ORIGINAL ARTICLE

New fluorescent sensor for antimony and transition metal cations based on rhodamine amide-arm homotrioxacalix[3]arene

Chong Wu · Wen-Juan Zhang · Xi Zeng · Lan Mu · Sai-Feng Xue · Zhu Tao · Takehiko Yamato

Abstract A new fluorescent sensor **1** based on the rhodamine amide-armed homotrioxacalix[3]arene was synthesized, and its sensing behavior toward metal ions was investigated by UV–vis and fluorescence spectroscopies. Upon the addition of metal cations (Sb^{3+}, Fe^{3+}, Ni^{2+}), a significant fluorescent enhancement in the range of 500–600 nm and colorimetric change was observed.

Keywords Fluorescent sensor · Homotrioxacalix[3]arene · Rhodamine · Antimony and transition metal cations

Introduction

The design and synthesis of new chemosensors for heavy and transition metal (HTM) cations is an important subject in the field of supramolecular chemistry due to their significant importance in chemical, biological, and environmental assays [1–4]. Particular interests in this regard are fluorescent sensors because they allow nondestructive and quick detection by a simple fluorescent enhancement (turn-on) or quenching (turn-off) response [5–8]. Fluorescent chemosensors, which combine two fundamental functional units: a fluorophore and an ionophore. The part of ionophore can selectively bind the substrate, and the part of fluorophore is attached to the vicinity of the binding site for signal detection and transduction. The probes not only provide a means of detection to investigate the process of molecular recognition, but also can be used as the architectures for assembling the OFF–ON fluorescent switching. The rhodamine framework is an ideal mode to act as the fluorophore of fluorescent chemosensors due to its particular properties. It is well known that many derivatives of rhodamine undergo an equilibrium between spirolactam and ring-opened amide, and the two forms always exhibit completely different fluorescent properties. Rhodamine-based OFF/ON-type fluorescent probes have received increasing interests on different metal ions in recent years [9–14].

Calixarenes are useful building blocks for the design of molecular receptors able to bind neutral or charged species. Their potential applications as sensing agents have received increasing interest [15–19]. Especially, linkage of fluorogenic compounds to appropriately functionalized calixarenes as ion receptors has afforded such efficient fluorescence chemosensors possessing abilities to selectively sense specific chemical species [20–25].

Herein, we report a new fluorescent sensor **1** for heavy and transition metal cations. We choose rhodamine as a fluorophore moiety to incorporate to the homotrioxacalix[3]arene skeleton. The homotrioxacalixarene adopts the cone conformation to form a cavity to encapsulate target ions. Strong signal output in neutral aqueous environments of recognition, high sensitivity made **1** to be a potential powerful candidate as a practical fluorescent sensor for

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heavy and transition metal cations. This is the first example of rhodamine-based homotrioxacalix[3]arene fluorescent chemosensor.

Results and discussion

As depicted in Scheme 1, sensor **1** was synthesized from **2** and **3** in the presence of excess DCC and HoBt. After the column chromatography using chloroform/ethyl acetate(1:1) as eluent, **1** was obtained as a white solid in 82% yield. The finial product **1** was well characterized by ^{1}H NMR, ^{13}C NMR, ESI–MS, and elemental analysis. The ^{1}H NMR spectrum shows three singlets for the *tert*-butyl protons at $\delta = 1.04$ ppm, Ar*OCH$_2$CO* and the aromatic protons at $\delta = 4.11$ and 6.93 ppm, and a pair of doublets for the Ar*CH$_2$OCH$_2$*Ar protons, suggesting a D_{3h}-symmetrical structure of **1**. These indicate that **1** has a cone conformation [26, 27].

A acetonitrile aqueous at pH 7 of 1 mM tris-HCl buffer solution was selected for the spectral investigation. The nitrate salts of Fe^{3+}, Ag^+, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}; chlorate salts of Sb^{3+}, Cu^{2+}, Fe^{2+}, Zn^{2+} and perchlorate salts of Mg^{2+}, Na^+, K^+ ions were used to evaluate the metal ion binding properties of compound **1** in tris-HCl buffer (pH = 7) acetonitrile aqueous. The fluorescence spectra were obtained by excitation of the rhodamine fluorophore at 555 nm. Both the excitation and emission slits were 5 nm.

