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Methoxy Functionalisation: Exerting Synthetic Control of the Supramolecular and Electronic Structure of Nitrogen-doped nanographenes

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Supporting information

S1. Materials and methods

General Methods: Unless otherwise stated, all reactions were carried out under nitrogen or argon with dry solvent, freshly distilled under anhydrous conditions. All chemicals were purchased from Sigma Aldrich unless otherwise stated.

NMR spectra were recorded in $CDCl_3$ with (i) Bruker Avance DPX-400 spectrometer (operating at 400.1 MHz for ^1H, 100.6 MHz for ^{13}C), (ii) Bruker AV-600 spectrometer (600.1 MHz for ^1H, 150.6 MHz for ^{13}C). ^1H and ^{13}C NMR spectra were referenced relative to TMS ($\delta = 0.00$ ppm) ^{13}C NMR spectra were proton-decoupled. Chemical shifts (δ) are reported in ppm and coupling contants in Hz. IR spectra (reported in cm^{-1}) of neat samples were recorded with a Perkin–Elmer Spectrum-One FT-IR spectrometer equipped with a Universal-ATR sampling accessory. Electrospray mass spectra were recorded with a Micromass-LCT spectrometer, and accurate mass spectra were referenced against leucine enkephalin (555.6 $gmol^{-1}$) and reported to within 5 ppm. MALDI-TOF mass spectra were recorded with a Waters MALDI-QTOF Premier spectrometer by using an α-cyano-4-hydroxycinnamic acid matrix, and accurate mass spectra were referenced against [Glu1]-fibrinopeptide B (1570.6 $gmol^{-1}$) and reported to within 5 ppm. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin.

Electrochemical Measurements: Cyclic voltammetry was performed by using a CH instruments Electrochemical Analyser Model 600B. Cyclic voltammograms were measured on 1 mM solutions of ligands in CH_2Cl_2 by using tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as supporting electrolyte. A standard three-electrode cell was employed with a glassy carbon working electrode, a Pt wire counter electrode, and an SCE as the reference electrode. Potentials are quoted vs. the ferrocene/ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. Solutions were degassed for several minutes by nitrogen bubbling before the experiments were performed, and a flow of nitrogen over the solution was maintained for the duration of the experiment.

Photophysical Measurements: UV/Vis absorption spectra were recorded as optically dilute solutions (10^{-5} to 10^{-6} M) in 1x1 cm^2 quartz cuvettes with a Shimadzu UV-2450 spectrophotometer. Corrected steady-state solution (ca. 10^{-6} M) spectra at 298K were recorded with a Horiba–Jobin–Yvon Fluorolog 3-22 spectrometer with double grating emission and excitation monochromators. Low temperature measurements were carried out within a thin tube in a quartz Dewar filled with liquid nitrogen. A Jobin–Yvon FluoroHub single-photon counting controller fitted with a 340 nm Jobin–Yvon NanoLED was used to measure lifetimes, which were determined from the observed decays by using DataStation v2.4. Emission quantum yields of the solutions were measured by the Demas and Crosby[1] method and were measured relative to quinine sulfate in 0.5 m H_2SO_4 (Φem = 0.546),[2] for compounds **6**, **7** and relative to coumarin 6 in ethanol (Φem = 0.78)[3] for compound **2**. Corrections were made for the difference in refractive index of the sample and reference solutions.

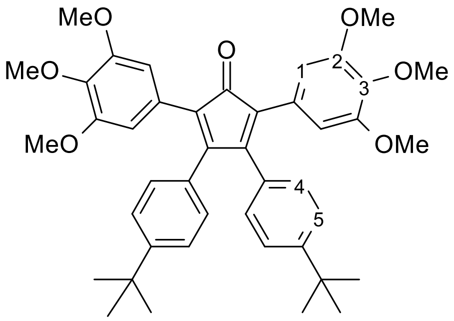
Crystal structure determination:

Single crystal analyses were carried out on a Brüker SMART APEX CCD diffractometer using graphite monochromised Mo-Kα (λ = 0.71073Å) radiation at the temperatures given following data. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarization effects and for absorption by SADABS. The structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons.

Single crystals of **3** suitable were grown by slow evaporation of a $CH_2Cl_2/CHCl_3/CH_3OH$ solution of the compound. Single crystals of **2** were obtained by slow evaporation of a $CHCl_3$ solution layered with CH_3OH. Very small crystals of **6** were grown from the evaporation of a CH_2Cl_2/CH_3OH solution of the compound.

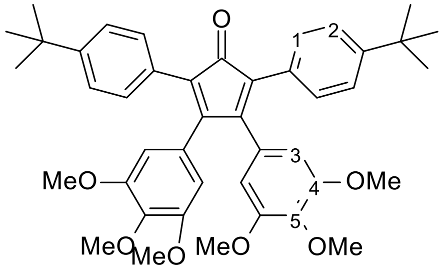
S2. Synthetic procedures

(a) 3,4-bis(4-*tert*-butylphenyl)-2,5-bis(3,4,5-*tri*-methoxyphenyl) cyclopenta-2,4-dienone



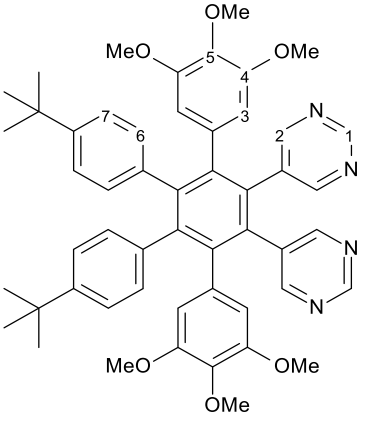
Compound was prepared by modifying a related literature procedure.[4] A solution mixture of 1,3-bis(3,4,5-*tri*-methoxyphenyl)propan-2-one (250 mg, 0.64 mmol), and 1,2-bis(4-*tert*-butylphenyl)ethane-1,2-dione (200 mg, 0.62 mmol) in ethanol (1.5 mL) were refluxed until all the solids were dissolved and then a solution of potassium hydroxide (17.5 mg, 0.33 mmol) in ethanol (1.5 mL) was added in two portions through the condenser. The reaction mixture was refluxed for a further 20 min. The resulting purple precipitate was filtered, washed with cold ethanol and dried under vacuum. (230 mg, 53%). **M.p.** 272-276 ºC. **ESI-MS** (acetonitrile) calculated for $C_{43}H_{49}O_7$, $(M+H)^+$ *m/z* 677.3478; found, 677.3500. **^{1}H NMR** ($CDCl_3$, 20 °C, 400 MHz, δ in ppm): 7.25 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H^5), 6.95 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H^4), 6.51 (s, 4H, H^1), 3.86 (s, 6H, $-C^3OCH_3$), 3.61 (s, 12H, $-C^2OCH_3$) and 1.29 (s, 18H, $-C(CH_3)_3$). **^{13}C NMR** ($CDCl_3$, 20 °C, 100 MHz, δ in ppm): 201.0 (1C, C=O), 154.6 (2C, $C_{quat/Cp}$), 152.7 (4C, $C_{quat/aryl}$), 151.8 (2C, $C_{quat/aryl}$), 137.4 (2C, $C_{quat/aryl}$), 130.2 (2C, $C_{quat/aryl}$), 129.1 (4C, C^4), 126.2 (2C, $C_{quat/aryl}$), 124.9 (4C, C^5), 124.3 (2C, $C_{quat/Cp}$), 107.1 (4C, C^1), 60.9 (2C, $–C^3OCH_3$), 55.6 (4C, $–C^2OCH_3$), 34.7 (2C,$-C(CH_3)_3$) and 31.2 (6C, $-C(CH_3)_3$). **EA:** found C, 76.32; H, 7.05; calcd. (%) for $C_{43}H_{48}O_7$: C, 76.30; H, 7.15. **IR** (neat) νbar in cm^{-1}: 3115, 3003 ($CH_{aromatic}$), 2953, 2905, 2867 (CH_3 stretch), 1702 (C=O), 1607, 1497 (C=C), 1461, 1363 (CH_3 bend), 1246, 1183, 1123 (OCH_3) and 854, 779 ($CH_{aromatic}$ bend).

(b) 2,5-bis(4-*tert*-butylphenyl)-3,4-bis(3,4,5-*tri*-methoxyphenyl) cyclopenta-2,4-dienone



Same procedure as S2a was followed using 1,2-bis(3,4,5-*tri*-methoxyphenyl)ethane-1,2-dione (200 mg, 0.51 mmol) and 1,3-bis(4-*tert*-butylphenyl)propan-2-one (165 mg, 0.51 mmol) as starting material. The resulting precipitate was dark brown. (290 mg, 84%); **M.p.** 228-232 ºC. **ESI-MS** (acetonitrile) calculated for $C_{43}H_{48}O_7Na$, $[M+Na]^+$ *m/z* 699.3298; found, 699.3316. **^{1}H NMR** ($CDCl_3$, 20 °C, 400 MHz, δ in ppm): 7.36 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H^1), 7.24 (d, $^3J_{HH}$ = 8.5 Hz, 4H, H^2), 6.22 (s, 4H, H^3), 3.79 (s, 6H, $-C^5OCH_3$), 3.46 (s, 12H, $-C^4OCH_3$) and 1.34 (s, 18H, $-C(CH_3)_3$). **^{13}C NMR** ($CDCl_3$, 20 °C, 100 MHz, δ in ppm): 200.1 (1C, C=O), 152.9 (2C, $C_{quat/Cp}$), 152.2 (2C, $C_{quat/aryl}$), 150.2 (2C, $C_{quat/aryl}$), 137.9 (2C, $C_{quat/aryl}$), 129.3 (4C, C^2), 127.8 (2C, $C_{quat/aryl}$), 127.7 (2C, $C_{quat/aryl}$), 124.8 (2C, $C_{quat/Cp}$), 124.5 (4C, C^1), 106.9 (4C, C^3), 60.1 (2C, $-C^5OCH_3$), 55.3 (4C, $-C^4OCH_3$), 34.0 (2C, $-C(CH_3)_3$) and 30.5 (6C, $-C(CH_3)_3$). **EA**: found C, 75.96; H, 7.07; calcd. (%) for $C_{43}H_{48}O_7{\cdot}0.2C_2H_5OH$: C, 75.92; H, 7.23. **IR** (neat) νbar in cm^{-1}: 3083, 3013 ($CH_{aromatic}$), 2960, 2933, 2909, 2874 (CH_3 stretch), 1702 (C=O), 1576, 1499 (C=C), 1452, 1347 (CH_3 bend), 1239, 1124, 1002 (OCH_3) and 856, 779 ($CH_{aromatic}$ bend).

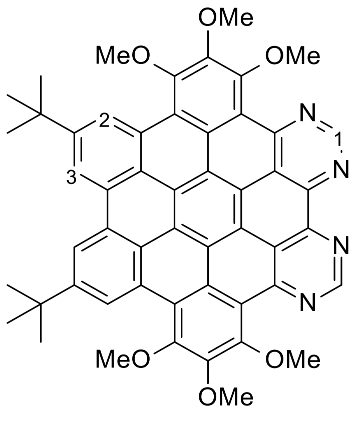
(c) 1,2-dipyrimidyl-3,6-bis(3,4,5-*tri*-methoxyphenyl)-4,5-bis(4-*tert*-butylphenyl)benzene (1)



1

A mixture of 3,4-bis(4-*tert*-butylphenyl)-2,5-bis(3,4,5-*tri*-methoxyphenyl) cyclopenta-2,4-dienone (1.0 g, 1.48 mmol), di(pyramid-3,5-yl)acetylene[5] (0.27 g, 1.48 mmol) and benzophenone (3.5 g, 19.21 mmol) were heated under reflux over a sand bath for 1 h in a round bottom flask attached to an air condenser. The product was purified by column chromatography (SiO_2, dichloromethane followed by dichloromethane/methanol (20:1) once the benzophenone had eluted) and recrystallised from methanol to give the compound as a white solid (1.08 g, 88%). **M.p.** 254-258 ºC. **ESI-MS** (toluene) calculated for $C_{52}H_{55}N_4O_6$, $(M+H)^+$ *m/z* 831.4122; found, 831.4096. ^{1}**H NMR** ($CDCl_3$, 20 °C, 400 MHz, δ in ppm): 8.89 (br s, 2H, H^1), 8.33 (br s, 4H, H^2), 6.94 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H^7), 6.72 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H^6), 5.97 (s, 4H, H^3), 3.69 (s, 6H, $-C^5OCH_3$), 3.42 (s, 12H, $-C^4OCH_3$) and 1.15 (s, 18H, $-C(CH_3)_3$). ^{13}**C NMR** ($CDCl_3$, 20 °C, 150 MHz, δ in ppm): 157.9 (2C, C^1), 156.1 (4C, C^2), 152.3 (C_{quat}), 148.8 ($C_{quat/}$), 141.3 (C_{quat}), 136.6 (C_{quat}), 136.5 (C_{quat}), 133.7 (C_{quat}), 132.7 (C_{quat}), 130.4 (4C, C^6), 123.8 (4C, C^7), 109.5 (4C, C^3), 60.9 (2C, $–C^5OCH_3$), 55.9 (4C, $–C^4OCH_3$), 34.2 (2C,$-C(CH_3)_3$) and 31.1 (6C, $-C(CH_3)_3$). **EA**: found C, 75.09; H, 6.56; N, 6.71; calcd. (%) for $C_{52}H_{54}N_4O_6$: C, 75.16; H, 6.55; N, 6.74. **IR** (neat) νbar in cm^{-1}: 3056, 3010 ($CH_{aromatic}$), 2963, 2902, 2870 (CH_3 stretch), 1578, 1508 (C=C), 1547, 1425 (C=N), 1404, 1347 (CH_3 bend), 1238, 1188, 1136 (OCH_3) and 833, 772 ($CH_{aromatic}$ bend).

