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## Impeller-like dodecameric water clusters in metal–organic nanotubes

Tien-Wen Tseng,<sup>\*,a</sup> Tzuoo-Tsair Luo,<sup>b</sup> and Kai-Hsiang Lu<sup>a,b</sup>

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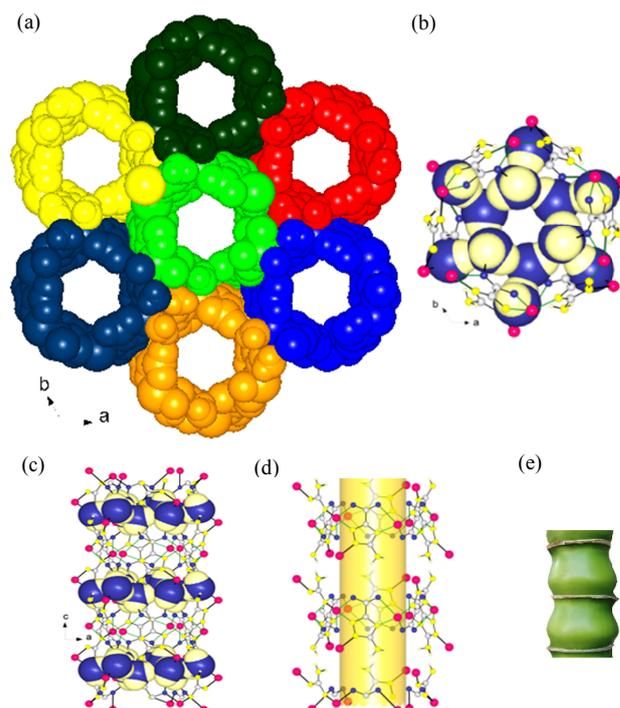
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5 A triazole ligand bearing a carboxylate and an amino groups has been incorporated into a nanotubular copper(II)–organic framework, in which the impeller-like (H<sub>2</sub>O)<sub>12</sub> water clusters were trapped in the nanotubes and can be encapsulated reversibly and precisely.

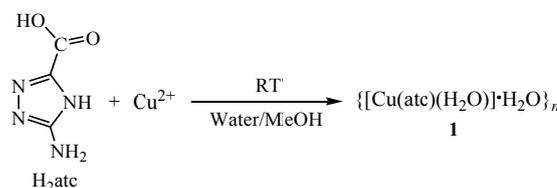
10 The development of metal–organic nanotubes (MONTs) has become a topic of major interest, since they are amenable to structural engineering and have some unique transport and storage properties.<sup>1</sup> Thanks to effective design and synthesis strategies, it is now possible to construct highly rigid and porous  
15 MONTs from judiciously selected organic and inorganic building blocks.<sup>2</sup> The structures of these tubular materials can be adjusted or regulated through the insertion/removal of the guest molecules,<sup>3</sup> but the preparation of MONTs, especially materials comprised of large and regular-shaped units, continues to be a  
20 challenge.<sup>4</sup> To date, a variety of water clusters with different sizes and shapes have been identified, which provide the associated information to permit the anomalous behavior of bulk water to be better understood.<sup>5–9</sup> To develop new nano materials with intriguing properties, getting an understanding of how  
25 water molecules or guests are regularly nano-confined becomes a major focus; however, an understanding based on the water clusters that are trapped in MONTs is limited.<sup>8</sup>

