

Supporting Information

Synthesis and Surface Self-Assembly of [3]Rotaxane-Porphyrin Conjugates: Toward the Development of a Supramolecular Surface Tweezer for C₆₀

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Determination of electrode surface

The surface area was determined by the CV of the $\text{Fe}(\text{CN})_6^{3-}$ redox at different scan rate and using the following relationship:¹

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$$

where i_p = peak current

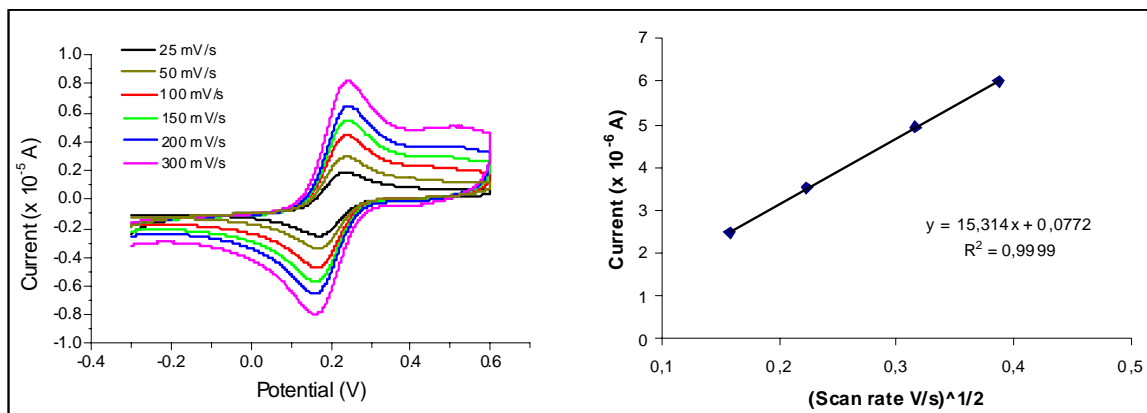
A = electrode surface area (cm^2)

D = diffusion coefficient ($0,76 \times 10^{-5} \text{ cm}^2/\text{s}$ for $\text{Fe}(\text{CN})_6^{3-}$ at 25°C in 0.1 M KCl)

C = concentration of $\text{Fe}(\text{CN})_6^{3-}$ ($1 \times 10^{-6} \text{ mol/cm}^3$)

v = scan rate (V/s)

From CV results:



The result agrees with the relationship of the peak current and scan rate:

$$(2.69 \times 10^5) n^{3/2} A D^{1/2} C = 1.5314 \times 10^{-5}$$

$$A = 2.12 \times 10^{-2} \text{ cm}^2$$

Determination of the surface coverage

The surface coverage can be determined by the surface CV at different scan rates using the following relationship:

