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Base-Induced Self-Assembly for One-Dimensional Coordination Polymers via Chiral Pendant-Armed Schiff Base Mononuclear Pb(II) Macrocycles

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Supporting Information

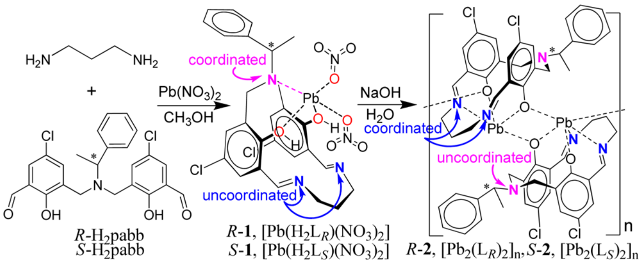
ABSTRACT: A pair of 18-membered [1 + 1] chiral pendant-armed Schiff base macrocyclic mononuclear Pb(II) complexes with an unusual N_1O_2 coordination mode, synthesized from two chiral isomeric dialdehyde components, can be further self-assembled to one-dimensional ribbon coordination polymers by adding NaOH as a base to remove two phenolic protons.

Crystal engineering of coordination polymers has been widely investigated because of its importance for material science.[1] With the simplest topological type of coordination array,[2] one-dimensional (1D) coordination polymers and their ease of formation by self-assembly allow researchers to incorporate functions at the metal centers or in the backbone of the organic linkers very easily, in order to develop functional polymeric materials with interesting magnetic, electrical, mechanical, and optical properties.[3] Until now, chemists have achieved many kinds of 1D coordination polymers such as linear, zigzag, ribbon, helical, ladder, stair, and rotaxane structural architectures.[4]

However, since the chelating effects of macrocyclic backbones originated from their multiple N and O donors, self-assembly based on the metallomacrocyclic building blocks is very challenging.[5] A practical strategy is using rigid and planar metallomacrocycles with weak-coordinated apical ligands as building blocks, introducing different strong-coordinated linkers to replace weak-coordinated apical ligands, and assembling further into coordination polymers without altering the basal coordination configuration of metal centers. In our previous studies, Schiff base dinuclear macrocyclic zinc(II) complexes with weak-coordinated solvent molecules and counterions at the axial positions have been used as building blocks to assemble a series of 1D coordination polymers without changing their rigid basal $Zn_2N_4O_2$ coordination plane.[5e,f]

Recently, we have tried to extend 2,6-diformyl-4-chlorophenol to chiral pendant-armed dialdehydes and used them to react with diamines to prepare chiral pendant-armed Schiff base macrocyclic complexes in the presence of certain metal ion template. Herein we design and prepare a pair of new extended dialdehydes (*R*-H_2pabb and *S*-H_2pabb) with chiral pendant arms (Schemes SI1 and SI2, Supporting Information), and they are reacted with 1,3-propanediamine by the Pb(II) ion template. As a result, two 18-membered [1 + 1] mononuclear Schiff base macrocyclic Pb(II) complexes (*R*-**1** and *S*-**1**) have been obtained (Scheme 1). X-ray single-crystal diffraction analysis of *R*-**1** reveals that an unusual N_1O_2 coordination mode for the pendant-armed dialdehyde component has been found for the central Pb(II) ion, where two strong intramolecular O−H···N hydrogen bonds are observed between the phenolic protons and the Schiff base nitrogen atoms to block the coordination of Schiff base units.

