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Lanthanide Cerium(III) Tris(pyrazolyl)borate Complexes: Efficient Blue Emitters for Doublet Organic Light-Emitting Diodes

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ABSTRACT: Organic light-emitting diodes (OLEDs) have had commercial success in displays and lighting. Compared to red and green OLEDs, blue OLEDs are still the bottleneck because the high-energy and long-lived triplet exciton in traditional blue OLEDs causes the short operational lifetime of the device. As a new type emitter, lanthanide complexes with a 5d–4f transition could have short excited-state lifetimes on the order of nanoseconds. To achieve a high-efficiency 5d–4f transition, we systematically tuned the steric and electronic effects of tripodal tris(pyrazolyl)borate ligands and drew a full picture of their Ce(III) complexes. Intriguingly, all of these complexes show bright blue emission with high photoluminescence quantum yields exceeding 95% and short decay lifetimes of 35-73 ns both in the solid powder and in dichloromethane solutions. Using the Ce(III) complex emitter, we show a blue OLED with a maximum external quantum efficiency of 14.1% and a maximum luminance of 33,160 cd m⁻², and the specific electroluminescence mechanism of direct exciton formation on the Ce(III) ion with a near-unity exciton utilization efficiency is also confirmed. The discovered photoluminescence and electroluminescence property–structure relationships may shed new light on the rational design of highly efficient lanthanide-based blue emitters and their optoelectronic devices such as OLEDs.

KEYWORDS: tris(pyrazolyl)borate, lanthanide, photoluminescence, 5d-4f transition, organic light-emitting diode, electroluminescence, optoelectronic

INTRODUCTION

An organic light-emitting diode (OLED) is an emerging display and lighting technology, especially for lightweight and flexible devices. To achieve OLEDs with high efficiency, longterm stability, and low cost, fluorescence,¹ phosphorescence,² thermally activated delayed fluorescence,³ and organic radical⁴ materials have been subsequently investigated as emitters during the past three decades. To date, blue OLEDs are still the bottleneck as compared to red and green OLEDs; one of the main issues is that the long-lived and highly reactive "hot" triplet excitons cause a trade-off between a high exciton utilization efficiency and a long operational lifetime in traditional blue OLEDs. Thus, many efforts have been devoted to designing a blue-light emission material with a short triplet lifetime to maintain its electrochemical stability.⁵ In this context, open-shell molecules such as luminescent organic donor-acceptor-type radicals^{4,6-8} and lanthanide complexes with a 5d-4f transition⁹⁻¹⁵ are worthy of in-depth research since high efficiency and a short excited-state lifetime could be realized in such molecules simultaneously.

There are few reports on highly efficient luminescent lanthanide complexes with a 5d-4f transition. The main reason is because the lanthanide ions (e.g., Ce^{3+} , Eu^{2+} , Yb^{2+} ,

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Scheme 1. Synthetic Scheme of Tp Ligands and Corresponding Ce(III) Complexes



and Sm²⁺)-based radiative 5d-4f transition can be easily quenched by the environment, such as the vibration of ligands and solvent molecules.¹⁶ Besides, low-valent lanthanide ions are susceptible to oxidation. Thus, the compactness of the coordination sphere is necessary for the molecular design, as inspired by the phenomenon that efficient 5d-4f transitions have been obtained in several Ce3+- or Eu2+-doped inorganic solid compounds. The classic tris(pyrazolyl)borate (Tp) ligand together with various substituted forms have been developed into one of the most versatile tripodal ligands since the mid-1960s.^{17–19} The facile manipulation of the substituents either on the 3- (R^1) , 4- (R^2) , and 5- (R^3) sites of the pyrazolyl rings or on the boron atom (R^4) implies the possibility of controlling the electronic structure and coordination sphere to a great extent. Hence, the sterically crowded ligand skeleton and attendant protection offered by the substituents may be conducive to efficient 5d-4f luminescence of the central lanthanide ion.

