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Air stable and efficient rare earth Eu(II) hydro-tris(pyrazolyl)borates complexes with tunable emission color

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Experimental Section

General remarks. ^{1}H NMR spectra were recorded on Bruker 400 MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were performed in positive/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. The steady-state and transient photoluminescence spectra were recorded on an Edinburgh FLS980 photoluminescence spectrometer. Absolute PL quantum yields were measured using Hamamatsu C9920-02 PL quantum yield measurement system with integrating sphere. The synthesis process of the complexes was carried out in the glove box. The purity of EuI_2 is 99.9999%, bought from Beijing Hawk Science & Technology Co., Ltd. THF and n-hexane were dried over sodium/benzophenone and freshly distilled under nitrogen atmosphere prior to use. Dichloromethane were dried over calcium hydride. All glassware was oven-dried at 120 °C for at least 1 h before using. The synthesis of 3, 5-diphenylpyrazole, 3-methyl-5-phenyl-1H-pyrazole, KTp^{Ph2}, $KTp^{Ph,Me}$ and $Eu(Tp^{Me2})_2$ was according to the literatures[1-3]. 5-Phenyl-1H-pyrazole was purchased from commercial supplier.

Synthesis of KTp^{Ph}: 5-Phenyl-1H-pyrazole (2.65 g, 18.4 mmol) and potassium borohydride (0.332 g, 6.15 mmol) were added to a 100 mL single-necked flask. Protected by nitrogen, the mixture was warmed gradually. At 90 °C, potassium borohydride was dissolved in melted 5-phenyl-1H-pyrazole, and hydrogen evolution began. The reaction progress can be monitored by measuring the volume of released hydrogen. Slowly heated to 150 °C, about three equivalents of hydrogen were obtained. The reaction mixture was stirred for 2 h and cooled to room temperature. The mixture was added to hot dichloromethane and filtered to give a white solid. Yield 83 %. ^{1}H NMR($(CD_3)_2CO$, 400 MHz): δ 6.51 (d, J = 2.0 Hz, 3H); 7.20 (t, J = 7.3 Hz, 3H); 7.34 (t, J = 7.6 Hz, 6H); 7.50 (d, J = 2.0 Hz, 3H); 7.78 (d, J = 7.3 Hz, 6H).

Synthesis of $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$: At room temperature, adding 30 mL THF solution of EuI_2 (0.300 g, 0.737 mmol) into 30 mL THF solution of two equivalents of $KTp^{Ph,Me}$, KTp^{Ph} or KTp^{Ph2}. After mixing, orange-red, yellow and

bright yellow-green turbid liquid were formed for $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$, respectively. The mixture was stirred overnighted and the solvent was removed under reduced pressure. For $Eu(Tp^{Ph,Me})_2$, yielded an orange-red solid, which was purified by crystallization from dichloromethane and hexane. Yield 84.3%. Anal. Calc. for $C_{60}H_{56}B_2EuN_{12}$: C, 64.41; H, 5.05; N, 15.02. Found: C, 64.11; H, 4.92; N, 14.93. For $Eu(Tp^{Ph})_2$, pure orange crystals were obtained by recrystallization from 50 mL hot toluene. Yield 71.7%. Anal. Calc. for $C_{54}H_{44}B_2EuN_{12}$: C, 62.69; H, 4.29; N, 16.25; Found: C, 61.87; H, 4.26; N, 16.28. For $Eu(Tp^{Ph2})_2$, pure product was obtained by sublimation at 320 °C under high vacuum (10^{-5} Pa). Yield 20.0%. Anal. Calc. for $C_{90}H_{68}B_2EuN_{12}$: C, 72.49; H, 4.60; N, 11.27; Found: C, 72.04; H, 4.51; N, 11.32.

X-Ray crystallography: The X-ray diffraction (XRD) data were collected on a Rigaku Mercury CCD di□ractometer. The radiation used in the XRD analysis is the graphite-monochromated Mo Kα emission line (λ = 0.71069 Å). XRD data were collected by using the CrystalClear software. Structural refinements were conducted with SHELXL-97 or SHELXL-2013 software. The crystallographic data collected for these complexes are provided in the Supporting Information. The structures were submitted to the Cambridge Crystallographic Data Centre (CCDC 2010439, 2010438 and 2010437 for $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$, respectively).

