Supplementary Information

Supramolecular Hydrogel Based on Amphiphilic Calix[4]arene and Its Application in the Synthesis of Silica Nanotubes

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Materials and general methods

Materials. Dichloromethane was dried with calcium chloride overnight and distilled under a nitrogen atmosphere before use. All other reagents were analytical grade and used as received without further purification unless specified.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in deuterated solvents. Mass spectrum was measured on a Bruker BioApex FTMS instrument. Field emission scanning electron microscopy (FE-SEM) images were taken on 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. Dynamic light scattering (DLS) was measured on a Horiba LB-550 Particle Size Analyzer.

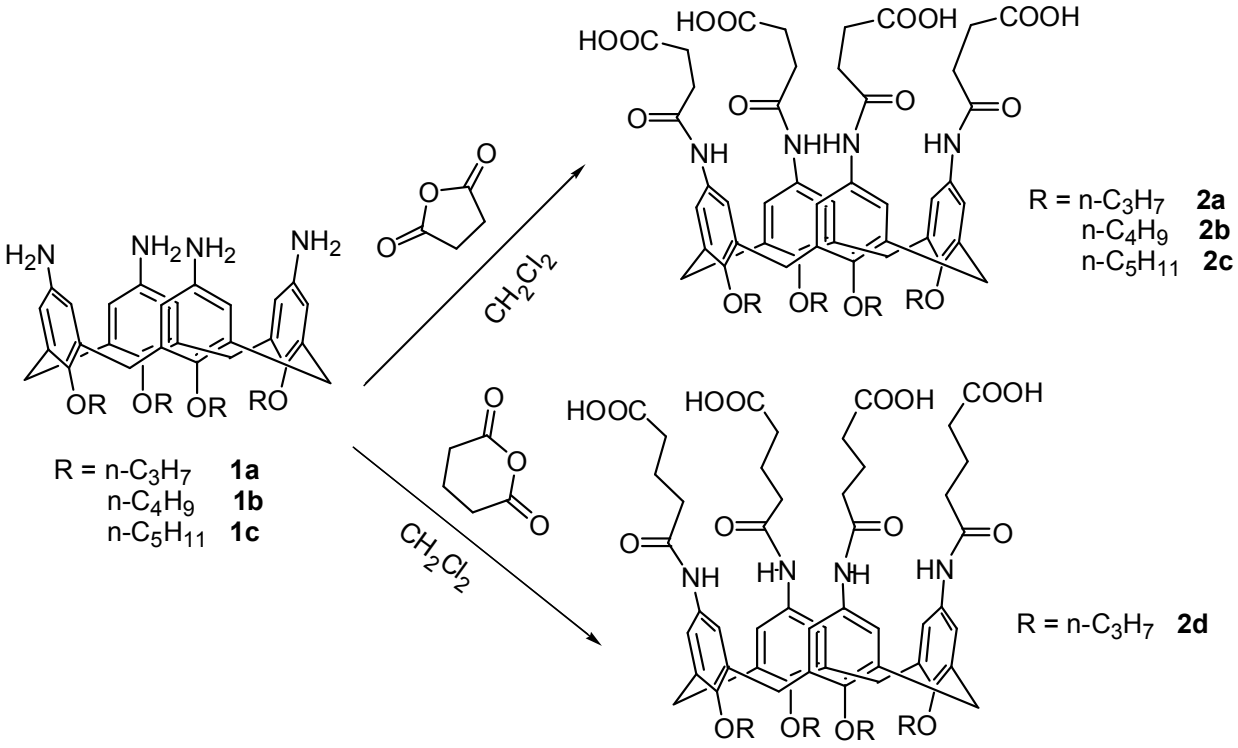
Preparation of gels. To a solution of one amphiphilic calix[4]arene in ethanol was added deionized water by a syringe. The resultant suspension was shaken gently for several minutes and then let it stand at room temperature till a gel formed.

Preparation of electron microscopy sample. The SEM sample was prepared by dropping the suspension or gel on the glass surface and dried at ambient condition. The SEM image was obtained after platinum sputtering treatment. The TEM sample was prepared by dropping the suspension on the surface of copper wire mesh substrate and then dried under room temperature before the TEM experiment.

Synthetic procedure of silica nanotubes. Under gently stirring at room temperature with magnetic stir at the rate about 60 r/min, 0.020 mL of solution of tetraethoxylsilane (0.134 mmol) and 3-

aminopropyltrimethoxysilane (0.05 mmol) in methanol (1.9 ml) was added into the hydrogel of 2a (2.5 mM, 2 mL) by a syringe. The reaction mixture was then allowed to stand for 12 h at room temperature. The precipitates were collected by centrifugation and washed with boiling triethylamine (2×10 mL), and then with boiling THF (3×10 mL) for 2 h, respectively, in order to remove the calixarene template. Finally, white silica powders were obtained.

Synthesis of the amphiphilic calix[4]arenes 2a – 2d



Scheme S1 The synthetic routes of the amphiphilic calix[4]arenes **2a** – **2d**.

Compound **1a** – **1c** [1] (0.46 mmol) was dissolved in dry dichoromethane (5 mL) into which a solution of corresponding anhydride (0.51 mmol) in dry dichoromethane (5 mL) was added dropwise. After the addition was finished, the reaction mixture was continued to stir for 2 hours at room temperature. As the reaction proceeded, a large amount of white precipitates appeared. Upon completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was re-crystallized with ethanol and water to give a white powder.

Compound 2a: yield: 93%; M.p.: 246.2 – 248.5 ^{o}C; IR (KBr): ν (cm^{-1}) 3312, 2962, 2928, 2875, 2658, 1722, 1658, 1604, 1548, 1217, 1005, 866; ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 6.88 (s, 8H), 4.47 (d, J = 13.2 Hz, 4H), 3.87 (t, J = 7.6 Hz, 8H), 3.12 (d, J = 13.2 Hz, 4H), 2.64 (t, J = 5.6 Hz, 8H), 2.57 (t, J = 5.6 Hz, 8H), 2.00 – 1.95 (m, 8H), 1.04 (t, J = 7.6 Hz, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm)

175.0, 170.9, 153.0, 134.7, 132.2, 120.5, 76.7, 30.7, 30.7, 28.6, 23.0, 9.4; ES^+ HRMS m/z calcd for $C_{56}H_{68}O_{16}N_4Na$ 1075.4528 [M+Na], found 1075.4506 [M+Na].

Compound 2b: yield: 90%; M.p.: 224.5 – 225.8 ^oC; IR (KBr): *v* (cm^{-1}) 3305，2959, 2870, 1723, 1658.5, 1603, 1548, 1470, 1417, 1213, 868; ^1H NMR (400MHz, DMSO-d_6): δ (ppm) 12.04(s, 4H), 9.56 (s, 4H), 6.92 (s, 8H), 4.33 (d, *J* = 12.8 Hz, 4H), 3.81 (t, *J* = 6.8 Hz, 8H), 3.06 (d, *J* = 12.8 Hz, 4H), 2.44 (m, 16H), 1.91 – 1.84 (m, 8H), 1.45 – 1.39 (m, 8H), 0.97 (t, *J* = 7.6 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.3, 169.7, 152.2, 134.5, 133.6, 119.8, 75.0, 32.2, 31.3, 31.2, 29.2, 19.4, 14.4; ES^+ HRMS m/z calcd for $C_{60}H_{76}O_{16}N_4Na$ 1131.5154 [M+Na], found 1131.5148 [M+Na].

