REVIEW ARTICLE

Non-covalent strategy for activating separation and detection functionality by use of the multifunctional host molecule thiacalixarene

Nobuhiko Iki

Abstract This review article proposes a non-covalent strategy for activating separation and detection functionality; this strategy acts not through extensive organic synthesis to a covalently constructed molecular receptor, but by combining a simple molecular platform with a chemical "field" or functional component. For such a platform, we employed thiacalixarenes—calixarenes in which the bridging methylene groups are replaced with sulfur—to demonstrate usefulness of the non-covalent strategy and the multifunctionality of thiacalixarene. Thiacalixarene exhibits inherent abilities to recognize metal ions by coordinating with the bridging sulfur and adjacent phenol oxygen, as well as to include organic guest molecules in the cavity. Moreover, the non-covalent coupling of thiacalixarene provides systems with functions higher than thiacalixarene by itself. The functions described in this paper are as follows: (1) a 200-fold pre-concentration of heavy metal ions such as Cu^{II}, Cd^{II}, and Pb^{II}; (2) a pre-column derivatization reagent for the highly selective and sensitive determination of Ni^{II}, Al^{III}, Fe^{III}, and Ti^{IV} at sub-ppb levels with reversed-phase HPLC; (3) the self-assembled formation of a luminescence receptor with Tb^{III} ions for the detection of 10^{-10} M levels of 1-ethylquinolinium guest; and (4) a sensing system for 10^{-9} M levels of Ag^{I} ions by the formation of the Ag^{I}-Tb^{III}-thiacalixarene ternary supramolecular complex. These examples support the non-covalent strategy as a highly promising way to obtain functions beyond that of a molecular platform. In addition, these diverse functions indicate the multifunctionality of thiacalixarene as well as its suitability to the non-covalent strategy, since the inherent functional groups—such as the bridging sulfur, phenol oxygen, p-substituent, aromatic ring, and hydrophobic cavity—synergistically perform the functions.

Introduction

The chemical recognition of molecules and ions is the base for functions that enable the sensing, separation, transport, and catalytic conversion of substances [1]. In a biological system, biomolecules with specific recognition abilities play vital roles in maintaining life. Such molecules have attracted and motivated chemists to design artificial receptors as capable and precise as biomolecules at chemical recognition. So far, efforts have been devoted to the synthesis of receptors—three-dimensional arrangements of functional groups interacting with a guest molecule at multiple points to construct a specific binding unit—which are then jointed with signaling groups responsible for signal read-out. The covalent attachment of the signaling group to a specific binding group is a straightforward strategy for obtaining a synthetic receptor and is termed here as the "covalent strategy" (Fig. 1). Usefulness of this strategy has been demonstrated by many examples of a wide variety of receptors with various guest-binding and signaling moieties. Absorption [2], fluorescence [3–5], luminescence [6, 7], circular dichroism [8, 9], and redox [10–13], have been utilized for the read-out of guest binding. Of these options, fluorescence is highly versatile because it is susceptible to changes such as excimer formation/dissociation, photo-induced electron

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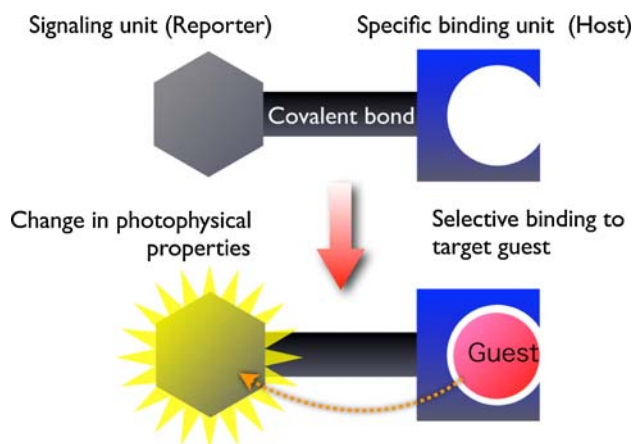e-mail: iki@orgsynth.che.tohoku.ac.jp

Fig. 1 Covalent strategy to design molecular receptors

	X	R
calix[4]arene	CH_2	*t*-Bu, *t*-Oct, etc.
thiacalix[4]arene	S	*t*-Bu, *t*-Oct
sulfinylcalix[4]arene	SO	*t*-Bu, *t*-Oct
sulfonylcalix[4]arene	SO_2	*t*-Bu, *t*-Oct
TCAS	S	SO_3^-
SO_2CAS	SO_2	SO_3^-

Scheme 1 Structure of *p*-substituted calix[4]arenes

transfer, charge transfer, and energy transfer caused by binding of the host moiety to a guest [3–5]. On the other hand, owing to their bowl-shaped structure to include guest molecules, calixarene [14–16] and cyclodextrin [17] have been utilized as a binding moiety for guests; their selectivity is further enhanced by the introduction of appropriate functional groups. To recognize metal ions, crown ethers and macrocyclic ligands have also been utilized by considering factors that affect selectivity, such as the ring size, affinity of donor atoms to analyte cations, and the stereochemistry of the resulting complex [18].

The covalent strategy has been derived on the premise that two different processes occur in guest sensing: molecular recognition and signaling. Although this strategy is useful, it does not provide much scope for alternative methods to design receptors or sensing systems. In the last decade, we discovered the recognition ability of thiacalixarene (Scheme 1) toward metal ions and organic guest molecules and applied it to sensing and separation [19–21]. It should be noted that the beginning of the thiacalixarene study was initiated not by the intention to design receptor molecules but by serendipity, as in the case of the discovery of calixarene [22]. Thiacalixarene was found in a reaction mixture for synthesizing a linear oligomer of *p*-alkylphenol joined with sulfide bridges at the *ortho* position. Afterwards, we successfully found a facile protocol to obtain the cyclic oligomer *p-tert*-butylthiacalix[4]arene [23]. From the synthetic point of view, the bridging sulfur drew much attention as a pivot for various modifications, such as oxidation to SO and SO_2 [24] and nucleophilic aromatic substitution [25]. In addition, protocols to introduce functional groups into phenol moiety should be transferrable from conventional methods employed in calixarene chemistry [20].[1] Elaborate modification of thiacalix[4]arene scaffold should produce receptor molecules selective to a
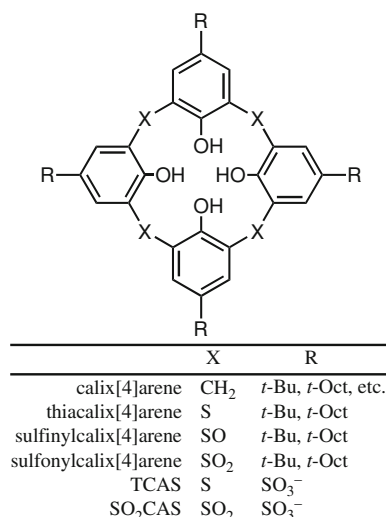
certain class of guest. However, we chose an alternative "non-covalent strategy"; we combined thiacalixarenes with other components and "chemical fields" to activate higher-order functions than simple recognition without relying on the covalent attachment of functional groups onto thiacalixarenes (Fig. 2). Here, we demonstrate the potential and usefulness of this strategy to activate functions related to highly selective and sensitive detection and separation.

