Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI)……..

Towards technomimetic spoked wheels: Dynamic hexakis-heteroleptic coordination at a hexakis-terpyridine scaffold

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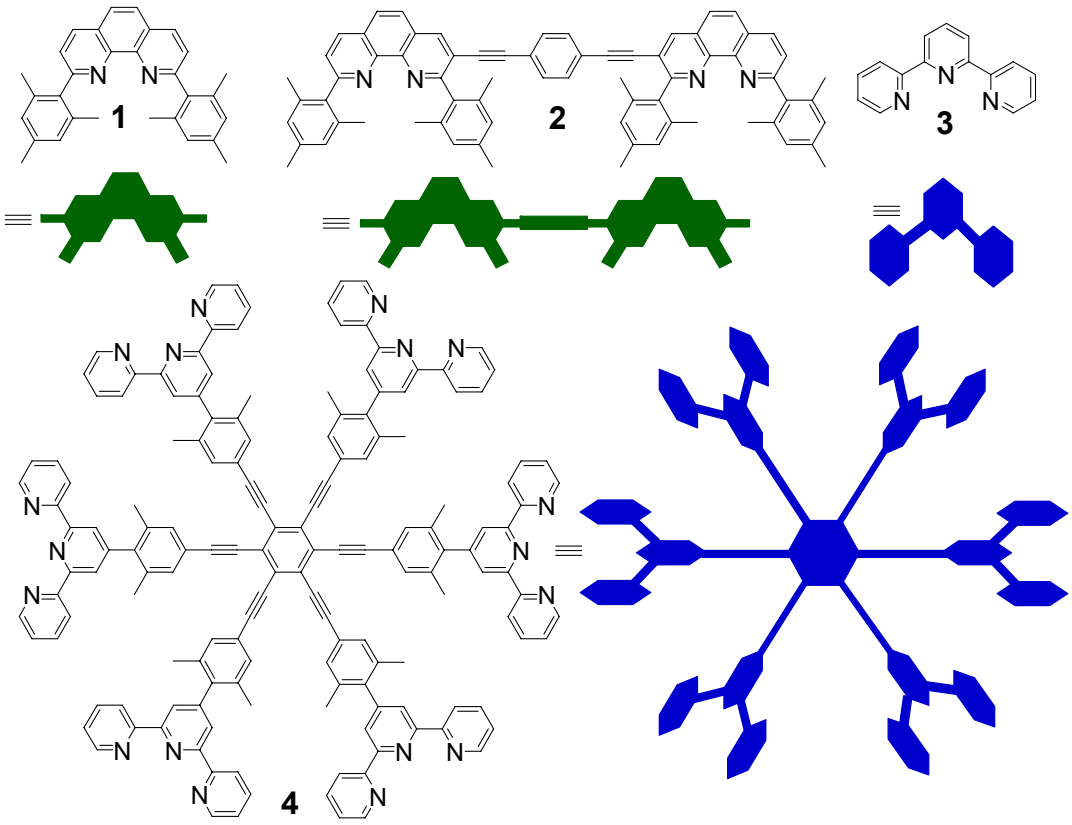
Chart S1. Ligands used for the present study.



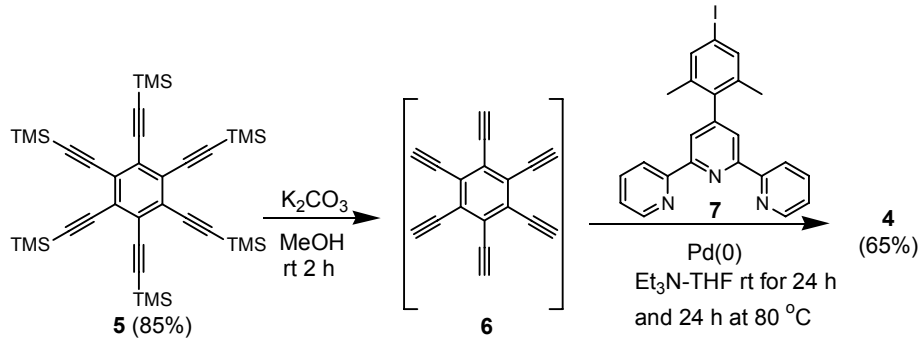
Experimental:

General. ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker AC 200 (200 MHz) or Avance 400 (400 MHz) machines. NMR analysis was conducted at room temperature mainly in deuterated dichloromethane unless specified otherwise. $[Cu(MeCN)_4]PF_6$ was prepared according to the known procedure.[1] Positive ESI-MS spectra were recorded on a LCQ Deca Thermo Quest instrument, scanning the *m/z* range 200-4000. Typically, each time 25 scans were accumulated for one spectrum. The samples were introduced in the ES source at a flow rate of 10 mL/min. Typical ESI-MS conditions used in this study: the sheath gas flow rate, spray voltage, capillary voltage and tube lense offset were set at 50 (arb), 5 (kV), 200 °C, 41 (V) and 5 (V) respectively, in order to avoid fragmentation. Assignment of ions was further confirmed by comparison of their isotopic pattern with the calculated ones and also by collisional fragmentations. UV/Vis spectra (for the complexes) were recorded on a Tidas II spectrophotometer using dichloromethane as the solvent. Molecular modelling was done with the MM +force field as implemented in Hyperchem 6.02. Hyperchem® 6.02 Release for Windows by Hypercube, Inc. **2000**. MM + force field.

(1) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90–92.

Synthesis. Chart S1 depicts phenanthrolines **1**,**2** and terpyridines **3**,**4** used as building blocks for the present study. Terpyridine **3** was purchased and used as received. Synthesis of compounds **1**[2] and **2**[3] was achieved along established protocols elaborated in our group. In Scheme S1, the synthesis of **4** (hexakis[4'-(4-ethynyl-2,6-dimethylphenyl)-2,2':6',2''-terpyridyl]benzene), is described. The first step involved the synthesis of hexakis-(trimethylsilylethynyl)benzene (**5**)[4] *via* a Sonogashira-Negishi coupling.[5] Deprotection of **5** using K_2CO_3 in methanol led to hexakis(ethynyl)benzene (**6**).[6] Since **6** was found to be very unstable, it was not purified for the ensuing step. The final step employed a Sonogashira coupling reaction between **6** and **7**[7] in presence of Pd(0) and CuI as catalyst. For this step exclusion of oxygen was crucial, because traces thereof in the reaction mixture led to a notorious and inseparable mixture of products.

Scheme S1. Synthesis of hexakis[4'-(4-ethynyl-2,6-dimethylphenyl)-2,2':6',2''-terpyridyl]-benzene (**4)**.



Procedure for the synthesis hexakis[4'-(4-ethynyl-2,6-dimethylphenyl)-2,2':6',2''-terpyridyl]benzene (4): To a degassed solution of hexakis(trimethylsilylethynyl)benzene (**5**) (118 mg, 0.180 mmol) in THF (10 mL) and methanol (10 mL) was added K_2CO_3 (248.0 mg, 1.79 mmol) and water (0.1 mL). The resulting mixture was stirred at room temperature for 2 h. After addition of water (30 mL) the mixture was extracted with diethyl ether, washed with water, and dried over Na_2SO_4. After removal of the solvents, dry THF (10 mL) and toluene (10 mL) were added immediately to the white solid **6** while purging thoroughly with argon. To the solution was added triethylamine (8.0 mL), 4'-(4-iodo-2,6-dimethylphenyl)-2,2':6',2''-terpyridine (**7**) (583 mg, 1.26 mmol) and CuI (12.0 mg, 63.0 μmol). Finally, after an addition

(2) Kalsani, V.; Ammon, H.; Jäckel, F.; Rabe, J. P.; Schmittel, M. *Chem. Eur. J.* **2004**, *10*, 5481–5492.
(3) (a) Schmittel, M.; Michel, C.; Wiegrefe, A.; Kalsani, V. *Synthesis* **2001**, 1561–1567.
(4) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *03*, 2419–2421.
(5) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *03*, 2419–2421.
(6) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.*, **1999**, *28*, 107–119.
(7) Schmittel, M.; Kalsani, V.; Mal, P.; Bats, J. W. *Inorg. Chem.* **2006**, *45*, 6370–6377.

of $Pd(PPh_3)_4$ (124.0 mg, 0.107 mmol) to the degassed mixture, the mixture was stirred at room temperature for 24 h and at 80 °C for additional 24 h under argon atmosphere. The reaction mixture was diluted with dichloromethane, washed successively with 2N KOH and brine, dried over Na_2SO_4, and concentrated. The crude mixture was purified by column chromatography on neutral alumina with CH_2Cl_2, ethyl acetate and triethylamine (90:9:1) to afford **4** (262 mg, 65%) as brownish powder.

