

A novel microporous MOF with the capability of selective adsorption of xylenes†

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A novel 3D metal–organic framework (MOF) with 2D rhombic channels was synthesized for selective adsorption of *p*-xylene from xylene isomers by acting as a molecular sieve.

As the initial raw materials, xylene isomers are widely used in the field of the chemical industry. *p*-xylene (pX), one of the xylene isomers, is required for the manufacture of polyethylene terephthalate (PET) which can be further utilized to make polyester fiber, resin, film and blown beverage bottles. Because of such great economic worth, a great deal of pX is produced every year. However, due to the closely matched boiling points (138 °C–144 °C), separation of xylenes by distillation is almost infeasible. Up to now, two methods have been used to separate xylene isomers: crystallization and adsorption. Compared to crystallization, adsorption which has high efficiency is gaining broader acceptance in separation of xylenes.

Metal–organic frameworks (MOFs), as a new class of porous materials, receive much attention for their potential practical applications; such applications being considered include optoelectronic properties, luminescence, magnetism, sensing, catalysis.^{1–14} Recently, adsorption of MOFs has been performed with a number of small molecules.^{15–19} However, as far as we know, studies on the selective adsorption and separation of small molecules are few,^{20–26} especially those on xylene isomers are quite rare.^{27–32}

Based on the above issues, here we report a novel three-dimensional flexible open microporous MOF (JUC-77) with 2D rhombus-shaped channels. The sorptions of benzene, toluene and three xylene isomers have been measured. The isotherms indicate that JUC-77 has potential capability for separating pX from the other two xylene isomers, acting as a molecular sieve because the size of channels in JUC-77 is between the sizes of pX and those of the other two xylene isomers. To the best of our knowledge, separation capabilities of porous MOFs reported in the literature are mainly due to the interaction between adsorbate and channel of material, and material such as JUC-77 which has potential capability of exploiting a molecular sieving process for separating pX from xylene isomers has not been reported.

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JUC-77-DMF ([In(OH)(OBA)]·DMF; H₂OBA = 4,4'-oxybis(benzoic acid)) was synthesized under mild conditions. The structure was determined by single-crystal X-ray diffraction at 298 K,[†] and molecular guest (DMF) was determined by TGA and FT-IR (Fig. S2 and S4). As shown in Fig. 1a, In^{III} is coordinated with six oxygen atoms, four of them at the equatorial sites are from four different OBA²⁻ ligands and the other two oxygen atoms from the μ₂-OH groups are at the axial position. Hexacoordinated In^{III} share axial μ₂-OH groups with each other to form infinite ···In–OH–In–OH··· zigzag chains. The ∠C8–O3–C7 of OBA ligand is 119.9° and the two aromatic rings of OBA are tilted with an angle of 66.5°, which are similar to the results reported³³ (Fig. 1b). Because of such geometry of OBA²⁻ ligand, the zigzag chains are linked perpendicularly with each other by OBA²⁻ ligand to form a 3D structure (Fig. 1c). Meanwhile two groups of the perpendicular and disconnected 1D channels are formed along [110] and [1-10] directions.

The fully desolvated JUC-77 (see ESI) used for sorption is verified by TGA, IR and PXRD (Fig. S3–5). The N₂ sorption measurements of JUC-77 at 77 K indicate a reversible type-I isotherm. (Fig. 2) The Langmuir and the BET surface area are 1066 m² g⁻¹ and 976 m² g⁻¹, respectively. The HK model

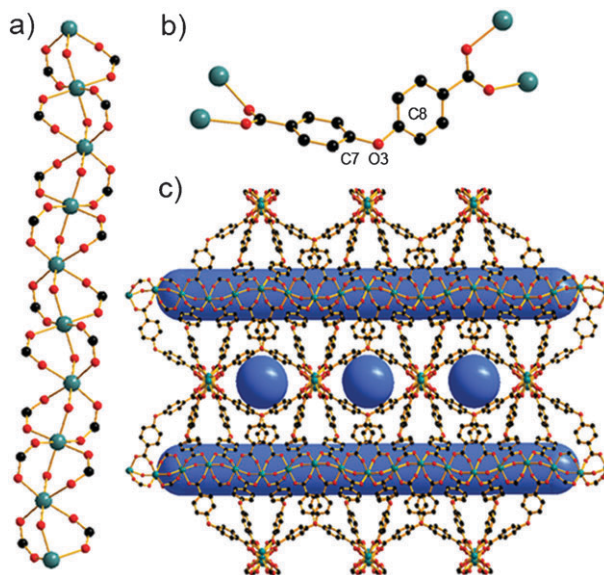


Fig. 1 (a) Ball-and-stick representation of the infinite ···In–OH–In–OH··· zigzag chains of JUC-77; (b) OBA²⁻ ligand connects with four different In atoms; (c) view of the 3D framework along the [110] direction. The 1D channel is shown in blue. In: cyan, C: black, O: red. H atoms omitted for clarity.

