Porous Assemblies

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Self-Assembly of a Homochiral Nanoscale Metallacycle from a Metallosalen Complex for Enantioselective Separation**

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Coordination-driven self-assembly provides unique opportunities to design and prepare ordered arrays of molecules and clusters, and has led to significant progress in the construction of metal–organic assemblies with potentially exploitable functions, from ion exchange to gas storage to separations to catalysis.[1,2] Of particular interest to us are elegant works on coordination-linked porphyrin arrays that demonstrate the feasibility of constructing a large family of *meso*-metalloporphyrin cycles and boxes based on complementary coordination interactions between coordinatively unsaturated central metal atoms and coordinating sidearms.[3] This assembling process is especially effective for the construction of discrete cyclic arrays, in that appropriately designed components are almost automatically self-assembled to form large arrays, thus providing an associated entropic advantage.[3c] However, such a direct approach has thus far received less attention in other supramolecular systems.[4,5]

Metallosalen-based architectures (salen = *N*,*N'*-ethylenebis(salicylideneaminato)) have diverse potential applications in catalysis and separations,[6,7] which motivated us to examine the self-assembly of enantiopure complementary metallosalen complexes through coordination, with the aim of generating well-defined enzyme-like chiral cavities and functionalities for enantioselective processes. With a few notable exceptions, metal–organic assemblies have not been explored for chirotechnology.[8,9]

Herein, we report the efficient self-assembly of a chiral porous macromolecule from the semiflexible pyridyl-functionalized metallosalen [ZnL] using coordination bonds (Figure 1).[6a] Single crystals of the robust metallomacrocycle show a reversibly and controllably dynamic behavior induced by external stimuli, and remarkably, can be used to separate small racemic alcohols with an enantioselectivity of up to 99.8% *ee*.

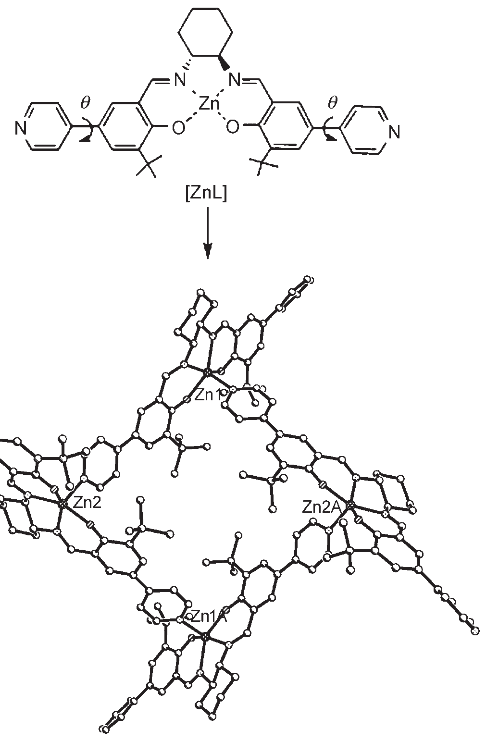

Figure 1. Assembly of a $[Zn_4L_4]$ macrocycle from self-complementary {ZnL} building blocks.

Heating $Zn(NO_3)_2{\cdot}6H_2O$ and H_2L (1:1) in a mixture of DMF and CH_3CN afforded light-yellow, rod-like crystals in high yield. The product is stable in air and insoluble in water and common organic solvents, and was formulated as $[Zn_4L_4]{\cdot}4CH_3CN$ (**1**·$4CH_3CN$) on the basis of elemental analysis, IR spectroscopy, and thermogravimetric analysis (TGA).

A single-crystal X-ray diffraction study performed on **1**·$4CH_3CN$ reveals a metallomacrocycle constructed from four [ZnL] molecules by the complementary coordination of the pyridyl groups to the metal centers (Figure 1).[10] Compound **1**·$4CH_3CN$ crystallizes in the tetragonal chiral space group $P4_2$, with a crystallographic C_2 axis passing through the center; thus, half of the tetramer is in the asymmetric unit. Each Zn center adopts a square-pyramidal geometry with the

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equatorial plane occupied by the N_2O_2 donors of one L ligand and the apical position by one pyridine group of another L ligand. The Zn−N and Zn−O bond lengths range from 2.045(6) to 2.123(6) Å and from 1.944(6) to 1.993(4) Å, respectively, while the zinc centers are located 0.44 and 0.42 Å above the plane formed by N_2O_2 coordination toward the axial pyridyl group. Each {ZnL} unit thus uses one terminal pyridyl group to coordinate to a Zn atom, thus building a tetramer with one pyridine group remaining uncoordinated. The coordinated pyridine groups are almost coplanar with the basal salen plane defined by the ZnN_2O_2 core and two attached aromatic rings with small dihedral angles of 11.4 and 15.3°, while the uncoordinated pyridine groups are twisted by 33.9 and 36.5° from coplanarity.

