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Synthesis, crystal structure and luminescent properties of a novel coordination polymer built on Eu^{III} and 1,2,4,5-tetrakis(diphenylphosphinyl)benzene

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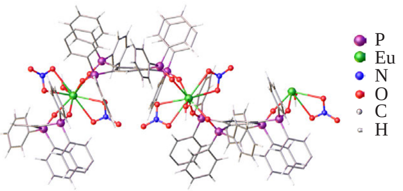
The reaction of 1,2,4,5-tetrakis(diphenylphosphinyl)benzene with Eu(ONO_2)$_3$·6H_2O led to the formation of a new coordination polymer exhibiting a bright red glow when excited in a wide ultraviolet range (Q_{in} = 19.9%).



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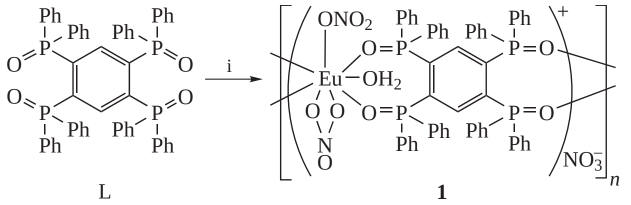
The synthesis and study of functional coordination polymers or metal–organic frameworks (MOFs) have attracted the attention of specialists in the field of coordination chemistry.[1,2] Among the compounds of this class, metal–organic complexes have been discovered whose properties are in demand in a wide range of applications, including nonlinear optics, catalysis, magnets and luminescent materials.[3–9] The first reports on the luminescent properties of MOFs were published in the early 2000s and have since attracted the attention of many researchers.[10–12]

This paper presents for the first time data on the synthesis of a new MOF **1**, obtained by reacting a tetraphosphinyl ligand with europium(III) nitrate, and also discusses its structure and photophysical properties. Our experiments have shown that the interaction of Eu(ONO_2)$_3$·6H_2O with 1,2,4,5-tetrakis(diphenylphosphinyl)benzene (L) in a 1 : 1 molar ratio in a methanol solution (25 °C, 45 min) leads to the formation of a coordination polymer $\{[EuL(H_2O)(NO_3)_2](NO_3)\}_n$ **1** in a yield of 68% (Scheme 1).†



Scheme 1 *Reagents and conditions*: i, Eu(ONO_2)$_3$·6H_2O, MeOH, 25 °C.

The composition of MOF **1** was established based on elemental analysis and X-ray diffraction data.‡ The independent part of the unit cell of complex **1** contains a europium(III) cation located on the twofold rotation axis, half of the ligand L, a water molecule and two and a half nitrate anions. Phosphine oxide bridges two europium(III) cations through four oxygen atoms. Unlike the previously reported tetrakis(diphenylphosphoryl)benzene complexes,[13,14] in which pairs of phosphoryl groups at positions 2,3 and 5,6 are pointed in opposite directions from the six-membered ring, in complex **1** all four oxygen atoms are located on the same side relative to the mean plane of the benzene ring. This conformation allows for intramolecular stacking interactions between two pairs of phenyl rings with intercentroid distances as short as 3.58(1) Å and an interplanar angle of 2.3(6)°.

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† *Synthesis of coordination polymer* $\{[EuL(H_2O)(NO_3)_2](NO_3)\}_n$ **1**. A solution of Eu(ONO_2)$_3$·6H_2O (0.1 mmol) in MeOH (2 ml) was added dropwise with stirring to a solution of ligand L (0.1 mmol) in MeOH (3 ml). The mixture was stirred at room temperature for 3 h and left overnight. Transparent almost colorless crystals were separated by decantation, washed with MeOH and dried at 62 °C *in vacuo* (0.1 Torr). The yield of crystalline complex **1** was 70%, mp > 360 °C (decomp.). Found (%): C, 52.38; H, 3.18; N, 3.28; P, 10.52. Calc. for $C_{54}H_{44}EuN_3O_{14}P_4$ (%): C, 52.65; H, 3.25; N, 3.41; P, 10.08.

