

Supporting Information

New D- π -A dyes incorporating dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP)-based π -spacers for efficient dye-sensitized solar cells

Jingwen Jia, Yu Chen*, Liangsheng Duan, Zhe Sun, Mao Liang, Song Xue*

Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

Corresponding author: Fax: +86-22-60214252; E-mail address: cytjut@163.com;

xuesong@ustc.edu.cn.

Experimental details

Treatment on solvents and reactants

N,N-Dimethylformamide was dried by 200 mesh molecular sieve. Acetonitrile, dichloromethane and chloroform were distilled from calcium hydride under nitrogen atmosphere. Ethanol was distilled from magnesium rod. The other solvents and chemicals used in this work were analytical grade and used without further purification. Phosphorus oxychloride was freshly distilled before use.

The fabrication of a TiO₂ electrode

The titania paste consisted of 18wt.% TiO₂, 9 wt.% ethyl cellulose and 73 wt.% terpineol was used for made nanocrystalline films by screen-printing technique on a precleaned fluorine-doped tin oxide (FTO) conducting glass (Nippon Sheet Glass, Hyogo, Japan, sheet resistance of 14Ω/sq), which was deployed as the negative electrode of DSSCs. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 M titanium tetrachloride solution in a water saturated desiccator at 70 °C for 30 min and sintered again to give a mesoscopic TiO₂ film.

¹H NMR and ¹³C NMR data of 7a-c, 8a-c, JW1, JW2 and JW3

7a, green fluorescence oil (59.0% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (s, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 4.6 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.21 (s, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 4H), 6.96 (d, *J* = 6.5 Hz, 2H), 6.92 (d, *J* = 4.7 Hz, 2H), 6.90 (d, *J* = 3.1 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 4H), 6.40 (d, *J* = 8.1

Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 4H), 1.85–1.76 (m, 4H), 1.53–1.43 (m, 4H), 1.40–1.34 (m, 8H), 0.94 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 155.62, 144.07, 142.47, 140.43, 139.14, 138.75, 133.38, 132.33, 132.22, 131.65, 131.53, 128.57, 128.44, 126.97, 126.72, 124.27, 122.89, 121.19, 121.19, 120.18, 116.61, 115.29, 112.14, 110.23, 68.28, 31.61, 29.34, 25.77, 22.62, 14.04 .

7b, green fluorescence oil (64.2% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.50 (d, $J = 8.5$ Hz, 1H), 8.40 (d, $J = 3.3$ Hz, 1H), 7.70 (d, $J = 2.0$ Hz, 1H), 7.65 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.53 (d, $J = 7.1$ Hz, 2H), 7.44 (t, $J = 7.0$ Hz, 4H), 7.32 (d, $J = 8.7$ Hz, 2H), 7.27 (d, $J = 3.4$ Hz, 1H), 7.23 (s, 1H), 7.08 (d, $J = 8.9$ Hz, 4H), 6.94 (d, $J = 4.2$ Hz, 2H), 6.91 (d, $J = 2.8$ Hz, 2H), 6.85 (d, $J = 8.9$ Hz, 4H), 3.96 (t, $J = 6.5$ Hz, 4H), 3.07–2.88 (m, 6H), 2.21–2.07 (m, 6H), 1.85–1.76 (m, 5H), 1.54–1.44 (m, 6H), 1.37 (dd, $J = 9.0, 5.2$ Hz, 9H), 0.94 (t, $J = 6.9$ Hz, 6H), 0.63–0.56 (m, 24H). ^{13}C NMR (101 MHz, CDCl_3): δ 155.80, 155.60, 153.74, 153.54, 148.32, 145.17, 144.83, 143.95, 143.85, 142.08, 140.47, 140.17, 140.03, 138.55, 138.38, 138.24, 138.03, 137.48, 129.00, 126.93, 126.68, 126.53, 126.13, 125.57, 124.74, 124.57, 123.69, 122.42, 122.35, 120.32, 117.40, 116.43, 115.29, 110.48, 68.28, 68.28, 39.43, 31.61, 29.33, 26.93, 25.76, 22.61, 17.38, 14.83, 14.04.

