

# Supporting Information

## A Crown Ether-Containing Copolyimide Membranes with Improved Free Volume for CO<sub>2</sub> Separation

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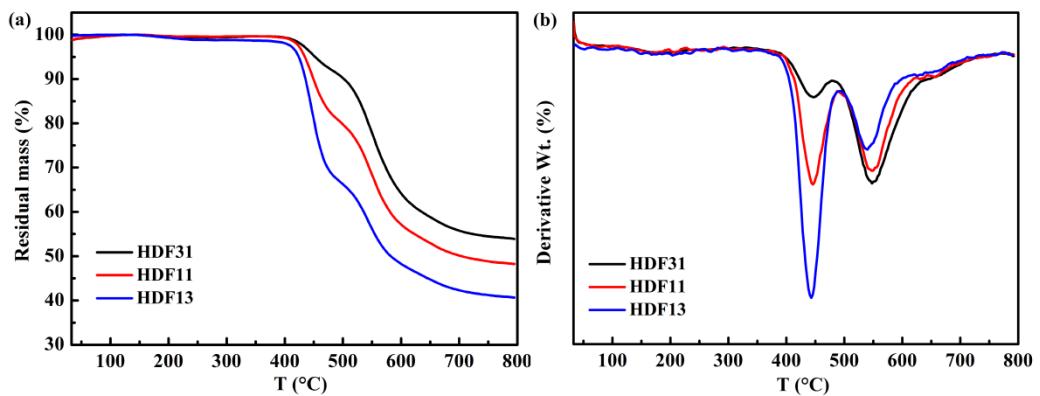
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**Table S1.** Mechanical Properties of HDF Copolyimide Membranes

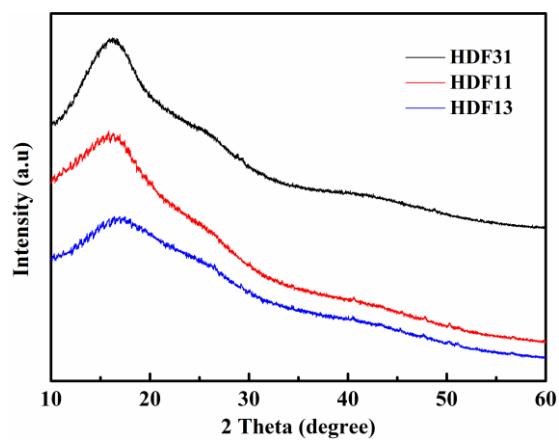
membranes	tensile Strength (MPa)	Young's modulus (MPa)	elongation at break (%)
HDF31	68.71 $\pm$ 2.87	1718 $\pm$ 120	7.50 $\pm$ 0.62
HDF11	65.23 $\pm$ 3.21	1630 $\pm$ 104	5.92 $\pm$ 0.41
HDF13	36.36 $\pm$ 2.66	820.5 $\pm$ 51	4.54 $\pm$ 0.29

**Table S2.** Solubility of HDF Copolyimide Membranes

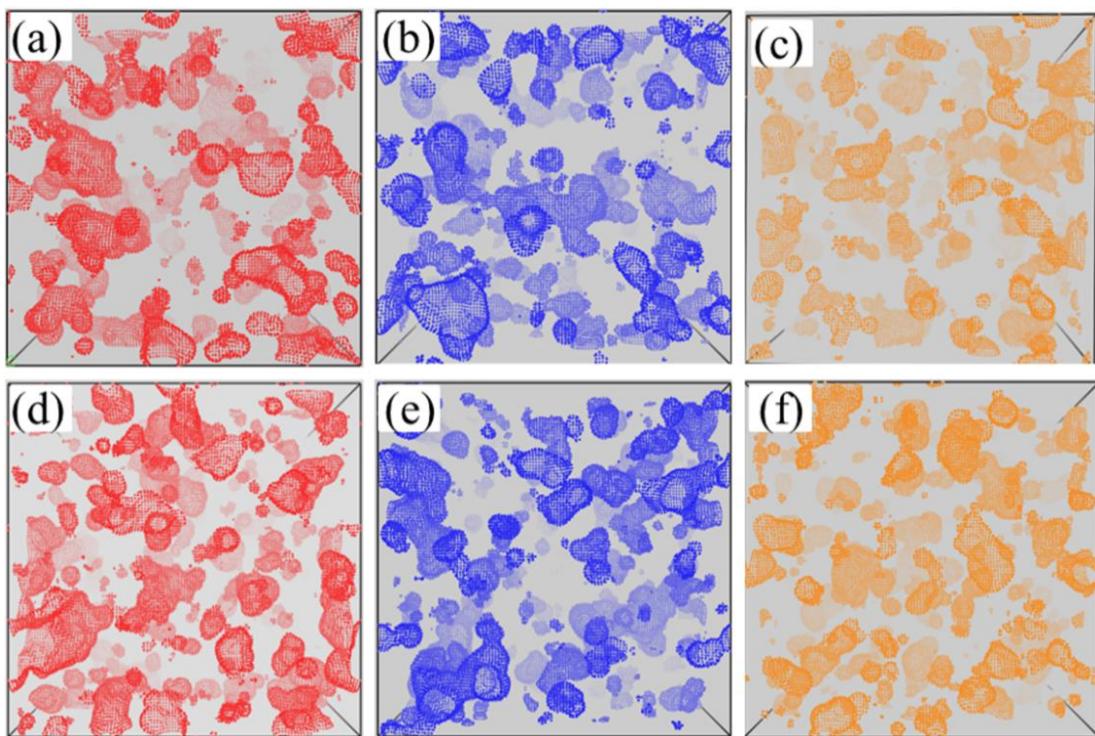
membranes	solvents					
	NMP	DMSO	DMF	DMAc	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>
HDF31	+	+	+	+	+	+
HDF11	+	+	+	+	+	+
HDF13	+	+	+	+	+	+



