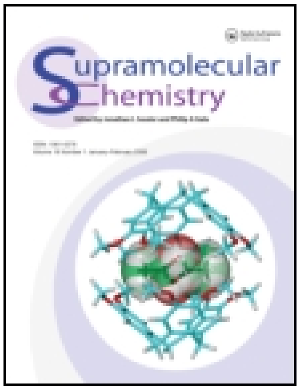

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Designing strategies for supramolecular luminescent complex of lanthanide-heterometal assembly

Nobuhiko Iki [a]

[a] Graduate School of Environmental Studies, Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai, 980-8579, Japan

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Designing strategies for supramolecular luminescent complex of lanthanide–heterometal assembly

Nobuhiko Iki*

Graduate School of Environmental Studies, Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan

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Luminescent complexes consisting of lanthanide, heterometal and ligands can provide supramolecular functions such as extended luminescent lifetime, near-infrared emission and sensing, which result from the heterometal assembly and cannot be realised with a lanthanide homonuclear complex. In this article, kinetic and thermodynamic strategies to construct such supramolecular complexes are reviewed. The kinetic strategy owes to the kinetic inertness of the intermediary homonuclear complex, but allows use of a wide variety of di- or multitopic ligands including relatively simple ones. On the other hand, the ligand used in the thermodynamic strategy so far has been designed with covalent joining of the selective binding sites as exemplified by the highly sophisticated triple-helical complexes. With the view of avoiding elaborate synthesis of ligands in the thermodynamic strategy, supramolecular functional complexes consisting of thiacalixarene, Ag^I and lanthanide are described, suggesting the possibility of a small simple ligand to serve as a building block in the thermodynamically obtained supramolecular complex.

Keywords: supramolecular complex; lanthanide luminescence; heterometal assembly; thiacalixarene

Introduction

In the last two decades, sensitised luminescence of the lanthanide (Ln) complex has attracted increasing attention of scientists in coordination, supramolecular, analytical and materials chemistry because of its characteristic features such as emission in the visible to near-infrared (NIR) region, large Stokes shift, sharp emission band and long luminescence lifetime (*1–4*). From the practical point of view, these features are advantageous to be applied to highly efficient luminescence labels for biomolecules (*5–8*) and materials (*9–15*). For instance, the long lifetime allows time-resolved detection of biomolecules labelled with a Ln complex by differentiating the long-lived emission signal from the background fluorescence and the scattered light with short lifetimes. The time-resolved detection thus leads to highly sensitive immunoassay and bioimaging with high signal/noise ratio. In the wavelength domain, shifting the emission wavelength from the visible to NIR region is also advantageous not only because of the feasibility in spectral resolution of the emission from the excitation bands but also of the ability to transmit deeply into biotissues. With increasing attention to the potential applicability of these luminescent functions to highly precise biomeasurement and high-performance luminescent materials, the target of leading researches in this area has clearly shifted from the mere synthesis of ligands by covalently joining a Ln-binding moiety and an antenna chromophore to construction of a heteronuclear supramolecular complex via designing of a sophisticated ditopic ligand-enabling recognition of Ln and secondary metal ions such as d-block (M) and another f-block lanthanide ions (Ln′) (*1–3*, *16–19*). The scope of this mini-review is to describe the designing strategies adopted in the recent development of luminescent heterometal complexes to lead to the emergence of supramolecular functions, such as controlled luminescence lifetimes, NIR emission, energy migration and sensing of ions, surpassing the ones obtained with conventional Ln–ligand binary systems. The strategy dealt with ranges from the kinetic stepwise to thermodynamic single-step ones (Figure 1) including the simplified approach using thiacalixarene, shedding light on the possibility of a simple building block to avoid the covalent, elaborate design in the thermodynamic strategy.

Kinetic strategy

Unlike the case of a luminescent complex containing only one kind of Ln ion, preparation of a supramolecular Ln–heterometal complex requires distinction of two kinds of metal ions, which are accommodated in two or more different

