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Electronic Supplementary Material

Metal-organic framework MIL-101(Cr) as sorbent of porous membrane- protected micro-solid-phase extraction for the analysis of six phthalate esters from drinking water: a combination of experimental and computational study

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1. Chemical structures, three-dimensional structures and molecular epidermis structures of six PAEs.

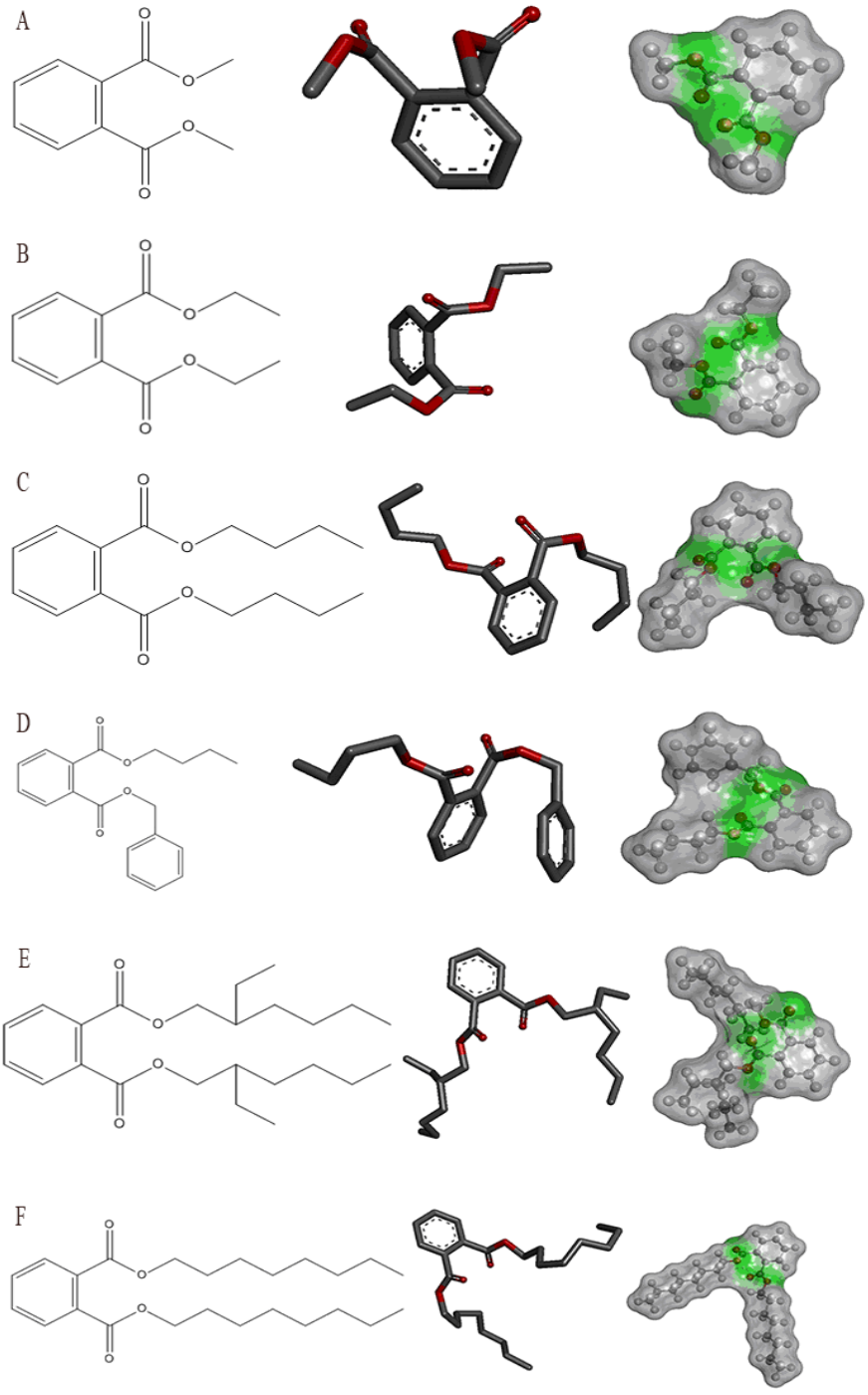


Fig.S1 Chemical structures, three-dimensional structures and molecular epidermis structures of six PAEs. A. DMP, B. DEP, C. DBP, D. BBP, E. DEHP and F. DNOP.

