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Supporting Information

Permanent Cavities in Ionic Liquids Created by Metal-Organic Polyhedra

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Section 1. Supporting Text

Viscosity Measurement

Viscosity measurements were carried out on the viscosity meter (Anton Paar Lovis 2000 ME) using falling ball automated technique. Liquid samples were combined with a ball along with a capillary of different diameters (1.59, 1.8 and 2.5 mm) to measure the viscosities. Before that, liquid samples were calibrated with standard liquids (N7.5, N26 and N100 viscosity oil).

After considering the temperature uncertainty (which was around 0.02 K), measurement deviation of the viscometer was calculated to be 1%. The viscosity measurements were repeated three times, and the average values are reported.

Karl Fischer Titration

The titration for analyzing water content in ionic liquid was carried out by using Automatic Karl Fischer Moisture Analyzer (PEiOU, V100). The sample was heated at 100 °C for 24 h before the analysis to remove absorbed moisture. The result shows that the water content in the synthesized IL is 0.39 wt%.

Considering the previous studies on the performance of ILs (especially, imidazolium and NTf₂ containing hydrophobic ILs) for CO₂ solubility in the presence of water (0.5 to 1.5 wt%) which shows no or very minor effect since H-bonding of H₂O with NTf₂ does not eliminate any NTf₂/CO₂ interactions,¹⁻⁴ the effect of 0.39 wt% of H₂O in the current IL(NTf₂) on the solubility of CO₂ should be very scarce, if any.

PALS Analysis

The materials used for positron annihilation lifetime spectroscopy (PALS) were prepared by a conventional fast-fast coincidence system (Key Laboratory of Nuclear Solid State Physics Hubei Province). When testing the sample, a ²²Na positron source was used and the sample was sealed in the sample box with 7 μ m thick Mylar film. Two sealed samples clamped the positron source and this structure is similar to the sandwich, and the Mylar film side faced toward the source.

The lifetime (τ 3) and the associated intensity (I3) were employed for the measurement of the available cavities in the obtained ionic liquid (IL) and porous ionic liquids (PILs). The average pore cavity present in IL and PILs was calculated with τ 3 (ns) using the Tao-Eldrup equation,^{5,6} which is as following:

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} (S1)$$

where *R* is the free-volume of radius (Å) and $R_0=R+\Delta R$. Here, ΔR was determined empirically to be 1.656 Å.

Gas Separation Tests

Mixed gas permeation tests are carried out to test the gas separation performance of composite membranes via a constant pressure/variable volume method.^{7–9} The gas permeance was calculated from the average value of at least three test results calculated by the following equation:

$$P = \frac{1}{\Delta_P \cdot A} \cdot \frac{273.15}{273.15 + T} \cdot \frac{P_{atm}}{76} \cdot \frac{dV}{dt} (S2)$$

where *P* is the gas permeance (1 GPU =10⁻⁶ cm³ (STP) cm⁻² s⁻¹ cm Hg), *A* is the effective area of membrane, Δ_P is the trans-membrane pressure (atm), *P*_{atm} represents the atmospheric pressure (atm), *T* is the testing temperature (°C), and dV/dt represents the volumetric displacement rate in the bubble flow meter.

A mixture of CO_2/N_2 (or CH₄) (50 vol%: 50 vol%) was employed as the feed gas, while Ar was chosen as the sweep gas. The mixed gas permeation test was measured at 1 atm and 25 °C. The component of the mixed gas was detected by gas chromatography (Agilent 7820A, USA). The selectivity of binary gas mixtures can be calculated as follows:

$$a_{A/B} = \frac{y_A / y_B}{x_A / x_B} (S3)$$

where x and y are the volumetric fraction of the one component in the feed and permeate side, respectively.

