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Supporting Information

Effect of Structural Engineering of π-Spacer on Anti-aggregation of D-A-π-A Dye

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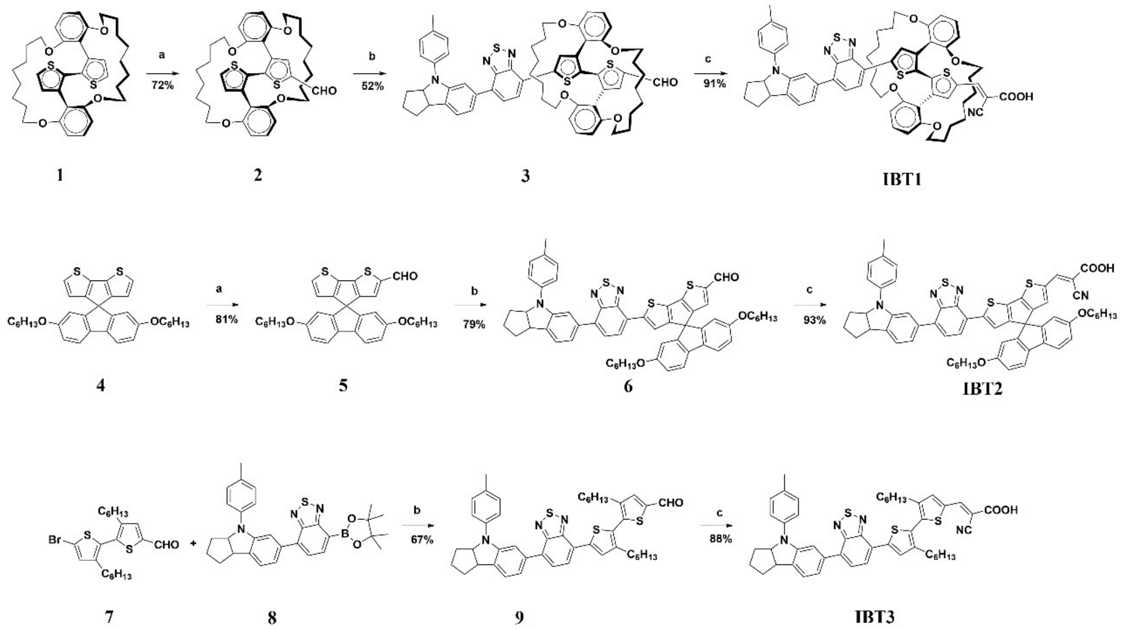
1. Synthetic routes of the dyes **IBT1–3**



a. $POCl_3$, DMF, 1,2-dibromoethane, 80 ^{o}C; b. $Pd(PPh_3)_4$, Na_2CO_3, ethanol, H_2O, toluene, 100 ^{o}C; c. piperidine, cyanoacetic acid, $CHCl_3$, 75 ^{o}C

2. Experimental details of the new compounds

Synthesis of compound **2**

To a solution of compound **1** (300 mg, 0.5 mmol) in 1,2-dichloroethane (20 mL), DMF (0.12 mL, 1.5 mmol) was added in one portion, then $POCl_3$ (0.14 mL, 1.5 mmol) was added dropwise at 0 ^{o}C under argon. The mixture was stirred at the same temperature for 1 h, then heated to 70 ^{o}C and maintained for 5 h. After cooling to room temperature, 0.1 M NaOH aqueous solution (10 mL) was added, and the mixture was extracted three times with CH_2Cl_2 (50 mL). The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (PE : EA= 10:1) to give desired compound **2** as a yellow solid in 72% yield (227 mg), mp 277.1 – 279.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.39 – 7.33 (m, 3H), 7.11 (d, J = 4.8 Hz, 1H), 6.75 (d, J = 4.8 Hz, 1H), 6.62 (d, J = 8.4 Hz, 4H), 3.94 (m, 8H), 1.62 – 1.49 (m, 8H), 1.16 – 1.06 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.07, 158.68, 158.18, 144.85, 141.17, 138.51, 134.27, 132.29, 131.31, 130.88, 130.42, 130.27, 125.20, 113.83, 113.50, 104.77, 104.38, 67.77, 67.69, 28.43, 28.40, 27.39, 27.36, 24.14, 24.06. HRMS (m/z) calcd for $C_{37}H_{42}NaO_5S_2$ $[M+Na]^+$ 653.2366; found: 653.2359.

Synthesis of compound **3**

To a solution of compound **2** (145 mg, 0.23 mmol) in 20 mL $CHCl_3$, NBS (45 mg, 0.25 mmol) was dissolved in 10 mL $CHCl_3$ and add into above solution dropwise. After this reaction was stirred at room temperature overnight, 15 mL water was added to this mixture. The mixture was extracted three times with CH_2Cl_2 (45 mL). The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product direct for next reaction without further purification. Above crude product was dissolved in 25 mL toluene, compound **8** (119 mg, 0.23 mmol) and Na_2CO_3 (73 mg, 0.69 mmol) were added, 2 mL ethanol, 2 mL H_2O and $Pd(PPh_3)_4$ (26 mg, 0.023 mmol) were added subsequently. The reaction mixture was stirred under an argon atmosphere at 100 ^oC for 24 h. After cooling to room temperature, 50 mL water was added into the mixture, the mixture was extracted three times with CH_2Cl_2 (45 mL). The combined organic ingredients were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (PE : EA= 10:1) to give desired compound **3** as a red solid in 52% yield (121 mg), mp 163.1 – 165.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.91 (s, 1H), 7.72 – 7.68 (m, 2H), 7.59 (s, 2H), 7.44 – 7.38 (m, 3H), 7.22 – 7.17 (m, 4H), 6.99 (s, 1H), 6.69 – 6.56 (m, 4H), 4.89 – 4.80 (m, 1H), 4.10 – 3.80 (m, 9H), 2.34 (s, 3H), 2.12 – 2.02 (m, 1H), 2.00 – 1.86 (m, 2H), 1.87 – 1.75 (m, 1H), 1.59 – 1.51 (m, 10H), 1.25 – 0.95 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.03, 158.71, 158.26, 154.09, 148.37, 144.72, 141.29, 140.20, 138.81, 138.63, 135.39, 135.38, 135.32, 132.92, 131.85, 131.72, 131.67, 130.54, 130.49, 129.84, 128.81, 128.76, 127.36, 126.16, 125.46, 125.28, 124.89, 124.73, 120.30, 114.03, 113.45, 107.43, 104.85, 104.55, 69.31, 67.82, 55.46, 50.17, 45.47, 35.20, 33.77, 28.46, 27.44, 27.35, 24.50, 24.18, 24.17, 20.86. HRMS (m/z) calcd for $C_{61}H_{61}N_3NaO_5S_3$ $[M+H]^+$ 1034.3666; found: 1034.3671.

Synthesis of compound **IBT1**

In argon atmosphere, compound **3** (95 mg, 0.094 mmol), piperidine (58 mg, 0.68 mmol), and cyanoacetic acid (24 mg, 0.28 mmol) were dissolved in chloroform (30 mL) and refluxed for 16 h. After cooling to room temperature, moderate water (30 mL) was added. Then, the mixture was extracted several times with CH_2Cl_2 (45 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$ and evaporated to remove the solvent. The crude product was purified by chromatography on a silica gel column (CH_2Cl_2 : CH_3OH= 20:1) to afford a desired compound **IBT1** as a red solid in 91% yield (100 mg), mp 212.1 – 213.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.95 (s, 1H), 7.74 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.44 – 7.38 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 6.0 Hz, 1H), 6.70 – 6.66 (m, 4H), 4.85 (t, J = 8.4 Hz, 1H), 4.04 – 3.90 (m, 9H), 2.34 (s, 3H), 1.71 – 1.42 (m, 10H), 1.21 – 1.02 (m, 16H). ^{13}C NMR (100 MHz, THF) δ 158.61, 158.24, 153.91, 152.87, 148.15, 144.19, 140.20, 139.62, 138.28, 135.21, 134.97, 133.29, 132.74, 132.63, 132.49, 131.86, 131.23, 130.40, 130.30, 129.95, 129.59, 129.48, 128.63, 127.34, 125.77, 125.37, 124.99, 124.58, 120.09, 120.03, 116.70, 113.74, 113.34, 107.10, 104.68, 104.41, 69.10, 67.54, 67.45, 45.40, 35.14, 33.61, 29.66, 28.50, 28.36, 27.40, 22.61, 20.28, 13.73. MALDI-TOF-MS calcd for $C_{64}H_{62}N_4O_6S_3$ 1078.383, found 1078.555.

