Electronic Supplementary Information

for

Doubly N-confused isophlorin: Synthesis, structure and copper coordination

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Experimental general

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Preparative separation was performed by silica gel column chromatography (KANTO Silica Gel 60 N, spherical, neutral, 63–210 μm). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 pre-coated aluminum sheets. ^{1}H-NMR (300 or 600 MHz), ^{19}F-NMR (564 MHz) and ^{13}C-NMR (150 MHz) spectra were recorded on a JEOL JNM-AL 300 FT-NMR spectrometer and Bruker Avance III HD600SB spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent and internal standard signals ($CDCl_3$: 7.26 ppm and CD_2Cl_2: 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C). Trifluoroacetic acid (0.02% in $CDCl_3$) was used as external reference for ^{19}F (δ = –76.5 ppm). UV-vis-NIR spectra were measured on a Shimadzu UV-3150PC spectrometer. Fluorescence spectra were recorded on Horiba Fluorolog photospectrometer in a 10 mm quartz fluorescence cuvette. High resolution mass (HRMS) spectra were obtained in fast atom bombardment (FAB) mode with 3-nitrobenzyl alcohol (NBA) as a matrix on a JEOL LMS-HX-110 spectrometer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out on a CH Instrument Model 620B (ALS) with electrochemical system utilizing the three-electrode configuration consisting of a glassy carbon (working electrode), platinum wire (counter electrode) and Ag/AgCl (reference electrode) in dichloromethane with *n*-tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-20AB equipped with a YMC R-ODS-5 column (4.6 × 250 mm) and an SPD-M10A photodiode array detector.

Preparation of 2, 3 and 4-Cu

2,12-Phenylthio-5,10,15,20-tetrakis(pentafluorophenyl)-3,13-diaza-21,23-dicarba-isophlorin, 2:

Compound **1**[1] (20.0 mg, 20.6 μmol) was dissolved in a mixture of CH_2Cl_2 (5 mL) and benzenethiol (10.5 mL, 103 μmol) and stirred for 1 h at room temperature. The solution color changed from dark red to yellow. After removing the solvent *in vacuo*, the residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (1:1) as eluent. Recrystallization from hexane/CH_2Cl_2 yielded 2.70 mg of compound **2** as yellow crystals;

Yield: 11 %, R_f = 0.15 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR (600 MHz, CD_2Cl_2, ppm): δ = 9.15 (s, 2H, inner NH), 8.29 (d, J = 2.6 Hz, 2H, inner CH), 8.14 (s, 2H, outer NH), 7.20–7.15 (m, 4H, Ph-H), 7.12–7.07 (m, 2H, Ph-H), 6.74–6.70 (m, 4H, Ph-H), 6.32 (d, J = 5.5 Hz, 2H, β-H), 6.27 (d, J = 5.5 Hz, 2H, β-H); ^{13}C NMR (150 MHz, CD_2Cl_2, ppm): δ = 146.61, 146.60, 145.54, 145.47, 145.38, 140.17, 139.01, 137.51, 137.35, 135.58, 130.28, 129.26, 129.20, 127.75, 126.13, 125.07, 118.97, 117.84, 113.91, 112.16, 94.66, 87.97; ^{19}F NMR (564 MHz, CD_2Cl_2, ppm): δ = −139.35 ~ −139.65 (m, 4F, *o*-Ph-F), −139.65 ~ −139.95 (m, 4F, *o*-Ph-F), −155.15 ~ −155.80 (m, 2F, *p*-Ph-F), −157.25 ~ −157.90 (m, 2F, *p*-Ph-F), −161.70 ~ −162.55 (m, 4F, *m*-Ph-F), −163.55 ~ −164.40 (m, 4F, *m*-Ph-F); HRMS (FAB): calcd for $C_{56}H_{19}F_{20}N_4S_2$ $[M]^+$, 1192.0810; found 1192.0807 with errors of 0.3 ppm; UV-Vis (CH_2Cl_2): λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$) = 438.7 (11.6).

2,12-Phenylthio-5,10,15,20-tetrakis(pentafluorophenyl)-3,13-diaza-21,23-dicarbaporphyrin, *trans*-N_2CP-$(SC_6H_5)_2$, 3:

Al_2O_3 (37 mg, 360 μmol) was added to a CH_2Cl_2 solution (5 mL) of **2** (4.30 mg, 3.61 μmol), and

the mixture was stirred for 3 h at room temperature. After removing the solvent *in vacuo*, silica gel column chromatography (CH_2Cl_2 as eluent) was performed to separate the yellow fraction. After evaporation, the residue was recrystallized from hexane/CH_2Cl_2 to give 4.30 mg of the species **3** as yellow crystals;

Yield: ~100%, R_f = 0.44 (CH_2Cl_2). ^{1}H NMR (600 MHz, CD_2Cl_2, ppm): δ = 8.52 (d, J = 4.6 Hz, 2H, β-H), 8.36 (d, J = 4.6 Hz, 2H, β-H), 7.67–7.63 (m, 4H, Ph-H), 7.45–7.37 (m, 6H, Ph-H), −2.69 (br, 2H, inner NH), −4.05 (s, 2H, inner CH); ^{13}C NMR (150 MHz, CD_2Cl_2, ppm): δ = 167.13, 151.12, 147.66, 146.91, 145.98, 145.27, 144.56, 142.86, 141.23, 139.78, 139.21, 138.49, 136.98, 135.18, 135.02, 129.64, 129.52, 129.02, 126.52, 126.42, 113.86, 105.44; ^{19}F NMR (564 MHz, CD_2Cl_2): δ = −138.33 (d, J = 5.6 Hz, 4F, *o*-Ph-F), −138.72 (d, J = 5.6 Hz, 4F, *o*-Ph-F), −155.13 (t, J = 22.6 Hz, 2F, *p*-Ph-F), −154.52 (t, $^3J_{FF}$ = 22.6 Hz, 2F, *p*-Ph-F), −163.70 ~ −163.95 (m, 4F, *m*-Ph-F), −163.81 (t, $^3J_{FF}$ = 5.6, 22.6 Hz, 4F, *m*-Ph-F); HRMS (FAB): calcd for $C_{56}H_{19}F_{20}N_4S_2$ $[M+H]^+$, 1191.0732, found 1191.0747 with errors of 1.3 ppm; UV-Vis (CH_2Cl_2): λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$) = 395.5 (3.4), 482 (13.6), 578 (0.91), 627 (0.66), 813 (0.50).

2,12-Phenylthio-5,10,15,20-tetrakis(pentafluorophenyl)-3,13-diaza-21,23-dicarbaporphyrin-ato copper (III), 4-Cu:

To a mixture CH_2Cl_2/MeOH solution (5 mL, 4:1 (v/v)) of porphyrin (**2**) (1.91 mg, 1.60 μmol), $Cu(OAc)_2$ (1.45 mg, 8.0 μmol) was added under aerobic condition. The resulting solution was stirred at room temperature for 30 min. The solution color changed from yellow to green. After removing the solvent *in vacuo*, the residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 (1:1) as eluent, Recrystallization from hexane/CH_2Cl_2 afforded 1.98 mg of **4-Cu** as green crystals;

Yield 99%, R_f = 0.24 (hexane: CH_2Cl_2 =1:1). ^{1}H NMR (600 MHz, CD_2Cl_2, ppm): δ = 8.96 (br s, 1H, outer NH), 8.26 (d, J = 5.4 Hz, 2H, β-H), 8.20 (d, J = 5.4 Hz, 2H, β-H), 7.92–7.85 (m, 2H, Ph-H), 7.82–7.70 (m, 5H, Ph-H), 7.55–7.43 (m, 3 H, Ph-H); ^{13}C NMR (150 MHz, CD_2Cl_2, ppm): δ = 179.49, 173.28, 158.97, 152.95, 149.48, 147.84, 147.05, 146.44, 145.42, 144.94, 144.79, 143.68, 142.34, 141.12, 140.00, 138.51, 138.03, 137.11, 136.07, 135.33, 133.79, 132.58, 132.17, 131.72, 130.46, 130.25, 129.58, 129.41, 128.90, 128.59, 128.27, 126.37, 125.94, 124.44, 121.07, 114.02, 111.65, 108.45, 106.05, 101.55; ^{19}F NMR (564 MHz, CD_2Cl_2, ppm): δ = −136.85 ~ −137.05 (dd, J = 5.6 Hz, 2F, *o*-Ph-F), −137.85 ~ −138.05 (dd, J = 5.6 Hz, 2F, *o*-Ph-F), −138.15 ~ −138.45 (m, 4F, *o*-Ph-F), −151.42 (t, J = 22.6 Hz, 1F, *p*-Ph-F), −151.65 (t, J = 22.6 Hz, 1F, *p*-Ph-F), −153.18 (t, J =22.6 Hz, 1F, *p*-Ph-F), −156.40 (t, J = 22.6 Hz, 1F, *p*-Ph-F), −160.35 ~ −160.55 (dt, J = 5.6, 22.6 Hz, 2F, *m*-Ph-F), −160.85 ~ −161.05 (dt, J = 5.6, 22.6 Hz, 2F, *m*-Ph-F), −162.10 ~ −162.30 (dt, J = 5.6, 22.6 Hz, 2F, *m*-Ph-F), −164.55 ~ −164.80 (dt, J = 5.6, 22.6 Hz, 2F, *m*-Ph-F); HRMS (FAB): calcd for $C_{56}H_{15}CuF_{20}N_4S_2$, 1249.9715; found 1249.9694 with errors of 1.7 ppm; UV-Vis (CH_2Cl_2): λ_{max}[nm] (ε, 10^4 $M^{-1}cm^{-1}$) = 357 (7.9), 469 (4.5), 509 (2.0), 611 (5.7), 722 (0.9), 794 (1.5).

[1] H. Maeda, A. Osuka and H. Furuta, H. *J. Am. Chem. Soc.* 2003, **125**, 15690.

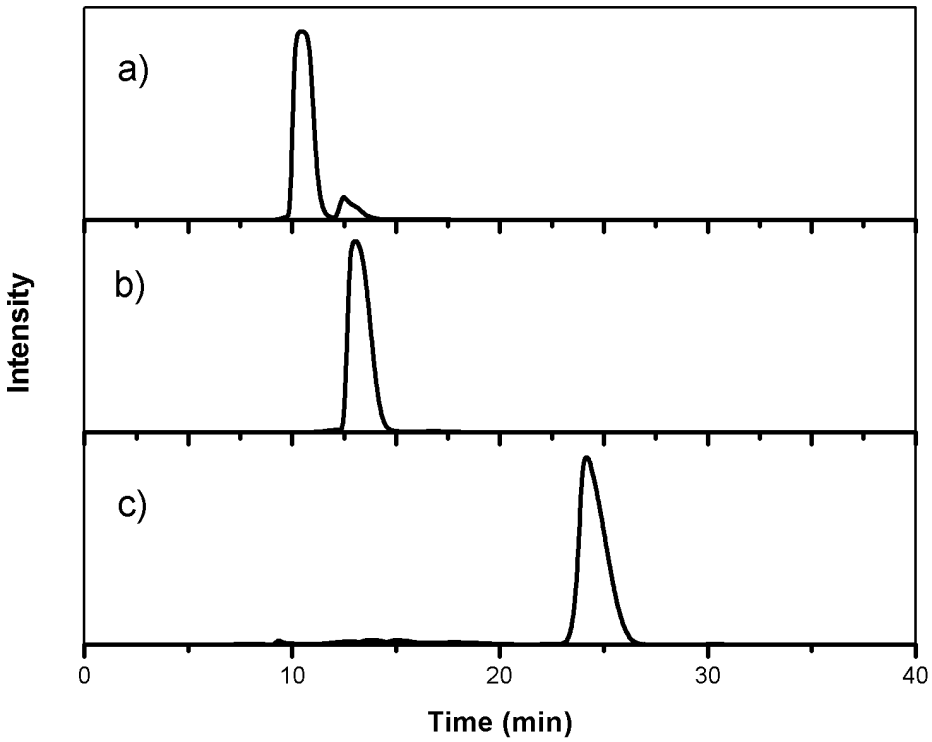


Fig. S1. HPLC charts of (a) **2**, (b) **3** and (c) **4-Cu** with a YMC R-ODS-5 column (4.6 × 250 mm) using CH_3CN. Constant flow rate was 0.5 mL/min.

