Highly efficient and air-stable Eu(II)-containing azacryptates ready for organic light-emitting diodes

Jiayi Li¹,², Liding Wang¹,², Zifeng Zhao¹,², Boxun Sun¹, Ge Zhan¹, Huanyu Liu¹, Zuqiang Bian¹ & Zhiwei Liu¹✉

Divalent europium 5d-4f transition has aroused great attention in many fields, in a way of doping Eu²⁺ ions into inorganic solids. However, molecular Eu²⁺ complexes with 5d-4f transition are thought to be too air-unstable to explore their applications. In this work, we synthesized four Eu²⁺-containing azacryptates EuX₂-N₈ (X = Br, I, n = 4, 8) and systematically studied the photophysical properties in crystalline samples and solutions. Intriguingly, the EuI₂-N₈ complexes exhibit near-unity photoluminescence quantum yield, good air-/thermal-stability and mechanochromic property (X = I). Furthermore, we proved the application of Eu²⁺ complexes in organic light-emitting diodes (OLEDs) with high efficiency and luminance. The optimized device employing EuI₂-N₈ as emitter has the best performance as the maximum luminance, current efficiency, and external quantum efficiency up to 25470 cd m⁻², 62.4 cd A⁻¹, and 17.7%, respectively. Our work deepens the understanding of structure-property relationship in molecular Eu²⁺ complexes and could inspire further research on application in OLEDs.

¹Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Rare Earth Materials Chemistry and Applications, Beijing Engineering Technology Research Centre of Active Display, College of Chemistry and Molecular Engineering, Peking University, 100871 Beijing, China. ²These authors contributed equally: Jiayi Li, Liding Wang, Zifeng Zhao. ✉email: zwliu@pku.edu.cn
The 5d–4f transition in lanthanides (Ln) has been studied for decades on the luminescent mechanism and potential applications in various fields. For the well-established luminescence of lanthanide ions, f-f transition can be observed under ambient conditions, while the 5d–4f transition is usually absent due to thermally quenching by fast intersystem crossing from 4f→5d to 4f configuration. In divalent lanthanide systems, 5d–4f transition is much more prominent for its spin-allowed nature and the stabilization of the 5d orbitals.

Among all Ln2+ ions, Eu2+ ions exhibit strong 5d–4f transition and great applications for two reasons: (1) the 5d level is near or below 6P7/2, decreasing the multiphoton relaxation, (2) the reduction potential of Eu3+/Eu2+ is not too negative. The research on luminescent properties of Eu2+ ions can be roughly divided into two categories: Eu2+-dopants in inorganic matrix and molecular Eu2+ complexes. The first one has been extensively studied while the latter remains unexplored in many aspects. The physicochemical properties of Eu2+-complexes are mainly studied using cyclopentadienyls, hydrotris(pyrazolyl)borates, silylamides and their derivatives as ligands. Recently, Allen et al. reported series of Eu2+-containing azacryptates and azaligands which have aroused growing interest for their attractive luminescent properties, photo-redox catalytic performance and magnetic resonance imaging.

The uniqueness of 5d–4f luminescent mechanism enables Eu2+ complexes to have great potential in high-performance organic light-emitting diodes (OLEDs), a technology that has successfully been commercialized in cutting-edge displays and is under developing in solid-state lighting. To reach 100% theoretical exciton utilization efficiency (EUE), which is the key parameter to enhance the energy efficiency, phosphorescence, thermally activated delayed fluorescence (TADF), organic and radical materials were discovered in succession and applied as emitters in OLEDs. Comparing with the traditional f-f transition and other currently used emitters, divalent europium compounds have the following significant advantages: (i) short decay lifetime: the f-f transition is spin-forbidden with long lifetimes up to milliseconds, strongly limiting their maximum luminescence, while 5d–4f transition is spin-allowed with typical lifetimes in nanosecond scale, which significantly reduce the excited-state quenching to reach higher luminescence and lower efficiency roll-off; (ii) high EUE: Eu2+ ion exhibits a unique transition for the open-shell electron configuration. In divalent lanthanide systems, 5d orbitals have lower energy than 4f orbitals, thus the 5d–4f transition is more likely to be spin-allowed.

