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A Cu(II) metallocycle for the reversible self-assembly of coordination-driven polyrotaxane-like architectures†

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We report the design and synthesis of a Cu(II) metallocycle (**1**) and use the possibility to expand the Cu(II) coordination sphere to self-assemble mechanically interlocked species *via* interpenetration. Metallocycle **1** can be used as a platform to reversibly assemble a 1D + 1D → 1D coordination-driven polyrotaxane (**3**), where **1** acts as the hosting ring as well as the stopper, and 4,4′-bipyridine is the guest-axle. A coordinating solvent can substitute the 4,4′-bipyridine axle to disassemble the polyrotaxane (**3** → **2**) that is easily restored by further adding 4,4′-bipyridine (**2** → **3**). Other polyrotaxanes can be isolated by reacting **1** with pyridine (**4**) and phenylpyridine (**5**). Interconversion among the presented species is demonstrated and ensured by the open position of each copper center in platform **1**.

Introduction

Mechanically interlocked molecular architectures, *i.e.* molecules that are entangled as a consequence of their topology, have attracted increasing attention.[1] The rapid growth of coordination polymers and MOFs chemistry offered a great opportunity to explore structural interlocking, interpenetration and entanglement.[2] Many interlocked topologies of coordination polymers are based on rotaxane- and catenane-like motifs.[2] However, entanglement deriving from metal ion and ligand self-assembly has been found in coordination polymers, essentially by serendipity. The only way to introduce by design rotaxane architectures into 1D, 2D and 3D networks is to use ligands that can thread an organic ring leading to the so called MORFs (metal–organic rotaxane frameworks), as firstly pioneered by Kim[3a] and Loeb to develop molecular machine-like components in an ordered array.[3b,c] Many MOFs can be structurally described as interlinked polyhedra and clusters *via* a hierarchical assembly of these platforms. This picture is confirmed by experimental evidence where MOFs have been prepared starting from discrete metal organic polyhedra (MOP) or clusters[4] interlinked to give a framework due to ditopic ligands. This step-by-step bottom–up approach can also be extended to the preparation of polymeric interlocked species, provided that suitable molecular platforms are used. In this context, coordination-driven cycles, boxes and capsules endowed with peculiar host–guest properties are ideal building blocks to develop new interlocked architectures. In 1994, Fujita firstly reported a [2]catenane[5a] that quantitatively self-assembled from two preformed Pd(II)-based metallocycles and, in 1999, the first example of an interpenetrated metallo-capsule.[5b] Since then, the possibility to obtain interlocked species starting from metallo-cycles or -capsules has been reported by several authors.[6] On the other hand, the self-assembly of infinite interlocked chains such as polycatenanes[7] based on discrete coordination-driven boxes and cages is not very common, and rotaxane oligomers,[8] poly-*pseudo*-rotaxanes[7d] or polyrotaxanes[9] are even more rare. Winpenny and collaborators demonstrated how to elegantly synthesize main-chain [*n*]rotaxane oligomers,[8a,b] a daisy chain[8c] and a 1D polyrotaxane[9a] based on ion-paired hybrid inorganic–organic structures where dialkylammonium axles thread the monoanionic $[Cr_7NiF_8(O_2C^tBu)_{16}]^-$ ring. Lu *et al.*[7d] firstly reported on a 2D poly-*pseudo*-rotaxane based on a discrete stool-like metallocycle. Lee *et al.*[9b] described a 1D polyrotaxane constructed starting from a discrete dicopper metallocycle and a ditopic pyridyl ligand, where the two building blocks react to form both a 1D coordination polymer (the axle) and a discrete rectangular box (the ring) threaded by an infinite chain.

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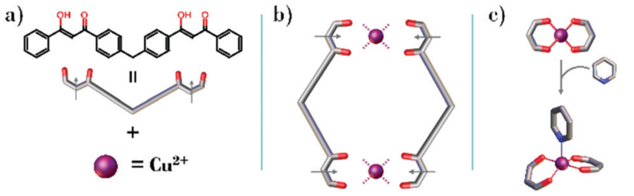

Fig. 1 Building blocks (a) for the Cu(II) platform self-assembly (b). Grey arrows: ligand coordination vectors. (c) Coordination expansion of the metal centre.

