Tracking down a key parameter responsible for low brightness

of lanthanide-based OLEDs

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1. Materials and Methods

1.1 Materials

Substances purchased from commercial sources were used without further purification unless otherwise stated: EuCl₃·6H₂O (99.99%, Sigma Aldrich); Bathophenanthroline (Bphen, 99%, Sigma Aldrich); pentafluorobenzoic acid (Hpfb, 99%, Sigma Aldrich), 2-fluorobenzoic acid (Hmfb, 99%, Sigma Aldrich), acetic acid (Hoac, Sigma Aldrich), pivalic acid (Hpiv, Sigma Aldrich), acetylacetone (Hacac, Sigma Aldrich), thenoyltrifluoroacetone (Htta, 99%, Sigma Aldrich), ethanol (Sigma Aldrich), methanol (Sigma Aldrich), aqueous ammonia solution (Sigma Aldrich).

Hacac and Htta were purified by distillation and recrystallization from ethanol, respectively, before being used in the synthesis of the complexes.

1.2 Methods

Simultaneous thermal analysis (TA) was performed on a NETZSCH STA449 F1 thermal analyzer at a heating rate of 10 ° C/min (sample weighed in 5-10 mg) in air. The composition of the gas phase formed during the decomposition of the samples was studied using a QMS 403C Aeolos quadrupole mass spectrometer combined with a thermal analyzer. Mass spectra were recorded for mass numbers 18 (H₂O), 44 (CO₂), and 46 (ethanol).

Nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker Avance-400 instrument (400 MHz) in the range of 0–16 ppm. at the Center for Collective Use of the Moscow State University Lomonosov. The data were processed using the 1D NMR Processor software package (ACD Labs).

Powder X-ray diffraction experiments were carried out in the θ - θ geometry of Bragg-Brentano reflection recording using a silicon holder on a Bruker D8 Advance diffractometer (λ (Cu-K α) = 1.5418 Å, K β filter on the reflected beam, variable slits, 1D detector LynxEye); as well as in ω -2 θ geometry of recording for transmission according to Bragg-Brentano between Mylar[®] films on a Bruker D8 Advance Vario diffractometer (λ (Cu-K α 1) = 1.54060 Å, K α 1 Ge (111) monochromator on the primary beam, 1D LynxEye detector). Diffraction patterns were recorded in the 2 θ angle range from 4 ° to 50 ° with a step of 0.020 ° and a rate of 2 ° / min. Diffraction data were processed using TOPAS 5.0 software.

Single crystal X-ray diffraction was performed on a Bruker APEX II Duo single crystal diffractometer (Mo-K α radiation, $\lambda = 1.7902$ Å) at 120 K. All crystal structures were solved by direct methods and then refined by the least squares method using the isotropic-anisotropic full-matrix approximation | Fhkl | 2 in Olex2 software package using SHELX software. The absorption was taken into account using the SADABS program. Hydrogen atoms bound to carbon atoms were added automatically and refined using a rigid body (AFIX command). The positions of the remaining hydrogen atoms were determined from the peaks of the difference electron density map; their positions were refined with restrictions on the length of the covalent bond of the hydrogen atom with the nearest atom.

Photoluminescence spectra, excitation spectra, and luminescence decay curves for powders and films were measured on a FluoroMax Plus spectrofluorometer from Horiba Scientific using a tunable xenon lamp as the excitation source. The wavelengths corresponding to the maxima in the excitation spectra were chosen as the excitation wavelength λ_{ex} . The excitation spectra were recorded at wavelengths $\lambda_{em} = 612$ nm, corresponding to the position of the emission maxima in the photoluminescence spectra of the Eu³⁺ complexes. The lifetimes of the excited state were found from the analysis of the luminescence decay curves using the exponential function:

$$y = y_o + B \exp\left(-\frac{t}{\tau}\right)$$

where y is the measured luminescence intensity at time t after the lamp pulse, B is the luminescence intensity at the time t = 0, τ is the observed lifetime of the excited state, y_0 is the background signal. All luminescence decay curves turned out to be perfect single-exponential functions. The determination of the quantum yield of photoluminescence for powders and films was carried out by the absolute method using a PTI KSPHERE-Petite integrating sphere on a FluoroMax Plus spectrofluorometer. The absolute method for measuring the quantum yield of photoluminescence ^[1] requires measuring: (1) L_{empty} , the integral intensity of the light emerging from the sphere when an empty cell is illuminated at the excitation wavelength (Rayleigh scattering band), (2) L_{sample} is the same integral scattering intensity, when a sample is placed in the cell, (3) E_{empty} is the integrated intensity of the entire luminescence spectrum of an empty cell; (4) E_{sample} is the integrated intensity of the entire luminescence spectrum of the cell with the sample. The absolute quantum yield is defined as:

$$PLQY = \frac{E_{sample} - E_{empty}}{L_{empty} - L_{sample}} \cdot 100\%$$

Photoelectron Yield Spectroscopy (PYS) was performed using a custom-built thin film ionization energy system. The sample, which was a film of the test substance on an ITO substrate, and a copper electrode that collected the emitted electrons were placed in a vacuum chamber. During measurements, a pressure of $1 \cdot 10^{-5}$ mbar was maintained in the chamber. The distance between the copper electrode and the sample was 2 cm. An ENERGETIQ laser (LDLSEQ-99) was used as light source. The wavelength with a spectral width of 2 nm was changed by a diffraction monochromator grating MYM-1. The sample was irradiated through a 2 × 15 mm slit in the copper electrode. A cylindrical lens with a short focal length was placed between the monochromator and the quartz window of the vacuum cryostat, which provided illumination of a large area of the sample, 5 × 15 mm. A voltage of 50 V was applied to the electrodes to improve the measurement accuracy, since the signal is amplified by one order of magnitude compared to the signal without an applied voltage. The ITO electrode under the film of the complexes under study prevented the charging of the sample, which could reduce the signal quality. A Keithley617 electrometer with a built-in voltage source was used to supply voltage as well as to measure electric current. The photoelectron yield Y(hv) was calculated as:

$$Y(hv) = \frac{I(hv)}{P(hv)},$$

where I (hv) is the number of emitted electrons, and P(hv) is the number of incident photons with energy hv.

The relationship between the photoelectron yield and the ionization energy E_{ioniz} can be expressed as a power law:

$$Y(hv) = a(hv - E_{ioniz})^n,$$

where α is a constant corresponding to the signal amplitude and an exponent $n \approx 2.5$ for semiconductors ^[2]. To calculate E_{ioniz} , a graph of $Y^{2/5}(hv)$ was plotted and the linear part of the $Y^{2/5}(hv)$ curve was extrapolated to $Y^{2/5}(hv) = 0$.

The energy gap E_g of the compounds under study was determined from photoconductivity measurements using the same setup as for PYS measurements. Instead of a copper electrode for collecting electrons, we used an aluminum electrode deposited on a film of the studied complex (ITO/complex/Al). The threshold photoconductivity energy E_{th} can be estimated from the spectrum of the quantum yield of photoconductivity $\beta(hv)$. The $\beta(hv)$ values were estimated by the equation ^[3]:

$$\beta(hv, U) = \frac{j_{ph}(hv, U)}{k(hv)I(hv)g(hv)'}$$

where j_{ph} is the photocurrent density at a given photon energy hv and applied voltage U, I(hv) is the light intensity (photons/cm²s), k(hv) is the transmission of a semitransparent electrode, g(hv)is a coefficient.

In crystals of the anthracene type, the spectral dependence $\beta(hv)$ in the near-threshold region can be approximated as:

$$\beta(hv) = A(hv - E_{th})^n,$$

where n \approx 5/2, and E_{th} is the intrinsic conductivity threshold. The photoconductivity threshold E_{th} correlates with the adiabatic band gap.

The absorption spectra of thin films were recorded using an Ocean Optics HR4000CG-UV-NIR spectrometer in the range from 200 nm to 1100 nm.

The mobility of charge carriers in thin films was measured using the Photo-CELIV method, which consists in recording a transient current signal at a linearly increasing electric field voltage applied to the sample. Samples for determining the mobility were prepared as follows: a layer of the compound under study (d = 100 nm) and an aluminum layer (80 nm) were successively deposited on an ITO-glass substrate coated with a dielectric layer of SiO₂ (70 nm) as a counter electrode. The SiO₂ layer is blocking for both types of charge carriers, i.e. prevents injection of charge carriers from ITO. When measuring the transient current of holes, a linearly increasing positive potential was applied to the ITO; therefore, the holes were extracted on an aluminum electrode. The SiO₂ layer prevented the injection of holes from the ITO electrode. In this case, the contribution of the electron current to the signal can be neglected, since the SiO₂ layer also blocked it. To measure the electron mobility, the polarity of the voltage applied to the sample was reversed.

The characteristic time t_{max} corresponding to the maximum value of the transient current was determined from the transient current curve. The mobility of charge carriers μ was calculated by the formula:

$$\mu = \frac{2 \times d^2}{A \times (t_{max})^2},$$

where d is the thickness of the composite layer, A is the rate of change of the applied voltage.

Surface morphology, roughness and thickness of thin films were characterized by NTegra AuraFM (Russia, 2005) in a semi-contact mode at 25 ° C using Micromash NSC15/AIBS probes. The observed surface structures were analyzed using the Nova 1.0.26 software.

