

Supplementary Information

Microtubes and Hollow Microspheres Formed by Winding of Nanoribbons from Self-Assembly of Tetraphenylethylene Amide Macrocycle

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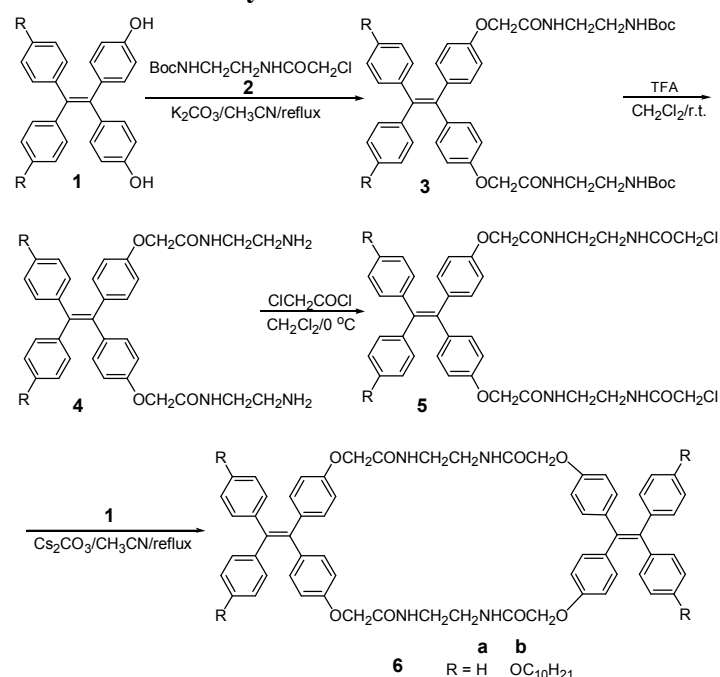
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Materials: Dichloromethane was dried with anhydrous calcium chloride overnight and distilled under a nitrogen atmosphere before used. Acetonitrile was dried with anhydrous potassium carbonate overnight and distilled under a nitrogen atmosphere. All other reagents were analytical grade and used as received without further purification unless specified. Deionized water was used in the experiments.

Measurements. ¹H NMR and ¹³C NMR spectra were measured on a Bruker AV400 spectrometer at 298 K in deuterated solvents. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer (KBr pellet). Mass spectrum was measured on an IonSpec 4.7 Tesla FTMS instrument. Field emission scanning electron microscopy (FE-SEM) images were acquired with a FEI Sirion 200 electron microscope operating at 5 kV or 10 kV. Transmission electron micrographs (TEM) were recorded on an electron microscope at 200 kV. Fluorescence emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. X-ray analysis of single-crystal was performed on a Bruker Smart Apex CCD diffractometer. Powder X-ray diffraction (XRD) pattern were measured on a χ 'Pert PRO diffraction instrument.

Synthesis of TPE amide macrocycle 6.



Synthesis of compound 3: To a solution of compound 1^[1] (1.0 mmol) in anhydrous acetonitrile (10 mL) was added potassium carbonate (3.0 mmol). The reaction mixture was stirred for 30 minutes at room temperature. A solution of compound 2^[2] (2.4 mmol) in dry acetonitrile (5 mL) was added and the mixture was refluxed for 20 h under a nitrogen atmosphere. After acetonitrile was removed under vacuum, CH₂Cl₂ (30 mL) was added and the mixture was washed twice with water. The solution was dried over anhydrous sodium sulfate and concentrated to afford a crude product, which was purified by flash column chromatography (silica gel, dichloromethane: methanol V/V 40/1) to afford 3.

Compound 3a: a white powder, yield: 82%; M.p.: 190.0 – 190.9 °C; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.17 (s, 1H), 7.12 – 7.06 (m, 6H), 7.01 – 7.09 (m, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 6.66 (d, *J* = 8.8 Hz, 4H), 4.96 (s, 2H), 4.40 (s, 4H), 3.46 – 3.41 (m, 4H), 3.29 – 3.27 (m, 4H), 1.42 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.8, 156.6, 155.7, 143.8, 140.4, 139.2, 137.5, 132.8, 131.3, 127.7, 126.4, 113.9, 79.7, 67.1, 40.2, 40.0, 28.4; IR (KBr): ν (cm⁻¹) 3362, 3324, 2977, 2930, 1695, 1604, 1518, 1443, 1251, 1171, 1059, 837, 699, 604.

Compound 3b: a white powder, yield: 78%; M.p.: 117.1 – 119.2 °C; ¹H NMR

(CDCl₃, 400 MHz): δ (ppm) 7.08 (s, 2H), 6.95 (d, J = 8.8 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.67 (d, J = 8.8 Hz, 4H), 6.62 (d, J = 8.8 Hz, 4H), 4.83 (s, 2H), 4.41 (s, 4H), 3.87 (t, J = 6.4 Hz, 4H), 3.47 – 3.42 (m, 4H), 3.29 (s, 4H), 1.75 – 1.70 (m, 4H), 1.43 – 1.40 (m, 22H), 1.30 – 1.27 (m, 24H), 0.88 (t, J = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.9, 157.6, 156.5, 155.4, 139.8, 138.2, 137.3, 136.2, 132.7, 132.4, 113.9, 113.6, 79.7, 67.9, 67.2, 40.3, 39.9, 31.9, 29.53, 29.52, 29.4, 29.3, 28.4, 26.1, 22.6, 14.1; IR (KBr): ν (cm⁻¹) 3419, 3332, 3070, 2925, 2855, 1690, 1665, 1606, 1537, 1512, 1450, 1365, 1244, 1178, 1060, 832, 572.

Synthesis of compound 4: To a solution of compound **3** (0.4 mmol) in anhydrous acetonitrile (10 mL) at 0 °C was added trifluoroacetic acid (1 mL, 13.9 mmol) dropwise. After the addition was finished, the reaction mixture was continued to stir for 3 h under a nitrogen atmosphere at room temperature. The reaction mixture was adjusted with sodium hydroxide aqueous solution to pH > 12. Then it was washed with water and brine in order before dried over anhydrous sodium sulfate. Upon filtered, the filtrate was evaporated to dryness to give pure product.

Compound 4a: a white powder, yield: 91%; M.p.: 93.1 – 95.0 °C; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.12 – 7.09 (m 6H), 7.02 – 6.94 (m, 10H), 6.67 (d, J = 8.8 Hz, 4H), 4.43 (s, 4H), 3.40 – 3.36 (m, 4H), 2.85 (t, J = 6.0 Hz, 4H), 1.34 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.4, 155.7, 143.8, 140.4, 139.2, 137.6, 132.8, 131.3, 127.8, 126.4, 113.9, 67.2, 41.7, 41.3; IR (KBr): ν (cm⁻¹) 3333, 3050, 2928, 2871, 1665, 1598, 1506, 1441, 1239, 1177, 1058, 835, 835, 700.

Compound 4b: a white powder, yield: 93%; M.p.: 80.1 – 81.9 °C; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 6.96 (t, J = 6.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.66 (d, J = 8.8 Hz, 4H), 6.62 (d, J = 8.8 Hz, 4H), 4.44 (s, 4H), 3.87 (t, J = 6.4 Hz, 4H), 3.41 – 3.36 (m, 4H), 2.85 (t, J = 6.4 Hz, 4H), 1.77 – 1.70 (m, 8H), 1.42 – 1.27 (m, 28H), 0.88 (t, J = 7.2 Hz, 10H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 168.6, 157.6, 155.4, 139.7, 138.3, 137.2, 136.2, 132.8, 132.5, 113.9, 113.6, 67.8, 67.2, 41.6, 41.3, 31.9, 29.57, 29.55, 29.4, 29.34, 29.32, 26.1, 22.7, 14.1; IR (KBr): (cm⁻¹) 3341, 3039, 2925, 2854, 1663, 1605, 1510, 1471, 1439, 1385, 1349, 1290, 1242, 1176, 1057, 830, 604.

Synthesis of compound 5: To a solution of compound **4** (0.2 mmol) and triethylamine (0.4 mL, 2.9 mmol) in 50 mL dichloromethane at 0 °C was added a solution of . chloroacetyl chloride (0.1 mL, 2.4 mmol) in 5 mL dry dichloromethane dropwise. After the addition was finished, the reaction mixture was continued to stir for 2 hours atmosphere at room temperature. Then it was washed twice with water, dried over anhydrous sodium sulfate and concentrated to dryness. Upon filtering, the filtrate was evaporated to dryness. The residue was re-crystallized with dichloromethane and methanol to give pure product.