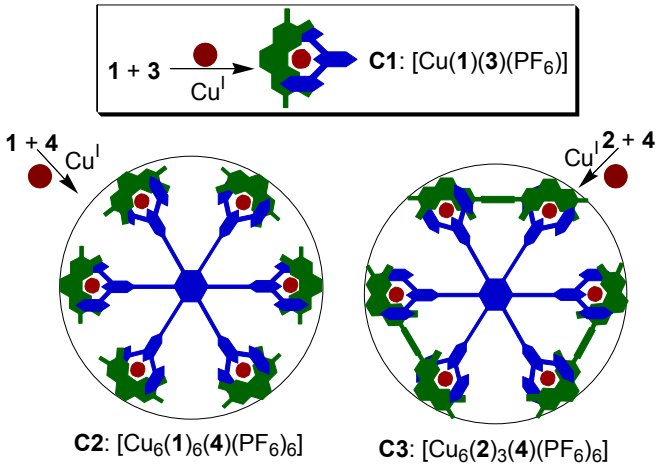
Hexakis(trimethylsilylethynyl)benzene (**5**): Yield 85%; mp 224.7 °C (from DSC analysis) (lit[8] > 300 °C); ^{1}H NMR ([D]Chloroform, 25 °C, 400 MHz): δ= 0.28 ppm (s, 54H); ^{13}C NMR ([D]Chloroform, 25 °C, 100 MHz): δ= 127.9, 105.2, 101.0, 0.01 ppm.

Hexaethynylbenzene (6): Yield (quantitative); ^{1}H NMR ([D_6]Dimethylsulfoxide, 25 °C, 400 MHz): δ= 4.96 ppm (s, 6H); ^{13}C NMR ([D_6]Dimethylsulfoxide, 25 °C, 400 MHz): δ= 127.7, 91.6, 79.3 ppm.

Hexakis[3,5-dimethyl-1,4-(2,2':6',2''-terpyridine-4'-yl)phenylethynyl]benzene (**4**): Mp > 300 °C; ^{1}H NMR ([D_2]Dichloromethane, 25 °C, 400 MHz): δ= 8.67 (d, J = 8.0 Hz, 12H), 8.60-8.57 (m, 12H), 8.35 (s, 12H), 7.86 (dt, J = 8.0, 2.0 Hz, 12H), 7.64 (s, 12H), 7.29 (ddd, J = 8.0, 5.0, 1.0 Hz, 12H), 2.16 ppm (s, 36H); ^{13}C NMR ([D_2]Dichloromethane, 25 °C, 100 MHz): δ= 156.4, 156.2, 150.9, 149.5, 141.4, 137.1, 136.4, 131.3, 127.9, 124.2, 122.6, 121.7, 121.3, 100.3, 87.6, 21.0 ppm; IR (KBr): ν = 3051, 2955, 2920, 2360, 2201, 1605, 1584, 1565, 1467, 1442, 1389, 1262, 1119 cm^{-1}; ESI-MS: *m/z* (%): 2236.5 (23) $[M]^+$: (calcd for $[C_{156}H_{109}N_{18}]$ $[M+H]^+$: 2234.9); 1118.9 (81) $[M+2H]^{2+}$ (calcd for $[C_{156}H_{110}N_{18}]^{2+}$: 1118.0); 746.9 (100) $[M+3H]^{3+}$ (calcd for $[C_{156}H_{111}N_{18}]^{3+}$: 745.6); elemental analysis calcd (%) for $C_{156}H_{108}N_{18}.2CH_2Cl_2$: C 78.92, H 4.69, N 10.49; found: C 79.17, H 4.88, N 10.08.

(8) (a) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489–2496; (b) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Engl*. **1986**, *25*, 268–269.

Scheme S2. Cartoon representations for the construction of the Assemblies.



General procedure for the formation of the assemblies: The supramolecular assemblies were prepared by mixing stoichiometric amounts of phenanthrolines and terpyridines with $[Cu(MeCN)_4]PF_6$ in dichloromethane. The mixing sequence was as followed: first phenanthroline and Cu^I were added and dissolved in dichloromethane, then to the clear solution the corresponding amount of terpyridine was added. The resulting dark red solution was analyzed without any purification by ESI-MS, ^{1}H NMR, ^{13}C NMR, IR and elemental analysis.

C1 $[Cu(\mathbf{1})(\mathbf{3})]^+$: > 300 °C; ^{1}H NMR ([D$_2$]Dichloromethane, 25 °C, 400 MHz): δ= 8.60 (d, J = 8.0 Hz, 2H, phenanthroline), 8.17 (s, 2H; phenanthroline), 8.03 (t, J = 8.0 Hz, 1H; terpyridine), 7.93 (d, J = 8.0 Hz, 2H; terpyridine), 7.76 (d, J = 8.0 Hz, 2H; phenanthroline), 7.73 (d, J = 8.0 Hz, 2H; terpyridine), 7.59 (d, J = 4.0 Hz, 2H; terpyridine), 7.49 (t, J = 8.0 Hz, 2H; terpyridine), 7.06-7.02 (m, 2H; terpyridine), 6.30 (s, 2H; (phenanthroline) mesityl H), 1.97 (s, 6H; (phenanthroline) mesityl *p*-CH$_3$), 1.58 ppm (s, 12H; (phenanthroline) mesityl *o*-CH$_3$); ^{13}C NMR ([D$_2$]Dichloromethane, 25 °C, 100 MHz): δ= 159.2, 153.2, 152.9, 148.1, 144.3, 138.1, 137.8, 137.2, 136.5, 135.3, 128.1, 127.9, 127.0, 126.9, 124.7, 123.1, 121.8, 116.9 (aromatic), 20.9, 20.0 ((phenanthroline) mesityl CH$_3$) ppm; IR (KBr): ν = 2915, 2857, 1610, 1583, 1480, 1446, 1377, 1298 cm^{-1}; ESI-MS: *m/z* (%): 714.3 (100) $[M]^+$: (calcd for $[CuC_{45}H_{39}N_5]^+$: 712.3); elemental analysis calcd (%) for $CuC_{45}H_{39}N_5.1/2CH_2Cl_2$: C 60.57, H 4.48, N 7.77; found: C 60.77, H 4.38, N 7.53.

