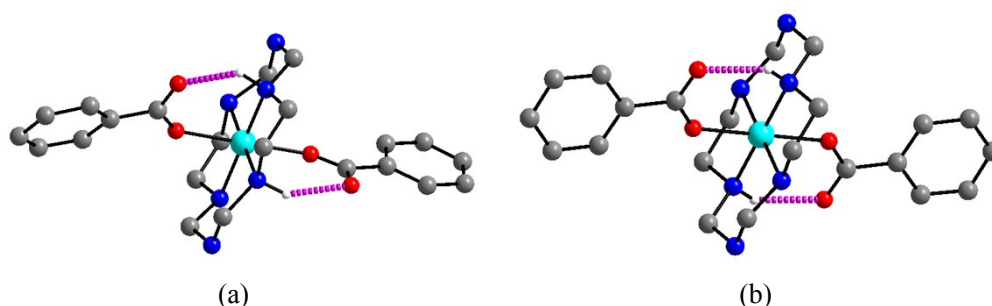


**Electronic supplementary information of:**  
**Tunable Gas Adsorption Property of Porous Coordination Polymers**  
**by the Modification of Macrocyclic Metallic Tecton**

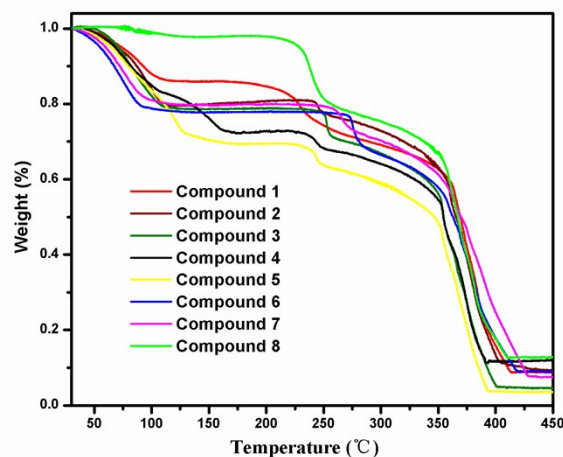
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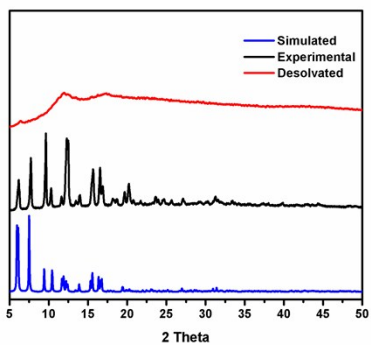


**Fig. S1.** The formed N-H...O<sub>carboxylate</sub> hydrogen bonds extend in different directions. Mode (a) in compounds **1-3** and **8**, mode (b) in compounds **4-7**.

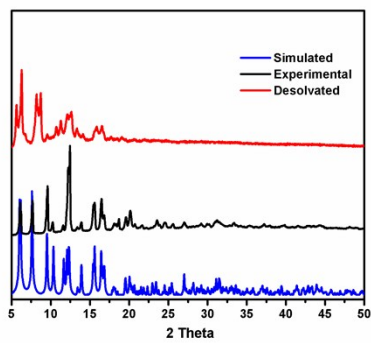


**Fig. S2.** TGA curves of compounds **1-8**. TGA of **1-8** demonstrate that they lose all guests in the range of 30-100°C (found 13.5%, calculated 13.1% for **1-7H<sub>2</sub>O**), 30-100°C (found 19.6%, calculated 19.8% for **2**), 30-100°C (found 21.2%, calculated 20.0% for **3**), 30-160°C (found 28.1%, calculated 27.6% for **4**), 30-130°C (found 27.9%, calculated 26.4% for **5**), 30-100°C (found 22.1%, calculated 21.8% for **6**), 30-100°C (found 20.3%, calculated 19.7% for **7**) and 30-120°C (found 2.3%, calculated 5.0% for **8**), respectively.

