Supporting information

Synthesis of bio-based polycarbonate via one-step melt polycondensation of isosorbide and dimethyl carbonate by dual site-functionalized ionic liquid catalysts

Zifeng Yang,[a, b] *Xue Li,* [a] *Fei Xu,*[*, a, c] *Weiwei Wang,*[a] *Yongqing Shi,*[a] *Zhencai Zhang,*[a]

Wenjuan Fang,[a] *Lei Liu,*[a] *and Suojiang Zhang*[*, a, b]

[a] CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences,

Beijing 100190, China

[b] School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

[c] Zhongke Langfang Institute of Process Engineering, Langfang 065001, China

Corresponding authors

Email address:

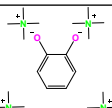
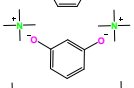
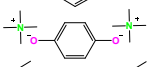
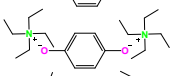
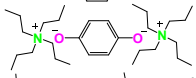
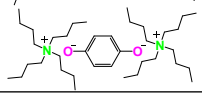
[*]Suojiang Zhang: sjzhang@ipe.ac.cn

[*] Fei Xu: fxu@ipe.ac.cn

Materials

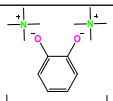
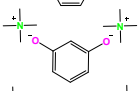
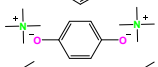
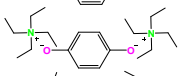
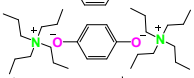
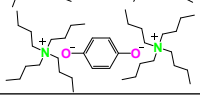
Dimethyl carbonate (99%), isosorbide (98%), phenol (PH, 99.5%), pyrocatechol (PY, 99%), resorcinol (RE, 99%), hydroquinone (HQ, 99%), tetramethylammonium hydroxide solution ([N_{1111}] OH, 25 wt % in H_2O), tetraethylammonium hydroxide solution ([N_{2222}] OH, 25 wt % in H_2O), tetrapropylammonium hydroxide solution ([N_{3333}] OH, 25 wt % in H_2O), tetrabutylammonium hydroxide solution ([N_{4444}] OH, 40 wt % in MeOH) were bought from Aladdin Co. Ltd. Isosorbide was purified by recrystallization for four times in acetone, and the other chemicals were used without any further purification.

Table S1. The terminal groups of the oligomer by different ILs catalyst [a]

Entry	Catalyst	Oligomer terminal groups [b]							
		Methylation	Endo-CH_3	Exo-CH_3	Endo-CH_3 /Exo-CH_3	-OH	Endo-OH	Exo-OH	Endo-OH /Exo-OH
1		0.332	0.163	0.169	0.96	0.119	0.067	0.052	1.29
2		0.256	0.121	0.135	0.90	0.073	0.041	0.032	1.28
3		0.197	0.096	0.101	0.96	0.060	0.033	0.027	1.22
4		0.057	0.026	0.031	0.84	0.186	0.106	0.080	1.33
5		0.129	0.051	0.078	0.71	0.207	0.122	0.085	1.39
6		0.154	0.066	0.088	0.75	0.242	0.139	0.103	1.35

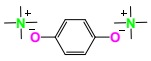
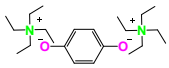
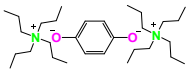
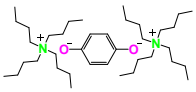
[a] (1) Transesterification: 101 kPa, (160 °C, 60 min)-(180 °C, 60 min). (2) Polycondensation: 5 Pa, 230 °C, 60 min, n(DMC):n(ISB)= 7:1, and catalyst amount of 8×10^{-4} mol. [b] The peak integration of the proton from isosorbide in the repeating unit (peak 3 at δ 4.88 ppm in Figure. 1) was normalized to be 1, and the contents of other terminal groups at the end of the polymer chain were calculated on this basis.

Table S2. The terminal groups of the PIC by different ILs catalyst [a]

Entry	Catalyst	PIC terminal groups [b]							
		Methylation	Endo-CH_3	Exo-CH_3	Endo-CH_3/ Exo-CH_3	-OH	Endo-OH	Exo-OH	Endo-OH/ Exo-OH
1		0.267	0.146	0.121	1.21	0.035	0.020	0.015	1.33
2		0.249	0.131	0.118	1.11	0.026	0.014	0.012	1.17
3		0.235	0.142	0.093	1.53	0.077	0.045	0.032	1.41
4		0.018	0.011	0.007	1.57	0.071	0.040	0.031	1.29
5		0.047	0.028	0.019	1.47	0.050	0.029	0.021	1.38
6		0.078	0.050	0.028	1.84	0.077	0.045	0.032	1.41

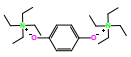
[a] (1) Transesterification: 101 kPa, (160 °C, 60 min)-(180 °C, 60 min). (2) Polycondensation: 5 Pa, 230 °C, 60 min, n(DMC):n(ISB)= 7:1, and catalyst amount of 8×10^{-4} mol. [b] The peak integration of the proton from isosorbide in the repeating unit (peak 3 at δ 4.88 ppm in Figure. 1) was normalized to be 1, and the contents of other terminal groups at the end of the polymer chain were calculated on this basis.

Table S3 Catalysts screening for synthesizing PIC via melt polycondensation of ISB and DMC [a]

Entry	Catalyst	ISB Con.[c] (%)	PIC terminal groups [b]			Molecular weight [d] (g/mol)
			-OH	Methylation	Carboxymethylation	M_w
1		98	0.077	0.235	0.377	21700
2		98	0.071	0.018	0.421	23300
3		91	0.050	0.047	0.337	17600
4		86	0.077	0.078	0.321	14500

[a] (1) Transesterification: 101 kPa, (160 °C, 60 min)-(180 °C, 60 min). (2) Polycondensation: 5 Pa, 230 °C, 60 min, n(DMC):n(ISB)= 7:1, and catalyst amount of 8×10^{-4} mol. [b] The peak integration of the proton from ISB in the repeating unit (peak 3 at δ 4.88 ppm in Figure 1) was normalized to be 1, and the contents of other terminal groups were calculated on this basis. [c] Determined by GC. [d] Determined by DMF-GPC using polystyrene standards (RI detector). The average of date was obtained by three times measurements to ensure the accuracy of the results.

