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Mixed-matrix materials using metal-organic polyhedra with enhanced compatibility for membrane gas separation

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Synthesis of PdMOP precursors

$PdbpyCl_2$ was synthesized following a previously published procedure.[1] 1.773 g (10.0 mmol) $PdCl_2$ and 100 mL CH_3CN were mixed and heated to 70°C for an hour. The hot solution was filtered into a 500-mL round bottom flask with 1.562 g (10.0 mmol) 2,2'-bpy in 200 mL CH_3CN, then stirred overnight. The orange needle-like solid product was isolated (19.80 g, 83% yield) and washed with CH_3CN and $(CH_3)_2CO$. ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ (ppm) = 9.14 (d, 2H, ^3J = 6.6 Hz, 3,3'-pyridine), 8.58 (d, 2H, ^3J = 7.9 Hz, 6,6'-pyridine), 8.36 (t, 2H, ^3J = 8.6 Hz, 4,4'-pyridine), 7.81 (t, 2H, ^3J = 7.3 Hz, 5,5'-pyridine).

$Pdbpy(ONO_2)_2$ was synthesized using a previously published procedure.[1] 1.00 g (3.00 mmol) $PdbpyCl_2$ in 280 mL 1 M HNO_3 was heated to 70°C. Then 0.509 g (3.00 mmol) $AgNO_3$ dissolved in minimal amount of H_2O was added to the mixture and stirred overnight. White AgCl solid precipitated immediately upon addition of $AgNO_3$. The mixture was centrifuged, decanted, and filtered to remove the white solid. The crude product was isolated by solvent removal in vacuo. This solid was washed with 50-mL portions of CH_3CN at least three times then dissolved in H_2O. The pure yellow powder product was isolated (1.16 g) at quantitative yield after solvent removal in vacuo. ^{1}H NMR (400 MHz, D_2O, 25°C): δ (ppm) = 8.36 (td, 2H, ^3J = 8.1 Hz, 3,3'-pyridine), 8.31 (m, 2H, 6,6'-pyridine), 8.27 (m, 2H, 4,4'-pyridine), 7.74 (ddd, 2H, ^3J = 7.5, 5.9, 1.7 Hz, 5,5'-pyridine).

TPT preparation was adapted from a previously published procedure.[2, 3] 1.0 g (3.8 mmol) 18-crown-6 and 0.225 g (4.0 mmol) KOH were dissolved in 5 mL CH_3OH with stirring for 10 min. The solution was concentrated to remove CH_3OH in a hood. To this oil, 10 g (96 mmol) of 4-cyanopyridine was added. The mixture was transferred into a 25 mL Teflon-lined stainless steel reactor and heated at 200°C for 7 h. After cooling to room temperature, the brown solid was washed with 50-mL portions of hot pyridine three times to give a white solid. The white solid was dissolved in 50 mL dilute HCl, reprecipitated with aqueous NH_3, filtered, washed with 50 mL portions of CH_3CN at least three times, then dried in a vacuum oven at 80°C overnight to afford 25% yield (2.5 g). ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C): δ (ppm) = 8.93 (d, 6H, ^3J = 5.3 Hz, pyridine H^{α}), 8.60 (d, 6H, ^3J = 5.8 Hz, pyridine H^{β}).