C2 $[Cu_6(\mathbf{1})_6(\mathbf{4})]^{6+}$: > 300 °C; ^{1}H NMR ([D$_2$]Dichloromethane, 25 °C, 400 MHz): δ= 8.61 (d, J = 8.0 Hz, 12 H; phenanthroline), 8.20 (s, 12H; phenanthroline), 7.91 (s, 12H; terpyridine),

7.78 (d, J = 8.0 Hz, 12H; terpyridine), 7.77 (s, 12H; terpyridine), 7.72 (d, J = 8.0 Hz, 12H; phenanthroline), 7.65 (d, J = 4.0 Hz, 12H; terpyridine), 7.44 (td, J = 8.0, 1.0 Hz, 12H; terpyridine), 7.06 (dd, J = 8.0, 4.0 Hz, 12H; terpyridine), 6.23 (s, 24H; (phenanthroline) mesityl H), 2.28 (s, 36H; (terpyridine) CH_3), 1.85 (s, 36H; (phenanthroline) mesityl *p*-CH_3), 1.54 ppm (s, 72H; (phenanthroline) mesityl *o*-CH_3); ^{13}C NMR ([D_2]Dichloromethane, 25 °C, 100 MHz): δ= 159.1, 153.7, 152.4, 150.7, 148.1, 144.2, 139.7, 138.0, 137.9, 137.4, 137.3, 136.7, 136.1, 135.2, 131.6, 128.2, 127.5, 127.0, 126.9, 125.1, 123.5, 123.5, 121.8 (aromatic), 99.8, 87.9 (ethynyl), 21.0, 20.8, 19.9 (benzyl) ppm; IR (KBr): ν = 2919, 2855, 2376, 2199, 1609, 1582, 1476, 1420 cm^{-1}; ESI-MS: *m/z* (%): 1849.5 (6) $[M]^{3+}$: (calcd for $[Cu_6C_{336}H_{276}N_{30}.3PF_6]^{3+}$: 1850.1); 1350.9 (100) $[M]^{4+}$: (calcd for $[Cu_6C_{336}H_{276}N_{30}.2PF_6]^{4+}$: 1351.4); 1052.0 (91) $[M]^{5+}$: (calcd for $[Cu_6C_{336}H_{276}N_{30}.PF_6]^{5+}$: 1052.0); 1351.4); 852.7 (9) $[M]^{6+}$: (calcd for $[Cu_6C_{336}H_{276}N_{30}]^{6+}$: 852.5); elemental analysis calcd (%) for $Cu_6C_{336}H_{276}N_{30}.6PF_6.4CH_2Cl_2$: C 64.57, H 4.53, N 6.64; found: C 64.28, H 4.41, N 6.36.

C3 $[Cu_6(\mathbf{2})_3(\mathbf{4})]^{6+}$: > 300 °C; ^{1}H NMR ([$D_2$]Dichloromethane + [$D_3$]Acetonitrile (4:1), 25 °C, 400 MHz): δ= 8.65 (d, J = 8.0 Hz, 6H; phenanthroline), 8.63 (s, 6H; phenanthroline), 8.24 (d, J = 9.0 Hz, 6H; phenanthroline), 8.17 (d, J = 8.0 Hz, 6H; phenanthroline), 7.96 (s, 12H; terpyridine), 7.87 (d, J = 8.0 Hz, 12H; terpyridine), 7.83 (s, 12H; terpyridine), 7.75 (d, J = 8.0 Hz, 6H; phenanthroline), 7.61-7.52 (m, 24H; terpyridine), 7.08 (t, J = 4.0 Hz, 12H; terpyridine), 6.50 (s, 12H; phenyl), 6.24 (s, 12H; phenanthroline), 6.15 (s, 12H; phenanthroline), 2.42 (s, 18H; terpyridine CH_3), 2.22 (s, 18H; (terpyridine) CH_3), 1.96 (s, 18H; (phenanthroline) mesityl *p*-CH_3), 1.94 (s, 18H; (phenanthroline) mesityl *p*-CH_3), 1.45 (s, 36H; (phenanthroline) mesityl *o*-CH_3), 1.43 (s, 36H; (phenanthroline) mesityl *o*-CH_3) ppm; ^{13}C NMR ([D_2]Dichloromethane + [D_3]Acetonitrile (4:1), 25 °C, 100 MHz): δ= 161.0, 159.4, 153.1, 152.0, 150.3, 147.8, 143.9, 142.4, 139.9, 137.6, 137.5, 137.3, 137.2, 137.1, 136.7, 136.5, 136.3, 136.0, 135.3, 134.9, 131.4, 131.3, 131.1, 128.4, 127.8, 127.6, 127.6, 127.2, 127.0, 126.8, 126.4, 125.0, 123.1, 123.0, 122.5, 121.9, 121.8 (aromatic), 99.6, 96.8, 88.8, 87.6 (ethynyl), 21.0, 20.7, 20.6, 20.4, 19.4, 19.1 (benzyl) ppm; IR (KBr): ν = 2920, 2855, 2379, 2201, 1609, 1462, 1401 cm^{-1}; ESI-MS: *m/z* (%): 1972.2 (5) $[M]^{3+}$: (calcd for $[Cu_6C_{366}H_{282}N_{30}.3PF_6]^{3+}$: 1972.2); 1442.9 (69) $[M]^{4+}$: (calcd for $[Cu_6C_{366}H_{282}N_{30}.2PF_6]^{4+}$: 1442.9); 1125.2 (100) $[M]^{5+}$: (calcd for $[Cu_6C_{366}H_{282}N_{30}.PF_6]^{5+}$: 1125.3); 913.5 (18) $[M]^{6+}$: (calcd for $[Cu_6C_{366}H_{282}N_{30}]^{6+}$: 913.5); elemental analysis calcd (%) for $Cu_6C_{366}H_{282}N_{30}.6PF_6.4CH_2Cl_2$: C 66.42, H 4.37, N 6.28; found: C 66.62, H 4.36, N 6.12.

Figure S1. ^{1}H NMR Spectrum of **5** ([D]Chloroform, 25 °C, 400 MHz)

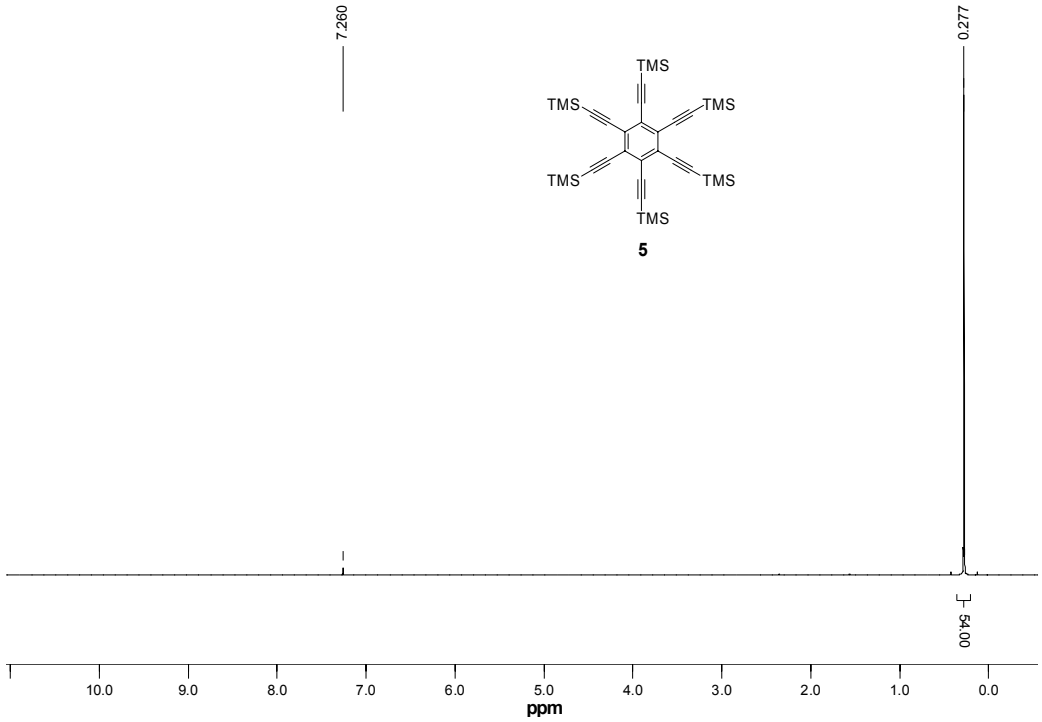


Figure S2. ^{13}C NMR Spectrum of **5** ([D]Chloroform, 25 °C, 100 MHz)