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*Email: iki@m.tohoku.ac.jp

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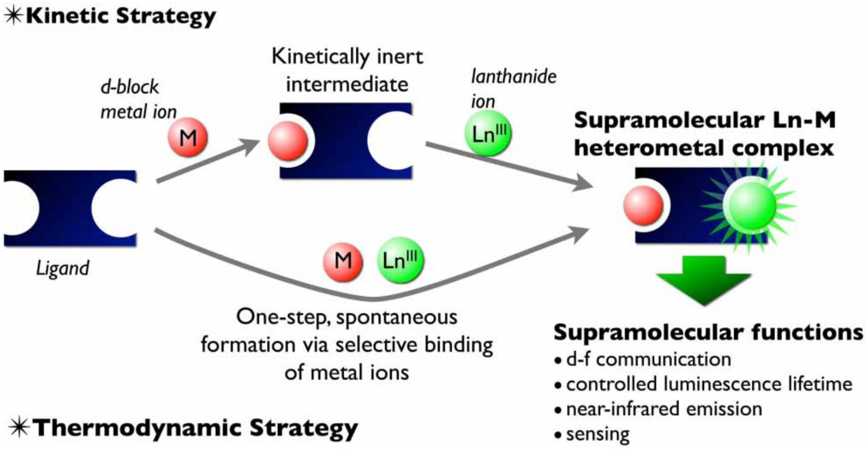
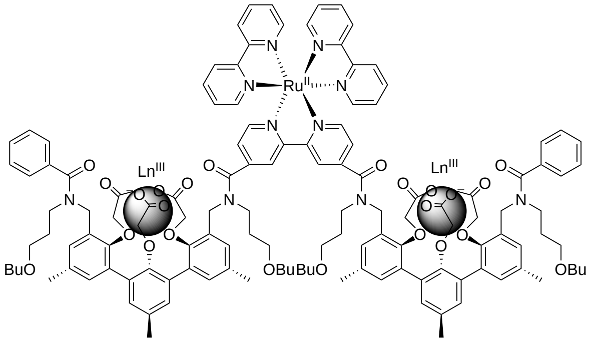


Figure 1. Schematic illustration of kinetic and thermodynamic strategies for the construction of a supramolecular luminescent lanthanide–heterometal complex.

sites in a ligand at the same time. Design of such coordination system has been realised by two different strategies: kinetic and thermodynamic ones (Figure 1). In this review, we first look at some successful examples adopting the kinetic strategy and then move onto the thermodynamic one.

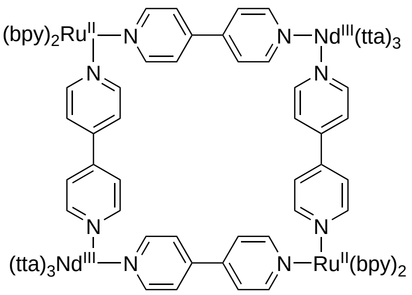
The kinetic strategy relies on the stepwise construction of the supramolecular complex. First, a homonuclear metal complex is formed as a precursor, followed by the reaction with secondary metal ions to form the supramolecular complex. Here, the incoming metal ion should not replace the metal ion already existing in the precursor. Hence, the precursor should be kinetically inert. Usually, hexacoordinate complex of a d^6 metal ion with an α-diimine ligand, square-planar complex of a d^8 metal ion and Ln complexes with a multidentate ligand are known to have sufficient kinetic stability, which are then used as a precursor to bind to the secondary metal ion.

The first example of luminescent complexes of Ln sensitised by the d-block metal complex was reported by van Veggel et al. (*20*, *21*). The ligand (**L1**) consists of a 2,2′-bipyridine (bpy) unit for binding to Ru^{II} and two units of a *m*-terphenyl-based ligand for Ln^{III}. The ligand **L1** was first reacted with Nd or Yb to form the kinetically stable precursor [Ln$_2$**L1**] via ligation of the three carboxymethoxy moieties of the *m*-phenylene moiety, and then with [Ru(bpy)$_2$Cl$_2$] by replacing the Cl$^-$ with the vacant bpy moiety of [Ln$_2$**L1**] to form the ternary complex [RuLn$_2$**L1**]$^{2+}$(**1**). The complex emits NIR light upon excitation at 450 nm of the ^{1}MLCT band of [Ru(bpy)$_3$]$^{2+}$. Scrutiny of the luminescent properties of the [Ru(bpy)$_3$]$^{2+}$ unit allowed determination of the sensitisation process to be through energy transfer from the ^{3}MLCT state to the lanthanide centre. Thus, it has been shown that introducing a d-block metal complex as a sensitiser into a Ln complex is a useful way to excite the Ln centre by visible light to obtain NIR luminescence.



