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Ionic liquid polymer materials with tunable nanopores controlled by surfactant aggregates: A novel approach for CO₂ capture

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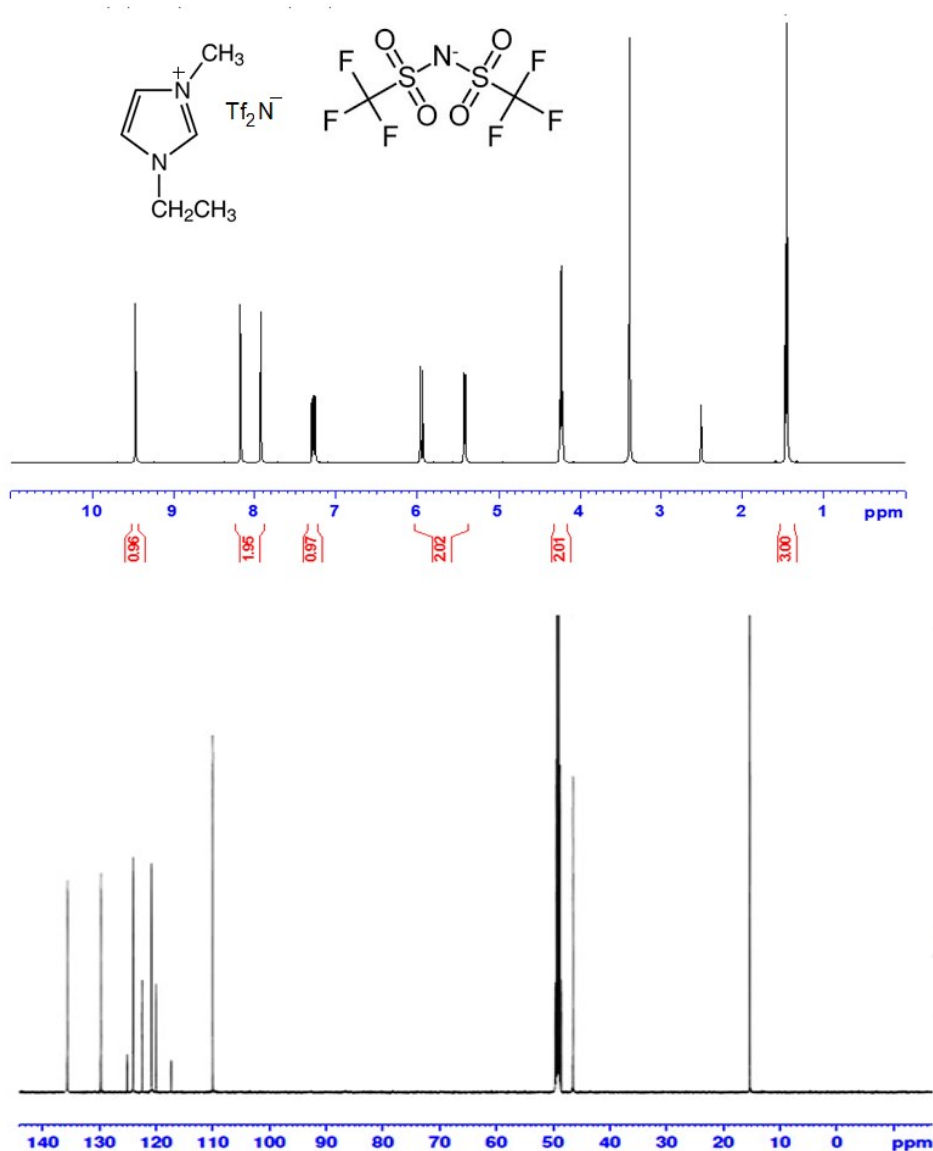
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$^1\text{H NMR}$ (500MHz; MeOD, δ/ppm): 9.51 (s, 1H, N-CH-N); 8.22 (s, 1H; N-CH-CH-N); 7.89 (s, 1H, N-CH-CH-N); 7.33 (dd, 1H, N-CH-CH₂); 5.95 (dd, 1H, N-CH-CH₂), 5.39 (dd, 2H, N-CH-CH₂); 4.273 (q, 2H, N-CH₂-CH₃); 1.44 (t, 3H, CH₂-CH₃).

$^{13}\text{C NMR}$ (500MHz; MeOD, δ/ppm): 14.89, 49.12, 110.05, 119.50, 121.10, 122.05, 124.25, 130.50, 136.05.

