Electronic Supplementary Information

Aggregation behavior of N-alkyl imidazolium-based poly (ionic liquid)s in organic solvent

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Table S1 Physical state, yield, and molecular weight of poly [$C_n VIm^+$][Br^-]

Samples	Physical state	Yield	Molecular weight	
			Mn	PDI
poly[$C_8 VIm^+$][Br^-]	Yellow power	78%	16855	1.52
poly[$C_{12} VIm^+$][Br^-]	White power	80%	12379	1.72
poly[$C_{16} VIm^+$][Br^-]	White power	76%	10841	1.58

Table S2. Solubility of PILs in different solvents at 298.15K

	H_2O	$CHCl_3$	n-PrOH	DMF	toluene	DMSO	dioxane	ethyl acetane	THF	acetone
poly[$C_8 VIm^+$][Br^-]	N	Y	Y	Y	N	Y	swollen	N	Y	N
poly[$C_{12} VIm^+$][Br^-]	N	Y	Y	N	N	swollen	N	N	swollen	N
poly[$C_{16} VIm^+$][Br^-]	N	Y	Y	N	N	N	N	N	N	N
poly[$C_{16} VIm^+$] [BF_4^-]	N	Y	N	Y	N	Y	swollen	N	Y	swollen

Table S3. Experimental conductivity (κ , $\mu S \cdot cm^{-1}$) of poly [C_nVIm^+][Br^-] in n-PrOH

	Concentration	Temperature (K)				
	(mol/L)×10^5	298.15	303.15	308.15	313.15	318.15
poly[C_8VIm^+][Br^-]	0.3	0.95	0.83	0.95	0.99	1.09
	0.6	1.12	1.09	1.23	1.34	1.51
	1.2	1.56	1.52	1.89	2.07	2.32
	1.8	1.98	2.14	2.47	2.75	3.08
	2.4	2.51	2.76	3.09	3.29	3.76
	3.0	2.83	3.17	3.75	3.99	4.76
	3.6	3.22	3.71	4.28	4.63	5.08
	4.2	3.78	4,44	4.91	5.23	5.51
	4.8	4.11	4.86	5.35	5.55	5.98
	5.4	4.49	5.05	5.65	5.91	6.32
	6.0	4.64	5.43	5.91	6.25	6.78
	6.6	4.97	5.71	6.25	6.56	7.15
	7.2	5.21	5.89	6.51	6.92	7.46
	7.8	5.42	6.21	6.92	7.27	7.89
	8.4	5.66	6.45	7.16	7.55	8.22
	9.0	6.01	6.74	7.48	7.89	8.63
poly[$C_{12}VIm^+$][Br^-]	0.3	0.77	0.86	1.01	1.03	1.08
	0.6	11.02	1.11	1.31	1.31	1.41
	1.2	1.44	1.55	1.74	1.91	2.08
	1.8	1.88	1.95	2.22	2.46	2.69
	2.4	2.24	2.58	2.69	3.14	3.53
	3.0	2.75	3.03	3.16	3.74	4.18
	3.6	3.12	3.44	3.74	4.26	4.77
	4.2	3.47	3.84	4.14	4.75	5.04
	4.8	3.95	4.17	4.65	4.94	5.34
	5.4	4.39	4.59	4.92	5.28	5.69
	6.0	4.63	4.88	5.19	5.64	6.04
	6.6	4.82	5.16	5.50	5.98	6.36
	7.2	5.08	5.4	5.79	6.23	6.69
	7.8	5.29	5.71	6.10	6.58	7.02
	8.4	5.55	6.02	6.42	6.86	7.3
	9.0	5.78	6.25	6.73	7.21	7.62
poly[$C_{16}VIm^+$][Br^-]	0.3	0.52	0.58	0.78	0.83	0.94
	0.6	0.63	0.91	0.94	1.02	1.13
	1.2	0.92	1.13	1.29	1.44	1.64
	1.8	1.27	1.46	1.71	1.88	2.14
	2.4	1.64	1.81	2.03	2.22	2.52
	3.0	2.01	2.17	2.49	2.71	2.93

	3.6	2.37	2.57	2.77	3.03	3.23
	4.2	2.67	2.85	3.01	3.19	3.48
	4.8	2.86	3.04	3.24	3.43	3.72
	5.4	3.07	3.26	3.45	3.71	4.03
	6.0	3.19	3.42	3.67	3.96	4.32
	6.6	3.39	3.62	3.85	4.14	4.47
	7.2	3.58	3.84	4.07	4.39	4.63
	7.8	3.74	3.99	4.28	4.59	4.89
	8.4	3.89	4.17	4.48	4.83	5.1
	9.0	4.08	4.36	4.69	5.08	5.38

