

Electronic Supplementary Information (ESI) for

**Dual-responsive vesicles formed by an amphiphile appended two
tetrathiafulvalene units in aqueous solution**

Xiao-Jun Wang,^{a,b} Ling-Bao Xing,^{a,c} Bin Chen,^a Ying Quan,^b Chen-Ho Tung^a and Li-Zhu Wu^{*a}

^aKey Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, the Chinese Academy of Sciences, Beijing 100190, P. R. China

^bJiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.

^cSchool of Chemical Engineering, Shandong University of Technology, Zibo 255049, P. R. China.

*Corresponding author. E-mail: lzwu@mail.ipc.ac.cn

Fax: +86 10-8254 3580

Experimental

General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium/benzophenone ketyl and CaH₂ under a nitrogen atmosphere prior to use, respectively. 2-Iodotetrathiafulvalene^[S1] and N-Boc-propylenediamine^[S2] were prepared according to the literature procedures.

NMR spectra were obtained on a Bruker Avance 400 spectrometer (400 MHz ¹H NMR and 100 MHz ¹³C NMR) at room temperature. Chemical shifts (δ) are reported in parts per million (ppm) using the solvent residual signal as an internal reference (CDCl₃, $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). Coupling constants (J) are given in hertz. Each resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublets), *m* (multiplet), or *br* (broad signal). Mass spectra (EI, ESI, MALDI-TOF) were obtained in the positive ion mode on a Waters GCT Premier, Waters-QTOF and Bruker Daltonics Microflex spectrometer, respectively. UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer, equipped with a temperature controller bath.

Dynamic Light Scattering (DLS) data were collected on a DynaPro NanoStar (Wyatt Technology) with a gallium-arsenide diode laser of 658 nm emission. The instrument has a temperature-controlled sample holder (precision of 0.1 °C) for a quartz cuvette of 10 μ L. Scattering data were collected at an angle of $\theta = 90^\circ$ and processed using the software program DYNAMICS V6, version 6.3.40. The autocorrelation functions were analyzed with the CONTIN method.

Cryo-transmission electron microscopy (cryo-TEM)^[S3] was performed on FEI Tecnai 20 and JEM 2200FS. A 3- μ L aliquot of sample was pipetted onto a glow discharged Quantifoil copper grid coated with holey carbon support film in the environmental chamber of a Vitrobot with RH of 100% at room temperature. The excess solution was blotted with a piece of filter paper, resulting in the formation of thin films suspended the mesh holes, and the samples were quickly plunged into a reservoir of liquid ethane (cooled by liquid nitrogen) at its melting temperature. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) for further observation at -174 °C operating at 200 kV.

Synthetic procedure of 1:

3: To a CH₂Cl₂ (30 mL) solution of **2** (4.02 g, 5.3 mmol) was added 15 mL trifluoroacetic acid (TFA), and the mixture was stirred at room temperature for over 2 h. Then, an excess of triethylamine was added to neutralize TFA in the ice-water bath. To the resulting mixture was added DMF (30 mL), 3,5-diiodobenzoic acid (1.98 g, 5.3 mmol), and then PyBOP (3.31 g, 6.4 mmol). The solution was stirred at room temperature for another 1.5 hour and then poured into water (200 mL), extracted with CH₂Cl₂ (3 × 120 mL). The combined organic layer were washed with brine for more than 8 times to remove DMF, dried over Na₂SO₄ and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 100/1) to give **3** as colorless oil (4.39 g, 4.3 mmol, 81%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 2H), 8.14 (s, 1H), 7.77 (br, 1H), 7.31 (br, 1H), 7.18 (s, 2H), 4.23-4.18 (m, 6H), 3.83 (t, *J* = 4.8 Hz, 4H), 3.78 (t, *J* = 5.0 Hz, 2H), 3.72-3.69 (m, 6H), 3.66-3.61 (m, 12H), 3.54-3.48 (m, 10H), 3.36 (s, 3H), 3.34 (s, 6H), 1.81 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 164.8, 152.3, 147.4, 141.1, 137.8, 135.6, 129.3, 107.0, 94.6, 72.3, 71.8, 70.6, 70.5, 70.4, 70.3, 69.6, 68.8, 58.9, 36.7, 36.5, 29.3. MALDI-TOF-MS: *m/z* calcd for C₃₈H₅₈I₂N₂O₁₄: 1020.7, found: 1043.2 [M+Na]⁺.

