

Efficient CO₂ capture by metallo-supramolecular polymers as fillers to fabricate polymeric blend membrane

Liangliang Dong,^a Yuping Sun ^a, Chunfang Zhang^{*a}, Dan Han ^a, Yunxiang Bai ^a and
Mingqing Chen^{*a}

^aThe Key Laboratory of Food Colloids and Biotechnology, Ministry of Education,
School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122,

Jiangsu, China

* Corresponding author: E-mail address: mqchen@jiangnan.edu.cn, Fax: +86-510-85917763; Tel: +86-510-85917019; E-mail address: zcf326@163.com, Fax: +86-510-85917763; Tel: +86 510-85917090.

Materials and Methods: The PEBA (grade 2533) copolymer (comprise 80 wt% of poly(tetramethylene oxide) [PTMO] and 20 wt% Nylon-12[PA12]) was supplied by Arkema. The PEO-PPO-PEO triblock copolymer was purchased from Aldrich and has the average composition EO₁₀₀PO₆₅EO₁₀₀. 4'-chloro-2,2':6',2"-terpyridine (97%) was purchased from Sun Chemical Technology (shanghai) Co. Ltd. CO₂ and N₂ were supplied by Wuxi Xinnan Chemical Gas Co. Ltd., China, and were of at least 99.99 % purity. Gases were used without further purification. All other reagents were of analytical grade and used without further purification. ¹H-NMR spectra were recorded on a BUKER 400 MHz in CDCl₃ using the residual solvent peak as reference. FTIR measurements were characterized by a FTLA 2000 type Fourier transform infrared (FT-IR) spectrometer. UV-Vis spectrum was recorded on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.). SEM and EDAX images were obtained with a Hitachi S4800 equipped with an EDAX system (Octane Super). DSC curves of were obtained through a Perkin-Elmer (DSC 8000). TGA measurements were examined with a METTLER 1/1100SF Thermogravimetric analyzer (TGA). Mechanical properties were performed at room temperature using an electronic universal testing machine (Shenzhen, China) with a crosshead speed of 10 mm/min.

1 Experimental Procedures

1.1 Synthesis of F127-Tpy

The synthesis was carried out according to a modified literature procedure.¹ 4'-chloro-2,2':6',2"-terpyridine (0.5 g, 1.87 mmol), PEO₁₀₀-PPO₆₅-PEO₁₀₀ (4.153 g, 0.78 mmol) and powdered potassium hydroxide (0.35 g, 6.22 mmol) were reacted in dry DMSO at 70 °C for 2 days. The reaction mixture was added into saturated NaCl solution and filtered. After dried, the crude product was dissolved in chloroform and then filtered. The filtrate was precipitated in *n*-hexane twice, and the product was obtained as a pale yellow gel.

1.2 General procedure for the synthesis of F127-Tpy-M

The F127-Tpy and the metal salt (Zn(CH₃COO)₂·2H₂O, Co(CH₃COO)₂·4H₂O, FeCl₃·6H₂O and CuCl₂·2H₂O) in a molar ratio of 2:1 were dissolved in 5 mL of MeOH and stirred for 4 hours under refluxing. The reaction mixture was dried under vacuum, and the dark color product was isolated obtained.

1.3 Preparation of blend membranes

PEBA2533 was dissolved at a concentration of 10 wt% in *n*-butanol for 3 h at 353 K. Different amounts of F127-Tpy were added to the polymer solutions and dissolved instantaneously. The solutions were then stirred for another 1 h to ensure homogeneous mixtures.

Membranes were prepared by controlled solvent evaporation of the above-mentioned solutions. The polymer solutions were cast onto clean Teflon plates and dried at room temperature for at least 48 hours under a fume hood. In order to guarantee complete removal of *n*-butanol, they were further dried at vacuum drying oven at 40 °C for another 12 h. The obtained blend membranes were designated as PEBA2533/X-Y, where X is F127, F127-Tpy and F127-Tpy-M, Y is the wt% of F127, F127-Tpy and F127-Tpy-M out of the mass of PEBA2533. The thickness of prepared membranes was about 100-110 μm.

