Switchable Foam Control by a New Surface-active Ionic Liquid

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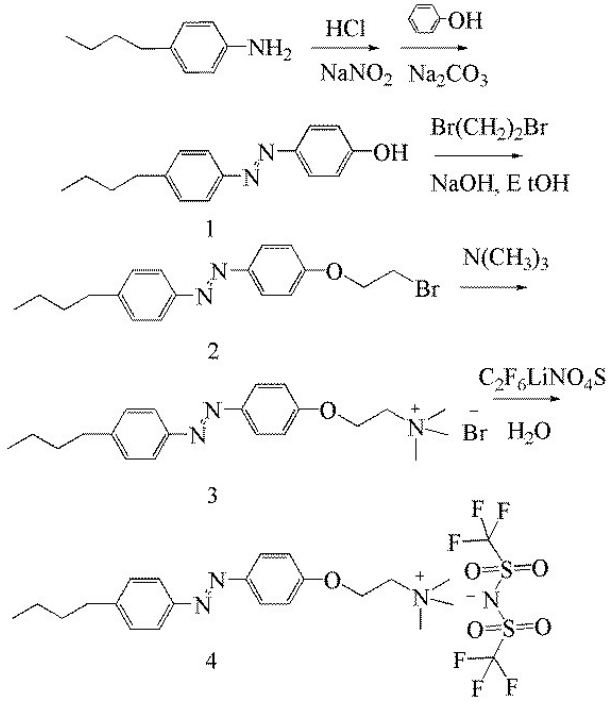
The purities and the suppliers of the chemicals used in the synthesis of [BAzoTMA][NTf_2] are listed in Table S1. The synthesis route of [BAzoTMA][NTf_2] is shown in scheme S1.

Table S1 Purities and suppliers of chemicals

Chemical [a]	supplier	Purity [b]
4-butylaniline	Aladdin	0.99
Sodium nitrite	Sinopharm Chemical Reagent Co.	0.99
Phenol	Aladdin	0.99
Sodium carbonate	Sinopharm Chemical Reagent Co.	0.98
1,2-dibromoethane	Aladdin	0.98
Trimethylamine	Aladdin	0.35 [c]
Lithium bis(trifluoromethane sulfonyl)imide	Aladdin	0.99
DTAB	Aladdin	0.99

[a] all chemicals are used as received; [b] mass fraction; [c] 35% mass fraction in aqueous solution.



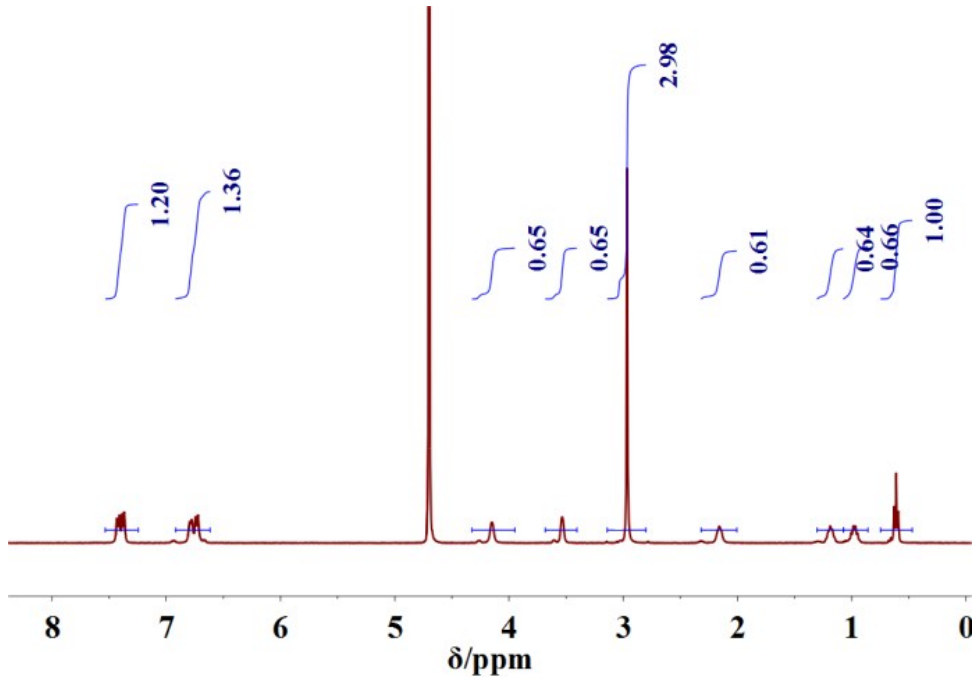
Scheme S1. Synthesis route of [BAzoTMA]-[NTf_2]

