Supplementary Information

Colour tuning of blue electroluminescence using bipolar carbazole-oxadiazole molecules in single-active-layer organic light emitting devices (OLEDs)

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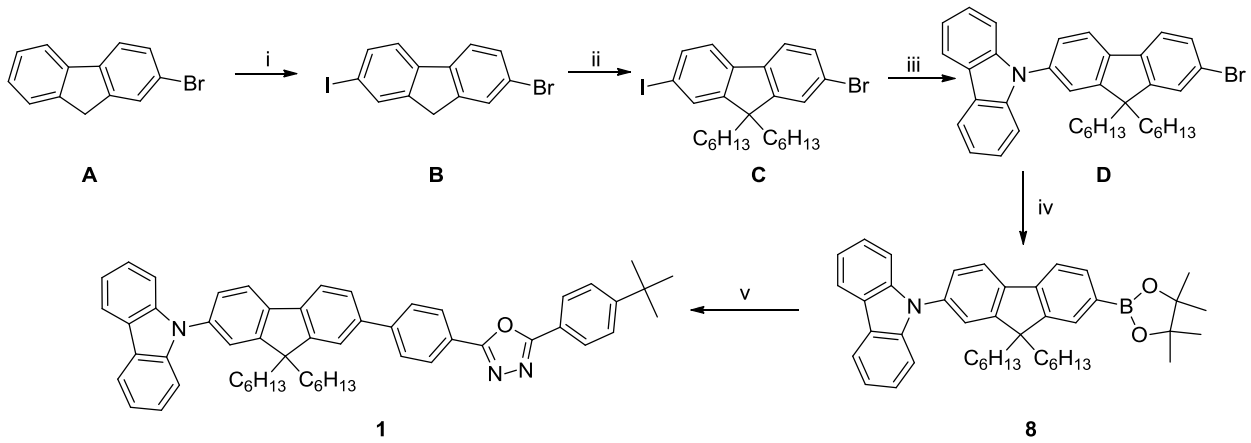
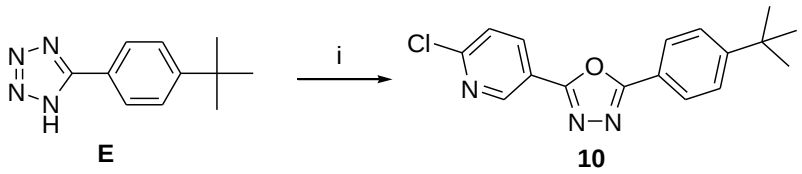
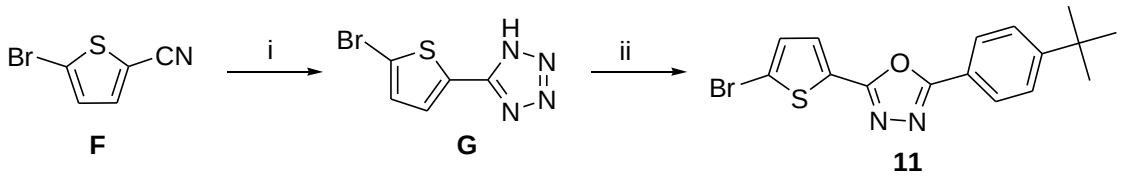


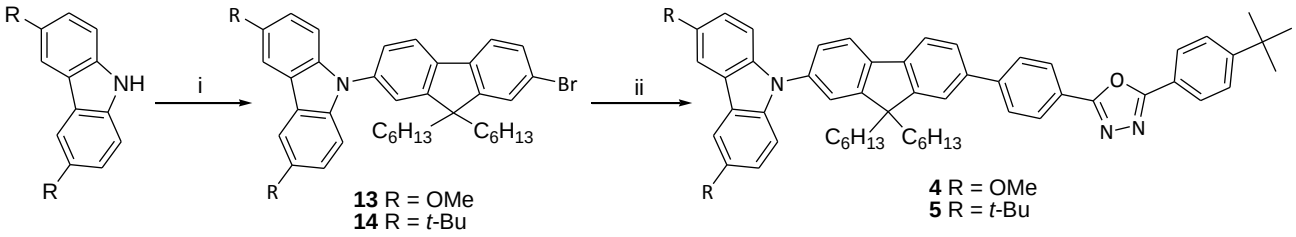
Scheme S1. Synthesis of **1** as previously described[1]: i) AcOH, H_2SO_4, KIO_3, I_2, 80 ^oC, 18 h; ii) tetra-*n*-butylammonium chloride, NaOH, *n*-bromohexane, RT, 20 h; iii) carbazole, CuI, 1,10-phenanthroline, K_2CO_3, DMF, 120 ^oC, 40 h; iv) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, -78 ^oC – RT, 15 h; v) 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, $Pd(PPh_3)_2Cl_2$, NaOH (aq), THF, reflux, 15 h.



Scheme S2. Synthesis of **10**: i) 6-chloronicotinoyl chloride, pyridine, 100 ^oC, 3 h.

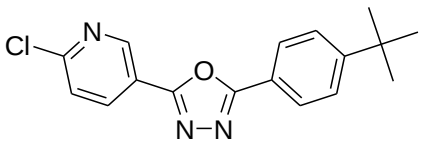


Scheme S3. Synthesis of **11**: i) NH_4Cl, NaN_3, DMF, 120 ^oC, 15 h; ii) 4-*tert*-butylbenzoyl chloride, pyridine, 100 ^oC, 15 h.



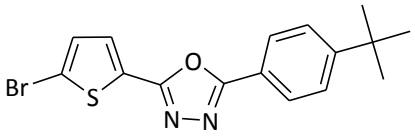
Scheme S4. Synthesis of **4** and **5**: i) 2-iodo-7-bromo-9,9-dihexylfluorene, CuI, 1,10-phenanthroline, DMF, 120 ^oC, 15 h, 93% for **13**, 73% for **14**; ii) $Pd(PPh_3)_2Cl_2$, NaOH (aq), THF, reflux, 15 h; 73% for **4**, 77% for **5**.

2-(4-*Tert*-butylphenyl)-5-(6-chloropyridin-3-yl)-1,3,4-oxadiazole, 10



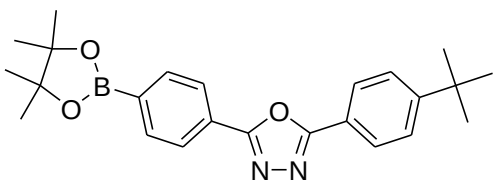
5-(4-*Tert*-butylphenyl)-1*H*-tetrazole[2] **E** (1.62 g, 8.00 mmol) and 6-chloronicotinoyl chloride (1.55 g, 8.80 mmol) were dissolved in pyridine (30 cm^3). The mixture was stirred and heated to 100 °C for 3 h. The reaction mixture was then cooled and poured onto water precipitating a pale yellow solid. The solid was filtered and recrystallised from ethanol to give **10** as white crystals (1.73 g, 69 %). ^{1}H NMR (700 MHz, DMSO-d_6): δ 9.12 (1H, dd, *J* = 2.4, 0.7 Hz), 8.51 (1H, dd, *J* = 8.3, 2.5 Hz), 8.06 (2H, d, J = 8.7 Hz), 7.78 (1H, dd, *J* = 8.3, 0.7 Hz), 7.67 – 7.60 (1H, d, J = 8.7 Hz), 1.31 (s, 9H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ 165.01, 161.84, 155.78, 153.42, 148.26, 138.02, 127.19, 126.72, 125.58, 120.76, 120.02, 35.34, 31.26 ppm; HRMS calcd for $C_{17}H_{17}N_3O^{35}Cl$: 314.1060. Found: 314.1063; Mp. 172.0 – 173.0 °C.

2-(5-Bromothiophen-2-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 11



5-Bromothiophene-2-carbonitrile[3] **F** (8.00 g, 42.5 mmol) was dissolved in anhydrous DMF (80 cm^3) to which ammonium chloride (2.70 g, 51 mmol) and sodium azide (3.31 g, 51 mmol) were added. The mixture was heated to 120 °C for 15 h. The reaction mixture was cooled, poured onto water and acidified to pH 3 with aqueous HCl to precipitate 5-(5-bromothiophen-2-yl)-1*H*-tetrazole **G** as a white solid which was used without purification. To a solution of **G** (9.61 g) in pyridine (50 cm^3) 4-*tert*-butylbenzoyl chloride (9.75 cm^3, 49.9 mmol) was added and the solution was heated to 100 °C for 15 h. The reaction mixture was cooled and poured onto water to precipitate a product which was filtered, washed with water and dried under high vacuum. The product was purified by chromatography on silica with DCM as eluent; the solid obtained was recrystallised from ethanol to give **11** as white crystals (11.4 g, 43 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.02 – 7.99 (2 H, m), 7.56 (1 H, d, *J* = 3.9), 7.55 – 7.51 (2 H, m), 7.14 (1 H, d, *J* = 3.9) 1.36 (9 H, s); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.18, 159.52, 155.55, 131.05, 129.65, 126.78, 126.06, 120.63, 117.79, 53.40, 35.09, 31.08; GC-MS (EI+) *m/z* 364 (M^+, 45 %), 349 (55 %), 161 (100); HRMS calcd for $C_{16}H_{16}N_2OS^{79}Br$: 363.0167. Found: 363.0152; Mp. 179.8 – 181.3 °C.

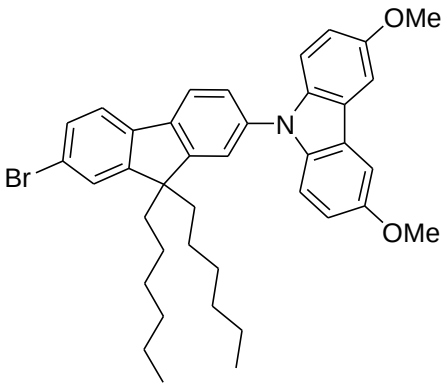
2-(4-*Tert*-butylphenyl)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole, 15



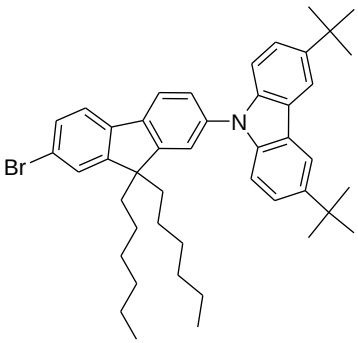
To a flame dried flask under an atmosphere of argon 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **9**[4] (1.50 g, 4.2 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.17 g, 4.6 mmol) and potassium

acetate (1.24 g, 12.6 mmol) were added. Anhydrous DMF was added and the mixture was degassed for 30 min. To this stirred solution $PdCl_2$(dppf) (10 mg, 0.1 mmol) was added and the reaction mixture was heated to 80 °C for 15 h. The reaction mixture was cooled, washed with brine and extracted with DCM. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel with 9 : 1 (v/v) petroleum ether : ethyl acetate as eluent to yield **15** as a white solid (1.41 g, 83 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.12 (2 H, d, *J* = 8.3), 8.07 (2 H, d, *J* = 8.6), 7.95 (2 H, d, *J* = 8 .3), 7.54 (2 H, d, *J* = 8.6), 1.37 (18 H, s), 1.36 (9 H, s); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.78, 164.38, 155.36, 135.27, 126.81, 126.16, 126.02, 125.90, 121.05, 84.19, 35.08, 31.10, 24.87; HRMS calcd for $C_{24}H_{30}{}^{10}BN_2O_3$: 404.2386. Found: 404.2389; Mp. 198.0 – 198.5 °C.

9-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-3,6-dimethoxy-9*H*-carbazole, 13



To a flame dried flask under an atmosphere of argon 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene **C**[5] (1.00 g, 1.85 mmol), 3,6-dimethoxy-9*H*-carbazole[6] (0.42 g, 1.85 mmol), copper iodide (0.03 g, 0.19 mmol), 1,10-phenanthroline (0.07 g, 0.37 mmol) and potassium carbonate (0.51 g, 3.7 mmol) were added. The flask was evacuated and backfilled with argon. Degassed DMF (8 cm^3) was added to the reagents *via* the septum. The mixture was stirred and heated to 120 °C for 40 h. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography on silica with 98 : 2 (v/v) petroleum ether : DCM as eluent to yield **13** as a white solid (1.10 g, 93 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (1 H, d, *J* = 7.8), 7.66 – 7.58 (3 H, m), 7.57 – 7.50 (4 H, m), 7.38 (2 H, d, *J* 8.9), 7.09 (2 H, dd, *J* 8.9, 2.5), 3.99 (6 H, s), 2.06 – 1.94 (4 H, m), 1.24 – 1.05 (12 H, m), 0.82 (6 H, t, *J* 7.1), 0.79 – 0.65 (4 H, m); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.30, 153.43, 152.42, 139.65, 139.05, 137.55, 136.58, 130.47, 126.51, 125.72, 123.90, 121.58, 121.52, 121.43, 121.17, 115.47, 110.93, 103.20, 56.39, 55.93, 40.47, 31.79, 29.86, 24.11, 22.85, 14.33; HRMS calcd for $C_{39}H_{45}NO_2{}^{79}Br$: 638.2634. Found: 638.2622; Mp. 92.0 – 91.5 °C.