Table S4[a]. Experimental conductivity (κ , $\mu S \cdot cm^{-1}$) of poly [$C_{16}VIm^+$][Br^-] in n-PrOH/water mixed solvents

poly[$C_{16}VIm^+$][Br^-] concentration	Water content in mixed solvents (vol. %)			
(mol/L)×10^5	7	8	9	10
0.3	1.78	1.95	2.02	2.14
0.6	1.98	2.09	2.24	2.44
1.2	2.32	2.51	2.74	3.05
1.8	2.72	2.97	3.27	3.78
2.4	3.16	3.44	3.77	4.43
3.0	3.56	3.86	4.25	5.02
3.6	3.97	4.36	4.76	5.44
4.2	4.34	4.74	4.99	5.61
4.8	4.65	4.85	5.18	5.82
5.4	4.76	5.03	5.33	5.99
6.0	4.89	5.11	5.48	6.17
6.6	5.02	5.31	5.62	6.38
7.2	5.15	5.44	5.79	6.53
7.8	5.29	5.61	5.94	6.75
8.4	5.33	5.77	6.09	6.92
9.0	5.49	5.93	6.27	7.14

Table S4[b]

poly[$C_{16}VIm^+$][Br^-] concentration	Water content in mixed solvents (vol. %)	
(mol/L)×10^5	15	20
0.12	1.98	-
0.24	2.16	2.11
0.36	2.36	2.48
0.48	2.57	2.84
0.60	2.74	3.26
0.72	2.97	3.44
0.84	3.21	3.57
0.96	3.38	3.69
1.06	3.61	3.82
1.32	3.93	4.12
1.50	4.05	4.29
1.80	4.28	4.56
2.10	4.42	4.88
2.40	4.62	5.17

Note: the conductivity for poly [$C_{16}VIm^+$][Br^-] in mixed solvents with 15 and 20 vol.% water is

listed in Table S4[b] because samples with more exact data of poly [$C_{16}VIm^+$][Br^-] concentration are required in order to obtain CAC value.

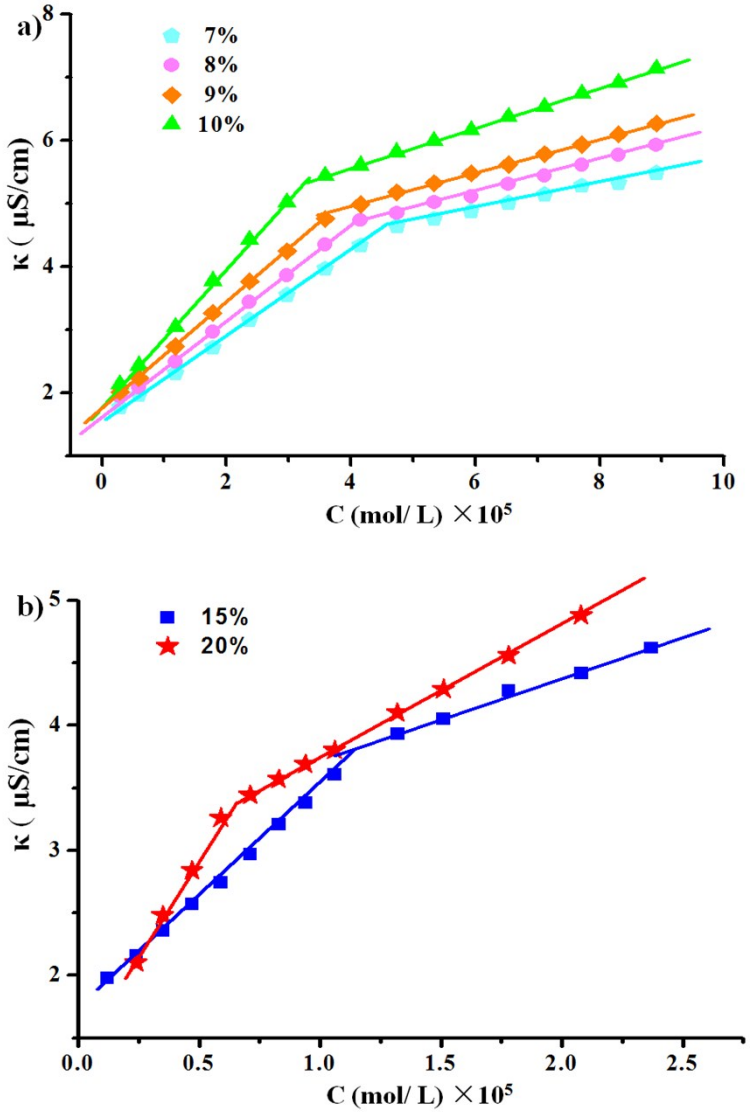

Fig S1. Plots of electrical conductivity, κ, against concentration of poly [$C_{16}VIm^+$][Br^-] in n-PrOH/water mixed solvents with different water content. (a) the water content is in the range of 7-10%, and (b) the water content is between 15% and 20%. The exact conductivity data used in Fig. S1are listed in Table S4[a] and Table S4[b].

