Supporting Information for

Structure Manipulation in Triptycene-Based Polyimides through Main Chain Geometry Variation and its Effect on Gas Transport Properties

Jennifer R. Weidman, Shuangjiang Luo, Qinnan Zhang, Ruilan Guo*

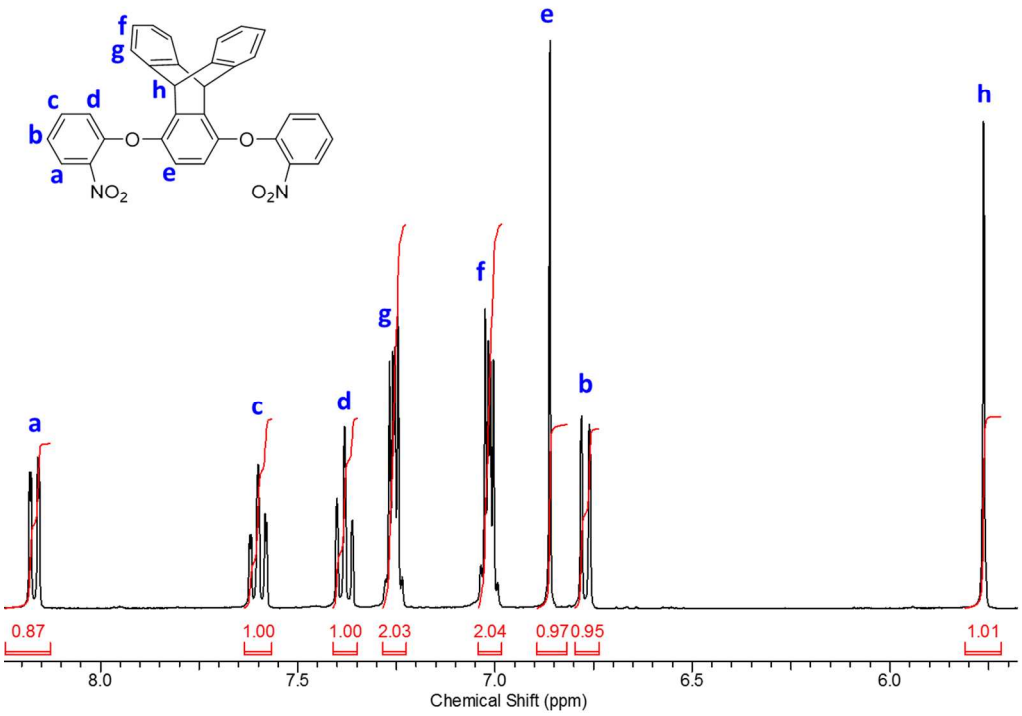
University of Notre Dame, Department of Chemical and Biomolecular Engineering, Notre Dame, IN 46556

* Corresponding author, +1-574-631-3453 (tel), +1-574-631-0317 (fax),

rguo@nd.edu

Synthesis Details:

1,4-bis(nitrophenoxy)triptycene (1): 1,4-dihydroxytriptycene was synthesized as reported in our previous paper. [1] To make the 1,4-bis(nitrophenoxy)triptycene, the following were combined in a 100 mL 2-neck flask equipped with a magnetic stir bar: 1,4-dihydroxytriptycene (2.0 g, 0.007 mol), potassium carbonate (2.12 g, 0.015 mol), and dimethylformamide (DMF) (20 mL). The mixture was allowed to stir at room temperature for 40 min and then 1-fluoro-2-nitrobenzene (1.97 g, 0.014 mol) was added. The reaction mixture was put on to reflux under nitrogen protection at 151 °C for 8 h. After cooling, the mixture was precipitated in a mixture of methanol and water (1:1 v/v, 120 mL), collected, and dried under vacuum at 100 °C overnight. (yield = 90%).