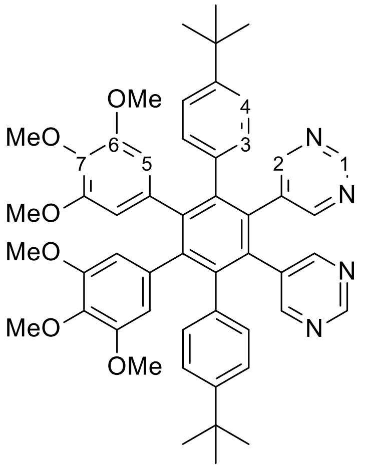
(d) Di-*peri*-(*tert*-butylbenzo)-di-*peri*-(*tri*-methoxybenzo)-di-*peri*-(pyrimidino)-coronene (2)



2

A solution of iron (III)chloride (0.425 g, 2.62 mmol) in nitromethane (3 mL) was added dropwise to a stirred solution of **1** (0.1 g, 0.12 mmol) in dichloromethane (30 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for 4 h the reaction was quenched by addition of methanol (20 mL). The product was isolated by crystallisation from dichloromethane to give brick-red crystals (52 mg, 53%). **ESI-MS** (toluene) calculated for $C_{52}H_{43}N_4O_6$, $[M+H]^+$ *m/z* 819.3183; found, 819.3170.**^{1}H NMR** ($CDCl_3$, 20 °C, 600 MHz, δ in ppm): 10.46 (s, 2H, H^2), 10.21 (br s, 2H, H^1), 9.48 (br s, 2H, H^3), 4.43 (s, 12H, -OC*H*$_3$), 4.33 (s, 6H, -OC*H*$_3$) and 1.90 (s, 18H, -C(C*H*$_3$)$_3$).**^{13}C NMR** ($CDCl_3$, 20 °C, 150 MHz, δ in ppm): 156.1 (1C, C_{quat}), 156.0 (1C, C^1), 154.7 (C_{quat}), 154.3 (C_{quat}), 150.2 (C_{quat}), 150.0 (C_{quat}), 149.0 (C_{quat}), 129.7 (C_{quat}), 128.8 (C_{quat}), 126.8 (C_{quat}), 124.8 (2C, C^2), 122.5 (C_{quat}), 122.0 (C_{quat}), 120.9 (C_{quat}), 120.4 (C_{quat}), 119.1 (2C, C^3), 118.6 (C_{quat}), 118.3 (C_{quat}), 115.7 (C_{quat}), 61.9 (2C, –O*C*H$_3$),61.3 (2C, –O*C*H$_3$), 60.8 (2C, –O*C*H$_3$), 35.9 (2C,-*C*(CH$_3$)$_3$), 31.9 (6C, -C(*C*H$_3$)$_3$). **EA**: found C, 70.55; H, 4.89; N, 6.10; calcd. (%) for $C_{52}H_{42}N_4O_6\cdot CH_2Cl_2$: C, 70.43; H, 4.91; N, 6.20. **IR** (neat) νbar in cm^{-1}: 3174 ($CH_{aromatic}$), 2937, 2902, 2863 (CH_3 stretching), 1601 (C=C), 1576 (C=N), 1395 (CH_3 bending), 1374, 1257 (OCH_3) and 831, 747 ($CH_{aromatic}$ bending).

(e) 1,2-dipyrimidyl-3,6-bis(4-*tert*-butylphenyl)-4,5-bis(3,4,5-*tri*-methoxyphenyl) benzene (3)



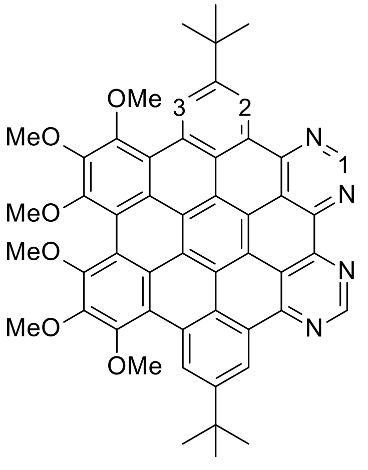
3

Same procedure in S2c was followed using 2,5-bis(4-*tert*-butylphenyl)-3,4-bis(3,4,5-*tri*-methoxyphenyl)cyclopenta-2,4-dienone (1.0 g, 1.48 mmol), di(pyramid-3,5-yl)acetylene[5] (0.27 g, 1.48 mmol) and benzophenone (3.5 g, 19.21 mmol). The product was isolated as a white solid (1.23 g, 82%). **M.p**. 284-288 ºC. **ESI-MS** (acetonitrile) calculated for $C_{52}H_{54}N_4O_6Na$, $[M+Na]^+$ *m/z* 853.3941; found, 853.3934. **^{1}H NMR** ($CDCl_3$, 20 °C ,400 MHz, δ in ppm): 8.81 (s, 2H, H^1), 8.23 (s, 4H, H^2), 7.03 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H^4), 6.76 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H^3), 6.05 (s, 4H, H^5), 3.69 (s, 6H, -C^7OC*H*$_3$), 3.40 (s, 12H, -C^6OC*H*$_3$) and 1.17 (s, 18H, -C(C*H*$_3$)$_3$); **^{13}C NMR** ($CDCl_3$, 20 °C, 150 MHz, δ in ppm): 158.1 (4C, C^2), 156.1 (2C, C^1), 152.1 (4C, C_{quat}), 149.7 (2C, C_{quat}), 142.2 (2C, C_{quat}), 141.6 (2C, C_{quat}), 136.4 (2C, C_{quat}), 135.7 (2C, C_{quat}), 134.9 (2C,

C_{quat}), 133.9 (2C, C_{quat}), 133.4 (2C, C_{quat}), 130.8 (4C, C^3), 124.6 (4C, C^4), 109.3 (4C, C^5), 60.9 (2C, $–C^7OCH_3$), 55.9 (4C, $–C^6OCH_3$), 34.3 (2C,-$C(CH_3)_3$) and 31.1 (6C, -$C(CH_3)_3$). **EA**: found C, 73.56; H, 6.42; N, 6.51; calcd. (%) for $C_{52}H_{54}N_4O_6 \cdot 1.1CH_3OH$: C, 73.62; H, 6.79; N, 6.47. **IR** (neat) νbar in cm^{-1}: 3041, 3024 ($CH_{aromatic}$), 2954, 2905, 2867 (CH_3 stretch), 1582, 1507, (C=C), 1549, 1464 (C=N), 1394, 1362 (CH_3 bend), 1237, 1125 (OCH_3) and 825, 772 ($CH_{aromatic}$ bend).

(f) Di-*peri*-(*tert*-butylbenzo)-di-*peri*-(*tri*-methoxybenzo)-di-*peri*-(pyrimidino) -coronene (4) and partially fused 5/6 N-HSB

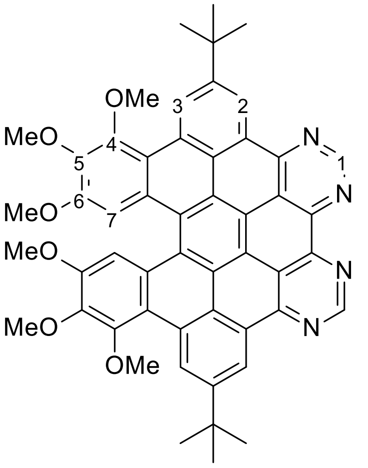
Iron(III) chloride (0.425 g, 2.62 mmol) in nitromethane (3 mL) was added dropwise to a solution containing **3** (0.10 g, 0.12 mmol) in dichloromethane (30 mL). An argon stream was bubbled through the reaction mixture throughout the entire reaction. After stirring for 4 h the reaction was quenched by addition of methanol (20 mL). The products were isolated by column chromatography (SiO_2, diethyl ether/hexane 4:1). Two major fractions were collected; the first dark orange fraction was dried and afforded a dark orange solid which was recrystallised from chloroform/methanol to give **4** as a dark orange solid (19.7 mg, 20%.). Similarly, solvent removal of the second set of brick-red fractions afforded 5/6-fused product which was further recrystallised from chloroform/methanol. (9.8 mg, 10%).



4

ESI-MS (toluene) calculated for $C_{52}H_{43}N_4O_6$, $(M+H)^+$ *m/z* 819.3183; found, 819.3156. **^{1}H NMR** (CD_3CN, 20 °C, 600 MHz, δ in ppm): 10.48 (br s, 2H, H^3), 9.79 (br s, 2H, H^1), 9.77 (br s, 2H,

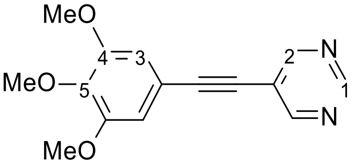
H^3), 4.49 (s, 6H, -OCH_3), 4.36 (s, 3H, -OCH_3), 4.34 (s, 3H, -OCH_3), 4.11 (s, 6H, -OCH_3) and 1.86 (s, 18H, -C(CH_3)$_3$). ^{13}C NMR and EA were not obtained due to low yield.



5/6 N-HSB

ESI-MS (toluene) calculated for $C_{52}H_{45}N_4O_6$, $(M+H)^+$ *m/z* 821.3339; found, 821.3312. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ in ppm): 10.50 (br s, 2H, H^1), 9.92 (br s, 2H, H^7), 9.81 (s, 2H, H^2), 9.53 (s, 2H, H^3), 4.35 (s, 6H, -C^4OCH_3), 4.29 (s, 6H, -C^5OCH_3), 3.96 (s, 6H, -C^6OCH_3) and 1.81 (s, 18H, -C(CH_3)$_3$). ^{13}C NMR and EA were not obtained due to low yield.

