

Supporting Information

Hydrogen bond donor functionalized poly(ionic liquid)s for efficient synergistic conversion of CO₂ to cyclic carbonates

Haibin Gou, Xifei Ma, Qian Su, Lei Liu, Ting Ying, Wei Qian, Li Dong, and Weiguo Cheng,*

*Corresponded to: Weiguo Cheng; Tel/Fax: +86 10 8262 7080 (E-mail: wgcheng@ipe.ac.cn)

Table of Contents

1. Synthesis of different poly(ionic liquid)s.....	2
2. ¹ H NMR of ionic liquids monomers and PILs.....	2
3. FT-IR spectra of PILs.....	4
4. Element analysis of PILs.....	5
5. Thermogravimetric analysis (TGA) of the PILs	5
6. DSC tests.....	6
7. The EDS spectra of HPIL-7	7
8. The catalytic performance of VHPImBr/HEMA mixtures and HPILs.....	7
9. ¹ H NMR of the different chemical shift in PO and HEMA system.....	8

1. Synthesis of different poly(ionic liquids)

The **s-PIL-1** was synthesized through the free radical polymerization of IL monomers, TMPTA as the cross-linker, and AIBN as the initiator (ILs:TMPTA=6:1, in molar ratio). Typically, VCEImBr(1.5 g), TMPTA(0.3 g) and AIBN(50 mg) was dissolved in 30 mL methanol, then the Schlenk line was used to replace the air with N₂. Subsequently, the mixture solution was stirred at 70 °C for 24 hours. Then the product was precipitated from methanol, washed with ethanol and dried in vacuum at 50 °C for 12 hours. The **s-PIL-2** was synthesized in the same way, only changed VCEImBr with VHPIImBr. The s-PILs cannot dissolve in conventional solvent.

The HPILs were synthesized through the free radical polymerization of ILs monomer, HEMA with different molar ratio, TMPTA as the cross-linker, and AIBN as the initiator. Typically, VCEImBr(1.5 g), HEMA(0.395 g), TMPTA(0.3 g) and AIBN(50 mg) was dissolved in 30 mL methanol, then the Schlenk line was used to replace the air with N₂, Subsequently, the mixture solution was stirred at 70 °C for 24 hours. Then the solution were precipitated from ethanol, and washed dried in vacuum at 50 °C for 12 hours. The HPIL was termed as **HPIL-1**, the other HPILs was synthesized in the same way, the molar ratio of ILs: TMAPTA: HEMA was list in **Table S1**.

Table S1. The synthesis methods for PILs catalysts

Entry	ILs: TMAPTA: HBDs	Termed
1	VCEImBr: TMPTA: HEMA=6:1:3	HPIL-1
2	VCEImBr: TMPTA: HEMA=6:1:6	HPIL-2
3	VCEImBr: TMPTA: HEMA=6:1:9	HPIL-3
4	VCEImBr: TMPTA: HEMA=6:1:12	HPIL-4
5	VHPIImBr: TMPTA: HEMA=6:1:3	HPIL-5
6	VHPIImBr: TMPTA: HEMA=6:1:6	HPIL-6
7	VHPIImBr: TMPTA: HEMA=6:1:9	HPIL-7
8	VHPIImBr: TMPTA: HEMA=6:1:12	HPIL-8
9	VHPIImBr: TMPTA: HEMA=6:0.5:9	HPIL-9
10	VHPIImBr: TMPTA: HEMA=6:2:9	HPIL-10

