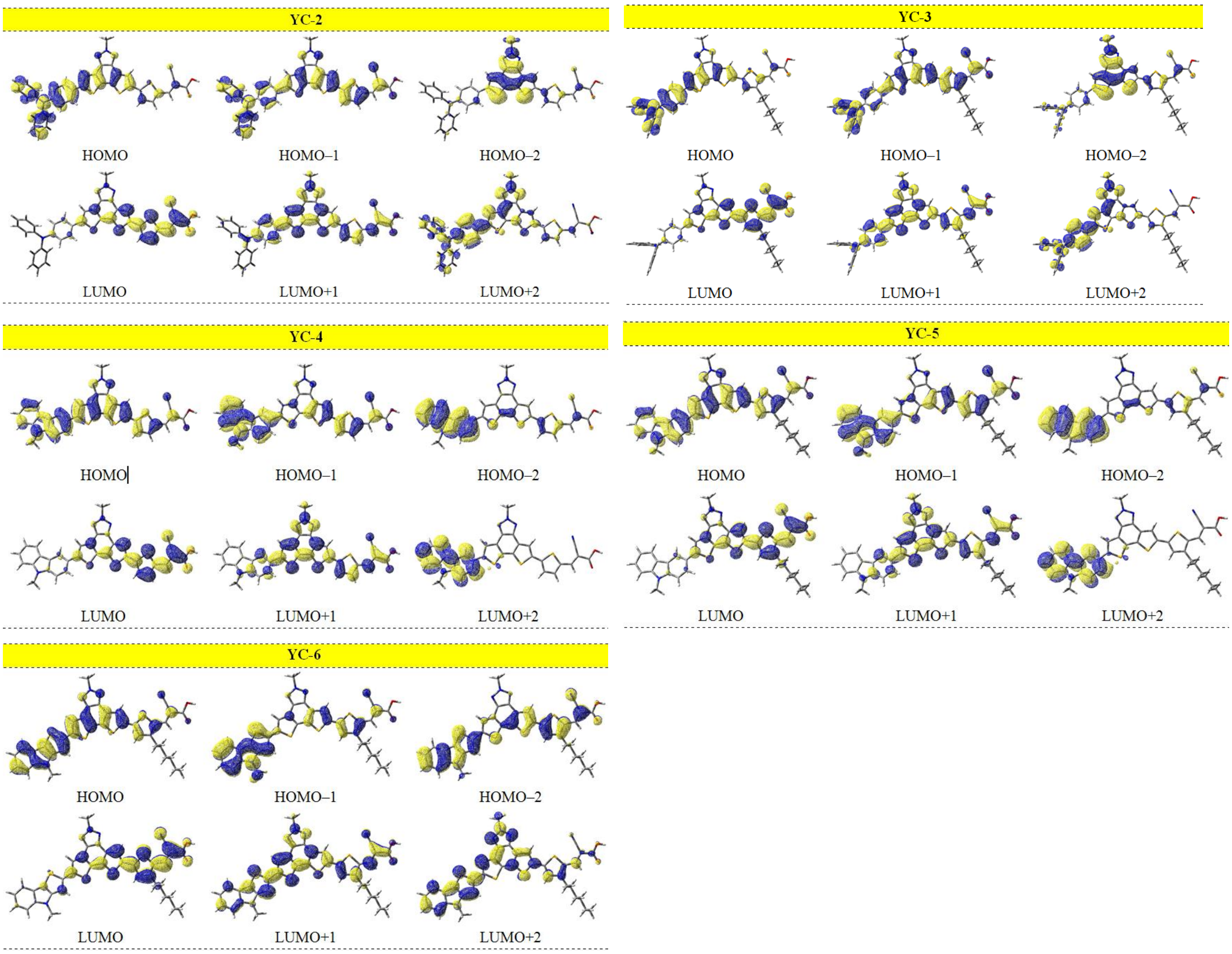


Fig. S5 Selected frontier orbitals of the dyes.

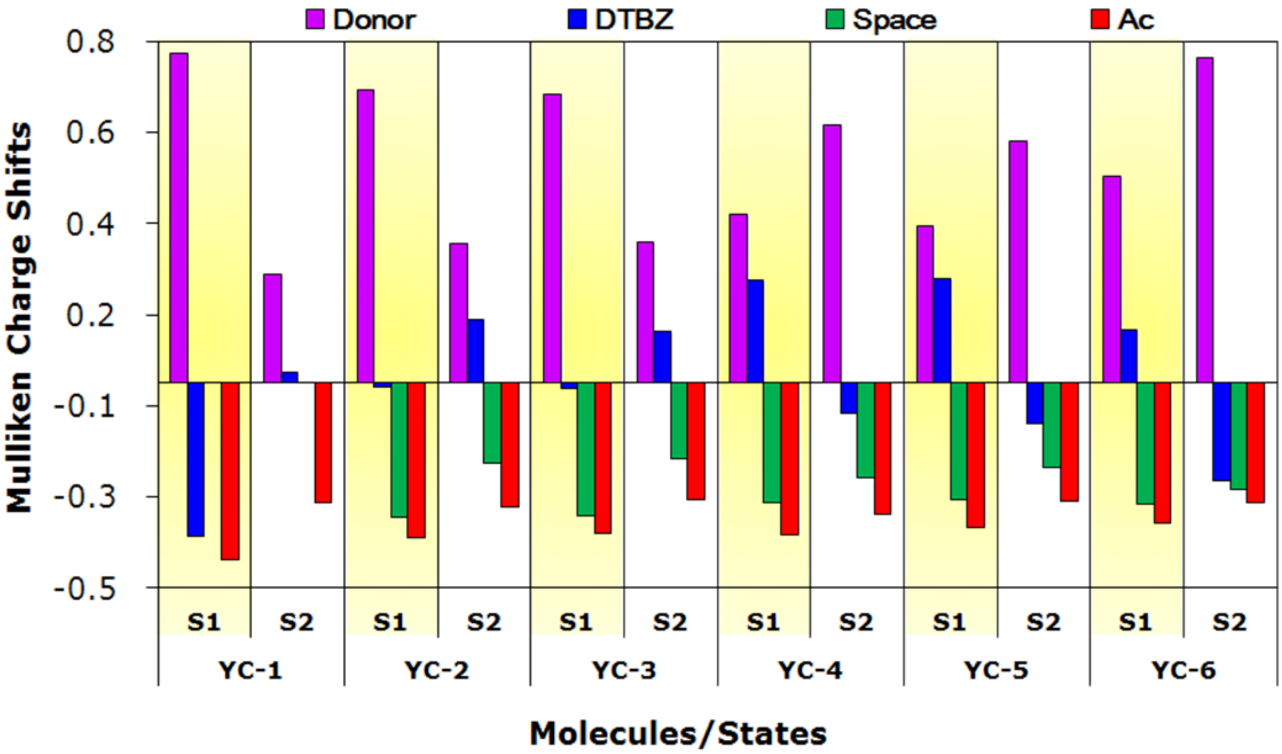


Fig. S6 Plot of the difference in the Mulliken charges between the ground and the excited states.

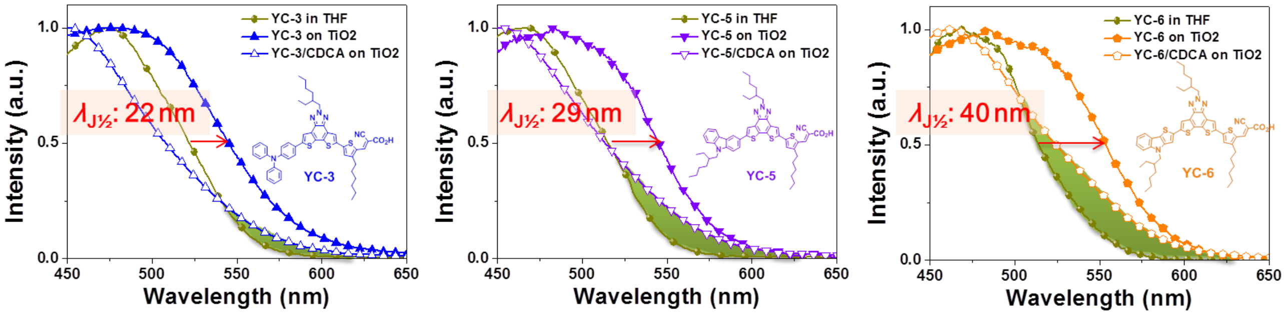


Fig. S7 Absorption spectra of **YC-6** in THF and on the TiO_2 film in comparison with that of **YC-3** and **YC-5**.

