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Fine tuning the steric hindrance of Eu(II) tris(pyrazolyl)borate complex for blue organic light-emitting diode

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Methods

General Methods: ^{1}H NMR spectra were recorded on Bruker 400MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were performed in negative ion mode on Bruker Apex IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were conducted on a VARIO elemental analyzer from Elementar Analysensysteme GmbH.

Photophysical Measurements: Photophysical measurements were conducted in a nitrogen condition. Ultraviolet-visible absorption spectra were measured by Shimadzu UV-3600Plus UV-VIS-NIR spectrometer. Excitation and emission spectra were recorded on Edinburgh FLS980 fluorescence spectrophotometer. Luminescence decay lifetimes were obtained on a single photon counting spectrometer from Edinburgh FLS980 with laser as the excitation source. The data were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments. Absolute photoluminescence quantum yields were measured using Hamamatsu C9920-02 PL quantum yield measurement system with integrating sphere.

Single Crystal Structure Measurements: The single crystal X-ray diffraction (XRD) data were collected on Rigaku Mercury CCD diffractometer. The radiation used in the XRD analysis is the graphite-mon chromated Mo Kα emission line (λ= 0.71069 Å). XRD data were collected by using the CrystalClear software. Structural refinement was conducted with SHELXL-2014/7 software.

Thermal Stability Measurement: Thermal gravimetric analysis (TGA) was carried out on a Q600SDT instrument at an elevation temperature rate of 10 °C min^{-1} under 100 mL min^{-1} nitrogen flow.

Cyclic Voltammetry (CV) Measurement: CV was carried out under inert atmosphere protection in dichloromethane solution with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl wire pseudo-reference electrode with ferrocene as the external standard. Cyclic voltammogram was obtained at a scan rate of 100 mV s^{-1}.

OLEDs Fabrication and Measurements: Indium tin oxide (ITO) patterned anode was commercially available with a sheet resistance of 14 Ω square^{-1} and a thickness of 80 nm. ITO substrates were cleaned with deionized water and ethanol. The organic and metal layers were deposited in different vacuum chambers with a base pressure better than 1×10^{-4} Pa. The active area for each device is 4 mm^2. All electric testing and optical measurements were performed under ambient conditions with encapsulation of devices in a glovebox. The electroluminescence spectra, current density-voltage-luminance, and EQE characteristics were measured by computer controlled Keithley 2400 source meter and absolute EQE measurement system (C9920-12) with photonic multichannel analyzer (PMA-12, Hamamatsu Photonics).

Experimental Section

All chemical reagents used in the synthesis process were commercially available and were used as received unless otherwise mentioned. 3-ethyl-1*H*-pyrazole, 3-cyclohexyl-1*H*-pyrazole and 3-(adamantan-1-yl)-1*H*-pyrazole were synthesized according as reported methods[1-3].

Synthesis of ligands

Synthesis of KTp^{Et}: KBH$_4$ (0.85 g, 16 mmol) and 3-ethyl-1*H*-pyrazole (5.00 g, 52.0 mmol) were mixed in a 50 mL flask, and the mixture was heated slowly to 190 °C under nitrogen atmosphere until 3 equiv. of H$_2$ evolved. After cooling down, the resulting solid was loaded into a thermal sublimator. With a gradient temperature of 260-120 °C and a pressure of ~ 8 Pa, 3.78 g KTp^{Et} was obtained as white powder. Yield: 71%. ^{1}H NMR (DMSO-d_6): δ 7.15-7.13 (3H, d), 5.78-5.76 (3H, d), 2.51-2.44 (6H, q), 1.15-1.09 (9H, t). ESI-MS negative: calcd. for $C_{15}H_{22}BN_6^-$ 297.20, found 297.20.

Synthesis of KTp^{iPr}: Similarly to that of KTp^{Et}, instead of KBH$_4$ (0.39 g, 7.2 mmol) and 3-isopropyl-1*H*-pyrazole (2.78 g, 25.2 mmol) were used. With a gradient temperature of 260-120 °C and a pressure of ~ 8 Pa, 1.75 g KTp^{iPr} was obtained as white powder. Yield: 64%. ^{1}H NMR (DMSO-d_6): δ 7.12-7.09 (3H, d), 5.80-5.77 (3H, d), 2.88-2.77 (3H, m), 1.17-1.03 (18H, d). ESI-MS negative: calcd. for $C_{18}H_{28}BN_6^-$ 339.25, found 339.25.