2 Characterization techniques and results

2.1 FTIR analysis

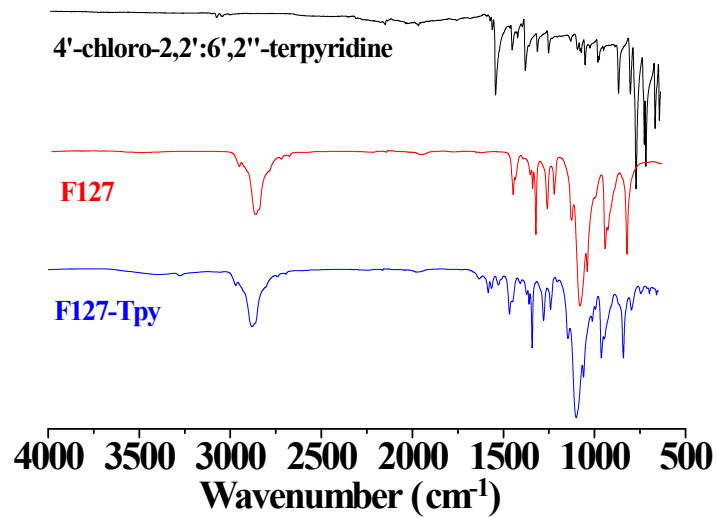


Fig.S1 FTIR spectra of F127, F127-Tpy and 4'-chloro-2,2':6',2''-terpyridine

2.2 ¹H NMR analysis

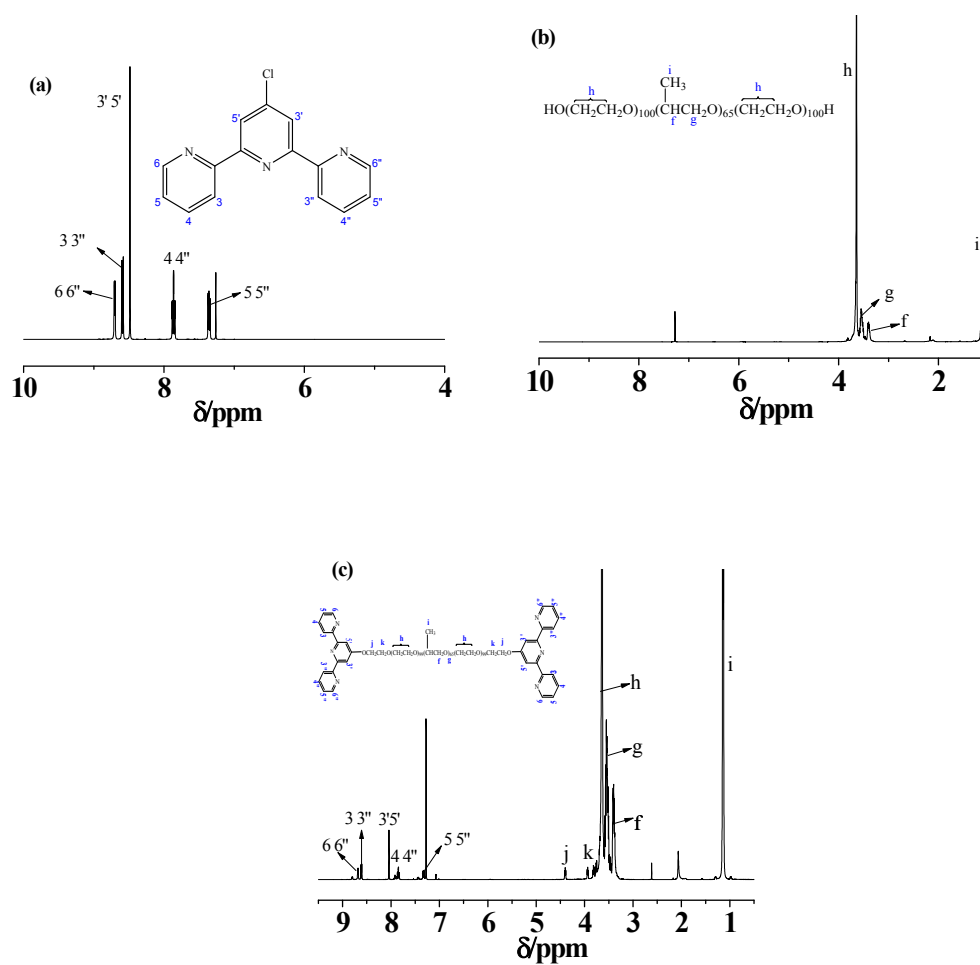


Fig.S2 ¹H NMR spectra of 4'-chloro-2,2':6',2''-terpyridine (a), F127 (b) and F127-Tpy (c)