2',7'-Bis(hexyloxy)spiro[cyclopenta[2,1-*b*:3,4-*b*']dithiophene-4,9'-fluorene]-2-carbaldehyde (**5**)

Compound **5** (253 mg, 81%) was synthesized from compound **4** with the similar procedure as that of compound **2** as a yellow solid, mp 112.3 – 113.6 ^{o}C. ^{1}H NMR (400

MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 4.8 Hz, 1H), 7.11 (s, 1H), 6.90 – 6.88 (m, 2H), 6.52 – 6.51 (m, 1H), 6.36 – 6.28 (m, 2H), 3.81 (d, J = 6.4 Hz, 4H), 1.71 – 1.64 (m, 4H), 1.42 – 1.34 (m, 4H), 1.29 – 1.24 (m, 8H), 0.86 (t, J = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.51, 159.27, 158.73, 155.67, 148.87, 144.90, 144.07, 137.25, 134.47, 130.63, 130.30, 122.05, 120.15, 114.39, 109.81, 68.28, 61.87, 31.57, 29.26, 25.69, 22.55, 14.01. HRMS (m/z) calcd for $C_{34}H_{37}O_3S_2$ $[M+H]^+$ 557.2179; found: 557.2182.

2',7'-Bis(hexyloxy)-6-(7-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)spiro[cyclopenta[2,1-*b*:3,4-*b*']dithiophene-4,9'-fluorene]-2-carbaldehyde (**6**)

Compound **6** (103 mg, 79%) was synthesized from compound **5** with the similar procedure as that of compound **3** as a red solid, mp 93.2 – 94.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.75 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.43 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.13 (s, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.92 (d, J = 8.2 Hz, 2H), 6.42 (s, 2H), 4.90 – 4.80 (m, 1H), 3.82 (t, J = 6.4 Hz, 4H), 2.34 (s, 3H), 1.71 – 1.62 (m, 4H), 1.43 – 1.33 (m, 2H), 1.28 – 1.20 (m, 12H), 0.93 – 0.76 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.37, 159.62, 158.85, 155.77, 153.89, 152.46, 149.14, 148.63, 145.51, 145.05, 144.43, 140.05, 138.49, 135.40, 134.53, 133.77, 131.82, 130.40, 129.86, 128.97, 126.85, 125.78, 125.72, 125.48, 124.21, 120.54, 120.41, 120.26, 114.57, 109.95, 107.41, 69.34, 68.30, 62.28, 45.44, 35.26, 33.73, 31.59, 29.30, 25.71, 24.48, 22.57, 20.87, 14.03. HRMS (m/z) calcd for $C_{58}H_{56}N_3O_3S_3$ $[M+H]^+$ 938.3478; found: 938.3477.

(E)-3-(2',7'-Bis(hexyloxy)-2-(7-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)spiro[cyclopenta[2,1-*b*:3,4-*b*']dithiophene-4,9'-fluoren]-6-yl)-2-cyanoacrylic acid (**IBT2**)

IBT2 (95 mg, 93%) was synthesized from compound **6** with the similar procedure as that of compound **IBT1** as a black solid, mp 193.1–195.1 °C. ^{1}H NMR (400 MHz, THF-d_8) δ 8.03 (s, 1H), 7.74 – 7.59 (m, 2H), 7.58 – 7.43 (m, 4H), 7.41 – 7.32 (m, 1H), 7.23 (s, 1H), 7.06 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 7.6 Hz, 4H), 6.82 – 6.70 (m, 3H), 6.38 (s, 2H), 4.73 – 4.57 (m, 1H), 3.78 – 3.59 (m, 5H), 2.17 (s, 3H), 2.00 – 1.83 (m, 1H), 1.79 – 1.70 (m, 2H), 1.70 – 1.63 (m, 1H), 1.52 – 1.43 (m, 4H), 1.39 – 1.31 (m, 2H), 1.28 – 1.06 (m, 12H), 0.71 – 0.57 (m, 6H). ^{13}C NMR (100 MHz, THF) δ 159.04, 155.91, 153.60, 152.31, 148.16, 145.44, 145.06, 145.02, 144.99, 144.97, 140.22, 138.94, 138.82, 134.96, 134.50, 133.01, 131.16, 129.53, 129.41, 128.72, 127.04, 125.80, 125.34, 125.23, 125.22, 125.20, 124.33, 124.13, 120.52, 119.96, 117.64, 114.40, 109.56, 106.99, 69.07, 67.76, 62.25, 45.35, 35.06, 33.53, 31.57, 29.67, 25.66, 22.47, 19.93, 13.39. MALDI-TOF-MS calcd for $C_{61}H_{56}N_4O_4S_3$ 1004.364, found 1004.572.

3,3'-Dihexyl-5'-(7-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-[2,2'-bithiophene]-5-carbaldehyde (**9**)

To a mixture of compound **7** (103 mg, 0.23 mmol), compound **8** (119 mg, 0.23 mmol) and Na_2CO_3 (73 mg, 0.69 mmol) in 25 mL toluene, 2 mL ethanol, 2 mL H_2O and $Pd(PPh_3)_4$ (26 mg, 0.023 mmol) were added subsequently. The reaction mixture was stirred under an argon atmosphere at 100 °C for 24 h. After cooling to room temperature, 50 mL water was added, the mixture was extracted three times with CH_2Cl_2 (30 mL). The combined organic ingredients were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (PE : EA= 30:1) to give desired compound **9** as a red solid in 67% yield (114 mg), mp 66.5 – 68.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.01 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.78 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.02 (d, J = 8.4 Hz, 1H), 4.86 (d, J = 6.6 Hz, 1H), 3.93 (t, J = 9.6 Hz, 1H), 2.68 – 2.61 (m, 4H), 2.35 (s, 3H), 2.09 (t, J = 11.6 Hz, 1H), 1.98 – 1.94 (m, 2H), 1.84 – 1.76 (m, 1H), 1.66 – 1.57 (m, 6H), 1.36 – 1.21 (m, 12H), 0.87 – 0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.85, 154.09, 152.85, 148.56, 144.07, 143.74, 142.54, 140.50, 140.13, 139.94, 137.72, 135.40, 133.76, 131.74, 129.86, 128.94, 128.85, 128.08, 127.06, 126.14, 125.98, 125.56, 123.99, 120.35, 107.45, 69.34, 45.48, 35.26, 33.77, 31.69, 31.64, 30.82, 30.59, 29.32, 29.22, 29.07, 29.01, 24.51, 22.66, 22.62, 20.88, 14.15, 14.13. HRMS (m/z) calcd for $C_{45}H_{50}N_3NaOS_3$ $[M+H]^+$ 744.3111; found: 744.3092.

(E)-2-Cyano-3-(3,3'-dihexyl-5'-(7-(4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-[2,2'-bithiophen]-5-yl)acrylic acid (**IBT3**)

Under argon atmosphere, compound **9** (92 mg, 0.124 mmol), piperidine (74 mg, 0.87 mmol), and cyanoacetic acid (32 mg, 0.37 mmol) were dissolved in chloroform (30 mL) and refluxed for 16 h. After cooling to room temperature, moderate water (30 mL) was added. Then, the mixture was extracted with CH_2Cl_2 (30 mL) several times, and the organic layers were combined, dried over anhydrous $MgSO_4$ and evaporated to remove the solvent. The crude product was purified by chromatography on a silica gel column (CH_2Cl_2 : CH_3OH= 20:1) to afford a desired compound **IBT3** as a red solid in 88% yield (88 mg), mp 91.5 – 93.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.00 (s, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.61 (d, J = 7.2 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 1H), 2.69 – 2.60 (m, 4H), 2.34 (s, 3H), 2.12 – 2.03 (m, 1H), 1.96 – 1.91 (m, 2H), 1.86 – 1.78 (m, 1H), 1.71 – 1.57 (m, 6H), 1.32 – 1.21 (m, 12H), 0.88 – 0.83 (m, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 154.04, 152.78, 148.48, 145.97, 144.13, 143.86, 140.55, 140.15, 139.77, 138.48, 135.48, 135.37, 133.60, 131.68, 130.32, 129.84, 128.97, 128.90, 128.06, 127.08, 126.03, 125.96, 125.76, 125.53, 124.00, 120.30, 116.93, 107.44, 100.67, 69.31, 45.46, 35.23, 33.76, 31.70, 31.61, 30.80, 30.58, 29.74, 29.71, 29.24, 29.15, 24.50, 22.63, 20.86, 14.16, 14.11. MALDI-TOF-MS calcd for $C_{48}H_{50}N_4O_2S_3$ 810.309, found 810.201.