Considering that the Ce(III) ion has natural advantages, 11,20,21 such as good air stability, a high energy level for

easy access to blue light, the shortest excited-state lifetime (nanosecond scale) in the observed lanthanide ions, and low cost due to quantitative superiority on Earth (more than copper), we adopted tris(pyrazolyl)borate derivatives as the ligands and synthesized a series of Ce(III) complexes: $Ce(R_4Tp3R^1,4R^2,5R^3)_3$ ($R^1 = R^2 = R^3 = R^4 = H$, 1; $R^1 = R^3$ = R^4 = H, R^2 = Me and Br, **2-Me** and **2-Br**; $R^1 = R^2 = R^3 = H$, R^4 = pyrazolyl, isopropyl, and *n*-butyl, 4-Pz, 4-^{*i*}Pr, and 4-^{*n*}Bu) and $Ce(Tp^{3Me,5Me})_2 dmpz$ ($R^1 = R^3 = Me$, $R^2 = R^4 = H$, dmpz =dimethylpyrazole anion, 3-Me). Encouragingly, all of the complexes demonstrated bright blue luminescence with high photoluminescence quantum yields (PLQYs) and short decay lifetimes arising from the compact coordination of Ce(III) as characterized by single-crystal X-ray diffraction. Further investigation of these doublet luminescent Ce(III) complexes in OLEDs allowed us to achieve efficient blue OLEDs and disclose the electroluminescence process of direct exciton formation on the central Ce(III) ion.

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Figure 1. ORTEP drawings and coordination polyhedrons of representative Ce(III) complexes: (a) **3-Me**, (b) **4-**ⁱ**Pr**, (c) **1**, and (d) **4-Pz**. (e) Coordination geometry of the four Ce(III) complexes (from top to bottom): dodecahedron in **3-Me**, bicapped-trigonal prism in **4-**ⁱ**Pr**, and tricapped-trigonal prism in **1** and **4-Pz**. All hydrogens are omitted for clarification. Atom notation: Ce, yellow; C, gray; N, blue; B, pink.

Table 1. Photophysical Data for Ce(III) Complexes in Solid Powder or Dissolved at 10^{-3} M Concentration in Dichloromethane (Solid/Solution)

complex	excitation ^{<i>a</i>} λ_{ex} (nm)	emission $\lambda_{\rm em}$ (nm)	CIE coordinates	PLQY Φ_{PL} (%)	lifetime τ (ns)	$k_{\rm r}^{\ b} (10^7 \ {\rm s}^{-1})$	$k_{\rm nr}^{\ b} (10^6 \ {\rm s}^{-1})$
1	346 (363)	424/-	(0.16, 0.07)/-	100/-	40/-	2.5/-	0.0/-
2-Me	336 (369)	416/444	(0.15, 0.05)/(0.14, 0.12)	100/100	37/58	2.7/1.7	0.0/0.0
2-Br	337 (358)	432/444	(0.16, 0.08)/(0.14, 0.12)	96/100	35/53	2.7/1.9	1.1/0.0
3-Me	392 (412)	471/481	(0.16, 0.32)/(0.19, 0.31)	100/100	63/73	1.6/1.4	0.0/0.0
4-Pz	380 (372)	445/448	(0.14, 0.13)/(0.14, 0.14)	100/100	46/62	2.2/1.6	0.0/0.0
4- ⁱ Pr	395 (412)	448/447	(0.14, 0.16)/(0.14, 0.14)	100/95	49/62	2.0/1.5	0.0/0.8
4- ⁿ Bu	352 (342)	441/444	(0.14, 0.11)/(0.14, 0.12)	100/100	46/62	2.2/1.6	0.0/0.0
Ce-1 ^c	354	464/433	(0.15, 0.13)/(0.15, 0.08)	82/100	42/53	2.0/1.9	4.3/0.0
Ce-2 ^c	353	476/-	(0.18, 0.40)/-	100/-	57/-	1.8/-	0.0/-

^{*a*}Maximum experimental excitation peak wavelengths of the Ce(III) complexes. Calculated vertical absorption wavelengths (λ_{abs}) are given in parentheses. ^{*b*} k_r and k_{nr} are obtained from equations $k_r = \Phi_{PL}/\tau$ and $k_{nr} = (1 - \Phi_{PL})/\tau$. ^{*c*}Obtained from refs 12 and 13.