Compound 2c: yield: 89%; M.p.: 256.9 – 228.7 ^oC; IR (KBr): ν (cm^{-1}) 3308, 2962, 2958, 2920, 2865, 1720, 1661, 1604, 1550, 1471, 1213, 867; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.54 (s, 4H), 6.91 (s, 8H), 4.33 (d, *J* = 12.8 Hz, 4H), 3.86 (t, *J* = 6.8 Hz, 8H), 3.06 (d, *J* = 12.8 Hz, 4H), 2.45 (m, 16H), 1.88 (m, 8H), 1.38 – 1.37 (m, 16H), 0.92 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.3, 169.7, 152.2, 134.5, 133.6, 119.8, 75.3, 31.3, 31.1, 29.8, 29.2, 28.4, 22.8, 14.4; ES^+ HRMS m/z calcd for $C_{64}H_{84}O_{16}N_4Na$ 1187.5780 [M+Na], found 1187.5812 [M+Na].

Compound 2d: yield: 90%; M.p.: 241.9 – 243.0 ^oC; IR (KBr): ν (cm^{-1}) 3321, 2963, 2875, 1714, 1654.8, 1603, 1548, 1470, 1417, 1218, 867; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 11.95 (s, 4H), 9.47 (s, 4H), 6.94 (s, 8H), 4.34 (d, *J* = 12.8 Hz, 4H), 3.77 (t, *J* = 6.8 Hz, 8H), 3.06 (d, *J* = 12.8 Hz, 4H), 2.24 – 2.20 (m, 16H), 1.92 – 1.87 (m, 8H), 1.75 – 1.72 (m, 8H), 0.96 (t, *J* = 7.6 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.6, 170.4, 152.3, 134.5, 132.6, 119.9, 76.9, 35.6, 33.5, 31.3, 23.1, 20.9, 10.6; ES^+ HRMS m/z calcd for $C_{60}H_{76}O_{16}N_4Na$ 1131.5154 [M+Na], found 1131.5167 [M+Na].

References

1. F. Sansone, E. Chierici, A. Casnati and R. Ungaro, *Org. Biomol. Chem.*, 2003, **1**, 1802; Z. Li, J. Ma, J. Chen, Y. Pan, J. Qiang and L. Wang, *Chin. J. Chem.*, 2009, **27**, 2031.

Supporting figures

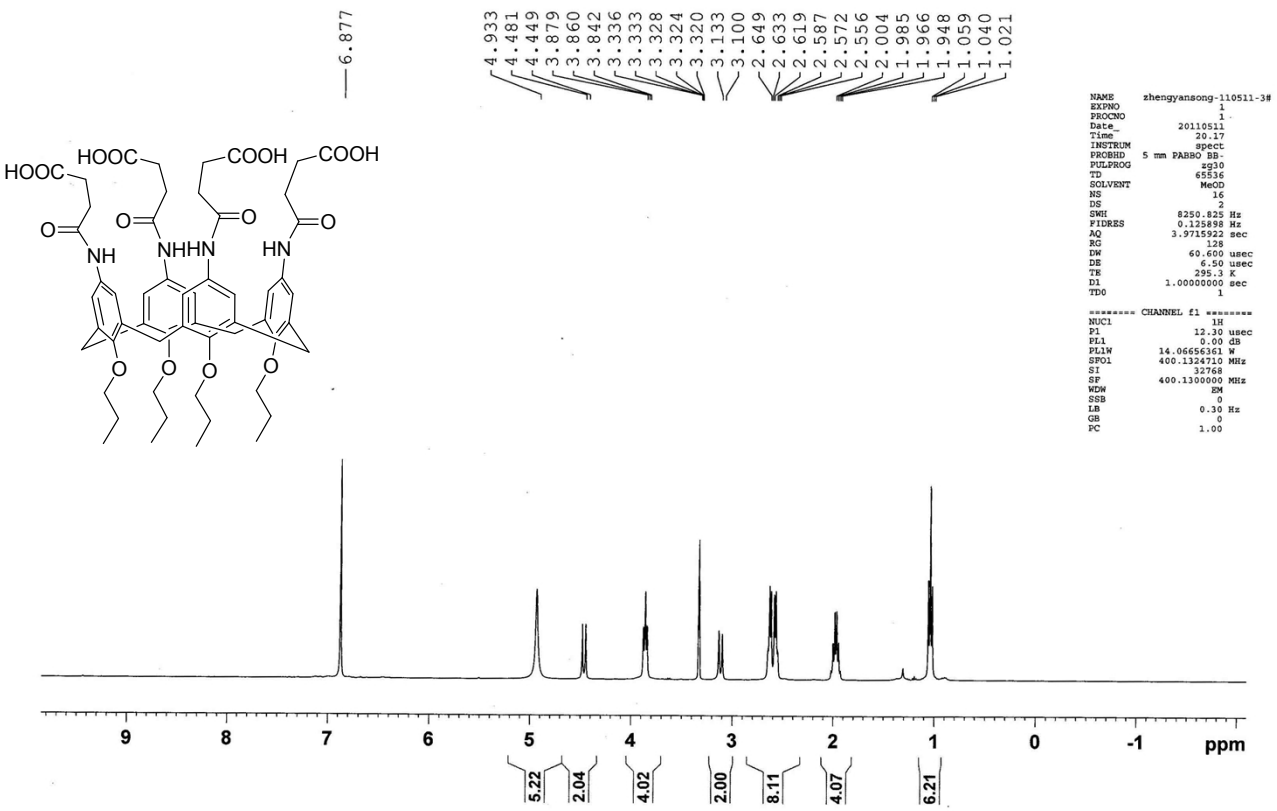


Figure S1. ^{1}H NMR spectrum of **2a** in CD_3OD.