Compound 5a: a white powder, yield 80%; M.p.: 218.8 – 221.0 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 8.26 (t, *J* = 5.2 Hz, 2H), 8.10 (t, *J* = 5.2 Hz, 2H), 7.16 – 7.09 (m, 6H), 6.96 (d, *J* = 6.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.74 (d, *J* = 6.8 Hz, 4H), 4.38 (s, 4H), 4.03 (s, 4H), 3.22 – 3.17 (m, 8H); ¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) 168.3, 166.7, 156.6, 144.1, 140.0, 139.7, 136.8, 132.4, 131.1, 128.3, 126.7, 114.5, 67.2, 43.1, 39.2, 38.4; IR (KBr): ν (cm⁻¹) 3329, 3079, 2950, 1660, 1543, 1442, 1228, 1056, 836, 699.

Compound 5b: a white powder, yield 83%; M.p.: 172.1 – 174.0 °C; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.19 (s, 2H), 7.08 (t, *J* = 5.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.66 (d, *J* = 8.8 Hz, 4H), 6.62 (d, *J* = 8.8 Hz, 4H), 4.43 (s, 4H), 4.02 (s, 4H), 3.87 (t, *J* = 6.4 Hz, 4H), 3.54 – 3.48 (m, 8H), 1.77 – 1.70 (m, 4H), 1.42 – 1.27 (m, 28H), 0.88 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 169.5, 167.0, 157.6, 155.3, 139.9, 138.4, 137.1, 136.2, 132.8, 132.5, 113.9, 113.6, 67.9, 67.1, 42.5, 40.4, 39.0, 31.9, 19.6, 29.5, 29.4, 29.34, 29.31, 26.1, 22.7, 14.1; IR (KBr): ν (cm⁻¹) 3322, 3041, 2924, 2854, 1652, 1555, 1512, 1443, 1409, 1387, 1290, 1244, 1176, 1053, 831, 574.

Synthesis of macrocyclic compound 6: A mixture of **1** (0.2 mmol) and cesium carbonate (0.40 mmol) in anhydrous acetonitrile (20 mL) was stirred for 0.5 h at room temperature under nitrogen atmosphere before **5** was added. After the reaction mixture was refluxed for 24 h under nitrogen atmosphere, the acetonitrile was removed under vacuum and CH₂Cl₂ was added. The resultant mixture was washed

twice with water, dried over anhydrous sodium sulfate, and concentrated to dryness. The residue was purified by flash column chromatography (silica gel, 40:1dichloromethane/methanol V/V) to give **6**.

Compound 6a: a white powder, yield 34%; M.p.: 313.0 – 314.8 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 7.98 (s, 4H), 7.14 – 7.08 (m, 12H), 6.93 (d, *J* = 6.4 Hz, 8H), 6.79 (d, *J* = 8.8 Hz, 8H), 6.66 (d, *J* = 8.8 Hz, 8H), 4.32 (s, 8H), 3.22 (s, 8H); IR (KBr): ν (cm⁻¹) 3345, 3053, 2925, 2853, 1663, 1604, 1541, 1508, 1443, 1242, 1219, 1055, 835, 700; ESI⁺ HRMS *m/z* calcd for C₆₄H₅₆O₈N₄Na 1031.3996 [M+Na], found 1031.4014 [M+Na].

Compound 6b: a white powder, yield: 32%; M.p.: 218.1 – 220.0 °C; IR (KBr): ν (cm⁻¹) 3427, 3343, 3036, 2927, 2855, 1676, 1605, 1510, 1467, 1442, 1385, 1358, 1289, 1243, 1175, 1111, 1056, 832, 598; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 6.93 (s, 4H), 6.88 (d, *J* = 4.8 Hz, 8H), 6.86 (d, *J* = 4.8 Hz, 8H), 6.61 (d, *J* = 4.8 Hz, 8H), 6.59 (d, *J* = 4.8 Hz, 8H), 4.36 (s, 8H), 3.86 (t, *J* = 6.4 Hz, 8H), 3.53 (s, 8H), 1.77 – 1.70 (m, 8H), 1.42 – 1.27 (m, 56H), 0.88 (t, *J* = 7.2 Hz, 12H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 169.2, 157.7, 155.3, 139.8, 138.4, 137.0, 136.1, 132.7, 132.5, 113.9, 113.6, 67.9, 37.1, 39.0, 31.9, 29.58, 29.57, 29.4, 29.35, 29.32, 26.1, 22.7, 14.1; APCI⁺ HRMS *m/z* calcd for C₁₀₄H₁₃₇O₁₂N₄ 1635.0267 [M+H], found 1635.0269 [M+H].

[1] X.-F. Duan, J. Zeng, J.-W. Lü, Z.-B. Zhang, *J. Org. Chem.* **2006**, *71*, 9873-9876.

[2] A.-M. Fanning, S. E. Plush, T. Gunnlaugsson, *Chem. Commun.* **2006**, *42*, 3791-3793.

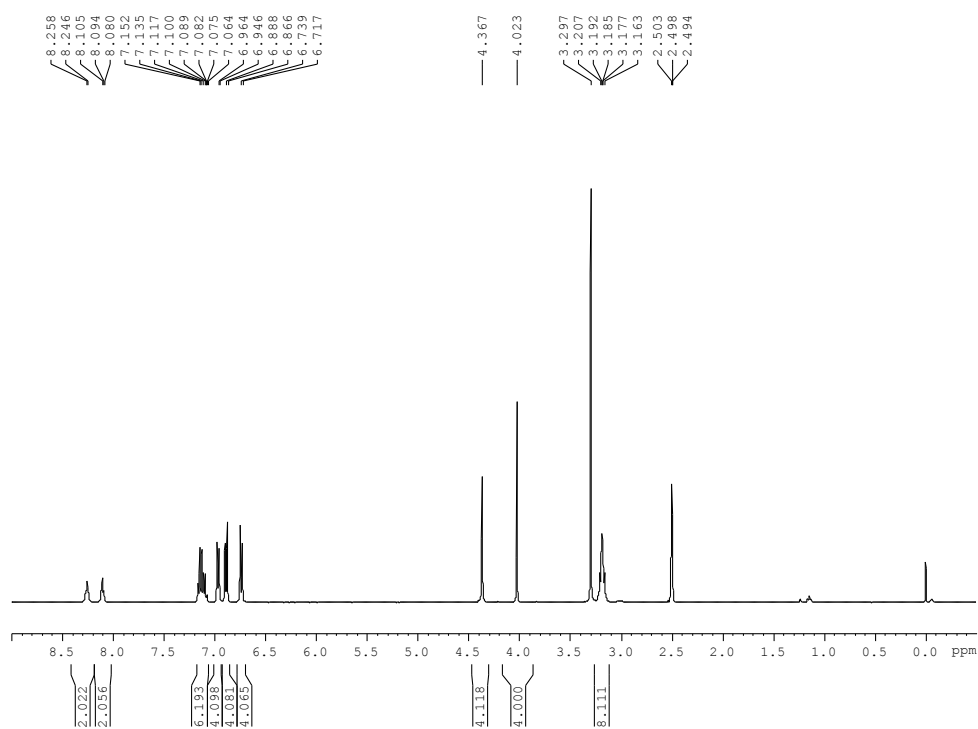


Fig. S1. ¹H NMR spectrum of **5a** in DMSO-d₆.

