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Fine-Tuned Visible and Near-Infrared Luminescence on Self-Assembled Lanthanide-Organic Tetrahedral Cages with Triazole-**Based Chelates**

Shi-Yu Wu,^{†,‡,§} Xiao-Qing Guo,^{†,‡,§} Li-Peng Zhou,[†][®] and Qing-Fu Sun^{*,†,‡}[®]

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Supporting Information

ABSTRACT: The construction of well-defined lanthanide complexes emitting in both the visible and near-infrared regions is of great importance due to their widespread applications in phosphors, light-emitting diodes, biosensors/ probes, optical communications, etc. In comparison to the well-known mononuclear and dinuclear lanthanide complexes, multinuclear lanthanide supramolecular edifices with bright luminescence are still scarce. Herein, we report the coordination self-assembly of strongly luminescent lanthanide-organic tetrahedral Ln₄L₄ cages with a series of tris(tridentate) ligands based on the triazole chelates. Among them, the new ligand L3 with triazole-pyridine-



triazole (TPT) chelates manifests an excellent sensitization toward all of the lanthanide ions (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) that emit in both the visible and near-infrared regions, with a record luminescent quantum yield for $Tb_4(L3)_4$ ($\Phi =$ 82%) being obtained. In contrast, ligands with amido-pyridine-triazole (APT) or TPA chelates show much weaker sensitization ability. Energy levels for all ligands were measured, and TD-DFT calculations were employed to shed light on the sensitization mechanism. Finally, white-light emission systems formed by combining the desired luminescent compounds have been demonstrated. Our strongly luminescent LOPs provide new candidates for photochemical supramolecular devices.

INTRODUCTION

Lanthanides, a series of peculiar elements in the periodic table with similar atomic radii and chemical properties, hold unique photophysical properties due to their shielded 4f electrons. Sharp linelike emission bands, long lifetimes, and large Stokes/ anti-Stoke shifts of the lanthanide luminescence facilitate their various applications, such as phosphors, light-emitting diodes, biosensors/probes, and so on.²⁻⁵ However, the absorptions arising from the direct 4f-4f transitions of lanthanides are very weak (with molar absorption coefficient $\varepsilon < 10^2 \text{ M}^{-1} \text{ cm}^{-1}$) due to the Laporte symmetry-forbidden rules.⁶ As such, stimulations of luminescence on inorganic lanthanide nanoparticles or clusters often suffer from low brightness ($B = \varepsilon \Phi$, where Φ stands for the photoluminescent quantum yield) and require the irradiation of a high-power laser source. On the other hand, numerous strong luminescent lanthanide-organic complexes, especially 3D lanthanide-organic frameworks, have been reported,⁸⁻¹¹ where suitable ligands containing chromophores with strong absorption are used to sensitize the lanthanide through the so-called "antenna effect".^{12,13} However, realization of the near-infrared (NIR) luminescence still represents a great challenge in these lanthanide complexes due to the vibrational quenching from organic ligands or coordinating solvent molecules.^{14,15} So far, NIR-emitting lanthanide (Ln = Pr, Nd, Sm, Dy, Ho, Er, Tm, Yb) complexes often suffer from relatively low intensity and short lifetime in comparison to their visible-emitting Eu and Tb counterparts. Known strategies to enhance the NIR emission of lanthanide complexes include the use of fluorinated ligands^{16,17} or d-block metalloligands^{18–20} as sensitizers.

Coordination self-assembled 3D supramolecular cages have received growing attention in the past decades, owing to their versatile structures as exquisite edifices displaying distinct inner space and diverse functional sites.^{21–29} Various supramolecular cages based on transition metals have been designed and reported.³⁰⁻⁴⁰ In sharp contrast, research on lanthanidedirected self-assembly has clearly lagged behind,⁴¹⁻⁴⁴ because of the lability and unpredictability of lanthanide coordination numbers and geometries. Though supramolecular mononuclear clathrate compounds, bundles, and dinuclear helicates with lanthanides have been comprehensively investigated,^{45–49} the rational design of 3D supramolecular lanthanide polyhedra is still in its infancy.⁵⁰⁻⁵³