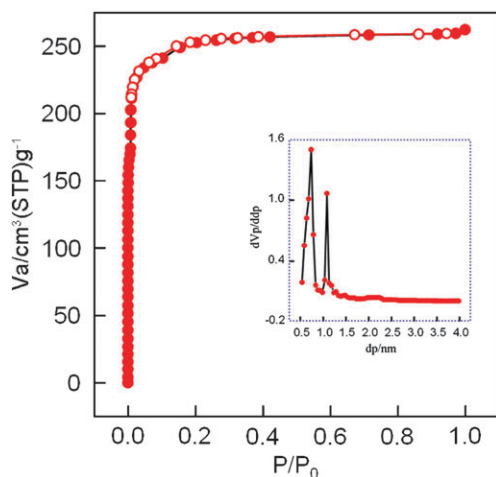


Fig. 2 N_2 sorption isotherm of JUC-77 at 77 K ($P_0 = 1$ atm). Filled circle: sorption; open circle: desorption. Inset: micropore size distribution.

indicates that the diagonal sizes of the rhombic pores in JUC-77 are $10.8 \times 7.3 \text{ \AA}^2$, consistent with the X-ray analysis. To study the sorption and preferential adsorption capability of JUC-77, benzene, toluene, pX, *m*-xylene (mX), *o*-xylene (oX) were chosen as probes by considering that the dimensions of the adsorptive molecules are close to that of the channel (Table 1).

Whether the adsorbate can enter into a pore is determined by the size and the shape of not only the adsorbate, but also the channel. Xylenes can be seen as cuboids, and the shape of JUC-77's channel is rhombic (See ESI, Scheme S1). Whether the organic molecule can be adsorbed by JUC-77 is decided by whether the rectangle formed by MIN-1 and MIN-2 of the molecule can go through the rhombic channel perpendicularly or not. The rectangles formed by MIN-1 and MIN-2 of benzene, toluene and pX can enter into the rhombic channel easily, but those of oX and mX can't. These assumptions are also confirmed by the simulation in MS software.³⁵ (Fig. 3) Based on the results of the simulations, it's suggested that JUC-77 has a capability of preferential adsorption for pX.

The sorption behavior of the benzene features a reversible type-I isotherm (Fig. 4), it reaches saturation at about $P/P_0 = 0.11$. And the sorption isotherm of pX is very different from that of benzene. The little loading and low slope indicate that pX can't enter the channel easily in the range of $P/P_0 < 0.4$, because JUC-77 is in the form of NP (narrow pore)³⁶ at the

Table 1 Dimensions of adsorptive molecules (\AA)^{c,34}

	<i>x</i>	<i>y</i>	<i>z</i>	MIN-1 ^a	MIN-2 ^b
benzene	6.628	7.337	3.277	3.277	6.628
toluene	6.625	4.012	8.252	4.012	6.625
pX	6.618	3.810	9.146	3.810	6.618
oX	7.269	3.834	7.826	3.834	7.269
mX	8.994	3.949	7.315	3.949	7.258

^a MIN-1 (size of the adsorptive in the minimum dimension). ^b MIN-2 (second minimum dimension for molecular orientations that enable a molecule to enter the channel). ^c Each atom surrounded by a van der Waals sphere.

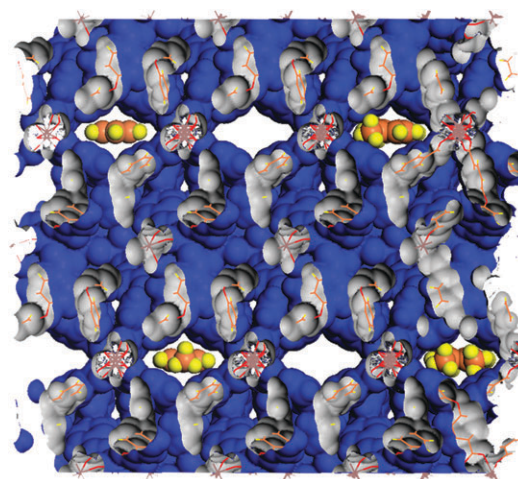


Fig. 3 Simulation for comparison of the dimensions of the adsorptive molecules and those of the channel in MS, benzene (upper-left); pX (lower-left); oX (upper-right); mX (lower-right). Orange: C; yellow: H.

