# *Supporting Information*

## Tailoring the micropore structure of 6FDA-based network polyimide membranes for advanced gas separation by decarboxylation

*YuXuan Zhao, Hongyan Wang*[*]*, Xiangyun Liu,*

*Xueping Zong, Jiangzhou Luo*[*] *,Song Xue*

School of Chemistry & Chemical Engineering, Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, Tianjin University of Technology, Tianjin, 300384, China

*Corresponding authors: hywang@email.tjut.edu.cn; luojz@email.tjut.edu.cn

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## Section S1. Experimental Procedures

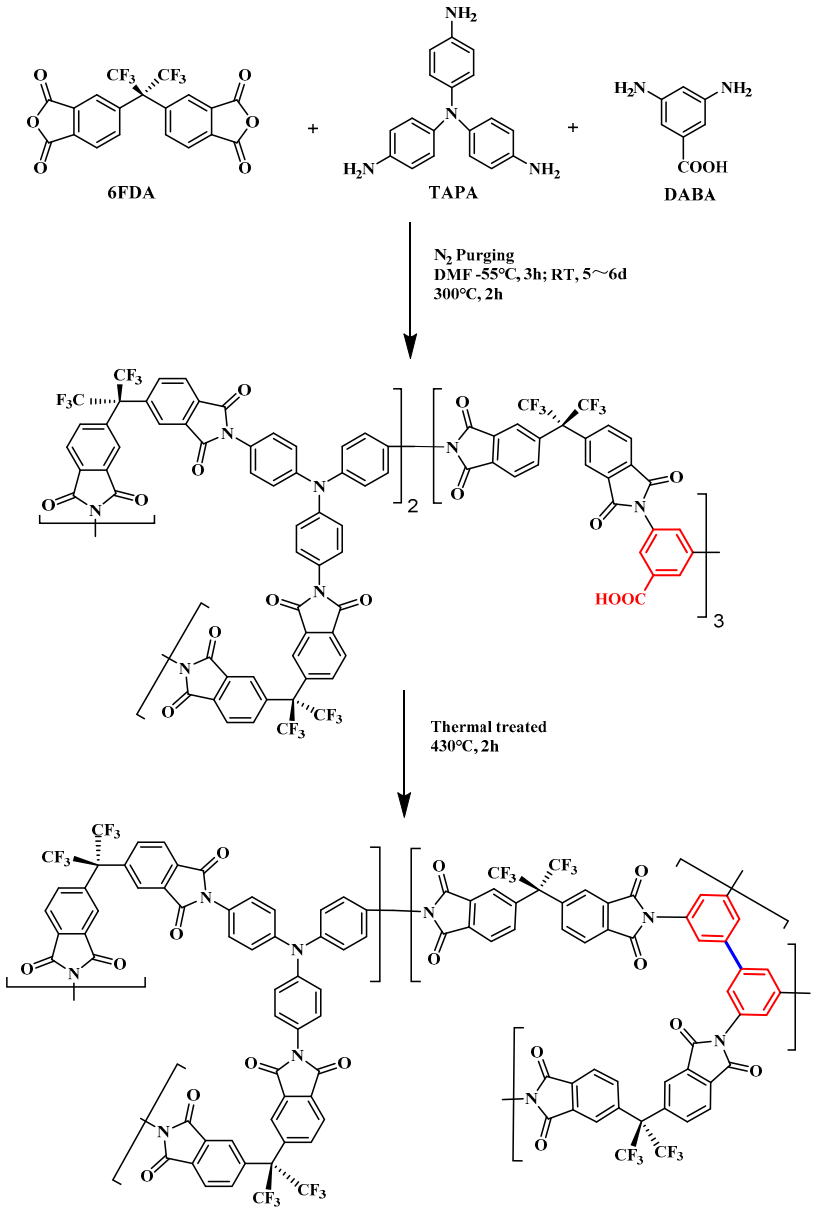
### Section S1.1 Gel contents measurement

