Supporting Information

Conformationally-Restricted Bicarbazoles with Phenylene Bridges Displaying Deep-Blue Emission and High Triplet Energies: Systematic Structure-Property Relationships

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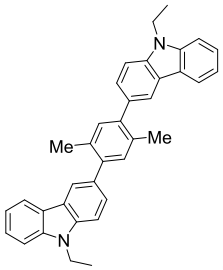
General information

All commercially available chemicals were used without further purification. Reactions requiring an inert atmosphere were performed under a blanket of argon gas, which was dried over a phosphorus pentoxide column. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent-purification system. Column chromatography was performed using 40–60 μm mesh silica gel. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel (Merck, silica gel 60F254) and visualized using UV light (254, 315, 365 nm). NMR spectra were recorded on Bruker Avance 400 MHz and Varian Mercury 400 MHz spectrometers. Melting points were determined in open-ended capillaries using a Stuart Scientific SMP3 melting point apparatus at a ramping rate of 1 °C/min. Atmospheric solids analysis probe (ASAP) mass spectra were recorded on a Waters Xevo QTOF spectrometer. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. Differential scanning calorimetry (DSC) was performed in a nitrogen atmosphere using a Mettler Toledo DSC 3 instrument. The compounds were heated at a rate of 10 ^{o}C /min. UV-Vis and photoluminescence spectra for all samples were obtained using Shimadzu UV-3600 and Jobin Yvon Luminescence spectrometers (FluoroMax-3). For cyclic voltammetry measurements the electrochemical cell comprised a platinum disc working electrode, a silver wire reference electrode and a platinum wire counter electrode. Data were recorded at room temperature using 1.0 mM concentrations of all compounds in 0.1 M solutions of *n*-Bu_4NBF_4, 99% (Sigma Aldrich) in dichloromethane (CH_2Cl_2), CHROMASOLV®, 99.9% (Sigma Aldrich) at a scan

rate of 100 mV s^{-1} and were calibrated against a ferrocene/ferrocenium redox couple as internal standard.

Synthetic details



1a

Under an atmosphere of Ar, 3-bromo-9-ethylcarbazole **3** (150 mg, 0.55 mmol), bridge **A** (90 mg, 0.25 mmol), $Pd(OAc)_2$ (1 mg, 2 %) and SPhos (4 mg, 4%) were dissolved in degassed toluene (10 mL) prior to addition of an aqueous K_3PO_4 (2.7 M, 1.6 mL, 4.4 mmol) and heated to reflux for 20 h. Upon cooling the reaction mixture was diluted with EtOAc (25 mL) and washed with water (25 mL) then dried over $MgSO_4$ prior to removal of solvent under reduced pressure and evaporation of solvent under reduced pressure. Purification was achieved by column chromatography (10% EtOAc/hexane) followed by recrystallization from EtOAc/hexane to yield the product as a white crystalline solid (56 mg, 45%). mp. 222-224°C

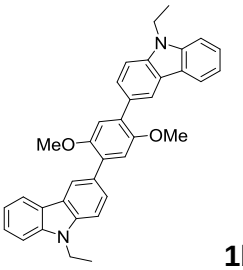
^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.23 (d, J = 7.5 Hz, 2H), 8.19 (d, J = 1.6 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.50 (dd, J = 8.4, 1.6 Hz, 2H), 7.48 (ddd, J = 8.3, 7.2, 1.2 Hz, 2H), 7.27 (s, 2H), 7.24 – 7.18 (m, 2H), 4.50 (q, J = 7.2 Hz, 4H), 2.33 (s, 6H), 1.37 (t, J = 7.1 Hz, 6H)

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 140.6, 139.9, 138.5, 132.2, 132.1, 131.9, 126.9, 125.8, 122.23, 122.16, 120.7, 120.6, 118.7, 109.1, 108.7, 37.0, 20.0, 13.8

MS ($ASAP^+$): m/z = 493.2 [$M+H^+$]

HRMS ($ASAP^+$): m/z = calculated for $C_{36}H_{33}N_2$ [$M+H^+$]: 493.2644; found: 493.2642

Elemental analysis: Found C, 87.58; H, 6.58; N, 5.49 Calculated C, 87.77; H, 6.55; N, 5.69



1b

Under argon, bridge **B** (117 mg, 0.30 mmol) and **3** (186 mg, 0.68 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (25 mg, 0.02 mmol) and K_2CO_3 (300 mg, 2.17 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure.

Purification was achieved by column chromatography (10% THF/hexane) followed by recrystallisation from toluene/methanol to give **1b** as a white crystalline powder (68 mg, 43%). mp. 247-249 °C (blackens)

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

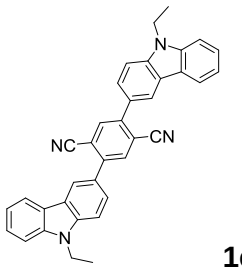
^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.30 (d, *J* = 1.7 Hz, 2H), 8.16 (d, *J* = 7.5 Hz, 2H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 2H), 7.21 (ddd, *J* = 7.9, 7.1, 1.0 Hz, 2H), 7.14 (s, 2H), 4.50 (q, *J* = 7.1 Hz, 4H), 3.83 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 6H)

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 150.3, 139.7, 138.5, 129.9, 128.7, 127.3, 125.5, 122.4, 122.1, 120.8, 120.2, 118.6, 114.9, 108.9, 108.2, 56.1, 37.0, 13.7

MS (ASAP): m/z = 525.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{36}H_{33}N_2O_2$ [M+H$^+$]: 525.2542; found: 525.2535

Elemental analysis: Found C, 81.75; H, 5.99; N, 5.12 Calculated C, 82.41; H, 6.15; N, 5.34



1c

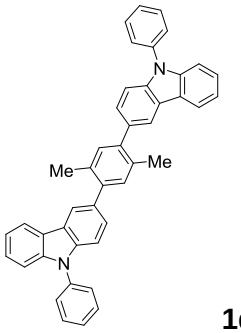
Under argon, bridge **C** (95 mg, 0.25 mmol) and **3** (173 mg, 0.63 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) and K_2CO_3 (242 mg, 1.75 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$. Purification was achieved by column chromatography (10% THF/hexane) followed by recrystallisation from toluene/methanol to give **1c** as a bright yellow crystalline powder (45 mg, 35%). mp. 294-297 °C (blackens)

1H-NMR (400 MHz, DMSO-d_6): δ = 8.52 (d, J = 1.8 Hz, 2H), 8.30 (s, 2H), 8.23 (d, J = 7.7 Hz, 2H), 7.88 – 7.74 (m, 4H), 7.64 (d, J = 8.2 Hz, 2H), 7.52 (ddd, J = 8.2, 7.1, 1.2 Hz, 2H), 7.34 – 7.20 (m, 2H), 4.54 (q, J = 7.1 Hz, 4H), 1.44 (t, J = 7.1 Hz, 6H)

13C-NMR (101 MHz, DMSO-d_6): δ = 143.5, 140.0, 139.8, 135.3, 126.2, 126.1, 122.7, 122.1, 121.0, 120.5, 119.2, 117.6, 114.5, 109.3, 109.2, 37.2, 13.7

MS (ASAP): m/z = 516.2 [M+2H$^+$]

HRMS (ASAP): m/z = calculated for $C_{36}H_{26}N_4$: 514.2157, found: 514.2162



1d

Under argon, bridge **A** (66 mg, 0.25 mmol) and 9-phenyl-3-bromocarbazole **4** (202 mg, 0.63 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) and K_2CO_3 (242 mg, 1.75 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (10% EtOAc/hexane) followed by recrystallisation from EtOAc/hexane to give **1d** as a white crystalline powder (41 mg, 31%). mp. 249-251 °C

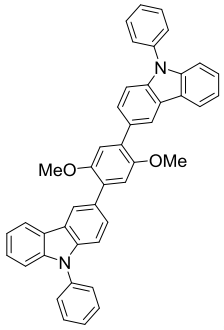
N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.26 (d, J = 7.7 Hz, 2H), 8.21 (s, 2H), 7.76 – 7.67 (m, 4H), 7.70 – 7.62 (m, 4H), 7.60 – 7.51 (m, 2H), 7.51 – 7.39 (m, 8H), 7.34 – 7.26 (m, 2H), 7.28 (s, 2H), 2.39 (s, 6H)

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 140.39, 140.38, 139.0, 136.9, 133.1, 132.1, 132.0, 130.0 (2C), 127.4, 127.2, 126.4 (2C), 126.1, 122.82, 122.78, 120.7, 120.5, 119.9, 109.5, 109.0, 19.9

MS (ASAP): m/z = 589.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{44}H_{33}N_2$ [M+H$^+$]: 589.2644; found: 589.2651



1e

Under argon, bridge **B** (98 mg, 0.25 mmol) and **4** (202 mg, 0.63 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) and K_2CO_3 (242 mg, 1.75 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure.

Purification was achieved by column chromatography (10% EtOAc/hexane) followed by recrystallisation from EtOAc/hexane to give **1e** as a white crystalline powder (74 mg, 48%). mp. 294-295 °C

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

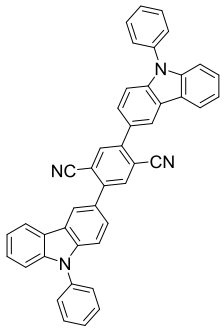
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.40 (dd, *J* = 1.7, 0.6 Hz, 2H), 8.26 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.77 – 7.69 (m, 5H), 7.69 – 7.62 (m, 5H), 7.60 – 7.51 (m, 2H), 7.49 – 7.40 (m, 6H), 7.30 (ddd, *J* = 7.9, 6.0, 2.1 Hz, 2H), 7.16 (s, 2H), 3.21 (s, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 150.3, 140.4, 139.1, 136.9, 130.00, 129.97 (2C), 129.8, 127.8, 127.4, 126.4 (2C), 126.0, 122.9, 122.6, 121.0, 120.4, 119.9, 114.9, 109.5, 108.8, 56.1

MS (ASAP): m/z = 621.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{44}H_{33}N_2O_2$ [M+H$^+$]: 621.2542; found: 621.2558

Elemental analysis: Found C, 84.97; H, 5.23; N, 4.38 Calculated C, 85.14; H, 5.20; N 4.51



1f

Under argon, bridge **C** (95 mg, 0.25 mmol) and **4** (202 mg, 0.63 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (21 mg, 0.02 mmol) and K_2CO_3 (242 mg, 1.75 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (0-20% toluene/hexane) followed by recrystallisation from toluene/methanol to give **1f** as a yellow crystalline powder (50 mg, 33%). mp. 347-348 °C (luminescence observed between 313-319 °C)