## Chemical-recognition ability of thiacalixarenes

There is no doubt that calixarenes are versatile molecular platforms with almost unlimited possibilities [14–16, 26–30]. This versatility owes to their three-dimensional structure with controllable conformations and the ease of chemical modification at the wider and narrower rims. For instance, calixarenes have been applied to ligands for metal extraction, sensors, and catalysis [14–16, 31, 32]. In many cases, ligand groups are attached to phonolic oxygen or at the *para* position in the typical covalent approach. There are a smaller number of examples where calixarene acts by itself as a ligand by coordinating with phenol O^- [29][2] or an aromatic ring [33–35]. Therefore, it can be said that a vast majority of calixarene chemistry relies on the covalent strategy.

What distinguishes thiacalixarene most from classical calixarene is the bridging sulfur, which is a potential metal binding site due to the lone pair of electrons and vacant 3*d* orbitals (Fig. 2). With this in mind, we first revealed the coordination ability of *p-tert*-butylthiacalix[4]arene towards the first-row transition metal ions by solvent extraction [36].

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[1] Chap. 3.

[2] Chapters 28–30.

Fig. 2 Non-covalent strategy to activate function of higher order by combination of thiacalixarene with chemical field or functional components
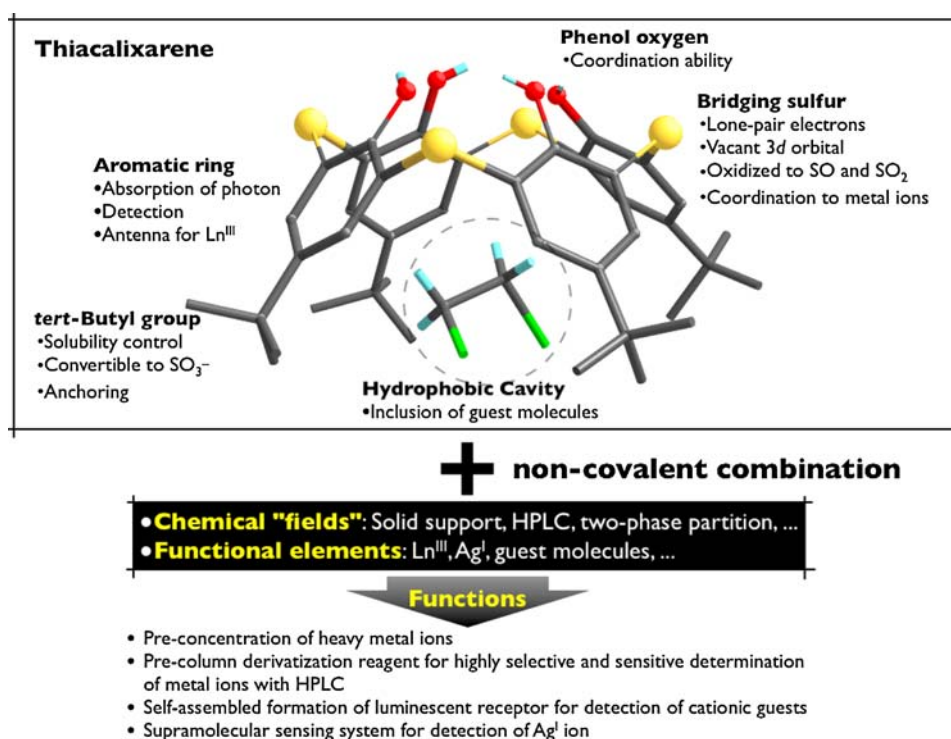

X-ray analysis for a Zn^{II} complex of thiacalix[4]arene proved that with adjacent phenol O^- donors, the bridging sulfur is able to coordinate to metal ions [37]. Furthermore, an extension of metal species to 40 different kinds revealed that thiacalix[4]arene is able to extract metal ions with soft to intermediate characteristics on the basis of the "hard and soft acids and bases" rule [38]. In addition, the coordination selectivity of thiacalix[4]arene towards metal ions can be controlled by the oxidation state of the bridging sulfur; sulfonylcalix[4]arene with SO_2 bridges coordinates to hard metal ions, and sulfinylcalix[4]arene with SO bridges coordinates to both hard and soft ions depending upon the disposition (Fig. 3). To date, thia-, sulfinyl-, and sulfonylcalix[4]arenes have been used as ligands to assemble multi-metal cores to form cluster complexes [39].

Another aspect of thiacalixarene is the hydrophobic cavity. For instance, *p-tert*-butylthiacalix[4]arene is able to include common organic solvent molecules in the solid states [40]. In aqueous solutions, thiacalix[4]arene-*p*-tetrasulfonate (TCAS) includes organic molecules such as halomethane [41], alcohols [42], DMF, DMSO [43], monosubstituted benzenes [44], and ferrocene derivatives [45]. Notably, according to X-ray analysis the hydrophobic cavity of thiacalix[4]arene is about 10% larger than the one for calix[4]arene [40]. Consequently, thiacalix[4]arene has a higher ability to include guest molecules such as halomethanes and water-miscible organic molecules in D_2O than calix[4]arene does [41, 43].

The characteristic features of thiacalixarene are summarized in Fig. 2. Besides the bridging sulfur and slightly extended hydrophobic cavity, thiacalixarene has moieties such as phenol oxygen, the aromatic ring, and R at the *para* position. As shown in the figure, thiacalixarene has different types of functional groups responsible not only for metal and guest recognition but also for light absorption, solubility control, anchoring to solid support, etc. Furthermore, by adopting the non-covalent strategy, higher functions have been successfully activated, such as the pre-

Fig. 3 Coordination selectivity of thiacalix[4]arenes arising from oxidation states of the bridging sulfur
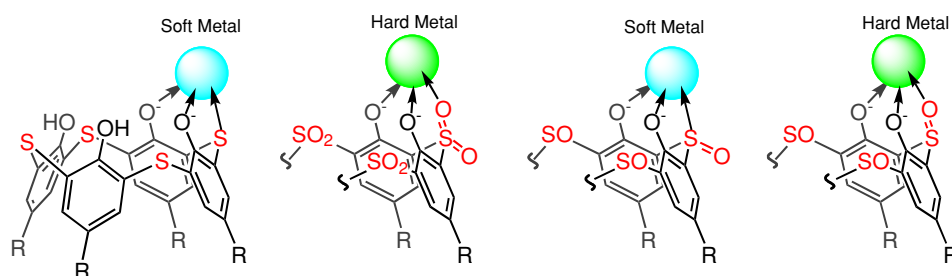
concentration of heavy metal ions [46, 47], the pre-column derivatization reagent for the highly selective and sensitive determination of metal ions with HPLC [48, 49], the self-assembling formation of the luminescence receptor for detection of cationic guests [50], and a supramolecular sensing system for the Ag^I ion [51] (Fig. 2).

