

Supplementary Materials: Carbon–Carbon Composite Membranes Derived from Small-Molecule-Compatibilized Immiscible PBI/6FDA-DAM-DABA Polymer Blends

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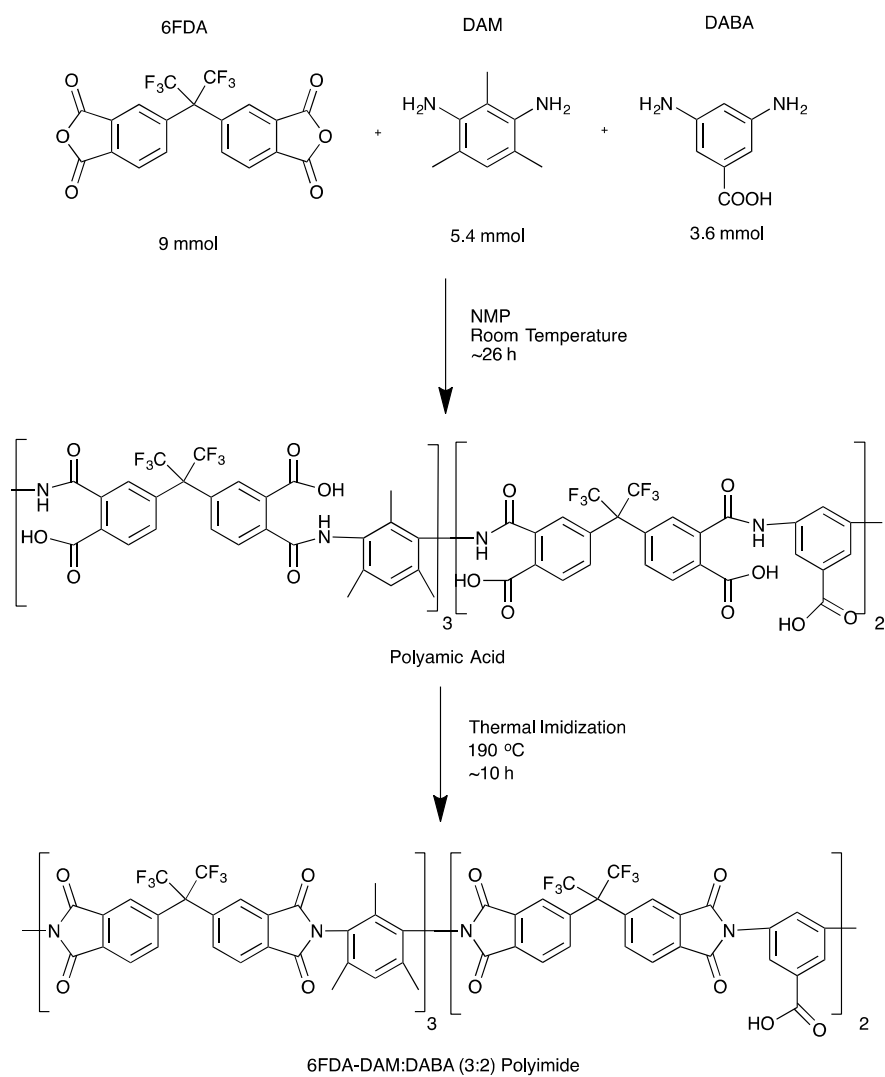


Figure S1. Synthesis route for 6FDA-DAM:DABA [3:2], (6FDD).