Figure 1a shows the UV–vis spectral variation of **1** upon the gradual addition of Sb^{3+}. The colorless free **1** solution exhibited almost no absorption peak in the visible wavelength range (>400 nm), which indicates **1** exists as a spirocyclic form. Moreover, the spirocyclic form of **1** was also confirmed by the distinctive spirocycle carbon at $\delta = 65.64$ ppm in the ^{13}C NMR spectra [28]. Upon the addition of the Sb^{3+}, a new absorption band centered at 556 nm appears, which induces a color change from colorless to pink (Fig. 1b). The nonlinear fitting of the titration curve and the Job's plot (Fig. 1c) imply that a 3:1 stoichiometry is most possible for the binding of Sb^{3+} by **1**.

The complexation of Sb^{3+} by **1** was also investigated by means of fluorescence titration. As shown in Fig. 2a, upon the addition of Sb^{3+}, a new emission centered at 557 nm appears, and the intensity increases gradually along with a remarkable orange fluorescence (Fig. 2b). The linear fitting of the titration curve assumed a 3:1 stoichiometry of Sb^{3+}-**1** complex (Fig. 2a inset). The Job's plot (Fig. 2c) reveals a 3:1 binding stoichiometry of Sb^{3+}-**1** complex. Both UV–vis and fluorescence data lead to a significant OFF–ON signal.

The selective coordination studies of **1** were then extended to related heavy, transition, and main group metal ions by UV–vis spectroscopy. As shown in Fig. 3, addition of Sb^{3+}, Fe^{3+}, Ni^{2+} cations (50 equiv) into the solution of **1**, Sb^{3+} creates a remarkable enhanced (353-fold) absorbance. However Fe^{3+} displayed a 169-fold enhancement, and Ni^{2+} provides 51 folds of emission enhancement. In contrast, 50 equiv of others cations (Fe^{2+}, Cu^{2+}, Co^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Na^+, K^+) show almost no increase in absorbance. These imply that **1** can serve as naked-eye detection for Sb^{3+}, Fe^{3+} and Ni^{2+}.

The selective fluorimetric response of **1** to all the tested metal ions was also studied, and a similar result also arises from the fluorescence spectra (Fig. 4). The respective emission enhancements upon addition of 50 equiv of Sb^{3+}, Fe^{3+}, Ni^{2+} are 527-fold, 357-fold, 224-fold. Besides unexpected 57-fold (Cu^{2+}) and 40-fold (Fe^{2+}) emission enhancements were arised, almost no emission enhancement could be observed upon addition of 50 equiv of other
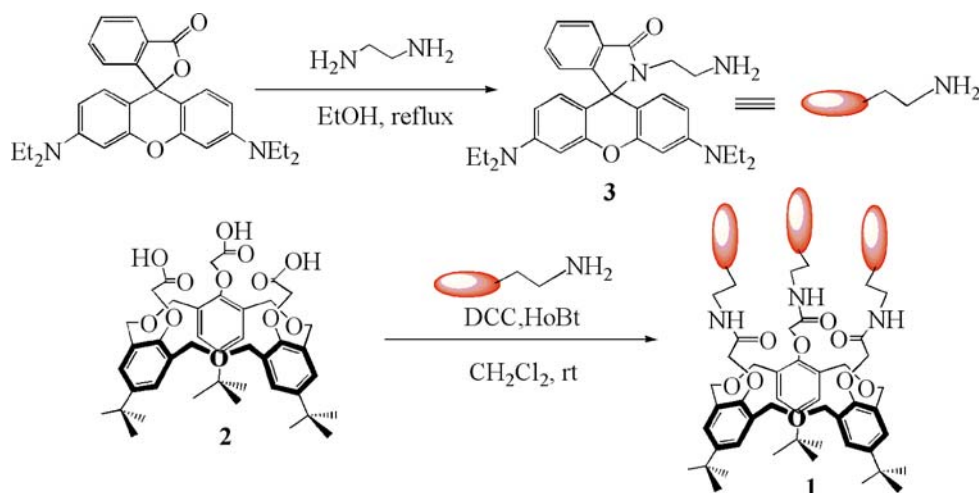
Scheme 1 Synthesis of compound **1**

