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Crystal structure and fluorescence sensing properties of tetramethoxyresorcinarene functionalized Schiff bases

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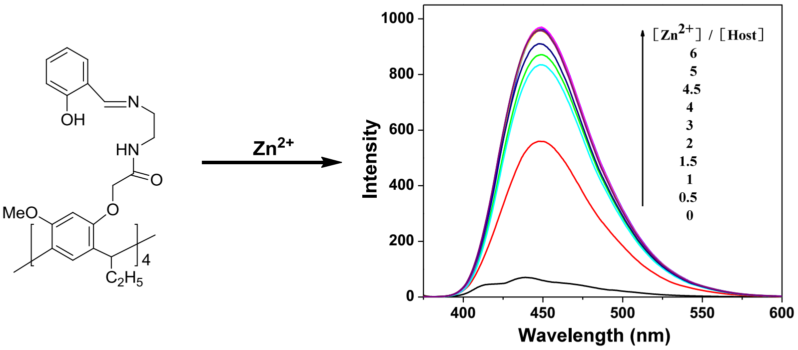
GRAPHICAL ABSTRACT



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ABSTRACT

A series of tertamethoxyresorcinarene functionalized Schiff bases were conveniently prepared by the reaction of resorcinarene ester derivatives with excess of ethylenediamine and then condensation with salicylaldehyde. The single crystal analysis of five products shows that tetramethoxyresorcinarenes existed in *chair* conformation. The complexing properties of these polydentated ligands to transition metal ions were studied by UV–Vis and fluorescence spectroscopy. The results demonstrate that these polydentated ligands are more efficient for recognition of Zn^{2+} in preference to other metal ions, accompanying a remarkable fluorescence intensity enhancement. Taking **4a** as an example, it exhibits a 13-fold fluorescence enhancement upon the addition of 3 equiv. of Zn^{2+} in CH_3OH/CH_3CN (1:9 v/v) solution.

Introduction

In recent years, fluorescent chemosensors have received extensive attention because they are of significant importance in the fields of analytical chemistry, life sciences, medical analysis, and environmental monitoring [1–5]. Sensitive zinc ion sensors are extensively required because zinc plays vital roles in many biological processes such as gene transcription, immune function, and mammalian reproduction [6–8]. A great deal of efforts have been contributed to design fluorescent probes for detecting Zn^{2+}, however, most of these Zn^{2+} sensors exhibit poor selectivity due to the interference of related cation (Cd^{2+}). It is still desirable to develop new molecular fluorescent sensors for zinc ions in preference to many other related ions [9,10].

As a new star of calixarene family, tetramethoxyresorcinarenes were prepared by Lewis acid catalyzed condensation of 3-alkoxy-

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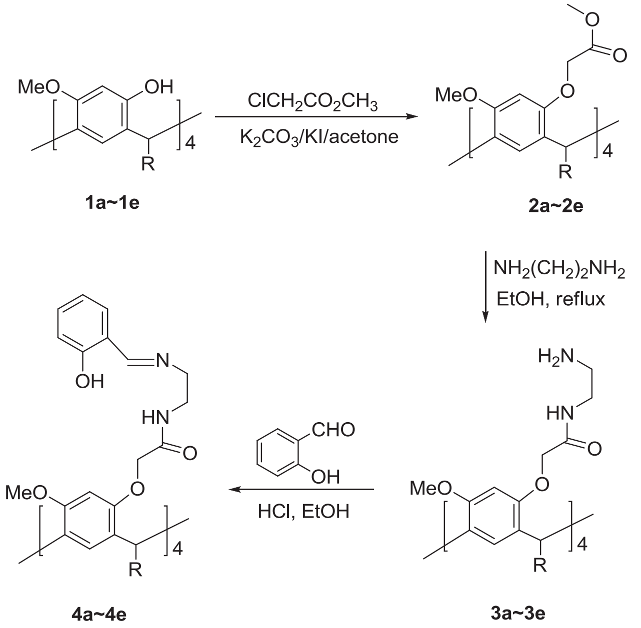
phenol with aliphatic aldehydes, which have attracted much interest in the field of supramolecular chemistry [11–14]. Tetramethoxyresorcinarenes have been used as not only artificial receptors for molecular recognition but also convenient building blocks to construct more sophisticated nanostructured supramolecular architectures [15–17]. The structural features mainly depend on the complexation of tetramethoxyresorcinarenes toward a variety of neutral compounds [18,19]. In addition, introducing metal ligands into the resorcinarenes frameworks is the most common way to improve the binding ability between the metal ions and the tetramethoxyresorcinarenes. For example, Ogden synthesized the tetramethoxyresorcinarene picolyl ether derivatives and obtained the interesting copper and nickel complex polymers [20]. Salorinne and Nissinen have synthesized tetramethoxyresorcinarene derivatives functionalized with the bis-crown ethers units and studied the complexation properties of the compounds toward alkali metal cations [21–23]. Schiff bases with N-ligating groups have attracted increasing attention because they are known to form strong complexes with transition metal ions and recently were used as ionophores in sensors for cations determination [4,24]. However, the design and syntheses of resorcinarene ligands remains challenging. In this respect, the chemical modification of N-ligating groups in resorcinarene prompted us to take up the design and synthesis of molecular receptors **4a–4e** which were obtained by a series of reactions, remain we wish to report transition metal complexing properties of a series of novel tetramethoxyresorcinarene derivatives. By using the fluorescence spectroscopy, we will demonstrate that these polydentated ligands are more efficient for recognition of Zn^{2+} in preference to other metal ions.