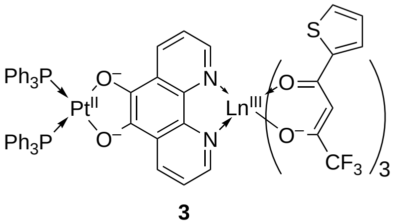
1 [RuLn$_2$**L1**]$^{2+}$

The preparation of NIR-emissive [RuLn$_2$**L1**]$^{2+}$ greatly owes to the design of the ligand **L1** obtained by covalent joining of the Ln- and Ru-binding moieties, which was implemented via elaborate multistep synthesis. By contrast, a more simple and straightforward preparation of the Ln–Ru heterometal complex exhibiting NIR light has been realised by self-assembly of a kinetically inert precursor [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ with Ln(tta)$_3$ (tta = thenoyltrifluoroacetone) in a 2:2 ratio through the coordination of one of 4,4′-bpy nitrogen to the Ln centre (Ln = Nd, Yb) (*22*). The resulting complex **2** has a unique square-shaped structure and emits NIR light upon excitation at 420 nm. The success in preparation of such Ln–Ru heterometal assembly strongly suggests the versatility of the stepwise construction using a kinetically inert precursor as the building units.



2

Ward et al. (*18*, *23*, *24*) showed the usefulness of a Pt^{II}-based antenna unit in the stepwise construction of NIR-emissive dinuclear complexes. A ditopic ligand such as 5,6-dihydroxy-1,10-phenanthroline and 2,3-bis(2-pyridyl)pyrazine is first reacted with Pt to obtain the kinetically inert precursor, 'complexes as ligand' as they say, which then is reacted with $[Ln(dik)_3]$ luminophores (dik = 1,3-diketonato) by coordination with the vacant α-diimine unit to the Ln centre to afford the dinuclear complexes **3** and **4**. In each complex, excitation into the Pt-centred absorption band results in characteristic NIR luminescence from the Nd, Yb or Er centres.



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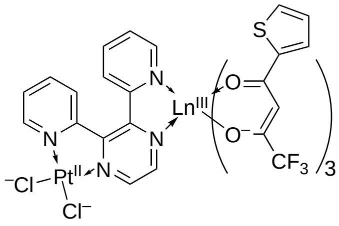
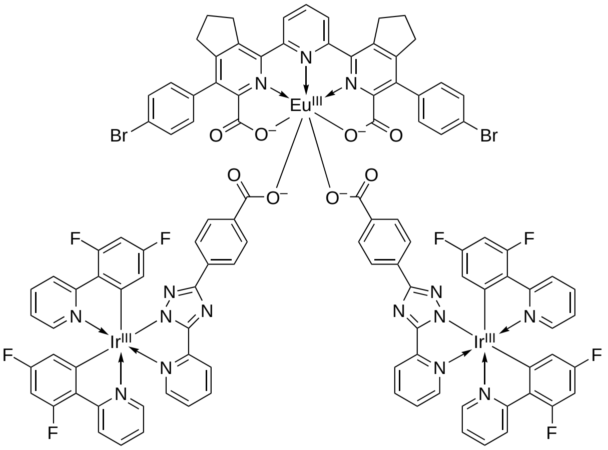


4

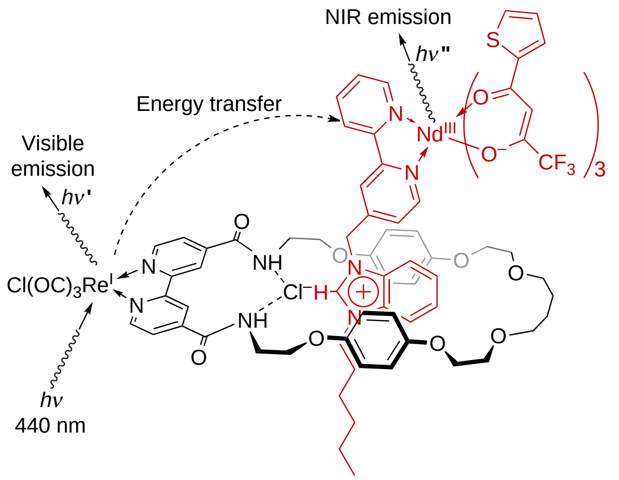
Owing to the kinetic inertness and luminescent properties akin to $[Ru(bpy)_3]^{2+}$, d^6 metal complexes of Ir^{III} and Re^{I} with the α-diimine(like) ligand have also been used as the antenna moiety. For instance, mixed d–f complexes consisting of $[Re(CO)_3Cl(\alpha\text{-diimine})]$ and $[Ln(dik)_3]$ were prepared in the same 'complexing ligand' + luminophore fashion (*25*). An Ir precursor analogous to luminescent $[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) having a carboxyphenyl group is preformed and mixed with an Eu-terpyridine-based complex giving an adduct complex (**5**), in which the carboxy group unidentately coordinates to the Eu centre (*26*). Interestingly, the Ir centre emits blue-green light, the energy of which is high enough to be transferred to the low-lying excitation state ($^5D_0$) of the Eu centre to emit red light. The dual emission results in exhibition of white light, which greatly owes to the supramolecular nature of the Ir–Eu heteronuclear complex formed by the assembly of kinetically inert building units.



