Electronic Supplementary Material (ESI) for RSC Advances.

Calix[4]arene-based low molecular mass gelators to form gels in organoalkoxysilanes

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CONTENS

1. Preparation of Compounds CMA, CDA and CTA

The compound of *p*-tert-Butylcalix[4]arene was synthesized according to a literature method, [1] and the compound CDE was synthesized in a similar way as described in our earlier reports.[2,3] The CME and CTE were prepared according to a slightly modified literature procedure described in. [4-7] The subsequent hydrolysis of esters to give desired compounds CMA, CDA and CTA.

Synthesis of CME. Under nitrogen, a mixture of p-tert-Butylcalix[4]arene (0.65 g, 1 mmol), potassium carbonate (0.14 g, 1 mmol) and Potassium iodide (0.017 g, 0.1 mmol) were heated at reflux for 0.5 h in acetone (30 mL). Ethyl chloroacetate (in 20 mL acetone, 0.1 mL, 1 mmol) was slowly added with stirring. The mixture was then refluxed for 10 h, followed by the evaporation of the solvent. The residue was dried and dissolved/suspended in chloroform. The organic system was extracted with 10% hydrochloric acid 3 times, and then collected and dried with anhydrous magnesium sulfate. The resulting clear solution was evaporated to dryness. The crude product as prepared was firstly purified by column chromatography (silicone gel, 200–300 mesh; dichloromethane-petroleum ether (60~90℃) ether, v : v = 5 : 2) to yield the white solid CME (0.35 g, 47%). ^{1}H NMR ($CDCl_3$/ Me_4Si, 600 MHz) δ (ppm): 1.19 (s, 9H, -$C(CH_3)_3$), 1.20 (s, 18H, -$C(CH_3)_3$), 1.23 (s, 9H, -$C(CH_3)_3$), 1.41 (t, J = 6.0 Hz, 3H, -CH_3), 3.43 (d, J = 12.0 Hz, 4H, -$ArCH_2Ar$-), 4.31 (d, J = 12.0 Hz, 2H, -$ArCH_2Ar$-), 4.42 (q, J = 12.0 Hz, 2H, -CH_2CH_3), 4.49 (d, J = 12.0 Hz, 2H, -$ArCH_2Ar$-), 4.88 (s, 2H, -$ArOCH_2$), 6.98 (d, 2H, -ArH), 7.05 (d, 4H, -ArH), 7.09 (s, 2H, -ArH), 9.25 (s, 2H, -OH), 10.22 (s, 1H, -OH). MS (ESI): m/z calcd for [$(M+Na)^+$]: 757.4444, found: 757.4434.

Synthesis of CTE. p-tert-Butylcalix[4]arene (4.0 g, 6 mmol), potassium carbonate (5.0 g, 36 mmol), Potassium iodide (4.0 g, 24 mmol) and excess ethyl chloroacetate (5.1 mL, 48 mmol) were heated at reflux for 24 h in acetone (90 mL) under a nitrogen atmosphere. Ethyl chloroacetate (2.5 mL, 24 mmol) was then added. The mixture was refluxed again for 7 d. The solvents were evaporated and the residue partitioned

between 10% hydrochloric acid and chloroform. The organic layer was separated and dried (anhydrous magnesium sulfate) and the solvents were evaporated. The crude product re-crystallization from ethanol to give CTE (4.8 g, 80%) as white crystals. ^{1}H NMR ($CDCl_3$/ Me_4Si, 600 MHz) δ (ppm): 1.07 (s, 36H, -C(CH_3)$_3$), 1.29 (t, J = 6.0 Hz, 12H, -CH_3), 3.20 (d, J = 12.0 Hz, 4H, -ArCH_2Ar-), 4.21 (q, J = 6.0 Hz, 8H, -CH_2CH_3), 4.81 (s, 8H, -ArOCH_2), 4.87 (d, J = 12.0Hz, 4H, -ArCH_2Ar-), 6.78 (s, 8H, -ArH). MS (ESI): m/z calcd for [(M+Na)$^+$]: 1015.5548, found: 1015.5565.

