

Electronic Supplementary Information (ESI) for

Push-pull Type Alkoxy-wrapped *N*-annulated Perylenes for Dye-Sensitized Solar Cells

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1. Synthetic procedures and characterization data

Compound 5. To the solution of compound **4** (892 mg, 1.46 mmol) in DCM (200 mL) was slowly added NBS (260 mg, 1.46 mmol) in portion over half an hour at 0 °C. The mixture was stirred at 0 °C for 30 min. The reaction mixture was quenched with water (50 mL). The organic layer was washed with water, and then washed with saturated brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexanes : DCM = 6 : 1) to give compound **5** as a yellow solid (705 mg, 70%). ¹H NMR (CDCl₃, 300 MHz): δ ppm = 8.65-8.70 (m, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.80-7.91 (m, 4H), 7.56 (d, *J* = 8.7 Hz, 1H), 6.63 (s, 2H), 3.91 (t, *J* = 6.3 Hz, 4H), 2.51 (s, 3H), 1.32-1.37 (m, 4H), 0.97-1.03 (m, 4H), 0.82-0.87 (m, 16H), 0.72 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ ppm = 155.77, 139.69, 133.43, 132.66, 130.74, 130.08, 129.06, 128.22, 125.32, 125.21, 124.75, 124.71, 124.59, 124.54, 123.59, 121.11, 120.77, 119.28, 117.46, 117.29, 116.99, 115.49, 113.73, 106.75, 69.04, 31.50, 28.97, 28.93, 28.89, 25.73, 22.45, 22.38, 13.93. HR-MS (APCI, *m/z*): calcd. for C₄₃H₄₉BrNO₂ ([M+1]), 690.2941; found, 690.2940 (error: -0.2 ppm).

Compound 6. To a solution of **5** (69 mg, 0.1 mmol) in DCM (10 mL) was added several drops of trifluoroacetic acid under argon atmosphere at room temperature. After the mixture was stirred for 10 minutes, *N*-iodosuccinimide (22.4 mg, 0.1 mmol) was added into the mixture. After stirring for half an hour, the mixture was poured into water. The aqueous layer was extracted with DCM, and the combined organic phase was washed with saturated brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced vacuum and the residue was purified by column chromatography (silica gel, DCM: hexane = 1:6) to afford **6** as an yellow solid (49 mg, 60%). ¹H NMR (CDCl₃, 300 MHz): δ ppm = 8.67-8.71 (m, 2H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 7.85-7.92 (m, 3H), 6.63 (s, 2H), 3.95 (t, *J* = 6.3 Hz, 4H), 2.51 (s, 3H), 1.36-1.41 (m, 4H), 0.82-1.00 (m, 20H), 0.70 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ ppm = 155.58, 140.03, 133.59, 132.76, 130.45, 130.25, 130.13, 129.36, 128.21, 126.17, 125.69, 125.44, 125.15, 124.34, 123.87, 121.61, 121.51, 119.32, 117.91, 117.75, 116.84, 113.04, 106.51, 92.09, 69.02, 31.51, 29.05, 28.97, 28.89, 25.81, 22.44, 22.42, 13.92. HR-MS (APCI, *m/z*): calcd. for C₄₃H₄₈BrINO₂ ([M+1]), 816.1908; found, 816.1891 (error: - 2.0 ppm).

Compound 7. To a suspended solution of **6** (82 mg, 0.1 mmol), 4-ethylnyl-*N,N*-bis(4-(hexyloxy)phenyl)aniline (**2**, 37 mg, 0.08 mmol), and tetrakis(triphenylphosphine)palladium (5.5 mg, 0.005 mmol) in THF (10 mL) was added CuI (2 mg, 0.01 mmol), triethylamine (2 ml) under argon. The reaction mixture was stirred at 70 °C for 24 h. The crude compound was extracted into ethyl acetate, washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (silica gel,

DCM : hexanes = 1 : 4) to yield a dark yellow solid (52 mg, 45% yield). ^1H NMR (CDCl_3 , 500 MHz): δ ppm = 8.69-8.72 (m, 2H), 8.56 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.88-7.92 (m, 3H), 7.80 (s, 1H), 7.45 (d, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 9.0 Hz, 4H), 6.92 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 9.0 Hz, 4H), 6.63 (s, 2H), 3.96 (t, J = 6.5 Hz, 4H), 3.92 (t, J = 6.5 Hz, 4H), 2.50 (s, 3H), 1.75-1.82 (m, 4H), 1.45-1.49 (m, 4H), 1.35-1.38 (m, 12H), 0.95-1.00 (m, 4H), 0.81-0.94 (m, 22H), 0.66 (t, J = 6.5 Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ ppm = 155.82, 155.77, 148.59, 140.17, 139.91, 139.62, 133.62, 132.75, 132.28, 130.56, 130.16, 129.76, 128.24, 126.96, 125.39, 125.09, 124.89, 124.55, 124.49, 124.01, 121.39, 121.28, 119.46, 119.19, 119.15, 117.75, 117.56, 117.37, 117.20, 115.35, 114.78, 113.29, 106.63, 93.78, 86.41, 69.03, 68.28, 31.60, 31.52, 29.69, 29.32, 29.01, 28.93, 28.89, 25.79, 25.76, 22.61, 22.43, 22.39, 14.02, 13.94. HR-MS (APCI, m/z): calcd. for $\text{C}_{75}\text{H}_{86}\text{BrN}_2\text{O}_4$ ($[\text{M}+1]$), 1157.5765; found, 1157.5757 (error: -0.7 ppm).

Compound 10. A 100 mL Schlenk flask was charged with **7** (115 mg, 0.1 mmol), pinacolborane (63 mg, 0.5 mmol), triethylamine (102 mg, 1.0 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (4 mg, 0.005 mmol) and 1,2-dichloroethane (10 mL) under argon. The reaction mixture was stirred at 90 °C overnight. After removal of the solvent, the crude compound was extracted into ethyl acetate, washed with brine and water, and dried over anhydrous sodium sulfate. The starting material **7** was almost gone, so the residue was used for next step without purification. To the suspension of the residue, **9** (58 mg, 0.12 mmol), and tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol) in toluene (5 mL) was added potassium carbonate aqueous solution (2 M, 0.4 mL) under argon. The reaction mixture was refluxed for 24 h and then water (5 mL) added. The crude compound was extracted with ethyl acetate three times, followed by washing with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate : hexanes = 1 : 50) to yield a viscous red oil (72 mg, 50% yield over two steps). ^1H NMR (CDCl_3 , 300 MHz): δ ppm = 9.85 (s, 1H), 8.72-8.74 (m, 2H), 8.56 (d, J = 8.0 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.93(t, J = 8.0 Hz, 1H), 7.87(t, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.73 (s, 1H), 7.61 (s, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.32 (s, 1H), 7.09 (d, J = 9.0 Hz, 4H), 6.92 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 9.0 Hz, 4H), 6.64 (s, 1H), 3.90-3.96 (m, 8H), 2.49 (s, 3H), 1.94-1.98 (m, 4H), 1.77-1.81 (m, 4H), 1.45-1.49 (m, 4H), 1.35-1.40 (m, 14H), 1.10-1.23 (m, 14H), 1.08-1.11 (m, 4H), 0.76-0.95 (m, 36H), 0.65 (t, J = 7.5 Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ ppm = 182.47, 163.02, 157.40, 155.85, 155.82, 149.42, 148.62, 148.40, 142.86, 140.18, 139.87, 134.59, 133.56, 133.29, 132.31, 130.89, 130.57, 129.80, 128.95, 127.83, 127.06, 126.99, 125.13, 124.94, 124.47, 124.21, 123.78, 121.70, 121.25, 121.20, 119.47, 119.16, 118.15, 117.83, 117.56, 117.01, 115.37, 114.79, 113.44, 106.70, 93.96, 88.46, 69.06, 68.31, 54.22, 37.74, 31.63, 31.51, 29.71, 29.6, 29.33, 29.04, 29.00, 28.89, 25.81, 25.77, 24.71, 22.62, 22.59, 22.43, 22.41, 14.04, 13.94. HR-MS (APCI, m/z): calcd. for $\text{C}_{97}\text{H}_{115}\text{N}_2\text{O}_5\text{S}_2$ ($[\text{M}+1]$), 1451.8242; found, 1451.8238 (error: -0.3 ppm).

QB4. To a suspended solution of **1** (77 mg, 0.1 mmol), 4-ethylnyl-*N,N*-bis(4-(hexyloxy)phenyl)aniline (**2**, 56 mg, 0.12 mmol), 4-ethylnylbenzoic acid (**3**, 18 mg, 0.12mmol), triethylamine (2 ml) and tetrakis(triphenylphosphine)palladium (5.5 mg, 0.005 mmol) in THF (10 mL) was added CuI (2 mg, 0.01 mmol) under argon. The reaction mixture was stirred at 70 °C for 24 h. The crude compound was extracted into ethyl acetate, washed with brine and water, then acidified with 2 M hydrochloric acid aqueous solution (3 mL) and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/10, v/v) in turn as the eluent to yield a dark red powder (37 mg, 30%). ¹H NMR (THF-d₈, 500 MHz): δ ppm = 8.80 (d, *J* = 6.5Hz, 2H), 8.57 (t, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.89-7.94 (m, 2H), 7.84 (s, 1H), 7.75 (m, 3H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 4H), 6.88 (m, 6H), 6.79 (s, 2H), 3.93-3.98 (m, 8H), 2.51 (s, 3H), 1.75-1.79 (m, 4H), 1.48-1.51 (m, 4H), 1.29-1.37 (m, 12H), 0.78-0.96 (m, 26H), 0.64 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm = 163.51, 155.94, 155.83, 148.63, 140.12, 139.98, 134.02, 133.19, 132.30, 131.35, 130.68, 130.16, 129.75, 129.64, 126.99, 125.38, 124.17, 123.89, 121.42, 121.26, 120.16, 119.40, 118.94, 118.85, 118.16, 117.73, 115.34, 114.64, 113.35, 106.75, 94.20, 88.42, 69.07, 68.28, 31.60, 31.53, 29.69, 29.00, 28.92, 25.81, 25.75, 22.61, 22.43, 22.41, 14.03, 13.93. HR-MS (APCI, *m/z*): calcd. for C₈₄H₉₁N₂O₆ ([M+1]), 1223.6872; found, 1223.6881 (error: +0.8 ppm). Anal. Calcd for C₈₄H₉₀N₂O₆: C, 82.45; H, 7.41; N, 2.29%. Found: C, 82.43; H, 7.44; N, 2.26%.