RESULTS AND DISCUSSION

Synthesis and Structure. The overall stepwise synthetic routes are outlined in Scheme 1. The synthesis of Tp ligands can be carried out by two methods depending on the substituents, starting from BH_4^- (Method 1)²² or R⁴B(OH)₂ (Method 2).²³ The Ce(III) complexes were obtained by reacting Ce(CF₃SO₃)₃²⁴ with 3 equiv of Tp ligands and further purified by recrystallization or sublimation. As shown in the scheme, the structures of the Ce(III) complexes vary according to the different substituents. The Tp^{3Me,5Me} ligand with two methyl substituents forms the unexpected structures in the upper row. Oxygen is introduced in complexes Ce-1 and Ce-2 as a new and stronger coordination atom by the addition of water in the reaction system.^{12,13,25} However, without water, the reaction would afford complex 3-Me consisting of two

Tp^{3Me,5Me} ligands and one 3,5-dimethylypyrazole ion.²⁶ The B–N bond cleavage during coordination results from big steric hindrance of the Tp^{3Me,5Me} ligand, which twists the pyrazolyl rings and weakens B–N bonds.²⁷ The case of no substituents on the Tp ligand leads to complex 1, which is a classic nine-coordinated complex comprised of three Tp ligands as a result of much less tension in the ligands.^{28,29} Complexes 2-Me and 2-Br are also nine coordinated because the substituents on the 4 site of the pyrazolyl ring have basically no impact on the coordination sphere. Substituents on the boron ought to have a small effect, such as in complexes 4-Pz and 4-^{*n*}Bu; however, we still found complex 4-^{*i*}Pr as an exception. One of the three ^{*i*}PrTp ligands is bidentate, and we attribute this to the increased steric hindrance.

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Figure 2. Photophysical properties of the Ce(III) complexes in solid powder. (a) Excitation spectra. (b) Emission spectra. (c) CIE coordinates and general mechanism of the photophysical process. (d) Transient photoluminescence decay curves.



Figure 3. Structure-property relationship of the Ce(III) complexes. (a) Calculation of the Tolman cone angle ($\theta_{\text{cone angle}}$) of a single threecoordinated Tp ligand, and $\overline{\theta}$ is the average of all of the $\theta_{\text{cone angle}}$ values in the complex. (b) $E_{\text{em}} - \overline{\theta}$ relationship. (c) $\overline{r}_{\text{Ce-N}} - \overline{\theta}$ relationship. (d) % $V_{\text{Bur}} - \overline{\theta}$ relationship.

The Ce(III) complexes were all structurally authenticated by single-crystal X-ray diffraction (SC-XRD) analysis, and their crystallographic data are listed in Table S1. The eight or nine coordination contributes to the good encapsulation of the Ce(III) ion. According to the coordination geometry, four representative SC-XRD structures, i.e., **3-Me**, **4**-^{*i*}**Pr**, **1**, and **4**-**Pz**, are demonstrated in Figure 1, and the others are shown in Figure S1. For the eight-coordinated complexes **3-Me** and

4-^{*i*}**Pr**, the former exhibits a dodecahedron geometry while the later a bicapped-trigonal prismatic geometry. For the 1-type structures, including complexes **1**, **2**-**Me**, and **2**-**Br**, the Ce(III) atom is nine coordinated to the N atoms of three ligands with a D_{3h} -symmetric tricapped-trigonal prismatic coordination geometry. Meanwhile, the molecules themselves show C_3 symmetry. For the nine-coordinated **4**-**Pz**-type structures, including complexes **4**-**Pz** and **4**-^{*n*}**Bu**, they also have the

tricapped-trigonal prismatic geometry like 1-type structures; however, there is no symmetry either in the coordination geometry or in the molecule.

