Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Carbon Dioxide Separation from Flue Gas by Mixed Matrix Membranes with Dual Phase Microporous Polymeric Constituents

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Materials and Preparation

All chemicals were purchased from Sigma Aldrich and were used without any further purification. BILP-101 and PIM-1 was synthesized based on the previous reports.[1,2] Thermogravimetric analysis (TGA) was performed using a TGA Q500 thermal analysis system. Powder X-ray diffraction (PXRD) was collected by Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Ka. Surface area measurements were performed using an Autosorb 1 from Quantachrome. Scanning electron microscopy (SEM) was performed using an FEI Quanta 600 scanning electron microscope. ^{1}H (300 MHz) NMR spectrum was recorded on a Bruker AVANCE III 300 spectrometer. Fourier transform infra-red (FT-IR) Spectra were collected by using a Bruker vertex 70.

Preparation of BILP-101

BILP-101 was synthesized by the experimental procedure reported by Sekizkardes *et al.* [1] 1,2,4,5-benzenetetramine tetrahydrochloride (100 mg, 0.35 mmol), 70 mL anhydrous DMF, and a stirrer-bar. The resultant homogeneous solution was cooled to -30 ^{o}C and treated drop-wise with 1,3,5-triformylbenzene (40 mg, 0.23 mmol) dissolved in anhydrous DMF (17 mL). The temperature was maintained around - 40 ^{o}C for 1 hour and warm to room temperature overnight. After air introduction for 15 min., the reaction mixture was transferred to oven and heated gradually to 130 ^{o}C and kept for two days to afford a fluffy light brown powder. The solid was washed with DMF, acetone, water, 1 M HCl, 1 M NaOH, water, and acetone. Dried product was vacuumed to give BILP-101 as a fluffy brown powder (72 mg, yield 92%).

Preparation of PIM-1

BILP-101 was synthesized by the experimental procedure reported by Budd *et al.*[2] 3,3,3`,3`-tetramethyl-1-1``-spirobisindane-5,5`,6,6`-tetrol (12.4 mmol, 4.1 g) and 2,3,5,6-tetra-fluorophthalonitrile (12.4 mmol, 2.4 g) were dissolved in dry DMF (120 mL). K_2CO_3 was added in the solution and the reaction was stirred at 65^{o}C for three days. Water (110 mL) was added after cooling the reaction mixture and the product was afforded by filtration. Further purification was performed by reprecipitation from $CHCl_3$ solution with MeOH and a bright yellow solid product was afforded (5.12 g, yield 92 %), after thermal activation at 120 ^{o}C.

