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PAPER

Hg^{2+} recognition by triptycene-derived heteracalixarenes: selectivity tuned by bridging heteroatoms and macrocyclic cavity†

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The binding properties of triptycene-derived oxacalixarenes containing 1,8-naphthyridine subunits **1a** and **1b** toward metal ions were investigated in detail by spectroscopic methods. A couple of new N,O-bridged diazadioxacalixarenes **2a**, **2b** were synthesized and their binding properties to metal ions were also evaluated. The results showed that the oxacalixarene **1a**, a *cis*-isomer with a boat-like 1,3-*alternate* conformation and a symmetrical cavity structure, exhibited a highly selective fluorescence response toward Hg^{2+} ions, while **1b**, **2a** and **2b** did not show selective response towards any specific metal ions. Such selectivity can thus be controlled by the bridging heteroatoms and cavity structures of the macrocycles. Moreover, it was found that the fluorescence of **1a** was considerably quenched upon the addition of Hg^{2+}, and a 1 : 2 stoichiometry host–guest complex was proposed on the basis of the Job plot and ^1H NMR titrations.

Introduction

The development of new classes of macrocyclic hosts has always been one of the most important topics in host–guest chemistry. Over the past few years, heteracalixarenes,[1] in which the carbon linkages between the aromatic units are replaced by heteroatoms, have attracted growing interest in calixarene chemistry because of their readily availability, tunable cavities and potential applications in supramolecular chemistry. Oxacalixarenes,[1d] or oxa[1_n]-*meta*-cyclophanes, are an important class of heteracalixarenes and could be efficiently synthesized by the nucleophilic aromatic substitution reactions of *m*-diphenol with appropriate electrophilic reagents. Although more and more sophisticated oxacalixarenes have been synthesized and documented in the recent literature,[2] the application of this new class of macrocycles in supramolecular chemistry remains largely unexplored, and only a few examples have been reported of their binding properties to cations, anions or neutral guest molecules.[2d–f,2k,3]

In recent years, we have devoted ourselves to the synthesis of triptycene-derived hosts and their applications in supramolecular chemistry.[4] Consequently, different kinds of novel macrocycles including triptycene-derived calixarenes[5] and triptycene-derived heteracalixarenes[6] have been reported. More recently, we also synthesized two novel triptycene-derived oxacalixarenes containing 1,8-naphthyridine units **1a** and **1b** as a pair of diastereomers (Fig. 1), and found that they showed highly efficient complexation abilities toward fullerenes C_{60} and C_{70},[6c] and could also be utilized as new molecular wheels for the templated synthesis of [2]rotaxanes.[6a]

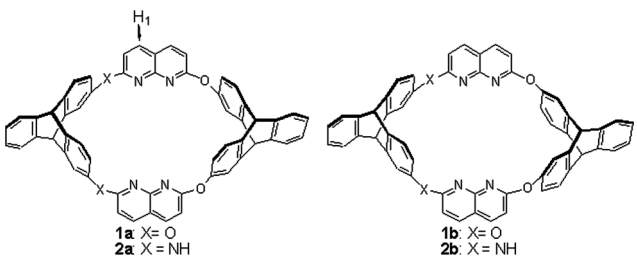

Fig. 1 Chemical structures of triptycene-derived heteracalixarenes **1**–**2**.

1, 8-Naphthyridine (napy) and its derivatives have found wide applications in many domains of chemistry including supramolecular chemistry, such as the recognition and sensing of carbohydrates,[7] amino acids[8] and guanine.[9] However, there are very few reports about the derivatives of 1,8-naphthyridine as optical sensors for transition and heavy metal ions.[10] As a part of our ongoing work exploring the applications of triptycene-derived heteracalixarenes, we report herein the recognition properties of triptycene-derived oxacalixarenes **1a** and **1b** towards metal ions. Moreover, we also synthesized a couple of new N,O-bridged diazadioxacalixarenes[11] **2a** and **2b** (Fig. 1), and evaluated their binding properties towards metal ions. The results showed that among the four macrocycles only **1a** showed high selectivity and sensitivity complexation ability towards Hg^{2+} ion,[12,13] and this selectivity was considerably influenced by the bridging heteroatoms and cavity structures of the macrocycles.