$$i_p = (9.39 \times 10^5) n^2 A \Gamma v$$

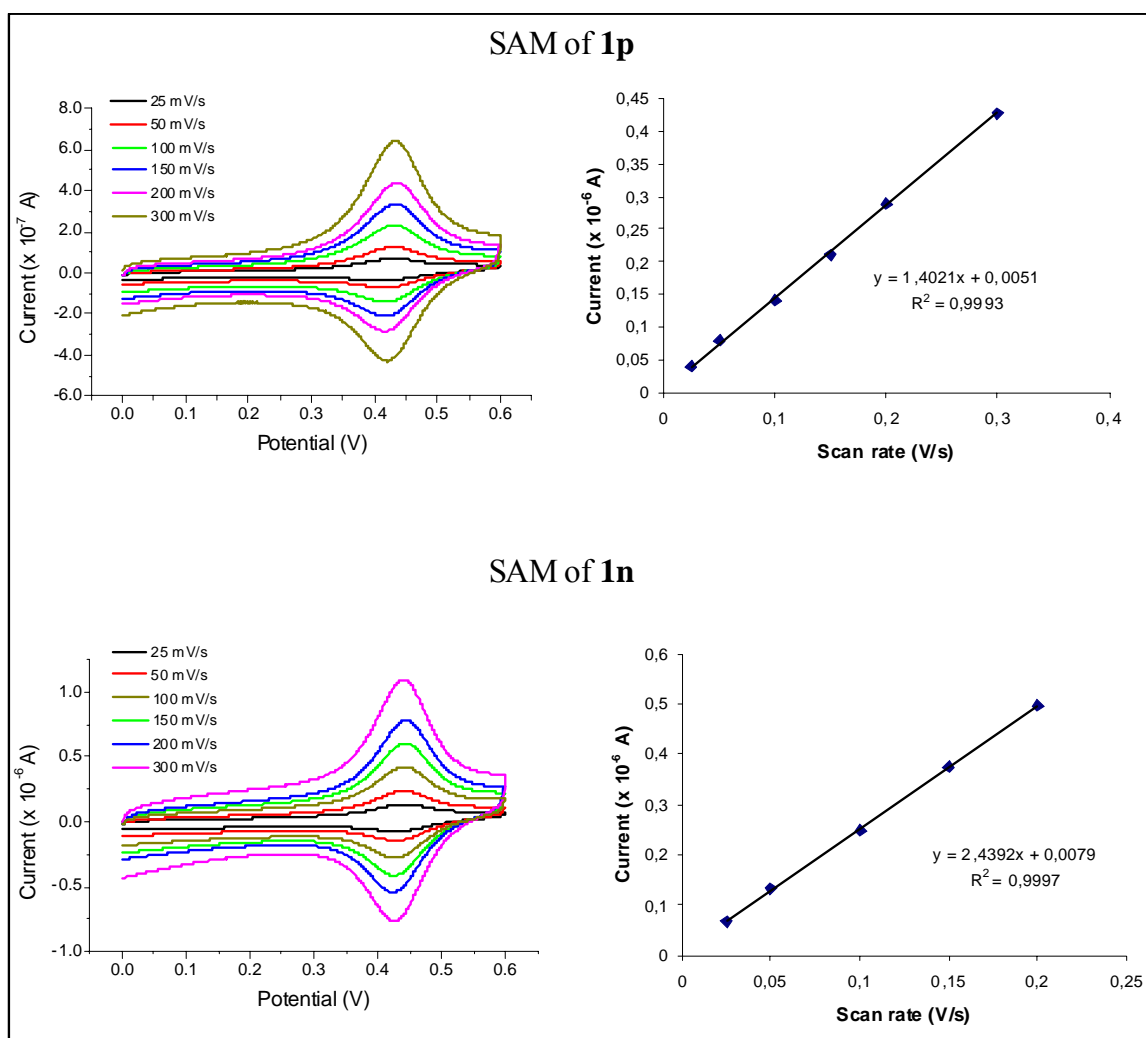
where i_p = peak current

A = electrode surface coverage area ($2.12 \times 10^{-2} \text{ cm}^2$)

Γ = surface coverage (mol/cm²)

v = scan rate (V/s)

From CV results:



These results agree with the relationship of the peak current and scan rate

For **1p**: (in this case, a working electrode with $A = 2.06 \times 10^{-2} \text{ cm}^2$ was used)

$$(9.39 \times 10^5) n^2 A \Gamma = 1.4021 \times 10^{-6}$$

$$\Gamma = 7.26 \times 10^{-11} \text{ mol/cm}^2$$

This number corresponds to the surface coverage of the ferrocene unit of **1p**. Therefore, it needs to be divided by 2 to obtain the surface coverage of **1p**.

$$\Gamma = 3.63 \times 10^{-11} \text{ mol/cm}^2 = 0.219 \text{ molecules/nm}^2 = 4.57 \text{ nm}^2/\text{molecule}$$

For **1n**: (in this case, a working electrode with $A = 2.12 \times 10^{-2} \text{ cm}^2$ was used)

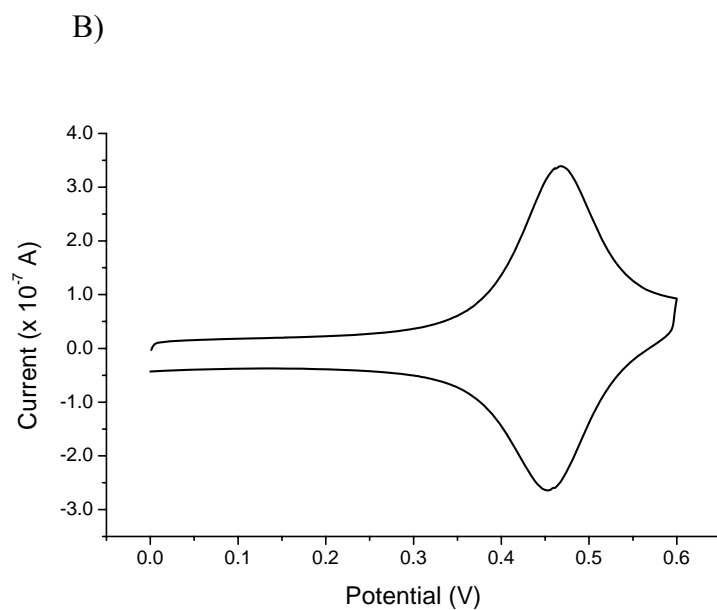
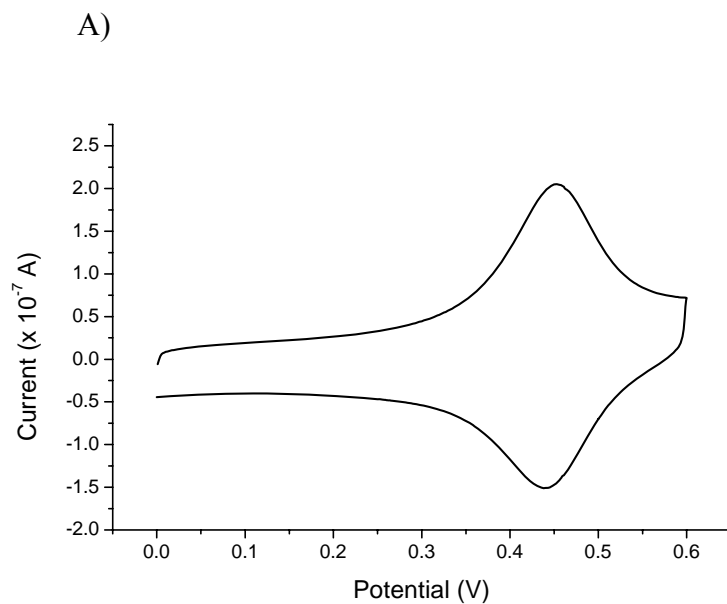
$$(9.39 \times 10^5) n^2 A \Gamma = 2.4392 \times 10^{-6}$$

