Electronic Supplementary Information

Highly Facilitated Permeation and Oxygen Enrichment from Air through Polyvinylimidazole Membrane Ligated with Kinetically Oxygen Interacting Cobaltporphyrin

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Selection of porous support

Dense polymer membranes were attempted to be coated utilizing porous membranes of various materials and pore geometries, including these composed of cellulose acetate, polytetrafluoroethylene, and polysulfone, as porous supports. However, a uniform dense membrane of CoTPP-OIm could not be prepared using these porous supports due to the infiltration of CoTPP-OIm into their pores. On the other hand, a uniform membrane without pinholes or defects was prepared on the polyacrylonitrile ultrafiltration porous support. By appropriately adjusting the coating conditions, such as solvent, the concentration of CoTPP-OIm, coating atmosphere, etc., membranes of varying thickness were successfully prepared on the porous support. The membrane thickness and nitrogen permeability coefficient (P_{N2}) in Barrer are presented in Fig. S1 together with the nitrogen permeance (Q_{N2}) in Gas Permeation Unit (GPU) defined as Eqn S1 and S2:

$$1 \text{ GPU} = 10^{-6} \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \tag{S1}$$

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3 \text{ (STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \tag{S2}$$

The independence of P_{N2} from CoTPP-OIm membrane thickness (Table S1) supported that the CoTPP-OIm membrane was coated without infiltrating the pores of the polyacrylonitrile porous support.

Table S1 Q_{N2} and P_{N2} of the CoTPP-OIm membranes with different thicknesses

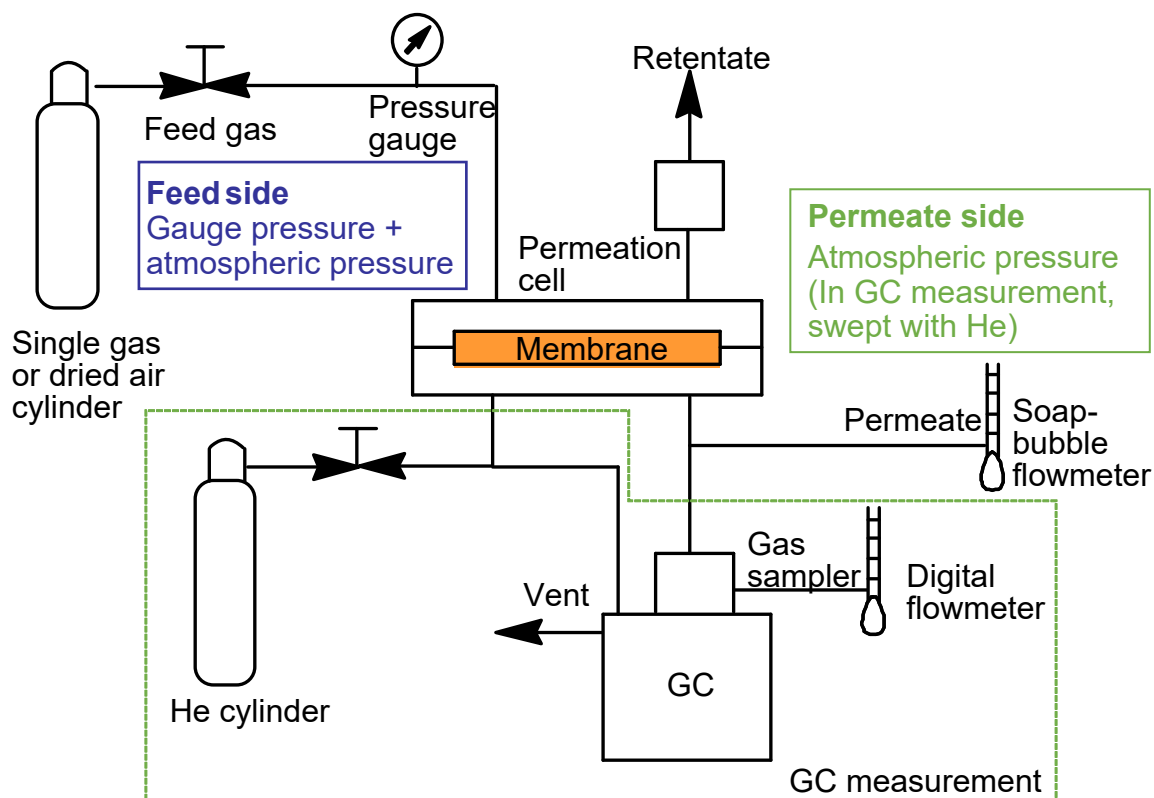| Membrane thickness [nm]	Q_{N2} [GPU]	$10^2 \, P_{N2}$ [Barrer]
85	0.93	7.9
120	0.73	8.7
160	0.51	8.1
230	0.37	8.5