5

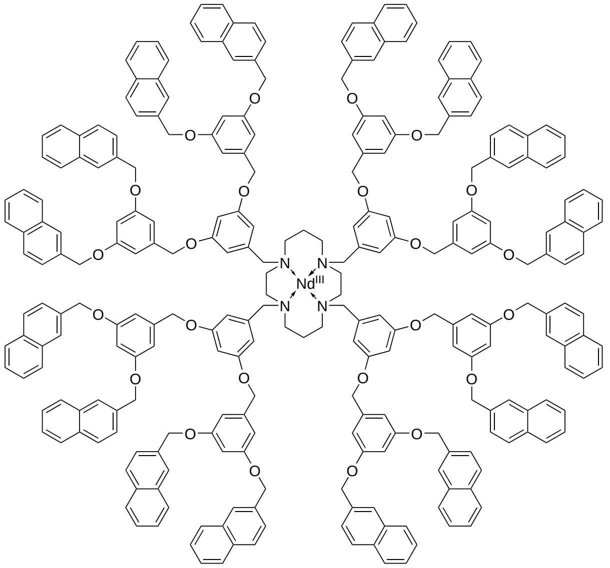
In supramolecular chemistry, rotaxane and dendrimer are one of the typical molecular motifs with functionalities such as switching (*27*, *28*) and light harvesting (*29*), respectively. There have been attempts to adopt these motifs to lanthanide–heterometal luminescent complexes. For instance, a [2]pseudorotaxane **6** facilitating through-space energy transfer from antenna Re^{I}-complex to Nd^{III} centre has been reported (*30*). The Re centre is coordinated by a bpy derived with a macrocycle, the N–H protons of which are hydrogen bonded to a Cl^- ion associated with a benzimidazolium moiety of the Nd complex to form a rotaxane-like structure. Interestingly, the Re and Nd centres are not bridged by a single ligand, but are brought together through the formation of [2]pseudorotaxane. The formation is signalled via sensitised NIR emission from the Nd, showing that even such non-coordinative interaction can be used to realise d–f communication.

Formation of a supramolecular associate, as well as the NIR emission function, between Nd^{III}-dendrimer **7** and



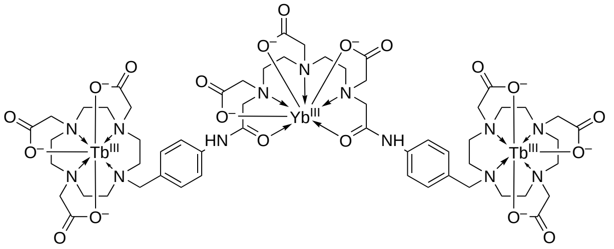
6

$[Ru(bpy)_2(CN)_2]$ has been recently exemplified (*31*). The dendrimer ligand consists of a cyclam core having 12 dimethoxybenzene and 16 naphthyl units. Although the dendrimer can act as a light-harvesting antenna, the Nd-dendrimer **7** is unable to emit NIR light by itself. In the presence of $[Ru(bpy)_2(CN)_2]$, however, the CN^- nitrogen coordinates to the Nd centre to form the supramolecular assembly, in which the harvested energy is once transferred to the ^{1}MLCT state of $[Ru(bpy)_2(CN)_2]$ and further transferred to the Nd centre via the ^{3}MLCT state to result in the emission of NIR light from the Nd centre. Thus, self-assembly of the simple Ru complex with Nd-dendrimer **7** produced a new function, NIR emission sensitised by the dendrimer.



