ELECTRONIC SUPPLEMENTARY INFORMATION

Terbium-based OLED luminance increase by 50% through reducing the excited state lifetime due to the introduction of gold nanoparticles

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1. Experimental Section

The synthesis of TDZP

The ligand [1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline (TDZP) was prepared using a straightforward and efficient methodology in four steps from phenanthroline.

The synthesis of Tb(czb)₃TDZP

The multi-ligand terbium complex was synthesized according to the reaction equations (2):

 $Tb(NO_3)_3TDZP + 3(NEt_3H)czb + TDZP = 3(NEt_3H)NO_3 + Tb(czb)_3TDZP \downarrow$ (2)

A solution of 0.4 mmol (NEt₃H)czb in 15 ml of ethanol was added to 0,13 mmol of Tb(czb)₃TDZP in 15 ml of ethanol. The precipitate was centrifuged and dried in the air.

The synthesis of gold nanoparticles

Gold nanoparticles were synthesized by the Frens method (3):

 $C_6H_5O_7Na_3 + HAuCl_4 = GNP$ (gold nanoparticles) + citrate oxidation products (3) Hydrogen tetrachloraurate HAuCl_4·3.5H_2O was dissolved in 25 ml of distilled water. The molar concentration of HAuCl_4 was 1*10⁻⁴ M. A solution of sodium citrate $C_6H_5O_7Na_3\cdot5.5H_2O$ (0.4 M) in 2.5 ml of distilled water was also obtained. Both solutions were brought to a boil at a temperature of 100 ° C for 10-15 minutes. After that, 0.25 ml from a solution with sodium citrate was added to a solution of hydrogen tetrachloraurate. Following 5 minutes, the resulting solution acquired a blue colour, 10 minutes after that, the solution acquired a wine-red colour, which indicates the formation of a colloidal solution of gold nanoparticles.

All reagents, solvents, host materials and layers of the OLED heterostructure were purchased from commercial sources. The following reagents were used as starting reagents for the synthesis of complexes: $Tb(NO_3)_3 \cdot 6H_2O$ (99.9%, Sigma Aldrich); triethylamine NEt₃ (p.), 4- (diphenylamino)benzoic acid Hczb (synthesized by PhD in Chemistry Medvedko), TDZP (synthesized by PhD in Chemistry Medvedko). The following solvents were used: ethanol (EtOH, 95%, p.), tetrahydrofuran (THF, 99.9%, Sigma Aldrich), chlorobenzene (C₆H₅Cl, chem.p.), DMSO-d⁶ (>99.98%, Euriso-top). OLED heterostructure layers were used as materials: glass substrate with ITO (25×25×0.7 mm, 15 ohms/sq. meter), PEDOT:PSS (1:6, H₂O, 2.6%, Lumtec), poly-TPD (Ossila), TPBi (99.5%, Lumtec), LiF (99.99%, Lumtec), Al (p., 99.98%).

Powder X-ray diffraction (PXRD) was performed by using Bruker D8 Advance $[\lambda(Cu-K\alpha) = 1.5418$ Å; Ni filter, Bragg-Brentano geometry] with a step size of 0.020°. The pattern was indexed by using SVD-Index [2] as implemented in the TOPAS 5 software [3]. Then, the powder pattern was refined using the Pawley method.

Thermal analysis was carried out on a thermoanalyzer STA 409 PC Luxx (NETZSCH, Germany) in the temperature range of 20–1000 °C in air and at a heating rate of 10° min⁻¹. The evolved gases were simultaneously monitored during the TA experiment using a coupled QMS 403C Aeolos

quadrupole mass spectrometer (NETZSCH, Germany). The mass spectra were registered for the species with the following m/z values: 18 (corresponding to H_2O), 44 (corresponding to CO_2).

IR spectra in the ATR mode were recorded on a spectrometer FTIR Nikolet iS50 in the region of 500–4000 cm⁻¹.

¹H NMR spectra were recorded from the DMSO-d₆ solutions with a Bruker Avance 600 NMR spectrometer.

Dynamic light scattering measurements were carried out using the Malvern Zetasizer Nanodevice equipped with a 10 MW HeNe-laser with a wavelength of 632.8 nm with a backscattering configuration at a temperature of 25.0 ± 0.2 °C.

Absorption spectra of colloidal solutions were obtained using a Perkin-Elmer Lambda 35 UV/vis Spectrometer (Perkin Elmer) scanning spectrophotometer.

TEM (transmission electron microscopy) analysis was performed using Libra 200 MC TEM (Zeiss, Germany). The capture of microphotographs of TEM was performed on a CCD camera (Gatan, USA) with a matrix size of 4096×4096 pixels.

Emission and excitation spectra of thin films were recorded using a FluoroMax Plus spectrophotometer upon excitation with a xenon lamp. Luminescence lifetime measurements were recorded and detected on the same system. All luminescence decays proved to be perfect single-exponential functions. Photoluminescence quantum yields in the visible range were determined with the FluoroMax Plus spectrophotometer at room temperature upon excitation into ligand states according to an absolute method using an integration sphere. The modified de Mello *et al.* [2] method requires the measurement of L_a , the integrated intensity of light exiting the sphere when the empty cuvette is illuminated at the excitation wavelength (Rayleigh scattering band); L_c , the same integrated intensity at the excitation wavelength when the sample is introduced into the sphere; E_a the integrated intensity of the entire emission spectrum of the empty cuvette; and E_c the integrated intensity of the entire emission spectrum of the sample. The absolute quantum yield is then given by:

$$PLQY = \frac{E_c - E_a}{L_a - L_c} \times 100\%$$

The determination of the **photoluminescence quantum yield** for powders and films was carried out by an absolute method using the integrating sphere PTI KSPHERE-Petite on a FluoroMax Plus spectrofluorimeter.

