



# Managing the luminescence efficiency of the organic compounds of Europium(III) through the obtaining technology



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A series of coordination organic compounds based on the trivalent  $Eu^{3+}$  ion were synthesized and optimized:  $Eu(o-MBA)_3phen$ ,  $Eu(DBM)_3(Ph_3PO)_1 \cdot H_2O$  and  $Eu(TTA)_3(Ph_3PO)_2$ . The efficiency of the photoluminescence (PL) emission of these coordination compounds depend on preparation technology, specifically on the optimal choice of the ligands. The photoluminescence spectrum measured in the range 500 – 750 nm exhibits a number of narrow (atomic-like) emission bands with the FWHM less than 10 nm. These PL emission bands are attributed to optical transitions in the  $4f$  orbital of the ion. PL experimental results were analyzed in the framework of Judd-Ofelt theory and the characteristic luminescence parameters were obtained: PL lifetime constant, quantum yield,  $\Omega$  coefficient, the probability for electric dipole transitions, etc.

The rare earth-energy energy cover  $4f$  is a stable heat shield that is protected by  $5s$  and  $5p$  levels with spherical symmetry where no direct electron energy transfer takes place. According to Laporte's rule, electronic transitions in the  $4f$  electronic shell of the  $Eu$  element are forbidden. To solve this problem we have synthesized on the base of  $Eu^{3+}$  the coordination compounds with different ligands, which are deformed the energy states of the ion and in such way favoring energy transitions in  $4f$  shell. As ligands were elected: tris(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion) (TTA)3, tris(*o*-methylbenzoic acid) (*o*-MBA)3, tris(1,3-diphenylpropane-1,3-dione)(DBM)3, bis(triphenyl- $\lambda$ -phosphanone)(( $Ph_3PO$ )2), 1,10-phenanthroline (*Phen*). Coordinating compounds (CCEu)  $Eu(o-MBA)_3Phen$ ,  $(Eu(DBM)_3(Ph_3PO)H_2O)$  and  $Eu(TTA)_3(Ph_3PO)_2$  were synthesized. The maximal number of ligands for coordination with  $Eu^{3+}$  ion is 12.