The metal–ligand bond in Eu2+-complexes is directly related to the coordination geometry. In Eu2+-complexes, the center Eu is coordinated by eight nitrogen atoms and thus has a distorted hula-hoop structure, while the eight iodide ions intersperse therein (see Supplementary Fig. 1). The crystal structures of EuX2–8N8 complexes were chosen as emitters in OLEDs for their high efficiency and good thermal/air stability. As a breakthrough, the optimized device using Eu2+-N8 complexes exhibits excellent performance with a maximum EQE of 17.7% and a maximum luminance of 25470 cd m−2.

Results

Synthesis and structural analysis. The four Eu2+ complexes EuX2–8N8 complexes were synthesized in glovebox by mixing EuX2 and corresponding ligands in methanol. The purified products were identified by elemental analysis. Then, single-crystal X-ray diffraction (SCXRD) was performed to investigate the coordinate geometry of these Eu2+-containing azacryptates (Fig. 1). EuBr2–N8 crystallizes in space group P21/n and one unit contains two azacryptate cations, four bromide ions in the outer sphere and four methanol. The N8 ligands have two possible conformations, 50% for each. Thus, the Eu2+ center, coordinated by eight nitrogen atoms from two ligands, adopts an unusual geometry with averagely half in square antiprism and half in distorted cube. Likely, the same coordinate geometry is found in EuI2–N8, which crystallizes in a higher-symmetry space group of Cmc21 without solvent. There are two sets of [Eu(N8)2]2+ with different orientations in one cell, locating in the edge center and body center, while the eight iodide ions intersperse therein (see Supplementary Fig. 1). The crystal structures of EuX2–8N8 show that the center Eu2+ is coordinated by eight nitrogen atoms and one halide ion as a distorted “hula-hoop” geometry, with the other halide in the outer sphere as a counterion, which are consistent with the reported structures. As shown in Table 1, the bond lengths of Eu–N in EuX2–8N8 are relatively shorter than those in EuX2–8N4, indicating the N8 complexes have stronger coordinate interaction between Eu2+ and ligands. Considering the charge separation in crystals, the EuX2–8N8 compounds behave more like ionic crystals with relatively stronger electrostatic attraction between the counterion halides and the [Eu(N8)2]2+ ions.

Photophysical properties. To systematically study the photophysical properties of Eu2+ complexes, steady-state spectra and transient spectra were collected. Crystalline powder of EuX2–8N8 shows orange-red emissions with maximum wavelength (λmax) of 605 nm (X = Br) and 613 nm (X = I), respectively (Fig. 2). Changing the azacryptates from N8 to N4, the EuX2–8N4 complexes exhibit strong hypsochromic shift induced by the weaker crystal field of N4 ligands, with λmax of 510 nm (X = Br) and 515 nm (X = I). The lifetimes for these complexes were found to be hundreds of nanoseconds (Table 2, Supplementary Fig. 2), within the expected range for 5d–4f transition. Full widths at half maximum (FWHMs) for these complexes in solid powder (40–45 nm) are relatively narrow comparing with luminescent materials featuring in charge-transfer (CT) mechanisms. The excitation bands of these complexes are broad and featureless, ranging from 230 to 500 nm (EuX2–8N8) and 230 to 600 nm (EuX2–8N4) as shown in Supplementary Fig. 3. Based on aforementioned photophysical studies and considering that the ligands in our system are saturated organic compounds with high-energy levels, it is reasonable to rule out the possibilities of ligand-metal charge transfer (LMCT). Hence, the excitation and emission processes can be regarded as the electronic transitions in Eu2+ ion, where the ground state is 4f5[8S7/2] and the excitation state is 4f6[7F0]5dF, specifically.
Due to the insolubility of Eu$_2$-$N_4$ in common solvents, we only studied the photophysical properties of Eu$_2$-$N_4$ in methanol solution (1.5 mM) under N$_2$ atmosphere. The Eu$_2$-$N_4$ solutions show bright yellow emission with $\lambda_{\text{max}}$ of 579 nm, and the emission spectra of the two complexes are almost identical. The emission is red-shifted by about 70 nm comparing with their solid samples, which is presumed to be caused by the differences in conformation of N$_8$ ligand in Eu$_2$-$N_4$. The emission is red-shifted by about 70 nm comparing with their solid samples, which is presumed to be caused by the differences in conformation of N$_8$ ligand in Eu$_2$-$N_4$. The transition from 4$^2$F$_{5/2}$ to 5d$_{5/2}$ and from 4$^2$F$_{7/2}$ to 5d$_{5/2}$, respectively.

