

Electronic Supporting Information

for

Redox-dependent self-sorting toggles a rotary nanoswitch

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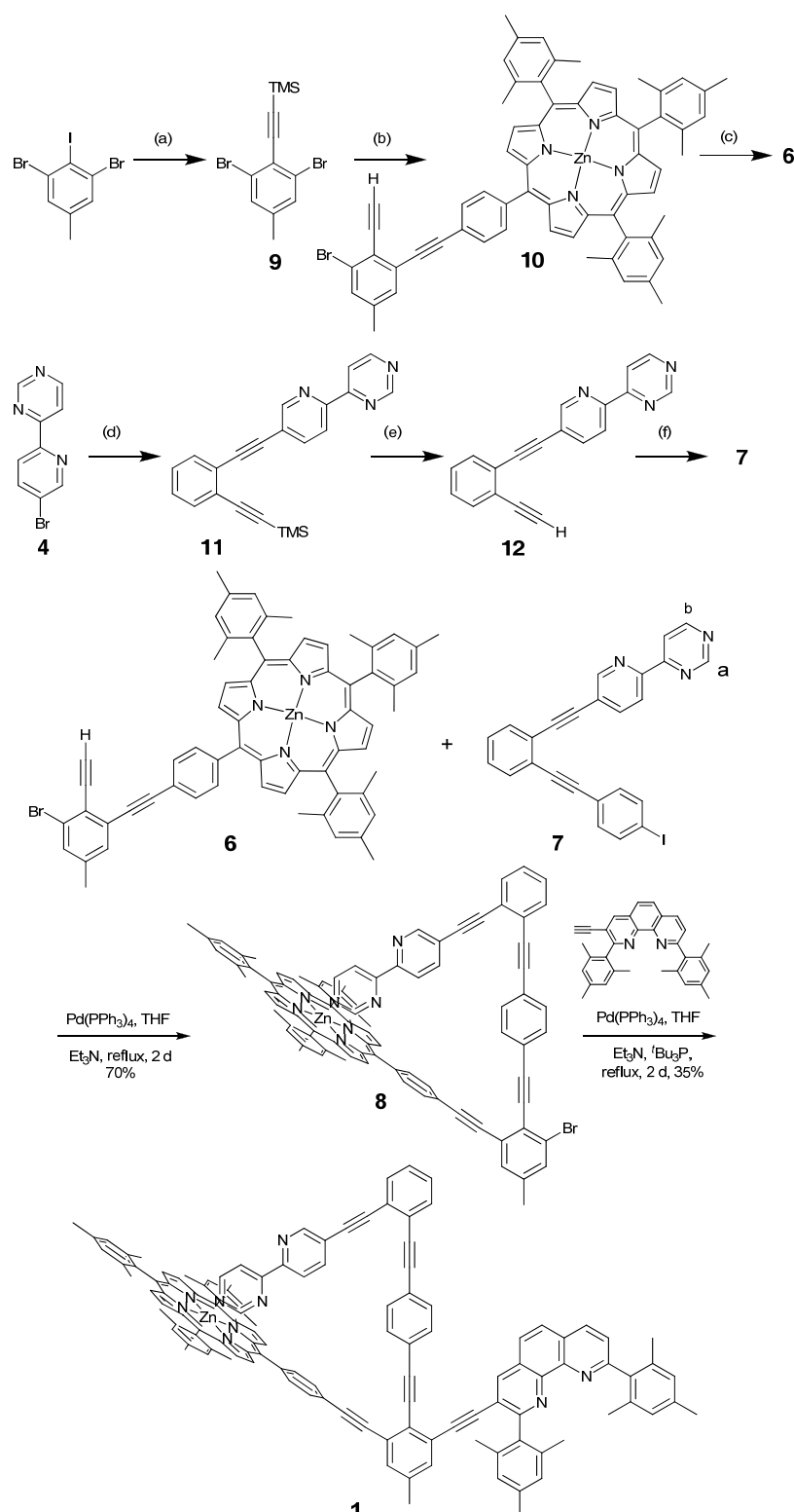
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General Information

Synthesis and Characterisation

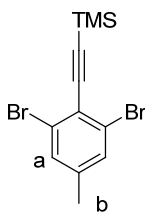
The commercially available reagents were used without any further purification. All solvents were distilled prior to use for column chromatography. Thin-layer chromatography (tlc) was performed using tlc plates (silica gel 60 F₂₅₄, Merck). Silica gel 60 was used for column chromatography. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer using the deuterated solvent as the lock and residual protiated solvent as the internal reference. In the assignments, the chemical shift (in ppm) is given first, followed by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublet of doublets, dt: doublet of triplets, m: multiplet), the number of protons implied, the value of the coupling constants in Hertz if applicable, and finally the assignment of the proton where ever possible. The numbering of the carbon atoms in the molecular formulae shown in the experimental section is only used for the assignment of the NMR signals and is not in accordance with the IUPAC nomenclature rules. Anhydrous tetrahydrofuran (THF) and benzene were distilled over potassium. Diethyl ether was distilled over sodium/benzophenone. Triethyl amine and DMF were dried over calcium hydride. The melting points of compounds were measured on a Büchi melting point apparatus (BÜCHI 510) and were uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1750. Electro spray ionisation mass spectra (ESI-MS) were recorded using a Thermo-Quest LCQ Deca. Microanalyses were performed on a Euro elemental analyzer from EuroVector. Absorption spectra were taken on a Cary 100 UV spectrophotometer in quartz cuvettes with 1 cm length.

Synthesis - Overview



Scheme S1. Synthesis of compounds **6** and **7**. (a) TMSA, $\text{Pd(PPh}_3)_4$, CuI, C_6H_6 , Et_3N , 80 °C, 8 h, 87%; (b) zinc(II)-5-(4-ethynylphenyl)-10,15,20-trimesitylporphyrin, $\text{Pd(PPh}_3)_4$, DMF, Et_3N , 80 °C, 2 d, 70%; (c) THF-MeOH, aq. KOH, rt, 24 h, 98%; (d) ((2-ethynylphenyl)ethynyl)trimethylsilane, $\text{Pd(PPh}_3)_4$, DMF, Et_3N , 80 °C, 18 h, 94%; (e) THF, MeOH, aq. KOH, 12 h, 93%; (f) 1,4-diiodobenzene, $\text{Pd(PPh}_3)_4$, DMF, Et_3N , 80 °C, 2 d, 58%. The transformation of **6** + **7** to **1** has been described earlier.¹

[(2,6-Dibromo-4-methylphenyl)ethynyl]trimethylsilane (9)²



1,3-Dibromo-2-iodo-5-methylbenzene (5.00 g, 13.3 mmol), cuprous iodide (50.0 mg, 26.3 μmol) and tetrakis(triphenylphosphine)palladium (100 mg, 86.5 μmol) were loaded in a Schlenk tube under nitrogen atmosphere. Then dry benzene (20 mL), dry triethylamine (20 mL), and trimethylsilylacetylene (9.25 mL, 65.5 mmol) were added under a steady flow of nitrogen. The flask was sealed and heated at 80 °C for 8 h. The reaction mixture was cooled to room temperature, then the solvents were evaporated. The solid part was dissolved in DCM and washed with water. The organic layer was separated and dried over sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by chromatography on silica using hexane ($R_f = 0.4$) as eluent.

Yield: 4.01g (11.6 mmol, 87%)

Melting point: 75 °C.

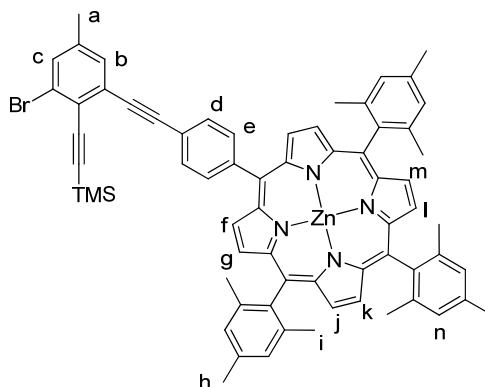
IR (KBr): ν 3060, 2959, 2899, 2164, 1727, 1593, 1527, 1451, 1381, 1334, 1251, 1189, 1044, 900, 880, 763, 711, 633, 589, 565, 538, 453 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 0.29 (s, 9 H, TMS-H), 2.29 (s, 3 H, b-H), 7.35 (d, $^4J = 0.4$ Hz, 2 H, a-H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ -0.2, 20.8, 101.7, 104.1, 124.0, 126.1, 131.9, 140.7 ppm.

Elemental analysis (C₁₂H₁₄Br₂Si•0.2 CH₃COCH₃): Calcd. C, 42.46; H, 4.33. Found C, 42.41; H, 4.08.

Zinc(II)-5-(4-(6-bromo-4-methyl-2-ylethynyl)ethynyltrimethylsilane)phenyl-10,15,20-trimesitylporphyrin (10**)³**



Zinc(II)-5-(4-ethynylphenyl)-10,15,20-trimesitylporphyrin (550 mg, 664 μmol) and **9** (460 mg, 1.33 mmol) were placed in a three-neck round-bottom flask under argon atmosphere. After addition of dry DMF (30 mL) and dry triethylamine (30 mL), the mixture was deaerated and tetrakis(triphenylphosphine)palladium (40.0 mg, 34.6 μmol) was added as solid. The reaction mixture was heated at 80 $^{\circ}\text{C}$ for 48 hours, after which it was evaporated to dryness under vacuum. The residue obtained was dissolved in 50 mL of DCM, washed with water (2×30 mL) and dried over sodium sulfate. The resulting solid obtained after evaporating the solvents was chromatographed ($R_f = 0.4$ in 50% DCM in hexane) over silica gel using 10% DCM in hexane as eluent to furnish the required product **10** as a violet solid. The compound was finally purified by bio-beads SX-3 (BioRad) using toluene as eluent (2nd fraction).

Yield: 510 mg (466 μmol , 70%)

Melting point: > 300 $^{\circ}\text{C}$.

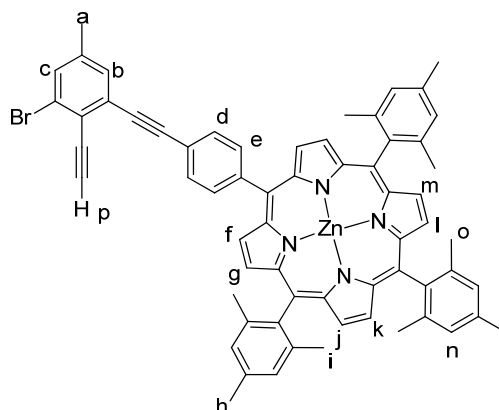
IR (KBr): ν 2917, 2853, 2731, 2361, 2210, 2157, 1593, 1523, 1478, 1446, 1376, 1335, 1250, 1204, 1102, 1062, 998, 953, 851, 798, 759, 722, 684 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 0.43 (s, 9 H, TMS-H), 1.81 (bs, 18 H, i-H), 2.43 (s, 3 H, a-H), 2.66 (s, 9 H, h-H), 7.30 (bs, 6 H, n-H), 7.49 (bs, 2 H, b-, c-H), 7.96 (d, $^3J = 8.0$ Hz, 2 H, d/e-H), 8.18 (d, $^3J = 8.0$ Hz, 2 H, e/d-H), 8.69 (bs, 4 H, j-, k-, l-, m-H), 8.74 (d, $^3J = 4.4$ Hz, 2 H, f-H), 8.83 (d, $^3J = 4.4$ Hz, 2 H, g-H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 0.1, 21.1, 21.5, 21.6, 21.7, 29.7, 88.8, 94.0, 102.0, 103.4, 118.6, 118.7, 118.9, 122.0, 124.7, 125.7, 127.6 (3 C), 127.7, 129.9, 130.6, 131.0, 131.1, 131.2, 131.7, 132.9, 134.3, 137.4, 138.9, 139.0, 139.2 (2 C), 139.4, 143.5, 149.4, 149.6, 149.7, 149.8 ppm.

