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Quest for Zeolite-like Supramolecular Assemblies: Self-Assembly of Metal-Organic Squares via Directed Hydrogen Bonding

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Abstract: Our conceived approach based on the directed assembly of functional metal-organic squares (MOSs), 4-membered ring (4MR) building units, permitted the construction of two novel zeolite-like supramolecular assemblies (ZSAs), namely [Co₄(ImDC)₄(En)₄·9H₂O·1.5DMF] (ZSA-10) and [Co₄(ImDC)₄(En)₄·7H₂O] (ZSA-11) (H₃ImDC = 4,5-imidazoledicarboxylic acid, En = ethylenediamine, DMF = N,N-dimethylformamide). The elected MOSs encompass both *trans*- and *cis*-coordinated nodes, offering complementary peripheral functional groups for their directed assembly into zeolite-like topologies via supramolecular hydrogen bonding interactions. Distinctly, ZSA-10 possesses the underlying MER zeolite topology and is the only pure MER framework material (without any supporting templates) exhibiting permanent porosity up to now. ZSA-11 has the underlying ABW topology together with one type of narrow channel.

Zeolite-like metal-organic frameworks (ZMOFs) are a distinct class of metal-organic frameworks (MOFs) with unique structural features including their underlying topologies akin to zeolites and forbidden self-interpenetration.¹ Markedly, ZMOFs are suitable targets in MOF chemistry for the attainment of periodic porous solids with ionic exchange properties, and/or extra-large cavities and large surface areas.² Nevertheless, the construction of new ZMOFs with underlying zeolite topologies remains an ongoing challenge in reticular chemistry.

To date, several synthetic strategies have been deployed for the design and construction of ZMOFs including the use of: (i) 4-connected nodes as rigid and directional single-metal-ion molecular building blocks (MBB);^{2c,3} (ii) ditopic angular linkers, to substitute O²⁻ in the conventional inorganic zeolites, affording decorated and/or expanded ZMOFs;^{1c,2d,4} (iii) elaborate secondary building units (SBUs) or supermolecular building blocks (SBBs) including metal-organic squares (MOSs) or metal-organic cubes (MOCs).⁵ Rationally in the near past, we introduced and explored MOSs as a four-membered ring (4MR) SBU, the most abundant SBU in conventional zeolites with over 80 zeolite structures based on 4MR (Scheme 1a), for the construction of zeolite-like supramolecular assemblies (ZSAs).^{5c} Noticeably to access readily functional 4MR MOSs, we employed imidazoledicarboxylate-like ligands as bridging linkers due to their potential to present peripheral uncoordinated oxygen centers when chelated to a metal ion in N,O-bis(monodentate) fashion, and bis(monodentate) diamines as capping ligands.

Scheme 1. (a) Formation of the 4MR SBU in zeolite structures and the corresponding quadrilateral MOS in ZSA materials; (b) formation of the new *cis*, *trans*-MOS SBU.

Conceivably, the deliberately exposed amino functionalities from the capping ligands offer additional hydrogen-bonding sites on the periphery of the molecular squares, the only hydrogen bond donor, is disposed/ready to form predictable and controlled N-H...O hydrogen bonds with the carboxyl oxygen on the ligand, the only hydrogen bond acceptor, and afford the directed assembly of ZSAs. Indeed, we successfully synthesized ZSA-1 with GIS underlying topology and ZSA-2 with RHO topology by regulating the *cis/trans* isomerism of the 6-coordinated metal.^{5c} It is to be noted that such a class of novel supramolecular framework materials, based supramolecular hydrogen bonding interactions, exhibit excellent stability, permanent porosity, and distinctive gas adsorption/separation performances.^{5b,5c,5e} To gain further insights on the assembly of aforementioned ZSAs, we closely analyzed the orientation and connectivity of the 4MR MOS in the resultant crystal structures and found that the directionality and orientation of the hydrogen bonds dictates and governs the formation of different types of composite building units (CBUs) and chains. Particularly, in ZSA-1, four *trans*-coordinated Co³⁺ ions afford four 1,2-propanediamine (1,2-PDA) molecules to be arranged nearly in the plane of the *trans*-MOS, leading to the