2. MOF crystal structures of MIL-101(Cr) and MIL-100(Fe).

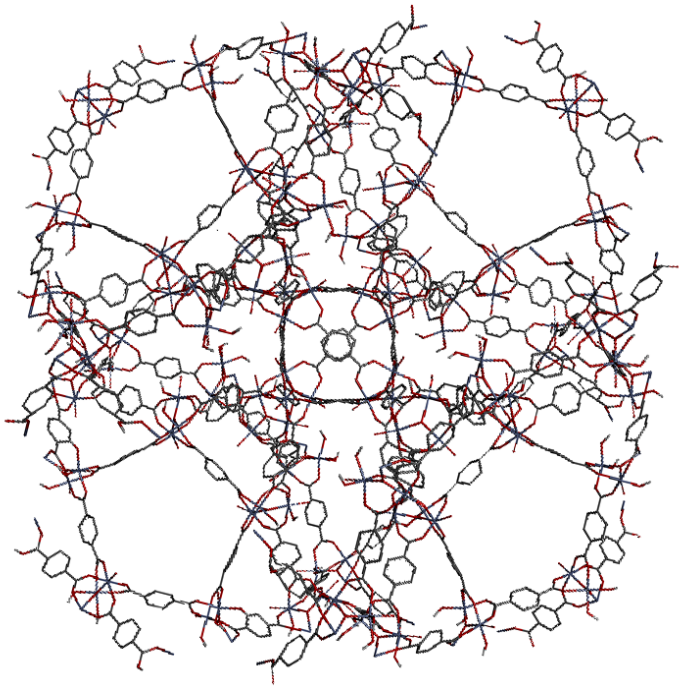


Fig.S2 (A) Structures of MIL-101.

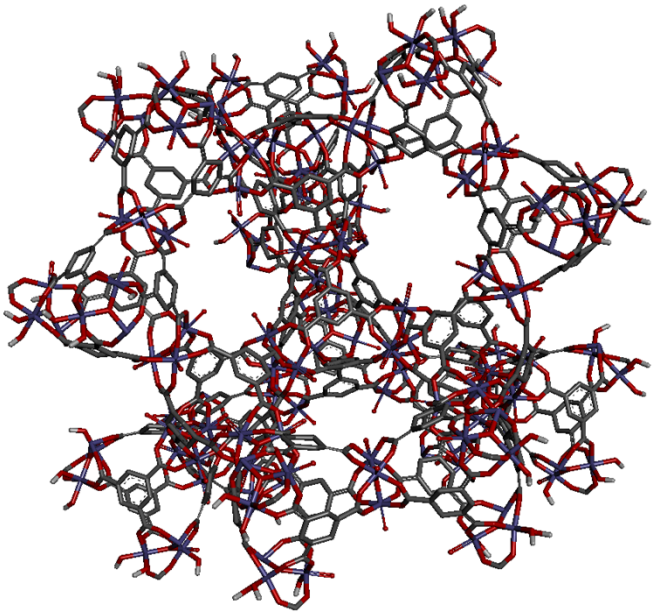


Fig.S2 (B) Structures of MIL-100.

Two types of MOF crystal structures of MIL-101(Cr) and MIL-100(Fe) were taken from the Cambridge Crystallographic Data Centre (CCDC). These MOFs were modeled by all-atom rigid frameworks of single unit cell.

3. Synthesis of MIL-100(Fe).

MIL-100(Fe) was synthesized by hydrothermal methods following reference [1] reported by Férey et al along with a slight modification: 1,3,5-BTC (687.5 mg), iron powder (299.5 mg), hydrofluoric acid (0.2 mL) and concentrated nitric acid (0.19 mL) were mixed with ultrapure water (20 mL). The obtained mixture was transferred to a Teflon lined bomb. Then, the Teflon lined bomb was sealed, placed in an oven and heated at 150 °C for 12 h. The light orange solid product was obtained by filtration and washed with ultrapure water. The as-synthesized MIL-100(Fe) was further purified by a two-step procedure using hot water and ethanol. The highly purified MIL-100(Fe) was evacuated in vacuum at 150 °C for 12 h to form activated MIL-100(Fe).

