Supplementary Information for

Highly Stable Polysulfone Anion Exchange Membranes Incorporated with Bulky Alkyl Substituted Guanidinium Cation

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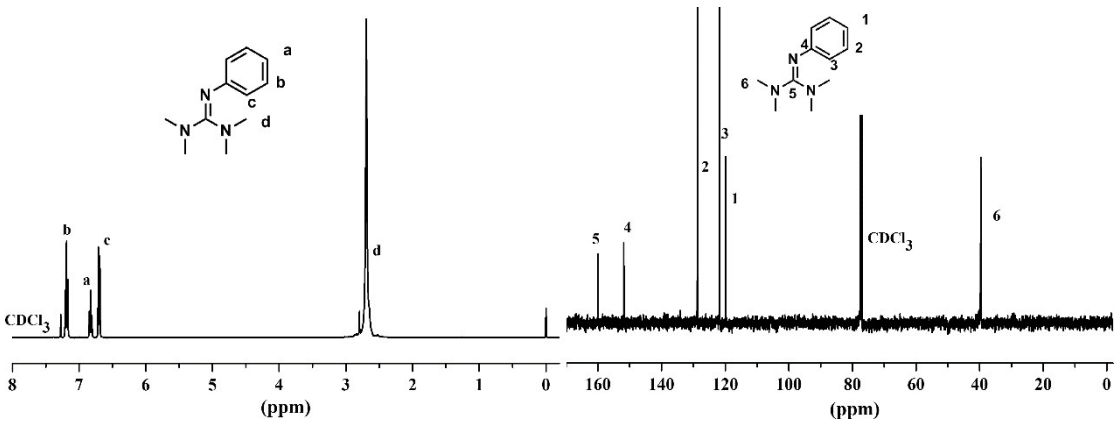
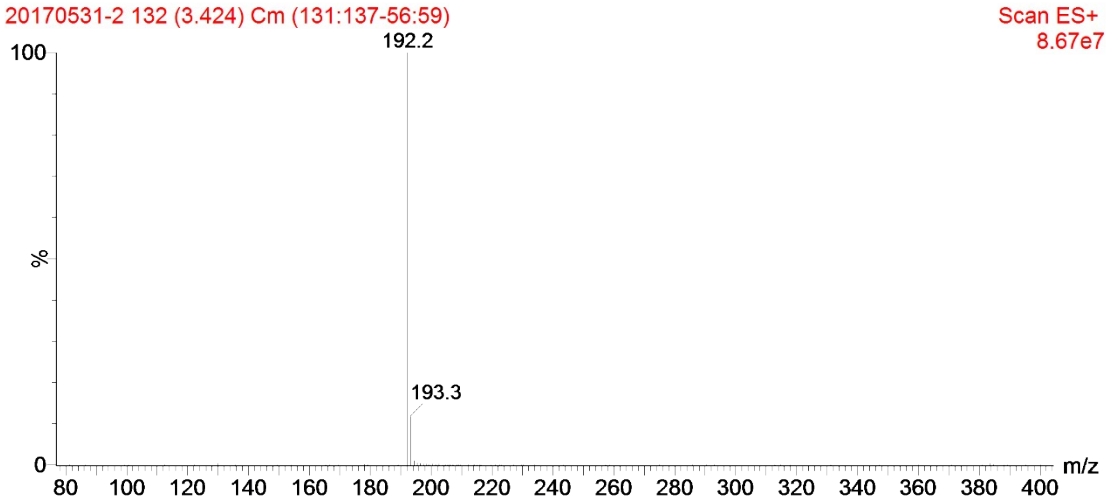
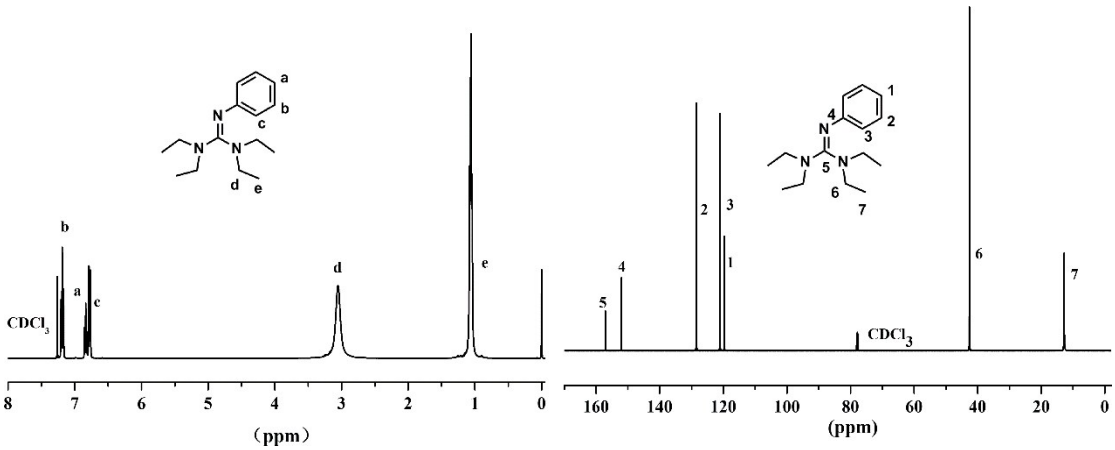
Contents

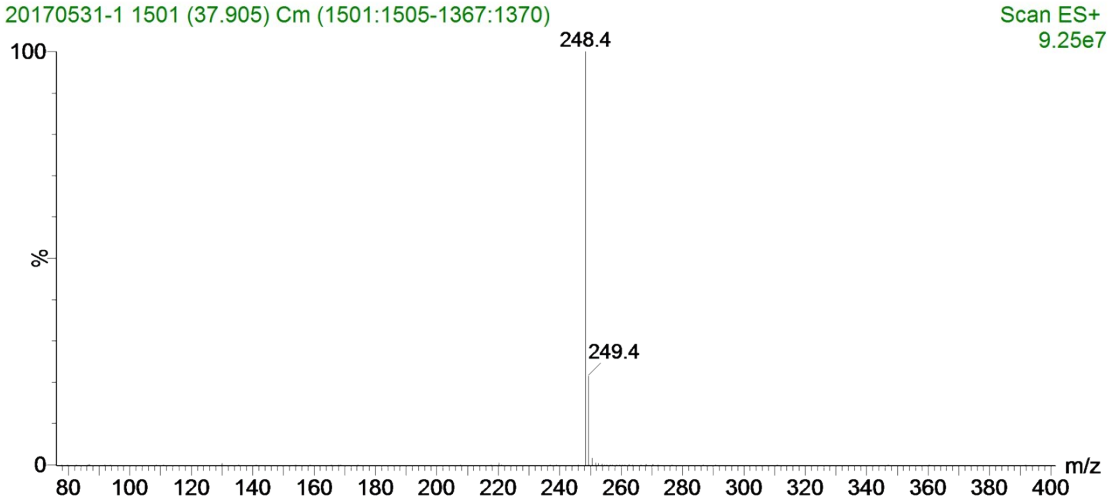
***1,1,3,3-tetramethyl-2-phenylguanidine*(G1)** yield: 97.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 (2H, t), 6.83 (1H, t), 6.69 (2H, d), 2.69 (12H, s); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 159.40, 151.48, 128.31, 121.53, 119.56, 39.63 ; HRMS (ESI): 192.2 $[M+H]^+$.