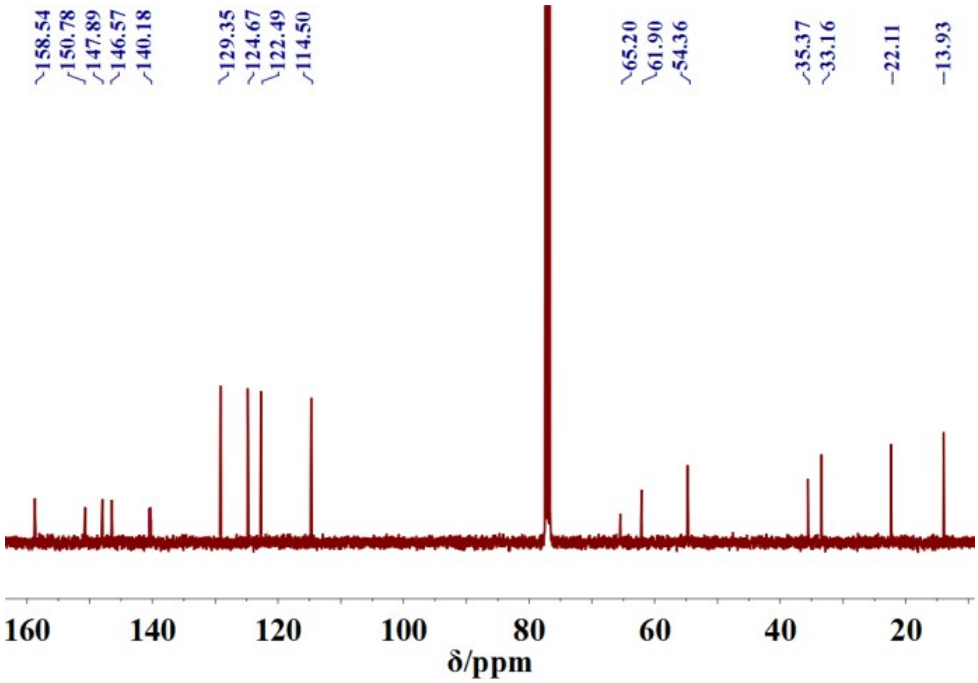
Synthesis of [BAzoTMA]Br, [DTA][NTf_2] and [BAzoTMA][NTf_2]: 15ml concentrated HCl aqueous solution was added into the round-bottom flask containing 50mmol 4-butylaniline placed in an ice bath. Then 50mmol sodium nitrite and 10ml cold water were added to the mixture and stirred for 1 hour with temperature being controlled near 0℃. Thereafter, 50mmol phenol and 120mmol sodium carbonate were dissolved in 15ml water and added to the above solution followed by stirred for 1 hour. The resulting precipitate (product 1) was filtered and washed by water and hexane for three times and dried under vacuum at 60℃ for 12 hours. 20mmol product 1 and 50mmol sodium hydroxide were dissolved in 100ml ethanol (solution I). 60mmol 1,2-dibromoethane was dissolved in 20ml ethanol and the solution was added slowly into solution I, followed by refluxed at 80℃ for 8 hours. The precipitate NaBr was removed and the filtrate was set for one day. The precipitate from the

