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Supporting Information

for

Boronic Ester-based Dynamic Covalent Ionic Liquid Gels for Self-healable, Recyclable and Malleable Optical Devices

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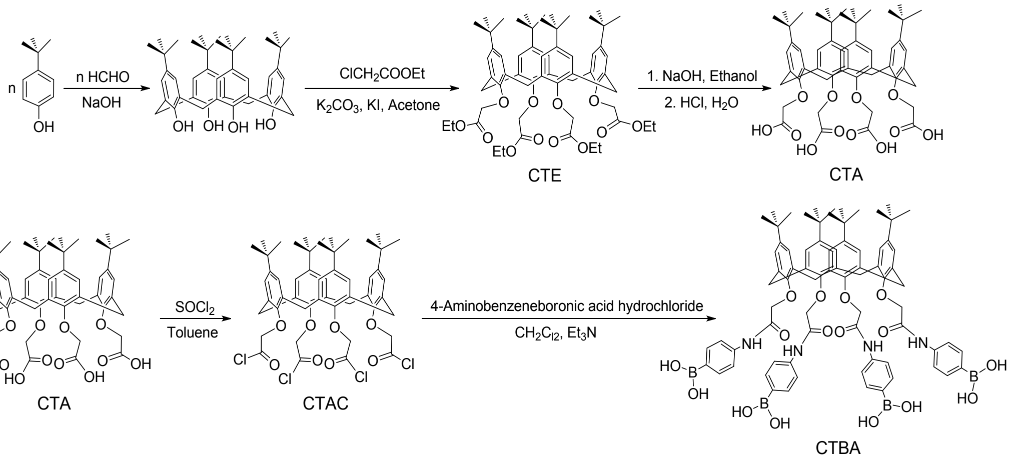
1. Experimental Section

1.1 Reagents and Materials

4-tert-Butylphenol (>98.0%) was purchased from TCI Tokyo Chemical Industry Co., Ltd., 4-aminobenzeneboronic acid hydrochloride was purchased from Soochiral Chemical Science & Technology Co., Ltd., poly(vinyl alcohol) (MW~31000) was from Shanghai Aladdin Bio-Chem Technology Co., Ltd., ethyl chloroacetate (99%), 1-butyl-3-methylimidazolium tetrafluoroborate (>98.0%) and diphenyl ether (99%) are products of J&K Technology Co., Ltd. These reagents were used without further purification. Other reagents were of analytical grade and used without further purification unless otherwise specified.

1.2 Synthetic Route for CTBA



Scheme S1. The synthetic route for CTBA.

1.3 Preparation of Compound CTBA

p-tert-Butylcalix[4]arene was prepared from the base-catalyzed condensation of 4-tert-butylphenol with formaldehyde by a literature method,[1] and the compounds CTE and CTA were synthesized in the way as described in our earlier reports. [2, 3]

Synthesis of CTAC: A suspension of CTA (3 g, 3.405 mmol) in 200 mL of Toluene was prepared by stirring the mixture at room temperature under nitrogen, then $SOCl_2$ (4.95 mL, 68.1 mmol) was slowly added with stirring, then the system was slowly heated to reflux (~80℃), and then refluxed with stirring for 10 hours. Finally, the solvent was evaporated under reduced pressure. The residues as generated were washed with dried methylbenzene to remove unreacted $SOCl_2$, then dissolved in

CH_2Cl_2, and then 4-aminophenylboronic acid and a small amount of triethylamine was added to the solution at room temperature under stirring. The reaction was finished 2 hours later. The solvent was evaporated under reduced pressure, then $CHCl_3$ was added under stirring. The organic layer was wash with equivalent volume of HCl solution (3 mol/L) for 3 times, then dried over anhydrous Mg_2SO_4 for 30 minutes, and then evaporated to dryness under reduced pressure. Absolute ethanol was added until yellow solution was formed. To the solution, an appropriate amount of petroleum ether was added. The solution as obtained was placed in a fridge over night. The yellow powders precipatated were collected and dried for characterization (0.86 g, 23%). ^1H NMR, ^{13}C NMR and high-resolution mass spec data of CTBA are depicted in **Figure S7, Figure S8 and Figure S9**, respectively.