Synthesis of KTp^{Cy}: KBH_4 (0.38 g, 7.0 mmol) and 3-cyclohexyl-1*H*-pyrazole (4.00 g, 26.6 mmol) were mixed in a 50 mL flask, and the mixture was heated slowly to 200 °C under nitrogen atmosphere until 3 equiv. of H_2 evolved. Then, toluene (15 mL) was added to avoid the aggregation of product. The resulting solid was filtered, washed with hexane, and dried under vacuum. 2.33 g KTp^{Cy} was obtained as white powder. Yield: 66%. ^{1}H NMR (DMSO-*d*$_6$): δ 7.11-7.05 (3H, d), 5.79-5.71 (3H, d), 2.54-2.42 (3H, m), 1.92-1.78 (6H, m), 1.77-1.59 (9H, m) .1.38-1.11 (15H, m). ESI-MS negative: calcd. for $C_{27}H_{40}BN_6^-$ 459.34, found 459.34.

Synthesis of KTp^{tBu}: Similarly to that of KTp^{Et}, instead of KBH_4 (0.29 g, 5.4 mmol) and 3-(*tert*-butyl)-1*H*-pyrazole (2.00 g, 16.1 mmol) were used. With a gradient temperature of 260-120 °C and a pressure of ~ 8 Pa, 1.58 g KTp^{tBu} was obtained as white powder. Yield: 70%. ^{1}H NMR (DMSO-*d*$_6$): δ 6.98-6.93 (3H, d), 5.84-5.77 (3H, d), 1.22-1.16 (27H, s). ESI-MS negative: calcd. for $C_{21}H_{34}BN_6^-$ 381.29, found 381.29.

Synthesis of KTp^{Ad}: Similarly to that of KTp^{Cy}, instead of KBH_4 (0.23 g, 4.3 mmol) and 3-(adamantan-1-yl)-1*H*-pyrazole (3.00 g, 14.8 mmol) were used. 1.87 g KTp^{Ad} was obtained as white powder. Yield: 67%. ^{1}H NMR (DMSO-*d*$_6$): δ 6.96-6.91 (3H, d), 5.80-5.75 (3H, d), 2.00-1.93 (9H, m), 1.87-1.81 (18H, m), 1.73-1.67 (18H, m). ESI-MS negative: calcd. for $C_{39}H_{52}BN_6^-$ 615.43, found 615.43.

Synthesis of Eu(II) complexes

Synthesis of Eu-Et: EuI_2 (0.27 g, 0.67 mmol) and KTp^{Et} (0.45 g, 1.3 mmol) were added to a 50 mL flask with 20 mL dry tetrahydrofuran in a glovebox. The mixture was stirred overnight at room temperature and then the solvent was removed under vacuum. The resulting solid was loaded into a thermal sublimator. With a gradient temperature of 170-100 °C and a pressure of ~ 10^{-4} Pa, 0.25 g Eu-Et was obtained as orange-yellow powder. Yield: 50%. Anal. calcd for $C_{30}H_{44}B_2EuN_{12}$: C 48.28, H 5.94, N 22.52; found: C 48.34, H 5.89, N 22.34.

Synthesis of Eu-iPr: Similarly to that of Eu-Et, instead of EuI_2 (0.11 g, 0.27 mmol) and KTp^{iPr} (0.20 g, 0.53 mmol) were used. With a gradient temperature of 170-120 °C and a pressure of ~ 10^{-4} Pa, 0.13 g Eu-iPr was obtained as yellow powder. Yield: 58%. Anal. calcd for $C_{36}H_{56}B_2EuN_{12}$: C 52.06, H 6.80, N 20.24; found: C 52.24, H 6.98, N

19.97.

