

A pyrene-functionalized triazole-linked hexahomotrioxacalix[3]arene as a fluorescent chemosensor for Zn^{2+} ions

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ABSTRACT: A new pyrenyl appended hexahomotrioxacalix[3]arene **L** featuring 1,2,3-triazole linkers was synthesized as a fluorescent chemosensor for Zn^{2+} in mixed aqueous media. It exhibited high affinity toward Zn^{2+} , and the monomer and excimer emission of the pyrene moieties could be adjusted. The binding stoichiometry of the **L**• Zn^{2+} complex was determined to be 1:1, and the association constant (K_a) was found to be $7.05 \times 10^4 \text{ M}^{-1}$. The binding behaviour with Zn^{2+} has been confirmed by ¹H NMR spectroscopic analysis.

Keywords: Hexahomotrioxacalix[3]arene, Fluorescent chemosensor, Pyrene, Zn^{2+}

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Highlight:

- A new pyrenyl appended hexahomotrioxacalix[3]arene **L** featuring 1,2,3-triazole linkers was synthesized and characterized.
- **L** exhibits a high affinity and selectivity for Zn^{2+} ion relative to most other competitive metal ions evidenced by ratiometric fluorescence changes.
- Chemosensor **L** had a detection limit of 1.42×10^{-7} M, which allowed for the detection of submicromolar concentrations of Zn^{2+} .
- The three triazole ligands of the C_3 -symmetric hexahomotrioxacalix[3]arene scaffold exhibit a synergistic action to recognize Zn^{2+} .

1. Introduction

The development of new chemosensors for the efficient detection of heavy and transition metal (HTM) ions **is** currently a task of prime importance for medical, environmental and biological applications [1–2]. Among different types of chemosensors, fluorescent chemosensors generally offer distinct advantages in terms of sensitivity, selectivity and response time. Thus the design and synthesis of new fluorescent chemosensors for the selective recognition of the HTM ions **have** attracted considerable interest in recent years [3–4].

Fluorescent chemosensors normally consist of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore). An effective fluorescence chemosensor must convert the event of recognition by the ionophore into an easily monitored and highly sensitive fluorescence signal [5]. As fluorogenic units, photoactive pyrenyl substituents are very attractive due to their long fluorescence lifetime, pure blue fluorescence, strong and well characterized emissions and chemical stabilities [6]. **In particular, the** monomer and excimer emissions are observed at considerably different wavelengths depending on the relative proximity **of the** pyrene moieties [7].

Calixarenes have been extensively used as molecular **platforms** for the design and construction of different kinds of excellent receptors in molecular recognition by easy chemical modifications. As **a** new generation of **calixarenes**, hexahomotrioxacalix[3]arenes are related to both calixarenes and crown ethers,

and possess a three-dimensional cavity with a C_3 symmetric structure. They exhibit characteristic affinities for metal cations [8–9], ammonium cations [10–11], and fullerene derivatives [12–13]. In other words, use of the hexahomotrioxacalix[3]arene as the platform has potential application in the development of novel fluorescence chemosensors.

The Cu(I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides (‘Click’ reaction) has provided a straightforward molecular linking strategy adopted in a wide range of synthetic applications [14–17]. The resulting 1,2,3-triazole group served not only as an efficient covalent linker, but also a binding site for specific metal cations and anions. On the basis of the wonderful complexation between triazole and metal cations, a number of triazole-based fluorescent chemosensors have been reported [18–20]. However, to date, triazole has been scarcely exploited for the functionalization of the hexahomotrioxacalix[3]arene scaffold.

Taking advantage of the easily-synthesized triazole binding site and the excellent fluorescent properties of pyrene, it prompted us to explore the possibility of introducing the pyrene at the hexahomotrioxacalix[3]arene for metal cation recognition. In the present manuscript, we reported the synthesis and fluorometric properties of pyrenyl appended hexahomotrioxacalix[3]arene **L** which was found to exhibit high selectivity towards Zn^{2+} in mixed aqueous media.

2. Experimental

2.1. General

Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. All the solvents used were dried and distilled by the usual procedures before use. All melting points were determined using a Yanagimoto MP-S1. ^1H NMR and ^{13}C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and a Varian-400MRvnmrs400 with SiMe_4 as an internal reference: J -values are given in Hz. IR spectra were measured as KBr pellets or as liquid films on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by a Shimadzu UV-3150UV-vis-NIR spectrophotometer. Fluorescence spectroscopic studies of compounds in solution were performed in a semi-micro fluorescence cell (Hellma®, 104F-QS, 10×4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by a Yanaco MT-5.

2.2. Synthesis

Compounds **1** [21], **2** [22] and **3** [23] were prepared following the reported procedures.