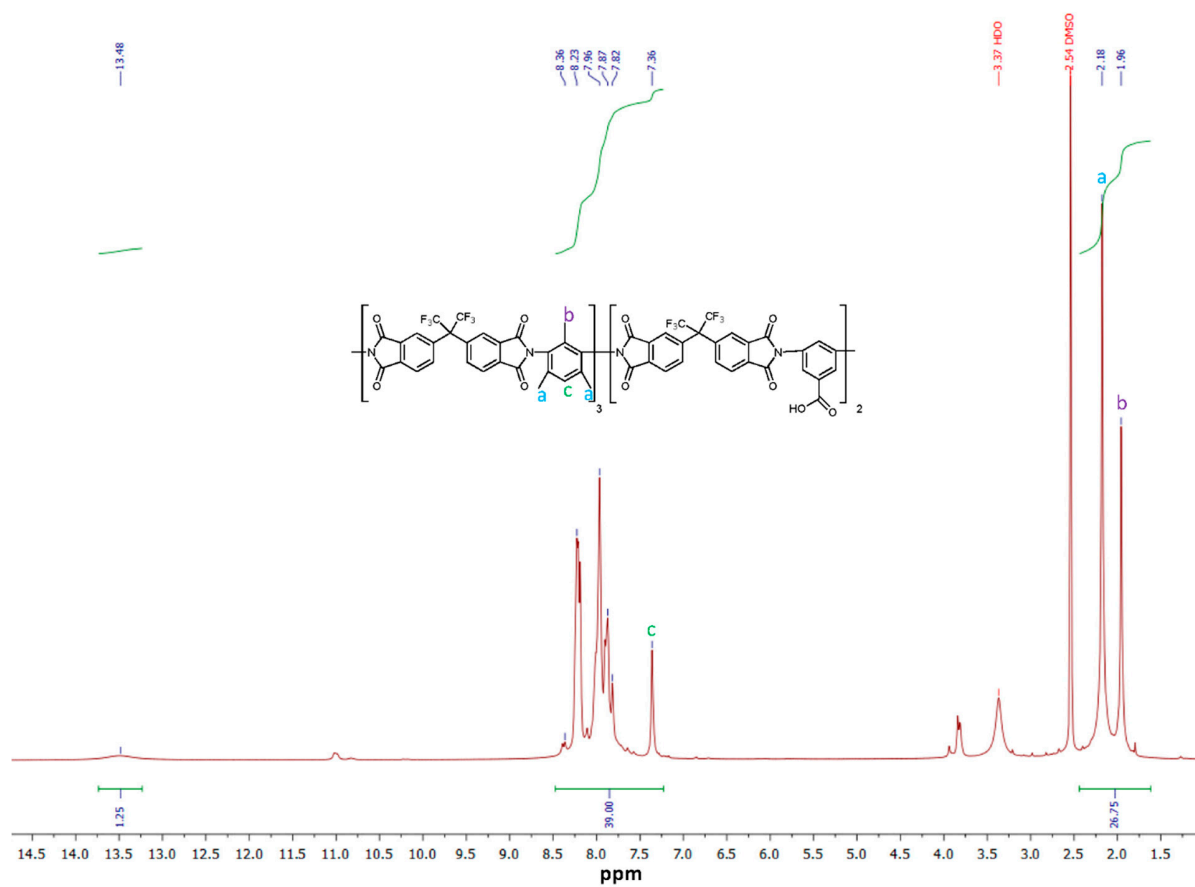


Figure S2. ^1H NMR spectrum of 6FDD in $\text{DMSO-}d_6$. Reported chemical shifts in [70,71].

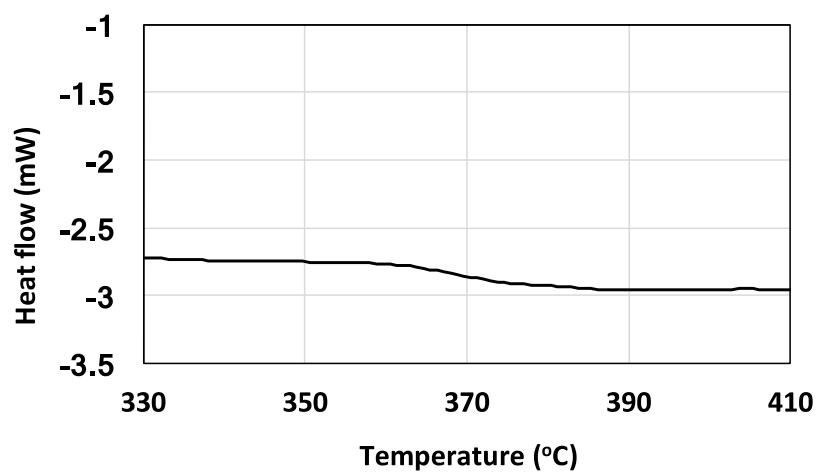


Figure S3. Differential scanning calorimetry of 6FDD at a scan rate of 10 °C/min in UHP N₂ at 50 mL/min. T_g = 370 °C - 375 °C, reported T_g = 387 °C [72].