The gel contents of network PIs in DMF solvent were respectively measured by extracting the membrnaes with solvent for 24 h. The insoluble part was dried at 150 ºC for 24 h to constant weight. The gel contents were obtained via the following Equation

$$\text{Gel } \% = \frac{W_1}{W_0}$$

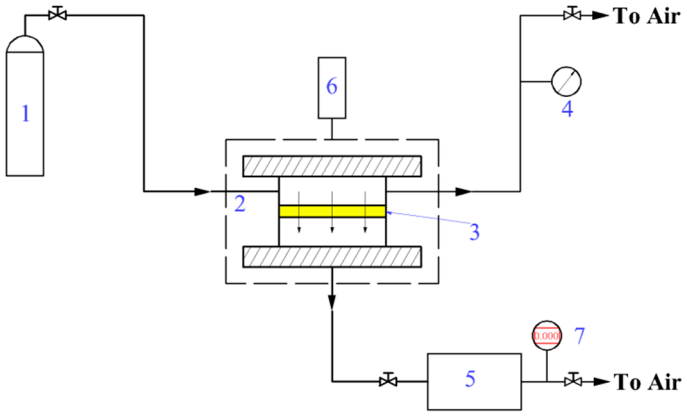
where $W_0$ and $W_1$ are the original weights and the insoluble part weights of the PI membranes, respectively [1-4].

## Section S2. Supplementary Figures



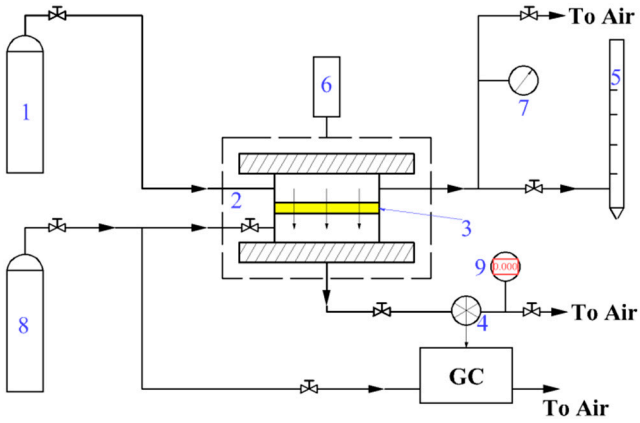

**Scheme S1.** Synthesis of 6FDA-DABA:TAPA(3:2) network PI and its thermally treated membrane 6FDA-DABA:TAPA(3:2)-430

(a)




1 Feed Gas 2 Membrane Cell 3 Separation Membrane 4 Pressure Gauge
5 Constant Volume Variable Pressure Device 6 Temperature Controller
7 DIGITAL TEST GAUGE

(b)




1 Feed Gas 2 Membrane Cell 3 Separation Membrane 4 Six-way valve
5 Soap Film Gas Flow Meter 6 Temperature Controller 7 Pressure Gauge
8 Sweep Gas and Carrier Gas 9 DIGITAL TEST GAUGE (YK-120B)