1,4-bis(aminophenoxy)triptycene (2): 1,4-bis(nitrophenoxy)triptycene (**1**) (3.33 g, 0.006 mol), 10% Pd/C catalyst (0.17 g), and alcohol (135 mL) were added to a 250 mL 2-neck round bottom flask equipped with a magnetic stir bar and brought to reflux at 78 °C. Hydrazine monohydrate (5.50 g, 0.11 mol) was then added dropwise. The reaction mixture was allowed to reflux for 8 h. The alcohol was then removed under vacuum. The product was dissolved in a minimal amount of hot DMF and the catalyst was removed via vacuum filtration through packed Celite®. The

DMF solution as then precipitated in water. The diamine monomer (**2**) was collected and dried under vacuum at 100 °C overnight (yield = 81%).

^{1}H NMR spectra of intermediates of 2,6-triptycene-based monomers:

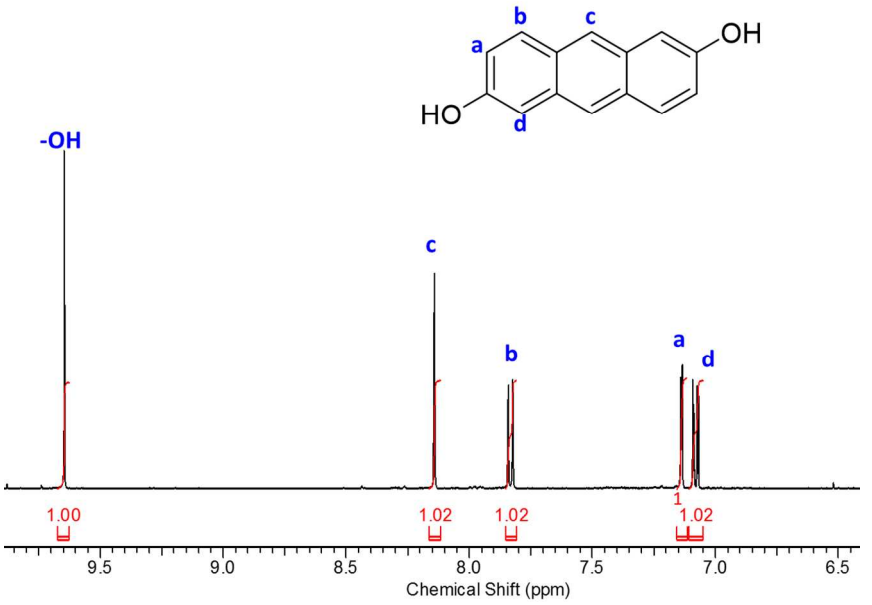


Figure S1. ^{1}H NMR spectrum of 2,6-dihydroxytriptycene in DMSO-d_6

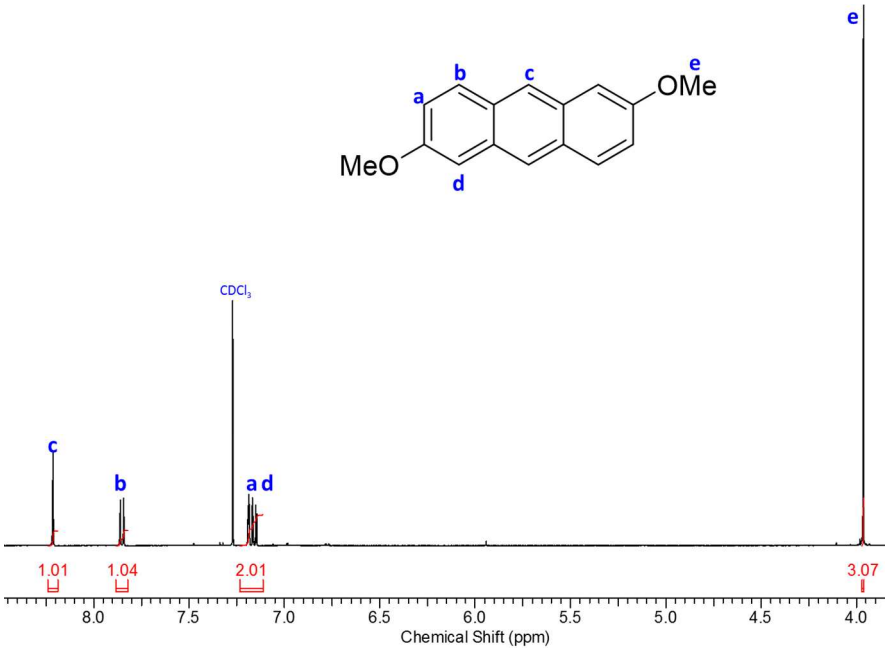


