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Supporting Information

Controlled Synthesis of Sugar-Containing Poly(ionic liquid)s

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Materials

4-Vinylpyridine (4VP, 96%), 1-phenylethylchloride (1-PECl, 97%), methyl 2-chloropropanoate (2-MCP, 97%), 3-bromo-1-propanol (PropanolBr, 97%), lithium tetrafluoroborate ($LiBF_4$, 99.9%), lithium hexafluorophosphate ($LiPF_6$, 97%) and bis(trifluoromethane)sulfonimide lithium salt (Tf_2NLi, 99%) were purchased from Aladdin (China) and used directly. *Tris*(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized according to a previously reported procedure and stored at -25°C under an inert atmosphere before use.[1-2] (3*S*,4*S*,5*S*,6*R*)-2-(3-bromopropoxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (ManBr) and (2*S*,3*R*,4*S*,5*S*,6*R*)-2-(3-bromopropoxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (GluBr) were synthesized according to a previously reported procedure.[3] Copper (I) chloride (CuCl, 99.99%, Sigma-Aldrich) was washed sequentially with acetic acid and ethanol two times and dried under vacuum. Membrane dialysis (1K MWCO) was obtained from Spectrum Laboratories. All other reagents and solvents were obtained at General-Reagent from Aladdin (China) and used without further purification unless otherwise stated.

Instrumentation and analysis

^1H NMR spectra were recorded with a Bruker AV 500M spectrometer using deuterated solvents obtained from Aladdin. Monomer conversion for 4VP was calculated by comparing the integral of vinyl protons with that from the polymer backbones. The number-average molecular weight (M_n) and molecular weight distribution (M_w / M_n) were determined by Waters 1515 size exclusion chromatography (SEC) in *N, N*-

dimethylformamide (DMF) at 40 °C with a flow rate of 1.00 mL min^{-1}, which was equipped with 2414 refractive index (RI) and 2489 UV detectors, a 20 μm guard column (4.6 mm × 30 mm) followed by three Waters Styragel columns (HR_1, HR_3, and HR_4) and autosampler. Narrow linear polystyrene standards in the range of 540 to 7.4×10^5 g mol^{-1} were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS5 FTIR spectrometer using an iD7 diamond attenuated total reflectance optical base. The X-ray photoelectron survey spectrum was performed by Thermo Scientific K-Alpha+ with Al Kα radiation. The binding activity of sugar-containing PILs with Con A was tested by measuring the absorbance at 420 nm using a SHIMADZU UV-2600 UV/Vis spectrophotometer.

Synthesis of P4VP by Cu(0)-RDRP

The polymerization of P4VP is performed under nitrogen protection and the typical procedures are shown as follow. Me_6TREN (0.24 mmol, 64 μL), CuCl (0.24 mmol, 24 mg) and 1.5 mL H_2O were added to one 30 mL vial with a magnetic stir bar. After rapid disproportionation, purple Cu(0) powders were observed at the bottom of the blue solution. The mixture was degassed for 15 min *via* nitrogen bubbling. After that, a pre-degassed mixture of 4VP (18 mmol, 1.89 g), 1-PECl (0.6 mmol, 84 mg) or 2-MCP (0.6 mmol, 73 mg) in 1.5 mL DMSO was added into the blue suspension containing Cu(0) powders *via* a gas tight syringe. The vial was then sealed for polymerization under ambient temperature (5 ~ 10 ℃). During the polymerization, reaction mixture was carefully taken out at defined time periods for analysis. The sample for ^1H NMR was directly diluted with DMSO-d_6. Catalyst residues were removed by filtering through a column of neutral alumina prior to SEC analysis.

When the stirring stopped, the polymer solution generated a biphasic system. Crude polymer product could be sucked away by a syringe. In order to obtain high-purity polymer products, the residual monomer, catalysts and other impurities could be removed by dialysis (MWCO 1000Da) against water for one day following lyophilization.

Quaternization reaction with organobromine compounds

In a typical reaction, P4VP (210 mg, ~ 2 mmol 4VP unit), 3-bromo-1-propanol (834 mg, 6 mmol) and 5 ml of DMSO were charged to a 25 mL, round-bottomed flask equipped with a stir bar. The result mixture bubbled for 15 min with N_2 and stirred at 80 °C for 2 days. DMSO and excess 3-bromo-1-propanol were removed by dialysis against water for two days following lyophilization.