QB5. To a suspended solution of **7** (58 mg, 0.05 mmol), compound **8** (17 mg, 0.06 mmol), triethylamine (2 ml) and tetrakis(triphenylphosphine)palladium (5.5 mg, 0.005 mmol) in THF (10 mL) was added CuI (2 mg, 0.01 mmol) under argon. The reaction mixture was stirred at 70 °C for 24 h. The crude compound was extracted into ethyl acetate, washed with brine and water, then acidified with 2 M hydrochloric acid aqueous solution (3 mL) and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/10, v/v) in turn as the eluent to yield a dark red powder (23.7 mg, 35%). ¹H NMR (THF-d₈, 500 MHz): δ ppm = 8.94 (d, *J* = 8.0 Hz, 1H), 8.1-8.85 (m, 2H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.17-8.23 (m, 4H), 7.92-8.06 (m, 5H), 7.76 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 4H), 6.88 (m, 6H), 6.81 (s, 2H), 3.94-4.00 (m, 8H), 2.53 (s, 3H), 1.75-1.79 (m, 4H), 1.43-1.51 (m, 4H), 1.36-1.38 (m, 12H), 0.91-0.94 (m, 18H), 0.79-0.81 (m, 8H), 0.56-0.61 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (CDCl₃, 125MHz): δ ppm = 169.02, 156.08, 155.88, 149.02, 140.16, 140.04, 134.24, 132.33, 131.65, 130.50, 129.28, 128.48, 127.01, 125.63, 127.01, 125.63, 125.21, 124.22, 121.46, 121.32, 120.24, 119.43, 119.14, 118.92, 117.83, 115.39, 114.46, 106.83, 94.32, 85.54, 69.14, 68.31, 31.93, 31.62, 31.54, 29.70, 29.36, 29.34, 29.01, 28.95, 28.93, 25.81, 25.77, 22.69, 22.62, 22.42, 14.10, 14.03, 13.92. HR-MS (APCI, *m/z*): calcd. for C₉₀H₉₃N₄O₆S ([M+1]), 1357.6810; found,

1357.6818 (error: +0.6 ppm). Anal. Calcd for C₉₀H₉₂N₄O₆S: C, 79.61; H, 6.83; N, 4.13%. Found: C, 79.64; H, 6.85; N, 4.15%.

QB6. To a stirred solution of **11** (43 mg, 0.03 mmol) and cyanoacetic acid (10 mg, 0.12 mmol) in chloroform (5mL) was added piperidine (25 mg, 0.3 mmol). The reaction mixture was refluxed under argon for 18 h and then acidified with 2 M hydrochloric acid aqueous solution (5mL). The crude product was extracted by chloroform, washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by flash column chromatography with chloroform and methanol/chloroform (1/10, v/v) in turn as the eluent to yield a dark red powder (40 mg, 87%). ¹H NMR (THF-d₈, 500 MHz): δ ppm= 8.79 (broad, 2H), 8.55 (m, 2H), 8.38 (s, 1H), 7.73-7.92 (m, 5H), 7.49 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 4H), 6.88 (m, 6H), 6.78 (s, 2H), 3.93-3.99 (m, 8H), 2.49 (s, 3H), 2.05-2.07 (m, 4H), 1.75-1.79 (m, 4H), 1.46-1.51 (m, 4H), 1.22-1.41(m, 14H), 1.20-1.24 (m, 14H), 1.09-1.11 (m, 4H), 0.79-0.86 (m, 36H), 0.64 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (THF-d₈, 75 MHz): δ ppm= 161.49, 156.21, 154.79, 154.38, 147.44, 138.60, 133.52, 132.13, 131.81, 130.63, 129.64, 129.38, 129.17, 128.26, 127.73, 126.31, 125.50, 123.63, 123.40, 122.66, 122.31, 120.45, 119.88, 117.55, 117.35, 116.43, 116.24, 116.08, 115.29, 113.69, 113.17, 111.52, 105.00, 92.37, 86.61, 67.23, 66.36, 52.68, 36.17, 30.18, 30.14, 30.14, 30.07, 28.19, 27.89, 27.62, 27.53, 27.49, 24.42, 24.33, 21.13, 21.07, 20.92, 19.97, 11.98, 11.93. HR-MS (APCI, *m/z*): calcd. for C₁₀₀H₁₁₆N₃O₆S₂ ([M+1]), 1518.8300; found, 1518.8295 (error: -0.4 ppm). Anal. Calcd for C₁₀₀H₁₁₅N₃O₆S₂: C, 79.06; H, 7.63; N, 2.77%. Found: C, 79.07; H, 7.66; N, 2.79%.

2. Additional spectra

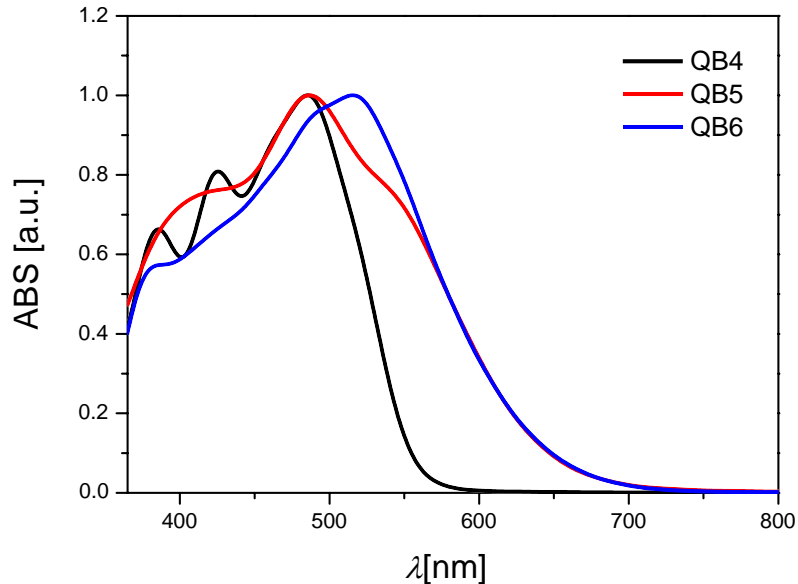


Fig. S1. The UV-Vis absorption spectra of **QB4** (black), **QB5** (red) and **QB6** (blue) adsorbed on TiO₂.

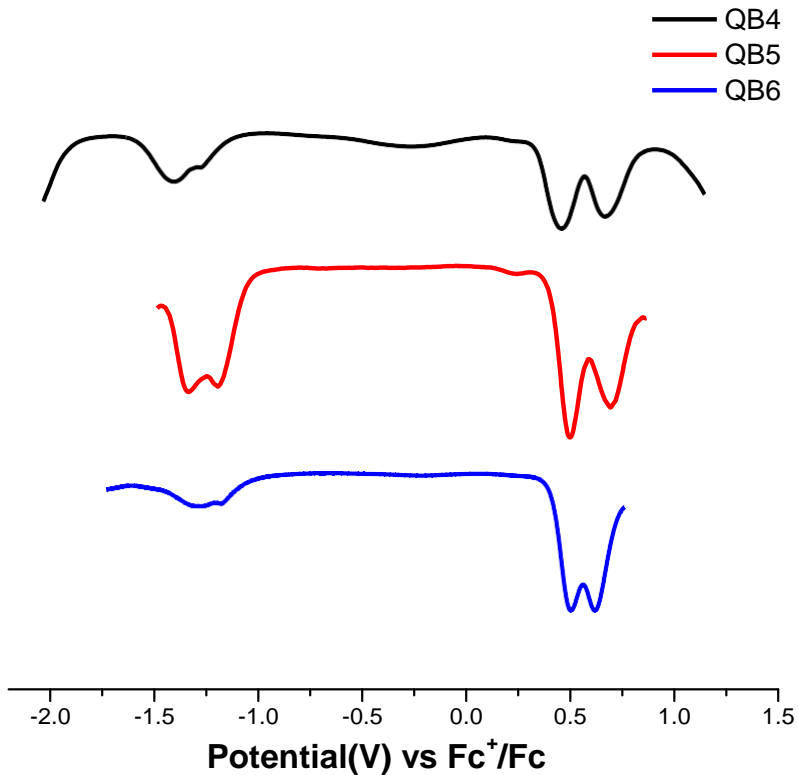


Fig. S2. Differential pulse voltammograms recorded in dry DCM with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte.

3. DFT Calculations

The geometries of **QB4-QB6** were optimized using Gaussian 09 package,¹ utilizing the B3LYP level of theory with basis set 6-31G(d), in the gas phase. Excitation energy was computed using time dependent density functional theory (TDDFT) with 6-31G(d) basis set in the B3LYP optimized geometry. Molecular orbital contributions were determined using GaussSum 3.0 package.² Hydrogen atoms are omitted for clarity.

Table S1. Optimized geometry, calculated HOMO and LUMO profiles and energy levels of **QB4** (B3LYP/6-31G*).

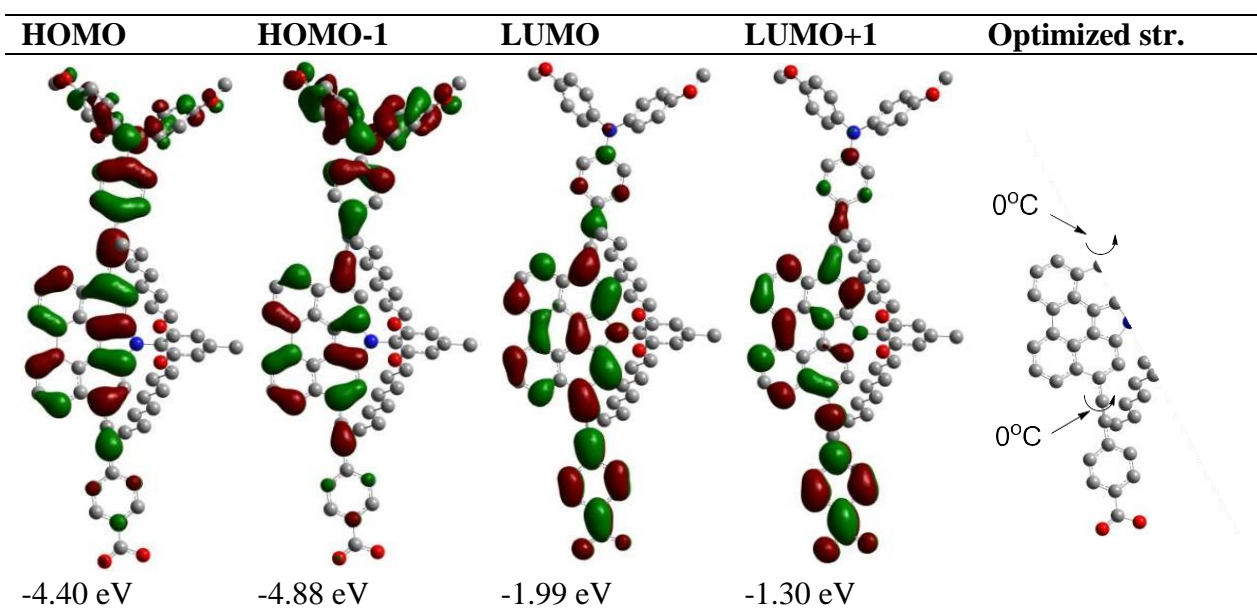
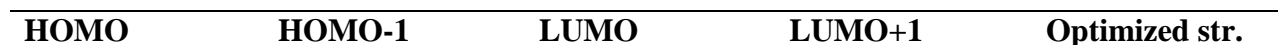


Table S2. Optimized geometry, calculated HOMO and LUMO profiles and energy levels of **QB5** (B3LYP/6-31G*).