Synthesis of CMA, CDA and CTA. A suspension of CME (0.37 g, 0.5 mmol), CDE (1.64 g, 2 mmol) or CTE (1.98 g, 2 mmol), and 15% NaOH (10 mL) in 75 mL of ethanol , and the mixture was stirred and heated under reflux for 2 d. The residue was diluted with cold distilled water (100 mL), then hydrochloric acid (3 M) was added with vigorous stirring until the pH value reached 1, and then the formed solid was collected via filtration. Finally, the residue was dried in air and dissolved in chloroform. The solution was first washed with hydrochloric acid (3 M) and brine, and was then dried and concentrated to afford white solid CMA (0.32 g, 90%), CDA (1.37 g, 90%) or CTA (1.58 g, 90%). For CMA: ^{1}H NMR ((CD_3)$_2$SO/ Me_4Si, 600 MHz) δ (ppm): 1.17 (d, J = 12.0 Hz, 36H, -C(CH_3)$_3$), 3.45 (d, J = 12.0 Hz, 4H, -ArCH_2Ar-), 4.10 (d, J = 18.0 Hz, 2H, -ArCH_2Ar-), 4.39 (d, J = 18.0 Hz, 2H, -ArCH_2Ar-), 4.71 (s, 2H, -ArOCH_2), 7.03 (d, 2H, -ArH), 7.12 (s, 2H, -ArH), 7.18 (d, 2H, -ArH), 7.23 (s, 2H, -ArH). MS(ESI): m/z calcd for [(M+Na)$^+$]: 729.4131, found: 729.4137. For CDA: ^{1}H NMR ($CDCl_3$/ Me_4Si, 300 MHz) δ (ppm): 1.08 (s, 18H, -C(CH_2)$_3$), 1.25 (s, 18H, -C(CH_2)$_3$), 3.47 (d, J = 12.0 Hz, 4H, -ArCH_2Ar-), 4.18 (d, J = 15.0 Hz, 4H, -ArCH_2Ar-), 4.70 (s, 4H, -ArOCH_2), 6.97 (s, 4 H, -ArH), 7.07 (s, 4H, -ArH). MS (ESI): *m/z* calcd for [(M+Na)$^+$]: 787.4186, found: 787.4175. For CTA: ^{1}H NMR (CD_3)$_2$SO/ Me_4Si, 600 MHz) δ (ppm): 1.06 (s, 36H, -C(CH_3)$_3$), 3.22 (d, J = 12.0 Hz, 4H, -ArCH_2Ar-), 4.58 (s, 8H, -ArOCH_2), 4.78 (d, J = 12.0 Hz, 4H, -ArCH_2Ar-), 6.92 (s, 12H, -ArOCH_2). MS (MALDI-TOF): *m/z* calcd for [(M+Na)$^+$]: 903.43, found: 903.63.