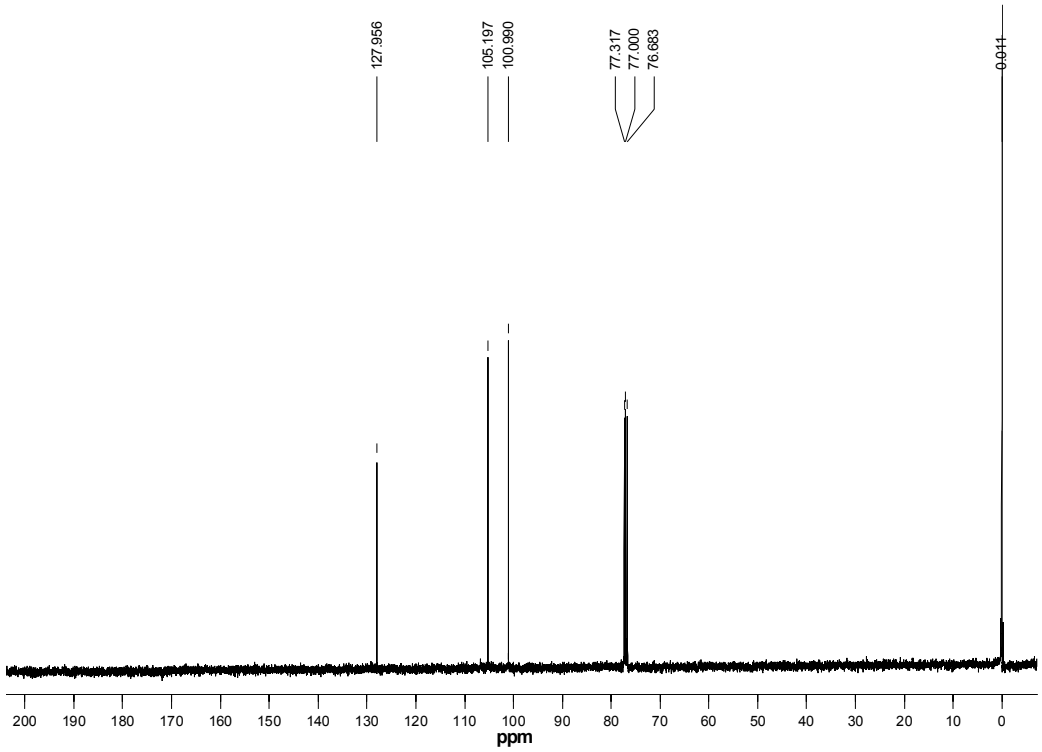


Figure S3. ^{1}H NMR Spectrum of **6** ([D_6]Dimethylsulfoxide, 25 °C, 400 MHz).

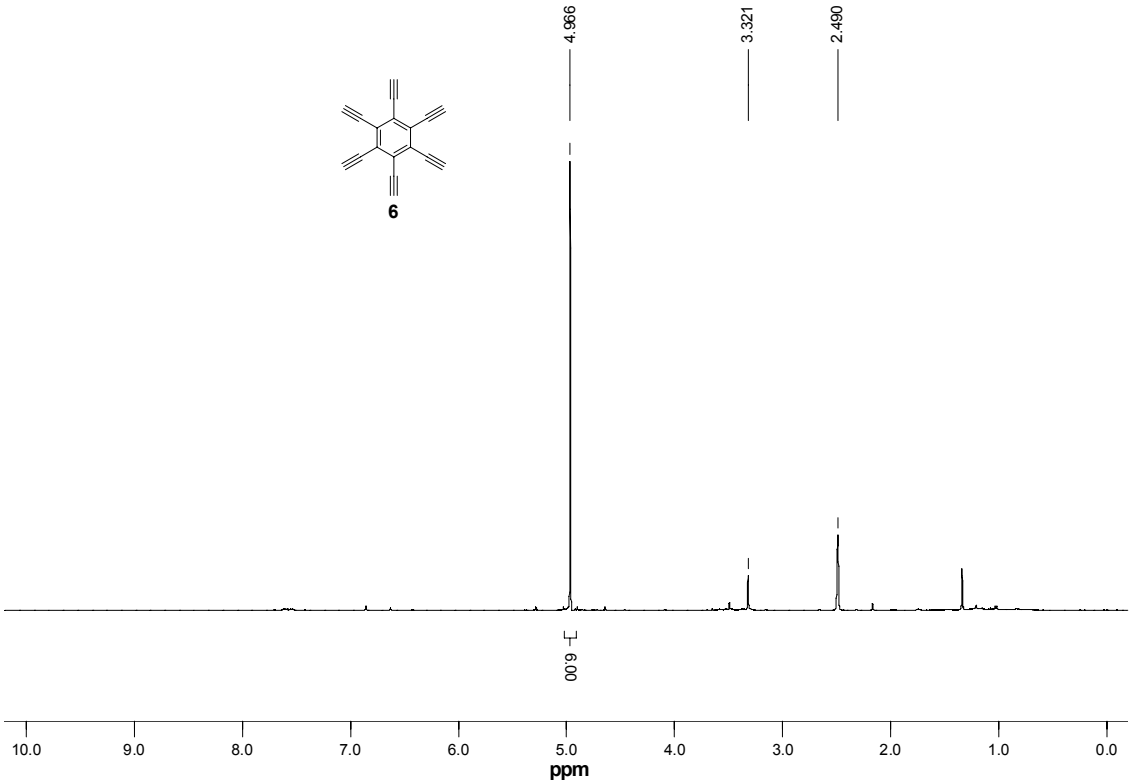


Figure S4. ^{13}C NMR Spectrum of **6** ([D_6]Dimethylsulfoxide, 25 °C, 100 MHz).

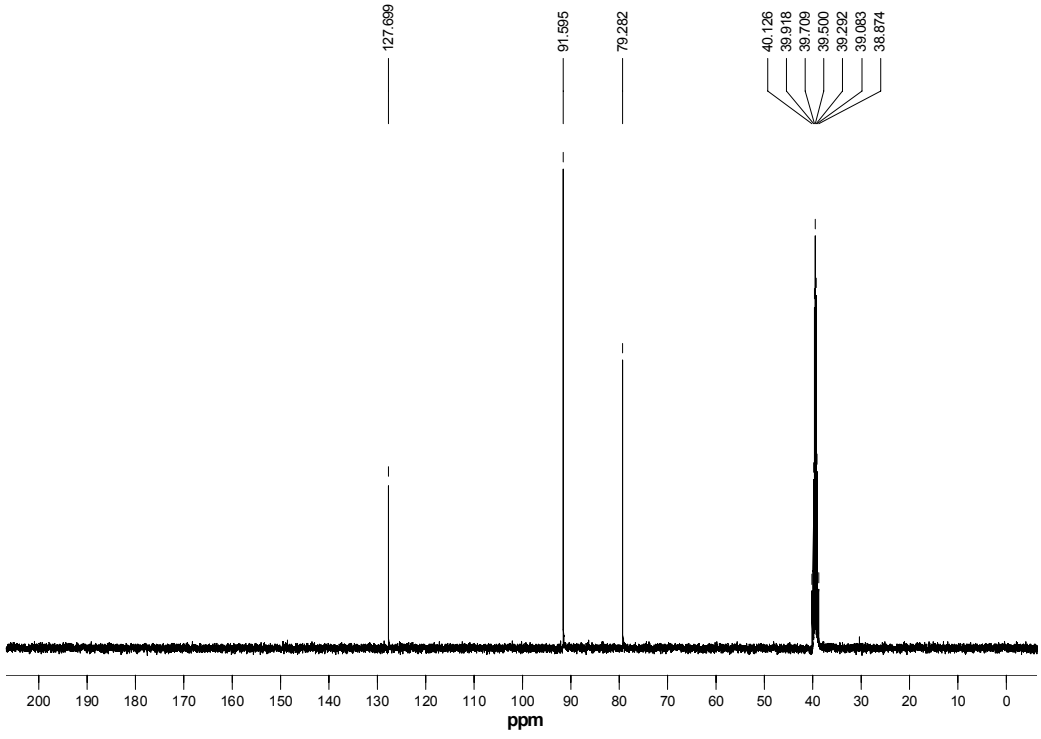


Figure S5. ^{1}H NMR Spectrum of **4** ([D_2]Dichloromethane, 25 °C, 400 MHz).