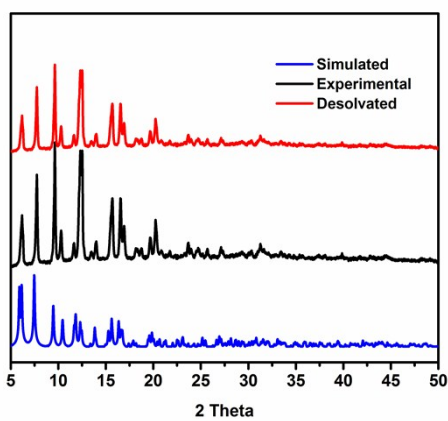
(a)



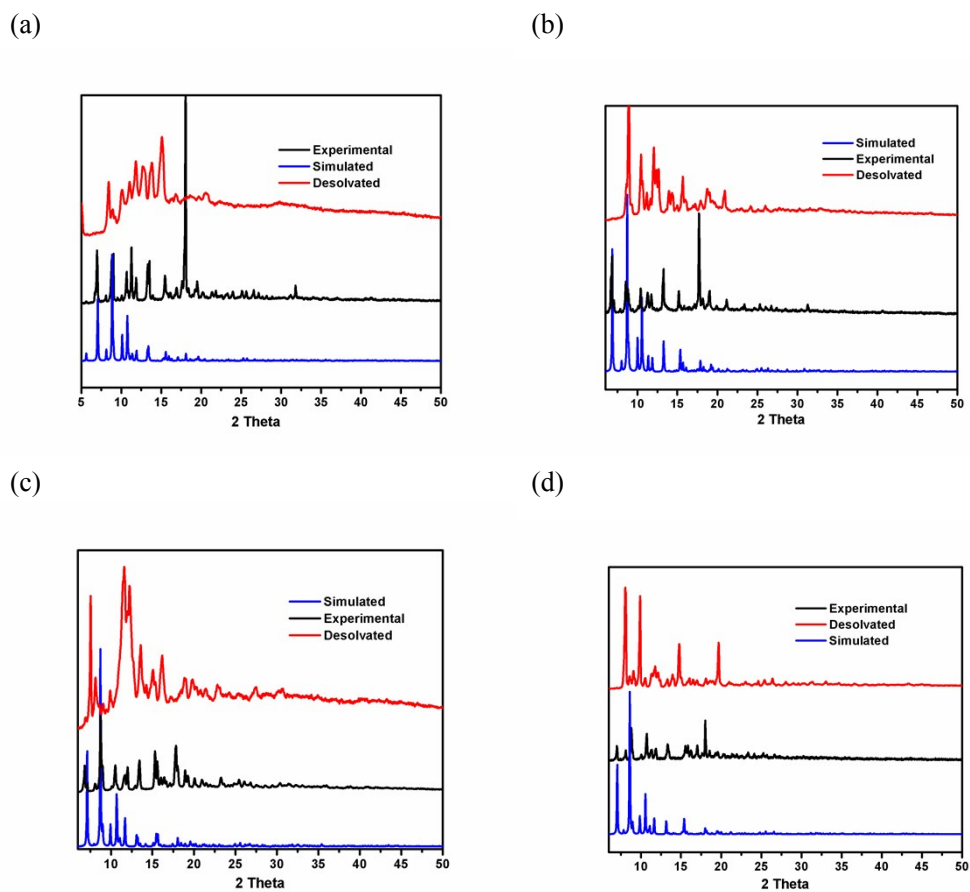
(b)



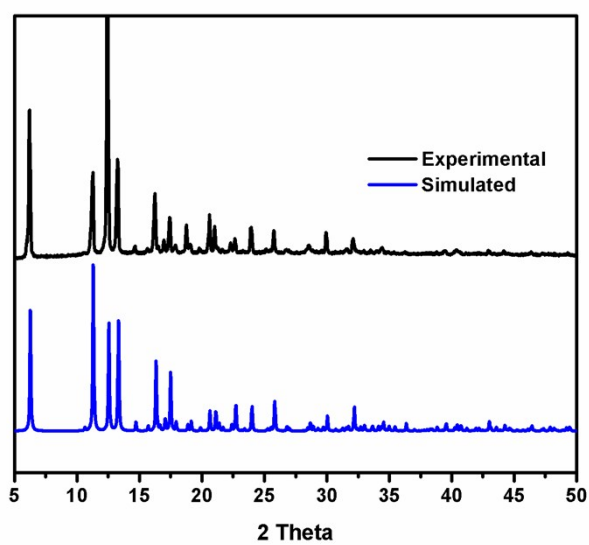
(c)