7

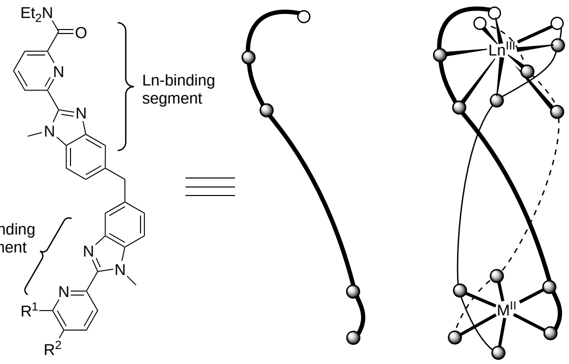
If the Ln-containing precursor is kinetically stable enough, a site-specific Ln–Ln′ heterometal complex can also be obtained without the formation of unwanted Ln_2 and Ln'_2 homo–dinuclear complexes and a Ln′–Ln site-confused complex to open the way to study and utilise the f–f communication. By virtue of the high kinetic stability of the Ln complex with a DOTA-like macrocyclic ligand (DOTA = 1,4,7,10-tetraaza-cyclododecane-*N*, *N*′, *N*″, *N*‴-tetraacetic acid), the first successful example of the Tb–Yb heteronuclear complex has been reported by Faulkner and Pope (*32*). The Tb-macrocycle precursor having an amino group is covalently attached to two distal carboxy groups of 1,1,4,7,7-diethylenetriamine pentaacetic acid (DTPA) to form diterbium(III) intermediate, which was then reacted with $Yb(CF_3SO_3)_3$ to accommodate Yb in the DTPA moiety to afford the Tb_2Yb complex **8**. Irradiation of the absorption band of Tb at 488 nm resulted in the observation of Yb-centred NIR emission at 980 nm, showing the first example of energy transfer from the Tb centre to Yb. Usefulness of the Ln–DOTA motifs for the stepwise construction of the Ln–Ln′ heterolanthanide complex has been further exemplified with EuTb (*33*), $EuTb_2$ (*34*), Nd_2Yb_2 (*35*) and TbYb (*36*) heterometal systems exhibiting supramolecular functions such as f–f energy transfer and dual luminescence.



8

Thermodynamic strategy

In the thermodynamic strategy, a mixture of Ln, M and ligand spontaneously and eventually gives the supramolecular complex with a desired structure. Practically speaking, this step is easy to implement, but the greatest issue is to design the ligand capable of precise differentiation of the metal ions with two different binding sites. In theory, such binding sites could be designed by considering the properties of metal ions such as hard/soft nature, ionic radius, coordination number and charge of the metal ion. However, the number of studies adopting the thermodynamic strategy less than that of the kinetic one suggests the difficulty of the thermodynamic strategy. So far, the most successful examples of this strategy have been reported by the group of Piguet and Bünzli (*37–42*). With an intention to add structural and synthetic flexibility of the ligand as well as ability of fine-tuning of the complexation properties towards Ln, they constructed a tripodal spacer of the ligand by using an octahedral complex of d-block metal ions. The designed ligands **L2** and **L3** have a segment structure consisting of an α-diimine moiety for the d-block metal ion and an *O*,*N*,*N*-tridentate segment for Ln binding (*37*, *38*). Mixing of the components spontaneously gives the triple-helical complex $[\mathrm{MLn}\mathbf{L2}_3]^{5+}$(**9**) in solution ($\mathrm{Ln} = \mathrm{La^{III}}{-}\mathrm{Lu^{III}}$, $\mathrm{M} = \mathrm{Fe^{II}}, \mathrm{Zn^{II}}$). The solid-state structure of $[\mathrm{ZnLn}\mathbf{L2}_3]^{5+}$ shows that the Zn centre is in a pseudo-octahedral coordination environment and Ln is in a pseudo-tricapped trigonal-prismatic one (*39*). It can be said that the presence of Zn is essential to bring three ligands to provide Ln a pre-organised coordination environment to result in high thermodynamic stability of the complex.



L2 : R^1 = H, R^2 = CH_3
L3 : R^1 = CH_3, R^2 = H

● : N
○ : O

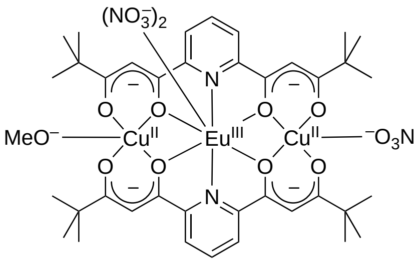
9 $[\mathrm{MLnL_3}]^{n+}$
(L = **L2** or **L3**)

As a supramolecular function, d–f communication was found in the $\mathrm{Eu^{III}}{-}\mathrm{Fe^{II}}$ complex systems (*38*, *40*). In the complex $[\mathrm{EuFe}\mathbf{L2}_3]^{5+}$, the emission from Eu is completely quenched via energy transfer from $\mathrm{Eu^{III}}$ to $\mathrm{Fe^{II}}$ caused by overlapping of the broad and intense $\mathrm{Fe^{II}}$-centred $^1\mathrm{MLCT} \leftarrow {}^1\mathrm{A}_1$ absorption with $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_j$ emission of Eu. On the other hand, the luminescence of Eu remains in the case of $[\mathrm{EuFe}\mathbf{L3}_3]^{5+}$, in which $\mathrm{Fe^{II}}$ adopts a high spin $^5\mathrm{T}_2$ electronic ground state configuration to reduce the spectral overlap. The structural difference between the ligands **L2** and **L3** only exists in the α-diimine moiety, suggesting that the fine-tuning of the coordination environment of the $\mathrm{Fe^{II}}$ influences the spin state to control the quenching of Eu-centred emission.

