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From Bola-Surfactant Templated Bimetal Phosphites to the Design of Crystalline Inorganic Mesoporous Frameworks

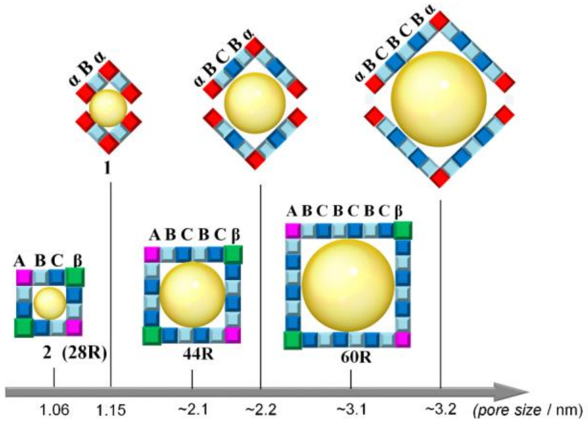
Hui-Lin Huang, Wen-Yen Huang, and Sue-Lein Wang*

The development of new porous materials is one of the most active research fields in crystalline inorganic solids, and interesting topologies and structure-related properties are continually discovered from these appealing structures.[1,2] It is constantly a huge challenge in constructing new structures by design because the ability to control the formation of any specific inorganic units is still limited.[3] Even though some small building units such as tetrahedral nodes in zeolites or other readily-formed metal clusters are quite helpful in constructing three-dimensional nets, a lack of selective connections of these units results in unpredictable and random connectivity sequences. If certain types of inorganic building units (or even building modules) of interest, can reproduce in reactions of different templating systems and to replicate the same connection message to the new structure, a high possibility of designing new series for unlimited pore augmentation can be expected.

Recently, we demonstrated that by using long-linear-alkyl chain monoamines as templates, one can achieve remarkable inorganic crystalline frameworks of the NTHU-13 system with channels unprecedentedly expanded from 24-membered ring (24R) to 72R and apertures from 0.69–3.5 nm.[4] Unlike mesoporous structures, which generally display ambiguous, amorphous walls,[5] crystalline wall structures in the NTHU-13 system were observed to be constructed of the same inorganic building modules in a specific sequence. This finding suggests that creating new topologies that are designable toward mesoscale may become feasible if these building modules can form repeatedly in another templating system.

Bola-surfactant templates, which present similar molecular structure to monoamine ones, are linear-long-alkyl chain diamines with two hydrophilic ends. Commercially available large-sized bola-surfactant, for example, 1,12-diaminododecane (DADD), has been used as biomimetic template for forming 2D lamellar silicas or mesolamellar metal phosphates,[6] or as porogens for creating 3D frameworks with extra-large channels (Table S1).[7,8] Taking into account its molecular shape and the ability in creatin crystalline inorganic structure with extra-large channels, DADI could be a suitable template for reproducing the desired buildin modules.

Herein, we present the use of DADD as template t successfully create a new channel-like structure c $(H_2DADD)_3[Ga_2FZn_5(OH)_5(HPO_3)_8]\cdot 9H_2O$ (**1**) and a new 28R channel structure of $(H_2DADD)_2[GaFZn_7(H_2O)_4(HPO_3)_{10}]\cdot 4H_2$((**2**), with breakthroughs not only in reproducing all requeste building modules (*vide infra*) but also in forming differer topologies from NTHU-13. By using these particular module reported in this work, two series can be rationally designed, wit predictable formulae, wall structures, and channel expansion from micro- to mesoscale (Scheme 1).



Scheme 1. Schematic drawing of channel expansions and wall structures of **1** (to and **2** (bottom). Hypothetical structures with pore sizes > 2 nm were designed wit BC pair as the proliferation unit (see text).

Crystals of **1** and **2** were observed to form concurrently when a reaction mixture of zinc lactate (0.122 g, 0.5 mmol), Ga_2O_3 (0.047 g, 0.25 mmol), 5M H_3PO_3 (0.6 mL, 3 mmol), DADD (0.4 g, 2 mmol), HF (40%, 0.2 mL), and water (10 mL) was heated at 120˚C for 2 days. As the dwelling time was extended to 3 days, crystals of **2** were unobserved in the product, instead, **1** was obtained as a major product, indicating that **1** was more thermally stable between the two phases. Unfortunately, most crystals of **1** were contaminated by unknown grains embedded deeply inside, causing difficulty to get the pure phase

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of **1**. In contrast, **2** was prepared as a pure phase (See Experimental Section) with a yield of 85% based on Zn, allowing us to further investigate its interesting properties. Single-crystal structure analysis was performed to determine the structures and chemical formulae (Table S2 and Figure S1),[9] which were corroborated by elemental analysis (EA) and thermogravimetric analysis (TGA) (Figure S3). The EA data confirmed the stoichiometry of organic amines for **2**. The found/calculated percentages were C, 15.64/15.43; H, 4.61/4.20; and N, 3.15/2.99.