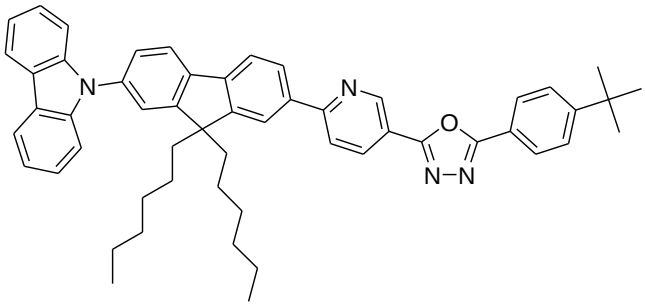


9-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-3,6-di-*tert*-butyl-9*H*-carbazole, 14

To a flame dried flask under an atmosphere of argon 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene (1.00 g, 1.85 mmol), 3,6-di-*tert*-butyl-9*H*-carbazole[7] (0.52 g, 1.85 mmol), copper iodide (0.03 g, 0.19 mmol),

1,10-phenanthroline (0.07 g, 0.37 mmol) and potassium carbonate (0.51 g, 3.7 mmol) were added. The flask was evacuated and backfilled with argon. Degassed DMF (8 cm^3) was added to the reagents *via* the septum. The mixture was stirred and heated to 120 °C for 40 h. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography on silica with 98 : 2 (v/v) petroleum ether : DCM as eluent. The product **14** was obtained as a white solid (1.00 g, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 1.6 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.62 (d, 1H), 7.56 – 7.48 (m, 5H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 0.7 Hz, 1H), 7.37 (s, 1H), 2.03 – 1.92 (m, 4H), 1.48 (s, 18H), 1.22 – 0.99 (m, 12H), 0.86 – 0.61 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.82, 152.20, 151.09, 141.88, 138.24, 137.78, 136.29, 129.18, 125.24, 124.46, 122.58, 122.39, 120.35, 120.26, 120.14, 119.85, 115.34, 108.16, 54.67, 39.24, 33.76, 31.03, 30.54, 28.62, 22.84, 21.60, 13.06; HRMS calcd for $C_{45}H_{56}N^{79}Br$: 689.3596. Found: 689.3611; Mp. 77.0 – 79.5 °C.

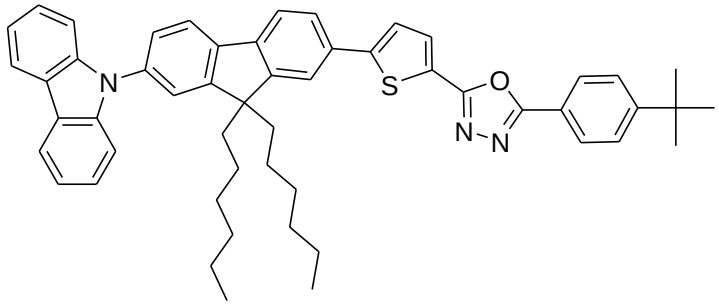
2-(6-(7-(9*H*-carbazol-9-yl)-9,9-dihexyl-9*H*-fluoren-2-yl)pyridin-3-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 2



To a flame dried flask under an atmosphere of argon 9-(9 , 9 - dihexyl - 7 - (4,4,5,5 – tetramethyl - 1,3,2 -dioxaborolan-2-yl) - 9H - fluoren-2-yl)-9H-carbazole **8** (0.20 g, 0.32 mmol) and 2-(4-*tert*-butylphenyl)-5-(6-chloropyridin-3-yl)-1,3,4-oxadiazole **10** (0.12 g, 0.38 mmol) were added. Anhydrous THF (30 cm^3) and NaOH (0.5 g in 5 cm^3) were added to the flask. The mixture was degassed for 1 h. To this mixture $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.02 mmol) was added and the mixture was heated to reflux for 15 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product **2** was isolated as a pale yellow solid (0.18 g, 72 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 9.47 (1 H, d, *J* = 2.2), 8.52 (1 H, dd, *J* = 8.3, 2.2), 8.21 – 8.15 (4 H, m), 8.12 (2 H, d, *J* = 8.3), 8.03 (1 H, d, *J* = 8.3), 8.01 – 7.96 (1 H, m), 7.92 (1 H, d, *J* = 7.9), 7.64 – 7.56 (4 H, m), 7.50 – 7.41 (4 H, m), 7.33 (2 H, dd, *J* = 10.7, 3.9), 2.20 – 2.04 (4 H, m), 1.40 (9 H, s), 1.21 – 1.04 (12 H, m), 0.87 – 0.81 (4 H, m), 0.79 (6 H, t, *J* = 7.2); ^{13}C NMR (176 MHz, $CDCl_3$): δ 165.03, 162.54, 159.93, 155.68, 153.31, 151.87, 147.81, 142.30, 140.97, 139.60, 137.21, 136.96, 134.78, 126.90, 126.50, 126.15, 125.92, 125.87, 123.41, 121.86, 121.57, 121.36, 120.82, 120.38, 120.34, 120.28, 119.93, 118.49, 109.76, 55.70, 40.29, 35.14, 31.52, 31.12,

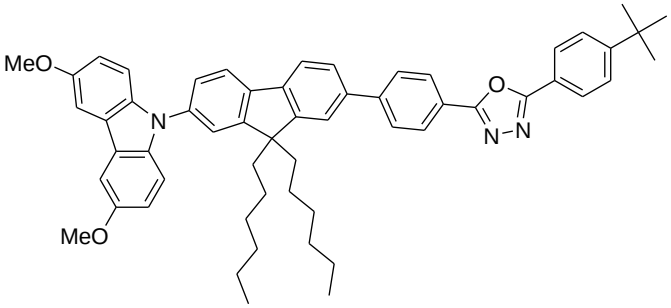
29.62, 23.95, 22.54, 13.99; HRMS calcd for $C_{54}H_{57}N_4O$: 777.4532. Found: 777.4551; Mp. 110.0 – 111.5 °C. Purity was judged to be >99% by HPLC analysis.

2-(5-(7-(9*H*-carbazol-9-yl)-9,9-dihexyl-9*H*-fluoren-2-yl)thiophen-2-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 3



To a flame dried flask under an atmosphere of argon 9-(9 , 9 - dihexyl - 7 - (4,4,5,5 – tetramethyl - 1,3,2 -dioxaborolan-2-yl) - 9H - fluoren-2-yl)-9H-carbazole **8** (0.4 g, 0.64 mmol) and 2-(5-bromothiophen-2-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **11** (0.28 g, 0.77 mmol) were added. Anhydrous THF (30 cm^3) and NaOH (0.5 g in 5 cm^3) were added to the flask. The mixture was degassed for one hour. To this mixture $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.02 mmol) was added and the mixture was heated to reflux for 15 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product **3** was isolated as a pale yellow solid (0.42 g, 84 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (2 H, d, *J* 7.8), 8.09 (2 H, d, *J* 8.5), 7.97 – 7.91 (1 H, m), 7.85 (1 H, d, *J* 3.8), 7.83 (1 H, d, *J* 7.8), 7.74 (1 H, dd, *J* 7.8, 1.6), 7.70 (1 H, d, *J* 1.3), 7.62 – 7.55 (4 H, m), 7.51 – 7.43 (5 H, m), 7.36 – 7.31 (2 H, m), 2.14 – 2.02 (4 H, m), 1.40 (9 H, s), 1.25 – 1.07 (12 H, m), 0.89 – 0.76 (10 H, m); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.10, 160.58, 155.39, 152.90, 152.11, 149.70, 141.12, 140.98, 139.51, 136.86, 132.23, 130.53, 126.79, 126.06, 125.94, 125.39, 123.83, 123.71, 123.42, 121.82, 121.12, 120.92, 120.52, 120.42, 120.40, 119.96, 109.76, 55.63, 40.28, 35.11, 31.50, 31.13, 29.61, 23.93, 22.54, 14.01; HRMS calcd for $C_{53}H_{55}N_3OS$: 781.4066. Found: 781.4071; Mp. 102.0 – 105.0 °C. Purity was judged to be >99% by HPLC analysis.

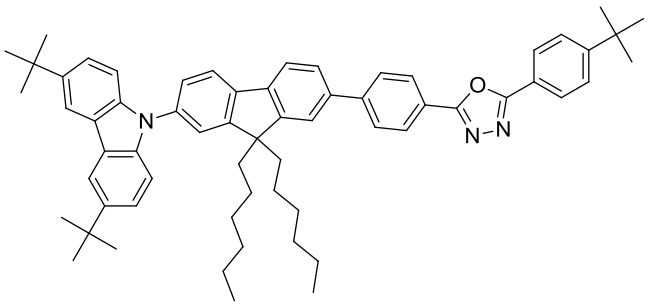
2-(4-*Tert*-butylphenyl)-5-(4-(7-(3,6-dimethoxy-9*H*-carbazol-9-yl)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazole, 4



To a flame dried flask under an atmosphere of argon 9-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-3,6-dimethoxy-9*H*-carbazole **13** (0.50 g, 0.78 mmol), 2-(4-*tert*-butylphenyl)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl)-1,3,4-oxadiazole **15** (0.32 g, 0.78 mmol) were added. Anhydrous THF (30 cm^3) and NaOH (0.7 g in 5 cm^3) were added to the flask. The mixture was degassed for one hour. To this mixture $Pd(PPh_3)_2Cl_2$ (0.01 g, 0.02 mmol) was added and the mixture was heated to reflux for 15 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product **4** was isolated as a pale yellow solid (0.48 g, 73 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.26 (2 H, d, *J* = 8.3), 8.11 (2 H, d, *J* = 8.5), 7.93 (1 H, d, *J* = 8.4), 7.90 – 7.82 (3 H, m), 7.70 (1 H, dd, *J* = 7.8, 1.6), 7.67 (1 H, d, *J* = 1.2), 7.60 (2 H, d, *J* = 2.5), 7.58 (2 H, d, *J* = 8.5), 7.56 – 7.53 (2 H, m, *J* = 4.1, 1.9), 7.39 (2 H, d, *J* = 8.8), 7.08 (2 H, dd, *J* = 8.9, 2.5), 3.98 (6 H, s), 2.15 – 2.00 (4 H, m), 1.40 (9 H, s), 1.22 – 1.05 (12 H, m), 0.89 – 0.72 (10 H, m); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.69, 164.31, 155.35, 154.03, 152.86, 151.89, 144.66, 140.56, 139.25, 138.85, 137.18, 136.40, 127.70, 127.36, 126.80, 126.34, 126.06, 125.42, 123.62, 122.69, 121.47, 121.35, 121.15, 120.99, 120.26, 115.18, 110.68, 103.00, 56.15, 55.55, 40.29, 35.10, 31.49, 31.13, 29.61, 23.92, 22.53, 14.00; HRMS calcd for $C_{57}H_{62}N_3O_3$: 836.4791. Found: 836.4827; Mp. 109.0 – 110.5 °C. Purity was judged to be >99% by HPLC analysis.

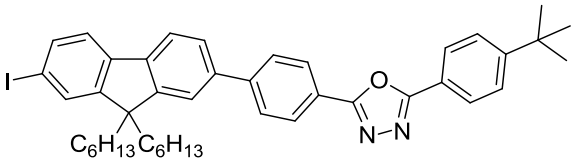
2-(4-*Tert*-butylphenyl)-5-(4-(7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazole, 5



To a flame dried flask under an atmosphere of argon 9-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-3,6-di-*tert*-butyl-9*H*-carbazole **14** (0.30 g, 0.43 mmol), 2-(4-*tert*-butylphenyl)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole **15** (0.18 g, 0.43 mmol) were added. Anhydrous THF (30 cm^3) and NaOH (0.5 g in 5 cm^3) were added to the flask. The mixture was degassed for one hour. To this mixture $Pd(PPh_3)_2Cl_2$ (0.01 g, 0.02 mmol) was added and the mixture was heated to reflux for 15 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product **5** was isolated as a white solid (0.30 g, 77 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.26 (2 H, d, *J* 8.2), 8.18 (2 H, d, *J* 1.8), 8.11 (2 H, d, *J* 8.4), 7.93 (1 H, d, *J* 8.3), 7.90 – 7.84 (3 H, m), 7.70 (1 H, dd, *J* 7.8, 1.4), 7.67 (1 H, s), 7.61 – 7.54 (4 H, m), 7.50 (1 H, dd, *J* 8.6, 1.8), 7.42 (3 H, d, *J* 8.6), 2.12

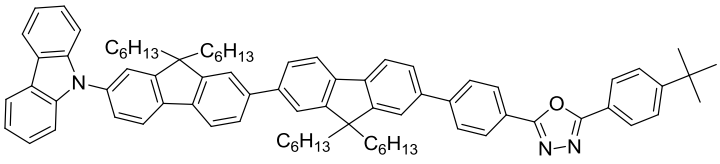
– 2.01 (4 H, m), 1.49 (18 H, s), 1.39 (9 H, s), 1.21 – 1.08 (12 H, m), 0.85 – 0.76 (10 H, m); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.69, 164.32, 155.37, 152.78, 151.92, 144.70, 142.83, 140.64, 139.30, 139.23, 138.82, 137.19, 127.71, 127.37, 126.81, 126.33, 126.06, 125.42, 123.56, 123.38, 122.68, 121.46, 121.41, 121.16, 120.96, 120.25, 116.31, 109.20, 55.56, 40.33, 35.11, 34.74, 32.03, 31.53, 31.14, 29.65, 23.93, 22.57, 14.03; HRMS calcd for $C_{63}H_{74}N_3O$: 888.5832. Found: 888.5859; Mp. 137.0 – 139.0 °C. Purity was judged to be >99% by HPLC analysis.

