



Photoluminescence Properties of New Dinuclear [Eu(μ_2 -OC₂H₅)(btfa)(NO₃)(phen)]₂phen and Mononuclear Eu(TTA)₃(Ph₃PO)₂ Complexes

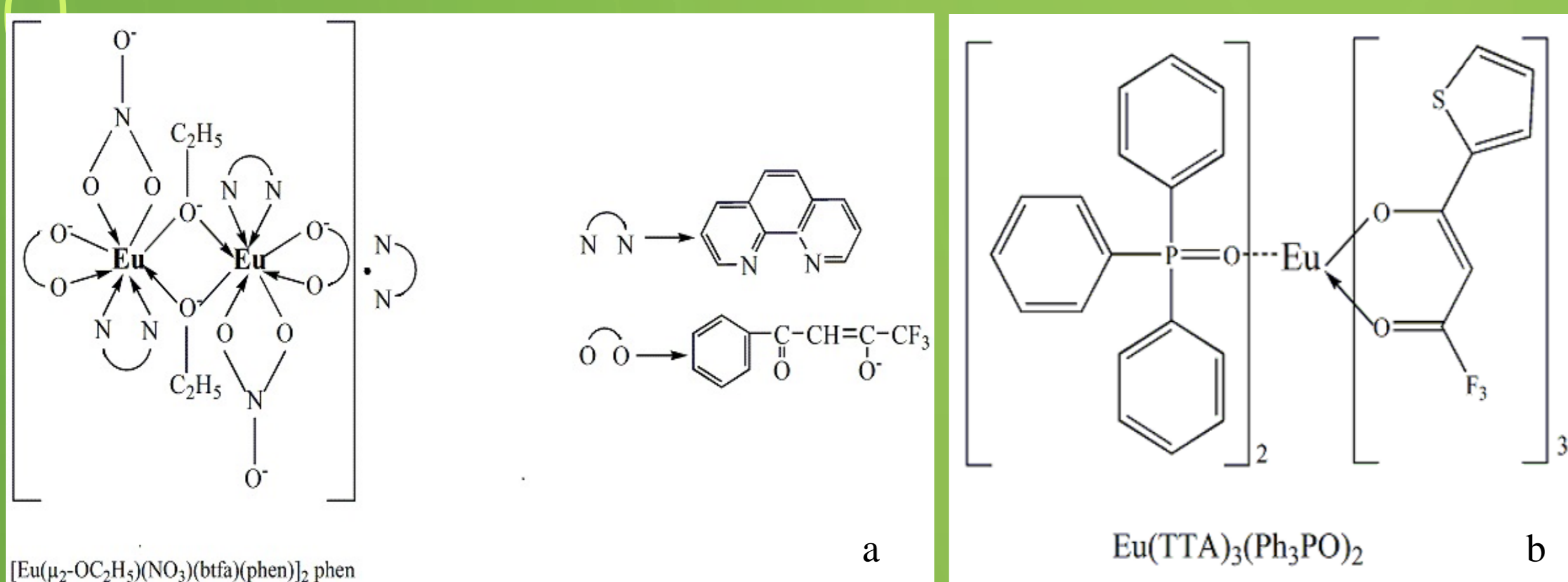
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A new dinuclear complex Europium(III) bis[(μ_2 -ethoxy)(benzoyl trifluoroacetato)(nitrate) (1,10-phenanthroline) europium(III)]₂ 1,10-phenanthroline, hereafter [Eu(μ_2 -OC₂H₅)(btfa)(NO₃)(phen)]₂phen and the mononuclear complex Eu(TTA)₃(Ph₃PO)₂ were synthesized and characterized by photoluminescence (PL) spectroscopy. The PL emission spectra of the powder samples of the compounds were recorded in the temperature range 10.7 – 300 K. Both complexes show rare metal-centered luminescence in the energy range characteristic of the Eu³⁺ ion (580 - 710 nm) with emission bands according to ion selection rule. The emission bands in the PL are attributed to the internal 4f → 4f radiative transitions of the Eu³⁺ ion ⁵D₀ → ⁷F_i (i = 0 → 4) and, in addition, to the splitting of each level caused by the influence of the electric field of the ligands of the complex. Due to the splittings, each level is divided into 2i+1 sublevels, which are well observed in the mononuclear compound Eu(TTA)₃(Ph₃PO)₂ centered at 580, 595, 615, 650, and 698 nm. However, in the PL spectrum of the dinuclear compound, the splits show a double number of splits (2(2i + 1)), which indicates the presence of two positions of the Eu³⁺ ion in the molecule and which are not optically equivalent.