Pre-concentration of heavy-metal ions [46, 47]

Although thiacalix[4]arene can recognize soft metal ions, the ability is merely the binding of a ligand to a metal ion in solutions. Similarly, water-soluble TCAS is able to bind to heavy-metal ions in aqueous solutions; this is simply a reaction between two entities in a homogeneous solution. In order to derive higher functions such as separation, TCAS should be placed or fixed in a "field" to convert recognition to spatial separation. To do this, we immobilized TCAS onto a solid support in a non-covalent manner: using the -SO$_3^-$ group as an anchoring group for cationic sites of an anion-exchange resin (Fig. 4). Simply soaking Amberlite$^®$ IRA-900 in an aqueous solution of TCAS and stirring for 10 h conveniently produced TCAS-immobilized resin [46]. Although the procedure for the preparation of the resin is much simpler than that of chelating resins constructed with multi-step organic synthesis, no leakage
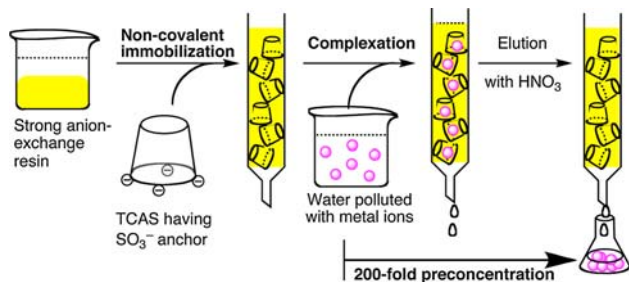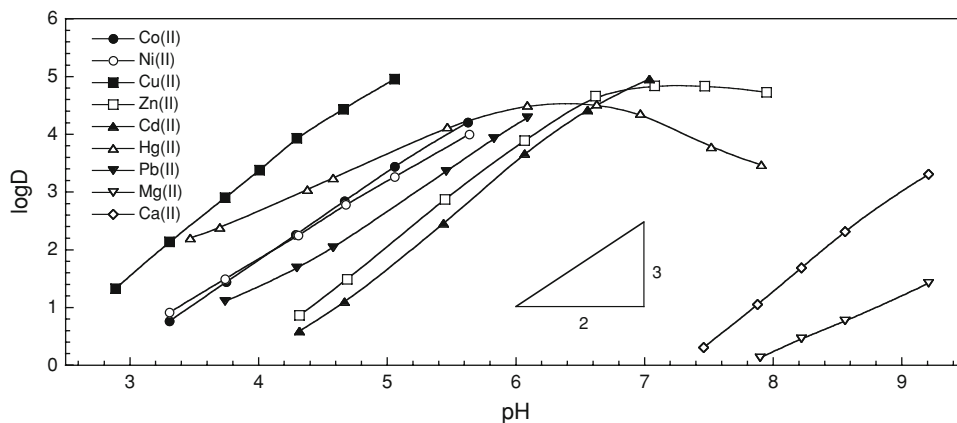
Fig. 4 Schematic drawing of preparation and operation of TCAS-immobilized resin

of TCAS was observed. In batchwise experiments, the dependence of the distribution ratio (D)—for the metal ions (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Hg^{II}, and Pb^{II}) in the resinous phase—on pH showed the quantitative adsorption of heavy metal ions in the slightly acidic to neutral pH region (Fig. 5).

$$D = C_{M,resin}/C_{M,aq} \tag{1}$$

where $C_{M,resin}$ and $C_{M,aq.}$ are the concentrations of metal ions (in mol cm^{-3}) in the resinous and aqueous phases, respectively. The linear relation of log D vs. pH suggests ligation of the phenol O$^-$ of TCAS on the resin. On the other hand, hard metal ions were barely adsorbed, showing that the selectivity of the resin was determined by TCAS. In a continuous adsorption scheme using a column packed with the resin, the above-mentioned heavy-metal ions were completely removed (>99.98%) from the aqueous solutions before its breakthrough point (Fig. 6), where 1% of the metal ions in the feed leaked out the column. The breakthrough capacity varied from 88-fold of the bed volume for Ni^{II} to 460-fold for Hg^{II}.
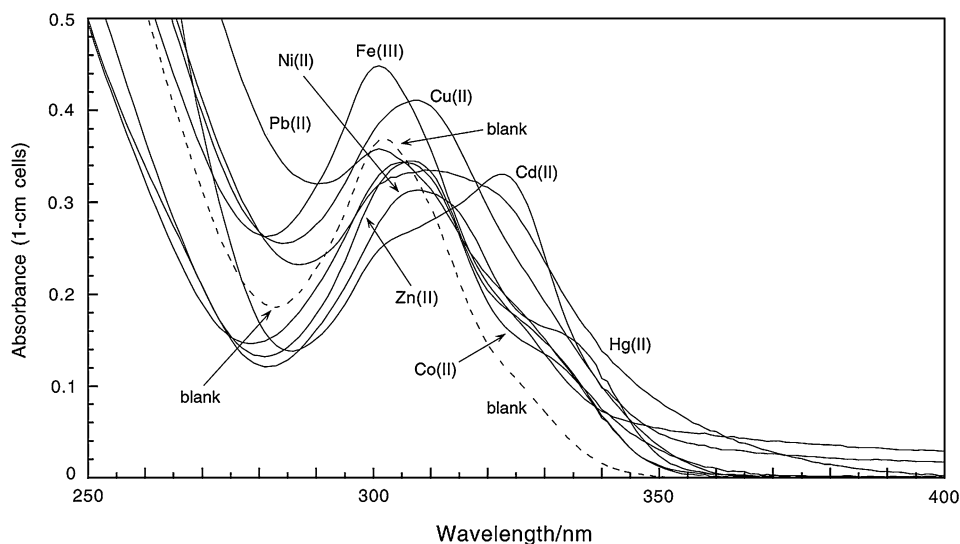
A drawback of the resin retarding practical application is the operating speed: the feed rate was as slow as 0.1 cm^3 min^{-1}, and increasing the rate resulted in a decrease of the break-through capacity. Changing the solid support to a hydrophilic one, however, allowed the fast adsorption of heavy metal ions. We used a dextran-based anion-exchanger QAE-Sephadex$^®$ A-25 as the solid support to improve the adsorption kinetics [47]. A column adsorption system with the TCAS-loaded Sephadex A-25 enabled the rapid collection and pre-concentration of Cu^{II}, Cd^{II}, and Pb^{II}. Passing 100 cm^3 of a water sample (pH 8.0) through a column at a flow rate of 10 cm^3 min^{-1}, followed by elution with 0.5 cm^3 of 1 M HNO$_3$ afforded a 200-fold pre-concentration of the analyte elements. This method was applied to determine sub-ppb levels of Cu^{II}, Cd^{II}, and Pb^{II} in seawater through graphite-furnace atomic-absorption spectrometry (GFAAS) without any interference.