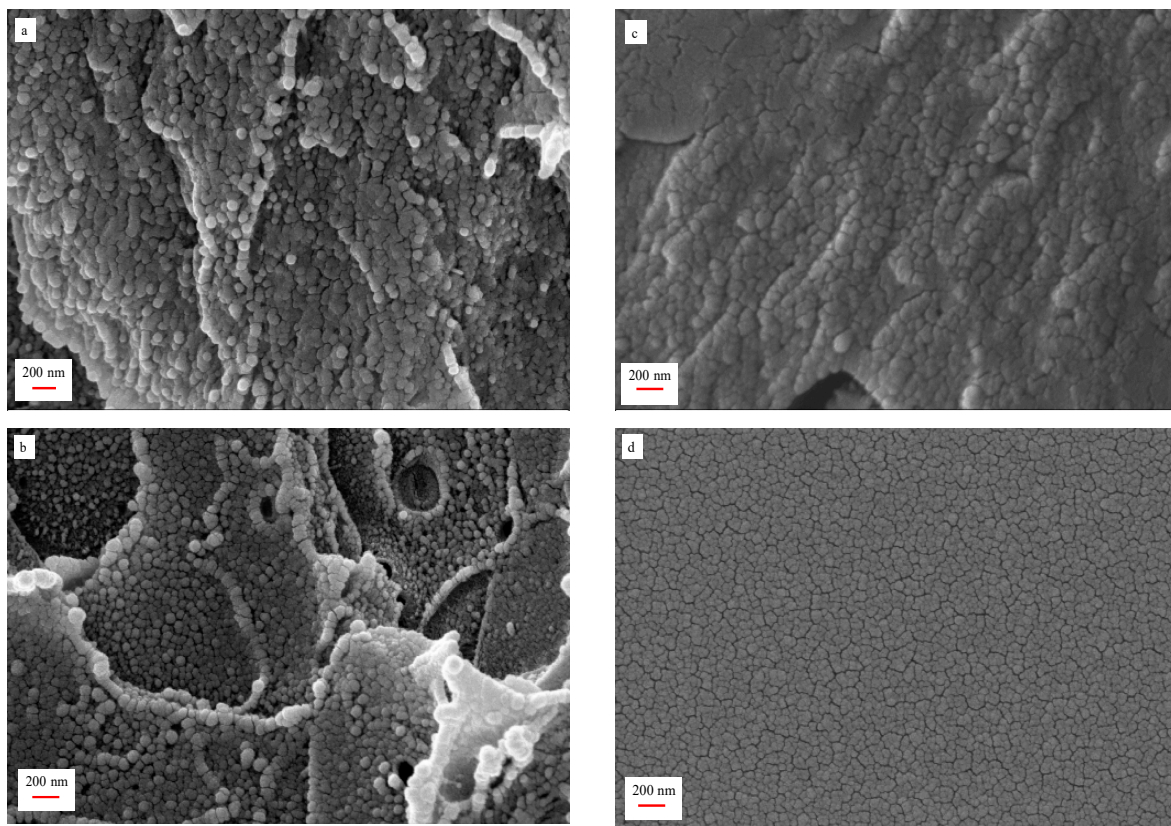


Figure S4. Cross-section SEM images of: a) PBI, b) 6FDD, c) PBI CMSM, d) 6FDD CMSM.

