Molecular Recognition Under Interfacial Conditions: Calix[4]pyrrole-based Cross-linkable Micelles for Ion Pair Extraction

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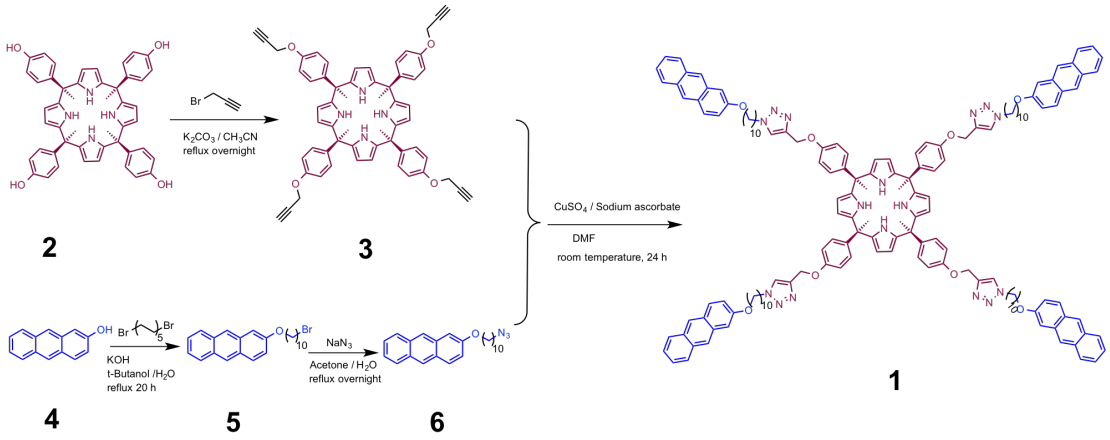
Supporting Information

1. Materials and Methods

All reagents were commercially available and used as supplied without further purification. Compounds **2**,[S1] **5**,[S2] and **6**[S2] were prepared according to published procedures. NMR spectra were recorded on a Varian 400 spectrometer and chemical shifts are reported in ppm using TMS as the reference standard. Low-resolution electrospray ionization mass spectra were recorded with an Ion Spec Fourier Transform mass spectrometer (9.4 T). Transmission electron microscopy (TEM) investigations, scanning electron microscopy, and EDX elemental analyses were carried out on a HITACHI S-5500 SEM/STEM instrument. Dynamic light scattering (DLS) measurements were carried out using a 200-mW polarized laser source Nd: YAG (λ = 532 nm). Polarized scattered light data were collected at 90° in the self-beating mode using a Hamamatsu R942/02 photomultiplier. The signals were sent to a Malvern 4700 submicrometer particle analyzer system. The UV-vis spectra of the product were acquired using a UV-2550 spectrophotometer (Shimadzu, Japan). The solutions were equilibrated for 15 min before making the measurements. Fluorescence spectra were recorded using a LS-55B fluorimeter (Perkin-Elmer, Inc., USA) with the excitation wavelength set to 370 nm. The solutions were equilibrated for 10 min before carrying out the measurements.

2. *Synthesis of **1***

Scheme S1. Synthesis of **WC4P**



Compound **3:** Compound **2** (2.00 g, 2.70 mmol) was dissolved in CH_3CN (150 mL). K_2CO_3 (2.24 g, 16.20 mmol) was added and the reaction mixture was stirred to apparent homogeneity. Propargyl bromide (1.93 g, 16.20 mmol) was added and the reaction mixture was stirred under N_2 at reflux overnight. The volatiles were evaporated off and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with first H_2O and then brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to give a crude solid. Column chromatography (silica gel; hexanes : ethylene acetate = 4 : 1, eluent) afforded a white solid (1.57 g, 65%). The ^1H NMR spectrum of **3** is shown in Figure S1. ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ (ppm): 7.65 (s, 4H), 7.05 (d, J = 8 Hz, 8H), 6.85 (d, J = 8 Hz, 8H), 5.74 (S, 8H), 4.66 (S, 8H), 2.53 (S, 4H), 1.94 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 ^oC) δ (ppm): 156.0, 141.3, 136.6, 128.5, 113.8, 106.1, 78.6, 75.6, 55.8, 44.0, 28.4.

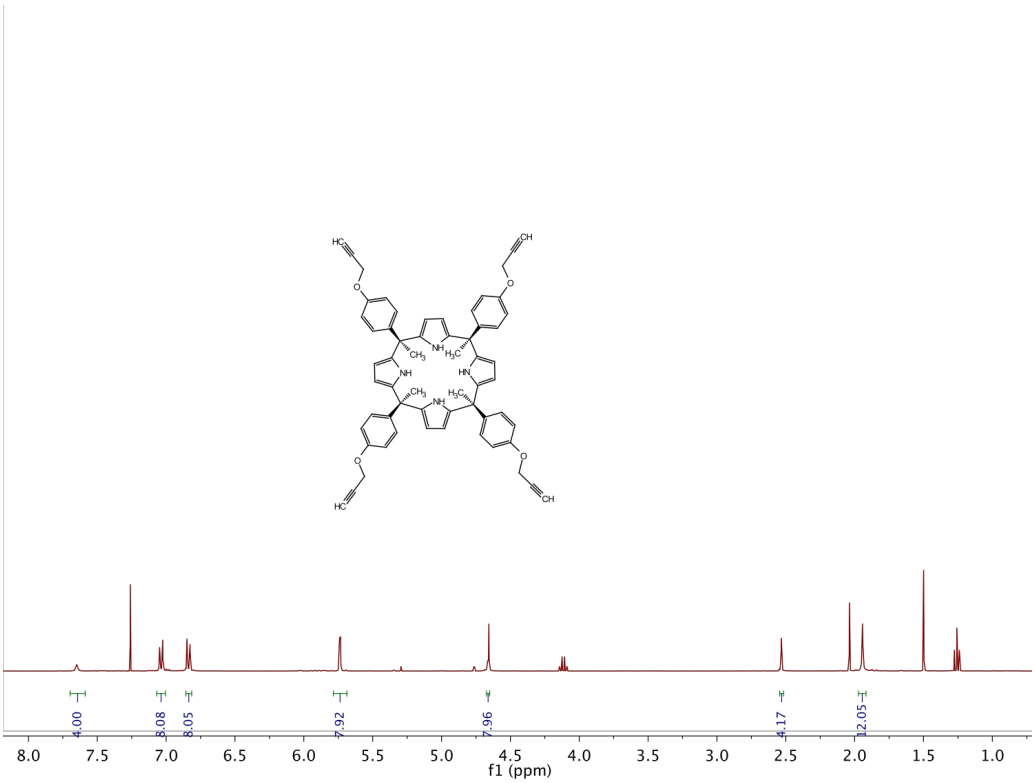


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **3**.