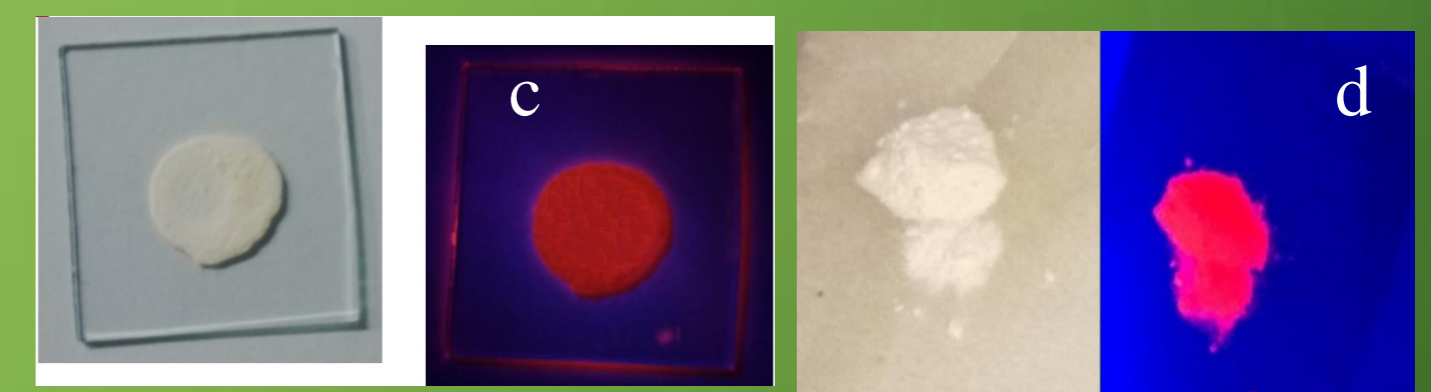
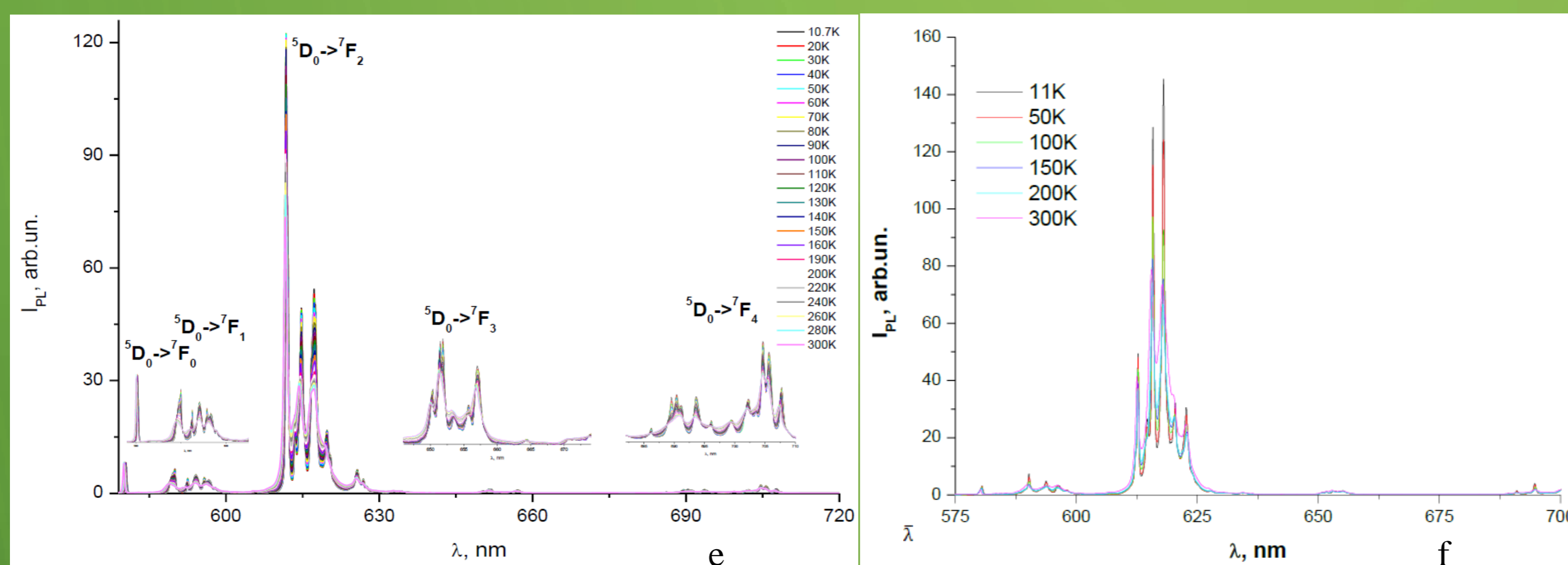


The chemical structure formula: a) Dinuclear [Eu(μ_2 -OC₂H₅)(btfa)(NO₃)(phen)]₂phen Complexes; b) Mononuclear Eu(TTA)₃(Ph₃PO)₂ Complexes.