Figure S1: ^{1}H (300 MHz) spectrum of PIM-1

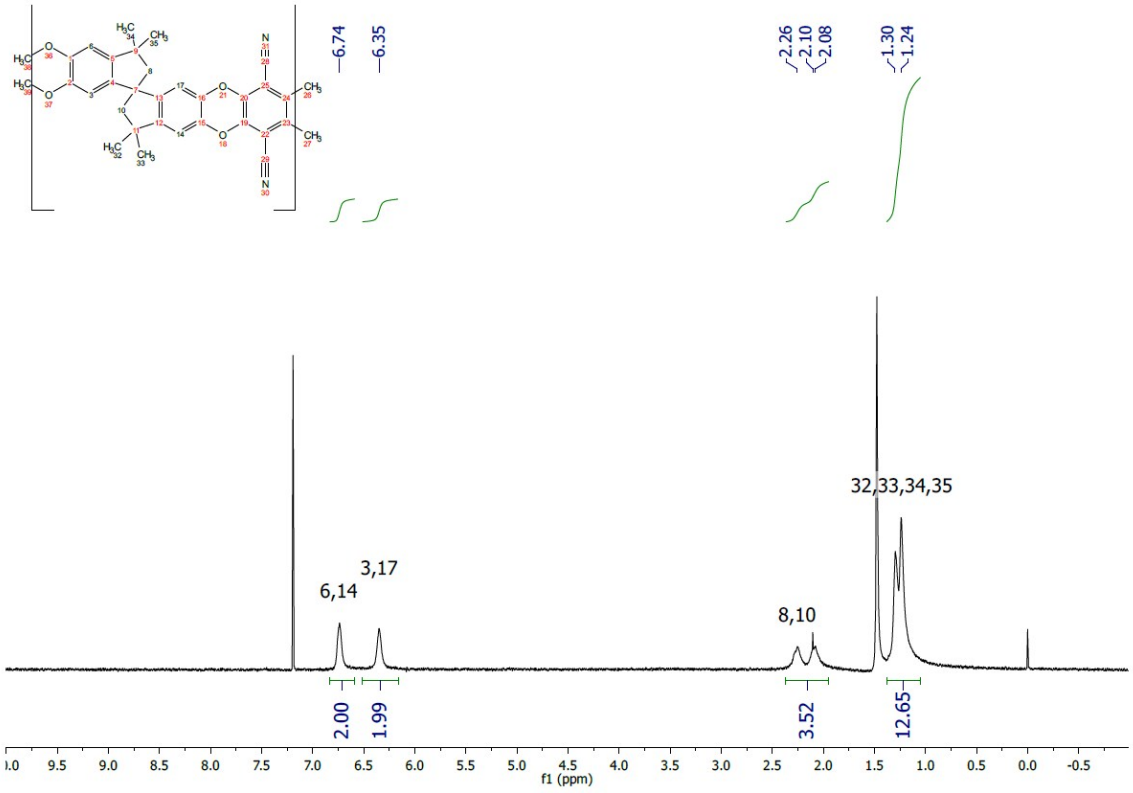


Figure S2: FT-IR spectrum (400-4000 cm^{-1}) of PIM-1