1.4 FTIR Measurements

All FTIR measurements were performed on a Bruker VERTEX70 V infrared spectrometer. The testing scale was from 400 to 4000 cm^{-1} with 128 scans for each sample. The KBr pellet was obtained by mixing a small amount of the sample and anhydrous KBr powder. The FTIR measurements were carried out at room temperature.

1.5 Micro-rheological Characteristics

The evolution of viscoelastic properties of the mixture solvent gel of CTBA with PVA at a total concentration of 45% (*w*/*v*) during gelation process were tracked by an optical micro-rheometer (Rheolaser Lab, from Formulaction, French). Fumed silica (hydrophilic, BET surface: 200 m^2/g, was from Aladdin Industrial Corporation) were adopted as probing particles. In the experiment, fumed silica (10 mg) and 4 mL solution of H_2O/EtOH (9/1, *v*/*v*) were placed into a sealed flat-bottomed cylindrical glass cell of 4 mL with a 14.5 mm diameter. Sonication was conducted on the mixture at room temperature for 30 min to make the probing particles disperse better. Gelators were added to the suspension (PVA was dissolved before CTBA addition), and the system was stirred (500 rpm) until CTBA completely dissolved. The glass cell was then immediately placed in the sample chamber of the instrument at 30 °C. During the test, the speckle image of the sample, which was generated by the interfering backscattering wave of the incident laser at 650 nm caused by the Brownian motion of the particles, was recorded by a multi-pixels detector.

Unlike conventional rheological measurements, this method shows no obvious perturbation towards the gelation of the system owing to no stress or strain applied. The micro-rheology, also called passive micro-rheology, involves measuring the time-dependent diffusion of tracer particles in the systems under study. This is done by employing multiple particles tracking to measure the ensemble-averaged mean square displacement (MSD) of the probe particles, of which time-cure superposition for the MSD curves was applied to analyze viscoelastic properties of the systems.[4]

As described in literatures,[5] SLB (solid-liquid balance) is a parameter defined as the ratio between liquid and solid behavior. For systems with SLB values greater than 1, they are pure viscous liquids, for those the values are in between of 0.6 and 1, the systems tend to viscous liquids, and for the systems, the value equals to 0.5, they reach a critical point of liquid-solid transition. Finally, the systems with SLB values greater than 0.3, but smaller than 0.5, they are typical elastic solids including gels. There are systems, of which their SLB values are equal to 0.4, and they are pure elastic solid.

1.6 Rheological Measurements

Rheological measurements were carried out by using a stress-controlled rheometer (TA instrument, AR-G-2) equipped with a steel-coated parallel-plate geometry (20 mm in diameter). The gap between the two plates was fixed at ~1000 μm. The following procedure was used to load the gel sample: 1 mL of mixture solvent and gelator were stirred until the gelator dissolved, then poured in a cylindrical PTFE molds (26 mm in diameter) at room temperature. The measurements were started after the gels formed 12 hours later. A solvent-trapping device was placed above the plate to avoid solvent evaporation during the measurement. Temperature sweeping at a constant heating rate was performed, which provides information about gel-sol transformation of the sample.