Elemental analysis ($\text{C}_{67}\text{H}_{59}\text{N}_4\text{ZnBrSi}$): Calcd. C, 73.58; H, 5.44; N, 5.12. Found C, 73.89; H, 5.84; N, 5.12.

Zinc(II)-5-(4-(3-bromo-2ethynyl-4-methyl-1-ylethynyl)benzene)phenyl-10,15,20-trimesitylporphyrin (6)



Compound **10** (450 mg, 411 μmol) was dissolved in a mixture of methanol (30 mL) and THF (50 mL) in a 250 mL round-bottom flask. A 1 N solution of KOH in water (30 mL) was added slowly. After stirring for 24 h at room temperature, the solution was neutralised with saturated NH_4Cl and extracted with DCM (3×50 mL). The organic layer was dried over sodium sulfate. After removing the solvent under reduced pressure, the desired product **6** was afforded as a violet solid.

Yield: 410 mg (401 μmol , 98%)

Melting point: > 300 $^\circ\text{C}$.

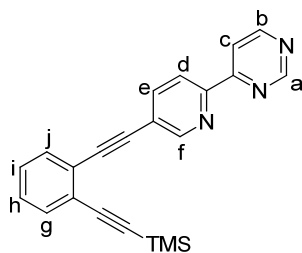
IR (KBr): ν 3096, 2965, 2916, 2210, 1812, 1602, 1594, 1524, 1478, 1445, 1377, 1336, 1204, 1063, 998, 799, 723, 649, 644, 560, 418 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 1.85 (s, 12 H, i-H), 1.86 (s, 6 H, o-H), 2.42 (s, 3 H, a-H), 2.64 (s, 9 H, h-H), 3.77 (s, 1 H, p-H), 7.29 (s, 6 H, n-H), 7.48 (bs, 2 H, b-,c-H), 7.94 (d, $^3J = 8.0$ Hz, 2 H, d/e-H), 8.24 (d, $^3J = 8.0$, 2 H, e/d-H), 8.72 (s, 4 H, j-, k-, l-, m-H), 8.79 (d, $^3J = 4.8$ Hz, 2 H, g-H), 8.88 (d, $^3J = 4.8$ Hz, 2 H, f-H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 21.1, 21.5, 21.7, 21.8, 29.7, 81.0, 85.2, 88.4, 94.2, 118.0, 119.0 (2 C), 121.9, 125.8, 127.6 (2 C), 128.2, 130.0, 130.8, 131.1, 131.2, 131.4, 131.8, 133.0, 134.4, 137.4 (2 C), 137.9, 138.9, 139.0, 139.3 (2 C), 140.0, 143.6, 149.6, 149.7, 149.9, 150.0 ppm.

Elemental analysis ($\text{C}_{64}\text{H}_{51}\text{N}_4\text{ZnBr} \cdot 0.5 \text{ MeOH}$): Calcd. C, 74.67; H, 5.15; N, 5.40. Found C, 74.91; H, 5.55; N, 5.16.

4-(5-((2-((Trimethylsilyl)ethynyl)phenyl)ethynyl)pyridin-2-yl)pyrimidine (11)



((2-Ethynylphenyl)ethynyl)trimethylsilane⁴ (140 mg, 706 μmol) and 4-(5-bromopyridin-2-yl)pyrimidine⁵ (163 mg, 690 μmol) were placed into a three-neck round-bottom flask under nitrogen atmosphere. 20 mL of dry DMF and 20 mL of dry triethylamine were added. After deaerating the solution by bubbling nitrogen through it for 1 h, solid tetrakis(triphenylphosphine)palladium (40.0 mg, 34.6 μmol) was added and the reaction mixture was heated at 80 °C for 18 h. Solvents were evaporated, then DCM and water were added. The layers were separated and the aqueous layer was extracted with dichloromethane (3 \times 30 mL). The solution was evaporated to dryness and the solid part was purified (R_f = 0.4 in 10% EtOAc in DCM) by column chromatography using 3% ethyl acetate in DCM as eluent.

Yield: 230 mg (651 μmol , 94%)

Melting point: 90 - 92 °C.

IR (KBr): ν 3055, 3024, 2957, 2923, 2851, 2216, 2157, 1956, 1642, 1579, 1529, 1456, 1390, 1309, 1247, 1161, 1096, 1022, 991, 872, 841, 751, 698, 667, 524, 495 cm^{-1} .

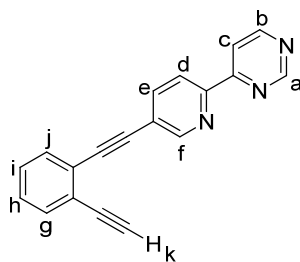
¹H NMR (400 MHz, CDCl₃): δ 0.28 (s, 9 H, SiMe₃), 7.31-7.33 (m, 2 H, g-, j-H), 7.52-7.57 (m, 2 H, h, i-H), 7.99 (dd, ³ J = 8.4 Hz, ⁴ J = 2.4 Hz, 1 H, e-H), 8.39 (d, ³ J = 4.8 Hz, 1 H, b-H), 8.51 (d, ³ J = 8.4 Hz, 1 H, d-H), 8.86-8.89 (m, 2 H, f-, c-H), 9.30 (bs, 1 H, a-H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 0.0, 89.7, 93.4, 99.2, 103.1, 117.7, 121.0, 122.3, 125.0, 125.9, 128.3, 128.7, 131.9, 132.4, 139.6, 151.9, 152.4, 158.1, 158.7, 162.0 ppm.

Mass Spectrum (ESI): [C₂₂H₁₉N₃Si + H⁺] Calcd. m/z = 354.1. Found m/z = 354.3.

Elemental analysis (C₂₂H₁₉N₃Si•0.5THF): Calcd. C, 74.00; H, 5.95; N, 10.79. Found C, 74.37; H, 5.79; N, 10.63.

4-(5-((2-Ethynylphenyl)ethynyl)pyridin-2-yl)pyrimidine (12)



Compound **11** (230 mg, 651 μmol) was dissolved in 50 mL of THF. 1 N KOH in methanol (30 mL) was added and the mixture stirred for 12 h at room temperature. The solvents were evaporated and the solid residue was dissolved in dichloromethane (50 mL). Water was added and the organic layer was separated. After extraction of the aqueous phase, the combined organic layers were evaporated to dryness to afford the product as yellow solid.

Yield: 170 mg (604 μmol , 93%).

Melting point: > 300 $^{\circ}\text{C}$.

IR (KBr): ν 3055, 3024, 2955, 2922, 2802, 2215, 2153, 1569, 1526, 1453, 1386, 1306, 1245, 1156, 1092, 1020, 874, 843, 756, 697, 662, 641, 595 cm^{-1} .

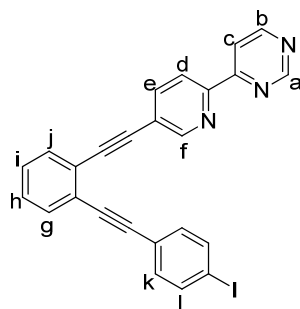
^1H NMR (400 MHz, CDCl_3): δ 3.41 (s, 1 H, k-H), 7.33-7.40 (m, 2 H, g-, j-H), 7.56-7.60 (m, 2 H, h-, i-H), 8.00 (dd, $^3J = 8.4$ Hz, $^4J = 2.4$ Hz, 1 H, e-H), 8.38 (dd, $^3J = 5.6$ Hz, $^4J = 1.2$ Hz, 1 H, b-H), 8.51 (dd, $^3J = 8.4$ Hz, $^5J = 0.8$ Hz, 1 H, d-H), 8.87-8.89 (m, 2 H, f-, c-H), 9.30 (d, $^4J = 1.2$ Hz, 1 H, a-H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 81.6, 81.9, 89.9, 93.0, 117.6, 121.0, 122.2, 124.9, 125.3, 128.7, 128.8, 131.9, 132.7, 139.6, 152.1, 152.5, 158.1, 158.7, 162.0 ppm.

Mass Spectrum (ESI): $[\text{C}_{19}\text{H}_{11}\text{N}_3 + \text{H}^+]$ Calcd. $m/z = 282.1$. Found $m/z = 282.3$.

Elemental analysis ($\text{C}_{19}\text{H}_{11}\text{N}_3 \cdot 0.166 \text{ CH}_2\text{Cl}_2$): Calcd. C, 77.91; H, 3.87; N, 14.22. Found C, 78.14; H, 3.77; N, 13.90.

4-(5-((2-((4-Iodophenyl)ethynyl)phenyl)ethynyl)pyridin-2-yl)pyrimidine (7)



Compound **12** (150 mg, 533 μmol) and 1,4-diiodobenzene (1.76 g, 5.33 mmol) were dissolved in dry DMF (25 mL) and dry triethylamine (25 mL) in a 100 mL three-neck round-bottom flask equipped with a reflux condenser under nitrogen atmosphere. After the solvent had been deaerated with nitrogen for 1 h, tetrakis(triphenylphosphine)palladium (50.0 mg, 43.2 μmol) was added and heated at 80 $^{\circ}\text{C}$ for 2 days. The solvents were removed under reduced pressure and residue was dissolved in dichloromethane (50 mL). The organic layer was washed with water, dried over sodium sulfate, and evaporated to dryness. The solid residue was purified (R_f = 0.4 in 10% EtOAc in DCM) using column chromatography (2% ethyl acetate in dichloromethane) to furnish the pure product **7** as a yellow solid.

Yield: 150 mg (310 μmol , 58%).

Melting point: Decomposition > 204 $^{\circ}\text{C}$.

IR (KBr): ν 3042, 2360, 2337, 2217, 1944, 1896, 1734, 1637, 1578, 1528, 1488, 1456, 1388, 1313, 1226, 1121, 1056, 1006, 949, 836, 812, 781, 687, 666, 487 cm^{-1} .