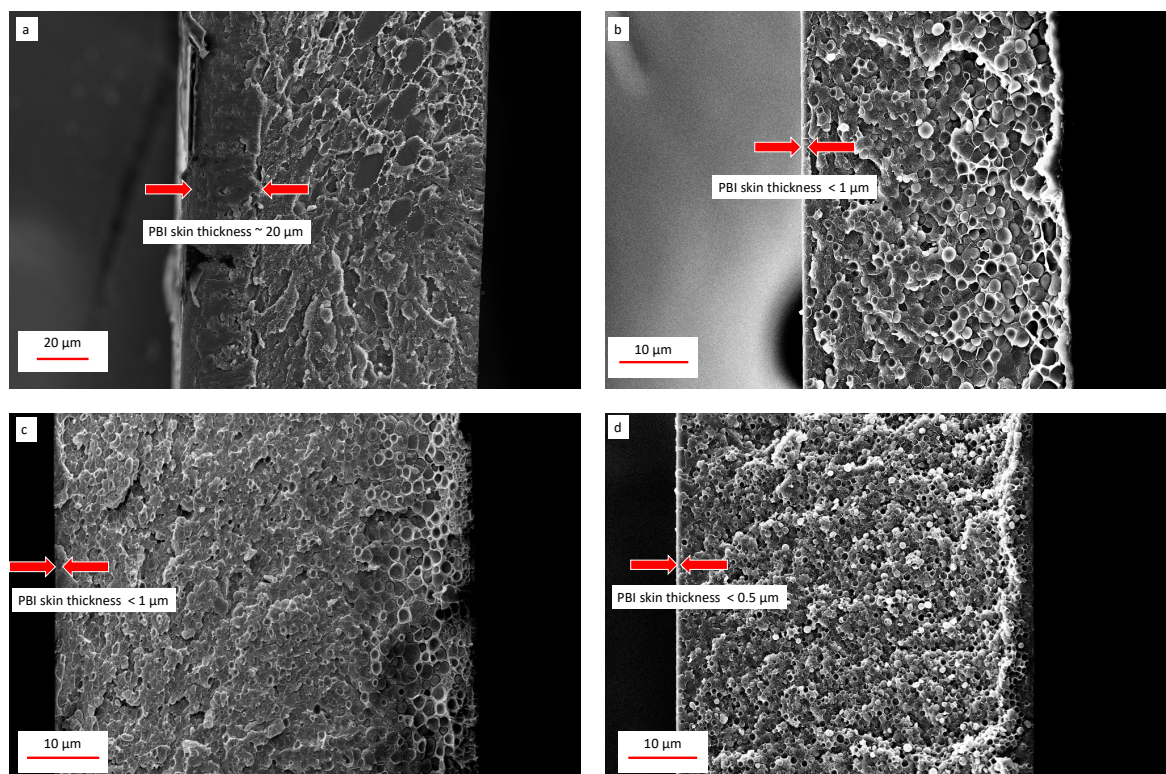


Figure S5. Cross-section SEM images of immiscible polymer blend membranes: a) 0DuD-6FDD:PBI, b) 5DuD-6FDD:PBI, c) 9DuD-6FDD:PBI, d) 17DuD-6FDD:PBI.

