Supporting Information

A comparative study on the design and application of new benzimidazolium Gemini ionic liquids for curing interfacial properties of crude oil–water system

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Number of Pages: 14

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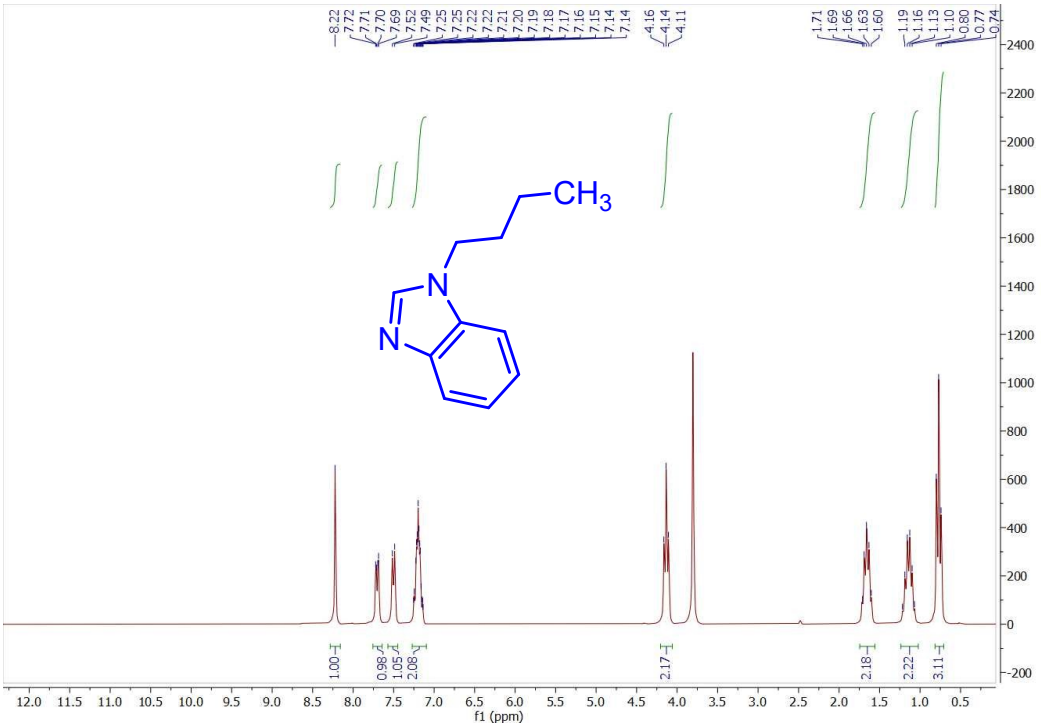

Figure S1. ^{1}H NMR spectrum of 1-butyl-1*H*-benzo[*d*]imidazole.

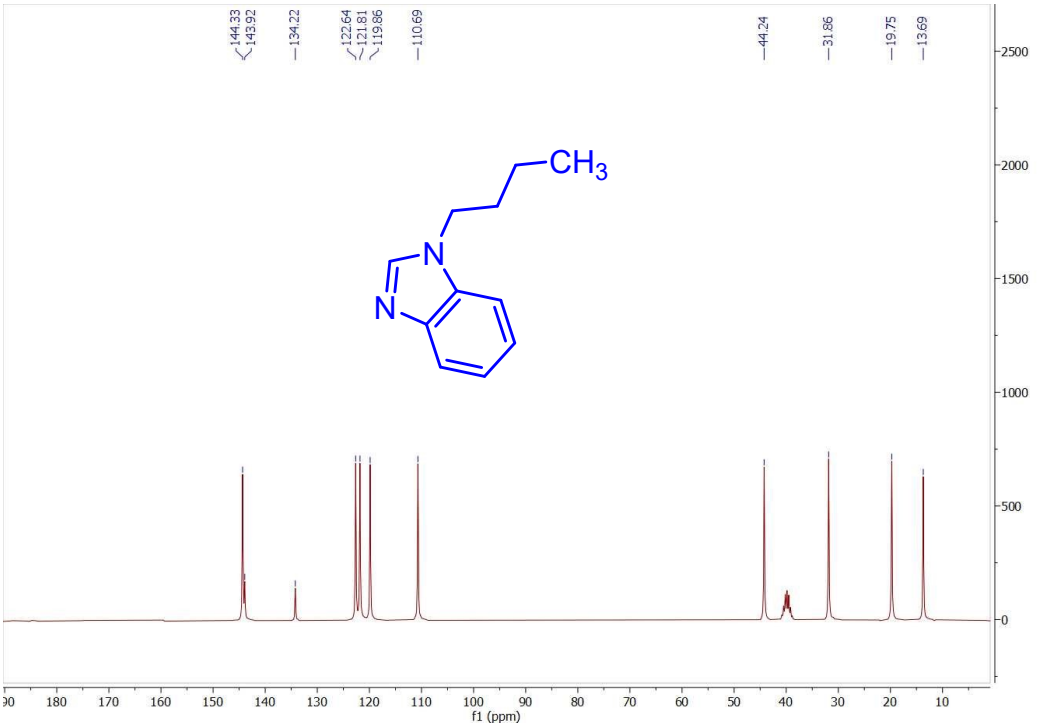

Figure S2. ^{13}C NMR spectrum of 1-butyl-1*H*-benzo[*d*]imidazole.

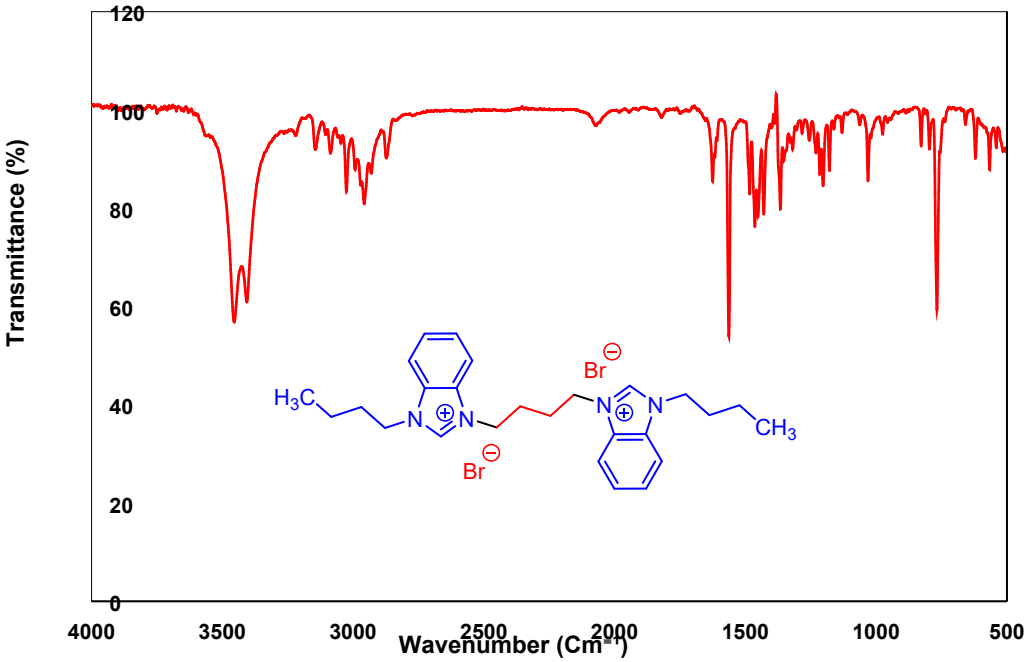

Figure S3. FT-IR spectrum of synthesized [C_4benzim-C_4-benzimC_4][Br_2].