2.2.1. General procedure for synthesis of compound **L**.

Copper iodide (10 mg) was added to compound **1** (200 mg, 0.27 mmol) and 1-azidomethylpyrene (230 mg, 0.89 mmol) in a 30 mL mixture of THF/H₂O (5:1, v/v) and the mixture was heated at 70 °C for 24 h. The resulting solution was cooled and extracted twice with chloroform. The chloroform layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The residue obtained was purified over silica gel column eluting with 1:1 hexane/chloroform to give the desired material **L** (295 mg, 72 %) as a white solid. m.p. 214–216 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.27–1.31 (t, 9H, COOCH₂CH₃, *J* = 6.8 Hz), 4.17–4.20 (d, 6H, ArCH₂(*eq*)O, *J* = 13.2 Hz), 4.19–4.24 (q, 6H, COOCH₂CH₃, *J* = 6.8 Hz), 4.31 (s, 6H, ArO–CH₂–triazole), 4.31–4.34 (d, 6H, ArCH₂(*ax*)O, *J* = 13.2 Hz), 5.78 (s, 6H, triazole–CH₂–pyrene), 7.29 (s, 3H, triazole–H), 7.39 (s, 6H, ArH), 7.64–7.66 (d, 3H, pyrene–H, *J* = 8.0 Hz), 7.80–7.88 (m, 12H, pyrene–H), 7.90–7.94 (t, 6H, pyrene–H, *J* = 8.0 Hz), 7.98–8.00 (d, 3H, pyrene–H, *J* = 8.0 Hz), 8.02–8.04 (d, 3H, pyrene–H, *J* = 8.0 Hz). ¹³C NMR (100 MHz, CDCl₃) δ = 14.26, 51.84, 60.56, 66.94, 68.86, 121.73, 123.40, 124.67, 125.48, 125.59, 126.06, 126.13, 126.90, 127.04, 127.27, 127.94, 128.64, 128.72, 130.80, 131.06, 131.66, 131.78, 143.59, 158.23, 165.40. FABMS: *m/z* 1510.56 (M⁺), 1511.57(M+H⁺). Anal. calcd for C₉₃H₇₅N₉O₁₂ (1510.64): C 73.94, H 5.00, N 8.34. found: C 73.89, H 5.04, N 8.36.

2.2.2. General procedure for synthesis of compound **L'**.

Copper iodide (10 mg) was added to compound **2** (200 mg, 0.98 mmol) and 1-azidomethylpyrene (252 mg, 0.98 mmol) in a 30 mL mixture of THF/H₂O (5:1, v/v) and the mixture was heated at 70 °C for 24 h. The resulting solution was cooled and

extracted twice with chloroform. The chloroform layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The residue obtained was purified over silica gel column eluting with 1:1 hexane/chloroform to give the desired material **L'** (340 mg, 75 %) as a white solid. m.p. 153–154 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.34–1.37 (t, 3H, $\text{COOCH}_2\text{CH}_3$, J = 6.8 Hz), 4.29–4.34 (q, 2H, $\text{COOCH}_2\text{CH}_3$, J = 6.8 Hz), 5.13 (s, 2H, $\text{ArO}-\text{CH}_2$ -triazole), 6.27 (s, 2H, triazole- CH_2 -pyrene), 6.89–6.91 (d, 2H, ArH , J = 8.4 Hz), 7.37 (s, 1H, triazole- H), 7.91–7.93 (d, 2H, ArH , J = 8.4 Hz), 7.97–7.99 (d, 1H, pyrene- H , J = 8.0 Hz), 8.04–8.15 (m, 4H, pyrene- H), 8.20–8.26 (m, 4H, pyrene- H). ^{13}C NMR (100 MHz, CDCl_3) δ = 14.32, 52.53, 60.62, 61.98, 114.23, 121.78, 122.68, 123.39, 124.41, 124.91, 125.06, 125.85, 125.98, 126.40, 127.15, 127.70, 128.36, 129.13, 129.30, 130.50, 131.12, 131.44, 132.19, 143.76, 161.68, 166.19. FABMS: m/z 461.17 (M^+). Anal. calcd for $\text{C}_{93}\text{H}_{75}\text{N}_9\text{O}_{12}$ (461.51): C 75.47, H 5.02, N 9.10. found: C 75.42, H 5.04, N 9.14.

3. Results and discussion

3.1. Synthesis

Insert Scheme 1 in here

The synthetic route for chemosensor **L** is described in Scheme 1. The Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of compound **1** with 1-azidomethylpyrene under Click conditions afforded the desired chemosensor **L** in 72 % yield. Compound **L'** was also synthesized in 75 % yield as a reference compound by a similar procedure. The ^1H NMR spectrum of **1** exhibited two singlets at δ 2.06 and 2.44 ppm for the $\text{C}\equiv\text{CH}$ protons (relative intensity 1 : 2), and two

singlets at δ 7.99 and 8.06 ppm for the aromatic protons (relative intensity 1 : 2). Furthermore, the resonances for the $ArCH_2OCH_2Ar$ bridging methylene protons appeared as three pairs of doublets in the region of δ from 4.15 to 5.04 ppm. These signals correspond to a *partial-cone* conformation **1**.

