

RESEARCH ARTICLE

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12, 3073Ionic radius-dependent self-assembly of
lanthanide organic polyhedra: structural diversities
and luminescent properties†Jing Su,^{a,b,c} Fan Yin,^a Xiao-Fang Duan,^a Jing-Yao Zhou,^a Li-Peng Zhou,^a
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The synthesis of nonclassical polyhedra is at the forefront of supramolecular research because of their unique anisotropic interior cavities. However, due to the difficulty in controlling the topology of Ln supramolecular systems, the preparation of nonclassical lanthanide organic polyhedra (LOPs) remains a challenge. Herein, we explore the ionic radius-dependent self-assembly of LOPs using a rectangular tetrapropyl ligand **L**. Owing to the rectangular geometry of the ligand panels (rather than square), its assembly with lanthanide ions located in the middle of the Ln series afforded an irregular tetragonal antiprismatic Ln₈L₄ (Ln = Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺ and Ho³⁺) with two faces unoccupied with **L** ligands. Interestingly, this tetragonal antiprism possessed an oblate internal cavity that binds to four THF molecules in the solid-state structure. With an increase in radius, the larger La³⁺ and Nd³⁺ ions produced Ln₄L₂ with a distinct sandwich square architecture. In contrast, the smaller Er³⁺ and Lu³⁺ ions gave rise to a mixture of both Ln₈L₄ and Ln₆L₃. On adding excess Ln³⁺ ions, a structural transformation from Ln₈L₄ to Ln₆L₃ occurred. Structural comparisons of La₄L₂ and Sm₈L₄ revealed that the differences in architecture within these systems were governed by both the ionic radii of the lanthanides and conformational flexibility of the ligands. Photophysical investigations revealed that the ligand **L** exhibited a sensitizing ability toward Sm³⁺, Tb³⁺ and Dy³⁺ ions, displaying their characteristic luminescence emission, with a new record-setting luminescent quantum yield of 92.74% observed for Tb₈L₄. This work provides new insights into the effect of lanthanide size on the resulting assemblies and opens new avenues to develop nonclassical LOPs.

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Introduction

Over the past two decades, preparation of self-assembled metal organic polyhedra has emerged as one of the most active research areas in supramolecular chemistry owing to their diverse potential applications, which include, but are not limited to, supramolecular catalysis,^{1–5} molecular recognition and separation,^{6–11} drug delivery^{12–15} and guest binding.^{16–22} In this context, the advancement of lanthanide organic polyhedra (LOPs) is of particular interest. This interest is driven by

the intrinsic optical, catalytic and magnetic properties of Ln ions,^{23–27} which can be integrated into the final LOPs by the Ln center. However, research on synthesizing such LOPs remains in its infancy compared to transition coordination assemblies, and only a limited number of such supramolecular architectures have been reported.^{28,29} This is primarily caused by the variable coordination numbers, weak coordination abilities, diverse coordination geometries, and poor stereochemical preferences of Ln ions.

Octanuclear LOPs with cubic or tetragonal prismatic architectures can be constructed by combining the C₂ symmetric ditropic tridentate or C₄ symmetric tetra-tropic tridentate ligands with nine-coordinated Ln centers. They typically form cubic structures that can be represented by the formulas Ln₈L₁₂ (L = C₂-symmetric ligands) or Ln₈L₆ (L = C₄-symmetric ligands) based on the geometric matching principle between the ligand and Ln³⁺ ions, which was proposed by Raymond and co-workers.³⁰ To date, several Ln₈L₁₂ or Ln₈L₆ compounds have been successfully developed by our group and other groups.^{31–36} Nevertheless, most of the reported Ln₈L₁₂ or Ln₈L₆ assemblies exhibit high-symmetry structures with

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regular Archimedean or Platonic geometries. In contrast, non-classical Archimedean or Platonic octanuclear LOPs with missing linkers or faces have been rarely reported^{37,38} owing to the challenges associated with controlling the topology of Ln supramolecular systems.