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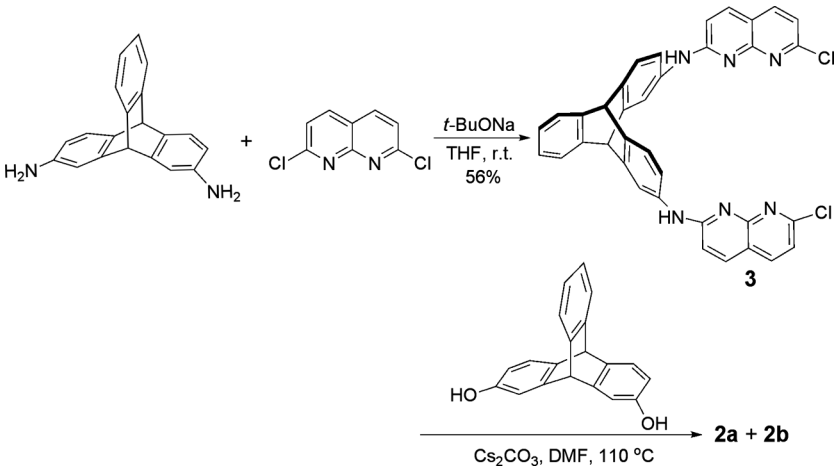
† Electronic supplementary information (ESI) available: Copies of ^1H and ^{13}C NMR spectra. Fluorescence and UV-vis spectra. CCDC reference numbers 819712 (**2b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05515a



Scheme 1 Synthesis of triptycene-derived heteracalixarenes **2a** and **2b**.

Results and discussion

Synthesis and structures of triptycene-derived heteracalixarenes

Oxacalixarenes **1a** and **1b** as a pair of diastereomers have been synthesized previously.[6a] Similarly, diazadioxacalixarenes **2a** and **2b** were synthesized by a two-step fragment coupling method. As shown in Scheme 1, reaction of 2,7-diaminotriptycene[6d] with 2,7-dichloro-1,8-naphthyridine in the presence of a large excess of *t*-BuONa afforded the [1 + 2] product **3** in 56% yield. Then, the macrocyclization from the reaction of compound **3** and 2,7-dihydroxytriptycene gave the target molecules **2a** and **2b** in 22% and 16% yield, respectively. X-Ray crystallographic analysis of **2b**[14] showed that it is a *trans*-isomer and adopts a curved boat-like conformation similar to that of **1b**[6a] (Fig. 2). We also found that by virtue of C–H$\cdots\pi$ ($d_{\text{C–H}\cdots\pi}$ = 2.83 Å for a, and 2.88 Å for b) interactions between the aromatic protons of the naphthyridine subunits in one macrocycle and the phenyl rings of the triptycene subunits in its adjacent macrocycles, $\pi\cdots\pi$ ($d_{\pi\cdots\pi}$ = 3.32 Å for c, and 3.34 Å for d) interactions between the naphthyridine subunits of two adjacent macrocycles (Fig. 2c), **2b** could assemble into a tubular architecture viewed along the *b*-axis (Fig. 2d).

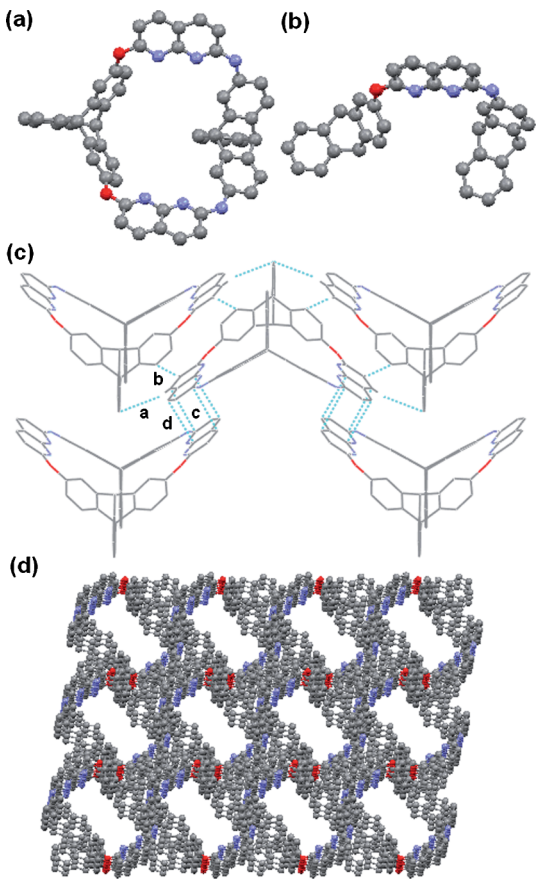


Fig. 2 (a) Top view and (b) side view of **2b**, (c) The noncovalent interactions between the adjacent molecules, and (d) a tubular architecture viewed along the *b* axis.

