Supramolecular Multi-Component Self-Assembly of Shape Adaptive Nanoprisms: Wrapping up C_{60} with Three Porphyrin Units

Supporting Information

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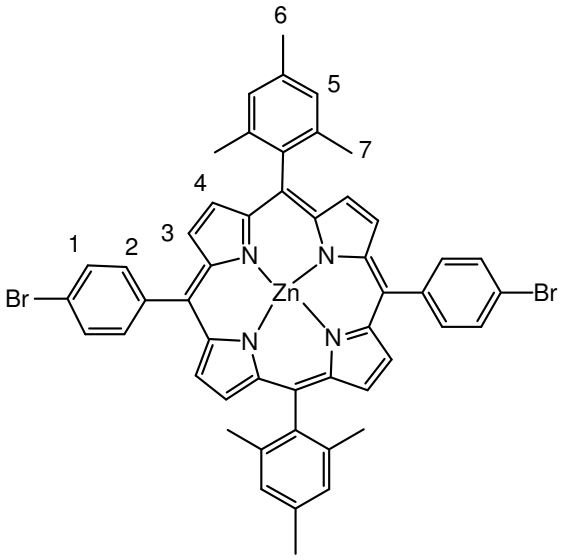
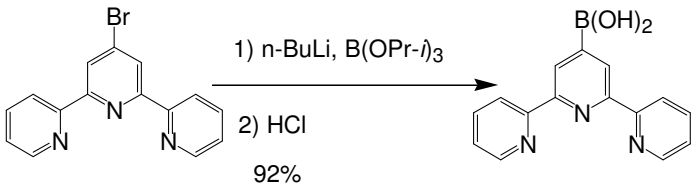
General

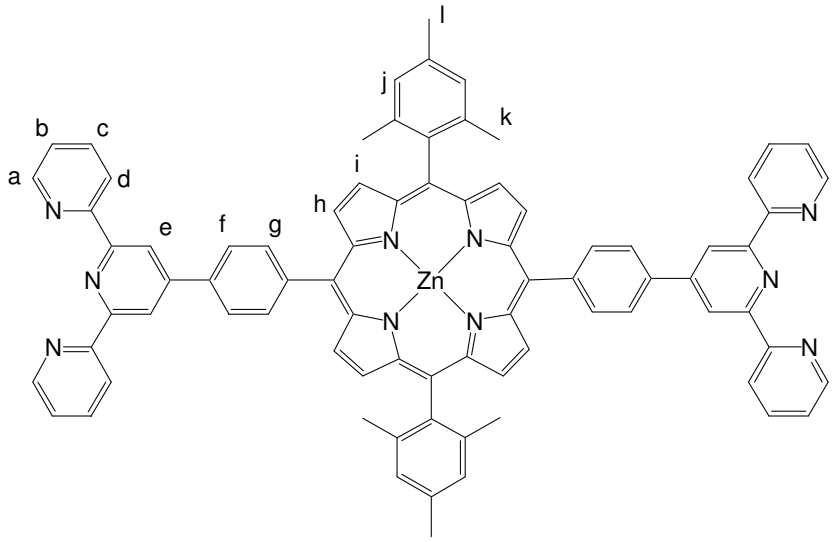
All reagents were commercially available and used without further purification. The purification and drying of the used solvents was accomplished according to standard methods. Thin-layer chromatography was performed using thin-layer chromatography plates (Silica Gel 60 F_{254}, Merck). Silica Gel 60 was used for column chromatography. Confirmation of the structures of all products was obtained by ^{1}H NMR and ^{13}C NMR spectroscopy (Bruker Avance 400 spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference). Numbering of carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signal and is not in accordance with the IUPAC nomenclature rules. Melting points were taken using an apparatus of Dr. Tottoli (Büchi) and are uncorrected. Electrospray mass spectra (ESI-MS) were recorded using a ThermoQuest LCQ Deca. The purity of all compounds was checked by thin-layer chromatography on SiO_2 (silica gel 60 F254, Merck). Infrared spectra were recorded on a Perkin Elmer 1750 FT-IR spectrometer with the software of IRDM 1700. UV/Vis was recorded on a Varian Cary 100 Bio UV/visible Spectrometer, cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were recorded on a Parstat 2273 instrument from Princeton Applied Research.



Zinc(II)-5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrin (**1**): A solution of 5-mesityldipyrromethane (624 mg, 2.36 mmol) and 4-bromo-benzaldehyde (437 mg, 2.36 mmol) in CH_2Cl_2 (236 mL) was treated with TFA (323 µL, 4.19 mmol) at room temperature under nitrogen for 30 min. Dichloro dicyano quinone (807 mg, 3.54 mmol) was added and the reaction mixture was stirred for 3 h. Then the mixture was filtered through a short pad of silica and the volume of the filtrate was reduced to 60 mL. $Zn(OAc)_2 \cdot 2H_2O$ (300 mg, 1.37 mmol) in methanol (10 mL) was added and the reaction mixture was stirred at room temperature overnight. Chromatography ($CHCl_3$) afforded **1** as a purple solid (380 mg, 0.413 mmol, 35%). mp: >300 °C; IR (KBr): $\tilde{\nu}$ = 3442, 2970, 1524, 1484, 1442, 1336, 1206, 1072, 999, 832, 800, 723, 519, 480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, *J* = 26 Hz, 4H, 3-H), 8.82 (d, *J* = 26 Hz, 4H, 4-H), 8.13 (d, *J* = 7.5 Hz, 4H, 2-H), 7.90 (d, *J* = 7.5 Hz, 4H, 1-H), 7.31 (s, 4H, 5-H), 2.66 (s, 6H, 6-H), 1.85 (s, 12H, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 149.9, 141.8, 139.3, 139.0, 137.7, 135.9, 132.2, 131.2, 129.9, 127.8, 122.3, 119.8, 118.9, 29.9, 21.8; Anal calcd for $C_{50}H_{38}Br_2N_4Zn \bullet 0.5H_2O$: C, 64.64; H, 4.23; N, 6.03; found: C, 64.43; H, 4.13; N, 6.01.

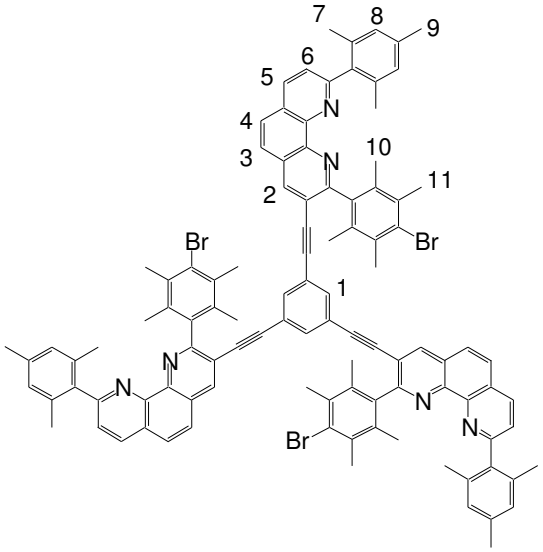


2,6-Di(pyridin-2-yl)pyridin-4-yl-4-boronic acid (**2**): 4-Bromoterpyridine (1.50 g, 4.80 mmol) and triisopropyl borate (1.40 mL, 6.06 mmol) were dissolved in 40 mL of THF under nitrogen. The mixture was cooled to −40 °C, and 2.4 mL of n-butyllithium (solution: 2.5 M in hexanes, 6.00 mmol) was added dropwise over 10 min. After the reaction mixture had been stirred for an additional 30 min at −40 °C, it was allowed to warm to room temperature whereupon 100 mL of 2 N HCl solution was added. The aqueous phase was separated and neutralized with 5 N aqueous NaOH, with a white solid precipitating as the pH approached 7. The aqueous mixture was saturated with solid NaCl and extracted with three 150 mL portions of THF. The solvent was removed from the combined organic layers under reduced pressure to furnish **2** as a white solid (1.22 g, 4.42 mmol), which was used for next reaction without further purification and characterization.



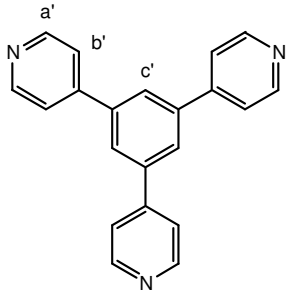
Zinc(II)-5,15-bis-(4-[2,2';6',2'']terpyridin-4'-yl-phenyl)-10,20-dimesitylporphyrin (**BT3**): 2,6-di(pyridin-2-yl)pyridin-4-yl-4-boronic acid (**2**, 600 mg, 2.16 mmol zinc(II)-5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrin (**1**, 200 mg, 0.217 mmol), $Pd(PPh_3)_4$ (100 mg, 86.5 μmol), PPh_3 (250 mg, 0.953 mmol) and Na_2CO_3 (6.00g, 56.6 mmol) were dissolved in a solvent mixture of toluene (20 mL), THF (20 mL) and H_2O (20 mL) in a 100 mL round-bottomed flask. After the mixture had been degassed using five vacuum/nitrogen back-fill cycles, it was heated to reflux for 4 days under nitrogen. The mixture was cooled to room temperature and diluted with 100 mL of water and 200 mL of dichloromethane. The aqueous layer was separated and extracted with 2x100 mL of dichloromethane. The combined organic layers were dried over $MgSO_4$, and concentrated on a rotary evaporator under reduced pressure to afford a purple solid. After several times of size exclusion chromatography using toluene as eluent, **BT3** was received as a purple solid (160 mg, 0.131 mmol, 60%). mp:

>300 °C; IR (KBr): $\tilde{\nu}$ = 3417, 2919, 2851, 1605, 1584, 1566, 1466, 1441, 1408, 1387, 1337, 1263, 1204, 997, 792, 740, 720. 661, 651, 622 cm^{-1}; ^1H NMR (400 MHz**,** $CDCl_3$: CD_3OD (4:1)): δ = 8.96 (s, 4H, e-H), 8.83 (d, *J* = 4.6 Hz, 4H, h-H), 8.71 (m_c, 8H, a-, d-H), 8.70 (d, *J* = 4.6 Hz, 4H, i-H), 8.35 (d, *J* = 8.0 Hz, 4H, g-H), 8.24 (d, *J* = 8.0 Hz, 4H, f-H), 7.93 (dt, *J* = 1.6 Hz, *J* = 8.0 Hz, c-H), 7.39 (ddd, *J* = 1.6 Hz, *J* = 5.0 Hz, *J* = 8.0 Hz, 4H, b-H), 7.23 (s, 4H, j-H), 2.58 (s, 6H, l-H), 1.82 (s, 12H, k-H); ^{13}C NMR (100 MHz**,** $CDCl_3$: CD_3OD (4:1)), δ = 156.3, 156.1, 150.6, 149.9, 149.8, 149.1, 144.5, 139.6, 139.3, 137.4, 137.3, 137.1, 135.2, 131.9, 130.7, 127.6, 125.3, 124.2, 121.9, 119.3, 119.1, 119.0, 21.7, 21.4; ESI-MS: calcd. for $[M+H]^+$: *m/z* 1223.4, found: *m/z* 1223.9, calcd. for $[M+2H]^{2+}$: *m/z* 612.2, found: *m/z* 612.4; Anal calcd for $C_{80}H_{58}N_{10}Zn \bullet 0.75CH_2Cl_2$: C, 75.27; H, 4.65; N, 10.87; found: C, 75.66; H, 4.94; N, 10.12.



1,3,5-Triiodobenzene (37.6 mg, 80.0 µmol), 2-(4-bromo-2,3,5,6-tetramethylphenyl)-3-ethynyl-9-mesityl-1,10-phenanthroline (145 mg, 270 µmol), $[Pd(PPh_3)_4]$ (14 mg, 12 µmol) were suspended in benzene (20 mL) and triethylamine (10 mL) under nitrogen. The reaction mixture was heated at 60 °C for 12 h and monitored by ESI-MS. It was then diluted with dichloromethane (100 mL) and washed with saturated NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The solid residue was purified by column chromatography (silica, ethylacetate:hexane 5:95) to obtain product **TP** as a light yellow solid (95.0 mg, 56.8 µmol, yield 71%). mp: >300°C; IR (KBr): $\tilde{\nu}$ = 2918, 2207, 1613, 1585, 1534, 1506, 1436, 1382, 1158, 844, 771, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 3H, 2-H), 8.31 (d, *J* = 8.0 Hz, 3H, 6-H), 7.93 (d, *J* = 9.0 Hz, 3H, 3-H), 7.90 (d, *J* = 9.0 Hz, 3H, 4-H), 7.59 (d, *J* = 8.0 Hz, 3H, 5-H), 6.69 (s, 3H, 1-H), 6.93

(s, 6H, 8-H), 2.49 (s, 18H, 7-H), 2.32 (s, 9H, 9-H), 2.12, (s, 18H, 10-H), 2.03 (s, 18H, 11-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 160.7, 145.9, 145.1, 139.2, 138.8, 138.0, 137.5, 136.2, 135.9, 133.9, 133.8, 133.6, 129.3, 128.5, 127.7, 127.3, 126.9, 125.7, 125.4, 123.6, 119.5, 93.5, 88.3, 21.1, 21.0, 20.6, 18.7; ESI-MS: calcd. for $[M+H]^+$: *m/z* 1673.6, found: *m/z* 1673.7, calcd. for $[M+2H]^{2+}$: *m/z* 837.3, found: *m/z* 837.5, calcd. for $[M+3H]^{3+}$: *m/z* 558.5, found: *m/z* 558.6; Anal. Calcd. for $C_{106}H_{91}Br_3N_6 \bullet 2H_2O$: C, 73.82; H, 5.55; N, 4.87; found C, 73.60; H, 5.17; N, 4.65.



1,3,5-Tribromobenzene (157 mg, 500 µmol), 4-pyridineboronic acid (250 mg, 2.03 mmol), [1,1'-bis(diphenyl-phosphino)ferrocene]palladium(II) chloride (1:1 complex with dichloromethane, 80mg, 98.0 µmol) and Na_2CO_3 (1.60 g, 15.1 mmol) were dissolved in a mixture of dioxane (20.0 mL) and H_2O (20.0 mL). After the mixture had been degassed by bubbling through a nitrogen flow for 10 min, it was heated to reflux for 2 days. Then, the mixture was cooled and dichloromethane (100 mL) was added. The organic phase was separated and washed twice with 40 mL of H_2O. After the solvent had been removed under reduced pressure, the solid residue was purified by chromatography on alumina to afford 1,3,5-trispyridylbenzene as a white solid (133 mg, 430 µmol, 86%). mp: >300°C; IR (KBr): $\tilde{\nu}$ = 3447, 3040, 1591, 1551, 1501, 1402, 1326, 1073, 992, 817, 611, 528 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD (4:1)): δ = 8.59 (d, *J* = 5.0 Hz, 6H, a'-H), 7.87 (s, 3H, c'-H), 7.59 (dd, *J* = 1.6 Hz, 5.0 Hz, 6H, b'-H); ^{13}C NMR (100 MHz, $CDCl_3$:CD_3OD (4:1)): δ = 149.8, 148.0, 140.1, 126.5, 122.2; ESI-MS: calcd. for $[M+H]^+$: *m/z* 310.1, found: *m/z* 310.6, calcd. for $[M+2H]^{2+}$: *m/z* 155.6, found: *m/z* 156.0; Anal. Calcd. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58; found C, 81.38; H, 4.96; N, 13.37.