^{1}H Nuclear Magnetic Resonance spectra of MOPs

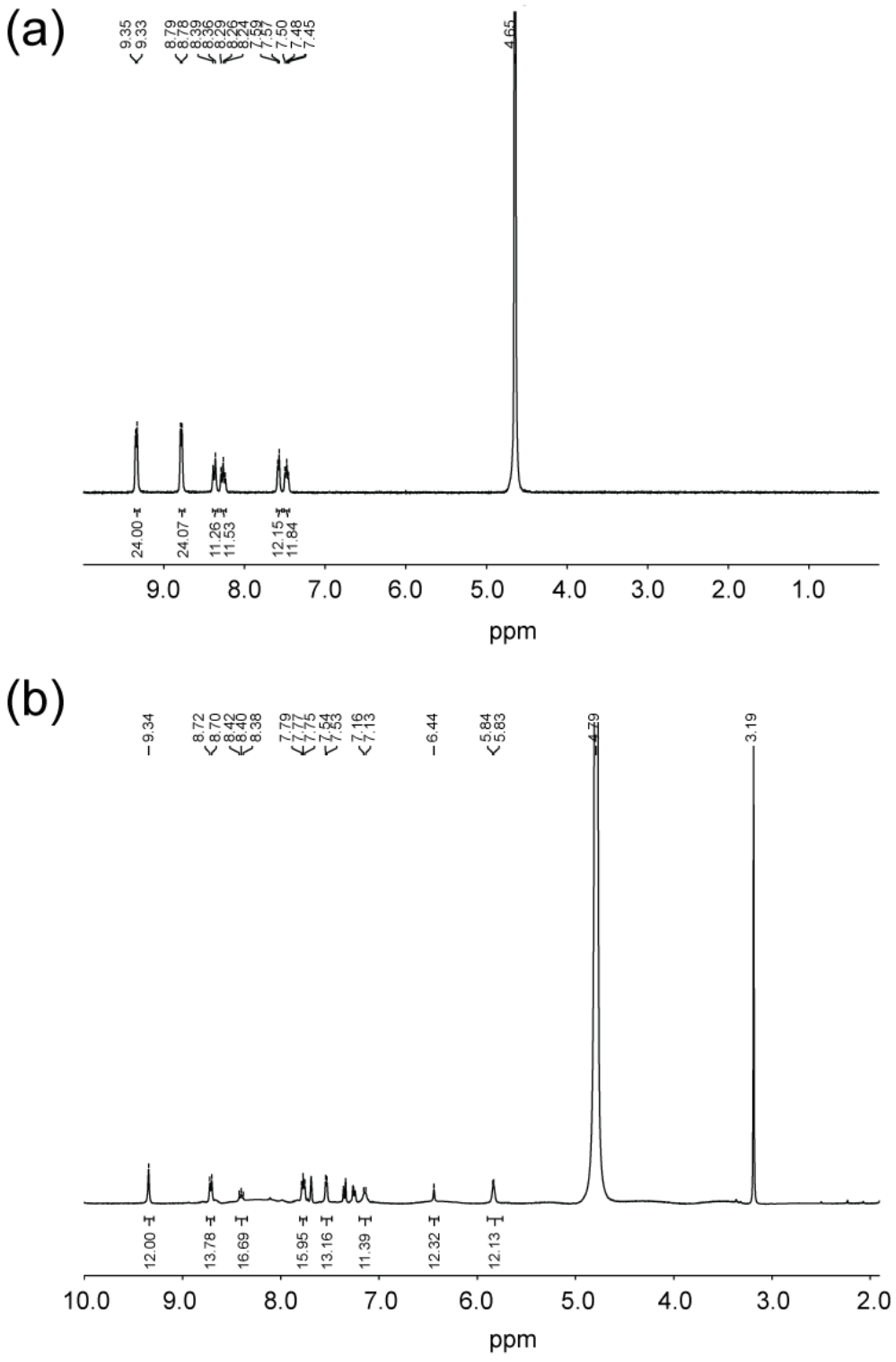

Figure S1. ^{1}H NMR spectra of (a) **PdMOP** in D_2O and (b) **FeMOP** in DMSO-d_6.