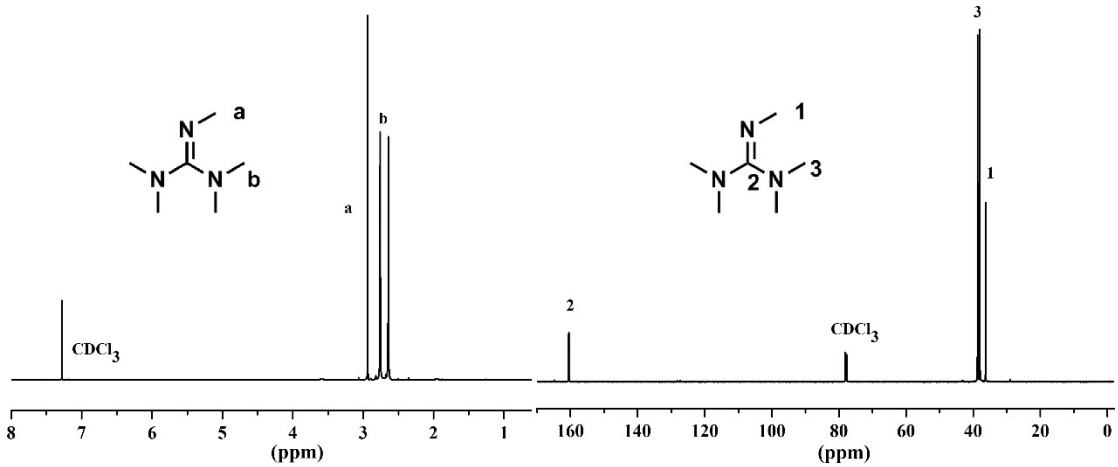


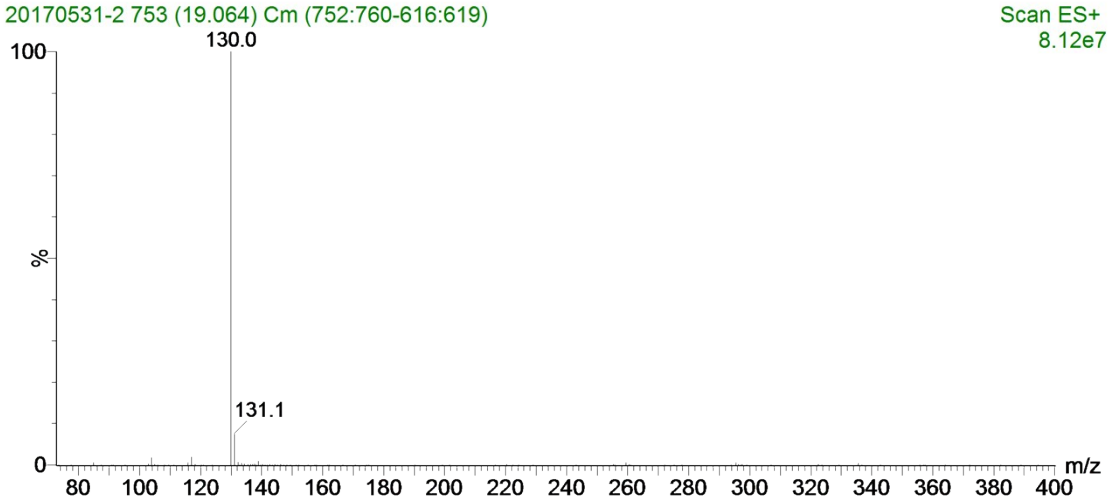
***1,1,3,3-tetraethyl-2-phenylguanidine*(G2)** yield: 94.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 (2H, t), 6.83 (1H, t), 6.77 (2H, d), 3.05 (8H, s), 1.04(12H, t); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 156.61, 151.83, 128.31, 121.08, 119.56, 42.11, 12.8; HRMS (ESI): 248.4 $[M+H]^+$.



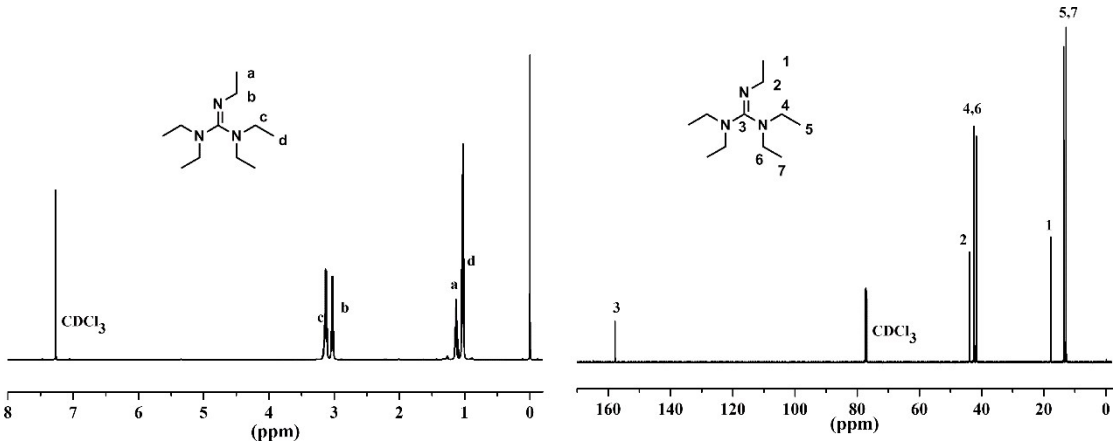


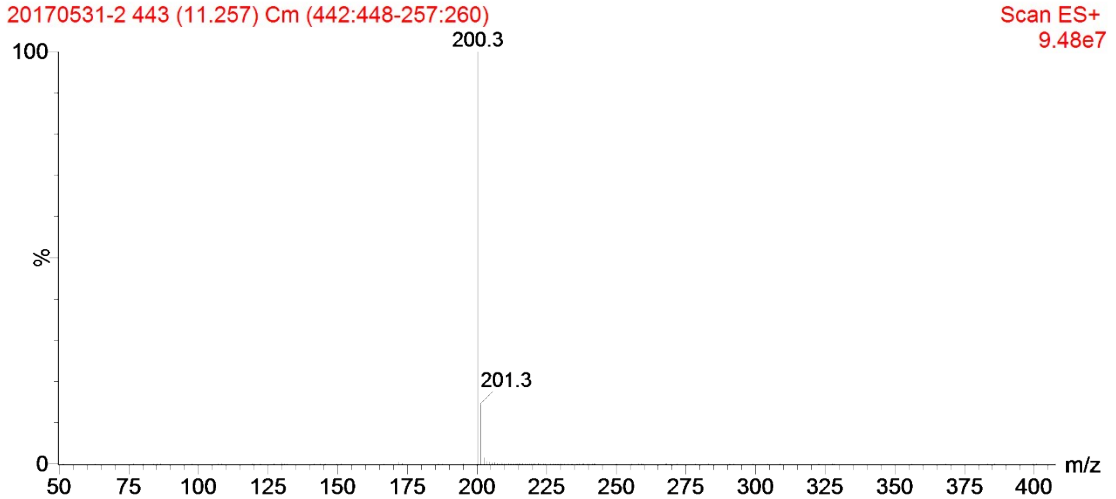
***1,1,2,3,3-pentamethylguanidine*(G3)** yield: 90.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.92 (3H, s), 2.74 (6H, s), 2.64 (6H, s); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 160.49, 38.06, 35.73; HRMS (ESI): 130.0 $[M+H]^+$.



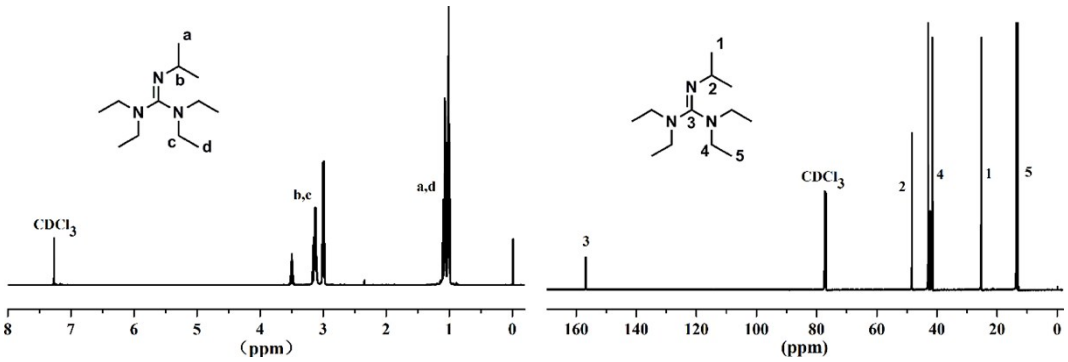


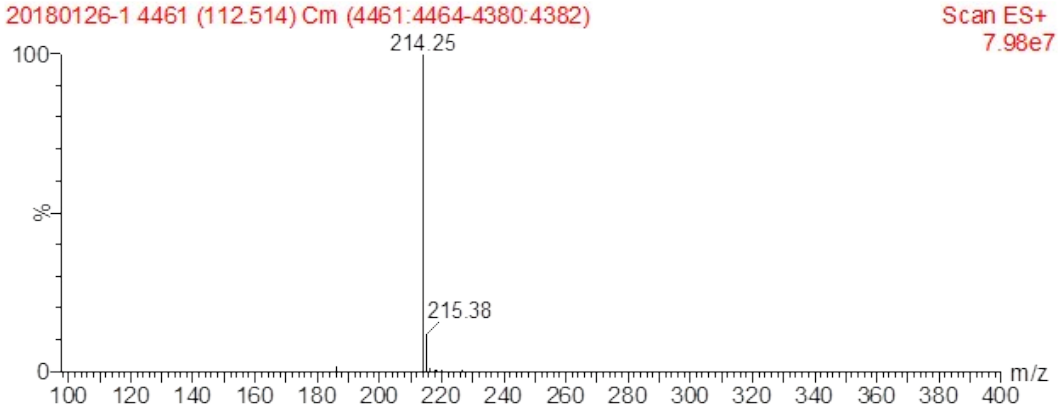
***1,1,2,3,3-pentaethylguanidine*(G4)** yield: 97.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.01(2H, t), 3.11 (8H, mq), 1.01(8H, m), 1.13 (2H, d); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 157.78, 43.76, 42.13, 41.32, 17.42, 13.46, 11.84 ; HRMS (ESI): 200.3 $[M+H]^+$.