OLED fabrication was carried out in an ISO8 class clean room (P.N. Lebedev Physical Institute, Moscow, Russia) or ISO7 class clean room (Institute of Solid State Physics, Riga, Latvia) in an argon atmosphere. The substrates were sonicated in the following media: aqueous NaOH solution, distilled water, acetone, and 2-propanol for 15 min. Poly(3,4ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) hole injection layer (40 nm thick) was deposited from an aqueous solution (5 ml) onto a preheated (70 °C) ITO support, after which the support was rotated for 60 seconds at 2000 rpm. The deposited film was annealed in air at 80 °C for 60 minutes. A hole-transport layer of poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine (PolyTPD) was deposited from a solution in chlorobenzene (c = 5 g/L) at a speed of 2000 rpm. The emission layer was applied from a solution in chloroform (c = 5 g/L) onto the heterostructure at a speed of 1500 rpm or thermally evaporated at a pressure below 10⁻⁶ mm Hg. The electron transport layer (OXD-7 or TPBi), the electron-injection layer (LiF) and the cathode (Al) were thermally evaporated (Univex-300, Leybold Heraeus) at a pressure below 10⁻⁶ mm Hg. Their thickness (20 nm, 1 nm and ~ 100 nm, respectively) was controlled by a quartz indicator.

Electroluminescence spectra were measured on a time-correlated PicoQuant photon counting mode system used as a conventional spectrofluorometer. The spectral resolution was 4 nm. All measurements were carried out in the same configuration, which made it possible to quantitatively compare the electroluminescence spectra after dividing by the integration time. The brightness of the light-emitting diodes was measured using a TKA-PKM luxmeter in the range of 380-750 nm.

2. Synthesis of the complexes

2.1 [Eu(pfb)₃(Bphen)] · Solv and [Eu(mfb)₃(Bphen)]

Homo-ligand $\text{Eu}(L)_3 \cdot \text{Solv} (L = \text{pfb}^-, \text{mfb}^-)$ were synthesized by the interaction of an excess of freshly precipitated europium hydroxide obtained by reaction (1.1) with solutions of pentafluorobenzoic acid (Hpfb) and 2-fluorobenzoic acid (Hmfb), respectively, in ethanol (reaction (1.2)). The reaction mixture was stirred for 30 min at 80 ° C, then excess europium hydroxide was filtered off and the resulting filtrate was evaporated to dryness.

$$\operatorname{EuCl}_{3} \cdot 6\operatorname{H}_{2}\operatorname{O} + 3\operatorname{NH}_{3} \cdot \operatorname{H}_{2}\operatorname{O} \to \operatorname{Eu}(\operatorname{OH})_{3} \downarrow + 3\operatorname{NH}_{4}\operatorname{Cl} + 6\operatorname{H}_{2}\operatorname{O}$$
(1.1)

$$Eu(OH)_3 + 3HL \rightarrow Eu(L)_3 \cdot Solv + 3H_2O \qquad L = pfb^-, mfb^- \qquad (1.2)$$

$$\operatorname{Eu}(L)_{3} \cdot \operatorname{Solv} + \operatorname{Bphen} \to [\operatorname{Eu}(L)_{3}(\operatorname{Bphen})] \cdot \operatorname{Solv} \downarrow \qquad L = \operatorname{pfb}^{-}, \operatorname{mfb}^{-} \qquad (1.3)$$

Mixed-ligand complexes were synthesized by reaction (1.3). A solution of 1 mmol of BPhen in 30 ml of ethanol was added to a solution of 1 mmol of $Eu(L)_3 \cdot Solv$ (L = pfb⁻, mfb⁻) in

20 ml of ethanol; no precipitate formed immediately. The reaction mixture was stirred overnight at 100 ° C under reflux, then cooled to room temperature. The formed precipitate was filtered off, washed with cold ethanol, and dried in air.

2.2 [Eu(oac)₃(Bphen)]

Europium acetate $Eu(oac)_3 \cdot xH_2O$ was synthesized by the reaction of Eu_2O_3 (10 mmol) with acetic acid (60 mmol) in boiling water, followed by evaporation of the resulting solution in air (reaction (2.1)).

$$Eu_{2}O_{3} + 6 CH_{3}COOH + (2x-3) H_{2}O = 2 Eu(CH_{3}COO)_{3} \cdot xH_{2}O$$
(2.1)

$$Eu(oac)_3 \cdot xH_2O + Bphen = [Eu(oac)_3 \cdot Bphen] + xH_2O$$
(2.2)

The synthesis of the mixed-ligand complex [**Eu(oac)**₃**Bphen**] was carried out according to reaction (2.2) in two ways:

Method 1. A solution of 2 mmol Bphen in 30 ml of ethanol was added to a solution of 2 mmol of $Eu(oac)_3 \cdot xH_2O$ in 10 ml of a mixture of water-ethanol (1: 1); no precipitate was formed immediately. The reaction mixture was stirred on a magnetic stirrer for one hour at 90 ° C. Upon evaporation of the mixture to half of the volume, a precipitate formed. The reaction mixture was cooled to room temperature, the precipitate was filtered off, washed with a cold water-ethanol mixture, and dried in air.

Method 2. A solution of 2 mmol Bphen in 30 ml of methanol was added to a suspension of 2 mmol of $Eu(oac)_3 \cdot xH_2O$ in 60 ml of methanol. The reaction mixture was stirred for 4 h at 80 ° C, during which complete dissolution of the suspension was observed. Then the solution was stripped to 2/3 of the volume, while precipitation was observed. The solution was cooled to room temperature, the precipitate was filtered off and washed with cold methanol.

2.3 [Eu(piv)₃(Bphen)]

A solution of a mixture of 1 mmol of $EuCl_3 \cdot 6H_2O$ and 1 mmol of Bphen in 25 ml of ethanol was added to a solution of a mixture of 3.5 mmol of Hpiv and 3 mmol of NEt₃ in 25 ml of ethanol; no precipitate was formed immediately (reaction (3)):

3 Hpiv + 3 NEt₃ + Bphen + EuCl₃·6H₂O = [Eu(piv)₃Bphen] \downarrow + 3 NHEt₃Cl + 9 H₂O (3)

The reaction mixture was stirred for 2 h at 80 ° C, after which the solution was evaporated to half of its volume, while precipitation was observed. The solution was cooled to room temperature, the precipitate was filtered off and washed with cold ethanol.

2.4 [Eu (tta)₃(Bphen)]

A solution of 1 mmol of $EuCl_3 \cdot 6H_2O$ in 20 ml of ethanol was added to a solution of a mixture of Htta (3.3 mmol), NEt₃ (3 mmol), and Bphen (1 mmol) in 30 ml of ethanol, and precipitation was observed (reaction (4)):

3 Htta + 3 NEt₃ + Bphen + EuCl₃·6H₂O = [Eu(tta)₃Bphen] \downarrow + 3 NHEt₃Cl + 9 H₂O (4)

The reaction mixture was stirred for 2 h at 60 $^{\circ}$ C, then the precipitate was filtered off, washed with cold ethanol and dried in air.

2.5 [Eu(acac)₃(Bphen)]

A solution of 1 mmol of $EuCl_3 \cdot 6H_2O$ in 20 ml of ethanol was added to a solution of a mixture of Hacac (3.3 mmol), NEt₃ (3 mmol), and Bphen (1 mmol) in 30 ml of ethanol; no precipitate was formed immediately (reaction (5)).

3 Hacac + 3 NEt₃ + Bphen + EuCl₃·6H₂O = [Eu(acac)₃Bphen] + 3 NHEt₃Cl + 9 H₂O (5)

The reaction mixture was stirred for 2 h at 60 ° C, during which no precipitate was formed. Then the solution was cooled to room temperature, after which 15 ml of water were added. The formed precipitate was filtered off and dried in air. The resulting product was recrystallized twice from ethanol.

2.6 The choice of synthesis and purification methods

The choice of synthesis methods was based on published data on the synthesis of europium mixed-ligand complexes with phenanthroline or its derivatives. Thus, the synthesis of aromatic carboxylates $[Eu(pfb)_3Bphen] \cdot Solv$ and $[Eu(mfb)_3Bphen]$ was carried out according to the well-known technique ^[4–6] of the interaction of the homoligand $Eu(L)_3 \cdot Solv$ ($L = pfb^-$, mfb⁻) complex and a Bphen neutral ligand in ethanol solution. The advantage of this technique lies in the simplicity of controlling the stoichiometric ratio, since only two reagents are involved in the reaction.

The synthesis of the $[Eu(oac)_3Bphen]$ and $[Eu(piv)_3Bphen]$ aliphatic carboxylates by the same technique was impossible, since their corresponding homoligand complexes were insoluble in ethanol. For the $[Eu(oac)_3Bphen]$ complex, an attempt was made to conduct the synthesis in a solvent mixture EtOH:H₂O (4:1), since Eu(oac)₃·xH₂O is soluble in water. When the reagents were mixed, a precipitate did not form, and when the reaction mixture was evaporated to half the volume, a precipitate formed, which, however, according to the PXRD data, represented mostly the initial Bphen. Later, single crystals of $[Eu_2(oac)_6(Bphen)_2]$ ·2Bphen·2EtOH were obtained from this reaction mixture. Therefore, a search for an individual solvent was made in which it would be possible to carry out the synthesis. It turned out that when a suspension of Eu(oac)₃·xH₂O was introduced into a solution of Bphen in methanol, it was dissolved, and when the mixture was evaporated to 2/3 of the volume, a precipitate was observed, which contained the desired complex.

