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Programmed single step self-assembly of a [2 × 2] grid architecture built on metallic centers of different coordination geometries

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A novel type of 2 × 2 grid type architecture incorporating two ions of different geometries results from the single step directed self-assembly of a bischelating ligand combining bridged bidentate and tridentate complexation subunits, designed so as to lead to the ion selective and toposelective introduction of two Zn(II) and two Cu(I) cations at well-defined, diagonally located positions of, respectively, octahedral and tetrahedral coordination geometry.

Self-assembly has proven to be a highly valuable process in the construction of elaborate architectures starting from simple building blocks.[1] The information encoded in molecular scaffolds may be read by algorithms based on hydrogen bonding,[1,2] donor/acceptor[1b] interactions and metal ion coordination,[1] in a supramolecular processing manner.[3]

Metal coordination chemistry has allowed to direct the self-assembly towards the generation of discrete well-defined metallosupramolecular architectures, yielding a variety of outputs such as linear and circular helicates,[1,4] racks,[5] cages[6] and grids[7] based on the preferred coordination geometry of the metal center and the structure of the ligands.

The regularity of the networks expressed in grid-type architectures[7] makes them attractive objects for nanotechnology and information storage, since they yield ordered 2D array of ion dots.[1a] Homometallic grids can be constructed on the basis of tetrahedral (Cu^I, Ag^I)[7a–c] or octahedral (Zn^{II}, Co^{II}, Fe^{II}, *etc.*)[7d–g] coordination geometry with ligands containing respectively bidentate or tridentate complexation subunits. The resulting homometallic complexes display a variety of interesting electrochemical[7f] and magnetic[7g] properties.

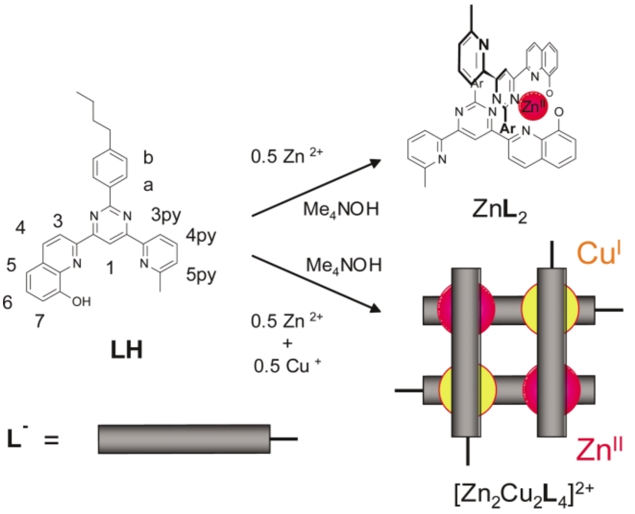
The construction of heterometallic [2 × 2] grids presenting different precisely located metal cations has been achieved by stepwise strategies.[8] Along the way towards self-organization by selection,[9] as seen in the generation of mixed ligand grids[7c] and the selective assembly of ligand components in a dynamic library of ligands,[10] it is particularly valuable to devise procedures allowing the spontaneous assembly of mixed metal grids by selection from a mixture of metal ions and ligand(s) under the control of the processing of suitable binding information through specific coordination algorithms.

We now report the ion selective and toposelective self-assembly of mixed metal [2 × 2] grid architectures combining two cations of octahedral and two cations of tetrahedral coordination geometry with four identical ligands, presenting two different coordination subunits, in a single step from a mixture of ligands and cations. Such a process bears relation to the self-assembly of heterotopic double helicates.[11]

Ligand **LH** (Scheme 1)[12] was designed so as to offer a bidentate unit of α,α′-bipyridine type as a privileged binding site for tetrahedral coordination, and a tridentate unit including a 8-hydroxyquinoline group, destined to accommodate octahedral coordination geometry. The latter further provides tunability through its acido-basic activity. The bidentate and tridentate sites share a bridging pyrimidine unit participating in both complexations.

Treating ligand **LH** with half an equivalent of each zinc triflate and copper tetrakisacetonitrile tetrafluoroborate in a $CDCl_3$–CD_3OD–CD_3CN (2:1:1) mixture in the presence of one equivalent of tetramethylammonium hydroxide, gave a deep purple solution of the complex $[Zn_2Cu_2\mathbf{L}_4]^{2+}$. Its ^1H NMR spectrum is displayed in Fig. 1(c), together with the spectra of the free anionic ligand and that of the red $Zn\mathbf{L}_2$ complex.[12] The peaks were assigned on the basis of their COSY and ROESY 2D proton NMR spectra.

