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Synthesis, complexation, and fluorescence behavior of 3,4-dimethylthieno[2,3-b]thiophene carrying two monoaza-15-crown-5 ether groups

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ABSTRACT

A novel fluoroionophore 1 based on 3,4-dimethylthieno[2,3-b]thiophene bearing two monoaza-15-crown-5 ethers at 3- and 4-positions was prepared. UV–vis and fluorescence responses of compound 1 upon the addition of alkali and alkaline earth metal cations were evaluated in acetonitrile solution. Receptor 1 showed unique response for Ba^{2+} due to the formation of an intramolecular sandwich complex.

1. Introduction

Fluorescent chemosensors-molecules that change their fluorescence in response to substrate representation an extremely sensitive optical method for the real-time monitoring of molecular interactions [1]. Such chemosensors are finding increased use in fields as diverse as biology, medical analysis, and environmental monitoring [1a]. The majority of fluorescent chemosensors operate by one of three mechanisms: (1) suppression of photoinduced electron transfer or enhancement of heavy-atom quenching; (2) variation of the distance between two fluorophores, modulating the efficiency of interchromophore energy transfer; and (3) alteration of the microenvironment of a solvatochromic fluorophore (e.g., by displacement from a cyclodextrin cavity) [2].

The design of fluorescent chemosensors for the detection of specific analytes has attracted a growing interest during the last two decades [1]. Considerable attention has been devoted to the development of selective sensors for alkali and alkali-earth cations since in situ detection of such analyte is needed in different research areas (e.g., environmental and life sciences). For example, selective fluorescent sensors for cesium were studied aimed at the detection of $^{137}Cs^{+}$ in the nuclear reactor wastes [3,4]. The detection of intracellular Ca^{2+} is performed worldwide by employing the fluorescent chemosensors developed by Tsien [5].

On the other hand, because of the increased industrial use of the barium compounds as well as their enhanced discharge, toxic properties and other adverse effects [6], the problems should encourage the development of new detection systems for this analyte. Therefore, the design of novel and specific chemosensors for barium seems to be particularly desirable.

Owing to the well-known ability of crown ethers to host *s*-block metals [7], many fluorescent chemosensors designed in recent years for alkali and alkali-earth ions contain at least one crown ether moiety (or a related derivative) which behaves as a "recognition subunit" connected to one or more fluorophores [1b,8]. In these systems, the output signal following the crown/cation interaction involves a change in the emission properties of the fluorophore(s) and is often related to a photoinduced electron transfer (PET) process [9]. Other examples involving different mechanisms e.g., photoinduced energy transfer [10], excimer or exciplex formation [11], conformational change [12], and proton transfer [13], have also been reported.

Bis(crown ether) derivatives, in which two crown ether moieties are linked by a flexible aliphatic chain, in some cases form more stable complexes with metal cations and show a higher cation-binding selectivity compared to the monocyclic analogues [14]. This is due to the ability of bis(crown ethers) to form intramolecular

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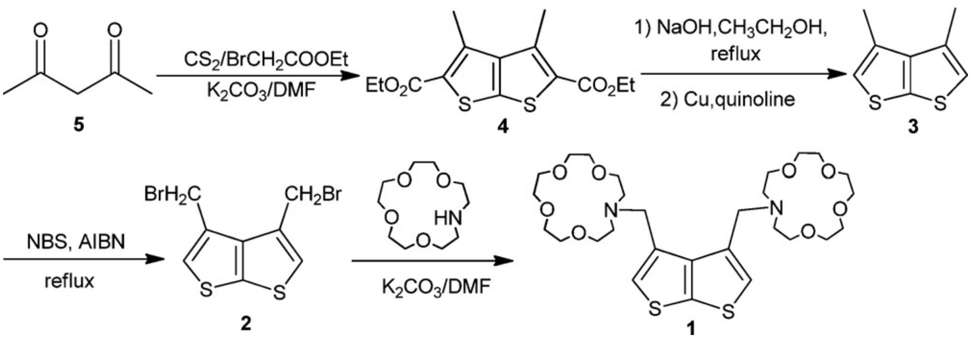


Scheme 1. Synthetic route to the fluorescence chemosensor **1**.

sandwich-type complexes with particular cations whose size is larger than the cavity size of the crown ether ring.

In this paper, we report the behavior of a novel 3,4-dimethylthieno[2,3-b] thiophene bearing two monoaza15-crown-5 moieties at 3- and 4-positions (**1**) (Scheme 1), which displays a strong fluorescence enhancement upon interaction with Ba^{2+}. This selective enhancement is ascribed to the formation of the intramolecular sandwich complex.

