Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information (ESI)

Anion Exchange: A Novel Way for Preparing Hierarchal Porous Structure of Poly(ionic liquid)s

Li Qin, Binshen Wang, Yongya Zhang, Li Chen and Guohua Gao*

* *Shanghai Key Laboratory of Green Chemistry and Chemical Processes,*
School of Chemistry and Molecular Engineering, East China Normal University,
North Zhongshan Road 3663, Shanghai 200062, China, Fax: (+)86-21-62233323,

e-mail:ghgao@chem.ecnu.edu.cn

1. Materials

CO_2 was supplied by Dumaoai factory with a purity of 99.999%. Epoxides were purchased from TCI. 1-Vinylimidazole was purchased from Alfa Aesar. Divinyl benzene (DVB) was purchased from Aldrich and the inhibitor was removed by distillation. The other chemicals were supplied by Sinopharm. All chemicals were used without further purification

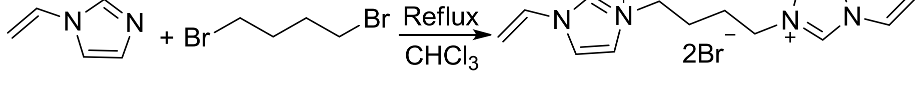
2. Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Ascend 400 spectrometer with tetramethylsilane as the internal standard at 400 MHz and 100 MHz, respectively. ^{13}C solid-state MAS NMR spectra were recorded at a frequency of 100 MHz, a spinning rate of 9.0 kHz, and a recycling delay of 4 s using a VARIANVNMRS-400WB spectrometer under one pulse conditions. Morphology and microstructure of dry PILs particles was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM with an Energy Dispersive X-ray Spectrometer was operated on a Hitachi S-4800 microscope and TEM was performed on a FEI Tecnai G2 F30 microscope working at 300 kV. The Fourier Transform Infrared spectroscopy (FTIR) was recorded on KBr pellets ranging from 4000 to 400 cm^{-1}using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere from 20 ^{o}C to 800 ^{o}C with a heating rate of 10 $^{o}C\cdot min^{-1}$ by using a Mettler Toledo TGA/SDTA851 apparatus. The high resolution mass spectrum (HR-MS) was performed by Bruker Compass DataAnalysis 4.0 on Bruker micrOTOF II 10293 instrument. The inductively coupled plasma analysis was performed by IRIS Intrepld II XSP inductively coupled plasma atomic emission spectrometer. All samples (50 mg) were dissolved in concentrated HNO_3 aqueous and diluted to 100 mL before ICP analysis. The specific surface area and pore information were measured on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer at -196 ^{o}C by Ar adsorption–desorption. The BET (Brunauer, Emmett, and Teller) specific surface area was calculated using adsorption data acquired at a relative pressure (P/P0) range of 0.05–0.22. The pore size distribution (PSD) curves were calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm and Horvath-Kawazoe method. The samples were pretreated at 150 ^{o}C under vacuum for 6 h. Differential scanning calorimetry (DSC) was performed on a Netzsch 204F1 in a nitrogen atmosphere. The sample was first heated from 40 to 100 ^{o}C and held at this temperature for 3 min, and then cooled to -50 ^{o}C and heated again from -50 to 100 ^{o}C, at a heating or cooling rate of 10 $^{o}C\times min^{-1}$. CHN elemental analyses were performed on an ElementarVarioELIII CHN elemental analyzer. GC analysis was performed by using a Shimadzu GC-14B equipped with a capillary column DM-1701 (30 m × 0.32 mm × 0.25 mm) and a flame ionization detector using biphenyl and dodecane as internal standards. Melting points were determined using a Beijing Tech instrument X-4 apparatus and are uncorrected.

3. Syntheses

3.1. Synthesis of monomers

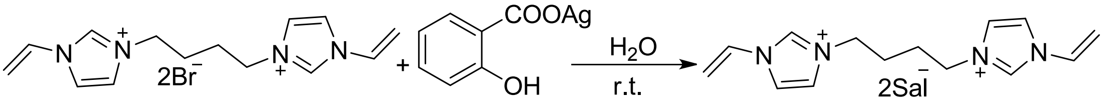
Synthesis of 1,4-butanediyl-3,3'-bis-1-vinylimidazolium dibromide (BVImBr)



1,4-butanediyl-3,3'-bis-1-vinylimidazolium dibromide (BVImBr) was synthesized according to ref. [S1] with minor modification: 1-Vinylimidazole (16.48 g, 0.175 mol) and 1,4-dibromobutane (17.31 g, 0.08 mol) were dissolved in chloroform (30 mL) in a 100 mL round-bottom flask. After the mixture was stirred under reflux for 24 h, the top phase was removed. Then the oily residue was washed three times with diethyl ether and dried at 25 °C for 6 h under vacuum. White powder solid was obtained in the yield of 98% (31.72 g).

^{1}H NMR (400 MHz, [d$_6$]DMSO, TMS): δ (ppm) 9.65 (s, 2H), 8.24 (s, 2H), 7.98 (s, 2H), 7.33 (dd, J = 8.8 Hz, J = 15.6 Hz, 2H), 5.99 (dd, J = 2.4 Hz, J = 15.6 Hz, 2H), 5.44 (dd, J = 2.4 Hz, J = 8.8 Hz, 2H), 4.29 (t, J = 5.6 Hz, 4H), 1.89-1.86 (m, 4H). ^{13}C NMR (100 MHz, [d$_6$]DMSO, TMS): δ (ppm) 135.44, 128.86, 123.22, 119.17, 108.69, 48.36, 25.69. mp 150.3-151.8 °C. HR-MS (ESI): m/z [M + Br]$^+$ Calcd for $C_{14}H_{20}N_4Br^+$ 323.0871, Found 323.0859.

Synthesis of 1,4-butanediyl-3,3'-bis-1-vinylimidazolium disalicylate (BVImSal)



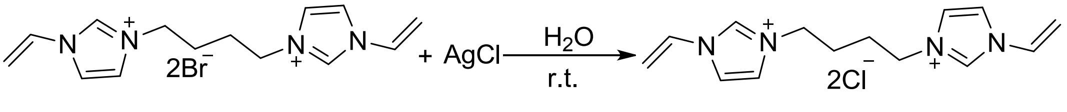
Silver salicylate was precipitated from the mixture of sodium salicylate with silver nitrate and dried in oven at 60 °C to a constant weight.

BVImBr (20.21 g, 0.05 mol) was dissolved in deionized water (50 mL). Silver salicylate (25.72 g, 0.105 mol) was added to the solution. After the mixture was stirred overnight at room temperature under dark for 12 h, precipitate was removed in dark room. Then filtrate was concentrated and dried under vacuum to give a white powder in the yield of 91% (23.59 g).

^{1}H NMR (400 MHz, [d$_6$]DMSO, TMS): δ (ppm) 16.53 (s, 2H), 9.76 (s, 2H), 8.24 (s, 2H), 7.93 (s, 2H), 7.64 (dd, J = 2.4 Hz, J = 8.0 Hz, 2H), 7.31 (dd, J = 8.8 Hz, J = 15.6 Hz, 2H), 7.12-7.08 (m, 2H), 6.57 (dd, J = 8.0 Hz, J = 15.6 Hz, 4H), 5.96 (dd, J = 2.4 Hz, J = 15.6 Hz, 2H), 5.43 (dd, J = 2.4 Hz, J = 8.8 Hz, 2H), 4.26 (t, J = 5.6 Hz, 4H), 1.86-1.83 (m, 4H).^{13}C NMR (100 MHz, [d$_6$]DMSO, TMS): δ (ppm) 171.31, 163.02, 135.62, 131.14, 129.83, 128.89, 123.19, 120.68, 119.18, 115.73, 115.68, 108.62, 48.38, 25.72. mp 125.1-126.7 °C. HR-MS (ESI): m/z [M + 2Sal + Na]$^+$ Calcd. for

$C_{28}H_{30}N_4O_6$ 541.2063, Found 541.2065. Ag residual 0.0075 wt%.

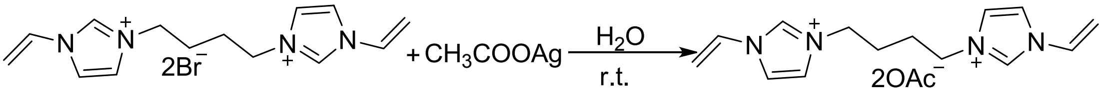
Synthesis of 1,4-butanediyl-3,3'-bis-1-vinylimidazolium dichloride (BVImCl)



BVImBr (4.04 g, 0.01 mol) was dissolved in deionized water (20 mL). Silver chloride (3.58 g, 0.025 mol) was added to the solution. After the mixture was stirred at room temperature under dark for 12 h, precipitate was removed in dark room, filtrate was concentrated and dried under vacuum to give a white powder in the yield of 88% (2.76 g)[S2, S3].

^{1}H NMR (400 MHz, [d$_6$]DMSO, TMS): δ (ppm) 10.12 (s, 2H), 8.35 (s, 2H), 8.11 (s, 2H), 7.40 (dd, J = 8.8 Hz, J = 15.6 Hz, 2H), 6.08 (dd, J = 2.4 Hz, J = 15.6 Hz, 2H), 5.42 (dd, J = 2.4 Hz, J = 8.8 Hz, 2H), 4.36 (t, J = 5.6 Hz, 4H), 1.90-1.87(m, 4H).^{13}C NMR (100 MHz, [d$_6$]DMSO, TMS): δ (ppm) 135.66, 128.89, 123.23, 119.21, 108.55, 47.99, 25.59. mp 169.8-171.2 °C. HR-MS (ESI): m/z $[M + Cl]^+$ Calcd. for $C_{14}H_{20}N_4Cl^+$ 279.1376, Found 279.1370. Ag residual 0.0062 wt%.