Optical microscope images of the mixed-matrix membranes

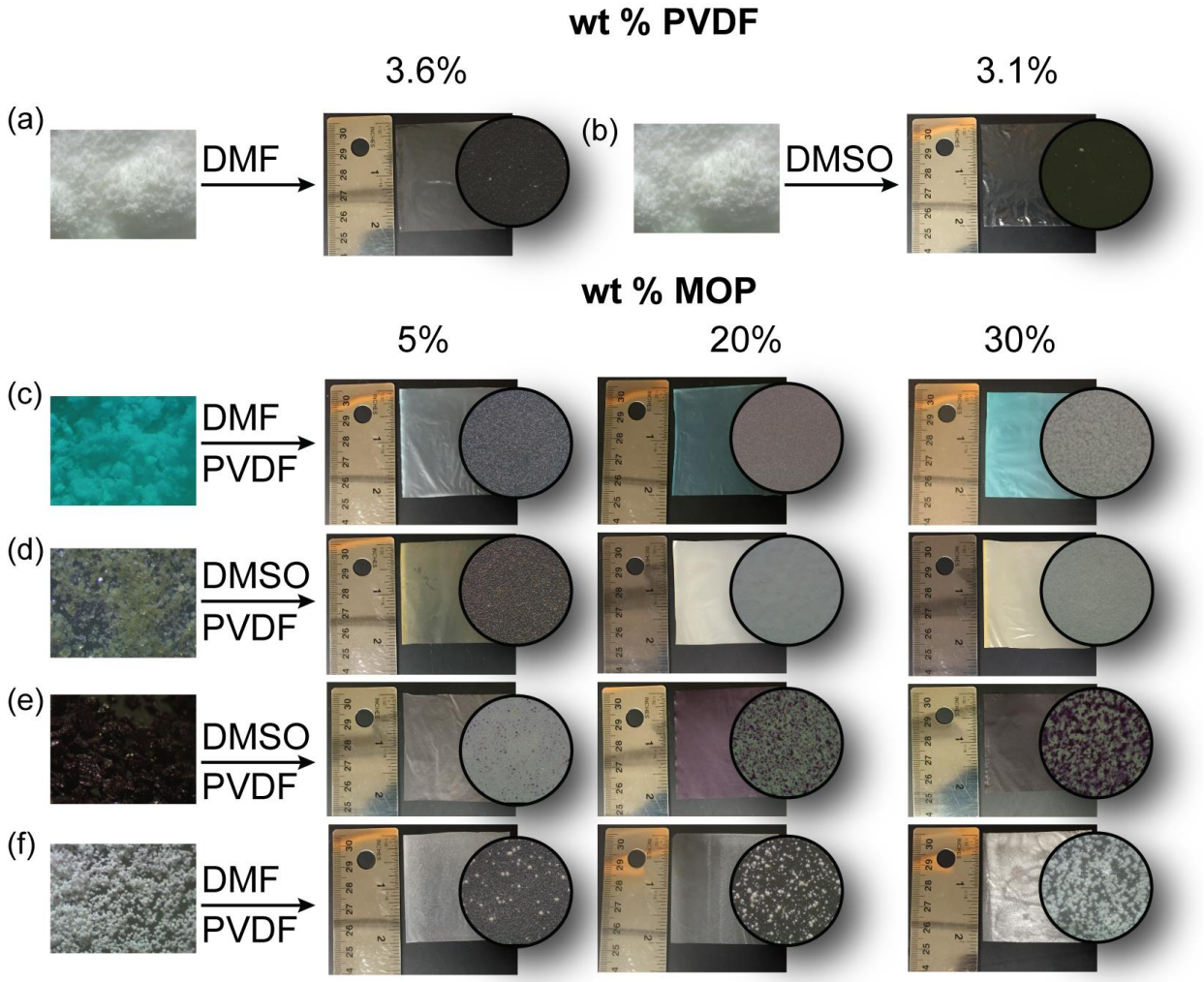

Figure S2. Optical microscope images at 5.0 magnification of polymer and MOP/MOF membranes: (a) PVDF in DMF; (b) PVDF in DMSO; (c) **CuMOP**; (d) **PdMOP**; (e) **FeMOP**; and (f) MOF-5.

