Electronic Supplementary Information

Acid-base indicators for non-polar solvent via anionexchange of polymeric ionic liquids with anionic dyes

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1. Materials and methods

Phthalic anhydride (PA, purity 299.7%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and dried under vacuum at 60 °C for 24 h. Epichlorohydrin (ECH, purity 299.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and purified by distillation under reduced pressure. Ethylene glycol (initiator, purity 299.0%) was purchased from Ling Feng Chemical Reagent Co., Ltd (Shanghai, China). 1-Methylimidazole (MIM, purity 299.0%) was purchased from Adamas Chemical Reagent Co., Ltd (Shanghai, China) and used without futher purification. Methyl orange (MO, Ind) and methyl blue (MB, BS) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) used without futher purification. N.Nand Dimethylformamide(DMF, purity≥99.5%), dichloromethane($\geq 99.5\%$), acetone (purity 299.5%) were purchased from Ling Feng Chemical Reagent Co., Ltd (Shanghai, China) and purified by distillation under reduced pressure. Acetic acid (Ac, purity 299.5%) was purchased from Ling Feng Chemical Reagent Co., Ltd (Shanghai,

China). Isopropylamine (IPA, purity≥99.0%) were purchased from Alfa Aesar (China).

Measurement of 1HNMR spectra was conducted on a Bruker Avance 400 spectrometer (Bruker BioSpin, Switzerland) operating at 300 MHz in DMSO-d6. Fourier transformed infrared (FT-IR) spectra were obtained on a Nicolet 8700 FT-IR spectrometer. The molecular weights and dispersity indices were determined using Polymer Laborato GPC-50. UV-Vis spectra were recorded on a Perkin Elmer lambda35 UV-vis spectrometer.

2. Synthesis of polyester and PIL-Cl

In a clean three-necked flask equipped with a condenser with bulbed inner tube, a constant pressure funnel and a magnetic stirrer, PA (29.60g, 0.2mol) and ethylene glycol (0.13g, 2mmol) were completely dissolved in DMF (50ml) . ECH (18.50g, 0.2mol) was added dropwise to the above solution under vigorous stirring in a dry nitrogen atmosphere. The reaction mixture was kept at 100 °C for 10 h. After the reaction was completed, the mixture was cooled to room temperature. A small amount of the mixture was poured into a large amount of cold deionized water. The precipitate was washed with deionized water for several times . The obtained polyester was dried at 35 °C for 2 days in a vacuum oven.

After removing remaining unreacted ECH from the above reaction mixture, MIM was added dropwise in a 1.5:1 molar MIM/Cl ratio. The stiried reaction mixture was kept at 90 °C for 4 days. After the grafting reaction was completed, the mixture was cooled to room temperature, and then poured into a large amount of acetone. The precipitate was washed with acetone for several times. The resulting polymer PIL-Cl was dried at 35 °C for 2 days in a vacuum oven.

The ¹HNMR spectra of polyester and PIL-Cl are presented in Fig. 1. The characteristic signal peaks of polyester are at 3.92 (e), 4.50 (c) and 5.47 ppm (d). Comparing with the ¹HNMR spectrum of polyester, the ¹HNMR spectrum of PIL-Cl shows new signals at 3.83ppm (i) and 9.0-9.6 ppm (h), which are attributed to the protons from MIM groups. This confirms the successful synthesis of PIL-Cl. The

grafting ratio of MIM groups is calculated to about 60% by comparing the integral of peaks h at 9.0-9.6 ppm with the integral of peaks ArH and MIH at 7-8 ppm. FTIR spectra are also used to characterize polyester and PIL-Cl (shown in Fig. S1). Compared with polyester, the new absorption bands at 1171 cm⁻¹ and 1578 cm⁻¹ in the FTIR spectrum of PIL-Cl are characteristic absorption peaks of MIM groups, indicating the successful preparation of PIL-Cl. The molecular weights of polyester are measured by GPC (Fig. S2) while Mn is 4200 Da, Mw is 5400 Da and PDI is 1.286. Owning to the strong polarity, PIL-Cl molecules were absorbed in chromatograhic column and it caused the molecular weights of PIL-Cl could not be accurately measured. Therefore, the molecular weight (Mn) of PIL-Cl is calculated according to the grafting ratio of MIM groups and the result is about 5100 Da.



Figure S1. The FT-IR spectra of polyester and PIL-Cl.



Figure S2. The GPC chromatogram of polyester.

3. Synthesis of PIL-MO

MO (0.61g, 1.86mmol) was completely dissolved in deionized water (500ml). PIL-Cl (0.50g) dissolved in deionized water (50ml) was added dropwise over 2 h in a 1.2:1 molar MO/Cl ratio. The reactant mixture was kept stirred for 1 day in room temperature, and then the red precipitate was collected and washed with deionized water for several times. The obtained product PIL-MO was dried for 2days in a vacuum oven.