$$\Gamma = 1.23 \times 10^{-10} \text{ mol/cm}^2$$

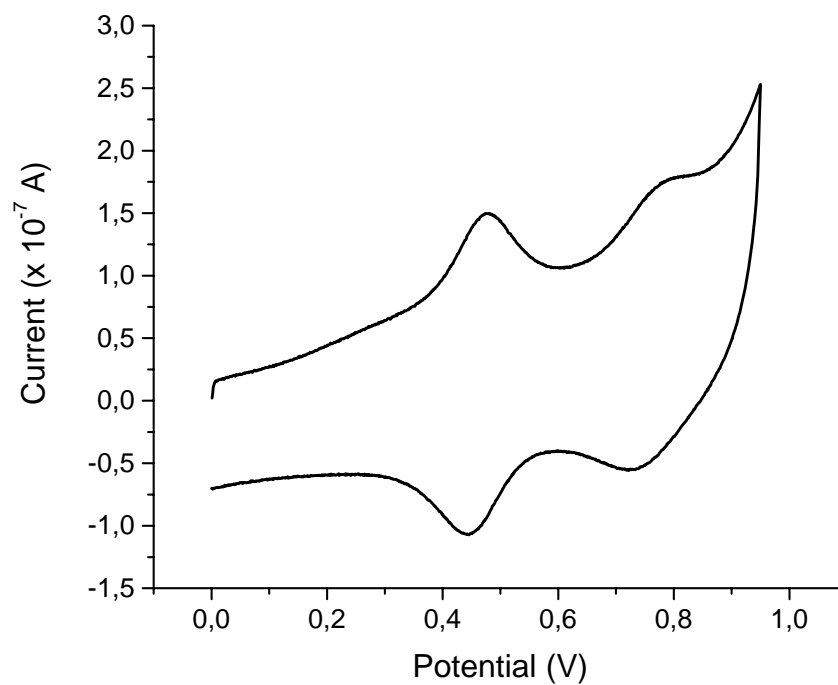
This number corresponds to the surface coverage of the ferrocene unit of **1p**. Therefore, it needs to be divided by 2 to obtain the surface coverage of **1p**.

$$\Gamma = 6.13 \times 10^{-11} \text{ mol/cm}^2 = 0.369 \text{ molecules/nm}^2 = 2.71 \text{ nm}^2/\text{molecule}$$

Cyclic voltammograms of (a) **1p** and (b) **1n** on a Au bead working electrode in 0.1 M TBAPF₆ in CH₂Cl₂ at room temperature. The counter electrode was a Pt wire, and the reference electrode was Ag/AgCl. Scan rate was 100 mV/s.



Cyclic voltammograms of **ZnP-1p** on a Au bead working electrode in 0.1 M TBAPF₆ in CH₂Cl₂ at room temperature. The counter electrode was a Pt wire, and the reference electrode was Ag/AgCl. Scan rate was 100 mV/s.



XPS data

Chemical composition of the functionalised gold surfaces

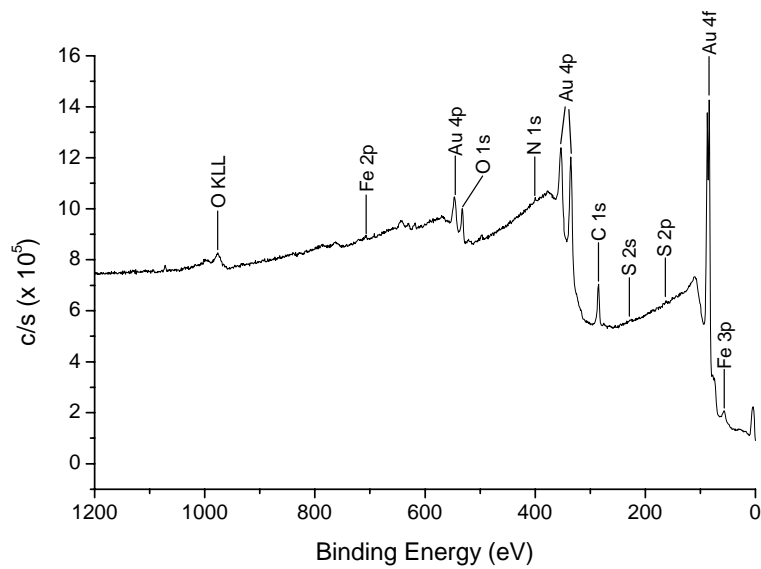
	SAM 1p	SAM 1n	SAM 1p with porphyrin 8	SAM 1n with porphyrin 8
C 1s	49.5	57.0	57.9	64.3
Au 4f	31.2	23.5	23.9	18.2
O 1s	16.2	16.7	12.6	11.8
N 1s	1.2	1.4	2.5	3.9
Cu 2p _{3/2}	0.0	0.0	1.8	0.9
S 2p	1.4	0.8	0.8	0.6
Fe 2p _{3/2}	0.5	0.6	0.4	0.3

