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## Multi-responsive metal-organic lantern cages in solution<sup>†</sup>

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Soluble copper-based  $M_4L_4$  lantern-type metal-organic cages bearing internal amines were synthesized. The solution state integrity of the paramagnetic metal-organic cages was demonstrated using NMR, DLS, MS, and AFM spectroscopy. 1D supramolecular pillars of pre-formed cages or covalent host-guest complexes selectively formed upon treatment with 4,4'-bipyridine and acetic anhydride, respectively.

Modern self-assembly synthetic protocols readily provide a plethora of capsule-like molecules in differing sizes and shapes,<sup>1–4</sup> yet functional group incompatibilities can interfere with the assembly of pyridine and imine based coordination cages from ligands bearing Lewis basic groups<sup>5,6</sup> and subsequent interactions with nucleophilic guests. The robust carboxylate-based secondary building units of metal–organic frameworks (MOFs), and their capsule-like cousins, metal organic polyhedra (MOPs),<sup>7–9</sup> however, readily tolerate embedded reactive groups<sup>10,11</sup> and can be post-synthetically modified (PSM) using standard organic reactions to covalently attach functional groups not present in the initial ligands.<sup>12,13</sup>

The majority of MOP reports focus on solid state structure<sup>14–16</sup> and much about MOP formation and solution state behavior remains unexplored.<sup>17–20</sup> First, nearly all MOPs utilize the paramagnetic copper( $\pi$ ) paddlewheel SBU that unfortunately renders NMR analyses, which offer powerful insight into the solution integrity and host–guest behavior of artificial molecular capsules, obtuse due to the hyperfine shift.<sup>21</sup> Second, carboxylate based MOPs are neutral and often poorly soluble. Here we report (i) the preparation of two multi-responsive, soluble lantern-type M<sub>4</sub>L<sub>4</sub> metal–organic cages, (ii) their crystallographic and <sup>1</sup>H NMR analyses and post-assembly transformations to give (iii) extended 1D supramolecular coordination polymers and (iv) a covalently bound guest complex (Scheme 1) in response to reactive guest substrates.

Lantern-type  $M_2L_4^{22,23}$  or  $M_4L_4^{24,25}$  cages assemble from four bent organic ligands and two metal ions or two square-paddlewheel SBUs, respectively, to provide a simple host framework. Methoxy and decyloxy groups on the central phenyl ring of curved ligands L1 and L2 improve cage solubility (Fig. 1a) and, as hyperfine coupling operates *via* delocalization of unpaired electron spin density through the  $\sigma$  and  $\pi$  framework and through-space dipolar coupling, we predicted that distant alkoxy groups would remain unaffected by the paramagnetic SBUs and provide a spectroscopic tag for NMR analyses. Finally, internal amines serve as embedded nucleophiles for the covalent binding of guests.

Methoxy and decyloxy amino ligands **L1** and **L2** were synthesized in five steps from *p*-anisidine and 4-decyloxyaniline, respectively. After dibromination, subsequent Sonogashira reactions were used to install ethynyl spacers and *m*-benzoic acid groups. Ligand **L1** was reacted with Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in DMSO at 85 °C for 16 hours to afford green crystals suitable for structure determination (Fig. 1a). Single crystal X-ray diffraction analysis confirmed the M<sub>4</sub>L<sub>4</sub> lantern-type cage structure containing two copper paddlewheel SBUs (Fig. 1b).‡ Cage **1** is an oblate spheroid where the major axis is ~2.5 nm, *i.e.* distance between oxygen atoms in opposing exotopic methoxy groups, and the minor axis ~ 1.5 nm, *i.e.* the distance between the outer copper atoms. The internal amino groups define a smaller spheroid with a



 $\label{eq:scheme1} \begin{array}{l} \mbox{Cartoon representation of $M_4L_4$ lantern cages and guest responsive post-assembly supramolecular assembly and internal bond formation. \end{array}$ 

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Fig. 1 (a) Assembly of lantern shaped cages 1 and 2 from multi-functional ligands L1 and L2 and (b) single crystal X-ray (SXRD) structures of methoxy amino cage 1 and decyloxy amino cage 2. Apical and included solvent molecules and ligand disorder removed for the sake of clarity. See ESI† for details.

volume of 680 Å<sup>3</sup>, a major axis of 1.2 nm (distance between opposing nitrogen atoms), and a minor axis of 0.9 nm (distance between inner copper atoms). In spite of the open cage framework,  $\pi$ -stacking interactions between cages render a dense structure without continuous solvate channels (Fig. S28, ESI†).