With the view of application to time-resolved NIR luminescence detection, the $[\mathrm{CrYb}\mathbf{L2}_3]^{6+}$ complex is noteworthy to show controllability of the lifetime of Yb-centred luminescence in the NIR region (*41*). Unlike the $\mathrm{Zn^{II}}$ and $\mathrm{Fe^{II}}$ ions, $\mathrm{Cr^{III}}$ is kinetically inert, which may end up with several kinetically stable intermediary species. To circumvent such inconvenience, they employed kinetically labile $\mathrm{Cr^{II}}$ at the initial step of the formation of the triple helix, followed by the oxidation of $\mathrm{Cr^{II}}$ to $\mathrm{Cr^{III}}$. The excitation of the $[\mathrm{Cr}(\alpha\text{-diimine})_3]^{3+}$ chromophore of the triple helix with visible light results in NIR emission with a lifetime $\tau = 1.96$ ms. Since the intrinsic lifetime of the excited state of $\mathrm{Yb^{III}}$ is 20 μs, the lifetime of NIR emission from the Yb centre of $[\mathrm{CrYb}\mathbf{L2}_3]^{6+}$ increases by two orders. This results from the slower rate of energy transfer from $\mathrm{Cr^{III}}$ to $\mathrm{Yb^{III}}$ ($2.4 \times 10^2\,\mathrm{s^{-1}}$) than the intrinsic deactivation rate of $\mathrm{Yb^{III}}$ ($5 \times 10^4\,\mathrm{s^{-1}}$). The helical heterometal complex thus obtained shows not only NIR emission but also an increase in the lifetime, which cannot be realised by any conventional Yb–organic ligand complex. The controllability of the lifetime is truly one of the supramolecular functions originating from the synergy of Ln, M and the neatly designed segmental ligand. They further pursue the helical complex towards a Ln–Ln′ heterolanthanide system with the expectation of f–f communication (*42*). However, the discrimination of the lanthanides with the segmental ligand in a thermodynamically controlled fashion is still insufficient to yield mixtures of homo- and heterolanthanide complexes.

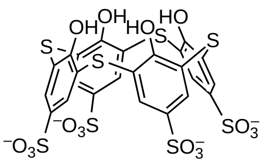
Towards a simpler ligand design in the thermodynamic strategy

As shown above, the segmental ligand has succeeded in the formation of a structurally defined triple-helical complex having the supramolecular function originating from the d–f intermetallic communication. The greatest part of the function owes to the programme embedded in the ligand, the design of which still relies on the covalent joining of functional segments. As compared to the simplicity of ligands employed in the kinetic stepwise strategy to obtain complexes such as **2**–**4**, the segmental ligands are rather intricate and therefore require elaborate multistep synthesis. A question arises whether any simpler ligands are able to form a luminescent Ln–M heterometal complex in a single step. Recently, there have been reported some examples using fairly simple molecules for the construction of the heterometal complexes. For example, Hasegawa et al. (*43*) reported a luminescent $\mathrm{Eu^{III}}{-}\mathrm{Cu^{II}}$ heteronuclear complex **10** spontaneously formed with a relatively simple molecular motif, 2,6-(acetoacetyl)pyridine. In the complex, each acetoacetyl moiety is linked by $\mathrm{Cu^{II}}$ to form a cryptate-like ligand to coordinate to the Eu centre with a pyridyl moiety. Because of the high Lewis acidity of the Eu centre, the adjacent O atom weakly coordinated to the Cu centre to result in the red shift of the d–d band. This makes the efficiency of Eu → Cu energy migration low to enable Eu-centred emission (luminescence quantum yield $\Phi = 2.2 \times 10^{-6}$, lifetime $\tau = 9.4 \times 10^{-2}$ ms in DMF). This has demonstrated that a relatively simple tritopic ligand can serve as a building block to thermodynamically form a Ln–M heterometal complex. Other simple ditopic ligands such as isonicotinate are shown to form multidimensional infinite metal-organic frameworks with M and Ln ions (*44*–*46*), although the primary purpose of these studies is on the formation of a porous structure in the solid state rather than luminescent functions in the solution state. These suggest that there remains a great possibility to construct a luminescent heteronuclear complex through a one-step thermodynamic assembly of a small, simple ligand.