3. ^{1}H NMR and ^{13}C NMR Spectra of the new compounds

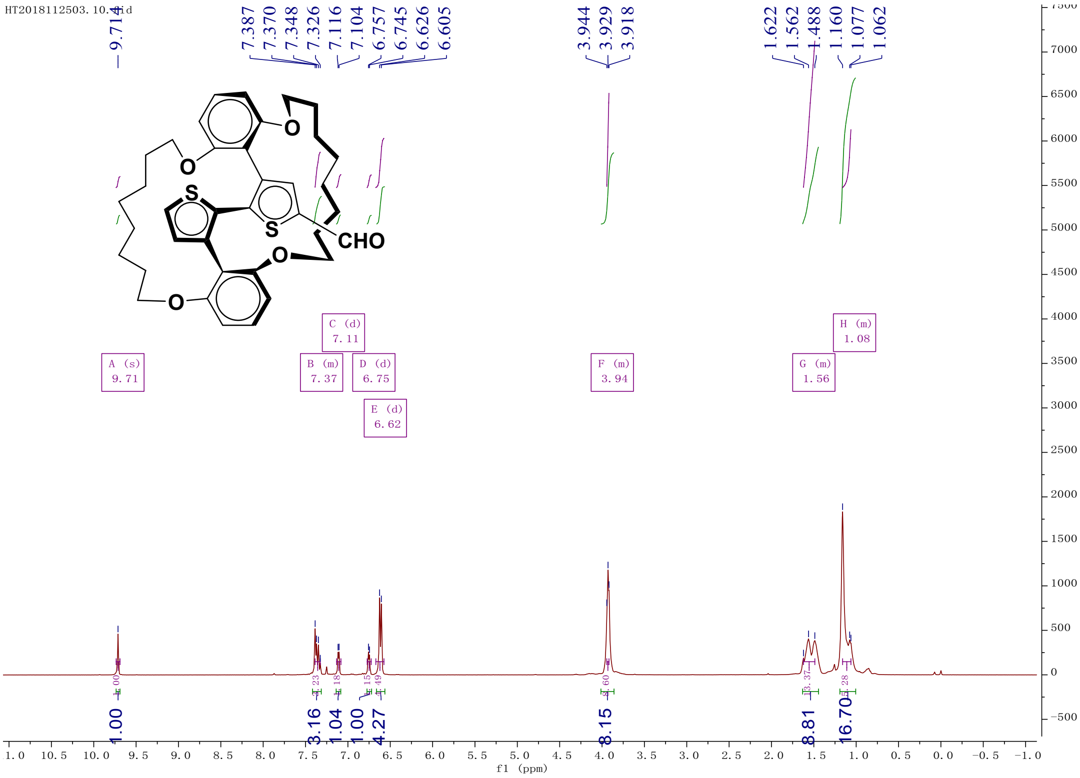


Fig. S1 ^{1}H NMR Spectrum of **2**

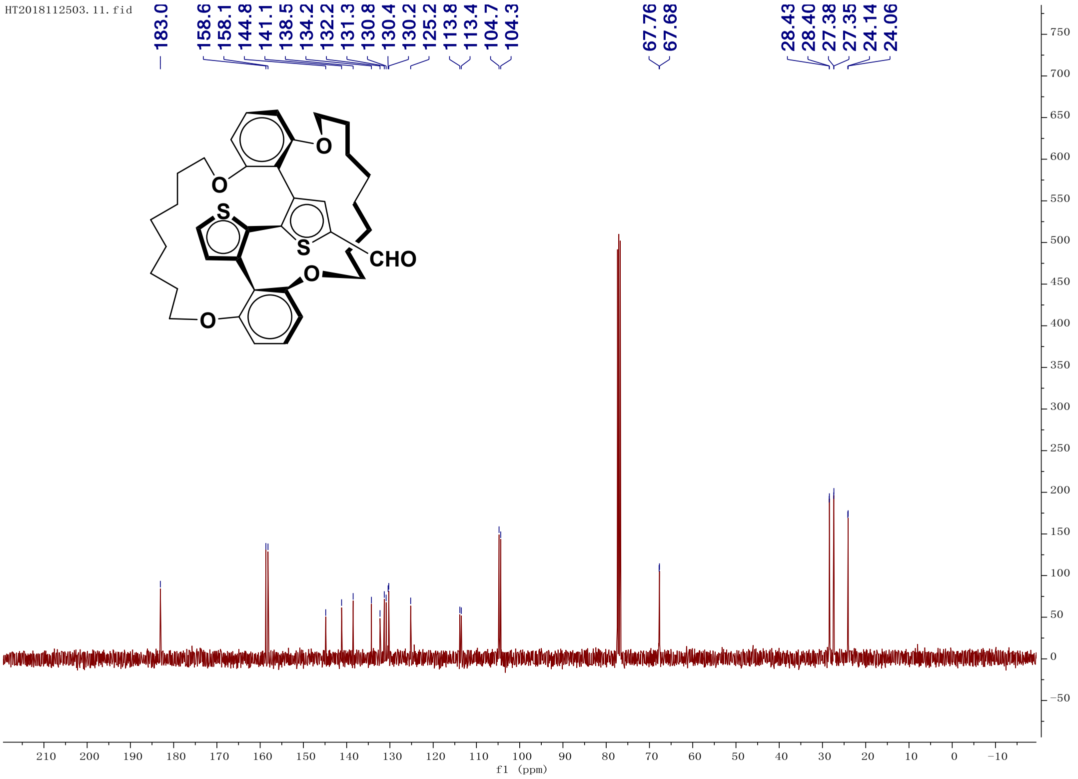


Fig. S2 ^{13}C NMR Spectrum of **2**

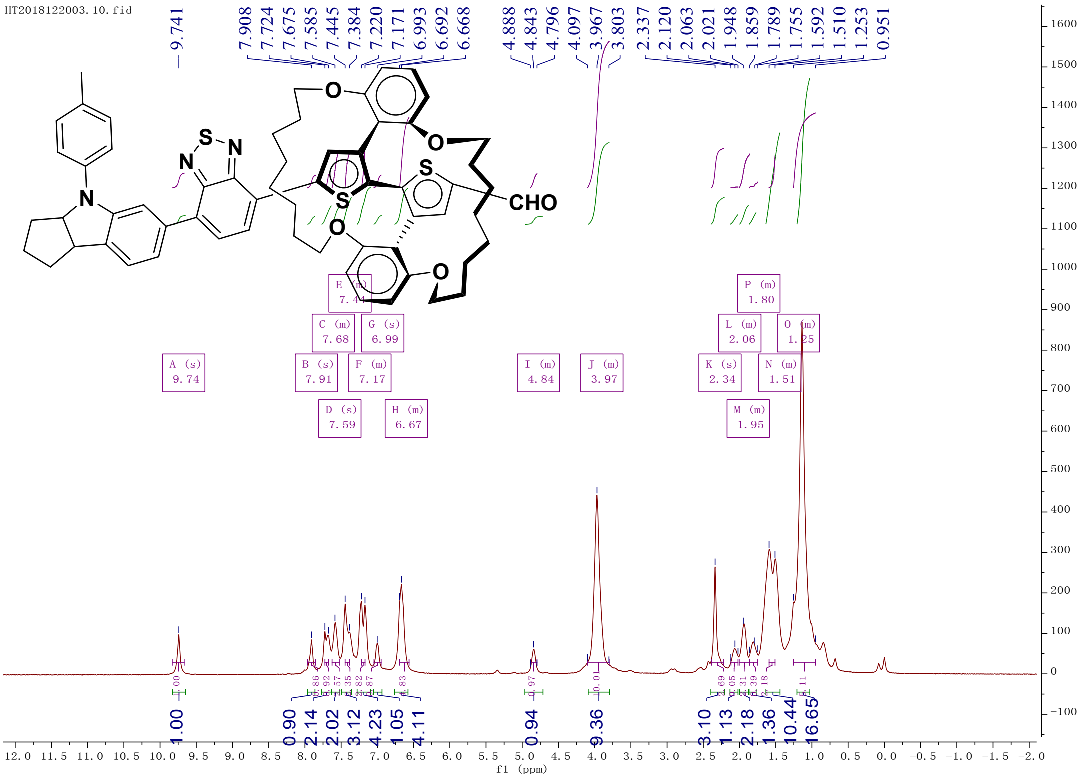


Fig. S3 ^{1}H NMR Spectrum of **3**

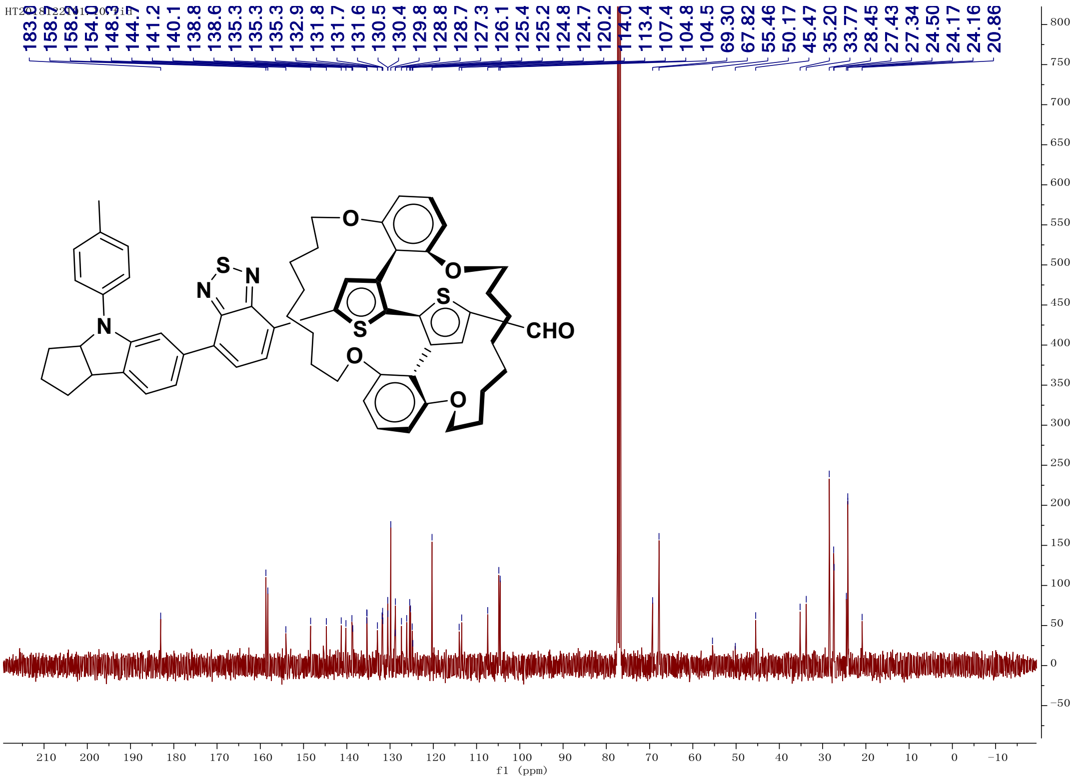


Fig. S4 ^{13}C NMR Spectrum of **3**

