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Supporting Information

Rational Syntheses of Helical π-Conjugated Oligopyrrins with a Bipyrrole Linkage: Geometry Control of Bis-Copper(II) Coordination

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Contents

Experimental

General

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (MERCK). ^{1}H NMR spectra were obtained using a Bruker AM 400 spectrometer with tetramethylsilane (TMS) used as the internal standard. ^{13}C NMR spectra were recorded at 100 MHz and chemical shifts were reported relative to $CDCl_3$ (δ = 77.00) in ppm. HRMS were performed using a Waters LCT Premier XE spectrometer. MALDI-TOF-MS was measured using AB Sciex 4800 Plus MALDI TOF/TOF Analyzer with dithranol as the matrix. UV-vis absorption spectra were recorded on a Varian Cary 500 spectrophotometer and Shimadzu UV-3150PC spectrometer equipped with a UNISOKU CoolspeK cryostat. EPR spectra were obtained on a Bruker EMX spectrometer equipped with an Oxford ESR900 cryostat. The g-value was calibrated by using a Mn^{II} reference. Magnetic susceptibility measurement was performed on a Quantum Design MPMS5S SQUID magneto/susceptometer. Chiral separation was performed on an HPLC (Shimadzu, SCL-10A) equipped with chiral stationary columns (e.g., SUMICHIRAL OA-3100, DAICEL CHIRALPAC IA and IB-3) with various solvent combinations. CD spectra were recorded on a JASCO J-1500 Circular Dichroism Spectrometer equipped with a PTC-517 Single Cell Peltier Holder.

Crystallography

X-ray analyses were performed on a SMART APEX equipped with CCD detector (Bruker) using MoKα (graphite, monochromated, λ = 0.71069 Å) radiation or CuKα (graphite, monochromated, λ = 1.54178 Å) radiation. The structures were solved by the direct method of SHELXS-97 and refined using the SHELXL-97 program.[1] The positional parameters and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and refined riding on their corresponding carbon atoms.

Crystal data for **P8:** $C_{92}H_{22}Cl_8F_{40}N_8O_2$, *Mr* = 2320.82, monoclinic, space group $P2_1/n$, a = 17.2568(16), b = 14.4839(11), c = 18.3034(18), α = 90°, β = 96.4540(10)°, γ = 90°, V = 4545.9(7) Å^3, Z = 2, R_1 = 0.0694, wR_2 = 0.2426 (all data), GOF = 1.020.

P6-Cu2: $C_{70}H_{24}Cu_2F_{30}N_6O_4S_2$, *Mr* = 1774.15, monoclinic, space group $P2_1/n$, a = 11.1752(5), b = 16.3892(8), c = 37.510(3), α = 90.00°, β = 93.3750(10)°, γ = 90.00°, V = 6858.1(7)Å^3, Z = 4, R_1 = 0.0620, wR_2 = 0.1383 (all data), GOF =1.027.

P7-Cu2: $C_{83}H_{23}Cu_2F_{35}N_{10}O_2$, *Mr* = 1984.19, monoclinic, space group $P2_1/c$, a = 15.2047(18), b = 23.710(3), c = 25.959(3), α = 90.00°, β = 103.577(2)°, γ = 90.00°, V = 9096.5(18) Å^3, Z = 4, R_1 = 0.0668, wR_2 = 0.2036 (all data), GOF = 1.077.

P8-Cu2: $C_{92}H_{24}Cl_8Cu_2F_{40}N_8O_2$, *Mr* = 2443.87, monoclinic, space group $P2_1/c$, a = 17.0506(17), b = 14.6158(13), c = 23.435(2), α = 90.00°, β = 129.005(2)°, γ = 90.00°, V = 4538.4(7) Å^3, Z = 2, R_1 = 0.1071, wR_2 = 0.3196 (all data), GOF = 1.032.

P8-Zn2: $C_{94}H_{29}Zn_2F_{40}N_{11}O_2$, *Mr* = 2235.02, triclinic, space group *P-1*, a = 13.1330(14), b = 16.1932(13), c = 20.7009(16), α = 81.3170(10)°, β = 86.431(2)°, γ = 83.3480(10)°, V = 4318.1(7) Å^3,

Z = 2, R_1 = 0.0702, wR_2 = 0.1647 (all data), GOF = 1.005.

CCDC 1060306 (**P8**), 1060309 (**P6-Cu2**), 1060310 (**P7-Cu2**), 1060311 (**P8-Cu2**) and 1455046 (**P8-Zn2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculation Details

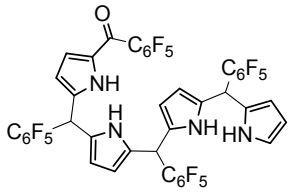
We employed density functional theory (DFT) calculations to optimize the geometries of compounds **P8** and copper complexes, **P6-Cu2, P7-Cu2, P8-Cu2**, using the hybrid (U)B3LYP functional[2] and the double-zeta basis set, 6-31G(d).[3] For copper atoms, the Los Alamos effective core potential basis set LANL2DZ was used.[4] Grimme's dispersion correction (version D.01)[5] was employed in DFT calculations. All calculations were carried out using the Gaussian09 program package.[6]

Electrochemical Measurements

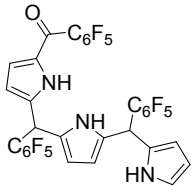
Cyclic voltammetry was carried out at 298 K using CHI-730C Electrochemical Workstation. A three-electrode cell was used for cyclic voltammetric measurements, consisting of a platinum or glassy carbon working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity containing the solvent/supporting electrolyte mixture.

Absolute dichloromethane (CH_2Cl_2) was purchased from Sigma-Aldrich and used as received and tetra-n-butylammonium perchlorate (TBAP) was purchased from Fluka Chemika, recrystallized from ethanol, and dried under vacuum at 40 °C for at least one week prior to use.

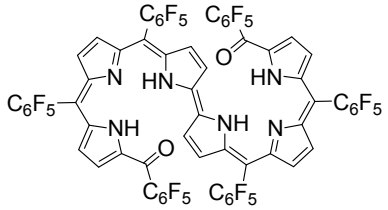
Synthetic Procedures



1: A THF solution of PhMgBr (30 mL, 22.5 mmol, 0.75 M) was added to a stirred solution of 5,10,15-tris(pentafluorophenyl) bilane[8] (4 g, 4.99 mmol) in toluene (150 mL) under nitrogen. The mixture was stirred at ambient temperature for 10 min and then cooled to 0 °C. A solution of (S)-2-pyridyl pentafluorobenzothioate[9] (1.52 g, 4.99 mmol) in THF (20 mL) was then added dropwise over 20 min. The solution was maintained at 0 ℃ for 20 min. Then, the mixture was allowed to warm to room temperature. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was partitioned between CH_2Cl_2 and water. Then, the CH_2Cl_2 phase was separated and washed with water, dried over sodium sulfate, and evaporated in vacuo. The residue was separated by silica gel column chromatography, using hexane/CH_2Cl_2= 1/2 (v/v) as the eluent to afford **1** as a clear yellowish oil (1.71 g, 27.6%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.83 (d, J = 17.9 Hz, 1H, NH), 8.35 ~ 8.16 (m, 3, NH), 6.73 (s, 1H, αH), 6.65 (s, 1H, βH), 6.14 (d, J = 2.5 Hz, 1H, βH), 6.10 ~ 5.98 (m, 3, βH), 5.98 ~ 5.86 (m, 3, βH), 5.83 (s, 2H, meso CH), 5.79 (s, 1H, meso CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.37, 146.11, 143.67, 140.48, 139.15, 136.51, 131.35, 129.54, 129.19, 127.73, 126.21, 126.05, 122.66, 118.23, 118.16, 111.32, 109.37, 108.79, 108.27, 108.18, 107.83, 33.10. HRMS : m/z; $[M+H]^+$, calcd for $C_{44}H_{17}F_{20}N_4O$: 997.1083; found: 997.1085.

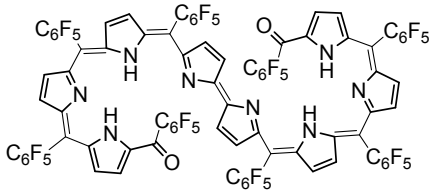


2: A THF solution of PhMgBr (14.1 mL, 9.69 mmol, 0.7 M) was added to a stirred solution of 5,10-bis(pentafluorophenyl)tripyrrane[7] (1.8 g, 3.23 mmol) in toluene (100 mL) under Ar. The mixture was stirred at ambient temperature for 10 min and then cooled to 0 °C. A solution of pentafluorobenzoyl chloride (816 mg, 3.55 mmol) in THF (5 mL) was then added dropwise over 10 min. The solution was maintained at 0 °C for 10 min. Then, the mixture was allowed to warm to room temperature. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was partitioned between CH_2Cl_2 and water. Then, the CH_2Cl_2 phase was separated and washed with water, dried over sodium sulfate, and evaporated in vacuo. The residue was separated by silica gel column chromatography, using hexane/CH_2Cl_2= 1/1 (v/v) as the eluent to afford **2** as a white solid (1.0 g, 1.31 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.96 (br s, 1H, NH), 8.34 (br s, 1H, NH), 8.16 (br s, 1H, NH), 6.74 (s, 1H, αH), 6.64 (s, 1H, βH), 6.14 (d, J = 2.5 Hz, 1H, βH), 6.07 (s, 1H, βH), 6.04 (br s, 1H, βH), 6.01 (br s, 1H,), 5.95 (s, 1H, βH), 5.86 (s, H, meso CH), 5.85 (s, H, meso CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.37, 140.86, 135.78, 131.90, 131.68, 131.60, 129.81, 129.71, 129.54, 128.66, 128.58, 127.48, 126.80, 124.84, 124.70, 124.64, 122.99, 121.73, 121.69, 120.70, 118.92, 118.65, 118.18, 117.56, 110.45, 110.19, 107.80, 102.06, 47.43, 29.73, 21.54; HRMS : m/z; $[M-H]^-$, calcd for $C_{33}H_{11}F_{15}N_3O$: 750.0663; found: 750.0658.

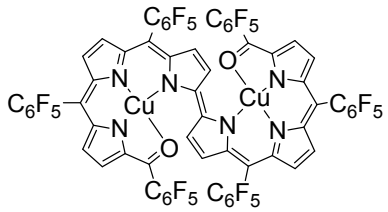


P6: A solution of DDQ (26.4 mg, 0.116 mmol) in CH_2Cl_2 (20

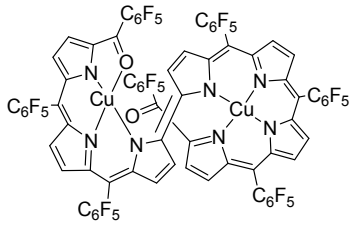
mL) was added slowly to a CH_2Cl_2 solution of **2** (21.7 mg, 0.029 mmol) and the resulting solution was stirred at room temperature for 2 h. After removal of the solvent, the residue was separated by silica gel column chromatography using CH_2Cl_2/hexane = 1/3 (v/v) as the eluent. The purple fraction corresponding to **P6** gradually decomposed during the chromatography and was unstable in the air. HRMS: *m*/*z*; $[M+H]^+$, calcd for $C_{66}H_{17}F_{30}N_6O_2$ 1495.0934; found: 1495.0936.



P8: A solution of DDQ (2.8 g, 6.24 mmol) in CH_2Cl_2 (2 L) was added slowly to a CH_2Cl_2 solution of **1** (3.1 g, 1.56 mmol) and the resulting solution was stirred at room temperature for 2 h. After removal of the solvent, the residue was separated by silica gel column chromatography using CH_2Cl_2/hexane = 1/4 (v/v) as the eluent. The maroon fraction afforded **5**. Recrystallization from CH_2Cl_2 and hexane gave **P8** as dark crystals (1.3 g, 42.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) (major diastereomer) δ = 13.14 (br s, 2H, NH), 12.08 (br s, 2H, NH), 7.26 (s, 2H, βH), 6.90 (d, *J* = 4.8 Hz, 2H, βH), 6.71 (s, 2H, βH), 6.66 (s, 2H, βH), 6.44 (s, 3, βH), 6.37 (s, 3, βH), 6.05 (s, 2H, βH). UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε [10^5mol^{-1}dm^{3}cm^{-1}]) = 347 (0.298), 505 (0.271), 639 (0.141), 1073 (0.142). IR (KBr, cm^{-1}): 3447 (s), 1653 (s), 1647 (s), 1636 (m), 1521 (m), 1505 (w), 1497 (m), 1405 (m), 1328 (m), 1249 (m), 1045 (m), 989 (w), 668 (w). HRMS: *m*/*z*; $[M+H]^+$, calcd for $C_{88}H_{20}F_{40}N_8O_2$:1981.1148; found: 1981.1185.

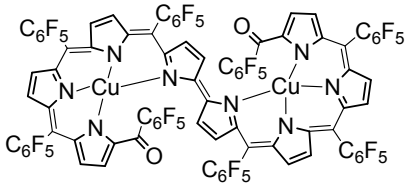


P6-Cu2: A solution of DDQ (200 mg, 0.896 mmol) in CH_2Cl_2 (20 mL) was added slowly to a CH_2Cl_2 solution of **2** (168 mg, 0.224 mmol) and the resulting solution was stirred at room temperature for 2 h. Then, a solution of excess $Cu(OAc)_2$ in MeOH was added slowly to the CH_2Cl_2 solution of **P6** and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was then purified by silica gel chromatography using CH_2Cl_2/hexane as an eluent to provide complex **P6-Cu2** as a brown fraction (80 mg, 44%). UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε [10^5 mol^{-1}dm^{3}cm^{-1}]) = 338 (0.221), 441 (0.42), 541 (0.098), 591 (0.096), 941 (0.119), 1065 (0.448), 1255 (0.036). IR (KBr, cm^{-1}): 3448 (s), 2927 (w), 1649 (m), 1518 (s), 1490 (s), 1458 (m), 1437 (m), 1327 (w), 1309 (w), 1212 (s), 1062 (m), 989 (s), 964 (m), 943 (m), 749 (w). MS (MALDI-TOF, *m*/*z*): [M] calcd for: $C_{66}H_{12}F_{30}N_6O_2Cu_2$: 1615.9135, found: 1615.830. Anal. Calcd for **P6-Cu2** · 2(C_6H_{14}): C, 52.33; N, 4.69; H, 2.25; Found: C, 52.41; N, 4.59; H, 2.14.

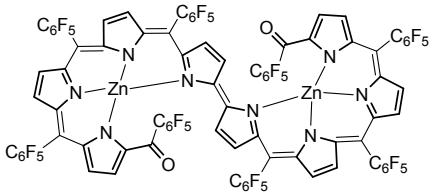


P7-Cu2: A solution of DDQ (228.8 mg, 1.0 mmol) in CH_2Cl_2 (50 mL) was added slowly to a CH_2Cl_2 solution of **1** (223 mg, 0.224 mmol) and **2** (168 mg, 0.224 mmol). The resulting solution was stirred at room temperature for 2 h. Then, a solution of excess $Cu(OAc)_2$ in MeOH was added slowly to the CH_2Cl_2 solution

and the resulting solution was stirred at room temperature for 5 h. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was then purified by silica-gel chromatography using CH_2Cl_2/hexane as the eluent. Successive three fractions afforded complexes **P8-Cu2** (161 mg, 35%), **P7-Cu2** (76 mg, 16%), and **P6-Cu2** (72 mg, 35%). UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε [$10^5 mol^{-1}dm^3cm^{-1}$]) = 367 (0.348), 385 (0.348), 507 (0.252), 696 (0.059), 1242 (0.112). IR (KBr, cm^{-1}): 3448 (m), 2924 (w), 2852 (w), 1648 (w), 1520 (s), 1490 (s), 1458 (m), 1321 (m), 1201 (m), 1066 (w), 989 (s), 962 (w), 946 (w). HRMS for **P7-Cu2**: *m*/*z*; $[M+H]^+$, calcd for $C_{77}H_{15}F_{35}N_7O_2Cu_2$: 1859.9320; found: 1859.9297. Anal. Calcd for **P7-Cu2** · 1.1(C_6H_{14}): C, 51.34; N, 5.01; H, 1.52; Found: C, 51.55; N, 4.94; H, 1.53.