2. Experimental

2.1. Materials and general methods

All chemicals were purchased from Aladdin Reagent Company (Shanghai, China). All the solvents except the chromatographically pure acetonitrile were of analytic grade. All other chemicals were purchased from aladdin and used as received. ^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCE 400 MHz spectrometer with chemical shifts reported in ppm (in $CDCl_3$; TMS as internal standard). GC–MS analyses were obtained from an Agilent7890A GC/5975C MSD(EI) instrument, and MALDI-TOF MS analyses were performed on an Bruker autoflex III smartbeam instrument using 2,5-dihydroxy-benzoic acid (DHB) as the matrix. The microanalyses were obtained with an elementar vario EL III analyzer. UV–vis spectra was recorded on a Lambda 25 spectrophotometer. Fluorescence spectra obtained on a photoluminescent spectra was taken on a Perkin-Elmer LS55 luminescence spectrometer using a xenon lamp as the light source, with 10 nm excitation slit widths, 20 nm emission slit widths and excitation wavelength at 300 nm. All solutions of fluorescent chemosensor **1** and were prepared in chromatographically pure acetonitrile without special efforts to exclude water or air. Both of absorption and fluorescence titrations were carried out with a concomitant addition of small volumes of metal ion aqueous solutions to acetonitrile solution of compound **1** (metal salts: $NaClO_4$, KCl, $CaCl_2$, $CdCl_2$, $MgSO_4$, $MnSO_4$, $Ni(ClO_4)_2{\cdot}6H_2O$, $SrCl_2{\cdot}6H_2O$, $BaCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$, $HgCl_2$, $LiClO_4$).

2.2. Synthesis routes and the characterization data

Fluorescent chemosensor **1** was synthesized according to the similar methods reported previously [15]. The structures of these compounds are shown in Scheme 1 together with their abbreviations.

*2.2.1. Synthesis of diethyl 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylate (**4**) and 3,4-dimethylthieno[2,3-b]thiophene (**3**)*

Diethyl 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylate (**4**) [15] and 3,4-dimethyl thieno[2,3-b]thiophene (**3**) [15] were prepared following the already published procedures.

*2.2.2. Synthesis of 3,4-bis(bromomethyl)thieno[2,3-b]thiophene (**2**) [16]*

To a solution of 3,4-dimethylthieno[2,3-b]thiophene (**3**) (25.2 g, 0.15 mol) and NBS (52 g, 0.3 mol) in CCl_4 (100 mL), AIBN (0.60 g) was added. The mixture was refluxed for 5 h. After the reaction was complete, the crude mixture was filtered at a room temperature to remove succinimide, and the filtrate was evaporated. Compound **2** were purified by recrystallization from petroleum ether.

Yield: 86%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43(s, 2H), 4.96(s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ 142.1, 140.1, 130.6, 129.2, 27.1 ppm. GC–MS: m/z 325[M+]. Anal. Calcd for $C_8H_6Br_2S_2$: C, 29.47; H, 1.85; S, 19.67. Found C, 29.55; H, 1.88; S, 19.69.

*2.2.3. Synthesis of 3,4-bis((1,4,7,10-tetraoxa-13-azacyclo-pentadecan-13-yl)methyl)thieno[2,3-b]thiophene (**1**)*

To a solution of 3,4-bis(bromomethyl)thieno[2,3-b]thiophene (**2**) (0.1 g, 0.3 mmol) and 1,4,7,10-tetraoxa-13-azacyclopentadecane (0.134 g, 0.6 mmol) in DMF (6 mL), dried potassium carbonate (0.086 g) and tetrabutylammonium bromide (0.01 g) was added. The reaction mixture was stirred at 30 °C for 24 h. After the reaction was complete, the crude mixture was filtered at a room temperature. The mixture solution was extracted with ethyl acetate (20 mL), and the combined organic layer was washed with water (10 mL). The residue was purified by flash column chromatography (neutrality alumina, ethyl acetate) to give yellow oily liquid.

Yield: 76%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24(s, 2H), 3.93(s, 4H), 3.66–3.59(m, 32H), 2.86–2.83(t, 8H) ppm.^{13}C NMR ($CDCl_3$, 400 MHz): δ 144.7, 138.5, 133.9, 125.4, 71.1, 70.6, 70.2, 70.0, 56.0, 54.8 ppm. MALDI-TOF-MS: m/z 625 $[M+Na]^+$. Anal. Calcd for $C_{28}H_{46}N_2O_8S_2$: C, 55.79; H, 7.69; N, 4.65; S, 10.64; Found C, 55.84; H, 7.82; N, 4.68; S, 10.72.