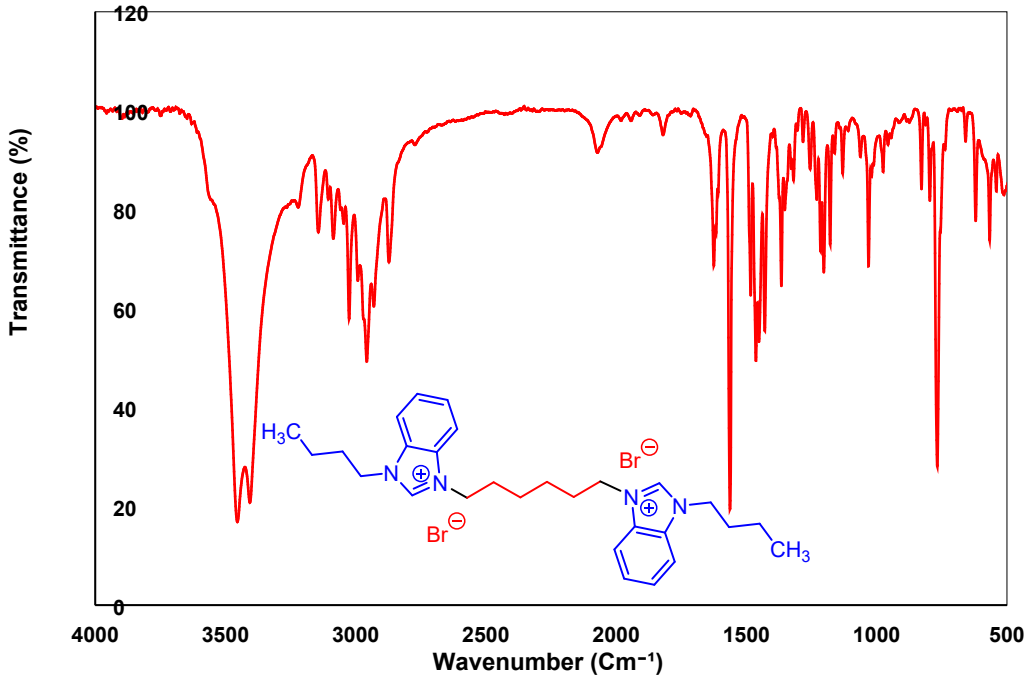

Figure S4. FT-IR spectrum of synthesized [C_4benzim-C_6-benzimC_4][Br_2].

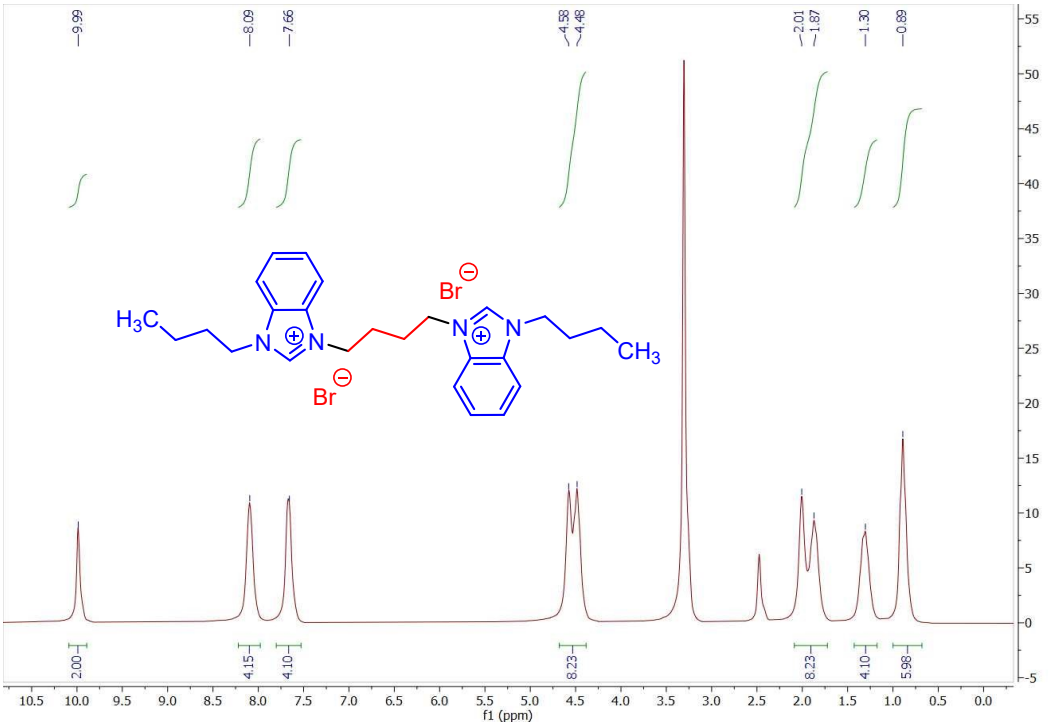

Figure S5. ^{1}H NMR spectrum of synthesized [C_4benzim-C_4-benzimC_4][Br_2].

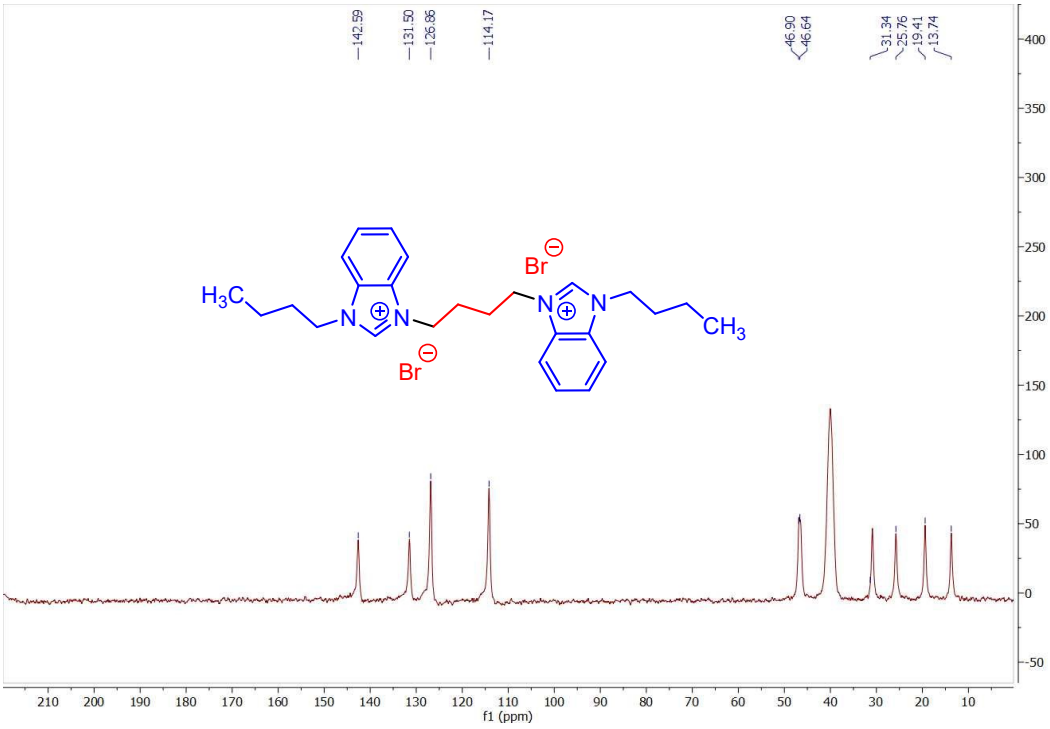

Figure S6. ^{13}C NMR spectrum of synthesized [C_4benzim-C_4-benzimC_4][Br_2].

