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# Ionic radius-dependent self-assembly of lanthanide organic polyhedra: structural diversities and luminescent properties†

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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 tetrapropic 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 Ln<sub>8</sub>L<sub>4</sub> (Ln = Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup> and Ho<sup>3+</sup>) 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 La<sup>3+</sup> and Nd<sup>3+</sup> ions produced Ln<sub>4</sub>L<sub>2</sub> with a distinct sandwich square architecture. In contrast, the smaller Er<sup>3+</sup> and Lu<sup>3+</sup> ions gave rise to a mixture of both Ln<sub>8</sub>L<sub>4</sub> and Ln<sub>6</sub>L<sub>3</sub>. On adding excess Ln<sup>3+</sup> ions, a structural transformation from Ln<sub>8</sub>L<sub>4</sub> to Ln<sub>6</sub>L<sub>3</sub> occurred. Structural comparisons of La<sub>4</sub>L<sub>2</sub> and Sm<sub>8</sub>L<sub>4</sub> 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 Sm<sup>3+</sup>, Tb<sup>3+</sup> and Dy<sup>3+</sup> ions, displaying their characteristic luminescence emission, with a new record-setting luminescent quantum yield of 92.74% observed for Tb<sub>8</sub>L<sub>4</sub>. 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,<sup>1–5</sup> molecular recognition and separation,<sup>6–11</sup> drug delivery<sup>12–15</sup> and guest binding.<sup>16–22</sup> 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,<sup>23–27</sup> 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.<sup>28,29</sup> 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 C<sub>2</sub> symmetric ditropic tridentate or C<sub>4</sub> symmetric tetra-tropic tridentate ligands with nine-coordinated Ln centers. They typically form cubic structures that can be represented by the formulas Ln<sub>8</sub>L<sub>12</sub> (L = C<sub>2</sub>-symmetric ligands) or Ln<sub>8</sub>L<sub>6</sub> (L = C<sub>4</sub>-symmetric ligands) based on the geometric matching principle between the ligand and Ln<sup>3+</sup> ions, which was proposed by Raymond and co-workers.<sup>30</sup> To date, several Ln<sub>8</sub>L<sub>12</sub> or Ln<sub>8</sub>L<sub>6</sub> compounds have been successfully developed by our group and other groups.<sup>31–36</sup> Nevertheless, most of the reported Ln<sub>8</sub>L<sub>12</sub> or Ln<sub>8</sub>L<sub>6</sub> 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<sup>37,38</sup> 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,<sup>39–42</sup> stoichiometry,<sup>43,44</sup> concentration,<sup>31,45,46</sup> anions,<sup>47,48</sup> pH<sup>49,50</sup> and some others.<sup>51,52</sup> Among these factors, the selection of metal ions is particularly significant in the design of metal organic polyhedra.<sup>39–42</sup> 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 Ln<sup>3+</sup> 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.<sup>7,53</sup> Recently, our group developed a post-synthetic transmetalation self-assembly strategy for creating near infrared emitting Yb<sub>8</sub>L<sub>6</sub> cube, which cannot be achieved using a direct synthesis method.<sup>34</sup> A deeper understanding of the specific role of Ln<sup>3+</sup> 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<sub>2n</sub>L<sub>n</sub> (*n* = 2, 3 and 4) assemblies with the unsaturated metal sites: sandwich square Ln<sub>4</sub>L<sub>2</sub>, the triangular prism Ln<sub>6</sub>L<sub>3</sub>, and the unique twisted tetrahedron prism Ln<sub>8</sub>L<sub>4</sub>. 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 Sm<sub>8</sub>L<sub>4</sub>, Tb<sub>8</sub>L<sub>4</sub> and Dy<sub>8</sub>L<sub>4</sub> were investigated.

## Results and discussion

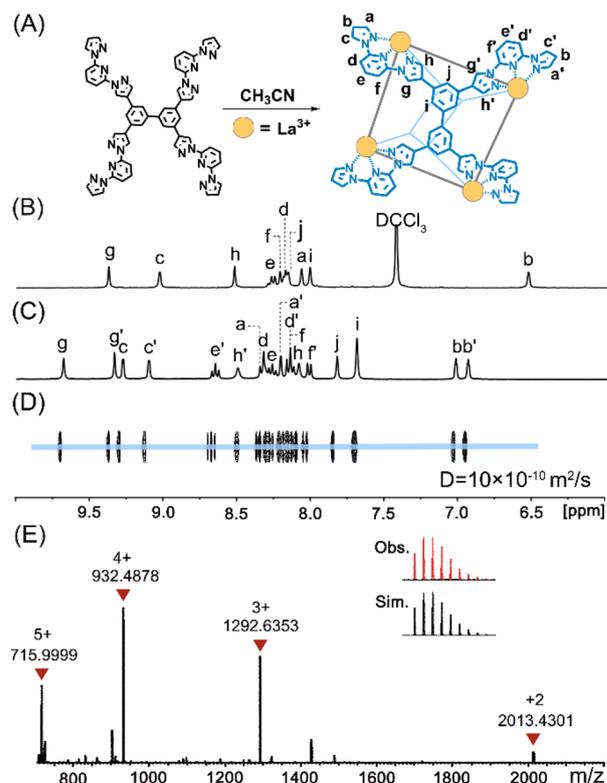
### Ligand design, synthesis and assembly with lanthanides