Fig. 1 a UV–vis titration spectra of **1** (25 μM) upon gradual addition of Sb^{3+}. **b** Changes in color. **c** Job's plot ($[Sb^{3+}] + [\mathbf{1}] = 50$ μM)
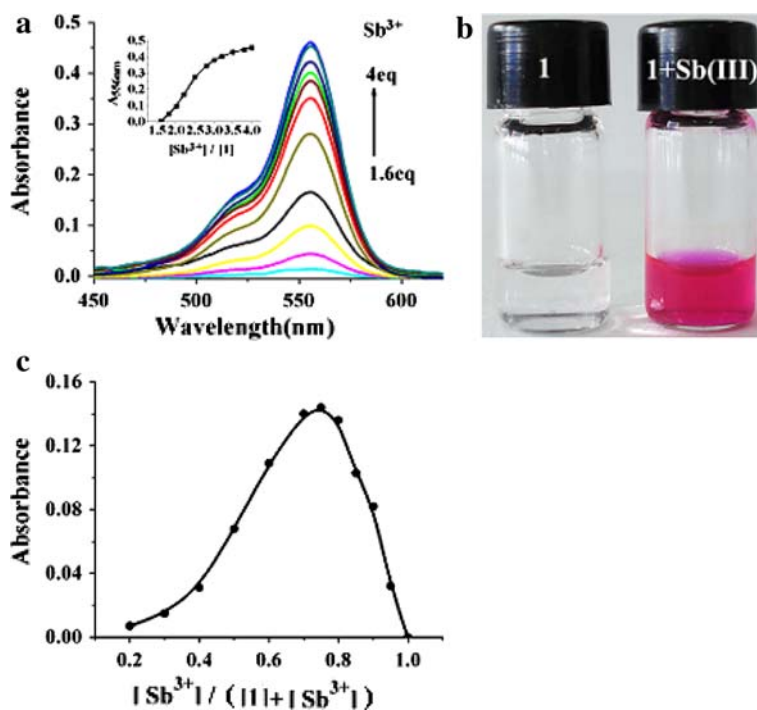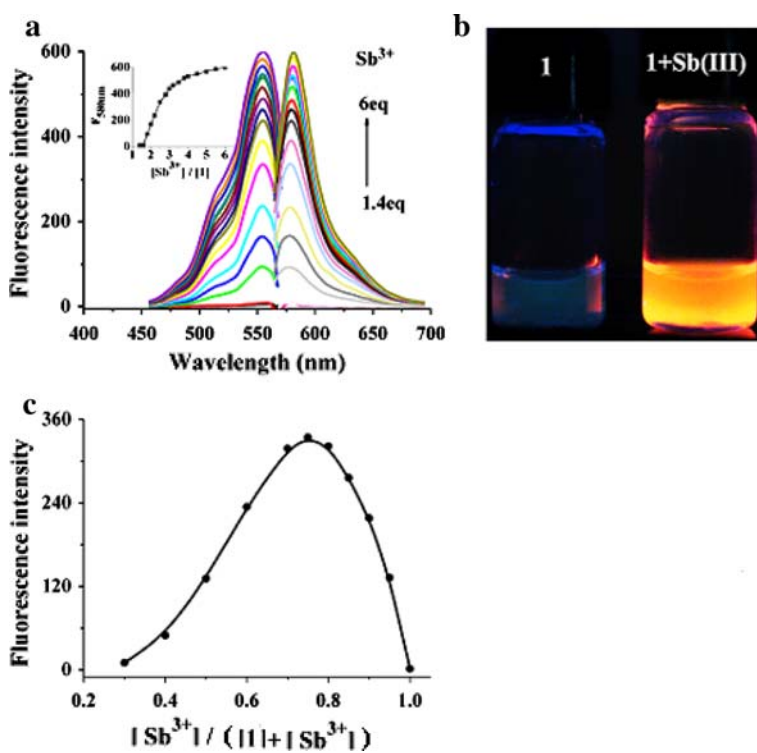

Fig. 2 a Fluorescence titration spectra of **1** (25 μM) upon gradual addition of Sb^{3+}. **b** Changes in color (excitation at 555 nm). **c** Job's plot ($[Sb^{3+}] + [\mathbf{1}] = 50$ μM)

cations. Therefore, probe **1** can acts as a potential turn-on fluorescent chemosensor for Sb^{3+}, Fe^{3+} and Ni^{2+}. The fluorescence quantum yields of **1** with 10 equiv of Sb^{3+}, Fe^{3+} and Ni^{2+} are determined to be 0.11, 0.10 and 0.09, respectively, using rhodamine B as a standard ($\Phi = 0.89$) [29].