Molecular Dynamic Simulation

Molecular dynamics simulations were conducted using the Forcite module in Accelrys Materials Studio 7.0 software.¹⁰ The initial configuration was constructed with one MOP cluster and one cation (+2 charge) and two anion of the ionic liquid packed in a large cubic box of (4.0 x 4.0 x

4.0 nm³). The simulations were carried out by implementing Universal forcefield (UFF) along with charge equilibration method (Q_{eq}) addressing point charges of the system to explain that IL molecule is not possible to enter the inner cavity of the MOP cage.

The calculation details are as follows: NPT ensembles with fixed pressure (100 kPa) and temperature (298 K) were selected to conduct the equilibrium run, where the time step and total equilibrium time-run were set as 1.0 fs and 50 ns, respectively. The final configurations of the equilibrium run were retaken as the initial models for the production run under NVT conditions, where the time step and total equilibrium time-run were set as 1.0 fs and 25 ns, respectively. For all the dynamic calculations, a cut off distance of 15.5 Å were applied to both van der Waals and electrostatic potential. For each computed frame within the production run, movies were generated to interpret the movements of the studied models.

Simulation Studies for Calculating Formation Energy (Ef)

The simulations based on semi-empirical methods were performed by employing the PM7 Hamiltonian as modified by Throssel and Frisch for continuous potential energy surfaces, which had been implemented in the Gaussian-16 package. Fully relaxed geometry optimizations were performed under the tight termination criteria, and self-consistent field procedures of full accuracy were performed with tight convergence, without any orbital symmetry constraints.

Section 2. Supporting Figures



Fig. S1. The ¹H NMR spectrum of ligand L1 [1,3-di(pyridin-4-yl)benzene] with all of the prominent chemical shifts.



Fig. S2. The ¹H NMR spectrum of 1 depict all the prominent chemical shifts [(400 MHz, DMSO-d₆), δ (ppm): 9.45 (s, 4H), 8.55 (s, 1H), 8.44 (s, 4H), 8.11 (s, 2H), 7.71 (s, 1H)] belong to the protons of the ligand 1,3-di(pyridin-4-yl)benzene.



Fig. S3. The MS spectra obtained from **1** $[Pd_{12}(L1)_{24}]$ $(NO_3^{2^-} salt)$ depicting all the prominent fragmentation patterns. MALDI-MS: prominent peaks (m/z) for $[Pd_{12}(L_1)_{24}]^{n+}$ (n = 6-14) are found as $[Pd_{12}(L_1)_{24}]^{6+} = 1181.1$, $[Pd_{12}(L_1)_{24}]^{7+} = 1127.1$, $[Pd_{12}(L_1)_{24}]^{8+} = 1083.1$, $[Pd_{12}(L_1)_{24}]^{9+} = 1173.2$, $[Pd_{12}(L_1)_{24}]^{10+} = 1029.2$, $[Pd_{12}(L_1)_{24}]^{11+} = 975.1$, $[Pd_{12}(L_1)_{24}]^{12+} = 930.1$. $[Pd_{12}(L_1)_{24}]^{13+} = 875.1$, $[Pd_{12}(L_1)_{24}]^{14+} = 823.1$.



Fig. S4. FTIR spectra obtained from 1 $[Pd_{12}(L1)_{24}]$ exhibiting characteristic absorption peaks by the respective functional groups available.



Fig. S5. TG and DTG analytical results of 1 $[Pd_{12}(L1)_{24}]$ illustrating the weight loss (%) and its derivative against the temperature.



Fig. S6. The ¹H NMR spectrum of precursor [3,5-dibromo-N-(3-(triethoxysilyl)propyl)aniline] with chemical shifts [(400 MHz, DMSO-d₆), δ (ppm): 0.66 (t, 2H); 1.16 (t, 3H); 1.75 (m, 2H); 3.47 (t, 2H); 3.75 (q, 2H); 4.36 (s, 1H); 6.74 (s, 1H); 7.25 (s, 1H)].