2. Supplementary Tables and Figures

Table S1. The gelation behavior of different ratios of CTBA to PVA in H_2O/EtOH (9/1, *v*/*v*) at room temperature.

n_{CTBA}:n_{PVA} (Gelators)	0.5:2	1:2	1.5:2	2:2
Gelation Time	---	---	5 h	---
Result	VS	VS	G	PG
Gel sample	---	---		---

Note: VS: viscous solution; G: gel; PG: partial gel

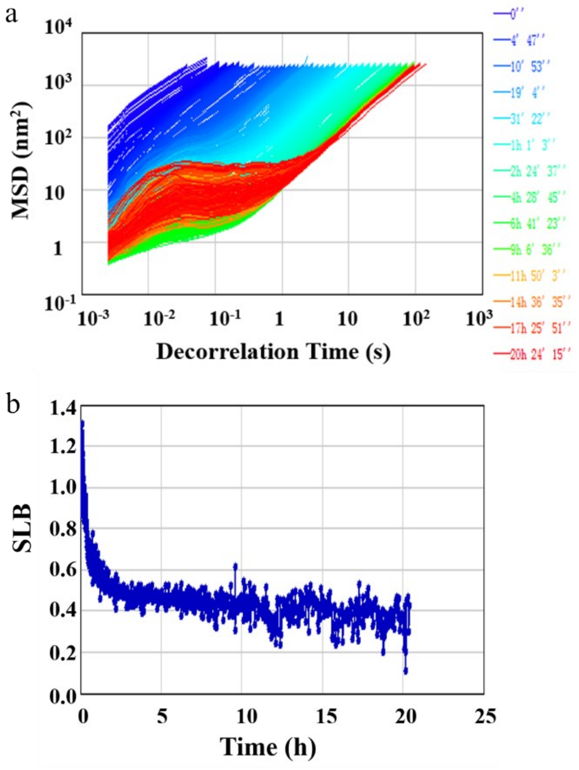


Figure S1. a) Time-dependent MSD traces of a mixture solvent gel of CTBA with PVA at a total concentration of 45% (*w*/*v*) in the dynamic cross-linking process, as well as plots of SLB against time (b).