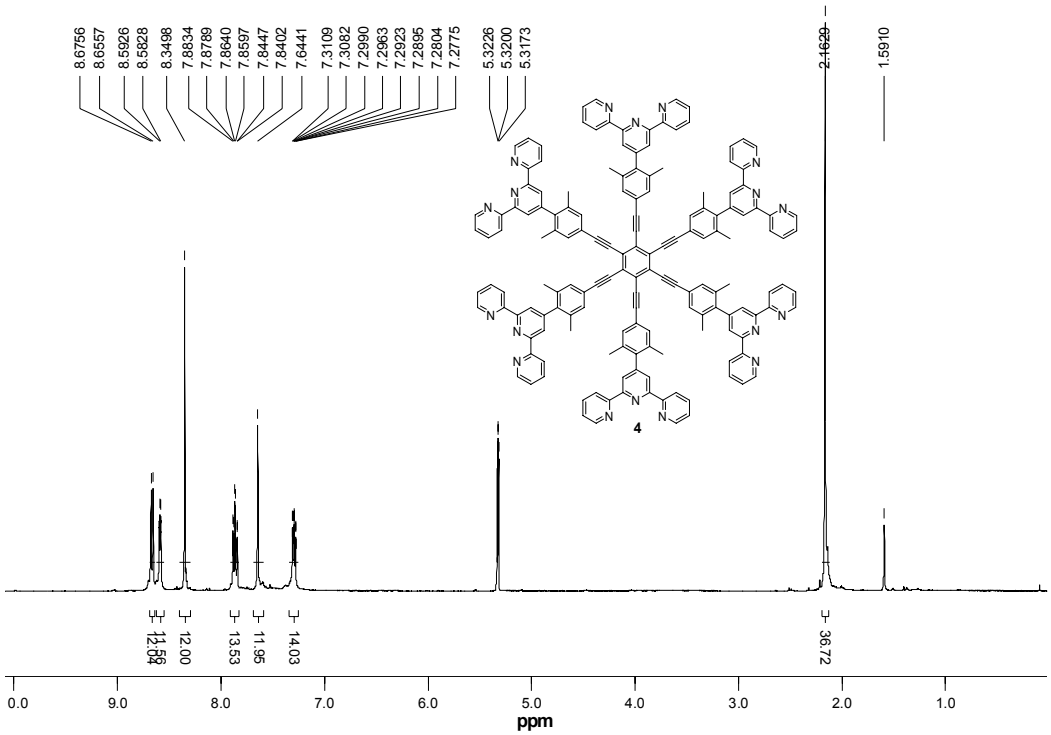


Figure S6. ^{13}C NMR Spectrum of **4** ([D_2]Dichloromethane, 25 °C, 100 MHz).

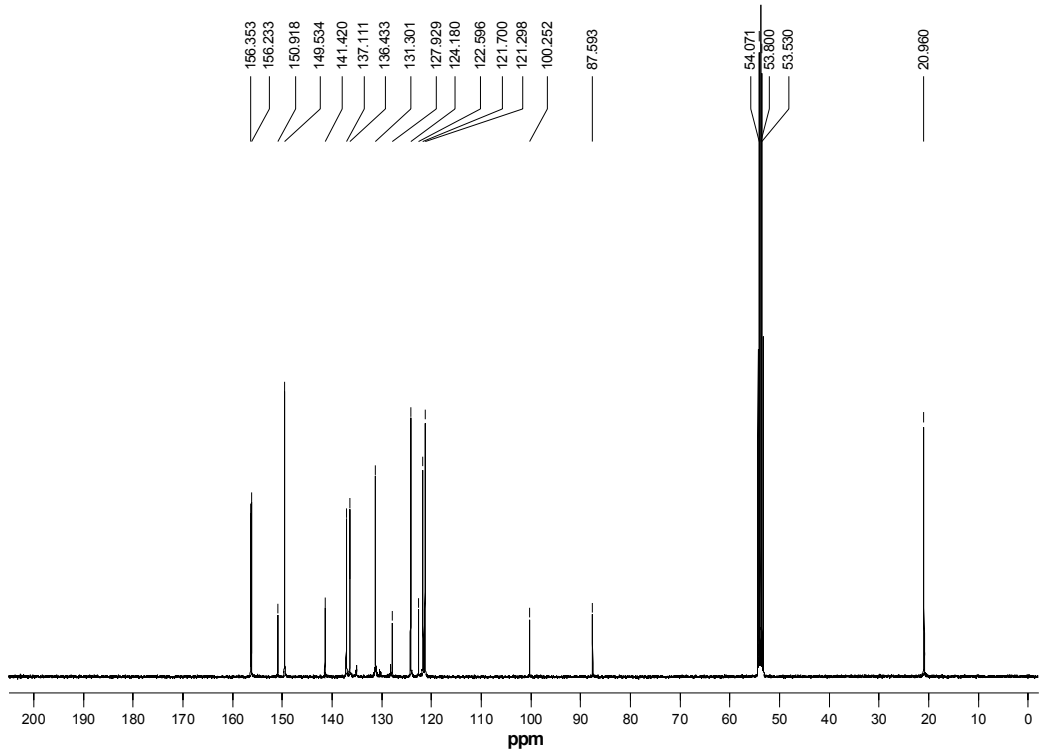


Figure S7. ^{1}H NMR Spectrum of **C1** $[Cu_6(\mathbf{1})(\mathbf{3})(PF_6)]$ ($[D_2]$Dichloromethane, 25 °C, 400 MHz).

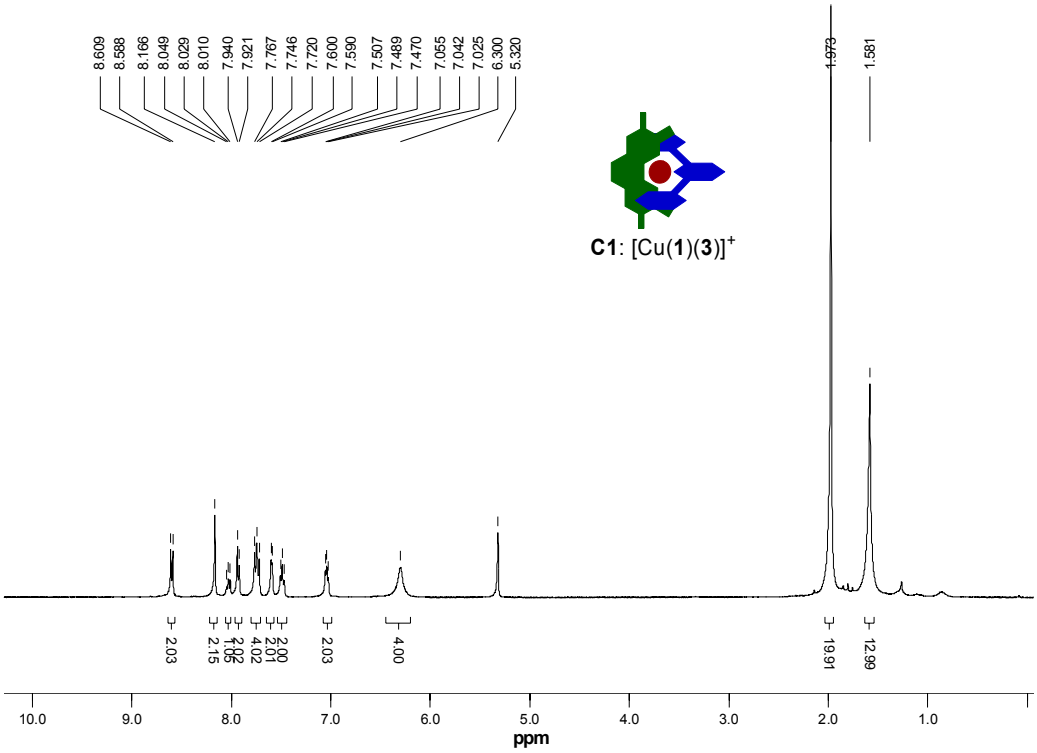


Figure S8. ^{13}C NMR Spectrum of **C1** $[Cu_6(\mathbf{1})(\mathbf{3})(PF_6)]$ ($[D_2]$Dichloromethane, 25 °C, 100 MHz, (*) acetone impurity).

