

Photochemical and oxidative cyclisation of tetraphenylpyrroles

Jayne L. Ferguson,^a Marie A. Squire^a and Christopher M. Fitchett^{a,b}

^a School of Physical and Chemical Sciences, University of Canterbury, Christchurch, New Zealand.

^b Email: chris.fitchett@canterbury.ac.nz.

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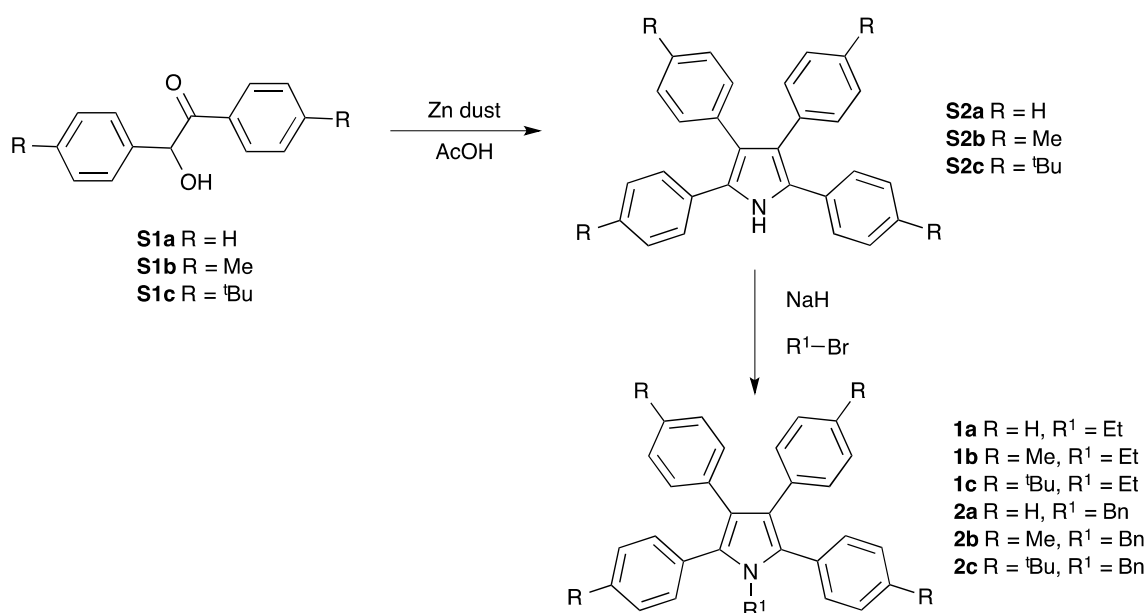
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Synthesis Details

Experimental Details

Unless specified all chemicals were reagent grade, purchased from suppliers and used as received. Water was purified by reverse osmosis in-house. Where anhydrous solvents were required, HPLC-grade solvent was either distilled from standard drying agents or dried by passing over a sealed column of activated alumina. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Except where otherwise specified, all reactions were carried out in air. All infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR instrument operating in diffuse reflectance mode with samples prepared as KBr mulls. The following abbreviations are used: s: strong, m: medium, w: weak, sh: shoulder, br: broad. All spectra were recorded on a Varian INOVA 500, Varian Unity 300, or an Agilent 400-MR instrument operating at 500, 300 and 400 MHz, respectively, for ^1H , and 125, 75 and 125 MHz, respectively, for ^{13}C . All samples were dissolved in commercially available deuterated solvents CDCl_3 and CD_3CN . Spectra were referenced to the residual solvent peaks and/or tetramethylsilane (TMS). ^1H - ^1H -COSY, HSQC and HMBC experiments were employed where required, using standard Varian and Agilent pulse sequences. Mass spectra were recorded on either a DIONEX Ultimate 3000 or Bruker MaXis 4G spectrometer, both of which were operated in high resolution positive ion electrospray mode. Samples were dissolved and diluted to the required concentration in HPLC grade acetonitrile or methanol. UV/Visible spectra were recorded on a Varian CARY UV/Visible spectrometer in the range 225 – 800 nm for dichloromethane and 200 – 800 nm for acetonitrile. Samples were measured at room temperature in quartz cuvettes of path length 1 cm and approximate capacity 3 mL. Emission spectra were recorded on a Horiba Fluorolog-3 spectrometer in the range 300 – 600 nm for dichloromethane. Samples were measured at room temperature in quartz cuvettes of path length 1 cm and approximate capacity 3 mL.

The following compounds were prepared according to literature methods, and all characterisation data were found to be consistent with that provided; 4,4'-dimethylbenzoin, **S1b**,¹ 4,4-di-tertbutylbenzoin, **S1c**,² NH-2,3,4,5-tetraphenylpyrrole, **S2a**,³ NH-2,3,4,5-tetra(4-methylphenyl)pyrrole, **S2b**, NH-2,3,4,5-tetra(4-tertbutylphenyl)pyrrole **S2c**,⁴ and N-ethyl-2,3,4,5-tetraphenylpyrrole, **1a**.⁵

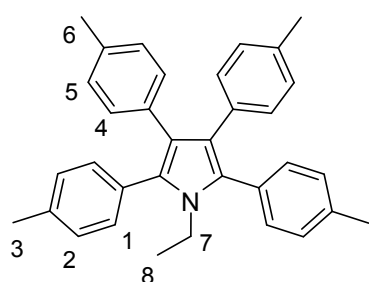


Scheme S1. Synthesis of N-Ethyl and N-Benzyl tetraphenylpyrroles (**1a-c** and **2a-c**).

General procedure for the synthesis of N-ethyl-2,3,4,5-tetraarylpyrroles, **1b** and **1c**, and N-benzyl-2,3,4,5-tetraarylpyrroles, **2a** – **2c**

Following a modified literature procedure:⁵ a round bottom flask was flushed with N₂ and the appropriate NH-2,3,4,5-tetraarylpyrrole was added followed by 25 mL dry dimethylformamide. The solution was cooled to 0 °C using an ice bath and sodium hydride was added. The solution was stirred at 0 °C for 10 minutes and then ethyl bromide or benzyl bromide was added and the solution stirred at room temperature overnight. The resulting solution was poured into 100 mL water and extracted with 3 x 75 mL ethyl acetate. The combined organic layers were washed with 3 x 200 mL water, dried with sodium sulfate and the solvent removed *in vacuo*. The solid obtained was recrystallised from ethyl acetate/hexanes.

Synthesis of N-ethyl-2,3,4,5-tetra(4-methylphenyl)pyrrole, **1b**

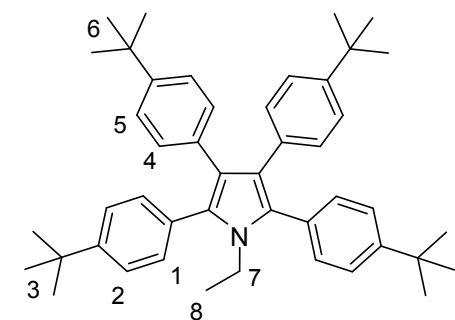


S2b (0.300 g, 0.702 mmol), sodium hydride (0.050 g, 2.1 mmol), ethyl bromide (0.095 g, 0.06 mL, 0.845 mmol). Yield: 0.220 g (69%). m.p. 161 – 165 °C; ¹H NMR (500MHz, CDCl₃): δ_H 7.21 (d, 4H, *J* = 8 Hz, H1), 7.12 (d, 4H, *J* = 8 Hz, H2), 6.82 (s, 8H, H4, H5), 3.84 (q, 2H, CH₂, *J* = 7 Hz, H7), 2.36 (s, 3H, CH₃, H3), 2.21 (s, 3H, CH₃, H6), 0.95 (t, 3H, CH₃, *J* = 7 Hz, H8); ¹³C NMR (125MHz, CDCl₃): δ_C 136.8, 134.0, 132.8, 131.3, 130.6, 130.4, 128.8, 128.1, 121.7, 39.3 C7, 21.3 C3, 21.1 C6, 16.7 C8; ESMS calc for C₃₄H₃₄N ([**1b** + H]⁺) = 456.2686, found 456.2693; IR (KBr)ν/cm⁻¹: 2973 m, br, 1522 s, 1498 s,

1338 m, 1114 m, 1021 s, 834 m, sh, 817 s, 741 m, 524 s; UV-Vis λ_{max} (ε): 256 nm (22312), 289 nm (14988); Emission λ_{max}: 392 nm.

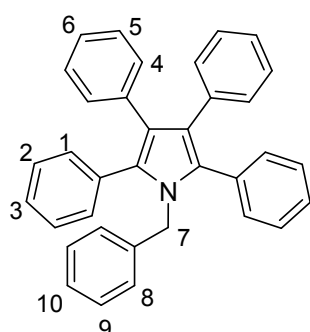
Synthesis of N-ethyl-2,3,4,5-tetra(4-*tert*butylphenyl)pyrrole, **1c**

S2c (0.340 g, 0.571 mmol), sodium hydride (0.04 g, 1.71 mmol), ethyl bromide (0.075 g, 0.05 mL, 0.685 mmol). Yield: 0.140 g (39%). m.p. 171 – 174 °C; ¹H NMR (500MHz, CDCl₃): δ_H 7.31 (d, 4H, *J* = 8 Hz, H1), 7.25 (d, 4H, *J* = 8 Hz, H2), 6.99 (d, 4H, *J* = 8 Hz, H4), 6.84 (d, 4H, *J* = 8 Hz, H5), 3.85



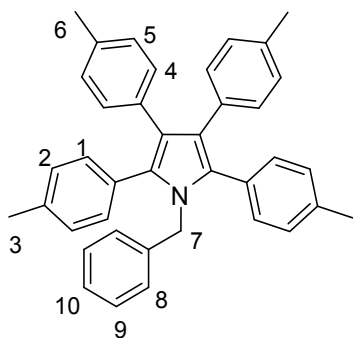
(q, 2H, CH₂, *J* = 7 Hz, H7), 1.32 (s, 9H, H3, H3', H3''), 1.22 (s, 9H, H6, H6', H6''), 0.94 (t, 3H, CH₃, *J* = 7 Hz, H8); ¹³C NMR (125MHz, CDCl₃): δ_C 171.2 C2a, C5a, 149.8 C1a, 147.1 C4a, 132.8, 131.1 C2, 130.7 C5, 130.5, 130.4, 124.8 C1, 124.0 C4, 121.9, 34.5 C7, 34.2 C3, 31.3 C6, 16.7 C8; ESMS calc for C₄₆H₅₇NNa ([**1c** + Na]⁺) = 646.4389, found 646.4381; IR (KBr)ν/cm⁻¹: 2961 s, br, 1739 w, 1462 m, 1362 m, 1269 m, 836 s, 569 m; UV-Vis λ_{max} (ε): 255 nm (24323), 287 nm (17437); Emission λ_{max}: 393 nm.