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.<sup>34,54–59</sup> 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.<sup>60,61</sup> 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.<sup>62,63</sup> However, this motif has been less explored in preparing rare earth coordination compounds.<sup>64,65</sup> Consequently, we opted to introduce bpp tridentate chelating units into the tetra-tropic ligand, and its assembly with Ln<sup>3+</sup> 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 La<sub>4</sub>L<sub>2</sub>

When 2.0 equiv. of ligand **L** was treated with 4.0 equiv. of La(OTf)<sub>3</sub> in acetonitrile at 70 °C for 30 min, the turbid suspension of the ligand gradually turned into a homogeneous clear solution. The <sup>1</sup>H NMR spectrum clearly indicates the generation of La<sub>4</sub>L<sub>2</sub> assembly. Compared with the highly symmetric free **L**, the <sup>1</sup>H NMR spectrum of La<sub>4</sub>L<sub>2</sub> showed 2-fold desymmetrization of the **L** (Fig. 1B and C), in agreement with the D<sub>2</sub> point symmetry of a sandwich square. The DOSY spectrum dis-



**Fig. 1** (A) Self-assembly of **L** with La(OTf)<sub>3</sub>. <sup>1</sup>H NMR spectra (400 MHz, 298 K) of **L** in CDCl<sub>3</sub> (B) and La<sub>4</sub>L<sub>2</sub> in CD<sub>3</sub>CN (C). (D) DOSY spectra of La<sub>4</sub>L<sub>2</sub>. (E) ESI-TOF-MS of La<sub>4</sub>L<sub>2</sub> with the inset showing the observed and simulated isotopic patterns of the +4 peak.



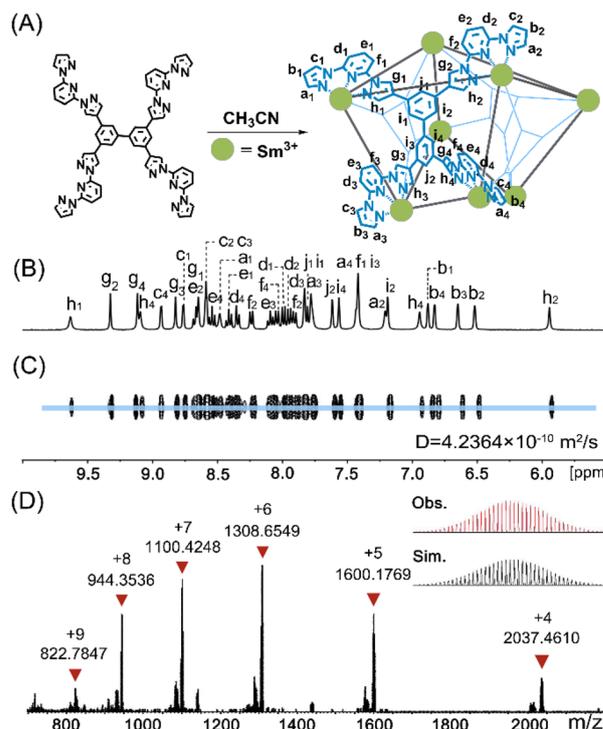
plays a single diffusion band with a diffusion coefficient of  $10 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , corresponding to a hydrodynamic radius of 12.72 Å for  $\text{La}_4\text{L}_2$  calculated using the Stokes–Einstein equation (Fig. 1D). As shown in Fig. 1E, high-resolution ESI-TOF-MS clearly suggests the presence of sandwich square assembly with a molecular formula of  $\text{La}_4(\text{L})_2(\text{OTf})_{12}$ . A set of prominent peaks was assigned according to the consecutive loss of  $\text{OTf}^-$  counter ions. For example, peaks with  $m/z = 715.9999$ , 932.4878, 1292.6353 and 2013.4301 correspond to  $[\text{La}_4(\text{L})_2(\text{OTf})_7]^{5+}$ ,  $[\text{La}_4(\text{L})_2(\text{OTf})_8]^{4+}$ ,  $[\text{La}_4(\text{L})_2(\text{OTf})_9]^{3+}$  and  $[\text{La}_4(\text{L})_2(\text{OTf})_{10}]^{2+}$ , respectively. Moreover, the isotopic pattern of each assignment was in line with the simulated one (Fig. 1E, inset).