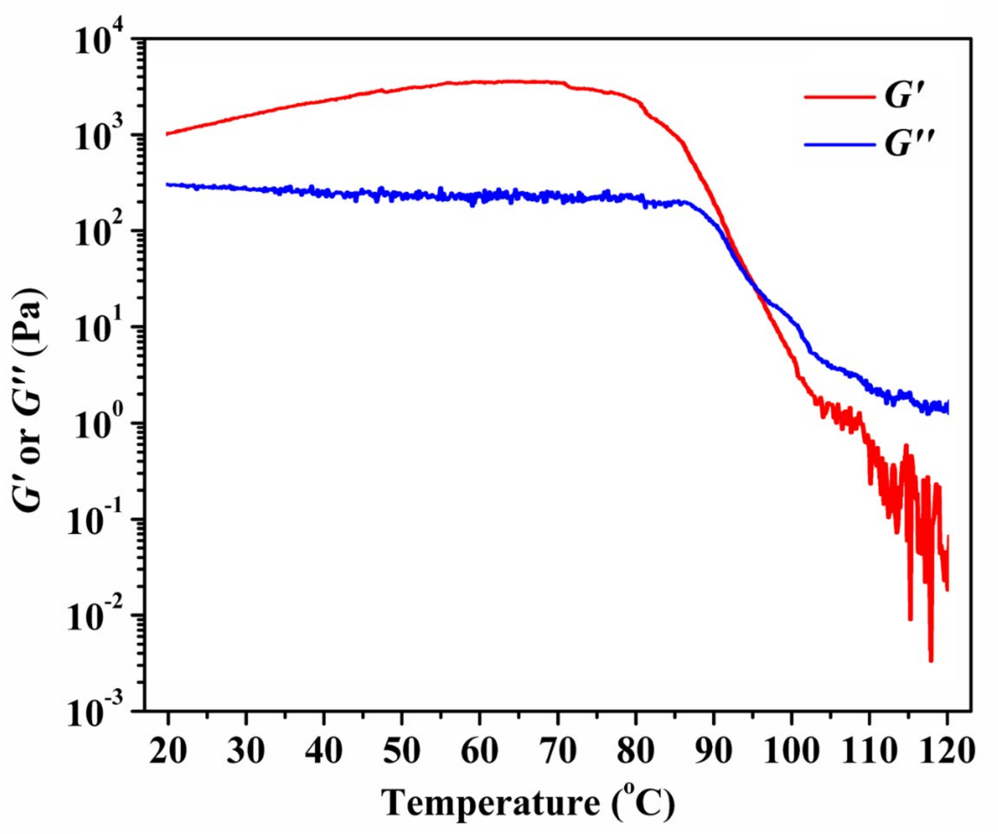


Figure S2. The storage modulus (G') and loss modulus (G'') of the IL gel change with variation of temperature.

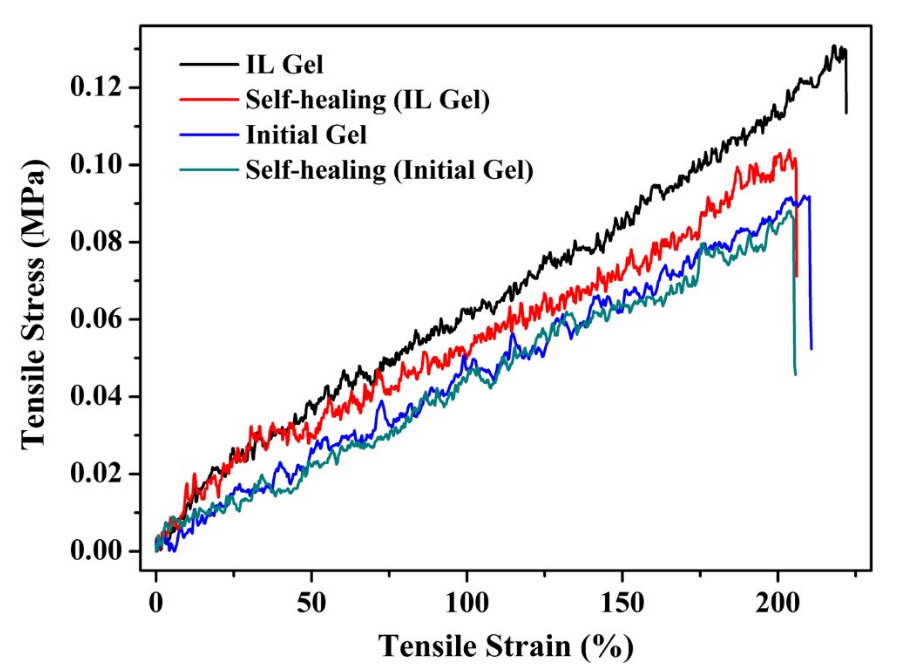


Figure S3. The tensile stress-strain curves of the initial mixture solvent gels, the IL gels and the relevant self-healed gels.

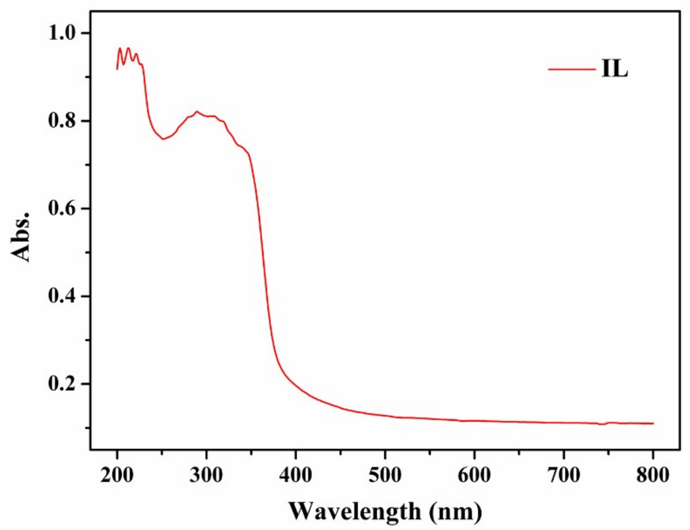


Figure S4. A typical UV-vis absorption spectrum of the IL-gels as prepared.