Single crystals of cage 2 were obtained from slow vapor diffusion of MeOH into a DMA solution of ligand L2 and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O over one week (Fig. 1a). X-ray diffraction analysis confirmed the isostructural lantern-type cage 2 with decyloxy chains (Fig. 1b).‡ The core framework of cage 2 is identical to that of cage 1 with similar distances and volumes. Opposing decyloxy chains are either both fully extended or bent in an anti-fashion to facilitate an interwoven, tightly packed structure (Fig. S31, ESI†). Conveniently, alkoxy tetramino cages 1 and 2 both proved sufficiently soluble ( $\sim 1 \text{ mM}$ ) in polar solvents, *i.e.* DMF, DEF, DMA and DMSO, and, given the efficient synthesis of cage 1, we used 1 for solution studies.

<sup>1</sup>H NMR analyses of crystals of cage 1 dissolved in DMF-d<sub>7</sub> revealed a single set of peaks broadened due to strong magnetic coupling with the paramagnetic metal centers (Fig. 2). The methoxy alkyl protons A and aromatic aniline protons B, however, are sufficiently distanced from the metal centers such that the corresponding signals remain well resolved at  $\delta = 6.85$ and 3.64 ppm ( $\Delta \delta \sim -0.25$  ppm). Signals from internal amino hydrogens appeared at  $\delta \sim 6.6$  ppm but are quite broad due to through space dipolar coupling with the copper centers. A single band was observed in the diffusion ordered spectroscopy (DOSY) NMR spectrum at  $\log D = -8.91$  ( $D = 10.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) from cage protons A and B which substantiates the existence of a single complex in solution (Fig. 2c).<sup>26</sup> It should be noted that the observed diffusion coefficient of cage 1 is faster than that of the free ligand L1,  $\log D = -9.08 \ (D = 8.32 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}).$ The apparent discrepancy in observed diffusion rates arises



**Fig. 2** Structural analysis of cage **1** in solution. <sup>1</sup>H NMR spectrum (500 MHz, 300 K) of DMF-d<sub>7</sub> solution of (a) **L1** and (b) <sup>1</sup>H NMR and (c) DOSY spectrum from a DMF-d<sub>7</sub> solution of redissolved crystals of cage **1**. (d) Particle size and distribution from dynamic light scattering measurements of cage **1** in DMF (observed diameter = 2.4 nm), (e) AFM image from a DMF solution of cage **1** on mica slide showing (f) single particles with *ca.* 2.2 nm in height.

from enhanced nuclear relaxation ( $T_1 \& T_2$ ) from dipolar coupling with the unpaired copper electrons, termed paramagnetic relaxation enhancement.<sup>27</sup> Cage 2 exhibits a similar augmentation in observed diffusion rate (Fig. S23, ESI<sup>†</sup>).

Dynamic light scattering (DLS) measurements support the solution integrity of cage **1** with the observation of small particles of 2.4 nm in diameter (Fig. 2d). AFM analysis of a DMF solution of cage **1** cast on a mica surface after drying provided clean images of spherical particles of *ca.* 2.2 nm in height (Fig. 2e and f). Finally, LTQ Linear Ion-Trap and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LTQ-FTMS) unambiguously confirmed the solution state  $M_4L_4$  composition with prominent signals at m/z = 977.83, 965.33 and 411.33 which were assigned to  $[1 \cdot Cu]^{2+}$ ,  $[1 \cdot Ca]^{2+}$  and  $[L1]^+$  based on FTICR isotope patterns (Fig. S39, ESI<sup>+</sup>).<sup>28</sup>

Although crystallization is slow, cage **1** quickly assembles in solution at room temperature. Using the methoxy signals **A** as a spectroscopic handle, the quantitative formation of a single complex could be observed by <sup>1</sup>H NMR upon titration of a DMSO-d<sub>6</sub> solution of ligand **L1** with copper acetate at room temperature (Fig. S18, ESI<sup>†</sup>). Cage formation can also be followed by fluorescence spectroscopy as ligand emission is severely quenched upon metal coordination (Fig. S25, ESI<sup>†</sup>). No intermediate species were observed using either method. Variable temperature <sup>1</sup>H NMR spectroscopy revealed that once formed, cage **1** is stable throughout the range of the spectrometer, *i.e.* 223 K to 323 K (Fig. S19, ESI<sup>†</sup>).