The structures of **1** and **2** share similar porous topology and building module. The 2D structure of **1** crystallizes in the space group *C*2/*c* and features a channel-like topology on the *ab* plane, with nearest and farthest interlayer-free distances of 2.12 Å and 20.14 Å, respectively (Figure 1a). On the other hand, the 3D framework of **2** crystallizes in the space group *Ibca* and features a diamond-shaped 28R-channel structure with free pore size of ~10.6 Å (Figure 1b). The void space in **2** reached 50.8%, which is higher than that in the 36R-channel structure of Cacoxenite (44.5%).[10] Five particular modules—$_\infty[GaF(HPO_3)_2]^{2-}$ (block A), $_\infty[Ga_2FZn(OH)_5(HPO_3)_4]^{6-}$ (block α), $_\infty[Zn(HPO_3)]$ (blocks B and β), and $[Zn(HPO_3)_2(H_2O)_4]^{2-}$ (block C)—comprise the structures of **1** or **2** (Figure 1c). Blocks α and A are negatively-charged zincogallium/gallium phosphite infinite chains; block C is a negatively-charged zinc phosphite cluster; blocks β and B are neutral polymorphs. Block B consists of a zinc phosphite 4R infinite chain, while block β can be viewed as a rearrangement of 4R units into a new 8R channel (Figures S8 and S10). Since **1** needed a longer reaction time to form than **2**, we speculated that block α was likely formed of blocks A and C. A comparison of thermodynamic or kinetic stability among these blocks has been made. The thermodynamic stability sequence can be sorted as B > α > C ≈ A > β; and the kinetic stability sequence can be sorted as A ≈ B > C > β > α. The unique layer structure of **1** can be described as an infinite linkage of αBα, while the wall structure of **2** is built from a sequence of A(BC)β(CB)A. Interestingly, the connecting sequence in **2** was the same as that in 28R-NTHU-13, but **2** possessed a lower symmetry (orthorhombic) than that of 28R-NTHU-13 (tetragonal). The successful preparation of **2** represents that using DADD was efficient in reproducing these particular building modules. It is worth to note that in the previously monoamine-templated NTHU-13 system, blocks A, B, and C repeatedly appeared in the pore augmentation process, while block β only appeared in 28R-NTHU-13, which was templated by *n*-hexylamine. The elongation of carbon chain of monoamines had no effect on the reproduction of block β. However, by using DADD instead of monoamines, we successfully produced block β again.

The DADD templates were clearly resolved in both **1** and **2** (Figure 2). In **1**, two types of protonated DADD were observed: one bent and the other straight (Figure 2), and they had intra-molecule N-to-N distances of 11.49 Å and 16.07 Å, respectively (Figure S6). Similar to **1**, two types of protonated DADD were observed in **2**: one with a longer N-to-N distance of 15.24 Å and the other with a shorter N-to-N distance of 14.58 Å (Figure S6). In both structures, the positively charged N heads interacted with the inorganic framework through hydrogen bonds (donor to acceptor distances are between 2.76 ~ 3.06 Å) (Figure S7).

TG analyses showed that removal of lattice water molecules began at *ca*. 50˚C for both **1** and **2**, and could be completely removed before 150˚C (Figure S3). Variable temperature powder X-ray diffraction (VT-PXRD) measurements showed that the structure of **2** could sustain up to 200˚C (Figure S11). From VT-PXRD patterns, we observed that two peaks representing the (004) and (040) planes merged into one peak upon heating to 100˚C (**2-T**$_1$) (Figure 3b), indicating a higher symmetry. Peaks from the pattern of **2-T**$_1$ were indexed,[11] revealing that the cell transformed into a tetragonal system with *a* (or *b*) = 52.103 Å. Toward 200˚C, low-angle peaks shifted slightly to higher angles (**2-T**$_2$), suggesting shrinkage of the crystal cell. Interestingly, **2-T**$_1$ and **2-T**$_2$ were discovered to transform back into the orthorhombic phase with exposure to humidity. The transformation between tetragonal and orthorhombic phases was reversible by heating and rehydration. To understand which part in the structure supported the symmetry transformation, we replaced the Ga centers by Al