One intriguing aspect of metal organic polyhedra is their dynamic and reversible metal–ligand bonds, which can be utilized to modify their structure by changing factors such as metal ions,^{39–42} stoichiometry,^{43,44} concentration,^{31,45,46} anions,^{47,48} pH^{49,50} and some others.^{51,52} Among these factors, the selection of metal ions is particularly significant in the design of metal organic polyhedra.^{39–42} The differences in the radii of metal centers can endow the cages with an extra degree of flexibility through the rearrangement of the coordination chelating unit, resulting in the generation of some new species. Along this line, a gradual change in the effective ionic radius across the lanthanide series, known as “lanthanide contraction”, makes Ln³⁺ ions ideal candidates for these studies. For example, Hooley and our team demonstrated that the Ln-selective self-assembly can occur through multivalency and cooperativity, which have potential utilization in Ln separation using a supramolecular approach.^{7,53} Recently, our group developed a post-synthetic transmetalation self-assembly strategy for creating near infrared emitting Yb₈L₆ cube, which cannot be achieved using a direct synthesis method.³⁴ A deeper understanding of the specific role of Ln³⁺ ions in the self-assembly process can facilitate the rational design of LOPs and promote the discovery of novel Ln supramolecular architectures that go beyond traditional approaches. Consequently, more examples of ionic radius-dependent self-assembly of LOPs are required.

Based on the considerations mentioned above, we report the design and synthesis of a rectangular tetra-tropic tridentate ligand, **L**, derived from 2,6-di[pyrazol-1-yl]pyridine (bpp) chelating moieties. Its self-assembly with lanthanide ions leads to a series of distinct Ln_{2n}L_n (*n* = 2, 3 and 4) assemblies with the unsaturated metal sites: sandwich square Ln₄L₂, the triangular prism Ln₆L₃, and the unique twisted tetrahedron prism Ln₈L₄. These assemblies were characterized by a combination of NMR, mass spectrometry, and single-crystal X-ray analysis. We found that the formation of these assemblies depends on the ionic radii of the Ln series as well as the varying conformation of the ligands. Additionally, the photophysical properties of Sm₈L₄, Tb₈L₄ and Dy₈L₄ were investigated.

Results and discussion

Ligand design, synthesis and assembly with lanthanides

The tetra-tropic ligands are commonly employed to fabricate octanuclear metal organic polyhedra. However, the square geometry of these ligand panels results in a regular cubic configuration of octanuclear assemblies.^{34,54–59} To create octanuclear assemblies using the nonclassical Archimedean or Platonic solids, designing ligands with rectangular panels may be a promising strategy, as recently demonstrated by Nitschke

et al. in their subcomponent self-assembled transition-based metal–organic architectures.^{60,61} In addition, tetra-tropic ligands contain very complex conformations, which can enhance the structural complexity and diversity after coordination with metal ions. The 2,6-di[pyrazol-1-yl]pyridine (bpp) and its derivatives are widely used tridentate coordination units in constructing transition metal complexes.^{62,63} However, this motif has been less explored in preparing rare earth coordination compounds.^{64,65} Consequently, we opted to introduce bpp tridentate chelating units into the tetra-tropic ligand, and its assembly with Ln³⁺ ions generally afforded octanuclear LOPs. The tetra-tropic tridentate ligand **L** was synthesized by Suzuki coupling (the experimental details are shown in the Experimental section of the ESI†) and was characterized by NMR.

Synthesis and characterization of La₄L₂

When 2.0 equiv. of ligand **L** was treated with 4.0 equiv. of La(OTf)₃ in acetonitrile at 70 °C for 30 min, the turbid suspension of the ligand gradually turned into a homogeneous clear solution. The ¹H NMR spectrum clearly indicates the generation of La₄L₂ assembly. Compared with the highly symmetric free **L**, the ¹H NMR spectrum of La₄L₂ showed 2-fold desymmetrization of the **L** (Fig. 1B and C), in agreement with the D₂ point symmetry of a sandwich square. The DOSY spectrum dis-