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formation of the double crankshaft chain (*dcc*). However, studies suggest that the orientation of hydrogen bonding makes *trans*-MOS can only be arranged in parallel and therefore cannot form double-ring structures (Figure S1 and S2). Distinctly, in **ZSA-2**, *cis*-coordinated In^{3+} affords two opposite ligands to be positioned in the plane of the square and perpendicular to the other two ligands, meanwhile the four 1,2-diaminocyclohexane (1,2-DACH) molecules deviate from the MOS plane and are no longer located in the four corners of the MOS. Correspondingly, the orientation of hydrogen bond affords the possibility to form double-eight ring (*d8r*) structures, but it cannot form such as double zigzag chains (*dzc*) (Figure S1 and S3). Inspired by the above considerations and in line with our continuous quest for the discovery of new ZSAs, we decide to pursue and explore the prospect to construct a MOS that mutually combines *cis*- and *trans*-coordination and offers the potential to form both double rings and various chains in their resultant ZSA materials.

It is to be noted that the deployed solvent systems for the synthesis of extended solids play a major role in the formation of different SBU. Specifically, **ZSA-1** is synthesized by hydrothermal reaction whereas **ZSA-2** is synthesized by solvothermal reaction. Reasonably, we recognized the possibility to access new MOS by adjusting the ratio of water and organic solvents in the reaction media. Indeed, reaction of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, 4,5-imidazoledicarboxylic acid (H_3ImDC), ethylenediamine (En), and HNO_3 in DMF/ H_2O , afforded the formation of a new type of MOS that encompasses both *cis*- and *trans*-coordinated Co^{3+} . In the resultant new MOS, two Co^{3+} ions are octahedrally coordinated in a *trans*- CoN_4O_2 manner whereas the other two are coordinated in a *cis*- CoN_4O_2 manner and arranged in ABB model, resulting in only one ImDC^{3-} ligand positioned in the plane of the MOS whereas the other three are perpendicular to the plane (Scheme 1b). Evidently, the new MOS can be divided into two parts: *cis*-part and *trans*-part, suggesting the plausible possibility to provide completely different hydrogen bonds orientations. If we specify the direction of MOS as shown in Scheme 1b, when only considering the formation of ladder-like hydrogen bonds, along the X-axis direction, the unique *dzc* structure can be formed by the $\cdots(\text{trans-cis})\cdots(\text{cis-trans})\cdots(\text{trans-cis})\cdots$ arrangement (Figure S4). However, the opposite sides of the MOS along the Y-axis direction share the same composition of one *cis*-Co and one *trans*-Co, which are alternately arranged up and down through hydrogen bonding to form a *dcc* structure, that is similar to the chains in **ZSA-1** (Figure S2 and S4). It is to be mentioned that when four MOSs are arranged vertically according to $\cdots(\text{trans-cis})\cdots(\text{trans-cis})\cdots(\text{trans-cis})\cdots$ arrangement, *d8r* structures can be successfully constructed (Figure S4). Therefore, such a brand-new MOS can not only form the CBUs and chains of both **ZSA-1** and **ZSA-2**, but also can build the *dzc* structure that they cannot form, making it possible to construct new ZSA materials.

By adjusting the ratio of DMF and H_2O around 1:1, red polyhedral crystals of **ZSA-10** were prepared. In the crystal structure of **ZSA-10**, as a typical feature of the ZSA materials, the 4MR MOSs are woven together by hydrogen bonds to form a porous three-dimensional (3D) supramolecular structure. As shown in Figure 1a, b and Figure S4, four MOSs are connected end-to-end to form a typical *d8r* structure with the inside diameter of 10.5 Å. Another larger Paulingite (*pau*) cage is composed of four MOSs that connect two *d8rs*, and forms classic *dcc* structures in the Z-axis direction at the same time. The maximum diameter of the *pau*

cage is 22.9 Å (Figure S4). Each individual MOS self-assembles through H-bonds to form an extended structure with the MER zeolite underlying topology (Figure 1c, d and Figure S6). From the viewpoint of reticular chemistry, each MOS can be regarded as a quadrangle and the interlaced hydrogen bonds form a type of nonplanar hexagon. Therefore, the entire structure can be regarded as a **mer-y** net which is woven by hydrogen bonds (Figure 1e). **ZSA-10** contains three types of intersecting channels with the window size of 4.6×8.0 Å, 10.5×10.5 Å and 4.1×13.9 Å (Figure 1f and Figure S6). It is noteworthy that the MER type ZMOFs are scarce and to the best of our knowledge, only ZIF-10 (including $\text{MeMeCH}_2\text{@ZIF-10}$), ZIF-60, CdIF-2 and $[\text{Zn}(\text{3-pbc})]\cdot\text{H}_2\text{O}\cdot 0.5\text{H}_2\text{O}$ four MER type MOFs have been reported thus far.^{1a,1d,7}