Scheme 1. Schematic Illustration for the Synthesis of [1 + 1] Chiral Macrocyclic Mononuclear Pb(II) Complexes and Their Relative 1D Ribbon Coordination Polymers



R-H_2pabb
S-H_2pabb

R-**1**, $[Pb(H_2L_R)(NO_3)_2]$
S-**1**, $[Pb(H_2L_S)(NO_3)_2]$

R-**2**, $[Pb_2(L_R)_2]_n$, *S*-**2**, $[Pb_2(L_S)_2]_n$

Considering the unsaturated coordination of macrocyclic donors and the presence of two weak-coordinated nitrate anions, we think it is possible to destroy the O−H···N hydrogen bonds by removing the phenolic protons and nitrate anions accordingly based on the electroneutrality principle. As a result, several coordination sites of the Pb(II) ion can be spared and the Schiff base units can be coordinated at the same time, so further self-assembly could be fulfilled just by varying the coordination geometry without adding additional bridging linkers. By following this strategy, a pair of chiral 1D coordination polymers *R*-**2** and *S*-**2** has been successfully produced by base-induced linker-free self-assembly, where chiral Pb(II) macrocycles *R*-**1** and *S*-**1** serve as building blocks, together with the significant alteration of flexible pendant arms stemmed from the cleavage of Pb−N coordinative bond.

The two chiral *N*-modificatory dialdehydes (*R*-H_2pabb and *S*-H_2pabb) were prepared by the reaction between *R*- or *S*-1-

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phenylethylamine and 5-chloro-3-(chloromethyl)-2-hydroxybenzaldehyde involving continuous two-step nucleophilic substitutions.[6] The construction of Schiff base macrocycle was carried out by the 1:1 condensation between *R*- or *S*-H_2pabb and certain diamine in the participancy of certain metal ion template.[7] It is found that the combination of Pb(II) ion and 1,3-propanediamine is somewhat a "perfect match" in the effective formation of [1 + 1] mononuclear Schiff base metallomacrocycles for this pair of chiral pendant-armed dialdehydes. This means that the size, charge, and coordination geometry of Pb(II) ion fits well with the flexibility of dialdehyde and diamine precursors to organize the final Schiff base macrocyclic ligands H_2L_R and H_2L_S. In fact, some other metal ions (Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, and Pd) and diamines [1,2-cyclohexanediamine, 1,2-bis(2-aminoethoxy)ethane, and 1,2-benzenediamine][8] with different sizes and flexibility have been used under the same experimental conditions, but the products were very complicated and difficult to isolate and purify. As we have mentioned before, two phenolic protons and nitrate anions in *R*-**1** and *S*-**1** can be removed by adding a base like NaOH to adjust the pH value in the range 8−9,[9] and the final products *R*-**2** and *S*-**2** have been obtained, accompanied by a color change of the reaction solution from red to yellow green. The single crystals of macrocyclic complexes *R*-**1** and *R*-**2** suitable for X-ray diffraction analysis were grown from the acetonitrile−methanol mixture by slow evaporation in air at room temperature for 2 weeks. However, attempts to obtain high-quality single crystals of *S*-**1** and *S*-**2** for X-ray diffraction determination have not been successful.

A strong FT-IR absorption peak is found to be 1666 and 1668 cm^{-1} in *R*-H_2pabb and *S*-H_2pabb, corresponding to the presence of aldehyde groups in their molecular structures. In contrast, this absorption peak disappears and a new absorption peak is observed at 1640 and 1638 cm^{-1} in chiral macrocyclic complexes *R*-**1** and *S*-**1**, respectively, indicating the transformation from the aldehyde groups to the Schiff base C═N units. Moreover, the characteristic Schiff base C═N absorption peak is significantly shifted to the same 1631 cm^{-1} in 1D coordination polymers *R*-**2** and *S*-**2**, suggesting its variation from uncoordinated to coordinated mode, which can be further verified by the following X-ray single-crystal structures. In addition, the CD spectra of two chiral dialdehydes and four Pb(II) complexes, which can reflect and verify the different chirality of compounds, have been recorded for comparison. The results reveal that the *R* isomers give Cotton effects that are mirror images of their respective *S* isomers (Figure SI2, Supporting Information), agreeing well with the enantiomeric nature of these chiral compounds.