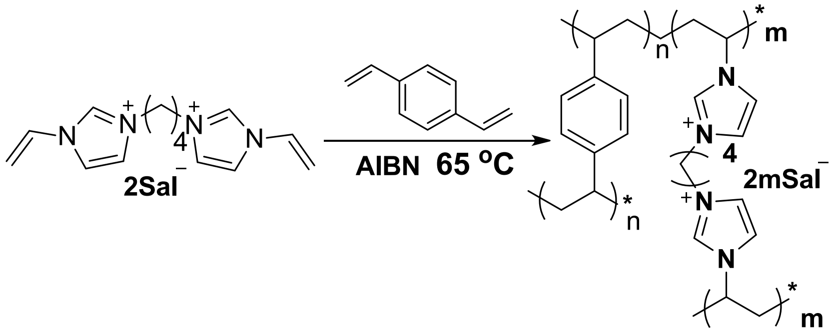
Synthesis of 1,4-butanediyl-3,3'-bis-1-vinylimidazolium diacetate (BVImOAc)



BVImBr (4.04 g, 0.01 mol) was dissolved in deionized water (20 mL). Silver acetate (4.17 g, 0.025 mol) was added to the solution. After the mixture was stirred at room temperature under dark for 12 h, precipitate was removed in dark room. Then filtrate was concentrated and dried under vacuum to give a yellow oil in the yield of 91% (3.30 g) [S4-S7].

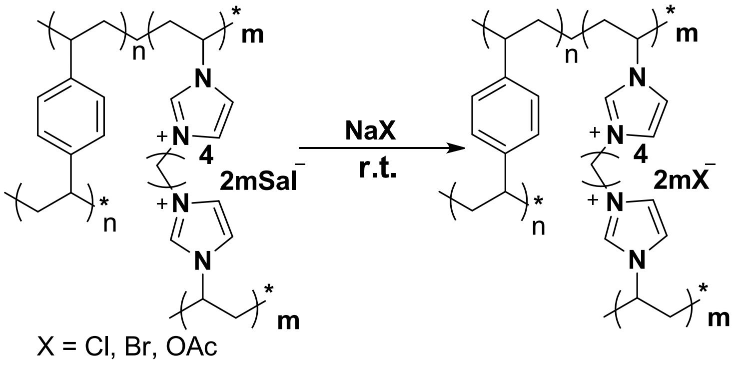
^{1}H NMR (400 MHz, [d$_6$]DMSO, TMS): δ (ppm) 10.66 (s, 2H), 8.26 (s, 2H), 8.05 (s, 2H), 7.41 (dd, J = 8.8 Hz, J = 15.6 Hz, 2H), 6.04 (dd, J = 2.4 Hz, J = 15.6Hz, 2H), 5.38 (dd, J = 2.4 Hz, J = 8.8 Hz, 2H), 4.35 (t, J = 6.2 Hz, 4H) , 1.88-1.85 (m, 4H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, [d$_6$]DMSO, TMS): δ (ppm) 173.46, 136.91, 129.09, 123.15, 119.13, 108.15, 48.46, 25.56, 25.38. HR-MS (ESI): m/z [M +2OAc + Na]$^+$ Calcd. for $C_{18}H_{26}N_4O_4$ 385.1852, Found 385.1852. Ag residual 0.029 wt%.

3.2. Synthesis of cross-linked PILs (PBVImSal) by direct polymerization



The cross-linked PILs were prepared by radical copolymerization of DVB and IL monomers using AIBN as initiator in methanol. 1,4-Butanediyl-3,3'-bis-1-vinylimidazolium disalicylate (20.74 g, 0.04 mmol), DVB (10.41 g, 0.08 mmol) and AIBN (1.63 g, 5 wt%) were dissolved in methanol (100 mL), and the mixture was stirred at reflux for 24 h. The solvent was removed by decantation. The residue was washed with diethyl ether and water. The product was dried under vacuum at 50 °C for 12 h. Yellow powder was obtained in the yield of 79% (24.58 g).

3.3. Synthesis of porous PILs by anion exchange (AE-PIL-X)

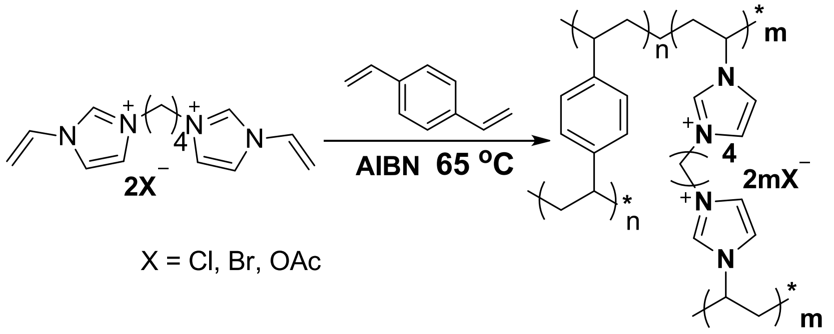


The porous PILs (AE-PIL-Cl) were prepared by the anion exchange of PBVImSal and NaCl. PBVImSal (5.0 g) was added to saturated NaCl aqueous solution with stirring at room temperature for 12 h several times until the salicylate was exchanged completely. The product was washed with deionized water and dried under vacuum at

50 °C for 12 h. White powder was obtained in the yield of 73% (3.67 g).

AE-PIL-Br and AE-PIL-OAc were synthesized by the similar procedure.

3.4. Synthesis of cross-linked PILs (DS-PIL-X) by direct polymerization



The nonporous PILs with different anions (DS-PIL-Cl, DS-PIL-Br and DS-PIL-OAc), were directly synthesized by the copolymerization of corresponding 1,4-butanediyl-3,3'-bis-1-vinylimidazolium monomers with DVB under identical conditions.

4. Characterization

4.1. Energy Dispersive X-ray Spectra of IL monomers

The energy dispersive X-ray analysis showed that no bromide and silver remained in BVImCl, BVImSal and BVImOAc, which indicated the bromide in BVImBr has been successfully exchanged by other anions.

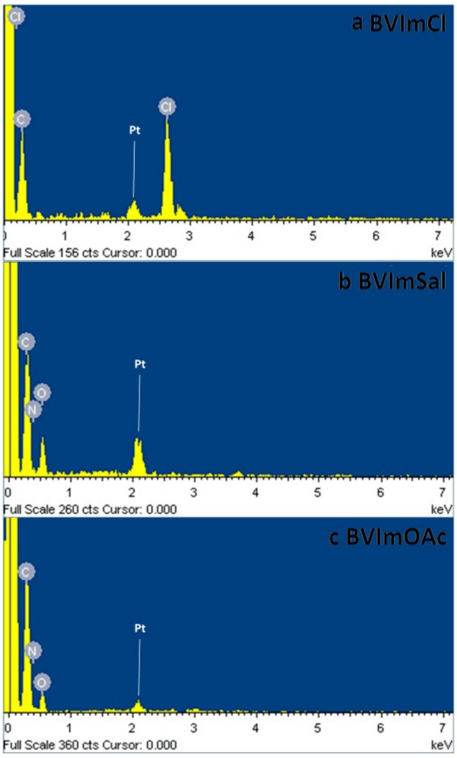
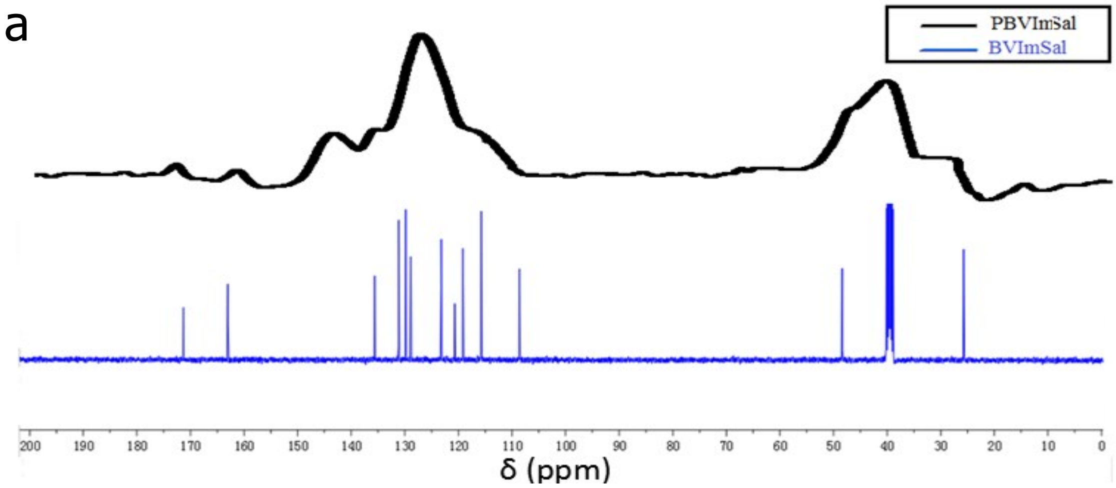


Fig. S1 EDX spectra of IL monomers a) BVImCl; b) BVImSal; c) BVImOAc.