‡ *Crystal data for* **1**. $C_{54}H_{44}EuN_3O_{14}P_4$ (M = 1230.73), orthorhombic, space group $C222_1$, a = 16.182(3), b = 18.729(4) and c = 18.010(4) Å, V = 5458.1(19) Å^3, Z = 4, d_{calc} = 1.498 g cm^{-3}, T = 100.0(2) K, μ = = 1.538 mm^{-1}, $F(000)$ = 2480, 21113 reflections were measured, 7254 independent reflections (R_{int} = 0.0537) were used in further refinement. The refinement converged at wR^2 = 0.169 and GOF = 1.049 for independent reflections [R_1 = 0.060 calculated on F^2 for 6075 observed reflections with $I > 2\sigma(I)$]. The measurements were carried out on a Rayonix SX165 detector of the ‘Belok/XDS’ station of the NRC ‘Kurchatov Institute’, which provides silicon monochromatized synchrotron radiation (λ = 0.7527 Å). The structure was solved by the direct method, non-hydrogen atoms were localized in difference synthesis of electron density and refined anisotropically on F^2 using the SHELXTL[17] and OLEX2[18] programs. Two of the phenyl rings and one nitrate anion are disordered in two positions, and the non-hydrogen atoms of these fragments were refined isotropically. Some fragments were refined using SADI, DFIX and FLAT instructions. A solvent mask was applied to treat the diffuse contribution of highly disordered solvent molecules to the overall scattering without specific atom positions. Hydrogen atoms were added to ideal positions using the riding model.

CCDC 2306751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

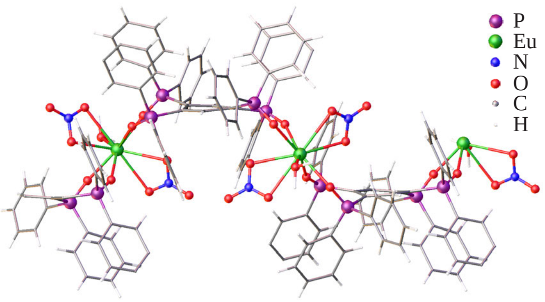

Figure 1 Fragment of infinite $[EuL(H_2O)(NO_3)_2]^+$ chains in coordination polymer **1**.

The metal atom coordinates two anions, one water molecule and one ligand, forming the $Eu^{III}O_9$ coordination polyhedron. The *r*(Eu–O) distances with water molecules are longer than those with the phosphine oxide and are 2.488(17) and 2.342(6)–2.366(6) Å, respectively. The coordinated anion is disordered, so the *r*(Eu–O) values for it vary from 2.21(2) to 2.77(2) Å. In general, the structure of the $[EuL(H_2O)(NO_3)_2]^+$ complex consists of chains running parallel to the crystallographic *c*-axis (Figure 1). The Eu···Eu distance in such a zigzag chain is 9.887(2) Å, and the Eu···Eu···Eu angle is 131.24(2)°. For comparison, the M···M distances in $[Eu_2L(NO_3)_6(H_2O)_2]$ and $[Tb_2L(NO_3)_6(H_2O)_2]$ dimers[13] and $[MnL(DMFA)_2]$ chains[14] with the same tetraphosphine oxide are 10.811(5), 10.777(5) and 10.299(1) Å, respectively.

To assess the luminescent properties of complex **1**, a number of photophysical studies were carried out.[§] Figure 2 illustrates the optical excitation and luminescence spectra of complex **1** in the solid phase at cryogenic (77 K) and room temperature (300 K). The complex under study exhibits ion-centered luminescence upon excitation in a wide spectral range from 280 to 470 nm. Broad bands in the excitation spectra from 280 to 370 nm with a maximum at 328 nm are associated with sensitizing luminescence due to electronic transitions within the ligand environment. Additionally, low-intensity narrow bands are observed in the spectra, corresponding to direct excitation of the Eu^{3+} ion *via* the transitions $^7F_0 \rightarrow ^5D_4$ (360–375 nm), $^7F_0 \rightarrow ^5L_6$ (400 nm) and $^7F_0 \rightarrow ^5D_2$ (464 nm).[15] This behavior indicates a relatively efficient sensitization of luminescence specifically through the ligand environment.