2. ¹H NMR of ionic liquids monomers and PILs

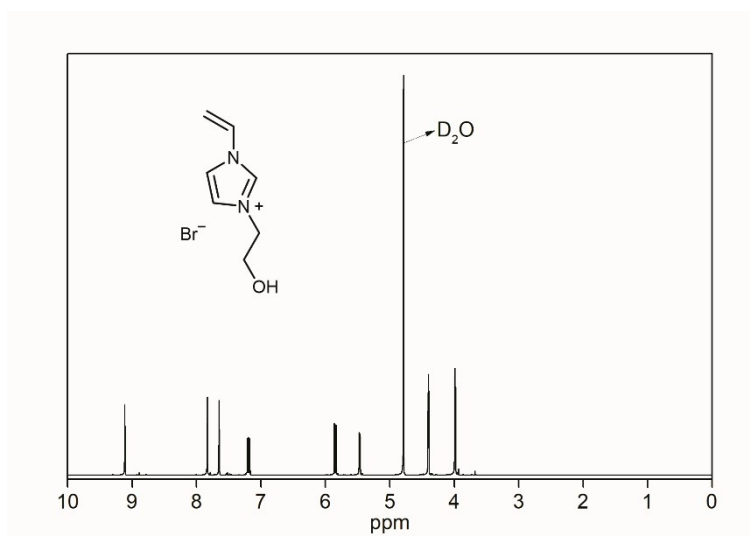


Fig. S1 The ¹H NMR spectrum of VHEImBr

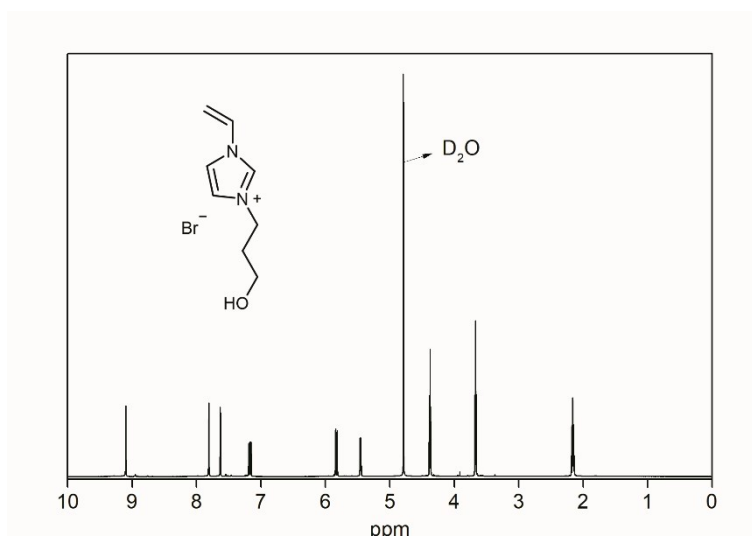


Fig. S2 The ^1H NMR spectrum of VHPImBr

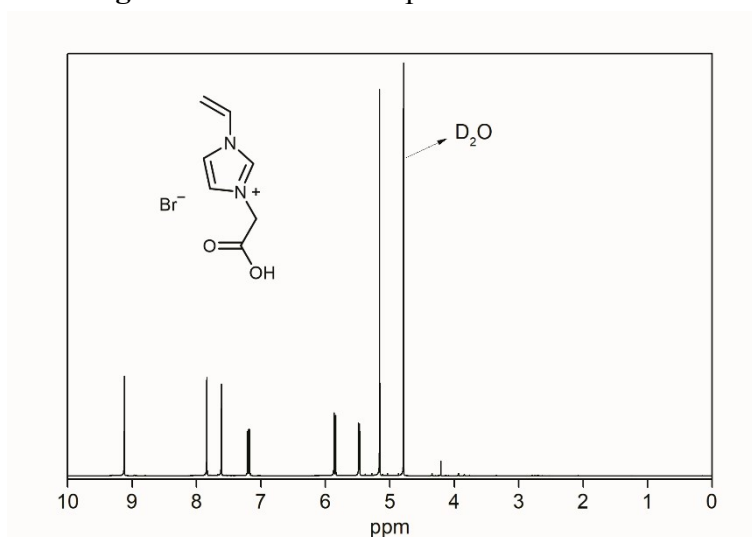


Fig. S3 The ^1H NMR spectrum of VCMImBr

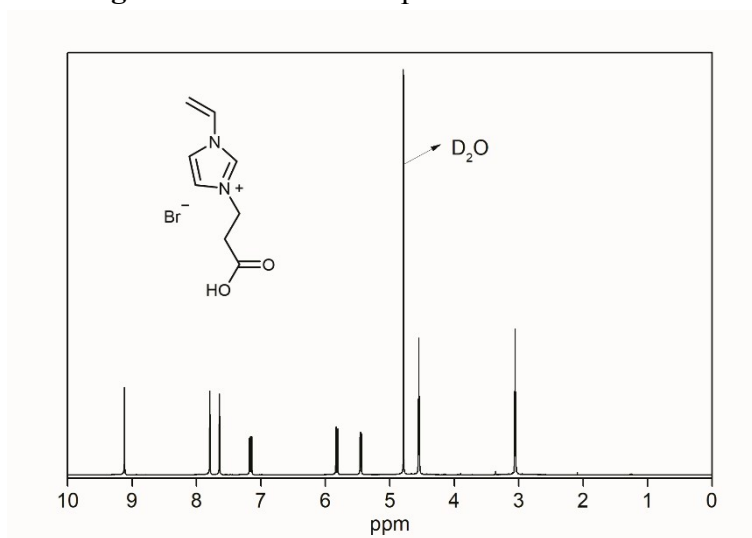


Fig. S4 The ^1H NMR spectrum of VCEImBr

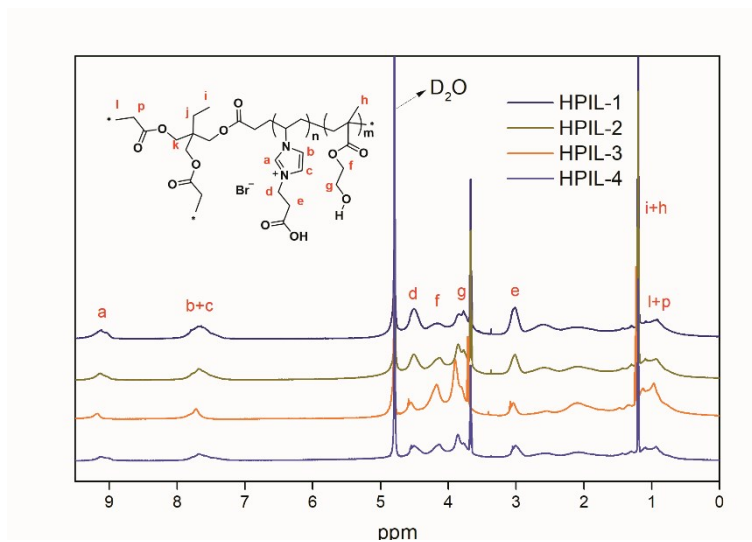


Fig. S5 The ^1H NMR spectra of HPIL-1, HPIL-2, HPIL-3 and HPIL-4

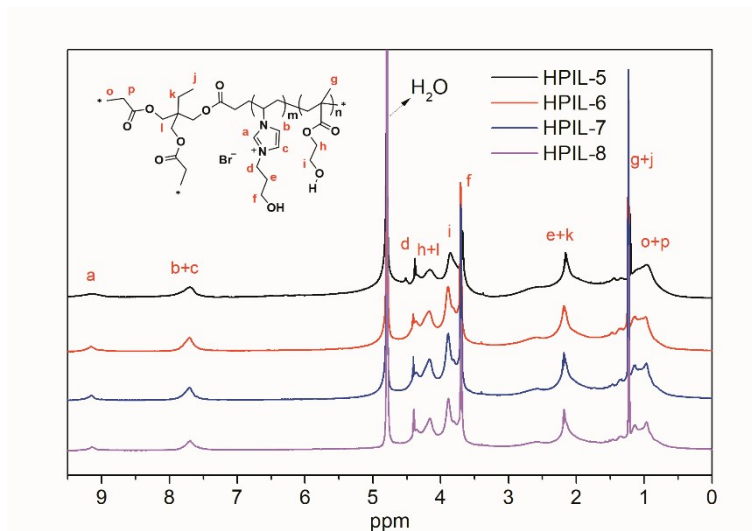