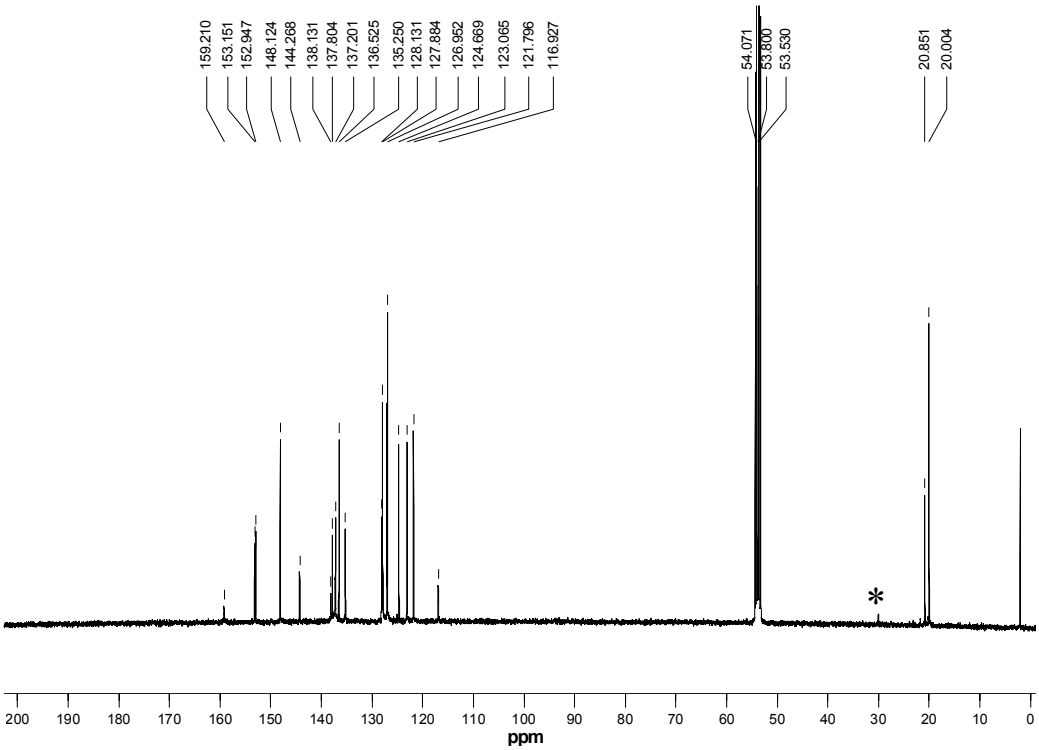


Figure S9. ^{1}H NMR Spectrum of **C2** $[Cu_6(\mathbf{1})_6(\mathbf{4})(PF_6)_6]$ ([D_2]Dichloromethane, 25 °C, 400 MHz).

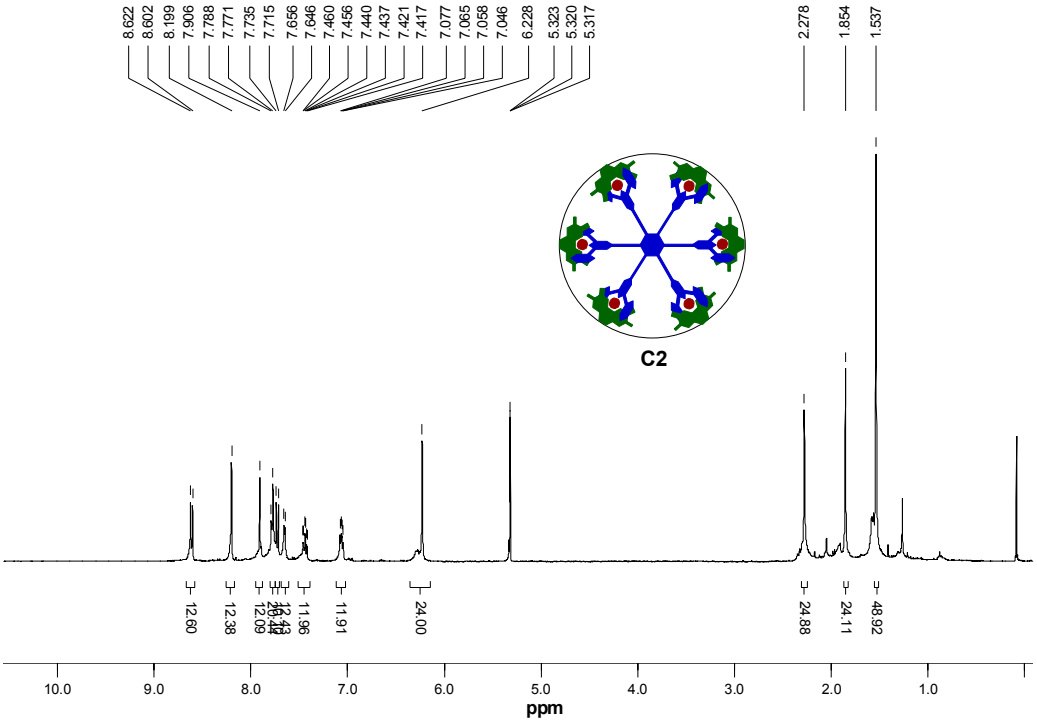


Figure S10. ^{13}C NMR Spectrum of **C2** $[Cu_6(\mathbf{1})_6(\mathbf{4})(PF_6)_6]$ ([D_2]Dichloromethane, 25 °C, 100 MHz, (*) acetone impurity).

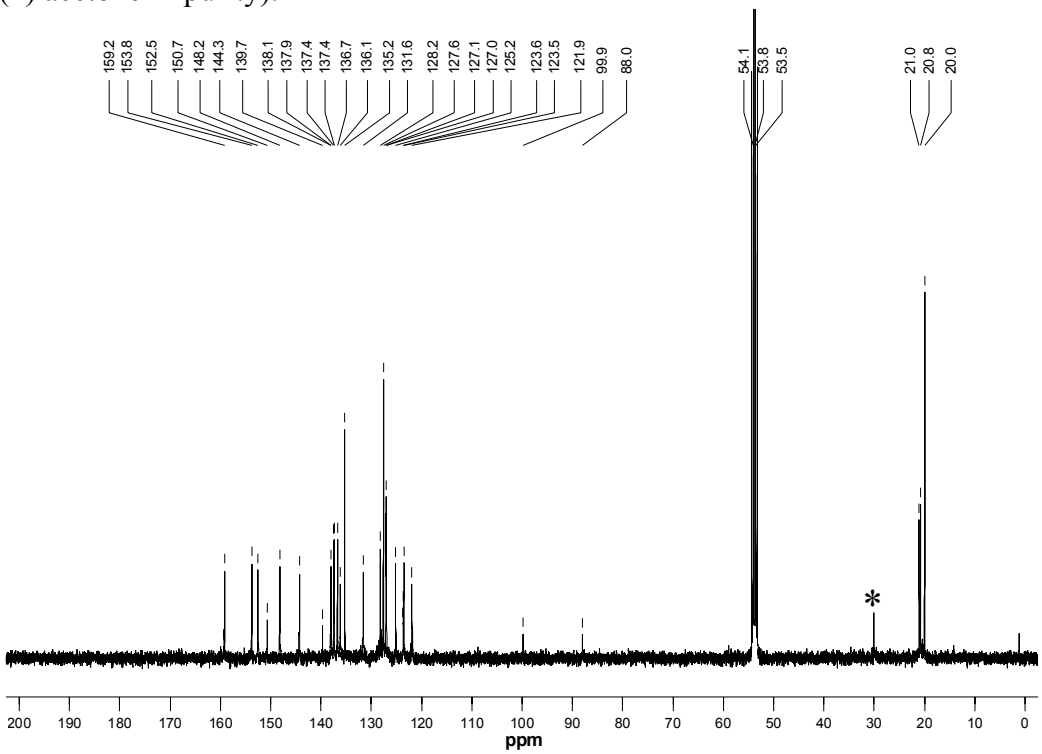


Figure S11. ^{1}H NMR Spectrum of **C3** $[Cu_6(\mathbf{2})_3(\mathbf{4})(PF_6)_6]$ ($[D_2]$Dichloromethane + $[D_3]$Acetonitrile (4:1) 25 °C, 400 MHz).

