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Innovative Multipodal Ligands Derived from Tröger's Bases for the Sensitization of Lanthanide(III) Luminescence

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To An, in loving memory

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Abstract: We describe the synthesis and characterization of the first family of multipodal ligands with a Tröger's base framework designed for the preparation of luminescent lanthanide(III) complexes. Eight ligands were designed and synthesized using different strategies, including alkylation reactions, amide couplings and Ugi multicomponent reactions. All ligands bear carboxylate groups for the coordination of the lanthanide(III) ion, with lanthanide(III) sensitizing units consisting of the Tröger's base framework itself or attached benzamides. Upon irradiation of the chromophoric ligands, the green terbium(III) emission was efficiently generated, whereas the europium(III) emission signal was negligible. The geometry and the substitution pattern of the ligands allow the control of the stoichiometry of the species formed and the Tb(III) luminescence sensitization efficiency, showing that *para*–substitution patterns are more efficient than *meta*–substitution ones for the formation of coordination compounds with lower Tb(III)/ligand ratio. We propose that the formed species are self–assembled 2:2 or 2:4 metallosupramolecular structures.

Introduction

Research in the field of luminescent lanthanide(III) complexes is in constant growth, driven by their remarkable and unmatched optical and magnetic properties. The narrow emission bands in the visible region of the electromagnetic spectrum of several lanthanide(III) ions (Ln[III]), such as europium(III) or terbium(III) combined with the large energy difference between excitation and emission bands and long luminescence lifetimes, are unique advantages in various fields of research such as the design of sensors, probes or light emitting devices, among others.[1–3]

Due to the extremely low light absorption of free Ln[III] ions as a result of the forbidden nature of most of f–f transitions, it is essential to create suitably functionalized ligands that ensure both coordination of Ln[III] ions and the sensitization of their emission by the so–called "antenna effect", in order to emit a sufficient number of photons to allow their use in the desired applications.[4–6]

In addition, luminescent Ln[III] ions need to be protected from the environment in order for their excited states not to be deactivated by overtones of –OH, –NH and –CH vibrations which would result in a significant decrease of their emission intensity.[7] One pertinent strategy to achieve this goal is by using ligand systems that will achieve the complete coordination of the Ln[III] ions, preventing the binding of solvent molecules such as water to the Ln[III]. In this work, flexible podand ligands were designed, synthetized and derivatized to orient their binding units around the Ln[III] ion, coordinating it efficiently and thus protecting it from their chemical environment.[1,6,8–14]

Podands possess the advantages of synthetic accessibility and versatility, and have been used for the grafting of functionalized pendant arms onto a convenient framework such as a small aromatic ring, in a similar fashion to the attachment to macrocycles such as cyclen derivatives or calixarenes.[4,5,14,15] In view of the eight or larger number of coordination sites of Ln[III] ions, this strategy is particularly suitable for the design of ligands with bidentate or tridentate pendant arms, as required for the complete and efficient coordination of Ln[III] ions.

The efficiency of the luminescence sensitization process depends on multiple factors, starting with the light absorption of the ligand followed by an adequate intersystem crossing path to

populate the triplet state centered on the organic chromophore, the most common feeding level from which the energy is transferred to the accepting electronic level of the Ln^{III} ion. The consideration of the energy of the triplet state, the distance between the antenna and the Ln^{III} ion as well as the multiple potential quenching processes and paths are crucial in the design of a Ln^{III} complex. In particular, according to the empirical rules established mainly for the complexes formed with visible-emitting Eu(III) and Tb(III) ions, the energy of the triplet state of the ligand should be located between 2500 and 4000 cm^{-1} above the lowest emitting level of the Ln^{III} ion in order to maximize the efficiency of the energy transfer and to minimize the risk of back energy transfer processes.[4,5,14,16,17]

In this respect, derivatives of Tröger's bases (6H,12H–5,11– methanodibenzo[b,f][1,5]diazocines, TBs), are a new type of scaffold for the design of controlled and unique architectures in the field of lanthanide coordination chemistry. In these molecules, the rigid V–shaped geometry allows the control over the location of different substituents to obtain predictable geometries (Figure 1).

TBs consist of two aromatic rings fused together by a bicyclic aliphatic methanodiazocine unit, and possess a methylene bridge that prevents the pyramidal inversion of the two nitrogen atoms and generates a geometry where the aromatic rings are located

almost perpendicular to each other. This rigid configuration makes TBs C_2–symmetric chiral molecules with a hydrophobic cavity. Due to these unique characteristics, TBs have countless potential applications in different fields, such as molecular recognition, catalysis, drug development, bioorganic and supramolecular chemistry and optical and optoelectronic devices, among others.[18–21]
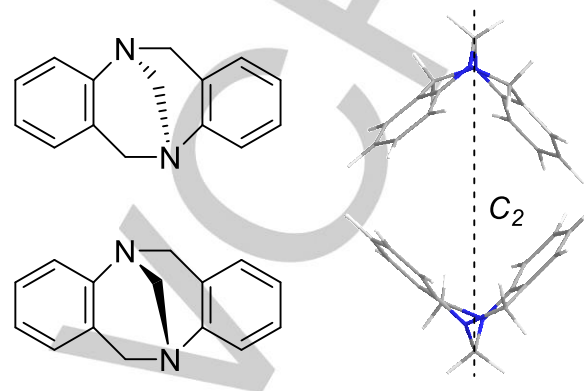

Figure 1. Chemical and simulated three-dimensional structure (Chem3D 15.0, MM2) of TB's framework (top: R,R; bottom: S,S)