filtrate was then filtered and washed by water and ethanol, and dried under vacuum to obtain product 2. Thereafter, 5mmol product 2 was dissolved in 100ml THF and trimehtylamine gas was bubbled through the solution for 30 min, and the solution was left for 2 days in room temperature. The precipitate from the solution was filtered and washed by THF for three times, and dried under vacuum. Thereafter, the raw product was recrystallized twice from ethanol to get product 3 (**[BAzoTMA]Br**). 1mmol product 3 and 1.2mmol lithium bis(trifluoromethane sulfonimide) were dissolved in 50ml CH_2Cl_2 and stirred in room temperature for 24h. The mixture was centrifuged and the transparent liquid was collected. Then, the CH_2Cl_2 was rotary evaporated and the obtained solid was dried under vacuum at 60℃ to get orange colored solid product 4 (**[BAzoTMA] [NTf_2]**). The total yield was about 20%.

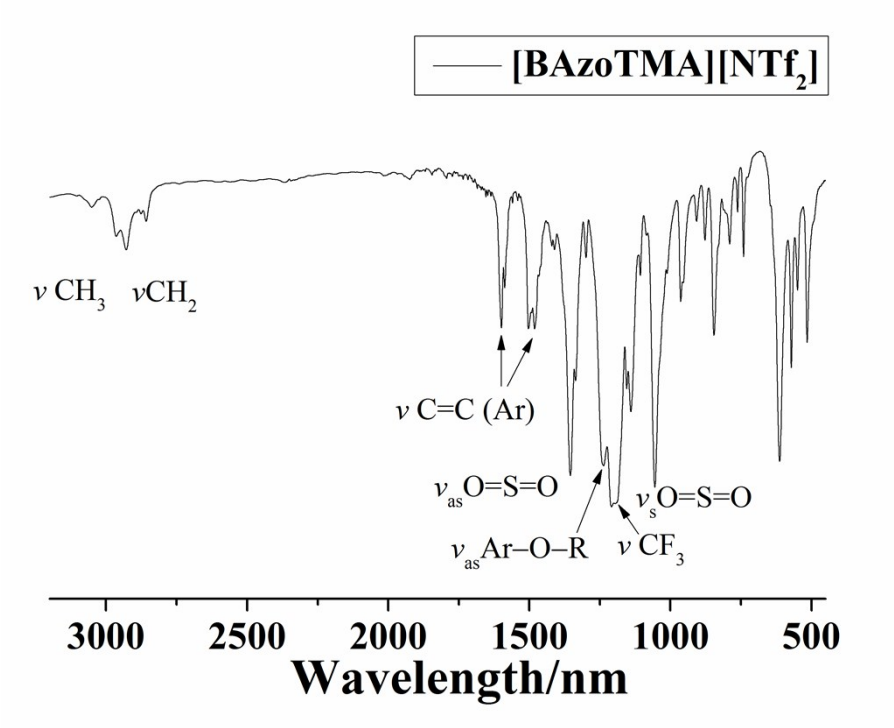
The synthetic route of **[DTA][NTf_2]** is as follow: 2.0 mmol DTAB and 2.2 mmol Lithium bis(trifluoromethane sulfonimide) were dissolved in 50ml deionized water and stirred in room temperature for 2h. Then, the precipitate was collected by filtration and washed by deionized water, and dried under vacuum for 24h to get the white solid product. The total yield was about 80%.

The product **[BAzoTMA][NTf_2]** was characterized by ^{1}HNMR ((D_2O, 400MHz): δ_{ppm} 0.61 (t, 3H), 0.9-1.05 (m, 2H), 1.1-1.25 (m, 2H), 2.16 (t, 2H), 2.95 (s, 9H), 3.55 (t, 2H), 4.15 (t, 2H), 6.50-7.50 (m, 8H)) and by ^{13}CNMR (($CDCl_3$, 500MHz): δ_{ppm} 13.93, 22.11, 33.16, 35.37, 54.36, 61.90, 65.20, 114.50, 122.49, 124.67, 129.35, 140.17, 146.57, 147.89, 150.78, 158.54).