To obtain sugar-containing PILs, P4VP (210 mg, ~ 2 mmol 4VP unit), bromine-containing mannose (ManBr, 1.8 g, 6 mmol) or glucose (GluBr, 1.8 g, 6 mmol) and 5 ml DMSO were charged to a 25 mL, round-bottomed flask equipped with a stir bar. The result mixture bubbled for 15 min with N_2 and stirred at 80 °C for 2 or 5 days. DMSO and excess bromine-containing sugar were removed by dialysis against water for two days following lyophilization.

Anion exchange reactions with different salts

Pyridinium-based poly(ionic liquid)s (P4VP-PropanolBr, 227 mg; P4VP-GluBr, 284 mg; P4VP-ManBr, 300 mg) and 1.5 mmol of salts (141 mg of $LiBF_4$, 228 mg of $LiPF_6$

or 431 mg of $LiTf_2N$) were dissolved in 5 mL H_2O and reacted at 40 ℃ for 12h. Nine PILs with varied anions could be recovered after dialysis against water following lyophilization.

Lectin-binding assay

Turbidimetric assay was adopted to measure the bind ability with Con A, which was carried out following a previously described procedure by Kiessling.[4] Con A (1 mg mL^{-1}) was fully dissolved in HBS buffer (HEPES 10 mM, NaCl 150 mM, and $CaCl_2$ 1 mM, adjusted to pH 7.4 and filtered with 0.2 μm nylon filters). The exact concentration of Con A was determined by using the UV absorbance at 280 nm [$A = 1.37 \times (\text{mg mL}^{-1}$ Con A)]. The solution was then diluted to 2 μM. PILs in HBS buffer (50 μL, 200 μM) and extra 500 μL HBS buffer was added into a 5 mL microcuvette. Then the Con A solution (500 μL) was rapidly injected into the cuvette. The absorbance of the mixture was quickly recorded at 420 nm for 60 min every 3 s. The relative rate of interaction was determined by a linear fit of the steepest portion of the initial aggregation. Each experiment was repeated three times.

Antibacterial Testing

Antibacterial testing and analysis were carried out according to a previously described method by Gillies et al.[5] The antibacterial activity of a serials of PILs was evaluated against *E.coli* (ACTCC 29522) by suspending the bacteria in phosphate buffer (PBS 0.3 mM KH_2PO_4, pH = 7.2 ± 0.2) and inoculating given concentrations of the samples. During the test, *E.coli* was first cultivated in sterilized Luria-Bertani (LB) broth and incubated for 12 hours at 37 ℃ with a shaking incubator (175 rpm). The resulting bacterial broth culture was then pelletized by centrifugation, washed with phosphate buffer three times, and then diluted to a concentration of 2 x 10^9 colony forming units (CFUs) per mL for *E. coli*, as determined by optical density (OD) at 600 nm (2.0 for *E. coli*). The suspensions were then diluted to 2 x 10^5 CFUs/mL to provide the stock solution for all bacterial testing. To investigate the antibacterial performance of PILs [P4VP-PropanolBr, P4VP-GluBr, P4VP-ManBr, P4VP-PropanolBF_4, P4VP-GluBF_4, P4VP-ManBF_4,], varied amounts of samples (1, 3, 5mg) were dissolved in 500 μL PBS buffer and then 500 μL diluted microbial solution (2 x 10^5 CFUs per mL) was added. Blank were made by 500μL PBS buffer added to 500 μL diluted stock solution as control. The resultant suspensions were incubated at 37 °C in a shaking incubator for 1 h 30 minutes. After that, 5 μL suspensions were taken to spread on the LB agar plate and incubated for 12 hours at 37 °C. Testing was completed in technical and biological quintuplicates.