The UV-visible spectra (Supplementary Fig. 4) show that EuX$_2$-$N_8$ complexes have high-energy absorption around 250 nm ($\varepsilon > 1000$ L mol$^{-1}$ cm$^{-1}$) and low-energy absorption peak at 404 nm ($\varepsilon = 644$ L mol$^{-1}$ cm$^{-1}$, $X = Br$) and 405 nm ($\varepsilon = 512$ L mol$^{-1}$ cm$^{-1}$, $X = I$), respectively, which is consistent with their excitation bands. The large molar absorptivity is on par with the reported Eu$^{2+}$ complexes due to the Laporte- and spin-allowed nature of $f-d$ transition$^{10,11,31}$. The time-dependent density functional theory (TD-DFT) calculation was conducted for EuX$_2$-$N_8$ and EuBr$_2$-$N_4$. The calculation prediction of EuX$_2$-$N_8$ is very close to the experimental data. For the N$_4$ complex, EuBr$_2$-$N_4$ has two possible conformations (high symmetry: cubic geometry and low symmetry: square antiprism), and calculation result suggests that the different conformations exhibit distinct absorption bands.

Interestingly, Eu$_2$-$N_8$ exhibits mechanochromic property, showing a fluorescence color change from green to yellow under moderate mechanical grinding in Fig. 2e. The emission spectra show that a new peak emerges in a longer wavelength region after grinding. Then the excitation and transient spectra of 515 nm and grinding. Then the excitation and transient spectra of 515 nm and 580 nm in the ground sample were collected to probe possible explanation as shown in Supplementary Fig. 5 and Fig. 2f. The similar excitation characteristics and a slightly longer decay of the new peak at 580 nm infer that the longer-wavelength emission is still from Eu$^{2+}$ center at a marginally different coordination environment. We tentatively attribute the mechanochromic property to the change in ligand conformation upon grinding, resulted from the relatively weak lattice energy of Eu$_2$-$N_8$. And the reversible process is essentially recrystallization in certain solvent atmosphere, like methano$^{32-34}$. Furthermore, the longer-wavelength emission can be pronouncedly enhanced by fast precipitation in antisolvent.

Table 1 The bond lengths (distances) around Eu$^{2+}$ center in Eu$_2$-$N_8$.

