## **Supporting Information**

## Microporous Polyimides with Functional Groups for Adsorption of Carbon Dioxide and Organic Vapors

Guiyang Li,<sup>ab</sup> Biao Zhang,<sup>a</sup> Jun Yan<sup>a</sup> and Zhonggang Wang<sup>\*a</sup>

<sup>a</sup> Department of Polymer Science and Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

<sup>b</sup> Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, China

Email: zgwang@dlut.edu.cn

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Sample	Theoretical value			Measured value		
	С	Н	N	С	Н	Ν
MPI-6FA	63.11	2.52	4.67	62.54	2.73	4.29
API-6FA	65.56	3.21	4.25	64.98	3.22	4.11
MPI-BPA	75.99	3.58	6.22	73.52	3.76	5.39
MPI-BTA	74.21	3.17	5.87	72.49	3.72	5.29

**Table S1**. Elemental analysis data of microporous polyimides

**Table S2**  $K_H$ ,  $A_o$  and  $A_1$  values of CO<sub>2</sub> adsorption in the microporous polyimides.

Sample	T/K	<i>K<sub>H</sub></i> / mol/(g Pa)	$A_0 / \ln(\text{mol}/(\text{g Pa}))$	$A_1$ / g/mol
MPI-6FA	273	$1.481 \times 10^{-7}$	-15.508	-798.404
	298	$5.102 \times 10^{-8}$	-16.791	-666.895
API-6FA	273	1.113×10 <sup>-7</sup>	-16.011	-717.668
	298	3.592×10 <sup>-8</sup>	-17.142	-373.790
MPI-BPA	273	1.388×10 <sup>-7</sup>	-15.790	-904.057
	298	4.140×10 <sup>-8</sup>	-17.000	-673.458
MPI-BTA	273	$1.866 \times 10^{-7}$	-15.494	-1063.009
	298	$5.237 \times 10^{-8}$	-16.765	-876.878



Figure S1. X-ray diffractions of the four polyimide networks.



**Figure S2.** Experimental pure component isotherms for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> at 273 K (dot), and their single-site Langmuir-Freundlich fitting curves for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> (solid) for microporous polyimides.



**Figure S3.** IAST selectivities for  $0.15/0.85 \text{ CO}_2/\text{N}_2$  mixture ( $\blacksquare$ , blue) and  $0.05/0.95 \text{ CO}_2/\text{CH}_4$  mixture ( $\blacktriangle$ , red) for the four microporous polyimides.



**Figure S4.** Adsorption selectivities of  $CO_2$  over  $CH_4$  and  $N_2$  for MPI-6FA, API-6FA, MPI-BTA and MPI-BPA from initial slope calculated according to their adsorption isotherms of  $CO_2$  (blue),  $CH_4$  (red) and  $N_2$  (green) at 273 K.



Figure S5. Virial plots of CO<sub>2</sub> adsorption in microporous polyimides at 273 and 298 K.