Atomic ratios of the functionalised surfaces

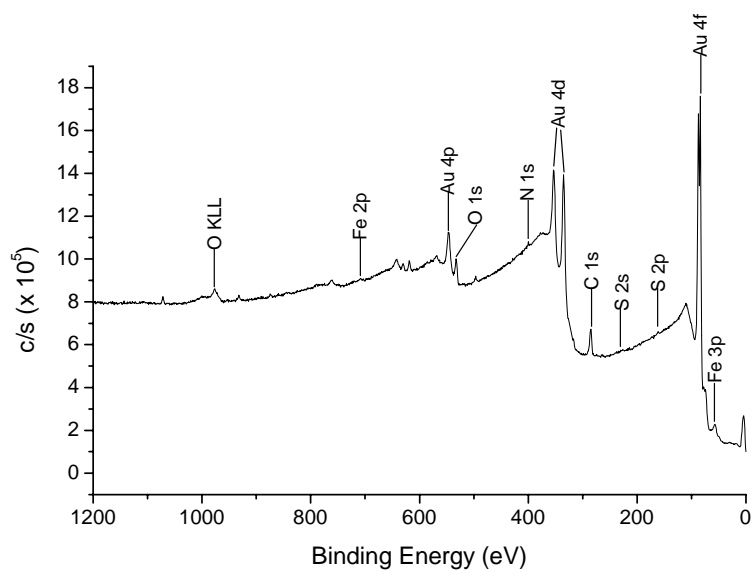
	SAM 1p		SAM 1n		SAM 1p with porphyrin 8		SAM 1n with porphyrin 8	
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
O 1s / C 1s	0.33	0.19	0.29	0.19	0.22	0.11	0.18	0.11
N 1s / C 1s	0.02	0.08	0.03	0.08	0.04	0.08	0.06	0.08
S 2p / C 1s	0.03	0.03	0.01	0.03	0.01	0.02	0.01	0.02
Cu 2p _{3/2} / C 1s	0.00	0.00	0.00	0.00	0.03	0.00	0.01	0.00
Fe 2p _{3/2} / C 1s	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01

Survey XPS of the (a) **1n** SAM and (b) **1p** SAM on Au substrate.

A)

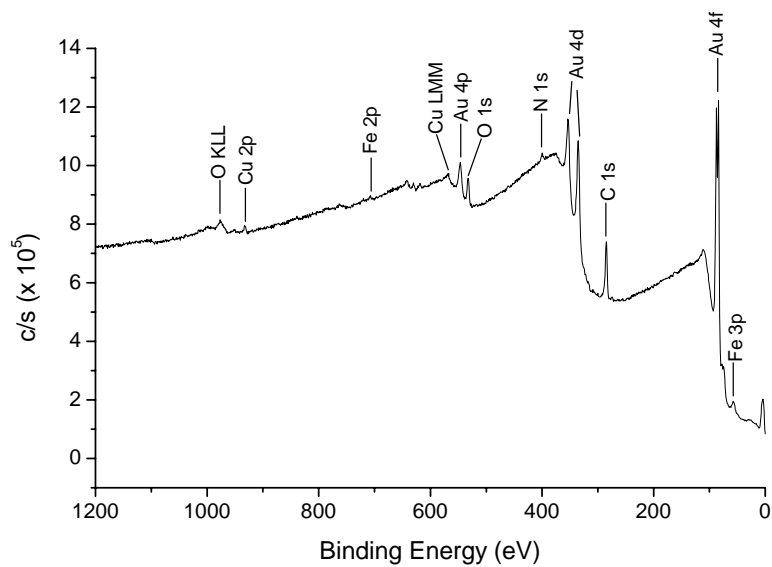


B)

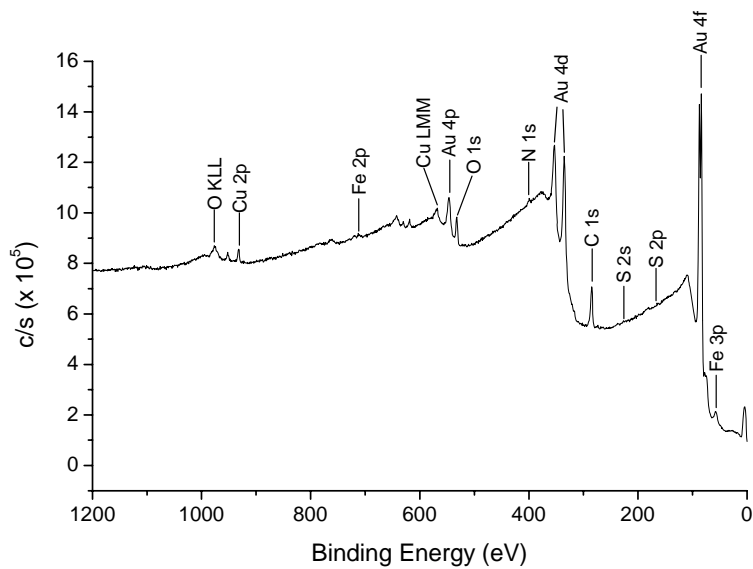


Survey XPS of the (a) **P-1n** SAM and (b) **P-1p** SAM on Au substrate.

A)

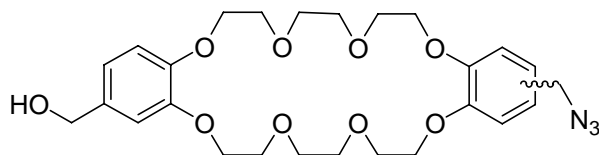


B)



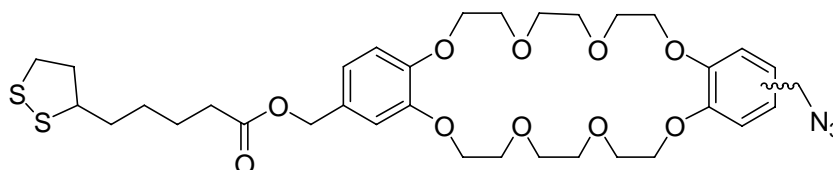
2. Experimental Data for compounds 4-5, 1p, Zn-8

General Synthetic Methods. ^1H and ^{13}C NMR spectra were recorded on a Varian AS400 apparatus in appropriate deuterated solvent solution at 298 K. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. High resolution mass spectroscopy (HRMS) was performed on a Agilent model 62-10 MS-TOF. IR spectra were obtained on a Bomem model MB-100 FTIR. Solvents were purified using a solvent purifying system from Vacuum Atmospheres Company. All other reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out using silica gel (40-63 μm purchased from Silicycle). Thin layer chromatography (TLC) was carried out on glass plates coated with silica gel F-254 purchased from Silicycle. Compounds **2**,² **3**,² **6**,³ **7**⁴ and **8**⁵ were prepared using literature procedures.