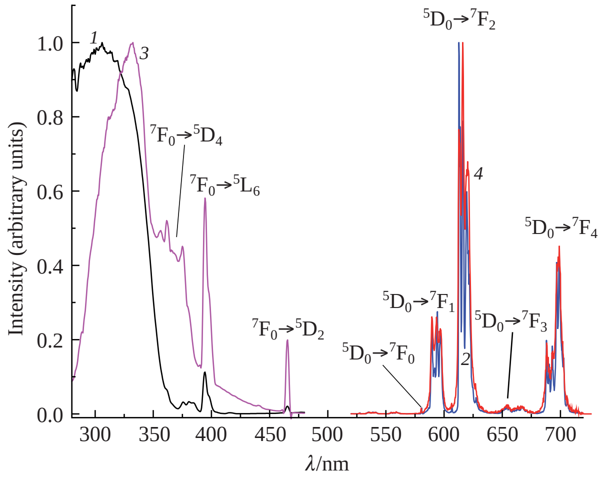

Figure 2 (*1*),(*3*) Optical excitation and (*2*),(*4*) luminescence spectra of complex **1** in the solid phase at temperatures of (*1*),(*2*) 77 and (*3*),(*4*) 300 K. Excitation spectra were measured at a recording wavelength of 615 nm, and fluorescence spectra were recorded at an excitation source wavelength of 335 nm.

Table 1 Energies of Stark components of *f**–*f* transitions of the Eu^{3+} ion in complex **1**.

*f**–*f* transition	Energy/cm^{-1}
$^5D_0 \rightarrow ^7F_0$	17220
$^5D_0 \rightarrow ^7F_1$	16950, 16840, 16750
$^5D_0 \rightarrow ^7F_2$	16320, 16230, 16150, 16090
$^5D_0 \rightarrow ^7F_3$	15290, 15020
$^5D_0 \rightarrow ^7F_4$	14530, 14490, 14430, 14360, 14300, 14270, 14220, 14170

The photoluminescence spectra of complex **1** exhibit narrow spectral bands corresponding to electronic transitions of Eu^{3+}: $^5D_0 \rightarrow ^7F_0$ (578–582 nm), $^5D_0 \rightarrow ^7F_1$ (585–600 nm), $^5D_0 \rightarrow ^7F_2$ (605–630 nm), $^5D_0 \rightarrow ^7F_3$ (645–660 nm) and $^5D_0 \rightarrow ^7F_4$ (700–710 nm). The assignment of individual *f**–*f* transitions to Eu^{3+} spectral lines (Table 1) is based on published data.[16] Fluorescence/phosphorescence contributions from the ligand environment are not observed in the luminescence spectra, indicating a relatively efficient transfer of excitation energy from the ligand to the central ion.

The ion-centered luminescence bands of Eu^{3+} at room temperature are inhomogeneously broadened, which makes it difficult to analyze the Stark structures of the energy levels of Eu^{3+} and the symmetry of the coordination environment of complex **1**. Registration of the emission of the complex at 77 K made it possible to resolve the structure of the ion-centered luminescence bands. Table 1 also presents the energies of the Stark components of *f**–*f* transitions of Eu^{3+} for the compound under study.

The transition $^5D_0 \rightarrow ^7F_0$ is not subject to Stark splitting, so the observation of multiple fluorescence spectral bands in the range from 575 to 585 nm would indicate the presence of different types of emission centers. For complex **1**, only one maximum is observed in the specified spectral range, which confirms the presence of one type of emission center.

Figure 3 shows the luminescence decay curves of complex **1** in the solid phase at temperatures of 77 and 300 K under optical excitation through the ligand environment (335 nm) and under direct excitation of the ion (395 nm) recorded at a wavelength of 615 nm (hypersensitive transition $^5D_0 \rightarrow ^7F_2$).

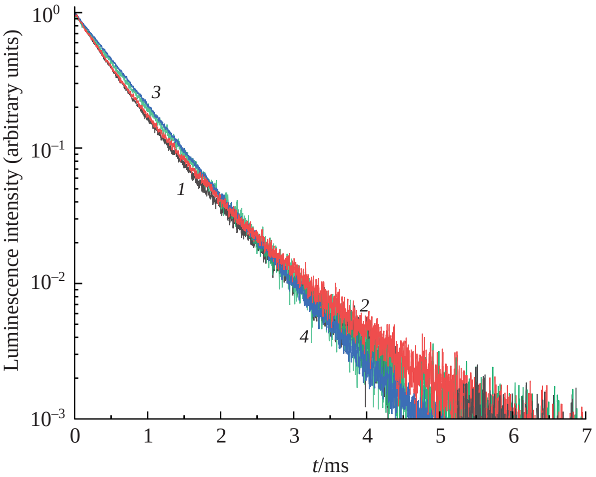

Figure 3 Luminescence decay curves of complex **1** at temperatures of (*1*),(*2*) 77 and (*3*),(*4*) 300 K (*2*),(*4*) under direct ion excitation (395 nm) and (*1*),(*3*) under ligand excitation (335 nm).