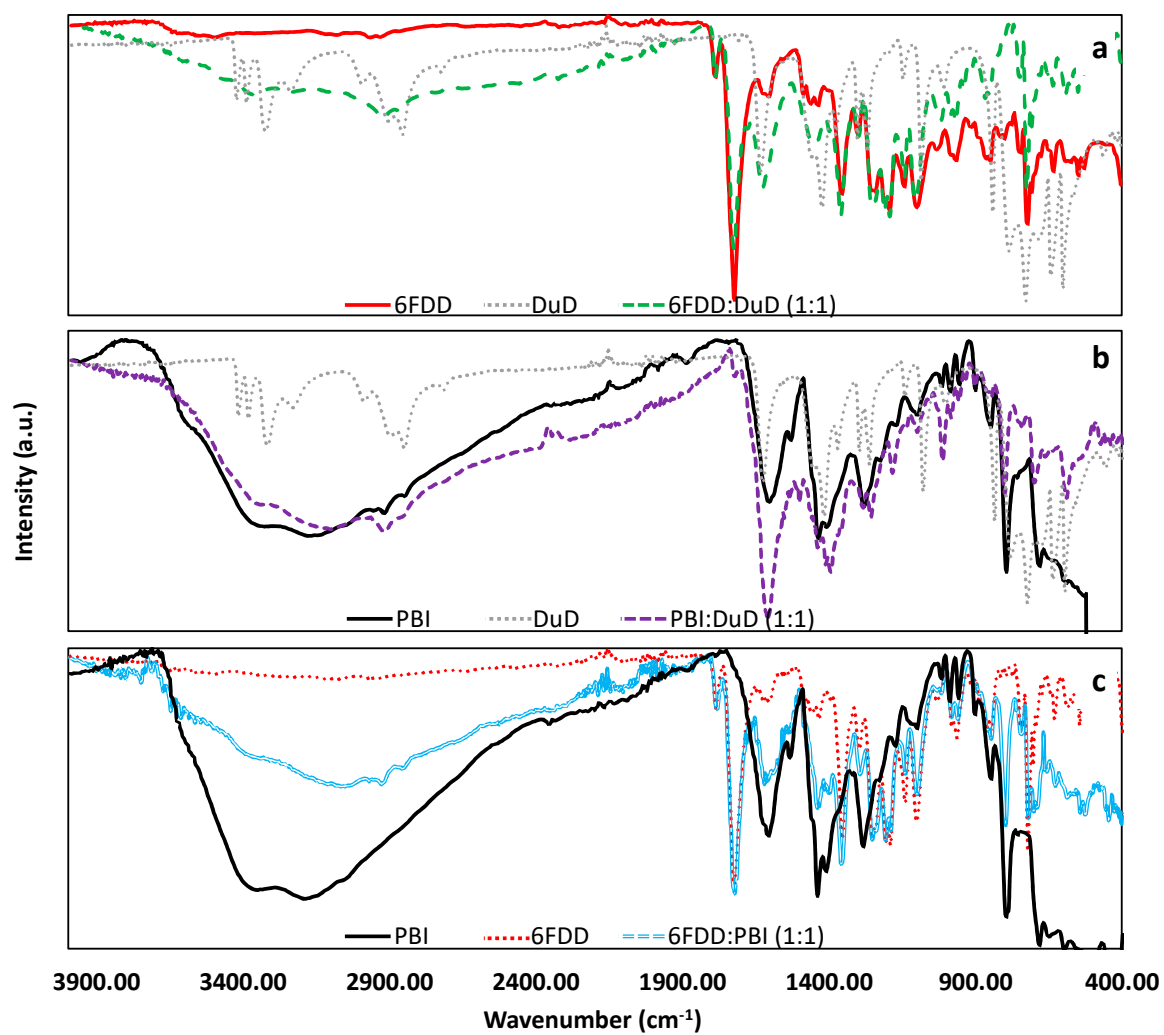


Figure S6. ATR-FTIR spectra of the prepared membranes: a) 6FDD:DuD, b) PBI:DuD, c) 6FDD:PBI.

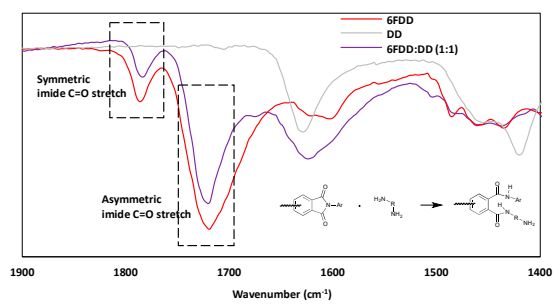


Figure S7. FTIR spectra of 6FDD, DD, and 6FDD:DD [1:1]

Supplementary equations

Gas transport models for immiscible polymer blends [58]:

a) Parallel model:

$$P = \Phi_c P_c + \Phi_d P_d \quad \text{Eq.1}$$

b) Series model:

$$P = P_c P_d / (\Phi_c P_d + \Phi_d P_c) \quad \text{Eq. 2}$$

c) Maxwell's model:

$$P = P_c \left[\frac{P_d + 2P_c - 2\Phi_d(P_c - P_d)}{P_d + 2P_c + \Phi_d(P_c - P_d)} \right] \quad \text{Eq. 3}$$

Where P is the permeability of the blend, Φ_c and Φ_d are the volume fractions of the continuous and discontinuous phases, respectively, and P_c and P_d are their experimental permeabilities.

d) Equivalent box model:

$$P = P_1 \Phi_{1p} + P_2 \Phi_{2p} + \Phi_S^2 \left/ \left[\frac{\Phi_{1s}}{P_1} + \frac{\Phi_{2s}}{P_2} \right] \right. \quad \text{Eq. 4}$$

where:

$$\Phi_S = \Phi_{1s} + \Phi_{2s}$$

$$\Phi_{1p} = [(\Phi_1 - \Phi_{1cr}) / (1 - \Phi_{1cr})]^{T_1}$$

$$\Phi_{2p} = [(\Phi_2 - \Phi_{2cr}) / (1 - \Phi_{2cr})]^{T_2}$$

$$\Phi_{1s} = \Phi_1 - \Phi_{1p}$$

$$\Phi_{2s} = \Phi_2 - \Phi_{2p}$$

and P_1 and P_2 are the permeabilities of components 1 and 2, Φ_{1cr} and Φ_{2cr} are the critical threshold percolation values, and T_1 and T_2 are the critical universal exponents.

References:

58. Robeson, L.M. Polymer Blends in Membrane Transport Processes. *Ind. Eng. Chem. Res.* **2010**, *49*, 11859–11865.
70. Kumar, A.; Tateyama, S.; Yasaki, K.; Ali, M.A.; Takaya, N.; Singh, R.; Kaneko, T. ¹H NMR and FT-IR dataset based structural investigation of poly(amic acid)s and polyimides from 4,4'-diaminostilbene, *Data in Brief* **2016**, *7*, 123–128.
71. Kim, Y.J.; Glass, T.E.; Lyle, G.D.; McGrath, J.E. Kinetic and mechanistic investigations of the formation of polyimides under homogeneous conditions, *Macromolecules* **1993**, *26*, 1344–1358.
72. Qiu, W.; Chen, C.-C.; Xu, L.; Cui, L.; Paul, D.R.; Koros, W.J. Sub-*T_g* cross-linking of a polyimide membrane for enhanced CO₂ plasticization resistance for natural gas separation, *Macromolecules* **2011**, *44*, 6046–6056.