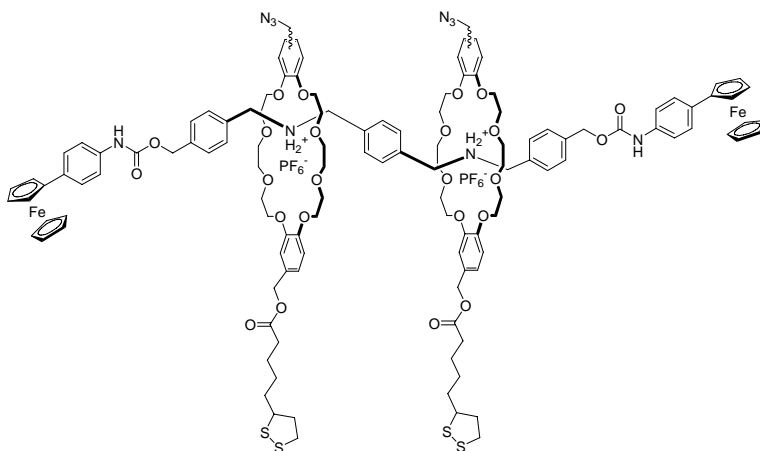


Compound 4. An oven-dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with **3** (1.76 g, 3.46 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (527 mg, 3.46 mmol), diphenylphosphoryl azide (952 mg, 3.46 mmol) and DMF (35 mL). The mixture was stirred for 20 h at room temperature. The solution was poured in water and extracted twice with chloroform. The combined organic layers were washed several times with water and dried over MgSO_4 . The solvent was removed under reduced pressure and the resulting orange oil was purified by column chromatography (silica gel, ethyl acetate followed by ethyl acetate/methanol 98:2 as eluent) to provide 627 mg of the title product as a white solid (34%). M.P. 87-90 $^{\circ}\text{C}$. IR (NaCl): ν 3369, 2925, 2099, 1513, 1264 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): 6.85 (m, 6H); 4.57 (s, 2H); 4.23 (s, 2H); 4.14 (br s, 8H); 3.91 (br s, 8H); 3.83 (s, 8H); 1.92 (br s, 1H). ^{13}C NMR (100 MHz,

CDCl₃, ppm): 149.13; 149.07; 149.06; 149.05; 148.44; 148.42; 134.38; 134.36; 128.4; 121.4; 120.0; 114.0; 113.9; 113.7; 113.0; 71.41; 71.38; 70.0; 69.9; 69.6; 69.54; 69.52; 69.4; 65.21; 65.19; 54.7. HRMS: Calculated for C₂₆H₃₅N₃O₉: 551.2712 [M + NH₄]⁺. Found: 551.2715.

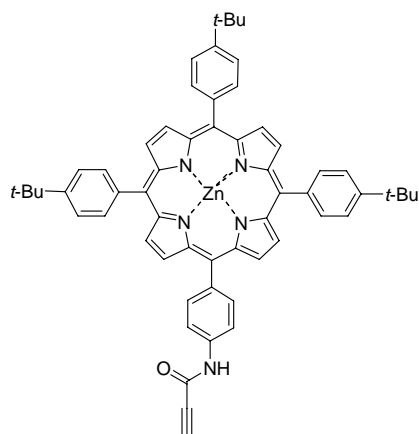


Compound 5. An oven-dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with **4** (600 mg, 1.12 mmol), (±)-lipoic acid (440 mg, 1.34 mmol), dicyclohexylcarbodiimide (DCC) (254 mg, 1.23 mmol), 4-(dimethylamino)pyridine (DMAP) (13 mg, 0.11 mmol) and dichloromethane (22 mL). The mixture was stirred for 16 h at room temperature and the reaction was stopped by addition of water. The mixture was extracted twice with dichloromethane and the organic layers were combined and dried over MgSO₄. The solvent was removed under reduced pressure and the resulting yellow oil was purified by column chromatography (silica gel, ethyl acetate as eluent) to provide 775 mg of the title product as a yellow solid (96%). M.P. 53-54 °C. IR (NaCl): ν 3449, 2931, 2099, 1515, 753 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, ppm): 6.88 (m, 2H); 6.83 (m, 4H); 5.01 (s, 2H); 4.24 (s, 2H); 4.15 (br s, 8H); 3.92 (br s, 8H); 3.83 (s, 8H); 3.54 (m, 1H); 3.13 (m, 2H); 2.44 (m, 1H); 2.34 (m, 2H); 1.89 (m, 1H); 1.67 (m, 4H); 1.45 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): 173.4; 149.1; 149.0; 148.9; 129.0; 128.3; 121.8; 121.4; 114.4; 113.9; 113.7; 113.6; 71.3; 69.9; 69.5; 66.2; 56.4; 54.7; 40.2; 38.5; 34.6; 34.1; 28.7; 24.7. HRMS: Calculated for C₃₄H₄₇N₃O₁₀S₂: 739.3041 [M + NH₄]⁺. Found: 739.3147.