The four pairs of *tert*-butyl groups of the {ZnL} units are organized such that they partly cover two sides of the cyclic tetramer along its crystallographic twofold axis, thus generating four hydrophobic pockets, each of which is occupied by one CH_3CN molecule (Figure 2). The four guest molecules interact with each other to afford a distorted tetrahedron. The guest-templating effect in **1** is inferred from the presence of weak hydrophobic interactions between the ligand methyl groups and solvent methyl groups. The maximum size of the cyclic tetramer is 3.1 nm, while the diagonals of the aperture on each face are 5.5×8.2 Å^2 (based on the atomic van der Waals radii). The separations between adjacent zinc atoms are 11.8974(5) and 11.9302(5) Å, and between opposite zinc atoms 15.0783(6) and 15.4947(6) Å. Compound **1** is a rare nanoscale chiral molecular container that has been crystallographically characterized.[11]

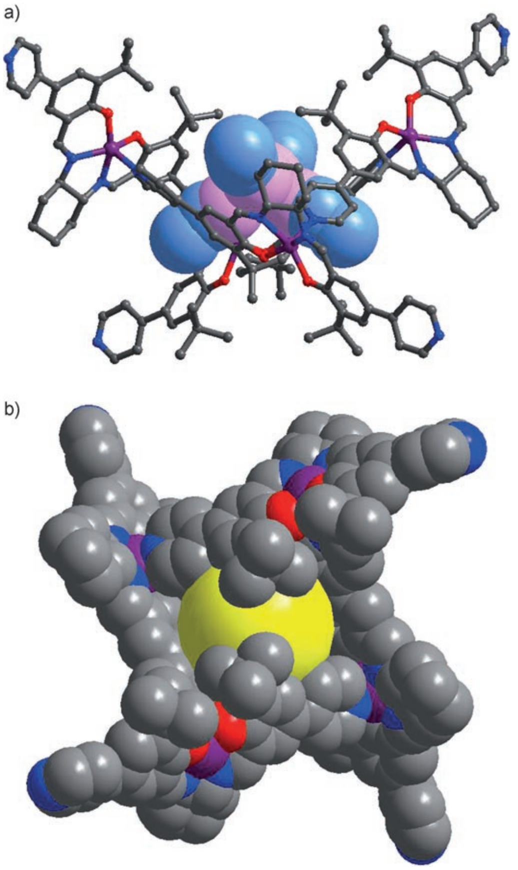


Figure 2. a) A view showing the inclusion of four CH_3CN molecules in **1**; b) Space-filling model of **1** (the cavity is highlighted by a yellow sphere, and the guest molecules are omitted for clarity).

The two edges of adjacent $[Zn_4L_4]$ tetramers are related by a 4_2 screw axis and thus are ideally positioned to interact by π–π stacking between the extended π-conjugated parts of {ZnL} units (shortest plane–plane separation: 3.37 Å). Each tetramer is surrounded by four adjacent analogues of the same handedness through four pairs of such π–π stacking interactions. As a result, the atoms in the {ZnL} conjugated system are polarized alternately; all the pairs of atoms facing each other in the two conjugated systems are oppositely polarized and hence should attract each other strongly.[12] The face-to-face intermolecular π–π interactions in **1** thus lead to a neutral, porous 3D structure (Figure 3). Equilateral-triangle-shaped zigzag channels with each side measuring 7.0 Å result from stacking of the tetramers along the [110] or [$1\bar{1}0$] direction. Furthermore, rhombus-shaped channels with dimensions of 4.0×5.5 Å^2 result from the arrangement of four adjacent tetramers in the (110) planes. This supramolecular structure is further stabilized by CH···π interactions (C−H···π 2.92 and 3.04 Å) between the butyl groups and the coordinated pyridine rings of adjacent tetramers and CH···π (2.85 Å) and CH···N (3.09 Å) interactions between the uncoordinated pyridyl groups and aromatic rings of the