Here, we describe a Cu(II) metallocycle ($[Cu_2(L)_2]$, **1**) that is used to reversibly assemble an interlocked 1D + 1D → 1D polyrotaxane ($\{[Cu_2(L)_2]bipy\}_n$, **3**) *via* coordination chemistry and supramolecular tools. Metallocycle **1** is large enough to host molecules in its pocket and to be threaded with an axle. In **3**, metallocycle **1** acts as the hosting ring as well as the stopper, and 4,4′-bipyridine (bipy) is the guest axle. The process is fully reversible since a coordinating solvent (dimethylacetamide, DMA) easily disassembles the polyrotaxane **3** forming the compound $\{[Cu_2(L)_2](DMA)_2\}$ (**2**). The same metallocycle also reacts with pyridine (py) and phenyl-pyridine (phpy) leading to the discrete assemblies **4** $\{[Cu_2(L)_2](py)_2\}$ and **5** $\{[Cu_2(L)_2](DMA)(phpy)\}$ that in the solid state adopt other polyrotaxane-like motifs. Moreover, interconversion among the different species here presented is enabled by the coordination chemistry of the open position at each copper site. In fact, the platform is a $[Cu_2(L)_2]$ metallocycle self-assembled starting from a Cu(II) source and a bis-β-diketone (L) ligand with a two-fold symmetry. Lindoy and coworkers have previously shown how metallocycles bearing transition metals that can expand their coordination act as platforms to hierarchically assemble extended metallo-supramolecular assemblies.[10] According to L coordination vectors and Cu(II)-β-diketonate coordination geometry, each Cu site is expected to adopt an approximate square planar geometry with the possibility of expanding its coordination by reacting with molecules bearing σ-donor atoms (Fig. 1). As we have previously demonstrated, this strategy can be used to select a triangular metallo-supramolecular host from a constitutional dynamic library through specific interactions with σ-donor guests.[11]

Conceptually, the preparation of the presented polyrotaxanes involves a two step-process. In the first step, we prepared a metallocycle **1** with hosting properties and metal ions that can expand their coordination sphere. In the second step, a σ-donor molecule is coordinated at the platform through the metal open sites and, simultaneously, is used to thread a second metallocycle.

Results and discussion

Metallocycle **1** was prepared in quantitative yield combining a chloroform solution of L‡ and copper acetate in methanol. The ligand L has been prepared using a two step-procedure and fully characterized as described in the ESI.† The obtained green powder of **1** is soluble in highly coordinating solvents such as DMA, DMF and pyridine and is slightly soluble in THF. Dark green single crystals of $\{[Cu_2(L)_2]\cdot 2(CHCl_3)\}$, $\mathbf{1}\cdot 2CHCl_3$, were obtained by pentane vapor diffusion in a chloroform/THF solution or using the reactant diffusion technique of the two building blocks. Metallocycle **1** hosts two chloroform molecules that have hydrogen interactions with the oxygen atoms of L ($O\cdots HCCl_3$, *ca.* 2.5 Å, Fig. 2a). The metallocycle involves two Cu^{2+} ions and two ligands that bind in a distorted square planar coordination to the metal centres. The two metal ions are located at a distance of 12.5 Å, while the two central carbons of the ligand spacer have a distance of 11.1 Å. Thanks to its flat shape, platform **1** packs on layers stabilized by stacking interactions (Fig. S9, ESI†). By dissolving **1** in DMA, an emerald green solution was obtained suggesting a change in Cu^{2+} coordination geometry. The vapor diffusion of diethyl ether or diisopropyl ether in a **1** DMA solution led to the quantitative crystallization of the compound $\{[Cu_2(L)_2](DMA)_2\}$ (**2**, Fig. 2b), where a DMA molecule coordinates each copper center in the apical position of a distorted square pyramid. These results confirm that **1** has the desired features to act as a platform for the formation of polyrotaxanes *via* coordination and supramolecular tools: (i) a pocket with hosting properties and (ii) the ability to coordinate other species. To explore this possibility, we decided to use 4,4′-bipyridine (bipy) for the following features: (i) it has σ-donor atoms to coordinate **1**, (ii) it is a ditopic ligand that can lead to the formation of a chain of "**1**-bipy" alternating units, and finally (iii) its dimensions are compatible with the metallocycle pocket size.