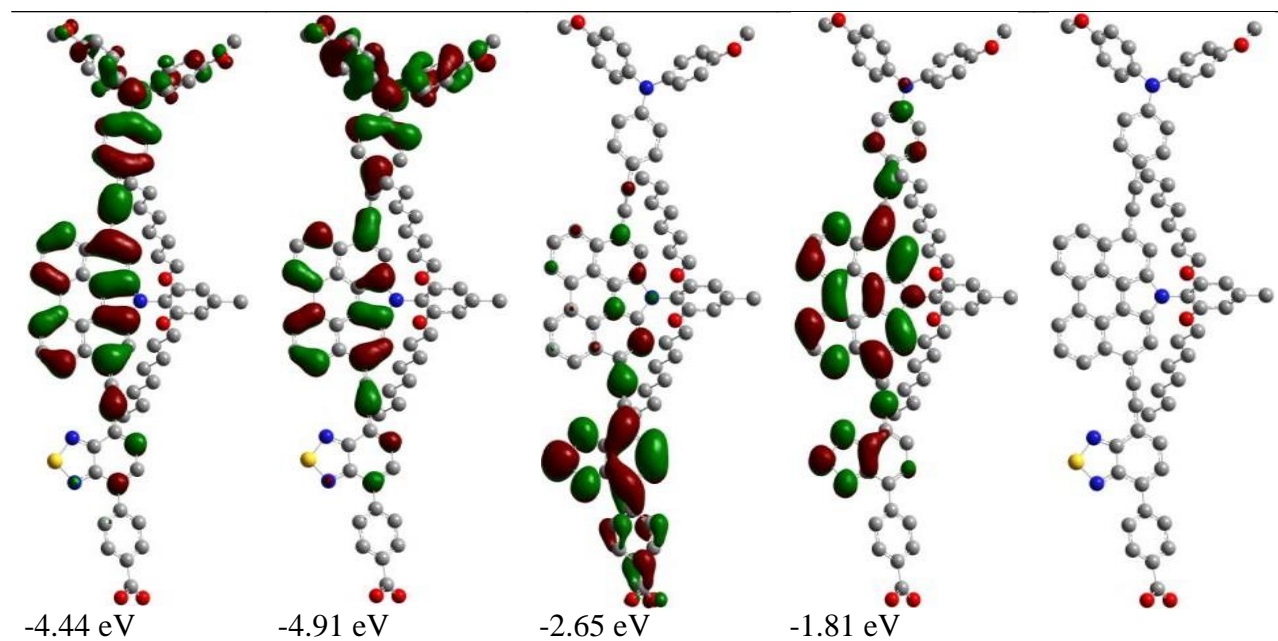


Table S3. Optimized geometry, calculated HOMO and LUMO profiles and energy levels of **QB6** (B3LYP/6-31G*).

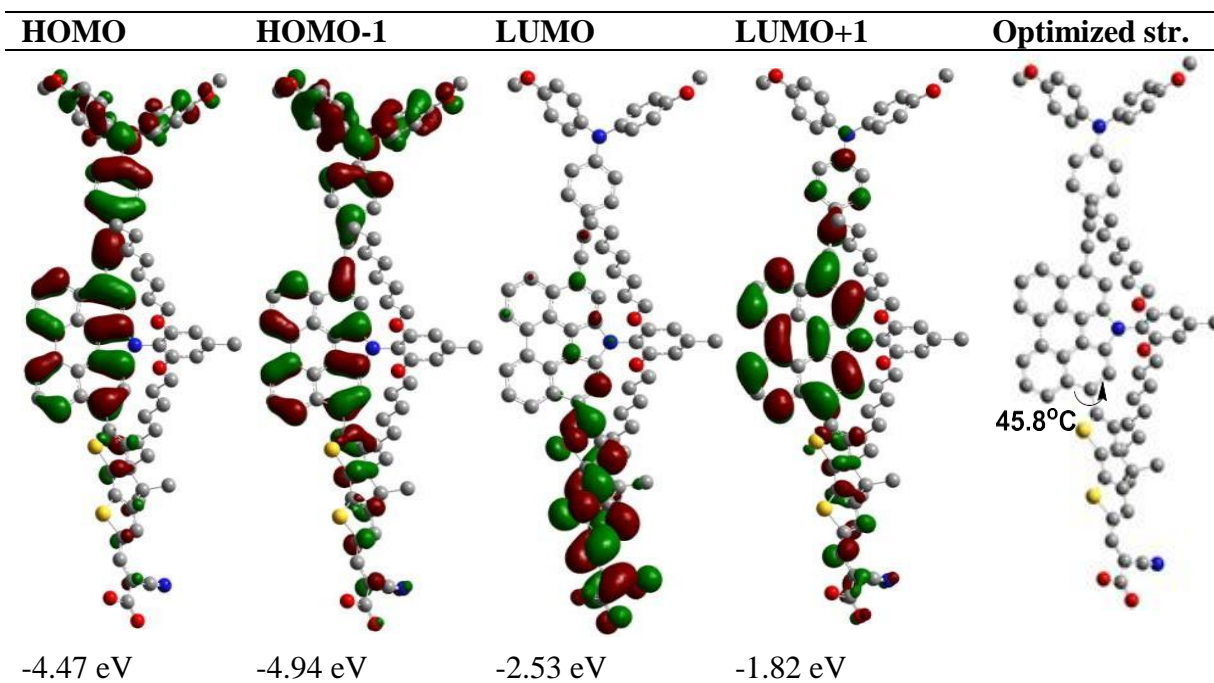


Table S4. TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength (f) and compositions of major electronic transitions of **QB4**.

Energy (cm ⁻¹)	Wavelength (nm)	<i>f</i>	Major contributions
17703.18544	564.8700927	1.6204	HOMO→LUMO (99%)
21583.5456	463.3159067	0.2077	H-1→LUMO (98%)
22794.99872	438.6927204	0.0288	HOMO→L+1 (95%)
24639.60144	405.8507206	0.0744	H-2→LUMO (91%)
26442.26304	378.1824568	0.4494	HOMO→L+2 (91%)
26890.7104	371.8756348	0.0161	H-1→L+1 (91%)
28410.26944	351.9853981	0.012	H-1→L+3 (12%), HOMO→L+3 (84%)
28803.06416	347.1852836	0.0778	H-4→LUMO (28%), H-3→LUMO (57%)
29033.74032	344.4268596	0.119	H-5→LUMO (22%), H-4→LUMO (45%), H-3→LUMO (25%)
29182.14736	342.6752623	0.1264	H-5→LUMO (75%), H-4→LUMO (14%)
29506.38448	338.909703	0.0016	HOMO→L+4 (82%)
30218.57696	330.9222672	0.0557	H-2→L+1 (61%), H-1→L+2 (15%)
30602.49952	326.7706938	0.0368	H-7→LUMO (24%), H-1→L+2 (48%)
30788.00832	324.8017831	0.0123	H-7→LUMO (55%), H-2→L+1 (22%), H-1→L+2 (13%)
31211.45232	320.3952158	0.0127	H-1→L+2 (13%), HOMO→L+5 (22%), HOMO→L+6 (36%)
31665.5456	315.8006537	0.0812	H-6→LUMO (14%), H-1→L+7 (10%), HOMO→L+7 (72%)
32037.36976	312.1354866	0.0008	HOMO→L+5 (61%), HOMO→L+6 (28%)
32125.2848	311.2812871	0.0285	H-6→LUMO (82%), HOMO→L+7 (12%)
32268.04592	309.9041084	0.0012	H-8→LUMO (40%), HOMO→L+6 (13%), HOMO→L+10 (19%)
32531.79104	307.3916216	0.0337	H-1→L+3 (12%), HOMO→L+8 (20%),

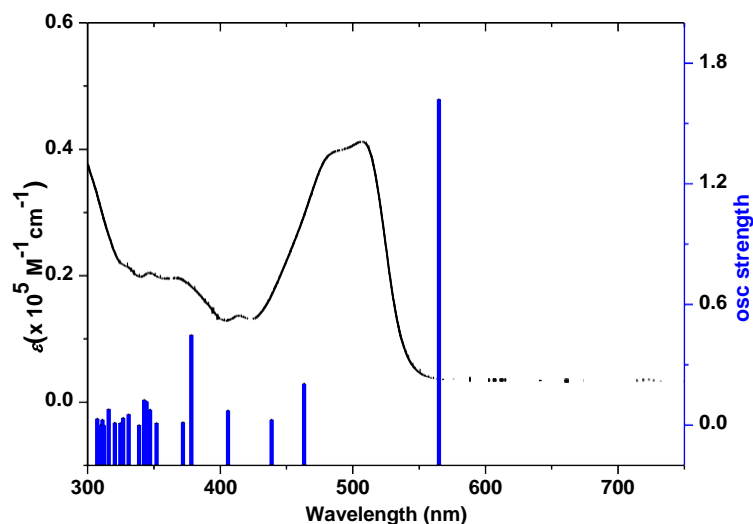


Fig. S3. UV-Vis spectrum and calculated stick spectrum for **QB4**.

Table S5. TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength (f) and compositions of major electronic transitions of **QB5**.