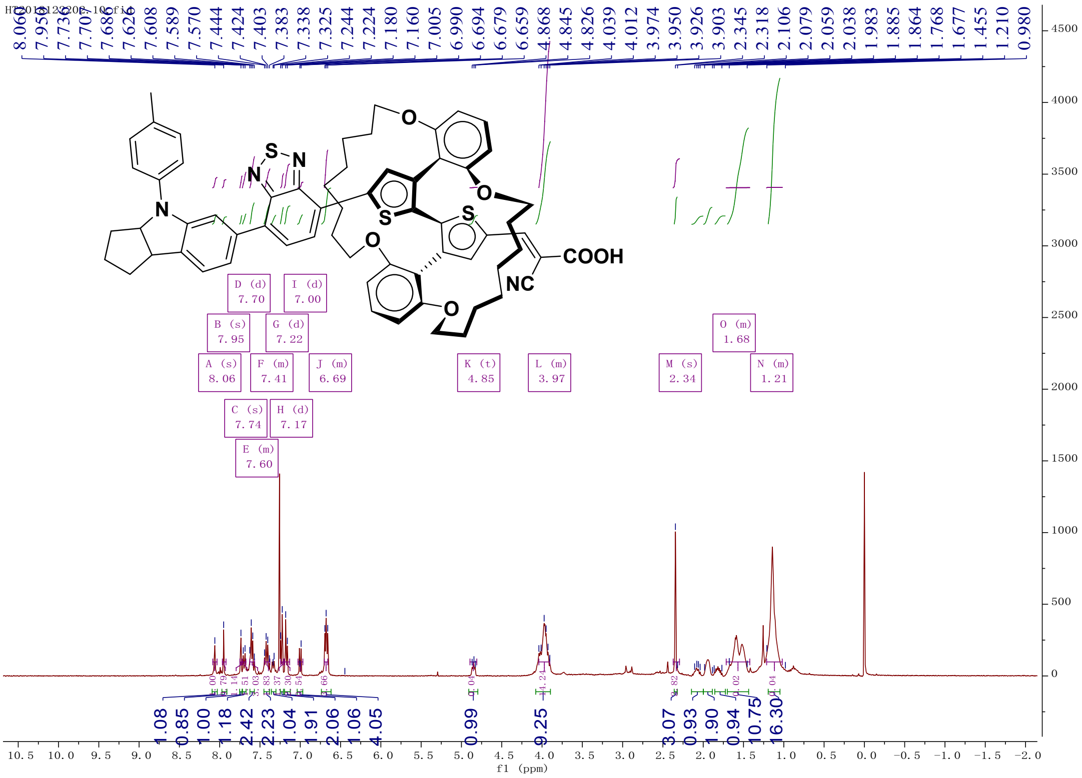


Fig. S5 ^{1}H NMR Spectrum of **IBT1**

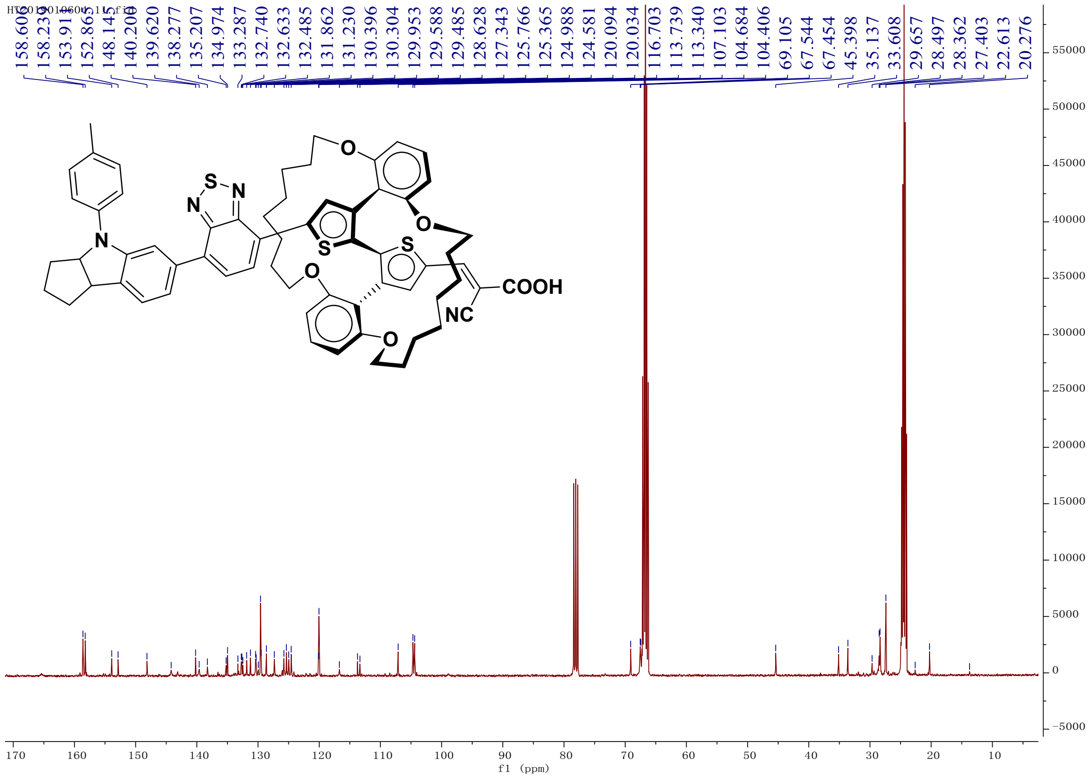


Fig. S6 ^{13}C NMR Spectrum of **IBT1**

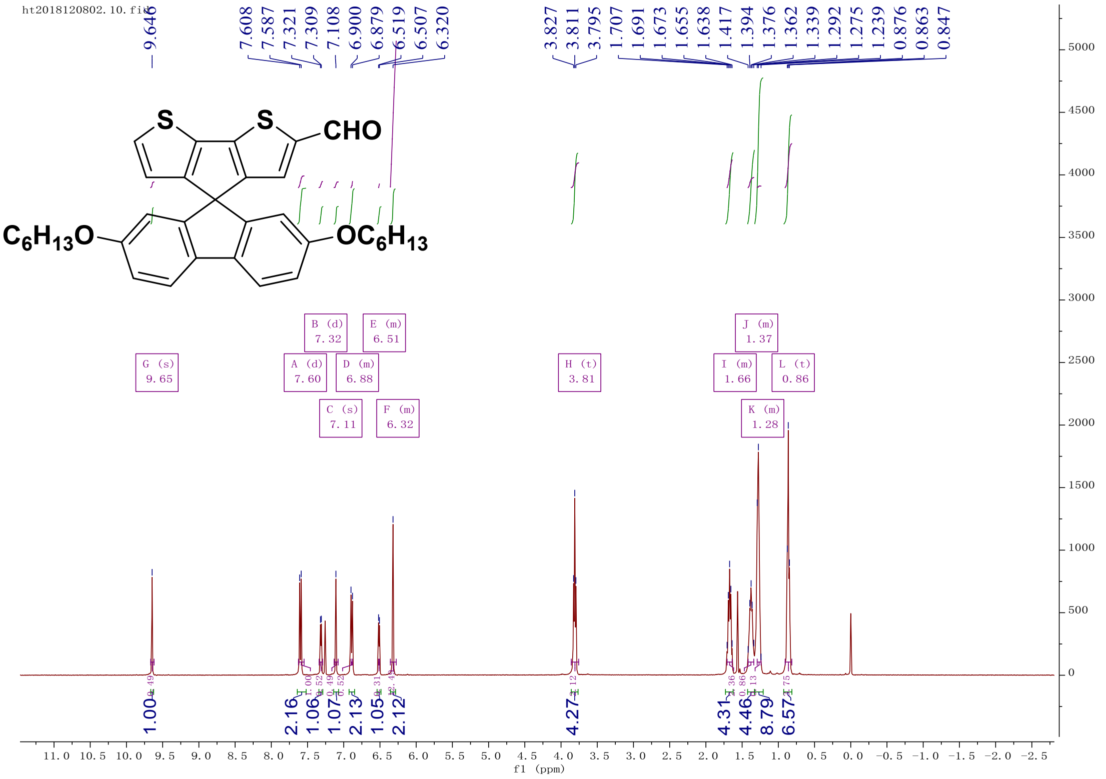


Fig. S7 ^{1}H NMR Spectrum of **5**

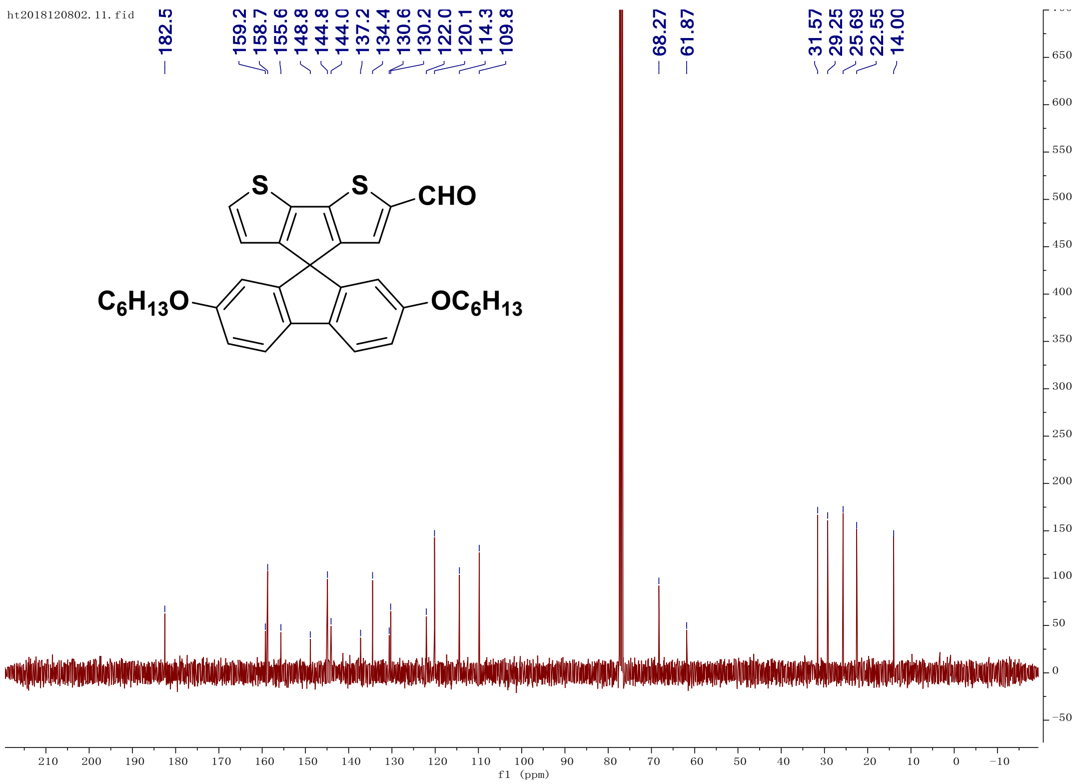


Fig. S8 ^{13}C NMR Spectrum of **5**

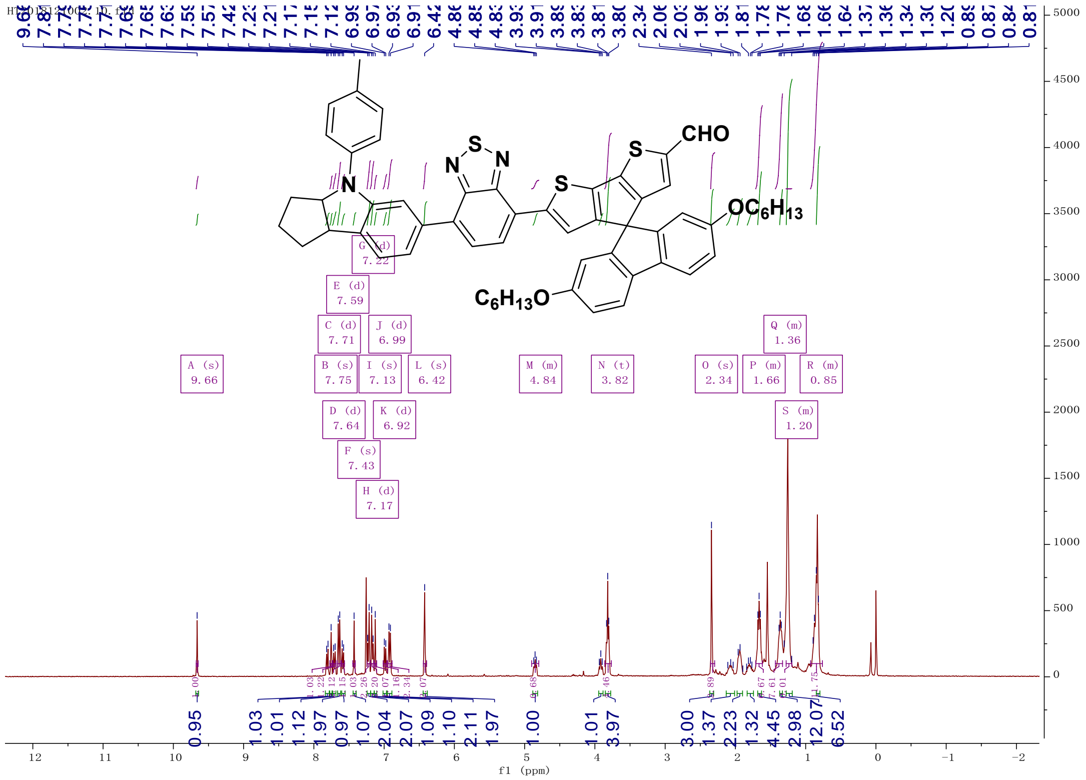