Fig. 5 The effect of solution pH on the equilibrium distribution ratio (D) for metal ions onto TCAS-loaded resin. TCAS-loaded resin: 0.80 cm^3. Volume of solution: 20.0 cm^3. Initial concentration of metal ions: 0.10 mmol dm^{-3}

Fig. 6 Column breakthrough profile for the adsorption of metal ions by TCAS-loaded resin. Resin bed: 0.80 cm^3 (5.0 mm i.d. × 40 mm high). Concentration of metal ions in feed solution: 0.50 mmol dm^{-3}. Solution pH: 6.5. Feed rate: 0.10 cm^3 min^{-1} (7.5 beds h^{-1})
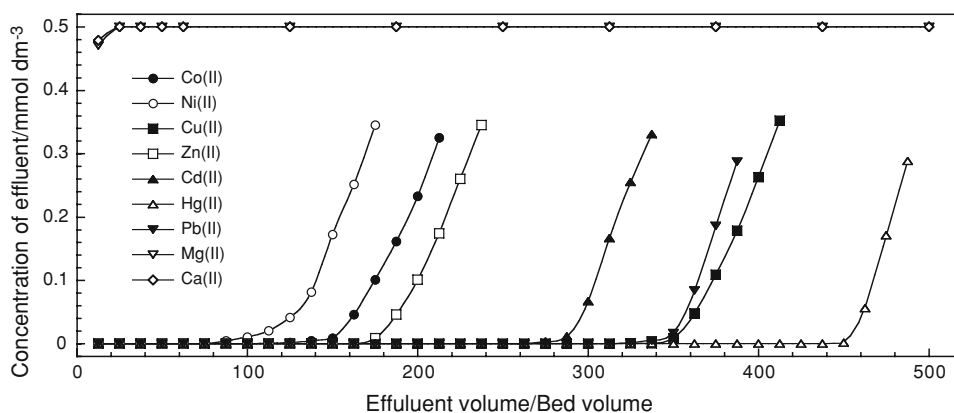
Thus, the non-covalent immobilization of TCAS onto a solid support by using its anchoring -SO$_3^-$ group successfully produced chelating resin for the separation and pre-concentration of heavy metal ions (Fig. 4). In addition to electrostatic immobilization, we succeeded in immobilizing *p-tert*-butylsulfinylcalix[4]arene onto the moderately polar acrylic resin XAD-7 through van der Waals interaction [52]. Stir-mixing the chloroform solution of *p-tert*-butylsulfinylcalix[4]arene with XAD-7 gave sulfinylcalix[4]arene-impregnated resin, which was able to adsorb more than 90% of Nb^V from an aqueous solution at a pH of approximately 5.4. Also, the adsorbed Nb^V was quantitatively desorbed with 9 M H$_2$SO$_4$. Interestingly, the adsorption of Ta^V on the resin was negligible; therefore, the separation of Nb^V from Ta^V was conveniently achieved. Thus, thiacalixarenes fixed onto a solid support show higher functions such as separation, removal, and pre-concentration; this suggests that the non-covalent strategy of placing calixarene in a "field" from a homogeneous solution is highly promising in extending functions beyond recognition.

Pre-column derivatization reagent for the highly selective and sensitive determination of metal ions with HPLC [48, 49]

TCAS has inherent coordinating sites and photo-absorbing groups, suggesting that it may act as a spectrophotometric reagent. However, TCAS is a very weak reagent in terms of selectivity for complex formation and detection. For the former, it forms complexes with metal ions of soft to intermediate character as shown in the previous section. In addition, the spectral selectivity of metal complexes with TCAS is not good, since complexes of TCAS show very similar absorption spectra to that of free TCAS arising from the π-π* transition of the aromatic ring (Fig. 7). To apply TCAS to the spectrophotometric detection of metal ions, there are two ways depending upon the strategies. The first is to covalently attach an auxiliary functional group to enhance the selectivity of coordination to a metal ion. This has been quite successful in the calixarene area to obtain highly selective ionophores for ion-selective electrodes [53, 54]. The second is the non-covalent strategy, which we

Fig. 7 Absorption spectra of TCAS (2 × 10^{-5} mol dm^{-3}) in the presence of various metal ions (2 × 10^{-5} mol dm^{-3} each) at pH 6.0 (0.01 M MES-NaOH buffer) after heating at 60°C for 30 min

adopted by combining TCAS with another field: reversed-phase high-performance liquid chromatography (RP-HPLC) with a spectrophotometric detector [48].

In this scheme, TCAS was used as a chelating reagent to form complexes, which were introduced into the RP-HPLC system using an *n*-octadecylsilanized silica-type Chromolith^{TM} Performance RP-18e column. The eluent contained the tetra-*n*-butylammonium (TBA$^+$) ion to retain and separate anionic TCAS species. Among the 14 kinds of common metal ions tested (Al^{III}, Ca^{II}, Cd^{II}, Co^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Hg^{II}, Mg^{II}, Mn^{II}, Ni^{II}, Pb^{II}, V^V, and Zn^{II}), only Ni^{II} ion was detected as the TCAS chelate in the HPLC
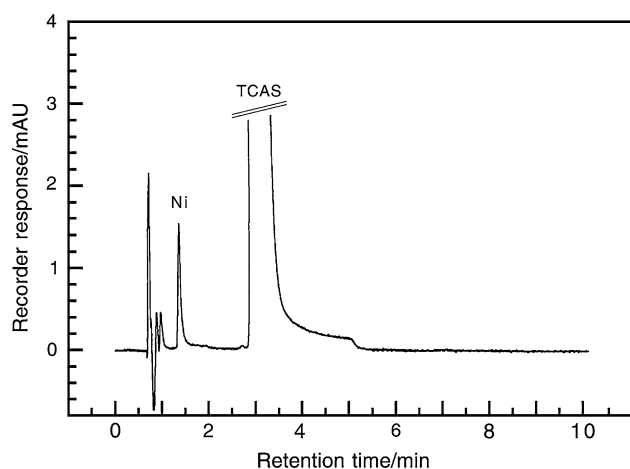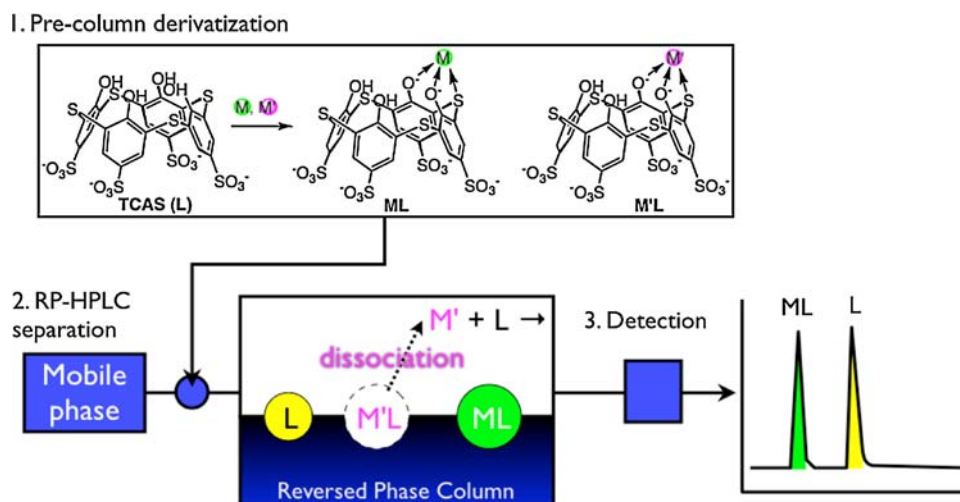