Metal ion binding studies of 1a

We firstly investigated the binding property of oxacalixarene **1a** to various metal ions by fluorescence spectroscopy in CH_3CN solution. Macrocycle **1a** showed a strong emission band maximum at 450 nm when excited at 327 nm, which can be attributed to the emission from the 1,8-naphthyridine fluorophore. Upon interaction with 5 equiv. of various metal ions (as perchlorate salts), Hg^{2+} ions alone exhibited effective fluorescence quenching among the tested metal ions (Fig. 3a). The fluorescence was quenched remarkably and the intensity at 450 nm was dramatically reduced by about 97% in the presence of Hg^{2+} ions (I/I_0 = 0.03, where I and I_0 represent the fluorescence intensity in the presence and absence of metal ions, respectively). The origin of the fluorescence quenching may result from the electron or energy transfer from the excited naphthyridine fluorophore to the Hg^{2+} ion. Alkali and alkaline earth metal ions showed no interaction with **1a**, which may be due to their hard acid properties. Other transition and heavy metal ions produced insignificant fluorescence changes where I/I_0 ranged from 0.90 to 0.99, and only Cu^{2+} ions showed a somewhat quenched fluorescence intensity (I/I_0 = 0.80).

It is known that the distance of the nitrogen atoms between the two face-to-face naphthyridine moieties in **1a** is about 8.8 Å, while the M^{n+}–N distance in metal complexes of naphthyridine normally falls within the range of 2.0–2.2 Å,[15] thus it is unlikely to form

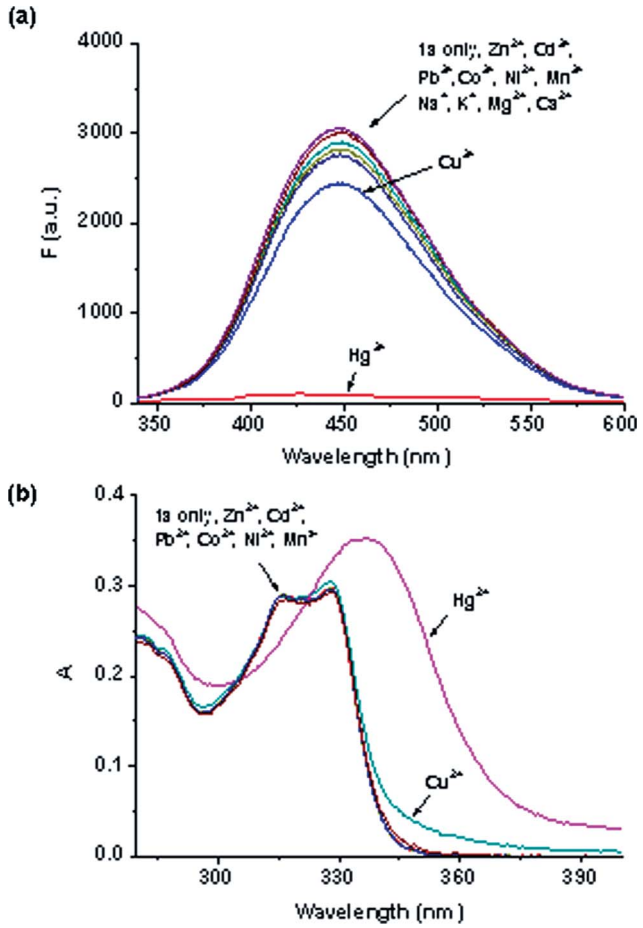


Fig. 3 (a) Fluorescence and (b) absorption spectra of **1a** (10 μM in CH_3CN) in the absence and presence of 5 equiv. of metal ions.