Fig. S9 ^{1}H NMR Spectrum of **6**

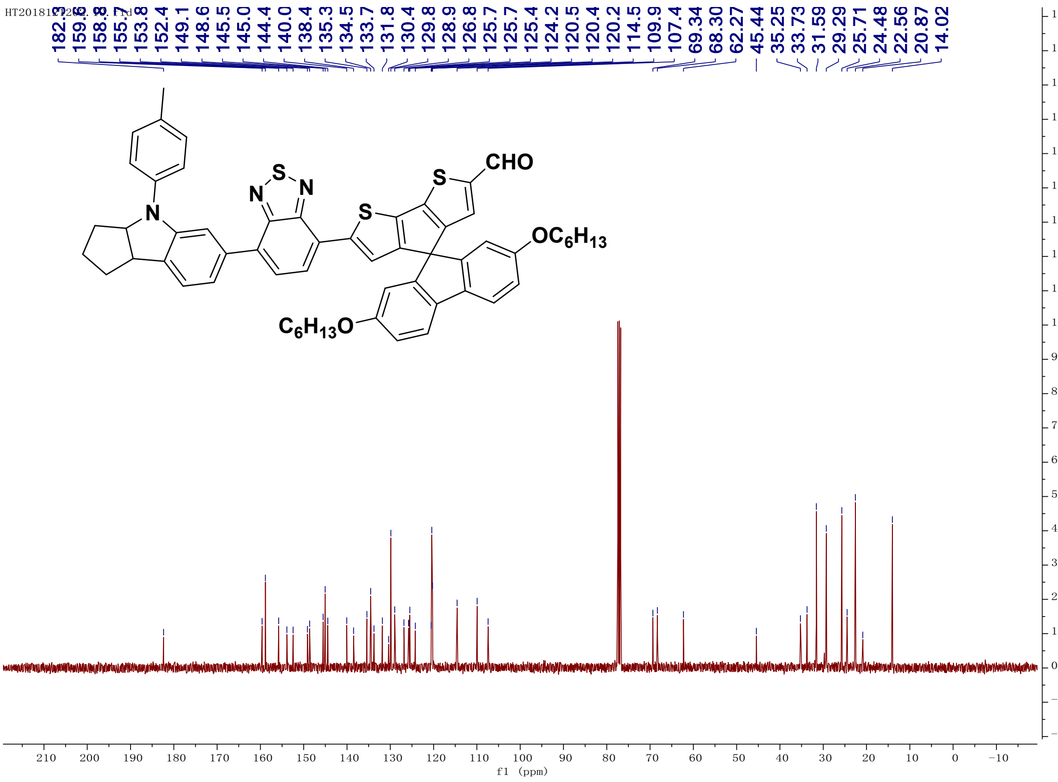


Fig. S10 ^{13}C NMR Spectrum of **6**

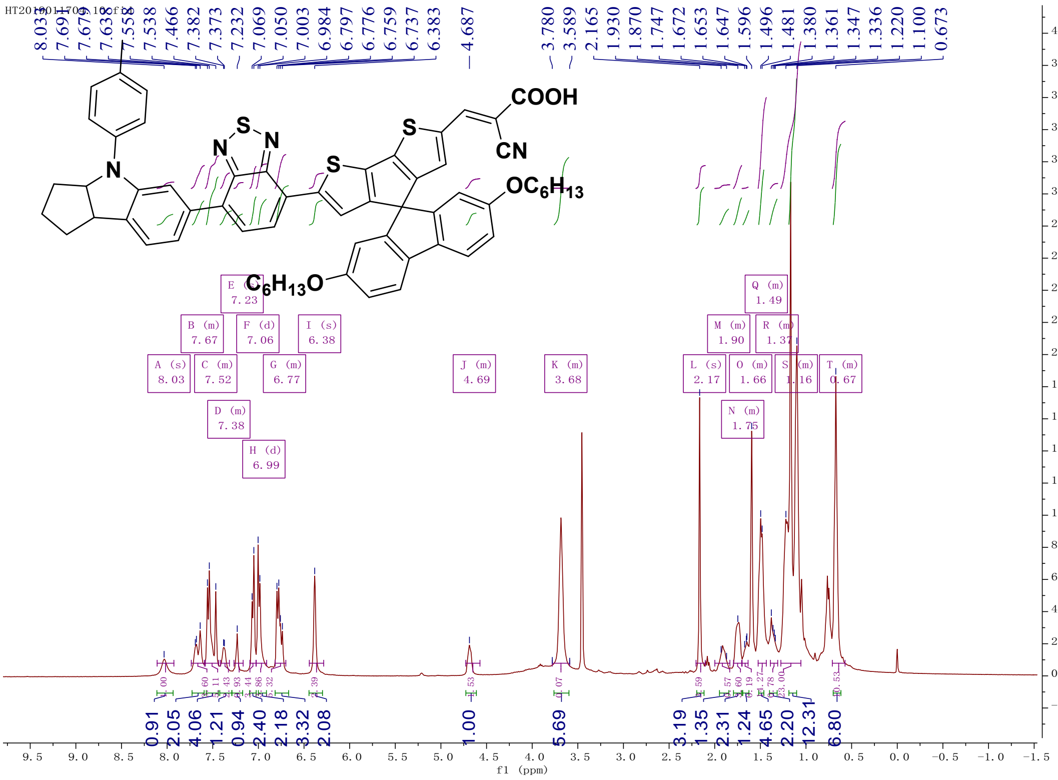


Fig. S11 ^{1}H NMR Spectrum of **IBT2**

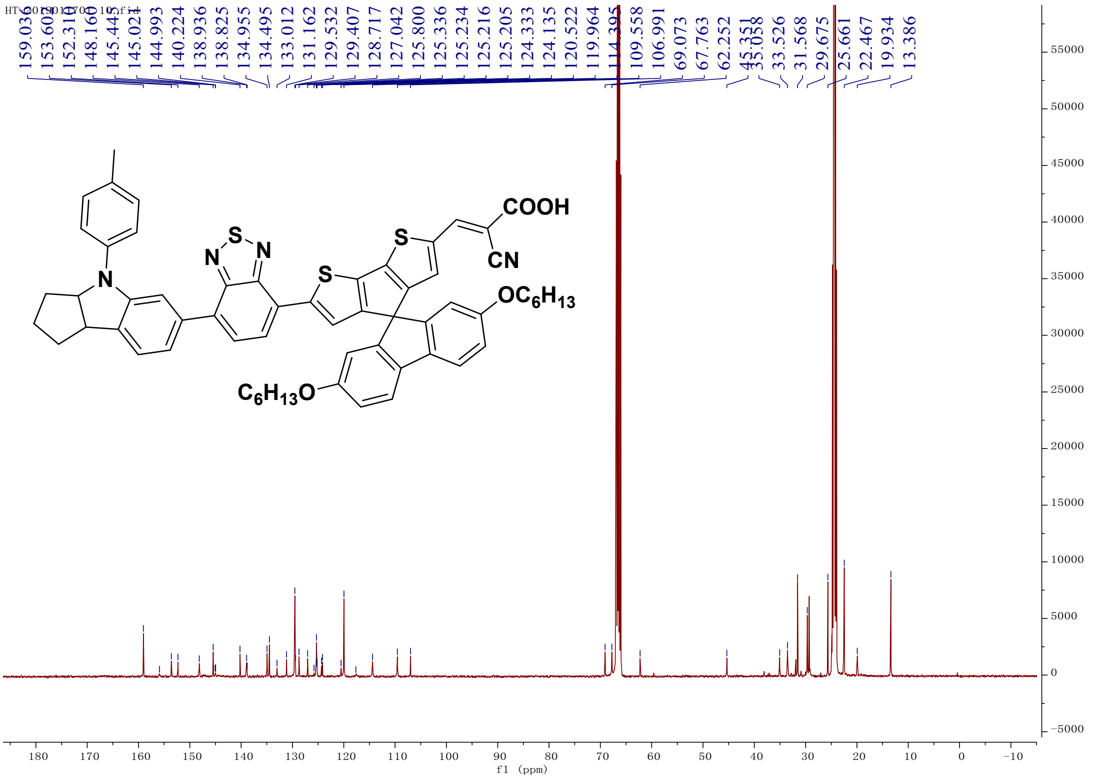


Fig. S12 ^{13}C NMR Spectrum of **IBT2**

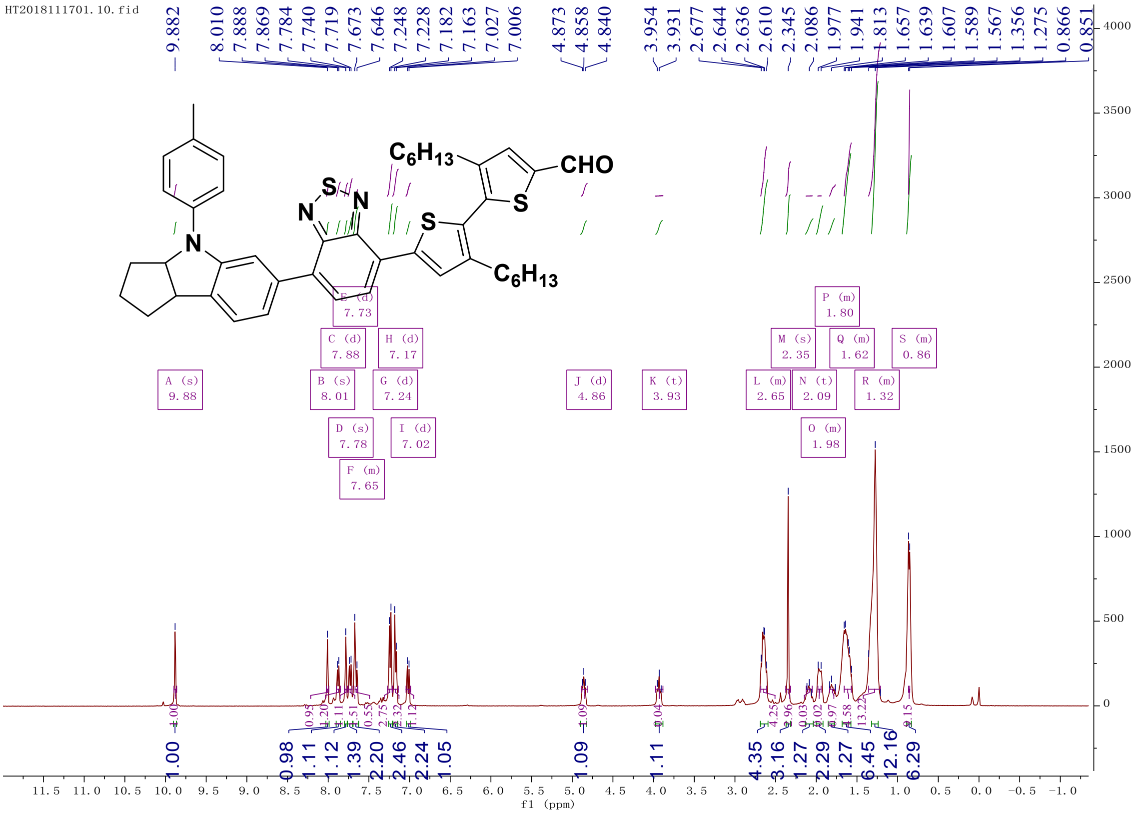


Fig. S13 ^{1}H NMR Spectrum of **9**