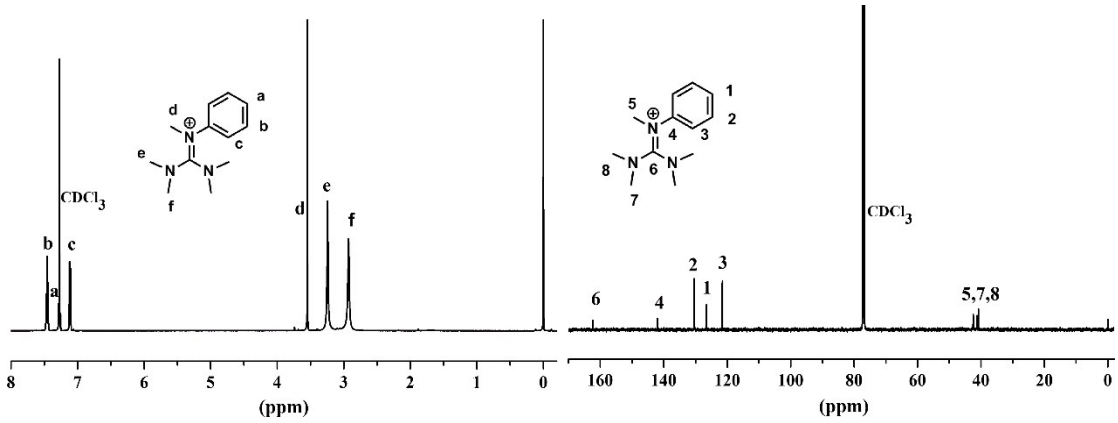


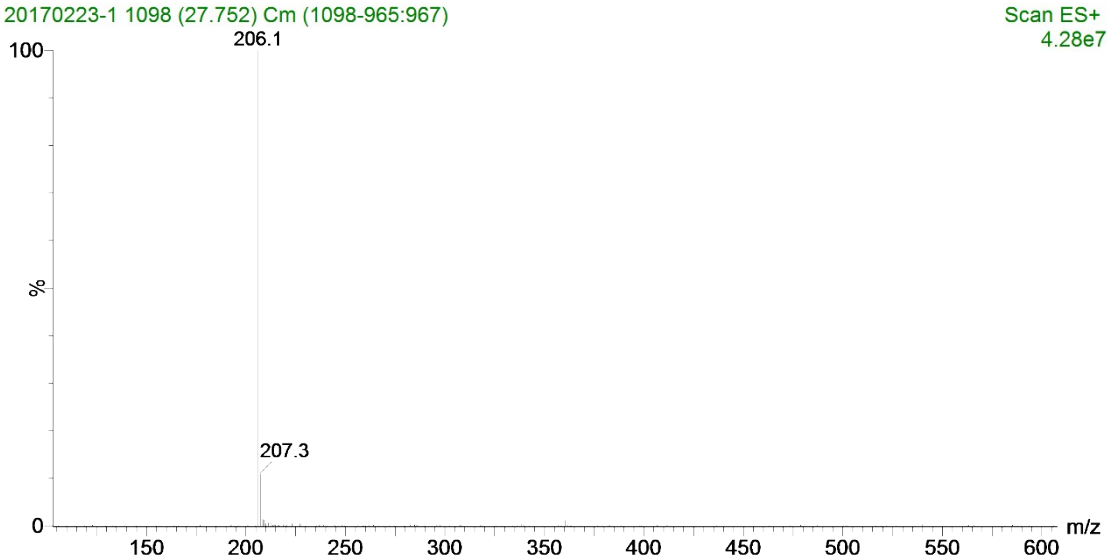
1,1,3,3-tetraethyl-2-isopropylguanidine **(G5)** yield: 93.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.49 (1H, m), 2.98-3.11 (8H, m), 1.02(18H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 156.91, 48.03, 43.07, 25.41, 13.62; HRMS (ESI): 214.25 $[M+H]^+$.



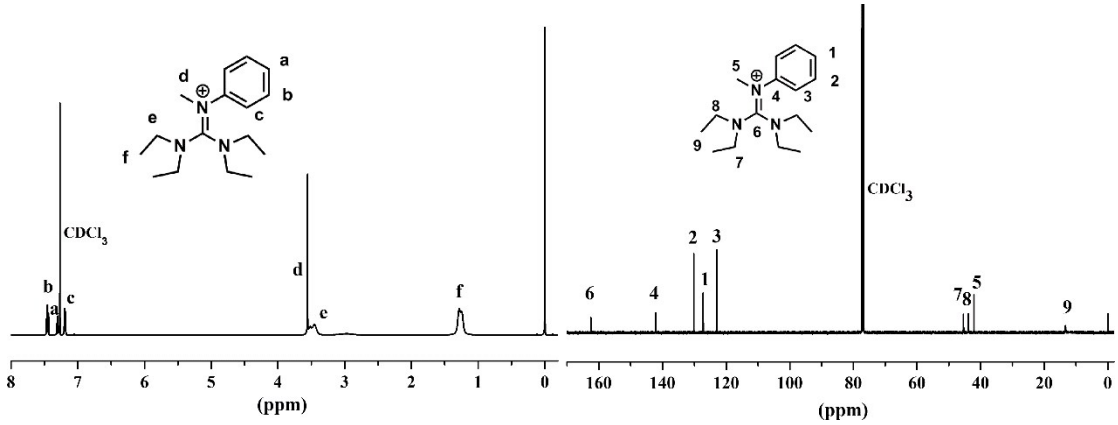


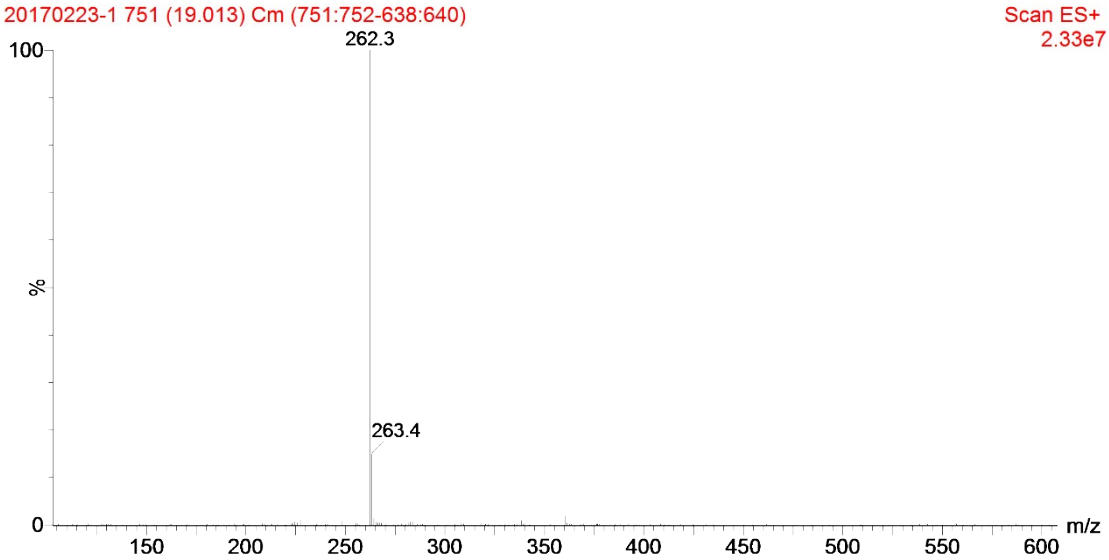
***N-(bis(dimethylamino)methylene)-N-methylbenzenaminium iodide*(M1),** yield: 99.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (2H, t), 7.27 (1H, t), 7.11 (2H, d), 3.55 (3H, s), 3.24(6H, s), 2.93(6H, s); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 162.33, 142.04, 130.38, 126.52, 121.52, 42.44, 41.23, 40.81; HRMS (ESI): 206.1 $[M]^+$.