For $[Eu(piv)_3Bphen]$, it was not possible to select a solvent in which it would be possible to carry out the synthesis according to the above procedure, therefore, the synthesis was carried out by an exchange procedure between EuCl₃Bphen and (NHEt₃)piv in ethanol. Solutions of the initial reagents were obtained *in situ* by mixing ethanol solutions of EuCl₃.6H₂O (1 equiv.) and Bphen (1 equiv.), with NEt₃ (3 equiv.) and Hpiv (3.5 equiv.). Triethylamine NEt₃ was chosen as the base, and not a stronger base — KOH or NaOH, in order to prevent the formation of hydroxo complexes. Upon evaporation of the reaction mixture to half the volume, the desired mixed-ligand complex precipitated.

Table S 1 Synthesis, purification and results of obtaining single crystals of the investigated

Complex	Synthesis scheme	Purification	Single crystal	
Eu(pfb) ₃ Bphen·Solv	Eu(pfb) ₃ + Bphen = ↓ Solvent EtOH	Washing by EtOH	obtained from THF	
Eu(mfb) ₃ Bphen	Eu(mfb) ₃ + Bphen = ↓ Solvent EtOH	Washing by EtOH	obtained from toluene before ^[6]	
Eu(tta) ₃ Bphen	EuCl ₃ + Bphen + 3Htta + 3 NEt ₃ =↓ Solvent EtOH	Washing by EtOH	not obtained	
Eu(acac) ₃ Bphen	EuCl ₃ + Bphen + 3Hacac + 3 NEt ₃ Solvent EtOH Precipitation by addition of H ₂ O	Recrystallization from EtOH	obtained from EtOH	
	Eu(OAc) ₃ + Bphen Solvent EtOH-H ₂ O (4:1) Precipitation by evaporation to half- volume	Washing by EtOH	co-crystal of complex and Bphen obtained from EtOH	
	Eu(OAc) ₃ ↓ + Bphen _(solution) Solvent MeOH Dissolving of suspension Precipitation by evaporation to half-volume	Washing by MeOH	not obtained	
Eu(piv) ₃ Bphen	EuCl ₃ + Bphen + 3Hpiv + 3NEt ₃ Solvent EtOH Precipitation by evaporation to half- volume	Washing by EtOH	obtained from EtOH	

complexes

The synthesis of β -diketonates [Eu(tta)₃Bphen] and [Eu(acac)₃Bphen] was carried out according to the exchange technique, which is most often used in the literature for the synthesis of lanthanide β -diketonates with phenanthroline derivatives ^[7,8]. The advantage of this technique lies

in the simplicity of the synthesis, since it does not require preliminary synthesis of homogeneous ligand complexes. It is important to note that the [Eu(tta)₃Bphen] complex precipitated during synthesis, while the [Eu(acac)₃Bphen] complex was precipitated by addition of water.

All complexes that precipitated during the synthesis were purified from possible impurities of the starting reagents by thorough washing with an appropriate solvent: ethanol or methanol. The [Eu(acac)₃Bphen] complex, obtained by salting out with water, was purified by recrystallization from ethanol. The methods of synthesis, purification, and the results of obtaining single crystals of the complexes studied in the work are summarized in Table S 1.

3. Structure of the complexes

3.1 Single-crystal X-ray diffraction: Coordination environment of Eu³⁺

crystals obtained by slow evaporation Some single were of solutions: $[Eu_2(pfb)_6(Bphen)_2(H_2O)_2] \cdot 2THF$ from [Eu(pfb)₃(Bphen)]·Solv in tetrahydrofuran, [Eu₂(piv)₆(Bphen)₂]·2EtOH from [Eu(piv)₃(Bphen)] in ethanol, and [Eu(acac)₃(Bphen)] from its ethanolic solution. Single crystals of [Eu2(oac)6(Bphen)2]·2Bphen·2EtOH were obtained by slow evaporation of the reaction mixture of Eu(oac)₃·xH₂O and Bphen in a 1:4 v:v water:ethanol mixture. Structures of all single crystals were determined by X-ray diffraction (Table S 2). The structure of [Eu(mfb)₃Bphen] was previously determined by some of us ^[6]. Single crystals of the individual complex [Eu(oac)₃Bphen], as well as of [Eu(tta)₃Bphen], could not be isolated, but we obtained at least one structure for each class of anionic ligands studied in this work.

In the structures of $[Eu_2(oac)_6(Bphen)_2] \cdot 2Bphen \cdot 2EtOH$ and $[Eu_2(piv)_6(Bphen)_2] \cdot 2EtOH$, the europium ion exhibits CN = 9 due to the fact that two of the four bridging ligands possess $\mu_2:\kappa^1 - \kappa^1$ coordination mode and other two ligands possess $\mu_2:\kappa^2 - \kappa^1$ coordination mode (Table S 2). At the same time, in the structures of $[Eu_2(pfb)_6(Bphen)_2(H_2O)_2] \cdot 2THF$ and $[Eu_2(mfb)_6(Bphen)_2] \cdot Toluene$, the europium ion exhibits CN = 8 due to $\mu_2:\kappa^1 - \kappa^1$ coordination mode of all four bridging ligands (Table S 2). It is interesting to note that in the $[Eu_2(pfb)_6(Bphen)_2(H_2O)_2] \cdot 2THF$ structure, competition is observed between the anionic ligand and the water molecules that are present in the tetrahydrofuran solution: each europium ion coordinates one water molecule, while the coordination mode of pfb⁻ changes from typical κ^2 to κ^1 . Apparently, this is due to the fact that pentafluorobenzoic acid is the strongest acid (pK_a(Hpfb) = 1.48, pK_a(Hmfb) = 3.27, pK_a(Hoac) = 4.76, pK_a(Hpiv) = 5.03), and, therefore, its anion is the worst complexing agent. In the structure of the mixed-ligand β -diketonate [Eu(acac)₃(Bphen)], the europium ion exhibits a CN = 8 typical for this class of compounds.

The resulting structures obey the general tendencies of lanthanide mixed-ligand complexes with phenanthroline derivatives, as shown by a CSD search, provided below. Thus, aromatic and aliphatic carboxylates are dimers, while $[Eu(acac)_3(Bphen)]$ is monomeric. Interestingly, in the structure of $[Eu_2(oac)_6(Bphen)_2]$ ·2Bphen·2EtOH co-crystal, the second Bphen molecule is not coordinated by the europium ion, and thus the typical dimeric fragment found in the structures of lanthanide carboxylates with phenanthroline derivatives is retained.

 Table S 2 The crystal structures, molecular packing and Eu³⁺ coordination environment of

 the studied complexes

Crystal structures	Molecular packing	Coordination environment of Eu ³⁺							
	$[Eu_2(pfb)_6(Bphen)_2(H_2O)_2] \cdot 2THF$ Spacegroup = P2 ₁ /c; R=4.62%								
		XX							
	[Eu ₂ (mfb) ₆ (Bphen) ₂]·Toluene ^[6]								
A A A A		XX							
$[Eu_2(piv)_6(Bphen)_2] \cdot 2EtOH$									
	Spacegroup $- r - 1$; $K - 3.19\%$								



3.2 CSD analysis of lanthanide complexes with Phen derivatives

Since the objects of study are mixed-ligand complexes of europium with bathophenanthroline, it is important to compare their structure with that of mixed-ligand complexes with phenanthroline derivatives. The Cambridge Structural Database (CSD) contains 1999 structures of lanthanide complexes with phenanthroline derivatives (April 2020), including 1220 carboxylate structures and 239 β -diketonates. The complexes crystallize in the lower crystal systems: triclinic and monoclinic, most often in space groups P-1 or P21/c. The structure of these two classes of compounds is strikingly different.

Among 1220 structures of lanthanide carboxylates with phenanthroline derivatives, 100 complexes have a monomeric structure, 498 have a dimeric structure, 559 are coordination polymers, and the remaining 63 are tri- and tetramers. Thus, the most common are dimeric and polymeric structures, this is primarily due to the fact that the carboxylate group can be bidentate, or bridging (**Fig. S 1**a). It is important to note that coordination polymers are observed when there

are several carboxy groups in the ligand, as, for example, in the case of fumaric acid Hfum (**Fig. S** 1b).



Fig. S 1 a) Dimeric structure of $[Dy_2(OAc)_6(Phen)_2]^{[9]}$ and b) Polymeric structure of $[Er(fum)_3(Phen)]_{\infty}^{[10]}$

The analysis of the coordination numbers of lanthanide ions shows that CN = 8 is observed in 576 structures, CN = 9 in 652 structures, and 55 more structures contain lanthanide ions with CN>9. There is no preference for any specific CN value, and occurrence of CN = 8 or CN = 9 is determined by the bridging function of the carboxy group: $\mu_2:\kappa^1-\kappa^1$ or $\mu_2:\kappa^2-\kappa^1$, while solvent molecules practically do not affect the coordination number, since they are rarely located in the first coordination sphere of the lanthanide ion due to competition with the neutral ligands.

At the same time, among 239 structures of lanthanide β -diketonates with phenanthroline derivatives, the overwhelming majority – 210 complexes – have a monomeric structure, and only 29 have a dimeric structure. This preference for the formation of monomeric structures is due to the fact that β -diketonate anions are characterized by a unique κ^2 coordination due to the formation of a stable six-membered ring (Fig. S 2a, b). The found dimeric structures are due to bridging OHgroups (Fig. S 2c) or to polydentate neutral ligands. An analysis of the coordination numbers of lanthanide ions shows that in almost all structures the ions exhibit CN = 8 (190 structures), in another 12 structures, CN = 9 and in 8 structures, CN = 10. The dominant CN = 8 is observed in all structures with composition [Ln(β -diketonate)₃Phen], and a rare CN> 8 is realized due to the entry of solvent molecules or a second molecule of the neutral ligand into the first coordination sphere of the lanthanide ion (Fig. S 2d).