Synthesis of N-benzyl-2,3,4,5-tetraphenylpyrrole, **2a**



S2a (1.60 g, 4.17 mmol), sodium hydride (0.30 g, 12.51 mmol), benzyl bromide (0.86 g, 0.60 mL, 5.01 mmol). Yield: 1.30 g (68%). m.p. 186 – 188 °C; ¹H NMR (500MHz, CDCl₃): δ_H 7.20 – 7.13 (m, 15H), 7.04 (d, 4H, *J* = 7 Hz), 6.98 (d, 4H, *J* = 7 Hz), 6.76 (d, 2H, *J* = 7 Hz), 5.08 (s, 2H, CH₂, H7); ¹³C NMR (125MHz, CDCl₃): δ_C 139.2, 135.6, 132.8, 131.9, 131.5, 130.9, 128.2, 128.0, 127.9, 127.4, 127.3, 126.7, 126.0, 125.1, 122.6, 48.2 C7; ESMS calc for C₃₅H₂₈N ([**2a** + H]⁺) = 462.2216, found 462.2225; IR (KBr)ν/cm⁻¹: 3063 w, 3030 w, 1601 m, 1501 m, 1337 m, 1073 w, 1028 w, 757 m, 739 m, 703 s; UV-Vis λ_{max} (ε): 251 nm (27416), 291 nm (16018); Emission λ_{max}: 392 nm.

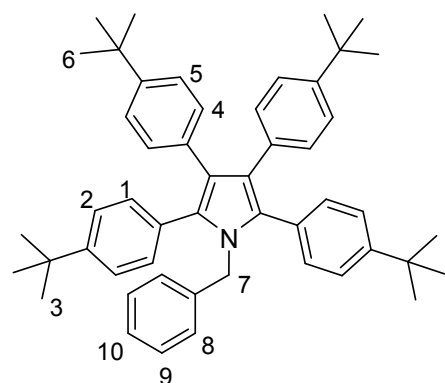
Synthesis of N-benzyl-2,3,4,5-tetra(4-methylphenyl)pyrrole, **2b**



S2b (1.40 g, 3.28 mmol), sodium hydride (0.25 g, 9.82 mmol), benzyl bromide (0.68 g, 0.45 mL, 3.94 mmol). Yield: 1.30 g (75%). m.p. 213 – 217 °C; $^1\text{H NMR}$ (500MHz, CDCl_3): δ_{H} 7.14 (d, 2H, $J = 7.5$ Hz, H8), 7.04 (d, 4H, $J = 7.5$ Hz, H1), 6.98 (d, 4H, $J = 7.5$ Hz, H2), 6.85 (s, 9 H), 6.74 (d, 2H, $J = 7$ Hz), 5.02 (s, 2H, CH_2 , H7), 2.27 (s, 3H, CH_3 , H3), 2.22 (s, 3H, CH_3 , H6); $^{13}\text{C NMR}$ (125MHz, CDCl_3): δ_{C} 139.5, 136.8, 134.1, 132.8, 131.6, 131.4, 130.6, 130.0, 128.7, 128.1, 128.0, 126.5, 126.0, 122.2, 48.0 C7, 21.2 C3, 21.1 C6; ESMS calc for $\text{C}_{39}\text{H}_{36}\text{N}$ ($[\mathbf{2b} + \text{H}]^+$) = 518.2842, found 518.2852; IR (KBr) ν/cm^{-1} : 3027 w, sh, 2917 w, 1520 s, 1494 s, 1454 s, 1351 s, 1113 m, 836 s, 824 s,

734 m, 525 m; UV-Vis λ_{max} (ϵ): 253 nm (25573), 284 nm (16291); Emission λ_{max} : 396 nm.

Synthesis of N-benzyl-2,3,4,5-tetra(4-tertbutylphenyl)pyrrole, **2c**

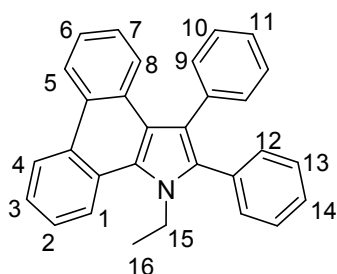


S3c (0.80 g, 1.34 mmol), sodium hydride (0.10 g, 4.02 mmol), benzyl bromide (0.27 g, 0.2 mL, 1.61 mmol). Yield: 0.40 g (43%). m.p. 277 – 282 °C; $^1\text{H NMR}$ (500MHz, CDCl_3): δ_{H} 7.18 (d, 4H, $J = 8.5$ Hz, H8), 7.11 – 7.09 (m, 7H), 7.02 (d, 4H, $J = 8.5$ Hz, H4), 6.90 (d, 4H, $J = 8.5$ Hz, H5), 6.69 – 6.67 (m, 2H), 5.00 (s, 2H, CH_2 , H7), 1.27 (s, 9H, CH_3 , H3), 1.23 (s, 9H, CH_3 , H6); $^{13}\text{C NMR}$ (125MHz, CDCl_3): δ_{C} 149.8, 127.3, 139.6, 132.8, 131.7, 131.2, 130.4, 130.1, 127.9, 126.4, 126.2, 124.7, 124.0, 122.3, 48.3 C7, 34.6, 34.2, 31.4 C3, 31.3 C6; ESMS calc for $\text{C}_{51}\text{H}_{60}\text{N}$ ($[\mathbf{2c} + \text{H}]^+$) = 686.4720, found 686.4743; IR (KBr) ν/cm^{-1} : 2965 s, 2902 w, sh, 2867 w, sh, 1495 w, 1362 m, 1268 w, 1130 w, 1019 w, 837 m, 820 w, 564 w; UV-Vis λ_{max} (ϵ): 253 nm (26405), 289 nm (17660); Emission λ_{max} : 399 nm.

General procedure for the photocyclisation reactions

In an oven dry quartz tube flushed with argon, 400 mL of dry toluene was added followed by sparging with argon for 5 minutes. The appropriate N-substituted-2,3,4,5-tetraarylpyrrole was added, along with I_2 and propylene oxide. The solution was sparged with argon for 15 minutes and then irradiated with 300 nm light in a Rayonet photoreactor overnight with argon bubbling through the solution continuously. The solution was then washed with 200 mL $\text{Na}_2\text{S}_2\text{O}_3$ solution and 100 mL water, dried over MgSO_4 and the solvent removed *in vacuo*. The residue was purified by flash column chromatography.

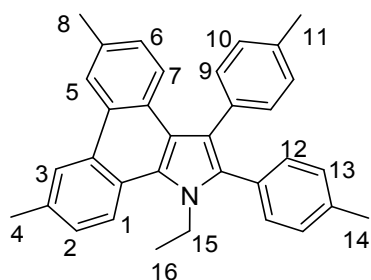
Synthesis of N-ethyl-2,3-diphenyl-dibenzo[e,g]indole, **3a**



1a (0.150 g, 0.375 mmol), I_2 (0.310 g, 1.24 mmol), propylene oxide (2 mL), purification with flash column chromatography (SiO_2 , 3:2 hexanes:dichloromethane). Yield: 0.110 g (73%). m.p. 174 – 175 °C; $^1\text{H NMR}$ (400MHz, CDCl_3): δ_{H} 8.82 (d, 1H, $J = 8.8$ Hz, H4), 8.68 (d, 1H, $J = 8.8$ Hz, H5), 8.45 (d, 1H, $J = 8.8$ Hz, H1), 7.78 (d, 1H, $J = 8.4$ Hz, H8), 7.66 (t, 1H, $J = 7.2$ Hz, H2), 7.58 (t, 1H, $J = 7.2$ Hz, H3), 7.43 (t, 1H, $J = 7.2$ Hz, H7), 7.36 – 7.22 (m, 11H, H6, H9, H10, H11, H12, H13, H14), 4.55 (q, 2H, CH_2 , $J = 7.2$ Hz, H15), 1.47 (t, 3H, CH_3 , $J = 7.2$ Hz, H16); $^{13}\text{C NMR}$ (125MHz, CDCl_3): δ_{C} 137.4 C1aa, 132.4,

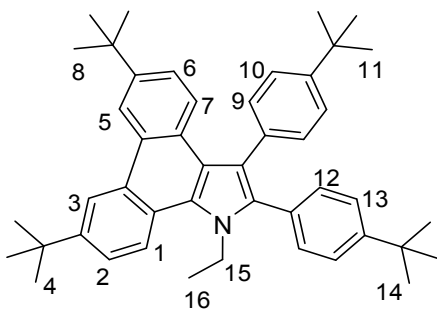
131.6, 131.5, 129.3, 128.1, 128.0, 127.8, 126.5 C2, 126.4, 126.1 C12aa, 124.3, 124.2 C4, 124.1 C8, 123.9 C3, 123.8 C7, 123.2 C5, 121.4 C1, 41.9 C15, 16.2 C16; ESMS calc for $\text{C}_{30}\text{H}_{24}\text{N}$ ($[\mathbf{3a} + \text{H}]^+$) = 398.1903, found 398.1905; IR (KBr) ν/cm^{-1} : 3056 w, 2991 w, 1608 m, 1516 m, 1442 m, 1354 m, 1171 w, 1069 w, 1028 m, 750 s, 725 s, 705 s; UV-Vis λ_{max} (ϵ): 267 nm (65681), 296 nm (28569), 319 nm (16423), 365 nm (2655); Emission λ_{max} : 394 nm.

Synthesis of N-ethyl-2,3-di(4-methylphenyl)-6,9-dimethyl-dibenzo[e,g]indole, **3b**



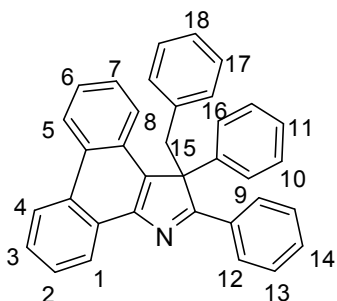
1b (0.150 g, 0.329 mmol), I₂ (0.270 g, 1.09 mmol), propylene oxide (1.5 mL), purification with flash column chromatography (SiO₂, 3:2 hexanes:dichloromethane). Crystals suitable for X-ray crystallography were obtained by diffusion of methanol into a benzene solution of **3b**. Yield: 0.110 g (71%). m.p. 168 – 170 °C; ¹H NMR (400MHz, CDCl₃): δ_H 8.59 (s, 1H, H3), 8.45 (s, 1H, H5), 8.30 (d, 1H, J = 8.4 Hz, H1), 7.66 (d, 1H, J = 8 Hz, H7), 7.45 (d, 1H, J = 9.2 Hz, H2), 7.23 – 7.19 (m, 4H), 7.13 – 7.07 (m, 5H), 4.49 (q, 2H, CH₂, J = 7.2 Hz, H15), 2.63 (s, 3H, CH₃, H4), 2.52 (s, 3H, CH₃, H8), 2.35 (s, 6H, CH₃, H11, H14), 1.43 (t, 3H, CH₃, J = 7.2 Hz, H16); ¹³C NMR (125MHz, CDCl₃): δ_C 137.5, 137.3 C13a, 135.6 C10a, 134.4, 133.0 C2a, 132.7 C6a, 131.5, 131.3, 129.6, 129.1, 128.8 C2, 128.7, 127.8, 127.5, 127.4, 126.9, 126.8, 124.1 C3, 123.9 C7, 123.0 C5, 122.2, 121.3 C1, 119.2, 118.8, 41.7 C15, 21.8 C11, 21.7 C14, 21.3 C8, C4, 16.2 C16; ESMS calc for C₃₄H₃₂N ([**3b** + H]⁺) = 454.2529, found 454.2521; IR (KBr)v/cm⁻¹: 2916 s, br, 1908 w, 1527 s, 1453 s, 1373 m, 1351 m, 1024 m, 821 s, 804 s, 745 m, 548 m; UV-Vis λ_{max} (ε): 268 nm (61052), 301 nm (27660), 323 nm (14852), 374 nm (3140); Emission λ_{max}: 394 nm, 405 nm.