General procedure for preparation of **P1**, **P2**, **P3** and **R1**: Ligand **TP** (3.72 mg, 2.22 µmol) and $[Cu(MeCN_4)]PF_6$ (2.49 mg, 6.66 µmol) were dissolved in a mixture of dichloromethane and acetonitrile (5.0 mL : 5.0 mL). After a clear yellow solution had formed, a solution of

ligand **BT1** (1.80 mg, 3.33 µmol) in dichloromethane was added dropwise. Then solvents were removed from the resulting dark red solution, and the solid residue was analysed by ESI-MS, ^{1}H NMR, UV-Vis and elemental analysis without any further purification.

P1 [Cu_6(**TP**)$_2$(**BT1**)$_3$(PF_6)$_6$]: IR (KBr): $\tilde{\nu}$ = 2920, 1608, 1475, 1399, 1158, 843, 770, 558 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN = 8:2): δ = 8.67-8.78 (m, 12H), 8.17-8.32 (m, 24H), 7.98-8.08 (m, 12H), 7.80-7.82 (m, 6H), 7.50-7.62 (m, 24H), 7.12 (s, 12H), 6.66 (s, 6H), 6.31 (s, 12H), 1.68-1.84 (m, 54H), 1.38-1.52 (m, 54H), 1.25 (s, 18H); ESI-MS: Calcd. for [M-3PF_6^-]$^{3+}$: *m/z* 1927.7, found: *m/z* 1927.4, Calcd. for [M-4PF_6^-]$^{4+}$: *m/z* 1409.5, found: *m/z* 1409.4, Calcd. for [M-5PF_6^-]$^{5+}$: *m/z* 1098.6, found: *m/z* 1098.2, Calcd. for [M-6PF_6^-]$^{6+}$: *m/z* 891.4, found: *m/z* 891.4.

P2 [Cu_6(**TP**)$_2$(**BT2**)$_3$(PF_6)$_6$]: IR (KBr): $\tilde{\nu}$ = 2921, 2209, 1607, 1475, 1421, 1385, 1158, 844, 770, 557 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN = 8:2): δ = 8.79-8.81 (m, 6H), 8.63-8.67 (m, 6H), 8.25-8.27 (m, 12H), 7.76-7.93 (m, 24H), 7.46-7.60 (m, 42H), 7.12 (s, 12H), 6.98 (s, 6H), 6.18 (s, 12H), 2.13-2.19 (m, 36H), 1.69-1.88 (m, 54H), 1.46 (s, 36H), 1.41 (s, 18H), 1.25 (s, 18H); ESI-MS: Calcd. for [M-4PF_6^-]$^{4+}$: *m/z* 1527.7, found: *m/z* 1527.6, Calcd. for [M-5PF_6^-]$^{5+}$: *m/z* 1192.4, found: *m/z* 1192.7, Calcd. for [M-6PF_6^-]$^{6+}$: *m/z* 969.5, found: *m/z* 969.4.

P3 [Cu_6(**TP**)$_2$(**BT3**)$_3$(PF_6)$_6$]: IR (KBr): $\tilde{\nu}$ = 3448, 2917, 2212, 1607, 1475, 1427, 1384, 996, 843, 792, 558 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN = 8:2): δ = 8.78-8.88 (m, 18H), 8.44-8.75 (m, 36H), 8.15-8.42 (m, 24H), 7.85-8.13 (m, 12H), 7.72-7.92 (m, 12H), 7.42-7.68 (m, 24H), 6.85-7.32 (m, 24H), 6.75 (s, 6H), 6.32 (s, 12H), 2.20-2.55 (m, 36H), 1.67-1.88 (m, 54H), 1.40-1.66 (m, 81H), 1.25 (s, 9H); ESI-MS: Calcd. for [M-4PF_6^-]$^{4+}$: *m/z* 1922.6, found: *m/z* 1921.9, Calcd. for [M-5PF_6^-]$^{5+}$: *m/z* 1509.1, found: *m/z* 1513.5, Calcd. for [M-6PF_6^-]$^{6+}$: *m/z* 1233.4, found: *m/z* 1233.0.

R1 [Cu_3(**TP**)(**Terpy**)$_3$(PF_6)$_3$]: mp: >300 C; IR (KBr): $\tilde{\nu}$ = 3442, 2919, 2212, 1584, 1506, 1446, 1384, 1158, 843, 770, 558 cm^{-1}; ESI-MS: Calcd. for [M-2PF_6^-]$^{2+}$: *m/z* 1354.0, found: *m/z* 1353.6, Calcd. for [M-3PF_6^-]$^{3+}$: *m/z* 854.3, found: *m/z* 855.0; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.73 (s, 3H, 2-H), 8.64 (d, *J* = 8.3 Hz, 3H, 6-H), 8.26 (d, *J* = 9.1 Hz, 3H, 3-H), 8.20 (d, *J* = 9.1 Hz, 3H, 4-H), 8.08 (t, *J* = 7.6 Hz, 3H, f"-H), 8.00 (d, *J* = 7.6 Hz, 6H, e"-H), 7.85 (d, *J* = 7.8 Hz, 6H, d"-H), 7.78 (d, *J* = 8.3 Hz, 3H, 5-H), 7.64 (t, *J* = 7.8 Hz, 6H, c"-H), 7.48 (d, *J* = 6.4 Hz, 6H, a"H), 7.08 (dd, *J* = 6.4 Hz, *J* = 7.8 Hz, 6H, b"H), 6.59 (s, 3H, 1-H), 6.26 (s, 6H, 8-H), 1.90 (s, 9H, 9-H), 1.77 (s, 18H, 10-H), 1.48, (s, 18H, 7-H), 1.37 (s, 18H,

11-H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 160.5, 160.0, 152.4, 152.3, 147.9, 144.0, 142.8, 139.4, 138.7, 138.1, 138.0, 137.3, 137.2, 137.0, 135.0, 134.5, 133.5, 132.8, 129.4, 128.7, 128.1, 127.9, 127.7, 127.4, 126.5, 124.8, 123.2, 122.8, 122.0, 117.0, 94.3, 87.1, 20.7, 20.5, 19.8, 18.2; Anal. Calcd. for $C_{150}H_{120}Br_3Cu_3F_{18}N_{15}P_3$•$2CH_2Cl_2$: C, 57.63; H, 3.95; N, 6.63; found: C, 57.52; H, 4.01; N, 6.69.

General procedure for preparation of **P4**, **P5** and **P6:** Ligand **tpy1** (0.47 mg, 1.1 μmol in dichloromethane), **tpy2** (0.34 mg, 1.1 μmol in dichloromethane) and C_{60} (0.80 mg, 1.1 μmol in carbon disulphide) were added dropwise to a solution of **P3** in acetonitrile to form **P4**, **P5** and **P6**, respectively. After removal of the solvents, the resulting solid residues were analyzed by ESI-MS, ^{1}H NMR, ^{13}C NMR, UV-Vis and elemental analysis without any further purification.

P4 [Cu_6(**TP**)$_2$(**BT3**)$_3$(**tpy1**)$(PF_6)_6$]: IR (KBr): $\tilde{\nu}$ = 3430, 2918, 2206, 1604, 1476, 1428, 1202, 995, 844, 793, 558 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN = 8:2): δ = 8.76-8.85 (m, 12H), 8.46-8.74 (m, 36H), 8.20-8.42 (m, 18H), 8.05-8.20 (m, 12H), 7.77-8.03 (m, 18H), 7.44-7.72 (m, 24H), 7.05-7.30 (m, 24H), 6.82-7.02 (m, 12H), 6.72 (s, 6H), 6.34 (s, 12H), 5.5-40-5.50 (m, 6H), 2.40-2.60 (m, 36H), 2.20-2.35 (m, 18H), 2.03-2.18 (m, 54H), 1.40-1.78 (m, 72H), 1.25 (s, 9H); ESI-MS: Calcd. for [M-5PF_6^-]$^{5+}$: *m/z* 1593.8, found: *m/z* 1593.7, Calcd. for [M-6PF_6^-]$^{6+}$: *m/z* 1304.0, found: *m/z* 1304.8; Anal. Calcd. for $C_{480}H_{369}Br_6Cu_6F_{36}N_{45}P_6Zn_3$• $4CH_2Cl_2$: C, 64.35; H, 4.21; N, 6.98; found: C, 64.24; H, 4.17; N, 7.01.

P5 [Cu_6(**TP**)$_2$(**BT3**)$_3$(**tpy2**)$(PF_6)_6$]: mp: >300°C; IR (KBr): $\tilde{\nu}$ = 3433, 2917, 2213, 1605, 1477, 1428, 1337, 1202, 995, 843, 793, 558 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN (8:2)): δ = 8.81 (d, *J* = 4.3 Hz, 12H, h-H) 8.75 (s, 6H, 2-H), 8.66-8.70 (m, 18H, i-, 6-H), 8.42 (s, 12H, e-H), 8.29 (d, *J* = 9.1 Hz, 6H, 3-H), 8.20-8.29 (m, 12H, d-H), 8.20 (d, *J* = 9.1 Hz, 6H, 4-H), 8.04-8.06 (m + d, *J* = 7.8 Hz, 24H, f-, g-H), 7.91 (s, 3H, c'-H), 7.83 (d, *J* = 8.0 Hz, 6H, 5-H), 7.65 (t, *J* = 7.8 Hz, 12H, c-H), 7.58 (d, *J* = 5.4 Hz, 12H, a-H), 7.32 (s, 12H, j-H), 7.14 (dd, *J* = 5.4 Hz, *J* = 7.8 Hz, 12H, b-H), 6.86 (s, 6H, 1-H), 6.33 (s, 12H, 8-H), 5.71 (br s, 6H, a'-H), 5.13 (br s, 6H, b'-H), 2.66 (s, 18H, l-H), 1.85 (s, 18H, 9-H), 1.76 (s, 36H, K-H), 1.64 (s, 36H, 11-H), 1.52 (s, 36H, 7-H), 1.38 (s, 36H, 10-H); ^{13}C NMR (150 MHz, CD_2Cl_2/CD_3CN (8:2)): δ = 159.2, 158.9, 152.2, 151.6, 149.2, 148.9, 147.2, 146.0, 144.2, 143.2, 142.1, 139.1, 138.8, 138.5, 138.4, 138.0, 137.3, 137.0, 136.7, 136.6, 136.2, 135.8, 134.9, 134.3, 133.6, 132.5, 132.0, 131.4, 129.9, 128.3, 128.2, 128.0, 127.3, 127.1, 127.0, 126.8, 126.7, 125.6, 125.0,

124.2, 122.3, 121.4, 121.3, 120.8, 120.4, 119.6, 118.4, 118.3, 118.2, 92.6, 85.8, 20.9, 20.5, 19.8, 19.4, 18.8, 17.2; ESI-MS: Calcd. for $[M\text{-}5PF_6^-]^{5+}$: *m/z* 1571.0, found: *m/z* 1570.5, Calcd. for $[M\text{-}6PF_6^-]^{6+}$: *m/z* 1285.0, found: *m/z* 1284.3; Anal. Calcd. for $C_{471}H_{363}Br_6Cu_6F_{36}N_{45}P_6Zn_3 \bullet 5CH_2Cl_2$: C, 63.49; H, 4.18; N, 7.00; found: C, 63.24; H, 4.11; N, 7.05.

P6 $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{C_{60}})(PF_6)_6]$: mp: >300°C; IR (KBr): $\tilde{\nu}$ = 3450, 2917, 2214, 1606, 1585, 1476, 1428, 1383, 996, 843, 792, 557 cm^{-1}; ^1H NMR (400 MHz, CD_3CN): δ = 8.85 (d, *J* = 8.3 Hz, 6H, 6-H), 8.77 (s, 6H, 2-H), 8.65-8.50 (m, 36H, e-, h-, i-H), 8.39 (d, *J* = 9.1 Hz, 6H, 3-H), 8.32 (d, *J* = 8.0 Hz, 12H, g-H), 8.27 (d, *J* = 9.1 Hz, 6H, 4-H), 7.96 (d, *J* = 8.3 Hz, 6H, 5-H), 7.93 (d, *J* = 8.0 Hz, 12H, f-H), 7.56-7.54 (m, 12H, d-H), 7.45-7.38 (m, 12H, c-H), 7.31-7.29 (m, 12H, a-H), 7.01-7.03 (m, 12H, b-H), 6.98 (s, 12H, j-H), 6.60 (s, 6H, 8-H), 6.58 (s, 6H, 8-H), 6.50 (s, 6H, 1-H), 2.08 (s, 18H, l-H), 2.07 (s, 18H, 9-H), 1.84 (s, 36H, k_1-, 11_1-H), 1.82 (s, 18H, 7_1-H), 1.68 (s, 18H, 7_2-H), 1.64 (s, 18H, 11_2-H), 1.62 (s, 18H, 10_1-H), 1.34 (s, 18H, k_2-H), 1.28 (s, 18H, 10_2-H); ^{13}C NMR (100 MHz, CD_3CN): δ = 160.8, 160.6, 154.4, 154.2, 154.0, 152.8, 150.8, 150.0, 149.8, 149.2, 148.8, 145.8, 144.9, 143.6, 141.0, 140.2, 139.6, 139.4, 139.2, 138.9, 138.5, 138.4, 138.0, 137.4, 137.0, 136.7, 136.2, 136.0, 134.8, 134.3, 134.1, 133.9, 133.8, 132.5, 131.9, 131.5, 131.0, 129.8, 129.7, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 127.2, 126.9, 126.7, 126.4, 125.4, 123.9, 123.5, 123.1, 121.9, 121.0, 119.7, 119.4, 94.4, 88.1, 24.2, 21.4, 21.3, 21.1, 21.0, 20.2, 20.1, 19.8, 18.8, 18.7; ESI-MS: Calcd. for $[M\text{-}5PF_6^-]^{5+}$: *m/z* 1653.3, found: *m/z* 1652.9, Calcd. for $[M\text{-}6PF_6^-]^{6+}$: *m/z* 1353.6, found: *m/z* 1353.2; Anal. Calcd. for $C_{520}H_{348}Br_6Cu_6F_{36}N_{42}P_6Zn_3 \bullet 5CH_2Cl_2$: C, 65.69; H, 3.83; N, 6.25; found: C, 65.56; H, 3.70; N, 6.21.