Table S4. The terminal groups of the oligomer and PIC by $[N_{2222}]_2$ [HQ] catalyst [a]

Entry	Catalyst	Stage	Time(h)	Terminal groups [b]							
				Methylation	Endo-CH_3	Exo-CH_3	Endo-CH_3/ Exo-CH_3	-OH	Endo-OH	Exo-OH	Endo-OH/ Exo-OH
1		Transesterification	1	0.080	0.034	0.067	0.51	0.659	0.348	0.311	1.12
2			2	0.057	0.026	0.031	0.84	0.186	0.106	0.080	1.33
3		Polycondensation	1	0.018	0.011	0.007	1.57	0.071	0.040	0.031	1.29
4			2	0.015	0.009	0.006	1.50	0.045	0.028	0.017	1.65
5			3	0.016	0.01	0.006	1.60	0.035	0.021	0.014	1.50

[a] (1) Transesterification: 101 kPa, 160-180 °C. (2) Polycondensation: 5 Pa, 230 °C, 60 min, n(DMC):n(ISB)= 7:1, and catalyst amount of 8×10^{-4} mol. [b] The peak integration of the proton from isosorbide in the repeating unit (peak 3 at δ 4.88 ppm in Figure. 1) was normalized to be 1, and the contents of other terminal groups at the end of the polymer chain were calculated on this basis.

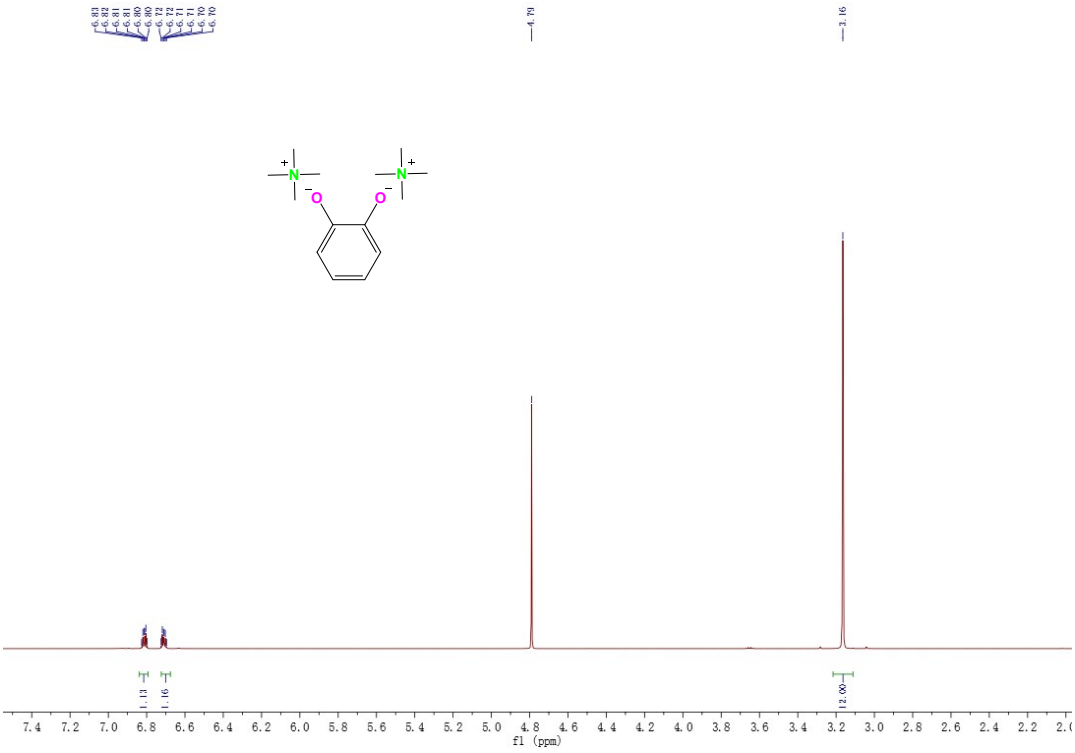


Fig. S1 The ^{1}H NMR spectrum of $[N_{1111}]_2$ [PY] (D_2O).

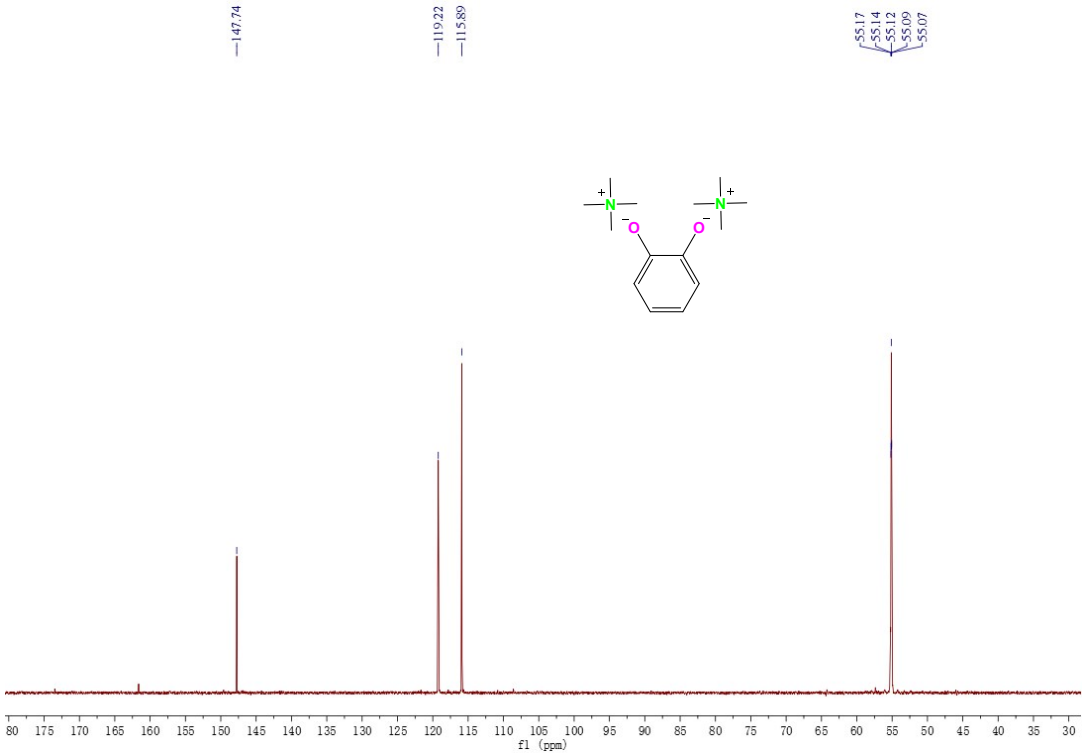


Fig. S2 The ^{13}C NMR spectrum of $[N_{1111}]_2$ [PY] (D_2O).

$[N_{1111}]_2$ [PY]: ^{1}H NMR (600 MHz, D_2O) δ: 3.16 (24H, s, 8×CH_3), 6.71 (2H, m), 6.81 (2H, m). ^{13}C NMR (600 MHz, D_2O) δ: 147.7, 119.2, 115.9, 55.1.