Figure S1 $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of the synthesized [veim][Tf₂N] monomer.

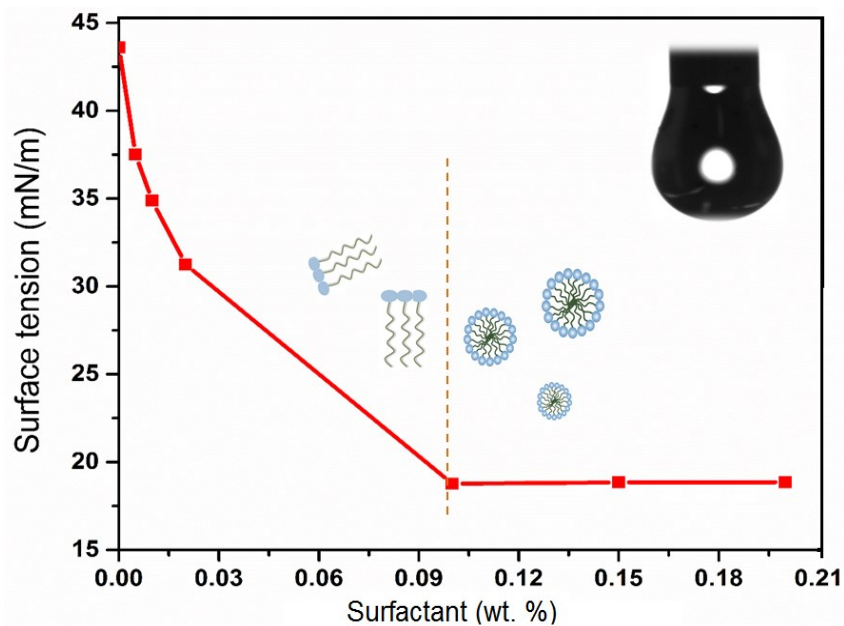


Figure S2 Determination of critical micelle concentration (CMC) of surfactant from the surface tension curve with respect to the surfactant weight percentage in [veim][Tf₂N]-chloroform solution.

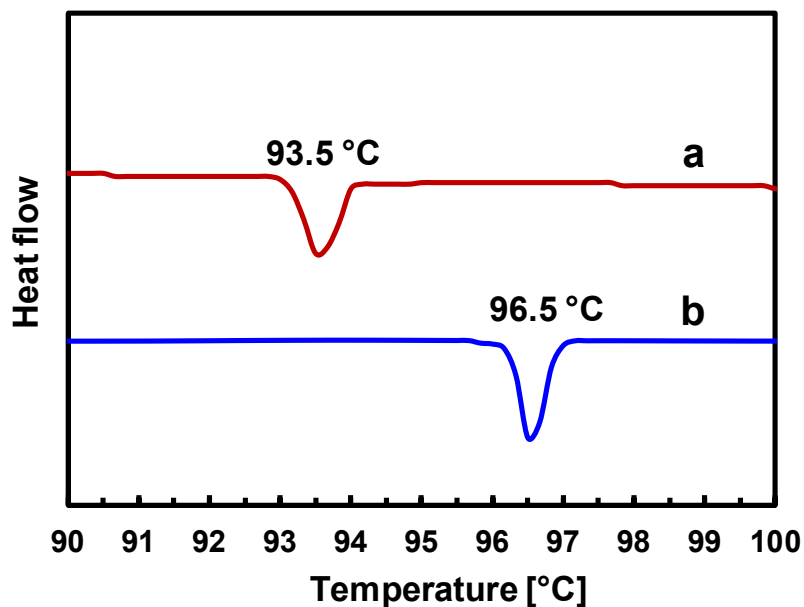


Figure S3 Differential scanning calorimetry (DSC) cooling curves of polymers (a) poly[veim][Tf₂N] and (b) 10 wt% SMI-poly[veim][Tf₂N] at 10 °C/min. The minima indicate exothermic events.