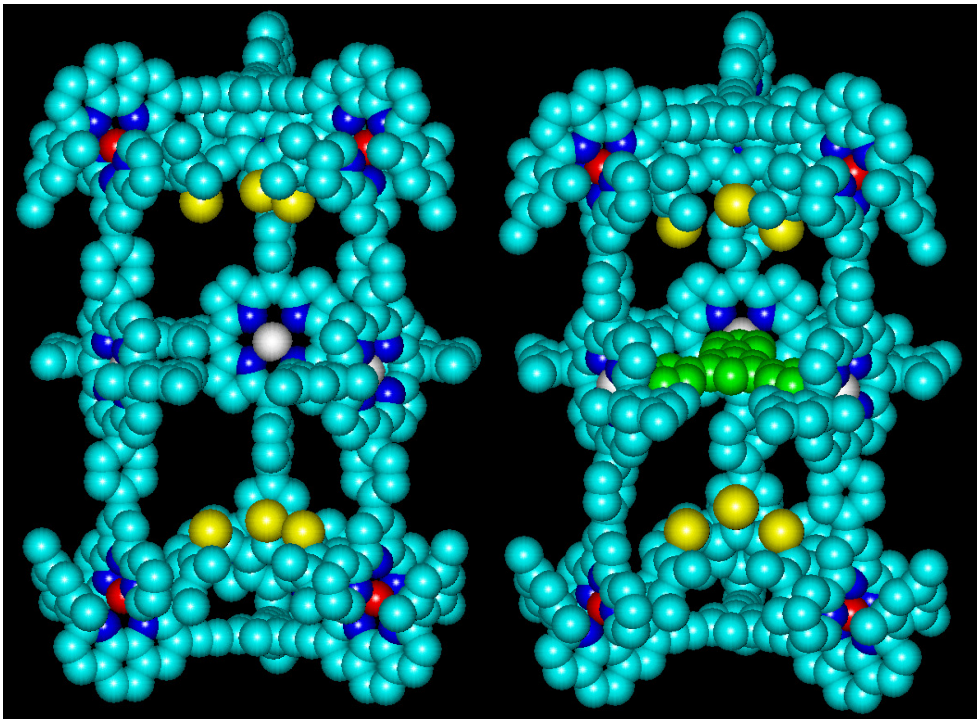
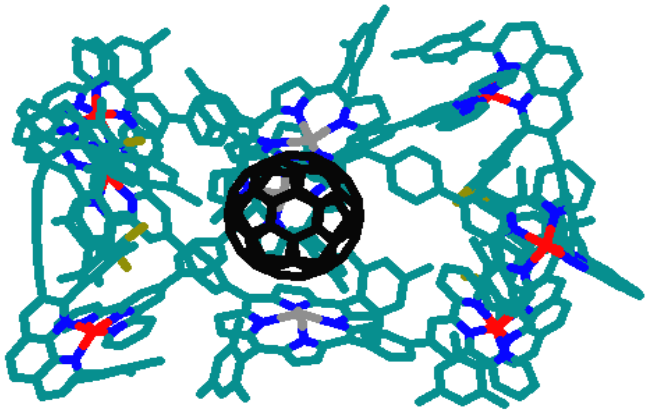
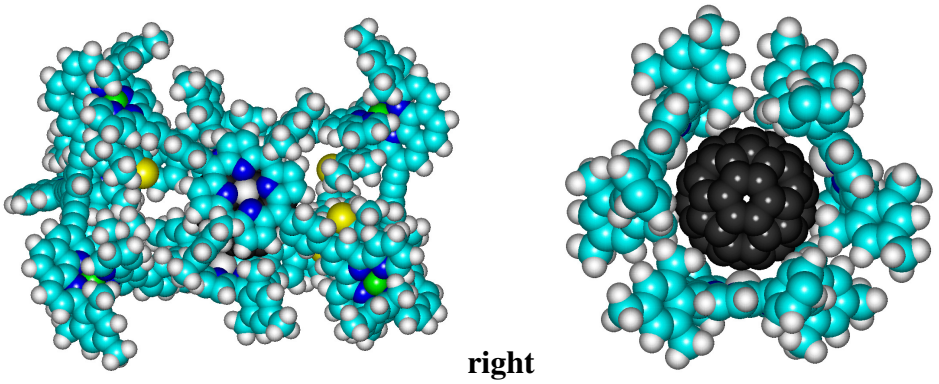


Figure S1. Side view of the space-filling model of prisms **P3** (left) and **P5** (right) generated from force field modelling (HyperChem®). The atoms and **tpy2** are colour coded for clarity: carbon: cyan; nitrogen: blue; bromine: yellow; copper: red; zinc: white; **Tpy2** ligand: green.

Top

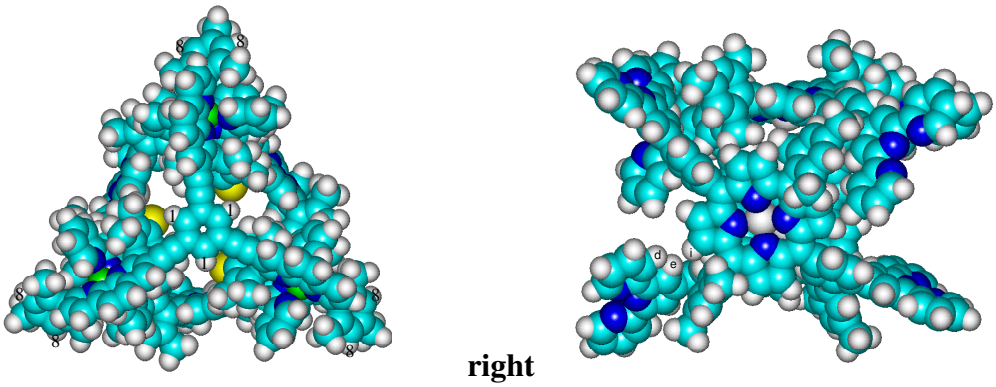


Middle



left **right**

Bottom



left **right**

Figure S2. Side view of prism **P6** generated from force field modelling (HyperChem®)**:** stick model (top) and space-filling model (middle, left). Middle right: Arrangement of three porphyrin units around the C_{60} unit. Bottom left: Positioning of l-H (**TP**) in the shielding region of the duryl group. Bottom right: Possible contact of d-H with i-H

The atoms are color coded for clarity: hydrogen: white; carbon: cyan; nitrogen: blue; bromine: yellow; copper: red; zinc: grey.

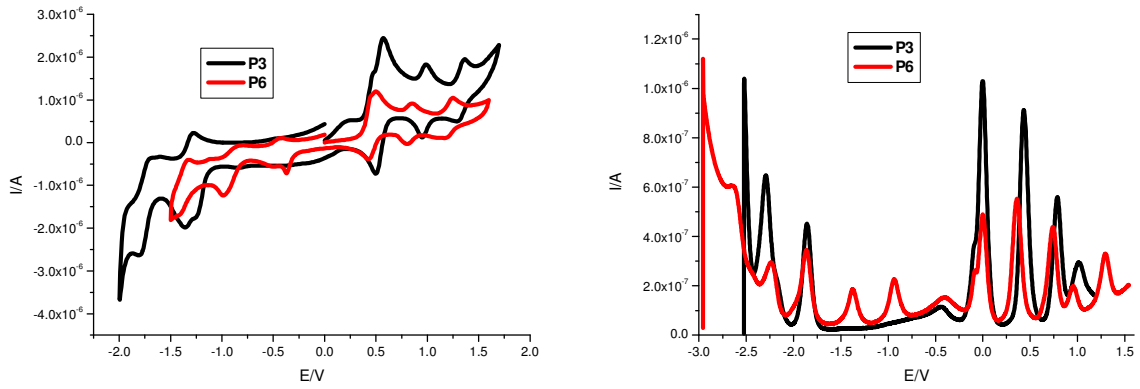


Figure S3. CVs (left) and DPVs (right) of **P3** (black) and **P6** (red) measured in a mixture of actonitrile and THF (1:1) using ferrocene as internal standard.

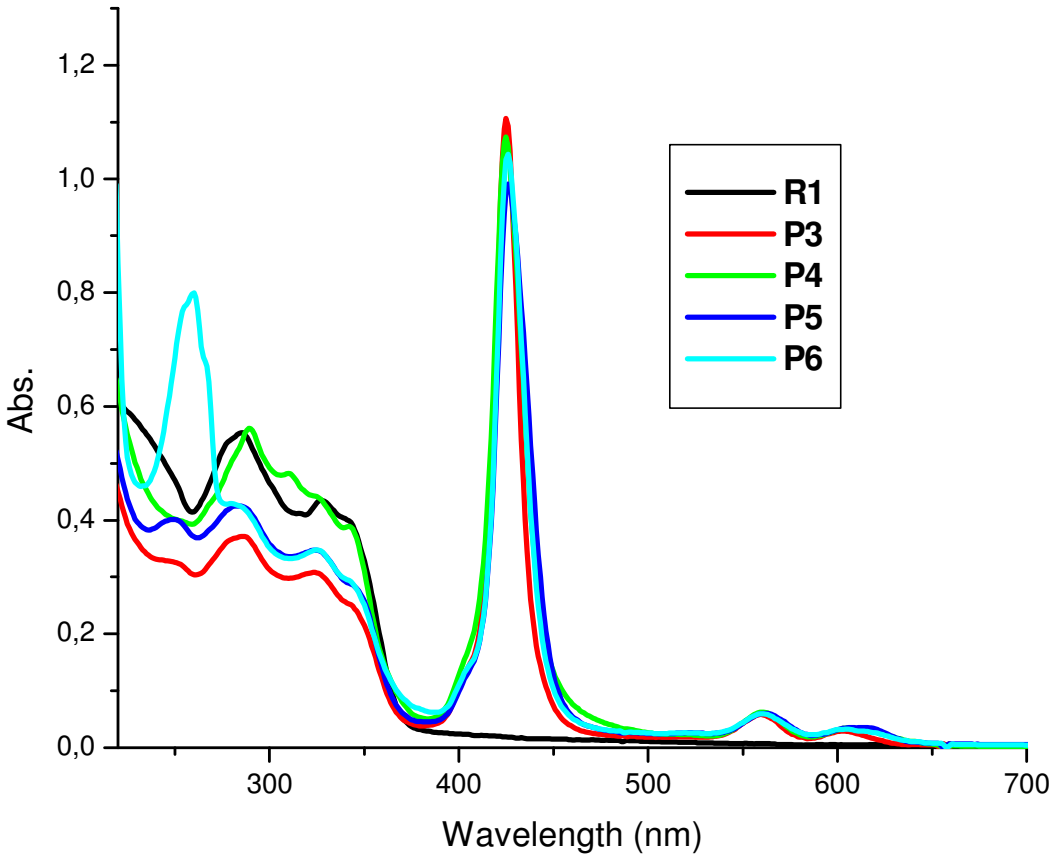


Figure S4. UV-Vis spetra of **R1**, **P3**, **P4**, **P5** and **P6**.

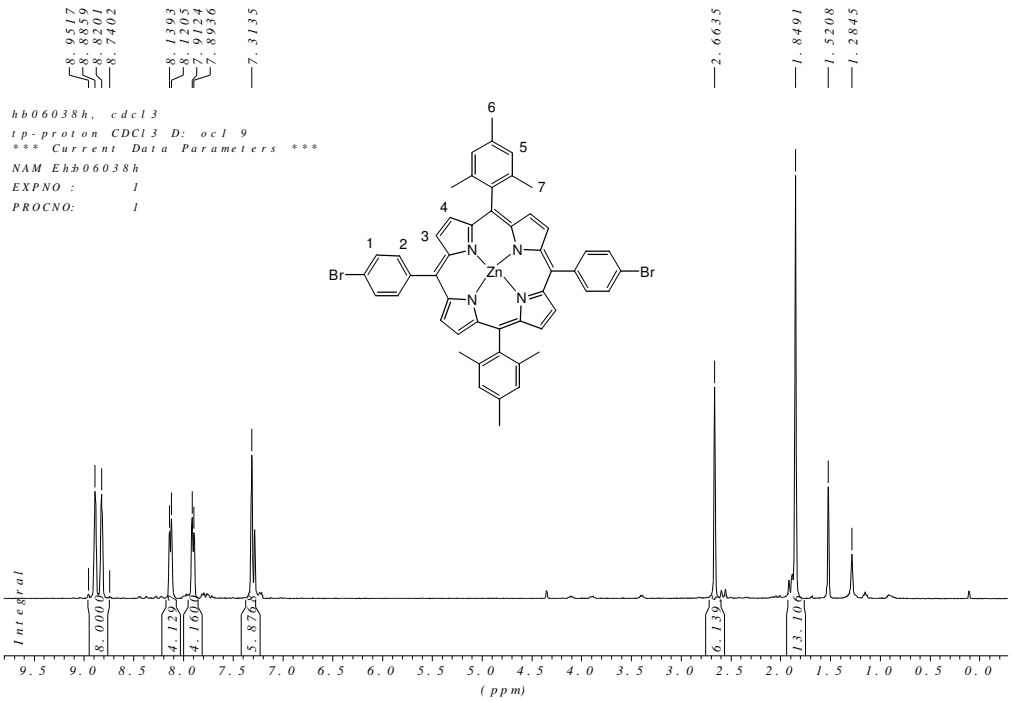


Figure S5. ^{1}H NMR spectrum of zinc(II)-5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrin (**1**)

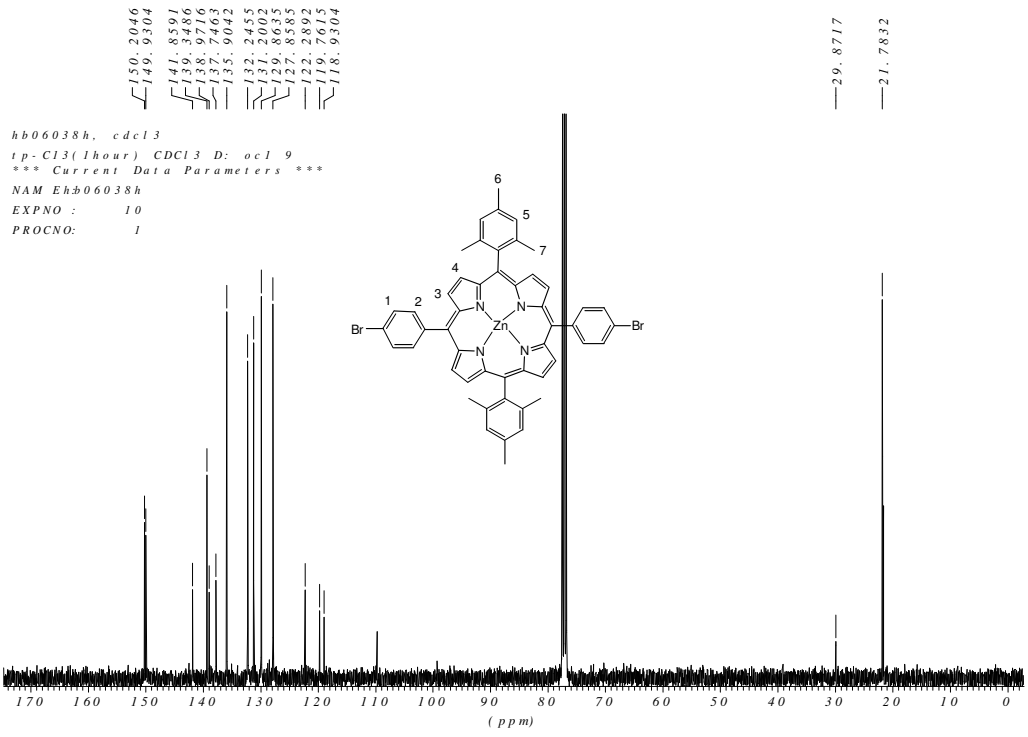


Figure S6. ^{13}C NMR spectrum of zinc(II)-5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrin (**1**)