A chloroform solution of L and bipy was layered with a dichloromethane buffer and then with a methanol solution of $Cu(CH_3COO)_2$. The slow reactant diffusion led to the for-

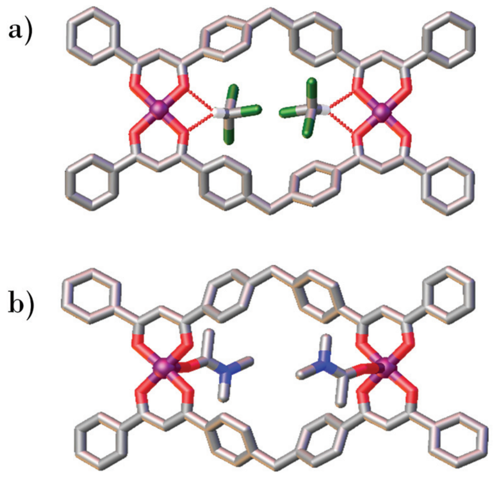

Fig. 2 (a) Structure of **1**, $\{[Cu_2(L)_2]\cdot 2CHCl_3\}$. (b) Structure of **2**, $\{[Cu_2(L)_2]_2(DMA)_2\}$. Colour code: C grey, O red, Cl green, Cu purple; H is omitted for clarity, except in $CHCl_3$ molecules (white).

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‡ L: 1-(4-{[4-(3-oxo-3-phenylpropanoyl)phenyl]methyl}phenyl)-3-phenylpropane-1,3-dione.

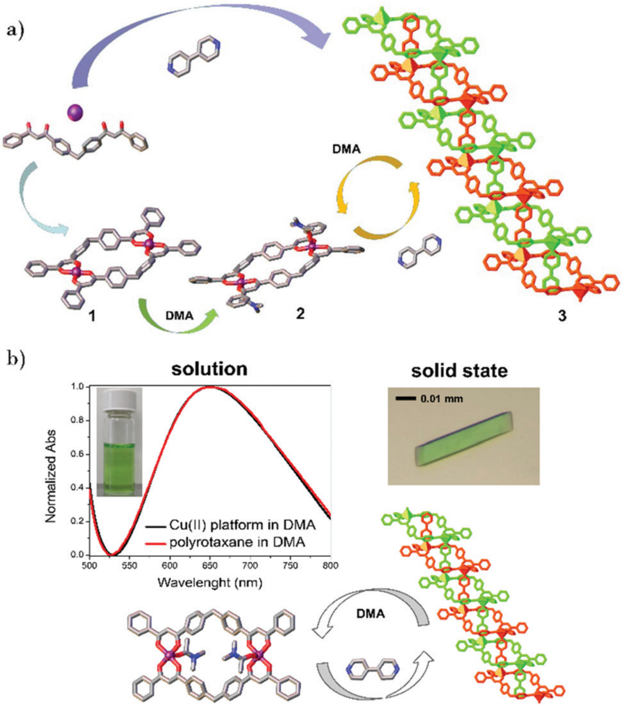

Fig. 4 (a) Self-assembly of polyrotaxane **3** *via* a one-pot reaction or through the Cu(II) platform (**1** → **2** → **3**). (b) Scheme of the reversible polyrotaxane formation. UV-Vis of the metallocycle **1** and of the dissolved polyrotaxane **3** (inset: DMA solution of **3**), and a single crystal of **3**.

