

Supporting Information

for

Scaffolding a cage-like 3D framework by coordination and constitutional dynamic chemistry

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Abbreviations used:

DCM: dichloromethane

THF: Tetrahydrofuran

DMSO: Dimethyl sulfoxide

TBAF: Tetrabutylammonium fluoride

Synthesis

General

All commercial reagents were used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use. Silica gel (60-230 mesh) was used for column chromatography. ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 MHz, whereas DOSY NMR was recorded on a Varian VNMR-S 600 MHz spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, br = broad and m = multiplet. The numbering of carbon atoms in the molecular formulae is only used for assignment of NMR signals and thus is not necessarily in accordance with IUPAC nomenclature rules. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Melting points were measured on a Büchi SMP-20 instrument. Infrared spectra were recorded using a Varian 1000 FT-IR instrument. Elemental analysis measurements were done using the EA 3000 CHNS. The numbering of the compounds follows the scheme in the publication. Compounds **10**,¹ **18**,² (precursors for **6** and **8**, respectively) and ligand **5**³ were synthesized according to known procedures. Energy minimized structures were obtained using the MM⁺ forced field as implemented in Hyperchem[®] 8.0.

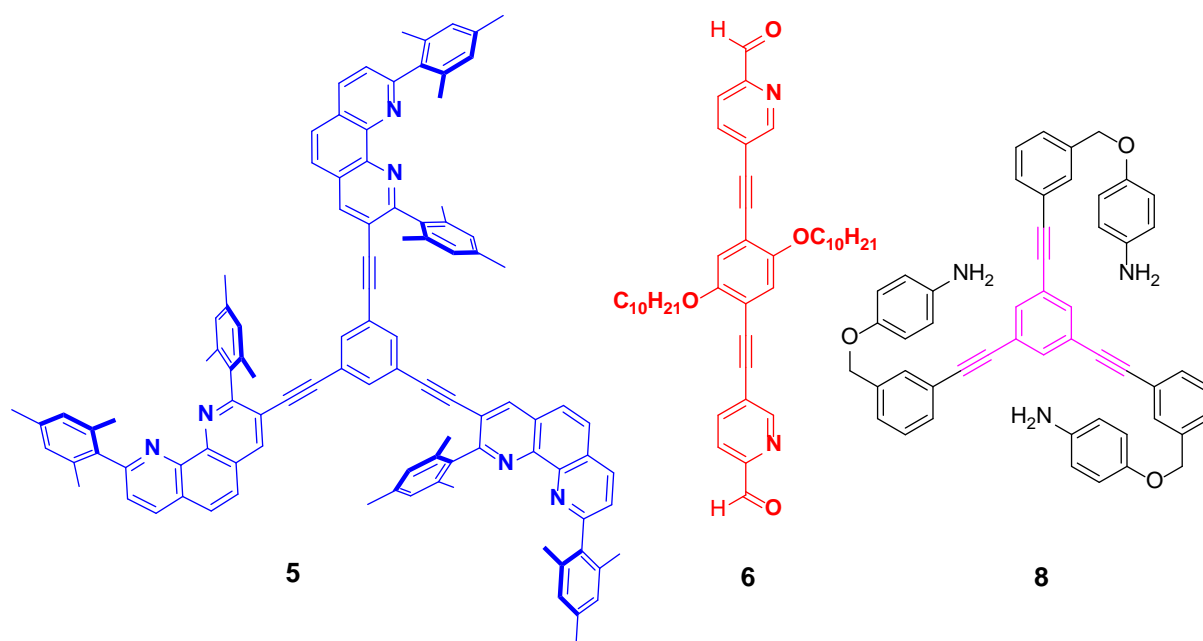
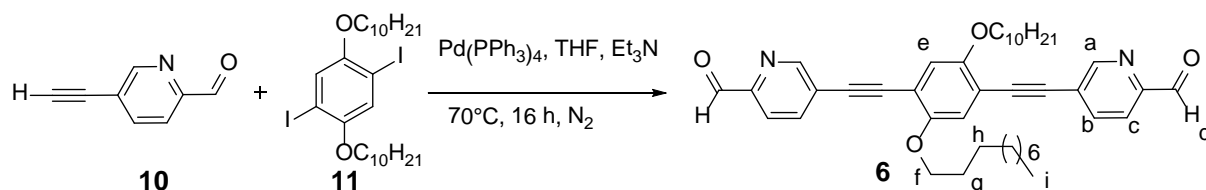


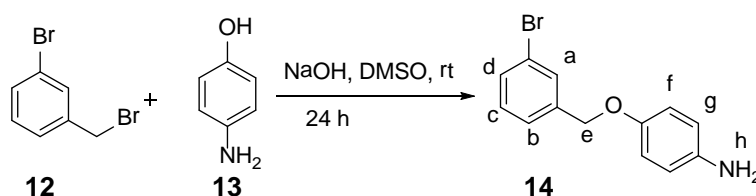
Chart 1. Ligands used in present study.

Synthesis of 5,5'-(2,5-bis(decyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)dipicolinaldehyde (**6**).



In an oven-dried 250-mL three-neck round-bottom flask, a mixture of 5-ethynylpicolinaldehyde (**10**, 202 mg, 1.54 mmol), 1,4-bis(decyloxy)-2,5-diiodobenzene (**11**, 495 mg, 0.77 mmol) and Pd(PPh₃)₄ (35.6 mg, 30.8 μmol) were stirred in dry THF (80 mL) and NEt₃ (20 mL) at 70 °C for 16 h under nitrogen. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in DCM and washed with water (200 mL). After drying over Na₂SO₄, the solvent was evaporated to furnish the crude product. The desired compound was obtained as a yellow solid after purification using column chromatography (SiO₂, CH₂Cl₂:MeOH = 100:1, *R_f* = 0.35 [DCM]). Yield 60%; mp 114 °C; ¹H NMR (400 MHz, CDCl₃): δ = 10.09 (s, 2 H, d-H), 8.90 (s, 2 H, a-H), 7.96 (m, 4 H, [b, c]-H), 7.06 (s, 2 H, e-H), 4.06 (t, ³*J* = 6.4 Hz, 4 H, f-H), 1.90-1.83 (m, 4 H, g-H), 1.58-1.50 (m, 4 H, h-H), 1.42-1.24 (m, 24 H, -(CH₂)₆-), 0.86 (t, ³*J* = 6.8 Hz, 6 H, i-H); ¹³C NMR (100 MHz, CDCl₃): δ = 192.5, 153.9, 152.4, 150.9, 139.2, 124.9, 121.0, 116.7, 113.7, 92.8, 91.3, 69.6, 31.9, 29.6, 29.5, 29.3, 29.3, 29.2, 26.0, 22.7, 14.1; IR (KBr) ν 2917, 2850, 2360, 2207, 1705, 1576, 1505, 1471, 1418, 1393, 1360, 1290, 1220, 1207, 1117, 1049, 1020, 925, 889, 842, 766, 733, 721; ESI-MS: *m/z* (%) 649.7 (100) [M+H]⁺; Anal calcd for C₄₂H₅₂N₂O₄: C, 77.74; H, 8.08; N, 4.32; found: C, 77.94; H, 8.23; N, 4.61.

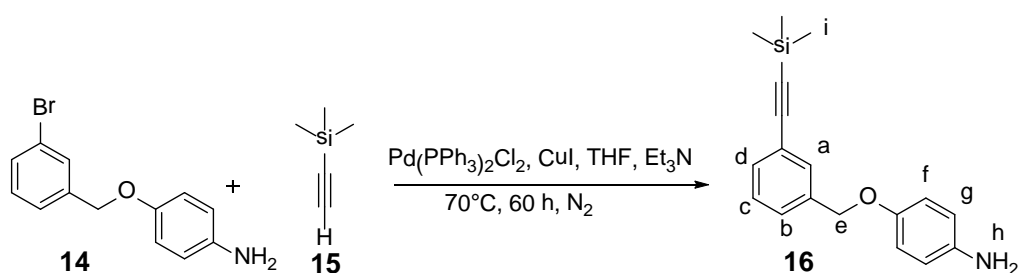
Synthesis of 4-(3-bromobenzyloxy)aniline (**14**).



In a 100-mL single-neck round-bottom flask, 1-bromo-3-(bromomethyl)benzene (**12**, 2.50 g, 10.0 mmol), NaOH (800 mg, 20.0 mmol), 4-aminophenol (**13**, 2.18 g, 20.0 mmol) were stirred in DMSO (30 mL) at room temperature for 24 h. The solvent was distilled off and the residue was washed by water (200 mL). The product was then extracted by DCM (3 × 100 mL). The crude compound was purified by column chromatography (SiO₂, CH₂Cl₂:MeOH =

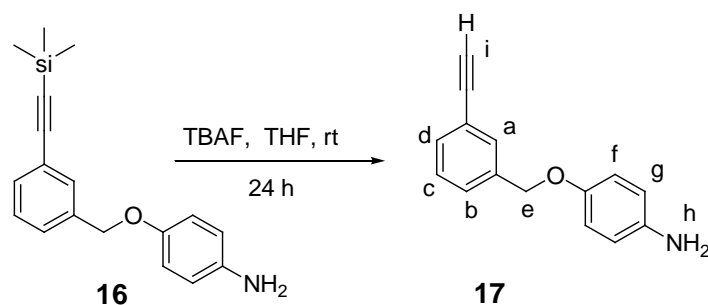
100:1, R_f = 0.26 [DCM]) to afford an off-white solid. Yield 39%; mp 52-54 °C; ^1H NMR (400 MHz, CDCl_3): δ = 7.59 (s, 1 H, a-H), 7.44 (d, 3J = 7.6 Hz, 1 H, [b/d]-H), 7.34 (d, 3J = 8.0 Hz, 1 H, [b/d]-H), 7.24 (dd, 3J = 8.0 Hz, 3J = 7.6 Hz, 1 H, c-H), 6.80 (d, 3J = 8.8 Hz, 2 H, f-H), 6.64 (d, 3J = 8.8 Hz, 2 H, g-H), 4.95 (s, 2H, e-H), 3.41 (br, 2H, h-H); ^{13}C NMR (100 MHz, CDCl_3): δ = 151.6, 140.4, 139.8, 130.8, 130.3, 130.0, 125.8, 122.5, 116.3, 116.0, 69.8; IR (KBr) ν 3305, 2910, 2360, 1589, 1572, 1507, 1467, 1425, 1370, 1294, 1235, 1169, 1096, 1070, 1014, 892, 866, 812, 792, 764, 690, 669; Anal calcd for $\text{C}_{13}\text{H}_{12}\text{BrNO} \cdot \frac{1}{3}\text{H}_2\text{O}$: C, 54.95; H, 4.49; N, 4.93; found: C, 54.98; H, 4.10; N, 5.18.

Synthesis of 4-(3-((trimethylsilyl)ethynyl)benzyloxy)aniline (**16**).



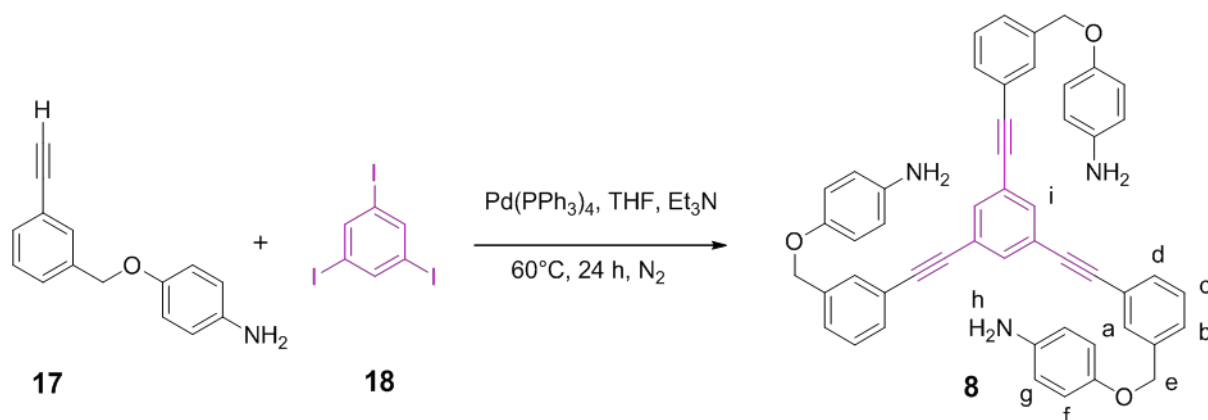
4-(3-Bromobenzyloxy)aniline (**14**, 1.60 g, 5.75 mmol), ethynyltrimethylsilane (**15**, 1.13 g, 11.5 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (404 mg, 575 μmol), CuI (110 mg, 575 μmol), dry and degassed THF (30 mL) and NEt_3 (20 mL) were stirred in a Schlenk tube at 70°C for 60 h under nitrogen. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was purified by (SiO_2 , CH_2Cl_2 , R_f = 0.20 [DCM]) furnishing the target as a brown solid. Yield 48%; mp 42°C ; ^1H NMR (400 MHz, CDCl_3): δ = 7.54 (s, 1 H, a-H), 7.41 (d, 3J = 7.6 Hz, 1 H, [b/d]-H), 7.36 (d, 3J = 8.0 Hz, 1 H, [b/d]-H), 7.30 (dd, 3J = 8.0 Hz, 3J = 7.6 Hz, 1 H, c-H), 6.80 (d, 3J = 8.8 Hz, 2 H, f-H), 6.64 (d, 3J = 8.8 Hz, 2 H, g-H), 4.95 (s, 2H, e-H), 3.44 (br, 2H, h-H), 0.26 (s, 9 H, i-H); ^{13}C NMR (100 MHz, CDCl_3): δ = 151.8, 140.3, 137.7, 131.3, 130.8, 128.4, 127.4, 123.3, 116.3, 116.0, 104.9, 94.3, 70.2, -0.1; IR (KBr) ν 3404, 2957, 2360, 2145, 1603, 1509, 1480, 1456, 1361, 1300, 1236, 1175, 1055, 920, 838, 823, 784, 754, 687; Anal calcd for $\text{C}_{18}\text{H}_{21}\text{NOSi}$: C, 73.17; H, 7.16; N, 4.74; found: C, 72.99; H, 7.19; N, 4.78.

Synthesis of 4-(3-ethynylbenzyloxy)aniline (**17**).



In an oven-dried 100-mL single-neck round-bottom flask, TBAF·3H₂O (1.17 g, 3.71 mmol) and 4-(3-((trimethylsilyl)ethynyl)benzyloxy)aniline (**16**, 1.00 g, 3.38 mmol) were stirred in THF (80 mL), at room temperature for 24 h. After removal of THF the residue was dissolved in DCM and washed several times with water. The solvent was removed under reduced pressure and the residue was purified by chromatography (SiO₂, CH₂Cl₂, *R_f* = 0.13 [DCM]) to give the product as a brown solid. Yield 85%; mp 68 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.56 (s, 1 H, a-H), 7.44 (d, ³*J* = 7.6 Hz, 1 H, [b/d]-H), 7.41 (d, ³*J* = 7.6 Hz, 1 H, [b/d]-H), 7.33 (dd, ³*J* = 7.6 Hz, ³*J* = 7.6 Hz, 1 H, c-H), 6.80 (d, ³*J* = 8.8 Hz, 2 H, f-H), 6.64 (d, ³*J* = 8.8 Hz, 2 H, g-H), 4.96 (s, 2H, e-H), 3.44 (br, 2H, h-H), 3.08 (s, 1 H, i-H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.7, 140.3, 137.8, 131.5, 131.0, 128.5, 127.8, 122.3, 116.3, 116.0, 83.5, 77.3, 70.1; IR (KBr) ν 3414, 3342, 3194, 2914, 2360, 1609, 1584, 1481, 1468, 1428, 1379, 1330, 1294, 1229, 1172, 1127, 1092, 1023, 914, 883, 851, 827, 799, 778, 714, 680; Anal calcd for C₁₅H₁₃NO·½H₂O: C, 78.58; H, 6.01; N, 6.11; found: C, 78.37; H, 5.65; N, 6.42.