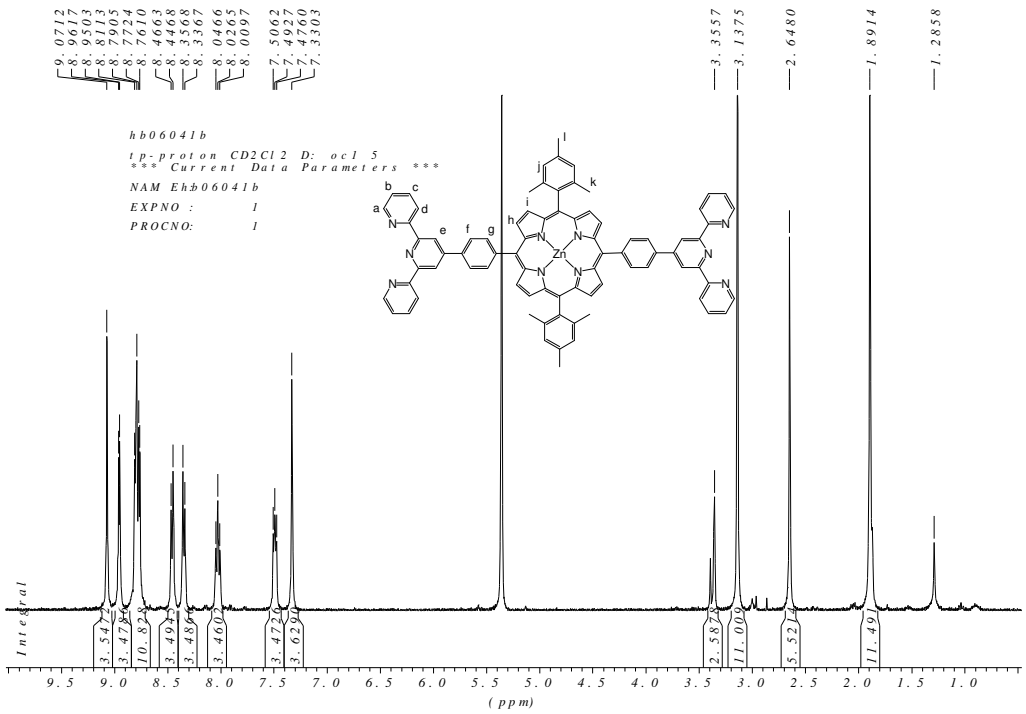


Figure S7. ^{1}H NMR spectrum of **BT3.**

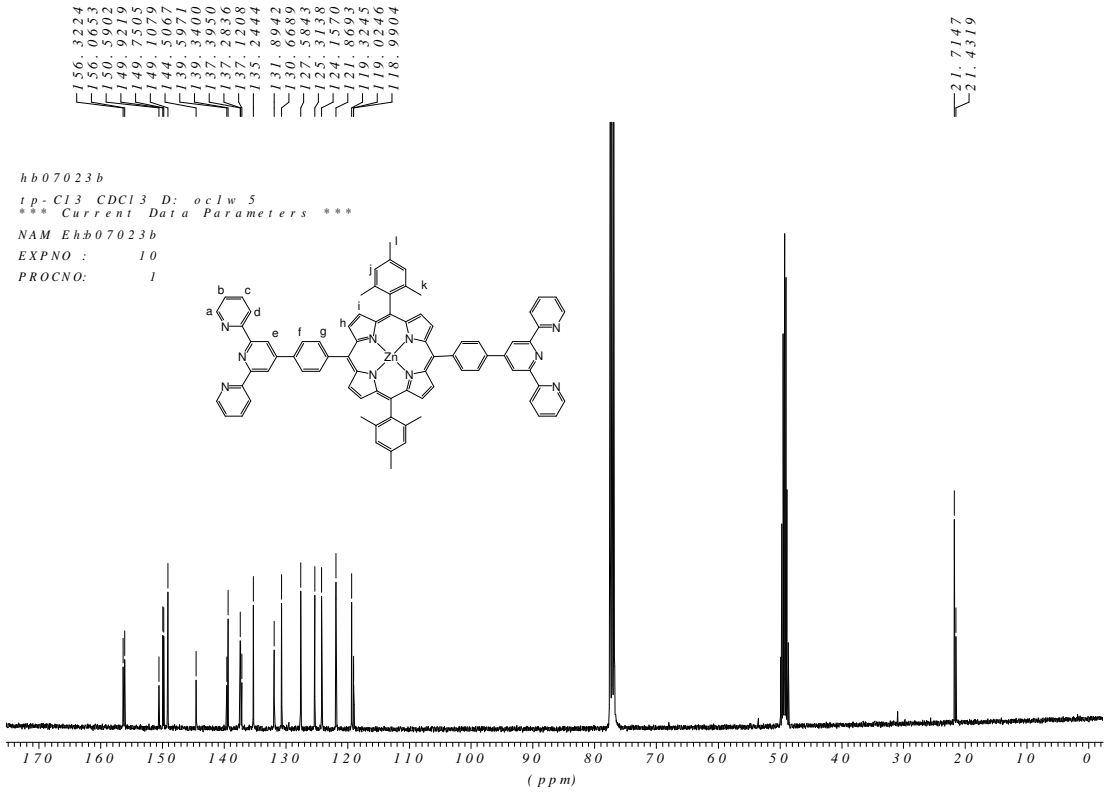


Figure S8. ^{13}C NMR spectrum of **BT3.**

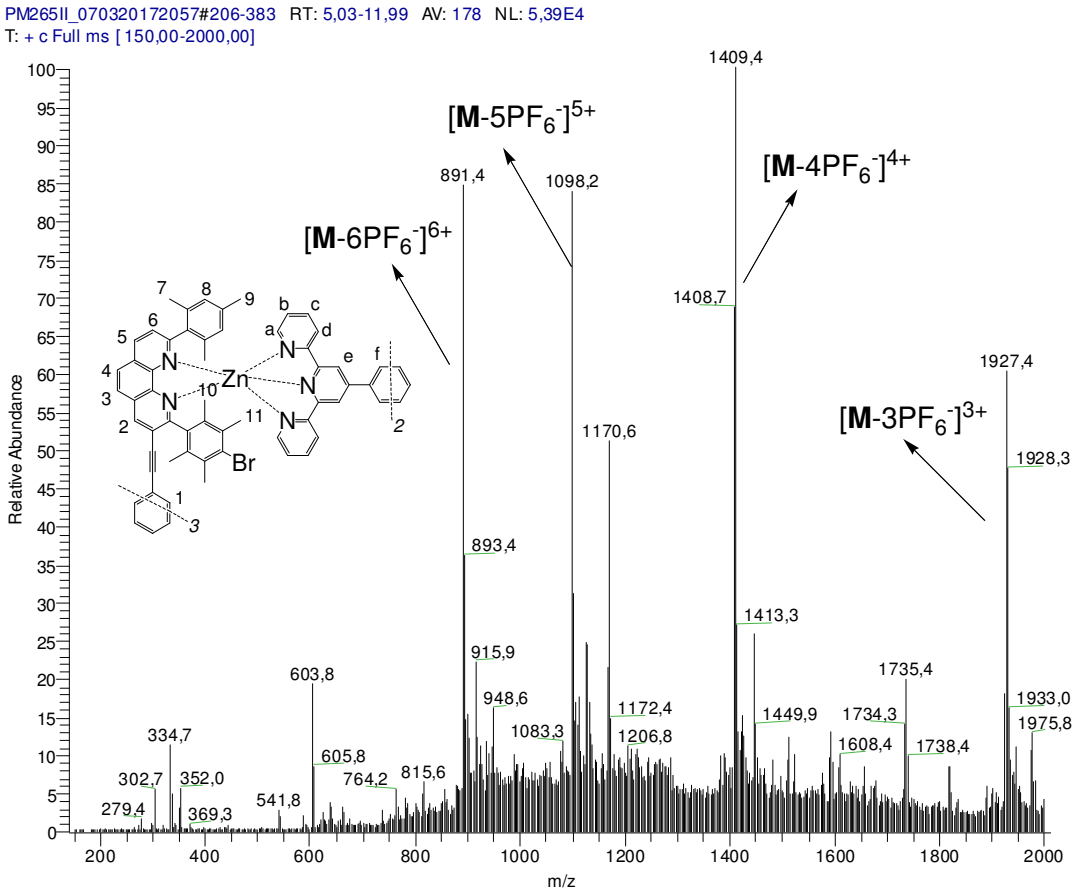


Figure S9. ESI-MS of **P1** $[Cu_6(\mathbf{TP})_2(\mathbf{BT1})_3(PF_6)_6]$.

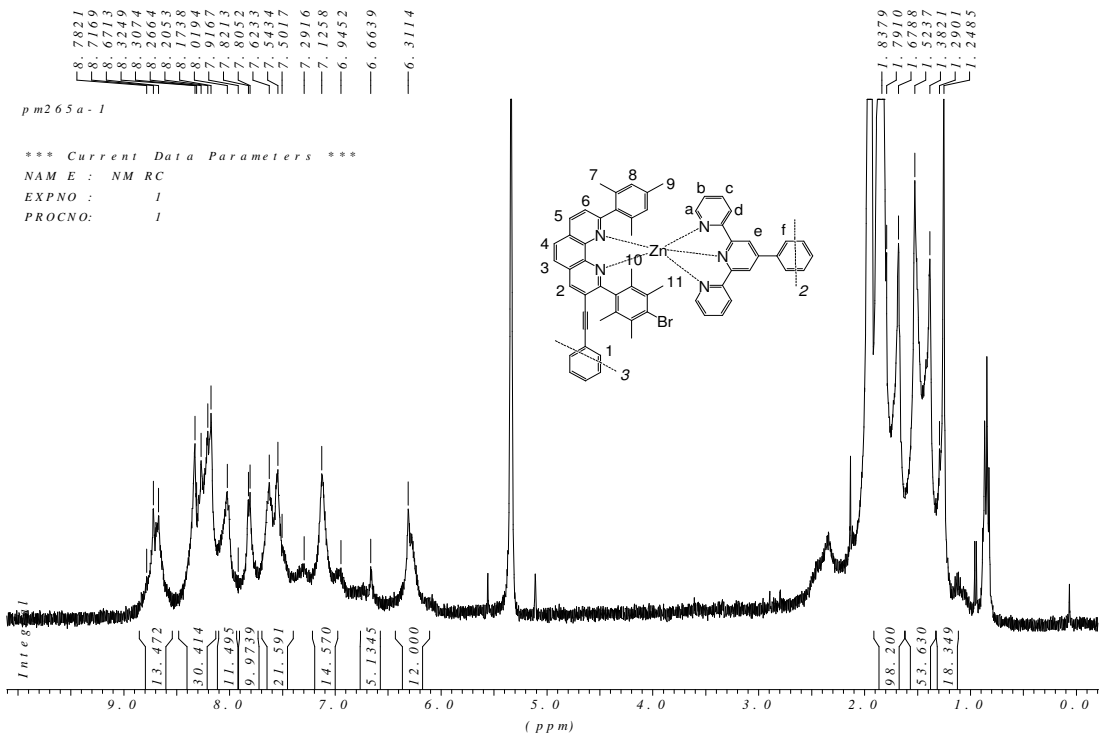


Figure S10. ^{1}H NMR spectrum of **P1** $[Cu_6(\mathbf{TP})_2(\mathbf{BT1})_3(PF_6)_6]$.

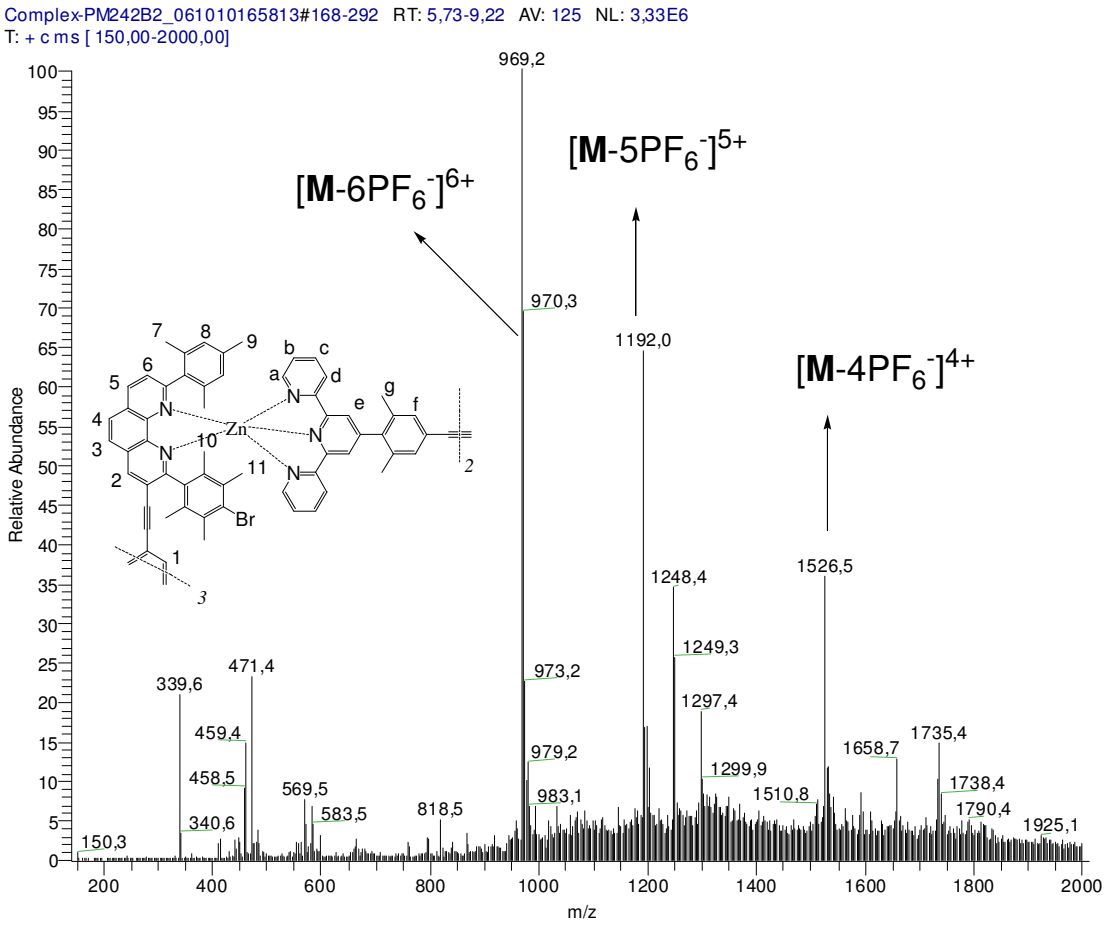


Figure 11. ESI-MS of **P2** $[Cu_6(\mathbf{TP})_2(\mathbf{BT2})_3(PF_6)_6]$.

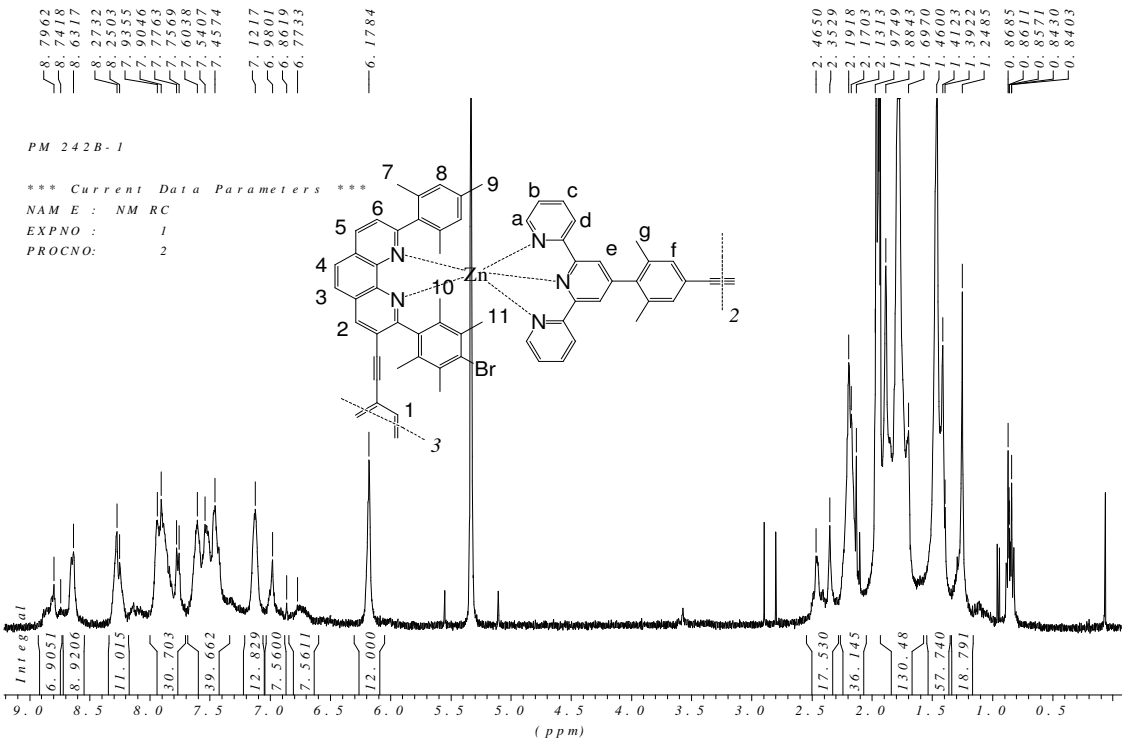


Figure S12. ^{1}H NMR spectrum of **P2** $[Cu_6(\mathbf{TP})_2(\mathbf{BT2})_3(PF_6)_6]$.