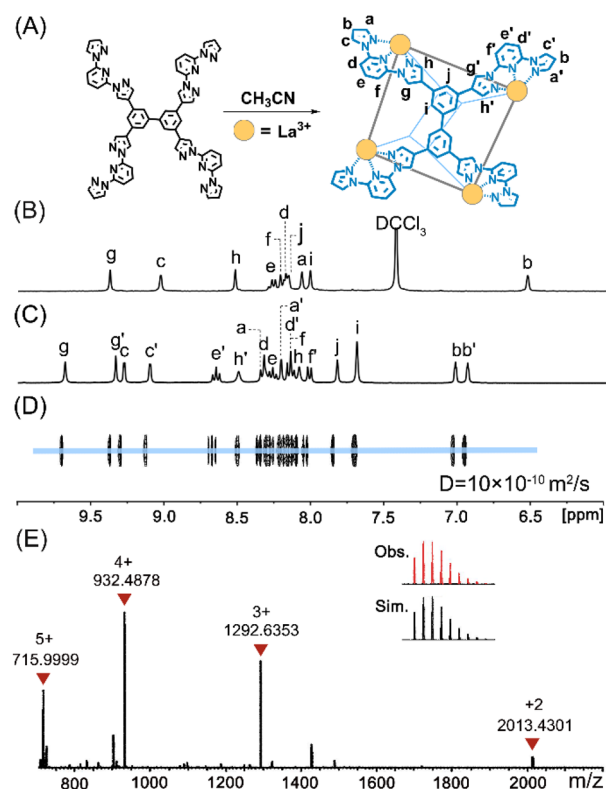


Fig. 1 (A) Self-assembly of **L** with La(OTf)₃. ¹H NMR spectra (400 MHz, 298 K) of **L** in CDCl₃ (B) and La₄L₂ in CD₃CN (C). (D) DOSY spectra of La₄L₂. (E) ESI-TOF-MS of La₄L₂ with the inset showing the observed and simulated isotopic patterns of the +4 peak.



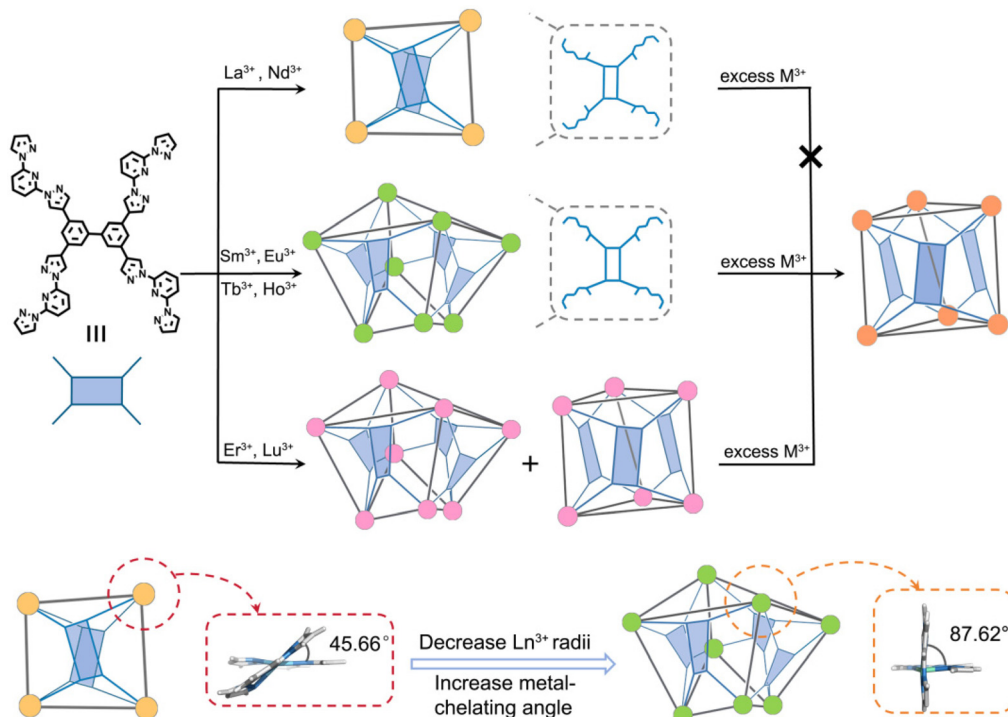


Fig. 3 ESI-MS of Lu_6L_3 (A) and Sm_6L_3 (B) complexes with the insets showing the observed and simulated isotopic patterns of the +5 peak.

