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Serrated Single-Wall Metal-Organic Nanotubes (SWMONTs) for Benzene Adsorption

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Abstract: A self-assembled functionalized metal-organic nanotubes, compound **1** has been hydrothermally synthesized using 5-(3-methyl-5-phenyl-4*H*-1, 2, 4-triazol-4-yl) isophthalic acid (H_2**L**) with Zn(II) ions. Compound **1** possesses one dimensional (1D) nanotubular architecture. Luminescent studies show that compound **1** displays strong blue emission at room temperature. Benzene adsorption results show t that the latter adsorbed benzene only on the outside walls, while the former adsorbed benzene also on the inside walls since the holes through the walls enabled benzene to reach the inside tubules.

Since the discovery of carbon nanotubes (CNTs) in 1991, discrete nanotubular materials emerged as an attractive topic, because the inner and outer spaces of such compounds exhibit exclusive properties and can be exploited for a variety of applications in nanotechnology and materials science [1]. Metal-organic frameworks (MOFs) are known as porous organic-inorganic hybrid materials, usually identified as a subgroup of complexes. MOFs are becoming an advanced research hotspot in chemical and materials sciences, due to the interesting structural topologies and their potential as functional materials in structure-dependent applications, such as gas storage and separation, sensing, catalysis, and drug delivery [2, 21-25]. Lots of organic, inorganic, and biologic materials have been used for the construction of synthetic nanotubes(SNTs). CNTs and SNTs represent a remarkable class of functional materials due to their applications in gas storage, separation, catalysis and sensors [3-6]. Synthetic nanotubes(SNTs), especially single-wall metal-organic nanotubes(SWMONTs) are not much explored so far. A few single-wall metal-organic nanotubes(SWMONTs) have been synthesized and crystallographically characterized. Some SWMONTs show interesting catalytic properties. For instance, Wu et al reported assembly and post-modification of a metal-organic nanotube(MONT) by linking up the bent organic ligands and the tetra-coordinated zinc cations for highly efficient catalysis [7]. While some other literatures only reported synthesis of SWMONTs. Garcia et al reported a single-walled metal-organic nanotube, $\{[Cu_3(\mu_3\text{-}OH)(H_2O)_3(Glytrz)_3]\cdot SiF_6\cdot 8H_2O\cdot X\}_\infty$, built from a simple synthon [8]. Xiao et al reported a 4-connected anionic metal-organic nanotube constructed from indium isophthalate, type, commonly observed in 4-connected structures such as SiO_2. Three In^{3+} sites are alternatively connected into a ring by three 1,3-BDC anions. These rings are stacked along the unit cell *c* axis forming an infinite tube [9]. Lu et al reported an unusual cobalt(II)-based single-walled metal-organic nanotube, in which a two-side-open box that acts as a secondary building unit (SBU) [10]. Zheng et al reported a novel 1D independent metal-organic nanotube based on cyclotriveratrylene ligand [11].

On the other hand, only a few SWMONTs show adsorption properties. Sun et al self-assembled an interesting SWMONT by threading molecular squares (formed by Zn^{II} and 4,4'-bipyridine) infinitely with the 5-amino-2,4,6-triiodoisophthalic acid ligand; interestingly it showed high thermal stability as well as reversible and fast adsorption of $(H_2O)_{12}$ cluster [12]. Navrotsky et al reported a porous metal-organic nanotube and its unique water exchange and uptake, which has been investigated by acid solution calorimetry, thermal analysis, and water adsorption calorimetry [13].

A lot of MOFs have been tested for the adsorption of small

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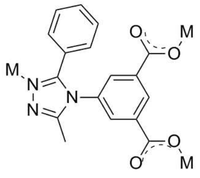
molecules in the vapor phase, and some of them revealed significant adsorption selectivity and separation potential. It is well known that benzene, as a very important chemical, is a typical volatile organic compound (VOC) of great social and environmental significance [14]. The preferential adsorption of benzene is usually due to the size/shape-based selective adsorption in a rigid MOF. While hydrophobic effect between sorbates and pore surfaces of MOFs could also be used to clarify the preferential adsorption in MOFs. It was demonstrated that these hydrophobic channels only allow organic solvent molecules to be adsorbed while excluding H_2O [15]. Herein, we report the synthesis of one self-assembled functionalized SWMONTs, $[Zn(\mathbf{L})(H_2O)]_n{\cdot}nH_2O$ (**1**) based on 5-(3-methyl-5-phenyl-4*H*-1, 2, 4-triazol-4-yl) isophthalic acid ($H_2\mathbf{L}$), with 1D channels of about 10.88×6.92×15.10 $Å^3$. Serrated phenyl structure could be seen on inner wall of SWMONTs. Based on the structure of SWMONTs, benzene adsorption could be investigated.