mation of two different types of crystals: long dark green needles, identified as **1**, and tiny light green needles, identified as $\{[Cu_2(L)_2](bipy)\}_n$, **3**. Compound **3** can be prepared as a pure compound and in quantitative yield by mixing a DMA solution of **1**, hence having in solution the species **2**, with bipy, to give a light green microcrystalline powder as confirmed by comparison of the experimental PXRD pattern with the simulated one (Fig. S6b†). In **3**, the copper centers coordinate a bipy molecule in the apical position of a distorted square pyramidal geometry. This leads to the development of a stair-like polymeric 1D chain (Fig. 3a). However, the structure of **3** is much more complex, with the two 1D chains being interlocked in parallel (Fig. 3b), resulting in a system that can be classified as a 1D + 1D → 1D coordination-driven polyrotaxane (Fig. 3c).[2b] The Cu(II) platform acts as the hosting ring as well as the stopper, and 4,4′-bipyridine is the guest-axle of the rotaxane-like unit. In fact, a bipy molecule coordinated two metallocycles **1** to form a 1D chain and it is at the same time hosted by a third metallocycle of a second chain. Small variations in the metallocycle dimension are observed if compared to **1** and **2** with a Cu⋯Cu distance of 12.0 Å, while the two central carbon atoms of the ligand spacer have a distance of 11.8 Å. The distance Cu-bipy-Cu is 11.5 Å. The bipy unit inside the **1** pocket has hydrogen interactions with oxygen atoms of L (ESI,† O⋯HC, *ca.* 2.6 Å). Only four examples of 1D + 1D → 1D polyrotaxanes based on metallocycle rings have been reported so far.[12] However, in these cases the metallocycle does not exist in solution as a discrete unit. In contrast, in the case here described, the polyrotaxane can be self-assembled starting from the single building blocks (Cu^{2+}, L, and bipy) in a one-pot reaction as well as starting from the metallocycle platform **1** coupled to bipy (Fig. 4a). This allowed us also to easily reverse the polyrotaxane formation. In fact, in the presence of a coordinating solvent, such as DMA, polyrotaxane **3** is disassembled since DMA substitutes the bipy axle coordinating the copper ions and leading to compound **2**. UV-Vis analysis showed that a DMA solution of the Cu(II) platform and the dissolved polyrotaxane in DMA have the same spectrum. Once disassembled, the entangled system is easily and quantitatively restored by adding more bipy and isolated as a polycrystalline powder (Fig. 4b). The microcrystalline powder obtained has been characterized *via* PXRD. The resulting diffractogram is in very good agreement with the calculated one (Fig. S6b†) as observed from the single crystal data of **3**, confirming the nature and purity of the compound. Determining the self-assembly pathway of a coordination polyrotaxane is not an easy task. The ESI-MS of a diluted **1**·THF solution (10^{-5} M)

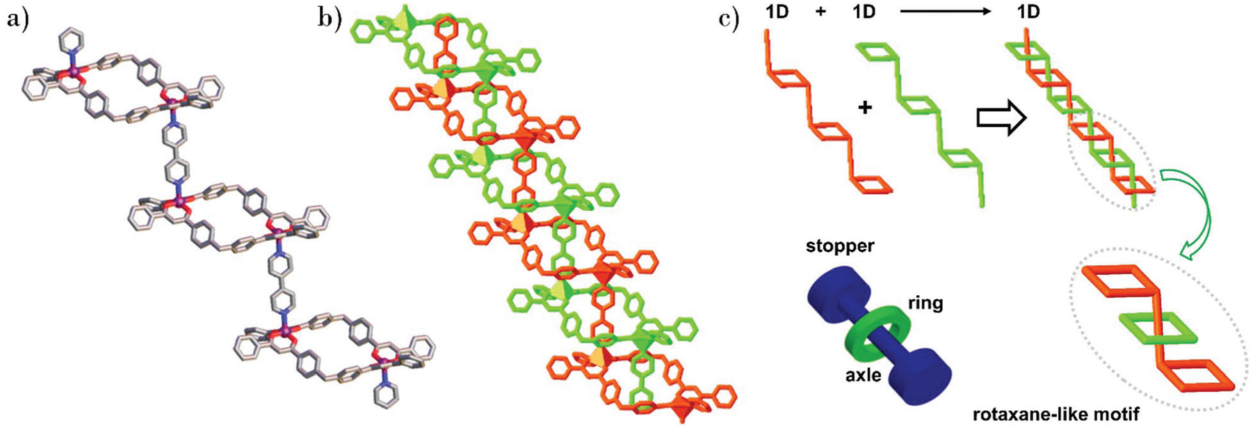

Fig. 3 Polyrotaxane **3**, $\{[Cu_2(L)_2](bipy)\}_n$. (a) A single polymeric chain of "**1**-bipy" alternating units. (b) Two interlocked chains giving the polyrotaxane. (c) Schematic representation of the 1D + 1D → 1D coordination-driven polyrotaxane and of the rotaxane-like motif.