nation geometry (Fig. S51 and Table S3†). The dihedral angles between metal-chelating planes around the La^{3+} node are 44.67, 46.02, 46.20 and 45.74° for La1, La2, La3 and La4, respectively (Fig. S52†). Owing to one whole La_4L_2 molecule

being observed in the asymmetric unit, its point symmetry in the solid-state structure is C_1 rather than the solution state point symmetry D_2 . This behavior should be caused by the different coordinated solvents and different numbers of coordinated OTf^- anions at the La centers, which reduced the symmetry of La_4L_2 in the solid state. Thus, if we remove the coordination solvents and coordinated OTf^- anions, the point symmetry of La_4L_2 can be regarded as D_2 with slight deviations from perfect geometry, which is consistent with the findings from ^1H NMR (*vide supra*). The four La^{3+} ions form a twisted square, with La–La distances of 11.56, 12.55, 11.44 and 12.42 Å (Fig. 4B). In La_4L_2 , the two ligands bearing conformation mode A (Fig. 4B and Table S6†) are located above and below the La_4 square, resulting in the metal centers with the same Δ or Λ configuration (Fig. S53†). The distances between the two corresponding phenyl rings belonging to the panels of two ligands, which exhibited a “face-to-face” arrangement mode, were measured to be 3.99 Å and 4.02 Å (Fig. 4C, top). These values indicate the presence of an intermolecular π - π stacking interaction between the two ligands. Furthermore, the average torsion angle between the phenyl ring of the ligand’s panel in La_4L_2 is 27.60° (Fig. 4B).

The definitive confirmation of the structure for Sm_8L_4 assembly was provided by a single-crystal diffraction analysis. Crystallographic analysis shows that Sm_8L_4 crystallizes in a tetragonal space group, with one quarter of the cage molecule present in the asymmetric unit (Fig. S54†), featuring a twisted tetragonal antiprismatic structure. The asymmetric unit of Sm_8L_4 consists of two crystallographic independent Sm^{3+} ions,



Scheme 1 Ionic radius-dependent self-assembly of LOPs based on rectangular tetra-tropic ligands.



