## **Electronic Supplementary Information**

#### Amine post-functionalized POSS-based porous polymers exhibiting

### simultaneously enhanced porosity and carbon dioxide adsorption

#### properties

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Fig. S1. (a) The FT-IR spectra of HPP-1, HPP-1-EDA at 24 h and 72 h; (b) the FT-IR spectra were enlarged from 2000 cm<sup>-1</sup> to 800 cm<sup>-1</sup>



**Fig. S2.** (a) The FT-IR spectra of HPP-1, HPP-1-HDA at 24 h and 72 h; (b) the FT-IR spectra were enlarged from 2000 cm<sup>-1</sup> to 800 cm<sup>-1</sup>



Fig. S3. TGA curves of HPP-1, HPP-1-EDA and HPP-1-HDA under  $N_2$  at 10 °C min<sup>-</sup>

<sup>1</sup> from 30°C to 800°C



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Fig. S9 Ten cycles of CO<sub>2</sub> uptakes of HPP-1-EDA (a) and HPP-1-HDA (b) at 273 K.

After saturation, the sample was regenerated with a temperature swing to 80°C and

then under vacuum.

# Henry's Law selectivity of CO<sub>2</sub> over N<sub>2</sub> for HPP-1, HPP-1-EDA and HPP-1-HDA at 298 K

A nice fitting of  $CO_2$  and  $N_2$  isotherms has been calculated based on Toth isotherm model.<sup>[1,2]</sup>

$$q = q_{sat} \frac{b^{1/t} P}{(1+b^t)^{1/t}}$$

where q is the uptake in mmol  $g^{-1}$ ,  $q_{sat}$  is the saturation uptake in mmol  $g^{-1}$ , P is the pressure in torr, t and b are parameters which are specific for adsorbent pairs.

The Henry law constant K, quantifies the extent of the adsorption of a given adsorbate by a solid. The magnitude of K depends on the properties of both adsorbate and solid. For the Toth isotherm, the Henry law constant is defined by the following equation:

$$K = \lim_{P \to 0} \left(\frac{dq}{dP}\right) = b^{1/t} q_{sa}$$

Finally, the Henry's Law selectivity  $S_{\alpha/\beta}$  of gas  $\alpha$  over  $\beta$  is given by the following equation:



Fig. S10 Toth model fitting of  $CO_2$  (a) and  $N_2$  (b) adsorption isotherms of HPP-1 at



Fig. S11 Toth model fitting of CO<sub>2</sub> (a) and N<sub>2</sub> (b) adsorption isotherms of HPP-1-

EDA at 298 K



Fig. S12 Toth model fitting of  $CO_2$  (a) and  $N_2$  (b) adsorption isotherms of HPP-1-

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