7c, green fluorescence oil (60.5% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.8$ Hz, 2H), 7.30 (s, 1H), 7.28 (d, $J = 2.9$ Hz, 2H), 7.08 (d, $J = 7.6$ Hz, 9H), 7.05 (s, 1H), 6.91 (d, $J = 8.3$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 4H), 4.04 (t, $J = 6.5$ Hz, 3H), 3.96 (t, $J = 6.5$ Hz, 6H), 1.87–1.78 (m, 6H), 1.54–1.45 (m, 6H), 1.39 (dd, $J = 8.1, 4.7$ Hz, 12H), 0.95 (t, $J = 6.6$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3): δ 157.57, 155.57, 148.23,

144.41, 144.24, 142.13, 141.86, 140.51, 132.59, 129.10, 128.85, 126.89, 126.65, 124.35, 120.45, 120.36, 116.66, 115.46, 115.28, 111.92, 110.17, 68.28, 31.62, 29.35, 25.78, 22.63, 14.06.

8a, orange solid (56.1% yield). M.p.: 73-75 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.87 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.18 (s, 1H), 7.14 (d, *J* = 9.1 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 4H), 7.01 (d, *J* = 5.8 Hz, 2H), 6.98 (d, *J* = 6.3 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 4H), 6.47 (d, *J* = 7.1 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 4H), 1.84–1.76 (m, 4H), 1.51–1.45 (m, 4H), 1.39–1.34 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 182.65, 155.83, 148.99, 147.81, 143.78, 143.03, 140.57, 140.13, 137.66, 130.91, 129.65, 127.98, 127.36, 127.20, 127.01, 126.93, 125.80, 124.61, 123.26, 122.27, 119.79, 119.27, 117.36, 115.34, 115.26, 109.39, 68.28, 31.61, 29.33, 25.77, 22.62, 14.05. HRMS (ESI) (*m/z*): [M]⁺ calcd. For C₅₉H₅₆N₃O₃S₃, 950.3406; found: 950.3433.

8b, orange solid (43.5% yield). M.p.: 63-65 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.92 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.42 (d, *J* = 7.4 Hz, 1H), 8.38 (d, *J* = 7.5 Hz, 1H), 7.87 (s, 1H), 7.70 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 6.9 Hz, 4H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.28 (s, 1H), 7.18 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 5H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 4H), 3.96 (t, *J* = 6.5 Hz, 4H), 3.00–2.87 (m, 6H), 2.23–2.09 (m, 6H), 1.87–1.76 (m, 4H), 1.55–1.26 (m, 15H), 0.98–0.90 (m, 6H), 0.62 (dd, *J* = 22.6, 9.3 Hz, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 182.70, 156.13, 155.82, 153.74, 153.47, 148.96, 148.22, 147.47, 145.53, 145.05, 144.79,

143.38, 140.18, 140.06, 139.90, 139.19, 137.19, 136.97, 130.90, 127.35, 126.91, 126.65, 126.22, 125.79, 125.36, 124.79, 124.54, 122.47, 122.36, 119.86, 119.45, 116.78, 115.34, 114.90, 109.56, 68.29, 39.65–39.27, 31.61, 29.33, 25.77, 22.62, 19.20, 17.40, 14.76–14.45, 14.04. HRMS (ESI) (m/z): [M]⁺ calcd. For C₈₆H₉₆N₂O₃S₂, 1269.6862; found: 1269.6823.

8c, orange solid (64.2% yield). M.p.: 68-69 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.83 (s, 1H), 7.66 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 2.3 Hz, 3H), 7.07 (d, *J* = 2.2 Hz, 3H), 7.03 (s, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.90–1.77 (m, 6H), 1.56–1.46 (m, 6H), 1.42–1.35 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 182.74, 167.72, 158.20, 155.76, 148.85, 148.66, 147.34, 143.82, 140.19, 131.38, 130.92, 129.26, 128.84, 128.14, 127.29, 126.88, 124.68, 119.86, 119.52, 115.67, 115.29, 114.27, 109.34, 68.26, 31.62, 29.33, 25.77, 22.63, 14.06. HRMS (ESI) (m/z): [M]⁺ calcd. For C₅₃H₆₁N₂O₄S₂, 853.3994; found: 853.4044.