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Introduction of lanthanides into coordination self-assembly will not only diversify the metallasupramolecular structures but also bring new functionality. From 2015, we reported a series of studies on the self-assembly of multicomponent supramolecular lanthanide edifices, including their ligand design principles, stereoselectivity, ligand and metal self-sorting behavior, luminescent photoswitching, and sensing.^{43,53–62} Bright visible-emitting tetrahedral cages with Eu and Tb have been realized by modification of the widely used pyridine-2,6diacarboxamide (pcam)-based ligands with oxazoline (L1) and triazole (L2) chelating groups (Scheme 1).^{56,60} In the latter

Scheme 1. Strongly Luminescent Lanthanide-Organic Tetrahedral Ln_4L_4 Cages Based on Tris(tridentate) Ligands with Different Chelating Groups



case, an unprecedented photoluminescent quantum yield ($\Phi = 56.6\%$) for Eu₄(**L2**)₄ was obtained. However, it is worth pointing out that the NIR emission of lanthanide-organic polyhedra (LOPs) has been rarely discussed so far. These precedents motivate our further study on the ligand effects toward the luminescence of LOPs, especially on their NIR emission properties.

Herein, we report fine-tuned luminescence on a series of Ln_4L_4 -type cages constructed by two new ligands (L3 and L4) with the triphenyltriazine core. We find that the fully conjugated L3, with TPT chelating groups, manifests excellent sensitization ability toward all the emitting lanthanide ions (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) covering both the visible and NIR regions. A record luminescent quantum yield for $Tb_4(L3)_4$ is reached ($\Phi = 82\%$). As a control, L4 with an amido-pyridine-triazole (APT) chelate that differs from the known L2 only in the relative position of the amido and triazole groups exhibits weaker sensitization ability on the LOPs. Finally, white-light emission systems have also been obtained by combining the desired luminescent compounds.

RESULTS AND DISCUSSION

Synthesis and Characterization. Ligands L3 and L4 were straightforwardly synthesized from bridging C_3 -symmetry 2,4,6-triphenyl-1,3,5-triazine and versatile arms by a Cu¹-catalyzed azide–alkyne cycloaddition (CuAAC) reaction⁶³ or an HATU condensation reaction.⁶⁴ Both ligands were fully characterized by NMR and high-resolution ESI-TOF-MS (see the experimental section in the Supporting Information for details).

Ligand L3 (1 equiv) was treated with $Ln(OTf)_3$ (1.1 equiv) in a mixed CD_3CN/CD_3OD (v/v 4/1) solvent and stirred for 3 h at 50 °C, affording a homogeneous faint yellow solution (Figure 1A). ¹H NMR spectra (Figure 1B,C) indicate the formation of a single species with high symmetry. In contrast



Figure 1. (A) Self-assembly from L3 to $Eu_4(L3)_4$. ¹H NMR spectra of (B) L3 (600 MHz, DMSO- d_{67} 298 K) and (C) $Eu_4(L3)_4(OTf)_{12}$ (400 MHz, CD₃CN/CD₃OD, 298 K). (D) DOSY spectrum and (E) ESI-TOF-MS measurement of $Eu_4(L3)_4(OTf)_{12}$ with insets showing the observed and simulated isotopic patterns for $[Eu_4(L3)_4(OTf)_4]^{8+}$.

with free L3, the proton signals of the complex show clear shifting and broadening after coordination with the paramagnetic Eu ion. Protons on pyridine are shifted dramatically upfield ($\Delta \delta = 1.2-2.7$ ppm), and two protons on different triazole groups display upfield shifts of 0.46 and 1.23 ppm, respectively. Moreover, H_i on the terminal isopropyl splits into two doublets with equal integrals, indicating their rigidified orientation in line with the C_3 -symmetry coordination geometry of Eu ion. A diffusion-ordered ¹H NMR (DOSY) spectrum also confirms the formation of a single species with a radius of 1.01 nm as calculated by the Stokes-Einstein equation (diffusion coefficient $D = 5.61 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, Figure 1D). ESI-TOF-MS analysis further confirms the composition of the complex, where a series of peaks corresponding to $[Ln_4(L3)_4(OTf)_{12-n}]^{n+}$ are found with finely resolved isotope distribution perfectly matching the simulated results (Figure 1E and Figure S73). Moreover, $Ln_4(L3)_4$ shows good stability and solubility in common medium-polarity solvents, including CH₃CN, CH₃OH, and CH₃NO₂ (Figure S25). Thermogravimetric analysis (TGA) suggests that this cage remains stable below 380 °C (Figure S91).

