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Synthesis, Characterization and Coordination Properties of a Novel Thiacalix[4]arene with Diagonal Quinolin-8-yloxy Pendants

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A novel conic thiacalix[4]arene derivative (1) with diagonal quinolin-8-yloxy pendants via oxyethylene spacer has been synthesized in one step. The coordination properties of the new ligand towards Ni^{2+}, Co^{2+} and Zn^{2+} ions were studied by UV–vis, fluorescent spectra and ^1H NMR titration. The results showed that 1 formed very stable complexes with the three metal ions, and the stoichiometries of 1-Ni^{2+}, 1-Co^{2+} and 1-Zn^{2+} were 1:1, 1:2 and 1:2, respectively.

Keywords: Thiacalix[4]arene; 8-Hydroxyquinoline; Coordination; Transition metal; Fluorescence

INTRODUCTION

Thiacalixarene is a new member of the calixarene family in which epithio groups replace the methylene bridges of traditional calixarene [1]. The presence of sulfur atom bridges in thiacalix[4]arenes results in potentially useful properties, mostly unknown in the chemistry of classical calixarenes, such as excellent complexation ability toward transition metals [2] in combination with chemical modification (oxidation) [3,4] of bridge units and different conformational preferences [5]. Since *p-tert*-butylthiacalix[4]arene was accessible in multi-grams scale by a simple synthetic procedure [6], thiacalixarenes have become attractive candidates as molecular platforms for constructing more sophisticated host molecules [7–12]. In recent years, the synthesis, characterization and application of fluorescent molecular sensors based on calixarenes have been the focus of much attention. Linkage of fluorogenic compounds (such as anthracene [13], pyrene [14,15], phenanthroline [16], dipyridine [17], hydroxyquinoline [18,19]) to appropriately functionalized calixarenes as ion receptors has afforded efficient fluorescence molecular chemosensors possessing abilities to selectively sense specific chemical species. But very few of such examples based on thiacalix[4]arene were known till now [20,21].

8-Hydroxyquinoline is one of the most extensively investigated ligand, after EDTA, in coordination chemistry [22]. An important property that makes 8-hydroxyquinoline even more attractive as a chelator is the appreciable change in its fluorescence upon metal binding. Therefore, 8-hydroxyquinoline has been used extensively to construct highly sensitive fluorescent molecular sensors for sensing of metal ions of important biological and environmental significance [23–26].

In view of the above, it seemed of interest to us to couple the 8-hydroxyquinoline moieties to thiacalix[4]arene. However, it is impossible to couple the 8-hydroxyquinoline to calixarenes directly, as we all know, oligooxyethylene is a well known segment to construct host for complexing metal ions [27]. We thought if using ω-quinolin-8-yl-oxyethyloxyethyl-tosylate as reactant, the 8-quinolinyl and diethylene glycol segment could be induced to thiacalixarene directly and simultaneously. This can fix the conformation and improve the coordination ability of thiacalix[4]arene. On the other hand, the thiacalix[4]arene derivative is fluorescent and may be used as a fluorescent molecular chemosensor or probe towards metal ions. To the best of our knowledge, thiacalix[4]arene derivatives with 8-hydroxyquinoline moieties have never been reported in the literature. Herein we report the synthesis and characterization of a novel thiacalix[4]arene with diagonal quinolin-8-yloxy pendants **1** (Scheme 1).

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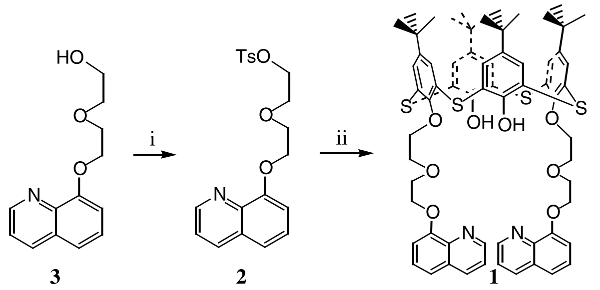


i: p-tosyl chloride, Pyridine/CH_2Cl_2
ii: p-*tert*-butylthiacalix[4]arene, K_2CO_3/Toluene

SCHEME 1

Its coordination properties towards Ni^{2+}, Co^{2+} and Zn^{2+} ions were investigated by UV–vis and fluorescent spectra and ^1H NMR titration.