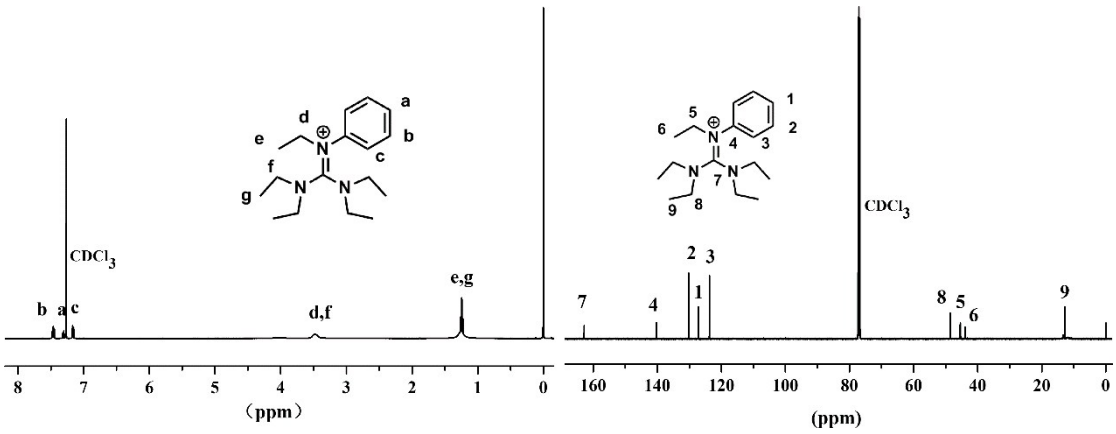


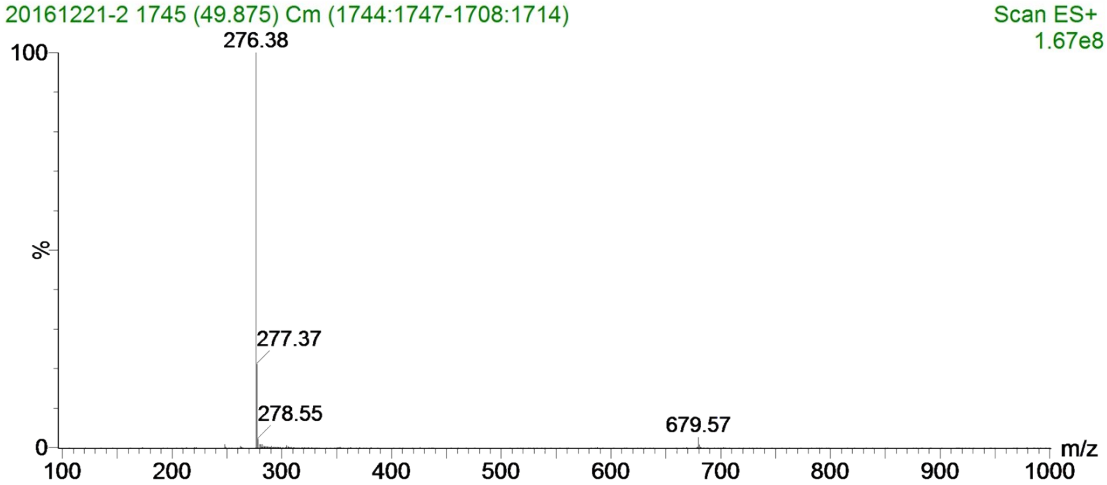
***N-(bis(diethylamino)methylene)-N-methylbenzenaminium iodide*(M2),** yield: 98.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 (2H, t), 7.30 (1H, t), 7.18 (2H, d), 3.56 (3H, s), 3.45(8H, s), 1.28(12H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 162.54, 142.15, 130.18, 127.20, 123.00, 45.40, 43.83, 42.09, 13.32; HRMS (ESI): 262.3 $[M]^+$.



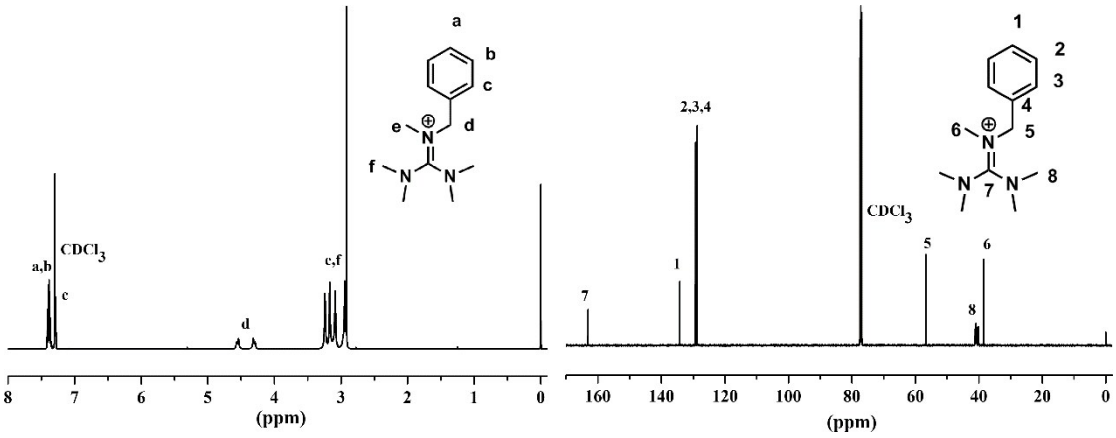


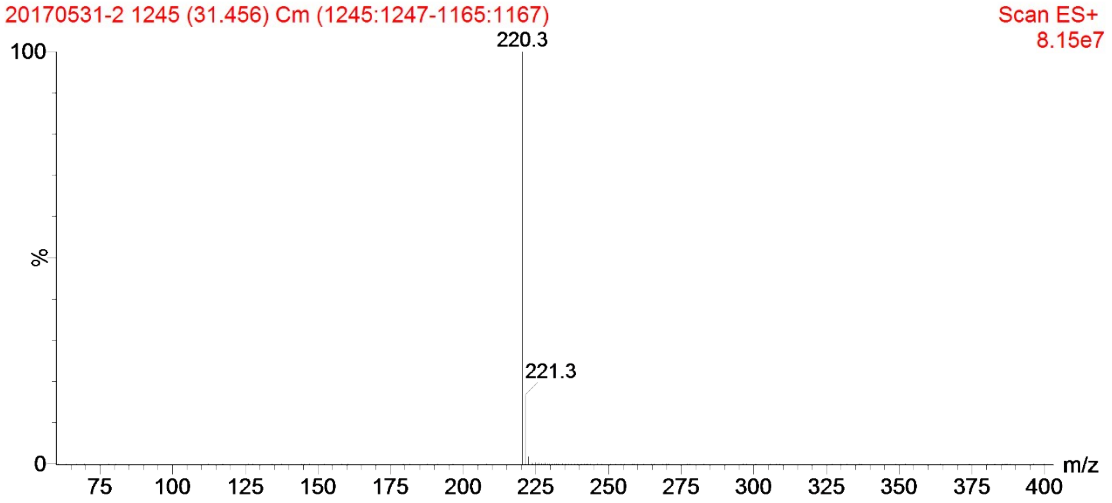
***N-(bis(diethylamino)methylene)-N-ethylbenzenaminium iodide* (M3),** yield: 99.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (2H, t), 7.30 (1H, t), 7.17 (2H, d), 3.48 (10H, s), 1.24(15H, t); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 162.83, 140.30, 130.16, 127.15, 123.72, 48.56, 45.42, 43.93, 13.26; HRMS (ESI): 276.38 $[M]^+$.



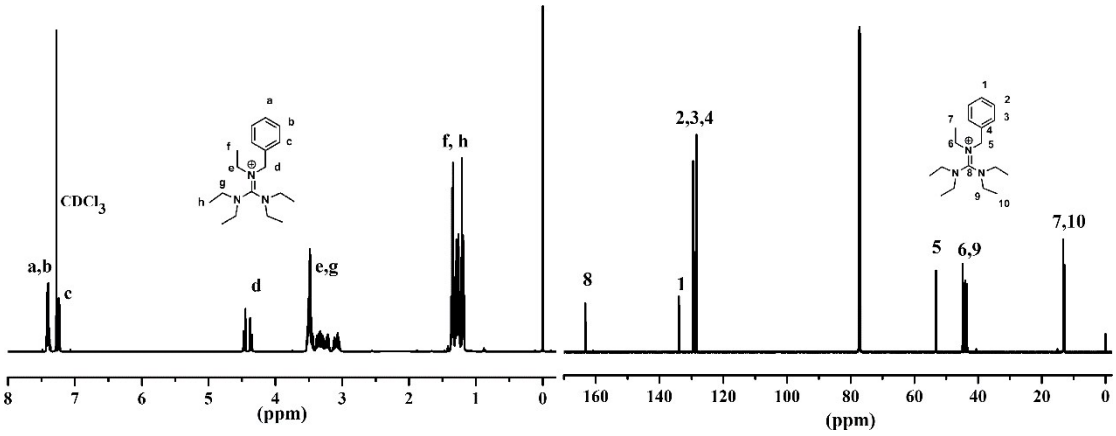


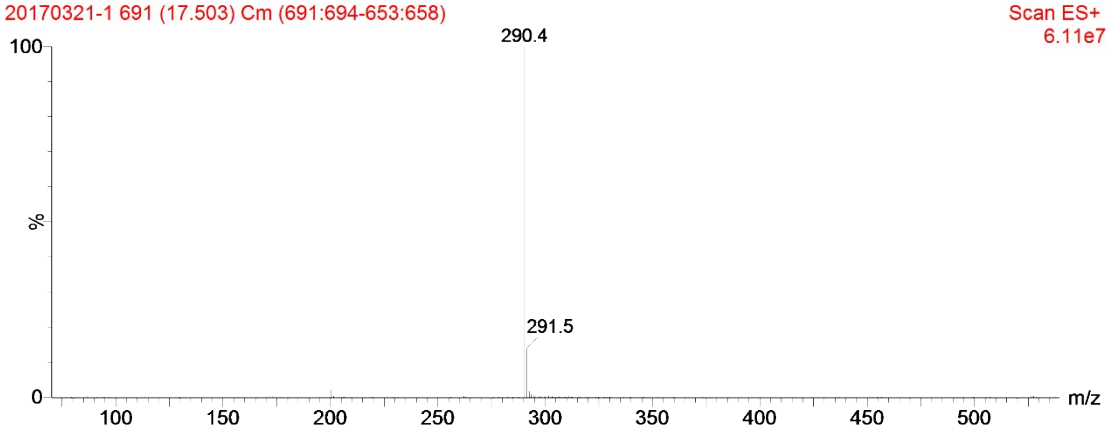
N-(bis(dimethylamino)methylene)-N-methyl-1-phenylmethanaminium chloride **(M4),** yield: 95.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.20-7.40 (5H, m), 4.30 (2H, q), 4.45 (2H, q), 2.93-3.18 (15H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 163.01, 134.21, 129.10, 127.92, 56.54, 40.13, 38.55 ; HRMS (ESI): 220.3 $[M]^+$.