1H NMR spectra of **L** showed the disappearance of the three terminal alkyne protons, whereas the new singlet appearing around $\delta = 7.29$ ppm was attributed to the protons of the newly formed triazole groups. Moreover, the other peaks were observed as three singlets assignable to the protons in the $ArOCH_2$, triazole- CH_2 , and aromatic protons, and a pair of doublet for the $ArCH_2OCH_2Ar$ methylene protons. These findings supported the conclusion that the hexahomotrioxacalix[3]arene skeleton was immobilized in the *cone* conformation. These spectral properties also indicated that **L** possesses a C_3 symmetry, which was further corroborated by the ^{13}C NMR spectrum. **L** should theoretically show a *partial-cone* conformation, but interestingly the conformation converted from the *partial-cone* **1** to *cone* **L** during the ‘click’ reaction. In this process, the Cu(I) might be employed as a metal template, which can hold the alkyne groups on the same side of the hexahomotrioxacalix[3]arene and the conformation was immobilized to the *cone* [24–25]. The Cu(I) not only catalyzed the cycloaddition of alkynes and azides, but also produced a metal template effect. It is worth highlighting that this synthesis approach opens up a new strategy to synthesize the *cone* conformational hexahomotrioxacalix[3]arene derivatives.

3.2. Spectral characteristics of compounds **L** and **L'** for metal cations

The chemosensor behaviour of **L** was investigated by fluorescence measurements in CH₃CN/H₂O (10:1, v/v) upon excitation at 343 nm. As shown in Figure 1, the fluorescence spectra of **L** display very weak monomer emission (380 nm and 398 nm) but strong excimer emission (around 484 nm). The formation of the excimer band indicates a strong face-to-face π - π stacking between the neighbouring pyrene units. Dilution experiments at different concentrations of **L** revealed that the excimer emission resulted from the intramolecular excimer, rather than the intermolecular excimer (Figure S7, ESI). To get an insight into the binding properties of **L** toward metal cations, we first investigated the fluorescence changes upon addition of a wide range of metal cations including Li⁺, Na⁺, K⁺, Cs⁺, Ag⁺, Cu²⁺, Pb²⁺, Zn²⁺, Co²⁺, Ni²⁺, Cr³⁺, Cd²⁺ and Hg²⁺ in CH₃CN/H₂O. The fluorescence changes are depicted in Figure 1. Addition of Zn²⁺ to the solution of **L** induced obvious ratiometric changes, where the monomer emission increases as its excimer emission declines. By contrast, no significant spectral changes were observed upon addition of most of the other metal cations apart from Cu²⁺ and Hg²⁺ where quenching was observed. These results suggest that complexations between **L** and Zn²⁺, Cu²⁺ and Hg²⁺ ions through intermolecular interaction might be proposed.

Insert Figure 1 in here

To further investigate the chemosensor properties of **L**, fluorescence titration experiments of **L** with metal ions were performed. In the titration of **L** with Zn²⁺ in CH₃CN/H₂O (Figure 2), the fluorescence intensity of the monomer emission bands (at 380 and 398 nm) gradually increased with a concomitant decrease of the excimer

emission (484 nm) as the concentration of Zn^{2+} increased. Upon the addition of 10 equiv. of Zn^{2+} , the intensity of the monomer emission of **L** at 380 nm increased by 10-fold while that for the excimer emission at 484 nm decreased by about 20 % (Figure S8, ESI). This may be attributed to the flexibility of the triazole groups of **L** enabling them to adopt the appropriate geometry for the binding of Zn^{2+} ion. Thus, it is likely that the three triazole units of **L** formed a selective binding pocket for Zn^{2+} ions. The coordination forces move the pyrene moieties far away from each other inhibiting the π - π stacking of the pyrene moieties which is necessary for the generation of excimer emission. The binding stoichiometry of the **L**• Zn^{2+} complex was determined by the Job's plot (Figure S9, ESI), which indicated the formation of a 1:1 complex between **L** and Zn^{2+} . On the basis of the 1:1 stoichiometry, the association constant (K_a) of the **L**• Zn^{2+} complex was calculated to be $7.05 \times 10^4 \text{ M}^{-1}$. It was found that chemosensor **L** had a detection limit of $1.42 \times 10^{-7} \text{ M}$ (Figure S10, ESI), which allows for the detection of submicromolar concentrations of Zn^{2+} .