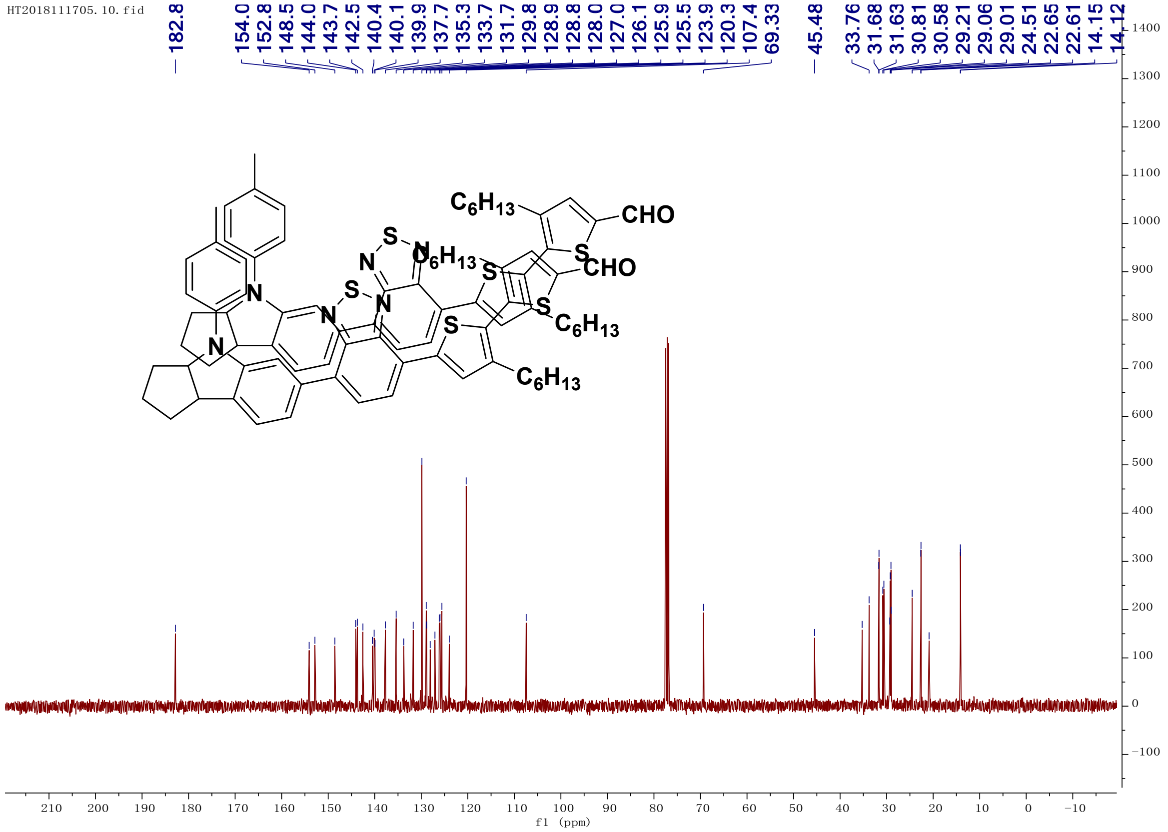


Fig. S14 ^{13}C NMR Spectrum of **9**

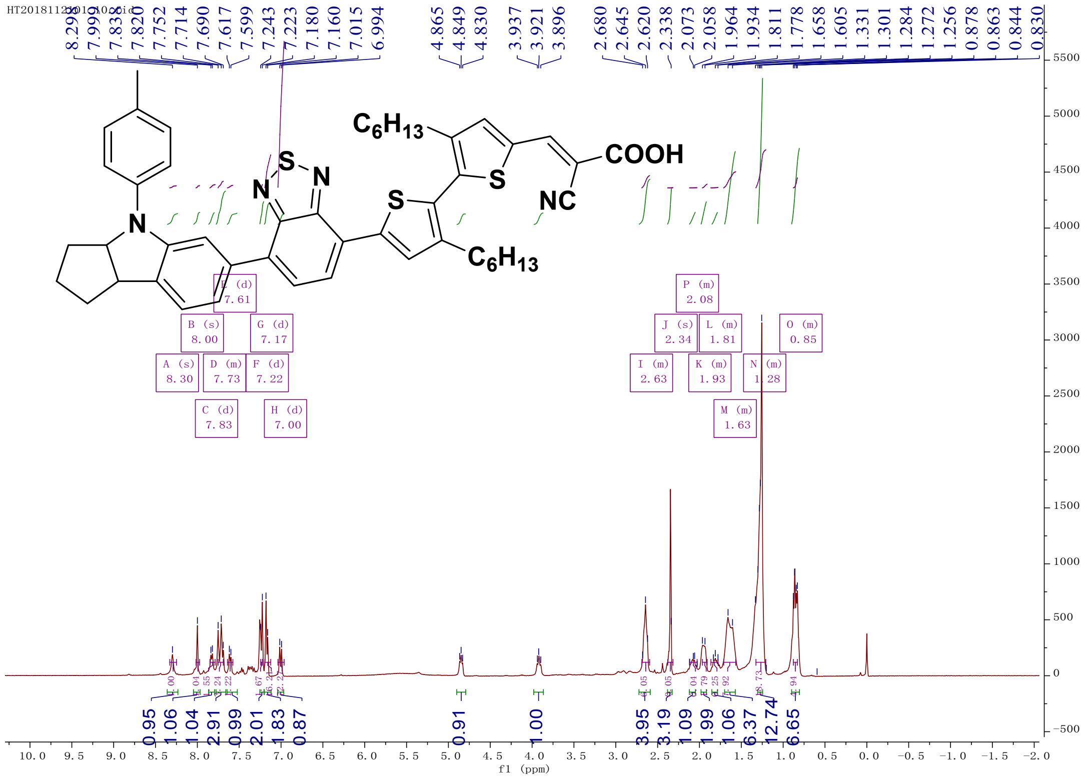


Fig. S15 ^{1}H NMR Spectrum of **IBT3**

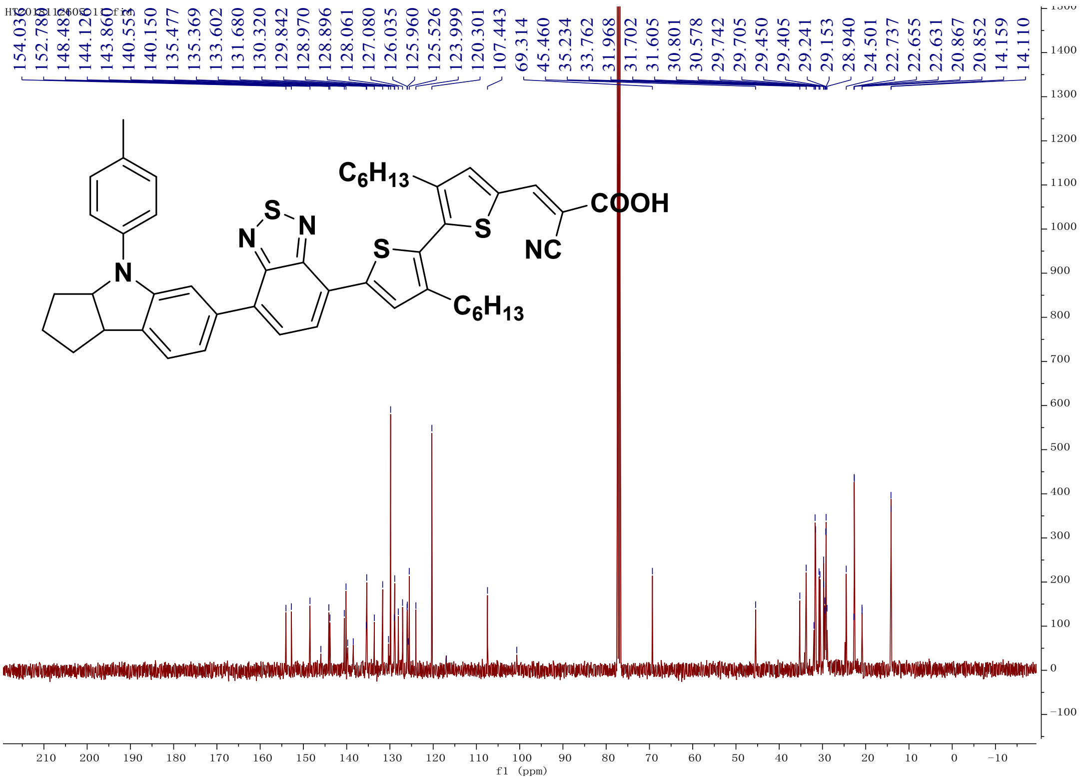


Fig. S16 ^{13}C NMR Spectrum of **IBT3**

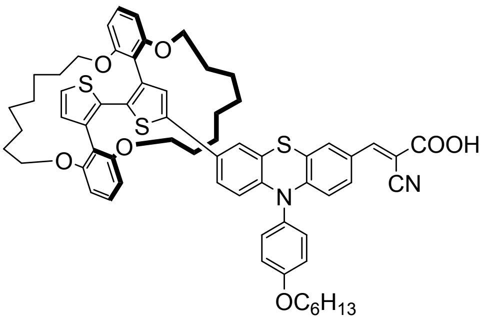


Figure S17. Chemical structure of dye **PH2**

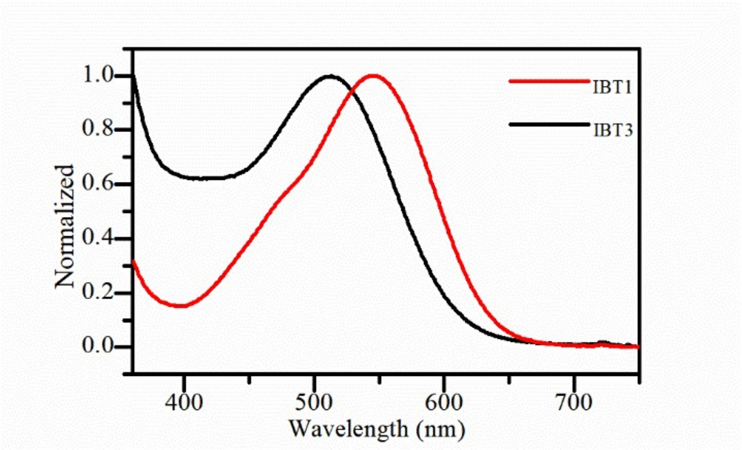