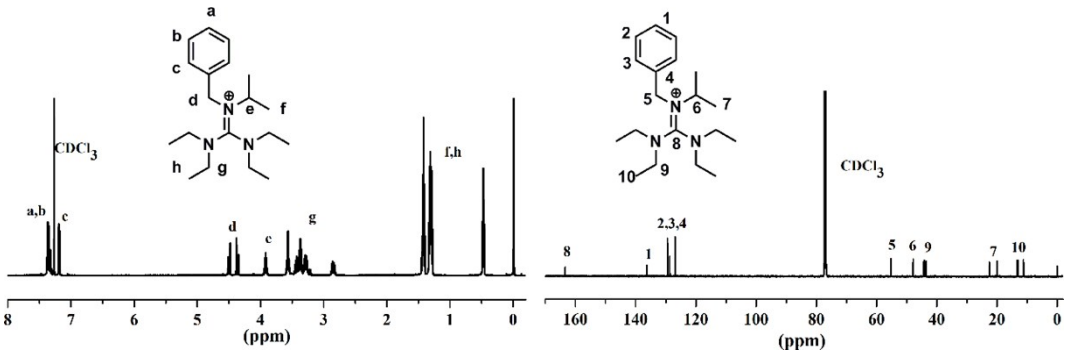


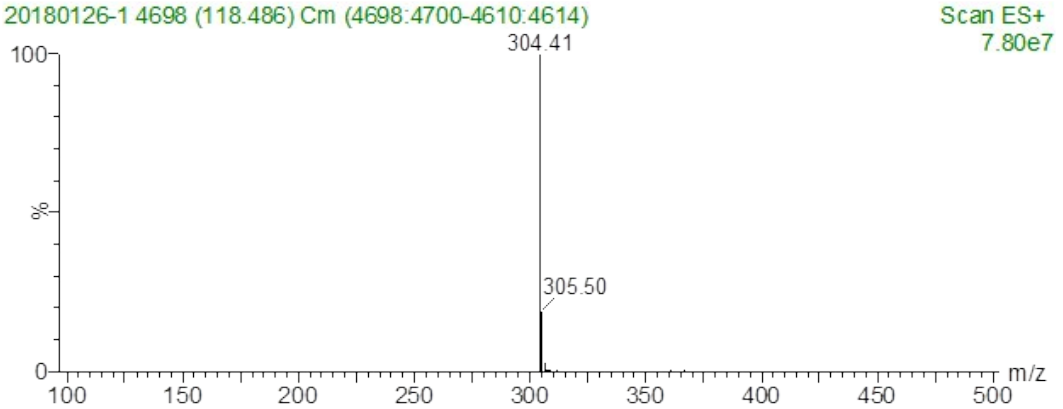
N-benzyl-N-(bis(diethylamino)methylene)ethanaminium chloride **(M5),** yield: 98.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (3H, m), 7.23 (2H, d), 4.45 (2H, q), 3.00-3.55 (10H, m), 1.15-1.40(15H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 163.23, 133.89, 129.46, 129.15, 128.40, 53.27, 44.91, 44.03, 13.24,13.12 ; HRMS (ESI): 290.4 $[M]^+$.



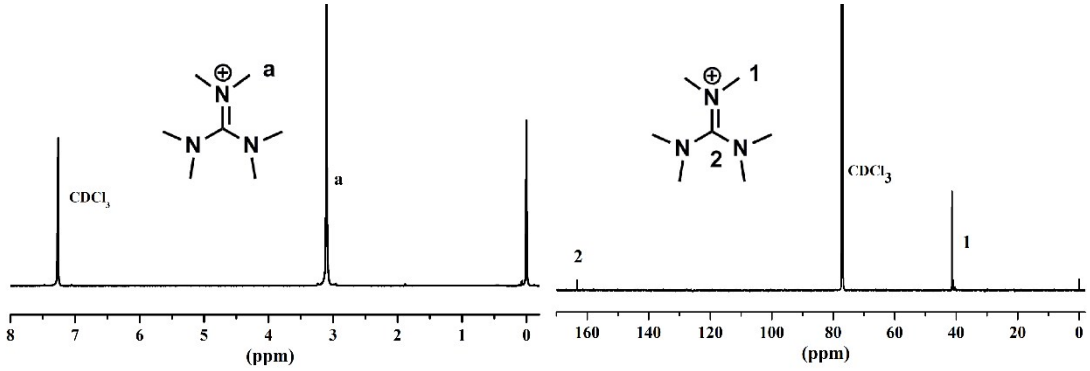


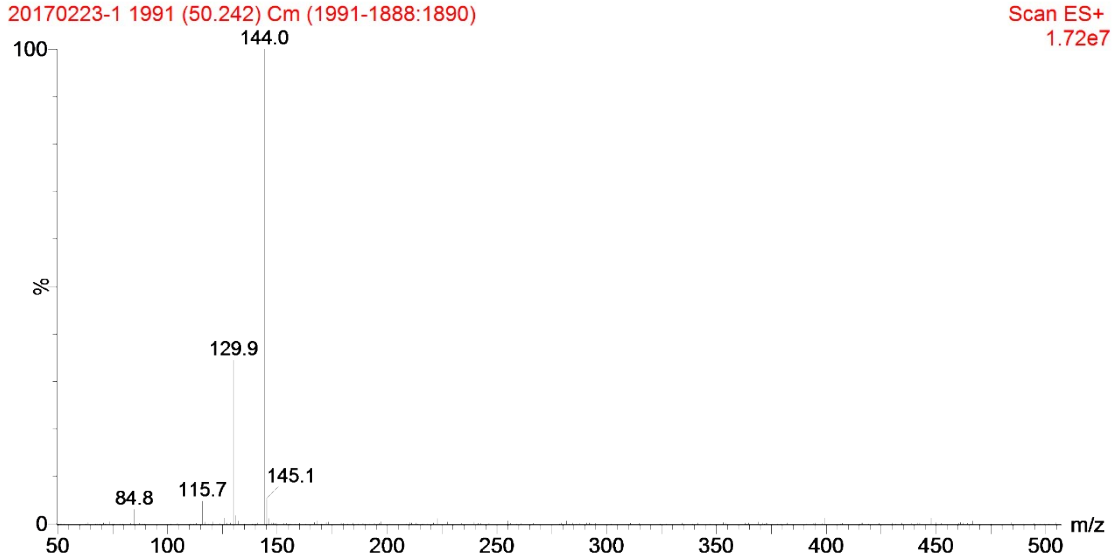
N-benzyl-N-(bis(diethylamino)methylene)propan-2-aminium chloride **(M6),** yield: 80.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (3H, m), 7.19 (2H, d), 4.48 (2H, q), 3.92 (1H, m), 2.85-3.57 (8H, m), 0.45-1.41(18H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 163.40, 135.91, 129.42, 128.79, 126.90, 55.33, 48.03, 44.03, 43.61, 22.06, 20.45, 12.88, 10.71 ; HRMS (ESI): 304.41 $[M]^+$.