**Figure S1.** Flow chart of gas transport testing for **(a)** pure gas, **(b)** mixed gas.

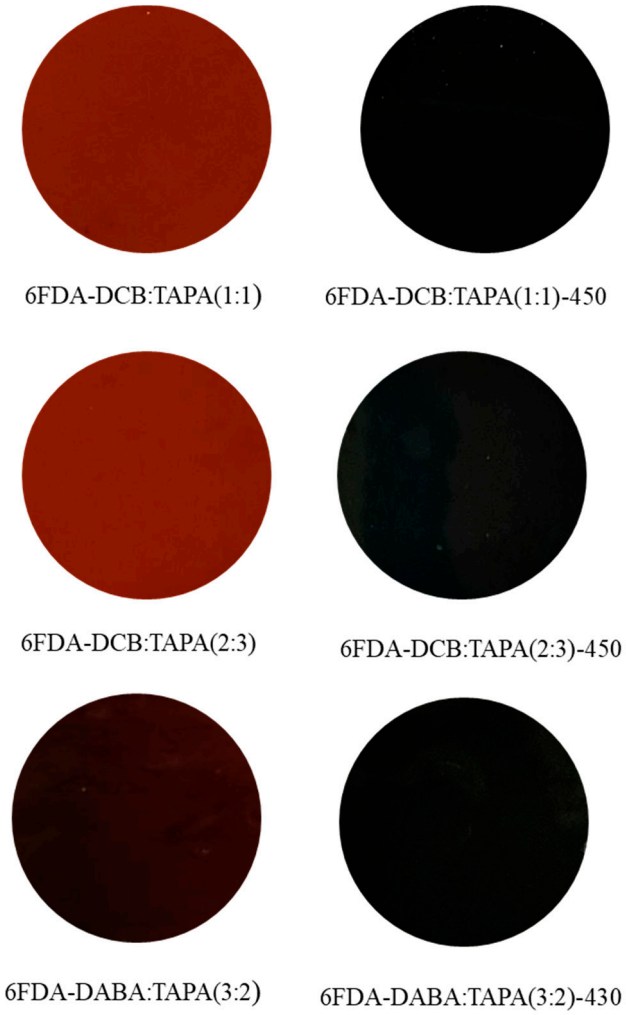



**Figure S2.** Optical pictures of prepared network PIs and their thermally treated membranes.

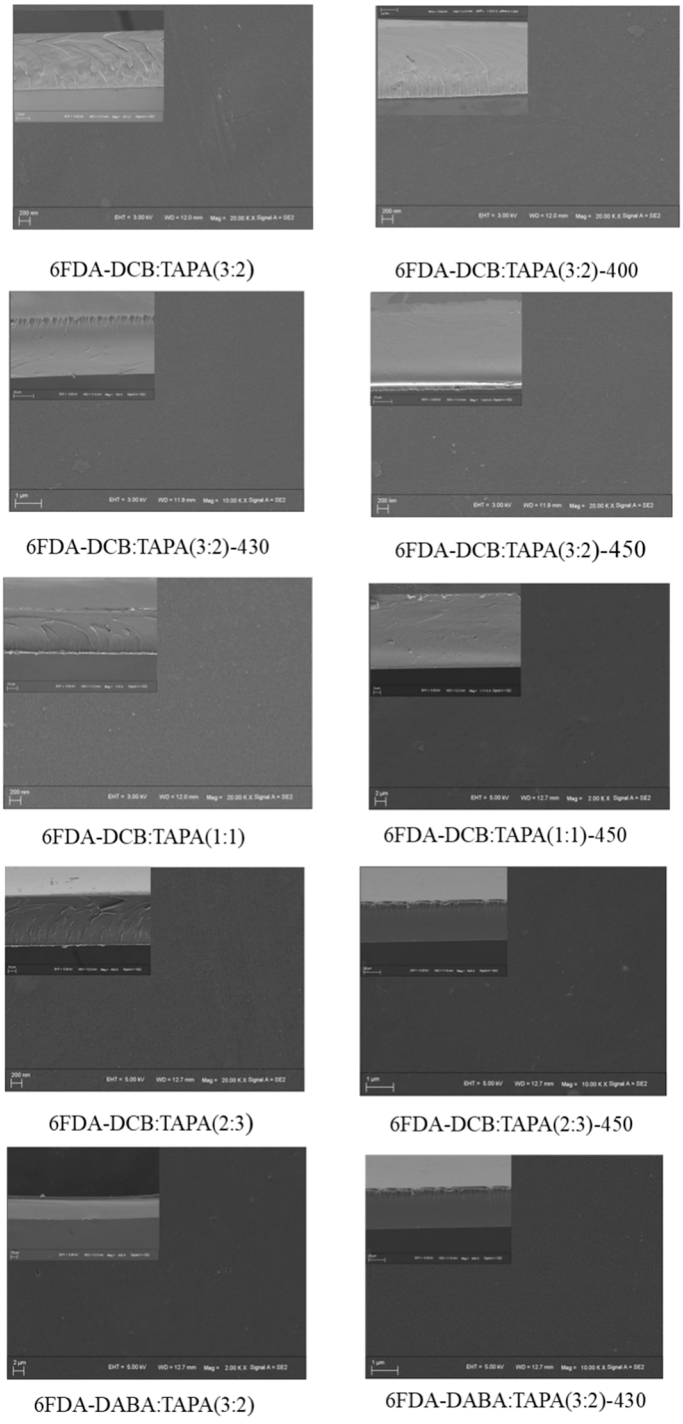



**Figure S3.** SEM images of prepared network PIs and their thermally treated membranes.

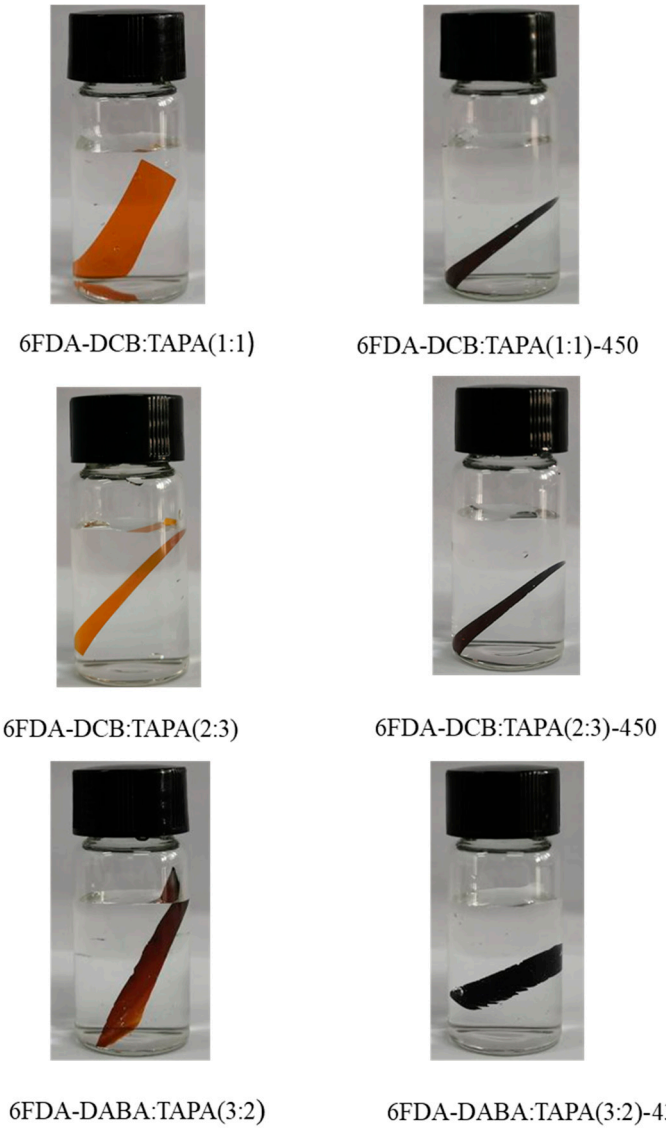



**Figure S4.** Solubility test of prepared network PIs and their thermally treated membranes.

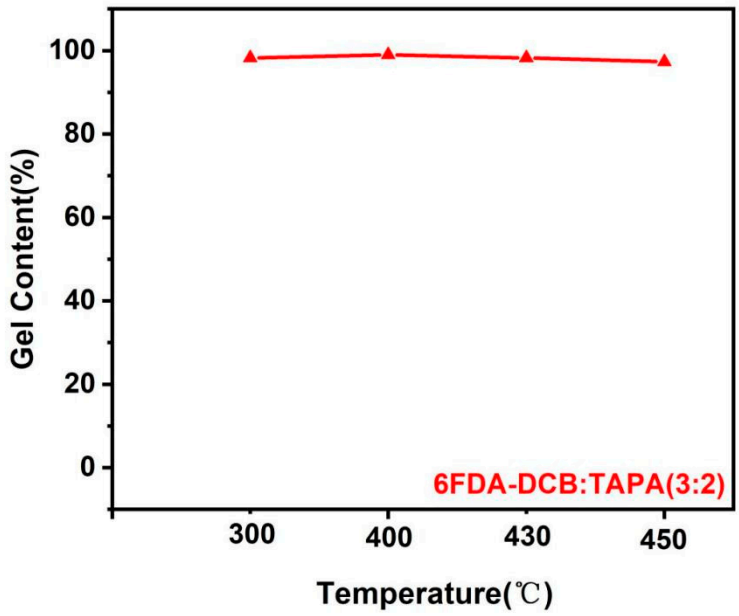



**Figure S5.** Gel contents of 6FDA-DCB: TAPA (3:2).

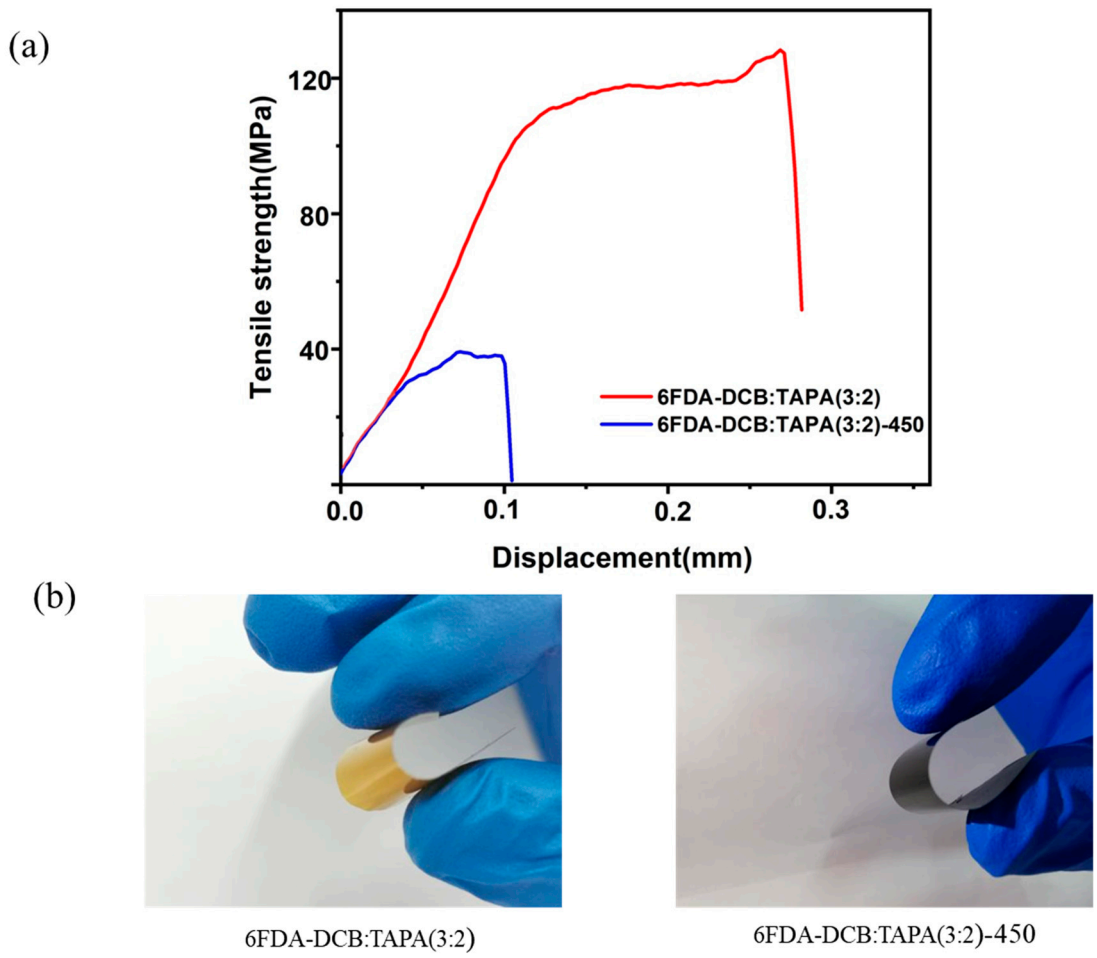