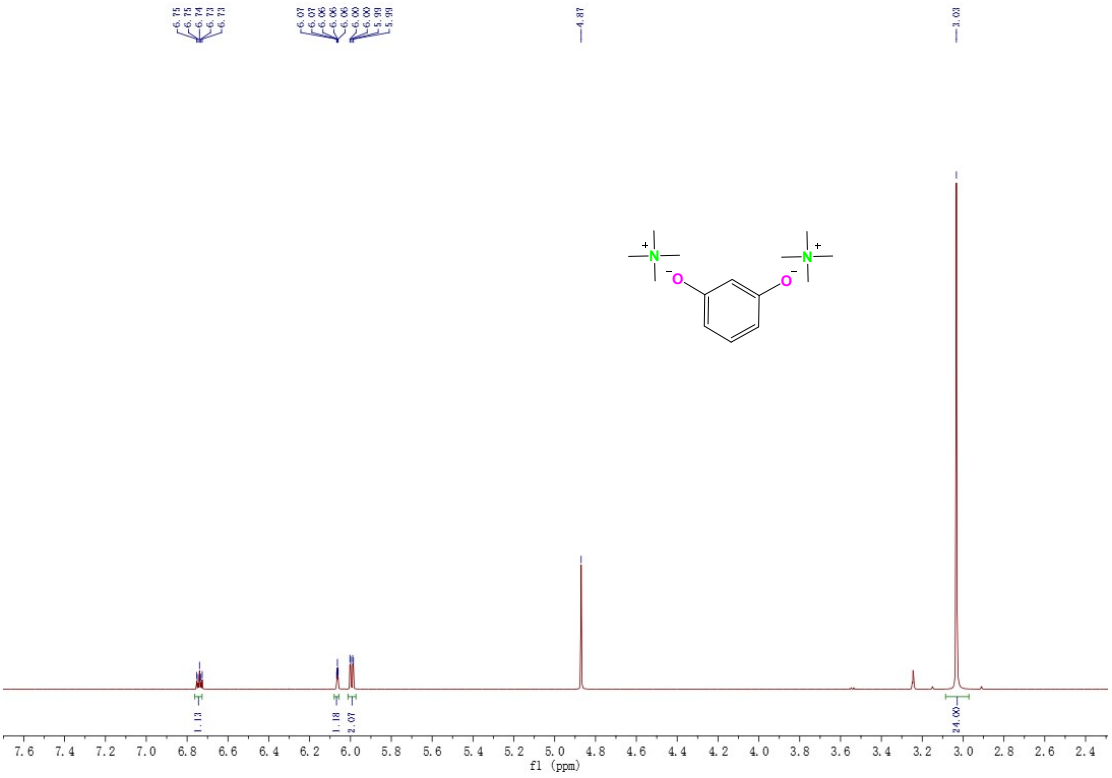


Fig. S3 The ^{1}H NMR spectrum of $[N_{1111}]_2$ [RE] (CD_3OD).

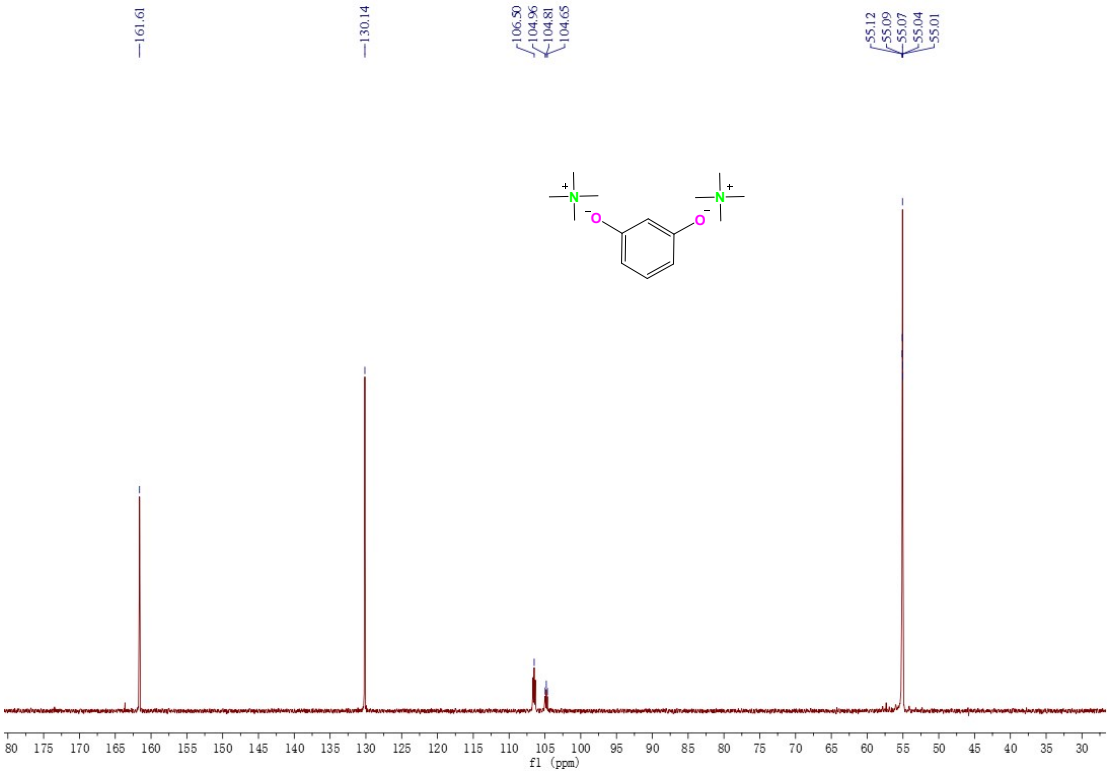


Fig. S4 The ^{13}C NMR spectrum of $[N_{1111}]_2$ [RE] (D_2O).

$[N_{1111}]_2$ [RE]: ^{1}H NMR (600 MHz, CD_3OD) δ: 3.03 (24H, s, 8×CH_3), 6.00 (2H, m), 6.07 (1H, m), 6.74 (1H, m). ^{13}C NMR (600 MHz, D_2O) δ: 161.6, 130.1, 106.5, 104.8, 55.1.