Synthesis of Eu-Cy: EuI_2 (0.16 g, 0.39 mmol) and KTp^{Cy} (0.40 g, 0.80 mmol) were added to a 50 mL flask with 20 mL dry tetrahydrofuran in a glovebox. The mixture was stirred overnight at room temperature. After removing insoluble substance, the solvent was removed under vacuum. The resulting solid was recrystallized from *n*-hexane, 0.21 g Eu-Cy was obtained as yellowish green powder. Yield: 50%. Anal. calcd for $C_{54}H_{80}B_2EuN_{12}$: C 60.57, H 7.53, N 15.70; found: C 60.60, H 7.61, N 15.72.

Synthesis of Eu-tBu: Similarly to that of Eu-Et, instead of EuI_2 (0.48 g, 1.2 mmol) and KTp^{tBu} (1.00 g, 2.4 mmol) were used. With a gradient temperature of 180-120 °C and a pressure of ~ 10^{-4} Pa, 0.58 g Eu-tBu was obtained as pale green powder. Yield: 54%. Anal. calcd for $C_{42}H_{68}B_2EuN_{12}$: C 55.15, H 7.49, N 18.38; found: C 55.20, H 7.44, N 18.44.

Synthesis of Eu-Ad: Similarly to that of Eu-Cy, instead of EuI_2 (0.31 g, 0.76 mmol) and KTp^{Ad} (0.50 g, 0.76 mmol) were used. 0.40 g Eu-Ad was obtained as pale green powder after recrystallization from *n*-hexane and tetrahydrofuran. Yield: 50%. Anal. calcd for $C_{47}H_{68}BEuIN_6O_2$: C 54.34, H 6.60, N 8.09; found: C 54.12, H 6.37, N 8.02.

Table S1 Crystallographic data for Eu(II) complexes.

Compound	Eu-tBu	Eu-Ad
Formula	$C_{42}H_{68}B_2EuN_{12}$	$C_{47}H_{68}BEuIN_6O_2$
Mw	914.66	1038.74
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$I2/a$
a (Å)	11.0607(2)	27.6985(3)
b (Å)	21.0152(4)	15.4209(2)
c (Å)	20.7561(3)	21.5097(2)
α (°)	90	90
β (°)	99.181(2)	95.0190(10)
γ (°)	90	90
V (Å^3)	4762.80(15)	9152.33(18)
Z	4	8
T (K)	180.00(10)	180.00(10)
θ range (°)	2.2230-28.3260	2.1400-29.1210
d_{calc} (g·cm^{-3})	1.276	1.508
F (000)	1908	4232
Crystal size (mm)	0.05×0.02×0.01	0.3×0.2×0.15
Absorp. coeff. (mm^{-1})	1.358	2.089
Index range	$-14 \leq h \leq 14$ $-28 \leq k \leq 28$ $-28 \leq l \leq 27$	$-37 \leq h \leq 35$ $-21 \leq k \leq 20$ $-29 \leq l \leq 22$
Reflns collected	35214 (R_{int} = 0.0293)	53504 (R_{int} = 0.0228)
Indep. reflns	12060	11615
Refns obs. [$I > 2\sigma(I)$]	9671	10486
data/restr/paras	12060/24/567	11615/0/523
GOF	1.036	1.044
R_1/wR_2 [$I > 2\sigma(I)$]	0.0318/0.0670	0.0207/0.0519
R_1/wR_2 (all data)	0.0472/0.0714	0.0244/0.0533
Largest diff. peak & hole (e/Å^3)	1.026/-0.506	1.278/-0.762

Table S2 The selected bond lengths of Eu-tBu, Eu-Ad and Eu-Et.

Eu-tBu	Bond length/Å	Eu-Ad	Bond length/Å	Eu-Et	Bond length/Å
Eu-N1	2.595	Eu-N1	2.581	Eu-N1	2.598
Eu-N2	2.644	Eu-N2	2.648	Eu-N2	2.576
Eu-N3	2.623	Eu-N3	2.633	Eu-N3	2.617
Eu-N4	2.650	Eu-I	3.207	Eu-N4	2.585
Eu-N5	2.697	Eu-O1	2.648	Eu-N5	2.589
-	-	Eu-O2	2.651	Eu-N6	2.612