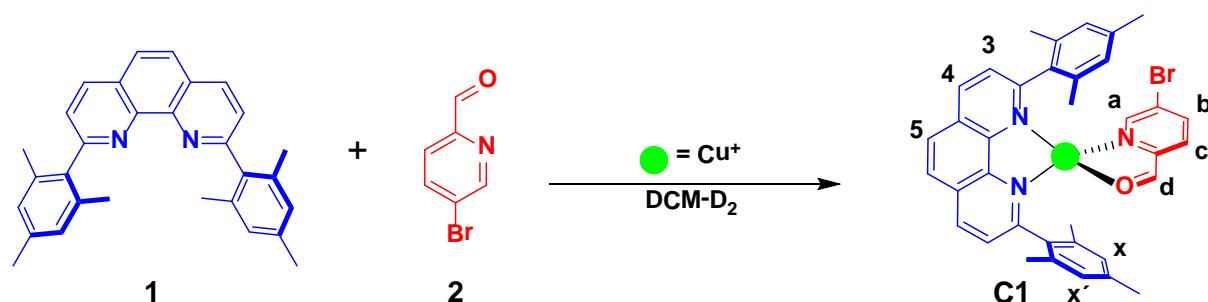
Synthesis of 4,4',4''-(3,3',3''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(benzene-3,1-diyl))tris(methylene)tris(oxy)trianiline (**8**).



In an oven-dried 250-mL three-neck round-bottom flask, a mixture of 1,3,5-triiodobenzene (**18**, 455 mg, 1.00 mmol), 4-(3-ethynylbenzyloxy)aniline (**17**, 737 mg, 3.30 mmol), Pd(PPh₃)₄ (185 mg, 0.16 mmol) were stirred in dry and degassed THF (40 mL) and NEt₃ (20 mL) at

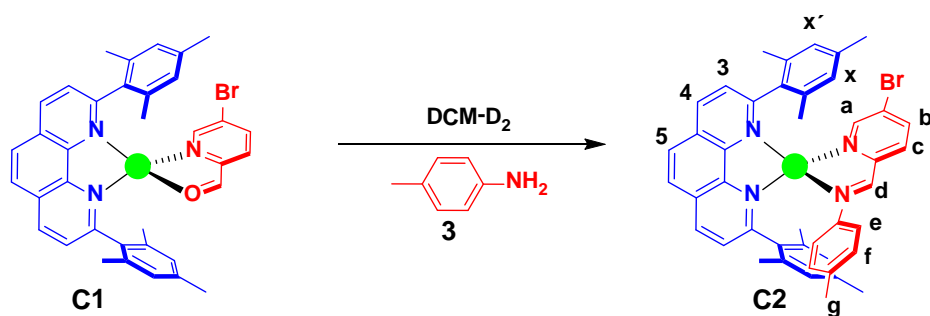
60°C for 24 h under nitrogen. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was purified by chromatography (SiO₂, CH₂Cl₂:CH₃OH = 100:1, *R_f* = 0.35 [DCM/MeOH = 20:1]) to afford **8** as a brown solid. Yield 51%; mp 70 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.67 (s, 3 H, i-H), 7.63 (s, 3 H, a-H), 7.51 (d, ³*J* = 7.6 Hz, 3 H, [b/d]-H), 7.44 (d, ³*J* = 7.6 Hz, 3 H, [b/d]-H), 7.39 (dd, ³*J* = 7.6 Hz, ³*J* = 7.6 Hz, 3 H, c-H), 6.80 (d, ³*J* = 8.8 Hz, 6 H, f-H), 6.63 (d, ³*J* = 8.8 Hz, 6 H, g-H), 5.00 (s, 6H, e-H), 3.48 (br, 6H, h-H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.8, 140.3, 138.0, 134.1, 131.0, 130.5, 128.6, 127.6, 124.0, 123.0, 116.4, 116.1, 90.4, 87.9, 70.2; IR (KBr) ν 3353, 2360, 1602, 1582, 1507, 1433, 1374, 1226, 1121, 1020, 876, 822, 782, 688; ESI-MS: *m/z* (%) 742.4 (100) [M+H]⁺, 371.7 (8) [M+2H]²⁺; Anal calcd for C₅₁H₃₉N₃O₃•0.5CH₃OH: C, 81.61; H, 5.45; N, 5.54; found: C, 81.71; H, 5.38; N, 5.53.

Synthesis of complex C1.



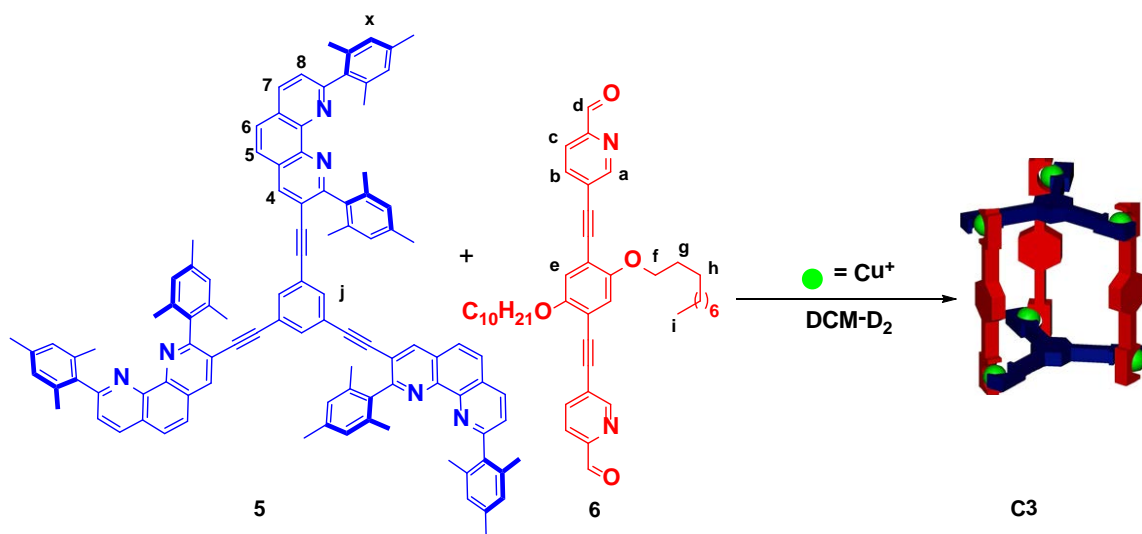
2,9-Dimesityl-1,10-phenanthroline (**1**, 4.46 mg, 10.7 μmol), 5-bromopicolinaldehyde (**2**, 1.99 mg, 10.7 μmol), and [Cu(MeCN)₄]PF₆ (3.99 mg, 10.7 μmol) were loaded in a NMR tube and dissolved in CD₂Cl₂. The resultant mixture was subjected to analytical characterization without any further purification. Yield quantitative; mp 90 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 9.63 (s, 1 H, d-H), 8.69 (d, ³*J* = 8.4 Hz, 2 H, 4-H), 8.33 (s, 1 H, a-H), 8.18 (d, ³*J* = 7.6 Hz, 1 H, b-H), 8.17 (s, 2 H, 5-H), 7.89 (d, ³*J* = 8.4 Hz, 2 H, 3-H), 7.71 (d, ³*J* = 7.6 Hz, 1 H, c-H), 6.71 (s, 4 H, [x, x']-H), 2.14 (s, 6 H, Me), 1.93 (s, 12 H, Me); ¹³C NMR (100 MHz, CDCl₃): δ = 190.4, 160.4, 150.3, 147.9, 144.0, 140.2, 139.1, 139.1, 137.2, 135.7, 128.2 (3C), 128.0, 127.1, 127.0, 21.0, 20.2; IR (KBr) ν 3353, 1670, 1612, 1544, 1479, 1357, 1206, 1145, 1094, 1035, 831; ESI-MS: *m/z* (%) 665.9 (100) [M-PF₆]⁺. Anal calcd for C₃₆H₃₂BrCuF₆N₃OP: C, 53.31; H, 3.98; N, 5.18; found: C, 53.25; H, 4.10; N, 5.20.

Synthesis of complex C2.



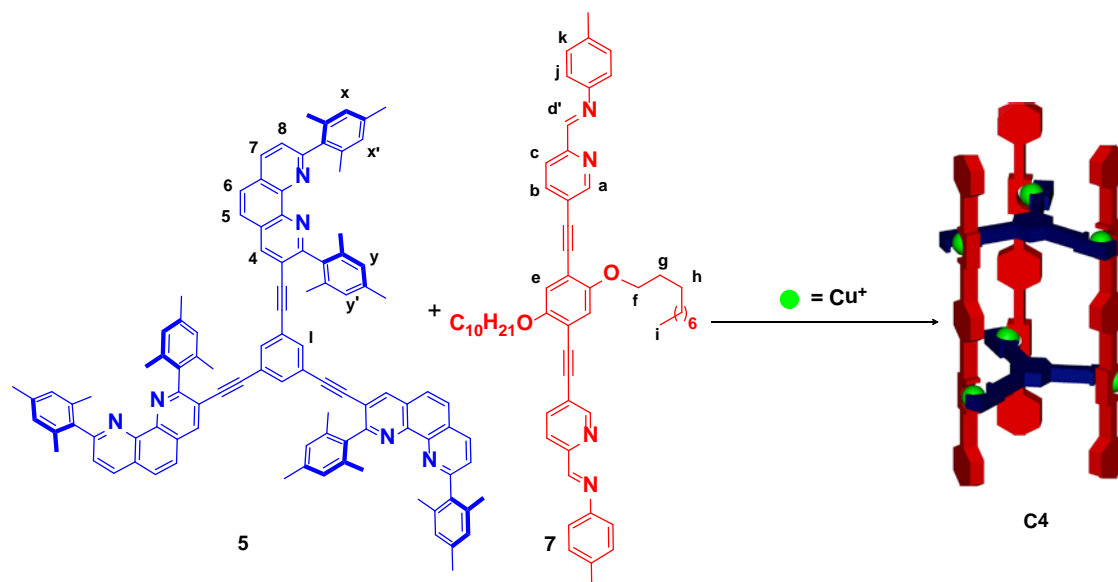
p-Tolylamine (**3**, 1.28 mg, 11.9 μ mol) was added into a NMR tube loaded with a solution of complex **C1** (9.69 mg, 11.9 μ mol) in CD_2Cl_2 , and the mixture was subjected to analytical characterization without any further purification. Yield quantitative; mp 110 $^\circ\text{C}$; ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.69 (d, 3J = 8.0 Hz, 2 H, 4-H), 8.30 (s, 1 H, d-H), 8.25 (d, 4J = 1.6 Hz, 1 H, a-H), 8.21 (s, 2 H, 5-H), 8.09 (dd, 3J = 8.2 Hz, 4J = 1.6 Hz, 1 H, b-H), 7.85 (d, 3J = 8.0 Hz, 2 H, 3-H), 7.41 (d, 3J = 8.2 Hz, 1 H, c-H), 7.01 (d, 3J = 8.4 Hz, 2 H, [e/f]-H), 6.98 (d, 3J = 8.4 Hz, 2 H, [e/f]-H), 6.49 (s, 2 H, [x/x']-H), 6.40 (s, 2 H, [x/x']-H), 2.28 (s, 6 H, g-H), 2.06 (s, 6 H, Me), 1.82 (s, 6 H, Me), 1.48 (s, 6 H, Me); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.8, 152.5, 149.4, 149.3, 144.0, 143.5, 140.6, 139.6, 138.7, 138.1, 137.3, 135.4, 135.1, 130.3, 128.4, 128.1, 127.7, 127.5, 127.2, 127.1, 124.4, 123.1, 21.2, 20.9, 20.3, 19.7; IR (KBr) ν 3353, 1612, 1580, 1506, 1479, 1377, 1094, 1021; ESI-MS m/z (%) 755.1 (100) $[\text{M}-\text{PF}_6]^+$; Anal calcd for $\text{C}_{43}\text{H}_{39}\text{BrCuF}_6\text{N}_4\text{P}\cdot\text{H}_2\text{O}$: C, 56.25; H, 4.50; N, 6.10; found: C, 56.27; H, 4.27; N, 6.20.

Synthesis of nanoprism C3.



Trisphenanthroline (**5**, 6.26 mg, 4.49 μmol), dipicolinaldehyde (**6**, 4.37 mg, 6.74 μmol), and $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (5.02 mg, 13.5 μmol) were loaded in a NMR tube and dissolved in CD_2Cl_2 . The resultant mixture was then analyzed by ESI-MS, ^1H NMR, ^{13}C NMR, IR and elemental analysis without any further purification. Yield quantitative; mp >260 $^\circ\text{C}$; ^1H NMR (400 MHz, CD_2Cl_2): δ = 9.64 (s, 6 H, d-H), 8.78 (s, 6 H, 4-H), 8.70 (d, 3J = 8.4 Hz, 6 H, 7-H), 8.28 (s, 6 H, a-H), 8.22 (d, 3J = 8.8 Hz, 6 H, [5/6]-H), 8.19 (d, 3J = 8.8 Hz, 6 H, [5/6]-H), 8.11 (d, 3J = 8.0 Hz, 6 H, [b/c]-H), 7.91 (d, 3J = 8.4 Hz, 6 H, 8-H), 7.84 (d, 3J = 8.0 Hz, 6 H, [b/c]-H), 7.13 (s, 6H, e-H), 6.71 (s, 6H, j-H), 6.68 (s, 24 H, x-H), 4.06 (t, 3J = 6.4 Hz, 12 H, f-H), 2.15 (s, 18 H, Me), 2.10 (s, 18 H, Me), 1.94 (s, 36 H, Me), 1.92 (s, 36 H, Me), 1.85-1.78 (m, 12 H, g-H), 1.51-1.43 (m, 12 H, h-H), 1.31-1.12 (m, 72 H, $-(\text{CH}_2)_6-$), 0.80 (t, 3J = 6.4 Hz, 18 H, i-H); ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 190.7, 162.1, 160.9, 154.4, 150.9, 147.1, 143.9, 142.8, 140.9, 139.5, 139.3, 139.2, 139.2, 137.3, 136.2, 135.8, 135.7, 135.1, 128.6, 128.2 (2C), 128.1 (2C), 127.9 (2C), 127.3, 126.7, 123.2, 122.2, 117.1, 113.9, 95.1, 94.8, 90.5, 86.8, 69.8, 32.1, 29.8, 29.7, 29.5, 29.5, 26.2, 22.9, 21.1, 21.0, 20.1, 19.7, 14.2; IR (KBr) ν 2923, 2854, 2360, 2208, 1671, 1586, 1558, 1506, 1458, 1206, 1030, 832; ESI-MS: 1849.4 (10) $[\text{M}-3\text{PF}_6]^{3+}$, 1350.9 (100) $[\text{M}-4\text{PF}_6]^{4+}$, 1051.7 (70) $[\text{M}-5\text{PF}_6]^{5+}$; Anal calcd for $\text{C}_{330}\text{H}_{324}\text{Cu}_6\text{F}_{36}\text{N}_{18}\text{O}_{12}\text{P}_6$: C, 66.22; H, 5.46; N, 4.21; found: C, 66.44; H, 5.36; N, 4.22.

