

## Metal-Ion Sensing Europium(III) Complexes with Bidentate Phosphine Oxide Ligands Containing a 2,2'-Bipyridine Framework

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

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Novel Eu<sup>III</sup> complexes with bidentate phosphine oxide ligands containing a bipyridine framework, *i.e.*, [3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine]tris(hexafluoroacetylacetonato)europium(III) ([Eu(hfa)<sub>3</sub>(BIPYPO)]) and [3,3'-bis(diphenylphosphoryl)-6,6'-dimethyl-2,2'-bipyridine]tris(hexafluoroacetylacetonato)europium(III) ([Eu(hfa)<sub>3</sub>(Me-BIPYPO)]), were synthesized for lanthanide-based sensor materials having high emission quantum yields and effective chemosensing properties. The emission quantum yields of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] were 71 and 73%, respectively. Metal-ion sensing properties of the Eu<sup>III</sup> complexes were also studied by measuring the emission spectra of Eu<sup>III</sup> complexes in the presence of Zn<sup>II</sup> or Cu<sup>II</sup> ions. The metal-ion sensing and the photophysical properties of luminescent Eu<sup>III</sup> complexes with a bidentate phosphine oxide containing 2,2'-bipyridine framework are demonstrated for the first time.

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**Introduction.** – The design of chemosensors for the selective detection of a specific analyte such as a cation, anion, or molecule is a topic of considerable interest, due to their widely ranging application field [1]. Considerable efforts have been devoted to the elaboration of luminescent chemosensors for various analytes in the last two decades [1][2]. A large number of luminescent organic dyes [3], metal complexes [4], and polymers [5] with attached chemosensing units has been reported. We here focus on lanthanide complexes as luminophores [6]. Luminescent lanthanide complexes with attached chemosensing units have been also focused upon as effective sensory molecules [7–10]. *Parker, Gunnlaugsson*, and co-workers have, for example, studied luminescent lanthanide cyclen complexes for selective detection of HCO<sub>3</sub><sup>–</sup> anion [7]. *Ziessel, Tsukube*, and co-workers have reported luminescent lanthanide complexes for effective halogen-anion and chiral-molecule sensing [8][9].

Those luminescent lanthanide complexes with chemosensing properties are expected to contain chemosensing units for effective sensing properties. For example, Eu<sup>III</sup> complexes with Zn<sup>II</sup> ion sensing properties have been reported [10], although the emission quantum yield of the Eu<sup>III</sup> complex is relatively small ( $\Phi = 7.4\%$ ). Previous chemosensing lanthanide complexes contained numerous C–H chemical bonds close to the metal center, which led to the radiationless transition *via* vibrational relaxations of these complexes [11]. To enhance the emission quantum yields of lanthanide complexes having chemosensing units, the coordination sites of the organic ligands should be composed of low-vibrational-frequency (LVF) modes for the suppression of

vibrational relaxation [11]. In earlier studies, we have reported on the suppression of radiationless quenching in fluid lanthanide(III) systems by complexing the lanthanide(III) ion with diketonato ligands having C–F bonds composed of LVF modes, such as the hexafluoroacetylacetonato (hfa) ligand [12]. Such a LVF ligand, with the C–H bonds replaced by C–F bonds, is effective in the suppression of the radiationless transition *via* vibrational relaxation in the lanthanide complex. We have also observed that Eu<sup>III</sup> complexes with the LVF ligands hexafluoroacetylacetonato (hfa) and triaryl phosphine oxide (P=O: 1125 cm<sup>-1</sup>) show relatively high emission quantum yields ( $\Phi > 60\%$  in (D<sub>6</sub>)acetone) [13][14]. The LVF phosphine oxides with attached chemosensing units are expected to be promising ligands for luminescent lanthanide complexes having high emission quantum yields and effective chemosensing properties.