RESULTS AND DISCUSSION

Synthesis

The reaction of 2-(2-(quinolin-8-yloxy)ethoxy)ethanol (**3**) [28] with p-tosyl chloride in pyridine/CH_2Cl_2 at 0°C afforded 2-(2-(quinolin-8-yloxy)ethoxy)ethyl tosylate (**2**) in 63.7% yield conveniently. A p-*tert*-butylthiacalix[4]arene derivative (**1**) with diagonal 8-hydroxyquinoline moieties was obtained by further treatment of p-*tert*-butylthiacalix[4]arene with 2.5 equiv. **2** in refluxing toluene for 24 hours, in the presence of 5 equiv. K_2CO_3.

UV–vis Spectra Study

The coordination properties of **1** with Ni^{2+}, Co^{2+} and Zn^{2+} were investigated by UV–vis spectra in acetonitrile, and in all cases the counterpart anion was ClO_4^-. Take the absorption spectra of **1**-Co^{2+} system as an example (Fig. 1), the characteristic absorption bands of free ligand at 285, 301 nm ascribed to π–π* transitions in the thiacalix[4]arene phenolic groups, and that at 313 nm ascribed to π–π* transitions in the 8-hydroxyquinoline groups. With the addition of Co^{2+} ion to the solution of receptor **1** in CH_3CN (1.0×10^{-4} M), the absorption strength of the thiacalix[4]arene at 285, 301 nm decreased gradually and a new peak appeared at 340 nm, which reflected the electronic perturbation induced by the coordination of the metal ion. The absorbance values at 340 nm increased gradually upon the addition of Co^{2+}. The similar phenomena were observed for the **1**-Ni^{2+} and **1**-Zn^{2+} systems.

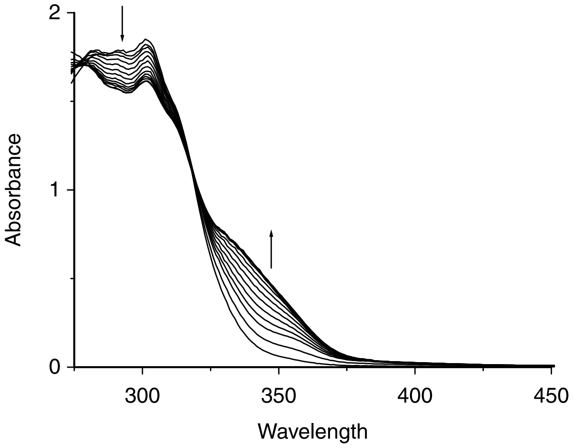


FIGURE 1 UV–vis titration curves for the **1**-Co^{2+} system in CH_3CN at 25°C, equivalent of Co^{2+} ion: 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 3 and 3.5.

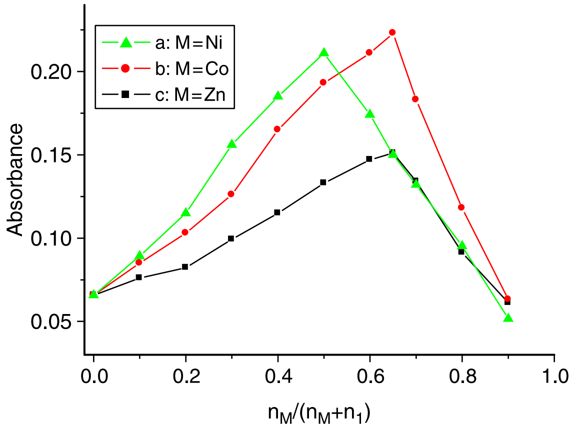


FIGURE 2 Job plot for the mixture of **1** and $M(ClO_4)_2$ in CH_3CN. The absorbance at 340 nm is plotted against the molar fraction of M^{2+}. (a) M = Ni; (b) M = Co; (c) M = Zn.

The continuous variation method [29] was used to determine the stoichiometric ratios of the receptor **1** with Zn^{2+}, Co^{2+} and Ni^{2+} ions. The total concentration of host (**1**) and guest (M^{2+}) was constant (1.0×10^{-4} M), with a continuously variable molar fraction of guest ($n_M/(n_1 + n_M)$). Figure 2 shows the Job plot of **1** with the three metal ions at 340 nm. The absorbance of **1**-Ni^{2+} complex approaches a maximum when the molar fraction of guest is 0.5, which means that receptor **1** and Ni^{2+} only form a 1:1 complex; while the positions of the maximum absorbance of both **1**-Co^{2+} and **1**-Zn^{2+} complexes are at about 0.65, indicating that host **1** forms 1:2 complexes with Co^{2+} and Zn^{2+} ions.