### Synthesis and characterization of $\text{Sm}_8\text{L}_4$

Previous studies have demonstrated that the generation of lanthanide architectures is sensitive to the radius of lanthanide ions.<sup>34,40,53,66–69</sup> Consequently, we hypothesize that using lanthanide ions bearing a smaller radius than  $\text{La}^{3+}$  ions may lead to the development of a different architecture during the self-assembly process. To our delight, when  $\text{Sm}(\text{OTf})_3$  was employed as the metal source at the same 2 : 1 metal-to-ligand ratio as  $\text{La}_4\text{L}_2$ , a noticeably different  $^1\text{H}$  NMR spectrum was observed, suggesting the formation of a new species. Based on the NMR, ESI-MS, and single-crystal X-ray diffraction data (*vide infra*), the newly formed species is a tetragonal antiprismatic  $\text{Sm}_8\text{L}_4$  LOP. Analysis of  $^1\text{H}$  NMR spectroscopy uncovered a different molecular symmetry compared to  $\text{La}_4\text{L}_2$ . Unlike the two sets of signals for the ligand arms found in  $\text{La}_4\text{L}_2$ , we detected four sets of ligand arm signals after substituting  $\text{La}(\text{OTf})_3$  with  $\text{Sm}(\text{OTf})_3$  (Fig. 2B). The proton signals are completely assigned based on  $^1\text{H}$ - $^1\text{H}$  COSY and NOE 2D spectra (Fig. S14 and S15<sup>†</sup>). Because the four sets of proton signals exhibit equal intensity on the  $\text{Sm}_8\text{L}_4$  cage, we conclude that there is only one magnetically distinct ligand, which is in agreement with its  $S_4$  symmetry observed on the solid-state structure (*vide infra*). Evidence for the exclusive formation of a sole species in solution was offered by  $^1\text{H}$  diffusion ordered spectroscopy (DOSY), where all signals were located in a single band (Fig. 2C), from which the kinetic diameter of 30.03 Å could be estimated. To verify the stoichiometry of the  $\text{Sm}^{3+}$  assembly, the ESI-MS spectrum was recorded using acetonitrile as the solvent. The observed peaks at  $m/z = 822.7847$ , 944.3536, 1100.4248, 1308.6549, 1600.1769 and 2037.4610 belong to the fragments  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{15}]^{9+}$ ,  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{16}]^{8+}$ ,  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{17}]^{7+}$ ,  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{18}]^{6+}$ ,  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{19}]^{5+}$  and  $[\text{Sm}_8(\text{L})_4(\text{OTf})_{20}]^{4+}$ , respectively. The ESI-MS result certifies a tetragonal prism composition of  $\text{Sm}_8\text{L}_4$  assembly.

### Synthesis and characterization of $\text{Lu}_6\text{L}_3$

With the above fascinating finding, we are curious to know whether a new assembly will be formed when using the even smaller  $\text{Lu}^{3+}$  ion. By replacing the metal source of  $\text{Sm}^{3+}$  with  $\text{Lu}^{3+}$ , we observed a distinct  $^1\text{H}$  NMR pattern that showed more complicated signals compared with  $\text{Sm}_8\text{L}_4$  species (Fig. S21<sup>†</sup>). It was impossible to make a detailed proton assign-



**Fig. 2** (A) Self-assembly of L with  $\text{Sm}(\text{OTf})_3$ . (B)  $^1\text{H}$  NMR spectra (400 MHz, 298 K) of  $\text{Sm}_8\text{L}_4$  in  $\text{CD}_3\text{CN}$ . (C) DOSY spectra of  $\text{Sm}_8\text{L}_4$ . (D) ESI-TOF-MS of  $\text{Sm}_8\text{L}_4$  with the inset showing the observed and simulated isotopic patterns of the +6 peak.

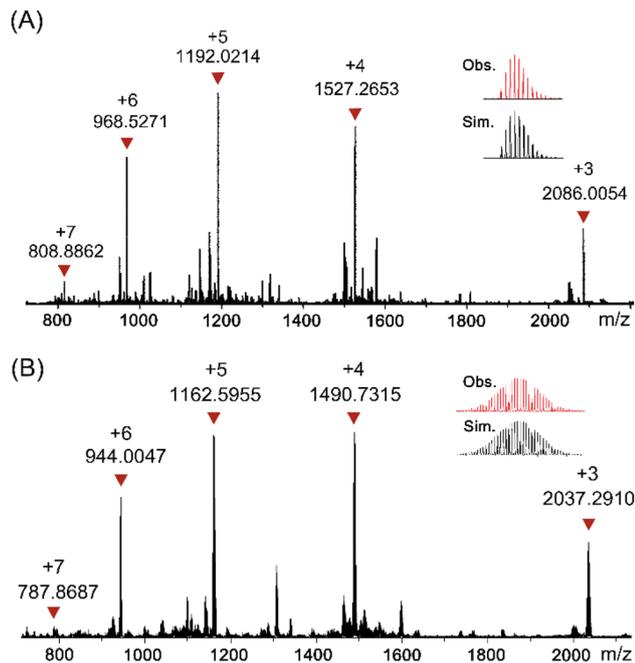
ment because of obvious line broadening and overlapping signals. However, the ESI-MS spectrum indicated the formation of mixed  $\text{Lu}_6\text{L}_3$  and  $\text{Lu}_8\text{L}_4$  (Fig. S42<sup>†</sup>).