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

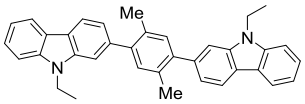
It was not possible to obtain a solution of suitable concentration for ^{13}C-NMR spectroscopy.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.64 (d, *J* = 1.8 Hz, 2H), 8.36 (s, 2H), 8.33 (d, *J* = 7.8 Hz, 2H), 7.81 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.77 – 7.71 (m, 4H), 7.71 – 7.66 (m, 4H), 7.62 – 7.57 (m, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.34 (m, 2H)

MS (ASAP): m/z = 611.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{44}H_{27}N_4$ $[M+H]^+$: 611.2236; found: 611.2247

Elemental analysis: Found C, 85.99; H, 4.27; N, 9.01 Calculated C, 86.53; H, 4.29; N 9.17



2a

Under argon, bridge **A** (108 mg, 0.41 mmol) and 9-ethyl-2-bromocarbazole **5** (250 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (10% THF/hexane) followed by recrystallisation from toluene/methanol to give **2a** as a white crystalline solid (61 mg, 30%). mp. >256 °C (blackens)

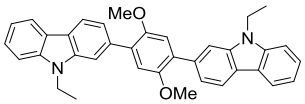
N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.16 (d, *J* = 8.0 Hz, 2H), 8.14 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 1.4 Hz, 2H), 7.46 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.30 (s, 2H), 7.24 – 7.18 (m, 2H), 7.21 (dd, *J* = 7.9, 1.4 Hz, 2H), 4.50 (q, *J* = 7.1 Hz, 4H), 2.38 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 140.9, 139.8, 139.4, 138.7, 132.0, 131.8, 125.4, 122.1, 121.0, 120.1, 120.0, 119.7, 118.6, 109.2, 108.8, 36.9, 19.9, 13.7

MS (ASAP): m/z = 493.3 $[M+H^+]$

HRMS (ASAP$^+$): m/z = calculated for $C_{36}H_{33}N_2$ $[M+H^+]$: 493.2644; found: 493.2639



2b

Under argon, bridge **B** (160 mg, 0.41 mmol) and **5** (250 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 min.

Upon cooling, the tube was opened and the reaction mixture poured into water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with 2M HCl (2 x 25 mL) and water (2 x 25 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and charcoal was added to the filtrate which was then stirred for 30 minutes before being filtered over celite. Solvent was removed under reduced pressure. Purification was by recrystallisation from toluene/methanol to give **2b** as a white crystalline solid (61 mg, 31%). mp. 287-289 °C

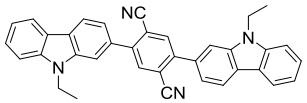
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.0 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.52 – 7.41 (m, 8H), 7.26 – 7.22 (m, 2H), 7.18 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 6H), 3.86 (s, 6H), 1.47 (t, *J* = 7.2 Hz, 6H)

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.1, 140.6, 140.1, 136.0, 131.5, 125.7, 123.1, 122.2, 120.7, 120.6, 120.1, 119.0, 115.8, 109.7, 108.6, 56.9, 37.7, 14.0

MS (ASAP): m/z = 525.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{36}H_{33}N_2O_2$ [M+H$^+$]: 525.2542; found:525.2559

Elemental analysis: Found C, 82.13; H, 6.13; N, 5.22 Calculated C, 82.41; H, 6.15; N, 5.34



2c

Under argon, bridge **C** (156 mg, 0.41 mmol) and **5** (250 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (0-20% toluene/hexane) followed by recrystallisation from toluene/methanol to give **2c** as yellow crystals (38 mg, 18%). mp. >310 °C (blackens)

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

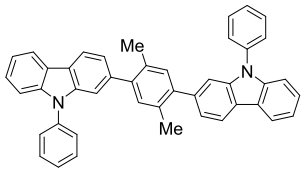
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.42 (s, 2H), 8.33 (d, *J* = 7.8 Hz, 2H), 8.22 (d, *J* = 7.7 Hz, 2H), 7.99 (d, *J* = 1.7 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.45 (m, 4H), 7.26 (td, *J* = 7.5, 0.9 Hz, 2H), 4.56 (q, *J* = 7.0 Hz, 4H), 1.44 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 143.9, 140.3, 139.4, 135.4, 132.7, 126.3, 123.0, 121.6, 120.7, 120.6, 119.3, 119.1, 117.5, 114.8, 109.7, 109.1, 37.1, 13.7

MS (ASAP): m/z = 515.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{36}H_{27}N_4$ [M+H$^+$]: 515.2236; found: 515.2222

Elemental analysis: Found C, 83.63; H, 5.09; N 10.71, Calculated C, 84.02; H, 5.09; N, 10.89



2d

Under argon, bridge **A** (108 mg, 0.41 mmol) and 9-phenyl-2-bromocarbazole **6** (293 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (10% EtOAc/hexane) followed by recrystallisation from toluene/methanol to give **2d** as a white crystalline solid (100 mg, 41%). mp. 178-181 °C

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

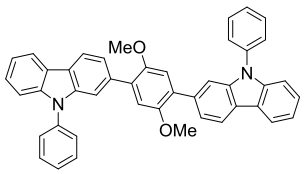
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.25 – 8.19 (m, 4H), 7.70 – 7.65 (m, 4H), 7.65 – 7.59 (m, 4H), 7.56 – 7.48 (m, 2H), 7.48 – 7.37 (m, 4H), 7.34 – 7.26 (m, 4H), 7.27 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.16 (s, 2H), 2.29 (s, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 141.3, 141.0, 140.7, 139.8, 137.4, 132.6, 132.3, 130.6 (2C), 128.0, 127.1 (2C), 126.5, 123.3, 122.2, 121.9, 120.9, 120.64, 120.55, 110.4, 110.0, 20.4

MS (ASAP): m/z = 589.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{44}H_{32}N_2$ [M$^+$]: 588.2565; found: 588.2594

Elemental analysis: Found C, 89.72; H, 5.47; N 4.67, Calculated C, 89.76; H, 5.48; N, 4.76.



2e

Under argon, bridge **B** (160 mg, 0.41 mmol) and **6** (293 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and extracted with $CHCl_3$ (3 x 25 mL). The combined organic extracts were washed with 2M HCl (2 x 25 mL) and water (2 x 25 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and charcoal was added to the filtrate which was then stirred for 30 minutes before being filtered over celite. Solvent was removed under reduced pressure. Purification was by recrystallisation from toluene/methanol to give **2e** as a white crystalline solid (118 mg, 46%). mp. 216-219 °C

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

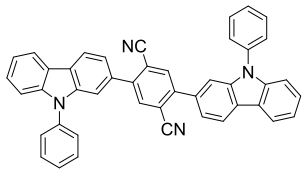
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.21 (dd, *J* = 8.1, 0.7 Hz, 2H), 8.21 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.73 – 7.62 (m, 8H), 7.59 (dd, *J* = 1.5, 0.6 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.46 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.44 – 7.41 (m, 4H), 7.29 (ddd, *J* = 8.0, 4.6, 3.4 Hz, 2H), 7.05 (s, 2H), 3.75 (s, 6H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 150.8, 141.1, 140.5, 137.5, 136.4, 130.8, 130.5 (2C), 127.9, 127.0 (2C), 126.5, 123.3, 122.3, 122.2, 120.9, 120.6, 120.3, 115.5, 111.0, 110.0, 56.7

MS (ASAP): m/z = 621.2 [M+H$^+$]

HRMS (ASAP): m/z = calculated for $C_{44}H_{33}N_2O_2$ [M+H$^+$]: 621.2542; found: 621.2557

Elemental analysis: Found C, 85.04; H, 5.27; N 4.32, Calculated C, 85.14; H, 5.20; N 4.51



2f

Under argon, bridge **C** (156 mg, 0.41 mmol) and **6** (293 mg, 0.91 mmol) were added to a microwave vial containing $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and K_2CO_3 (400 mg, 2.87 mmol) and suspended in a degassed mixture of DMF (3 mL) and H_2O (1 mL) before the vial was sealed. The vial was then heated at 120 °C in a microwave reactor for 25 minutes. Upon cooling, the tube was opened and the reaction mixture poured into water and filtered. The solids thus obtained were then dissolved in dichloromethane and dried over $MgSO_4$ prior to removal of solvent under reduced pressure. Purification was achieved by column chromatography (0-20% toluene/hexane) followed by recrystallisation from toluene/methanol to give **2f** as yellow crystals (99 mg, 40%). Mp. 320-322 °C (luminescence observed above 290 °C)

N.B. Addition of a few drops of CS_2 to the NMR sample was required to inhibit aggregation and obtain well-resolved NMR spectra.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.43 (dd, J = 8.1, 0.6 Hz, 1H), 8.36 – 8.28 (m, 2H), 7.73 – 7.68 (m, 5H), 7.59 (dd, J = 8.1, 1.6 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.50 (dd, J = 6.8, 1.3 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.35 (ddd, J = 8.0, 6.7, 1.3 Hz, 1H)

^{13}C NMR (101 MHz, DMSO-d_6): δ = 192.4, 143.8, 140.8, 139.8, 136.4, 135.2, 133.3, 130.1 (2C), 127.6, 126.9, 126.5 (2C), 123.5, 122.2, 121.0, 120.7, 120.4, 117.2, 114.8, 110.2, 109.7