All other $Ln_4(L3)_4$ species (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb) and $Ln_4(L4)_4$ (Ln = Sm, Eu, Gd, Tb, Dy) were synthesized according to the above protocol, and their structures were confirmed by a combination of NMR (for Ln = Sm, Eu, Yb only) and high-resolution ESI-TOF-MS (see the experimental section in the Supporting Information for details).

Self-sorting is a very attractive topic within coordinationdriven self-assembly; $^{54,65-67}$ hence, we checked the self-sorting behavior of ligands L3 and L4 with the lanthanide metals. ¹H NMR (Figure S92) and ESI-TOF-MS (Figure S93) suggest a strong ligand self-sorting potential, but such a behavior is not complete. No change was observed in ¹H NMR when Eu₄(L3)₄ and Eu₄(L4)₄ were blended together after 48 h (Figure S92c), indicating the thermodynamic stability of these cages. However, mixed-ligand self-assembly of L3, L4 ,and Eu(OTf)₃ showed that the self-sorted Eu₄(L3)₄ and Eu₄(L4)₄ were the major products, along with some additional peaks indicating that new species were also obtained, which were found to be $[Eu_4(L3)_3(L4)]$ and $[Eu_4(L3)(L4)_3]$ by ESI-TOF-MS.

Single crystals of $Eu_4(L3)_4$ and $Eu_4(L4)_4$ suitable for X-ray diffraction were obtained by slowly diffusing CH_2Cl_2 into a solution of the complex after roughly 2 weeks. As shown in Figure 2, both complexes give rise to the standard tetrahedral



Figure 2. Single-crystal X-ray structures of (A) $Eu_4(L3)_4(OTf)_{12}$ and (B) $Eu_4(L4)_4(OTf)_{12}$ (atom colors: red, Eu; yellow, C; white, H; pink, O; blue, N).

structures with four C_3 -symmetry ligands and four ninecoordinated europium ions defining the faces and vertices, respectively. Eu₄(L3)₄ crystallizes in the C2/*c* space group with half of the cage skeleton (two unique L3 and two Eu ions) in the asymmetric unit. In contrast, Eu₄(L4)₄ crystallized in a space group of much higher symmetry (*P*43*n*), so that only one-third of the L4 and Eu ions are located in the asymmetric unit. The Eu–Eu distances in Eu₄(L3)₄ and Eu₄(L4)₄ are measured to be 19.0 and 16.9 Å, respectively. Thus, a larger inner cavity for Eu₄(L3)₄ is defined. Consistent with a previous report,⁶⁰ the four metal centers on both tetrahedral cages exhibit a cooperative $\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda$ chirality. As none of them crystallize in a chiral space group, two enantiomers coexist in both crystals.

Photophysical Properties. The UV–vis absorption and luminescence spectra of L3 and L4 are shown in Figure 3A. The maximum absorption peaks of the two ligands are located at 320 and 334 nm, with molar extinction coefficients (ε) of 1.83 × 10⁴ and 6.11 × 10⁴ M⁻¹ cm⁻¹, respectively. Interestingly, the absorption of L4 shows a clear red shift and relatively higher molar extinction coefficient in comparison to L3. On excitation at 330 nm, the ligands' fluorescence spectra show maximum emission positions at 400 and 450 nm for L3 and L4, respectively. UV–vis absorption spectra of typical Ln₄(L3)₄ and Ln₄(L4)₄ complexes (Ln = Eu, Tb, Sm, Dy) were also measured and displayed very small red shifts (<13 nm) in comparison with the free ligands, with high molar



Figure 3. (A) UV–vis absorption, excitation, and fluorescence spectra of L3 (CH₂Cl₂, 1×10^{-5} M, $\lambda_{ex} = 330$ nm)and L4 (CH₂Cl₂, 1×10^{-5} M, $\lambda_{ex} = 366$ nm); (B) Emission spectra of Ln₄(L3)₄ complexes (CH₃CN, 1×10^{-5} M) in the visible region (Ln = Eu, Tb, Sm, Dy).