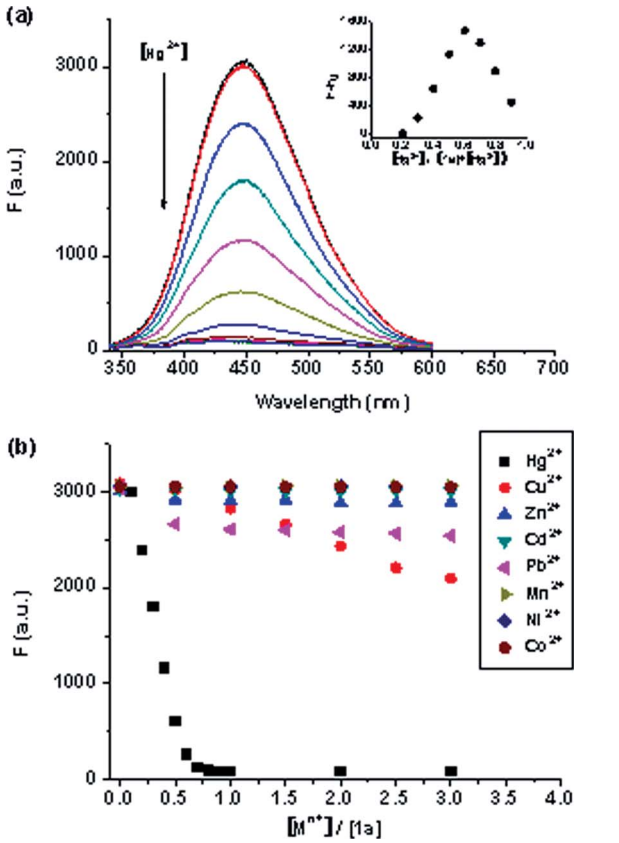


Fig. 4 (a) Fluorescence titrations of **1a** (10 μM in CH_3CN) with Hg^{2+} (0–3 equiv.). The inset shows the Job plot between **1a** and Hg^{2+}; total concentration is 10 μM. (b) Fluorescence titration profiles of **1a** (10 μM in CH_3CN) with metal ions at 450 nm.

a 1 : 1 host–guest complex resulting from a cooperative binding of the two naphthyridine moieties. The binding stoichiometry between the **1a** and Hg^{2+} was determined by Job plot experiments. Consequently, the maximum fluorescence change of the complex was obtained when the mole fraction of the Hg^{2+} had reached about 0.67, which is characteristic of a host–guest binding in a 1 : 2 stoichiometry.

Given the binding stoichiometry between the host and the guest, the binding constants could be calculated from the fluorescence titration experiments. As shown in Fig. 4a, the intensity of the emission band at 450 nm was gradually decreased upon addition of increasing amounts of Hg^{2+} ions, and reached the saturation point when about 1.0 equiv. of Hg^{2+} was added. Further addition of Hg^{2+} induced no obvious spectroscopy changes. This observation indicated a considerable affinity of macrocycle **1a** toward the Hg^{2+}. The titration curves were analyzed by the Hyperquad 2003 program[16] and the binding constants were calculated to be log K_{11} = 7.59(3) and log K_{12} = 12.40(13). Titrations of **1a** with other transition and heavy metal ions were also carried out (Fig. 4b), as discussed above, and only Cu^{2+} induced moderate fluorescence quenching upon addition of excess salts. The binding constants for the **1a**/Cu^{2+} complex were found to be logK_{11} = 3.91(6) and logK_{12} = 8.55(1), which are 3–4 orders of magnitude lower than that of Hg^{2+}. These results showed that macrocycle **1a** could recognize Hg^{2+} with high sensitivity and selectivity over other metal ions.

The complexation between macrocycle **1a** with metal ions in the ground-state was also studied by UV-vis spectroscopy (Fig. 3b). **1a** showed an absorption band maximum at 327 nm ($\varepsilon_{327\,nm}$ = 2.9 × 10^4 M^{-1} cm^{-1}) along with a shoulder peak at 315 nm ($\varepsilon_{315\,nm}$ = 2.8 × 10^4 M^{-1} cm^{-1}). Upon the addition of various metal ions, only Hg^{2+} induced significant spectroscopy changes; other metal ions induced negligible changes except for Cu^{2+}, which produced a slightly increased intensity at about 340 nm. The UV-vis titrations showed that upon addition of increasing amounts of Hg^{2+}, the intensity of the absorption band at 315 nm was gradually decreased while the band at 327 nm underwent a continuous red-shift to 340 nm with concomitant increased intensity. No well-defined isosbestic points were observed throughout the titrations, which may be due to the fact that it was not a simple 1 : 1 host–guest complex equilibrium. The remarkable changes of the absorption bands of **1a** in the presence of Hg^{2+} confirmed that the fluorescence spectroscopy changes could be mostly attributed to the strong host–guest complexation in the ground-state.