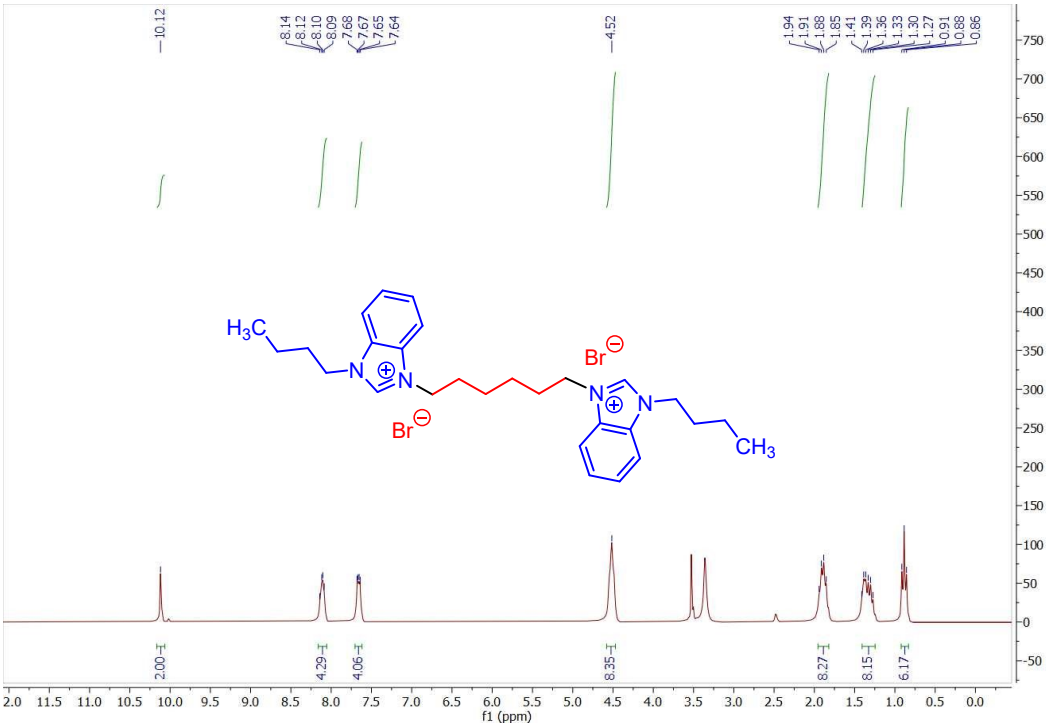

Figure S7. ^{1}H NMR spectrum of synthesized [C_4benzim-C_6-benzimC_4][Br_2].

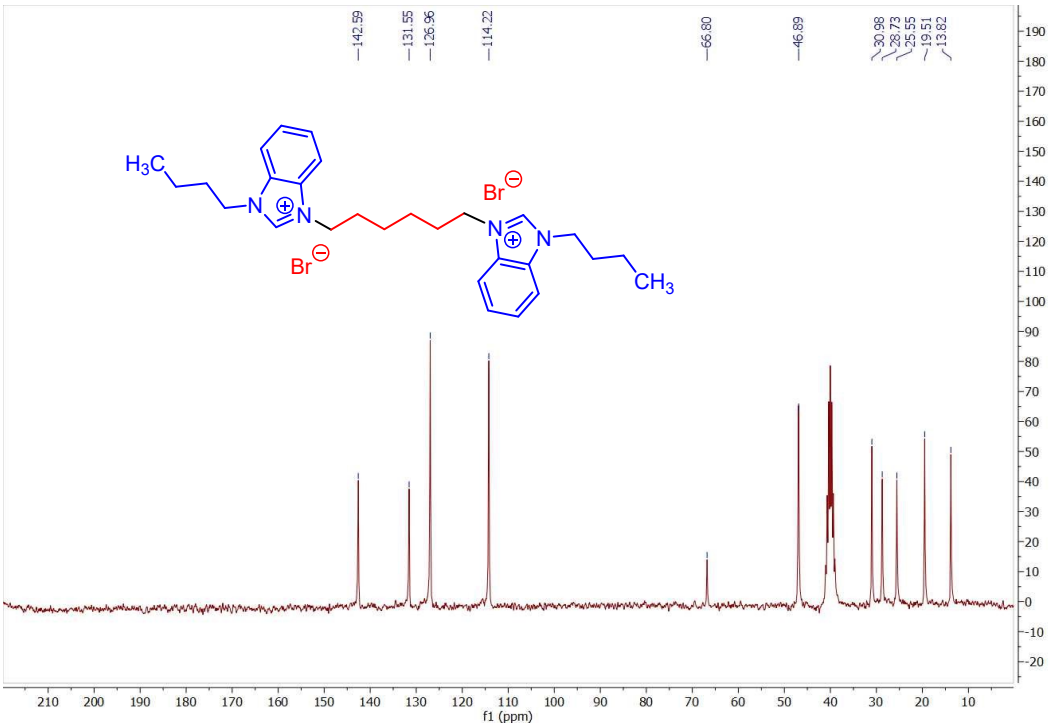

Figure S8. ^{13}C NMR spectrum of synthesized [C_4benzim-C_6-benzimC_4][Br_2].