It is known that an excess of metal can trigger an initial assembly transformation into a new species.<sup>68</sup> Inspired by this, we explored the effect of metal excess on the structure. The  $^1\text{H}$  NMR titration experiment indicates that the broadening and overlapping signals evolve into a set of well-resolved peaks once the metal-to-ligand ratio reaches 4 : 1 (Fig. S22<sup>†</sup>), which consists of ten different signals. This simplified  $^1\text{H}$  NMR spectrum was also observed by directly assembling the  $\text{Lu}^{3+}$  ion with L in a metal-to-ligand ratio of 4 : 1. The ESI-MS spectrum of the above solution demonstrates the presence of the hexanuclear complex with chemical formula  $\text{Lu}_6\text{L}_3$  (Fig. 3A), where the three tetra-topic tridentate ligand L may cover the rectangular faces of  $\text{Lu}_6\text{L}_3$ , and gives a trigonal prism structure (Scheme 1).

### Crystal structural analysis of $\text{La}_4\text{L}_2$ and $\text{Sm}_8\text{L}_4$

The slow diffusion of diethyl ether into the acetonitrile of  $\text{La}_4\text{L}_2$  for one week led to high-quality single crystals suitable for X-ray structural analysis. Single crystal X-ray diffraction analysis reveals that  $\text{La}_4\text{L}_2$  crystallizes in the monoclinic  $P2_1/n$  space group with a sandwich square structure (Fig. 4A). The asymmetric unit of  $\text{La}_4\text{L}_2$  consists of one complete  $\text{La}_4\text{L}_2$  molecule (Fig. S50<sup>†</sup>), where all four  $\text{La}^{3+}$  ions are ligated by ten donor atoms and adopt a bicapped square antiprism coordi-



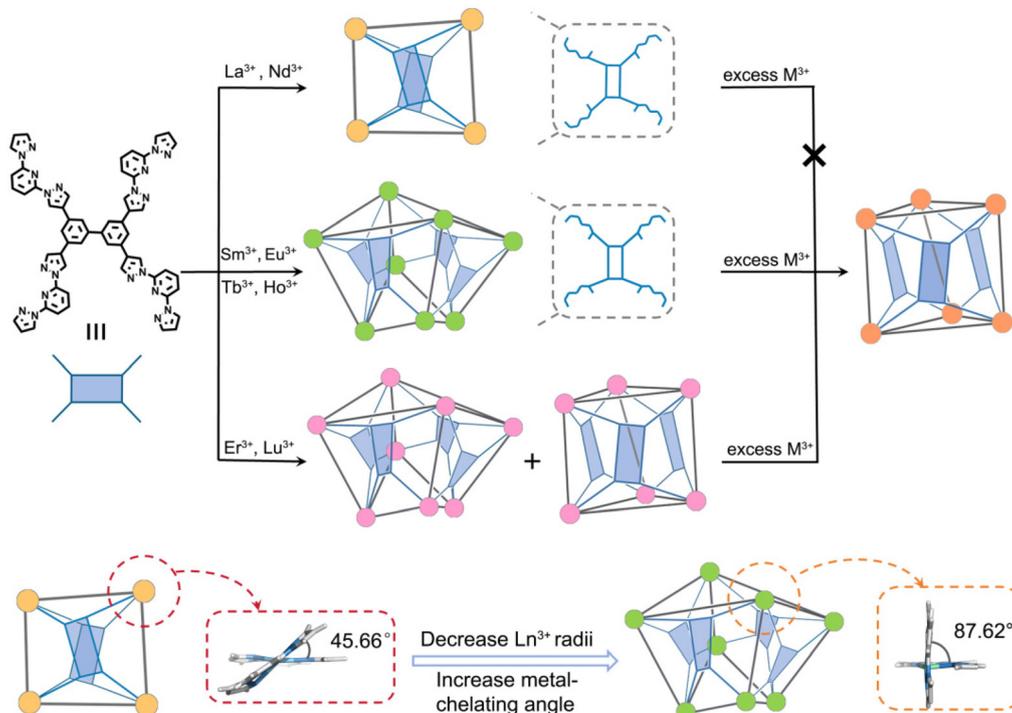


**Fig. 3** ESI-MS of  $\text{Lu}_6\text{L}_3$  (A) and  $\text{Sm}_6\text{L}_3$  (B) complexes with the insets showing the observed and simulated isotopic patterns of the +5 peak.

nation geometry (Fig. S51 and Table S3†). The dihedral angles between metal-chelating planes around the  $\text{La}^{3+}$  node are 44.67, 46.02, 46.20 and 45.74° for La1, La2, La3 and La4, respectively (Fig. S52†). Owing to one whole  $\text{La}_4\text{L}_2$  molecule