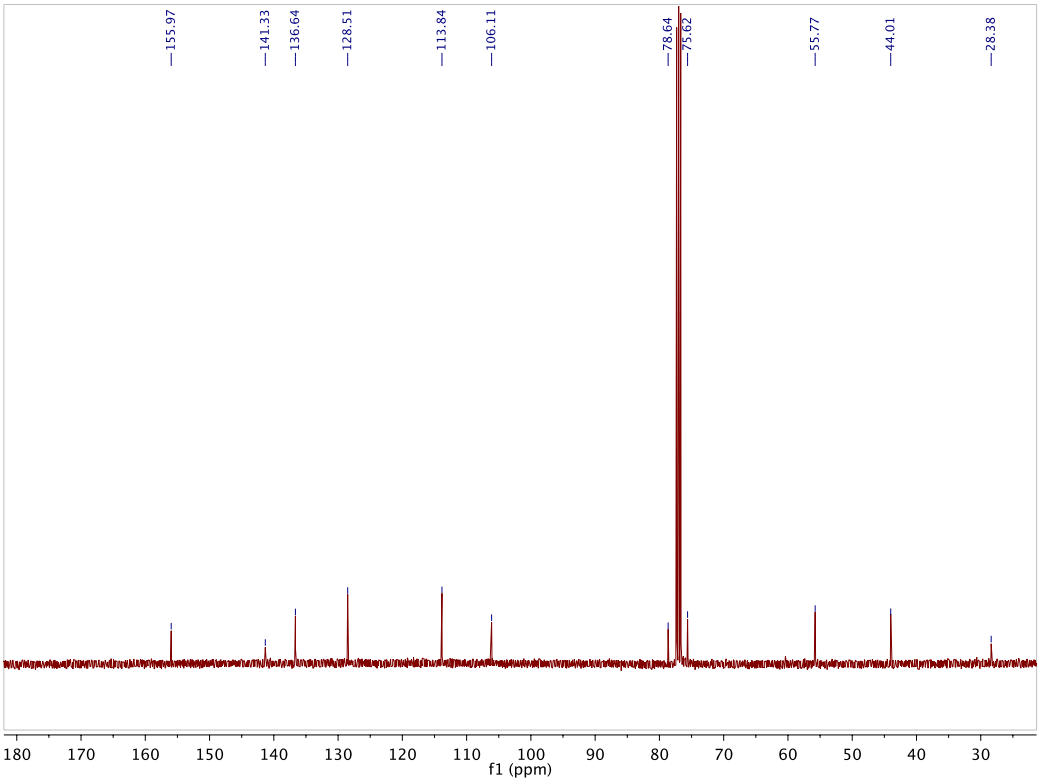


Figure S2. ^{13}C NMR spectrum (400 MHz,$CDCl_3$, 25 ^{o}C) of **3**.

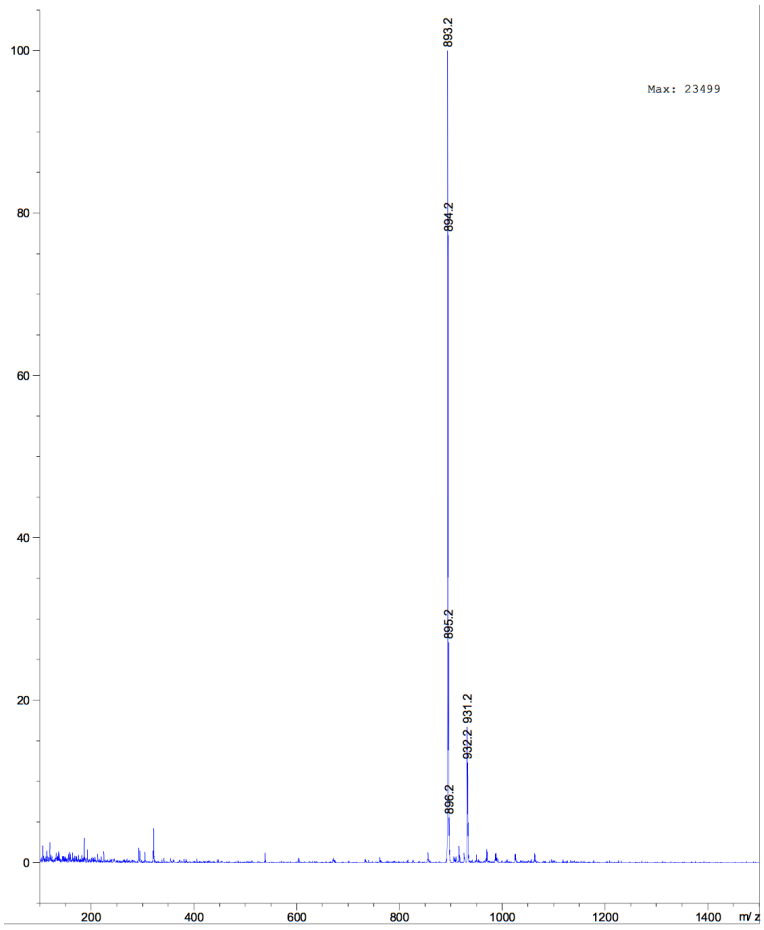


Figure S3. Electrospray ionization mass spectrum of **3**.

Compound **1**: A solution of **3** (0.1 mmol, 127 mg), **6** (0.6 mmol, 222 mg), sodium ascorbate (0.2 mmol, 44.6 mg), and $CuSO_4$ (0.02 mmol, 5.6 mg) in DMF (50 mL) was stirred at room temperature for 24 h. After removal of the volatiles in vacuo, the crude product was purified by column chromatography over silica gel (CH_2Cl_2/MeOH = 20:1, eluent) to afford **1** (209 mg, 87%). The ^{1}H NMR spectrum of **3** is shown in Figure S4. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ^{o}C) δ (ppm): 8.32 (s, 4H), 8.24 (s, 4H), 7.96-7.89 (m, 12H), 7.77 (s, 4H), 7.59 (s, 4H), 7.43-7.36 (m, 8H), 7.19-7,12 (m, 8H), 7.03 (d, J = 8 Hz, 8H), 6.88 (d, J = 8 Hz), 5.75 (s, 8H), 5.12 (s, 8H), 3.30-4.26 (m, 8H), 4.10-4.09 (m, 8H), 1.93-1.80 (m, 21H), 1.55-1.46 (m, 24H), 1.39-1.26 (m, 32H); ^{13}C NMR (400 MHz, CD_2Cl_2, 25 ^{o}C) δ (ppm): 156.7, 136.9, 132.8,132.1, 130.2, 129.6, 128.5, 128.1, 127.4, 126.0, 125.5, 124.3, 123.9, 122.7, 120.8, 113.7, 106.0, 104.1, 68.0, 62.0, 50.3, 44.0, 30.2, 29.4, 29.3, 29.29, 29.2, 28.93, 26.42, 26.05.