Fig. S6 The ^1H NMR spectra of HPIL-5, HPIL-6, HPIL-7 and HPIL-8

3. FT-IR spectra of PILs

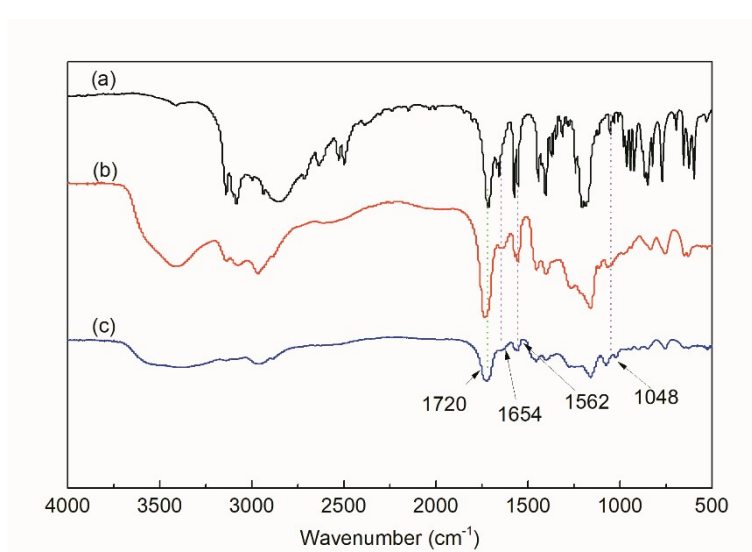


Fig. S7 The FT-IR spectra of (a) VCEImBr, (b) s-PIL-1 and (c) HPIL-3

4. Element analysis of PILs

Table S2. The element analysis of all PILs

Entry	PILs	C content (%)	H content (%)	N content (%)
1	HPIL-1	45.58	6.28	5.14
2	HPIL-2	47.15	6.69	4.05
3	HPIL-3	47.11	6.08	3.88
4	HPIL-4	51.11	7.31	2.71
5	HPIL-5	49.32	6.80	4.07
6	HPIL-6	49.72	6.97	3.56
7	HPIL-7	50.04	7.23	3.11
8	HPIL-8	50.92	7.39	2.08
9	HPIL-9	48.32	7.18	4.23
10	HPIL-10	48.39	7.00	4.13