2-(4-*Tert*-butylphenyl)-5-(4-(9,9-dihexyl-7-iodo-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazole, 17



A solution of 2-(4-*tert*-butylphenyl)-5-(4-(9,9-dihexyl-7-trimethylsilyl)-9*H*-fluorene-2-yl)phenyl) -1,3,4 -oxadiazole **16** (0.63 g, 0.92 mmol) in DCM (20 cm^3) was cooled to 0 °C in an ice bath. To this stirred solution 1M iodine monochloride (1.5 cm^3, 1.5 mmol) was added. The reaction mixture was stirred for 1.5 h, quenched with aqueous sodium thiosulfate, extracted into DCM, washed with brine, concentrated under reduced pressure and the product was recrystallised from ethanol to give **17** as white crystals (0.64 g, 93 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.24 (2H, d, J = 8.5 Hz), 8.10 (2H, d, J = 8.6 Hz), 7.82 (2H, d, J = 8.5 Hz), 7.76 (1H, d, J = 7.8 Hz), 7.70 (1H, d, J = 1.2 Hz), 7.69 (1H, dd, J = 7.9 and 1.2 Hz), 7.64 (1H, dd, J = 7.8 and 1.6 Hz), 7.59 (1H, d, J = 1.2 Hz), 7.57 (1H, d, J = 8.5 Hz), 7.48 (1H, d, 8.3 Hz), 2.00 (4H, m), 1.39 (9H, s), 1.09 (12H, m), 0.78 (6H, t, J = 7.3 Hz), 0.67 (4H, m) ppm; ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.68, 164.27, 155.43, 153.42, 151.05, 144.60, 140.28, 140.10, 139.24, 135.96, 132.12, 127.68, 127.35, 126.79, 126.25, 126.05, 122.70, 121.59, 121.35, 121.11, 120.26, 92.88, 55.50, 40.22, 35.09, 31.41, 31.12, 29.58, 23.75, 22.54, 13.97; MS (EI+): 736 (M+, 100%); Anal. Calcd. For $C_{43}H_{49}IN_2O$: C, 70.10; H, 6.70; N, 3.80. Found: C, 70.34; H: 6.77; N: 3.72; Mp: 139.5 – 140.9 ^{o}C.

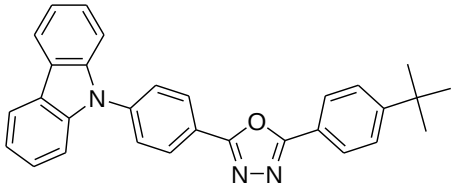
2-(4-(7'-(9*H*-carbazol-9-yl)-9,9,9',9'-tetrahexyl-2,2'-bi(9*H*-fluoren)-7-yl)phenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 6



To a flame dried flask under an atmosphere of argon 9-(9,9-dihexyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-yl)-9*H*-carbazole **8** (0.20 g, 0.32 mmol) and 2-(4-*tert*-butylphenyl)-5-(4-(9,9-dihexyl-7-iodo-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazole **17** (0.26 g, 0.35 mmol) were added. Anhydrous THF (30 cm^3) and NaOH (0.5 g in 5 cm^3) were added to the flask. The mixture was degassed for one hour. To this mixture $Pd(PPh_3)_2Cl_2$ (0.01 g, 0.02 mmol) was added and the mixture was heated to reflux for 15 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined

organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product **6** was isolated as a white solid (0.32 g, 91 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.27 (2 H, d, *J* 6.8), 8.20 (2 H, d, *J* 7.9), 8.12 (2 H, dd, *J* 8.2, 1.3), 7.96 (1 H, d, *J* 7.5), 7.87 (4 H, dd, *J* 17.4, 8.1), 7.79 – 7.64 (6 H, m), 7.64 – 7.54 (4 H, m), 7.54 – 7.40 (4 H, m), 7.33 (2 H, t, *J* 7.3), 2.21 – 2.01 (8 H, m), 1.40 (9 H, s), 1.23 – 1.05 (24 H, m), 0.97 – 0.72 (20 H, m); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.69, 164.35, 155.33, 152.86, 151.96, 151.91, 151.82, 144.83, 141.07, 141.02, 140.81, 140.70, 140.09, 139.81, 139.58, 138.64, 136.36, 127.69, 127.37, 126.81, 126.37, 126.29, 126.22, 126.07, 125.90, 125.83, 123.38, 122.62, 121.86, 121.51, 121.49, 121.19, 120.85, 120.37, 120.23, 120.16, 119.86, 109.81, 60.37, 55.55, 55.44, 40.38, 40.30, 35.11, 31.51, 31.46, 31.15, 29.67, 29.63, 23.95, 23.85, 22.56, 22.54, 14.02, 14.01; HRMS calcd for $C_{80}H_{90}ON_3$ 1108.7078. Found: 1108.7090; Mp. 113.5 – 115.0 °C. Purity was judged to be >99% by HPLC analysis.

2-(4-(9*H*-carbazol-9-yl)phenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 7



To a flame dried flask under an atmosphere of argon 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **9** (0.4 g, 1.12 mmol), 9*H*-carbazole (0.22 g, 1.34 mmol) and potassium carbonate (0.46 g, 3.36 mmol) were added. Anhydrous toluene (10 cm^3) was added to the reagents and degassed for 1 hr. To this stirred solution palladium (II) acetate (7.5 mg, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (29 mg, 0.10 mmol) were added and the reaction mixture heated to reflux for 22 h. The reaction mixture was cooled, washed with brine and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography on silica gel first with 7 : 3 (v/v) petroleum ether : diethyl ether as eluent and then a second time with DCM as eluent. The product was recrystallised from acetonitrile to yield **7** as colourless crystals (0.27 g, 54 %). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.39 (2 H, d, *J* = 8.5), 8.17 (2 H, d, *J* = 7.7), 8.11 (2 H, d, *J* = 8.5), 7.79 (2 H, d, *J* = 8.5), 7.59 (2 H, d, *J* = 8.5), 7.51 (2 H, d, *J* = 8.2), 7.49 – 7.42 (2 H, m), 7.37 – 7.31 (2 H, m), 1.39 (9 H, s); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.88, 163.78, 155.52, 140.80, 140.29, 128.52, 127.24, 126.82, 126.19, 126.11, 123.77, 122.63, 120.99, 120.54, 120.45, 109.69, 35.12, 31.11; HRMS calcd for $C_{30}H_{26}N_3O$: 444.2076. Found: 444.2074; Mp. 171.5 – 173.0.

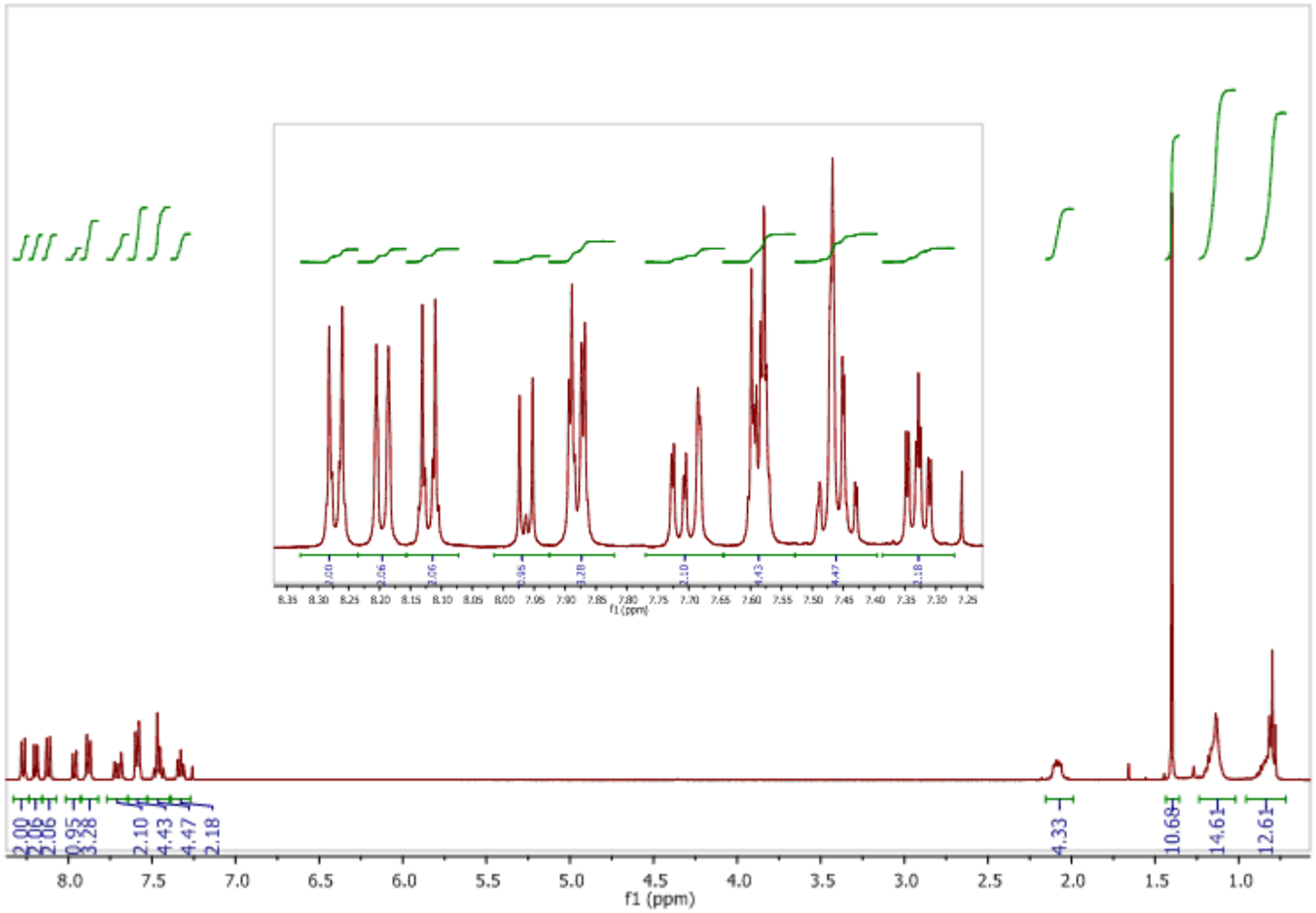


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$. The inset shows an expansion of the aromatic region.