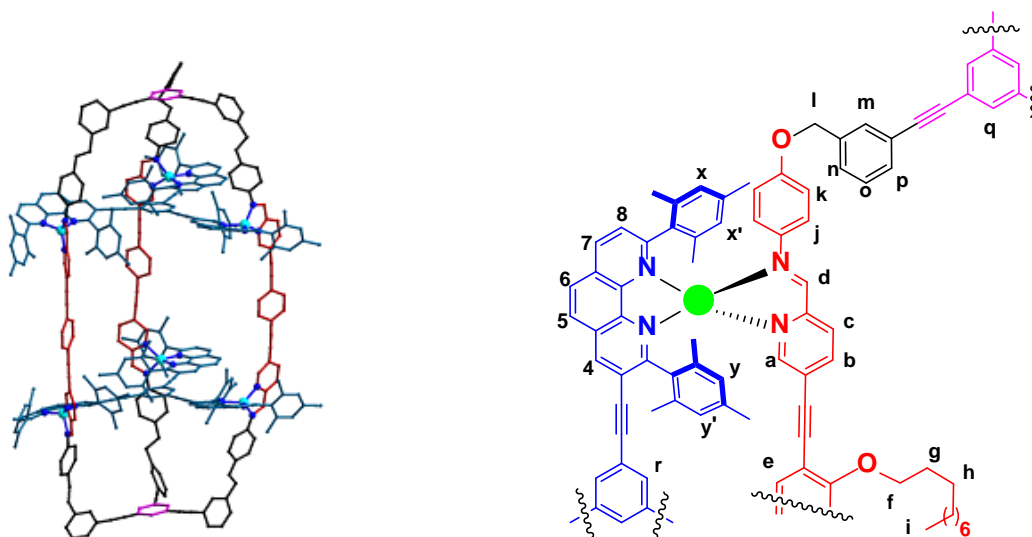
Synthesis of nanoprism C4.



p-Tolylamine (**3**, 1.40 mg, 13.1 μmol) was added into a NMR tube loading with a solution of nanoprism **C3** (13.0 mg, 2.18 μmol) in $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}$ (3:1), and the mixture was placed in a ultrasonic bath at room temperature for 2 h. Yield quantitative; mp > 260 $^\circ\text{C}$; H NMR (400

MHz, CD₂Cl₂:CD₃CN (3:1)): δ = 8.70 (d, 3J = 7.6 Hz, 6 H, 7-H), 8.69-8.61 (br, 6 H, 4-H), 8.33 (s, 6 H, d'-H), 8.27 (d, 3J = 8.8 Hz, 6 H, [5/6]-H), 8.25 (d, 3J = 8.8 Hz, 6 H, [5/6]-H), 8.17 (br, 6 H, a-H), 7.98 (d, 3J = 8.4 Hz, 6 H, [b/c]-H), 7.84 (d, 3J = 7.6 Hz, 6 H, 8-H), 7.50 (d, 3J = 8.4 Hz, 6 H, [b/c]-H), 6.99 (br, 30 H, [k, j, e-H]), 6.61-6.58 (br, 6 H, l]-H), 6.47 (s, 6H, [x/x' or y/y']-H), 6.39 (s, 3H, [x/x' or y/y']-H), 6.30 (s, 9H, [x/x' or y/y']-H), 6.20 (s, 6H, [x/x' or y/y']-H), 3.91 (br s, 12 H, f-H), 2.24 (s, 30 H, Me), 2.11 (s, 18 H, Me), 1.89 (s, 30 H, Me), 1.76 (br, 48 H, Me), 1.50-1.41 (m, 12 H, g-H), 1.31-1.26 (m, 12 H, h-H), 1.10-0.96 (m, 72 H, -(CH₂)₆-), 0.72 (t, 3J = 6.0 Hz, 18 H, i-H); ¹³C NMR (100 MHz, CD₂Cl₂:CD₃CN (3:1)): δ = 161.7, 160.0, 154.0, 153.2, 150.4, 149.2, 143.6, 142.6, 140.3, 138.9, 138.8, 138.8, 138.5, 138.0, 137.2, 136.2, 135.6, 135.2, 134.9, 130.0, 128.7, 128.0 (2C), 127.9, 127.7, 127.6, 127.4 (2C), 126.5, 124.5, 123.1, 122.9, 121.9, 116.7, 113.7, 93.3, 93.2, 90.9, 87.0, 69.4, 31.9, 29.4, 29.3, 29.1, 25.9, 25.8, 22.7, 20.9, 20.6, 20.1, 19.7, 19.5, 19.0, 18.9, 14.0; IR (KBr) ν 2922, 2360, 2341, 1584, 1542, 1507, 1458, 1376, 1217, 1029, 833; ESI-MS: 1485.0 (100) [M-4PF₆]⁴⁺, 1159.0 (24) [M-5PF₆]⁵⁺, 941.7 (12) [M-6PF₆]⁶⁺; Anal calcd for C₃₇₂H₃₆₆Cu₆F₃₆N₂₄O₆P₆•3CH₂Cl₂: C, 66.48; H, 5.53; N, 4.96; found: C, 66.77; H, 5.28; N, 5.03.

Synthesis of cage C5.



In an oven-dried 100-mL round-bottom flask trisphenanthroline (**5**, 3.59 mg, 2.58 μ mol), dipicolinaldehyde (**6**, 2.51 mg, 3.86 μ mol), trianiline (**8**, 1.91 mg, 2.58 μ mol), and [Cu(MeCN)₄]PF₆ (2.88 mg, 7.73 μ mol) were dissolved in acetonitrile/DCM (6:1) and refluxed for 3 days. After obtaining a reddish brown solution from the initial yellow solution, the solvents were evaporated and the solid was subjected to analytical characterization

without any further purification. Yield quantitative; mp >300 °C; ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}$ (1:6)) δ = 8.87 (s, 2 H, 4-H), 8.84 (d, 3J = 8.0 Hz, 4 H, 7-H), 8.74 (d, 3J = 8.0 Hz, 2 H, 7-H), 8.62 (s, 4 H, 4-H), 8.39(d, 3J = 8.8 Hz, 4 H, [5/6]-H), 8.31(d, 3J = 8.8 Hz, 4 H, [5/6]-H), 8.32 (s, 6 H, d-H), 8.23 (d, 3J = 8.6 Hz, 2 H, [5/6]-H), 8.18(d, 3J = 8.6 Hz, 2 H, [5/6]-H), 8.15 (d, 4J = 1.6 Hz, 6 H, a-H), 7.96 (d, 3J = 8.0 Hz, 4 H, 8-H), 7.92 (dd, 3J = 8.4 Hz, 4J = 1.6 Hz, 6 H, b-H), 7.89 (d, 3J = 8.0 Hz, 2 H, 8-H), 7.77 (dd, 3J = 7.6 Hz, 3J = 7.6 Hz, 6 H, o-H), 7.68 (d, 3J = 7.6 Hz, 6 H, [p/n]-H), 7.61 (d, 3J = 7.6 Hz, 3J = 7.6 Hz, 6 H, [p/n]-H), 7.59 (s, 6 H, m-H), 7.49 (d, 3J = 8.4 Hz, 6 H, c-H), 7.11 (d, 3J = 8.8 Hz, 12 H, [j/k]-H), 7.03 (s, 6 H, [e/q/r]-H), 6.93 (s, 6 H, [e/q/r]-H), 6.82 (d, 3J = 8.8 Hz, 12 H, [j/k]-H),), 6.56 (s, 6 H, [x/x' or y/y']-H), 6.22 (s, 6 H, [x/x' or y/y']-H), 6 12(s, 6 H, [x/x' or y/y']-H), 5.91 (s, 6 H, [x/x' or y/y']-H), 5.61 (s, 6 H, [e/q/r]-H), 5.41 (s, 12 H, l-H),), 3.81-3.86 (m, 6H, f-H), 3.73-3.78 (m, 6H, f-H), 2.40(s, 6 H, CH_3), 2.36 (s, 6H, CH_3), 2.04 (s, 12H, CH_3), 2.01 (s, 12H, CH_3), 1.88 (s, 18H, CH_3), 1.87 (s, 18H, CH_3), 1.67 (s, 12H, CH_3), 1.65 (s, 12H, CH_3), 1.47 (s, 12H, CH_3), 1.40-1.45 (m, 12 H, g-H), 1.22-1.27 (m, 12 H, h-H), 0.70-0.88 (m, 72 H, $-(\text{CH}_2)_6-$), 0.51 (t, 3J = 6.8 Hz, 18H, i-H); IR (KBr) ν 2920, 1578, 1502, 1462, 1220, 1164, 1029, 837, 691; ESI-MS: 1694.7 (45) $[\text{M}-4\text{PF}_6]^{4+}$, 1327.2 (100) $[\text{M}-5\text{PF}_6]^{5+}$, 1081.9 (18) $[\text{M}-6\text{PF}_6]^{6+}$; Anal calcd for $\text{C}_{432}\text{H}_{390}\text{Cu}_6\text{F}_{36}\text{N}_{24}\text{O}_{12}\text{P}_6\cdot 3\text{CH}_2\text{Cl}_2$: C, 68.60; H, 5.24; N, 4.41; found: C, 68.87; H, 5.23; N, 4.46.

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

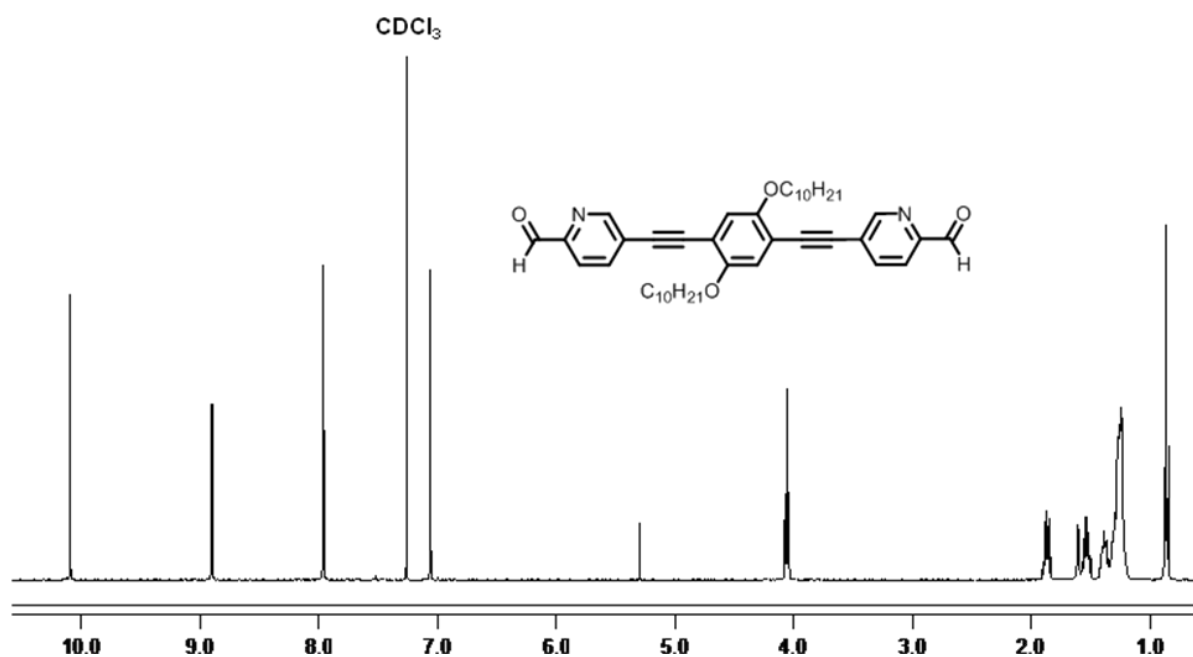


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **6**.

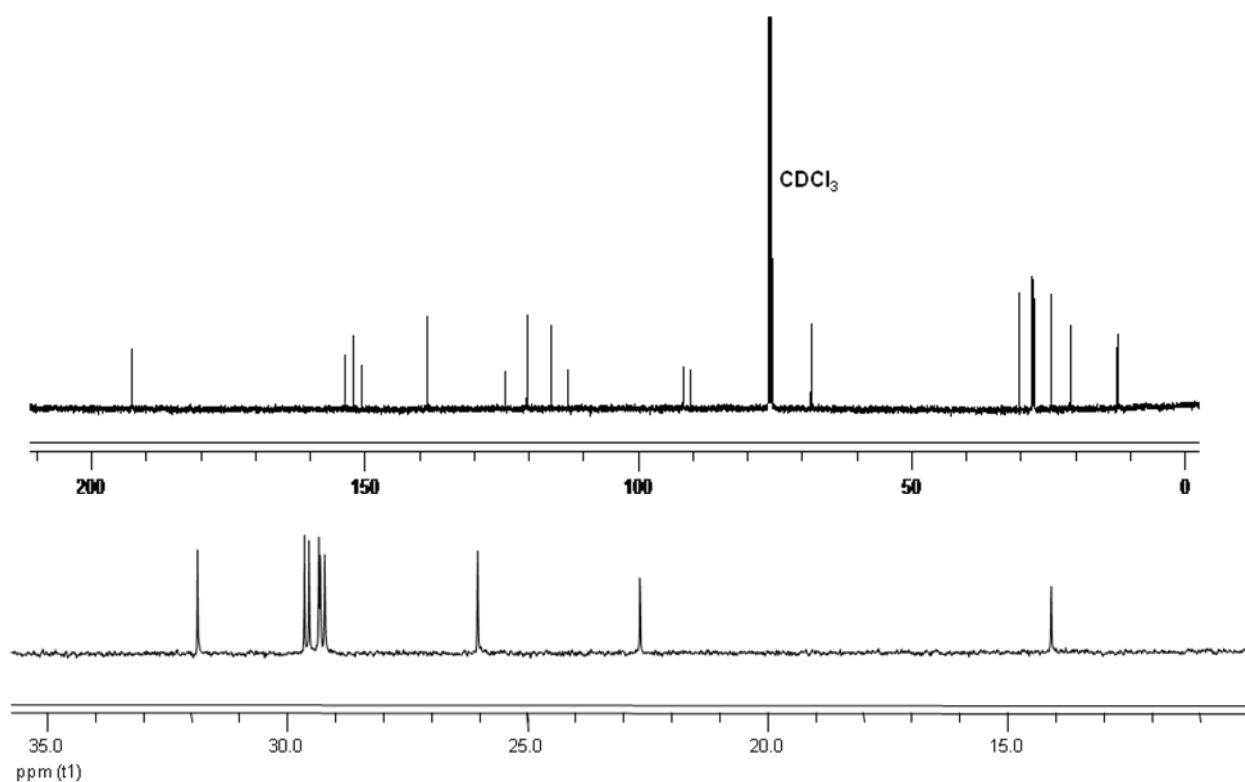


Figure S2. Full ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **6**. An expanded part of the spectrum is shown in the spectrum at bottom.

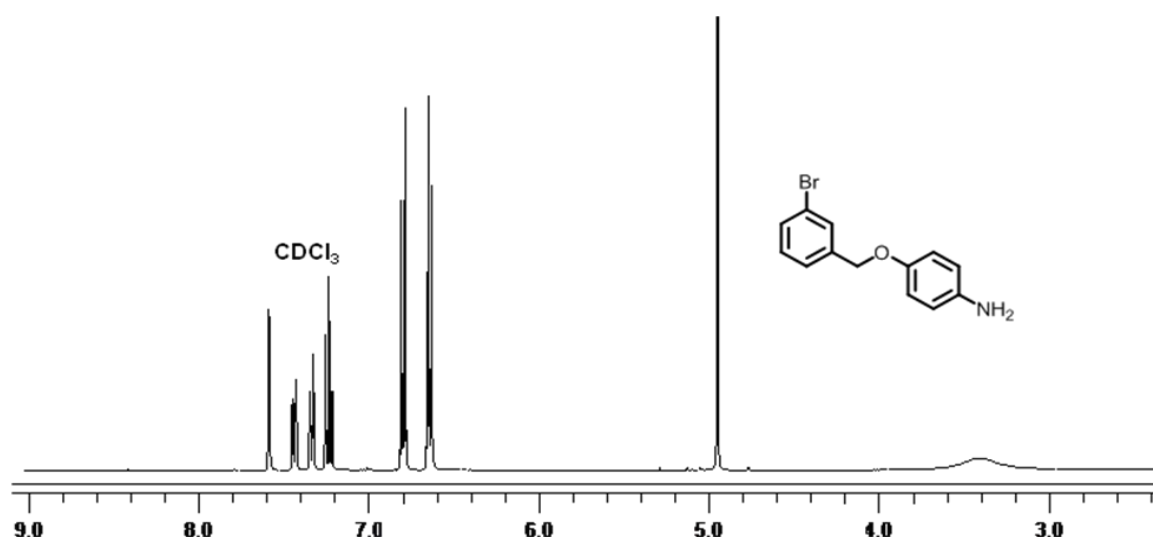


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **14**.

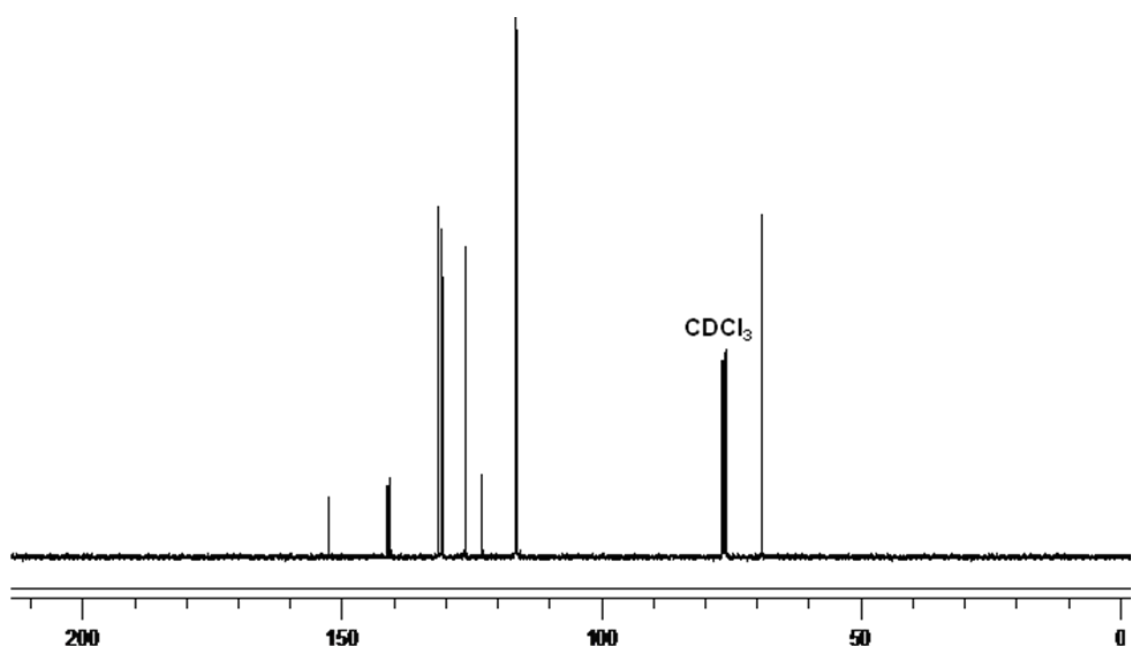


Figure S4. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **14**.