Cage 1 possesses two potential reactive sites, the Lewis acidic apical positions of the copper atoms and the Lewis basic internal amines. Initially solvent ligands occupy the apical positions but are labile and undergo exchange upon dissolution. Crystals of as-synthesized cage 1 were dissolved in DMF and diffusion of



Fig. 3 Reaction scheme and SXRD crystal structure showing the postassembly modification of pre-assembled cage 1, in solution, to give the 1D supramolecular chain of cages 3. Apical and included solvent molecules and ligand disorder removed for the sake of clarity. See ESI† for details.

 $Et_2O$  gave X-ray quality single crystals of cage 1' where the apical DMSO molecules were replaced with DMF (Fig. S32, ESI†).‡

Supramolecular 1D coordination polymers of metal–organic cages 3 formed in the presence of bridging bipyridine ligands. The pillars of linked cages assembled from a DMF solution of preassembled cage 1 and 4,4'-bipyridine upon diffusion of diethyl ether at room temperature over one week (Fig. 3). X-ray analysis of the green crystals elucidated well-ordered polymeric columns of cages connected by 4,4'-bipyridines bridging the copper SBUs.‡ One molecule of methanol is bound to each of the internal coppers as 4,4'-bipyridine is too large to fit within the cage. The pillars of cages align along a single axis with neighboring cages snugly packed (Fig. S34, ESI†). Bridging bipyridines and disordered DMF solvent molecules occupy the interstitial voids. We emphasize that attempts to crystallize the pillars from the primary building blocks failed. The supramolecular 1D columns only assemble from solutions of the pre-formed cage 1.

Reaction of the internal amines provided a covalent hostguest complex upon treating a DMF solution of cage 1 with acetic anhydride. After 4 d, the solvent was removed in vacuo and the recovered solid washed with copious MeOH, dissolved in DMF and precipitated with diethyl ether. The green solid was digested with HCl and extracted. <sup>1</sup>H NMR analysis of the released ligands in DMSO-d<sub>6</sub> revealed the presence of a second set of signals (Fig. 4, in red) which include a new signal at  $\delta$  2.1 ppm, corresponding to the acetamide methyl, and an amide N-H proton signal at  $\delta$  9.8 ppm. Integration indicates a  $\sim\!25\%$  conversion or approximately one acetamide guest per host. Molecular modeling indicates the inclusion of a second substrate is disfavored due to steric interactions (Fig. S45, ESI<sup>+</sup>). Post-assembly synthetic modification occurs only in solution. Soaking crystals of the as-synthesized cage 1 in acetic anhydride yielded only the starting ligand L1 after digestion. Presumably this is due to poor guest diffusion through narrow channels in the crystal lattice. Unlike previous reports on the PSM of cages, which focus on external modifications,<sup>29-33</sup> the internal covalent binding of guest molecules remains rare.34-36



Fig. 4 Post-assembly covalent modification of cage **1**: (a) reaction scheme showing amide bond formation with cage **1** and (b) <sup>1</sup>H NMR spectra (500 MHz, 300 K, DMSO-d<sub>6</sub>) of digested cage **4** showing 3:1 mixture of free amine **L1** and amide ligand **L1**'.

In summary, we designed, prepared and characterized two highly soluble  $M_4L_4$  metal organic cages with four internal amino groups. Pendant alkoxy groups serve to increase solubility and function as spectroscopic tags for NMR analyses. DOSY and VT NMR spectroscopy was used for the first time to demonstrate the solution integrity of carboxylate based cages. Once assembled, the metalorganic cages serve as supramolecular building blocks<sup>37,38</sup> for the construction of 1D supramolecular coordination polymers. The amines enabled the successful covalent tethering of molecular guests within a metal-organic cage using post-synthetic protocols. Ongoing work is focused on the inclusion of functional guests within soluble metal-organic cages and for the controlled assembly of functional supramolecular architectures.