4.2. ^{13}C MAS NMR of PILs and ^{13}C NMR of IL monomers



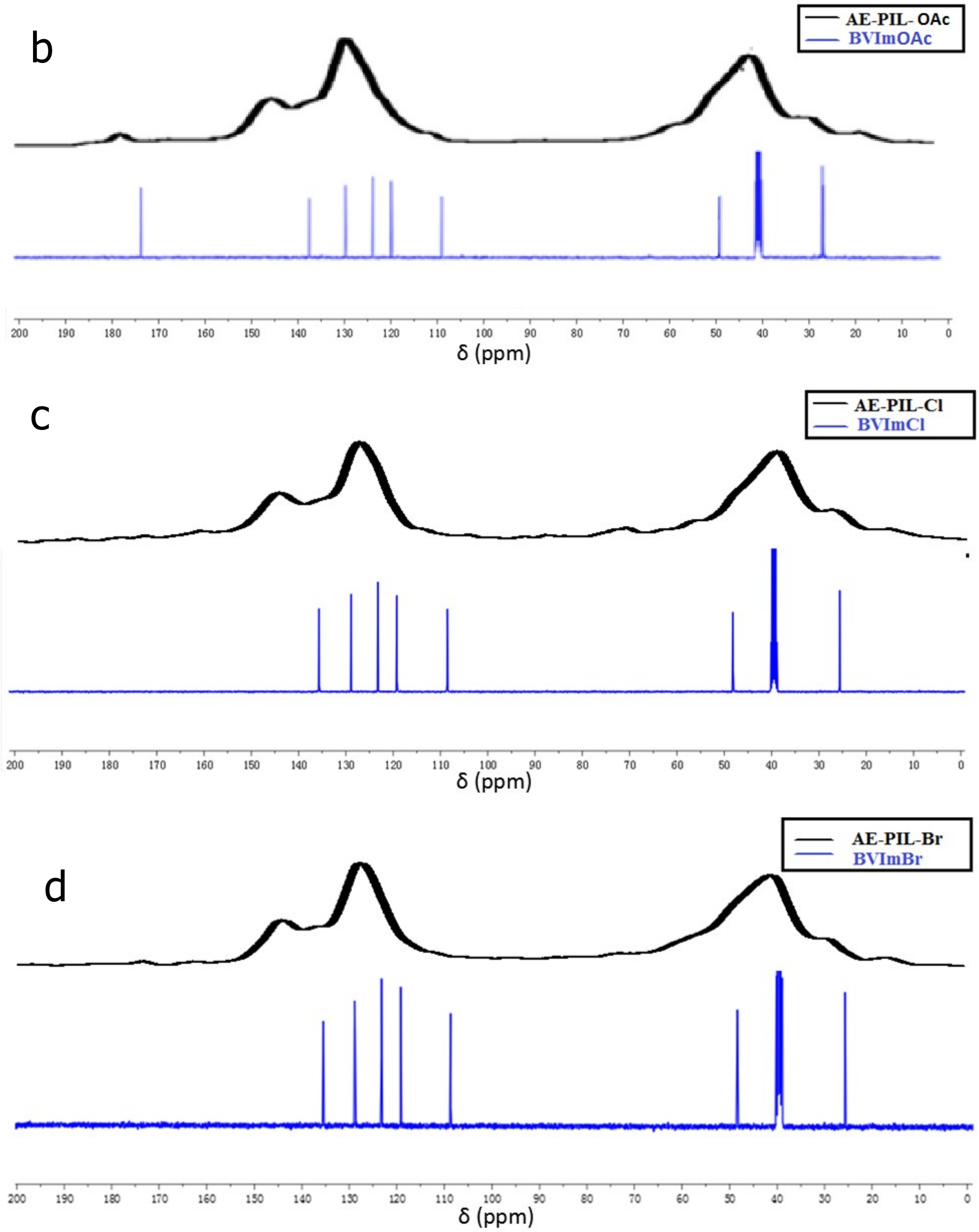
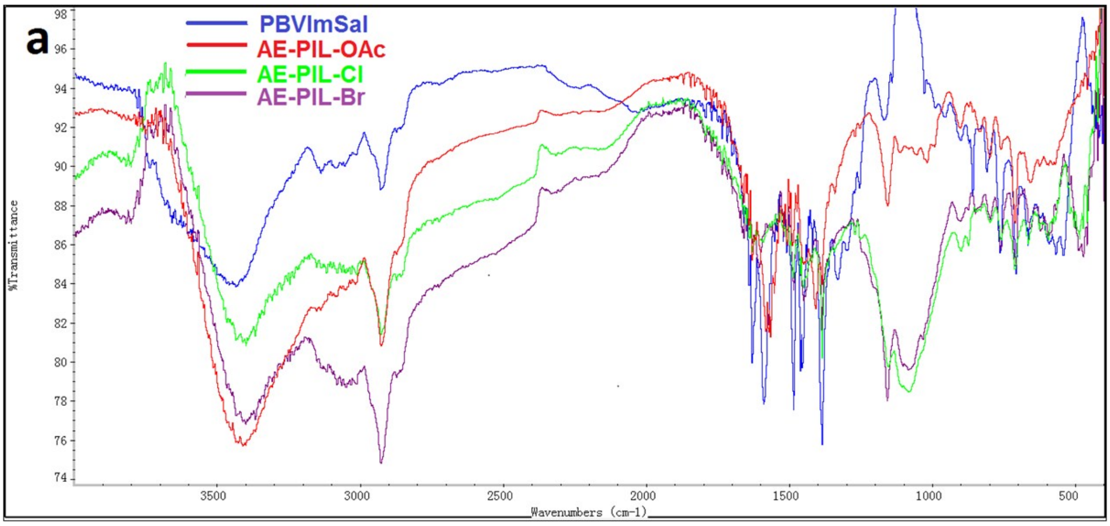


Fig. S2 ^{13}C NMR spectra of IL monomers and ^{13}C MAS NMR of PILs. a) BVImSal and PBVImSal; b) BVImOAc and AE-PIL-OAc; c) BVImCl and AE-PIL-Cl; d) BVImBr and AE-PIL-Br.

4.3. Fourier Transform Infrared spectroscopy



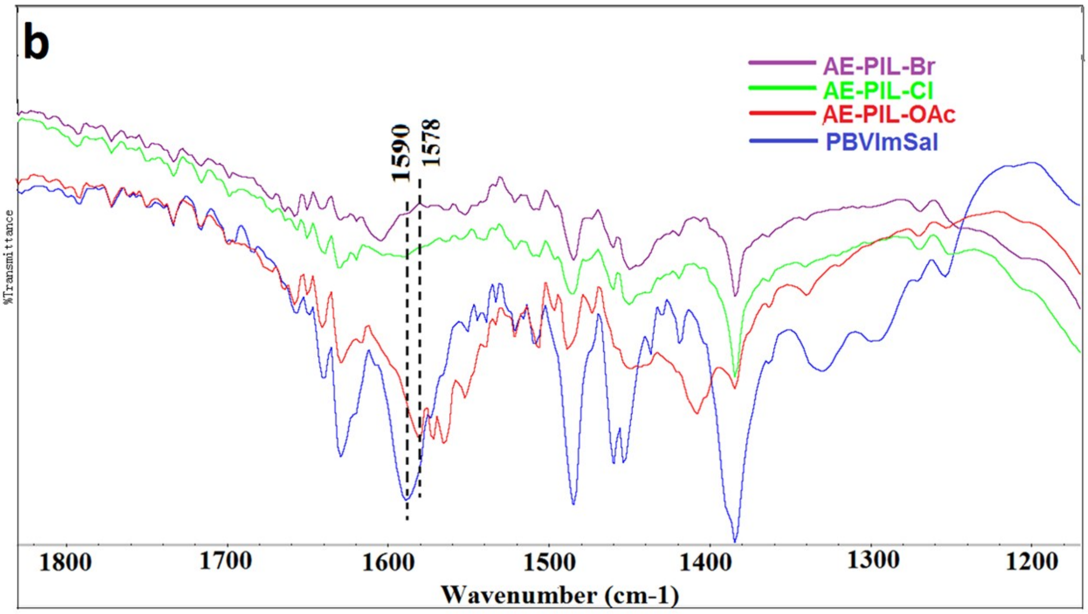
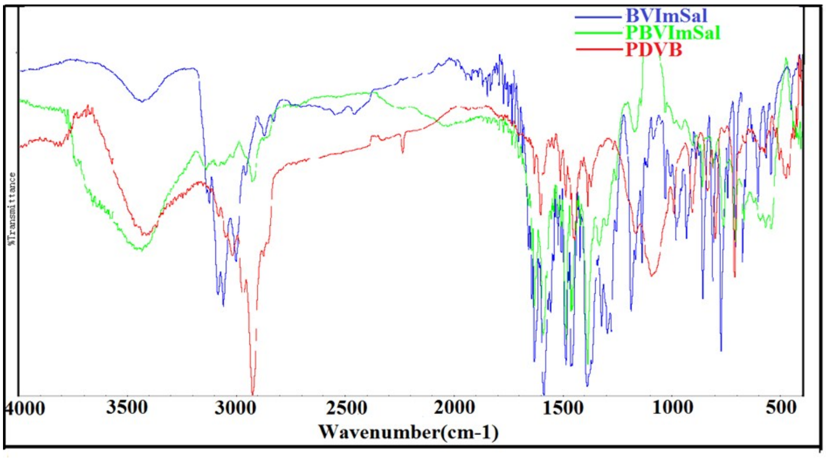
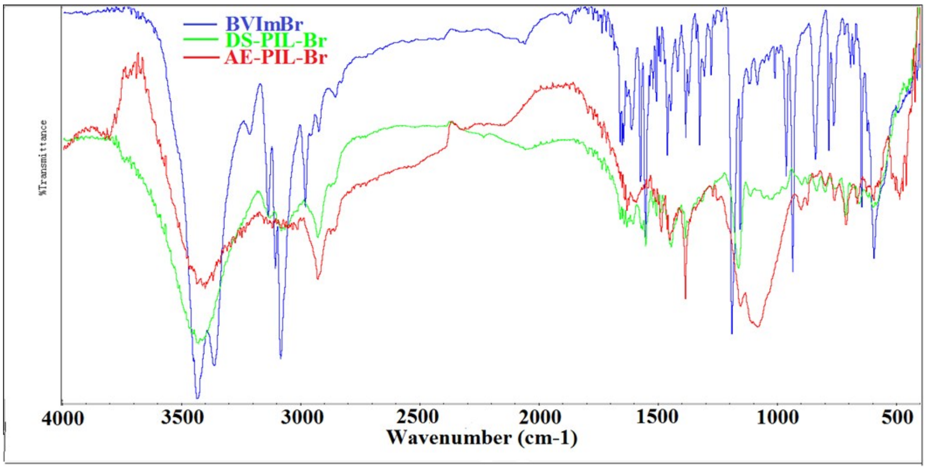
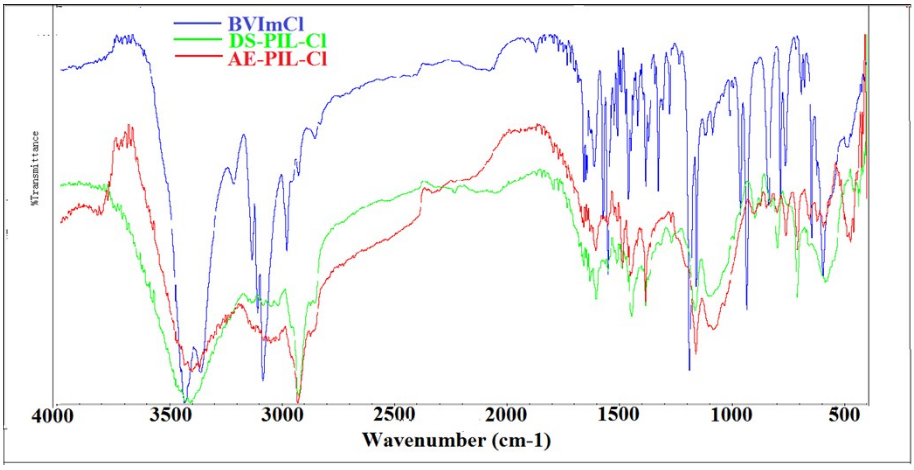