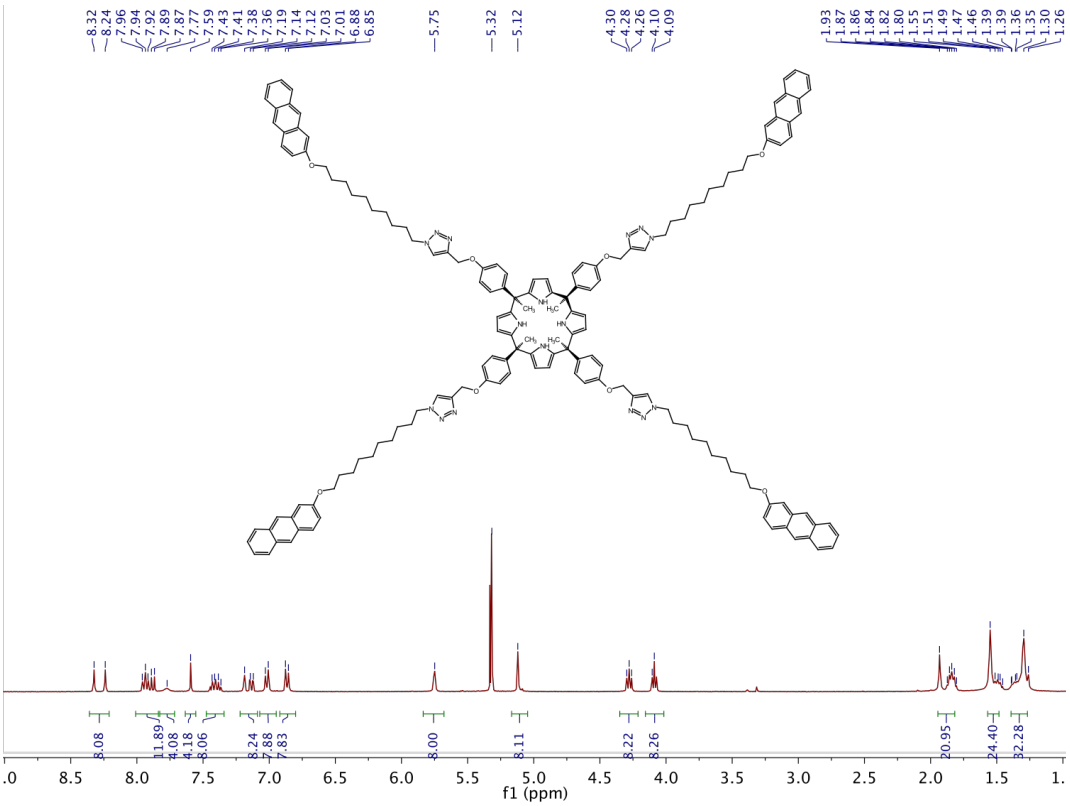


Figure S4. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 25 ^{o}C) of **1**.

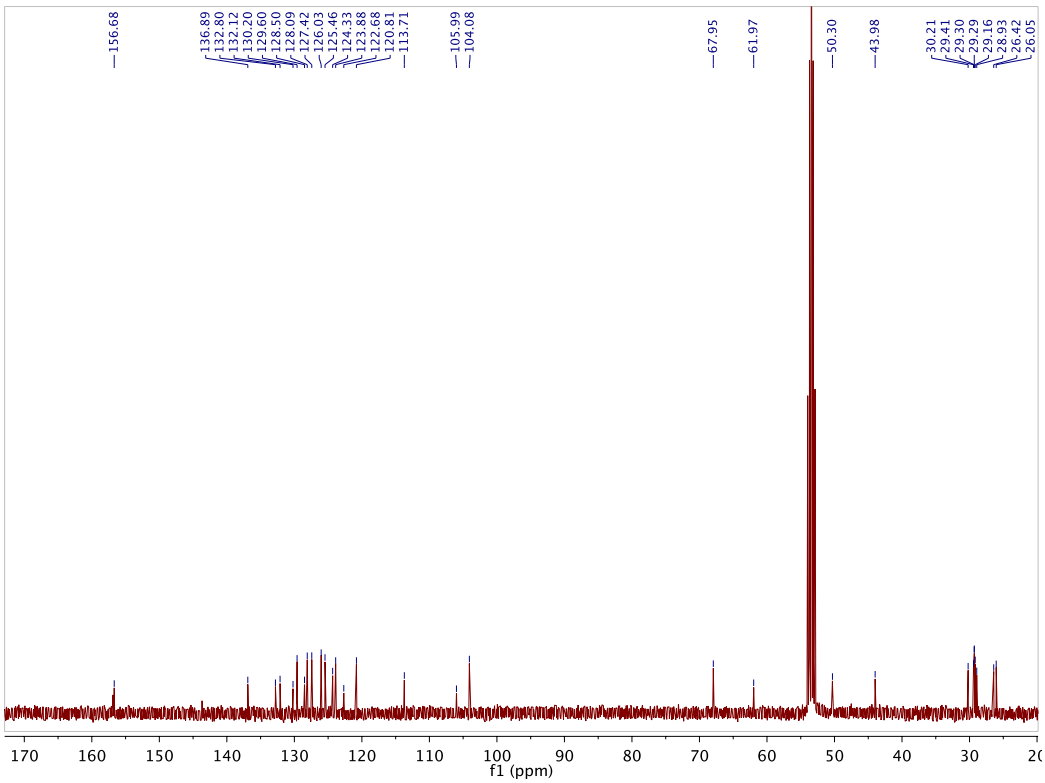


Figure S5. ^{13}C NMR spectrum (400 MHz, CD_2Cl_2, 25 ^{o}C) of **3**.