Fluorescent Spectra Study

Due to its high sensitivity, fluorescent titration was carried out to investigate the complexation constants of **1** with Ni^{2+}, Co^{2+} and Zn^{2+} ions. The emission spectra ($\lambda_{ex} = 322$ nm) of **1** (0.1 mM) with various concentrations of $Ni(ClO_4)_2$ or $Co(ClO_4)_2$ in acetonitrile are shown in Fig. 3. It can be seen that the fluorescence intensity ($\lambda_{em} = 394$ nm) of **1** decreases continually, but the position of the emission maximum has no significant change upon addition of Ni^{2+} or Co^{2+}. 1 Equiv. Ni^{2+} or 2 equiv. Co^{2+} almost completely quenched the fluorescence of **1**, which probably resulted from the very efficient and

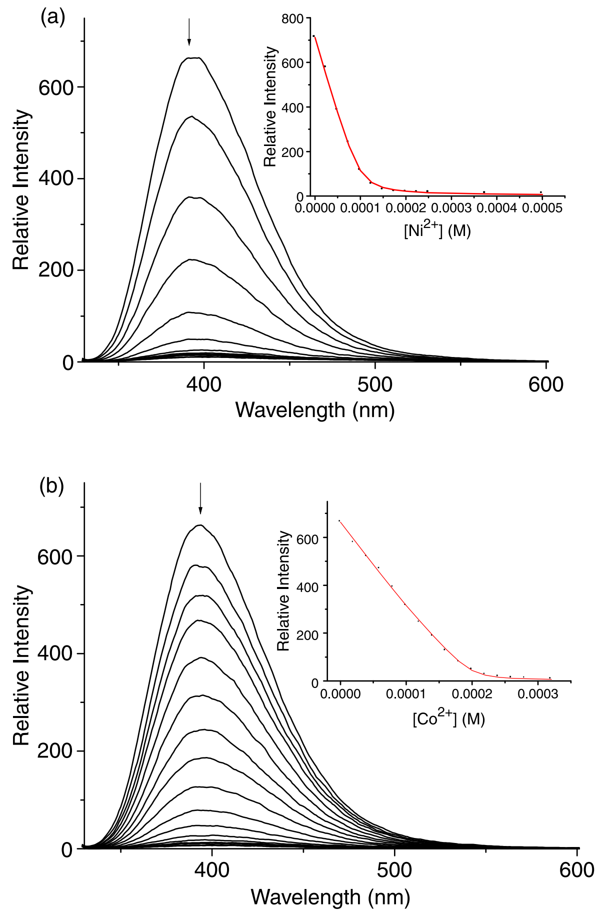


FIGURE 3 The change of fluorescence spectra of **1** (0.1 mM) in CH_3CN at 25°C upon addition of $M(ClO_4)_2$, $\lambda_{ex} = 322$ nm. The insert shows the nonlinear fitting curve of change in F_{max} (394 nm) values with respect to the concentrations of M^{2+} ion. (a) M = Ni, equivalent of Ni^{2+} ion: 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 3.75 and 5; (b) M = Co, equivalent of Co^{2+} ion: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8 and 3.2.

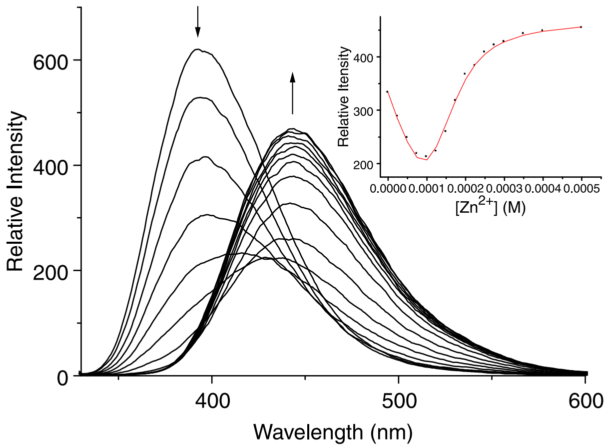
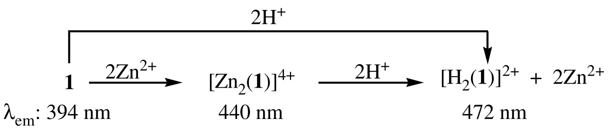