extinction coefficients $\varepsilon > 10^5$ at 320 nm (Figures S32 and S34). Complexes with different lanthanides display shapesimilar absorption bands, suggesting that the nature of the lanthanide ions only slightly affects their absorbance.⁶⁸

First of all, the photoluminescence of all the complexes with L3 and L4 are systematically compared in the visible region (Table 1, Figure 3B and Figures S37-S48). L3 with the TPT chelates could universally sensitize Eu, Tb, Sm, and Dy with lifetimes of 2.711, 1.526, 0.14, and 0.028 ms, respectively. For $Eu_4(L3)_4$, the characteristic emission bands (579, 593, 616, 649.5, 694 nm) of europium are observed under an excitation of 330 nm, corresponding to the ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J = 0-4) transitions. In comparison to the known $Eu_4(L2)_4$, the introduction of the second triazole group gives no improvement in the quantum yield of $Eu_4(L3)_4$ ($\Phi = 22.5\%$). However, L3 shows excellent sensitization ability on $Tb_4(L3)_4$ $(\Phi = 82\%)$ and Sm₄(L3)₄ ($\Phi = 3.2\%$). It is worth pointing out that the quantum yield of $Tb_4(L3)_4$ was a new record for multinuclear LOPs. In contrast, L4 with the APT chelates displays relatively poor sensitization ability on the lanthanide tetrahedra. For example, the quantum yield for $Eu_4(L4)_4$ is determined to be Φ = 8.9%. Meanwhile, the emission band of L4 could be clearly observed in the cases of $Tb_4(L4)_4$ and $Sm_4(L4)_4$. No characteristic luminescence of Dy is observed in the case of $Dy_4(L4)_4$.

To gain further insight into the differences observed in visible emission on the complexes, phosphorescence spectra of $Gd_4(L3)_4$ and $Gd_4(L4)_4$ were tested at 77 K under an Ar atmosphere using gating technique, from which the triplet state energy levels of L3 and L4 are estimated to be 22421 and 20704 cm⁻¹, respectively (Figures S50 and S51).⁶⁹ The triplet state energy level of L3 is higher than that of L2 (21858 cm⁻¹)⁶⁰ and 5221 cm⁻¹ higher than the energy level of ⁵D₀ of Eu^{III}, causing decreased sensitization efficiency. However, such a high energy level of L3 better suits the emitting ⁵D₄ energy level of Tb^{III} (20500 cm⁻¹), with an energy gap of 1921 cm⁻¹. The much lower ligand level of L4 could only sensitize Eu and Sm, and the energy gap is too small to sensitize Tb. Nonetheless, in comparison to the previous oxazoline-based

Table 1. Photophysical Data	for Typical Ln ₄ L ₄	Cages Emitting in t	he Visible Region
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LOP	$\varepsilon_{\rm max}~(10^5~{ m M}^{-1}~{ m cm}^{-1})$	$\lambda_{\rm ex}$ (nm)	au (ms)	$\Phi_{ m sens}$ (%)	$\Phi_{ m overall}$ (%)
$Eu_4(L3)_4$	3.059	332	2.711	45	22.5
$Tb_4(L3)_4$	2.057	330	1.526		82
$Sm_4(L3)_4$	4.061	333	0.14		3.2
$Dy_4(L3)_4$	2.426	330	0.028		2.9
$Eu_4(L4)_4$	4.284	365	1.913	22	8.9

 $Eu_4(L1)_{47}^{56}$ $Eu_4(L4)_4$ with the triazole chelates still has a better luminescence quantum yield (from 1.4% to 8.9% under the same experimental conditions). Thus, we conclude that triazole is a better sensitization group in similar lanthanide-organic tetrahedral systems.