Fig. S2 FT-IR spectra of AE-PIL-X ranging from: a) 4000 to 400 cm^{-1}; b) 1800 to 1100 cm^{-1}.


BVImSal
PBVImSal
PDVB
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


BVImBr
DS-PIL-Br
AE-PIL-Br
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


BVImCl
DS-PIL-Cl
AE-PIL-Cl
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

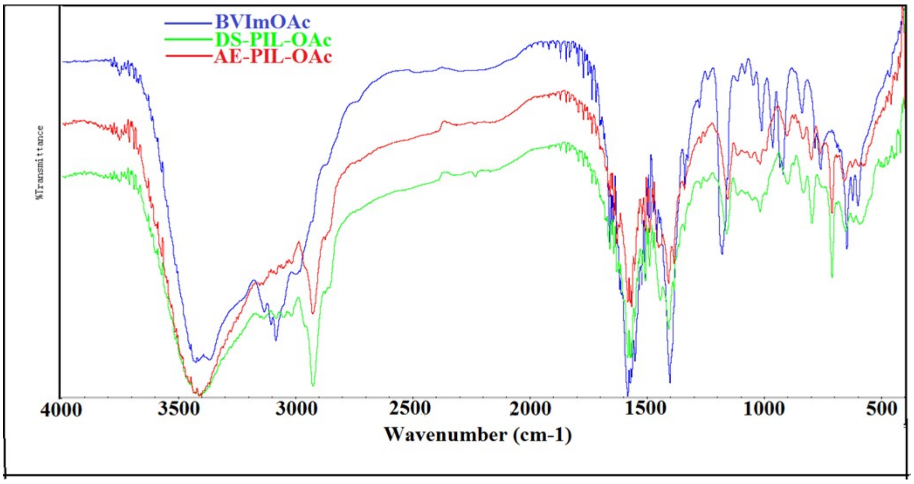
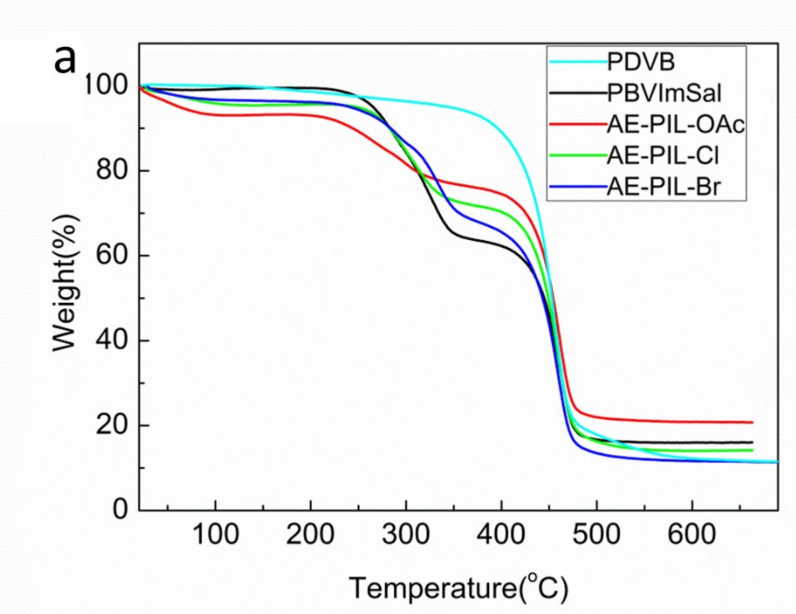
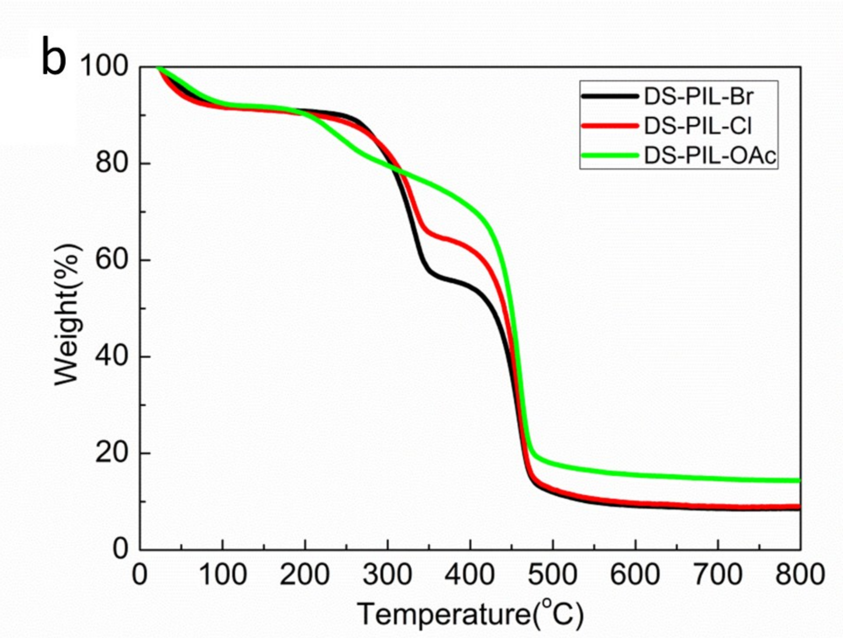


Fig. S3 FT-IR spectra of PILs bearing same anion with different synthetic methods.

AE-PIL-X and DS-PIL-X, bearing the same anion showed similar FT-IR spectra.