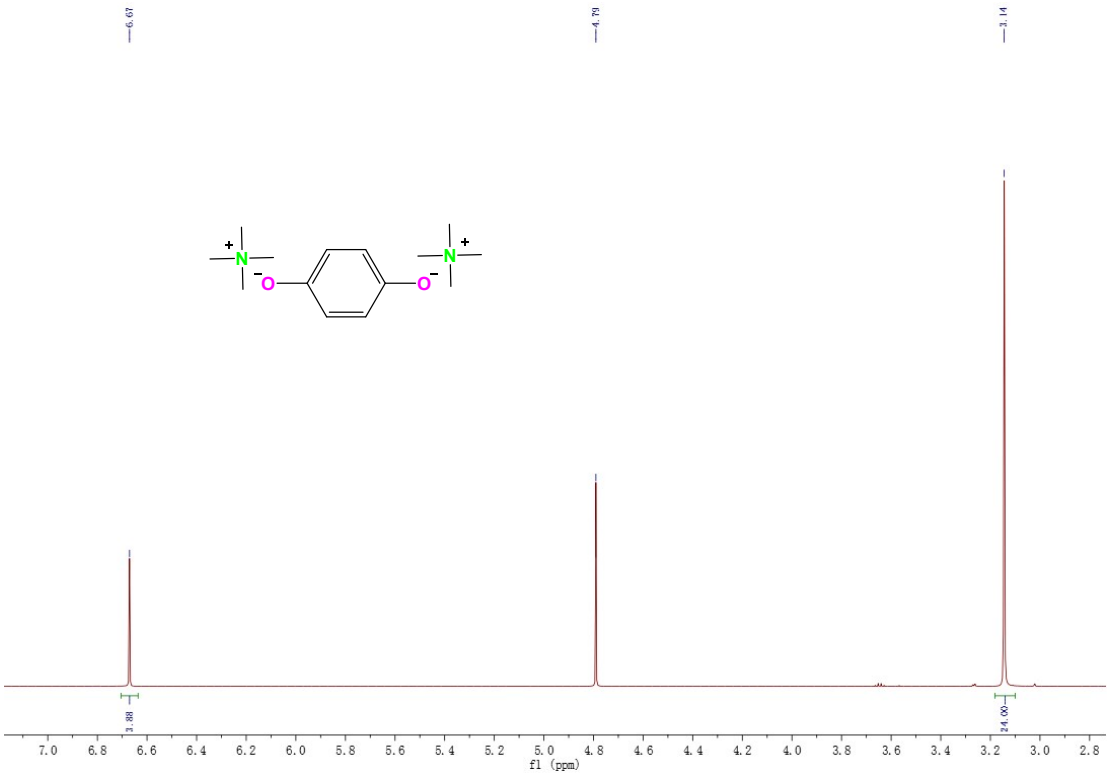


Fig. S5 The ^{1}H NMR spectrum of $[N_{1111}]_2$ [HQ] (D_2O).

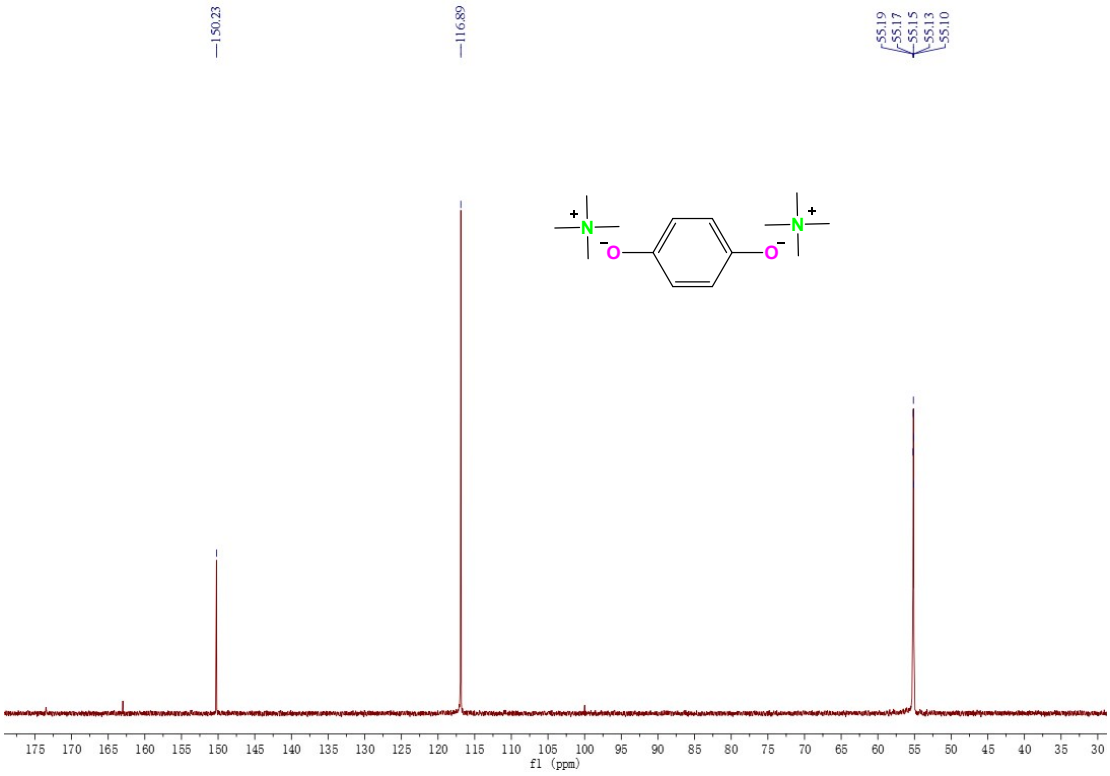


Fig. S6 The ^{13}C NMR spectrum of $[N_{1111}]_2$ [HQ] (D_2O).

$[N_{1111}]_2$ [HQ]: ^{1}H NMR (600 MHz, D_2O) δ: 3.14 (24H, s, 8×CH_3), 6.67 (4H, s,). ^{13}C NMR (600 MHz, D_2O) δ: 150.2, 116.9, 55.1.

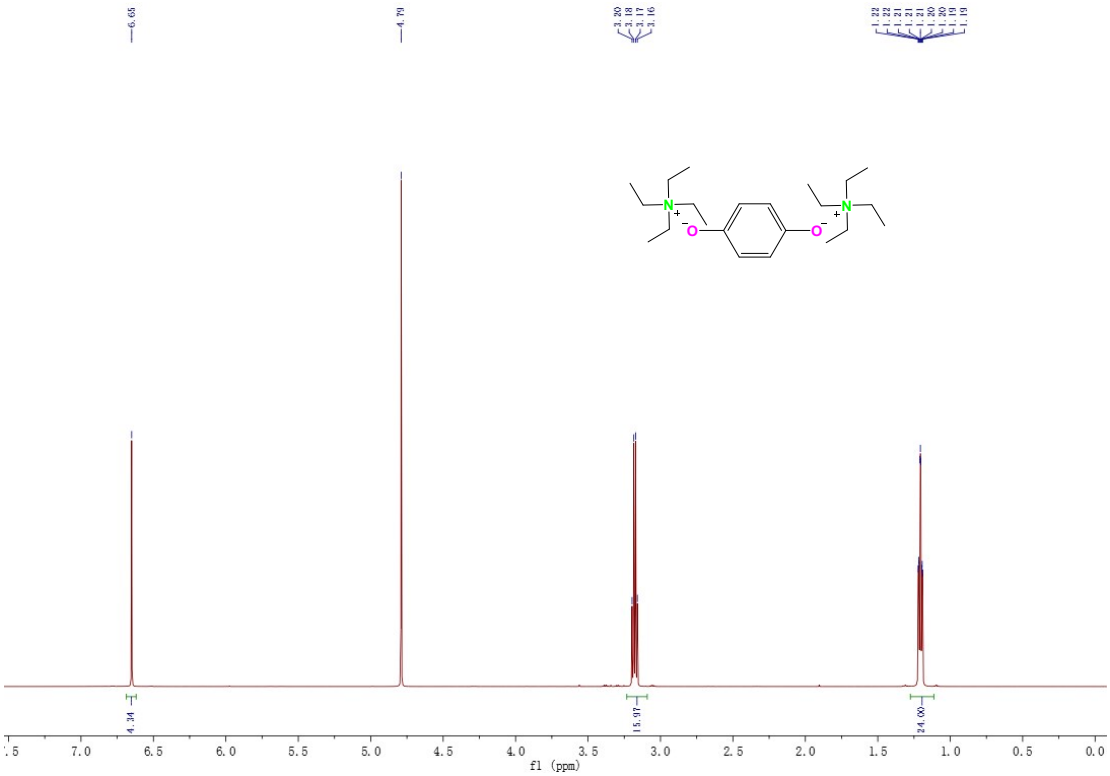


Fig. S7 The ^{1}H NMR spectrum of $[N_{2222}]_2$ [HQ] (D_2O).

