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Novel Crown Ether and Salen Metal Chelation Driven Molecular Pincers

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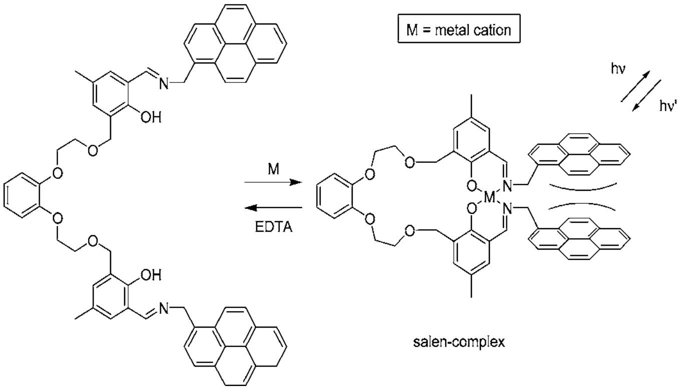
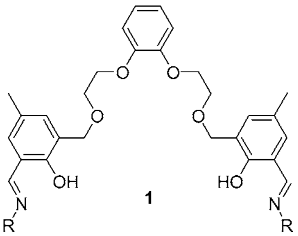
ABSTRACT



The synthesis of novel metal chelation driven molecular pincers based on crown ether and salen ligand substructures are described. Their functionality was monitored by fluorescence spectroscopy using pyrene groups as fluorescence probes. The pincer was shown to function reversibly with respect to metal chelation with Zn^{2+} and also to chelate ditopically with 100 mol % of Zn^{2+} and 100 mol % Li^{+} or 200 mol % of Li^{+} ion.

The control of molecular-scale mechanical movements is a highly desired objective in the construction of molecular devices and machines.[1] When the movements generated are related to opening, closing, and translocation functions, these molecular-scale devices are often called molecular tweezers,[2] scissors,[3] hinges,[4] or pincers.[5] All of these systems exhibit molecular units that are able to switch between two or more states of geometry.

A convenient way to control molecular movements between different geometries is metal chelation. Chelation driven steering of conformation can be achieved using pyridine,[6] amine,[4b] and ether[7] ligands. Additionally, crown ethers have been widely applied as supramolecular binders for cationic species, especially for alkali metals, since the pioneering work of C. J. Pedersen.[8,9]



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Salens are widely applied strongly coordinating ligands for a variety of transition metal ions. Their metal complexes

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have been used for many applications such as asymmetric catalysis,[10] sensing,[11] and DNA cleavage.[12] To the best of our knowledge, however, thus far reversible Salen complex formation has not been used to control molecular movements.

Reynolds and Reddinger have previously shown that the closed ring Salen-crown ether molecules are able to perform dual-ion cocomplexation;[11a] we instead extend this type of ditopic metal chelation to open ring Salen-crown ether molecules. Herein we report a novel molecular pincer structure **1**, in which Salen and crown ether functionalities are combined to give a distinct closing and locking mechanism (and the driving force for the molecular pincer). The proposed mechanism for this type of chelator is shown in Figure 1. In the pincer molecule, the Salen moiety is the primary metal chelator, in which phenolate groups act as anionic binding sites (Figure 1). The crown ether part is an additional tetradentate metal chelator.

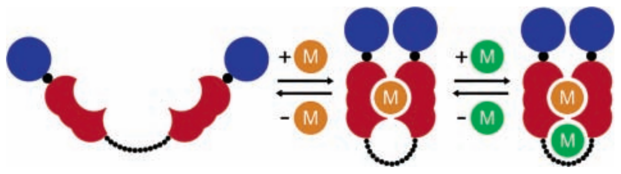
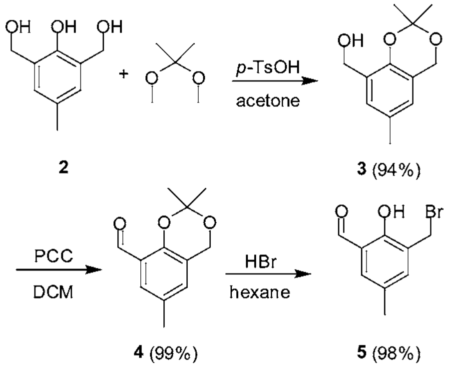


Figure 1. Schematic illustration of metal chelation adjustable molecular pincers. The structure on the left depicts ditopic metal chelation.