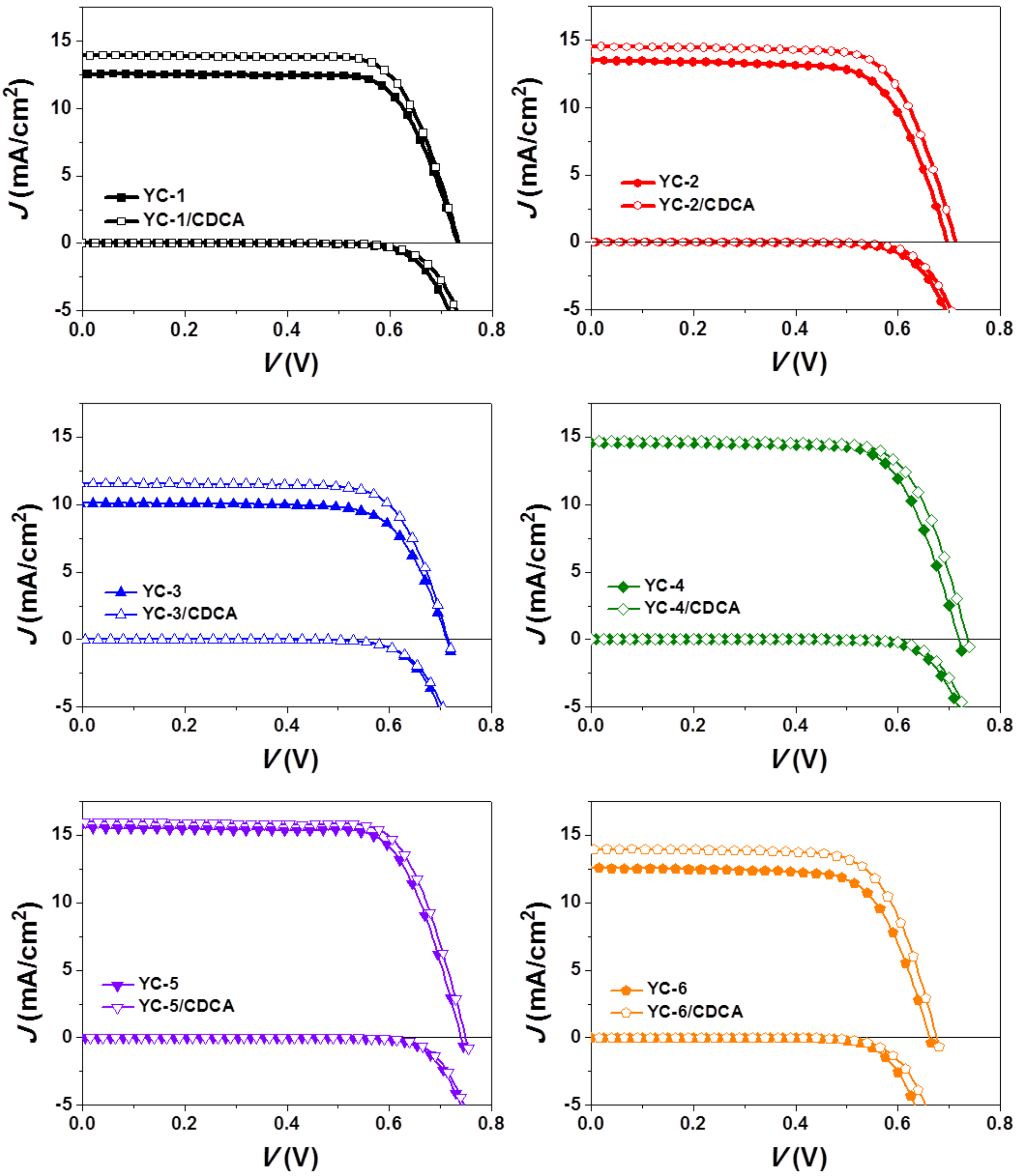


Fig. S8 *J*−*V* curves of DSSCs based on the dyes with and without CDCA as coadsorbent.

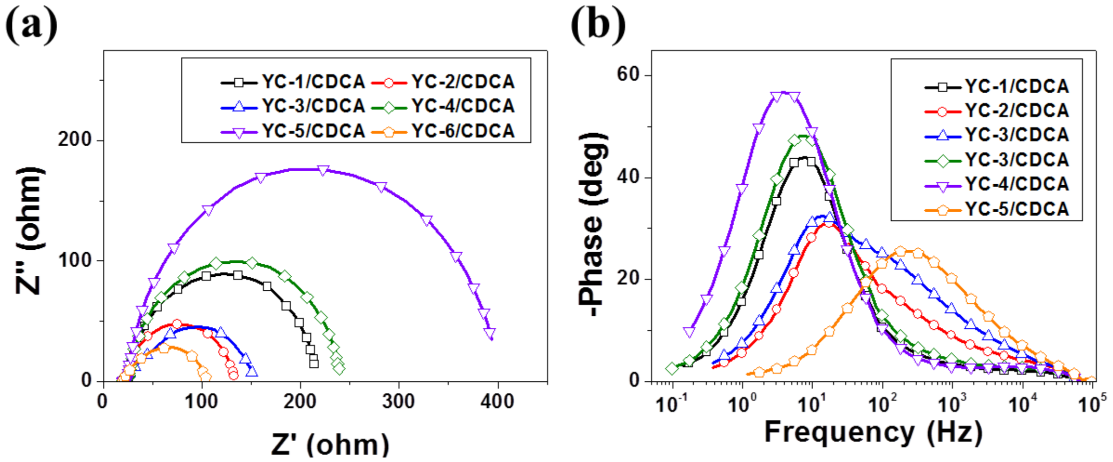


Fig. S9 (a) Nyquist and (b) Bode plots of the DSSCs with the dyes and CDCA in the dark.

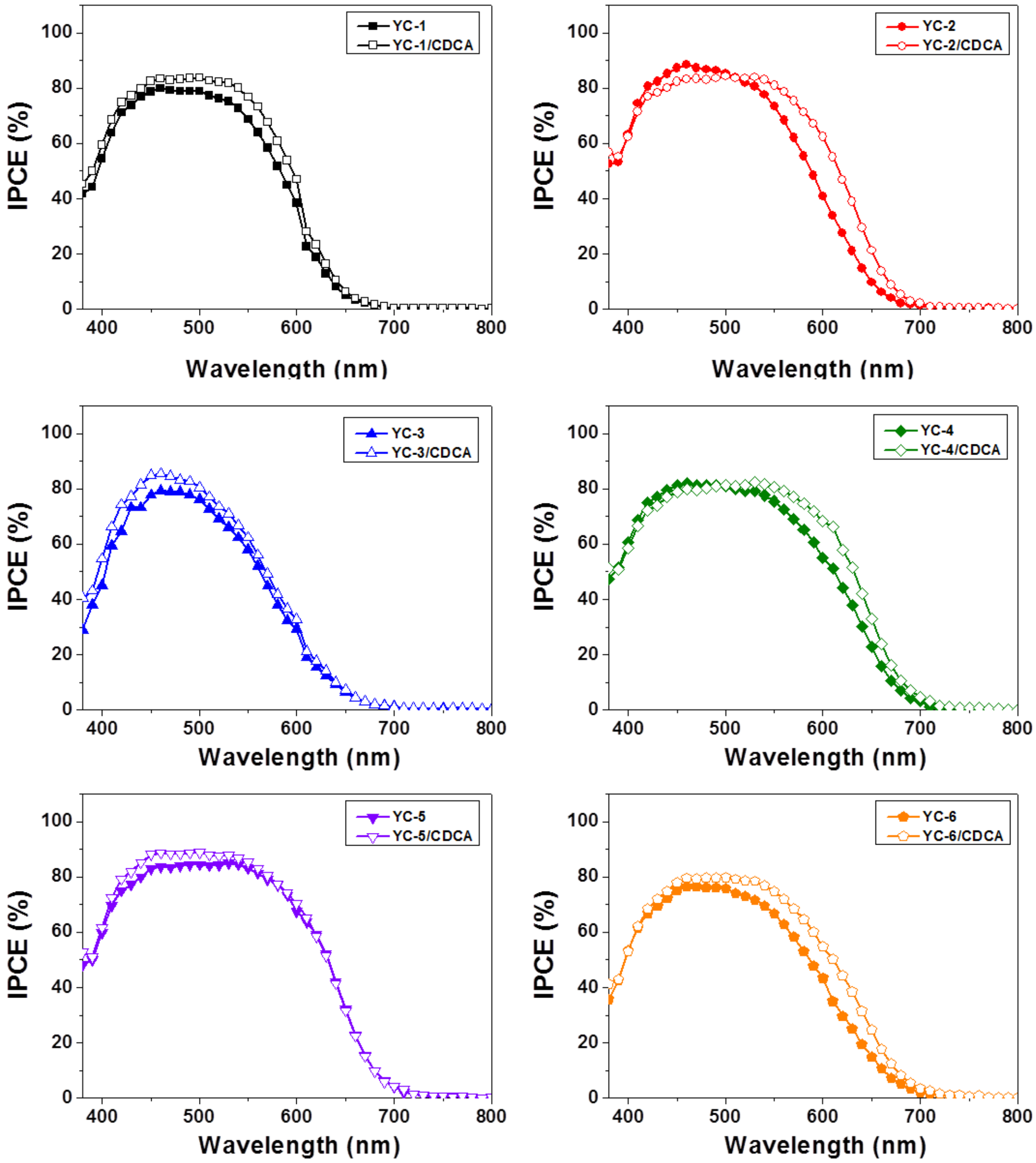
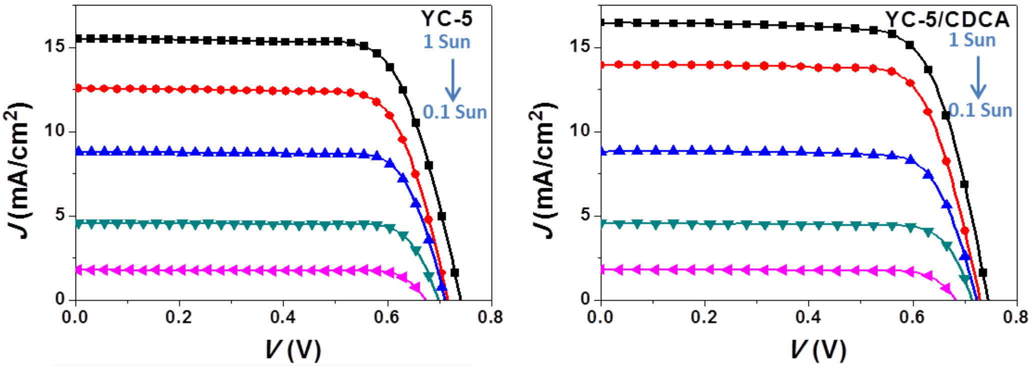
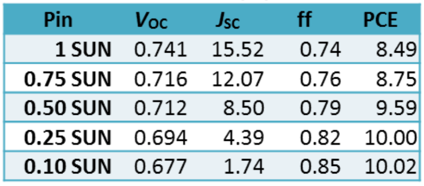
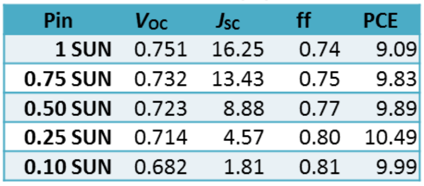


Fig. S10 IPCE plots of DSSCs based on the dyes with and without CDCA as coadsorbent.