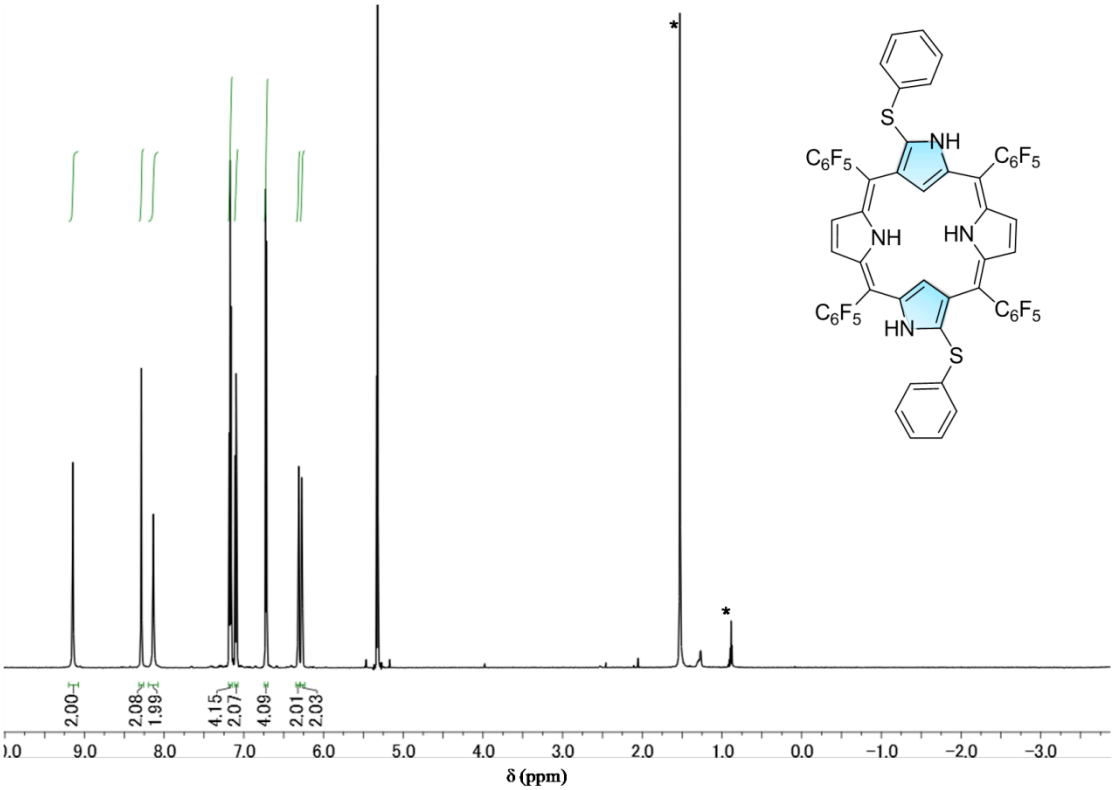


Fig. S2. ^{1}H NMR spectrum of **2** in CD_2Cl_2. Asterisks indicate the peaks of residual solvents and impurities.

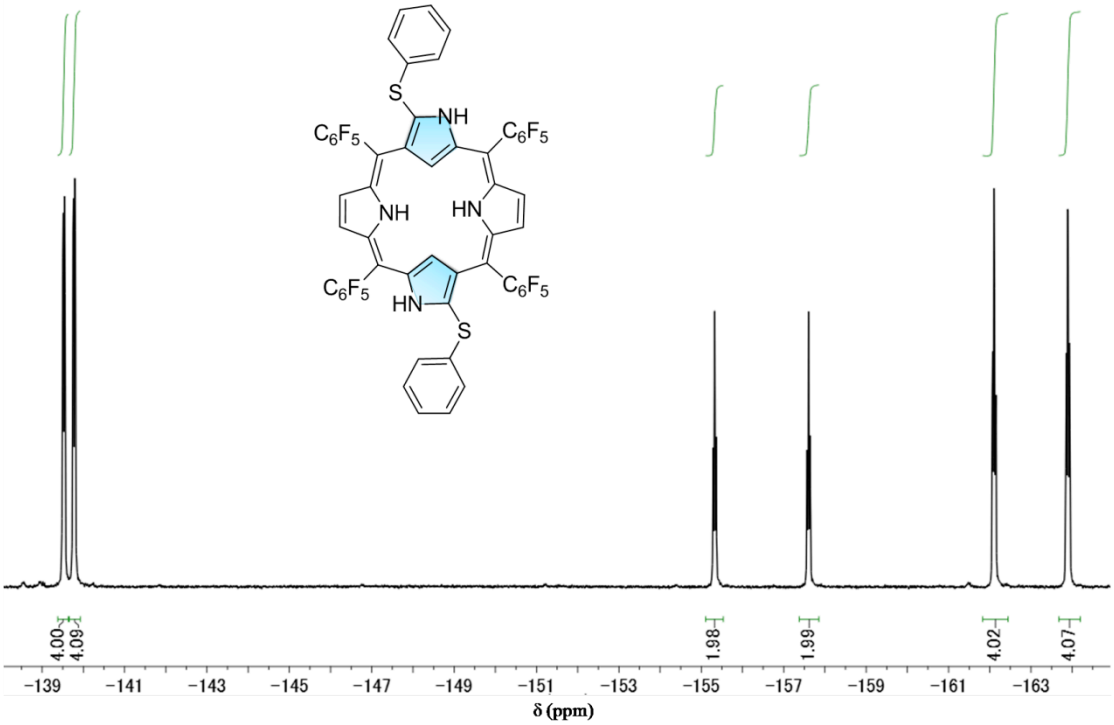


Fig. S3. ^{19}F NMR spectrum of **2** in CD_2Cl_2.

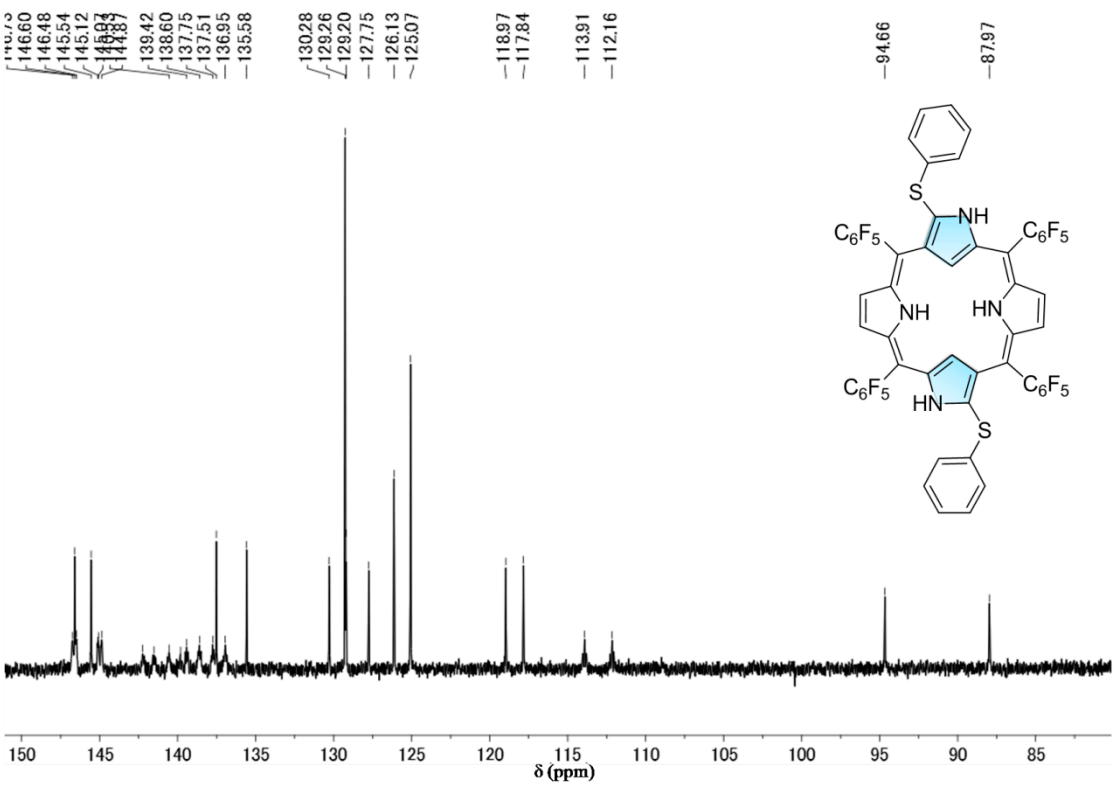


Fig. S4. ^{13}C NMR spectrum of **2** in CD_2Cl_2.