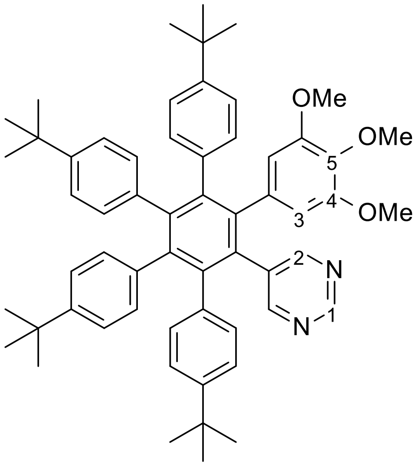
(g) (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene



5-bromo-1,2,3-trimethoxybenzene (247 mg, 1 mmol) and 5-ethynylpyrimidine (104 mg, 1 mmol) were added to a solution of DMF (0.5 mL) and DIPA (1.5 mL) bubbled over nitrogen. To this solution, triphenylphosphine (23 mg, 0.087 mmol), bis(triphenylphosphine) palladium(II)dichloride (15 mg, 0.021 mmol) and copper(I) iodide (4 mg, 0.02 mmol) were added and the mixture was irradiated at 150 W, 115 °C for 25 min. After cooling, the brown suspension was extracted with 2 x 50 mL of Et_2O, filtered and washed with saturated NH_4Cl (2 x 25 mL), water (2 x 25 mL) and then dried over $MgSO_4$. Off white crystals were obtained when the filtrate was concentrated in *vacuo*. Crystals were washed with cold methanol. **(**122 mg, 45%). **M.p.** 136-140 ºC. **ESI-MS** (dichloromethane) calculated for $C_{15}H_{15}N_2O_3$ $[M+H]^+$ *m/z* 271.1083;

found 271.1077. **^{1}H-NMR** (400 MHz, 20 °C, $CDCl_3$, δ in ppm): 9.18 (s, 1H, H^1), 8.90 (s, 2H, H^2), 6.82 (s, 2H,H^3), 3.93 (s, 9H, OC*H$_3$*).**^{13}C-NMR** (150 MHz, 20 °C ,$CDCl_3$, δ in ppm): 157.8 (2C, C^2), 155.6 (1C, C^1), 152.8 (2C, C^4), 139.2 (1C, C^5), 116.2 (C_{quat}), 108.5 (2C, C^3), 96.2 (C_{quat}), 81.2 (C_{quat}), 60.6 (1C, –C^{5}OCH$_3$), 55.8 (2C, –C^{4}OCH$_3$). **EA**: found C, 66.03; H, 4.93; N, 10.04 calcd. (%) for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22, N, 10.36. **IR** (neat) νbar in cm^{-1}: 3067, 3013 ($CH_{aromatic}$), 2928, 2834(CH_3 stretch), 2209 (C≡C), 1578, 1541, 1505, (C=C), 1469 (C=N), 1355, (CH_3 bend), 1237, 1120 (OCH_3) and 822, 765 ($CH_{aromatic}$ bend).

(h) Synthesis of 1-pyrimidyl-3,4,5,6-tetrakis(4-*tert*-butylphenyl)-2-(3,4,5-trimethoxyphenyl) benzene (5)

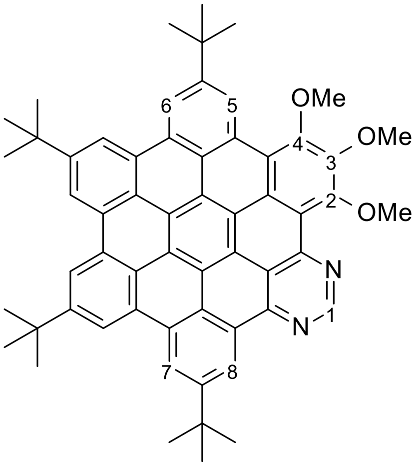


5

A mixture of 2,3,4,5-tetra(4-*tert*-butylphenyl)cyclopenta-2,4-dienone[5] (100 mg, 0.164 mmol), 3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene (44 mg, 0.164 mmol) and benzophenone (450 mg, 2.47 mmol) were heated to reflux over a sand bath for 2 h in a round bottom flask attached to an air condenser. The colour changed from purple to brown after 2h. After cooling, the product was purified by column chromatography (SiO_2, dichloromethane followed by dichloromethane:methanol, 10:0.2 once the benzophenone had eluted) and recrystallized from hexane/methanol to give off-white crystals of **5** (75 mg, 54%). **M.p.** 260-264 °C, **ESI-MS** (chloroform) calculated for $C_{59}H_{67}N_2O_3$ $[M+H]^+$ *m/z* 851.5152; found 851.5160. **^{1}H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 8.77 (s, 1H, H^1), 8.29 (s, 2H, H^2), 6.94 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^{Ar}), 6.92 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^{Ar}), 6.85 (m, 4H, H^{Ar}), 6.74 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H^{Ar}), 6.71 (m, 4H, H^{Ar}), 6.66 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H^{Ar}), 6.02 (s, 2H, H^3), 3.69 (s, 3H, -C^{5}OC*H$_3$*), 3.42 (s, 6H, $-\mathrm{C}^4\mathrm{OC}H_3$), 1.15 (s, 18H, $-\mathrm{C}(\mathrm{C}H_3)_3$), 1.12 (s, 18H, $-\mathrm{C}(\mathrm{C}H_3)_3$). **^{13}C NMR** (150 MHz, 20 °C, $\mathrm{CDCl_3}$, δ in ppm): 157.8 (2C, C^2), 155.0 (1C, C^1), 152.1 ($\mathrm{C_{quat}}$), 148.7 ($\mathrm{C_{quat}}$), 148.2 ($\mathrm{C_{quat}}$), 147.98 ($\mathrm{C_{quat}}$), 147.96 ($\mathrm{C_{quat}}$), 142.5 ($\mathrm{C_{quat}}$), 141.6 ($\mathrm{C_{quat}}$), 141.0 ($\mathrm{C_{quat}}$), 140.9 ($\mathrm{C_{quat}}$), 140.0 ($\mathrm{C_{quat}}$), 137.2 ($\mathrm{C_{quat}}$), 137.2 ($\mathrm{C_{quat}}$), 136.9 ($\mathrm{C_{quat}}$), 136.3 ($\mathrm{C_{quat}}$), 136.2 ($\mathrm{C_{quat}}$), 135.6 ($\mathrm{C_{quat}}$), 134.7 ($\mathrm{C_{quat}}$), 132.1 ($\mathrm{C_{quat}}$), 131.0 (2C, *C*H), 130.83 (2C, *C*H), 130.72 (2C, *C*H), 130.69 (2C, *C*H), 124.0 (2C, *C*H), 123.5 (2C, *C*H), 123.26 (2C, *C*H), 123.25 (2C, *C*H), 109.9 (2C, C^3), 60.9 (1C, $-\mathrm{C}^5\mathrm{O}C\mathrm{H_3}$), 55.9 (2C, $-\mathrm{C}^4\mathrm{O}C\mathrm{H_3}$), 34.19 (1C,$-C(\mathrm{CH_3})_3$), 34.15 (1C,$-C(\mathrm{CH_3})_3$), 34.08 (1C,$-C(\mathrm{CH_3})_3$), 34.07 (1C,$-C(\mathrm{CH_3})_3$), 31.15 (3C, $-\mathrm{C}(C\mathrm{H_3})_3$), 31.13 (6C, $-\mathrm{C}(C\mathrm{H_3})_3$), 31.10 (3C, $-\mathrm{C}(C\mathrm{H_3})_3$). **EA**: found C, 82.93; H, 7.64; N, 3.19; calcd. (%) for $\mathrm{C_{59}H_{66}N_2O_3}$: C,83.25; H, 7.82; N, 3.29. **IR** (neat) νbar in cm^{-1}: 2961, 2905, 2867 ($\mathrm{CH_3}$ stretch), 1583, 1509 (C=C), 1555, 1462 (C=N), 1509, 1404, 1361 ($\mathrm{CH_3}$ bend), 1238, 1188, 1128 ($\mathrm{OCH_3}$) and 833, 779 ($\mathrm{CH_{aromatic}}$ bend).

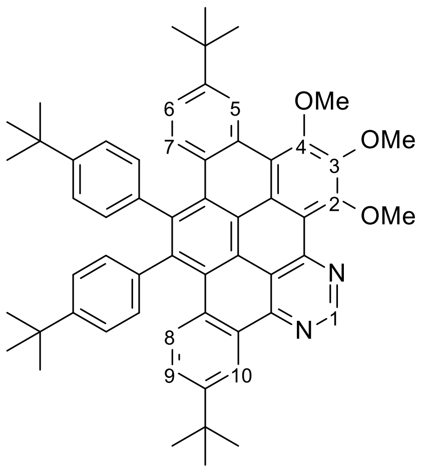
(i) Synthesis of di-*peri*-(*tert*-butylbenzo)-*peri*-(*tri*-methoxybenzo)-*peri*-(pyrimidino)-coronene (6) and partially fused N- ½ HSB (7)

A solution of iron-(III)chloride (320 mg, 1.97 mmol) in nitromethane (2 mL) was added dropwise to a stirred solution of 1-pyrimidyl-3,4,5,6-tetrakis(4-*tert*-butylphenyl)-2-(3,4,5-trimethoxyphenyl)benzene (50 mg, 0.058 mmol) in dichloromethane (30 mL). The reaction was stirred with argon bubbling through the solution, at room temperature for 24 h and then quenched through addition of methanol (20 mL). The solvent was removed and the product was extracted into chloroform, washed with water, and dried over $\mathrm{MgSO_4}$. Following preparative thin-layer chromatography ($\mathrm{SiO_2}$, dichloromethane) two main bands were observed. Extraction and subsequent drying of the orange band yielded fully fused product as a dark yellow solid (20 mg, 40%) and the yellow band yielded the half-fused product as a yellow solid. (10 mg, 20%).



6

M.p >300°C. **ESI-MS** (dichloromethane) calculated for $C_{59}H_{55}N_2O_3$ $[M+H]^+$ *m/z* 839.4213; found 839.4214. **^{1}H-NMR** (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 10.43 (s, 1H, H^5), 10.13 (s, 1H, H^1), 10.02 (s, 1H, H^8), 9.51 (s, 1H, H^7), 9.39 (s, 1H), 9.38 (s, 1H, H^6), 9.37 (s, 1H), 9.36 (s, 1H), 9.34 (s, 1H), 4.46 (s, 3H, $-C^3OCH_3$), 4.41 (s, 3H, $-C^2OCH_3$), 4.25 (s, 3H, $-C^4OCH_3$), 1.87 (s, 9H, $-C(CH_3)_3$), 1.86 (s, 9H $-C(CH_3)_3$), 1.85 (s, 9H $-C(CH_3)_3$), 1.84 (s, 9H $-C(CH_3)_3$). **^{13}C NMR** (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 155.5 (1C, C^1), 154.4 (C_{quat}), 153.7 (C_{quat}), 153.4 (C_{quat}), 150.1 (C_{quat}), 149.8 (C_{quat}), 149.6 (C_{quat}), 149.56 (C_{quat}), 148.53 (C_{quat}), 130.8 (C_{quat}), 130.7 (C_{quat}), 130.5 (C_{quat}), 130.4 (C_{quat}), 130.0 (C_{quat}), 129.6 (C_{quat}), 129.0 (C_{quat}), 128.9 (C_{quat}), 127.6 (C_{quat}), 125.7 (C_{quat}), 124.9 (1C, C^5), 123.6 (C_{quat}), 123.5 (C_{quat}), 123.3 (C_{quat}), 122.5 (1C, C^7), 121.9 (1C, C^8), 121.5 (C_{quat}), 121.3 (C_{quat}), 121.0 (1C, C_{quat}), 120.7 (1C, C_{quat}), 119.9 (1C, C_{quat}), 119.2 (1C, C_{quat}), 119.18 (1C, C^6), 119.14 (1C, *C*H), 119.0 (1C, *C*H), 118.95 (1C, *C*H), 118.85 (1C, *C*H), 117.4 (2C, C_{quat}), 116.5 (2C, C_{quat}), 62.2 (1C, $–C^3OCH_3$), 61.6 (2C, $–C^2OCH_3$), 61.0 (2C, $–C^4OCH_3$), 35.9 (2C,$-C(CH_3)_3$), 35.8 (2C,$-C(CH_3)_3$), 32.01 (1C,$-C(CH_3)_3$), 32.0 (2C,$-C(CH_3)_3$), 31.9 (1C,$-C(CH_3)_3$). **IR** (neat) νbar in cm^{-1}: 3179 ($CH_{aromatic}$), 2955, 2863 (CH_3 stretching), 1603 (C=C), 1580 (C=N), 1393 (CH_3 bending), 1364, 1257 (OCH_3) and 868, 747 ($CH_{aromatic}$ bending). Satisfactory EA could not be obtained due to the aromatic core's resistance to thermal decomposition.[5,6]