Figure 1. Single crystal structure of **ZSA-10**: (a) ball-and-stick representations of the 4MR-MOS SBU and two simplified ways of hydrogen bonds; (b) *d8r* and the *pau* cage; (c) ball-and-stick model of the 3D supramolecular framework; (d) schematic representation of the MER topology showing the hydrogen bonds and MOS SBUs; (e) linked quadrangles and hexagons representations of the **mer-y** net in reticular chemistry; (f) CPK model of the framework via X-axis.

Manifestly, red block crystals of **ZSA-11** were synthesized by adjusting the ratio of DMF and H_2O around 2:1. **ZSA-11** shares the same MOS as in **ZSA-10** but it forms a completely different *dzc* structure (Figure 2a, b, c). Different *dzc* structures are further connected by hydrogen bonds to form an extended structure with ABW zeolite underlying topology (Figure 2d, e and Figure S7). From structural perspective and considering its reticular chemistry

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assembly, it can be regarded as a structure with interwoven threads and rings. The H-bonds form a type of 4_1 helix and weaves the quadrangles into a supramolecular **sra-wy** net (Figure 2f). **ZSA-11** contains a very narrow channel along the X-axis with a trapezoid window, of which the longer side is approximately 2.945 Å (Figure 2g). Such a small size is similar to zeolite 3A, widely used as a desiccant.⁸

Figure 2. Single crystal structure of **ZSA-11**: (a, b and c) representations of the *dzc* structure; (d) ball-and-stick model of the 3D supramolecular framework; (e) schematic representation of the ABW topology showing the hydrogen bonds and MOS SBUs; (f) mixed threads and rings representations of the **sra-wy** net in reticular chemistry; (g) representation of the narrow and irregular channel in **ZSA-11**.

As described above, the direction of H-bonds and the associated arrangements of MOSs are equally important factors governing the construction of different ZSAs. Correspondingly, the solvent, particularly the ratio of DMF/H₂O, was found to play a critical role in the synthesis and the assembly process (Figure S5). Specifically, when the ratio of DMF/H₂O gradually decreases from 2:1 to 1:2, **ZSA-11**, **ZSA-10** and another large amount of red flake crystals (**compound a**, Figure S8), which have been confirmed not zeolite-like phase in turn, were obtained. The boundaries between the obtained phases were not particularly clear and resulted easily in a mixture phase. To further explore the effect of H₂O on the ZSA structure formation, we soaked **ZSA-10** and **ZSA-11** in water. As a result, it was found that there was no significant change for **ZSA-10** in water (Figure S10) but **ZSA-11** exhibited obviously single-crystal-to-single-crystal (SCSC) transformation and turned into **compound a** (Figure S14). This interesting phenomenon further confirms that H₂O plays an important role in the construction of hydrogen bonding structures. To date, only one MER type MOF (MeMeCH₂@ZIF-10) which was constructed by employing a bulky macrocyclic template to support the structure has been confirmed to be porous.^{7a,7b,9} The N₂ sorption for **ZSA-10** at 77 K exhibited type-I adsorption isotherm behavior, characteristic of a microporous material with permanent

porosity (Figure 3a). The apparent BET surface area of **ZSA-10** was calculated to be 724 m²/g (Langmuir 979 m²/g). The experimental micropore volume was calculated to be 0.38 cm³/g, which was found lower than the theoretical values of 0.69 cm³/g, indicating the plausible contraction/partial collapse of the framework. Nevertheless, **ZSA-10** is the only pure MER framework material (without any supporting templates) exhibiting permanent porosity.^{7b} Although it is still unknown why MOFs based on MER topology are highly unstable, the noted porosity of **ZSA-10** may permit to understand such a discrepancy.