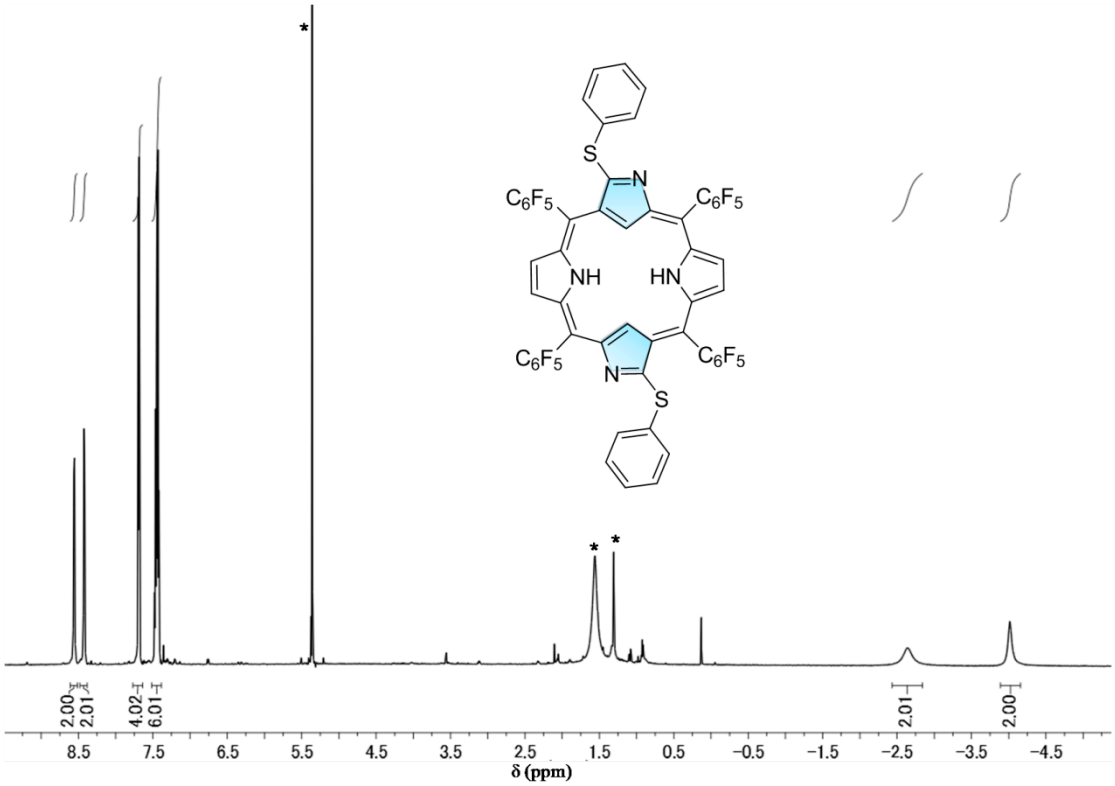


Fig. S5. ^{1}H NMR spectrum of **3** in CD_2Cl_2. Asterisks indicate the peaks of residual solvents and impurities.

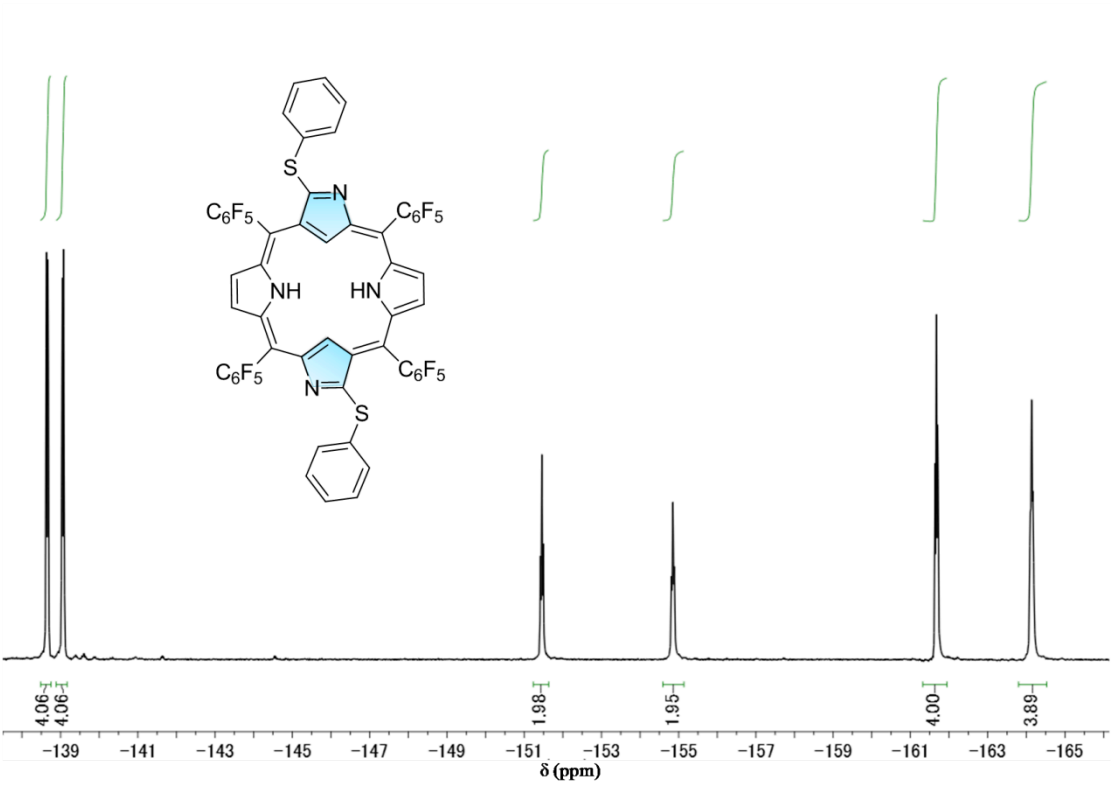


Fig. S6. ^{19}F NMR spectrum of **3** in CD_2Cl_2.

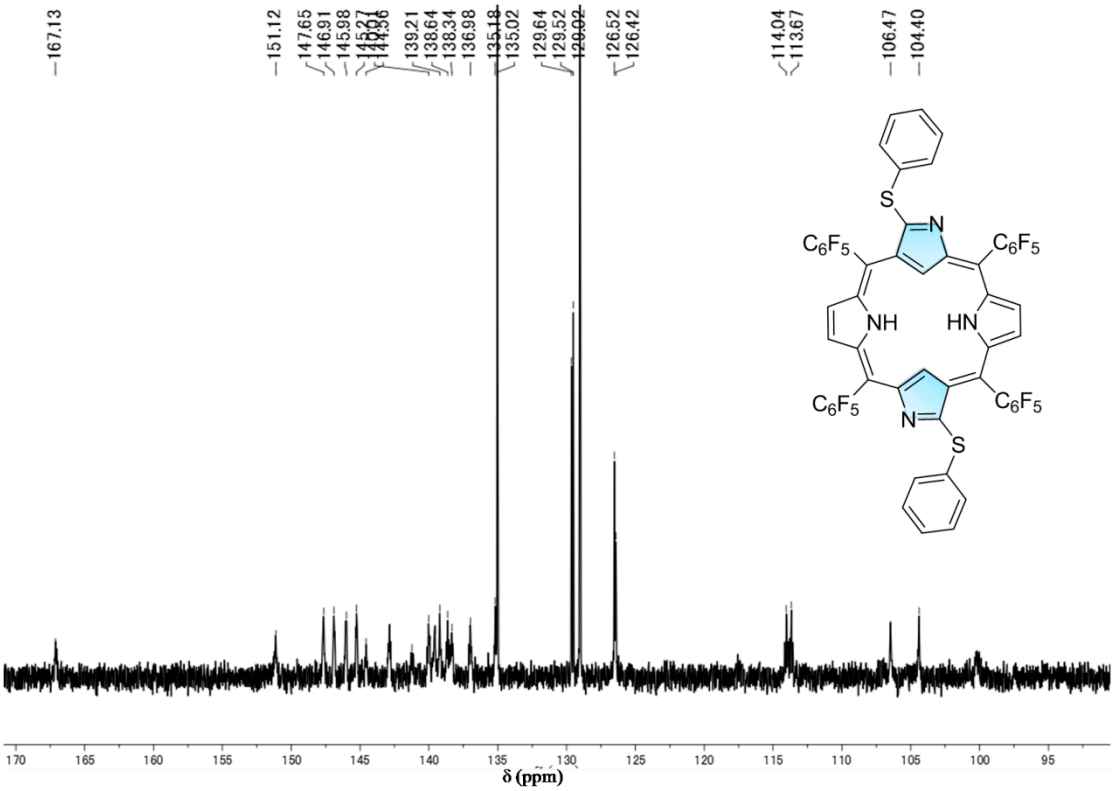


Fig. S7. ^{13}C NMR spectrum of **3** in CD_2Cl_2.

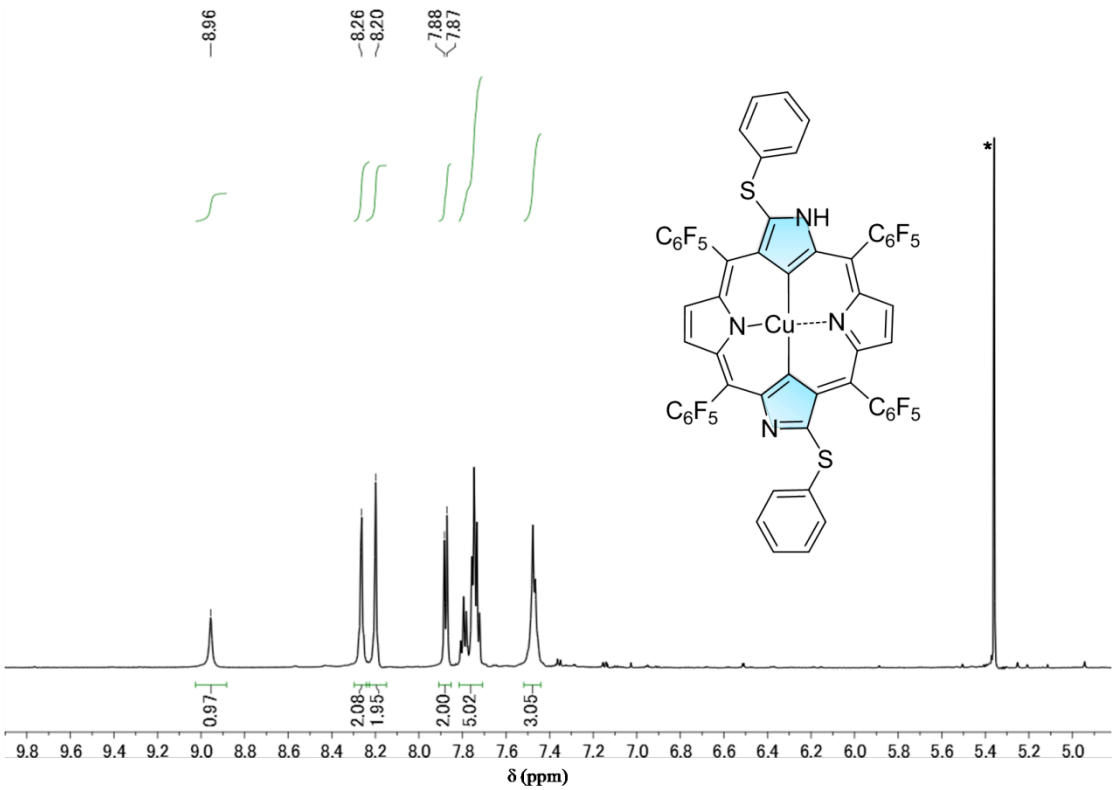


Fig. S8. ^{1}H NMR spectrum of **4-Cu** in CD_2Cl_2. Asterisk indicates the residual solvent peak.