2. Supplementary Figures

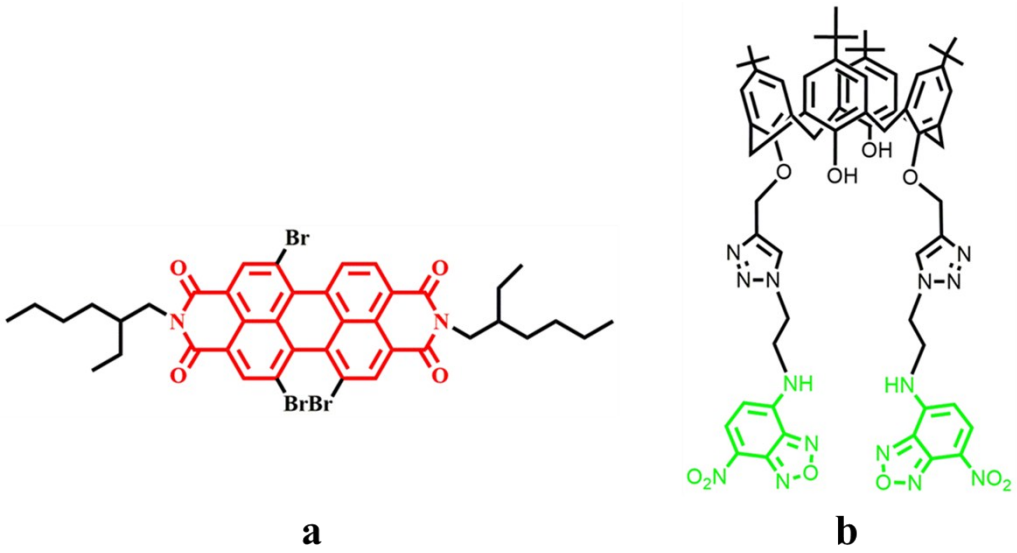

Figure S1 Molecular structures of the fluorescent probes empployed: a) perylene bisimide derivative **1**; b) NBD derivative **2**.

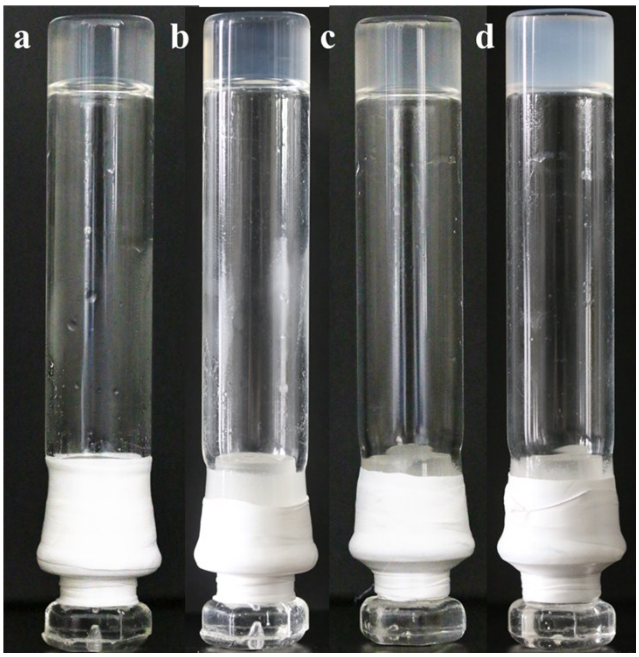

Figure S2 Pictures of freshly prepared gels at a gelator concentration of 2.0% (w/v, a: CTA/PTMS, c: CTA/PTES), and after one month storage in sealed tubes at room temperature (b: CTA/PTMS, d: CTA/PTES).

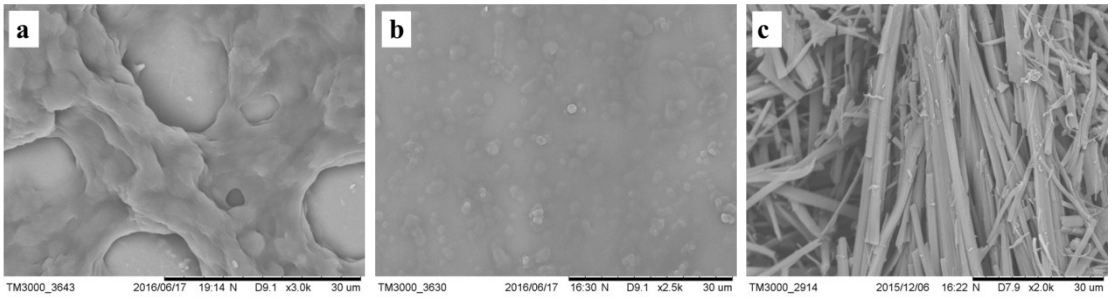

Figure S3 SEM images of the xerogels of CTA from: a) PTMS, b) PTES, and c) CCl_4.