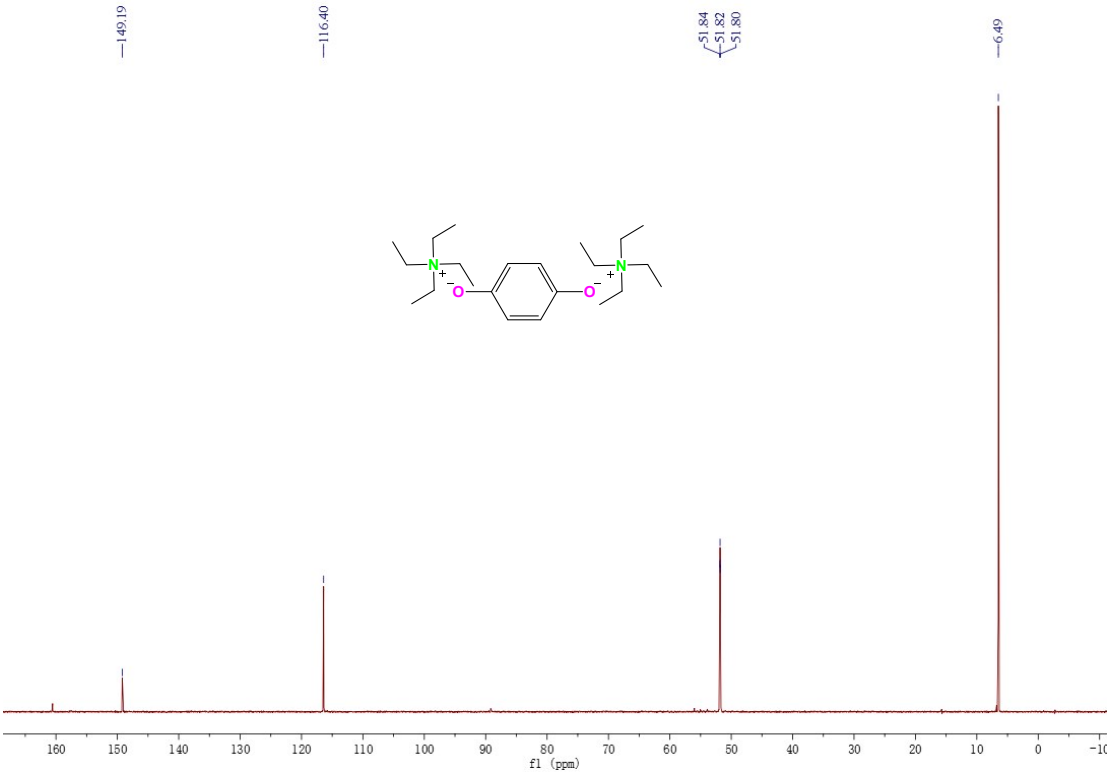


Fig. S8 The ^{13}C NMR spectrum of $[N_{2222}]_2$ [HQ] (D_2O).

$[N_{2222}]_2$ [HQ]: ^{1}H NMR (600 MHz, D_2O) δ: 1.21 (24H, m, 8×CH_3), 3.18 (16H, m, 8×CH_2), 6.65 (4H, s,). ^{13}C NMR (600 MHz, D_2O) δ: 149.2, 116.4, 55.8, 6.5.

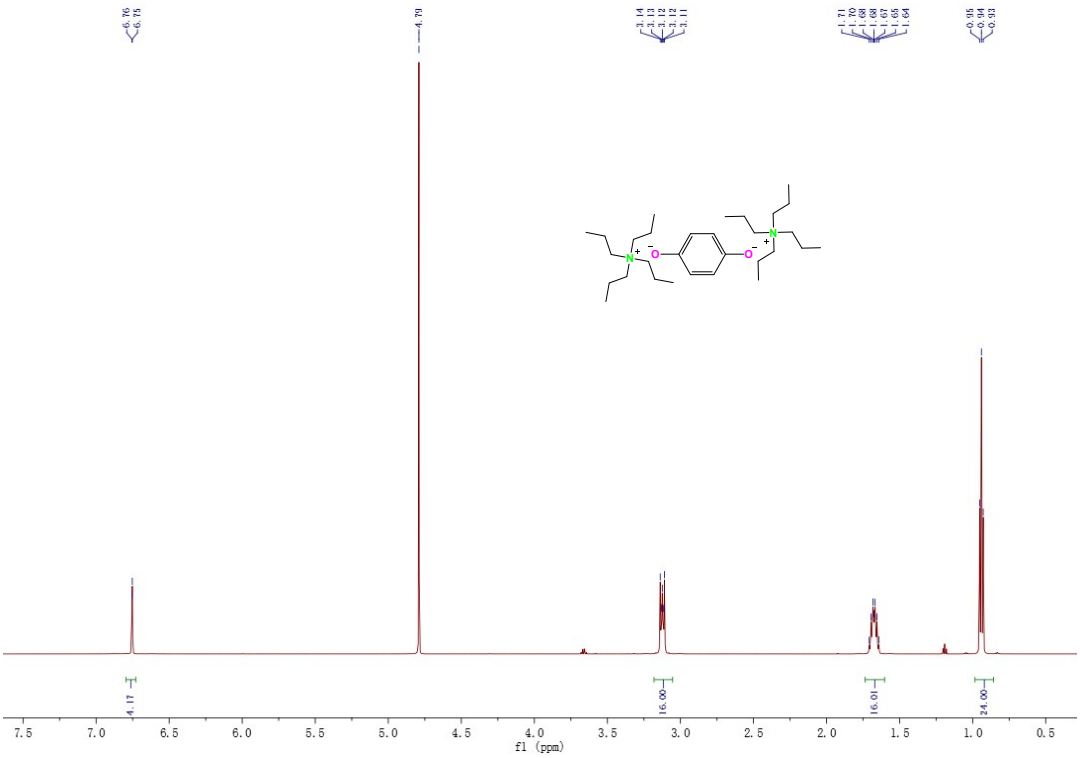


Fig. S9 The ^{1}H NMR spectrum of $[N_{3333}]_2$ [HQ] (D_2O).