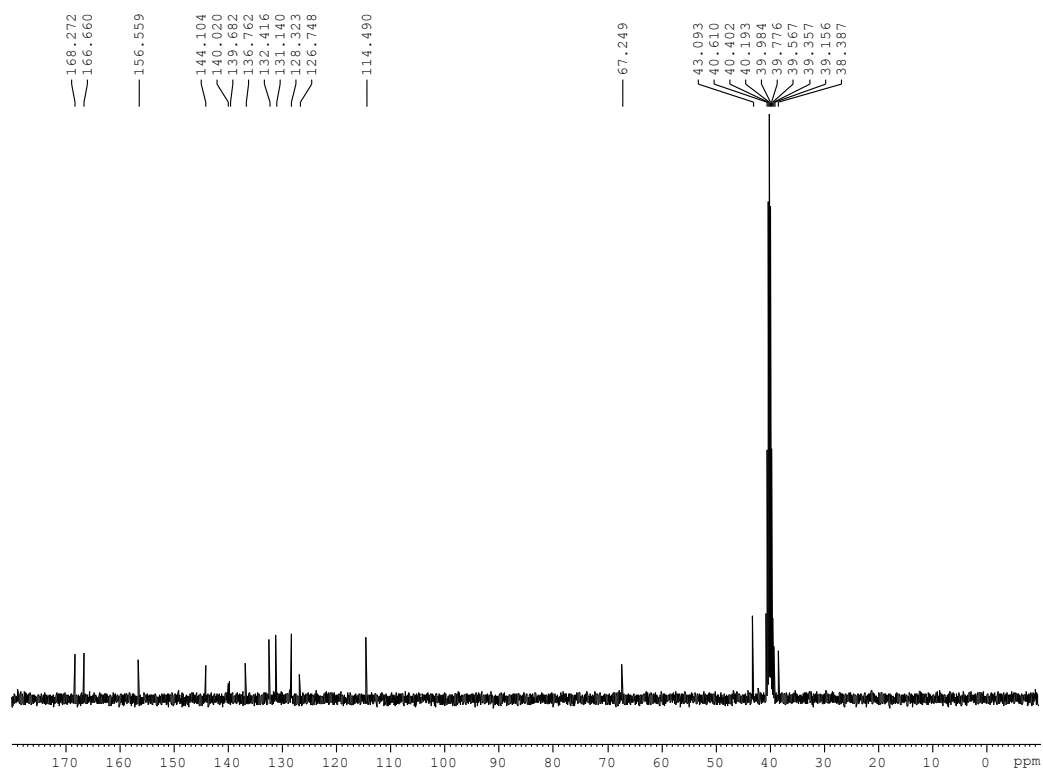


Fig. S2. ¹³C NMR spectrum of **5a** in DMSO-d₆.

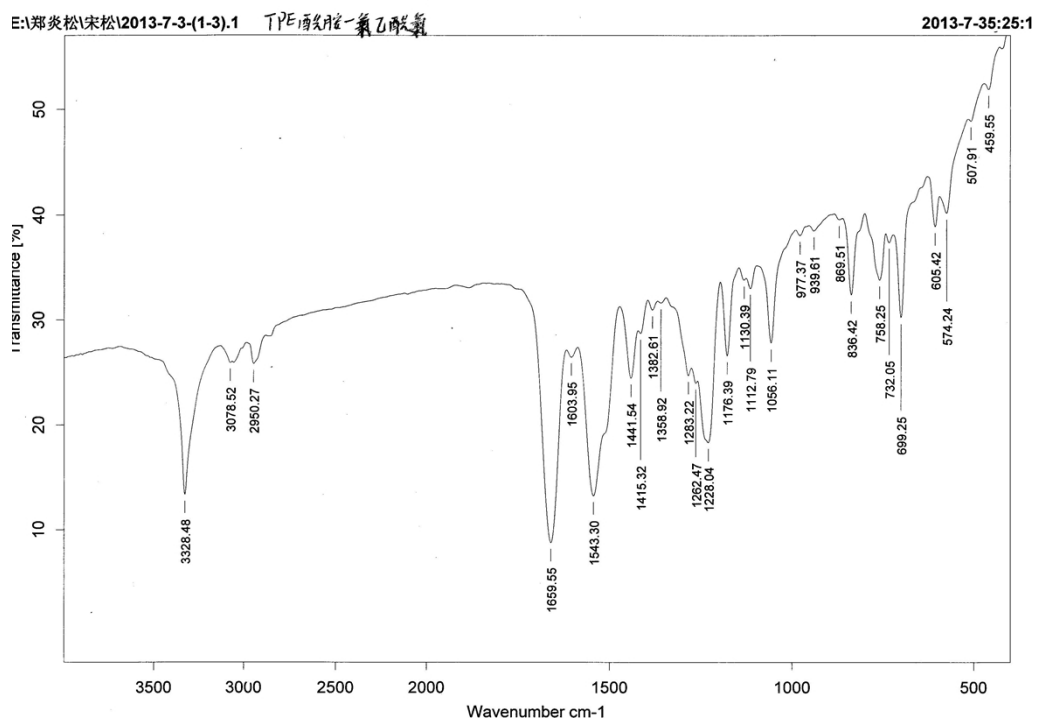


Fig. S3. IR spectrum of **5a**.

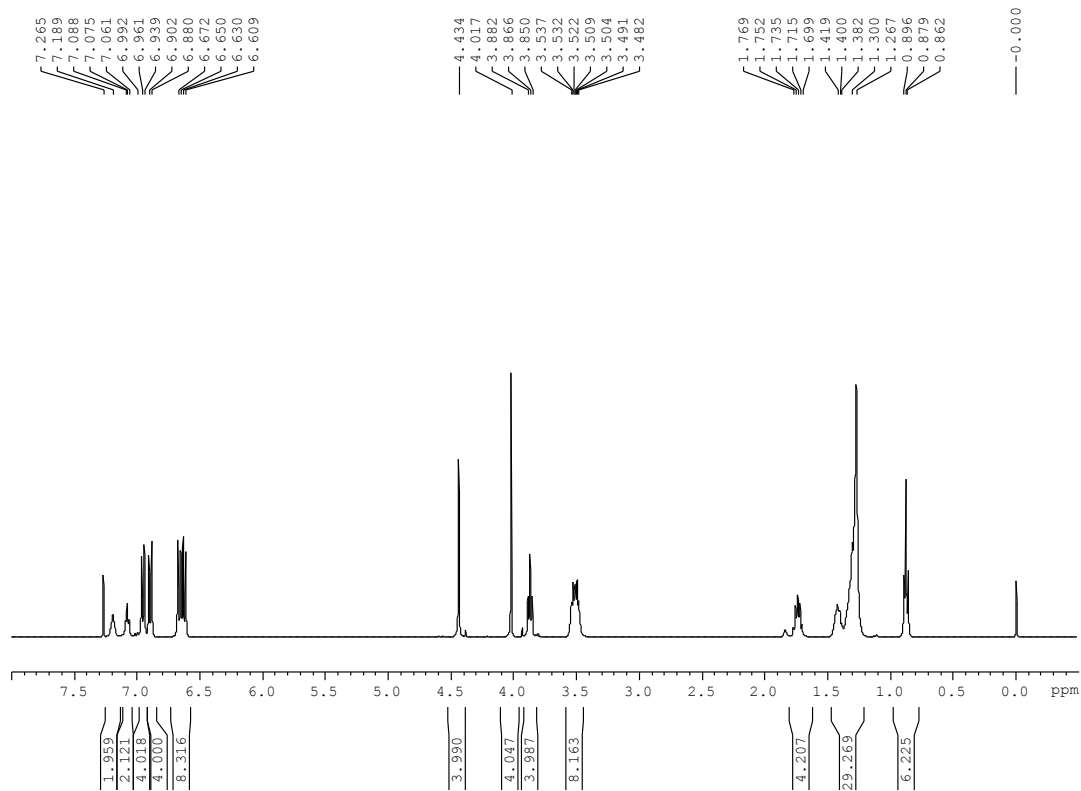


Fig. S4. ¹H NMR spectrum of **5b** in CDCl₃.