Synthesis of N-ethyl-2,3-di(4-tertbutylphenyl)-6,9-ditertbutyl-dibenzo[e,g]indole, **3c**



1c (0.06 g, 0.0962 mmol), I₂ (0.081 g, 0.317 mmol), propylene oxide (1 mL), purification with flash column chromatography (SiO₂, 3:2 hexanes:dichloromethane). Yield: 0.040 g (69%). m.p. 230 – 232 °C; ¹H NMR (400MHz, CDCl₃): δ_H 8.82 (s, 1H, H3), 8.68 (s, 1H, H5), 8.37 (d, 1H, J = 8.4 Hz, H1), 7.74 (d, 1H, J = 8.4 Hz, H7), 7.71 (d, 1H, J = 8.4 Hz, H2), 7.34 – 7.21 (m, 9H), 4.52 (q, CH₂, J = 7 Hz, H15), 1.57 (s, 9H, CH₃, %4), 1.52 (s, 9H, CH₃, H8), 1.44 (s, 18H, CH₃, H11, H14), 1.34 (t, 3H, CH₃, J = 7 Hz, H16); ¹³C NMR (125MHz, CDCl₃): δ_C 150.3 C2, 148.9 C6, 145.9 C13, 145.7 C10, 137.7, 134.5, 131.3, 131.1, 129.6, 129.1, 127.3, 127.1, 126.9, 124.7, 124.6, 124.2, 124.1, 123.8, 122.3 C7, 121.1 C1, 119.8 C3, 119.4 C5, 119.0, 118.7, 41.7 C15, 34.9, 34.8, 34.6, 34.6, 31.5 C4, 31.4, C8, 31.3 C11, C14, 16.3 C16; ESMS calc for C₄₆H₅₆N ([**3c** + H]⁺) = 622.4407, found 622.4421; IR (KBr)v/cm⁻¹: 2961 s, 2903 m, sh, 2868 m, sh, 1461 m, 1362 s, 1266 m, 1022 w, 850 w, 600 w; UV-Vis λ_{max} (ε): 269 nm (64653), 298 nm (30069), 324 nm (16262), 371 nm (3291); Emission λ_{max}: 390 nm, 400 nm.

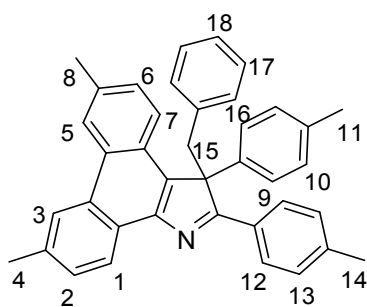
Synthesis of 3-benzyl-2,3-diphenyl-dibenzo[e,g]indole, **4a**



2a (0.150 g, 0.325 mmol), I₂ (0.270 g, 1.07 mmol), propylene oxide (1.5 mL), purification with flash column chromatography (SiO₂, 3:2 hexanes:dichloromethane). Yield: 0.005 g (4%). m.p. 218 – 220 °C; ¹H NMR (500MHz, CDCl₃): δ_H 8.78 (d, 1H, J = 8 Hz, H4), 8.72 (m 2H, H5), 7.93 (d, 2H, 7 Hz), 7.89 (d, 1H, 7.6 Hz, H1), 7.68 (m, 2H, H6), 7.60 (t, 1H, J = 6.8 Hz, H3), 7.52 (t, 1H, J = 7.6 Hz, H2), 7.45 – 7.27 (m, 10H), 6.81 (t, 1H, J = 7.6 Hz, H18), 6.63 (t, 2H, J = 7.6 Hz, H17), 6.11 (d, 2H, J = 7.6 Hz, H16), 4.32 (d, 1H, J = 12.4 Hz, H15), 4.05 (d, 1H, J = 12.4 Hz, H15); ¹³C NMR (125MHz, CDCl₃): δ_C 145.9, 131.8, 131.5, 129.5, 128.9, 128.7, 128.6 C16, 127.1, 127.0 C2, 126.9 C17, 126.8 C18, 126.6, 125.6 C3, 124.9 C4, 124.0, 123.4 C1, 122.7 C5, 67.8 C15a, 40.7 C15; ESMS calc for C₃₅H₂₆N ([**4a** + H]⁺) = 460.2060, found 460.2070; IR (KBr)v/cm⁻¹: 3060 w, 3028 w, 1524 m, 1493 m, 1443 m, 1315 w, 1027 w, 753 s, 725 m, 702 s, 526 m; UV-Vis λ_{max} (ε): 258 nm (40432), 291 nm (23671), 301 nm (17474), 364 nm (13590); Emission λ_{max}: 453 nm.

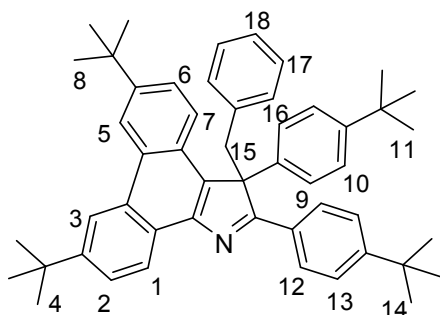
Synthesis of 3-benzyl-2,3-di(4-methylphenyl)-6,9-dimethyl-dibenzo[e,g]indole, **4b**

2b (0.150 g, 0.290 mmol), I₂ (0.150 g, 0.608 mmol), propylene oxide (1.5 mL), purification with flash column chromatography (SiO₂, 3:2 hexanes:dichloromethane). Crystals suitable for X-ray crystallography were obtained by diffusion of methanol into a benzene solution of **4b**. Yield: 0.007 g (5%). m.p. 274 – 276 °C; ¹H NMR (400MHz, CDCl₃): δ_H 8.54 (s, 1H, H3), 8.49 (s, 1H, H5), 7.85 (d, 2H, J = 7.6 Hz, H12), 7.78 (d, 1H, J = 8.4 Hz, H1), 7.49 (d, 1H, J = 7.6 Hz, H7), 7.33 (d, 1H, J = 7.6 Hz, H2); 7.27 (m, 2H, H9), 7.20 (d, 2H, J = 7.6 Hz, H13), 7.12 (m, 3H, H6, H10), 6.80 (t, 1H, J = 7.2 Hz, H18), 6.63 (t, 2H, J = 7.2 Hz, H17), 6.13 (d, 2H, J = 7.2 Hz, H16), 4.27 (d, 1H, J = 12.8 Hz, H15), 4.00 (d, 1H, J = 12.8 Hz, H15), 2.64 (s, 3H, CH₃), 2.60 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.30 (s, 3H, CH₃); ¹³C NMR (125MHz, CDCl₃): δ_C 148.6 C4a, 140.5 C14a, 136.7, 136.6, 136.0, 135.9, 134.9, 134.6, 131.3, 131.0, 130.0, 129.6 C11, 129.3, 129.0 C16, 128.5 C2, 128.3 C12, 128.2 C7, 126.9 C17, 126.3 C18, 126.0, 124.9, 124.6, 123.7, 123.1 C1, 122.5 C5, 68.1 C15a, 40.7 C15, 22.3 C4, 22.1 C8, 21.6 C14, 21.1 C11; ESMS calc for C₃₉H₃₄N ([**4b** + H]⁺) = 516.2686, found 516.2694; IR (KBr)ν/cm⁻¹: 3032 w, 2918 m, br, 1608 w, 1509 s, 1311 w, 1183 m, 1021 w, 819 s, 809 m, sh, 763 w, 739 w, 701 s, 524 s; UV-Vis λ_{max} (ε): 262 nm (30986), 281 nm (24451), 294 nm (19158), 306 nm (13655), 375 nm (9741); Emission λ_{max}: 463 nm.



Synthesis of 3-benzyl-2,3-di(4-tertbutylphenyl)-6,9-ditertbutyl-dibenzo[e,g]indole, **4c**

2c (0.150 g, 0.219 mmol), I₂ (0.190 g, 0.722 mmol), propylene oxide (1.5 mL), purification with flash column chromatography (SiO₂, 7:3 hexanes:dichloromethane). Yield: 0.006 g (4%). m.p. 251 – 252 °C; ¹H NMR (400MHz, CD₂Cl₂): δ_H 8.79 (s, 1H, H3), 8.74 (s, 1H, H5), 8.61 (d, 1H, J = 8.8 Hz, H7), 7.89 (d, 3H, J = 8.4 Hz, H1, H12), 7.78 (d, 1H, J = 8.8 Hz, H6), 7.64 (d, 1H, J = 7.6 Hz, H2), 7.44 (d, 2H, J = 8.8 Hz, H13), 7.36 (d, 2H, J = 8 Hz, H9), 7.31 (m, br, 2H, H10), 6.83 (t, 1H, J = 7.6 Hz, H18), 6.60 (t, 2H, J = 7.6 Hz, H17), 6.19 (d, 2H, J = 7.6 Hz, H16), 4.35 (d, 1H, J = 12.4 Hz, H15), 4.08 (d, 1H, J = 12.4 Hz, H15), 1.47 (s, 9H, CH₃, H4), 1.45 (s, 9H, CH₃, H8), 1.31 (s, 9H, CH₃, H14), 1.23 (s, 9H, CH₃, H11); ¹³C NMR (125MHz, CD₂Cl₂): δ_C 135.8, 135.5, 129.0, 128.1, 126.9, 126.2, 125.8, 125.5, 125.2, 125.0, 124.1, 123.0, 119.6, 118.3, 67.4 C15a, 40.5 C15, 31.2 C4, 31.1 C8, 30.9 C14, 30.8, C11; ESMS calc for C₅₁H₅₈N ([**5c** + H]⁺) = 684.4564, found 684.4583; IR (KBr)ν/cm⁻¹: 2961 s, 2905 m, sh, 2868 m, sh, 1606 w, 1507 m, 1363 m, 1264 m, 111 w, 1017 w, 838 m, 700 m; UV-Vis λ_{max} (ε): 262 nm (43251), 279 nm (34494), 295 nm (28320), 307 nm (19733), 375 nm (15564); Emission λ_{max}: 461 nm.