3. Results and discussion

The working principle of sensor **1** is schematically depicted in the graphical Fig. 1. In this mechanism, uncomplexed **1** is supposed to show quenched fluorescence (turn off) as a result of photoinduced electron transfer (PET) from the two aza-15-crown-5 donors to the thieno[2,3-b]thiophene moieties. After complexation with metal cations, the electrondonating ability of the two monoaza-15-crown-5 moieties is attenuated because of cation-π attraction [17]. This effect will in turn suppress the PET process to result in fluorescence enhancement (turn on). Fig. 1 shows that sensor **1** consists of one conjugated group, but it exhibits almost no fluorescence emission in acetonitrile (concentration: 2.0×10^{-6} M, excited at 300 nm, ‘off-state’), which is resulting from PET process.

It was known that crown ethers could bind certain metal ions, which inspired us to test the presence of special metal ions by inspecting the changes of fluorescence intensity of complex **1** in the presence of metal ions. The alkali metal cations (Li^+, Na^+, K^+), alkaline-earth metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and heavy and

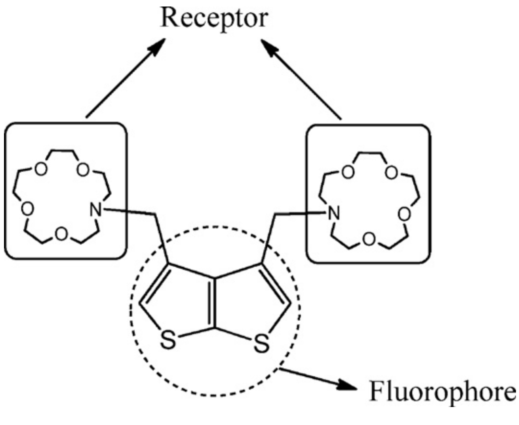


Fig. 1. The compound **1**.

transition metal (HTM) cations (Ni^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) were used to evaluate the binding ability. Consequently, when different metal ions (50 equiv.) were added in the acetonitrile solution of the sensor **1**, the different degree fluorescent enhancements of sensor **1** have happened in some alkaline metal ions, alkaline-earth metal ions and heavy and transition metal (HTM) cations (Fig. 2). Surprisingly, **1** displayed a large chelation-enhancement fluorescence (CHEF) [18] with only Ba^{2+} among these metal ions. The experimental data ($I_{complex}/I_{free\mathbf{1}}$) demonstrated that **1** is a highly sensitive and selective sensor for Ba^{2+} in acetonitrile solution. However, under the same conditions, no obvious changes were observed for other widely tested metal ions. Because of its strong complex properties among its relatives [19–21], it was important to note that molecular recognition can result from a selective binding or selective response. Metal ions of the same family show quite similar binding properties, and the alkaline-earth metal ions may bind the O and N [22]. But the large distinctions are still extant among the alkaline-metal ions, such as the relative fluorescence enhancement intensity of Ba^{2+} reaches to (22.67), which is three times than the Sr^{2+} (7.43) and much more than the Ca^{2+} (1.59). Among the divalent alkaline-metal ions, with the increasing of the ion diameter, the fluorescence yields of their complexes increased. These results suggested that Ba^{2+} ions might bind much stronger with host **1** than other tested metal ions. Thus, complex **1** could acts as a Ba^{2+} selective supramolecular fluorescence probe.

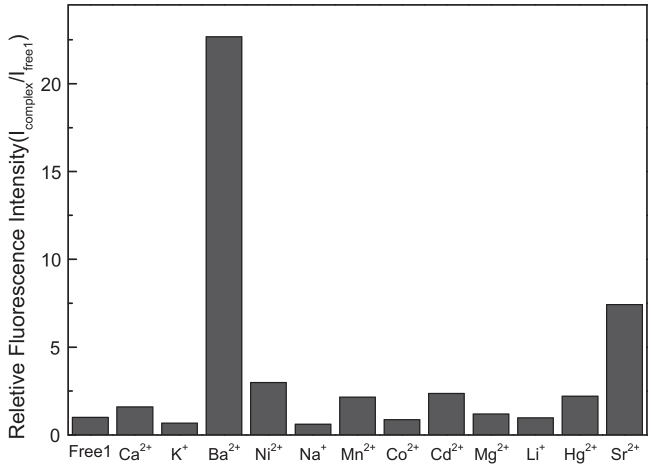


Fig. 2. The relative fluorescence enhancement intensity of compound **1** (2.0×10^{-6} M) in acetonitrile solution at room temperature upon addition of various metal cations. The excitation wavelength was at 300 nm, and the concentration of metal cations was 50 equiv. of compound **1**.