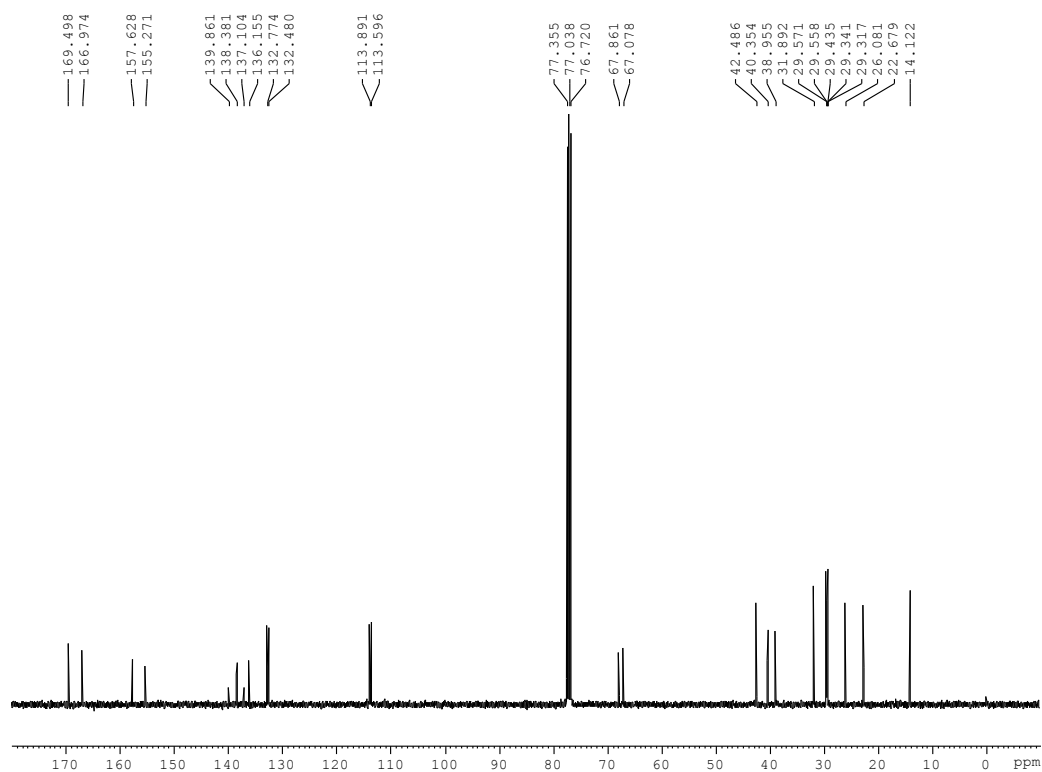


Fig. S5. ^{13}C NMR spectrum of **5b** in CDCl_3 .

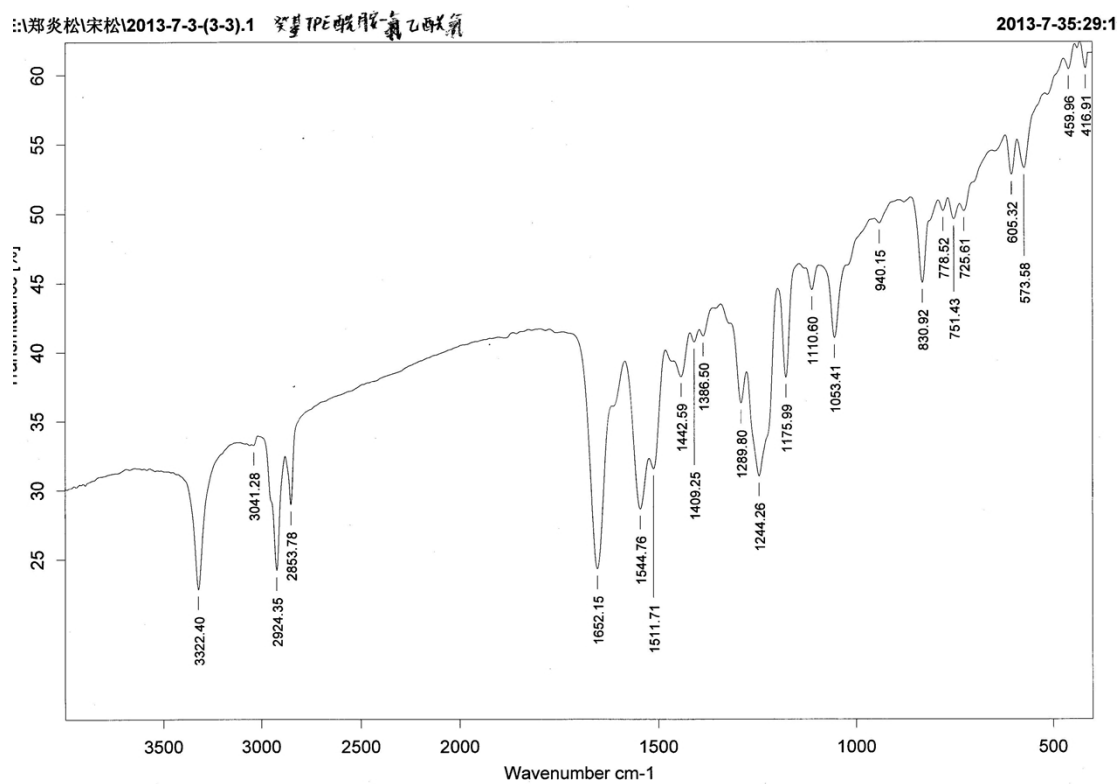


Fig. S6. IR spectrum of **5b**.

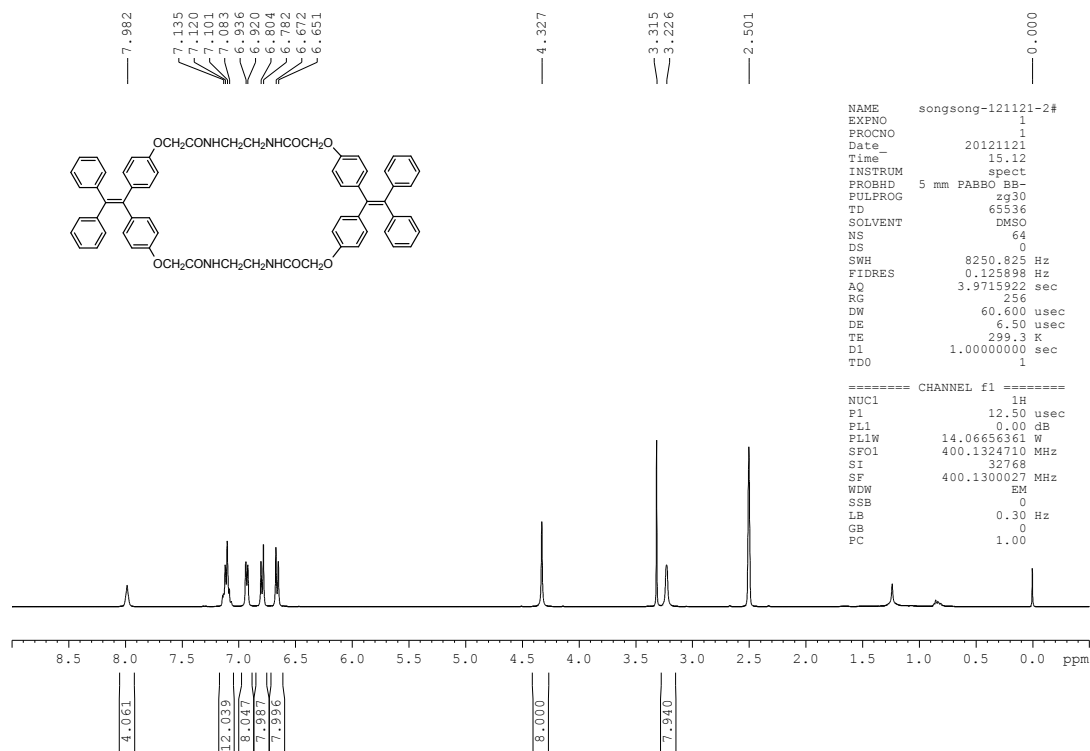


Fig. S7. ¹H NMR spectrum of **6a** in DMSO-d₆.

