Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information to accompany

Back to the future: asymmetrical DπA 2,2′-bipyridine ligands for homoleptic copper(I)-based dyes in dye-sensitized solar cells

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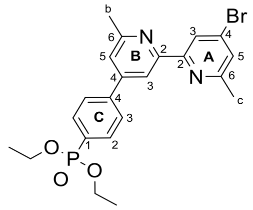
Experimental section

Syntheses



8 4,4′-Dibromo-6,6′-dimethyl-2,2′-bipyridine (**7**) (941 mg, 2.75 mmol, 3.0 eq), diethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylphosphonate (312 mg, 917 µmol, 1.0 eq), Pd(PPh3)4 (20.1 mg, 17.4 µmol, 1.9 mol%) and Na_2CO_3 (389 mg, 3.67 mmol, 4.0 eq) were loaded into a microwave vial. After three vacuum-N_2 cycles, the solids were dissolved in N_2-degassed mixture Toluene/H_2O N_2-degassed mixture (9:1, 13.2 mL). The reaction vessel was sealed and set under stirring at 90 °C overnight. After cooling to room temperature, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, and then dried by rotavaporation. The excess of 4,4′-Dibromo-6,6′-dimethyl-2,2′-bipyridine was removed and recovered by recrystallization from EtOAc. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2:EtOAc in 2:1 ratio). The product was further recrystallized from Et_2O, collected and dried *in vacuo*. The product was isolated as white crystals (278 mg, 585 µmol, 63.8%).

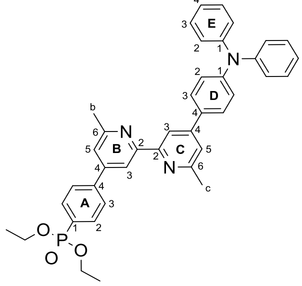
^{1}H NMR (500 MHz, $CDCl_3$ + d-TFA) δ/ ppm 8.25 (s, 1H, H^{A3}), 8.33 (s, 1H, H^{B3}), 8.05 (dd, J = 13.4, 7.9 Hz, 2H, H^{C2}), 7.94 – 7.88 (overlapping m, 3H, H^{B5+C3}), 7.77 (d, J = 1.4 Hz, 1H, H^{A5}), 4.23 (m, 4H, $H^{Et\text{-}CH2}$), 2.97 (s, 3H, $H^{CH3\text{-}b}$), 2.73 (s, 3H, $H^{CH3\text{-}a}$), 1.39 (t, J = 7.0 Hz,6H, $H^{Het\text{-}CH3}$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ + d-TFA) δ/ ppm 160.3 (C^{A6}), 156.9 (C^{B6}), 146.4 (C^{B2}), 145.8 (C^{A2}), 139.1 (d, $^4J_{CP}$ = 3.32 Hz, C^{C4}), 138.4 (C^{A4}), 133.3 (d, $^2J_{CP}$ = 10.6 Hz, C^{C2}), 131.1 (C^{A5}), 131.1 (C^{B4}), 130.3 (d, $^1J_{CP}$ = 193.6 Hz, C^{C1}), 128.2 (d, $^3J_{CP}$ = 15.8 Hz, C^{C3}), 126.1 (C^{B5}), 124.4 (C^{A3}), 120.0 (C^{B3}), 64.2 (d, $^2J_{CP}$ = 6.1 Hz, $C^{Et\text{-}CH2}$), 22.6 (C^{CH3a}), 21.0 (C^{CH3b}), 16.22 (d, $^3J_{CP}$ = 6.4 Hz, $C^{Et\text{-}CH3}$).

^{31}P{^{1}H} NMR (202 MHz, 298 K, $CDCl_3$ + d-TFA) δ/ppm 17.0 (s, P).

HR ESI-MS *m/z* 475.0774 $[M+H]^+$ (calc. 475.0781).

Found: C 55.47, H 4.840, N 5.79; $C_{22}H_{24}BrN_2O_3P$ requires C 55.59, H 5.09, N 5.89.



3e Compound **8** (259 mg, 545 µmol, 1.0 eq), 4-(Diphenylamino)phenylboronic acid (189 mg, 654 µmol, 1.2 eq), $Pd(PPh_3)_4$ (12.0 mg, 10.4 µmol, 1.9 mol%) and Na_2CO_3 (231 mg, 2.18 mmol, 4.0 eq) were loaded into a microwave vial. After three vacuum-N2 cycles, the solids were dissolved in N_2-degassed Toluene/H_2O mixture (9:1, 9.25 mL). The reaction vessel was sealed and set under stirring at 90 °C overnight. After cooling to room temperature, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, and then dried by rotavaporation. The product was recrystallized from EtOAc, filtered and rinsed with small portions of EtOAc, then dried *in vacuo*. Product was isolated as canary yellow crystals. (228 mg, 356 µmol, 65.4%).

^{1}H NMR (500 MHz, $CDCl_3$ + d-TFA) δ/ ppm 8.57 (s, 1H, H^{C3}), 8.54 (s, 1H, H^{B3}), 8.01 – 7.90 (overlapping m, 4H, H^{A2+A3}), 7.72 (d, *J* = 8.6 Hz, 2H, H^{D2}), 7.67 (s, 1H, H^{C5}), 7.60 (s, 1H, H^{B5}), 7.36 (t, J = 7.8 Hz, 4H, H^{E3}), 7.20 (overlapping m, 6H, H^{E2+E4}), 7.14 (d, J = 8.6 Hz, 2H, H^{D3}), 4.17 (m, 4H, $H^{Et\text{-}CH2}$), 2.99 (s, 3H, H^{CH3c}), 2.76 (s, 3H, H^{CH3b}), 1.36 (t, *J* = 7.0 Hz, 6H, $H^{Et\text{-}CH3}$).

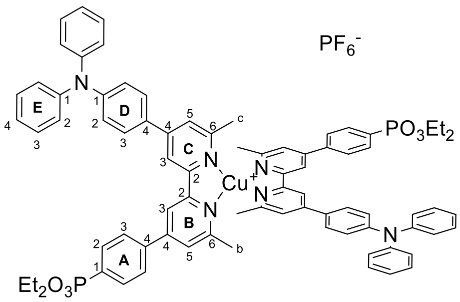
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$ + d-TFA) δ/ ppm 160.3 (C^{B6}), 156.2 (C^{C4}), 154.7 (C^{C6}), 152.1 (C^{B4}), 151.9 (C^{D1}), 149.9 (C^{C2}), 147.8 (C^{B2}), 146.3 (C^{E1}), 141.4 (C^{A4}), 140.0 (d, C^{A1}), 132.9 (d, $^{2}J_{CP}$ = 11 Hz, C^{A2}), 129.9 (C^{E3}), 129.0 (C^{D3}), 127.8 (d, $^{3}J_{CP}$ = 15 Hz, C^{A3}), 126.2 (C^{E2}), 125.8 (C^{D4}), 125.2 (C^{E4}), 124.3 (C^{B5}), 122.2 (C^{C5}), 121.0 (C^{D2}), 119.3 (C^{B3}), 118.9 (C^{C3}), 63.2 (d, $^{2}J_{CP}$ = 5.7 Hz, $C^{Et\text{-}CH2}$), 24.3 (C^{CH3b}), 20.5 (C^{CH3c}), 16.4 (d, $^{3}J_{CP}$ = 6.5 Hz, $C^{Et\text{-}CH3}$).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, $CDCl_3$ + d-TFA) δ/ppm 17.9 (s, P).

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 246 (ε/dm^{-3} mol^{-1} cm^{-1} 45,650), 298 (27,840); 353 (23,740).

HR ESI-MS *m/z* 640.2721 $[M+H]^{+}$ (calc. 640.2724).

Found: C 73.97, H 5.946, N 6.25; $C_{40}H_{38}N_3O_3P$ requires C 75.10, H 5.99, N 6.27.



[Cu(3e)₂][PF₆] Compound **3e** (10.6 mg, 16.6 µmol, 2.0 eq) was loaded in a round bottom flask and dissolved in CH_2Cl_2 (5 mL). After addition of $[Cu(CH_3CN)_4][PF_6]$ (3.09 mg, 8.28 µmol, 1.0 eq), the mixture was set under stirring overnight. The solvent was removed by rotavaporation, the solids dried in *in vacuo*. The product was isolated as a red solid (12.3 mg, 8.27 µmol, >99%).

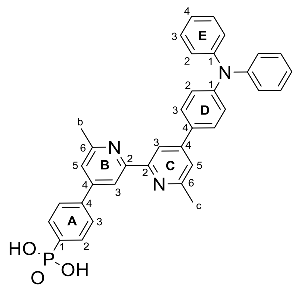
^{1}H NMR (500 MHz, acetone-d_6) δ/ ppm 9.08 (s, 2H, H^{B3}), 9.00 (s, 2H, H^{C3}), 8.17 (dd, *J* = 8.2, 3.6 Hz, 4H, H^{A3}), 8.07 (s, 2H, H^{B5}), 8.02 – 7.94 (overlapping m, 10H, $H^{A2+C5+D3}$), 7.39 (m, 8H, H^{E3}), 7.21 – 7.12 (overlapping m, 16H, $H^{E2+E4+D2}$), 4.14 (m, 8H, $H^{Et\text{-}CH2}$), 2.48 (s, 6H, H^{CH3b}), 2.45 (s, 6H, H^{CH3c}), 1.32 (t, J = 7.1 Hz, 12H, $H^{Et\text{-}CH3}$).

$^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6) δ/ ppm 158.8 (C^{B6}), 158.5 (C^{C6}),153.8 (C^{B2}),153.3 (C^{C2}),150.7 (C^{D1}),150.1 (C^{B4}),148.0 (C^{E1}), 141.7 (d, $^{4}J_{CP}$ = 3.2 Hz, H^{A4}), 133.3 (d, $^{2}J_{CP}$ = 9.9 Hz, H^{A2}), 131.8 (d, $^{1}J_{CP}$ = 187.4 Hz, C^{A1}), 130.6 (C^{E3}), 130.4 (C^{E4}), 130.4 (C^{D4}), 129.3 (C^{D3}), 128.5 (d, $^{3}J_{CP}$ = 14.9 Hz, H^{A3}), 126.1 (C^{D2}), 124.8 (C^{B5}), 123.6 (C^{C5}), 123.0 (C^{E2}), 119.0 (C^{B3}), 118 (C^{C3}), 62.7 (d, $^{2}J_{CP}$ = 5.5 Hz, $H^{Et\text{-}CH2}$), 25.4 (C^{CH3b}), 25.1 (C^{CH3c}), 16.7 (d, $^{3}J_{CP}$ = 6.0 Hz, $H^{Et\text{-}CH3}$); C^{C4} not resolved in HMBC.

$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, acetone-d_6) δ/ppm 16.7 (s, P^{PO3Et2}), -144.2 (hept, $^{1}J_{PF}$ = 707.4 Hz, P^{PF6}). UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 259 (ε/dm^{-3} mol^{-1} cm^{-1} 62,130), 321 (47,890), 494 (33,630).

HR ESI-MS *m/z* 1341.4587 $[M-PF_6]^{+}$ (calc. 1341.4592).

Found: C 63.16, H 5.48, N 5.21; $C_{80}H_{76}CuF_6N_6O_6P_3$ requires C 64.58, H 5.15, N 5.65.



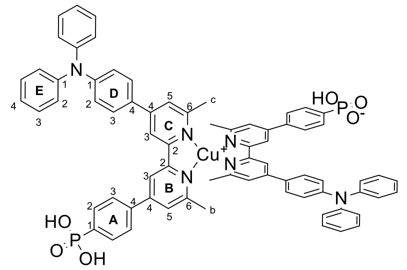
3 Compound **3e** (99.8 mg, 156 µmol, 1.0 eq) was loaded in a round bottom flask and dissolved in anhydrous CH_2Cl_2 (3 mL). TMSBr (82.4 µL, 624 µmol, 4.0 eq) was added dropwise into the reaction mixture and stirred under nitrogen at rt overnight. The solvent was removed by rotavaporation and the residue redissolved in the smallest amount of MeOH. Addition of Et_2O afforded precipitation of the product, which was filtered and rinsed with small portions of Et_2O, then dried *in vacuo*. The product was isolated as a red solid (71.7 mg, 123 µmol, 78.8%).

^{1}H NMR (500 MHz, CD_3OD) δ/ ppm 8.79 (s, 1H, H^{C3}), 8.65 (s, 1H, H^{B3}), 8.13 (s, 1H, H^{C5}), 8.07 (dd, J = 8.3, 3.4 Hz, 2H, H^{A3}), 8.03 (d, J = 9.0 Hz, 2H, H^{D3}), 7.99 (m, 2H, H^{A2}), 7.95 (d, J = 1.4 Hz, 1H, H^{B5}), 7.39 (m, 4H, H^{E3}), 7.20 (overlapping m, 6H, H^{E2+E4}), 7.12 (d, J = 8.9 Hz, 2H, H^{D2}), 2.91 (s, 3H, H^{CH3c}), 2.83 (s, 3H, H^{CH3b}).

$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ/ ppm 161.2 (C^{B6}), 157.7 (C^{C4}), 156.1 (C^{C6}), 153.2 (C^{D1}), 152.4 (C^{B4}), 149.6 (C^{C2}), 149.3 (C^{B2}), 147.8 (C^{E1}), 141.2 (C^{A4}), 135.2 (d, $^{1}J_{CP}$ = 188.8 Hz, C^{A1}), 132.9 (d, $^{2}J_{CP}$ = 10.3 Hz, C^{A2}), 130.9 (C^{E3}), 130.5 (C^{D2}), 128.5 (d, $^{3}J_{CP}$ = 14.9 Hz, C^{A3}), 127.3 (C^{D4}), 127.3 (C^{E2}), 126.2 (C^{E4}), 125.5 (C^{B5}), 123.7 (C^{C5}), 121.7 (C^{D2}), 119.6 (C^{B3}), 118.9 (C^{C3}), 23.8 (C^{CH3b}), 20.5 (C^{CH3c}).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, CD_3OD) δ/ppm 14.9 (s, P).

HR ESI-MS *m/z* 582.1958 $[M-H]^{-}$ (calc. 582.1952).



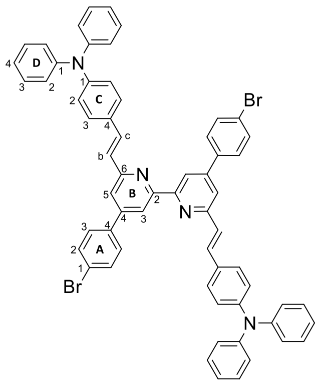
[Cu(3)₂] Compound **3** (60.3 mg, 103 µmol, 2.0 eq) was loaded in a round bottom flask and dissolved in MeOH (4 mL). After addition of $[Cu(CH_3CN)_4][PF_6]$ (19.3 mg, 51.7 µmol, 1.0 eq), the mixture was set under stirring for 1 h. The solvent was reduced to a minimum volume by rotavaporation. Et_2O was added to the reaction mixture to afford precipitation. The precipitate was filtered, rinsed with small portions of Et_2O, then dried *in vacuo*. The product was isolated as a red solid (52.3 mg, 42.5 µmol, 82.3%).

^{1}H NMR (500 MHz, acetone-d_6) δ/ ppm 9.00 (d, *J* = 1.8 Hz, 2H, H^{C3}), 8.89 (s, 2H, H^{B3}), 8.25 (s, 2H, H^{C5}), 8.09 – 8.03 (overlapping m, 8H, H^{A3+D3}), 8.01 (s, 2H, H^{B5}), 7.93 (dd, *J* = 12.9, 8.1 Hz, 4H, H^{A2}), 7.43 (m, 8H, H^{E3}), 7.27 – 7.19 (overlapping m, 12H, H^{E2+E4}), 7.10 (d, *J* = 8.9 Hz, 4H, H^{D2}), 2.98 (s, 6H, H^{CH3c}), 2.78 (s, 6H, H^{CH3b}).

^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ/ ppm 160.3 (C^{B6}), 156.9 (C^{C4}), 155.9 (C^{C6}), 152.0 (C^{B4}), 151.6 (C^{D1}), 148.2 (C^{C2}), 147.7 (C^{B2}), 147.2 (C^{E1}), 140.2 (C^{A4}), 135.3 (d, $^1J_{CP}$ = 191.2 Hz, C^{A1}), 132.6 (d, $^2J_{CP}$ = 10.3 Hz, C^{A2}), 130.8 (C^{E3}), 130.4 (C^{D3}), 128.3 (d, $^3J_{CP}$ = 14.5 Hz, C^{A3}), 127.0 (C^{E2}), 126.8(C^{D4}), 126.1(C^{E4}), 125.5(C^{B5}), 123.8(C^{C5}), 121.2(C^{D2}), 119.4 (C^{B3}), 118.5 (C^{C3}), 23.6 (C^{CH3b}), 20.9 (C^{CH3c}).

^{31}P{^{1}H} NMR (202 MHz, 298 K, acetone-d_6) δ/ppm 14.6 (s, P).

HR ESI-MS *m/z* 1227.3244 $[M-H]^-$ (calc. 1227.3195).



10 The procedure was adapted from literature.[1] Compound **9** (2.580 g, 5.22 mmol, 1.0 eq), 4-(diphenylamino)benzaldehyde (5.707 g, 20.9 mmol, 4.0 eq) were loaded in an autoclave vessel. After sequential addition of anhydrous DMF (100 mL) and TMSCl (3.0 mL, 23.5 mmol, 4.5 eq), the reaction vessel was sealed and heated at 173 °C for 48 h. After allowing the vessel to cool down to 4 °C ca. (easing of internal pressure), the reaction mixture was slowly added to water (1 L ca.) while stirring homogeneously. The aqueous phase was filtered and the precipitate was redissolved in CH_2Cl_2 and collected in a round-bottom flask, then removed the organic phase by rotavaporation. After addition of CH_2Cl_2 (20 mL), the suspension was filtered and dried *in vacuo*. The product was isolated as yellow powder (1.657 g, 1.65 mmol, 31.6 %). Alternatively, the product could be purified by column chromatography (SiO2, CH_2Cl_2/CHX, 3:1). Crystals for X-ray diffraction were grown by slow CH_2Cl_2 evaporation.

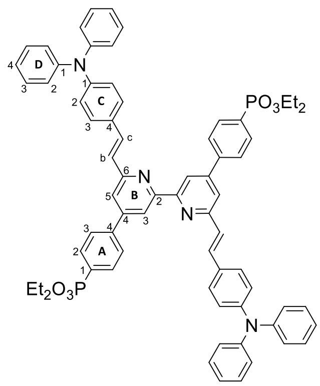
^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm 8.61 (d, *J* = 1.6 Hz, 2H, H^{B3}), 7.76 (d, *J* = 16.0 Hz, 2H, H^c), 7.70 – 7.65 (overlapping m, 8H, H^{A2+A3}), 7.58 (d, *J* = 1.6 Hz, 2H, H^{B5}), 7.50 (d, *J* = 8.5 Hz, 4H, H^{C3}), 7.29 (m, 8H, H^{D3}), 7.22 (d, *J* = 16.0 Hz, 2H, H^b), 7.14 (d, *J* = 7.3 Hz, 8H, H^{D2}), 7.10 – 7.04 (overlapping m, 8H, H^{D4+C2}).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm 156.8 (C^{B2}), 156.3 (C^{B6}), 148.8 (C^{B4}), 148.3 (C^{C1}), 147.5 (C^{D1}), 138.0 (C^{A8}), 132.4 (C^{A2}), 130.6 (C^{C4}), 129.5 (C^{D3}), 129.0 (C^{A3}), 128.3 (C^{C3}), 125.0 (C^{D2}), 123.5 (C^{D4}), 123.5 (C^{D4}), 123.1 (C^{C2}), 119.7 (C^{B5}), 117.6 (C^{B3}).

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 295 (ε/dm^{-3} mol^{-1} cm^{-1} 90,705), 398 (76,104)

HR ESI-MS *m/z* 1005.1976 $[M+H]^+$ (calc. 1005.1985).

Found: C 73.35, H 4.28, N 5.67; $C_{62}H_{44}Br_2N_4$ requires C 74.11, H 4.41, N 5.58.



4e Compound **10** (601 mg, 598 µmol, 1.0 eq), HPO_3Et_2 (309 µL, 330 mg, 2.39 mmol, 4.0 eq), Cs_2CO_3 (487 mg, 1.49 mmol, 2.5 eq), $Pd(dba)_2$ (34.4 mg, 59.8 µmol, 10 mol%), Ruphos (56.9 mg, 120 µmol, 20 mol%) were loaded in a microwave vial. After three cycles of vacuum-N2, the reaction mixture was dissolved with N2-degassed THF (8 mL), then set at 90 °C for 18 h. The reaction vessel was allowed to cool down to rt. The reaction mixture was transferred in a separatory funnel and water added. The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The organic layers were washed with Brine (20 mL), back-extracted with an additional portion of CH_2Cl_2. After drying over $MgSO_4$, the crude mixture was brought to dryness by rotavaporation. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 with Ethyl Acetate gradient changing from 19:1 to 9:1 to 4:1 to 2:1). The product was further purified by recrystallization from CHX/$CHCl_3$ solvent mixture, then dried *in vacuo*. Isolated as yellow powder (382 mg, 341 µmol, 57.1%).

^{1}H NMR (500 MHz, $CDCl_3$) δ/ ppm 8.67 (d, *J* = 1.6 Hz, 2H, H^{B3}), 7.99 (m, 4H, H^{A2}), 7.91 (m, 4H, H^{A3}), 7.78 (d, *J* = 16.0 Hz, 2H, H^c), 7.63 (d, *J* = 1.6 Hz, 2H, H^{B5}), 7.51 (d, J = 8.7 Hz, 4H, H^{C3}), 7.28 (m, 8H, H^{D3}), 7.23 (d, *J* = 16.0 Hz, 2H, H^b), 7.14 (m, 8H, H^{D2}), 7.10 – 7.04 (overlapping m, 8H, H^{C2+D4}), 4.17 (m, 8H, $H^{Et\text{-}CH2}$), 1.37 (t, *J* = 7.1 Hz, 12H, $H^{Et\text{-}CH3}$).

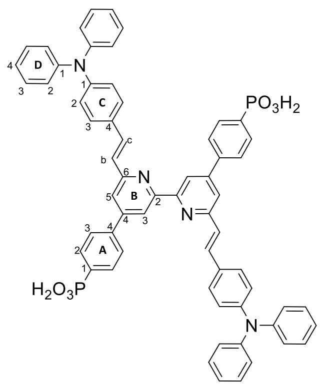
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ/ ppm 156.7 (C^{B2}), 156.4 (C^{B6}), 148.9 (C^{B4}), 148.4 (C^{C4}), 147.5 (C^{D1}), 143.1 (C^{A4}), 133.1 (C^c), 132.7 (d, $^2J_{CP}$ = 10.0 Hz, C^{A2}), 130.5 (C^{C1}), 129.5 (C^{D3}), 129.1 (d, $^1J_{CP}$ = 188.4 Hz, C^{A1}), 128.3 (C^{C3}), 127.5 (d, $^3J_{CP}$ = 15.63 Hz, C^{A3}), 126.3 (C^b), 125.0 (C^{D2}), 123.5 (C^{D4}), 123.1 (C^{C2}), 120.1 (C^{B5}), 117.9 (C^{B3}), 62.4 (d, $^2J_{CP}$ = 5.37 Hz, $C^{Et\text{-}CH2}$), 16.6 (d, $^3J_{CP}$ = 6.52 Hz, $C^{Et\text{-}CH3}$).

$^{31}P\{^1H\}$ NMR (202 MHz, 298 K, $CDCl_3$) δ/ppm 18.2 (s, P).

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 267 (ε/dm^{-3} mol^{-1} cm^{-1} 71,150), 401 (59,850).

HR ESI-MS *m/z* 1119.4361 $[M+H]^+$ (calc. 1119.4374).

Found: C 74.65, H 5.78, N 5.29; $C_{62}H_{44}Br_2N_4$ requires C 75.12, H 5.76, N 5.01.



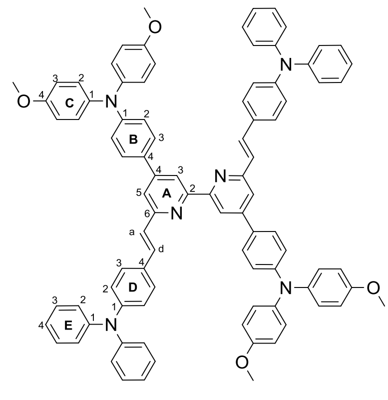
4 Compound **4e** (122 mg, 109 µmol, 1.0 eq) was loaded in a round-bottom flask and dissolved with anhydrous CH_2Cl_2 (20 mL). TMSBr (575 µL, 4.36 mmol, 40 eq) was added dropwise into the reaction mixture and stirred under N_2 at room temperature for 7 h. The solvent was removed by rotavaporation and the residue was redissolved with the smallest amount of MeOH. Addition of Et_2O afforded precipitation of the product, which was filtered and rinsed with small portions of Et_2O, then dried *in vacuo*. The product was isolated as a deep purple solid (65.8 mg, 65.3 µmol, 59.9%).

^{1}H NMR (500 MHz, DMSO-d_6) δ/ppm 8.72 (d, *J* = 1.6 Hz, 2H, H^{B3}), 8.20 (s, 2H, H^{B5}), 8.11 (dd, *J* = 8.3, 3.1 Hz, 4H, H^{A3}), 8.00 (d, *J* = 16.1 Hz, 2H, H^c), 7.89 (m, 4H, H^{A2}), 7.66 (m, 4H, H^{C3}), 7.46 (d, *J* = 16.1 Hz, 2H, H^b), 7.36 (m, 8H, H^{D3}), 7.16 – 7.08 (overlapping m, 12H, H^{D2+D4}), 7.00 (m, 4H, H^{C3}).

$^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ/ ppm 149.3 (C^{B4}), 147.9 (C^{C1}), 146.7 (C^{D1}), 139.1 (C^{A4}), 135.4 (d, $^1J_{CP}$ = 175.5 Hz, C^{A1}), 134.4 (C^c), 131.4 (C^{A2}), 129.7 (C^{D3}), 129.6 (C^{C4}), 128.7 (C^{C3}), 127.1 (C^{A3}), 124.8 (C^{D2}), 124.5 (C^b), 123.8 (C^{D4}), 122.0 (C^{C2}), 120.2 (C^{B5}), 117.4 (C^{B3}); C^{B2}, C^{B6} not resolved in HMBC.

$^{31}P\{^1H\}$ NMR (202 MHz, 298 K, DMSO-d_6) δ/ppm 11.9 (s, P).

HR ESI-MS *m/z* 1005.2972 $[M-H]^-$ (calc. 1005.2976).



5 Compound **10** (300 mg, 299 µmol, 1.0 eq), 4,4'-Dimethoxydiphenylamine (171 mg, 747 µmol, 2.5 eq), NaOtBu (172 mg, 1.79 mmol, 6.0 eq), $Pd(dba)_2$ (17.2 mg, 29.9 µmol, 10 mol%), Ruphos (28.5 mg, 59.8 µmol, 20 mol%) were loaded in a microwave vial. After three cycles of vacuum-N2, the reaction mixture was dissolved with N2-degassed THF (4 mL), then set at 90 °C for 18 h. The reaction vessel was allowed to cool down to rt. The reaction mixture was transferred into a separatory funnel and water (20 mL) added. The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The organic layers were washed with Brine (20 mL), back-extracted with an additional portion of CH2Cl2. After drying over $MgSO_4$, the crude mixture was brought to dryness by rotavaporation. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/CHX, from 3:1 to CH_2Cl_2), then dried *in vacuo*. The product was isolated as orange crystalline powder (351.2 mg, 270 µmol, 90.2%).

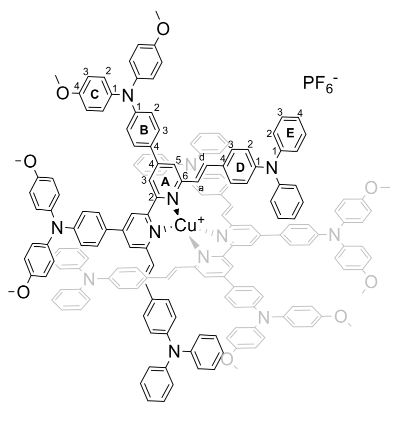
^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.60 (s, 2H, H^{A3}), 7.75 (d, *J* = 16.0 Hz, 2H, H^d), 7.66 (d, *J* = 8.3 Hz, 4H, H^{B3}), 7.57 (s, 2H, H^{A5}), 7.50 (m, 4H, H^{D3}), 7.27 (m, 8H, H^{E3}), 7.21 (d, *J* = 16.0 Hz, 2H, H^a), 7.15 – 7.10 (overlapping m, 16H, H^{C2+E2}), 7.09 – 7.02 (overlapping m, 12H, $H^{B2+D2+E4}$), 6.87 (m, 8H, H^{C3}), 3.81 (s, 12H, H^{OCH3}).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm 156.9 (C^{A2}), 156.4 (C^{C4}), 155.8 (C^{A6}), 149.8 (C^{B1}), 148.0 (C^{D1}), 147.6 (C^{E1}), 140.6 (C^{C1}), 132.1 (C^d), 131.1 (C^{D4}), 130.0 (C^{B4}), 129.5 (C^{E3}), 128.2 (C^{D3}), 127.9 (C^{B3}), 127.2 (C^a), 127.2 (C^{C2}), 124.9 (C^{E2}), 123.3 (C^{D2}), 123.3 (C^{E4}), 120.1 (C^{B2}), 119.1 (C^{A5}), 117.1 (C^{A3}), 115.0 (C^{C3}); C^{A4} not resolved in HMBC.

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 298 (ε/dm^{-3} mol^{-1} cm^{-1} 69,600), 385 (91,570).

HR ESI-MS *m/z* 1301.5699 [M+H]$^+$ (calc. 1301.5688).

Found: C 82.71, H 5.91, N 6.38; $C_{90}H_{72}BrN_6O_4$ requires C 83.05, H 5.58, N 6.46.



[Cu(5)₂][PF₆] Compound **5** (82.0 mg, 63.0 µmol, 2.0 eq) was loaded in a round-bottom flask and dissolved in CH_2Cl_2/CH_3CN mixture (10 mL). After addition of $[Cu(CH_3CN)_4][PF_6]$ (11.7 mg, 31.5 µmol, 0.5 eq) the mixture was set under stirring for 2 h. The reaction mixture was dried by rotavaporation and redissolved in the minimal amount of CH_2Cl_2. Then Et_2O was added to the reaction mixture to afford precipitation of the product. The precipitate was collected, washed with small amounts of Et_2O and dried *in vacuo*. Isolated as brown solid (63.9 mg, 31.5 µmol, 72.1%).

^{1}H NMR (500 MHz, acetone-d$_6$) δ/ppm 8.64 (d, *J* = 1.6 Hz, 4H, H^{A3}), 8.09 (d, *J* = 1.7 Hz, 4H, H^{A5}), 7.68 (d, *J* = 8.9 Hz, 8H, H^{B3}), 7.54 (d, *J* = 16.4 Hz, 4H, H^d), 7.22 (m, 16H, H^{E3}), 7.08 (d, *J* = 9.0 Hz, 16H, H^{C2}), 7.07 – 7.03 (overlapping m, 6H, H^{a+E4}), 6.95 (d, *J* = 9.0 Hz, 8H, H^{C3}), 6.89 – 6.84 (overlapping m, 32H, $H^{B2+D2+E2}$), 6.70 (m, 8H, H^{D3}), 3.83 (s, 24H, H^{OCH3}).

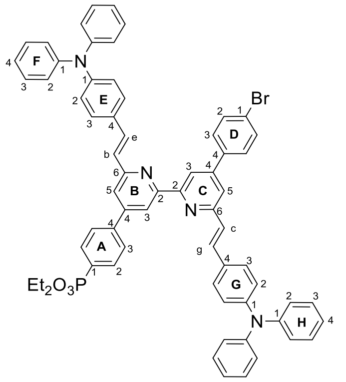
^{13}C{^{1}H} NMR (126 MHz, acetone-d$_6$) δ/ ppm 158.0 (C^{C4}), 156.0 (C^{A6}), 154.3 (C^{A2}), 151.4 (C^{A4}), 150.5 (C^{B1}), 149.2 (C^{D1}), 148.0 (C^{E1}), 140.5 (C^{C1}), 134.6 (C^d), 130.4 (C^{E3}), 130.2 (C^{D4}), 129.0 (C^{B3}), 128.7 (C^{C2}), 128.7 (C^{D3}), 128.2 (C^{B4}), 126.3 (C^a), 125.8 (C^{E2}), 124.6 (C^{E4}), 122.7 (C^{D2}), 119.2 (C^{B2}), 119.1 (C^{A5}), 118.5 (C^{A3}), 115.9 (C^{C3}).

^{31}P{^{1}H} NMR (202 MHz, 298 K, acetone-d$_6$) δ/ppm -142.5 (hept, $^1J_{PF}$ = 703.3 Hz, P^{PF6}).

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 299 (ε/dm^{-3} mol^{-1} cm^{-1} 141,040), 413 (141,040).

HR ESI-MS m/z 2664.0470 [M–PF_6]$^+$ (calc. 2664.0521).

Found: C 71.64, H 5.20, N 5.18; $C_{160}H_{136}N_{10}O_{10}P_3$ requires C 73.09, H 5.21, N 5.33.



6eBr Compound **10** (901 mg, 897 µmol, 3.0 eq), HPO_3Et_2 (46.3 µL, 49.6 mg, 359 µmol, 1.2 eq), Cs_2CO_3 (195 mg, 598 µmol, 2.0 eq), Pd(dppf)Cl_2 (17.5 mg, 23.9 µmol, 6.66 mol%) were loaded in a microwave vial. After three vacuum-N_2 cycles, the reaction mixture was dissolved in N_2-degassed Toluene (24.8 mL), then set at 110 °C for 18 h. The reaction vessel was allowed to cool down to rt. The crude mixture was brought to dryness by rotavaporation, then redissolved in $CHCl_3$ and filtered through a celite plug. The crude mixture was dried again and purified by column chromatography (SiO_2, CH_2Cl_2 with EtOAc gradient changing from 19:1 to 9:1 to 4:1 to 2:1), then dried *in vacuo*. The product was isolated as yellow powder (202 mg, 190 µmol, 63.6%).