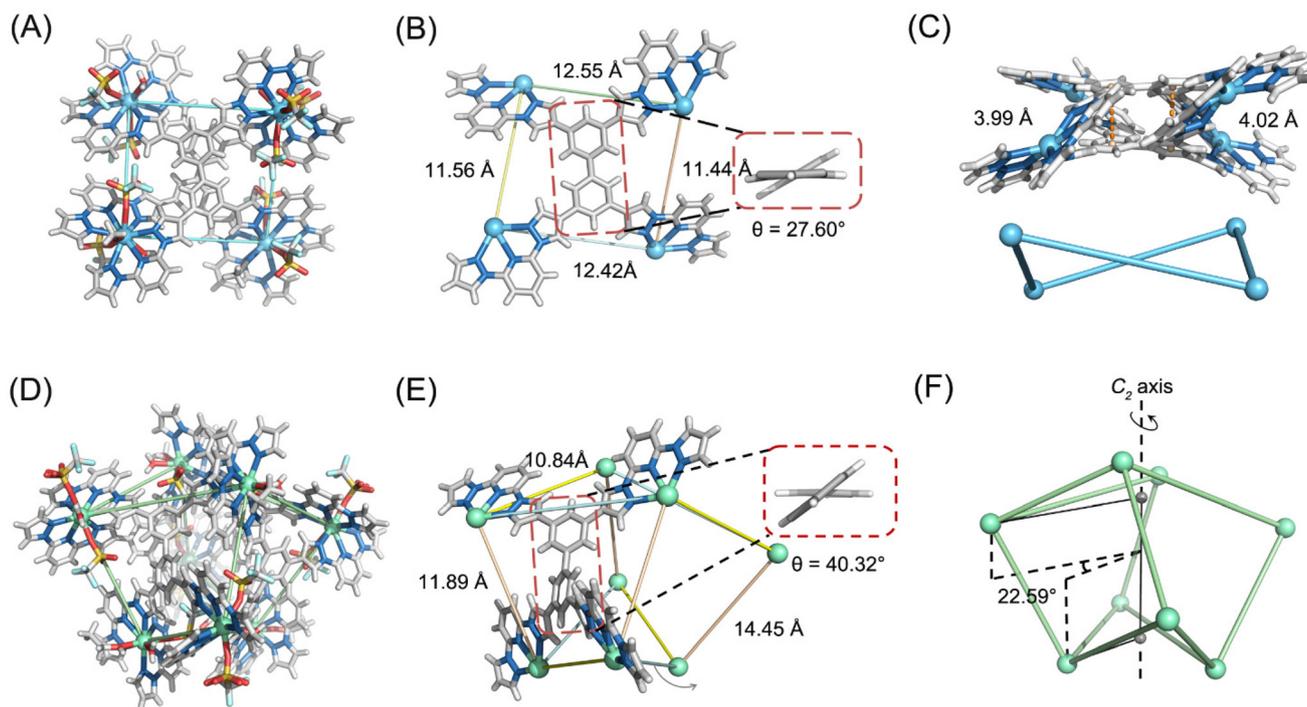
being observed in the asymmetric unit, its point symmetry in the solid-state structure is  $C_1$  rather than the solution state point symmetry  $D_2$ . This behavior should be caused by the different coordinated solvents and different numbers of coordinated  $\text{OTf}^-$  anions at the La centers, which reduced the symmetry of  $\text{La}_4\text{L}_2$  in the solid state. Thus, if we remove the coordination solvents and coordinated  $\text{OTf}^-$  anions, the point symmetry of  $\text{La}_4\text{L}_2$  can be regarded as  $D_2$  with slight deviations from perfect geometry, which is consistent with the findings from  $^1\text{H}$  NMR (*vide supra*). The four  $\text{La}^{3+}$  ions form a twisted square, with La–La distances of 11.56, 12.55, 11.44 and 12.42 Å (Fig. 4B). In  $\text{La}_4\text{L}_2$ , the two ligands bearing conformation mode A (Fig. 4B and Table S6†) are located above and below the  $\text{La}_4$  square, resulting in the metal centers with the same  $\Delta$  or  $\Lambda$  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  $\pi$ - $\pi$  stacking interaction between the two ligands. Furthermore, the average torsion angle between the phenyl ring of the ligand’s panel in  $\text{La}_4\text{L}_2$  is 27.60° (Fig. 4B).