In compound **1**, the ligand $\mathbf{L}^{2-}$ presents one coordination mode (see Scheme 1: configuration μ3). Compound **1** crystallized in the rhombohedral system with the *R-3* space group. As shown in Figure 1a, the asymmetric unit of **1** consists of one crystallographically independent Zn(II) ion, one $\mathbf{L}^{2-}$ ligand, one coordinated water molecule and one lattice water molecule. Each Zn(II) atom is coordinated in a tetrahedron defined by three oxygen atoms from two different $\mathbf{L}^{2-}$ ligands and one coordinated water molecule (Zn1-O3A, 1.949(2) Å; Zn1-O1, 1.977(3) Å; Zn1-O5, 1.991(3) Å) and one nitrogen atom from another $\mathbf{L}^{2-}$ ligand (Zn1-N3B, 2.037(3) Å). The $\mathbf{L}^{2-}$ ligands and Zn(II) ions connected to 1D tube (Figure 1b)., which could be described as hexagonal structure along the ab-plane. There exist 1D channels of about 10.88×6.92×15.10 $Å^3$, which are filled with free water molecules. Serrated phenyl structure could be seen on inner wall of SWMONTs along the bc-plane (Figure S1). Three benzene rings are in a plane. No literature has been reported that there is any specific group within SWMONTs. And the 1D tubes were connected to a 3D MOF by hydrogen bonds (Figure 1c). From a topological perspective, each Zn(II) ion links three nearest $\mathbf{L}^{2-}$ ligands, so we can define it as a 3-connected node. Thus, the 1D tube can be described as a SP 1-periodic net topology (Figure 1d).



Scheme 1. Coordination Modes of the ligand $\mathbf{L}^{2-}$ in **1**.

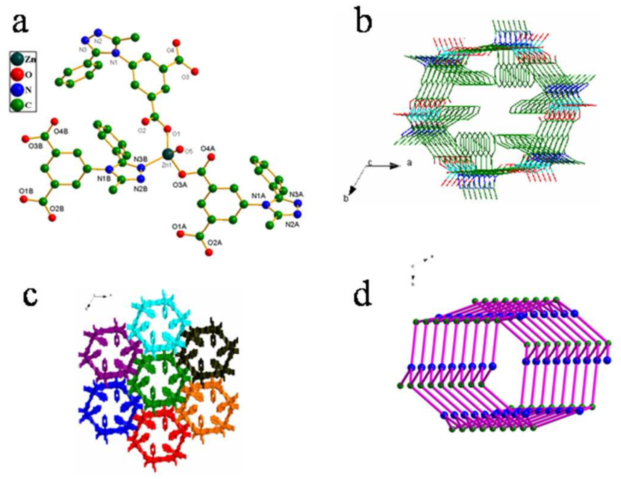


Figure 1. (a) Coordination environment of the Zn^{II} ion (All hydrogen atoms and solvent molecules are omitted for clarity). **(b)** Structure of 1D tube for **1** (All solvent molecules are omitted for clarity). **(c)** 3D structure of **1** running along the ab-plane. **(d)** Topology of **1** along the ab-plane.

The TGA were carried out on the crystalline samples in the N_2 atmosphere with a heating rate of 10 °C /min in the temperature range 25-950 °C. The TG curve of compound **1** is illustrated in Figure S2 (Supporting information). The TG curve of compound **1** shows the first stage of weight loss from 25 °C to 220 °C (9.2 % contrast to theoretical 8.52 %), which is attributed to the release of one guest water molecule and one coordinated water molecule. There is a platform time from 220 °C to 390 °C. The second stage of weight loss occurs from 390 °C to 950 °C. The degradation of compound **1** is incomplete. The TG curve of activated **1** shows the first stage of weight loss from 140 °C to 220 °C (5.12 % contrast to theoretical 4.26 %), which is attributed to the release of one coordinated water molecule. There is overlapping temperature between the weight loss of benzene/SWMONTs and the release of the coordinated water molecule (140-220□). Once the influence of coordinated water was taken out, weight loss of benzene could be obtained (Table S1, Figure 2a and 2b). We could predict that the latter adsorbed benzene only on the outside walls, while the former adsorbed benzene also on the inside walls since the holes through the walls enabled benzene to reach the inside tubules. We can see that desorption rate of benzene was slightly accelerated and the desorption temperature was higher after being left in air for 3–17 days. Figure 2a and 2b show that the desorption quantity of benzene from benzene/SWMONTs became small, at about 2.91%, after the specimen was left in air for 17 days. The desorption temperature increased during the first 3 days, and became constant after the specimen was left in air for 8 days. Then the desorption temperature increased [16]. Previous vapor-adsorption study of MOFs is usually indicative of selectivity toward benzene over cyclohexane. As for SWMONTs, no data are available for reference. Compared to oxydic single-wall carbon nanohorns(SWNHox), the weight loss of benzene/SWMONTs (5.77%) was lower than that of benzene/SWNHox (8%) due to benzene desorption at first, while the weight loss of benzene/SWMONTs (2.91%) was close to that for benzene/SWNHox (lower than 3%) , but higher than that for benzene/SWNH(0.6%) after 2 weeks.