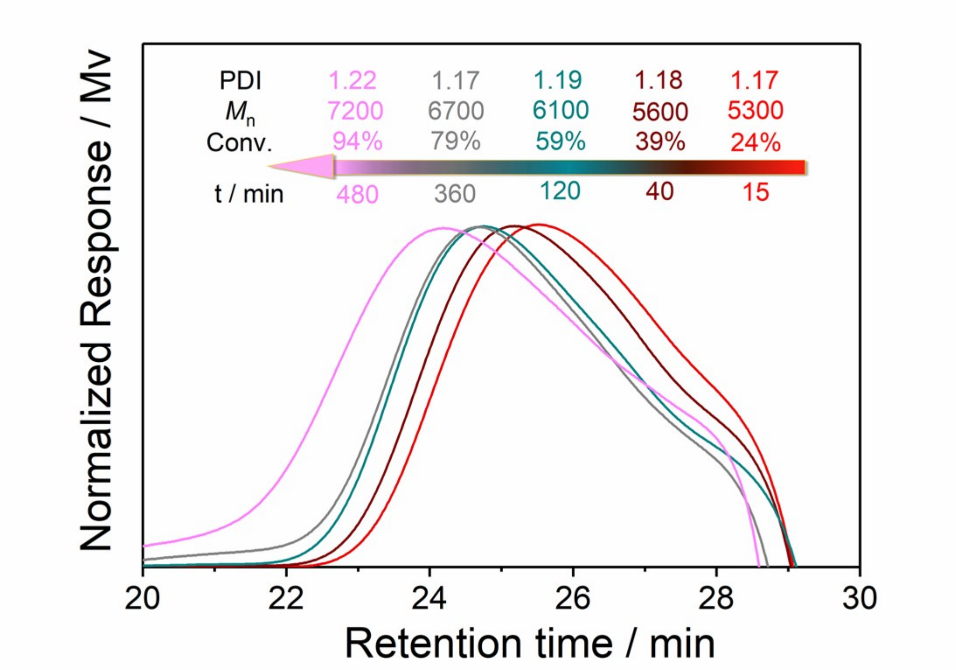

Figure S1. SEC elution traces of P4VP by Cu(0)-RDRP using 1-PECl as the initiator (DMSO/water solution, ambient temperature).

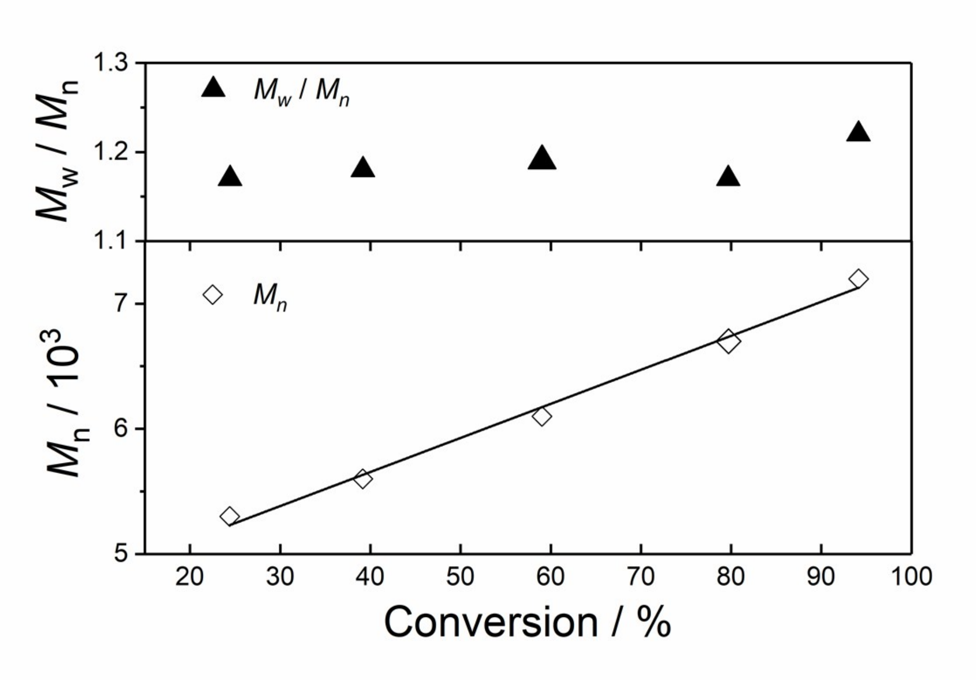

Figure S2. Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) as a function of monomer conversion for P4VP by Cu(0)-RDRP using 1-PECl as the initiator (DMSO/water solution, ambient temperature).