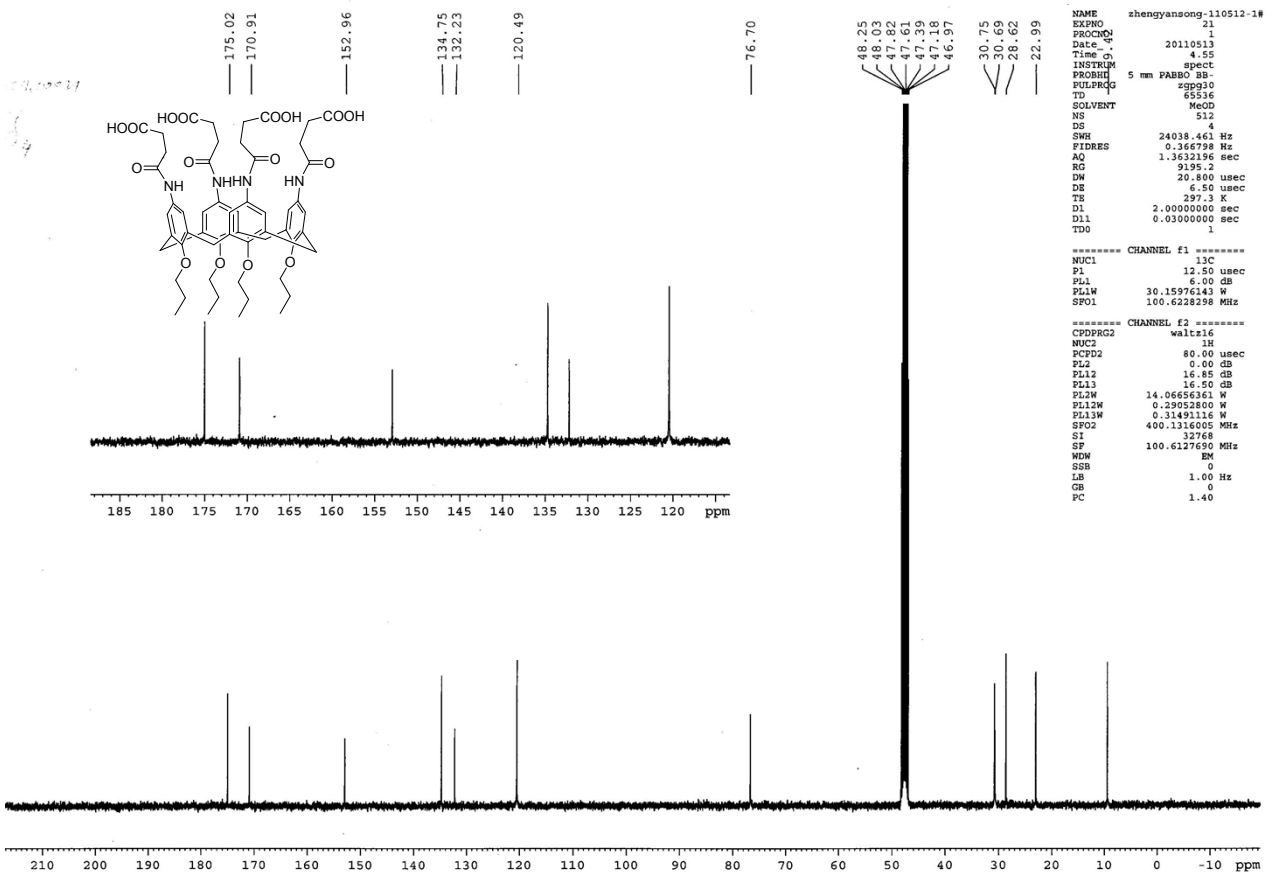


Figure S2. ^{13}C NMR spectrum of **2a** in CD_3OD.

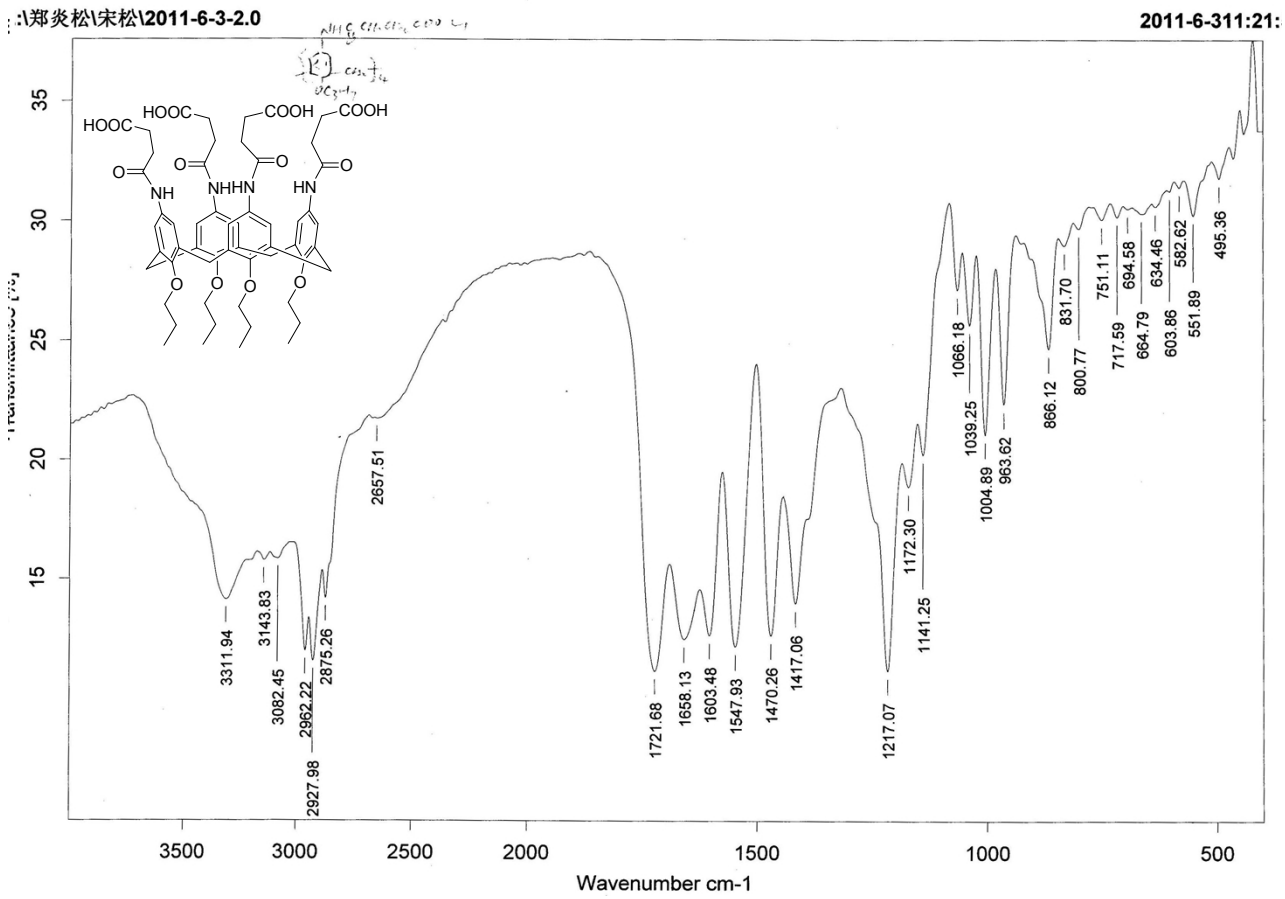


Figure S3. IR spectrum of **2a**.

Mass Spectrum List Report

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Comment			

Acquisition Parameter

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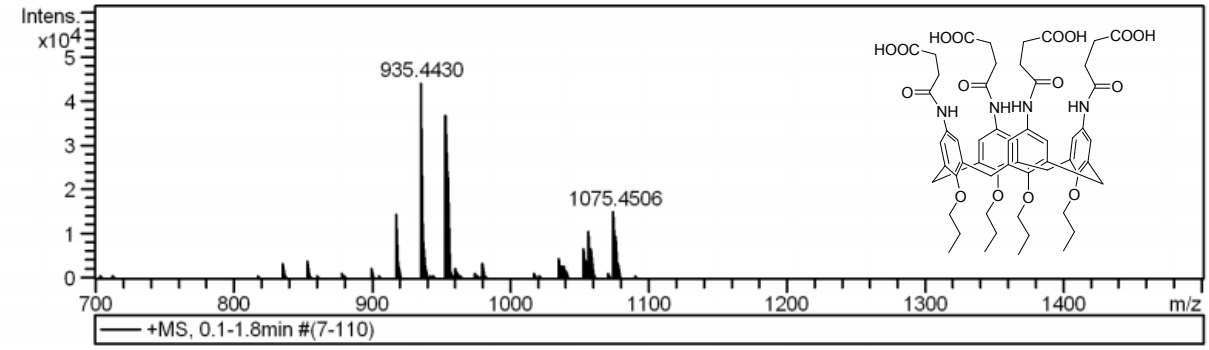

Figure S4. HRMS spectrum of **2a**.