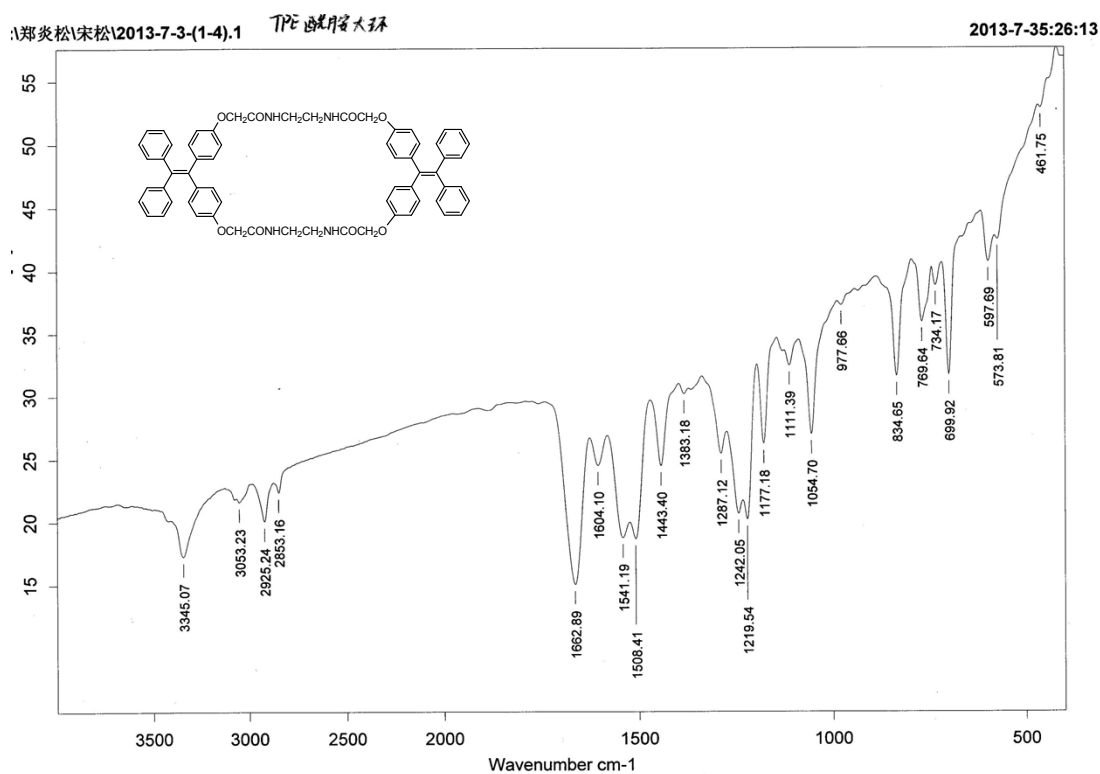


Fig. S8. IR spectrum of **6a**.

Mass Spectrum List Report

Analysis Info

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Acquisition Date 3/14/2014 4:47:04 PM

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10401

Acquisition Parameter

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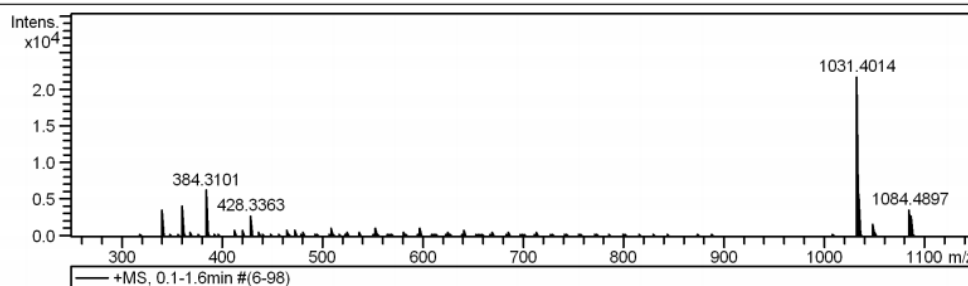


Fig. S9. HRMS spectrum of **6a**.

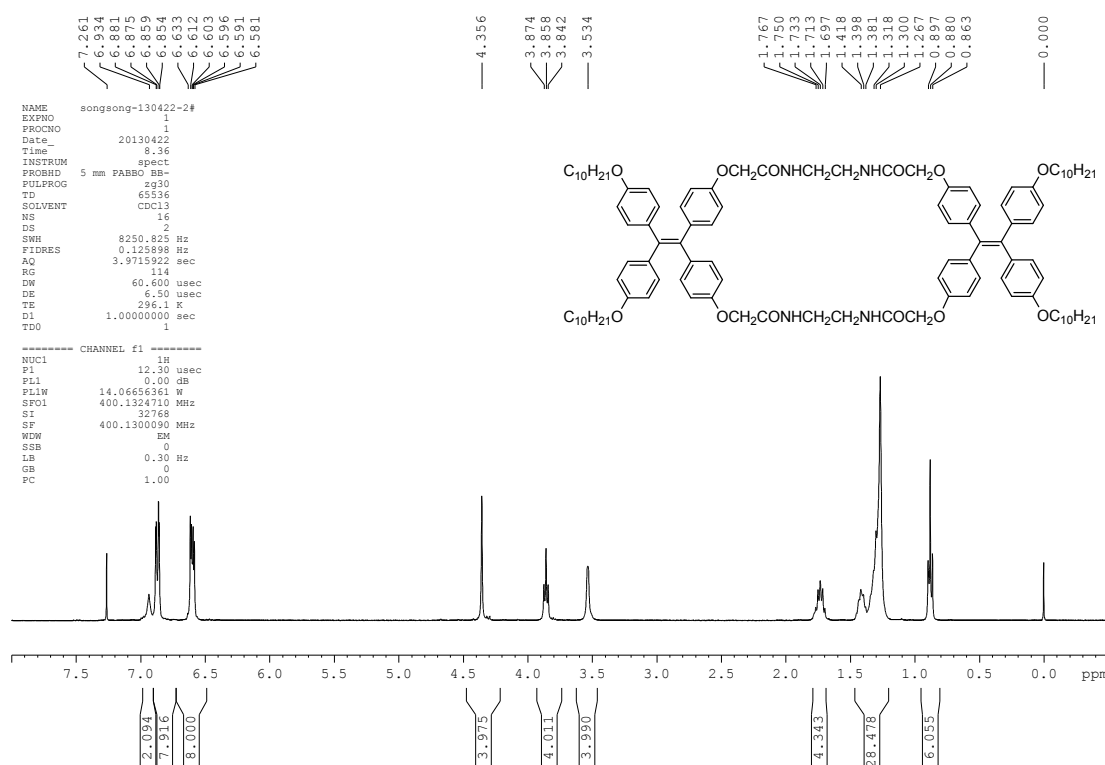


Fig. S10. ¹H NMR spectrum of **6b** in CDCl₃.

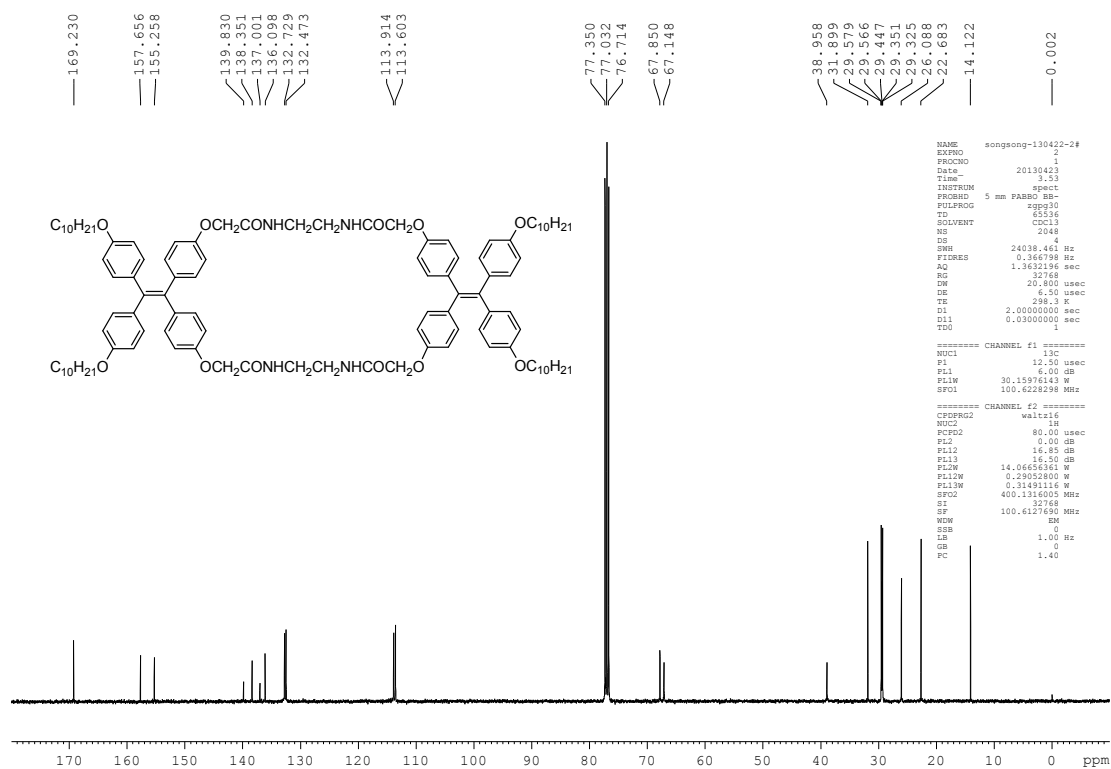


Fig. S11. ¹³C NMR spectrum of **6b** in CDCl₃.

