

Supramolecular Co-adsorption on TiO₂ to Enhance the Efficiency of Dye-Sensitized Solar Cells

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1. Materials

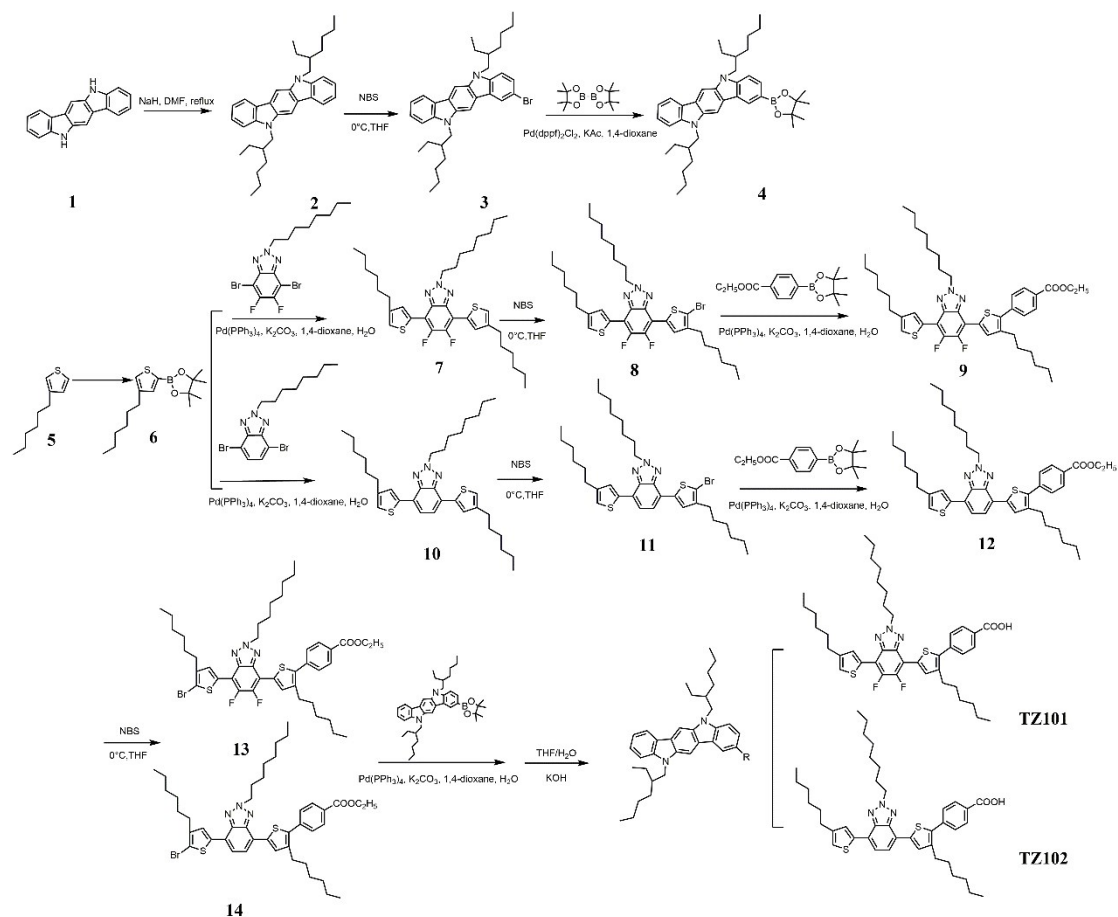
All the solvents and chemicals were purchased from Energy Chemical and used as received unless specifically stated. 18-NRT transparent Titania paste was purchased from Dyesol. The copper electrolyte, (Cu^{III}(tmby)₂TFSI_{1/2}), was purchased from Dyenamo AB., Sweden. The counter electrodes (Pt-coated FTO conducting glass) and Surlyn films (25 μm), TPP200 were achieved from Dalian HeptaChroma SolarTech Co. Ltd.

2. Measurements

¹H NMR spectra were recorded (VARIAN INOVA 500 MHz spectrometer, USA) using tetramethyl silane as standard. MS data were obtained by means of GCT CA156 (UK), HP1100 LC/MSD (USA), and LC/Q-TOF MS (UK). The absorption spectra were recorded on HP8453 (USA). Electrochemical redox potentials were obtained by performing cyclic voltammetry (CV) on an electrochemical workstation (BAS100B, USA). The *J*-*V* curves are recorded at a scan rate of 10 mV s⁻¹. The incident photon-to-current conversion efficiency (IPCE) spectra were obtained by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan). A standard silicon solar cell was used as reference before the measurement.

Ultraviolet photoelectron spectra (UPS) were carried out in an integrated ultrahigh vacuum (UHV) system equipped with multi-technique surface analysis system photoelectron spectrometer (Thermo Fisher, ESCALAB XI+, UK). An Ar ion gun was performed for 15 s before measuring. The scale of the binding energy (BE) was calibrated against Au (4f_{7/2}). UPS were measured with a negative bias voltage (-10 V) applied to the samples using the He (I) (21.2 eV) line in order to shift the spectra from the spectrometer threshold.

3. Synthesis of AJ502, TZ101, TZ102 dyes



Scheme S1. The synthetic routes of **TZ101**

Compound 2 (5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-b] carbazole): A mixture of Indolo [3, 2-*b*] carbazole, 5, 11-dihydro (1) (3 g, 11.7 mmol), NaH (0.62 g, 25.8 mmol) were dissolved in 70 mL DMF and stirred 1 h under room temperature. Then, 2-ethylhexyl bromide (5.0 g, 25.8 mmol) was added and the mixture was allowed to reflux overnight. The cooled resulting liquid was extracted with CH₂Cl₂ and water, dried with MgSO₄. The organic solvent was removed under reduced pressure and the product was purified by silica gel chromatography using petroleum ether: CH₂Cl₂ = 5:1 as yellow oil (80.3%). IR (cm⁻¹) 3051 $\nu_{\text{=CH}}$; 2971 $\nu_{\text{-CH}^{\text{as}}}$; 2853 $\nu_{\text{-CH}^{\text{s}}}$; 1605, 1509, 1475 ν benzene ring; 1467 δ_{CH} ; 1370 $\nu_{\text{-C-N}}$; 721 $\nu_{\text{-(CH}_2\text{)}_n}$. ¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J*=7.5 Hz, 2H), 7.99 (s, 2H), 7.48 (t, *J*=7.5 Hz, 1H), 7.40 (d, *J*=8.0 Hz, 2H), 7.23 (t, *J*=7.0 Hz, 2H), 4.31 - 4.23 (m, 4H), 2.22 - 2.18 (m, 2H), 1.51 - 1.38 (m, 12H), 1.36 - 1.26 (m, 4H), 0.97 - 0.87 (t, 12H). (GC/Q-TOF, *m/z*) Calculated for C₃₄H₄₄N₂ (M⁺): 480.3504; Found, 480.3507.

Compound 3 (2-bromo-5,11-bis(2-ethylhexyl)-5,11-dihydroindolo [3,2 -*b*] carbazole): Compound 2 (2 g, 4.2 mmol) was added in 30 mL THF, NBS (0.74 g, 4.2 mmol) was added slowly under ice bath. The mixture was extracted with CH₂Cl₂ and water and dried with MgSO₄ after string for 2 h. The solvent was removed by rotary evaporation and the product was obtained by chromatography using CH₂Cl₂: petroleum ether (PE) = 1:5 as yellow oil (64.1%). IR (cm⁻¹) 3053 $\nu_{\text{=CH}}$; 2953 $\nu_{\text{-CH}^{\text{as}}}$; 2863 $\nu_{\text{-CH}^{\text{s}}}$; 1611, 1511, 1475 ν benzene ring; 1467 δ_{CH} ; 1376 $\nu_{\text{-C-N}}$; 721 $\nu_{\text{-(CH}_2\text{)}_n}$. ¹H NMR (500 MHz, CDCl₃) δ 8.27 (s, 1H), 8.19 (d, *J*=8.0 Hz, 1H), 7.94 (s, 2H), 7.53- 7.47 (m, *J*=8.5 Hz, 2H), 7.39 (t, *J*=7.0 Hz, 2H), 7.23 (t, *J*=7.0 Hz, 1H), 4.31-4.23 (m, 4H), 2.18 - 2.13 (m, 2H), 1.53 - 1.38 (m, 12H), 1.35-1.26 (m, 4H), 0.97-0.87 (t, 12H). (GC/Q-TOF, *m/z*). Calculated for C₃₄H₄₃N₂Br (M⁺): 558.2610; Found, 558.2613.