JW1, red solid (78.9% yield). M.p.: 115-117 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.30 (s, 1H), 7.84 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 4.7 Hz, 2H), 7.10 (s, 1H), 6.99 (t, *J* = 3.4 Hz, 2H), 6.98 (d, *J* = 2.7, 2H), 6.87 (d, *J* = 3.5, 2H), 6.71 (t, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 7.4 Hz, 2H), 6.62 (d, *J* = 4.7 Hz, 4H), 6.581 (d, *J* = 6.3 Hz, 1H), 6.48 (d, *J* = 6.9 Hz, 2H), 6.38 (d, *J* = 5.1 Hz, 4H), 3.97 (t, *J* = 9.2 Hz, 4H), 1.82–1.78 (m, 4H), 1.31–1.27 (m, 8H), 1.37–1.33 (m, 4H), 0.92 (t, *J* = 6.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 161.83, 159.61, 140.14, 138.22, 135.10, 133.75, 132.61,

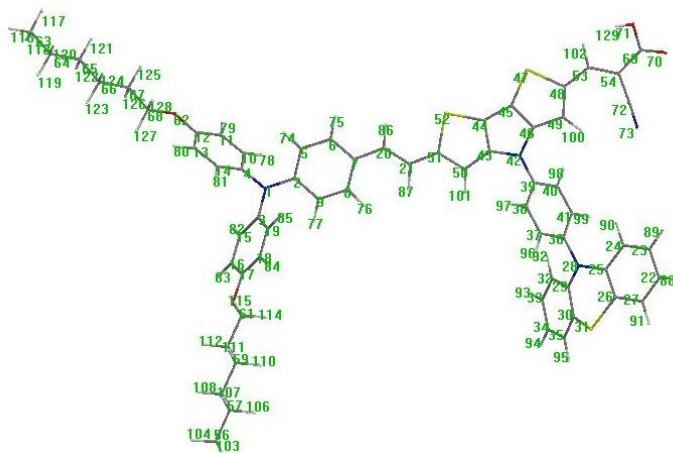
131.24, 130.82, 129.86, 128.41, 128.13, 127.52, 124.37, 123.93, 123.53, 122.54, 116.01, 115.64, 94.26, 69.74, 33.07, 30.04, 26.14, 22.81, 15.26. HRMS (ESI) (m/z): [M]⁺ calcd. For C₆₂H₅₇N₄O₄S₃, 1017.3464; found: 1017.3475.

JW2, red solid (65.4% yield). M.p.: 110-112 °C. ¹H NMR (400 MHz, CDCl₃) δ8.84 (s, 1H), 8.26(d, *J* = 2.2 Hz, 1H), 8.03(d, *J* = 5.5 Hz, 1H), 7.96 (d, *J* = 4.2 Hz, 1H), 7.74 (s, 1H), 7.70 (d, *J* = 8.8 Hz 1H), 7.64 (s, 1H), 7.59 (d, *J* = 5.6 Hz, 1H), 7.47 (t, *J* = 2.2 Hz, 1H), 7.40 (t, *J* = 3.2 Hz, 1H), 7.38 (d, *J* = 4.8 Hz, 1H), 7.29 (t, *J* = 5.6 Hz, 1H), 7.20 (t, *J* = 8.8 Hz, 1H), 7.05 (s, 1H), 7.01(d, *J* = 5.4 Hz, 2H), 6.98 (d, *J* = 8.6Hz, 2H), 6.76 (d, *J* = 5.6Hz, 4H), 6.53 (d, *J* = 2.6 Hz, 2H), 6.48 (d, *J* = 6.5 Hz, 4H), 3.93 (t, *J* = 5.2 Hz, 4H), 2.19 (t, *J* = 4.8Hz, 12H), 2.02–1.98 (m, 4H), 1.52–1.49 (m, 8H), 1.44-1.40 (m, 16H), 0.94 (t, *J* = 3.4Hz, 24H). ¹³C NMR (101 MHz, CDCl₃) δ160.84, 159.72, 153.66, 150.51, 148.40, 142.23, 140.17, 140.21, 139.25, 138.39, 137.30, 137.00, 135.17, 132.40, 130.93, 129.40, 129.87, 128.82, 128.78, 127.40, 126.82, 126.52, 125.72, 123.88, 122.35, 119.89, 115.62, 115.31, 114.03, 99.99, 68.19, 46.23, 38.73, 30.35, 29.68, 28.91, 23.74, 18.24, 14.08, 14.01. HRMS (ESI) (m/z): [M]⁺ calcd. For C₈₉H₉₈N₃O₄S₂, 1336.6920; found: 1336.6920.