Here, we report on novel luminescent Eu<sup>III</sup> complexes with bidentate phosphine oxide ligands containing a 2,2'-bipyridine framework, *i.e.*, [3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine]tris(hexafluoroacetylacetonato)europium(III) ([Eu(hfa)<sub>3</sub>(BIPYPO)]) and [3,3'-bis(diphenylphosphoryl)-6,6'-dimethyl-2,2'-bipyridine]tris(hexafluoroacetylacetonato)europium(III) ([Eu(hfa)<sub>3</sub>(Me-BIPYPO)]) (Figs. 1, a and b). The bipyridine frameworks in these bidentate phosphine oxide ligands are expected to perform as chemosensing units for catching of a metal cation such as a Zn<sup>II</sup> ion. The metal-ion sensing properties of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] were estimated by measuring the emission spectra of the Eu<sup>III</sup> complex in the presence of a Zn<sup>II</sup> or Cu<sup>II</sup> ion. We also compared the metal-ion sensing and the emission properties of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] with those Eu<sup>III</sup> complexes containing a 1,1'-biphenyl framework, *e.g.*, [Eu(hfa)<sub>3</sub>(BIPHEPO)] (Fig. 1, c) [14]. In the present study, metal-ion sensing and the emission properties of luminescent Eu<sup>III</sup> complexes with bidentate phosphine oxide ligands containing a 2,2'-bipyridine framework are demonstrated for the first time.

**Results and Discussion.** – *Emission Properties.* The emission spectra of the Eu<sup>III</sup> complexes [Eu(hfa)<sub>3</sub>(BIPHEPO)], [Eu(hfa)<sub>3</sub>(BIPYPO)], and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] in (D<sub>6</sub>)acetone under excitation at 465 nm (<sup>7</sup>F<sub>0</sub>–<sup>5</sup>D<sub>2</sub> transition band of Eu<sup>III</sup>) are shown in Fig. 2. The spectra are normalized with respect to the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> (magnetic-dipole) transition at 580 nm that is known to be insensitive to the ligand field [13a]. Emission bands were observed at around 579, 592, 615, 650, and 700 nm, and are attributed to the f–f transitions <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>J</sub> (J = 0, 1, 2, 3, 4, resp.). The strongest emission band at around 615 nm (<sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub>) is due to the electric-dipole transition. [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] showed the characteristic narrow emission band which agreed well with that of [Eu(hfa)<sub>3</sub>(BIPHEPO)]. The spectral shape of a hypersensitive transition band is generally affected by the coordination structure of the Eu<sup>III</sup> complex [15]. These results indicate that the coordination structures of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] in (D<sub>6</sub>)acetone are much similar to that of [Eu(hfa)<sub>3</sub>(BIPHEPO)].

The emission quantum yields of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] in (D<sub>6</sub>)acetone are summarized in the Table. [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] show relatively high emission quantum yields ( $\Phi \approx 70\%$ ). The time-resolved emission profiles of [Eu(hfa)<sub>3</sub>(BIPYPO)] and [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] revealed mono-exponential decays with lifetimes in the millisecond time in

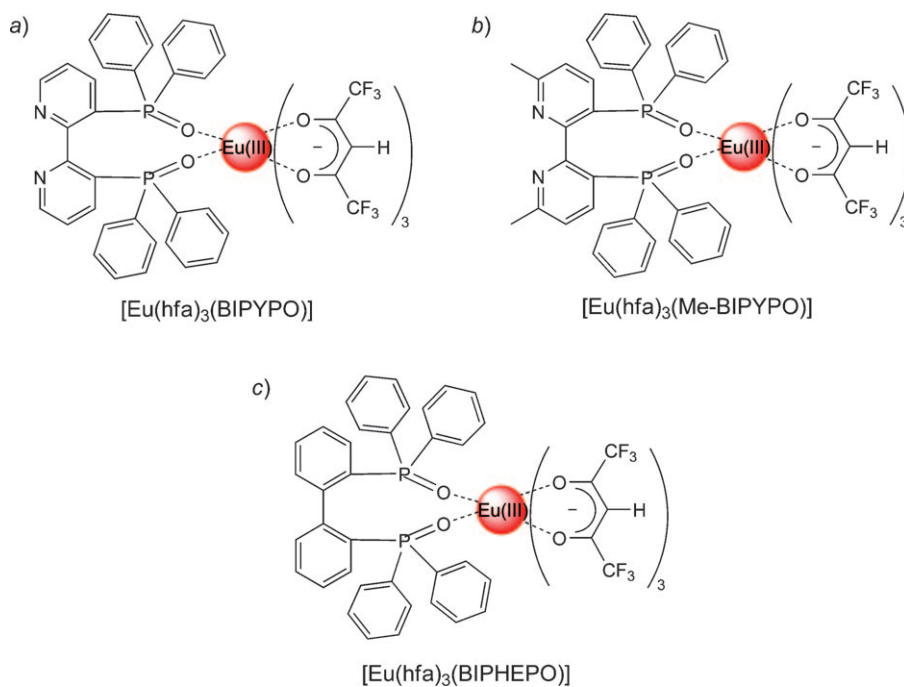


Fig. 1. Chemical structures of a)  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ , b)  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$ , and c)  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$