Pin	V_{OC}	J_{SC}	ff	PCE
1 SUN	0.741	15.52	0.74	8.49
0.75 SUN	0.716	12.07	0.76	8.75
0.50 SUN	0.712	8.50	0.79	9.59
0.25 SUN	0.694	4.39	0.82	10.00
0.10 SUN	0.677	1.74	0.85	10.02



Pin	V_{OC}	J_{SC}	ff	PCE
1 SUN	0.751	16.25	0.74	9.09
0.75 SUN	0.732	13.43	0.75	9.83
0.50 SUN	0.723	8.88	0.77	9.89
0.25 SUN	0.714	4.57	0.80	10.49
0.10 SUN	0.682	1.81	0.81	9.99

Fig. S11 *J*–*V* curves of the DSSCs based on the **YC-5** sensitizers with and without CDCA as coadsorbent under the different illumination.

Table S1. Calculated low-lying transition for the dye molecules[a]

Dye	State	Excitation[b]	λ_{cal} (eV)	f[c]	Δ(Mulliken charge),[d] |e|
YC-1	S_1	H → L (99%)	2.17	0.64	DG: 0.72, DTBZ: -0.34, Ac: -0.39
	S_2	H1 → L (92%), H → L1 (7%)	2.96	0.66	DG: 0.24, DTBZ: 0.02, Ac: -0.26
	S_3	H2 → L (98%)	3.22	0.05	DG: -0.03, DTBZ: 0.49, Ac: -0.45
YC-2	S_1	H → L (100%)	2.04	0.77	DG: 0.64, DTBZ: -0.01, T: -0.29, Ac: -0.34
	S_2	H1 → L (95%)	2.64	0.86	DG: 0.31, DTBZ: 0.14, T: -0.17, Ac: -0.27
	S_3	H → L1 (89%)	2.96	0.29	DG: 0.45, DTBZ: -0.23, T: -0.07, Ac: -0.14
YC-3	S_1	H → L (99%)	2.10	0.77	DG: 0.63, DTBZ: -0.01, T6: -0.29, Ac: -0.33
	S_2	H1 → L (95%)	2.66	0.83	DG: 0.31, DTBZ: 0.11, T6: -0.17, Ac: -0.26
	S_3	H → L1 (90%)	2.99	0.27	DG: 0.44, DTBZ: -0.23, T6: -0.07, Ac: -0.14
YC-4	S_1	H → L (99%)	2.23	1.06	DG: 0.37, DTBZ: 0.22, T: -0.26, Ac: -0.33
	S_2	H1 → L (96%)	2.84	0.40	DG: 0.57, DTBZ: -0.07, T: -0.21, Ac: -0.29
	S_3	H2 → L (85%), H → L1 (5%)	3.02	0.15	DG: 0.68, DTBZ: -0.10, T: -0.27, Ac: -0.31
YC-5	S_1	H → L (99%)	2.27	1.10	DG: 0.34, DTBZ: 0.23, T6: -0.26, Ac: -0.32
	S_2	H1 → L (95%)	2.87	0.39	DG: 0.53, DTBZ: -0.09, T6: -0.18, Ac: -0.26
	S_3	H2 → L (88%), H → L1 (8%)	3.07	0.12	DG: 0.69, DTBZ: -0.14, T6: -0.26, Ac: -0.29
YC-6	S_1	H → L (100%)	2.11	1.12	DG: 0.45, DTBZ: 0.12, T6: -0.26, Ac: -0.31
	S_2	H1 → L (94%)	2.68	0.29	DG: 0.71, DTBZ: -0.22, T6: -0.23, Ac: -0.26
	S_3	H2 → L (52%), H → L1 (46%)	2.81	0.56	DG: 0.34, DTBZ: -0.12, T6: -0.08, Ac: -0.14

[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.

[d] The difference of the Mulliken charge between the ground state and excited state.

Table S2. Dipole moments of the dye molecules

	Dipole Moment (Debye)			
	x	y	z	total
YC-1	4.76	5.30	1.07	7.20
YC-2	7.35	–0.47	–0.17	7.37
YC-3	6.78	–2.48	0.49	7.23
YC-4	8.04	–2.58	–0.66	8.47
YC-5	6.86	–5.04	–0.73	8.55
YC-6	4.47	–4.76	–0.54	6.56

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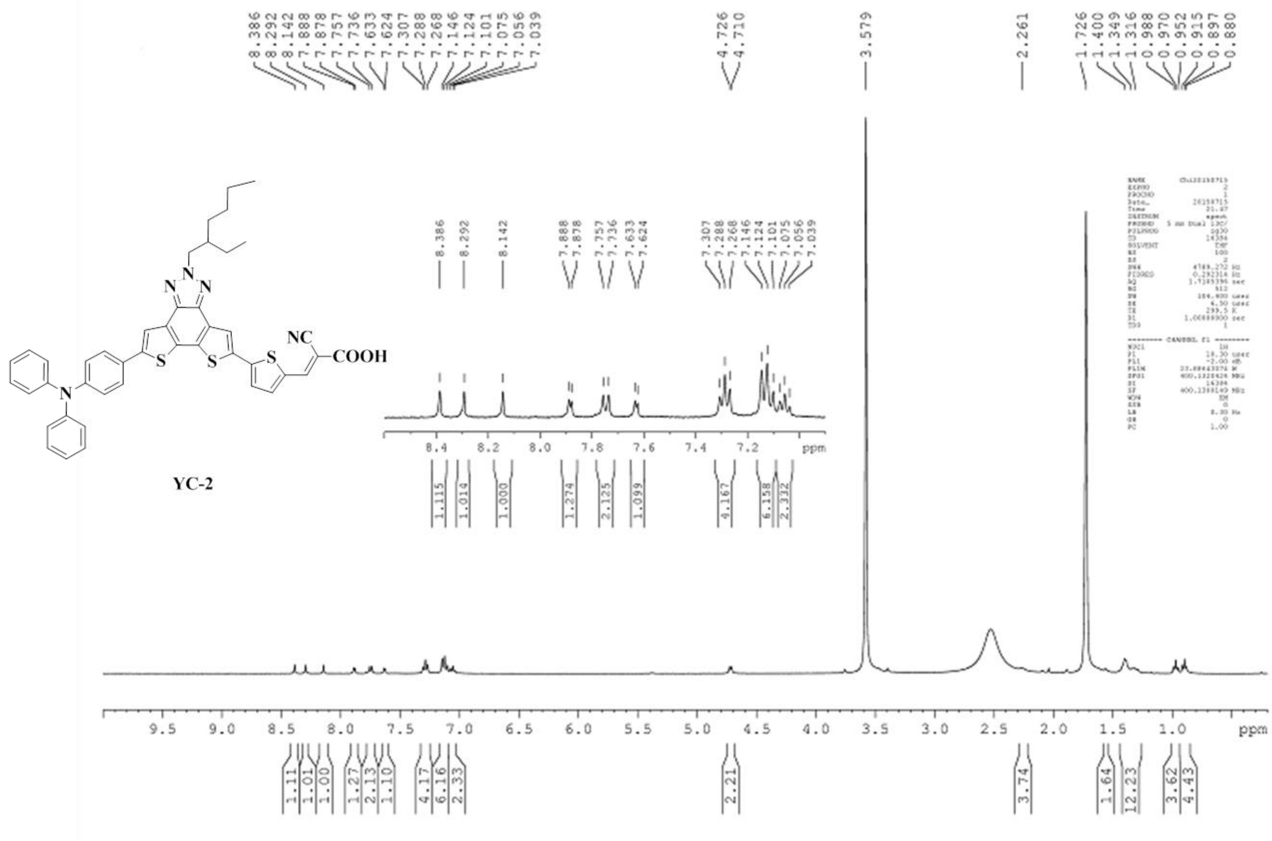
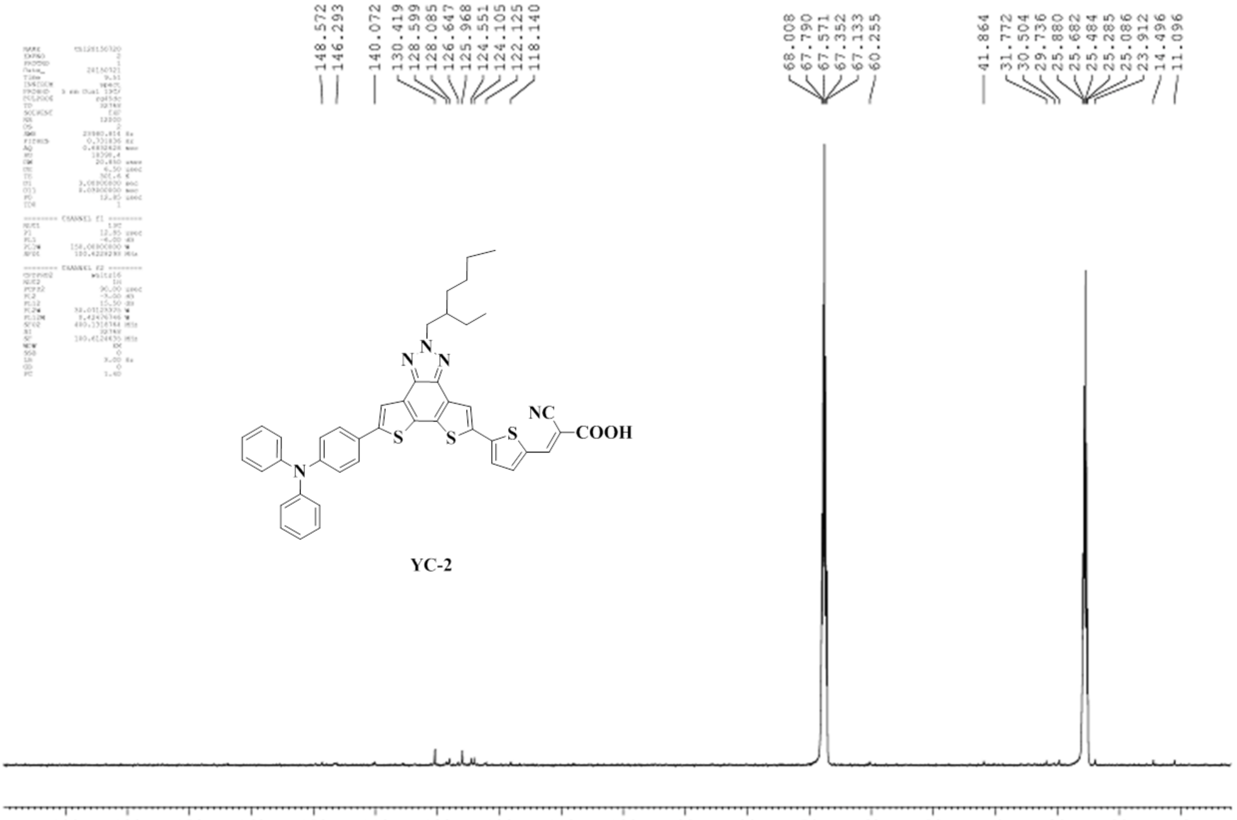