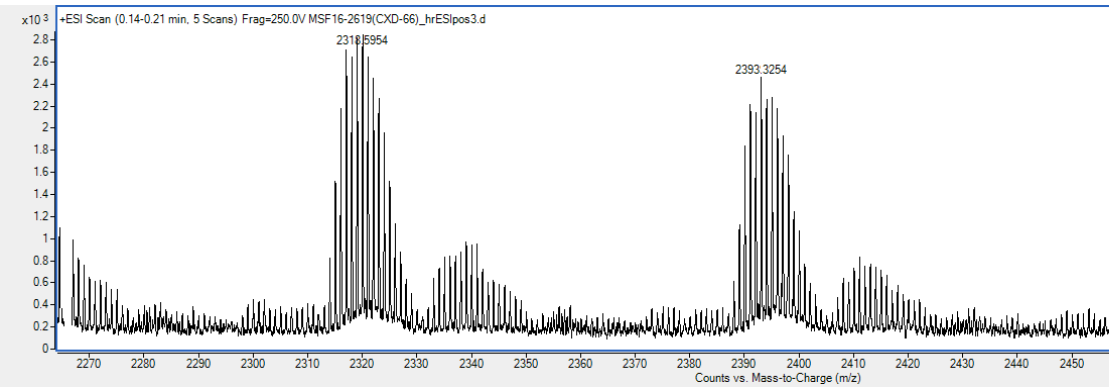
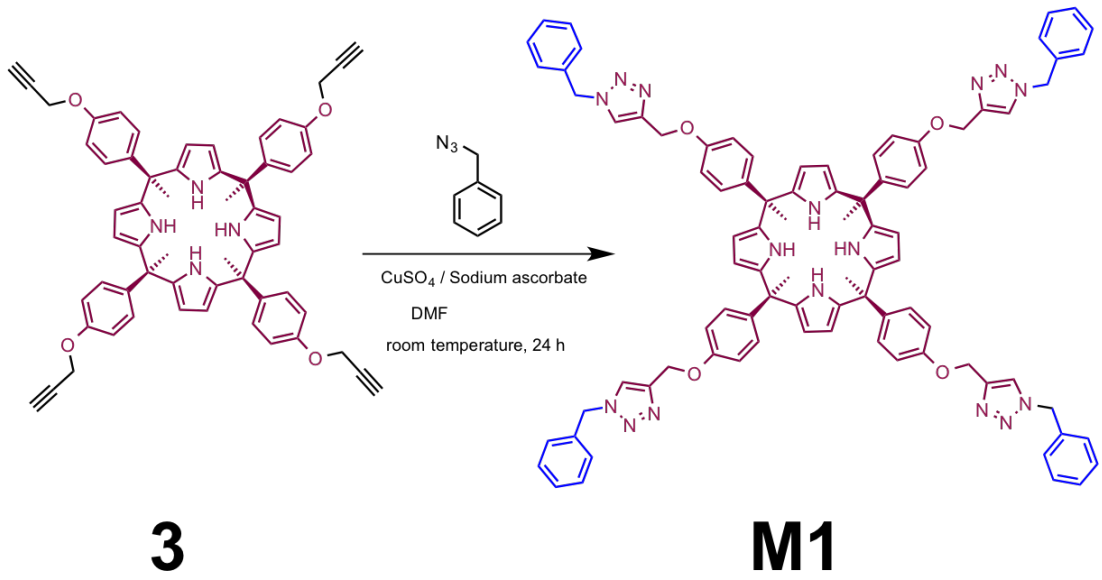


Figure S6. High-resolution electrospray ionization mass spectrum of **1**.

*3. Synthesis of **M1***

Scheme S1. Synthesis of **M1**



Compound **M1**: A solution of **3** (0.1 mmol, 127 mg), benzyl azide (0.6 mmol, 80 mg), sodium ascorbate (0.2 mmol, 44.6 mg), and $CuSO_4$ (0.02 mmol, 5.6 mg) in DMF (50 mL) was stirred at room temperature for 24 h. After removal of the volatiles in vacuo, the crude product was purified by column chromatography over silica gel (CH_2Cl_2/MeOH = 20:1, eluent) to afford **M1** (130 mg, 91%). The ^{1}H NMR spectrum of **M1** is shown in Figure S7. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ^{o}C) δ (ppm): 7.70 (s, 4H), 7.59 (s, 4H), 7.35-7.34 (m, 12H), 7.26-7.25 (m, 8H), 7.02 (d, J = 8Hz, 8H), 6.85 (d, J = 8Hz, 8H), 5.73 (s, 8H), 5.49 (s, 8H), 5.32 (s, 8H), 5.12 (s, 8H), 1.93(s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ (ppm): 156.6, 144.5, 141.0, 129.1, 128.8, 128.5, 128.1, 122.7, 113.7, 106.0, 62.1, 54.2, 44.0, 28.3.

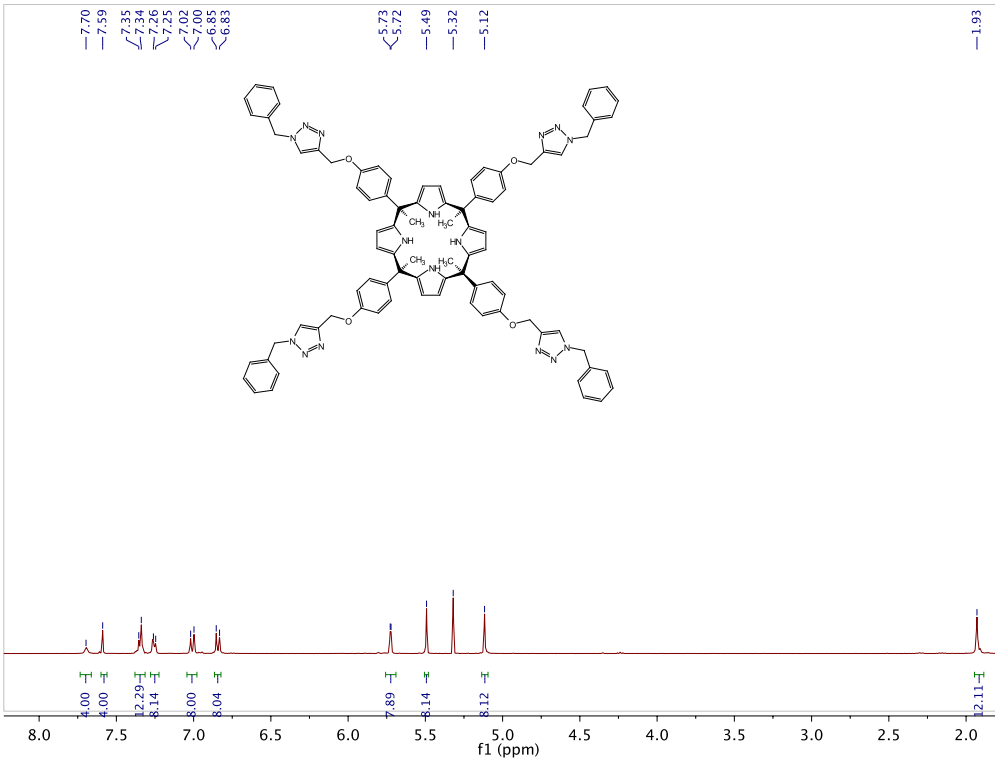


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 25 ^{o}C) of **M1**.