Figure S18. Normalized absorption spectra of the dyes **IBT1** and **IBT3**

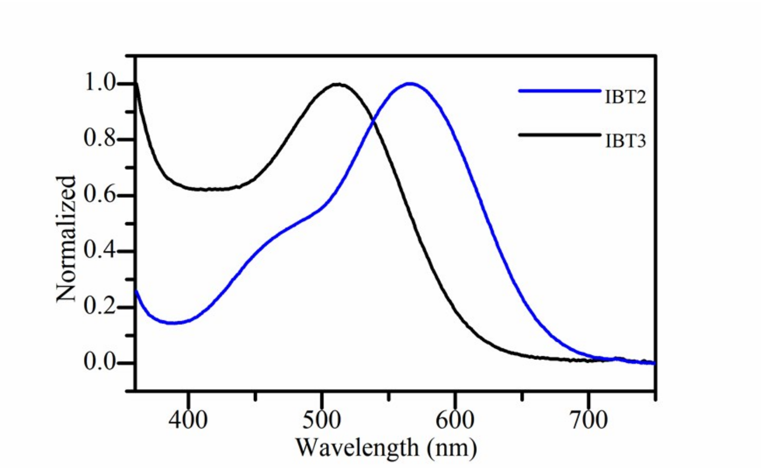


Figure S19. Normalized absorption spectra of the dyes **IBT2** and **IBT3**

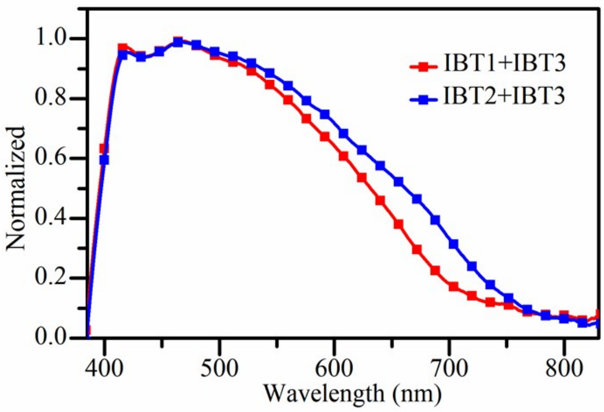


Figure S20. Normalized absorption spectra of the two cosensitized photoanodes (**IBT1**+ **IBT3** and **IBT2** + **IBT3**)

