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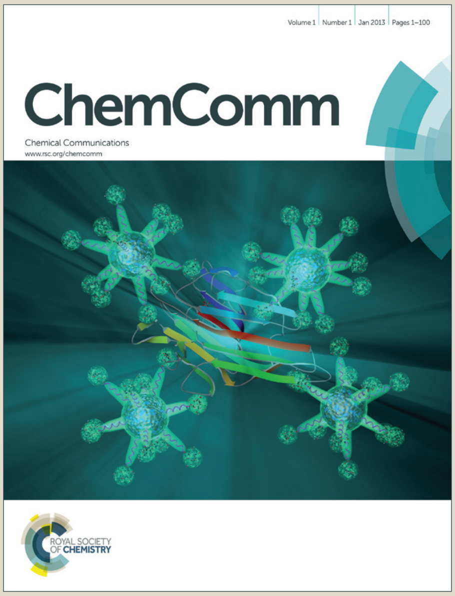

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ARTICLE TYPE

Enhancement of adsorption selectivity for MOFs under mild activation and regeneration conditions

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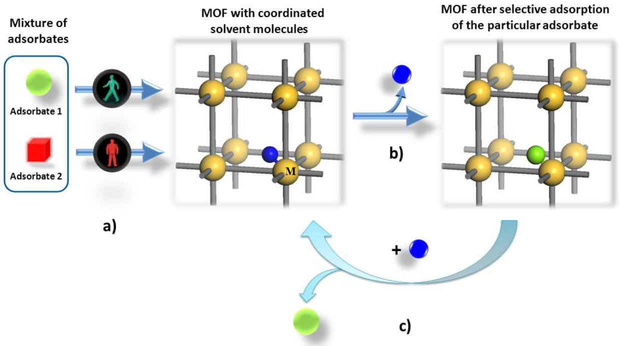
A new concept has been proposed and proven through the model experiments for enhancing adsorption selectivity of metal-organic frameworks (MOFs) and reducing the energy cost during the activation and regeneration processes.

In recent years, metal-organic frameworks (MOFs) have attracted considerable attention on the area of selective adsorption and separation because of their adjustable pore sizes[1-3], surface environments[4-6] and low energy cost in separation process[7] compared with distillation method. However, in order to remove the coordinated solvent molecules completely to obtain open metal sites and larger void volume,[8] activation and regeneration at as high temperature as possible are still indispensable for most of MOF materials,[9] which cost much additional energy. Therefore, it is necessary to find new methods to improve the ability and broaden the application scale of MOFs on the area of selective adsorption and separation under mild activation conditions or even room temperature. In this contribution, we proposed a new method to separate homologues under mild activation condition based on the exchange reaction between coordinated molecules in MOFs and target adsorbates. The concept has been verified by model experiments, and single crystal to single crystal (SC-SC) transformations have been utilized to trace the whole procedures stepwisely and to confirm the strategy as well as to illustrate the mechanism in detail.



Scheme 1. Proposed process of selective separation in MOFs with the coordinated solvent. (a) Selective adsorption process based on the different coordination abilities of adsorbates; (b) exchange reaction between the coordinated molecule and the particular adsorbate; (c) recovery of the material under suitable condition.

The general construction of the concept is illustrated in Scheme 1. Normally, the coordinated solvent molecules in a MOF can be substituted by other types of solvent, and the coordination abilities of different solvent molecules towards the metal centres in a MOF differ from each other significantly. Based on this fact, it is possible to utilize given coordinated molecule to decide which adsorbate can be absorbed by MOFs and which cannot: if the adsorbate coordinates more strongly with metal ions than the original coordinated molecule, the original coordinated molecule will be substituted and the adsorbate will be caught by MOFs; otherwise, the original coordinated molecule will stay at its coordination position, and the adsorbate cannot be absorbed by MOFs. As a result, we just need to remove the free solvent molecules in the crystal lattice under mild conditions, and further heating and/or evacuation for the removal of coordinated solvent molecules are no longer demanded. Besides, the used MOFs can be regenerated by exchange reaction as well to release the adsorbate and recover the original coordinated molecule in MOFs.