|          | EuBr$_2$-$N_4$ | Eu$_2$-$N_8$ | EuBr$_2$-$N_8$ | Eu$_2$-$N_8$ |
|----------|---------------|--------------|----------------|--------------|
| Eu-X     | 4.9097(3)     | 5.3019(2)    | 3.3129(8)      | 3.6170(4)    |
| Eu-N1$^b$| 2.660(3)      | 2.671(5)     | 2.907(6)       | 3.027(3)     |
| Eu-N2$^b$| 2.691(4)      | 2.724(5)     | 2.830(15)      | 2.790(3)     |
| Eu-N3$^b$| 2.689(4)      | 2.712(6)     | 2.837(6)       | 2.839(4)     |
| Eu-N4$^b$| 2.683(3)      | 2.672(6)     | 2.932(5)       | 3.040(3)     |
| Eu-N5$^b$| 2.686(4)      | 2.724(5)     | 2.792(5)       | 2.761(3)     |
| Eu-N6$^b$| 2.725(4)      | 2.671(5)     | 2.716(5)       | 2.789(3)     |
| Eu-N7$^b$| 2.723(3)      | 2.672(6)     | 2.773(6)       | 2.758(3)     |
| Eu-N8$^b$| 2.689(4)      | 2.712(6)     | 2.738(12)      | 2.819(3)     |

$^a$The Eu$_2$-$N_8$ structures only have one Eu-X distance, while in Eu$_2$-$N_4$, one halide directly bonds to center Eu$^{2+}$ ion (inner sphere) and the other is in the outer sphere.

$^b$The labels for nitrogen atoms in Eu$_2$-$N_4$ is named as 1-4 and 5-8 for two N$_4$ ligands. The labels in Eu$_2$-$N_8$ are shown in Fig. 1.

Fig. 1 The crystal structure of four Eu$^{2+}$ complexes. ORTEP drawings of the crystal structures of (a) EuBr$_2$-$N_4$, (b) Eu$_2$-$N_4$, (c) EuBr$_2$-$N_8$, and (d) Eu$_2$-$N_8$, respectively. The coordination polyhedrons (from top to bottom): square antiprism in Eu$_2$-$N_4$, distorted cube in EuBr$_2$-$N_8$, distorted “hula-hoop” in EuBr$_2$-$N_8$ and Eu$_2$-$N_8$. The nitrogen atoms are similarly located at 280 nm and 410 nm, attributed to the transition from 4$^2$F$_{5/2}$ to 5d$_{5/2}$ and from 4$^2$F$_{7/2}$ to 5d$_{5/2}$, respectively. At the labels for nitrogen atoms in Eu$_2$-$N_4$ structures only have one Eu-N bond to center Eu$^{2+}$ ion, while in Eu$_2$-$N_8$, one halide directly bonds to center Eu$^{2+}$ ion (inner sphere) and the other is in the outer sphere.
(tetrahydrofuran) to get amorphous powder of EuI$_2$–N$_8$. As shown in Fig. 2f, the emission shifts to a longer wavelength of 560 nm and the decay lifetime also increases from crystalline to amorphous state. However, a similar phenomenon was not observed in EuBr$_2$–N$_8$ (Supplementary Fig. 6), which indicates that EuBr$_2$–N$_8$ has a higher lattice energy, so it is harder to change the ligand conformation by such small mechanical stimulation.

**Thermal and air stability.** Thermal properties of these four compounds are studied by thermogravimetric analysis (TGA), which is of great significance for their further applications in OLEDs. The deposition temperature ($T_{\text{d,corr}}$ corresponding to 5% weight loss) are around 270 °C, 265 °C, 393 °C, and 436 °C for EuBr$_2$–N$_4$, EuI$_2$–N$_4$, EuBr$_2$–N$_8$, and EuI$_2$–N$_8$ in Fig. 3a, respectively. After 550 °C, the unchanged residue weight percentages of these compounds should be the mass percentage of metal halides, for that the decomposition process is tentatively attributed to the break of coordinate bonds followed by sublimation of organic ligands. Then the relative error (RE) of residue weight is calculated to verify that speculation. As shown in Supplementary Table 2, the REs of EuX$_2$–N$_4$ are reasonably low (~3%) while the REs of EuX$_2$–N$_8$ are too high (~6% and ~10% for X = Br, I, respectively). The element analysis is employed to exclude the possibility of impurities in EuX$_2$–N$_8$. Thus, we believe these EuX$_2$–N$_8$ compounds undergo both decomposition and sublimation around $T_{\text{d}}$ which will result in a large deviation in the final weight percentage.