As part of our ongoing efforts to explore functional crystalline materials,<sup>10</sup> we report on a unique type of MOF,  $\{[\text{Cu}(\text{atc})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$  (**1**), comprised of Cu(II) and the ligand atc<sup>2-</sup> (atc<sup>2-</sup> = 3-amino-1,2,4-triazolate-5-carboxylate). Compound **1** was found to be: 1) a porous and robust MOF; 2) composed of a framework consisting of corner-shared metal–organic nanotubes with an interior channel diameter of  
35 8.5 Å; 3) with a unique impeller-like dodecameric water cluster (H<sub>2</sub>O)<sub>12</sub> being regularly confined within the MONT so as to resemble a bamboo culm; 4) the water clusters can be encapsulated reversibly and with high-precision. To the best of our knowledge, metal–organic nanotubes that contain regularly  
40 trapped impeller-like (H<sub>2</sub>O)<sub>12</sub> water clusters resembling a bamboo culm, in which the water clusters participate in a reversible dehydration/rehydration process are quite rare. This phenomenon appears to be astonishing and unprecedented.

Green crystals of **1** were synthesized by the reaction of  
45 copper(II) nitrate dihydrate and 3-amino-4H-1,2,4-triazol-5-carboxylic acid (H<sub>2</sub>atc) in a water/MeOH solvent diffusion



**Fig. 1** Crystal structures of **1**: (a) top view of the tubular structure; (b) top view of the impeller-like water cluster (H<sub>2</sub>O)<sub>12</sub> in the space-filling mode; (c) water clusters were trapped within in the nanotube; (d) a dehydrated nanotube; (e) a bamboo culm.

Scheme 1 Synthesis of compound **1**

system at room temperature through a single-step, self-  
90 organization process† (Scheme 1). The appropriate choice of the H<sub>2</sub>atc ligand with specific functional groups and geometry was found to be a major factor for successfully producing this nanotube-based structure. To achieve a tubular framework **1**, it appears that the scaffold of the atc<sup>2-</sup> ligand plays a crucial role  
95 because of its suitable  $\mu_3$ -( $\kappa^3\text{N}, \text{O}^1:\text{O}^2$ ) bridging mode. However (and fortunately), the synthesis allowed entire scaffold of the

atc<sup>2-</sup> ligand to be retained, unlike the situation in which the atc<sup>2-</sup> ligand was completely *in situ* decarboxylated under hydrothermal conditions.<sup>11</sup>

A single-crystal X-ray diffraction analysis revealed that compound **1** crystallized in the rhombohedral space group *R*-3 and possessed a nanotubular framework. The asymmetric unit of **1** consisted of one Cu<sup>II</sup> center, one atc<sup>2-</sup> ligand, one coordinated water molecule, and one guest water molecule. Analysis of the local symmetry of the metal cation showed that the Cu(II) center was located on a special position (site occupancy factor (SOF) = 1/3) containing a threefold axis of rotation. Each Cu<sup>II</sup> center was bound to one nitrogen atom, two pairs of atoms from three distinct atc<sup>2-</sup> ligands, and one coordinated water molecule (O3) in a distorted octahedral environment (Fig. S2, ESI†). Two atc<sup>2-</sup> ligands are bridged to two Cu(II) centers and form a dinuclear copper cluster, which functions as a building unit. As shown in Fig. 1, these copper cluster units are extended, leading to the formation of a single-walled corner-shared metal-organic nanotube (MONT) with an exterior wall diameter of up to 15.1 Å and an interior channel diameter of 8.5 Å. To analyse the topology of the structure of **1**, it can be simplified by considering that a building block is linked to four neighbour ones, giving rise to a pseudo 4-connected node, as shown in Figs. S3a and S3b. Thus, the entire connectivity of framework **1** shows an *nbo*-type topology (Fig. S3c, ESI†).<sup>12</sup>

Overall, there are six guest water molecules (O4) hydrogen-bonded together to form a core hexameric water cluster, which is further linked to six adjacent coordinated water molecules (Fig. S4, Table S3, ESI†). Finally, these water molecules are assembled into dodecameric clusters. Interestingly, a geometry of this water cluster (H<sub>2</sub>O)<sub>12</sub> indicates that it is impeller-like (Fig. 1b), a formation that has not been previously reported.<sup>8a,9</sup> In addition, owing to the fact that these water clusters are regularly encapsulated in the nanotubes, the overall structure of MONT **1** resembles a bamboo culm (Fig. 1d).