4.4. Thermogravimetric analysis





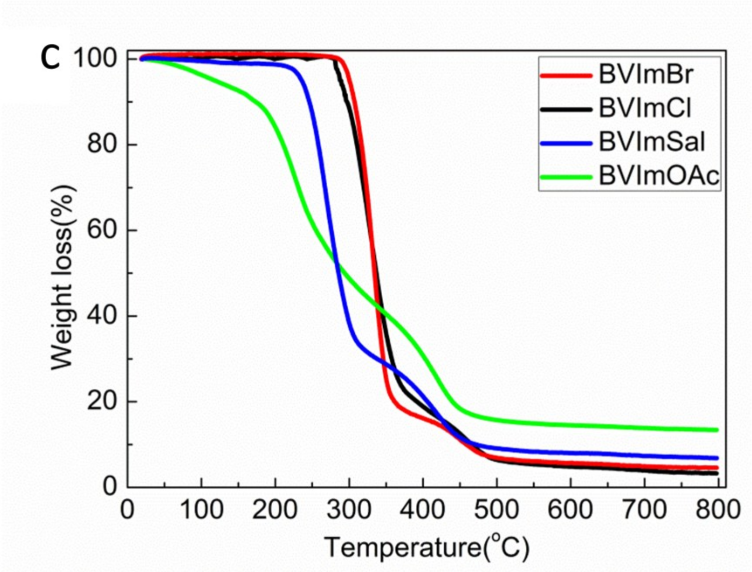


Fig. S5 TGA of a) AE-PIL-X; b) DS-PIL-X; c) IL monomers

4.5. Difference scanning calorimeter analysis

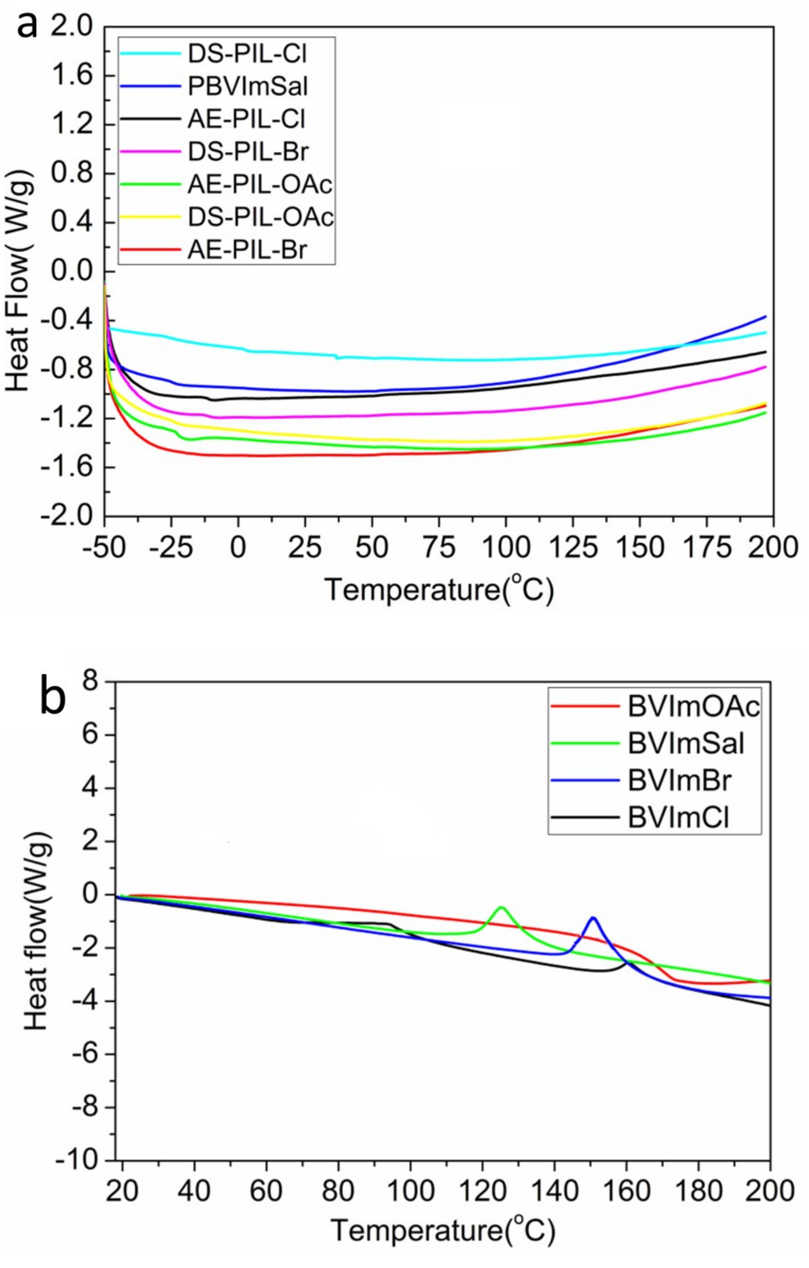


Fig. S6 DSC of a) AE-PIL-X and DS-PIL-X; b) IL monomers

4.6. Argon sorption isotherms

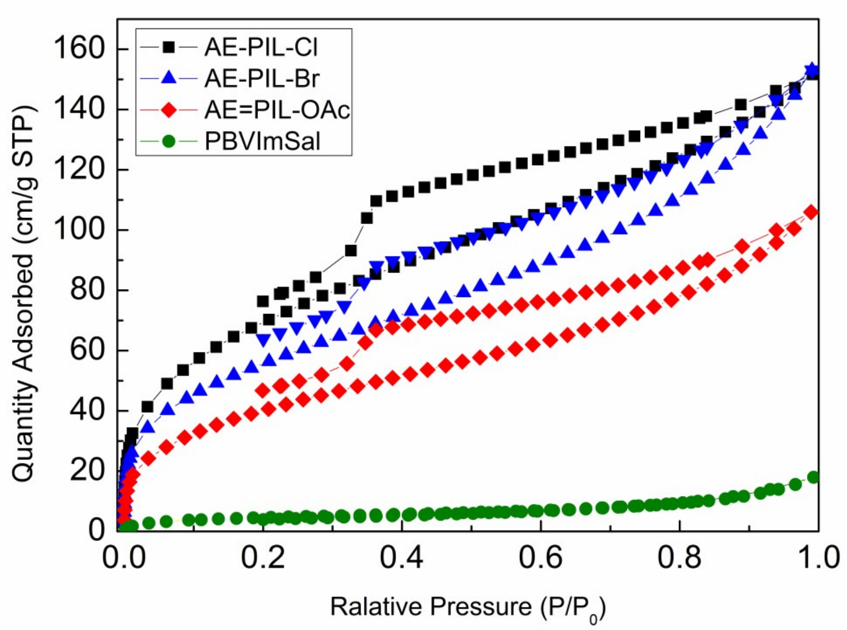
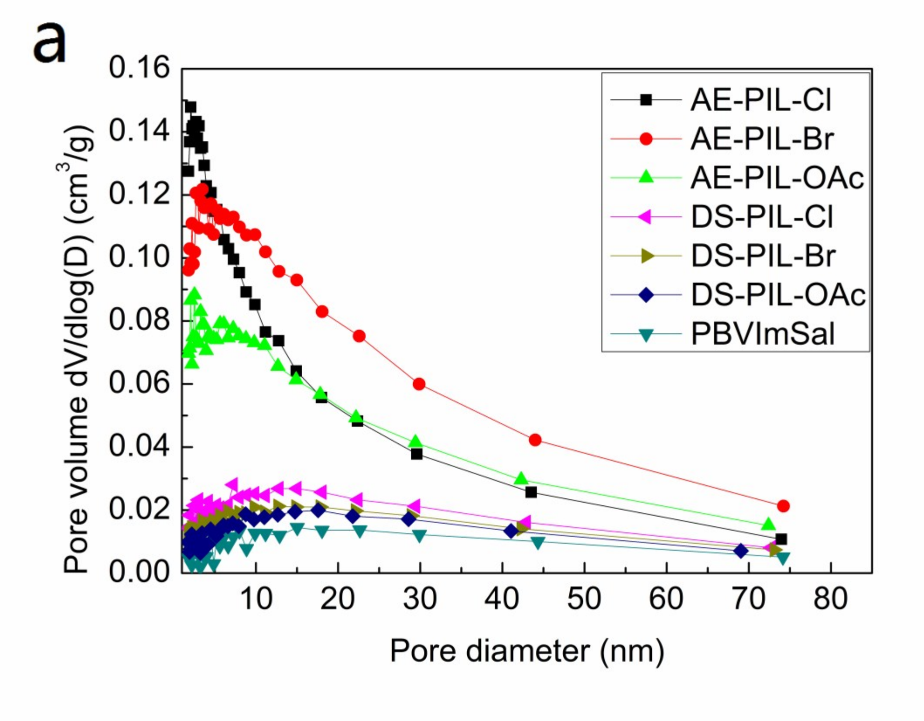
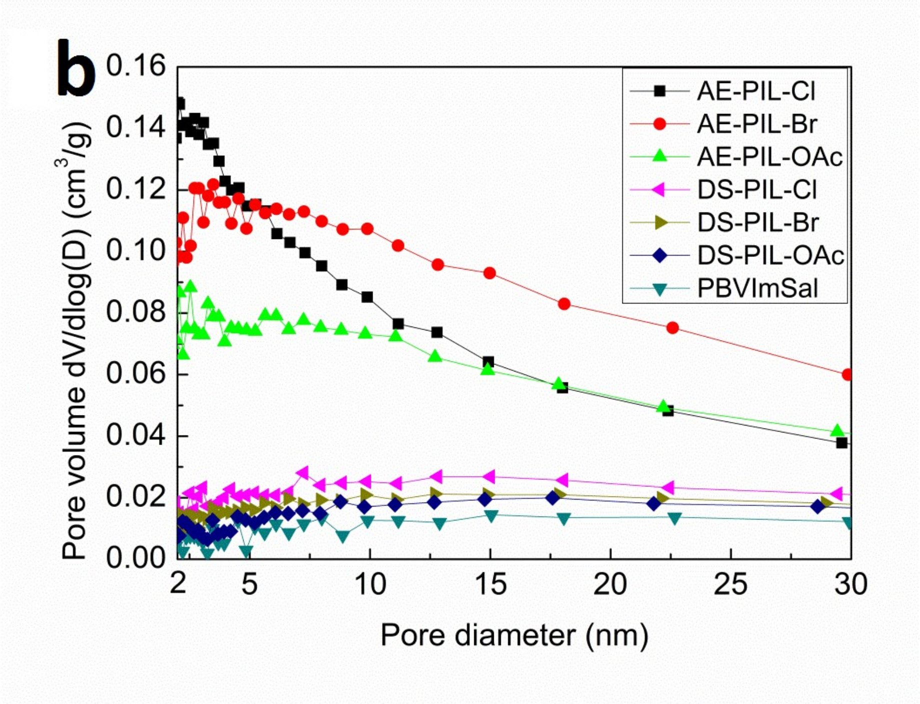


Fig. S7 Argon sorption isotherms of PILs.