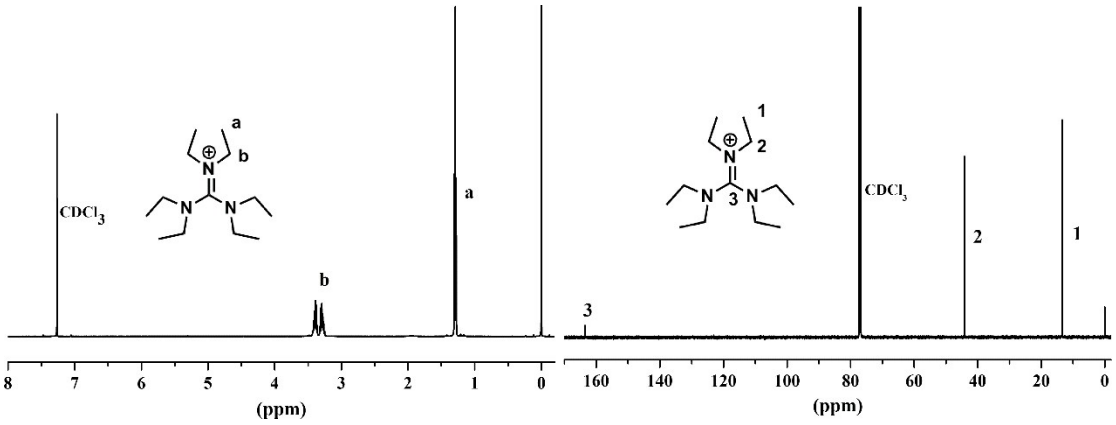


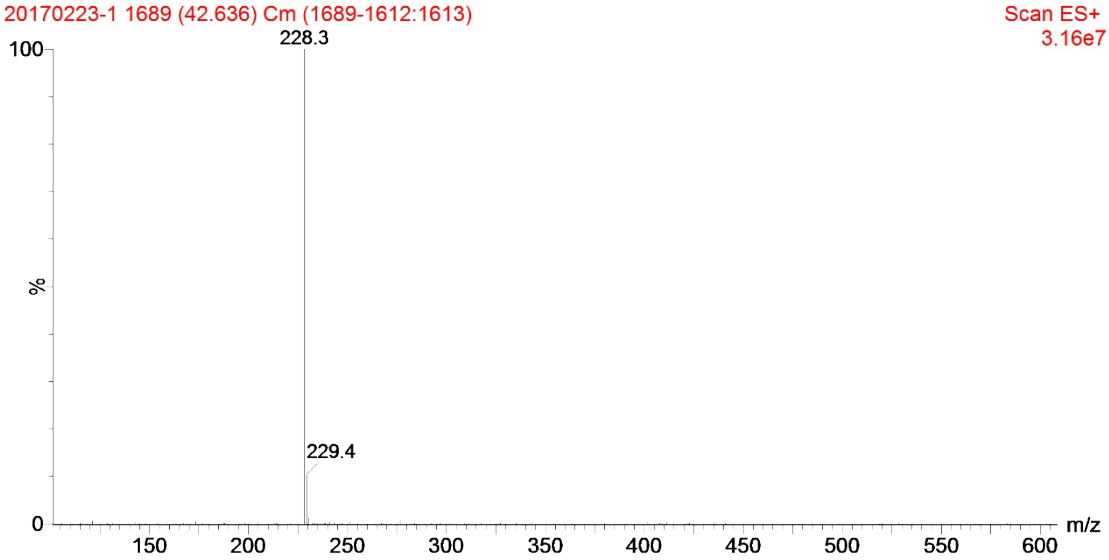
***N-(bis(dimethylamino)methylene)-N-methylmethanaminium iodide*(M7),** yield: 99.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.10 (12H, s); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 163.36, 41.41; HRMS (ESI): 144.0 $[M]^+$.



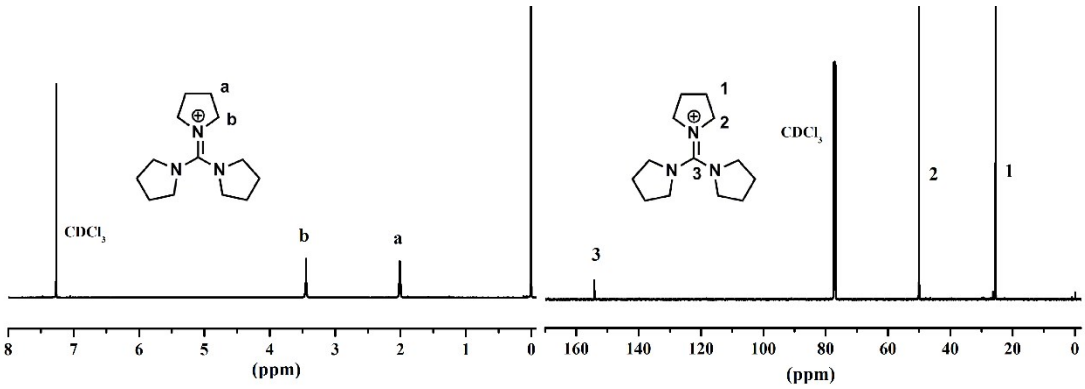


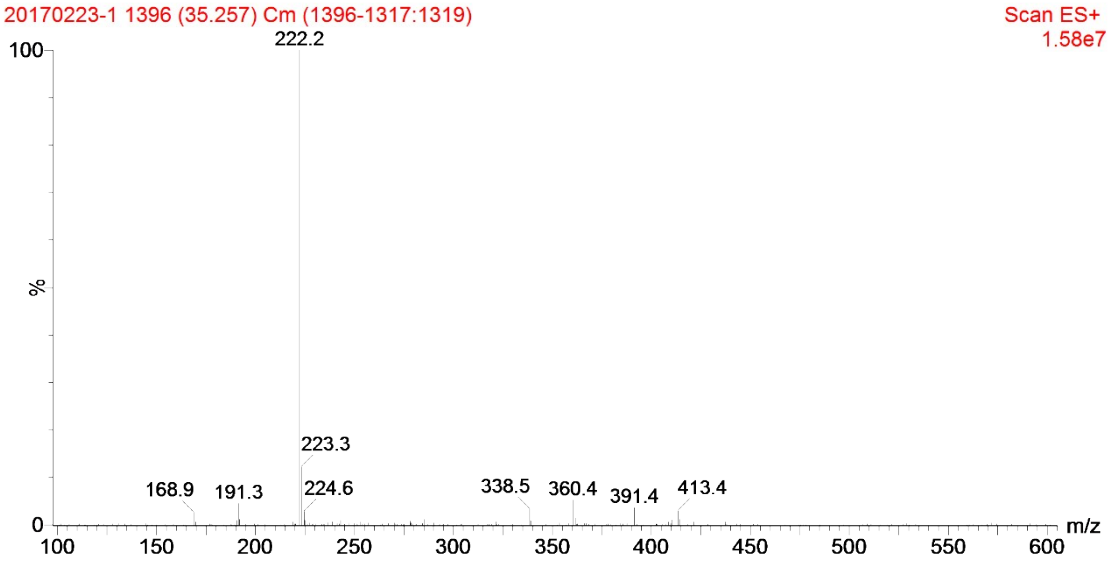
***N-(bis(diethylamino)methylene)-N-ethylethanaminium iodide*(M8),** yield: 97.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.38 (12H, m), 1.29 (18H, t); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 163.54, 44.21, 13.39; HRMS (ESI): 228.3 $[M]^+$.