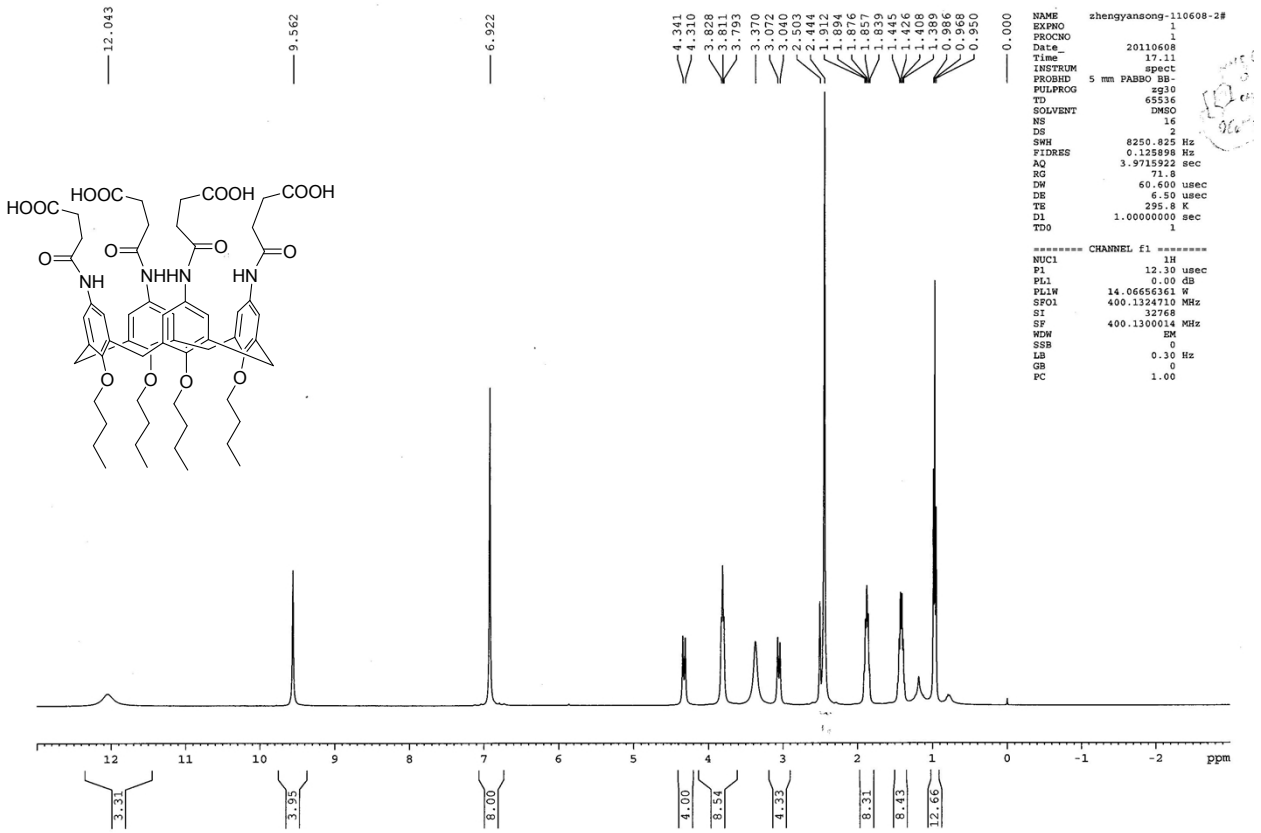

Figure S5. ^{1}H NMR spectrum of **2b** in DMSO-d_6.

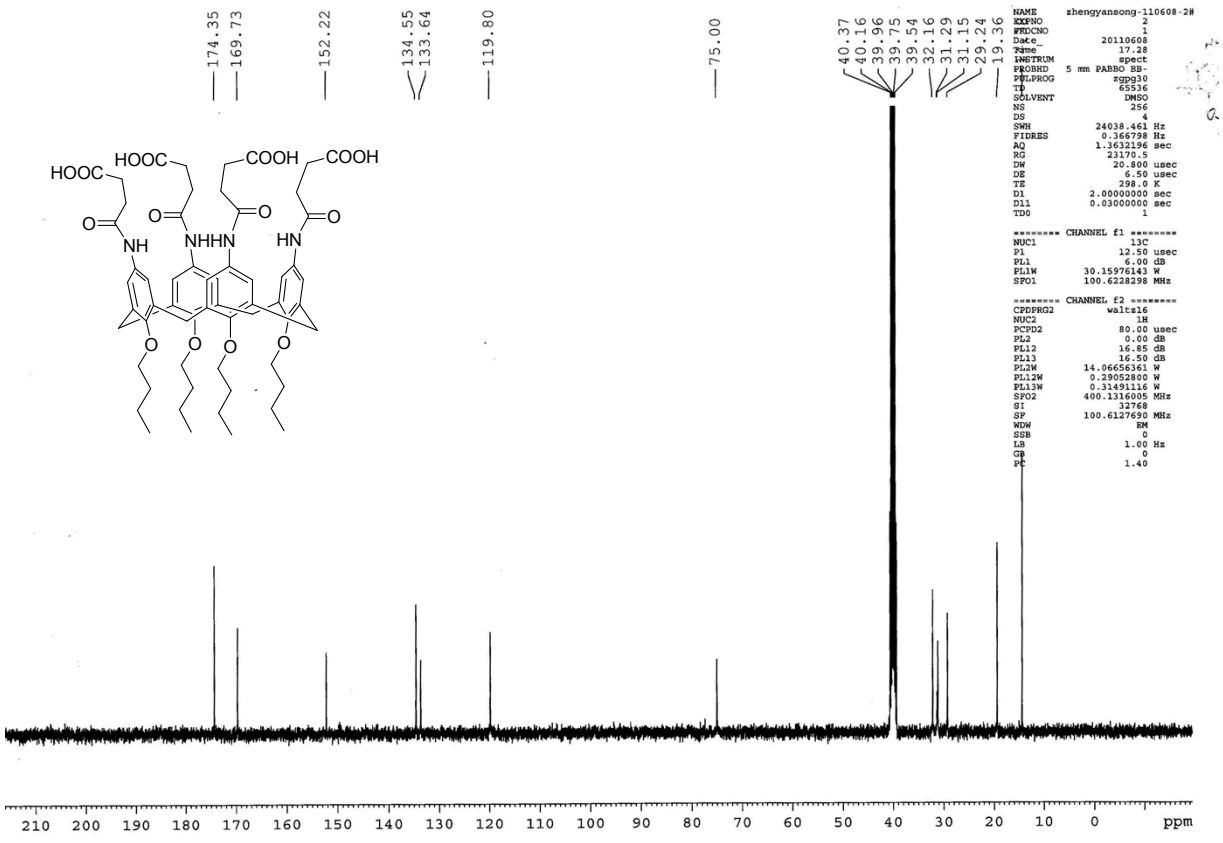

Figure S6. ^{13}C NMR spectrum of **2b** in DMSO-d_6.