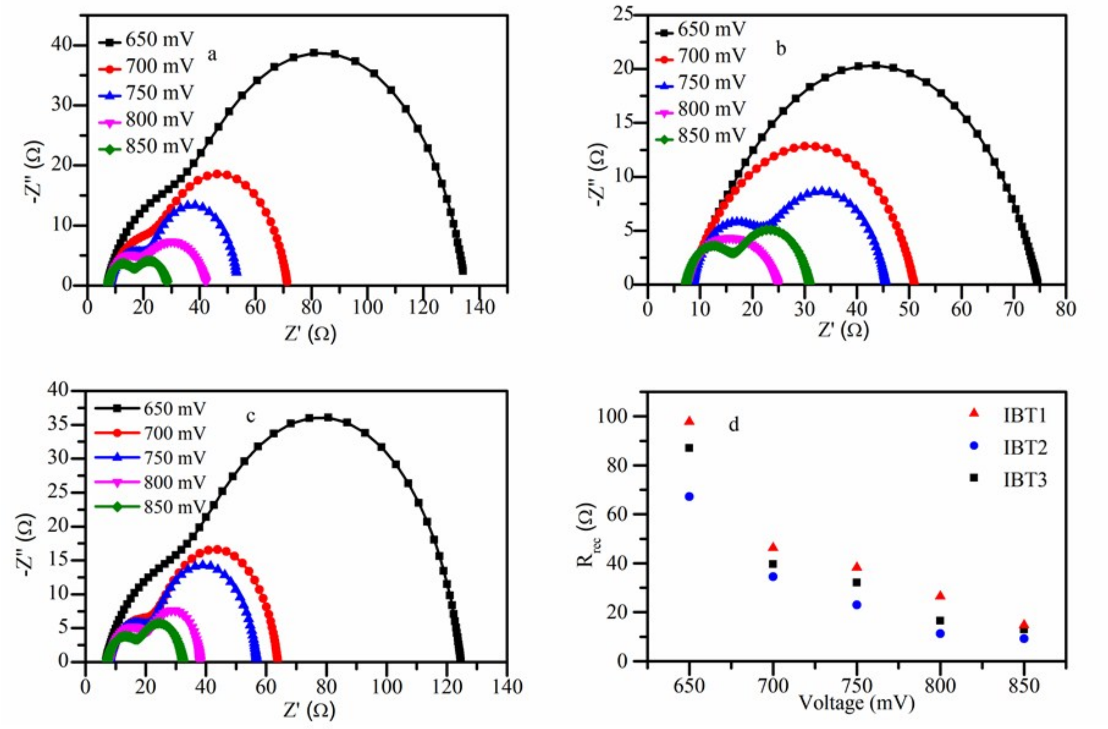


Figure S21. Electrochemical impedance spectroscopy of the three devices at different applied biases (a) **IBT1**; (b) **IBT2**; (c) **IBT3**; (d) the charge recombination resistance (R_{rec}) as a function of the potential

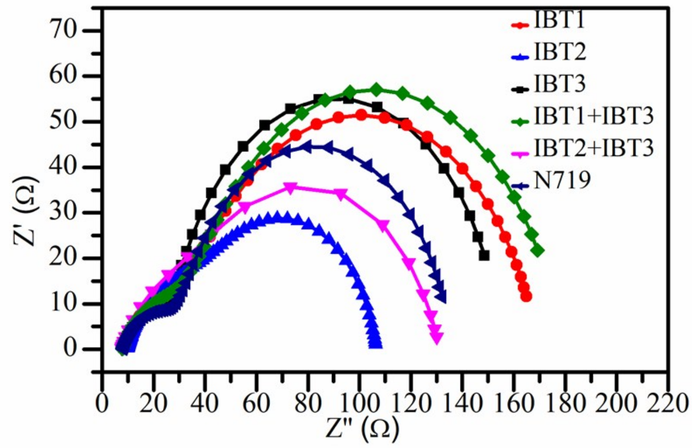


Figure S22. Nyquist (a) of electrochemical impedance spectra (EIS) for six DSSCs