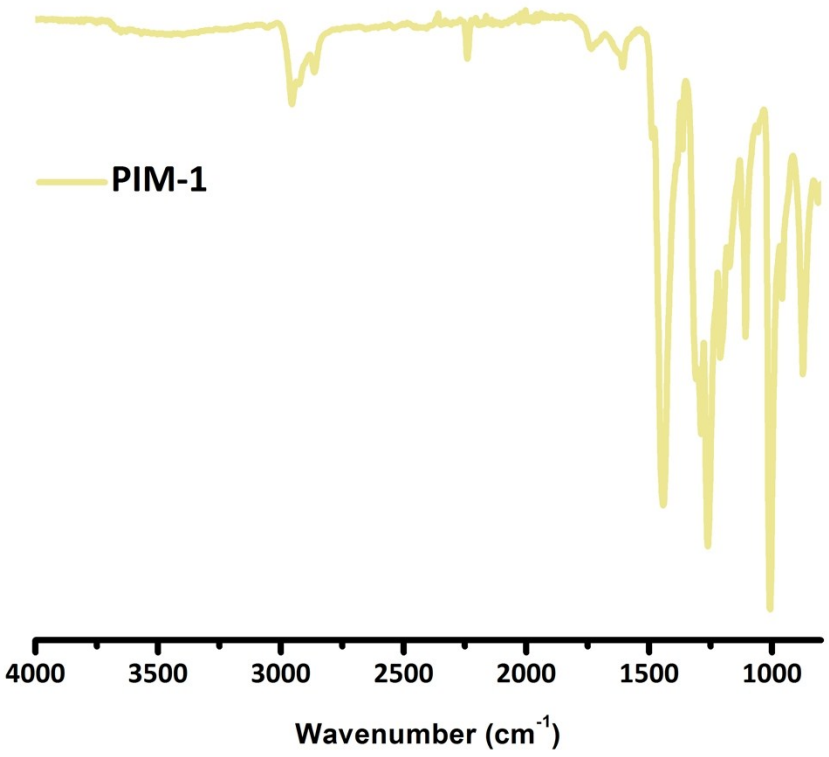


Figure S3: FT-IR spectrum (1000-4000 cm^{-1}) of BILP-101

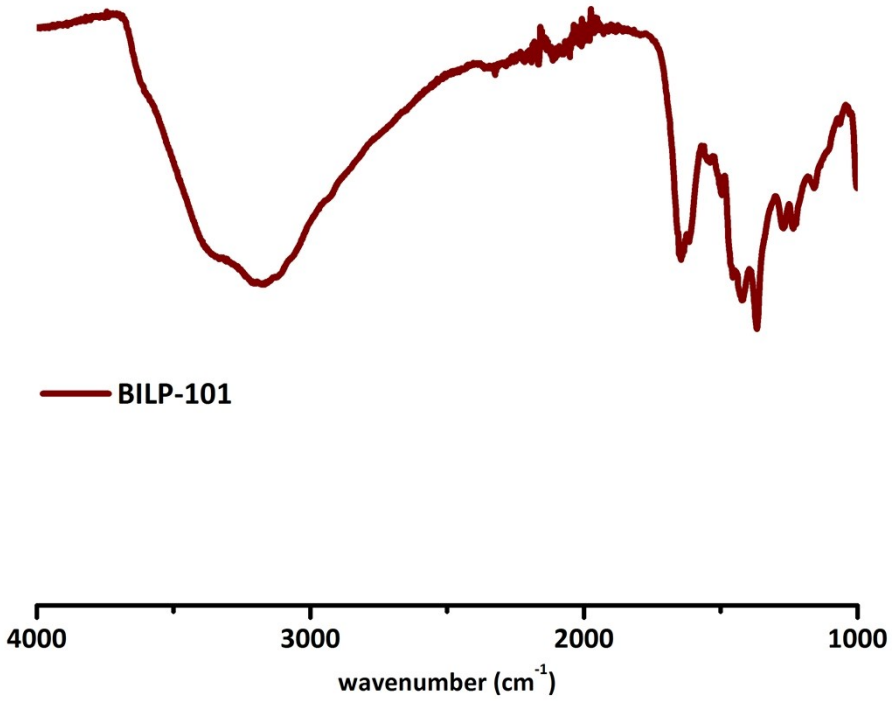
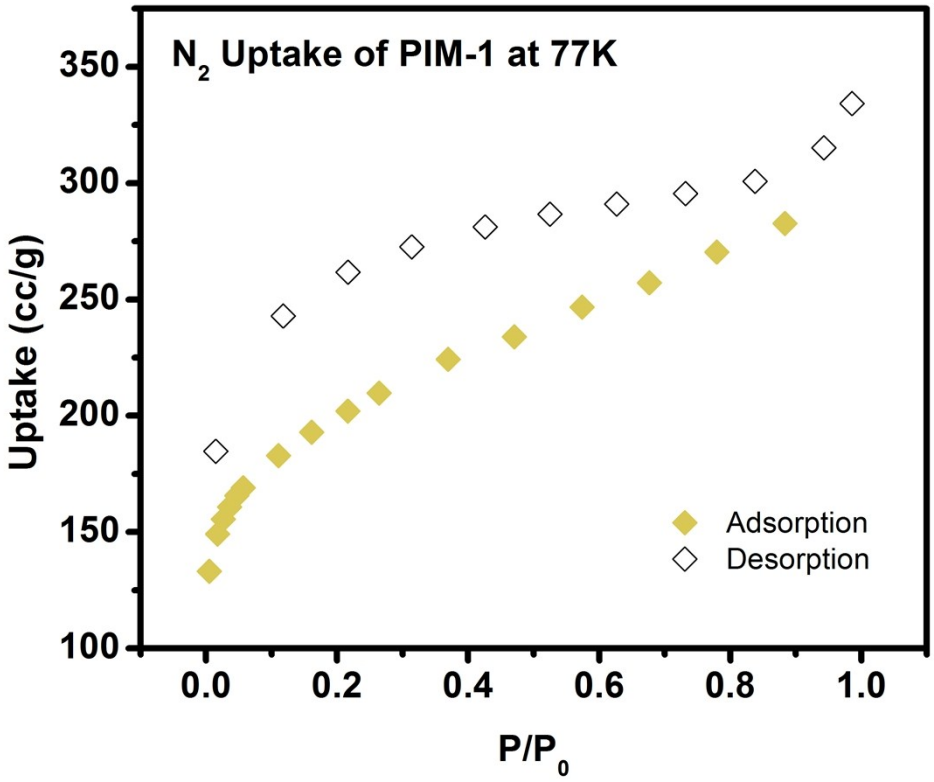