2.3 FTIR analysis

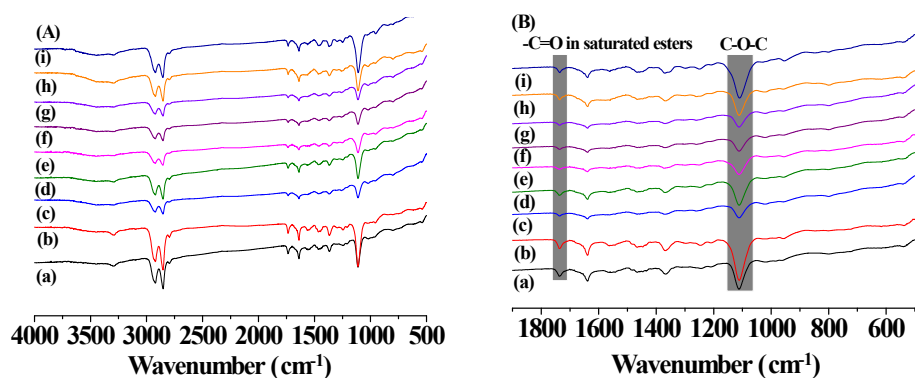


Fig.S3 (A),(B)FTIR spectra of PEBA2533/F127-Tpy-M blend membranes ((a) PEBA2533, (b) PEBA2533/F127-Tpy-Co-30, (c) PEBA2533/F127-Tpy-Co-80, (d) PEBA2533/F127-Tpy-Fe-30, (e) PEBA2533/F127-Tpy-Fe-80, (f) PEBA2533/F127-Tpy-Cu-30, (g) PEBA2533/F127-Tpy-Cu-80, (h) PEBA2533/F127-Tpy-Zn-30, (i) PEBA2533/F127-Tpy-Zn-80)

2.4 SEM and EDAX analysis

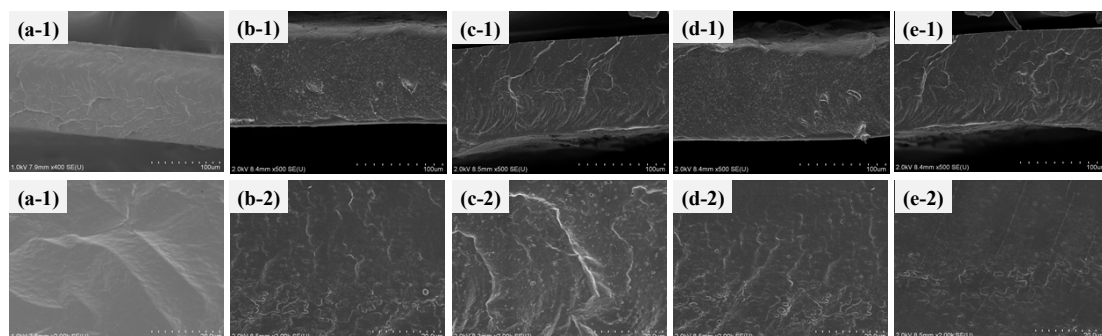


Fig. S4 SEM images of the cross section of PEBA2533 and PEBA2533/F127-Tpy-M membranes (a): PEBA2533; (b) PEBA2533/F127-Tpy-Co-60 membranes; (c) PEBA2533/ F127-Tpy-Fe-60 membranes; (d) F127-Tpy-Cu-60 membranes; (e) F127-Tpy-Zn-60 membranes