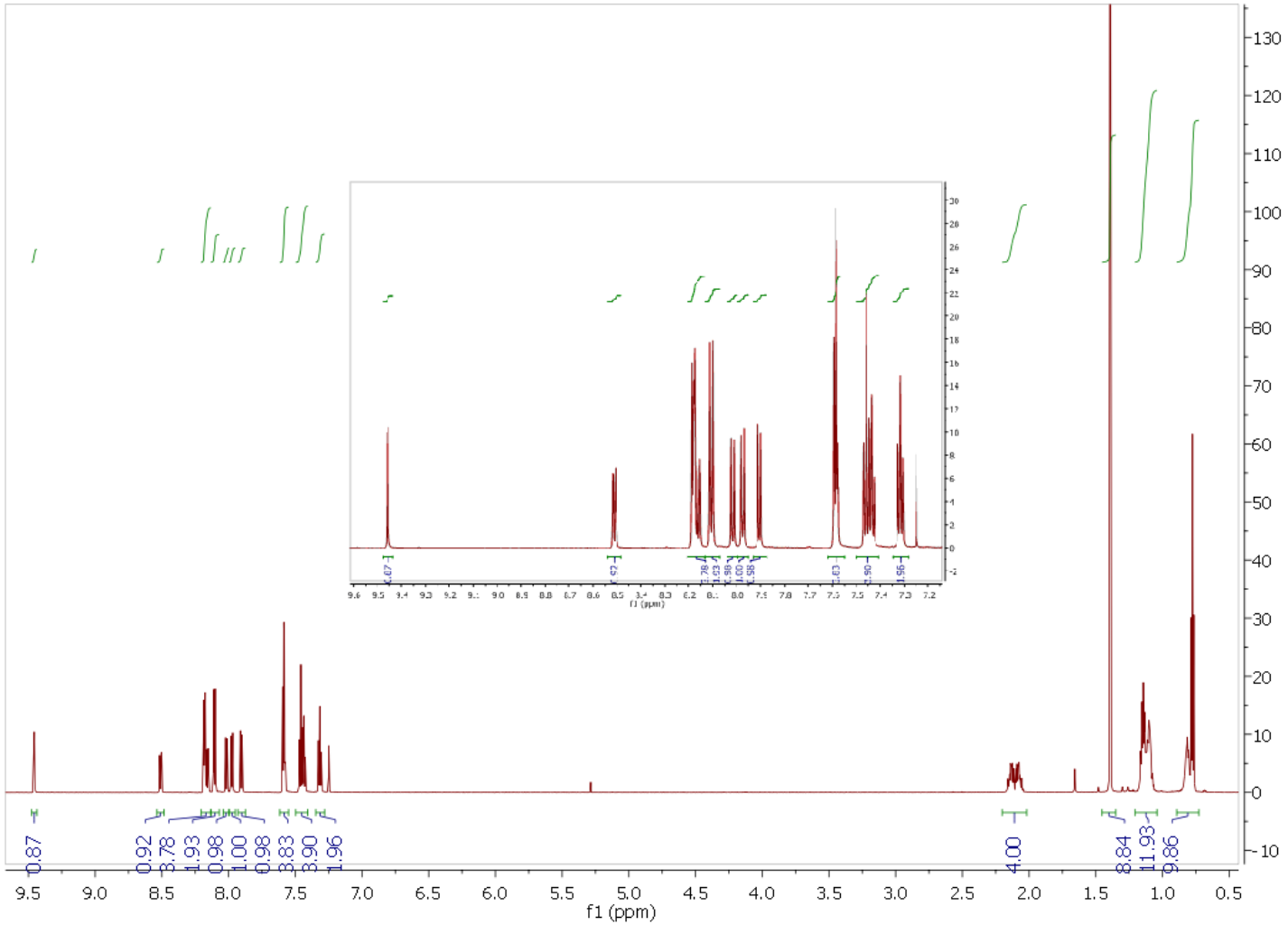


Figure S2. ^{1}H NMR spectrum of **2** in $CDCl_3$. The inset shows an expansion of the aromatic region.

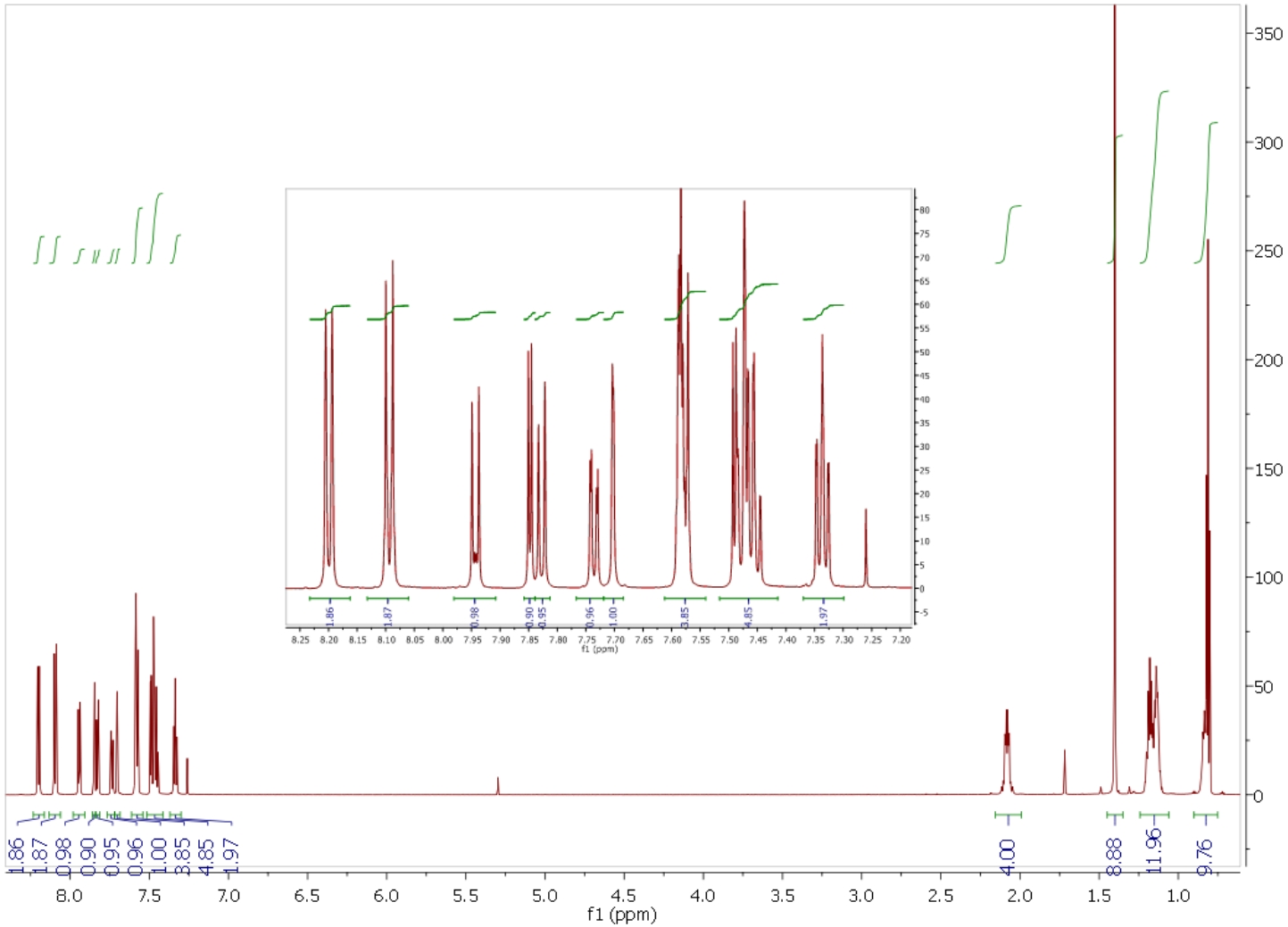


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$. The inset shows an expansion of the aromatic region.

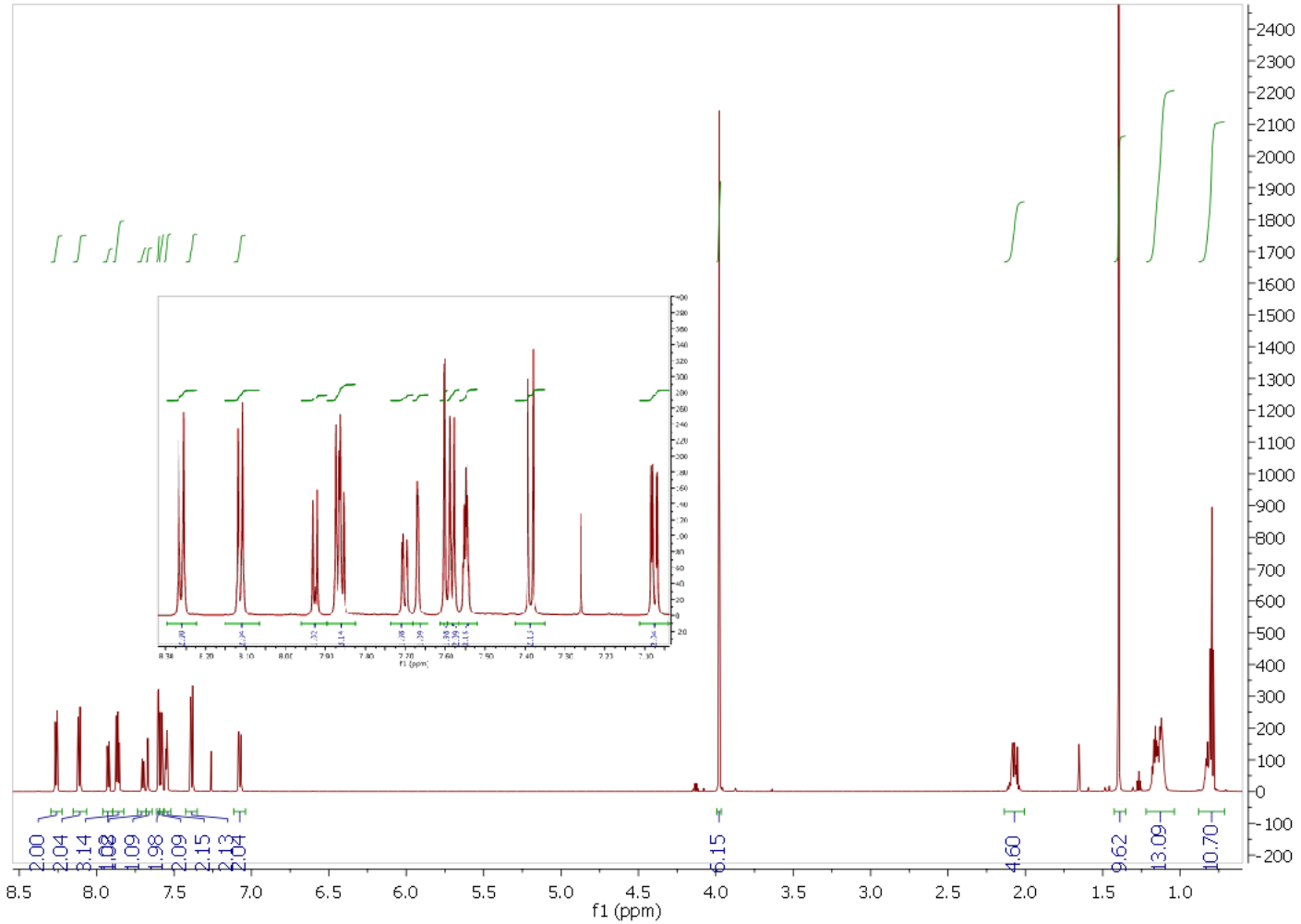


Figure S4. ^{1}H NMR spectrum of **4** in $CDCl_3$. The inset shows an expansion of the aromatic region.

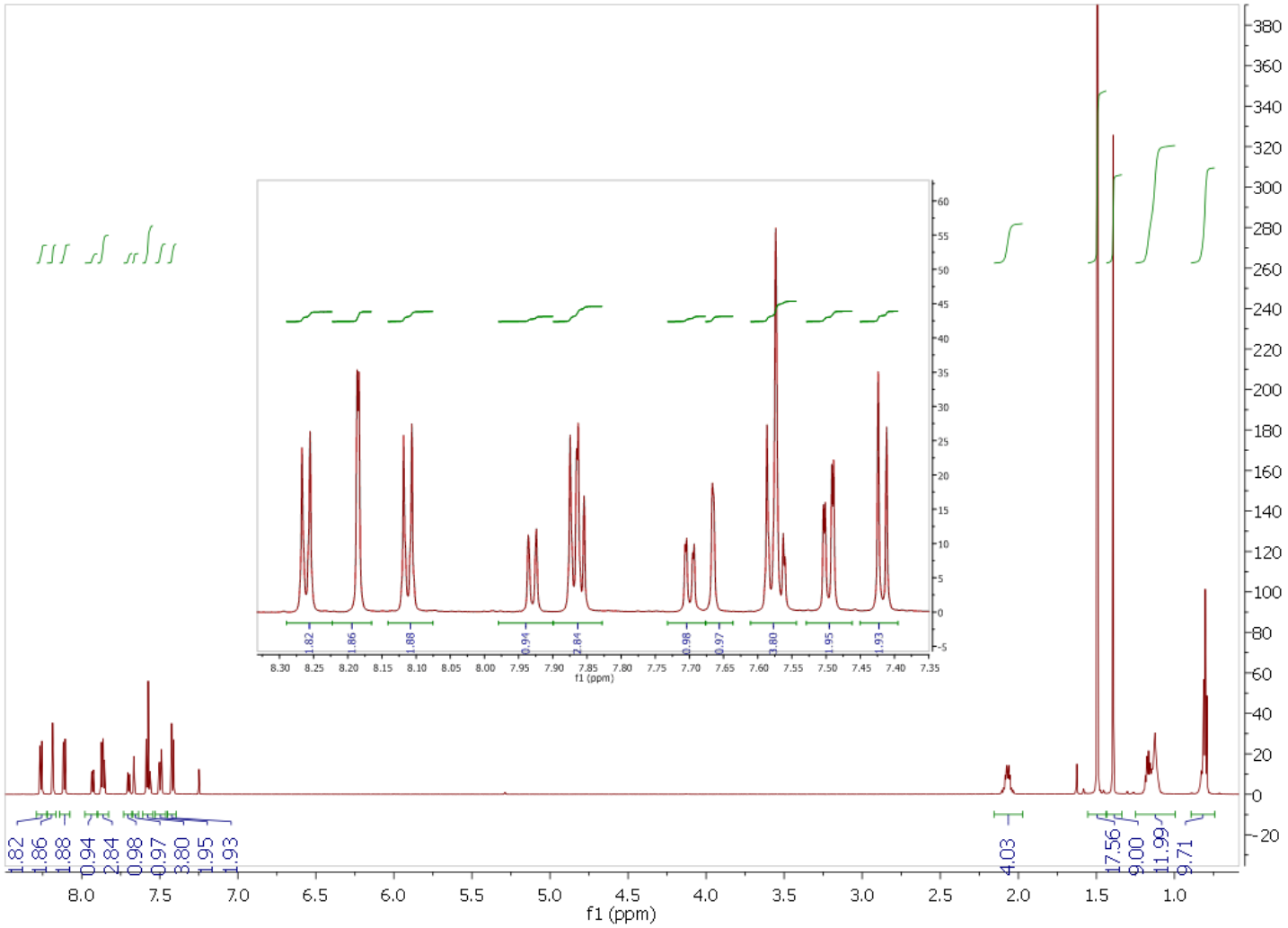


Figure S5. ^{1}H NMR spectrum of **5** in $CDCl_3$. The inset shows an expansion of the aromatic region.