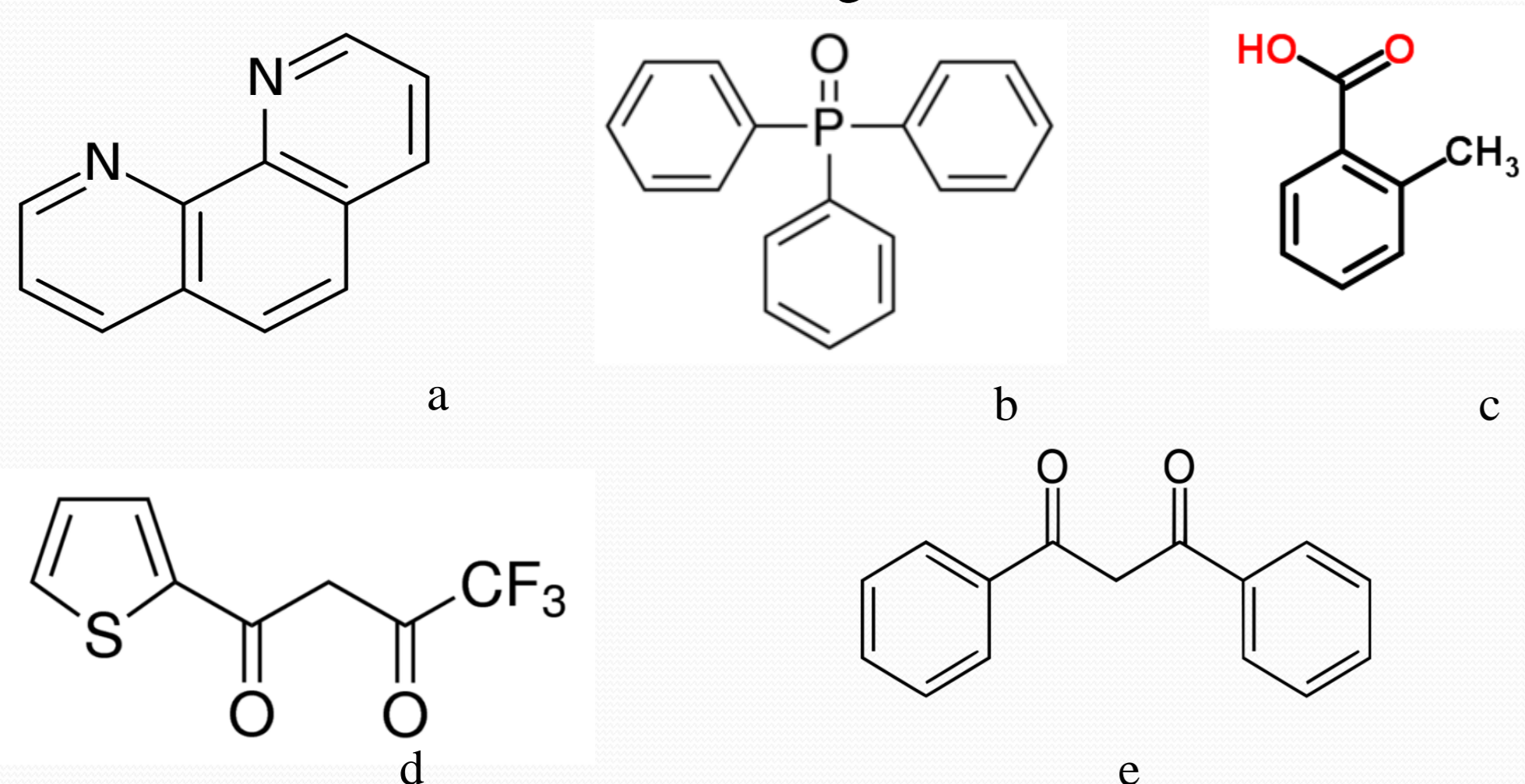


Fig. 1. Illustration of chemical structure of the ligands used in preparation of organic rare-earth coordination compounds: a) Phen; b) ( $Ph_3PO$ )<sub>2</sub>; c) *o*-MBA; d) TTA; e) DBM.