The selectivity of **1** for Sb^{3+} were further tested when coexist with other cations (Figs. 5, 6). The increases of absorbance and fluorescence intensity resulting from the addition of the Sb^{3+} were not influenced by the subsequent addition of miscellaneous cations except for Fe^{3+}, Fe^{2+}, Cu^{2+}, these cations enhanced the Sb^{3+}-induced **1** spectrum
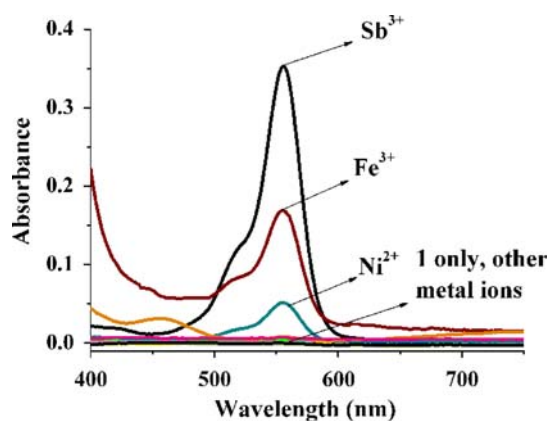
Fig. 3 Absorption spectra of **1** (5 μM) in the absence and presence of different metal ions (50 equiv)
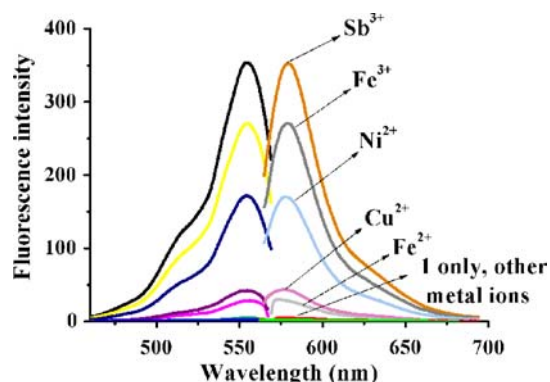

Fig. 4 Fluorescence spectra of **1** (5 μM) in the absence and presence of different metal ions (50 equiv)
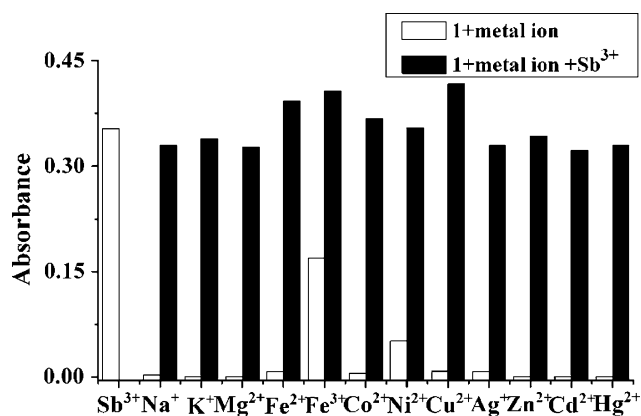

Fig. 5 Absorbance response of **1** (5 μM) to various cations and selectivity of **1** for Sb^{3+} in the presence of other cations. *White bars* represent the addition of the appropriate metal ion (50 equiv). *Black bars* represent the addition of Sb^{3+} (50 equiv) to the solution

response a little. All of these results indicated that the high selectivity of **1** for Sb^{3+} over other competing cations except in test condition.
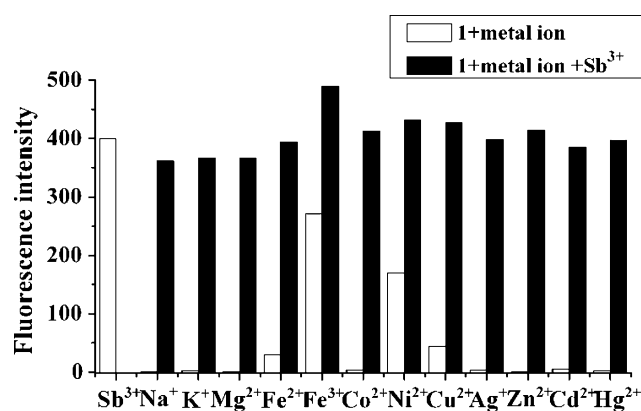