Fig. S 2 a) k²-coordination of β-diketonates, and structures of b) [Sm(acac)₃(Phen)] ^[11],
c) [Er₂(hfa)₆(OH)₂(Phen)₂] ^[12], and d) [La(hfa)₃(Phen)₂] ^[13].

If we narrow down the consideration to complexes of europium with bathophenanthroline (Bphen), then today there are only 11 structures in the CSD base: 9 structures of carboxylates, namely [Eu(bz)₃(Bphen)], where bz⁻ is the benzoate anion (Fig. S 3a), [Eu(mfb)₃(Bphen)] Toluene, where mfb⁻ is 2-fluorobenzoate anion (Fig. S 3b), and 7 structures $[Eu(piv)_3(Bphen)]$ ·Solv, where piv⁻ is pivalate anion (Fig. S 4); one structure of β -diketonate [Eu(cpta)₃(Bphen)], where cpta⁻ is 1- (4-chlorophenyl)-4.4.4-trifluoro-butanedionate-1,3) (Fig. S 4a), and one structure of $[Eu(L)_3(Bphen)]$, where L= tetraphenylimidodiphosphinate (Fig. S 4b).

All Eu(carb)₃(Bphen)·Solve (carb⁻ = bz⁻, mfb⁻, piv⁻) complexes obey general tendencies in the structure of lanthanide carboxylates with phenanthroline derivatives: they are all dimers, and the coordination number of the europium ion varies from CN = 8 up to CN = 9, depending on which bridging function the ligand is operating: $\mu_2:\kappa^1-\kappa^1$ or $\mu_2:\kappa^2-\kappa^1$.



Fig. S 3 Structures of a) $[Eu_2(bz)_6(Bphen)_2]^{[14]}$ and b) $[Eu_2(mfb)_6(Bphen)_2]$. Toluene ^[15].

Interestingly, all structures with different solvation compositions $[Eu_2(piv)_6(Bphen)_2]$ ·Solv (Solv = 0.75H₂O, 1.5EtOH, 2EtOH) are formed from one reaction mixture in a 95% ethanol solution. The complexes crystallize in different space groups – C2/c, I2/a, and P-1, respectively. When heated in the range 58-125 °C, de-solvation occurs with the formation of three different structures $[Eu_2(piv)_6(Bphen)_2]$ in space groups C2/c, I2/a, and P21, respectively. Thus, the space group and the overall structure of the $[Eu_2(piv)_6(Bphen)_2]$ ·Solv (Solv = 0.75H₂O, 1.5EtOH) complexes are retained, while for $[Eu_2(piv)_6(Bphen)_2]$ ·2EtOH, a phase transition with increasing syngony is observed ^[16].

It is particularly interesting to consider the diversity of structures of europium pivalates with bathophenanthroline. Of the 7 pivalate structures, only 6 are unique, namely, three $[Eu_2(piv)_6(Bphen)_2]$ ·Solv structures with different solvation compositions Solv = 0.75H₂O, 1.5EtOH, 2EtOH, and three different structures of the same composition $[Eu_2(piv)_6(Bphen)_2]$. The seventh structure duplicates the structure of $[Eu_3(piv)_6(Bphen)_2]$ ·1.5EtOH, but due to other experimental conditions and subsequent processing, they exhibit only a small difference in the unit cell parameters.



b) $[Eu_2(piv)_6(Bphen)_2]$ ·1.5EtOH, c) $[Eu_2(piv)_6(Bphen)_2]$ ·2EtOH and d) $[Eu_2(piv)_6(Bphen)_2]$.

The last two structures [Eu(cpta)₃(Bphen)] and [Eu(L)₃(Bphen)] have a monomeric structure with CN = 8, which is also typical for lanthanide β -diketonates with phenanthroline

derivatives. It is important to note that L = tetraphenylimidodiphosphinate is not a member of the β -diketone class, but is chemically related.



Fig. S 5 Structures of a) $[Eu(cpta)_3(Bphen)]^{[17]}$ and b) $[Eu(L)_3(Bphen)]^{[18]}$.

3.3 Powder X-ray diffraction

Powdered samples of the complexes were analyzed by powder X-ray diffraction to prove the individuality of the obtained compounds. PXRD revealed that for $[Eu(acac)_3Bphen]$ the structure calculated from its powder pattern by Rietveld's method (Fig. S 10) is identical with its single crystal structure. The diffraction patterns for $[Eu(oac)_3Bphen]$, $[Eu(pfb)_3Bphen]$, $[Eu(mfb)_3Bphen]$, and $[Eu(tta)_3Bphen]$ also prove their individuality but they could only be indexed and refined by the Le Bail method (Fig. S 6-Fig. S 9). Space groups were identified in the analysis of systematic extinction of reflections. The correctness of indexing was also verified by comparing the found unit cell volume with the theoretical one, on the basis that the average nonhydrogen atom in the structures of organic compounds and coordination compounds with organic ligands is ~ 18 Å³.

The diffraction pattern of [Eu(piv)₃Bphen] was impossible to index; however, according to PXRD data no impurities of the initial reagents were found. Unit cell parameters are reported in Table S 3.



Fig. S 6 XRD pattern of [Eu(pfb)₃Bphen]. Blue traces are experimental ones while red traces and patterns are calculated; grey traces show differences between experimental and calculated data.



Fig. S 7 XRD pattern of [Eu(mfb)₃Bphen]. Blue traces are experimental ones while red traces and patterns are calculated; grey traces show differences between experimental and

calculated data.



Fig. S 8 XRD pattern of [Eu(tta)₃Bphen]. Blue traces are experimental ones while red traces and patterns are calculated; grey traces show differences between experimental and

calculated data.



Fig. S 9 XRD pattern of [Eu(oac)₃Bphen] described by Le Bail method. Blue traces are experimental ones while red traces and patterns are calculated; grey traces show differences between experimental and calculated data.



Fig. S 10 XRD pattern of [Eu(acac)₃Bphen] described by Rietveld method. Blue traces are experimental ones while red traces and patterns are calculated; grey traces show differences between experimental and calculated data.

L=	Space group	V (Å ³)	a (Å)	b (Å)	c (Å)	α()	β()	γ()
pfb⁻	P-1	2220.5(3)	12.5834(8)	13.6925(8)	13.8021(9)	103.508(5)	83.582(6)	77.146(5)
mfb⁻	P-1	1901.2(2)	11.5736(4)	13.0897(5)	13.9977(4)	113.570(7)	100.543(6)	85.961(5)
oac-	P2/c or Pc	2858.2(1)	13.4556(2)	9.4459(2)	25.7344(6)		119.094(1)	
tta⁻	P21/c	4886.6(2)	14.0866(3)	22.6046(6)	19.7565(5)		129.033(4)	
acac-	P-1	1829.4(2)	11.9674(5)	12.1362(4)	14.2330(7)	95.605(3)	105.660(3)	109.951(3)

Table S 3 Unit cell parameters for powdered [Eu(L)₃Bphen] complexes

4. Characterization of the complexes

4.1 ¹H NMR Spectroscopy

¹H NMR spectroscopy in DMSO-d₆ at room temperature was used for determining the ratio of anionic and neutral ligands in the composition of the complexes, since the ¹H NMR spectra of mixed-ligand complexes contain a combination of signals from both types of ligands. It turned out that for all the $[Eu(L)_3Bphen]$ complexes, this ratio was exactly one molecule of the neutral ligand for three anionic ligands (Fig. S 11-Fig. S 15). So, the ratio of the integrated intensities of the signals of the neutral ligand BPhen and the signals of the anionic ligand mfb⁻ was 16:12, which points to the occurrence of exactly one molecule of the neutral ligand in the complex for three anionic ligands and one Eu^{3+} ion (Fig. S 11). For the $[Eu(oac)_3Bphen]$, $[Eu(piv)_3Bphen]$, $[Eu(tta)_3Bphen]$ and $[Eu(acac)_3Bphen]$ complexes, the ratio of anionic to neutral ligands was confirmed similarly (Fig. S 12-Fig. S 15).







Fig. S 12 ¹H NMR spectra of [Eu(oac)₃Bphen] (top) and Bphen (bottom) in DMSO-d⁶.



Fig. S 13 ¹H NMR spectra of [Eu(piv)₃Bphen] (top) and Bphen (bottom) in DMSO-d⁶.



Fig. S 14 ¹H NMR spectra of [Eu(tta)₃Bphen] (top) and Bphen (bottom) in DMSO-d⁶.



Fig. S 15 ¹H NMR spectra of [Eu(acac)₃Bphen] (top) and Bphen (bottom) in DMSO-d⁶.

A separate task was to determine the ratio of anionic and neutral ligands in the [Eu(pfb)₃Bphen] complex, since there are no protons in the pentafluorobenzoate anion. To solve this problem, ¹H NMR with an external standard was used ^[5]. We selected trioctylphosphine oxide (TOPO) as an external standard, since all its protons are alkyl and, therefore, their signals lie in the range of 0-2 ppm, therefore, TOPO signals do not overlap with BPhen aromatic proton signals. The following procedure was used to determine the ligand ratio. Samples of the complex and S22

TOPO powders were weighed, the ratios of the amounts of substances were calculated, and the theoretical ratios of the integrated intensities were calculated for the possible compositions $[Eu(pfb)_3Bphen]$ (16:108) and $[Eu(pfb)_3(Bphen)_2]$ (16:70). The ratio of the integrated intensities of the signals of the neutral BPhen ligand and the signals of the external TOPO standard according to ¹H NMR in DMSO-d₆ was 16:103 (Fig. S 16). Comparing these ratios with theoretical values, we concluded that one molecule of the neutral ligand is included in the complex.