General procedure for oxidative cyclodehydrogenation using FeCl₃ dissolved in nitromethane

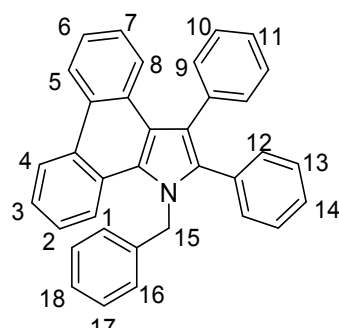
In an oven dry schlenk tube cooled under vacuum and backfilled with argon was added iron (III) chloride and placed back under vacuum for 15 minutes. In an oven dry three-necked round bottom flask cooled whilst flushing with argon was added the appropriate N-substituted-2,3,4,5-tetraarylpyrrole (~ 0.150 g), and the solid was flushed with argon for five minutes. 150 mL dry dichloromethane was added and the solution was stirred with argon bubbling through for five minutes. The schlenk tube was refilled with argon and the iron (III) chloride was dissolved in nitromethane. The nitromethane solution was added dropwise to the dichloromethane solution and the solution was stirred with argon bubbling through for six hours, then the bubbling argon was removed and the solution was stirred under argon overnight. The reaction was quenched with 100 mL methanol and then 100 mL water was added. The layers were separated and the organic layer was washed with 50mL of water, dried with MgSO₄ and the solvent removed *in vacuo*. Purification by flash

column chromatography was attempted usually using SiO₂, 9:1 hexanes : ethyl acetate or SiO₂ 4:1 hexanes:ethyl acetate.

General procedure for oxidative cyclodehydrogenation using FeCl₃ added to the reaction as a solid

In an oven dry schlenk tube cooled under vacuum and backfilled with argon was added iron (III) chloride and placed back under vacuum for 15 minutes. To an oven dried three-necked round bottom flask cooled whilst flushing with argon was added the appropriate N-substituted-2,3,4,5-tetraarylpyrrole, and the solid was flushed with argon for five minutes. 150 mL dry dichloromethane was added and the solution was stirred with argon bubbling through for five minutes. The schlenk tube was refilled with argon and the solid iron (III) chloride was added in one go to the dichloromethane solution. The solution was stirred with argon bubbling through for six hours, then the bubbling argon was removed and the solution was stirred under argon overnight. The reaction was quenched with 100 mL methanol and then 100 mL water was added. The layers were separated and the organic layer was washed with 50 mL of water, dried with MgSO₄ and the solvent removed *in vacuo*. Purification by flash column chromatography was attempted usually using SiO₂, 9:1 hexanes:ethyl acetate or SiO₂, 4:1 hexanes:ethyl acetate.

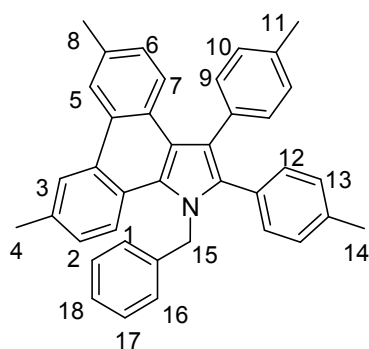
Synthesis of N-benzyl-2,3-diphenyl-dibenzo[e,g]indole, **5a**



2a (0.150 g, 0.325 mmol), iron (III) chloride (0.81 g, 4.87 mmol), purification with flash column chromatography (SiO₂, 9:1 hexanes:ethyl acetate). Crystals suitable for X-ray crystallography were obtained by diffusion of methanol into a benzene solution of **5a**. Yield: 0.045 g (30%). m.p. 243 – 244 °C; ¹H NMR (400MHz, CDCl₃): δ_H 8.77 (d, 1H, *J* = 8.4 Hz, H4), 8.68 (d, 1H, *J* = 8.8 Hz, H5), 8.15 (d, 1H, *J* = 8.4 Hz, H1), 7.84 (d, 1H, *J* = 8.8 Hz, H8), 7.48 – 7.27 (m, 17H, H3, H2, H6, H7), 7.13 (d, 2H, *J* = 8 Hz, H9), 5.73 (s, 2H, CH₂, H15); ¹³C NMR (125MHz, CDCl₃): δ_C 138.8, 138.6, 137.3, 131.7, 131.6, 131.4, 129.3, 128.9, 128.8, 128.2, 127.9, 127.8, 127.6, 127.2, 126.6, 126.3,

126.2, 125.8, 124.2 C8, 124.0, 123.9, 123.8 C4, 123.2 C5, 121.8 C1, 119.7, 119.6, 51.1 C15; ESMS calc for C₃₅H₂₆N ([**5a** + H]⁺) = 460.2060, found 460.2056; IR (KBr)ν/cm⁻¹: 3056 w, br, 1608 m, 1512 m, 1441 m, 1357 m, 1031 m, 761 s, 728 s, 701 s; UV-Vis λ_{max} (ε): 267 nm (62766), 294 nm (28055), 318 nm (17661), 365 nm (3071); Emission λ_{max}: 394 nm.

Synthesis of N-benzyl-2,3-di(4-methylphenyl)-6,9-dimethyl-dibenzo[e,g]indole, **5b**

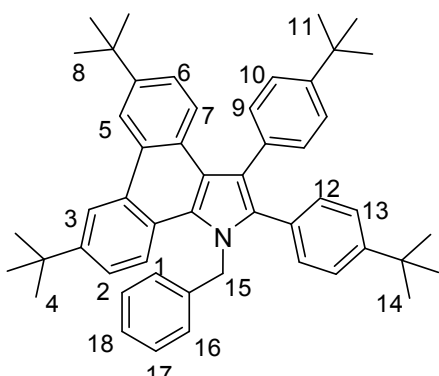


2b (0.150 g, 0.290 mmol), iron (III) chloride (0.71 g, 4.35 mmol), purification with flash column chromatography (SiO₂, 9:1 hexanes:ethyl acetate). Crystals suitable for X-ray crystallography were obtained by diffusion of methanol into a benzene solution of **5b**. Yield: 0.057 g (38%). m.p. 256 – 257 °C; ¹H NMR (400MHz, CDCl₃): δ_H 8.53 (s, 1H, H3), 8.45 (s, 1H, H5), 7.99 (d, 1H, *J* = 7.2 Hz, H1), 7.71 (d, 1H, *J* = 7.2 Hz, H7), 7.30 – 7.25 (m, 4H), 7.23 (d, 1H, *J* = 7.2 Hz, H2), 7.17 (d, 1H, *J* = 7.2 Hz, H6), 7.14 – 7.10 (m, 5H), 7.05 (d, 2H, *J* = 6.4 Hz, H9), 6.96 (d, 2H, *J* = 6.4 Hz, H10), 5.67 (s, 2H, CH₂, H15), 2.53 (s, 6H, CH₃, H4, H8), 2.39 (s, 3H, CH₃, H14), 2.27 (s, 3H, CH₃, H11); ¹³C NMR (125MHz, CDCl₃): δ_C 138.9, 138.2, 137.3, 135.8, 134.4,

133.1, 132.9, 131.4, 131.2 C9, 129.2, 129.0, 128.9 C2, 128.6 C10, 127.8, 127.6 C2, 127.5, 127.0, 126.9, 125.8, 124.1 C7, 123.8 C3, 123.0 C5, 121.7 C1, 119.0, 51.3 C15, 21.8 C4, 21.7 C8, 21.3 C14, 21.2 C11; ESMS calc for C₃₉H₃₄N ([**5b** + H]⁺) = 516.2686, found 516.2684; IR (KBr)ν/cm⁻¹: 2914 w, br, 1525 s, 1496 m, 1453 s, 1355 s,

1033 w, 1024 w, 955 w, 821 s, 806 m, 749 s, 732 s, 547 m; UV-Vis λ_{\max} (ϵ): 269 nm (64982), 299 nm (30645), 322 nm (17828), 373 nm (3551); Emission λ_{\max} : 393nm, 403 nm.

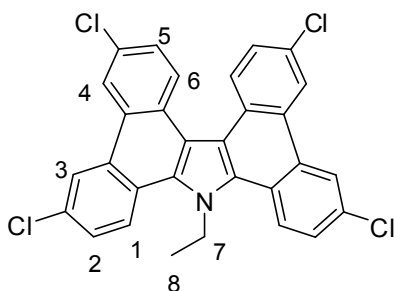
Synthesis of N-benzyl-2,3-di(4-*tert*butylphenyl)-6,9-ditertbutyl-dibenzo[*e,g*]indole, **5c**



2c (0.150 g, 0.219 mmol), iron (III) chloride(0.53 g, 3.28 mmol), purification with flash column chromatography (SiO_2 , 9:1 hexanes:ethyl acetate). Crystals suitable for X-ray crystallography were obtained by diffusion of methanol into a benzene solution of **5c**. Yield: 0.038 g (25%). m.p. 294 – 295 °C; ^1H NMR (400MHz, CDCl_3): δ_{H} 8.75 (s, 1H, H3), 8.66 (s, 1H, H5), 8.04 (d, 1H, $J = 7.2$ Hz, H1), 7.79 (d, 1H, 6.8 Hz, H7), 7.40 (d, 1H, $J = 7.2$ Hz, H2), 7.35 – 7.24 (m, 8H), 7.13 (s, br, 4H, H9), 7.05 (d, 2H, $J = 6.4$ Hz, H10), 5.71 (s, 2H, CH_2 , H15), 1.45 (s, 18H, CH_3 , H4, H8), 1.36 (s, 9H, CH_3 , H14), 1.24 (s, 9H, CH_3 , H11); ^{13}C NMR (125MHz, CDCl_3): δ_{C} 150.24, 149.0, 145.9, 139.2, 138.3, 134.4, 131.2, 130.9 C10, 129.1, 128.9, 128.8, 127.9, 127.4, 127.0, 125.9,

124.8, 124.6, 124.1 C2, 123.9 C7, 121.6 C1, 119.5 C3, 119.4, 118.8 C5, 51.0 C15, 34.9, 34.8, 34.5, 34.5, 31.5 C4, 31.4 C8, 31.3 C14, 31.2 C11; ESMS calc for $\text{C}_{51}\text{H}_{58}\text{N}$ ($[\mathbf{5c} + \text{H}]^+$) = 684.4564, found 684.4580; IR (KBr) ν/cm^{-1} : 2961 s, 2903 w, sh, 2867 w, sh, 1456 w, 1361 m, 1265 w, 1025 w, 839 w, 599 w; UV-Vis λ_{\max} (ϵ): 269 nm (62144), 296 nm (29750), 323 nm (17470), 369 nm (3472); Emission λ_{\max} : 389 nm, 399 nm.

Synthesis of 3,6,12,15-tetrachloro-9-ethyl-tetrabenzo[*a,c,g,i*]carbazole, **6**



1a (0.180 g, 0.450 mmol), FeCl_3 (3.37 g, 20.61 mmol), upon attempting to dissolve in dichloromethane to purify by column chromatography a solid formed. This solid was filtered, and washed with a small amount of dichloromethane to give **7**. Yield: 0.044 g (18%). m.p. °C 306 – 307 ; ^1H NMR (500MHz, CDCl_3): δ_{H} 8.69(d, 1H, $J = 9$ Hz, H1), 8.67 (s, 2H, H3), 8.57 (s, 2H, H4), 8.42 (d, 2H, $J = 9$ Hz, H6), 7.68 (d, 2H, $J = 9$ Hz, H5), 7.53 (d, 2H, $J = 9$ Hz, H2), 5.15 (q, 2H, CH_2 , $J = 7$ Hz, H7), 1.69 (t, 3H, CH_3 , $J = 7$ Hz, H8); ^{13}C NMR (125MHz, CDCl_3): δ_{C} 135.3, 132.0, 131.4, 131.0, 128.6,

127.9, 127.1, 127.0, 126.9, 124.4, 123.9, 123.8, 117.3, 45.2 C7, 16.1 C8; ESMS calc for $\text{C}_{30}\text{H}_{17}\text{Cl}_4\text{N}$ ($[\mathbf{6} + \text{K}]^+$) = 571.9723, found 571.9791; IR (KBr) ν/cm^{-1} : 2975 w, 2925 w, 1566 s, 1518 m, 1433 s, 1350 m, 1131 m, 1100 m, 1027 m, 953 m, 875 s, 802 s, 697 w, 541 w.