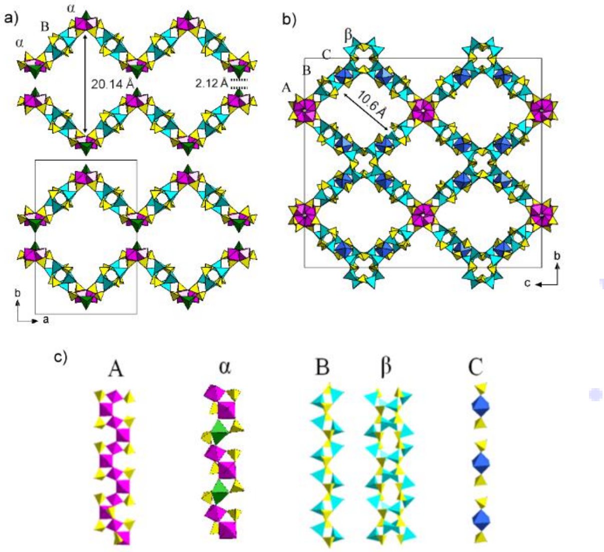

Figure 1. Crystal structures for **1** and **2**. a) Quasi-channel structure of **1** along the axis, showing the channel-like topology with nearest and farthest interlayer-fre distances. b) 28R channels along the *a*-axis, showing a diamond-shaped windo with a free diameter of 10.6 Å. c) Five inorganic building modules compris structures of **1** and **2**. Tetrahedra of Zn in cyan, P in yellow, trigonal-bipyramid of Z in green, octahedra of Zn in blue, and Ga in pink.

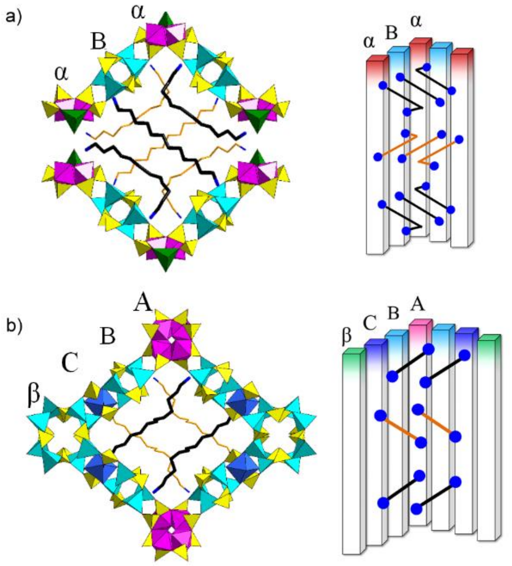

Figure 2. Schematic drawing of structure connectivity and the arrangement DADD in **1** (a) and **2** (b). Various stick colors represent DADD residing at various depths along the channel.

(**2-Al**) and Fe (**2-Fe**) (Table S2) for gaining some clues. The difference in crystal radii between Al and Fe was about 17 %; however, the difference in cell volume between **2-Al** and **2-Fe** was only 0.9 %, indicating that block A is a rigid part in **2**. In addition, when comparing Ga-to-Ga distances (block A) and Zn-to-Zn distances (block β) in orthorhombic **2** with those in tetragonal 28R-NTHU-13, we observed more significant differences in block β than block A (Figure S12). Therefore, block β could be considered as a "soft" joint to support the framework transformation process.

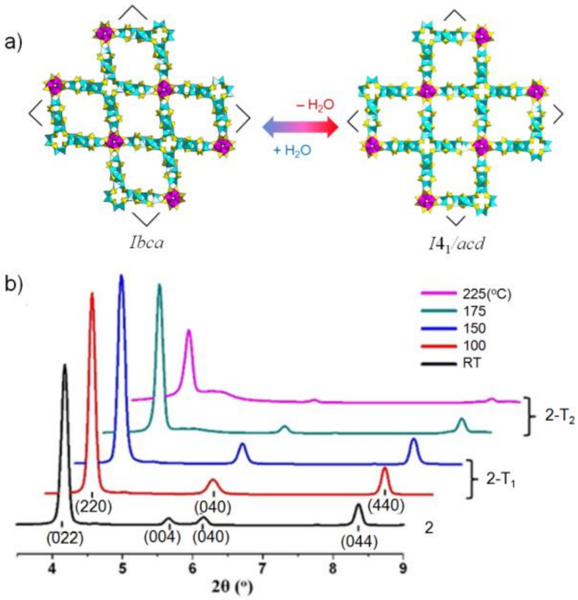

Figure 3. Framework symmetry transformation of **2**. a) Reversible framework transformation between orthorhombic and tetragonal phases triggered by the loss of lattice water molecules upon heating. b) VT-PXRD patterns with plane indexes showing two peaks representing the (004) and (040) planes merged into one peak upon heating.