Figure 3. (a) N₂ sorption isotherm and pore size distribution for **ZSA-10**; (b) CO₂ sorption isotherms for **ZSA-10**; (c) CO₂/CH₄ gas mixture adsorption selectivity predicted by IAST at 298 K under 1 bar for **ZSA-10**; (d) N₂, CO₂, H₂ and H₂O vapor sorption isotherms for **ZSA-11**.

In addition, due to the very high Lewis basic sites (LBSS) density (4.08 nm⁻³) introduced by En molecules, **ZSA-10** exhibited outstanding CO₂ storage capacities of 121 cm³/g at 273K and 88 cm³/g at 298K (Figure 3b), which were even higher than -NH₂ functionalized **ZSA-7** and reached the highest one among ZSAs series to date. Also, it is among the highest adsorption values for ZMOFs (Table S9). Considering the partial collapse of the framework, therefore, **ZSA-10** offers a higher CO₂ storage prospect. Moreover, **ZSA-10** exhibits relatively high natural gas selectivity separation (Figure 3c and Figure S19-23), especially for CO₂ over CH₄ (25.9 for CO₂/CH₄ = 0.5/0.5 and 73.6 for CO₂/CH₄ = 0.05/0.95, respectively, under 1 bar at 298 K), which surpasses many reported MOFs under the same conditions.^{5b, 10} Because **ZSA-11** has a very narrow and irregular channel similar to zeolite 3A, most of the gas molecules (such as N₂, CO₂ and H₂) and organic solvent molecules (such as DMF) cannot enter the channel (Figure 3d and Figure S16). As shown in Figure 3d, **ZSA-11** exhibits a typical type-I adsorption isotherm for H₂O, and reaches a total water sorption capacity of 206 cm³/g at P/P₀ = 0.95.

In conclusion, we successfully isolated and revealed a new type of MOS that afforded the synthesis of two new ZSA materials with MER and ABW underlying topologies. The introduction of this distinct MOS attests to the prospect of constructing new ZSA materials, and at the same time magnifies the plausible use of 4MR SBUs for the construction of ZMOFs.