FIGURE 4 The change of fluorescence spectra of **1** (0.1 mM) in CH_3CN at 25°C upon addition of $Zn(ClO_4)_2$, $\lambda_{ex} = 322$ nm, equivalent of Zn^{2+} ion: 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75, 3, 3.5, 4 and 5. The insert shows the nonlinear fitting curve of change in fluorescent intensity (435 nm) values with respect to the concentrations of Zn^{2+} ion.

thermodynamically allowed electron or energy transfer from the quinoline fluorophore to the metal center [30]. The graphs in the top right corner of Fig. 3(a) and 3(b) illustrate the fluorescence intensity change of receptor solution upon addition of Ni^{2+} and Co^{2+} ions at 394 nm, respectively. It can be concluded that the stoichiometries of **1**-Ni^{2+} and **1**-Co^{2+} are 1:1 and 1:2, respectively, which are in accordance with the results calculated by the Job plot method.

It should be noted that the emission spectra of **1** (0.1 mM) with various concentrations of $Zn(ClO_4)_2$ in acetonitrile is quite different from that of **1** with $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ (Fig. 4). When the ratio of $[Zn^{2+}]/[\mathbf{1}]$ is less than 1, the position of the emission maximum has no obvious change, but the fluorescence intensity ($\lambda_{em} = 394$ nm) decreases gradually upon addition of Zn^{2+} ion; when the ratio of $[Zn^{2+}]/[\mathbf{1}]$ is in the range of 1 to 1.5, the position of the emission maximum shifts from 394 nm to 440 nm; when the ratio of $[Zn^{2+}]/[\mathbf{1}]$ increases from 1.5 to 2, the position of maximum remains unchanged, but the fluorescence intensity ($\lambda_{em} = 440$ nm) increases quickly; when the ratio of $[Zn^{2+}]/[\mathbf{1}]$ is larger than 2, the fluorescence intensity ($\lambda_{em} = 440$ nm) increases slightly, and the position of maximum has no evident change. From these, we can know that the formation of $[Zn(\mathbf{1})]^{2+}$ quenches the fluorescence of **1**, and that the formation of $[Zn_2(\mathbf{1})]^{4+}$ results in 46 nm red shift and enhancement of the fluorescence.

Figure 5 shows the fluorescence changes upon addition of toluene-4-sulfonic acid to **1** (a), and the 2:1 complex (b) formed between Zn^{2+} and **1**. As can be seen from the figure, when excesses equivalent toluene-4-sulfonic acid was added, the relative emission intensity of the both cases decreased along with different red shifts of the emission spectra, and they arrived the same final state, suggesting that the addition of acid result in the protonation of **1** and the dissociation of $[Zn_2(\mathbf{1})]^{4+}$.



^{1}H NMR Study

^{1}H NMR spectroscopy has been widely used to investigate receptor–substrate interactions, and it can provide details of the interactions between the host and the guest [31,32]. In the ^{1}H NMR spectra of **1**, the resonance signals of the *tert*-butyl protons appear as two singlets at 0.75 and 1.32 ppm in a ratio of 1:1, and the signals of ArH appear at 6.88 and 7.57 ppm in a ratio of 1:1, too. These indicate that **1** possesses high symmetry and exists in cone or 1,3-alteration conformation. In order to get the exact conformation of **1**, we studied its two-dimensional