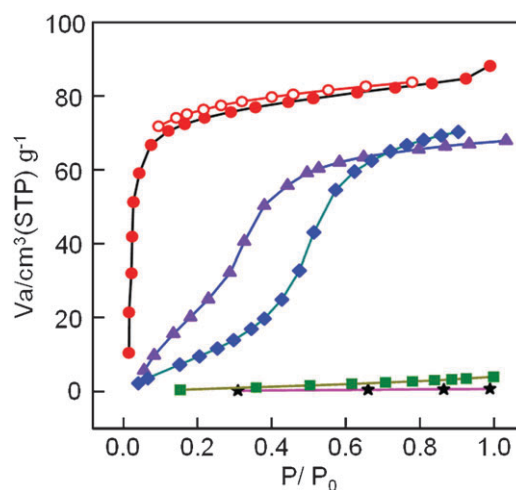


Fig. 4 Vapor adsorption and desorption of JUC-77 with benzene and the vapor adsorption of toluene, xylenes at 298 K. P_0 is saturated vapor pressure; solid circle: adsorption of benzene; open circle: desorption of benzene; triangle: adsorption of toluene; rhombus: adsorption of pX; star: adsorption of oX; rectangle: adsorption of mX.

beginning (Fig. S5), and transforms into LP (large pore) form slowly when the pressure is increased. In the $0.4 < P/P_0 < 0.6$ region, the LP form becomes preponderant, then pX molecules enter the channel easily, so the slope of the sorption isotherm becomes abrupt, and the uptake increases rapidly. It reaches saturation after $P/P_0 = 0.6$. On the other hand, as the same as our analysis above, adsorption of mX, oX features typical type-III isotherms shown in Fig. 4, which means mX and oX are not allowed to get into the channel. These results imply that JUC-77 has potential capability for separating pX from xylenes by acting as a molecular sieve.

In conclusion, we have successfully synthesized a novel 3D flexible framework, JUC-77, with permanent 2D rhombic channels. The results of adsorption indicate that JUC-77 has potential capability for separating pX from xylene isomers by acting as a molecular sieve. Meanwhile, such porous MOF material may be used as the shape-selective catalyst^{6,9} in

producing pX. Our future work will focus on exploring those potential applications of JUC-77.

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Notes and references

† Crystal data: $\text{InC}_{14}\text{H}_9\text{O}_6$; $M = 388.03$, colorless block, orthorhombic, space group $Fddd$ (No. 70), $a = 19.2396(9)$, $b = 20.3017(9)$, $c = 46.143(2)$ Å, $V = 18023.4(14)$ Å³, $Z = 32$, $T = 298$ K, $\rho_c = 1.144$ g cm⁻³, $\lambda = 0.71073$ Å, $2\theta_{\text{max}} = 56.58^\circ$, 28 635 reflections collected, 5280 unique ($R_{\text{int}} = 0.0588$). Final $\text{Goof} = 1.000$, $R_1 = 0.0698$, $wR_2 = 0.2191$, R indices based on 3397 reflections with $I > 2\sigma(I)$ (refinement on F^2). (Table S1). The routine SQUEEZE was applied to the structures in order to remove diffuse electron density associated with badly disordered DMF molecules.³⁷ This had the effect of dramatically improving the agreement indices. Crystallographic data for this paper and selected bond lengths and angles are displayed in Tables S1 and S2.