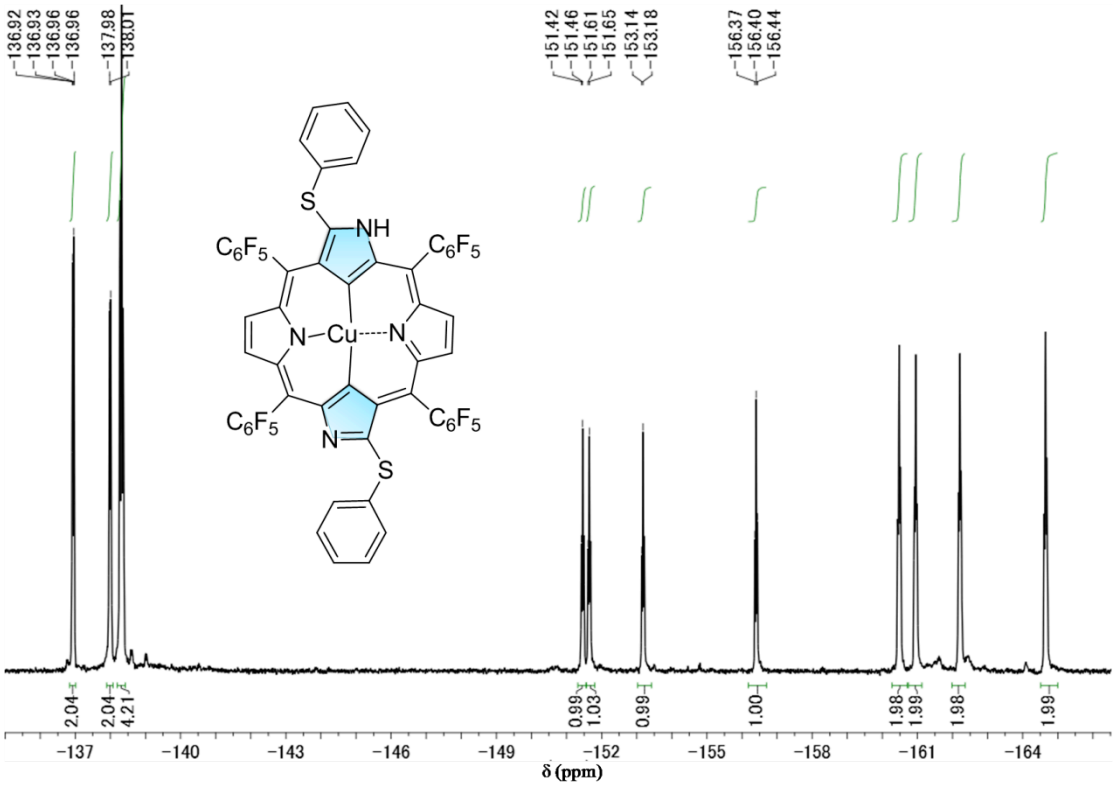


Fig. S9. ^{19}F NMR spectrum of **4-Cu** in CD_2Cl_2.

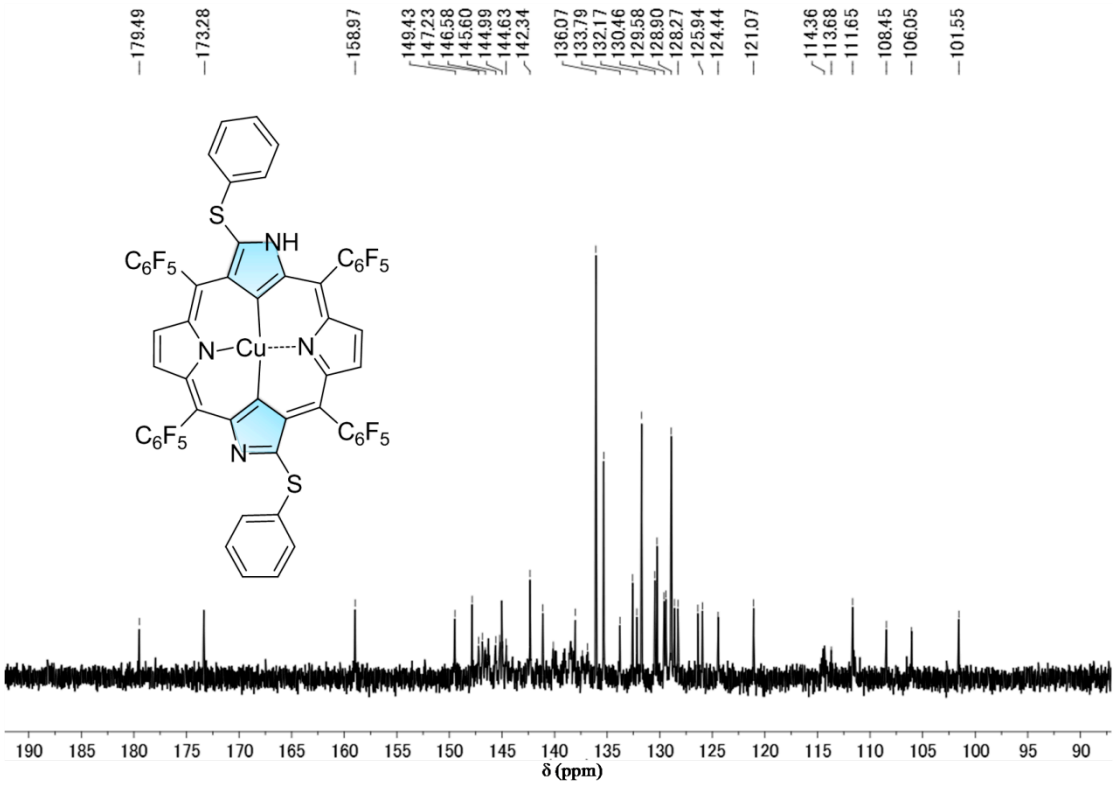


Fig. S10. ^{13}C NMR spectrum of **4-Cu** in CD_2Cl_2.

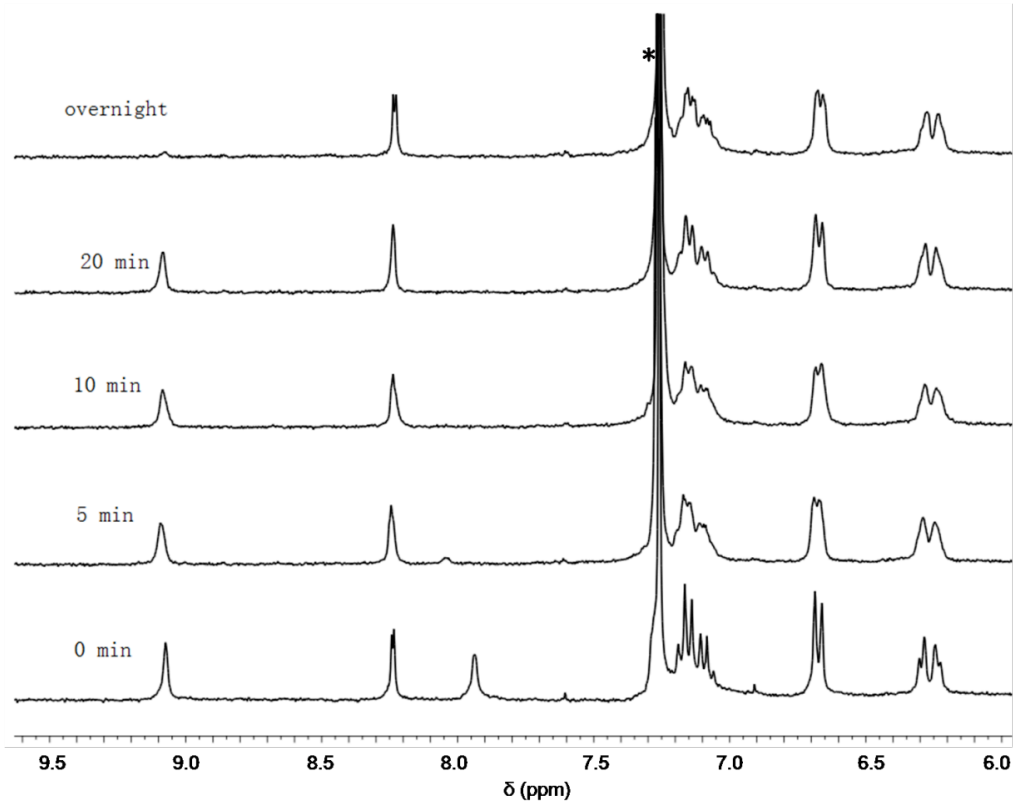


Fig. S11. ^{1}H NMR spectral changes of **2** (in $CDCl_3$) upon addition of D_2O. Asterisk indicates the residual solvent peaks.

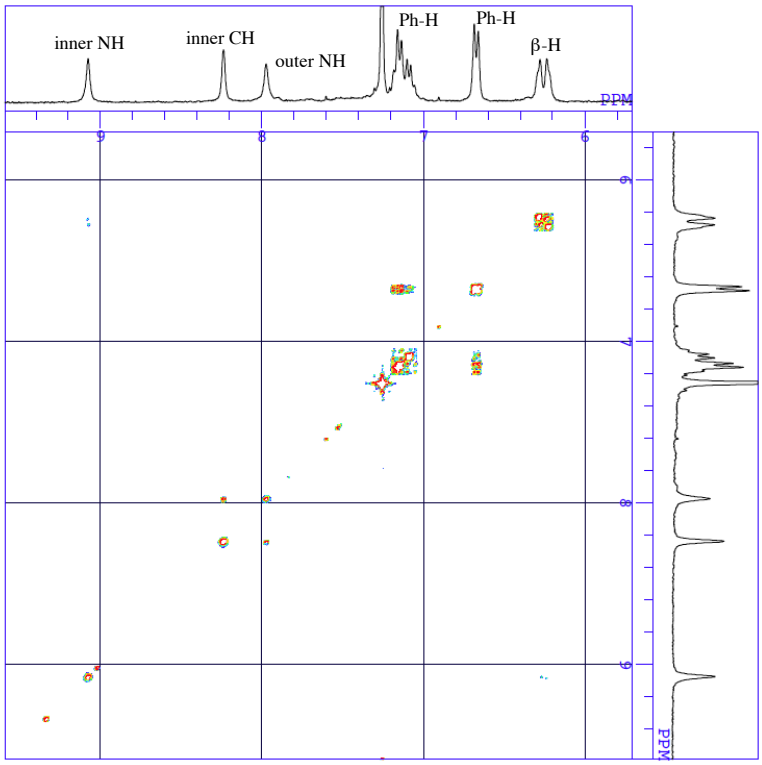


Fig. S12. ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$.

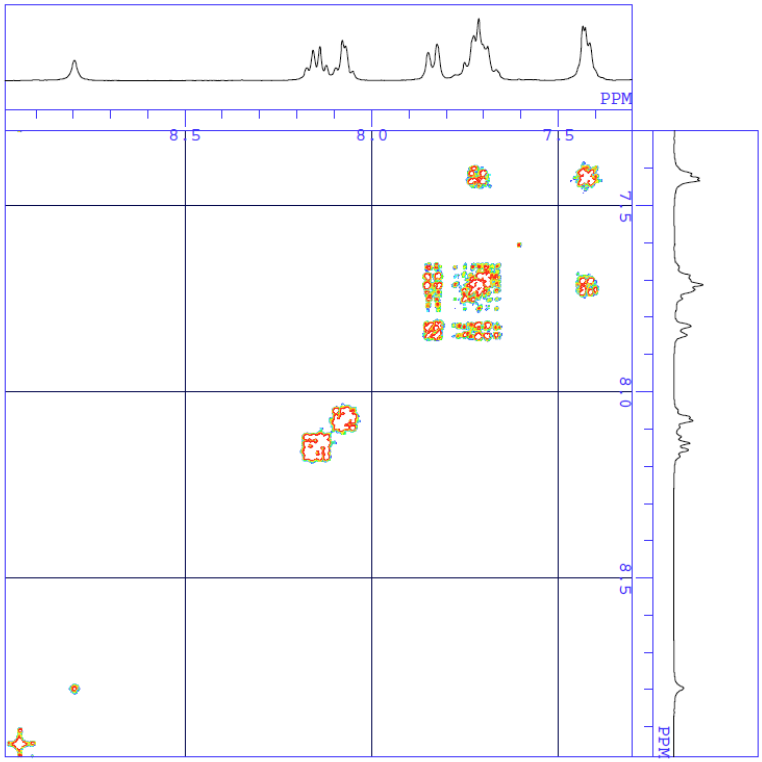


Fig. S13. ^{1}H-^{1}H COSY spectrum of **4-Cu** in $CDCl_3$.