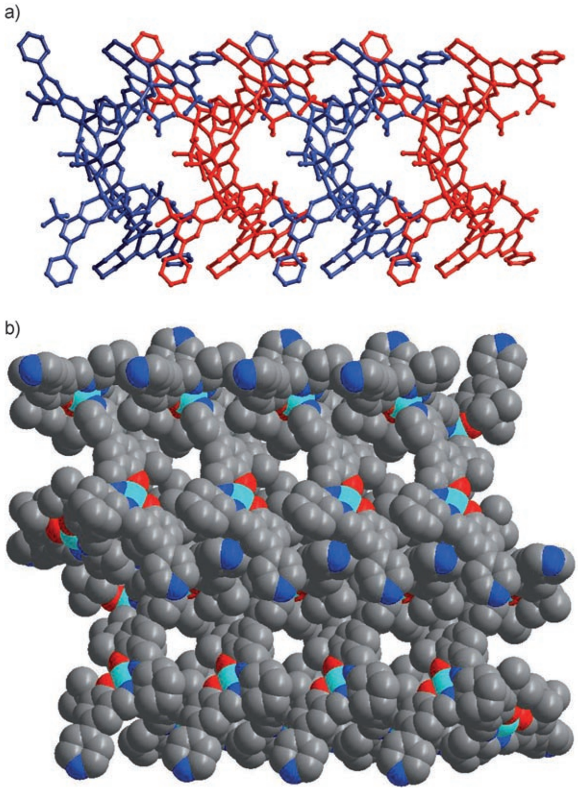


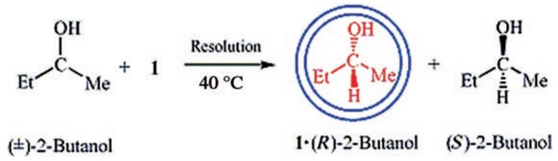
Figure 3. a) A view of the packing of $[Zn_4L_4]$ macrocycles along the *c* axis; b) Space-filling model showing the open channels along [110] direction within the 3D supramolecular structure of **1** (the included guest molecules are omitted for clarity).

{ZnL} units. Calculations using the PLATON program indicate that **1** has 14.5% of its total volume occupied by solvent molecules.[13] TGA revealed that the guest molecules could be removed at 80–150 °C (Figure S12 in the Supporting Information).

A remarkable feature of **1** is that it undergoes reversible single-crystal to single-crystal structural transformations in response to guest removal and uptake. After the guests have been removed completely by heating at 40 °C in a vacuum for 2 h, the individual crystals remain transparent with no apparent fracturing, but their color transforms from light yellow to deep yellow. The single-crystal structure revealed that the four CH_3CN molecules escaped. The cell volume decreases by 2.3%; the shorter *a* axis contracts, while the long *c* axis remains unchanged (Table S1 in the Supporting Information). Although the tetramer skeleton is intact, the {ZnL} units undergo obvious rotational rearrangements upon desolvation. In particular, the dihedral angles between the coordinated pyridine groups and the salen basal planes decrease from 11.4 and 15.3° in **1**·4 CH_3CN to 7.8 and 8.8° in **1**, owing to the axial rotation of the pyridine rings. As a result, intermolecular π–π interactions in the evacuated sample are strengthened significantly, even leading to an unprecedented color transformation of the crystals. This change can be detected from their visible spectra, which exhibits a bathochromic shift from 353 for **1**·4 CH_3CN to 391 nm for the apohost **1** (Figure S14 in the Supporting Information).