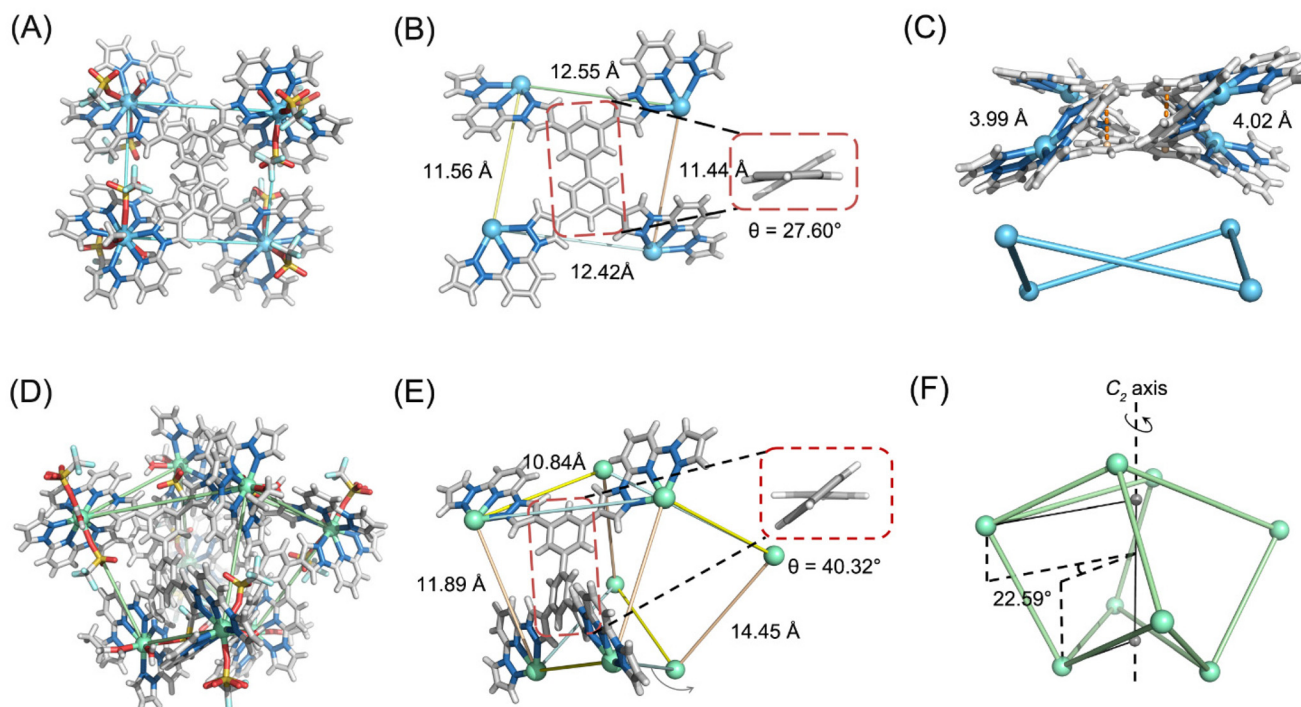


Fig. 4 (A) X-ray single-crystal structure of La_4L_2 . (B) Ligand conformation with the La–La distances and average torsion angle between phenyl rings in La_4L_2 . (C) π – π stacking interaction between the panels of two ligands. (D) X-ray single-crystal structure of Sm_8L_4 . (E) Ligand conformation with the Sm–Sm distances and average torsion angle between phenyl rings in Sm_8L_4 . (F) Twist angle of Sm_8L_4 , which is defined as the dihedral angle between Sm^{3+} (top face)···centroid (top face)···centroid (bottom face) face and centroid (top face)···centroid (bottom face)··· Sm^{3+} (bottom face) face.

both with a coordination number of nine: the Sm1 atom has a tricapped trigonal prism geometry, while the Sm2 atom has a capped square antiprism geometry (Fig. S55 and Table S4†). For Sm1 and Sm2, the dihedral angles between the metal-chelating planes around the Sm^{3+} center are 86.47 and 88.77°, respectively (Fig. S56†). Research into the molecular structure of Sm_8L_4 shows that each ligand bridged four Sm^{3+} ions located on the side face of the twisted tetragonal antiprism. The top and bottom faces of tetragonal antiprism are empty. Moreover, the torsion angle between the phenyl ring of the ligand's panel in Sm_8L_4 is 40.32° (Fig. 4E), leading to the four Sm^{3+} centers on the side face of the tetragonal antiprism not being in the same plane. This result generates the formation of a distorted square on the side face of the tetragonal antiprism. Four such distorted squares together form the highly twisted tetragonal antiprism. The edge length of the tetragonal antiprismatic Sm_8L_4 is 11.89 Å, and the side lengths of the up and bottom distorted squares in the tetragonal antiprismatic Sm_8L_4 are 10.84 Å and 14.45 Å, respectively (Fig. 4E). As shown in Fig. S57,† each tetragonal antiprismatic Sm_8L_4 cage consists of a 1 : 1 ratio of Δ - Sm^{3+} and Λ - Sm^{3+} metal vertices, where each Sm^{3+} center is surrounded by the nearest neighbors of the opposite chiral configuration. On each face of the tetragonal antiprism, the Δ - Sm^{3+} and Λ - Sm^{3+} centers are arranged alternately. Such a distribution of metal chiral within Sm_8L_4 gives rise to an overall achiral S_4 molecular symmetry, in which the C_2 rotation axis runs through the centers of the up

and bottom faces of tetragonal antiprism (Fig. 4F). The twist angle, defined as the dihedral angle between the face constructed by the top face Sm^{3+} , centroids of the top and bottom faces, is measured to be 22.59° (Fig. 4F). The tetragonal antiprism provides an oblate internal cavity (Fig. S60†), which is different from the pseudospherical or prolate cavities formed by the tetragonal prism.^{60,61,70,71} This cavity feature makes the cage suitable for binding small planar guest molecules. To our delight, we found in the crystal structure that four THF molecules occupy the oblate cavity of Sm_8L_4 (Fig. S61†). ¹H NMR titration experiment indicates a fast-exchange binding dynamic mode, and the apparent association constants (K_a) for THF are determined to be 127 M^{-1} by applying the Hill function (Fig. S63 and S64†). After removing the THF molecules, the cavity volume of Sm_8L_4 was calculated to be 594.52 Å³ using the MoloVol program.⁷²