7

M.p >300°C. **ESI-MS** (dichloromethane) calculated for $C_{59}H_{61}N_2O_3$ $[M+H]^+$ *m/z* 845.4682; found 845.4672. **^{1}H-NMR** (600 MHz, 20 °C, CDCl$_3$, δ in ppm): 9.92 (s, 1H, H^1), 9.58 (s, 1H, H^5), 9.43 (s, 1H, H^{10}), 8.03 (d, $^3J_{HH}$ = 9.04 Hz, 1H, H^8), 7.85 (d, $^3J_{HH}$ = 9.03 Hz,1H, H^7), 7.34 (d, $^3J_{HH}$ = 9.03 Hz, 1H, H^6), 7.23 (overlapping with CHCl$_3$, 2H, H^{Ar}), 7.13 (m, 3H, H^9 and H^{Ar}), 7.05 (m, 4H, H^{Ar}), 4.30 (s, 3H, -OC^3H_3), 4.25 (s, 3H, -OC^4H_3), 4.12 (s, 3H, -OC^2H_3), 1.47 (s, 9H, -C(CH_3)$_3$), 1.39 (s, 9H, -C(CH_3)$_3$), 1.33 (s, 9H, -C(CH_3)$_3$), 1.26 (s, 9H, -C(CH_3)$_3$). **^{13}C NMR** (150 MHz, 20 °C, CDCl$_3$, δ in ppm): 155.1 (1C, C^1), 154.1 (C$_{quat}$), 153.6 (C$_{quat}$), 153.2 (C$_{quat}$), 152.7 (C$_{quat}$), 150.0 (C$_{quat}$), 149.7 (C$_{quat}$), 149.3 (C$_{quat}$), 148.9 (C$_{quat}$), 148.1 (C$_{quat}$), 140.7 (C$_{quat}$), 140.1 (C$_{quat}$), 140.09 (C$_{quat}$), 139.96 (C$_{quat}$), 131.86 (1C, *C*H), 131.2 (1C, *C*H), 130.3 (C$_{quat}$), 129.69 (1C, C^8), 129.59 (1C, *C*H), 128.9 (1C, C^7), 128.3 (C$_{quat}$), 128.2 (C$_{quat}$), 127.2 (1C, C^6), 126.7(C$_{quat}$), 125.5 (C$_{quat}$), 124.6 (1C, *C*H), 124.1 (1C, C^9), 123.8 (C$_{quat}$), 123.5 (1C, C^{10}), 123.4 (1C, *C*H), 121.2 (1C, C^5), 120.8 (C$_{quat}$), 120.3 (C$_{quat}$), 117.8 (C$_{quat}$), 115.4 (C$_{quat}$), 62.1 (1C, –C^{3}O*C*H$_3$), 61.68 (1C, –C^{4}O*C*H$_3$), 61.66 (1C, –C^{2}O*C*H$_3$), 35.0 (2C,-*C*(CH$_3$)$_3$), 34.5 (1C,-*C*(CH$_3$)$_3$), 34.4 (1C,-*C*(CH$_3$)$_3$), 31.43 (3C, -C(*C*H$_3$)$_3$), 31.36 (3C, -C(*C*H$_3$)$_3$), 31.33 (6C, -C(*C*H$_3$)$_3$). **IR** (neat) νbar in cm^{-1}: 3174 (CH$_{aromatic}$), 2868, (CH$_3$ stretching), 1601 (C=C), 1578 (C=N), 1391 (CH$_3$ bending), 1374, 1259 (OCH$_3$) and 831, 747 (CH$_{aromatic}$ bending). Satisfactory EA could not be obtained due to the aromatic core's resistance to thermal decomposition.[5,6]

S3. ^{1}H and ^{13}C NMR Spectra

^{1}H NMR Spectroscopy

All the products were fully characterized using NMR spectroscopy (^{1}H, ^{13}C, HSQC, HMBC, NOE) and mass spectrometry. The ^{1}H NMR spectra of the three fully fused compounds **2**, **4** and **6** all show well-separated singlets in their aromatic regions (Figure S3-1)

The spectra of **2** and **4** are simplified by the C_{2v} symmetry of these molecules. It is interesting to note that the protons responsible for the most downfield singlets in the spectra of both **2** and **6** are not located on the carbon between the two nitrogen atoms in the pyrimidyl ring, as observed for the other members of the non-methoxy (N-heterosuperbenzene or N-HSB) family.[5,7] HMBC and NOE experiments reveal that these signals belong to the protons adjacent to the –OMe groups in both **2** and **6**. Compound **4** was assigned by comparison, as its low yield precluded in-depth investigation. The half-cyclised **7** shows additional doublets in the aromatic region due to its unfused or "free" phenyl rings (see below).

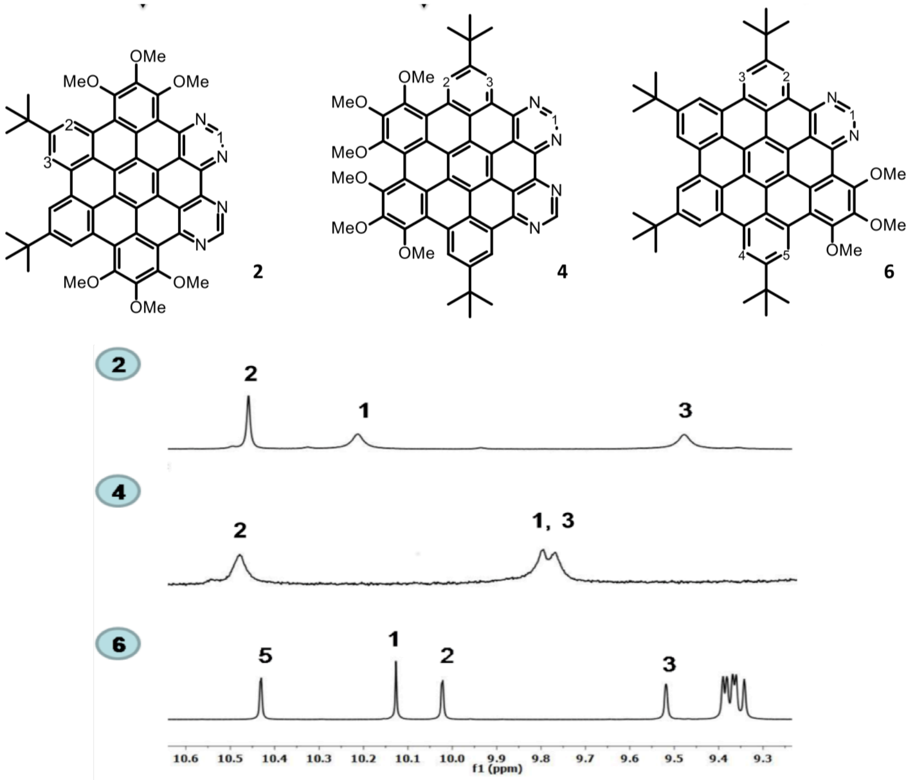
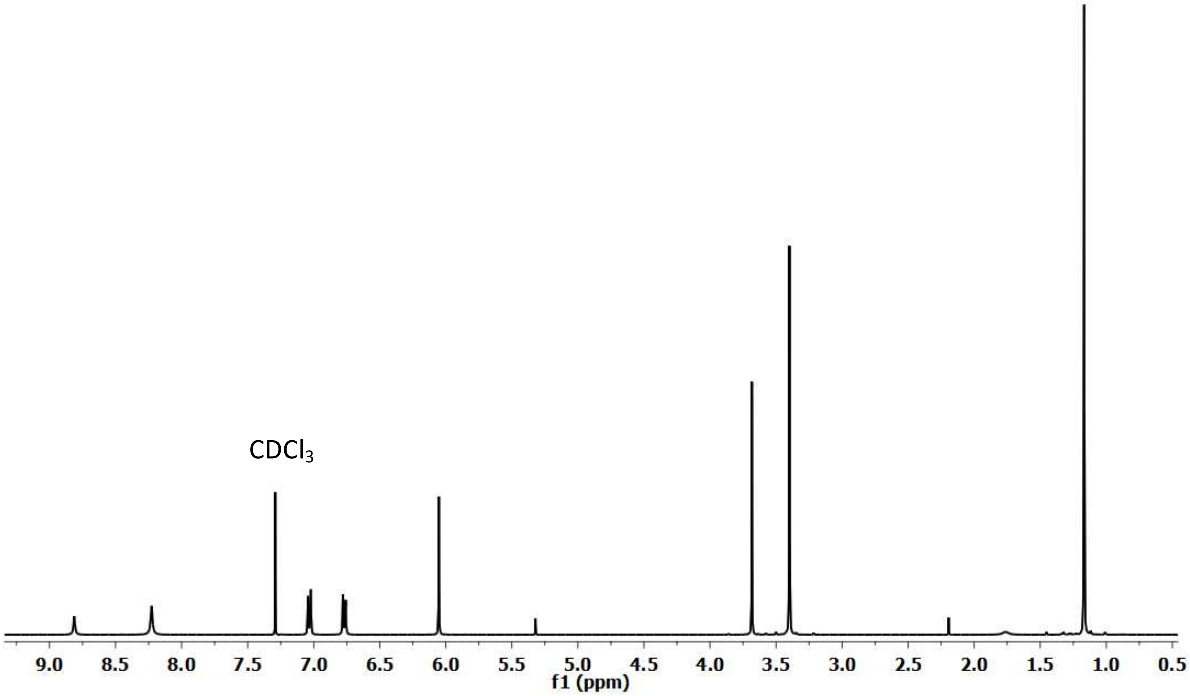
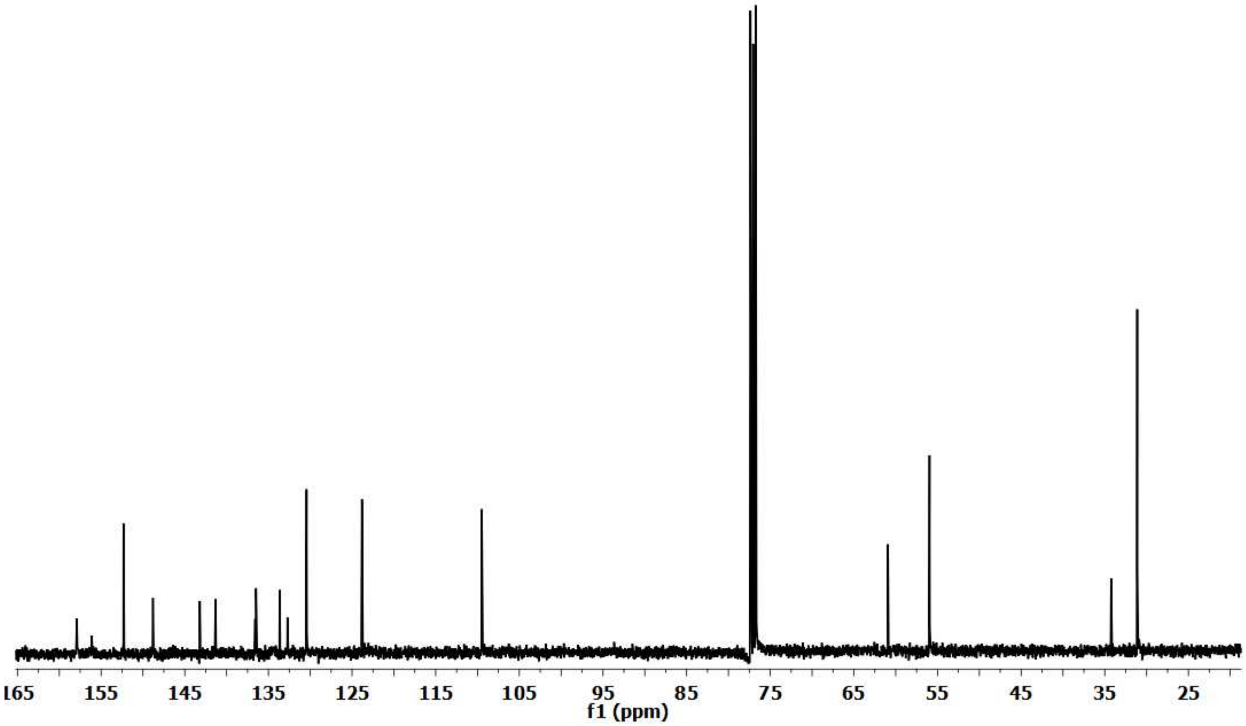


*Figure S3-1. Aromatic region ^{1}H NMR spectra (R.T., 600 MHz, $CDCl_3$) of **2**, **4** and **6**.*