Compound 4 (5,11-bis(2-ethylhexyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-dihydroindolo[3,2-*b*] carbazole): Compound 3(1.5 g, 2.68 mmol), bis(pinacolato) diboron (0.68 g, 2.68 mmol), KAc (1.31 g, 13.4

mmol) was added into 50 mL 1,4-dioxane and bubbled with nitrogen for 15min. After that, the Pd (dppf)₂Cl₂ (0.16 g, 2.1 mmol) were added into the flask. The mixture was allowed to heat at 85 °C for 12 h under nitrogen atmosphere and then extracted with CH₂Cl₂ and water. The product was obtained by chromatography using CH₂Cl₂: petroleum ether = 1:2 after removing the organic solvent as yellow solid (67.3%). Melting point: 60-62 °C. IR (cm⁻¹) 3054 ν_{=CH}; 2961 ν_{-CH^{as}}, 2853 ν_{-CH^s}; 1613, 1511, 1485 ν benzene ring; 1467 δ_{-CH}; 1376 ν_{-C-N}; 721 ν_{-(CH₂)_n}. ¹H NMR (500 MHz, CDCl₃) δ 8.68 (s, 1H), 8.17 (d, *J*=8.0 Hz, 1H), 8.01 (s, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 7.91 (s, 1H), 7.54- 7.50 (t, *J*=8.0 Hz, *J*=7.5 Hz, 1H), 7.36 (d, *J*=8.5 Hz, 2H), 7.23 (m, *J*=7.5 Hz, 1H), 4.22-4.13 (m, 4H), 2.25 - 2.07 (m, 2H), 1.47 - 1.24 (m, 28H), 0.97 - 0.87 (t, 12H). (GC/Q-TOF, *m/z*) Calculated for C₄₀H₅₅BN₂O₂ (M⁺): 606.4357; Found, 606.4352.

Compound 6 was synthesized followed the cited literature procedures.¹

Compound 7 (5,6-difluoro-4,7-bis(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazole): Compound 6 (2.0 g, 6.8 mmol) and 4,7-dibromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3] triazole (1.0 g, 2.36 mmol) and K₂CO₃ (4.7 g, 34.0 mmol) were added into 70 mL 1,4-dioxane and 15 mL H₂O. The mixed solution was bubbled with nitrogen for 15min. After that, the Pd (PPh₃)₄ (0.78g, 0.68mmol) were added into the flask. The mixture was allowed to heat at 85 °C for 12 h under nitrogen atmosphere. The resulting reaction was extracted with CH₂Cl₂ and water and the organic solvent was washed three times.^{2,3} The product was purified by silica gel chromatography using petroleum ether: CH₂Cl₂ = 7:1 as light-yellow powder (74.3%). Melting point: 71-73 °C. IR (cm⁻¹) 3097 ν_{=CH}; 2961 ν_{-CH^{as}}, 2854 ν_{-CH^s}; 1600, 1485 ν benzene ring; 1580 ν_{-C=N}; 1457 δ_{-CH}; 1445-ν_{-C-N(electron-withdrawing group)}; 1370 ν_{-C-N}; 722 ν_{-(CH₂)_n}. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (s, 2H), 7.06 (s, 2H), 4.74 (t, 2H), 2.66 (t, 4H), 2.14-2.08 (m, 2H), 1.66 - 1.60 (m, 4H), 1.47 (m, 2H), 1.36 - 1.19 (m, 20H), 0.85-0.78 (t, 9H). (GC/Q-TOF, *m/z*). Calculated for C₃₄H₄₇F₂N₃S₂ (M⁺): 599.3179; Found, 599.3169.

Compound 10 (4,7-bis(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazole) was synthesized as light-yellow powder with the same procedure for Compound 7. Melting point: 67-69 °C. IR (cm⁻¹) 3040 ν_{=CH}; 2956 ν_{-CH^{as}}, 2857 ν_{-CH^s}; 1600, 1505, 1485 ν benzene ring; 1575 ν_{-C=N}; 1469 δ_{-CH}; 1443-ν_{-C-N(electron-withdrawing group)}; 1379 ν_{-C-N}; 726 ν_{-(CH₂)_n}. ¹H NMR (500 MHz, CDCl₃) δ 7.91 (s, 2H), 7.74 (s, 2H), 7.04 (s, 2H), 4.83 (t, 2H), 2.67 (t, 4H), 2.20-2.17 (m, 2H), 1.70-1.68 (m, 4H), 1.43 (m, 2H), 1.39 - 1.19 (m, 20H), 0.89-0.77 (t, 9H). (GC/Q-TOF, *m/z*) Calculated for C₃₄H₄₉N₃S₂ (M⁺): 563.3368; Found, 563.3359.

Compound 8 (4-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluoro-7-(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3] triazole) Compound 7 (0.5 g, 0.83 mmol) was added in 30 mL THF under ice bath, and then N-Bromosuccinimide (NBS) (0.15 g, 0.83 mmol) was added slowly in 5 h, and then string overnight at room temperature. The reaction mixture was poured onto water and extracted with CH₂Cl₂ and the solvent was removed under reduced pressure. The compound 8 was rapidly purified by chromatography (petroleum ether: CH₂Cl₂=2:1) without serious separation after removing the organic solvent as yellow solid. Because the bromine produced is too difficult to separate from the raw material in mixed product.

Compound 11 (4-(5-bromo-4-hexylthiophen-2-yl)-7-(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3] triazole) was synthesized as light-yellow powder with the same procedure for Compound 8.

Compound 9 (ethyl 4-(5-(5,6-difluoro-7-(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-3-hexylthiophen-2-yl)benzoate):The crude compound 8, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl propionate (0.138 g, 0.5 mmol), K₂CO₃(0.3 g, 2.2 mmol), Pd(PPh₃)₄ (0.05 g, 0.044 mmol) were added into 50 mL 1,4-dioxane and 10mL H₂O under N₂ atmosphere. The mixture was heated at 85 °C for overnight. The organic was extracted with CH₂Cl₂ and water and the solvent were removed by rotary evaporation. The residue was purified by chromatography (petroleum ether: CH₂Cl₂=2:1) to provide compound 9 as yellow solid. Melting point: 53-55 °C. IR (cm⁻¹) 3040 ν_{=CH}; 2956 ν_{-CH^{as}}, 2857 ν_{-CH^s}; 1605, 1505, 1485 ν benzene ring; 1584 ν_{-C=N}; 1720 ν_{-C=O}; 1469 δ_{-CH}; 1446-ν_{-C-N(electron-withdrawing group)}; 1369 ν_{-C-N}; 726 ν_{-(CH₂)_n}. ¹H NMR (500 MHz, CDCl₃) δ 8.16 (s, 1H), 8.12 (d, *J* = 8.0

Hz, 2H), 8.10 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.14 (s, 1H) 4.80 (t, 2H), 4.42 (q, 2H), 2.77 (t, 4H), 2.20-2.17 (m, 2H), 1.70-1.68 (m, 4H), 1.43 (m, 2H), 1.39-1.19 (m, 23H), 0.89-0.77 (t, 9H). (GC/Q-TOF, m/z). Calculated for $C_{43}H_{55}F_2N_3O_2S_2$ (M^+): 747.3704; Found, 747.3711.