Fig. S 16 ¹H NMR spectrum of a mixture of Eu(pfb)₃Bphen and TOPO in DMSO-d⁶.

4.2 Thermal analysis

Thermal stability of the [Eu(L)₃(Bphen)] complexes was assessed by thermal analysis (Fig. S 17). These data, together with mass spectrometry detection of evolved gaseous substances (Fig. S 17b,c) and XRD data of the residue (Fig. S 17d,e), point to the complexes with L = mfb⁻, oac⁻, piv⁻, acac⁻, and tta⁻ not containing coordinated solvent molecules, unlike [Eu(pfb)₃Bphen]. Mass-spectrometry data show that at this stage a mixture of water (m/z = 18) and ethanol (m/z = 46) is released, but their exact ratio could not be determined. Thus, for this complex, it is more correct to assign the composition as [Eu(pfb)₃Bphen]·Solv (Solv = H₂O + EtOH). With further decomposition of the complex, a sharp exothermic effect is observed at ~200 °C, which apparently corresponds to an explosion, and then further thermal destruction of the complex occurs, which indicates thermal instability of the complex.

The complexes with $L = acac^{-}$ starts to decompose around 200 °C while the other ones are stable up to ~ 290 °C. Decomposition occurs in two steps and finally leads, above 600 °C, to the formation of either Eu₂O₃ or, for complexes with fluorinated ligands, to a mixture of Eu₂O₃ and EuOF (Fig. S 17d,e). Detailed weight loss analysis is given in Table S 4.



Fig. S 17 a) TGA curves of the studied complexes and b) TGA curves with mass spectrometric detection of gaseous substances for [Eu(pfb)₃Bphen]·Solv. c) TGA curve with mass spectrometric detection of gaseous substances for [Eu(tta)₃Bphen]. d,e) PXRD data for samples after thermal analysis of d) [Eu(piv)₃Bphen] (black) and [Eu(pfb)₃Bphen]·Solv (blue),

e) [Eu(oac)₃Bphen] (black), [Eu(acac)₃Bphen] (red) and [Eu(tta)₃Bphen] (blue).

The phases formed after decomposition of the complexes were determined using XRD data (Fig. S 17b,c). It turned out that the $[Eu(L)_3(Bphen)]$ complexes, where $L = oac^-$, piv⁻, acac⁻ decompose with the formation of europium oxide Eu_2O_3 , while the fluorine-containing complexes for which $L = pfb^-$, mfb⁻, tta⁻, decompose with the formation of a mixture of Eu_2O_3 oxide and EuOF

oxofluoride. Interestingly, even in the case of the [Eu(pfb)₃Bphen]·Solv complex containing a perfluorinated anionic ligand, the europium fluoride phase EuF₃ does not form.

Knowing into which final compounds the complexes decompose, the theoretical percentage of the mass of the residue (Δ m/m) was calculated based on the assumed composition of the complex. In the case of L = oac⁻, piv⁻, acac⁻, this corresponds to the formation of ¹/₂ equiv. Eu₂O₃, while for fluorine-containing complexes we assumed formation of ¹/₂ equiv. Eu₂O₃ and 1 eq. EuOF (since the phase ratio of Eu₂O₃ and EuOF after decomposition is unknown), implying that the true theoretical value should be between these two limiting cases. Comparison of theoretical values (Δ m/m) with experimental (Δ m/m) ratio for each complex confirms that the complex includes three anionic ligands and one neutral one (Table S 4).

		Residual (Δm/m), %,	Residual (Δm/m),	Residual (Δm/m),	
Complex	M, g/mol	clcd for ½ Eu ₂ O ₃	%, clcd for EuOF	%, found	
Eu(pfb) ₃ Bphen·Solv	1150	15.3%	16.3%	15.6%	
Eu(mfb) ₃ Bphen	901	19.5%	20.7%	20.0%	
Eu(oac) ₃ Bphen	661	26.6%		26.4%	
Eu(piv) ₃ Bphen	787	22.3%		21.8%	
Eu(tta) ₃ Bphen	1147	15.3%	16.3%	15.4%	
Eu(acac) ₃ Bhpen	781	22.5%		22.1%	

Table S 4 Analysis of the mass loss of the studied complexes.

5. Photophysical and electronic properties of complexes and composite films

5.1 Powdered samples of the complexes

Excitation and luminescence spectra were recorded for powders (Fig. S 18), thin films (Fig. S 19), and composite thin films (Fig. S 20-Fig. S 25), since the complexes were synthesized in the form of powder, but will be used in OLEDs in the form of thin films (pure and composite; spin-coated from CHCl₃, 5 mg/ml).



Fig. S 18. a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of powders [Eu(L)₃Bphen], L = mfb⁻, oac⁻, piv⁻, acac⁻, tta⁻, and [Eu(pfb)₃Bphen]·Solv (Solv = H₂O + EtOH)

(room temperature).



Fig. S 19. a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of thin

films of Eu(L)₃Bphen (room temperature).

The luminescence spectra of powders and pure thin films coincide and contain only characteristic europium bands (${}^{5}D_{0} \rightarrow {}^{7}F_{j}$, j = 0...4). It should be noted, that the intensity of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in the case of [Eu(tta)₃Bphen] and [Eu(acac)₃Bphen] β -diketonates is much higher than in the case of [Eu(L)₃Bphen] carboxylates (L = pfb⁻, mfb⁻, oac⁻, piv⁻).

The excitation spectra of the powders (Fig. S16a) present a broad intense band arising from the organic subsystem, spanning the range 250–350 nm (450 nm for L = tta⁻) and featuring several maxima, one around 280 nm and others around 340 and 360-370 nm. In addition, two narrow lowintensity bands are seen, which arise from the europium ion and correspond to the ${}^{5}L_{6}\leftarrow {}^{7}F_{0,1}$ (~390 nm) and ${}^{5}D_{2}\leftarrow {}^{7}F_{0,1}$ (~460 nm) transitions. In the case of thin films (Fig. S 19b), the shape of the excitation band due to the organic subsystem changes substantially for [Eu(L)₃Bphen] (L = pfb⁻, mfb⁻, oac⁻, piv⁻, acac⁻): only one maximum remains at 280 nm, which corresponds mainly to excitation through Bphen, with shoulders around 310 and 350 nm. On the other hand, for [Eu(tta)₃Bphen] for which the molar absorption coefficient ε (tta⁻) is comparable to ε (Bphen) ^[8], unlike the ε values for L = pfb⁻, mfb⁻, oac⁻, piv⁻, acac⁻, the shape of the excitation band, with two maxima, is retained. Another difference between the powder and thin film excitation spectra is the disappearance of the f-f transitions in the latter one; one explanation could be that for the thin films, absorption by Eu(III) sites occurs in a reduced depth (10 nm) while it occurs in a much larger volume for the powder samples.

The quantum yields of photoluminescence (PLQY) were measured upon excitation into the organic ligand, and for most of powders were very high (Main text, Table 1, row 1). The quantum yields of $[Eu(oac)_3Bphen]$ and $[Eu(piv)_3Bphen]$ complexes are 85% and result from sensitization by Bphen, since the aliphatic anionic ligands do not have sensitization ability. The quantum yields of $[Eu(L)_3Bphen]$ (L=mfb⁻, tta⁻) are 90%, which is slightly higher, possibly due to additional sensitization by the anionic ligands. For the $[Eu(pfb)_3Bphen] \cdot Solv$ complex, the quantum yield decreases down to 60%, which is due to quenching by coordinated solvent molecules. The

quantum yield for the [Eu(acac)₃Bphen] complex was only 20% despite the introduction of an effective sensitizer, Bphen, which is apparently due to the presence of a charge transfer state from the acac⁻ ligand to the metal ion (LMCT) ^[19]. The quantum yields for films (Main text, Table 1, row 3) are lower than for powders, which could be attributed to the quenching by oxygen, despite the annealing.

The observed lifetimes of the excited state are different for all complexes (Main text, Table 1, rows 2, 4), but it is important to note that for complexes with β -diketonates they are significantly lower than for carboxylates, both aromatic and aliphatic.

5.2 Thin composite films

To increase the mobility of charge carriers of the emission layer and/or to optimize the energy structure of OLEDs, the approach of introducing emitters into the host is often used. It is important that the energy is transferred from the host to the emitter, since in the case of using such composite films, the exciton is generated mainly in the host material.



Fig. S 20 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of [Eu(oac)₃Bphen] thin film and Host:[Eu(oac)₃Bphen] composite films, where Host = CBP, mCP, TcTa (room temperature)

To study the energy transfer from the widely used hole transport hosts CBP (4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl), mCP (1,3-bis(*N*-carbazolyl)benzene), TcTa (tris(4-carbazoyl-9-

ylphenyl)amine) to emitters, we studied the photoluminescent properties of Host: $[Eu(L)_3Bphen]$ (10 wt%) composite thin films, which were deposited by spin-coating from the host and complex mixture in chloroform (Fig. S 20-Fig. S 25).



Fig. S 21 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of

 $[Eu(piv)_3Bphen]$ thin film and Host: $[Eu(piv)_3Bphen]$ composite films, where Host = CBP, mCP, TcTa (room temperature).



Fig. S 22 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of [Eu(acac)₃Bphen] thin film and Host:[Eu(acac)₃Bphen] composite films, where Host = CBP, mCP, TcTa (room temperature).