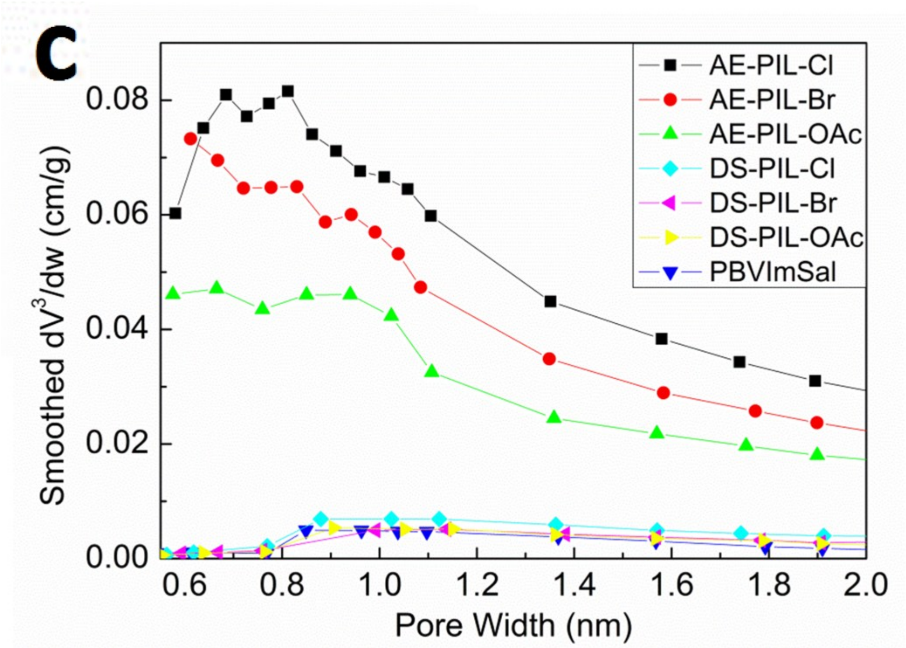


Fig. S8 Pore size distributions of AE-PIL-X and DS-PIL-X. Pore diameter/width: a) 2-80 nm; b) 2-30 nm; c) 0.6-2.0 nm.

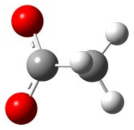
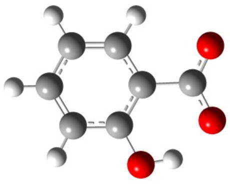
4.7. Element analysis

Table S1 The element analysis of PILs.

Entry	PILs	N(%)	C(%)	H(%)	Im[a] (mmol/g)	Im[b] (mmol/g)
1	PBVImSal	5.14	72.63	7.04	1.9	2.6
2	AE-PIL-Cl	5.22	70.14	7.52	1.9	3.5
3	AE-PIL-OAc	4.49	72.76	7.83	1.6	3.2
4	AE-PIL-Br	4.54	66.82	7.19	1.6	3.0
5	DS-PIL-Cl	4.48	72.82	7.76	1.6	3.5
6	DS-PIL-OAc	4.66	71.47	8.38	1.7	3.2
7	DS-PIL-Br	6.21	63.29	7.51	2.1	3.0

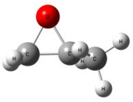
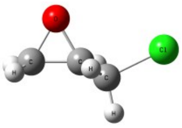
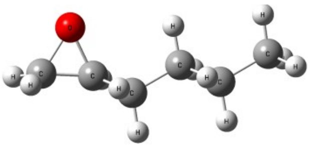
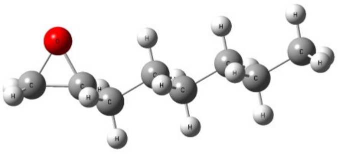
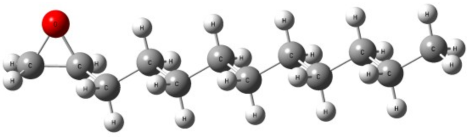
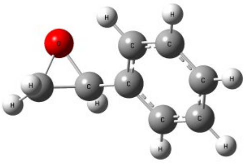
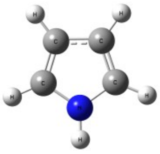
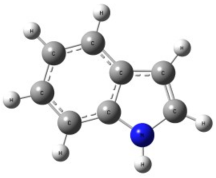
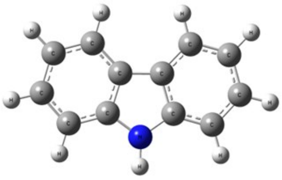
[a] The mole amount of imidazolium was calculated by nitrogen content. [b] The theoretical value of PIL was calculated according to initiate ratio of IL monomers and DVB.

Table S2 Optimized geometries of anions using Gaussian5 at b3lyp/6-311g (d, p) level.

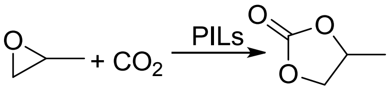
Entry	Anion	Structure	Dimensions
1	Bromide		~1.14*1.14Å^2
2	Chloride		~0.99*0.99Å^2
3	Acetate		~3.22*2.88Å^2
4	Salicylate		~6.05*4.53Å^2

5. Catalysis

Table S3 Optimized geometries of substrates using Gaussian5 at b3lyp/6-311g (d, p) level [S8, S9].

Entry	Substrate	Optimized Structure	Dimensions
1	Propylene oxide		~4.35*3.12Å^{2}
2	Epichlorohydrin		~5.02*3.12Å^{2}
3	1,2-Epoxyhexane		~8.21*3.12Å^{2}
4	1,2-Epoxyoctane		~10.78*3.12Å^{2}
5	1,2-Epoxydodecane		~15.92*3.12Å^{2}
6	Styrene oxide		~7.27*4.28Å^{2}
7	Pyrrole		~4.24*4.20Å^{2}
8	Indole		~6.65*4.28Å^{2}
9	Carbazole		~8.98*5.41Å^{2}

5.1. The cycloaddition reactions of epoxides and CO_2



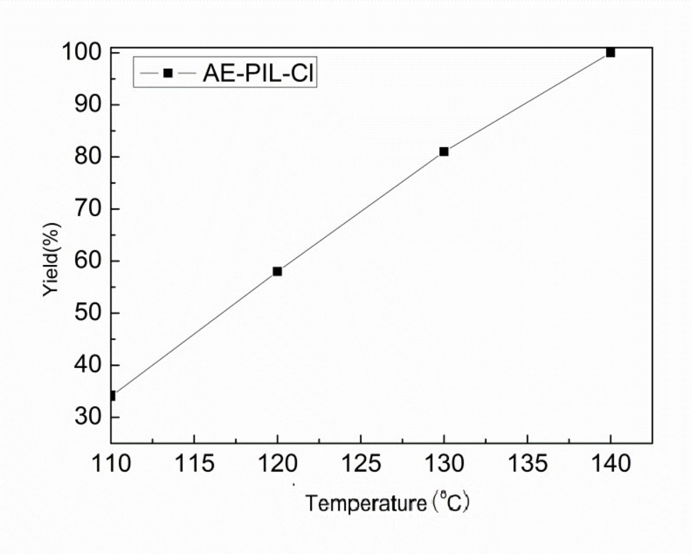


Fig. S9 The effect of reaction temperature on the activity of AE-PIL-Cl in the reaction of CO_2 and propylene oxide. Reaction condition: Propylene oxide (10 mmol), CO_2 (1 MPa), catalyst (1 mol% based on imidazolium), 6 h.

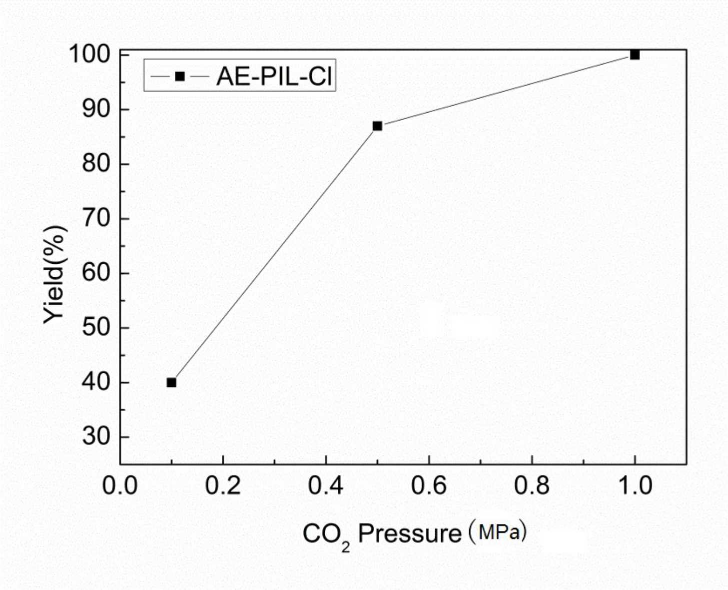


Fig. S10 The effect of CO_2 pressure on the activity of AE-PIL-Cl in the reaction of CO_2 and propylene oxide. Reaction condition: Propylene oxide (5 mmol), catalyst (1 mol% based on imidazolium), 140 °C, 6 h.