To obtain more details about the complexation between **1a** and Hg^{2+}, ^1H NMR titrations were carried out. As illustrated in Fig. 5, the resonance signals of H_1 protons on the *para*-position of naphthyridine nitrogen atoms appeared at δ 8.17 ppm, and gradually broadened and disappeared when about one equiv. of $Hg(ClO_4)_2$ were added. Meanwhile, a new set of signals at about δ 8.79 ppm gradually appeared which were assigned to the H_1 protons of the complex. At this point, we assumed that a 1 : 1

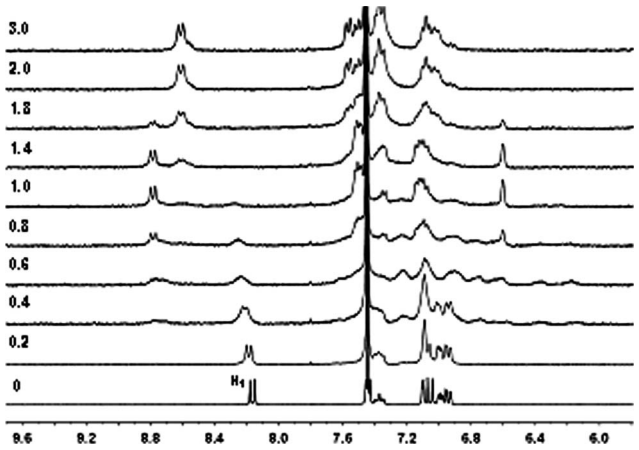


Fig. 5 ^{1}H NMR titrations of **1a** (2 mM in $CDCl_3$–CH_3CN, 2 : 1, v/v) with Hg^{2+} (0–3 equiv.) at 298 K.

1a–Hg^{2+} complex was formed. The results also indicated that the complex was very stable in solution, and the exchange between **1a** and **1a**–Hg^{2+} was slow on the NMR time scale. Further addition of $Hg(ClO_4)_2$ induced similar changes, that is, the signals of the H_1 protons at δ 8.79 ppm gradually disappeared and another new set of signals at about δ 8.61 ppm were observed. Changes of both signals disappeared when about 2 equiv. of $Hg(ClO_4)_2$ were added; again, we attributed this to the formation of a 1 : 2 stoichiometry complex **1a**–$(Hg^{2+})_2$. A considerable downfield shift could also be observed for the water signal at δ 2.1 ppm upon the addition of $Hg(ClO_4)_2$, which suggested that the water molecules were probably involved in the metal ion coordination processes.

For other metal ions, because of the paramagnetic properties of Cu^{2+}, the complexation between **1a** and Cu^{2+} was not suitable for investigation by NMR spectroscopy, so we chose Zn^{2+} ions. Because macrocycle **1a** showed a very weak affinity toward Zn^{2+} as observed in the fluorescence and UV-vis spectroscopy studies, the changes in the NMR spectra of **1a** in the presence of Zn^{2+} were obviously different from that of Hg^{2+} (see the ESI†). The resonance signals of the H_1 protons showed a small downfield shift to δ 8.33 ppm ($\Delta\delta = 0.16$ ppm) even at 3 equiv. of excess Zn^{2+}. The spectra also exhibited only one set of signals throughout the titration, indicating that a relatively weak host–guest interaction and a fast exchange equilibrium between the host and the complex existed on the NMR time-scale.