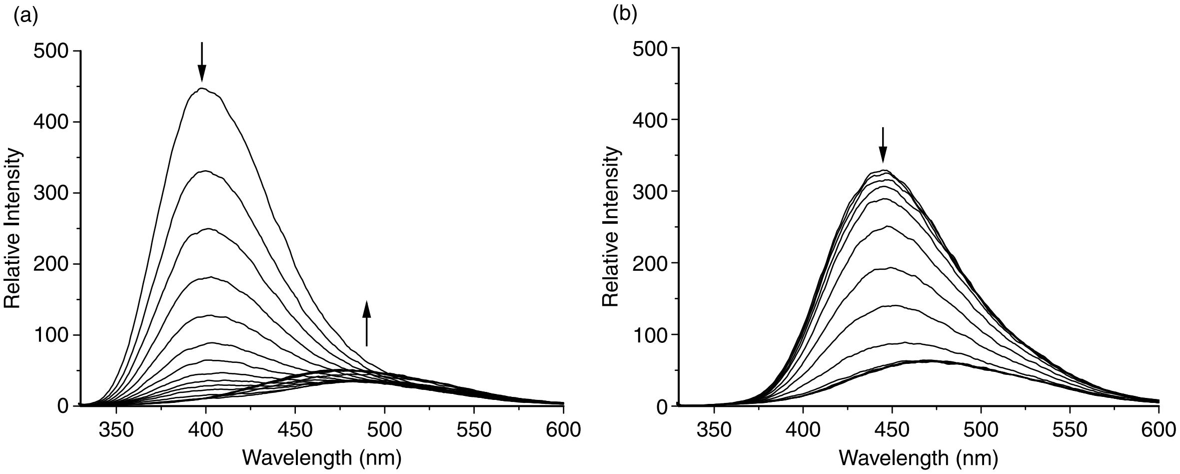


FIGURE 5 (a) The change of fluorescence spectra of **1** (0.1 mM) in CH_3CN at 25°C upon addition of toluene-4-sulfonic acid, $\lambda_{ex} = 322$ nm, equivalent of H^+ ion: 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6; (b) The change of fluorescence spectra of $[Zn_2(\mathbf{1})]^{4+}$ (0.1 mM) in CH_3CN at 25°C upon addition of toluene-4-sulfonic acid, $\lambda_{ex} = 322$ nm, equivalent of H^+ ion: 0, 0.25, 0.5, 0.75, 1.0, 2.0, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6.

$^1H-^1H$ NOESY spectra. As shown in Fig. 6, the NOESY spectrum of **1** displays clear NOE cross-peak between the protons of the two different *tert*-butyl (peak A), as well as that between the protons of the two different ArH (peak B). In addition, the variable temperature ^1H NMR experiments of **1** show that the ^1H NMR spectra has no changes from 15°C to −10°C, which means the conformation of **1** is fixed between the temperatures. These results confirm that **1** is in conic conformation at room temperature.

The high symmetry of receptor **1** will benefit the formation of chelate complex between the two quinoline moieties and metal ions. To examine the nature of interaction between **1** and Zn^{2+} ion, a standard ^1H NMR titration experiment was carried out in $CDCl_3-CD_3OD$ (4:1, V/V) using a constant

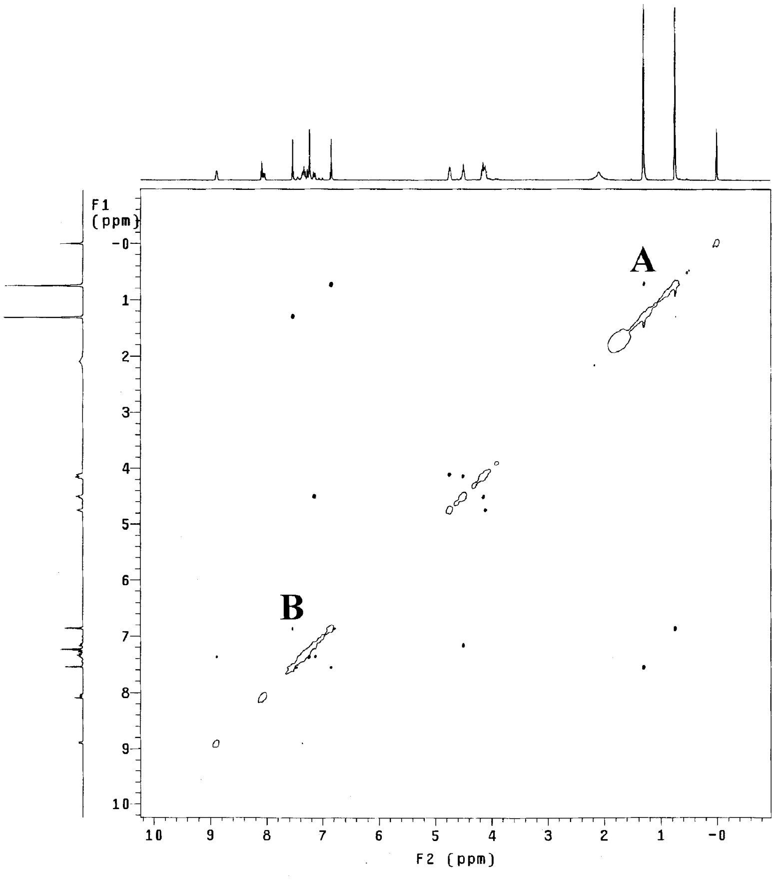


FIGURE 6 $^1H-^1H$ NOESY spectrum of 1 in $CDCl_3$ at room temperature.