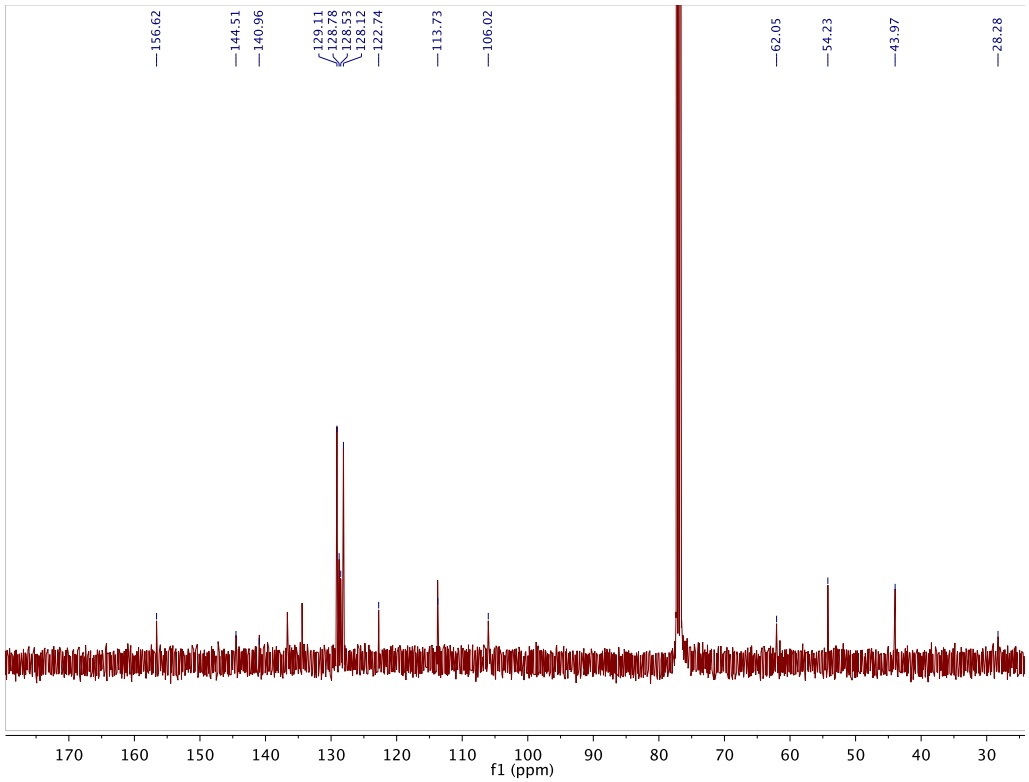


Figure S8. ^{13}C NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **M1**.

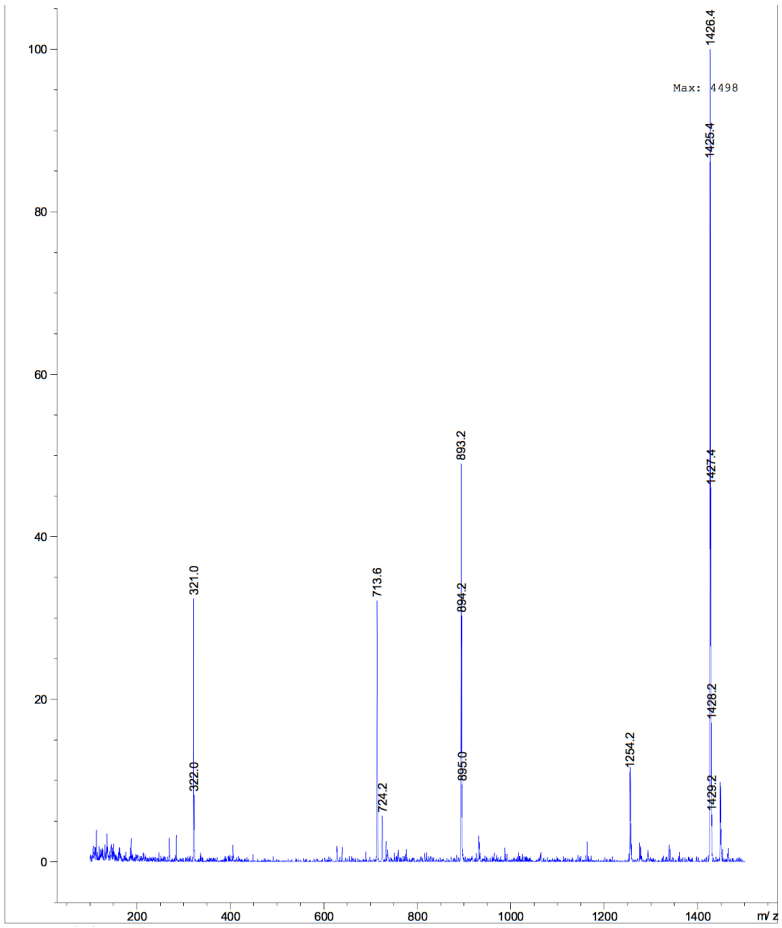


Figure S9. Electrospray ionization mass spectrum of **M1**.