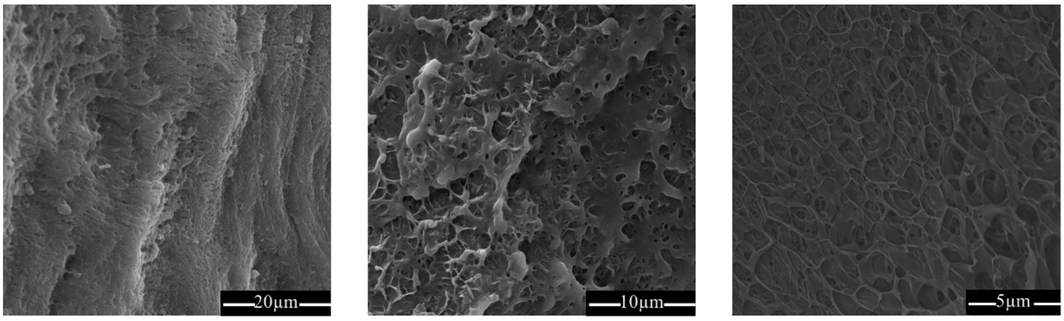


Figure S5. Scanning electron microscopy (SEM) images of the xerogel of a water-ethanol mixture solvent gel with different magnifications.

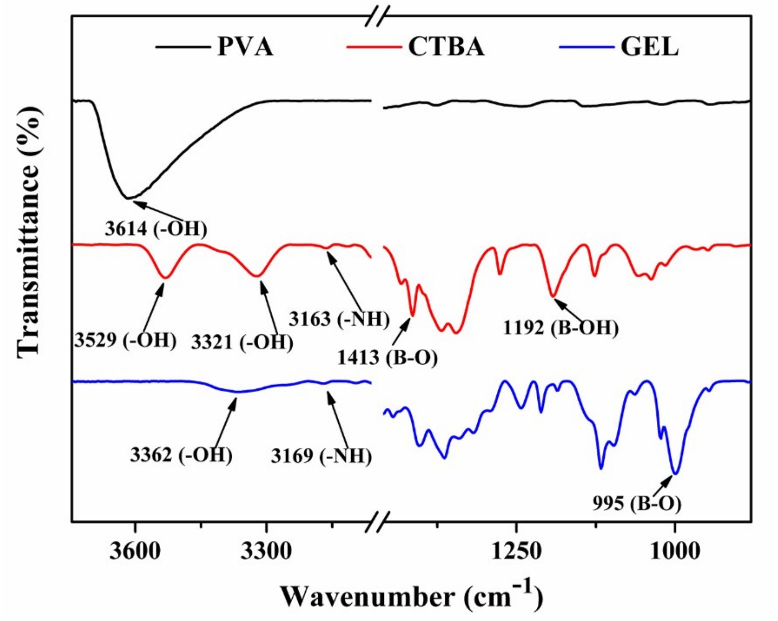


Figure S6. FTIR spectra of PVA, CTBA and the xerogel of a water-ethanol mixture solvent gel.