Extensive attempts to crystallize the Lu_6L_3 were unsuccessful. This failure may be attributed to the presence of excess Lu^{3+} ions in the solution, which could disrupt the crystallization process by promoting the formation of amorphous or poorly ordered competing phases rather than desired Lu_6L_3 single crystals.

To gain insight into the structural changes related to lanthanides, we conducted detailed structural analyses of the two assemblies. Our analysis indicates that both the central lanthanide ions and the conformation of the ligands play a crucial role in the selective formation of the resulting assem-



blies. First, the La^{3+} and Sm^{3+} ions, which have different radii and exhibit different coordination numbers, give rise to the assemblies with different nuclearities. For example, the La^{3+} ion, the largest along the lanthanide series, has a coordination number of ten in La_4L_2 . This results in a small average dihedral angle between the metal-chelating planes around the La^{3+} node (Avg: 45.66°), promoting the formation of a sandwich square structure. In contrast, the smaller Sm^{3+} ion has a coordination number of nine in Sm_8L_4 . This reduction in the coordination number allows for enough space to increase the dihedral angle between the metal-chelating planes surrounding the Sm^{3+} center, which is essential for the formation of higher nuclearity assemblies. Consequently, a larger average dihedral angle was obtained around the Sm^{3+} node in Sm_8L_4 (Avg: 87.62°), leading to the generation of higher nuclearity Sm_8L_4 . Second, the ligand **L** in La_4L_2 and Sm_8L_4 displays different conformations: mode A for La_4L_2 and mode D for Sm_8L_4 (Fig. 4B, E and Table S6[†]). Third, the average torsion angle between the phenyl ring of the ligand's panel in La_4L_2 and Sm_8L_4 is different: 27.60° in La_4L_2 and 40.32° in Sm_8L_4 . Because the metal nodes in La_4L_2 and Sm_8L_4 each contain the same two coordinated bpy moieties, it can be assumed that the main reason for such structural change stems from the decreased lanthanide radius and varied ligand conformation.

Effect of Ln ions on supramolecular architecture

After characterizing the assemblies of La_4L_2 , Sm_8L_4 and Lu_6L_3 , we determine whether these assemblies were exclusively formed by their corresponding La^{3+} , Sm^{3+} and Lu^{3+} ions, or if they could also be created with alternative lanthanide ions. Specifically, we wanted to investigate whether the structure is affected by ionic radii. To explore this, we conducted further studies using other selected lanthanides (Nd^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} and Er^{3+}), which span the Ln series and offer a range of ionic radii. The experiments were carried out using 2:1 ratios of lanthanide triflates ($\text{Ln} = \text{Nd}^{3+}$, Eu^{3+} and Er^{3+}) and **L** in acetonitrile. For the Nd^{3+} ion, the mass spectrum analysis supported the formation of the Nd_4L_2 complex (Fig. S28[†]), similar to the results obtained with the La^{3+} ion. However, when the Nd^{3+} ion was replaced with Eu^{3+} ions, the mass spectrum data revealed the production of octanuclear Eu_8L_4 complexes (Fig. S32[†]), similar to those observed with Sm^{3+} ions. In contrast, the use of the Er^{3+} ion resulted in a mixture of self-assembled species, including Er_8L_4 and Er_6L_3 supramolecular architectures, as evidenced by its mass spectrum (Fig. S40[†]). Clearly, the structures of assemblies are influenced by the tiny difference in ionic radii across the Ln series, which is consistent with the previous reports.^{34,40,53,66–69} The larger lanthanide cations, such as La^{3+} and Nd^{3+} , can form sandwich square structure Ln_4L_2 , while the lanthanides positioned in the middle of the series, such as Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} (Fig. S30–S39[†]), can produce tetragonal antiprism Ln_8L_4 . In contrast, the smaller lanthanide ions ($\text{Ln} = \text{Er}^{3+}$ and Lu^{3+}) yield a mixture of both Ln_8L_4 and Ln_6L_3 (Fig. S40–S43[†]). It is important to highlight that our observations differ from previous reports, which suggested that