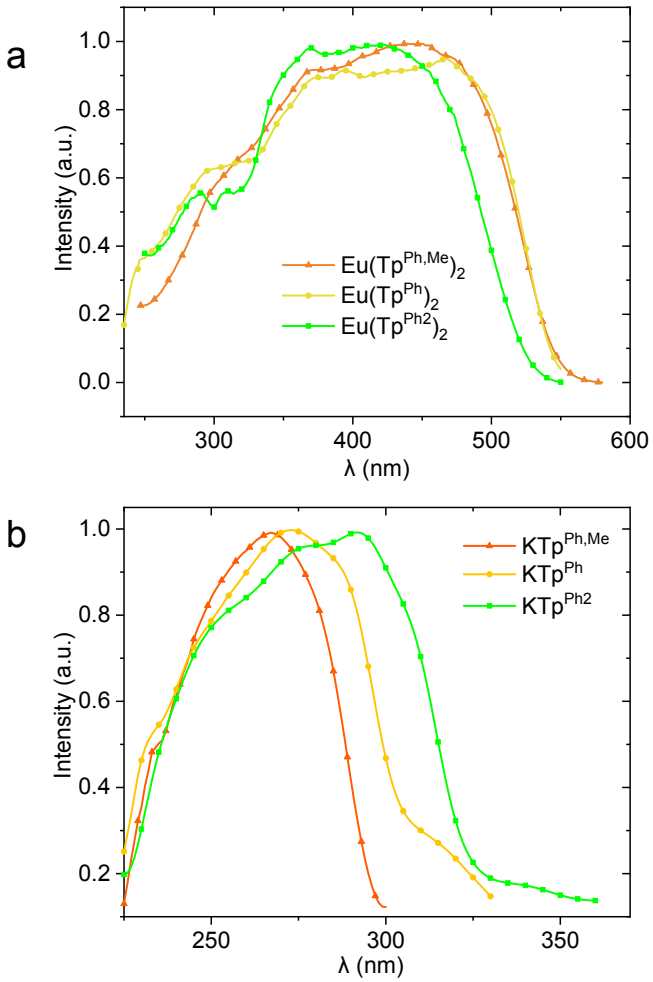

Figure S1. (**a**) Solid excitation spectra of $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$, which were tested at their maximum emission wavelengths of 617 nm, 578 nm and 538 nm, respectively. (**b**) Solid excitation spectra of $KTp^{Ph,Me}$, KTp^{Ph} and KTp^{Ph2}, which were tested at an emission wavelength of 315 nm, 350 nm and 380 nm, respectively.

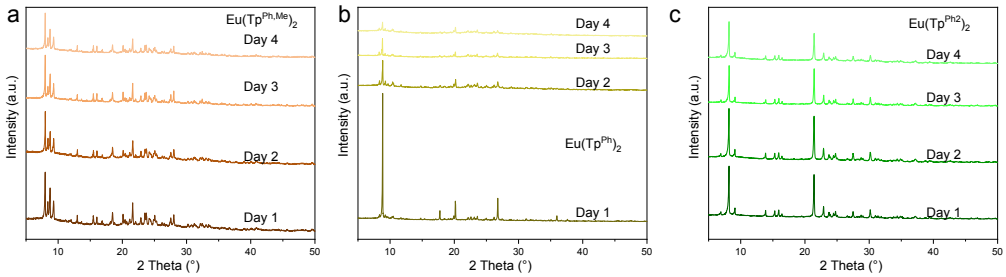

Figure S2. The time dependent XRD spectra of $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$ in air.

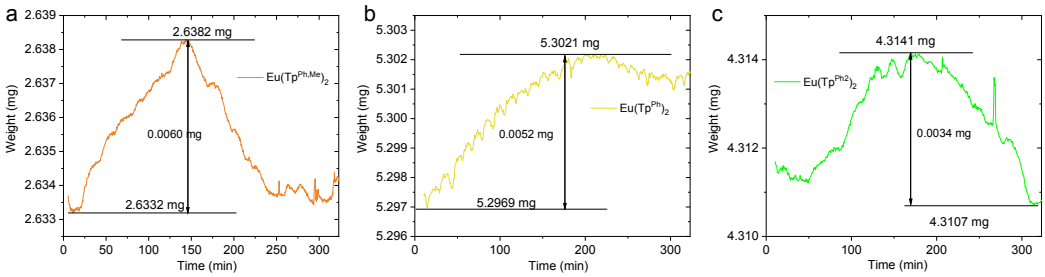

Figure S3. Mass change (TG) of $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$ under an air flow (25 °C).