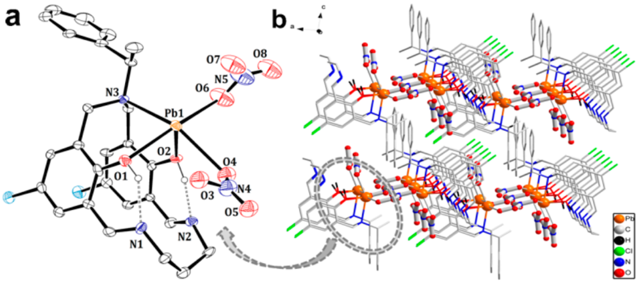

Figure 1. (a) ORTEP drawing of *R*-**1** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and only the phenolic protons are shown. (b) View of molecular packing of *R*-**1** down the *b*-axis. Hydrogen atoms are omitted for clarity.

From the X-ray structure analyses of *R*-**1** and *R*-**2** derived from dialdehyde *R*-H_2pabb,[10] it is known that they have the same 18-membered [1 + 1] Schiff base macrocyclic ligand except that two phenolic protons are present in *R*-**1**. Nevertheless, there are extraordinary differences between them. On the one hand, *R*-**1** is a mononuclear macrocyclic Pb(II) complex, which is countered by two weak-coordinated nitrate anions, displaying an unusual coordination fashion (Figure 1a). The central Pb(II) is five-coordinated by two phenolic oxygen atoms (O1 and O2), a tertiary nitrogen atom (N3), and two oxygen atoms (O4 and O6) from two nitrate anions. The coordination configuration of the Pb(II) center in *R*-**1** can be described as a distorted pyramid with a τ value of 0.077.[11] Two bond lengths between the phenolic oxygen atoms and the central Pb(II) ion are 2.346(8) and 2.294(7) Å, which are much shorter than the other three (2.624(5), 2.666(9), and 2.817(11) Å). The dihedral angles between pendant-armed phenol ring and two phenolic rings are 82.2(7) and 76.8(8)°, respectively. It is worth pointing out that the two Schiff base nitrogen atoms are uncoordinated, which is different from most of the reported Schiff base macrocylic complexes with the common N_2O_2 coordination mode. Instead, two strong intramolecular O−H···N hydrogen bonds are observed between the Schiff base nitrogen atoms and the phenolic protons (Table SI2, Supporting Information). It is suggested that the formation of hydrogen bonds will stabilize the dynamic imine bonds and block the coordination of Schiff base units simultaneously. Moreover, intramolecular π−π interactions are observed between two parallel phenolic rings with a centroid-to-centroid separation of 3.503(9) Å (Figure 1b).

On the other hand, *R*-**2** is a 1D coordination polymer which is self-assembled from *R*-**1** via the addition of NaOH. Accompanied by the deprotonation process, two nitrates have been eliminated according to the electroneutrality principle, and two imine nitrogen atoms take part in the coordination with the central Pb(II) ion. As a result, the conventional and stable N_2O_2 coordination mode is formed in *R*-**2**, where the above-mentioned three longer coordinative bonds in *R*-**1** have been cleaved. A dinuclear repeating unit is formed in 1D coordination polymer *R*-**2**, where two central Pb(II) ions display distinguishable coordination environment (Figure 2a). Pb1 is twisted six-coordinate octahedronal, while Pb2 is distorted five-coordinate trigonal bipyramidal (τ = 0.975). The dihedral angles between the pendant-armed phenol ring and two phenolic rings are 36.7(8) and 47.9(9)°, respectively. Three of four phenolic oxygen atoms (O1, O3, and O4) serve

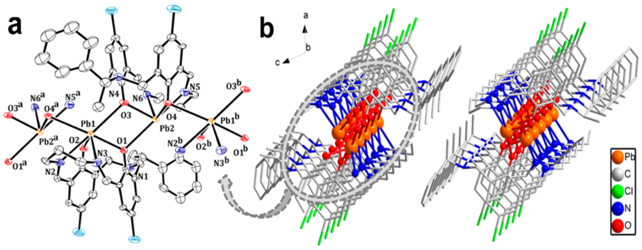

Figure 2. (a) ORTEP drawing of *R*-**2** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. (b) View of packing structure of 1D ribbon coordination polymer *R*-**2** down the *b*-axis. Hydrogen atoms are omitted for clarity.

as the μ_2-bridges linking adjacent Pb(II) ions forming an infinite 1D ribbon coordination polymer along the crystallographic *b* axis (Figure 2b). Additionally, intramolecuar $\pi-\pi$ interactions are observed between two parallel phenolic rings with the centroid-to-centroid separations of 3.569(10) and 3.607(10) Å.