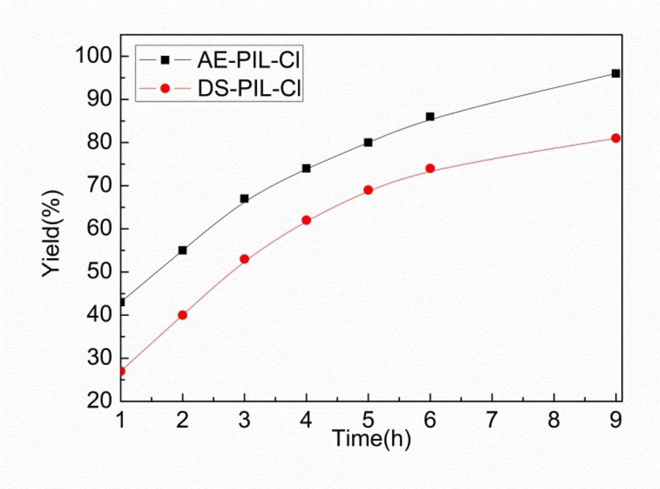
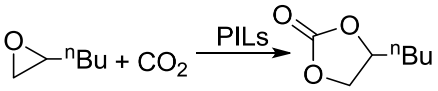
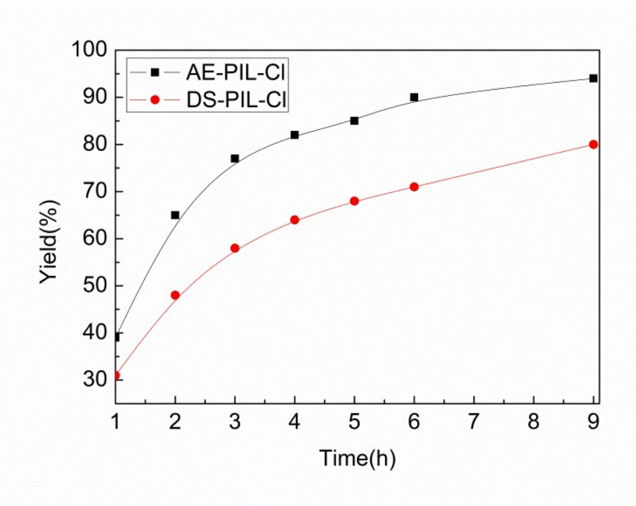
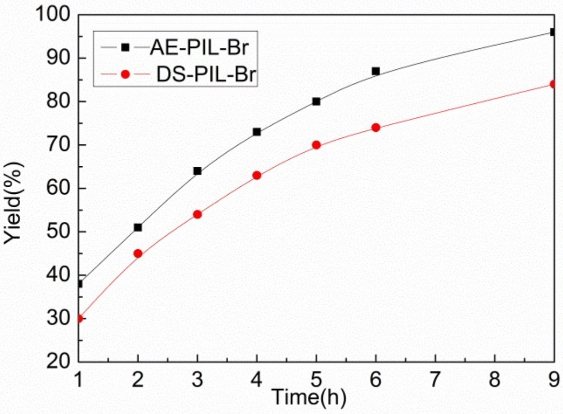


Fig. S11 The activity of AE-PIL-Cl and DS-PIL-Cl in the reaction of CO_2 and propylene oxide. Reaction condition: Propylene oxide (5 mmol), CO_2 (1 MPa), catalyst (0.5 mol% based on imidazolium), 140 °C.







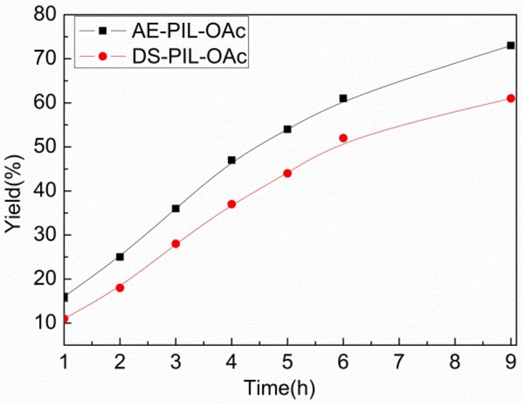


Fig. S12 The activity of AE-PIL-X and DS-PIL-X in the reaction of CO_2 and 1,2-epoxyhexane. Reaction condition: 1,2-Epoxyhexane (5 mmol), CO_2 (1 MPa), catalyst (1 mol% based on imidazolium), 140 ^{o}C.

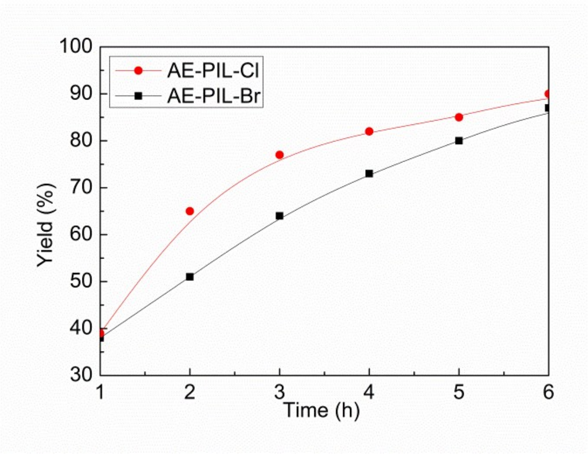
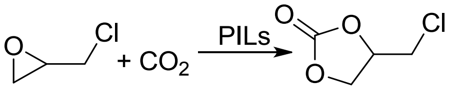


Fig. S13 The activity of AE-PIL-Cl and AE-PIL-Br in the reaction of CO_2 and 1,2-epoxyhexane. Reaction condition: 1,2-Epoxyhexane (5 mmol), CO_2 (1 MPa), catalyst (1 mol% based on imidazolium), 140 °C.



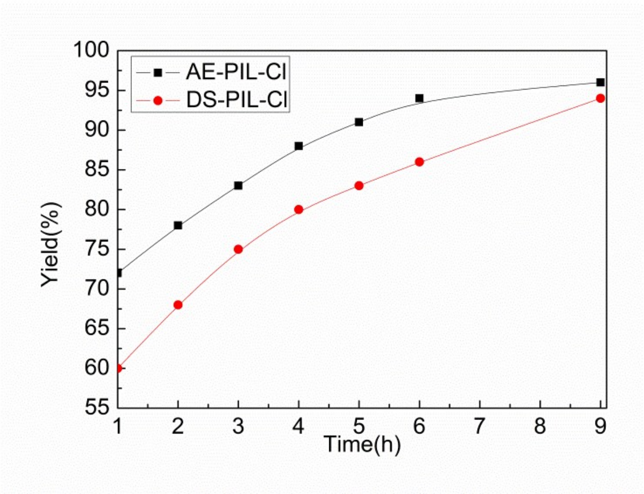
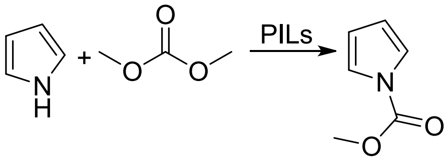


Fig. S14 The activity of AE-PIL-Cl and DS-PIL-Cl in the reaction of CO_2 and epichlorohydrin. Reaction condition: Epichlorohydrin (5 mmol), CO_2 (1 MPa), catalyst (1 mol% based on imidazolium), 140 °C.

5.2. The N-heterocyclic carbomethoxylation reactions



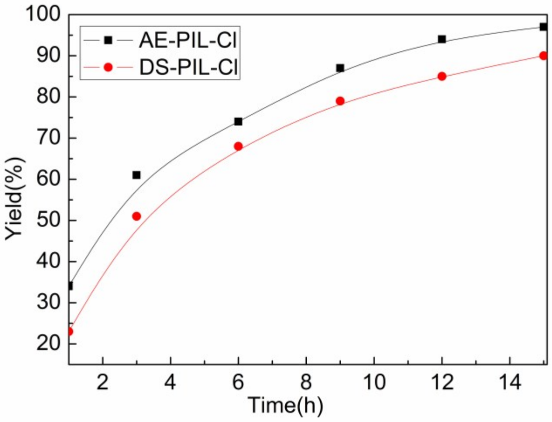


Fig. S15 The activity of AE-PIL-Cl and DS-PIL-Cl in pyrrole carbomethoxylation reaction. Reaction condition: Pyrrole (1 mmol), DMC (10 mL), catalyst (10 mol% based on imidazolium), 110 °C.