Fig. S7. The ¹H NMR spectrum of ligand L2 [3,5-di(pyridin-4-yl)-N-(3-(triethoxysilyl)propyl)aniline] with chemical shifts [(400 MHz, DMSO-d₆), δ (ppm): 0.94 (t, 2H); 1.19 (t, 3H); 1.55 (m, 2H); 3.31 (t, 2H); 3.79 (q, 2H); 4.05 (s, 1H); 7.17 (s, 1H); 7.52 (s, 1H); 7.66 (s, 1H); 8.67 (s, 1H)].



Fig. S8. The ¹H NMR spectrum of **2** depict all the prominent chemical shifts [(400 MHz, DMSO-d₆), δ (ppm): 0.85 (t, 2H); 1.23 (t, 3H); 1.48 (m, 2H); 3.17 (t, 2H); 4.02 (q, 2H); 4.05 (s, 1H); 7.14 (s, 1H); 7.62 (s, 1H); 8.18 (s, 1H); 9.37 (s, 1H)] belong to the protons of the ligand 3,5-di(pyridin-4-yl)-N-(3-(triethoxysilyl)propyl)aniline (the asterisk peaks are due to signal noises).



Fig. S9. The MS spectra obtained from **2** $[Pd_{12}(L2)_{24}]$ (NO₃²⁻ salt) depicting the characteristic fragmentation patterns. MALDI-MS: prominent peaks (m/z) for $[Pd_{12}(L_2)_{24}]^{n+}$ (n = 7–12) are found as $[Pd_{12}(L_2)_{24}]^{7+} = 1562.1$, $[Pd_{12}(L_2)_{24}]^{8+} = 1409.8$, $[Pd_{12}(L_2)_{24}]^{9+} = 1299.9$, $[Pd_{12}(L_2)_{24}]^{10+} = 1277.1$, $[Pd_{12}(L_2)_{24}]^{11+} = 1257.1$, $[Pd_{12}(L_2)_{24}]^{12+} = 1169$. Note: the noise in the fragmentation patterns of MOP **2** was due to the presence of water (see Figure S8).



Fig. S10. The FTIR spectra obtained from 2 $[Pd_{12}(L2)_{24}]$ exhibiting the absorption peaks by the available functional groups. As can be seen, the vibration of Si–O bond emerged at the absorbance peak 1019 cm⁻¹.



Fig. S11. TG and DTG analytical results of 2 $[Pd_{12}(L2)_{24}]$ depicting the weight loss (%) and its derivative as per the rise in temperature.



Fig. S12. The ¹H NMR spectra obtained from IL(NTf₂) exhibiting the chemical shifts [(400 MHz, DMSO-d₆), δ (ppm): 0.91 (t, 3H); 1.28 (m, 2H); 1.79 (m, 2H); 3.51 (s, 8H); 3.79 (t, 2H); 4.20 (t, 2H); 4.35 (t, 2H); 7.76 (d, 1H); 7.79 (d, 1H); 9.13 (s, 1H)].



Fig. S13. The ¹³C NMR spectra obtained from IL(NTf₂) exhibiting the chemical shifts (δ) belong to the carbons available [(100 MHz, DMSO-d6), δ (ppm)]: 13.61, 19.23, 31.72, 49.07, 60.19, 70.21, 122.89, 123.29, 136.80 and 171.89. The asterisk peaks are due to signal noises.



Fig. S14. The FTIR spectra obtained from $IL(NTf_2)$ depicting the absorption peaks by the available functional groups.



Fig. S15. Comparisons of the initial (a), and final (b) configuration of the molecular dynamics simulations boxes for the IL-cage interaction in order to illustrate the bulkiness of IL molecule.



Fig. S16. The addition of methanol (CH₃OH) was carried out to mitigate the viscosity of $IL(NTf_2)$ and to better disperse 1 in the mixture. Notably, 1 was found not soluble in the neat CH₃OH.