	R^1	R^2	R^3
3a	H	N(CH$_2$COOH)$_2$	H
3b	N(CH$_2$COOH)$_2$	H	H
3c	N(CH$_2$COOH)$_2$	H	N(CH$_2$COOH)$_2$

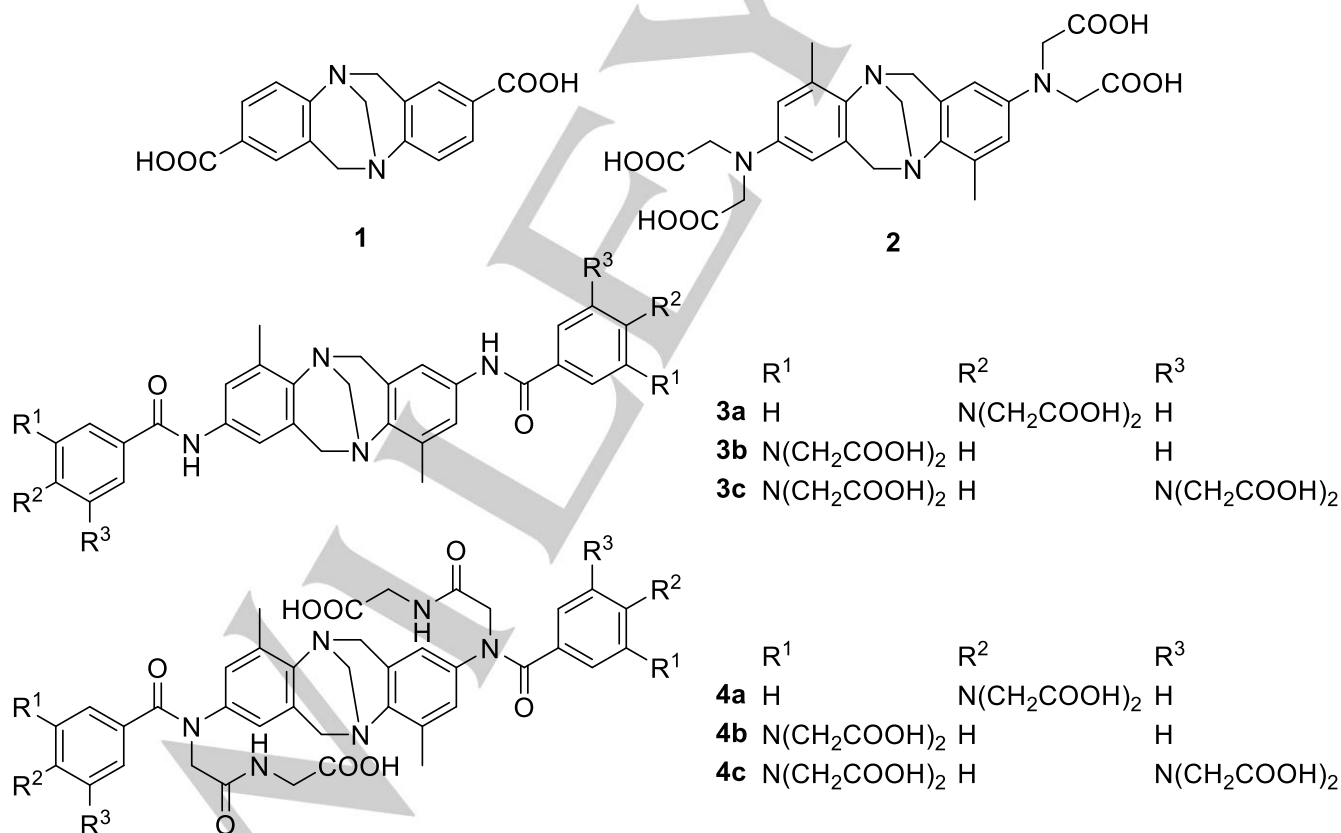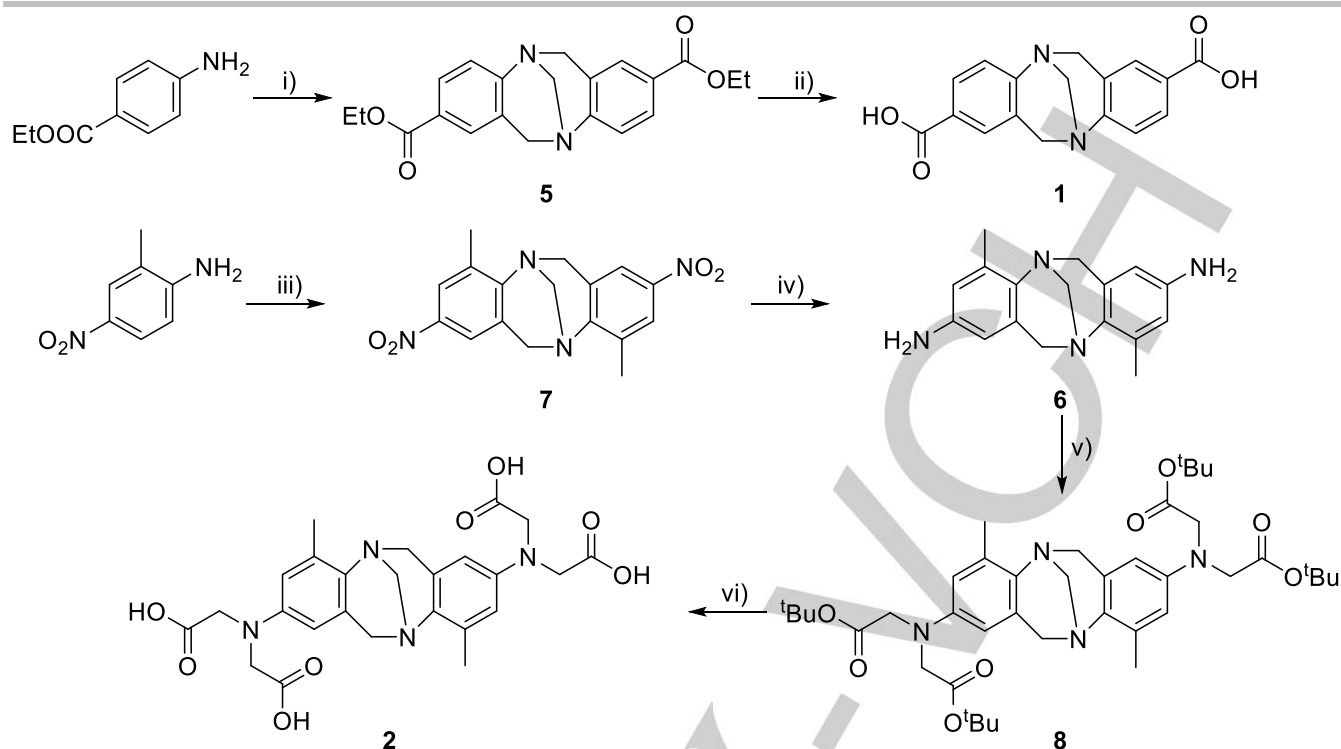|	R^1	R^2	R^3
4a	H	N(CH$_2$COOH)$_2$	H
4b	N(CH$_2$COOH)$_2$	H	H
4c	N(CH$_2$COOH)$_2$	H	N(CH$_2$COOH)$_2$

Figure 2. Chemical structures of the multipodal ligands **1**–**4** designed using TB's frameworks.