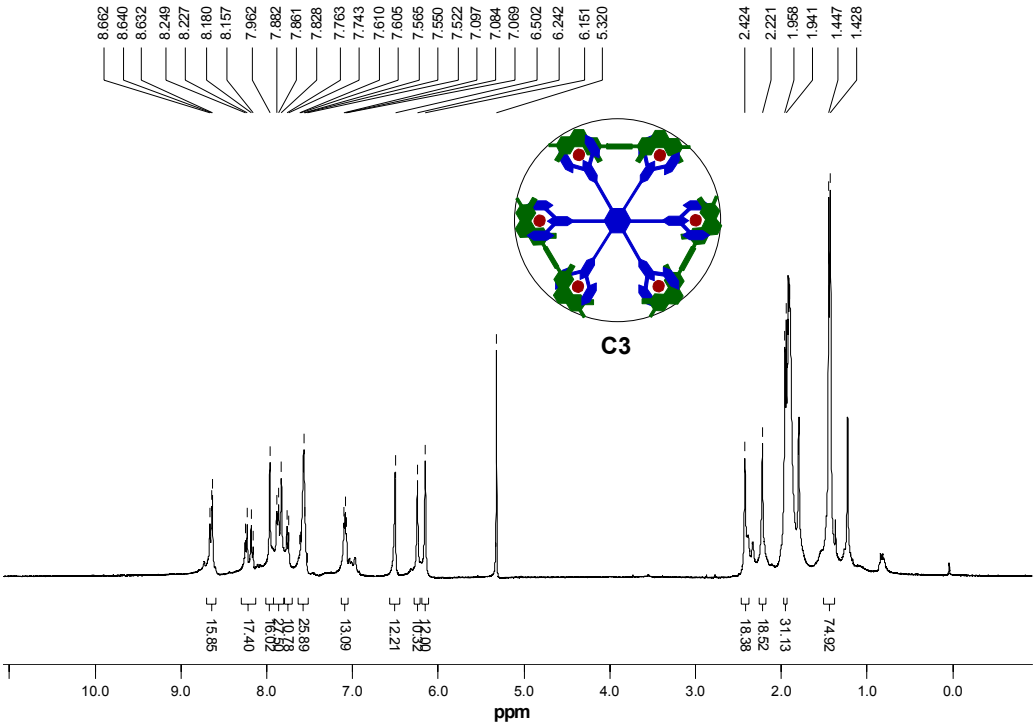


Figure S12. ^{13}C NMR Spectrum of **C3** $[Cu_6(\mathbf{2})_3(\mathbf{4})(PF_6)_6]$ ($[D_2]$Dichloromethane + $[D_3]$Acetonitrile (4:1) 25 °C, 100 MHz, (*) acetone impurity).

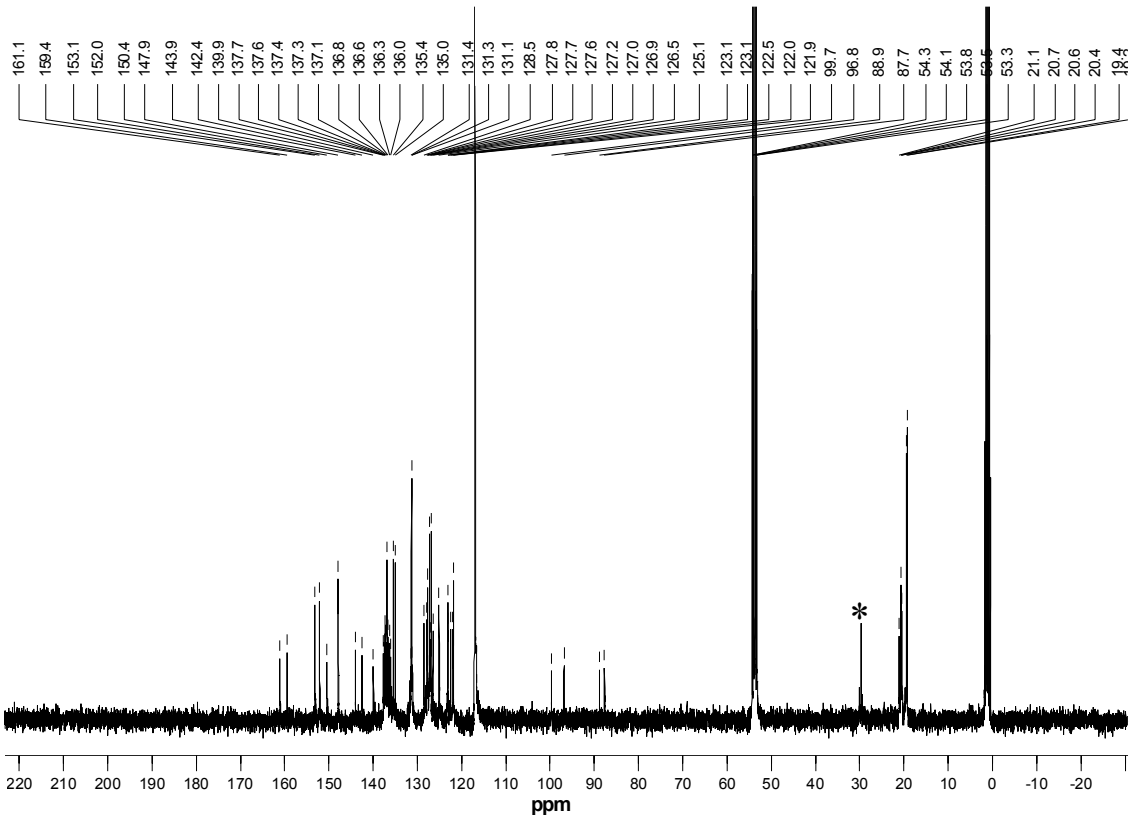


Figure S13. ESI-MS spectrum of **4** and the experimental isotopic distribution (black lines) for the 3+ (746.4) and 2+ (1119.1) charged species along with its calculated one (red lines). Inset shows the spectrum at high capilary voltage and low tube lense offset.