Results and discussions

Synthesis and characterization

The general synthetic route for the expected tetramethoxyresorcinarenes with functional Schiff bases derivatives was shown in Scheme 1. The tetramethoxyresorcinarenes **1a–1e** (R = C_2H_5, *i*-C_3H_7, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_7H_{15}) and tetramethoxyresorcinarene acetate **2a–2e** were prepared by the previously reported procedure [25]. The ammonolysis of tetramethoxyresorcinarene *O*-acetate **2a–2e** was carried out in a mixture of ethanol and toluene with excess of ethyelenediamine to obtain the corresponding tetramethoxyresorcinarene amide derivatives **3a–3e** as white solid in excellent yields (86–91%). Then the acylamide derivatives were used to react with salicylaldehyde in refluxed ethanol, after 8 h, the target tetramethoxyresorcinarene functionalized Schiff bases **4a–4e** were obtained in good yields (62–89%).



Scheme 1. Synthesis of tetramethoxyresorcinarene Schiff bases **4a–4e**. R = C_2H_5, $CH(CH_3)_2$, *n*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_7H_{15}.

The IR spectra of **3a–3e** shows that the stretching vibration of carbonyl group occurs at 1680 cm^{-1}, while for the carbonyl group of ester occurs at 1760–1770 cm^{-1}, which indicates the formation the amide bond. Also, the tetramethoxyresorcinarene functionalized Schiff bases **4a–4e** were confirmed by the appearance of the peak at 1632 cm^{-1} in their IR spectra. In order to determine the structures of the expected tetramethoxyresorcinarene functionalized Schiff bases **4a–4e**, ^1H NMR spectra can be used as a powerful tool to investigate the outcome of the reaction. The protons of **4a–4e** usually give one set of chemical shifts for the characteristic groups in the molecules, which suggest that the whole molecule have the C_4 symmetry. Taking **4a** for example, two downfield singlets (δ = 12.93, 7.82 ppm) are attributed to protons of the four hydroxy groups and the four CH=N units, respectively. Two upfield proton signals (δ = 4.44, 3.51 ppm) are assigned to the protons of the four bridging CH units and the four methoxy groups respectively. On the other hand, the two proton signals observed at 4.31 and 4.07 ppm with germinal coupling *J* = 14.4 Hz belongs to the $—OCH_2CO—$ groups, indicating that the two protons in $—OCH_2CO—$ group are in the different environment. All the above observations demonstrate that the whole molecule exist in an symmetric conformation.

Crystal structures

To obtain further information of the tetramethoxyresorcinarene functionalized Schiff bases in the solid state, X-ray diffraction analyses were performed. Thus, the single crystal structures of tetramethoxyresorcinarenes **1b, 1c, 1e, 2b** and **4c** were successfully determined. The crystal data and refinement details were listed in Table 1. The perspective views with the partial atomic numbering scheme are shown in Figs. 1–5, respectively. From the structures of **1b**, **1c** and **1e**, it can be clearly shown that the four isopropyl, *n*-pentyl and *n*-heptyl groups are located in the lower rim direction, which indicates the structures of **1b**, **1c** and **1e** adopt *rccc* (all *cis*) conformation. In those structures, the four resorcinol units in the macrocycle were divided into two groups with two resorcinol rings almost perpendicular to the other two resorcinol rings, which suggest the resorcinarene in C_4 crown conformation with much distorted in a propeller-like manner. As illustrated in Figs. 1–3.

The molecular structures of tetramethoxyresorcinarene *O*-acetate **2b** (Fig. 3) adopts the *boat* conformation with two resorcinol rings in almost perpendicular position and the other two resorcinol rings in nearly horizontal position. Thus, the two methoxycarbonylmethoxy groups in the resorcinarene stretch to upside and the other two methoxycarbonylmethoxy groups stretch to horizontal direction. In the molecular structure of tetramethoxyresorcinarene Schiff base **4c**, the resorcinarene core retains the *boat* conformation with two resorcinol rings in nearly horizontal position, which caused the corresponding to four Schiff base moieties into two kinds of circumstance.

Complex formation with transition metal ions

The metal ions binding properties of the above prepared tetramethoxyresorcinarenes Schiff bases with nitrate salts of various transition metal ions were investigated by UV–Vis and fluores-