5. Thermogravimetric analysis (TGA) of the PILs

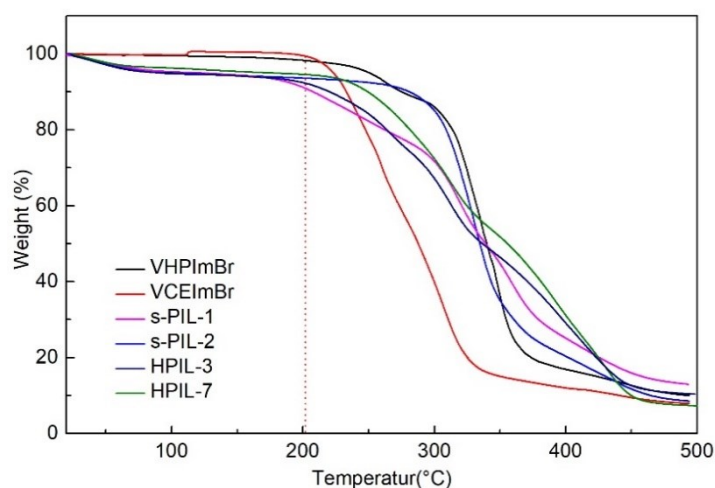


Fig. S8 The TGA curves of different ILs and PILs

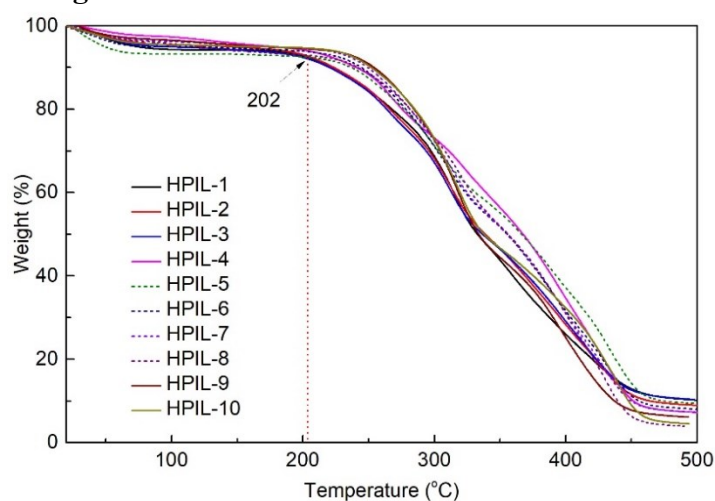


Fig. S9 The TGA curves of different HPILs

6. DSC tests

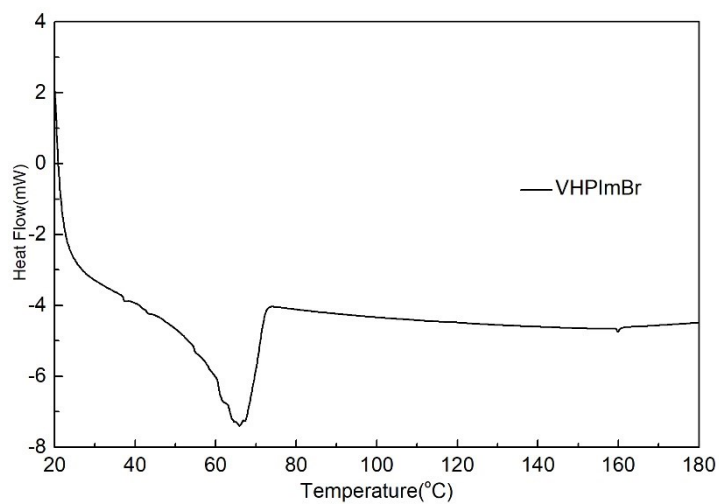


Fig. S10 The DSC spectrum of VHPImBr

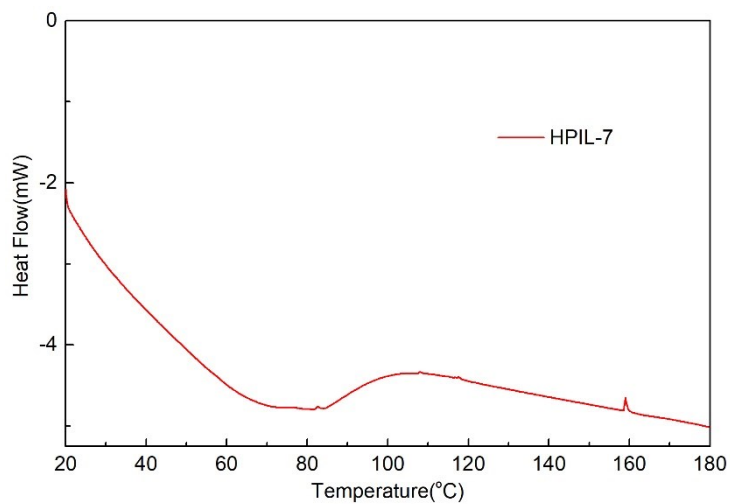


Fig. S11 The DSC spectrum of HPIL-7

7. The EDS spectra of HPIL-7

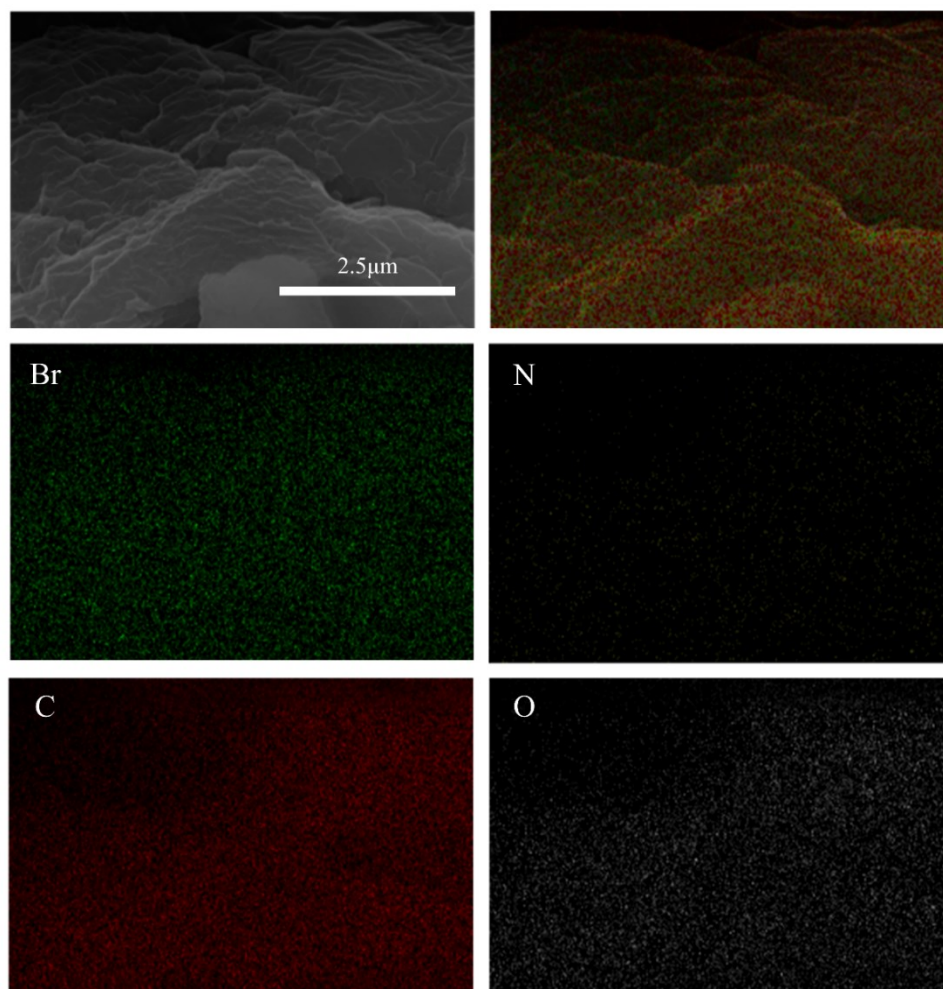


Fig. S12 The EDS spectra of HPIL-7