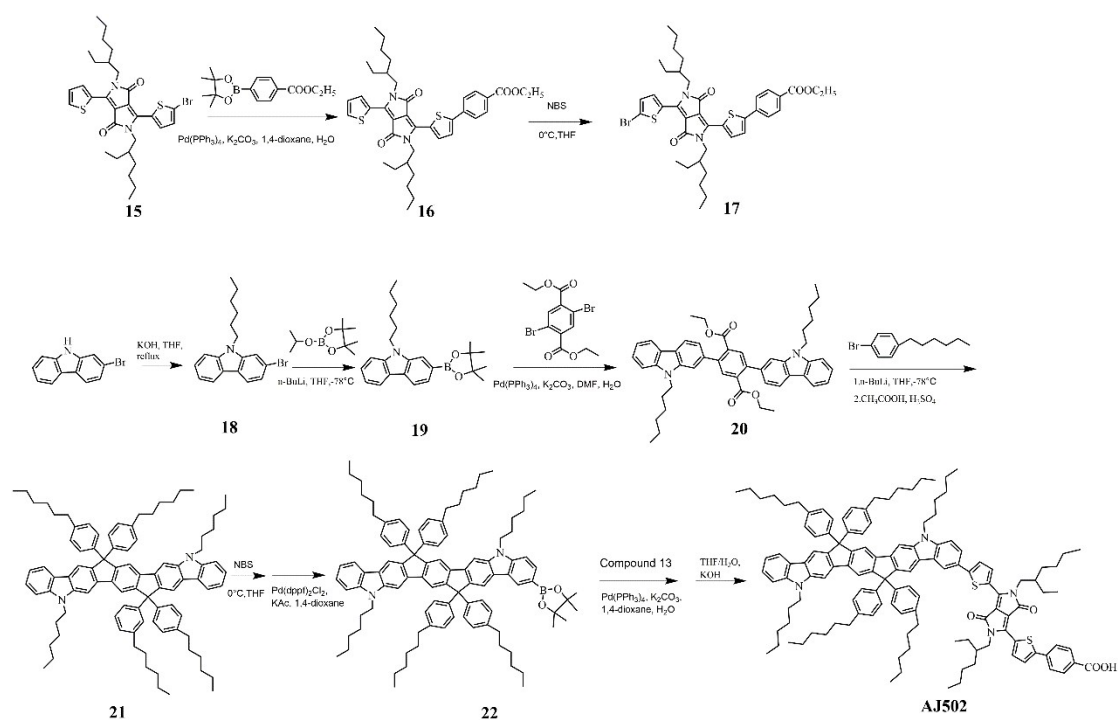
Compound 12 (ethyl 4-(3-hexyl-5-(7-(4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophen-2-yl)benzoate) was synthesized as light-yellow powder with the same procedure for Compound 9. Melting point: 50-52°C. IR (cm^{-1}) 3061 ν_{-CH} ; 2956 $\nu_{-CH^{as}}$, 2846 ν_{-CH^s} ; 1600, 1504, 1464 ν benzene ring; 1572 $\nu_{-C=N}$; 1720 $\nu_{-C=O}$; 1469 δ_{-CH} ; 1440 ν_{-C-N} (electron-withdrawing group); 1379 ν_{-C-N} ; 726 $\nu_{-(CH_2)_n}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 2H), 7.96 (d, 2H), 7.67 (s, 1H), 7.60 (s, $J = 8.5$ Hz, 1H), 7.58 (s, 1H), 6.97 (s, 1H) 4.85 (t, 2H), 4.44 (q, 2H), 2.67 (t, 4H), 2.21-2.17 (m, 2H), 1.7 - 1.68 (m, 4H), 1.45 (m, 2H), 1.45 - 1.19 (m, 23H), 0.92 - 0.85 (t, 9H). (GC/Q-TOF, m/z). Calculated for $C_{43}H_{57}N_3O_2S_2$ (M^+): 711.3892; Found, 711.3889.

Compound 13 (ethyl 4-(5-(7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-3-hexylthiophen-2-yl)benzoate): was synthesized as light-yellow oil with the same procedure for Compound 7. IR (cm^{-1}) 3061 ν_{-CH} ; 2962 $\nu_{-CH^{as}}$, 2841 ν_{-CH^s} ; 1605, 1516, 1458 ν benzene ring; 1581 $\nu_{-C=N}$; 1710 $\nu_{-C=O}$; 1469 δ_{-CH} ; 1449 ν_{-C-N} (electron-withdrawing group); 1379 ν_{-C-N} ; 1281 ν_{-C-O-C} ; 726 $\nu_{-(CH_2)_n}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.11 (d, $J = 8.0$ Hz, 2H), 7.91 (s, 1H), 7.59 (d, $J = 8.5$ Hz, 2H), 4.77 (t, 2H), 4.42 (q, 2H), 2.74 (t, 1H), 2.63 (t, 4H), 1.70-1.68 (m, 4H), 1.45 (m, 2H), 1.37 - 1.18 (dd, 23H), 0.89 (d, 9H). (GC/Q-TOF, m/z). Calculated for $C_{43}H_{54}BrF_2N_3O_2S_2$ (M^+): 825.2809; Found, 825.2812.

Compound 14 (ethyl 4-(5-(7-(5-bromo-4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-3-hexylthiophen-2-yl)benzoate) was synthesized as light-yellow oil with the same procedure for Compound 13. IR (cm^{-1}) 3051 ν_{-CH} ; 2956 $\nu_{-CH^{as}}$, 2862 ν_{-CH^s} ; 1610, 1510, 1458 ν benzene ring; 1569 $\nu_{-C=N}$; 1715 $\nu_{-C=O}$; 1469 δ_{-CH} ; 1442 ν_{-C-N} (electron-withdrawing group); 1385 ν_{-C-N} ; 1281 ν_{-C-O-C} ; 726 $\nu_{-(CH_2)_n}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 2H), 7.95 (s, 2H), 7.72 (s, 1H), 7.67 (s, 1H), 7.57 (d, $J = 8.5$ Hz, 2H), 4.82 (t, 2H), 4.42 (q, 2H), 2.77 (t, 4H), 2.23-2.17 (m, 2H), 1.71-1.66 (m, 4H), 1.47 (m, 2H), 1.43-1.16 (m, 23H), 0.91-0.78 (t, 9H). (GC/Q-TOF, m/z). Calculated for $C_{42}H_{56}BrF_2N_3O_2S_2$ (M^+): 789.2997; Found, 789.2989.

TF101 (4-(5-(7-(5-(5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-b]carbazol-3-yl)-4-hexylthiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-3-hexylthiophen-2-yl)benzoic acid): Compound 13 (200 mg, 0.25 mmol), compound 4 (150 mg, 0.25 mmol), K_2CO_3 (13.8 mg, 1 mmol) in 35 mL 1,4-dioxane, 10 mL H_2O was added under N_2 . After that, the Pd (PPh_3)₄ (28 mg, 0.025 mmol) were added into the flask. The mixture was allowed to heat at 85 °C for 12 h and then extracted with CH_2Cl_2 and water. The combined organic layers are dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a yellow solid, which is purified by chromatography on silica gel using CH_2Cl_2 : CH_3OH (20:1, v/v) to afford 273 mg orange solid (78%). After then, the product was dissolved in H_2O (10 mL), and THF (30 mL), KOH (0.38 g, 0.07 mmol) dissolved in water was added and refluxed 20 h. After cooling to room temperature, 2 M HCl was added slowly in 2 h for neutralizing to pH=1-3, the organic was collected and evaporated to obtain an orange solid. The residue was purified by chromatography using CH_2Cl_2 to provide **TZ101** as an orange solid (260 mg). Melting point: 88-90 °C. IR (cm^{-1}) 3057 ν_{-CH} ; 2953 $\nu_{-CH^{as}}$, 2849 ν_{-CH^s} ; 1598, 1504 ν benzene ring; 1583 $\nu_{-C=N}$; 1687 $\nu_{-C=O}$; 1469 δ_{-CH} ; 1446 ν_{-C-N} (electron-withdrawing group); 1385 ν_{-C-N} ; 1281 ν_{-C-O-C} ; 727 $\nu_{-(CH_2)_n}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.22 (s, 1H), 8.19 (s, 1H), 8.17 (s, 1H), 8.13 (d, $J = 8.5$ Hz, 2H), 7.99 (s, 2H), 7.64 (d, 1H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.44-7.39 (m, $J = 8.5$ Hz, 2H), 7.22 (m, $J = 7.5$ Hz, 1H), 4.80 (t, 2H), 4.25 (d, 4H), 2.88 (d, 2H), 2.23 (m, 2H), 1.81 (m, 4H), 1.58 - 1.22 (m, 32H), 1.00 - 0.83 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) 171.4, 142.7, 142.2, 141.6, 140.4, 140.1, 138.8, 138.5, 137.8, 136.8, 136.7, 132.9, 131.8, 130.5, 129.3, 128.5, 127.9, 127.3, 125.7, 123.9, 123.1, 122.7, 122.5, 121.0, 120.1, 117.95, 110.6, 108.9, 99.1, 72.2, 67.9, 61.8, 56.8, 47.8, 39.4, 31.8, 31.1, 29.7, 29.5, 29.3, 28.9, 26.6, 24.6, 23.1, 22.6, 14.1, 11.0. MS (MALDI-TOF) Calculated for $C_{75}H_{93}F_2N_5O_2S_2$ (M^+): 1197.6739; Found, 1197.6781.