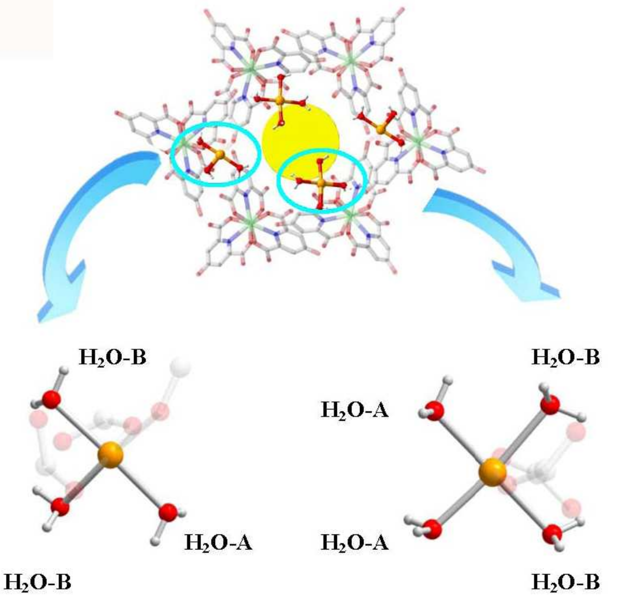


Figure 1. The 1D channel of complex **1** and the chemical environment of coordinated water molecules (H_2O-A and H_2O-B). The free water molecules have been omitted for clarity.

In order to verify the concept, we selected the selectivity adosrption of MOF towards MeOH and EtOH as model experiment, which is a typical isolation in most chemical fields, and is especially important nowadays to obtain sustainable energy source, such as bioethanol.[10] The hetero-metal-organic framework (HMOF),[11] $\{[Eu(CAM)(HCAM)_2Mn_2(H_2O)_7]\cdot 7H_2O\}_n$ (**1**) (H_3CAM = chelidamic acid monohydrate), was synthesized as a representative adsorpiton material. The structure of **1** was constructed by Mn^{2+} ion and the second building unit $[Eu(HCAM)_2(CAM)]$. Adjacent $[Eu(HCAM)_2(CAM)]$ units are connected through $[Mn(H_2O)_4]^{2+}$ and $[Mn(H_2O)_3]^{2+}$ to form an infinite 2D structure. The hydrogen bonding interaction between carboxylate O atoms and OH groups links the 2D coordination sheets to a 3D framework, in which 1D channels are observed with an average size of ca. 10.2×6.5 Å.. The kinetic diameters of EtOH and MeOH molecules are 3.626 Å and 4.530 Å, respectively. Clearly, comparing with the size of the channel, both MeOH and EtOH molecules can enter the channel of **1**.

There are two types of coordinated water molecules involved in both $[Mn(H_2O)_4]^{2+}$ and $[Mn(H_2O)_3]^{2+}$ units: toward the channel center (H_2O-A) and toward the wall of channel (H_2O-B), respectively, as specified in Figure 1. Depending on the steric hindrance effect, H_2O-A are able to be substituted by other molecules, while H_2O-B are stable in the framework of **1**.[12] Consequently, small molecules with different abilities for substituting H_2O-A could be distinguished during their adsorption process in **1**, which could thus enable **1** to separate corresponding homologues.

The reactivity of MeOH and EtOH to substitute H_2O-A in **1** was tested and compared with each other at first through SC-SC transformation process. When a selected crystal of **1** was exposed in EtOH vapor atmosphere for 24 h, the single crystal X-ray diffraction (SCXRD) reveals a formation of $\{[Eu(CAM)(HCAM)_2Mn_2(H_2O)_7]\cdot H_2O\cdot 0.33C_2H_5OH\}_n$ (**2**) and exhibits no change on H_2O-A. The crystal of **2** was then exposed in MeOH vapor instead of EtOH, and a new crystalline product was obtained after 10 h. The crystal structure of the product reveals a formation of $\{[Eu(CAM)(HCAM)_2Mn_2(CH_3OH)_3(H_2O)_4]\cdot 2.08H_2O\cdot 0.25CH_3OH\}_n$ (**3**) indicating the replacement of H_2O-A by MeOH. Remarkably, when we continued to expose this crystal of **3** into a water atmosphere for 24 h, the MeOH molecules were substituted by H_2O and the crystal of **1** was regenerated. The whole SC-SC transformation cycle is summarized in Figure 2. Although the Lewis base of EtOH is stronger than that of MeOH, the stereo-hindrance effect between the EtOH and framework could prevent the EtOH molecules to substitute H_2O-A on Mn^{2+} ions. The SC-SC transformation procedures described above proved that it is possible for **1** to selectively adsorb MeOH and EtOH through utilizing their different coordination abilities towards Mn^{2+}, and H_2O-A could be utilized to decide which type of molecules can be involved in the substitution-absorption-separation process.