UV-vis Absorbtion and Emmision Spectroscopy

The normalised UV-vis absorption and emission spectra for **1a – 1c**, **2a – 2c**, **3a – 3c**, **4a – 4c** and **5a – 5c** are shown below. There is a clear difference the absorption and emission spectra between the precursor compounds and partially fused products. Fine structure and some vibronic coupling can be seen in the absorption spectra of the cyclodehydrogenated and photocyclised compounds, **3a – 3c**, **4a – 4c** and **5a – 5c**, as a result of rigidity being introduced to the system through the formation of a carbon-carbon bond. The formation of a carbon-carbon bond increasing the π -conjugation results in a red shift of the λ_{max} in the absorption spectra. The shape of the absorption spectra remain consistent for each type of compound and the spectra are not affected by peripheral substitution of the aryl rings or substitution on the nitrogen atom. The substitution on the peripheral aryl rings are only weakly electron donating

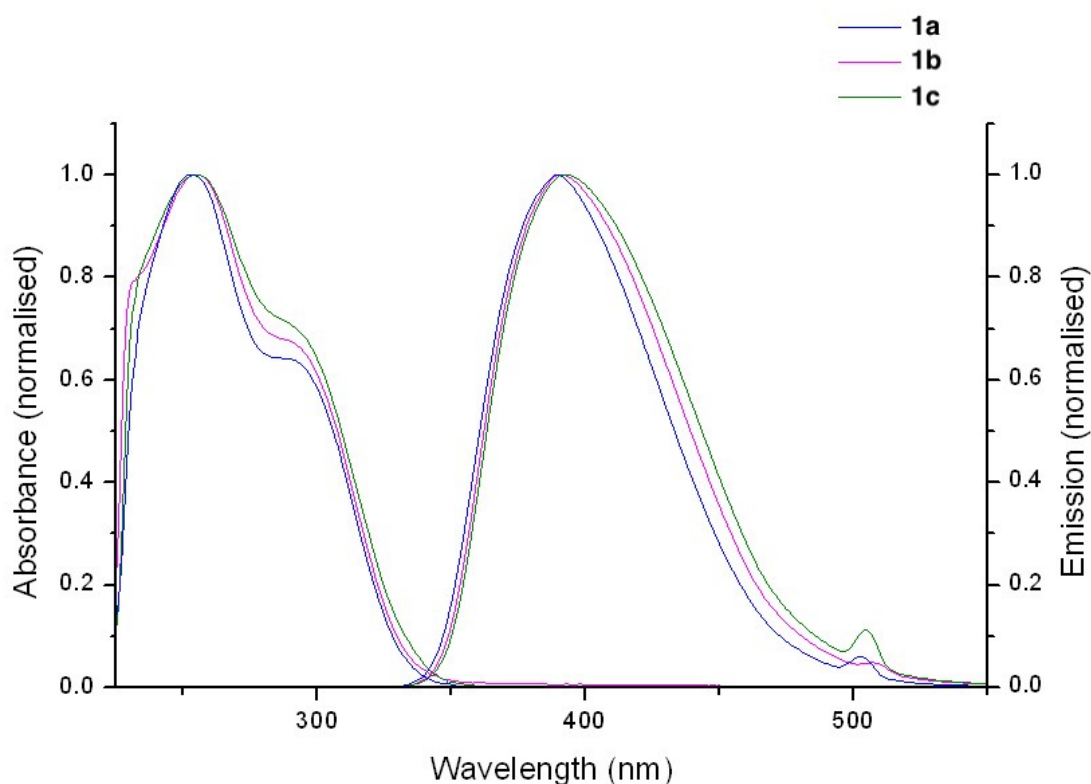


Figure S1. Normalized UV/visible and photoluminescence spectra of **1a**, **1b** and **1c**, all measured in deoxygenated dichloromethane at room temperature, concentrations $\sim 10^{-6}$ mol.L $^{-1}$.

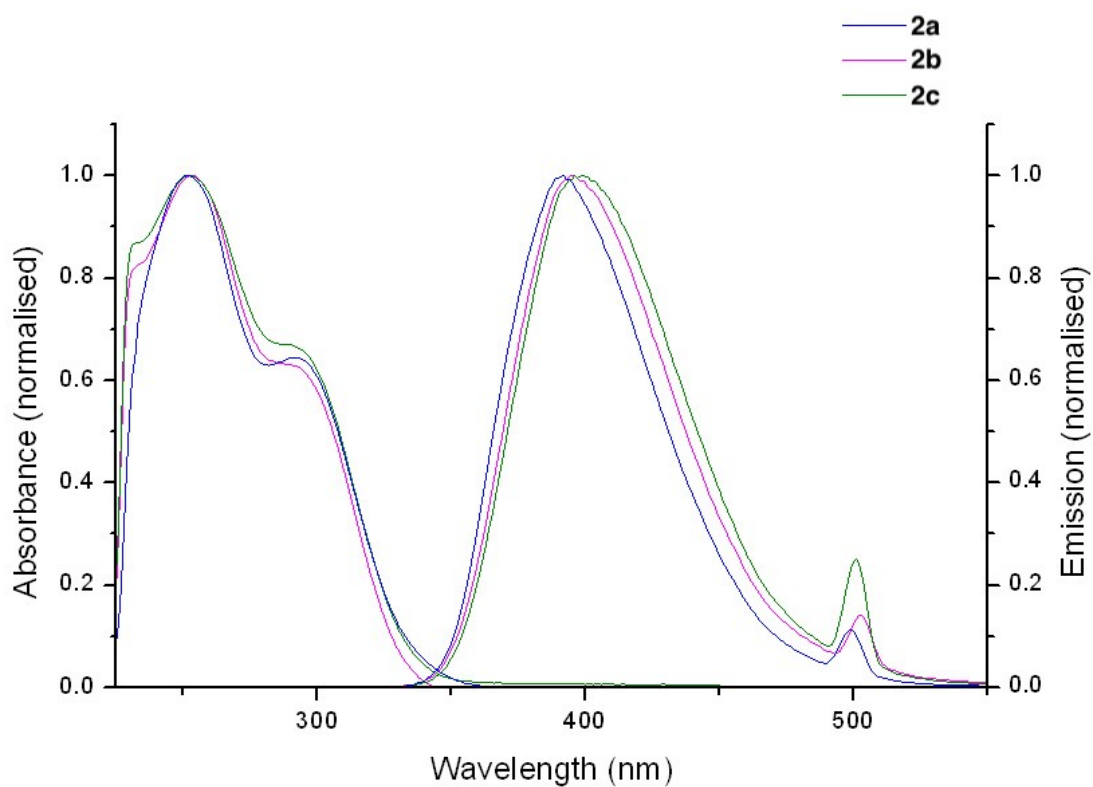


Figure S2. Normalized UV/visible and photoluminescence spectra of **2a**, **2b** and **2c**, all measured in deoxygenated dichloromethane at room temperature, concentrations $\sim 10^{-6}$ mol.L $^{-1}$.

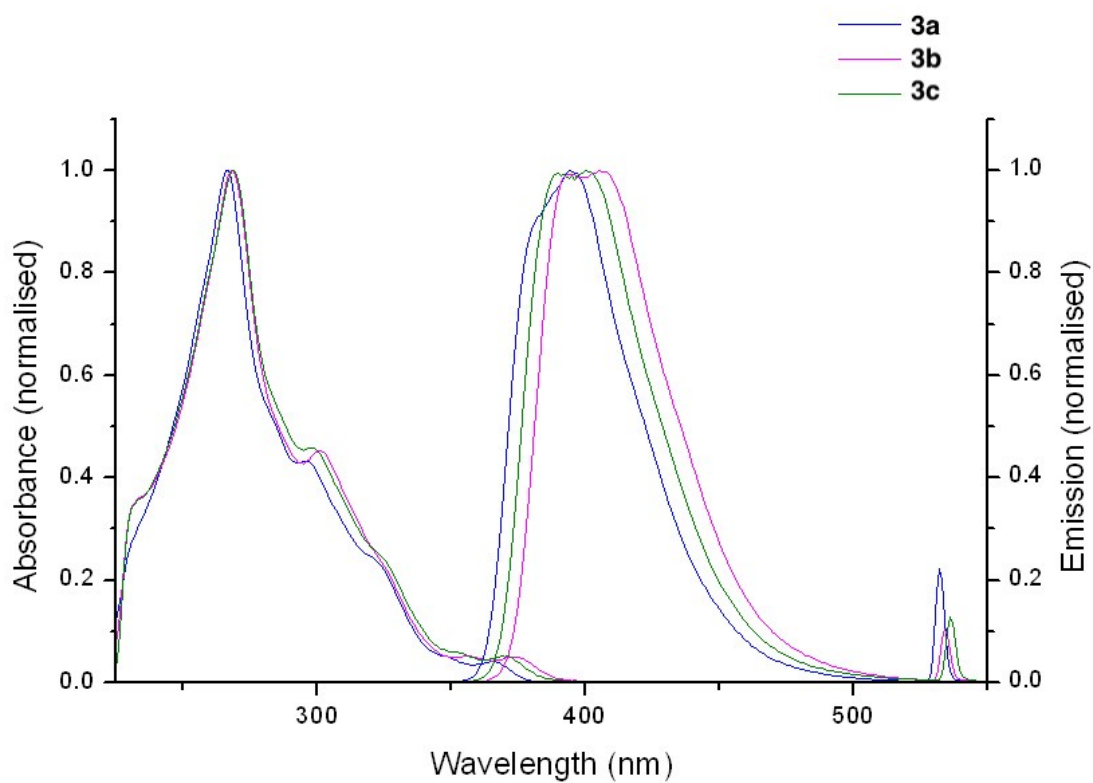


Figure S3. Normalized UV/visible and photoluminescence spectra of **3a**, **3b** and **3c**, all measured in deoxygenated dichloromethane at room temperature, concentrations $\sim 10^{-6}$ mol.L $^{-1}$.