Photoluminescence Properties. The photophysical data of all of the Ce(III) complexes are summarized in Table 1. Complexes 1 and 3-Me have been reported before; nevertheless, their luminescent properties were investigated here for the first time.^{26,28,29} All of the Ce(III) complexes showed bright blue luminescence with high PLQYs over 95% under ultraviolet excitation. The photophysical properties of these complexes in the solid powder are shown in Figure 2. The solid powder could be excited by UV-vis light (220-480 nm) and exhibits several emission peaks with decent Commission Internationale de l'Eclairage (CIE) coordinates in the blue light area (Figure 2a-c). Analogous to the typical Ce(III)activated phosphors,²⁰ the dual peak with an energy difference of around 2000 cm⁻¹ is derived from two terminating levels, ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$, as depicted in Figure 2c. Intriguingly, there are more than two emission peaks in the solid powder of complexes 1, 2-Me, and 2-Br, which may come from two excited states with different energies. The Gaussian-fitting results of the emission spectra are shown in Figures S2-S8 and Table S2. We also confirmed the split of the peaks by measuring the low-temperature photoluminescence of the solid powder (Figures S9-S15 and Table S3). The luminescence intensity decreases in a monoexponential relationship with a fitting result of 35-63 ns (Figure 2d). The excited-state lifetime is in a reasonable range compared to the common values (from 10^{-7} to 10^{-8} s) from the literature.^{11,16} The subtle differences of the decay lifetimes among these Ce(III) complexes may depend on the rigidity of the molecular structure, resulting in various radiative transition constants (k_r) and nonradiative transition constants (k_{nr}) .

Substituents on the Tp ligand improve the solubility significantly, and all of the complexes except 1 could be dissolved in common solvents. The photophysical properties of these complexes in dichloromethane solution are shown in Figure S16. Ultraviolet–visible (UV–vis) absorption spectra indicate that all of the complexes exhibit a high molar extinction coefficient at a wavelength around 240 nm, which could be attributed to the π – π * transition of the pyrazole ring,^{30,31} and the absorption bands between 250 and 450 nm could be assigned to the 4f–5d absorption of the Ce(III) cation (Figure S16a).³² The excitation and emission spectra have similar features with those of the solid powder, and the fitted excited-state lifetimes are 53–73 ns (Table 1, Figures S16b–d and S3–S8, and Table S4).

All of the Ce(III) complexes show high PLQYs, and the emission energy (E_m) differs, which peaked our interest in the structure-property relationship. The E_m is deduced from the lowest energy emission peak by Gaussian fitting corresponding to the transition from the lowest 5d orbital to the ${}^2F_{7/2}$ energy level of Ce³⁺. The steric effect of the Tp ligands is usually quantified with the average Tolman cone angle $(\overline{\theta})$, and the calculation method is depicted in Figure 3a.³³ The coordination sphere is represented by the average Ce–N bond distance (\overline{r}_{Ce-N}) and the percentage of buried volume (% V_{Bur}),³⁴ which measure the compactness of the first coordination sphere. All of the analytical data are summarized in Table 2. The E_m decreases as the $\overline{\theta}$ increases, as plotted in Figure 3b. To further look into the reason for the tendency, we plot the relationship of \overline{r}_{Ce-N} and % V_{Bur} vs $\overline{\theta}$ (Figure 3c,d).

Table 2. Structural and Property Data for Ce(III) Complexes

complex	$\overline{ heta}$ (°) ^{<i>a</i>}	$E_{\rm em} ({\rm eV})^{b}$	$\overline{r}_{\text{Ce-N}}$ (Å) ^c	$%V_{\rm Bur}^{\ \ d}$
1	181.0	2.74	2.677	94.4
2-Me	182.0	2.74	2.671	93.6
2-Br	182.5	2.70	2.667	93.7
4- ⁿ Bu	182.9	2.64	2.667	94.3
4-Pz	183.4	2.61	2.656	94.7
4- ⁱ Pr	185.6	2.57	2.605	93.4
3-Me	222.0	2.46	2.575	90.7
Ce-1 ^e	223.8	2.64	2.642	91.2
Ce-2 ^e	227.5	2.41	2.603	92.0

^{*a*}Average Tolman cone angle of all of the three-coordinated Tp ligands. ^{*b*}Emission energy deduced from the lowest energy emission peak by Gaussian fitting. ^{*c*}Average Ce–N bond length. ^{*d*}Percentage of buried volume, hydrogen atoms are considered in the calculation, parameters adopted here are Bondi radii scaled by 1.17, sphere radius 3.5 Å, and mesh spacing value s = 0.10 Å. ^{*e*}Obtained from refs 12 and 13.