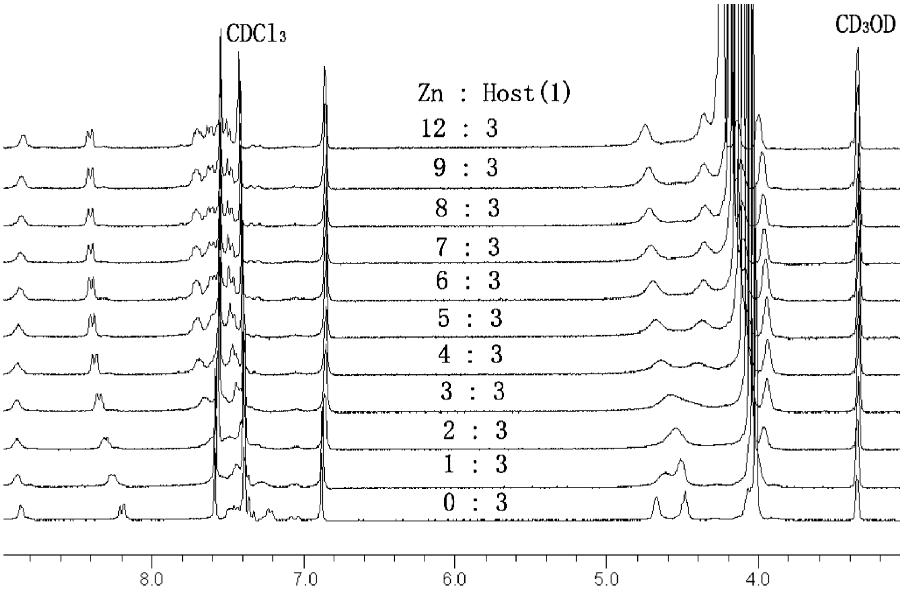


FIGURE 7 ^{1}H NMR spectra changes of **1** upon the addition of $Zn(ClO_4)_2$ (300 MHz, $CDCl_3$:CD_3OD = 4:1, [**1**] = 3.0 mM).

host concentration (3.0 mM) and an increasing concentration of Zn^{2+} ion at room temperature (Fig. 7). Upon the addition of Zn^{2+} ion, the resonance signals of ArH and the *tert*-butyl protons had no obvious changes, but the positions of the protons of quinoline and diethylene glycol in the ^{1}H NMR spectra exhibited dramatic changes up to the molar ratio of Zn^{2+} to **1** reaching 2:1, so it is the N atom of quinoline and the O atoms of diethylene glycol but not the sulfur atom bridges that participate in the Zn^{2+} ion binding. The peaks of 3,4,5,6,7-CH of quinoline were downfield shifted, which resulted from the reduction of electron-cloud density of quinoline by the coordination of metal ions.

In the literature [24], Jiang *et al.* found that the stoichiometries of the ether or ester of mono oxine with Zn^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+} ions were 1:1. The differences in stoichiometry of **1** with the three metal ions may be relative to the structures of the complexes formed. We speculate, the structure of 1:1 complex is that two quinoline moieties of **1** chelate a metal ion, and the structure of 1:2 complex is that each quinoline moiety binds a metal ion (Fig. 8).

BINDING CONSTANTS

In a supramolecular system, when the ligand absorbs light or emits fluorescence but the cations do not, in a titration experiment, the concentration of the ligand is kept constant and the metal ions are gradually added. The absorption spectrum or fluorescence spectrum is recorded as a function of cation concentration. Changes in these spectra upon complexation allow us to determine the stability constant of the complexes.