The coordination compounds presented in this work were synthesized in the Coordination Chemistry Laboratory of the Institute of Chemistry, Chisinau.

All chemicals were purchased from Aldrich Chemical Company.

The complex [Eu(μ_2 -OC₂H₅)(btfa)(NO₃)(phen)]₂phen (c) has been characterized by IR attenuated total reflectance (IR ATR) and PL spectroscopy. Under UV excitation the complex exhibits a bright red luminescence with the dominant emission band around 612 nm.



Photoluminescence spectra of the powder samples of the complexes [Eu(μ_2 -OC₂H₅)(btfa)(NO₃)(phen)]₂phen (e), Eu(TTA)₃(Ph₃PO)₂ (f) and dependenta intensității integrale a fiecărei tranziții de temperatură în intervalul 10.7 – 300 K. $\lambda_{exc} = 405$ nm, step = 0,125 nm, slit = 0,055 mm, Hamamatsu 9319.

The PL decay profile registered under N₂ laser pulsed excitation can be fitted by two-exponential function for compound [Eu(μ_2 -OC₂H₅)(NO₃)(phen)]₂phen and the average lifetime was calculated to be 1.07 ms and one-exponential function for compound Eu(TTA)₃(Ph₃PO)₂ with lifetime 0.80 ms. The absolute quantum yield and the ligand sensitization efficiency of compound [Eu(μ_2 -OC₂H₅)(NO₃)(phen)]₂phen were determined to be 49.2% and 78.7% respectively and 37%, and the ligand sensitization efficiency $\eta = 53,49\%$ for compound 2. From the analysis of the experimental data of PL spectra and decay the luminescence parameters of the studied compound were determined: barycenter of each emission level, probabilities of transition, luminescence parameter Ω , efficiency η , etc.

The parameters of photoluminescence transitions ⁵D₀ → ⁷F_i (i = 0, 1, 2, 3, 4) for Eu³⁺ based coordination mononuclear compounds [Eu(μ_2 -OC₂H₅)(NO₃)(phen)]₂phen $\lambda_{exc} = 405$ nm (powder).

T = 10.7 K	⁵ D ₀ → ⁷ F ₀	⁵ D ₀ → ⁷ F ₁	⁵ D ₀ → ⁷ F ₂	⁵ D ₀ → ⁷ F ₃	⁵ D ₀ → ⁷ F ₄
λ , nm	580.4075	589.9373	611.7868	651.4420	704.6708
S, nm	2.5325	21.1965	238.0805	1.8158	8.0813
$\bar{\lambda}$, nm	580.4480	593.4420	614.7017	653.7654	699.9826
S(⁵ D ₀ → ⁷ F _i)/S(⁵ D ₀ → ⁷ F ₁)	0.1194	1	11.2320	0.0856	0.3812
A _{0→i} (i = 0, ... 4)	5.8773	50	582.4034	4.7298	22.5777
β , %	0.95	8.12	94.6		3.66

Conclusion

The excitation spectrum demonstrates the antenna effect of energy transfer from the ligands.

The direct excitation of the Eu³⁺ ion is not observed and negligible,

The temperature dependence of FL in both compounds is not observed.

The integral FL intensity of compound [Eu(μ_2 -OC₂H₅)(NO₃)(phen)]₂phen is approximately 20 times higher than that of compound Eu(TTA)₃(Ph₃PO)₂.

Confirmation of the novelty

The novelty of the Eu complex was confirmed by two medals – one the silver and the other a golden medals, received at the international exhibitions this year; as well as by two patent applications we made – one in Moldova and the other in Romania.

1. Certificate of Priority from AGEPI of the Republic of Moldova No. 4194 2018.11.12, MD a 2018 0063, Deposit Date 2018.08.17

2. Certificate of Priority from OSIM, Romania, A/0000 din 07-01-2019, Compus coordonativ al Eu(III) de tip dinuclear cu liganzi micsti avind proprietati de luminescenta si procedeu de obtinere.

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