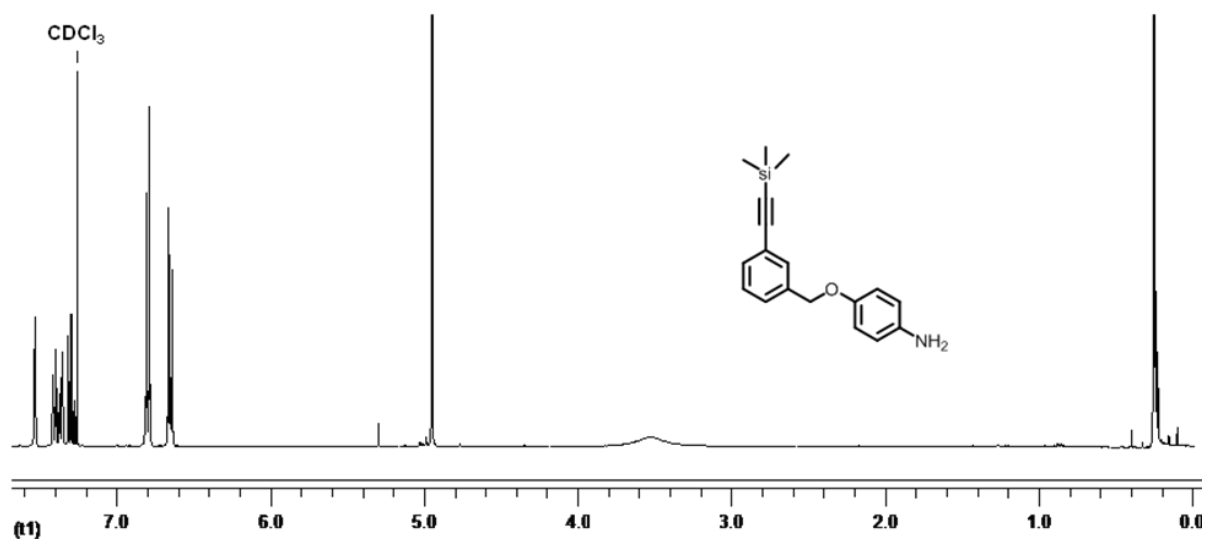


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3 , traces of DCM, 298 K) of **16**.

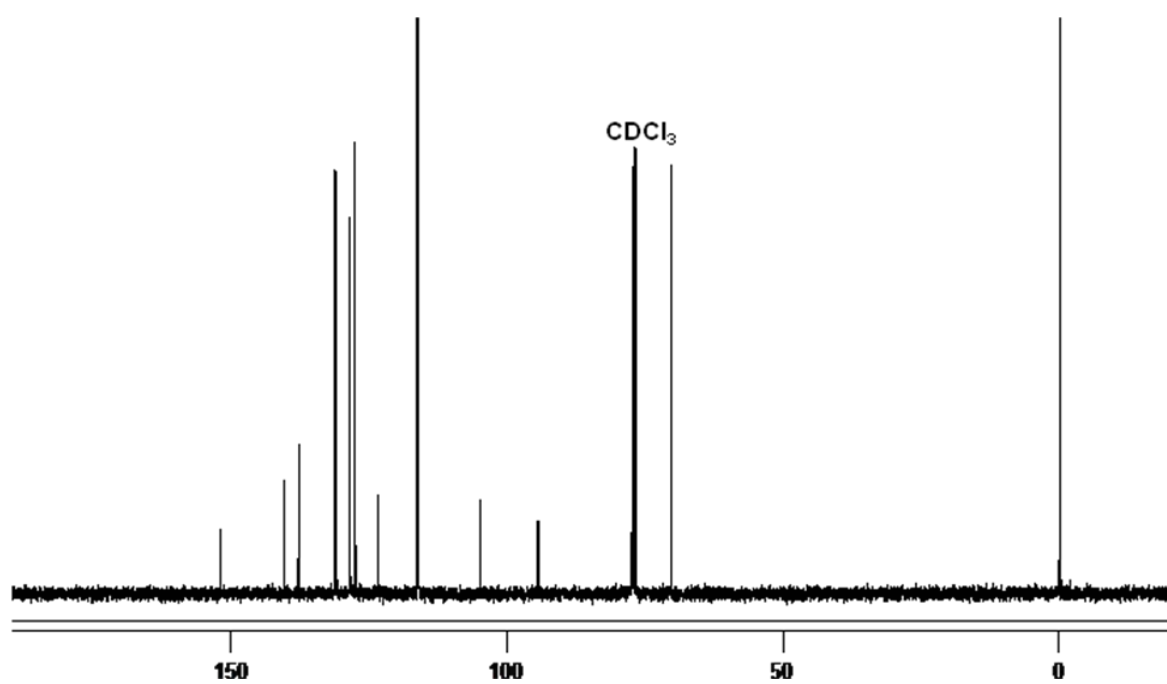


Figure S6. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **16**.

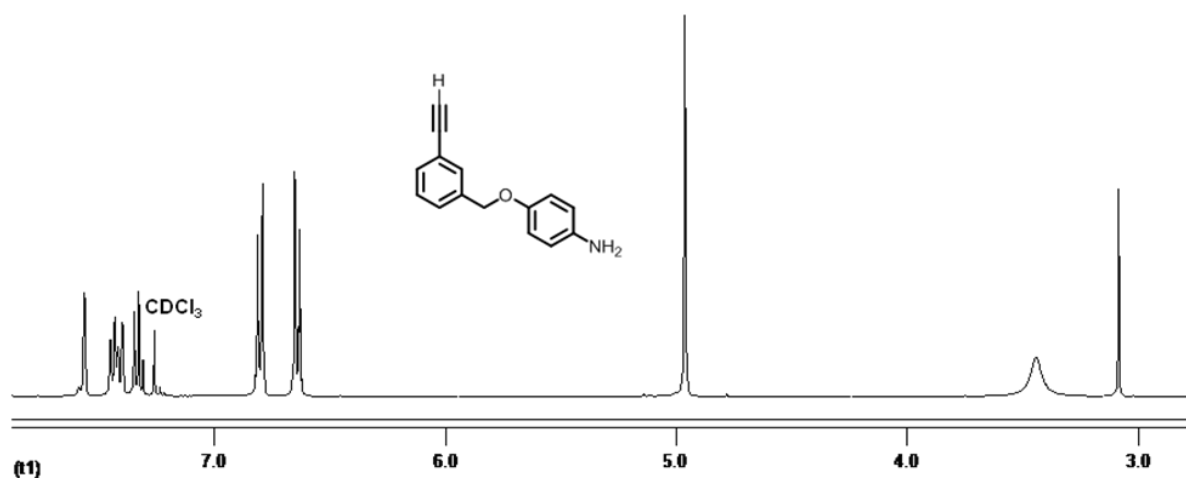


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **17**.

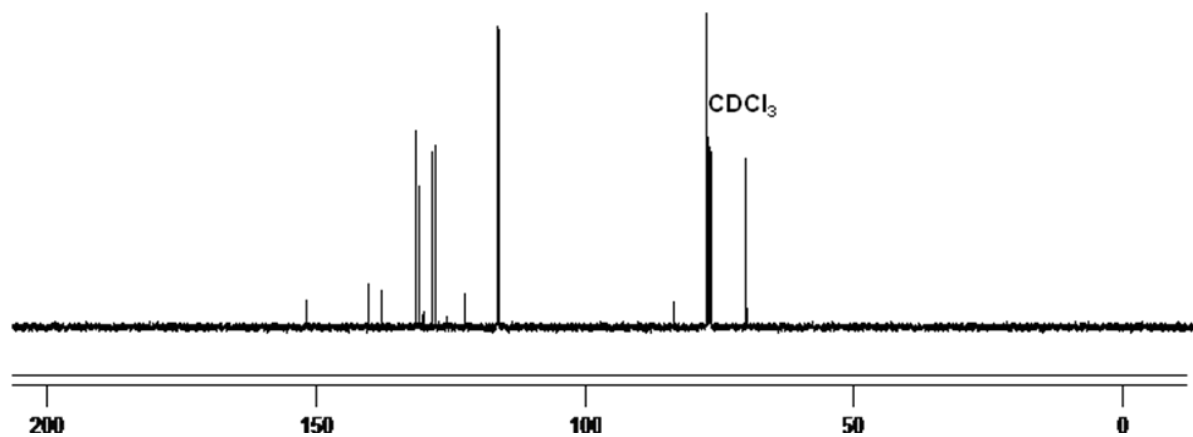


Figure S8. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **17**.

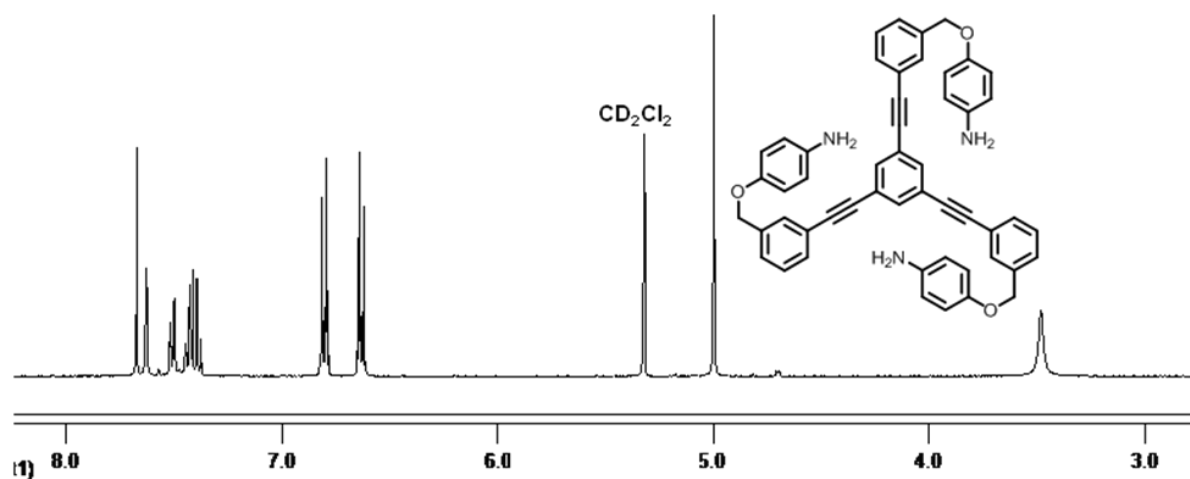


Figure S9. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of **8**.

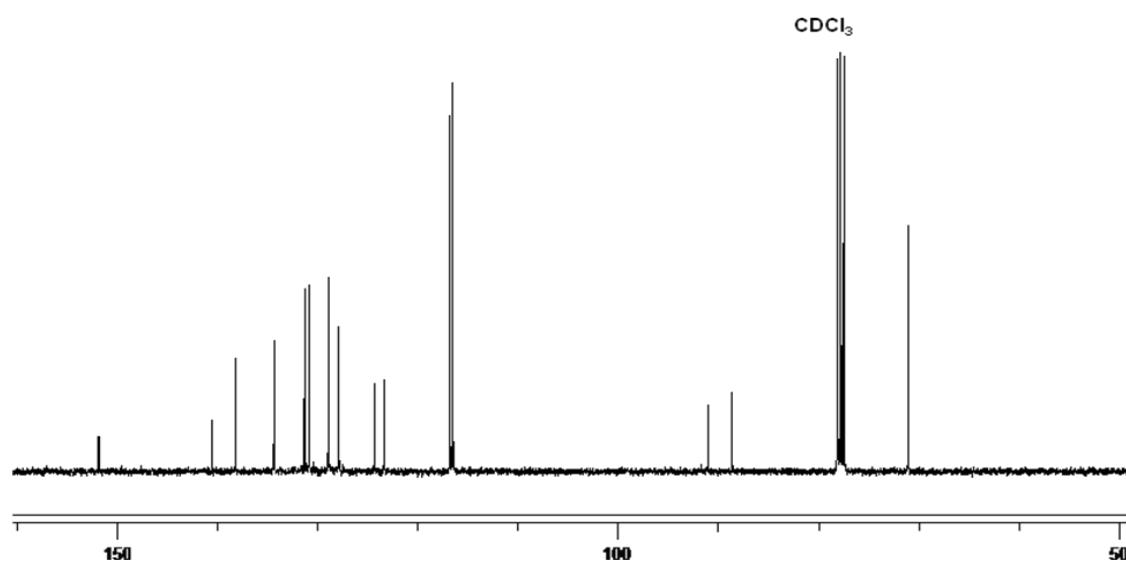


Figure S10. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **8**.

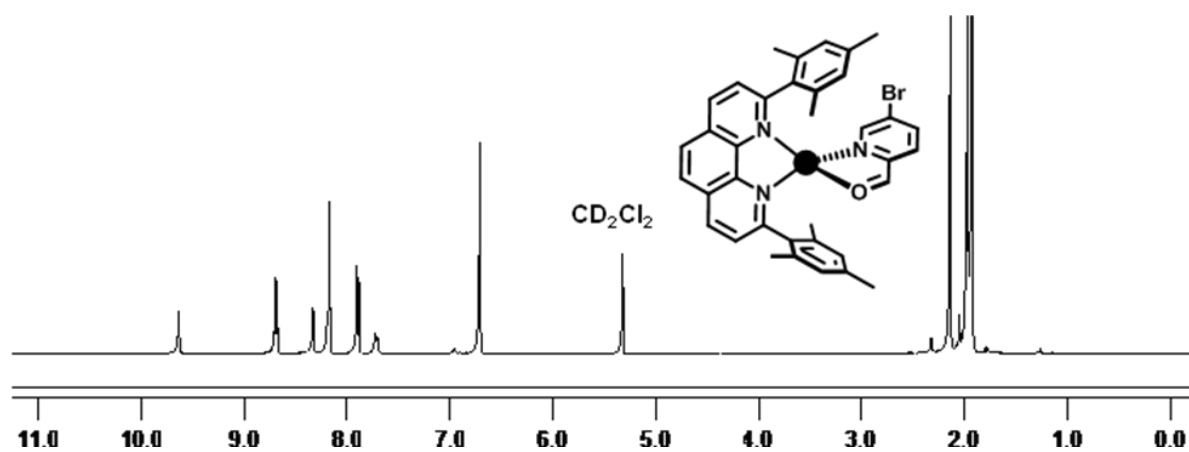


Figure S11. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of **C1**.

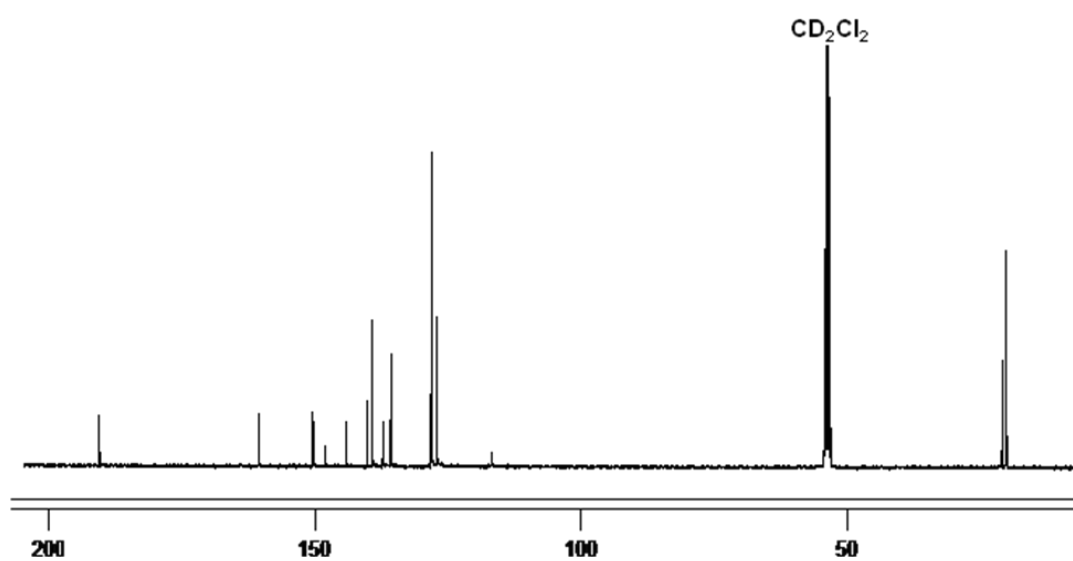


Figure S12. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of **C1**.