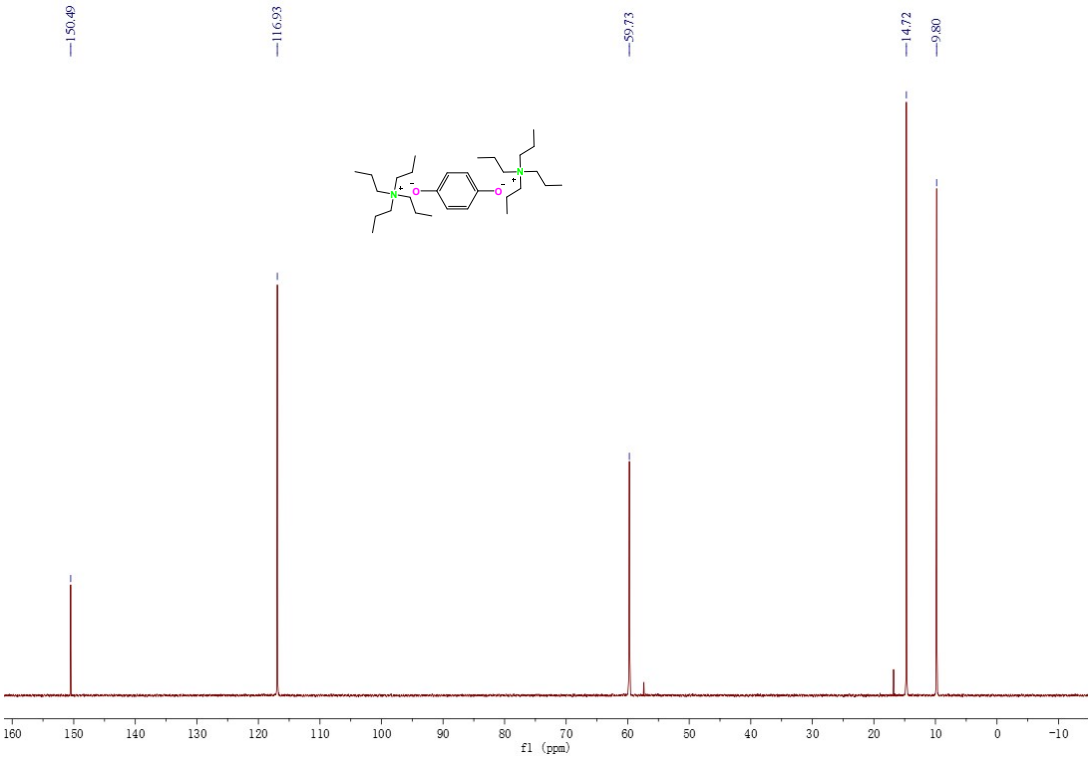


Fig. S10 The ^{13}C NMR spectrum of $[N_{3333}]_2^+$ $[HQ]^-$ (D_2O).

$[N_{3333}]_2$ [HQ]: ^{1}H NMR (600 MHz, D_2O) δ: 0.94 (24H, m, 8×CH_3), 1.68 (16H, m, 8×CH_2), 3.12 (16H, m, 8×CH_2),6.75 (4H, d,). ^{13}C NMR (600 MHz, D_2O) δ: 150.5, 116.9, 59.7, 14.7, 9.8.

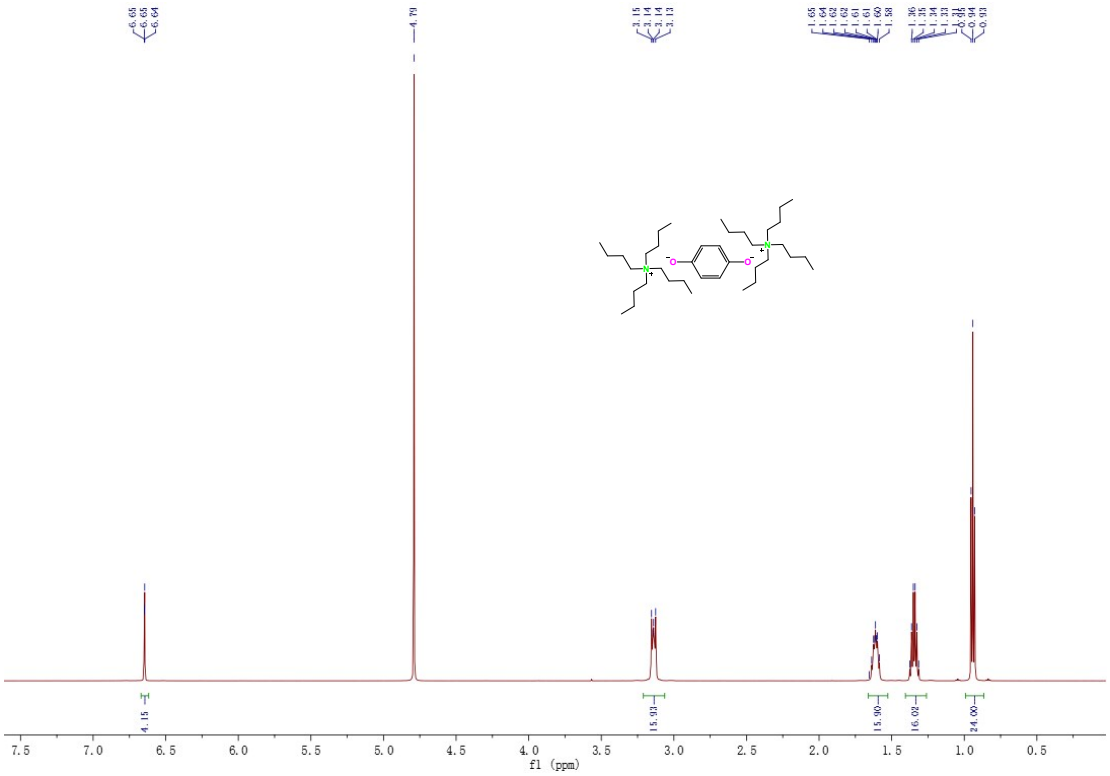


Fig. S11 The ^{1}H NMR spectrum of $[N_{4444}]_2$ [HQ] (D_2O).