( $D_6$ )acetone. The radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) rate constants estimated from the emission lifetimes and the emission quantum yields are also summarized in the *Table*. The radiative and nonradiative rate constants of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  and  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  were nearly similar to those of the corresponding  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$ . The radiative and nonradiative processes of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  and  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  in ( $D_6$ )acetone might not be affected by introducing the bipyridine framework in bidentate phosphine oxides. Generally, kinetics of the radiative rate of the emission from lanthanide complexes depends on the geometrical symmetry of their coordination structure [13]. We suggest that the geometrical symmetries of the coordination structure of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  and  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  are similar to that of  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$ .

In our previous study, we have reported that the coordination geometry of  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  is characterized as a square-antiprism structure (SAP) with eight coordinating O-atoms (8-SAP), and the two phosphine oxides of the BIPHEPO ligand are located on one square of the 8-SAP (*Fig. 3*) [14]. The two phosphine oxide sites in the BIPYPO and Me-BIPYPO ligands might also be located on one square of the 8-SAP. We consider that the characteristic structures of BIPYPO and Me-BIPYPO located in  $\text{Eu}^{\text{III}}$  complexes would provide the best conformation for chelation of a metal ion such as a bipyridine ligand in the case of transition-metal complexes.

*Metal-Ion-Sensing Properties.* The emission spectra of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  upon addition of  $\text{Zn}(\text{NO}_3)_2$  ion in ( $D_6$ )acetone under excitation at 465 nm are shown in

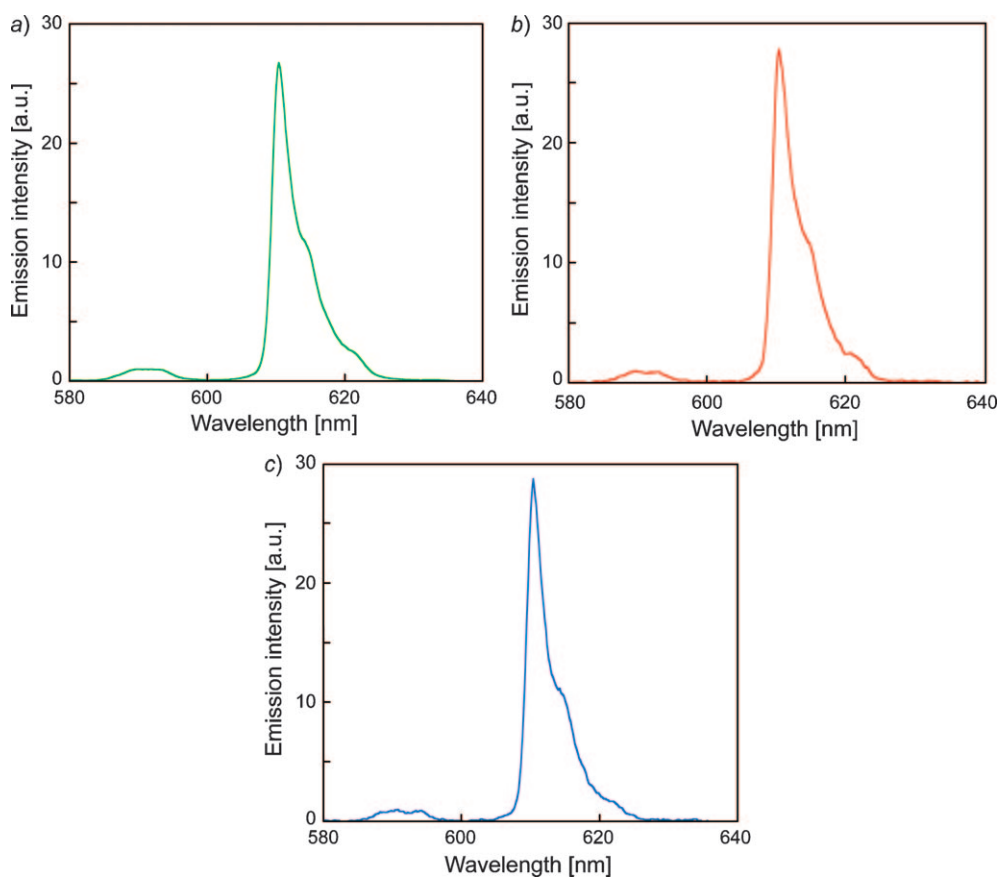


Fig. 2. Normalized emission spectra of a)  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ , b)  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$ , and c)  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPHEPO})]$  in  $(\text{D}_6)$ acetone under 465 nm. Emission spectra were normalized at 592 nm ( ${}^5\text{D}_0 - {}^7\text{F}_1$ ).