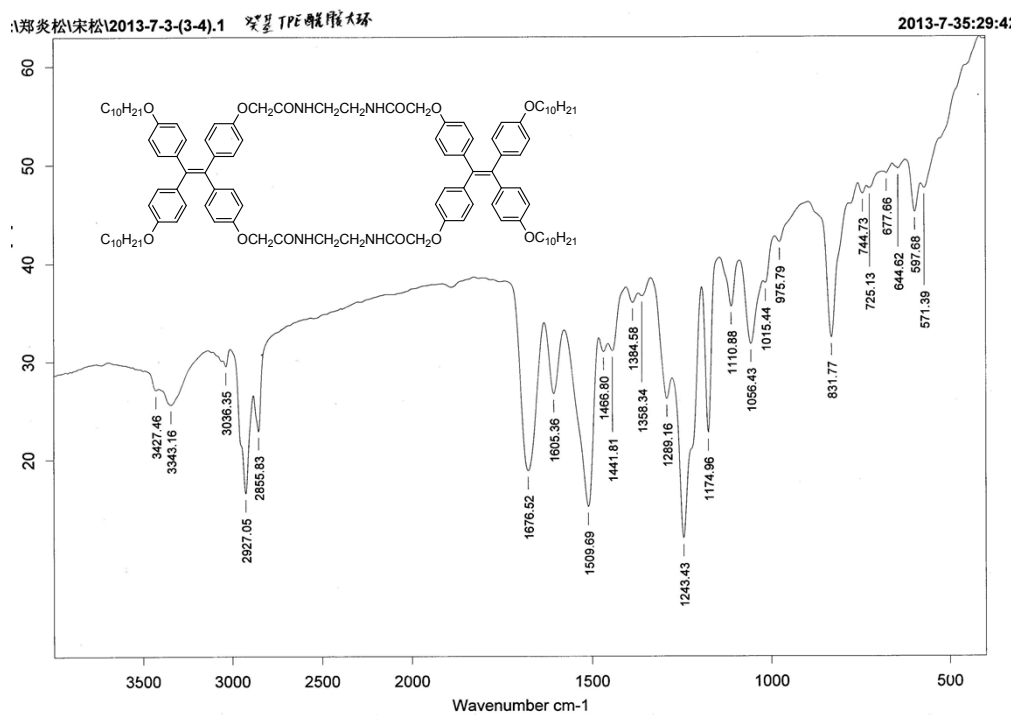


Fig. S12. IR spectrum of **6b**.

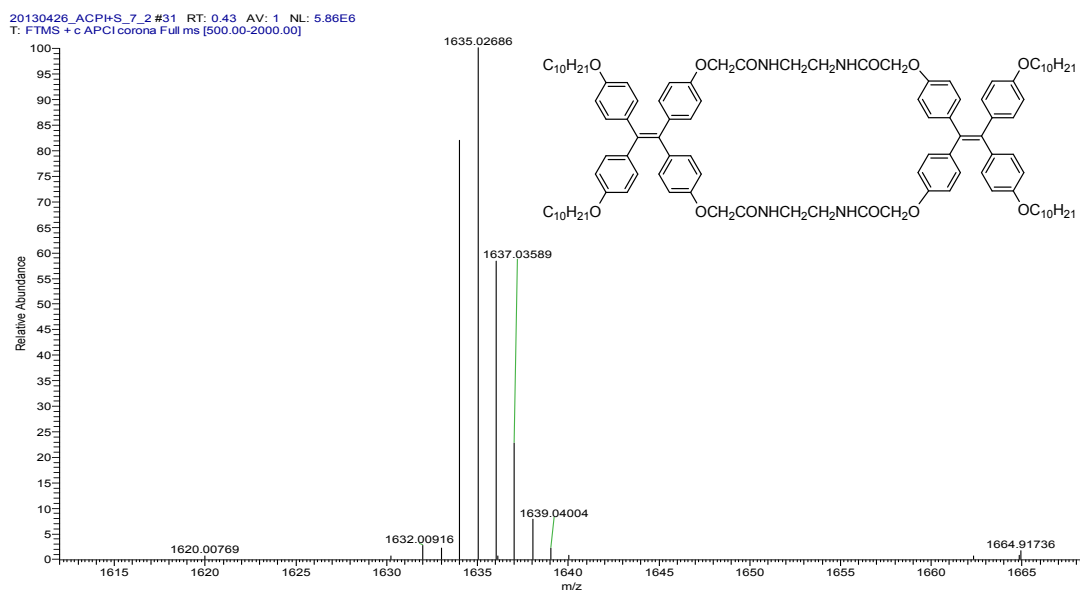


Fig. S13. HRMS spectrum of **6b**.

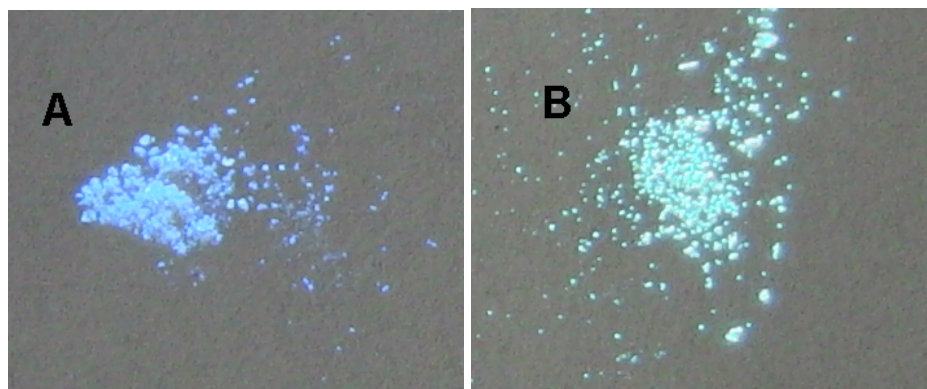


Fig. S14. Photos of dry powders of **6b** under 365 nm UV light obtained by centrifugation of suspensions in H₂O/THF with water of 70% (A) and 95% (B).