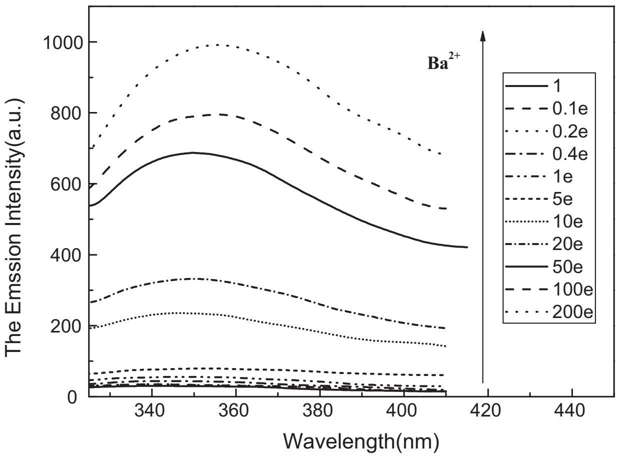


Fig. 3. Fluorescence spectra of compound **1** (2.0×10^{-6} M) upon the titration of Ba^{2+} (0–200 equiv.) in acetonitrile solution. Fluorescence intensity was regarded as a function of Ba^{2+} concentration.

To explore the recognition property of complex **1** to Ba^{2+} ions, we have also carried out fluorescence titration experiments. As shown in Fig. 3, upon the addition of Ba^{2+} into the solution of complex **1** in acetonitrile solution, the emission band in the region of 320–410 nm gradually increased. When Ba^{2+} was added, the nitrogen atom was involved in complexing with Ba^{2+} and lost its ability to donate an electron to the excited state of the thieno[2,3-b]thiophene ring. Thus, the addition of Ba^{2+} caused the recovery of the fluorescence which meant that the complexation for guest cations inhibit the PET occurring from the nitrogen atom in the two aza-15-crown-5 ethers to thieno[2,3-b]thiophene.

On the basis of the fluorescence titrations of **1**, we have determined the association constant K_a for Ba^{2+} to be 1.80×10^5, following the Benesi–Hildebrand-type analysis [23] (Fig. 4: $Y = A + BX$, $K_a = A/B$, $X = 1/[M^{n+}]$, $Y = I_0/(I_F - I_0)$; K_a: the association constant, I_0: the fluorescent intensity of sensor **1**, I_F: the fluorescent intensity of **1**-complex; $A = 0.27888$, $B = 1.55263 \times 10^{-6}$, $R^2 = 0.9312$, $K_a = A/B = 1.7962 \times 10^5$). The stoichiometry of the **1–Ba^{2+}** complex was also estimated to be 1:1 using Job's method [24] of continuous variation for the fluorescence data (Fig. 5). In the case of the complexation with Ba^{2+}, the complex approached a maximum when the mole fraction of guest ca. 0.5, suggesting 1:1 host–guest complexation.

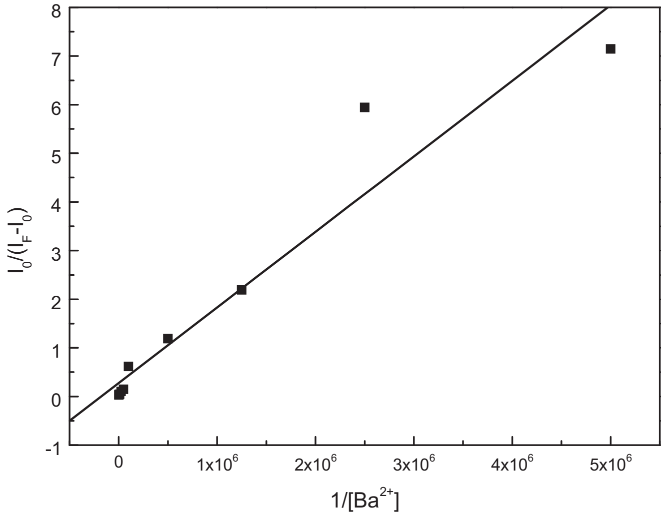


Fig. 4. The Benesi–Hildebrand analysis of compound **1** in different Ba^{2+} concentrations.