^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.66 (d, J = 1.6 Hz, 1H, H^{B3}), 8.62 (d, *J* = 1.6 Hz, 1H, H^{C3}), 7.99 (dd, *J* = 12.9, 7.9 Hz, 2H, H^{A2}), 7.91 (dd, *J* = 8.0, 3.8 Hz, 2H, H^{A3}), 7.77 (overlapping d, 2H, H^{e+g}), 7.71 – 7.65 (overlapping m, 4H, H^{D2+D3}), 7.63 (d, *J* = 1.6 Hz, 1H, H^{B5}), 7.59 (d, *J* = 1.6 Hz, 1H, H^{C5}), 7.51 (d, *J* = 8.2 Hz, 4H, H^{E3+G3}), 7.29 (t, *J* = 7.7 Hz, 8H, H^{F3+H3}), 7.23 (overlapping d, 2H, H^{b+c}), 7.14 (overlapping d, 8H, H^{F2+H2}), 7.10 – 7.04 (overlapping m, 8H, $H^{E2+G2+F4+H4}$), 4.18 (m, 4H, $H^{Et\text{-}CH2}$), 1.37 (t, *J* = 7.1 Hz, 6H, $H^{Et\text{-}CH3}$).

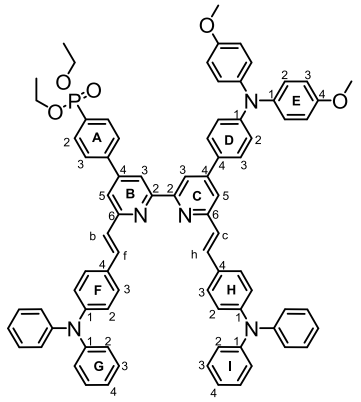
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ ppm 156.8 (C^{B2}), 156.7 (C^{C2}), 156.3 (C^{B6}), 156.3 (C^{B6}), 148.9 (C^{C4}), 148.8 (C^{B4}), 148.4 ($C^{E1/G1}$), 148.3 ($C^{E1/G1}$), 147.5 (C^{F1+H1}), 143.1 (d, $^4J_{CP}$ = 3.11 Hz, C^{A4}), 138.0 (C^{D4}), 133.0 (C^{e+g}), 132.4 (C^{D2}), 130.6 ($C^{E4/G4}$), 130.5 ($C^{E4/G4}$), 129.5 (C^{F3+H3}), 129.4 (C^{b+c}), 129.1 (d, $^1J_{CP}$ = 181.01 Hz, C^{A1}), 129.0 (C^{D3}), 128.3 (C^{E3+G3}), 127.5 (d, $^3J_{CP}$ = 14.8 Hz, C^{A3}), 125.0 (C^{F2+H2}), 123.7 (d, $^2J_{CP}$ = 10.0 Hz, C^{A2}), 123.5 (C^{F4+H4}), 123.5 (C^{D1}), 123.1 (C^{E2+G2}), 120.1 (C^{B5}), 119.8 (C^{C5}), 117.9 (C^{B3}), 117.6 (C^{C3}), 62.4 (d, $^2J_{CP}$ = 5.40 Hz, $C^{Et\text{-}CH2}$), 16.5 (d, $^3J_{CP}$ = 6.47 Hz, $C^{Et\text{-}CH3}$).

^{31}P{^{1}H} NMR (202 MHz, 298 K, $CDCl_3$) δ/ppm 18.2 (s, P).

UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 271 (ε/dm^{-3} mol^{-1} cm^{-1} 65,930), 400 (56,860).

HR ESI-MS *m/z* 1063.3190 $[M+H]^+$ (calc. 1063.3190).

Found: C 74.09, H 5.26, N 4.93; $C_{66}H_{54}BrN_4O_3P$ requires C 74.64, H 5.13, N 5.28.

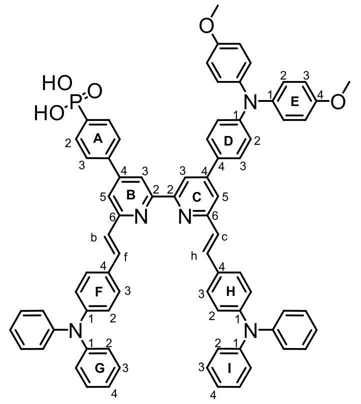


6e Compound **6eBr** (155 mg, 146 µmol, 1.00 eq), 4,4'-Dimethoxydiphenylamine (41.8 mg, 183 µmol, 1.25 eq), NaOtBu (21.0 mg, 219 µmol, 1.50 eq), Pd(dba)2 (4.2 mg, 7.3 µmol, 5 mol%), Ruphos (6.95 mg, 14.6 µmol, 10 mol%) were loaded in a microwave vial. After three vacuum-N2 cycles, the reaction mixture was dissolved in N_2-degassed Toluene (15 mL), then set at 90 °C for 18 h. The reaction vessel was allowed to cool down to rt. The reaction mixture was transferred in a separatory funnel and water added. The water emulsion containing most of the material was dissolved by addition of NaOH solution (3M, ca. 3 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The organic layers were brought to dryness by rotavaporation. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 with EtOAc, gradient from 39:1 to 29:1 after elution of main yellow band), then dried *in vacuo*. The product was isolated as deep orange crystalline powder (103 mg, 85.3 µmol, 58.4%).

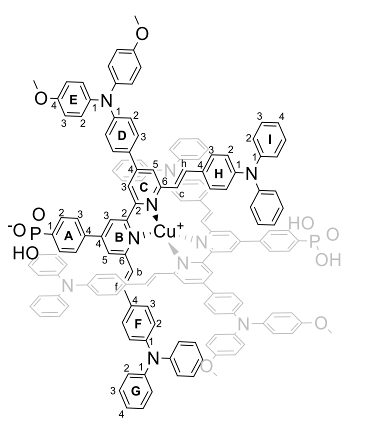
^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm 8.64 (d, *J* = 1.6 Hz, 1H, H^{B3}), 8.62 (d, *J* = 1.6 Hz, 1H, H^{C3}), 7.98 (dd, *J* = 12.9, 8.2 Hz, 2H, H^{A2}), 7.90 (dd, *J* = 8.2, 3.6 Hz, H^{A3}), 7.76 (overlapping d, 2H, H^{h+f}), 7.66 (m, 2H, H^{D3}), 7.60 (overlapping s, 2H, H^{B5+C5}), 7.51 (overlapping m, 4H, H^{F3+H3}), 7.30 – 7.27 (overlapping t, 8H, H^{G3+I3}), 7.22 (overlapping d, 2H, H^{b+c}), 7.16 – 7.11 (overlapping m, 12H, $H^{G2+I2+E2}$), 7.10 – 7.02 (overlapping m, 10H, $H^{D2+F2+G4+H2+I4}$), 6.87 (m, 4H, H^{E3}), 4.16 (m, 4H, $H^{Et\text{-}CH2}$), 3.82 (s, 6H, H^{OCH3}), 1.36 (t, *J* = 7.1 Hz, 6H, $H^{Et\text{-}CH3}$).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ/ ppm 157.2 (C^{B2}), 156.4 (C^{E4}), 156.2 (C^{B6}), 156.2 (C^{C2}), 155.9 (C^{C6}), 149.8 (C^{D1}), 148.8 (C^{B4}), 148.0 (C^{F1}), 148.0 (C^{H1}), 147.5 (C^{G1}), 147.5 (C^{I1}), 143.14 (d, $^4J_{CP}$ = 2.74 Hz, C^{A4}), 140.5 (C^{E1}), 132.9 (C^{f}), 132.7 (d, $^2J_{CP}$ = 10.2 Hz, C^{A2}), 132.4 (C^{h}), 130.8 ($C^{F4/H4}$), 130.7 ($C^{F4/H4}$), 129.8 (C^{D4}), 129.5 (C^{G3}), 129.5 (C^{I3}), 128.8 (d, $^1J_{CP}$ = 174.5 Hz, C^{A1}), 128.3 ($C^{F3/H3}$), 128.2 ($C^{F3/H3}$), 127.8 (C^{D3}), 127.5 (d, $^3J_{CP}$ = 15.2 Hz, C^{A3}),

127.2 (C^{E2}), 126.9 (C^{c}), 126.5 (C^{b}), 124.9 (C^{G2}), 124.9 (C^{I2}), 123.4 (C^{G4}), 123.4 (C^{I4}), 123.2 (C^{F2}), 123.2 (C^{H2}), 120.0 (C^{D2}), 119.9 (C^{C5}), 119.3 (C^{B5}), 117.9 (C^{B3}), 117.0 (C^{C3}), 115.0 (C^{E3}), 55.7 (C^{OCH3}),
62.4 (d, $^{2}J_{CP}$ = 5.4 Hz, C$^{Et\text{-}CH2}$), 16.6 (d, $^{3}J_{CP}$ = 6.3 Hz, C$^{Et\text{-}CH3}$); C4 not resolved in HMBC.
^{31}P{^{1}H} NMR (202 MHz, 298 K, $CDCl_3$) δ/ppm 18.3 (s, P).
UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 298 (ε/dm^{-3} mol^{-1} cm^{-1} 69,600), 385 (91,570).
HR ESI-MS *m/z* 1210.5025 [M+H]$^{+}$ (calc. 1210.5031).
Found: C 78.90, H 5.73, N 5.77; $C_{80}H_{68}N_5O_5P$ requires C 79.38, H 5.66, N 5.79.

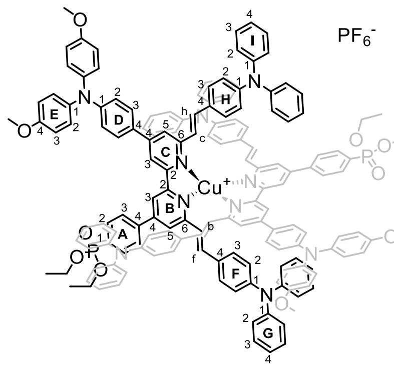


6 Compound **6e** (52.7 mg, 43.6 µmol, 1.0 eq) was loaded in a round-bottom flask and dissolved in anhydrous CH_2Cl_2 (5 mL). TMSBr (46.0 µL, 53.4 mg, 349 µmol, 8.0 eq) was added dropwise into the reaction mixture and stirred under N_2 at rt overnight. The solvent was removed by rotavaporation and the residue was redissolved with the smallest amount of MeOH/ CH_2Cl_2 (9:1). Addition of Et_2O afforded precipitation of the product, which was filtered and rinsed with small portions of Et_2O, then dried *in vacuo*. The product is isolated as a deep purple solid (41.85 mg, 36.3 µmol, 83.2%).
^{1}H NMR (500 MHz, DMSO-d$_6$) δ/ppm 8.66 (overlapping s, 2H, H^{B3+C3}), 8.35 (s, 1H, H^{B5}), 8.21 (s, 1H, H^{C5}), 8.09 (overlapping m, 4H, H^{A3+f+h}), 8.00 (d, *J* = 8.3 Hz, 2H, H^{D3}), 7.88 (dd, *J* = 12.6, 7.9 Hz, 2H, H^{A2}), 7.62 (overlapping t, *J* = 8.6 Hz, 4H, H^{F3+H3}), 7.55 (d, *J* = 16.2 Hz, 1H, H$^{b/c}$), 7.43 (d, *J* = 16.1 Hz, 1H, H$^{b/c}$), 7.36 (overlapping t, 8H, H^{G3+I3}), 7.17 – 7.07 (overlapping m, 16H, H$^{E2+G2+G4+I2+I4}$), 6.99 (overlapping m, 8H, H$^{E3+F2+H2}$), 6.87 (d, *J* = 8.5 Hz, 2H, H^{D2}), 3.77 (s, 6H, H^{OCH3}).
^{13}C{^{1}H} NMR (126 MHz, DMSO-d$_6$) δ/ ppm 156.6 (C^{E4}), 156.3 (C^{B6}), 155.8 (C^{C6}), 150.7 (C^{D1}), 149.4 (C^{B4}), 148.7 (C$^{F1/H1}$), 148.1 (C$^{F1/H1}$), 146.6 (C^{G1}), 146.6 (C^{I1}), 138.9 (C^{E1}), 138.8 (C^{A4}), 135.6 (d, $^{1}J_{CP}$ = 180.95 Hz, C^{A1}) 134.9 (C^{f}), 134.9 (C^{h}), 131.2 (d, $^{2}J_{CP}$ = 9.63 Hz, C^{A2}), 129.8 (C$^{G3/I3}$), 129.7 (C$^{G3/I3}$), 129.6 (C^{F4}), 129.6 (C^{H4}), 129.2 (C^{D3}), 129.0 (C$^{F3/H3}$), 128.6 (C$^{F3/H3}$), 127.6 (C^{E2}), 127.1 (d, $^{3}J_{CP}$ = 14.3 Hz, C^{A3}), 125.5 (C^{D4}), 125.4 (C$^{G4/I4}$), 124.8 (C$^{G2/I2}$), 124.3 (C$^{b/c}$), 124.3 (C$^{b/c}$), 124.2 (C$^{G4/I4}$), 123.9 (C$^{G2/I2}$), 121.9 (C^{F2}), 121.9 (C^{H2}), 120.8 (C^{C5}), 118.0 (C^{B3}), 117.7 (C^{D2}), 117.6 (C^{B5}), 117.1 (C^{C3}), 115.2 (C^{E3}), 55.3 (C^{OCH3}); B2, C2 and C4 not resolved in HMBC.
^{31}P{^{1}H} NMR (202 MHz, 298 K, DMSO-d$_6$) δ/ppm 11.9 (s, P).
HR ESI-MS *m/z* 1152.4263 [M−H]$^{-}$ (calc. 1152.4259).



[Cu(6)(6–H)] Compound **6** (37.9 mg, 32.8 µmol, 2.0 eq) was loaded in a round bottom flask and dissolved in a CH_2Cl_2/MeOH mixture (8 mL). After addition of [Cu(CH_3CN)$_4$][PF_6] (3.65 mL of a 4.49 mM solution, 16.4 µmol, 1.0 eq) the mixture was set under stirring overnight. The reaction mixture was dried by rotavaporation and redissolved in minimum amount of CH_2Cl_2/MeOH mixture. Then n-Hexane was added to the reaction mixture to afford precipitation of the product. The precipitate was filtered, washed with small amounts of n-hexane, then dried *in vacuo*. The product was isolated as a dark red powder (31.2 mg, 13.1 µmol, 80.1%).
^{1}H NMR (500 MHz, DMSO-d$_6$) δ/ppm 8.87 (s, 2H, H^{B3}), 8.81 (s, 2H, H^{C3}), 8.35 (s, 2H, H^{B5}), 8.18 (s, 2H, H^{C5}), 7.98 (dd, *J* = 8.1, 3.0 Hz, 4H, H^{A3}), 7.80 (dd, *J* = 12.6, 7.7 Hz, 4H, H^{A2}), 7.74 (d, *J* = 8.4 Hz, 4H, H^{D3}), 7.61 (overlapping d, 4H, H^{f+h}), 7.22 (overlapping t, 16H, H^{G3+I3}), 7.07 – 7.01

(overlapping m, 12H, H$^{E2+G4+I4}$), 6.97 (m, 8H, H^{E3}), 6.91 – 6.81 (overlapping m, 20H, H$^{b+c+G2+I2}$), 6.76 (d, *J* = 8.3 Hz, 4H, H^{D2}), 6.72 (overlapping d, 8H, H^{F3+H3}), 6.61 (overlapping d, 8H, H^{F2+H2}), 3.77 (d, *J* = 3.4 Hz, 12H, H^{OCH3}).
^{13}C{^{1}H} NMR (126 MHz, DMSO-d$_6$) δ/ ppm 156.5 (C^{E4}), 154.6 (C^{B6}), 154.5 (C^{C6}), 149.8 (C^{D1}), 148.6 (C^{B4}), 147.8 (C^{F1}), 147.8 (C^{H1}), 146.4 (C^{G1}), 146.4 (C^{I1}), 139.1 (C^{E1}), 138.6 (C^{A4}), 135.5 (d, $^{1}J_{CP}$ = 186.4 Hz, C^{A1}), 134.4 (C$^{f/h}$), 134.0 (C$^{f/h}$), 131.2 (C^{A2}), 129.6 (C^{G3}), 129.6 (C^{I3}), 128.7 (C^{F4}), 128.7 (C^{H4}), 128.3 (C^{D3}), 127.6 (C^{F3}), 127.6 (C^{H3}), 127.4 (C^{E2}), 127.1 (C^{A3}), 126.7 (C^{D4}), 126.6 (C^{b}), 126.6 (C^{c}), 124.7 (C^{G2}), 124.7 (C^{I2}), 123.8 (C^{G4}), 123.8 (C^{I4}), 121.3 (C^{F2}), 121.3 (C^{H2}), 119.7 (C^{B5}), 118.8 (C^{B3}), 118.5 (C^{C5}), 118.1 (C^{C3}), 117.8 (C^{D2}), 115.1 (C^{E3}), 55.3 (C^{OCH3}); B2, C2 and C4 not resolved in HMBC.
^{31}P{^{1}H} NMR (202 MHz, 298 K, DMSO-d$_6$) δ/ppm 12.2 (s, P).
HR MALDI-ToF-MS *m/z* 2369.7939 [M+H]$^+$ (calc. 2369.7955), m/z 2391.7764 [M+Na]$^+$ (calc. 2391.7774).



[Cu(6e)$_2$][PF$_6$] Compound **6e** (109.4 mg, 90.4 µmol, 2.0 eq) was loaded in a round-bottom flask and dissolved in CH_2Cl_2 (8 mL). After addition of [Cu(CH$_3$CN)$_4$][PF$_6$] (16.8 mg, 45.2 µmol, 1.0 eq), the mixture was set under stirring overnight. The reaction mixture was dried by rotavaporation and redissolved in Acetone (1 mL). Then n-hexane was added to the reaction mixture to afford precipitation of the product. This was collected, washed with small amounts of n-hexane and Et$_2$O, then dried *in vacuo*. The product was isolated as a red powder (91.2 mg, 34.7 µmol, 76.7%).
^{1}H NMR (500 MHz, acetone-d$_6$) δ/ppm 8.80 (d, *J* = 1.5 Hz, 2H, H^{B3}), 8.71 (d, *J* = 1.6 Hz, 2H, H^{C3}), 8.28 (s, 2H, H^{B5}), 8.13 (d, *J* = 1.5 Hz, 2H, H^{C5}), 7.99 (dd, *J* = 8.1, 3.5 Hz, 4H, H^{A3}), 7.91 (dd, *J* = 12.8, 7.9 Hz, 4H, H^{A2}), 7.68 (m, 4H, H^{D3}), 7.62 (d, *J* = 16.3 Hz, 2H, H^{f}), 7.58 (d, *J* = 16.3 Hz, 2H, H^{h}), 7.28 – 7.23 (overlapping t, 16H, H^{G3+I3}), 7.11 – 7.05 (overlapping m, 16H, H$^{b+c+E2+G4+I4}$), 6.97 (m, 8H, H^{E3}), 6.91 – 6.85 (overlapping m, 28H, H$^{D2+F3+G2+H3+I2}$), 6.69 (overlapping d, 8H, H^{F2+H2}), 4.09 (m, 8H, H$^{Et\text{-}CH2}$), 3.83 (s, 12H, H^{OCH3}), 1.29 (t, *J* = 7.0 Hz, 12H, H$^{Et\text{-}CH3}$).
^{13}C{^{1}H} NMR (126 MHz, acetone-d$_6$) δ/ ppm 158.1 (C^{E4}), 156.7 (C^{B6}), 156.2 (C^{C6}), 154.6 (C^{B2}), 153.4 (C^{C2}), 151.5 (C^{D1}), 150.8 (C^{C4}), 149.8 (C^{B4}), 149.4 (C^{F1}), 149.4 (C^{H1}), 147.9 (C^{G1}), 147.9 (C^{I1}), 141.9 (C^{A4}), 140.5 (C^{E1}), 135.7 (C^{f}), 135.2 (C^{h}), 132.2 (d, $^{1}J_{CP}$ = 188.8 Hz, C^{A1}), 130.4 (C^{E4}), 130.0 (C$^{F4/H4}$), 129.0 (C^{D3}), 128.8 (C$^{F3/H3}$), 128.7 (C^{E2}), 128.4 (C$^{F3/H3}$), 128.2 (C^{A3}), 128.1 (C^{D4}), 126.2 (C^{c}), 126.0 (C$^{G2/I2}$), 125.9 (C$^{G2/I2}$), 125.4 (C^{b}), 124.8 (C$^{G4/I4}$), 124.7 (C$^{G4/I4}$), 123.3 (C^{A2}), 122.4 (C^{F2}), 122.4 (C^{H2}), 121.1 (C^{B5}), 120.4 (C^{G3}), 120.4 (C^{I3}), 120.1 (C^{B3}), 119.8 (C^{C5}), 119.1 (C^{C3}), 119.1 (C^{D2}), 115.9 (C^{E3}), 62.7 (d, $^{2}J_{CP}$ = 5.5 Hz, C$^{Et\text{-}CH2}$), 55.9 (C^{OCH3}), 16.8 (d, $^{3}J_{CP}$ = 6.1 Hz, C$^{Et\text{-}CH3}$).
^{31}P{^{1}H} NMR (202 MHz, 298 K, acetone-d$_6$) δ/ppm 21.9 (s, P^{PO3Et2}), -139.0 (hept, $^{1}J_{PF}$ = 707.4 Hz, P^{PF6}).
UV-VIS (CH_2Cl_2, 10^{-5} mol dm^{-3}) λ/nm 297 (ε/dm^{-3} mol^{-1} cm^{-1} 124,240), 414 (134,030).
HR ESI-MS *m/z* 1240.9583 [M−PF$_6$]$^{2+}$ (calc. 1240.9601).
Found: C 71.64, H 5.20, N 5.18; $C_{160}H_{136}N_{10}O_{10}P_3$ requires C 73.09, H 5.21, N 5.33.

NMR Spectra

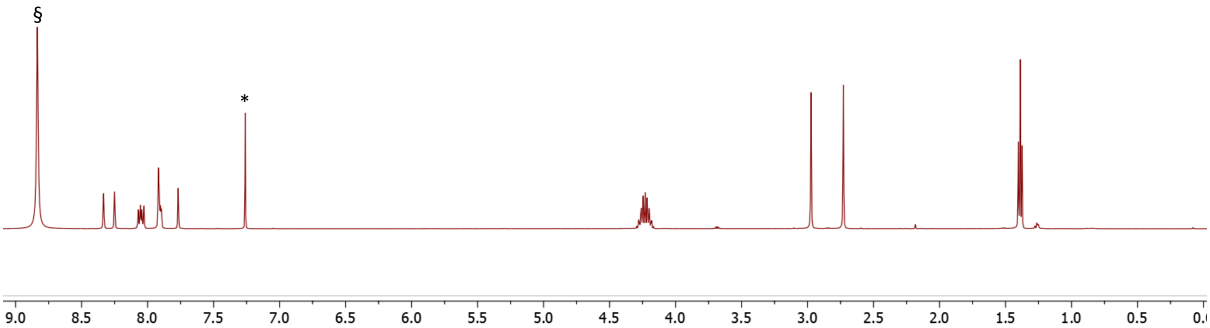


Figure S1*:* ^{1}H NMR spectrum (500 MHz, $CDCl_3$ + d-TFA, 298 K) of **8**. * = $CHCl_3$, § = H^{TFA}

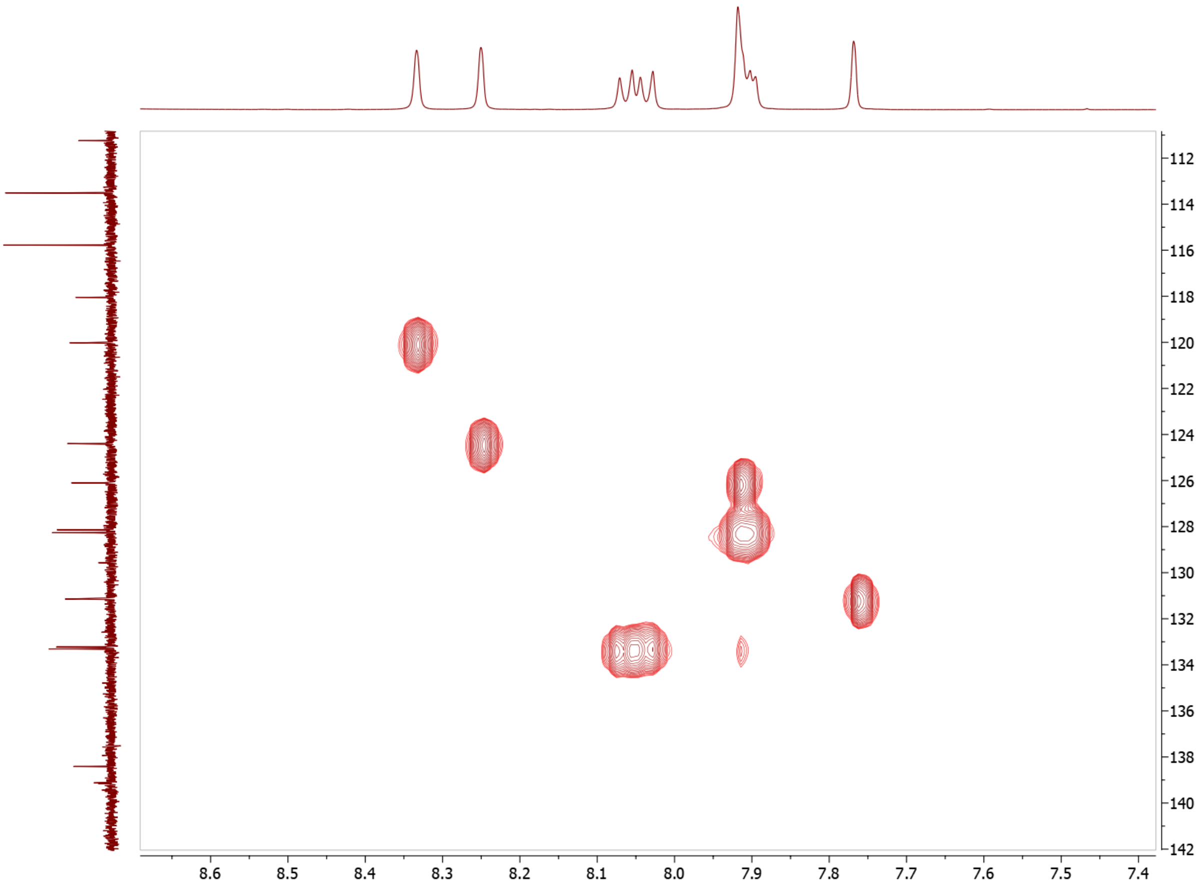


Fig. S2 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$ + d-TFA, 298 K) of **8**.

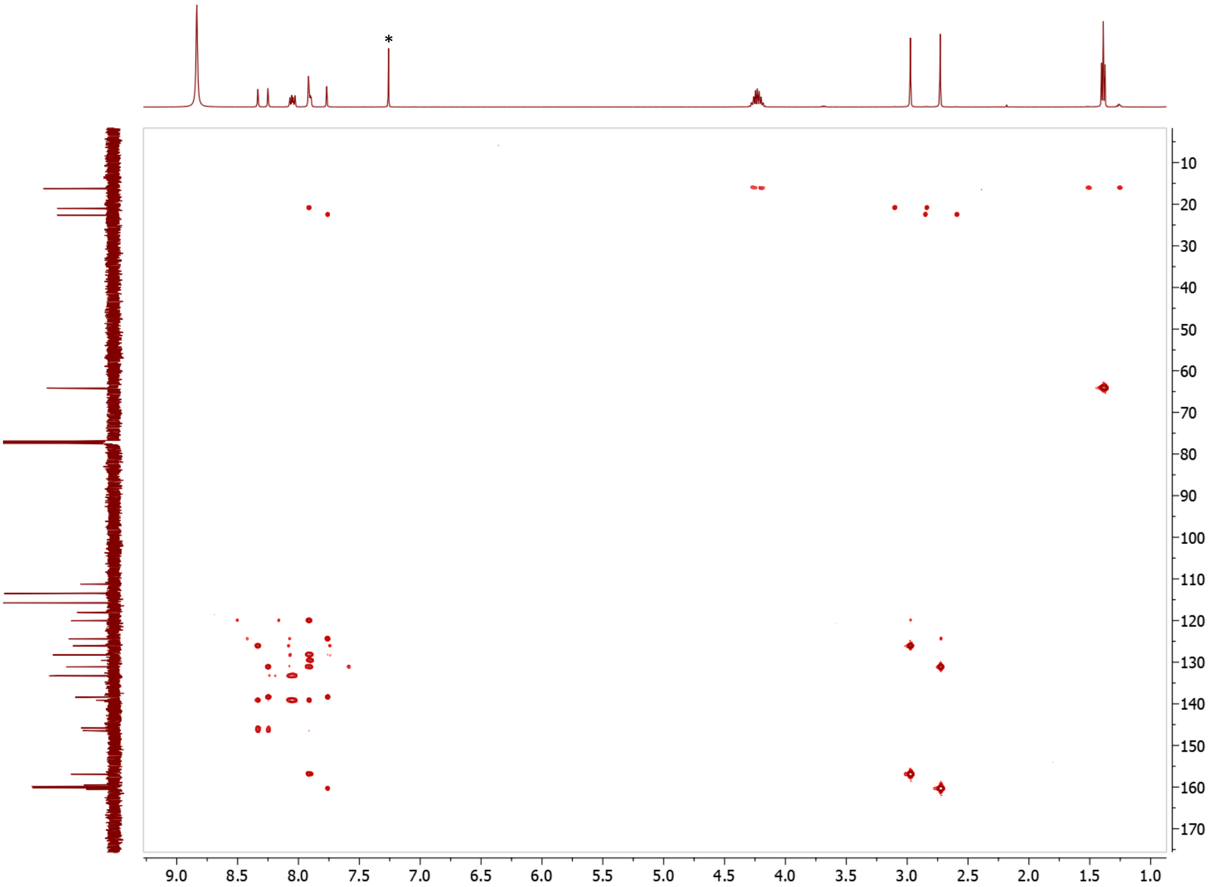


Fig. S3 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$ + d-TFA, 298 K) of **8**. * = $CHCl_3$.

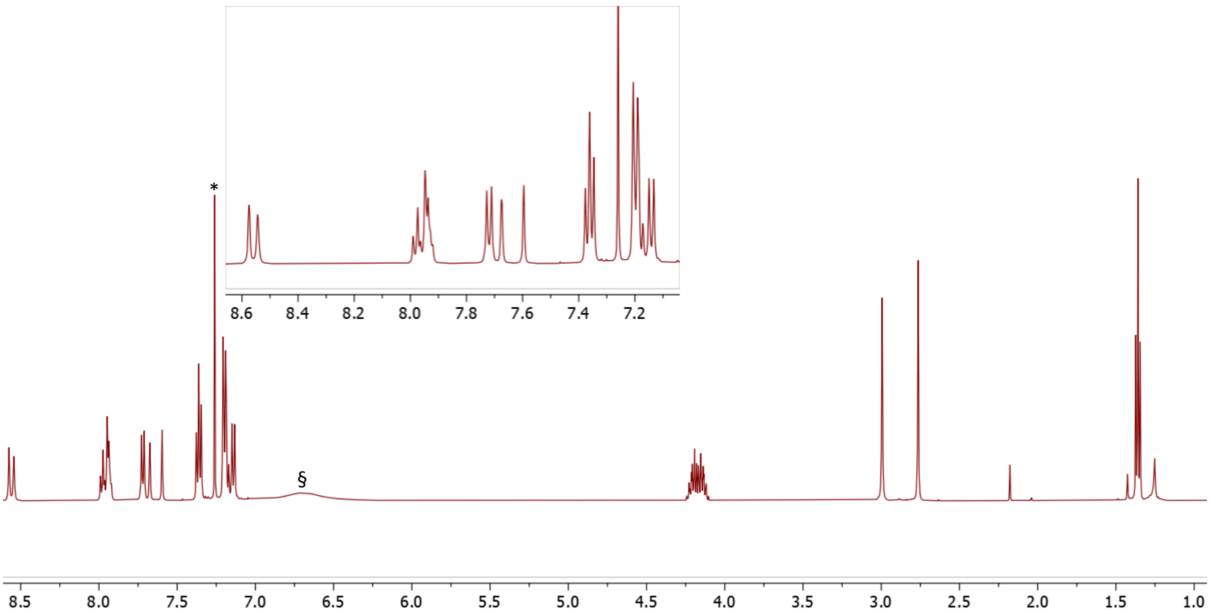


Figure S4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$ + d-TFA, 298 K) of **3e**. * = $CHCl_3$, § = H^{TFA}.

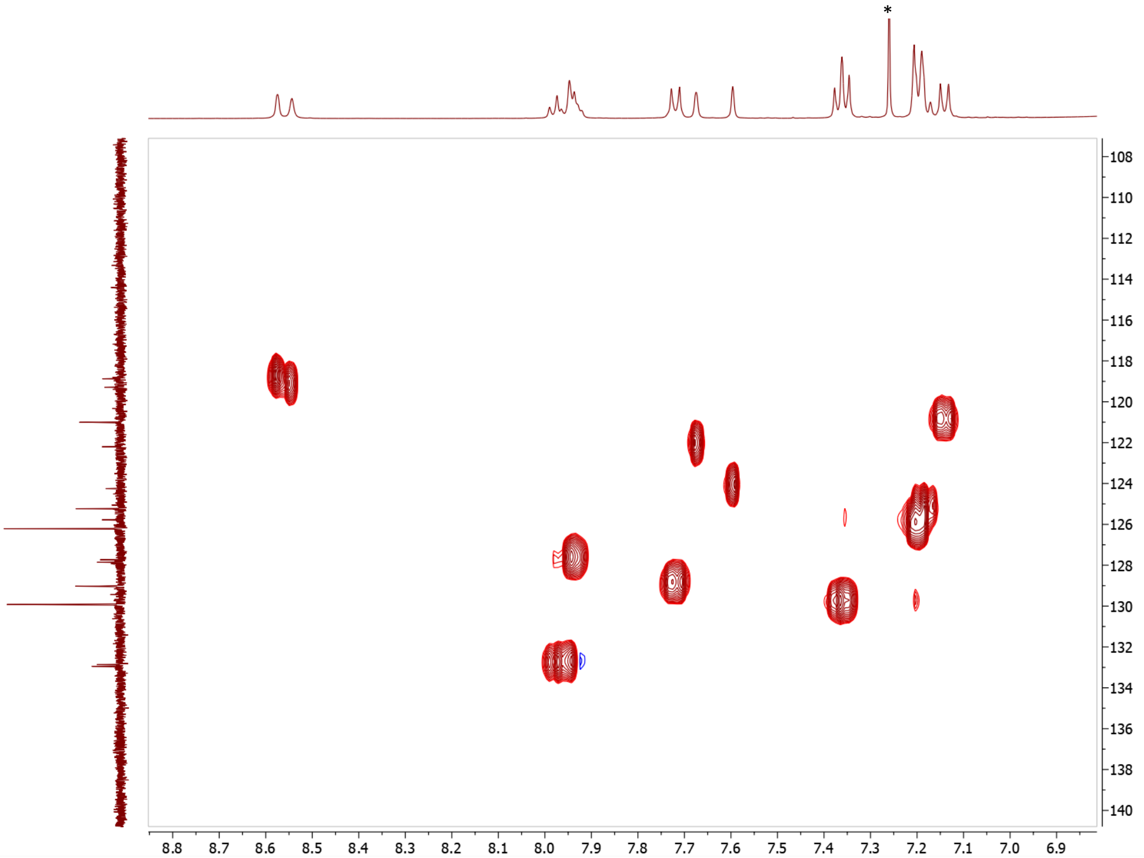


Fig. S5 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, $CDCl_3$ + d-TFA, 298 K) of **3e**. * = $CHCl_3$.