plus a stoichiometric amount of bipy gave a low intensity signal at m/z = 1199.4, compatible with the species $\{[Cu_2(L)_2](bipy) + H\}^+$. To gain more information on polyrotaxane formation we used pyridine (py) and phenylpyridine (phpy) as σ-donor molecules. These two molecules have very similar coordination behaviours compared to bipy, but not being divergent ditopic ligands they should lead to discrete systems. Platform **1** promptly dissolves in py to form an emerald green solution, and single crystals of $\{[Cu_2(L)_2](py)_2\}$ (**4**, Fig. 5a) were isolated from a DMA/py solution after partial evaporation. The distances between the two metal ions and between the two central carbon atoms of the ligand spacer deviate from the data found in **1**, **2** and **3** with values of 13.5 Å (Cu⋯Cu) and 9.9 Å (C⋯C). At variance to the other compounds, the σ-donor atom does not take the longer apical positions, but it lies on an equatorial site of the distorted square pyramids, and the apical positions are occupied by the oxygen atoms of L. Considering the short CH⋯CH contacts (2.6 Å) between two different phenyl rings in the apical position (Fig. 5b, dashed lines), a supramolecular 1D chain is formed in the solid state. Moreover, these terminal phenyl rings slightly penetrate other rings. Pairs of these 1D chains entangle, with each metallocycle of one chain threaded by a Ph⋯Ph axle of the other chain, establishing a 1D + 1D → 1D supramolecular polyrotaxane with the same intertwining of the coordination-driven polyrotaxane **3**. When dissolving **1** in DMA and adding an excess of phpy, single crystals of $\{[Cu_2(L)_2](DMA)(phpy)\}$ (**5**, Fig. 5c) were obtained by vapor diffusion of diethyl ether or diisopropyl ether. In this case, platform **1** coordinates two different molecules, *i.e.* DMA and phpy. Both the molecules take the apical position of a distorted square pyramid. At variance to the findings for the other compounds, the two molecules lie on the same side of the metallocycle. The two copper ions are located at a distance of 12.4 Å, while the two central carbon atoms of the ligand spacer have a distance of 10.9 Å; both values are very similar to those found in **1**, **2** and **3**. Also **5** shows interpenetration, with the DMA molecule of one ring threading a second one to give a 1D poly-*pseudo*-rotaxane (Fig. 5d).

Finally, as it is possible to reversibly assemble polyrotaxane **3** using the open coordination sites in platform **1**, we demonstrated that similar interconversion can be exploited among all the compounds here presented, as depicted in Fig. 6.

On the basis of the coordination and host–guest properties of platform **1** coupled to its tendency to form polyrotaxane-like motifs, as evidenced by compounds **4** and **5**, the pathway depicted in Fig. 7 for the formation of the 1D + 1D → 1D coordination-driven polyrotaxane **3** appears plausible. Starting from two building blocks (**1** and bipy, stage a), the pathway proceeds *via* the formation of $\{[Cu_2(L)_2](bipy)\}$ discrete units (stage b), as supported by ESI-MS analysis. This step may be followed by the formation of daisy chain-like motifs (stage c). Although we did not observe any evidence on the formation of these units, we reasoned that this should be the key step to form the interlocked architecture. The growth of the daisy chain (stage n) leads to the final 1D + 1D → 1D intertwined system.

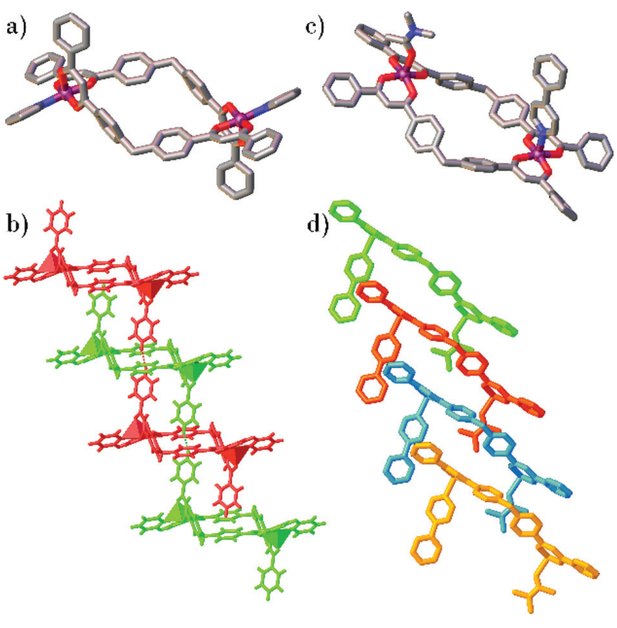

Fig. 5 (a) Structure of **4**, $\{[Cu_2(L)_2](py)_2\}$, and (b) its 1D + 1D → 1D polyrotaxane intertwining supported by CH⋯CH interactions (dashed lines). (c) Structure of **5**, $\{[Cu_2(L)_2]_2(phpy)(DMA)\}$, and (d) its 1D poly-*pseudo*-rotaxane motif (lateral view) with the DMA molecules threading the metallocycles.