Fig. 6 Fluorescence response of **1** (5 μM) to various cations and selectivity of **1** for Sb^{3+} in the presence of other cations. *White bars* represent the addition of the appropriate metal ion (50 equiv). *Black bars* represent the addition of Sb^{3+} (50 equiv) to the solution

After addition of excess ethylenediamine to a solution containing **1** with Sb^{3+}, Fe^{3+}, Ni^{2+}, both pink color and orange fluorescence immediately disappear. This indicates a reversible coordination of **1** with metal cations and rules out the occurrence of an irreversible chemical reaction [30–32]. Considering the behaviors of fluorescence and absorption spectra, the turn-on response of **1** to Fe^{3+} and Ni^{2+} may be explained by the spirocycle open–close mechanism, as is also the case for rhodamine-based chemosensors: the free probe **1** is the spirocyclic form, which is colorless and nonfluorescent, whereas the coordination of the amide carbonyl oxygen to cations leads to the spirocycle opening, resulting in an appearance of visible absorption and fluorescence.

Conclusion

we have presented a novel fluorescent sensor **1** based on a rhodamine amide-armed homotrioxacalix[3]arene, which showed a strong enhancement of visible color and fluorescence enhancement upon addition of Sb^{3+}, Fe^{3+}, Ni^{2+} while showing almost no response to other cations. Compound **1** may therefore be applicable as a homotrioxacalix[3]arene based rhodamine turn-on type fluorescent chemosensor. The obtained findings also indicate that various rhodamine-based chemosensors for HTM cations may easily be made by incorporating various ligand groups. The works are in progress in our laboratory.

Experimental

All the melting point determinations were performed on a Boetius apparatus and are uncorrected. NMR spectra

(500 MHz) were recorded on a Varian Nova spectrometer with SiMe$_4$ as an internal reference: *J*-values are given in Hz. ESI MS spectra were obtained on a HP LC-MSD spectrometer without using the LC part. IR spectra were measured for samples as KBr pellets in a Bruker Vertex 70 FT-IR spectrophotometer. UV spectra were measured by an Amersham Biosciences Ultrospec 5300 spectrophotometer. Elemental analyses were performed by Vario EL III Elemental Analyzer.

Materials

cone-7,15,23-tri-tert-butyl-25,26,27-tris[(N,N-diethylamino) methoxy]-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3] arene and *cone-7,15,23-tri-tert-butyl-25,26,27-tris[(hydro-xycarbonyl)methoxy]- 2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene* **2** were prepared according to the reported procedures [26, 33].

Preparation of cone-hexahomotrioxacalix[3]arene triacetic acid (2)

To a mixture of *cone-7,15,23-tri-tert-butyl-25,26,27-tris [(N,N-diethylamino)methoxy]-2,3,10,11,18,19-hexahomo-3, 11,19-trioxacalix[3]arene* (1.0 g, 1.14 mmol) in dioxane (35 mL) was added 1 M KOH aqueous solution (40 mL). After the mixture was refluxed for 3 days, it was condensed under reduced pressure, then acidified by hydrochloric acid to pH 1–2. The dispersion was extracted with ethyl acetate (2 × 30 mL). The combined extracts were washed with water (2 × 20 mL), saturated brine (20 mL), dried (Na$_2$SO$_4$) and condensed under reduce pressure. The residue was washed with small amount of diethyl ether to give the crude **2** as a colorless solid. Recrystallization from methanol gave **2** (730 mg, 85%) as colorless powder; m.p. 227–229 °C. ^{1}H NMR (500 MHz, CDCl$_3$):δ = 1.17 (s, 27 H, *t*Bu), 4.18 (t, J = 12.4 Hz, 6 H, ArCH$_2$O), 4.35 (s, 6 H, ArOCH$_2$), 4.89 (d, J = 12.4 Hz, 6 H, ArCH$_2$O), 6.93 (s, 6 H, Ar–H). ^{13}C NMR (CDCl$_3$/DMSO, 1:1): δ = 31.66, 34.25, 69.58, 70.62, 126.25, 131.15, 145.72, 153.16, 171.36. ESI–MS *m/z* 749.4 (M–H$^+$)$^+$. Anal. calcd for C$_{42}$H$_{54}$O$_{12}$: C 67.18, H 7.25, O 25.57; found C 67.37, H 7.39, O 25.24.