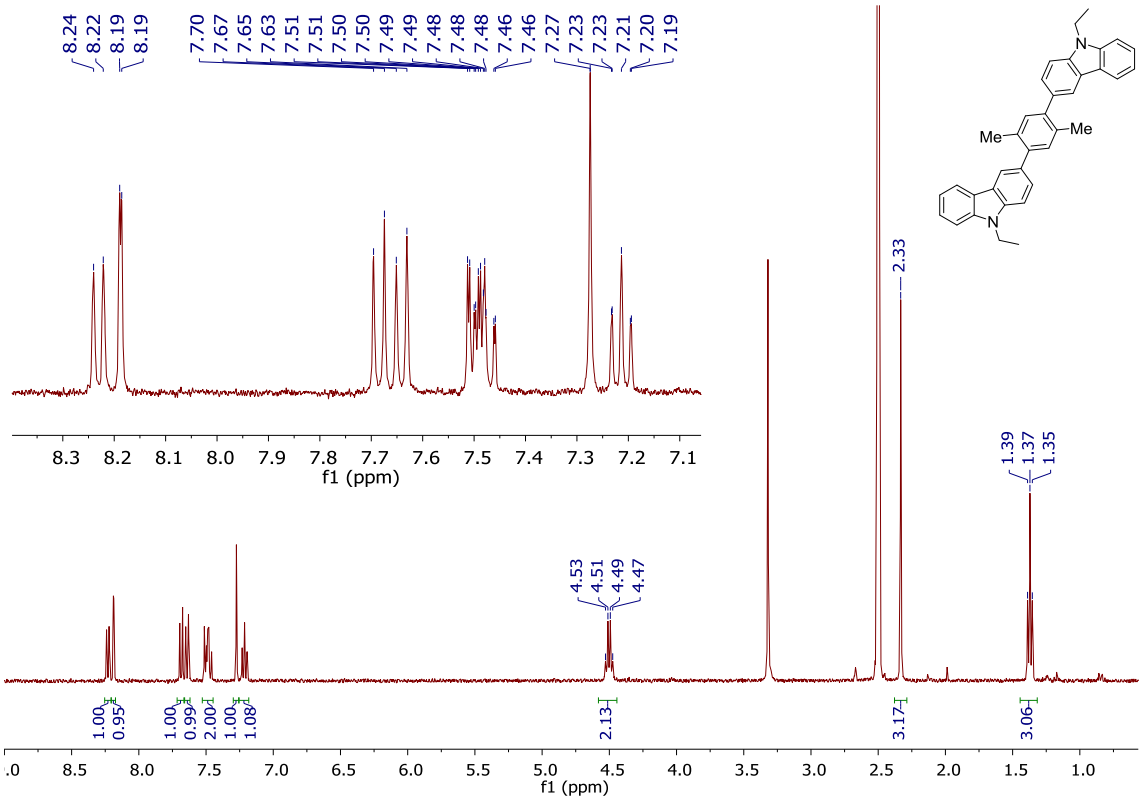
MS (ASAP): m/z = 611.2 [M+H$^+$].

HRMS (ASAP): m/z = calculated for $C_{44}H_{27}N_4$ [M+H]$^+$: 611.2236; found: 611.2257.

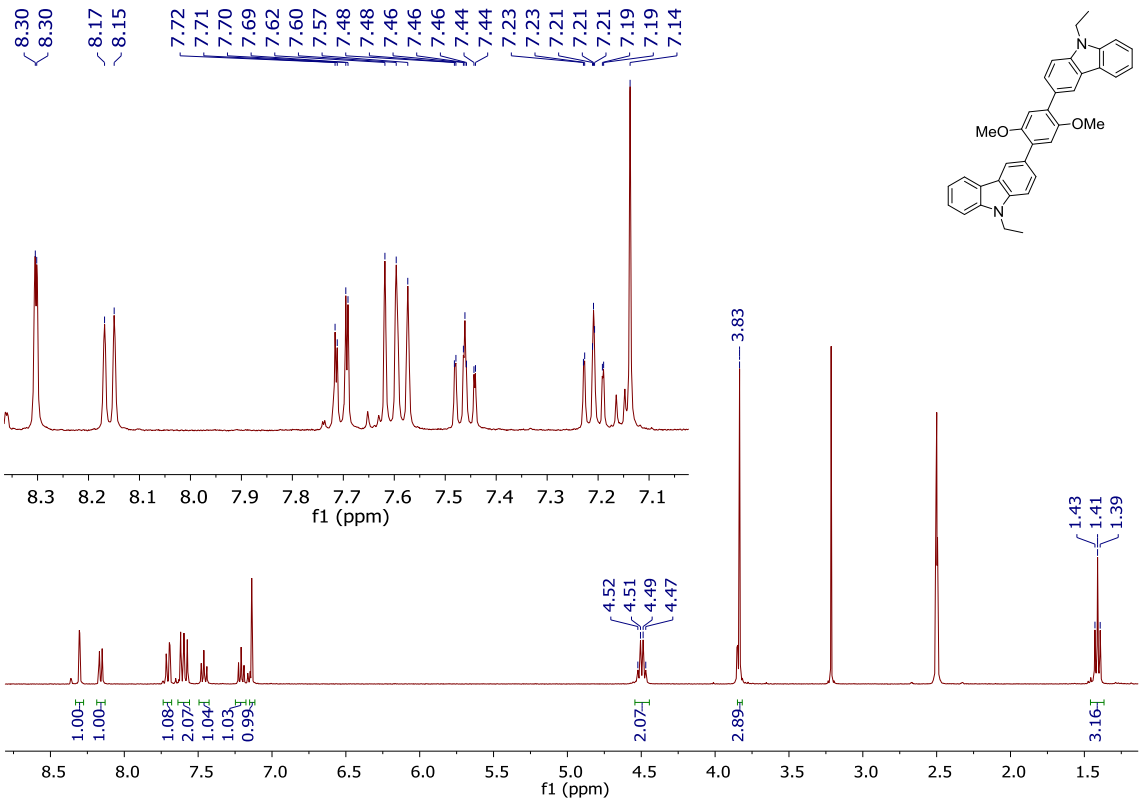
Elemental analysis: Found C, 86.51; H, 4.33; N, 8.99 Calculated C, 86.53; H, 4.29; N 9.17

Copies of ^{1}H NMR Spectra:

1a



1b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7.48
7.46
7.46
7.46
7.44
7.44
7.23
7.23
7.21
7.21
7.21
7.19
7.19
7.14
MeO
OMe
N
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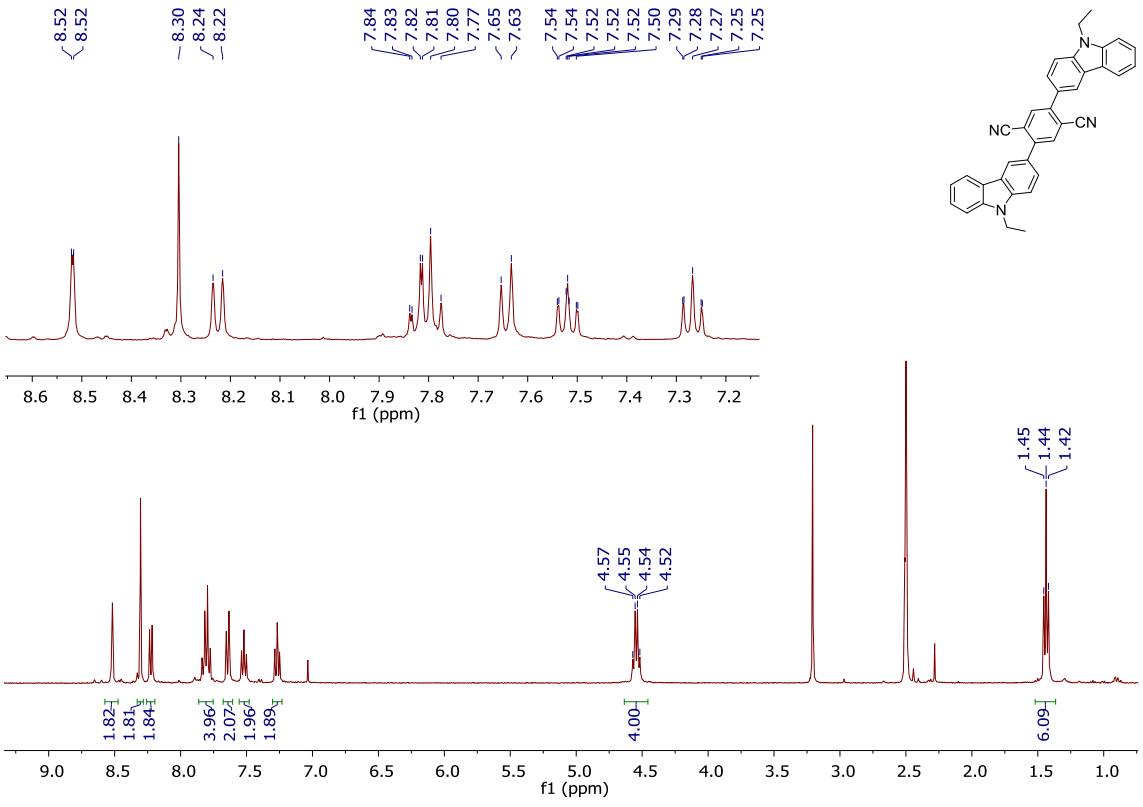
1.43
1.41
1.39
4.52
4.51
4.49
4.47
1.00
1.00
1.08
2.07
1.04
1.03
0.99
2.07
2.89
3.16
f1 (ppm)

1c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7.54
7.54
7.52
7.52
7.52
7.50
7.29
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7.25
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CN
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1.42
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4.55
4.54
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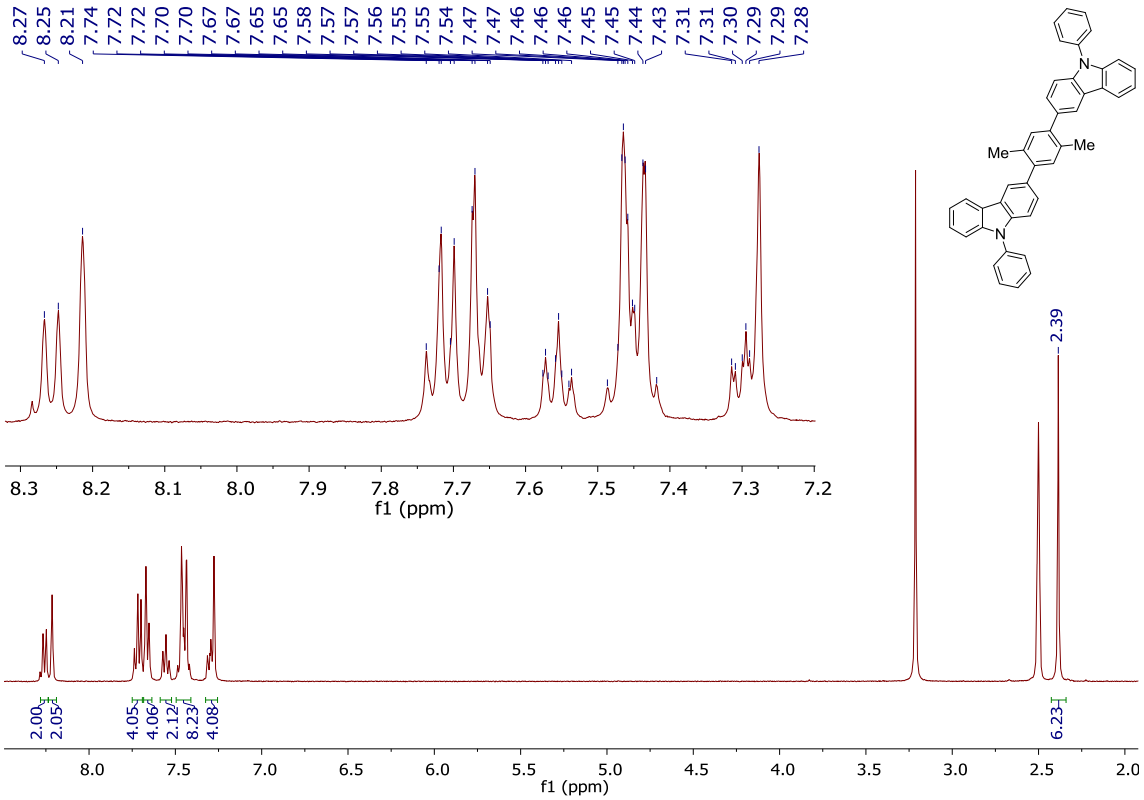
1.89
4.00
6.09
f1 (ppm)