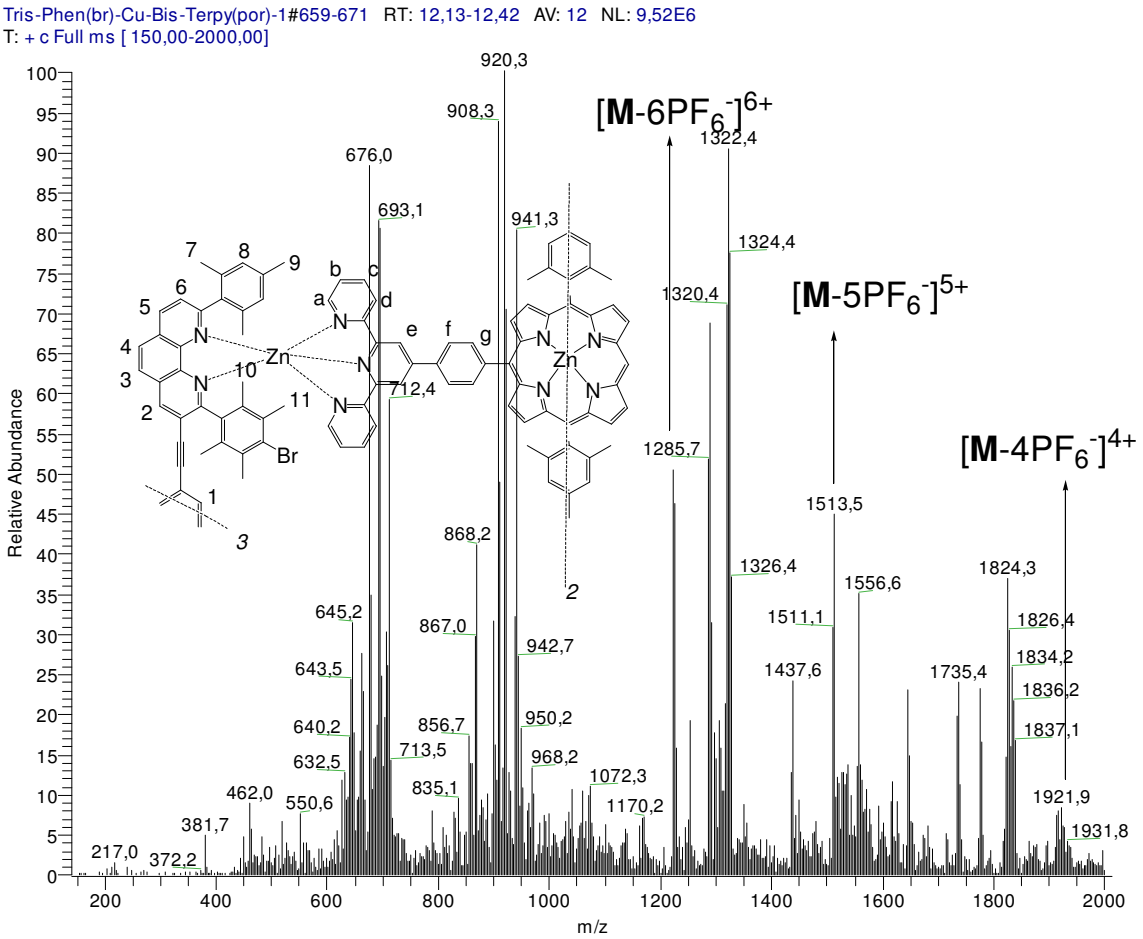


Figure S13. ESI-MS of **P3** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(PF_6)_6]$.

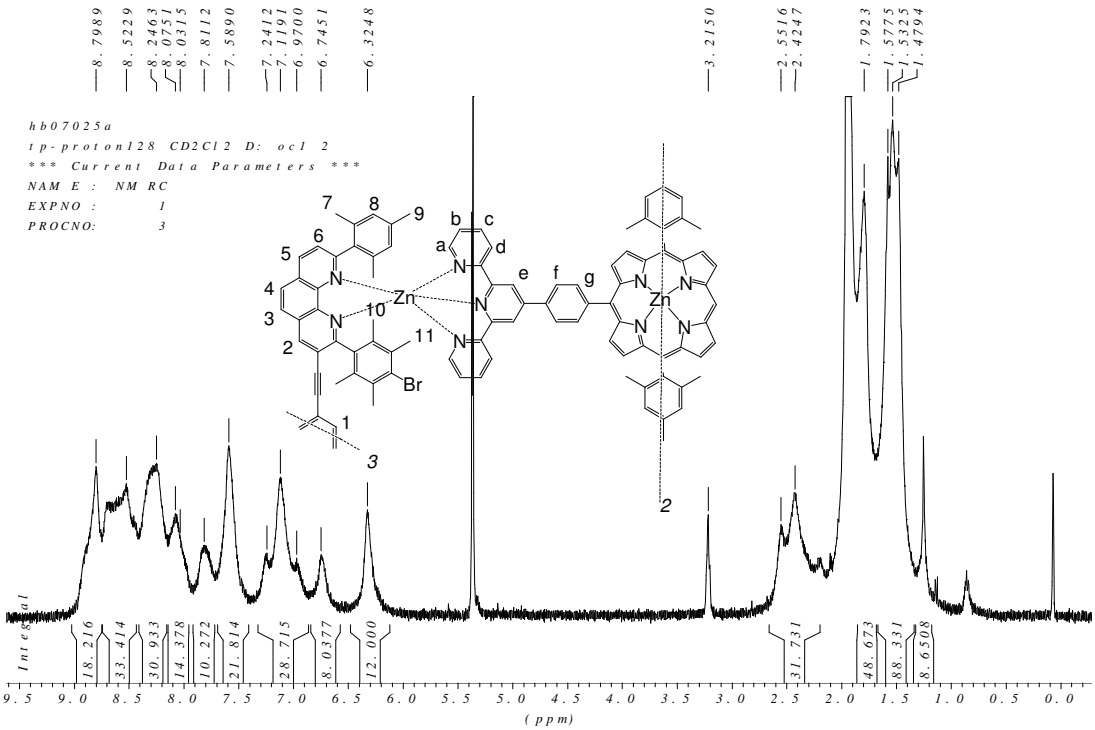


Figure S14. ^{1}H NMR spectrum of **P3** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(PF_6)_6]$.

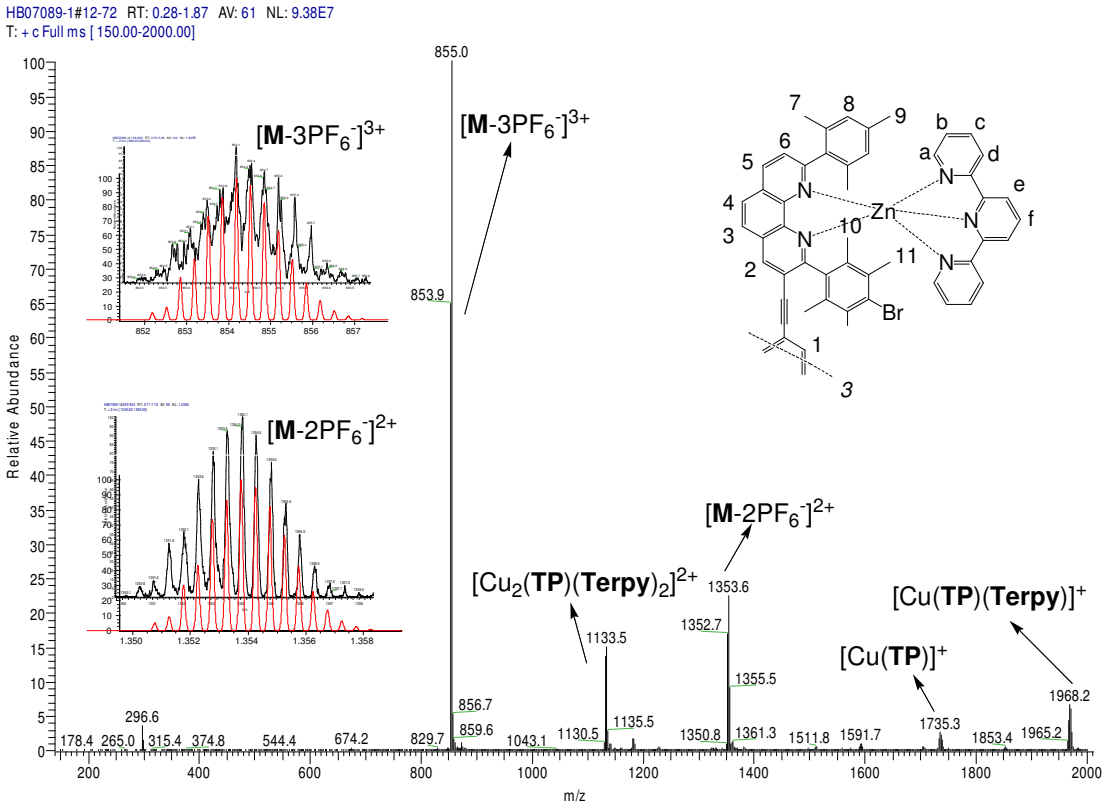


Figure S15. ESI-MS of **R1** [Cu_3(**TP**)(**Terpy**)$_3$(PF_6)$_3$].

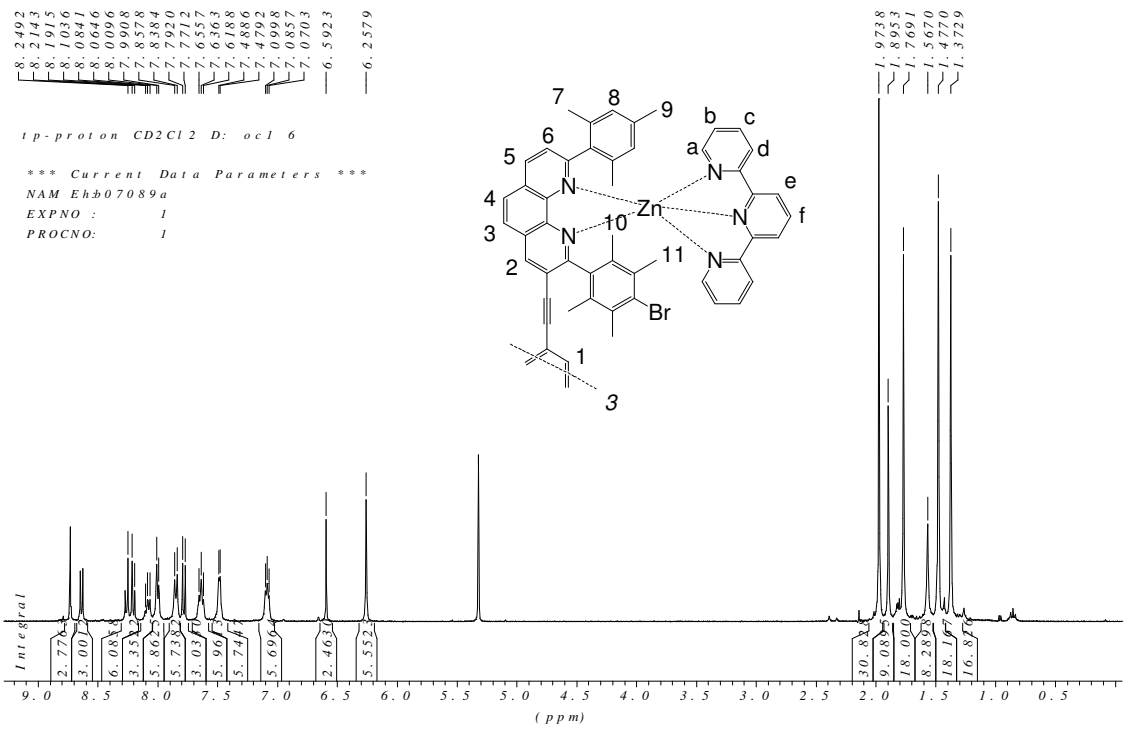


Figure S16. ^{1}H NMR spectrum of **R1** [Cu_3(**TP**)(**Terpy**)$_3$(PF_6)$_3$].

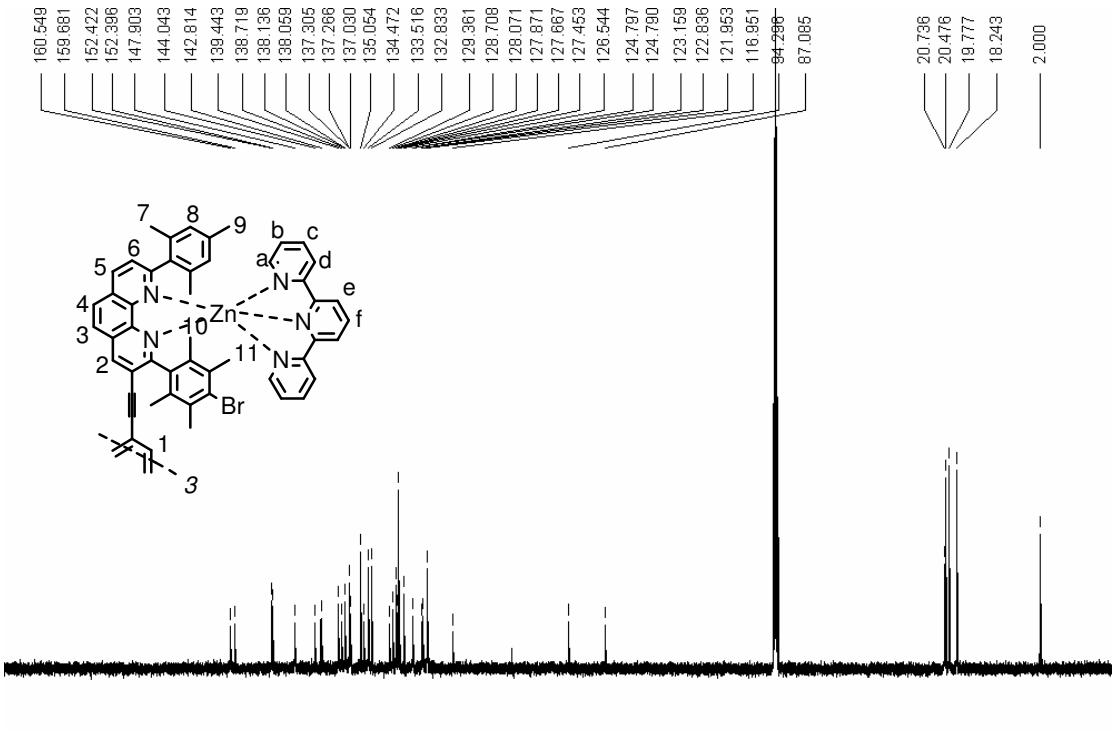


Figure S17. ^{13}C NMR spectrum of **R1** [Cu_3(**TP**)(**Terpy**)$_3$(PF_6)$_3$].