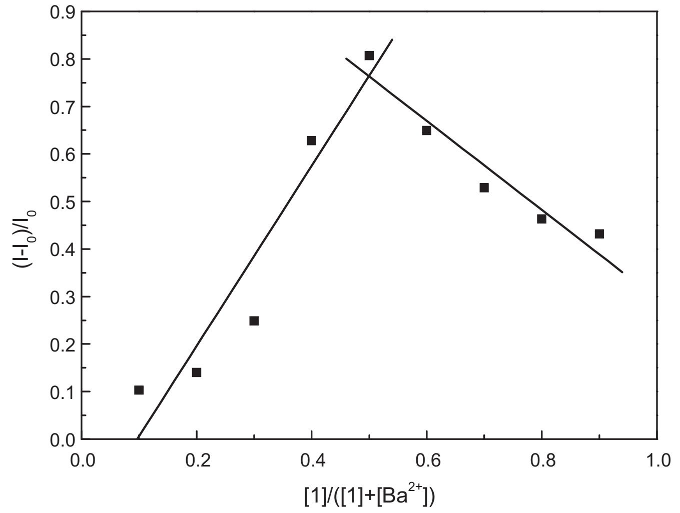


Fig. 5. Job plot for determining the stoichiometry of compound **1** and Ba^{2+}. The total concentration of compound **1** and Ba^{2+} was 2.0×10^{-6} M. Molar fraction was given by $[1]/([1]+[Ba^{2+}])$.

Owing to the known ability of monoaza15-crown-5 ether to interact with Ba^{2+} according to a sandwich-like mode [25], the results obtained from both spectrophotometric and spectrofluorimetric titration experiments can be explained by the formation of an adduct according to a formal 1:1 stoichiometry, in which the Ba^{2+} ions coordinate to two aza-15-crown-5 subunits belonging to different molecules of **1**. Spectrofluorimetric titration experiments performed on acetonitrile solution of the bis-crown compound **1** (10^{-6} M) with different cations showed that sensor **1** has selectivity for alkaline-earth metal ions with a relatively large diameter such as Ba^{2+}. The discriminative sensing behavior is likely originated from a complementarity of metal ions and the rigid binding pocket of **1** in terms of size matching and noncovalent (e.g., cation–dipole and cation–π) interactions.

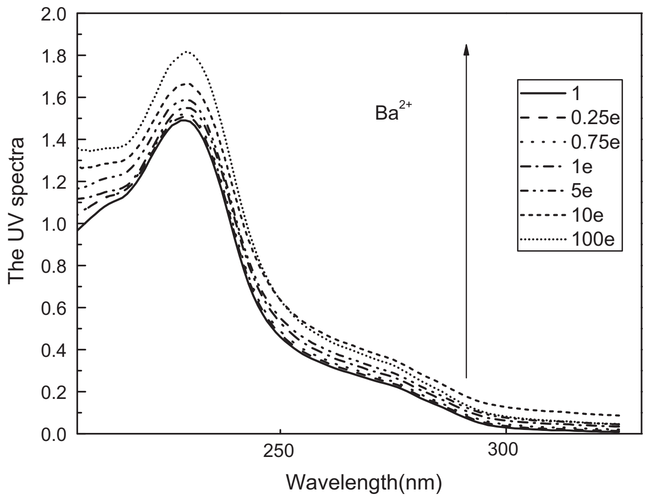
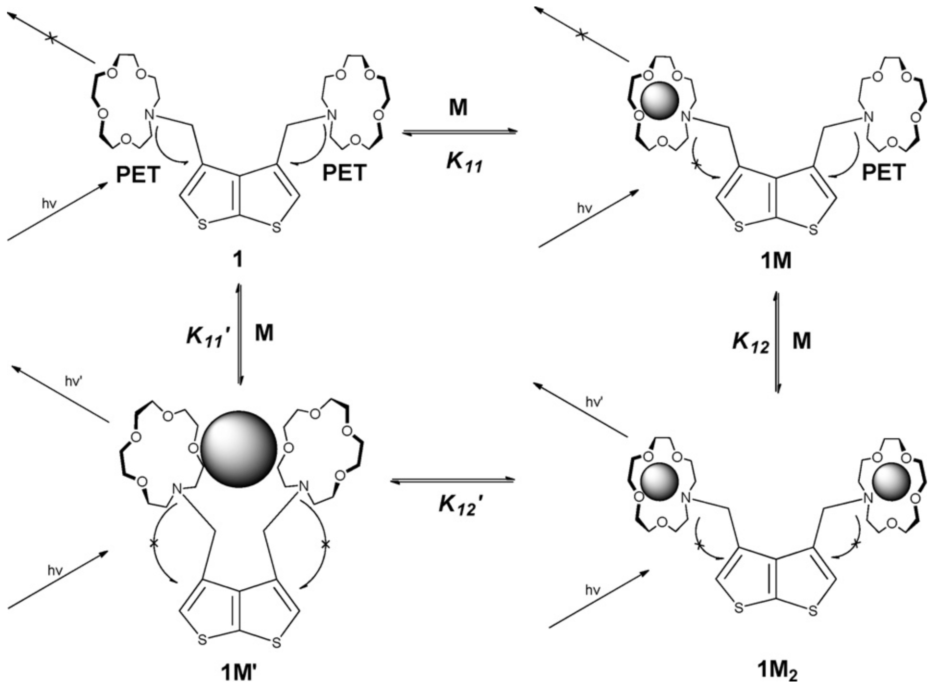