1 in $CDCl_3$

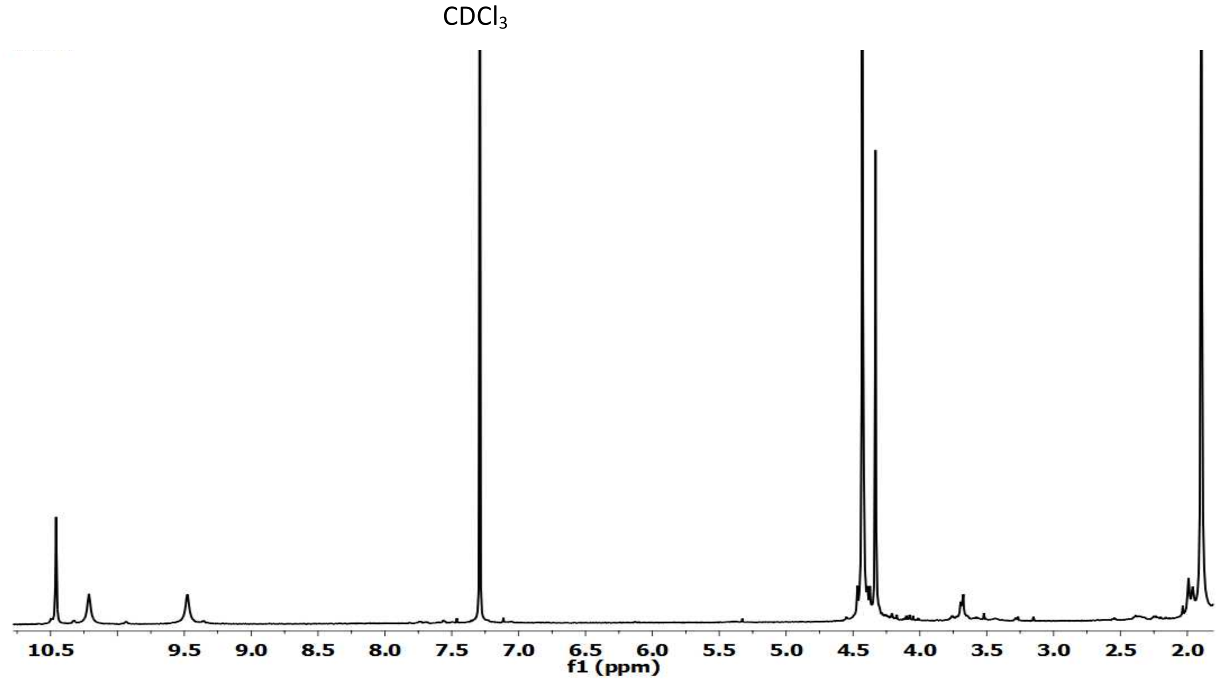


^{13}C NMR

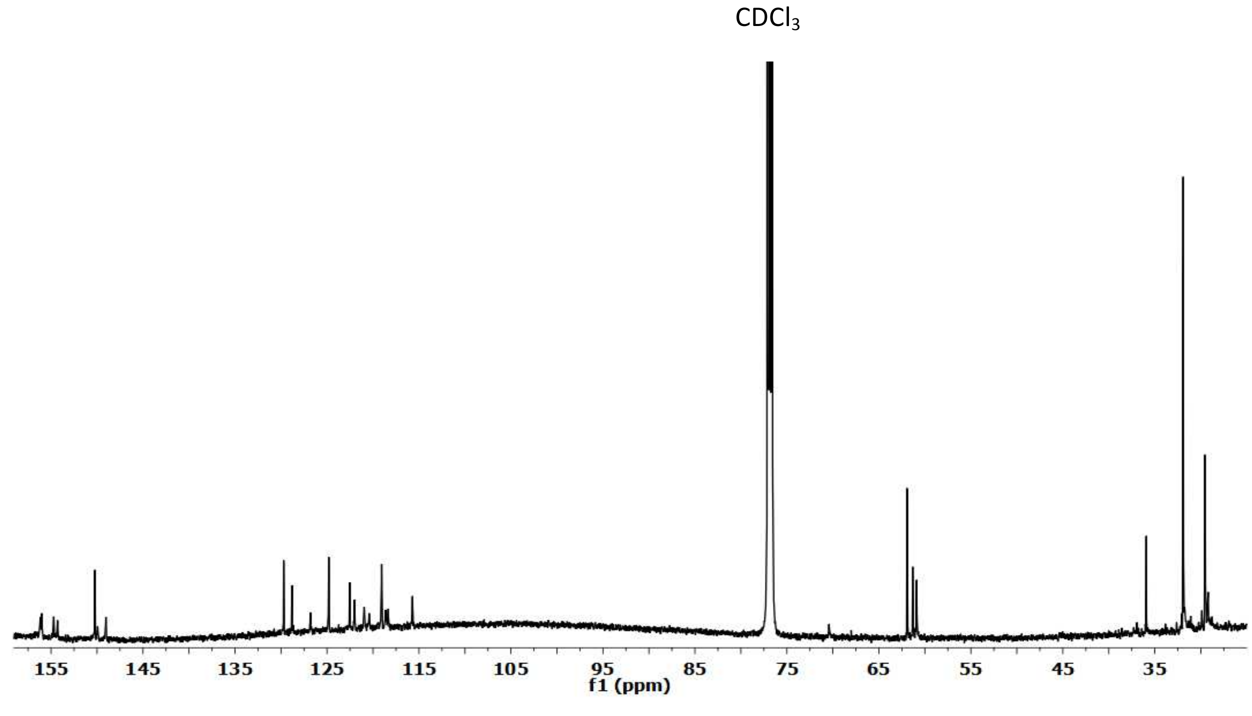


2 in $CDCl_3$

^1H -NMR

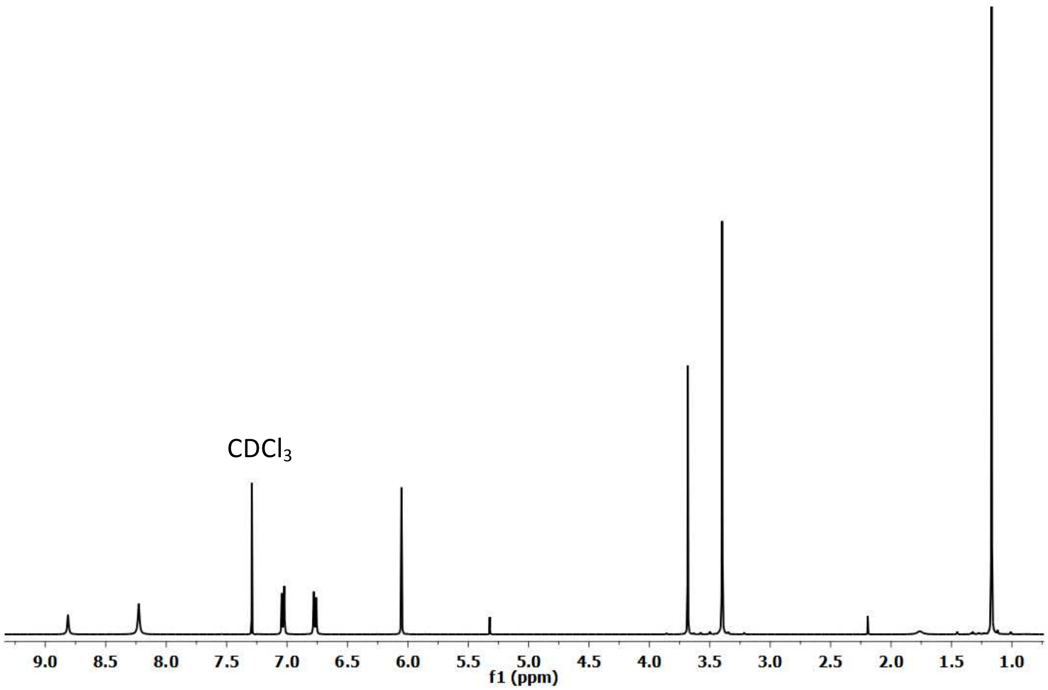


^{13}C-NMR

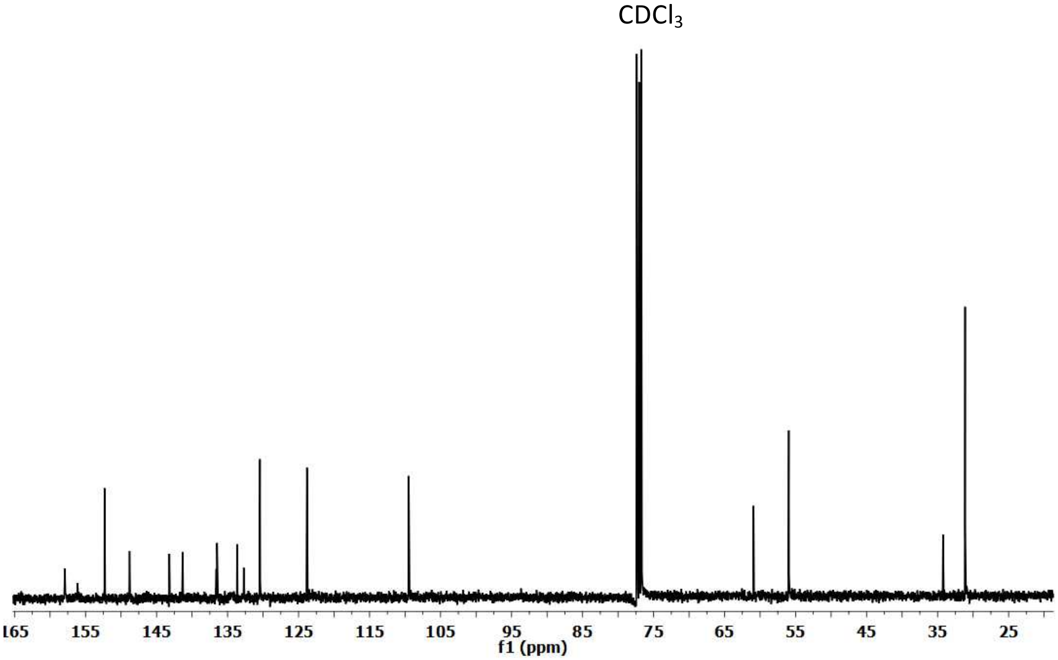


3 in $CDCl_3$

^{1}H –NMR

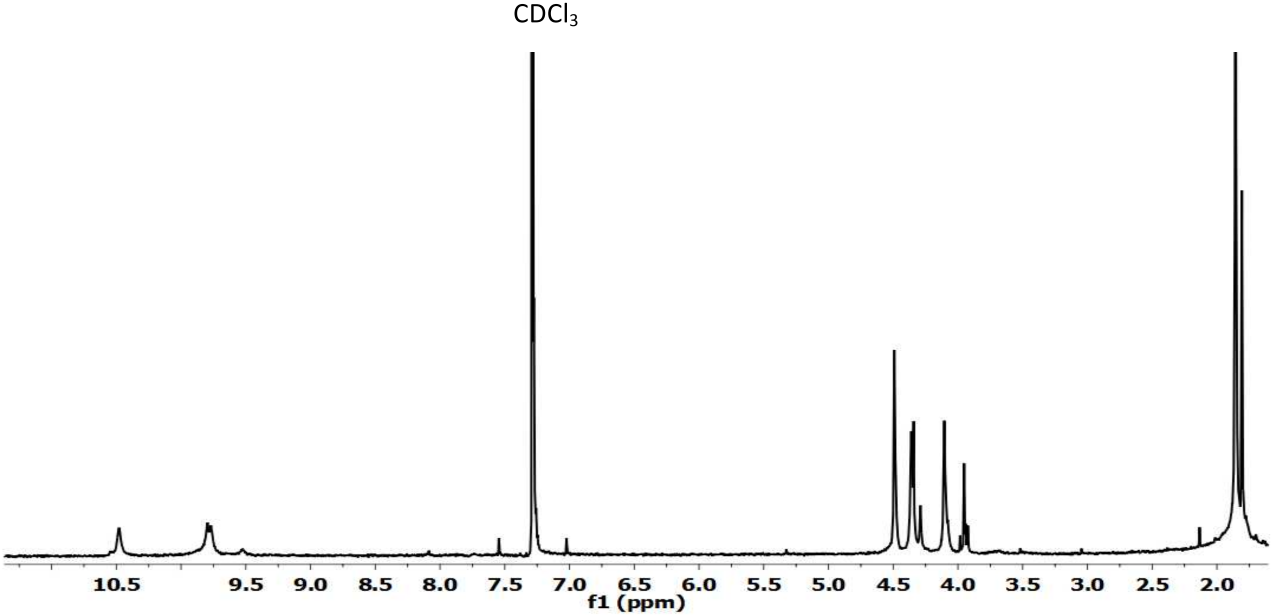


^{13}C-NMR



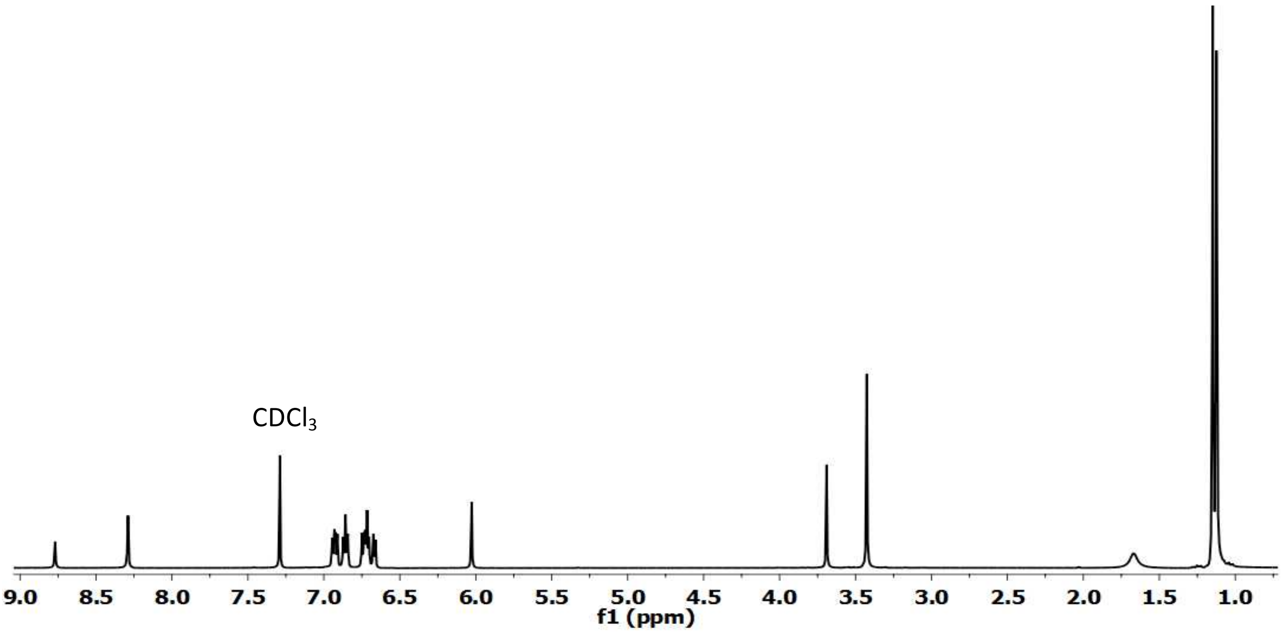
4 in $CDCl_3$

^1H –NMR

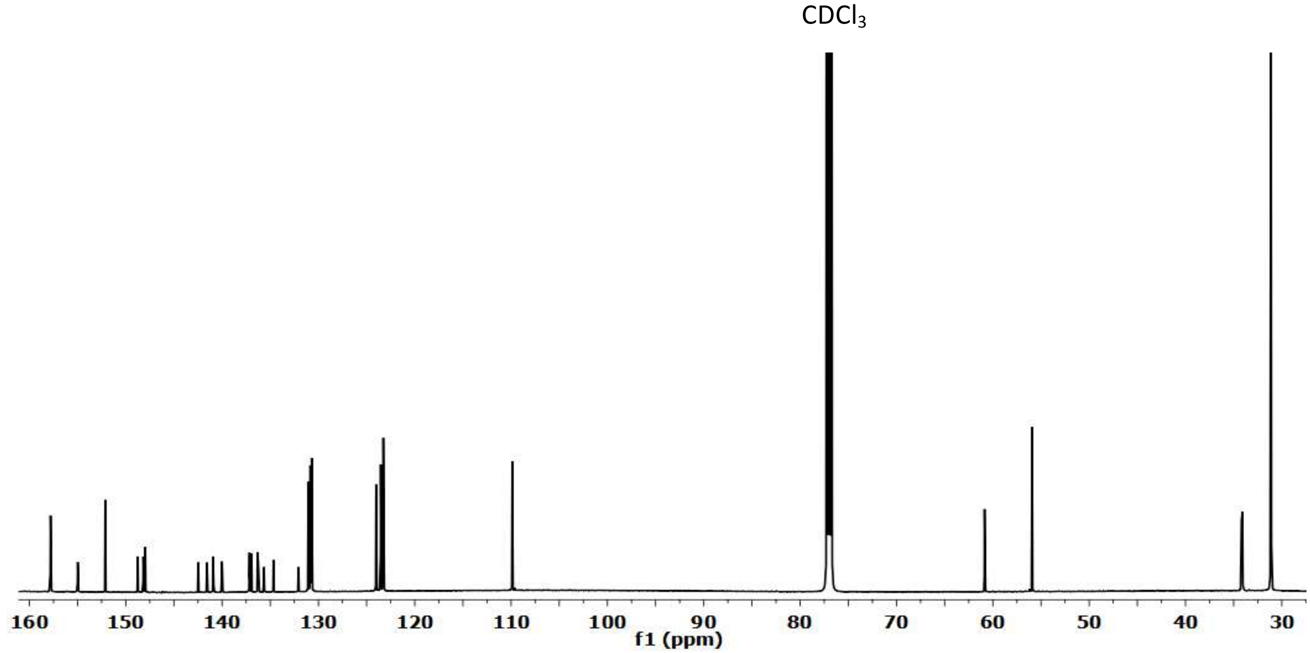


5 in $CDCl_3$

^1H –NMR

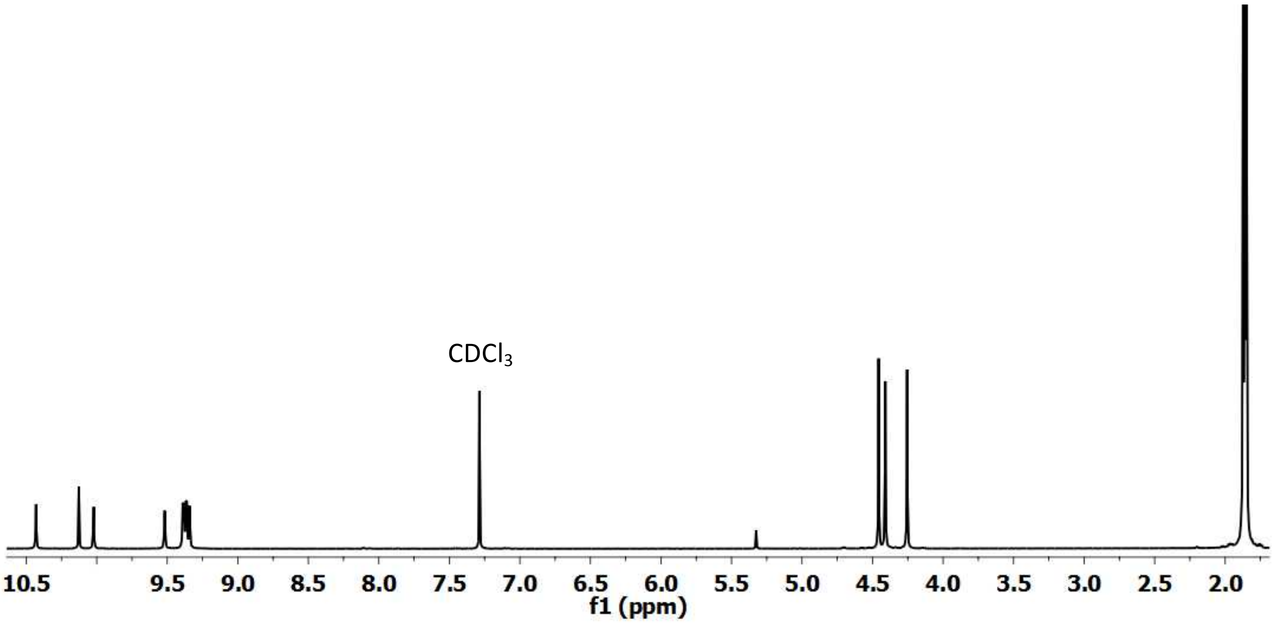


^{13}C-NMR

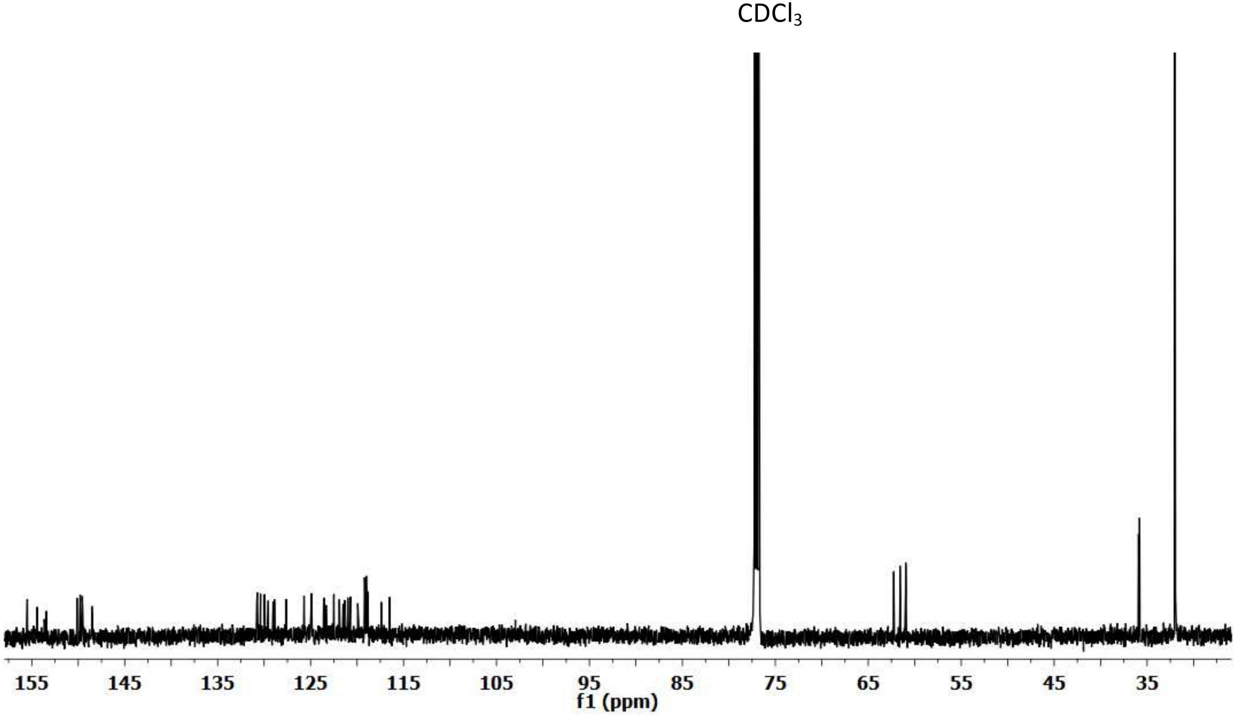


6 in CDCl$_3$

^{1}H –NMR

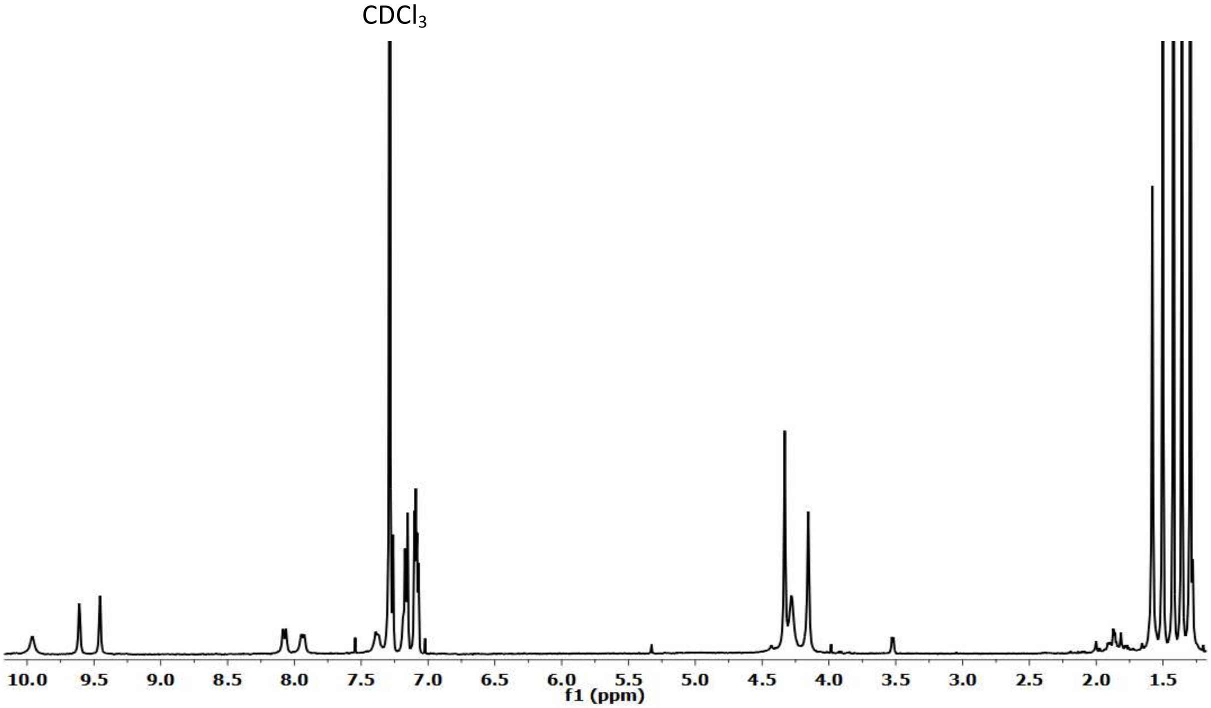


^{13}C-NMR

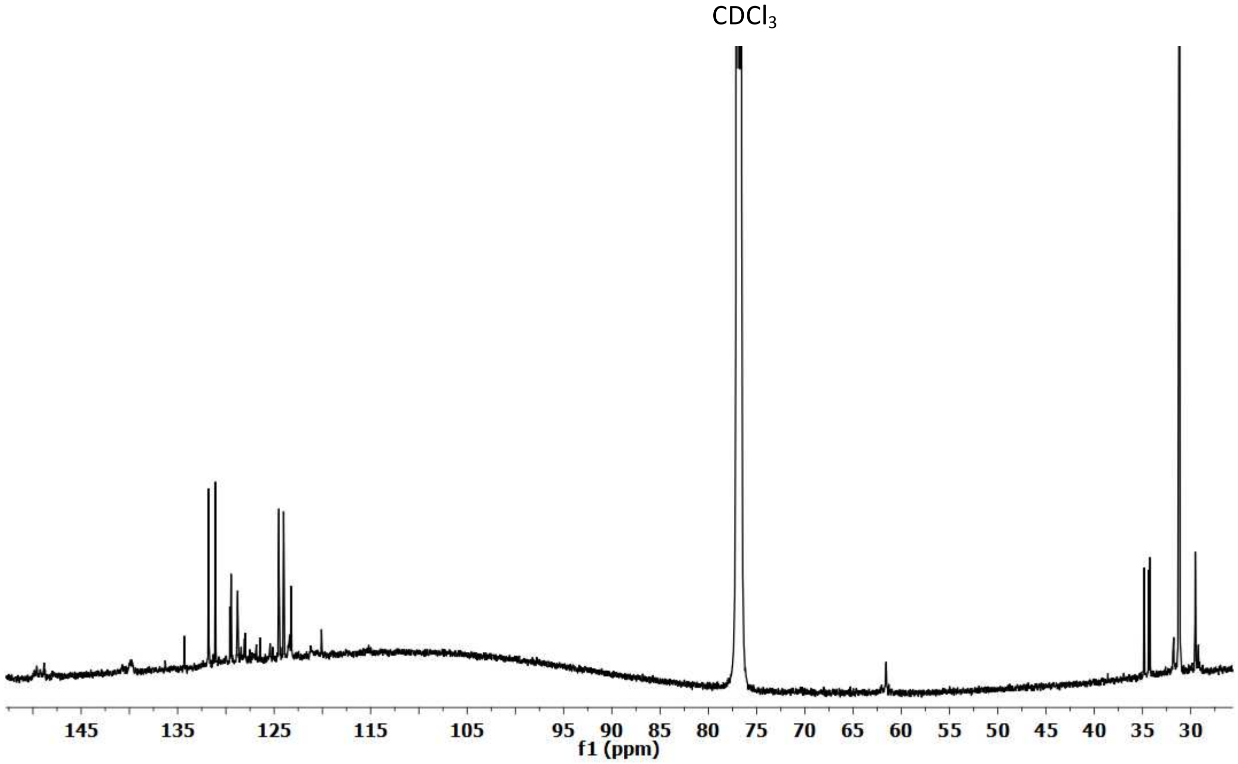


7 in CDCl$_3$

^{1}H –NMR



^{13}C-NMR

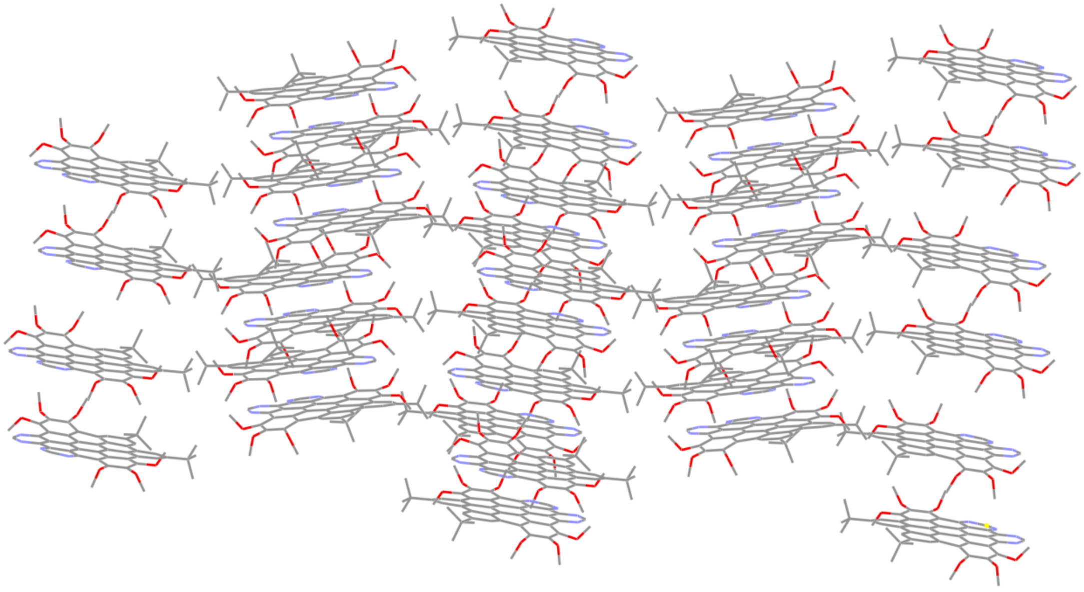


S4. X-ray crystal structures of 2, 3 and 6

S4a: Crystal data and structure refinement for **2**

Identification code	**2**	
Empirical formula	C208 H168 N16 O24	
Formula weight	3275.58	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 7.8968(11) Å	α = 90°.
	b = 31.810(4) Å	β = 105.408(5)°.

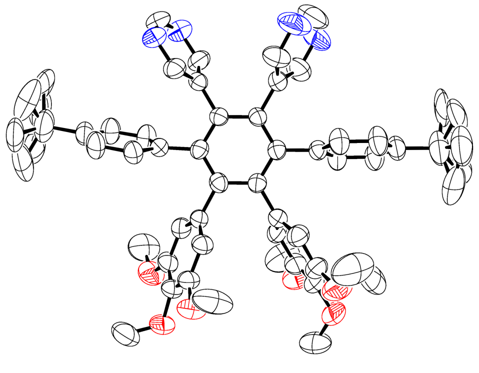
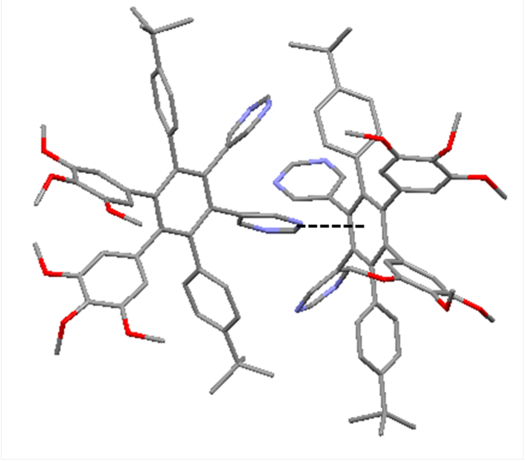