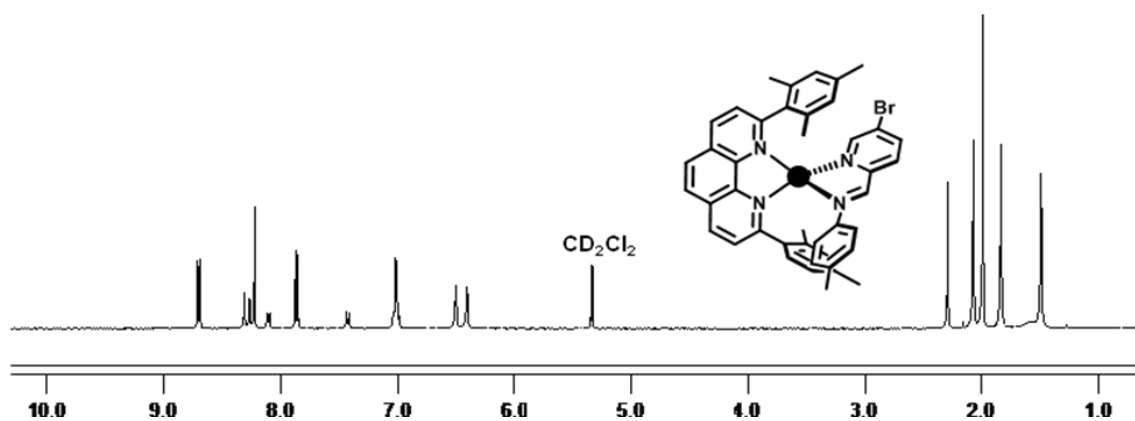


Figure S13. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of **C2**.

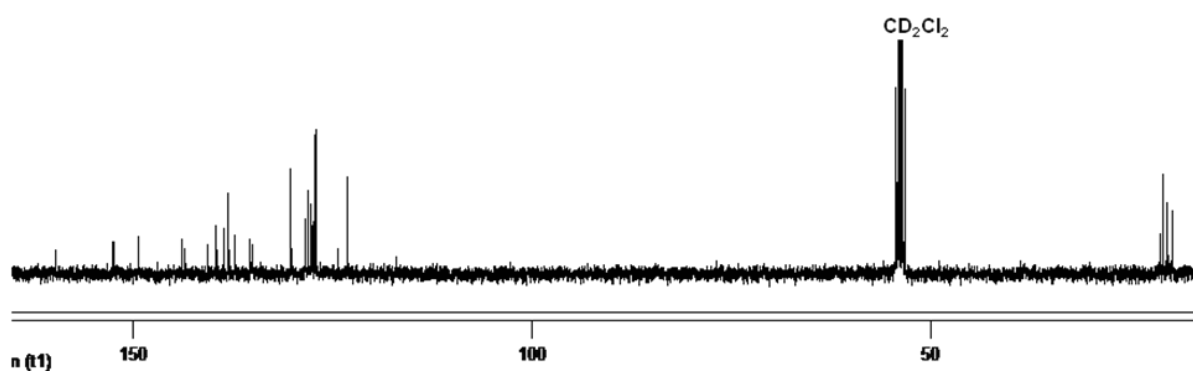


Figure S14. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of **C2**.

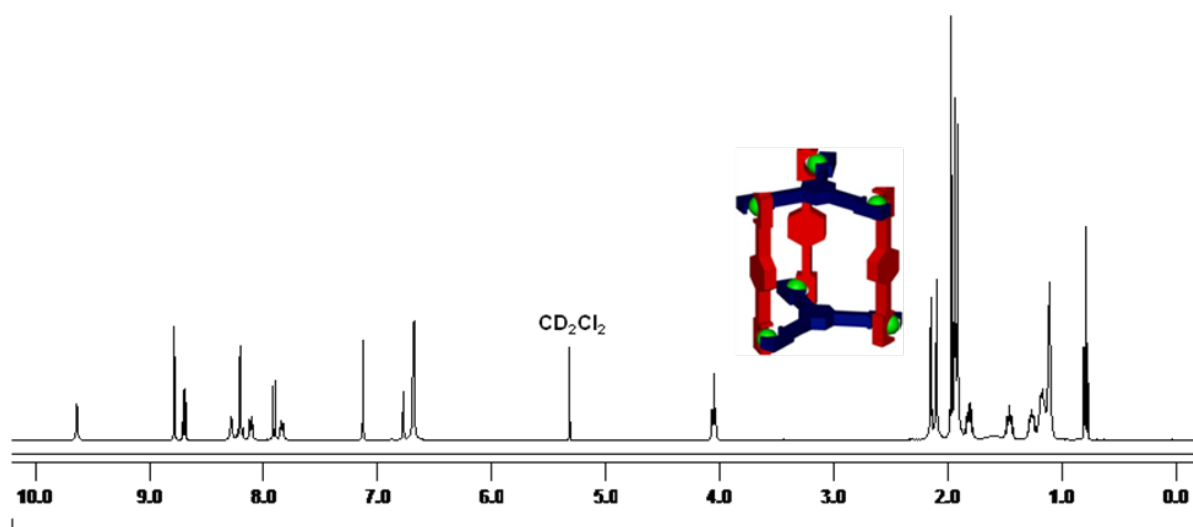


Figure S15. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of **C3**.

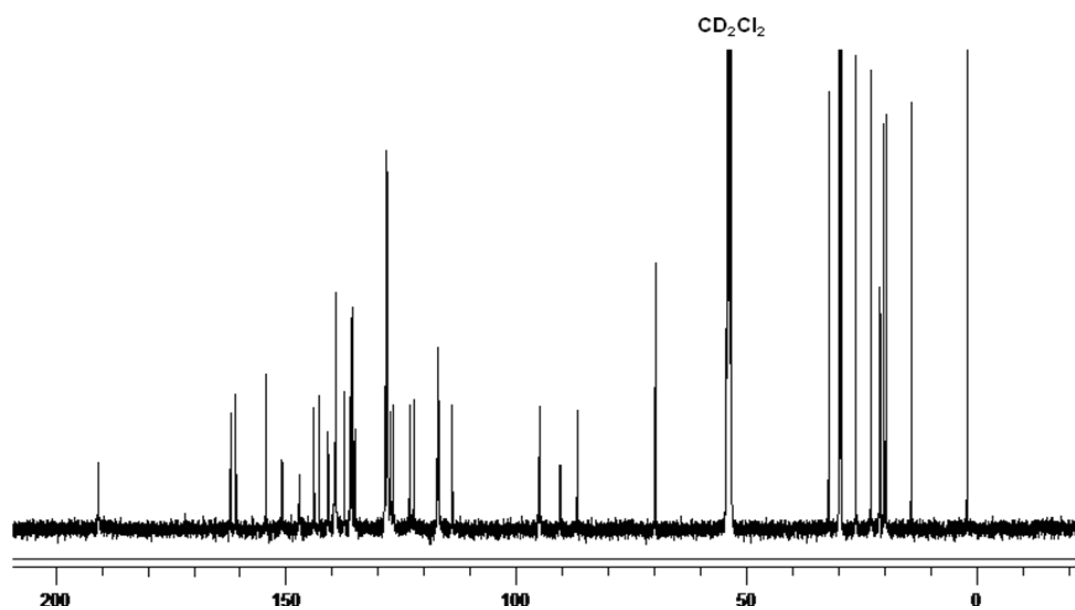


Figure S16. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2 , 298 K) of **C3**.

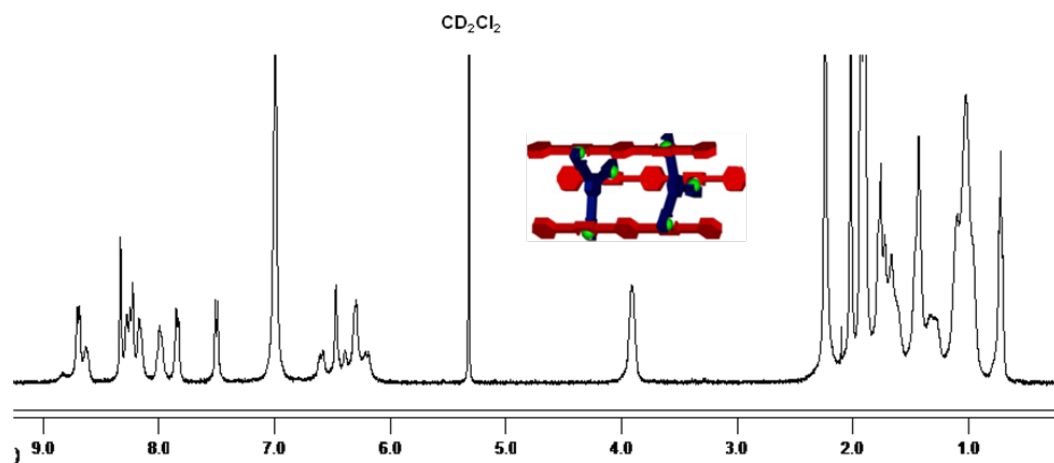


Figure S17. ^1H NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}(3:1)$, 298 K) of **C4**.

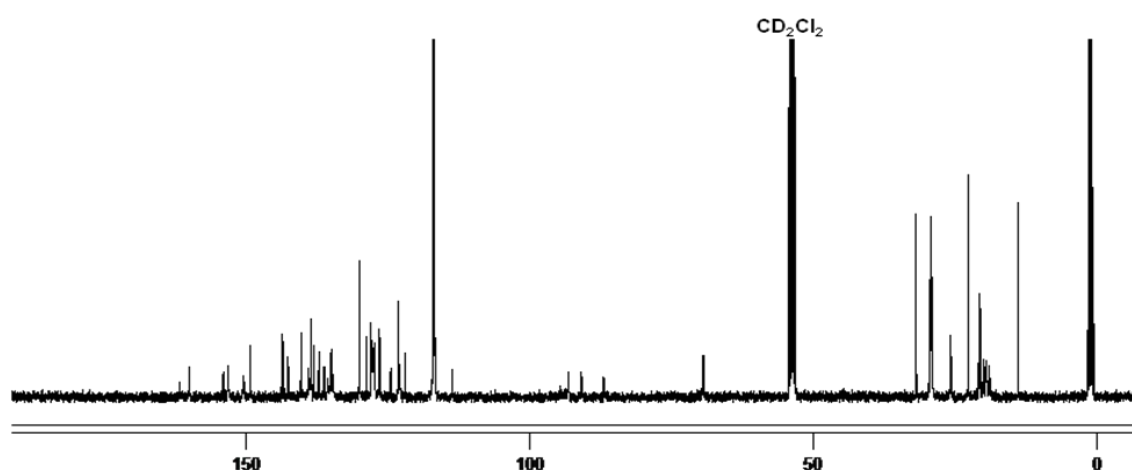


Figure S18. ^{13}C NMR spectrum (100 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}(3:1)$, 298 K) of **C4**.

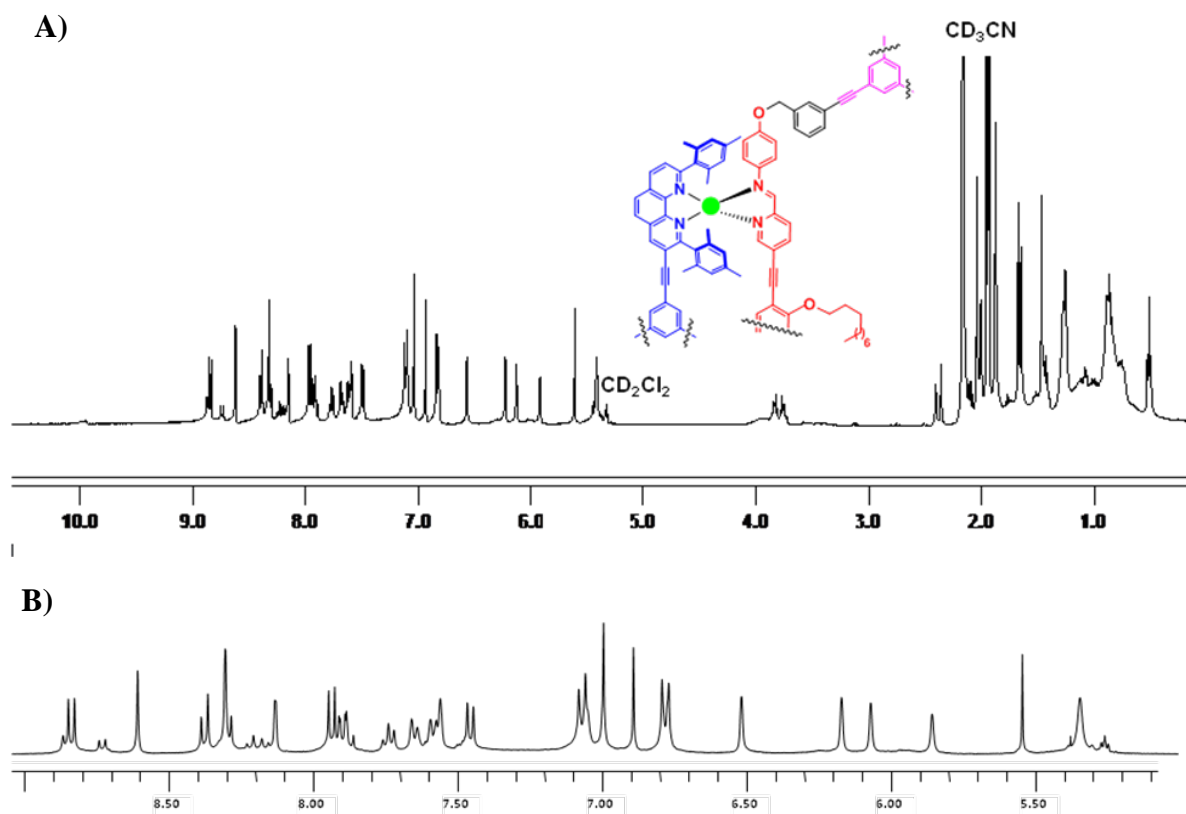


Figure S19. A) ^1H NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}$ (1:6), 298 K) of **C5**. B) Partial ^1H NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}$ (1:6), 298 K) of **C5**.

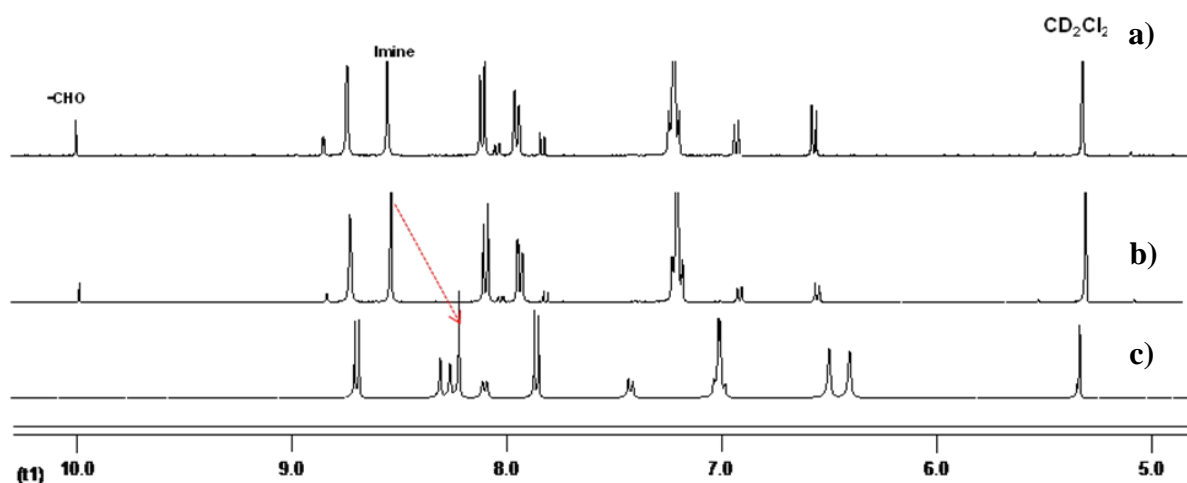
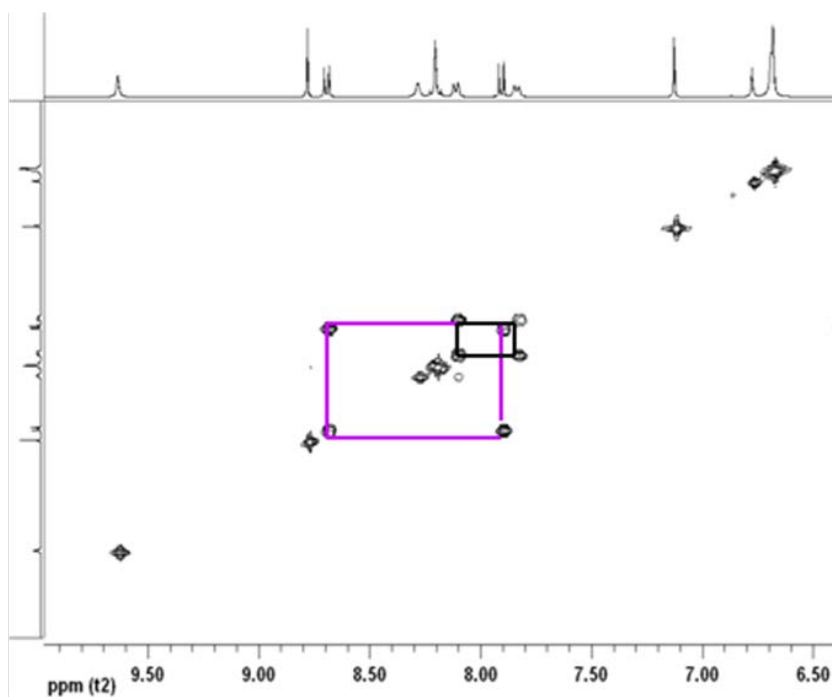


Figure S20. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of (a) an equimolar mixture of **2**, **3** after 24 h; (b) an equimolar mixture of **2**, **3** after 72 h; (c) an equimolar mixture of **1**, **2**, and **3** in presence of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$.