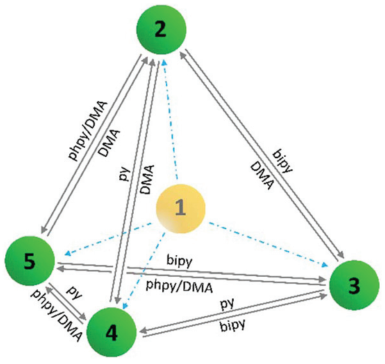

Fig. 6 Interconversion paths among the compounds here presented.

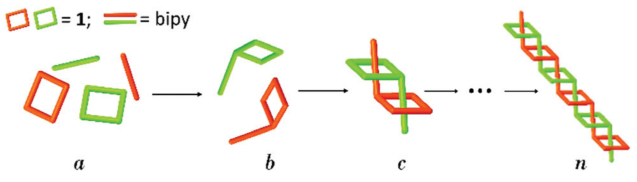

Fig. 7 (a) Proposed pathway for the formation of the 1D + 1D → 1D coordination-driven polyrotaxane **3**.

Conclusions

In conclusion, we have demonstrated how a discrete metallocycle can be used as a versatile platform to self-assemble polyrotaxane architectures. The proposed strategy to access these coordination-driven polymeric intertwined structures is to design and synthesize a metallocycle with two key features: (i) host–guest properties and (ii) metal centers prone to expand their coordination sphere. In a second step, such features are exploited by reacting the platform with suitable σ-donor molecules to obtain coordination-driven polyrotaxanes. Hence, the 1D + 1D → 1D polyrotaxane **3** was straightforwardly obtained by adding the ditopic bipy ligand to **1**. The formation of the polyrotaxane architecture is accompanied by a phase change from solution to a crystalline solid that can be easily disassembled in the presence of a coordinating solvent (**3** ⇄ **2**). The existence of **1** in solution as a discrete species is of paramount importance for the reversible process. In the same way, the coupling of platform **1** with py and phpy led to two discrete metallocycles (**4** and **5**). Upon crystallization, and due to the interpenetration of metallocycle pockets, we obtained a further 1D + 1D → 1D polyrotaxane supported by CH⋯CH interactions (**4**) and a poly-*pseudo*-rotaxane (**5**). A judicious use of the coordination chemistry of the metal open coordination sites also allowed the easy interconversion of each compound.

Experimental

Synthesis

Ligand L. Ligand L was prepared using a two step-procedure, (i) Friedel Crafts acylation and (ii) Claisen condensation, and characterized as described in the ESI.†

[$Cu_2(L)_2$] (1). *Method A*. A methanol solution (4 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (5.00 mg, 0.025 mmol) was quickly added to a chloroform solution (4 ml) of L (11.50 mg, 0.025 mmol). The instantaneous precipitation of an olive green solid was observed, and it was recovered by filtration and was washed with chloroform. Yield: 90%. Crystals of **1**·2CHCl$_3$ were isolated by pentane vapor diffusion in a **1**·chloroform/THF solution. Elemental analysis for **1**, $C_{62}H_{44}Cu_2O_8$: C 71.40%, H 4.33% (exp.); C 71.32%, H 4.25% (calc.).

Method B. Single crystals of **1**·2CHCl$_3$ were obtained using a reactant diffusion technique. A chloroform solution (4 ml) of L (11.50 mg, 0.025 mmol) was layered with dichloromethane (*ca.* 2.5 ml) and with a methanol solution (4 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (5.00 mg, 0.025 mmol). The test tube was stoppered and the solutions were let to diffuse slowly. After a few days, long dark green needles of **1** were obtained.

{[$Cu_2(L)_2$](DMA)$_2$} (2). 4.1 mg (0.004 mmol) of **1** were dissolved in the minimum volume of DMA (*ca.* 1 ml) to give an emerald green solution. The solution was stirred, heated at 50 °C for 1 hour and filtered. A slow diffusion of diethyl ether or diisopropyl ether vapor was carried out. After three days, needle-shaped light green crystals were quantitatively isolated and identified as **2**. Elemental analysis for **2**, $C_{70}H_{60}Cu_2NO_{10}$: C 69.91%, N 1.21%, H 4.95% (exp.); C 69.93%, N 1.16%, H 5.03% (calc.).