	c = 16.8438(18) Å	γ = 90°.
Volume	4079.0(9) Å^3	
Z	4	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	1720	
Crystal size	0.25 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.79 to 25.00°.	
Index ranges	-9<=h<=9, -37<=k<=37, -18<=l<=20	
Reflections collected	32299	
Independent reflections	7185 [R(int) = 0.0564]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.841579	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7185 / 0 / 571	
Goodness-of-fit on F^2	1.171	
Final R indices [I>2sigma(I)]	R1 = 0.1140, wR2 = 0.2646	
R indices (all data)	R1 = 0.1329, wR2 = 0.2750	
Largest diff. peak and hole	0.733 and -0.385 e.Å^{-3}	



Molecular packing of **2** along ‘a’ axis

S4b: Crystal data and structure refinement for **3**

3 crystallised in the monoclinic P2$_1$/n space group with four molecules in the unit cell. The molecule has a propeller-like structure, with the six aryl substituents twisted at angles varying from 64 - 82° from the plane of the central benzene ring. Molecules of **3** show T-shaped C-H···π interactions (3.409 Å, 70.39°) with one of the pyrimidyl rings and the central phenyl ring of the adjacent molecule. In addition, intermolecular O···H-C and N···H-C interactions contribute to form a self-assembled close packed arrangement.