Insert Figure 2 in here

On the other hand, the same fluorescence titration experiments were also carried out with Cu^{2+} and Hg^{2+} ions in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (Figure S11–S12, ESI). Addition of Cu^{2+} or Hg^{2+} caused a remarkable quenching of the fluorescence intensities of **L**, 5 equiv. Cu^{2+} or Hg^{2+} were enough to quench the emission of **L**. Heavy metal ions are well known to quench the fluorescence of nearby fluorophores via enhanced spin-orbital coupling [26], and/or photoinduced electron transfer (PET) [27]. As anticipated, Cu^{2+} and Hg^{2+} quenched the fluorescence of **L** through the heavy metal ion effect [28]

and/or the reversed PET [29]. In the latter case, when Cu^{2+} or Hg^{2+} was bound to the nitrogen atoms of the triazole units, the pyrene units probably behaved as PET donors and the triazole groups behaved as PET acceptors [30]. According to the fluorescence titration results, the association constants (K_a) were calculated to be 7.08×10^5 and $2.11 \times 10^5 \text{ M}^{-1}$ for Cu^{2+} and Hg^{2+} ions, respectively.

Additionally, we assumed that the three triazole ligands of the C_3 -symmetric hexahomotrioxacalix[3]arene scaffold can exhibit a synergistic action to bind Zn^{2+} . To further confirm this assumption, the monomeric compound **L'** was synthesized as a reference compound and the fluorescence properties were evaluated under the same analytical conditions as were used for **L**. As shown in Figure 3, the fluorescent spectra of **L'** was not significantly changed upon addition of Zn^{2+} ions and other metal cations. Consequently, these results allow us to confirm our hypothesis about the fluorescent sensitive and selective binding of Zn^{2+} ion requires the coordination of three triazole rings of **L**. It suggests that the C_3 symmetry of hexahomotrioxacalix[3]arene plays an important role in the coordination with Zn^{2+} .

Insert Figure 3 in here

An important aspect to evaluate chemosensors is their ability to detect metal ions selectively over other competing metal cations. To utilize compound **L** as an ion-selective fluorescence chemosensor for Zn^{2+} , competition experiments were carried out in the presence of Zn^{2+} mixed with other metal ions. As shown in Figure 4, no significant interference in detection of Zn^{2+} was observed in the presence of many

competitive metal ions except for Cu^{2+} and Hg^{2+} . These results suggested that **L** can be used as a Zn^{2+} selective ratiometric fluorescent chemosensor in the presence of most competing metal cations.

Insert Figure 4 in here

3.3. ^1H NMR binding studies

To support the results obtained by spectrophotometric experiments and to obtain additional information about the coordination mode of these metal cations with **L**, we performed ^1H NMR titration experiments. From the ^1H NMR spectra of **L** (Figure 5), upon the addition of 1.0 equiv. of Zn^{2+} ion to the solution of **L**, as expected, the chemical shift of proton H_d on the triazole groups exhibited a significant down-field shift by δ 0.47 ppm from 7.29 to 7.76 ppm. The two peaks of protons H_c and H_e proximal to the triazole also demonstrated a similar but smaller down-field shift from δ 4.31 to 4.39 ppm and δ 5.78 to 6.00 ppm, respectively, whereas the peaks of the protons on the distal ester moieties were only slightly affected. Particularly, the slight shift of proton H_c indicates that the oxygen atoms are not involved in the coordination with Zn^{2+} . These spectral changes suggested that Zn^{2+} can be selectively bound by the nitrogen atoms via the synergistic action of the three triazole groups. On the other hand, it should be noted that the protons H_a on the aromatic rings also experienced a down-field shift from δ 7.39 to 7.49 ppm and the $\text{ArCH}_2\text{OCH}_2\text{Ar}$ methylene protons H_b revealed an up-field shift from δ 4.34 to 3.67 ppm. Moreover, considerable down-field shifts of the pyrene peaks were also observed. These data further indicated that there must be a conformational change for **L** in the presence of Zn^{2+} ion. As a

matter of fact, it is believed that the conformation of hexahomotrioxacalix[3]arene can be pre-organized for the binding of Zn^{2+} ion in solution in a manner that is similar to the examples described by Shinkai and coworkers [31–32]. Based on the above results, a plausible binding mode of $\text{L}\cdot\text{Zn}^{2+}$ complex is therefore depicted in Figure 6. This binding mode is consistent with the fluorescence changes observed as the induced conformational alterations of the triazole groups upon 1:1 complexation. The formation of the $\text{L}\cdot\text{Zn}^{2+}$ complex probably reduces the π - π stacking interactions necessary for excimer emission, and enforces the separation of pyrene moieties leading to the concomitant increasing of monomer emission.