Using the PLATON software,<sup>13</sup> the extra-framework volume per unit cell of compound **1** was calculated to be 36.4%. A thermogravimetric analysis (TGA) of **1** showed that the water molecules are eliminated from the framework (calcd 16.0%; found 15.2%) when the temperature is increased from room temperature to about 245 °C, after which, the compound undergoes decomposition (Fig. S13, ESI†). Interestingly, the dehydrated sample reverts back to the original solid by rehydration in humid atmosphere at room temperature for 0.5 h, as indicated by the TGA results for the rehydrated material (Fig. S14, ESI†). Importantly, extensive powder X-ray diffraction (PXRD) results showed that the crystallinity of **1** does not undergo significant change upon dehydration at 110 °C for 1 h (see ESI†), and a reversible crystal-to-crystal transformation could be confirmed (Fig. S15, ESI†). Considering this highly precise reversible encapsulation of water molecules, the water molecules are able to effectively migrate through the nanotubes.

Variable temperature dependence of magnetic susceptibility of compound **1** was measured on powdered sample in the temperature range of 1.8–300 K at a 1.0 kG magnetic field. The magnetic susceptibility of compound **1** above 50 K obeyed the Curie-Weiss law very well (Fig. 3). The monotonic decrease in  $\chi_M T$  with temperature is characteristic of compound **1** with

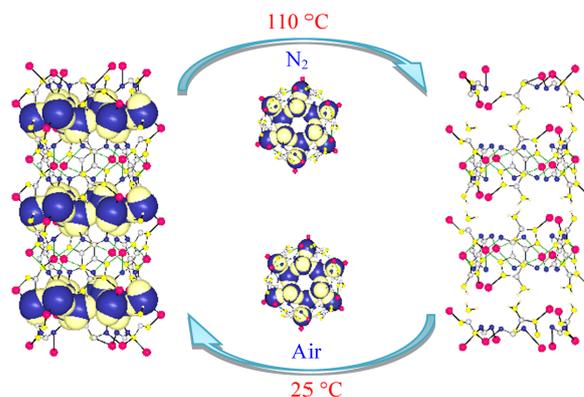


Fig. 2 Schematic view shows the reversible dehydration and hydration of water clusters in a nanotube.

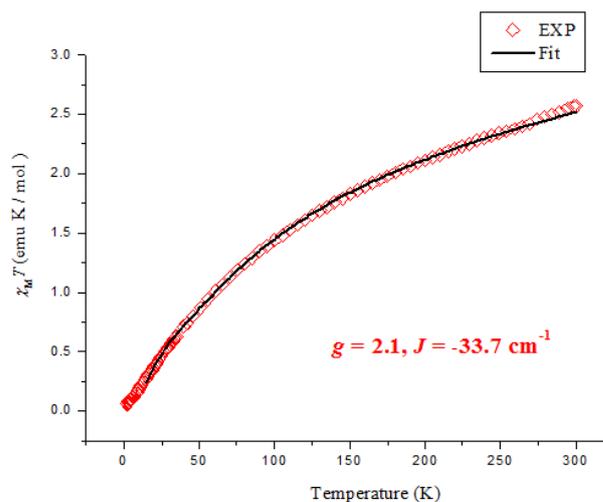


Fig. 3 Plots of  $\chi_M T$  vs.  $T$  for a microcrystalline sample of complex **1**. The solid line represents a least-squares fit of the data in the region 10–300 K to the van Vleck equation.

overall antiferromagnetic interactions and/or spin-orbital coupling within **1**. In addition, the magnetic data can be analyzed using a Heisenberg Hamiltonian according to a simple six-*J* model (Fig. S18, ESI†). The results of the fitting of the experimental data are shown as a solid line in Fig. 3, with final parameters being  $g = 2.1$ ,  $J = -33.7 \text{ cm}^{-1}$ , which is indicative of antiferromagnetic interactions.