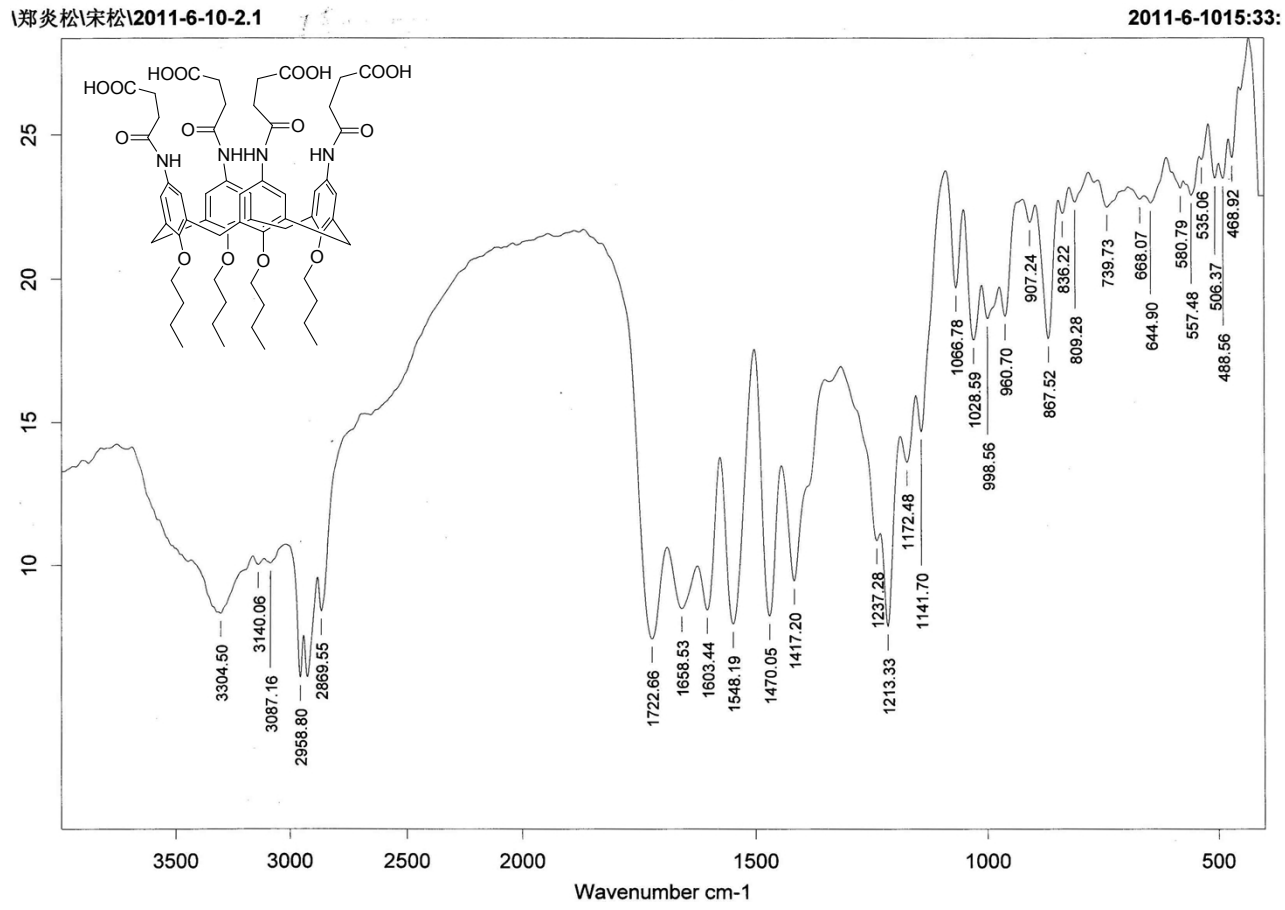

Figure S7. IR spectrum of **2b**.

Mass Spectrum List Report

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Comment			

Acquisition Parameter

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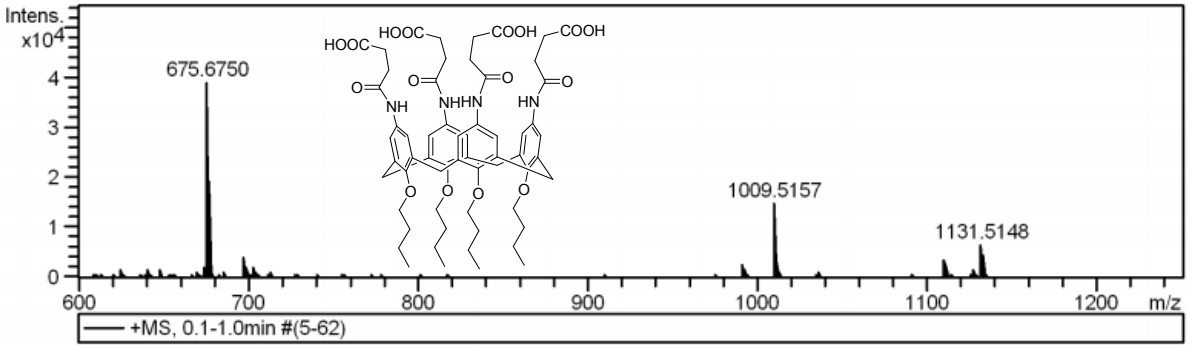

Figure S8. HRMS spectrum of **2b**.

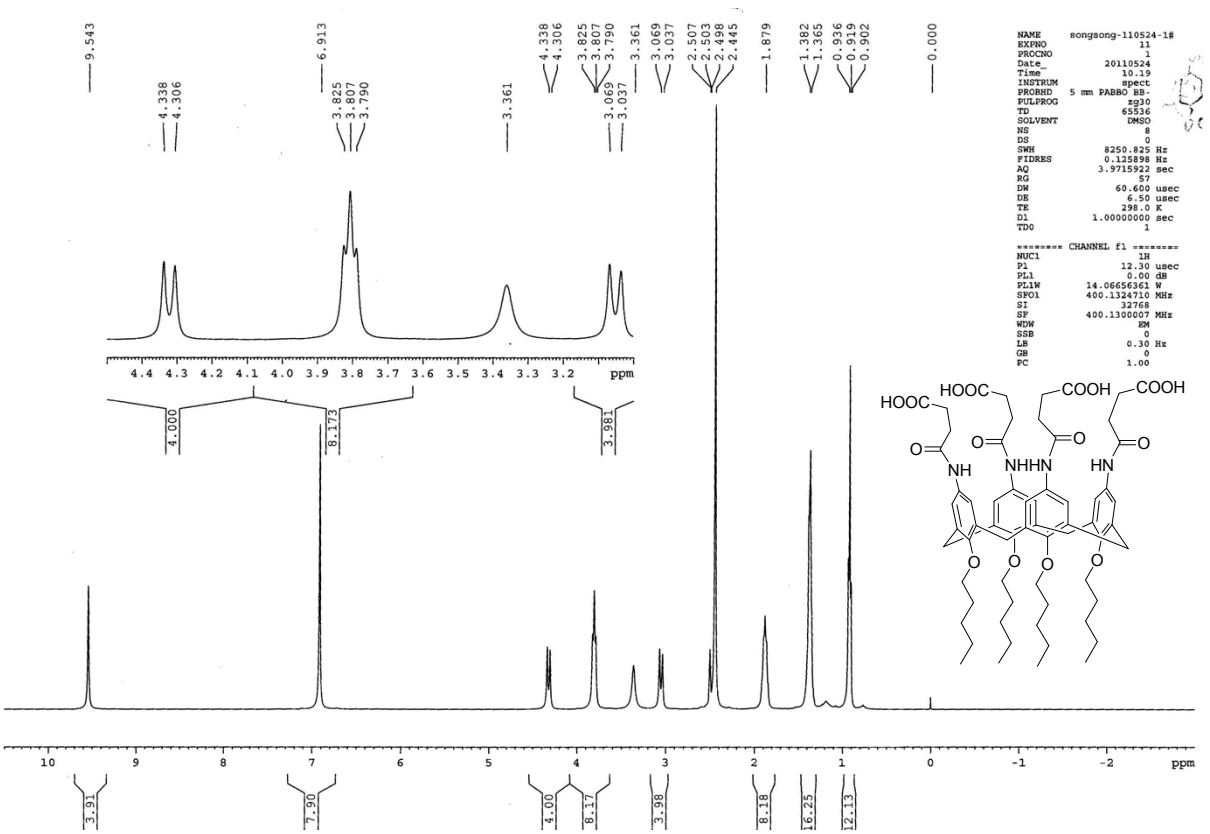

Figure S9. ^{1}H NMR spectrum of **2c** in DMSO-d$_6$.