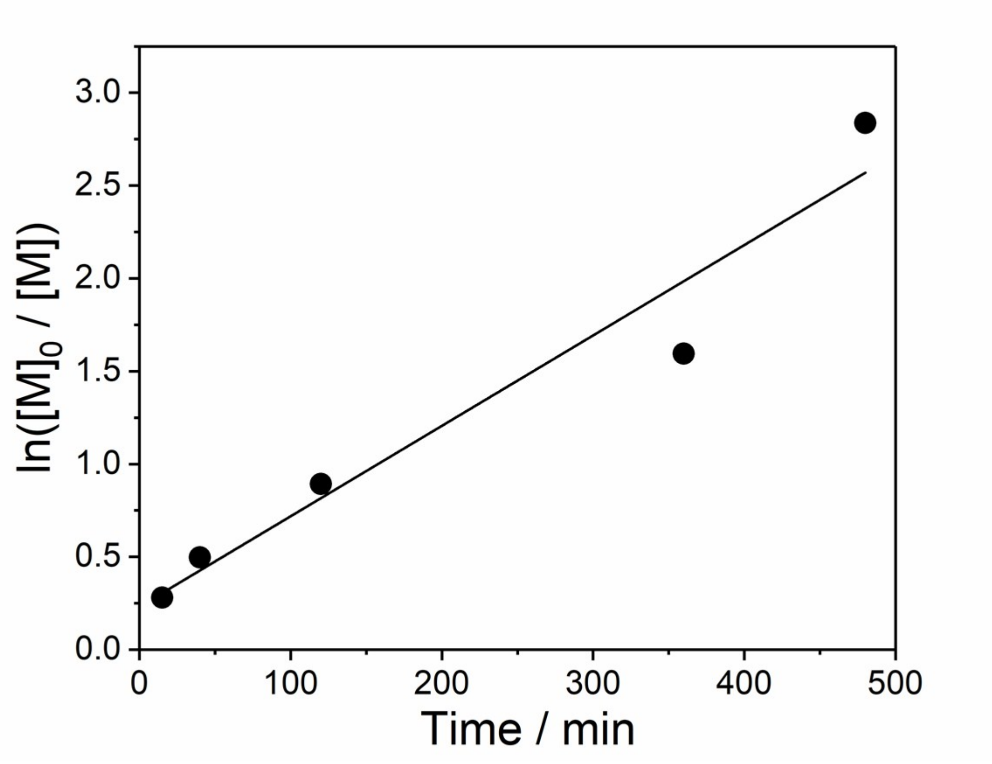

Figure S3. First-order kinetic plots of P4VP by Cu(0)-RDRP using 1-PECl as the initiator (DMSO/water solution, ambient temperature).

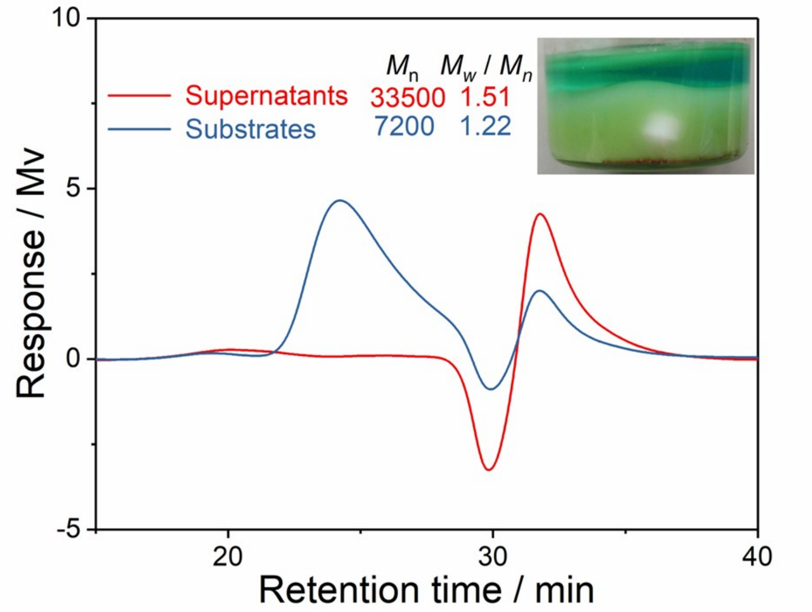

Figure S4. SEC elution traces of supernatants and substrates from the self-generating biphasic system after polymerization (inset) for P4VP by Cu(0)-RDRP using 1-PECl as the initiator (DMSO/water solution, ambient temperature).