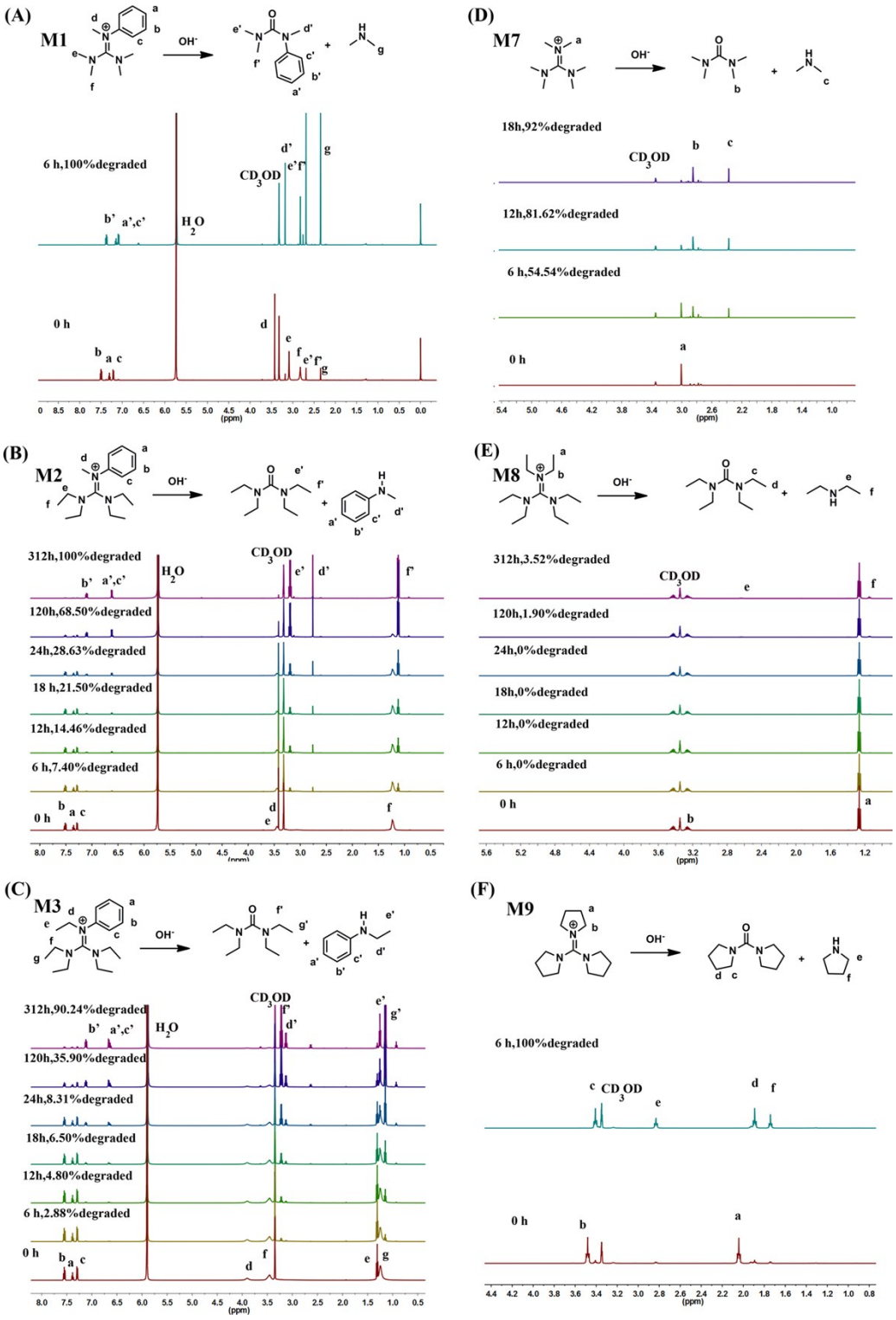


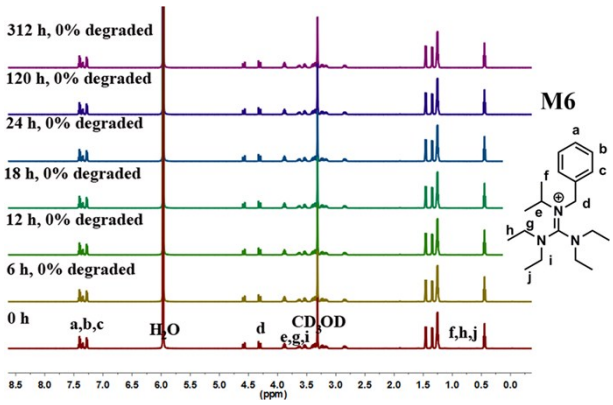
***1-(di(pyrrolidin-1-yl)methylene)pyrrolidin-1-ium chloride*(M9),** yield: 99.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.56 (8H, m), 2.02 (8H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 154.18, 26.32; HRMS (ESI): 222.2 $[M]^+$.





The degradation of guanidinium model compounds M1–M3, M6 and M7–M9:


(A)
M1
OH-
6 h,100%degraded
0 h
CD3OD
H2O
(ppm)
(B)
M2
OH-
312h,100%degraded
120h,68.50%degraded
24h,28.63%degraded
18 h,21.50%degraded
12h,14.46%degraded
6 h,7.40%degraded
0 h
(C)
M3
OH-
312h,90.24%degraded
120h,35.90%degraded
24h,8.31%degraded
18h,6.50%degraded
12h,4.80%degraded
6 h,2.88%degraded
0 h
(D)
M7
OH-
18h,92%degraded
12h,81.62%degraded
6 h,54.54%degraded
0 h
(E)
M8
OH-
312h,3.52%degraded
120h,1.90%degraded
24h,0%degraded
18h,0%degraded
12h,0%degraded
6 h,0%degraded
0 h
(F)
M9
OH-
6 h,100%degraded
0 h



Theoretical calculations were carried out using Gaussian03 and Gaussian09 program packages.[1,2] The geometric optimization of both the structures and transition states were initially carried out at the B3LYP/6-31+G(d) level. The connection of each transition state to associated structures or fragments was checked by the intrinsic reaction coordinate (IRC) method at the B3LYP/6-31+G(d) level. To get detailed orbital information, we performed the natural bond orbital (NBO) analysis.

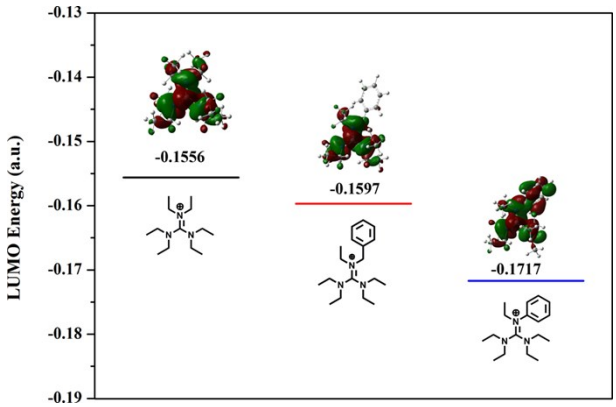
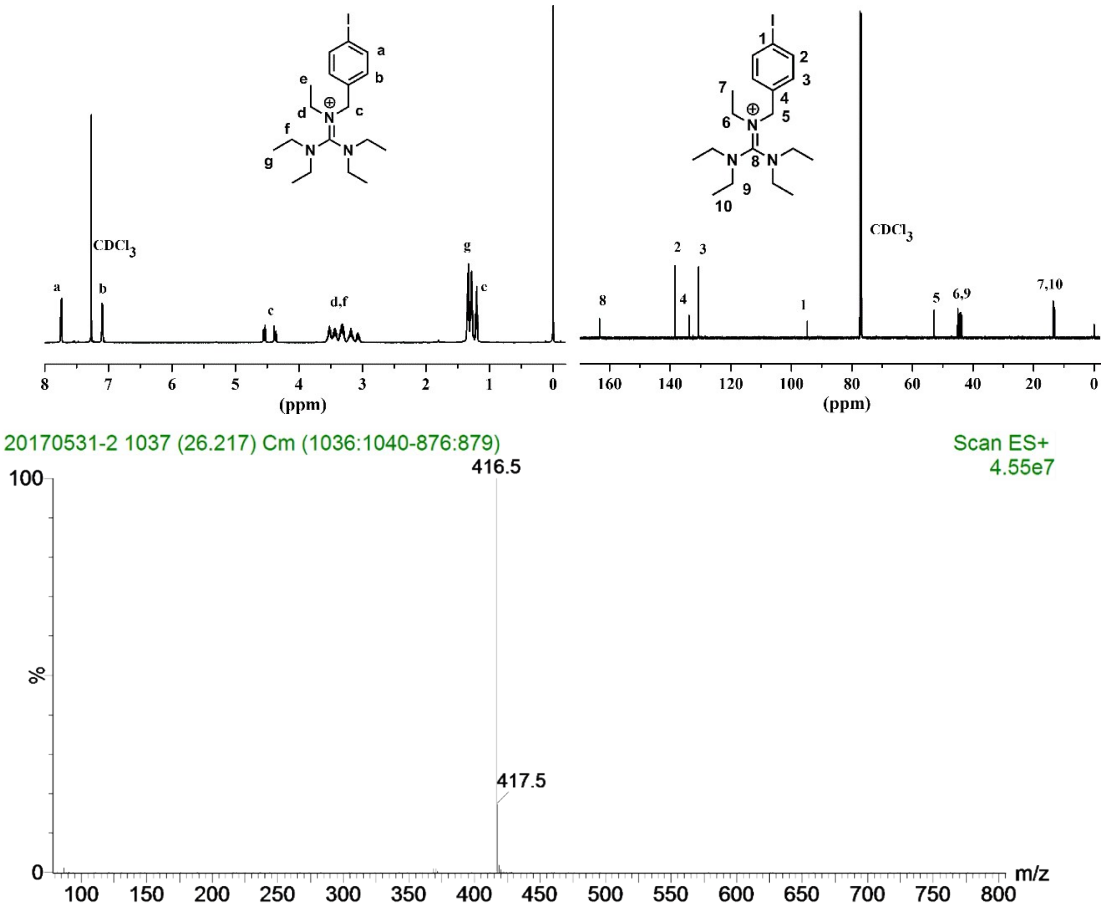


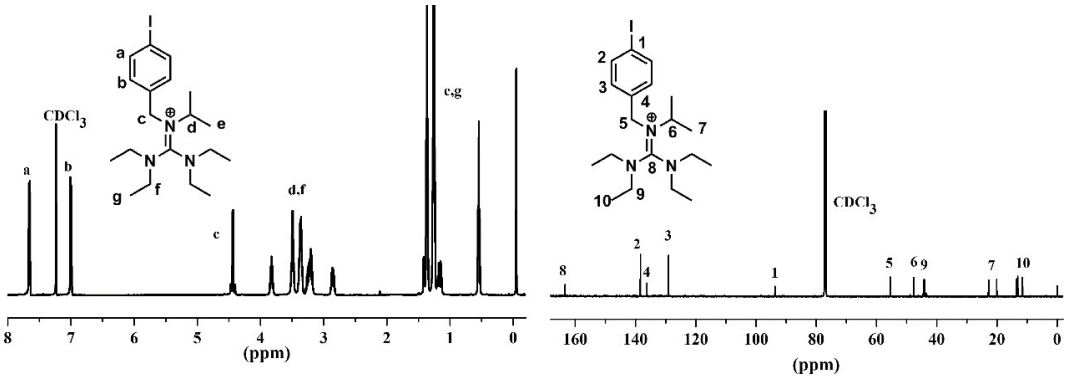
Figure S1. LUMO energy and isosurface of M3, M5 and M8.