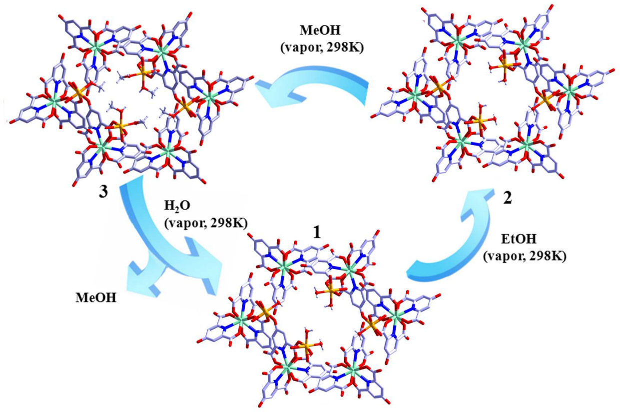


Figure 2. The SC-SC process of exchange reactions for H_2O-A in **1** with EtOH and MeOH at vapor. All free molecules were omitted for clarity.

For confirming the above concept further, adsorption selectivity of **1** towards MeOH and EtOH in vapor state was tested. Firstly, **1** was outgased at 85 ℃ under vacuum for 10 h to lose both free water molecules and H_2O-A molecules, after which $\{[Eu(CAM)(HCAM)_2Mn_2(H_2O)_4]\}_n$ (**1-85**) was obtained and confirmed by thermogravimetry (TG) and element analysis. As presented in Figure 3, the isotherm of MeOH shows a rapid increase at $P/P_0 < 0.1$ indicating **1-85** as a microporous material. When $P/P_0 > 0.1$ the isotherm increases smoothly and attains 187.4293 $cm^3\ g^{-1}$ at $P/P_0 = 0.9$. The EtOH isotherm shows the same tendency as for MeOH and a value of 131.7821 $cm^3\ g^{-1}$ at $P/P_0 = 0.9$. The selectivity molar ratio of **1-85** towards MeOH/EtOH at vapor state is 1.42. Considering all of the free water molecules and H_2O-A molecules have been removed, the selectivity is mainly caused by the different interactions between EtOH and MeOH with the framework of **1**.

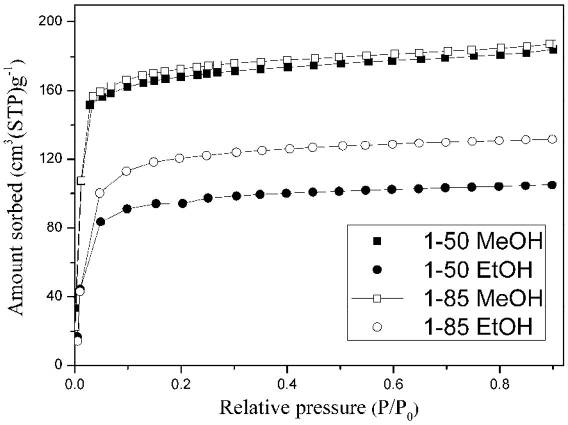


Figure 3. MeOH and EtOH vapor adsorption isotherm of **1-50** and **1-85**.