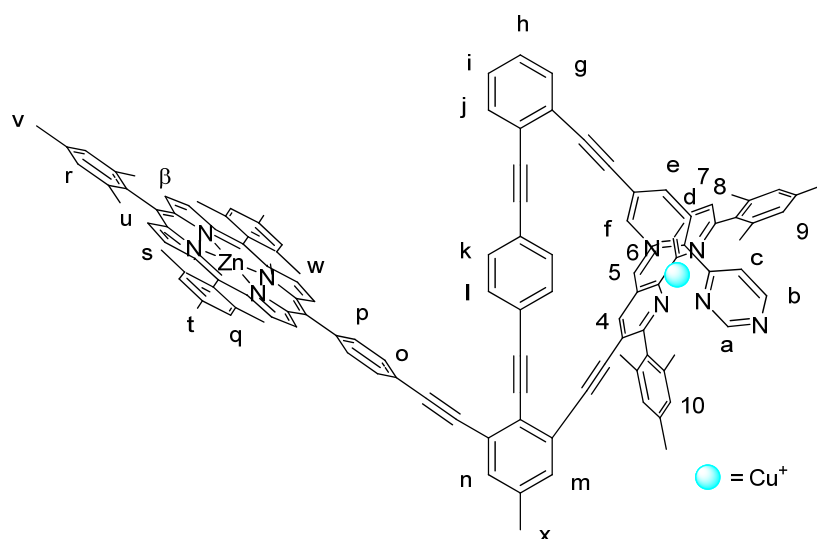
^1H NMR (400 MHz, CDCl_3): δ 7.28 (d, 3J = 8.4 Hz, 2 H, k/l-H), 7.35-7.40 (m, 2 H, g-, j-H), 7.58-7.62 (m, 2 H, h-, i-H), 7.71 (d, 3J = 8.4 Hz, 2 H, l/k-H), 7.98 (dd, 3J = 8.4 Hz, 4J = 2.0 Hz, 1 H, e-H), 8.40 (d, 3J = 5.2 Hz, 1 H, b-H), 8.51 (d, 3J = 8.4 Hz, 1 H, d-H), 8.86 (bs, 1 H, f-H), 8.89 (d, 3J = 5.2 Hz, 1 H, c-H), 9.31 (bs, 1 H, a-H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 89.3, 90.0, 93.0, 93.3, 94.7, 117.6, 121.0, 122.2, 122.5, 124.8, 125.7, 128.4, 128.9, 132.0, 132.1, 133.0, 137.7, 139.5, 151.9, 152.6, 158.1, 158.8, 161.9 ppm.

Mass Spectrum (ESI): $[\text{C}_{25}\text{H}_{14}\text{IN}_3 + \text{H}^+]$ Calcd. m/z = 484.0. Found m/z = 483.9.

Elemental analysis ($\text{C}_{25}\text{H}_{14}\text{N}_3\text{I}$): Calcd. C, 62.13; H, 2.92; N, 8.69. Found C, 62.26; H, 2.89; N, 8.49.

Complex [Cu(1)]PF₆ (complex published by us earlier,^{1b} data given for comparison)



CD₂Cl₂ was added to a 1:1 mixture of [Cu(CH₃CN)₄]PF₆ and **1**.^{1b} The mixture was sonicated for 2-3 min. and then analysed by NMR, ESI-MS and UV-vis.

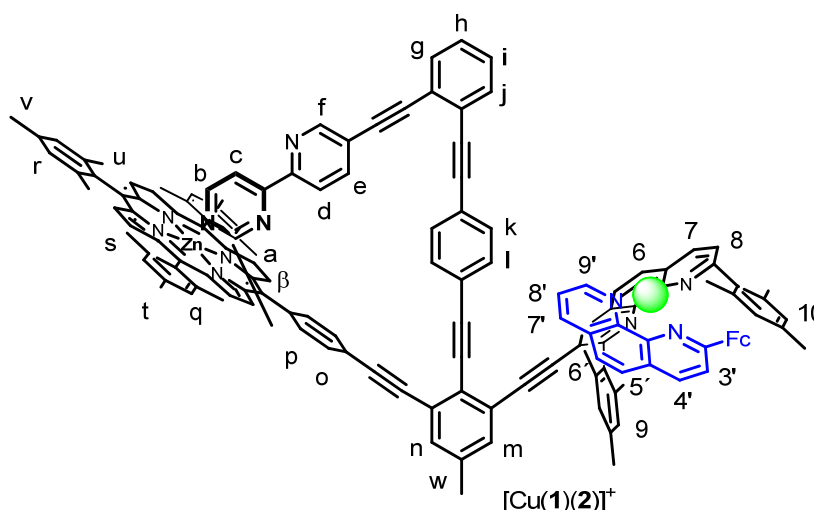
Yield: Quantitative. Melting point: Above 300 °C.

¹H NMR (400 MHz, CD₂Cl₂): δ = 1.09 (s, 3 H, CH₃), 1.64 (s, 3 H, CH₃), 1.71 (s, 3 H, CH₃), 1.79 (s, 6 H, s/w-H), 1.80 (s, 6 H, w/s-H), 1.82 (s, 6 H, u-H), 1.84 (s, 3 H, CH₃), 1.86 (s, 3 H, CH₃), 1.94 (s, 3 H, CH₃), 2.42 (s, 3 H, x-H), 2.61 (s, 9 H, v-, t-H), 5.93 (s, 1 H, 9/10-H), 6.16 (s, 1 H, 9/10-H), 6.26 (s, 1 H, 9/10-H), 6.37 (s, 1 H, 9/10-H), 7.28-7.31 (m, 10 H, q-, r-, a-, b-, k/l-H), 7.37-7.39 (m, 5 H, h-, i-, m/n-, l/k-H), 7.46-7.49 (m, 1 H, g/j-H), 7.54 (s, 1 H, n/m-H), 7.61-7.63 (m, 1 H, j/g-H), 7.67 (d, ³*J* = 4.8 Hz, 1 H, c-H), 7.85 (d, ³*J* = 8.4 Hz, 1 H, 8-H), 7.88 (d, ³*J* = 8.4 Hz, 1 H, d-H), 7.90 (d, ³*J* = 8.4 Hz, 2 H, o/p-H), 8.10 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.0 Hz, 1 H, e-H), 8.13 (s, 1 H, f-H), 8.20 (d, ³*J* = 8.4 Hz, 2 H, p/o-H), 8.21 (d, ³*J* = 8.8 Hz, 1 H, 5/6-H), 8.24 (d, ³*J* = 8.8 Hz, 1 H, 6/5-H), 8.67 (d, ³*J* = 8.4 Hz, 1 H, 7-H), 8.68 (d, ³*J* = 4.4 Hz, 2 H, β -H), 8.70 (d, ³*J* = 4.4 Hz, 2 H, β -H), 8.72 (d, ³*J* = 4.4 Hz, 2 H, β -H), 8.84 (d, ³*J* = 4.4 Hz, 2 H, β -H), 9.00 (s, 1 H, 4-H) ppm.

ESI-MS: *m/z* (%): 1799.4 (100) [Cu(**1**)]⁺. calcd 1799.6; see also Figure S21.

UV-Vis absorption: λ_{max} = 422 nm, ϵ = 5.09 × 10⁵ L mol⁻¹ cm⁻¹ (Soret band).

Complex $[\text{Cu(1)(2a)}]^+$ (complex published by us earlier,⁶ data given for comparison)



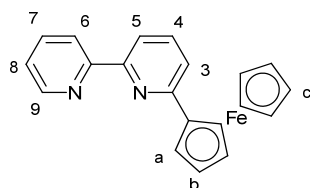
$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ was added to a CD_2Cl_2 solution of 2-ferrocenyl-1,10-phenanthroline (2a) and compound **1** in a 1:1.1 ratio. The purple solution was analysed by NMR without purification.

Yield: Quantitative. **MP:** Above 300 °C.

^1H NMR (400 MHz, CD_2Cl_2): δ 1.64 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 1.81 (s, 3 H, CH_3), 1.84 (s, 9 H, CH_3 -, u-H), 1.86 (s, 12 H, s-H), 1.88 (s, 3 H, CH_3), 2.27 (s, 3 H, w-H), 2.59 (s, 6 H, t-H), 2.61 (s, 3 H, v-H), 2.87 (d, $^3J = 5.6$ Hz, 1 H, b-H), 3.31 (d, $^3J = 1.2$ Hz, 1 H, a-H), 3.64-3.65 (m, 1 H, Fc-H), 3.71-3.73 (m, 1 H, Fc-H), 3.90 (s, 5 H, Fc-H), 4.22-4.23 (m, 1 H, Fc-H), 4.26-4.28 (m, 1 H, Fc-H), 6.11 (s, 1 H, 9/10-H), 6.15 (s, 1 H, 9/10-H), 6.16 (s, 1 H, 9/10-H), 6.30 (s, 1 H, 9/10-H), 6.55 (s, 1 H, m-H), 6.63 (dd, $^3J = 5.6$ Hz, $^5J = 1.2$ Hz, 1 H, c-H), 7.26 (s, 4 H, q-H), 7.28 (s, 2 H, r-H), 7.35 (td, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1 H, h/i-H), 7.40 (td, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1 H, i/h-H), 7.47 (d, $^3J = 8.4$ Hz, 2 H, k/l-H), 7.49-7.52 (m, 2 H, n-, g/j-H), 7.60-7.63 (m, 3 H, j/g-, l/k-H), 7.65-7.71 (m, 3 H, 8'-, d-, e-H), 7.78 (d, $^3J = 8.0$ Hz, 1 H, 8-H), 7.84 (d, $^3J = 8.8$ Hz, 1 H, 5'/6'-H), 7.86-7.88 (m, 3 H, o/p-, 6'/5'-H), 8.00 (d, $^3J = 8.8$ Hz, 1 H, 3'-H), 8.01 (d, $^3J = 8.0$ Hz, 2 H, p/o-H), 8.14 (d, $^3J = 8.8$ Hz, 1 H, 5/6-H), 8.22 (d, $^3J = 8.8$ Hz, 1 H, 6/5-H), 8.29 (d, $^3J = 8.8$ Hz, 1 H, 4'-H), 8.37-8.39 (m, 2 H, 7'-, 9'-H), 8.50 (dd, $^4J = 2.0$ Hz, $^5J = 0.8$ Hz, 1 H, f-H), 8.62 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.63 (d, $^3J = 8.0$ Hz, 1 H, 7-H), 8.68 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.69 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.71 (d, $^3J = 4.4$ Hz, 2 H, β -H), 8.81 (s, 1 H, 4-H) ppm.

UV-Vis: $\lambda_{\text{max}} = 429$ nm (Soret band, 10^{-6} M).