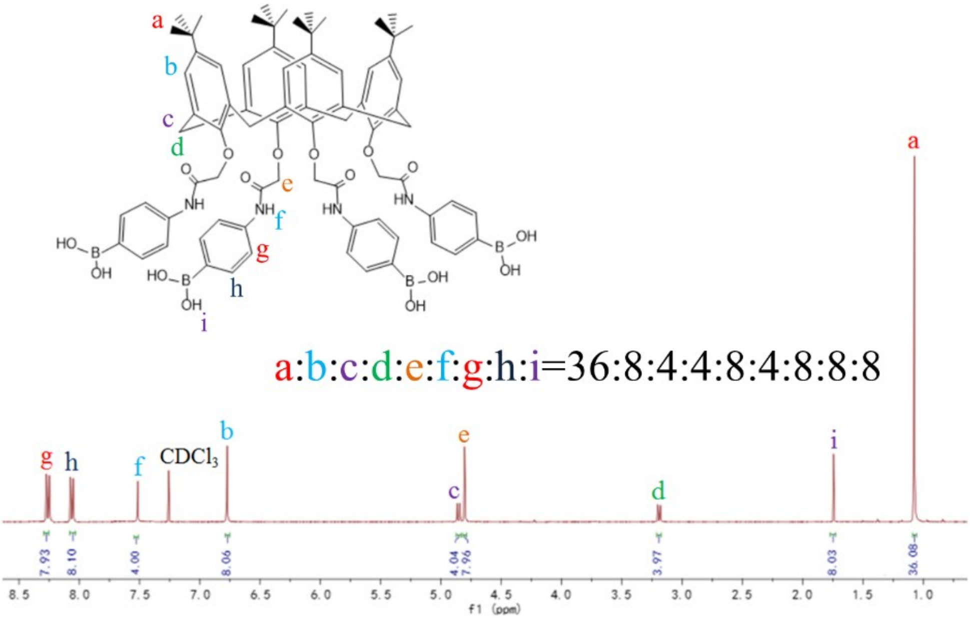


Figure S7. ^{1}H NMR spectrum of CTBA.