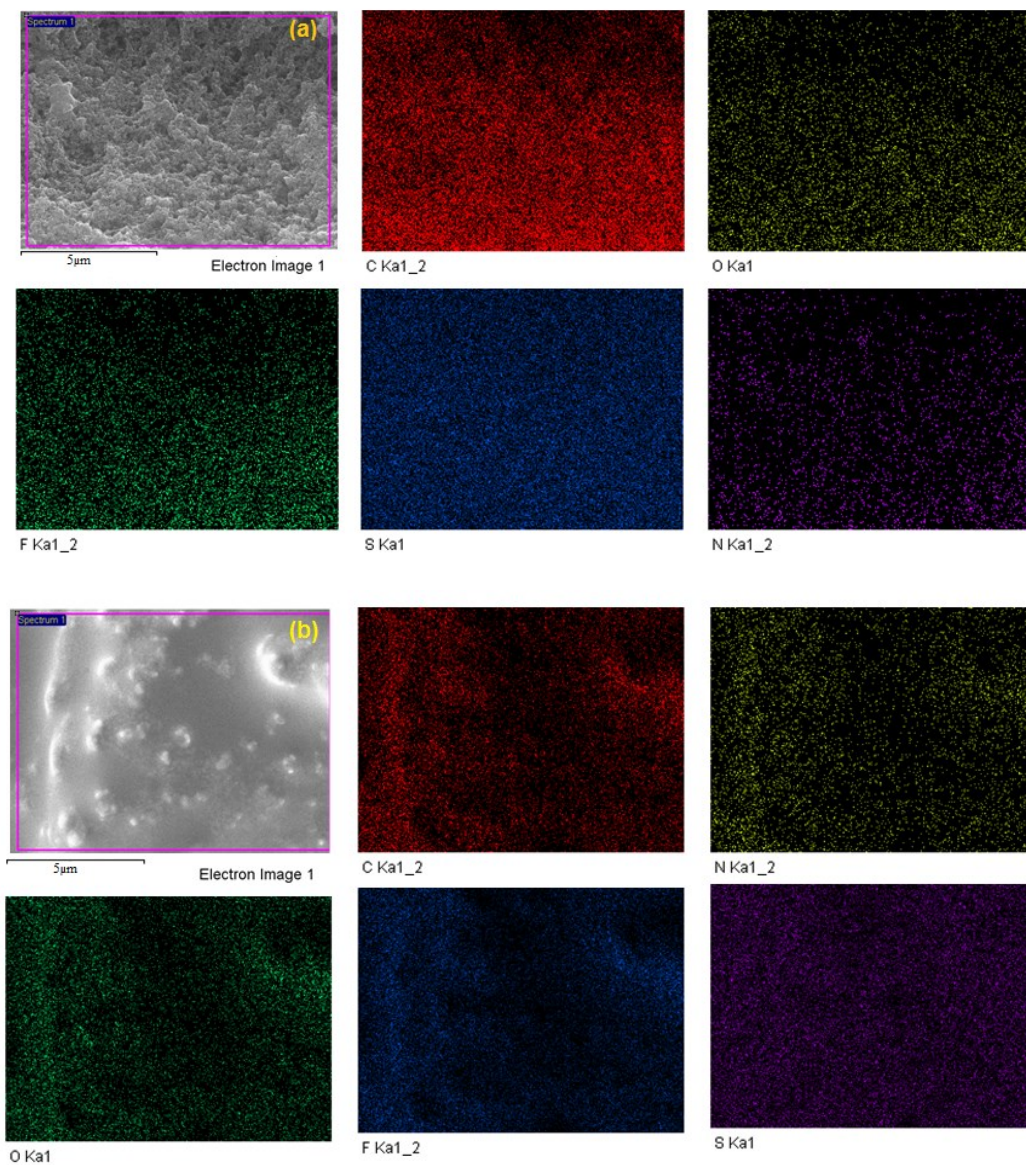


Figure S4 SEM images with energy dispersive X-ray (EDX) spectroscopic elemental mapping for (a) poly[veim][Tf₂N] alone, and (b) 1.0 wt% SMI-poly[veim][Tf₂N] composite. The mapping of individual elements i.e., C, O, F, S, N confirmed the uniform distribution of surfactant micelles within the poly[veim][Tf₂N] material.