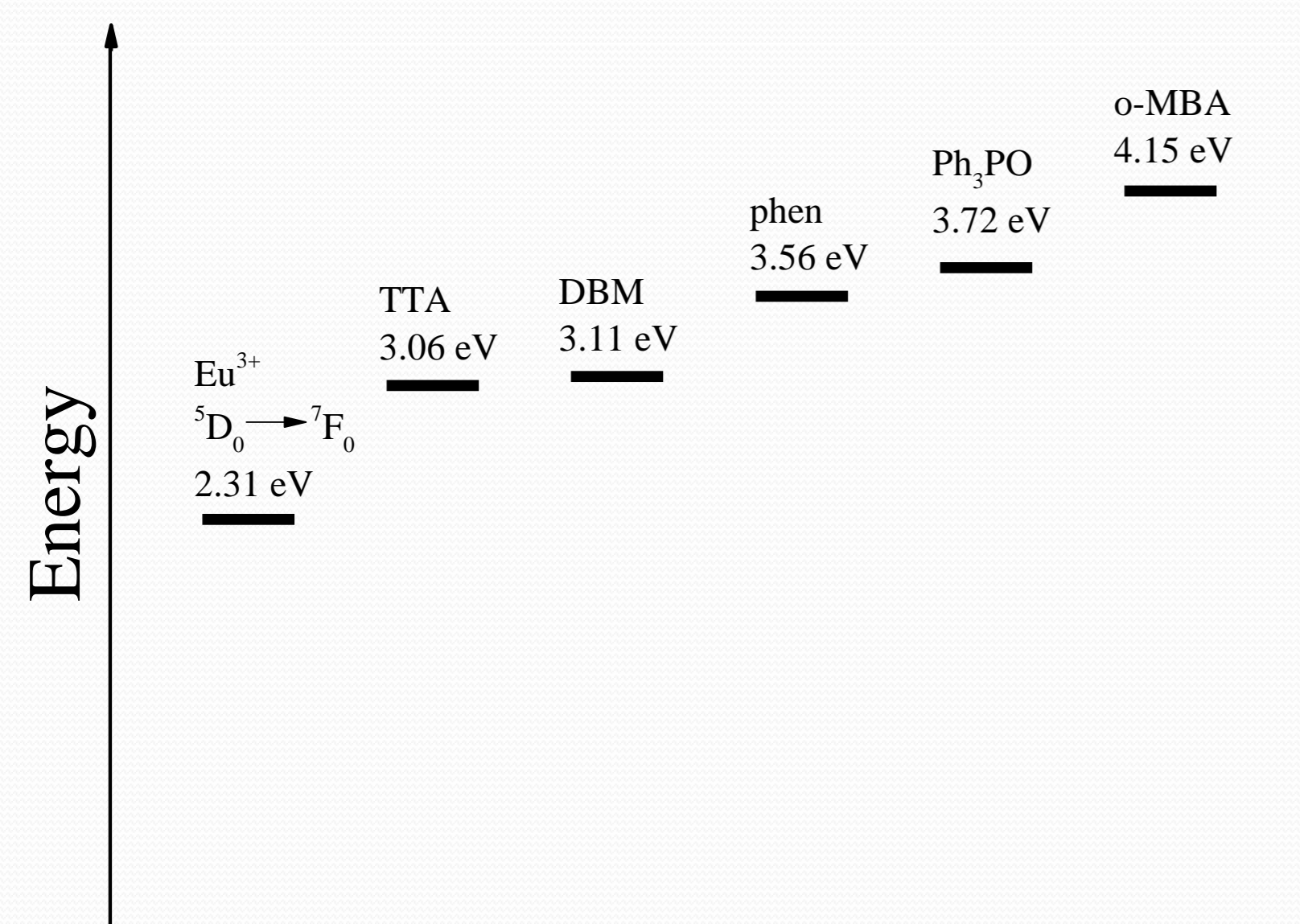


Fig. 2. Energy levels of ligands, determined for their use in the synthesis of coordination compounds.