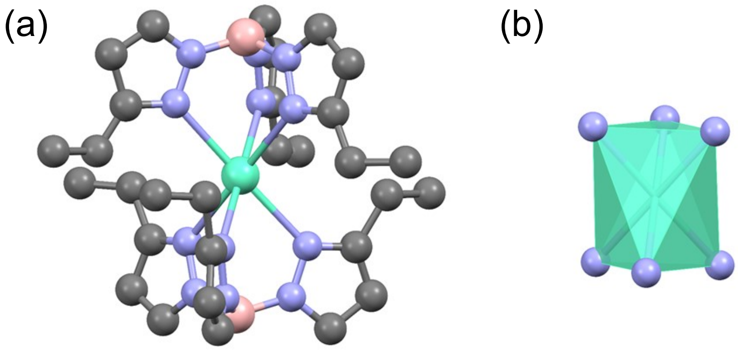

Fig. S1 (a) The coordination model, and (b) coordination polyhedron of Eu-Et.

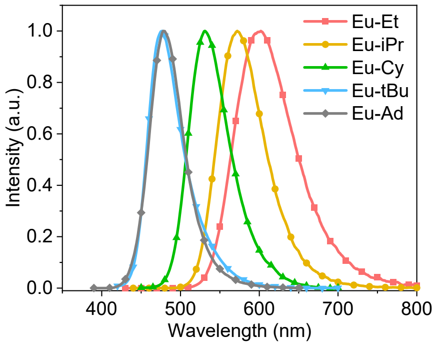

Fig. S2 The emission spectra of Eu(II) complexes in solid powder under the excitation of 280 nm.

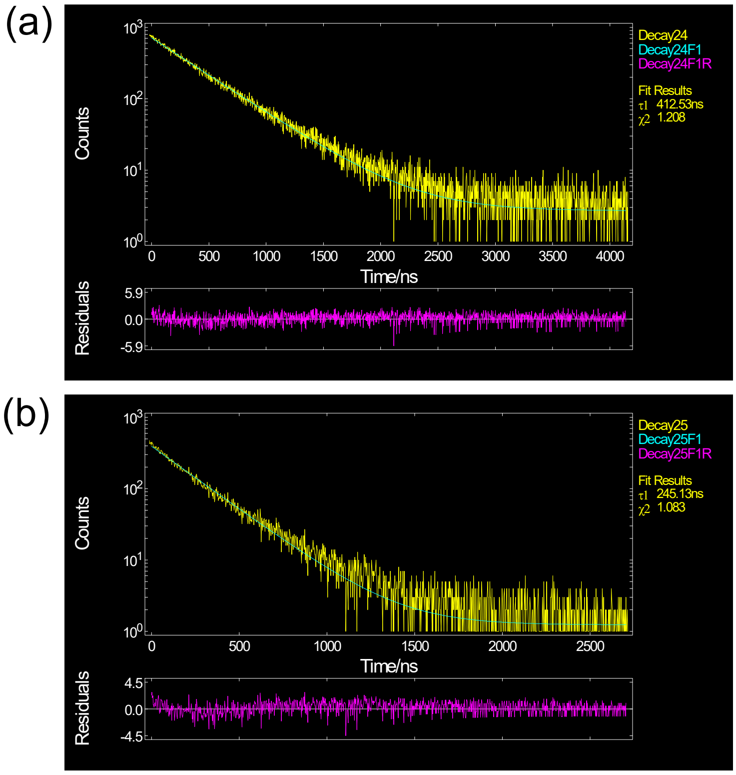

Fig. S3 The lifetime fitting curves of Eu-Et and Eu-iPr on FLS980.

Table S1 The original PLQY values of Eu(II) complexes during the two measurements.

Complex	Solid		Solution	
Eu-Et	31.9%	32.2%	4.98%	4.93%
Eu-iPr	16.9%	17.0%	10.3%	10.3%
Eu-Cy	82.8%	83.0%	1.63%	1.65%
Eu-tBu	95.5%	95.4%	89.2%	89.1%
Eu-Ad	98.1%	97.7%	58.0%	57.9%

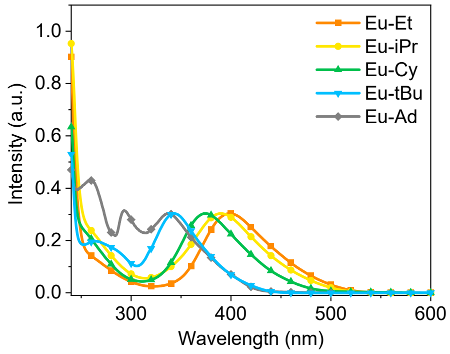

Fig. S4 Absorption spectra of Eu(II) complexes in dichloromethane solutions (10^{-3} M).