In the free ligand, the preferential *transoid* conformation of the pyridine-pyrimidine type unit is responsible for the high chemical shift of the signal of the pyrimidine proton 1, which directly faces two nitrogen atoms. It is displaced by 1 ppm on introduction of half an equivalent of Zn^{II}, mainly due to conformational change. Electro-spray mass spectrometry shows that two ligands assemble



Scheme 1 Ligand **LH** and its complexes $Zn\mathbf{L}_2$ and $[Zn_2Cu_2\mathbf{L}_4]^{2+}$.

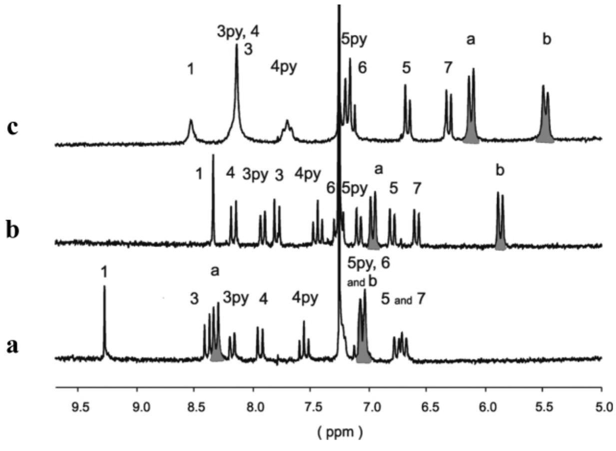


Fig. 1 ^1H NMR spectra of $\mathbf{L}^-$ in $CDCl_3$–CD_3OD 1.0:1.0 (a), $Zn\mathbf{L}_2$ in $CDCl_3$–CD_3OD 1.0:1.0 (b) and $[Zn_2Cu_2\mathbf{L}_4]^{2+}$ in $CDCl_3$–CD_3OD–CD_3CN 2.0:1.0:1.0 (c). The signals corresponding to protons a and b (Scheme 1) are highlighted in grey.

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with a zinc cation to form a 2:1 complex Zn**L**$_2$. Single crystal diffraction confirmed that the zinc cation recognizes the hard tridentate site in ligand **L**$^-$ and that it coordinates in a distorted octahedral fashion to the deprotonated hydroxyquinoline of two ligands.[12] Solution studies agree with this formulation. Upon complexation in a 2:1 ligand–metal mode, the signals of protons a and b are both shifted to lower values by approximately 1.2 ppm, as a result of both cation complexation and shielding by the phenyl ring.

In the case of the 1:0.5:0.5 ligand–zinc–copper mixture, the resulting deep purple complex displays a further decrease in shift of ~0.4 ppm for b and ~0.9 ppm for a, relative to Zn**L**$_2$ (1.6 and 2.2 ppm respectively relative to the free anionic ligand), suggesting that stacking is enhanced upon copper complexation.

The values of the chemical shifts closely resemble those obtained with pyrimidine bridged [2 × 2] grids based on octahedral centers,[7e] for which, however, the signals of both protons a and b are split, due to hindered rotation of the phenyl group within the grid architecture, which renders them inequivalent. In the present case, the two *ortho* a and *meta* b protons are equivalent on the NMR time scale. The signal for the b protons is actually broadened [Fig. 1(c)], indicative of intermediate rotation rate around the phenyl–pyrimidine bond. The mass spectral data agree with a 4:2:2 ligand–zinc–copper composition (peaks at 1018.2 and 2187 respectively for the 2+ species and the 1+ species with a triflate anion).

The grid type structure of the [Zn$_2$Cu$_2$**L**$_4$]$^{2+}$ complex was confirmed by single crystal diffraction (Fig. 2).‡ In contrast to the fully octahedral site homonuclear grids,[7d,e] this mixed tetrahedral/octahedral center [2 × 2] grid deviates from a strictly square geometry; it is diamond shaped with an angle of about 100° between the planes of the ligand at each octahedral Zn(II) site. The Cu–Zn distances (edges) range from 6.5 to 6.7 Å. These features correlate with a large difference in the length of the two diagonals, the Zn–Zn distance being much shorter (8.5 Å) than the Cu–Cu distance (10 Å). The phenyl groups are held within stacking between two parallel ligands, as in homonuclear octahedrally based [2 × 2] grids.[7e] Their orientation relative to the pyrimidine differs though, since the torsion angle is only 50° compared to the usual 90°. Two enantiomeric grids are present in the unit cell.

The complex cation [Zn$_2$Cu$_2$**L**$_4$]$^{2+}$ is the first [2 × 2] grid self-assembled from two cations of different coordination geometries. The generation of a well-defined species results from the proper reading of the electronic information (namely the coordination number and the hard/soft nature) of the binding sites by the cation effectors. The high coordination number hard zinc(II) cation recognizes the anionic tridentate unit while soft tetracoordinate copper(I) prefers to bind to the bipyridine type portion. The controlled introduction of two pairs of cations along the diagonals imposes a directionality to these systems, which may thereafter be translated at a supramolecular level in the 1D and 2D organization of grids into arrays.[13] In addition, preliminary mass spectrometry data show that zinc(II) can be replaced by copper(II) while preserving the tetrameric assembly. Hence, a single cation in two different (and possibly interconvertible) oxidation states may be used to assemble these architectures, which may open the door to electro-controlled self-assembled grids.