1d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Me
Me
N
N
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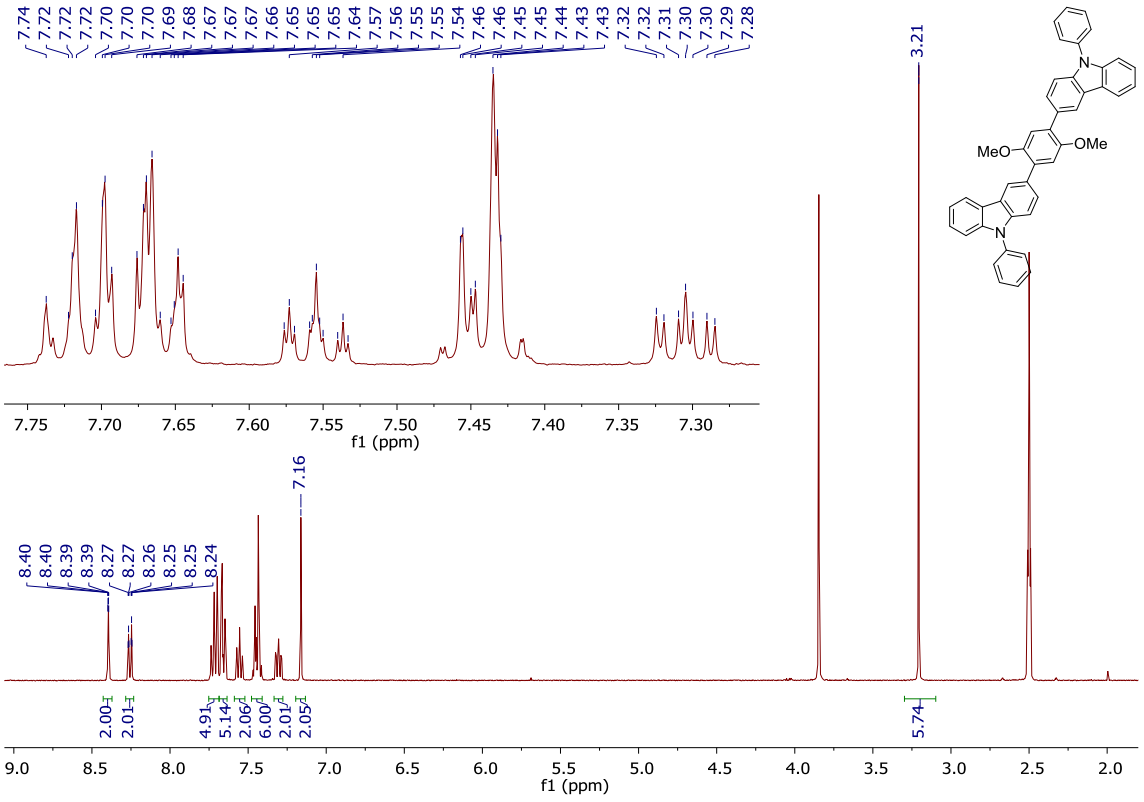
f1 (ppm)
2.00 2.05 4.05 4.06 2.12 8.23 4.08 6.23
f1 (ppm)

1e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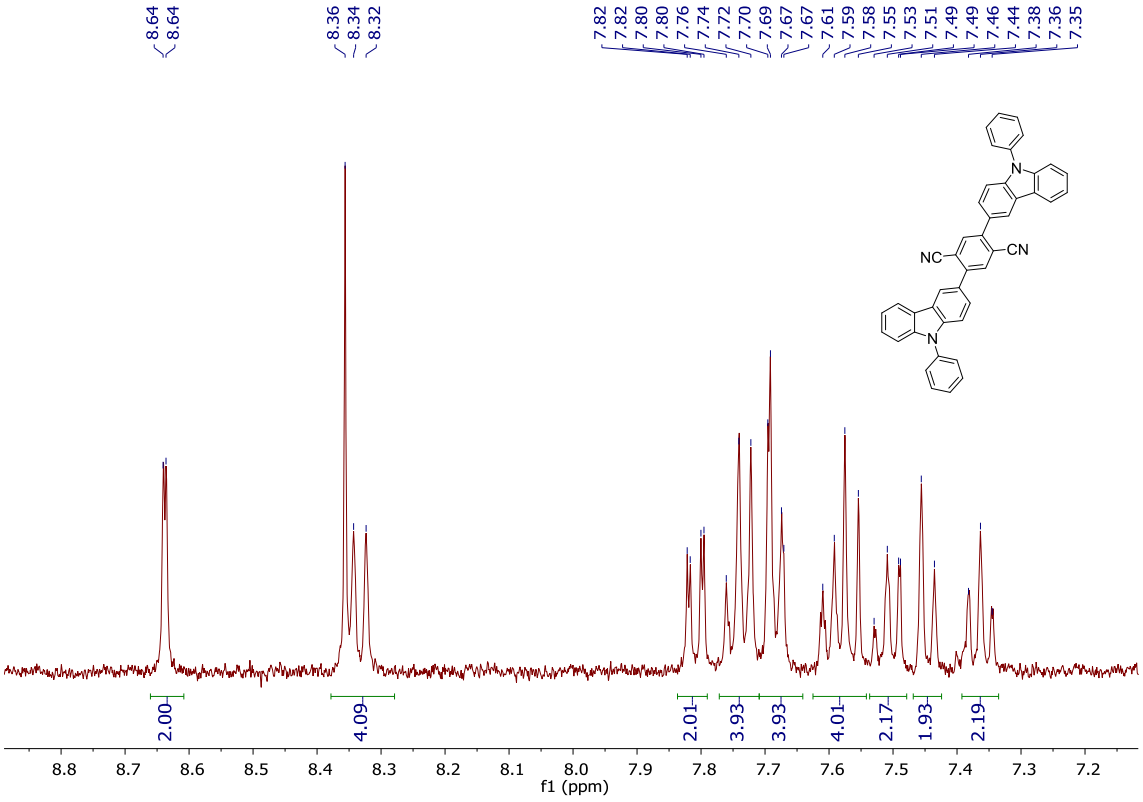
3.21
MeO
OMe
N
N
f1 (ppm)
7.16
8.40 8.40 8.39 8.39 8.27 8.27 8.26 8.25 8.25 8.24
2.00 2.01 4.91 5.14 2.06 6.00 2.01 2.05 5.74
f1 (ppm)

1f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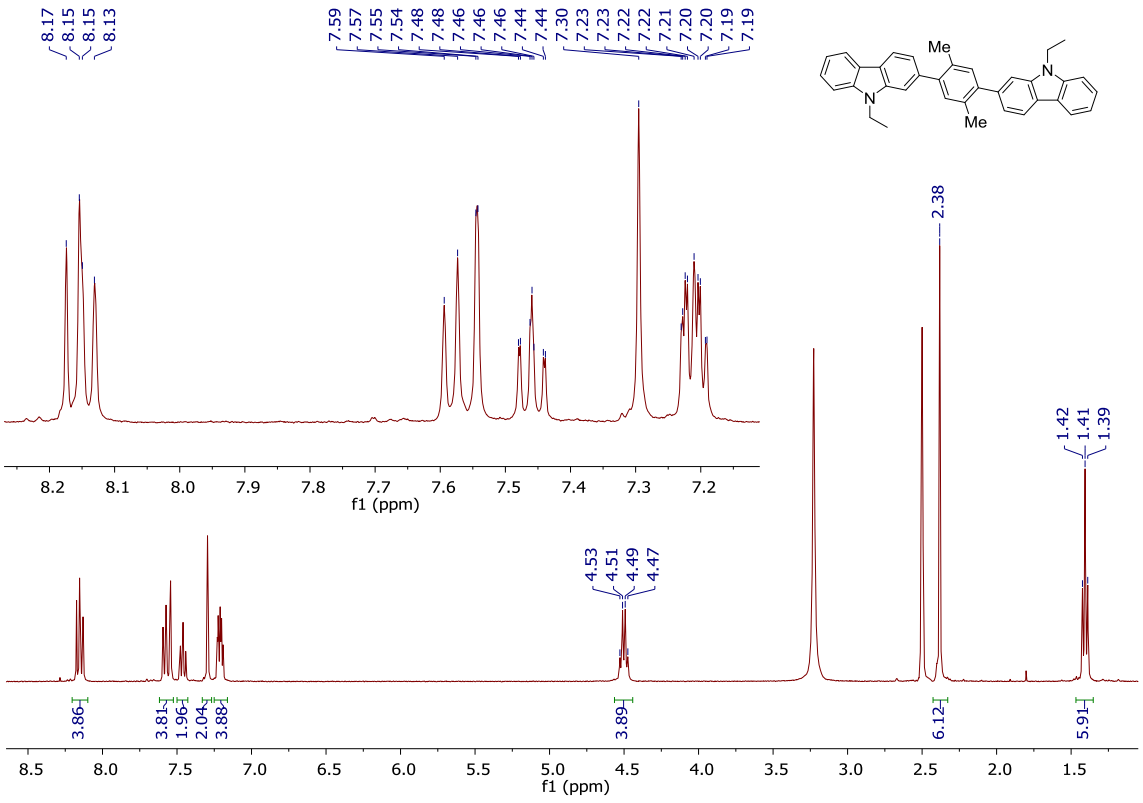
1.93
2.19
f1 (ppm)