8. The catalytic performance of VHPIImBr/HEMA mixtures and HPILs

Table S3 The catalytic performance of different molar ratio of VHPIImBr/HEMA in mixtures and HPILs

Entry	Molar ratio/HPILs	Sel.(%) ^b	Yield(%) ^b
1	VHPIImBr	>99	83
2	HEMA	—	trace
3	VHPIImBr:HEMA=1:0. 5	>99	75
4	VHPIImBr:HEMA=1:1	>99	87
5	VHPIImBr:HEMA=1:1. 5	>99	93
6	VHPIImBr:HEMA=1:2	>99	93
7 ^c	HPIL-5	>99	91

8 ^c	HPIL-6	>99	93
9 ^c	HPIL-7	>99	94
10 ^c	HPIL-8	>99	95

Reaction conditions: ^a PO (14.3 mmol), VHPImBr (1 mol% of PO), 105 °C, 2 MPa, 3 h. ^b Based on GC analysis. ^c The molar ratio of VHPImBr and HEMA in HPIL-5, HPIL-6, HPIL-7 and HPIL-8 were 1:0.5, 1:1, 1:1.5 and 1:2, respectively. (This corresponds to **Table S1**)

9. ¹H NMR of the different chemical shift in PO and HEMA system

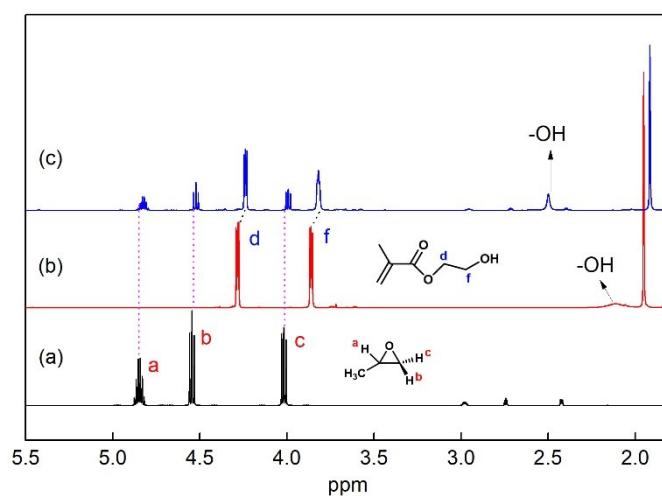


Fig. S13 Partial ¹H NMR spectra of PO, HEMA and PO+HEMA in CDCl₃
 (a) PO 30 uL, CDCl₃ 0.5 mL. (b) HEMA 10 uL, CDCl₃ 0.5 mL. (c) PO 30 uL,
 HEMA 10 uL, CDCl₃ 0.5 mL.