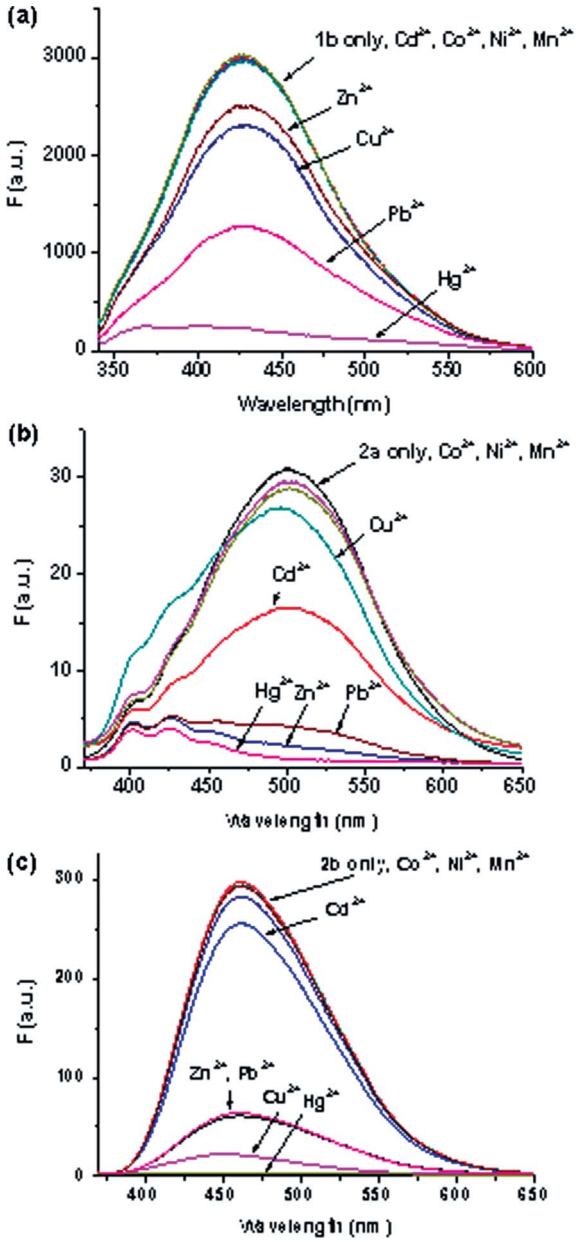


Fig. 6 Fluorescence spectra of (a) **1b**, (b) **2a**, and (c) **2b** (all were 10 μM in CH_3CN) in the absence and presence of 5 equiv. of metal ions.

Metal ion binding studies of 1b, 2a–b

Oxacalixarene **1b** was known to adopt a curved boat-like conformation and showed a different cavity structure from that of **1a** in the solid state. Consequently, it was interesting to find that **1b** showed different binding selectivity toward the metal ions from that of **1a** (Fig. 6a). Upon addition of 5 equiv. of various metal ions, the emission band maximum at 425 nm (λ_{ex} = 327 nm) of **1b** quenched significantly in the presence of Hg^{2+} (I/I_0 = 0.08) and Pb^{2+} (I/I_0 = 0.42). Moderate changes were observed after addition of Cu^{2+} (I/I_0 = 0.76) and Zn^{2+} (I/I_0 = 0.82), and other metal ions induced negligible spectroscopy changes. For diazadioxacalixarenes **2a** and **2b**, in which the two bridging oxygen atoms of **1a** and **1b** were replaced by N–H groups, none of them showed a selective spectroscopic response toward any specific metal ions (Fig. 6b–c). The fine-structure of the emission spectra of **1b** and **2a** could be observed in the presence of metal ions (Fig. 6a–b), which possibly resulted from changes in the vibration transition of the naphthyridine aromatic rings upon the complexation with metal ions. The binding constants of the metal complexes of **1b**, **2a**, **2b** were calculated and summarized in Table 1, which showed that the selectivity of these four macrocycles toward Hg^{2+} was related to their affinity with the ions, *i.e.* the order of binding constants of **1a–2b** with Hg^{2+} is: **1a** > **1b** > **2a** > **2b**, while the selectivity has a similar order. The diazadioxacalixarenes **2a** and **2b** showed poorer selectivity toward metal ions than the oxacalixarenes **1a** and **1b**. Correspondingly, some metal complexes of **2a** or **2b** have similar binding constants, while oxacalixarenes **1a** and **1b** both exhibited higher affinity toward Hg^{2+}. The different cavity structures induced different affinities towards the metal ions observed between **1a**

Table 1 Binding constants ($\log K_{11}$, $\log K_{12}$) for 1 : 2 complexation between **1a–2b** and metal ions calculated from fluorescence titrations in CH_3CN by Hyperquad 2003 program at 298 K[a,b]

	1a	1b	2a	2b
Hg^{2+}	7.59(3)	6.54(3)	6.59(10)	4.89(5)
	12.40(13)	11.00(3)	10.05(4)	10.78(5)
Cu^{2+}	3.91(6)	3.34(2)	7.64(3)	4.49(2)
	8.55(1)	7.37(4)	13.43(3)	9.59(2)
Zn^{2+}	n.d.	4.96(4)	6.40(7)	3.99(8)
		6.78(3)	10.64(3)	8.82(1)
Pb^{2+}	n.d.	4.62(1)	6.37(3)	4.37(11)
		7.64(2)	10.07(9)	9.24(2)
Cd^{2+}	n.d.	n.d.	5.61(5)	n.d.
			8.01(14)	

[a] n.d.: No obvious fluorescence spectral changes were shown, so K values were not determined. [b] The errors given in parentheses correspond to the standard deviation.

and **1b** as discussed above and this was also observed in the case of **2a** and **2b**. For example, the metal complexes of *cis*-isomer **2a** all showed larger binding constants than that of *trans*-isomer **2b**; macrocycle **2a** showed a comparatively high affinity toward Cd^{2+} with the binding constants of $\log K_{11} = 5.61(5)$ and $\log K_{12} = 8.01(14)$, while the fluorescence band maximum at 461 nm of **2b** showed only small changes ($I/I_0 = 0.93$) upon the addition of Cd^{2+}.