As we can see from the scatters, a bigger Tolman cone angle is accompanied by a shorter Ce–N bond distance (Figure 3c). This gives rise to the increased crystal field splitting and thus decreased emission energy. There are several models explaining the relationship between the amount of crystal field splitting and the metal–ligand bond distance, and the classical crystal field theory predicts a r^{-5} dependence.²⁰ However, the decrease in \overline{r}_{Ce-N} is relatively small among **2-Br**, **4**-"**Bu**, and **4**-**Pz**, which may not be enough to induce such a drop in emission energy. The reason may lie in the remarkable increase in the % V_{Bur} , which is another driving force for the compression of the coordination sphere (Figure 3d).

To further understand these Ce(III) complexes, we analyzed their electronic structures with time-dependent density functional theory (TD-DFT), and the data are provided in Table S5. The calculated excitation spectra and natural transition orbitals (NTOs) are shown in Figures \$17-\$30. As summarized in Figure 4, all of the nine-coordinated complexes are approximately C_3 symmetric, and the λ_{abs}^{-1} bands (the absorption peak with the lowest energy) are unambiguously assigned to the $4f_{z^3}/4f_{xyz} \rightarrow 5d_{z^2}$ transition. The λ_{abs}^{1} bands of the eight-coordinated 3-Me and 4-ⁱPr could be assigned to the $4f_{xyz} \rightarrow 5d_{x^2-y^2}$ transition, which indicates that the coordination geometry is a crucial inducer for the crystal field splitting. The 5d orbitals are predominantly nonbonding, but the orbitals involved for the absorption bands with higher energy have more characteristics of metal-to-ligand charge transfer (MLCT). The assumed nine-coordinated $4 \cdot i \mathbf{Pr'}$ is calculated to have a higher energy than the eight-coordinated 4-ⁱPr, accounting for the coordination number decrease.

OLEDs Application. Considering that these Ce(III) complexes all show high PLQYs, good thermal stability (Figure S31), and short excited-state lifetimes, it is worth investigating them as emitters in OLEDs with the vacuum thermal deposition method. We selected complexes **3-Me**, **4-Pz**, and **4-**^{*i*}**Pr** for electroluminescence device fabrication. These three complexes with a relatively low emission energy have large structural differences, providing us with a great opportunity to look into how the molecular structure makes a difference in the device performance. We fabricated the OLEDs **D1**, **D2**, and **D3** with the structure of indium tin oxide (ITO)/MoO₃ (2 nm)/MoO₃-doped *N*,*N*-dicarbazolyl-3,5-

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Figure 4. Calculated donor and acceptor natural transition orbitals (NTOs) corresponding to the transition at λ_{abs}^{1} (absorption peak with the lowest energy) in all of the Ce(III) complexes.

device	host:emitter	$V_{\rm on}^{\ a}$ (V)	EQE_{max}^{b} (%)	EQE_{1000}^{c} (%)	$L_{\rm max}^{d}~({\rm cd}{\cdot}{\rm m}^{-2})$	CIE ^e	
D1	mCP:3-Me	3.8	3.6	1.5	10 480	0.16, 0.28	
D2	mCP:4-Pz	4.2	0.55		108	0.16, 0.15	
D3	mCP:4- ^{<i>i</i>} Pr	4.2	1.1	0.41	1229	0.16, 0.25	
D4	BCPO:3-Me	3.2	14.1	12.6	33160	0.15, 0.23	
$dT_{\text{res}} = \frac{1}{2} b_{\text{res}} = \frac{1}{2} b_{r$							

^{*a*}Turn-on voltage, taken as the reference point at which the luminance is 1 cd·m⁻². ^{*b*}Maximum EQE. ^{*c*}EQE at 1000 cd·m⁻². ^{*d*}Maximum luminance. ^{*e*}CIE coordinates at 100 cd·m⁻².