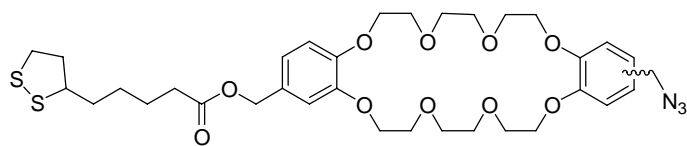
[3]rotaxane (1p). A 5 mL round bottom flask equipped with a magnetic stir bar was charged with **5** (119 mg, 0.16 mmol), **6** (50 mg, 0.08 mmol), acetonitrile (0.3 mL) and dichloromethane (0.3 mL). After 1 h, **7** (68 mg, 0.23 mmol) and dibutyltin dilaurate (6.5 mg, 0.01 mmol) were added. The mixture is stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the crude material was purified by column chromatography (silica gel, chloroform followed by chloroform/acetone 4:2 as eluent) to provide 61 mg of the title product as an orange solid (30%). M.P. dec. > 98 °C. IR (NaCl): ν 3397, 2099, 1516, 721, 753 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): 7.53 (br s, 4H); 7.39 (s, 8H); 7.26 (m, 6H); 7.15 (dd, 8H, $J = 21.7$ and 6.8 Hz); 6.71 (m, 12H); 4.97 (m, 8H); 4.62 (br s, 4H); 4.58 (s, 4H); 4.47 (br s, 4H); 4.27 (s, 4H); 4.19 (s, 4H); 4.00 (m, 26H); 3.72 (m, 16H); 3.53 (m, 18H); 3.09 (m, 4H); 2.40 (m, 2H); 2.33 (m, 4H); 1.84 (m, 2H); 1.63 (m, 8H); 1.42 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 173.5; 153.4; 147.36; 147.32; 147.29; 147.27; 147.20; 137.4; 135.9; 134.2; 132.7; 131.3; 129.9; 129.25; 129.21; 128.6; 127.7; 126.6; 121.5; 121.3; 118.81 à 118.67*; 112.66 à 112.50*; 112.38 à 112.23*; 85.1; 77.4; 70.7; 70.1; 69.6; 68.9; 68.1 à 67.1*; 66.2; 65.8; 56.4; 54.3; 52.3; 51.9; 40.2; 38.5; 34.5; 34.0; 28.7; 24.6. HRMS: Calculated for $\text{C}_{126}\text{H}_{150}\text{F}_{12}\text{Fe}_2\text{N}_{10}\text{O}_{24}\text{P}_2\text{S}_4$: 1213.4203 $[\text{M} - 2\text{PF}_6]^{2+}$. Found: 1213.4208.

* The number of carbon in these signals cannot be measured precisely.

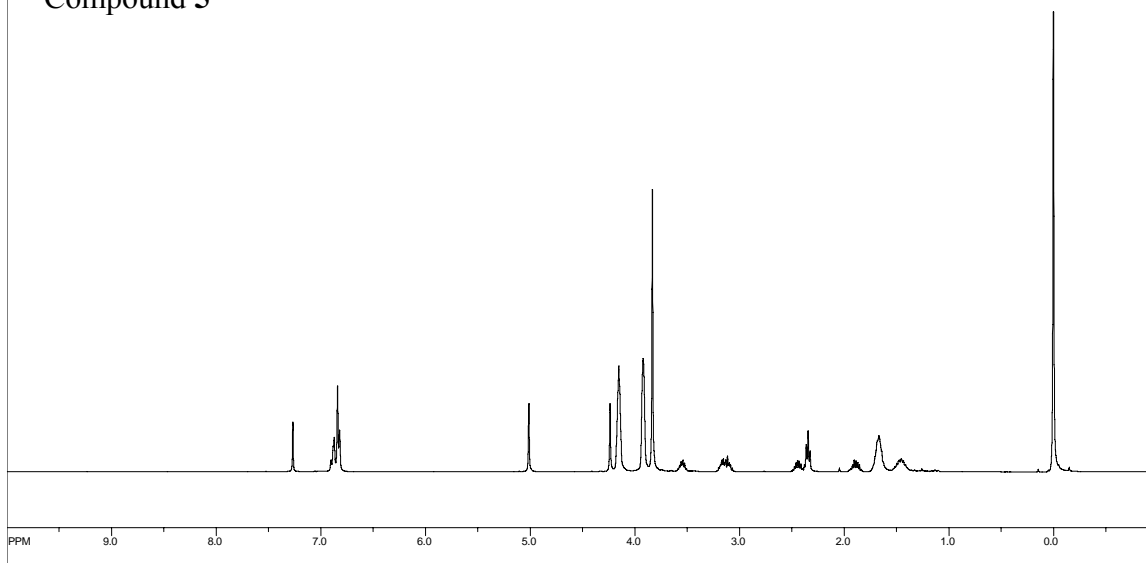


Zn-8. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with **8** (50 mg, 0.06 mmol) and dichloromethane (50 mL). To this mixture was added a solution of zinc(II) acetate (104 mg, 0.58 mmol) in methanol (2 mL). The mixture was heated to reflux for 20h and cooled at room temperature. The mixture was then washed three times with water and dried over MgSO_4 . The solvent was removed under reduced pressure and the resulting purple solid was purified by column chromatography (silica gel, dichloromethane as eluent) to provide 44 mg of the title product as a purple solid (80%). M.P. >260 °C. IR (NaCl): ν 3426, 2958, 1649, 998, 798 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): 8.99 (m, 6H); 8.92 (d, 2H, $J = 4.6$ Hz); 8.21 (d, 2H, $J = 8.2$ Hz); 8.14 (d, 6H, $J = 7.8$ Hz); 7.91 (d, 2H, $J = 8.2$ Hz); 7.84 (s, 1H); 7.77 (d, 6H, $J = 8.0$ Hz); 3.06 (s, 1H); 1.62 (s, 27H). HRMS: Calculated for $\text{C}_{59}\text{H}_{53}\text{N}_5\text{OZn}$: 912.3614 $[\text{M} + \text{H}]^+$. Found: 912.3602.