Fig. 8 Typical chromatograms for the sample containing 14 kinds of metal ions. Sample solution: concentration of metal ion, 2×10^{-7} M each of Al^{III}, Ca^{II}, Cd^{II}, Co^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Hg^{II}, Mg^{II}, Mn^{II}, Ni^{II}, Pb^{II}, V^V, and Zn^{II}; concentration of TCAS, 5×10^{-5} M; pH, 6.0 (0.01 M MES-NaOH buffer). Injection volume: 100 mm^3. Mobile phase: methanol-water mixture $(1 + 1$ m/m) containing TBABr (7.0 mmol kg^{-1}), sodium acetate (5.0 mmol kg^{-1}), and CyDTA (0.10 mmol kg^{-1}). Flow rate: 2.0 ml min^{-1}. Column: Chromolith Performance RP-18e (4.6 mm i.d. $\times$ 100 mm length). Detection wavelength: 310 nm

separation stage (Fig. 8), in spite of the fact that TCAS formed chelates with all these metal ions except for Al^{III}, Ca^{II}, and Mg^{II} at the pre-column chelation stage. Because of kinetic instability, the undetected metal-TCAS chelates seemed to be dissociated on an HPLC column where no added TCAS was present in the mobile phase (Fig. 9). Thus, combining TCAS with HPLC enabled the specific detection of Ni^{II} ion on the basis of kinetic stability. We have termed this scheme—consisting of pre-column chelation followed by RP-HPLC separation using an eluent not containing the ligand—as kinetic differentiation mode–HPLC (KD-HPLC) because the kinetic stability of the metal complexes is discriminated by the separation field [55]. The analytical performance of this TCAS-KD-HPLC system is also noted; the calibration graph for Ni^{II} ion gave a wide linear dynamic range (40-20,000 nM) with a very low detection limit (DL) (3σ base-line fluctuation) of 5.4 nM (0.32 ng ml^{-1}). The high sensitivity owes to the very low background absorption in the detection step, where excess ligands were separated from the Ni^{II} complex. The practical applicability of the KD-HPLC method with TCAS was demonstrated through the determination of trace Ni in coal fly ash.

Sulfonylcalix[4]arene-*p*-tetrasulfonate (SO$_2$CAS) was also used in the KD-HPLC scheme as a pre-column chelating reagent [49]. Metal ions with hard to intermediate characters (Al^{III}, Ca^{II}, Co^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Mg^{II}, Ni^{II}, Ti^{IV}, and Zn^{II}) were converted into SO$_2$CAS chelates in an acetic buffer solution (pH 4.7), thus showing the low selectivity of SO$_2$CAS. The chelates were injected into an RP-HPLC system and eluted using a methanol-water eluent (50 wt% methanol; pH 5.6) containing TBA$^+$ bromide (7.0 mmol kg^{-1}), acetate buffer (5.0 mmol kg^{-1}), and disodium eth-ylenediamine-*N,N,N',N'*-tetraacetate (0.10 mmol kg^{-1}). Under these conditions, Al^{III}, Fe^{III}, and Ti^{IV} were selectively detected from among 21 kinds of metal ions (Fig. 10). The

Fig. 9 Schematic drawing of KD-HPLC-TCAS system. L: TCAS ligand, M: Detected metal ion (i.e. Ni^{II}), M'L: metal complex which is kinetically unstable (labile) to dissociate on column
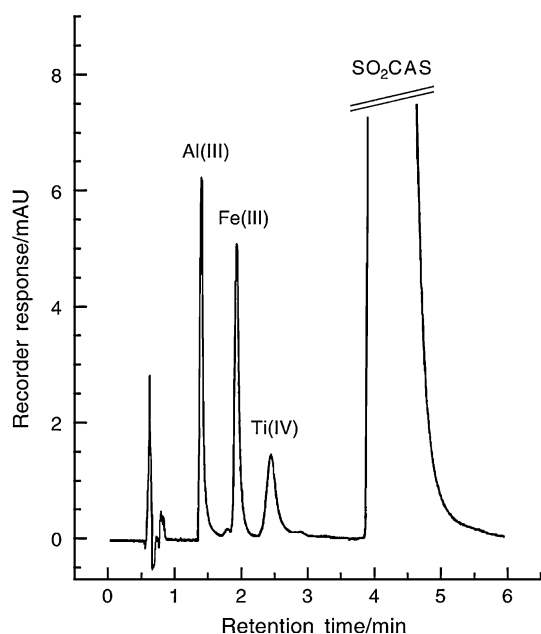
Fig. 10 Typical chromatogram for a sample containing 21 kinds of metal ions. Sample solution: concentration of metal ion, 5×10^{-7} mol dm^{-3} each of Al^{III}, Ba^{II}, Be^{II}, Ca^{II}, Cd^{II}, Co^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Ga^{III}, Hf^{IV}, Hg^{II}, In^{III}, Mg^{II}, Mn^{II}, Mo^{VI}, Ni^{II}, Ti^{IV}, V^{V}, Zn^{II}, and Zr^{IV}; concentration of SO$_2$CAS, 1×10^{-4} mol dm^{-3}; pH, 4.7 (0.01 mol dm^{-3} acetate buffer). Injection volume: 100 mm^3. Mobile phase: MeOH (50 wt%)-water mixture (pH 5.6) containing TBABr (7.0 mmol kg^{-1}), EDTA (0.1 mmol kg^{-1}), and acetate buffer (5.0 mmol kg^{-1}). Column: Chromolith^{TM} Performance RP-18e (4.6 mm i.d. × 100 mm length). Flow rate: 2.5 cm^3 min^{-1}. Detection wavelength: 330 nm

DLs on a 3σ blank basis were 8.8 nmol dm^{-3} (0.24 ng cm^{-3}) for Al^{III}, 7.6 nmol dm^{-3} (0.42 ng cm^{-3}) for Fe^{III}, and 17 nmol dm^{-3} (0.80 ng cm^{-3}) for Ti^{IV}. The practical applicability of the proposed method was checked using river and tap water samples.

Thus, introducing thiacalixarene ligands into RP-HPLC separation field has developed functions—such as selectivity based on kinetic differentiation and highly sensitive detection—with high practicability, suggesting the non-covalent strategy is feasible and a readily achievable approach to enhance selectivity and sensitivity without relying upon extensive synthesis.

Self-assembled formation of luminescence receptor for detection of cationic guests [50]

Energy-transfer, or ligand-sensitized, luminescence of lanthanide(III) (Ln^{III}) complex is Ln^{III}-centered luminescence, where the excitation energy is transferred from the ligand in the T_1 state (Fig. 11). Because of attractive features such as a long emission lifetime, sharp emission bands, emissions at long wavelengths, and a large Stokes
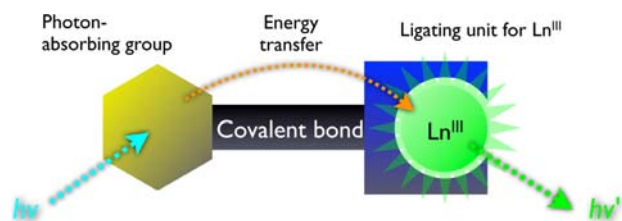

Fig. 11 Covalent strategy for designing ligands suitable to luminescence lanthanide(III) complex

shift, energy-transfer luminescence has been applied to light-emitting diodes [56, 57], displays, optical amplifiers [58], lasers, and bioanalyses [59–61]. To obtain strong emissions with a long lifetime, the ligand design is of key importance. So far, a wide variety of ligands for a luminescent Ln^{III} complex have been derived via the covalent joining of the ligating unit for Ln^{III} to an antenna group to absorb photons (Fig. 11). For the former, the ligand structure is designed to encapsulate Ln^{III} and expel the solvent water molecule responsible for quenching at the first coordination sites. For the latter, chromophores having a suitable T_1 level to excite an f electron at the Ln^{III} center with high efficiency are selected. In this regard, calix[4]-arene is an ideal platform to be O-alkylated with a chromophore and ligating groups to form a cage-shaped coordination environment [62].