The definitive confirmation of the structure for  $\text{Sm}_8\text{L}_4$  assembly was provided by a single-crystal diffraction analysis. Crystallographic analysis shows that  $\text{Sm}_8\text{L}_4$  crystalizes 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  $\text{Sm}_8\text{L}_4$  consists of two crystallographic independent  $\text{Sm}^{3+}$  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  $\text{La}_4\text{L}_2$ . (B) Ligand conformation with the La–La distances and average torsion angle between phenyl rings in  $\text{La}_4\text{L}_2$ . (C)  $\pi$ – $\pi$  stacking interaction between the panels of two ligands. (D) X-ray single-crystal structure of  $\text{Sm}_8\text{L}_4$ . (E) Ligand conformation with the Sm–Sm distances and average torsion angle between phenyl rings in  $\text{Sm}_8\text{L}_4$ . (F) Twist angle of  $\text{Sm}_8\text{L}_4$ , which is defined as the dihedral angle between  $\text{Sm}^{3+}$  (top face)–centroid (top face)–centroid (bottom face) face and centroid (top face)–centroid (bottom face)– $\text{Sm}^{3+}$  (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  $\text{Sm}^{3+}$  center are 86.47 and 88.77°, respectively (Fig. S56†). Research into the molecular structure of  $\text{Sm}_8\text{L}_4$  shows that each ligand bridged four  $\text{Sm}^{3+}$  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  $\text{Sm}_8\text{L}_4$  is 40.32° (Fig. 4E), leading to the four  $\text{Sm}^{3+}$  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  $\text{Sm}_8\text{L}_4$  is 11.89 Å, and the side lengths of the up and bottom distorted squares in the tetragonal antiprismatic  $\text{Sm}_8\text{L}_4$  are 10.84 Å and 14.45 Å, respectively (Fig. 4E). As shown in Fig. S57,† each tetragonal antiprismatic  $\text{Sm}_8\text{L}_4$  cage consists of a 1 : 1 ratio of  $\Delta$ - $\text{Sm}^{3+}$  and  $\Lambda$ - $\text{Sm}^{3+}$  metal vertices, where each  $\text{Sm}^{3+}$  center is surrounded by the nearest neighbors of the opposite chiral configuration. On each face of the tetragonal antiprism, the  $\Delta$ - $\text{Sm}^{3+}$  and  $\Lambda$ - $\text{Sm}^{3+}$  centers are arranged alternately. Such a distribution of metal chiral within  $\text{Sm}_8\text{L}_4$  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  $\text{Sm}^{3+}$ , 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.<sup>60,61,70,71</sup> 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  $\text{Sm}_8\text{L}_4$  (Fig. S61†). <sup>1</sup>H NMR titration experiment indicates a fast-exchange binding dynamic mode, and the apparent association constants ( $K_a$ ) for THF are determined to be 127  $\text{M}^{-1}$  by applying the Hill function (Fig. S63 and S64†). After removing the THF molecules, the cavity volume of  $\text{Sm}_8\text{L}_4$  was calculated to be 594.52 Å<sup>3</sup> using the MoloVol program.<sup>72</sup>

Extensive attempts to crystallize the  $\text{Lu}_6\text{L}_3$  were unsuccessful. This failure may be attributed to the presence of excess  $\text{Lu}^{3+}$  ions in the solution, which could disrupt the crystallization process by promoting the formation of amorphous or poorly ordered competing phases rather than desired  $\text{Lu}_6\text{L}_3$  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  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  ions, which have different radii and exhibit different coordination numbers, give rise to the assemblies with different nuclearities. For example, the  $\text{La}^{3+}$  ion, the largest along the lanthanide series, has a coordination number of ten in  $\text{La}_4\text{L}_2$ . This results in a small average dihedral angle between the metal-chelating planes around the  $\text{La}^{3+}$  node (Avg:  $45.66^\circ$ ), promoting the formation of a sandwich square structure. In contrast, the smaller  $\text{Sm}^{3+}$  ion has a coordination number of nine in  $\text{Sm}_8\text{L}_4$ . This reduction in the coordination number allows for enough space to increase the dihedral angle between the metal-chelating planes surrounding the  $\text{Sm}^{3+}$  center, which is essential for the formation of higher nuclearity assemblies. Consequently, a larger average dihedral angle was obtained around the  $\text{Sm}^{3+}$  node in  $\text{Sm}_8\text{L}_4$  (Avg:  $87.62^\circ$ ), leading to the generation of higher nuclearity  $\text{Sm}_8\text{L}_4$ . Second, the ligand **L** in  $\text{La}_4\text{L}_2$  and  $\text{Sm}_8\text{L}_4$  displays different conformations: mode A for  $\text{La}_4\text{L}_2$  and mode D for  $\text{Sm}_8\text{L}_4$  (Fig. 4B, E and Table S6<sup>†</sup>). Third, the average torsion angle between the phenyl ring of the ligand's panel in  $\text{La}_4\text{L}_2$  and  $\text{Sm}_8\text{L}_4$  is different:  $27.60^\circ$  in  $\text{La}_4\text{L}_2$  and  $40.32^\circ$  in  $\text{Sm}_8\text{L}_4$ . Because the metal nodes in  $\text{La}_4\text{L}_2$  and  $\text{Sm}_8\text{L}_4$  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  $\text{La}_4\text{L}_2$ ,  $\text{Sm}_8\text{L}_4$  and  $\text{Lu}_6\text{L}_3$ , we determine whether these assemblies were exclusively formed by their corresponding  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Lu}^{3+}$  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 ( $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$ ), which span the Ln series and offer a range of ionic radii. The experiments were carried out using 2:1 ratios of lanthanide triflates ( $\text{Ln} = \text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$ ) and **L** in acetonitrile. For the  $\text{Nd}^{3+}$  ion, the mass spectrum analysis supported the formation of the  $\text{Nd}_4\text{L}_2$  complex (Fig. S28<sup>†</sup>), similar to the results obtained with the  $\text{La}^{3+}$  ion. However, when the  $\text{Nd}^{3+}$  ion was replaced with  $\text{Eu}^{3+}$  ions, the mass spectrum data revealed the production of octanuclear  $\text{Eu}_8\text{L}_4$  complexes (Fig. S32<sup>†</sup>), similar to those observed with  $\text{Sm}^{3+}$  ions. In contrast, the use of the  $\text{Er}^{3+}$  ion resulted in a mixture of self-assembled species, including  $\text{Er}_8\text{L}_4$  and  $\text{Er}_6\text{L}_3$  supramolecular architectures, as evidenced by its mass spectrum (Fig. S40<sup>†</sup>). 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.<sup>34,40,53,66–69</sup> The larger lanthanide cations, such as  $\text{La}^{3+}$  and  $\text{Nd}^{3+}$ , can form sandwich square structure  $\text{Ln}_4\text{L}_2$ , while the lanthanides positioned in the middle of the series, such as  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Ho}^{3+}$  (Fig. S30–S39<sup>†</sup>), can produce tetragonal anti-prism  $\text{Ln}_8\text{L}_4$ . In contrast, the smaller lanthanide ions ( $\text{Ln} = \text{Er}^{3+}$  and  $\text{Lu}^{3+}$ ) yield a mixture of both  $\text{Ln}_8\text{L}_4$  and  $\text{Ln}_6\text{L}_3$  (Fig. S40–S43<sup>†</sup>). It is important to highlight that our observations differ from previous reports, which suggested that