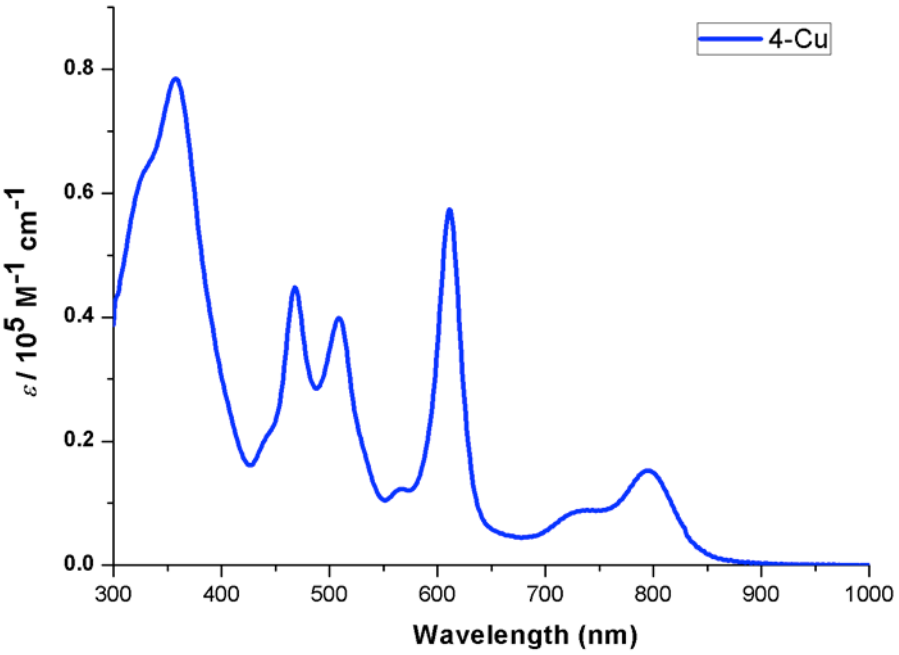


Fig. S14. UV/vis absorption spectrum of **4-Cu** in CH_2Cl_2.

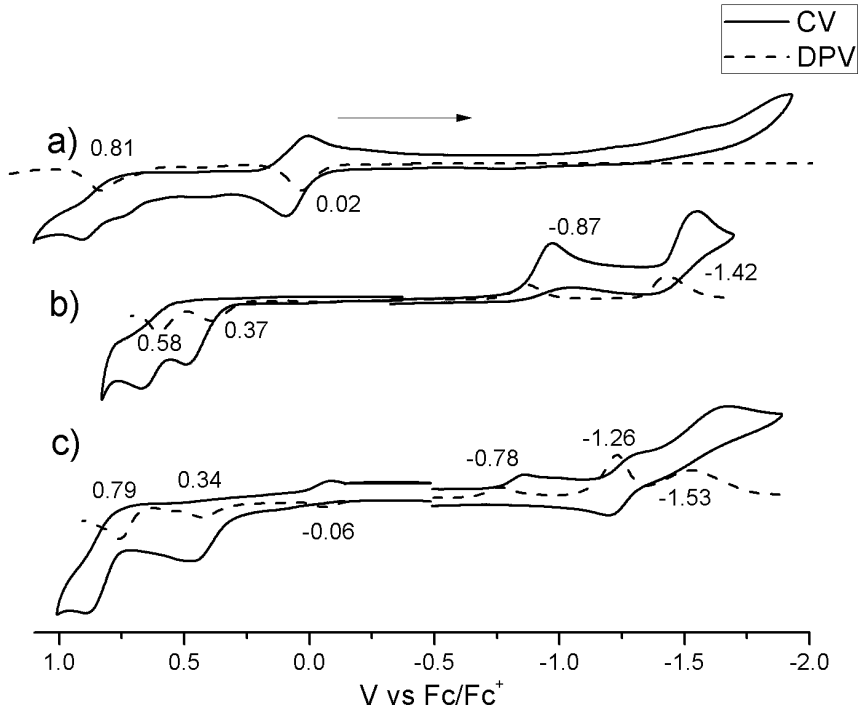


Fig. S15. Cyclic voltammograms (solid line) and differential pulse voltammograms (dashed line) of (a) **2**, (b) **3** and (c) **4-Cu** in the CH_2Cl_2 solution containing 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. All potentials were calibrated by a Fc/Fc^+ redox couple. Scan rate; 0.1 Vs^{-1}. The arrow indicates the direction of cyclic voltammetry measurements.

X-ray Crystallography

X-ray single crystal measurements for **2, 3** and **4-Cu** were carried out on a Rigaku RAXIS RAPID and Saturn 724 diffractometers. The structures were solved by the direct method (SIR2004)[2] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares procedures (SHELXL-97).[3] 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. All calculations except for refinement were performed by using CrystalStructure[4] software package of the Rigaku Corporation.

For mean deviation (m.d.) calculations, 24 atoms of the core macrocycle are selected to define the mean plane for all derivatives.

[2] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna (2005)

[3] G. M. Sheldrick, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

[4] CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000–2010). Tokyo 196-8666, Japan.

Table S1. Crystal data and structure analysis results for **2, 3** and **4-Cu**

	2	**3**	**4-Cu**
Formula	$C_{56}H_{20}F_{20}N_4S_2 \bullet H_2O$	$C_{56}H_{18}F_{20}N_4S_2$	$C_{56}H_{15}CuF_{20}N_4S_2 \bullet 2CH_2Cl_2$
Formula Weight	1210.90	1190.86	1421.26
Crystal system	monoclinic	monoclinic	orthorhombic
T (K)	123	100	100
Space group	$P2_1/n$	$P2_1/c$	$Pbca$
a (Å)	17.201(6)	11.9072(2)	31.3073(6)
b (Å)	15.424(4)	25.4953(5)	21.1481(4)
c (Å)	19.135(7)	24.1650(4)	16.0579(3)
α (deg)	90	90	90
β (deg)	111.208(5)	99.372(7)	90
γ (deg)	90	90	90
V (Å^3)	4733(3)	7238.0(3)	10631.8(3)
Z	4	6	8
D_{calc} (g cm^{-3})	1.699	1.639	1.776
Crystal size (mm)	0.15 x 0.06 x 0.02	0.22 x 0.10 x 0.08	0.24 x 0.20 x 0.13
$2\theta_{min}$, $2\theta_{max}$ (deg)	2.7, 55.1	6.9, 136.5	7.0, 136.5
No. of reflns measd (unique)	10844	13196	9730
No. of rflns measd ($I > 2\sigma(I)$)	5376	10735	8498
No. of parameters	854	1208	860
Goodness-of-fit	1.073	1.031	1.057
R_1	0.0820	0.0432	0.0665
wR_2 (all data)	0.2284	0.1138	0.1965
Δ (ε Å^{-3})	0.498, –0.493	0.379, –0.318	0.844, –1.631
Diffractometer	Saturn 724	R-AXIS RAPID	R-AXIS RAPID
CCDC number	1008503	1008504	1008505

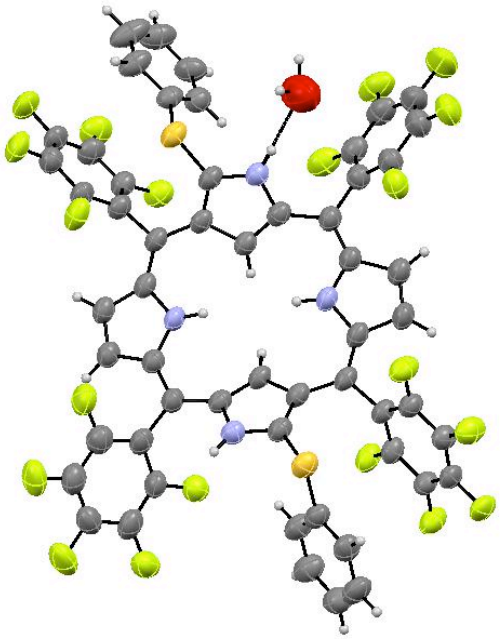


Fig. S16. X-ray crystal structure of **2** with a hydrogen-bonded water molecule. The thermal ellipsoids are scaled at the 50% probability level.

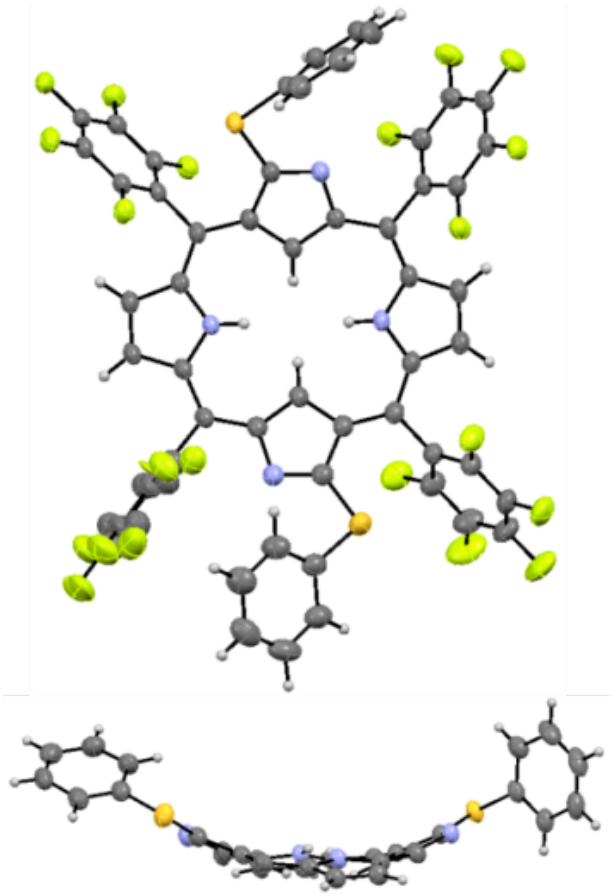


Fig. S17. X-ray crystal structure of another geometry of **3** found in the packing lattice. Pentafluorophenyl groups are omitted for clarity in the side view (bottom). The thermal ellipsoids are scaled at the 50% probability level. The structure was labeled as **3(2)** to differentiate the text one, **3(1)**.