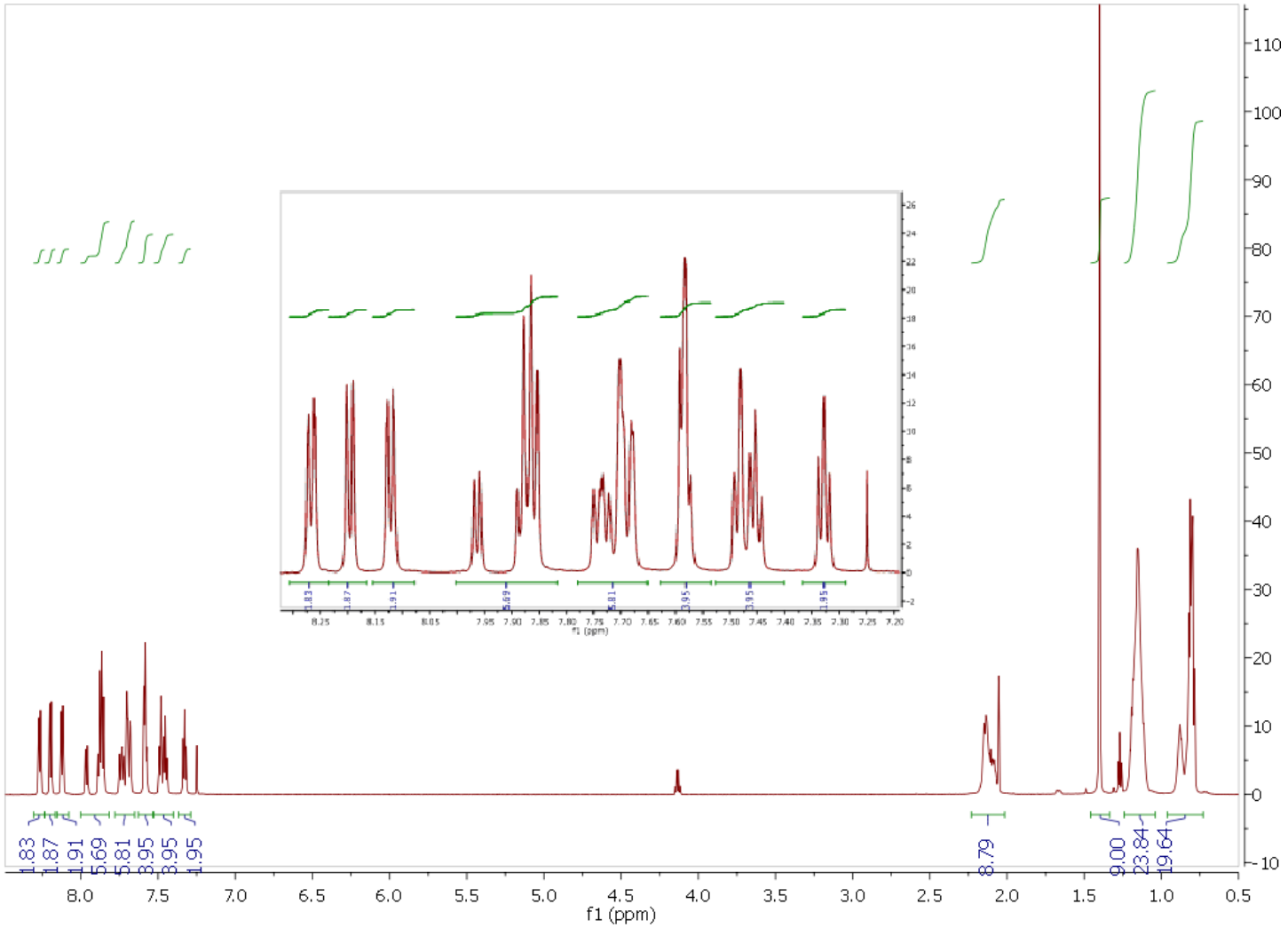


Figure S6. ^{1}H NMR spectrum of **6** in $CDCl_3$. The inset shows an expansion of the aromatic region.

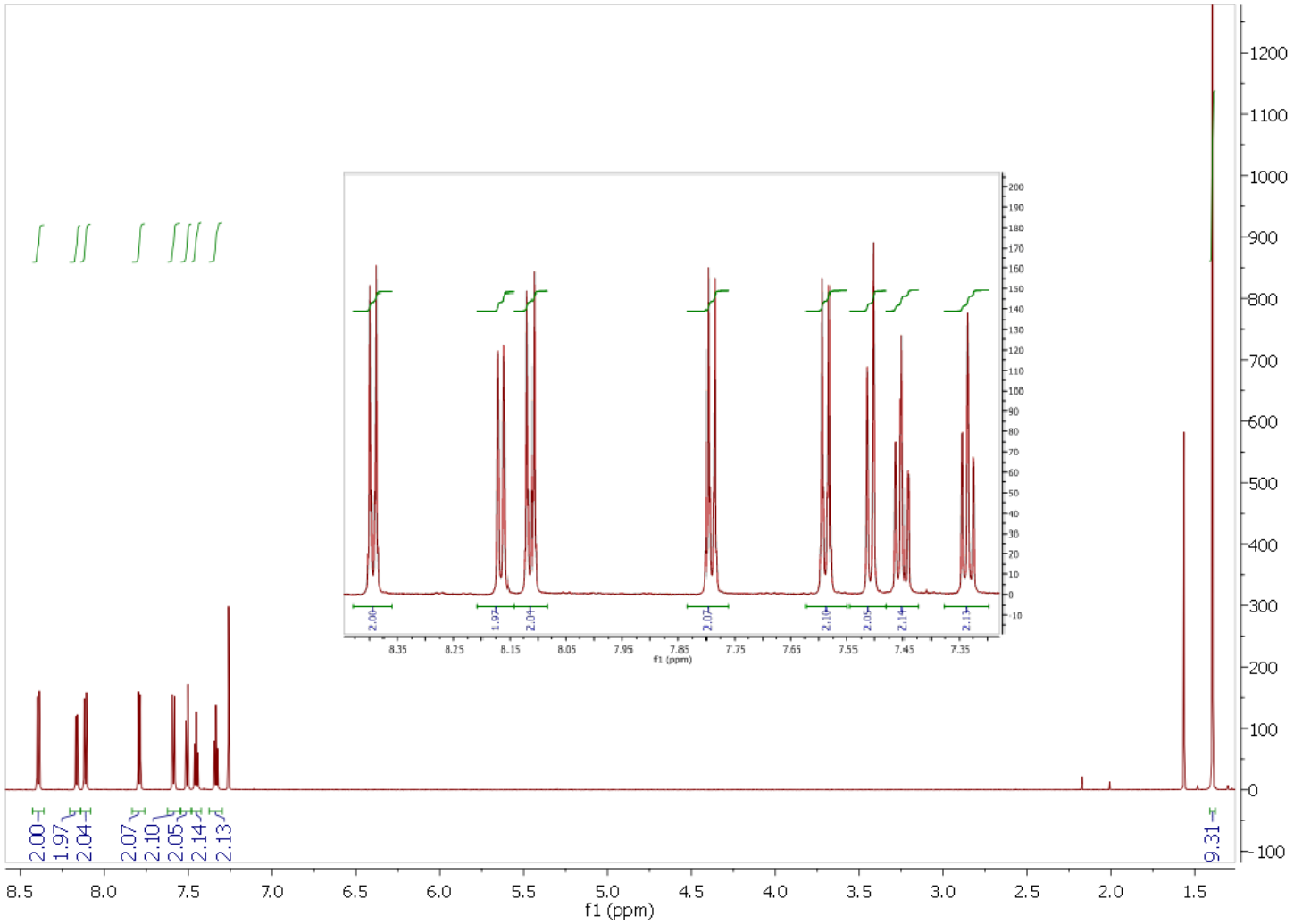


Figure S7. ^{1}H NMR spectrum of **7** in $CDCl_3$. The inset shows an expansion of the aromatic region.

Cyclic Voltammetry

Cyclic voltammetry experiments were carried out using a BASCV50W electrochemical workstation in a three-electrode cell equipped with a platinum disk (Ø 1.6 mm) working electrode, platinum wire counter electrode and a non-aqueous Ag/Ag^+ reference electrode (0.01 M $AgNO_3$ in dry MeCN), with iR compensation. CV data for compounds **1** and **2** were obtained in dry DCM (oxidations) and dry THF (reductions) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte, under an argon atmosphere. The potential of the reference electrode in benzonitrile (0.1 M Bu_4NPF_6) was checked against the ferrocene/ferrocenium couple (Fc/Fc^+), which showed the average potential against the reference electrode of +0.187 V.

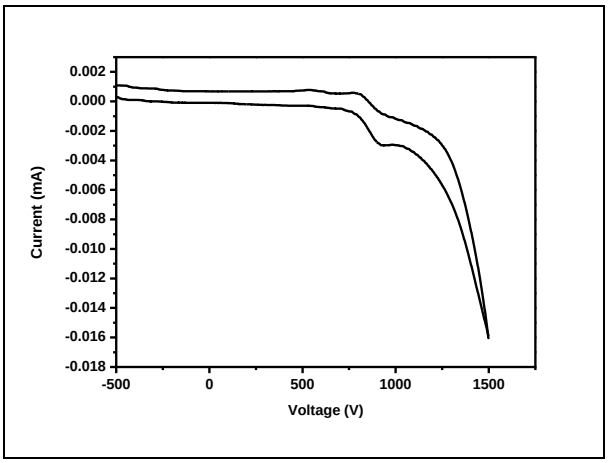


Figure S8. Cyclic voltammogram showing oxidation waves for **1** in DCM vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

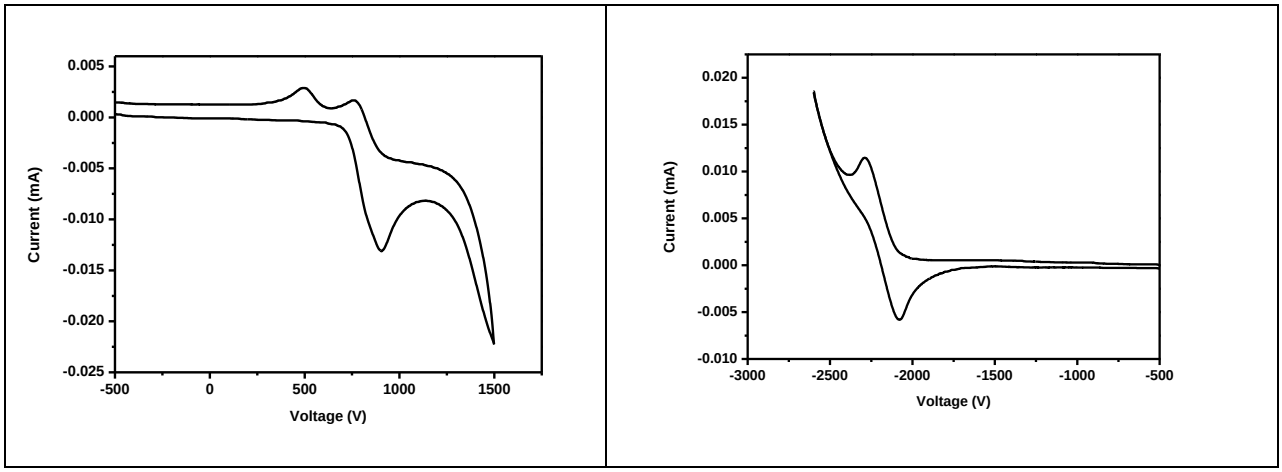


Figure S9. Cyclic voltammograms showing oxidation (left: in DCM) and reduction (right: in THF) waves for **2** vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