*4. UV-vis Spectrum of **M1** Recorded in the Presence of Different Salts*

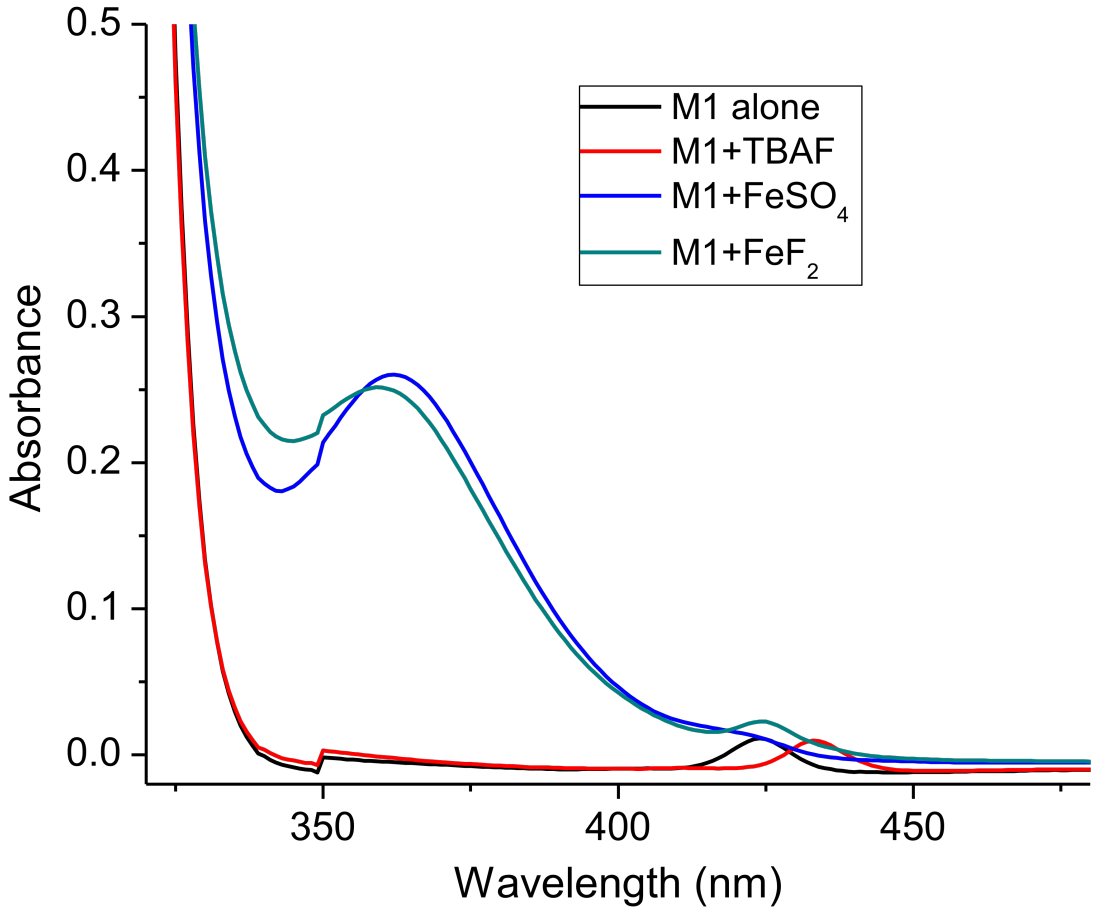


Figure S10. UV-vis spectrum of **M1** recorded in the presence of different salts

5. *Fluorescence Spectra of **1** Recorded in the Presence of Different Salts*

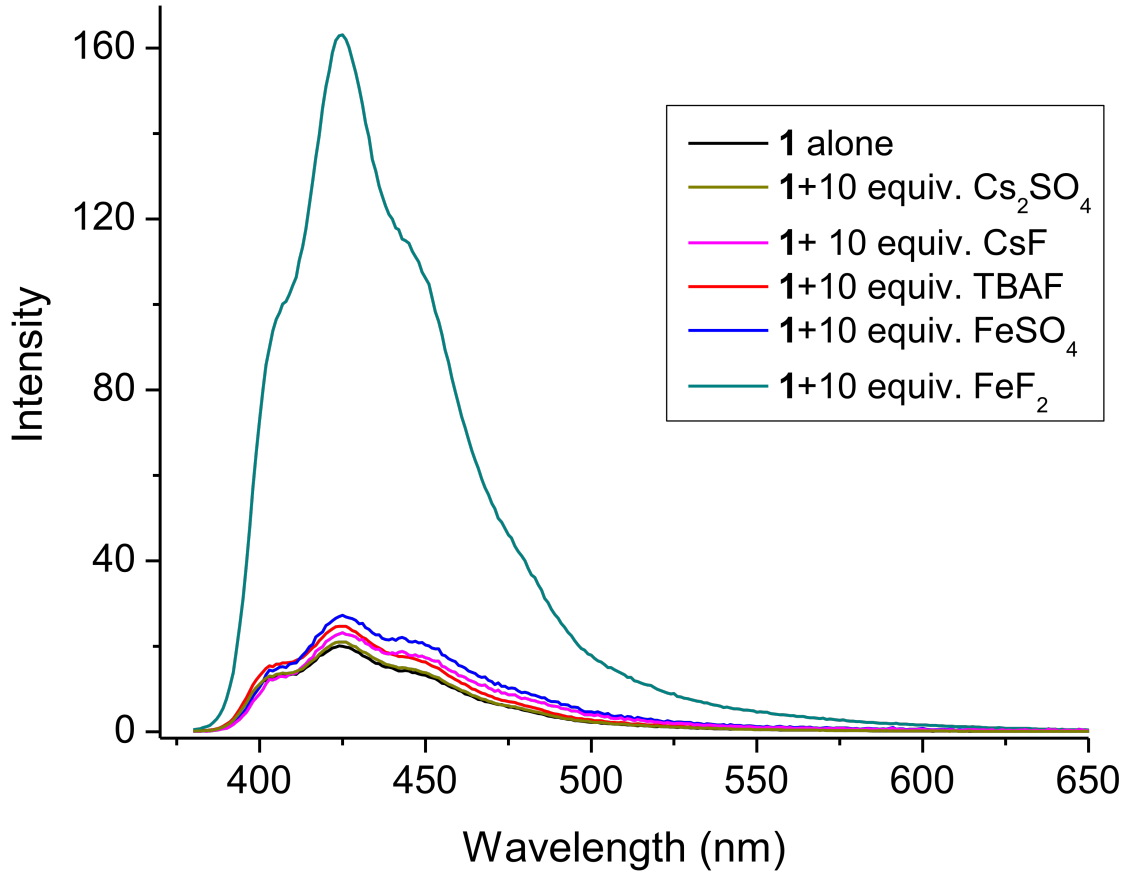


Figure S11. Fluorescence spectra (λ_{ex} = 370 nm) of **1** (8.0 μM) recorded in aqueous media (DMF:water 1:20, v/v) at 25 °C in the presence of different salts.