Insert Figure 5 and 6 in here

Furthermore, we also carried out ^1H NMR experiments so as to further seek the detailed information on the complexation of Cu^{2+} and Hg^{2+} with **L** (Figure S15, S16, ESI). Upon interaction with 0.3 equiv. Cu^{2+} ion, the peaks of H_a , H_b , H_c , H_d and H_e nearby to the triazole groups disappeared completely, and the signals of the pyrene units were blurred. Cu^{2+} is a paramagnetic ion and can therefore affect proton signals that are close to the Cu^{2+} binding site [33–34]. Interestingly, subsequent addition of ethylene diamine to the same NMR tube recovered all of the disappeared peaks immediately (Figure S15 e, ESI). It suggests that the binding process was considered to be reversible rather than an ion-catalyzed reaction. On the other hand, upon addition of 1.0 equiv. of Hg^{2+} ion, considerable changes were noted in the chemical shift of protons in the triazole groups of chemosensor **L**. Protons labelled as H_c , H_d and H_e , which are proximal to the triazole groups exhibited significant down-field

shift by $\Delta\delta = 0.31, 0.49$ and 0.39 ppm, respectively. These changes reflect the involvement of the triazole rings in the Cu^{2+} and Hg^{2+} ion binding. Thus, the complexation between the heavy metal ions and sensor **L** led to the quenching of the fluorescence emission through the heavy metal ion effect, and/or the reversed PET.

4. Conclusion

In summary, a new fluorescent chemosensor **L** based on a pyrene-functionalized triazole-linked hexahomotrioxacalix[3]arene was synthesized through the 'Click' reaction. During the synthetic process, the Cu(I) not only catalyzed the cycloaddition of alkynes and azides, but also produced a metal template effect. Chemosensor **L** exhibited a high affinity and selectivity for Zn^{2+} ion relative to most other competitive metal ions as evidenced by the ratiometric fluorescence changes. The Zn^{2+} -selective recognition depends on the synergistic action of the three triazole ligands. On comparison with another fluorescent chemosensor based on a calix[4]arene scaffold bearing two triazole-pyrene groups, which exhibited selective recognition to Zn^{2+} and Cd^{2+} [35], **L** exhibited exclusive selectivity towards Zn^{2+} . This may be attributed to the different conformation adopted by hexahomotrioxacalix[3]arene versus calix[4]arene. Hexahomotrioxacalix[3]arene with the unique C_3 symmetry is beneficial to the design and synthesis of highly selective chemosensors for specific metal cations. This work can expand the application of the hexahomotrioxacalix[3]arene skeleton in the design and synthesis of novel fluorescent chemosensors.

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Supplementary data

Electronic Supplementary Information (ESI) available: Details of the NMR spectra and titration experimental data.

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Figure captions

Scheme 1. The synthetic route of **L** and **L'**.

Figure 1. Fluorescence spectra of chemosensor **L** (1.0 μM) on addition of various metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Cd^{2+} and Hg^{2+} , 10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343$ nm.

Figure 2. Fluorescence spectra of chemosensor **L** (1.0 μM) upon addition of increasing concentrations of $\text{Zn}(\text{ClO}_4)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343$ nm.

Figure 3. Fluorescence spectra of **L'** (1.0 μM) on addition of various metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Cd^{2+} and Hg^{2+} , 10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343$ nm.

Figure 4. Fluorescence responses of **L** (1.0 μM) in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (10:1, v/v) to 10 μM various tested metal ions (black bar) and to the mixture 10 μM tested metal ions with 10 μM Zn^{2+} (red bar). I_0 is fluorescence intensity at 380 nm for free **L**, and I is the fluorescent intensity after adding metal cations.

Figure 5. The ^1H NMR spectra of **L** (3.0 mM) upon titration with $\text{Zn}(\text{ClO}_4)_2$ in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (10:1, v/v). (a) **L** only, (b c d and e) in the presence of 0.3, 0.5, 0.8, 1.0 equiv. of $\text{Zn}(\text{ClO}_4)_2$, respectively.

Figure 6. The plausible binding mode of **L** $\cdot\text{Zn}^{2+}$ complex.