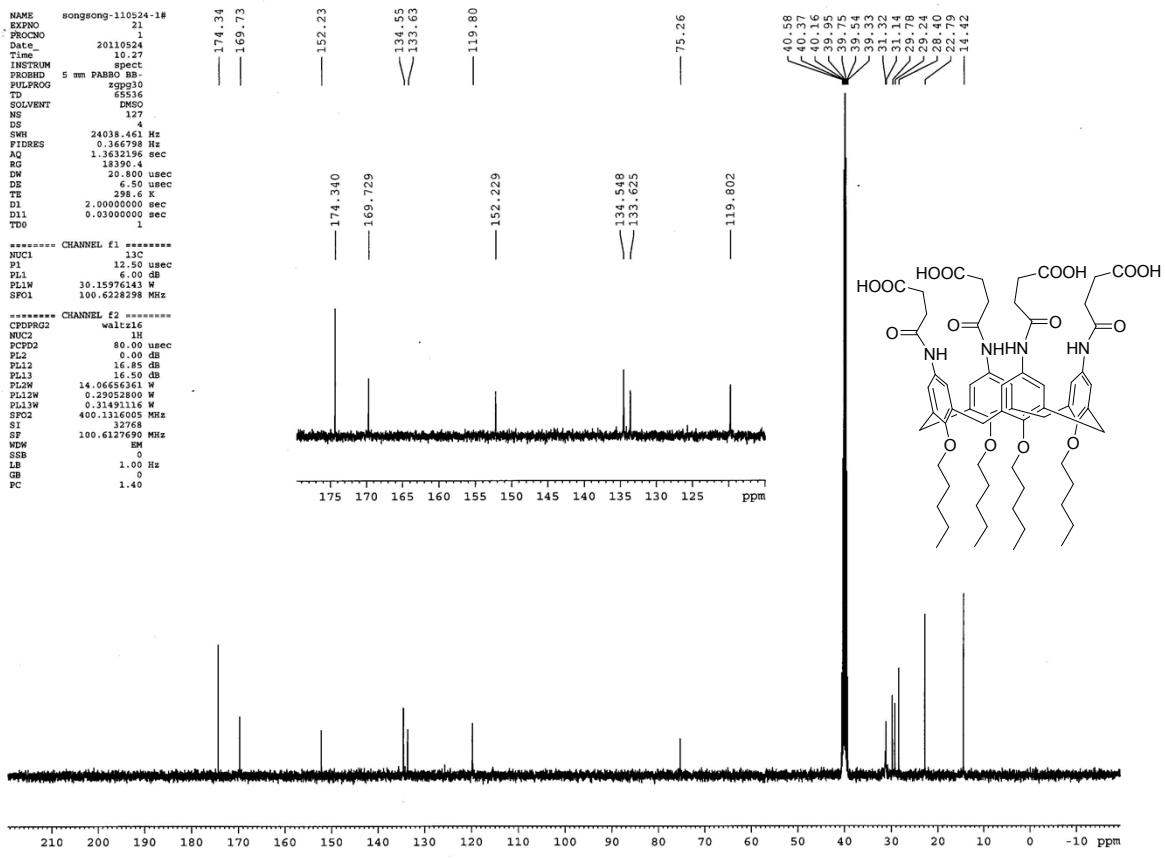

Figure S10. ^{13}C NMR spectrum of **2c** in DMSO-d$_6$.

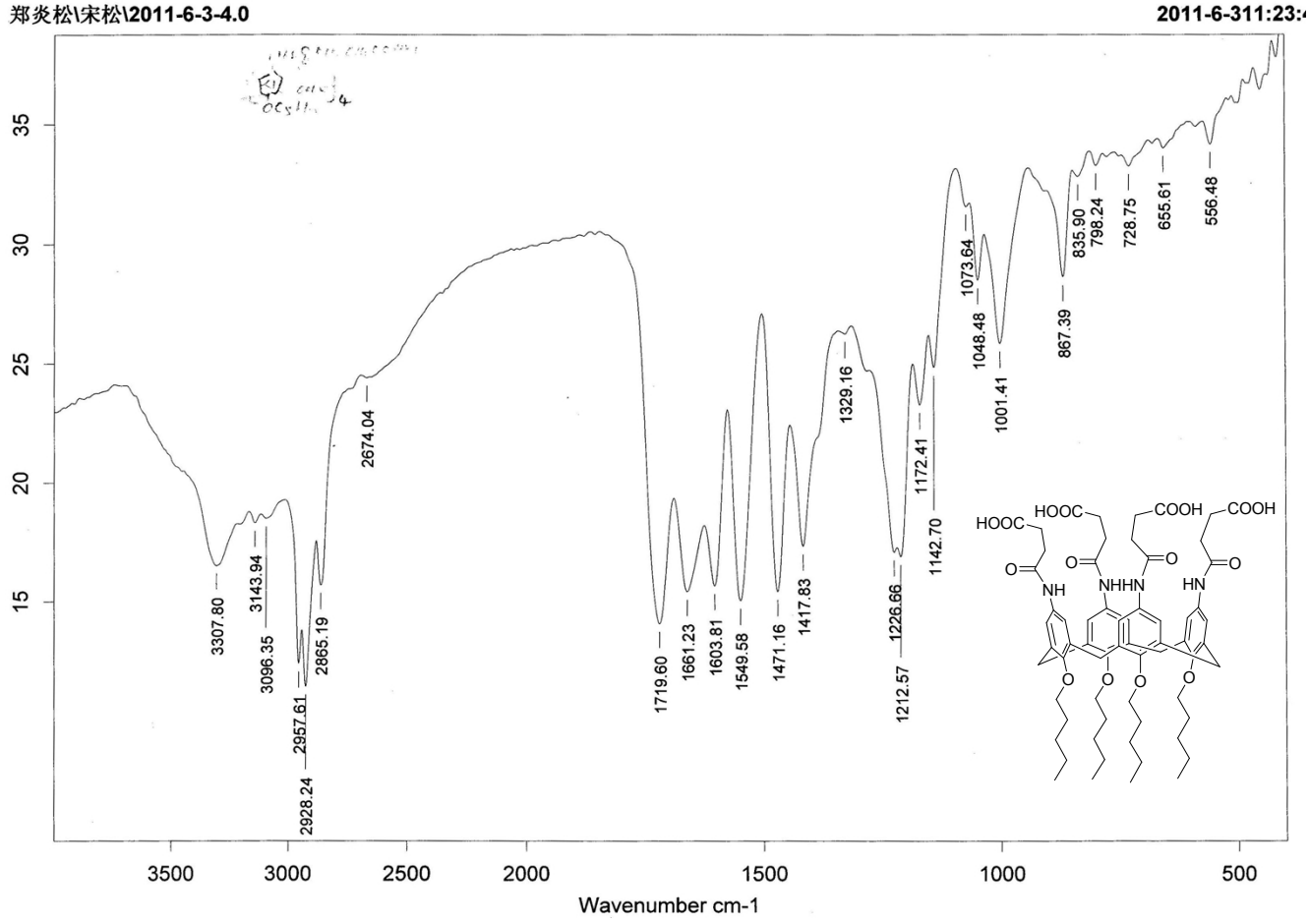

Figure S11. IR spectrum of **2c**.