Electron microscope images of the mixed matrix membranes

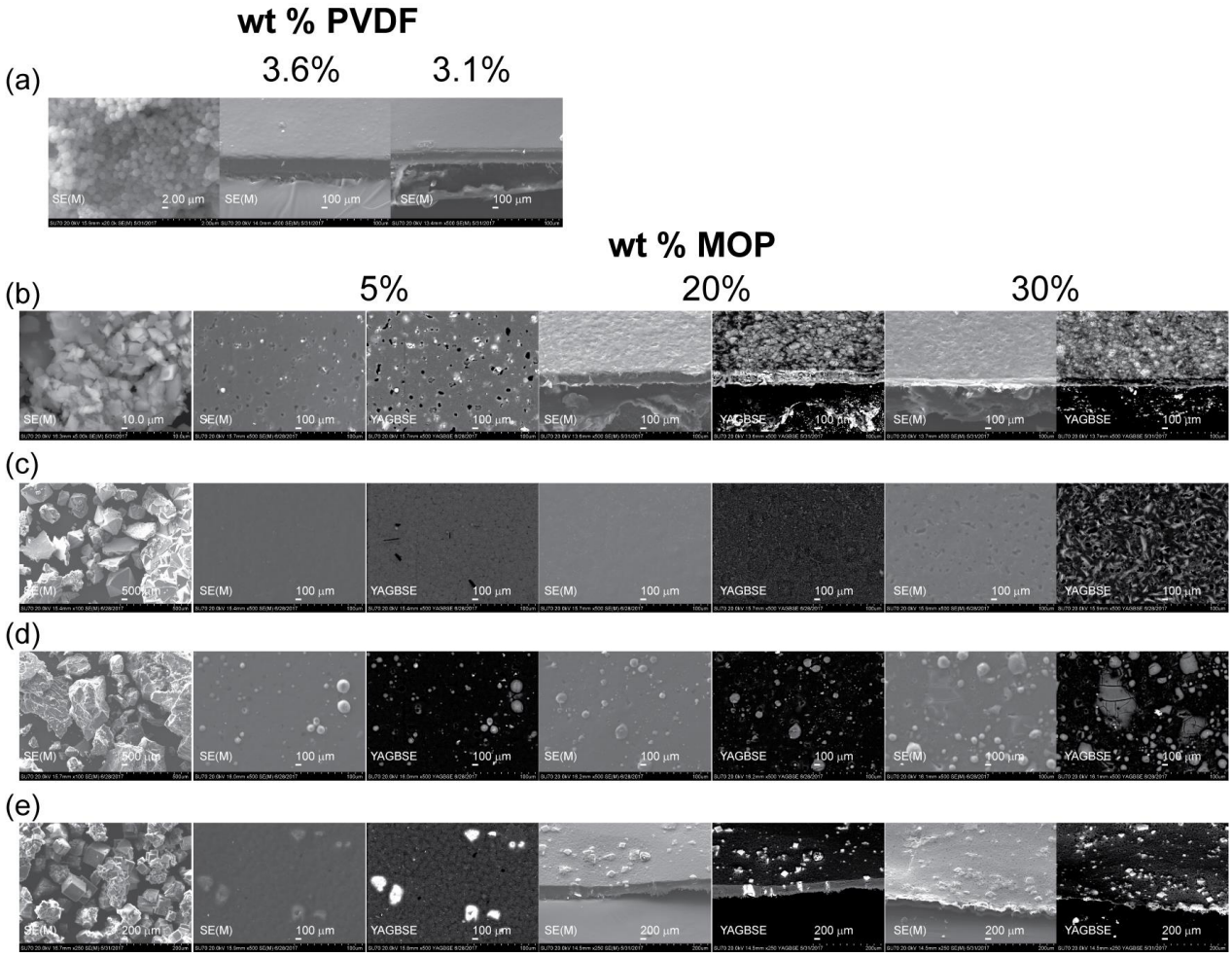

Figure S3. Electron microscope images: (a) SEM of PVDF powder and membranes in DMF and DMSO; (b) SEM/YAGBSE of **CuMOP** powder and membrane; (c) SEM/YAGBSE of **PdMOP** powder and membrane; (d) SEM/YAGBSE of **FeMOP** powder and membrane; and (e) SEM/YAGBSE of MOF-5 powder and membrane.