Figure S4: Full N_2 adsorption/desorption isotherm at 77K and pore size distribution for PIM-1 calculated by non-local density functional theory (NLDFT) model.



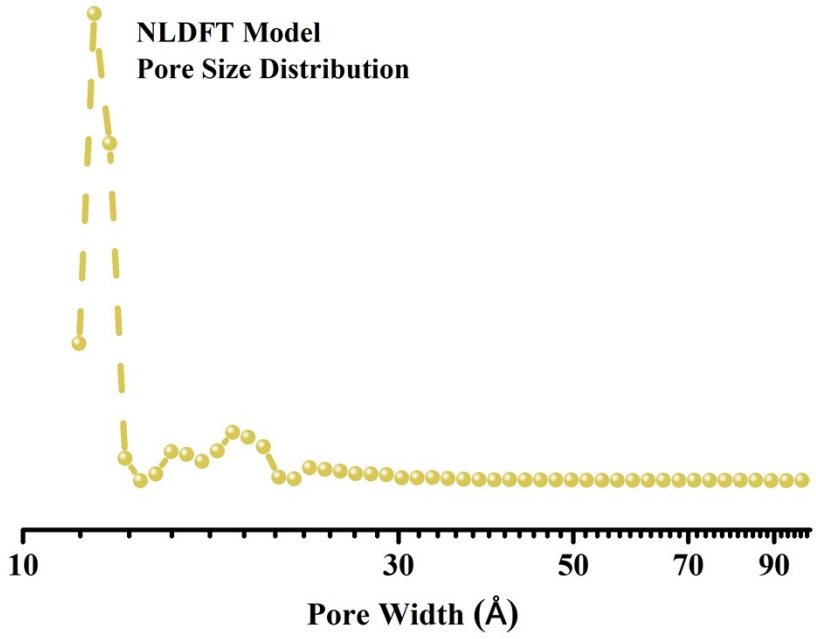


Figure S5: Thermogravimetric Analysis (TGA) of PIM-1 and PIM-1/BILP-101 MMMs.