4. Characterization of stability of MIL-101(Cr).

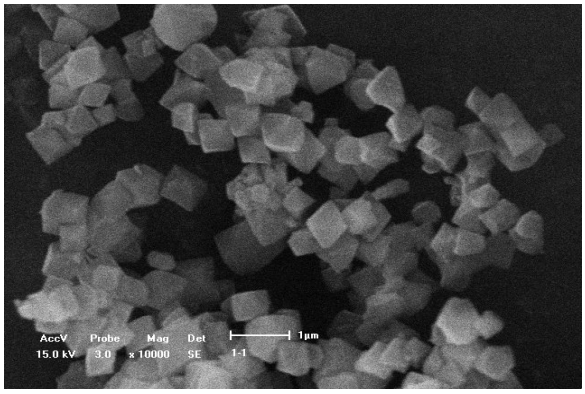
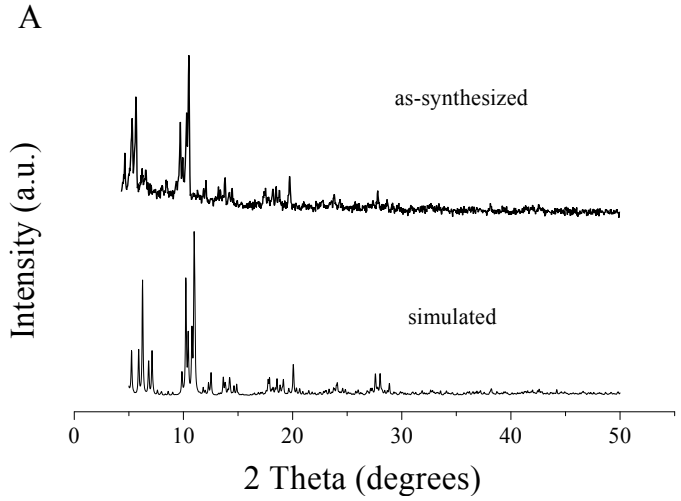
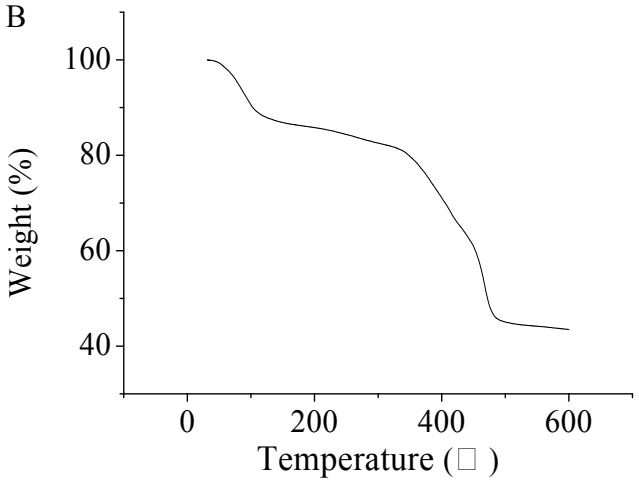


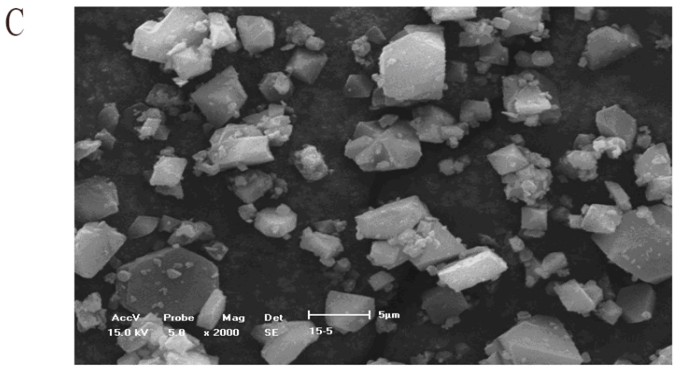
Fig. S3 SEM image of MIL-101(Cr) after 50 cycles of μ-SPE extraction.