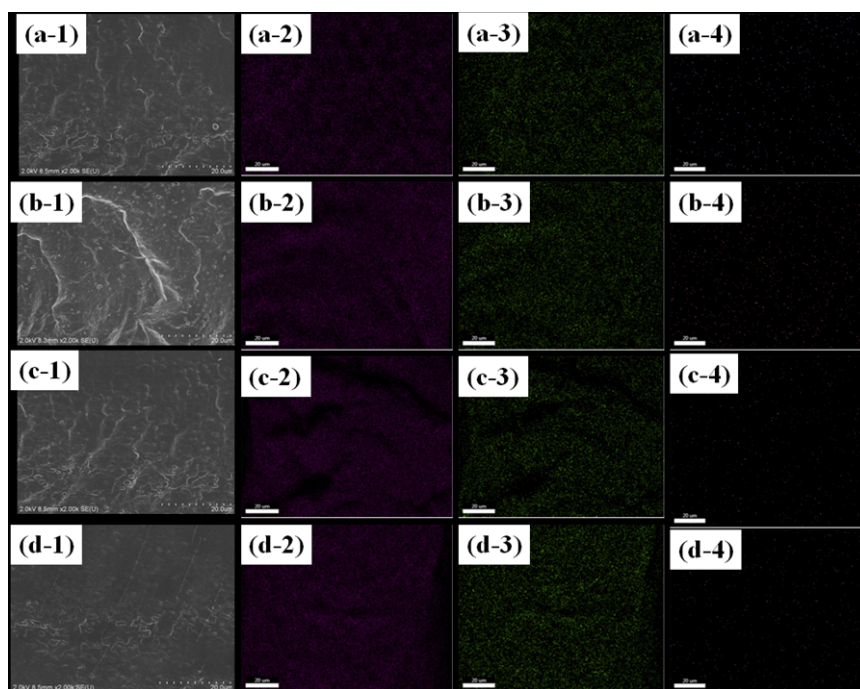
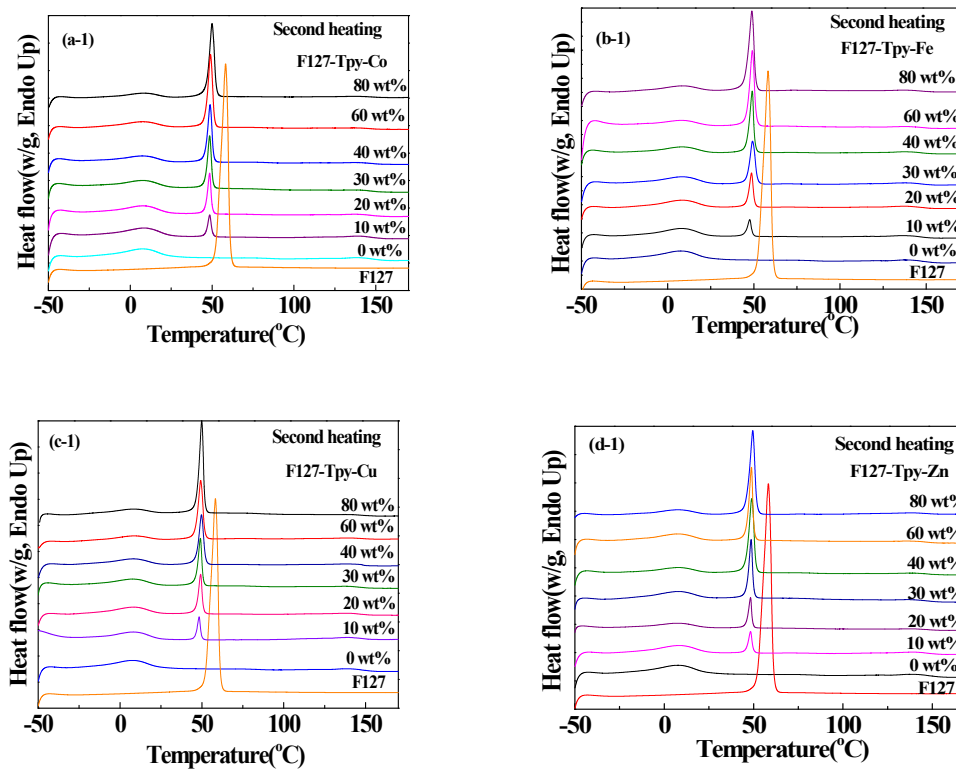


Fig.S5 EDAX mapping of PEBA2533/F127-Tpy-M-60 membranes.(a-2~d-2) C signal: purple, (a-3~d-3) O signal: green, (a-4) Zn signal: dark Green, (b-4) Fe signal: brown, (c-4) Co signal: blue, (d-4) Cu signal: light green