For a 1:1 system, we can calculate the complexation constant (K_s) by using the Eq. (1) [33,34]. For a 2:1 system, the successive complexation constants

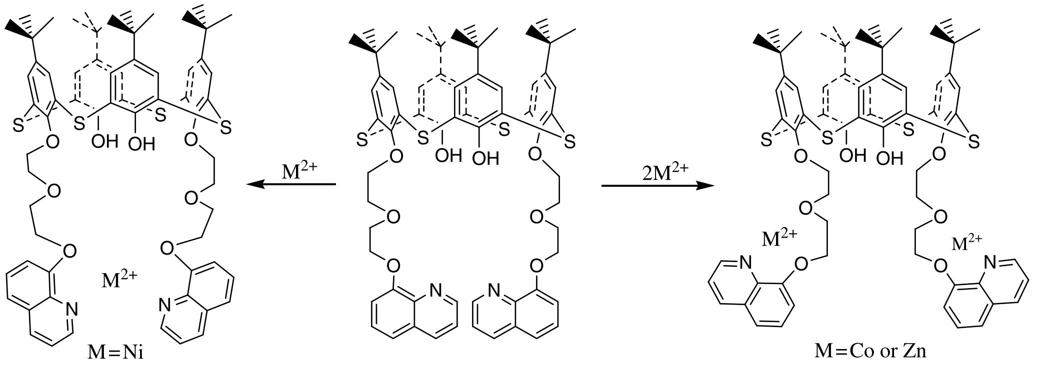


FIGURE 8 Proposed structures of the complexes of **1** with Ni^{2+}, Co^{2+} and Zn^{2+}.

TABLE I log *K* values for the complex formation of Ni^{2+},Co^{2+} and Zn^{2+} with host **1** in CH_3CN at 25°C

Reaction	Log *K*
$Ni^{2+} + \mathbf{1} \rightarrow [Ni(\mathbf{1})]^{2+}$	5.5
$Co^{2+} + \mathbf{1} \rightarrow [Co(\mathbf{1})]^{2+}$	6.8
$Co^{2+} + [Co(\mathbf{1})]^{2+} \rightarrow [Co_2(\mathbf{1})]^{4+}$	5.7
$Zn^{2+} + \mathbf{1} \rightarrow [Zn(\mathbf{1})]^{2+}$	6.1
$Zn^{2+} + [Zn(\mathbf{1})]^{2+} \rightarrow [Zn_2(\mathbf{1})]^{4+}$	4.7

(K_{11} and K_{21}) can be calculated according to the Eqs. (2) and (3) [29].

$$Y = Y_0 + \frac{Y_{\lim} - Y_0}{2}\left\{1 + \frac{c_M}{c_L} + \frac{1}{K_s c_L} - \left[\left(1 + \frac{c_M}{c_L} + \frac{1}{K_s c_L}\right)^2 - 4\frac{c_M}{c_L}\right]^{1/2}\right\} \quad (1)$$

$$K_{11}K_{21}[M]^3 + (K_{11} + 2K_{11}K_{21}c_L - K_{11}K_{21}c_M)[M]^2 + (K_{11}c_L - K_{11}c_M + 1)[M] - c_M = 0 \quad (2)$$

$$Y = \frac{Y_0 + c_L b K_{11}[M] + Y_{\lim}K_{11}K_{21}[M]^2}{1 + K_{11}[M] + K_{11}K_{21}[M]^2} \quad (3)$$

Where Y represents the absorbance or the fluorescence intensity; Y_0 is the absorbance or the fluorescence intensity of the free ligand; $Y_{\lim}$ is the limiting value of Y; c_L and c_M are the corresponding total concentration of ligand and cation; [M] is the concentration of free metal ion; b is the molar absorption coefficient or the fluorescence quantum yield. According to the nonlinear least squares analysis of Y versus c_M, the complexation constants (Ks, K_{11} and K_{21}) can all be obtained.

The complexation constants of **1** with Ni^{2+}, Co^{2+} and Zn^{2+} ions were calculated according to the nonlinear fitting method and listed in Table I. From the table, we can see that **1** formed very stable complexes with the three metal ions, the complexation constants are about 100 times higher than those of the thiacalix[4]arenes modified with dansyl moities [20,21].

CONCLUSION

In conclusion, we successfully synthesized a novel *p-tert*-butylthiacalix[4]arene receptor **1** conveniently. Its structure and conformation were verified by ESI-MS, ^{1}H NMR and ^{1}H–^{1}H NEOSY, its coordination properties toward Ni^{2+}, Co^{2+} and Zn^{2+} ions were studied by UV–vis, fluorescent spectra and ^{1}H NMR titration. The results showed that **1** formed very stable complexes with the three metal ions, and the stoichiometries of **1**-Ni^{2+}, **1**-Co^{2+} and **1**-Zn^{2+} were 1:1, 1:2 and 1:2, respectively. We believe that receptor **1** may have the potential use as the transition metals fluorescent probe and organic light-emitting diodes. Further studies along this line are being planned.