P8-Cu2: A CH_2Cl_2/methanol (40 mL/20 mL) solution of **P8** (100 mg, 0.051 mmol) was stirred in the presence of $Cu(OAc)_2$ (92.3 mg, 0.51 mmol) for 3 h under ambient conditions. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was then purified by silica gel chromatography using CH_2Cl_2/hexane as the eluent to provide complex **P8-Cu2** as a violet fraction (85.8 mg, 80%). UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε [$10^5 mol^{-1}dm^3cm^{-1}$]) = 357 (0.304), 565 (0.287), 1267 (0.076), 1453(0.166). IR (KBr, cm^{-1}): 3448 (s), 2066 (w), 1637 (m), 1560 (w), 609 (w). HRMS: *m*/*z*; $[M+H]^+$, calcd for $C_{88}H_{17}F_{40}N_8O_2Cu_2$: 2102.9428; found: 2103.9419. Anal. Calcd for **P8-Cu2** · 2(H_2O) · CH_2Cl_2: C, 48.04; N, 5.04; H, 1.00; Found: C,47.89; N, 5.01; H, 1.27.



P8-Zn2: A CH_2Cl_2/methanol (40 mL/20 mL) solution of **P8** (100 mg, 0.051 mmol) was stirred in the presence of $Zn(OAc)_2$ (92.3 mg, 0.51 mmol) for 2 h under ambient conditions. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was then purified by silica gel chromatography using CH_2Cl_2/hexane as the eluent to provide complex **P8-Zn2** as a purple fraction (89 mg, 84%). ^1H NMR ($CDCl_3$, 400 MHz (ppm), 298 K): δ = 6.21 (s, 1H, βH), 6.29 (d, *J* = 4.4 Hz, 1H, βH), 6.53 (s, 1H, βH), 6.57 (d, *J* = 4.8 Hz, 1H, βH), 6.65 (d, *J* = 4.8 Hz, 1H, βH), 6.69 (s, 1H, βH), 6.86 (d, *J* = 4.8 Hz, 1H, βH), 7.08 (d, *J* = 4.4 Hz, 1H, βH); UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε [$10^5 mol^{-1}dm^3cm^{-1}$]) = 354 (0.76), 564 (0.98), 1386 (0.18), 1561 (0.37). IR (KBr, cm^{-1}):3367 (m), 2923 (w), 2857 (w), 1654 (m), 1647 (m), 1636 (m), 1518 (s), 1508 (s), 1497 (s), 1490 (s), 1458 (m), 1420 (m), 1187 (s), 1159 (m), 1047 (m), 988 (s), 947 (m). MS (MALDI-TOF, *m*/*z*): [M] calcd for: $C_{88}H_{16}F_{40}N_8O_2Zn_2$: 2103.9340, found: 2103.9297.

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Characterization data for the compounds

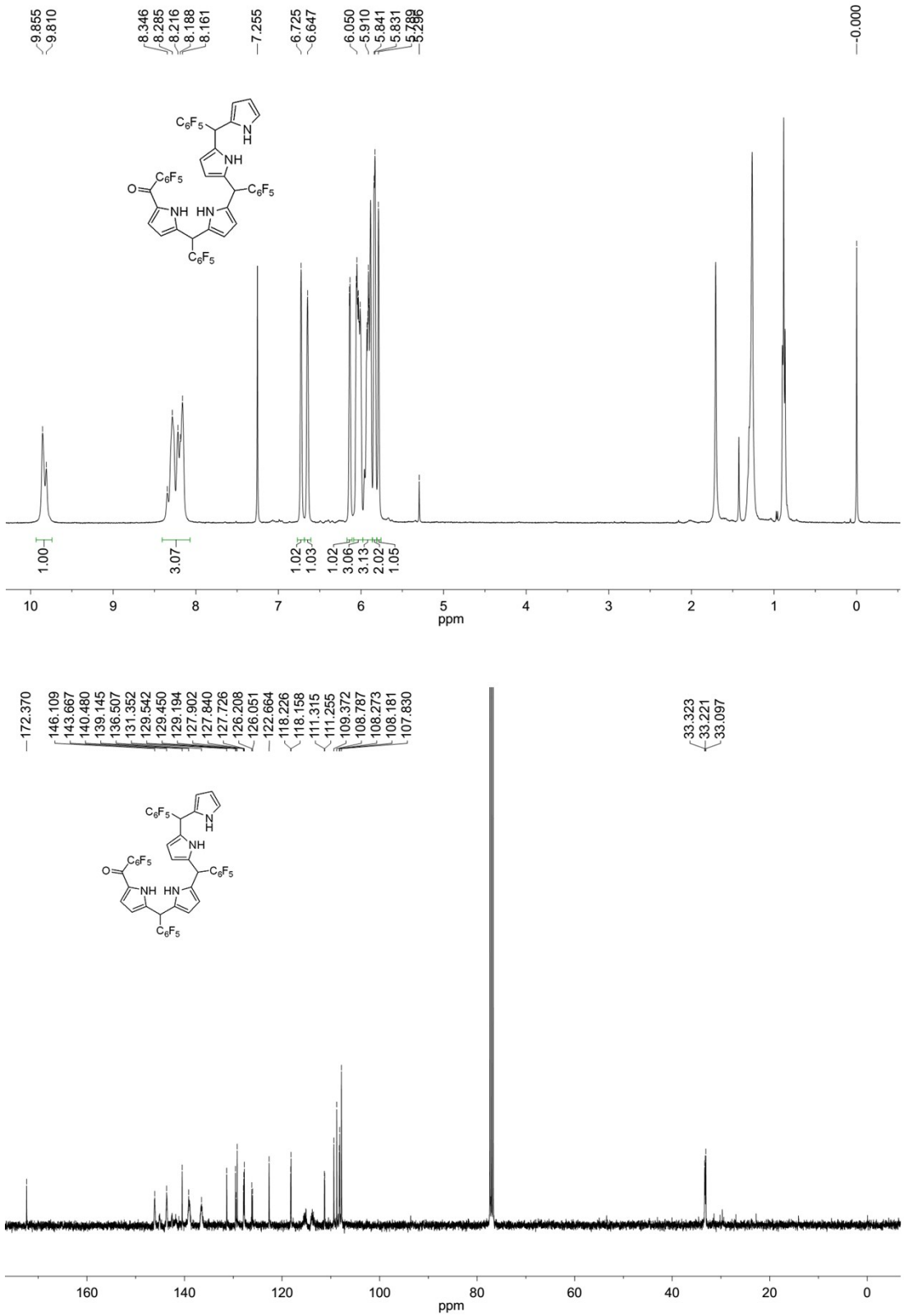

Figure S1. ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$

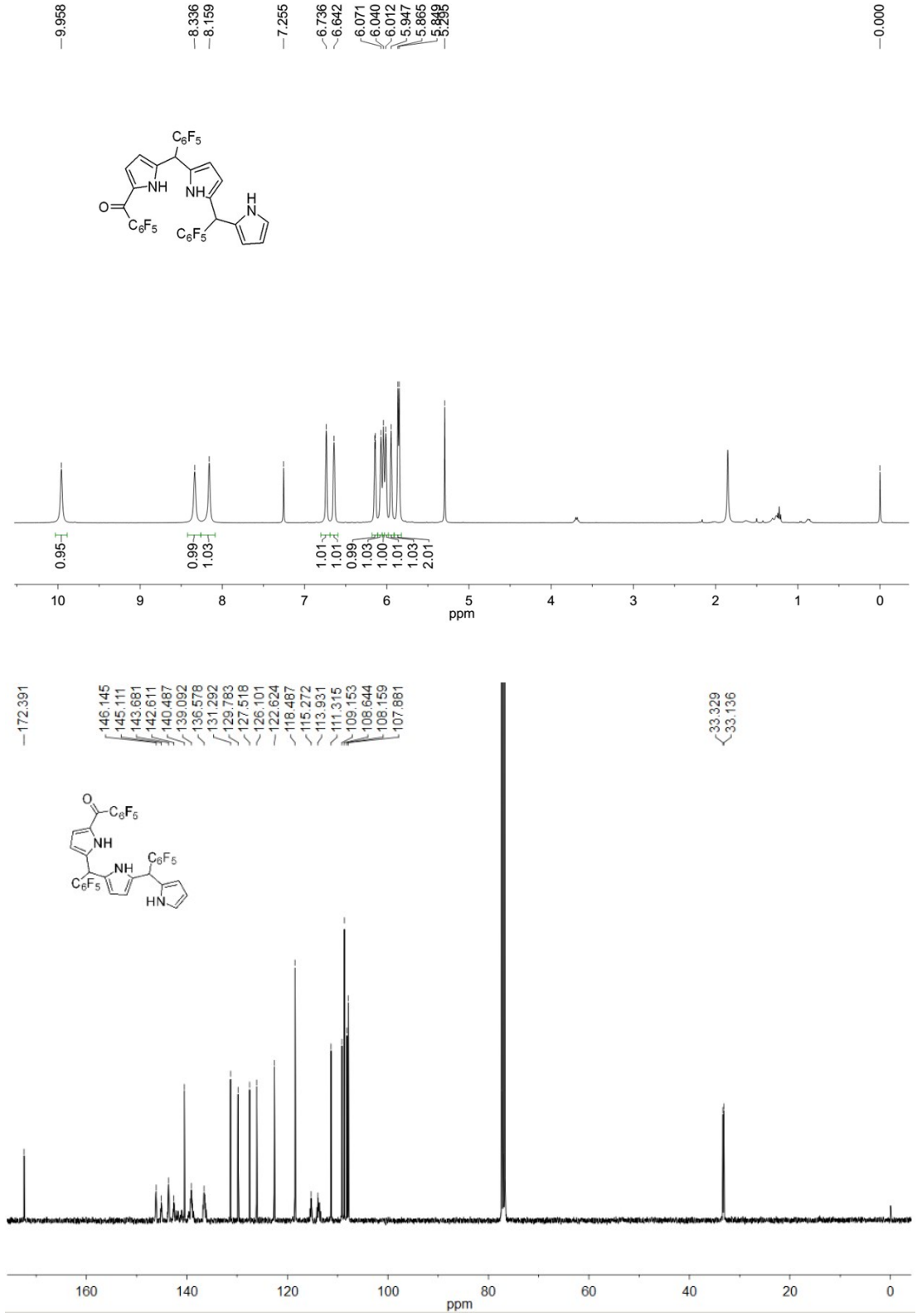

Figure S2. ^{1}H and ^{13}C NMR spectra of **2** in $CDCl_3$.

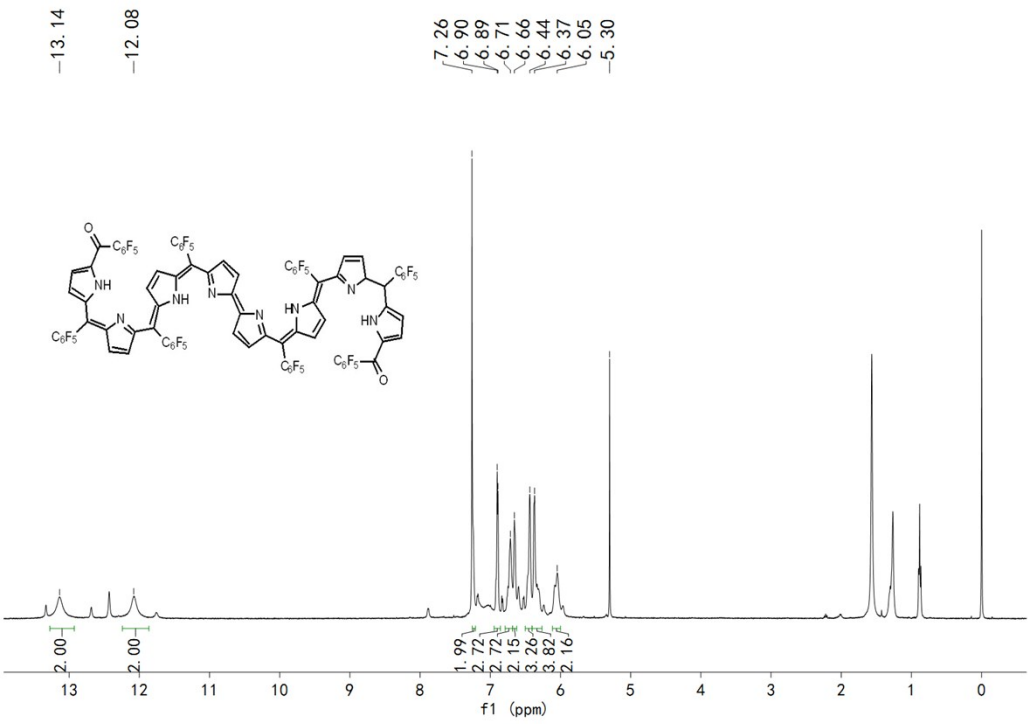

Figure S3. ^{1}H spectrum of **P8** in $CDCl_3$ at 298 K. (More than one sets of signals were observed because of the presence of isomers. Signals for the major diastereomer were assigned on the basis of the singlets for the pyrrolic NH protons at 13.14 and 12.08 ppm.)