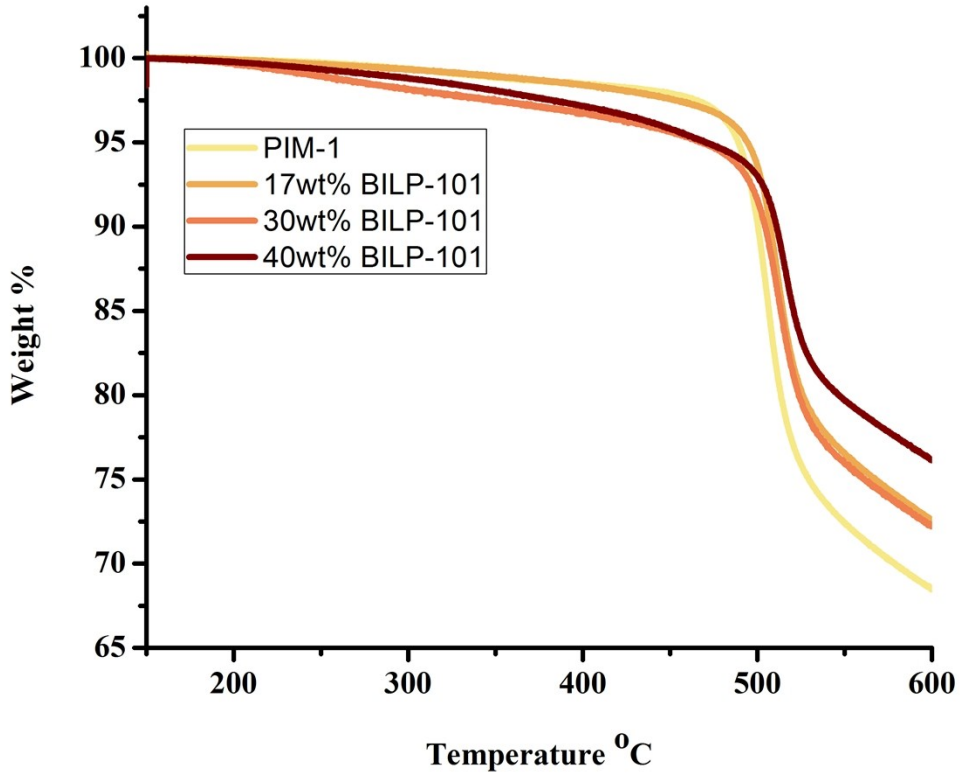


Figure S6: PXRD pattern for PIM-1 and PIM-1/BILP-101 MMMs.

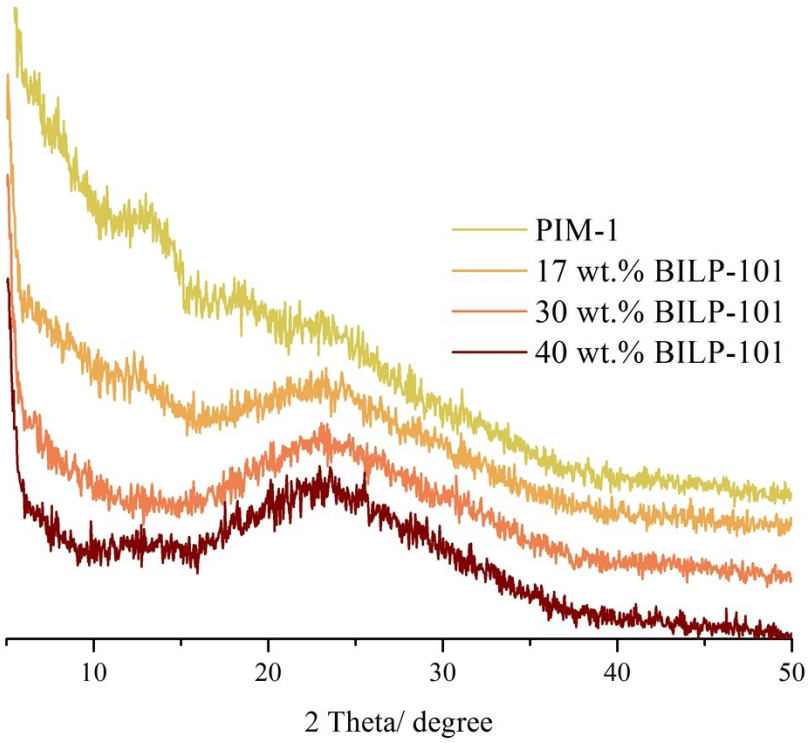
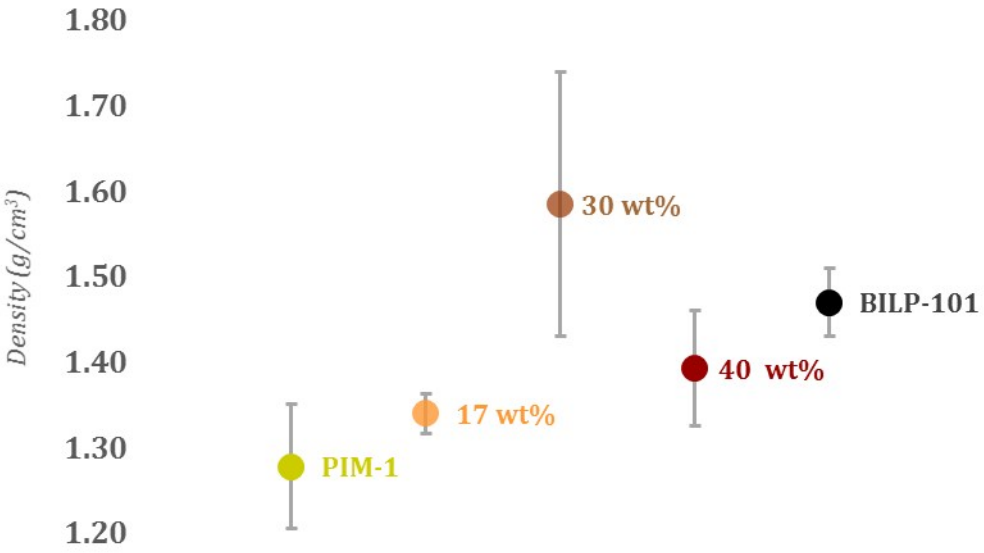
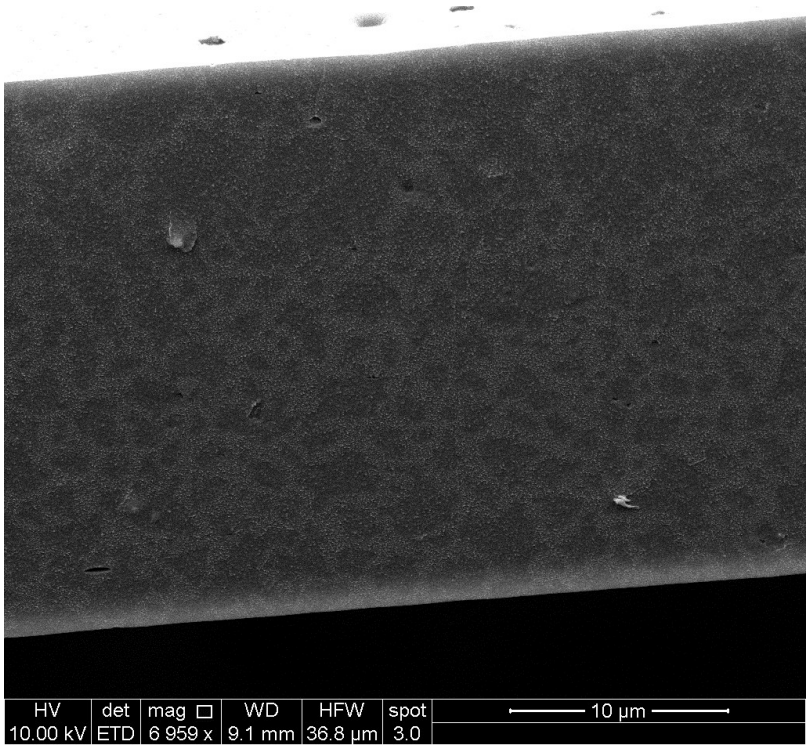