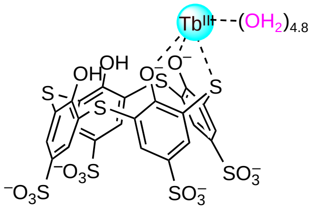


10

In the field of calixarene chemistry, it seems to be a common notion that introduction of ligating groups and/or chromophore to the calixarene skeleton is essential to construct the luminescent Ln complex (*47*), which is one of the typical examples of the covalent strategy. There are only a few exceptions; Tb^{III} complexes of calix[*n*]arene-*p*-sulphonates ($n = 4$, 6, 8) reported by Shinkai et al. (*48*), and lanthanide complexes of *p*-*tert*-butylcalix[*n*]arenes ($n = 5$, 8) (*49–51*) and of *p*-nitrocalix[8]arene by Bünzli and Ihringer (*52*), where the phenolic O$^-$ serves as the binding site and the aromatic moiety as the chromophore. Since we found a facile one-step method to prepare thiacalixarene (*53*, *54*), we have studied the function as a host molecule and a ligand (*55–57*). During the course of studying the complexation ability of thiacalix[4]arene-*p*-sulphonate (TCAS) to metal ions, we found sensitised luminescence of the Tb^{III} complex (**11**) in aqueous solutions (*58*). Unlike the classical calix[4]arene-*p*-sulphonate, TCAS provides not only phenolic O$^-$ but also the bridging S to Tb.

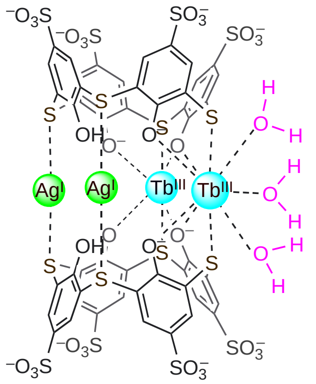


TCAS



11

Since the TCAS has O$_4$S$_4$ donor sets, the complex **11** still has vacant coordination sites which seem to retain coordination ability. In particular, the bridging S should have high affinity towards the soft Ag^I ion, which led to an idea to add the Ag^I ion to the binary system. As a result, the Ag$_2$·Tb$_2$·TCAS$_2$ complex (**12**) forms in aqueous solutions at pH around 6 (*59*). Moreover, in the presence of 20-fold excess of Ag^I and 50-fold excess of TCAS to Tb at pH 10, Ag$_2$·Tb·TCAS$_2$ (**13**) forms as a main luminescent species. The structure of **12** and **13** has been proposed; two TCAS ligands are linked by two S–Ag^I–S linkages to adopt a double-cone structure. Furthermore, each Tb ion of **12** accepts O$^-$,S,O$^-$ donation. By contrast, the Tb centre of **13** only accepts 8-fold O$^-$ donation. The photophysical properties of complexes **11**–**13** have been determined in H$_2$O. The luminescence quantum yield of **12** ($\Phi = 0.16$) is as large as that of **11** ($\Phi = 0.15$), but the luminescence lifetime τ ($= 1.09$ ms) is larger than that of **11** ($\tau = 0.73$ ms). For complex **13**, the yield Φ ($= 0.11$) is smaller, attributed to the low efficiency of photosensitisation ($\eta = 0.11$). By contrast, the τ value is exceptionally large (4.61 ms in H$_2$O!), which owes to the absence of coordinating water in **13** ($q = 0.1$). This is compatible with the proposed structure of **13**: Tb centre is shielded by a supramolecular cage of **13** to expel coordinated water responsible for quenching.



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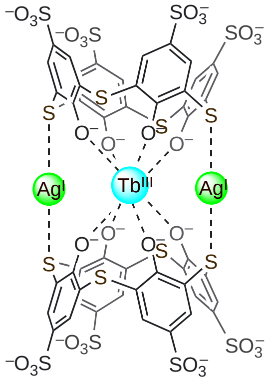
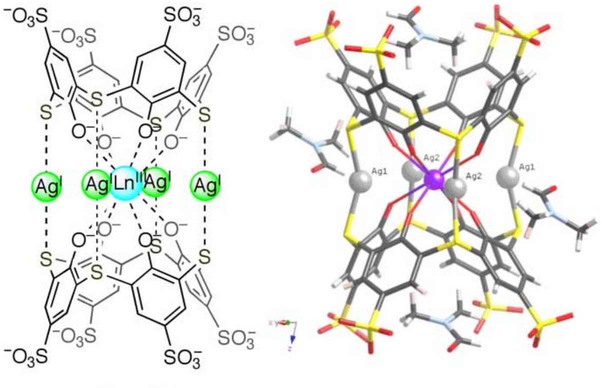