6. TEM-EDX Results

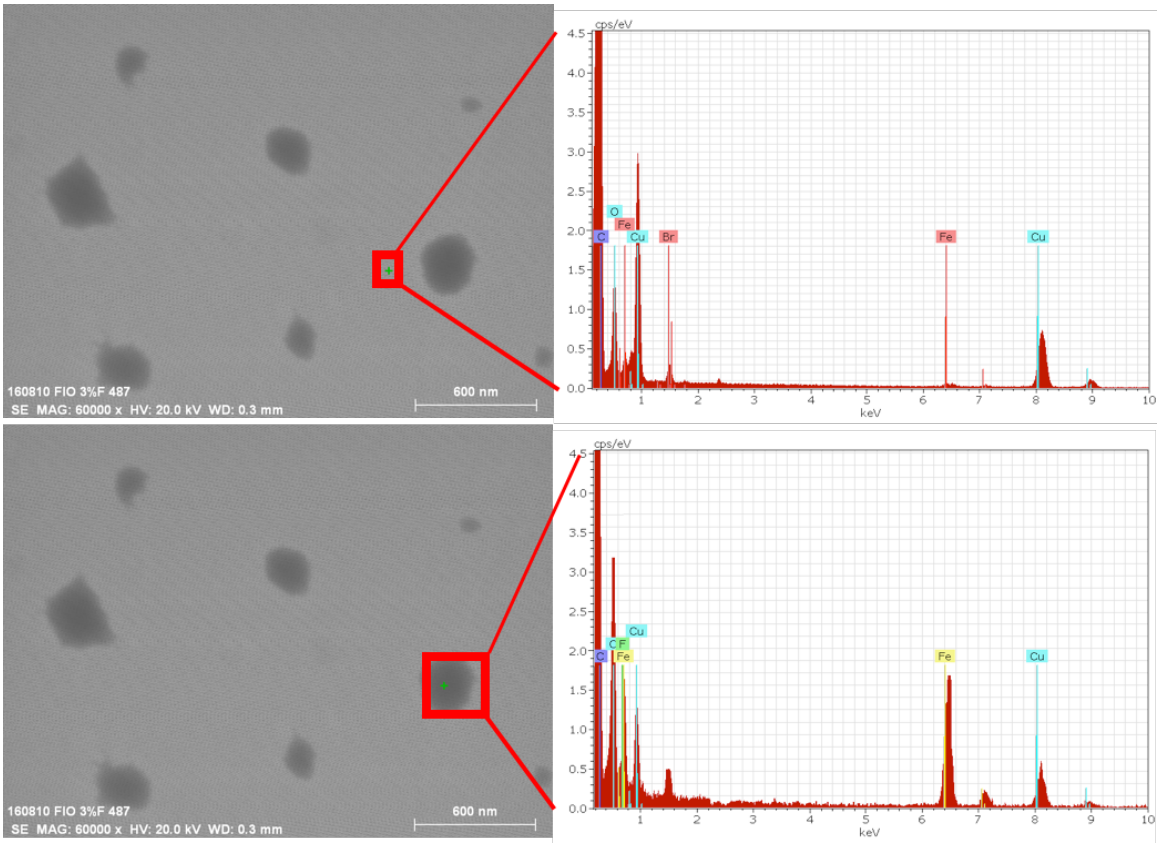


Figure S12. TEM-EDX results. Top) Spectrum of the background; bottom) spectrum recorded after loading the surface with the micelles formed from **1**•FeF_2 .

7. *SEM Images of Amphiphile **1***

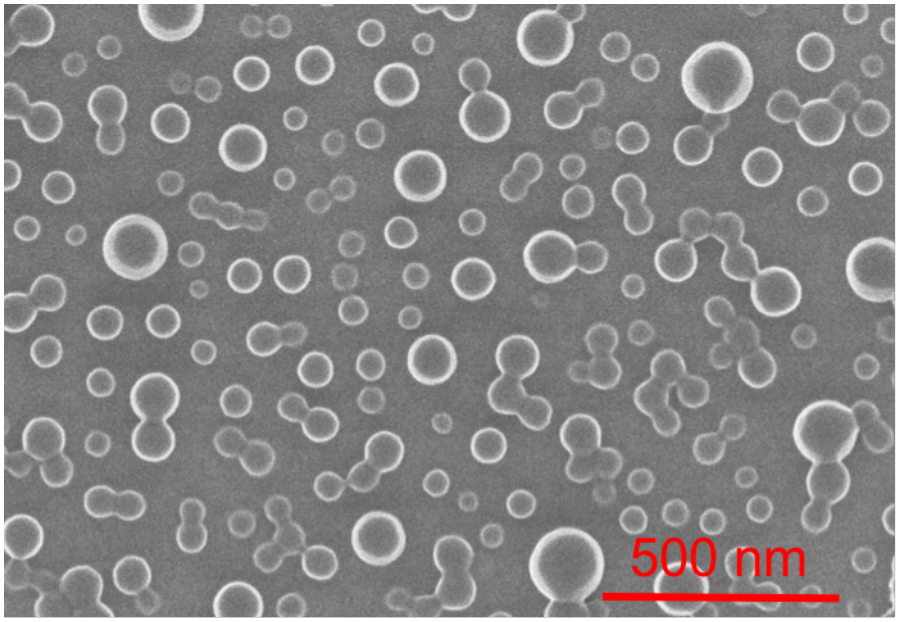


Figure S13. SEM images of the aggregates formed from amphiphile **1** after photoirradiation (365 nm) for 8 h.

8. *TEM Image of Amphiphile **1***

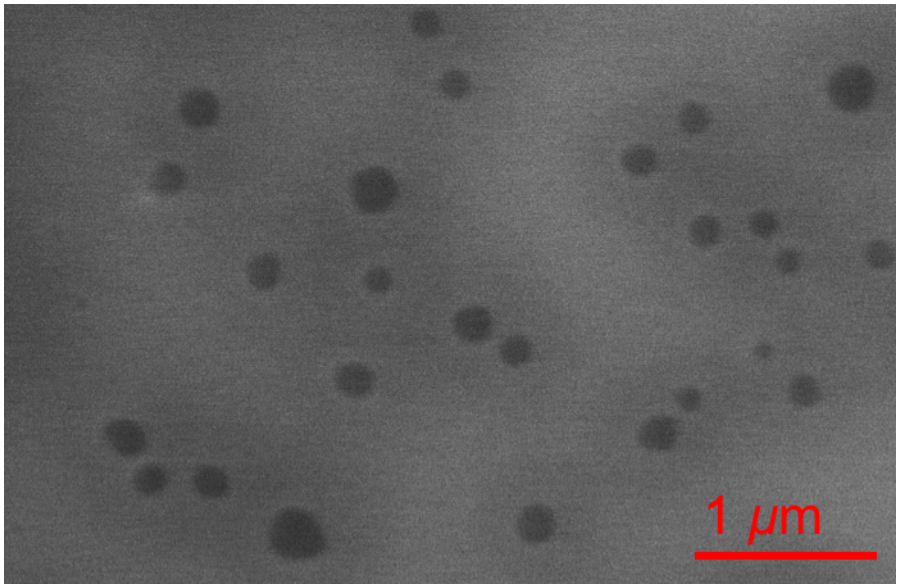


Figure S14. TEM images of the aggregates formed from **1** in the presence of one molar equivalent of FeF_2.

9. *TEM Image of **1** Alone*

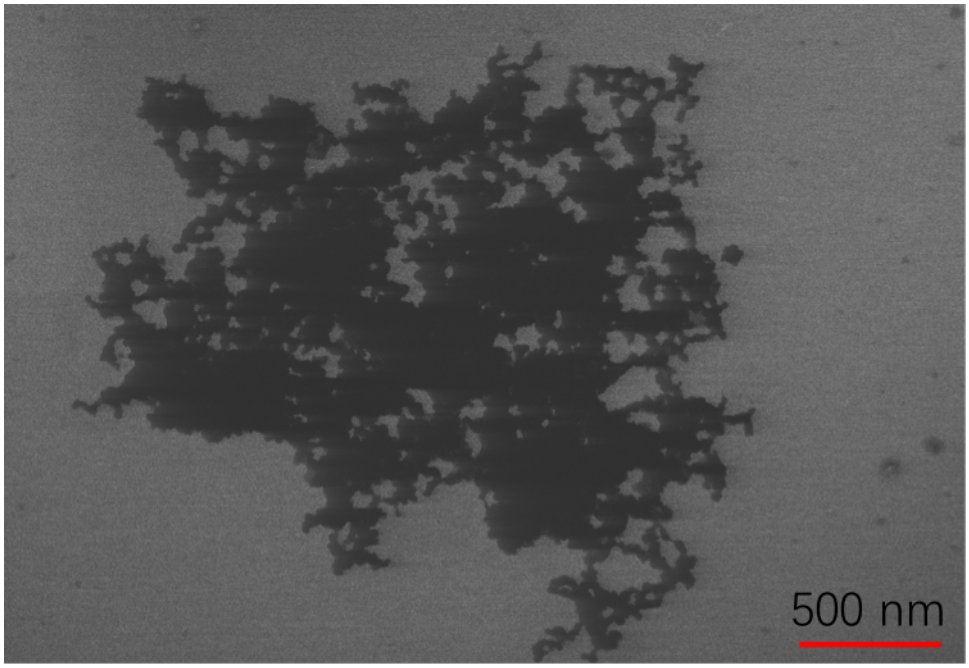


Figure S15. TEM images of the aggregates formed from **1** alone.