Figure S2. ^{1}H NMR spectrum of 2,6-dimethoxytriptycene in $CDCl_3$

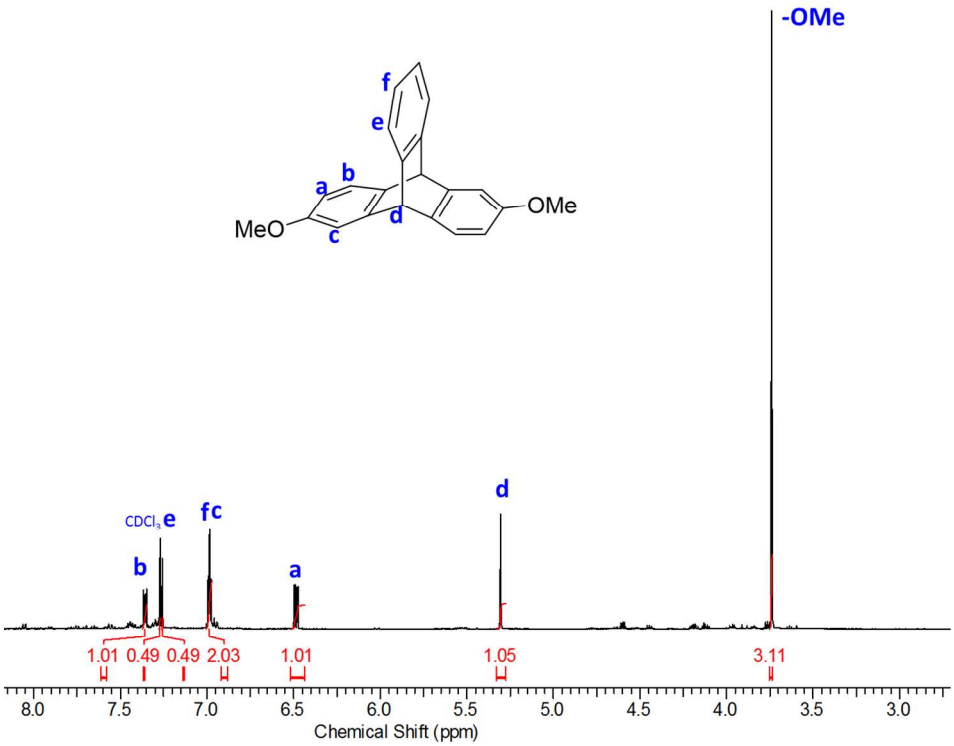


Figure S3. ^{1}H NMR spectrum of 2,6-dimethoxytriptycene in $CDCl_3$

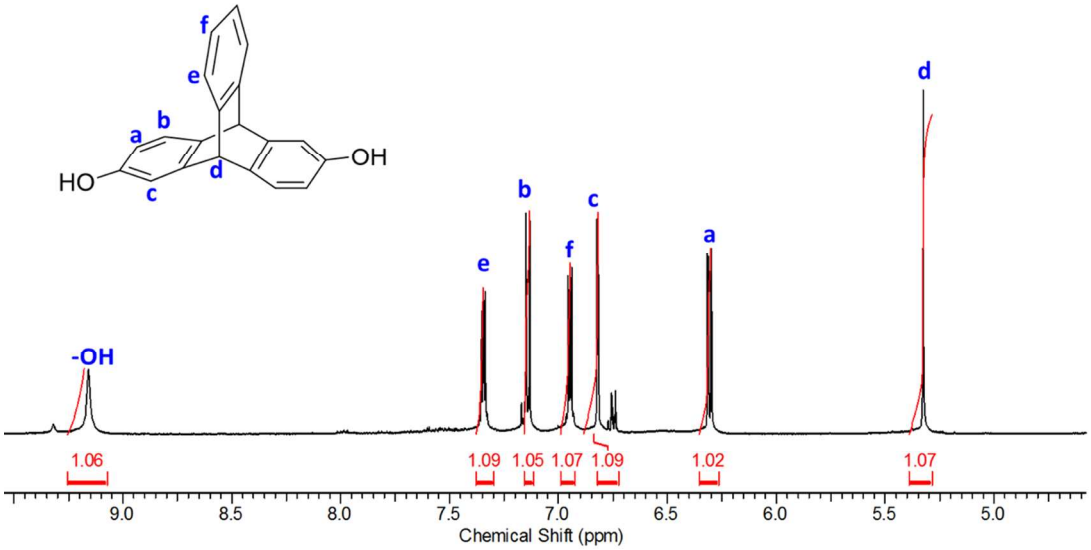


Figure S4. ^{1}H NMR spectrum of 2,6-dihydroxytriptycene in DMSO-d_6

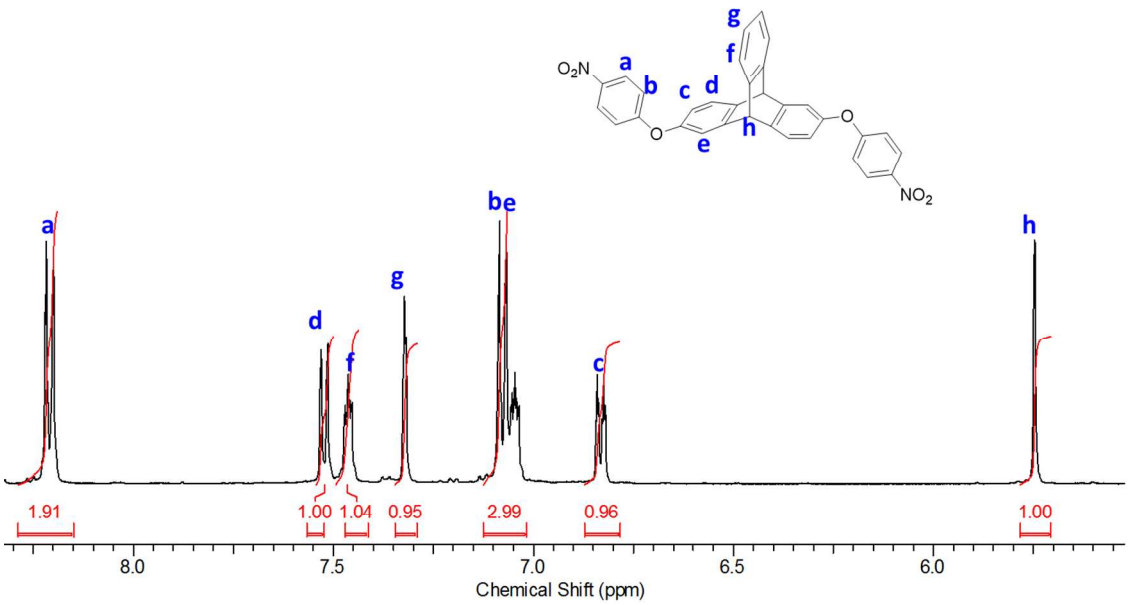


Figure S5. ^{1}H NMR spectrum of 2,6-bis(nitrophenoxy)triptycene in DMSO-d_6

Table S1: Pure gas permeabilities (Barrer) and selectivities at 3 atm and 35 °C.