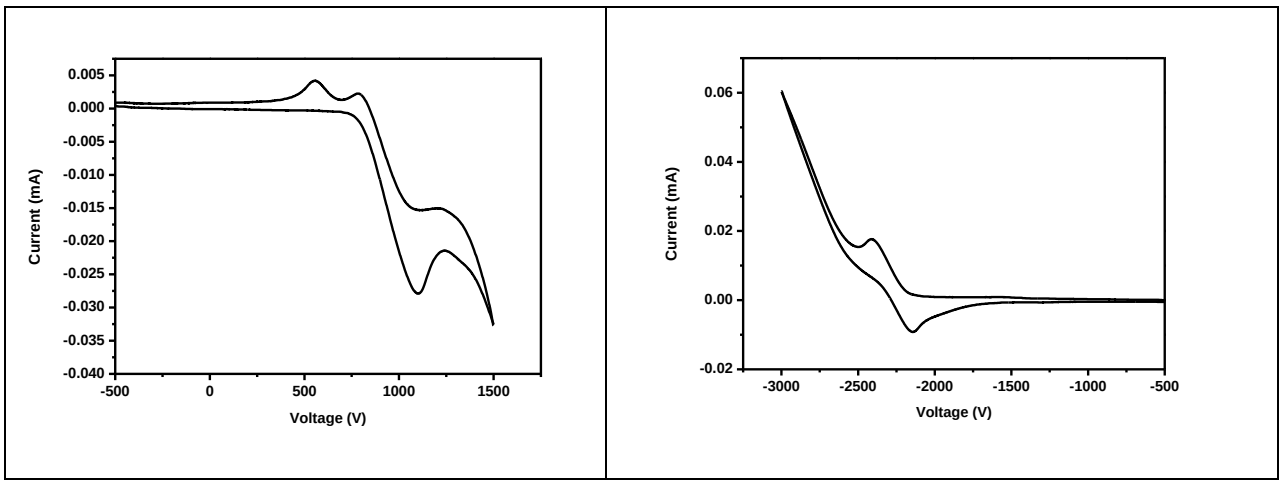


Figure S10. Cyclic voltammograms showing oxidation (left: in DCM) and reduction (right: in THF) waves for **3** vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

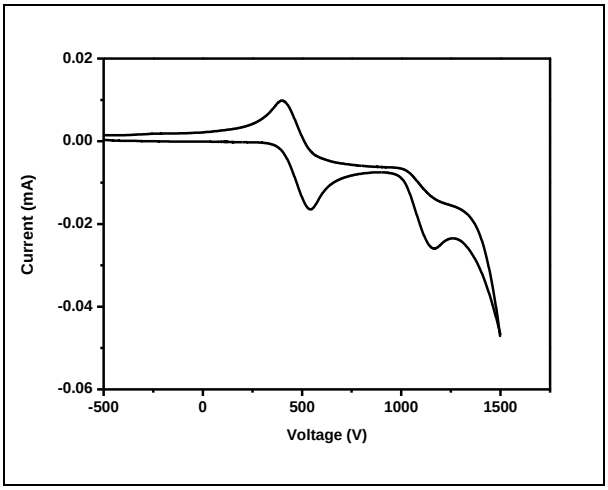


Figure S11. Cyclic voltammogram showing oxidation waves for **4** in DCM vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

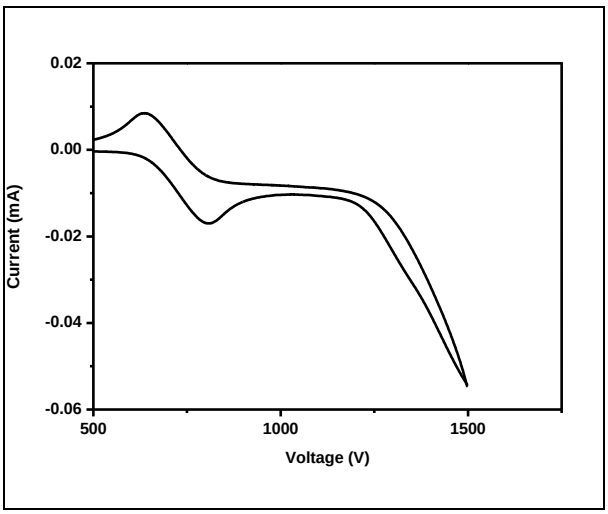


Figure S12. Cyclic voltammogram showing oxidation waves for **5** in DCM vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

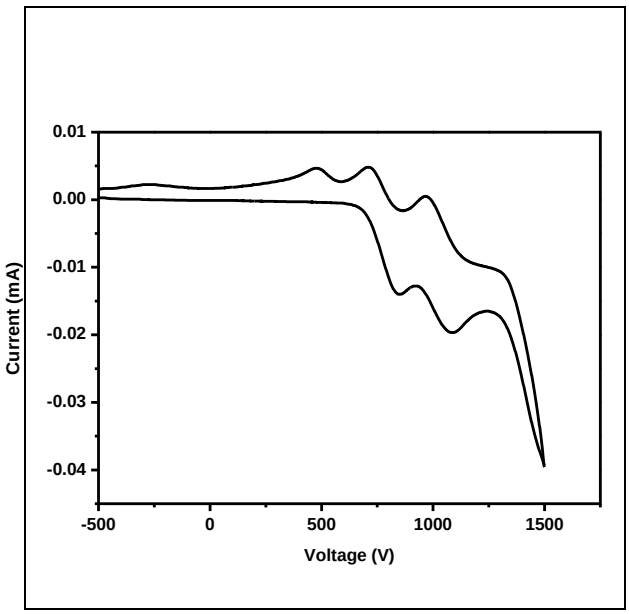


Figure S13.Cyclic voltammogram showing oxidation waves for **6** in DCM vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

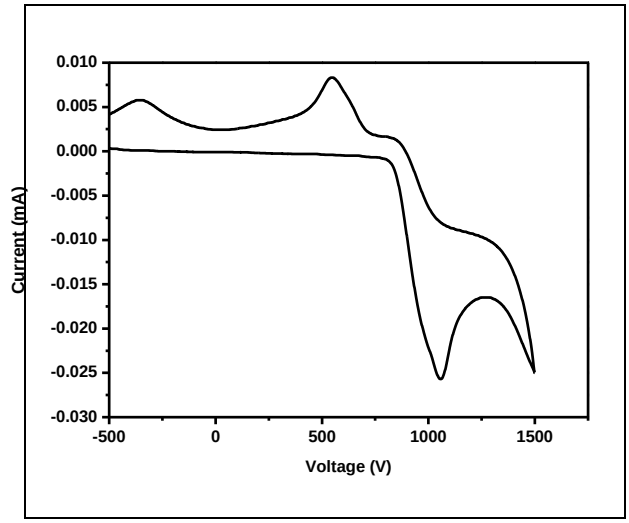


Figure S14. Cyclic voltammogram showing oxidation waves for **7** in DCM vs ferrocenium/ferrocene couple (FcH^+/FcH = 0.0 V).

Photophysical Studies: Solution Absorption and Emission Spectra

Absorption spectra of solutions of **1-7** in cyclohexane solution were recorded in quartz cuvettes of path length l = 1 cm with an absorbance, A, < 0.3 at 400 nm using a Unicam UV2-100 spectrometer operated with the Unicam Vision software. Baseline correction was achieved by reference to pure solvent. Extinction coefficients (ε, $dm^3\ mol^{-1}\ cm^{-1}$) were calculated using the Beer-Lambert law, $A = \varepsilon cl$, (c is the concentration, mol dm^{-3}) by recording the absorption spectrum for a sample weighed on an analytical balance. The excitation wavelengths for emission spectra were the absorption maxima.

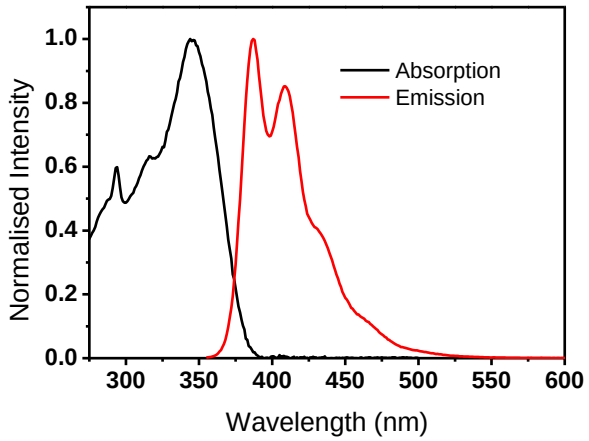


Figure S15. Absorption and emission spectra of **1** in cyclohexane solution with emission excitation at 345 nm.

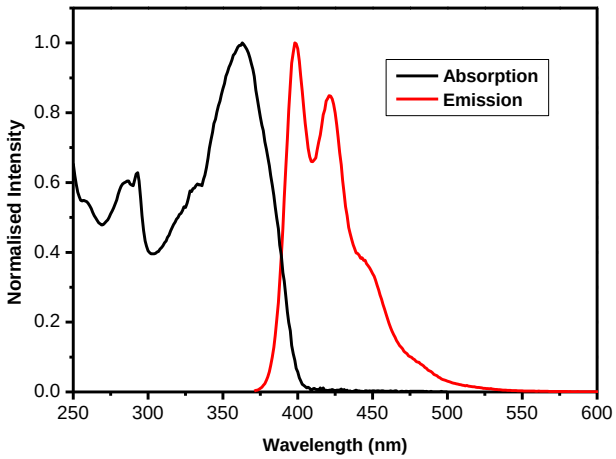


Figure S16. Absorption and emission spectra of **2** in cyclohexane solution with emission excitation at 363 nm.

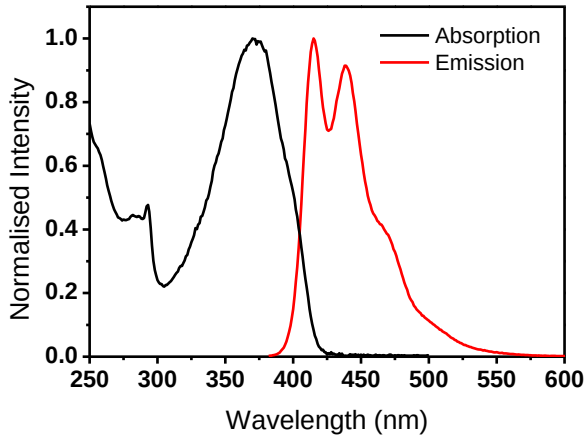


Figure S17. Absorption and emission spectra of **3** in cyclohexane solution with emission excitation at 371 nm.

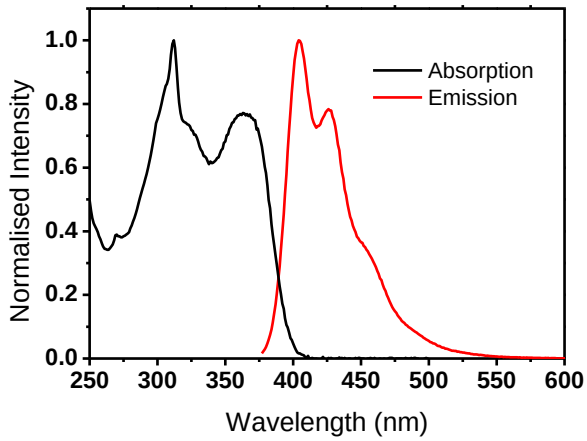


Figure S18. Absorption and emission spectra of **4** in cyclohexane solution with emission excitation at 364 nm.

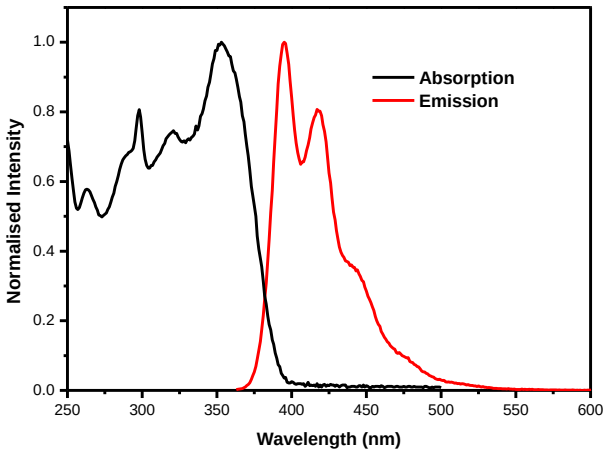


Figure S19. Absorption and emission spectra of **5** in cyclohexane solution with emission excitation at 339 nm.

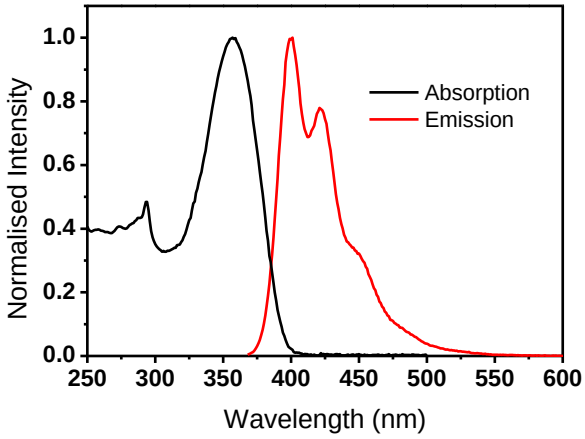


Figure S20. Absorption and emission spectra of **6** in cyclohexane solution with excitation at 357 nm.