13

In an attempt to isolate single crystals of **13** to prove the structure, we obtained ones of Ag$_4$·Tb·TCAS$_2$ (**14**) showing the double-cone structure formed with four instead of two S–Ag–S bridges, which supports the relevance of the proposed structure of **13** (*60*). Interestingly, the Tb ion is in O_8-cubic coordination geometry to be shielded from quenchable water molecules. This strongly suggests that the long lifetime of Tb emission in complex **13** results from the coordination environment identical to that of **14**. Taking advantages of the spontaneous formation of the O_8-cubic coordination, we recently studied the Ag–Nd–TCAS ternary system to show that $Ag_4 \cdot Nd \cdot TCAS_2$ (**15**) was formed in aqueous solutions and that the solid-state structure was isomorphous to **14** (*61*). The complex showed NIR luminescence upon irradiation of UV light with a quantum yield of 4.8×10^{-4} (in H_2O), which is quite large for NIR emission of Nd in aqueous solutions (*62*). As supramolecular functions, thus, long-lifetime emission from Tb and NIR emission from Nd centres in aqueous solution are obtained through the formation of the supramolecular cage to shield the Ln centre. Although these originated from the synergistic effect of the components, Tb, Ag and TCAS, the most important role was played by TCAS to sharply distinguish the two different metal ions by providing different ligating atoms on the basis of hard and soft selectivity to lead to the double-cone structure as well as the O_8-cubic coordination environment.



14 (Ln = Tb)
15 (Ln = Nd)

Crystal structure of **14**

The Ag–Tb–TCAS ternary system also gives another supramolecular function, highly sensitive detection of Ag^I (*63*). As mentioned above, ternary complex **12** forms at pH 6, while in the absence of Ag, the binary system does not give luminescent complex **11** at the same pH. This in turn means that the components Tb and TCAS should give the ternary complex **12** in accordance with the amount of Ag coexisting in the solution. As expected, the luminescence intensity from **12** increases as the concentration of Ag increases. Surprisingly, the detection limit of Ag^I at $S/N = 3$ is 3.2×10^{-9} M (0.35 ppb), showing that the system is more sensitive than the covalently designed fluorescent sensors to afford detection of Ag^I in the 10^{-6} M range (*64–66*). In addition to the large difference in the sensitivity, there is a fundamental difference between the Ag–Tb–TCAS sensing system and the fluorescent sensors. In a usual fluorescent metal-ion sensor designed with the covalent strategy, metal-binding moiety and signalling moiety, i.e. fluorophore, are covalently connected to exhibit the function through read-out of the change in the fluorescent property upon binding to the analyte ion. Thus, the detection functionality is programmed in the sensor structure. On the other hand, in the present Ag^I sensing system, the signalling moiety cannot be found in the components themselves (free Tb^{III} and TCAS), but was spontaneously formed in the presence of the analyte Ag^I. Therefore, the detection function of the ternary system is beyond the sum of functions of the components, endorsing the supramolecular ('beyond' molecule) nature of the system. Thus, TCAS has demonstrated that relatively simple ligands can thermodynamically form Ln–M heterometal complexes possessing a variety of supramolecular functions.

Conclusion

In this article, we have shown that the Ln–M–ligand ternary system can provide supramolecular functionalities such as NIR emission, long-emission lifetime and sensing, which are not obtained with Ln–ligand binary systems. In the kinetic strategy, the supramolecular complexes can be obtained by taking advantages of the kinetic stability of the intermediary homonuclear complex, which then reacted with the heterometal ion. This makes the molecular design of the ditopic ligand to be simple to avoid covalent, elaborate synthesis. Given the kinetic inertness of the intermediate, the combination of Ln, M and ligand is almost unlimited to show the versatility of the strategy. On the other hand, in the thermodynamic strategy, the mixing of the components spontaneously gives a thermodynamically stable ternary complex via differentiating the metal ions with the coordination sites of the ligand. In this strategy particularly, the key factor to determine the formation and function of the supramolecular complex is the ligand, so that it forms a supramolecular assembly displaying functionalities that are absent in the individual. One successful structural motif was provided by the rational design of the segmental ligands to form the triple-helical Ln–M complex, the function of which has been programmed in the ligand structure. In this sense, the thermodynamic strategy seems to require covalent design of the ligand to connect relevant functional groups to end up with complicated ligand design. However, the multifunctionality of TCAS emerging in the supramolecular complexes strongly suggests that a simple ligand can potentially give supramolecular complexes in the thermodynamic strategy. The challenge in this strategy is to seek such simple ligand having multitopic coordination sites with an ability to strictly distinguish M and Ln as well as with appropriate orientations to spontaneously construct the supramolecular complex.

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