Energy (cm ⁻¹)	Wavelength (nm)	f	Major contributions
12867.05168	777.1788168	0.7871	HOMO→LUMO (99%)
16704.66416	598.6352018	0.0871	H-1→LUMO (98%)
19064.65872	524.5307638	1.2649	HOMO→L+1 (96%)
20543.0832	486.7818478	0.0127	H-2→LUMO (98%)
22358.64976	447.2541995	0.0505	H-3→LUMO (57%), HOMO→L+2 (34%)
22896.62528	436.7455849	0.1381	H-1→L+1 (69%), HOMO→L+2 (22%) H-3→LUMO (26%), H-1→L+1 (25%),
23470.08944	426.0742178	0.023	HOMO→L+2 (41%)
24656.5392	405.5719223	0.0431	H-4→LUMO (91%)
25218.71152	396.5309644	0.0002	H-5→LUMO (99%)
26059.9536	383.7305374	0.0718	H-2→L+1 (75%), HOMO→L+3 (15%)
26660.03424	375.0932917	0.463	H-2→L+1 (12%), HOMO→L+3 (72%)
27081.05856	369.2617841	0.0337	H-1→L+2 (92%)
27223.81968	367.3253833	0.0015	H-7→LUMO (94%)
27657.74896	361.5623243	0.0006	H-6→LUMO (100%)
28140.8784	355.3549345	0.0238	HOMO→L+4 (65%)
28469.14832	351.2574345	0.0135	H-1→L+5 (13%), HOMO→L+5 (83%)
28807.09696	347.13668	0.0117	H-8→LUMO (71%), H-3→L+1 (17%)

28949.85808	345.4248367	0.0197	H-8→LUMO (15%), H-3→L+1 (62%)
29478.15488	339.2342581	0.0047	H-9→LUMO (46%), HOMO→L+7 (28%)
29816.10352	335.38923	0.0305	H-9→LUMO (19%), HOMO→L+7 (55%)

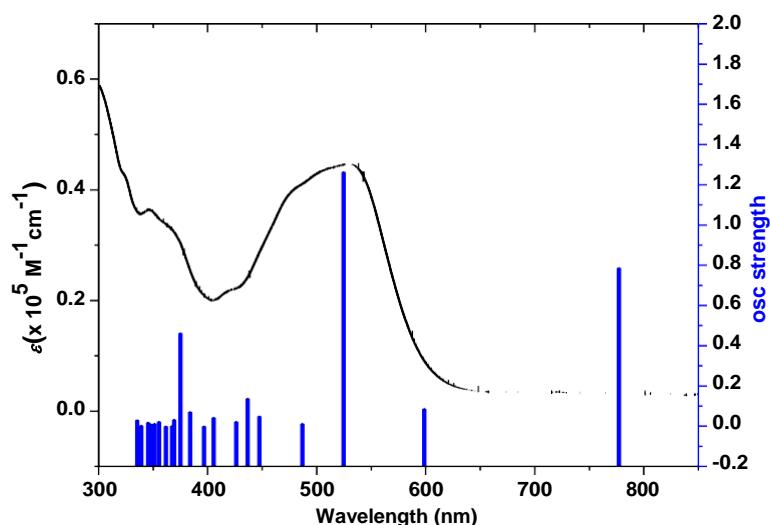


Fig. S4. UV-Vis spectrum and calculated stick spectrum for **QB5**.

Table S6. TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength (f) and compositions of major electronic transitions of **QB6**.

Energy (cm ⁻¹)	Wavelength (nm)	f	Major contributions
14048.66208	711.8115549	0.7166	HOMO→LUMO (99%)
17972.57648	556.403252	0.3114	H-1→LUMO (97%)
19202.58048	520.7633427	1.1229	HOMO→L+1 (91%)
22163.46224	451.1930443	0.0601	H-3→LUMO (79%), H-2→LUMO (13%)
22583.68	442.7976309	0.3385	H-3→LUMO (19%), H-2→LUMO (38%), H-1→L+1 (38%)
23790.29376	420.3394923	0.1337	H-2→LUMO (39%), H-1→L+1 (53%)
25943.80896	385.4484134	0.0257	H-4→LUMO (46%), H-2→L+1 (11%), HOMO→L+2 (23%), HOMO→L+3 (14%)
26164.8064	382.1927763	0.0423	H-4→LUMO (43%), HOMO→L+2 (37%)
26231.75088	381.217405	0.1818	H-3→L+1 (38%), HOMO→L+3 (42%)
26712.46064	374.3571262	0.0003	H-5→LUMO (98%)
26946.36304	371.1075957	0.408	H-3→L+1 (25%), HOMO→L+2 (26%), HOMO→L+3 (34%)
27014.92064	370.1658107	0.0266	H-3→L+1 (19%), H-2→L+1 (66%)

28530.44688	350.5027468	0.0126	H-1→L+4 (12%), HOMO→L+4 (83%)
28701.4376	348.4146035	0.0011	H-7→LUMO (93%)
28707.89008	348.3362926	0.001	H-6→LUMO (95%)
29328.13472	340.9695194	0.0168	HOMO→L+5 (81%)
30122.59632	331.976696	0.0066	H-8→LUMO (50%), H-1→L+2 (23%)
30291.97392	330.120448	0.163	H-4→L+1 (17%), H-1→L+3 (60%)
30499.25984	327.8768092	0.0006	H-9→LUMO (31%), H-4→L+1 (10%), H-1→L+2 (38%)
30950.93344	323.0920327	0.013	H-9→LUMO (26%), H-4→L+1 (30%), HOMO→L+7 (18%)

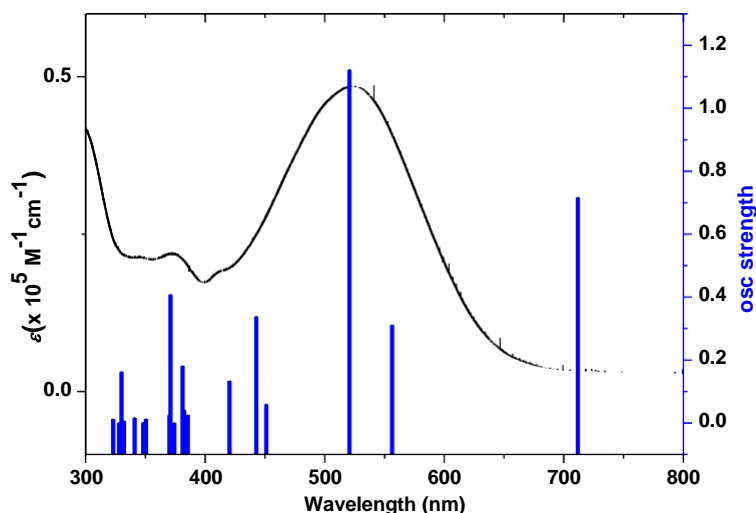


Fig. S5. UV-Vis spectrum and calculated stick spectrum for **QB6**.

Reference:

(11) *Gaussian 09*, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;

Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

(2) N.M. O'Boyle, A.L. Tenderholt and K.M. Langner. *J. Comp. Chem.* 2008, **29**, 839-845.

4. Photovoltaic properties

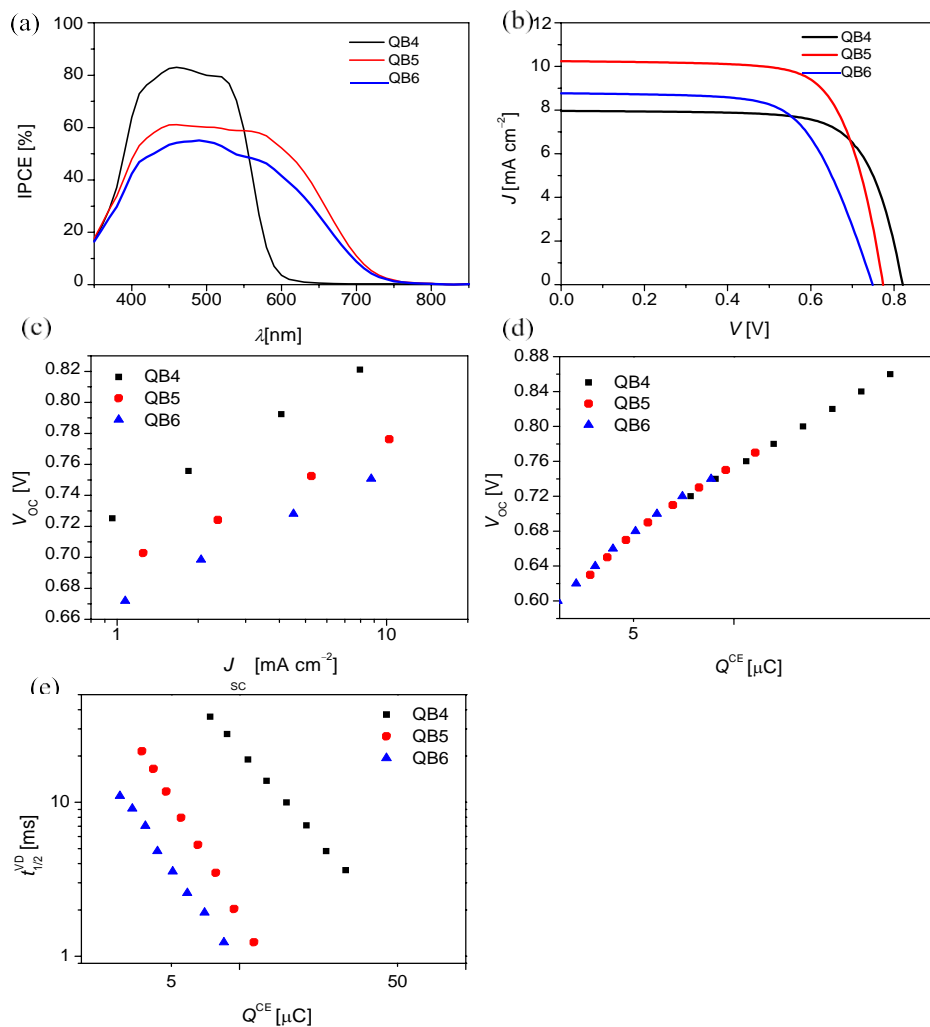


Fig. S6. (a) IPCEs spectra and (b) Current-voltage characteristics (c) Open-circuit photovoltage plotted as a function of short-circuit photocurrent density. (d) Plots of open-circuit photovoltage versus extracted charge. (e) Plots of lifetime of photoinjected electrons in titania as a function of extracted charge recorded for DSCs devices fabricated with the three dyes without the presence of CDCA.

Fig. S8. ^{13}C NMR spectrum (75 MHz, CDCl_3) of **5**.