TZ102 (4-(5-(7-(5-(5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-b]carbazol-2-yl)-4-hexylthiophen-2-yl)-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)-3-hexylthiophen-2-yl)benzoic acid) was synthesized as light-yellow powder with the same procedure for Compound TZ101. Melting point: 85-87 °C. IR (cm⁻¹) 3051 $\nu_{\text{=CH}}$; 2958 $\nu_{\text{-CH}}^{\text{as}}$, 2859 $\nu_{\text{-CH}}^{\text{s}}$; 1602, 1504 ν benzene ring; 1573 $\nu_{\text{-C=N}}$; 1682 $\nu_{\text{-C=O}}$; 1464 $\delta_{\text{-CH}}$; 1447 $\nu_{\text{-C-N}}$ (electron-withdrawing group); 1385 $\nu_{\text{-C-N}}$; 1276 $\nu_{\text{-C-O-C}}$; 727 $\nu_{\text{-(CH}_2\text{)}_n}$. ¹H NMR (500 MHz, CDCl₃) δ 8.32 (s, 1H), 8.21 (s, 1H), 8.19 (s, 1H), 8.13 (d, J = 8.5 Hz, 2H), 8.00 (s, 2H), 7.63(d, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.48 (d, 1H), 7.43-7.39 (m, 2H), 7.23 (m, J = 7.5 Hz, 1H), 4.86 (t, 2H), 4.27 (d, 4H), 2.78 (d, 2H), 2.22 (m, 2H), 1.81 (m, 4H), 1.48 - 1.31 (m, 32H), 0.95- 0.86 (m, 21H). ¹³C NMR (100 MHz, CDCl₃) 171.5, 142.2, 142.1, 141.6, 141.1, 140.4, 139.4, 136.9, 136.6, 130.9, 130.5, 129.8, 129.3, 129.0, 127.7, 127.2, 125.7, 125.2, 124.3, 123.0, 122.7, 122.6, 122.1, 121.0, 120.1, 117.9, 108.7, 99.1, 72.3, 61.8, 56.8, 47.8, 39.4, 31.8, 31.1, 30.1, 29.7, 29.3, 29.1, 28.9, 26.7, 24.6, 23.1, 22.7, 14.1, 11.06. MS (MALDI-TOF) Calculated for C₇₅H₉₅N₅O₂S₂ (M⁺): 1161.6927; Found, 1161.6946.



Scheme S2. The synthetic routes of **AJ502**

Compound 16 (ethyl 4-(5-(2,5-bis(2-ethylhexyl)-3,6-dioxo-4-(thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)thiophen-2-yl)benzoate): To a solution of compound 11 (1.0 g, 1.67 mmol), K₂CO₃ (1.15 g, 8.4 mmol), ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (0.5 g, 1.84 mmol), in 50 mL 1,4-dioxane and 10mL H₂O, After that, the Pd(PPh₃)₄ (0.2 g, 0.17 mmol) were added into the flask. The mixture was allowed to heat at 85 °C for 12 h. The mixture was allowed to stir overnight and extracted with CH₂Cl₂ and water. The organic solvent was removed under reduced pressure and the organic solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using CH₂Cl₂ :PE = 1:1 (v/v) to give the product as a blue-dark solid. (75%). Melting point: 156-158 °C. IR (cm⁻¹) 3076 $\nu_{\text{=CH}}$; 2952 $\nu_{\text{-CH}}^{\text{as}}$, 2859 $\nu_{\text{-CH}}^{\text{s}}$; 1605, 1504 ν benzene ring; 1668 $\nu_{\text{-C=O}}$ (acylamino); 1715 $\nu_{\text{-C=O}}$ (carbamido); 1464 $\delta_{\text{-CH}}$; 1442 $\nu_{\text{-C-N}}$; 1275 $\nu_{\text{-C-O-C}}$; 727 $\nu_{\text{-(CH}_2\text{)}_n}$. ¹H NMR (500 MHz, CDCl₃) δ 8.94 (d, J = 4.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 6 Hz, 1H),

7.56 (d, $J = 4.0$ Hz, 1H), 7.28 (d, $J = 5.0$ Hz, 1H), 4.43 (q, 2H), 4.10 - 4.00 (m, 4H), 1.92 (t, 2H), 1.42-1.24 (m, 22H), 0.99 - 0.81 (m, 6H). MS (MALDI-TOF) Calculated for $C_{39}H_{48}N_2O_4S_2$ (M^+): 672.3055; Found, 672.3043.

Compound 17 (ethyl 4-(5-(4-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)thiophen-2-yl)benzoate) was synthesized as blue-dark powder with the same procedure for Compound 3. Melting point: 175-1176 °C. IR (cm^{-1}) 3082 ν_{-CH} ; 2956 $\nu_{-CH^{as}}$, 2852 ν_{-CH^s} ; 1605, 1504 ν benzene ring; 1663 $\nu_{C=O(acylamino)}$; 1720 $\nu_{C=O(carbamido)}$; 1464 δ_{-CH} ; 1446 ν_{C-N} ; 1275 ν_{C-O-C} ; 727 $\nu_{(CH_2)n-}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.95 (d, $J = 4.0$ Hz 2H), 8.66 (d, $J = 4.5$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 4.5$ Hz, 1H), 7.22 (d, $J = 5.0$ Hz 1H), 4.43 (q, 2H), 4.10 - 4.00 (m, 4H), 1.92 (t, 2H), 1.42-1.24 (m, 22H), 0.99 - 0.81 (m, 6H). MS (MALDI-TOF) Calculated for $C_{39}H_{47}BrN_2O_4S_2$ (M^+): 750.2161; Found, 750.2158.

Compound 18 (2-bromo-9-hexyl-9H-carbazole)

A mixture of 2-bromo-9H-carbazole (5.0 g, 20.4 mmol), KOH (2.3g, 40.8 mmol) were dissolved in 70 mL THF and stirred 2 h under room temperature. Then, 2-ethylhexyl bromide (5.0 g, 30.6mmol) was added and the mixture was allowed to reflux overnight.^{4,5}The cooled resulting liquid was extracted with CH_2Cl_2 and water, dried with $MgSO_4$. The organic solvent was removed under reduced pressure and the product was purified by silica gel chromatography using petroleum ether: $CH_2Cl_2 = 5:1$ as white oil product (90.5%). IR (cm^{-1}) 3056 ν_{-CH} ; 2941 $\nu_{-CH^{as}}$, 2852 ν_{-CH^s} ; 1605, 1504 ν benzene ring; 1463 δ_{-CH} ; 1364 $\nu_{C-N(donor)}$; 727 $\nu_{(CH_2)n-}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, $J=8.0$ Hz, 1H), 7.94 (d, $J=8.5$ Hz, 1H), 7.54(s, 1H), 7.48 (t, $J=7.5$ Hz, 1H), 7.40 (d, $J=8.0$ Hz, 1H), 7.33 (d, $J=8.5$ Hz, 1H), 7.23 (t, $J=7.5$ Hz, 1H), 4.24 (t, 2H), 1.88 (m, 2H), 1.40-1.27 (m, 6H), 0.89-0.85 (m, 3H). MS (MALDI-TOF) Calculated for $C_{18}H_{20}BrN$: 329.0779 (M^+); Found, 329.0767.