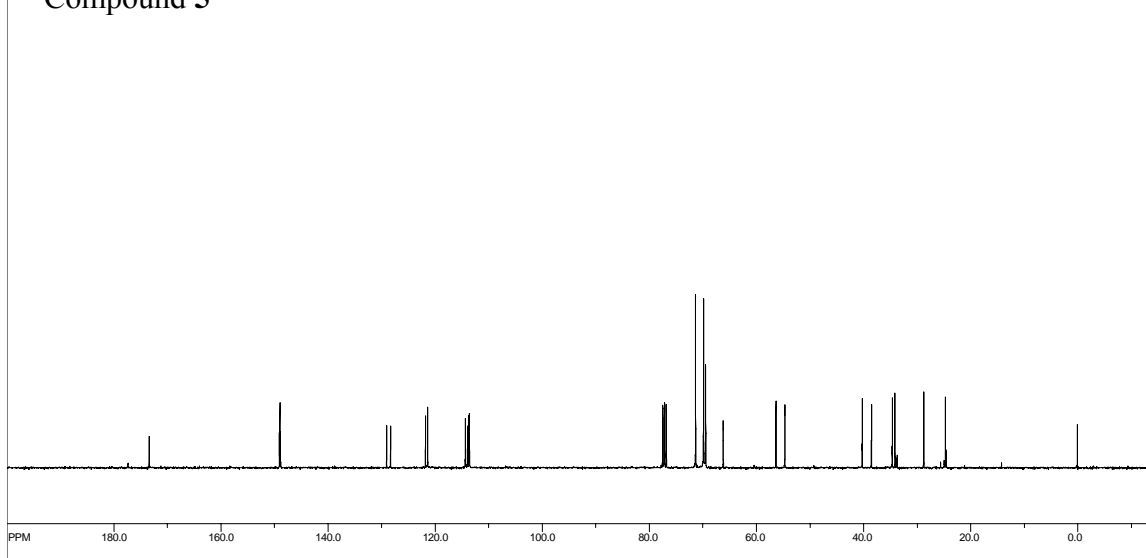
* The compound was not soluble enough to obtain clear ^{13}C NMR data.