Synthesis of 3

To a 100 mL flask, rhodamine B (1 g, 2.1 mmol) was dissolved in 50 mL ethanol. Ethylenediamine (1 mL, excess) was added dropwise to the solution and refluxed overnight (12 h) until the solution loses its red color and become clear. Then the mixture was cooled and solvent was removed under reduced pressure. Water (20 mL) was added to the resultant and extracted with CH$_2$Cl$_2$

(20 mL × 2). The combined organic phase was washed twice with water and dried over Na$_2$SO$_4$. The solvent was removed in vacuo, after that, the residue was recrystallized from ethanol and the light yellow cubic crystal **3** was obtained in a 76% yield; m.p. 216–218 °C. ^{1}H NMR (CDCl$_3$): δ = 1.16 (t, 12H, J = 6.4 Hz, *NCH$_2$CH$_3$*), 2.45 (t, 2H, J = 6.4 Hz, *NCH$_2$CH$_2$NH$_2$*), 3.20(t, 2H, J = 6.0 Hz, *NCH$_2$CH$_2$NH$_2$*), 3.33 (q, 8H, J = 6.8 Hz, *NCH$_2$CH$_3$*), 6.27 (d, 2H, J = 6.4 Hz, Ar–H), 6.37 (s, 2H, Ar–H), 6.43 (d, 2H, J = 6.4 Hz, Ar–H), 7.10 (s, 1H, Ar–H), 7.45 (t, 2H, J = 5.4 Hz, Ar–H), 7.90 (s, 1H, Ar–H). ^{13}C NMR (500 MHz, CDCl$_3$): δ = 170.20, 153.64, 153.24, 149.16, 132.93, 129.94, 128.18, 123.83, 123.05, 108.78, 104.04, 98.09, 66.63, 44.44, 41.14, 39.93, 12.74. ESI–MS *m/z* 485.3 (M + H$^+$)$^+$. Anal. calcd for C$_{30}$H$_{36}$N$_4$O$_2$: C 74.35, H 7.49, N 11.56, O 6.60; found C 73.66, H 7.57, N 11.72, O 7.05.

Synthesis of 1

HoBt (270 mg, 2.00 mmol) and **3** (2.70 g, 5.55 mmol) were added to a solution of **2** (500 mg, 0.667 mmol) in CH$_2$Cl$_2$ (50 mL). The mixture was then stirred at 0 °C while a solution of DCC (1.35 g, 13.55 mmol) in CH$_2$Cl$_2$ (50 mL) was added dropwise. The solution was stirred for 1 h at 0 °C and for an additional 24 h at room temperature. After completion, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, CHCl$_3$/ethyl(1:1) acetate) to give 881 mg of **1** as a colorless solid in 61.5% yield; m.p. 158–161 °C. ^{1}H NMR (500 MHz, CDCl$_3$):δ (ppm) 7.78 (d, 1H, J = 6.5 Hz, Ar–H), 7.35 (m, 2H, Ar–H), 7.00 (d, 1H, J = 6.5 Hz, Ar–H), 6.92(s, 2H, Ar–H), 6.45 (d, 2H, J = 8.8 Hz, Ar–H), 6.35 (d, 2H, J = 2.3 Hz, Ar–H), 6.22,6.24 (d, d, 2H, J = 2.7 Hz, Ar–H), 4.65 (d, 2H, J = 13 Hz, ArCH$_2$O), 4.38(d, 2H, J = 13 Hz, ArCH$_2$O), 4.05 (s, 2H, ArOCH$_2$), 3.24–3.28 (m, 10H, J = 8.5 Hz, *NCH$_2$CH$_3$*, *CH$_2$CH$_2$NHCO*), 3.10 (m, 2H, *OCNHCH$_2$CH$_2$*), 1.05–1.08 (m, 21H, *NCH$_2$CH$_3$*, *t*Bu); ^{13}C NMR (500 MHz, CDCl$_3$): δ = 169.02, 168.52, 154.35, 153.25, 152.51, 148.77, 146.40, 130.96, 130.49, 128.72, 126.48, 123.74, 122.90, 108.33, 105.37, 97.92, 73.56, 69.05, 65.24, 44.32, 39.82, 38.84, 34.30, 31.58, 12.74. ESI-Mass *m/z* (2,172.5) (M + Na + H)$^+$. Anal. calcd for C$_{132}$H$_{156}$O$_{15}$N$_{12}$: C 73.72, H 7.31, N 7.82, O 11.16; found C 73.66, H 7.38, N 7.72, O 11.24.