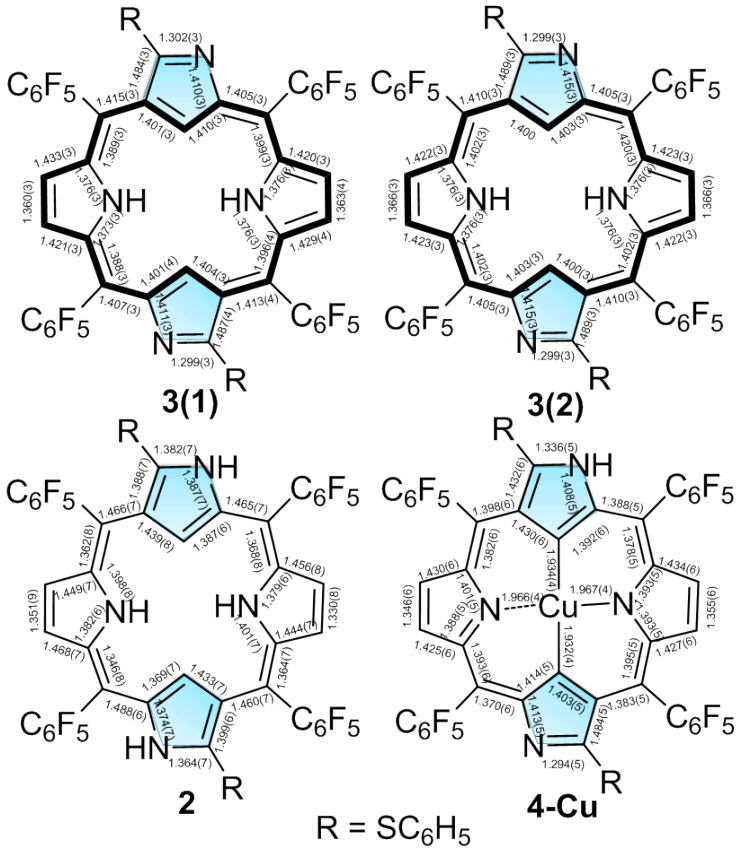


Fig. S18. Selected bond lengths (Å) of **2**, **3** and **4-Cu**.

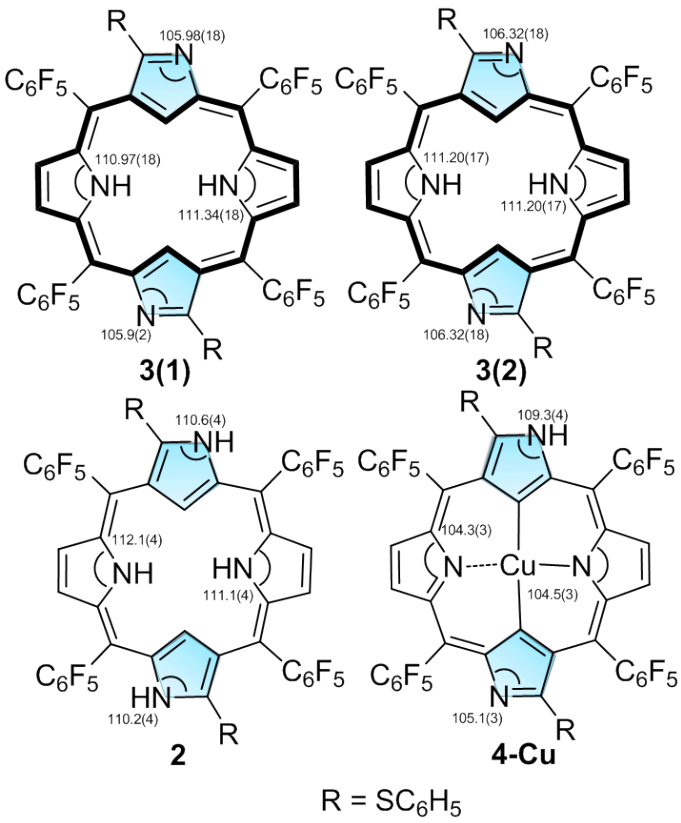


Fig. S19. Selected C-N-C angles (deg) of **2**, **3** and **4-Cu**.

Calculations details

Theoretical calculations were performed with the *Gaussian09*[5] program suite using a supercomputer.[6] All calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G(d,p) basis set for C, H, N, F atoms and LANL2DZ basis for Cu atom (denoted as 6-31LAN for **4-Cu**).[6] The NICS[7] value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries. To simulate the ground-state absorption spectra, the time-dependent (TD) DFT calculation was employed with B3LYP/6-31G(d,p) level.

[5] Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[6] (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

[7] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. v. E. Hommes, *J. Am. Chem. Soc.* 1996, **118**, 6317.

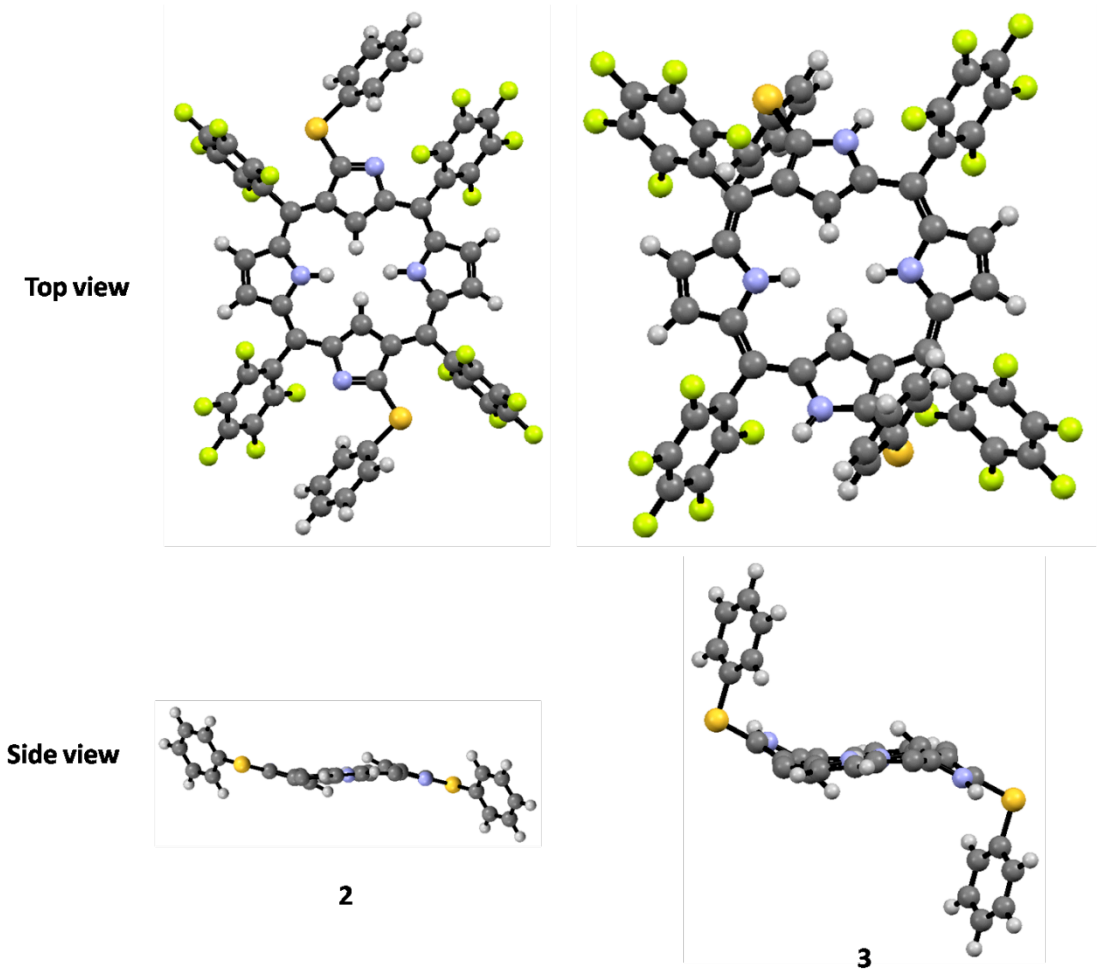


Fig. S20. Top view (left) and side view (right) of the optimized structures of (a) **2** and (b) **3** obtained by DFT (B3LYP/6-31G**) calculations.

Table S2. HOMA values calculated based on the x-ray structures and optimized structures[8]

	X-ray structures			optimized structures		
	EN	GEO	HOMA	EN	GEO	HOMA
2	0.170503	0.669012	0.160485	0.244994	0.44076	0.314246
3(1)	0.057982	0.092285	0.849732	0.153984	0.080676	0.765341
3(2)	0.080431	0.069235	0.850334			
4-Cu	0.023257	0.154799	0.821944	0.062803	0.221665	0.715532

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum\left[\mathrm{R}_{opt} - \mathrm{R}_i\right]^2$$
$$= 1 - \alpha\left(\mathrm{R}_{opt} - \mathrm{R}_{av}\right)^2 - \frac{\alpha}{n}\sum\left[\mathrm{R}_{av} - \mathrm{R}_i\right]^2$$
$$= 1 - \mathrm{EN} - \mathrm{GEO}$$

[8] T. M. Crygowski and M. Cyrański, *Tetrahedron* 1996, **52**, 1713 and 10255.

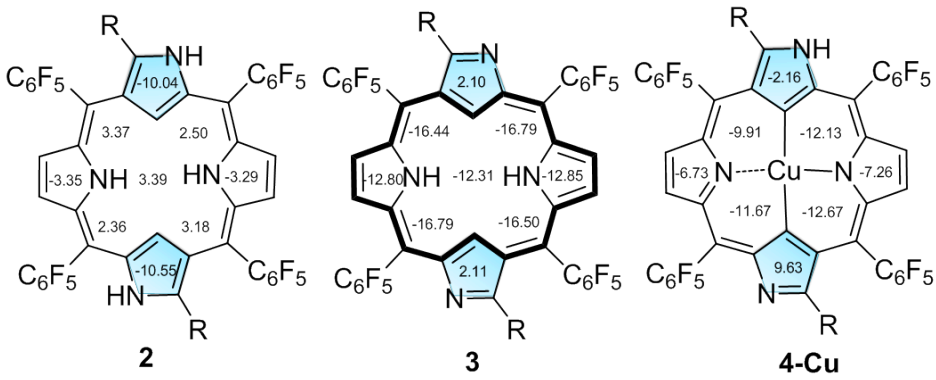


Fig. S21. NICS values (ppm) for **2**, **3** and **4-Cu** obtained by GIAO-B3LYP/6-31(d,p) (**2**, **3**) and GIAO-B3LYP/6-31G(d,p)/LANL2DZ (**4-Cu**) calculations. (R = SC_6H_5)