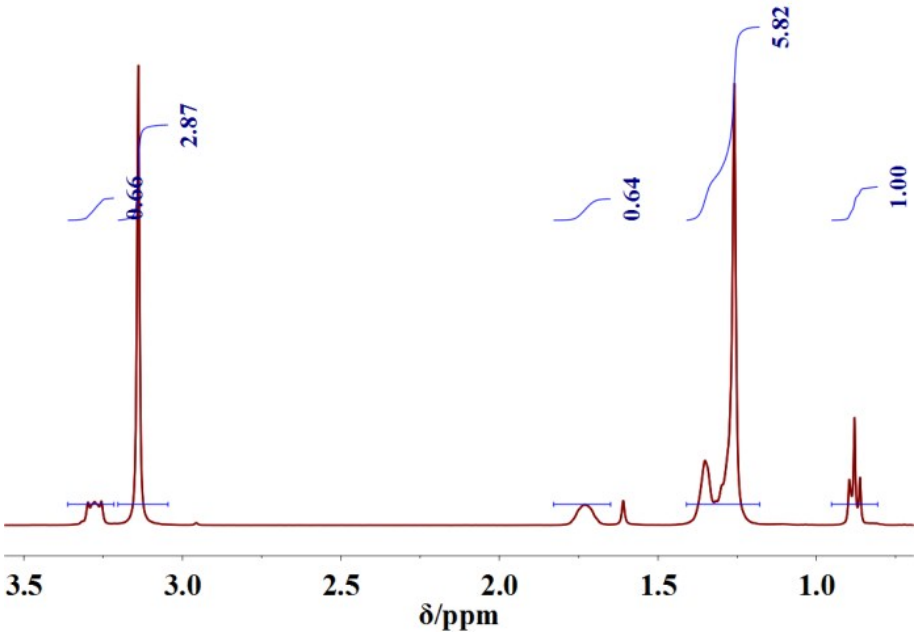

1.20
1.36
0.65
0.65
2.98
0.61
0.64
0.66
1.00
8
7
6
5
4
3
2
1
0
δ/ppm


158.54
150.78
147.89
146.57
140.18
129.35
124.67
122.49
114.50
65.20
61.90
54.36
35.37
33.16
22.11
13.93
160
140
120
100
80
60
40
20
δ/ppm

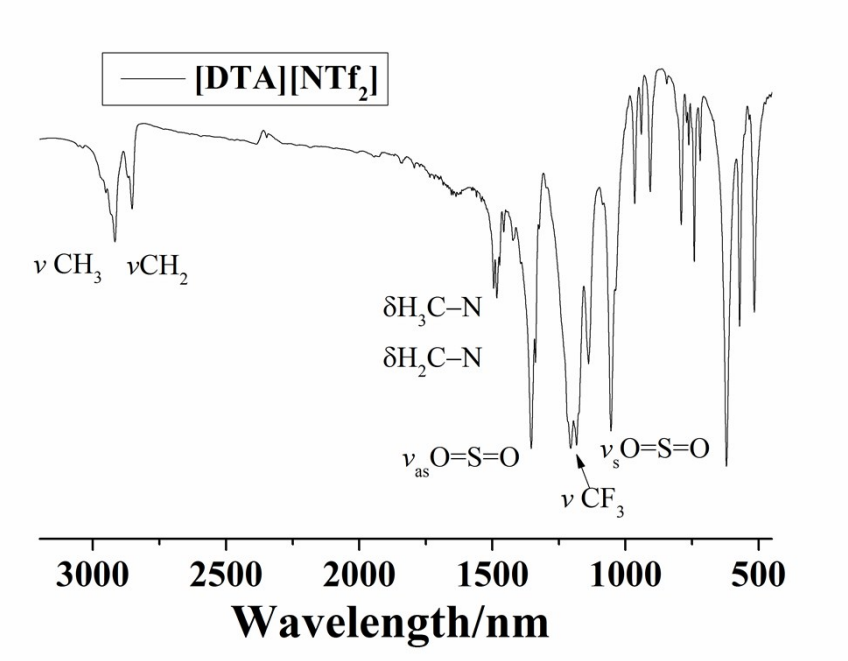
The FT-IR spectrum of **[BAzoTMA][NTf$_2$]:**