benzene (mCP: MoO₃, 20 wt %, 30 nm)/mCP (10 nm)/ mCP:3-Me, 4-Pz, or 4-ⁱPr (10 wt %, 20 nm)/1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB, 40 nm)/LiF (0.7 nm)/Al. The performance of these devices is shown in the Figure S32 and Table 3. Though the PLQYs of the three doped films (mCP:3-**Me**, mCP:**4-Pz**, and mCP:**4**-^{*i*}**Pr**) are 69, 34, and 52%, there are significant differences in the maximum luminance (L_{max}) and external quantum efficiency (EQE) among these three devices, i.e., they show $L_{\rm max}$ of 10 480, 108, and 1229 cd·m⁻² and maximum EQE of 3.6, 0.55, and 1.1%, respectively. In addition, there is no emission from mCP in device D1 (Figure 5a), which is different from devices D2 and D3. While the photoluminescence spectra indicate that the energy transfer from mCP to the three Ce(III) complexes is incomplete, we propose that the exciton formation in device D1 occurs mainly on 3-Me, more accurately on the Ce(III) ions since the OLED turns on below 4 V while the excitation energy of the ligands is around 5 eV.

To verify the proposed mechanism, we further fabricated hole-only devices with the structure of ITO/MoO₃ (2 nm)/mCP (40 nm)/mCP:**3-Me**, **4-Pz**, or **4-**ⁱ**Pr** (10 wt %, 20 nm)/mCP (40 nm)/MoO₃ (2 nm)/Al and electron-only devices with the structure of ITO/LiF (0.7 nm)/TmPyPB (40 nm)/mCP:**3-Me**, **4-Pz**, or **4-**ⁱ**Pr** (10 wt %, 20 nm)/TmPyPB (40 nm)/LiF (0.7 nm)/Al. The current density–voltage curves revealed that eight-coordinated **3-Me** and **4-**ⁱ**Pr** have rather poor hole transport mobility or good hole capture ability compared with nine-coordinated **4-Pz** (Figure 5b). On the other hand, the current densities of these electron-only devices are comparable (Figure 5c). In order to understand this phenomena, we fabricated more hole-only devices with the structure of ITO/MoO₃ (2 nm)/mCP (40 nm)/mCP:**3-Me** (0, 1, 2, and 5 wt %, 20 nm)/mCP (40 nm)/MoO₃ (2 nm)/Al.

The current density–voltage curves are shown in Figure S33. The current densities of mCP:**3-Me** (1, 2, and 5 wt %, 20 nm) are similar but much lower than the pure mCP. Therefore, it is ruled out that the reason for the low current density of the **3-Me** based hole-only device is its poor hole transport mobility, and the real reason should be its good hole capture ability. Besides, we found that the Ce(III) complexes have relatively shallow singly occupied molecular orbitals (SOMOs) compared with the highest occupied molecular orbitals (HOMOs) of host mCP (Figure S34). Thus, the eight-coordinated **3-Me** with the smallest % $V_{\rm Bur}$ has the shallowest SOMO and the strongest hole capture ability.

Considering the performance of hole-only and light-emitting devices of these three complexes, the electroluminescence mechanism for the 3-Me-based device is shown in the right part of Figure 5d. Due to the good hole capture ability of 3-Me, the current density is significantly reduced in the 3-Mebased hole-only device, while in the light-emitting device, 3-Me with a hole will acquire an electron to form an exciton and then return to the ground state by emitting a photon. In this situation, 3-Me could continue to trap holes, leading to the similar current density of device D1 to the other two devices (Figure S32). In comparison, 4-Pz and 4-^{*i*}Pr could not capture the hole completely like 3-Me, and there are excitons formed on the host material mCP in devices D2 and D3 as shown on the left side of Figure 5d. This is precisely because 3-Me avoids the incomplete energy transfer from the host material to the Ce(III) complex, so that there is no emission of mCP in the electroluminescence spectra, and the performance of the 3-Mebased device is significantly better than the remaining two devices.

Due to the good hole capture ability, **3-Me** is likely to be a better emitter for OLEDs. Therefore, we optimized the



Figure 5. Performance of the OLEDs and proposed electroluminescence mechanism. (a) Photoluminescence (PL) spectra of Ce(III) complexesdoped mCP films, and electroluminescence (EL) spectra of devices D1–D3. (b) Current density–voltage curves of hole-only devices. (c) Current density–voltage curves of electron-only devices. (d) EL mechanism of typical doped OLEDs and 3-Me-doped OLEDs. (e) PL spectrum of 3-Medoped BCPO film, and EL spectra of device D4 at different luminances. (f) Current density–voltage–luminance traces for device D4. (g) Power efficiency–luminance–EQE traces for device D4 inset with the device structure.