In particular, the framework integrity of **1** is sustained upon heating to 245 °C, thus making the vacant sites of the Cu<sup>II</sup> centers to be available. The water molecules are rapidly re-encapsulated into these dehydrated nanotubes via coordination and hydrogen-bonding interactions. After **1** is dehydrated, these possible open metal sites have the potential for use as a catalyst or heat recovery system.<sup>14</sup>

In summary, we report on the successful preparation of a robust metal-organic nanotubular framework, in which an impeller-like dodecameric water clusters were regularly stacked, permitting this MONT to resemble a bamboo culm. The unique impeller-like (H<sub>2</sub>O)<sub>12</sub> water clusters display reversible encapsulation with a high degree of precision. This phenomenon is currently astonishing and may provide an unusual insight into exploring the mysterious behaviours of water clusters in

nanotubes.

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## Notes and references

<sup>a</sup>Department of Chemical engineering, National Taipei University of Technology, Taipei 106, Taiwan. Fax: +886-2-2776-2383; Tel: +886-2-2771-2171 ext 2538; E-mail: f10403@ntut.edu.tw

<sup>b</sup>Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

†Electronic Supplementary Information (ESI) available: Experimental procedures, characterization and additional figures of **1**; dehydrated/rehydrated PXRD; CCDC 963169 contains the supplementary crystallographic data for this compound. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

‡Crystal data for **1**: C<sub>3</sub>H<sub>6</sub>CuN<sub>4</sub>O<sub>4</sub>, *M<sub>r</sub>* = 225.66, Rhombohedral, space group *R*-3, *a* = *b* = 21.5760(4) Å, *c* = 8.9043(4) Å, *V* = 3589.82(19) Å<sup>3</sup>, *T* = 100(2) K, *Z* = 18, θ<sub>max</sub> = 25.02°, MoK<sub>α</sub> radiation, λ = 0.71073 Å, μ = 2.721 mm<sup>-1</sup>, ρ = 1.832 Mg m<sup>-3</sup>. 11346 reflections measured, 1420 unique (*R*<sub>int</sub> = 0.0546), that were used in all calculations. Final *R<sub>f</sub>* = 0.0359 [*I* > 2σ(*I*)], w*R*<sub>2</sub> = 0.1117 (all data), GOF = 1.067.

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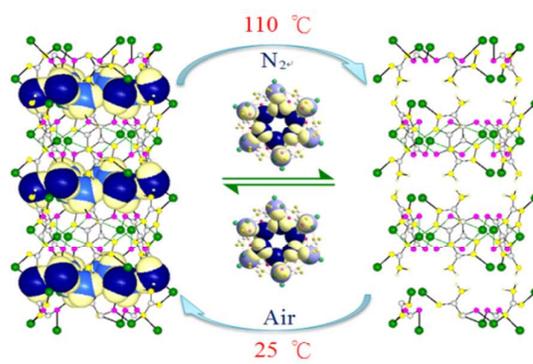
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## Impeller-like dodecameric water clusters in metal–organic nanotubes

Tien-Wen Tseng,<sup>\*,a</sup> Tzuoo-Tsair Luo,<sup>b</sup> Kai-Hsiang Lu<sup>a,b</sup>

<sup>a</sup>Department of Chemical Engineering, National Taipei University of Technology, Taipei 106, Taiwan.

<sup>b</sup>Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan.



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A triazole ligand, 3-amino-1,2,4-triazole-5-carboxylic acid ( $H_2atc$ ), bearing a carboxylate and an amino groups, has been incorporated into a nanotubular copper(II)–organic framework that displays an **nbo**-type topology, in which the impeller-like  $(H_2O)_{12}$  water clusters were trapped in the nanotubes that can be encapsulated reversibly and precisely.

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