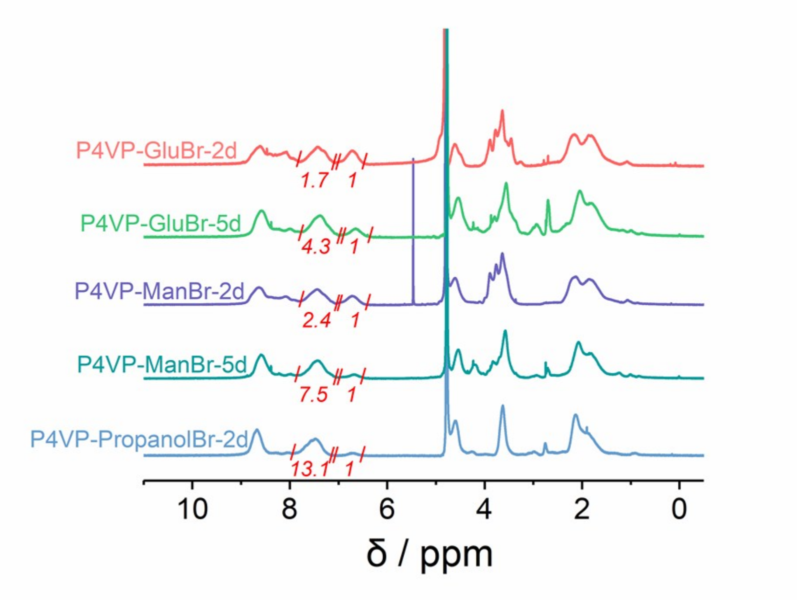

Figure S5. ^{1}H NMR spectra of P4VP-GluBr, P4VP-ManBr and P4VP-PropanolBr after quaternization for different time (Red digits represent the ratio of degree of quaternization).

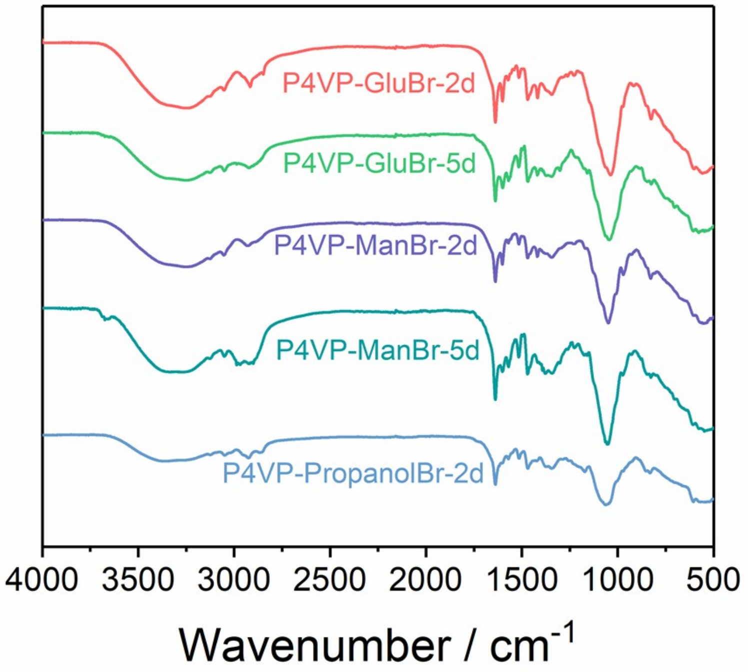

Figure S6. FTIR spectra of P4VP, P4VP-PropanolBr and P4VP-ManBr after quaternization for different time reaction time.