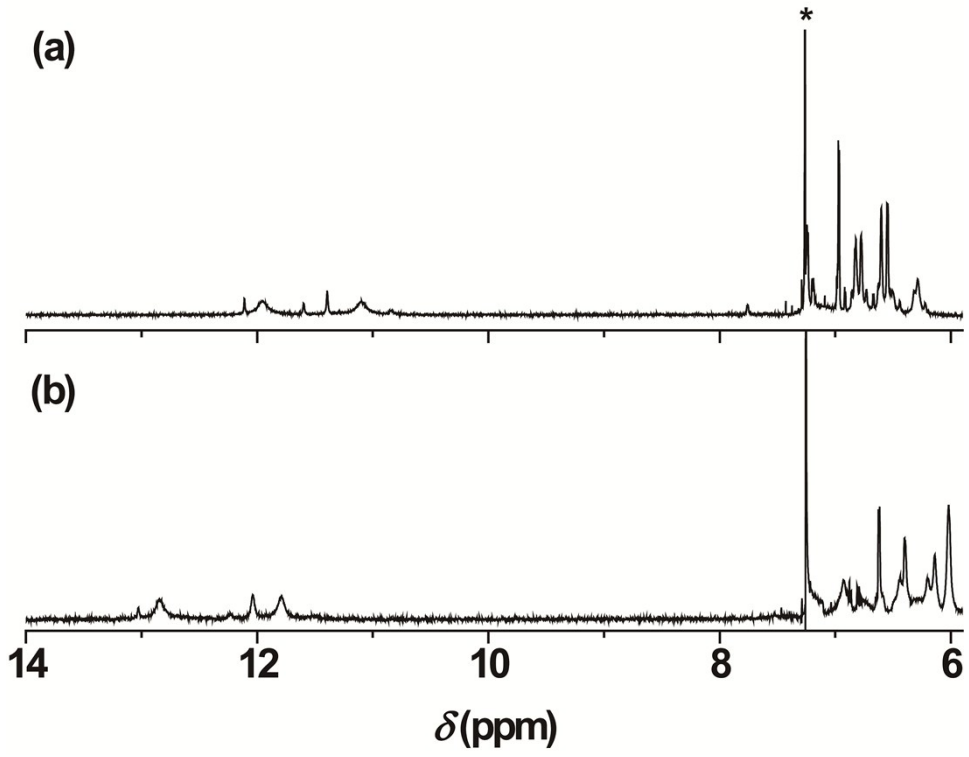

Figure S4. ^{1}H spectra of **P8** (a) in $CDCl_3$ and (b) in the presence of 1 drop of deuterated DMSO (DMSO-d_6) at 298 K

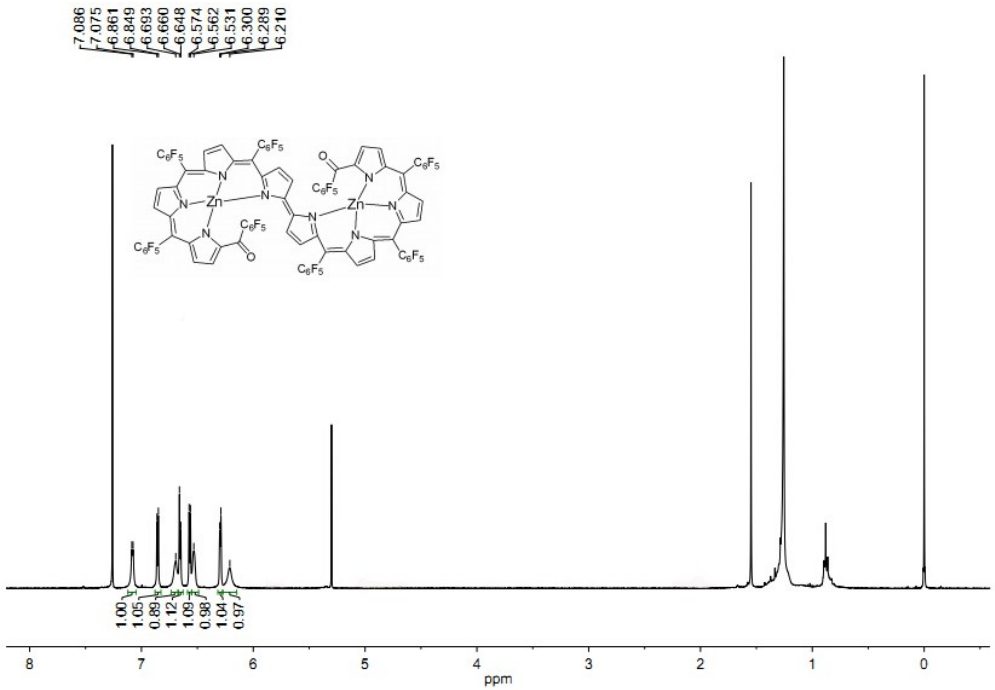

Figure S5. ^{1}H NMR spectrum of **P8-Zn2** in $CDCl_3$.

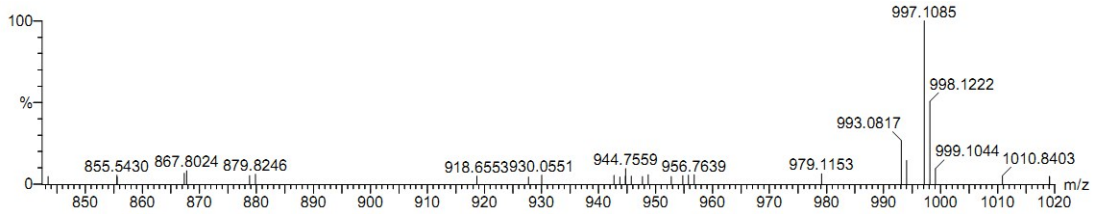

Figure S6. HRMS spectrum of **1** in MeOH.

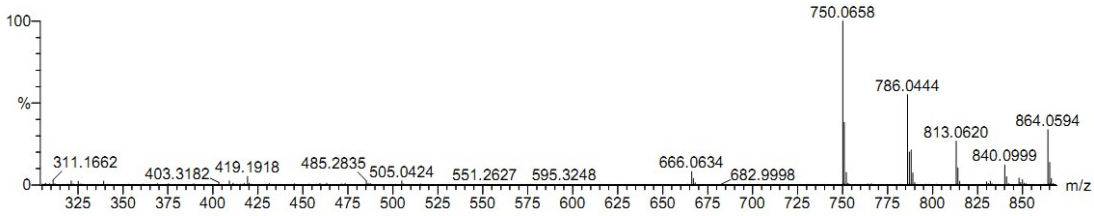

Figure S7. HRMS spectrum of **2** in MeOH.

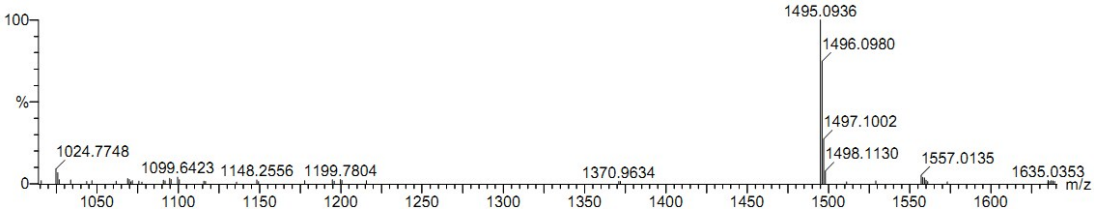

Figure S8. HRMS spectrum of **P6** in MeOH.

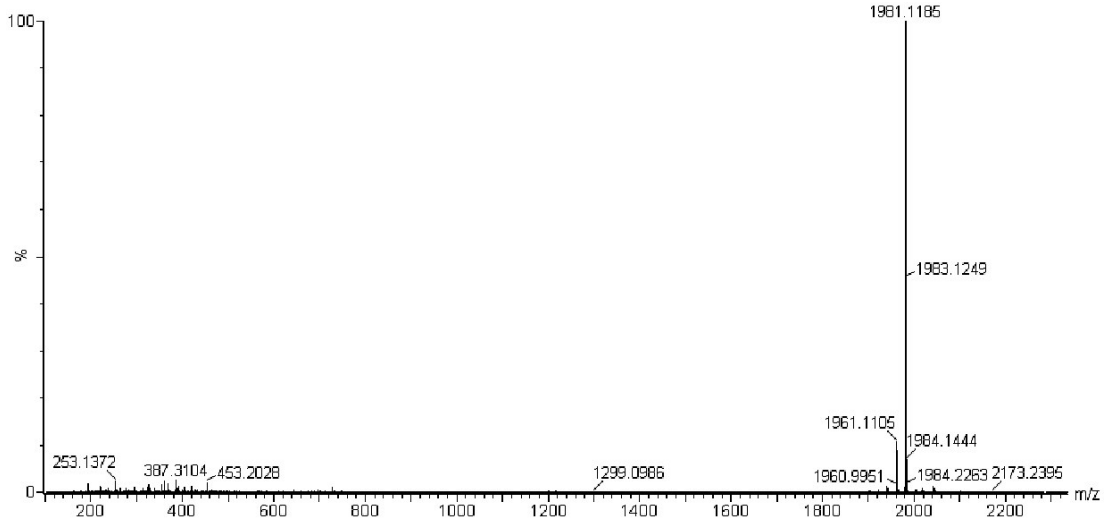

Figure S9. HRMS spectrum of **P8** in MeOH.

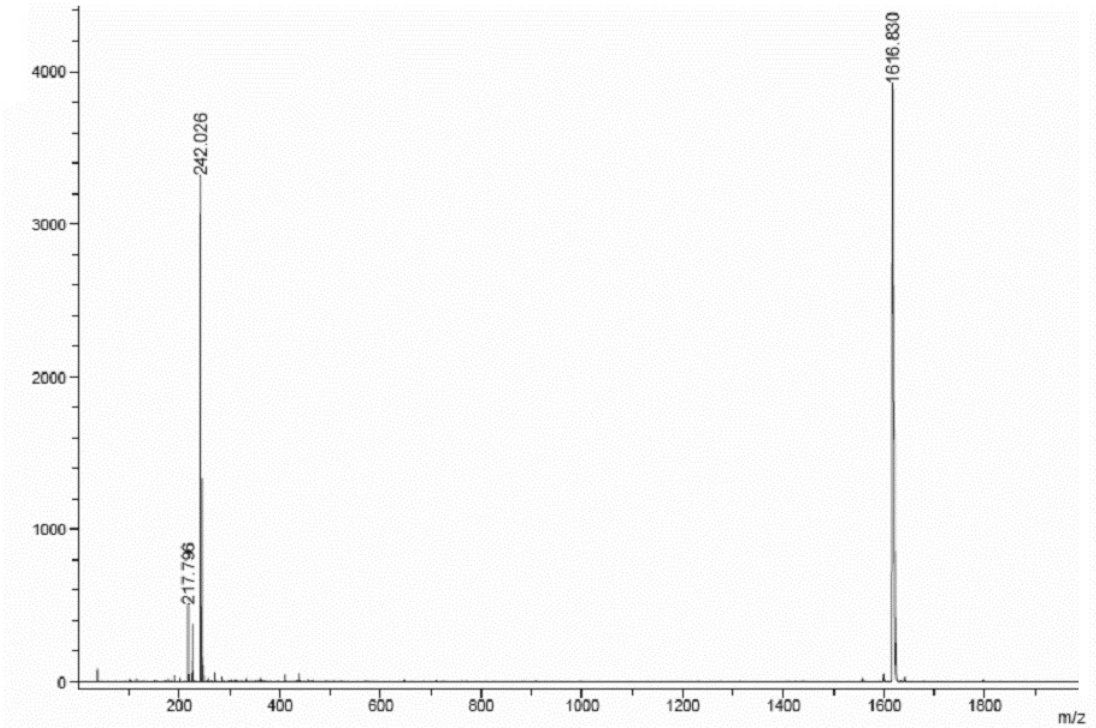

Figure S10. MALDI-TOF MS of **P6-Cu2**.

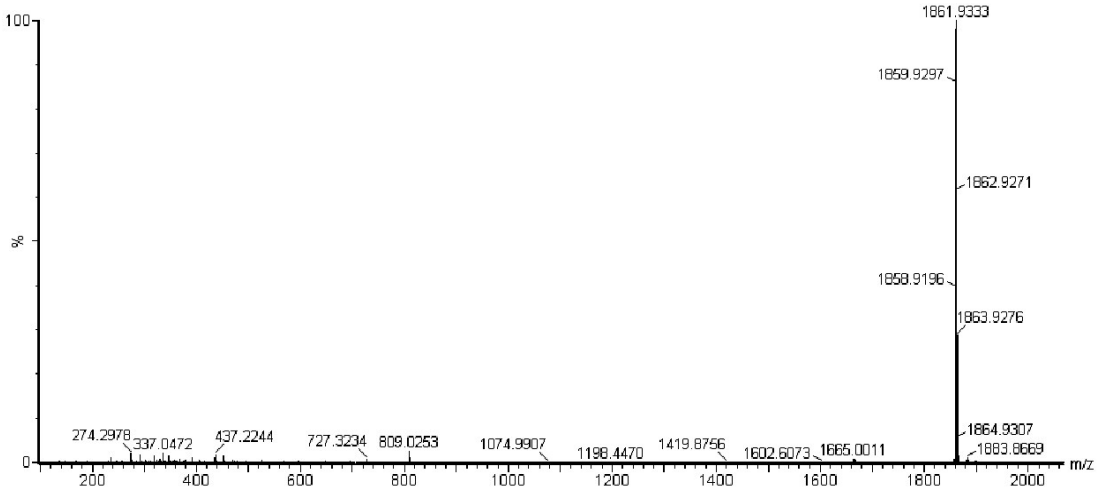

Figure S11. HRMS spectrum of **P7-Cu2** in MeOH.

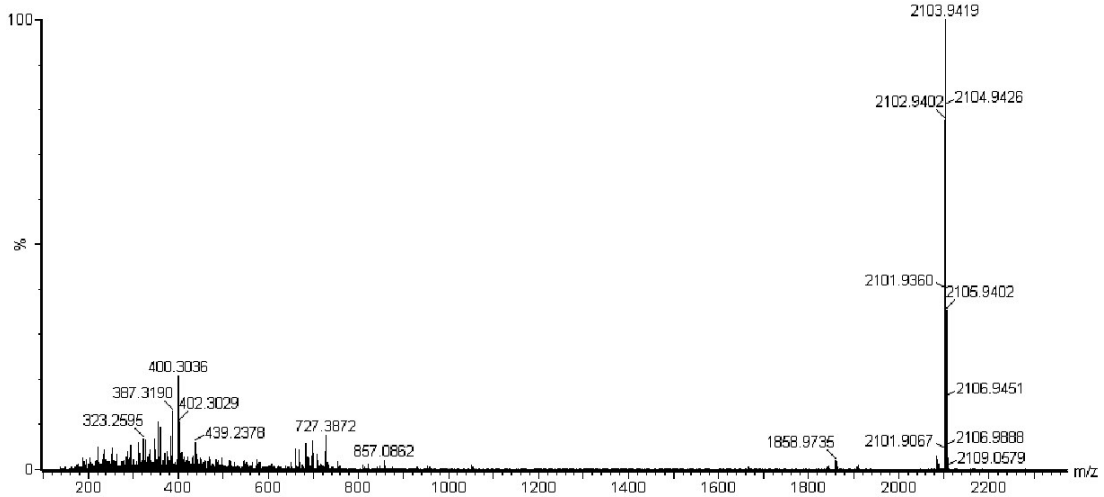

Figure S12. HRMS of **P8-Cu2** in MeOH.

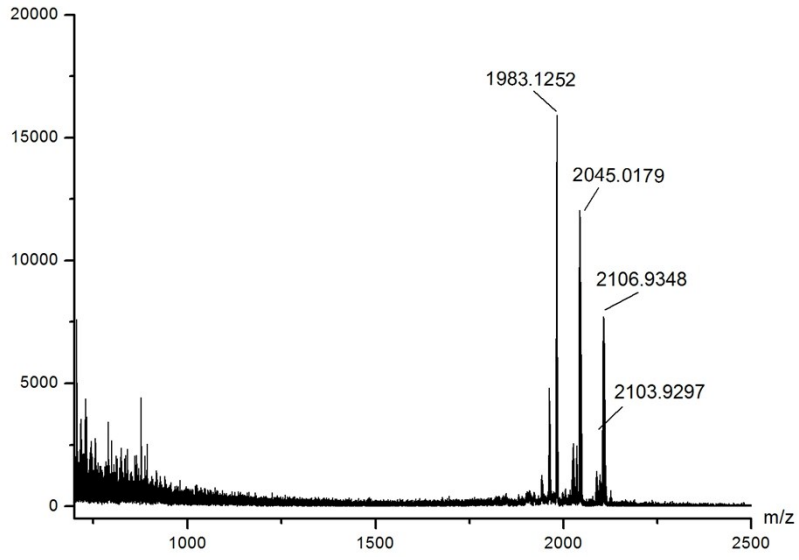

Figure S13. MALDI-TOF MS of **P8-Zn2**.

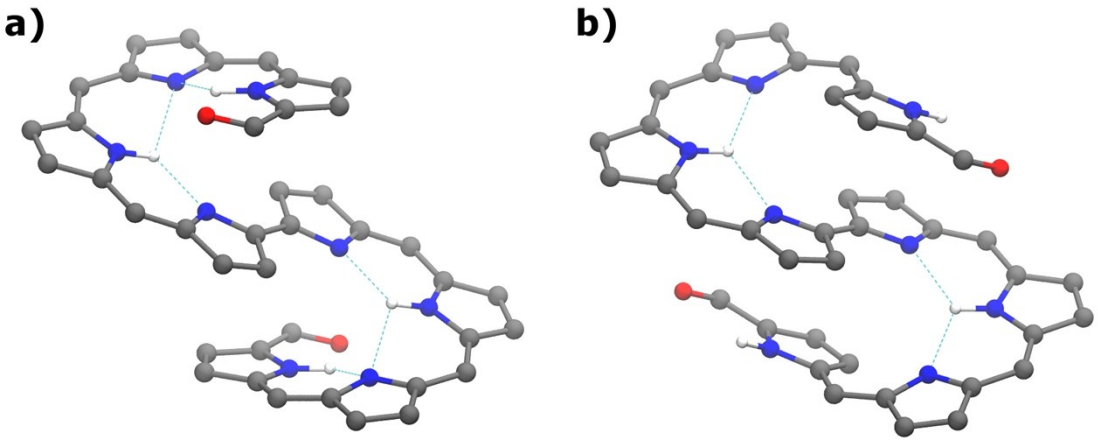

Figure S14. Optimized geometries of (a) **P8** and the possible isomers with opposite orientation of the carbonyl groups, (b) **P8'**. Pentafluorophenyl groups and hydrogen atoms of β-pyrrolic positions are omitted for clarity.