2a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7.44
7.44
7.30
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.19
Me
N
N
Me
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1.41
1.39
4.53
4.51
4.49
4.47
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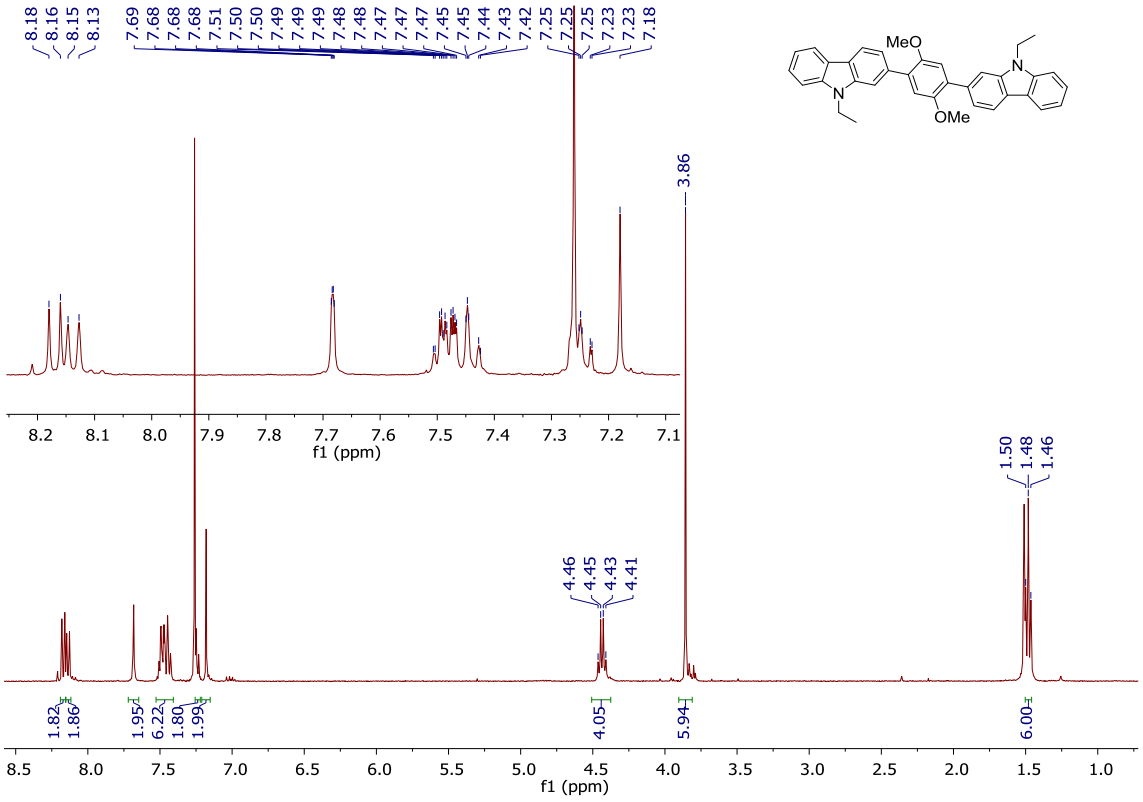
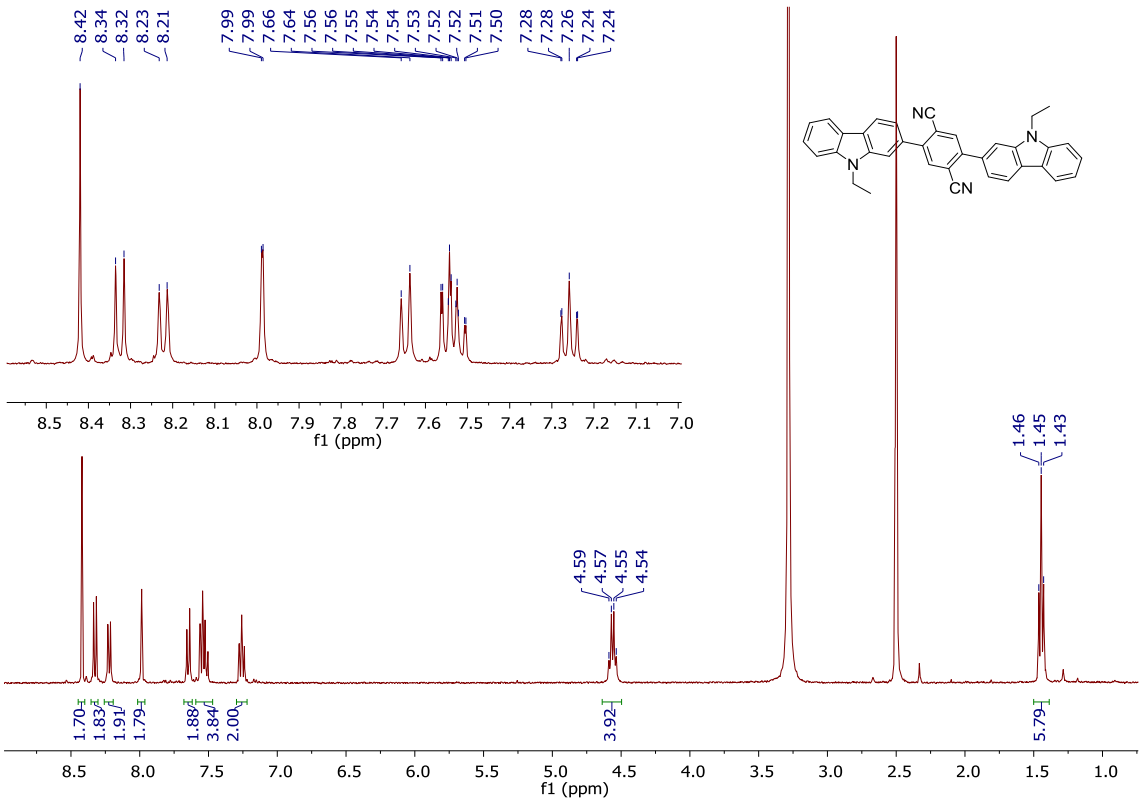
3.89
6.12
5.91
f1 (ppm)

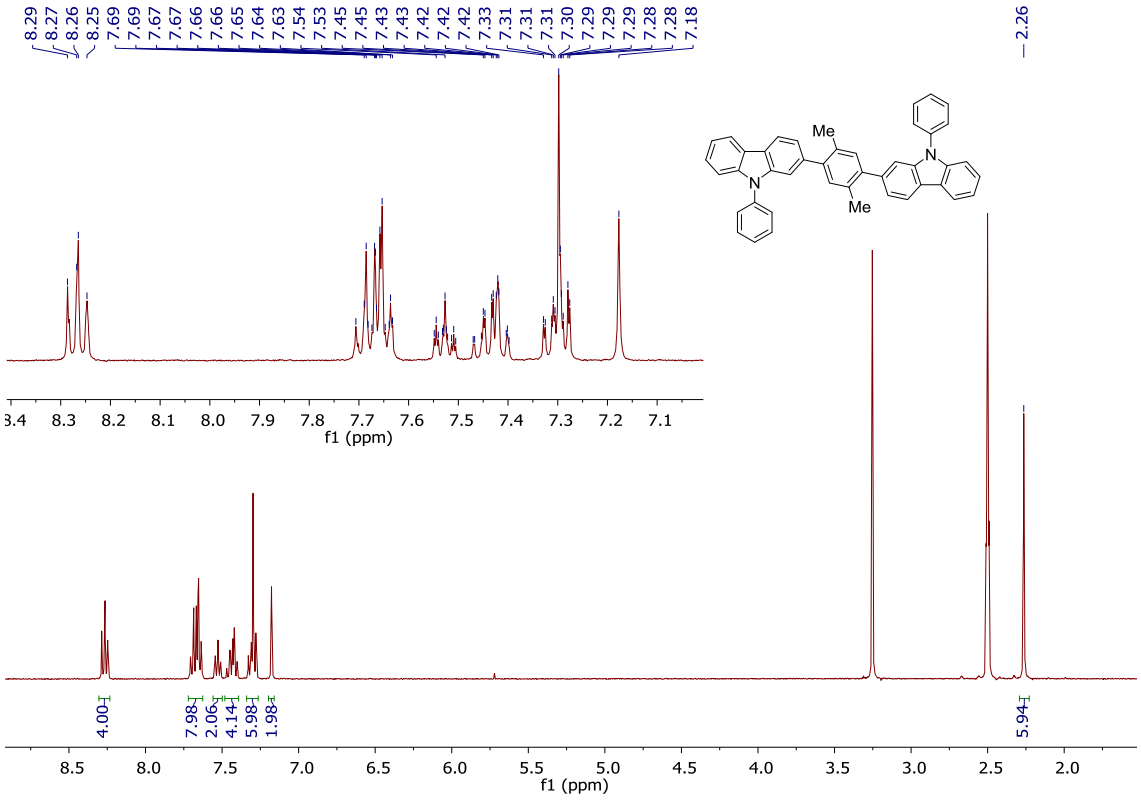
2b



2c



2d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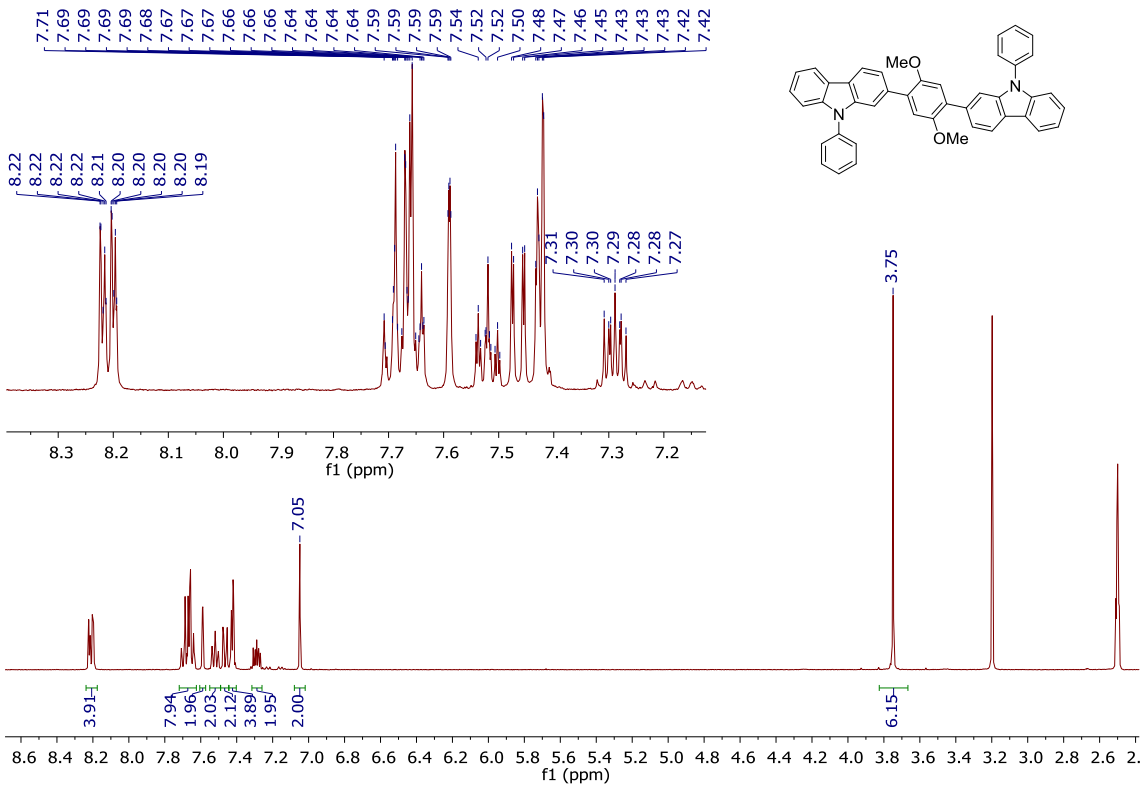
2.26
Me
Me
N
N
f1 (ppm)
4.00 7.98 2.06 4.14 5.98 1.98 5.94