4: Compound **3** (1.22 g, 1.2 mmol), CuI (7.6 mg, 0.04 mmol) and Pd(PPh₃)₄ (23 mg, 0.02 mmol) were added to the mixture of anhydrous THF (40 mL) and TEA (20 mL) under Ar. While stirring, trimethylsilylethyne (0.14 g, 1.40 mmol) was injected through syringe. The reaction mixture was stirred at 50-60 °C over night under Ar atmosphere and was monitored by TLC. Upon completion, the solution was evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 100/1) to give the compound **4** as colorless oil (0.94 g, 0.98 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 2H), 7.76 (br, 1H), 7.65 (s, 2H), 7.20 (s, 2H), 4.24-4.17 (m, 6H), 3.83 (t, *J* = 5.1 Hz, 4H), 3.77 (t, *J* = 5.0 Hz, 2H), 3.72-3.69 (m, 6H), 3.64- 3.60 (m, 12H), 3.53-3.46 (m, 10H), 3.35 (s, 3H), 3.33 (s, 6H), 1.79 (s, 2H), 0.22 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 165.9, 151.6, 140.1, 136.8, 134.6, 130.0, 129.0, 122.9, 106.2, 102.8, 94.9, 71.6, 71.2, 70.0, 69.9, 69.7, 69.0, 68.1, 58.2, 36.1, 35.8, 28.7. MALDI-TOF-MS: *m/z* calcd for C₄₈H₇₆N₂O₁₄Si₂: 961.3, found: 983.6 [M+Na]⁺.

5: To a CH₂Cl₂ (20 mL) and CH₃OH (30 mL) solution of **4** (2.12 g, 2.21 mmol) was added K₂CO₃

(13.8 g, 10 mmol). The solution was stirred at room temperature for 15 minutes and then poured into water (100 mL), extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layer were washed with 1 M HCl (1 × 100 mL) and brine (3 × 150 mL), dried over Na₂SO₄ and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 105/1) to give **5** as colorless oil (1.62 g, 1.99 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 1.4 Hz, 2H), 7.93 (br, 1H), 7.67 (s, 1H), 7.56 (br, 1H), 7.20 (s, 2H), 4.23-4.17 (m, 6H), 3.83 (t, *J* = 5.1 Hz, 4H), 3.78 (d, *J* = 5.3 Hz, 2H), 3.71-3.69 (m, 6H), 3.65-3.61 (m, 12H), 3.54-3.50 (m, 10H), 3.35 (s, 3H), 3.34 (s, 6H), 3.15 (s, 2H), 1.80 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 165.7, 151.7, 140.3, 137.1, 134.8, 130.7, 129.1, 122.3, 106.3, 81.5, 78.7, 71.8, 71.3, 70.1, 70.0, 69.9, 69.1, 68.2, 58.3, 36.4, 36.2, 28.8. MALDI-TOF-MS: *m/z* calcd for C₄₂H₆₀N₂O₁₄: 816.9, found: 817.5 [M]⁺, 839.5 [M+Na]⁺.

1: To the mixture of anhydrous THF (30 mL) and TEA (30 mL) were added **5** (0.23 g, 0.28 mmol), TTF-I (0.11 g, 0.34 mmol), CuI (1.9 mg, 0.01 mmol) and Pd(PPh₃)₄ (12 mg, 0.01 mmol) under Ar. The reaction mixture was refluxed over 12 hours under Ar atmosphere and was monitored by TLC. Upon completion, the solution was evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (CH₂Cl₂/CH₃OH, 90/1) to give the compound **1** as red oil (0.22 g, 0.18 mmol, 65%). ¹H NMR (400 MHz, THF-*d*₈) δ 8.19 (br, 1H), 7.99 (s, 2H), 7.85 (br, 1H), 7.70 (s, 1H), 7.24 (s, 2H), 6.94 (s, 2H), 6.54 (s, 4H), 4.18 (dd, *J* = 10.8, 5.7 Hz, 6H), 3.81 (t, *J* = 4.7 Hz, 4H), 3.74 (t, *J* = 4.6 Hz, 2H), 3.65 (dd, *J* = 10.0, 5.1 Hz, 6H), 3.56-3.54 (m, 12H), 3.49-3.42 (m, 10H), 3.27 (d, *J* = 3.9 Hz, 9H), 1.81 (t, *J* = 5.6 Hz, 2H). ¹³C NMR (101 MHz, THF) δ = 167.1, 165.7, 153.6, 142.7, 137.2, 137.0, 131.5, 130.8, 128.3, 123.9, 120.4, 120.1, 115.7, 115.0, 108.2, 107.6, 92.4, 82.8, 73.4, 73.1, 71.8, 71.6, 71.5, 70.8, 70.2, 59.1, 37.9, 37.6, 30.8. MALDI-TOF-MS: *m/z* calcd for C₅₄H₆₄N₂O₁₄S₈: 1221.6, found: 1221.5 [M]⁺. ESI-HRMS: *m/z* calcd for C₅₄H₆₄N₂O₁₄S₈: 1220.2123, found: 1220.2107 [M]⁺.