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Scheme 1. Synthetic pathways employed for the preparation of ligands **1** and **2**. i) (CH₂O)ₙ, TFA, 48 h, r.t., 93%; ii) LiOH(aq), THF, 8 h, Δ, 100 %; iii) (CH₂O)ₙ, TFA, 48 h, r.t., 87%; iv) Fe, HAcO, EtOH, 2 h, Δ, 99 %; v) *t*-butyl bromoacetate, DIPEA, MeCN, 4 d, Δ, 45 %; vi) TFA, CH₂Cl₂, 4 d, r.t., 100 %.

To the best of our knowledge, TBs have never been used as a scaffold for the design and preparation of luminescent complexes of Ln^{III} ions. Therefore, we envisioned herein the design and the synthesis of multipodal ligands built using a TB framework, with an increasing number of pendant arms and different organic chromophores–sensitizers of Ln^{III} emission. The introduction of carboxylate groups as coordinating units was chosen, taking into account the affinity of lanthanides for hard donor groups such as negatively charged oxygen atoms.[22] Moreover, aminobenzamides or anilines, including TB's aromatic rings themselves, that are known to possess important light absorption, were employed as the basic structures for sensitizing the emission of Ln^{III} ions through the antenna effect.[23–25] The work focuses on terbium(III) and/or europium(III) ions, that exhibit characteristic green or red emissions, respectively, in the visible region of the electromagnetic spectrum.

Therefore, eight multipodal TB ligands with increasing complexity and number of pendant arms were synthesized (**1–4**, Figure 2). Different synthetic strategies were employed, including robust and standard techniques such as alkylations or amide couplings and synthetically efficient multicomponent reactions (MCRs). The interaction of **1–4** with Tb(III) and Eu(III) triflates was studied by spectrophotometric and spectrofluorimetric titrations, and photophysical properties (quantum yields and observed luminescence lifetimes) of the most luminescent species were determined.

Results and Discussion

Design and synthesis of the ligands

As was previously mentioned, all TB ligands possess carboxylate groups for Ln^{III} coordination. The TB framework was envisioned as the lanthanide(III) ion sensitizing unit in ligands **1** and **2**, whereas the incorporation of benzamide groups to the TB skeleton to form aminobenzanilides was the chosen strategy for the families of ligands **3** and **4**. Each of these families consists of three ligands **a–c** that vary in the number and position of the substituents of the benzamide moiety. The detailed design and synthesis of the different ligands **1–4** will be discussed below.

Synthesis of ligands 1 & 2

The simplest ligand proposed here is the dicarboxylic–TB **1**, which holds the Tröger's base skeleton as the chromophoric antenna and two carboxylate groups for the coordination. Compound **1** has already been synthesized, but its interaction with Ln^{III} salts has never been explored.[26,27] Ligand **1** was obtained here in two steps according to the literature procedures with an overall yield of 93 % (Scheme 1). The *p*-aminobenzoate group, the building block used for synthetizing compound **1**, has already been described as being an effective sensitizer of terbium(III) luminescence.[28–30] The initial step, as in every synthetic route presented herein, was the preparation of the TB framework (in this case, diester **5**), by means of the acid–catalyzed condensation of the corresponding aniline with paraformaldehyde in trifluoroacetic acid.[27,31]

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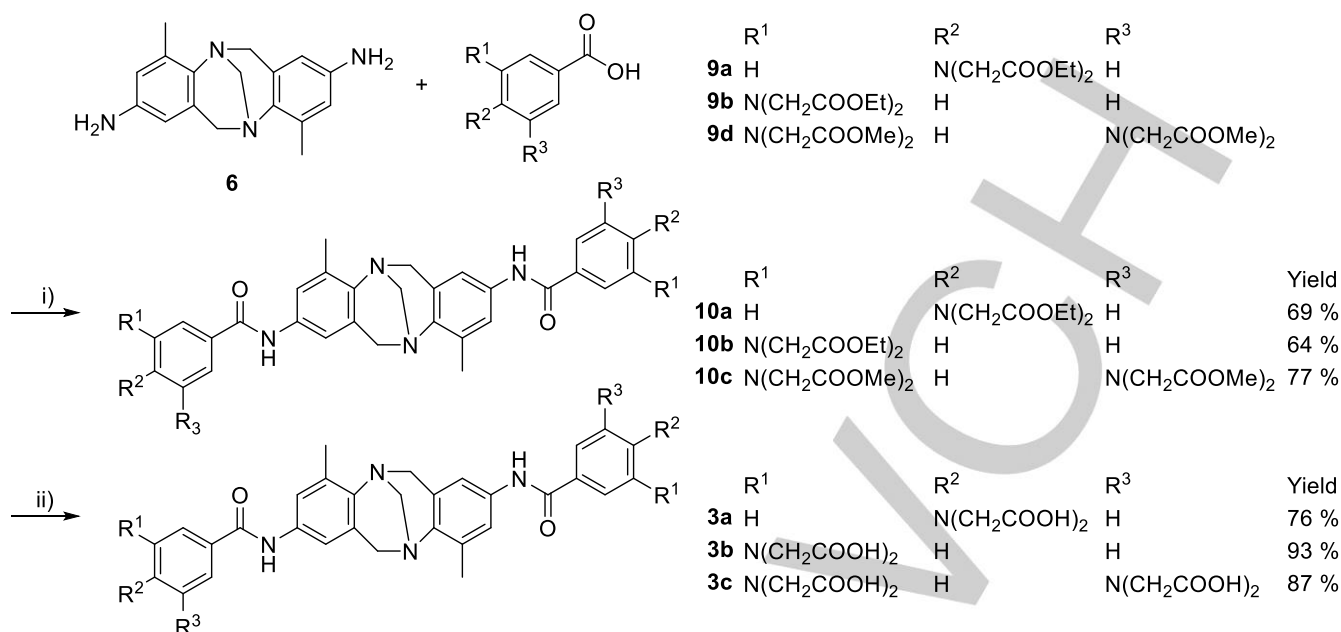
Scheme 2. Synthetic pathway employed for the preparation of ligands **3**. i) EDC·HCl, DMAP, CH₂Cl₂, overnight, r.t.; ii) a) KOH (aq.), MeOH, overnight, r.t.; b) HCl (aq).