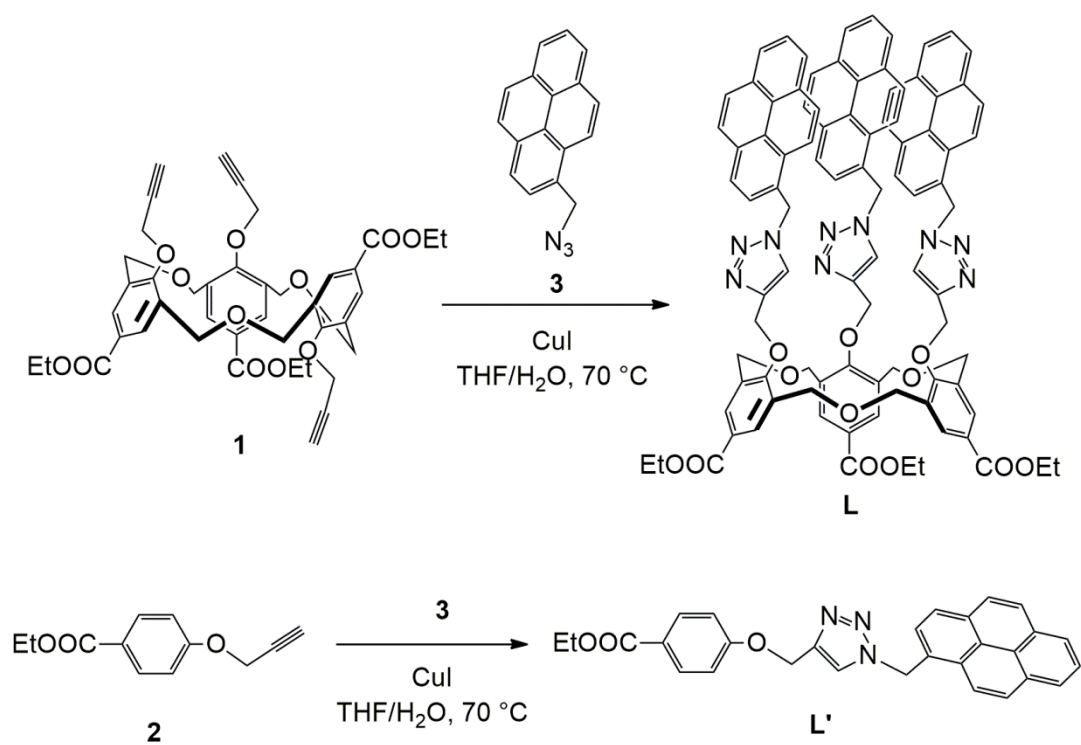
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Figure 1. Fluorescence spectra of chemosensor **L** (1.0 μM) on addition of various metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Cd^{2+} and Hg^{2+} , 10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343 \text{ nm}$.

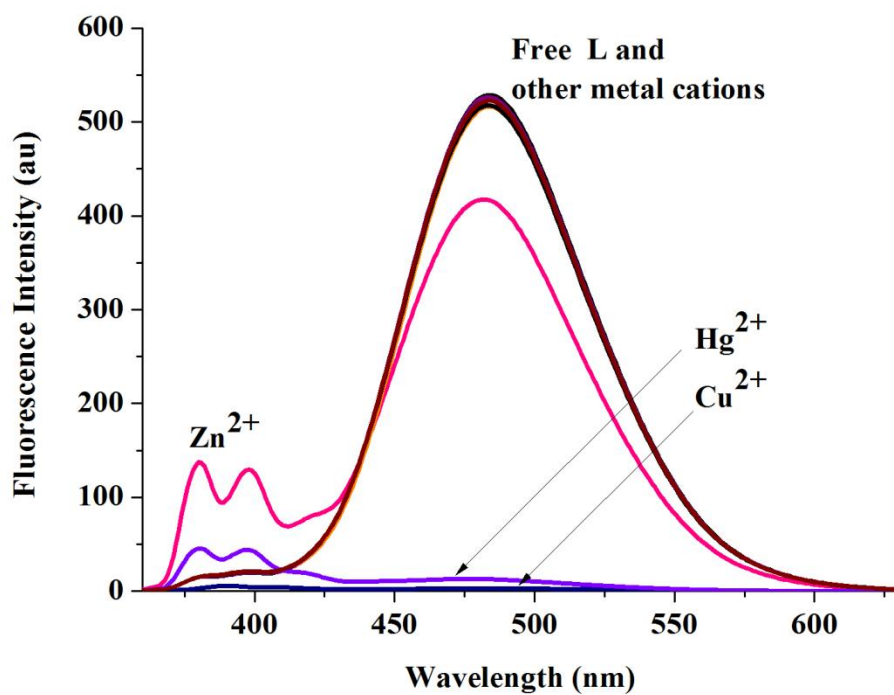


Figure 2. Fluorescence spectra of chemosensor **L** (1.0 μM) upon addition of increasing concentrations of $\text{Zn}(\text{ClO}_4)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343 \text{ nm}$.