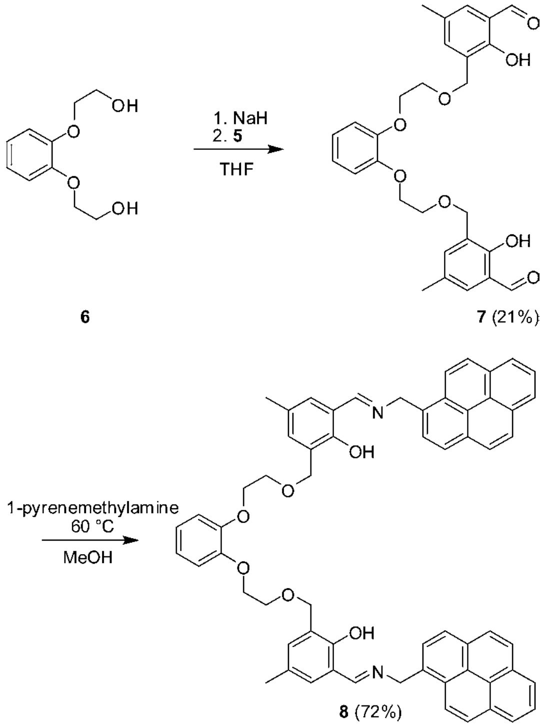
To demonstrate the pincers' functionality as a molecular device we have equipped the Salen pincers with pyrene groups to act as fluorescence reporters. By monitoring with fluorescence spectroscopy it is possible to observe the open and closed forms of the pincers: in a closed pincer structure, the pyrene groups are brought into close proximity, affording excimer fluorescence (Figures 1 and 2).[13]

For the pincer synthesis we have developed a concise two directional synthetic strategy. The crown ether segment is constructed from catechol and chloroethanol, whereas the Salen fragment is built from 2,6-bis(hydroxymethyl)phenol prior to their coupling to form the Salen crown backbone (Schemes 1 and 2).

Scheme 1



Scheme 2



2,6-Bis(hydroxymethyl)phenol **2** was treated with 2,2-dimethoxypropane in the presence of *p*-TsOH to afford the acetonide **3** in good yield. Oxidation of acetonide **3** with PCC gave aldehyde **4** in an excellent yield. Aldehyde **4** was treated with HBr gas, resulting simultaneous deprotection and bromination of benzylic hydroxyl group. Benzyl bromide **5** was collected in an excellent yield (Scheme 1).

1,2-Bis(2-hydroxyethoxy)benzene **6** was prepared according to a literature procedure.[14] Product **7** was obtained in

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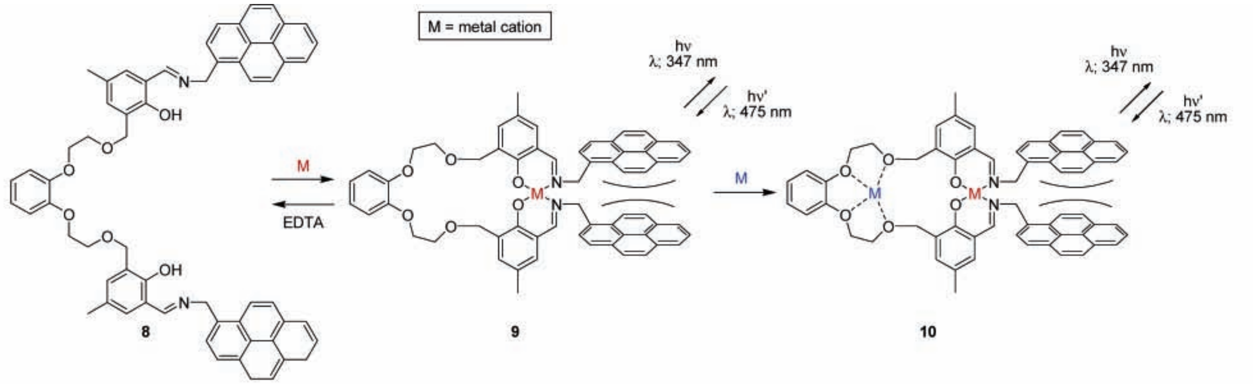