This crystal transformation is reversible and controllable. Upon exposure of the apohost **1** to the vapor of guest molecules such as CH_3CN, CH_3OH, and EtOH for two days at room temperature, the crystals reversibly transform back to the tetramers with stoichiometric uptake of the solvent. The bulk integrity of each individual crystal is maintained, as confirmed by powder XRD experiments, and the color reverts back to light yellow. The cell volume with CH_3CN reverts back, and the volume with EtOH increases by 3.9% and 1.7% (both the *a* and *c* axes expand) relative to the evacuated **1** and **1**·4 CH_3CN. From **1**·4 CH_3CN to **1**·4 EtOH, the dihedral angles between the coordinated pyridine rings and the salen basal planes increase as expected upon increasing the guest size (14.9 and 16.1° for **1**·4 EtOH). However, further studies have demonstrated that the cavity of **1** can only accommodate two molecules of 1-propanol and one molecule of 1-butanol, 2-butanol, or 3-methyl-2-butanol per tetramer and cannot accommodate 2-pentanol and 2-hexanol. A single-crystal structure of **1**·2-butanol (see below) shows that the degree of rotation of the coordinated pyridine rings to the basal salen plane (dihedral angles 11.2 and 11.3°) is smaller than those of **1**·4 CH_3CN and **1**·4 EtOH. The above results suggest that the potential barrier for the rotation of the pyridine rings in single crystals of **1** is very small and can be readily overcome by the inclusion of guest molecules. Whereas the amount of included guest is mainly determined by the cavity's volume, the host preferentially forms thermodynamically stable adducts through a process of lower energy barrier with guest molecules that fit the cavity in size and shape. Therefore, the dynamic motion of pyridine groups in **1** can be regulated by guest sorption and also endows the macromolecule with special molecular-recognition ability. For example, competitive-binding studies indicated **1** selectively includes alcohols in the order methanol > ethanol > 1-propanol > 1-butanol, but does not include chlorocarbons and nonpolar molecules. More interestingly, **1** exhibits excellent selectivity for the inclusion of acetonitrile over methanol and ethanol (Figure S13 in the Supporting Information). Notably, experimental information on the diffusion of guests in porous molecules and solids is scarce.[14] A detailed understanding of the dynamic process will no doubt allow systems with unmatched physical properties and functionalities to be designed.[15,16]

To investigate whether enantioselective separation can be achieved with the metallacycle, the crystalline sample of **1** was soaked in neat racemic 2-butanol in a sealed vial at 40 °C (Scheme 1). After two days, most crystals remained transparent with no apparent fracturing. The single-crystal structure clearly revealed that (*R*)-2-butanol is included in the cavity of **1** and the complex adduct is isostructural to **1**. This inclusion of 2-butanol is further supported by elemental analysis, TGA, and powder XRD (Figure S11 and S12 in the Supporting Information). Chiral GC analysis of the desorbed 2-butanol yielded an *ee* value of 99.8%, and the absolute *R* configuration was confirmed by comparing its optical rotation with that of the standard sample. Similar enantioselective inclusion was observed for racemic 3-methyl-2-butanol, whereby compound **1** exhibited remarkable sorption toward the *R* enantiomer over the *S* enantiomer as well. The *ee* value of the desorbed 3-methyl-2-butanol was determined to be 99.6% by chiral GC analysis. The resulting solid of **1** could be recycled and directly reused for the second cycle of resolving racemic 3-methyl-2-butanol with retention of crystallinity but with a small decrease in enantioselectivity (91.6% *ee* for the second cycle; Figure S15 in the Supporting Information). An alternative approach to recycle **1** is to recycle the {ZnL} units by using dilute HCl to dissociate the used powder and then regenerate **1** by crystallization. Further investigations on resolutions of other molecules and optimal recycling conditions are underway.



Scheme 1. Selective inclusion of (*R*)-2-butanol into the cavity of **1**.

In conclusion, this work illustrates the feasibility of producing a homochiral nanosized metallacycle from metallosalens with complementary coordination motifs. The dynamic cavity and chiral functionality presented by **1** make it an excellent host for a variety of guests with selectivity. Particularly, it can resolve small racemic alcohols with high enantioselectivity. The tunability of such a modular approach promises to lead to a variety of metallosalen-based nanostructures with unique and useful enantioselective functions.

Experimental Section

$\mathbf{1}\cdot 4\,CH_3CN$ and **1**: A mixture of $Zn(NO_3)_2\cdot 6\,H_2O$ (14.9 mg, 0.05 mmol), H_2L (29.5 mg, 0.05 mmol), DMF (3 mL), and CH_3CN (4 mL) was sealed in a 10-mL vial with a screw cap and heated at 80 °C for 12 h. The mixture was then cooled to room temperature, and light-yellow rod-like crystals were collected, washed with ether, and dried in air. Yield: 29.6 mg, 86 % based on Zn. Elemental analysis (%) calcd for $C_{160}H_{180}N_{20}O_8Zn_4$: C 69.31, H 6.54, N 10.10; found: C 69.04, H 6.46, N 10.01. The guest molecules can be readily removed to generate **1** by evacuating $\mathbf{1}\cdot 4\,CH_3CN$ at 40 °C for 2 h.