For comparison, the outgasing temperature for **1** was then reduced at 50 ℃ in order to remove all the free water molecules and retain all of H_2O-A molecules. $\{[Eu(HCAM)_2(CAM)Mn_2(H_2O)_7]\}_n$ (**1-50**) was obtained after the above outgassing process and the formula of the complex was confirmed by TG and element analysis. **1-50** shows the isotherm values of 184.1014 $cm^3\ g^{-1}$ for MeOH and 104.9267

$cm^3\ g^{-1}$ for EtOH, respectively. The selectivity molar ratio of **1-50** towards MeOH/EtOH vapor is 1.75. As we anticipated, excluding the selectivity which caused by the difference between the kinetic diameters of EtOH and MeOH, the selectivity molar ratio of **1-50** towards MeOH/EtOH vapor is 23% higher than that of **1-85**. The framework of **1-50** and **1-80** was maintained during the whole procedure, as confirmed by powder X-ray diffraction (PXRD) (See SI). The vapor adsorption result indicated that higher selectivity of **1** was obtained at lower activation temperature due to the different substitution activities between MeOH and EtOH towards the coordinated water molecules. Consequently, the feasibility of the concept based on exchange reactions between the coordinated molecule and adsorbates has been clearly confirmed by the results of vapor adsorption experiment.

In conclusion, the results of the SC-SC processes and vapor adsorption experiment unambiguously confirmed that our new concept based on exchange reactions between the coordinated molecule and adsorbates is feasible for the application of MOFs in the area of separation towards homologues. Based on the concept, the selectivity of MOF materials towards the selectivity adsorption of MeOH and EtOH has been enhanced under mild activation condition successfully. Since the removal of coordinated solvent molecules are no longer necessary, the energy-consumption and dissipation for the pre-activation of MOFs can be reduced remarkably.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of characterization, SC-SC experiments, sorption and saperation experiments, crystallographic data, TG and powder XRD. See DOI: 10.1039/b000000x/

1 (a) Y. Q. Lan, H. L. Jiang, S. L. Li and Q. Xu, *Adv. Mater.* 2011, **23**, 5015; (b) S. D. Burd, S. Q. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.* 2012, **134**, 3663; (c) Y. B. He, W. Zhou, R. Krishna and B. L. Chen, *Chem. Commun.*, 2012, **48**, 11813.

2 (a) Y. P. He, Y. X. Tan and J. Zhang, *Chem. Commun.*, 2013, **49**, 11323; (b) K. Suh, M. P. Yutkin, D. N. Dybtsev, V. P. Fedin and K. Kim, *Chem. Commun.*, 2012, **48**, 513.

3 (a) J. K. Sun, M. Ji, C. Chen, W. G. Wang, P. Wang, R. P. Chen and J. Zhang, *Chem. Commun.*, 2013, **49**, 1624; (b) K. Zhang, R. P. Lively, M. E. Dose, A. J. Brown, C. Zhang, J. Chung, S. Nair, W. J. Koros and R. R. Chance, *Chem. Commun.*, 2013, **49**, 3245; (c) B. S. Zheng, J. F. Bai, J. G. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.* 2011, **133**, 748; (d) G. Lu, O. K. Farha, W. N. Zhang, F. W. Huo and J. T. Hupp, *Adv. Mater.* 2012, **24**, 3970; (e) H. Y. Zhao, Z. Jin, H. M. Su, J. L. Zhang, X. D. Yao, H. J. Zhao and G. S. Zhu, *Chem. Commun.*, 2013, **49**, 2780.

4 (a) J. Teufel, H. Oh, M. Hirscher, M. Wahiduzzaman, L. Zhechkov, A. Kuc, T. Heine, D. Denysenko and D. Volkmer, *Adv. Mater.* 2013, **25**, 635; (b) R. El Osta, M. Frigoli, J. Marrot, N. Guillou, H. Chevreau, R. I. Walton and F. Millange, *Chem. Commun.*, 2012, **48**, 10639; (c) J. M. Roberts, B. M. Fini, A. A. Sarjeant, O. K. Farha, J. T. Hupp and K. A. Scheidt, *J. Am. Chem. Soc.* 2012, **134**, 3334.

5 (a) X. T. Rao, J. F. Cai, J. C. Yu, Y. B. He, C. D. Wu, W. Zhou, T. Yildirim, B. L. Chen and G. D. Qian, *Chem. Commun.*, 2013, **49**, 6719; (b) M. Wriedt, J. P. Sculley, A. A. Yakovenko, Y. G. Ma, G. J. Halder, P. B. Balbuena and H. C. Zhou, *Angew. Chem. Int. Ed.* 2012, **51**, 9804; (c) V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.* 2012, **134**, 12830.