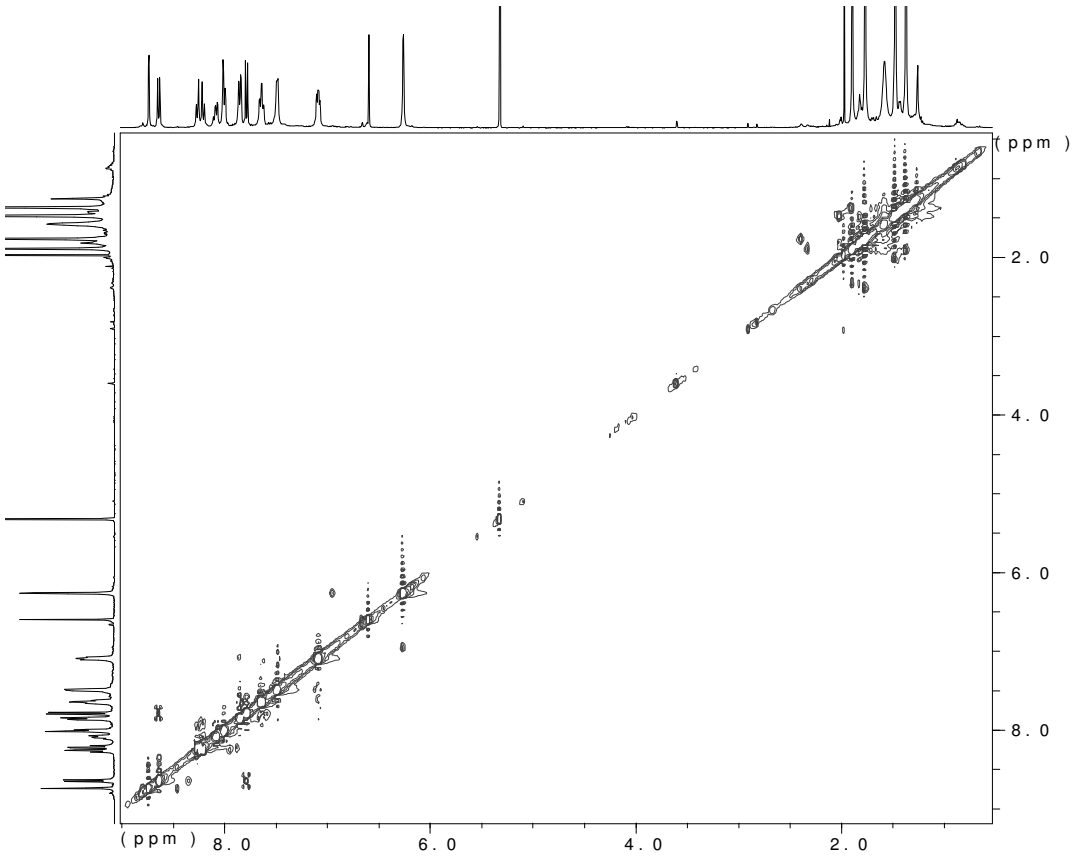


Figure S18. NOESY spectrum of **R1** [Cu_3(**TP**)(**Terpy**)$_3$(PF_6)$_3$].

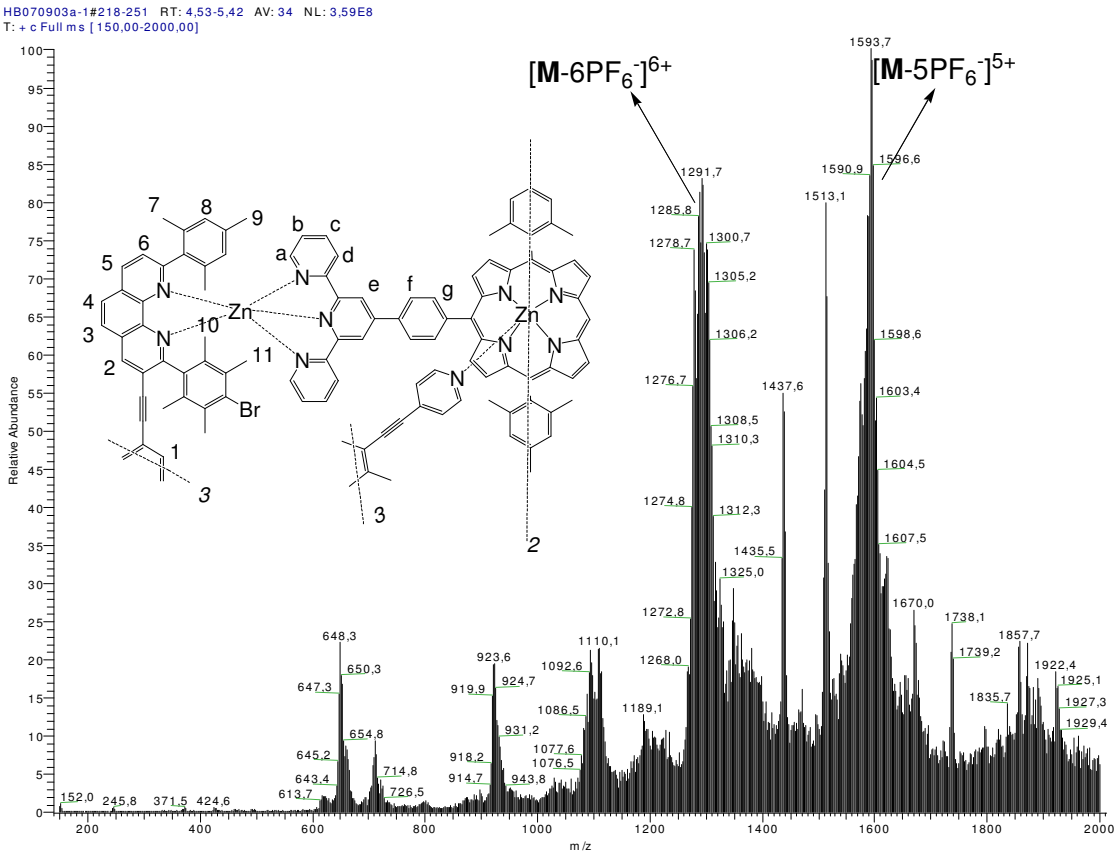


Figure S19. ESI-MS of **P4** [Cu_6(**TP**)$_2$(**BT3**)$_3$(**tpy1**)$(PF_6)_6$].

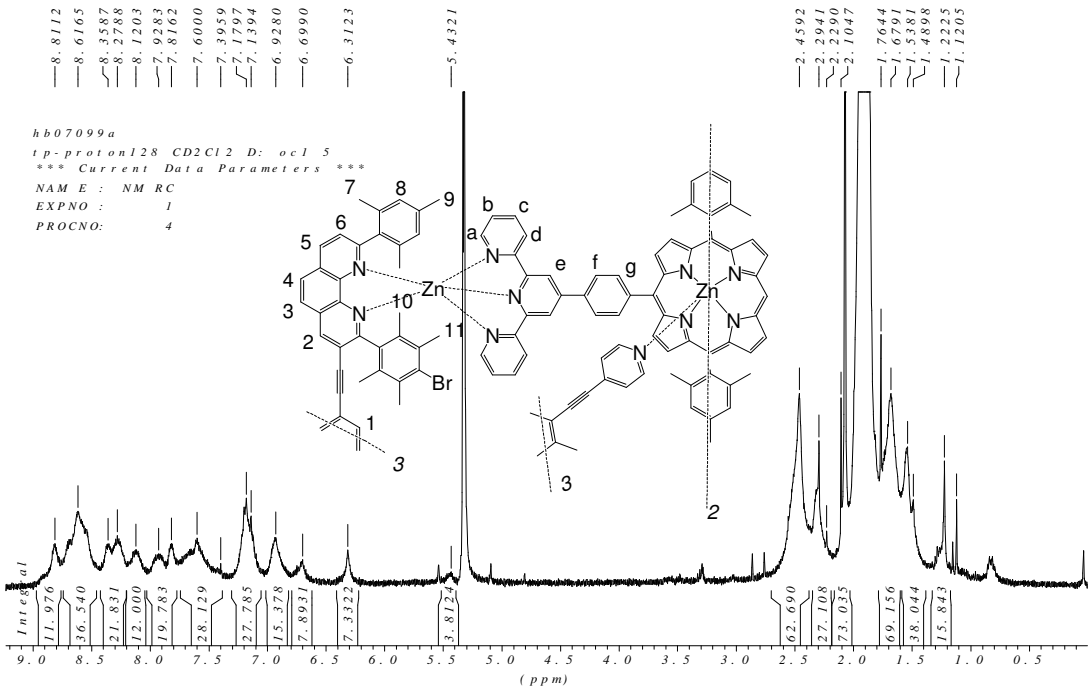


Figure S20. ^{1}H NMR spectrum of **P4** [Cu_6(**TP**)$_2$(**BT3**)$_3$(**tpy1**)$(PF_6)_6$].

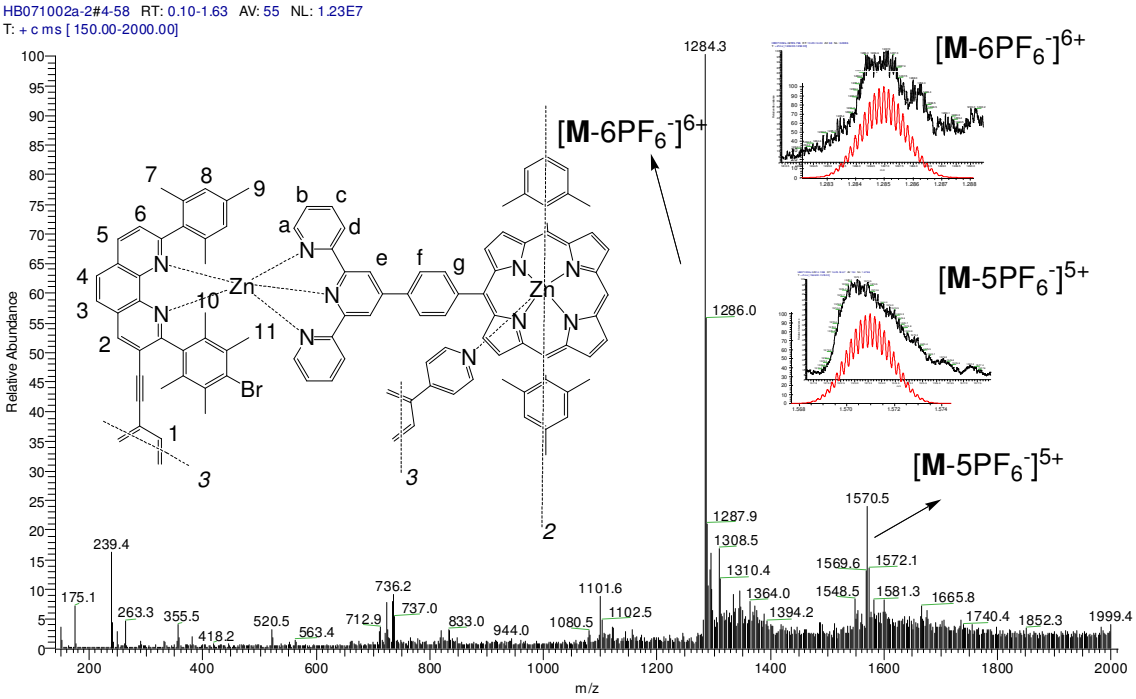


Figure S21. ESI-MS spectrum of **P5** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{tpy2})(PF_6)_6]$.

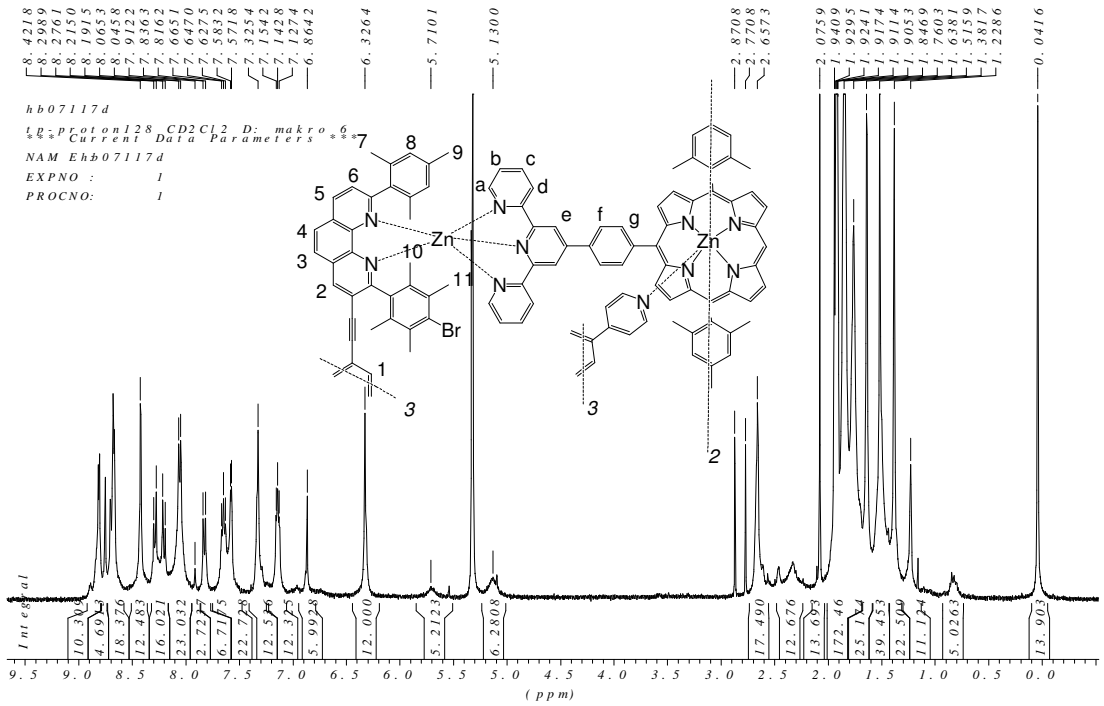


Figure S22. ^{1}H NMR spectrum of **P5** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{tpy2})(PF_6)_6]$.