8.386
8.292
8.142
7.888
7.878
7.757
7.736
7.633
7.624
7.307
7.288
7.268
7.146
7.124
7.101
7.075
7.056
7.039
4.726
4.710
3.579
2.261
1.726
1.400
1.349
1.316
0.988
0.970
0.952
0.915
0.897
0.880
NC
COOH
N
S
YC-2
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.115
1.014
1.000
1.274
2.125
1.099
4.167
6.138
2.332
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.11
1.01
1.00
1.27
2.13
1.10
4.17
6.16
2.33
2.21
3.74
1.64
12.23
3.62
4.43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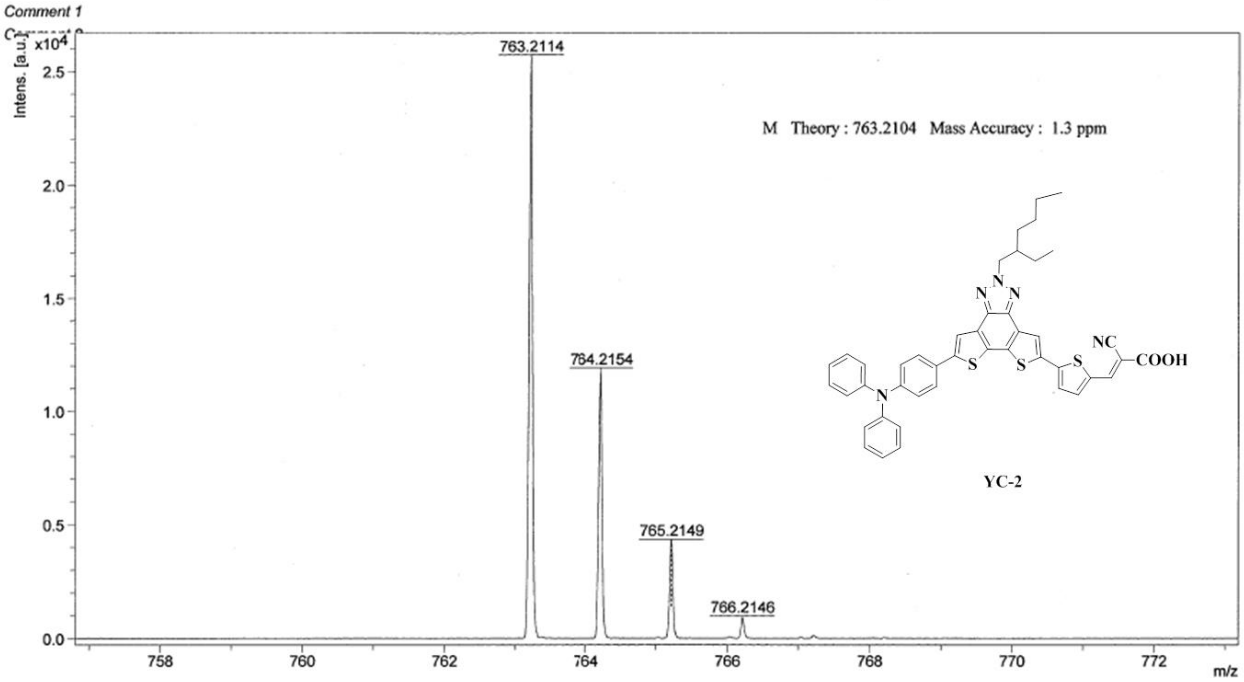
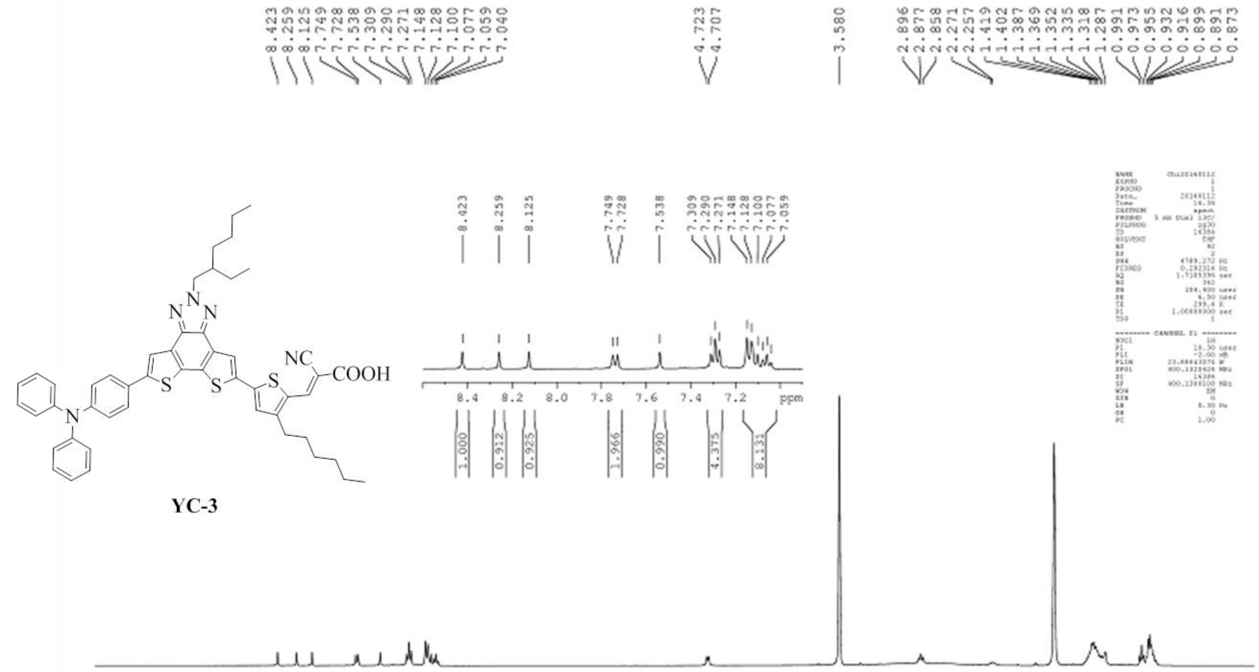
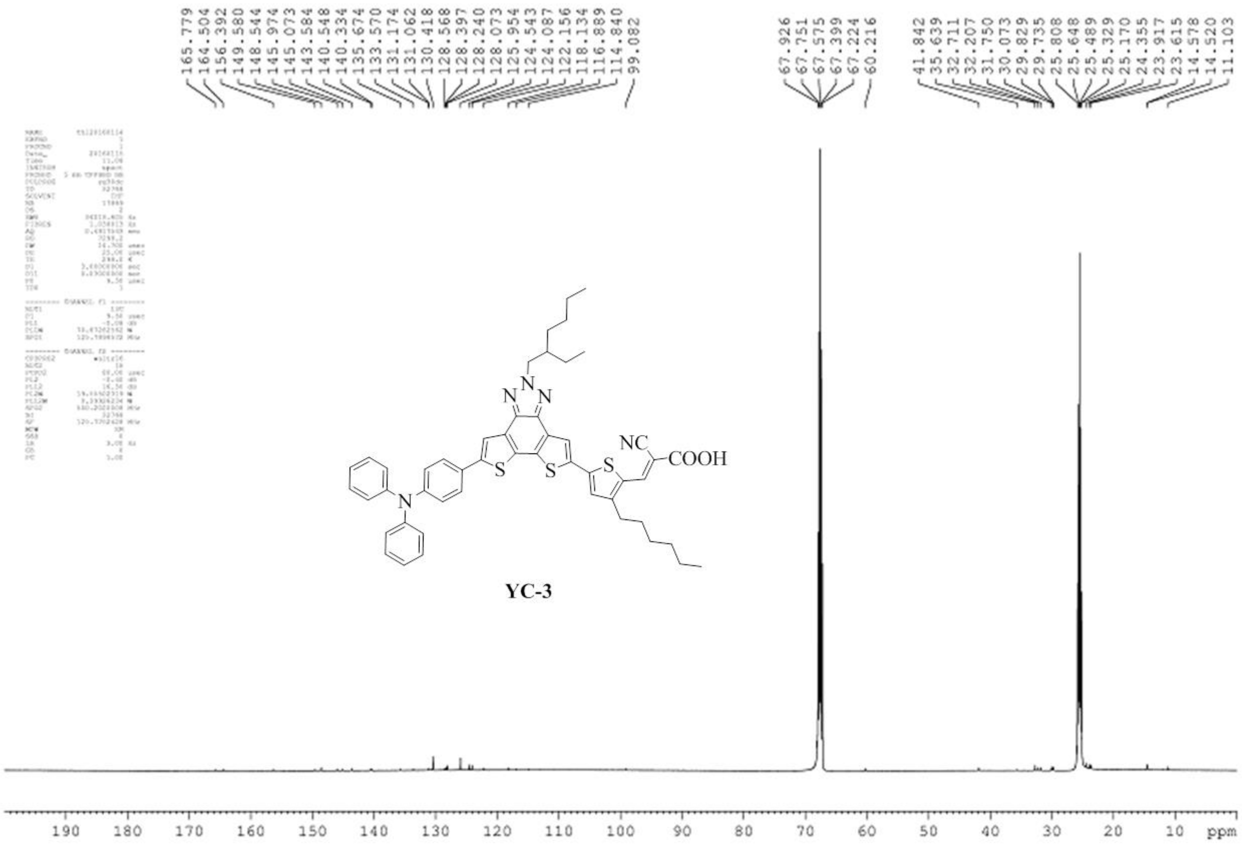
146.293
140.072
130.419
128.599
128.085
126.647
125.968
124.551
124.105
122.125
118.140
68.008
67.790
67.571
67.352
67.133
60.255
41.864
31.772
30.504
29.736
25.880
25.682
25.484
25.285
25.086
23.912
14.496
11.096
NC
COOH
N
S
YC-2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