The purity of the bulky crystalline sample was confirmed by PXRD. The PXRD pattern of compound **1** is illustrated in Figure S3 (Supporting information), which is in good agreement with simulated one, confirming the phase purity of the as-synthesized product.

The fluorescence emission spectrophotometry of compound **1** and the ligand was studied in the solid state at room temperature (Figure 3). Compound **1** shows luminescence with the emission maximum at 421 nm and 492 nm, upon excitation at 370 nm. The free ligand H_2**L** shows luminescence with the emission maximum at 431 nm, upon excitation at 370 nm. The luminescence may be attributed to the chelating and/or bridging effects of the ligands to the metal centers, which effectively increases the rigidity of the ligands and reduces the loss of energy *via* radiation less pathway. As its structure contains only one ligand, its emission behavior can be tentatively assigned to the coexistence of intraligand fluorescent emissions and ligand−metal charge transfer (LMCT) [17-20]. Luminescent studies show that compound **1** displays strong blue emission at room temperature(Figure 4).

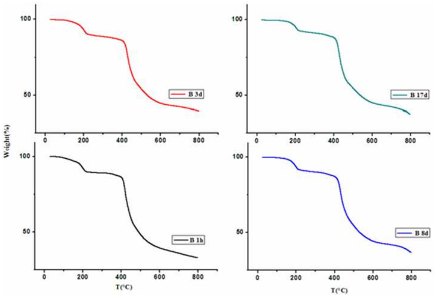


Figure 2a. Thermogravimetric profiles of benzene/compound **1** after stored for different time.

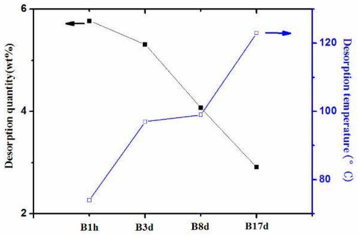


Figure 2b. Desorption quantities and temperatures of benzene/compound **1** after stored for different time.

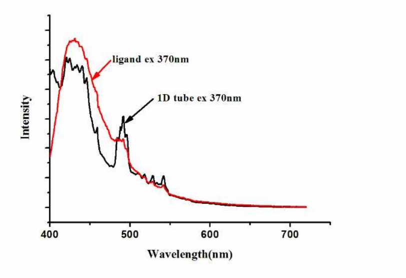


Figure 3. Solid state emission spectra for compound **1** and the ligand H_2**L** at room temperature.

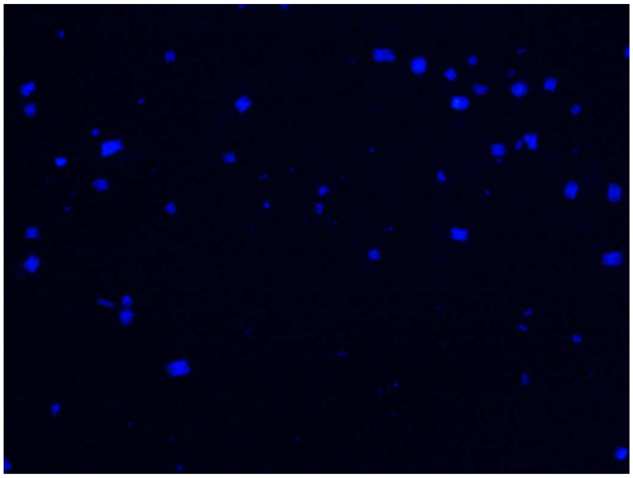


Figure 4. Blue emission of compound **1** at room temperature recorded by inverted fluorescence Microscope.

Conclusions

In conclusion, a novel SWMONTs, [Zn(**L**)(H_2O)$]_n$·nH_2O (**1**) has been hydrothermally synthesized. Benzene adsorption results show that benzene molecules on the outer could be gradually lost over time, while stable adsorption of benzene could be realized inside the tube. Compound **1** shows luminescence with the emission maximum at 421 nm and 492 nm, upon excitation at 370 nm. The free ligand H_2**L** shows luminescence with the emission maximum at 431 nm, upon excitation at 370 nm.