The second ligand, **2**, includes also the dibenzodiazocinic core as the chromophore, but in this case as a substituted *p*-phenylenediamine. These units have also been proven to be valuable for the sensitization of Tb(III) emission, which is consistent with the energy calculated by Matsui for the triplet state of a *p*-phenylenediamine.[32,33] Coordinating units in **2** are iminodiacetate groups, present at both ends of the molecule.

Ligand **2** was prepared using the diamino–TB **6** as precursor, which in turn was obtained in two steps from 2-methyl-4-nitroaniline as described by Kiehne et al., with the initial formation of dinitro–TB **7** and an overall yield of 86 %.[34] Compound **6** was alkylated as a second step with *tert*-butyl bromoacetate to give the tetra-*tert*-butyl ester **8**, which was finally deprotected to produce the tetraacid **2** with a 45 % yield from the diamino–TB (Scheme 1).[35] This compound was previously prepared by our group in our study of a six–armed tetrahydrophenomazine, but its lanthanide coordination properties were not studied.[36]

Synthesis of families of ligands 3 & 4

Ligands **3** and **4** are derivatives of aminobenzanilides, in which exocyclic nitrogen atoms are part of the coordinating iminodiacetate moiety. These compounds were chosen in order to attain a family of ligands with different numbers of coordinating units and substitution patterns, which should also impact their abilities to sensitize lanthanide(III) luminescence. To the best of our knowledge, the use of aminobenzamides in lanthanide(III) complexes has not been reported so far, and there is no information regarding the energies of their triplet states either.
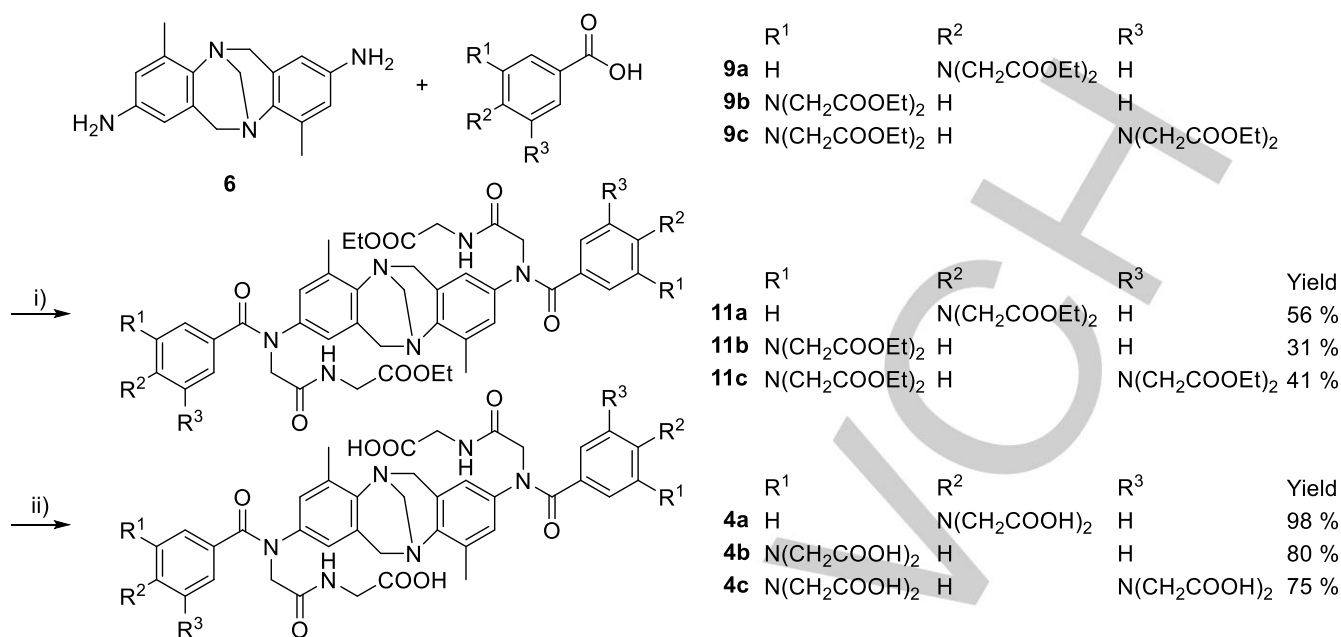
Synthetic pathways designed for the preparation of these compounds present a key step of reaction between a diamino–TB and an aminobenzoic acid derivative. These carboxylic acids were prepared in four steps starting from commercial nitrobenzoic

acids with overall yields of 64–94 %, as shown in Figure S1 (Supporting Information, SI). In every case, the first step was the protection of the acid moiety to obtain the *tert*-butyl nitrobenzoates, followed by the reduction of the nitro group to give the *tert*-butyl aminobenzoates. These amines were alkylated and finally the *tert*-butyl esters were hydrolyzed into the corresponding acids **9**.

Once the acids were obtained, final products **3** were synthesized in two steps (Scheme 2). Initially, the esters **10** were prepared through an amide coupling between the diamino–TB **6** and the appropriate acid **9**, using EDC·HCl (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) as coupling agent. The presence of this reagent yielded better results than with other commercially available activating agents such as dicyclohexyl carbodiimide (DCC) and carbonyl diimidazole (CDI).[37–39] The ester groups of the resulting compounds were finally hydrolyzed using aqueous potassium hydroxide, with overall yields of 52–67 % for the two–step procedure.[40]

Compounds **4** present N,N-disubstituted amides at each end of the TB, which incorporate an additional coordinating arm in respect to the family of ligands **3**, and were prepared using an Ugi MCR as the key step. MCRs are an effective synthetic strategy for the construction of compound libraries, and in this sense they can be used for the simultaneous introduction of several coordinating groups and/or chromophores into a selected framework. We took advantage of this powerful procedure for attaching pendant arms onto a TB's framework to create a family of compounds capable of coordinating the central Ln^III ion in a multisite fashion. In addition, the Ugi MCR is a soft and green synthetic tool, with high atom efficiency, low energy consumption (room temperature or mild heating reaction conditions) and that only requires small volumes of low–toxicity solvents such as alcohols or even water.[41,42] Remarkably, to the best of our knowledge, TBs have never been employed as substrates in Ugi MCRs.

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Scheme 3. Synthetic pathway employed for the preparation of ligands **4**. i) CH_2O, $CNCH_2COOEt$, MeOH, 5 d, 35 °C; ii) a) KOH (aq.), MeOH, overnight, r.t.