{[$Cu_2(L)_2$](bipy)}$_n$ (3). *Method A*. A methanol solution (4 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (5.00 mg, 0.025 mmol) was quickly added to a chloroform solution (4 ml) of L (11.50 mg, 0.025 mmol) and bipy (3.90 mg, 0.025 mmol). The instantaneous precipitation of a clear green solid was observed, and it was recovered by filtration and washed with chloroform. Yield: 95%. Elemental analysis for **3**, $C_{72}H_{52}Cu_2N_2O_8$: C 72.11%, H 4.30%, N 2.35% (exp.); C 72.05%, H 4.37%, N 2.33% (calc.).

Method B. 4.1 mg (0.004 mmol) of **1** were dissolved in a minimum volume of DMA (*ca.* 1 ml) to give an emerald green solution. A bipy (0.005 mmol) solution in THF was added to give a clear green solid in quantitative yield. Elemental analysis for **3**, $C_{72}H_{52}Cu_2N_2O_8$: C 71.95%, H 4.41%, N 2.37% (exp.); C 72.05%, H 4.37%, N 2.33% (calc.).

Method C (for single crystals suitable for SCXRD). A chloroform solution of L (11.85 mg), bipy (3.93 mg) and triethylamine (7.5 μl) was layered with dichloromethane and with a methanol solution of $Cu(CH_3COO)_2 \cdot H_2O$ (5.00 mg). The test tube was stoppered and the solutions were let to diffuse slowly. After a few days, two types of crystals were obtained: long dark green needles (yield: 50%) and tiny light green needles (yield: 25%). The first kind has been identified as **1** and the second one as **3** by single crystal XRD.

{[$Cu_2(L)_2$](py)$_2$} (4). 10 mg (0.01 mmol) of **1** were dissolved in a minimal amount of a DMA/py solution, mixed and heated for 1 hour and left undisturbed for slow evaporation. The DMA/py ratios used were: 9 : 1, 4 : 1, 7 : 3, 3 : 2, and 1 : 1. After a month, single crystals of **4** were obtained from the solutions with DMA/py ratios of 1 : 1, 2 : 3 and 3 : 7 (yield: 23%, 53% and 72%, respectively). Elemental analysis for **4**, $C_{72}H_{54}Cu_2N_2O_8$: C 72.02%, H 4.58%, N 2.31% (exp.); C 71.93%, H 4.53%, N 2.33% (calc.).

{[$Cu_2(L)_2$](DMA)(phpy)} (5). 10 mg (0.01 mmol) of **1** were dissolved in a minimal amount of a DMA solution. To this solution an excess of phpy was added. The mixture was stirred and heated for 1 hour. A slow diffusion of diethyl ether or diisopropyl ether vapor was carried out. After two days, plate-shaped light green crystals were quantitatively isolated and identified as **5**. Elemental analysis for **5**, $C_{77}H_{60}Cu_2N_2O_8$: C 72.75%, H 4.68%, N 2.27% (exp.); C 72.91%, H 4.77%, N 2.21% (calc.).

Interconversion experiments

Compound 3 from 2, 4 and 5. Compound **2**, or **4** or **5** was dissolved in a minimum amount of THF. To this mixture a bipy solution (THF) was added. A green microcrystalline precipitate was formed. The nature and purity of the compound were confirmed by PXRD (Fig. 5b).

Compound 4 from 2, 3 and 5. Compound **2**, or **3** or **5** was dissolved in a minimum amount of a 1 : 1 DMA/py solution. Slow evaporation led to single crystals of **4**. The nature and purity of the compound were confirmed by PXRD (Fig. 5c).

Compound 5 from 2, 3 and 4. Compound **2**, or **3** or **4** was dissolved in a minimum amount of a 1 M phpy solution in

DMA. Diethyl ether vapour diffusion led to the quantitative isolation of compound **5**. The nature and purity of the compound were confirmed by PXRD (Fig. 5d).

X-ray diffraction

Powder X-ray diffraction (PXRD). PXRD patterns were obtained with a Bruker D8 Advance diffractometer, in Bragg–Brentano geometry, equipped with a Göbel mirror using Cu Kα. The patterns were acquired in the 5–40° 2θ range (0.03° per step and 10 s per step).

Single crystal X-ray diffraction (SCXRD). The details of SCXRD data collections, crystal structures solution and refinement, and crystallographic tables for each compound are reported in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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