6-Ferrocenyl-2,2'-bipyridine (**2b**)⁷



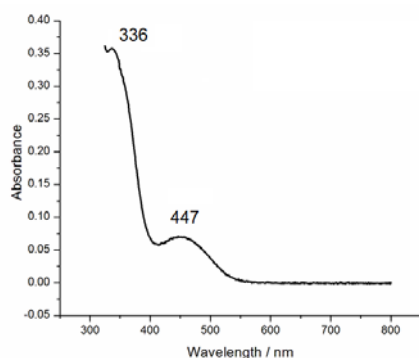
A 1.7 M solution of *tert*-butyllithium (11.3 mL) in hexane was slowly added to a cooled solution (0 °C) of ferrocene (3.81 g, 20.5 mmol) in THF (70 mL) under an inert atmosphere. The solution was stirred for 1 h at rt. Then 2,2'-bipyridine (2.00 g, 12.8 mmol) was added and the mixture stirred for another 4 h at rt. After neutralisation with saturated aqueous NH₄Cl solution (50 mL) and extraction with dichloromethane (3 × 60 mL), the organic layer was dried over MgSO₄. The concentrated reaction mixture (volume 50 mL) was subsequently stirred with MnO₂ (3.00 g, 34.5 mmol) for 12 h. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO₂) using DCM as eluent to obtain **2b** as reddish solid.

Yield: 1.31 g (3.84 mmol, 30%).

¹H NMR (400 MHz, CDCl₃): δ = 4.06 (s, 5 H, c-H), 4.42 (s, 2 H, b-H), 5.03 (s, 2 H, a-H), 7.30-7.33 (m, 1 H, 8-H), 7.43 (d, ³*J* = 8.0 Hz, 1 H, 3-H), 7.72 (t, ³*J* = 8.0 Hz, 1 H, 4-H), 7.85 (t, ³*J* = 8.0 Hz, 1 H, 7-H), 8.21 (d, ³*J* = 8.0 Hz, 1 H, 5-H), 8.58 (d, ³*J* = 8.0 Hz, 1 H, 6-H), 8.69 (d, ³*J* = 4.0 Hz, 1 H, 9-H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 67.4, 69.6, 69.8, 84.1, 117.6, 120.0, 121.2, 123.5, 136.7, 136.8, 149.0, 155.2, 156.6, 158.4 ppm.

UV-Vis (DCM): λ_{max} = 447 nm (ϵ = 536 L mol⁻¹ cm⁻¹).



NMR Spectra (sequenced by the synthetic strategy)

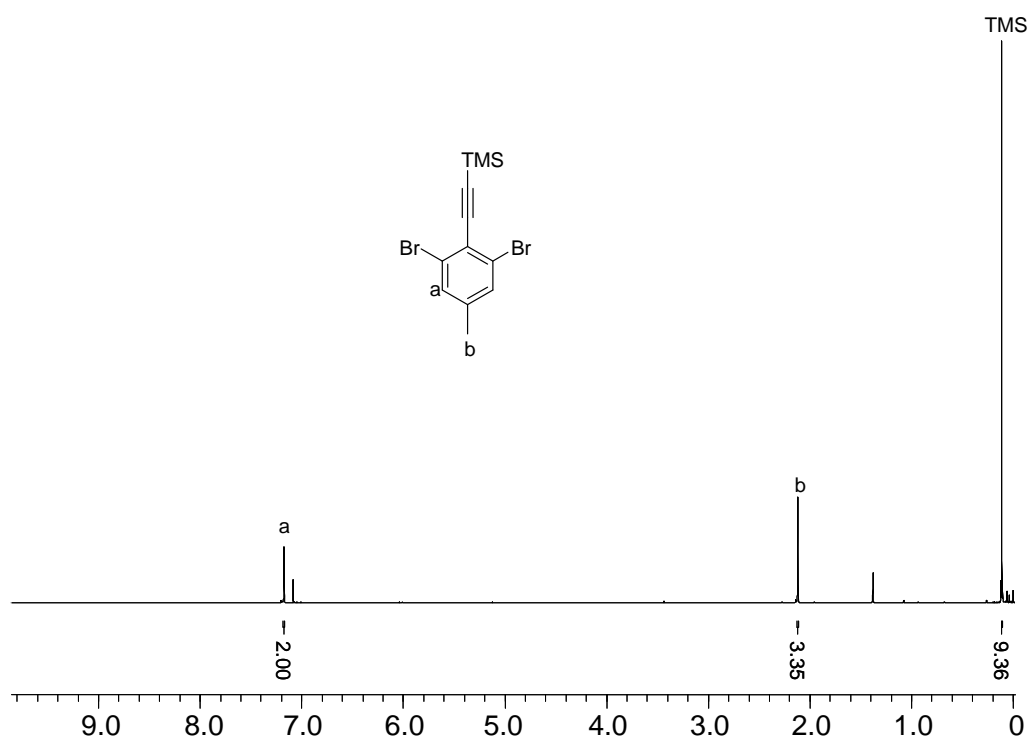


Figure S1. ^1H NMR (400 MHz, CDCl_3 , 298 K) of compound **9**.

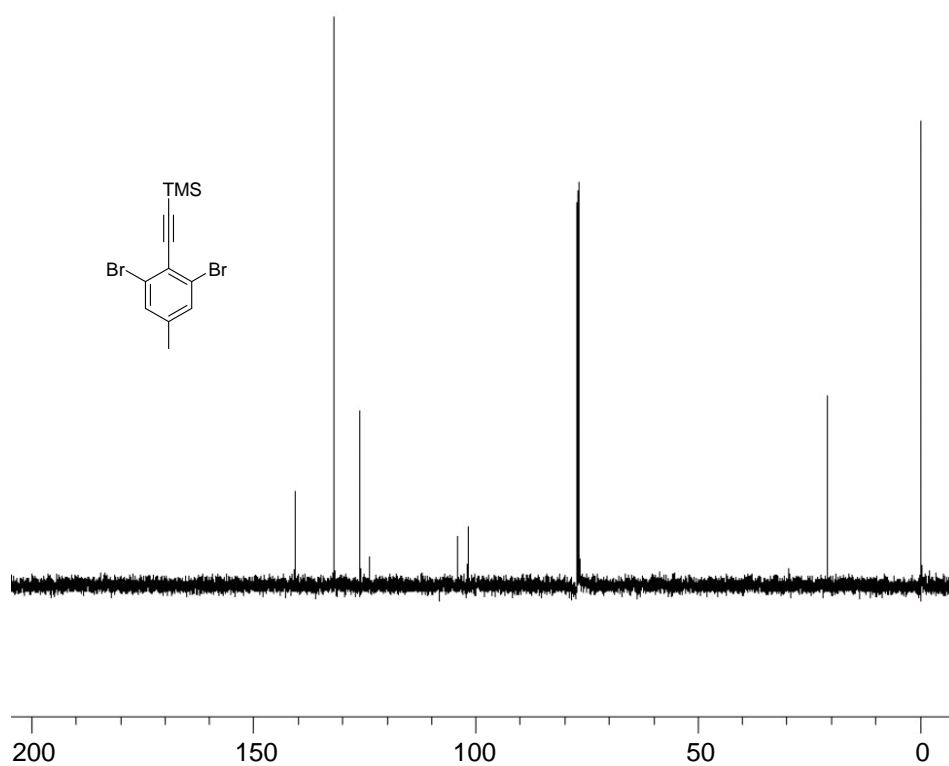


Figure S2. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) of compound **9**.

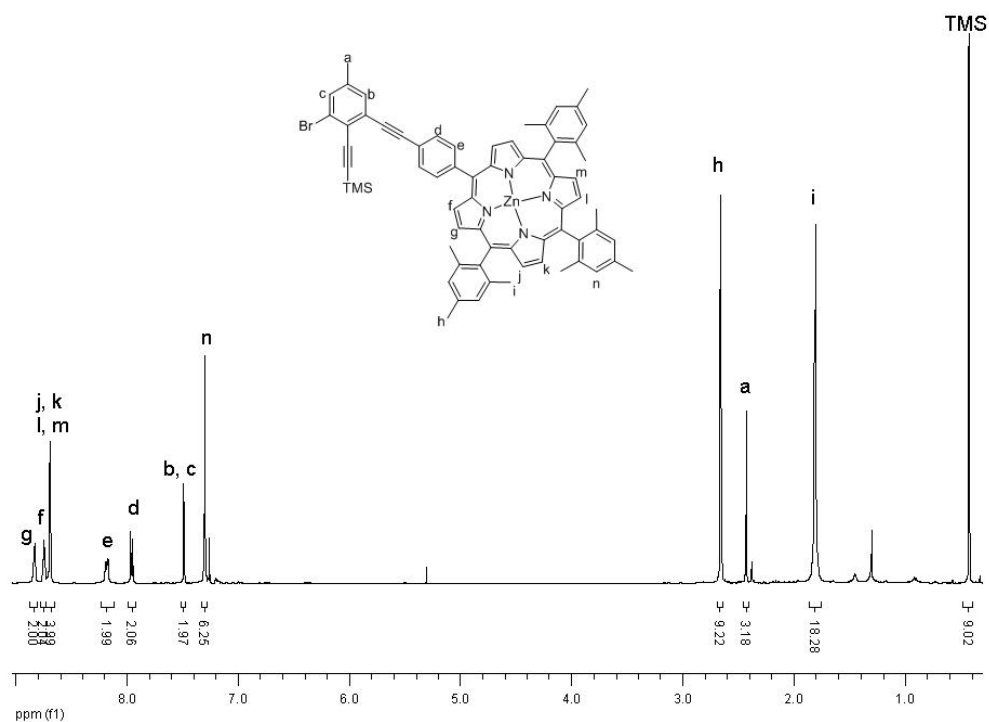


Figure S3. ^1H NMR (400 MHz, CDCl_3 , 298 K) of compound **10**.

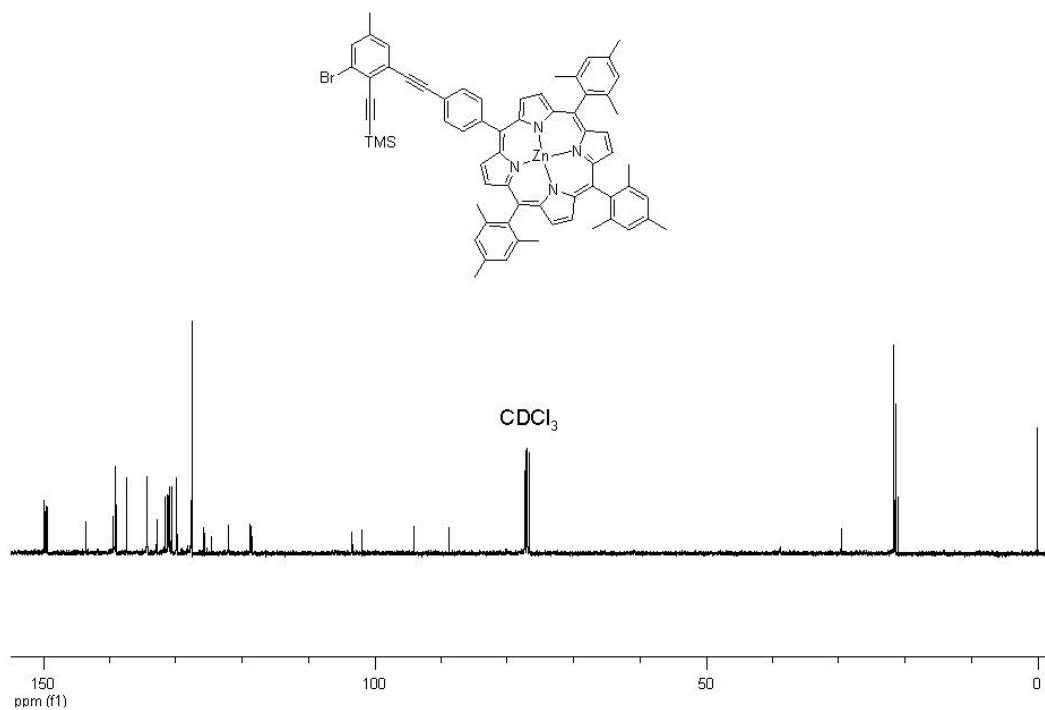


Figure S4. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) of compound **10**.