Ligands **4** were prepared in two steps (Scheme 3), starting with a double Ugi MCR involving the diamine **6** and two molecules of the corresponding acid **9**, formaldehyde and ethyl isocyanoacetate which yielded the esters **11** of the desired compounds in mild conditions.[42,43] The aldehyde was chosen for its high reactivity whereas the isonitrile allowed the incorporation of two additional coordinating arms. The ethyl ester groups of compounds **11** were finally hydrolyzed with potassium hydroxide, with yields in ranges of 25–55 %.[40]

Spectroscopic characterization of the ligands

The ligands **1**–**4** were characterized by 1D and 2D NMR spectroscopy, high resolution mass spectrometry (electrospray ionization, ESI), absorption and fluorescence spectroscopies (see SI). ^{1}H NMR spectra show in every case the typical pattern of the TB diazocinic core in the 3.5–5.0 ppm region, with a singlet originating from the bridgehead methylene between the two doublets of the inequivalent *exo* and *endo* protons of the diazocinic methylene groups ([2]J ≈ 17 Hz). Furthermore, the Ugi products were identified by the presence of the diagnostic signal of the methylene N*CH*$_2$CON that derives from the formaldehyde carbon atom. This signal is particularly easy to observe in bidimensional HSQC spectra as a cross peak in ca. 4 ppm for ^{1}H and ca. 55 ppm for [13]C.

The absorption spectra of TBs are usually characterized by a main absorption band centered at ca. 250 nm ascribed to [1]ππ* transitions and, in most cases, by a second red–shifted band sensitive to the substituents of the aromatic moieties.[25] The absorption and emission spectra of compounds **1**, **2**, **3c** and **4a** are shown in Figure 3, whereas the remaining spectra are presented in Figure S94 (SI). The photophysical results for all ligands are summarized in Table S1 (SI).

Absorption and emission spectra of **1** collected in methanol are very similar to those recently recorded by our group for a diisocyano–TB, which also holds an electron acceptor group.[24] The compound **1** presents a large Stokes shift (165 nm with respect to the red–shifted absorption maximum), which could be attributed to an intramolecular charge transfer state formed between the nitrogen donor atoms and the carboxylic acceptor groups, which are located in *para* position in respect to each other.[23,24]

The absorption spectrum of the compound **2** resembles that of the parent compound **6** and of other *p*-phenylenediamines, showing that the endomethylene bridge does not affect strongly the electronic transitions located on the dibenzodiazocinic framework and that the *p*-phenylenediamine structure is the origin of the spectroscopic features.[24,36,44] The red shifted absorption band observed for the compound **2** at 310 nm is less intense and energetic than in the case of the compound **1**, and the Stokes shift is substantially smaller for the former, with emission centered at 372 nm.

In the case of the benzanilides **3** and **4**, the presence of two additional aromatic rings generates absorption spectra that do not depend only on the TB framework. The substitution pattern of the benzamides is crucial, as it defines the extent of the conjugation of the aromatic system with the auxochrome.[23,45] In general, the *m*–substituted analogs (**3b**, **3c**, **4b** and **4c**) present similar absorption and emission spectra, with a main absorption band centered at ca. 250 nm and emission centered in the 410–445 nm spectral range. On the other hand, the *p*–substituted benzamides (**3a** and **4a**) show absorption spectra that are substantially red–shifted, with maxima ca. 310 nm, whereas their emission bands have smaller Stokes shifts with maxima below 400 nm.

Fluorescence quantum yields in methanol were determined using the relative method, and the values obtained were smaller than 1 % for all studied ligands except for **1**, that exhibits a quantum yield value of 4.6 %.
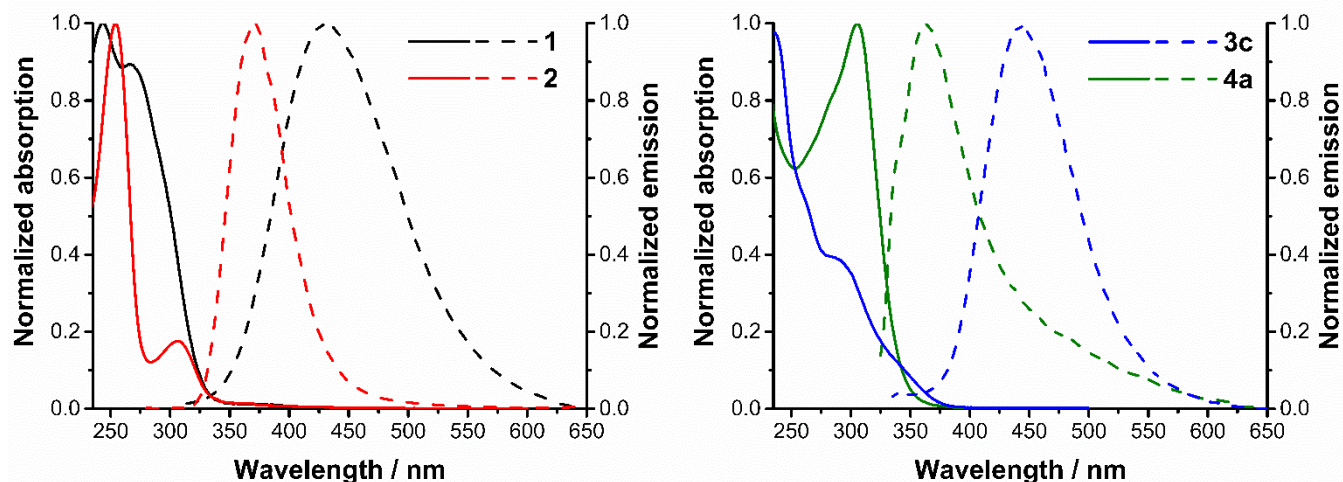
Figure 3. Normalized absorption (full lines) and emission (dashed lines) spectra of ligands **1** (black, λ_{exc} = 243 nm), **2** (red, λ_{exc} = 254 nm), **3c** (blue, λ_{exc} = 287 nm) and **4a** (green, λ_{exc} = 305 nm) in methanol.