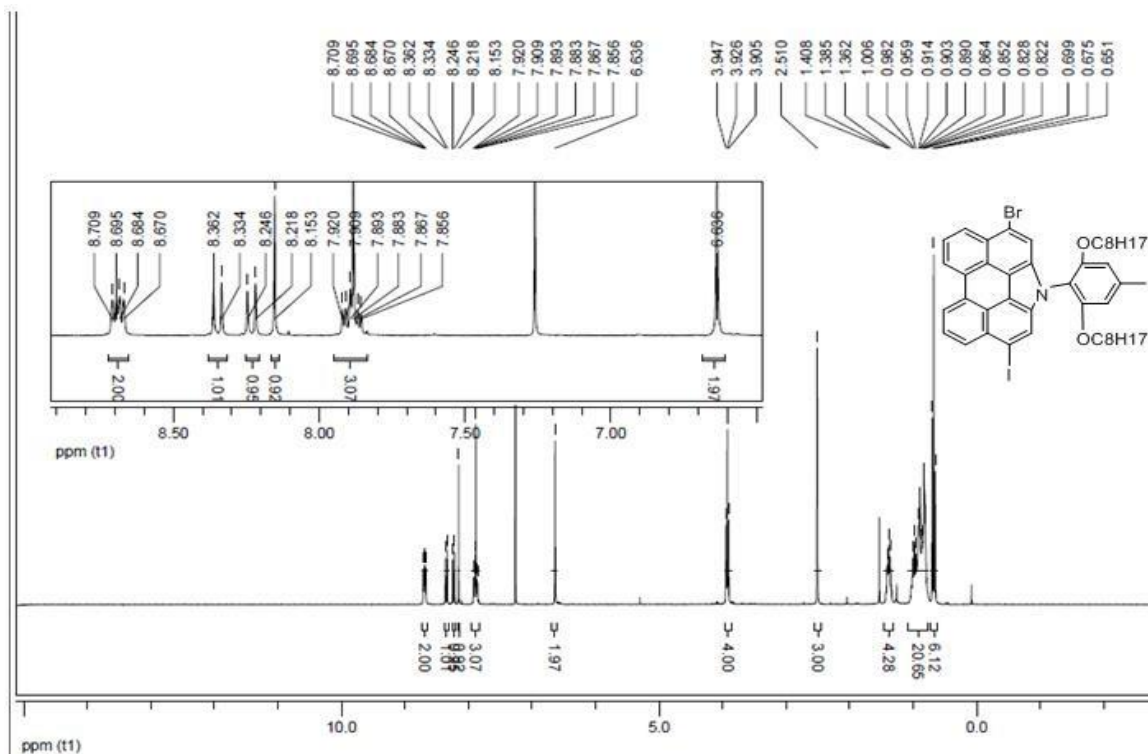


Fig. S9. ^1H NMR spectrum (300 MHz, CDCl_3) of **6**.

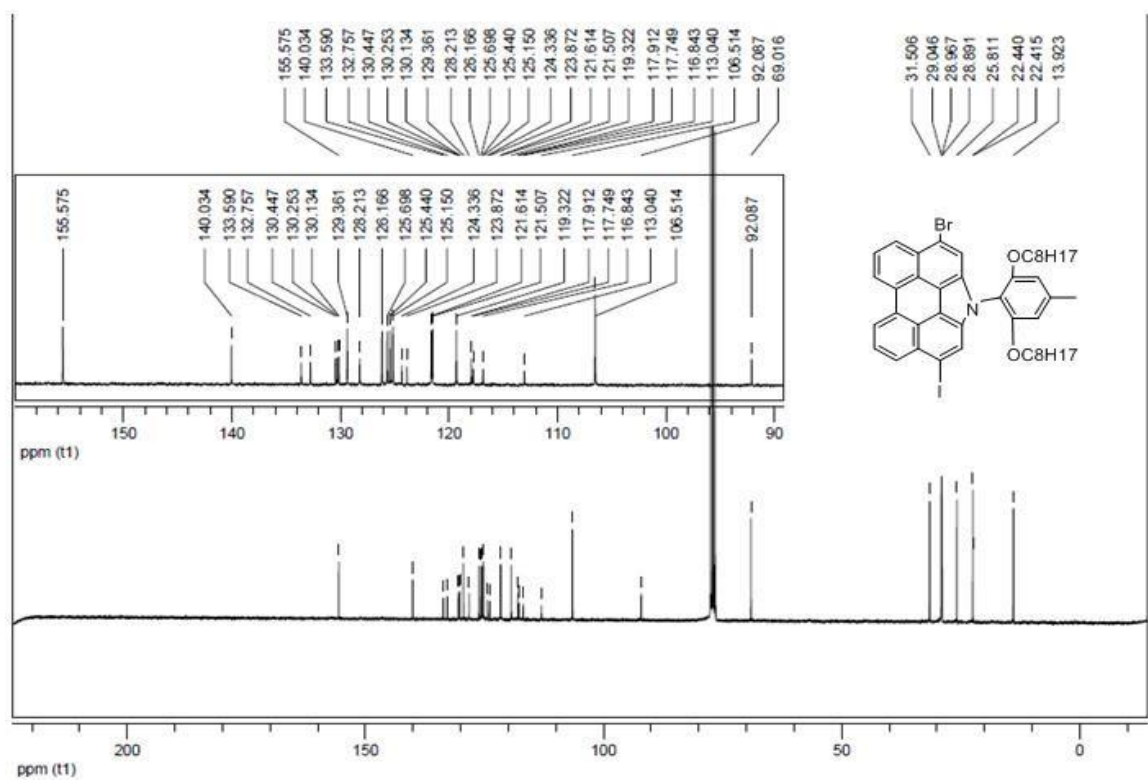


Fig. S10. ^{13}C NMR spectrum (75 MHz, CDCl_3) of **6**.

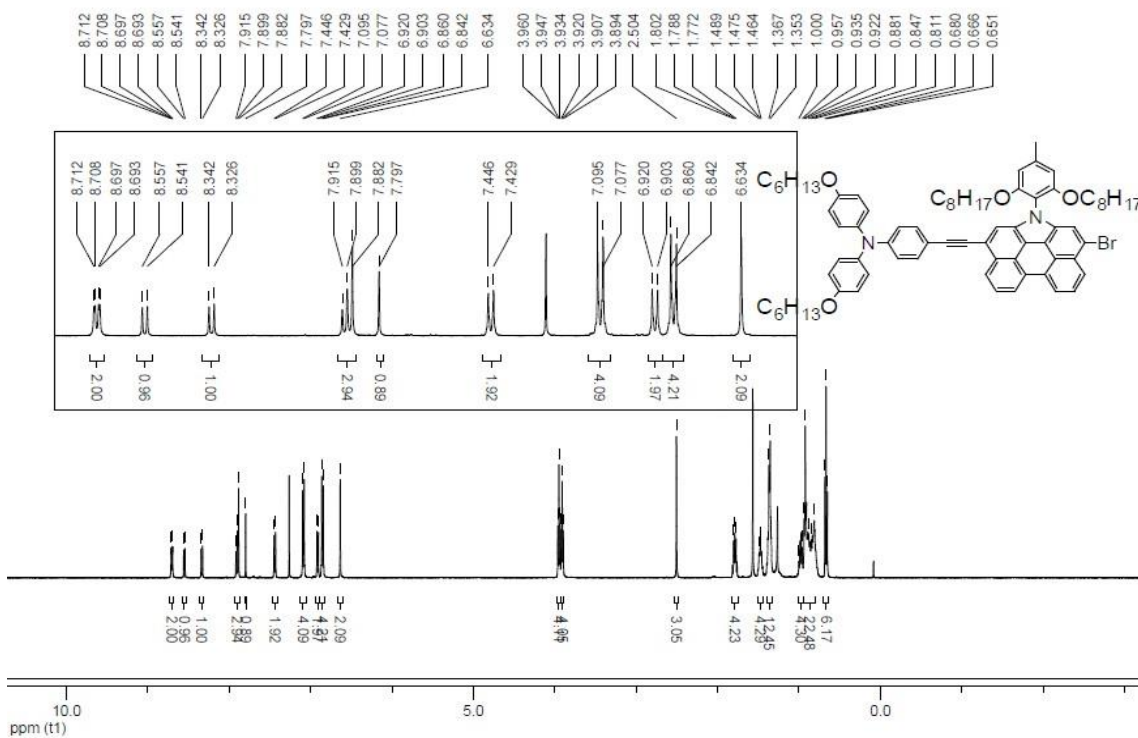


Fig. S12. ^{13}C NMR spectrum (125 MHz, CDCl_3) of **7**.

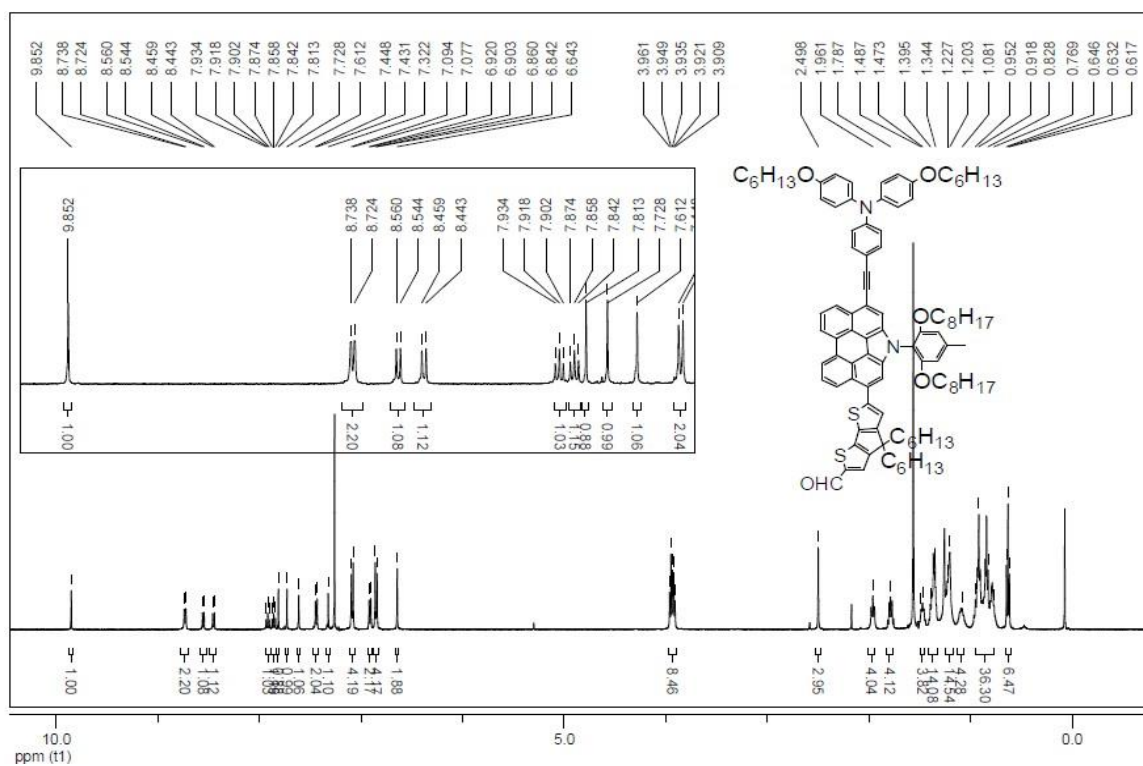


Fig. S13. ^1H NMR spectrum (500 MHz, CDCl_3) of **10**.