OLED manufacturing was carried out in an ISO8 class clean room (P.N. Lebedev Physics Institute, Moscow, Russia) in an argon chamber. The substrates were cleaned by ultrasound in the following media: aqueous solution of NaOH (30 min), distilled water (10 min), propanol-2 (10 min) and then dried under current N₂. A 50 nm thick PEDOT:PSS hole-injecting layer was applied from an aqueous solution (PEDOT:PSS + 10% H₂O) to an ITO substrate, after which the substrate was rotated for 1 minute at a speed of 2000 rpm. For OLEDs with gold nanoparticles a 50 nm thick PEDOT:PSS holeinjecting layer was applied from an aqueous solution with GNP (PEDOT:PSS + 10% GNP in H₂O) to an ITO substrate, after which the substrate was rotated for 1 minute at a speed of 2000 rpm. The deposited film was annealed in air at 120°C for 20 min. The poly-TPD hole-transport layer was applied from a solution in chlorobenzene (c = 5 g/l) at a speed of 2000 rpm for one minute, after which the film was annealed in an argon chamber at 100°C for 20 minutes. The emission layer Tb(czb)₃TDZP was applied from a solution in tetrahydrofuran (c = 5 g/l) at a speed of 1500 rpm for one minute, after which the film was annealed at 80°C for 10 minutes. The electron transport layer (TPBi), electron injection layer (LiF) and cathode (Al) were thermally sprayed (Univex-300 LeybordHeraeus) at a pressure below 10⁻⁵ mmHg. The thickness (20 nm, 1 nm and 150 nm, respectively) was controlled by a quartz indicator.

The electroluminescence spectra were taken using the Ocean Optics Maya 2000 Pro CCD spectrometer, sensitive in the range of 200-1100 nm. Volt-ampere curves were measured using two digital multimeters DT 838. The brightness of light-emitting diodes was measured using a luxmeter TKA-PCM.

2. ¹H-NMR spectra

¹H-NMR spectra of TDZP were obtained in DMSO-d₆ (Fig. S1).





Fig. S1. ¹H-NMR spectra of TDZP, Tb(NO₃)₃TDZP, Tb(czb)₃, Tb(czb)₃TDZP.

3. Photoluminescence spectra

In order to determine the triplet state energy of TDZP, the GdCl₃TDZP complex was synthesized. The phosphorescence spectra of this gadolinium complex were measured, and the maximum was

estimated (**Fig. S2**). The triplet energy of TDZP ligand was calculated ($T_1(TDZP) = 23000 \text{ cm}^{-1}$), which is quite close to the terbium energy of resonance level ($E({}^{5}D_{4}) = 20660 \text{ cm}^{-1}$).



Fig. S2. Normalized to [0;100] photoluminescence spectra of GdCl₃TDZP at 300 K and 77 K.

Excitation spectra and photoluminescence spectra were measured for the obtained thin film of Tb(czb)₃TDZP. In the excitation spectra, the maximum of the excitation band was at 335 nm (**Fig. S3a**). The photoluminescence spectrum is a set of four typical narrow emission bands of the terbium ion (**Fig. S3b**).



Fig. S3. a) Excitation spectra ($\lambda em = 545 \text{ nm}$), b) photoluminescence spectra of Tb(czb)₃TDZP thin film ($\lambda ex = 335 \text{ nm}$).

Tb(czb)₃TDZP lifetime of the excited state was 0,49 ms in the luminescence decay curve (Fig. S4).



Fig. S4. Luminescence decay curve of Tb(czb)₃TDZP thin film (λ em = 545 nm, λ ex = 335 nm).

4. Electroluminescent properties

J-V and L-V curves were also measured at backwards bias for OLED based on Tb(czb)₃TDZP without and with GNP (**Fig. S5**).



Fig. S5. L-I-V curves of excited state of OLEDs of Tb(czb)₃TDZP without and with GNP.

The electroluminescence spectra were measured at different turn-on voltages for OLED based on Tb(czb)₃TDZP without and with GNP (**Fig. S6**).



Fig. S6. Electroluminescence spectra of OLEDs of Tb(czb)₃TDZP a) without and b) with GNP.

Tb(czb)₃-based OLED demonstrated typical terbium electroluminescence spectra (**Fig. S7**). J-V and L-V curves were also measured for OLED based on Tb(czb)₃ without and with GNP (**Fig. S7b, c**) and luminescence decay curves of OLEDs. After the introduction of GNP, the lifetime of the excited state decreased by 0.02 ms (from 0.29 ms to 0.27 ms) (**Fig. S7d**).



Fig. S7. a) Electroluminescence spectra at U=3,5 V, maximum electroluminescence wavelength is 545 nm, b) J-V curves, c) L-V curves, and d) luminescence decay curves of OLEDs at (λem = 545 nm, λex = 335 nm).