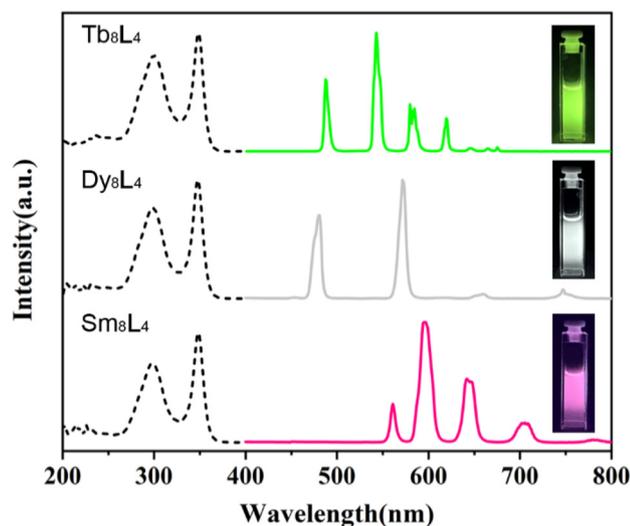
structural alternation was only caused by ionic radii without observing changes in ligand conformation.<sup>34,40,66–69</sup> In our case, however, the variation in the conformation of ligands was distinctly observed (*vide supra*).

Inspired by the structural transformation from  $\text{Lu}_8\text{L}_4$  to  $\text{Lu}_6\text{L}_3$ , we subsequently explore whether other lanthanide ions exhibit similar structural changes in the presence of excess  $\text{Ln}^{3+}$  ions. For  $\text{La}^{3+}$ , no changes were detected in the  $^1\text{H}$  NMR spectrum after adding excess  $\text{La}^{3+}$  ions into the solution of  $\text{La}_4\text{L}_2$  (Fig. S23<sup>†</sup>), indicating that excess  $\text{La}^{3+}$  ions do not trigger structural conversion. However, for  $\text{Sm}^{3+}$  ion, the NMR titration experiment of excess  $\text{Sm}^{3+}$  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  $^1\text{H}$  NMR signals was achieved (Fig. S24<sup>†</sup>). This high symmetry NMR spectrum is distinctly different from that of  $\text{Sm}_8\text{L}_4$  but similar to that of  $\text{Lu}_6\text{L}_3$ . This observation may suggest that the excess  $\text{Sm}^{3+}$  ions can induce the structural transformation from  $\text{Sm}_8\text{L}_4$  to  $\text{Sm}_6\text{L}_3$ , as the result obtained with  $\text{Lu}^{3+}$ . The measurement of the mass spectrum demonstrates that the molecular formula of the predominant product after structural transformation was  $\text{Sm}_6\text{L}_3$  (Fig. 3B). The observations presented above together with the result of the  $\text{Lu}^{3+}$  ion (*vide supra*) show that excess  $\text{La}^{3+}$  ions with larger radii are unable to drive structural transformation, while smaller  $\text{Ln}^{3+}$  ions, such as  $\text{Sm}^{3+}$  and  $\text{Lu}^{3+}$  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  $\text{La}_4\text{L}_2$  and Mode D in  $\text{Sm}_8\text{L}_4$ , Table S6<sup>†</sup>) and exhibits varying torsion angles between panel phenyl rings of the ligand's panel (Fig. 4B and E,  $27.60^\circ$  in  $\text{La}_4\text{L}_2$  and  $40.32^\circ$  in  $\text{Sm}_8\text{L}_4$ ) in the crystal structure of  $\text{La}_4\text{L}_2$  and  $\text{Sm}_8\text{L}_4$ , we infer that these differences may account for why  $\text{La}_4\text{L}_2$  is stable and does not undergo structural transformation, while  $\text{Sm}_8\text{L}_4$  is more labile and capable of such transformation.