Enhanced selectivity of 1a for Hg^{2+} by water

The complexation between oxacalixarene **1a** and Hg^{2+} is reversible: the quenched emission band of **1a** restored its intensity upon addition of a strong Hg^{2+} ligand, such as I^-. Large amounts of water could also restore the emission band probably due to the oleophilic properties and limited solubility in aqueous solution of **1a**. However, the intensity of emission bands of both **1a** and the **1a**–Hg^{2+} complex showed negligible changes in the presence of a small amount of water (<5%, v%). In particular, we found that the binding strength of macrocycle **1a** toward Cu^{2+} was greatly reduced, while the selectivity of **1a** toward Hg^{2+} was further enhanced in the CH_3CN–H_2O (98 : 2 v/v) system (Fig. 7a), although the binding constants of **1a**–Hg^{2+} complex were also decreased ($\log K_{11} = 6.35(2)$, $\log K_{12} = 10.73(4)$). We further carried out the competition experiments, and measured the fluorescence quenching ratios of **1a** by the treatment of 2 equiv. of Hg^{2+} in the presence of 5 equiv. of other metal ions including K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}. As shown in Fig. 7b, the background metal ions tested showed little or no interference with the sensing of Hg^{2+} ions, which demonstrated the outstanding selectivity of macrocycle **1a** toward Hg^{2+}.

One possible contribution for the high selectivity of **1a** toward Hg^{2+} over the other metal ions tested could result from the electronic and coordinating nature of the 1,8-naphthyridine ligand, and this result may also be rationalized by the very specific orientation of electron density for the two pyridinyl lone-pair electrons in the 1,8-naphthyridine moiety, which makes the naphthyridine ligand favor complex formation with a soft metal ion with a large radius such as Hg^{2+}. That the selectivity resulted from the macrocyclic cavity structure could be further supported by the metal ion binding investigations on a linear 1,8-naphthyridine derivative, such as 2,7-dimethoxy-1,8-naphthyridine (Dmnapy).[17]

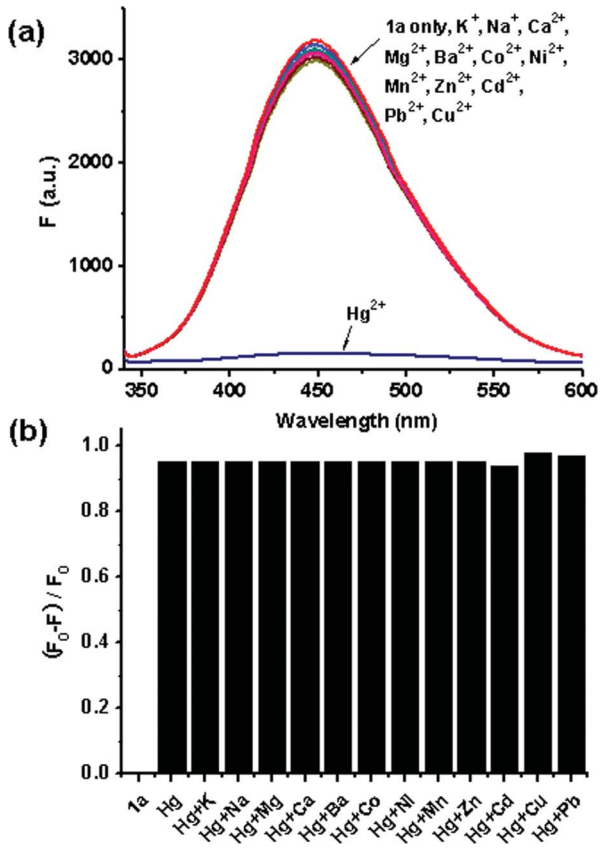


Fig. 7 (a) Fluorescence spectra of **1a** (10 μM in CH_3CN–H_2O, 98 : 2, v/v) in the absence and presence of 5 equiv. of metal ions. (b) Fluorescence quenching ratio of **1a** (10 μM in CH_3CN–H_2O, 98 : 2, v/v) after the addition of 2 equiv. of Hg^{2+} in the presence of 5 equiv. of other metal ions.

Fluorescence titration showed that the ligand Dmnapy exhibited different binding profiles from that of either macrocycle **1a** or **1b**, as well as **2a** and **2b** (see the ESI†).