 Molecular structure of **3**	 T-shaped C-H···π interactions (3.409 Å, 70.39°)

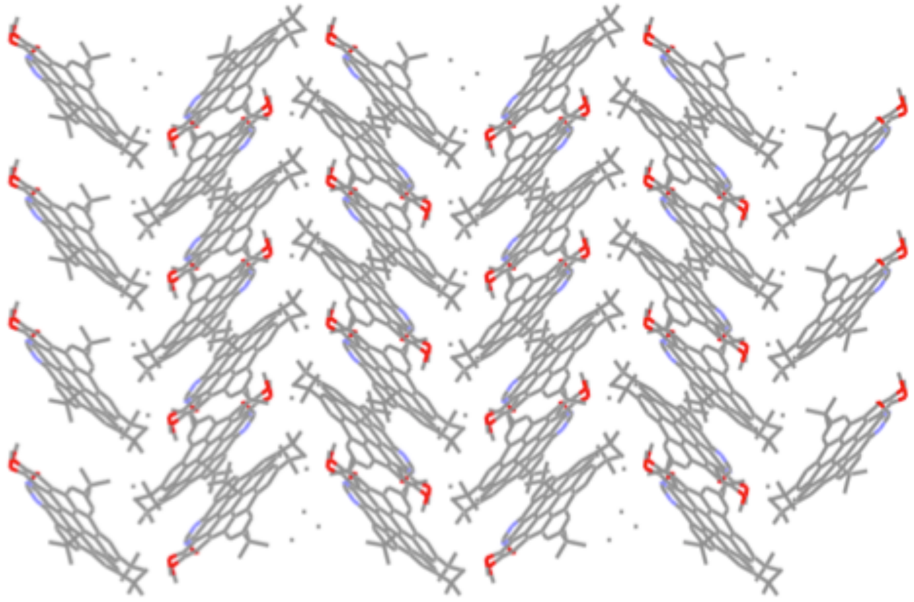
Identification code	**3**	
Empirical formula	C52 H54 N4 O6	
Formula weight	830.99	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.586(12) Å	α = 90°.
	b = 11.951(11) Å	β = 94.14(2)°.
	c = 31.96(3) Å	γ = 90°.
Volume	5176(8) $Å^3$	
Z	4	
Density (calculated)	1.066 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	1768	
Crystal size	0.16 x 0.09 x 0.07 mm^3	
Theta range for data collection	1.67 to 25.26°.	
Index ranges	-16<=h<=16, -14<=k<=14, -38<=l<=37	
Reflections collected	53620	
Independent reflections	9248 [R(int) = 0.1348]	
Completeness to theta = 25.26°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9951 and 0.9889	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9248 / 81 / 625
Goodness-of-fit on F^2	0.912
Final R indices [I>2sigma(I)]	R1 = 0.0732, wR2 = 0.1673
R indices (all data)	R1 = 0.1796, wR2 = 0.2082
Largest diff. peak and hole	0.305 and -0.237 e.Å^{-3}