Study of the interaction of ligands with Ln^{III} salts by spectrophotometric and spectrofluorimetric titrations

The sensitization of lanthanide(III) luminescence upon ligand irradiation was monitored through spectrofluorimetric titrations of **1**–**4** with europium(III) or terbium(III) triflates in methanol. Europium(III) emission intensity was found to be negligible for all studied ligands (data not shown), reflecting a relatively inefficient sensitization and/or the presence of strong quenching processes through ligand-to-metal charge transfer (LMCT) states.[16,17] The UV excitation into the ligand-centered bands in solutions containing Tb(OTf)$_3$ and **1**–**4** produces green luminescence with narrow emission bands centered at 488 nm, 545 nm, 585 nm and 620 nm that can be ascribed to the $^5D_4 \rightarrow {}^7F_J$ (J = 6–3) electronic transitions respectively (Figure 4). Therefore, these results show that all the new ligands can act as sensitizers of Tb(III) luminescence with various levels of efficiency.

In addition, the substitution pattern of the different ligands studied here proved to be crucial for the coordination modes with Tb(III). The Tb(III)/ligand stoichiometry of the most luminescent species present in solution were determined for **1**–**4** through spectrofluorimetric titrations. The results showed that the 1:2 Tb(III)/ligand ratio is optimal for the formation of the most luminescent complex formed with the *p*–substituted ligands **1**, **2** and **3a** and that 1:1 ratio is optimal for the *m*–substituted compounds **3b**–**c** and **4b**–**c**. The single exception to this behavior was observed with the *p*–substituted benzanilide ligand **4a**, for which the most luminescent species correspond to a 1:1 Tb(III)/ligand ratio which will be discussed below. Results obtained for the *p*–substituted ligands are depicted in Figure 4, whereas the remaining experiments are shown in Figure S95 (SI).

Ligands **2** and **3a** show a substantial decrease of the luminescence intensity when more than 0.5 equivalents of Tb(III) triflate are present in solution, which proves the formation of additional number of complexes possessing different molecular formulas. Initially, the 1:2 species are formed in deficiency of Tb(III), and at least one additional complex appears over 0.5

equivalents of lanthanide(III). In the case of **3a,** the most luminescent species corresponds to the formation of a 1:1 system, whereas the stoichiometry determination for **2** proved to be more challenging. The spectrophotometric titrations suggest the presence of 1:1 and 1:2 complexes for **3a** and the equilibrium between several coordination compounds for **2** (Figure S96, SI).

In contrast to the aforementioned ligands, the increase in lanthanide(III) luminescence intensity in the solutions formed by **4a**–**b** upon addition of less than one equivalent of Tb(III) presents an approximately sigmoidal profile, with a change in slope close to 0.5 equivalents of Ln^{III}. This behavior could indicate the initial formation of a 1:2 complex, after which the 1:1 system is formed when a larger amount of Tb(III) triflate is added.

Tb(III)-centered luminescence quantum yields (ϕ_{Tb}) were determined by the relative method for the most emissive species formed in solution of **1**–**4** and Tb(III) triflate. Observed luminescence lifetimes (τ) were determined from the corresponding decay curves (Figure S100, SI) obtained upon excitation at 355 nm and monitoring the Tb(III) emission at 545 nm ($^5D_4 \rightarrow {}^7F_5$ transition). Measurements were performed, when possible, in both methanol and monodeuterated methanol (CH$_3$OD), in order to assess the number of solvent molecules present in the inner coordination sphere of the lanthanide(III) using standard phenomenological equations.[46–48] Results are summarized in Table 1, and will be discussed below.

The 1:2 Tb(III)/ligand complex formed by **1** and Tb(III) possesses the most intense luminescence among all the compounds assessed, with a recorded quantum yield value of 21.0 %. For this compound, the coordination also induces the disappearance of the fluorescence arising from the chromophoric ligand itself, as can be seen in the full emission spectrum of the Tb(III)/ligand mixture (Figure S97, SI) indicating a more efficient transfer of the energy from the ligand to the accepting electronic levels of the Ln^{III} ion and explaining the higher Tb(III) luminescence quantum yield.
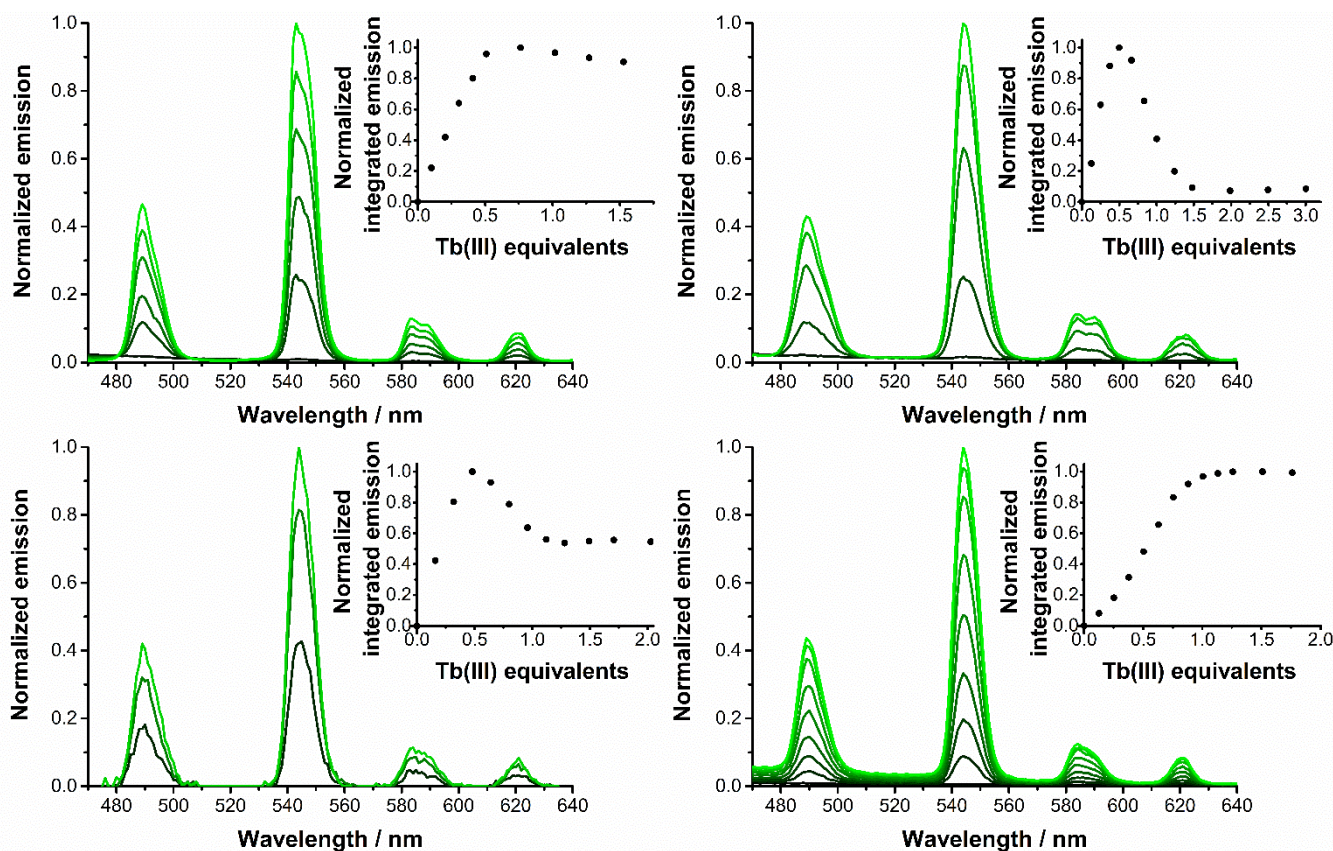
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Figure 4. Spectrofluorimetric titration of **1** (8.2×10^{-6} M, λ_{exc} = 280 nm, top left), **2** (8.1×10^{-6} M, λ_{exc} = 320 nm, top right), **3a** (2.0×10^{-6} M, λ_{exc} = 335 nm, bottom left) and **4a** (3.7×10^{-6} M, λ_{exc} = 315 nm, bottom right) with Tb(OTf)$_3$ in methanol. Inset: normalized integrated emission intensity of the four $^5D_4 \rightarrow {}^7F_J$ (J = 6–3) bands.