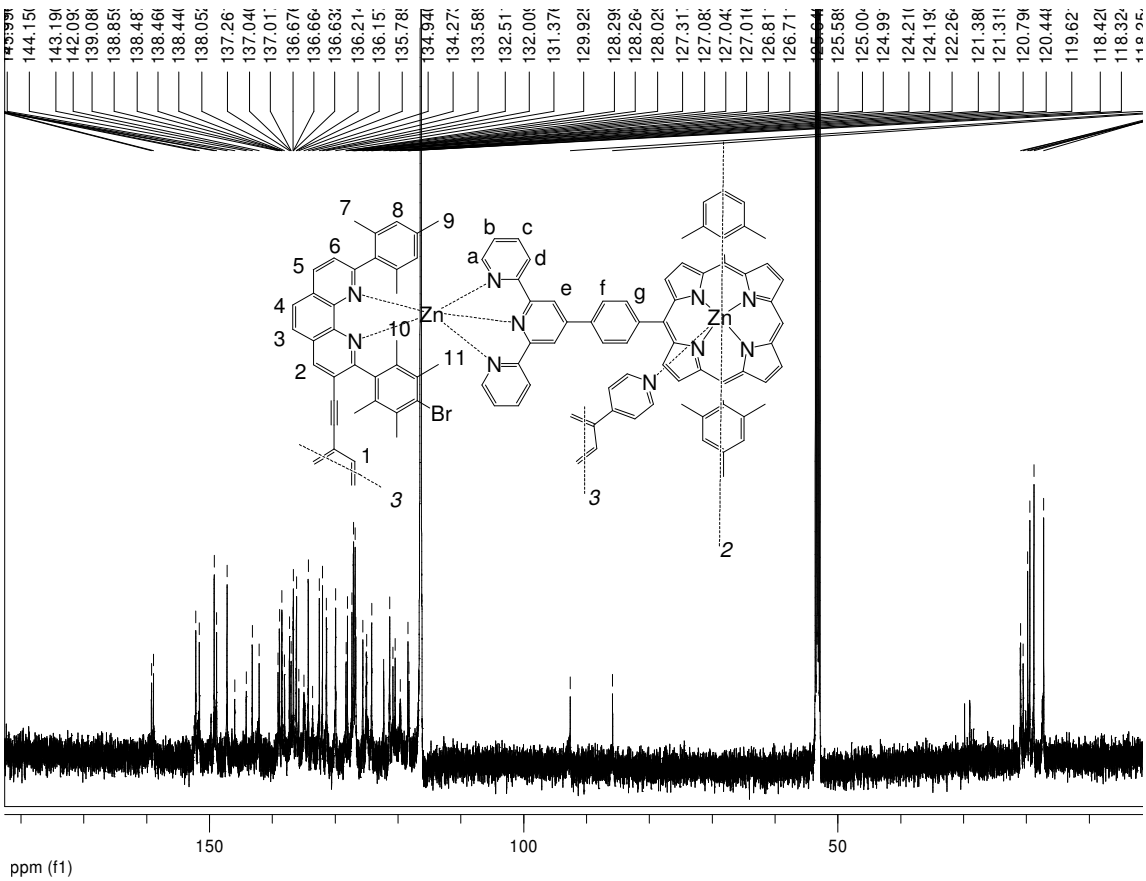


Figure 23. C^{13} NMR spectrum of **P5** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{tpy2})(PF_6)_6]$.

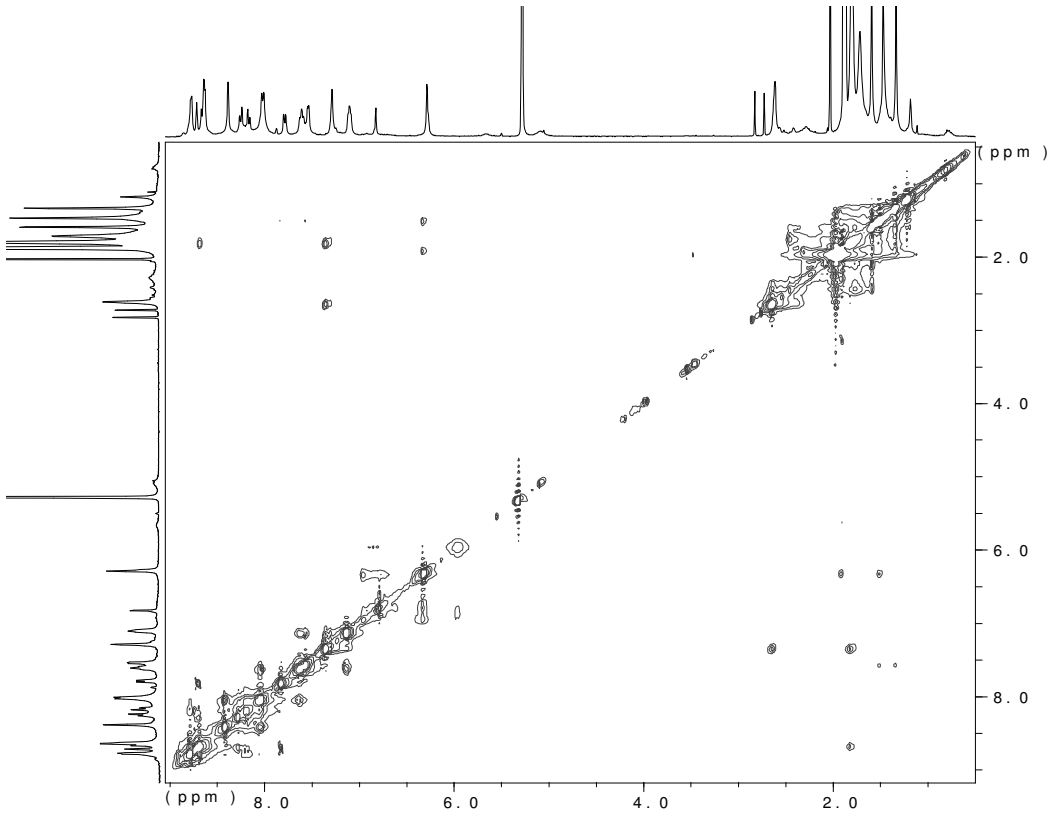


Figure S24. NOESY spectrum of **P5** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{tpy2})(PF_6)_6]$.

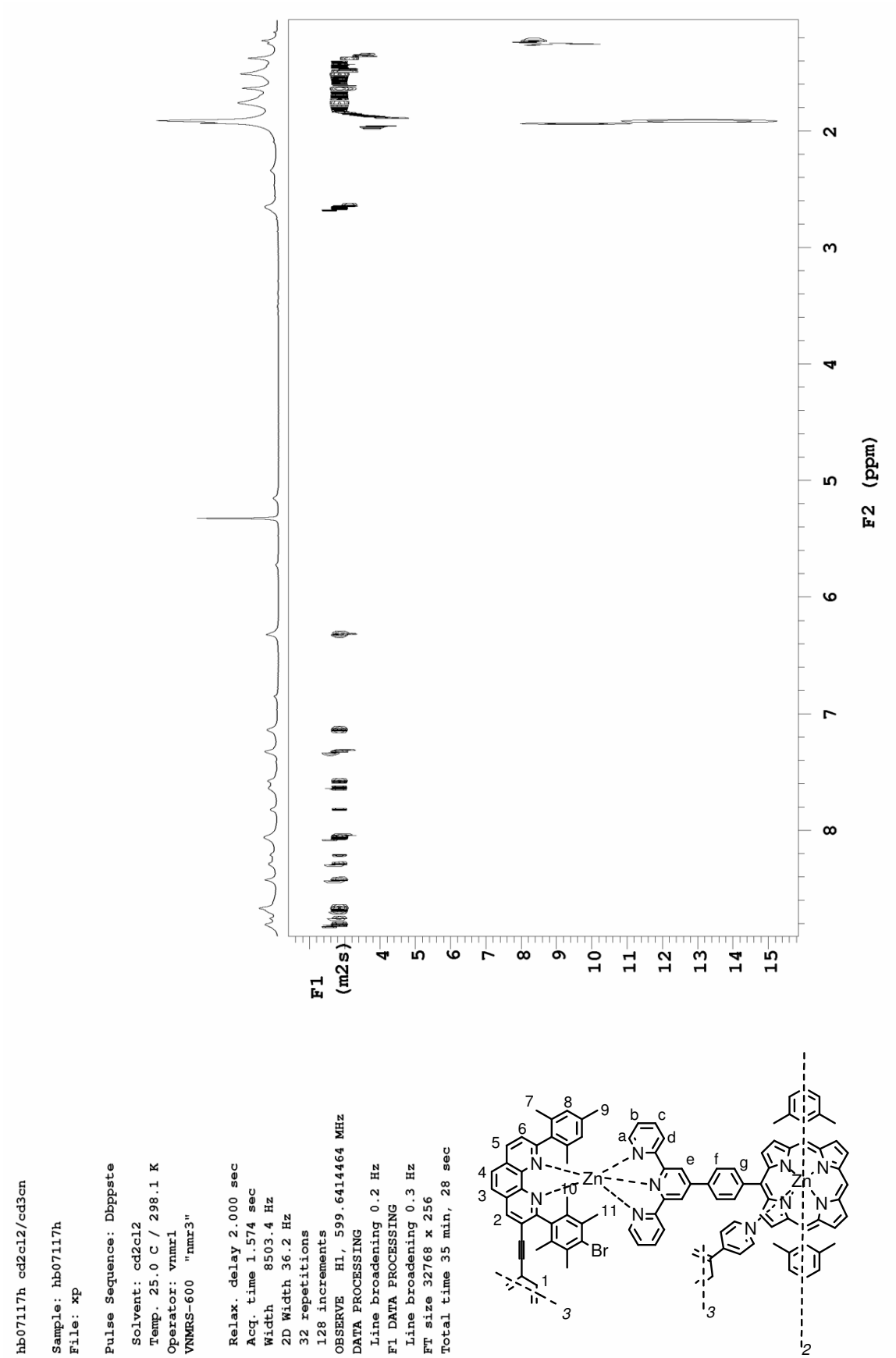


Figure S25. DOSY spectrum of **P5** [Cu_6(**TP**)$_2$(**BT3**)$_3$(**tpy2**)$(PF_6)_6$].

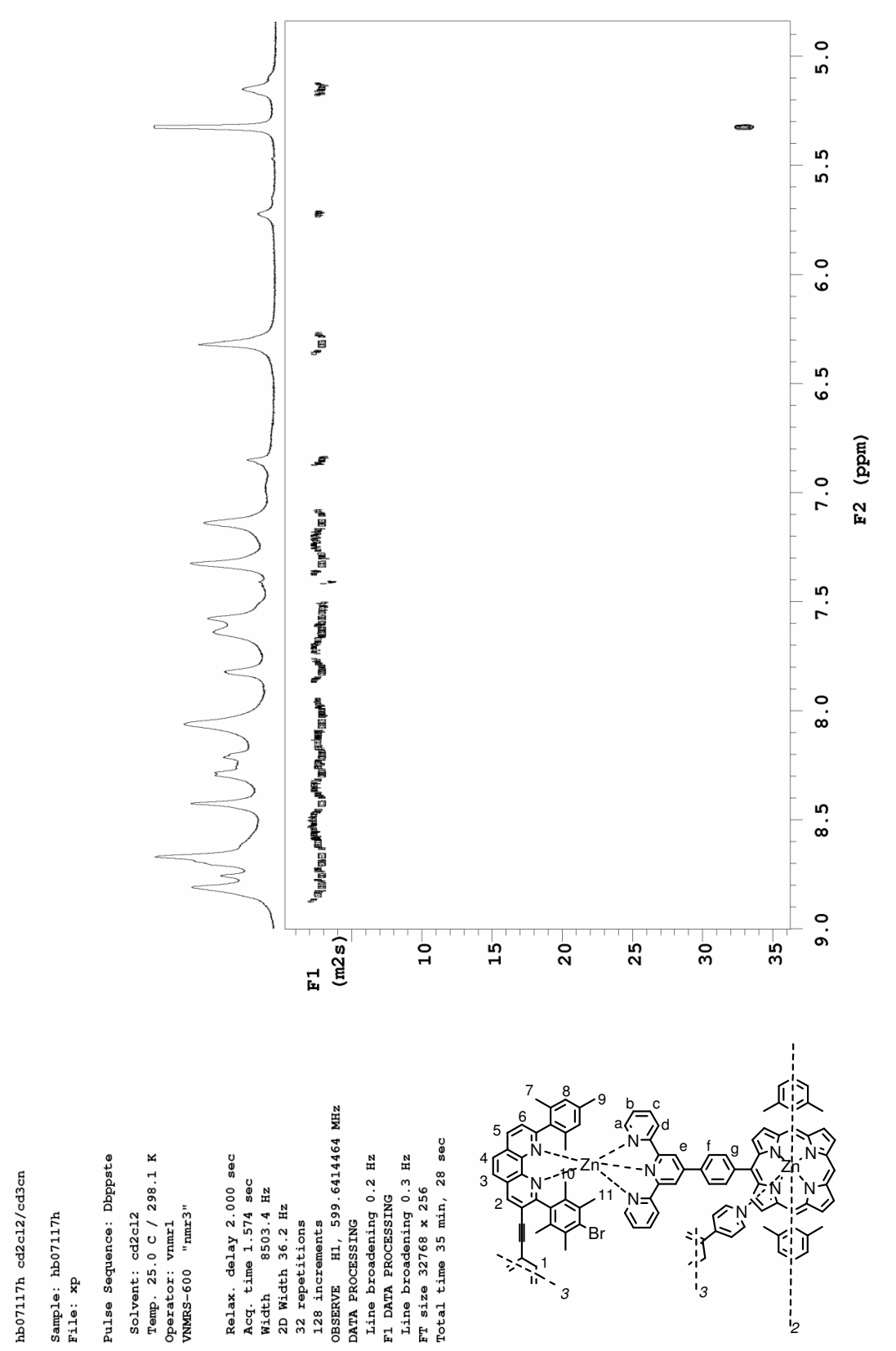


Figure S26. Aromatic part of DOSY spectrum of **P5** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(\mathbf{tpy2})(PF_6)_6]$ with increased signal intensity. Signals from **tpy2** (δ = 5.13 and 5.71 ppm) show up at the same diffusion coefficient as those of the prism host.

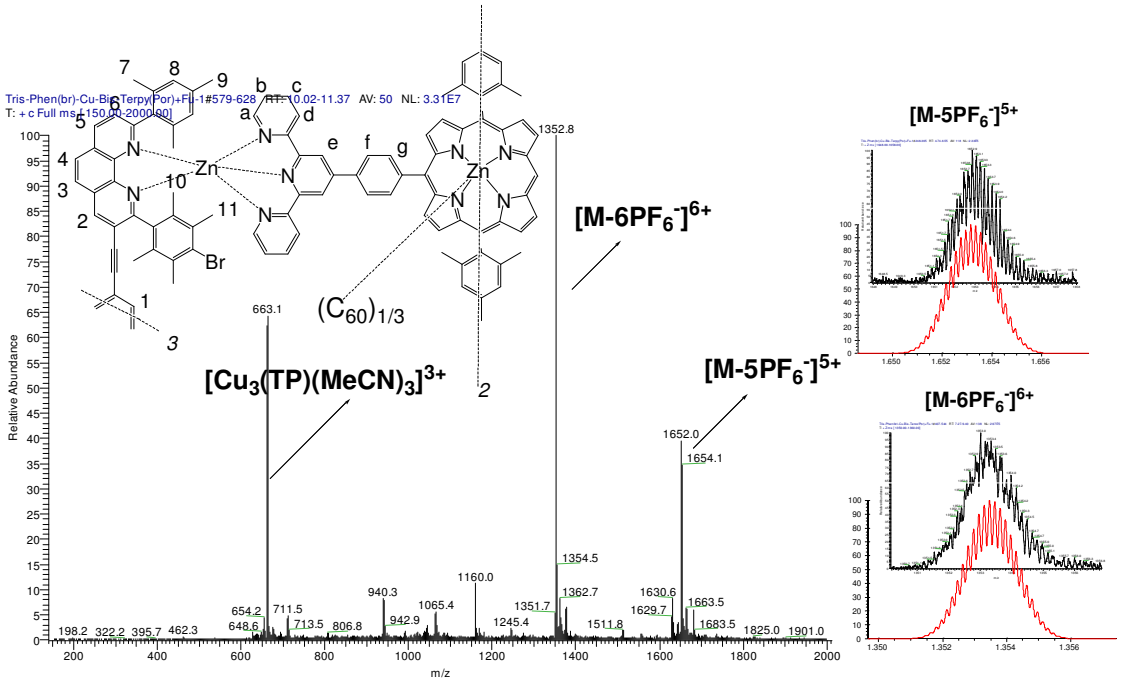


Figure S27. Left: ESI-MS spectrum of prism **P6** (=**M**) in acetonitrile. Right: experimental (black) and theoretical (red) isotopic splitting of 5+ and 6+ charged species of prism **P6**.