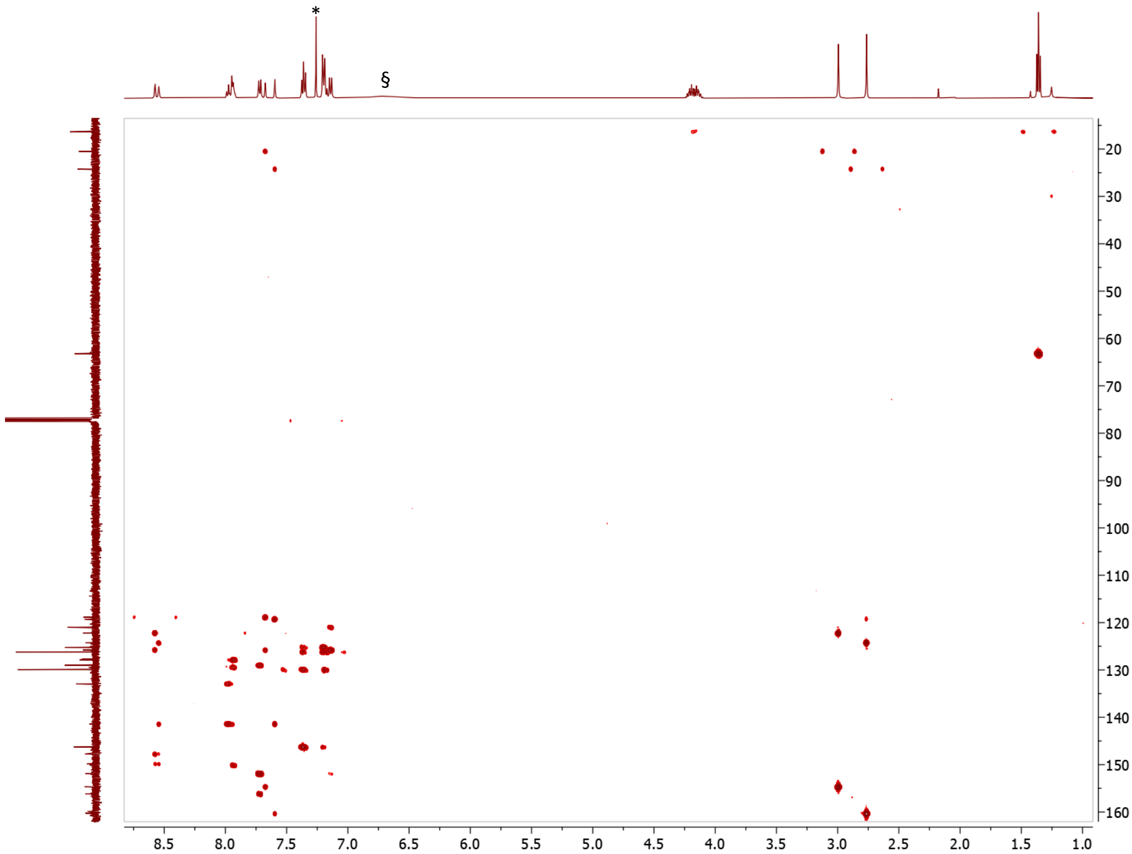


Fig. S6 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, $CDCl_3$ + d-TFA, 298 K) of **3e**. * = $CHCl_3$, § = TFA.

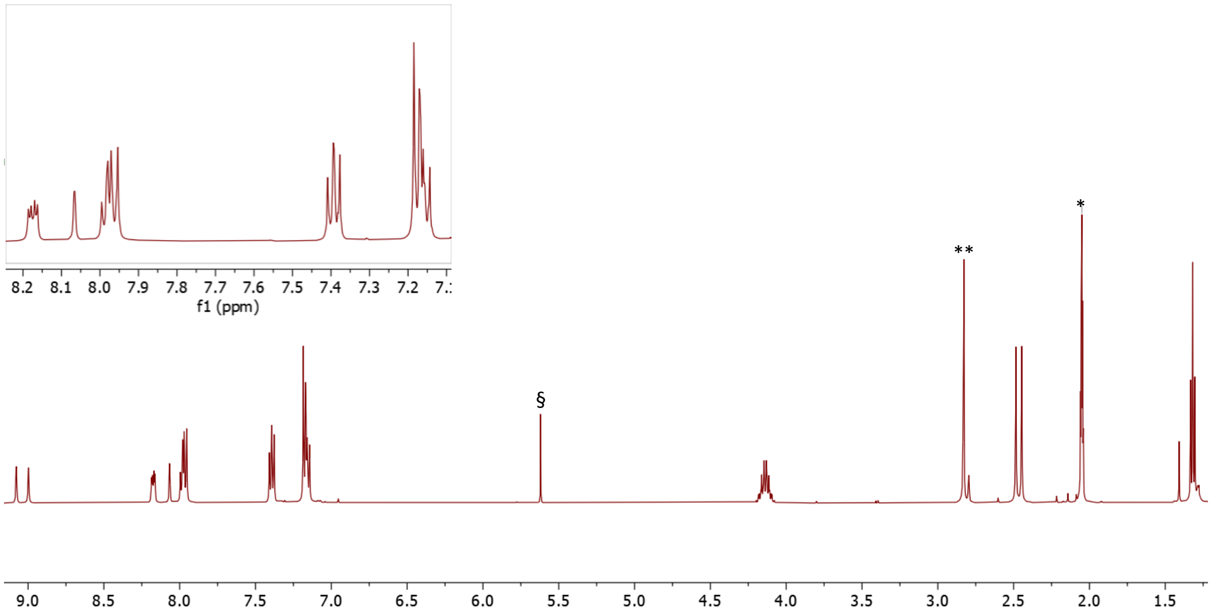


Fig. S7 ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(**3e**)$_2$][PF_6]. * = acetone-d_5, ** = H_2O and HDO, § = CH_2Cl_2.

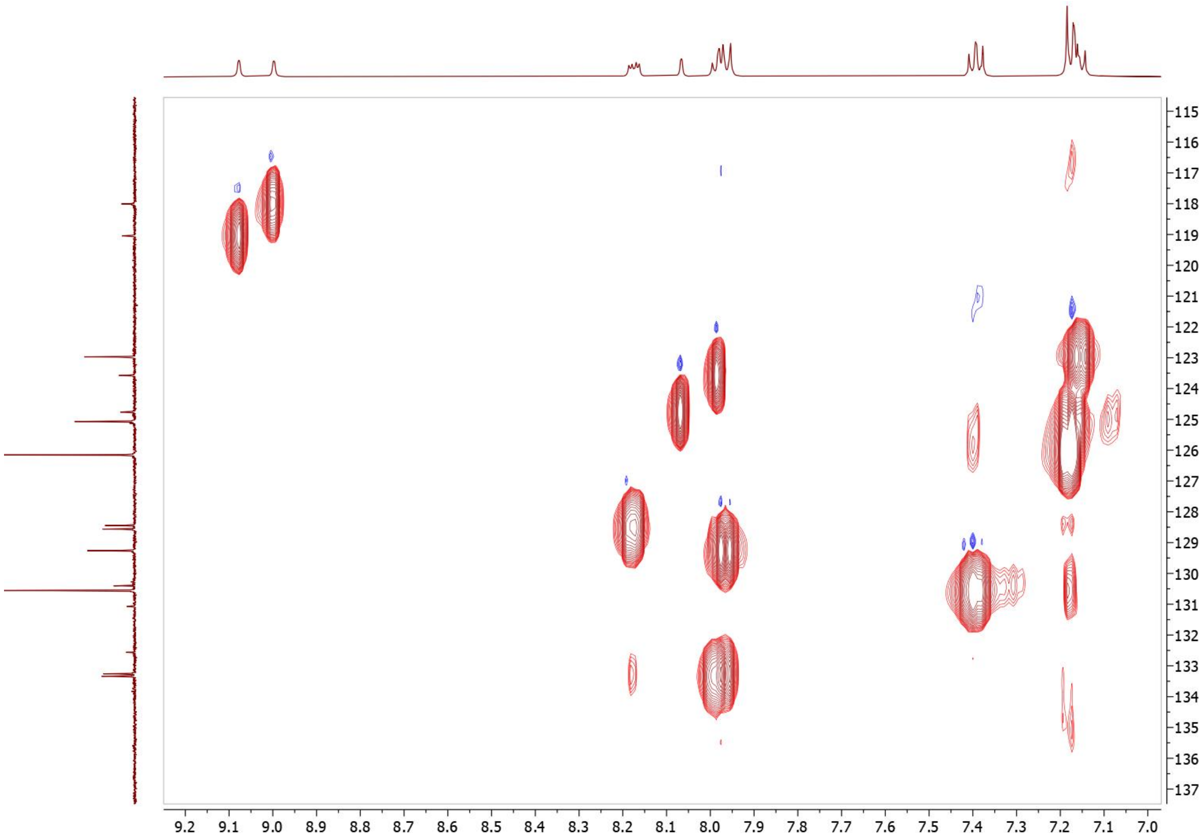


Fig. S8 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, acetone-d_6, 298 K) of [Cu(**3e**)$_2$][PF_6].

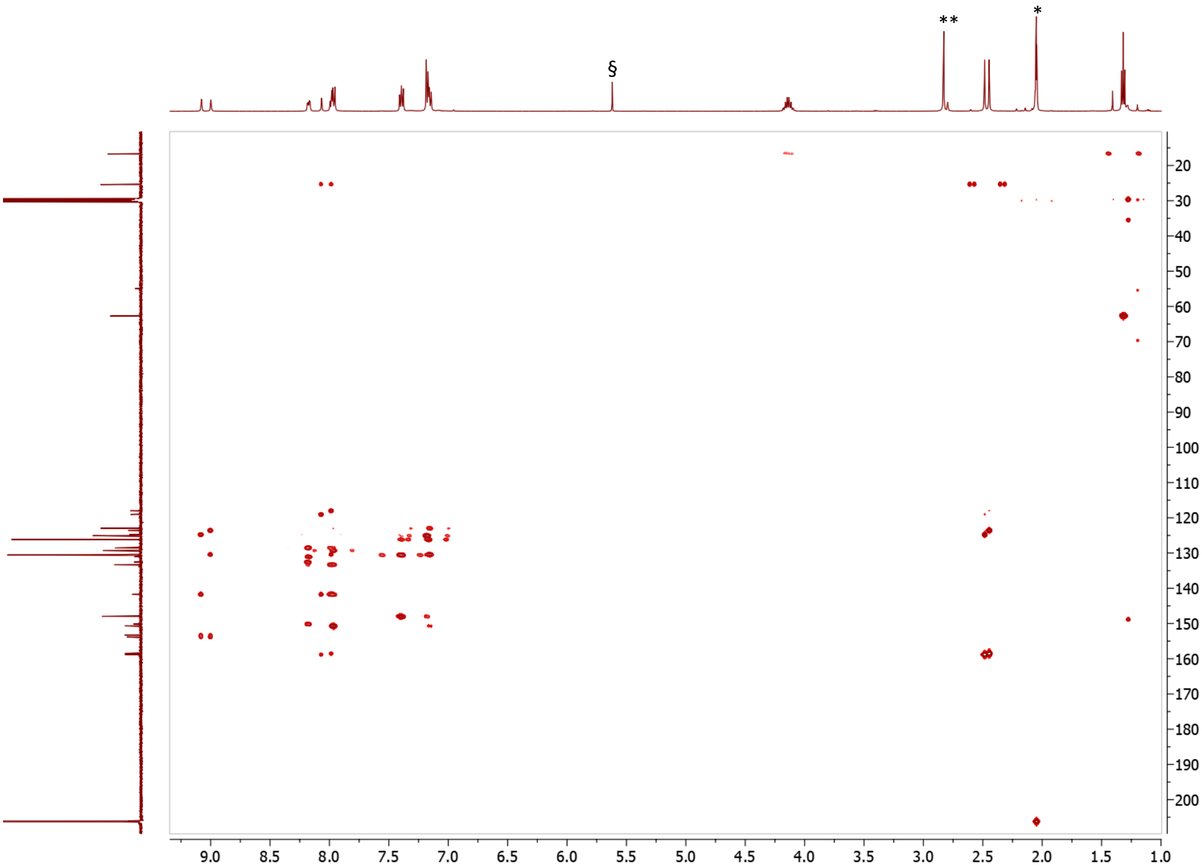


Fig. S9 Part of the HMBC spectrum (500 MHz, acetone-d$_6$, 298 K) of [Cu(**3e**)$_2$][PF$_6$]. * = acetone-d$_5$, ** = H_2O and HDO, § = CH_2Cl_2.

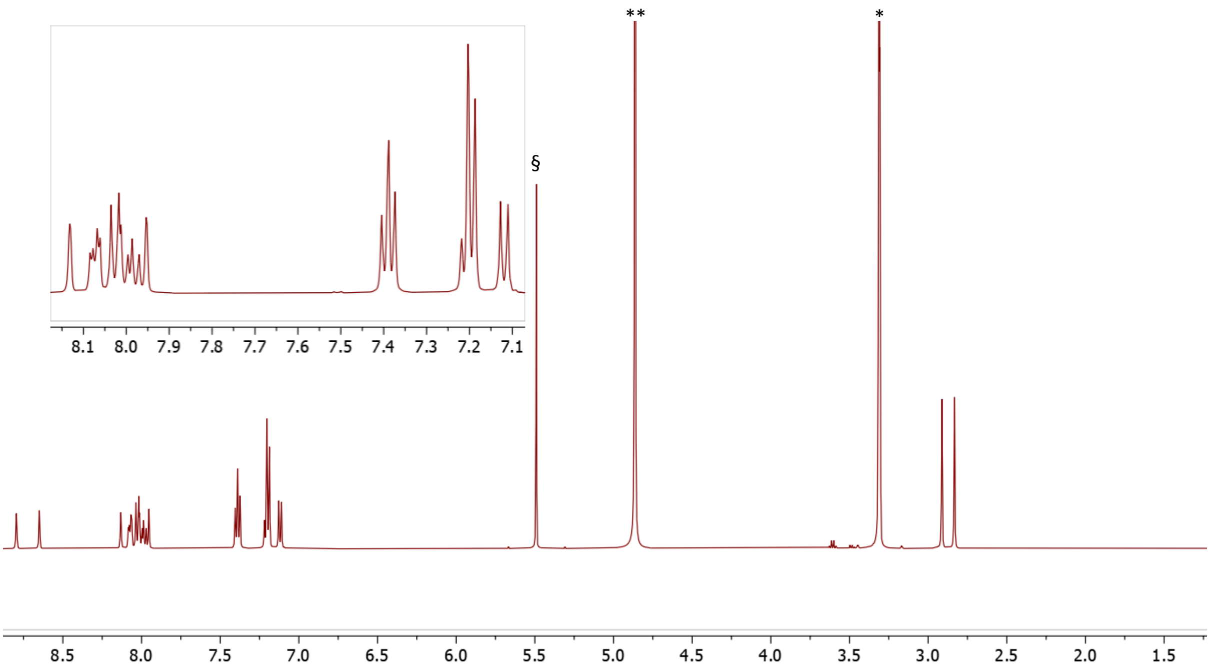


Fig. S10 ^{1}H NMR spectrum (500 MHz, CH_3OD, 298 K) of **3**. * = CH_3OD, ** = H2O, § = CH_2Cl_2.

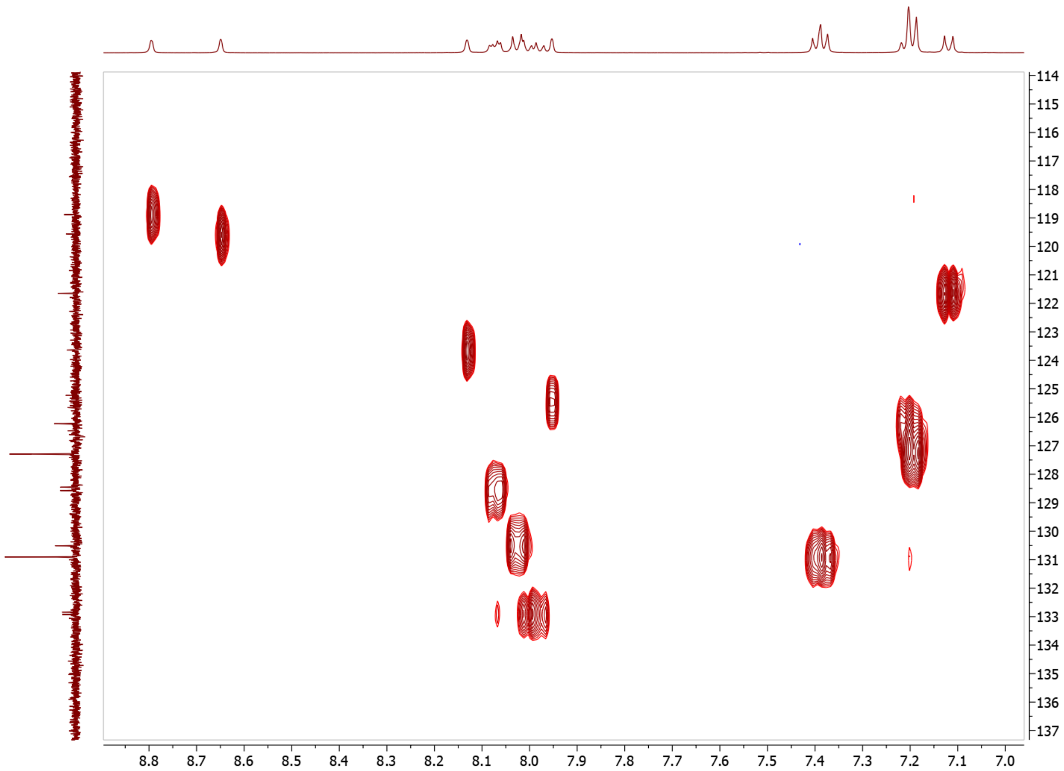


Fig. S11 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, CD_3OD, 298 K) of **3**.

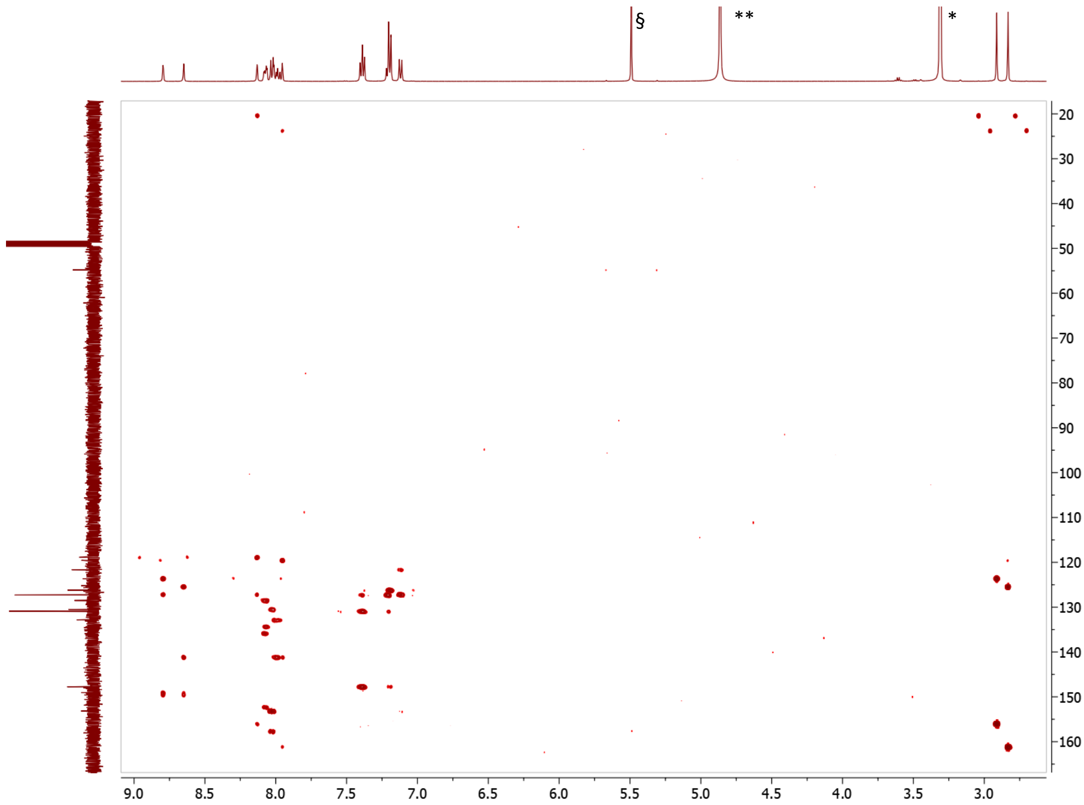


Fig. S12 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, CD_3OD, 298 K) of **3**. * = CH_3OD, ** = H_2O, § = CH_2Cl_2.

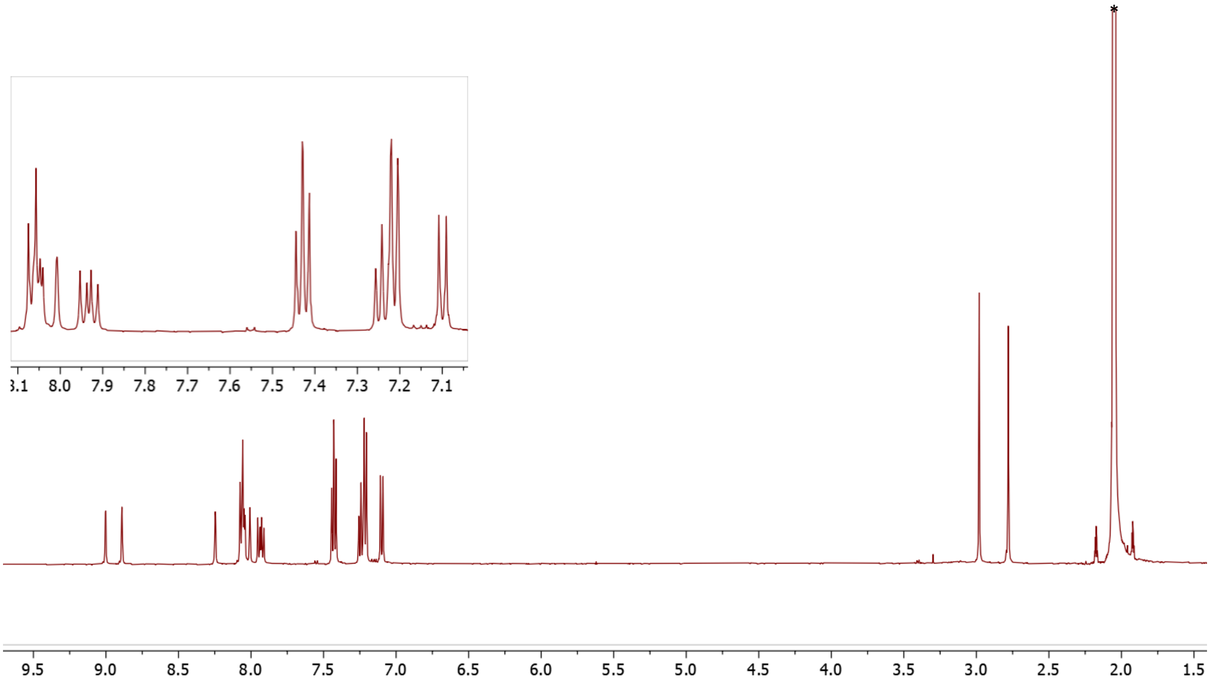


Fig. S13 ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(**3**)(**3**-H)]. * = acetone-d_5.

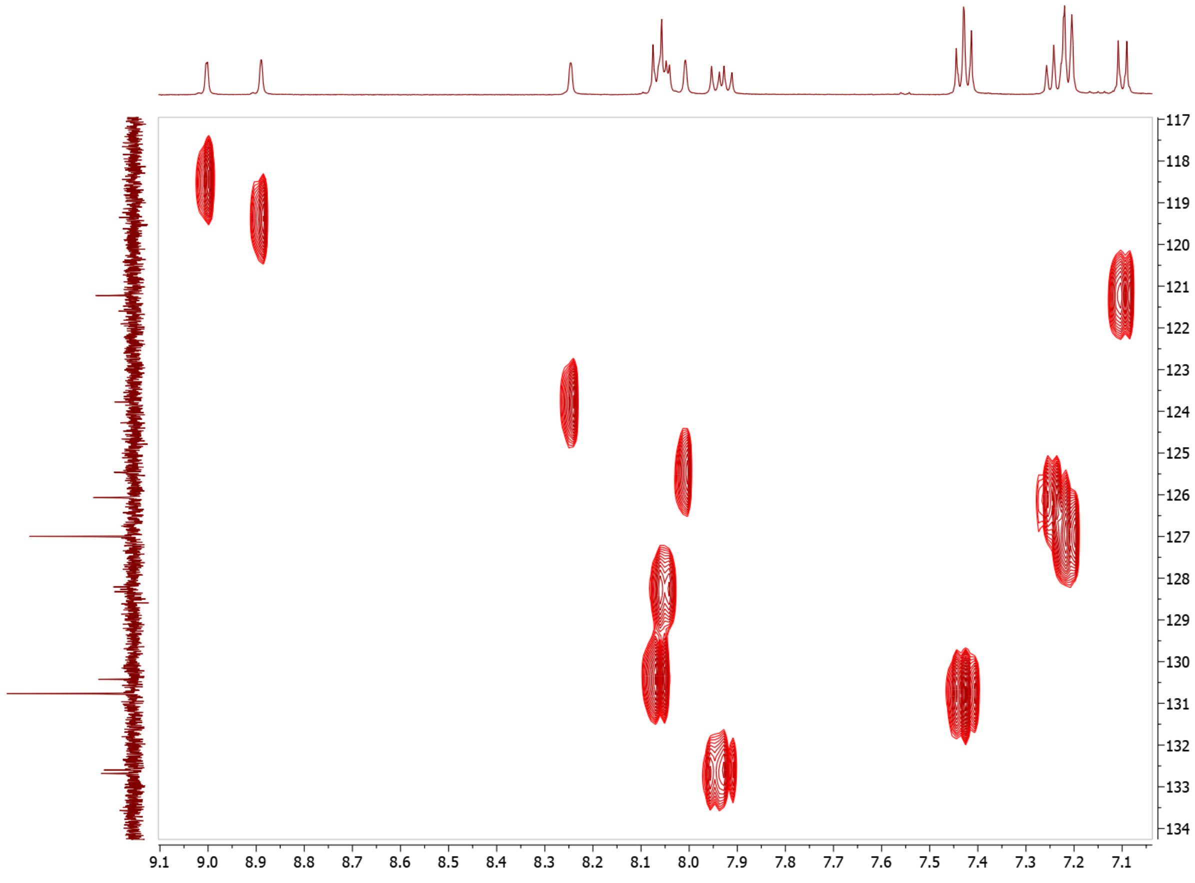


Fig. S14 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, acetone-d_6, 298 K) of [Cu(**3**)(**3**-H)].

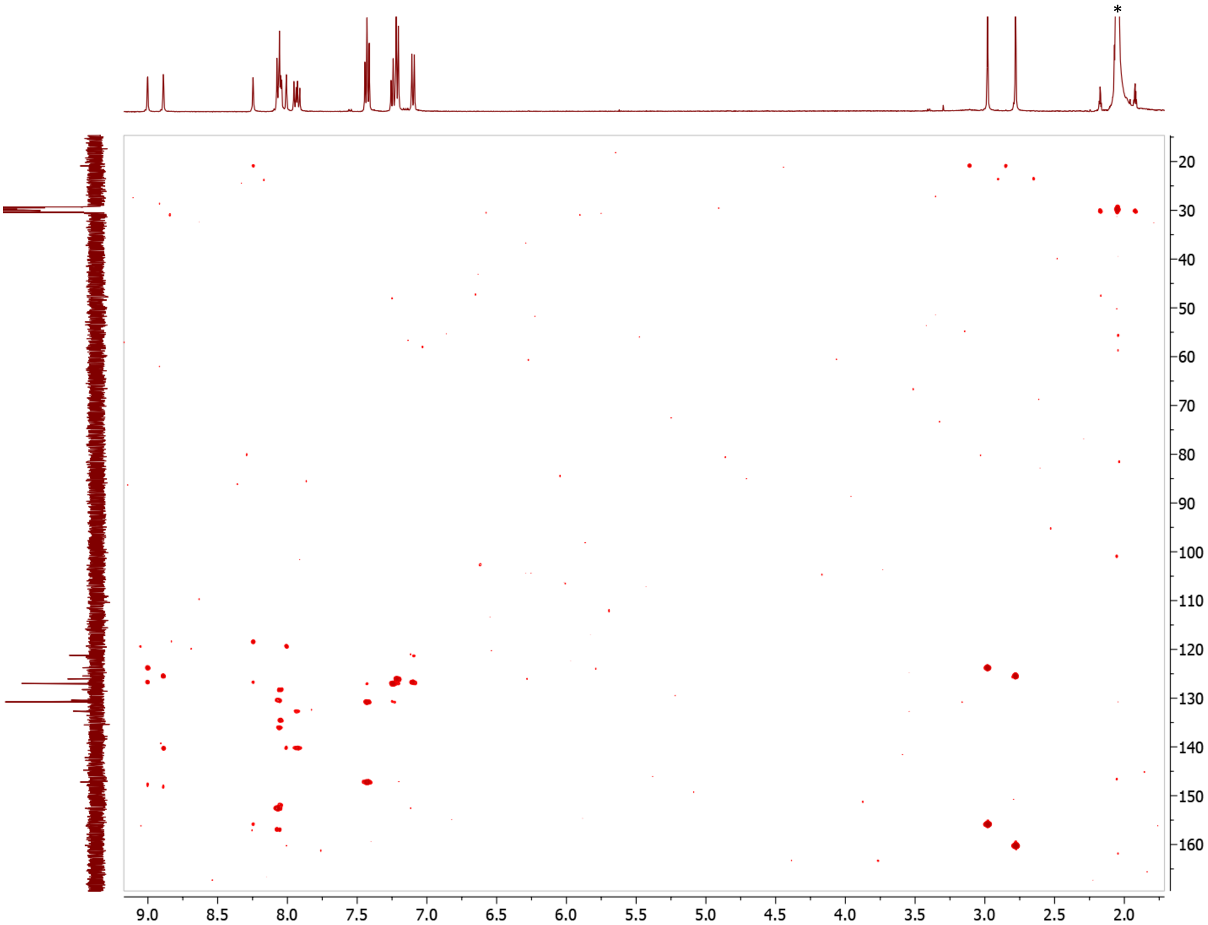


Fig. S15 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, acetone-d$_6$, 298 K) of [Cu(**3**)(**3**-H)]. * = acetone-d$_5$.

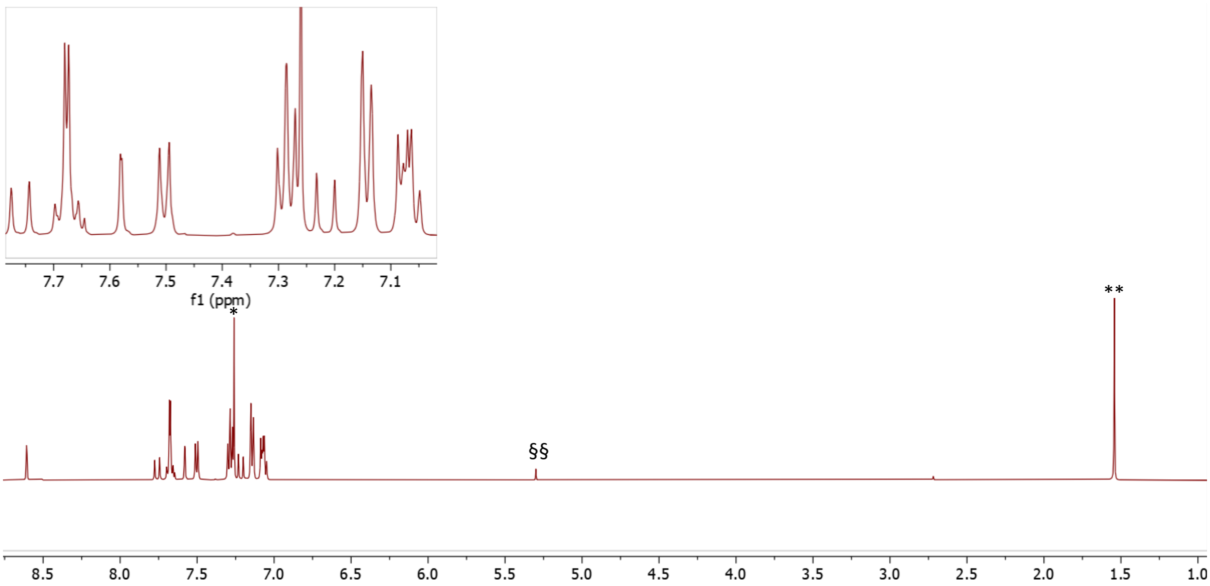


Fig. S16 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **10**. * = $CHCl_3$, ** = H_2O, § = TMS, §§ = CH_2Cl_2.