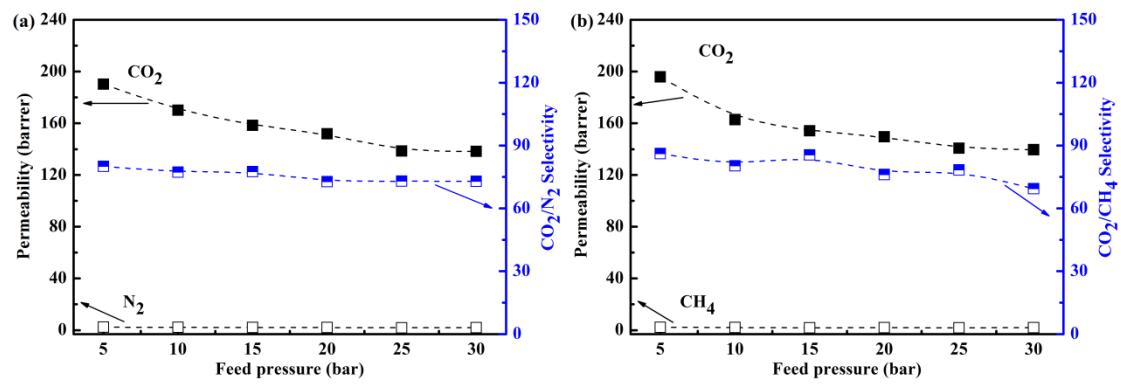
**Figure S1.** (a) TGA and (b) DTG curves of HDF co-polyimide membranes.



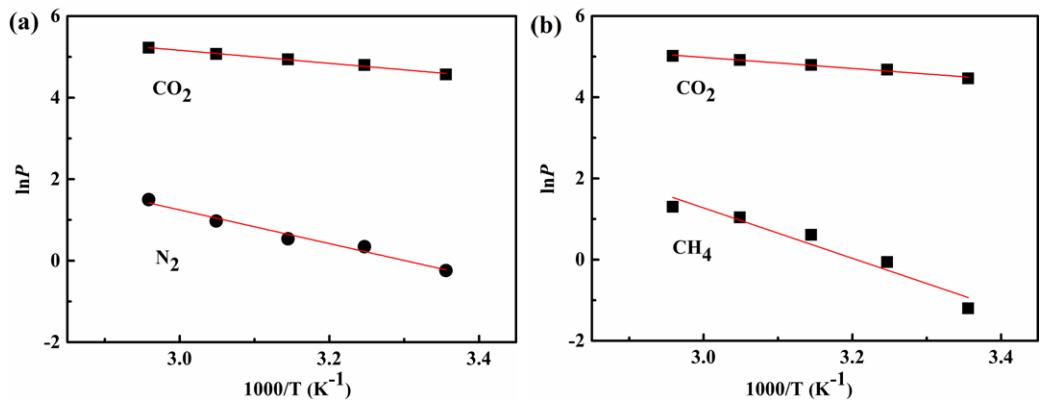
**Figure S2.** WAXD patterns of HDF co-polyimide membranes.



**Figure S3.** Three-dimensional representation of the CO<sub>2</sub> accessible free volume distribution and morphology of MDF and HDF co-polyimide membranes, the red, blue and orange shaded areas highlight the different crown ether contents: (a) MDF31; (b) MDF11; (c) MDF13; (d) HDF31; (e) HDF11; (f) HDF13.



**Figure S4.** Mixed-gas permeability coefficients and separation factor versus feed pressure of HDF31 co-polyimide membrane (a) CO<sub>2</sub>/N<sub>2</sub> mixed-gas (20/80 by volume); (b) CO<sub>2</sub>/CH<sub>4</sub> mixed-gas (10/90 by volume). (testing temperature of 35 °C)



**Figure S5.** The temperature dependence of permeability for HDF31 co-polyimide membrane (a)  $\text{CO}_2/\text{N}_2$  mixed-gas (20/80 by volume); (b)  $\text{CO}_2/\text{CH}_4$  mixed-gas (10/90 by volume). (testing pressure of 20 bar)