^1H - ^1H COSY NMR Spectra

a)



b)

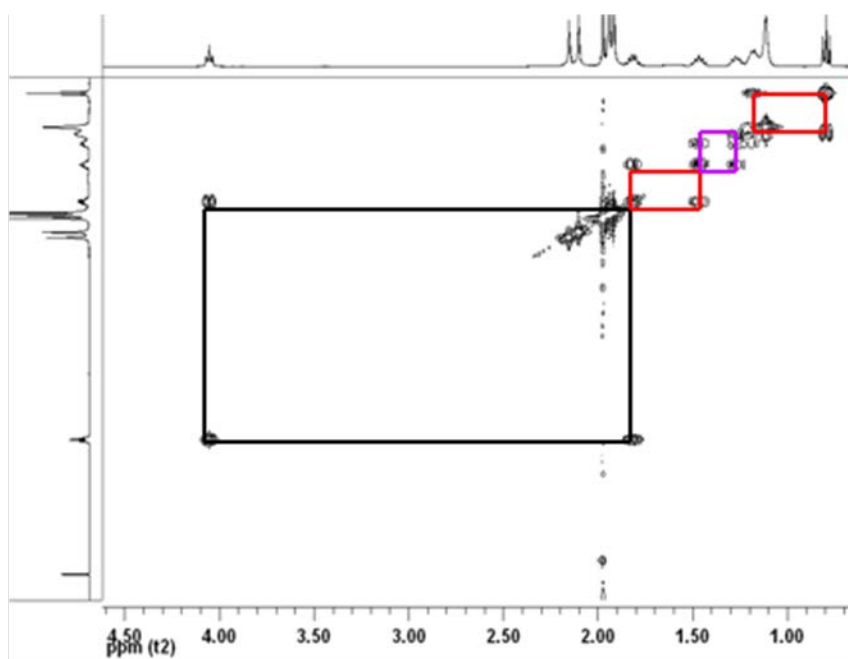


Figure S21. ^1H - ^1H COSY NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of **C3** (a) 10 to 6.5 ppm. (b) 4.5 to 1.0 ppm.

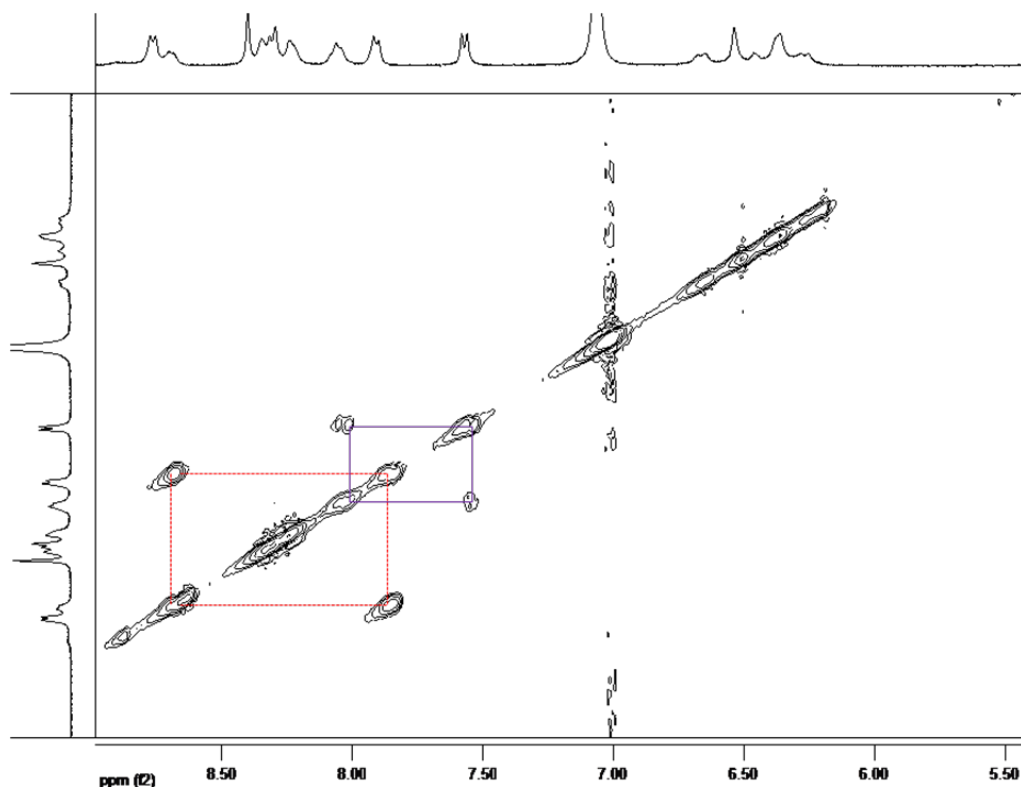


Figure S22. Partial ^1H - ^1H COSY NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}(3:1)$, 298 K) of **C4**

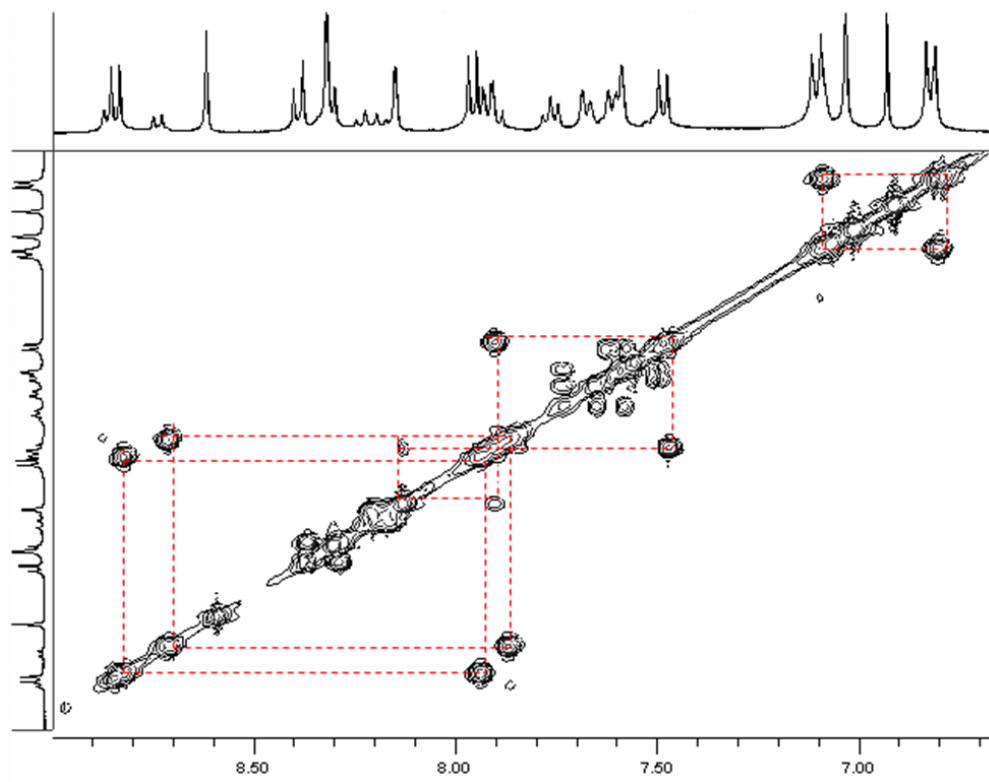


Figure S23. Partial ^1H - ^1H COSY NMR spectrum (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}(1:6)$, 298 K) of **C5**

DOSY NMR Spectra

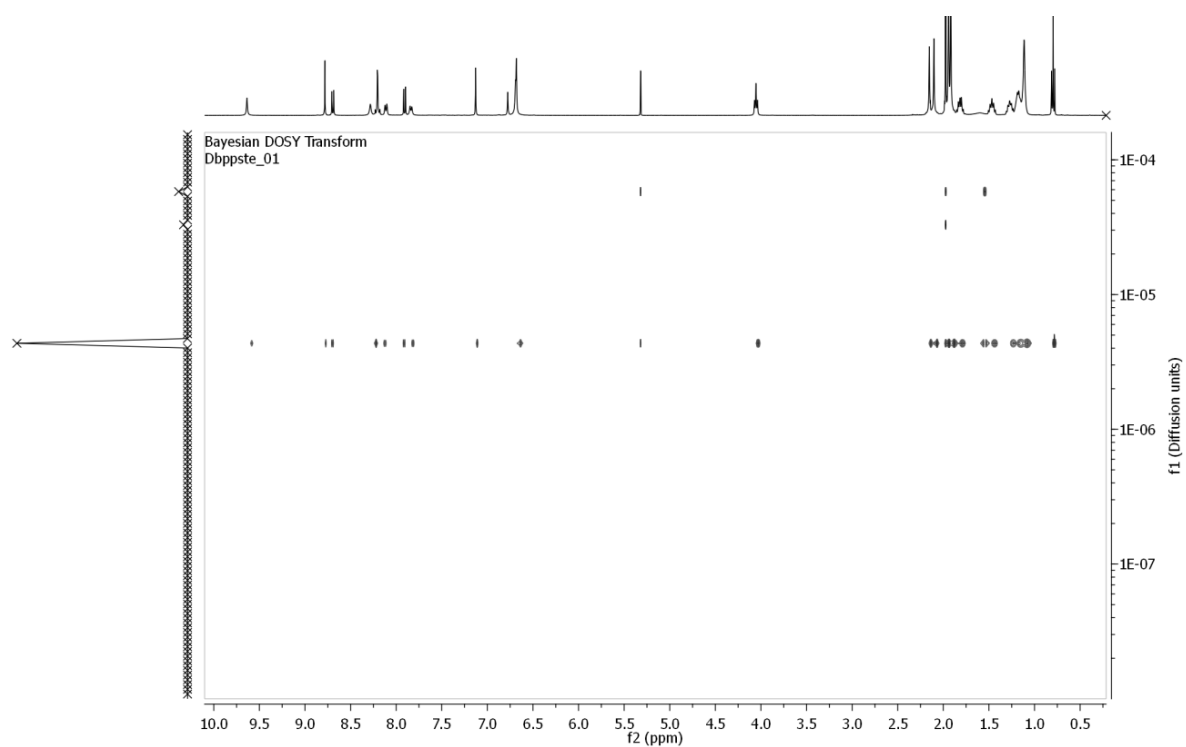


Figure S24. DOSY plot of nanoprism **C3** in CD_2Cl_2 .

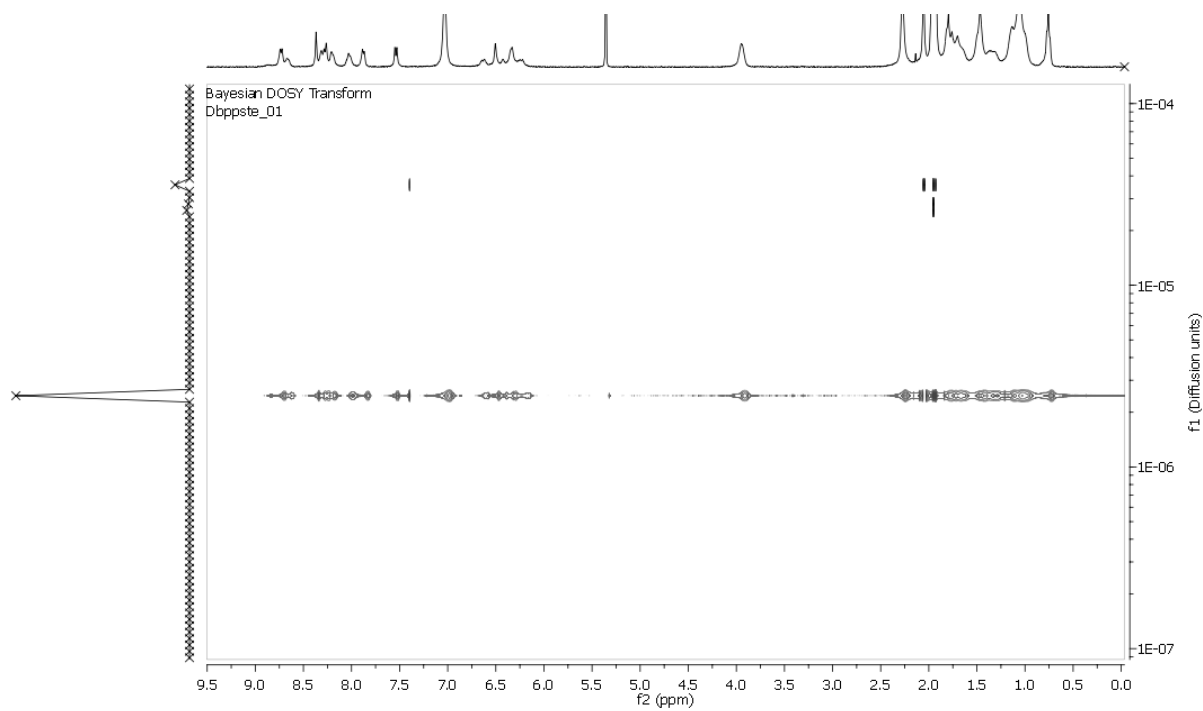


Figure S25. DOSY plot of nanoprism **C4** in $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}(3:1)$.

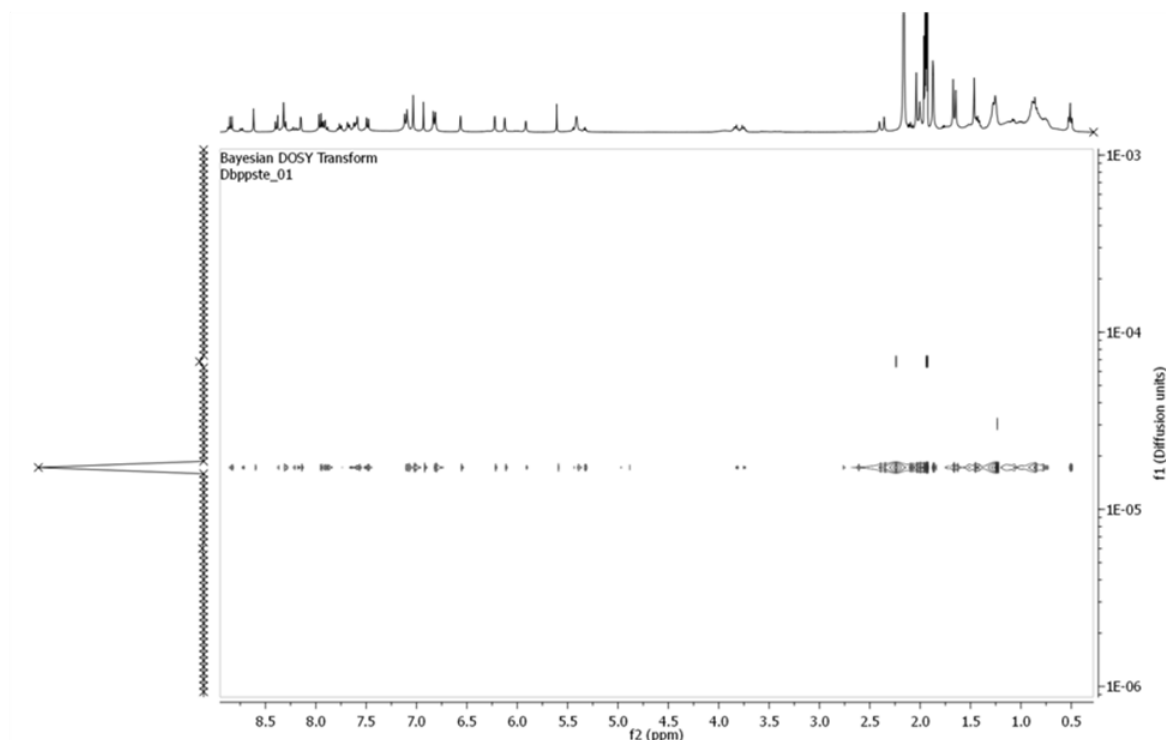


Figure S26. DOSY plot of cage **C5** in CD₂Cl₂:CD₃CN(1:6).