Table S1. Computed self-consistent field (SCF) energies of **P8** and its isomers.

Compound	SCF energy[a]	Relative energy[a]	VDW contrib.
P8	-7947.24002958 a.u.	0 kJ/mol	0 kJ/mol
P8'	-7947.23610366 a.u.	10 kJ/mol	35 kJ/mol

[a] Including the van der Waals contribution.

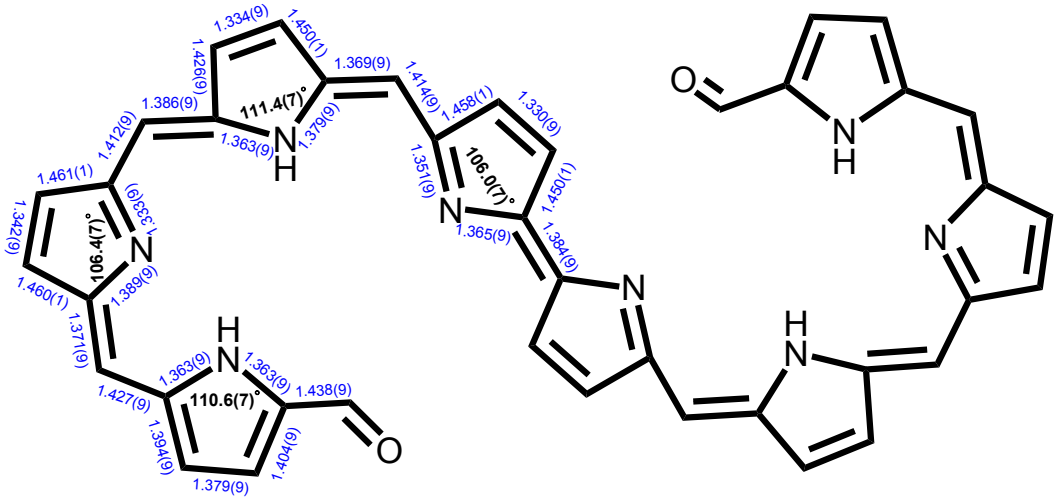

Figure S15. Selected bond (blue) lengths (Å) and angles (°) for the molecules of compound **P8** in the crystal structures. C_6F_5 groups are omitted for clarity.

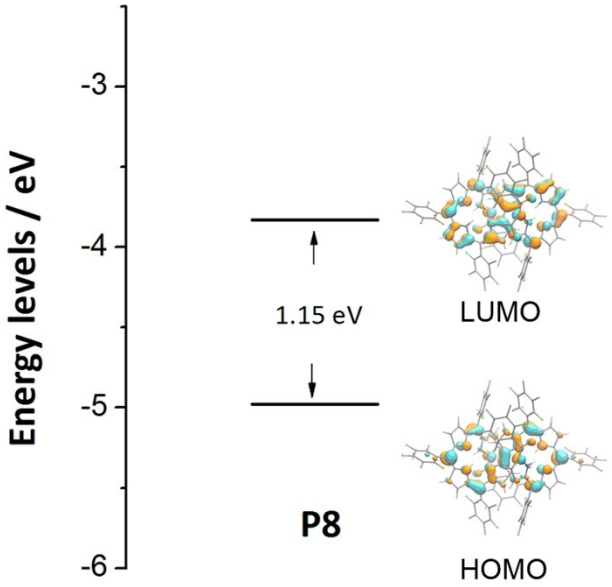

Figure S16. Energy levels of the frontier molecular orbitals of **P8**.

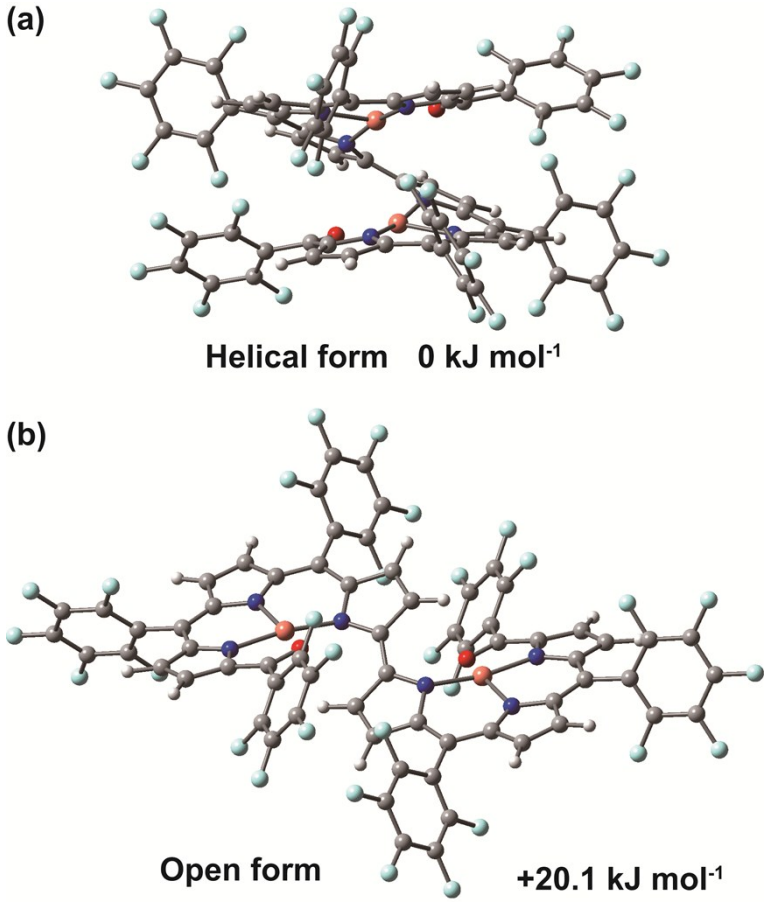

Figure S17. Optimized geometries of **P6-Cu2** (a) helical form and (b) the supposed open form.

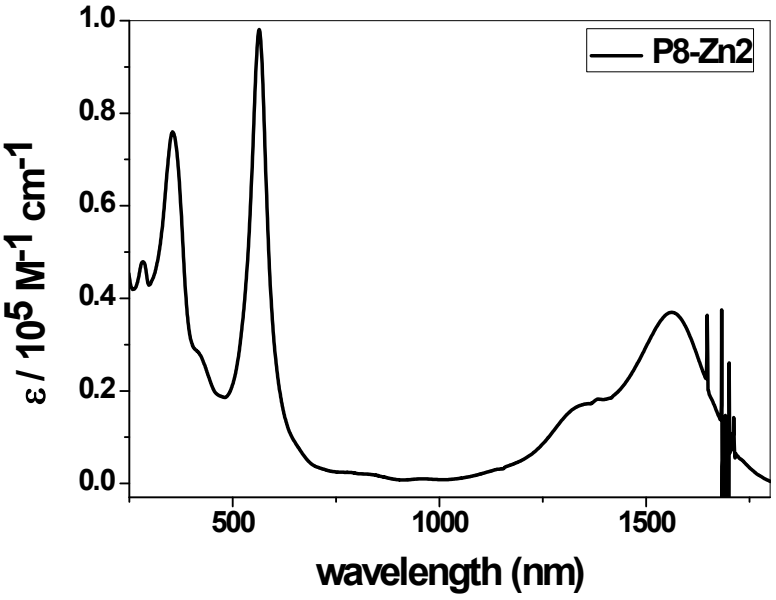

Figure S18. UV-vis-NIR absorption spectrum of **P8-Zn2** in CH_2Cl_2.

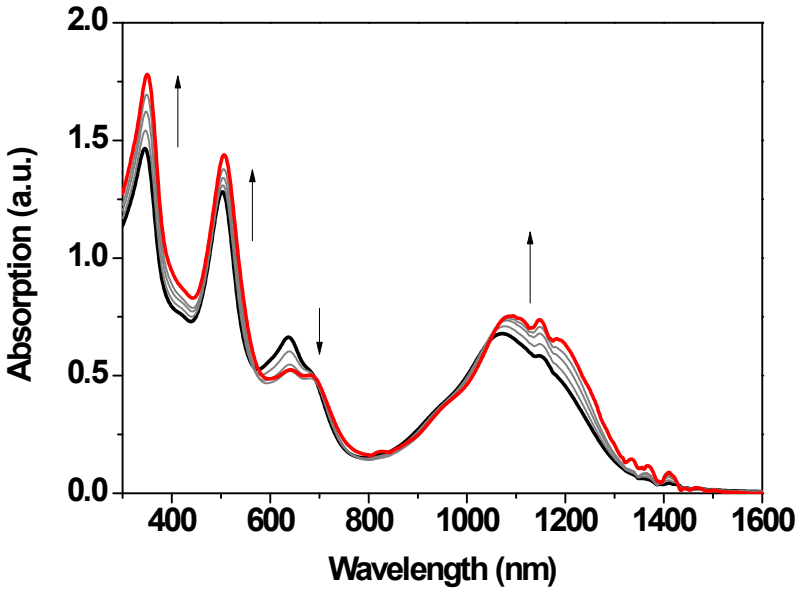

Figure S19. The changes of UV-vis-NIR absorption spectra of **P8** in CH_2Cl_2 upon lowering the temperature from 303 K (black line) to 223 K (red line).

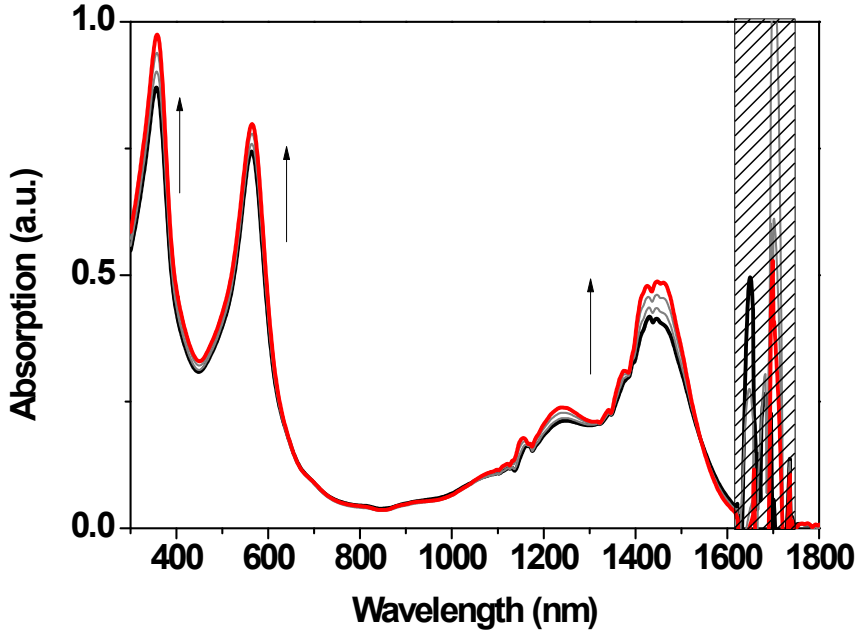

Figure S20. The changes of UV-vis-NIR absorption spectra of **P8-Cu2** in CH_2Cl_2 upon lowering the temperature from 283 K (black line) to 223 K (red line).

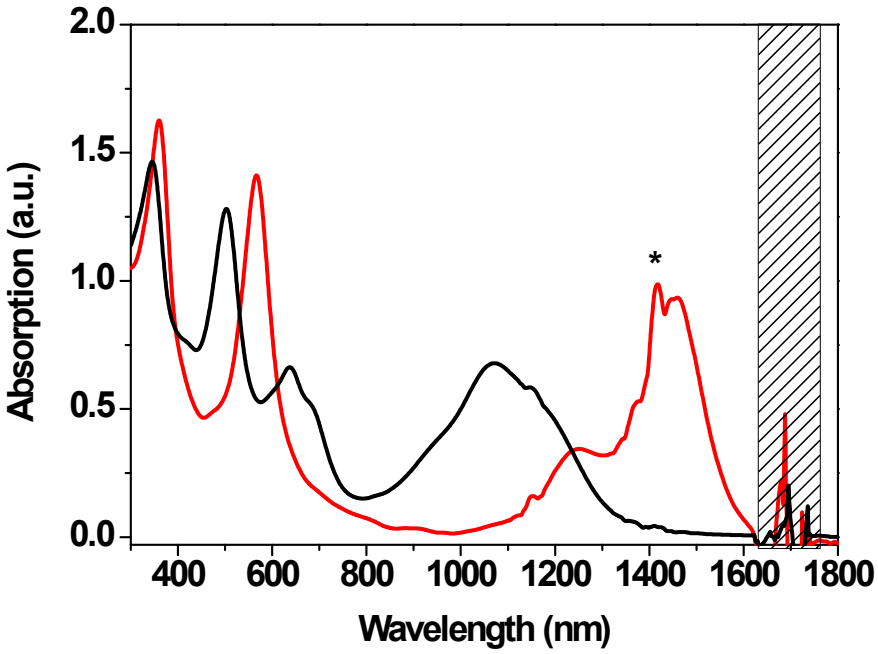

Figure S21. The change of UV-vis-NIR absorption spectrum of **P8** (black line) in CH_2Cl_2 upon addition of $Cu(OAc)_2$ salt (100 equiv) dissolved in MeOH at 243 K. The final spectrum was shown in red color.

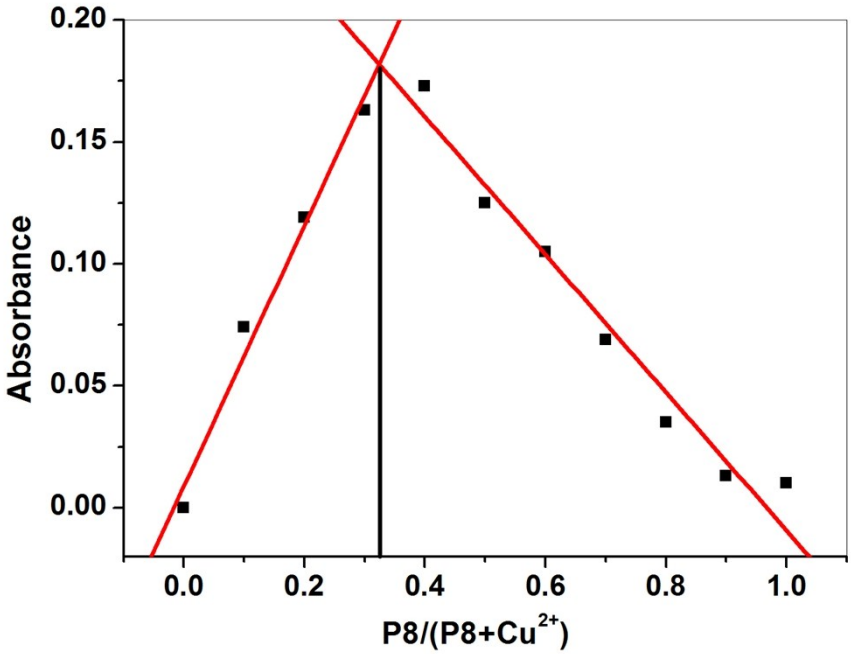

Figure. S22. Job's plot for determining the stoichiometry of **P8** and Cu^{2+} in MeOH.