Table. Characteristics of the Emission Properties of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ ,  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$ , and  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$ <sup>a</sup>

	$\Phi_{\text{r-t}}$ [%]	$\tau$ [ms]	$k_{\text{r}}$ [ $\text{s}^{-1}$ ] <sup>b</sup>	$k_{\text{nr}}$ [ $\text{s}^{-1}$ ] <sup>c</sup>
$[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$	71	1.16	$6.0 \cdot 10^2$	$2.5 \cdot 10^2$
$[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$	73	1.27	$5.8 \cdot 10^2$	$2.1 \cdot 10^2$
$[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$	60	1.27	$4.7 \cdot 10^2$	$3.2 \cdot 10^2$

<sup>a</sup>) The emission quantum yields ( $\Phi_{\text{r-t}}$ ) and the emission lifetimes ( $\tau$ ) in  $(\text{D}_6)$ acetone (1 mm) were measured by excitation at 465 nm ( ${}^7\text{F}_0 - {}^5\text{D}_2$ ) and 355 nm ( $\pi - \pi^*$  transition band of the hfa ligands), resp.

<sup>b</sup>) Radiative rate constant  $k_{\text{r}} = (\Phi_{\text{r-t}})/\tau$ . <sup>c</sup>) Nonradiative rate constant  $k_{\text{nr}} = (1/\tau) - k_{\text{r}}$ .

Fig. 4.a. We observed an effective decrease of the emission intensity of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  upon the addition of  $\text{Zn}^{\text{II}}$  ions. Normalized emission spectra with respect to

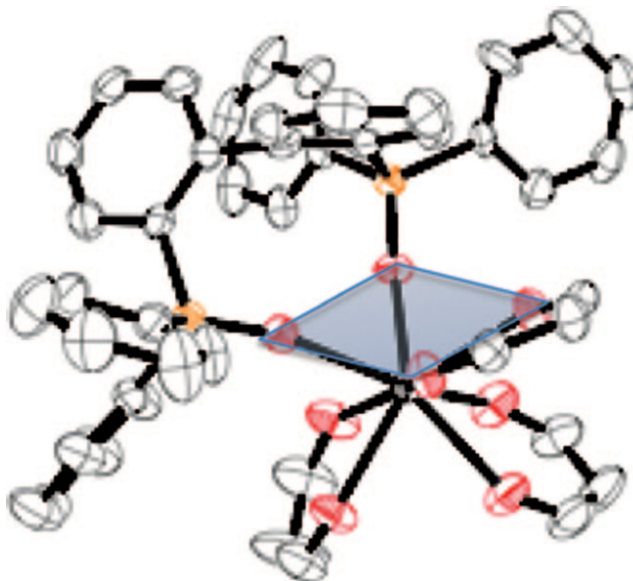


Fig. 3. ORTEP View of the  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  single crystal [14] ( $\text{CF}_3$  groups omitted for clarity)

the magnetic-dipole-transition intensities were not affected by the addition of  $\text{Zn}^{\text{II}}$  ion. These results indicate that the geometrical structure and radiative rate constant of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  were not affected by the addition of  $\text{Zn}^{\text{II}}$  ion. We also observed that the decrease ratio upon addition of  $\text{Zn}(\text{OTf})_2$  ( $\text{OTf}^- = \text{trifluoromethanesulfonate}$ ) was the same as that of  $\text{Zn}(\text{NO}_3)_2$ , and the absorption band of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  in the presence of  $\text{Zn}^{\text{II}}$  ion was not observed in the range from 500 nm to 800 nm. From these observations, the effective decrease of the emission intensity of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  on addition of  $\text{Zn}^{\text{II}}$  ion might be due to the increase of the nonradiative rate constant of the  $\text{Eu}^{\text{III}}$  complex. We consider that formation of dimer or trimer  $\text{Eu}^{\text{III}}$  complexes combined by  $\text{Zn}^{\text{II}}$  ions in ( $\text{D}_6$ )acetone might lead to an increase of the nonradiative process as a consequence of the excitation migration or cross-relaxation between  $\text{Eu}^{\text{III}}$  ions [16]. In contrast, the effective decrease of the emission intensity of  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  which also has a bidentate phosphine oxide ligand but containing the biphenylene framework was not observed.