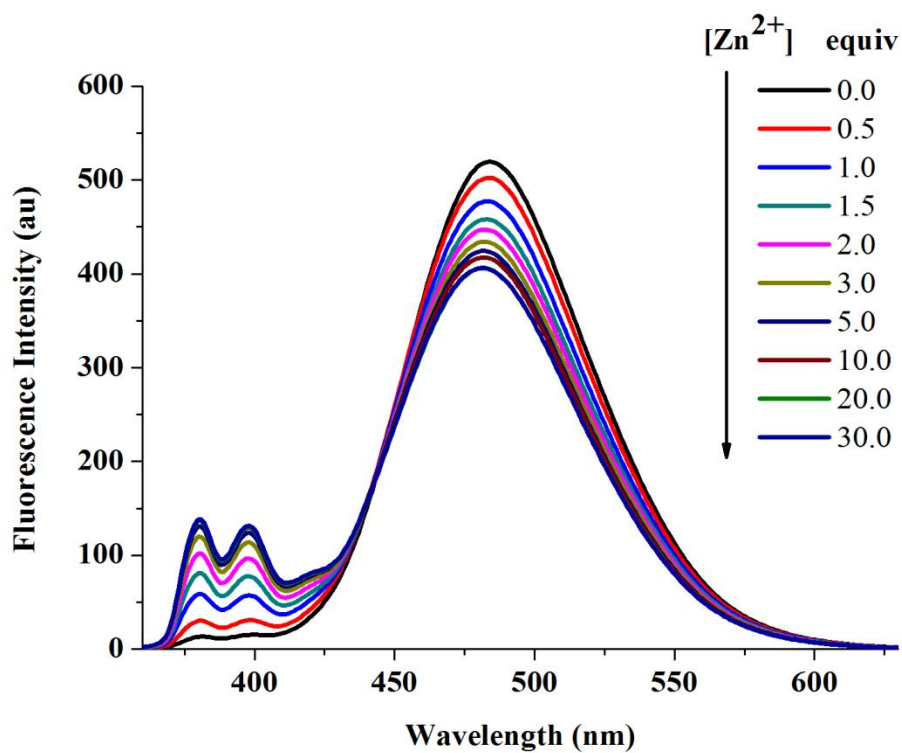


Figure 3. Fluorescence spectra of L' ($1.0 \mu\text{M}$) on addition of various metal ions (Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Cu^{2+} , Pb^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Cd^{2+} and Hg^{2+} , $10 \mu\text{M}$) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (10:1, v/v) at 298 K, $\lambda_{\text{ex}} = 343 \text{ nm}$.