2e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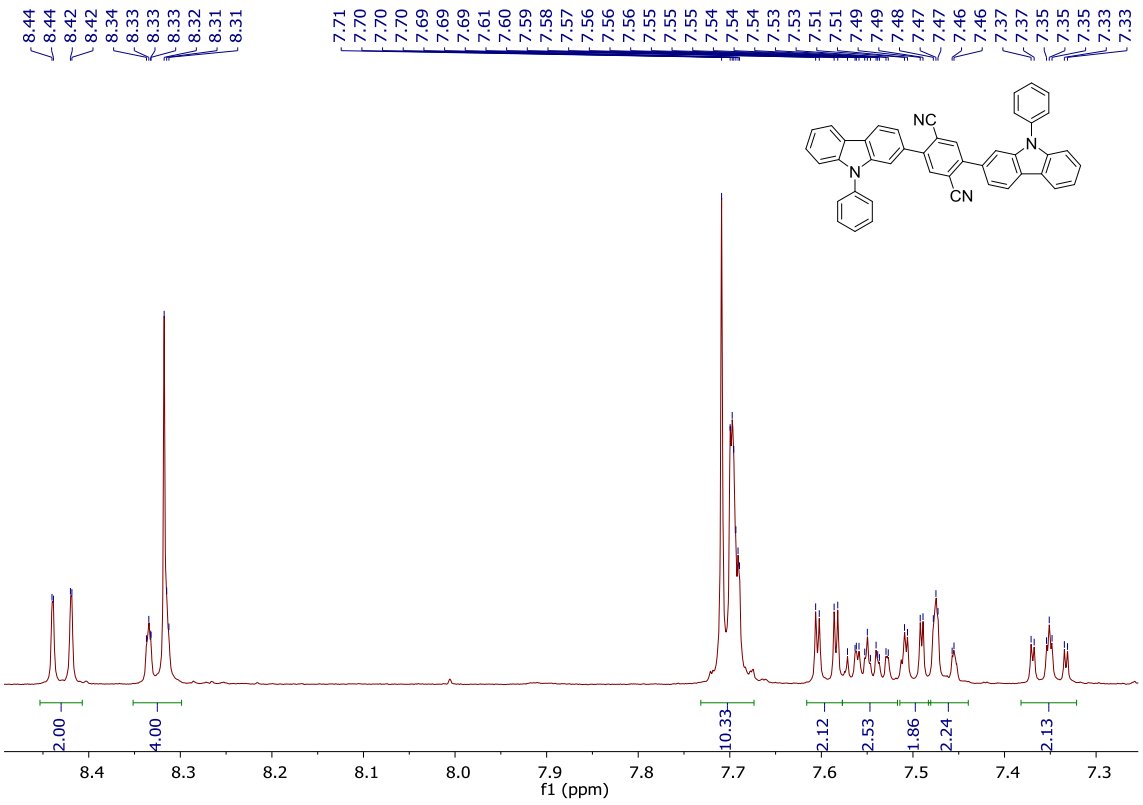
8.22 8.22 8.22 8.22 8.21 8.20 8.20 8.20 8.20 8.19
7.31 7.30 7.30 7.29 7.28 7.28 7.27
MeO
OMe
N
N
3.75
7.05
f1 (ppm)
3.91 7.94 1.96 2.03 2.12 3.89 1.95 2.00 6.15

2f



X-ray crystallography

The X-ray diffraction experiment for **1a** was carried out on a Bruker 3-circle D8 Venture diffractometer with a PHOTON 100 CMOS area detector, using Cu-K_α radiation from a IμS microsource with focussing mirrors, for **1c** on an Xcalibur κ-diffractometer with a Sapphire3 CCD area detector, using Mo-K_α radiation from an Enhance (Mo) source. Crystals were cooled to 120 K using Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostats. The structures were solved by direct methods using SHELXS 2013/1 software,[1] and refined by full-matrix least squares using SHELXL 2014/7[2] and OLEX2[3] software. Crystal data have been deposited with Cambridge Structural Database as CCDC-1547241 (**1a**) and 1547242 (**1c**).

Absorption Spectra

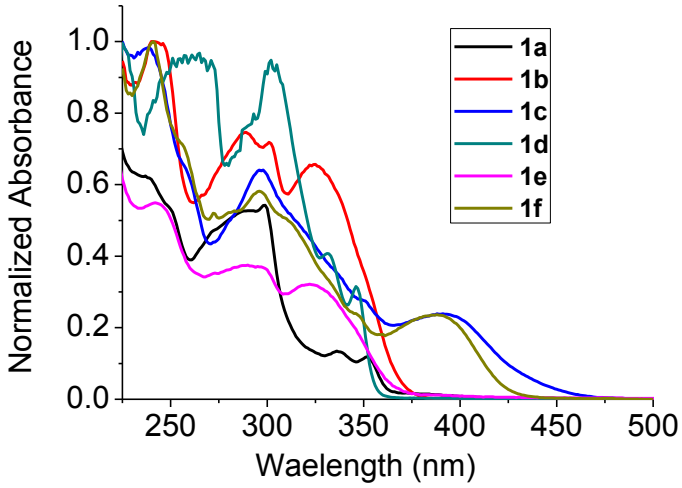


Figure S1. Absorption spectra for series 1 in zeonex (1:50 w/w) at room temperature

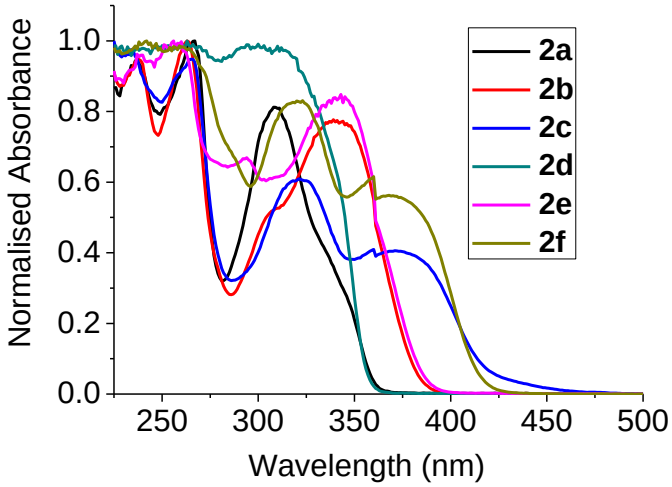
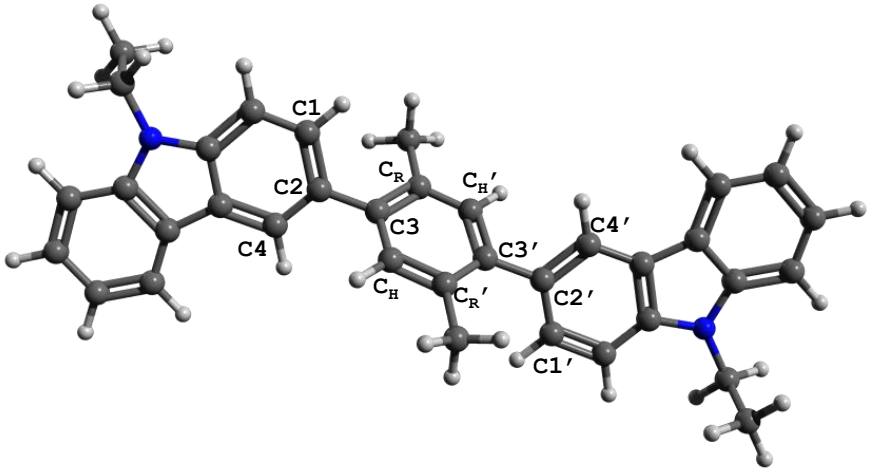


Figure S2. Absorption spectra for series 2 in zeonex (1:50 w/w) at room temperature. .

Computational studies

	LUMO+2 (eV)	LUMO+1 (eV)	LUMO (eV)	HOMO (eV)	HOMO-1 (eV)	HOMO-2 (eV)	E_g (eV)
7	-0.510	-0.574	-0.602	-4.882	-5.257	-5.539	4.280
1a	-0.266	-0.542	-0.558	-4.976	-5.205	-5.512	4.418
1b	-0.404	-0.473	-0.571	-4.798	-5.198	-5.413	4.227
1c	-0.850	-1.072	-1.978	-5.346	-5.542	-5.825	3.368
8	-0.579	-0.598	-0.668	-4.933	-5.283	-5.585	4.265
1d	-0.438	-0.568	-0.586	-5.023	-5.236	-5.56	4.437
1e	-0.453	-0.545	-0.622	-4.850	-5.229	-5.457	4.228
1f	-0.857	-1.112	-2.000	-5.366	-5.542	-5.854	3.366
9	0.088	-0.544	-1.080	-5.161	-5.255	-5.255	4.081
2a	0.168	-0.544	-0.858	-5.227	-5.229	-5.261	4.369
2b	0.211	-0.488	-0.999	-5.044	-5.128	-5.249	4.045
2c	-0.915	-1.390	-2.141	-5.508	-5.509	-5.672	3.367
10	-0.356	-0.556	-1.093	-5.179	-5.272	-5.274	4.086
2d	-0.336	-0.557	-0.875	-5.246	-5.248	-5.282	4.371
2e	-0.389	-0.504	-1.013	-5.062	-5.149	-5.271	4.049
2f	-0.908	-1.372	-2.121	-5.504	-5.505	-5.686	3.383

Table S1 Calculated (B3LYP/6-31G*) frontier orbital energy levels of compounds **1a-f**, **2a-f** and **7-10**.