In summary, we have reported a pair of new extended dialdehydes with chiral pendant arms (*R*-H_2pabb and *S*-H_2pabb), and their 18-membered [1 + 1] chiral mononuclear Schiff base macrocyclic Pb(II) complexes (*R*-**1** and *S*-**1**). It is noted that the Pb(II) ion exhibits an unusual N_1O_2 coordination mode in *R*- and *S*-**1**, where two Schiff base nitrogen atoms are blocked by strong intramolecular O−H···N hydrogen bonds with two phenolic protons and they are kept uncoordinated. Considering that unsaturated coordination of macrocyclic donors and the presence of two weak-coordinated nitrate anions in *R*-**1** and *S*-**1**, NaOH is used as a base to remove the phenolic protons, destroy the intramolecular O−H···N hydrogen bonds, eliminate two nitrate anions accordingly, and spare several coordination sites of the Pb(II) ion, which will make the rearrangement of coordination geometry possible. As a result, further self-assembly can be fulfilled and a pair of 1D ribbon coordination polymers (*R*-**2** and *S*-**2**) has been successfully produced without adding additional bridging linkers, where two Schiff base nitrogen atoms are coordinated with the central Pb(II) ion instead of the original weakly coordinated tertiary nitrogen atom and two nitrates.

In this work, we have demonstrated that a base-induced linker-free macrocyclic self-assembly can be achieved just by adding NaOH as a base to remove the phenolic protons of metallomacrocyclic precursors in the absence of any additional bridging linkers, thereby varying the coordination geometry of metal centers and facilitating the self-assembly process. This is different from our previously reported macrocyclic self-assembled strategy because the axially weak-coordinated solvent molecules and counterions of rigid and planar metallomacrocycles with strong-coordinated bridging ligands are replaced. We believe the results of this study could provide new insight into the supramolecular self-assembly of Schiff base macrocyclic complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, characterization data, crystallographic data (CIF). CCDC 996990−996991. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Crystal data for *R*-**1**: $C_{27}H_{27}Cl_2N_5O_8Pb$, M = 827.64, monoclinic, space group $P2_1$, a = 10.568(1) Å, b = 12.453(1) Å, c = 10.693(1) Å, $\alpha = \gamma = 90°$, β = 92.773(1)°, V = 1405.5(2) Å^3, T = 291(2) K, Z = 2, 9414 reflections measured, 5377 independent reflections (R_{int} = 0.030), Flack parameter, 0.022(9), the final R_1 = 0.0357 [$I > 2\sigma(I)$] and 0.0489 (all data), and the final wR_2 = 0.0774 [$I > 2\sigma(I)$] and 0.0823 (all data). CCDC 996990. Crystal data for *R*-**2**: $C_{54}H_{50}Cl_4N_6O_4Pb_2$, M = 1403.20, monoclinic, space group $C2$, a = 26.095(3) Å, b = 7.460(1) Å, c = 28.384(3) Å, $\alpha = \gamma = 90°$, β = 111.599(2)°, V = 5137.7(9) Å^3, T = 291(2) K, Z = 4, 17252 reflections measured, 7016 independent reflections (R_{int} = 0.077), Flack parameter, 0.096(14), the final R_1 = 0.0627 [$I > 2\sigma(I)$] and 0.0691 (all data), and the final wR_2 = 0.1692 [$I > 2\sigma(I)$] and 0.1749 (all data). CCDC 996991.

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