6 (a) Z. Zhang, W. Y. Gao, L. Wojtas, S. Ma, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem. Int. Ed.* 2012, **51**, 9330; (b) D. D. Zhou, C. T. He, P. Q. Liao, W. Xue, W. X. Zhang, H. L. Zhou, J. P. Zhang and X. M. Chen, *Chem. Commun.*, 2013, **49**, 11728; (c) P. Q. Liao, D. D. Zhou, A. X. Zhu, L. Jiang, R. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.* 2012, **134**, 17380.

7 (a) R. B. Eldridge, *Ind. Eng. Chem. Res.* 1993, 32, 2208-2212; (b) T. Ren, M. Patel and K. Blok, *Energy* 2006, **31**, 425.

8 (a) K. Gedrich, I. Senkovska, N. Klein, U. Stoeck, A. Henschel, M. R. Lohe, I. A. Baburin, U. Mueller and S. Kaskel, *Angew. Chem. Int. Ed.* 2010, **49**, 8489; (b) Z. Y. Gu and X. P. Yan, *Angew. Chem. Int. Ed.* 2010, **49**, 1477; (c) E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science* 2012, **335**, 1606; (d) A. L. Dzubak, L. C. Lin, J. Kim, J. A. Swisher, R. Poloni, S. N. Maximoff, B. Smit and L. Gagliardi, *Nat. Chem.* 2012, **4**, 810; (e) K. Sumida, D. Stuck, L. Mino, J. D. Chai, E. D. Bloch, O. Zavorotynska, L. J. Murray, M. Dinca, S. Chavan, S. Bordiga, M. Head-Gordon and J. R. Long, *J. Am. Chem. Soc.* 2013, **135**, 1083.

9 (a) X. S. Wang, S. Q. Ma, P. M. Forster, D. Q. Yuan, J. Eckert, J. J. Lopez, B. J. Murphy, J. B. Parise and H. C. Zhou, *Angew. Chem. Int. Ed.* 2008, **47**, 7263; (b) Z. Y. Guo, H. Wu, G. Srinivas, Y. M. Zhou, S. C. Xiang, Z. X. Chen, Y. T. Yang, W. Zhou, M. O'Keeffe and B. L. Chen, *Angew. Chem. Int. Ed.* 2011, **50**, 3178; (c) T. Borjigin, F. X. Sun, J. L. Zhang, K. Cai, H. Ren and G. S. Zhu, *Chem. Commun.*, 2012, **48**, 7613; (d) W. B. Yang, A. J. Davies, X. Lin, M. Suyetin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, J. E. Parker, C. C. Tang, M. W. George, P. Hubberstey, S. Kitagawa, H. Sakamoto, E. Bichoutskaia, N. R. Champness, S. H. Yang and M. Schroder, *Chem. Sci.* 2012, **3**, 2993. (e) P. Cui, Y. G. Ma, H. H. Li, B. Zhao, J. R. Li, P. Cheng, P. B. Balbuena and H. C. Zhou, *J. Am. Chem. Soc.* 2012, **134**, 18892.

10 (a) A. Shigematsu, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.* 2012, **134**, 13145. (b) S. Kim and B. E. Dale, *Biomass Bioenergy* 2004, **26**, 361;

11 (a) B. Zhao, P. Cheng, Y. Dai, C. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang and G. L. Wang, *Angew. Chem. Int. Ed.* 2003, **42**, 934; (b) B. Zhao, P. Cheng, X –C. Chen, C. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.* 2004, **126**, 3012; (c) X. Q. Zhao, P. Cui, B. Zhao, W. Shi and P. Cheng, *Dalton Trans.* 2011, **40**, 805; (d) X. Q. Zhao, B. Zhao, W. Shi, P. Cheng, D. Z. Liao and S. P. Yan, *Dalton Trans.* 2009, **38**, 2281.

12 M. C. Das and P. K. Bharadwaj, *J. Am. Chem. Soc.* 2009, **131**, 10942.