	τ_1 (°)	τ_2 (°)	τ_1' (°)	τ_2' (°)
7	37.2	37.2	–	–
1a	55.1	52.4	–	–
1b	45.9	42.3	43.5	41.8
1c	45.4	43.5	–	–
8	36.9	37.2	–	–
1d	55.1	52.2	–	–
1e	46.1	42.2	43.3	41.7
1f	45.8	43.7	–	–
9	37.4	37.2	–	–
2a	55.7	53.0	–	–
2b	46.6	42.9	43.9	42.2
2c	46.4	44.3	–	–
10	36.4	36.4	–	–
2d	54.8	52.5	–	–
2e	46.0	42.6	43.3	41.6
2f	45.7	43.9	–	–

Table S2. Calculated dihedral angles between bridge and carbazole for compounds **1**, **2** and **7**–**10** (τ_1 = ∠C1C2C3C_R, τ_2 = ∠C4C2C3C_H, τ_1' = ∠C1'C2'C3'C_R', τ_2' = ∠C4'C2'C3'C_H'). The structure of **1a** is shown to illustrate the numbering system adopted. For compounds **1b**,**e** and **2b**,**e** τ_1/τ_2 refer to the MeO_{eq} side of the bridge and τ_1'/τ_2' refer to the MeO_{ax} side of the bridge.

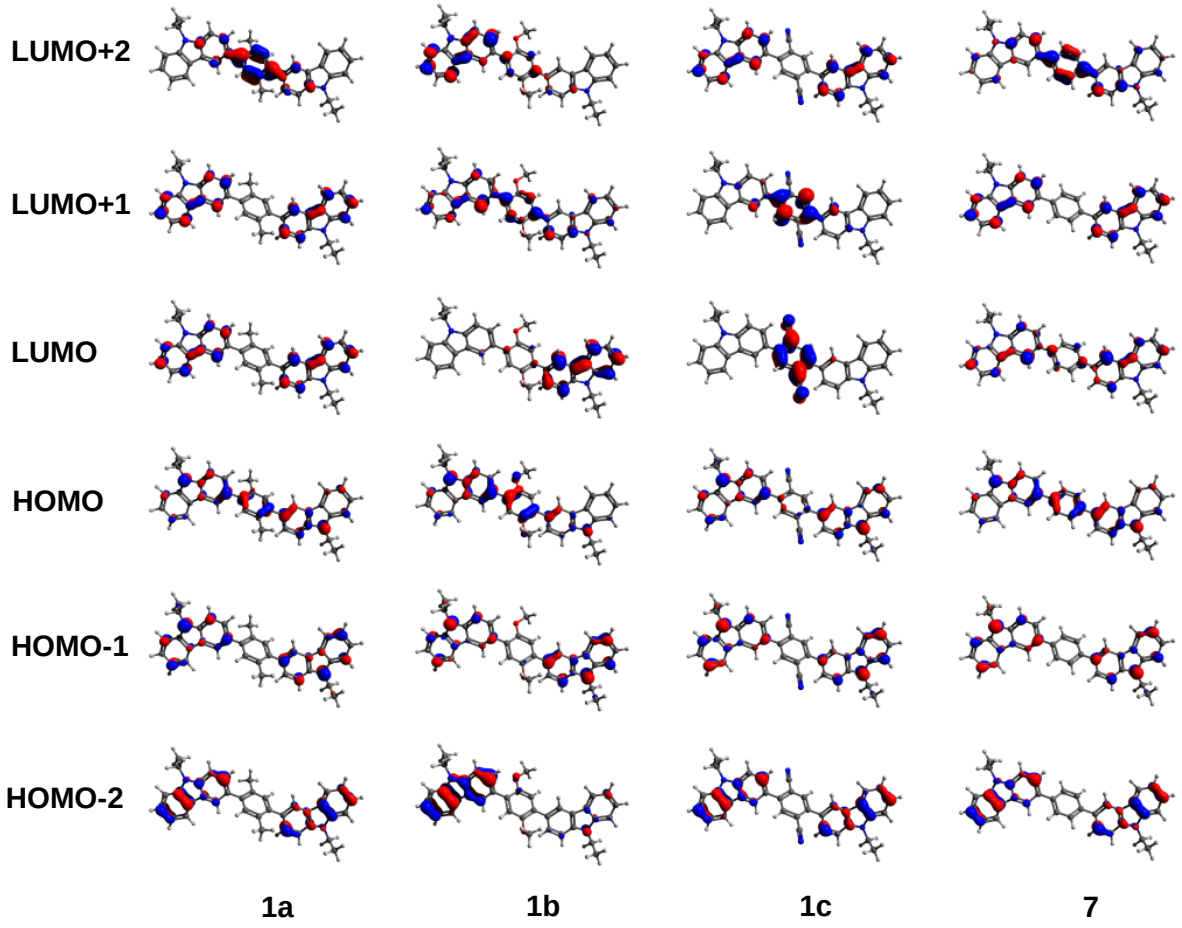


Figure S3 Frontier molecular orbital plots for the complete 3-substituted *N*-ethylcarbazolyl series **1a**−**c** and **7**.

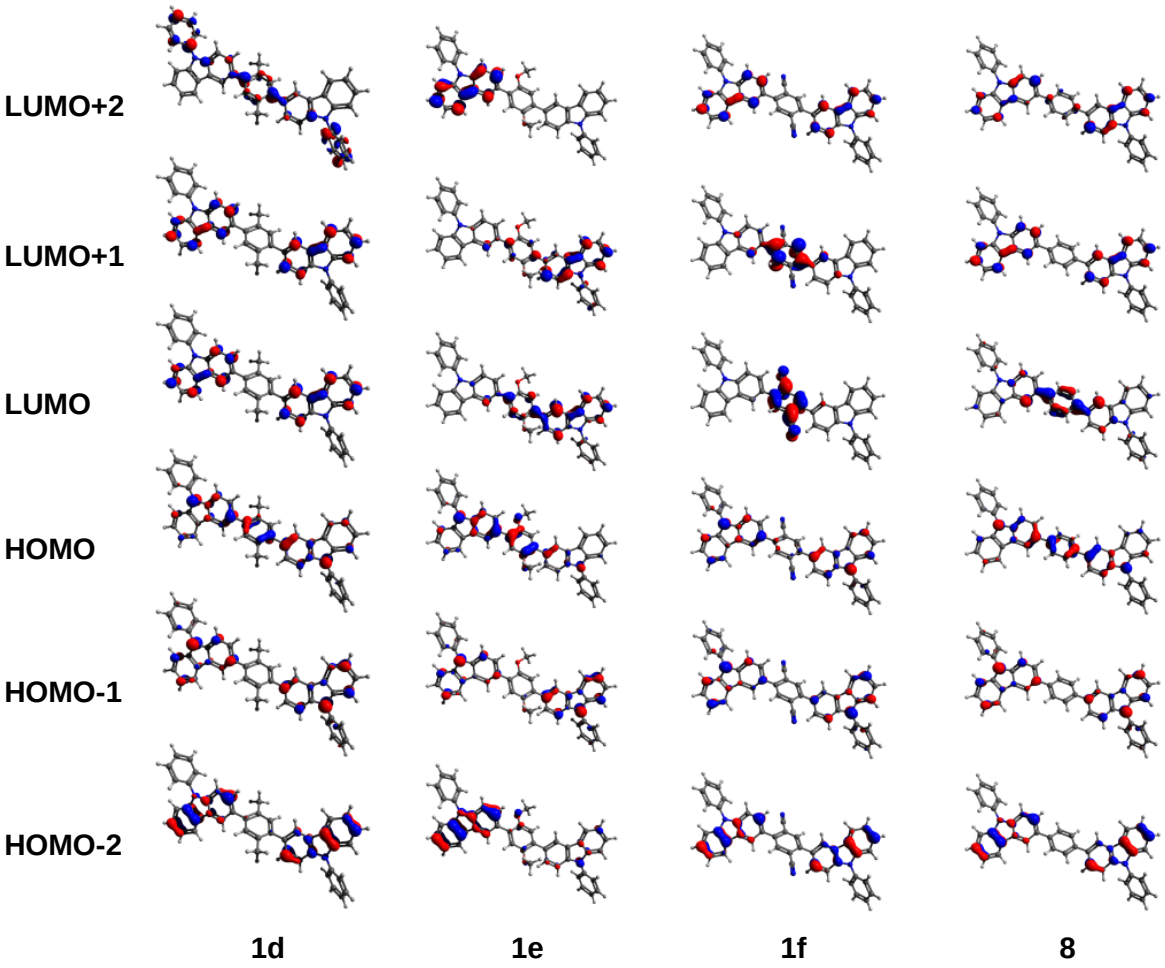


Figure S4 Frontier molecular orbital plots for the complete 3-substituted *N*-phenylcarbazolyl series **1d**–**f** and model compound **8**.