Fig S1 Flow diagram of the permeability measurement for the CoTPP-OIm membranes (2 cm diameter).
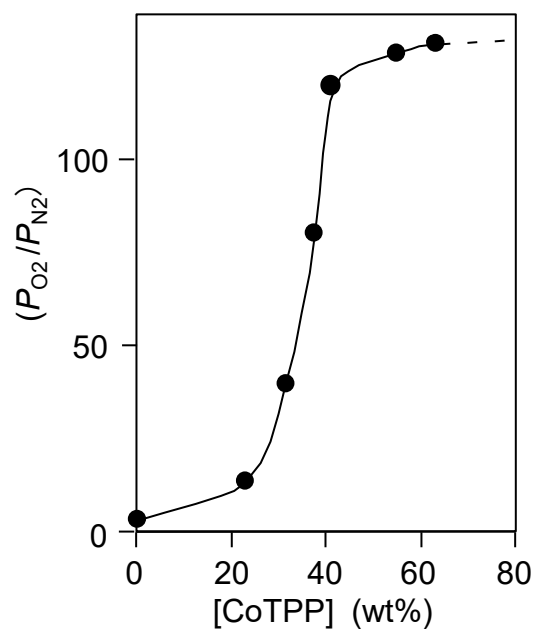
Fig S2 Effect of the CoTPP concentration on the O_2/N_2 permselectivity at $\Delta p = 1$ cmHg.

Table S2 Membrane thickness, glass transition temperature (T_g), and P_{N2} of the CoTPP-OIm membranes

$Co^{II}TPP$ [%] [a]	Membrane thickness [nm]	T_g [°C]	$10^2 P_{N2}$ [Barrer]
42	80	6.0	8.1
32	71	6.2	8.5
21	95	5.9	9.6
11	90	6.2	9.0
0	88	6.0	9.3

[a] Total (active $Co^{II}TPP$ + inactive $Co^{III}TPP$) concentration = constant 42 wt%.

CoTPP-OIm membrane

Quartz window
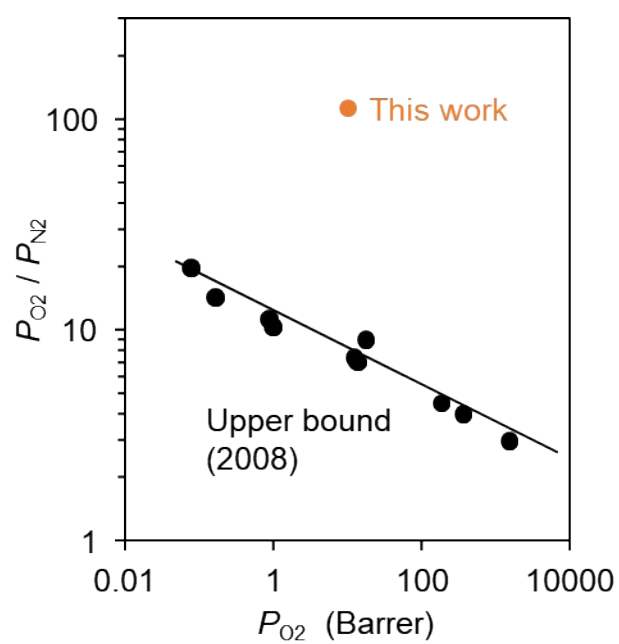
Fig S3 High-pressure cell for spectroscopic measurements.

Fig. S4 O_2/N_2 permselectivity *vs*. oxygen permeability for the CoTPP-OIm membrane in this study compared to Robeson's upper-bound correlation[S1].

Reference

S1   L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390–400.