In contrast, we have found that the sulfur-bridged calixarenes TCAS and SO$_2$CAS are able to form the 1:1 luminescent complexes Tb$^{III} \cdot$ TCAS and Tb$^{III} \cdot$ SO$_2$CAS, with Tb^{III} ions at a pH around 8.5 and 5.5 via coordination with a bridging group and the two adjacent phenol O$^-$ atoms (Fig. 12) [63]. Each complex exhibits strong luminescence from the $^5D_4$ excited state of the Tb^{III} center; the quantum yield and lifetime were estimated. It should be emphasized that these calixarenes intrinsically have both coordination and light-absorbing groups, which act cooperatively to fulfill the prerequisites of ligands for the luminescent Ln^{III} complex. By using the formation of Tb$^{III} \cdot$ TCAS and Tb$^{III} \cdot$ SO$_2$CAS, the detection of Tb^{III} ion at nano-molar levels was achieved [64]. Hence, TCAS and SO$_2$CAS are
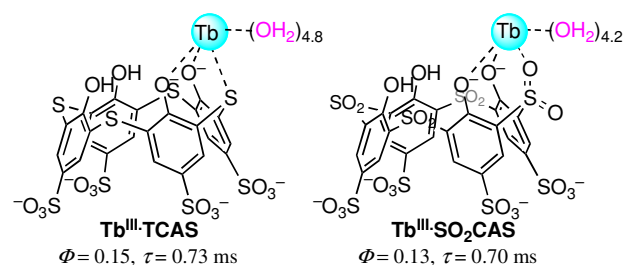

Fig. 12 Structure and photophysical properties of Tb^{III} complexes of TCAS and SO$_2$CAS. Φ: luminescence quantum yield, τ: luminescence lifetime. Each was determined at 25°C under N$_2$ atmosphere

highly promising ligands for energy-transfer luminescence without relying on the covalent strategy.

Since TCAS in the $Tb^{III} \cdot TCAS$ complex should adopt cone conformation by ligation with O^-, S, O^- atoms, it should retain a cone-shaped cavity which may further include certain guest molecules. If so, through the self-assembly of Tb^{III} and thiacalixarene a luminescent host molecule can be obtained without using the covalent strategy. Expecting a strong interaction with negatively charged sulfo groups at the wider rim of TCAS, we chose cationic guest molecules such as 1-ethylpyridinium ($EtPy^+$) and 1-ethylquinolinium (EtQ^+) ions (Fig. 13) to study the dependence of the luminescence intensity for each Tb^{III}-containing host on the guest concentration [50]. For instance, the addition of 10^{-7} M EtQ^+ to a solution of $Tb^{III} \cdot TCAS$ (2×10^{-6} M) caused quenching of the luminescence in accordance with the Stern-Volmer (SV) relationship (Eq. (2), $K_{SV,all} = 6.74 \times 10^6$ M^{-1}) (Fig. 14, open circle).

$$I_0/I - 1 = K_{SV,all}[G] \qquad (2)$$

where I_0 and I are the luminescence intensities in the absence and presence of the guest G respectively, [G] is the guest molarity, and $K_{SV,all}$ is the SV coefficient of the overall luminescence process. The detection limit of EtQ^+ on the basis of $S/N = 3$ was 6.71×10^{-10} M, confirming the high sensitivity of this system. The SV plot obtained with the luminescence lifetime (Fig. 14, closed circle) also showed a linear relation, suggesting a dynamic quenching mechanism of the $Tb^{III} \cdot TCAS$ luminescence by EtQ^+. In particular, the SV coefficient $K_{SV,Tb}$ ($= 6.50 \times 10^6$ M^{-1}) obtained with Eq. (3) was very close to $K_{SV,all}$ obtained with Eq. (2), meaning that quenching was predominantly caused by deactivation of the $^5D_4$ state of the Tb^{III} center.

$$\tau_0/\tau - 1 = K_{SV,Tb}[G] \qquad (3)$$

Here $K_{SV,Tb}$ is a SV coefficient for quenching of the Tb^{III} excited state because τ shows only the lifetime of the excited state. Since the luminescence lifetime of the $Tb^{III} \cdot$ TCAS host in the absence of EtQ^+ was determined to be
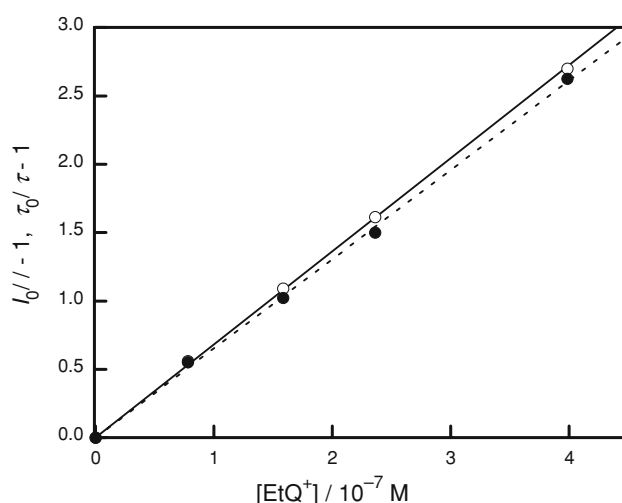

Fig. 14 Stern-Volmer plot for quenching of Tb^{III}-centered luminescence of $Tb^{III} \cdot TCAS$ host by EtQ^+ on the basis of luminescence intensity (open circle) and lifetime (closed circle). Conditions: $[Tb^{III}] = 2.0 \times 10^{-6}$ M, $[TCAS] = 2.0 \times 10^{-6}$ M, [buffer] $= 1.0 \times 10^{-3}$ M, pH 9.2; $\lambda_{ex}/\lambda_{em} = 313/543$ nm

$\tau_0 = 654$ μs, the quenching rate constant of the $^5D_4$ state ($k_{q,Tb}$) can be estimated using Eq. (4) with $k_{q,Tb} = 9.94 \times 10^9$ M^{-1} s^{-1}.

$$k_{q,Tb} = K_{SV,Tb}/\tau_0 \qquad (4)$$

The $k_{q,Tb}$ value indicates that the quenching rate is as fast as the diffusion-limited rate. Thus, the high sensitivity for detection of EtQ^+ with the quenching of the luminescence of $Tb^{III} \cdot TCAS$ owes to the long lifetime of Tb^{III} luminescence and the extremely fast quenching rate. This further suggests that sensitivity of fluorescence sensors on the basis of dynamic quenching is essentially less sensitive than the present system because fluorescence lifetime does not exceed 10^{-9} s and if k_q is as large as the diffusion-controlled rate (10^{10} M^{-1} s^{-1}), K_{SV}, which determines the sensitivity of the fluorescent sensor, should be in the range of 10 M^{-1}.