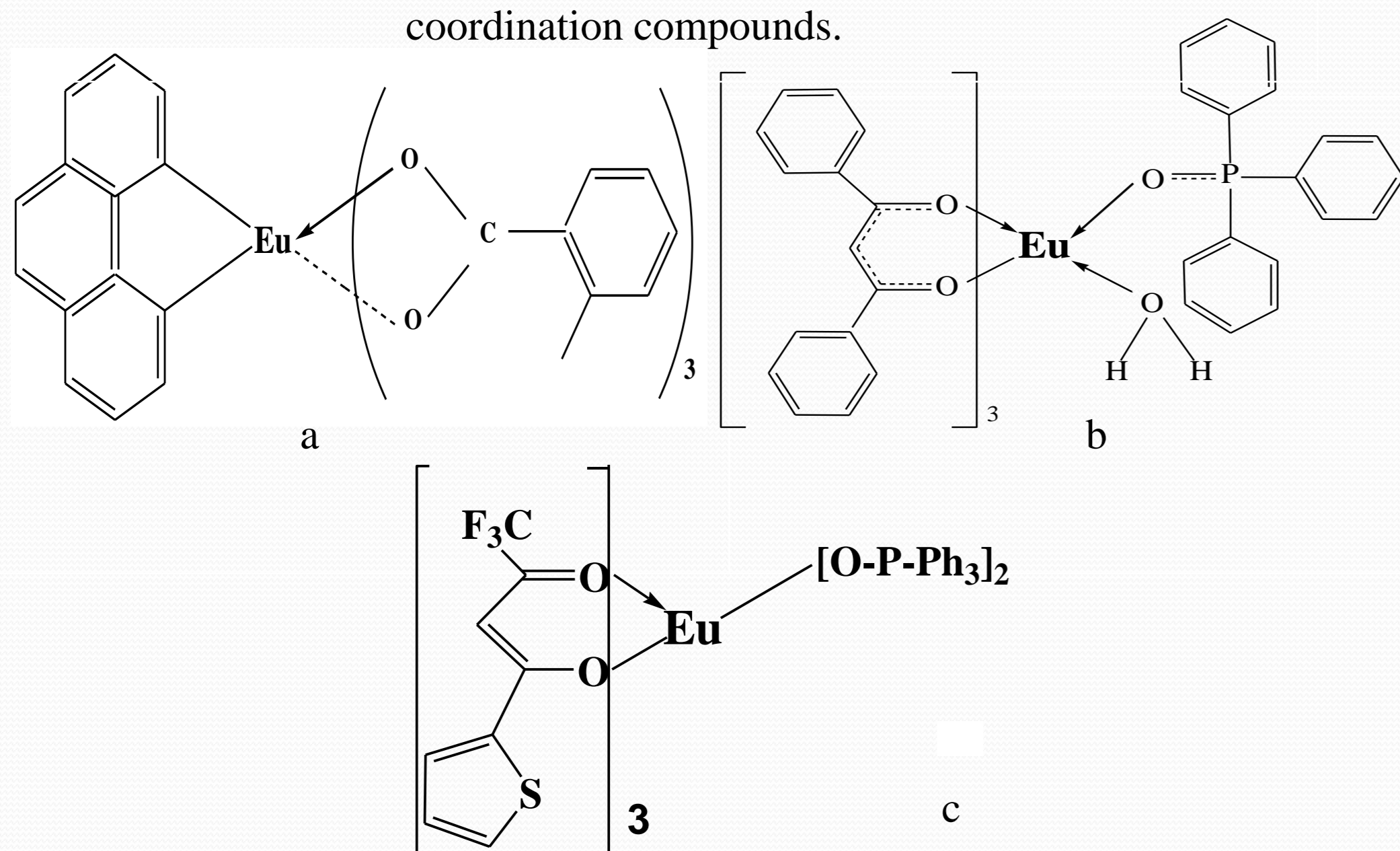


Fig. 3. Illustration of molecular structure of the compounds  $Eu(o-MBA)_3Phen$  (a),  $Eu(DBM)_3(Ph_3PO)_1 \cdot H_2O$  (b) and  $Eu(TTA)_3(Ph_3PO)_2$  (c).

## References

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## Experimental methods

Powder samples were characterized by PL spectroscopy. Photoluminescence emission spectra were recorded using different excitation sources with a MDR-23 single emission monochromator. A pulsed *nitrogen* laser at 337 nm with repetition rate 10-100 Hz and the pulse width 10 ns was used for excitation of  $Eu^{3+}$  ions in the charge transfer band. Another excitation light source was a Thorlabs LD at 405 nm. PL signal was detected in a photon counting mode with a Hamamatsu module H8259-01 with a counting unit C8855-01 connected to a PC. The spectral resolution for PL measurements was as low as 0.125 nm. For both the PL spectra and the quantum yield measurements the emission spectra were corrected for the instrument spectral sensitivity. The luminescence time decay was recorded using a *nitrogen* pulsed laser as a light source at the repetition rate 10 Hz. The PMT module H8259-01 with the pulse-counter C8855-01 provides time-resolved measurements with the resolution 50  $\mu$ s, which is sufficient for registration of PL relaxation in the range 50  $\mu$ s – 10 ms.

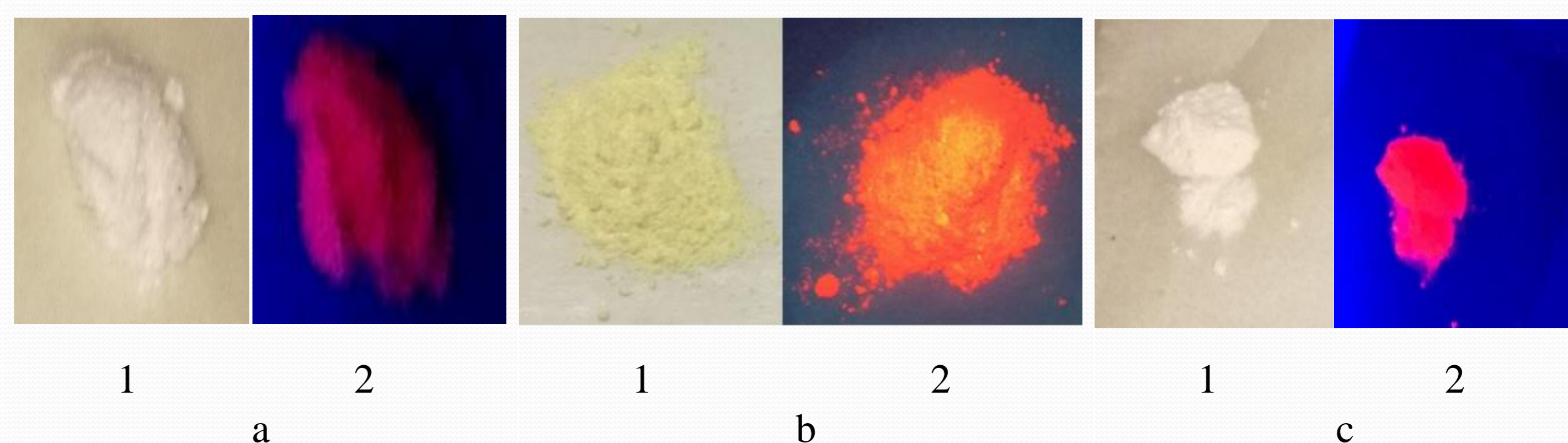


Figure 4. The images of the OCC  $Eu(o-MBA)_3Phen$  (a),  $Eu(DBM)_3(Ph_3PO)_1 \cdot H_2O$  (b) and  $Eu(TTA)_3(Ph_3PO)_2$  (c) powder samples: samples irradiated with white light(1) and irradiated with UV light(2).