Then the sublimation properties of these compounds were tested under high vacuum of 10$^{-5}$ Pa and gradient heating. The
EuBr$_2$–N$_8$ was found to be completely sublimable around 320 °C (tube temperature, which is different from the sample temperature) at a small scale of 50 mg. It is notable that there will be obvious decomposition at large-scale sublimation, probably due to the uneven heating in the sublimation boat. A similar property is found for EuI$_2$–N$_8$ with a higher sublimation temperature at 350 °C.

Considering the high thermal stability and near-unity PLQY, the N$_8$ complexes are potential candidates used in OLEDs as emitters. However, Eu$^{2+}$ ion is traditionally known to be easily oxidized to Eu$^{3+}$ by O$_2$, hence the air stability is a critical parameter in terms of further applications. To shed light on their air stability at room temperature, the PLQYs of EuX$_2$–N$_8$ were measured as the function of time. As shown in Fig. 3b where the PLQY value change reflects their respective air stability, the quantum yield of EuBr$_2$–N$_8$ does not change after exposure in air over 450 h and EuI$_2$–N$_8$ is metastable towards air. To explain the differences in stability for future design of Eu$^{2+}$ complexes, the analysis of buried volume (%$V_{bur}$) was calculated to estimate the steric protection by N$_8$ ligands as shown in Fig. 3c. d$^{35,36}$, %$V_{bur}$ is defined as the fraction of volume of ligand over the total volume of sphere centered on the metal. It determines the steric effect of a given ligand regard to the first coordination sphere (Supplementary Fig. 7). The two complexes all exhibit high %$V_{bur}$ values (77% to 75.1% for X = Br, I, respectively). EuBr$_2$–N$_8$ has a slightly higher %$V_{bur}$ than EuI$_2$–N$_8$ due to the closer distance between Eu$^{2+}$ and Br$^–$. Thus, the divergence in air stability between these two N$_8$ complexes is related to the different lattice energy considering the similar %$V_{bur}$. The EuI$_2$–N$_8$ has smaller lattice energy than EuBr$_2$–N$_8$ because of weaker static interaction and the existing of solvent methanol in crystal, which is also applied to explain their different mechanochromic behaviors.

**Electroluminescence performance.** Based on the photophysical and stability studies, the EuX$_2$–N$_8$ complexes are better candidates used in OLEDs as emitters. Prior to device fabrication, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the two complexes were deduced from their ultraviolet photoelectron spectroscopy (Supplementary Fig. 8) and ultraviolet absorption spectra data. Then, great efforts have been devoted to optimizing the device structure due to the lack of experiences of Eu$^{2+}$ complexes used in OLEDs. The EuBr$_2$–N$_8$ was first chosen for device optimization, which includes screening host materials, finding the best combination of hole transporting layer (HTL) and electron transporting layer (ETL), adjusting the thickness of the emission layer in Supplementary sections 1–4. Then, we followed the optimized conditions and further adjusted the doping concentration and the thickness of the emission layer of the EuI$_2$–N$_8$ device in Supplementary sections 5–6. The details of materials used, device optimization, and performance are shown in Supplementary Figs. 9–17 and Supplementary Tables 3–8.

On the base of the aforementioned process, the optimized OLED structure is ITO/MoO$_3$ (2 nm)/N,N′-bis(1-naphthalenyl)-N,N′-bis-phenyl-(1,1′-biphenyl)-4,4′-diamine (NPB, 50 nm)/cyclohexylidenbis[N,N′-bis(p-toly)aniline] (TPAC, 10 nm)/EuX$_2$–N$_8$:4,4′,4′″-tris(phenyl(m-tolyl)amino)triphenylamine (m-MTDATA, 25 nm)/diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSP01, 10 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen, 30 nm)/LiF (0.7 nm)/Al. The best EuBr$_2$–N$_8$ device gives pretty good performance with a turn-on voltage ($V_{on}$) of 6.2 V, a maximum luminance ($L_{max}$) of 10,200 cd m$^{-2}$, a maximum current efficiency (CE$_{max}$) of 52.8 cd A$^{-1}$ and a maximum EQE of 15.5%. While the champion device is obtained by using EuI$_2$–N$_8$ as the emitter, the $V_{on}$, $L_{max}$, CE$_{max}$ and EQE$_{max}$ are