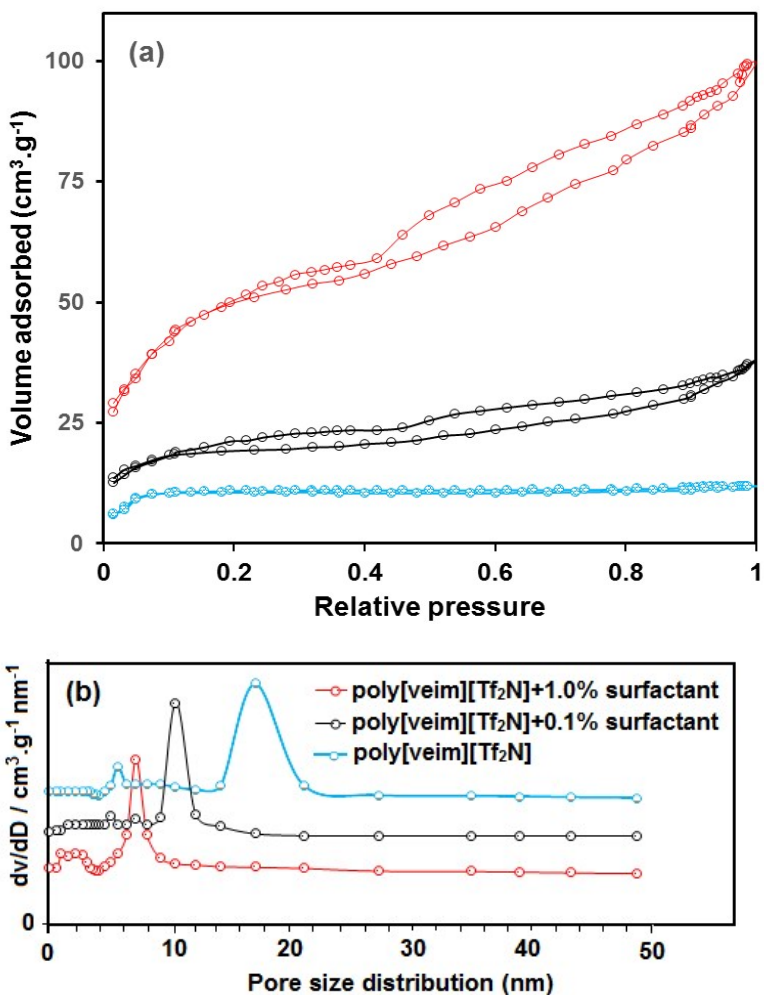


Figure S5 (a) N_2 sorption isotherms and the corresponding (b) pore size distribution curves of poly[veim][Tf₂N] alone (blue), 0.1 wt% SMI-poly[veim][Tf₂N] (black) and 1.0 wt% SMI-poly[veim][Tf₂N] (red) composites.