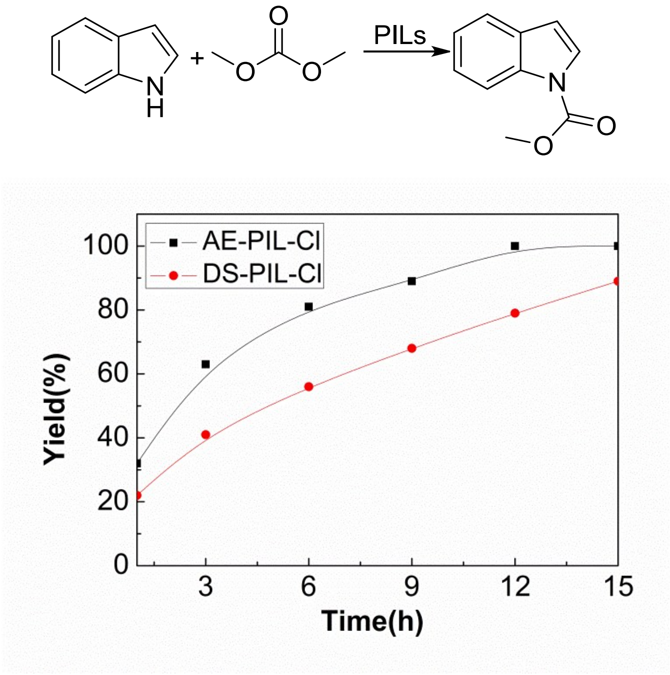


Fig. S16 The activity of AE-PIL-Cl and DS-PIL-Cl in indole carbomethoxylation reaction. Reaction condition: Indole (1 mmol), DMC (10 mL), catalyst (10 mol% based on imidazolium), 110 °C.

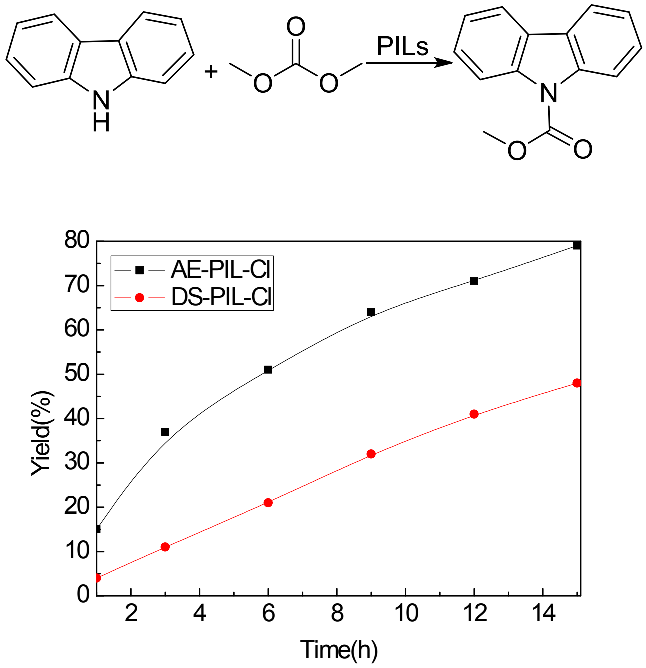


Fig. S17 The activity of AE-PIL-Cl and DS-PIL-Cl in carbazole carbomethoxylation reaction. Reaction condition: Carbazole (1 mmol), DMC (10 mL), catalyst (10 mol% based on imidazolium), 110 °C.

5.3. Recycle of catalyst

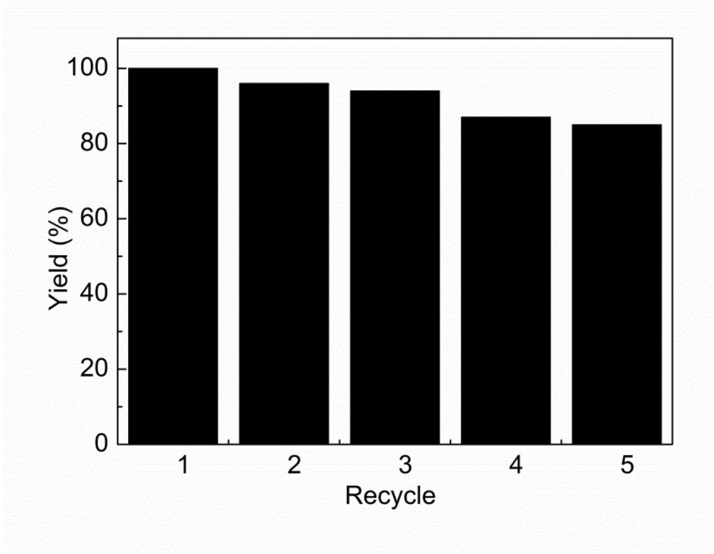
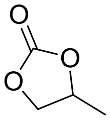


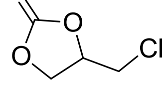
Fig. S18 The recycle of AE-PIL-Cl in the reaction of CO_2 and 1,2-epoxyhexane. Reaction condition: 1,2-Epoxyhexane (5 mmol), CO_2 (1 MPa), catalyst (1 mol% based on imidazolium), 140 ^{o}C.

The PILs can be easily recycled from the reaction mixture by simple centrifugation. No significant decrease of catalytic activity was observed after 5 runs of the catalysts.

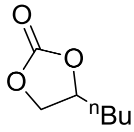
5.4. NMR data of products



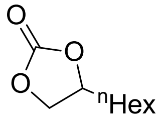
1,2-Propylene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 4.92-4.84 (m, 1H), 4.60 (t, J = 8.0 Hz, 1H), 4.04 (t, J = 8.0 Hz, 1H), 1.50 (dd, J = 3.0 Hz, J = 5.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 155.17, 73.70, 70.76, 19.42.



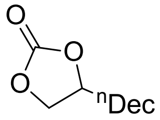
3-Chloro-1,2-propylene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 5.01-4.95 (m, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.39-4.35 (m, 1H), 3.81-3.77 (m, 1H), 3.72-3.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 154.24, 74.33, 66.99, 43.74.



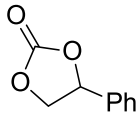
1,2-Hexene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 4.75-4.68 (m, 1H), 4.54 (t, J = 8.0 Hz, 1H), 4.07 (t, J = 8.0 Hz, 1H), 1.86-1.77 (m, 1H), 1.74-1.65 (m, 1H), 1.50-1.34 (m, 4H), 0.93 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 155.17, 77.14, 69.46, 33.58, 26.47, 22.28, 13.81.



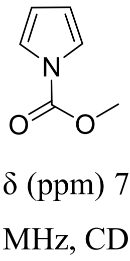
1,2-Octylene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 4.75-4.69 (m, 1H), 4.54 (t, J = 8.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 1.82-1.65 (m, 2H), 1.49-1.30 (m, 8H), 0.89 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 155.11, 77.11, 69.40, 33.80, 31.47, 28.74, 24.28, 22.40, 13.92.



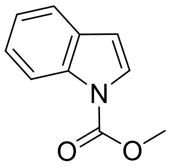
1,2-Dodecylene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 4.72-4.69 (m, 1H), 4.53 (t, J = 8.0 Hz, 1H), 4.07 (t, J = 8.0 Hz, 1H), 1.80-1.64 (m, 2H), 1.51-1.27 (m, 16H), 0.88 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 154.99, 77.06, 69.34, 33.84, 31.83, 29.50, 29.40, 39.30, 29.27, 29.11, 24.33, 22.61, 14.00.



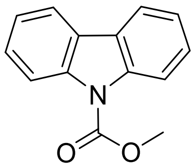
Styrene carbonate: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 7.46-7.40 (m, 3H), 7.35 (d, J = 8.0, 2H), 5.67 (t, J = 8.0 Hz, 1H), 4.79 (t, J = 8.0 Hz, 1H), 4.32 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 154.93, 135.87, 129.72, 129.23, 125.90, 78.04, 71.20.



Pyrrole-1-carboxylic acid methyl ester: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 7.26 (d, J=4.0 Hz, 2H), 6.23 (d, J = 4.0 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 150.80, 119.92, 112.32, 53.83.



Indole-1-carboxylic acid methyl ester: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 8.17 (d, J = 6.0Hz, 1H), 7.55-7.59 (m, 2H), 7.33 (t, J = 6.0 Hz, 1H), 7.24 (t, J = 6.0 Hz, 1H), 6.58 (d, J = 6.0Hz, 1H), 4.01(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 151.46, 135.16, 130.39, 125.42, 124.43, 122.93, 120.93, 115.03, 108.06, 53.69.



Carbazole-1-carboxylic acid methyl ester: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) 8.27 (d, J = 8.0Hz, 2H), 7.95 (d, J =8.0Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 4.11(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm) 152.83, 138.15, 127.10, 125.86, 123.26, 119.55, 116.15, 53.39.

Reference

[S1] Y. Xiong, J. Liu, Y. Wang, H. Wang and R. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 9114–9118.

[S2] Z. Cheng, X. Chu, Z. Sheng, J. Xu, H. Zhong and L. Zhang, *Mater. Lett.*, 2016, **168**, 99–102.

[S3] F. Bianchi, F. Bisceglie, S. Dugheri, G. Arcangeli, V. Cupelli, E. Borrello, L. Sidisky and M. Careri, *J. Chromatogr. A*, 2014, **1331**, 1– 9.

[S4] Y. Men, X. Du, J. Shen, L. Wang, Z. Liu, *Carbohydr. Polym.*, 2015, **121** 348–354.

[S5] L. P. Jameson and S. V. Dzyuba, *J. Nat. Prod.*, 2011, **74**, 310–313.

[S6] M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831–16840.

[S7] T. Zou, L. Lu, X. Liu, Z. Zhang, L. Wang, X. Fu, G. Gao, Y. Kou, M. He, *Chin. J. Chem.*, 2008, **26**, 1469–1480.

[S8] P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142−2145.

[S9] B. Ugale, S. S. Dhankhar and C. M. Nagaraja, *Inorg. Chem.*, 2016, **55**, 9757−9766.