Fig. 13 Schematic drawing of quenching detection of cationic guest molecules with use of a self-assembled luminescent host $Tb^{III} \cdot TCAS$
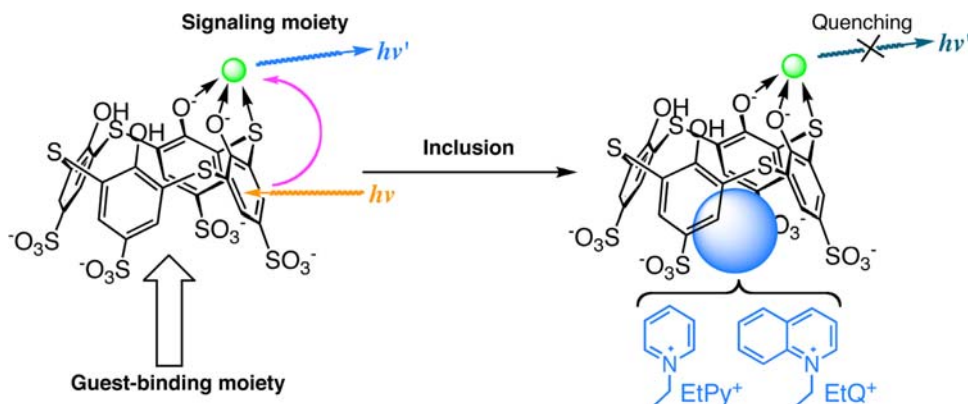
Thus, the self-assembled receptor consisting of Tb^{III} and TCAS was shown to be able to include a quinolinium guest to quench the ligand-sensitized luminescence of Tb^{III} with high sensitivity. Notably, thiacalixarene provides two functions: ligation to Tb^{III} and inclusion of guests (Fig. 13). The former makes it possible to form signal read-out moiety—or luminescent groups—through self-assembly, while the latter is responsible for guest recognition. A recent review on self-assembled fluorescence chemosensors described two types of sensors: a chemosensing ensemble and a template-assisted chemosensor [65]. In the former, a target guest and a reporter are in competition for the host. The displacement of the reporter causes a change in the photophysical properties which lead to the signal read-out. In the latter, the reporter and host self-assemble on a template surface. Upon binding to the host, the guest is held in close proximity to the reporter and may influence its photophysical properties. However, the present $Tb^{III} \cdot TCAS$ is not categorized into these systems because self-assembled $Tb^{III} \cdot TCAS$ has both reporter and host functions. Thus, TCAS is a multifunctional molecule in that it has inherent guest-binding moiety and forms signaling moiety with Tb^{III} in a non-covalent fashion (Fig. 13).

Supramolecular sensing system [51]

As we have seen, one of the most significant contributions of supramolecular chemistry is the development of a covalent strategy to design fluorescent chemosensors with high selectivity and sensitivity for heavy metal ions [2–4]. For instance, a fluorescence ratiometric sensor—where pyrene is attached as a signaling unit to a ligand having N,O donors—has been designed to enable the detection of Ag^{I} ions at micromolar levels in a 50:50 v/v EtOH-water mixture [66]. On the other hand, without use of the covalent strategy, sub-ppp levels of Tb^{III} ions were detected by

formation of the luminescence complex for $Tb^{III} \cdot TCAS$ [64]. As shown in the previous section, the hydrophobic cavity of $Tb^{III} \cdot TCAS$ can be used for detecting a cationic guest molecule. On the other hand, $Tb^{III} \cdot TCAS$ still retains vacant O^-, S, O^- donor sets, which drew our attention to study the interaction of $Tb^{III} \cdot TCAS$ with soft metal ions. Consequently, we found that TCAS, Tb^{III}, and Ag^{I} ions form the luminescent ternary complexes $Ag_2^{I} \cdot Tb_2^{III} \cdot TCAS_2$ and $Ag_2^{I} \cdot Tb^{III} \cdot TCAS_2$ at pHs of around 6 and 10, respectively (Fig. 15) [67]. Interestingly, the complex $Ag_2^{I} \cdot Tb^{III} \cdot TCAS_2$ exhibits Tb^{III}-centered luminescence with an exceptionally long lifetime (4.6 ms) in aqueous solutions. This owes to the absence of coordinating water molecules to Tb^{III} responsible for quenching. Such a coordination environment is constructed by self-assembly of TCAS ligands joined by $S–Ag^{I}–S$ bridges, as proven by the crystal structure of $Ag_4^{I} \cdot Tb^{III} \cdot TCAS_2$ (Fig. 15) [68]. Emphasis should be put on the fact that the components self-assemble to synergistically form a heterogeneous assembly, for which multiple ligating sites of TCAS play the most significant role.

In a Tb^{III}-TCAS binary system, only a small fraction of the Tb^{III} ions is complexed with TCAS at pH 6 because the quantitative formation is accomplished at pHs above 8.5 [63]. This suggests that the presence of the Ag^{I} ion can trigger formation of the ternary complex $Ag_2^{I} \cdot Tb_2^{III} \cdot TCAS_2$, leading to luminescence detection of Ag^{I} at a pH of 6. Accordingly, when $[Tb^{III}]_T = 1.0 \times 10^{-6}$ M and $[TCAS]_T = 2.0 \times 10^{-6}$ M at a pH of 6.1, the dependence of the luminescence intensity at 544 nm—assigned to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{III}—on the Ag^{I} concentration was investigated (Fig. 16) [51]. For a wide range of Ag^{I}, the intensity increases almost linearly as $[Ag^{I}]_T$ increases from the nanomolar to the sub-micromolar levels. This demonstrates that Ag^{I} can be detected with the formation of the ternary complex $Ag_2^{I} \cdot Tb_2^{III} \cdot TCAS_2$. When $[Ag^{I}]_T \leq 2.0 \times 10^{-8}$ M, a linear calibration curve was obtained by least-square fitting as shown in Eq. (5).
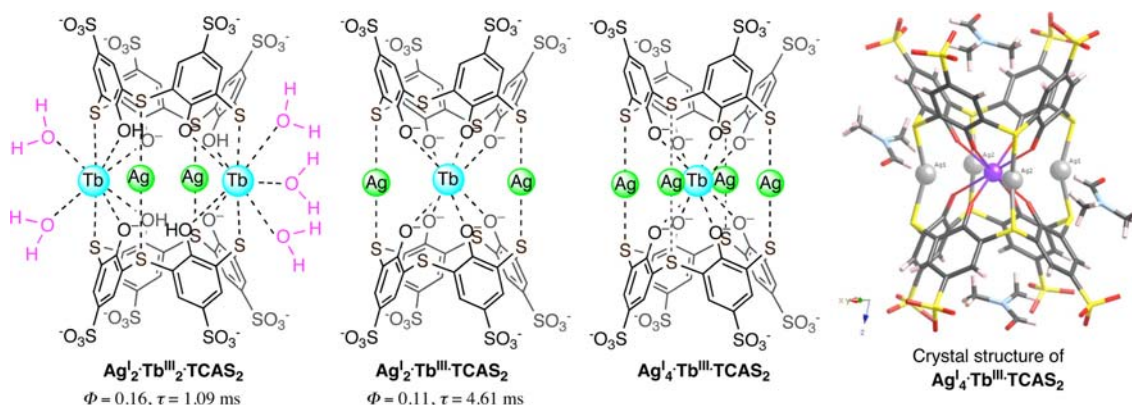