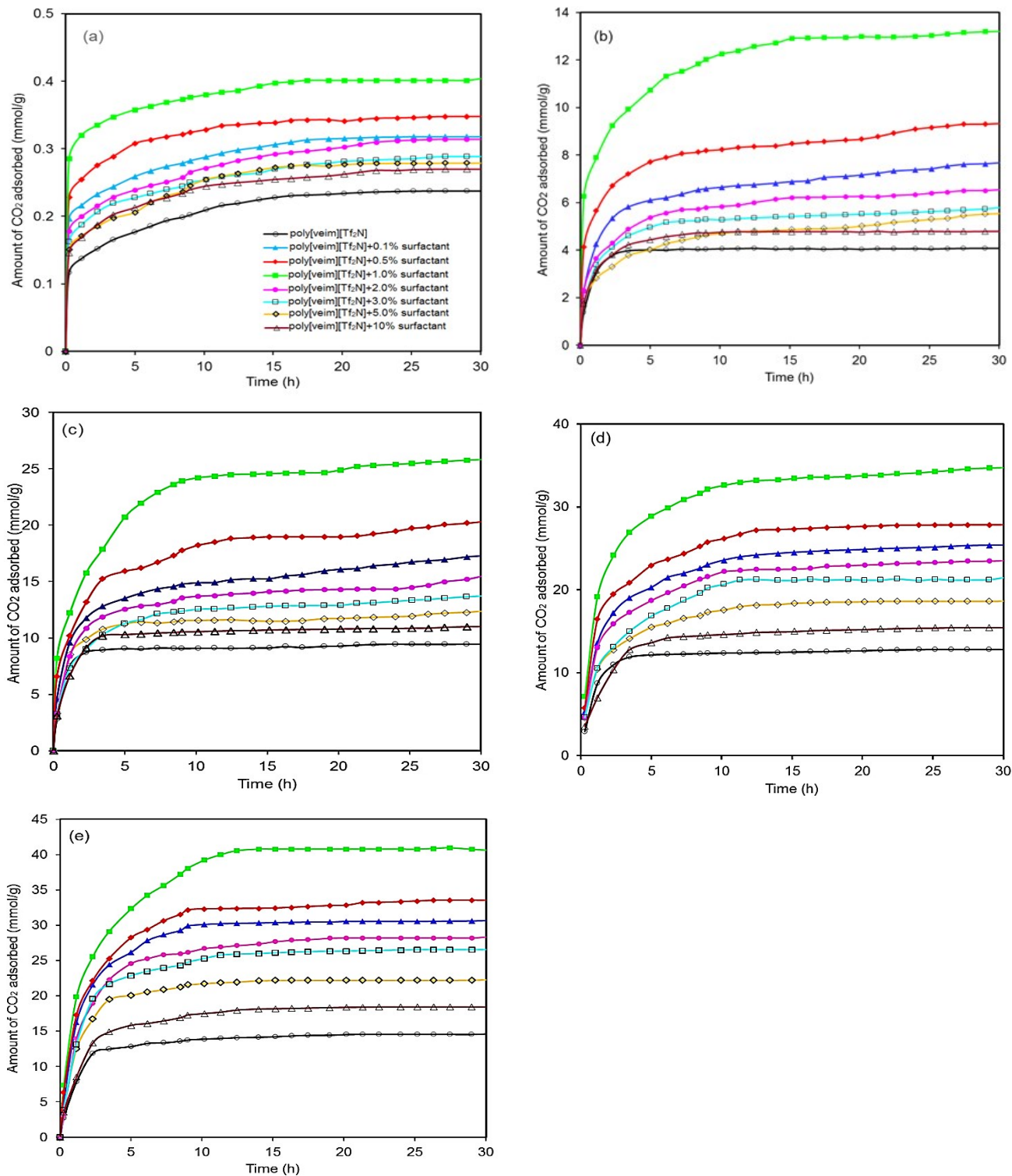


Figure S6 CO₂ sorption capacity of different poly[veim][Tf₂N] and its SMI-poly[veim][Tf₂N] materials at (a) 