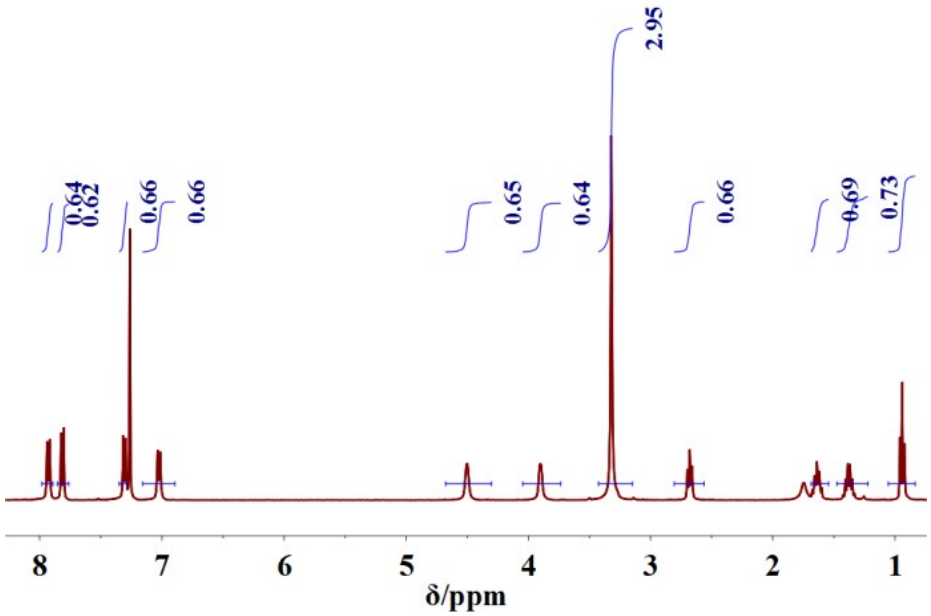
The product **[DTA][NTf$_2$]** was characterized by ^{1}HNMR ($CDCl_3$, 400MHz): δ_{ppm} 0.88 (t, 3H), 1.26-1.35 (m, 18H), 1.73 (t, 2H), 3.14 (s, 9H), 3.28 (t, 2H).



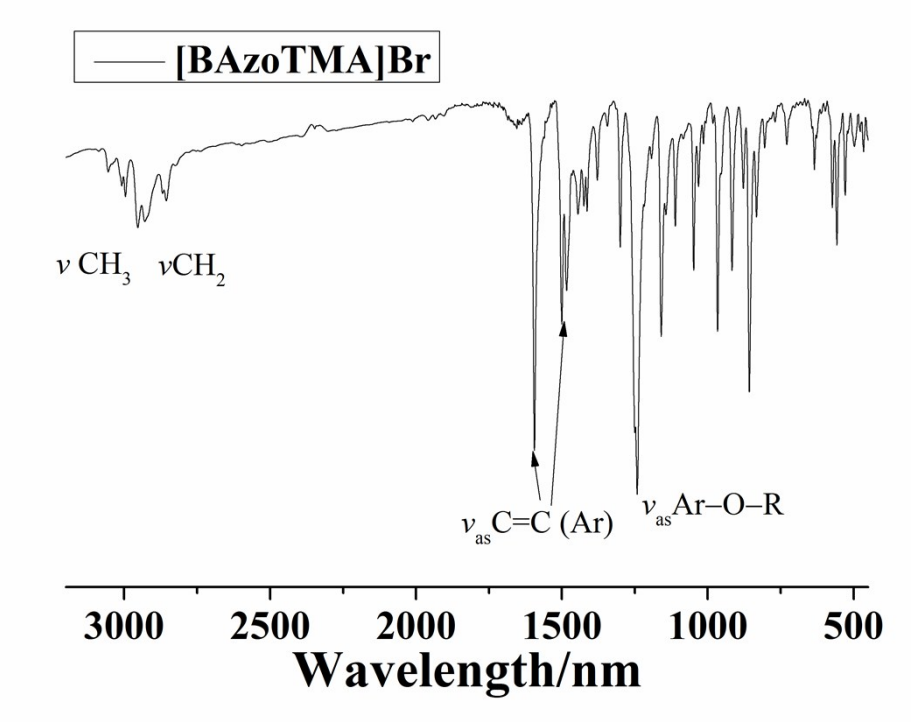
The FT-IR spectrum of **[DTA][NTf$_2$]:**