	Permeability (barrer)		Selectivity	
Fresh	H_2	O_2	H_2/N_2	O_2/N_2
6FDA-1,4-trip_*ortho*	29	2	104	7.1
6FDA-2,6-trip_*para*	30	-	74	-

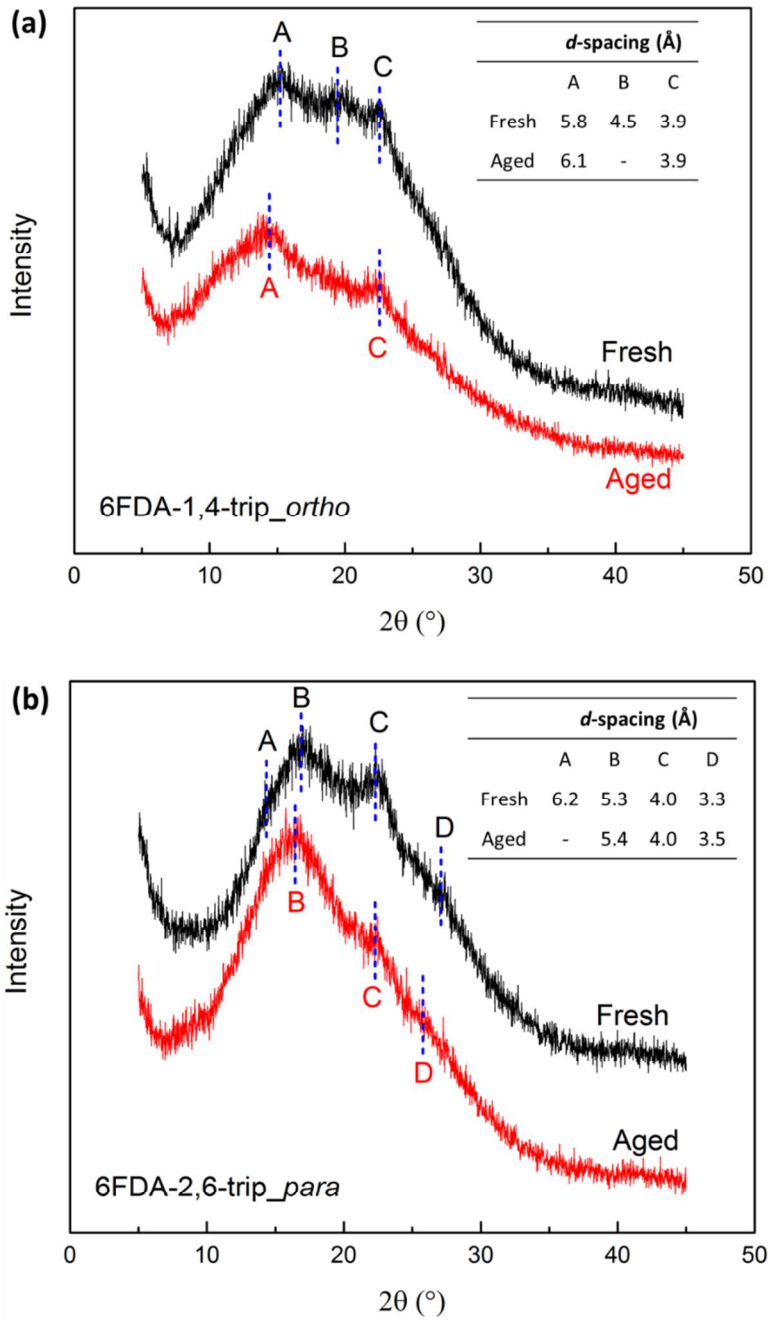


Figure S6. Wide-angle X-ray diffraction patterns of (a) fresh and aged (2.5 years) 6FDA-1,4-trip_*ortho* films and (b) fresh and aged (5 months) 6FDA-2,6-trip_*para* films.

References

[1] J.R. Wiegand, Z.P. Smith, Q. Liu, C.T. Patterson, B.D. Freeman, R. Guo, Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes, *J. Mater. Chem. A.* 2 (2014) 13309. doi:10.1039/C4TA02303J.