Comment 1
Intens. [a.u.]
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
763.2114
764.2154
765.2149
766.2146
758
760
762
764
766
768
770
772
m/z
M Theory : 763.2104 Mass Accuracy : 1.3 ppm
N
N
N
S
S
S
NC
COOH

YC-2

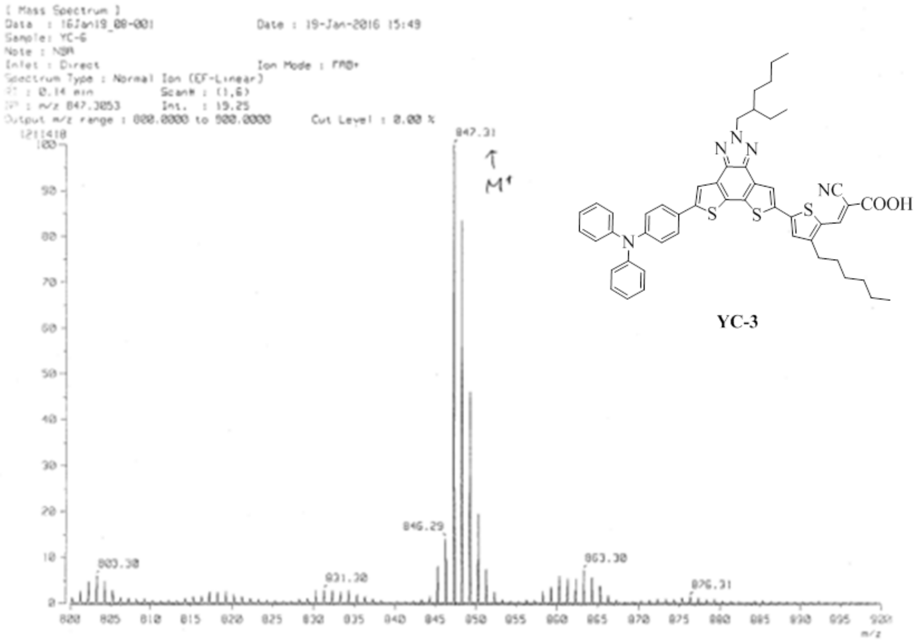

8.423
8.259
8.125
7.749
7.728
7.538
7.309
7.290
7.271
7.148
7.128
7.100
7.077
7.059
7.040
4.723
4.707
3.580
2.896
2.877
2.858
2.271
2.257
1.419
1.402
1.387
1.369
1.352
1.335
1.318
1.287
0.991
0.973
0.955
0.932
0.916
0.899
0.891
0.873
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.000
0.912
0.925
1.966
0.990
4.375
8.131
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.91
0.93
1.97
0.99
4.37
8.13
1.96
3.45
1.54
18.51
13.47
N
N
N
S
S
S
NC
COOH