Figure S7: Density measurements for PIM-1, BILP-101 and 17, 30, and 40 wt% BILP-101 in PIM-1 collected by a Helium pycnometer.



	ρ (g/cm^3)	mass (g)	estimated uncertainty (+ 1 mg)
PIM-1	*1.28*	*0.0138*	*0.07*
17 wt%	*1.34*	*0.0426*	*0.02*
30 wt%	*1.59*	*0.0065*	*0.15*
40 wt%	*1.39*	*0.0149*	*0.07*
BILP-101	*1.47*	*0.0252*	*0.04*

Figure S8. Cross-sectional SEM images for PIM-1



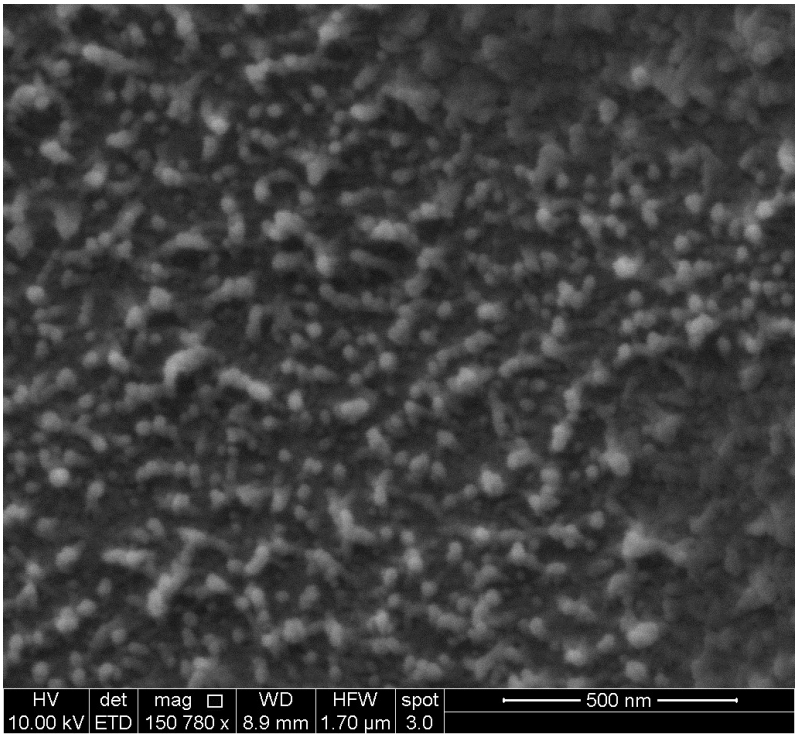
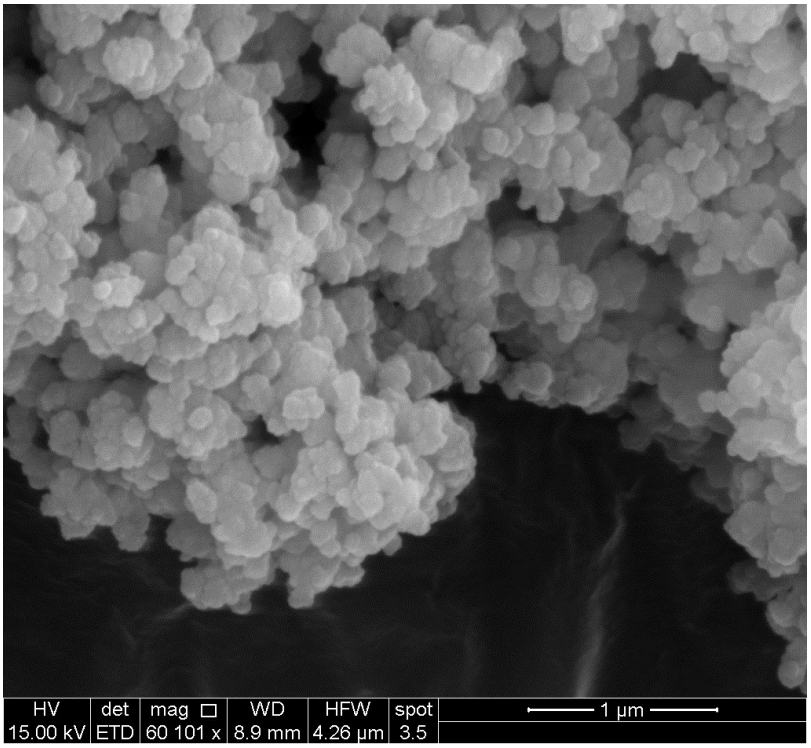
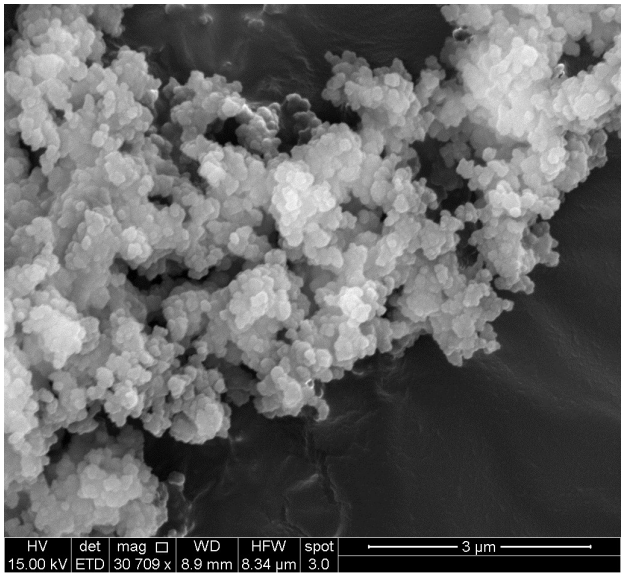


Figure S9: Cross-sectional SEM images for BILP-101





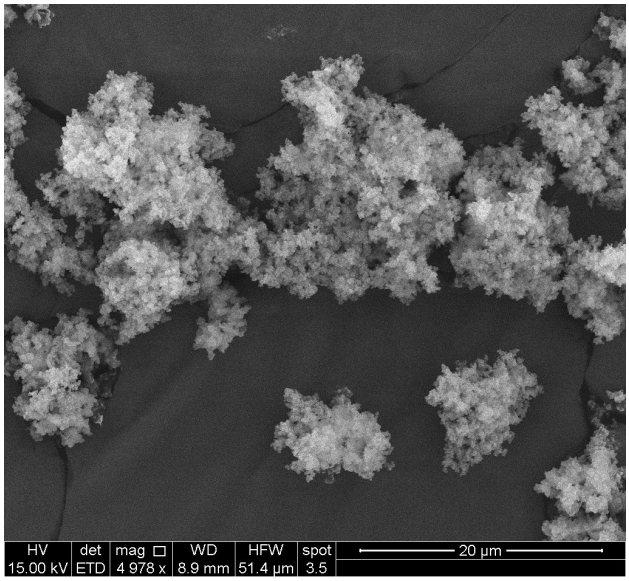
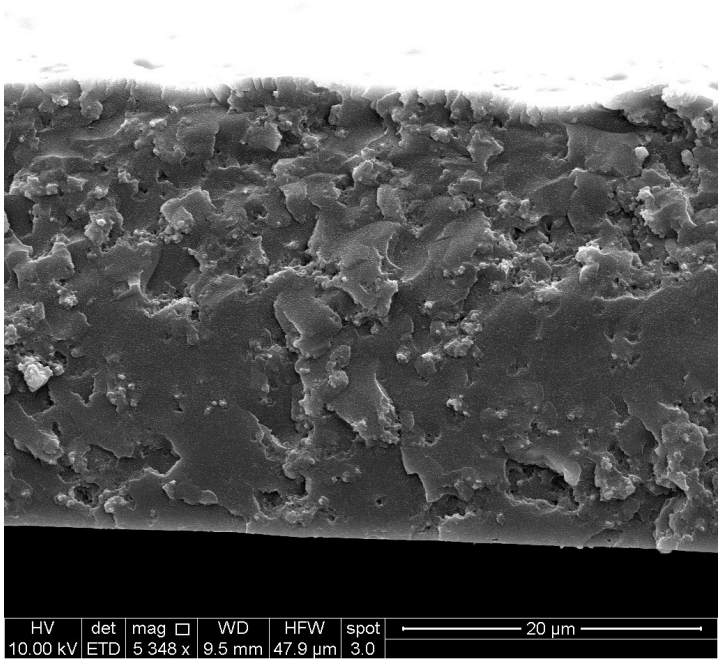