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## Notes and references

 $Crystal data for cage 1:^{39} C_{108}H_{84}Cu_4N_4O_{24}S_4 \cdot 0.56(O), M_r = 2213.95,$ green block:  $0.32 \times 0.14 \times 0.12$  mm, triclinic, *P*1, *a*, *b*, *c* = 14.935(5), 16.106(6), 16.995(6) Å, α, β, γ = 105.989(4)°, 109.453(4)°, 104.285(5)°, V = 3438(2) Å<sup>3</sup>, Z = 1, ρ = 1.069 g cm<sup>-3</sup>, Mo Kα, F(000) = 1136.5, μ = 0.73 mm<sup>-1</sup>, T = 100 K,  $2\theta_{max}$  = 31.398, 19.952 unique reflections used, 11.327 with  $I_o > 2\sigma(I_o)$ ,  $R_{int}$  = 0.048, 812 parameters, 490 restraints, GoF = 1.047,  $R = 0.0735 [I_0 > 2\sigma(I_0)]$ ,  $wR_2 = 0.2218$  (all reflections),  $1.43 < \Delta \rho < -1.20 \text{ e} \text{ Å}^3$ . Crystal data for cage 2:  $C_{137,18}H_{142,36}Cu_4N_4O_{24}$ .  $1.82(C_4H_9NO) 6.07(CH_4O) 2.14(H_2O), M_r = 2877.26$ , green block,  $0.21 \times$  $0.19 \times 0.15$  mm, monoclinic,  $P2_1/c$ , a, b, c = 18.2648(11), 27.0741(17), 16.6959(9) Å,  $\beta = 110.078(2)^{\circ}$ , V = 7754.4(8) Å<sup>3</sup>, Z = 2,  $\rho = 1.232$  g cm<sup>-</sup> Cu K $\alpha$ , F(000) = 3039.3,  $\mu = 1.21 \text{ mm}^{-1}$ , T = 100 K,  $\theta_{\text{max}} = 66.882$ , 13 282 unique reflections used, 11546 with  $I_{\rm o} > 2\sigma(I_{\rm o})$ ,  $R_{\rm int} = 0.022$ , 1267 parameters, 971 restraints, GoF = 1.046,  $R = 0.051 [I_0 > 2\sigma(I_0)]$ , w $R_2 =$ 0.146 (all reflections), 0.70  $< \Delta \rho < -0.46$  e Å<sup>3</sup>. Crystal data for cage 1':<sup>39</sup> C<sub>136.45</sub>H<sub>149.05</sub>Cu<sub>4</sub>N<sub>16.15</sub>O<sub>34.15</sub>,  $M_{\rm r}$  = 2815.82, green block, 0.18 ×  $0.14 \times 0.12$  mm, monoclinic, C2/c, a, b, c = 22.7256(6), 27.9980(6), 23.4326(5) Å,  $\beta$  = 91.8800(10)°, V = 14901.5(6) Å<sup>3</sup>, Z = 4,  $\rho$  = 1.255 g cm<sup>-1</sup> Cu Ka, F(000) = 5880,  $\mu = 1.273$  mm<sup>-1</sup>, T = 100 K,  $\theta_{max} = 66.911^{\circ}$ , 13 021 unique reflections used, 12 202 with  $I_{\rm o} > 2\sigma(I_{\rm o})$ ,  $R_{\rm int} = 0.0225$ , 1323 parameters, 2459 restraints, GoF = 1.066,  $R = 0.0584 [I_0 > 2\sigma(I_0)]$ , w $R_2 = 0.1574$  (all reflections),  $0.952 < \Delta \rho < -0.439$  e Å<sup>3</sup>. Crystal data for

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chain 3:<sup>39</sup> C<sub>56</sub>H<sub>38</sub>Cu<sub>2</sub>N<sub>3</sub>O<sub>11</sub>,  $M_r$  = 1055.97, blue rod, 0.21 × 0.12 × 0.10 mm, triclinic,  $P\bar{1}$ , *a*, *b*, *c* = 16.1748(7), 17.1245(8), 17.3765(8) Å,  $\alpha$ ,  $\beta$ ,  $\gamma$ : 61.699(2)°, 79.187(2)°, 79.168(2)°, *V* = 4135.1(3) Å<sup>3</sup>, *Z* = 2,  $\rho$  = 0.832 g cm<sup>-3</sup>, Cu K $\alpha$ , *F*(000) = 1082.0,  $\mu$  = 0.96 mm<sup>-1</sup>, *T* = 100 K,  $\theta_{max}$  = 66.940, 14174 unique reflections used, 9805 with  $I_o > 2\sigma(I_o)$ ,  $R_{int}$  = 0.081, 682 parameters, 350 restraints, GoF = 1.045, *R* = 0.108 [ $I_o > 2\sigma(I_o)$ ], w $R_2$  = 0.323 (all reflections), 1.43 <  $\Delta \rho$  < -1.49 e Å<sup>3</sup>.

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