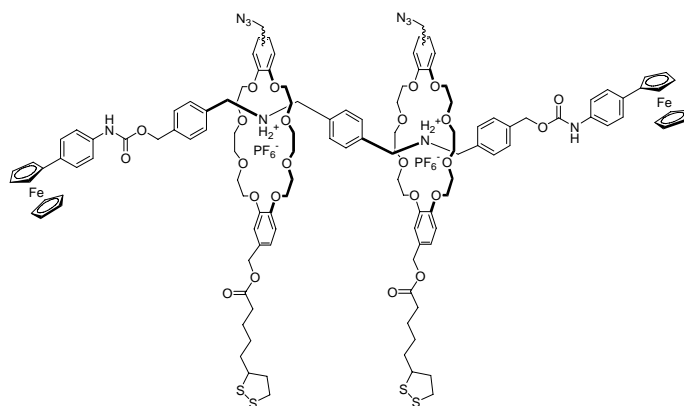


Compound **5**

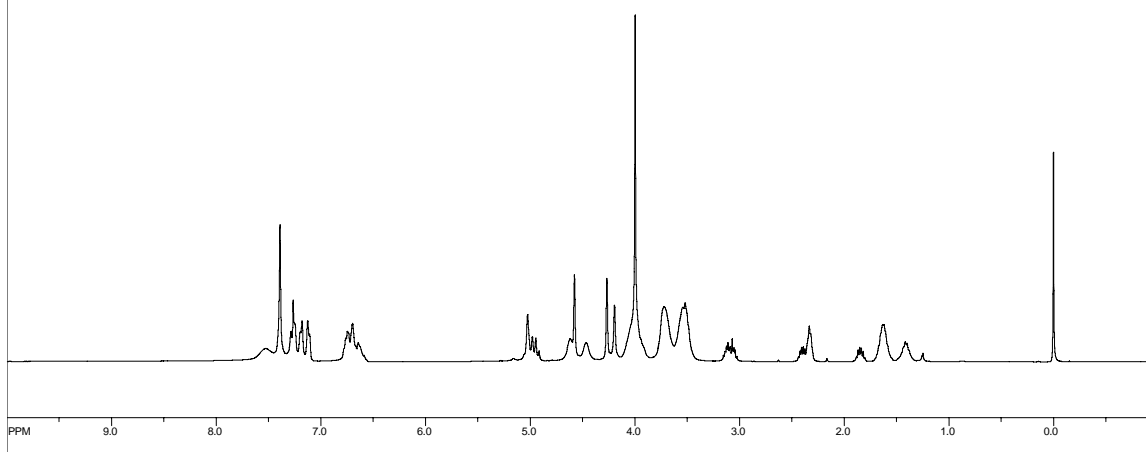


Compound **5**

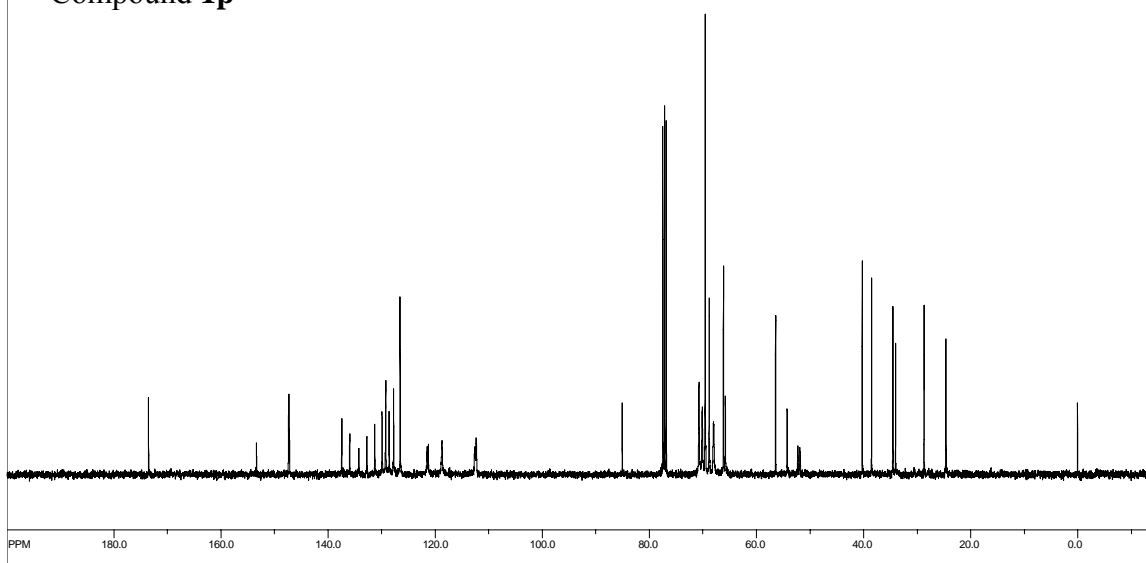


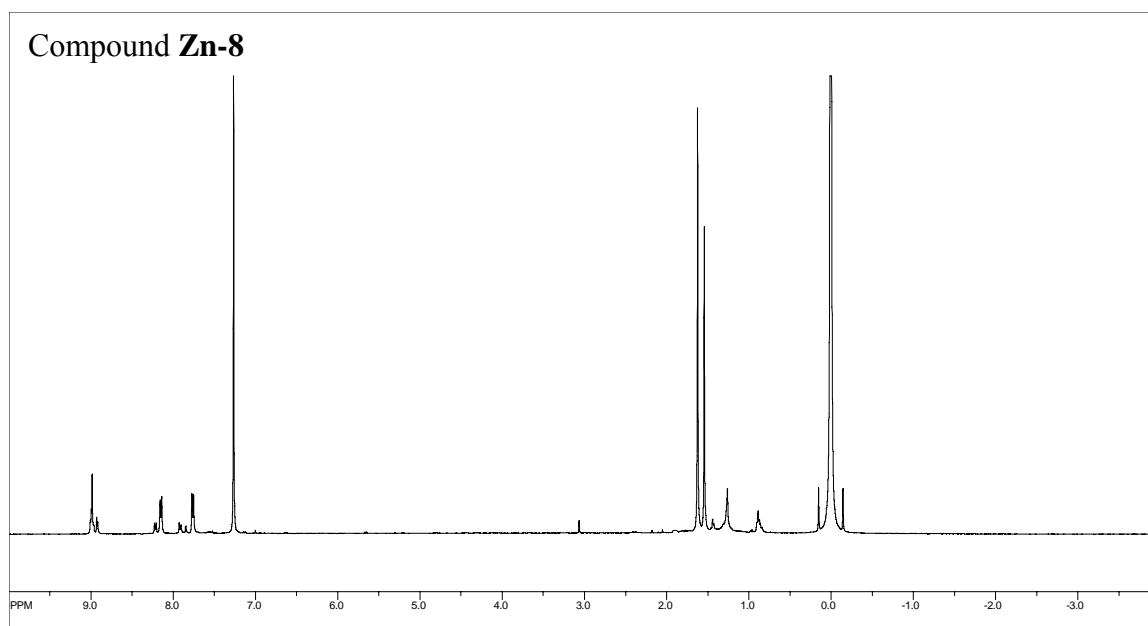
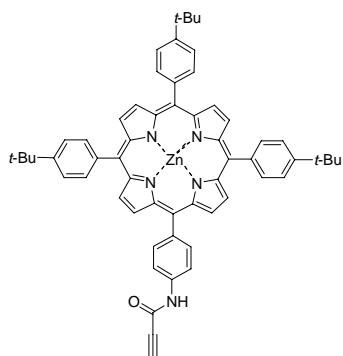


Compound **1p**



Compound **1p**





4. References

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- (3) Watanabe, N.; Yagi, T.; Kihara, N.; Takata, T. *Chem. Comm.* **2002**, 2720-2721.
- (4) Rajkumar, G. A.; Sandanayaka, A. S. D.; Ikeshita, K.-I.; Araki, Y.; Furusho, Y.; Takata, T.; Ito, O. *J. Phys. Chem. B* **2006**, *110*, 6516-6525.
- (5) Marois, J.-S.; Cantin, K.; Desmarais, A.; Morin, J.-F. *Org. Lett.* **2008**, *10*, 33-36.