EXPERIMENTAL

General

The melting points (uncorrected) were obtained from X6 microscopic melting point detector. The ^{1}H NMR and ^{1}H–^{1}H NOESY were recorded at 300 MHz on Varian Mercury-VX300 spectrometer. The chemical shifts were recorded in parts per million (ppm) with TMS as the internal reference. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrometer. Elemental analyses were determined by Perkin–Elmer 204B elemental autoanalyzer. ESI Mass spectra were determined using Finnigan LCQ Advantage mass spectrometer.

2-(2-(Quinolin-8-yloxy)ethoxy)ethyl 4-methylbenzenesulfonate (2)

To a cooled (0°C) yellow solution of 2-(2-(quinolin-8-yloxy)ethoxy) ethanol **3** (11.6 g, 0.05 mol) and pyridine (5.5 g, 0.07 mol) in methylene dichloride (30 mL), *p*-tosyl chloride (10.4 g, 0.06 mol, dissolved in 50 mL CH_2Cl_2) was added dropwise over a period of 2 hours. The resulting red solution was stirred overnight at room temperature and poured into 100 mL water. The aqueous phase was washed with additional methlene dichloride three times (50 mL each), and the combined organic phases were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by chromatography, eluting with chloroform. In this way, **2** (12.3 g) was obtained in 63.7% yield as a yellow oil, which was solidified after standing. m.p. 40–42°C. ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ: 2.39 (s, 3H, CH_3), 3.81 (t, $J = 4.5$ Hz, 2H, qui-$OCH_2CH_2OCH_2$), 3.99 (t, $J = 4.8$ Hz, 2H, qui-OCH_2CH_2), 4.20 (t, $J = 4.5$ Hz, 2H, qui-$OCH_2CH_2OCH_2CH_2$), 4.35 (t, $J = 5.4$ Hz, 2H, qui-OCH_2), 7.09–7.13 (m, 1H, 7-CH), 7.27 (d, $J = 8.1$ Hz, 2H, ArH), 7.40–7.51 (m, 3H, 3, 5, 6-CH), 7.77 (d, $J = 8.1$ Hz, 2H, ArH), 8.15 (d, $J = 8.7$ Hz, 1H, 4-CH), 8.94 (d, $J = 3$ Hz, 1H, 2-CH).

5,11,17,23-Tetra-*tert*-butyl-25,27-bi-hydroxy-26,28-bi-[2-(2-(2-(quinolin-8-yloxy)ethoxy)ethoxy)]-2,8,14,20-tetra-thiacalix[4]arene (1)

A mixture of *p-tert*-butylthiacalix[4]arene 1.44 g (2.0 mmol), **2** 1.95 g (5.0 mmol) and anhydrous K_2CO_3 1.38 g (10.0 mmol) in toluene was stirred under reflux for 24 hours. The solvent was removed by rotary evaporation under reduced pressure. The resulting red residue was treated with 50 mL pure water and then extracted with chloroform (50 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel to give 1.22 g of pale yellow solid (**1**) in 52.7% yield. m.p. 68–70°C ^1H NMR (300 MHz, TMS, $CDCl_3$)δ: 0.75 (s, 18H, $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$), 4.12–4.18 (m, 8H, qui-$\mathrm{OCH_2C}\mathit{H}_2\mathrm{OC}\mathit{H}_2\mathrm{CH_2}$), 4.51 (t, $J = 5.1$ Hz, 4H, qui-$\mathrm{OCH_2CH_2OCH_2C}\mathit{H}_2$), 4.76 (b, 4H, qui-$OCH_2$), 6.88 (s, 4H, ArH), 7.17 (d, $J = 7.5$ Hz, 2H, 7-CH), 7.30–7.47 (m, 6H, 3,5,6-CH), 7.57 (s, 4H, ArH), 8.06 (dd, $J = 1.5$ Hz, $J = 8.4$ Hz, 2H, 4-CH), 8.11 (s, 2H, OH), 8.91 (dd, $J = 1.5$ Hz, $J = 4.5$ Hz, 2H, 2-CH). ESI-MS (+): 1152.0 $[M + H]^+$. Anal. calcd. for $C_{66}H_{74}N_2O_8S_4$(1150.4): C, 68.84; H, 6.48; N, 2.43; Found: C, 68.45; H, 6.52; N, 2.48.

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