Compound **2** was discovered to display a blueish-white light under the excitation of 380-nm UV light. As shown in Figure 4, the photoluminescence (PL) emission curve is a broad band with maximum peak centered on 450 nm and CIE coordinates of (0.26, 0.30). The significant blueish-white emission (quantum yield ~4 %) may originate from diamine templates (Figure S12). A temperature-dependent PL experiment was conducted for **2**. The powder sample of **2** was gently heated from room temperature to 200℃, and PL intensity gradually decreased. This could be attributed to the thermal quench effect. However, at 210℃, the intensity was dramatically enhanced and was 20% stronger than that measured at room temperature. Since water is a well-known luminescence quencher, this phenomenon can be attributed to the complete elimination of lattice water molecules. With continuous heating beyond this temperature, PL intensity gradually decreased due to collapse of the framework.

The successful preparation of crystalline **1** and **2** provided us with new modules, α and β, respectively, to design additional two new expandable series (Scheme 1) based on the systematic expansion mechanism of NTHU-13, namely, the insertion of BC pair as the proliferation unit. For **1**, if we can discover a suitable reaction condition to form block C, then the quasi-channel of **1** could be expanded from 1.15 nm to mesoporous region with a general formula of $\alpha(BC)_nB\alpha$ ($n \geq 0$). On the other hand, for **2**, the channel expansion can be described by a general formula of $A(BC)_N\beta(CB)_NA$ ($N \geq 1$). Such expansion would result in new crystalline mesoporous structures with 44R (N = 2), 60R (N = 3), or even 76R (N = 4).

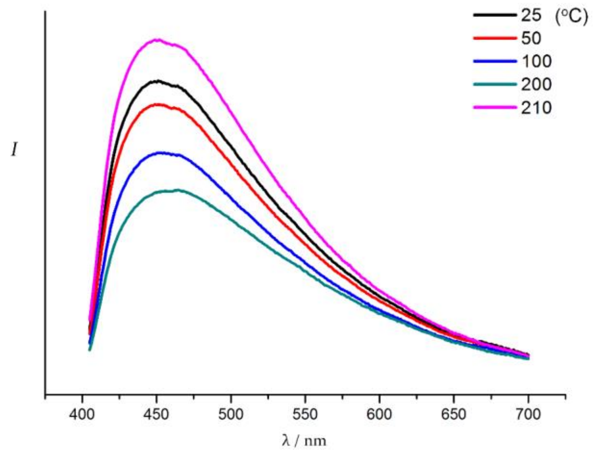

Figure 4. Variable-temperature PL emission spectra of **2** under the excitation of 38 nm UV light, showing that intensity was dramatically enhanced at 210˚C and w 20% stronger than that measured at room temperature.

In conclusion, by using bola-type surfactant, we hav successfully prepared **1** and **2** and achieved the controll formatio of particular inorganic modules. Compound **1** displays an unusua quasi-channel structure with a quasi-aperture of 1.15 nm. Th channel compositions and connectivity of **2** are similar to that c the tetragonal 28R-NTHU-13. However, **2** could experience symmetry-change to tetragonal. Such framework transformatio was not detected previously when monoamines were used t prepare NTHU-13. The use of bola-type surfactant may facilitat the discovery of potential mechanical property in association wit such flexible framework of **2** or perhaps NTHU-13. Intriguing P property and catalytic activity were observed. Catalytic result showed that **2** can be a good catalyst for the Knoevenage condensation reaction (Table S4). The preparation of crystalline and **2** provides successful replication of building modules whic are key to the predictive design of new inorganic mesoporou topologies, opening up more opportunities with bola-typ surfactant to create new crystalline inorganic mesoporou structures with pore sizes unattainable before.

Experimental Section

A major phase of needle-like crystals of **1** was obtained by heating a mixture of zi lactate (0.122 g, 0.5 mmol), Ga_2O_3 (0.047 g, 0.25 mmol), 5M H_3PO_3 (0.6 mL, mmol), DADD (0.4 g, 2 mmol), HF (40%, 0.2 mL), and water (10 mL) in a 23-m Teflon-lined, acid-digestion bomb at 120˚C for 72 h. Attempts to prepare a pu phase of **1** were tried with a soluble metal source of gallium nitrate but failed. The above reaction so far was an optimal condition for **1**. By reducing the amount of HF (40%, 0.1 mL) in the above reaction at 120˚C for 48 h, a pure phase of needle-like crystals of **2** was obtained. The yields (based on Zn) were 60% and 85% for **1** and **2**, respectively.

CCDC 1474949 and CCDC 1474950 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Bola-surfactant • Hydrothermal synthesis • Metal phosphite • Mesoporous materials • Synthesis design

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