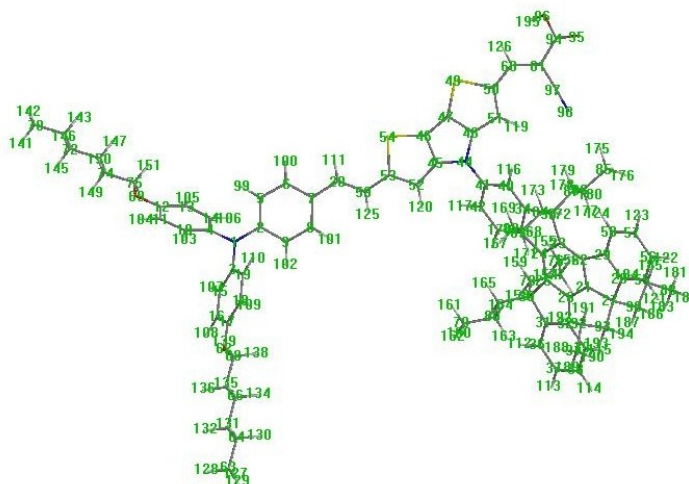
JW3, red solid (74.3% yield). M.p.: 92-94 °C. ¹H NMR (400 MHz, CDCl₃) δ8.21 (s, 1H), 7.61 (s, 1H), 7.12 (s, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 5.6 Hz, 2H), 7.07 (d, *J* = 2.2 Hz, 2H), 6.46 (d, *J* = 8.8Hz, 2H), 6.98 (d, *J* = 8.8Hz, 2H), 6.45 (d, *J* = 2.2 Hz, 4H), 6.55 (d, *J* = 6.5 Hz, 4H), 3.95 (t, *J* = 5.4 Hz, 6H), 2.19 –2.18 (m, 6H), 1.74-1.72 (m, 12H), 1.52–1.49 (m, 6H), 0.94 (t, *J* = 7.1 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ159.63, 155.23, 151.94, 142.22, 139.26, 137.81, 135.16, 132.39, 130.89,

129.87, 128.47, 127.20, 124.77, 124.71, 123.87, 117.35, 115.0, 114.90, 112.67,
101.58, 69.19, 38.72, 30.35, 28.91, 22.95, 14.00. HRMS (ESI) (m/z): [M]⁺ calcd. For
 $C_{56}H_{62}N_3O_5S_2$, 920.4053; found: 920.4131.