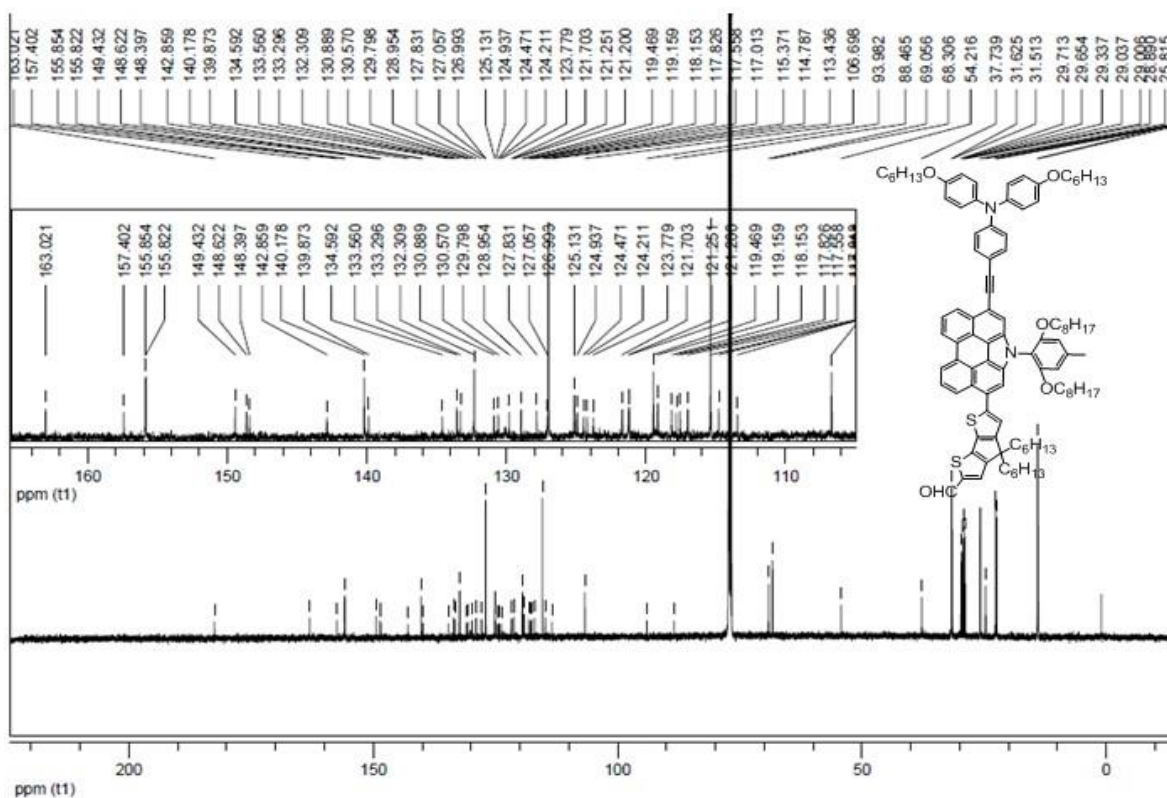


Fig. S14. ^{13}C NMR spectrum (125 MHz, CDCl_3) of **10**.

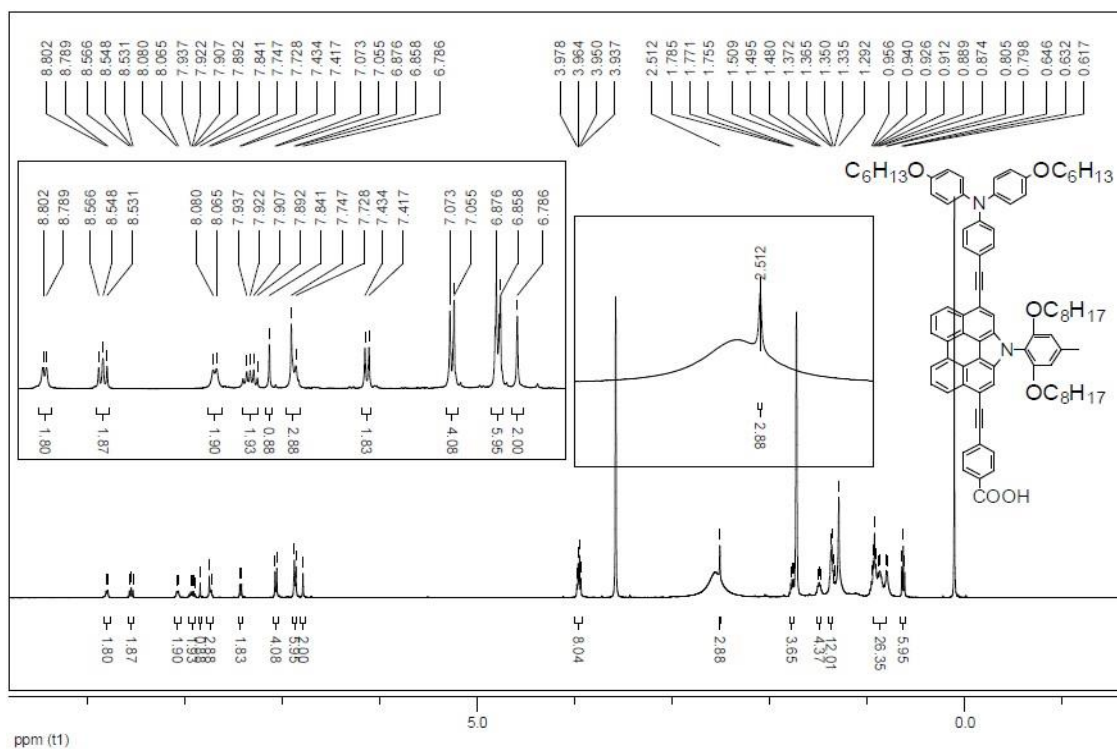


Fig. S15. ^1H NMR spectrum (500 MHz, THF-d_8) of **QB4**.

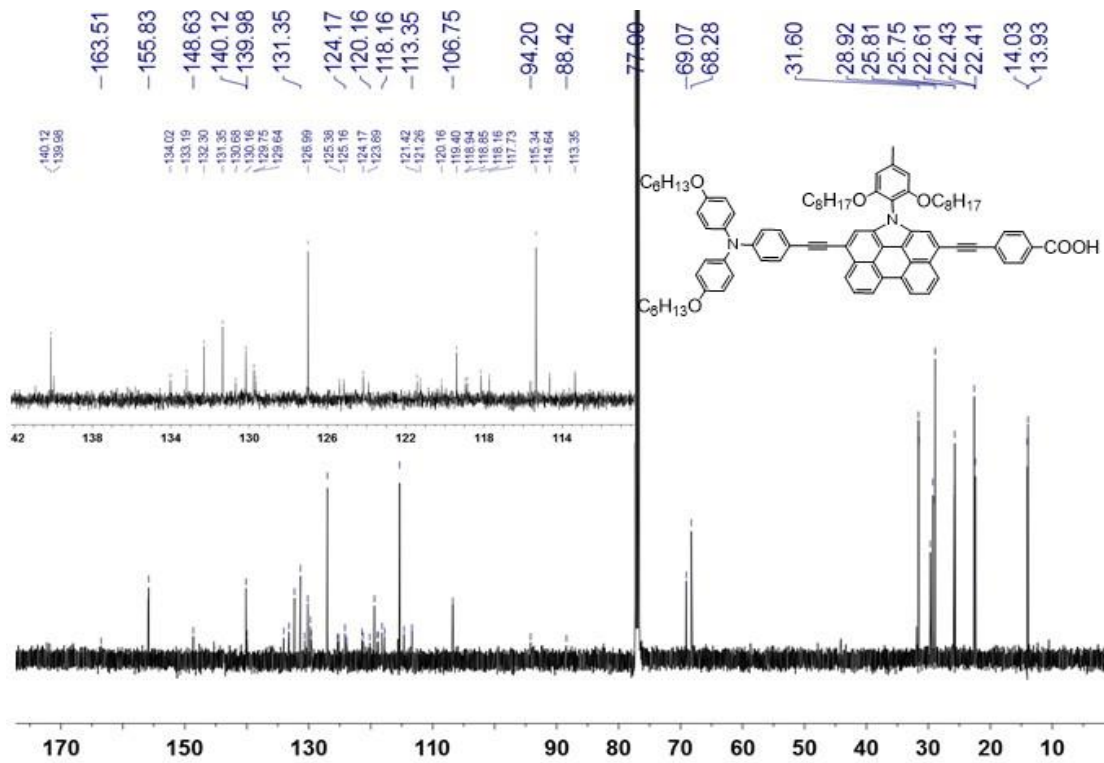


Fig. S18. ^{13}C NMR spectrum (125 MHz, CDCl_3) of **QB5**.