Fig. S17. The preparation of porous ionic liquid was also tried by dispersing 20 mg of 1 $[Pd_{12}(L1)_{24}]$ in 2 mL solution of IL(Br)/CH₃OH (1:1). However, after drying the mixture at 70 °C for 2 h, 1 was found precipitated at the bottom of the tube. This implies that the molecule size (3.75 nm x 1.86 nm x 1.12 nm) of IL(Br) was inferior than the average pore-aperture diameter (1.3 nm) of 1.



Fig. S18. The dispersion of 1 $[Pd_{12}(L1)_{24}]$ in 2 mL solution of commercial Im(NTf₂) and CH₃OH (1:1) has the same fate as of with IL(Br) (Fig. S17) owing to its very inferior molecular size than the average pore-aperture diameter (1.3 nm) of 1. As a result, Pd-MOP (1) precipitated at the bottom of the tube. In conclusion, the solvent molecule must be size-exterior relatively to the pore-aperture diameter of porous solid to obtain a porous liquid system.



Fig. S19. Different amounts of **1** $[Pd_{12}(L1)_{24}]$ were dispersed in IL(NTf₂) in order to find its solubility. After obtaining the respective porous ionic liquids (PIL-1-*x*%, where *x* is 1–5), 200 μ L of each PILs were mixed with 1 mL of CH₃OH, and the resulting solutions were kept under light. It was observed that the saturation for dissolving **1** in IL(NTf₂) was attained with >2% of its content (for example, PIL-1-5%, a colloidal solution apparent under light), while 2% making a clear solution.



Fig. S20. Compared ¹H NMR spectra (400 MHz, DMSO- d_6) of IL(NTf₂), PIL-1-2%, and PIL-1-5% dissolved in DMSO- d_6 (asterisks depict the peaks from the solvent and minor impurities).



Fig. S21. Cumulative ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of (a) **1** $[Pd_{12}(L1)_{24}]$ prepared in DMSO-*d*₆ with the magnified ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of (b) PIL-**1**-2% dissolved in DMSO-*d*₆. The arrows (blue) depict the emergence of NMR peaks at 8.98, 8.52, 8.41 and 8.18 ppm which represents **1** dissolved in IL(NTf₂) and confirms its presence. The change in the chemical shifts could be attributed to the interaction of IL(NTf₂) molecules at the periphery of Pd-MOP (**1**).



Fig. S22. As discussed in Figure S16, the addition of CH_3OH was carried out to mitigate the viscosity of $IL(NTf_2)$ and to better disperse 2 in the mixture. 2 was found not soluble in the neat CH_3OH .



Fig. S23. In order to observe the solubility of 2 $[Pd_{12}(L2)_{24}]$ in IL(NTf₂), the obtained PILs (200 μ L) were mixed with CH₃OH (1 mL). The resulting solutions were kept under light and it was observed that 0.5% of 2 is completely soluble in IL(NTf₂) while 2% of its content making a colloidal solution.



Fig. S24. Compared ¹H NMR spectra (400 MHz, DMSO- d_6) of IL(NTf₂), PIL-2-0.5%, and PIL-2-2% dissolved in DMSO- d_6 (asterisks depict the NMR peaks from the solvent and minor impurities).



Fig. S25. Cumulative ¹H NMR spectra (400 MHz, DMSO- d_6) of (a) 2 [Pd₁₂(L2)₂₄] prepared in DMSO- d_6 with the magnified ¹H NMR spectrum (400 MHz, DMSO- d_6) of (b) PIL-2-0.5% dissolved in DMSO- d_6 . As can be seen, arrows (blue) depict the NMR peaks appeared at 8.91, 8.22, 8.04, 7.59 and 7.44 ppm confirms the presence of 2 dissolved in IL(NTf₂). Some peaks seems shifted in the NMR spectrum of PIL-2-0.5% than the peaks appeared in NMR spectrum of 2, most probably due to the interaction of IL(NTf₂) molecules at the periphery of Pd-MOP 2.