YC-3



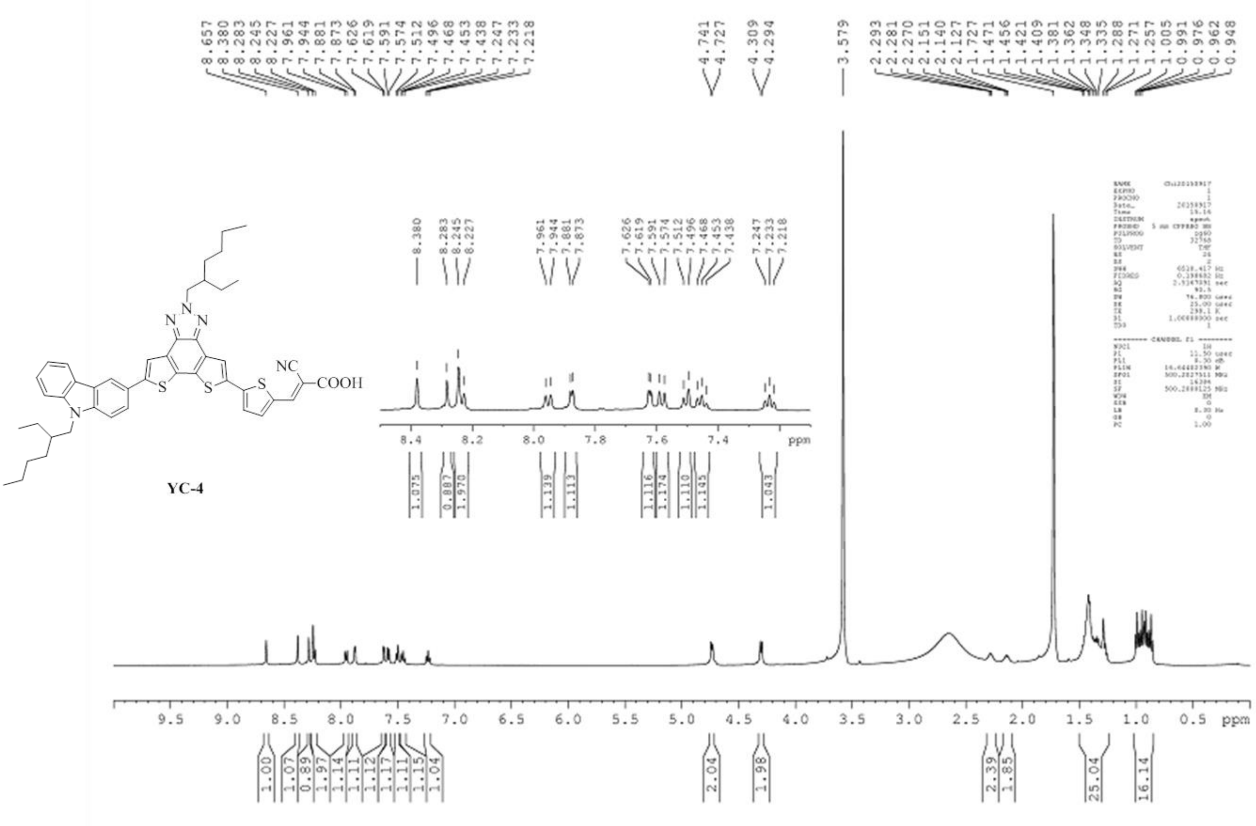
YC-3

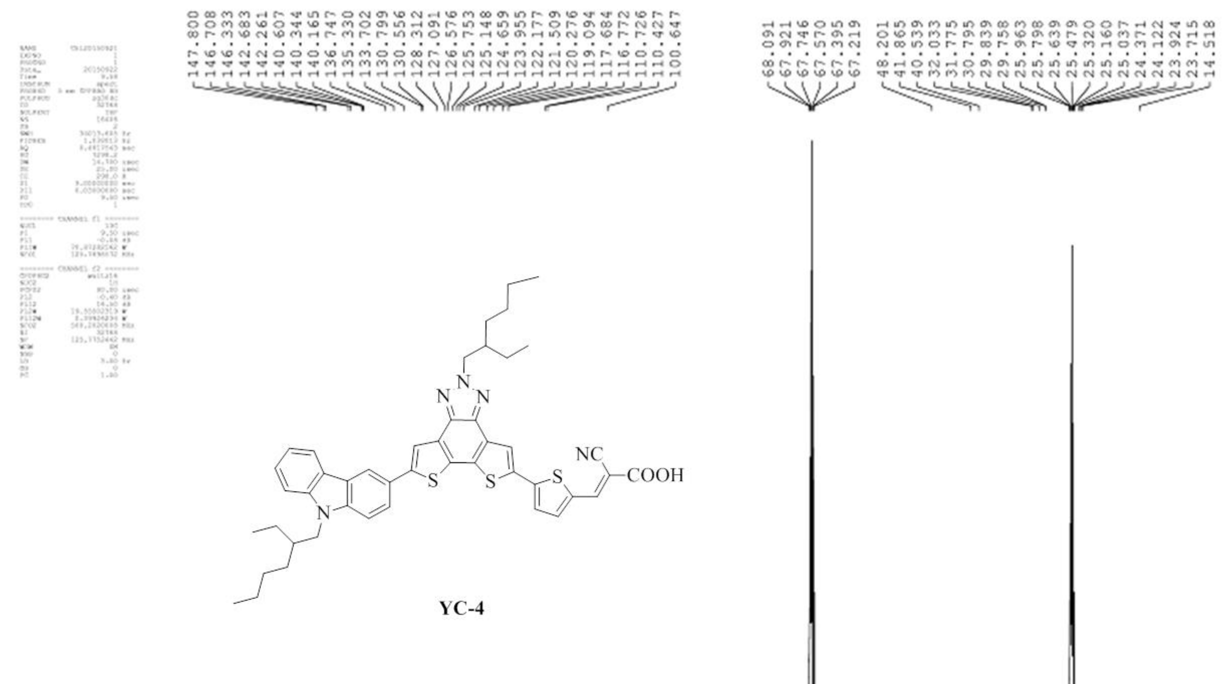
```
[ Elemental Composition ]                                        Page: 1
Data   : 16Jan19_08-001              Date : 19-Jan-2016 15:49
Sample: YC-6
Note : NBA
Inlet : Direct                       Ion Mode : FAB+
RT : 0.14 min                        Scan#: (1,6)
Elements : C 1000/0, H 1000/0, O 2/2, N 5/5, S 3/3
Mass Tolerance      : 10mmu
Unsaturation (U.S.) : -0.5 - 1000.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  847.3053   100.0     +0.5 /  +0.5   32.0  C 50 H 49 O 2 N 5 S 3 =847.3048
```

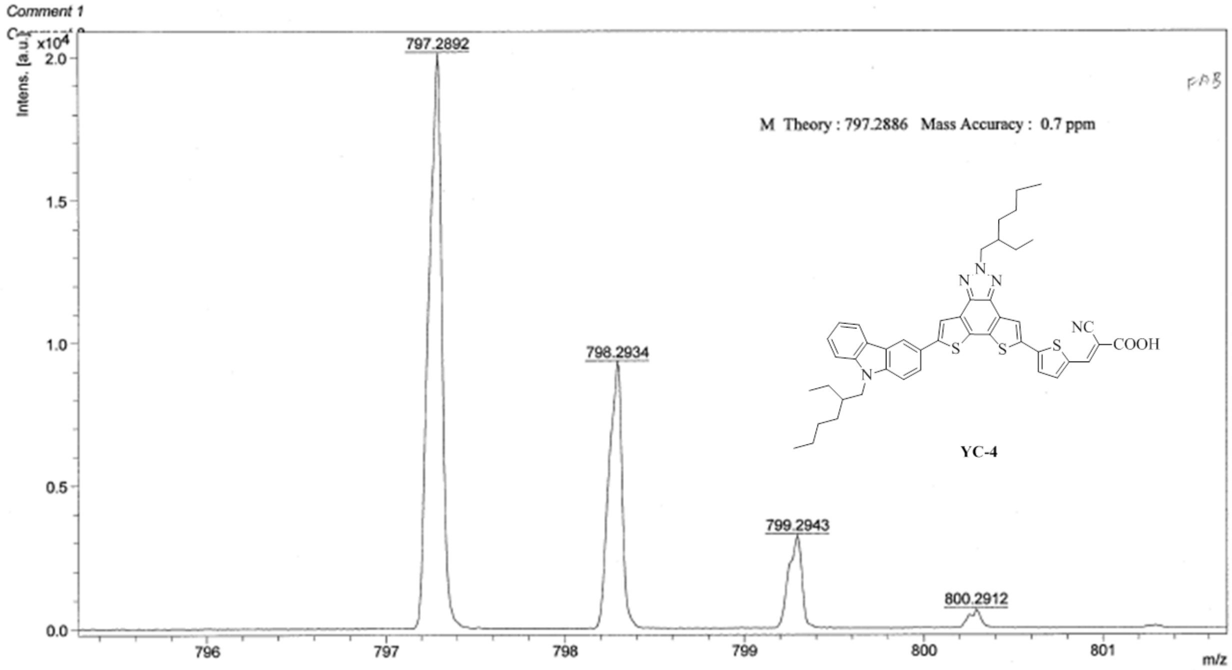


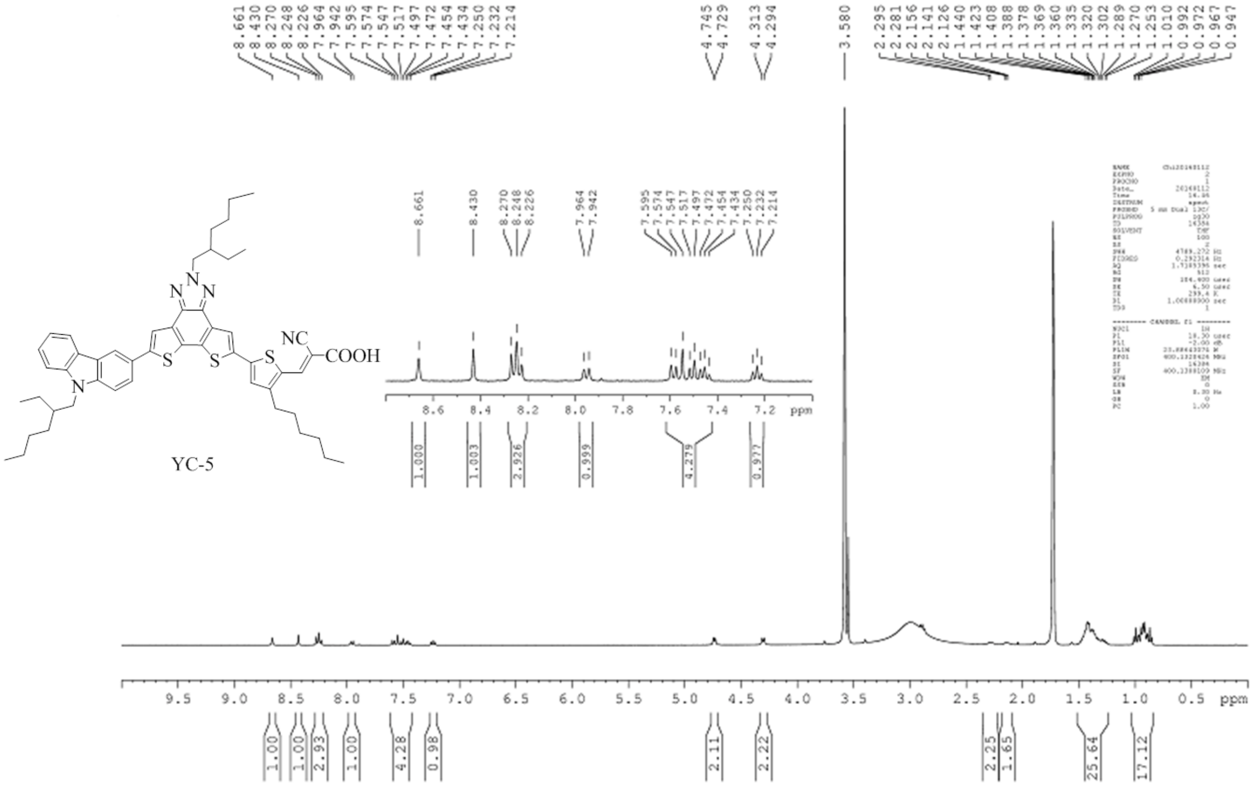
```
[ Mass Spectrum ]
Data   : 16Jan19_08-001              Date : 19-Jan-2016 15:49
Sample: YC-6
Note : NBA
Inlet : Direct                       Ion Mode : FAB+
Spectrum Type : Normal Ion (EF-Linear)
RT : 0.14 min            Scan# : (1,6)
BP : m/z 847.3053        Int.   : 19.25
Output m/z range : 800.0000 to 900.0000      Cut Level : 0.00 %
```