10. *DFT Calculations of the Complex Formed from **M1** upon Exposure to FeF_2*

All geometrical optimizations and frequency analyses were carried out with the Gaussian09 suite[S3] of programs at the B3LYP/6-31G*//B3LYP/6-31G* level. Frequency analyses were run to confirm that all the structures obtained were local minima.

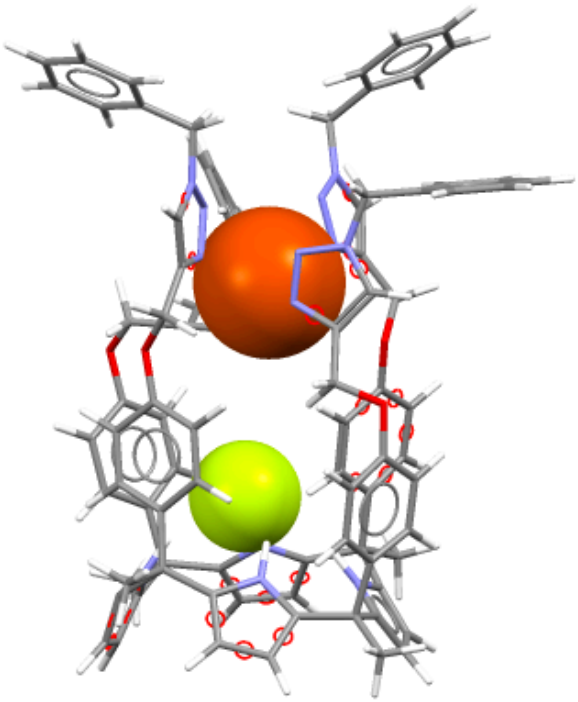


Figure S16. DFT optimized molecular model of the complex of receptor **M1** with FeF_2

11. Quantification of FeF_2 Extraction using ^{19}F NMR Spectroscopy

Quantification of the fluorine present in the water after extraction was carried out as follows: A DMF solution of **1** (2.0 mL, 10 mM) was added slowly into an aqueous solution of FeF_2 (10 mL, 30 mM) and subject to ultra-sound sonication for 2 h. After the multi-micelle formation, dialysis was carried out to remove the non-encapsulated salts. After dialysis, the solvent was removed and DMSO-d_6 (2.0 mL) was added to dissolve the sample. To the resulting sample, 2 μL (10.00 mM) of fluorobenzene was added as an internal ^{19}F NMR standard. At this juncture, ^{19}F NMR spectroscopic analyses were performed and the amount of FeF_2 was quantified *via* peak integration relative to the internal fluorobenzene standard.

12. ^{19}F NMR Spectroscopic Analyses

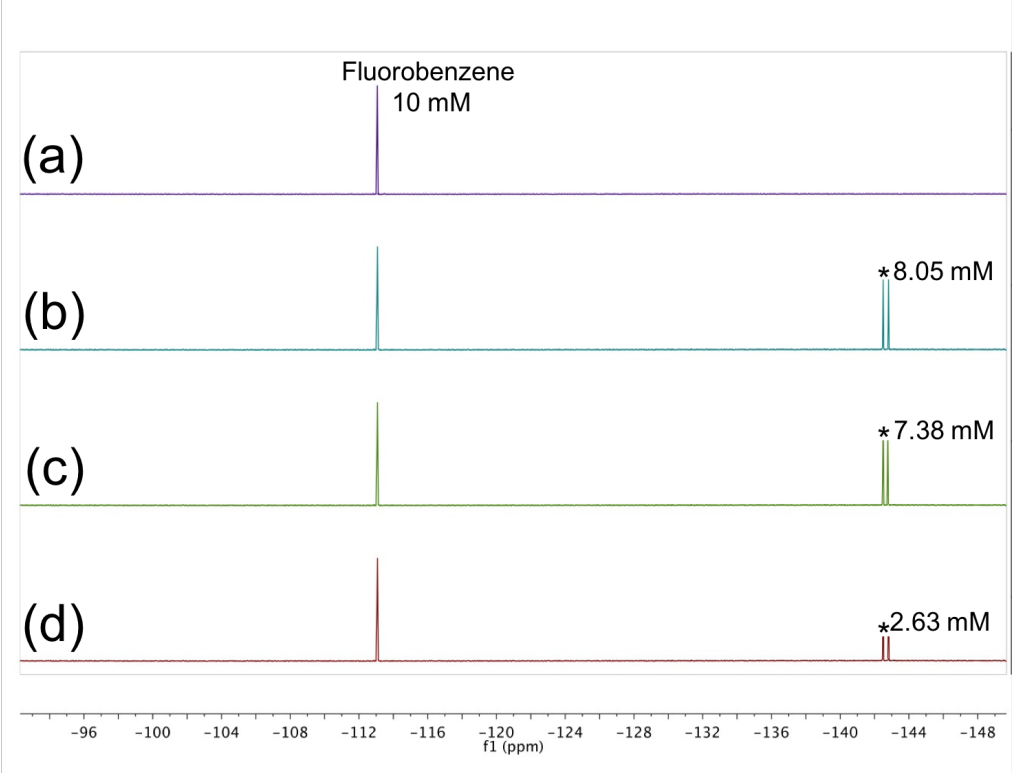


Figure S17. ^{19}F NMR spectra of (a) fluorobenzene in DMSO-d_6 (10 mM); (b) solid remaining after a DMF solution of **1** was mixed with FeF_2 (30 mM in H_2O), sonicated for 2 h, with 5 hours of photo-irradiation, dialyzed to remove free FeF_2, and redissolved in DMSO-d_6; (c) solid remaining after a DMF solution of **1** was mixed with FeF_2 (30 mM in H_2O), sonicated for 2 h, dialyzed to remove free FeF_2, and redissolved in DMSO-d_6; (d) solid remaining after a DMF solution of **M1** was mixed with FeF_2 as per the protocol in (b). *denotes signal ascribed to FeF_2

References:

S1. Anzenbacher, Jr, P.; Jursíková, K.; Lynch, V. M.; Gale, P. A.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 11021.

S2. Han, T.; Chen, C.-F. *J. Org. Chem.* **2008**, *73*, 7735.

S3. Gaussian 09, Revision E.01, 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, J. M.; 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.; and Fox, D. J., Gaussian, Inc., Wallingford CT, 2009.