Fig. 6. The UV–vis spectra of compound **1** (2.0×10^{-5} M) upon the titration of Ba^{2+} (0–100 equiv.) in acetonitrile. The concentration of compound **1** was regard as 1 equiv.

UV–vis spectral changes of **1** upon the addition of Ba^{2+} ions in acetonitrile solution were showed that they have the similar UV–vis absorption spectra except the intensity slight differences (Fig. 6). In general, when a crown ether and a chromophore which has no interaction site with guest cation are connected with a methylene spacer, there are only minor spectral changes upon the complexation with a guest. Furthermore when Ba^{2+} was added, the absorbance derived from fluorophore moiety was more obviously increased as their shapes do no shifted, which was proved the PET process.

The electronic properties of the thieno[2,3-b]thiophene derivative **1** were investigated by UV–vis absorption. In the high-energy region, an intense sharp band at 229 nm is absorptions due to the thieno[2,3-b]thiophene moieties, which are ascribed to the $\pi \rightarrow \pi^*$ transitions at the central thieno[2,3-b]thiophene core by comparison to the UV–vis data of other thieno[2,3-b]thiophene derivatives [17].

Plausible equilibria are illustrated in Scheme 2. For a 1:1 complex of **1**, two possible structures are formed, that is, a complex in



Scheme 2. The possible mechanism complex of **1** with metal ion.

which one azacrown is occupied with a metal ion and the other is unoccupied (**1M**) and an intramolecular sandwich complex (**1M′**). Meanwhile, in a certian extent, the structure of $\mathbf{1M_2}$ will be formed, but it is just a small proportion of the complex. The fluorescence intensities of **1M** and **1M′** are expected to be larger than that of free **1**, because the PET process is blocked by coordination of the nitrogen atoms to the metal ions. The UV–vis and fluorescence titrations of **1** with Ba^{2+} showed the pronounced spectral changes. A Job plot analysis of the fluorescence responses indicates the formation of 1:1 complex with Ba^{2+}. The ionic diameter for Ba^{2+} (2.70 Å) [26] is larger than the effective cavity diameter for aza-15-crown-5 (1.7–2.2 Å). Thus **1** forms the intramolecular sandwich complex with Ba^{2+} ($\mathbf{1–Ba^{2+}}$ in Scheme 2) as observed in the crystal structure of $(15\text{-crown-}5)_2Ba^{2+}$ complex [27]. Formation of a sandwich complex of **1** restricts rotation of thieno[2,3-b]thiophene rings and affects the electronic property of the thieno[2,3-b]thiophene skeleton. On the 1:1 complexation with barium ion, **1M′** is predominantly formed [28], therefore, the small UV–vis spectral changes and the modest fluorescence enhancements were observed.

4. Conclusion

We have synthesized a novel receptor based on 3,4-dimethylthieno[2,3-b]thiophene moiety for cation recognition. The receptor **1** shows distinctive UV–vis and fluorescence responses for Ba^{2+} due to restriction of the conformational change through the formation of the intramolecular sandwich complex. Selectivity of receptors would be tuned by substitution of aza-15-crown-5 moieties to appropriate functional groups. Further studies on this line are in progress. We believe that a variety of fluorophores can be effectively used in different media (for example in water/organic solvent mixtures and/or aqueous micellar solutions) in the future.

Acknowledgments

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