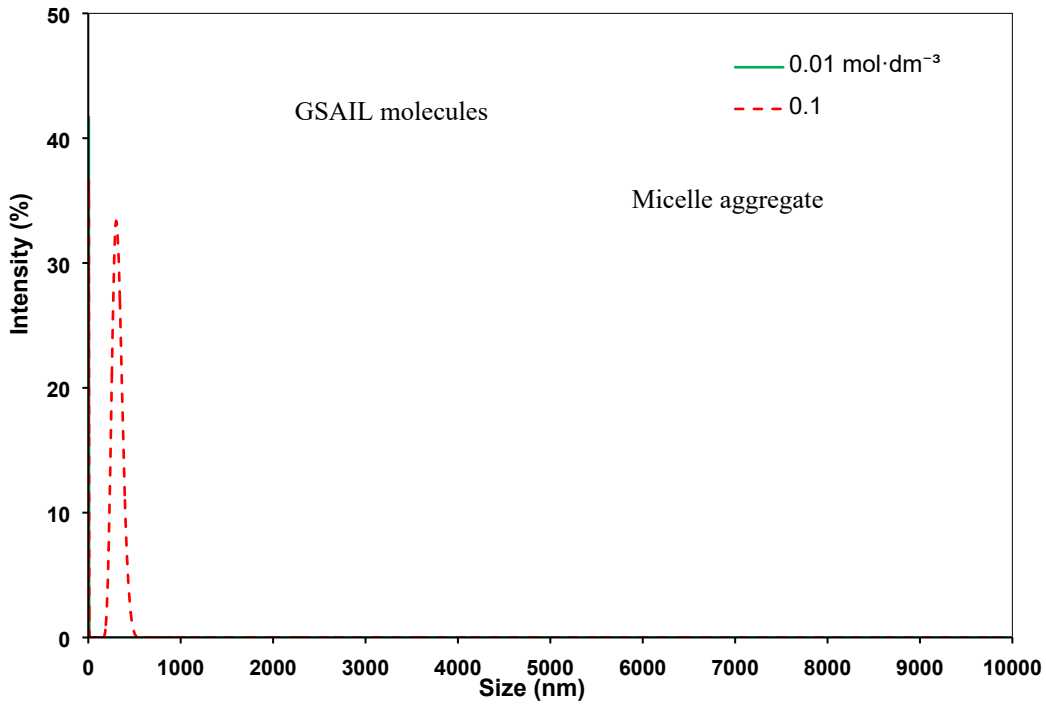

Figure S9. The DLS spectra of the of [C_4benzim-C_4-benzimC_4][Br_2] product before and after CMC.

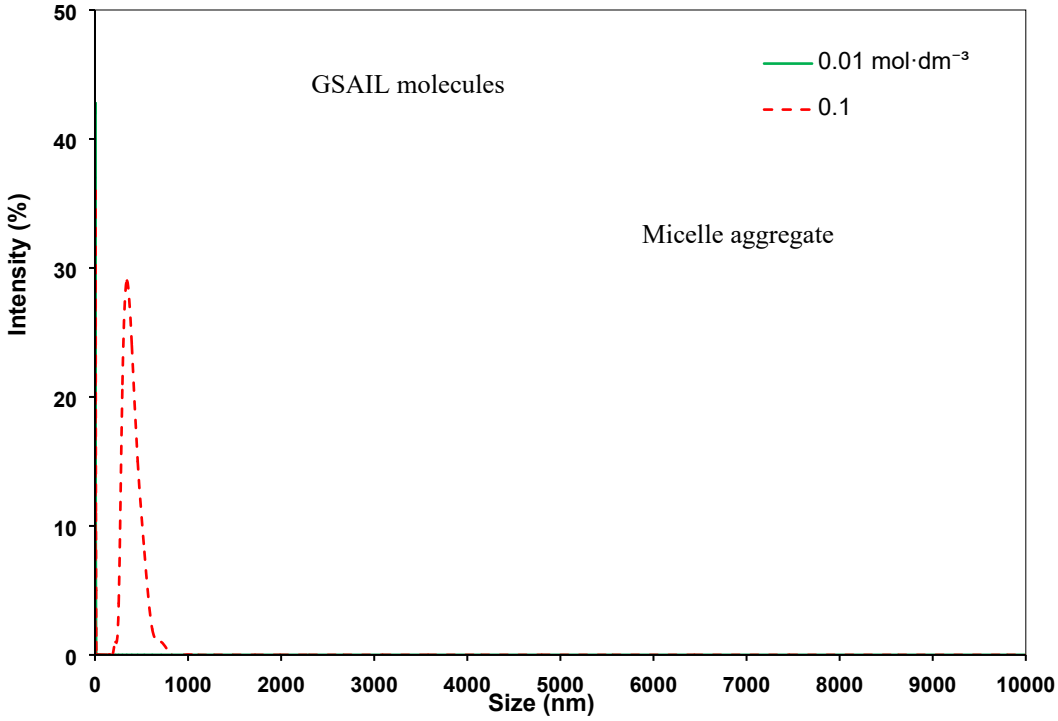

Figure S10. The DLS spectra of the of [C_4benzim-C_6-benzimC_4][Br_2] product before and after CMC.

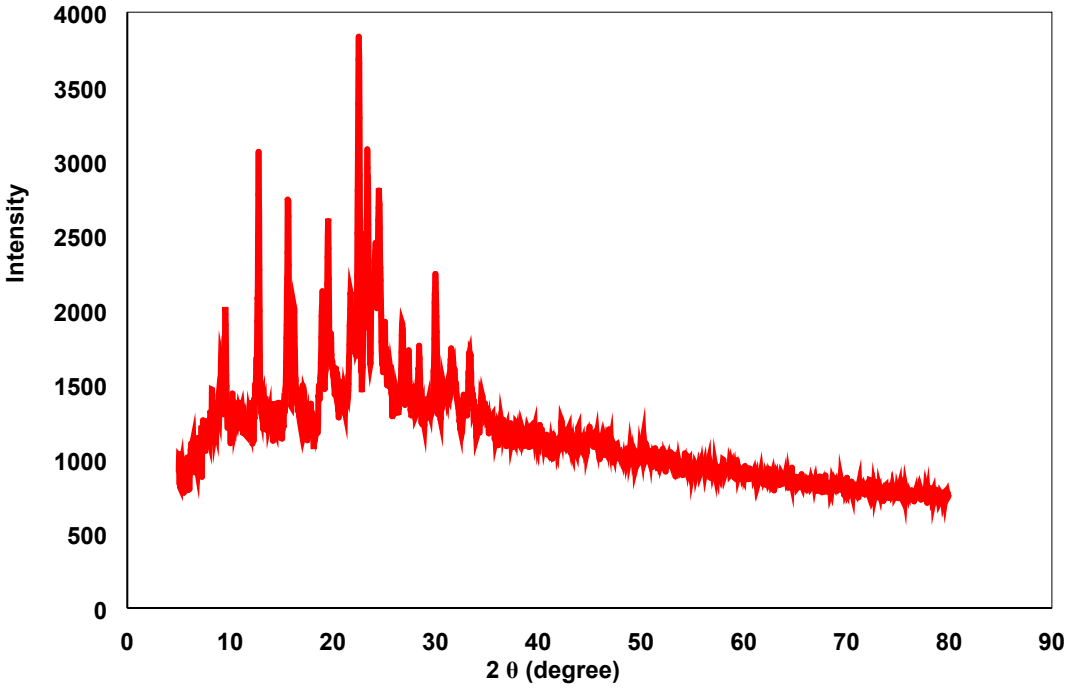

Figure S11. XRD pattern of synthesized [C_4benzim-C_4-benzimC_4][Br_2].