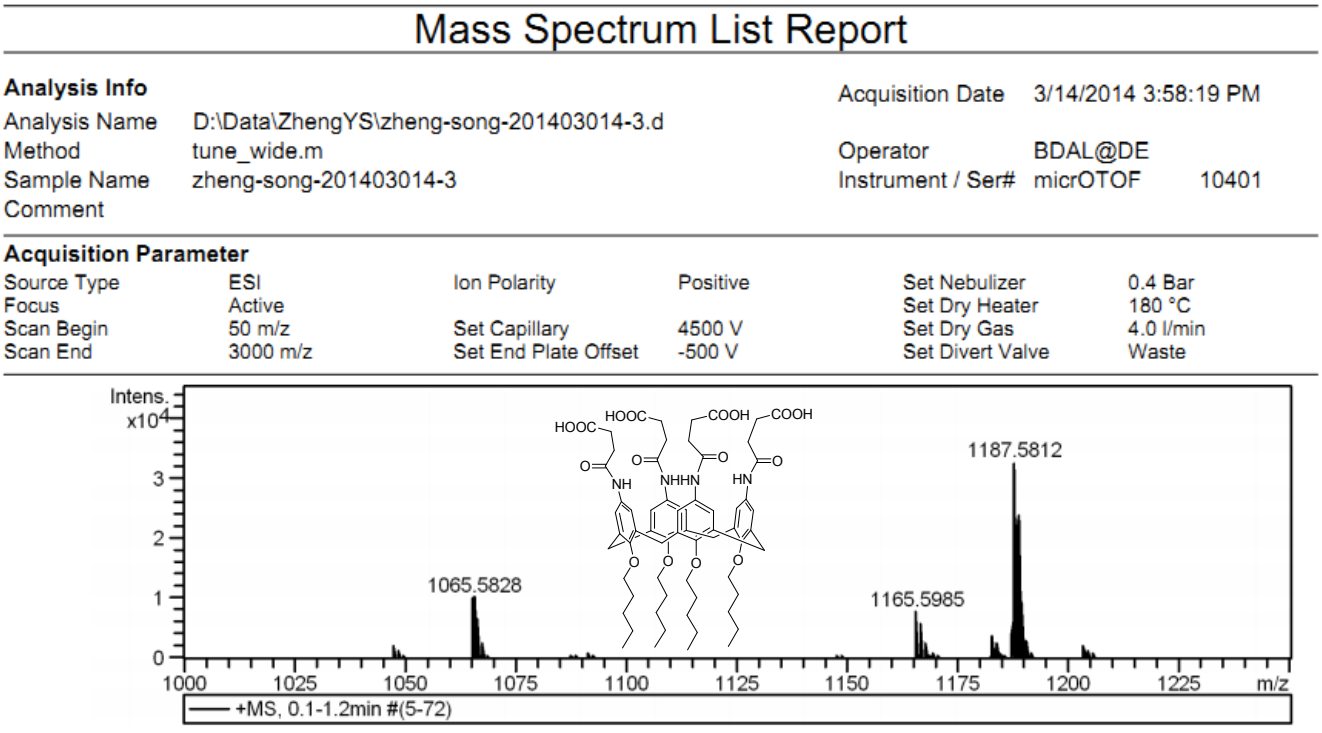

Figure S12. HRMS spectrum of **2c**.

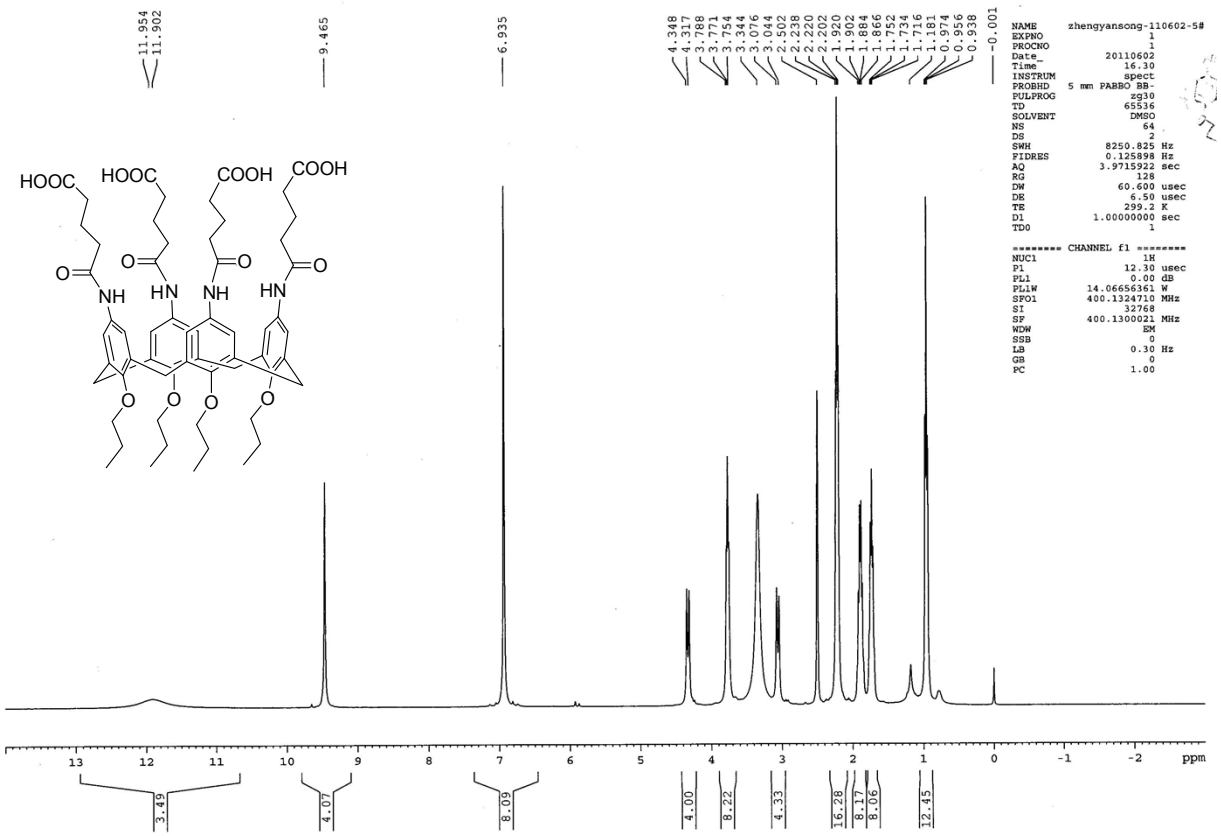

Figure S13. ^{1}H NMR spectrum of **2d** in DMSO-d_6.