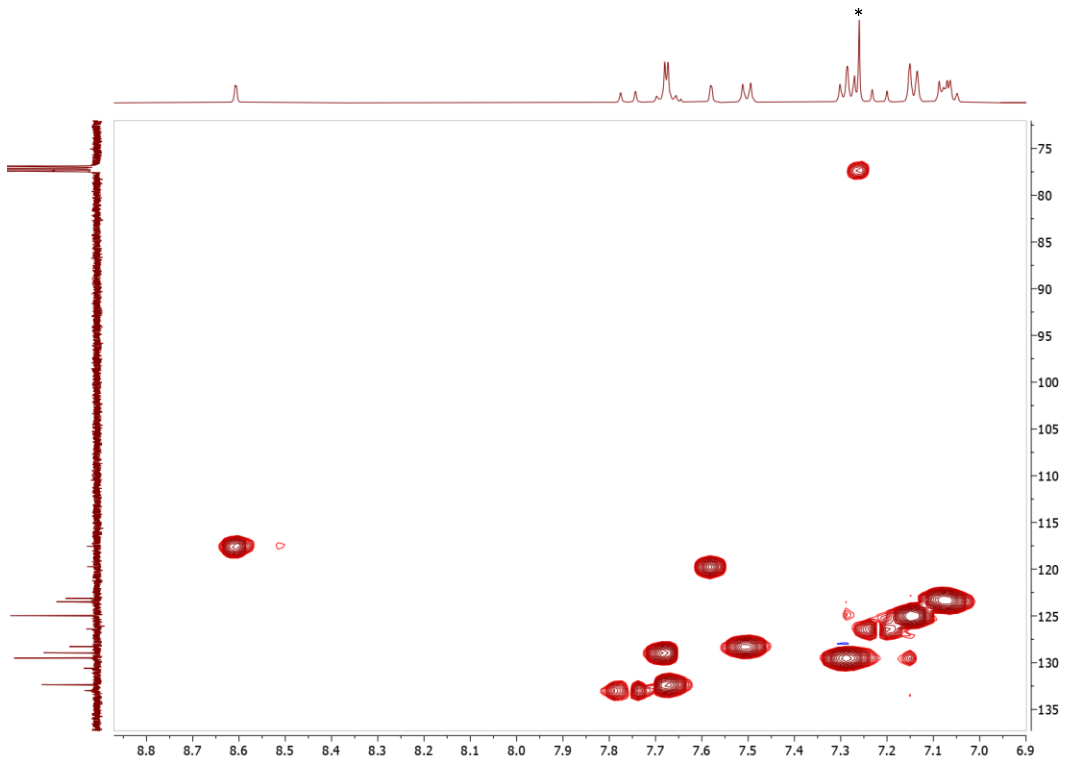


Fig. S17 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **10**. * = $CHCl_3$.

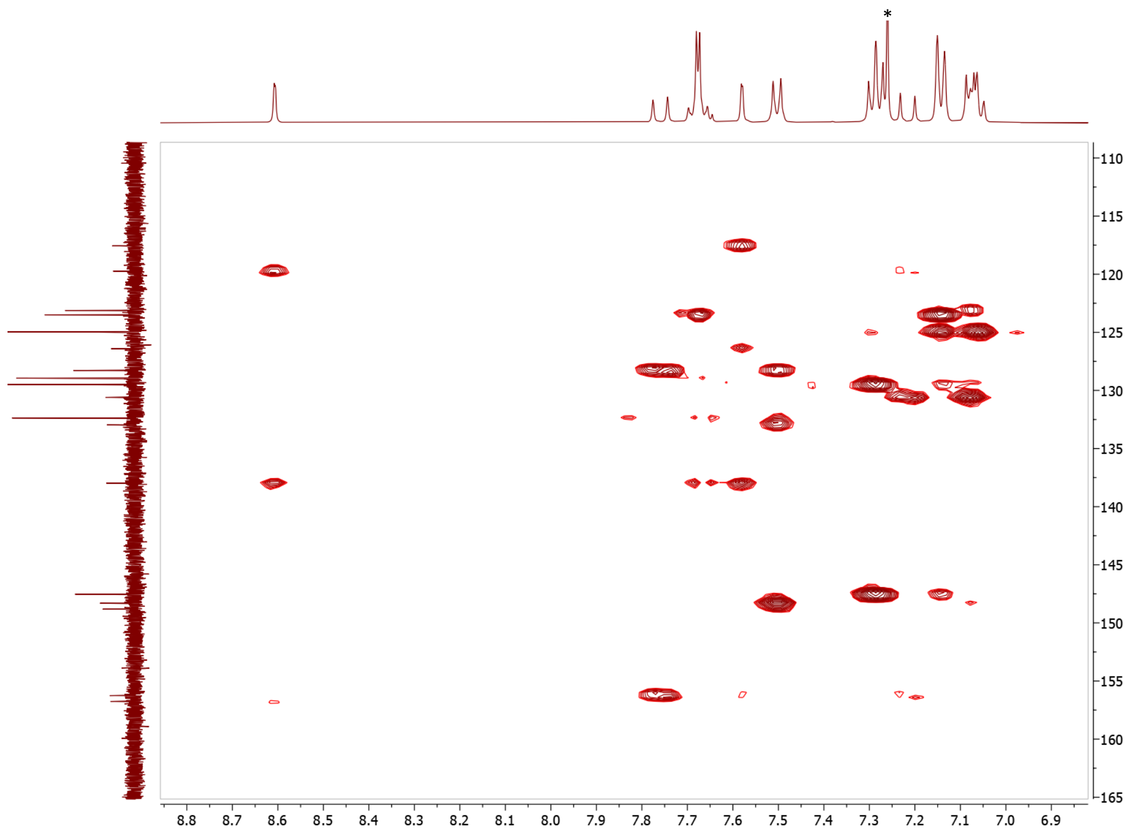


Fig. S18 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **10**. * = $CHCl_3$.

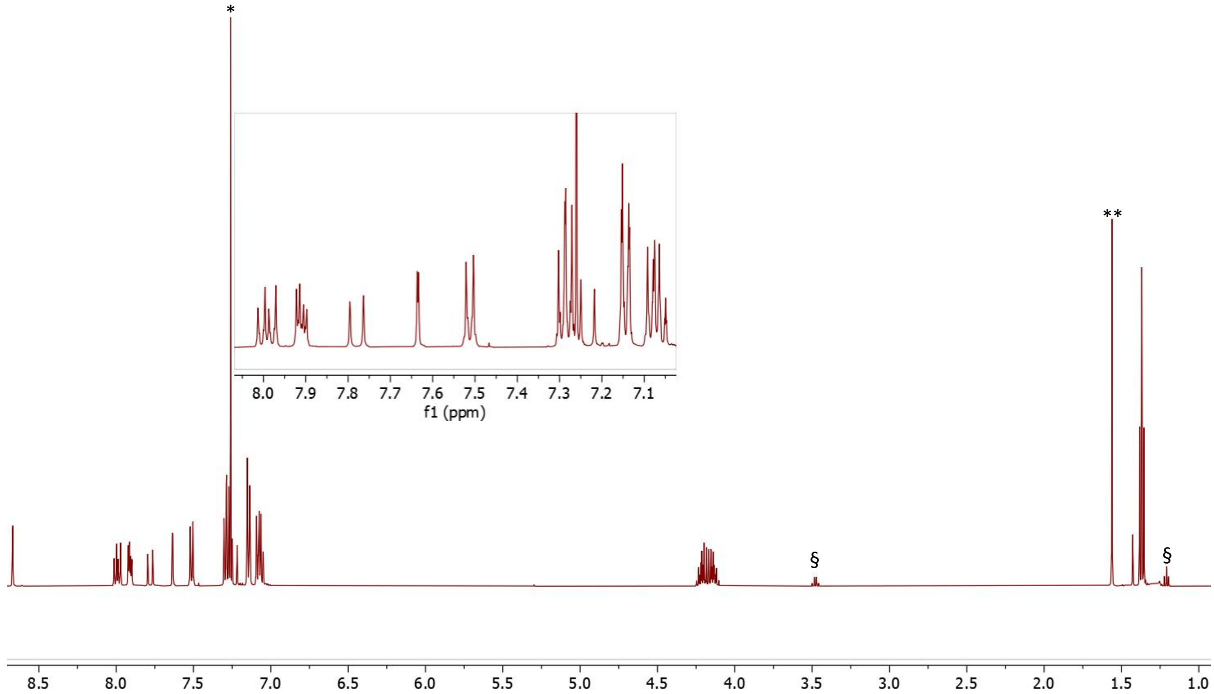


Fig. S19 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4e**. * = $CHCl_3$, ** = H_2O, § = Et_2O.

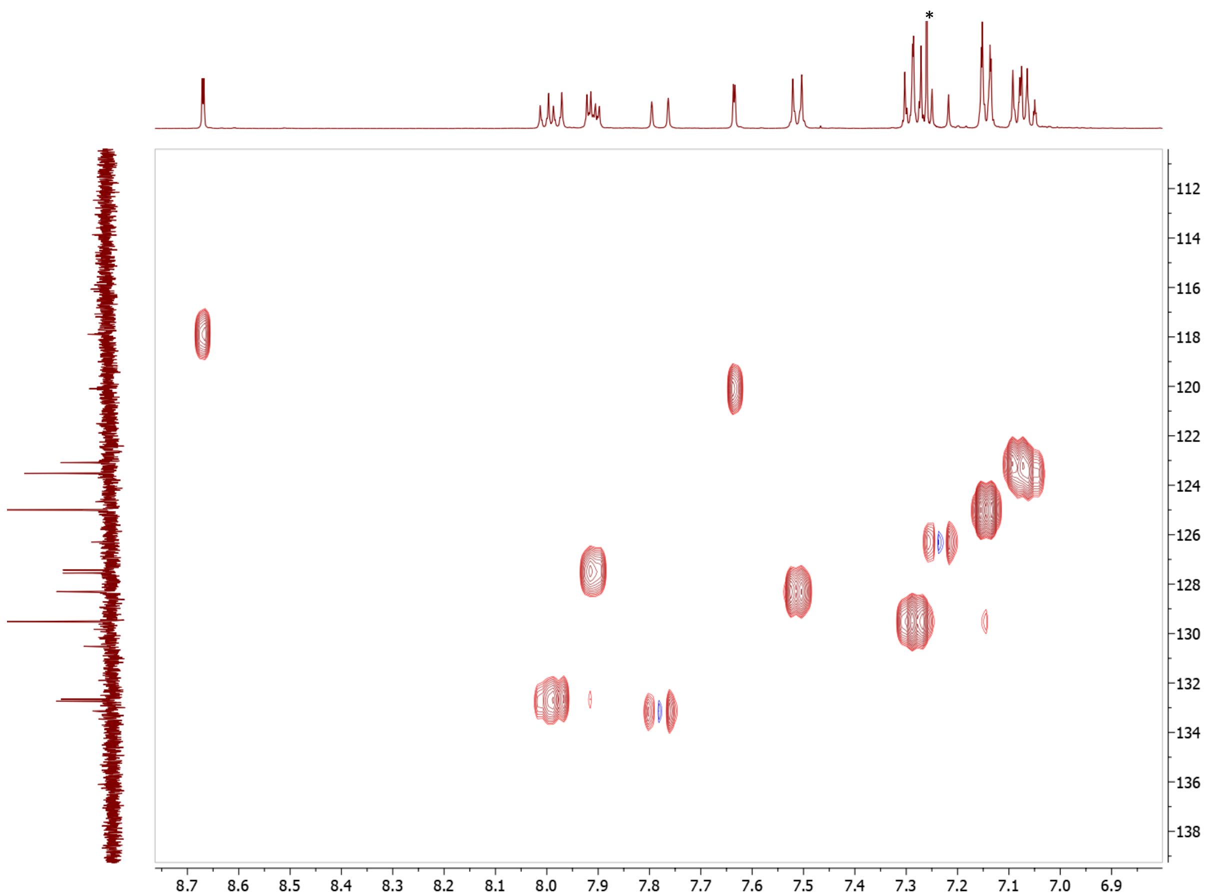


Fig. S20 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **4e**. * = $CHCl_3$.

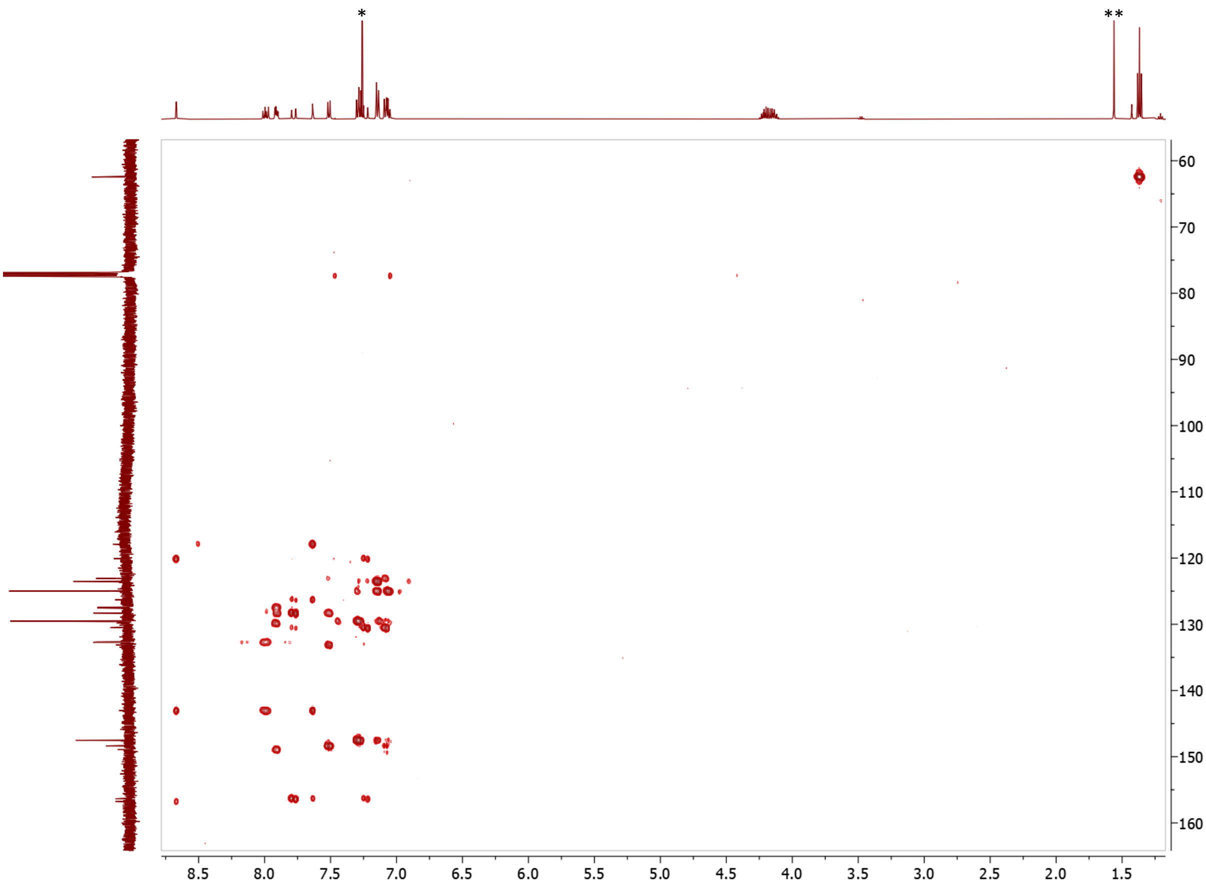


Fig. S21 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, $CDCl_3$, 298 K) of **4e**. * = $CHCl_3$, ** = H_2O, § = Et_2O.

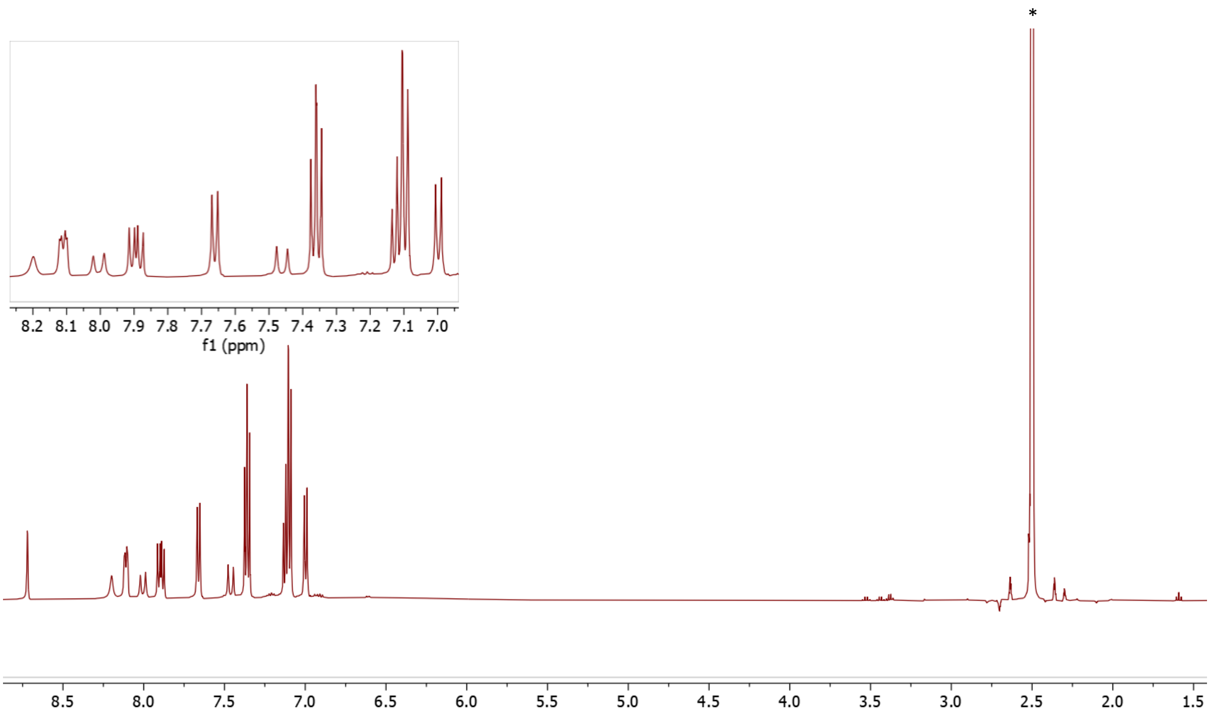


Fig. S22 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of **4**. * = DMSO-d_5.

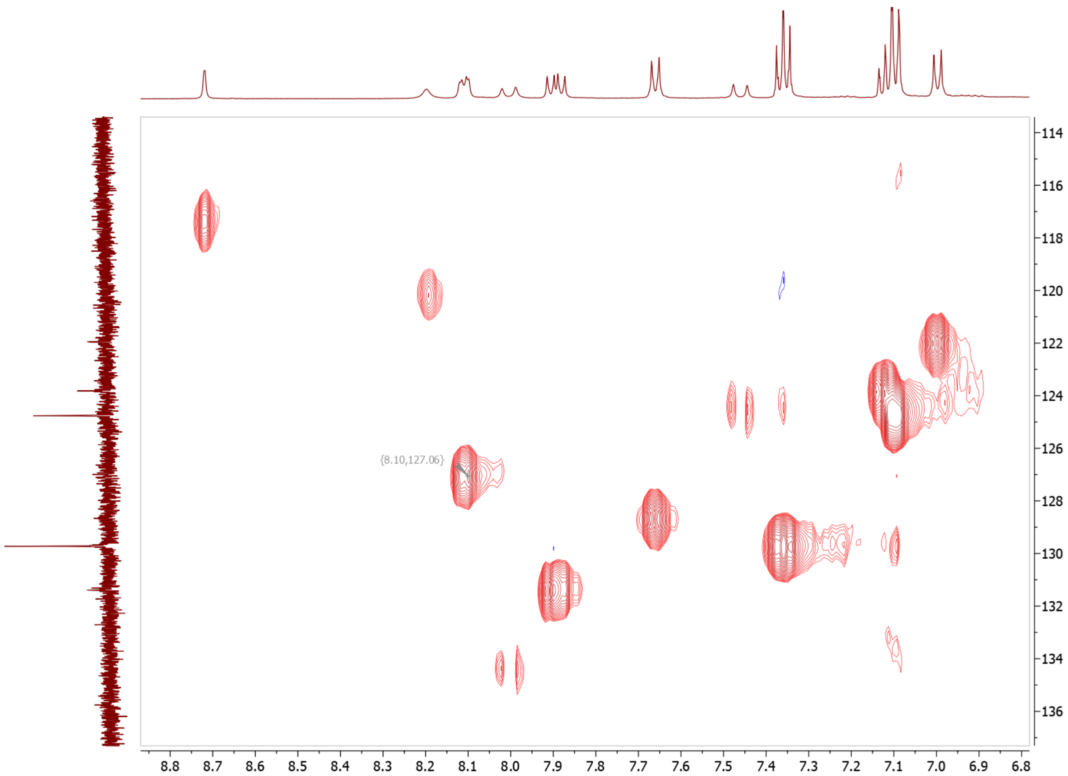


Fig. S23 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, DMSO-d$_6$, 298 K) of **4**.

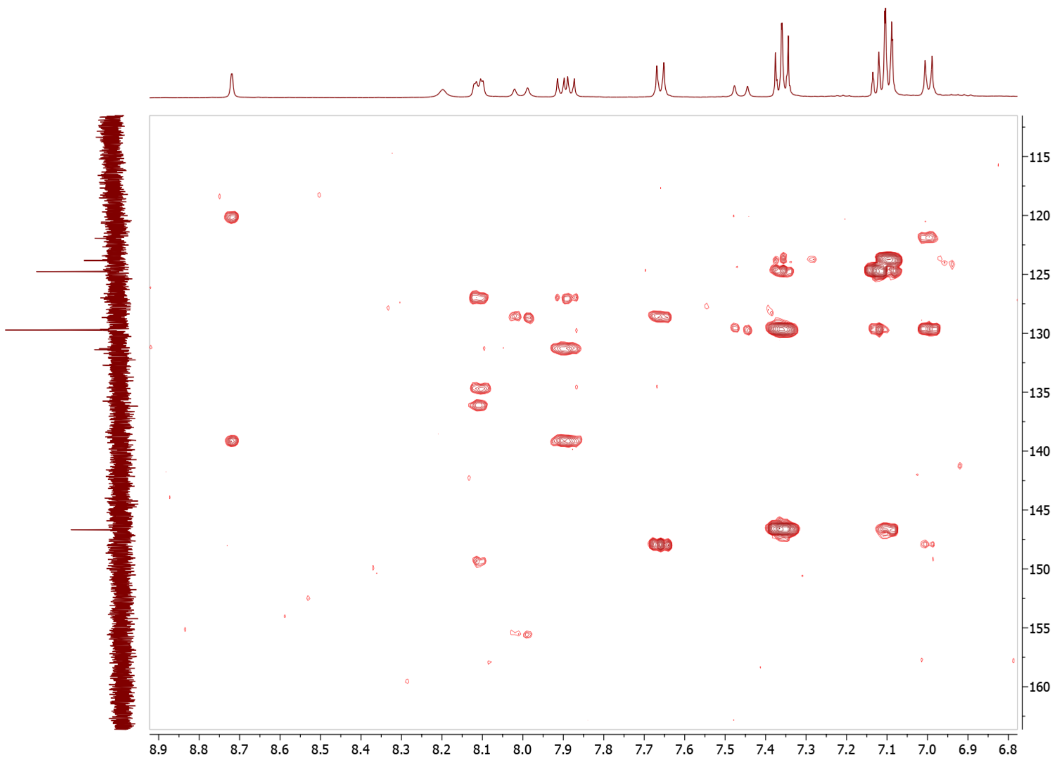


Fig. S24 The aromatic region of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, DMSO-d$_6$, 298 K) of **4**.

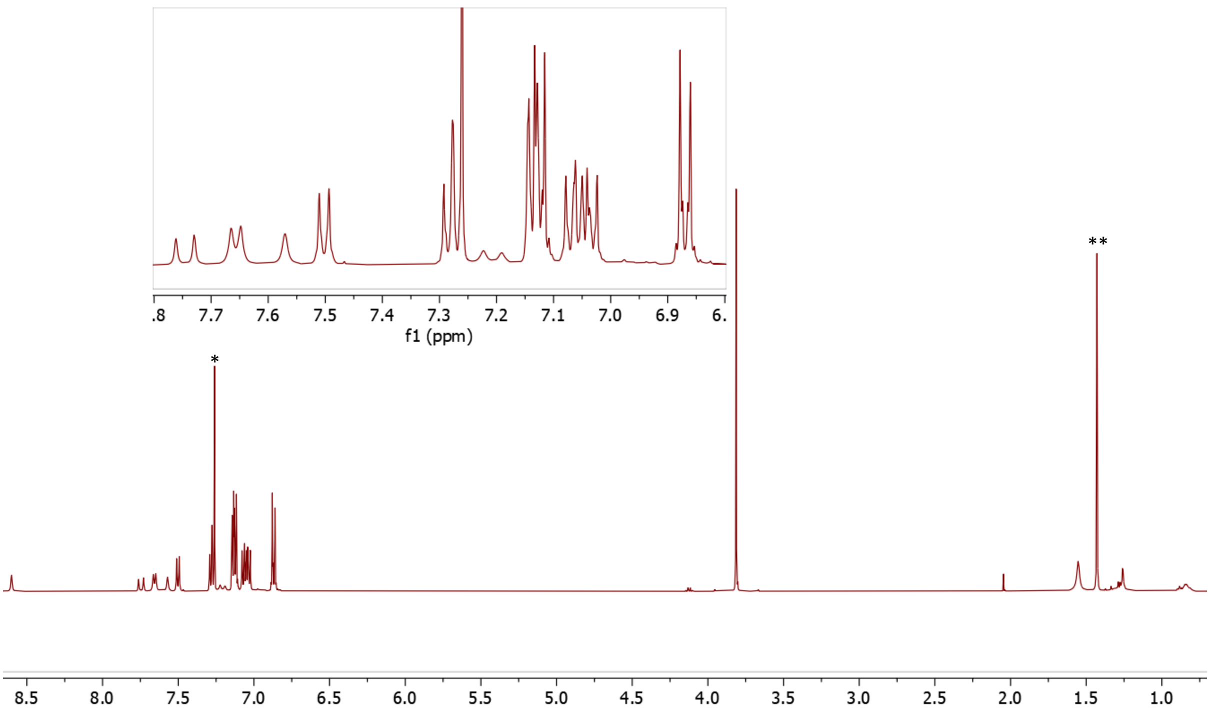


Fig. S25 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **5**. * = $CHCl_3$, ** = H_2O.

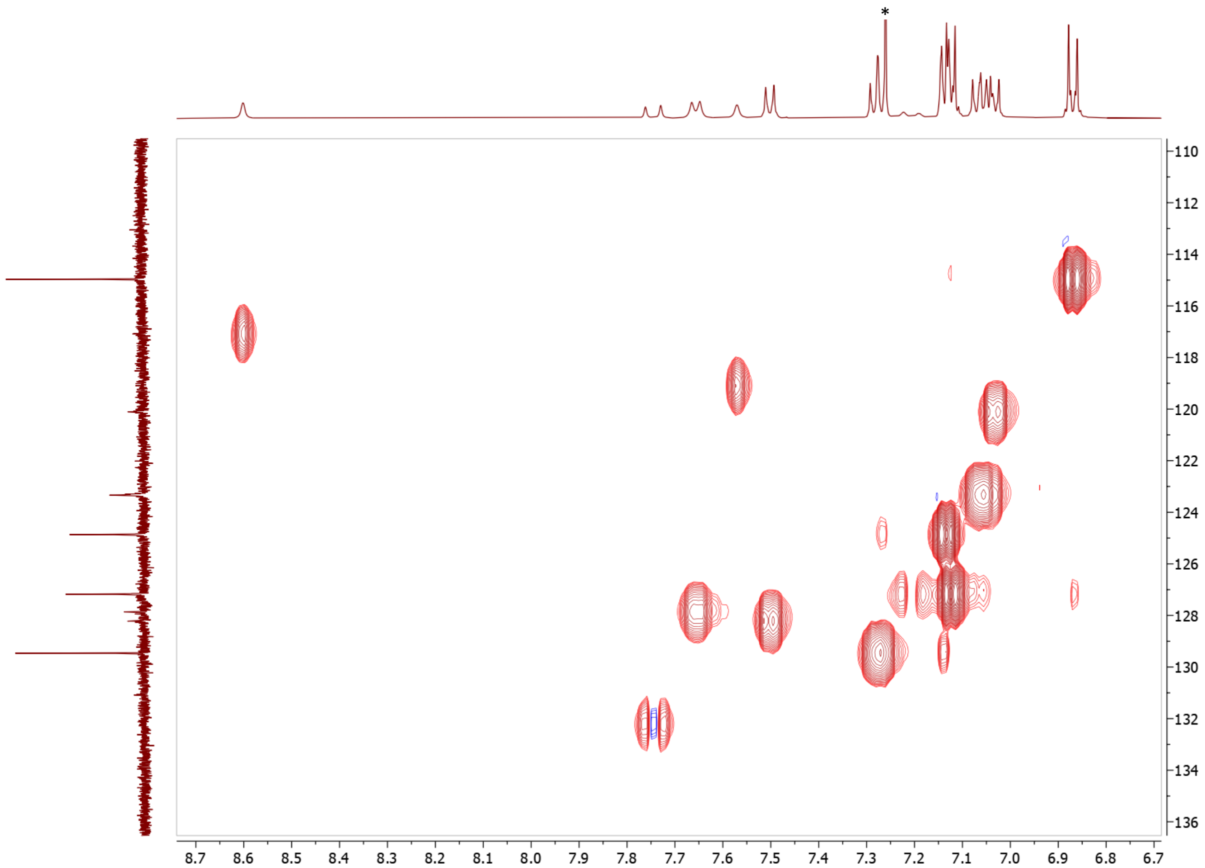


Fig. S26 The aromatic region of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **5**. * = $CHCl_3$.

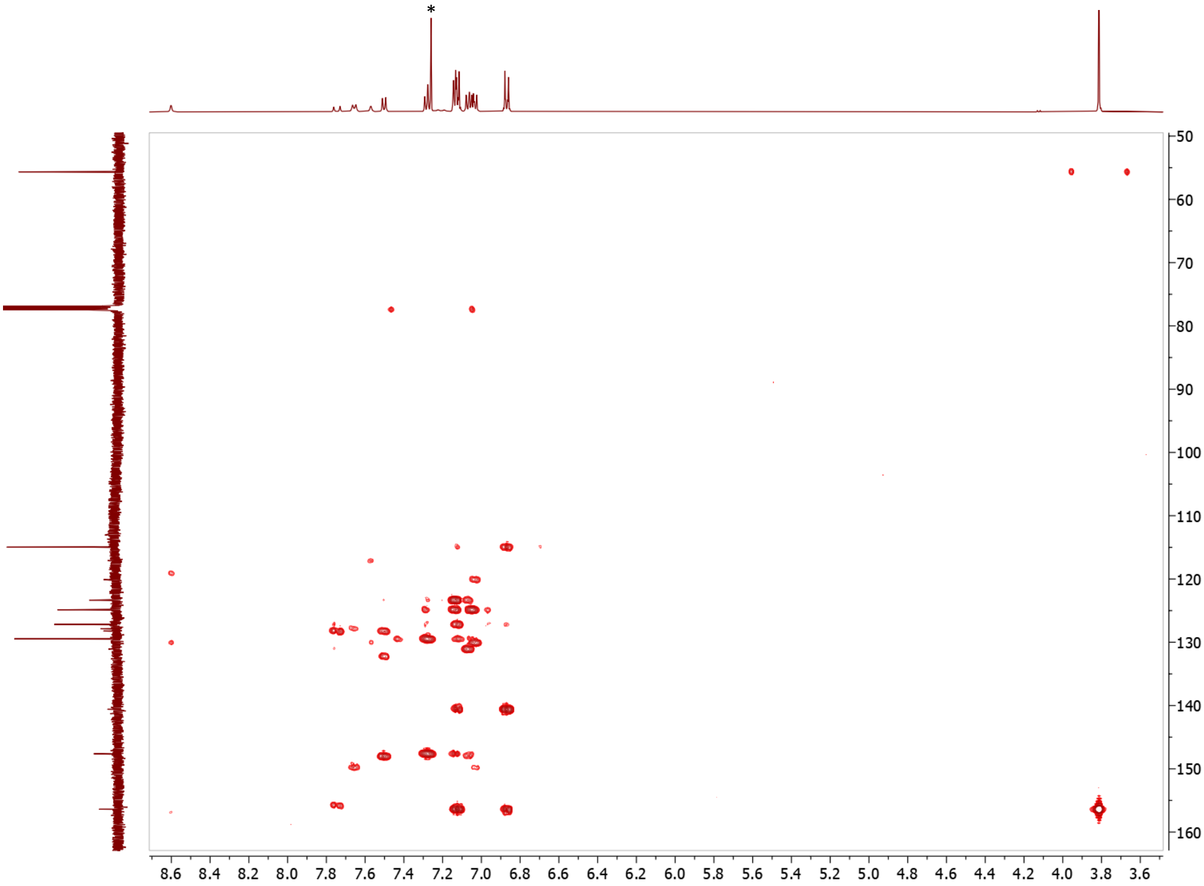


Fig. S27 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, $CDCl_3$, 298 K) of **5**. * = $CHCl_3$.

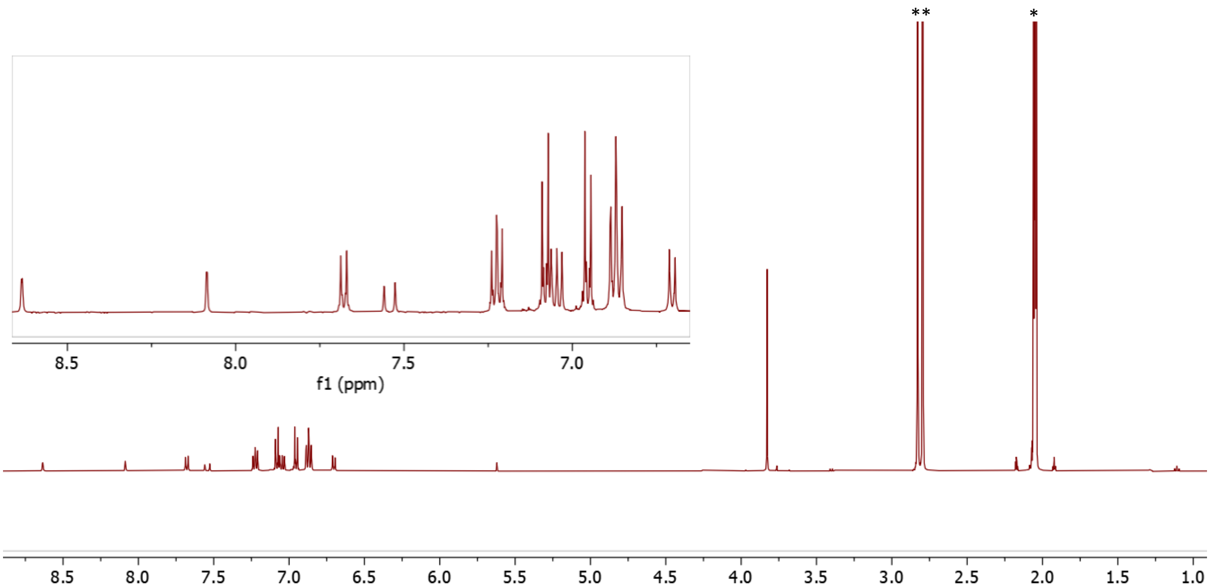


Fig. S28 ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of $[Cu(\mathbf{5})_2][PF_6]$. * = acetone-d_5, ** = H_2O and HDO.