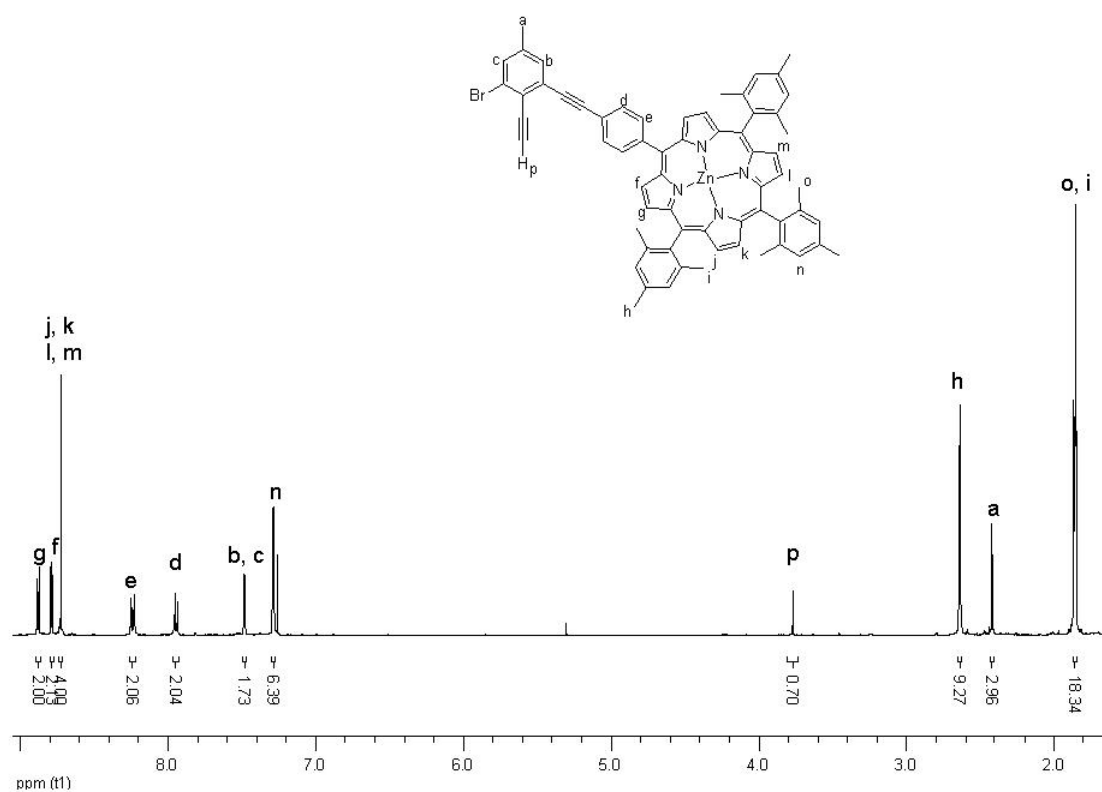


Figure S5. ^1H NMR (400 MHz, CDCl_3 , 298 K) of compound **6**.

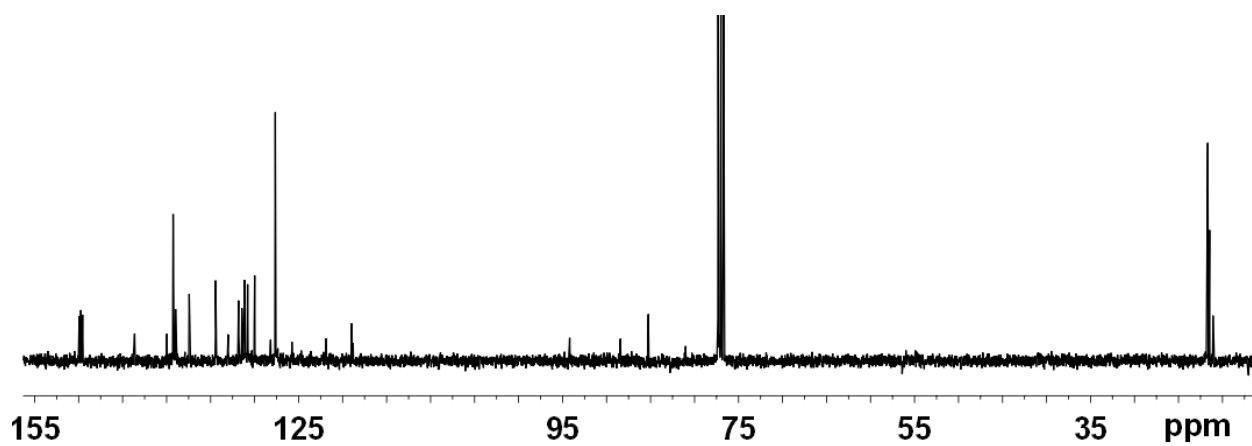


Figure S6. ^{13}C NMR (400 MHz, CDCl_3 , 298 K) of compound **6**.

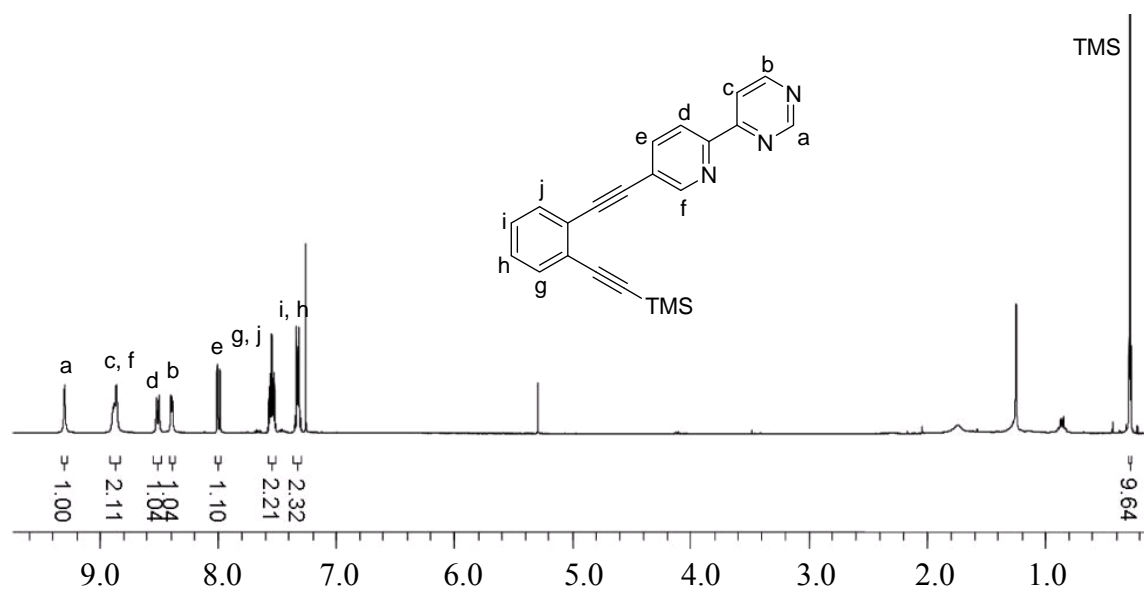


Figure S7. ^1H NMR (400 MHz, CDCl_3 , 298 K) of compound **11**

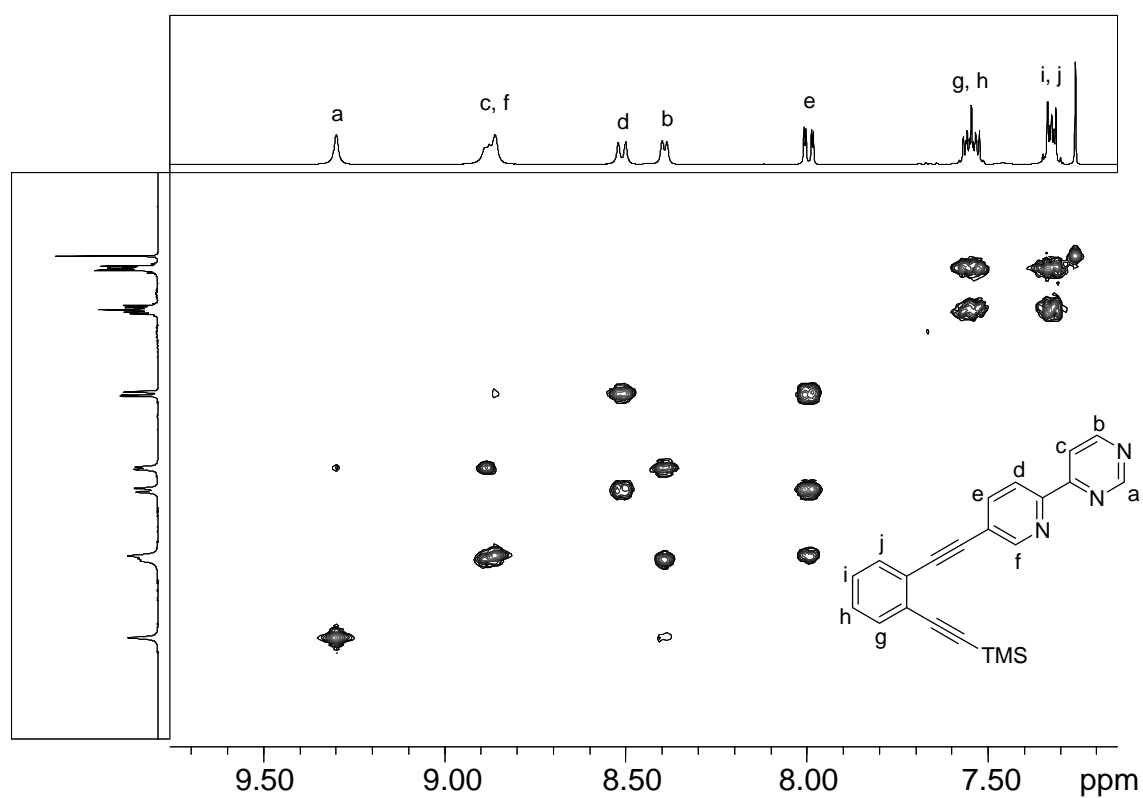


Figure S8. Partial ^1H - ^1H COSY NMR spectrum (400 MHz, CDCl_3 , 298 K) of **11**.