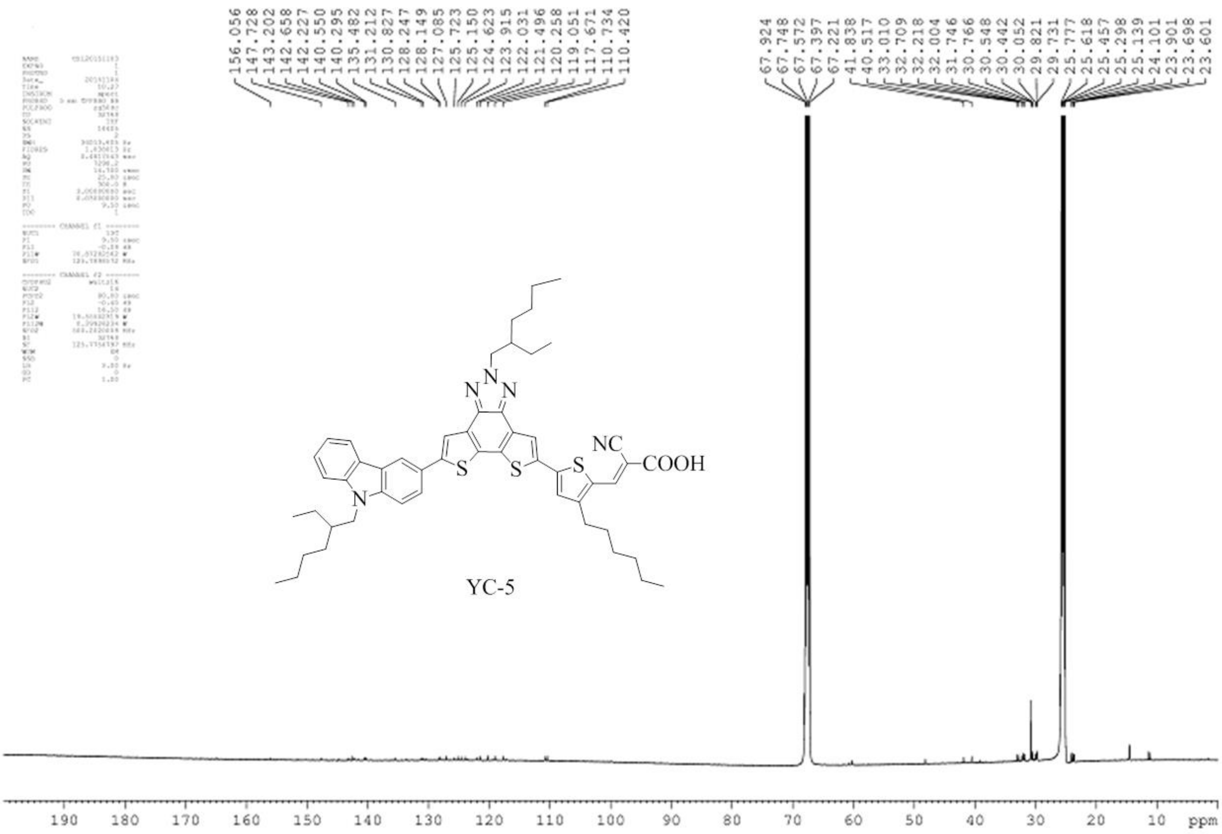
YC-3


8.657 8.380 8.283 8.245 8.227 7.961 7.944 7.881 7.873 7.626 7.619 7.591 7.574 7.512 7.496 7.468 7.453 7.438 7.247 7.233 7.218
4.741 4.727
4.309 4.294
3.579
2.293 2.281 2.270 2.151 2.140 2.127 1.727 1.471 1.456 1.421 1.409 1.381 1.362 1.348 1.335 1.288 1.271 1.257 1.005 0.991 0.976 0.962 0.948
NC
COOH
N
S
YC-4
8.4 8.2 8.0 7.8 7.6 7.4 ppm
1.075 0.887 1.970 1.139 1.113 1.116 1.174 1.110 1.145 1.043
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.07 0.89 1.97 1.14 1.11 1.12 1.17 1.11 1.15 1.04 2.04 1.98 2.39 1.85 25.04 16.14


147.800 146.708 146.333 142.683 142.261 140.607 140.344 140.165 136.747 135.330 133.702 133.799 130.556 128.312 127.091 126.576 125.753 125.148 124.659 123.955 122.177 121.509 120.276 119.094 117.684 116.772 116.726 110.427 100.647
68.091 67.921 67.746 67.570 67.395 67.219
48.201 41.865 40.539 32.033 31.775 30.795 29.839 29.758 25.963 25.798 25.639 25.479 25.320 25.160 25.037 24.371 24.122 23.924 23.715 14.518
NC
COOH
N
S
YC-4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Comment 1
Comment 2
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
797.2892
798.2934
799.2943
800.2912
FAB
M Theory : 797.2886 Mass Accuracy : 0.7 ppm
N
S
NC
COOH
YC-4
796
797
798
799
800
801
m/z

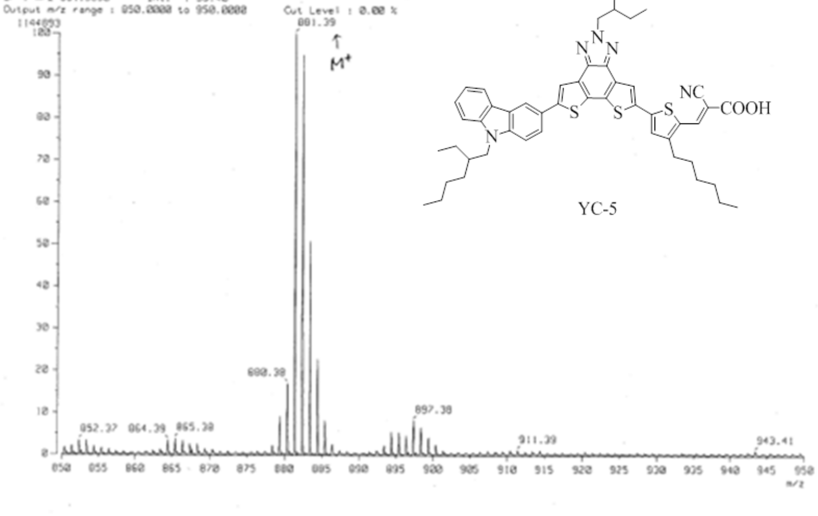

8.661 8.430 8.270 8.248 8.226 7.964 7.942 7.595 7.574 7.547 7.517 7.497 7.472 7.454 7.434 7.250 7.232 7.214
4.745 4.729
4.313 4.294
3.580
2.295 2.281 2.156 2.141 2.126 1.440 1.423 1.408 1.388 1.378 1.369 1.360 1.335 1.320 1.302 1.289 1.270 1.253 1.010 0.992 0.972 0.967 0.947
N
S
NC
COOH
YC-5
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
1.000 1.003 2.926 0.999 4.279 0.977
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.00 2.93 1.00 4.28 0.98 2.11 2.22 2.25 1.65 25.64 17.12