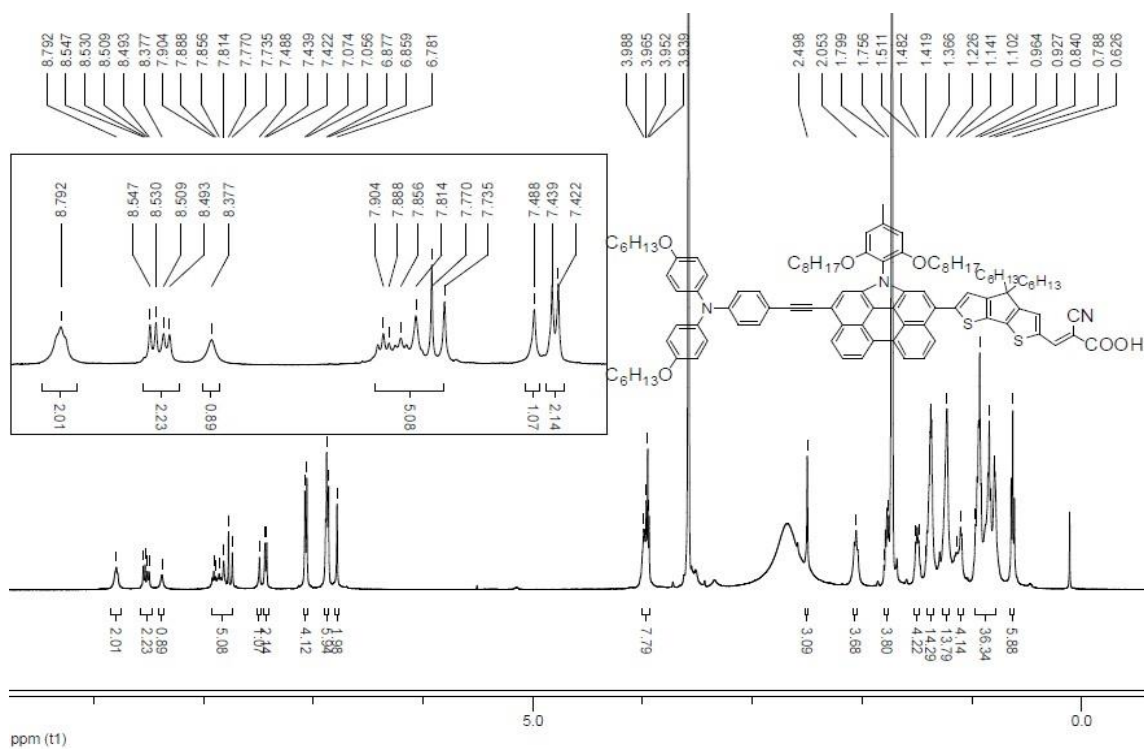


Fig. S19. ^1H NMR spectrum (500 MHz, THF-d_8) of **QB6**.

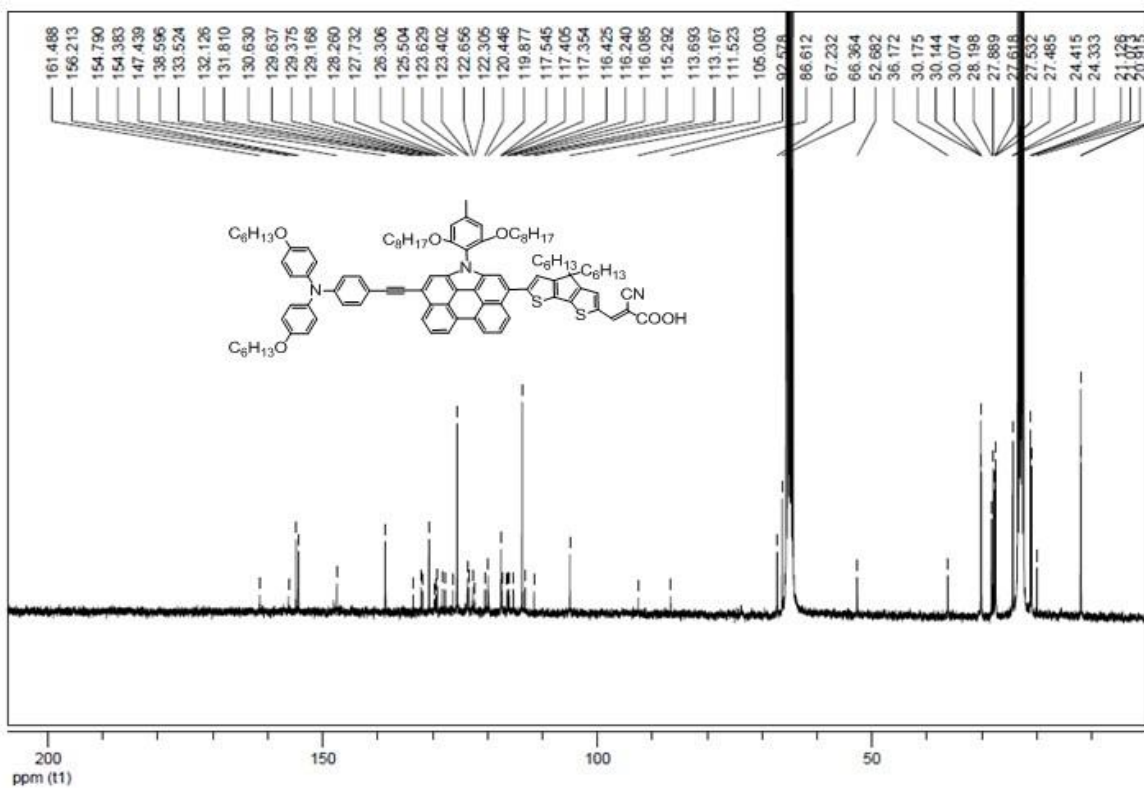


Fig. S20. ^{13}C NMR spectrum (125 MHz, THF- d_8) of **QB6**.

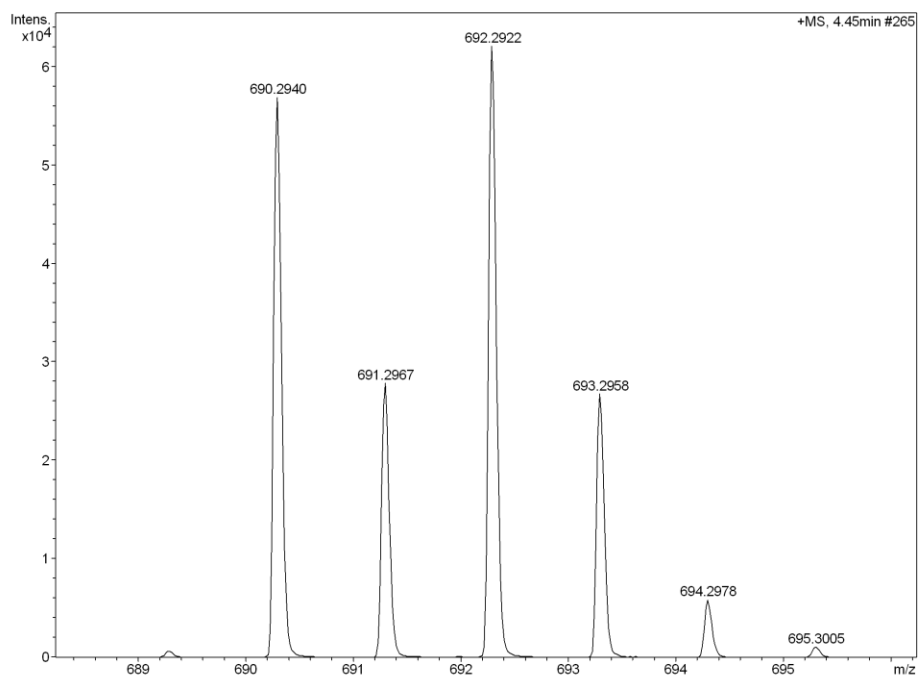


Fig. S21. HR mass spectrum (APCI) of compound **5**.

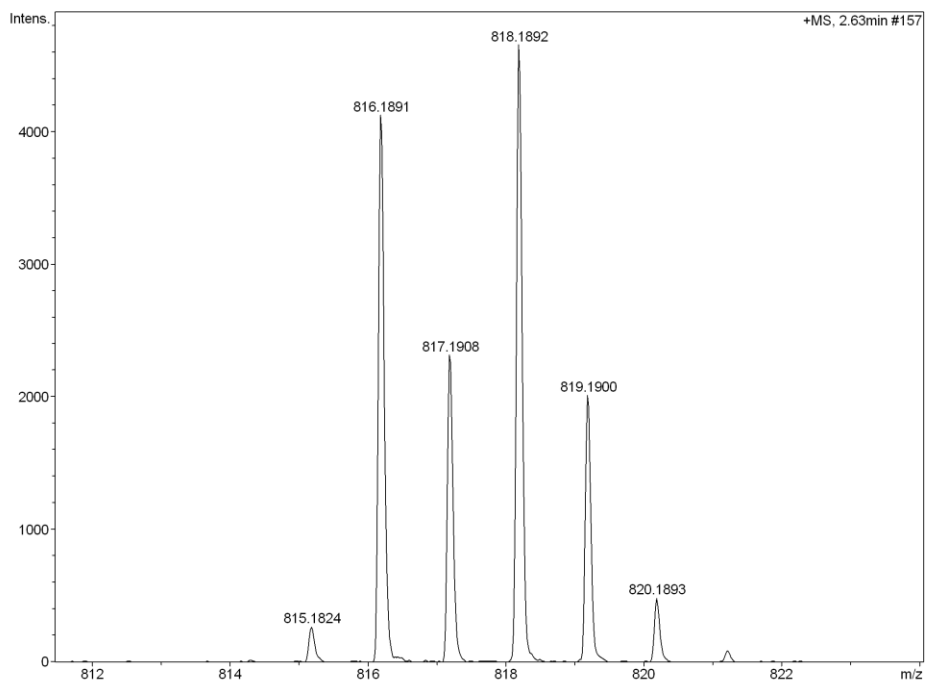


Fig. S22. HR mass spectrum (APCI) of compound **6**.

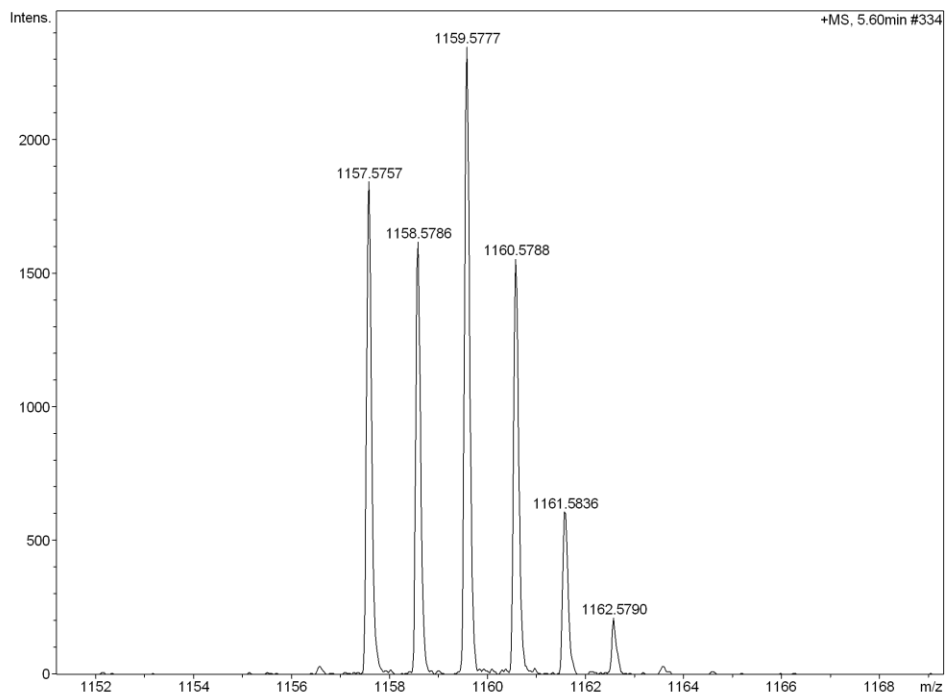


Fig. S23. HR mass spectrum (APCI) of compound **7**.