JW1



JW2



JW3

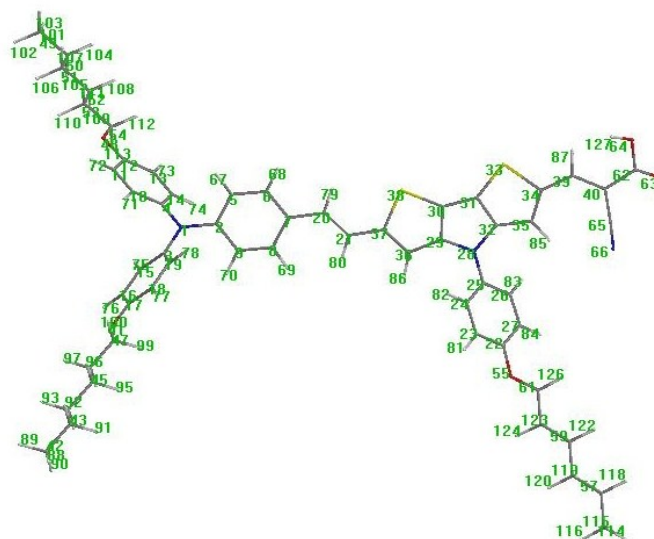
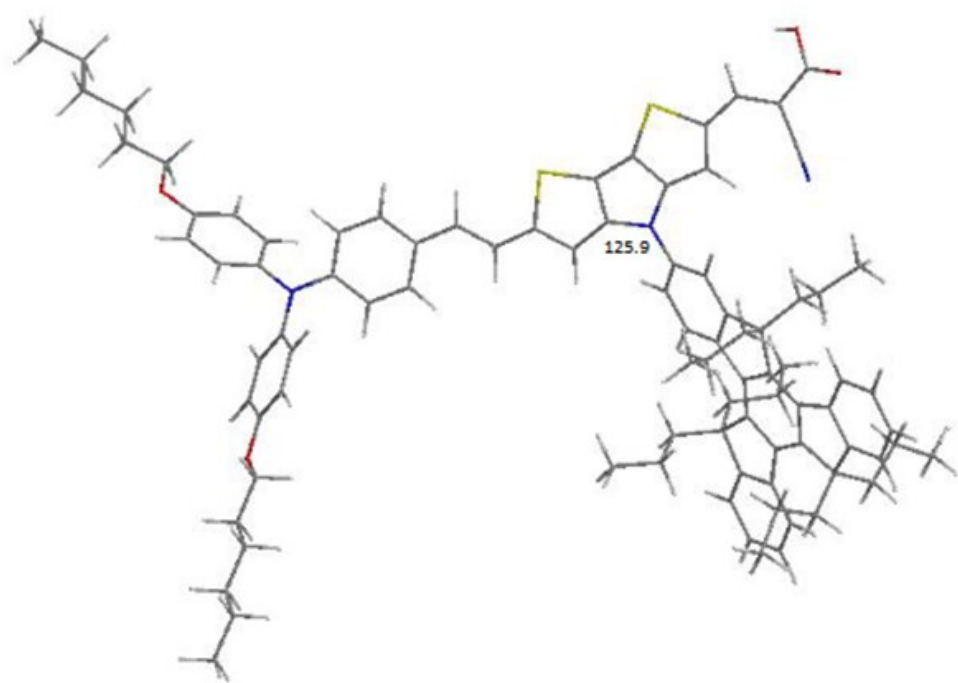
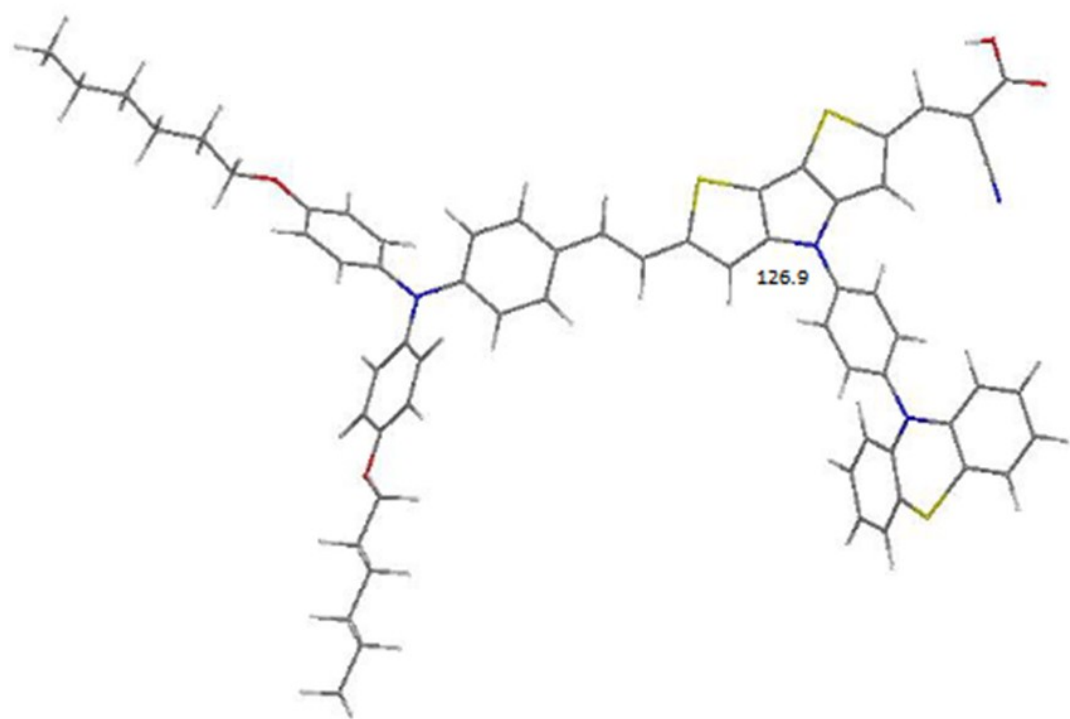


Fig. S1. The numbered structures of JW1, JW2 and JW3.