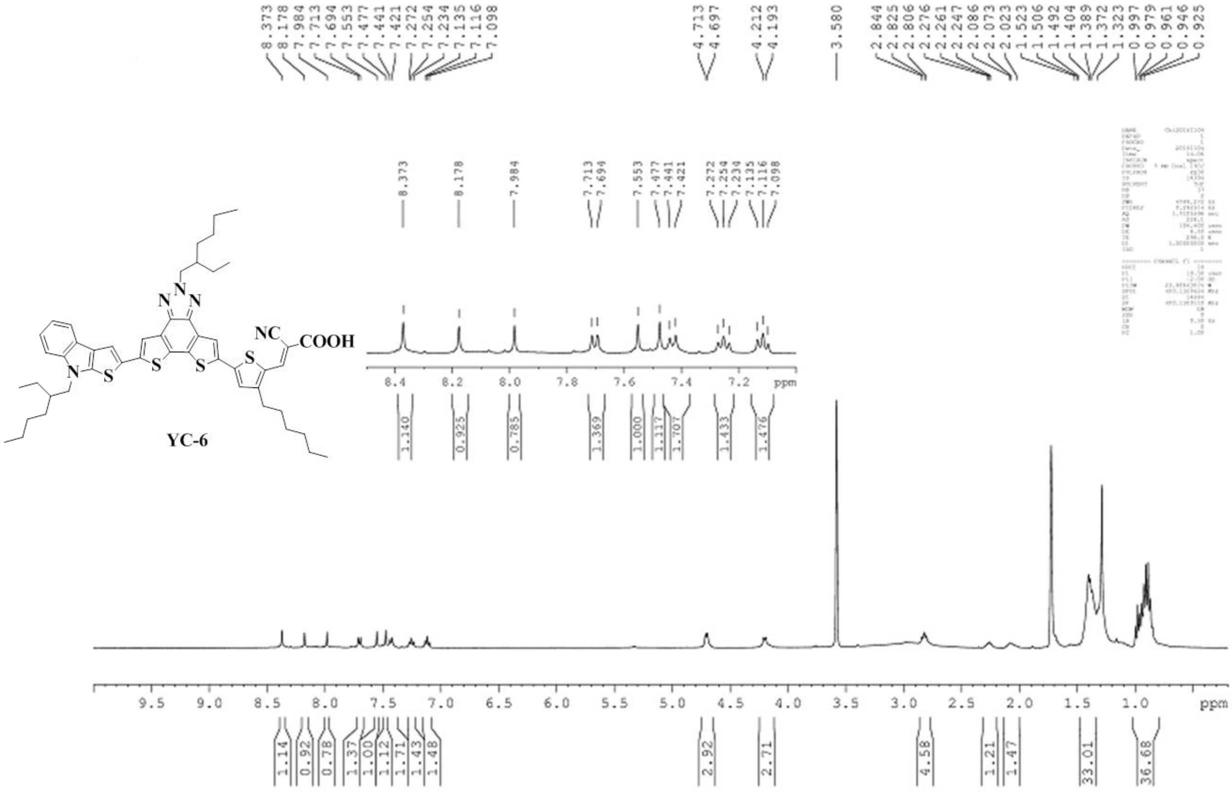
YC-5

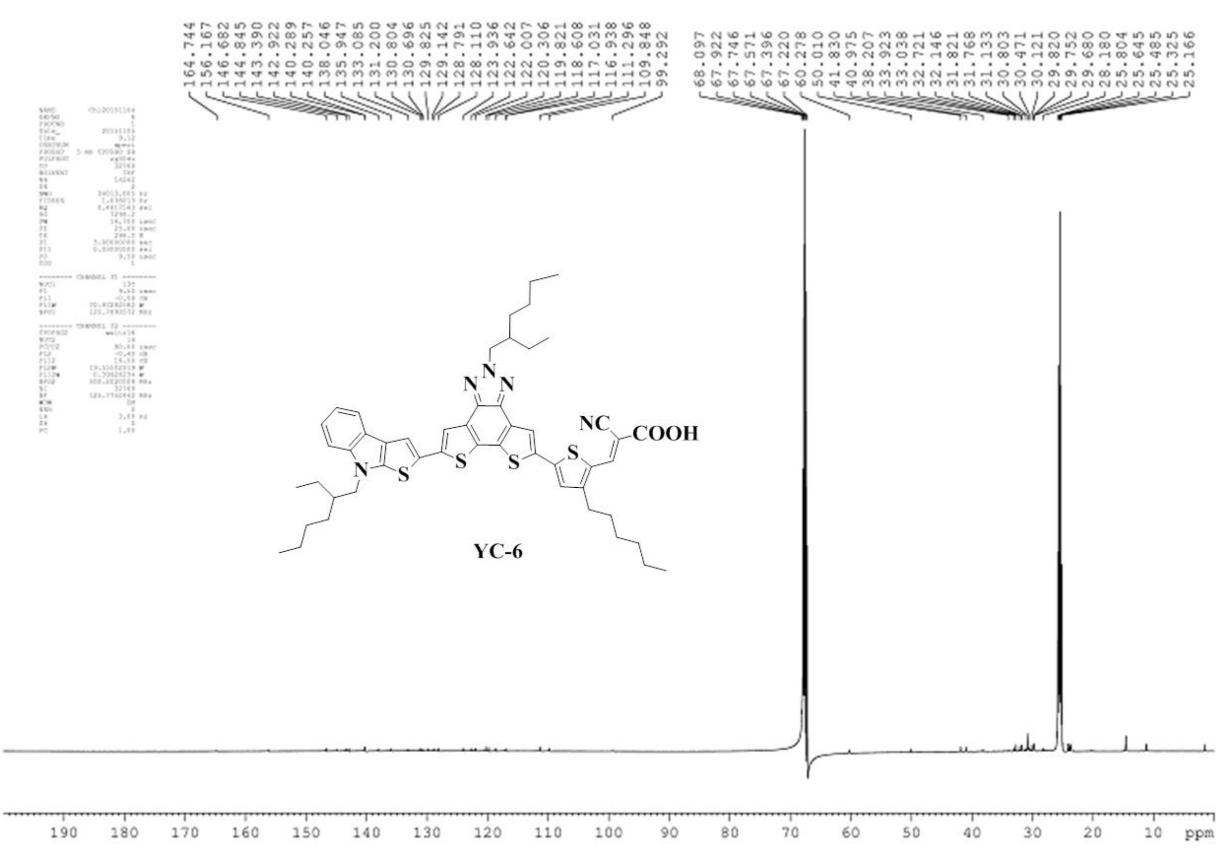
```
[ Elemental Composition ]                                        Page: 1
Data   : 15Sep10_05-001              Date : 10-Sep-2015 17:24
Sample: YC-4
Note : NBA
Inlet : Direct                       Ion Mode : FAB+
RT : 0.12 min                        Scan#: (3,5)
Elements : C 1000/0, H 1000/0, O 2/2, N 5/5, S 3/3
Mass Tolerance         : 10mmu
Unsaturation (U.S.) : -0.5 - 1000.0

Observed m/z  Int%    Err[ppm / mmu]    U.S.  Composition
  881.3850   100.0      +2.2 /   +1.9   29.0  C 52 H 59 O 2 N 5 S 3 = 881.3831
```

```
[ Mass Spectrum ]
Data  : 15Sep10_05-001                Date : 10-Sep-2015 17:24
Sample: YC-4
Note : NBA
Inlet : Direct                        Ion Mode : FAB+
Spectrum Type : Normal Ion [CF-Linear]
RT : 0.12 min             Scan# : (3,5)
BP : m/z 881.3850         Int.   : 36.40
Output m/z range : 850.0000 to 950.0000       Cut Level : 0.00 %
```



YC-5

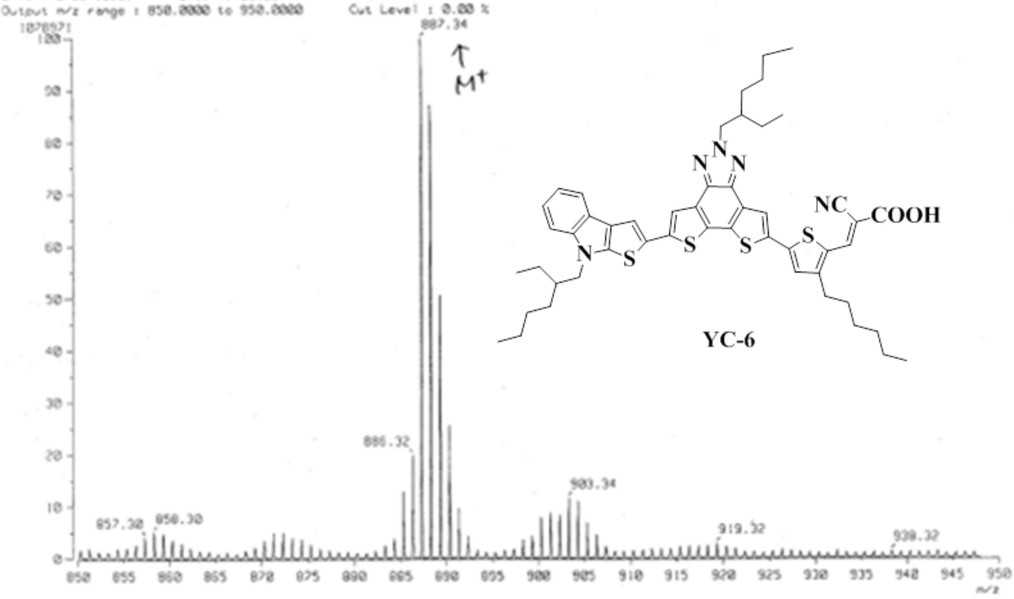

8.373
8.178
7.984
7.713
7.694
7.553
7.477
7.441
7.421
7.272
7.254
7.234
7.135
7.116
7.098
4.713
4.697
4.212
4.193
3.580
2.844
2.825
2.806
2.276
2.261
2.247
2.086
2.073
2.023
1.523
1.506
1.492
1.404
1.389
1.372
1.323
0.997
0.979
0.961
0.946
0.925
N
N
N
NC
COOH
N
S
S
S
S
YC-6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.140
0.925
0.785
1.369
1.000
1.117
1.707
1.433
1.476
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.14
0.92
0.78
1.37
1.00
1.12
1.71
1.43
1.48
2.92
2.71
4.58
1.21
1.47
33.01
36.68


164.744
156.167
146.682
144.845
143.390
142.922
140.289
140.257
138.046
135.947
133.085
131.200
130.804
130.696
129.825
129.142
128.791
128.110
123.936
122.642
122.007
120.306
119.821
118.608
117.031
116.938
111.296
109.848
99.292
68.097
67.922
67.746
67.571
67.396
67.220
60.278
50.010
41.830
40.975
38.207
33.923
33.038
32.721
32.146
31.821
31.768
31.133
30.803
30.471
30.121
29.820
29.752
29.680
28.180
25.804
25.645
25.485
25.325
25.166
N
N
N
NC
COOH
N
S
S
S
S
YC-6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

```
[ Elemental Composition ]                                          Page: 1
Data   : 15Nov13_03-002              Date : 13-Nov-2015 12:50
Sample: YC-5
Note : NBA
Inlet : Direct                       Ion Mode : FAB+
RT : 0.13 min                        Scan#: (1,5)
Elements : C 1000/0, H 1000/0, O 2/2, N 5/5, S 4/4
Mass Tolerance       : 20mmu
Unsaturation (U.S.) : -0.5 - 1000.0

Observed m/z  Int%   Err[ppm / mmu]   U.S.  Composition
  887.3391   100.0     -0.5 /  -0.4   29.0  C 50 H 57 O 2 N 5 S 4
```

= 887.3395

```
[ Mass Spectrum ]
Data   : 15Nov13_03-002          Date : 13-Nov-2015 12:50
Sample: YC-5
Note : NBA
Inlet : Direct                   Ion Mode : FAB+
Spectrum Type : Normal Ion [EF-Linear]
RT : 0.13 min          Scan# : (1,5)
BP : m/z 887.3391      Int.  : 20.58
Output m/z range : 850.0000 to 950.0000      Cut Level : 0.00 %
```



↑ M^+

YC-6