1.0 bar, (b) 5.0 bar, (c) 10 bar, (d) 15 bar and (e) 20 bar pressure.

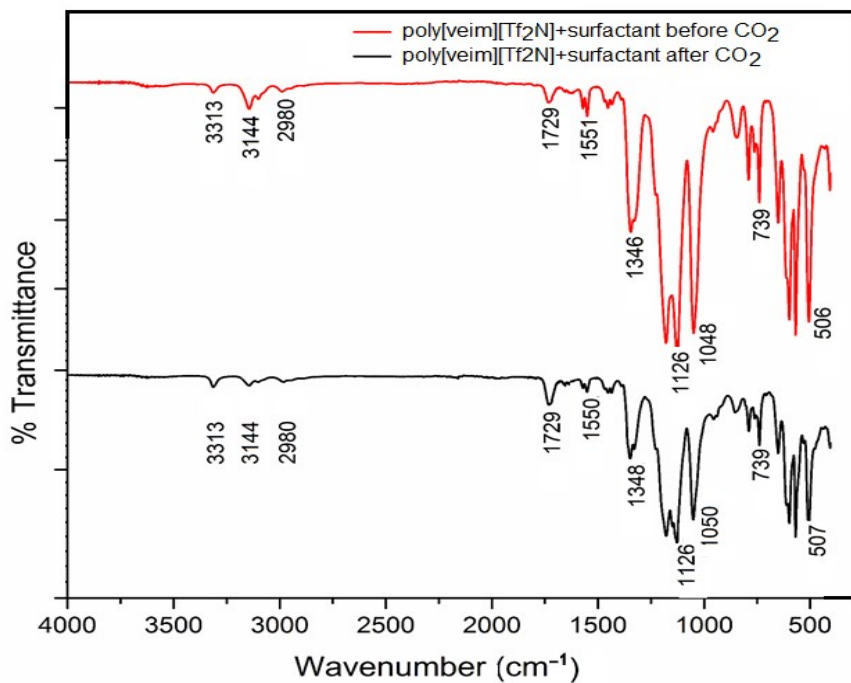
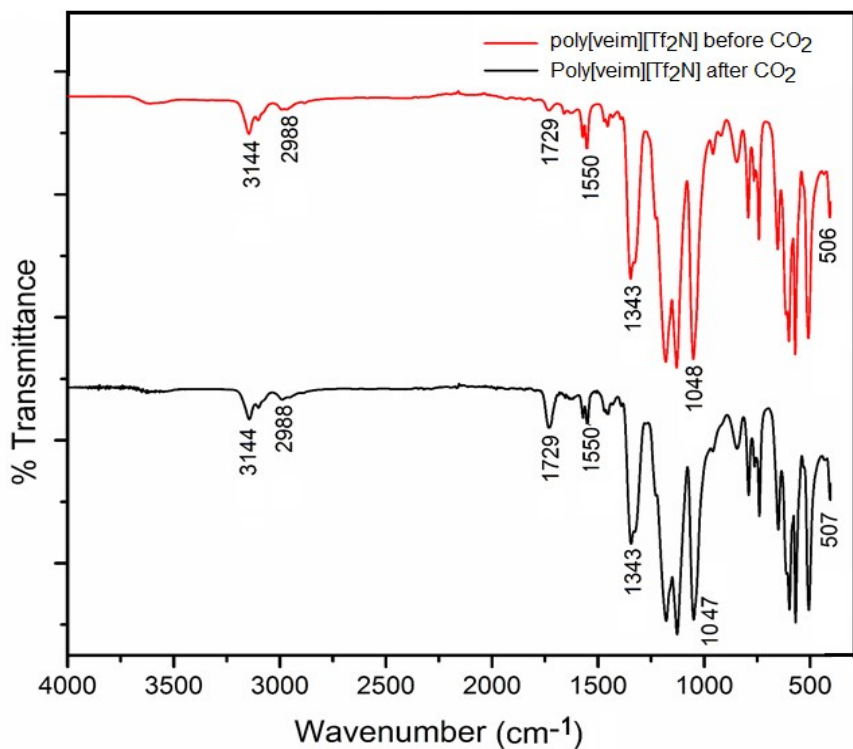