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- [1] a) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939-943; b) M. Eddaoudi, D. F. Sava, J. F. Eubank, K. Adil, V. Guillemin, *Chem. Soc. Rev.* **2015**, *44*, 228-249; c) Y. Liu, V. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488-1490; d) K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186-10191; e) Y. X. Tan, F. Wang, J. Zhang, *Chem. Soc. Rev.* **2018**, *47*, 2130-2144; f) J. P. Zhang, Y. B. Zhang, J. B. Lin, X. M. Chen, *Chem. Rev.* **2012**, *112*, 1001-1033; g) F. Yi, H. Yang, X. Zhao, P. Feng, and X. Bu, *Angew. Chem. Int. Ed.* **2019**, *58*, 2889-2892.
- [2] a) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2009**, *43*, 58-67; b) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 3875-3877; c) X. Luo, Y. Cao, T. Wang, G. Li, J. Li, Y. Yang, Z. Xu, J. Zhang, Q. Huo, Y. Liu, Eddaoudi, M. *J. Am. Chem. Soc.* **2016**, *138*, 786-789; d) N. T. Nguyen, H. Furukawa, F. Gandara, H. T. Nguyen, K. E. Cordova, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2014**, *53*, 10645-10648; e) B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature* **2008**, *453*, 207-211.
- [3] a) L. Sun, H. Xing, Z. Liang, J. Yu, R. Xu, *Chem. Commun.* **2013**, *49*, 11155-11157; b) D. Wang, T. Zhao, G. Li, Q. Huo, Y. Liu, *Dalton Trans.* **2014**, *43*, 2365-2368.
- [4] a) Y. Liu, V. Kravtsov, M. Eddaoudi, *Angew. Chem. Int. Ed.* **2008**, *47*, 8446-8449; b) Y. H. Tang, F. Wang, J. X. Liu, J. Zhang, *Chem. Commun.* **2016**, *52*, 5625-5628; c) D. F. Sava, V. Ch. Kravtsov, F. Nouar, L. Wojtas, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 3768-3770; d) Qi. Shi, W. Xu, R. Huang, W. Zhang, Y. Li, P. Wang, F. Shi, L. Li, J. Li, J. Dong, *J. Am. Chem. Soc.* **2016**, *138*, 16232-16235.
- [5] a) M. H. Alkordi, J. A. Brant, L. Wojtas, V. Ch. Kravtsov, A. J. Cairns, M. Eddaoudi, *J. Am. Chem. Soc.* **2009**, *131*, 17753-17755; b) J. Li, C. Dai, Y. Cao, X. Sun, G. Li, Q. Huo, Y. Liu, *J. Mater. Chem. A* **2017**, *5*, 21429-21434; c) S. Wang, T. T. Zhao, G. H. Li, L. Wojtas, Q. S. Huo, M. Eddaoudi, Y. L. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 18038-18041; d) D. F. Sava, V. Kravtsov, J. Eckert, J. F. Eubank, F. Nouar, M. Eddaoudi, *J. Am. Chem. Soc.* **2009**, *131*, 10394-10396; e) S. Wang, Y. Belmabkhout, A. J. Cairns, G. Li, Q. Huo, Y. Liu, M. Eddaoudi, *ACS Appl. Mater. Interfaces* **2017**, *9*, 33521-33527; f) K. Xing, R. Fan, S. Gai, X. Zheng, P. Wang, Y. Yang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 36081-36089; g) Q. Pang, B. Tu, E. Ning, Q. Li, D. Zhao, *Inorg. Chem.* **2015**, *54*, 9678-9680.
- [6] a) R. Ding, C. Huang, J. Lu, J. Wang, C. Song, J. Wu, H. Hou, Y. Fan, *Inorg. Chem.* **2015**, *54*, 1405-1413; b) L. L. Han, T. P. Hu, K. Mei, Z. M. Guo, C. Yin, Y. X. Wang, J. Zheng, X. P. Wang, D. Sun, *Dalton Trans.* **2015**, *44*, 6052-6061; c) G. Majano, O. Martin, M. Hammes, S. Smeets, C. Baerlocher, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2014**, *24*, 3855-3865; d) T. Qin, J. Gong, J. Ma, X. Wang, Y. Wang, Y. Xu, X. Shen, D. Zhu, *Chem. Commun.* **2014**, *50*, 15886-15889; e) B. Zheng, X. Sun, G. Li, A. J. Cairns, V. C. Kravtsov, Q. Huo, Y. Liu, M. Eddaoudi, *Cryst. Growth Des.* **2016**, *16*, 5554-5562.
- [7] a) M. Deng, X. Liu, Q. Zheng, Z. Chen, C. Fang, B. Yue, H. He, *CrystEngComm* **2013**, *15*, 7056-7061; b) J. R. Ramirez, H. Yang, C. M. Kane, A. N. Ley, K. T. Holman, *J. Am. Chem. Soc.* **2016**, *138*, 12017-12020; c) Y. Q. Tian, S. Y. Yao, D. Gu, K. H. Cui, D. W. Guo, G. Zhang, Z. X. Chen, D. Y. Zhao, *Chem. Eur. J.* **2010**, *16*, 1137-1141.
- [8] K.-M. Kim, H.-T. Oh, S.-J. Lim, K. Ho, Y. Park, C.-H. Lee, *J. Chem. Eng. Data* **2016**, *61*, 1547-1554.
- [9] O. Karagiari, W. Bury, A. A. Sarjeant, C. L. Stern, O. K. Farha, J. T. Hupp, *Chem. Sci.* **2012**, *3*, 3256-3260.
- [10] a) D. M. Chen, X. P. Zhang, W. Shi, P. Cheng, *Inorg. Chem.* **2015**, *54*, 5512-5518; b) M. H. Choi, H. J. Park, D. H. Hong, M. P. Suh, *Chem. Eur. J.* **2013**, *19*, 17432-17438; c) P. S. Nugent, V. L. Rhodus, T. Pham, K. Forrest, L. Wojtas, B. Space, M. J. Zaworotko, *J. Am. Chem. Soc.* **2013**, *135*, 10950-10953.

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A new type of MOS was successfully synthesized and employed for the construction of two new ZSA materials with MER and ABW underlying topologies. The introduction of this distinct MOS attests to the prospect of constructing new ZSA materials, and at the same time magnifies the plausible use of 4MR SBUs for the construction of ZMOFs.