The SEM images (Fig. S3) of MIL-101(Cr) after 50 cycles of μ-SPE experiments indicated that the structure of MIL-101(Cr) did not undergo any significant change.

5. Characterization of MIL-100(Fe).







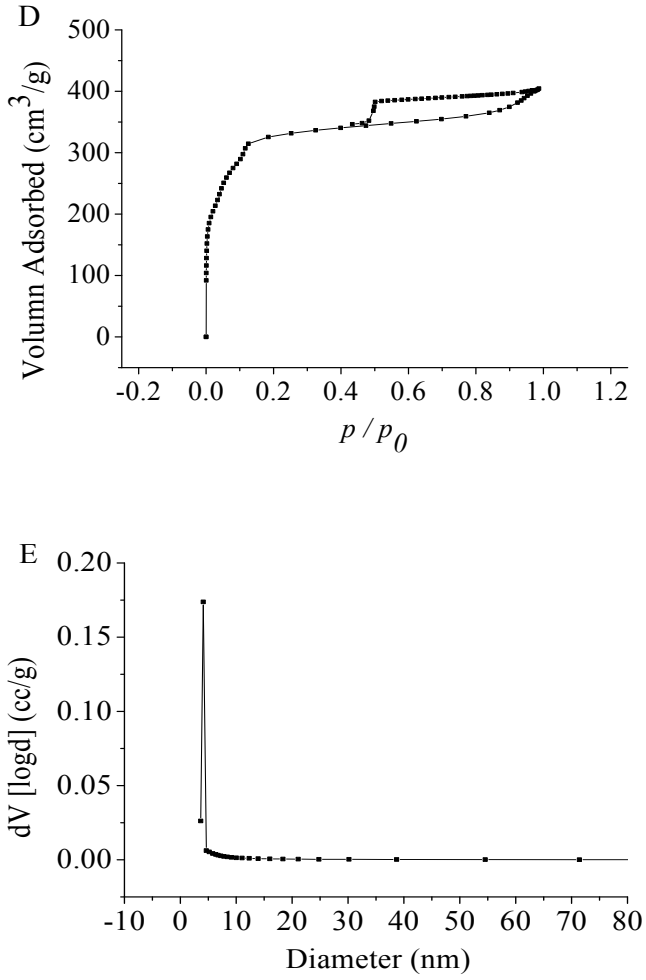


Fig. S4 (A) Comparison of the XRD pattern of the synthesized MIL-100(Fe) with the simulated one obtained by importing the crystal structure data cited in Reference No. 2 into the software of Mercury 1.4; (B) TGA curve of the synthesized MIL-100(Fe); (C) SEM image of the synthesized MIL-100(Fe); (D) N_2 adsorption-desorption isotherms of MIL-100(Fe); (E) The pore size distribution of the synthesized MIL-100(Fe).

The prepared MIL-100(Fe) was characterized by X-ray diffraction (XRD), TGA, scanning electron microscope (SEM), and N_2 adsorption-desorption test (Fig. S3).

The experimental XRD pattern of the synthesized MIL-100(Fe) was in good agreement with the simulated one, showing the successful preparation of MIL-

100(Fe). The prepared MIL-100(Fe) gave a BET surface area of 1225.53 m^2 g^{-1} with a pore volume of 0.6224 cm^3 g^{-1}. The TGA data revealed that the MIL-101(Cr) is stable up to 340 °C.