Calculation of hydrodynamic radii for **C3**, **C4**, **C5**.

For the calculation of the hydrodynamic radii r_H the diffusion coefficients D was used after averaging over all observable non-exchanging NMR signals.

The Stokes –Einstein equation⁴ was then used to compute the radius r_H .

$$r_H = k_B T / 6\pi\eta D$$

$$k_B = 1.38066 \times 10^{-23} \text{ N m K}^{-1}$$

From DOSY NMR data at 298 K

Compound	$D / \text{m}^2 \text{S}^{-1}$	$r_H / \text{\AA}$	Diameter / \AA
C3	4.56×10^{-10}	11.3	22.6
C4	4.44×10^{-10}	11.6	23.2
C5	5.43×10^{-10}	11.8	23.6

From MM⁺ calculation

Compound	V / nm^3	$r_H / \text{\AA}$	Diameter / \AA
C3	4.14	9.96	19.9
C4	3.91	9.77	19.5
C5	6.41	11.5	23.0

To compare the calculated (MM⁺ force field) diameter with the experimental DOSY data, we consider the volume of the nanoprisms **C3**, **C4** and cage **C5** as that of a corresponding sphere.

ESI-MS spectra

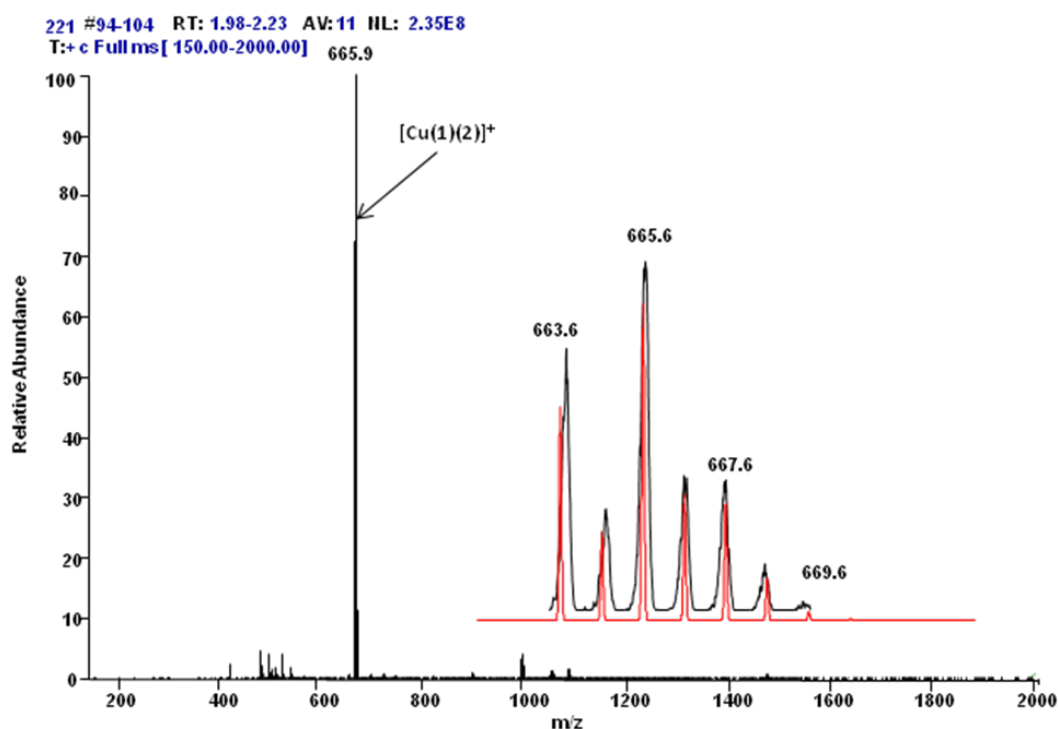


Figure S27. ESI-MS spectrum of **C1** = $[Cu(1)(2)](PF_6)$ (in DCM) and experimental isotopic distribution (black lines) along with calculated isotopic distribution (red lines) for the species $[Cu(1)(2)]^+$.

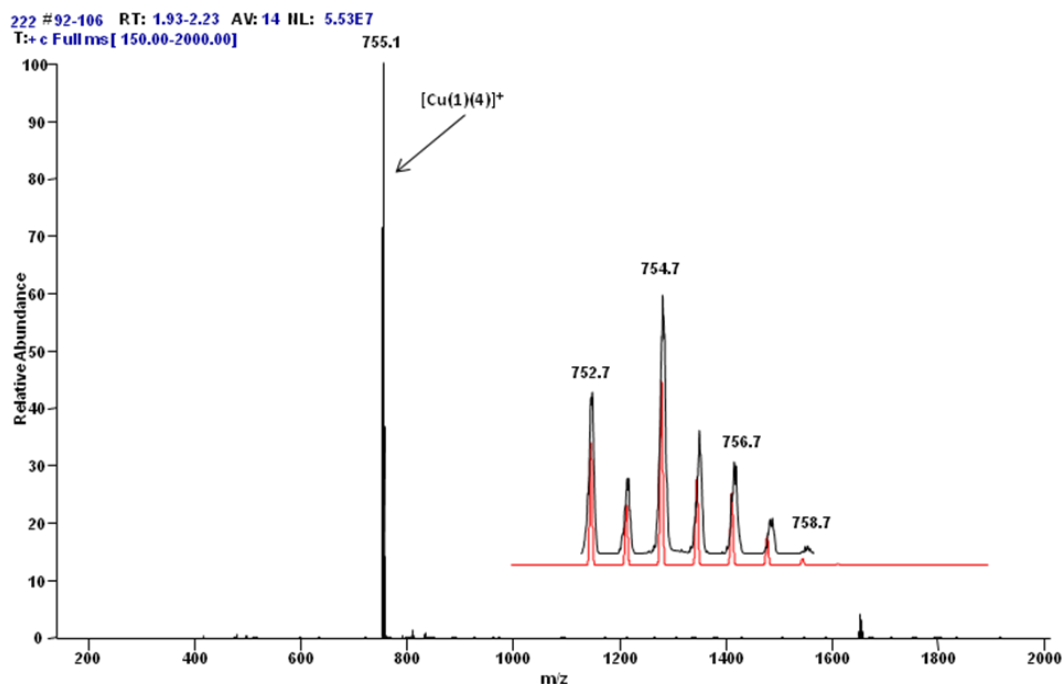


Figure S28. ESI-MS spectrum of **C2** = $[Cu(1)(4)](PF_6)$ (in DCM) and experimental isotopic distribution (black lines) along with calculated isotopic distribution (red lines) for the species $[Cu(1)(4)]^+$.

185-1 #282-297 RT: 5.38-5.93 AV: 16 HL: 6.33E5
T: + c Full ms [150.00-2000.00]

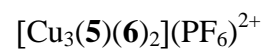
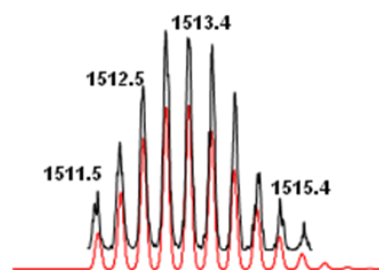
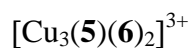
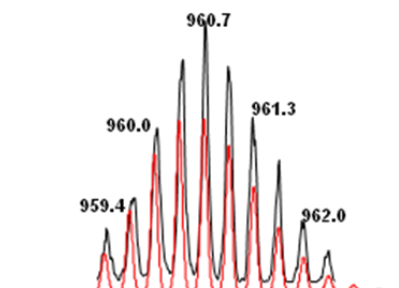
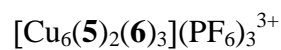
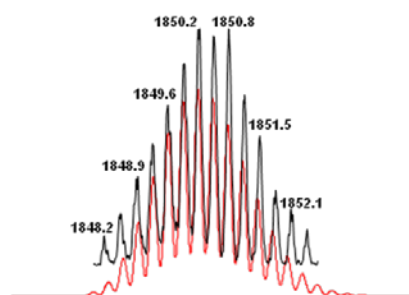
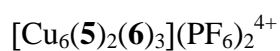
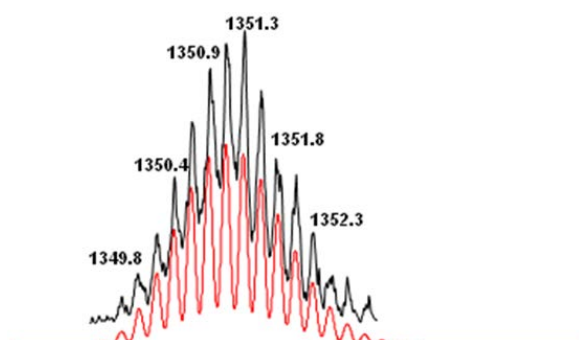
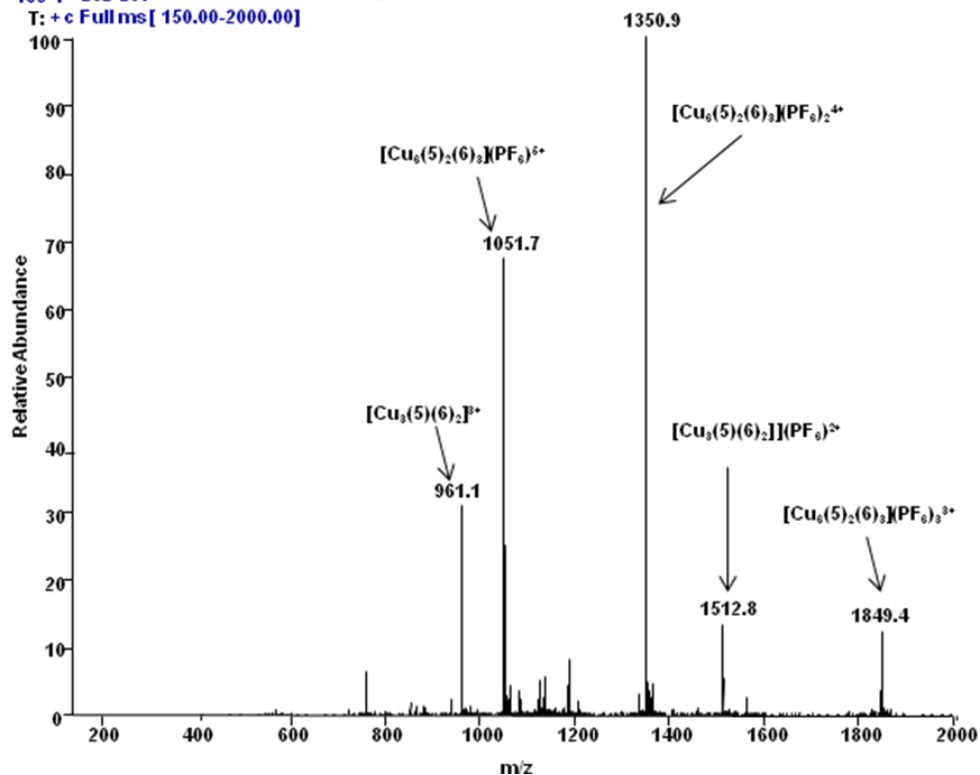


Figure S29. ESI-MS spectrum of **C3** = $[\text{Cu}_6(5)_2(6)_3](\text{PF}_6)_6$ (in DCM) and experimental isotopic distribution (black lines) along with calculated isotopic distribution (red lines) for the species $[\text{Cu}_3(5)(6)_2]^{3+}$, $[\text{Cu}_6(5)_2(6)_3](\text{PF}_6)_2^{4+}$, $[\text{Cu}_3(5)(6)_2](\text{PF}_6)^{2+}$, and $[\text{Cu}_6(5)_2(6)_3](\text{PF}_6)_3^{3+}$.

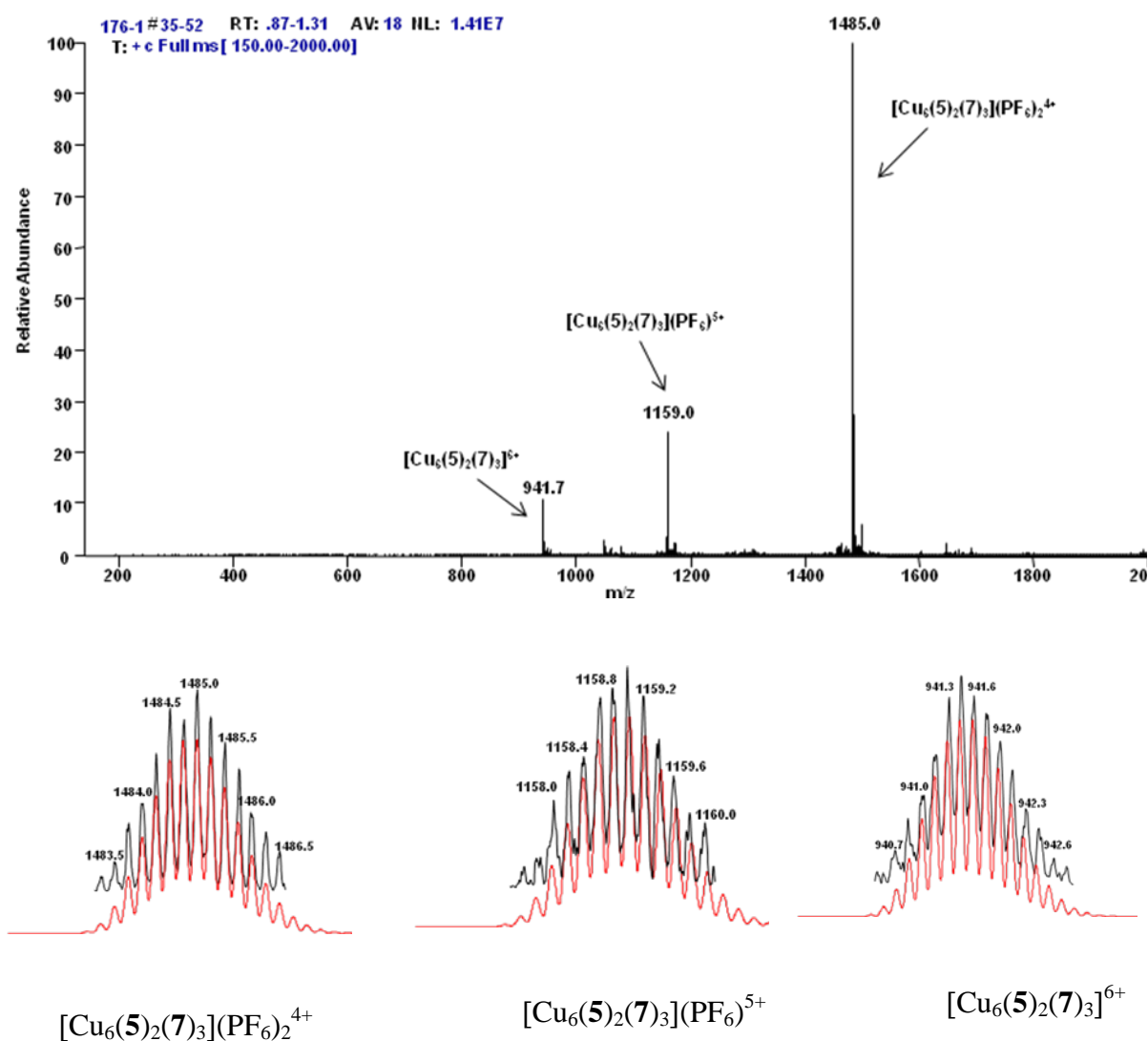


Figure S30. ESI-MS spectrum of **C4** = $[Cu_6(5)_2(7)_3](PF_6)_6$ (in DCM) and experimental isotopic distribution (black lines) along with calculated isotopic distribution (red lines) for the species $[Cu_6(5)_2(7)_3]^{6+}$, $[Cu_6(5)_2(7)_3](PF_6)^{5+}$, and $[Cu_6(5)_2(7)_3](PF_6)_2^{4+}$.