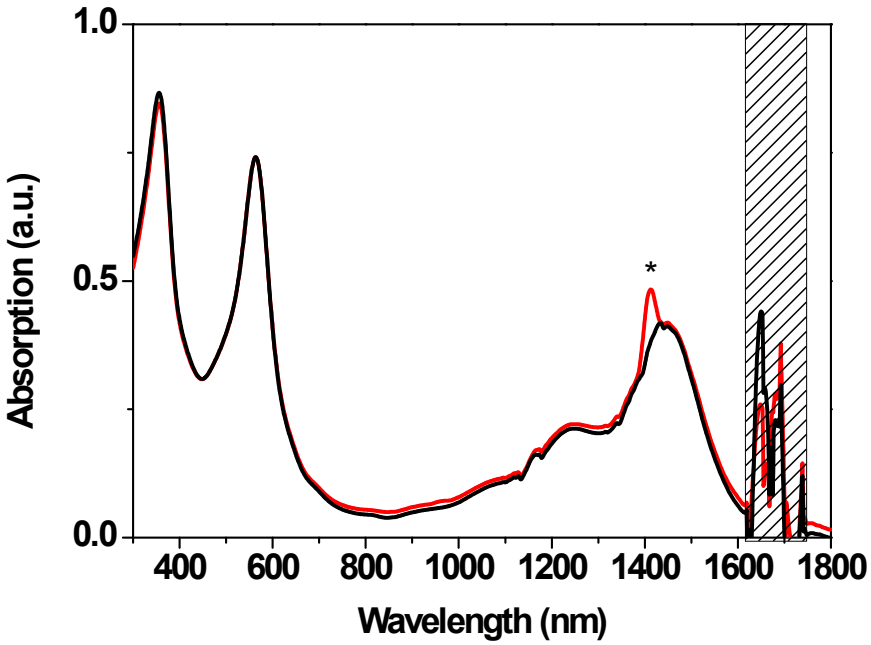

Figure S23. The change of UV-vis-NIR absorption spectra of **P8-Cu2** (black line) in CH_2Cl_2 upon addition of ethylenediaminetetraacetic acid (EDTA, 10 equiv) dissolved in MeOH at 303 K. The final spectrum was shown in red color. *: solvent noise peak.

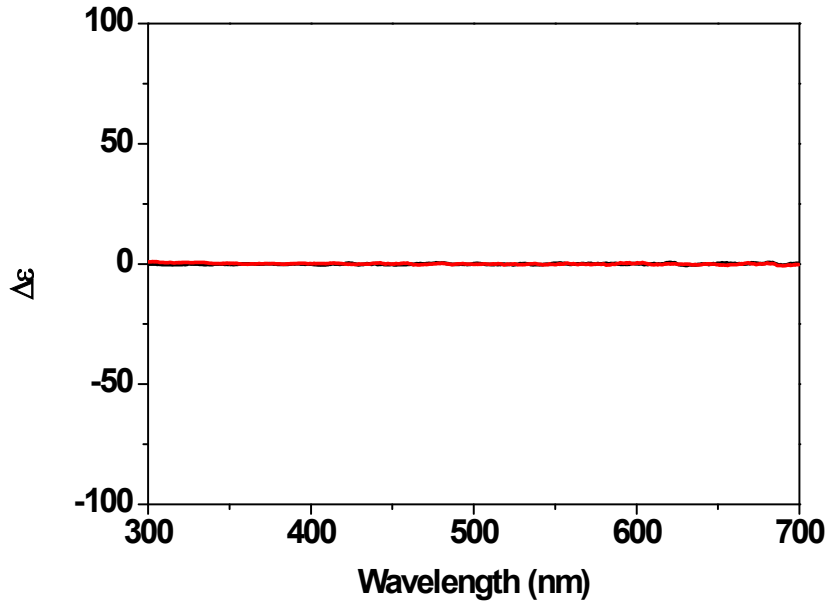

Figure S24. CD spectra of **P6-Cu2** in CH_2Cl_2 recorded at 293 K (black) and 273 K (red).

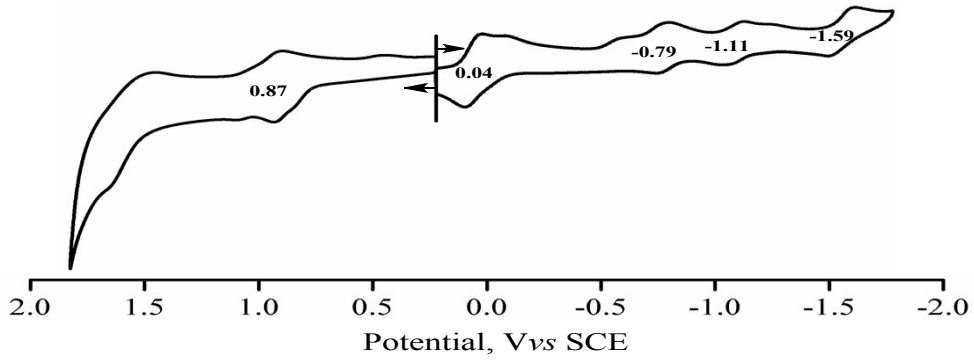

Figure S25. Cyclic voltammogram of **P8**.

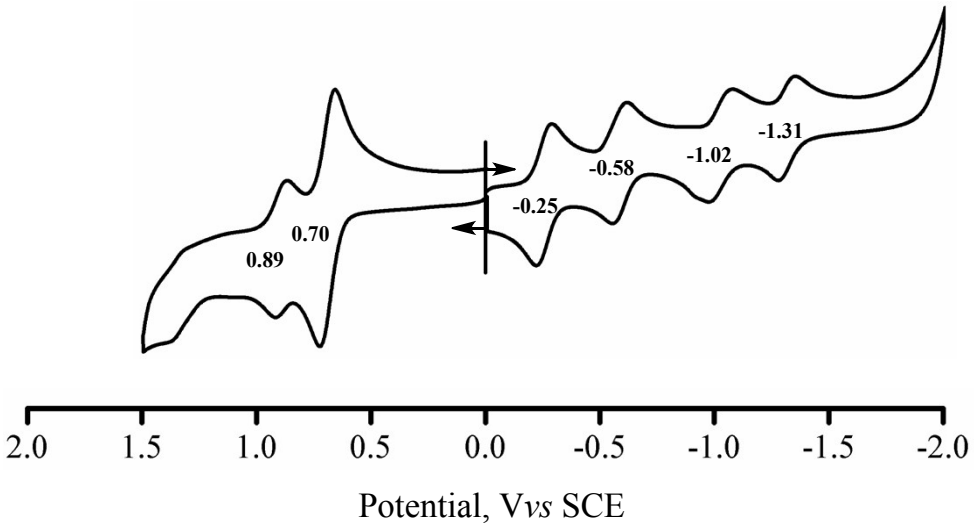

Figure S26. Cyclic voltammogram of **P6-Cu2**.

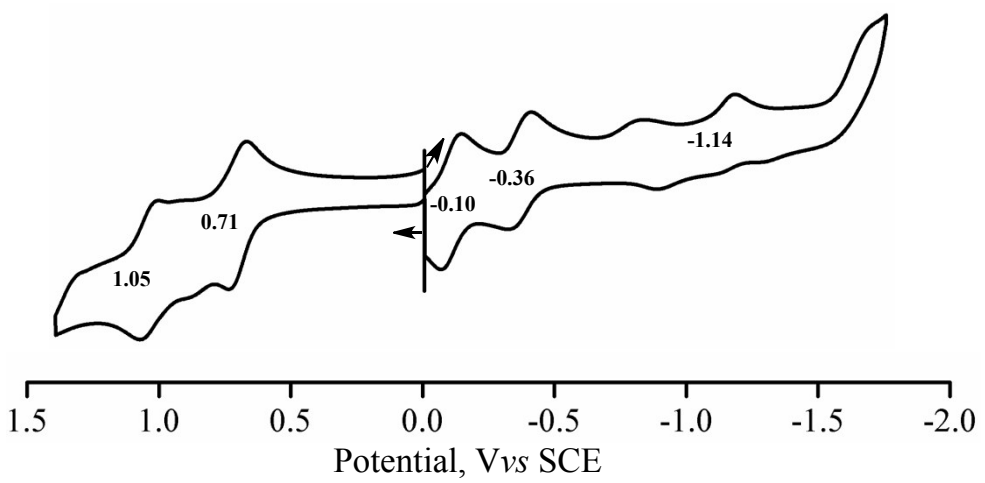

Figure S27. Cyclic voltammogram of **P7-Cu2**.

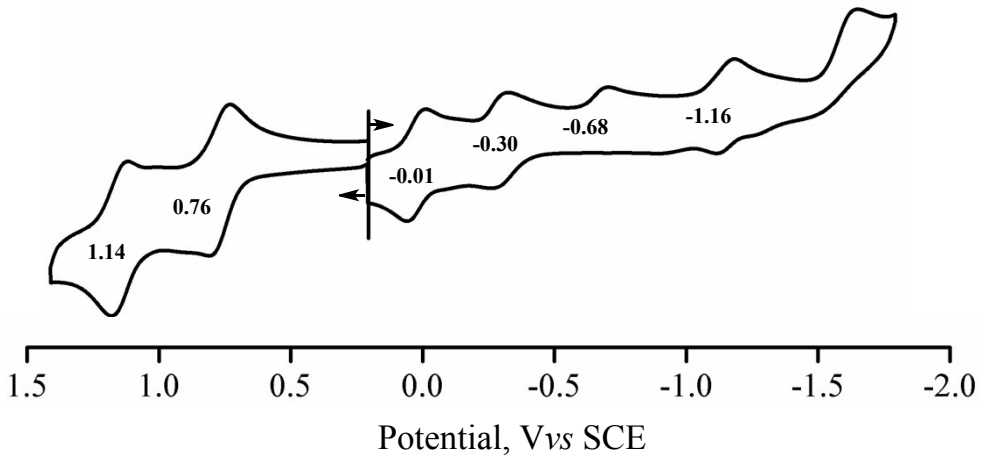

Figure S28. Cyclic voltammogram of **P8-Cu2**.

Table S2. Redox data for the compounds (SCE)

	Oxidation (V)			Reduction (V)					HOMO-LUMO gap[a] (eV)
	$E^{1/2}_{ox1}$	$E^{1/2}_{ox2}$	$E^{1/2}_{ox3}$	$E^{1/2}_{red1}$	$E^{1/2}_{red2}$	$E^{1/2}_{red3}$	$E^{1/2}_{red4}$	$E^{1/2}_{red5}$	
P8	0.87	--	--	0.04	-0.79	-1.11	--	-1.59	0.83
P6-Cu2	0.70	0.89	--	-0.25	-0.58	-1.02	-1.31	--	0.95
P7-Cu2	0.71	1.05	--	-0.10	-0.36	--	-1.14	--	0.81
P8-Cu2	0.76	1.14	--	-0.01	-0.30	-0.68	-1.16	--	0.77

[a]HOMO–LUMO gap = $E^{1/2}_{ox1} - E^{1/2}_{red1}$

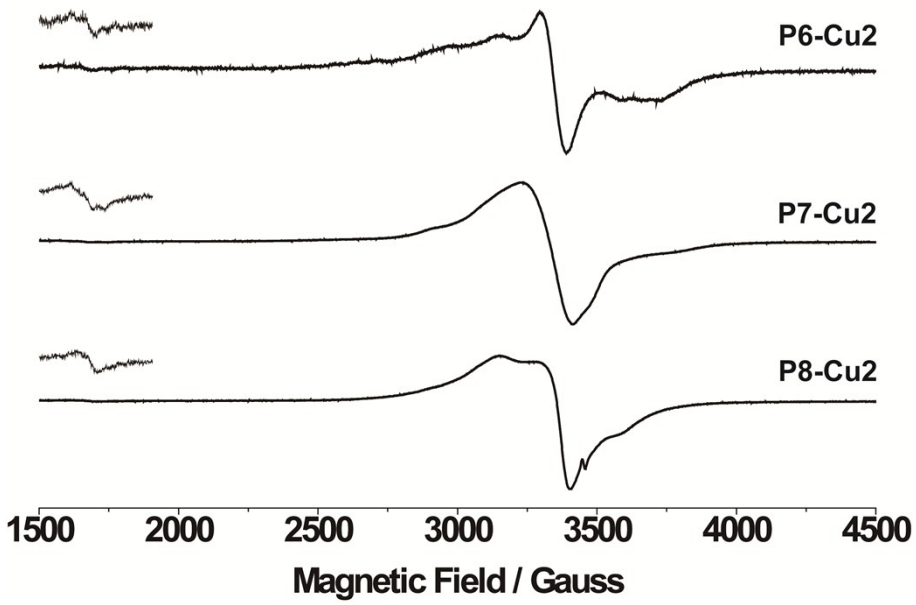

Figure S29. EPR spectra of solid samples of **P6-Cu2**, **P7-Cu2** and **P8-Cu2** recorded at 4K.

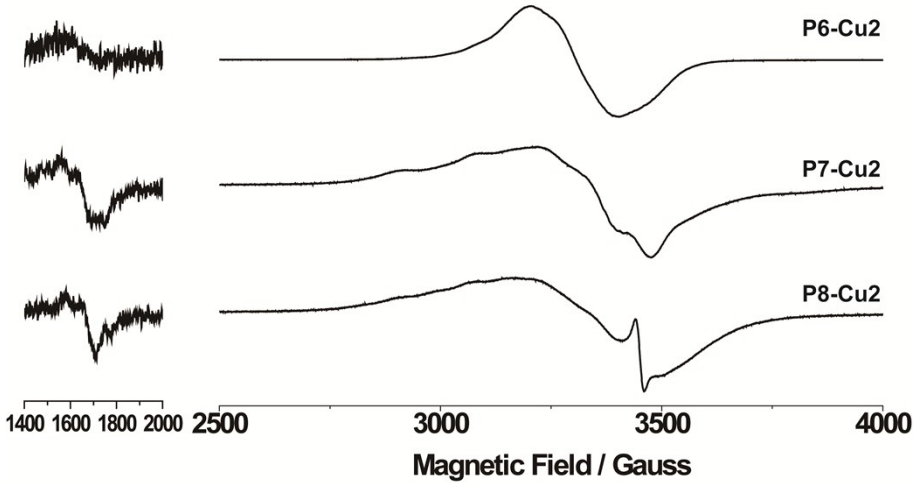

Figure S30. EPR spectra of frozen CH_2Cl_2 solutions of **P6-Cu2**, **P7-Cu2** and **P8-Cu2** recorded at 4K.

Table S3. Fitting parameters estimated by the Bleany-Bower equation.

	P6-Cu2[b]	**P7-Cu2**[b]	**P8-Cu2**[b]
J/k_B (K)	-11.4	-6.5	-4.3
θ (K)	-0.13	0	0
g (fixed)[a]	2.07	2.08	2.06

[a)] The values were obtained from EPR spectra. [b)] Including the temperature independent paramagnetic impurity of 6, 11, and 11 % for **P6-Cu2**, **P7-Cu2**, and **P8-Cu2**, respectively.