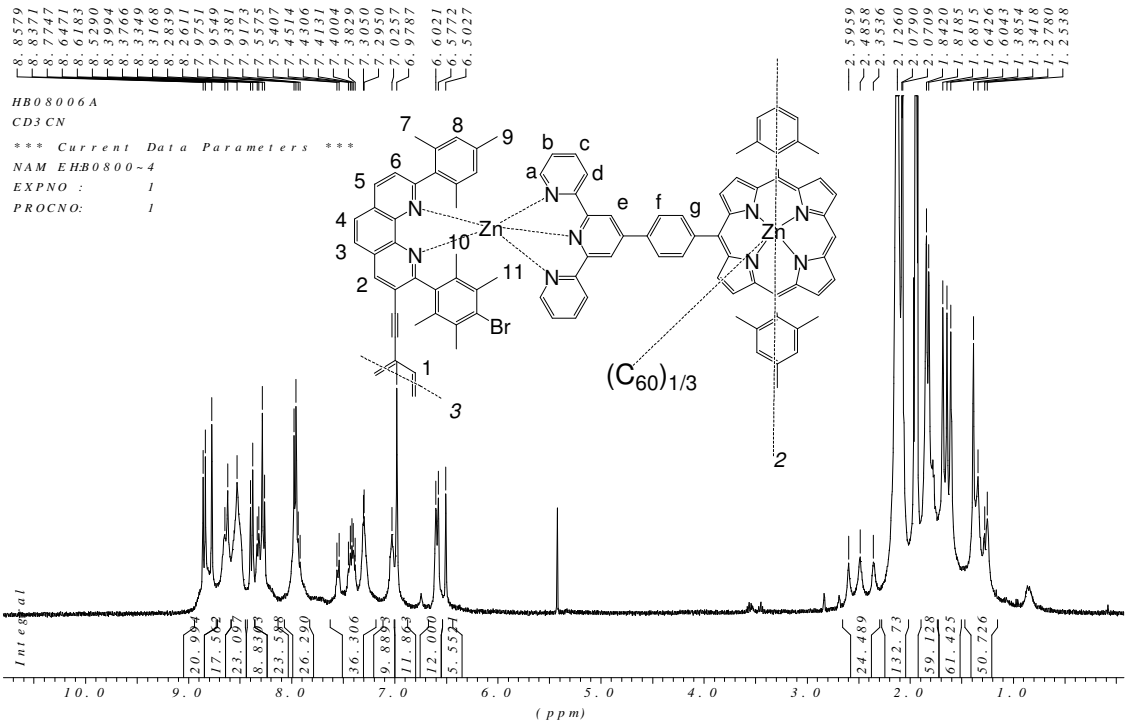


Figure S28. ^{1}H NMR spectrum of **P6** [Cu_6(**TP**)$_2$(**BT3**)$_3$(C_{60})(PF_6)$_6$].

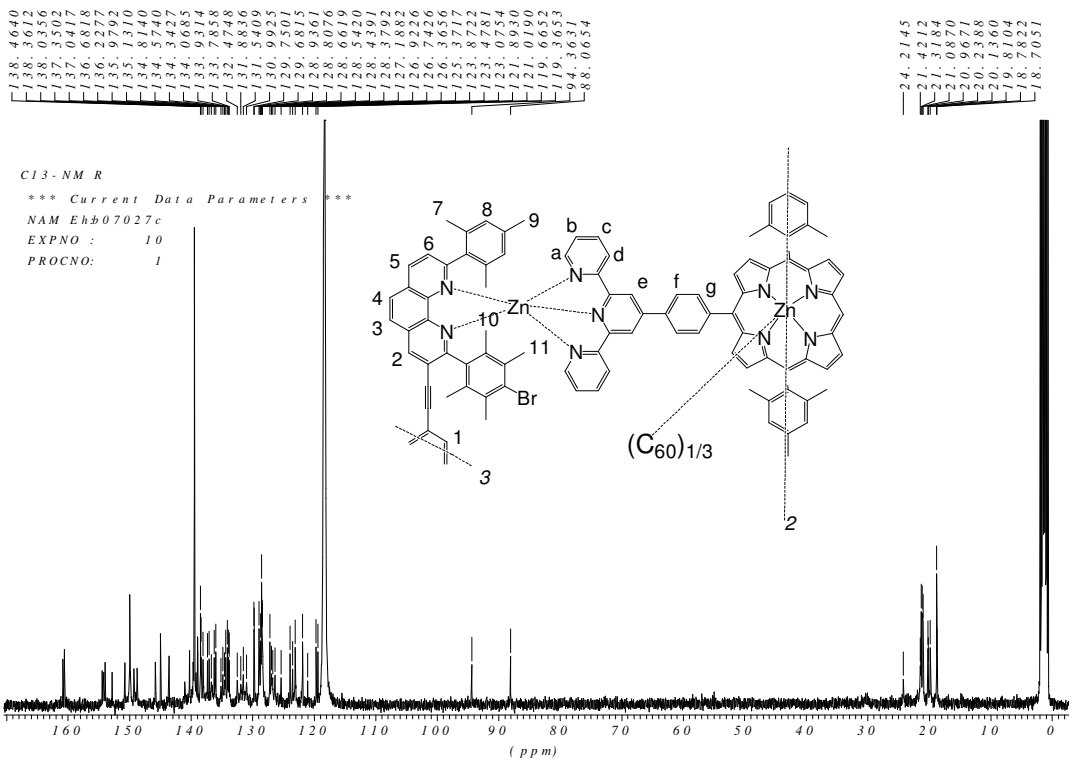


Figure S29. ^{13}C NMR spectrum of **P6** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(C_{60})(PF_6)_6]$.

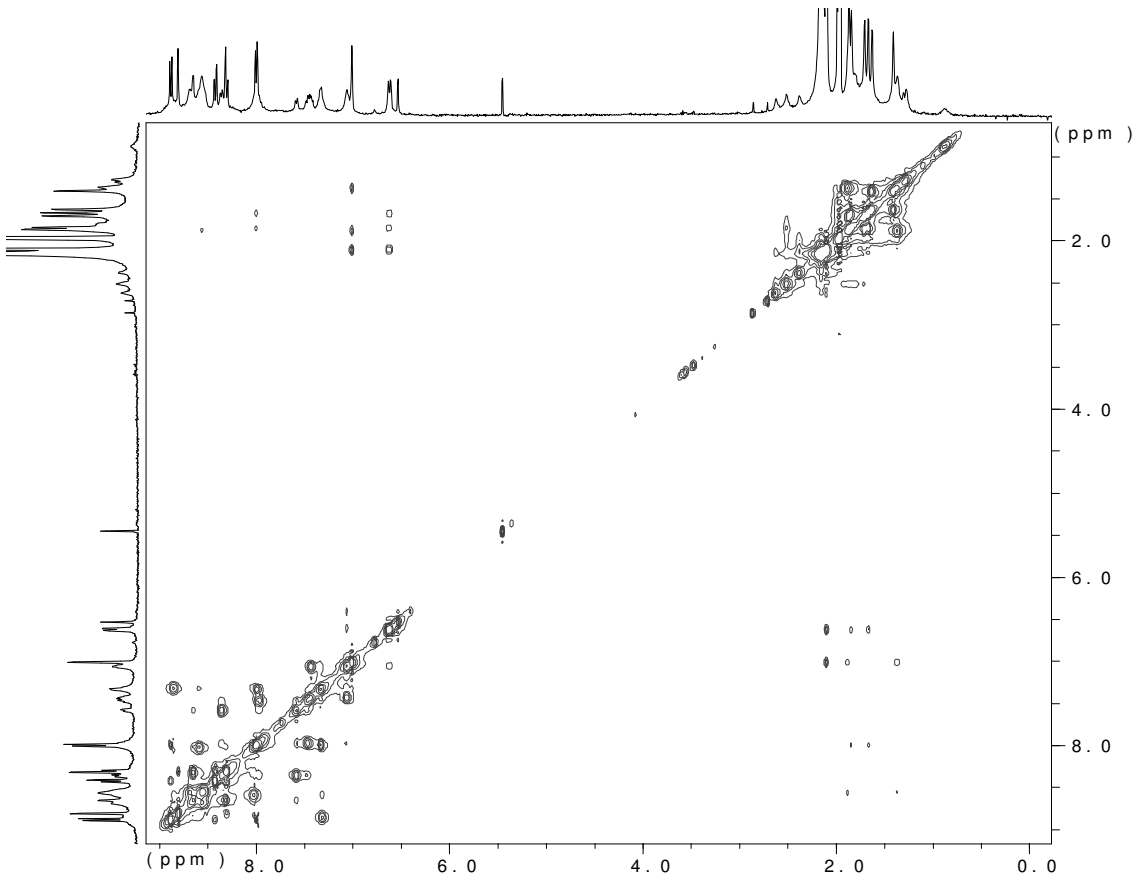


Figure S30. NOESY spectrum of **P6** $[Cu_6(\mathbf{TP})_2(\mathbf{BT3})_3(C_{60})(PF_6)_6]$.

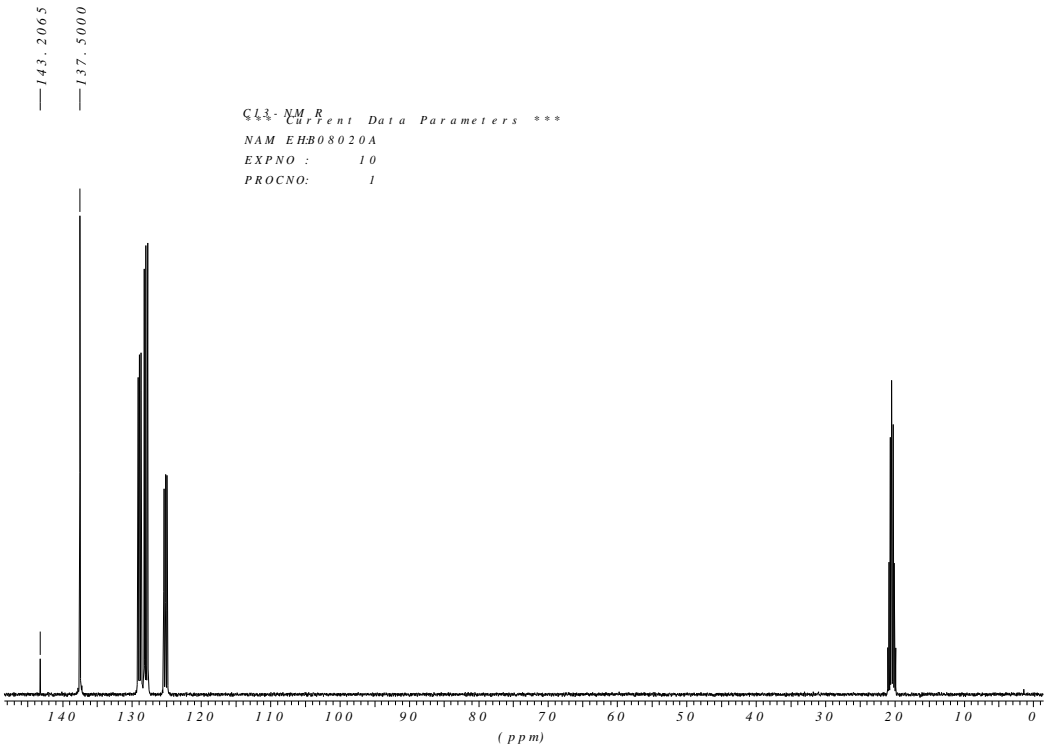


Figure S31. ^{13}C NMR spectrum of C_{60} measured in toluene-d_8 for 2 hours. C_{60} has a chemical shift of 143.2 ppm with the singlet signal of toluene-d_8 being set to 137.50 ppm.

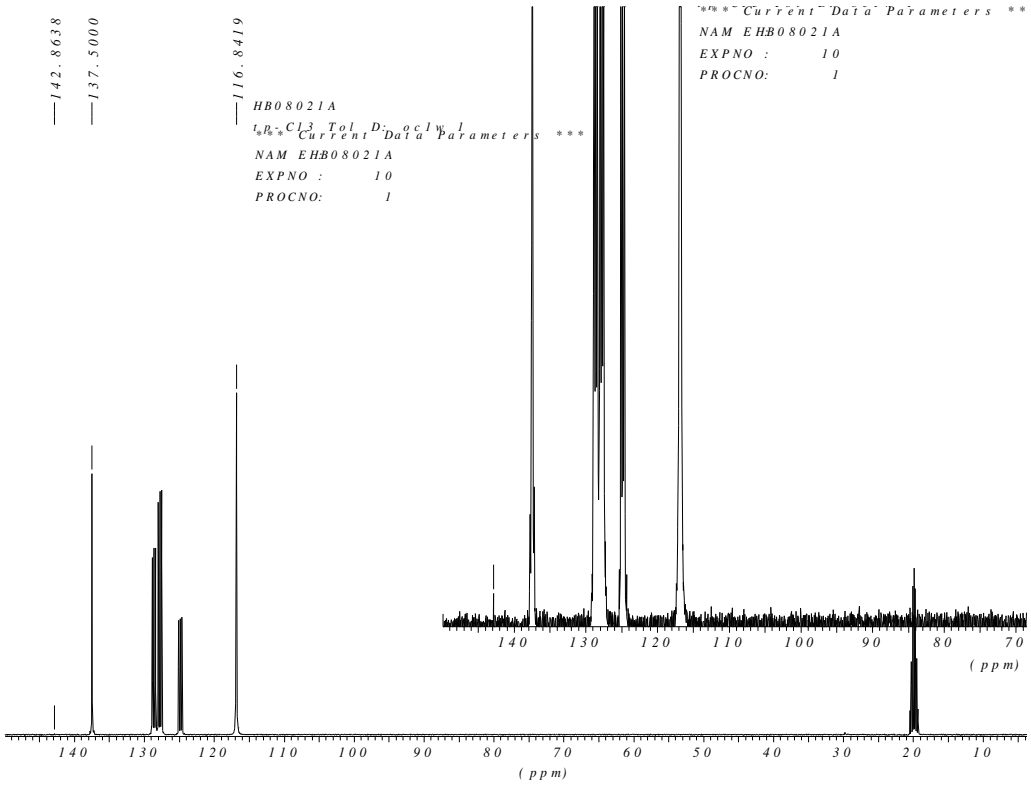


Figure S32. ^{13}C NMR spectrum of fullerene C_{60} measured over 48 hours in a mixture of acetonitrile-d_3 : toluene-d_8 (1 : 1). Due to the low solubility of C_{60} (0.031 mg/mL) in this mixture, only a tiny signal of C_{60} was observed at 142.9 ppm (with regard to toluene-d_8 set to 137.50 ppm). When we reference with regard to acetonitrile-d_3 (118.26 ppm) C_{60} shows up at 144.3 ppm.