Fig. 15 Schematic drawings of structures of Ag^{I}-Tb^{III}-TCAS ternary luminescent complexes of TCAS

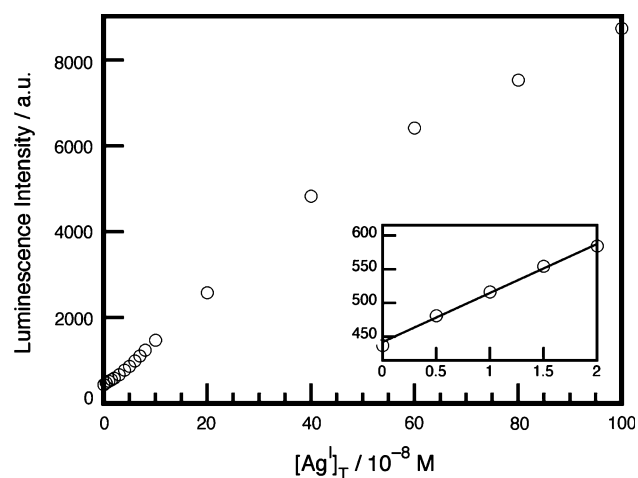**Fig. 16** Calibration graphs for Ag^I ion. The inset shows a calibration curve for a small Ag^I concentration range. Samples: $[Ag^I]_T = 0$–100×10^{-8} M, $[Tb^{III}]_T = 1.0 \times 10^{-6}$ M, $[TCAS]_T = 2.0 \times 10^{-6}$ M, $[MES \ buffer]_T = 2 \times 10^{-3}$ M (pH = 6.11). $\lambda_{ex} = 323$ and $\lambda_{em} = 544$ nm

$$\text{Luminescence intensity} = 76.5 \times 10^8 \times \left([Ag^I]_T / M \right) + 437 \tag{5}$$

Surprisingly, the detection limit (DL) at S/N = 3 was determined to be 3.2×10^{-9} M (0.35 ppb); this shows that the system is more sensitive than the covalently designed fluorescent sensors to be able to allow detection of Ag^I in the 10^{-6} M range [66, 69, 70]. Notably, the DL of Ag^I with $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ is lower than one for flame atomic absorption spectrometry (DL 3 ppb) and as low as inductively coupled plasma atomic emission spectroscopy (DL 0.2 ppb) [71].

In metal-ion sensors designed with the covalent strategy, the roles of each functional group are different (Fig. 1). On the other hand, in the present Ag^I sensing system, it is not obvious which moiety of $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ is responsible for the functions of binding and signaling. As shown in the schematic drawing of $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ (Fig. 15), TCAS has four O and four S donors that form the tetra-metal core $Ag_2^I Tb_2^{III}$. Further, there is an antenna to absorb photons, the energy of which is eventually transferred to the Tb^{III} center. Upon excitation, the Tb^{III} center emits light via the *f-f* transition. From the structural point of view, Tb^{III} ions accept two sets of O^-,S,O^--donations from the TCAS ligands. However, it is important to consider that in the Tb^{III}-TCAS binary system, Tb^{III} does not form a complex with TCAS at a pH of 6. Thus, analyte Ag^I is indispensable in linking two TCAS ligands via S–Ag^I–S bridges to promote the coordination of TCAS to Tb^{III} to form $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$. In fact, TCAS forms the 4:2 complex $Ag_4^I \cdot TCAS_2$ in the binary system with a pH of 6 [67]. In conclusion, multidentate and photon-absorbing TCAS, luminescent Tb^{III}, and analyte Ag^I with linear coordination
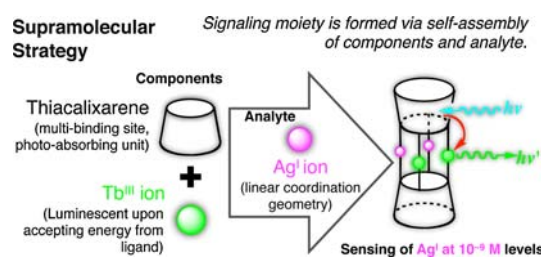

Fig. 17 Schematic drawing of supramolecular sensing system for Ag^I using formation of $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ ternary complex

geometry were synergistically assembled to form a supramolecular structure capable of sensing Ag^I ions at nanomolar levels (Fig. 17). Since the sensing function of this system originates from the supramolecular nature of the complex $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ and not from TCAS and Tb^{III} individually, the complex $Ag_2^I \cdot Tb_2^{III} \cdot TCAS_2$ truly demonstrates the "supramolecular strategy", [65, 72–74].[3] Here, it is very important to rationally design the molecules to form a supramolecular assembly displaying functionalities absent in the individual components.

Non-covalent strategy and multifunctionality of thiacalixarenes

As presented above, thiacalixarene was successfully applied to the separation and pre-concentration of heavy metal ions, the highly selective and sensitive determination of the Ni^{II} ion in the KD-HPLC scheme, luminescence-quenching detection of cationic guest molecules, and the supramolecular sensing of Ag^I. Because the functions derived from thiacalixarene are so diverse, thiacalixarene can be said to be truly multifunctional. Notably, this multifunctionality is activated not by the covalent attachment of functional groups but by the non-covalent combination of thiacalixarene with a field or other components. Moreover, such combinations are enabled by the synergy of functional groups inherent in thiacalixarenes such as bridging sulfurs, phenolic oxygens, phenyl groups, hydrophobic cavity, and anchoring groups. In this sense also, thiacalixarene is multifunctional. Emphasis should be put on the fact that the functionality of the total system consisting of thiacalixarene and the chemical field or components is beyond that of each component, exemplified by the four systems. Thus, the functions of systems derived from the non-covalent approach emerge in a non-linear fashion simply described by the mathematical formulation:

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[3] Examples of supramolecular sensing systems can be found in these reviews. Caution should be paid to the fact that many of the key components used in supramolecular sensing systems are designed by covalent strategy.

$$f(\text{whole system}) > f(\text{thiacalixarene}) + f(\text{field}) \\ + f(\text{component}) \tag{6}$$

where $f(x)$ denotes the chemical function of x. The selection of other fields and components to combine with thiacalixarene is full of possibilities, suggesting that the non-covalent strategy is ready for implementation. At the same time, it is challenging to rationally design a molecular platform—suitable for the non-covalent strategy to activate a higher functionality than mere chemical recognition—to surpass thiacalixarene.

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