2.5 DSC analysis



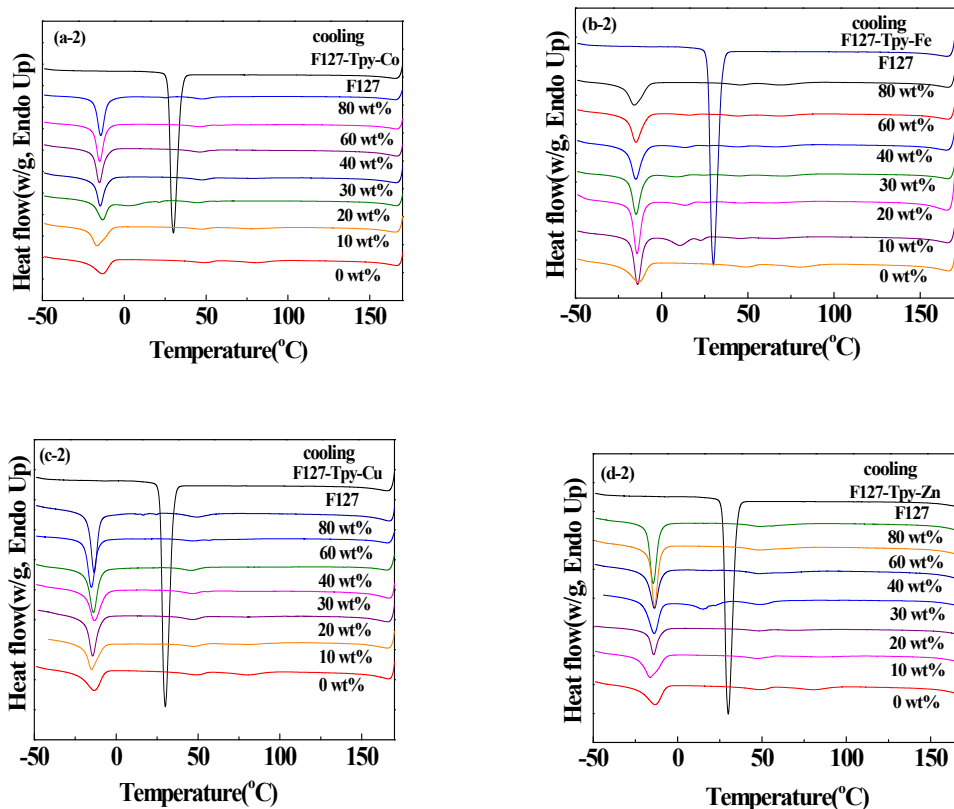


Fig. S6 DSC thermograms of the PEBA2533 and PEBA2533/F127-Tpy-M membranes; (a): PEBA2533 and PEBA2533/F127-Tpy-Co membranes (b):PEBA2533 and PEBA2533/ F127-Tpy-Fe membranes (c): PEBA2533 and PEBA2533/ F127-Tpy-Cu membranes (d): PEBA2533/F127-Tpy-Zn membranes

The low temperature melting point, T_m (PTMO), is ascribed to melting of crystals of the polyether blocks and occurs about 0-20 °C. The high temperature melting point, T_m (PA), is attributed to melting of polyamide crystals and exists approximately 140-160 °C. The melting of crystals of PEO of F127 occurs approximately 50-60 °C

Table S1 Heat of fusion (ΔH_m) and degree of crystallization (f_c) of PEBA2533 and PEBA2533/F127-Tpy-M membranes

Sample	F127-Tpy-M content (wt%)	ΔH_m for PEO (Jg ⁻¹)	f_c (PEO) (%) ^a	ΔH_m for PA (Jg ⁻¹)	f_c (PA) (%) ^a
PEBA2533	0	N/A	N/A	6.593	13.4
F127	0	114.8	83.41	N/A	N/A
	10	7.005	55.94	5.857	13.09
	20	12.91	56.17	2.716	6.63
	30	18.01	56.65	2.012	5.32
PEBA2533/F127-Tpy-Co	40	22.36	56.81	1.587	4.52
	60	29.36	56.89	1.296	4.21
	80	34.79	56.94	1.094	3.99
	10	5.298	42.30	4.493	10.05
	20	11.77	51.21	3.712	9.06
	30	16.91	53.16	3.265	8.63
	40	21.37	54.29	2.890	8.23
	60	29.76	57.67	2.082	6.77
PEBA2533/F127-Tpy-Fe	80	35.51	58.11	1.794	6.56
	10	6.983	55.76	5.429	12.14
	20	12.92	56.22	4.593	11.21
	30	17.99	56.59	4.059	10.73
	40	22.33	56.73	2.741	7.79
	60	29.39	56.95	1.838	5.98
PEBA2533/F127-Tpy-Cu	80	35.06	57.38	1.552	5.67
	10	6.595	52.66	5.970	13.35
	20	12.25	53.30	3.542	8.64
	30	17.69	55.65	3.001	7.93
	40	22.23	56.48	2.316	6.59
	60	29.39	56.95	1.529	4.97
PEBA2533/F127-Tpy-Zn	80	34.97	57.23	1.081	3.95

^a Degree of crystallinity was calculated by using Eq.(1), the final crystallinity is normalized by PEO or PA weight fractions.

$$f_c = \frac{\Delta H_m^0}{w\Delta H_m} \dots\dots\dots (1)$$

where ΔH_m is the enthalpy of formation of the crystalline PEO or PA phase (J/g), ΔH_m^0 is the enthalpy of formation of the pure crystal (for PEO 196.6 J/g² and for PA 246 J/g³), and w is the weight percent PEO or PA present in the blend.