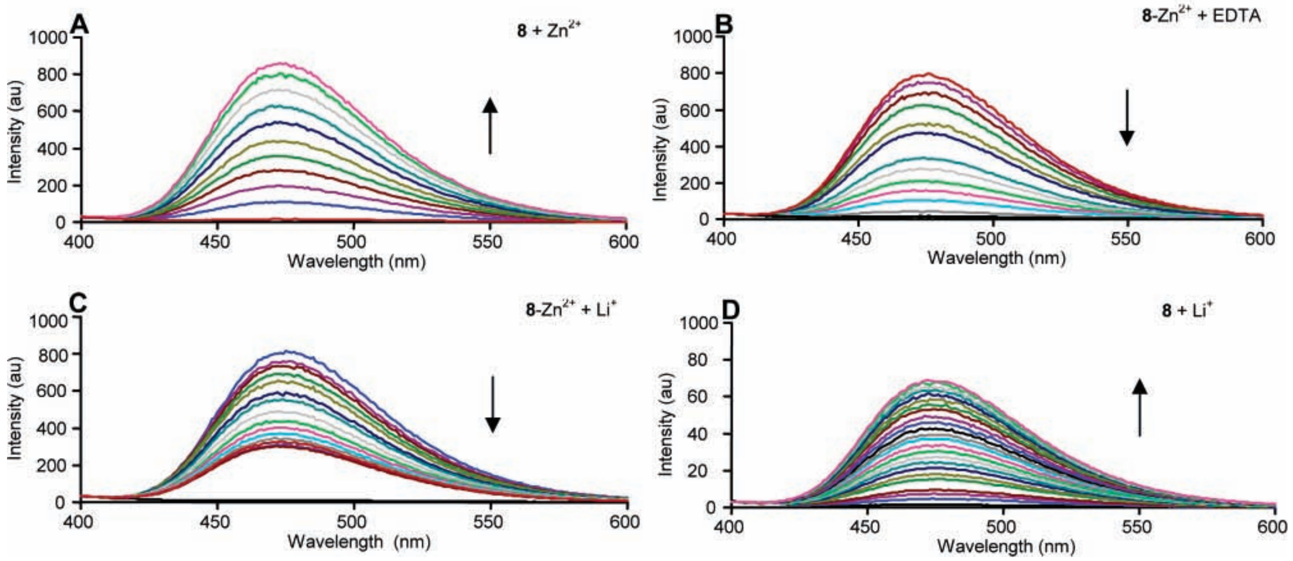

Figure 2. UV−vis spectra of the titration measurements. (A) Fluorescence spectral change of **8** (10 μM in 1:1 MeOH/THF, excitation at 347 nm) upon addition of $Zn(ClO_4)_2 \cdot 6H_2O$ (0, 10, 20, 30, 40. 50, 60, 70, 80, 90, 100 mol %). (B) Fluorescence spectral change of **8**−Zn^{2+} complex (10 μM in 1:1 MeOH/THF, excitation at 347 nm) with the addition of EDTA (0, 10, 20, 30, 40. 50, 60, 70, 80, 90, 100, 110, 120 mol %). (C) Fluorescence spectral change of **8**−Zn^{2+} complex (10 μM in 1:1 MeOH/THF, excitation at 347 nm) with the addition of LiCl (0, 10, 20, 30, 40. 50, 60, 70, 80, 90, 100, 110, 120, 130 mol %). (D) Fluorescence spectral change of **8** (10 μM in 1:1 MeOH/THF, excitation at 347 nm) with the addition of LiCl (0, 10, 20, 30, 40. 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230 mol %).

modest yield, by reaction of the sodium alcoholate of hydroxyethoxybenzene **6** with benzaldehyde **5**. The crown-Salen hinge with pyrene functionalities (**8**) was prepared by treating aldehyde **7** with 1-pyrenemethylamine (Scheme 2).

The pincer functionality and metal chelation ability of compound **8** was studied in MeOH/THF (1:1) solution by fluorescence spectroscopy. Without a chelated metal, compound **8** gave only weak fluorescence when excited at 347 nm. However, when the solution was titrated with metal ions an intense emission was observed at 475 nm. In the case of $Zn(ClO_4)_2$ the emission intensity increased until the concentration of ions reached 100 mol % (Figure 2A).

The reversibility of pincer function was tested by titration with EDTA, which is known to trap transition metal ions. The zinc complex **9** was titrated by portion-wise addition of EDTA to the pincer−Zn^{2+} complex solution. Upon titration, the fluorescence intensity decreased smoothly in an inverse manner compared to titration of **8** with Zn^{2+}. When 100 mol % of EDTA had been added the fluorescence intensity returned to the level of nonchelated **8** (Figure 2B).

The ditopic chelation ability of **8** was studied by adding LiCl to the pincer−Zn^{2+} complex solution. Upon titration, the emission fluorescence intensity dropped until 100 mol % of the metal ion had been added and then remained stable. We interpret this as being a consequence of Li^+ coordination to the crown ether moiety, causing a disturbance in the pyrene excimer structure of **10**, lowering the observed fluorescence intensity (Figure 2C).

Titration of **8** with LiCl indicated that ditopic chelation is also possible with a single metal ion: upon LiCl titration of **8** the emission intensity increased linearly until 200 mol % of LiCl was added (Figure 2D).

In summary, we have introduced a molecular pincer based on a reversible metal chelation driven Salen-crown ether concept. It should be possible to use a number of primary amines in the formation of the Schiff base Salen structure, thus creating a library of related pincer structures. Currently, we are studying how these pincers could be integrated into macroscopic structures and be employed in advanced materials.

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Supporting Information Available: Experimental procedures for the preparation of compound **8** and characterization for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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