Figure S10: Cross-sectional SEM images for 17 wt% BILP-101 in PIM-1



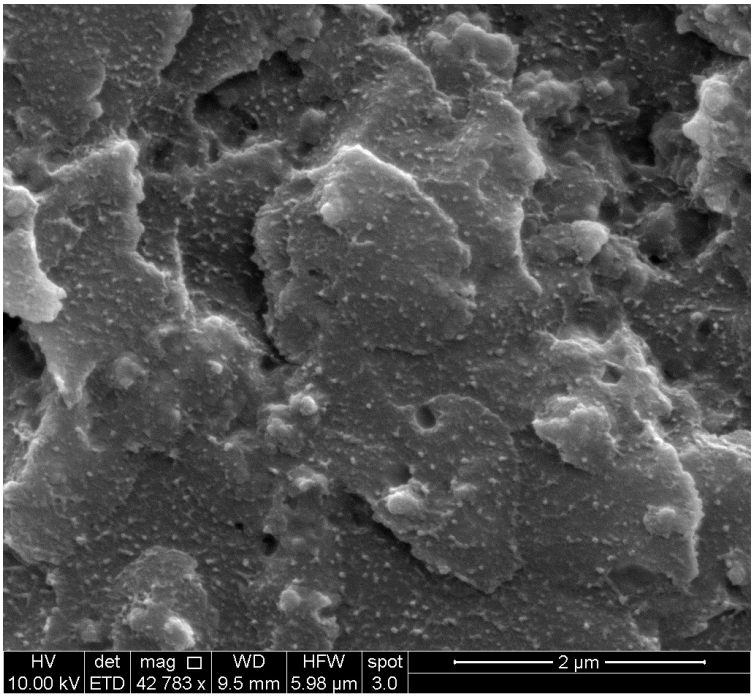
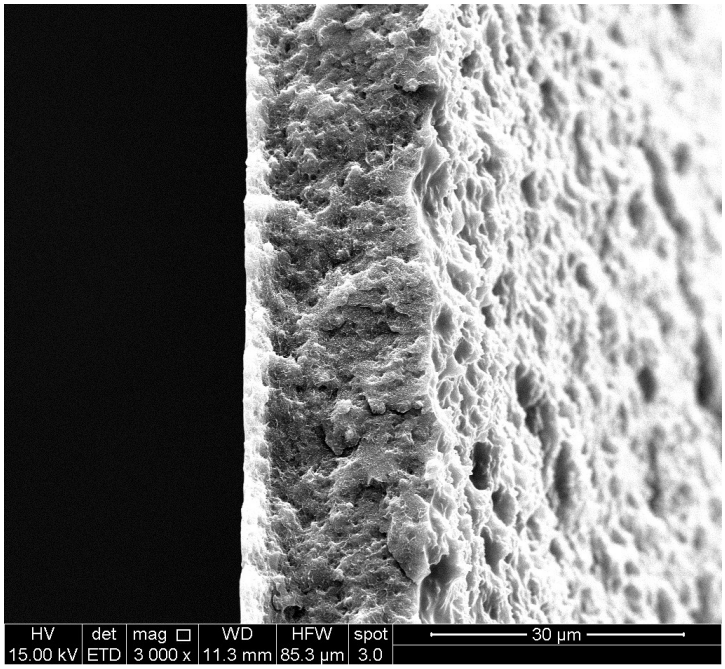