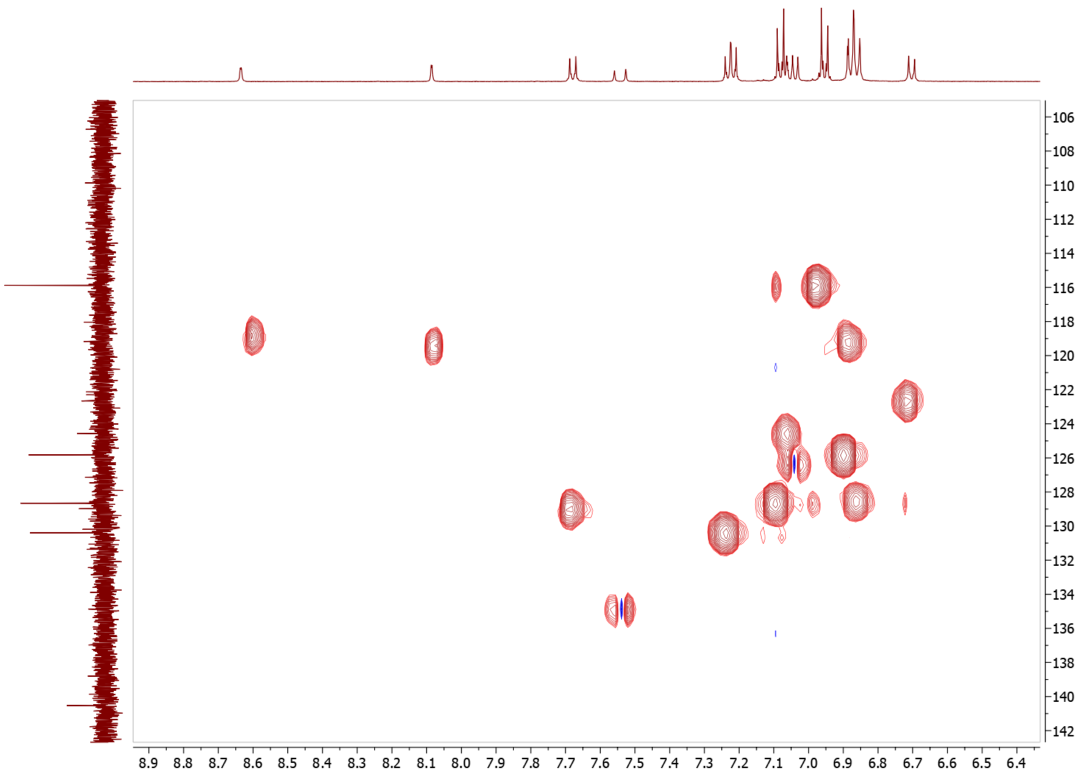


Fig. S29 The aromatic region of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d$_6$, 298 K) of [Cu(**5**)$_2$][PF$_6$].

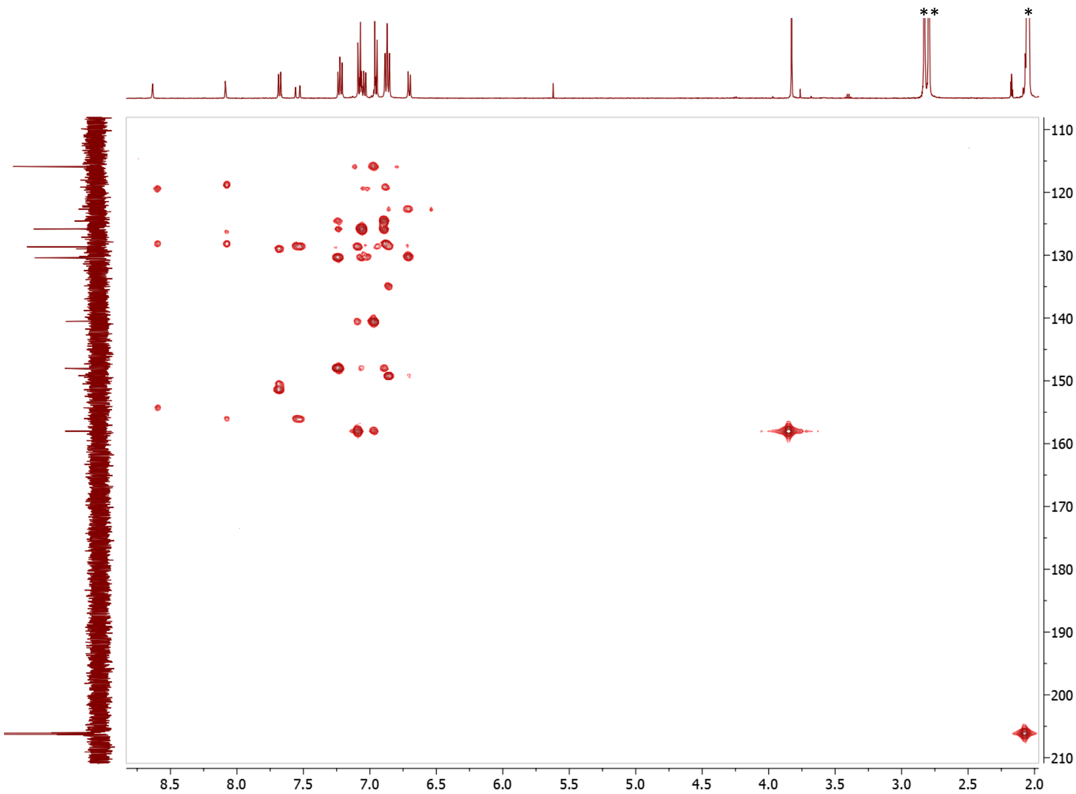


Fig. S30 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d$_6$, 298 K) of [Cu(**5**)$_2$][PF$_6$]. * = acetone-d$_5$, ** = H_2O and HDO.

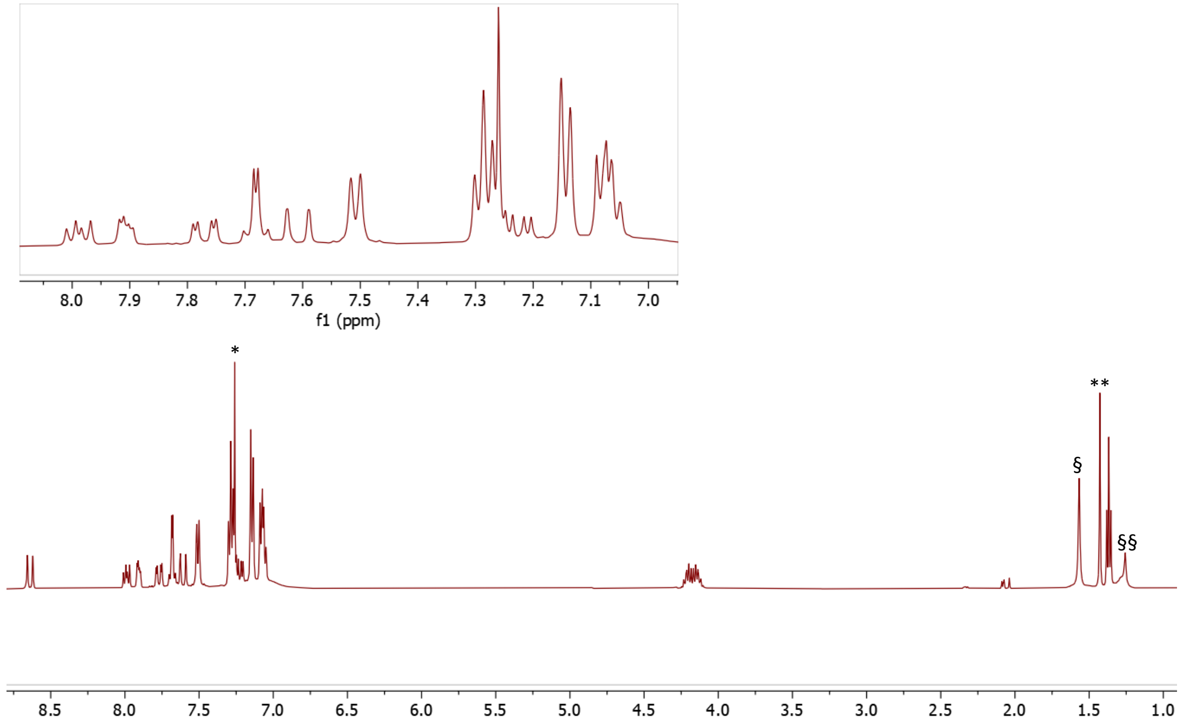


Fig. S31 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **6eBr**. * = $CHCl_3$, ** = H_2O, § = CHX, §§ = H-grease.

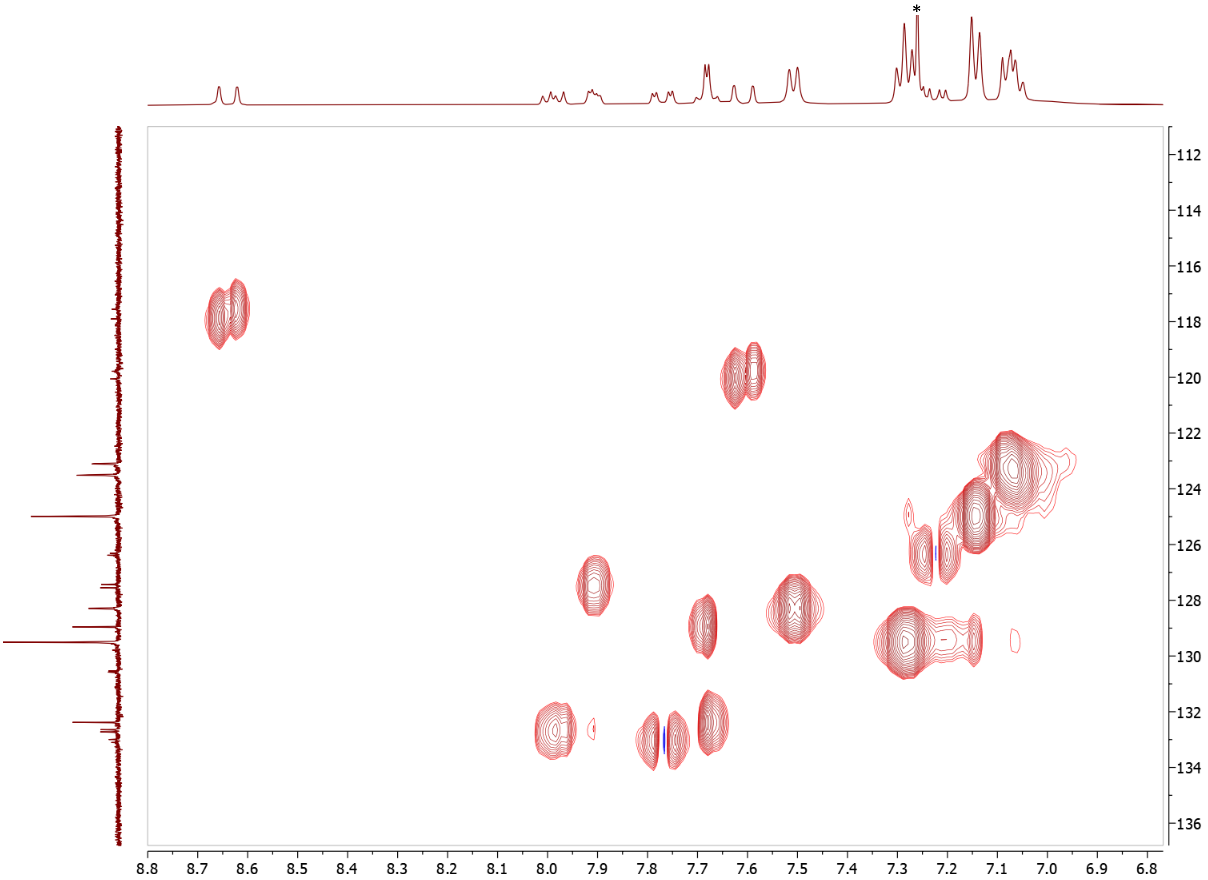


Fig. S32 The aromatic region of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **6eBr**. * = $CHCl_3$

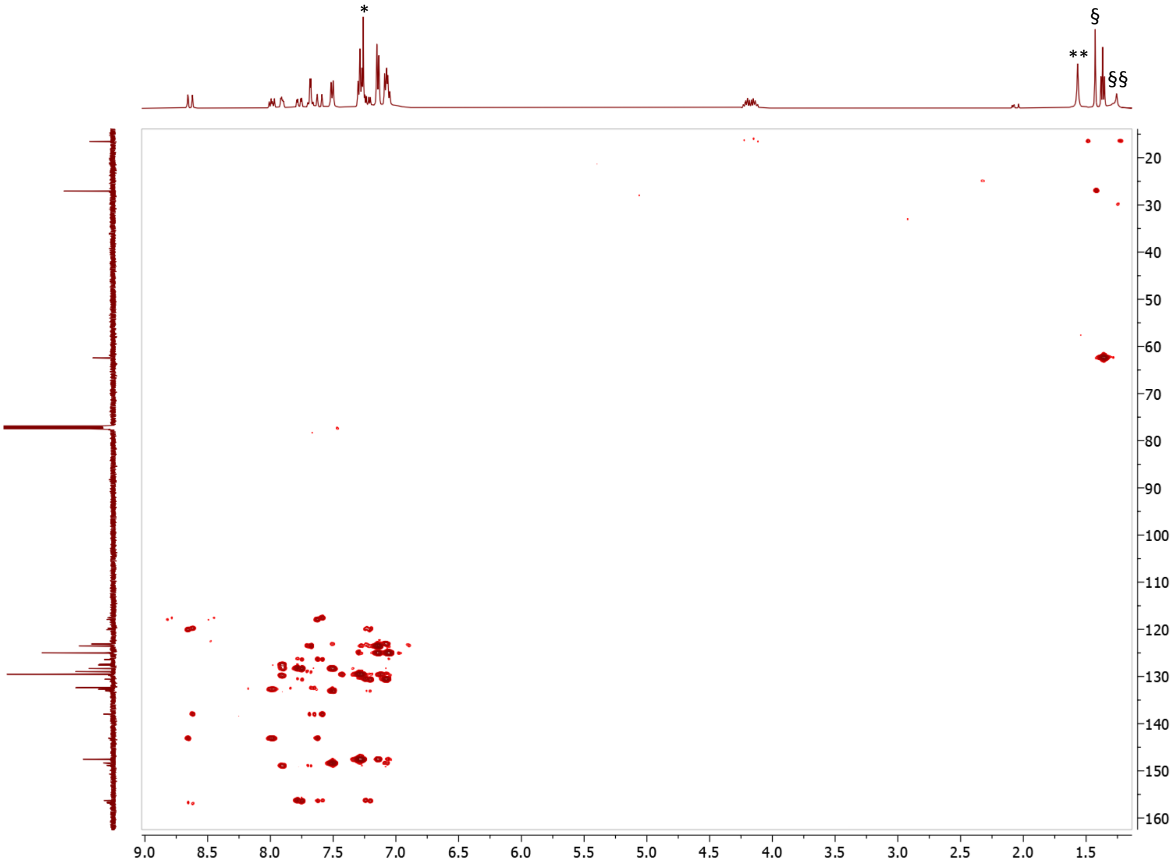


Fig. S33 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, $CDCl_3$, 298 K) of **6eBr**. * = $CHCl_3$, ** = H_2O, § = CHX, §§ = H-grease.

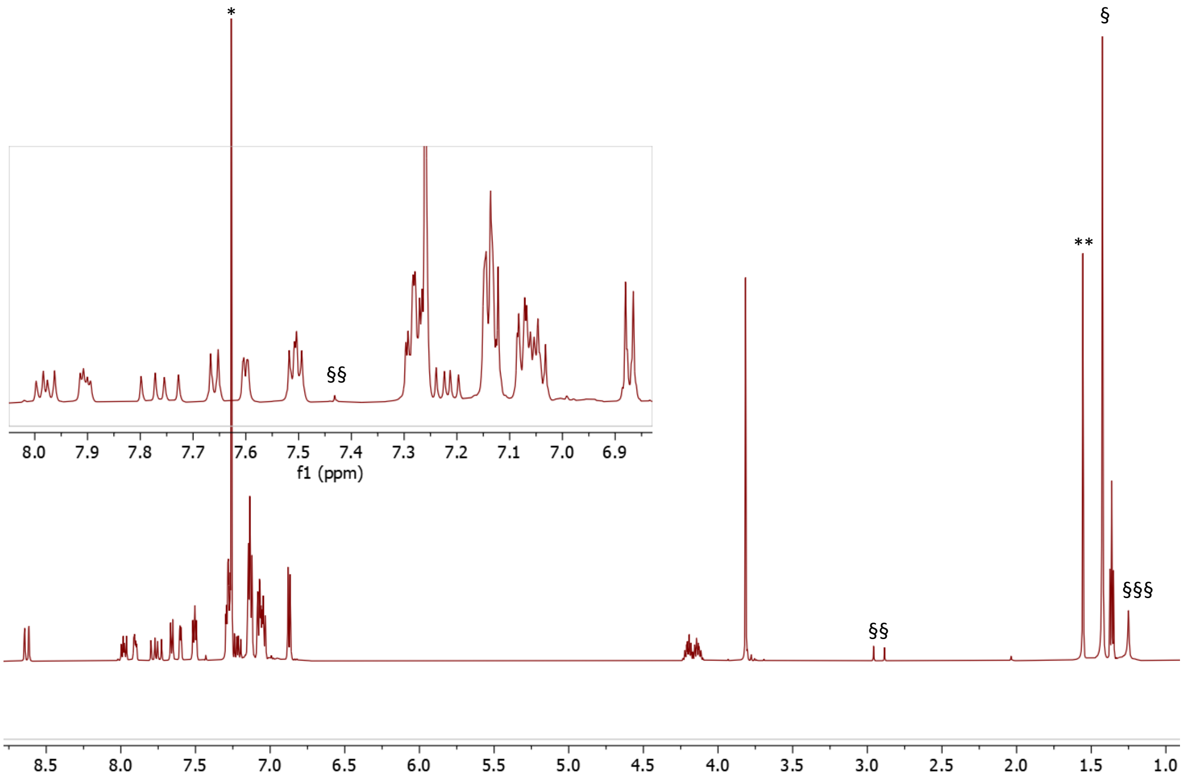


Fig. S34 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **6e**. * = $CHCl_3$, ** = H_2O, § = CHX, §§ = DMF, §§§ = H-grease.

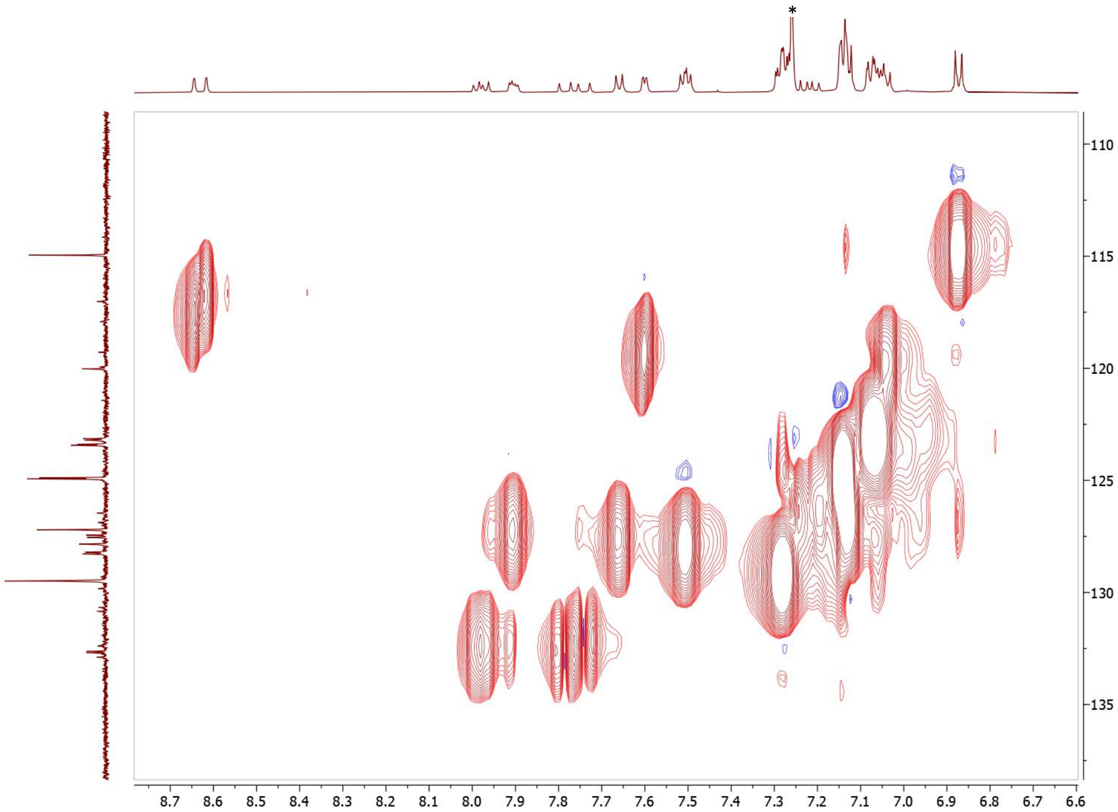


Fig. S35 The aromatic region of the HMQC spectrum (600 MHz ^{1}H, 151 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **6e**. * = $CHCl_3$

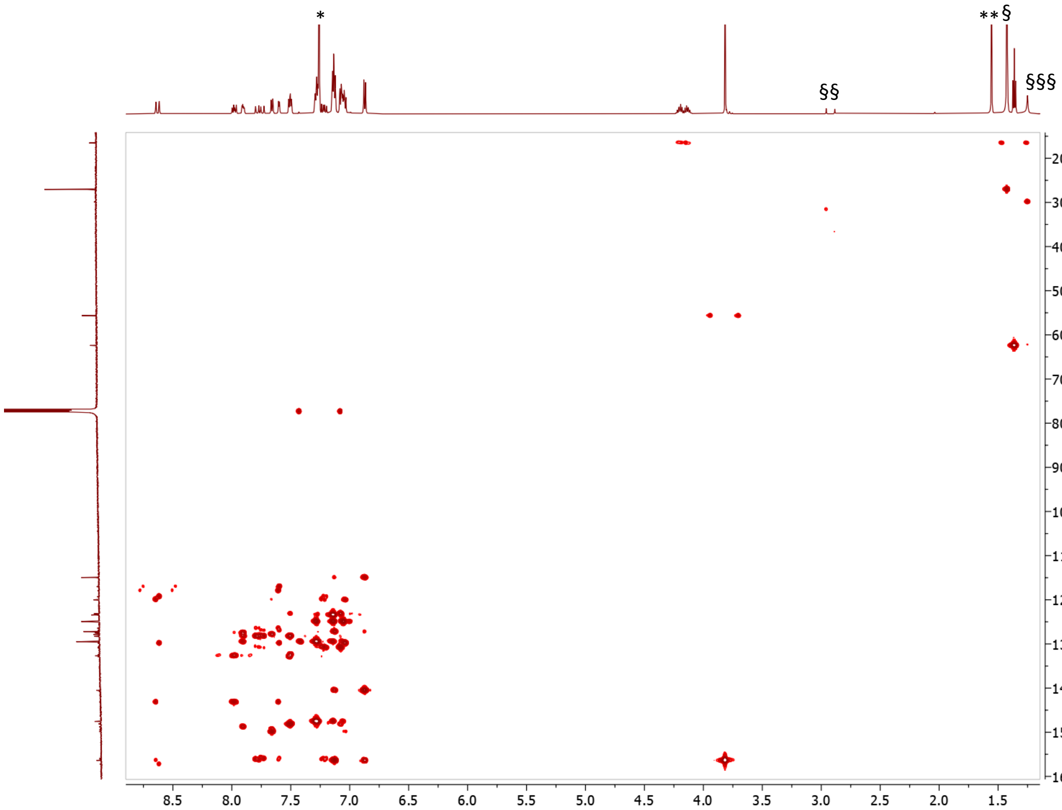


Fig. S36 Part of the HMBC spectrum (500 MHz ^{1}H, 151 MHz $^{13}C\{^{1}H\}$, $CDCl_3$, 298 K) of **6e**. * = $CHCl_3$, ** = H_2O, § = CHX, §§ = DMF, §§§ = H-grease.

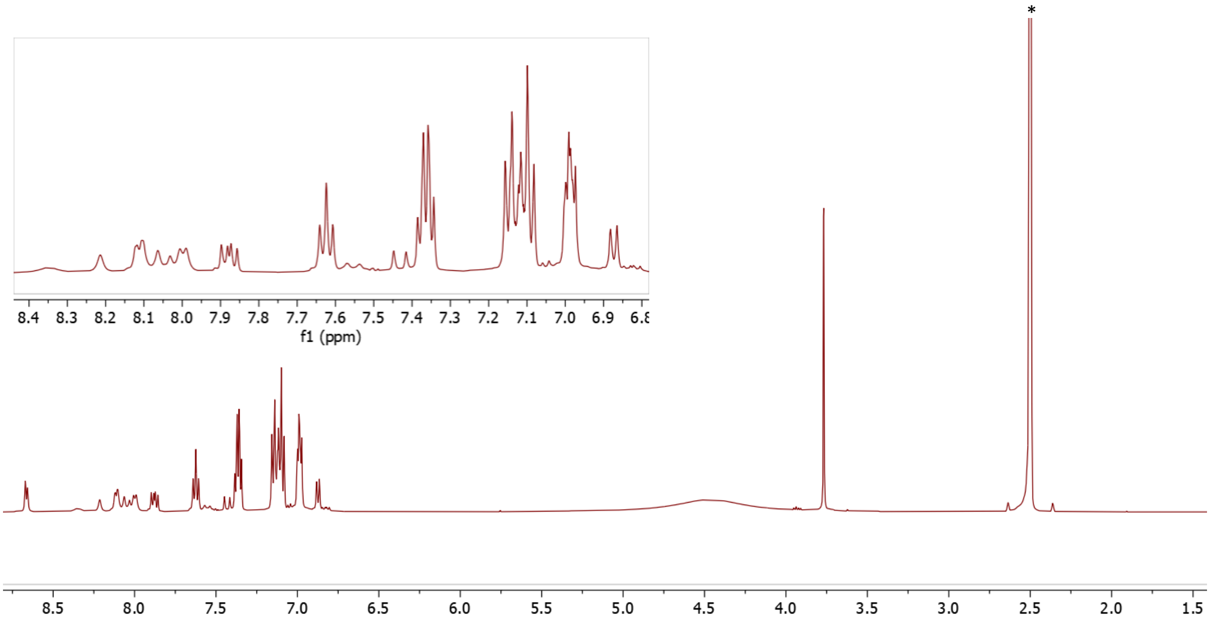


Fig. S37 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of **6**. * = DMSO-d_5.

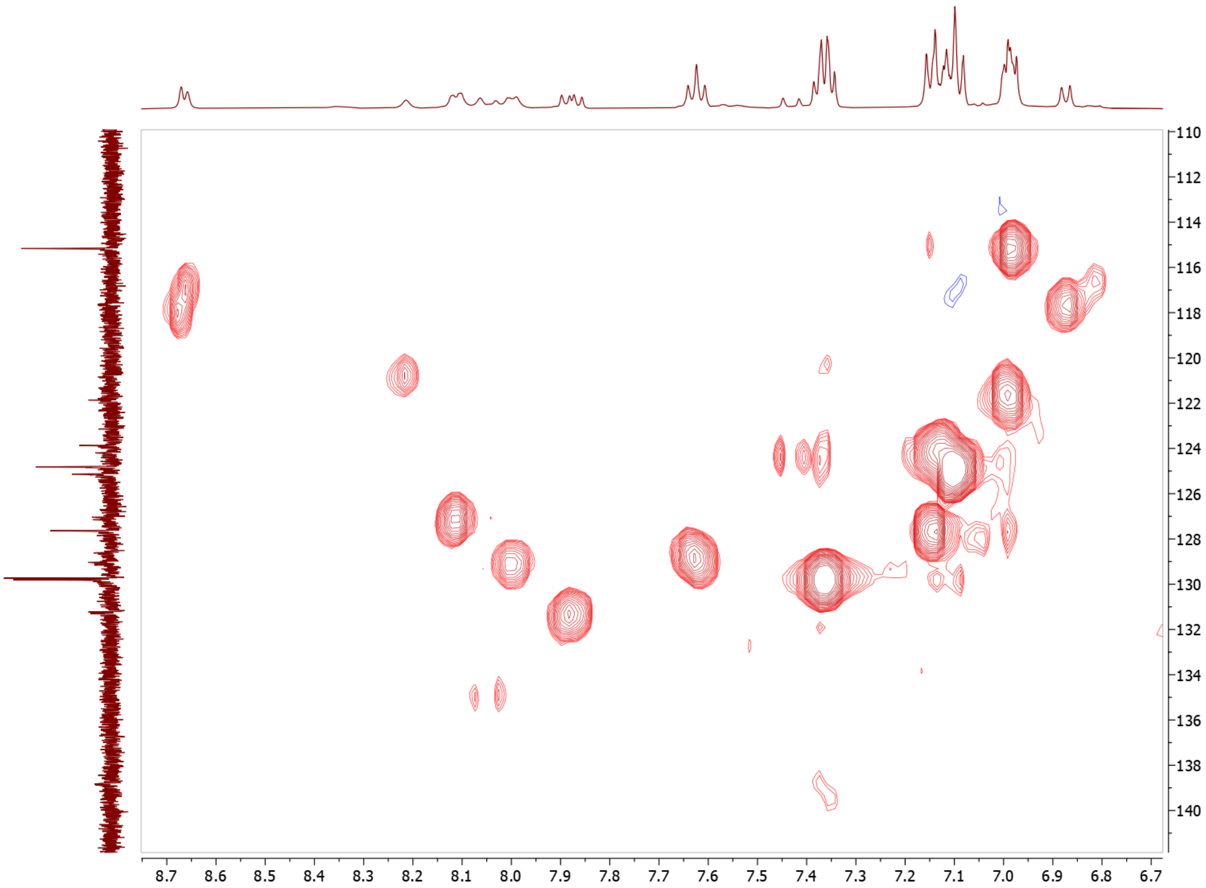


Fig. S38 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, DMSO-d_6, 298 K) of **6**.

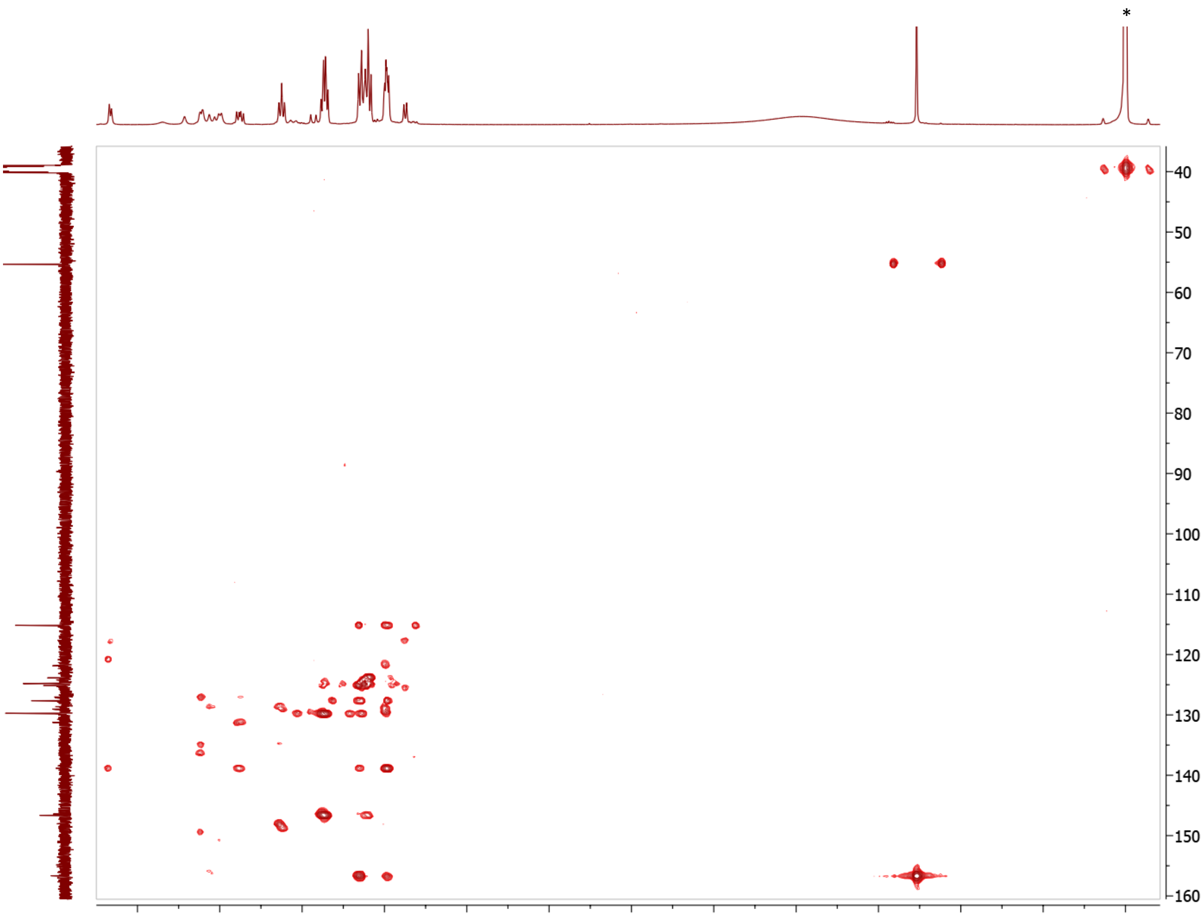


Fig. S39 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, DMSO-d$_6$, 298 K) of **6**. * = DMSO-d$_5$.