### Photophysical properties

The UV-vis absorption and luminescence spectra of **L** and  $\text{Ln}_8\text{L}_4$  ( $\text{Ln} = \text{Sm}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Dy}^{3+}$ ) were measured in a solution at room temperature. Luminescence analysis data show that the ligand **L** can sensitize  $\text{Sm}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  ions (Fig. 5). Upon the excitation wavelength of 345 nm, the complex  $\text{Tb}_8\text{L}_4$  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  $\text{Tb}^{3+}$  (Fig. 5, top). The quantum yield of  $\text{Tb}_8\text{L}_4$  in acetonitrile solution is up to 92.74% (Fig. S68<sup>†</sup>), which is higher than our previously reported tetrahedral  $\text{Tb}^{3+}$  cage with a record quantum yield of 82% in multinuclear LOPs.<sup>73</sup> Hence,  $\text{Tb}_8\text{L}_4$  represents a new record-setting quantum yield in multinuclear LOPs. The above results indicate that the ligand **L** has excellent sensitization efficiency towards  $\text{Tb}^{3+}$ . In contrast, the ligand **L** exhibits relatively poor sensitization ability on  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  ions because the quantum yield for  $\text{Sm}_8\text{L}_4$  and  $\text{Dy}_8\text{L}_4$  is determined to be





**Fig. 5** Excitation (black-dashed lines) and emission (solid color lines) spectra of  $\text{Tb}_8\text{L}_4$ ,  $\text{Dy}_8\text{L}_4$ , and  $\text{Sm}_8\text{L}_4$  in the visible region ( $c = 1 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ). Insets show the emission under a 365 nm UV light.

0.88% and 2.79% (Table S7<sup>†</sup>), respectively, which are lower than that of  $\text{Tb}_8\text{L}_4$ . Interestingly,  $\text{Dy}_8\text{L}_4$  shows single-component white-light emission when excited at 365 nm by UV light (Fig. 5, inset). Because the ligand **L** emits blue light (351 nm, Fig. S72<sup>†</sup>) and the  $\text{Dy}^{3+}$  ions mainly exhibit yellow light (572 nm, Fig. S72<sup>†</sup>), the single-component white-light emission of  $\text{Dy}_8\text{L}_4$  can be ascribed to the combination of **L**-centered emission and  $\text{Dy}^{3+}$ -centered emission. To elucidate the different sensitization abilities of ligand **L** to lanthanide ions, we measured the phosphorescence spectrum of the  $\text{Gd}_8\text{L}_4$  complex at low temperatures (Fig. S75<sup>†</sup>). The triplet energy level of the ligand was calculated to be  $22\,523\text{ cm}^{-1}$ , which is closer to the excitation energy level of  $\text{Tb}^{3+}$  ( $E = 20\,500\text{ cm}^{-1}$ ), meaning that ligand **L** exerts a favorable sensitization effect on  $\text{Tb}^{3+}$ .

## Conclusions

In summary, we reported the synthesis and characterization of a series of lanthanide  $\text{Ln}_{2n}\text{L}_n$  ( $n = 2, 3, 4$ ) assemblies with tetranuclear sandwich square, hexanuclear triangular prism and octanuclear tetragonal antiprism structures. The larger  $\text{La}^{3+}$  and  $\text{Nd}^{3+}$  ions favor the formation of sandwich square structure  $\text{Ln}_4\text{L}_2$ , while with a decrease in radius, the smaller  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  give rise to a different structure: the twisted tetragonal prism,  $\text{Ln}_8\text{L}_4$ . Meanwhile, even smaller  $\text{Er}^{3+}$  and  $\text{Lu}^{3+}$  ions lose the ability to form exclusively a single species, resulting instead in a mixture of the tetragonal prism,  $\text{Ln}_8\text{L}_4$ , and the trigonal prism,  $\text{Ln}_6\text{L}_3$ . Interestingly, the excess  $\text{Ln}^{3+}$  ions ( $\text{Ln} = \text{Sm}^{3+}$  and  $\text{Lu}^{3+}$ ) can trigger the structural transformation from  $\text{Ln}_8\text{L}_4$  to  $\text{Ln}_6\text{L}_3$ . The luminescence investigations revealed that the tetra-topic tridentate ligand based on 2,6-di[pyrazol-1-yl]pyridine can sensitize the luminescence emissions of

lanthanide ions simultaneously ( $\text{Sm}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ ). Moreover, a record high luminescence quantum yield ( $\Phi = 92.74\%$ ) was achieved for  $\text{Tb}_8\text{L}_4$  assembly. This work demonstrates that the ionic radii of lanthanide affect the resulting supramolecular architectures and that multidentate ligands with rectangular panels are excellent candidates for creating nonclassical Archimedean or Platonic lanthanide solids. Synthesizing additional rectangular multidentate ligands is currently being undertaken to further develop nonclassical LOPs.

## Author contributions

Q. F. S. and C. B. T. designed and supervised the project; J. S. completed the synthesis and performed the experiments; F. Y. solved all the crystal structures; X. F. D. and J. Y. Z. analyzed the experiment data; L. P. Z. contributed the mass experiments. S. J., C. B. T. and Q. F. S. wrote the manuscript; all the authors discussed the results and commented on the manuscript.

## Data availability

The data supporting this article have been included as part of the ESI.<sup>†</sup>

## Conflicts of interest

There are no conflicts to declare.

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