S4c: Crystal data and structure refinement for **6**

Identification code	**6**	
Empirical formula	C59 H54 N2 O3	
Formula weight	839.04	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 17.8254(6) Å	α= 90°.
	b = 10.8398(4) Å	β= 124.420(2)°.
	c = 29.3462(9) Å	γ = 90°.
Volume	4677.6(3) Å^3	
Z	4	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	0.564 mm^{-1}	
F(000)	1784	
Crystal size	0.16 x 0.14 x 0.08 mm^3	

Theta range for data collection	3.65 to 58.40°.
Index ranges	-19<=h<=14, -10<=k<=11, -23<=l<=32
Reflections collected	15062
Independent reflections	6139 [R(int) = 0.0359]
Completeness to theta = 58.40°	93.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9563 and 0.9151
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6139 / 21 / 623
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0681, wR2 = 0.1911
R indices (all data)	R1 = 0.0802, wR2 = 0.2003
Largest diff. peak and hole	0.693 and -0.358 e.Å^{-3}



Molecular packing of **6** along ‘a’axis

S5. UV-visible absorption spectra

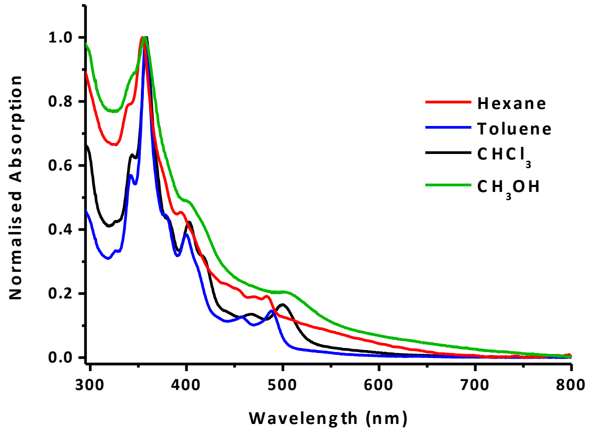
Table S1: Room temperature UV-Visible absorption spectral data ($CHCl_3$, ~10^{-6} M) and electrochemical data for compounds ***2****,* ***4****,* ***6*** *and 7 and reference compound tert-butyl N-HSB.*

Compound	Medium (T/K)	λ_{max} [nm] (ε x 10^4 /M^{-1} cm^{-1})	λ_{em}/nm (λ_{exc}/nm)	τ /ns (λ_{exc} / λ_{em} nm)[b]	Φ_{em}	Oxidation E_{pa}/ V[b]	Reduction $E_{1/2}$/V [ΔE_p/mV][c]
2	$CHCl_3$ (298)	291 (3.5), 342 (3.3), 359 (5.1), 380 (2.2), 404 (2.2), 417 (1.8), 468 (0.6), 500 (0.9)	554_{max} (360)	5.1 (340/554)	0.32	+0.65, +0.82, +1.03	-1.62 [79], -1.80 [78], -1.94 [89]
	C_4H_7N (77)	-	472, 482_{sh}, 505, 572_{max}, 622 (360)	41.1 (340/570)			
4	$CHCl_3$ (298)	290 (3.2), 343 (3.3), 359 (5.1), 380 (2.2), 403 (2.2), 417 (1.8), 470 (0.6), 500 (0.9)	550_{max} (360)	-	0.28	-	-
6	$CHCl_3$ (298)	297 (3.2), 328 (2.6), 343 (5.9), 359 (13.4), 377 sh (5.6), 396 (3.0), 448 (1.0), 477 (1.0)	483_{max}, 516, 552 (360)	8.3 (340/ 483)	0.53	+0.78, +0.997 [79]d	-2.02 [89], -2.34
	C_4H_7N (77)	-	476_{max}, 508, 545_{wk}, 566, 612 (400)	21.9 (340/ 470)			
7	$CHCl_3$ (298)	308 (6.8), 339_{sh} (3.7), 400 (1.7), 426 (1.4)	453_{max}, 487, 522_{sh}, (360)	7.9 (340/487)	0.21	+0.86	-2.10 [95]
	C_4H_7N (77)	-	428_{max}, 454, 473, 505, 570, 614_{wk} (360)	22.8 (340/475)			
tert-butyl **N-HSB** (4N)	Toluene (298)	290 (5), 323 (2.6), 339 (5.7) , 355 (13.7), 377 (35.4), 394 (3.2), 415 (1.5), 452 (1.0), 481(1.4)	494_{max}, 524_{sh}	13 (340/ 494)	0.4	+0.9	-1.56 [320], -2.00 [330]

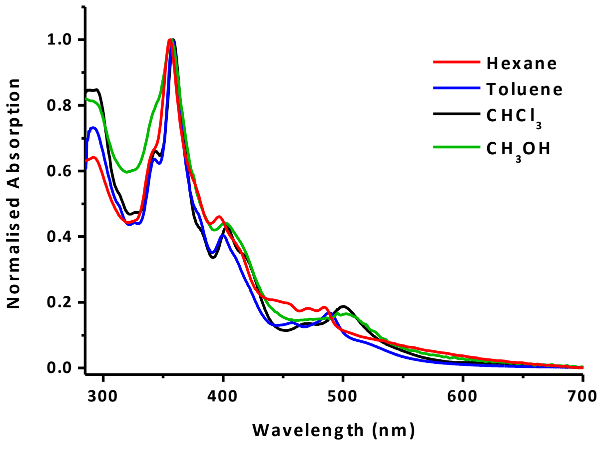
[a] In deoxygenated dichloromethane (0.1 M, $^nBu_4NPF_6$) at 298K, scan rate = 100 mVs^{-1}, reported vs. Fc/Fc^+; [b] Irreversible oxidation process, E_{pa}/V (anodic peak potential) quoted; [c] $\Delta E_p = E_{pa}-E_{pc}$, peak potential separation.; [d] Reversible oxidation process, $E_{1/2}$ /V [ΔE_p/mV] quoted.

Solvent dependency studies of **2**, **4**, **6** and **7**

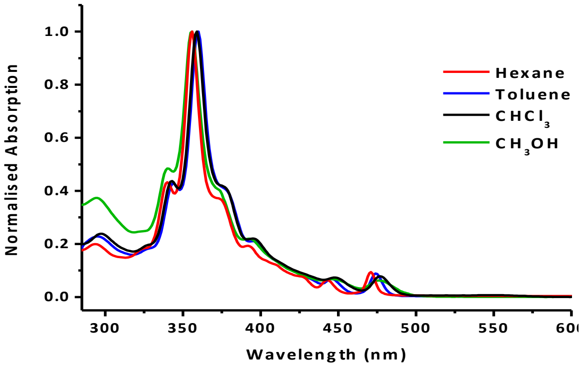
a) Compound **2**



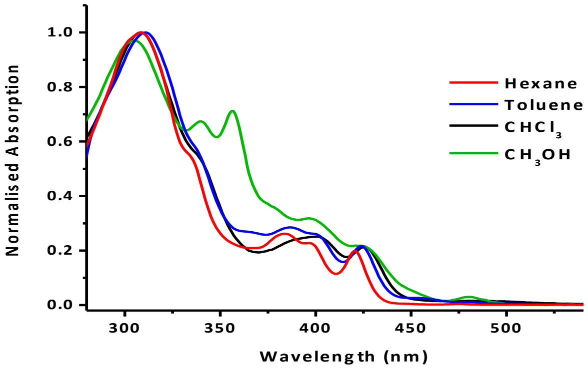
b) Compound **4**



c) Compound **6**



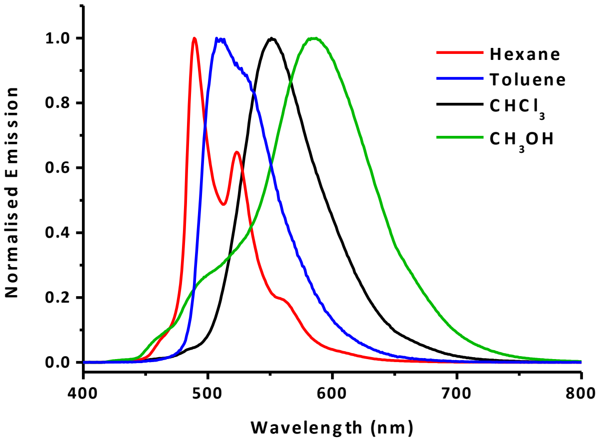
d) Compound **7**



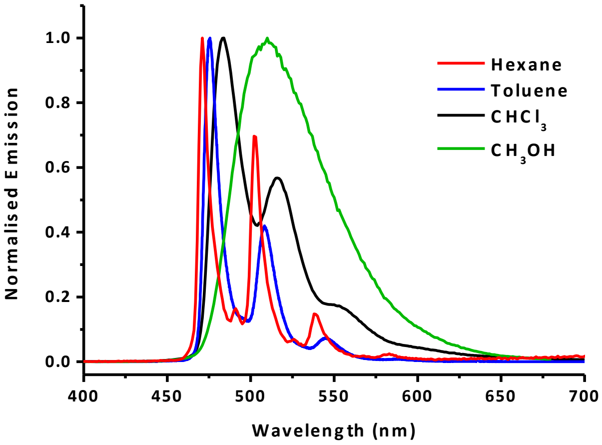
S6. Emission Spectra of 2, 6 and 7

Solvent dependency studies of **2**, **6** and **7**

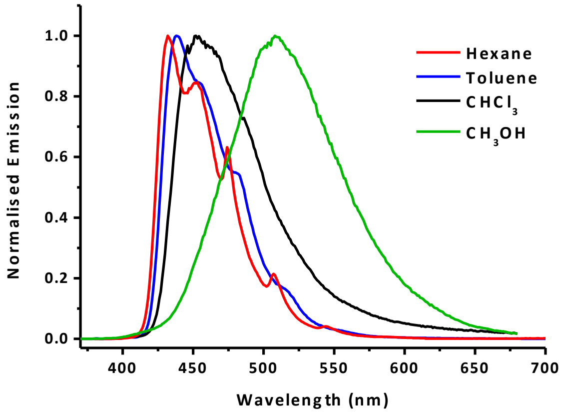
a) Compound **2**



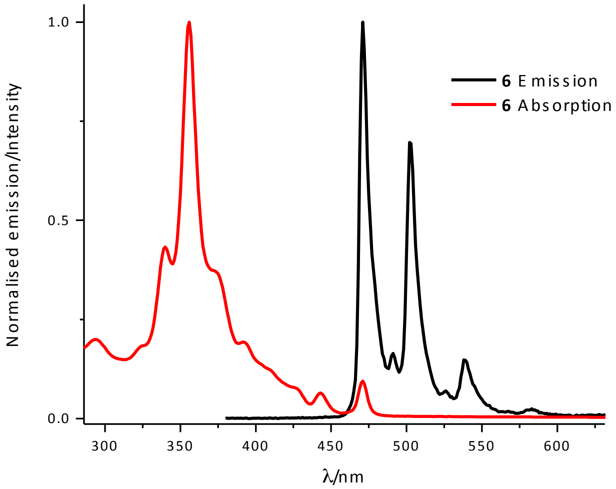
b) Compound **6**



c) Compound **7**



(d) Compound **6**, absorption and emission in chloroform, showing the clear 0-0 transition.



S7. References:

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