Figure S7 FT-IR spectra of (a) poly[veim][Tf₂N], and (b) 1.0 wt% SMI-poly[veim][Tf₂N] materials before and after CO₂ adsorption.

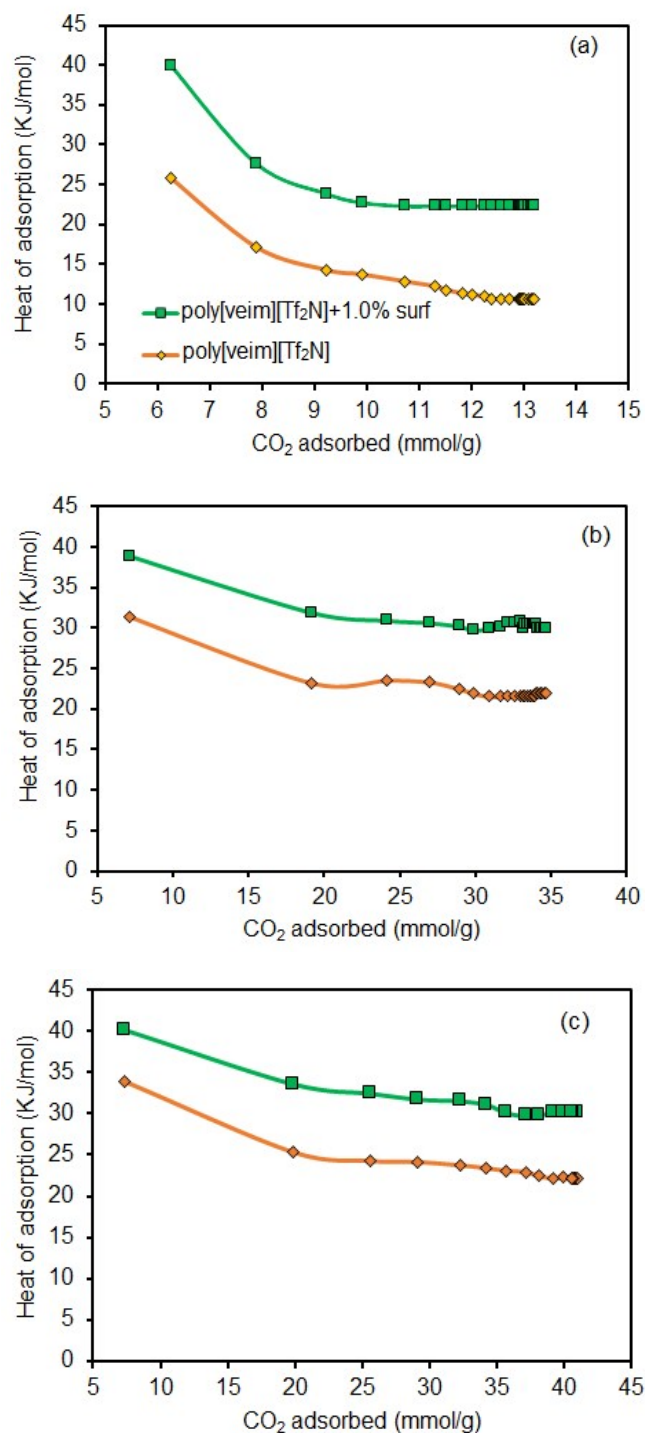


Figure S8 CO_2 isosteric heat of adsorption (Q_{st}) of poly[veim][Tf₂N] and 1.0 wt% SMI-poly[veim][Tf₂N] materials calculated at 298 K and 308 K using the Clausius-Clapeyron equation for (a) 5.0 bar, (b) 15 bar, and (c) 20 bar.

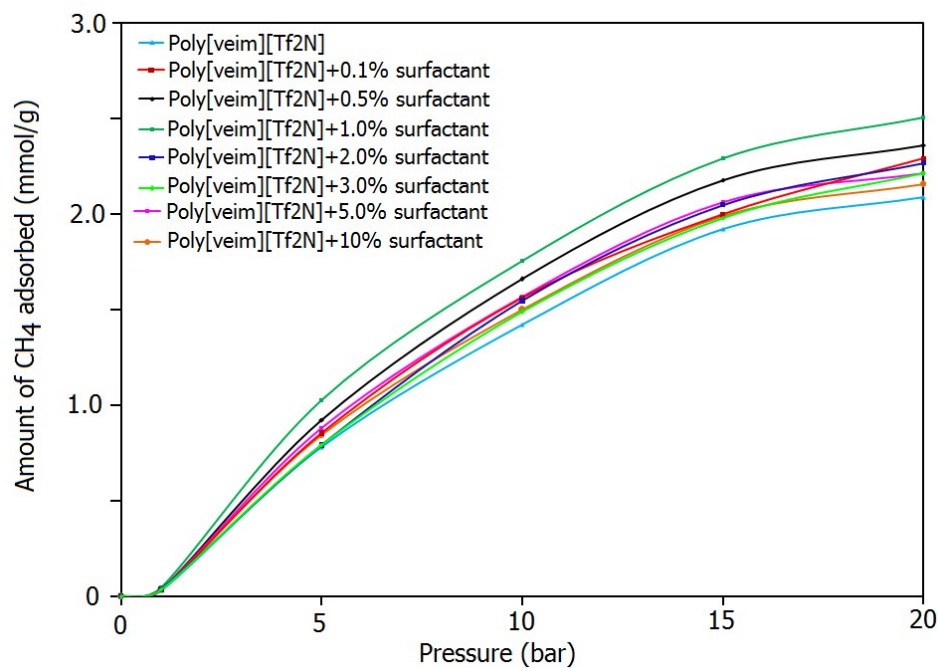


Figure S9 CH₄ sorption capacity of different poly[veim][Tf₂N] and its SMI-poly[veim][Tf₂N] materials measured at 1.0 bar, 5.0 bar, 10 bar, 15 bar, and 20 bar pressure.

Table S1 Elemental composition of poly[veim][Tf₂N] and its SMI-poly[veim][Tf₂N] materials in terms of weight percent (wt%) determined by EDX.

Sample name	Element content (wt%)				
	C	N	O	F	S
Poly[veim][Tf ₂ N]	43.6	8.4	10.8	12.7	20.9
Poly[veim][Tf ₂ N]+0.1% surfactant	39.2	10.3	13.4	15.0	12.1
Poly[veim][Tf ₂ N]+0.5% surfactant	38.9	10.8	12.2	18.1	13.7
Poly[veim][Tf ₂ N]+1.0% surfactant	36.8	11.3	11.2	21.4	14.4
Poly[veim][Tf ₂ N]+2.0% surfactant	33.6	11.8	14.0	24.6	13.3
Poly[veim][Tf ₂ N]+3.0% surfactant	31.6	12.4	13.9	27.4	11.2
Poly[veim][Tf ₂ N]+5.0% surfactant	28.3	13.7	13.2	32.5	10.1
Poly[veim][Tf ₂ N]+10% surfactant	24.3	15.1	12.2	37.1	9.8

Table S2 BET surface area, pore volume and average pore diameter of all synthesized SMI-ILPs.