6. Characterization of activated carbon.

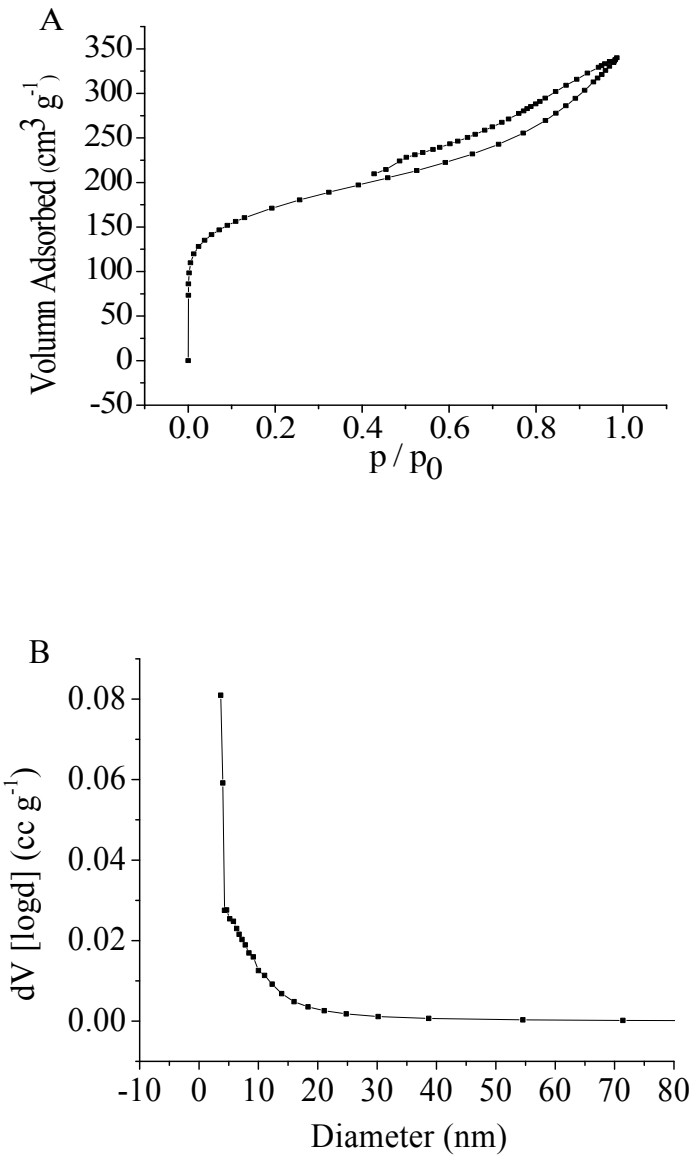


Fig.S5 (A) N_2 adsorption-desorption isotherms and (B) pore size distribution of activated carbon.

The activated carbon gave a BET surface area of 608.45 m^2 g^{-1} with a pore volume of 0.5217 cm^3 g^{-1}.