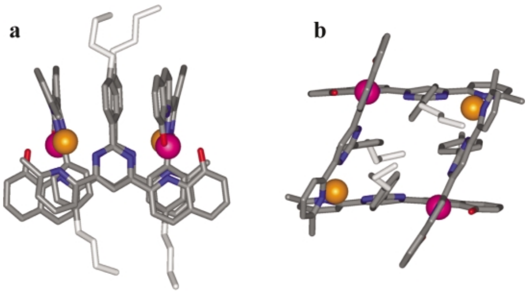

Fig. 2 Molecular structure of [Zn$_2$Cu$_2$**L**$_4$]$^{2+}$: (a) side view; (b) top view. The *n*-butyl chains are represented in light grey; solvent molecules and triflate anions are omitted for clarity. Stick and ball representation were used for the ligands and cations respectively.

The present results achieve the single step, programmed self-assembly of heteronuclear arrays of metal ions of well-defined geometry with ion selectivity and toposelectivity, a given metal ion being selected for binding at a precisely determined location. These features bear relation to the potential interest of such arrays for local information storage and addressing as well as to processes of self-organization by selection.[9]

Notes and references

‡ *Crystal data* for [Zn$_2$Cu$_2$**L**$_4$]$^{2+}$: $C_{232}H_{200}Cu_4N_{32}O_8Zn_4 \cdot 3BF_4 \cdot F_3CSO_3 \cdot 5CH_3OH \cdot 2H_2O$, M = 4685.76, purple prism, triclinic, a = 17.8009(3), b = 18.2756(3), c = 21.3141(4) Å, V = $5887.\underline{1}(2)$ Å^3, α = 17.80009(3), β = 66.993(5), γ = 67.425(5)°, space group $P\bar{1}$, Z = 1, μ = 0.842 mm^{-1}, 35 951 data measurements, 11 153 data measurements with $I > 3\sigma(I)$, R = 0.105, R_w = 0.137. Anions (BF$_4$ and triflate) are disordered in the crystal. See http://www.rsc.org/suppdata/cc/b4/b402854f/ for crystallographic data in CIF or other electronic format.

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 9; (*b*) D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.
2 D. C. Sherrington and K. A. Taskinen, *Chem. Soc. Rev.*, 2001, **30**, 83; M. J. Krische and J.-M. Lehn, *Struct. Bonding*, 2000, **96**, 3.
3 J.-M. Lehn, *Chem. Eur. J.*, 2000, **6**, 2097.
4 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
5 G. Hanan, C. Arana, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1996, **2**, 1292.
6 (*a*) P. N. W. Baxter, in *Comprehensive Supramolecular Chemistry, Vol. 9*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn, Pergamon, Oxford, 1996, p. 165; (*b*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.
7 (*a*) M.-T. Youinou, N. Rahmouni, J. Fischer and J. A. Osborn, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 733; (*b*) P. N. W. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284; (*c*) G. Hanan, D. Volkmer, U. S. Schubert, J.-M. Lehn, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1842; (*d*) J. Rojo, F. J. Romero-Salguero, J.-M. Lehn, G. Baum and D. Fenske, *Eur. J. Inorg. Chem.*, 1999, 1421; (*e*) M. Ruben, E. Breuning, M. Barboiu, J.-P. Gisselbrecht and J.-M. Lehn, *Chem. Eur. J.*, 2003, **9**, 291; (*f*) M. Ruben, E. Breuning, J.-M. Lehn, V. Ksenofontov, F. Renz, P. Guetlich and G. B. M. Vaughan, *Chem. Eur. J.*, 2003, **9**, 4422.
8 (*a*) D. M. Bassani, J.-M. Lehn, K. Fromm and D. Fenske, *Angew. Chem., Int. Ed.*, 1998, **37**, 2364; (*b*) L. Uppadine and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 240.
9 J.-M. Lehn, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4763.
10 J. R. Nitschke and J.-M. Lehn, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 11 970.
11 V. Smith and J.-M. Lehn, *Chem. Commun.*, 1996, 2733; J.-C. G. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897.
12 The synthesis and properties of ligand **L**H and of its complexes will be described in detail in a forthcoming paper: A. Petitjean, N. Kyritsakas and J.-M. Lehn, manuscript in preparation. All compounds had properties in agreement with their structure.
13 For grid arrays organized in two dimensions by hydrogen bonding recognition groups see: E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 1515.