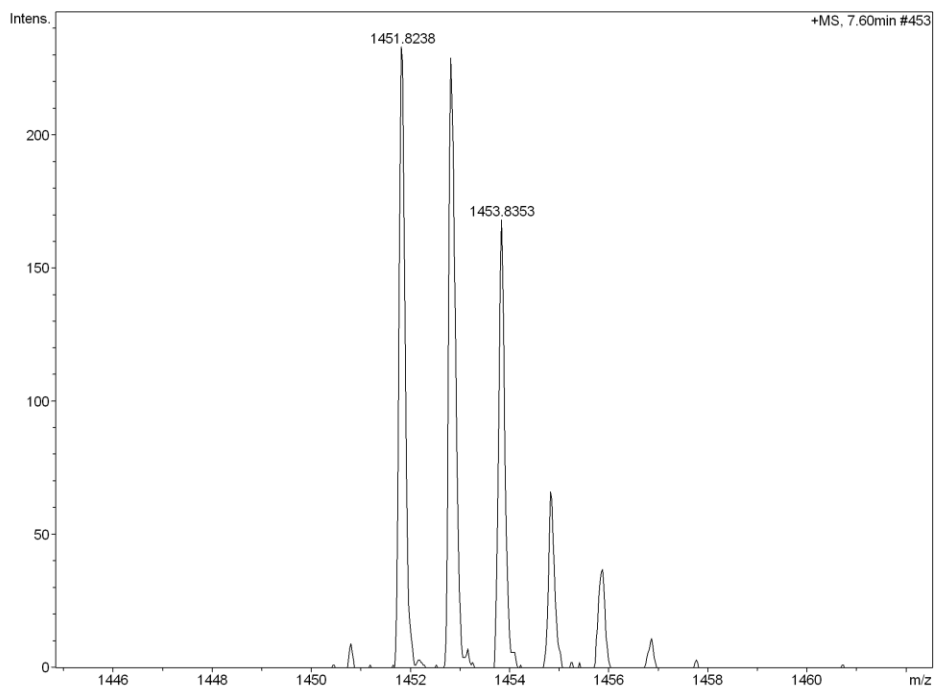


Fig. S24. HR mass spectrum (APCI) of compound **10**.

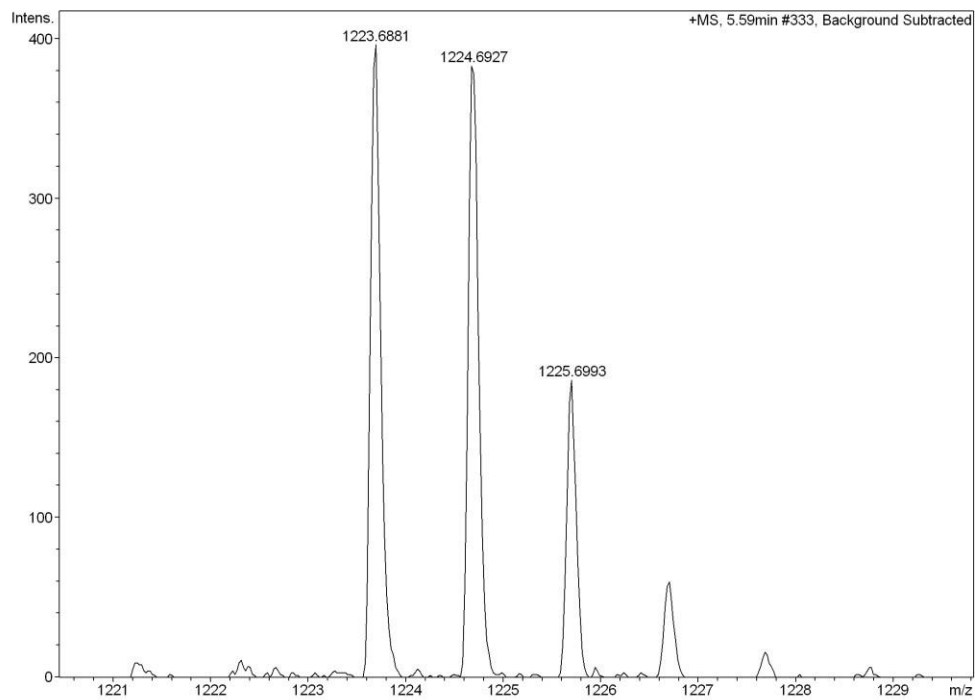


Fig. S25. HR mass spectrum (APCI) of compound **QB4**.

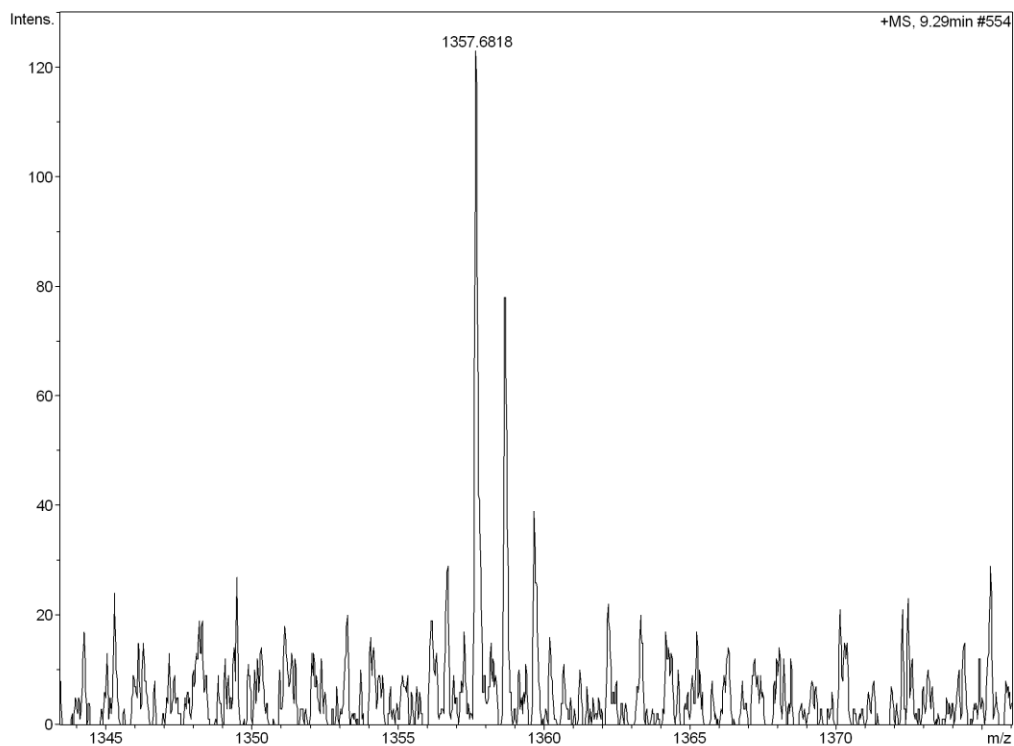


Fig. S26. HR mass spectrum (APCI) of compound **QB5**.

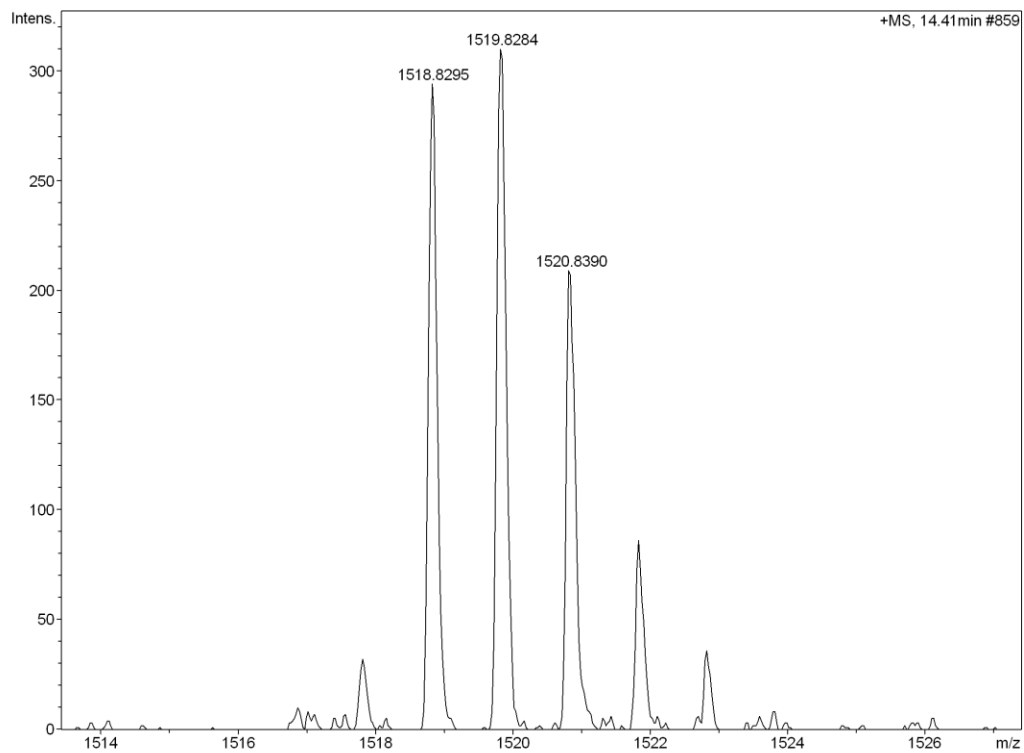


Fig. S27. HR mass spectrum (APCI) of compound **QB6**.