structural alternation was only caused by ionic radii without observing changes in ligand conformation.^{34,40,66–69} In our case, however, the variation in the conformation of ligands was distinctly observed (*vide supra*).

Inspired by the structural transformation from Lu_8L_4 to Lu_6L_3 , we subsequently explore whether other lanthanide ions exhibit similar structural changes in the presence of excess Ln^{3+} ions. For La^{3+} , no changes were detected in the ^1H NMR spectrum after adding excess La^{3+} ions into the solution of La_4L_2 (Fig. S23[†]), indicating that excess La^{3+} ions do not trigger structural conversion. However, for Sm^{3+} ion, the NMR titration experiment of excess Sm^{3+} ions showed the emergence of new NMR peaks when the metal-to-ligand ratio reached 2.8:1. At a ratio of 4:1, a set of high-symmetry ^1H NMR signals was achieved (Fig. S24[†]). This high symmetry NMR spectrum is distinctly different from that of Sm_8L_4 but similar to that of Lu_6L_3 . This observation may suggest that the excess Sm^{3+} ions can induce the structural transformation from Sm_8L_4 to Sm_6L_3 , as the result obtained with Lu^{3+} . The measurement of the mass spectrum demonstrates that the molecular formula of the predominant product after structural transformation was Sm_6L_3 (Fig. 3B). The observations presented above together with the result of the Lu^{3+} ion (*vide supra*) show that excess La^{3+} ions with larger radii are unable to drive structural transformation, while smaller Ln^{3+} ions, such as Sm^{3+} and Lu^{3+} ions, can facilitate such changes. This finding seems to go against traditional knowledge, that is, the smaller the radius of the lanthanide ions, the more stable the resulting complexes and the less likely to suffer structural transformations. Given that the ligand **L** adopts different conformations (mode A in La_4L_2 and Mode D in Sm_8L_4 , Table S6[†]) and exhibits varying torsion angles between panel phenyl rings of the ligand's panel (Fig. 4B and E, 27.60° in La_4L_2 and 40.32° in Sm_8L_4) in the crystal structure of La_4L_2 and Sm_8L_4 , we infer that these differences may account for why La_4L_2 is stable and does not undergo structural transformation, while Sm_8L_4 is more labile and capable of such transformation.

Photophysical properties

The UV-vis absorption and luminescence spectra of **L** and Ln_8L_4 ($\text{Ln} = \text{Sm}^{3+}$, Tb^{3+} , and Dy^{3+}) were measured in a solution at room temperature. Luminescence analysis data show that the ligand **L** can sensitize Sm^{3+} , Tb^{3+} and Dy^{3+} ions (Fig. 5). Upon the excitation wavelength of 345 nm, the complex Tb_8L_4 exhibits characteristic line-like emission peaks at 487 nm, 543 nm, 585 nm, and 620 nm, which correspond to $^5\text{D}_4 \rightarrow ^6\text{F}_J$ ($J = 6-3$) energy level transition of Tb^{3+} (Fig. 5, top). The quantum yield of Tb_8L_4 in acetonitrile solution is up to 92.74% (Fig. S68[†]), which is higher than our previously reported tetrahedral Tb^{3+} cage with a record quantum yield of 82% in multinuclear LOPs.⁷³ Hence, Tb_8L_4 represents a new record-setting quantum yield in multinuclear LOPs. The above results indicate that the ligand **L** has excellent sensitization efficiency towards Tb^{3+} . In contrast, the ligand **L** exhibits relatively poor sensitization ability on Sm^{3+} and Dy^{3+} ions because the quantum yield for Sm_8L_4 and Dy_8L_4 is determined to be



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