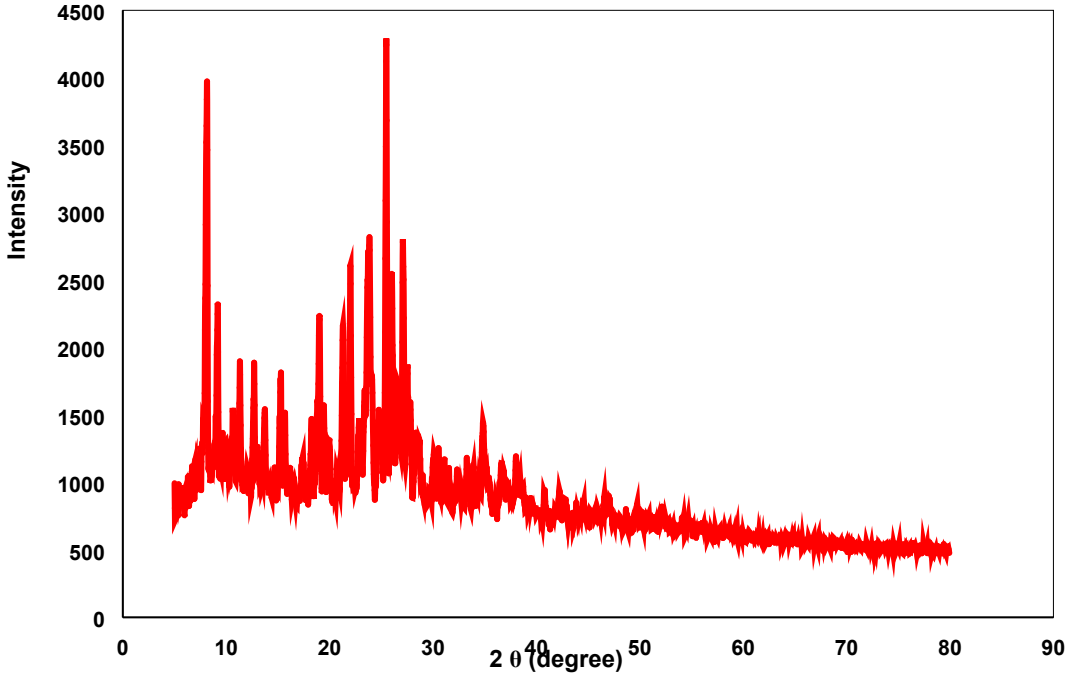

Figure S12. XRD pattern of synthesized [C_4benzim-C_6-benzimC_4][Br_2].

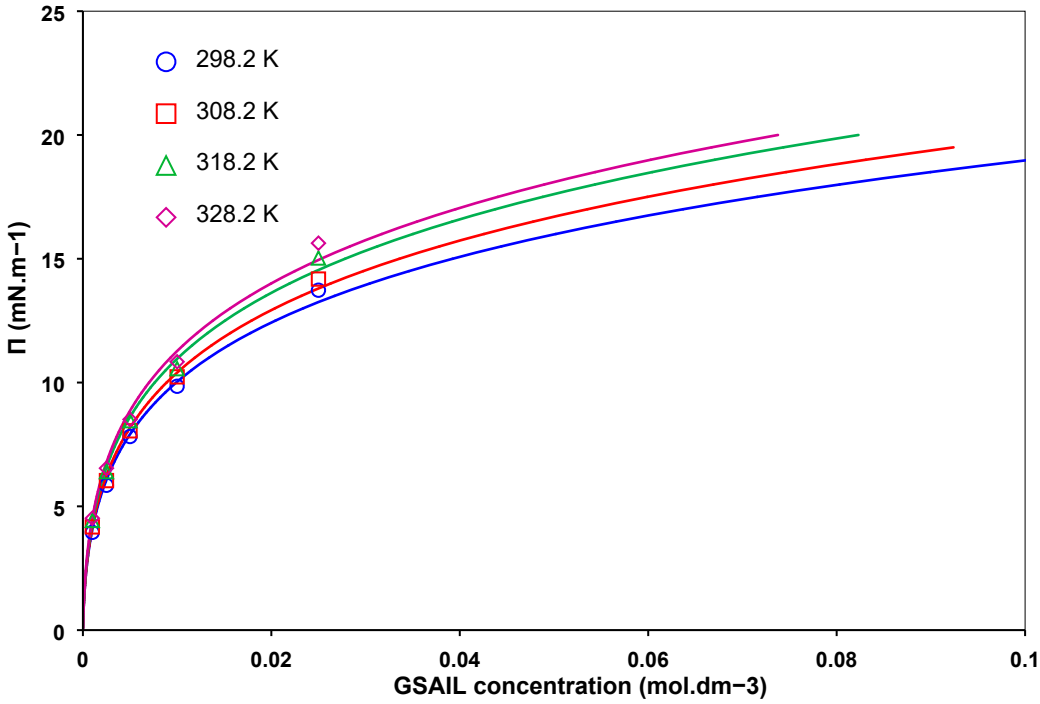

Figure S13. Fitted data with the Frumkin adsorption isotherm (solid lines) of [C_4benzim-C_4-benzimC_4][Br_2] at different temperatures.

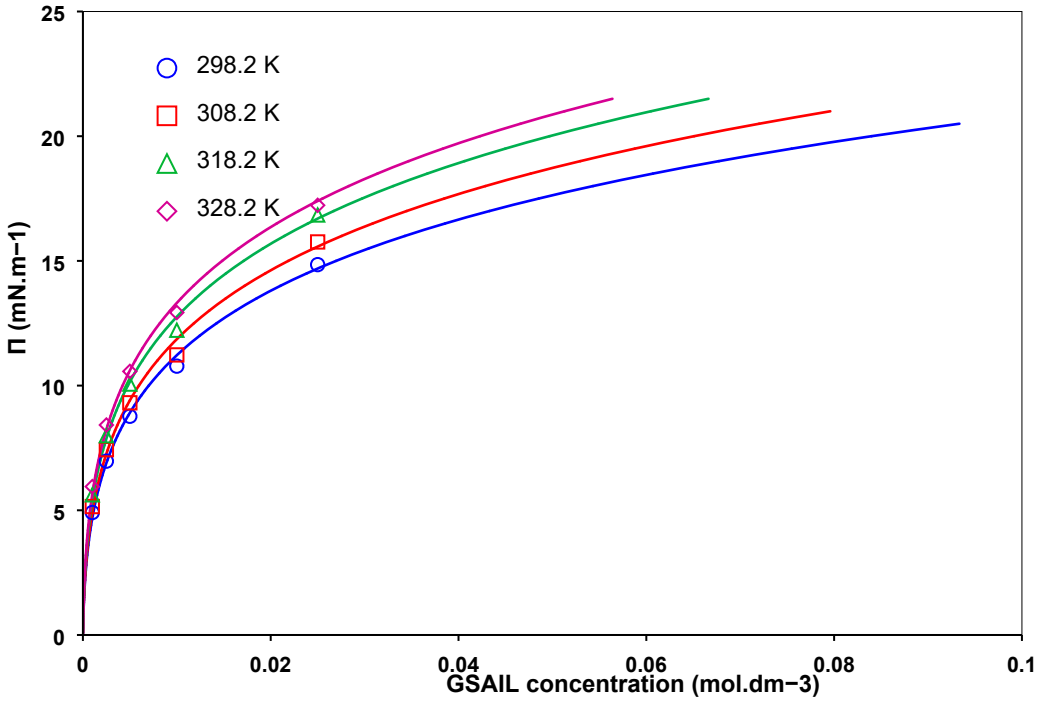

Figure S14. Fitted data with the Frumkin adsorption isotherm (solid lines) of [C_4benzim-C_6-benzimC_4][Br_2] at different temperatures.