2.6 TGA analysis

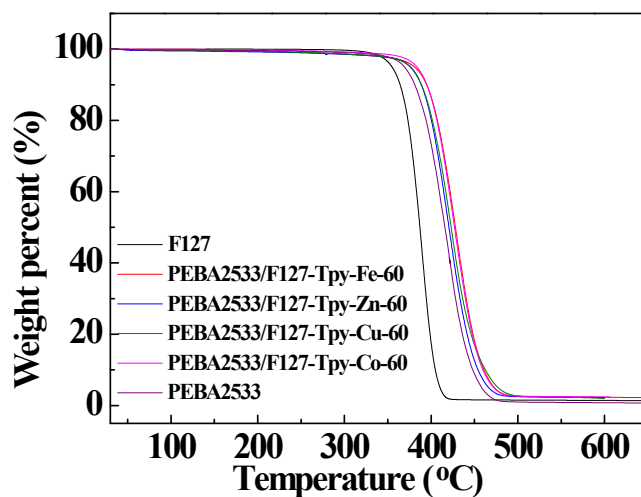


Fig. S7 TGA curves of F127, PEBA2533 and PEBA2533/F127-Tpy-M-60 membranes

2.7 Mechanical properties

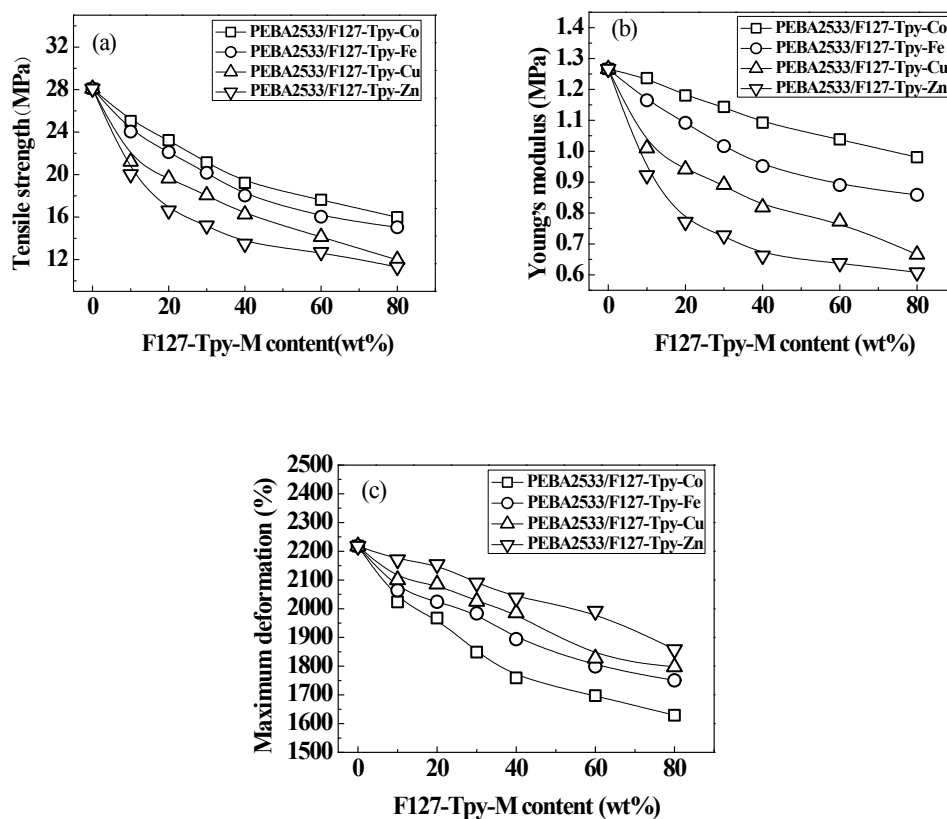


Fig. S8 Effect of F127-Tpy-M content on mechanical properties of PEBA2533/F127-Tpy-M membranes ((a) Tensile strength; (b) Young's modulus; (c) Maximum deformation)

2.8 Gas permeation experiments

Gas permeability experiments were evaluated for CO₂, N₂, O₂ and H₂ using the constant pressure/variable volume method at room temperature (25 °C). Fig. S9 shows the schematic representation of the gas permeation equipment. A circular sample with 13.80 cm² effective areas (*A*) was cut from membranes samples and placed in the stainless steel membrane module. The gas permeability of membranes was calculated by solution-diffusion mechanism^{4,5} as follows.

$$P = \frac{F}{A * \Delta p / L} \quad (2)$$

where *F* is the flux (cm³(STP)/min), *L* is membrane thickness (cm), *A* is the membrane effective area (cm²), Δ*P* is the pressure difference of membranes on both sides and *P* is permeability expressed in Barrer.

The permeability ratio for gas A and gas B which is called gas pair selectivity^{6,7}, is determined as follows.

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

where *P_A* and *P_B* are permeability of gas A and gas B, respectively. α_{*A/B*} is gas selectivity of gas A and gas B.