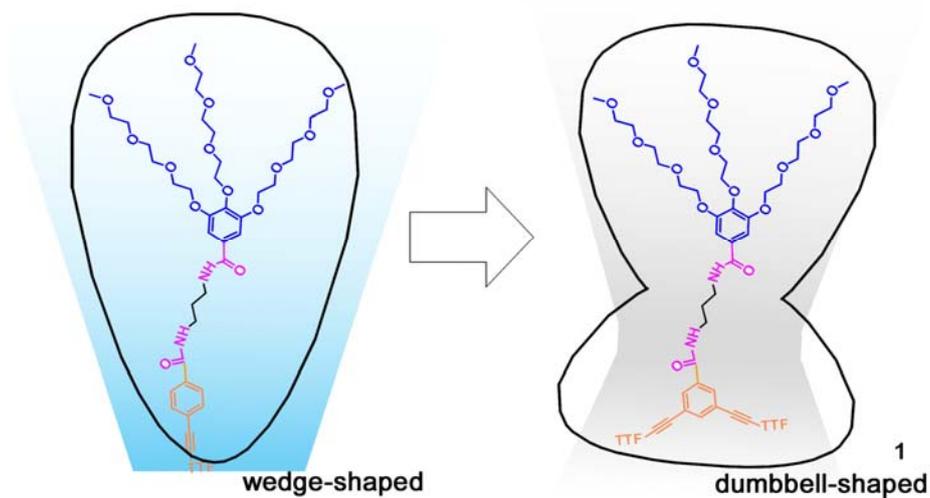


Fig. S1. The whole structural shape changing from wedge and dumbbell.

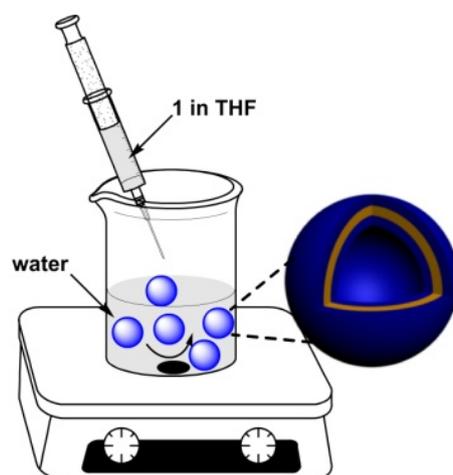


Fig. S2 Schematic representation for the preparation procedure of vesicles.

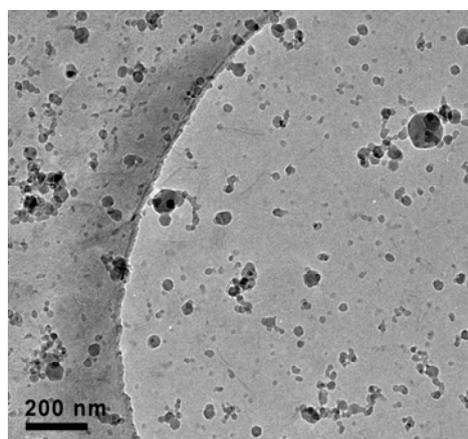


Fig. S3. The low magnification cryo-TEM image of the vesicles for amphiphile **1** obtained at concentration of 3.0×10^{-5} M in aqueous solution.