**Fig. S3.** XRD of simulated, experimental and desolvated compounds **1** (a), **2** (b) and **3** (c).

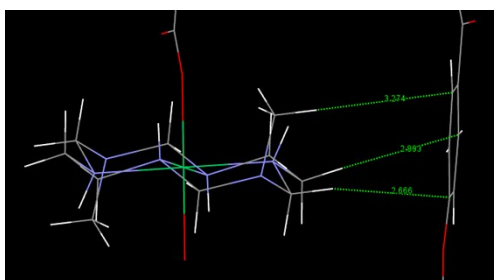


**Fig. S4.** XRD of simulated, experimental and desolvated compounds **4** (a), **5** (b), **6** (c) and **7** (d).

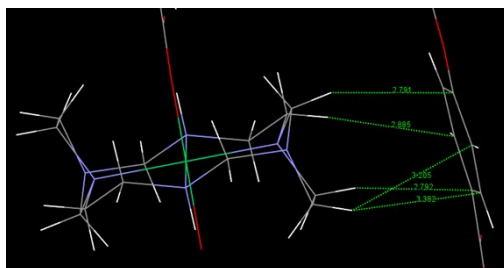


**Fig. S5.** XRD of simulated and experimental compound **8**.

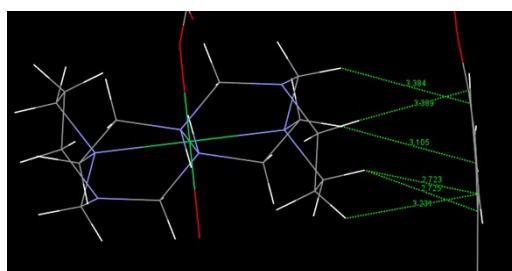
(a)



(b)

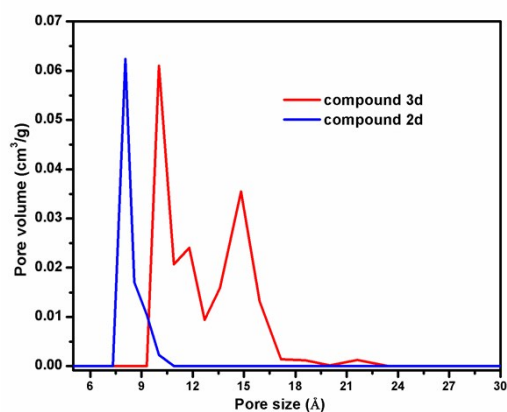


(c)



**Fig. S6.** Multipoint C-H... $\pi$  interactions in compounds **1**(a), **2**(b) and **3**(c).

(a)



(b)



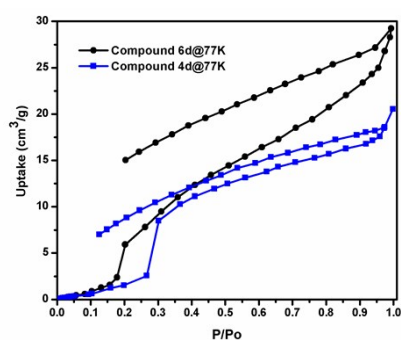
(c)



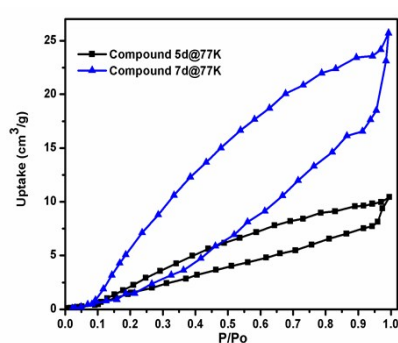
(d)



**Fig. S7.** (a) NLDFT pore size distribution of compound **2d** (blue) and compound **3d** (red). The unusually large pore sizes in compound **3d** (15 Å and 22 Å) should be related to the small size of the crystals, as shown in (b). Despite slow diffusion method is utilized, the crystal size is still not large enough, as shown in (c and d). When the sample **3d** with a small crystal size was used to measure the adsorption property, interstitial pores cannot be eliminated. As a result, some unusually large pore size and hysteresis were observed. As for other compounds, the crystals are large enough to avoid this problem.