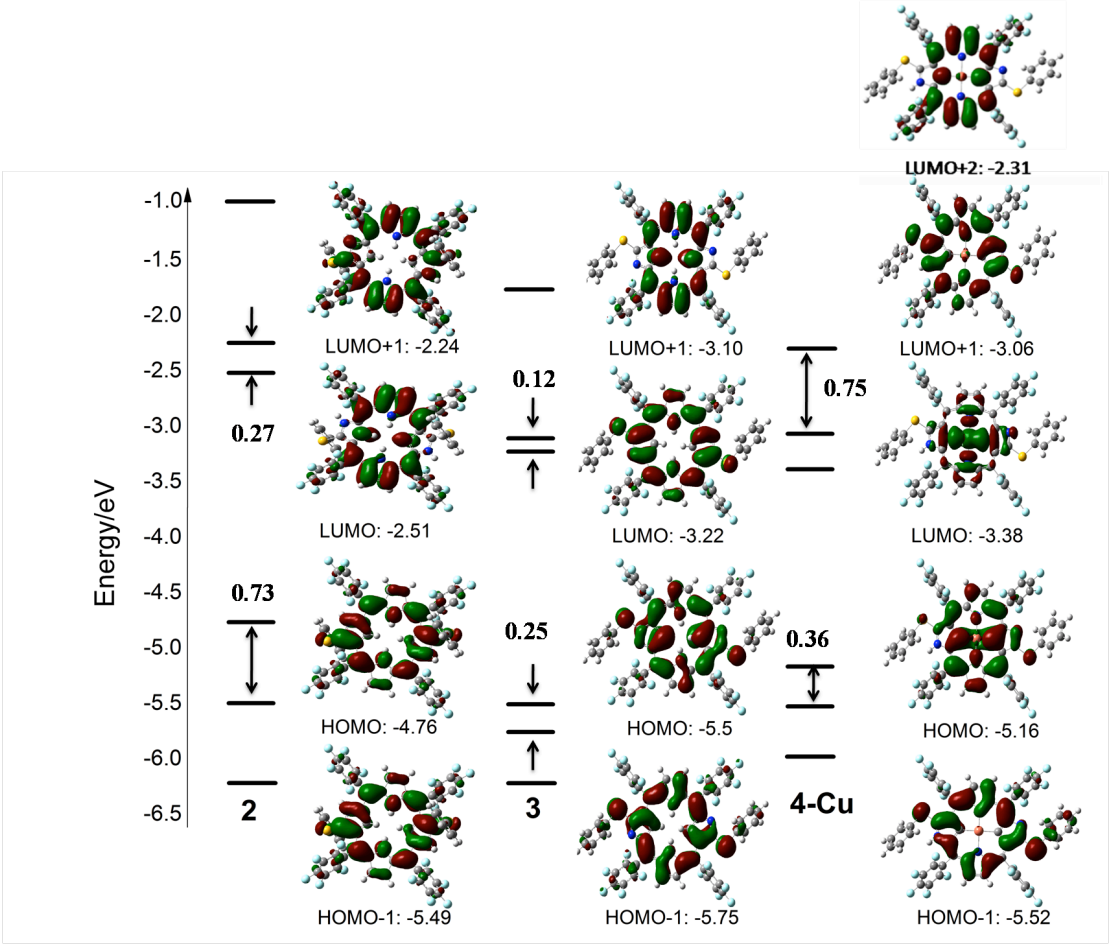


Fig. S22. MO diagrams of **2**, **3** and **4-Cu** obtained from the calculations at the B3LYP/6-31G(d,p) (**2**, **3**) and B3LYP/6-31G(d,p)/LanL2DZ (**4-Cu**) levels, respectively.

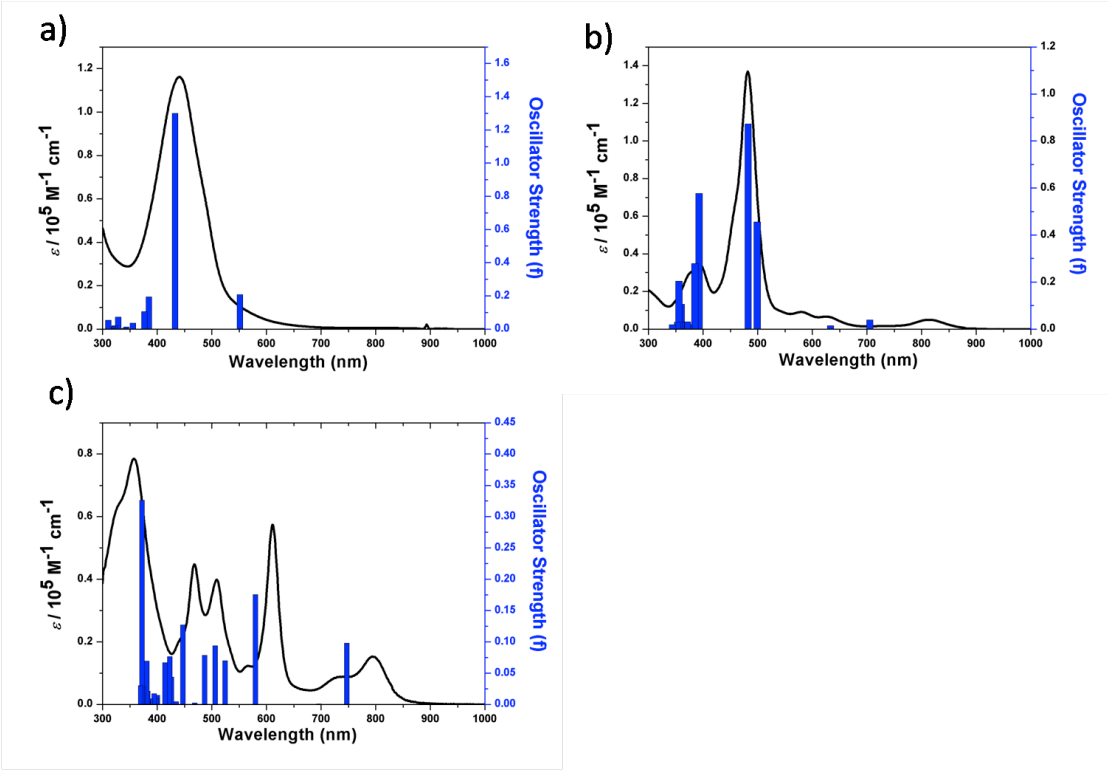
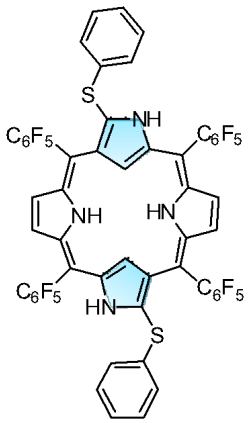


Fig. S23. TD-DFT (B3LYP/6-31G**) calculations for (a) **2**, (b) **3** and (c) **4-Cu** along with the experimental spectra in CH_2Cl_2.

Cartesian coordinates for optimized structures for 2, 3 and 4-Cu



2

Stoichiometry C56H20F20N4S2
Framework group C1[X(C56H20F20N4S2)]
Deg. of freedom 300
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.686406	-1.476711	0.083910
2	6	0	4.042154	-0.149283	0.126794
3	6	0	2.971282	0.589638	-0.396520
4	6	0	1.960289	-0.366161	-0.743921
5	6	0	2.417042	-1.643826	-0.416542
6	6	0	-1.522792	-4.192877	0.266981
7	6	0	-0.232968	-4.449406	-0.057389
8	6	0	0.470595	-3.186919	-0.225098
9	7	0	-0.495070	-2.209493	-0.056277
10	6	0	-1.736726	-2.753906	0.265087
11	6	0	1.814557	-2.971710	-0.429162
12	7	0	-3.686373	1.476699	-0.083989
13	6	0	-4.042117	0.149270	-0.126891
14	6	0	-2.971262	-0.589653	0.396456
15	6	0	-1.960267	0.366143	0.743861
16	6	0	-2.417018	1.643810	0.416488
17	6	0	-2.895122	-2.052904	0.492369
18	6	0	1.522833	4.192863	-0.266939
19	6	0	0.233013	4.449396	0.057443

20	6	0	-0.470577	3.186912	0.225072
21	7	0	0.495078	2.209480	0.056220
22	6	0	1.736740	2.753890	-0.265122
23	6	0	2.895132	2.052891	-0.492420
24	6	0	-1.814543	2.971701	0.429129
25	16	0	5.615889	0.308858	0.783411
26	6	0	5.342389	0.208270	2.572206
27	16	0	-5.615842	-0.308869	-0.783534
28	6	0	-4.132996	-2.807006	0.819465
29	6	0	-5.342336	-0.208207	-2.572324
30	6	0	-2.739792	4.129931	0.547607
31	6	0	4.133000	2.807006	-0.819494
32	6	0	2.739788	-4.129960	-0.547573
33	6	0	-4.580090	-1.178272	-3.234684
34	6	0	-4.409991	-1.096719	-4.616576
35	6	0	-5.011934	-0.065827	-5.341993
36	6	0	-5.951883	0.821117	-3.297700
37	6	0	-4.820648	-2.565471	2.017342
38	6	0	-6.000895	-3.225542	2.343965
39	6	0	-6.527902	-4.170729	1.466669
40	6	0	-5.871747	-4.439015	0.268535
41	6	0	-4.697412	-3.758893	-0.037899
42	6	0	2.903390	-5.089434	0.462937
43	6	0	3.783192	-6.162651	0.336372
44	6	0	4.554889	-6.289755	-0.815165
45	6	0	4.434455	-5.346505	-1.834213
46	6	0	3.538137	-4.291819	-1.692210
47	6	0	-3.538027	4.291780	1.692327
48	6	0	-4.434368	5.346435	1.834411
49	6	0	-4.554955	6.289660	0.815358
50	6	0	-3.783391	6.162555	-0.336267
51	6	0	-2.903561	5.089370	-0.462910
52	6	0	4.697331	3.758974	0.037834
53	6	0	5.871659	4.439117	-0.268578
54	6	0	6.527893	4.170772	-1.466655
55	6	0	6.000967	3.225510	-2.343920
56	6	0	4.820722	2.565423	-2.017321
57	6	0	4.580229	1.178416	3.234544
58	6	0	4.410139	1.096919	4.616441
59	6	0	5.012006	0.066001	5.341883
60	6	0	5.787950	-0.887735	4.682826
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62	9	0	-4.337651	-1.675095	2.894809
63	9	0	-6.620008	-2.975485	3.503414

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65	9	0	-6.379753	-5.335675	-0.585761
66	9	0	-4.124646	-4.017611	-1.229558
67	9	0	-2.204087	4.994496	-1.604373
68	9	0	-3.905992	7.057079	-1.323818
69	9	0	-5.406800	7.309486	0.942934
70	9	0	-5.167834	5.470034	2.945560
71	9	0	-3.440165	3.413298	2.697606
72	9	0	4.337803	1.674976	-2.894760
73	9	0	4.124470	4.017767	1.229432
74	9	0	6.379581	5.335855	0.585685
75	9	0	7.654790	4.818404	-1.775146
76	9	0	6.620152	2.975397	-3.503318
77	9	0	5.406705	-7.309614	-0.942668
78	9	0	2.203743	-4.994581	1.604294
79	9	0	3.905630	-7.057214	1.323907
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81	9	0	5.168040	-5.470112	-2.945282
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84	1	0	1.070398	-0.156507	-1.322420
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87	1	0	-0.311140	-1.222912	-0.096565
88	1	0	-4.251773	2.213485	-0.477592
89	1	0	-1.070383	0.156488	1.322371
90	1	0	2.287082	4.920737	-0.492306
91	1	0	-0.226891	5.420878	0.155908
92	1	0	0.311136	1.222900	0.096484
93	1	0	-6.553951	1.561389	-2.779885
94	1	0	-6.263023	1.687660	-5.243345
95	1	0	-4.881190	-0.010592	-6.418577
96	1	0	-3.815419	-1.847455	-5.128795
97	1	0	-4.136998	-1.993951	-2.674056
98	1	0	4.137200	1.994117	2.673898
99	1	0	3.815637	1.847722	5.128643
100	1	0	4.881272	0.010809	6.418470
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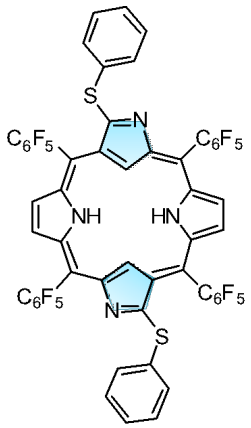
102	1	0	6.553863	-1.561417	2.779807