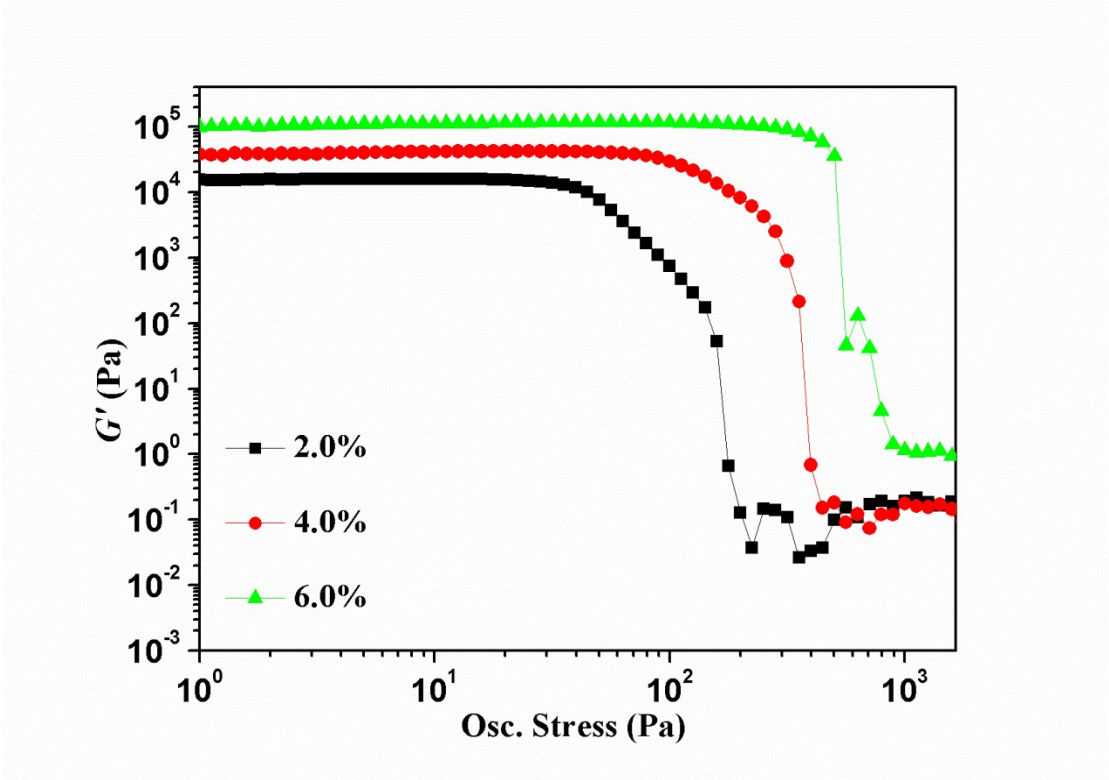

Figure S4 Evolution of *G′* as a function of the applied shear stress at different concentration of CTA in PTES (w/v).

3. Preparation of Test Paper for Ag^+ detection

The Ag^+ test papers were prepared generally as follows. A piece of filter paper was immersed in a hot solution of CTA/PTMS (6.0%, *w/v*, ~40 °C), then took out the paper, and then waiting a few minutes till the gel was formed. After that, the as treated paper was immersed in the CTA/CCl_4 solution of **2**. CCl_4 was evaporated within a few minutes after the paper was taken out from the as afore mentioned solution. The paper as obtained is ready for using in Ag^+ detection.