Sample name	BET Surface area ^a	Pore volume ^b	Pore size ^c
	(m ² /g)	(cm ³ /g)	(nm)
Poly[veim][Tf ₂ N]	27	0.14	20
Poly[veim][Tf ₂ N]+0.1% Surfactant	69	0.16	9
Poly[veim][Tf ₂ N]+0.5% Surfactant	132	0.29	8
Poly[veim][Tf ₂ N]+1.0% Surfactant	228	0.42	7
Poly[veim][Tf ₂ N]+2.0% Surfactant	208	0.31	6
Poly[veim][Tf ₂ N]+3.0% Surfactant	164	0.28	6
Poly[veim][Tf ₂ N]+5.0% Surfactant	127	0.20	6
Poly[veim][Tf ₂ N]+10% Surfactant	47	0.17	15

^a calculated from BET equation based on N₂ adsorption isotherms at 77 K in the relative pressure region of 0.22 < p/p₀ < 0.96.

^b calculated from N₂ adsorption-desorption isotherms.

^c peak pore size evaluated from BJH pore size determination.

Table S3 The CO₂ sorption data for poly[veim][Tf₂N] and its SMI-poly[veim][Tf₂N] materials between 1.0 to 20 bar pressure and at constant temperature of 298 K.

Sample name	Pressure (bar)				
	1	5	10	15	20
Poly[veim][Tf ₂ N]	0.24	4.08	9.47	12.80	14.62
Poly[veim][Tf ₂ N]+0.1% surfactant	0.32	5.30	12.37	18.62	22.28
Poly[veim][Tf ₂ N]+0.5% surfactant	0.35	7.68	17.29	25.37	30.68
Poly[veim][Tf ₂ N]+1.0% surfactant	0.41	13.21	25.82	34.75	41.31
Poly[veim][Tf ₂ N]+2.0% surfactant	0.31	9.33	20.34	27.82	33.52
Poly[veim][Tf ₂ N]+3.0% surfactant	0.29	6.54	15.49	23.54	28.39
Poly[veim][Tf ₂ N]+5.0% surfactant	0.28	5.69	13.72	21.52	26.53
Poly[veim][Tf ₂ N]+10% surfactant	0.27	4.80	10.98	15.45	18.42

Table S4 Comparison of CO₂ adsorption capacity of various IL based materials with the present study. *

Material	Temperature (K)	Pressure (bar)	CO ₂ adsorption capacity (mmol/g)	Reusability of material	Reference
Amine-functionalized PIL brushes on TiNTs	298	1.0	2.43	only 40% capacity retained after 2 cycles	[1]
Encapsulated [Emim][Tf ₂ N]	296	25	2.46	necessitated 25 bar pressure for the material desorption	[2]
[Hmim][Tf ₂ N]	296	25	3.05		
ILP- N-CNC-Fe-Si	298	1.0	2.14	nearly 90% reusable capacity retained after 20 cycles of use	[3]
PVIm-6-SCD	273	1.0	3.60	reusability of material tested for 6 cycles only	[4]
[APMIM]Br@NaY	298	1.0	4.94	280 °C needed for regeneration >90% capacity after 10 cycles	[5]
OMS-IL(AA)	298	1.0	0.61	high temperature (~107 °C) needed for regeneration	[6]
PMMA-[N1111][Gly]	308	1.0	2.14	not reported	[7]
CB-PCPs	273	1.0	2.0	not reported	[8]
SiO ₂ -P(VBTMA)(BF ₄)	303	1.0	0.40	not reported	[9]
P(SVImTf ₂ N)	273	1.0	0.46	not reported	[10]
SMI-poly[veim][Tf ₂ N]	298	1.0	0.41	found >96% capacity after	This study
		5.0	13.21	15 consecutive cycles	
		10	25.82	only 70 °C required for material	
		15	34.75	regeneration	
		20	41.32		

* Authors are aware of the problem to compare CO₂ adsorption and reusability of the materials under different pressures. We have performed a literature search to find the studies reported at similar conditions which we used for the SMI-poly[veim][Tf₂N] materials. However, we were unable to find the work conducted at similar operating pressure and temperature. The above Table is aimed to provide only some basic information that describes the efficiency of synthesized SMI-ILPs over other reported IL polymers in terms of CO₂ sorption particularly under high operating pressures and reusability under mild operating conditions.

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