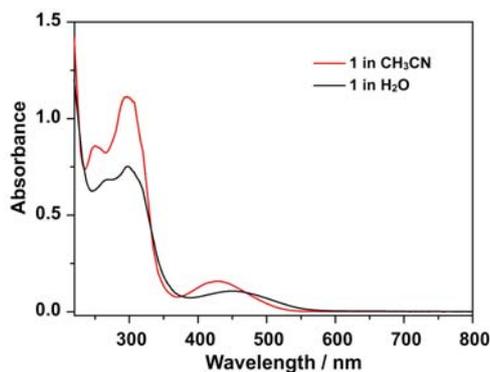


Fig. S4. UV-vis absorption spectra of **1** (2.7×10^{-5} M) in H_2O and CH_3CN at room temperature. The lower absorbance **1** in H_2O suggested the aggregates formation in aqueous solution.

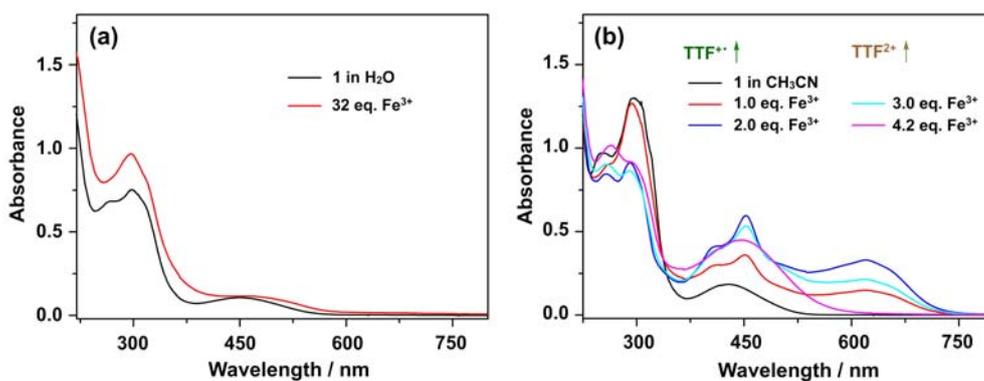


Fig. S5. Absorption spectral changes of **1** (2×10^{-5} M) in aqueous solution (a) and CH_3CN (b) with the different amount of $\text{Fe}(\text{ClO}_4)_3$. These results indicated that it is very difficult to oxidize the TTF unit of **1** in aqueous solution.

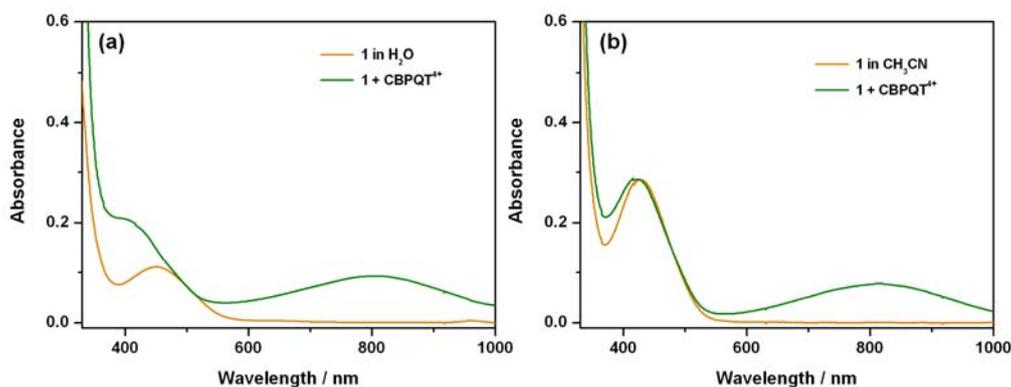


Fig. S6. Absorption spectra of **1** (2.5×10^{-5} M) in the absence and presence of CBPQT^{4+} (2.0 equiv) in H_2O (a) and CH_3CN (b).