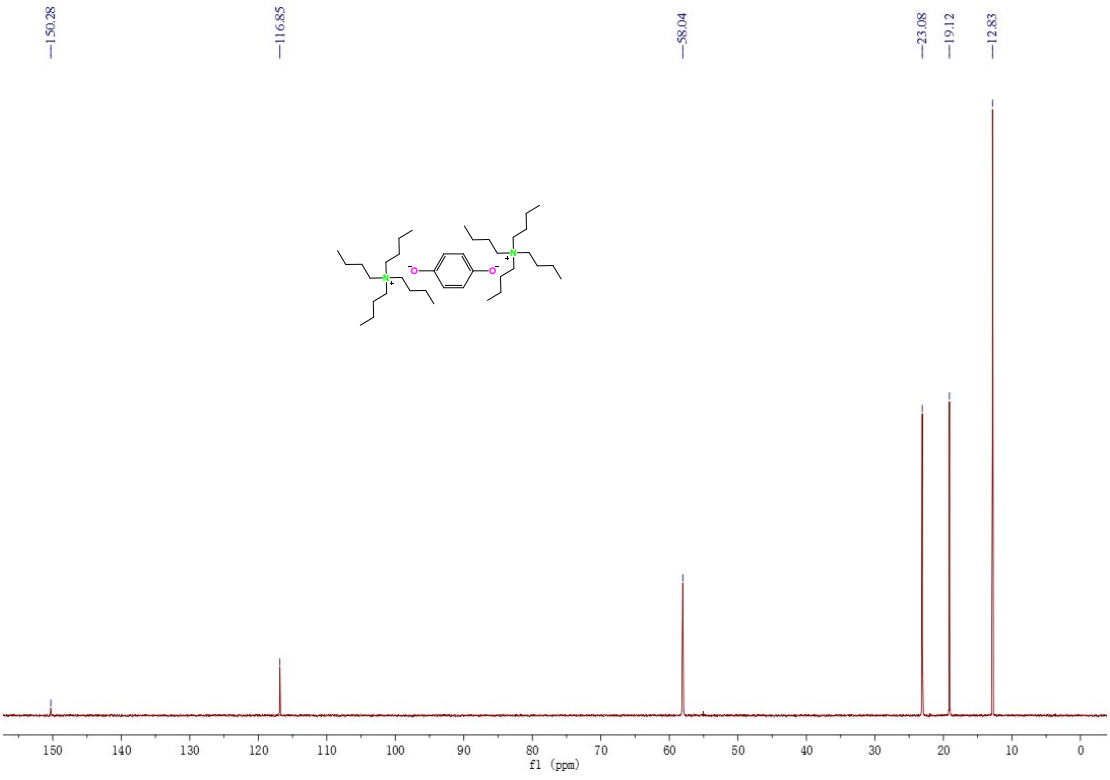


Fig. S12 The ^{13}C NMR spectrum of $[N_{4444}]_2$ [HQ] (D_2O).

$[N_{4444}]_2$ [HQ]: ^{1}H NMR (600 MHz, D_2O) δ: 0.94 (24H, m, 8×CH_3), 1.34 (16H, m, 8×CH_2), 1.61 (16H, m, 8×CH_2), 3.14 (16H, m, 8×CH_2), 6.65 (4H, t,). ^{13}C NMR (600 MHz, D_2O) δ: 150.3, 116.8, 58.0, 23.1, 19.1, 12.8.

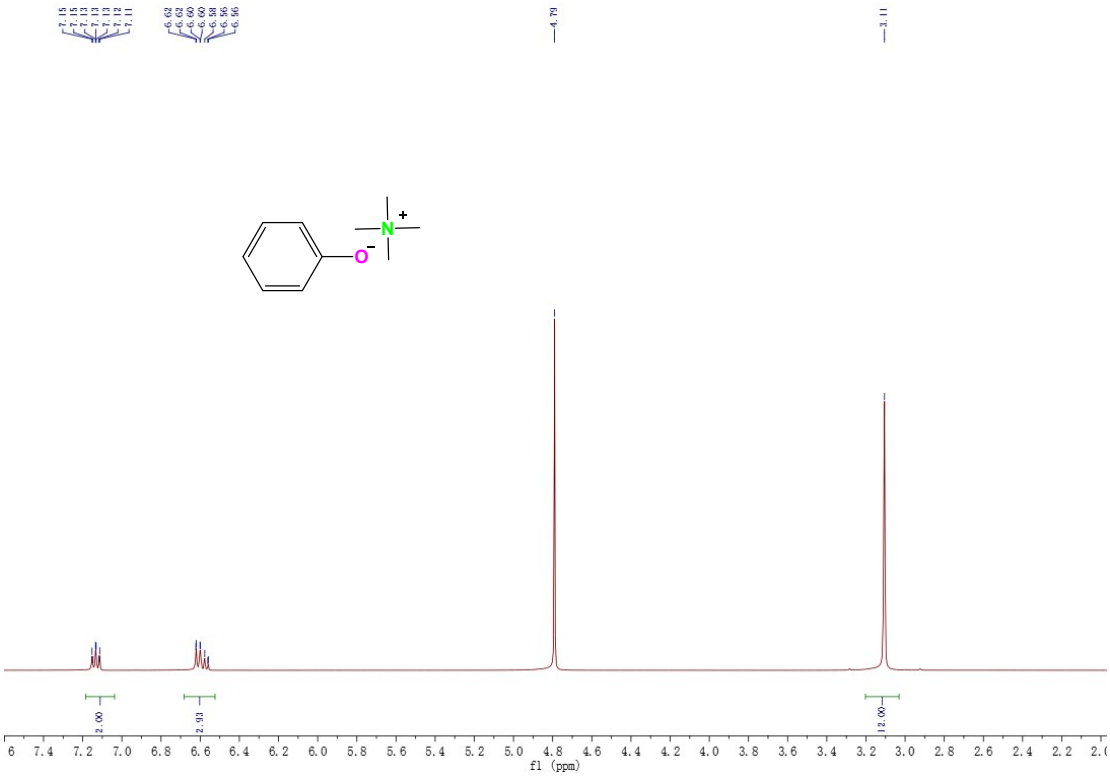


Fig. S13 The ^{1}H NMR spectrum of [N_{1111}] [PH] (D_2O).