7. Adsorptive capacity between MIL-101(Cr) and PAEs.

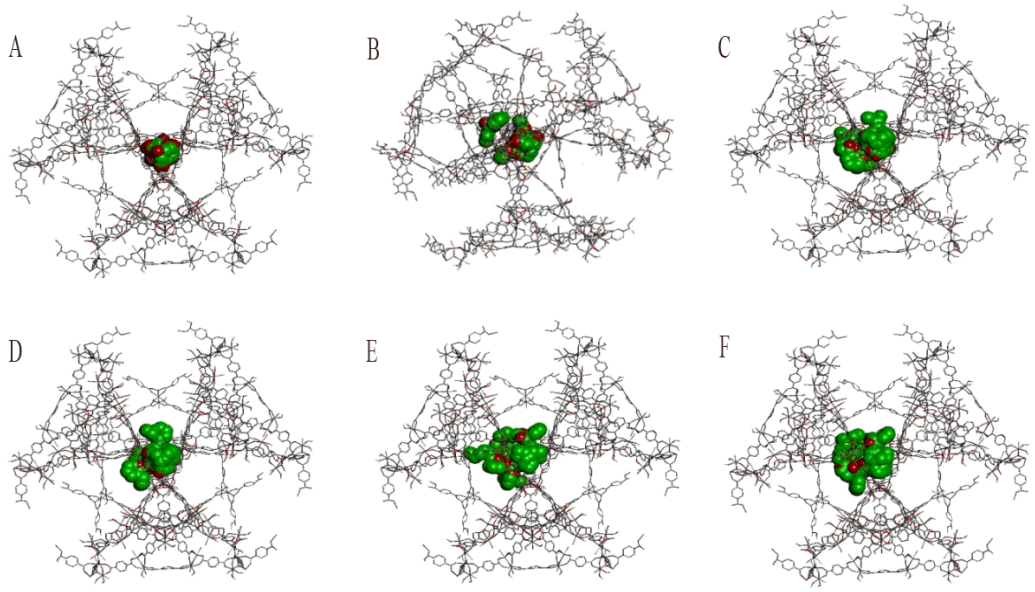


Fig. S6 Adsorptive capacity between MIL-101(Cr) and PAEs. MIL-101(Cr) binding with DMP (A), DEP (B), DBP (C), BBP (D), DEHP (E) and DNOP (F).

The adsorption capacity of the MOFs targeted on the specific PAEs was determined by putting several conformations of the PAEs with high adsorption efficiency on the same position of the MOFs at the same time. Fig.S6 shows the number of the better conformations for DMP, DEP, DBP, BBP, DEHP and DNOP combined with MIL-101(Cr) were 5, 6, 9, 7, 5 and 6 types, respectively. All of the conformations of PAEs were involved in the same district except DEP. There were two districts in the action spots in the case of DEP. Therefore, the adsorption capacity of MIL-101(Cr) towards BBP, DBP, DEHP, DMP, DNOP was 1 and the molar ratio of the host and the guest was 1:1; while, the adsorption capacity of MIL-101(Cr) towards DEP was 2 and the molar ratio of the host and the guest was 1:2.

Adsorption experiments were carried out with two phthalates (DMP and DEP) and a MOF material MIL-101(Cr). Upon the same extraction and analysis condition described in the manuscript, various concentrations of DMP (10, 60, 100, 120, 135, 140, 150, 160, 200 mg L^{-1} in water) and DEP (50, 150, 200, 250, 280, 300, 320, 350, 400 mg L^{-1} in water) were prepared, respectively. 10 mg of MIL-101(Cr) were used to adsorb the DMP or DEP by shaking for 12 h at room temperature. And then, the methanol desorption solution were analyzed by GC-MS method. The adsorption capacity (Q, mg g^{-1}) was calculated using the ratio of the mass of analytes to the mass of MIL-101(Cr). The relationships of adsorption capacities of MIL-101(Cr) towards DMP or DEP to the concentrations of DMP or DEP were presented in Fig. S7 and Fig. S8. It can be seen from the curves that the capacities of MIL-101(Cr) towards the two phthalates increased obviously with raising the initial concentrations of PAEs. And the maximum adsorption capacities of 285 mg g^{-1} for DMP and 603 mg g^{-1} for DEP were reached, respectively. It has been also noted that the maximum molar capacity of the DEP adsorbed by MIL-101(Cr) is around 1.8 times greater than DMP adsorbed by MIL-101(Cr) under the experimental conditions. While, in the molecular docking, the maximum molar capacity of the DEP adsorbed by MIL-101(Cr) was around 2 times greater than DMP adsorbed by MIL-101(Cr).

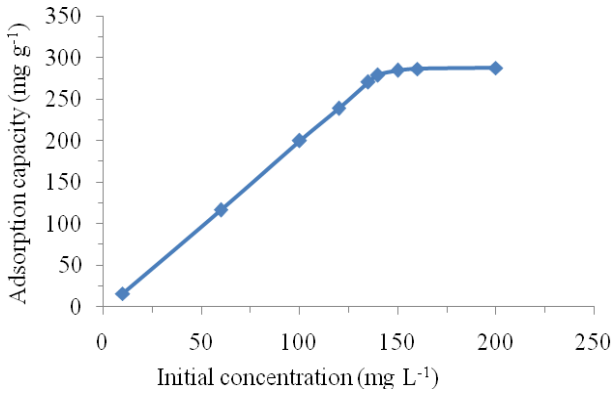


Fig. S7 Adsorption saturation curves of MIL-101(Cr) for DMP.