Figure S11: Cross-sectional SEM images for 30 wt% BILP-101 in PIM-1



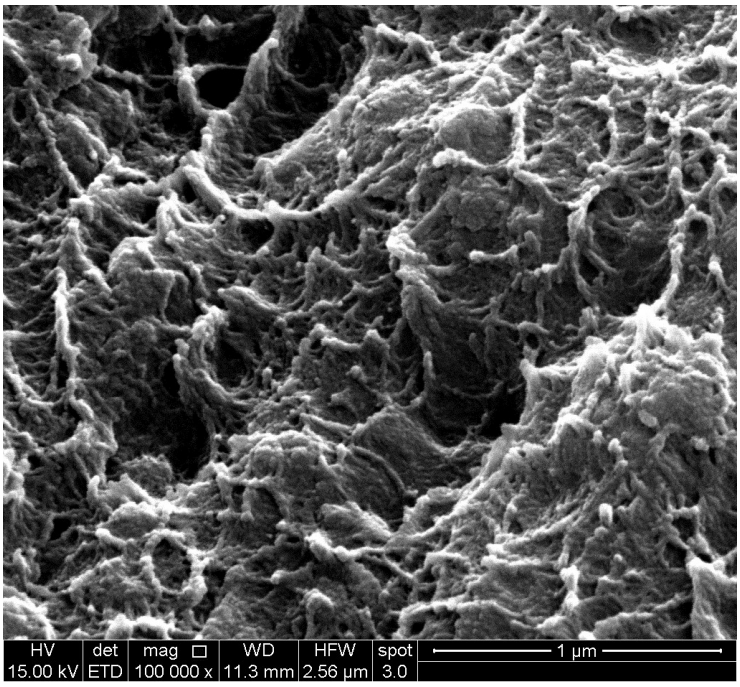
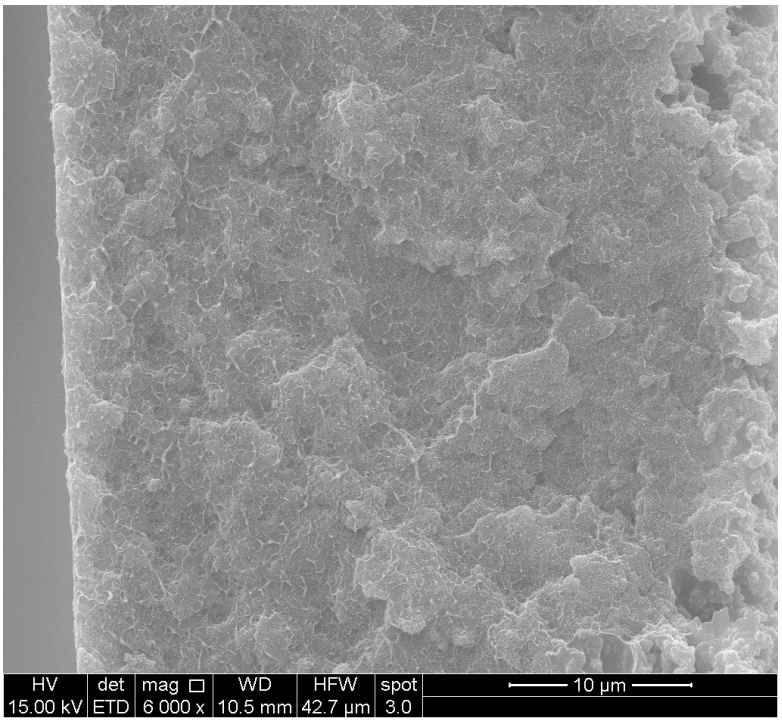


Figure S12: Cross-sectional SEM images for 40 wt% BILP-101 in PIM-1



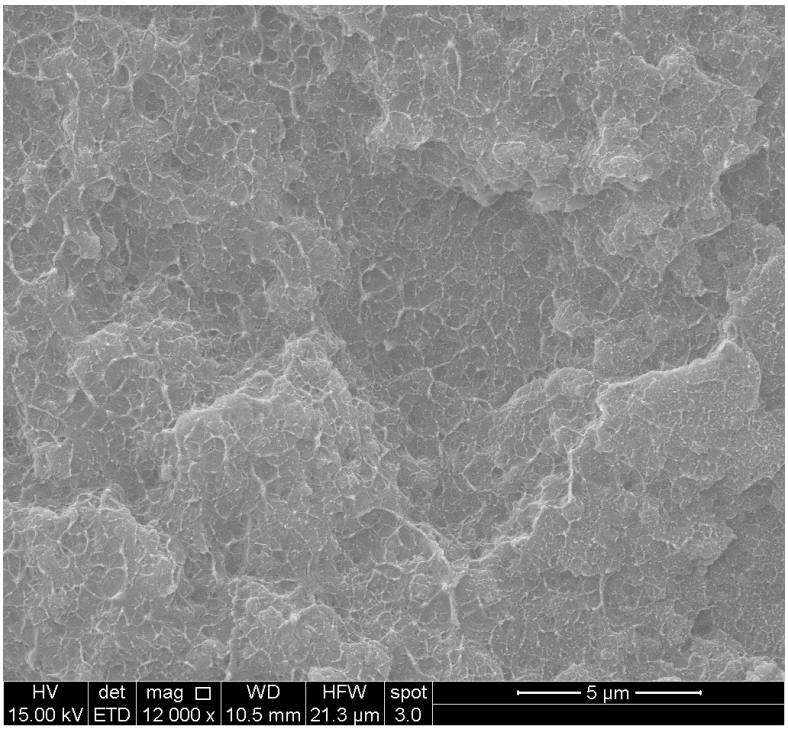


Table S1. 4 weeks aging data for 30 wt% BILP-101 in PIM-1.

30 wt% BILP-101 in PIM-1	**CO_2 permeability (Barrer)**	**CO_2/N_2 selectivity**
1 week	7200	15.3
2 week	6100	15.7
4 week	4600	16.7

References

1. A. K. Sekizkardes, J. T. Culp, T. Islamoglu, A. Marti, D. Hopkinson, C. Myers, H. M. El-Kaderi and H. B. Nulwala, *Chemical Communications*, 2015, **51**, 13393-13396.
2. P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chemical Communications*, 2004, 230-231.