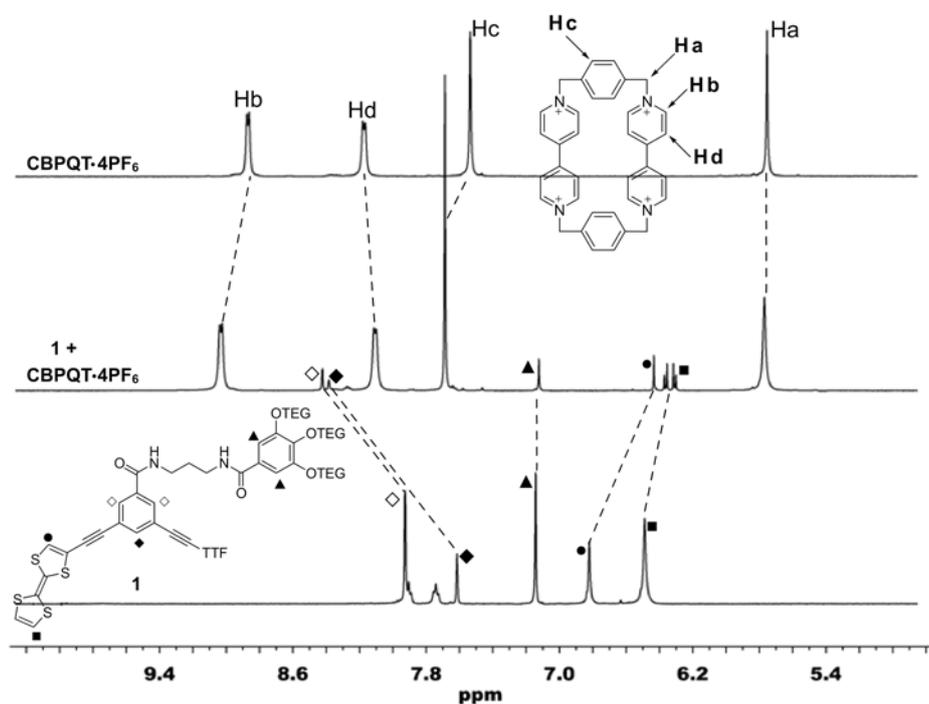


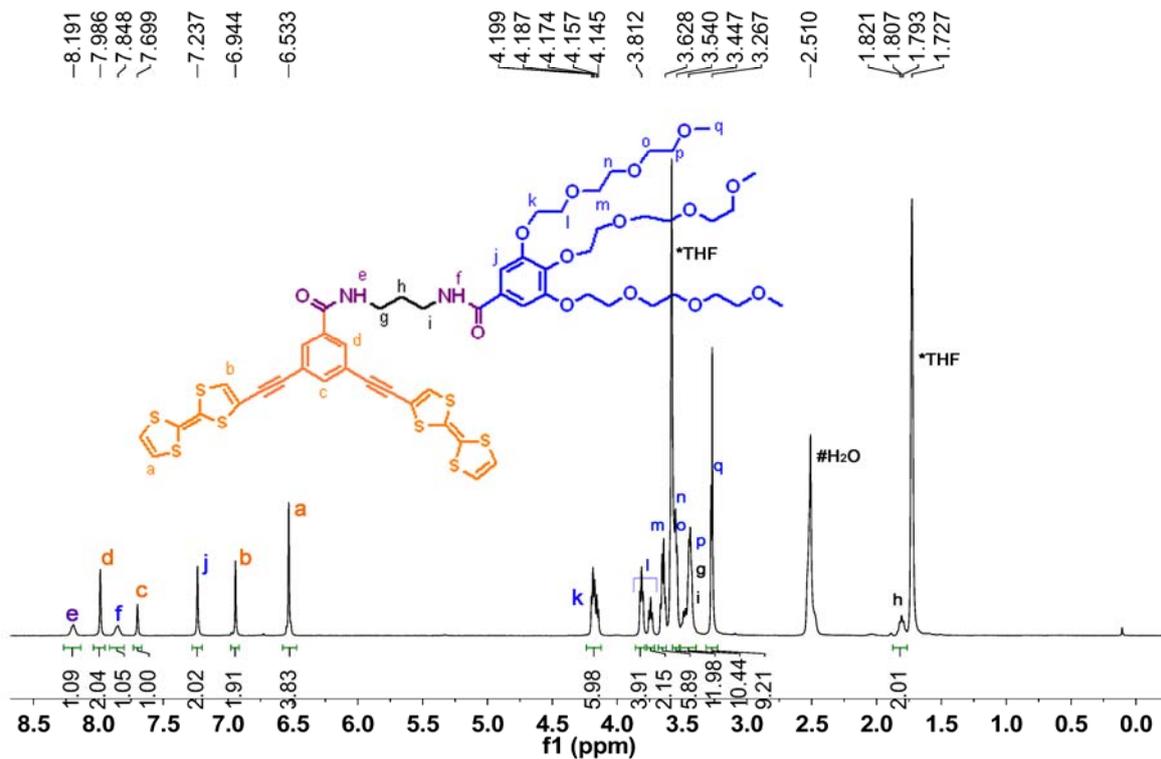
Fig. S7. Partial ^1H NMR spectra (400 MHz, CD_3CN , 298K) of **1** (1 mM, bottom), **1** + CBPQT^{4+} (middle), and CBPQT^{4+} (3 mM, top).