(a)

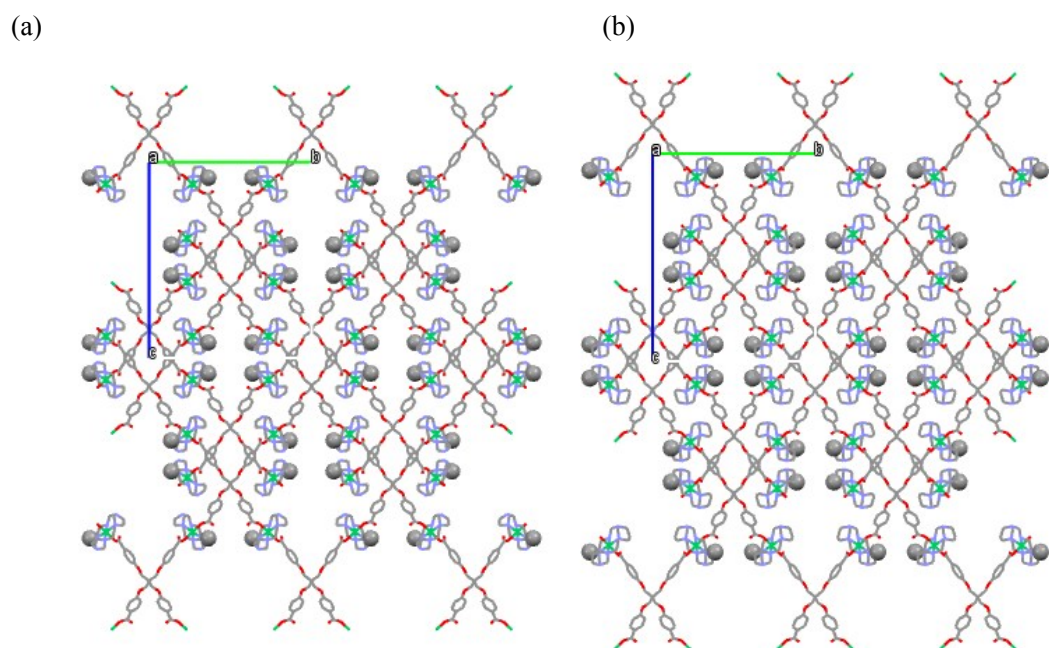


(b)

**Fig. S8.** N<sub>2</sub> sorption isotherms for compound **4d** and **6d** at 77 K (a). N<sub>2</sub> sorption isotherms for compounds **5d** and **7d** at 77 K (b).

The N<sub>2</sub> adsorption isotherms of **4d** and **6d** at 77 K exhibited two steps (Figure S8a). Multistep adsorption behavior in PCPs is ascribed to the structural transformation during the gas adsorption. And the transition pressure called gate opening pressure, which is 0.2 for **4d** and 0.3 for **6d**. The discrepancy of gate opening pressure is derived from the slighter different structure of the macrocyclic ligands L<sup>4</sup> and L<sup>6</sup>. Before the gate opening pressure, shrunk framework can't contain N<sub>2</sub> due to the small pore size. However, above the gate opening pressure, the pore size is expanded by the interaction of N<sub>2</sub>. Hence, it shows abrupt adsorption curve. The conclusion also can be proved by other macrocyclic metallic tectons based porous coordination polymers by using in-situ XRD measurements.<sup>S1</sup> In contrast to **4d** and **6d**, the N<sub>2</sub> sorption isotherm of **5d** and **7d** at 77 K show the absence of obvious multistep adsorption (Figure S8b). This difference could be due to the -CH<sub>3</sub> groups' supporting force of **5d** and **7d** after guest removal, which can be deduced from the single-crystal structures. Because the -CH<sub>3</sub> groups protruded into the pores (Figure S9), after activation, the deformation of **5d/7d** is smaller than **4d/6d**. Hence, the abrupt change of adsorption is not obvious. Compounds **4d-7d** show hysteresis in desorption of N<sub>2</sub>, also indicating the structural flexibility of the framework.