The product **[BAzoTMA]Br** was characterized by ^{1}HNMR ($CDCl_3$, 400MHz): δ_{ppm} 0.94 (t, 3H), 1.37-1.39 (m, 2H), 1.62-1.64 (m, 2H), 2.68 (t, 2H), 3.32 (s, 9H), 3.5 (t, 2H), 3.9 (t, 2H), 7.01-7.94 (m, 8H).



The FT-IR spectrum of **[BAzoTMA]Br:**



***Measurements of the Foamability and Foam Stability*.** Samples were shaken sufficiently in cylindrical tubes with plugs in five minutes. The heights of the foam and the solution were measured immediately after shake, therefore, the relative height of foam to the solution was calculated. The foam stability was studied by measurement of the time needed when the foam's height reduced to half of the original one.

***Measurement of Contact Angle*:** About 50μL aqueous solution of surfactant sample was dropped carefully onto a piece of polyethylene slide and allowed to equilibrate for 1min. Thereafter, the contact angle was determined by JC2000C, Zhongchen Digital Technic Apparatus Co. Ltd., Shanghai.

***Conductivity measurement*:** Conductivity measurements were performed with a digital conduct-meter supplied by Leici Co. Shanghai. The sample aqueous

solution was transferred into a cell which was placed in a water bath with temperature being controlled at 298.15±0.1K. The conductivity was measured after the sample being equilibrated for about 15 mins.

***Polarization Modulation infrared Reflection Absorption Spectroscopy*:** PM-IRRAS experiments were carried out with KSV NIMA BiolinSci, Sweden. About 1ml of the sample was dropped onto an ITO glass. Then the wavelength of 1000 ~ 2000 cm^{-1} was scanned and the corresponding spectrum was recorded.

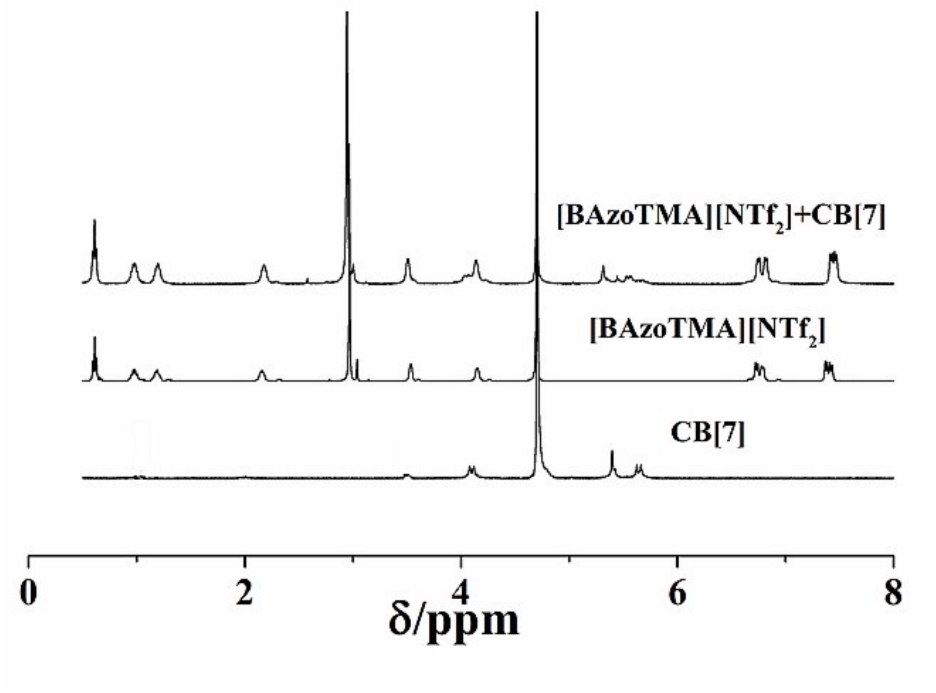


Figure S1. ^{1}HNMR spectrum profiles of CB[7] (0.05mM), **[**BAzoTMA][NTf_2] (0.05mM), and **[**BAzoTMA][NTf_2] (0.05mM) + CB[7] (0.05mM) in D_2O