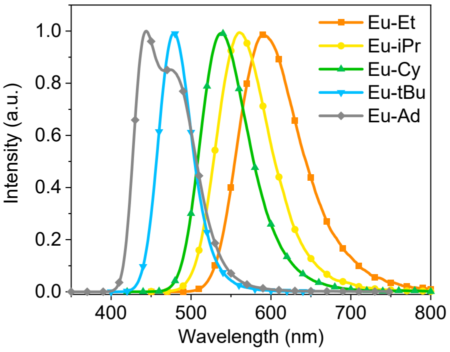

Fig. S5 Emission spectra of Eu(II) complexes in dichloromethane solutions (10^{-3} M). The excitation wavelengths for Eu-Et, Eu-iPr, Eu-Cy, Eu-tBu and Eu-Ad are 400, 400, 400, 360 and 340 nm, respectively.

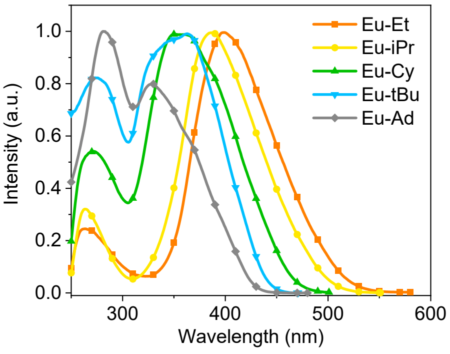

Fig. S6 Excitation spectra of Eu(II) complexes in dichloromethane solutions (10^{-3} M). The detecting wavelengths for Eu-Et, Eu-iPr, Eu-Cy, Eu-tBu and Eu-Ad are 590, 560, 570, 480 and 480 nm, respectively.

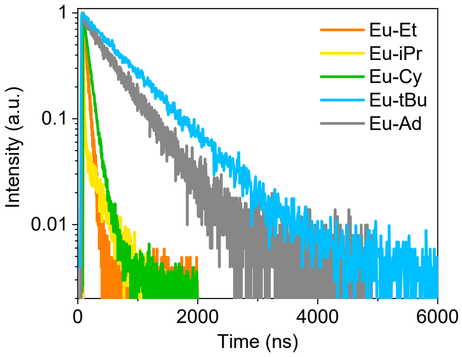

Fig. S7 Decay spectra of Eu(II) complexes in dichloromethane solutions (10^{-3} M). The excitation wavelength is 405 nm, and the detecting wavelengths for Eu-Et, Eu-iPr, Eu-Cy, Eu-tBu and Eu-Ad are 590, 560, 530, 480 and 470 nm, respectively.

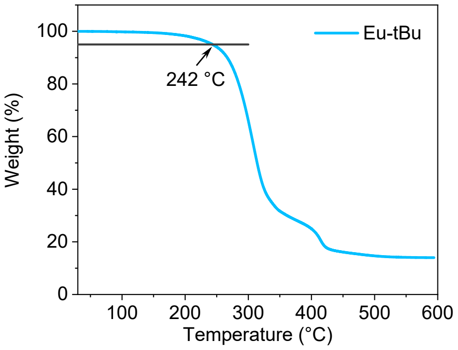

Fig. S8 Thermogravimetric analysis of Eu-tBu.

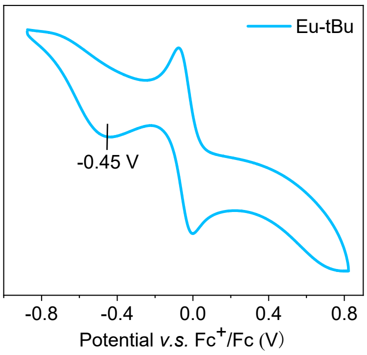

Fig. S9 Cyclic voltammetry curve of Eu-tBu recorder in dichloromethane with ferrocene as an internal standard.

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