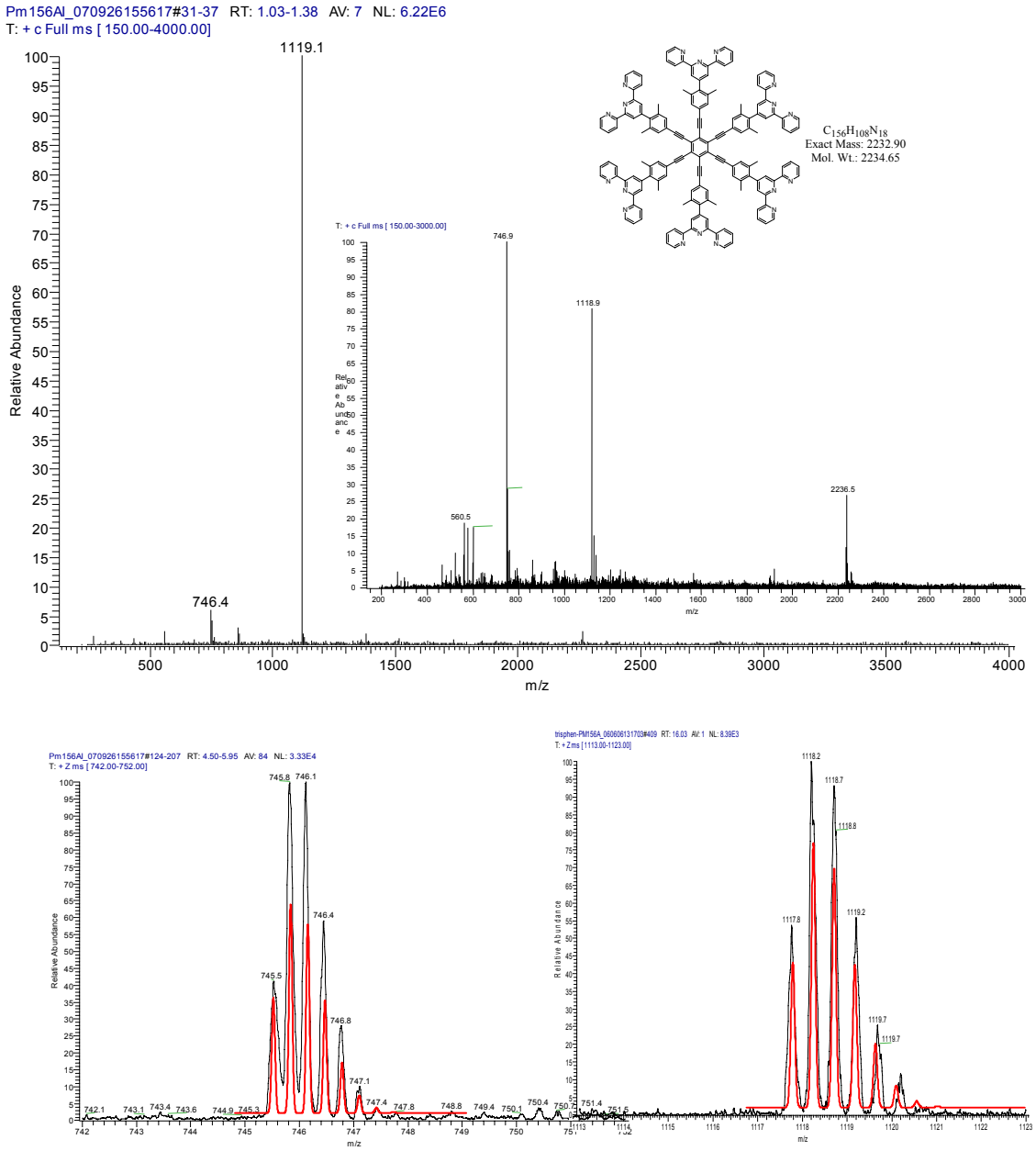


Figure S14. ESI-MS spectra of **C1** and the experimental isotopic distribution (black lines) for the 1+ charged species along with its calculated one (red lines).

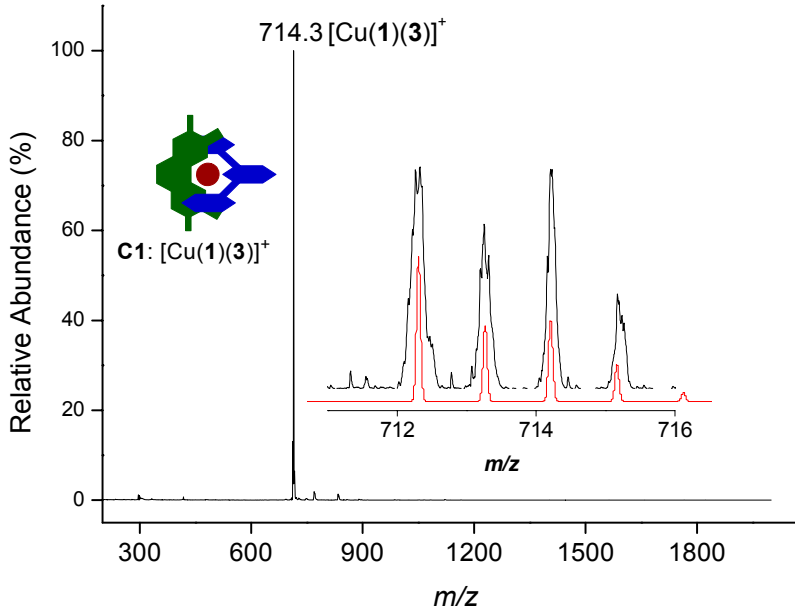


Figure S15. ESI-MS spectra of **C2** and the experimental isotopic distribution (black lines) for the 5+, 4+ and 3+ charged species along with its calculated one (red lines).

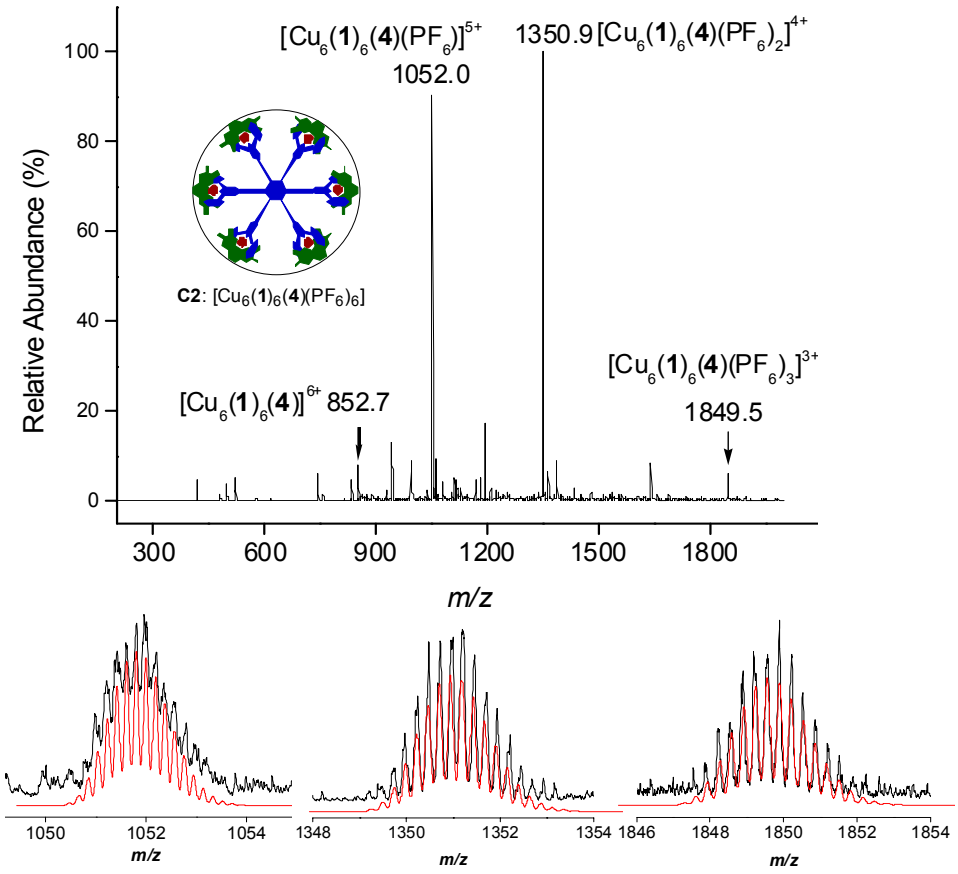


Figure S16. ESI-MS spectra of **C3** and the experimental isotopic distribution (black lines) for the 5+, 4+ and 3+ charged species along with its calculated one (red lines).