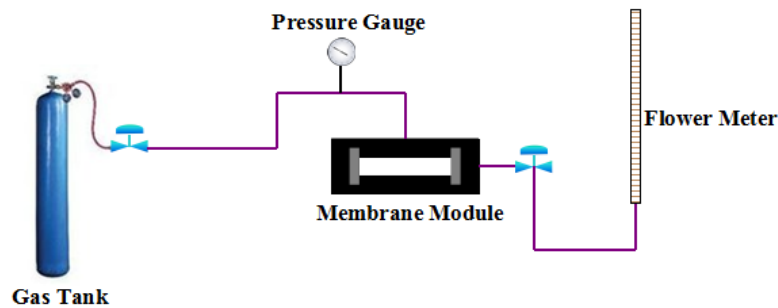


Fig. S9 Experimental apparatus for gas permeability

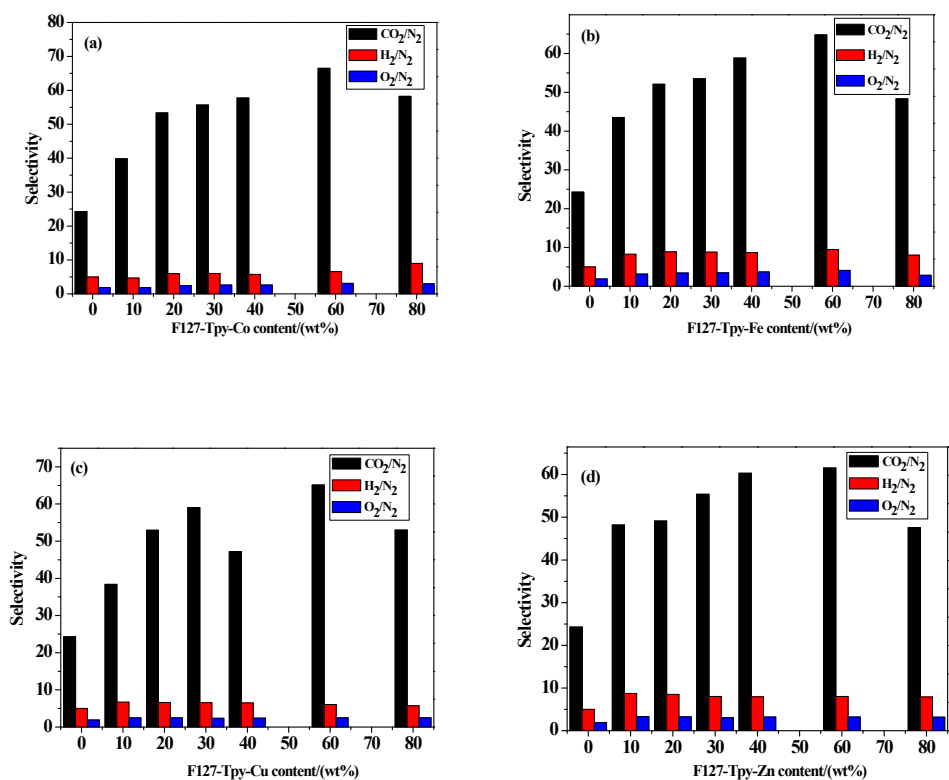


Fig. S10 CO₂/N₂, O₂/N₂ and H₂/N₂ selectivities at 298 K and 0.1 MPa: (a) PEBA2533/F127-Tpy-Co membranes, (b) PEBA2533/F127-Tpy-Fe membranes, (c) PEBA2533/F127-Tpy-Cu membranes, (d) PEBA2533/F127-Tpy-Zn membranes

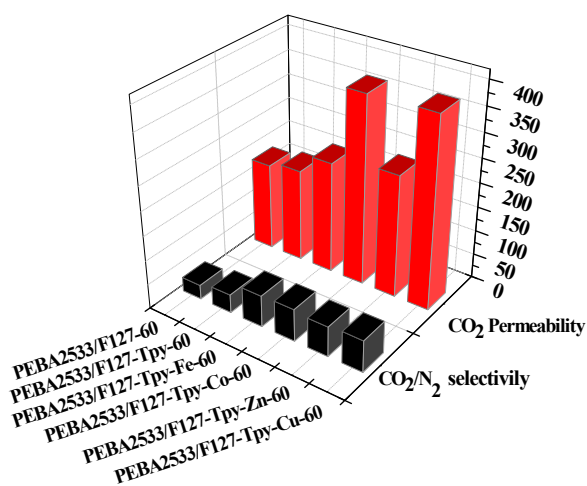
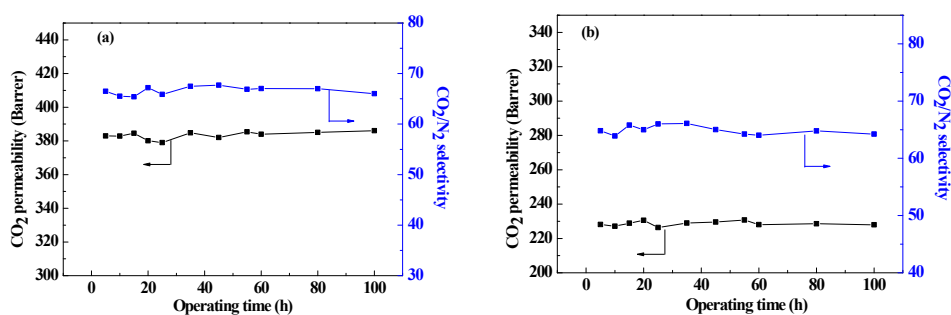


Fig. S11 CO₂ Permeability and CO₂/N₂ selectivity of PEBA2533/F127-Tpy-60, PEBA2533/F127-Tpy-M-60 and PEBA2533/F127-60

