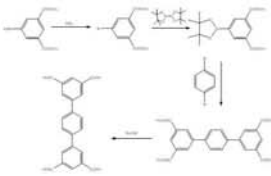
Solvothermal Synthesis of a Novel 3D Microporous Transition Metal-Organic Framework

*Jianfeng Cai, Guodong Qian**
Department of Materials Science and Engineering, State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China
E-mail: gdqian@zju.edu.cn; Tel. : +86-571-87952334; Fax: +86-571-87951234

Abstract: A new three-dimensional (3D) zinc based metal-organic frameworks (MOFs) containing terphenyl-3,3",5,5"-tetracarboxylic acid (TPTC) have been synthesized solvothermally and characterized by single crystal X-ray diffraction. $Zn_2(TPTC)(H_2O)_2$ (ZnTPTC), which crystallizes in the space group R−3m (a = 19.1771(7) Å, b = 19.1771(7) Å, c = 37.6412(13) Å, α = 90.00(4) ° , β= 90.00(4) ° , γ = 120(4) °), Pairs of Zn^{II} centers are bridged by four carboxylate groups, forming $\{Zn_2(O_2CR)_4\}$ paddle-wheel units. One H_2O molecule binds to each metal center along the paddle-wheel axis. Each $\{Zn_2(O_2CR)_4\}$ paddlewheel is linked to four terphenyl connectors, to give frameworks with NbO-type topologies. Interestingly, it can exhibit high Showed high thermal stability and will be an excellent framework of gas adsorption.



Scheme 1. The synthetic routes of TPTC

^{1}HNMR ([D_6] DMSO, 500 MHz): δ = 8.48 (t, J = 1.6 Hz, 1H), 8.44 (d, J = 2.1 Hz, 2H), 7.91 ppm (s, 2H);
Elemental analysis (%) calcd for TPTC($C_{22}O_8H_{14}$): C 65.03, H 3.47; found: C 64.87, H 3.59

The synthetic of ZnTPTC: a mixture of $Zn(NO_3)\cdot 6H_2O$ (1.5mg , 50 μmol) and TPTC (5 mg, 12.3 μmol) was suspended in 1.1 ml DMF/MeCN (10:1), and heated in a teflon (3 ml) vessel at 90° C for 48h

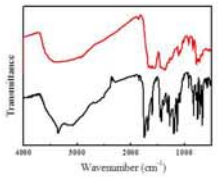


Fig 1. FT-IR of TPTC and ZnTPTC

IR spectrum shows that the C=O stretching peak at 1750cm^{-1} in TPTC shifted to 1655cm^{-1} in ZnTPTC, which indicated that the reaction of carboxylic group and Zn^{2+}.

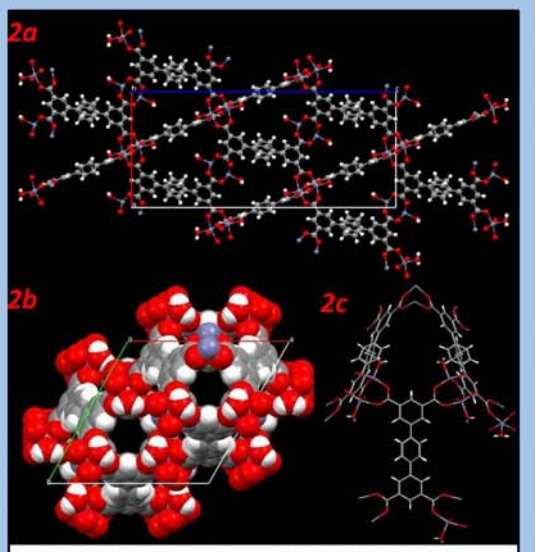
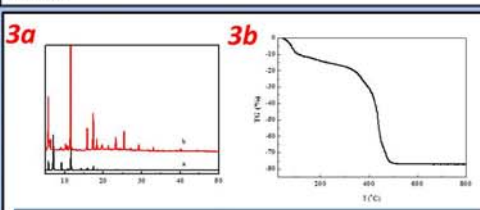


Fig 2. Crystal structure of ZnTPTC , Zn, blue; O, red; C, grey; H, white

The diameters of the channels are predefined by the geometry of $\{Zn_2(O_2CR)_4\}$ units and the span of the dicarboxylato moieties of the isophthalate groups on each terminus of the bridging ligands.
The diameters of the channels is approximately 0.5nm.



3a The experimental XRD patterns agreed well with the simulated for ZnTPTC
3b shows the weight loss of uncoordinated and coordinated water moleculesin the temperature range of ~90° C. The host framework is stable up to ca. 320° C.

Conclusion

- A Novel 3D zinc MOF, $Zn_2(TPTC)(H_2O)_2$, was synthesized by solvothermal reaction
- ZnTPTC has high thermal stability up to 320° C
- The diameters of the channels is approximately 0.5nm, and it will be an excellent framework for gas adsorption

研究所：无机所
导师：钱国栋
姓名：蔡建锋