[S1] H. S. Choi and M. P. Suh, *Angew. Chem. Int. Ed.* 2009, **48**, 6865.

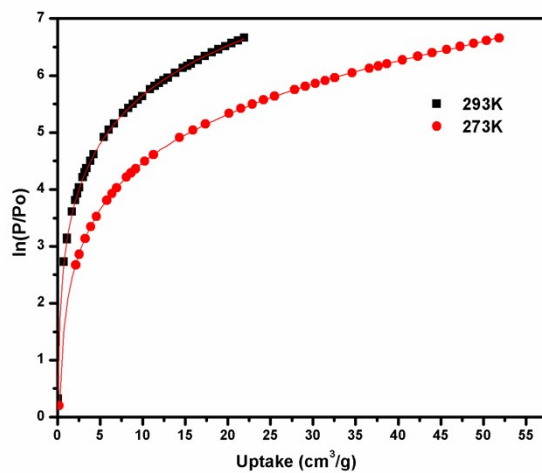


**Fig. S9.** The  $\text{-CH}_3$  groups decorated porous surface in compound **5** (a) and **7** (b), grey balls represent  $\text{-CH}_3$  groups.

### Calculation of sorption heat for CO<sub>2</sub> uptake using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad Q_{st} = -R \sum_{i=0}^m a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **3** at 273 and 293 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a<sub>i</sub> and b<sub>i</sub> are virial coefficients, and m and N are the number of coefficients used to describe the isotherms. Q<sub>st</sub> is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.



**Fig. S10.** CO<sub>2</sub> adsorption isotherms for compound **3d** with fitting by Virial 2 model. Fitting results: a<sub>0</sub> = -4455.35711, a<sub>1</sub> = -31.56418, a<sub>2</sub> = 0.19003, a<sub>3</sub> = 0.03293, a<sub>4</sub> = -0.000590541, a<sub>5</sub> = -4.05848E-6, b<sub>0</sub> = 18.13594, b<sub>1</sub> = 0.17328, b<sub>2</sub> = -0.00398; R<sup>2</sup> = 0.9997.



### IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO<sub>2</sub> and N<sub>2</sub> (measured at 273K) were fitted using a Langmuir-Freundlich (L-F) model:

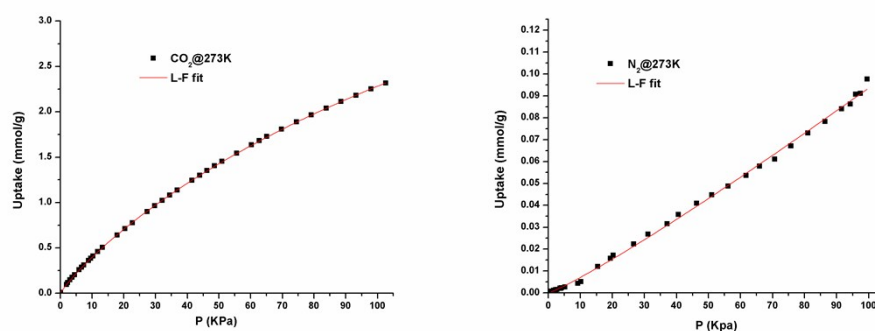
$$q = \frac{a * b * P^c}{1 + b * P^c}$$

Where  $q$  and  $P$  are adsorbed amounts and pressures of component  $i$ , respectively.

The adsorption selectivities for binary mixtures of CO<sub>2</sub>/N<sub>2</sub>, defined by:

$$S_{ij} = \frac{x_i * y_j}{x_j * y_i}$$

data were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz. Where  $x_i$  is the mole fraction of component  $i$  in the adsorbed phase and  $y_i$  is the mole fraction of component  $i$  in the bulk.



**Fig. S11.** CO<sub>2</sub> adsorption isotherms of compound **3a** with fitting by L-F model:  $a = 7.65337$ ,  $b = 0.00708$ ,  $c = 0.88927$ ,  $R^2 = 0.99997$ ;

N<sub>2</sub> adsorption isotherms of compound **3a** with fitting by L-F model:  $a = 0.886745$ ,  $b = 5.98477E-5$ ,  $c = 1.12548$ ,  $R^2 = 0.99808$ .