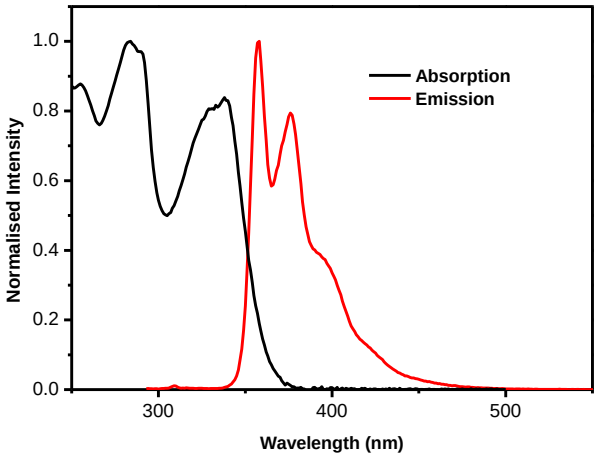


Figure S21. Absorption and emission spectra of **7** in cyclohexane solution with emission excitation at 339 nm.

Solvatochromism

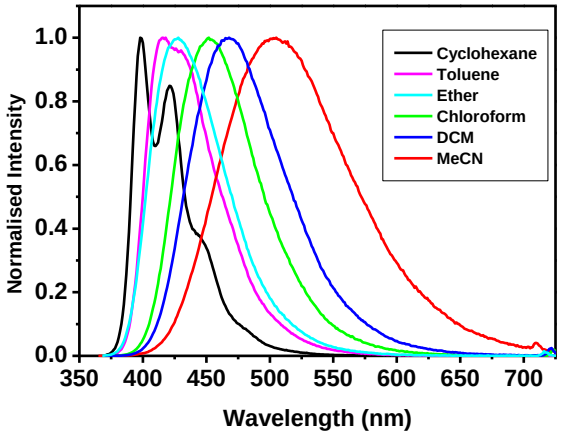


Figure S22. Emission spectra of **2** in various solvents.

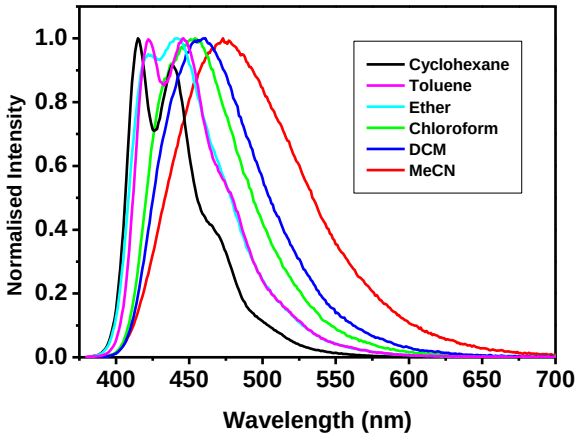


Figure S23. Emission spectra of **3** in various solvents.

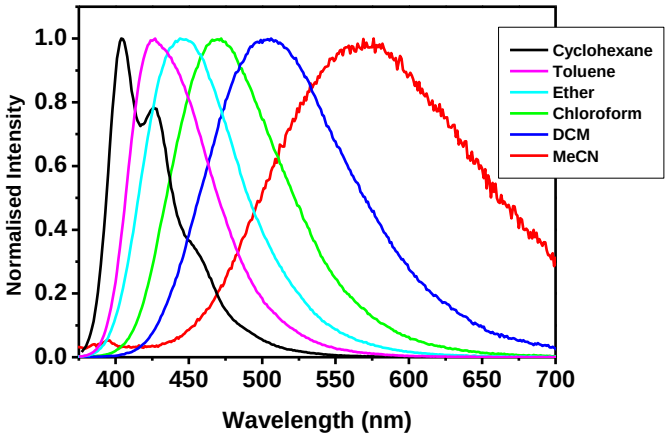


Figure S24. Emission spectra of **4** in various solvents.

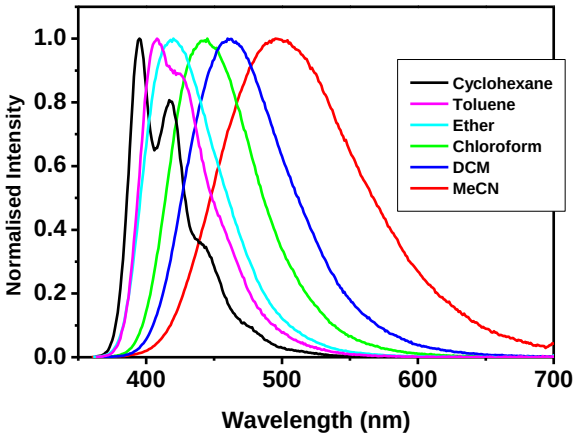


Figure S25. Emission spectra of **5** in various solvents.

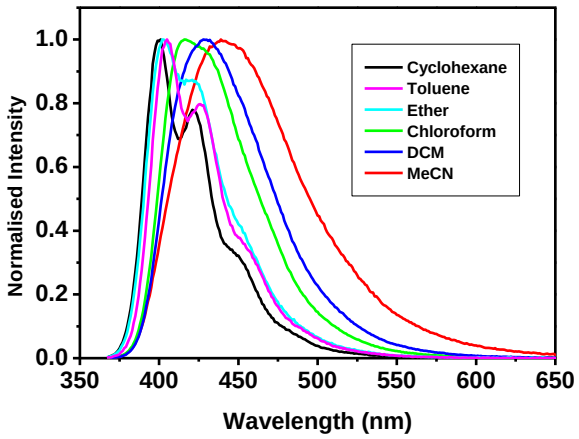


Figure S26: Emission spectra of **6** in various solvents.

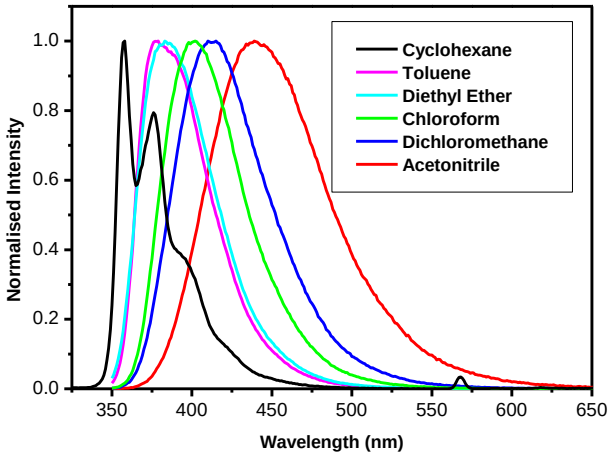


Figure S27: Emission spectra of **7** in various solvents.

Thin Film PL Spectra

Spectra are corrected for both the integrating sphere and detector.

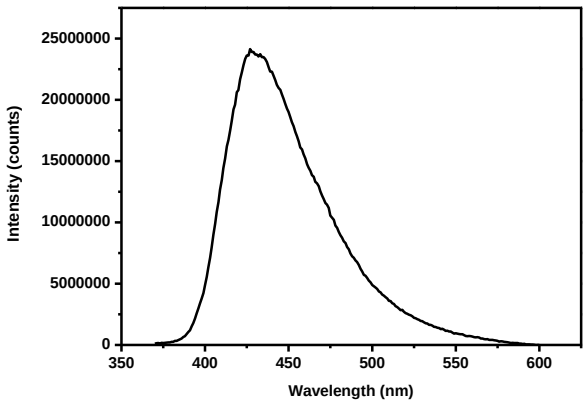


Figure S28. Photoluminescence spectrum of **1**, excitation wavelength (λ_{ex}) at 350 nm

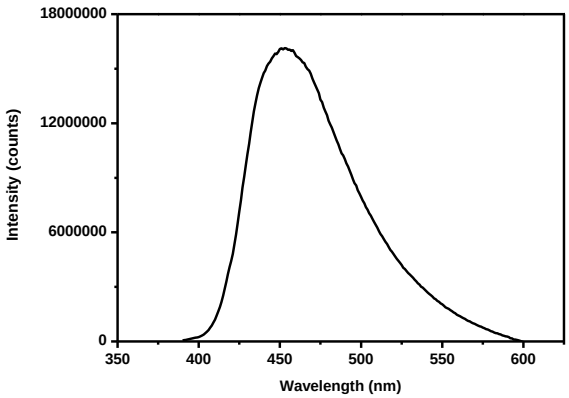


Figure S29. Photoluminescence spectrum of **2**, excitation wavelength (λ_{ex}) at 370 nm

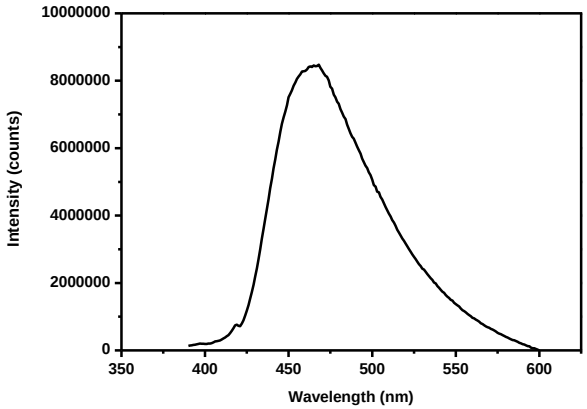


Figure S30. Photoluminescence spectrum of **3**, excitation wavelength (λ_{ex}) at 370 nm

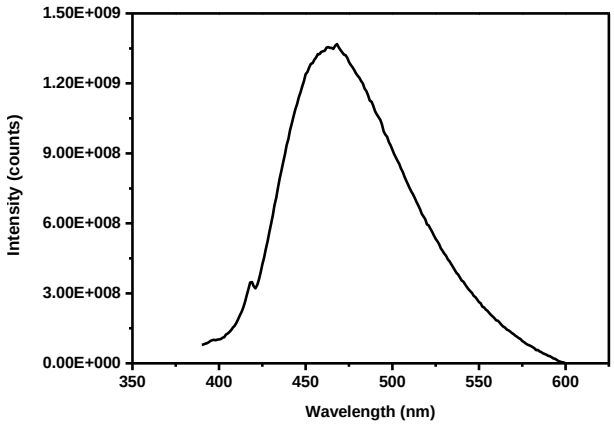


Figure S31. Photoluminescence spectrum of **4**, excitation wavelength (λ_{ex}) at 370 nm

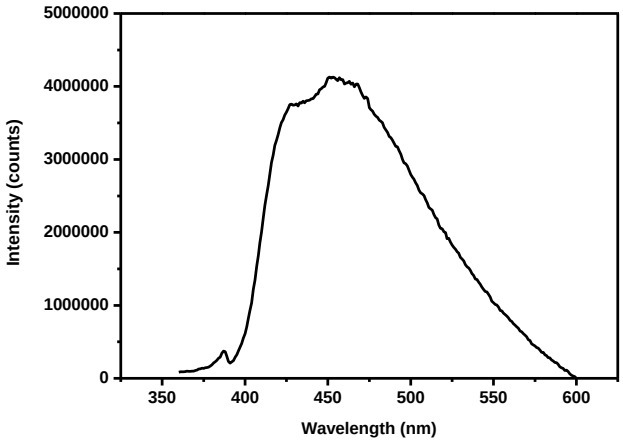


Figure S32. Photoluminescence spectrum of **5**, excitation wavelength (λ_{ex}) at 340 nm

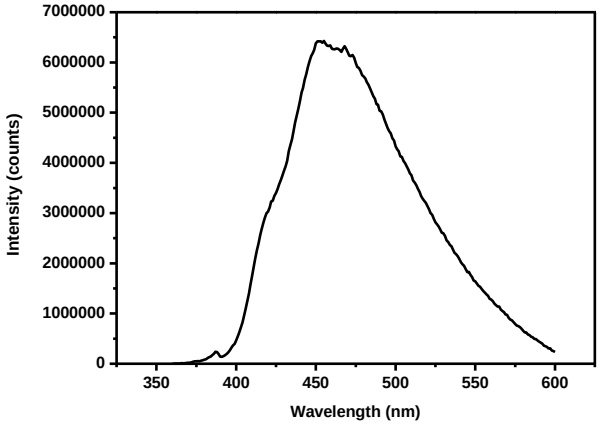


Figure S33. Photoluminescence spectrum of **6**, excitation wavelength (λ_{ex}) at 340 nm

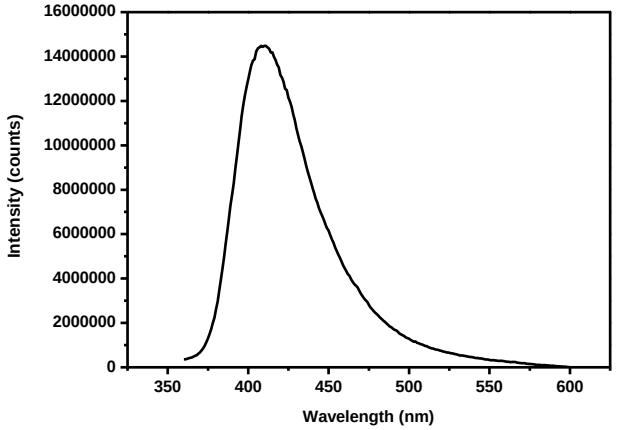
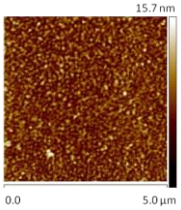
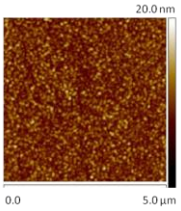
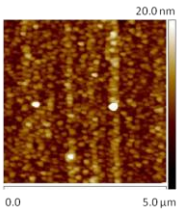
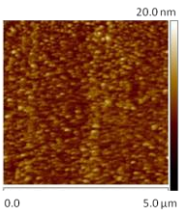
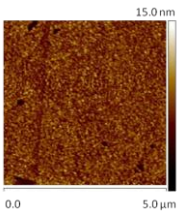
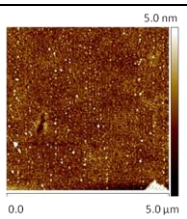
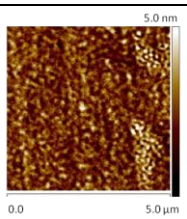