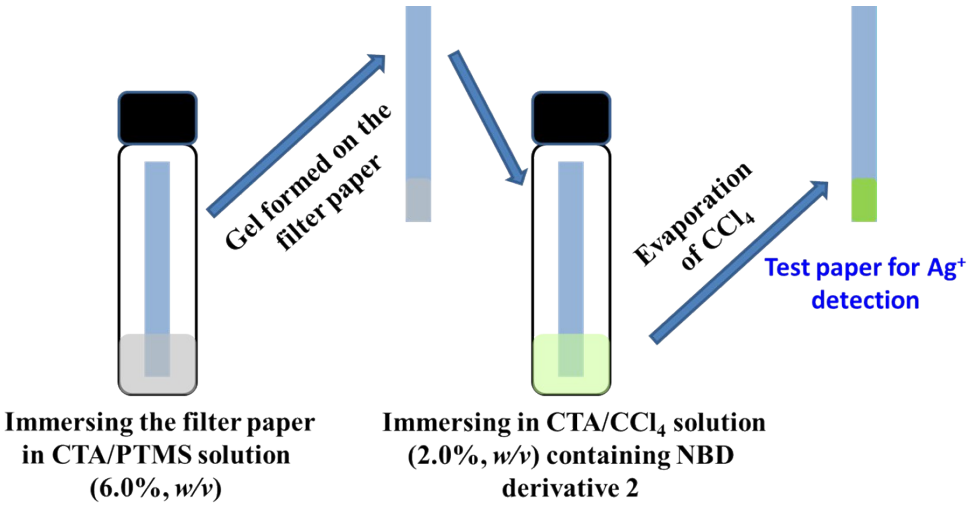

Figure S5 Schematic representation of the fabrication of a test paper for Ag^+ detection.

4. Preparation of Gel Model

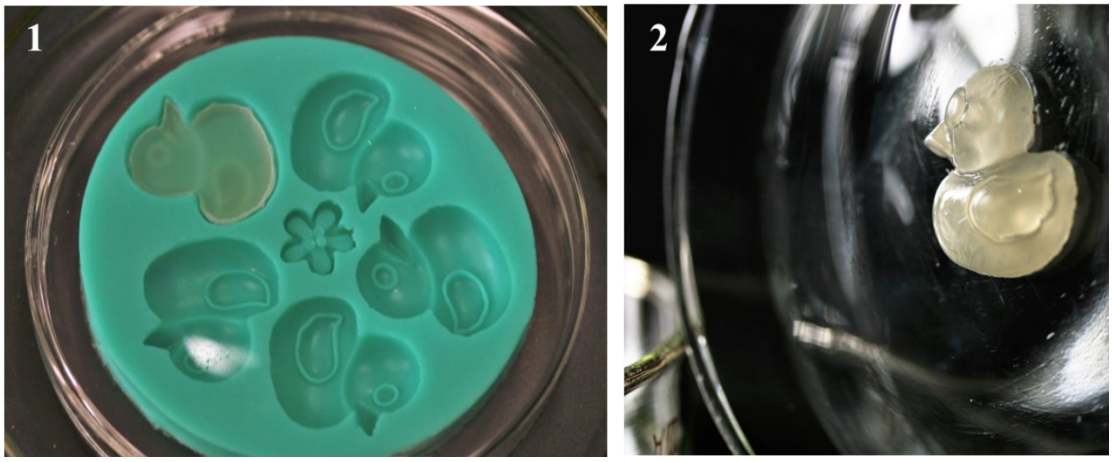

Figure S6 A 'duck' modeled with the CTA/PTMS gel.

Note: Depositing the PTMS gel of CTA (6.0%, w/v) into a duck template, and then the duck as produced was taken out of the template. In this way (melting-free deposition molding), a model duck was obtained.