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**Fig. 3** The thermal properties and buried volume calculation of EuX$_2$–N$_8$ compounds. **a** Thermogravimetric analysis (TGA) of EuX$_2$–N$_8$, where the 95%–weight line is shown to determine the $T_d$. **b** The change in PLQY of EuX$_2$–N$_8$ complexes in air. **c** Buried volume %$V_{bur}$ calculated of EuBr$_2$–N$_8$ (77.0%). **d** Buried volume %$V_{bur}$ calculated of EuI$_2$–N$_8$ (75.1%).
6.5 V, 25,470 cd m\(^{-2}\), 62.4 cd A\(^{-1}\), and 17.7\%, respectively. These results shown in Fig. 4 far exceed the only previously reported Eu\(^{2+}\)-based OLEDs, with EQE\(_{\text{max}}\) of 0.01\%, \(I_{\text{max}}\) of 10 cd m\(^{-2}\) and \(V_{\text{on}}\) of 20 V\(^{26}\). In addition, the electroluminescence lifetimes of the champion device are determined at 2.5 mA cm\(^{-2}\) and 10 mA cm\(^{-2}\), which are little shorter than tris(2-phenylpyridine) iridium (Ir(ppy)\(_3\)) based control device, a well-studied phosphorescence emitter in the same spectral region (Supplementary Fig. 18). It should be noted that both devices showed very short lifetime, since which is not only related to the emission material, but also host material, charge transport material, device fabrication, seal conditions, and so on\(^{37}\).

It is notable that the Eu\(_2\)N\(_8\) devices have rather high \(V_{\text{on}}\) values over 6 V considering the bandgap of host material is only 3 eV \((~400\) nm\)). To understand this phenomenon, the photophysical properties of films fabricated by doping 10 wt% Eu\(_2\)N\(_8\) in m-MTDATA onto quartz substrates in a vacuum chamber at high vacuum (10\(^{-3}\) Pa) were studied. The pure films of Eu\(_2\)N\(_8\) were also fabricated as reference. The emission of doping films is mainly located as two bands, where the 400–470 nm band \((\tau=1.2\) ns) is attributed as fluorescence from host materials and the 500–650 nm band \((\tau=10^2\) ns) is from Eu\(_2\)N\(_8\) in Supplementary Fig. 19. The excitation spectra show that in pure film, the two main excitation bands are located at around 320 nm and 390 nm, which is close to the studies showed in solution and solid state. The two doping films have almost identical excitation band at 350 nm, indicating the photoenergy first excites host materials and then transfers to doping Eu\(^{2+}\) complexes, without complete energy transfer in the photoluminescence process. Intriguingly, the electroluminescence spectra only exhibit emission from Eu\(^{2+}\) complexes with doping concentrations \((7\text{ wt%})\) lower than those in the photoluminescence study. Thus, we tentatively propose that the carrier recombination dominantly occurs in the doping materials instead of host materials, where the excitation of ligand results in a high \(V_{\text{on}}\).