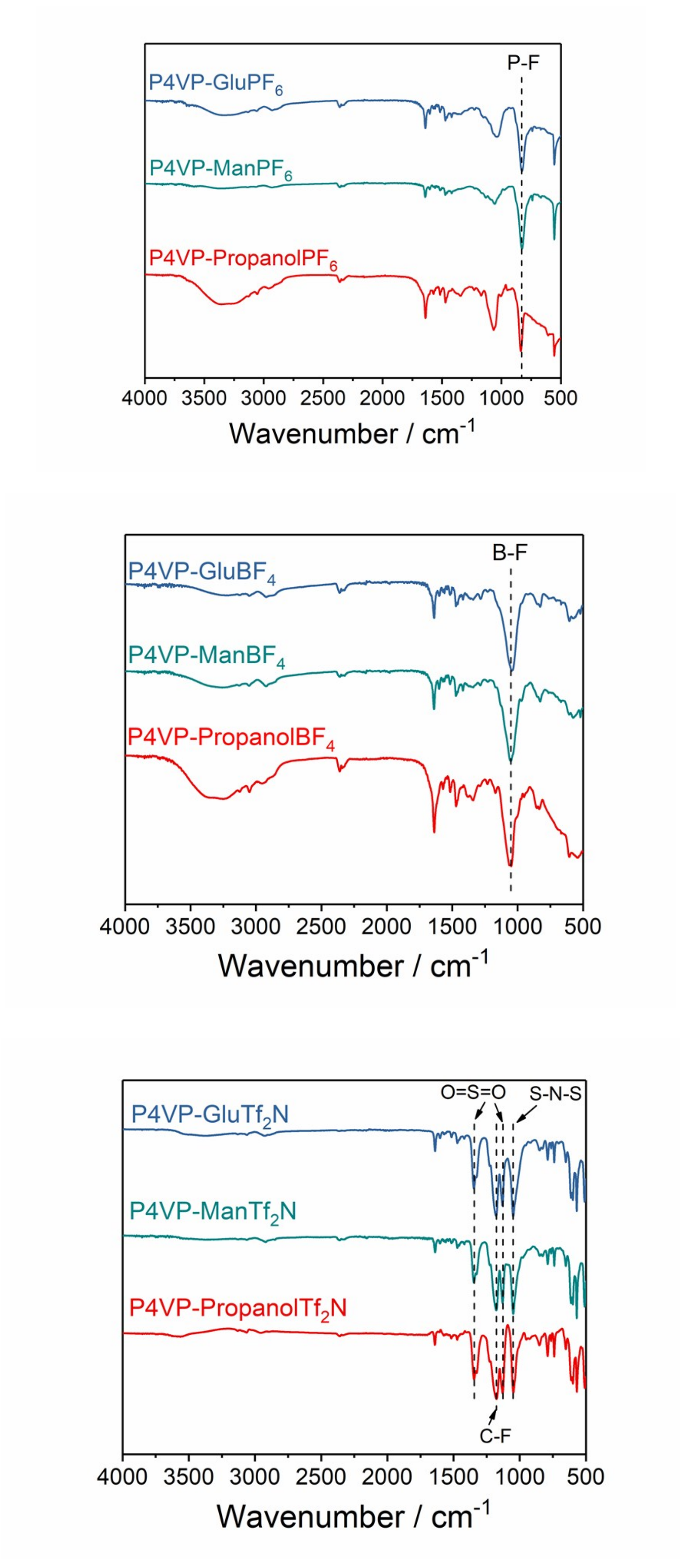

Figure S7. FTIR spectra of PILs after anion exchange reactions.

Table S1. Element concentration of P4VP-ManX as measured by XPS.

Polymer	C1s	O1s	N1s	F1s	Br3d	B1s	P2p	S2p
P4VP-ManBF_4	68.65%	19.25%	5.66%	4.39%	0.12%	1.93%	-	-
P4VP-ManPF_6	56.76%	13.79%	4.17%	21.57%	0.14%	-	3.57%	-
P4VP-ManTf_2N	54.17%	20.23%	5.70%	14.72%	0.09%	-	-	5.09%

Note: “-” was defined as no element detected in the corresponding polymer.

Table S2. Solubility of PILs in different solvents.

Polymer	Anion	Acetone	MeOH	DMF	DMSO	H_2O
P4VP-PropanolX	Br	-	+	-	+	+
	BF_4	-	+	-	-	+
	PF_6	-	x	-	-	-
	Tf_2N	+	+	+	+	x
P4VP-ManX	Br	-	+	-	+	+
	BF_4	-	+	-	x	+
	PF_6	-	x	-	-	-
	Tf_2N	+	+	+	+	x
P4VP-GluX	Br	-	+	-	+	+
	BF_4	-	+	-	x	+
	PF_6	-	x	-	-	-
	Tf_2N	+	+	+	+	x

Note: x was defined as slightly soluble and “+” “-” was defined as soluble and insoluble respectively.

Table S3. Initial binding rate for different PILs with Con A

Polymer	K_i (Abs/s)[a]
P4VP-PropanolBr	/
P4VP-PropanolBF_4	/
P4VP-GluBr	0.075
P4VP-GluBF_4	0.046
P4VP-ManBr	0.145
P4VP-ManBF_4	0.084

[a] The initial binding rate was calculated using the slope of the initial linear region of the absorbance plot.

References

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