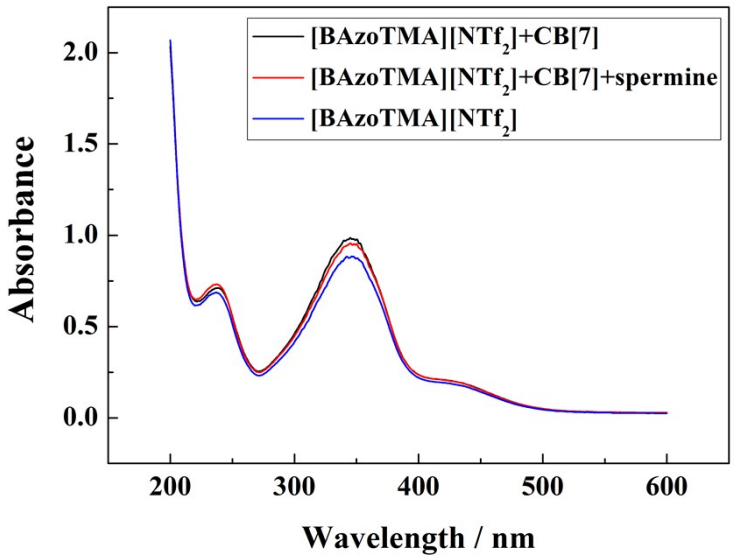


Figure S2. UV-vis spectra of **[**BAzoTMA][NTf_2] (0.05mM), **[**BAzoTMA][NTf_2] (0.05mM) + CB[7] (0.05mM), and **[**BAzoTMA][NTf_2] (0.05mM) + CB[7] (0.05mM) + spermine (0.05mM).

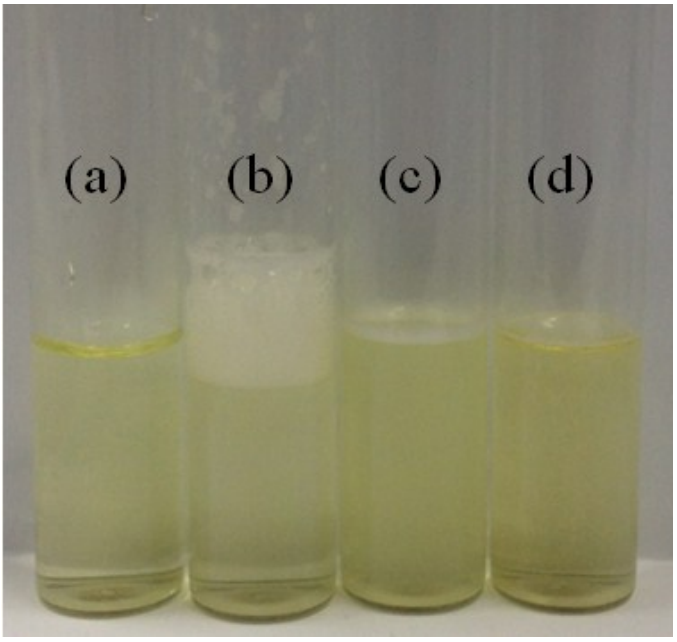


Figure S3. Photos of aqueous solutions of (a) **[**BAzoTMA][NTf_2]; (b) **[**BAzoTMA][NTf_2] + CB[7]; (c) **[**BAzoTMA][NTf_2] + CB[7] + 1-octanol; and (d) further addition of CB[7] to aqueous solution (c).