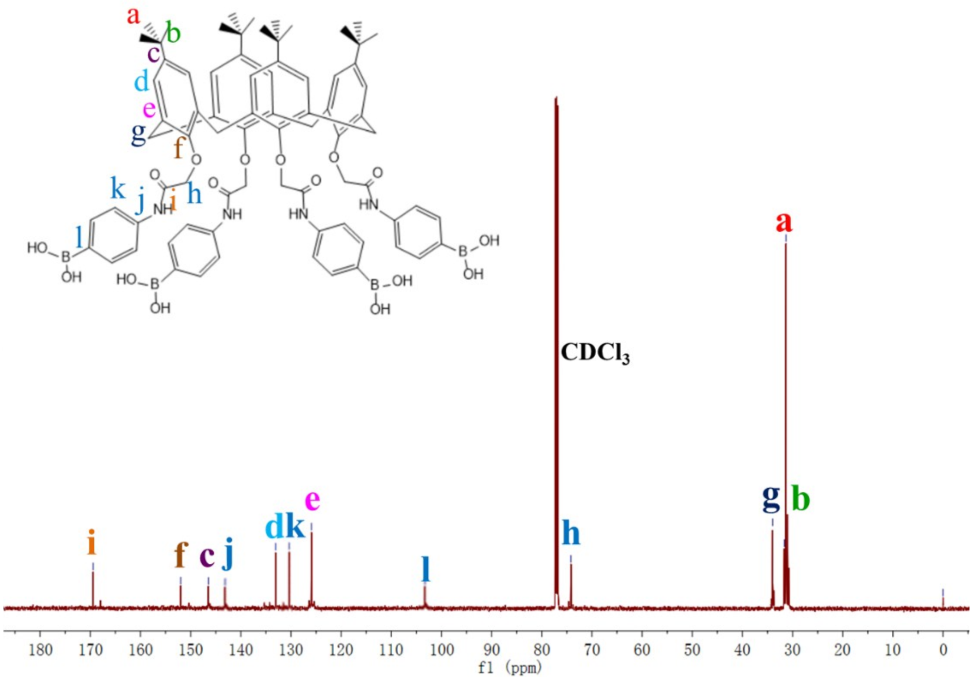
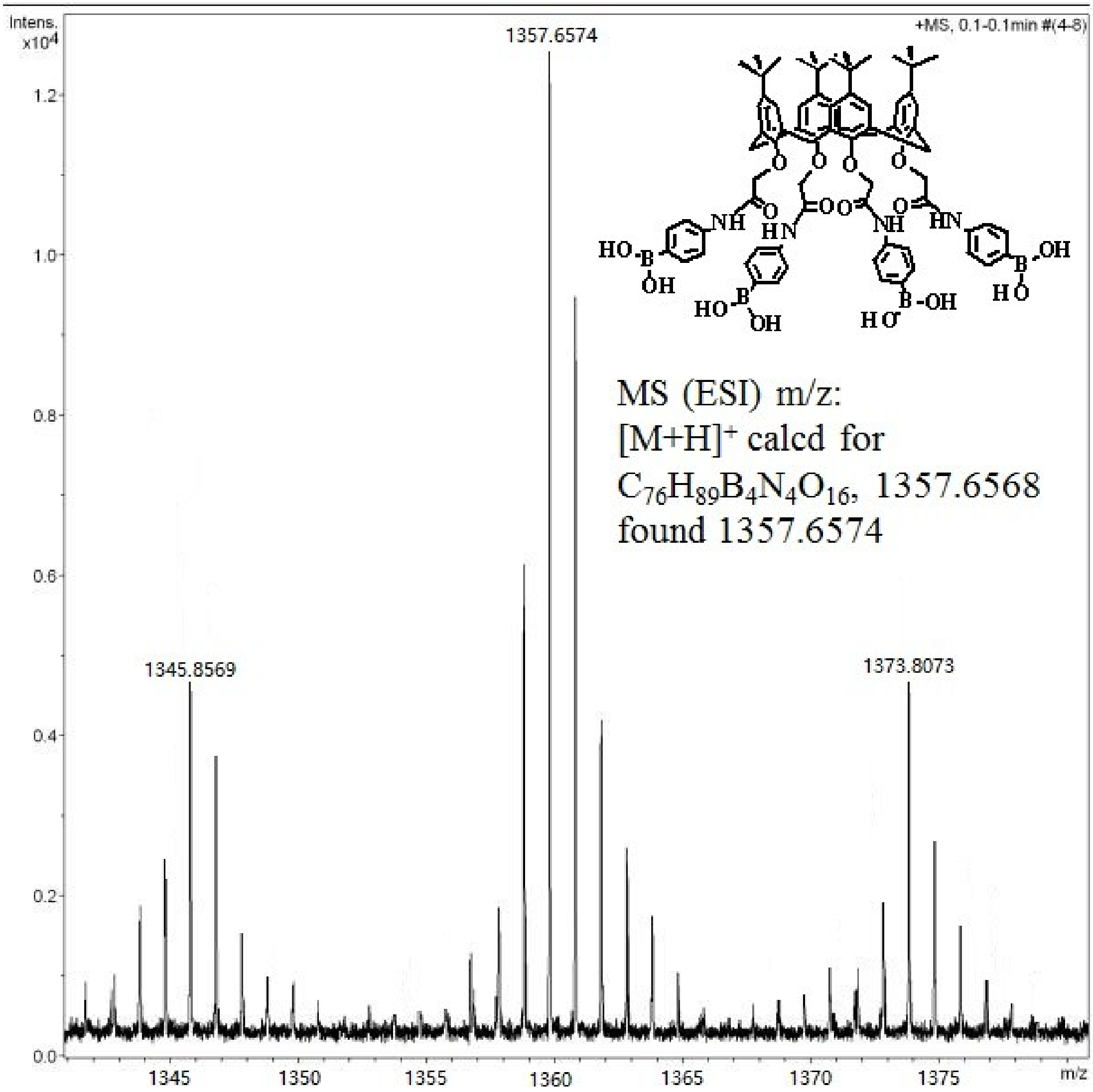


Figure S8. ^{13}C NMR spectrum of CTBA



MS (ESI) m/z:
$[M+H]^+$ calcd for $C_{76}H_{89}B_4N_4O_{16}$, 1357.6568
found 1357.6574

Figure S9. ESI mass spectrum of compound CTBA.

3. References

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