Fig. S26. Positron annihilation lifetime spectroscopic (PALS) analysis of Pd-MOP 1 where τ and I represents positron (e⁺) annihilation lifetime and intensity of lifetime, respectively. Based on τ 3 (ns) value by using the Tao-Eldrup equation (S1), the average cavity present in Pd-MOP is calculated as R = 6.67 Å.



Fig. S27. TG analyses of PIL-1-2% and PIL-2-0.5% depicts the slight enhancement of thermal stability than the neat $IL(NTf_2)$.



Fig. S28. DTG analytical results of IL(NTf₂), PIL-1-2%, and PIL-2-0.5%.



Fig. S29. Compared ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of fresh PIL-1-2% and after 15 months of time period. Insets are the digital images of freshly prepared PIL-1-2% and the same after 15 months.



Fig. S30. Compared ¹H NMR spectrum (400 MHz, DMSO- d_6) of fresh PIL-**2**-0.5% and after 15 months of time period. Insets are the digital images of fresh PIL-**2**-0.5% and the same after 15 months.



Fig. S31. Compared FTIR spectra of fresh PIL-1-2% and after 15 months of time period.



Fig. S32. Compared FTIR spectra of fresh PIL-2-0.5% and after 15 months of time period.



Fig. S33. CO₂ uptake analyses at low pressure (25 °C). PIL-**2**-0.5% (0.119 mmol g^{-1}) and PIL-**1**-2% (0.096 mmol g^{-1}) depict high CO₂ adsorption capacities which clearly indicate the role of cavities and functionality available in PILs than that of neat ionic liquid (0.082 mmol g^{-1}).



Fig. S34. Simulation studies for calculating the formation energy of CO₂ interacting at different locations of **1** [Pd₁₂(L1)₂₄] which is present as a cavity in PIL-**1**-2%. The energy of CO₂ molecule located inside the Pd₁₂(L1)₂₄ cage is more negative ($E_f = -32.2$) than that of located at the cage mouth i.e. $E_f = -31.1$. This implies that CO₂ molecules are easy to be captured by **1** in view of the negative formation energy ($E_f = -32.2$) of the complex structure CO₂-Pd₁₂(L1)₂₄ in PIL-**1**-2%.

 $E_{\rm f} = E \left[\mathrm{Pd}_{12}(\mathrm{L1})_{24} \text{ cage adsorbing the guest molecule} \right] - E \left[\mathrm{Pd}_{12}(\mathrm{L1})_{24} \text{ cage} \right] - E \left(\text{guest molecule} \right).$



Fig. S35. CO₂ adsorption capacity of Pd-MOP 1 (0.621 mmol g^{-1}) and Si-PdMOP 2 (0.629 mmol g^{-1}) at 25 °C.



Fig. S36. Comparative adsorption capacities of PIL-1-2% [type II PL, 0.096 mmol g^{-1}] and PIL-1-5% [type III PL, 0.136 mmol g^{-1}) at 25 °C. Apparently, PIL-1-5% has at most achieved 1.4 times the adsorption capacity of PIL-1-2% which do no justice with such high (5%) content of 1 in IL(NTf₂), probably because of its oversaturation and partial congregation in IL (see Fig. S19).



Fig. S37. Comparative CO₂ adsorption capacities (mmol g^{-1} , 25 °C) of IL(NTf₂) solutions containing dissolved ligands (L1 and L2) and Pd salt against neat IL(NTf₂). As can be seen, the presence of additional functionalities alone in IL was not found assisting in uprising CO₂ uptakes, and thus, an intrinsic cavity is required to captivate guest molecule which is observed with current PILs system.



Fig. S38. Comparative CO₂ adsorption capacities (25 °C) of fresh and 15 months old samples of PIL-1-2% and PIL-2-0.5%.



Fig. S39. Comparative CO₂ adsorption capacity (25 °C) of PIL-1-2% after each regeneration and reuse. As can be seen, there is negligible loss in CO₂ uptake after each adsorption cycle and confirms the reversibility/reusability of PILs system.