UV-Vis Spectra of MOPs and MOF-5 in their respective solvents

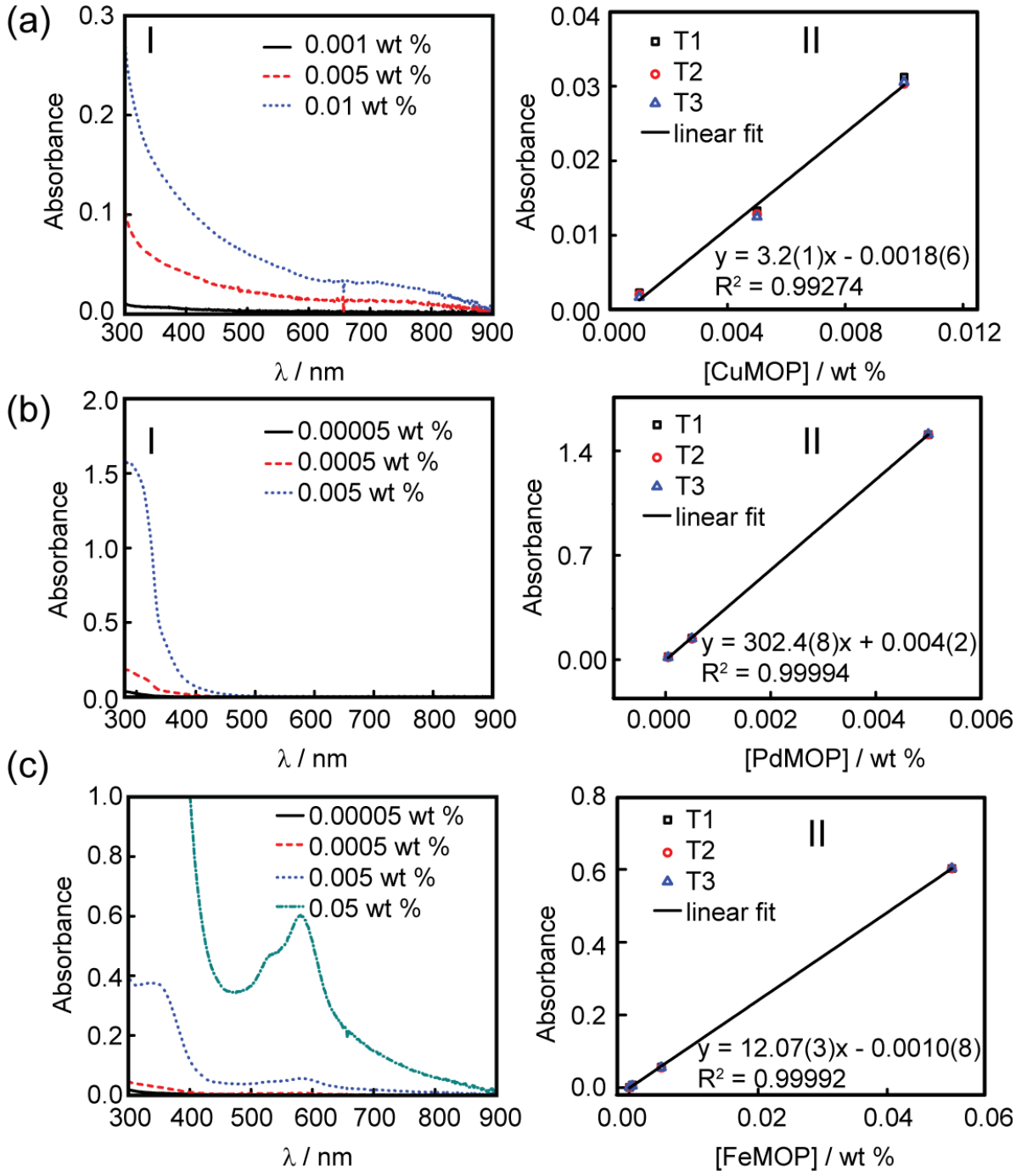

Figure S4. (I) UV-Vis spectra and (II) calibration curves for solubility determination of (a) **CuMOP** in DMF; (b) **PdMOP** in DMSO; and (c) **FeMOP** in DMSO.