Table S1. Bond angles (dihedral) and bond lengths of **JW1**, **JW2** and **JW3**

HTMs	Bond (dihedral) angle(°)		Bond length(Å)	
JW1	C(2)-C(1)-C(3)	120.936	C(21)-C(51)	1.432
	C(20)-C(21)-C(51)	126.311	C(20)-C(21)	1.362
	C(21)-C(51)-C(50)	127.024	C(42)-C(39)	1.426
	C(49)-C(42)-C(43)	126.885	C(48)-C(53)	1.417
	C(49)-C(48)-C(53)	131.768		
JW2	C(2)-C(1)-C(3)	120.871	C(41)-C(44)	1.429
	C(20)-C(21)-C(51)	126.217	C(53)-C(59)	1.433
	C(41)-C(44)-C(45)	125.943	C(50)-C(60)	1.416
	C(51)-C(53)-C(59)	132.013	C(20)-C(59)	1.362
	C(52)-C(53)-C(59)	121.230		
JW3	C(25)-C(28)-C(29)	126.850	C(25)-C(28)	1.430
	C(21)-C(37)-C(36)	127.104	C(21)-C(37)	1.433
	C(35)-C(34)-C(39)	131.883	C(34)-C(39)	1.417
	C(2)-C(1)-C(3)	121.060	C(20)-C(21)	1.361
	C(20)-C(21)-C(37)	126.242		



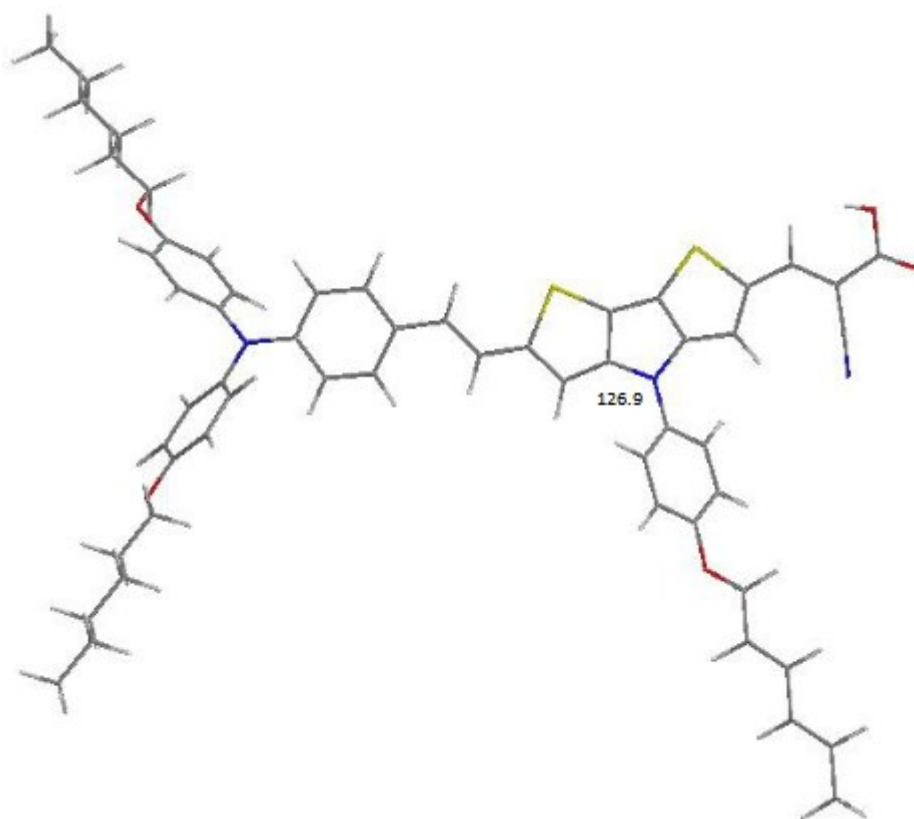


Fig. S2. The optimized geometries of **JW1**, **JW2** and **JW3**.