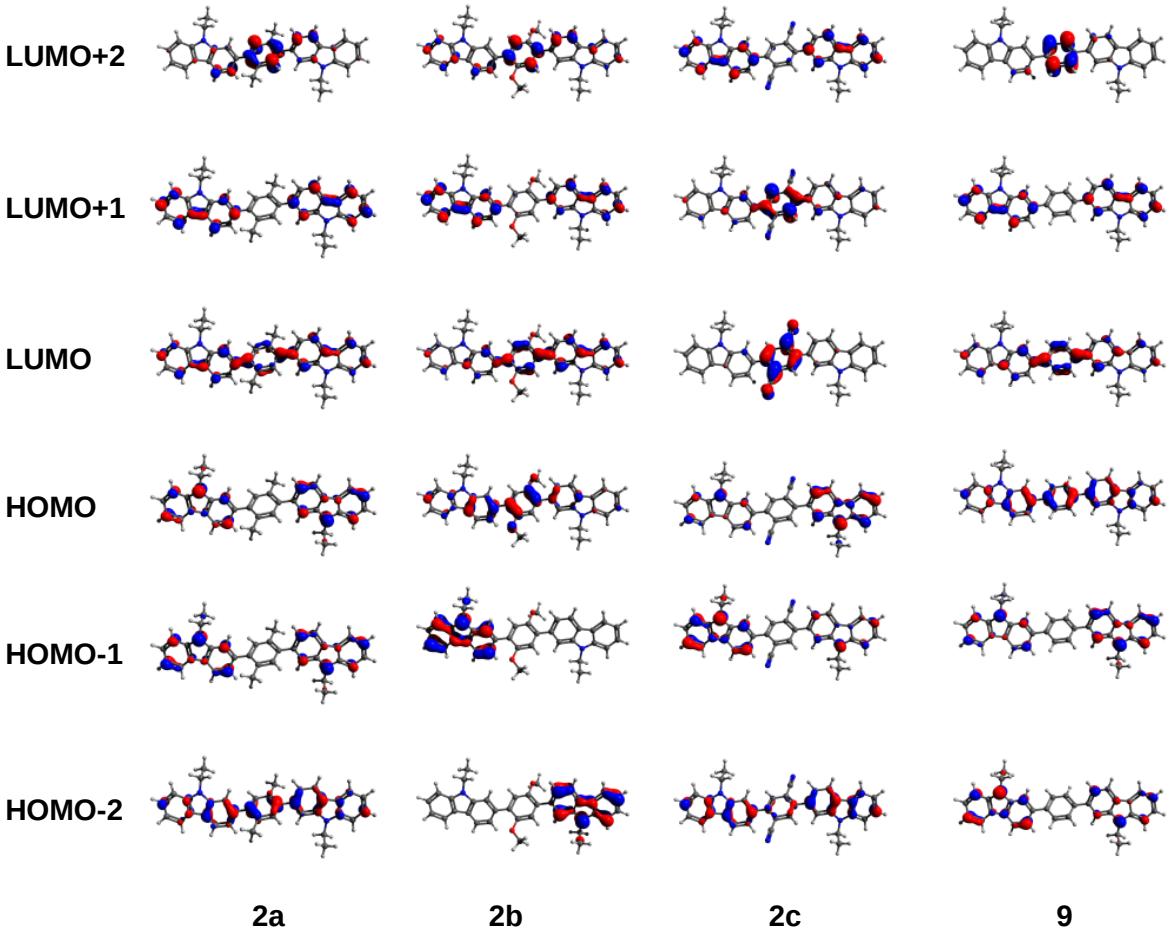


Figure S5 Frontier molecular orbital plots for the complete 2-substituted *N*-ethylcarbazolyl series **2a**−**c** and model compound **9**.

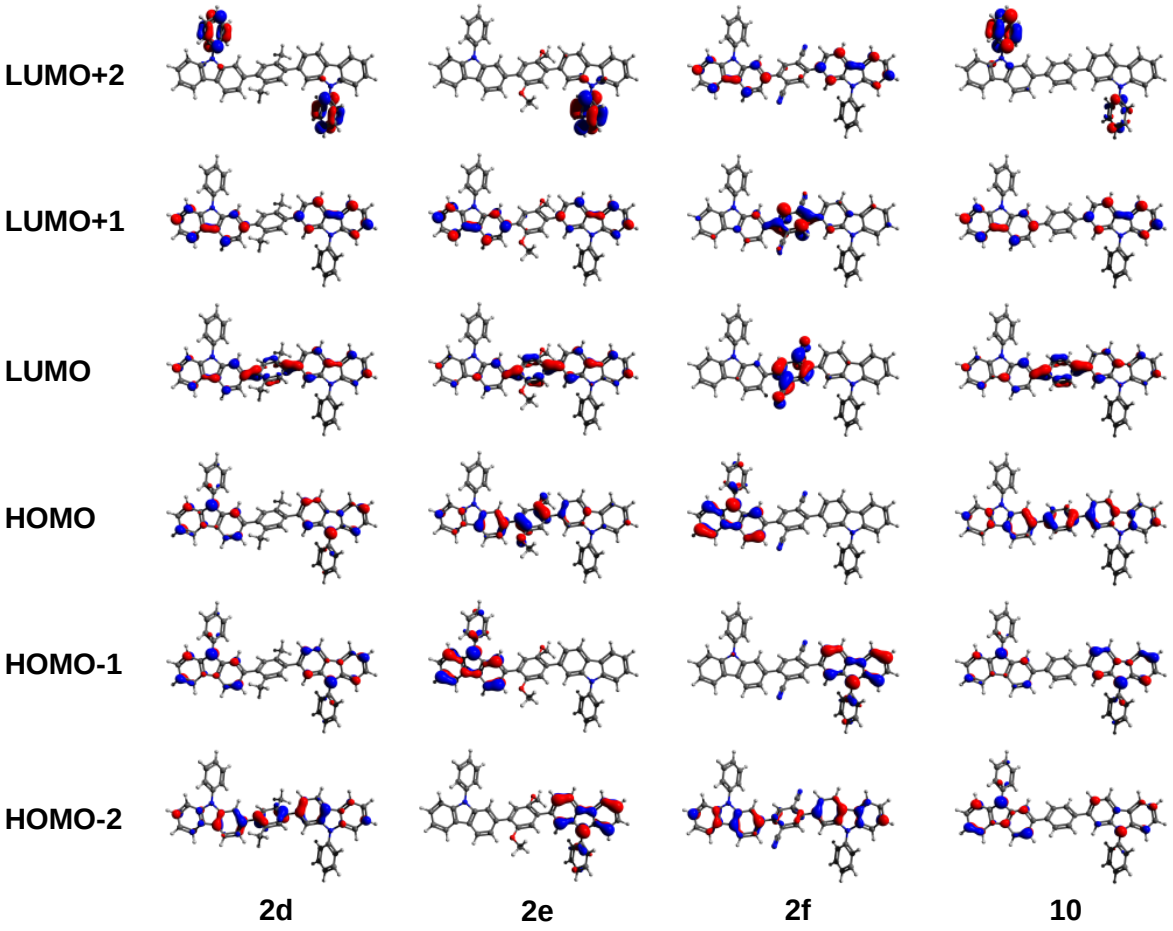


Figure S6 Frontier molecular orbital plots for the complete 3-substituted *N*-phenylcarbazolyl series **2d**−**f** and **10**.

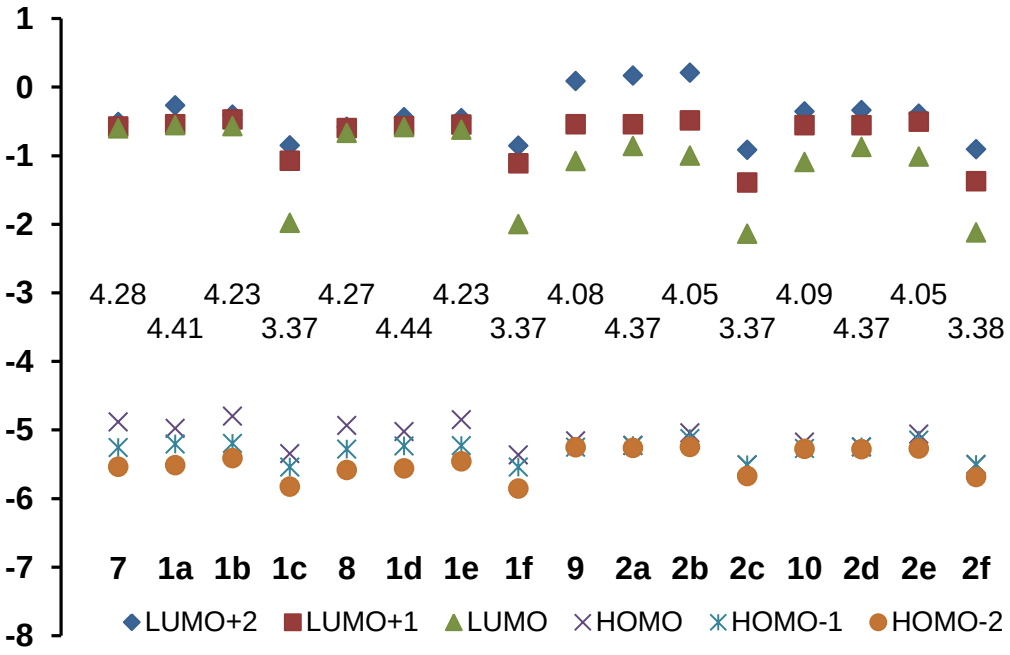


Figure S7 Calculated frontier orbital arrangements of compounds **1a-f** and **2a-f** highlighting the degeneracy in the LUMO manifold of series 1 and the HOMO manifold of series 2.

OLED Devices

Organic light emitting diode (OLED) devices were fabricated on cleaned indium tin oxide (ITO)-coated glass substrates of thickness 125 nm and possessing a sheet resistance of 20 Ω /square. Devices were prepared with the structure: ITO/ NBP (40 nm)/TAPC(10 nm)/18% FIrpic in CBP or in **2d** host(35 nm)/ TAZ(10 nm)/ TPBi(40 nm)/ LiF(0.8 nm)/ Al (100 nm) by thermal evaporation under a vacuum at a pressure of ca. $1x10^{-6}$ Torr. The emissive layer of FIrpic doped into CBP or **2d** was evaporated at a rate of < 1 Å/s, followed by 10 nm of TAZ as a hole blocking layer and 40 nm of TPBi as an electron injection and transport layer, then a deposition of a cathode which consist of a thin layer of 0.8 nm of LiF at a rate of < 0.1 Å/s, capped by a 100 nm layer of aluminium at a rate of 1 Å/s. All samples are encapsulated inside a glove box using DELO UV cured epoxy (KATIOBOND) and capped with 1.2x1.2 cm microscope glass slides then exposed to UV light for 3 min. NBP = *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine; TAPC = (1,1-bis{4-*N*,*N*-di(*p*-tolyl)amino]phenyl}cyclohexane); FIrpic = iridium(III) bis[4,6-(di-fluorophenyl)pyridinato-*N*,*C* 2′]picolinate; TAZ = 3-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-4*H*-1,2,4-triazole; TPBi = 2,2′,2″-(1,3,5-benzenetriyl)tris-[1-phenyl-1*H*-benzimidazole].

The current-voltage (*I*-*V*) characteristics and the devices' emission characteristics were measured using a calibrated integrating sphere and the data acquisition was controlled using a home-written NI LabView program which controlled an Agilent Technologies 6632B power supply. The electroluminescence (EL) spectra were measured using a calibrated Ocean Optics USB 4000 CCD spectrometer supplied with 400 µm UV/Vis fiber optic.

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