**Figure S6.** Mechanical properties of 6FDA-DCB:TAPA(3:2) and 6FDA-DCB:TAPA(3:2)-450. (a) Stress-strain curves (b)Bending experiment

## Section S3. Supplementary Tables

**Table S1.** Tensile strength and Elongation at break of 6FDA-DCB:TAPA(3:2) and 6FDA-DCB:TAPA(3:2)-450.

| PIs | Tensile strength(MPa) | Elongation at break(%) |
|---|---|---|
| 6FDA-DCB:TAPA(3:2) | 131 | 5.6 |
| 6FDA-DCB:TAPA(3:2)-450 | 38 | 2.2 |

**Table S2.** The pure gas diffusion coefficient (*D*), solubility coefficient (*S*), the diffusion selectivity ($\alpha_S$) and the solubility selectivity ($\alpha_D$) for all tested membranes at 0.2 MPa and 30 °C.

| PIs | D ($10^{-8}$·cm2·s-1) | | | | S ($10^{-2}$· cm3 ) (STP)·$cm^{-3}$·$cmHg^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | $N_2$ | $O_2$ | $CO_2$ | α($CO_2$/$N_2$) | $N_2$ | $O_2$ | $CO_2$ | α($CO_2$/$N_2$) |
| 6FDA-DCB:TAPA(3:2) | 1.1 | 3.15 | 7.2 | 6.5 | 0.96 | 2.79 | 5.44 | 5.6 |
| 6FDA-DCB:TAPA(3:2)-400 | 2.25 | 5.33 | 8.75 | 4 | 1.16 | 2.96 | 6.52 | 5.6 |
| 6FDA-DCB:TAPA(3:2)-430 | 3.23 | 6.48 | 12.43 | 3.9 | 1.32 | 3.27 | 7.1 | 5.4 |
| 6FDA-DCB:TAPA(3:2)-450 | 5.91 | 14.37 | 23.97 | 4.1 | 1.92 | 3.99 | 11.12 | 5.8 |