**Discussion**

In summary, four Eu\(^{2+}\)-containing azacryptates Eu\(_2\)N\(_8\) \((X = \text{Br, I, } n = 4, 8)\) were synthesized, showing promising photoluminescence properties: high PLQY \((~100\%\) for N\(_8\) complexes), short excited-state lifetime \((10^2\) ns\)) and easily tunable emission by ligand field. Intriguingly, Eu\(_2\)N\(_8\) exhibits reversible mechnochromic property under grinding, which is attributed to the potential flexibility of N\(_8\) ligand and recrystallization. Furthermore, the Eu\(_2\)N\(_8\) complexes were chosen as the emissive materials in OLEDs due to their good air-/thermal-stability. After optimization of design, the best device showed excellent performance with a maximum EQE of 17.7\% and luminance of 25,470 cd m\(^{-2}\). Our work deepens the understanding of photoluminescence and electroluminescence properties in Eu\(^{2+}\) complexes and proves their promising applications in OLEDs.

**Methods**

All chemical reagents used in the synthesis process were commercially available and were used as received unless otherwise mentioned. The N\(_8\) ligand was commercially available. \(^{1}H\)-NMR spectra were recorded on a Bruker-400 MHz NMR spectrometer. Tetramethylsilane (TMS) was used as an internal reference for the chemical shift correction, where 8(TMS) equals 0. Elemental analyses were performed on a VARIO EL analyzer (GmbH, Hanau, Germany). All the synthesis of Eu\(^{2+}\) complexes were conducted in glovebox. All spectral tests of solid Eu\(^{2+}\) complexes were carried out by paraffin encapsulation between two quartz plates and the solution was protected by capped cuvettes under N\(_2\) atmosphere. The commercially available paraffin was purified by oxidation using KMnO\(_4\) and column chromatography to remove fluorescent whitening agents.

**Synthesis.** 1,4,7,10,13,16,21,24-octaazahexacyclo[8.8.8]hexacosane (N\(_8\) ligand): The synthesis of N\(_8\) ligand is carried out by an improved version of a reported method\(^{36}\). Tris(2-aminoethyl)amine (4.9 g, 33.5 mmol), NEt\(_3\) (12 mL), and 2-propanol (250 mL) were added to a 2-neck 1-L round-bottom flask equipped with mechanical stirring and a drip funnel containing a dilute solution of glyoxal (7.5 g). The flask was cooled to \(-78\) °C and the glyoxal solution was added slowly \((1\text{ drop s}^{-1})\). After the completion of addition, the yellow solution was stirred at room temperature overnight. Then the solvent was removed under vacuum at 40 °C, yielding a yellow solid which was dispersed in 300 mL CHCl\(_3\) and stirred for 2 h with the generation of lots of yellow...
translucent gels. The gels were removed by filtration and the resulting CHCl3 was removed under vacuum at 40 °C. The crude intermediate was dissolved in 300 mL MeOH, cooled with ice water. Excess NaBr (14 g) was gradually added to the solution to prevent an intensive reaction. The cloudy solution was stirred for 4 h and the solvent was removed under vacuum yielding white solid, which was extracted by CHCl3 (200 mL×3). The removal of CHCl3 gave the crude product N8. Further purification was conducted by thermal gradient sublimation (160–80 °C) at low pressure (~5 Pa). 1H NMR (400 MHz, D2O): δ 2.79 (a, 12H), 2.75 (m, 12H), 2.58 (m, 12H). 

**Data availability**

All the data in manuscript and supporting information are available from the corresponding author upon reasonable request.

Received: 25 April 2020; Accepted: 24 September 2020; Published online: 15 October 2020

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**Acknowledgements**

This work was supported by the National Key R&D Program of China (2016YFB0400100, 2017YFA0205010), the Beijing Natural Science Foundation (220205), and High-performance Computing Platform of Peking University.
**Author contributions**
Z.L. proposed and designed this project. J.L., L.W., and Z.Z. conducted most of the experiments. B.S. and H.L. helped in synthesizing ligands. G.Z. measured the PLQY values. Z.L., Z.B., and J.L. discussed the results and wrote the manuscript.

**Competing interests**
The authors declare no competing interests.

**Additional information**
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-19027-x.

Correspondence and requests for materials should be addressed to Z.L.

Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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