Compound 19 (9-hexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole) The compound 8 (5.0 g, 13.2 mmol) was dissolved in dry 70 mL THF and stirred under room temperature. Then, n-BuLi (5.8 mL, 14.5 mmol) was added for 1h at -78 °C. After that, Keeping the temperature for 1h, followed isopropoxyboronic acid pinacol ester (2.7 g, 14.7 mmol) was added into the flask to stir overnight. The mixed liquid was extracted with CH_2Cl_2 and water, dried with $MgSO_4$. The organic solvent was removed under reduced pressure and the product was purified by silica gel chromatography using petroleum ether: $CH_2Cl_2 = 2:1$ as white oil product (80.2 %). Melting point: 82-84 °C. IR (cm^{-1}) 3051 ν_{-CH} ; 2971 $\nu_{-CH^{as}}$, 2862 ν_{-CH^s} ; 1600, 1504 ν benzene ring; 1463 δ_{-CH} ; 1374 $\nu_{C-N(donor)}$; 720 $\nu_{(CH_2)n-}$. 1H NMR (500 MHz, $CDCl_3$) δ 8.12(d, $J=7.0$ Hz, 2H), 7.87 (s, 1H), 7.69(s, $J=8.0$ Hz, 1H), 7.47 (t, $J=7.5$ Hz, 1H), 7.40 (d, $J=8.5$ Hz, 1H), 7.23 (t, $J=7.5$ Hz, 1H), 4.35 (t, 2H), 1.88 (m, 2H), 1.40-1.28 (m, 18H), 0.89-0.85 (m, 3H). MS (MALDI-TOF) Calculated for $C_{24}H_{32}BNO_2$ (M^+): 377.2526; Found, 377.2517.

Compound 20 (diethyl 2,5-bis(9-hexyl-9H-carbazol-2-yl) terephthalate): A mixture of compound 14(1.5 g 4.0 mmol), diethyl 2,5-dibromoterephthalate (3.0 g, 8 mmol), K_2CO_3 (2.76 g, 20 mmol) were added in 80 mL DMF and H_2O 16mL under nitrogen. The mixed solution was bubbled with nitrogen for 15min. After that, the Pd (PPh_3)₄ (0.46 g, 0.4 mmol) were added into the flask. The solution was allowed to heat at 110 °C for overnight, and the solvent was extracted with CH_2Cl_2 and H_2O . The organic solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel by CH_2Cl_2 : petroleum ether=1:2 to give the product as a yellow solid. (73.2%). Melting point: 168-169 °C. IR (cm^{-1}) 3056 ν_{-CH} ; 2956 $\nu_{-CH^{as}}$, 2862 ν_{-CH^s} ; 1605, 1580, 1450 ν benzene

ring; 1726 $\nu_{\text{C=O(carbamido)}}$; 1474 δ_{CH} ; 1369 $\nu_{\text{C-N(donor)}}$; 1276 $\nu_{\text{C-O-C}}$; 727 $\nu_{\text{(CH}_2\text{)}_n}$. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.14 (d, $J = 7.5$ Hz, 4H), 7.96 (s, 2H), 7.51-7.48 (m, 2H), 7.45-7.46 (d, $J = 7.5$ Hz, 4H), 7.27-7.24 (m, 4H), 4.34 (q, 4H), 4.09 (t, 4H), 1.92-1.86 (m, 4H), 1.52 (m, 4H), 1.43-1.27 (m, 14H), 0.88 (t, 6H). (GC/Q-TOF, m/z) Calculated for $\text{C}_{48}\text{H}_{52}\text{N}_2\text{O}_4$ (M^+): 720.3927; Found, 720.3931.

Compound 21 (5,14-dihexyl-8-(3-hexylphenyl)-8,17,17-tris(4-hexylphenyl)-5,8,14,17-tetrahydro-s-indaceno[1,2-b:5,6-b']dicarbazole): The 4-hexyl-1-bromobenzene (4.5 g, 18.7 mmol) were added in dry THF 70 mL under -78°C . After the reaction was stirred for 10 min, *n*-BuLi (8.2 mL, 20.5 mmol, 2.5 M in hexane) was added slowly for 40 min and kept the temperature for 1h, followed compound 20 (2.7 g, 3.7 mmol) was added into the flask to stir overnight. After that, the mixture was extracted with CH_2Cl_2 and H_2O , the solvent was removed under reduced pressure. Then, the solid was dissolved in CH_3COOH (100 mL), one drop of concentrated H_2SO_4 was added in the solvent. The solution was allowed to heat at 110°C for 6h. The mixture was extracted and the organic solvent was removed to give the product as a yellow solid. The crude product was purified by column chromatography on silica gel by CH_2Cl_2 : petroleum ether=1:5 to give the product as a yellow solid. (65.8%). Melting point: $85\text{-}87^\circ\text{C}$. IR (cm^{-1}) 3051 $\nu_{\text{=CH}}$; 2956 $\nu_{\text{-CH}^{\text{as}}}$; 2862 $\nu_{\text{-CH}^{\text{s}}}$; 1600, 1450 ν benzene ring; 1464 δ_{CH} ; 1363 $\nu_{\text{C-N(donor)}}$; 1276 $\nu_{\text{C-O-C}}$; 727 $\nu_{\text{(CH}_2\text{)}_n}$. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.20 (s, 2H), 7.89 (s, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.62 (s, 2H), 7.49-7.46 (t, $J = 7.5$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 8H), 7.22 (d, 2H), 7.08 (t, $J = 8.0$ Hz, 8H), 4.34 (q, 4H), 2.57-2.50 (m, 8H), 1.93-1.87(m, 4H), 1.60 - 1.56 (m, 8H), 1.33- 1.26 (m, 36H), 0.92-0.88 (t, 18H). (GC/Q-TOF, m/z) Calculated for $\text{C}_{92}\text{H}_{108}\text{N}_2$ (M^+): 1240.8513. Found, 1240.8520.

Compound 22 (5,14-dihexyl-8,8,17,17-tetrakis(4-hexylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,8,14,17-tetrahydro-s-indaceno[1,2-b:5,6-b']dicarbazole): NBS (0.28 g, 1.6 mmol) was added in a solution of compound 16 (2.0g, 1.6mmol) in 60 mL THF at 0°C in 2 h. The mixture was stirred overnight and then extracted with dichloromethane and water, the organic solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel by CH_2Cl_2 : petroleum ether =1:4 to give the product as a yellow solid. Then, to a mixture of the compound obtained 1.48 g (estimated the monobromide compound is 70%), bis(pinacolato) diboron (0.28 g, 1.12 mmol), KAc (0.55 g, 5.6 mmol) dissolved in 1,4-dioxane 50 mL in a round bottom flask. The mixed solution was bubbled with nitrogen for 15 min. After that, the $\text{Pd(dppf)}_2\text{Cl}_2$ (17 mg, 0.015 mmol) were added into the flask. is heated at 85°C for overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water, then purified by column chromatography on silica gel by CH_2Cl_2 : petroleum ether (1:2, v/v) to obtain yellow solid. Melting point: $129\text{-}131^\circ\text{C}$. IR (cm^{-1}) 3041 $\nu_{\text{=CH}}$; 2951 $\nu_{\text{-CH}^{\text{as}}}$; 2857 $\nu_{\text{-CH}^{\text{s}}}$; 1601, 1450 ν benzene ring; 1465 δ_{CH} ; 1363 $\nu_{\text{C-N(donor)}}$; 1273 $\nu_{\text{C-O-C}}$; 727 $\nu_{\text{(CH}_2\text{)}_n}$. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.21 (s, 1H), 8.12 (s, 1H), 8.05 (s, 1H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.94 (s, 2H), 7.89 (d, 1H), 7.77 (d, 1H), 7.62 (d, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz 8H), 7.22 (t, $J = 7.0$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 8H), 4.35 (t, 4H), 2.56 (d, 8H), 1.90 (m, 4H), 1.60 - 1.56 (m, 8H), 1.33- 1.26 (m, 48H), 0.99- 0.85 (m, 18H). MS (MALDI-TOF) m/z Calculated for $\text{C}_{98}\text{H}_{119}\text{N}_2\text{O}_2\text{B}$ (M^+): 1366.9365; Found, 1366.9357.