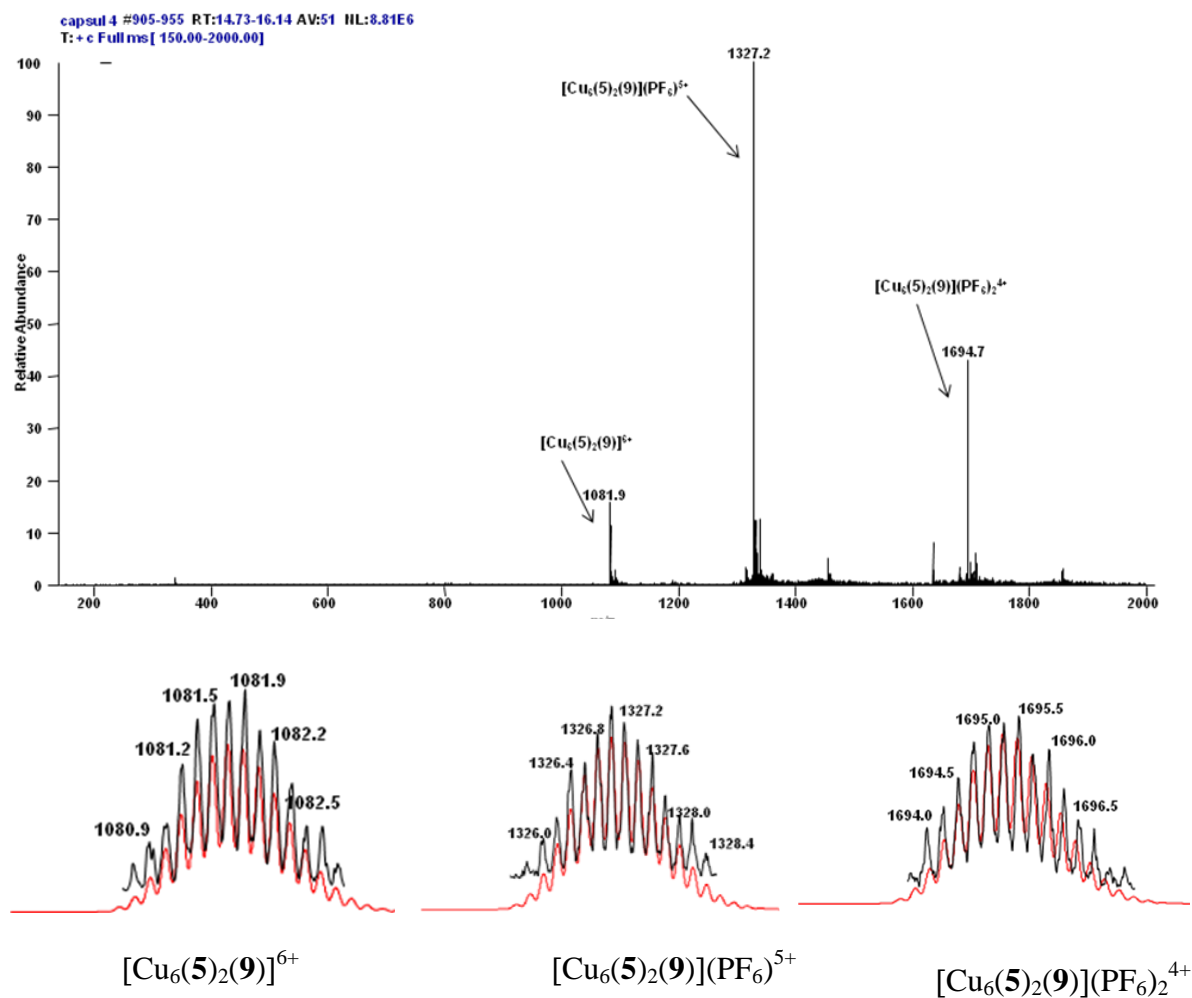


Figure S31. ESI-MS spectrum of **C5** = $[\text{Cu}_6(\mathbf{5})_2(\mathbf{9})](\text{PF}_6)_6$ (in CH_3CN) and experimental isotopic distribution (black lines) along with calculated isotopic distribution (red lines) for the species $[\text{Cu}_6(\mathbf{5})_2(\mathbf{9})]^{6+}$, $[\text{Cu}_6(\mathbf{5})_2(\mathbf{9})](\text{PF}_6)_5^+$, and $[\text{Cu}_6(\mathbf{5})_2(\mathbf{9})](\text{PF}_6)_2^{4+}$.

Energy minimized structures

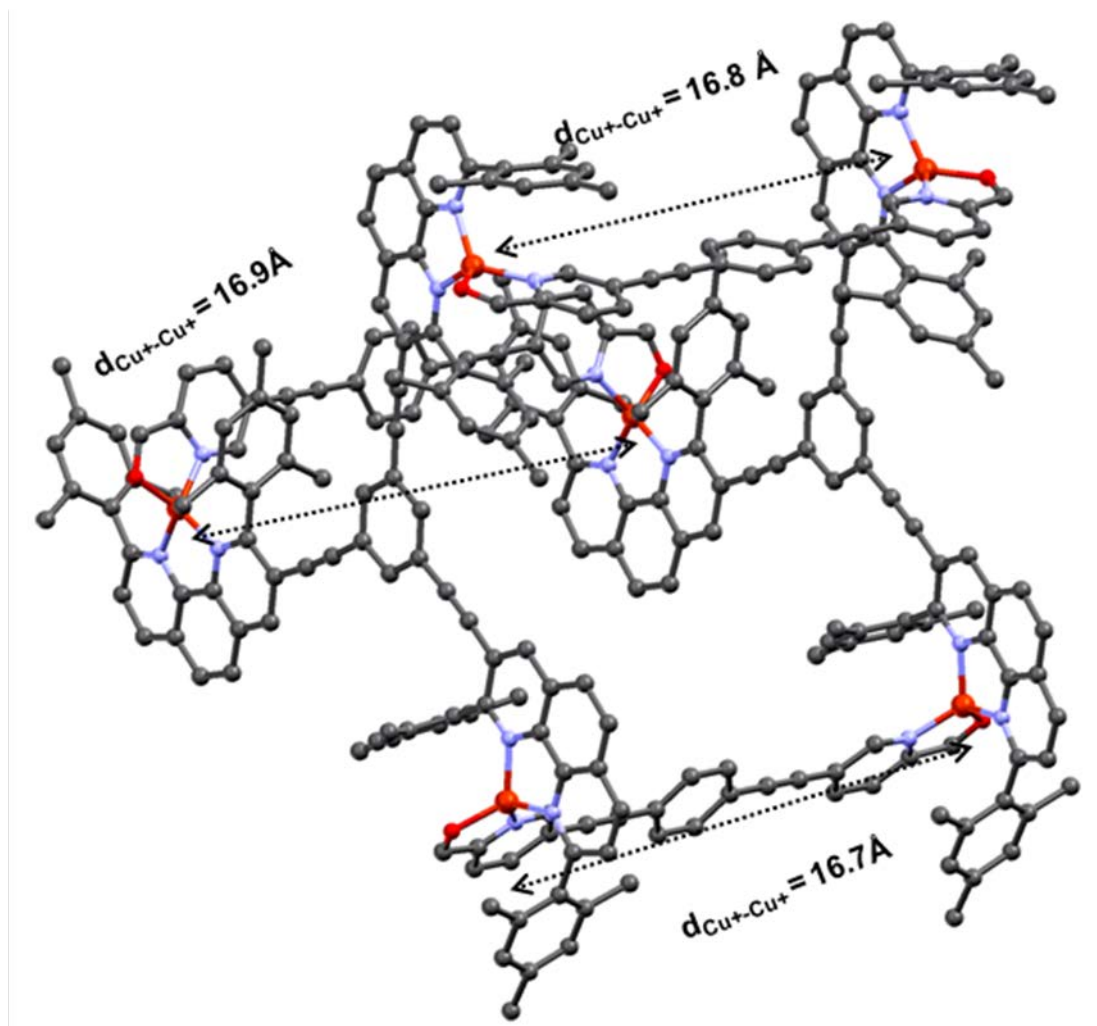


Figure S32. Energy minimized structure of the nanoprism **C3** with anticlockwise orientation of **5**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

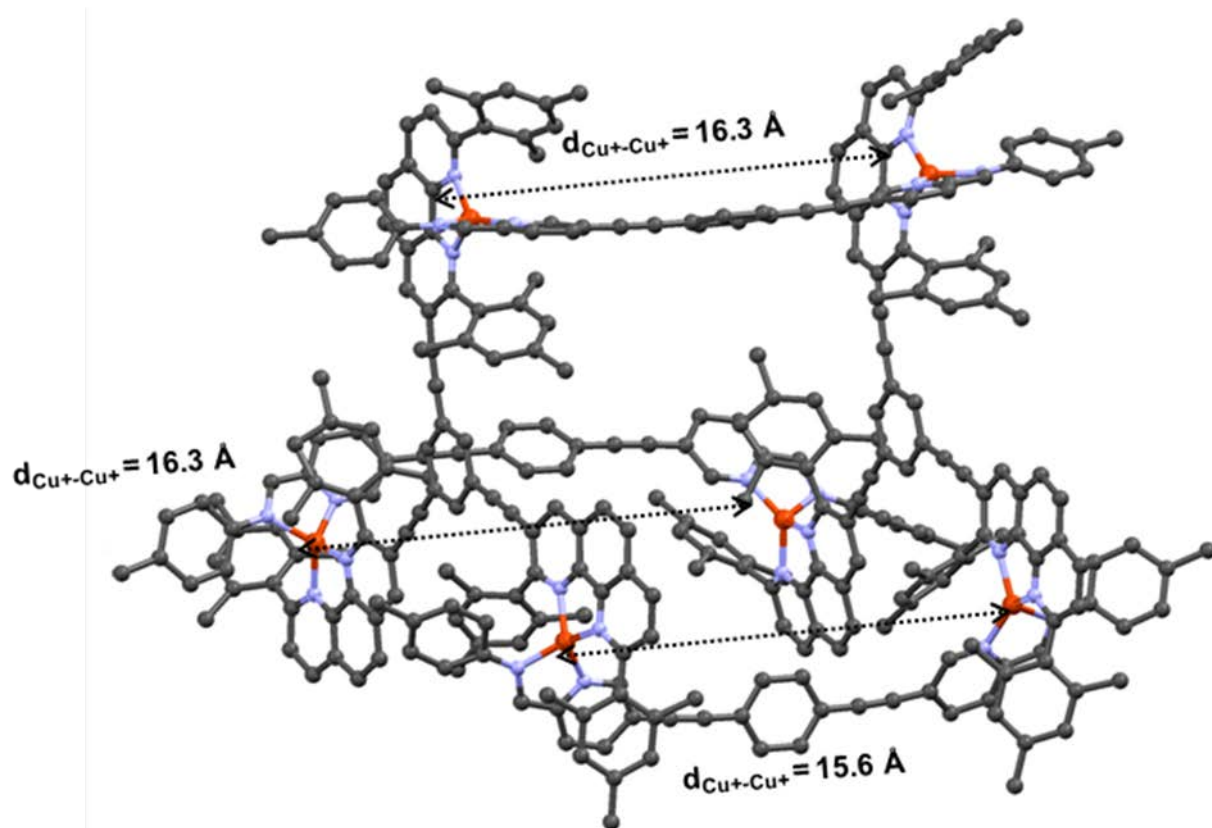


Figure S33. Energy minimized structure of the nanoprism **C4** with anticlockwise orientation of **5**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

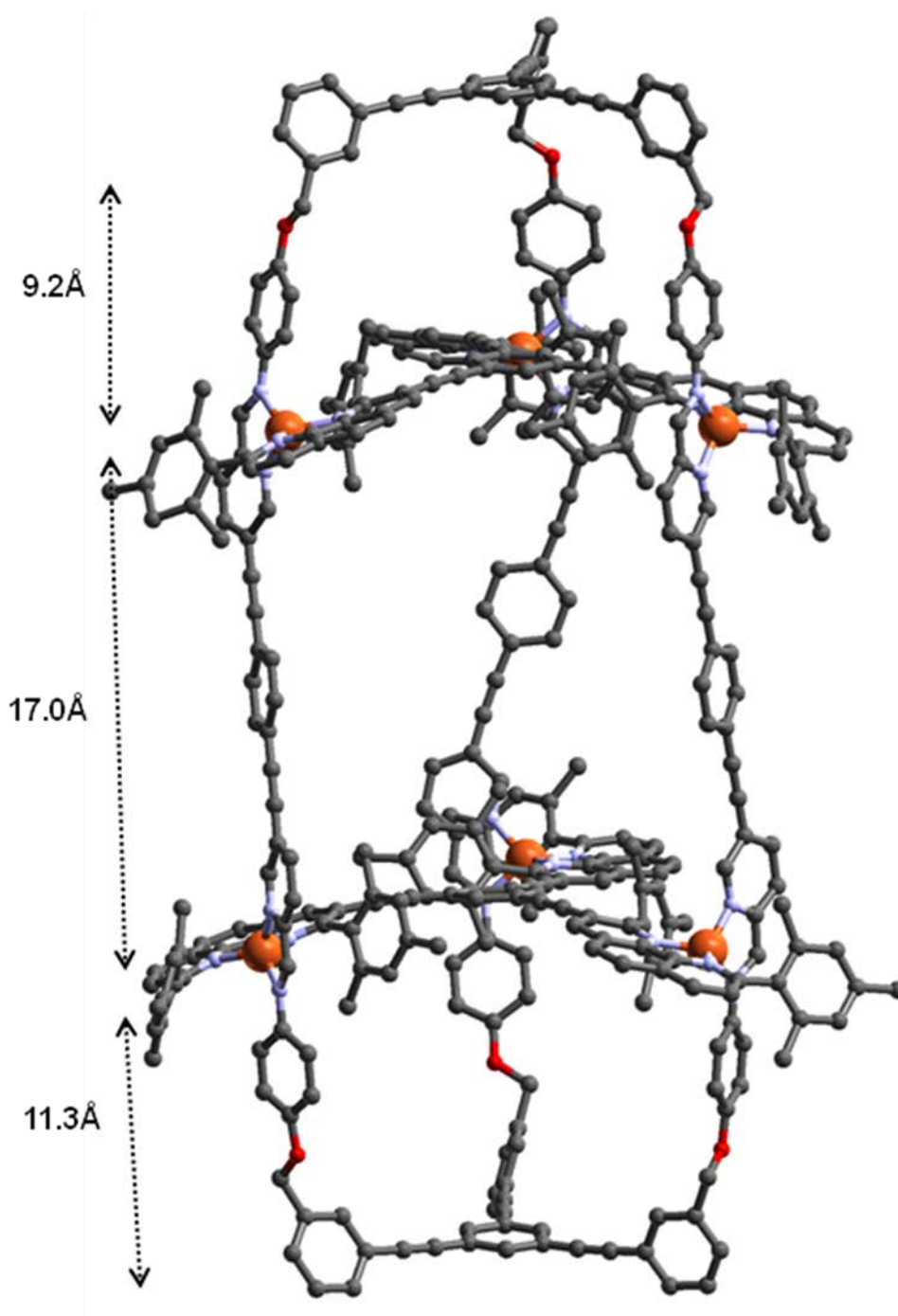


Figure S34. Energy minimized structure of the “formal” D_3 isomer of cage **C5**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

-
- (1) Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, *68*, 9907.
 - (2) Vatsadze, S. Z.; Titanyuk, I. D.; Chernikov, A. V.; Zyk, N.V. *Russ. Chem. Bull., Int. Ed.* **2004**, *53*, 471.
 - (3) Fan, J.; Bats, J. W.; Schmittel, M. *Inorg. Chem.* **2009**, *48*, 6838.
 - (4) Elias, H.-G. *Polymere: Von Monomeren und Makromolekülen zu Werkstoffen* Hüthig & Wepf Verlag: Zug, Heidelberg, Oxford, CT/USA **1996**.