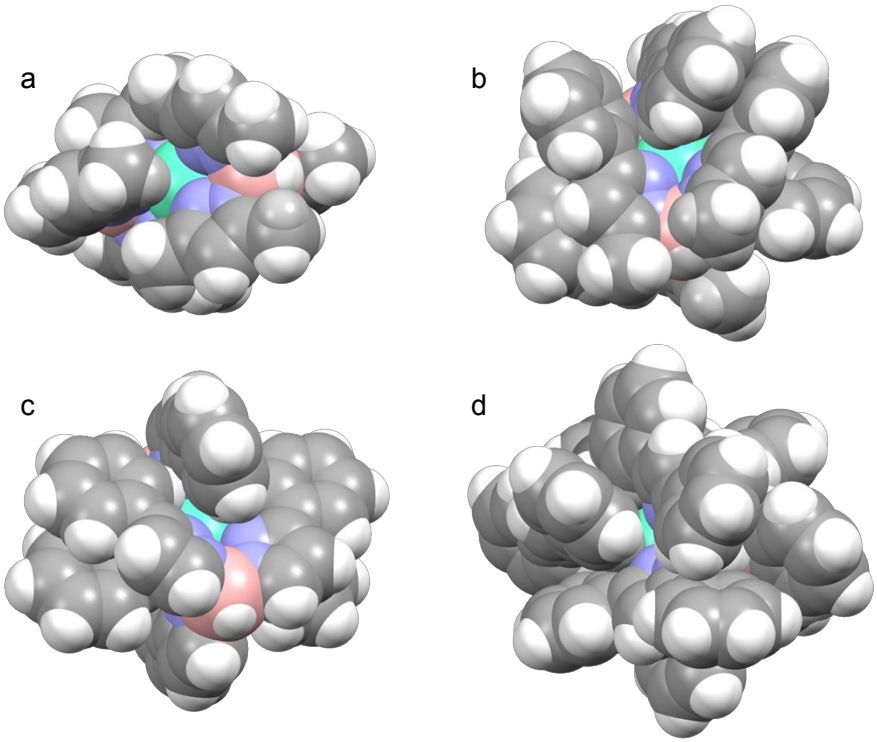

Figure S4. Spacefill view with the largest exposed area of $Eu(Tp^{Me2})_2$ (**a**), $Eu(Tp^{Ph,Me})_2$ (**b**), $Eu(Tp^{Ph})_2$ (**c**) and $Eu(Tp^{Ph2})_2$ (**d**). The blue-green sphere represents Eu, the pink one represents B, the purple blue one represents N, and the gray one represents C.

Table S1. Crystallographic data for $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$ and $Eu(Tp^{Ph2})_2$.

Compound	$Eu(Tp^{Ph,Me})_2$	$Eu(Tp^{Ph})_2$	$Eu(Tp^{Ph2})_2$
chemical formula	$C_{60}H_{56}B_2EuN_{12}$	$C_{54}H_{44}B_2EuN_{12}$	$C_{90}H_{68}B_2EuN_{12}$
formula weight	1118.74	1034.59	1491.14
crystal size (mm)	0.42×0.05×0.03	0.41×0.18×0.06	0.09×0.07×0.06
temperature (K)	180	180	180
radiation	0.71073	0.71073	0.71073
crystal system	Monoclinic	Triclinic	Trigonal
space group	C2/c	P-1	R-3:H
a(Å)	18.8271(3)	10.6292(3)	12.8521(2)
b(Å)	13.5315(2)	11.1934(5)	12.8521(2)
c(Å)	20.9847(3)	11.8422(5)	38.0462(9)
α(°)	90	63.474(4)	90
β(°)	96.110(1)	77.518(3)	90
γ(°)	90	67.401(4)	120
V(Å^3)	5315.67(14)	1162.15(9)	5442.4(2)
Z	4	1	3
$\rho_{(calc)}$ (g/cm^3)	1.398	1.478	1.365
F (000)	2292	525	2295
absorp. coeff. (mm^{-1})	1.232	1.402	0.922
θ range (deg)	2.043-27.483	2.078-27.485	2.817-27.478
reflns collected	33621	14346	7061
indep. reflns	6082	5335	2781
refns obs. [$I>2\sigma(I)$]	5769	5238	2626
data/restr/paras	6082/0/346	5335/0/316	2781/0/160
GOF	1.019	1.049	1.005
R_1/wR_2 [$I>2\sigma(I)$]	0.0190/0.0520	0.0371/0.0895	0.0285/0.0719
R_1/wR_2 (all data)	0.0214/0.0531	0.0377/0.1071	0.0316/0.0733

Table S2. Reported Eu(II) complexes with good PLQY at room temperature.

Complex	PLQY (%)	λ（nm）	Reference
$Eu(Tp^{ipr2})_2$	12	550	4
$Eu(C_5Ph_5)_2$	45	480	5
$Eu(C_5Ph_4)_2(dme)$	41	490	5
$Eu(Tp^{Me2})_2$	85	596	3
Eu(II)-containing aza-222 cryptate-Cl	26[a]	580	6
Eu(II)-containing aza-222 cryptate-I	47[a]	447	7
Eu(II)-15C5	28[a]	432	8
Eu $[(DME)Li(Cot)]_2$	25	485	9
$Eu(II)(Cp^{BIG})_2$	45[a]	412	10

[a] The PLQY was measured in solution. Others were measured in powder.

Table S3. PLQY values of $Eu(Tp^{Ph,Me})_2$, $Eu(Tp^{Ph})_2$, $Eu(Tp^{Ph2})_2$ and $Eu(Tp^{Me2})_2$.

t (day) / PLQY	0	1	2	4	10	11
$Eu(Tp^{Ph,Me})_2$	3%		3%	3%	3%	
$Eu(Tp^{Ph})_2$	19%	20%	20%	21%	17%	
$Eu(Tp^{Ph2})_2$	70%	66%	65%	64%	61%	70%
$Eu(Tp^{Me2})_2$	78%	5%	3%	2%		

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