| 6FDA-DCB:TAPA(1:1) | 1.1 | 2.98 | 6.71 | 6.1 | 1.44 | 3.1 | 6.93 | 4.8 |
| 6FDA-DCB:TAPA(1:1)-450 | 4.39 | 10.68 | 20.76 | 4.8 | 2.35 | 4.65 | 11.57 | 4.9 |
| 6FDA-DCB:TAPA(1:1) | 1.22 | 3.23 | 7.14 | 6 | 1.41 | 3.16 | 6.83 | 4.8 |
| 6FDA-DCB:TAPA(1:1)-450 | 3.38 | 11.11 | 18.78 | 5.7 | 2.82 | 4.19 | 12.52 | 4.4 |
| 6FDA-DABA:TAPA(3:2) | 1.19 | 2.6 | 6.43 | 5.8 | 1.17 | 3.91 | 5.32 | 4.5 |
| 6FDA-DABA:TAPA(3:2)-430 | 5.4 | 6.32 | 19.12 | 3.5 | 1.37 | 5.46 | 10.64 | 7.7 |

**Table S3.** Pure gas permeabilities and ideal selectivities for 6FDA-DCB:TAPA(3:2)-450 and 6FDA-DABA:TAPA(3:2)-430 with different test pressures at 30 °C.