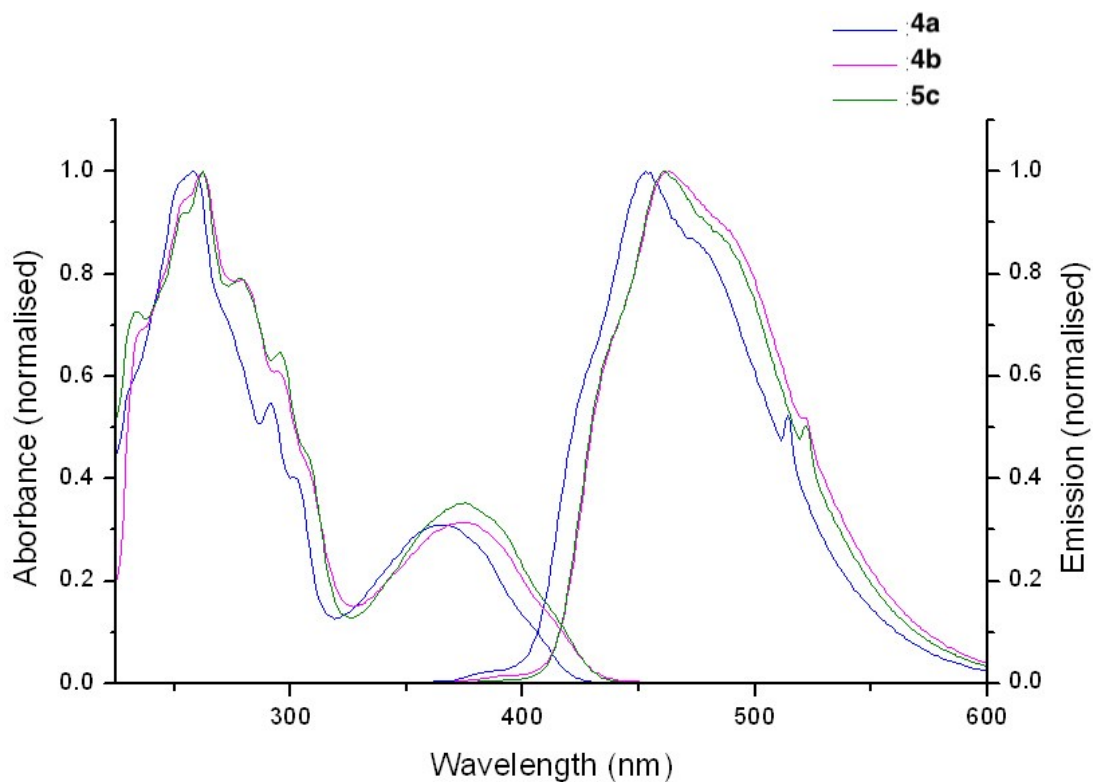


Figure S4. Normalized UV/visible and photoluminescence spectra of **4a**, **4b** and **4c**, all measured in deoxygenated dichloromethane at room temperature, concentrations $\sim 10^{-6}$ mol.L $^{-1}$.

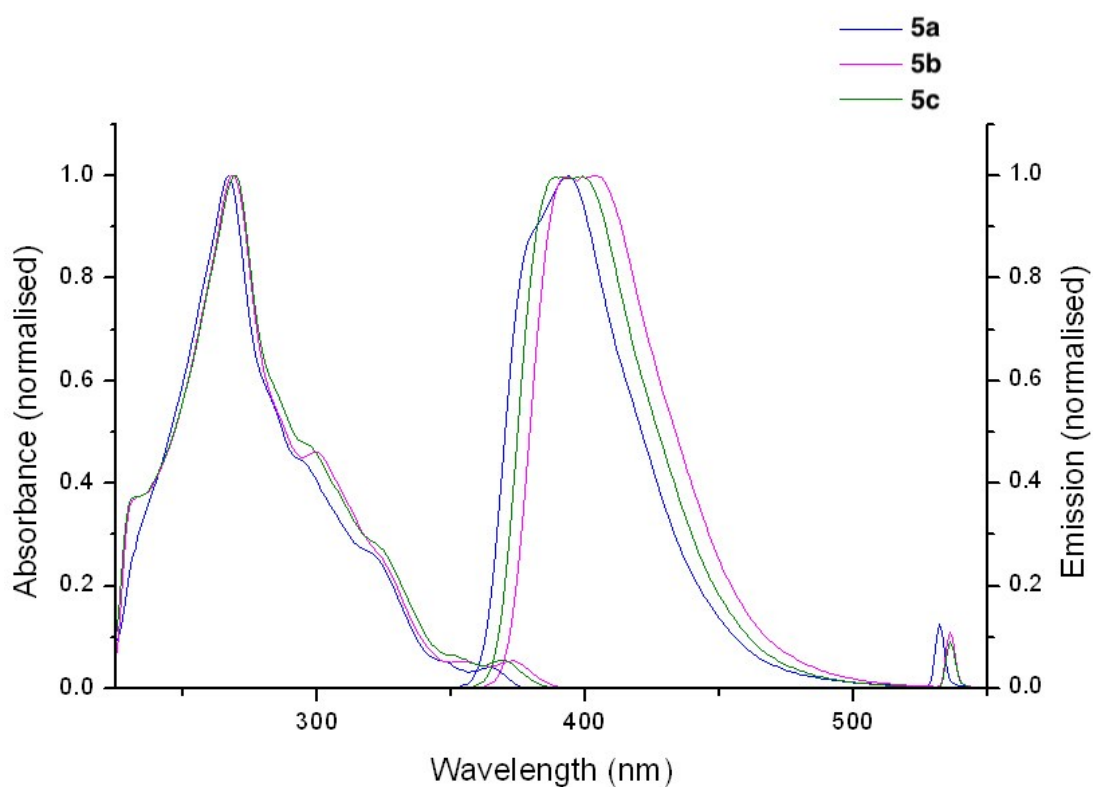


Figure S5. Normalized UV/visible and photoluminescence spectra of **5a**, **5b** and **5c**, all measured in deoxygenated dichloromethane at room temperature, concentrations $\sim 10^{-6}$ mol.L $^{-1}$.

Mass Spectrometry

The ESMS mass spectra collected for **1b**, **2b**, **3a**, **3b**, **3c**, **5a** and **5c** all showed the presence of oxidation products including MO and MO₂ which were not observed in the NMR spectra or via other spectroscopic techniques. The oxidation of suitable substrates during the electrospray experiment is well known.⁶ During the experiment the generation of the required cone voltage is achieved via a potential drop between the cone surface and the spectrometer allowing the oxidation of analyte molecules. The oxidation products of **3a**, **3b** and **3c** are detailed in Figures S4 – S6, respectively.

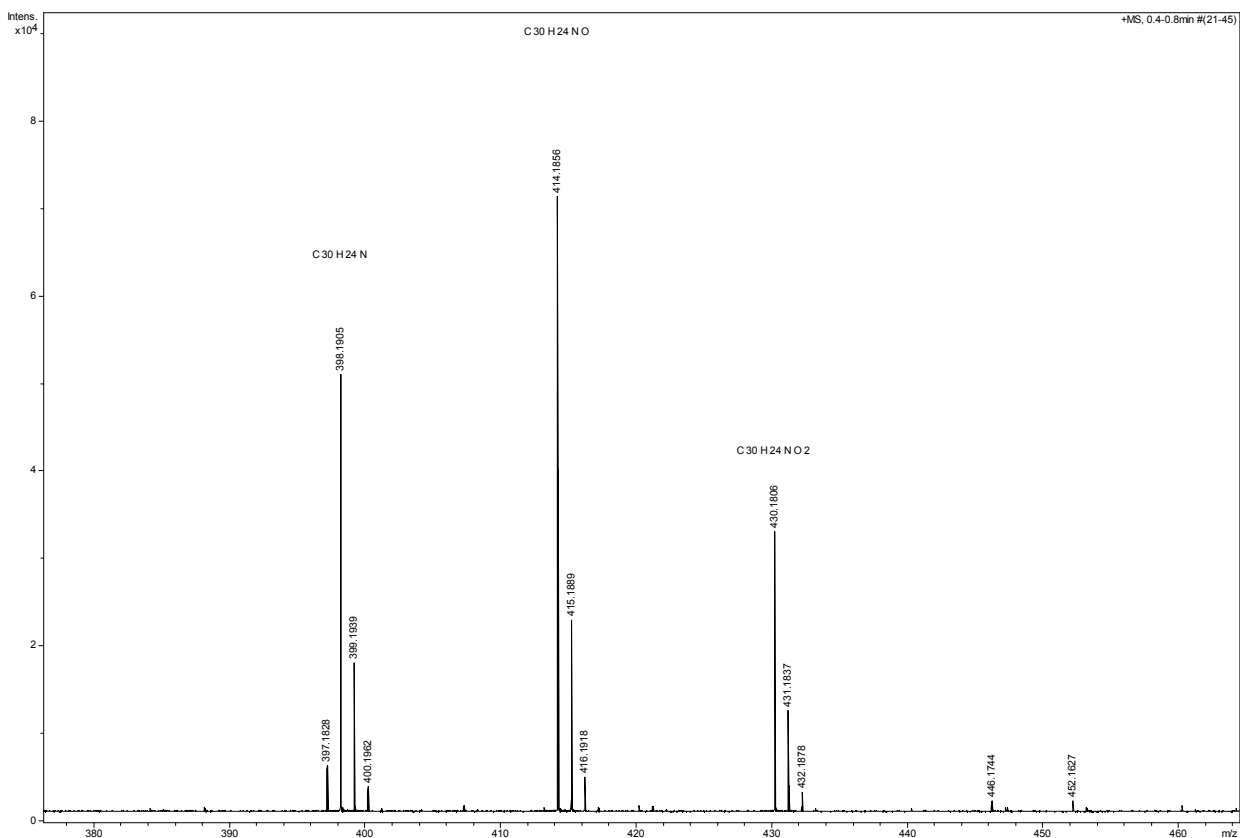


Figure S6. ESMS spectra of **3a** showing the observation of the oxidative electrolysis products C₃₀H₂₄NO [**3a** + H + O]⁺ (calc 414.1852, found 414.1856) and C₃₀H₂₄NO₂ [**3a** + H + 2O]⁺ (calc 430.1802, found 414.1806) along with the molecular ion C₃₀H₂₄N [**3a** + H]⁺ (calc 398.1903, found 398.1905).