Acknowledgement

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Appendix A. Supplementary data

CCDC 940997 for compound **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Notes and references

[1] Iijima, S. *Nature*, 1991, **354**, 56.

[2] Jiang, H.L.; Makal, T.A.; Zhou, H.C. *Coordination Chemistry Reviews*, 2013, **257**, 2232.

[3] Procopio, E.Q.; Linares, F.; Montoro, C.; Colombo, V.; Maspero, A.; Barea, E.; Navarro, J.A.R. *Angew. Chem.*, 2010, **122**, 7466.

[4] Ren, H.; Ben, T.; Wang, E.; Jing, X.; Xue, M.; Liu, B.; Cui, Y.; Qiu, S.; Zhu, G. *Chem. Commun.,* 2010, **46**, 291.

[5] Kuppler, R.J.; Timmons, D.J.; Fang, Q.R.; Li, J.R.; Makal, T. A.; Young, M.D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.C. *Coordination Chemistry Reviews*, 2009, **253**, 3042.

[6] Cui, Y.; Yue, Y.; Qian, G.; Chen. B. *Chem. Rev.*, 2012, **112**, 1126.

[7] Kong, G.Q.; Ou, S.; Zou, C.; Wu, C.D. *J. Am. Chem. Soc.*, 2012, **134**, 19851.

[8] Nayarassery, N.A.; Marinela, M.D.; Anil, D.N.; Alexandre, F.L.; Nicolo, C.; Koen, R.; Johan, S.; Jan, F.; Bao, L.S.; Yann, G. *Chem. Eur. J.*, 2015, **21**, 4300.

[9] Bu, F.; Xiao, S.J. *CrystEngComm*, 2010, **12**, 3385.

[10] Tseng, T.W.; Luo, T.T.; Su, C.C.; Hsu, H.H.; Yang, C.I.; Lu, K.L. *CrystEngComm*, 2014, **16**, 2626.

[11] Yu, J.T.; Sun, J.L.; Huang, Z.T.; Zheng, Q.Y. *CrystEngComm*, 2012, **14**, 112.

[12] Dai, F.N.; He, H.Y.; Sun, D.F. *J. Am. Chem. Soc.*, 2008, **130**, 14064.

[13] Sahu, S.K.; Unruh, D.K.; Forbes, T.Z.; Navrotsky, A. *Chem. Mater.*, 2014, **26**, 5105.

[14] Cheng, J.Y.; Wang, P.; Ma, J.P.; Liu, Q.K.; Dong, Y.B. *Chem. Commun.,* 2014, **50**, 13672.

[15] Murdock, C.R.; Jenkins, D.M. *J. Am. Chem. Soc.,* 2014, **136**, 10983.

[16] Fan, J.; Yudasaka, M.; Kasuya, Y.; Kasuya, D.; Iijima, S. *Chem. Phys. Lett.,* 2004, **397**, 5.

[17] Liu, J.; Zhang, H. B.; Tan, Y. X. *Inorg. Chem.,* 2014, **53**, 1500.

[18] Su, Z.; Fan, J.; Okamura, T. *Cryst. Growth Des.,* 2010, **10**, 1911.

[19] Sun, D.; Xu, H. R.; Yang, C. F. *Cryst. Growth Des.,* 2010, **10**, 4642.

[20] Zhang, S. Q.; Jiang, F. L.; Wu, M. Y. *Cryst. Growth Des.,* 2012, **12**, 1452.

[21] Zhu, Q. L.; Xu, Q. *Chem. Soc. Rev.,* 2014, **43**, 5468.

[22] Zhang, W.; Xiong, R. G. *Chem. Rev.,* 2012, **112**, 1163.

[23] Wang, C.; Zhang, T.; Lin, W. B. *Chem. Rev.,* 2012, **112**, 1084.

[24] Wu, H. H.; Gong, Q. H.; Olson, D. H.; Li, J. *Chem. Rev.,* 2012, **112**, 836.

[25] Lin, J. B.; Zhang, J. P.; Chen, X. M. *J. Am. Chem. Soc.*, 2010, **132**, 6654.

A table of contents entry

Title: Serrated single-wall metal-organic nanotubes (SWMONTs) for benzene adsorption

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A self-assembled functionalized metal-organic nanotubes, compound **1** has been hydrothermally synthesized.

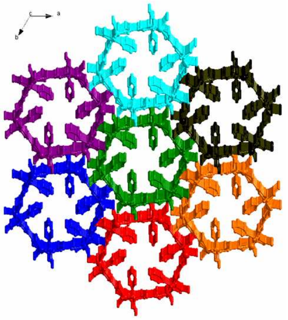

Figure 1. (c) 3D structure of **1** running along the ab-plane.