| PIs | Pressure (MPa) | P(Barrer) | | | α | |
|---|---|---|---|---|---|---|
| | | $N_2$ | $O_2$ | $CO_2$ | $O_2/N_2$ | $CO_2/N_2$ |
| 6FDA-DCB:TAPA (3:2)-450 | 0.2 | 10.99 | 49.09 | 169.49 | 4.5 | 15.4 |
| | 0.4 | 10.07 | 46.3 | 135.64 | 4.6 | 13.5 |
| | 0.6 | 9.58 | 44.25 | 119.31 | 4.6 | 12.5 |
| | 0.8 | 8.74 | 40.09 | 98.55 | 4.6 | 10.3 |
| | 1.0 | 8.13 | 38.2 | 92.03 | 4.7 | 11.3 |
| | 1.2 | 7.83 | 37.58 | 87.3 | 4.8 | 11.1 |
| 6FDA-DABA:TAPA (3:2)-430 | 0.2 | 6.3 | 30.9 | 141.39 | 4.9 | 22.4 |
| | 0.4 | 5.97 | 26.54 | 115.9 | 4.4 | 19.4 |
| | 0.6 | 5.62 | 26.2 | 93.07 | 4.7 | 16.6 |
| | 0.8 | 5.23 | 25.66 | 86.03 | 4.9 | 16.4 |
| | 1.0 | 4.91 | 25.28 | 84.81 | 5.1 | 17.3 |
| | 1.2 | 4.85 | 25.02 | 78.57 | 5.2 | 16.2 |

1 Barrer= $10^{-10}$ ($cm^3$ (STP)·cm)/($cm^2$·sec cmHg).

**Table S4.** Physical aging performances of 6FDA-DCB:TAPA(3:2)-450 and 6FDA-DABA:TAPA(3:2)-430 aged 30, 60, 90, and 120 days at 0.2 MPa and 30 °C.

| PIs | Days | P(Barrer) | | | α | |
|---|---|---|---|---|---|---|
| | | $N_2$ | $O_2$ | $CO_2$ | $O_2/N_2$ | $CO_2/N_2$ |
| 6FDA-DCB:TAPA (3:2)-450 | 0 | 11.32 | 57.29 | 266.6 | 5.1 | 23.6 |
| | 30 | 10.99 | 49.09 | 169.49 | 4.5 | 15.4 |
| | 60 | 9.4 | 43.87 | 138.14 | 4.7 | 14.7 |
| | 90 | 8.73 | 39.69 | 117.87 | 4.5 | 13.5 |
| | 120 | 8.29 | 37.41 | 102.35 | 4.5 | 12.3 |
| 6FDA-DABA:TAPA (3:2)-430 | 0 | 7.37 | 39.6 | 203.45 | 5.4 | 27.6 |
| | 30 | 6.3 | 30.9 | 141.39 | 4.9 | 22.4 |
| | 60 | 5.95 | 25.8 | 136.96 | 4.3 | 23 |
| | 90 | 5.51 | 23.71 | 130.67 | 4.3 | 23.7 |
| | 120 | 5.08 | 22.87 | 127.43 | 4.5 | 25.1 |

1 Barrer= $10^{-10}$ ($cm^3$ (STP)·cm)/($cm^2$·sec cmHg).

**Table S5.** Mixed gas separation performance for 6FDA-DCB:TAPA(3:2)-450 and 6FDA-DABA:TAPA(3:2)-430 membranes at 0.2 MPa and 30 °C.

| PIs | Mixed-gas $CO_2/N_2$ | Permeate gas concentration (v/v) | $P_{CO2}$ (Barrer) | $P_{N2}$ (Barrer) | α |
|---|---|---|---|---|---|
| 6FDA-DCB:TAPA (3:2)-450 | 15/85 | 80.8/19.2 | 230.66 | 9.67 | 23.9 |
| 6FDA-DABA:TAPA (3:2)-430 | 15/85 | 84.5/15.5 | 197.17 | 6.38 | 30.9 |

1 Barrer= $10^{-10}$ ($cm^3$ (STP)·cm)/($cm^2$·sec cmHg).

## Reference

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