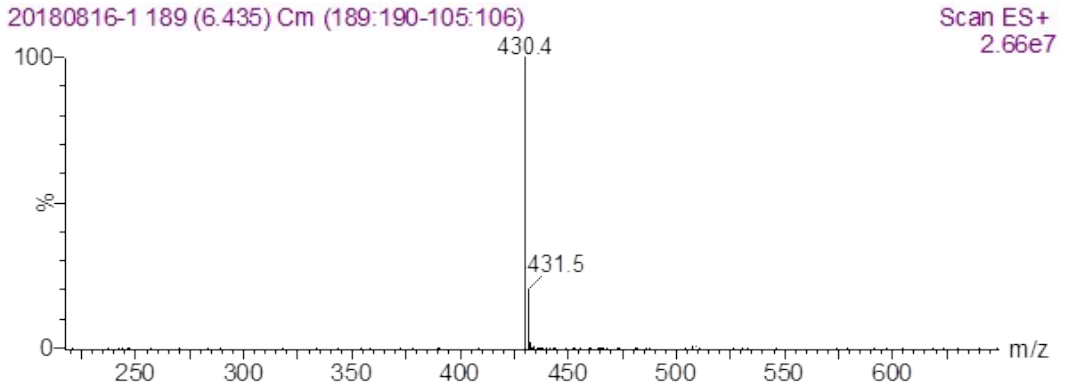
Guanidiniums functionalized aryl iodines: *N-(bis(diethylamino)methylene)-N-(4-iodobenzyl)ethanaminium* (GI-E). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (2H, d), 7.08 (2H, d), 4.52 (2H, q), 3.07-3.52 (10H, m), 1.19-1.35(15H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 163.32, 138.26, 133.48, 130.24, 94.37, 52.44, 44.51, 43.34, 13.42, 12.61; HRMS

(ESI): 416.5 $[M]^+$.

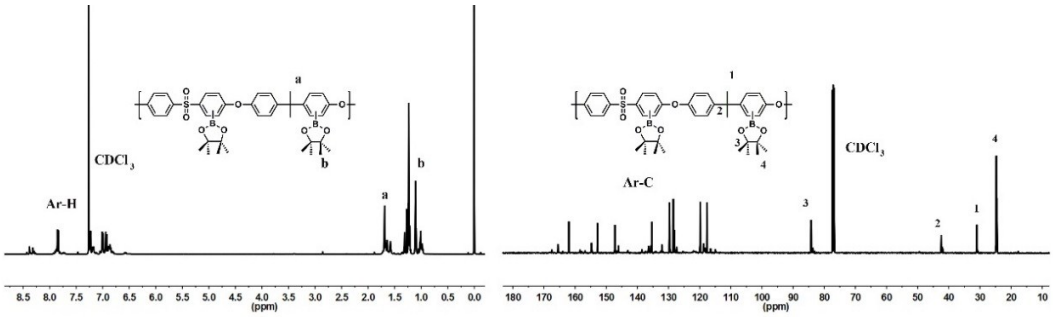


Guanidiniums functionalized aryl iodines: ***N-(bis(diethylamino)methylene)-N-(4-iodobenzyl)propan-2-aminium*** **(GI-P).** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65(2H, d), 7.01 (2H, d), 4.42 (2H, q), 2.84-3.84 (9H, m), 0.56-1.36(18H, m); ^{13}C NMR (100MHz, $CDCl_3$; ppm): δ 163.13, 138.61, 135.91, 129.15, 93.19, 55.60, 47.13, 43.88, 22.43, 20.18, 13.42, 11.80; HRMS (ESI): 430.4$[M]^+$.





PSU-Bpin. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30-8.38 (m, Ar-H), 7.74-7.90 (m, Ar-H),7.14-7.22 (m, Ar-H), 6.84-7.00 (m, Ar-H), 1.58-1.69 (m, 6H), 1.04-1.21 (20H, m); ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) 115.10-167.50 (Ar-C), 83.99, 42.31, 30.79, 24.49.



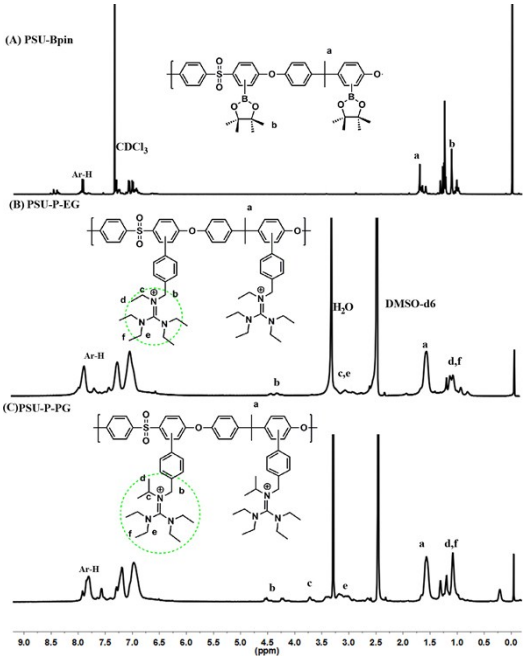


Figure S2. The ^{1}H NMR spectra of PSU-Bpin, PSU-P-EG and PSU-P-PG.

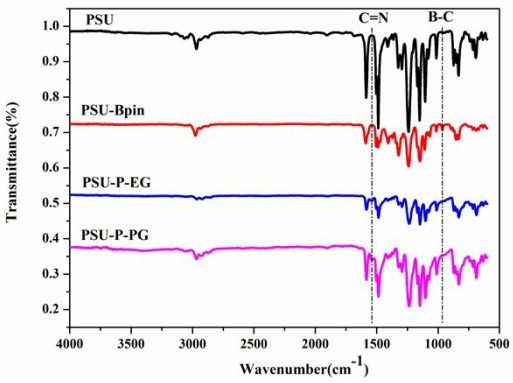


Figure S3. IR spectras of PSU-Bpin, PSU-P-EG and PSU-P-PG.

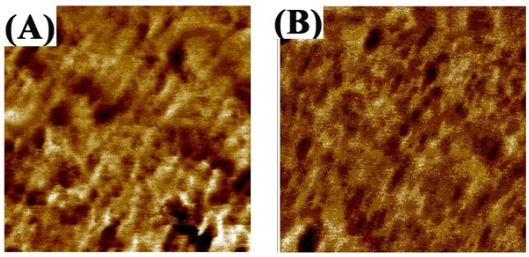


Figure S4. AFM phase images of (A) PSU-P-EG and (B) PSU-P-PG. Scan box dimensions are 500 nm × 500 nm.

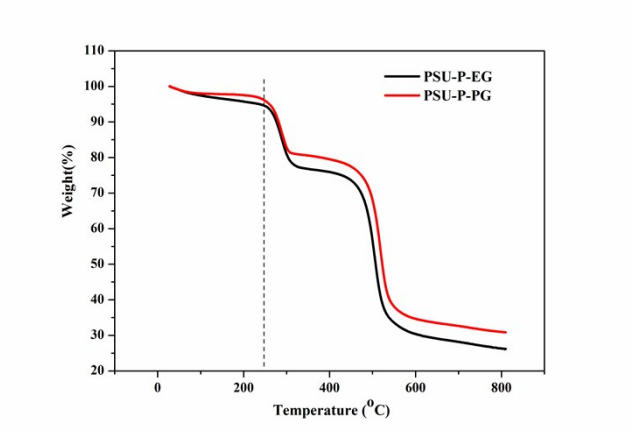


Figure S5. The TGA curves of PSU-P-EG and PSU-P-PG.

Table S1. Mechanical properties of PSU-P-EG and PSU-P-PG.

sample	TS[a] (MPa)	YM[a] (MPa)	EB[a](%)
PSU-P-EG	52.1	1489	9.9
PSU-P-PG	40.0	1160	5.7

[a] TS: Tensile strength; YM: Young's modulus; EB: Elongation at break.

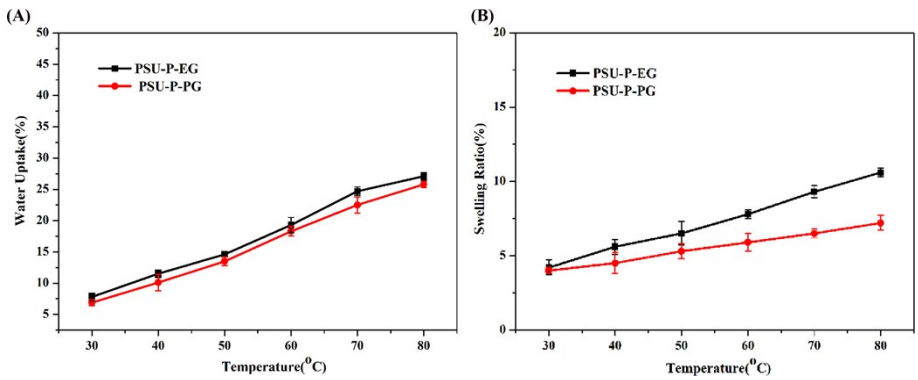


Figure S6. (A)Water uptake and (B) swelling ratio of PSU-P-EG and PSU-P-PG.

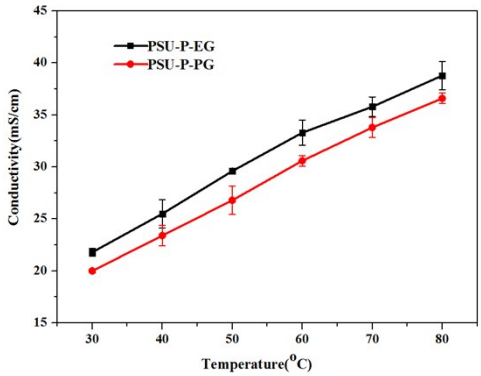


Figure S7. OH^- conductivity of PSU-P-EG and PSU-P-PG.

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