AJ502 (4-(5-(4-(5-(5,14-dihexyl-8,8,17,17-tetrakis(4-hexylphenyl)-5,8,14,17-tetrahydro-s-indaceno[1,2-b:5,6-b']dicarbazol-3-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-

yl)thiophen-2-yl)benzoic acid): To a solution of compound 22 (150 mg, 0.11 mmol), compound 17 (150 mg, 0.2mmol), K_2CO_3 (13.8 mg, 1 mmol) in 30 mL 1,4-dioxane and 5mL H_2O under nitrogen, the mixture was stirred overnight. The mixed solution was bubbled with nitrogen for 15min. After that, the $Pd(PPh_3)_4$ (12.7 mg, 0.011 mmol) were added into the flask. is heated at 85 °C for overnight. After cooling to room temperature, the mixture was extracted with dichloromethane and water. After removal of solvent, the crude product was purified on a silica-gel column chromatography with $CH_2Cl_2:CH_3OH=20:1$ as eluent to give a product as blue solid (66.3%). After then, the product was dissolved in H_2O (10 mL) and THF (30 mL), KOH (440 mg, 3.17 mmol) dissolved in water was added and refluxed 36 h. After cooling to room temperature, 2 M HCl was added slowly in 2 h for neutralizing to $pH=1-3$, the organic was collected and evaporated to obtain an orange solid. The residue was purified by chromatography using CH_2Cl_2 to provide **AJ502** as a dark blue solid (95%). Melting point:158-160 °C. IR (cm^{-1}) 3051 $\nu_{=CH}$; 2953 $\nu_{-CH^{as}}$, 2849 ν_{-CH^s} ; 1602, 1504 ν benzene ring;1657 $\nu_{-C=O(acylamino)}$; 1682 $\nu_{-C=O(carboxyl)}$; 1460 δ_{-CH} ; 1370 ν_{-C-N} ; 1271 ν_{-C-O-C} ; 727 $\nu_{-(CH_2)_m}$. 1H NMR (500 MHz, $CDCl_3$) δ 1H NMR (500 MHz, $CDCl_3$) 8.99 (d, $J = 4.0$ HZ, 2H), 8.26 (s, 2H), 8.14 (d, $J = 8.0$ HZ, 2H), 7.99 (s, 2H), 7.91 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.0$ HZ, 2H), 7.63 (s, 2H), 7.53 (d, $J = 4.0$ Hz, 1H), 7.50-7.46 (t, $J = 7.5$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz 2H), 7.30 (d, $J = 8.0$ Hz, 8H), 7.24 (d, $J = 5.0$ Hz, 1H), 7.22 (d, 1H), 7.09 (t, $J = 8.0$ Hz, 8H), 4.35(d, 4H), 4.13 (t,4H), 2.6-2.5 (m, 8H), 1.93-1.87 (m, 6H), 1.60 - 1.56 (m, 8H), 1.54- 1.26 (m, 58H), 1.05 - 0.77 (t, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) 169.9, 161.6, 161.1, 155.6, 152.0, 146.6, 144.3, 143.6, 141.5, 141.4, 141.1, 140.9, 140.7, 140.5, 140.3, 139.5, 139.2, 138.5, 138.2, 137.7, 137.4, 136.3, 133.6, 130.8, 130.5, 128.9, 128.8, 127.2, 125.4, 123.1, 120.2, 117.9, 108.8, 107.1, 99.7, 72.1, 64.5, 46.1, 43.2, 42.5, 39.4, 38.6, 35.6, 31.9, 31.7, 31.5, 31.2, 30.0, 29.6, 29.2, 27.2, 26.6, 23.7, 22.4, 14.2, 10.9. MS (MALDI-TOF) m/z Calculated for $C_{129}H_{150}N_4O_4S_2$ (M^+): 1883.1099; Found, 1884.1145.

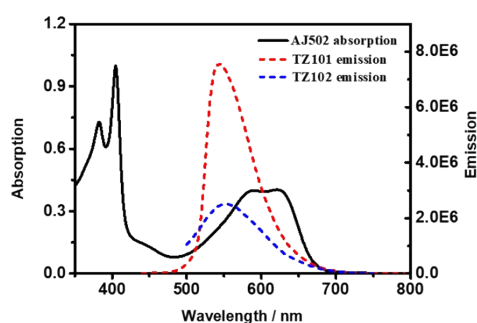
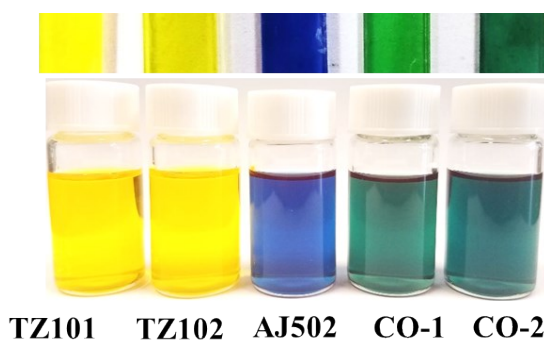


Figure S1. Emission spectra of single dye dissolved in PhMe



TZ101 TZ102 AJ502 CO-1 CO-2

Figure S2. The photographs of dyes and co-sensitizations in solution and on TiO₂ film.

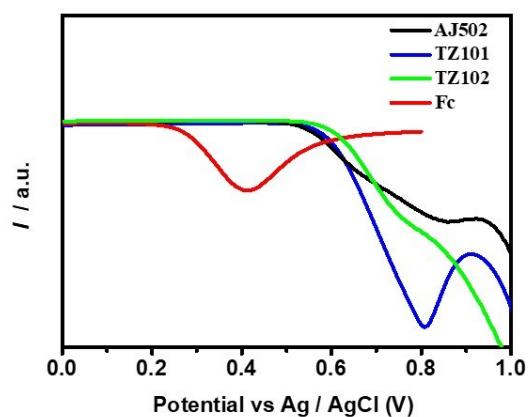


Figure S3. DPV curves of AJ502, TZ101, and TZ102 measured in acetonitrile with 0.1 M TBAPF₆ as supporting electrolyte. Fc/Fc⁺ added as inner standard.

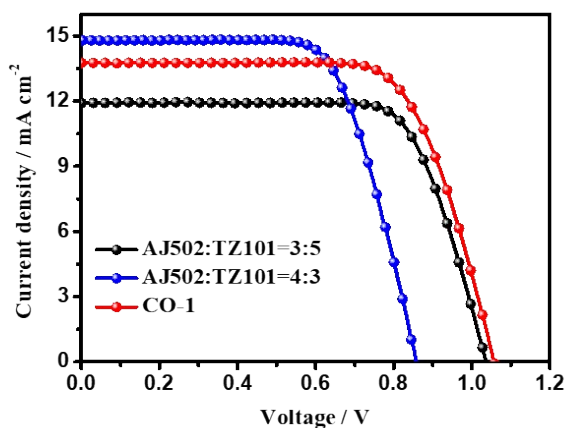


Figure S4. Data for devices based on different concentration ratios.