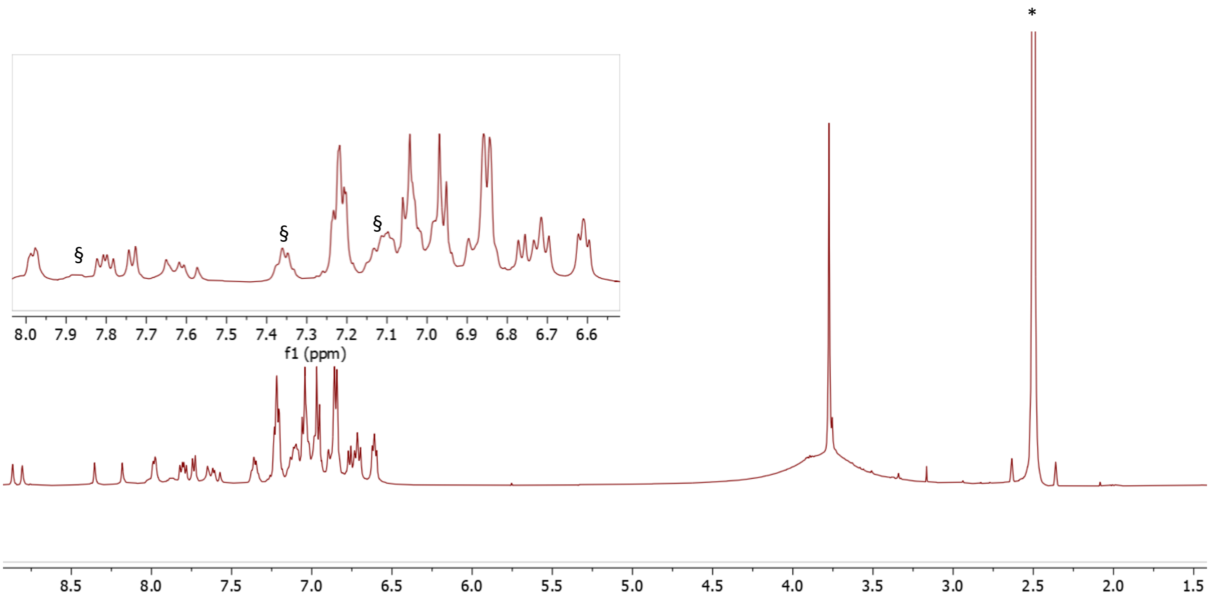


Fig. S40: ^{1}H NMR spectrum (500 MHz, DMSO-d$_6$, 298 K) of [Cu(**6**)(**6**-H)].* = DMSO-d$_5$, § = impurity.

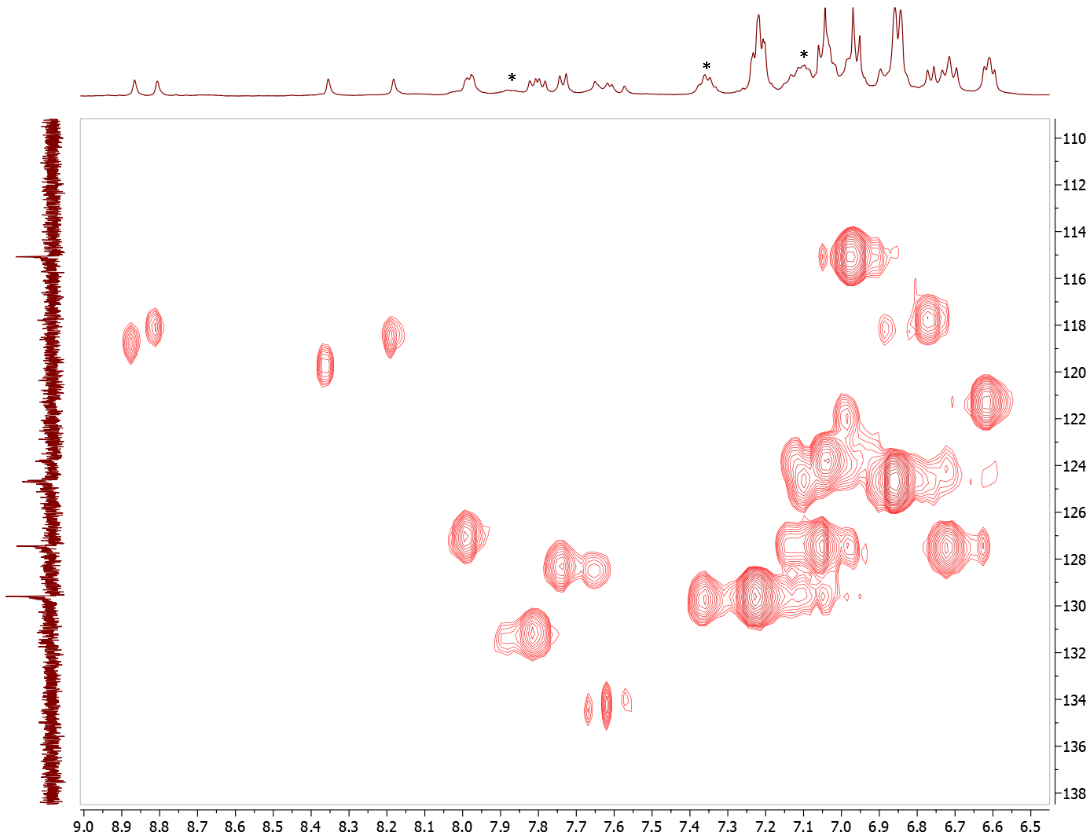


Fig. S41 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, DMSO-d$_6$, 298 K) of [Cu(**6**)(**6**-H)].* = impurity.

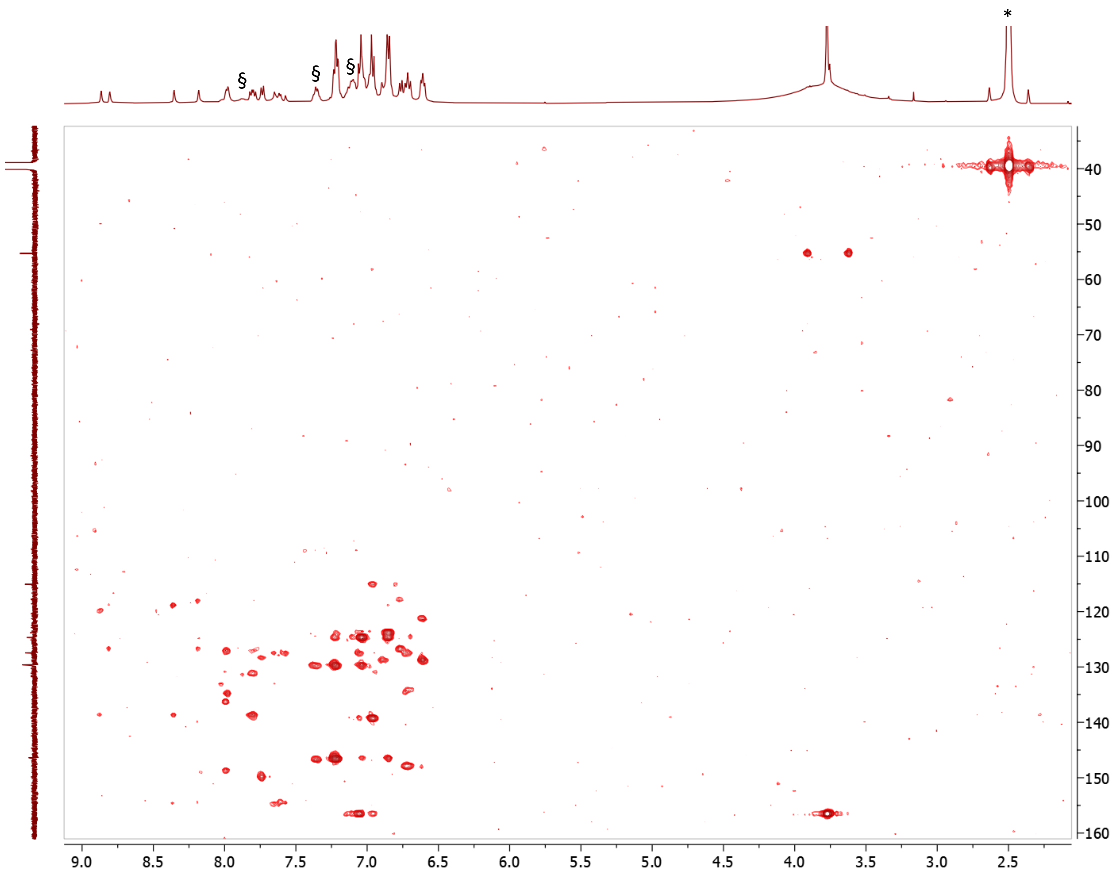


Fig. S42 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, DMSO-d$_6$, 298 K) of [Cu(**6**)(**6**-H)].* = DMSO-d$_5$, § = impurity.

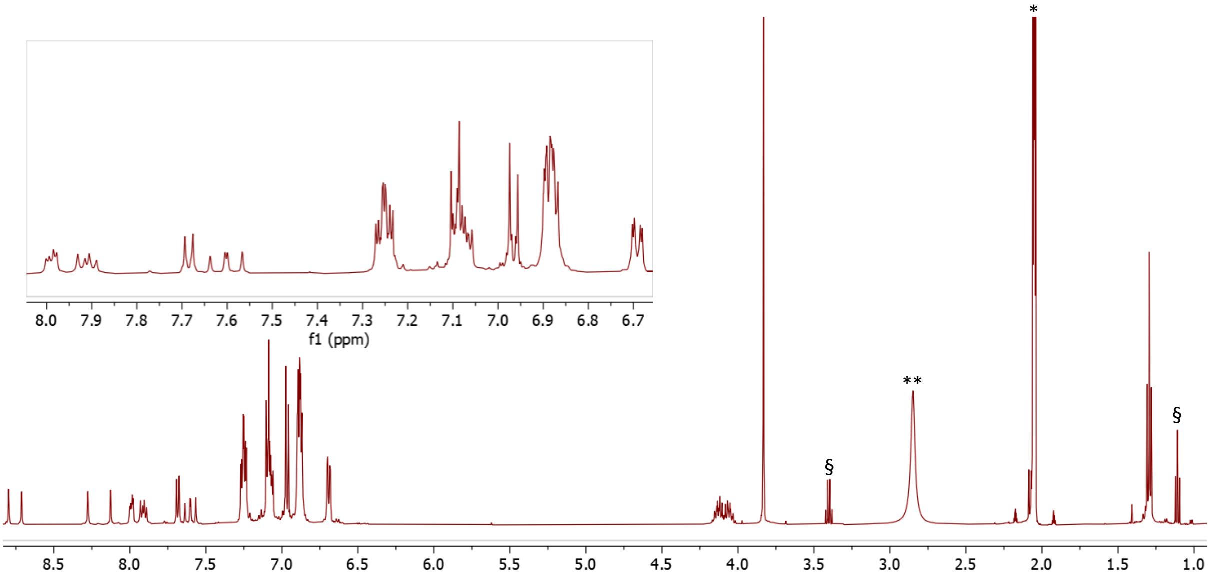


Fig. S43 ^{1}H NMR spectrum (500 MHz, acetone-d$_6$, 298 K) of [Cu(**6**)$_2$][PF$_6$]. * = acetone-d$_5$, ** = H_2O, § = Et_2O.

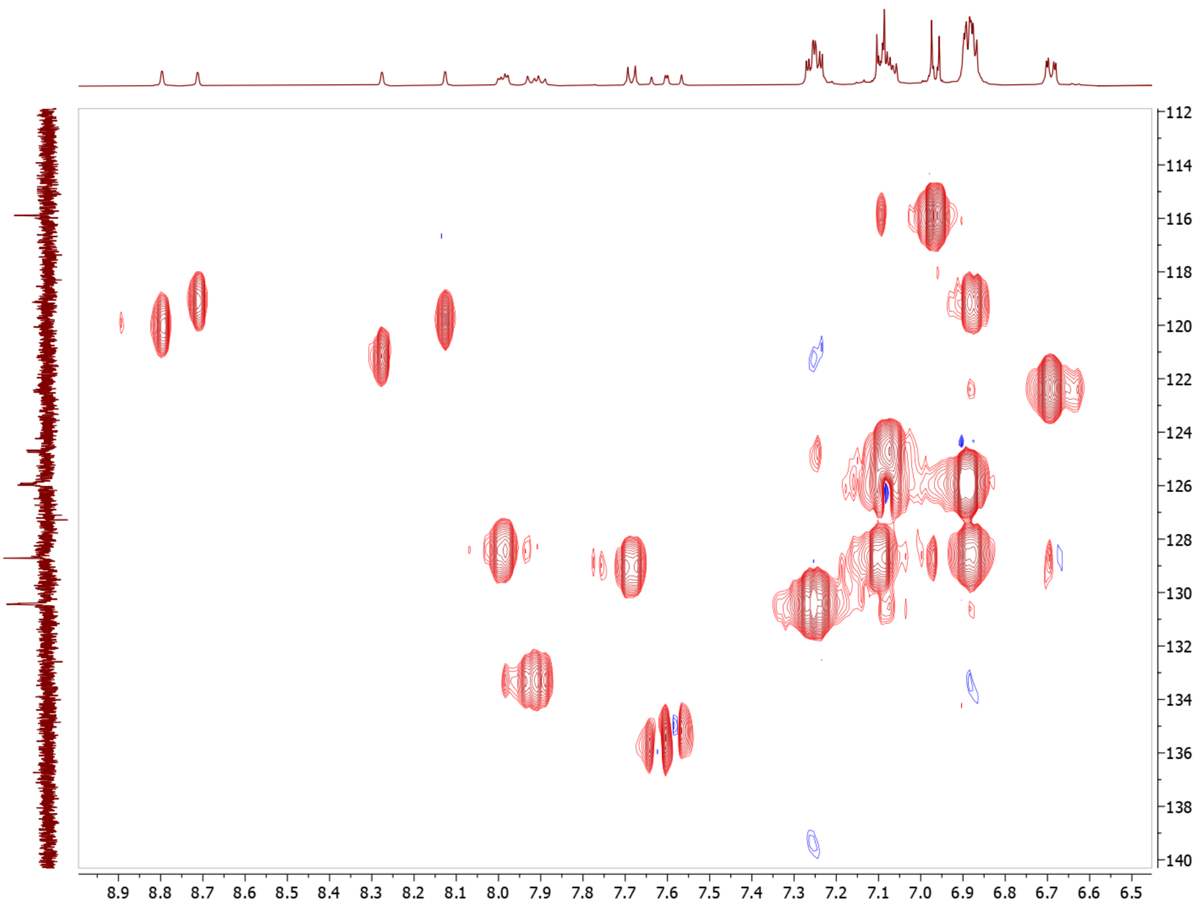


Fig. S44 The aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, acetone-d$_6$, 298 K) of [Cu(**6**)$_2$][PF$_6$].

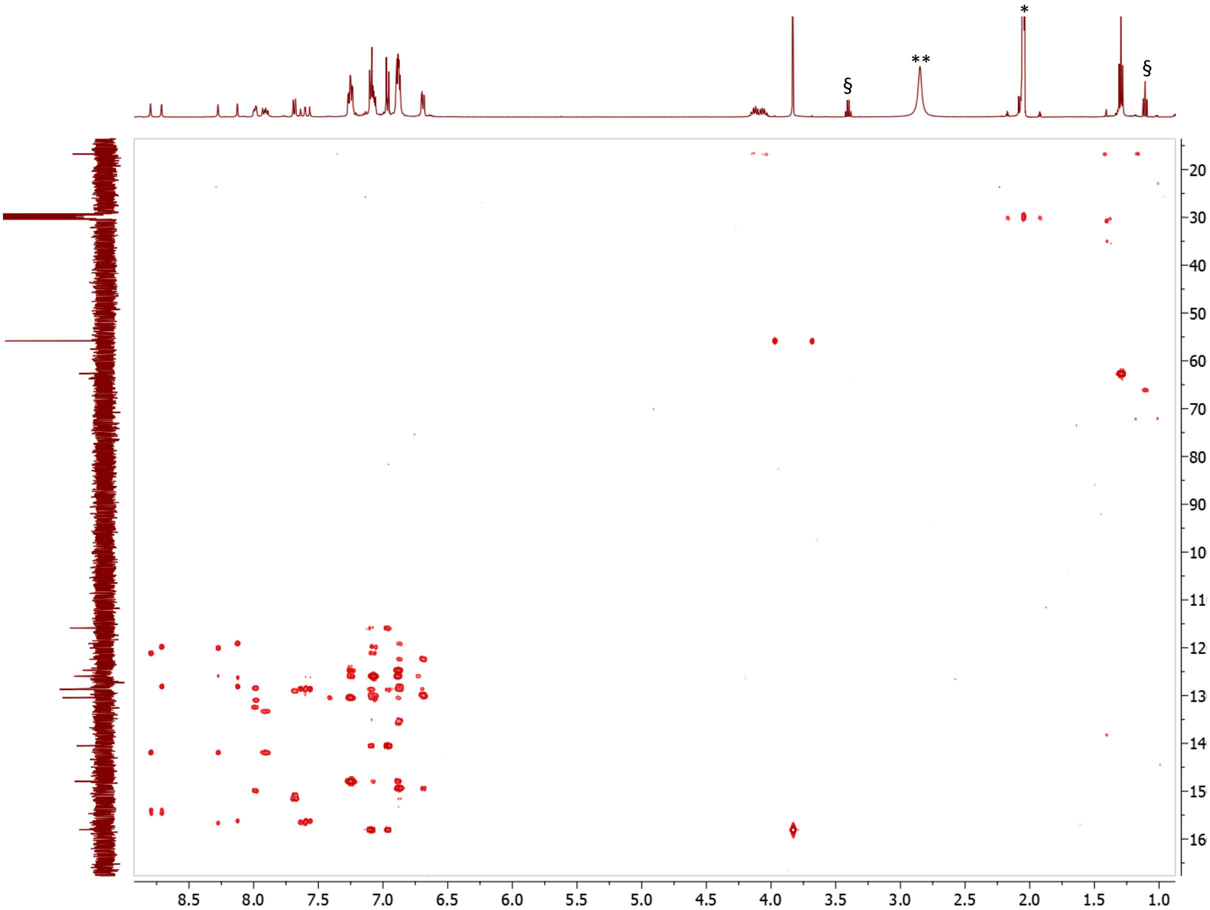


Fig. S45 Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, acetone-d_6, 298 K) of $[Cu(\mathbf{6})_2][PF_6]$. * = acetone-d_5, ** = H_2O, § = Et_2O.

FT-IR Spectra

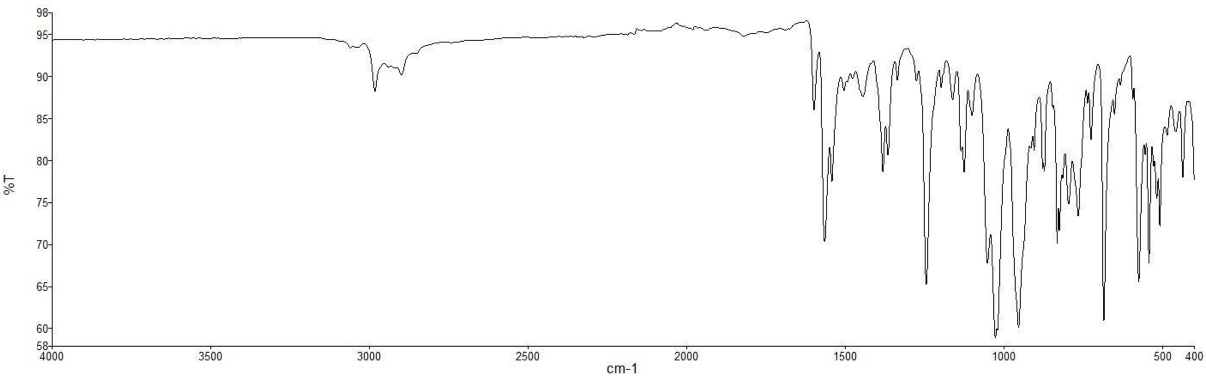


Fig. S46 The solid state FT-IR spectrum of **8**.

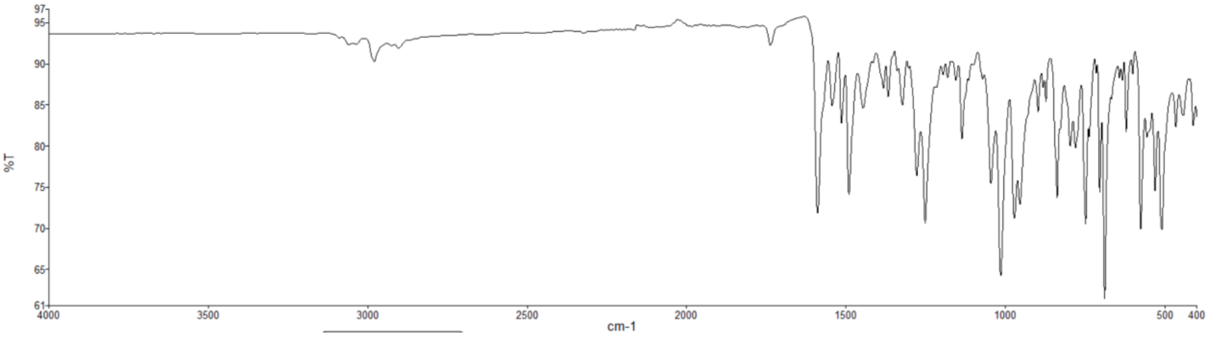


Fig. S47 The solid state FT-IR spectrum of **3e**.

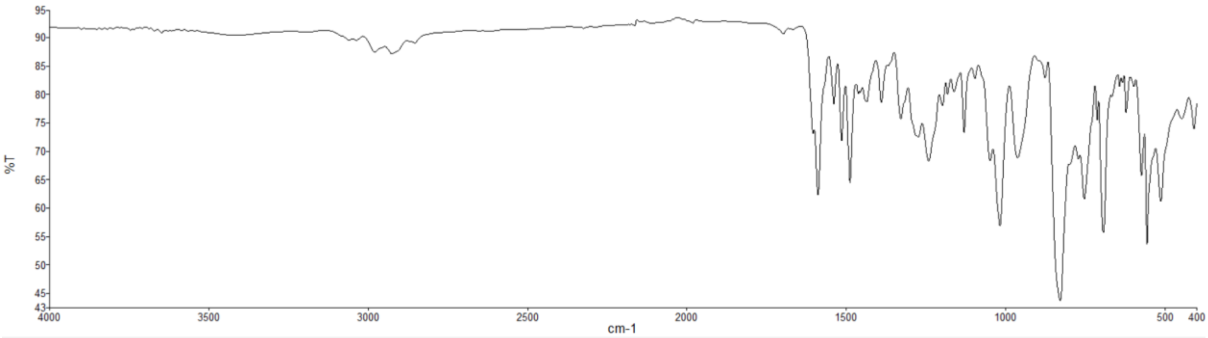


Fig. S48 The solid state FT-IR spectrum of [Cu(**3e**)$_2$][PF_6].

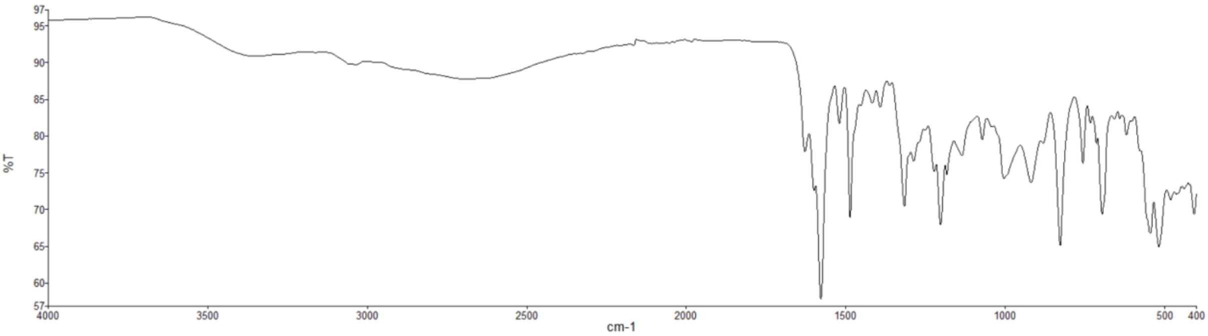


Fig. S49 The solid state FT-IR spectrum of **3**.

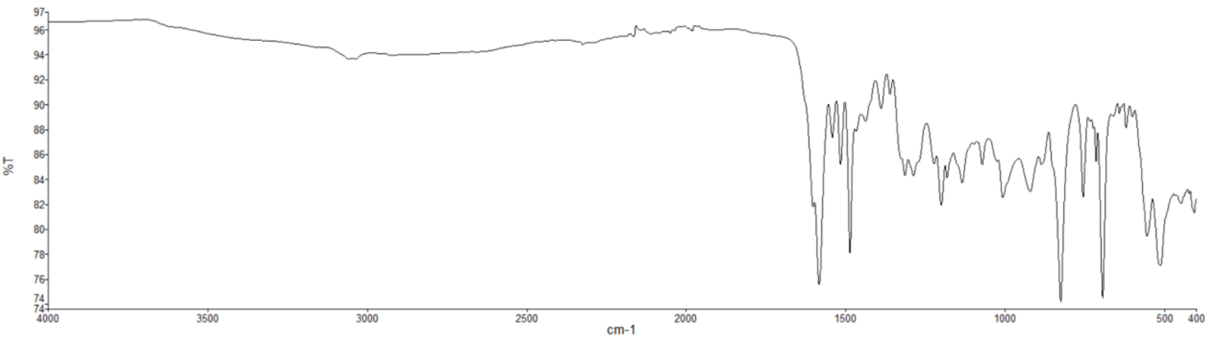


Fig. S50 The solid state FT-IR spectrum of [Cu(**3**)(**3**-H)].

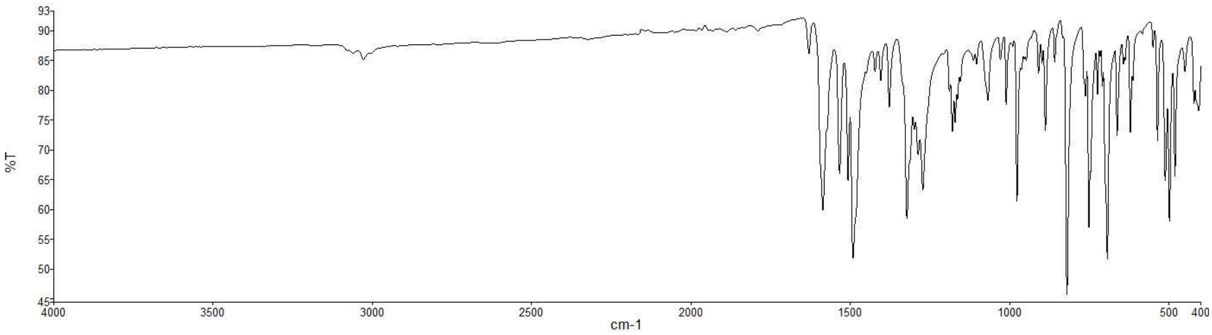


Fig. S51 The solid state FT-IR spectrum of **10**.

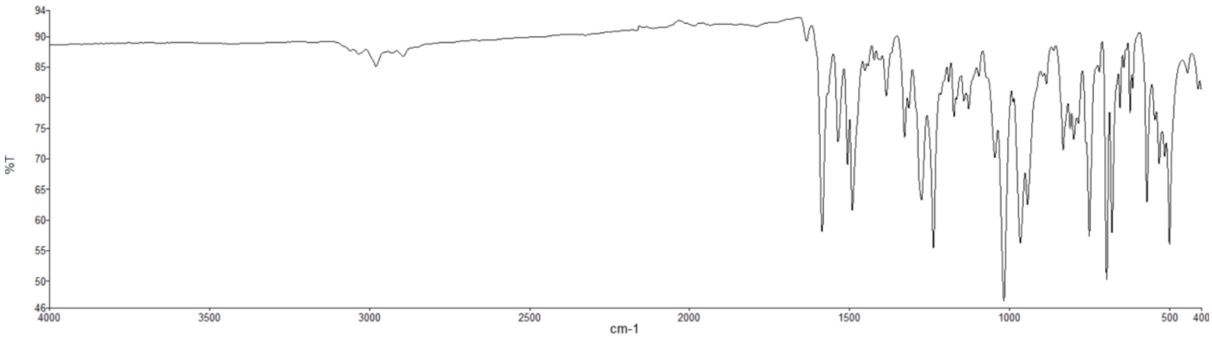


Fig. S52 The solid state FT-IR spectrum of **4e**.

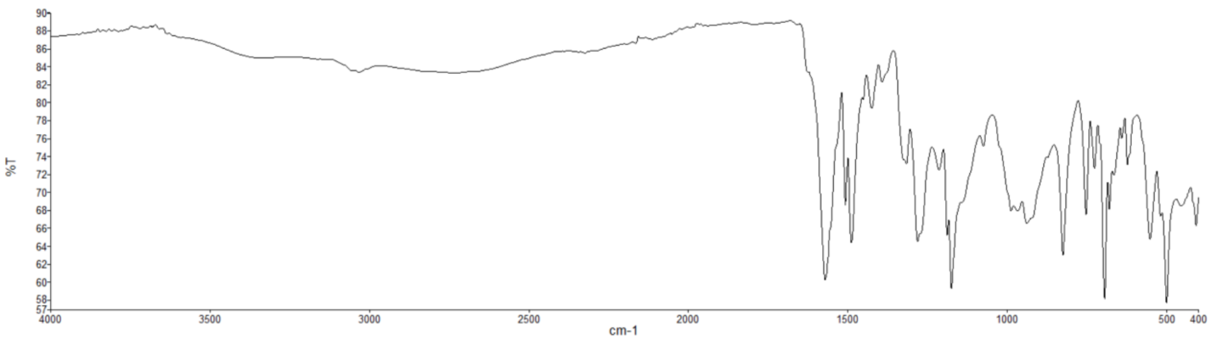


Fig. S53 The solid state FT-IR spectrum of **4**.

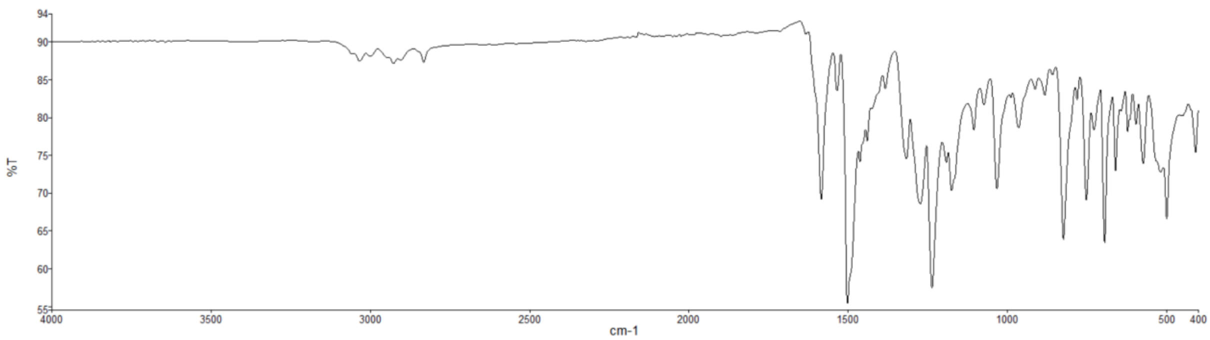


Fig. S54 The solid state FT-IR spectrum of **5**.

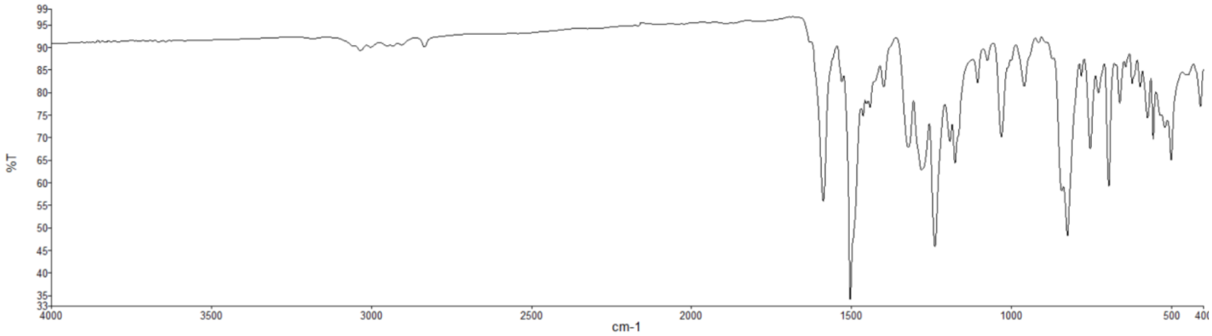


Fig. S55 The solid state FT-IR spectrum of $[Cu(\mathbf{5})_2][PF_6]$.

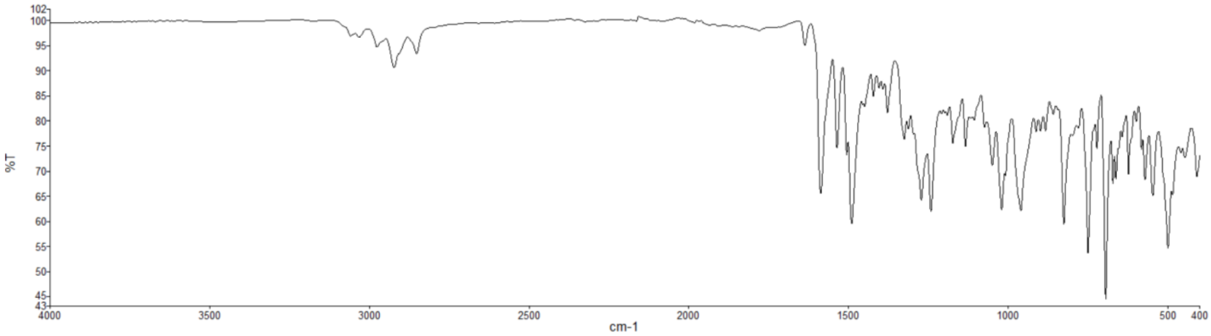


Fig. S56 The solid state FT-IR spectrum of **6eBr**.