Table 1. Tb(III)-centered quantum yields (ϕ_{Tb}) and luminescence lifetimes (τ) of the most emissive species formed in solution of **1–4** and Tb(III) triflate.

Ligand	Tb(III) / L [a]	ϕ_{Tb}[b] / %	τ[b] / ms	q[c]
1	1:2	21.0	1.4	0
2	1:2	0.6	1.0	0
3a	1:2	0.3	[d]	[d]
3b	1:1	< 0.1	[d]	[d]
3c	1:1	< 0.1	[d]	[d]
4a	1:1	3.2	1.0	0
4b	1:1	0.6	[d]	[d]
4c	1:1	< 0.1	[d]	[d]

[a] Tb(III)/ligand ratio for the most emissive species; [b] estimated experimental error is 10 %; [c] number of coordinated solvent molecules estimated from luminescence lifetime values in CH$_3$OH and CH$_3$OD;[46–48] [d] not determined.

Luminescence quantum yield recorded for the terbium(III) emission for the 1:2 Tb(III)/**2** species was determined as 0.6 %, showing that the emission sensitization process is significantly less efficient in this case in comparison to **1**. Moreover, although the ligand fluorescence is also reduced upon coordination, it remains clearly detectable in contrast to the almost complete fading observed for the 1:2 Tb(III)/**1** species (Figure S97, SI). The same phenomenon is observed for **3a**–**c** and **4b**–**c**, that exhibit luminescence quantum yields smaller than 1 % and for which the fluorescence arising from the ligand singlet state is superimposed with the Tb(III) emission. The weak luminescence intensity hampered luminescence lifetime measurements in most of these cases.

Interestingly, Tb(III) emission is much more intense than the ligand fluorescence in the complex formed with **4a**, and a Tb(III)-centered luminescence quantum yield value of 3.2 % was measured for 1:1 Tb(III)/**4a**. In addition, this compound has the advantage that its absorption spectrum is red–shifted in respect to the remaining of the ligands, a very desirable property for systems or applications in which the use of the harmful UV excitation under 320 nm (UVB and UVC) is not recommended. In fact, green emission was clearly visible by the naked eye under irradiation of 1:1 Tb(III)/**4a** at 365 nm by a commercial lamp.

Therefore, the photophysical properties of the Tb(III) complexes formed with TB ligands containing aminobenzanilides are highly dependent on the substitution pattern and on the nature of the lateral chains. Secondary benzanilides **3** produced in general less luminescent Tb(III) complexes than the tertiary analogs **4**, indicating a less efficient sensitization or the presence of enhanced deactivation pathways. In addition, the *m*–substitution pattern gave rise to less luminescent complexes than the *p*–substitution.

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Tb(III) observed luminescence lifetimes could only be measured for the complexes emitting significant green signals upon 355 nm excitation, and all of them lie in the millisecond timescale. The experimental luminescence decays could be adequately fitted with monoexponential functions, suggesting the presence of a single predominant emissive species and of a high level of similarity of coordination environments around Tb(III) ions (Figure S100, SI). Luminescence lifetime of the $^5D_4$ level of Tb (III) in the 1:2 Tb(III)/**1** species in CH_3OH or CH_3OD were found to be 1.4 ms in both cases. Similar results were obtained for Tb(III) species formed with the ligands **2** and **4a**, suggesting in each case that no solvent molecules are directly coordinated to the terbium(III) ion, and that the sites of the first coordination sphere are fully occupied by the ligand, providing a very efficient protection.[46,47]

The 1:2 Tb(III)/ligand ratio in the most emissive species and the absence of solvent molecules in the lanthanide inner coordination sphere allows us to hypothesize that the stoichiometry of the complexes formed by ligands **1** and **2** with Tb(III) should be 2:4. In the case of compound **1**, each Tb(III) ion would be coordinated by four carboxylate groups belonging to different molecules of the ligand. Each carboxylate moiety could occupy two coordination positions of the central ions (one with each oxygen atom) in a chelate fashion. As a consequence, the Tb(III) would have eight coordination sites occupied, preventing the coordination of solvent molecules and the corresponding quenching. For the ligand **2,** in order to occupy the eight coordination sites of the Tb(III), the latter would need to be coordinated either by only one of the two oxygen atoms of each carboxylate group in a monodentate fashion or by only one of the two carboxylates of each iminodiacetate moiety in a chelate fashion.[22]

A 2:4 system could thus be built with the octahedron generated by two rhombs intertwined by the axis that includes the Tb(III) ions, with each rhomb formed by two ligand molecules and two Ln^{III} ions (Figure 5). These rhomboidal structures, where two vertices are constituted by TBs bridges and the other two by lanthanide(III) ions, are of the same nature to the self–assembly compounds formed between TBs and different transition metal ions.[34,49–57] Even though the general stoichiometry of these coordination compounds is 2:2, the Lützen group proposed structures with two transition metal ions and three TB ligands, showing that a 2:4 structure could also be obtained from a steric point of view.[49,50] Similar 2:4 structures were reported for other self–assembled metallosupramolecular cages, including with lanthanide(III) ions.[58–66]