- X. D. Guo, G. S. Zhu, Q. R. Fang, M. Xue, G. Tian, J. Y. Sun, X. T. Li and S. L. Qiu, *Inorg. Chem.*, 2005, **44**, 3850.
- Q. R. Fang, G. S. Zhu, Z. Jin, M. Xue, X. Wei, D. J. Wang and S. L. Qiu, *Angew. Chem., Int. Ed.*, 2006, **45**, 6126.
- Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun and S. L. Qiu, *Inorg. Chem.*, 2006, **45**, 3582.
- T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.
- C. A. Bauer, T. V. Timofeeva, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Am. Chem. Soc.*, 2007, **129**, 7136.
- K. Barthelet, K. Adil, F. Millange, C. Serre, D. Riou and G. Férey, *J. Mater. Chem.*, 2003, **13**, 2208.
- B. L. Chen, Y. Yang, F. Zapata, G. N. Lin, G. D. Qian and E. B. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693.
- F. Gándara, B. Gomez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, D. M. Proserpio and N. Snejko, *Chem. Mater.*, 2008, **20**, 72.
- T. Uemura, S. Horike, K. Kitagawa and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 6781.
- Q. R. Fang, G. S. Zhu, Z. Jin, Y. Y. Ji, J. W. Ye, M. Xue, H. Yang, Y. Wang and S. L. Qiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 6638.
- M. Xue, G. S. Zhu, Y. X. Li, X. J. Zhao, Z. Jin, E. Kang and S. L. Qiu, *Cryst. Growth Des.*, 2008, **8**, 2478.
- Z. Y. Li, G. S. Zhu, X. D. Guo, X. J. Zhao, Z. Jin and S. L. Qiu, *Inorg. Chem.*, 2007, **46**, 5174.
- X. D. Guo, G. S. Zhu, F. X. Sun, Z. Y. Li, X. J. Zhao, X. T. Li, H. C. Wang and S. L. Qiu, *Inorg. Chem.*, 2006, **45**, 2581.
- M. R. Kishan, P. K. Thallapally and J. L. Atwood, *Chem. Commun.*, 2010, **46**, 538.
- H. L. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
- B. L. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.
- M. Latroche, S. Surbl, C. Serre, C. Mellot-Draznieks and G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 8227.
- R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- V. Finsy, L. Ma, L. Alaerts, D. E. D. Vos, G. V. Baron and J. F. M. Denayer, *Microporous Mesoporous Mater.*, 2009, **120**, 221.
- J. W. Yoon, S. H. Jhung, Y. K. Hwang, S. M. Humphrey, P. T. Wood and J. S. Chang, *Adv. Mater.*, 2007, **19**, 1830.
- B. L. Chen, O. M. Yaghi and S. Dai, *Angew. Chem., Int. Ed.*, 2006, **45**, 1390.
- K. H. Li, D. H. Olson, J. Y. Lee, W. H. Bi, K. Wu, T. Yuen, Q. Xu and J. Li, *Adv. Funct. Mater.*, 2008, **18**, 2205.
- L. Alaerts, M. Maes, M. A. v. d. Veen, P. A. Jacobs and D. E. D. Vos, *Phys. Chem. Chem. Phys.*, 2009, **11**, 2903.
- J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 6010.
- J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 5516.
- L. Alaerts, J. F. M. Denayer and V. D. E. Denayer, *Angew. Chem., Int. Ed.*, 2007, **46**, 4293.
- V. Finsy, C. E. A. Kirschhock, G. Vedts, M. Maes, L. Alaerts, D. E. D. Vos, G. V. Baron and J. F. M. Denayer, *Chem.-Eur. J.*, 2009, **15**, 7724.
- Q. K. Liu, J. P. Ma and Y. B. Dong, *Chem.-Eur. J.*, 2009, **15**, 10364.
- M. P. M. Nicolau, P. S. B́arcia, J. M. Gallegos, J. A. C. Silva, A. E. Rodrigues and B. L. Chen, *J. Phys. Chem. C*, 2009, **113**, 13173.
- L. Alaerts, J. F. M. Denayer and D. E. D. Vos, *J. Am. Chem. Soc.*, 2008, **130**, 14170.
- V. Finsy, H. Verelst, L. Alaerts, D. D. Vos, P. A. Jacobs, G. V. Baron and J. F. M. Denayer, *J. Am. Chem. Soc.*, 2008, **130**, 7110.
- C. Y. Sun and L. P. Jin, *J. Mol. Struct.*, 2006, **782**, 171.
- C. E. Webster, R. S. Drago and M. C. Zerner, *J. Am. Chem. Soc.*, 1998, **120**, 5509.
- Materials Studio simulation environment, version 4.3. (Accelrys software Inc., San Diego, CA, USA). Command used is Atoms Volumes & surfaces. Task: solvent surfaces, Analysis by vdW Surface command, CPK = 0.7.
- S. Bourrelly, G. Maurin, A. Vimont and G. Férey, *J. Am. Chem. Soc.*, 2010, **132**, 9488.
- A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.