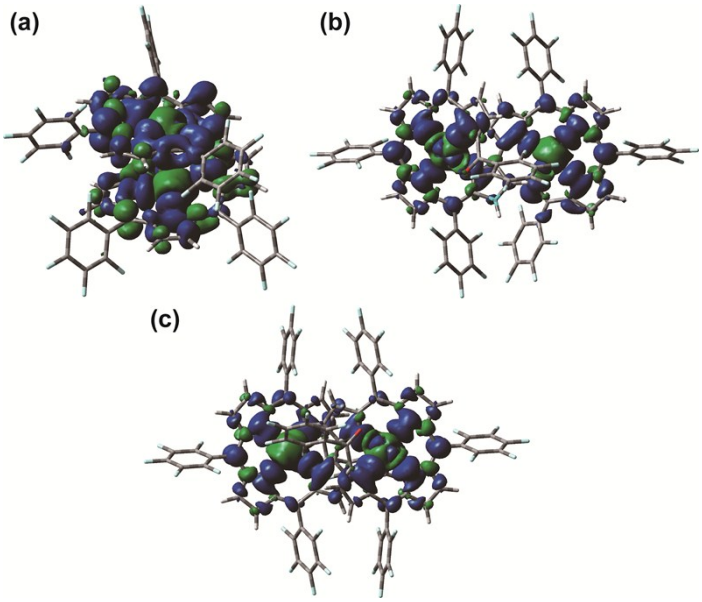

Figure S31. Spin density maps for a) **P6-Cu2**, b) **P7-Cu2** and c) **P8-Cu2** with isosurface values of 0.004 calculated by UB3LYP method (S =1).

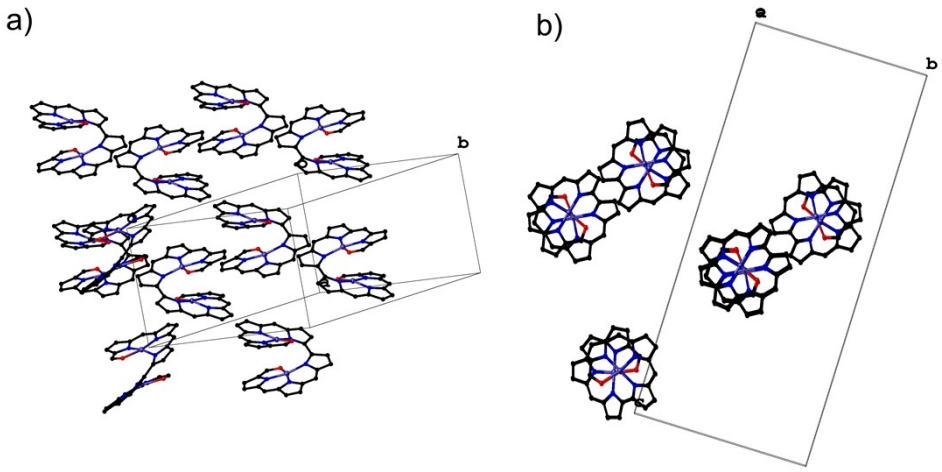

Figure S32. Complementary views of the packing of the molecules in the crystal **P6-Cu2**. Solvent molecules and meso aryl groups are omitted for clarity.

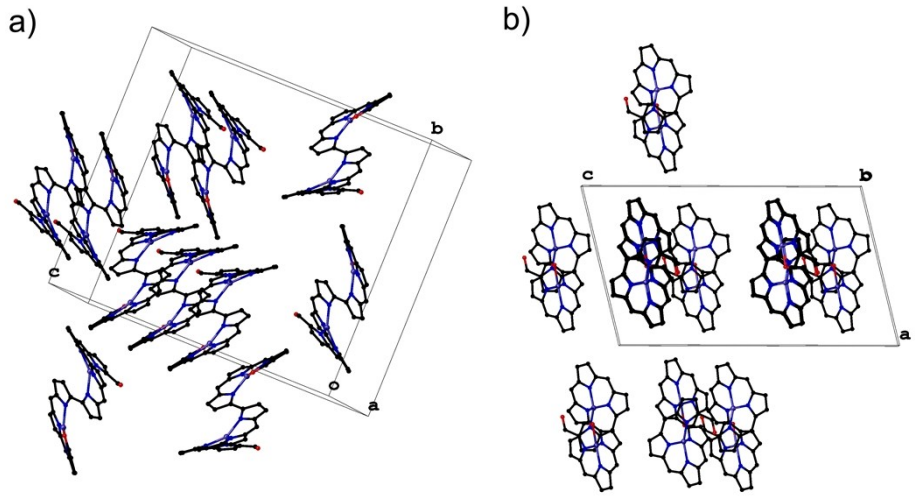

Figure S33. Complementary views of the packing of the molecules in the crystal **P7-Cu2**. Solvent molecules and meso aryl groups are omitted for clarity.

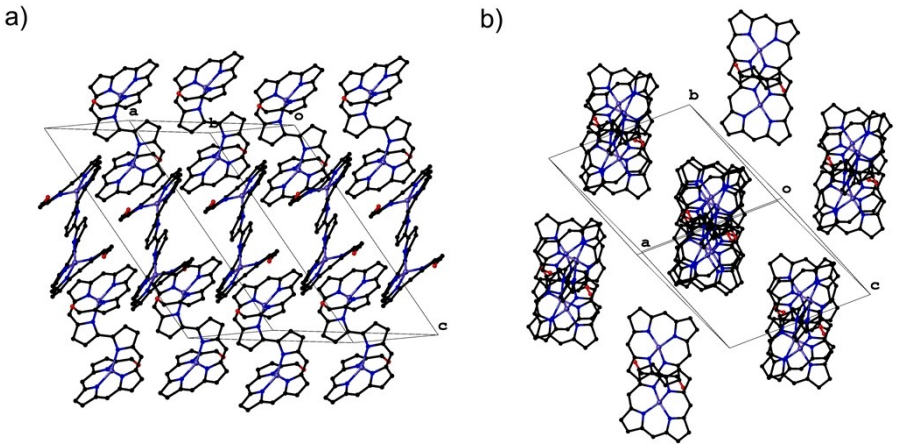

Figure S34. Complementary views of the packing of the molecules in the crystal **P8-Cu2**. Solvent molecules and meso aryl groups are omitted for clarity.

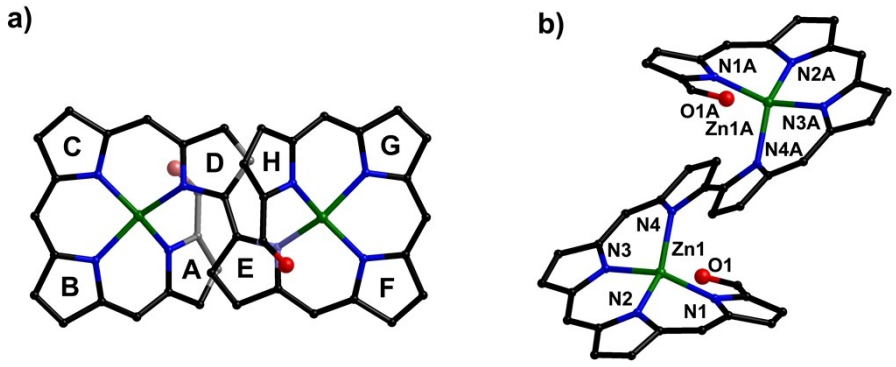

Figure S35. Crystal structure of **P8-Zn2**; (a) top view and (b) side view. C_6F_5 groups and the hydrogens attached to carbons are omitted for clarity.

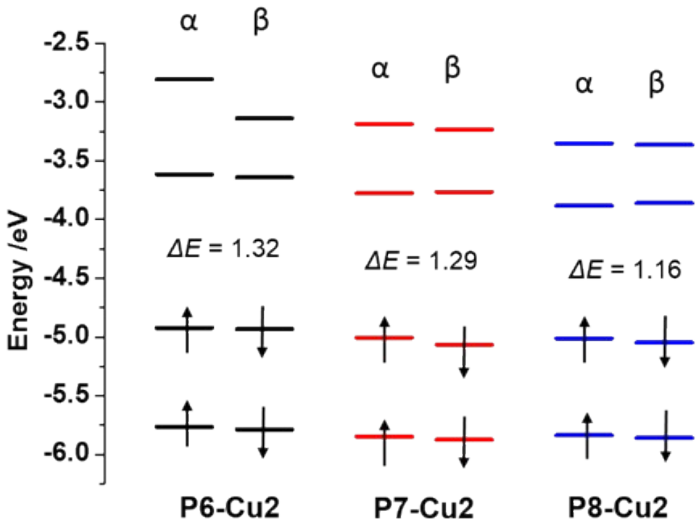

Figure S36. Energy levels of the frontier molecular orbitals of the copper complexes, **Pn-Cu2**.

Cartesian coordinates for all atoms of optimized geometries of P8 and its isomers (P8') and copper complexes, Pn-Cu2

P8 B3LYP(6-31G(d))

Row	Symbol	X	Y	Z
1	F	0.09638437	-4.772545271	4.691135039
2	F	1.715205517	-6.92074047	4.553011073
3	F	4.286026222	-6.655100609	3.696321245
4	F	5.210433954	-4.190272285	2.896678001
5	F	3.628476196	-2.050483302	3.04575712
6	F	2.339992047	4.923986795	5.356873265
7	F	3.379211781	6.248186509	7.458881832
8	F	3.210281037	5.190664042	9.97040626
9	F	1.970258238	2.790645631	10.35851535
10	F	0.897259638	1.46469076	8.271264315
11	F	-4.212962259	3.295726043	3.502025654
12	F	-6.539723892	4.460443146	2.843967327
13	F	-6.750569996	5.898579666	0.530922069
14	F	-4.594507284	6.15552301	-1.109889417
15	F	-2.286760384	4.880611072	-0.546048265
16	F	-5.607671924	1.278359045	2.391530197
17	F	-6.879036062	2.23209263	0.279795807
18	F	-6.276292517	1.341270588	-2.233800762
19	F	-4.349048551	-0.57542752	-2.561731538
20	F	-3.012010956	-1.507796949	-0.495951994
21	N	-1.199239884	-1.127607928	3.187708705
22	H	-1.024687808	-0.251951706	3.677976533
23	N	0.741486534	0.222597645	4.531220691
24	N	-0.348566758	2.606102379	3.545638758
25	H	-0.030046463	1.772370291	3.050259532
26	N	-0.518718165	1.357437786	1.135764094
27	O	-3.16001748	0.641843733	3.016853979
28	C	-2.235158231	-1.3675768	2.330731542
29	C	-2.02755123	-2.652292497	1.783653684
30	H	-2.66901087	-3.150865855	1.075536761
31	C	-0.833927768	-3.143037738	2.305621827
32	H	-0.355985409	-4.080100453	2.059296681
33	C	-0.306454619	-2.160735956	3.183730538
34	C	0.92192093	-2.129346013	3.92019642
35	C	1.373650234	-0.99982043	4.601580245
36	C	2.506792127	-0.917954934	5.519494119
37	H	3.177960182	-1.7268294	5.773066984
38	C	2.512873988	0.347713751	6.009441922

39	H	3.205704262	0.779740096	6.718548048
40	C	1.398845969	1.044094062	5.365883694
41	C	1.014934426	2.405340711	5.579413902
42	C	0.095785987	3.062670583	4.759906598
43	C	-0.620924123	4.293856693	5.013322913
44	H	-0.497781287	4.901051361	5.898507024
45	C	-1.494561642	4.495811567	3.985022924
46	H	-2.195860118	5.309546117	3.867880736
47	C	-1.31585019	3.426606503	3.031116674
48	C	-1.949710908	3.221616049	1.803901823
49	C	-1.534043635	2.211780417	0.888951646
50	C	-2.153303144	1.921798899	-0.405947783
51	H	-3.010867542	2.423101748	-0.822191263
52	C	-1.469499718	0.876504583	-0.934260281
53	H	-1.640893354	0.352534659	-1.861811493
54	C	-0.453945025	0.525609713	0.049453547
55	C	1.793204398	-3.327178045	3.876099269
56	C	1.347834903	-4.602257281	4.245928154
57	C	2.173413806	-5.721897779	4.179529641
58	C	3.490281649	-5.588559853	3.744681979
59	C	3.963778088	-4.335806908	3.360393666
60	C	3.1228476	-3.234015208	3.441094366
61	C	1.581627061	3.140366746	6.73345153
62	C	2.2250224	4.376955785	6.575446488
63	C	2.768881658	5.073566715	7.650892504
64	C	2.688615399	4.53341897	8.9326629
65	C	2.059650328	3.305137384	9.127456271
66	C	1.512587693	2.63171012	8.039070546
67	C	-3.166427222	4.01302678	1.492618574
68	C	-4.280538993	3.959905886	2.346778259
69	C	-5.492197074	4.564726424	2.022993794
70	C	-5.603102318	5.295614473	0.843627273
71	C	-4.502249067	5.409718712	-0.001634814
72	C	-3.310680108	4.769372047	0.32240477
73	C	-3.217091648	-0.283939182	2.206822429
74	C	-4.210918976	-0.15926973	1.073104752
75	C	-5.251352717	0.786775314	1.203650708
76	C	-5.942094865	1.28982079	0.106234786
77	C	-5.648360661	0.831590021	-1.176704769
78	C	-4.686891321	-0.158540033	-1.336044079
79	C	-3.994976179	-0.638351393	-0.227306197
80	C	0.453945025	-0.525609713	-0.049453547
81	N	0.518718165	-1.357437786	-1.135764094
82	C	1.469499718	-0.876504583	0.934260281

83	C	1.534043635	-2.211780417	-0.888951646
84	C	2.153303144	-1.921798899	0.405947783
85	H	1.640893354	-0.352534659	1.861811493
86	C	1.949710908	-3.221616049	-1.803901823
87	H	3.010867542	-2.423101748	0.822191263
88	C	1.31585019	-3.426606503	-3.031116674
89	C	3.166427222	-4.01302678	-1.492618574
90	N	0.348566758	-2.606102379	-3.545638758
91	C	1.494561642	-4.495811567	-3.985022924
92	C	4.280538993	-3.959905886	-2.346778259
93	C	3.310680108	-4.769372047	-0.32240477
94	H	0.030046463	-1.772370291	-3.050259532
95	C	-0.095785987	-3.062670583	-4.759906598
96	C	0.620924123	-4.293856693	-5.013322913
97	H	2.195860118	-5.309546117	-3.867880736
98	F	4.212962259	-3.295726043	-3.502025654
99	C	5.492197074	-4.564726424	-2.022993794
100	F	2.286760384	-4.880611072	0.546048265
101	C	4.502249067	-5.409718712	0.001634814
102	C	-1.014934426	-2.405340711	-5.579413902
103	H	0.497781287	-4.901051361	-5.898507024
104	F	6.539723892	-4.460443146	-2.843967327
105	C	5.603102318	-5.295614473	-0.843627273
106	F	4.594507284	-6.15552301	1.109889417
107	C	-1.398845969	-1.044094062	-5.365883694
108	C	-1.581627061	-3.140366746	-6.73345153
109	F	6.750569996	-5.898579666	-0.530922069
110	N	-0.741486534	-0.222597645	-4.531220691
111	C	-2.512873988	-0.347713751	-6.009441922
112	C	-2.2250224	-4.376955785	-6.575446488
113	C	-1.512587693	-2.63171012	-8.039070546
114	C	-1.373650234	0.99982043	-4.601580245
115	C	-2.506792127	0.917954934	-5.519494119
116	H	-3.205704262	-0.779740096	-6.718548048
117	F	-2.339992047	-4.923986795	-5.356873265
118	C	-2.768881658	-5.073566715	-7.650892504
119	F	-0.897259638	-1.46469076	-8.271264315
120	C	-2.059650328	-3.305137384	-9.127456271
121	C	-0.92192093	2.129346013	-3.92019642
122	H	-3.177960182	1.7268294	-5.773066984
123	F	-3.379211781	-6.248186509	-7.458881832
124	C	-2.688615399	-4.53341897	-8.9326629
125	F	-1.970258238	-2.790645631	-10.35851535
126	C	0.306454619	2.160735956	-3.183730538