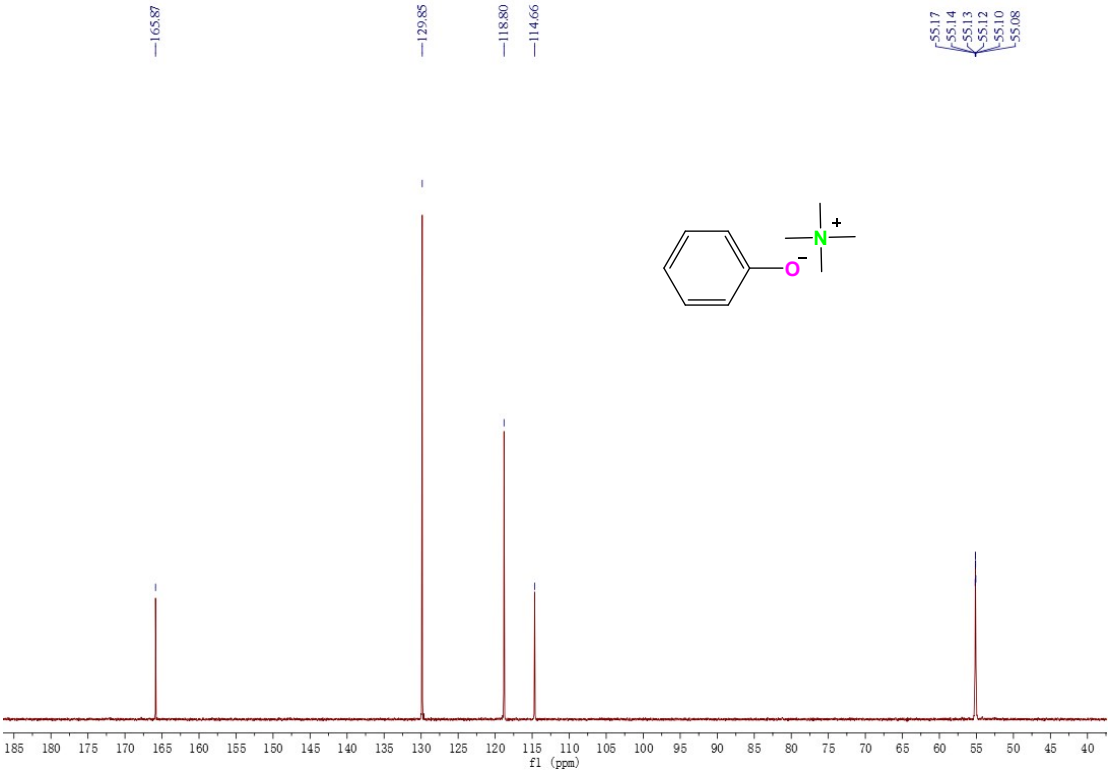


Fig. S14 The ^{13}C NMR spectrum of [N_{1111}] [PH] (D_2O).

[N_{1111}] [PH]: ^{1}H NMR (600 MHz, D_2O) δ: 3.11 (12H, s, 4×CH_3), 6.60 (3H, m), 7.13 (2H, m). ^{13}C NMR (600 MHz, D_2O) δ: 165.8, 129.8, 118.8, 114.7, 55.1.

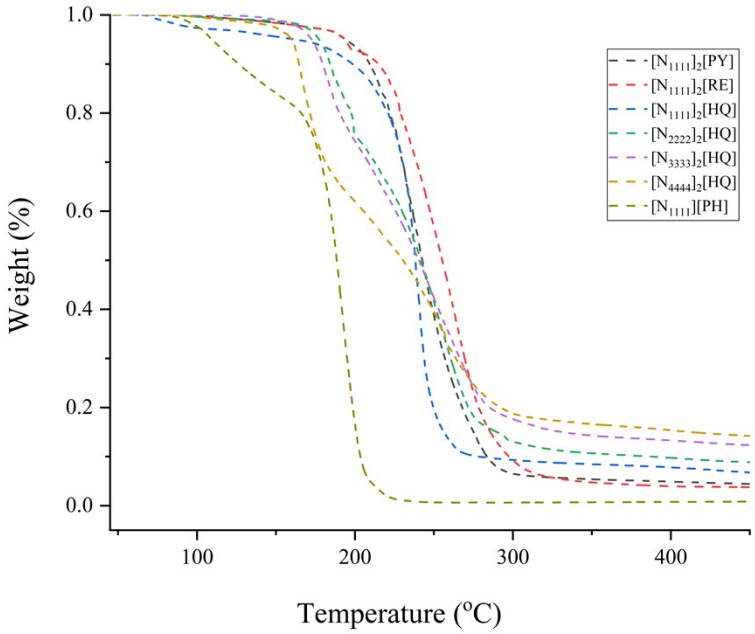


Fig. S15 TGA curves of ionic liquids

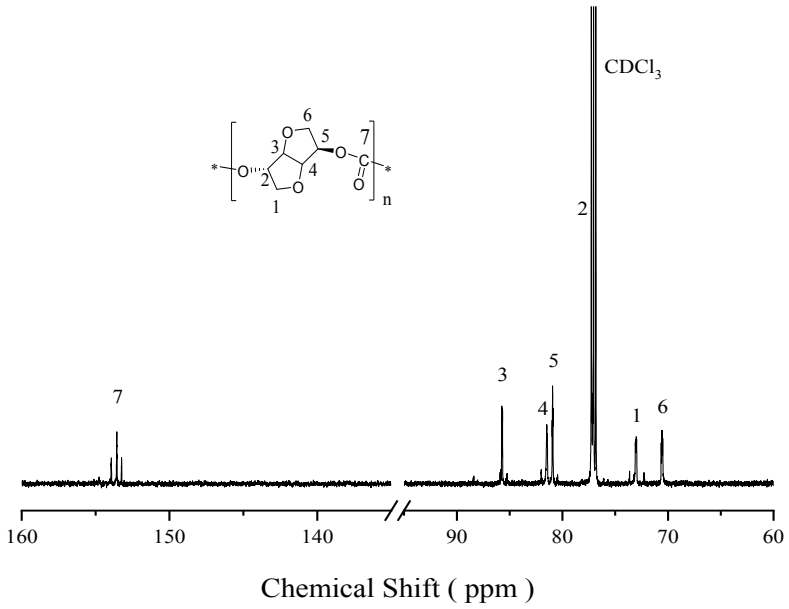


Fig. S16 The ^{13}C NMR spectrum of the PIC catalyzed by $[N_{2222}]_2^+$ $[HQ]^-$.

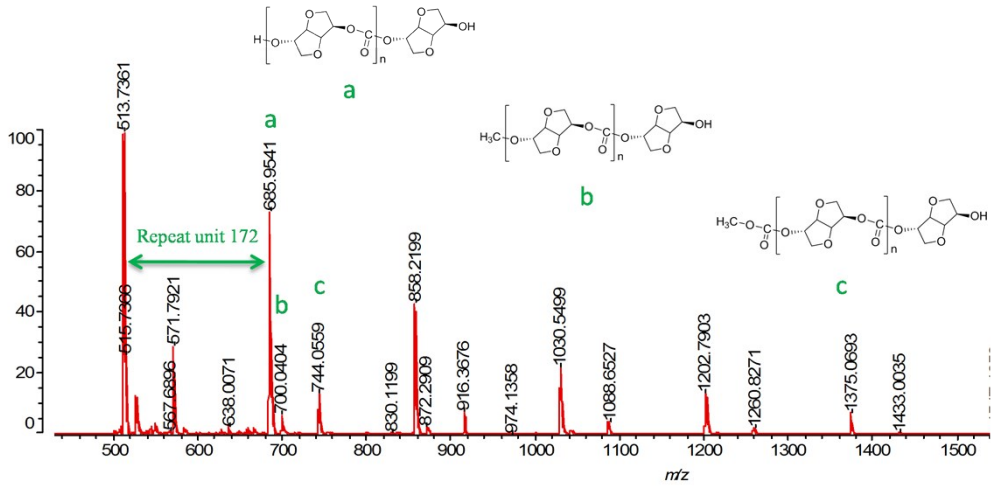


Fig. S17. The MALDI-TOF-MS spectrum of PIC prepared at initial stage of polycondensation.