Conclusions

In conclusion, the binding properties of two pairs of triptycene-derived heteracalixarenes towards metal ions were investigated in detail by spectroscopic methods. It was found that among the four macrocycles only oxacalixarene **1a**, a *cis*-isomer with a boat-like 1,3-*alternate* conformation and a symmetrical cavity structure, showed a highly selective response toward Hg^{2+}. Such selectivity is controlled by the bridging heteroatoms and cavity structure of the macrocycles. The results presented here suggest that **1a** can serve as a potential fluorescent probe for Hg^{2+}. Given its Hg^{2+} specificity, sensitivity and reversibility, modification of **1a** to make it water-soluble or further alteration to switch its detection mode from turn-off to turn-on would be further worthwhile.

Experimental section

General

Melting points, taken on an electrothermal melting point apparatus, are uncorrected. The NMR spectra were measured on a Bruker DMX300 NMR spectrometer. MALDI-TOF MS were obtained

on a Bruker BIFLEXIII mass spectrometer. Fluorescence spectra were measured on a Hitachi F-4500 spectrometer. Absorption spectra were measured on a Shimadzu UV-2401PC spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Chemistry, CAS. Metal ions as their perchlorate salts were commercial and used without further treatment.

Synthesis of trimer 3

Under an argon atmosphere, a mixture of 2,7-diaminotriptycene (284 mg, 1 mmol), 2,7-dichloro-1,8-naphthyridine (594 mg, 3 mmol), and *t*-BuONa (2.88 g, 30 mmol) in dry THF (50 mL) was stirred at room temperature for 24 h. Aqueous hydrochloric acid (4 M) was added to neutralize the excess base. Then, THF was removed and the resulting precipitate was collected, dried, and subjected to column chromatography (silica gel, 200–300 mesh) eluted with CH_2Cl_2/ethyl acetate (6 : 1), which afforded **3** as a yellow solid (340 mg, 56%). Mp: 259–261 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.00 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 9.3 Hz, 2H), 7.75 (s, 2H), 7.47–7.39 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 9.3 Hz, 2H), 7.06–7.02 (m, 4H), 5.49 (s, 2H). MALDI-TOF MS: m/z 609.2 $[M + H]^+$, 631.2 $[M + Na]^+$.

Synthesis of diazadioxacalixarenes 2a and 2b. Under an argon atmosphere, a mixture of **3** (304 mg, 0.5 mmol), 2,7-dihydroxytriptycene (143 mg, 0.5 mmol), and Cs_2CO_3 (488 mg, 1.5 mmol) in dry DMF (250 mL) was stirred at 110 °C for 48 h. The mixture was cooled down to room temperature, filtered, and concentrated under reduced pressure. The crude residue was dissolved in a mixture of CH_2Cl_2 and water. The organic fraction was separated, washed with water, dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography over silica gel (eluent: CH_2Cl_2/ethyl acetate, 5 : 1) to afford **2a** (90 mg, 22%) as a yellow solid and **2b** as a yellow-grey solid (65 mg, yield: 16%). **2a**: Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.43–7.24 (m, 8H), 7.21–7.19 (m, 2H), 7.10 (s, 2H), 7.02–6.98 (m, 4H), 6.91 (s, 2H), 6.83–6.81 (m, 4H), 6.73 (s, 2H), 5.35 (s, 1H), 5.31 (s, 1H), 5.29 (s, 1H), 5.22 (s, 1H). MALDI-TOF MS: m/z 823.5 $[M+H]^+$. Anal. Calcd for $C_{56}H_{34}N_6O_2{\cdot}0.5CH_2Cl_2{\cdot}CH_3CO_2C_2H_5$: C 76.21, H 4.55, N 8.81; found C 76.72, H 4.34, N 8.84%. **2b**: Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 2H), 7.84 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.46–7.24 (m, 10H), 7.21 (d, J = 7.8 Hz, 2H), 7.08–7.04 (m, 4H), 6.87 (d, J = 8.4 Hz, 2H), 6.57 –6.48 (m, 6H), 5.58 (s, 1H), 5.47 (s, 2H), 5.31 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 163.9, 156.4, 150.5, 146.9, 146.7, 146.5, 146.4, 146.2, 145.9, 141.2, 140.3, 139.7, 137.5, 137.2, 125.7, 125.5, 125.4, 124.3, 124.1, 123.8, 123.7, 123.5, 123.3, 119.7, 117.4, 117.1, 115.2, 111.9, 109.7. MALDI-TOF MS: m/z 823.5 $[M+H]^+$. Anal. Calcd for $C_{56}H_{34}N_6O_2{\cdot}CH_2Cl_2$: C 75.41, H 4.00, N 9.26; found C 75.31, H 4.32, N 8.97%.

Acknowledgements

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Notes and references

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