5. ^{1}H spectra for compounds CMA, CDA and CTA

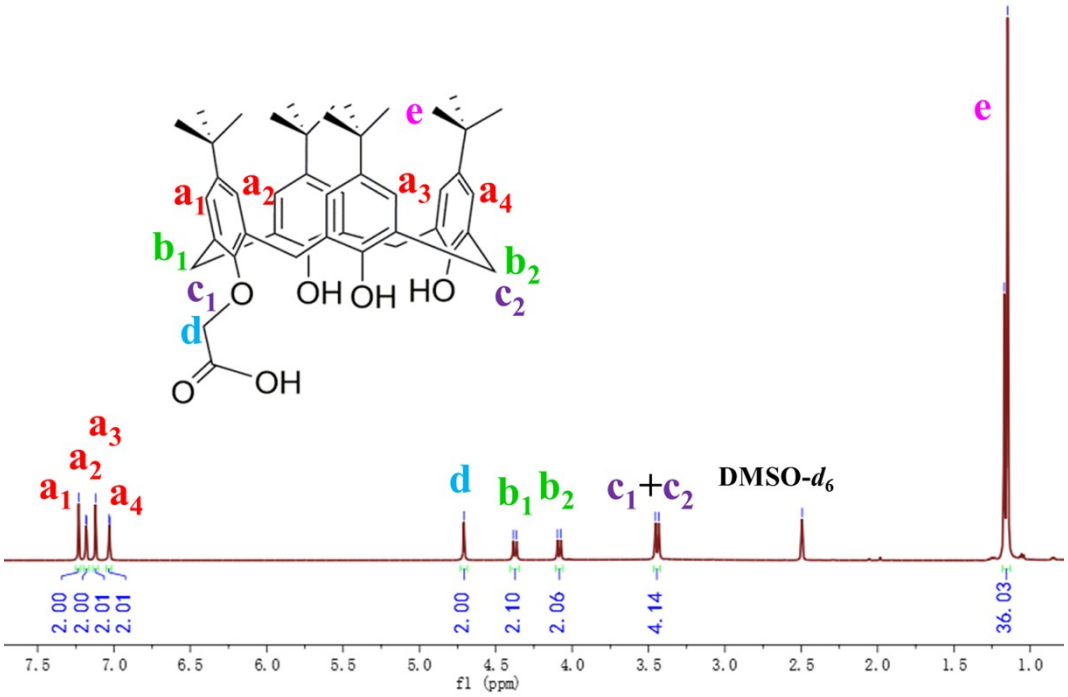

Figure S7 ^{1}H spectra for compound CMA.

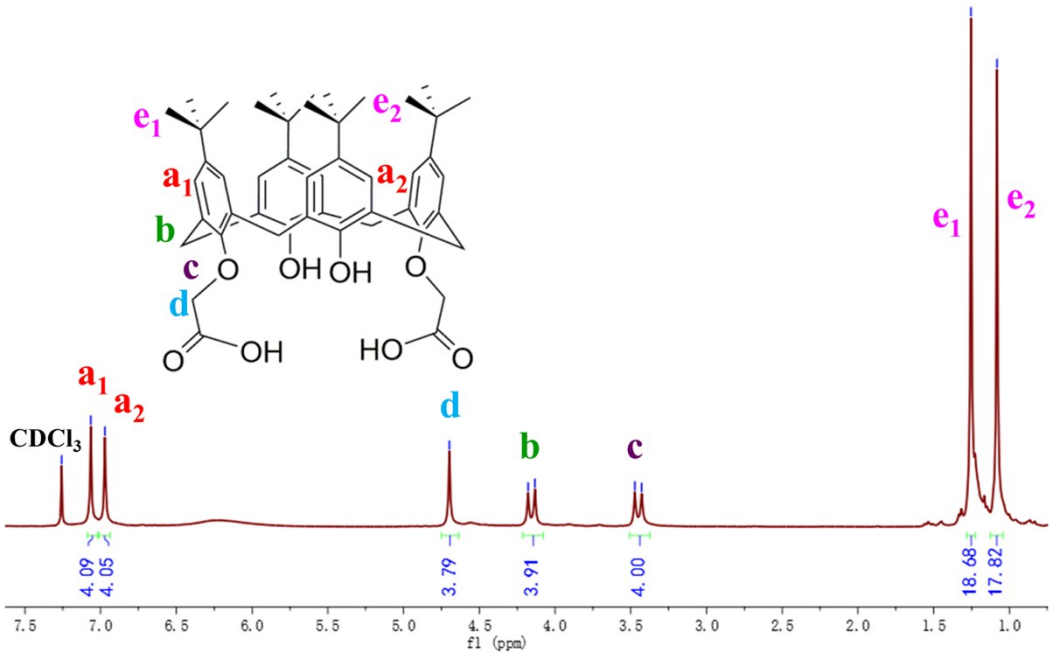

Figure S8 [1]H spectra for compound CDA.