structure of 3-Me-based OLEDs. After screening the host materials, we chose a bis[4-(N-carbazolyl)-phenyl]phenylphosphineoxide (BCPO):3-Me (10 wt %) film with a PLQY of 83% as the emission layer. The best performance is achieved in device D4 with a structure of ITO/MoO_3 (2 nm)/ 1-bis[4-[N,N'-di(4-tolyl)amino]phenyl]cyclohexane (TAPC,40 nm)/mCP (10 nm)/BCPO:3-Me (7 wt %, 25 nm)/ bathophenanthroline (Bphen, 40 nm)/LiF (0.7 nm)/Al. The electron-hole recombination still occurred on the Ce(III) ions as deduced from Figure 5e, and a short transient electroluminescence lifetime of 108 ns was observed (Figure \$35). The device exhibited a maximum EQE of 14.1%, a maximum luminance of 33160 cd m⁻², and CIE coordinates of (0.15, 0.23) at 100 cd m⁻² (Figure 5f and 5g). In order to estimate the exciton utilization efficiency (EUE) of the device, the orientation of the transition dipole moment vectors was measured with the polarization- and angle-dependent luminescence spectroscopy. As shown in Figure S36, the horizontal dipole ratio of the BCPO:3-Me film was 59%, which is lower than 67% of the isotropic distribution. Therefore, the outcoupling efficiency of this device is lower than 20%, and the EUE of 3-Me is higher than 85%.

Compared with Ce-1 and Ce-2 that we reported before,^{12,13} **3-Me** also showed a high EUE in the OLED device and the working mechanisms of Ce-1-, Ce-2-, and **3-Me**-based devices are the same. Although **3-Me** also shows a short excited-state lifetime which is in favor of fabricating OLEDs with a good working lifetime and low-efficiency roll off, the air stability and redox stability of **3-Me** are not good (Figures S37 and S38), which would reduce the device performance; thus, design and synthesis of Ce(III) complexes with good stability and high efficiency are underway.

CONCLUSION

In summary, we demonstrated a full synthesis map for tris(pyrazolyl)borate-based Ce(III) complexes with an aim to explore the efficient 5d–4f transition. By replacing different substituents, we manipulated the steric and electronic effects of the ligands and therefore the coordination sphere of the lanthanide Ce(III) ions. Consequently, all of the designed Ce(III) complexes exhibit blue 5d–4f transitions with high PLQYs over 95% and short decay lifetimes of tens of nanoseconds both in the aggregated solid powder and in diluted dichloromethane solution. The trial of Ce(III) complex

as the emitter in OLEDs gave efficient blue emission with a maximum EQE of 14.1% and a new electroluminescence mechanism of direct exciton formation on the Ce(III) ion. These insights may pave the way toward the targeted design of highly efficient blue OLEDs.

EXPERIMENTAL SECTION

Synthesis of 1. $Ce(CF_3SO_3)_3$ (1.17 g, 2.0 mmol) and KTp (1.56 g, 6.2 mmol) were dissolved in methanol separately with a total volume of 30 mL and then added to a 100 mL round-bottomed flask. The mixture was stirred for 16 h at room temperature, and the resulting white powder was filtered and dried. Pure 1 was obtained as a crystalline white powder after sublimation at 250 °C with a pressure of around 10^{-4} Pa (1.28 g, 1.64 mmol, 82%). Analysis (% calcd, % found for $C_{27}H_{30}B_3CeN_{18}$): C (41.62, 41.47), H (3.88, 3.71), N (32.36, 32.07).

Synthesis of 2-Me. Similar to that of 1, instead of $Ce(CF_3SO_3)_3$ (0.35 g, 0.60 mmol), KTp^{4Me} (0.56 g, 1.9 mmol) and 10 mL of methanol were used. Colorless crystals were obtained by sublimation (0.53 g, 0.58 mmol, 97%). Analysis (% calcd, % found for $C_{36}H_{48}B_3CeN_{18}$): C (47.75, 47.72), H (5.34, 5.30), N (27.85, 27.85).