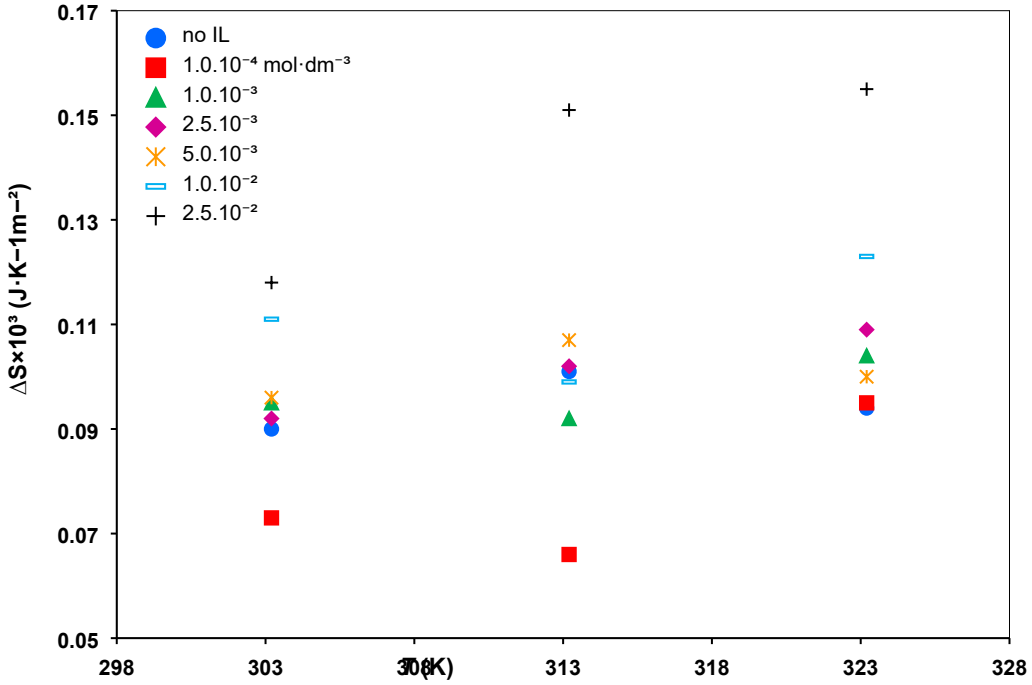

Figure S15. The interface entropy change as a function of temperature for different concentrations of [C_4benzim-C_4-benzimC_4][Br_2].

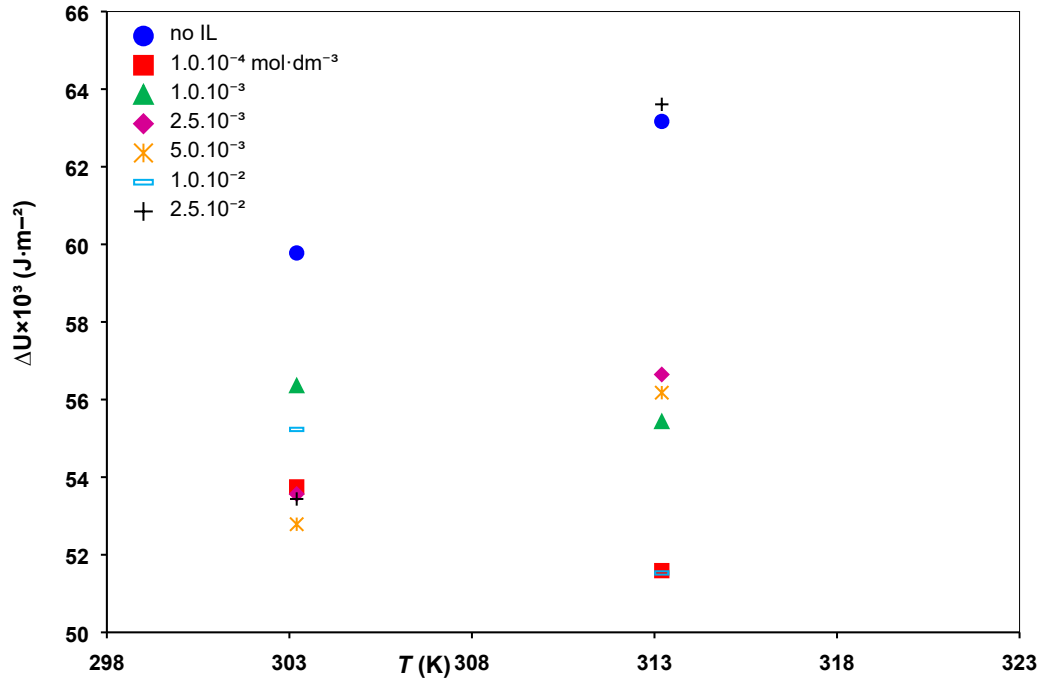

Figure S16. The interface energy change as a function of temperature for different concentrations of [C_4benzim-C_4-benzimC_4][Br_2].

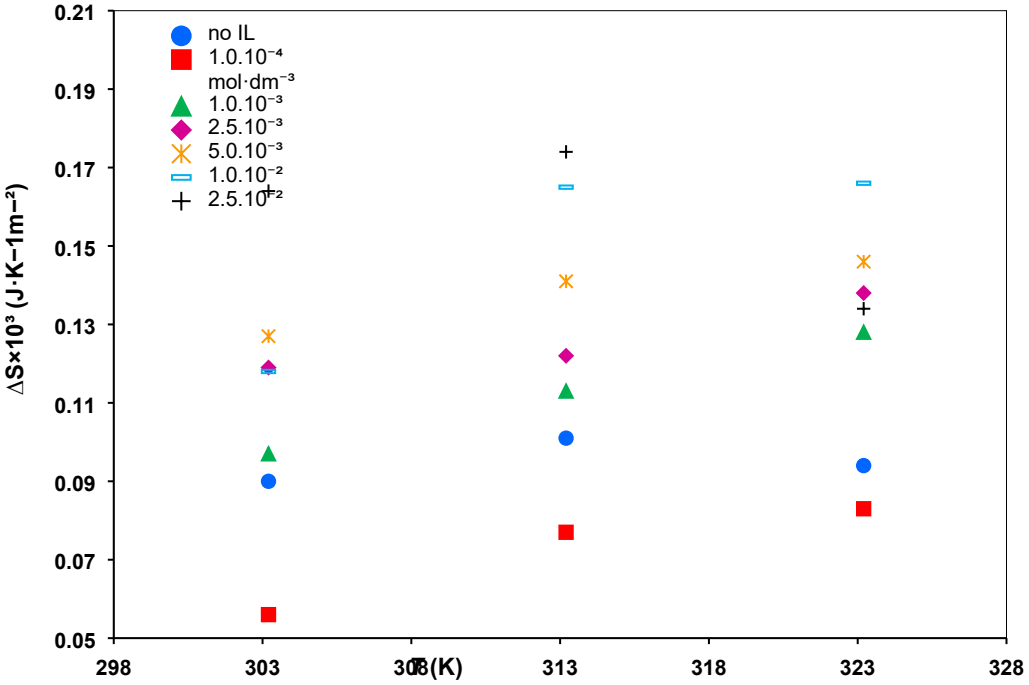

Figure S17. The interface entropy change as a function of temperature for different concentrations of [C_4benzim-C_6-benzimC_4][Br_2].