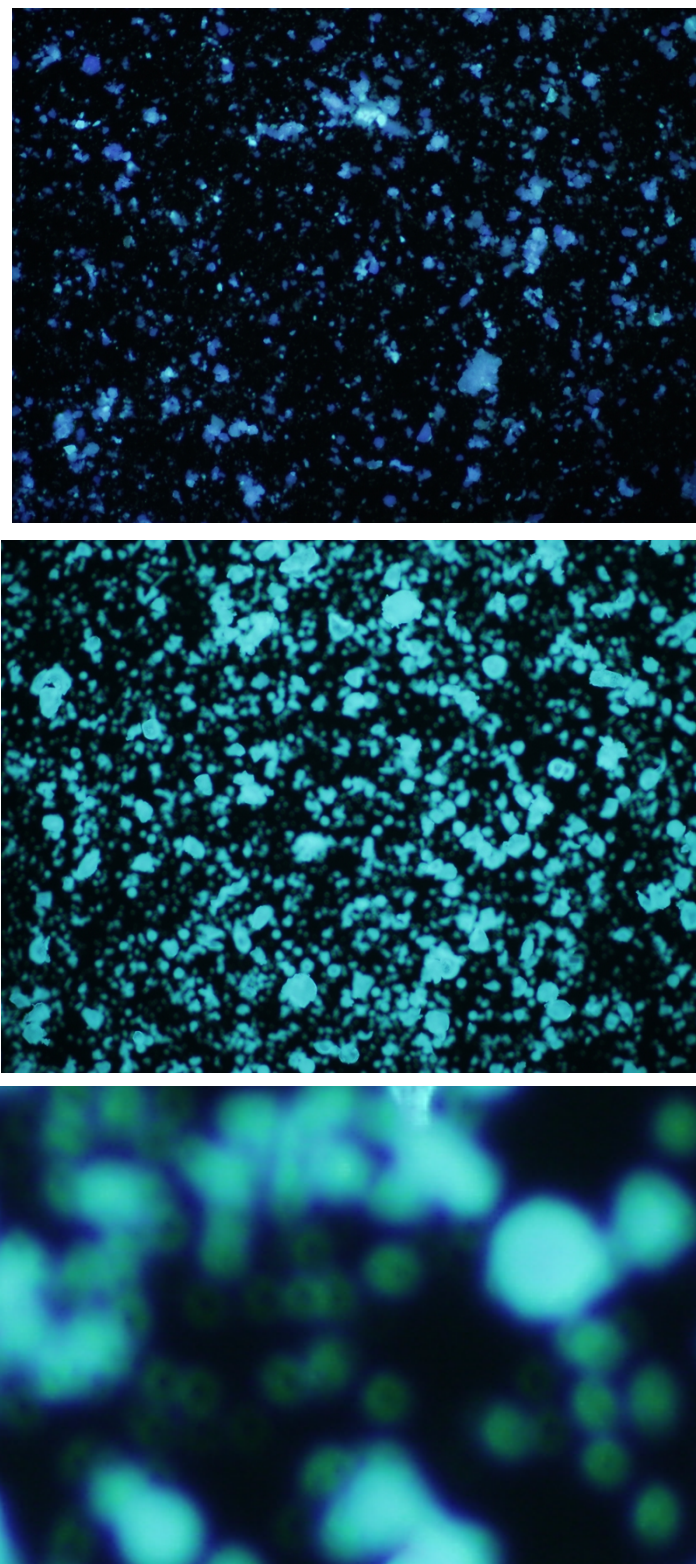


Fig. S15. Inverted fluorescence microscope images of dry powder of **6b** obtained by centrifugation of suspensions in H₂O/THF with water of 70% (top), 95% (middle) and partial magnification of the middle image (bottom, hollow microspheres could be made out).

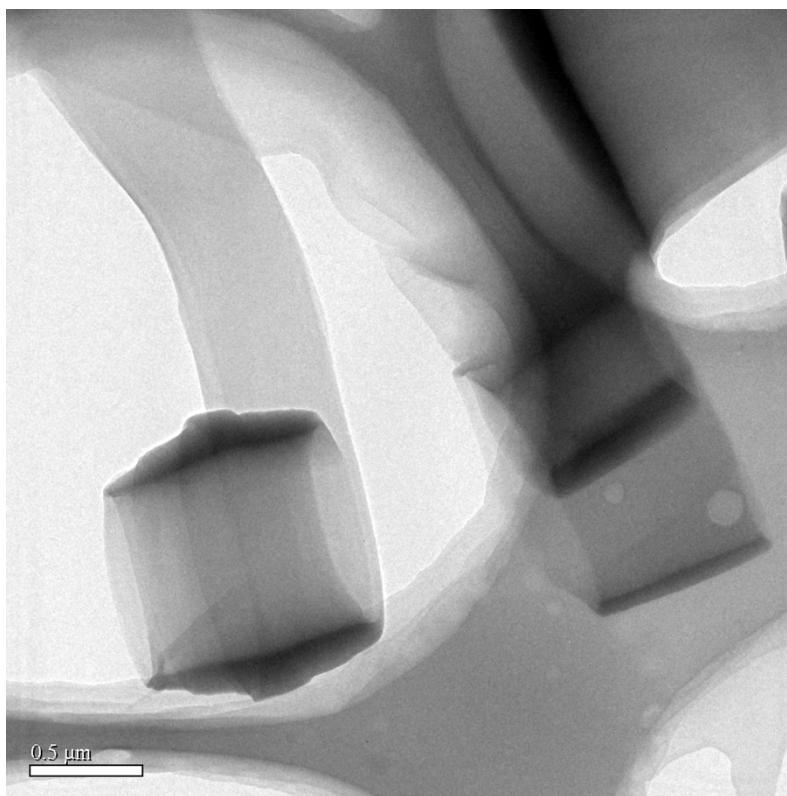


Fig. S16. TEM images of suspension of **6b** in H₂O/THF with 70% water. [**6b**]= 1.0×10^{-3} M.

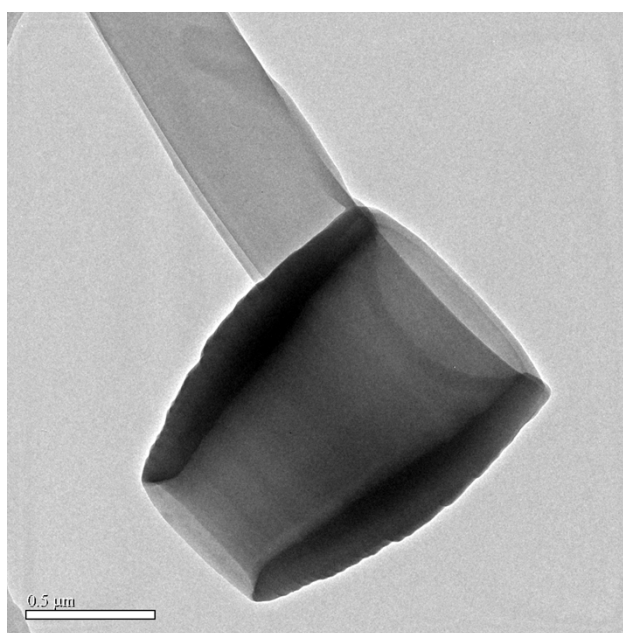


Fig. S17. TEM images of suspension of **6b** in H₂O/THF with 70% water. [**6b**]= 1.0×10^{-3} M.

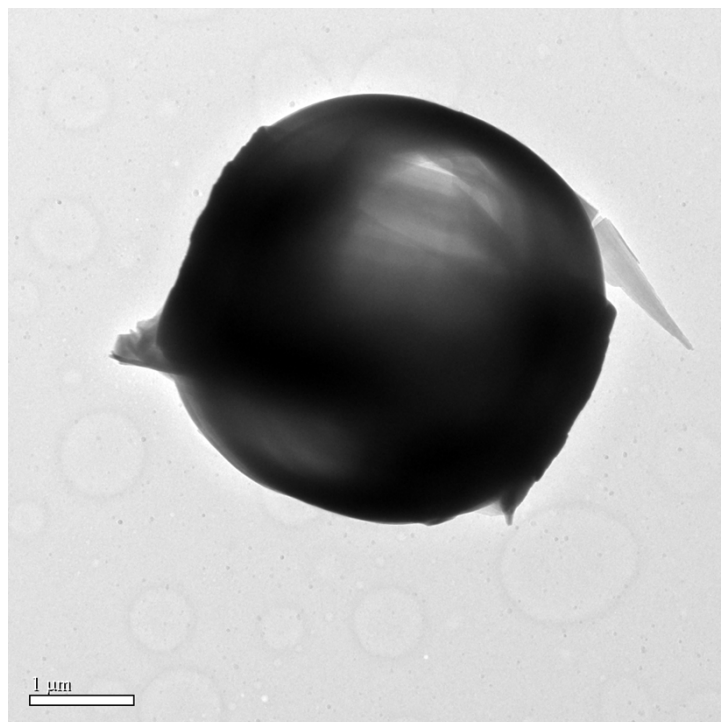


Fig. S18. TEM images of suspension of **6b** in H₂O/THF with 90% water. [**6b**]= 1.0×10^{-3} M.