Synthesis of 2-Br. Similar to that of 1, instead of $Ce(CF_3SO_3)_3$ (0.35 g, 0.60 mmol), KTp^{4Br} (0.92 g, 1.9 mmol) and 10 mL of methanol were used. Colorless crystals were obtained by sublimation (0.79 g, 0.53 mmol, 88%). Analysis (% calcd, % found for $C_{27}H_{21}B_3Br_9CeN_{18}$): C (21.78, 21.76), H (1.42, 1.48), N (16.93, 17.07).

Synthesis of 3-Me. Similar to that of 1, instead of $Ce(CF_3SO_3)_3$ (1.0 g, 1.7 mmol), $KTp^{3Me.5Me}$ (1.7 g, 5.0 mmol) and 30 mL of tetrahydrofuran (THF) were used. Light yellow crystals were obtained by sublimation at 190 °C with a pressure of around 10^{-4} Pa (1.2 g, 1.6 mmol, 94%). We improved the synthesis route by increasing 2 equiv of $KTp^{3Me.5Me}$, as reported before, to 3 equiv of $KTp^{3Me.5Me}$ with the yield increasing from 64% to 94%.⁶ Analysis (% calcd, % found for $C_{35}H_{51}B_2CeN_{14}$): C (50.67, 50.91), H (6.20, 6.06), N (23.64, 23.71).

Synthesis of 4-Pz. $Ce(CF_3SO_3)_3$ (1.76 g, 3.0 mmol) and KPzTp (3.15 g, 9.9 mmol) were dissolved in methanol separately with a total volume of 50 mL and then added to a 100 mL round-bottomed flask. The mixture was stirred overnight at room temperature before removing the solvent. The remaining solid was extracted with dichloromethane (DCM) to remove the byproduct KCF₃SO₃ through filtration. The filtrate was concentrated, dried, and sublimed at 260 °C with a pressure of around 10^{-4} Pa to obtain pale yellow crystals (0.65 g, 0.66 mmol, 22%). Analysis (% calcd, % found for $C_{36}H_{36}B_3CeN_{24}$): C (44.24, 44.11), H (3.71, 3.53), N (34.39, 34.26).

Synthesis of 4-^{*i*}**Pr.** Similar to that of 4-**Pz**, instead of $Ce(CF_3SO_3)_3$ (1.17 g, 2.0 mmol), Na'PrTp (1.72 g, 6.2 mmol) and 35 mL of DCM were used. The product was obtained by recrystallization from a mixed solution (DCM:hexane = 1:1) to obtain a crystalline white powder (1.23 g, 1.2 mmol, 60%). Analysis (% calcd, % found for $C_{36}H_{48}B_3CeN_{18}$ ·CH₂Cl₂): C (44.87, 44.70), H (5.09, 5.01), N (25.46, 25.09). A 0.57 g amount of product was taken out for further sublimation at 220 °C with a pressure of around 10^{-4} Pa (0.14 g, 0.15 mmol, 24%). Analysis (% calcd, % found for $C_{36}H_{48}B_3CeN_{18}$): C (47.75, 47.70), H (5.34, 5.18), N (27.85, 27.87).

Synthesis of 4-^{*n*}**Bu.** Similar to that of 4-**Pz**, instead of $Ce(CF_3SO_3)_3$ (1.17 g, 2.0 mmol), Na^{*n*}BuTp (1.81 g, 6.2 mmol) and 40 mL of THF were used. The product was obtained by recrystallization from a mixed solution (THF:hexane = 1:3) to obtain a white powder (1.26 g, 1.3 mmol, 65%). Analysis (% calcd, % found for $C_{39}H_{54}B_3CeN_{18}$): C (49.44, 49.19), H (5.74, 5.73), N (26.61, 26.22). A 0.55 g amount of product was taken out for further sublimation at 210 °C with a pressure of around 10^{-4} Pa to obtain a white powder (0.05 g, 0.05 mmol, 9%). Analysis (% calcd, % found for $C_{39}H_{54}B_3CeN_{18}$): C (49.44, 49.43), H (5.74, 5.66), N (26.61, 26.47).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c09718.

Methods, crystallographic information, spectroscopic data, DFT calculations, thermal property measurements, and other measurements (PDF)

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Notes

The authors declare no competing financial interest.

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