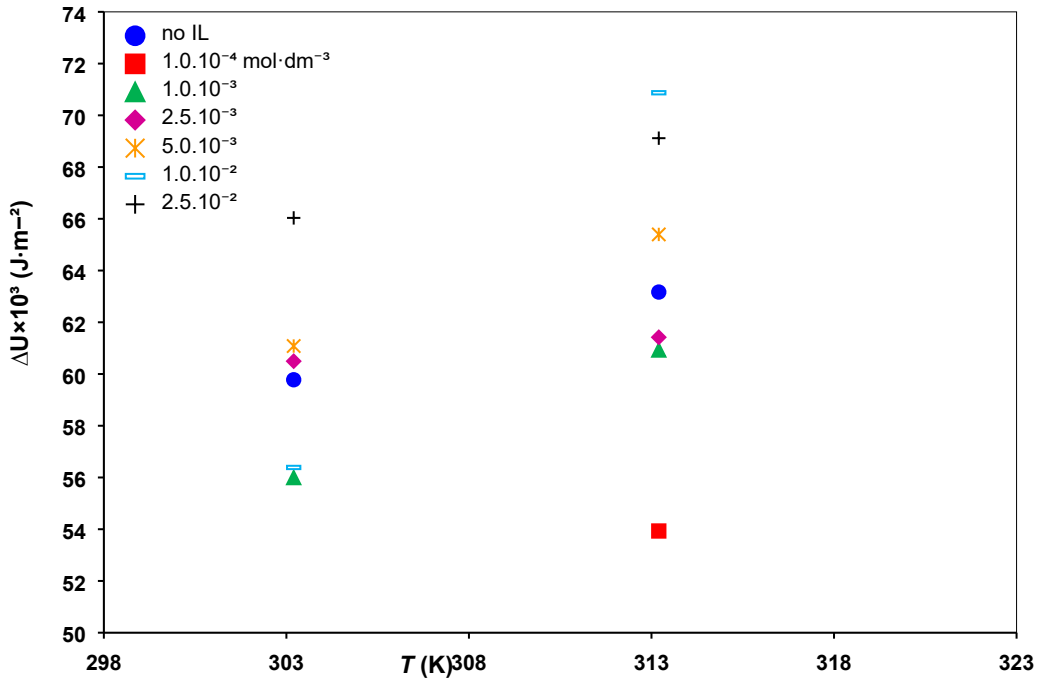

Figure S18. The interface energy change as a function of temperature for different concentrations of [C_4benzim-C_6-benzimC_4][Br_2].

Table S1. XRD data for the benzimidazolium GSAILs.

Entry	2 θ (degree)	Peak width [FWHM] (degree)	Size (nm)	Interplanar distance (nm)
[C_4benzim-C_4-benzimC_4][Br_2]				
1	9.55	0.41	19.16	0.93
2	12.77	0.42	19.21	0.69
3	15.63	0.73	11.01	0.57
4	19.40	0.55	14.76	0.46
5	19.51	0.75	10.74	0.45
6	22.52	0.39	20.76	0.39
7	23.39	0.81	10.06	0.38
8	24.52	0.22	36.61	0.36
9	29.96	0.73	11.29	0.30
[C_4benzim-C_6-benzimC_4][Br_2]				
1	8.14	0.29	27.84	1.08
2	9.18	0.52	15.32	0.96
3	11.30	0.49	16.15	0.78
4	12.70	0.44	18.08	0.70
5	15.20	0.39	20.54	0.58
6	19.02	0.49	16.30	0.47
7	22.01	0.31	25.93	0.40
8	23.85	0.70	11.56	0.37
9	25.49	0.21	39.14	0.35
10	25.95	0.47	17.41	0.34
11	27.10	0.31	26.18	0.33

Table S2. GSAILs concentrations, aqueous phase densities, ρ_{aq}, oil phase densities, ρ_{oil}, drop equatorial diameter, *D*, horizontal drop diameter at distance of *D* from drop top curvature point, *d*, drop volume, *V,* and IFT values, γ, at different temperatures[a] for benzimidazolium GSAILs.

T (K)	GSAIL concentration (mol·dm^{-3})	$\rho_{aq}\times10^{2}$ (g·cm^{-3})	$\rho_{oil}\times10^{2}$ (g·cm^{-3})	*D* (mm)	*d* (mm)	*V* (mm^{3})	γ (mN·m^{-1})
			[C_4benzim-C_4-benzimC_4][Br_2]				
298.2	0	99.70	89.00	6.36	5.14	196.25	32.94
	1.0×10^{-4}	99.71	89.00	6.18	4.34	154.8	31.98
	1.0×10^{-3}	99.73	89.00	5.30	3.49	91.19	28.03
	2.5×10^{-3}	99.74	89.00	4.59	2.78	57.38	26.13
	5.0×10^{-3}	99.75	89.00	5.08	3.43	82.05	24.16
	1.0×10^{-2}	99.77	89.00	3.22	0.01	69.25	22.13
	2.5×10^{-2}	100.04	89.00	4.44	3.04	55.53	18.25
	5.0×10^{-2}	100.09	89.00	4.32	3.10	53.17	15.28
	1.0×10^{-1}	100.10	89.00	4.28	3.08	51.43	14.87
308.2	0	99.37	88.50	6.21	4.94	178.46	32.04
	1.0×10^{-4}	99.41	88.50	6.17	4.31	168.21	31.25
	1.0×10^{-3}	99.43	88.50	4.89	3.82	107.69	27.08
	2.5×10^{-3}	99.44	88.50	5.31	3.22	88.77	25.21
	5.0×10^{-3}	99.45	88.50	5.00	3.39	78.77	23.20
	1.0×10^{-2}	99.47	88.50	5.12	3.39	82.77	21.02
	2.5×10^{-2}	99.74	88.50	4.41	3.08	55.27	17.07
	5.0×10^{-2}	99.79	88.50	4.59	3.28	63.40	14.24
	1.0×10^{-1}	100.07	88.50	4.48	3.18	58.44	13.81
318.2	0	98.80	88.00	6.14	4.13	162.91	31.03
	1.0×10^{-4}	98.91	88.00	5.45	4.03	150.92	30.59
	1.0×10^{-3}	98.93	88.00	4.88	4.85	97.44	26.16
	2.5×10^{-3}	99.04	88.00	4.87	3.59	92.75	24.19
	5.0×10^{-3}	99.05	88.00	4.99	3.43	78.71	22.13
	1.0×10^{-2}	99.17	88.00	5.12	3.40	82.85	20.03
	2.5×10^{-2}	99.24	88.00	4.66	3.24	64.57	15.56
	5.0×10^{-2}	99.49	88.00	3.53	1.86	24.68	12.52
	1.0×10^{-1}	99.77	88.00	5.79	3.55	84.20	12.39
328.2	0	98.06	87.60	4.42	5.75	154.18	30.09
	1.0×10^{-4}	98.21	87.60	4.25	3.84	125.80	29.64
	1.0×10^{-3}	98.33	87.60	4.10	3.93	104.47	25.12
	2.5×10^{-3}	98.44	87.60	4.63	3.46	96.28	23.10
	5.0×10^{-3}	98.51	87.60	5.12	3.37	82.71	21.13
	1.0×10^{-2}	98.67	87.60	4.58	3.09	66.78	18.80
	2.5×10^{-2}	98.74	87.60	4.55	3.23	61.16	14.01
	5.0×10^{-2}	98.89	87.60	4.61	3.15	61.78	10.87