In the ¹HNMR spectrum of PIL-MO, all the signals are attributed to the protons of PIL and MO groups. The signals at 3.83 ppm (i) , 4.69 ppm (c) , 5.74 ppm (d) and 9.18 ppm (h) are attributed to PIL containing polyester backbone and MIM groups, and the signals at 3.05ppm (n) and 6.82ppm (m) are attributed to MO groups. This confirms that PIL-MO is successfully obtained. Comparing the integral of peaks h with the integral of peaks m ($S_m/2S_h$), the conversion ratio from chloride ions to MO groups is calculated to about 100% which means that almost all chloride ions have been exchanged by MO anions. It have been further confirmed by comparing the integral of peaks n ($S_n/2S_i$). According to the extremely high conversion ratio, the molecular weight (Mn) of PIL-MO was calculated to about 7900 Da.

4. Synthesis of PIL-MB

MB (1g, 1.25mmol) was dissolved in deionized water (400ml). PIL-Cl (0.34g) dissolved in deionized water (50ml) was added dropwise to the above solution in a 1.2:1 molar MB/Cl ratio. The stirred mixture was kept in room temperature for 1 day. After full reaction, the purple precipitate was obtained and added into a large amount of dry dichloromethane (100ml) under vigorous stirring for 10h. After that, the precipitate was filtered out and the crude PIL-MB was left in the filtrate. By removal of dichloromethane on the rotary evaporator, PIL-MB was obtained.

In the ¹HNMR spectrum of PIL-MB, the signals at 3.84 ppm (i), 4.67 ppm (c), 5.72 ppm (d) and 9.17 ppm (h) are attributed to the protons of PIL and new signals appearing at 1-1.5 ppm, 4.83 ppm, 7.02 ppm, 7.28 ppm and 7.54 ppm are attributed to the protons of MB groups, and these peaks are also observed in the spectrum of MB (Fig. S3). This evidence proves the successful preparation of PIL-MB. By comparing the integral of peaks h with the integral of peaks ArH and MIH at 6.5-8 ppm, the conversion ratio of MB anions is calulated to about 84%. Moreover, the molecular weight (Mn) of PIL-MB is calculated to about 12000 Da.

Table S1. The molecular weights of polyester, PIL-Cl, PIL-MO, PIL-MB and PIL-
MO-MB

	Polyester	PIL-Cl	PIL-MO	PIL-MB	PIL-MOB
Mn	4.2×10^3	5.1x10 ³	7.9x10 ³	1.2x10 ⁴	9x10 ³

 Table S2. Solubility Table

	H ₂ O	DMSO	CH ₂ Cl ₂	CHCl ₃	$C_2H_4Cl_2$	$C_2H_2Cl_4$				
polyester	-	++	-	-	-	-				
PIL-Cl	++	++	-	-	-	-				
MO	+	++	-	-	-	-				
MB	+	++	-	-	-	-				
PIL-MO	-	++	++	+	++	++				
PIL-MB	-	++	++	++	++	++				
PIL-MO-	-	++	++	+	++	++				
MB										



5. Synthesis of PIL-MOB

MO (0.65g, 2mmol) and MB (1.59g, 2mmol) were dissolved together in deionized water (500ml). PIL-Cl (1.07g) dissolved in deionized water (100ml) was added dropwise to the solution in a 1.2:1 molar (MO+MB)/Cl ratio. The stirred mixture was kept in room temperature for 1 day. The black precipitate was collected and added into large amount of dry dichloromethane (100ml) under stirring for 10 h. And then the precipitate was filtered out and the crude PIL-MOB was left in the filtrate. Finally, PIL- MOB was prepared by removal of dichloromethane on the rotary evaporator.



Figure S4. The ¹HNMR spectrum of PIL-MO-MB

The characteristic signal peaks of PIL were observed at 3.85 ppm (i), 4.69 ppm (c), 5.74 ppm (d), 9.19 ppm (h). The characteristic signal peaks of MO groups were observed at 3.05 ppm (n) and 6.82 ppm (m). And the characteristic signal peaks of MB groups were located at 1-1.5 ppm and 4.83 ppm. It proved that PIL-MOB was successfully prepared. The total conversion ratio of MO and MB anions was surprisingly high and it was calculated to about 100%. Almost all chloride ions had been exchanged. The respective conversion ratios of MO anions and MB anions were calculated to about 76% and 24%.

6. Investigation of the acidic-indicating behavior of MO/H₂O solution.



Figure S5. Acidic chromism characterization of MO/H₂O. (a) Acid-indicating pictures of MO/H₂O at various concentrations of Ac. (b) The UV-vis absorption spectra of MO/H₂O at various concentrations of Ac.

7. Investigation of the basic-indicating behavior of MB/H₂O solution.



Figure S6. Basic chromism characterization of MB/H₂O. (a) Base-indicating pictures of MB/H₂O at various concentrations of IPA. (b) The UV-vis absorption spectra of MB/H₂O at various concentrations of IPA.

8. Investigation of the indicating behaviors of PIL-MO and PIL-MB

in other non-polar solvents.



$1,2\text{-Dichloroethane}(\mathrm{C}_{2}H_{4}\mathrm{Cl}_{2})$



1, 1, 2, 2-Tetrachloroethane($C_2H_2Cl_4$)



Figure S7. The indicating pictures of PIL-MO and PIL-MB in CHCl₃, $C_2H_4Cl_2$ and $C_2H_2Cl_4$.