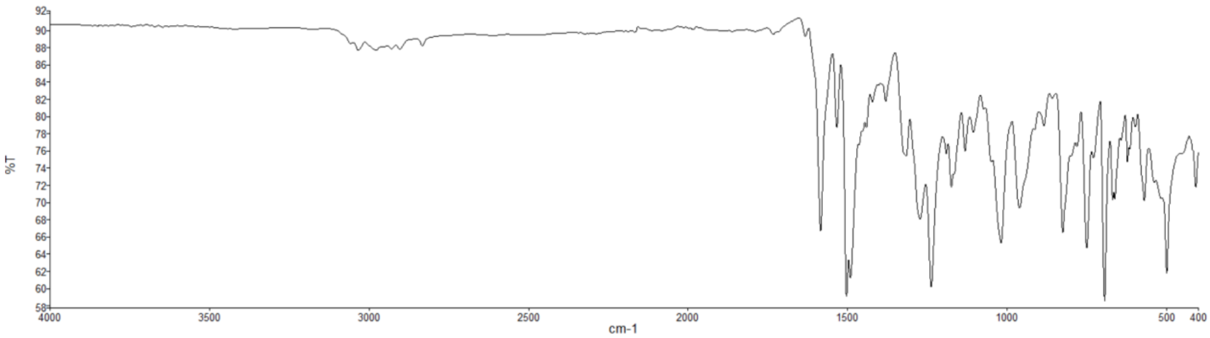


Fig. S57 The solid state FT-IR spectrum of **6e**.

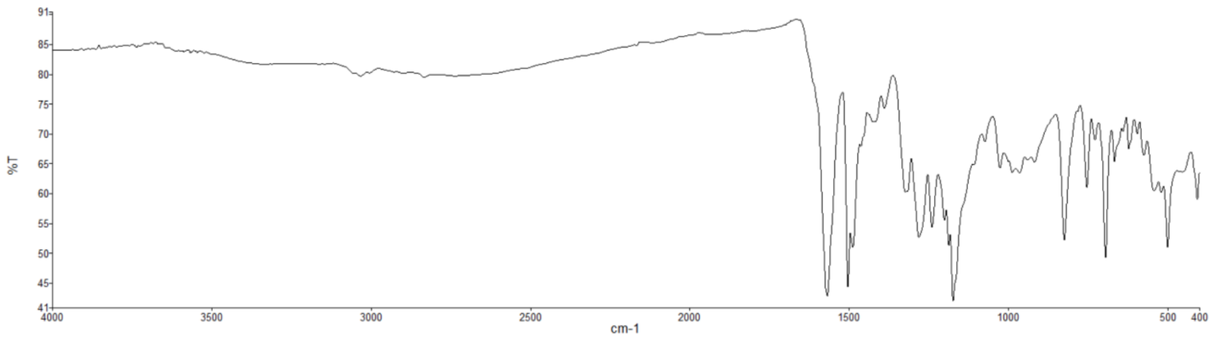


Fig. S58 The solid state FT-IR spectrum of **6**.

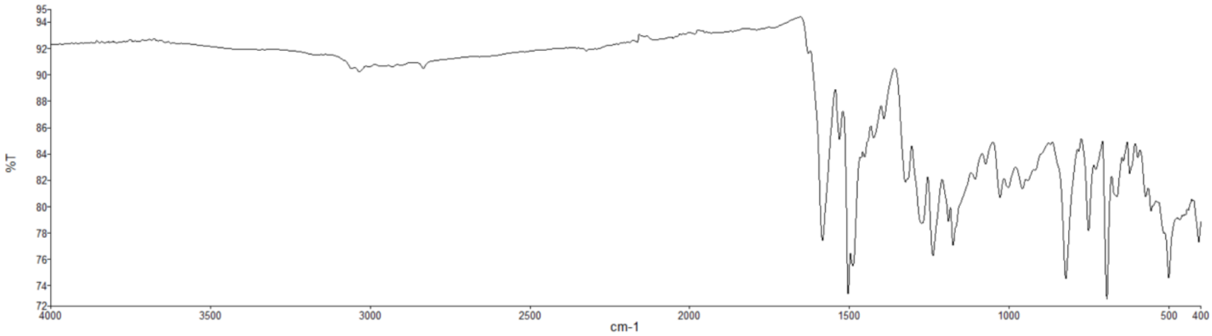


Fig. S59 The solid state FT-IR spectrum of [Cu(**6**)(**6**-H)].

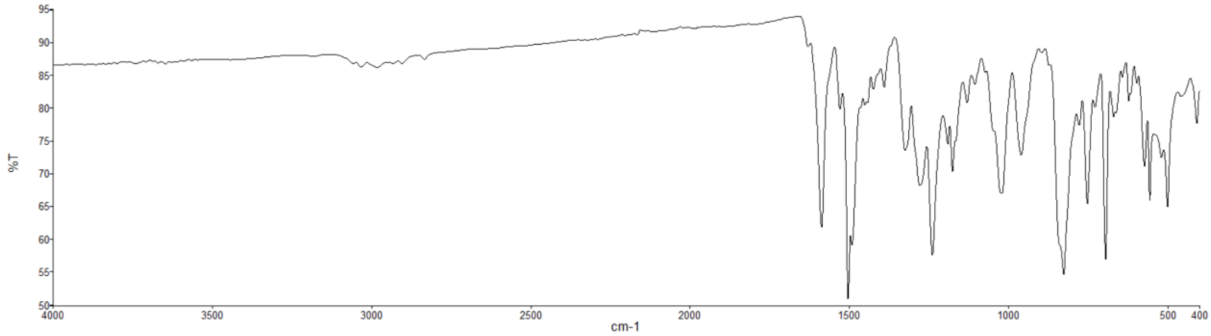


Fig. S60 The solid state FT-IR spectrum of [Cu(**6e**)$_2$][PF_6].

HR-MS Spectra

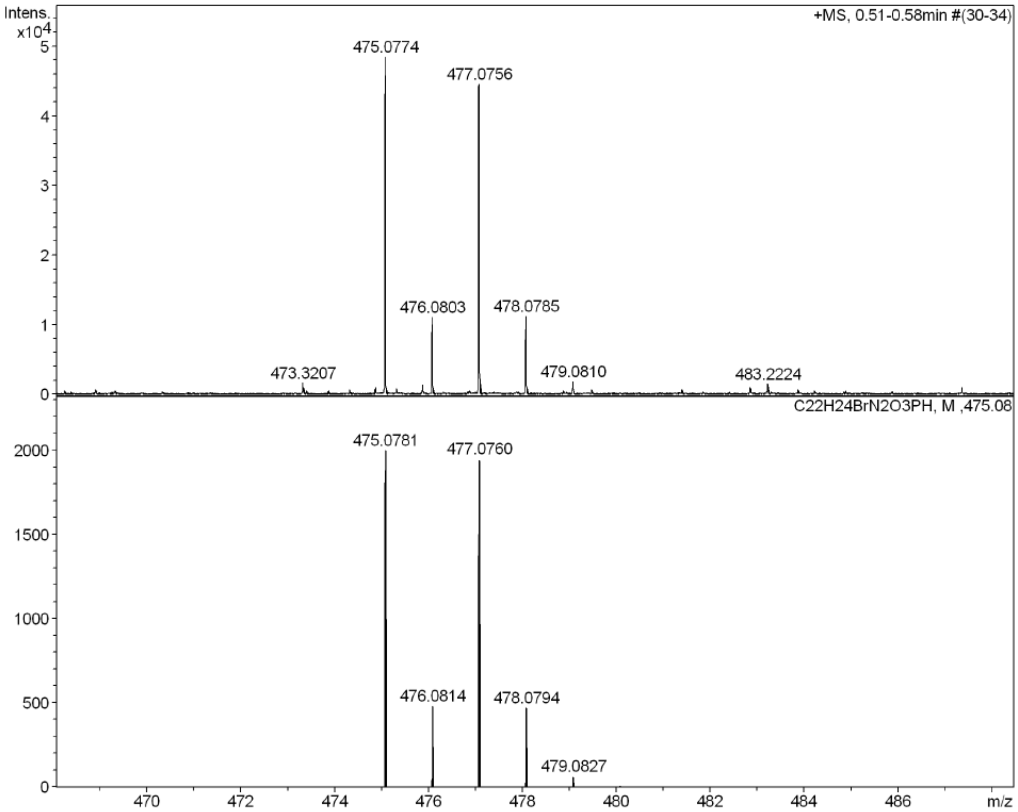


Figure S61 HR-ESI mass spectrum of **8** comparing the experimental isotope pattern for the base peak arising from $[M+H]^+$ (top) with the calculated isotope pattern (bottom).

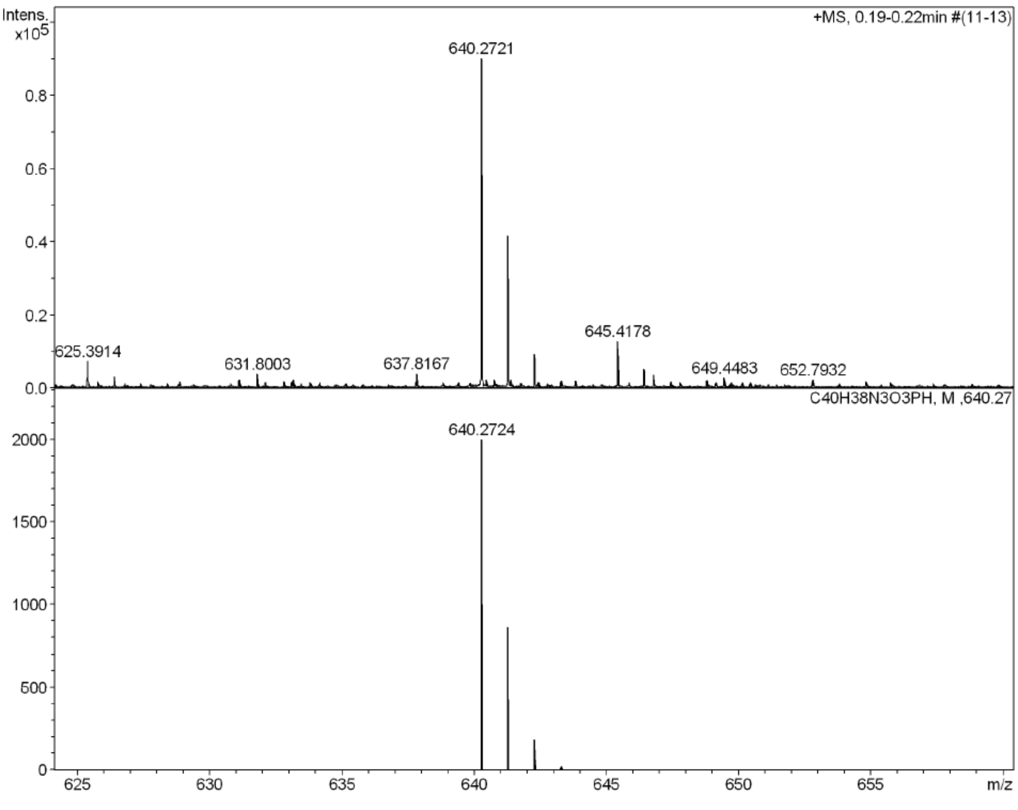


Figure S62 HR-ESI mass spectrum of **3e** comparing the experimental isotope pattern for the base peak arising from $[M+H]^+$ (top) with the calculated isotope pattern (bottom).

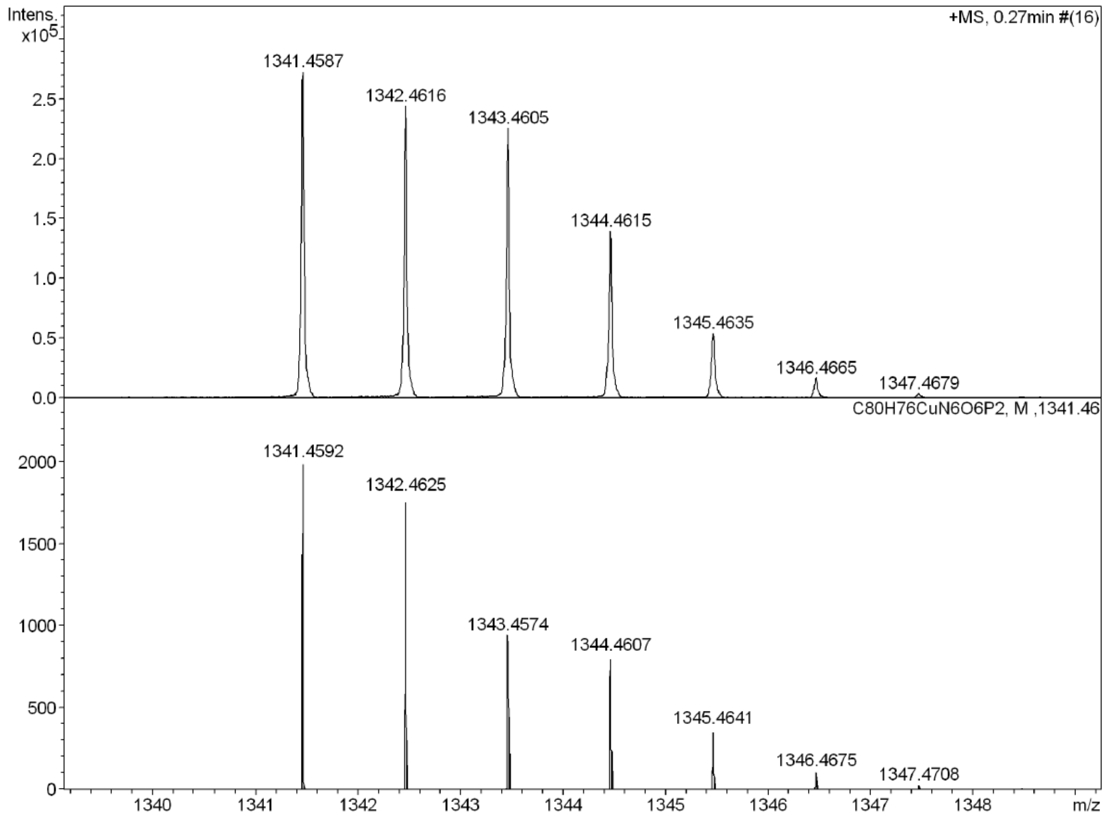


Figure S63 HR-ESI mass spectrum of [Cu(**3e**)$_2$][PF_6] comparing the experimental isotope pattern for the base peak arising from [M−PF_6]$^+$ (top) with the calculated isotope pattern (bottom).

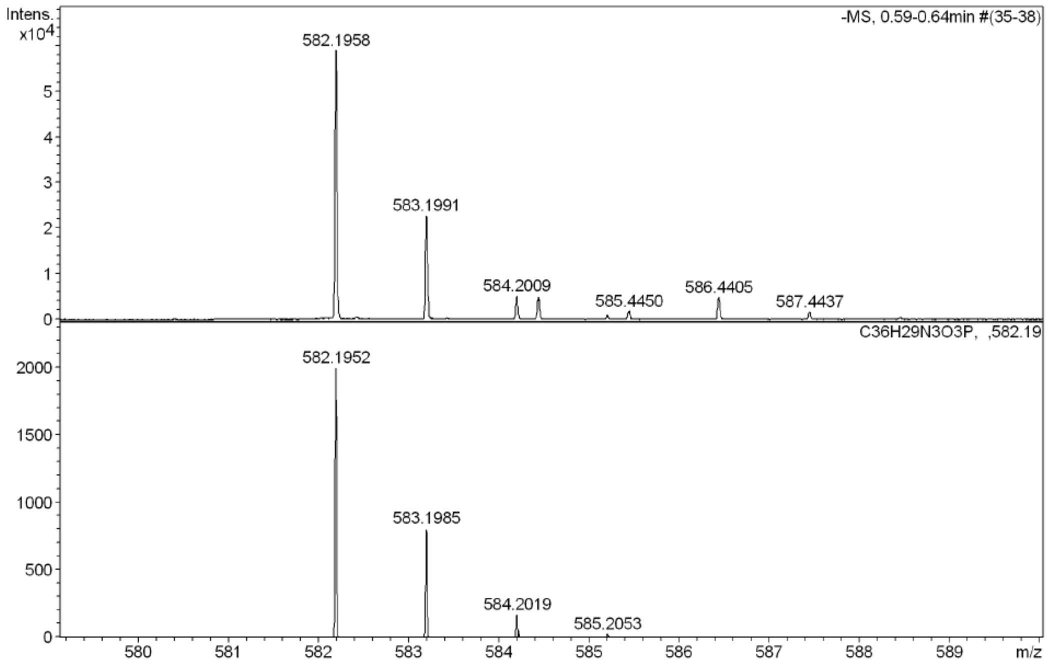


Figure S64 HR-ESI mass spectrum of **3** comparing the experimental isotope pattern for the base peak arising from [M−H]$^-$ (top) with the calculated isotope pattern (bottom).

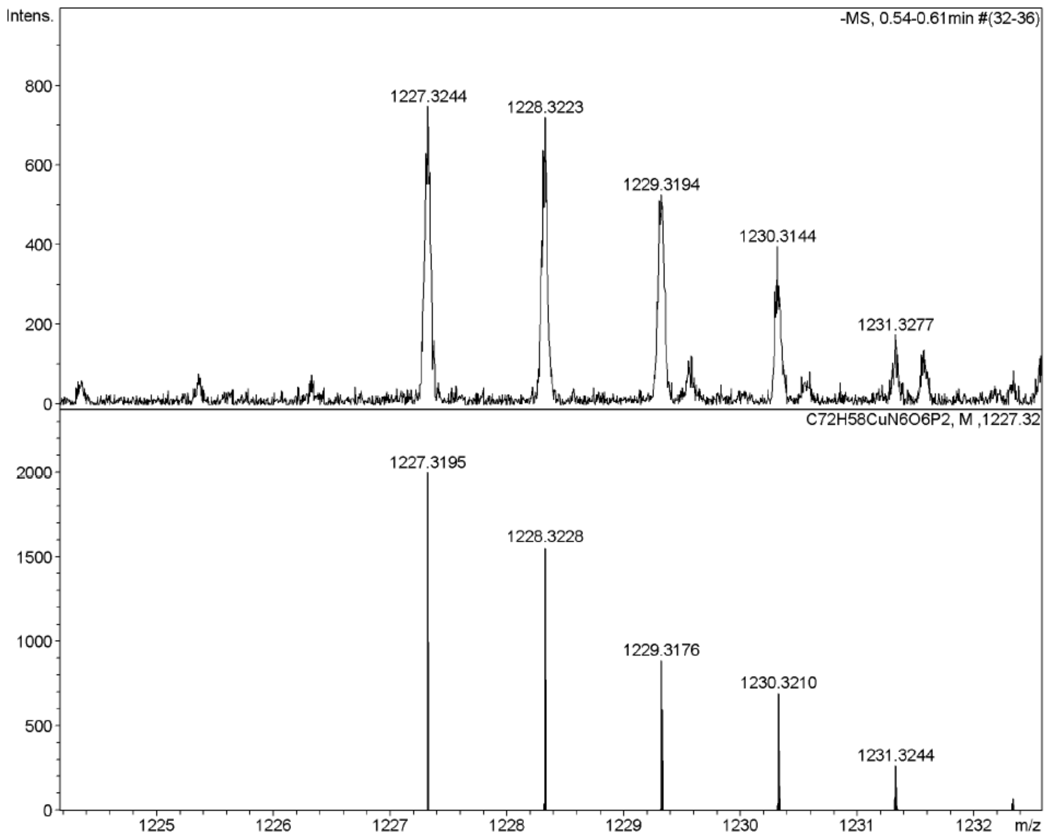


Figure S65 HR-ESI mass spectrum of [Cu(**3**)(**3**-H)] comparing the experimental isotope pattern for the base peak arising from [M–H]⁻ (top) with the calculated isotope pattern (bottom).

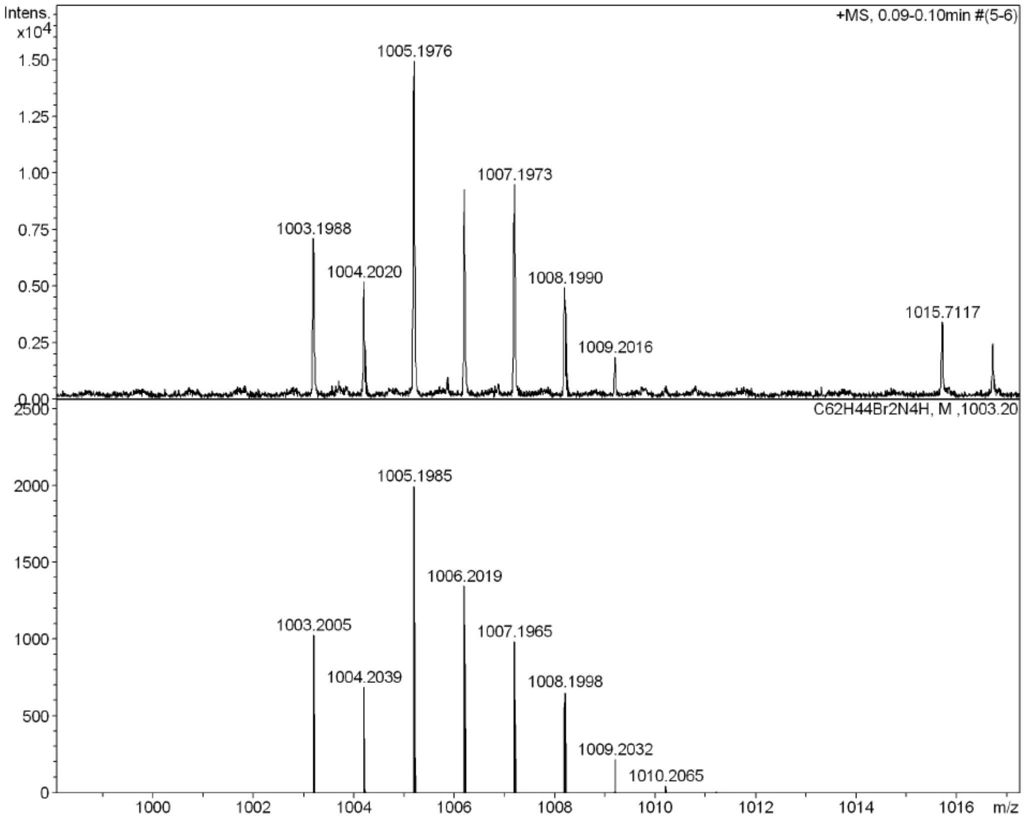


Figure S66 HR-ESI mass spectrum of **10** comparing the experimental isotope pattern for the base peak arising from [M+H]⁺ (top) with the calculated isotope pattern (bottom).

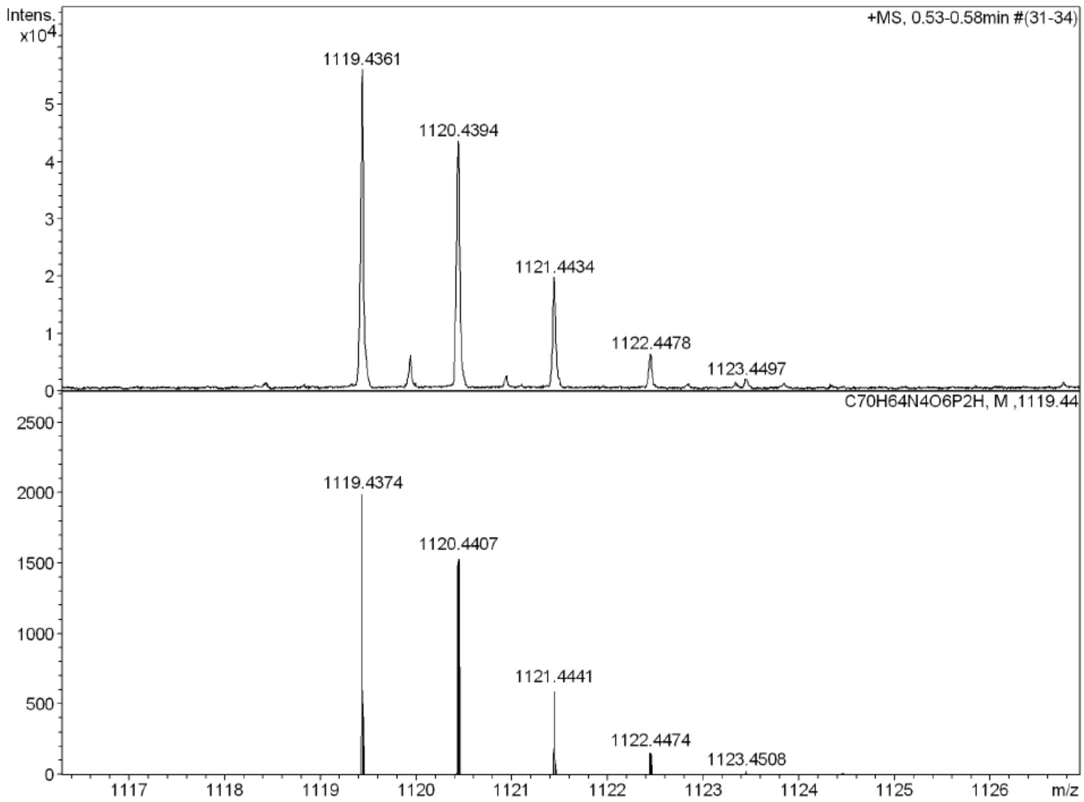


Figure S67 HR-ESI mass spectrum of **4e** comparing the experimental isotope pattern for the base peak arising from [M+H]$^+$ (top) with the calculated isotope pattern (bottom).

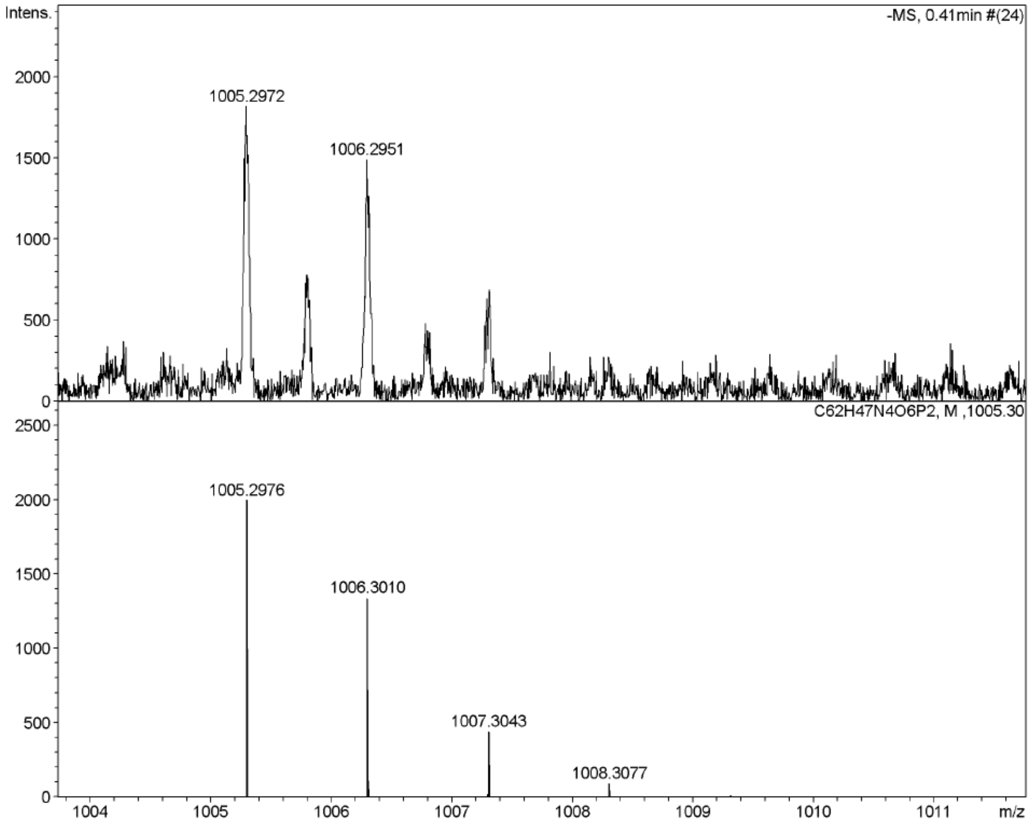


Figure S68 HR-ESI mass spectrum of **4** comparing the experimental isotope pattern for the base peak arising from [M–H]$^-$ (top) with the calculated isotope pattern (bottom).

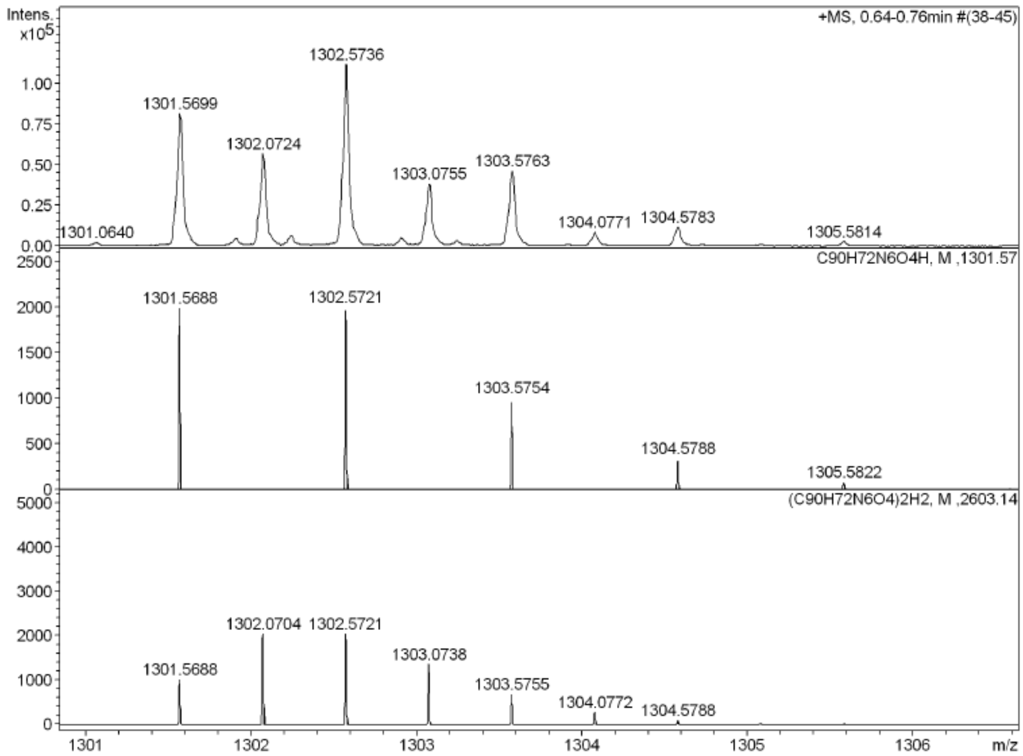


Figure S69 HR-ESI mass spectrum of **5** comparing the experimental isotope pattern for the base peak arising from $[M+H]^+$ (top) with the calculated isotope pattern (bottom).

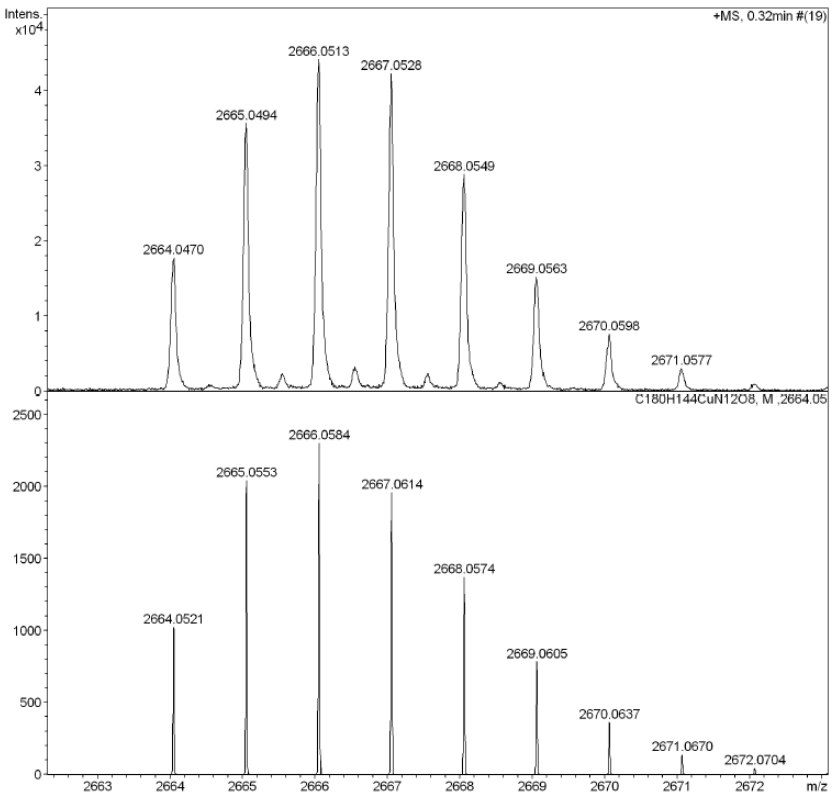


Figure S70 HR-ESI mass spectrum of $[Cu(\mathbf{5})_2][PF_6]$ comparing the experimental isotope pattern for the base peak arising from $[M-PF_6]^+$ (top) with the calculated isotope pattern (bottom).