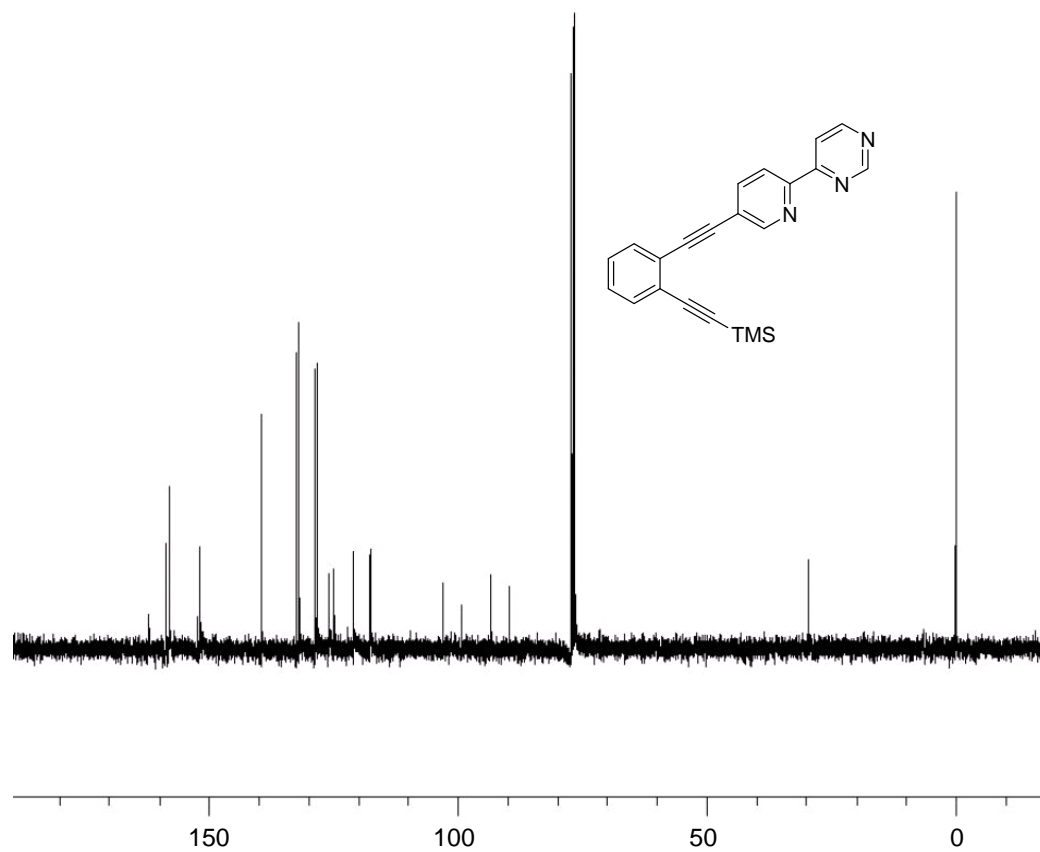


Figure S9. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) of compound **11**.

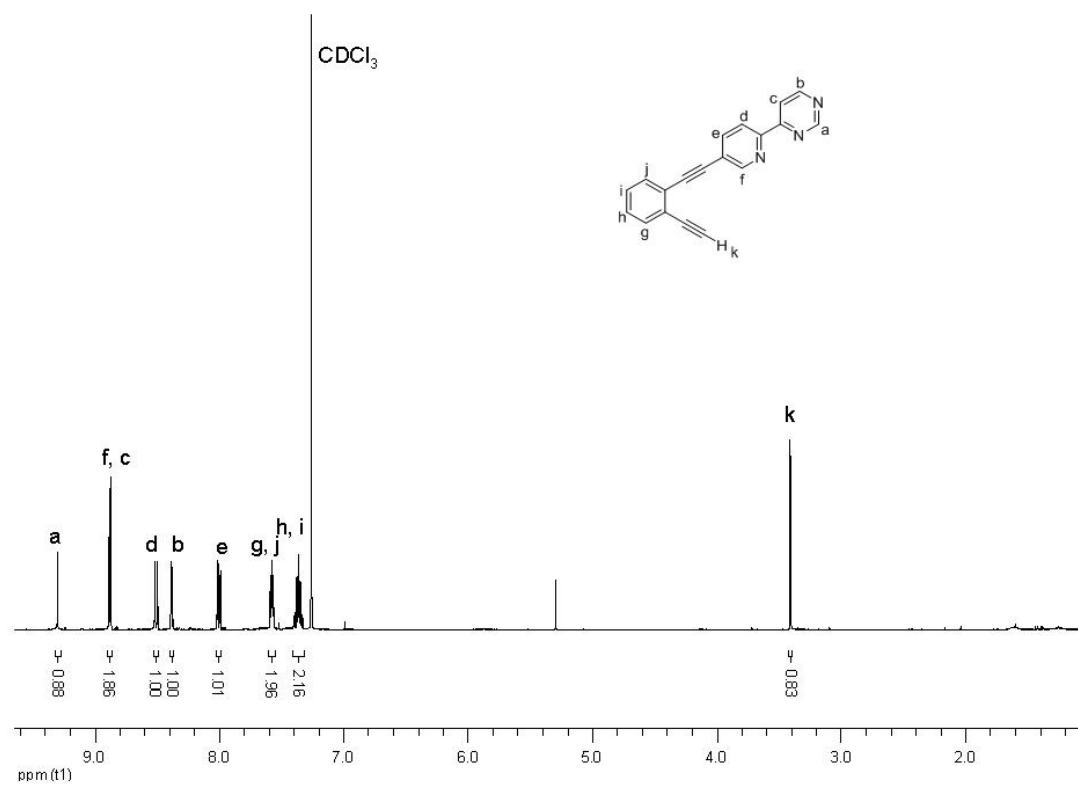


Figure S10. ¹H NMR (400 MHz, CDCl₃, 298 K) of compound **12**.

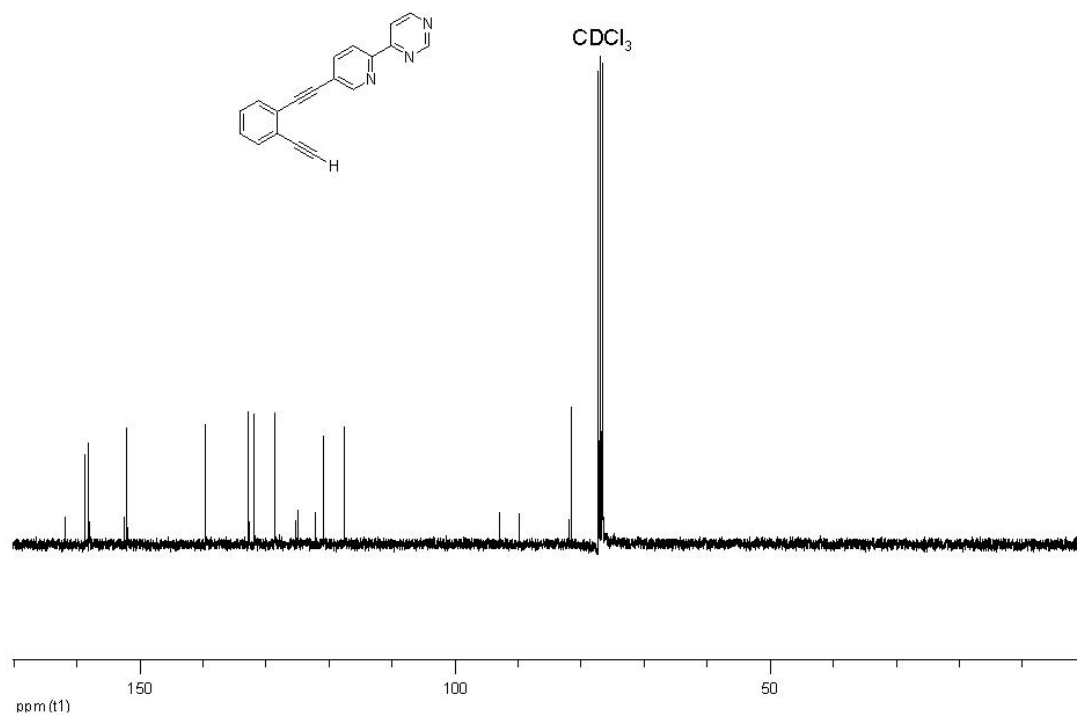


Figure S11. ¹³C NMR (100 MHz, CDCl₃, 298 K) of compound **12**.

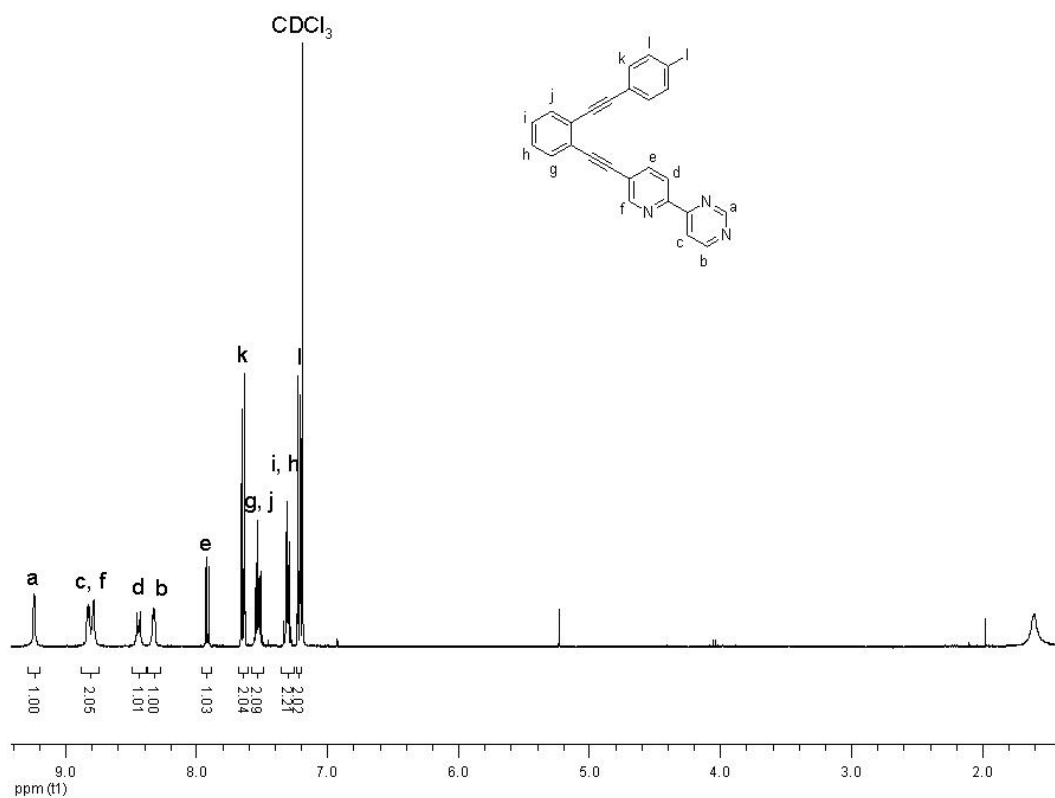


Figure S12. ¹H NMR (400 MHz, CDCl₃, 298 K) of compound 7.