3

Stoichiometry C56H18F20N4S2
Framework group C1[X(C56H18F20N4S2)]
Deg. of freedom 294
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.120151	0.616036	0.007894
2	6	0	4.118568	-0.685131	-0.020082
3	6	0	2.763277	-1.259372	0.243220
4	6	0	1.975984	-0.108609	0.473672
5	6	0	2.810112	1.019131	0.306400
6	6	0	-0.539484	4.380377	0.193629
7	6	0	0.821671	4.325150	0.365459
8	6	0	1.232158	2.956830	0.293041
9	7	0	0.076623	2.231687	0.099123
10	6	0	-1.033221	3.046157	0.020595
11	6	0	2.527135	2.405741	0.335072
12	7	0	-4.120072	-0.616036	-0.007875
13	6	0	-4.118482	0.685132	0.020079
14	6	0	-2.763159	1.259351	-0.243069
15	6	0	-1.975830	0.108585	-0.473385
16	6	0	-2.810008	-1.019143	-0.306260
17	6	0	-2.364921	2.613858	-0.133670
18	6	0	0.539570	-4.380381	-0.193498
19	6	0	-0.821581	-4.325165	-0.365362
20	6	0	-1.232083	-2.956854	-0.292895
21	7	0	-0.076549	-2.231698	-0.099013

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30	6	0	-3.686908	-3.337775	-0.311533
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32	6	0	3.686958	3.337789	0.311616
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42	6	0	3.873580	4.271323	-0.715976
43	6	0	4.987693	5.104928	-0.770636
44	6	0	5.970737	5.004078	0.209128
45	6	0	5.820652	4.081468	1.240643
46	6	0	4.693664	3.269412	1.283938
47	6	0	-4.693502	-3.269441	-1.283976
48	6	0	-5.820534	-4.081438	-1.240737
49	6	0	-5.970780	-5.003950	-0.209158
50	6	0	-4.987859	-5.104751	0.770734
51	6	0	-3.873700	-4.271204	0.716128
52	6	0	3.712516	-4.420954	-1.016540
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55	6	0	4.994425	-5.080743	1.354419
56	6	0	4.047561	-4.061880	1.320417
57	6	0	7.609345	-0.381312	-1.738367
58	6	0	8.671521	0.512435	-1.892543
59	6	0	8.955230	1.441541	-0.892439
60	6	0	8.181572	1.471175	0.271327
61	6	0	7.133706	0.569008	0.443637
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63	9	0	-5.605450	5.403589	-2.498235
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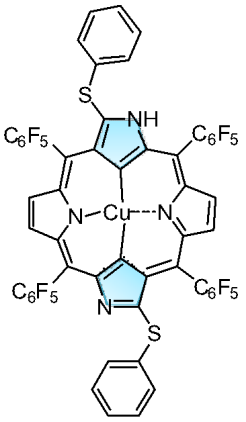
65	9	0	-4.950415	6.107949	2.130096

66	9	0	-3.114301	4.124550	2.177980
67	9	0	-2.976222	-4.375769	1.708052
68	9	0	-5.127703	-5.982540	1.770998
69	9	0	-7.050929	-5.787154	-0.161522
70	9	0	-6.773866	-3.967295	-2.177051
71	9	0	-4.595987	-2.400580	-2.298428
72	9	0	3.773382	-3.416015	2.459912
73	9	0	3.114499	-4.124479	-2.177845
74	9	0	4.950488	-6.107991	-2.129912
75	9	0	6.206731	-6.750430	0.204268
76	9	0	5.605157	-5.403938	2.498517
77	9	0	7.050841	5.787341	0.161440
78	9	0	2.975944	4.375972	-1.707748
79	9	0	5.127370	5.982829	-1.770827
80	9	0	4.596312	2.400439	2.298310
81	9	0	6.774094	3.967291	2.176842
82	6	0	-8.181492	-1.471095	-0.271921
83	1	0	1.001706	-0.096674	0.941783
84	1	0	-1.153079	5.268161	0.185906
85	1	0	1.486152	5.157560	0.540606
86	1	0	0.061119	1.238731	-0.036416
87	1	0	-1.001475	0.096647	-0.941346
88	1	0	1.153174	-5.268159	-0.185781
89	1	0	-1.486050	-5.157576	-0.540541
90	1	0	-0.061065	-1.238739	0.036505
91	1	0	-6.530615	-0.597104	-1.343703
92	1	0	-8.387456	-2.200613	-1.049130
93	1	0	-9.775458	-2.142108	1.016814
94	1	0	-9.267113	-0.486155	2.799598
95	1	0	-7.374508	1.094153	2.521849
96	1	0	7.374222	-1.093996	-2.522412
97	1	0	9.266747	0.486375	-2.800395
98	1	0	9.775321	2.142274	-1.017632
99	1	0	8.387640	2.200667	1.048532
100	1	0	6.530882	0.597099	1.343330



4-Cu

Stoichiometry C56H15CuF20N4S2
Framework group C1[X(C56H15CuF20N4S2)]
Deg. of freedom 288
Full point group C1 NOp 1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-4.143209	-0.523157	-0.080341
2	6	0	-4.162485	0.815137	-0.135029
3	6	0	-2.799251	1.259079	-0.184331
4	6	0	-1.962374	0.105499	-0.156549
5	6	0	-2.818228	-0.986844	-0.060290
6	6	0	0.512030	-4.231307	0.006024
7	6	0	-0.840784	-4.179442	0.080029
8	6	0	-1.216245	-2.792784	0.055329
9	7	0	-0.073898	-1.994572	0.013549
10	6	0	0.993526	-2.876601	-0.035908
11	6	0	-2.533963	-2.354379	0.046500
12	7	0	4.189253	0.596828	0.042038
13	6	0	4.168553	-0.696252	-0.041377
14	6	0	2.770272	-1.228203	-0.108940
15	6	0	1.946357	-0.089637	-0.117903
16	6	0	2.838552	1.000731	0.003146
17	6	0	2.353577	-2.557242	-0.093489
18	6	0	-0.499866	4.246209	-0.236269
19	6	0	0.850093	4.181240	-0.134613
20	6	0	1.203063	2.792689	-0.017042
21	7	0	0.072168	2.008341	-0.033187

22	6	0	-1.001254	2.898416	-0.171203
23	6	0	-2.350420	2.595682	-0.227570
24	6	0	2.534262	2.350191	0.059513
25	16	0	-5.664635	1.731793	-0.084230
26	6	0	-6.881663	0.429853	0.175283
27	16	0	5.640282	-1.670749	-0.090818
28	6	0	3.322170	-3.693378	-0.131428
29	6	0	6.956702	-0.457354	0.046931
30	6	0	3.641889	3.337605	0.171201
31	6	0	-3.316594	3.726954	-0.348334
32	6	0	-3.657984	-3.327291	0.147660
33	6	0	7.927917	-0.674513	1.030305
34	6	0	9.027159	0.182251	1.121258
35	6	0	9.146080	1.262683	0.247188
36	6	0	7.080576	0.617166	-0.842737
37	6	0	3.828439	-4.171433	-1.344100
38	6	0	4.722949	-5.236872	-1.398601
39	6	0	5.127762	-5.852495	-0.216299
40	6	0	4.634030	-5.405100	1.007429
41	6	0	3.739536	-4.338827	1.036507
42	6	0	-3.937115	-4.258050	-0.862963
43	6	0	-5.002547	-5.151629	-0.772990
44	6	0	-5.842047	-5.116721	0.338610
45	6	0	-5.603085	-4.195116	1.354611
46	6	0	-4.521425	-3.324334	1.252597
47	6	0	4.627381	3.449880	-0.816082
48	6	0	5.702817	4.322435	-0.687422
49	6	0	5.811954	5.124725	0.445333
50	6	0	4.842255	5.046409	1.441195
51	6	0	3.780259	4.156928	1.296630
52	6	0	-3.859153	4.085970	-1.587127
53	6	0	-4.752642	5.145533	-1.719901
54	6	0	-5.120858	5.876880	-0.592443
55	6	0	-4.594292	5.547447	0.655129
56	6	0	-3.701450	4.484315	0.763592
57	6	0	-7.827007	0.187000	-0.829021
58	6	0	-8.823078	-0.770017	-0.623447
59	6	0	-8.862626	-1.497359	0.567163
60	6	0	-7.913820	-1.259855	1.565853
61	6	0	-6.932664	-0.284550	1.382820
62	9	0	3.458659	-3.596022	-2.494683
63	9	0	5.192207	-5.673686	-2.572381
64	9	0	5.983752	-6.876411	-0.255825
65	9	0	5.019183	-6.003409	2.140607

66	9	0	3.278351	-3.931341	2.225953
67	9	0	2.876711	4.094755	2.286267
68	9	0	4.941860	5.814382	2.533197
69	9	0	6.839459	5.969277	0.572970
70	9	0	6.635959	4.395439	-1.648652
71	9	0	4.555300	2.713244	-1.932822
72	9	0	-3.214249	4.188440	1.974076
73	9	0	-3.524201	3.399236	-2.686459
74	9	0	-5.255530	5.466547	-2.916545
75	9	0	-5.975758	6.894848	-0.707691
76	9	0	-4.948903	6.251741	1.734634
77	9	0	-6.875021	-5.956558	0.425093
78	9	0	-3.173048	-4.307531	-1.959812
79	9	0	-5.237476	-6.026419	-1.755126
80	9	0	-4.328197	-2.449457	2.252973
81	9	0	-6.414637	-4.146349	2.419007
82	6	0	8.169263	1.480452	-0.728752
83	1	0	-4.970013	-1.101741	-0.050046
84	1	0	1.140272	-5.108695	-0.016109
85	1	0	-1.530216	-5.008252	0.136025
86	1	0	-1.112398	5.127029	-0.356835
87	1	0	1.558761	4.995247	-0.159298
88	1	0	6.320408	0.793784	-1.593141
89	1	0	8.245635	2.330217	-1.400052
90	1	0	9.994942	1.935711	0.326226
91	1	0	9.780657	0.009202	1.884143
92	1	0	7.820962	-1.504592	1.721682
93	1	0	-7.779998	0.742326	-1.760171
94	1	0	-9.559218	-0.953317	-1.400186
95	1	0	-9.631149	-2.249246	0.718605
96	1	0	-7.934846	-1.832153	2.487588
97	1	0	-6.204495	-0.088157	2.163285
98	29	0	-0.004022	0.004368	-0.091809