NIR-emitting lanthanide complexes have attracted increasing attention, as they are widely used for bioimaging, optical communication, and so on.^{3,9,70} However, research into the NIR emission properties of multinuclear lanthanide supramolecular cages is still rare. Inspired by the thrilling sensitization abilities of L3, isostructural $Ln_4(L3)_4$ complexes with NIR-emitting lanthanide centers were synthesized. As shown in Figure 4, the NIR emissions of $Ln_4(L3)_4$ (Ln = Dy,



Figure 4. Emission spectra of the $Ln_4(L3)_4$ complexes (CH₃CN, 1 × 10^{-5} M) in the NIR region (Ln = Tm, Dy, Sm, Yb, Ho, Pr, Nd, Er).

Tm, Nd, Sm, Yb, Pr, Er) are distinctly observed with the main character emission peaks corresponding to each lanthanide ion (for details see Figures S62–S69 and Table S3). For example, Nd₄(L3)₄ and Yb₄(L3)₄ exhibit characteristic NIR emission bands at 1068 and 978 nm, corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions, respectively. In all cases, the NIR lifetimes concentrate on a microsecond scale, and the maximum lifetime of 142 μ s is noted for Sm₄(L3)₄.

Perfluorinated ligand and d-block sensitizers have been proven successful to improve lanthanide NIR emission. From the above results, we propose that the use of a fully conjugated rigidified ligand provides an alternative strategy to improve the NIR emission. To test this assumption, the NIR spectra of Ln_4L_4 (L = L2, L3, L4) are compared (Table 2). For $Ln_4(L3)_4$, the distinct characteristic peaks of all eight lanthanides are observed. The weakest signal is noticed for $Ho_4(L3)_4$, but still a clear emission band is noticed at 974 nm, corresponding to its ${}^5F_5 \rightarrow {}^5I_7$ transition. In clear contrast, L2

Table 2. Comparison of the NIR Emission on $\mathrm{Ln}_4\mathrm{L}_4$ with Triazole-Based Ligands

	NIR emission							
	Pr	Nd	Sm	Dy	Ho	Er	Tm	Yb
L2	×	\checkmark	\checkmark		×	\checkmark	×	\checkmark
L3	\checkmark			\checkmark	\checkmark	\checkmark	\checkmark	
L4	×			×	×	×	×	

Article

could only sensitize Nd, Sm, Dy, Er, and Yb and L4 could only sensitize Nd, Sm, and Yb. Moreover, the most detectable NIR spectra of $Ln_4(L3)_4$ show a higher signal to noise ratio in comparison to $Ln_4(L2)_4$ and $Ln_4(L4)_4$ under the same conditions.

TD-DFT Calculations. TD-DFT calculations were performed to shed light on the relationship between the ligand structures and the photoluminescent performances of our lanthanide complexes. TD-DFT calculations and the experimental UV–vis spectra are displayed in Figure S31. According to the TD-DFT results, the calculated λ_{max} values of L2, L3, and L4 are located at 319, 317, and 331 nm, respectively, which agree very well with the experimental λ_{max} values (L2, 315 nm; L3, 320 nm, L4, 334 nm). The LUMOs of L2 and L3 focus on the central triphenyltriazine groups, while the LUMO of L4 extends to the peripheral pyridine groups. The HOMOs of L2 and L3 dominate on the tridentate chelates, while the HOMO of L4 is located on the phenyl rings (Figure 5A,B).



Figure 5. TD-DFT (B3LYP $6-31G^*$) calculated (A) LUMOs and (B) HOMOs and the charge density transfer diagrams (red, electronic increase; blue, electronic decrease) corresponding to the (C) strongest absorption bands of L2, L3, and L4.

The charge density transfer diagrams⁷¹ corresponding to the strongest absorption bands also suggest that the presence of the inner amido group on L4 has a dramatic influence on the electron transfer directions from central triphenyltriazine chromophores to peripheral chelates (Figure 5C), which may have a great effect on the energy transfer from the ligands to the lanthanide centers.

White-Light Emission. White-light-emitting diodes (WLEDs) have attracted a great deal of attention in recent years.^{72–75} In principle, an ideal white-light-emitting material should meet three main requirements: CIE coordinates (0.33,

0.33), a color rendition index (CRI) exceeding 80, and a correlated color temperature (CCT) between 2500 and 6500 K.⁷⁶ In addition, color stability, reproducibility, and quantum yield of the materials are also crucial for practical WLED application. Some pioneering works using lanthanides as stabilized light source have been reported.^{77–79} Recently, Gunnlaugsson's group reported the design of white-light emitters based on directed self-assembly of two f metals in solution, resulting in a successful emission of white light with CIE coordinates of (0.33, 0.34).⁸⁰ Due to the unpromising luminescence of previous LOPs architectures, their white-light regulation has never been studied before. Thus, the high quantum yields of our LOPs persuaded us to further study their WLE potentials.