It is worth noting that for a 1:2 system to exist, having one Tb(III) ion, two molecules of ligand **1**, and no solvent molecules in the lanthanide inner coordination sphere, both carboxylates of each TB should coordinate the same terbium(III) ion. This coordination mode is geometrically implausible, given the rigid structure of the ligand and the distance between both carboxylates (approximately 1 nm). Therefore this arrangement is not proposed.[67]

In addition, the experimental result showing that the Tb(III) luminescence intensity of the 2:4 complex is substantially larger than that of the 2:2 complexes formed with the ligands **2** and **3a** (Figure 4) is consistent with the fact that a lower lanthanide(III)/ligand ratio offers the possibility of a larger degree of occupancy of the coordination sites. This in turn would diminish the influence of non–radiative deactivation mechanisms due to vibrational coupling with solvent oscillators, thus increasing terbium(III) luminescence intensity.[4]

By analogy, we suggest that the actual coordination compounds obtained with 1:1 Tb(III)/ligand ratios (**3b**–**c** and **4a**–**c**) are 2:2 systems formed by rhomboidal structures with two terbium(III) ions located in two vertices and the diazocinic cores of the two TB ligands in the remaining ones (Figure 6). It should be noted, however, that the structures proposed for the Tb(III) coordination compounds where the q values could not be determined experimentally are hypothetical and are only suggested considering similar complexes.[34,49–57]

This hypothesis allows to rationalize the unusual sigmoidal profile observed in the titrations of **4a** and **4b**, as a response to a cooperative coordination process in which the formation of the 1:2 complex favors the access of a new lanthanide(III) ion, as observed for comparable systems such as the Eu(III) complex formed by a phosphine ligand recently described by Cotter et al.[68–70]

The ligand **4a** forms a 1:1 complex with Tb(III), even though it presents a *p*–substitution pattern. This result could be related to its larger volume and the presence of lateral chains that could prevent the formation of complexes with a larger number of ligands due to steric hindrance.

Figure 6. Schematic representation of the proposed structure for the 2:2 Tb(III)/ligand complexes formed with **3b**–**c** and **4a**–**c**.

Conclusion

In this work, we described for the first time that Tröger's bases are a promising scaffold for the design and the construction of luminescent lanthanide(III) compounds, either acting themselves as the antenna unit or incorporating additional chromophores, and that these ligands can be efficiently obtained by alternative synthetic strategies. Furthermore, we observed the formation of terbium(III) complexes with all the new ligands, with significant
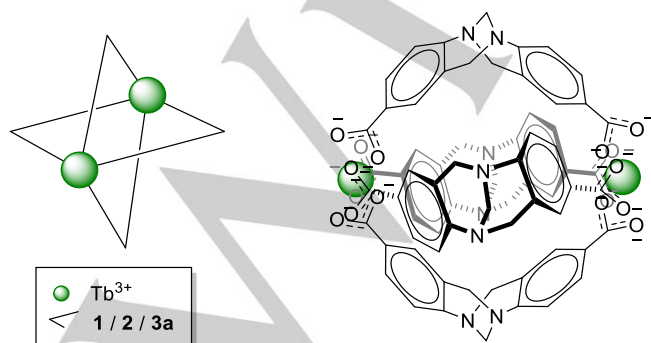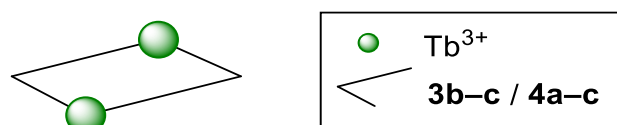

Figure 5. Schematic representation of the proposed structure for the 2:4 Tb(III)/ligand complexes formed by **1**, **2** and **3a** (left) and detailed representation structure for the 2:4 Tb(III)/**1** complex (right).

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differences in efficiencies of luminescence sensitization depending on the nature of the chromophoric unit present in each ligand.

We propose that the coordination compounds can be described as metallosupramolecular self–assembled rhomboidal structures, where each rhomb is formed by two terbium(III) ions, that occupy two vertices, and two ligand molecules, with their diazocinic cores occupying the remaining vertices. This situation would lead to the obtention of 2:2 and 2:4 Tb(III)/ligand complexes, the nature of the species formed being mainly dependent on the substitution pattern of the ligands combined with geometric and steric factors.

The Tb(III)-centered luminescence quantum yields of all the complexes were measured, as well as the luminescence lifetimes of the species with higher quantum yields, which lie in the millisecond timescale. Moreover, the similarity of Tb(III) luminescence lifetimes recorded in CH_3OH and CH_3OD suggest that no solvent molecules are present in the first inner coordination sphere of the terbium(III) ions.

Finally, it is worth noting that the high variability in geometries and emission properties of the complexes studied here was controlled by designing ligands possessing a common framework (a Tröger's base) and coordination units (carboxylate groups). TBs are versatile building blocks obtained with an efficient and rapid preparation that allow for a wide array of substituents to be incorporated or modified. In particular, TBs could be used in Ugi MCRs not only as an amine but also as an isocyanide or a carboxylic acid in order to obtain comparable products of this family but incorporating specifically designed chromophores, with different connectivities and geometries that would allow a fine tuning of the excitation wavelengths, a desirable feature in many applications.

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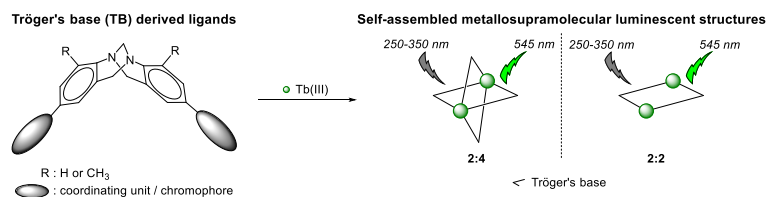
Specifically designed Tröger's base derived ligands that ensure the coordination and sensitization of luminescent terbium(III) ions were synthesized for the first time, using several strategies that include the powerful Ugi Multicomponent Reaction. Self–assembled 2:2 or 2:4 metallosupramolecular structures were formed, where stoichiometries and sensitization efficiency can be tuned by the geometry and the substitution patterns of the ligands.