A typical guest-exchange experiment: Freshly evacuated crystals of **1** (0.10 mmol, 25.5 mg) and neat EtOH (5 mL) or a mixture of EtOH (2 mL) and CH_2Cl_2 (3 mL) were placed in a 10-mL capped vial at 40 °C for two days. The resulting sample was then isolated by filtration and washed several times with ether. Based on elemental analysis and TGA, the product can be formulated as $\mathbf{1}\cdot 4\,EtOH$. Powder XRD indicates that crystals of **1** remain almost intact without loss of crystallinity. Similarly, the guest-exchanged products can be formulated as $\mathbf{1}\cdot 4$(guest) for methanol, $\mathbf{1}\cdot 2$(guest) for 1-propanol, and $\mathbf{1}\cdot$(guest) for 1-butanol, 2-butanol, and 3-methyl-2-butanol. These formulations were also confirmed by single-crystal X-ray crystallography for the ethanol and 2-butanol products.

Separation experiment: An evacuated sample of **1** (50 mg) and racemic 2-butanol (5 mL) or 3-methyl-2-butanol (5 mL) were put in a sealed vial at 40 °C for three days. The solid samples were filtered, washed with diethyl ether, and then loaded into a distillation setup and gently heated to 60 °C under vacuum while the volatile components were collected with a liquid nitrogen bath. Optical purity of the condensates was determined by GC using a Chiral-G-TA capillary column: 99.8 % *ee* (*R*) for acetylated 2-butanol and 99.6 % *ee* (*R*) for 3-methyl-2-butanol. Optical rotation: $[\alpha] = -14.7$ and $-3.2\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ ($c = 10\ \mathrm{g\,cm^{-3}}$ in CH_3OH, 20 °C) for 2-butanol and 3-methyl-2-butanol, respectively. Other experimental details are provided in the Supporting Information.

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[10] Crystal data for $\mathbf{1}\cdot 4\,CH_3CN$: Tetragonal, space group $P4_2$, $a = 25.9432(13)$, $c = 10.9287(12)$ Å, $V = 7355.6(10)$ Å^3, $Z = 2$, $T = 298$ K, $F(000) = 2928$, $\rho_{calcd} = 1.252\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 0.708\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), $R_1 = 0.0614$, $wR_2 = 0.1280$, Flack parameter $= 0.034(19)$, GOF $= 1.030$. **1**: Tetragonal, space group $P4_2$, $a = 25.949(4)$, $c = 10.677(2)$ Å, $V = 7189(2)$ Å^3, $Z = 2$, $T = 298$ K, $F(000) = 2752$, $\rho_{calcd} = 1.205\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 0.720\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), $R_1 = 0.0745$, $wR_2 = 0.1333$, Flack parameter $= 0.01(3)$, GOF $= 0.995$. $\mathbf{1}\cdot 4\,EtOH$: Tetragonal, space group $P4_2$, $a = 26.098(4)$, $c = 10.981(2)$ Å, $V = 7479(2)$ Å^3, $Z = 2$, $T = 298$ K, $F(000) = 2960$, $\rho_{calcd} = 1.240\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 0.698\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), $R_1 = 0.0670$, $wR_2 = 0.0718$, Flack parameter $= 0.04(3)$, GOF $= 0.825$. $\mathbf{1}\cdot 2$-butanol: Tetragonal, space group $P4_2$, $a = 25.9703(7)$, $c = 10.7390(6)$ Å, $V = 7243.0(5)$ Å^3, $Z = 2$, $T = 298$ K, $F(000) = 2936$, $\rho_{calcd} = 1.230\ \mathrm{g\,cm^{-3}}$, $\mu(Mo_{K\alpha}) = 0.717\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), $R_1 = 0.0549$, $wR_2 = 0.0950$, Flack parameter $= 0.00(3)$, GOF $= 0.953$. CCDC-651775, 651776, 651777, and 651778 contain the supplementary crystallographic data for this paper. 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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