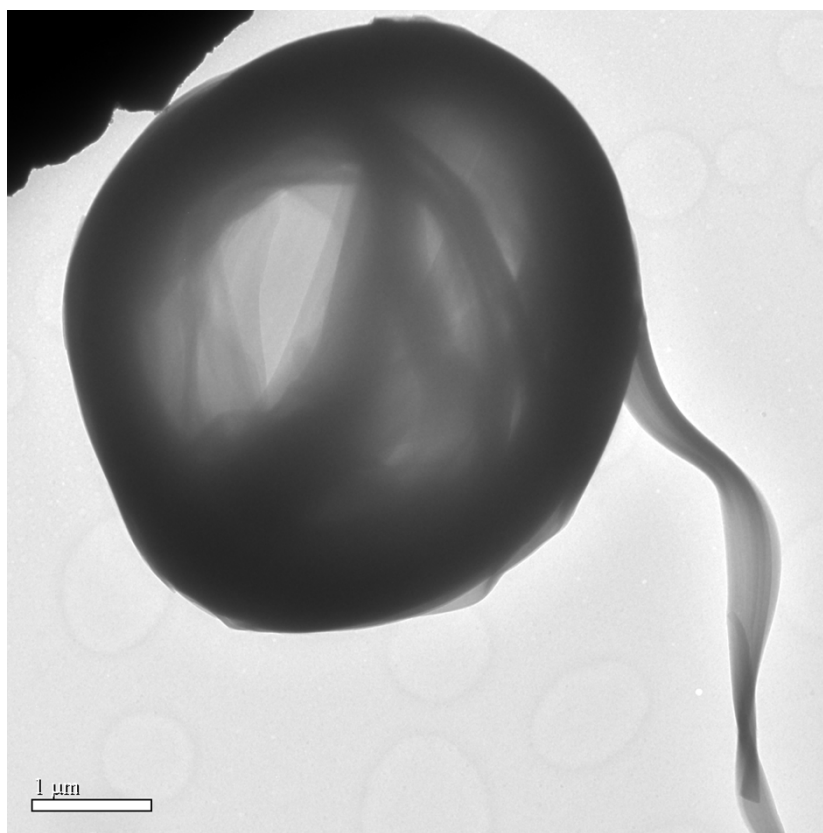


Fig. S19. TEM images of suspension of **6b** in H₂O/THF with 90% water. [**6b**]= 1.0×10^{-3} M.

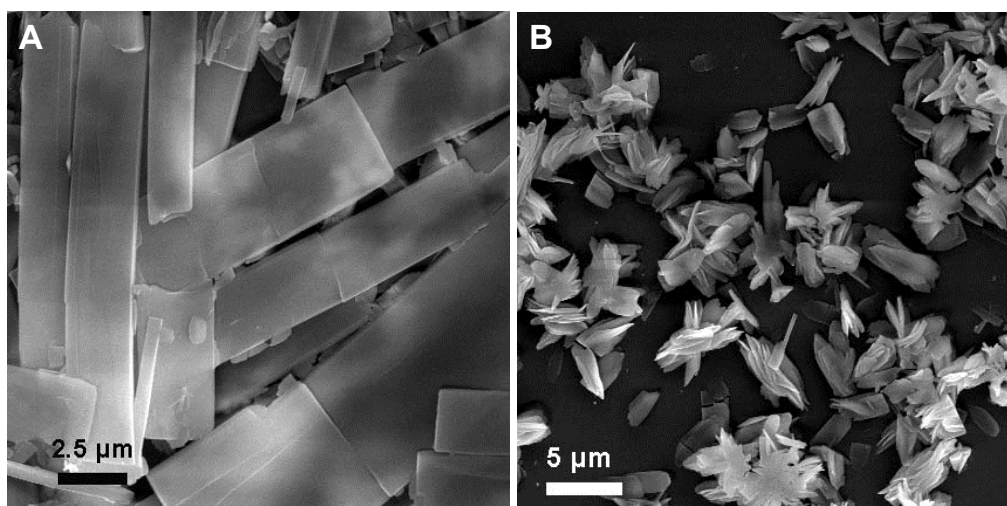


Fig. S20. FE-SEM images of suspension of **6a** in H₂O/DMF with water of 95%. [**6a**] = 1.0×10^{-3} M.

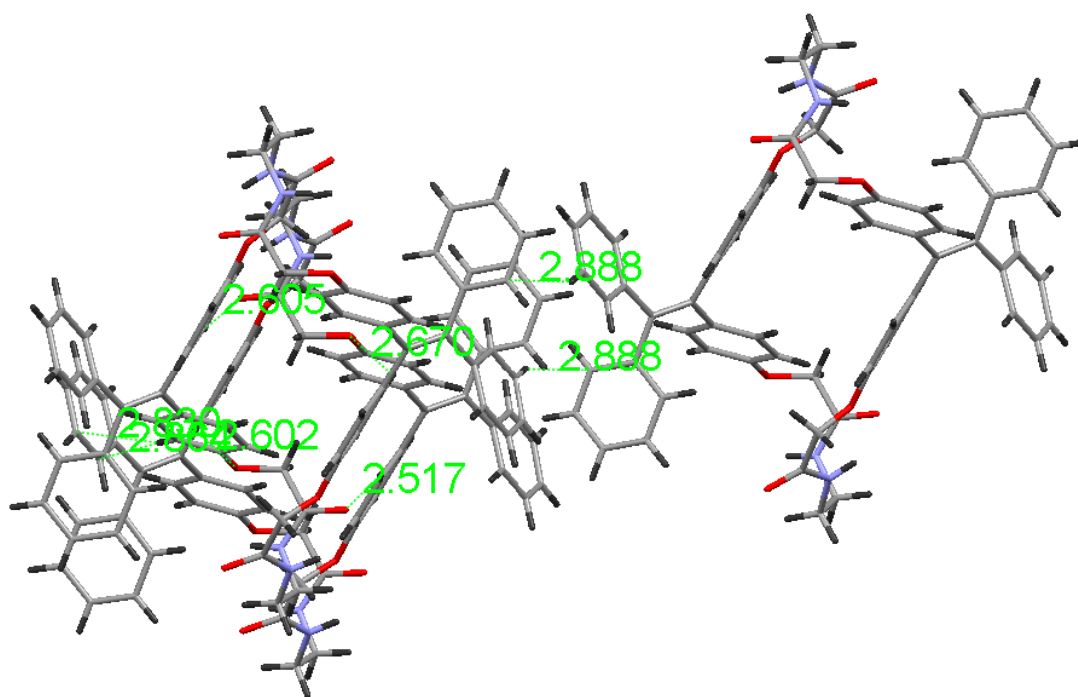


Fig. S21. Intermolecular interactions in crystal structure of **6a**. The solvent molecules are omitted for clarity.

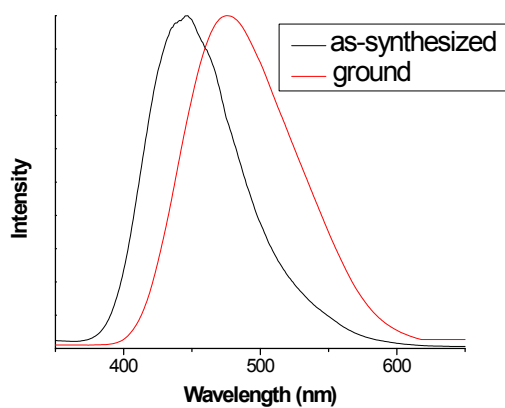


Fig. S22. Normalized fluorescence spectra of as prepared and ground powders of macrocycle **6a**.

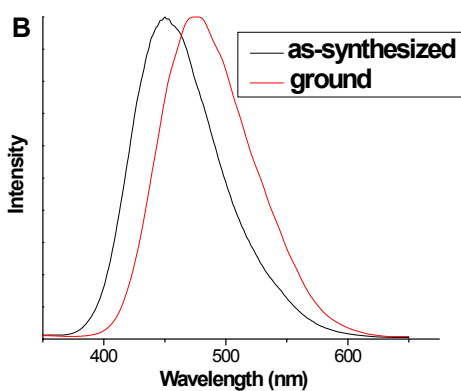


Fig. S23. Normalized fluorescence spectra of as prepared and ground powders of macrocycle **6b**.

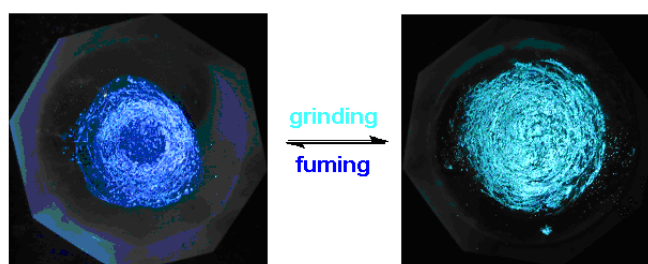


Fig. S24. Photos of powders of **6a** under a portable UV lamp after ground and fumed by chloroform alternately.