Table S1 Photovoltaic performance of DSSCs sensitized by different concentration ratios

| Dye | Concentration ratios | J_{sc} [mA·cm ⁻²] | V_{oc} [V] | FF [%] | PCE [%] |
|-------------|----------------------|---------------------------------|--------------|----------|---------|
| AJ502:TZ101 | 4:3 | 15.7 | 0.87 | 68.7 | 9.4 |
| AJ502:TZ101 | 3:5 | 11.9 | 1.03 | 73.6 | 9.1 |

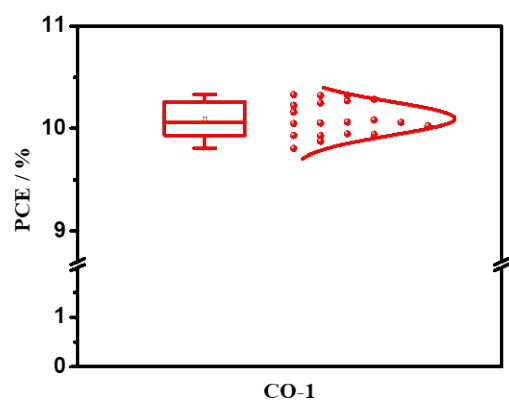


Figure S5. PCE performance based on 20 fresh devices sensitized by Co-1

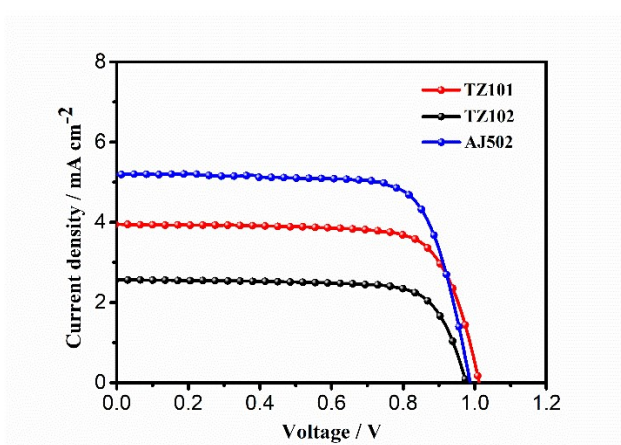


Figure S6. J - V curves of DSSCs sensitized by AJ502, TZ101, TZ102 with CDCA.

Table S2 Photovoltaic performance parameters of DSSCs sensitized by AJ502, TZ101, TZ102 with 2M CDCA

| Dye | J_{sc} [mA·cm ⁻²] | V_{oc} [V] | FF [%] | PCE [%] |
|-------|------------------------------------|-----------------|-------------|------------|
| AJ502 | 5.85 | 0.98 | 74.5 | 4.30 |
| TZ101 | 3.94 | 1.01 | 74.7 | 2.98 |
| TZ102 | 2.55 | 0.97 | 75.4 | 1.87 |

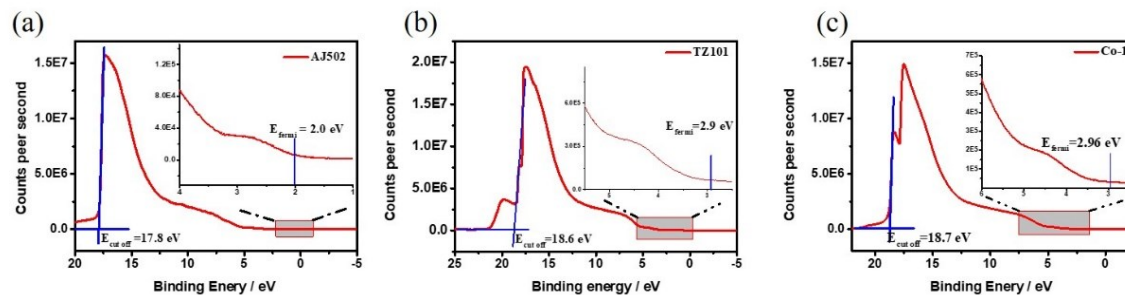


Figure S7. Ultraviolet Photoelectron Spectra of (a) AJ502, (b) TZ101, (c) Co-1 deposited on TiO₂

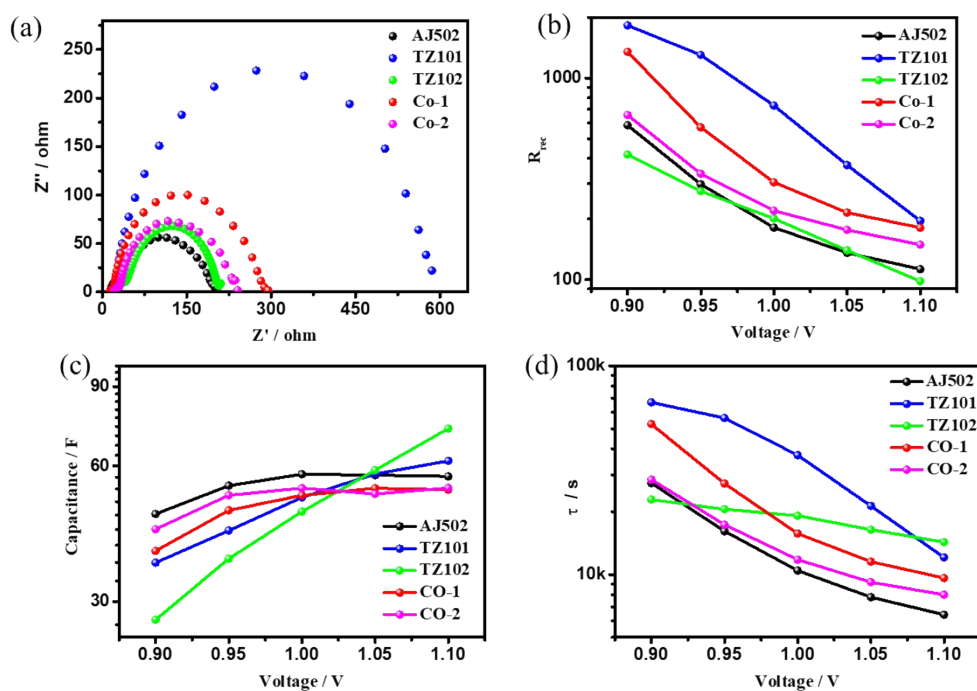


Figure S8. EIS analysis data: (a) Nyquist plots under forward bias of 1.05 V, (b) recombination resistance R_{rec} (c) chemical capacitance C_{μ} , and (d) electron lifetime τ plots.

Table S3. Photovoltaic parameters of containing DPP dyes based on traditional electrolyte redox couples under standard AM1.5G, 100 mW cm⁻² condition.

| Dyes | electrolyte | J_{sc} (mA cm ⁻²) | V_{oc} (V) | FF (%) | PCE (%) | Ref. |
|-------------|---|---------------------------------|--------------|--------|---------|------|
| DPP-I | I ⁻ /I ₃ ⁻ | 9.78 | 0.605 | 70 | 4.14 | 6 |
| DPP-II | I ⁻ /I ₃ ⁻ | 2.39 | 0.508 | 68 | 0.83 | 6 |
| QS-DPP-I | I ⁻ /I ₃ ⁻ | 10.73 | 0.659 | 61 | 4.32 | 7 |
| 3+ QS-DPP-I | I ⁻ /I ₃ ⁻ | 12.99 | 0.685 | 67 | 5.95 | 7 |
| DB | Co ²⁺ /Co ³⁺ | 13.21 | 0.757 | 72.7 | 7.3 | 8 |
| DB/D35 | Co ²⁺ /Co ³⁺ | 15.6 | 0.797 | 70.1 | 8.7 | 8 |
| DPP01 | I ⁻ /I ₃ ⁻ | 8.66 | 0.55 | 72 | 3.41 | 9 |
| DPP02 | I ⁻ /I ₃ ⁻ | 5.04 | 0.52 | 73 | 1.92 | 9 |
| DPP03 | I ⁻ /I ₃ ⁻ | 11.9 | 0.64 | 65 | 4.93 | 9 |
| DPP04 | I ⁻ /I ₃ ⁻ | 5.49 | 0.58 | 72 | 2.31 | 9 |
| DPP07 | I ⁻ /I ₃ ⁻ | 15.6 | 0.676 | 73 | 7.67 | 10 |
| | Co ²⁺ /Co ³⁺ | 15.5 | 0.735 | 76 | 8.74 | 10 |
| DPP10 | I ⁻ /I ₃ ⁻ | 12.4 | 0.655 | 70 | 5.67 | 10 |
| | Co ²⁺ /Co ³⁺ | 12.7 | 0.693 | 76 | 6.7 | 10 |
| DPP12 | I ⁻ /I ₃ ⁻ | 16.1 | 0.717 | 67 | 7.74 | 10 |
| | Co ²⁺ /Co ³⁺ | 14.3 | 0.737 | 76 | 8.01 | 10 |
| YCD01 | I ⁻ /I ₃ ⁻ | 13.4 | 0.76 | 73 | 7.43 | 11 |
| TDPP | I ⁻ /I ₃ ⁻ | 10.4 | 0.68 | 64 | 4.82 | 12 |
| SPS-01+TDPP | I ⁻ /I ₃ ⁻ | 15.2 | 0.72 | 74 | 8.1 | 12 |