[§] To record the photoluminescence and optical excitation spectra, as well as the quantum yield in the solid phase, a Horiba Jobin-Yvon Fluorolog QM-75-22-C spectrofluorimeter equipped with a Hamamatsu R13456 photomultiplier tube detector was used. The source of continuous excitation was a 75 W ArcTune xenon arc lamp. To measure the total quantum yield, the absolute method was employed using a GMP G8 integrating sphere G8. Luminescence decay was also recorded using a Horiba Jobin-Yvon Fluorolog QM-75-22-C spectrofluorimeter. The excitation source was a pulsed xenon lamp with a frequency of 100 Hz and a pulse duration of 50 µs.

Table 2 Times (t) and amplitudes (A) of luminescence decay for complex **1** upon excitation of luminescence at various wavelengths and temperatures (T).

Excitation wavelength/nm	T/K	t_1/μs	A_1 (arbitrary units)	t_2/μs	A_2 (arbitrary units)
335	77	450	0.75	940	0.25
335	300	640	0.99	–	–
395	77	450	0.70	950	0.30
395	300	630	0.95	–	–

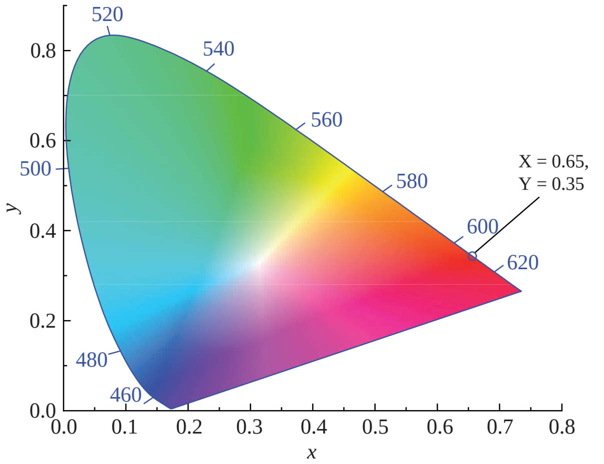

Figure 4 Chromaticity coordinates on the CIE 1931 color diagram for the luminescence of complex **1** when excited at a wavelength of 335 nm and a temperature of 300 K.

The luminescence decay curves of complex **1** at 300 K were fitted using a monoexponential function. The calculated lifetimes of the excited state are presented in Table 2. At 77 K, the kinetic curves can be described using a biexponential model. The component with a small amplitude contribution and a long decay time of approximately 950 μs can be attributed to residual phosphorescence of the ligand. The luminescence color diagram of this complex is presented in Figure 4.

The obtained key photophysical parameters of coordination polymer **1** are summarized in Table 3.

Table 3 Photophysical parameters of complex **1**.[a]

Complex	n	$I_{\mathrm{tot}}/I_{\mathrm{MD}}$	t_{rad}/ms	$k_{\mathrm{rad}}/\mathrm{s}^{-1}$	$k_{\mathrm{nrad}}/\mathrm{s}^{-1}$	$\tau_{\mathrm{obs}}^{-1}/\mathrm{s}^{-1}$	Q_{in} (%)	Q_{L} (%)	η
1	1.5	6.3	3.2	311.5	1275.0	1562.5	19.9	13.0	0.66

[a] Parameter designations: n is the refractive index of the medium, $I_{\mathrm{tot}}/I_{\mathrm{MD}}$ is the ratio of the integrated intensities of the total emission spectrum to the intensity of the magnetic dipole transition, t_{rad} is the radiative relaxation time, k_{rad} is the radiative relaxation rate constant, k_{nrad} is the nonradiative relaxation rate constant, τ_{obs}^{-1} is the reciprocal of the luminescence decay time, Q_{in} is the internal quantum yield, Q_{L} is the external quantum yield, and η is the sensitization efficiency coefficient.

In conclusion, a new coordination polymer of the Eu^{3+} ion with 1,2,4,5-tetrakis(diphenylphosphinyl)benzene has been synthesized. When excited in a wide ultraviolet range, this complex exhibits bright and efficient luminescence with CIE (Commission Internationale de l'Eclairage) color coordinates X = 0.65, Y = 0.35 and may be of interest in the creation of promising materials with luminescent properties.

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