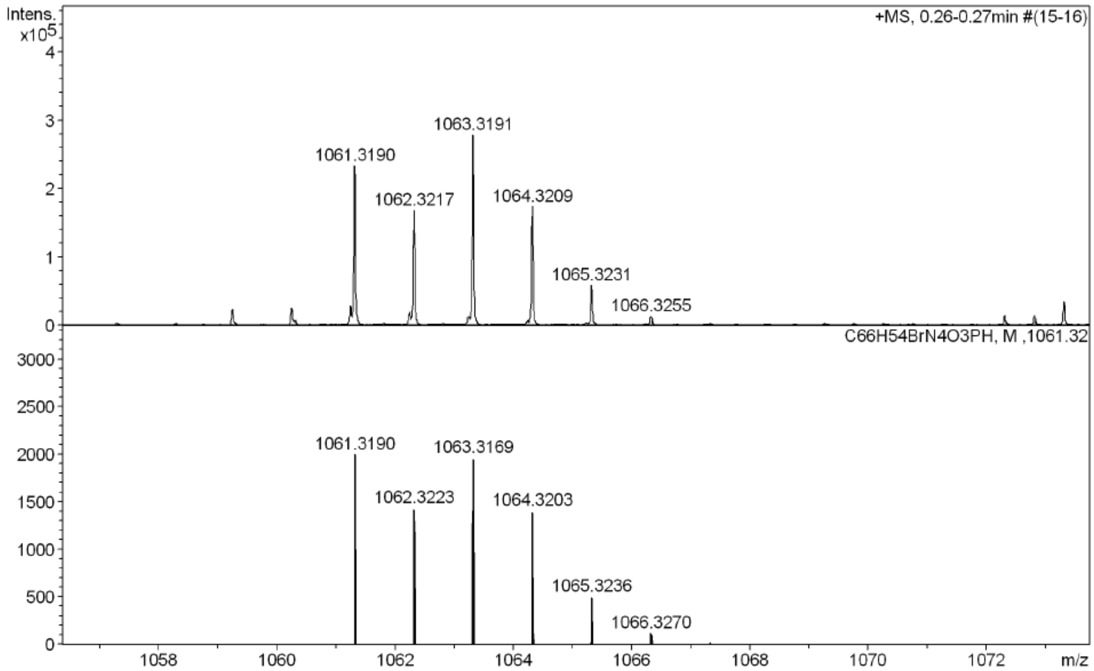


Figure S71 HR-ESI mass spectrum of **6eBr** comparing the experimental isotope pattern for the base peak arising from $[M+H]^+$ (top) with the calculated isotope pattern (bottom).

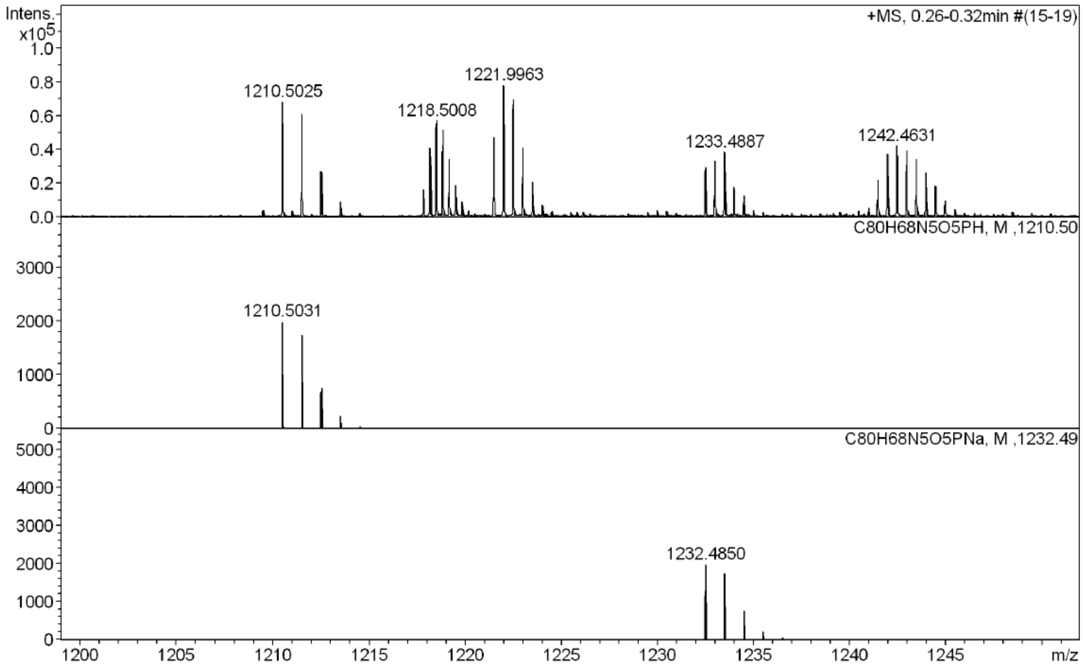


Figure S72 HR-ESI mass spectrum of **6e** comparing the experimental isotope pattern for the base peak arising from $[M+H]^+$ (top) with the calculated isotope patterns (bottom).

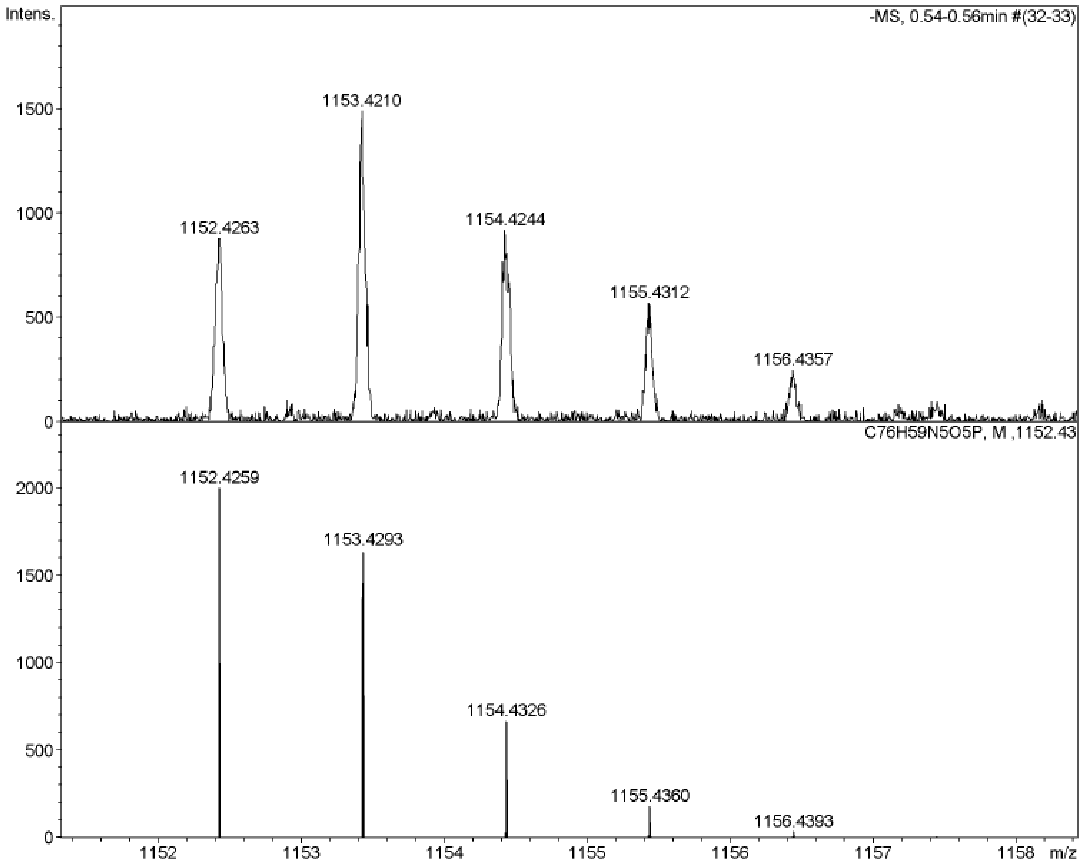


Figure S73 HR-ESI mass spectrum of **6** comparing the experimental isotope pattern for the base peak arising from [M–H]⁻ (top) with the calculated isotope pattern (bottom).

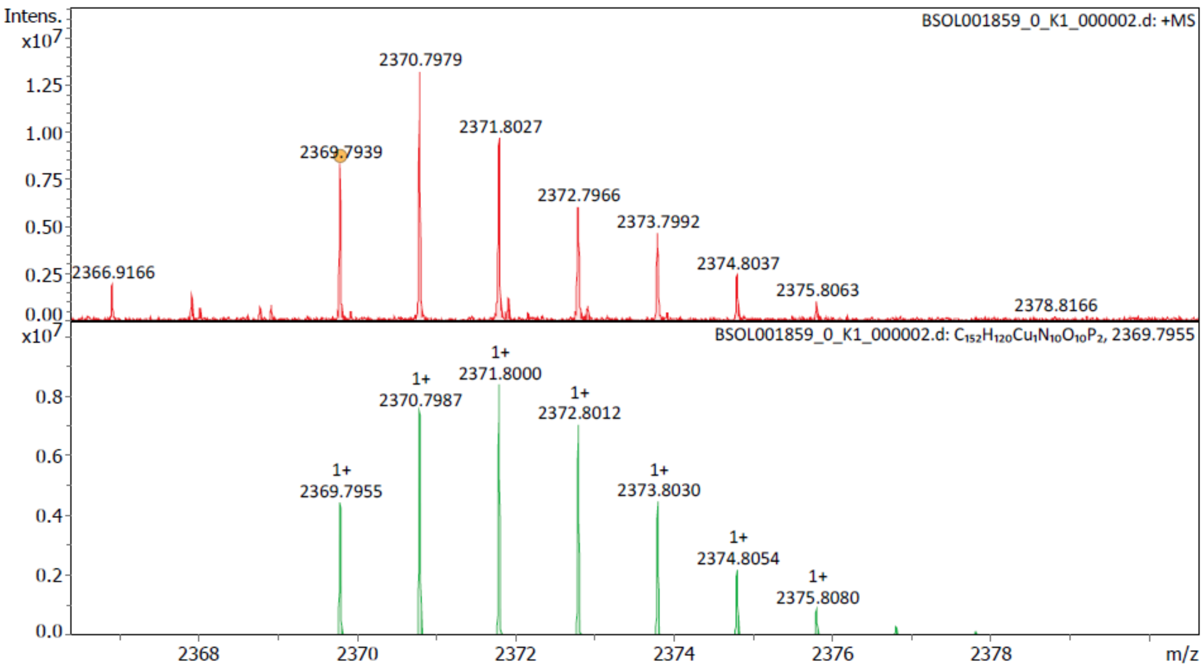


Figure S74 HR-MALDI-ToF-MS mass spectrum of [Cu(**6**)(**6**-H)] comparing the experimental isotope pattern for the base peak arising from [M+H]⁺ (top) with the calculated isotope pattern (bottom).

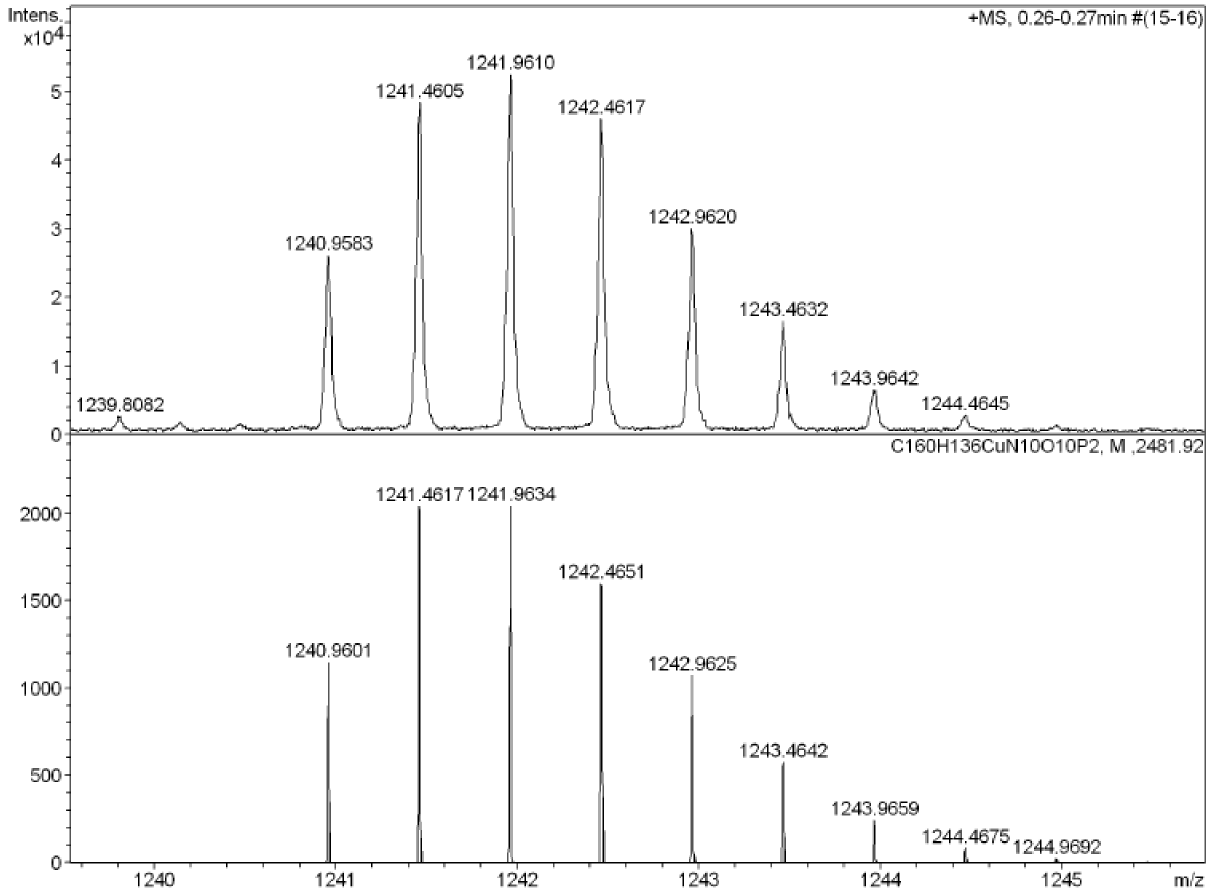


Figure S75 HR-MALDI-ToF-MS mass spectrum of $[Cu(\textbf{6e})_2][PF_6]$ comparing the experimental isotope pattern for the base peak arising from $[M - PF_6]^{2+}$ (top) with the calculated isotope pattern (bottom).

	Diffusion Coefficient/ $m^2\ s^{-1}$	Species	Peak used for calculation
Neat ligand	5.037×10^{-10}	L	7.84
Ligand:Cu 1:0.5	4.466×10^{-10}	CuL_2	7.45
Ligand:Cu 1:1	4.455×10^{-10}	CuL_2	7.45
Ligand:Cu 1:2	4.535×10^{-10}	CuL_2	7.45
Ligand:Cu 1:2	4.929×10^{-10}	CuL	7.36

Table S1 DOSY experiment data for ligand **5** and $[Cu(CH_3CN)_4][PF_6]$ in different ratios.

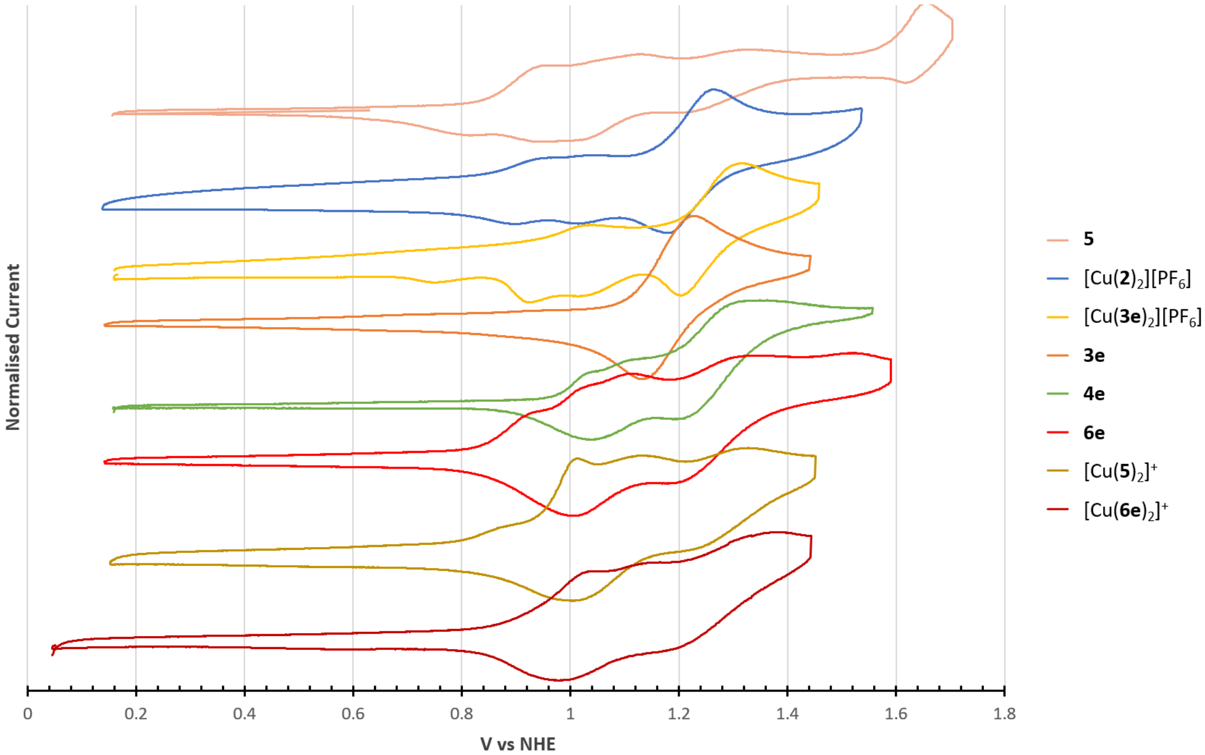


Fig. S76 Cyclic voltammograms of the investigated compounds.

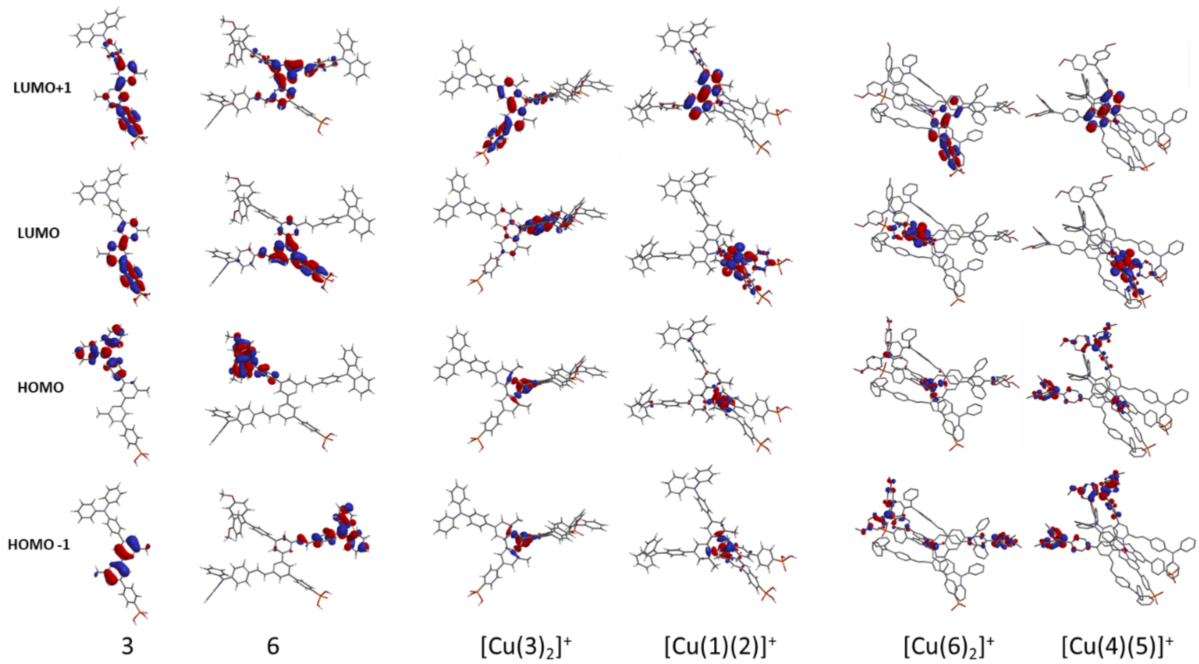


Fig. S77 MOs character of investigated compounds. From LUMO+1 to HOMO−1 from top to bottom, respectively. Calculated at a DFT level 6-31G* basis set in polar solvent with Spartan software.[3]

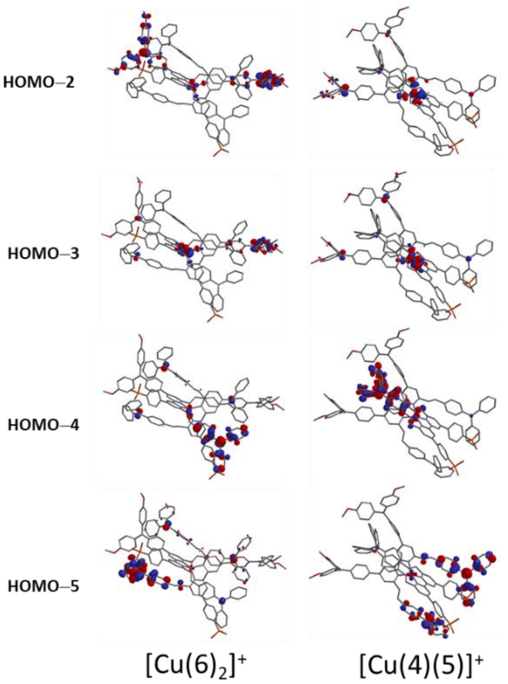


Fig. S78 MOs character of [Cu(**6**)$_2$]$^+$ and [Cu(**4**)(5)]$^+$. From HOMO–2 to HOMO–5 from top to bottom, respectively. Calculated at a DFT level 6-31G* basis set in polar solvent with Spartan software.[3]

	[Cu(**6**)$_2$]$^+$	[Cu(**4**)(**5**)]$^+$	[Cu(**3**)$_2$]$^+$	[Cu(**1**)(**2**)]$^+$
	E/ eV	E/ eV	E/ eV	E/ eV
LUMO+9	−0.93	−0.66	−0.52	−0.52
LUMO+8	−1.00	−0.91	−0.52	−0.56
LUMO+7	−1.10	−1.07	−0.64	−0.64
LUMO+6	−1.15	−1.16	−0.64	−0.66
LUMO+5	−1.23	−1.19	−1.09	−1.03
LUMO+4	−1.31	−1.31	−1.10	−1.11
LUMO+3	−1.54	−1.55	−1.50	−1.45
LUMO+2	−1.62	−1.66	−1.50	−1.59
LUMO+1	−1.89	−1.81	−1.90	−1.77
LUMO	−1.99	−2.03	−1.90	−1.97
HOMO	−4.76	−4.81	−4.86	−4.86
HOMO-1	−4.83	−4.85	−4.87	−4.87
HOMO-2	−4.90	−4.90	−5.19	−5.18
HOMO-3	−4.96	−4.94	−5.20	−5.21
HOMO-4	−5.10	−5.11	−5.48	−5.48
HOMO-5	−5.11	−5.13	−5.72	−5.72
HOMO-6	−5.15	−5.15	−6.19	−6.18
HOMO-7	−5.15	−5.17	−6.70	−6.66
HOMO-8	−5.50	−5.54	−6.71	−6.75
HOMO-9	−5.75	−5.81	−6.78	−6.78

Table S2 MOs energy values from single point DFT calculations Calculated at a DFT level 6-31G* basis set in polar solvent with Spartan software.[3]

Table S3 Day 3 J-V performance data for three sets of cells with dyes **3**, **4** and **6**.

Dye	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$η_{rel.}$/%
N719	15.02	615	59	5.42	100.0
3 c1	1.57	552	64	0.56	10.3
3 c2	1.91	580	62	0.69	12.7
3 c3	1.87	563	64	0.68	12.5
3 c4	1.66	559	64	0.60	11.0
3 average	**1.75 ± 0.16**	**564 ± 12**	**64 ± 1**	**0.63 ± 0.06**	**11.6 ± 1.2**
4 c1	4.30	551	71	1.69	31.1
4 c2	4.18	543	71	1.62	30.0
4 c3	3.98	541	72	1.54	28.5
4 c4	4.08	534	72	1.56	28.8
4 average	**4.13 ± 0.14**	**542 ± 7**	**72**	**1.60 ± 0.7**	**29.6 ± 1.2**
6 c1	4.68	598	65	1.83	33.7
6 c2	4.99	610	66	2.00	36.9
6 c3	5.01	595	61	1.80	33.3
6 c4	4.79	600	66	1.90	35.1
6 average	**4.87 ± 0.16**	**601 ± 6**	**64 ± 3**	**1.88 ± 0.09**	**34.7 ± 1.6**

Table S4 Day 7 J-V performance data for three sets of cells with dyes **3**, **4** and **6**.

Dye	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$η_{rel.}$/%
N719	15.02	615	59	5.42	100.0
3 c1	1.49	563	64	0.54	10.0
3 c2	1.83	591	61	0.66	12.2
3 c3	1.78	577	64	0.65	12.1
3 c4	1.56	570	63	0.56	10.3
3 average	**1.66 ± 0.17**	**575 ± 12**	**63 ± 1**	**0.60 ± 0.06**	**11.1 ± 1.2**
4 c1	4.17	550	70	1.60	29.5
4 c2	3.87	543	72	1.51	27.9
4 c3	3.54	546	72	1.39	25.7
4 c4	3.74	540	72	1.45	26.8
4 average	**3.83 ± 0.26**	**545 ± 5**	**71 ± 1**	**1.49 ± 0.09**	**27.5 ± 1.6**
6 c1	4.73	606	63	1.82	33.5
6 c2	4.28	616	67	1.75	32.4
6 c3	4.87	606	64	1.90	35.1
6 c4	4.75	608	66	1.90	35.1
6 average	**4.66 ± 0.26**	**609 ± 5**	**65 ± 1**	**1.84 ± 0.07**	**34.0 ± 1.3**

Table S5 Day 3 J-V performance data for sets of four or two cells for dyes [Cu(**3**)(**3**–H)], [Cu(**1**)(**2**)]$^+$, [Cu(**6**)(**6**–H)] and [Cu(**4**)(**5**)]$^+$.

Dye	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$η_{rel.}$/%
N719	15.02	615	59	5.42	100.0
[Cu(**3**)(**3**–H)][a] c1	4.81	639	59	1.81	33.4
[Cu(**3**)(**3**–H)][a] c2	3.77	634	63	1.51	27.8
[Cu(**3**)(**3**–H)][a] c3	4.31	639	62	1.70	31.4
[Cu(**3**)(**3**–H)][a] c4	4.61	636	63	1.85	34.1
[Cu(**3**)(**3**–H)] average	**4.37 ± 0.45**	**637 ± 3**	**62 ± 2**	**1.72 ± 0.15**	**31.7 ± 2.8**
[Cu(**1**)(**2**)]$^{+b,c}$ c1	3.86	553	64	1.36	25.0
[Cu(**1**)(**2**)]$^{+b,c}$ c2	4.49	539	62	1.51	27.9
[Cu(**1**)(**2**)]$^{+b,c}$ c3	3.61	542	63	1.22	22.6
[Cu(**1**)(**2**)]$^{+b,c}$ c4	4.07	546	59	1.32	24.4
[Cu(**1**)(**2**)]$^+$ average	**4.01 ± 0.37**	**545 ± 6**	**62 ± 2**	**1.35 ± 0.12**	**25.0 ± 2.2**
[Cu(**6**)(**6**–H)][a] c1	6.24	607	61	2.31	42.6
[Cu(**6**)(**6**–H)][a] c2	6.00	609	66	2.43	44.8
[Cu(**6**)(**6**–H)] average	**6.12 ± 0.17**	**608 ± 2**	**64 ± 4**	**2.37 ± 0.09**	**43.7 ± 1.6**
[Cu(**4**)(**5**)]$^{+c}$ c1	4.55	532	70	1.71	31.5
[Cu(**4**)(**5**)]$^{+c}$ c2	4.47	525	71	1.67	30.8
[Cu(**4**)(**5**)]$^{+c}$ c3	4.42	523	70	1.63	30.1
[Cu(**4**)(**5**)]$^{+c}$ c4	4.42	523	68	1.58	29.2
[Cu(**4**)(**5**)]$^+$ average	**4.47 ± 0.06**	**526 ± 4**	**70 ± 1**	**1.65 ± 0.05**	**30.4 ± 1.0**

[a]From electrodes functionalised with *method b*, see Fig. 7. [b]Set and parameters from our previous work.[2] From electrodes functionalised with *method a*.

Table S6 Day 7 J-V performance data for sets of four or two cells for dyes [Cu(**3**)(**3**–H)], [Cu(**1**)(**2**)]$^+$, [Cu(**6**)(**6**–H)] and [Cu(**4**)(**5**)]$^+$.

Dye	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$η_{rel.}$/%
N719	15.02	615	59	5.42	100.0
[Cu(**3**)(**3**–H)][a] c1	4.85	643	59	1.84	34.0
[Cu(**3**)(**3**–H)][a] c2	3.69	645	62	1.47	27.2
[Cu(**3**)(**3**–H)][a] c3	4.43	649	62	1.78	32.8
[Cu(**3**)(**3**–H)][a] c4	4.53	646	62	1.82	33.7
[Cu(**3**)(**3**–H)] average	**4.37 ± 0.49**	**646 ± 3**	**61 ± 1**	**1.73 ± 0.17**	**31.9 ± 3.2**
[Cu(**1**)(**2**)]$^{+}$[b,c] c1	4.16	567	63	1.48	27.4
[Cu(**1**)(**2**)]$^{+}$[b,c] c2	4.67	563	63	1.65	30.5
[Cu(**1**)(**2**)]$^{+}$[b,c] c3	3.79	560	64	1.36	25.1
[Cu(**1**)(**2**)]$^{+}$[b,c] c4	4.12	569	59	1.38	25.4
[Cu(**1**)(**2**)]$^+$ average	**4.18 ± 0.36**	**565 ± 4**	**62 ± 2**	**1.47 ± 0.13**	**27.1 ± 2.5**
[Cu(**6**)(**6**–H)][a] c1	5.65	618	62	2.17	40.1
[Cu(**6**)(**6**–H)][a] c2	5.73	627	64	2.32	42.7
[Cu(**6**)(**6**–H)] average	**5.69 ± 0.05**	**622 ± 6**	**63 ± 2**	**2.24 ± 0.10**	**41.4 ± 1.9**
[Cu(**4**)(**5**)]$^{+}$[c] c1	4.55	537	71	1.73	32.0
[Cu(**4**)(**5**)]$^{+}$[c] c2	4.44	533	71	1.69	31.2
[Cu(**4**)(**5**)]$^{+}$[c] c3	4.39	530	71	1.64	30.3
[Cu(**4**)(**5**)]$^{+}$[c] c4	4.55	522	65	1.55	28.7
[Cu(**4**)(**5**)]$^+$ average	**4.48 ± 0.08**	**531 ± 7**	**70 ± 3**	**1.65 ± 0.08**	**30.5 ± 1.4**

[a]From electrodes functionalised with *method b*, see Fig. 7. [b]Set and parameters from our previous work.[2] From electrodes functionalised with *method a*.

Table S7 Day 3 J-V performance data for three or four sets of cells derived from dipping of **3**-functionalised and **6**-functionalised electrodes into either 0.01, 0.1 or 1.0 mM solutions of [Cu($CH_3CN)_4$][PF_6].

Dye and Cell number	[Cu($CH_3CN)_4$][PF_6]/ mM	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$η_{rel.}$/%
N719	-	15.02	615	59	5.42	100.0
3 c1	0.01	3.06	583	69	1.23	22.7
3 c2	0.01	3.60	569	65	1.34	24.7
3 c3	0.01	3.47	578	69	1.38	25.5
3 c4	0.01	3.38	573	68	1.31	24.2
average	-	**3.38 ± 0.23**	**576 ± 6**	**68 ± 2**	**1.32 ± 0.06**	**24.3 ± 1.2**
3 c1	0.1	4.11	583	70	1.68	31.1
3 c2	0.1	4.06	581	72	1.69	31.2
3 c3	0.1	4.03	570	73	1.67	30.8
3 c4	0.1	4.23	602	70	1.79	33.0
average	-	**4.11 ± 0.09**	**584 ± 13**	**71 ± 1**	**1.71 ± 0.05**	**31.5 ± 1.0**
3 c1	1.0	2.16	542	65	0.76	14.0
3 c2	1.0	2.87	577	62	1.03	19.0
3 c3	1.0	2.85	573	61	0.99	18.2
average	-	**2.63 ± 0.41**	**564 ± 19**	**62 ± 2**	**0.92 ± 0.15**	**17.0 ± 2.7**
6 c1	0.1	6.84	580	64	2.53	46.8
6 c2	0.1	6.86	583	61	2.44	45.1
6 c3	0.1	6.79	579	61	2.40	44.3
6 c4	0.1	6.45	579	61	2.30	42.4
average	-	**6.74 ± 0.19**	**580 ± 2**	**62 ± 1**	**2.42 ± 0.10**	**44.6 ± 1.8**

Table S8. Day 7 J-V performance data for three or four sets of cells derived from dipping of **3**-functionalised and **6**-functionalised electrodes into either 0.01, 0.1 or 1.0 mM solutions of $[Cu(CH_3CN)_4][PF_6]$.

Dye and Cell number	$[Cu(CH_3CN)_4][PF_6]$/ mM	J_{SC}/mA cm^{-2}	V_{OC}/mV	FF/%	η/%	$\eta_{rel.}$/%
N719	-	15.02	615	59	5.42	100.0
3 c1	0.01	3.05	583	70	1.24	22.8
3 c2	0.01	3.41	568	68	1.31	24.2
3 c3	0.01	3.39	574	70	1.37	25.3
3 c4	0.01	3.41	565	69	1.32	24.4
average	-	**3.31 ± 0.18**	**572 ± 8**	**69 ± 1**	**1.31 ± 0.06**	**24.2 ± 1.0**
3 c1	0.1	3.97	564	73	1.62	30.0
3 c2	0.1	3.92	563	73	1.62	29.9
3 c3	0.1	3.92	557	74	1.62	30.0
3 c4	0.1	4.11	584	72	1.74	32.1
average	-	**3.98 ± 0.09**	**567 ± 11**	**73 ± 1**	**1.65 ± 0.06**	**30.5 ± 1.1**
3 c1	1.0	2.07	556	64.7	0.74	13.7
3 c2	1.0	2.82	591	62.3	1.04	19.2
3 c3	1.0	2.10	558	64.9	0.76	14.0
average	-	**2.33 ± 0.43**	**568 ± 20**	**64 ± 1**	**0.85 ± 0.17**	**15.7 ± 3.1**
6 c1	0.1	6.64	589	64	2.51	46.4
6 c2	0.1	6.70	591	61	2.43	44.9
6 c3	0.1	6.58	586	61	2.37	43.7
6 c4	0.1	6.47	590	61	2.32	42.9
average	-	**6.60 ± 0.09**	**589 ± 2**	**62 ± 2**	**2.41 ± 0.08**	**44.5 ± 1.5**

References

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