Fig. S 23 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of [Eu(tta)₃Bphen] thin film and Host:[Eu(tta)₃Bphen] composite films, where Host = CBP, mCP, TcTa (room temperature).



Fig. S 24 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of [Eu(mfb)₃Bphen] thin film and Host:[Eu(mfb)₃Bphen] composite films, where Host = CBP, mCP, TcTa (room temperature).



Fig. S 25 a) Excitation (λ_{em} =613 nm) and b) luminescence (λ_{ex} = 280 nm) spectra of [Eu(pfb)₃Bphen] thin film and Host:[Eu(pfb)₃Bphen] composite films, where Host = CBP, mCP, TcTa (room temperature).

All composite films show typical europium luminescence with bands (${}^{5}D_{0} \rightarrow {}^{7}F_{J}$, J = 0-4) of the same shape as in the spectra of the individual complexes. Preservation of the Stark splitting indicates the preservation of the europium coordination environment upon complex doping into the host. The shape of all the composite film excitation spectra differ from those of the films of the individual complexes: an additional through-host excitation band appears. For $[Eu(L)_3(Bphen])$ (L = oac⁻, piv⁻, acac⁻, mfb⁻, pfb;Fig. S 20-Fig. S 22, Fig. S 24-Fig. S 25), the additional band is clearly present, evidencing host—emitter energy transfer while for $[Eu(tta)_3(Bphen)]$ through-host excitation band overlaps with the intense through-tta⁻ band (Fig. S20).

The efficiency of the Host→complex energy transfer could not be estimated but it is clearly different for different hosts as illustrated by the PLQYs of composite films (Table S 5). The composite film PLQYs were determined under 300-nm excitation, at which both ligands and host absorb, and for CBP – also at 350 nm, at which excitation through CBP mainly occurs. PLQYs of composite films are lower than those of the corresponding individual films, and, more importantly, they are lower under 350 nm excitation, compared to 300 nm excitation, witnessing that energy

transfer efficiency is usually below 100%. An exception was the composite films $mCP:Eu(oac)_3Bphen$, $CBP:Eu(acac)_3Bphen$, and $mCP:Eu(acac)_3Bphen$, for which, taking into account the experimental error, energy transfer efficiency was almost quantitative. For Host = TcTa, energy transfer efficiency is so low, that it cannot be considered as a prospective host.

Eu(L)₃Bphen, where L= Host mfb⁻ pfb⁻ oacpiv⁻ tta⁻ acac⁻ 52 34 50 40 33 16 CBP 25* 2* 38* 38* 17* 62* mCP 45 47 60 39 50 15 ТсТа 25 20 16 28 15 12

Table S 5 PLQY of composite films Host:10%[Eu(L)₃Bphen] (λ_{ex} =300 nm, ±10%)

* λ_{ex} =350 nm

5.3 HOMO and LUMO determination

HOMO energies were determined for thin films by photoelectron yield spectroscopy as the ionization energy of the compounds (Main text, Table 1, row 8). LUMO energies were calculated as LUMO = HOMO-E_g, where the energy gap E_g was determined from photoconductivity measurements or was estimated from the absorption spectra of thin films (Main text, Table 1, row 9). The shape of the absorption spectra of thin films of $[Eu(L)_3(Bphen)]$ complexes, where L = pfb⁻, mfb⁻, oac⁻, piv⁻, acac⁻, is the same and practically coincides with the shape of the absorption spectrum of Bphen (Fig. S 26b), due to the molar absorption coefficient of Bphen being orders of magnitude greater than the molar absorption coefficients of anionic ligands L = pfb⁻, mfb⁻, oac⁻, piv⁻, acac⁻. At the same time, two absorption bands corresponding to the absorption of the Bphen and tta⁻ ligands are observed for [Eu(tta)₃(Bphen)]; a similar situation was observed with the excitation spectra of thin films. Therefore, the energy gap E_g^{opt} for all [Eu(L)₃(Bphen)] complexes, where L = pfb⁻, mfb⁻, oac⁻, piv⁻, acac⁻, was ~3.6 eV (~cm⁻¹), while for [Eu(tta)₃(Bphen)] it

amounted to ~3.1 eV (~ 25,000 cm⁻¹). At the same time, the energy gap for all complexes, determined from photoconductivity data, turned out to be very close and lies in the range of 2.55–2.68 eV. The LUMO values were calculated from HOMO values (Fig. S 26a) using these two sets of data, but when using E_g^{opt} , some of the obtained values do not reach 1 eV, which is atypical. Therefore, preference should be given to the value obtained from experiments on photoconductivity.

The obtained energies are in the range of the typical values for OLED emitters of various classes ^[20–23].



Fig. S 26 a) Determination of ionization energy and b) absorption spectra of thin films of complexes and a solution of Bphen in CH_3CN (concentration $1 \cdot 10^{-5}$ M).

6. OLED fabrication and characterization

6.1 Determination of the charge carrier mobility

Determination of the charge carrier mobility for nonvolatile lanthanide complexes is virtually impossible. Indeed, the time-of-flight method requires a large film thickness (> 1 μ m), which is impossible to obtain with high quality from solution of small molecules. The measurement of mobility in organic field effect transistors (OFET) requires the absence of defects in the film of an organic semiconductor; in addition, mobility in OFET is measured along the plane of the film, while in OLED, charge carriers move in the film in the perpendicular direction. Even

the Photo-CELIV method, which in principle is suitable for thin films with low charge mobility, has never been successfully used for films of lanthanide complexes deposited from a solution. The graphs below (Fig. S27) demonstrate typical transient current curves versus time during which the sawtooth signal was applied. For more accurate results, the curves were taken at least 10 times with the same parameters of the sawtooth signal. The maximum value of the electric field attainable in the sample is shown as the onset in the graphs.





Fig. S 27 Photo-Celiv current transients (e and h; electric field values are onsets) of $Eu(L)_3Bphen: L = a)$ tta, b) acac, c) pfb, d) mfb, e) oac, f) piv.

Complex	Electron mobility	Hole mobility
Complex	$\mu_{e}, cm^2 V^{-1} s^{-1}$	μ_h , cm ² V ⁻¹ s ⁻¹
Eu(mfb) ₃ Bphen	2.44.10-7	5.78.10-6
Eu(pfb) ₃ Bphen	3.33.10-5	1.87.10-6
Eu(oac) ₃ Bphen	3.71.10-5	5.39.10-5
Eu(piv) ₃ Bphen	2.02.10-5	2.42.10-6
Eu(tta) ₃ Bphen	8.40.10-7	7.30.10-4
Eu(acac) ₃ Bphen	8.51.10-6	3.06.10-5

Table S 6 The charge carrier mobility of the studied complexes.

However, in this study, we were able to determine the electron and hole mobility of all complexes by the Photo-CELIV method (Table S 6) ^[24]. It turned out that, as expected, Bphen provides electron mobility μ_e of complexes which reaches 10^{-5} cm² V⁻¹s⁻¹. However, it is important to note that the obtained electron mobility is lower than $\mu_e(Bphen) = 3.2 \cdot 10^{-4} \text{cm}^2 \text{V}^{-1}\text{s}^{-1}$. At the same time, most complexes demonstrated high hole mobility, reaching $\mu_h = 7.30 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ for [Eu(tta)₃Bphen].

6.2 Film deposition and morphology

The volatility (at 10^{-5} Torr) and the solubility (in CHCl₃ and THF) of the complexes was assessed prior to their thin film deposition. For the film deposition by spin-coating, solutions with a solute concentration of 5 mg/ml were usually used; therefore, instead of the exact solubility, the possibility to reach this concentration was determined. The solubility in CHCl₃ exceeds 10 mg/ml for all the complexes, but in THF only for [Eu(L)₃(Bphen)] (L = pfb⁻, piv⁻, tta⁻, and acac⁻), so CHCl₃ was further selected (Main text, Table 1, rows 12-13). Complexes [Eu(L)₃(Bphen)] (L = piv⁻, tta⁻, acac⁻) are volatile, while [Eu(L)₃(Bphen] (L = mfb⁻, pfb⁻, oac⁻) decompose under heating (Main text, Table 1, row 14).

The morphology of the spin-coated ITO/PEDOT:PSS/PolyTPD/Eu(L)₃Bphen films, studied by atomic force microscopy (AFM), revealed the same low root-mean-square roughness

of 1.1–1.4 nm for all complexes (Main text, Table 1, row 15), and the film thickness varied from 10 to 16.9 nm (Main text, Table 1, row 16).

In order to control the thickness of the films deposited by the VTE method, the volatile complexes $[Eu(piv)_3Bphen]$, $[Eu(tta)_3Bphen]$, and $[Eu(acac)_3Bphen]$ were pre-calibrated, for which AFM data were also used, and morphology of the deposited films were also studied. It turned out that both diketonates form smooth films, while $[Eu(piv)_3Bphen]$ forms an inhomogeneous film on which agglomerates are visible (Fig. S 28b). Based on the literature data on the film growth mechanisms ^[25], we suggest that this difference may be due to the fact that, unlike mixed-ligand β -diketonates, the $[Eu(piv)_3Bphen]$ complex has a dimeric structure, which affects the mechanism of film formation.



Fig. S 28 AFM scans of the [Eu(piv)₃Bphen] film in the ITO/PEDOT:PSS/PolyTPD heterostructure deposited by a) spin-coating and b) VTE.