Based on above results of Fig.2, Fig.S10 and Fig.S11, we think that there are two reasons to explain the effects of metallo-supramolecular polymers on the membrane separation performances. Firstly, we hypothesized that our metallo-supramolecular polymers may be just like flexible MOFs, in which the metal ions act as gas adsorbing centers and the flexible framework of polymer chains will circumvent the powdery texture. As we all know, the MOFs are well known for gas separation. Different MOFs have different effects on gas separation due to different metal precursors and organic ligands. So specific to our study, Co^{2+} have stronger coordination ability with Tpy and gas-metal interactions than Fe^{3+} , Cu^{2+} and Zn^{2+} , facilitating Co^{2+} and F127-Tpy to form flexible MOFs and enhancing the adsorption of CO_2 . Therefore, PEBA2533/F127-Tpy-Co membranes have high CO_2 permeabilities and CO_2 /light gas selectivities. The similar phenomenon is also reported by Nasr *et al*⁸ and Maqbool *et al*⁹ who point out that different metal ions have the different gas-metal interactions to affect membrane separation performances. Secondly, as stated above, to some extent, metallo-supramolecular polymer can form layers structure through self-assembly, which has been reported by Beck *et al*³² and Schott *et al*³³. This layer structure can increase interchain space, facilitating better diffusion of gas molecules. Due to strong coordination ability and big ionic radius (0.745 Å) for Co^{2+} , effect of “chain push back” of Co^{2+} is more significant than three other metal ions, resulting in increase of distance between molecular chains, enhancing diffusion of gas molecules and then having higher gas permeabilities and gas selectivities.



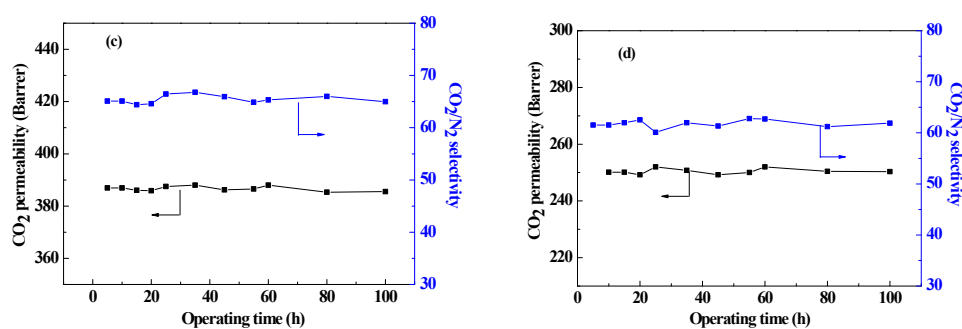


Fig. S12 Long-term gas separation performance test of the PEBA2533/F127-Tpy-M blend membranes up to 100 h at 298 K and 0.1 MPa: (a) PEBA2533/F127-Tpy-Co membranes, (b) PEBA2533/F127-Tpy-Fe membranes, (c) PEBA2533/F127-Tpy-Cu membranes, (d) PEBA2533/F127-Tpy-Zn membranes

The long-term operation stability is crucial for the industrial application of membrane. The long-term gas separation performances of the PEBA2533/F127-Tpy-M blend membranes at 60 wt % loading up to 100 h for CO₂/N₂ are shown in Fig. S12. During the entire test period, the CO₂ permeabilities and the selectivities of CO₂/N₂ keep stable, indicating a good operation stability.

References:

- 1 Y. C. Hu, K. H. Y. Chan, C. Y. S. Chung and V. W. W. Yam, *Dalton Trans.*, 2011, **40**, 12228-12234.
- 2 F. Zhang and B. Stühn, *Colloid. Polym. Sci.*, 2007, **285**, 371-379.
- 3 A. Xenopoulos and B. Wunderlich, *J. Polym. Sci., Part B: Polym. Phys.*, 1990, **28**, 2271-2290.
- 4 Y. F. Li, S. F. Wang, H. Wu, R. Guo, Y. Liu, Z. Y. Jiang, Z. Z. Tian, P. Zhang, X. Z. Cao and B. Y. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 6654-6663.
- 5 M. M. Talakesha, M. Sadegh, M. P. Chenar and A. Khosravi, *J. Membr. Sci.*, 2012, **415-416**, 469-477.
- 6 L. J. Cao, K. Tao, A. S. Huang, C. L. Kong and L. Chen, *Chem. Commun.*, 2013, **49**, 8513-8515.
- 7 C. J. Zhang, Y. L. Xiao, D. H. Liu, Q. Y. Yang and C. L. Zhong, *Chem. Commun.*, 2013, **49**, 600-602.
- 8 G. Nasr, T. Macron, A. Gilles, Z. Mouline and M. Barboiu, *Chem. Commun.*, 2012, **48**, 6 827-6829.
- 9 Q. Maqbool, A. Reddy M, S. Goswami, S. Konar and A. Srivastava, *J. Mater. Chem. A*, 2014, **2**, 2609-2615