Fig. S40. SEM images (a), (b), (c) and (d) depicting the thickness of PIL-2-0.5%, PIL-1-2%, $IL(NTf_2)$ coated PAN membrane, and neat PAN substrate while the images (e), (f), (g) and (h) depict the roughness of respective coatings, and the bare PAN membrane.

Sample	Tau 1	I1 (%)	Tau 2	I2 (%)	Tau 3 ^a	I3 (%) ^b	R ^c
Ionic liquid	0.125	16.372	0.436	64.414	2.987	19.213	9.18 Å
PIL-1-2%	0.125	11.165	0.428	70.027	3.090	18.809	9.60 Å
PIL-2-0.5%	0.125	11.630	0.430	69.388	3.083	18.982	9.55 Å

Table S1. PALS data obtained after the analyses of IL(NTf₂), PIL-1-2% and PIL-2-0.5%.

^{*a*}Tau = positron (e^+) annihilation lifetime; ^{*b*}I = intensity of lifetime; ^{*c*}R = Pore aperture

Table S2. Analytical data of PILs and IL(NTf₂) after viscosity measurements as a function of temperatures.

Temperature	Viscosity	Lovis kinetic	Lovis variation						
(°C)	(cP)	Viscosity	Coefficient						
		$(mm^2 s^{-1})$	(%)						
IL(NTf ₂)									
20.00	118.19	80.4	0.09						
25.00	87.92	55.9	0.43						
30.00	66.59	38.8	0.65						
35.00	52.27	25.9	0.46						
40.00	40.83	17.3	0.01						
45.00	32.02	11.5	0.07						
50.00	25.54	7.6	0.31						
PIL-2-0.5%									
20.00	142.44	89.55	0.50						
25.00	107.87	73.18	0.10						
30.00	84.73	52.97	0.03						
35.00	64.86	43.41	0.11						
40.00	51.929	38.66	0.10						
45.00	42.649	31.86	0.18						
50.00	34.065	25.54	0.14						
PIL-1-2%									
20.00	196.69	143.5	0.96						
25.00	147.11	107.7	0.26						
30.00	111.06	81.61	0.06						
35.00	85.686	63.17	0.70						
40.00	67.522	49.95	0.04						
45.00	55.866	41.47	0.13						
50.00	45.407	33.82	0.22						

Porous liquid	Туре	Bulky solvent	CO ₂ uptake	Ref.
			$(mmol g^{-1})$	
PIL-2-0.5%	II	$IL(NTf_2)^a$	0.89	This work
PIL-1-2%			0.61	
UiO-66@OS@PEGS	Ι	_	0.63	11
UiO-66-liquid	Ι	_	0.27	12
15-C-5-PL	II	15-C-5 ^b	0.38	
18-C-6-PL		18-C-6 ^c	0.43	13
ZSM-5-PL	III	$[DBU-PEG][NTf_2]^d$	0.46	14
ZIF-8-PL			1.56	
450-P[VHIm]Br-PEGS	Ι	-	1.05	15
450- P[VBBI]Br-PEGS			1.03	
H-ZSM-5-	III	[P66614][Br] ^e	0.46	16
liquid/[P66614][Br]				

Table S3. Comparative CO₂ adsorption capacities (at 10 bar, 25 °C) of various PLs with the currently prepared PILs.

 a IL(NTf₂) = 1,1'-(3,6,9,12,15,18,21,24-octaoxahexacosane-1,26-diyl)bis(3-butyl-1H-imidazol-3ium) di-trifluoromethanesulfonylamide; b 15-C-5 = 15-Crown-5; c 18-C-6 = Dicyclohexano-18-Crown-6; d [DBU-PEG][NTf₂] = 8,8'-(3,6-dioxaoctane-1,8-diyl)bis(1,8-Diazabicyclo[5.4.0]undec-7-en-8-ium)bis(trifluoromethanesulfonyl)imide; and e [P66614][Br] = Trihexyl(tetradecyl)phosphonium bromide.

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