	1.0×10^{-1}	99.17	87.60	4.60	2.97	53.30	10.72
			$[C_4benzim\text{-}C_6\text{-}benzimC_4][Br_2]$				
298.2	0	99.70	89.00	6.36	4.14	146.25	32.94
	1.0×10^{-4}	99.72	89.00	5.99	4.01	133.62	30.76
	1.0×10^{-3}	99.73	89.00	5.46	3.73	103.84	27.07
	2.5×10^{-3}	99.75	89.00	5.00	3.29	77.59	25.01
	5.0×10^{-3}	99.77	89.00	4.83	3.19	69.62	23.21
	1.0×10^{-2}	99.90	89.00	4.65	3.09	62.26	21.20
	2.5×10^{-2}	100.07	89.00	4.31	2.94	50.58	17.13
	5.0×10^{-2}	100.31	89.00	3.91	2.75	39.14	13.56
	1.0×10^{-1}	100.73	89.00	3.75	2.65	33.69	12.80
308.2	0	99.37	88.50	6.11	4.94	138.46	32.04
	1.0×10^{-4}	99.42	88.50	5.25	4.35	117.38	30.20
	1.0×10^{-3}	99.44	88.50	5.05	4.17	141.26	26.10
	2.5×10^{-3}	99.55	88.50	5.43	3.57	99.14	23.82
	5.0×10^{-3}	99.59	88.50	5.33	3.57	94.33	21.94
	1.0×10^{-2}	99.60	88.50	5.14	3.49	85.44	20.06
	2.5×10^{-2}	99.77	88.50	4.17	2.89	46.55	15.49
	5.0×10^{-2}	99.98	88.50	3.67	2.57	31.96	12.06
	1.0×10^{-1}	100.12	88.50	3.62	2.59	30.47	11.51
318.2	0	98.80	88.00	6.54	4.03	182.91	31.03
	1.0×10^{-4}	98.92	88.00	6.11	4.01	170.60	29.43
	1.0×10^{-3}	98.94	88.00	6.15	4.85	169.87	24.98
	2.5×10^{-3}	99.08	88.00	6.44	4.20	164.17	22.60
	5.0×10^{-3}	99.12	88.00	6.35	4.26	159.32	20.52
	1.0×10^{-2}	99.20	88.00	5.87	3.90	125.76	18.37
	2.5×10^{-2}	99.27	88.00	3.93	2.72	38.97	13.75
	5.0×10^{-2}	99.61	88.00	3.76	2.61	33.86	10.52
	1.0×10^{-1}	99.93	88.00	3.45	2.50	26.83	10.01
328.2	0	98.06	87.60	6.42	5.25	194.18	30.09
	1.0×10^{-4}	98.35	87.60	6.35	5.22	179.53	28.61
	1.0×10^{-3}	98.42	87.60	6.25	5.13	154.71	23.69
	2.5×10^{-3}	98.55	87.60	5.35	4.79	143.73	21.22
	5.0×10^{-3}	98.62	87.60	5.12	4.73	122.68	19.07
	1.0×10^{-2}	98.69	87.60	5.56	4.36	95.51	16.71
	2.5×10^{-2}	98.87	87.60	4.76	3.47	83.60	12.42
	5.0×10^{-2}	99.01	87.60	4.90	3.40	74.89	9.05
	1.0×10^{-1}	99.23	87.60	3.52	2.54	28.17	8.78

[a]The standard uncertainties u are $u(T) = 0.1$ K, u(concentration) $= 4\times10^{-6}$ mol·dm^{-3}, $u(\rho) = 0.01$ g·cm^{-3}, $u(D) = 1\times10^{-3}$ mm , $u(d) = 1\times10^{-3}$ mm, $u(V) = 1\times10^{-3}$ mm^3 and $u(\gamma) = 1\times10^{-3}$ mN·m.

Table S3. The maximum interface excess concentration, $\Gamma_{m,F}$, the minimum interface area occupied by each molecule, A_m, the Frumkin adsorption equilibrium constant, b_F, the molecular interaction parameter, β, the Gibbs free energy of adsorption, ΔG°_{ads}, and the Gibbs free energy of micellization, ΔG^{0}_{mic}, of imidazolium and benzimidazolium GSAILs at different temperatures.

GSAIL	T (K)	$\Gamma_{m,F}\times10^{6}$ (mol·m^{-2})	$A_m\times10^{36}$ (m^2)	b_F (dm^3·mol^{-1})	β	ΔG°_{ads} (kJ·mol^{-1})	ΔG^{o}_{mic} (kJ·mol^{-1})
[C_4im-C_2-imC_4][Br_2]	298.2	1.28	9.08	109.5	–1.5	–39.73	–0.49
	308.2	1.80	6.48	421.6	–1.9	–36.15	–0.51
	318.2	2.32	5.02	259.9	–2.5	–34.74	–0.53
	328.2	3.38	3.45	364.8	–6.1	–37.64	–0.56
[C_4im-C_4-imC_4][Br_2]	298.2	2.78	4.19	476.7	–4.1	–47.02	–0.003
	308.2	3.70	3.14	159.7	–5.0	–42.98	–0.01
	318.2	5.00	2.33	83.1	–6.8	–40.88	–0.03
	328.2	6.25	1.86	92.8	–9.9	–42.73	–0.06
[C_4im-C_6-imC_4][Br_2]	298.2	1.39	8.38	991.0	–6.1	–47.02	–0.25
	308.2	1.43	8.15	807.9	–7.7	–42.98	–0.27
	318.2	1.54	7.57	684.8	–8.5	–40.88	–0.30
	328.2	1.83	6.34	702.1	–10.2	–42.73	–0.34
[C_4benzim-C_4-benzimC_4][Br_2]	298.2	1.67	6.98	212.4	-4	–42.99	–9.46
	308.2	2.08	5.59	166.1	-4.8	–43.17	–10.02
	318.2	2.44	4.77	148.7	-5.4	–43.97	–10.62
	328.2	2.82	4.13	135.3	-6.2	–44.78	–11.28
[C_4benzim-C_6-benzimC_4][Br_2]	298.2	1.69	6.87	269.2	-3.9	–44.18	–9.82
	308.2	2.13	5.47	222.5	-4.7	–44.66	–10.43
	318.2	2.50	4.66	211.6	-5.3	–45.84	–11.10
	328.2	2.86	4.07	207.4	-6.1	–47.11	–11.95