6.3 OLED fabrication

To identify general tendencies of OLED characteristics dependence on the complex nature, the same OLED heterostructure ITO/PEDOT:PSS/polyTPD/**Eu(L)**₃**Bphen**/OXD-7/LiF/A1 was used first, in which the emissive layer was spin-coated from CHCl₃ (diodes -9 to -4, Table S 7) with standard hole-transport (PolyTPD, poly(4-butyl-N,N-diphenylaniline) and electron-transport layers (OXD-7, 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene) ^[26–28]. Then a better optimized structure was tested (diodes **0-6**, Table S 7) in which the complex was dispersed into CBP polymer (4,4'-bis(9-carbazolyl)-1,1'-biphenyl, 4,4-N,N'-dicarbazole-1,1'-biphenyl , 50 %) and the electron transport layer was replaced with TPBi (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) for OLEDs **1-6** (Table S 7).

Table S 7 List of OLED heterostructures indicating the deposition method of the emissive layer,as well as switch-on voltage and maximum luminance values of devices.

	EML			
		Heterostructure	U _{on} a,	L _{max} ,
OLED	deposition			
		ITO/PEDOT:PSS/polyTPD//LiF/Al	V	cd/m ²
	method			
-9	spin-coating	Eu(mfb) ₃ Bphen/OXD-7	7	<1
0	· · · · · · · · · · · · · · · · · · ·		7	<1
-8	spin-coating	Eu(pib) ₃ Bpnen/OAD-7		<1
-7	spin-coating	Eu(oac) ₃ Bphen/OXD-7	7	<1
-6	spin-coating	Eu(piv) ₃ Bphen/OXD-7	7	<1
-5	spin-coating	Eu(acac) ₃ Bphen/OXD-7	6	2
-4	spin-coating	Eu(tta) ₃ Bphen/OXD-7	4	8
-3	VTE	Eu(piv) ₃ Bphen/OXD-7	6	1
-2	VTE	Eu(acac) ₃ Bphen/OXD-7	13	8
-1	VTE	Eu(tta) ₃ Bphen/OXD-7	4	10
0	spin-coating	CBP:Eu(tta) ₃ Bphen/OXD-7	5	23
1	spin-coating	CBP:Eu(mfb) ₃ Bphen/TPBi	7	9
2	spin-coating	CBP:Eu(pfb) ₃ Bphen/TPBi	7	5
3	spin-coating	CBP:Eu(oac) ₃ Bphen/TPBi	7	5
4	spin-coating	CBP:Eu(piv) ₃ Bphen/TPBi	8	1
5	spin-coating	CBP:Eu(acac) ₃ Bphen/TPBi	5	50
6	spin-coating	CBP:Eu(tta) ₃ Bphen/TPBi	5	105

^aAs U_{on} value the voltage, where EL detectable with the naked eye appeared, was considered.

Electroluminescence (EL) spectra for OLEDs **-9** to **-4** are reported in Fig. S 29, along with current-voltage curves. It turned out that pairs of complexes with the anionic ligands of the same nature: aromatic carboxylates (Fig. S 29a), aliphatic carboxylates (Fig. S 29b) and β -diketonates

(Fig. S 29c) – behave similarly in OLEDs. Aromatic carboxylate based diodes -9 and -8 demonstrated moderate electroluminescence (EL) intensity, EL of aliphatic carboxylate based diodes -7 and -6 was barely visible, while diodes -5 and -4 based on β -diketonates demonstrated the most intense EL with the luminance up to 8 cd/m². The I-V curves of all -9 to -4 devices (Fig. S 29d) are typical and differ in current density.

Dispersion of the [Eu(tta)₃Bphen] complex into CBP (diode **0**) resulted in an almost 3-fold improvement in luminance while replacement of the electron transport layer brought a decisive improvement, luminance being further enhanced almost 5-fold to reach 105 cd/m² (diode **6**). Therefore OLEDs were fabricated with this structure for all the remaining complexes (diodes **1**-**5**). The steep slope on the double-logarithmic scale varies from 11.6 (acac) and 9.4 (pfb) to 4.8 (tta) indicating strong trap-filling regime at 3-9 voltage for all the diodes. The regime probably goes to trap-free space-charge limited current at higher voltages but its overshadowed by starting degradation.



Fig. S 29 Electroluminescence spectra of a) **-9** and **-8**, b) **-7** and **-6**, c) **-5** and **-4** devices and d) I-V curves of **-9** to-4 devices (double-logarithmic scale).

The effect of the deposition method on OLED characteristics, i.e. vacuum thermal evaporation (VTE), which is important nowadays ^[29], *vs* spin-coating, was tested on heterostructures with $L = piv^{-}$, acac⁻, and tta⁻ (OLEDs -3 to -1, Table S 7). Diodes -2 and -1 based on the volatile complexes [Eu(L)₃Bphen] (L = acac⁻, tta⁻,) with the same heterostructures as of OLEDs -6 and -5, but in which emitter films were deposited by the VTE method, were manufactured to study the effect of the deposition method on the OLED characteristics. OLED -3 based on [Eu(piv)₃Bphen] was unstable due to its film inhomogeneity.



Fig. S 30 I-V curves of a) OLEDs -4 and -1, b) OLEDs -5 and -2.

The I-V curves of the OLEDs -4 and -1 almost coincide, which indicates the same thickness of the emission layer. The maximum brightness of diode -1 was 10 cd/m^2 at the same current values, which is due to the greater resistance to degradation of the film obtained from the gas phase. From these data, it seems that VTE is only slightly superior to spin coating.

In order to increase OLED performance, the next step was to test all complexes in composite films with CBP matrix, and $[Eu(tta)_3Bphen]$ complex was tested as emitter, which showed the best results in OLED. Two diodes **0** and **6** were made, where the complex is introduced into the CBP host, which differ in the material of the electron transport layer, OXD-7 and TPBi.



Fig. S 31 I-V and L-V curves of a) OLED 0 (ETL = OXD-7) and b) OLED 6 (ETL = TPBi)

The use of the CBP host in OLED **0** leads to an increase in the current density and luminance ($L_{max} = 23$ cd/m², Fig. S 31a) in comparison with OLEDs -4 and -1, where [Eu(tta)₃Bphen] was not introduced into the host, which may be related both with increasing hole mobility of the emissive layer (μ_h (CBP) = 2·10⁻³ cm²V⁻¹s⁻¹), as well as optimization of the energy structure of the diode. Substituting the OXD-7 material of the electron transport layer with TPBi (OLED 8) leads to an even greater increase in luminance up to 105 cd/m², while the current density value does not increase (Fig. S 31b). This indicates an increase in the efficiency of the diode: indeed, the current efficiency increases from CE_{max} = 0,029 cd/A in OLED **0** to CE_{max} = 0,129 Cd/A in OLED **6**. An increase in efficiency of 4.5 times can be explained by the fact that the electron mobility of TPBi is μ_e (TPBi) = 3-8·10⁻⁵ cm² V⁻¹s⁻¹, while μ_e (OXD-7) = 1-4·10⁻⁵ cm² V⁻¹s⁻¹ is several times smaller; at the same time, the emission layer has high hole mobility (μ_h (CBP) = 2·10⁻³ cm² V⁻¹s⁻¹, μ_h (Eu(tta)₃Bphen) = 7.3·10⁻⁴ cm² V⁻¹s⁻¹). Therefore, an increase in the electron mobility of the electron transport layer leads to balance of electron and hole currents, as a result of which the efficiency of electroluminescence increases.

OLEDs 1-6 were prepared with the same heterostructure and revealed the same tendency. First, the use of CBP host leads to the increase of brightness, and second, β -diketonate-based OLEDs 5-6 are clearly superior to carboxylate-based OLEDs 1-4. Normalized electroluminescence (EL) spectra of OLEDs 1-6 and photoluminescence spectra of corresponding Eu(L)₃Bphen are presented below.



Fig. S 32 Normalized electroluminescence (EL) spectra of OLEDs 1-6 and photoluminescence spectra of corresponding $Eu(L)_3Bphen: L = a)$ mfb, b) pfb, c) oac, d) piv, e) acac, f) tta.

7. OLED literature analysis

7.1 Identifying the major factor curbing the brightness of

[Eu(L)₃BPhen)]-based OLEDs

To identify the critical parameters affecting the OLED luminance of the studied europium compounds, as well as those that hamper the final OLED characteristics, all the main physicochemical characteristics of the complexes were included in the analysis: the morphology of the formed thin films, the energy of the boundary orbitals, the mobility of charge carriers, the quantum yield of photoluminescence, and the lifetime of the excited state (Main text, Table 1). Since some complexes are non-volatile, all the thin films within the OLEDs were spin-coated in order to ensure impartial comparison. Correlations are displayed in Fig. 4 (Main text).

The morphology, namely, the rms roughness of the thin films, is **not** a key parameter affecting the EL of the lanthanide complexes. So, it is approximately the same for all $[Eu(L)_3Bphen]$ complexes (1.1-1.4 nm) but the complex with tta⁻ differ substantially in OLED performances. Besides, it is of the same level as of well-performing materials: for instance, the. rms roughness of the emissive layer of the BPyThIr material ($L_{max} = ~59\ 000\ cd/m^2$, EQE = 28.5%) is 1.69 nm ^[30].

The boundary orbitals energy does not unambiguously correlate with the OLED luminance. For instance, the HOMO and LUMO energies of $[Eu(mfb)_3Bphen]$ and $[Eu(tta)_3Bphen]$ are the same (HOMO = 4.9 eV and LUMO = 2.3 eV), however, the luminance of OLEDs based on $[Eu(tta)_3Bphen]$ is much higher.