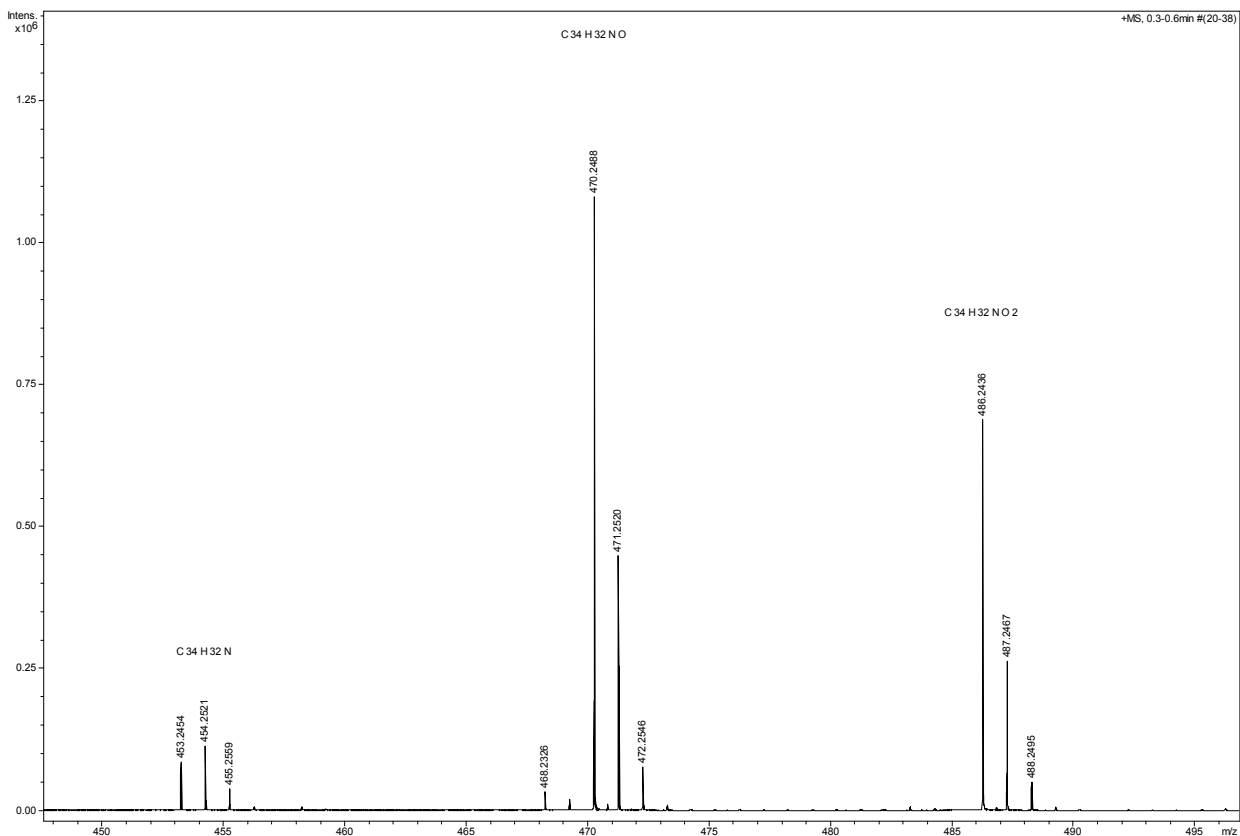


Figure S7. ESMS spectra of **3b** showing the observation of the oxidative electrolysis products C₃₄H₃₂NO [**3b** + H + O]⁺ (calc. 470.2478, found 470.2488) and C₃₄H₃₂NO₂ [**3b** + H + 2O]⁺ (calc. 486.2428, found 486.2436) along with the molecular ion C₃₄H₃₂N [**3b** + H]⁺ (calc. 454.2529, found 454.2521).

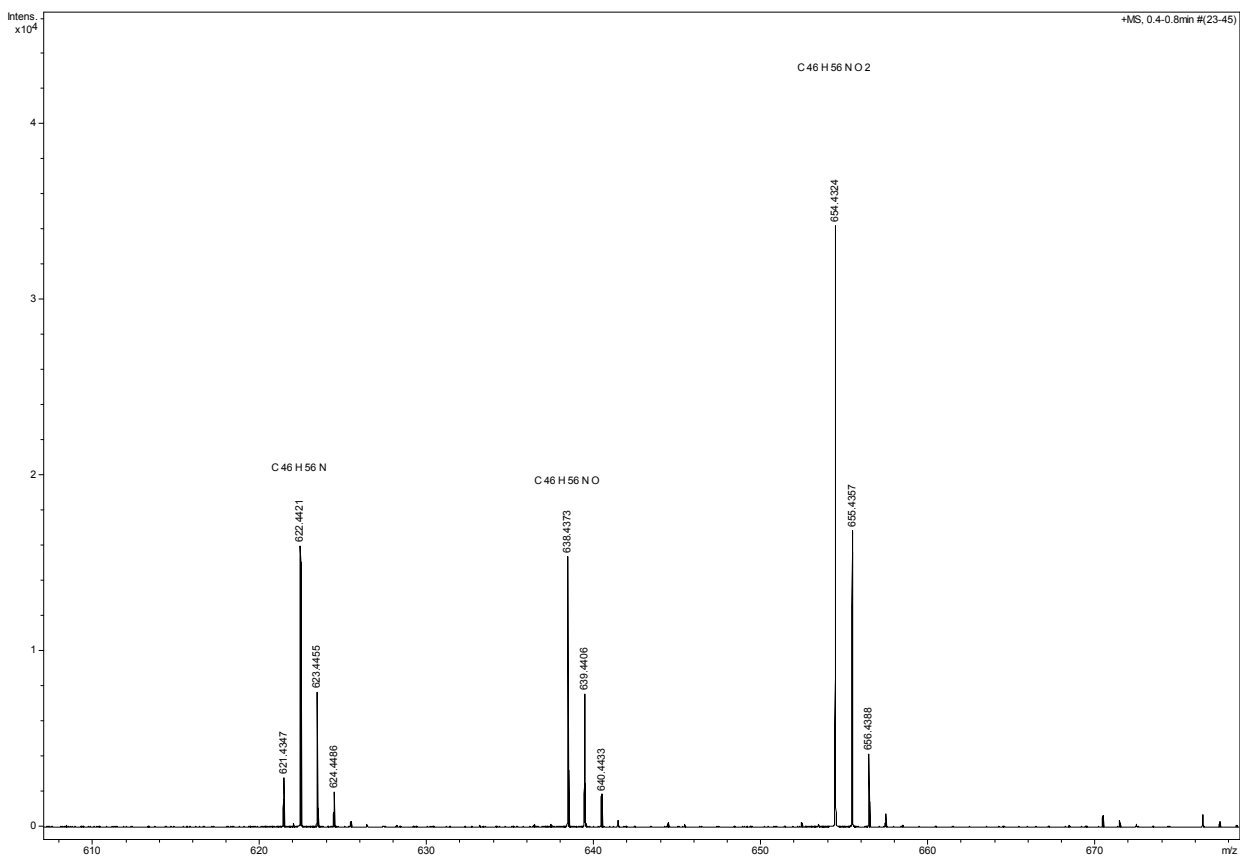


Figure S8. ESMS spectra of **3c** showing the observation of the oxidative electrolysis products C₄₄H₅₆NO [**3c** + H + O]⁺ (calc. 638.4356, found 638.4373) and C₄₄H₅₆NO₂ [**3c** + H + 2O]⁺ (calc. 654.4306, found 654.4324) along with the molecular ion C₄₄H₅₆N [**3c** + H]⁺ (calc. 622.4407, found 622.4421).

X-ray Crystallography

Crystals were mounted on a glass fiber under oil. Data were collected at 120(1) K on a Bruker APEXII area detector using graphite monochromised Mo K α ($\lambda = 0.71073$ Å) radiation for **6**, and on an Agilent Atlas area detector using microfocus graphite monochromised Cu K α ($\lambda = 1.5418$ Å) radiation for structures the remaining structures. The data reduction was performed using SAINT for structures 7, and CrysAlisPro for the other structures. Intensities were corrected for Lorentzian polarization effects and for absorption effects using multiscan methods. Space groups were determined from systematic absences and checked for higher symmetry. Structures were solved by direct methods using SHELXS⁷ and refined with full-matrix least squares on F^2 using SHELXL-97⁸ within OLEX-2.3.⁹ All non-hydrogen atoms were refined anisotropically, unless specified otherwise. Hydrogen atoms were included at geometrically estimated positions and refined with a riding model. Details of data collections and structure refinements for all structures are given in Table S1

The structure of **2b** contained a benzene solvate molecule disordered over two sites occupying the same space in the unit cell. The occupancy of the atoms totalled one, and the distances between the bonds were restrained to be equal. The thermal parameters of these groups were treated as anisotropic and were similar to those of **2b**.

Table S1– Crystal data and X-ray experimental details for complexes **3b**, **4b**, **5a**, **5b** and **6**.

Compound	3b	4b	5a	5b	6
Empirical formula	C ₄₀ H ₃₇ N	C ₃₉ H ₃₃ N	C ₃₅ H ₂₅ N	C ₄₅ H ₃₉ N	C ₃₀ H ₁₇ Cl ₄ N
Formula weight	531.70	515.66	459.56	593.77	533.24
Crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	P-1	P-1	P2 ₁ /c	P2 ₁ /c	P-1
Unit cell dimensions: a (Å)	9.8521(3)	10.2655(5)	10.1062(2)	5.95712(11)	9.9632(3)
b (Å)	10.1991(4)	11.6330(5)	13.1190(3)	24.7533(5)	11.2079(3)
c (Å)	16.8567(6)	12.7175(6)	18.1079(4)	22.2920(4)	11.9471(4)
α (°)	99.880(3)	109.469(4)	90	90	64.541(2)
β (°)	95.857(3)	101.265(4)	97.158(2)	94.0305(17)	74.712(2)
γ (°)	116.117(3)	91.218(4)	90	90	75.154(2)
Volume(Å ³)	1467.81(10)	1398.13(12)	2382.11(10)	3279.02(11)	1146.18(6)
Z	2	2	4	4	2
Density (calculated) (Mg/m ³)	1.203	1.225	1.281	1.203	1.545
Absorption coefficient (mm ⁻¹)	0.517	0.529	0.560	0.518	0.539
F(000)	568.0	548.0	968.0	1264.0	544.0
Crystal size (mm)	0.25 × 0.23 × 0.03	0.09 × 0.05 × 0.05	0.32 × 0.29 × 0.12	0.19 × 0.17 × 0.16	0.50 × 0.29 × 0.04
Theta range for data collection (°)	5.432 to 147.674	7.55 to 147.922	8.346 to 147.944	5.342 to 147.64	4.296 to 60
Reflections collected	15594	10379	9069	18660	29287
Independent reflections [R(int)]	5810 [0.0197]	5488 [0.0215]	4678 [0.0219]	6468 [0.0193]	6617 [0.0429]
Observed reflections (I>2σ(I))	5245	4674	3749	5731	4627
Data / restraints / parameters	5810/66/430	5488/0/365	4678/0/325	6468/0/419	6617/0/317
Goodness-of-fit on F ²	1.049	1.040	1.038	1.042	1.018
R ₁ [I>2σ(I)]	0.0407	0.0441	0.0418	0.0599	0.0391
wR ₂ (all data)	0.1124	0.1214	0.1131	0.1537	0.1095
Largest diff. peak/hole (e Å ⁻³)	0.22/-0.20	0.30/-0.23	0.54/-0.21	0.65/-0.28	0.43/-0.44