127	C	-1.793204398	3.327178045	-3.876099269
128	F	-3.210281037	-5.190664042	-9.97040626
129	N	1.199239884	1.127607928	-3.187708705
130	C	0.833927768	3.143037738	-2.305621827
131	C	-1.347834903	4.602257281	-4.245928154
132	C	-3.1228476	3.234015208	-3.441094366
133	H	1.024687808	0.251951706	-3.677976533
134	C	2.235158231	1.3675768	-2.330731542
135	C	2.02755123	2.652292497	-1.783653684
136	H	0.355985409	4.080100453	-2.059296681
137	F	-0.09638437	4.772545271	-4.691135039
138	C	-2.173413806	5.721897779	-4.179529641
139	F	-3.628476196	2.050483302	-3.04575712
140	C	-3.963778088	4.335806908	-3.360393666
141	C	3.217091648	0.283939182	-2.206822429
142	H	2.66901087	3.150865855	-1.075536761
143	F	-1.715205517	6.92074047	-4.553011073
144	C	-3.490281649	5.588559853	-3.744681979
145	F	-5.210433954	4.190272285	-2.896678001
146	O	3.16001748	-0.641843733	-3.016853979
147	C	4.210918976	0.15926973	-1.073104752
148	F	-4.286026222	6.655100609	-3.696321245
149	C	5.251352717	-0.786775314	-1.203650708
150	C	3.994976179	0.638351393	0.227306197
151	F	5.607671924	-1.278359045	-2.391530197
152	C	5.942094865	-1.28982079	-0.106234786
153	F	3.012010956	1.507796949	0.495951994
154	C	4.686891321	0.158540033	1.336044079
155	F	6.879036062	-2.23209263	-0.279795807
156	C	5.648360661	-0.831590021	1.176704769
157	F	4.349048551	0.57542752	2.561731538
158	F	6.276292517	-1.341270588	2.233800762

P8’ B3LYP(6-31G(d))

Row	Symbol	X	Y	Z
1	F	0.09638437	-4.772545271	4.691135039
2	F	1.715205517	-6.92074047	4.553011073
3	F	4.286026222	-6.655100609	3.696321245
4	F	5.210433954	-4.190272285	2.896678001
5	F	3.628476196	-2.050483302	3.04575712
6	F	2.339992047	4.923986795	5.356873265
7	F	3.379211781	6.248186509	7.458881832
8	F	3.210281037	5.190664042	9.97040626
9	F	1.970258238	2.790645631	10.35851535

10	F	0.897259638	1.46469076	8.271264315
11	F	-4.212962259	3.295726043	3.502025654
12	F	-6.539723892	4.460443146	2.843967327
13	F	-6.750569996	5.898579666	0.530922069
14	F	-4.594507284	6.15552301	-1.109889417
15	F	-2.286760384	4.880611072	-0.546048265
16	F	-5.607671924	1.278359045	2.391530197
17	F	-6.879036062	2.23209263	0.279795807
18	F	-6.276292517	1.341270588	-2.233800762
19	F	-4.349048551	-0.57542752	-2.561731538
20	F	-3.012010956	-1.507796949	-0.495951994
21	N	-1.199239884	-1.127607928	3.187708705
22	H	-1.024687808	-0.251951706	3.677976533
23	N	0.741486534	0.222597645	4.531220691
24	N	-0.348566758	2.606102379	3.545638758
25	H	-0.030046463	1.772370291	3.050259532
26	N	-0.518718165	1.357437786	1.135764094
27	O	-3.16001748	0.641843733	3.016853979
28	C	-2.235158231	-1.3675768	2.330731542
29	C	-2.02755123	-2.652292497	1.783653684
30	H	-2.66901087	-3.150865855	1.075536761
31	C	-0.833927768	-3.143037738	2.305621827
32	H	-0.355985409	-4.080100453	2.059296681
33	C	-0.306454619	-2.160735956	3.183730538
34	C	0.92192093	-2.129346013	3.92019642
35	C	1.373650234	-0.99982043	4.601580245
36	C	2.506792127	-0.917954934	5.519494119
37	H	3.177960182	-1.7268294	5.773066984
38	C	2.512873988	0.347713751	6.009441922
39	H	3.205704262	0.779740096	6.718548048
40	C	1.398845969	1.044094062	5.365883694
41	C	1.014934426	2.405340711	5.579413902
42	C	0.095785987	3.062670583	4.759906598
43	C	-0.620924123	4.293856693	5.013322913
44	H	-0.497781287	4.901051361	5.898507024
45	C	-1.494561642	4.495811567	3.985022924
46	H	-2.195860118	5.309546117	3.867880736
47	C	-1.31585019	3.426606503	3.031116674
48	C	-1.949710908	3.221616049	1.803901823
49	C	-1.534043635	2.211780417	0.888951646
50	C	-2.153303144	1.921798899	-0.405947783
51	H	-3.010867542	2.423101748	-0.822191263
52	C	-1.469499718	0.876504583	-0.934260281
53	H	-1.640893354	0.352534659	-1.861811493

54	C	-0.453945025	0.525609713	0.049453547
55	C	1.793204398	-3.327178045	3.876099269
56	C	1.347834903	-4.602257281	4.245928154
57	C	2.173413806	-5.721897779	4.179529641
58	C	3.490281649	-5.588559853	3.744681979
59	C	3.963778088	-4.335806908	3.360393666
60	C	3.1228476	-3.234015208	3.441094366
61	C	1.581627061	3.140366746	6.73345153
62	C	2.2250224	4.376955785	6.575446488
63	C	2.768881658	5.073566715	7.650892504
64	C	2.688615399	4.53341897	8.9326629
65	C	2.059650328	3.305137384	9.127456271
66	C	1.512587693	2.63171012	8.039070546
67	C	-3.166427222	4.01302678	1.492618574
68	C	-4.280538993	3.959905886	2.346778259
69	C	-5.492197074	4.564726424	2.022993794
70	C	-5.603102318	5.295614473	0.843627273
71	C	-4.502249067	5.409718712	-0.001634814
72	C	-3.310680108	4.769372047	0.32240477
73	C	-3.217091648	-0.283939182	2.206822429
74	C	-4.210918976	-0.15926973	1.073104752
75	C	-5.251352717	0.786775314	1.203650708
76	C	-5.942094865	1.28982079	0.106234786
77	C	-5.648360661	0.831590021	-1.176704769
78	C	-4.686891321	-0.158540033	-1.336044079
79	C	-3.994976179	-0.638351393	-0.227306197
80	C	0.453945025	-0.525609713	-0.049453547
81	N	0.518718165	-1.357437786	-1.135764094
82	C	1.469499718	-0.876504583	0.934260281
83	C	1.534043635	-2.211780417	-0.888951646
84	C	2.153303144	-1.921798899	0.405947783
85	H	1.640893354	-0.352534659	1.861811493
86	C	1.949710908	-3.221616049	-1.803901823
87	H	3.010867542	-2.423101748	0.822191263
88	C	1.31585019	-3.426606503	-3.031116674
89	C	3.166427222	-4.01302678	-1.492618574
90	N	0.348566758	-2.606102379	-3.545638758
91	C	1.494561642	-4.495811567	-3.985022924
92	C	4.280538993	-3.959905886	-2.346778259
93	C	3.310680108	-4.769372047	-0.32240477
94	H	0.030046463	-1.772370291	-3.050259532
95	C	-0.095785987	-3.062670583	-4.759906598
96	C	0.620924123	-4.293856693	-5.013322913
97	H	2.195860118	-5.309546117	-3.867880736

98	F	4.212962259	-3.295726043	-3.502025654
99	C	5.492197074	-4.564726424	-2.022993794
100	F	2.286760384	-4.880611072	0.546048265
101	C	4.502249067	-5.409718712	0.001634814
102	C	-1.014934426	-2.405340711	-5.579413902
103	H	0.497781287	-4.901051361	-5.898507024
104	F	6.539723892	-4.460443146	-2.843967327
105	C	5.603102318	-5.295614473	-0.843627273
106	F	4.594507284	-6.15552301	1.109889417
107	C	-1.398845969	-1.044094062	-5.365883694
108	C	-1.581627061	-3.140366746	-6.73345153
109	F	6.750569996	-5.898579666	-0.530922069
110	N	-0.741486534	-0.222597645	-4.531220691
111	C	-2.512873988	-0.347713751	-6.009441922
112	C	-2.2250224	-4.376955785	-6.575446488
113	C	-1.512587693	-2.63171012	-8.039070546
114	C	-1.373650234	0.99982043	-4.601580245
115	C	-2.506792127	0.917954934	-5.519494119
116	H	-3.205704262	-0.779740096	-6.718548048
117	F	-2.339992047	-4.923986795	-5.356873265
118	C	-2.768881658	-5.073566715	-7.650892504
119	F	-0.897259638	-1.46469076	-8.271264315
120	C	-2.059650328	-3.305137384	-9.127456271
121	C	-0.92192093	2.129346013	-3.92019642
122	H	-3.177960182	1.7268294	-5.773066984
123	F	-3.379211781	-6.248186509	-7.458881832
124	C	-2.688615399	-4.53341897	-8.9326629
125	F	-1.970258238	-2.790645631	-10.35851535
126	C	0.306454619	2.160735956	-3.183730538
127	C	-1.793204398	3.327178045	-3.876099269
128	F	-3.210281037	-5.190664042	-9.97040626
129	N	1.199239884	1.127607928	-3.187708705
130	C	0.833927768	3.143037738	-2.305621827
131	C	-1.347834903	4.602257281	-4.245928154
132	C	-3.1228476	3.234015208	-3.441094366
133	H	1.024687808	0.251951706	-3.677976533
134	C	2.235158231	1.3675768	-2.330731542
135	C	2.02755123	2.652292497	-1.783653684
136	H	0.355985409	4.080100453	-2.059296681
137	F	-0.09638437	4.772545271	-4.691135039
138	C	-2.173413806	5.721897779	-4.179529641
139	F	-3.628476196	2.050483302	-3.04575712
140	C	-3.963778088	4.335806908	-3.360393666
141	C	3.217091648	0.283939182	-2.206822429

142	H	2.66901087	3.150865855	-1.075536761
143	F	-1.715205517	6.92074047	-4.553011073
144	C	-3.490281649	5.588559853	-3.744681979
145	F	-5.210433954	4.190272285	-2.896678001
146	O	3.16001748	-0.641843733	-3.016853979
147	C	4.210918976	0.15926973	-1.073104752
148	F	-4.286026222	6.655100609	-3.696321245
149	C	5.251352717	-0.786775314	-1.203650708
150	C	3.994976179	0.638351393	0.227306197
151	F	5.607671924	-1.278359045	-2.391530197
152	C	5.942094865	-1.28982079	-0.106234786
153	F	3.012010956	1.507796949	0.495951994
154	C	4.686891321	0.158540033	1.336044079
155	F	6.879036062	-2.23209263	-0.279795807
156	C	5.648360661	-0.831590021	1.176704769
157	F	4.349048551	0.57542752	2.561731538
158	F	6.276292517	-1.341270588	2.233800762

P6-Cu2 in the triplet state (ub3lyp/6-31g(d)LAN)

Row	Symbol	X	Y	Z
1	Cu	0.542191	-0.825426	1.551622
2	Cu	-0.578923	-0.883789	-1.564603
3	F	-4.493553	0.829287	1.694426
4	F	-6.953579	0.107611	2.488418
5	F	-7.290658	-2.014128	4.171162
6	F	-5.124114	-3.410241	5.059719
7	F	-2.650489	-2.703479	4.295143
8	F	1.508115	3.879211	4.431129
9	F	2.180375	6.487905	4.615683
10	F	2.989834	7.855087	2.397417
11	F	3.118856	6.586341	-0.016809
12	F	2.444108	3.983903	-0.217461
13	F	5.167967	-1.890505	3.668005
14	F	7.673022	-2.864485	3.879849
15	F	8.893017	-4.000611	1.719486
16	F	7.576066	-4.140265	-0.671709
17	F	5.082184	-3.158373	-0.905399
18	F	-5.297049	-1.874666	-3.612532
19	F	-7.835973	-2.772443	-3.73213
20	F	-9.032828	-3.81042	-1.509946
21	F	-7.656953	-3.928415	0.849057
22	F	-5.128699	-3.023034	0.990671
23	F	-0.496316	4.321002	-0.304937
24	F	-1.034264	6.95481	-0.506231

25	F	-2.671865	7.873724	-2.489888
26	F	-3.756739	6.124442	-4.281213
27	F	-3.208731	3.490922	-4.111048
28	F	4.4714	0.654088	-1.729611
29	F	6.929671	-0.116258	-2.490522
30	F	7.249689	-2.277827	-4.123673
31	F	5.072515	-3.667377	-4.995101
32	F	2.6016	-2.911844	-4.263322
33	N	-0.271537	0.81505	2.101932
34	N	2.294021	0.090314	1.565228
35	N	1.29177	-2.425926	0.721854
36	N	-1.375621	-2.422748	-0.671859
37	N	-2.31459	0.06629	-1.682112
38	N	0.292516	0.727766	-2.114059
39	O	-1.329397	-1.524944	2.178277
40	O	1.276374	-1.651846	-2.184391
41	C	-2.098377	-0.569454	2.504247
42	C	-1.585729	0.762952	2.471237
43	C	-2.021752	2.078151	2.803083
44	H	-3.01343	2.36943	3.118637
45	C	-0.929982	2.90926	2.621964
46	H	-0.898093	3.978672	2.776894
47	C	0.169869	2.085884	2.201329
48	C	1.547917	2.410889	1.984997
49	C	2.521481	1.446906	1.724598
50	C	3.957172	1.665786	1.672388
51	H	4.44291	2.627564	1.762349
52	C	4.552668	0.452251	1.525639
53	H	5.611078	0.245045	1.452406
54	C	3.493154	-0.539514	1.446056
55	C	3.650662	-1.932356	1.26266
56	C	2.589694	-2.809198	0.945072
57	C	2.69555	-4.241443	0.735328
58	H	3.598522	-4.825574	0.842249
59	C	1.462783	-4.69196	0.366966
60	H	1.186951	-5.699313	0.085369
61	C	0.598201	-3.538691	0.301669
62	C	-0.704673	-3.53568	-0.21933
63	C	-1.589617	-4.674737	-0.257978
64	H	-1.334374	-5.678925	0.05301
65	C	-2.812438	-4.21201	-0.645025
66	H	-3.724855	-4.782951	-0.743756
67	C	-2.678387	-2.789065	-0.896218
68	C	-3.718715	-1.899303	-1.245882

69	C	-3.525631	-0.519488	-1.485393
70	C	-4.554528	0.506359	-1.517585
71	H	-5.613171	0.335929	-1.380389
72	C	-3.92663	1.699301	-1.692567
73	H	-4.384349	2.677591	-1.732459
74	C	-2.503724	1.432055	-1.82154
75	C	-1.499142	2.363914	-2.084894
76	C	-0.130185	1.996006	-2.294664
77	C	0.965986	2.764054	-2.816655
78	H	0.942087	3.815666	-3.067529
79	C	2.036201	1.900285	-2.973005
80	H	3.019801	2.146522	-3.347422
81	C	1.587599	0.622115	-2.533484
82	C	-3.472155	-0.905948	2.967746
83	C	2.067879	-0.722913	-2.529365
84	C	-4.607523	-0.207193	2.539201
85	C	-5.89034	-0.57107	2.934716
86	C	-6.065985	-1.660126	3.784202
87	C	-4.957143	-2.374873	4.232191
88	C	-3.681338	-2.002831	3.819134
89	C	1.952378	3.839688	2.100267
90	C	1.895187	4.522677	3.321152
91	C	2.238548	5.867619	3.432271
92	C	2.655028	6.566637	2.301243
93	C	2.723351	5.916422	1.071637
94	C	2.372843	4.571361	0.98338
95	C	5.027512	-2.489756	1.375267
96	C	5.736301	-2.433683	2.583315
97	C	7.030528	-2.933053	2.709539
98	C	7.654375	-3.516787	1.609076
99	C	6.979628	-3.591839	0.392645
100	C	5.689334	-3.079269	0.291167
101	C	-5.11264	-2.41869	-1.309122
102	C	-5.852304	-2.370364	-2.499152
103	C	-7.164669	-2.830949	-2.577633
104	C	-7.776785	-3.364794	-1.445694
105	C	-7.071931	-3.429775	-0.245811
106	C	-5.763465	-2.958176	-0.192367
107	C	-1.838369	3.808052	-2.196792
108	C	-1.294749	4.737476	-1.299763
109	C	-1.564795	6.099725	-1.387975
110	C	-2.402485	6.570156	-2.396941
111	C	-2.959146	5.674447	-3.307019
112	C	-2.669806	4.315463	-3.202811