Stoichiometry of metal complexation

To confirm the binding mechanism, IR spectrum of **1** (10 mM) was measured in acetonitrile (Fig. 7). The two amide carbonyl absorption of **1** at 1,685.18 cm^{-1} drastically shifts to lower frequency upon addition of 10 equiv of

Fig. 7 Infrared spectra of **1** (25 mM) measured in acetonitrile with or without 10 equiv of Sb^{3+}, Fe^{3+}, and Ni^{2+}, respectively
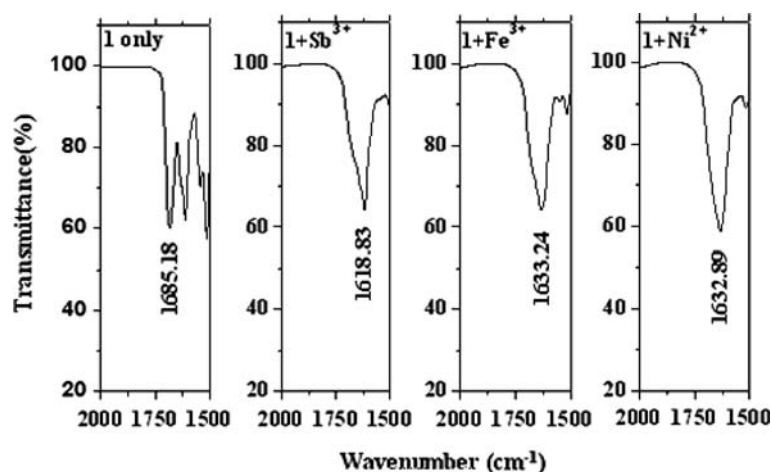
Scheme 2 The proposed mode for **1** binding with metal cation
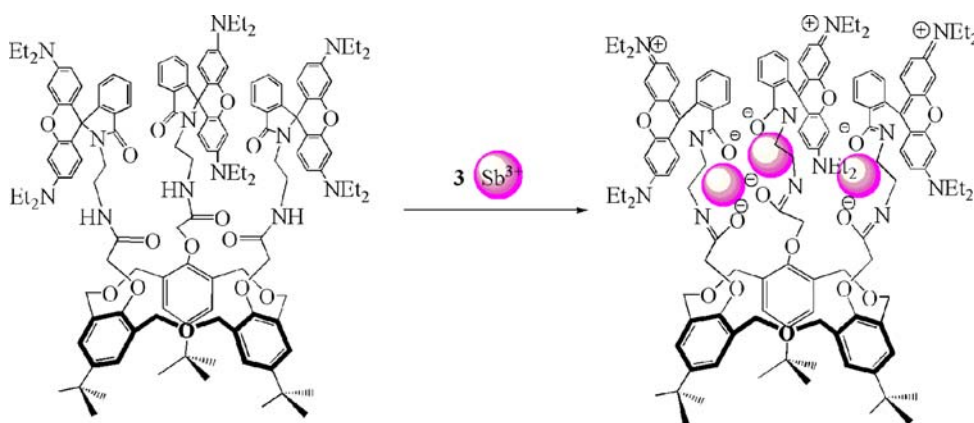
Sb^{3+} (1,618.83 cm^{-1}), Fe^{3+} (1,633.24 cm^{-1}), Ni^{2+} (1,632.89 cm^{-1}). These indicate that the amide carbonyl O of **1** is actually involved in the coordination with metal cations [34, 35]. Considering the Job's plot and the above experimental evidence, coordination of metal cation with **1** forms a 3:1 complex (Scheme 2), where the two binding sites (two amide carbonyl oxygen) within every arm of **1** form chelate pocket with cations.

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