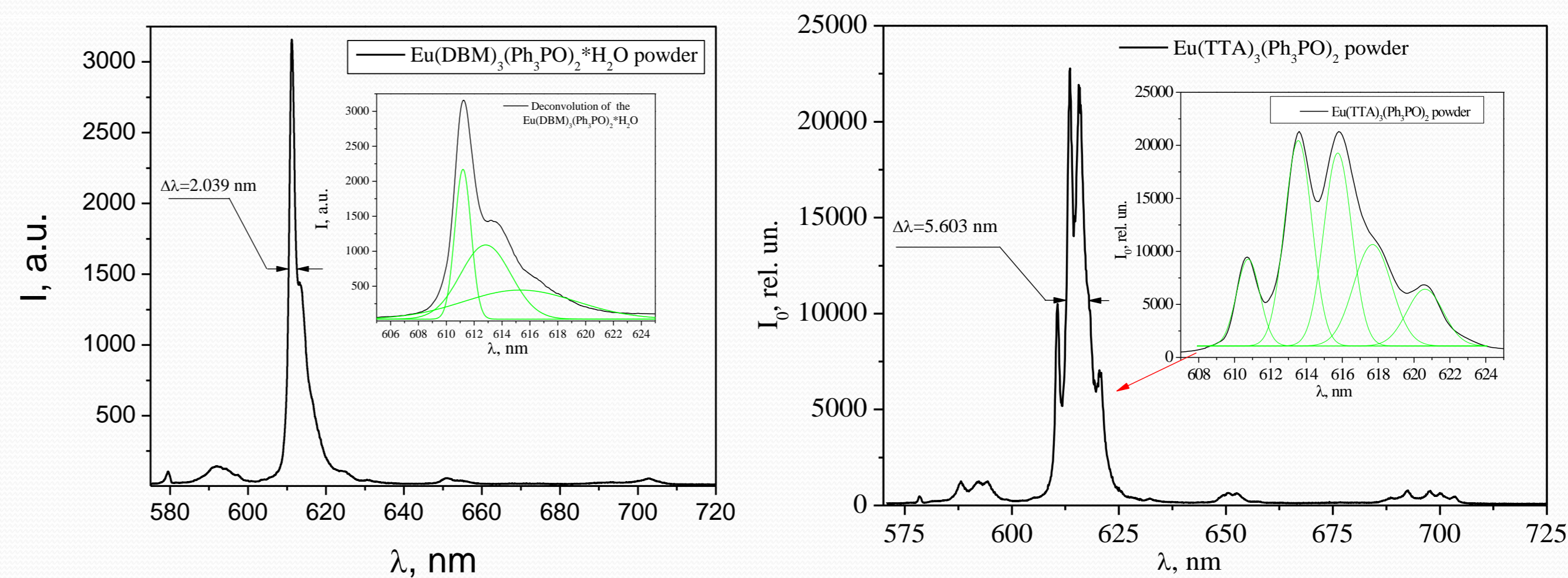


Fig. 5. Photoluminescence spectra of synthesized organic compounds (2) and (3). The full width at half maximum (FWHM) of the compounds were determined from the PL spectra. The excitation light source was a laser diode 405 nm.

$$\text{The Judd-Ofelt parameters were estimated: } \Omega_{0 \rightarrow j} = \frac{4e^2 \bar{\lambda}_{0 \rightarrow j}^3 A_{0 \rightarrow j}}{3hc^3 \chi \left\langle \left\langle {}^7F_j \left\| U^{(\lambda)} \right\| {}^5D_0 \right\rangle \right\rangle^2}$$

Table 1. Photoluminescence parameters for synthesized coordination compounds with  $Eu^{3+}$  ions.

Coordination compound	$E_g$ , eV	$\Delta\lambda$ , nm	$\tau$ , ms	$\eta$ , %	$A_p$ , s <sup>-1</sup>	$\Omega_2$ , cm <sup>2</sup>	$\Omega_4$ , cm <sup>2</sup>
$Eu(o-MBA)_3Phen$ (1)	3.40	9.45	1.09	28.23	400.71	$8.19 \times 10^{-20}$	$2.58 \times 10^{-20}$
$Eu(DBM)_3(Ph_3PO)_1 \cdot H_2O$ (2)	2.85	2.04	0.42	20.69	827.26	$1.91 \times 10^{-19}$	$2.22 \times 10^{-20}$
$Eu(TTA)_3(Ph_3PO)_2$ (3)	3.10	5.60	0.49	53.46	1165.58	$2.85 \times 10^{-19}$	$2.22 \times 10^{-20}$