Figure S34. Photoluminescence spectrum of **7**, excitation wavelength (λ_{ex}) at 340 nm

Table S1. Atomic Force Microscope Images

Compound Number	AFM Image	Thickness (nm)[a]	Surface Roughness, Ra (nm)[a]	Grain Size (nm)[b]
1		59	1.24	179
2		64	1.25	152
3		63	1.70	278
4		59	1.19	217
5		67	0.97	147
6		64	0.43	125
7		65	1.06	208

[a] ±5%; [b] ±10%

Computational details

All computations were carried out with the Gaussian 09 package.[8] The model ground state (S_0) geometries from various starting conformers were fully optimised with the B3LYP functional[9] with no symmetry constraints using the 6-31G* basis set[10] for all atoms. Similar results were obtained using a larger basis set 6-311G** and are not discussed here. Frequency calculations on these optimised geometries (**1a-7a**) at B3LYP/6-31G* revealed no imaginary frequencies. Predicted absorption data were obtained from TD-DFT calculations on the S_0 geometries. The MO diagrams and orbital contributions were generated with the aid of Gabedit[11] and GaussSum[12] packages, respectively. Molecular orbital compositions for optimised S_0 geometries of **1a-7a** are listed in Table S2.

Table S2. Molecular orbital compositions for optimised S_0 geometries of **1a-7a.** Cz = carbazolyl group, N = nitrogen atom at Cz, Fl = fluorene unit, py = pyridine unit, th = thiophene unit.

1a

	eV	Cz	N	Fl	C_6H_4	C_2N_2O	$C_6H_4{}^tBu$
L+2	-0.69	3	0	42	21	17	16
L+1	-1.18	2	0	40	3	21	34
LUMO	-1.80	1	0	30	34	23	11
HOMO	-5.28	53	20	23	2	1	0
H-1	-5.74	100	0	0	0	0	0
H-2	-5.81	12	3	29	24	19	13
H-3	-6.30	7	1	40	5	18	29

2a

	eV	Cz	N	Fl	py	C_2N_2O	$C_6H_4{}^tBu$
L+2	-0.89	1	0	30	67	2	0
L+1	-1.26	1	0	24	7	27	41
LUMO	-2.04	1	0	31	40	21	8
HOMO	-5.28	53	20	23	2	1	0
H-1	-5.74	100	0	0	0	0	0
H-2	-5.87	14	3	38	19	15	11
H-3	-6.38	5	0	31	5	21	37

3a

	eV	Cz	N	Fl	th	C_2N_2O	$C_6H_4{}^tBu$
L+2	-0.73	3	0	39	21	18	20
L+1	-1.22	2	0	33	6	24	36
LUMO	-1.97	1	0	32	39	20	8
HOMO	-5.26	45	18	26	7	3	1
H-1	-5.64	19	5	19	29	17	10
H-2	-5.75	100	0	0	0	0	0
H-3	-6.33	8	1	41	5	17	30

4a

	eV	$(MeO)_2Cz$	N	Fl	C_6H_4	C_2N_2O	$C_6H_4{}^tBu$
L+2	-0.71	94	1	2	1	1	1
L+1	-1.13	2	0	39	3	21	35
LUMO	-1.76	1	0	28	35	24	12
HOMO	-4.89	67	19	13	1	0	0
H-1	-5.43	100	0	0	0	0	0
H-2	-5.72	8	0	42	24	16	10
H-3	-6.22	6	0	36	6	21	31

5a

	eV	$^{t}Bu_2Cz$	N	Fl	C_6H_4	C_2N_2O	$C_6H_4{}^{t}Bu$
L+2	-0.66	4	0	41	21	17	16
L+1	-1.15	2	0	39	3	21	34
LUMO	-1.77	1	0	29	34	24	12
HOMO	-5.14	57	20	20	2	1	0
H-1	-5.59	100	0	0	0	0	0
H-2	-5.77	11	2	34	24	18	12
H-3	-6.27	7	0	39	5	19	30

6a

	eV	Cz	N	Fl(N)	Fl(C)	C_6H_4	C_2N_2O	$C_6H_4{}^{t}Bu$
L+2	-0.96	1	0	24	14	10	18	31
L+1	-1.37	2	0	44	18	6	15	15
LUMO	-1.80	0	0	10	32	29	19	9
HOMO	-5.22	44	17	27	10	1	0	0
H-1	-5.53	17	5	11	47	12	6	3
H-2	-5.71	100	0	0	0	0	0	0
H-3	-5.98	7	1	26	8	16	22	20

7a

	eV	Cz	N	C_6H_4	C_2N_2O	$C_6H_4{}^{t}Bu$
L+2	-0.79	98	1	1	0	0
L+1	-0.93	3	0	27	29	41
LUMO	-1.70	3	1	38	36	22
HOMO	-5.45	59	22	13	5	2
H-1	-5.85	100	0	0	0	0
H-2	-6.21	10	1	14	33	41
H-3	-6.89	99	0	1	0	0

To demonstrate how molecular rotations affect the total energies, nature of MOs, MO energies and TD-DFT data, three geometries of **1a** were looked at where the torsion angles are:

a) between the oxadiazole and phenylene groups at 90°
b) between the fluorene and phenylene groups at 0°
c) between the fluorene and phenylene groups at 90°.

Partially optimised geometries for **1a** with constrained dihedral angles were obtained using OPT(Z-MAT) to determine rotational barrier energies. While the rotation barrier between the oxadiazole and the phenylene ring is substantial at 6.5 kcal mol^{-1}, the two rotation barriers between fluorene and phenylene groups are only 1.9 and 2.9 kcal mol^{-1}. These small barriers indicate that compound **1a** is expected to have essentially free rotations between the three rings in solutions at ambient temperatures.

The effects of constrained torsion angles on the character and energy of the LUMO are obvious as the LUMO is fluorene-phenylene-oxadiazole in character as shown in Figures S35-S38 for the fully optimised geometry and for geometries with constrained angles. These variations are shown in the TD-DFT data with the values for the HOMO > LUMO transitions computed between 361 and 410 nm – a difference of ca 50 nm. While the computed data depend on the starting rotational isomer geometries, the predicted trends are in good agreement with experimental trends as all the fully optimised geometries have similar torsion angles between the rings.

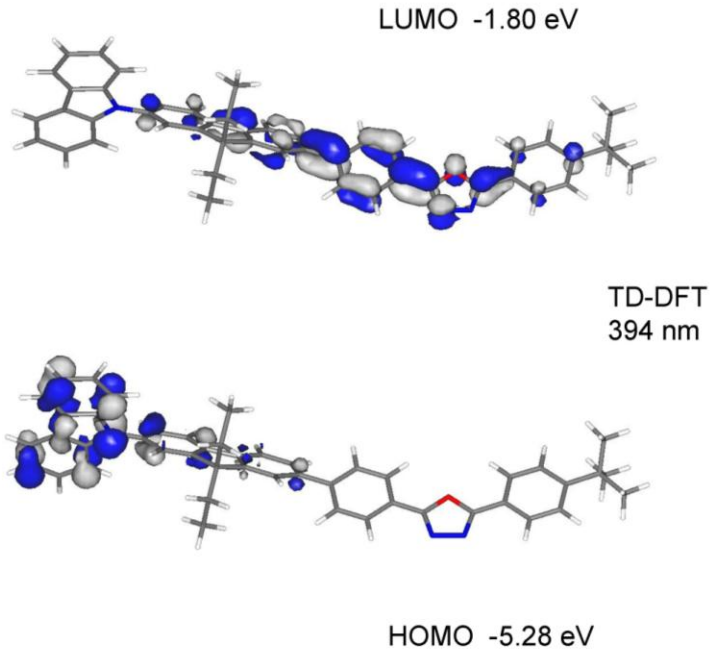


Figure S35. Optimised geometry of **1a** with frontier orbitals, orbital energies and calculated absorption value for HOMO > LUMO transition.

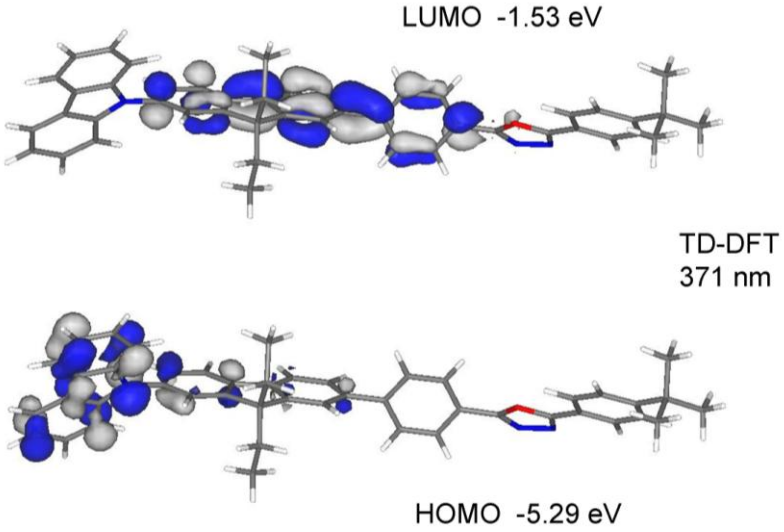


Figure S36. Geometry of **1a** with oxadiazole and C_6H_4 rings constrained at 90°.

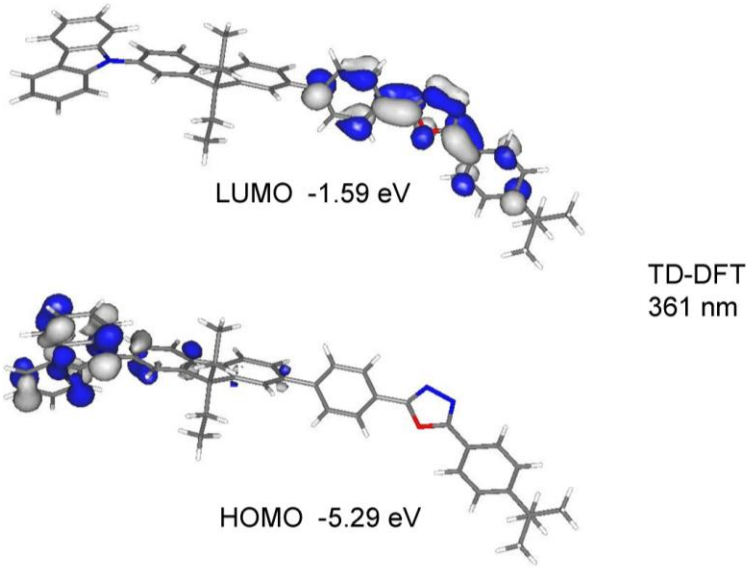


Figure S37. Geometry of **1a** with fluorene and C_6H_4 rings constrained at 90°.

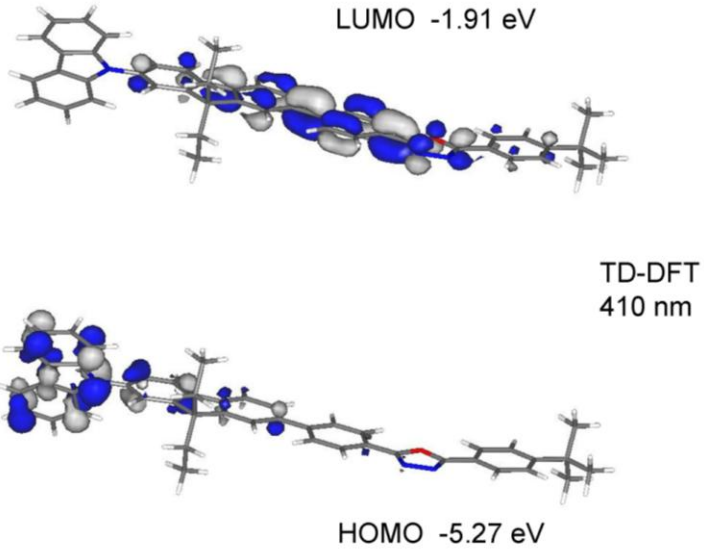


Figure S38. Geometry of **1a** with fluorene and C_6H_4 rings constrained at 0°.

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