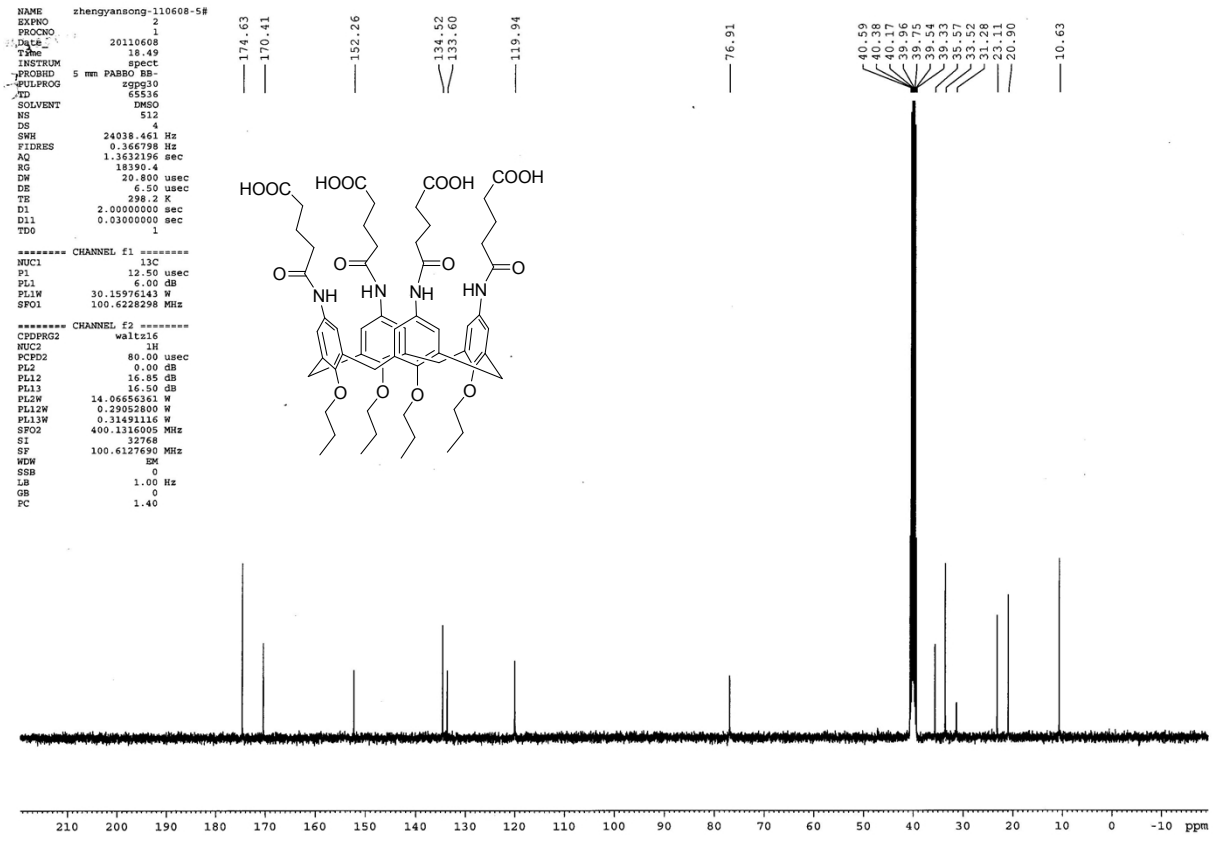

Figure S14. ^{13}C NMR spectrum of **2d** in DMSO-d_6.

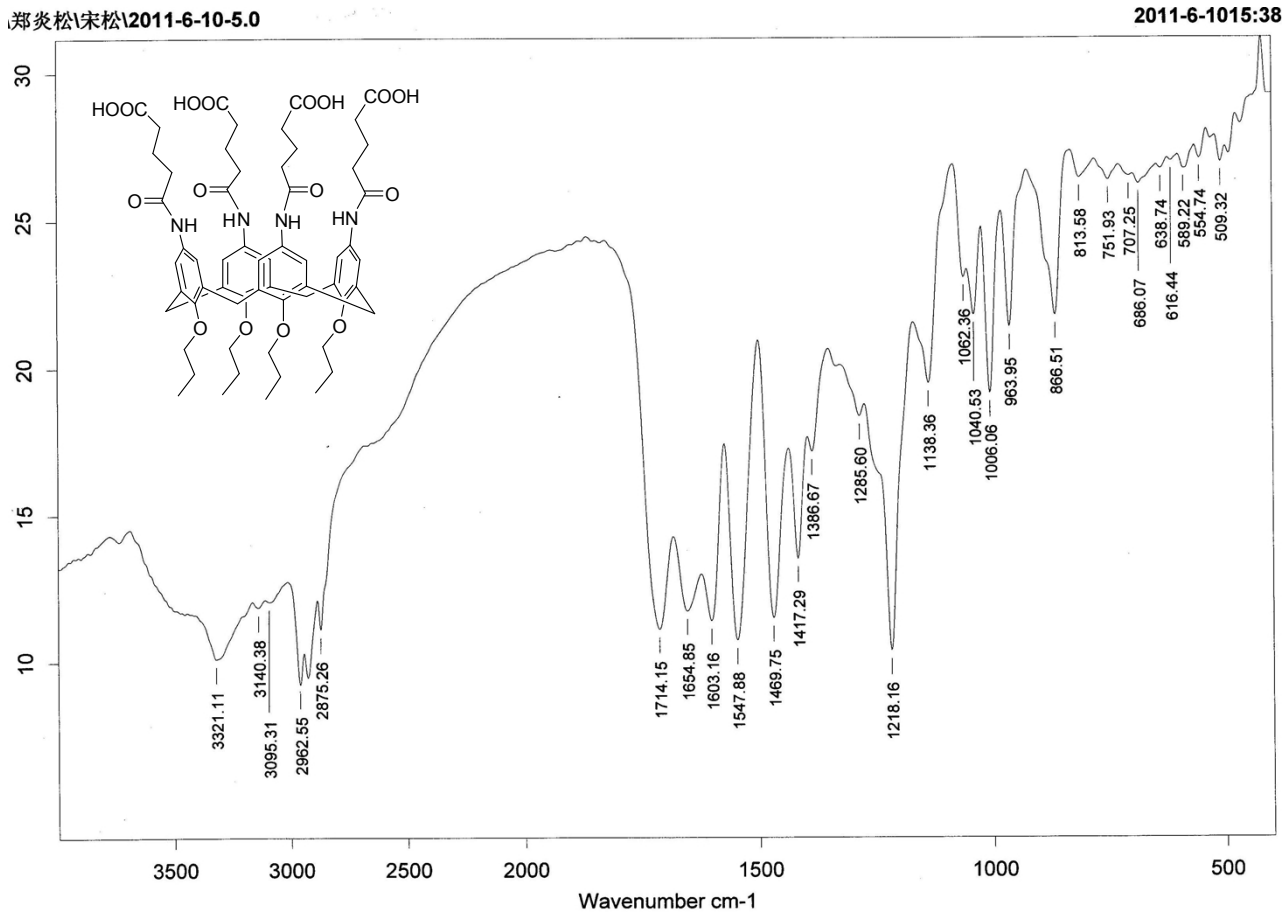

Figure S15. IR spectrum of **2d**.

Mass Spectrum List Report

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Comment			

Acquisition Parameter

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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

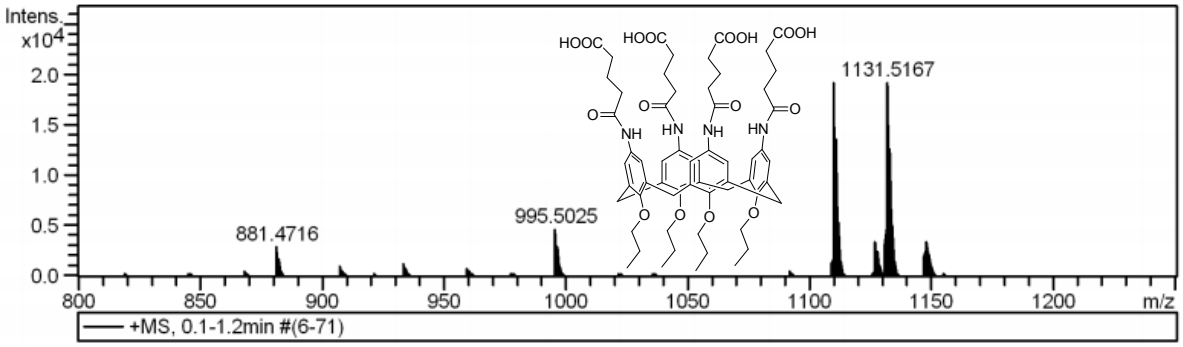

Figure S16. HRMS spectrum of **2d**.