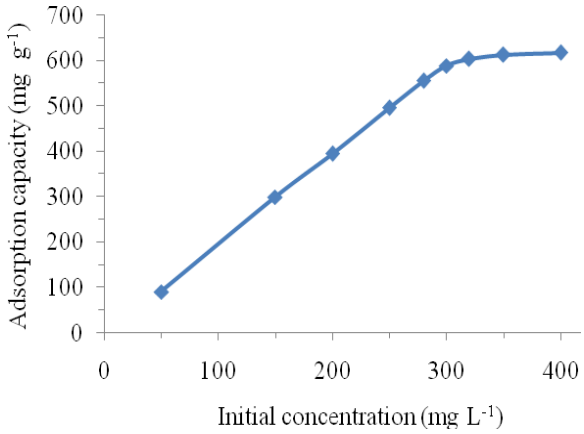


Fig. S8 Adsorption saturation curves of MIL-101(Cr) for DEP.

Higher adsorption capacity was obtained in the experiment than in the computational simulation. This could be due to many other possible interactions except the best adsorption sites of MIL-101(Cr) and PAEs. All of minor adsorption sites would facilitate and promote the adsorption behaviors of PAEs on the surface of porous MIL-101(Cr) in concert. However, we have chosen the highest density adsorption sites in molecular docking process. So our experimental values were higher than the calculated adsorption.

8. Adsorptive capacity between MIL-100 and PAEs.

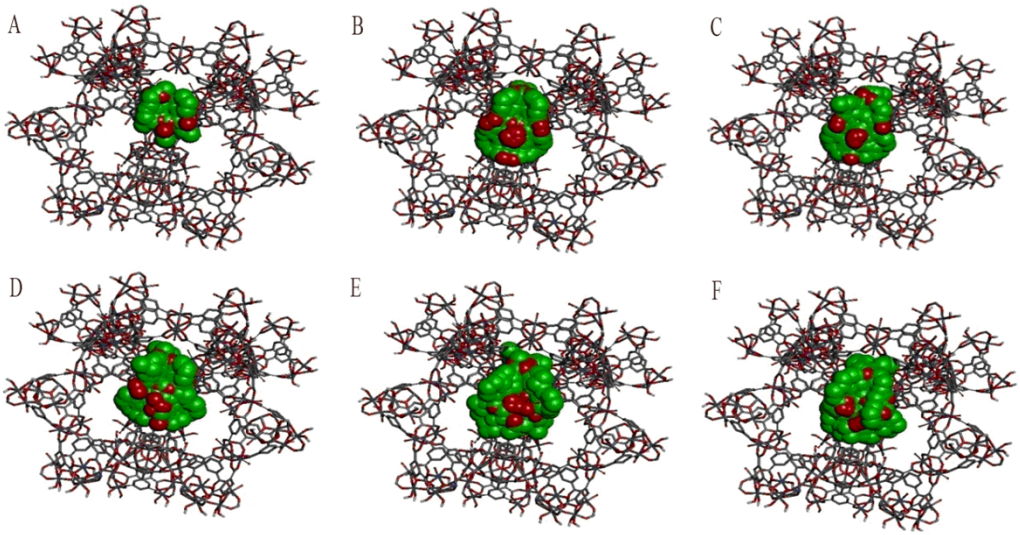


Fig.S9 Adsorptive capacity between MIL-100(Fe) and PAEs. MIL-100(Fe) binding with DMP (A), DEP (B), DBP (C), BBP (D), DEHP (E) and DNOP (F).

Fig.S9 shows the number of the better conformations for DMP, DEP, DBP, BBP, DEHP and DNOP combined with MIL-100(Fe) were 4, 10, 6, 8, 8 and 9 types, respectively. All of the conformations of PAEs were involved in the same district. Therefore, the adsorption capacity of MIL-100(Fe) towards all of the PAEs was 1 and the molar ratio of the host and the guest was 1:1.

9. References.

[1] J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues **and** G. Férey, *Angew. Chem. Int. Ed.* 2010, **49**, 5949-5952.

[2] P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki **and** G. Férey, *Chem. Commun.* 2007, **27**, 2820-2822.