In view of the weak blue emission performance of Gd₄L₄, we decided to choose the ligands as the blue-ray source. First of all, the quantum yields of all the ligands were determined and the best value was obtained for L2 ($\Phi_{L2} = 5.1\%$; $\Phi_{L3} = 1.7\%$; Φ_{L4} = 1.6%). Then, the concentration-dependent luminescence of L2 was measured to determine its blue-emitting performance in solution. An optimal concentration of 140 μM in CH_2Cl_2/CH_3OH (v/v 1/1) was confirmed, above which the broad featureless excimer luminescent band (at ca. 490 nm) became apparent (Figure S70). Under this condition, the CIE coordinates for the emission of the ligand was calculated to be (0.24, 0.27). Then the red $Eu_4(L2)_4$ and green $Tb_4(L2)_4$ emitters, with CIE coordinates of (0.65, 0.34) and (0.36, 0.54), respectively, were added to the ligand solution. Finally, the CIE coordinates for $[Eu_4(L2)_4]_2[Tb_4(L2)_4][L2]_{35}$ in $CH_2Cl_2/$ CH₃OH (v/v 1/1) solution was determined to be (0.33, 0.33), which is the ideal value for a WLE system (Figure 6).



Figure 6. (A) White-light emission of $[Eu_4(L2)_4]_2[Tb_4(L2)_4][L2]_{35}$ in CH₂Cl₂/CH₃OH (v/v 1/1) solution excited at 347 nm. (B) Shifts of the CIE coordinates for $[Eu_4(L2)_4]_x[Tb_4(L2)_4]_y[L2]_{35}$ with different amounts of $[Eu_4(L2)_4]$ and $[Tb_4(L2)_4]$ added (A, 0, 0; B, 0.5, 0.25; C, 1, 0.25; D, 1, 0.25; E, 2, 0.625; F, 2, 1) correspondingly ($c = 4 \mu M$ for Tb₄(L2)₄).

Generally, sharp emission of lanthanide compounds usually leads to low CRI values. However, the broad emission of L2 can efficiently overcome this drawback, giving a higher CRI value of 93 and moderate CCT of 4594 K. Moreover, the absolute quantum yield for such a system in solution was measured to be 8.0% by excitation at 347 nm. Moreover, white-light emission from $[Eu_4(L3)_4][Tb_4(L3)_4][L3]_{230}$ and $[Sm_4(L3)_4][Dy_4(L3)_4]_{7.5}[L3]_{80}$ was also achieved by using a similar method (Table S4 and SI). It is noteworthy that when the proportion of the three emitters was kept fixed, the resulting white-light emission demonstrated a good reproducibility and color stability for at least 1 month.

CONCLUSIONS

In summary, the luminescent properties of supramolecular lanthanide cages have been thoroughly investigated with a series of ligands featuring the triazole-based chelates. A record high luminescence quantum yield ($\Phi = 82\%$) in the visible region for a terbium cage was reached among all multinuclear LOPs. Moreover, a fully conjugated rigid ligand that can universally sensitize the LOPs luminescence spanning the visible and NIR regions was obtained. This study offers important design principles toward strongly NIR emitting LOPs. Moreover, these strongly luminescent LOPs provide new candidates for photochemical supramolecular devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00756.

Additional synthetic and structural details, crystallographic data, and additional figures and tables as described in the text (PDF)

Accession Codes

CCDC 1903502 and 1903518 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for Q.-F.S.: qfsun@fjirsm.ac.cn.

ORCID 💿

Li-Peng Zhou: 0000-0003-3820-2591

Qing-Fu Sun: 0000-0002-6419-8904

Author Contributions

[§]S.-Y.W. and X.-Q.G. contributed equally.

Notes

The authors declare no competing financial interest.

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