| | | | | | | |
|-------------------|---|-------|-------|----|-------|----|
| XW3 | I ⁻ /I ₃ ⁻ | 15.73 | 0.748 | 68 | 8.02 | 13 |
| XW3+XW4 | I ⁻ /I ₃ ⁻ | 19.96 | 0.728 | 74 | 10.75 | 13 |
| DPP13 | I ⁻ /I ₃ ⁻ | 16.2 | 0.705 | 68 | 7.67 | 14 |
| | Co ²⁺ /Co ³⁺ | 15.6 | 0.743 | 78 | 8.97 | 14 |
| DPP14 | I ⁻ /I ₃ ⁻ | 16.6 | 0.680 | 68 | 7.73 | 14 |
| | Co ²⁺ /Co ³⁺ | 15.2 | 0.716 | 76 | 8.23 | 14 |
| DPP15 | I ⁻ /I ₃ ⁻ | 16.9 | 0.684 | 65 | 7.44 | 14 |
| | Co ²⁺ /Co ³⁺ | 17.6 | 0.745 | 75 | 9.81 | 14 |
| DPP17 | I ⁻ /I ₃ ⁻ | 16.3 | 0.700 | 63 | 7.13 | 14 |
| | Co ²⁺ /Co ³⁺ | 17.9 | 0.761 | 74 | 10.1 | 14 |
| DPP07+NT35 | I ⁻ /I ₃ ⁻ | 16.9 | 0.69 | 71 | 8.31 | 15 |
| DPP07+D35 | I ⁻ /I ₃ ⁻ | 12.2 | 0.76 | 71 | 6.56 | 15 |
| ICD-1 | I ⁻ /I ₃ ⁻ | 16.65 | 0.708 | 73 | 8.61 | 16 |
| ICD-2 | I ⁻ /I ₃ ⁻ | 13.67 | 0.712 | 74 | 7.2 | 16 |

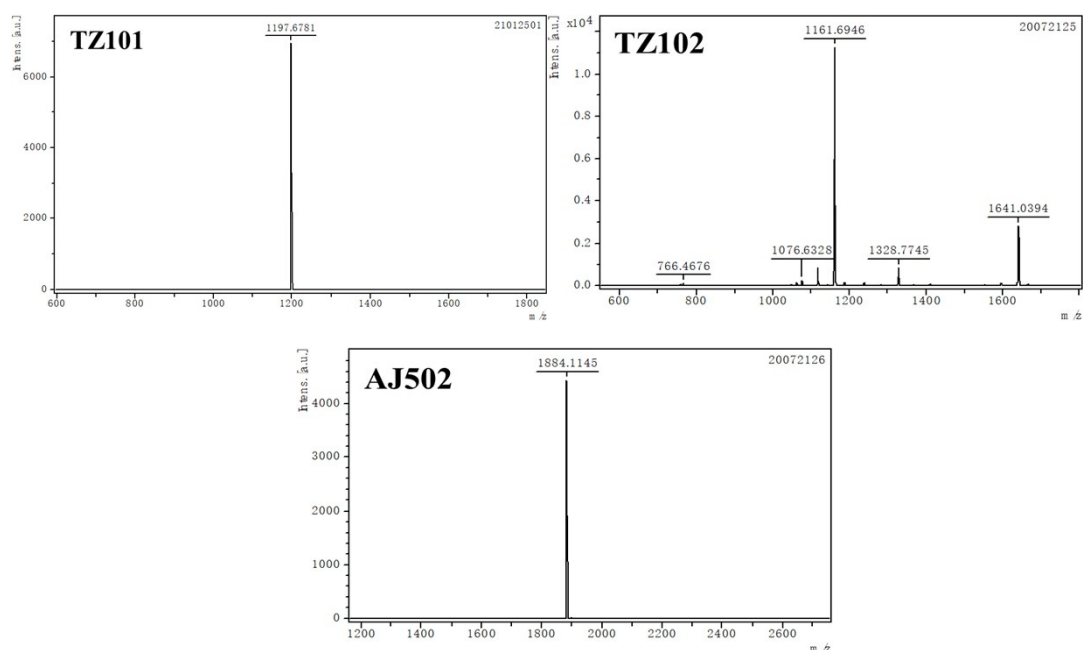


Figure S9. MALDI-TFO-MS of **TZ101**, **TZ102** and **AJ502**

References

- 1 H.-C. Chu, D. Sahu, Y.-C. Hsu, H. Padhy, D. Patra, J.-T. S. Lin, D. Bhattacharya, K.-L. Lu, K.-H. Wei, H.-C. Lin, *Dyes and Pigments* 2012, 93, 1488 - 1497.
- 2 P. J. Holliman, M. L. Davies, A. Connell, B. Vaca Velasco, T. M Watson, *Chem. Commun.* 2010, 46, 7256-7258.
- 3 K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, M. Hanaya, *Chem. Commun.* 2015, 51, 15894 - 15897.
- 4 C.-H. Yang, P.-Y. Chen, W.-J. Chen, T.-L. Wang, Y.-T. Shieh, *Electrochimica Acta* 2013, 107, 170 - 177.
- 5 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diao, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* 2011, 334, 629.
- 6 S. Qu, W. Wu, J. Hua, C. Kong, Y. Long, and H. Tian, *J. Phys. Chem. C* 2010, 114, 1343–1349.
- 7 Q. Wang, W. Wu, C.-L. Ho, L. Xue, Z. Lin, H. Li, Y. H. Lo, and W.-Y. Wong, *Eur. J. Inorg. Chem.* 2014, 5322–5330.

- 8 Y. Hao, Y. Saygili, J. Cong, A. Eriksson, W. Yang, J. Zhang, E. Polanski, K. Nonomura, S. M. Zakeeruddin, M. Gratzel, A. Hagfeldt and G. Boschloo, *ACS Appl. Mater. Interfaces*, 2016, 8, 32797-32804.
- 9 T. W. Holcombe, J. H. Yum, J. Yoon, P. Gao, M. Marszalek, D. Di Censo, K. Rakstys, M. K. Nazeeruddin and M. Gratzel, *Chem. Commun.*, 2012, 48, 10724-10726.
- 10 T. W. Holcombe, J.-H. Yum, Y. Kim, K. Rakstys and M. Grätzel, *J. Mater. Chem. A*, 2013, 1, 13978-13983.
- 11 M. Katono, T. Bessho, M. Wielopolski, M. Marszalek, J.-E. Moser, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *J. Phys. Chem. C*, 2012, 116, 16876-16884.
- 12 G. D. Sharma, M. S. Roy and S. P. Singh, *J. Mater. Chem.*, 2012, 22, 18788-18792.
- 13 X. Sun, Y. Wang, X. Li, H. Agren, W. Zhu, H. Tian and Y. Xie, *Chem. Commun.*, 2014, 50, 15609-15612.
- 14 J. H. Yum, T. W. Holcombe, Y. Kim, K. Rakstys, T. Moehl, J. Teuscher, J. H. Delcamp, M. K. Nazeeruddin and M. Gratzel, *Sci. Rep.*, 2013, 3, 2446.
- 15 J. H. Yum, T. W. Holcombe, Y. Kim, J. Yoon, K. Rakstys, M. K. Nazeeruddin and M. Gratzel, *Chem. Commun.*, 2012, 48, 10727-10729.
- 16 F. Zhang, K.-J. Jiang, J.-H. Huang, C.-C. Yu, S.-G. Li, M.-G. Chen, L.-M. Yang and Y.-L. Song, *J. Mater. Chem. A*, 2013, 1, 4858-4863.