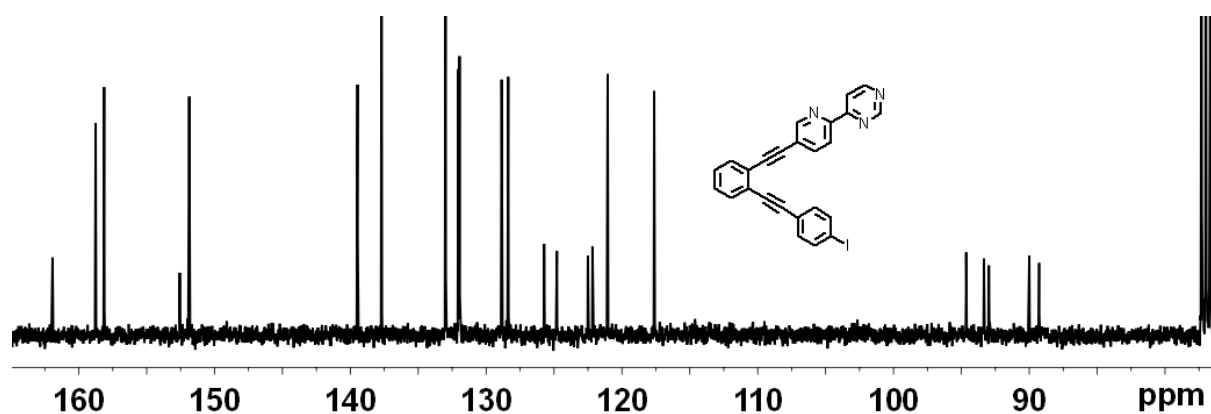


Figure S13. ¹³C NMR (100 MHz, CDCl₃, 298 K) spectrum of compound 7.

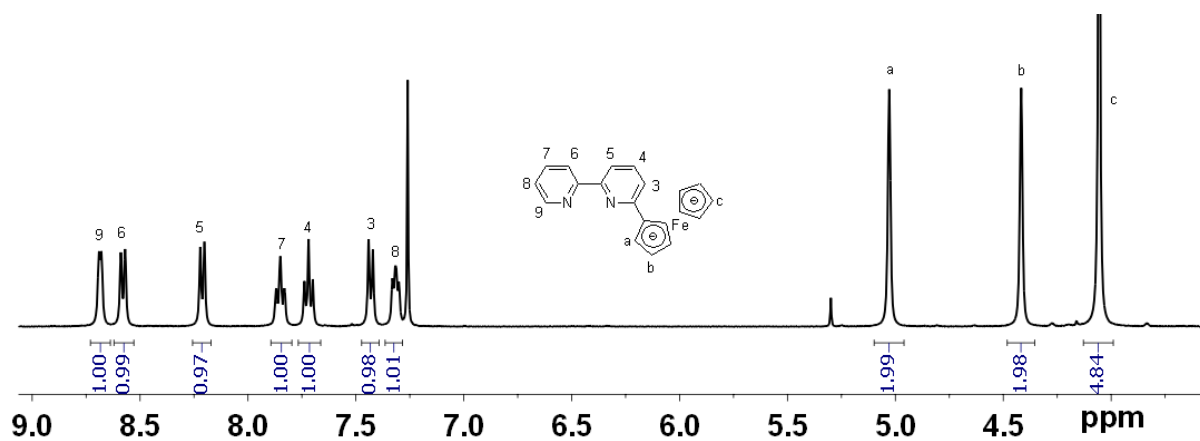


Figure S14. ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of compound **2b**.

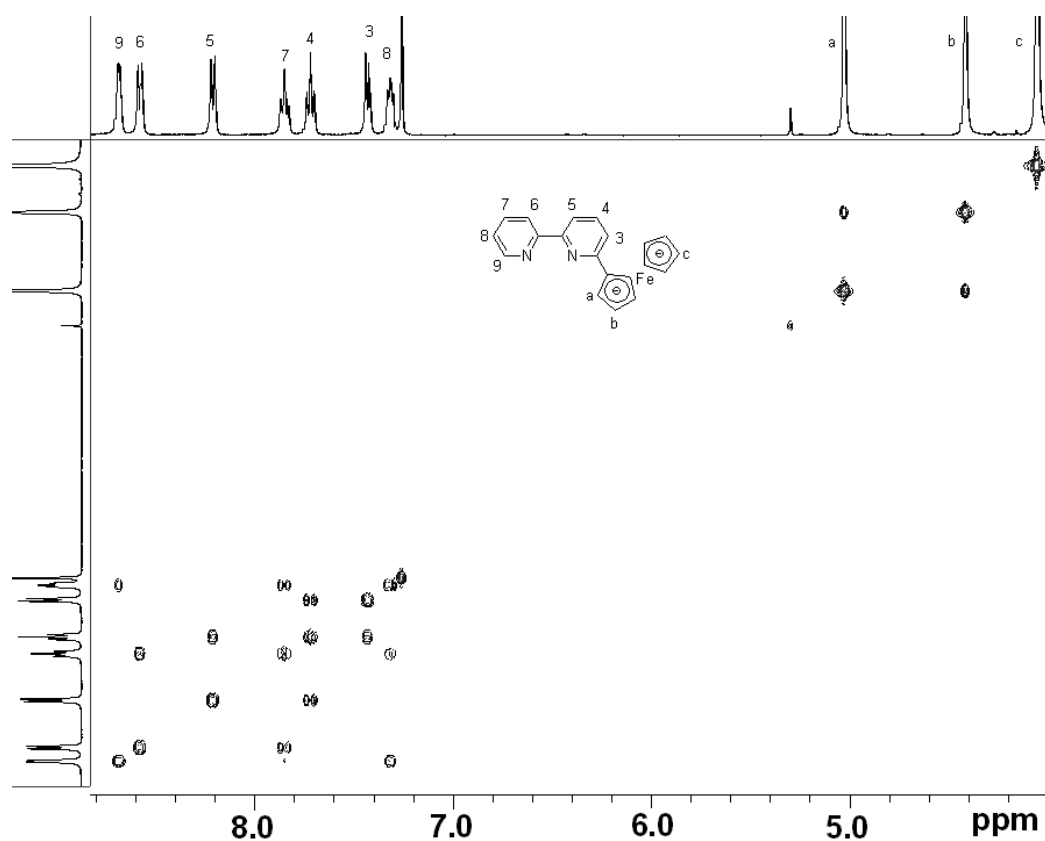


Figure S15. Partial ¹H-¹H COSY NMR spectrum (400 MHz, CDCl₃, 298 K) of compound **2b**.

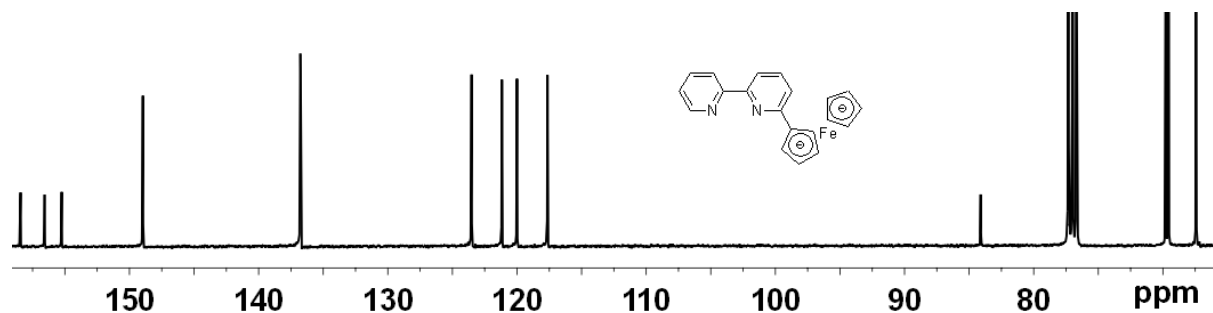


Figure S16. ¹³C NMR (100 MHz, CDCl₃, 298 K) spectrum of compound **2b**.

ESI-MS Spectra

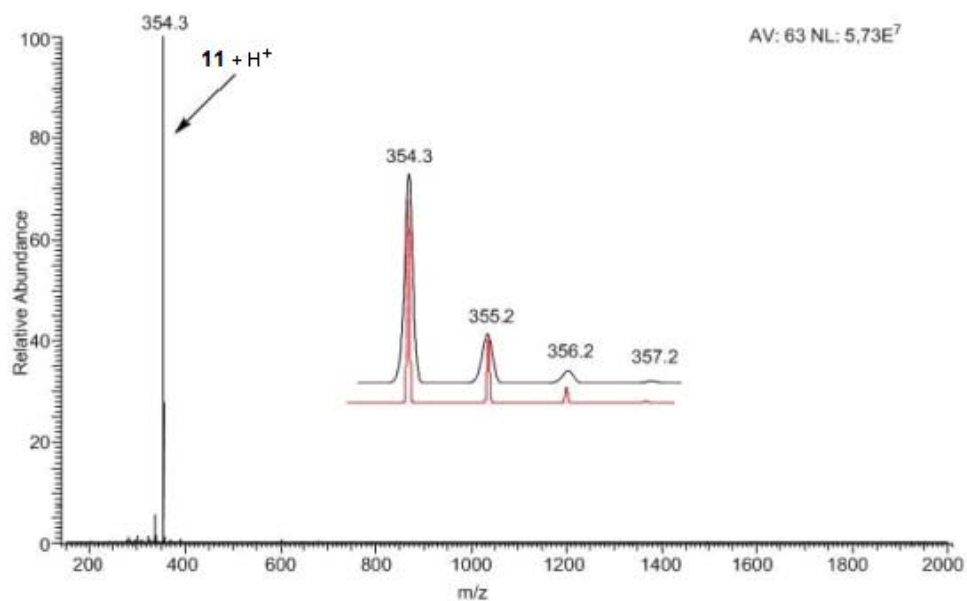


Figure S17. ESI-MS of compound 11.