113	C	3.438814	-1.095012	-2.973052
114	C	4.579534	-0.400772	-2.550726
115	C	5.860161	-0.789992	-2.929024
116	C	6.026969	-1.899653	-3.753354
117	C	4.91252	-2.61134	-4.192456
118	C	3.638796	-2.213963	-3.796866

P7-Cu2 in the triplet state (ub3lyp/6-31G*-LAN)

Row	Symbol	X	Y	Z
1	Cu	-3.084444	0.080864	0.548127
2	Cu	3.149415	-0.26376	-1.077332
3	N	-2.203162	1.351793	1.790904
4	N	-4.40376	1.493104	0.040873
5	N	-4.296523	-1.333211	-0.048415
6	N	-1.500985	-1.09306	-0.047611
7	N	1.598729	0.859267	-0.704932
8	N	4.423795	1.230246	-0.873669
9	N	4.63551	-1.468027	-1.156587
10	O	-2.045055	-1.183291	2.992308
11	O	2.221393	-1.960252	-1.86561
12	F	1.594401	0.095276	2.715867
13	F	3.565438	-0.679424	4.383652
14	F	2.957826	-1.840132	6.778948
15	F	0.356975	-2.226333	7.491371
16	F	-1.630608	-1.468893	5.832735
17	F	-3.921162	5.155157	2.987593
18	F	-3.574071	7.835973	2.945678
19	F	-2.432586	9.035026	0.777971
20	F	-1.653149	7.526296	-1.364215
21	F	-2.03736	4.859063	-1.353549
22	F	-8.490928	-0.830583	0.680359
23	F	-10.990811	-0.876916	-0.33989
24	F	-11.438606	-0.062217	-2.906114
25	F	-9.357859	0.794012	-4.449169
26	F	-6.849648	0.832941	-3.444029
27	F	-1.108279	-4.928616	-1.279992
28	F	-0.85629	-7.566322	-0.817054
29	F	-2.246631	-8.745438	1.216987
30	F	-3.881032	-7.241561	2.801912
31	F	-4.114562	-4.591175	2.382235
32	F	1.185176	4.725295	0.601556
33	F	0.805964	7.341472	0.12236
34	F	1.984655	8.534163	-2.034318
35	F	3.539243	7.058632	-3.72527

36	F	3.899832	4.425545	-3.285121
37	F	7.65765	0.702041	1.848324
38	F	10.312581	0.813362	2.321099
39	F	12.084963	0.194335	0.340839
40	F	11.176243	-0.532556	-2.126405
41	F	8.523731	-0.63241	-2.620157
42	F	3.479756	-5.457164	-0.538273
43	F	2.221515	-7.741777	-1.201997
44	F	0.50846	-7.799821	-3.320947
45	F	0.064102	-5.547296	-4.785477
46	F	1.297809	-3.247447	-4.140214
47	C	-1.210637	-0.32151	3.264121
48	C	-1.289421	1.03928	2.741534
49	C	-0.629012	2.215457	3.199212
50	H	0.128034	2.265033	3.969578
51	C	-1.186239	3.270965	2.508077
52	H	-0.937372	4.318364	2.602501
53	C	-2.186058	2.71702	1.644006
54	C	-3.125006	3.430383	0.852281
55	C	-4.198727	2.852565	0.169556
56	C	-5.327486	3.54617	-0.409462
57	H	-5.448963	4.619774	-0.453364
58	C	-6.210015	2.594194	-0.828682
59	H	-7.180875	2.753832	-1.275483
60	C	-5.613337	1.304648	-0.54113
61	C	-6.202467	0.028825	-0.786268
62	C	-5.572192	-1.192139	-0.526863
63	C	-6.12791	-2.521899	-0.755464
64	H	-7.11293	-2.729566	-1.148889
65	C	-5.174462	-3.42219	-0.407105
66	H	-5.233201	-4.499861	-0.469273
67	C	-4.000015	-2.66499	0.005097
68	C	-2.736096	-3.186481	0.323254
69	C	-1.554378	-2.396476	0.346394
70	C	-0.223307	-2.857269	0.692545
71	H	0.021952	-3.833419	1.086357
72	C	0.62925	-1.824856	0.45192
73	H	1.693994	-1.803658	0.623518
74	C	-0.166724	-0.73653	-0.07806
75	C	0.274579	0.472907	-0.628272
76	C	-0.561734	1.557307	-1.095028
77	H	-1.636055	1.523057	1.199591
78	C	0.256893	2.612733	-1.346874
79	H	-0.035917	3.595375	-1.682577

80	C	1.614488	2.183952	-1.06851
81	C	2.757173	3.011737	-1.094962
82	C	4.074986	2.542998	-0.884538
83	C	5.265345	3.346347	-0.662473
84	H	5.292778	4.42595	-0.614251
85	C	6.306719	2.485999	-0.507093
86	H	7.342333	2.739465	-0.328292
87	C	5.787238	1.135655	-0.655682
88	C	6.532427	-0.044776	-0.660571
89	C	5.960699	-1.32768	-0.942909
90	C	6.580954	-2.611643	-1.134651
91	H	7.634492	-2.830535	-1.028996
92	C	5.586773	-3.500138	-1.503198
93	H	5.704225	-4.550851	-1.728696
94	C	4.369728	-2.758293	-1.520223
95	C	3.006933	-2.960188	-1.889257
96	C	-0.087826	-0.656276	4.220753
97	C	1.256262	-0.462251	3.890829
98	C	2.28797	-0.859587	4.737073
99	C	1.979735	-1.459424	5.955905
100	C	0.648283	-1.6617	6.315422
101	C	-0.367624	-1.270841	5.446801
102	C	-2.988556	4.919011	0.821822
103	C	-3.370225	5.71684	1.904977
104	C	-3.193582	7.099007	1.897928
105	C	-2.613251	7.714035	0.790208
106	C	-2.222497	6.945332	-0.303367
107	C	-2.422875	5.568395	-0.278391
108	C	-7.584576	0.001885	-1.347722
109	C	-8.675743	-0.42951	-0.584332
110	C	-9.971004	-0.459033	-1.096585
111	C	-10.20186	-0.041471	-2.405386
112	C	-9.138277	0.397781	-3.191209
113	C	-7.851132	0.410933	-2.659503
114	C	-2.610835	-4.651701	0.546052
115	C	-1.791257	-5.46178	-0.253338
116	C	-1.654964	-6.828863	-0.03305
117	C	-2.364768	-7.434609	1.001303
118	C	-3.200437	-6.664534	1.807032
119	C	-3.312317	-5.294861	1.576289
120	C	2.559806	4.469745	-1.325446
121	C	1.773809	5.263705	-0.478072
122	C	1.568149	6.620492	-0.711302
123	C	2.168915	7.2329	-1.808194

124	C	2.965509	6.478302	-2.666371
125	C	3.145435	5.11892	-2.421866
126	C	7.997561	0.028779	-0.402464
127	C	8.499618	0.397974	0.851707
128	C	9.866748	0.459021	1.111487
129	C	10.773222	0.140177	0.103014
130	C	10.307	-0.233837	-1.155533
131	C	8.935864	-0.282932	-1.394007
132	C	2.437644	-4.265539	-2.316738
133	C	2.659412	-5.449121	-1.600508
134	C	2.013221	-6.637615	-1.924859
135	C	1.130598	-6.667222	-3.001528
136	C	0.900155	-5.511469	-3.744404
137	C	1.540189	-4.32681	-3.394952

P8-Cu2 in the triplet state (ub3lyp/6-31G*-LAN)

Row	Symbol	X	Y	Z
1	Cu	2.995281	0.491388	1.185869
2	F	2.88312	5.318106	2.791028
3	F	2.075361	7.872815	3.058416
4	F	0.344879	8.964121	1.252453
5	F	-0.55435	7.467433	-0.849999
6	F	0.276332	4.932221	-1.162331
7	F	6.876415	2.075746	-2.42891
8	F	9.418259	2.549093	-3.19841
9	F	11.482791	2.083261	-1.476063
10	F	10.97904	1.14507	1.036569
11	F	8.439141	0.681947	1.826746
12	F	3.098104	-4.450329	-0.439503
13	F	3.179554	-7.142677	-0.312187
14	F	3.952915	-8.384373	1.997413
15	F	4.614897	-6.89947	4.186757
16	F	4.488842	-4.200849	4.08585
17	F	-1.791695	-0.294642	2.875423
18	F	-4.057437	0.186731	4.25731
19	F	-3.962666	1.581617	6.60147
20	F	-1.580446	2.503135	7.550499
21	F	0.694939	2.046394	6.175039
22	N	1.289805	1.275726	0.392608
23	N	3.95545	2.078999	0.569833
24	N	4.618504	-0.641411	0.964799
25	N	2.250333	-0.843924	2.452088
26	O	1.481858	1.681565	3.421018
27	C	0.069731	0.657562	0.228671

28	C	-0.989612	1.604459	0.510076
29	H	-2.047028	1.387255	0.509971
30	C	-0.39243	2.800394	0.760281
31	H	-0.88101	3.734306	0.989929
32	C	1.039144	2.591674	0.64796
33	C	2.036594	3.600052	0.687983
34	C	3.407087	3.327891	0.531121
35	C	4.458894	4.28955	0.231893
36	H	4.32082	5.357488	0.136757
37	C	5.605318	3.58545	0.050631
38	H	6.581291	3.975253	-0.201569
39	C	5.286776	2.178404	0.263315
40	C	6.167004	1.096058	0.160908
41	C	5.808966	-0.256164	0.444449
42	C	6.643263	-1.424917	0.248979
43	H	7.645764	-1.42279	-0.154748
44	C	5.923136	-2.505985	0.667155
45	H	6.237416	-3.540601	0.678386
46	C	4.652179	-2.010219	1.144709
47	C	3.644294	-2.750508	1.770397
48	C	2.51193	-2.191695	2.419499
49	C	1.550365	-2.876691	3.232441
50	H	1.498353	-3.944157	3.392891
51	C	0.732089	-1.910762	3.779336
52	H	-0.079504	-2.059273	4.47812
53	C	1.199366	-0.658432	3.286116
54	C	1.603249	5.018216	0.813854
55	C	2.045352	5.819543	1.876594
56	C	1.634117	7.141824	2.030257
57	C	0.748627	7.700837	1.111662
58	C	0.290196	6.933952	0.043269
59	C	0.727014	5.620514	-0.100746
60	C	7.567738	1.36216	-0.272481
61	C	7.864101	1.843352	-1.554055
62	C	9.171165	2.091676	-1.966653
63	C	10.226839	1.851552	-1.089923
64	C	9.967805	1.369447	0.191576
65	C	8.65258	1.134677	0.584174
66	C	3.784444	-4.237918	1.823331
67	C	3.470447	-5.029505	0.715541
68	C	3.512559	-6.419743	0.761613
69	C	3.901245	-7.053397	1.939536
70	C	4.236893	-6.292683	3.057956
71	C	4.172155	-4.902314	2.991057

72	C	0.800504	0.690898	3.678731
73	C	-0.469762	0.856818	4.482251
74	C	-1.705671	0.387447	4.028776
75	C	-2.885856	0.629604	4.726828
76	C	-2.840309	1.348539	5.919136
77	C	-1.621373	1.824379	6.399675
78	C	-0.455437	1.585887	5.67684
79	F	-2.882764	-5.318077	-2.791141
80	F	-2.074955	-7.872779	-3.058429
81	F	-0.344706	-8.96408	-1.252239
82	F	0.554216	-7.4674	0.850349
83	F	-0.276577	-4.932229	1.162624
84	F	-6.876342	-2.075761	2.428998
85	F	-9.418171	-2.549115	3.19854
86	F	-11.482735	-2.08329	1.476227
87	F	-10.979027	-1.1451	-1.036414
88	F	-8.439144	-0.681973	-1.826635
89	F	-3.098017	4.450365	0.439421
90	F	-3.17934	7.142707	0.312015
91	F	-3.952808	8.384366	-1.997569
92	F	-4.614997	6.899422	-4.186825
93	F	-4.489033	4.200801	-4.085844
94	F	1.79152	0.294698	-2.875606
95	F	4.057284	-0.186686	-4.257457
96	F	3.962553	-1.581634	-6.601581
97	F	1.580353	-2.503204	-7.55061
98	F	-0.695051	-2.046454	-6.175186
99	N	-1.289774	-1.275688	-0.39266
100	N	-3.955419	-2.07899	-0.569783
101	N	-4.618514	0.641405	-0.964785
102	N	-2.250396	0.843919	-2.452145
103	O	-1.481978	-1.681569	-3.421137
104	C	-0.0697	-0.657511	-0.228747
105	C	0.989643	-1.604409	-0.510144
106	H	2.047058	-1.387203	-0.510051
107	C	0.392465	-2.800343	-0.760348
108	H	0.881055	-3.734248	-0.990008
109	C	-1.039109	-2.591641	-0.647979
110	C	-2.036549	-3.60003	-0.687955
111	C	-3.407043	-3.327878	-0.531074
112	C	-4.458835	-4.289543	-0.231811
113	H	-4.32075	-5.357478	-0.136656
114	C	-5.605265	-3.585454	-0.050544
115	H	-6.581229	-3.975265	0.201676

116	C	-5.28674	-2.178408	-0.263246
117	C	-6.166977	-1.09607	-0.160834
118	C	-5.808958	0.256152	-0.444395
119	C	-6.643259	1.4249	-0.248909
120	H	-7.645747	1.422767	0.154851
121	C	-5.923155	2.50597	-0.667117
122	H	-6.237442	3.540584	-0.678344
123	C	-4.652208	2.010212	-1.144702
124	C	-3.644347	2.750501	-1.770425
125	C	-2.511998	2.191689	-2.419553
126	C	-1.550444	2.87669	-3.232504
127	H	-1.498426	3.944157	-3.392937
128	C	-0.732189	1.910762	-3.779432
129	H	0.079381	2.059276	-4.478243
130	C	-1.199471	0.658428	-3.286228
131	C	-1.603185	-5.018195	-0.813775
132	C	-2.04513	-5.819516	-1.876585
133	C	-1.633862	-7.141792	-2.030202
134	C	-0.748491	-7.700803	-1.11149
135	C	-0.290215	-6.933924	-0.043027
136	C	-0.727077	-5.620496	0.100947
137	C	-7.567703	-1.36218	0.272579
138	C	-7.864043	-1.843372	1.554158
139	C	-9.171099	-2.091699	1.966778
140	C	-10.226789	-1.851579	1.090066
141	C	-9.967778	-1.369474	-0.191437
142	C	-8.65256	-1.134702	-0.584058
143	C	-3.784499	4.23791	-1.823367
144	C	-3.470417	5.029518	-0.715617
145	C	-3.512477	6.419755	-0.761732
146	C	-3.901199	7.05339	-1.939653
147	C	-4.236951	6.292655	-3.058027
148	C	-4.172256	4.902285	-2.99109
149	C	-0.800658	-0.690896	-3.678913
150	C	0.46962	-0.856824	-4.482414
151	C	1.705519	-0.387426	-4.028941
152	C	2.885713	-0.629586	-4.726974
153	C	2.840186	-1.348553	-5.919263
154	C	1.621261	-1.824419	-6.399803
155	C	0.455315	-1.585922	-5.676986
156	Cu	-2.995284	-0.491386	-1.18588