The charge carrier mobility of all complexes is different. Electron mobility is largest for $L = pfb^-$, oac⁻, and piv⁻, while the value for acac⁻ is only slightly smaller but it is the smallest for mfb⁻ and tta⁻. On the other hand, hole mobility is the largest for tta⁻, 14 and 23 times less for oac⁻ and acac⁻, respectively, while it is hundred of times less for the other emitting layers. However, we think that the charge carrier mobility is definitely **not** the decisive factor curbing the luminance, since, e.g. [Eu(oac)₃Bphen] demonstrates higher mobility of both electrons (5-fold) and holes (1.6-fold) than [Eu(acac)₃Bphen], but the luminance of the corresponding OLED is significantly

smaller (10-fold!). Moreover, the obtained hole mobility values of β -diketonate complexes are high even in comparison with other classes of OLED emitters, *e.g.* the hole mobility of the well-known FIrpic phosphorescent emitter is on the order of 10⁻⁶ cm²/V⁻¹s⁻¹ [31].

The photoluminescence quantum yield, which characterizes the efficiency of radiative relaxation, is directly proportional to the luminance within the same class of complexes, and it definitely affects the final OLED performance. However, this analysis makes it clear that PLQY is also **not** the decisive factor limiting lanthanide materials in comparison with compounds of other classes: e.g., PLQY of aromatic carboxylates is very high, reaches 90% and exceeds PLQY of [Eu(acac)₃Bphen], while the luminance of OLEDs based on mixed-ligand aromatic carboxylates in several times less.

7.2 Hypothesis verification

It should be noted that the direct analysis of the literature data is impossible due to several obvious reasons:

- 1. All the initially listed parameters affect the final brightness of the device;
- The obtained characteristics were measured under different experimental conditions, i.e. different OLED heterostructures, emitter film thickness, etc.;
- Bad results, i.e. low brightnesses, are not given quantitatively or not commented at all, which significantly hampers the analysis;
- OLED performance strongly depends on the quality of the fabrication conditions (cleanroom class, oxygen/water concentration, etc.), access to which is different by different research groups;
- 5. For the majority of compounds important data are missing, i.e. almost nobody characterize morphology, mobility, and even boundary orbital energy are rarely presented;
- 6. The photophysical properties, including lifetime, are usually also missing: if given, they are usually taken from other papers or measured by us for the sake of this work;

 Different lanthanide ions possess different properties, i.e. host selection is practically impossible for terbium complexes ^[32], etc.

N⁰	Emitter	Lifetime, µs	PLQY, %	LUMO, eV	HOMO, eV	rms roughness of EML, nm	OLED heterostructure	L _{max} , cd/m ²	depo sitio n	ref			
	β-DIKETONATES												
1	Eu(TTA) ₃						ITO/PMPS:Eu1/PBD/Mg:Ag	0.1	V	[33]			
2		350					ITO/TPD/Eu2:CBP(1%)/BCP/A1 q3/Mg:Ag	505	V	[34]			
3	Eu(TTA) ₃ phen	(2%CBP) [34]					ITO/PVK:PBD:Eu2/Ca/Al	30 at 20V	S	[36]			
4		139.1						137	V	[37]			
5	Eu(tta) ₃ SFXPO	1180 in cyclohexane	55 cyclo- hexane				ITO/PEDOT:PSS/PVK/CBP:PBD :Eu24/TPBi/LiF/Al	620	S	[38]			
6	Eu(nta) ₃ SFXPO	1120 in cyclohexane	60 cyclo- hexane				ITO/PEDOT:PSS/PVK/CBP:PBD :Eu26/TPBi/LiF/Al	430	S	[38]			
7	EuZnL(tta) ₂ (m-tfa)	1140	42	3.4	5.8		ITO/TPD/ Eu40 :CBP 10% /TPBI/LiF/A1	1982	V	[39]			
8	Eu ₂ (tta) ₆ (BuOXDTPA- Phen ₂)	n.a.	11.5 Solution	2.6	6.1		ITO/PEDOT:PSS/PVK:PBD:EuP P/LiF/A1	296 at 8.5V	S	[40]			
9	Eu(tta) ₃ (TNADAPO) ₂	n.a.	36.1	3	5.3		ITO/NPB/ Eu16 /BCP/Alq ₃ /Mg:A g	1158 at 18V	V	[41]			
0	Eu(TTA) ₃ (DPEPO)	n.a.	55.3 in CH ₂ Cl ₂				ITO/NPB/CBP:Eu- 19/BCP/Alq3/LiF/Al	632 at 25 V	V	[42]			
1							ITO/TPD/1%Eu:CBP/BCP/AlQ/ LiF/Al	800 at 24 V	V	[43]			
1 a	$Eu(11A)_3(1mPnen)$						ITO/TPD/1% Eu :CBP:FIrPic/BCP /AlQ/LiF/Al	1156 at 23.9 V	V	[44]			
2	Eu(TTA) ₃ Dppz	80 ë	5% ë		4.5 ^ë		ITO/NPB/CBP:Eu1/BCP/Alq3/M g:Ag	2046	V	[7]			

Table S 8 Comparison of some Eu-based OLED emitters.

							continueu			
13	Eu(DPDBM) ₃ DPPZ	30 μs (10%CBP)	36				ITO/m-MTDATA/NPB/ CBP: Eu64 /Bphen/Ala3/LiF/Al	2910	V	[45]
14		130	70				ITO/TPD/Eu54:PBD/Alq3/Mg:A	460	V	[46]
14 a	Eu(DBM) ₃ Phen	(10%CBP) ^[45]					ITO/MoO3/mCP/mCP:PO-T2T: Eu54/PO-T2T/LiF/A1	330	V	[47]
15	Eu(DBM) ₃ Bphen	440					ITO/TPD/Eu67/TAZ/LiF/A1	380	V	[48]
16	Eu(DBM) ₃ Bphen	420 (TPD 1:2)					ITO/TPD/TPD:Eu67/Eu67/TAZ/ LiF/Al	1000	V	[48]
17	Eu(dbm) ₃ DPPZ		27.1% (sol)	2.7	5.6	0.739	ITO/PEDOT:PSS/PVK/PFO:PBD :Eu-68/Ba/Al	1381	V	[49]
18	Eu(DBM) ₃ (DFPP)						ITO/TPD/Eu- 79:CBP:DCJTB/BCP/Alq3/LiF/A l	1200	V	[50]
19	Eu(DBM) ₃ EPBM						ITO/TPD/Eu-85/Alq3/Al	180	V	[51]
20	Eu(dbm) ₃ (BuOXD- Phen)		11.3 In DCM				ITO/PEDOT:PSS/PVK/PFO:PBD :EuP/Ba/Al	568 at 15V	S	[52]
21	Eu(DPM) ₃	49 [53]					ITO/TAPC/Eu- 91:BCP/BCP/Alq3/Mg:Ag/Ag	2123	V	[54]
22	[Eu(hfaa) ₃ (indazole) ₃]	997 (solid)	67 (CHCl ₃) 69 (solid)	2.9	5.7		ITO/CuPc/ Eu- 92:CBP/BCP/Alq3/LiF/Al	1750	V	[55]
23	NBu4[EuL4]	469	45%				ITO/PEDOT:PSS/CBP:OXD- 7:Eu-94/LiF/Al	1547 Exiplex EL	V	[56]
24	NBu4[EuL4]	780	80 (solid) 85 (5% PMMA film)	2.5	5.6		ITO/PEDOT:PSS/CBP:OXD- 7: Eu-95 /BCP/LiF/A1	1234	V	[57]
25	Eu(L1) ₃ (TPPO)(H ₂ O)	33.7	10%				ITO/NPB/CBP:Eu- 88/BCP/Alq3/Mg:Ag	247	V	[58]

Table S 8 Continued

							Johnmada			
				C	ARBOXYL	ATES				
26	Eu(BSA) ₃ phen						ITO/PVK:Eu97/LiF/Al	55	S	[59]
27	Eu(o-BBA) ₃ (phen)						ITO/PVK:Eu96/Al	n.a.	S	[60]
28	Eu(tfb) ₃ (BPhen) ₂	1610	45			0.9	ITO/PEDOT:PSS/PVK/Eu(tfb)3: 10Bphen/Bphen/Al	1	S	[4]
29	Eu(1) ₃ (Phen)	1450	90				ITO/PEDOT:PSS/PVK/Eu/TPBi/ Al	<1	S	[61]
30	Eu(2) ₃ (Phen)	1500	82				ITO/PEDOT:PSS/PVK/Eu/TPBi/ Al	<1	S	[61]
31	Eu(1) ₃ (BPhen)	1310	66				ITO/PEDOT:PSS/PVK/Eu/TPBi/ Al	10 at 15 V	S	[61]
32	Eu(2) ₃ (BPhen)	1400	70				ITO/PEDOT:PSS/PVK/Eu/TPBi/ Al	25 at 12V	S	[61]
33	Eu(pfb) ₃ (BPhen)	1000	80	1.7	5.2		ITO/PEDOT:PSS/poly-TPD/CBP (60 wt%):OXD-7 (30 wt%):Eu(pfb)3(BPhen) (10 wt%)/OXD-7/LiF/Al	9 at 17V	S	[5]
34	Eu(btz) ₃ Bphen	600	10	3.0	7.3		ITO/PEDOT:PSS/poly- TPD/Eu/TPBi/Al	<1	S	[62]
35	[Eu(EO ₃)(NO ₃)(Pic) (OH ₂) ₂] ⁺ (Pic) ⁻ (H ₂ O)						n/a	No light	S	[63]

Table S 8 Continued



Fig. S 33 Maximum luminance (cd m⁻²) versus inverse lifetime $(10^3 \times \mu s^{-1})$ for Eu-based OLEDs listed in Table 2.

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