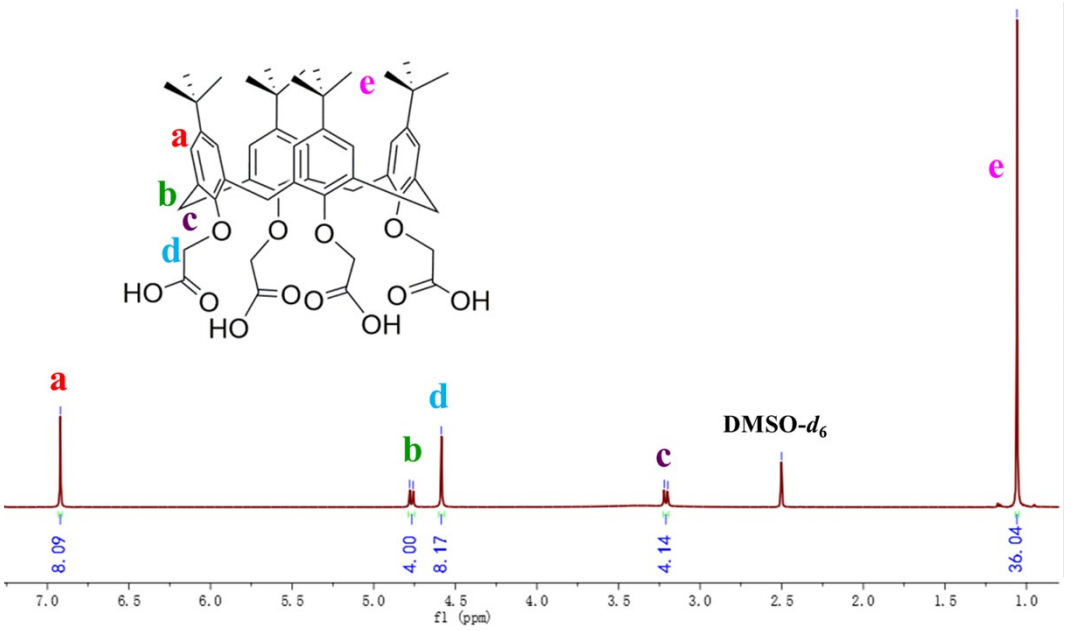

Figure S9 [1]H spectra for compound CTA.

6. MS spectra for compounds CMA, CDA and CTA

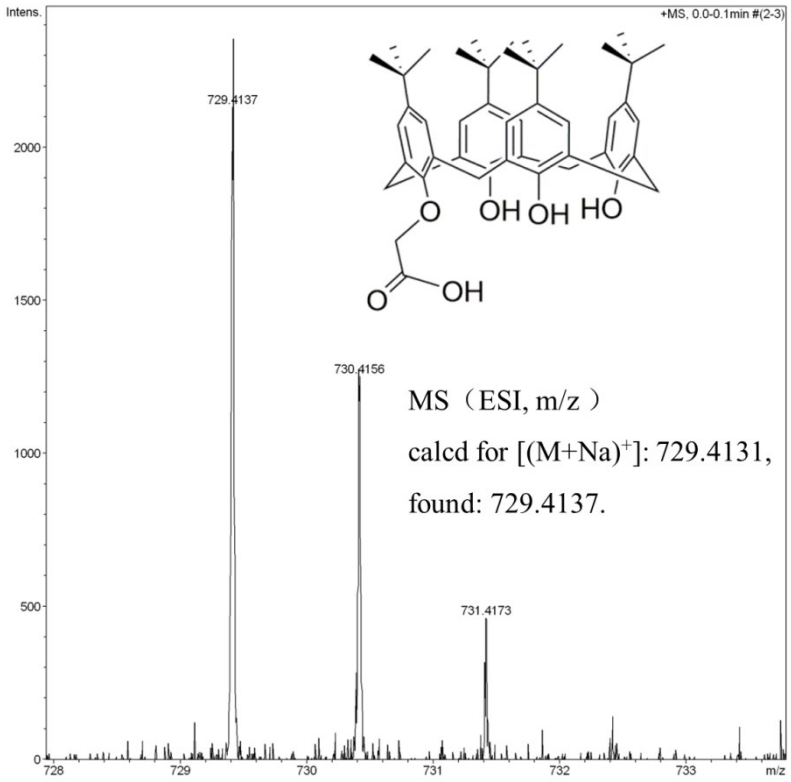

Figure S10 MS spectra for compound CMA.