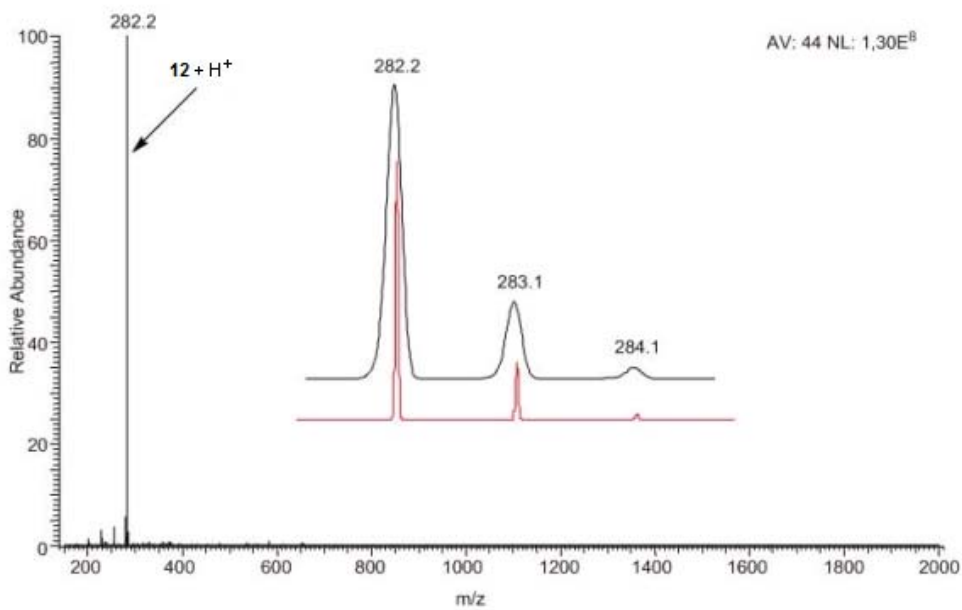


Figure S18. ESI-MS of compound 12.

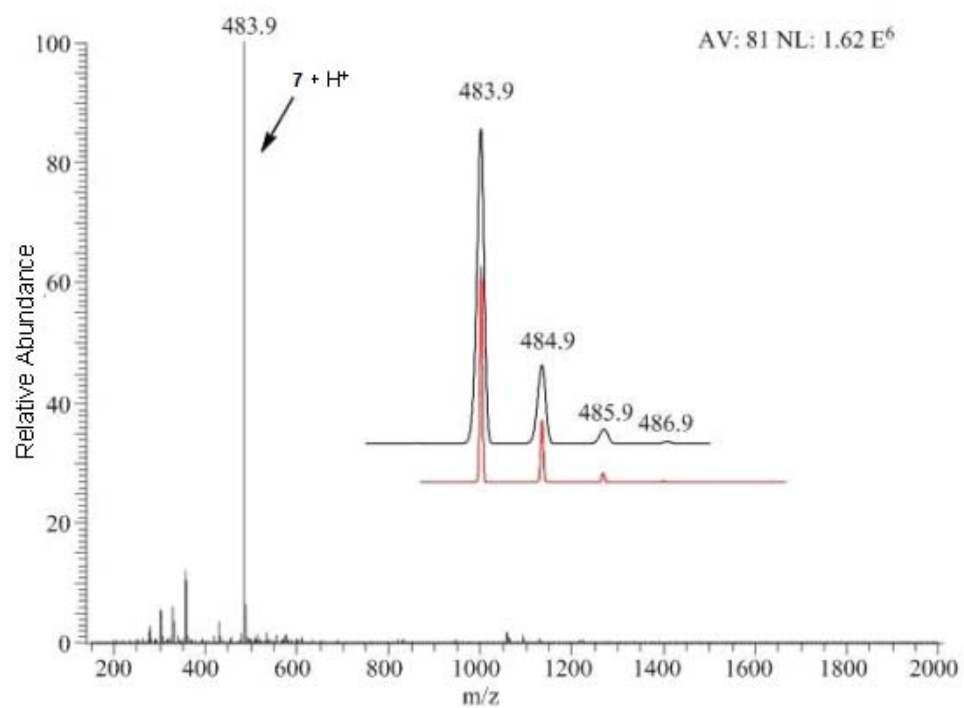


Figure S19. ESI-MS of compound 7.

Cyclic Voltammetry

The cyclic voltammetry (CV) experiments were carried out by using a standard three-electrode set-up (Pt working (1.0 mm diameter), Pt auxiliary electrode, and a silver wire as reference electrode) connected to a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System. After taking scans, the Ag electrode was calibrated using 2,4,6-triphenylpyrylium tetrafluoroborate as an internal standard ($E_{1/2} = -0.39$ V vs. SCE). If not mentioned otherwise, experiments were performed with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte under N₂ atmosphere.

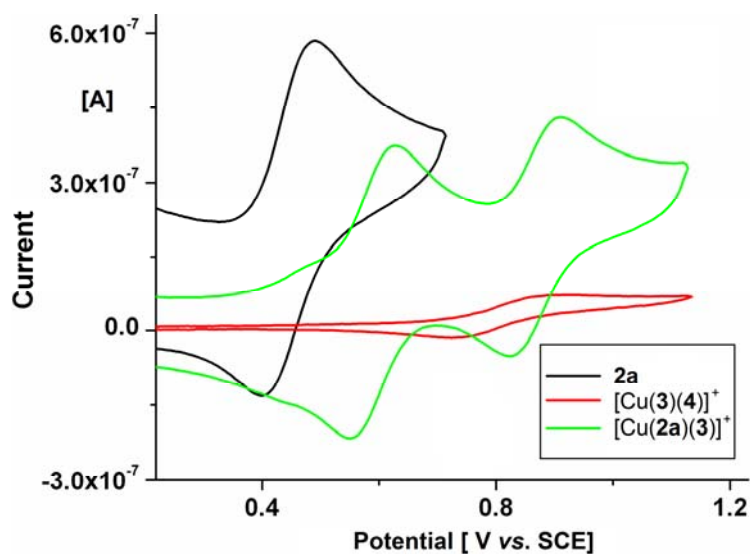


Figure S20. Cyclic voltammetry of model compounds / complexes (DCM, $\nu = 100$ mV s⁻¹).

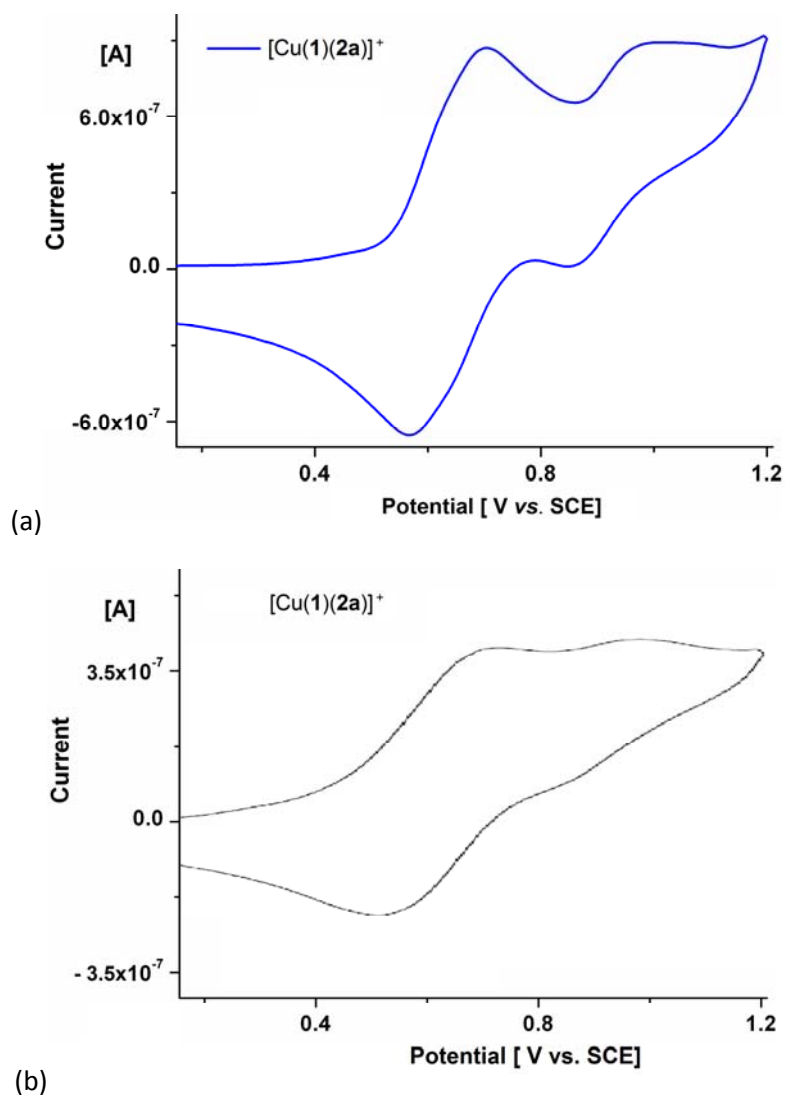


Figure S21. Cyclic voltammetry study of switch $[\text{Cu}(\mathbf{1})(\mathbf{2a})]^+$ (DCM, (a) $\nu = 100 \text{ mV s}^{-1}$) and (b) $\nu = 20 \text{ mV s}^{-1}$).

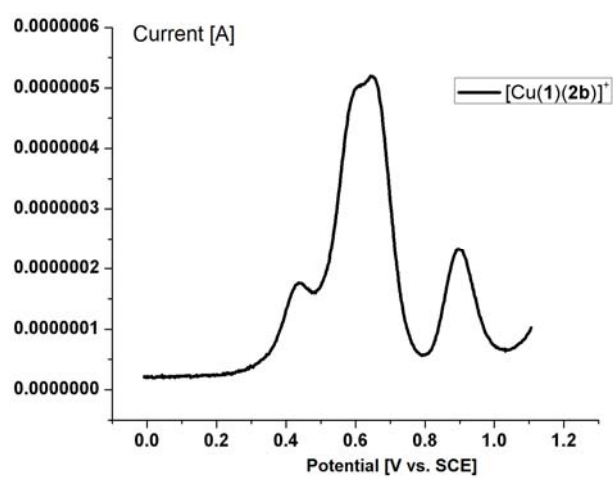


Figure S22. DPV study of nanoswitch $[\text{Cu}(\mathbf{1})]^+$ in presence of $\mathbf{2b}$ (DCM, $\nu = 100 \text{ mV s}^{-1}$).

References

- 1 (a) M. Schmittle, S. De and S. Pramanik, *Angew. Chem. Int. Ed.*, 2012, **51**, 3832. (b) M. Schmittle, S. Pramanik and S. De, *Chem. Commun.*, 2012, 48, 11730.
- 2 K. Tahara, S. Okuhata, J. Adisoejoso, S. Lei, T. Fujita, S. D. Feyter and Y. Tobe, *J. Am. Chem. Soc.*, 2009, **131**, 17583.
- 3 W. J. Youngblood, D. T. Gryko, R. K. Lammi, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 2002, **67**, 2111.
- 4 M. Ohkita, K. Ando, T. Suzuki and T. Tsuji, *J. Org. Chem.* 2000, **65**, 4385.
- 5 S. De, S. Pramanik and M. Schmittle, *Synthesis*, 2012, **44**, 2959.
- 6 S. De, S. Pramanik and M. Schmittle, *Angew. Chem. Int. Ed.*, 2014, **53**, 14255.
- 7 P. Edinç, A. M. Önal and S. Özkar, *J. Organomet. Chem.*, 2007, **692**, 1983.