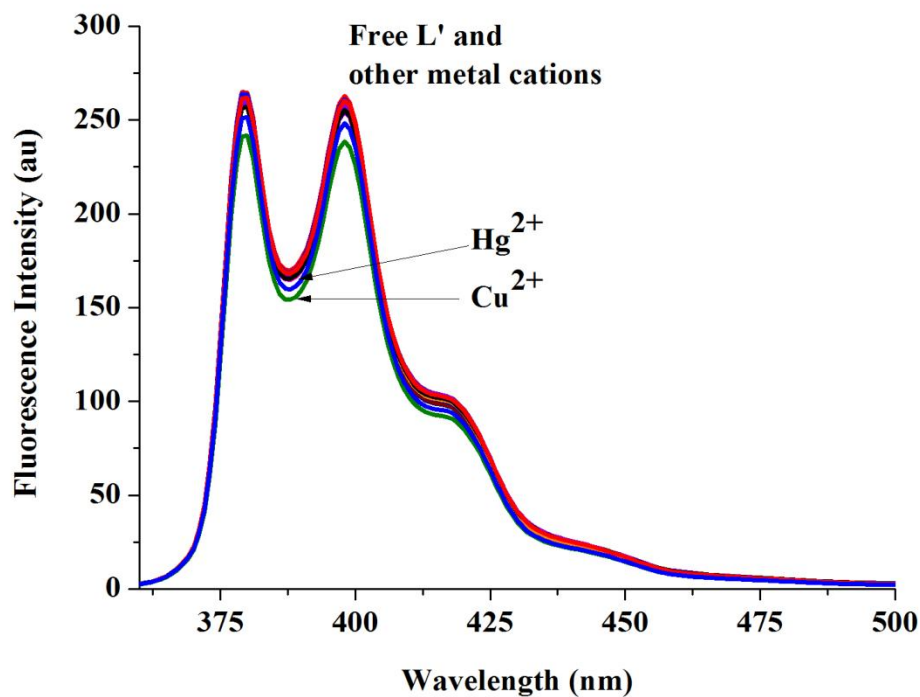


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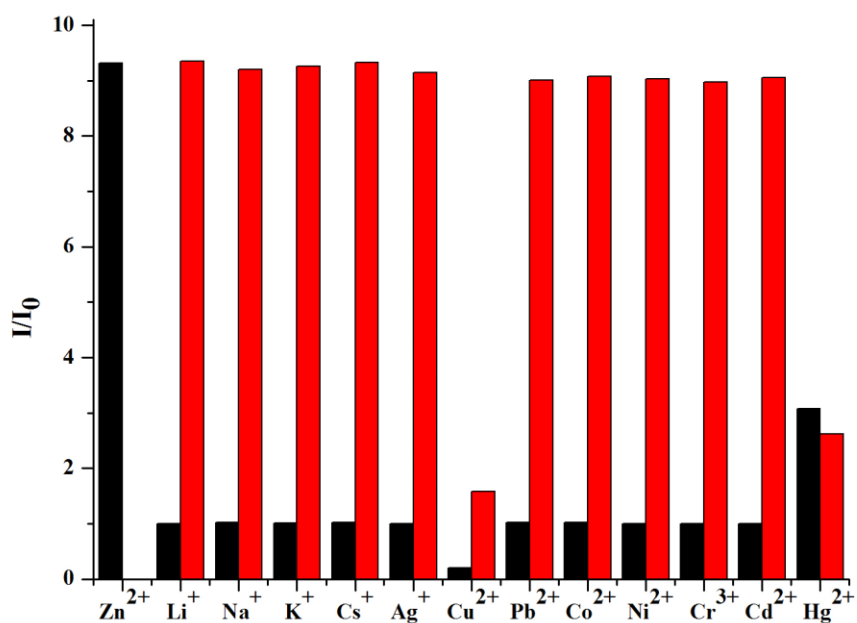


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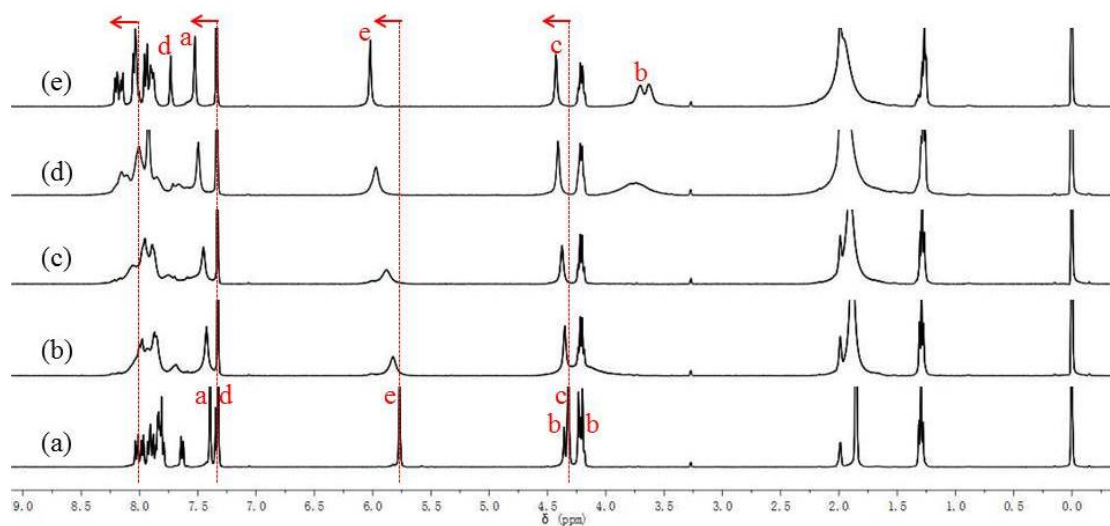
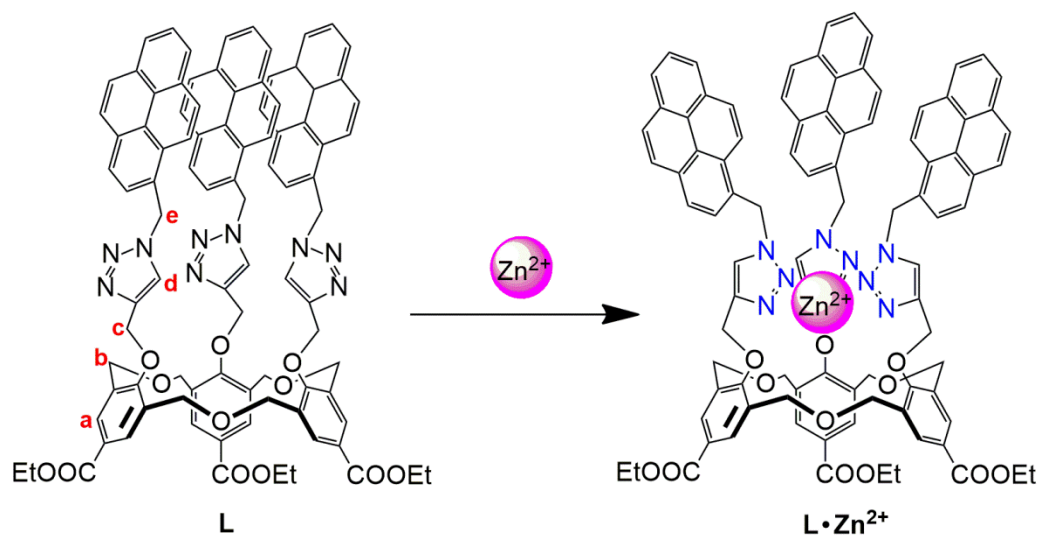


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