References:

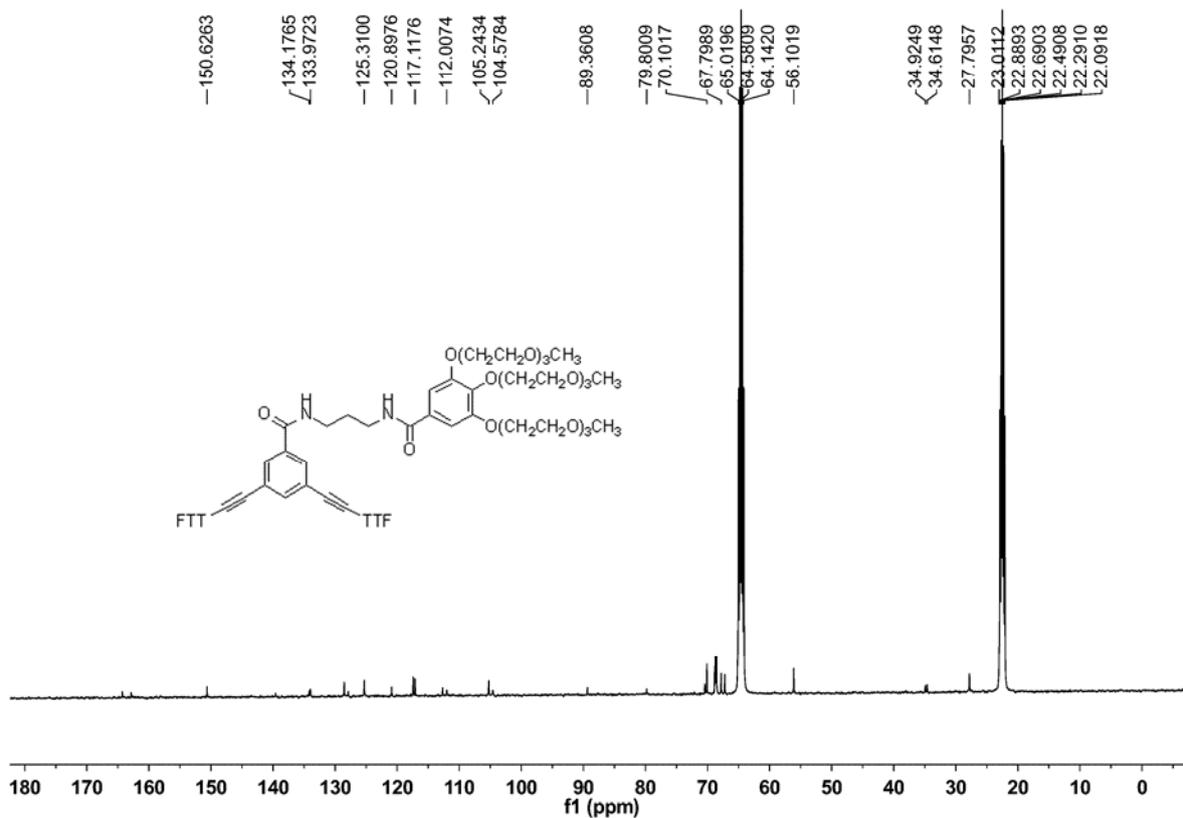
[S1] Green, D. C. *J. Org. Chem.* **1979**, *44*, 1476-1479.

[S2] Kurtan, T.; Nesnas, N.; Li, Y.-Q.; Huang, X.; Nakanishi, K.; Berova, N. *J. Am. Chem. Soc.* **2001**, *123*, 5962-5973.

[S3] Won, Y.-Y. *Korean J. Chem. Eng.* **2004**, *21*, 296-302.



¹H NMR of **1** in *d*₈-THF.



¹³C NMR of **1** in *d*₈-THF.