Table S5. Experimental conductivity (κ , $\mu S \cdot cm^{-1}$) of poly [$C_{16}VIm^+$][Br^-] in n-PrOH/acetone mixed solvents

poly[$C_{16}VIm^+$][Br^-]	Acetone content in mixed solvents (vol. %)					
(mol/L)×10^5	7	8	9	10	15	20
0.12	2.02	2.09	2.21	2.18	2.21	2.34
0.3	2.17	2.23	2.42	2.39	2.34	2.54
0.6	2.35	2.35	2.52	2.57	2.57	2.86
1.2	2.68	2.72	2.69	2.72	3.02	3.61
1.8	3.03	3.11	3.29	3.31	3.51	4.09
2.4	3.61	3.47	3.56	3.54	3.92	4.48
3.0	3.91	3.73	3.95	4.01	4.41	4.91
3.6	4.19	4.12	4.41	4.45	4.73	5.21
4.2	4.58	4.37	4.59	4.78	5.12	5.62
4.8	4.77	4,62	4.83	4.93	5.52	6.04
6.0	5.14	5.01	5.22	5.23	6.15	6.88
7.2	5.36	5.42	5.63	5.71	6.59	7.52

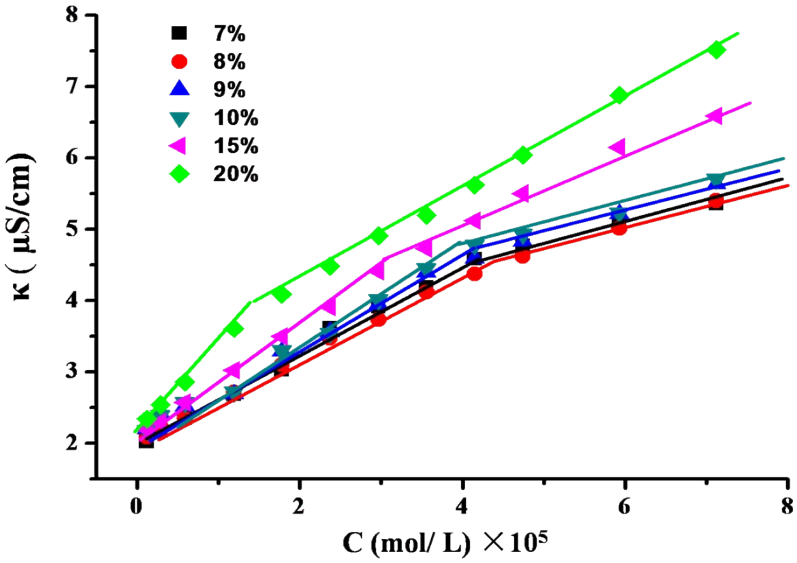

Fig S2. Plots of electrical conductivity, κ, against concentration of poly [$C_{16}VIm^+$][Br^-] in n-PrOH/acetone mixed solvents with acetone content varying in the range of 7-20%. The exact conductivity data used in Fig. S2 can be found in Table S5.

Table S6 Thermodynamic parameters for poly [$C_{16}VIm^+$][Br^-] in acetone-containing mixed solvents at 298.15K[a]

Acetone content in mixed solvents (vol. %)	CAC (mol/L)×10^5	β	$\Delta G^{\theta}_{m,n-\mathrm{Pr}OH/\mathrm{acetonee}}$ (KJ/mol)	$\Delta G^{\theta}_{m,alkyl}$ (kJ/mol)	$\Delta G^{\theta}_{m,\mathrm{acetone}}$ (KJ/mol)
0	4.61	0.44	-44.76	-1.65	0
7	4.25	0.46	-45.79	-1.69	-1.03
8	4.26	0.47	-45.53	-1.71	-0.77
9	4.20	0.44	-46.11	-1.69	-1.35
10	4.18	0.47	-46.17	-1.71	-1.41
15	2.94	0.43	-47.13	-1.75	-2.37
20	1.38	0.45	-49.56	-1.84	-4.80

[a]The data in Table S6 are obtained from the conductivity results as shown in Table S5.

The results in Table S6 indicate that the contribution of acetone to Gibbs free energy, $\Delta G^{\theta}_{m,\mathrm{acetone}}$, is more negative and CAC values decrease as increasing acetone content in mixed solvents. Obviously, the addition of acetone (another nonsolvent for poly [$C_{16}VIm^+$][Br^-]) is favorable for poly [$C_{16}VIm^+$][Br^-] aggregation.