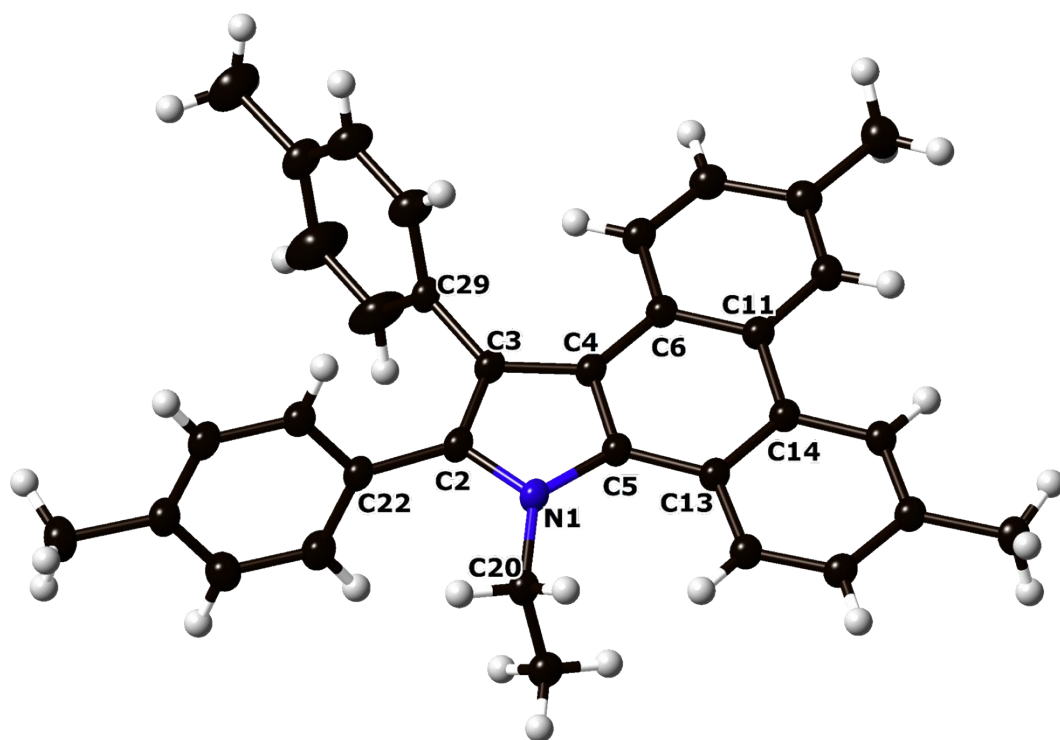


Figure S9. Structure of **3b**, with thermal ellipsoids shown at the 50% level. Selected Bond Lengths (Å): N1-C21.3847(13), N1-C5 1.3874(14), N1-C20 1.4663(14), C2-C3 1.3725(16), C2-C22, 1.4816(15), C3-C4 1.4309(15), C3-C29 1.4882(15), C4-C5 1.3986(15), C4-C6 1.4433(15), C5-C13 1.4478(14) C11-C14 1.4669(15). Selected Bond Angles (°): C2-N1-C5 108.23(9), C2-N1-C20 122.59(9), C5-N1-C20 128.80(9), N1-C2-C22 123.33(10), C3-C2-N1 109.72(10), C3-C2-C22 126.95(10), C2-C3-C4 106.68(10), C2-C3-C29 123.49(10), C4-C3-C29 129.82(10). Mean-plane twists of phenyl rings vs diphenyldibenz[e,g]pyrrole (°): 106.50(3) for C22-ring and 101.14(5) for C29-ring.

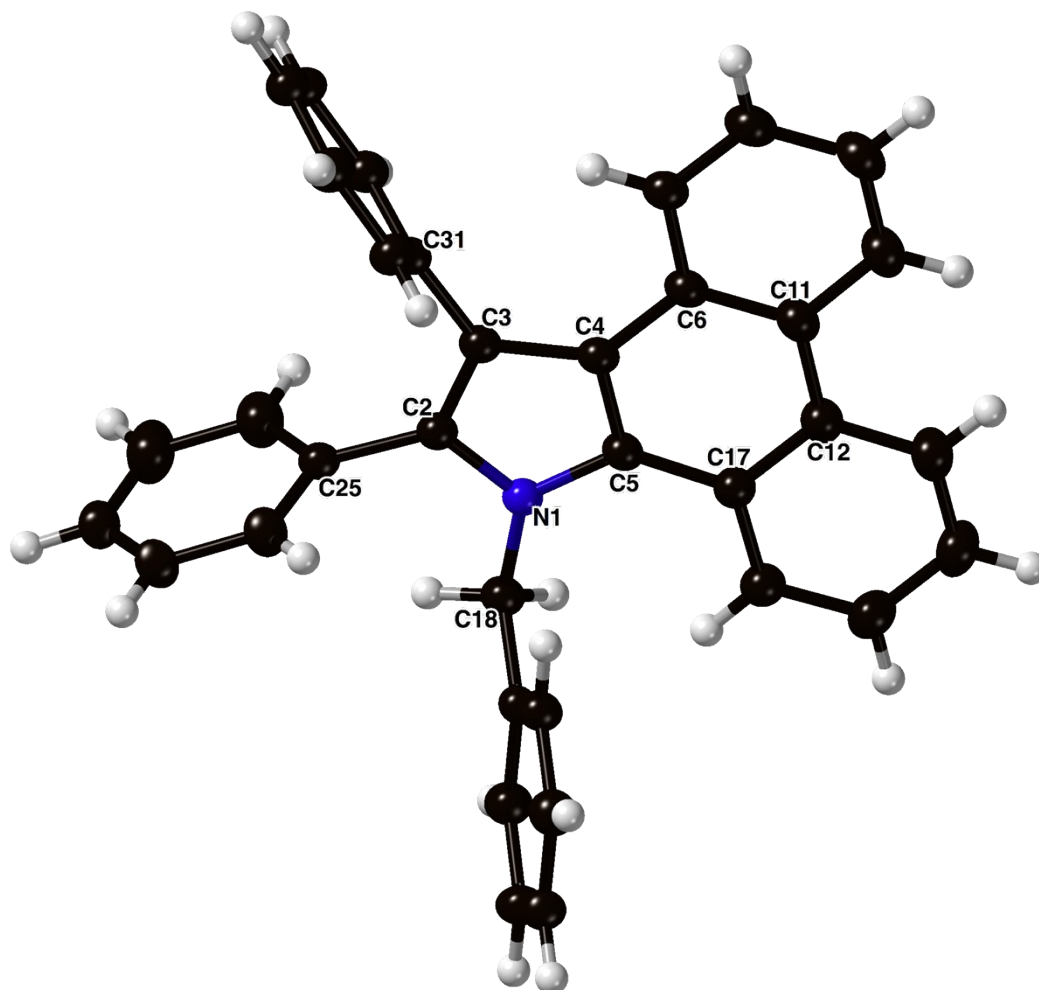


Figure S10. Structure of **5a**, with thermal ellipsoids shown at the %50 level. Selected Bond Lengths (Å): N1-C2 1.3862(18), N1-C5 1.3882(18), N1-C18 1.4605(17), C2-C3 1.3740(19), C2-C25 1.485(2), C3-C4 1.431(2), C3-C31 1.4859(19), C4-C5 1.4020(19), C4-C6 1.4439(19), C5-C17 1.442(2), C11-C12 1.467(2). Selected Bond Angles (°): C2-N1-C5 108.47(11), C2-N1-C18 122.40(12), C5-N1-C18 129.13(12), N1-C2-C25 121.38(12), C3-C2-N1 109.62(12), C3-C2-C25 128.96(13), C2-C3-C4 106.67(12), C2-C3-C31 123.92(13), C4-C3-C31 129.40(12). Mean-plane twists of phenyl rings vs diphenyldibenz[e,g]pyrrole (°): 87.16(5) for C25-ring, 77.19(4) for C31-ring and 79.43(4) for the benzyl ring.

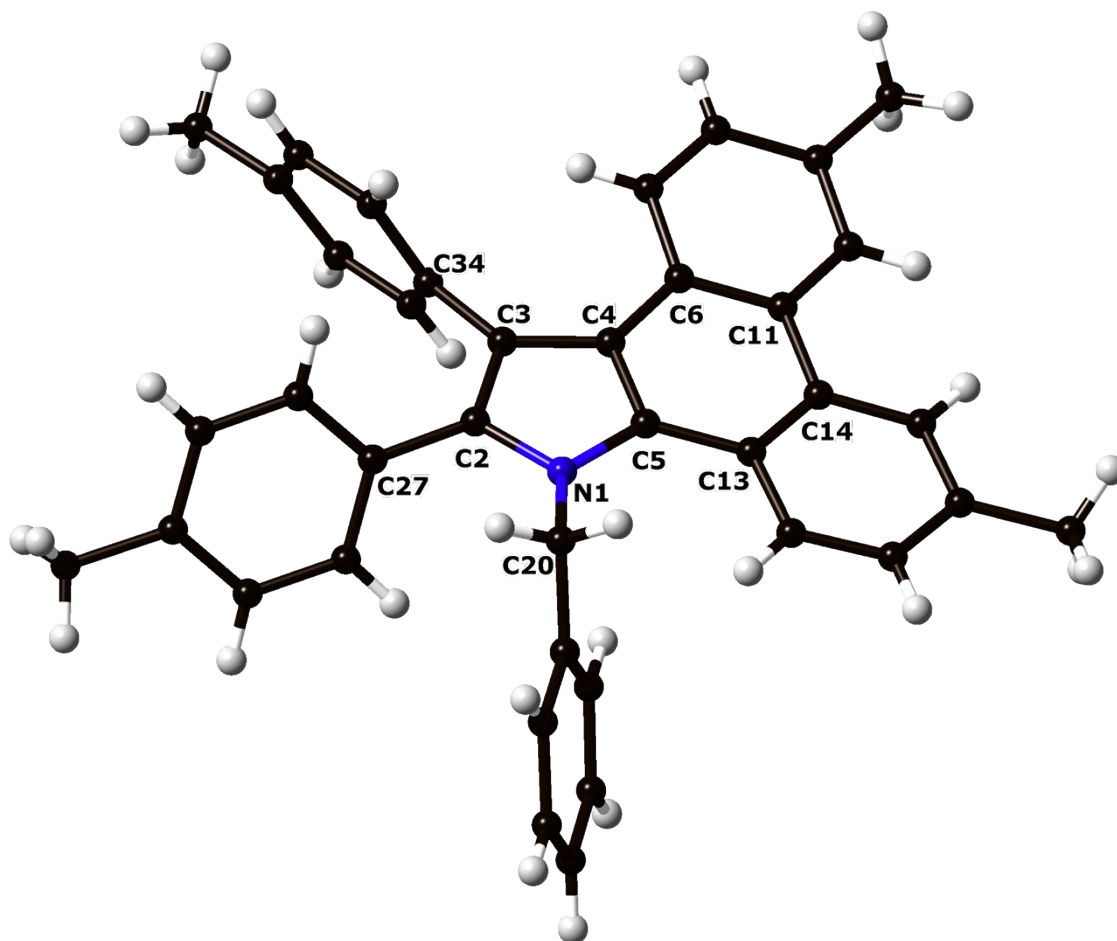


Figure S11. Structure of **5b**, with thermal ellipsoids shown at the %50 level. Selected Bond Lengths (Å): N1-C2 1.388(2), N1-C5 1.392(2), N1-C20 1.471(2), C2-C3 1.377(3), C2-C27 1.475(2), C3-C4 1.428(2), C3-C34 1.498(3), C4-C5 1.388(3), C4-C6 1.443(2), C5-C13 1.445(2), C6-C7 1.408(3), C11-C14 1.466(3), C2-N1-C5 108.23(14). Selected Bond Angles (°): C2-N1-C20 121.55(15), C5-N1-C20 127.78(15), N1-C2-C27 122.31(16), C3-C2-N1 109.17(15), C3-C2-C27 128.24(16), C2-C3-C4 106.88(15), C2-C3-C34 123.45(16), C4-C3-C34 128.55(16). Mean-plane twists of phenyl rings vs diphenyldibenz[e,g]pyrrole (°): 87.16(5) for C27-ring, 51.11(5) for C37-ring and 77.52(6) for the benzyl ring.

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