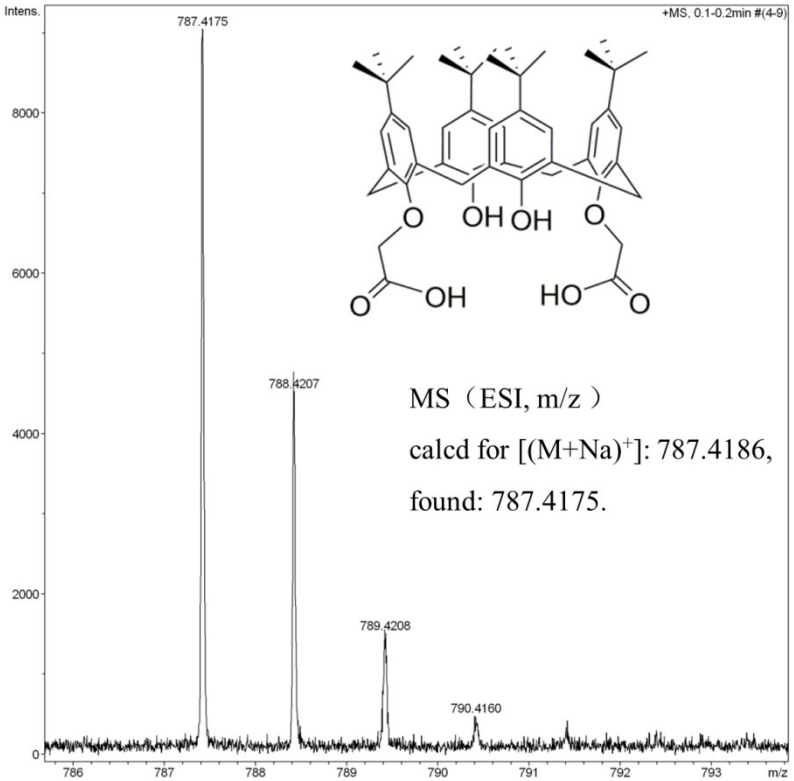

Figure S11 MS spectra for compound CDA.

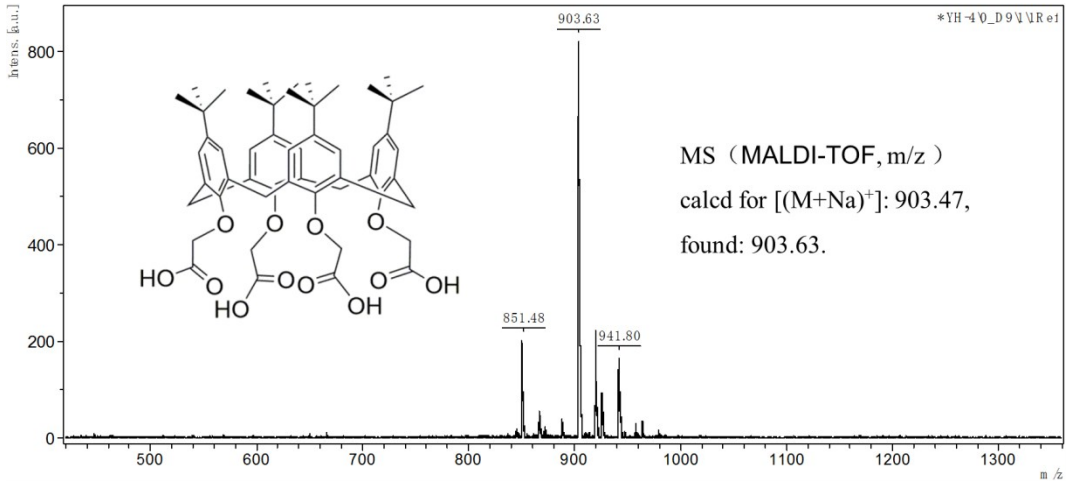

Figure S12 MS spectra for compound CTA.

7. References

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