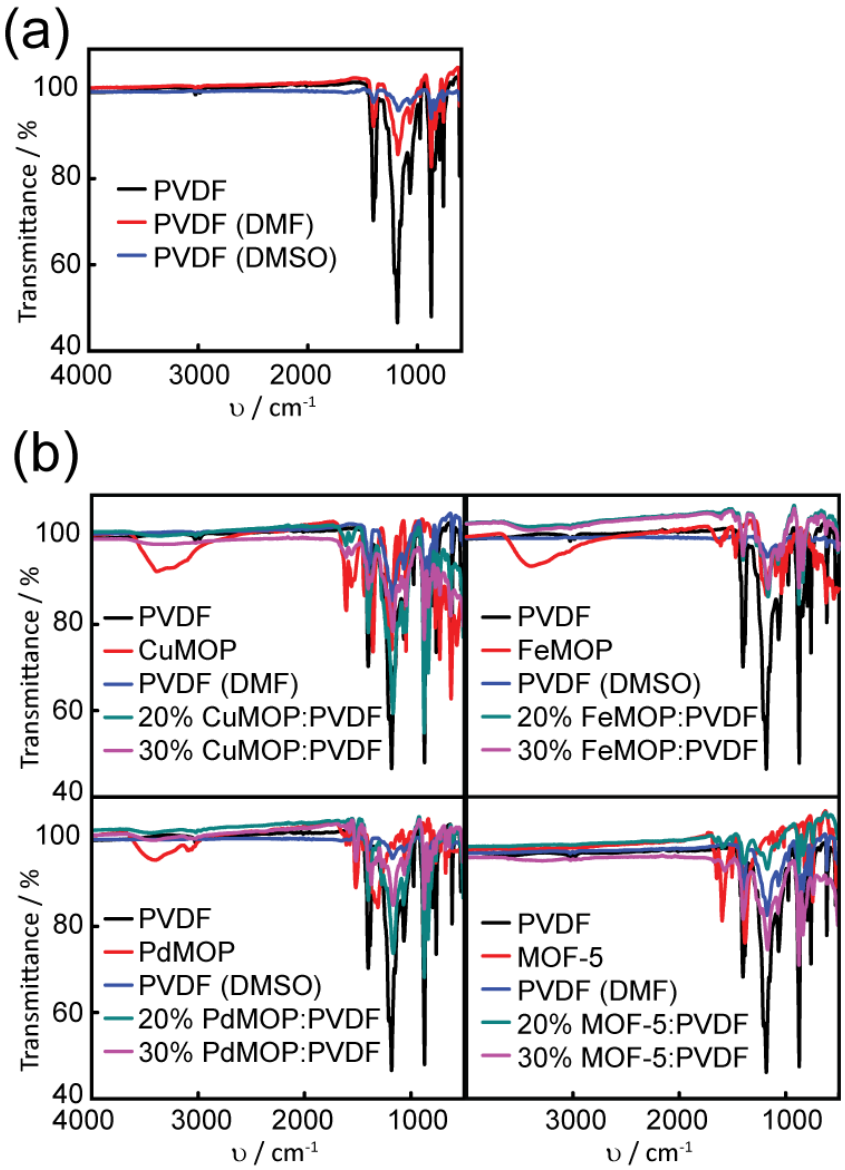

Figure S5. FT-IR spectra of (a) PVDF powder and membranes and (b) filler powders and membranes (**CuMOP**, **PdMOP**, **FeMOP**, and MOF-5).

Summary of Powder X-ray diffraction peaks from diffractograms of PVDF and MOP/MOF

Table S1. Values of 2θ and respective d spacing observed in the diffractograms of PVDF powder and membranes

Material	2θ	*d*, Å	PVDF phase
	18.34	4.833	
PVDF powder	19.90	4.459	α
	26.80	3.324	
	18.61	4.763	
PVDF film (DMF)	19.99	4.437	α
	26.48	3.363	
PVDF film (DMSO)	20.59	4.311	β

Table S2. Values of 2θ and respective d spacing observed in the diffractograms of **CuMOP** powder and membrane

Material	2θ	*d*, Å	PVDF phase
CuMOP powder	11.03	8.018	-
	11.82	7.484	
	12.67	6.984	
	13.51	6.549	
	15.37	5.760	
	16.92	5.236	
	18.43	4.811	
	18.99	4.669	
	19.51	4.547	
	20.32	4.366	
	21.38	4.153	
	23.60	3.766	
	24.22	3.672	
	26.18	3.401	
	29.55	3.020	
	30.37	2.941	
CuMOP film (20 wt %)	20.62	4.304	β

Table S3. Values of 2θ and respective d spacing observed in the diffractograms of **FeMOP** powder and membrane

Material	2θ	*d*, Å	PVDF phase
FeMOP powder	9.48	9.321	-
	10.49	8.426	
	16.07	5.509	
	23.56	3.772	
FeMOP film (20 wt %)	20.49	4.331	β

Table S4. Values of 2θ and respective d spacing observed in the diffractograms of **PdMOP** powder and membrane

Material	2θ	*d*, Å	PVDF phase
PdMOP powder	9.96	8.876	-
	14.25	6.210	
	23.59	3.769	
	27.84	3.202	
PdMOP film (20 wt %)	20.61	4.306	β

Table S5. Values of 2θ and respective d spacing observed in the diffractograms of MOF-5 powder and membrane

Material	2θ	*d*, Å	PVDF phase
MOF-5 powder	5.84	15.132	-
	6.80	12.982	
	8.79	10.054	
	9.52	9.282	
	9.75	9.064	
	11.34	7.800	
	12.11	7.304	
	13.67	6.470	
	14.67	6.035	
	15.42	5.743	
	16.66	5.316	
	17.64	5.024	
	17.95	4.938	
	18.51	4.789	
	19.15	4.632	
	20.04	4.428	
	20.59	4.310	
	22.40	3.965	
	23.17	3.836	
	24.24	3.668	
	24.56	3.621	
	24.92	3.569	
	25.54	3.485	
	26.48	3.364	
	28.88	3.089	
	29.69	3.006	
	31.23	2.862	
	31.62	2.827	
	32.15	2.782	
	32.74	2.733	
	34.70	2.583	
MOF-5 film (20 wt %)	8.82	10.014	β
	20.12	4.410	

References

1. S. Wimmer, P. Castan, F. L. Wimmer and N. P. Johnson, *J. Chem. Soc., Dalton Trans.*, 1989, DOI: 10.1039/DT9890000403, 403-412.
2. H. L. Anderson, S. Anderson and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, DOI: 10.1039/P19950002231, 2231-2245.
3. M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang and S.-R. Zhu, *Inorg. Chem.*, 2008, **47**, 4481-4489.