We also observed a drastic decrease of the emission intensity on addition of  $\text{Cu}^{\text{II}}$  ion to  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ , although the normalized emission spectra and the absorption band of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  in the range from 500 nm to 800 nm were not changed by this addition (Fig. 4, b). The decrease ratio on addition of  $\text{Cu}^{\text{II}}$  ion was larger than that of  $\text{Zn}^{\text{II}}$  ion. Previously, *Saladini* and co-workers have reported that the binding constant for the formation of a  $[\text{Cu}^{\text{II}}(\text{bipyridine})]$  complex ( $\log K = 8.0$ ) is larger than that of corresponding  $[\text{Zn}^{\text{II}}(\text{bipyridine})]$  complex ( $\log K = 5.3$ ) [17]. It seems that the drastic decrease of the emission spectra of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  on addition of  $\text{Cu}^{\text{II}}$  ion is caused by a strong affinity between the  $\text{Cu}^{\text{II}}$  ion and the bipyridine unit in the BIPYPO ligand.

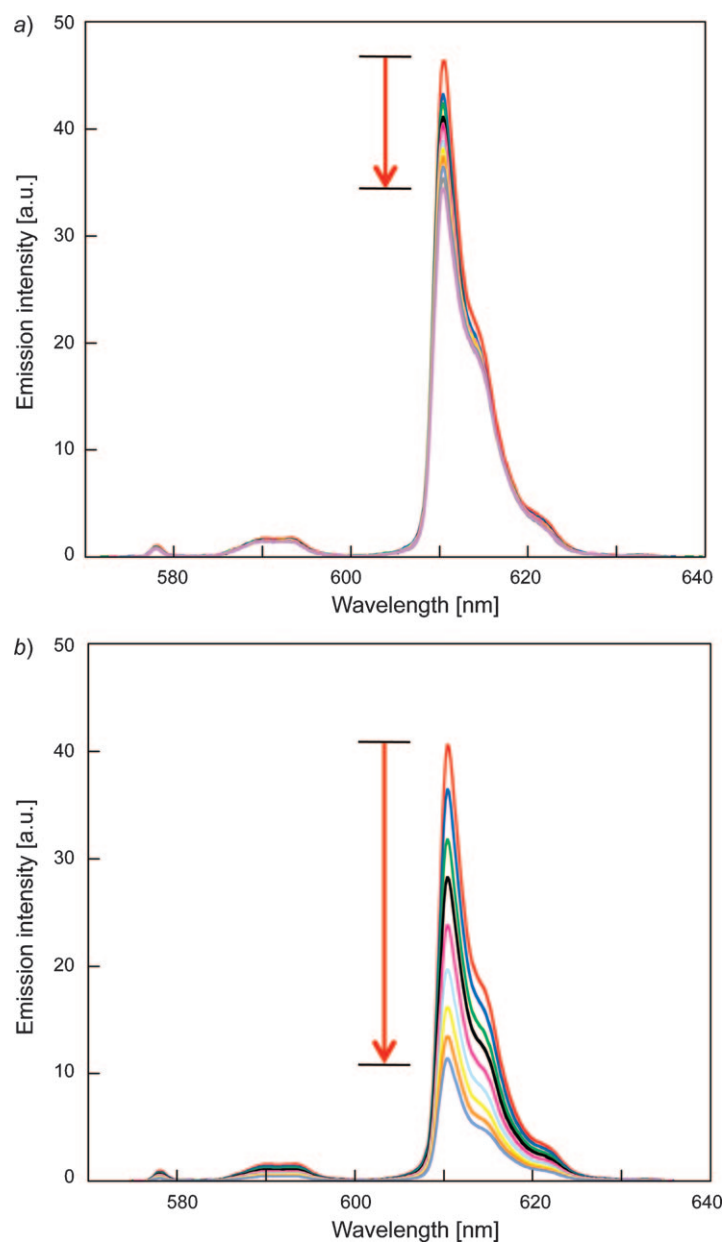


Fig. 4. Emission spectra (excitation at 465 nm) of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  (1 mM) in the presence of various concentrations of a)  $\text{Zn}^{\text{II}}$  or b)  $\text{Cu}^{\text{II}}$  (0.000, 0.025, 0.050, 0.075, 0.100, 0.125, 0.160, 0.175, and 0.200 equiv. of  $\text{Zn}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$  with respect to  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ )

The emission-intensity profiles of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ ,  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$ , and  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  in the presence of  $\text{Zn}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  ions (Fig. 5) show a

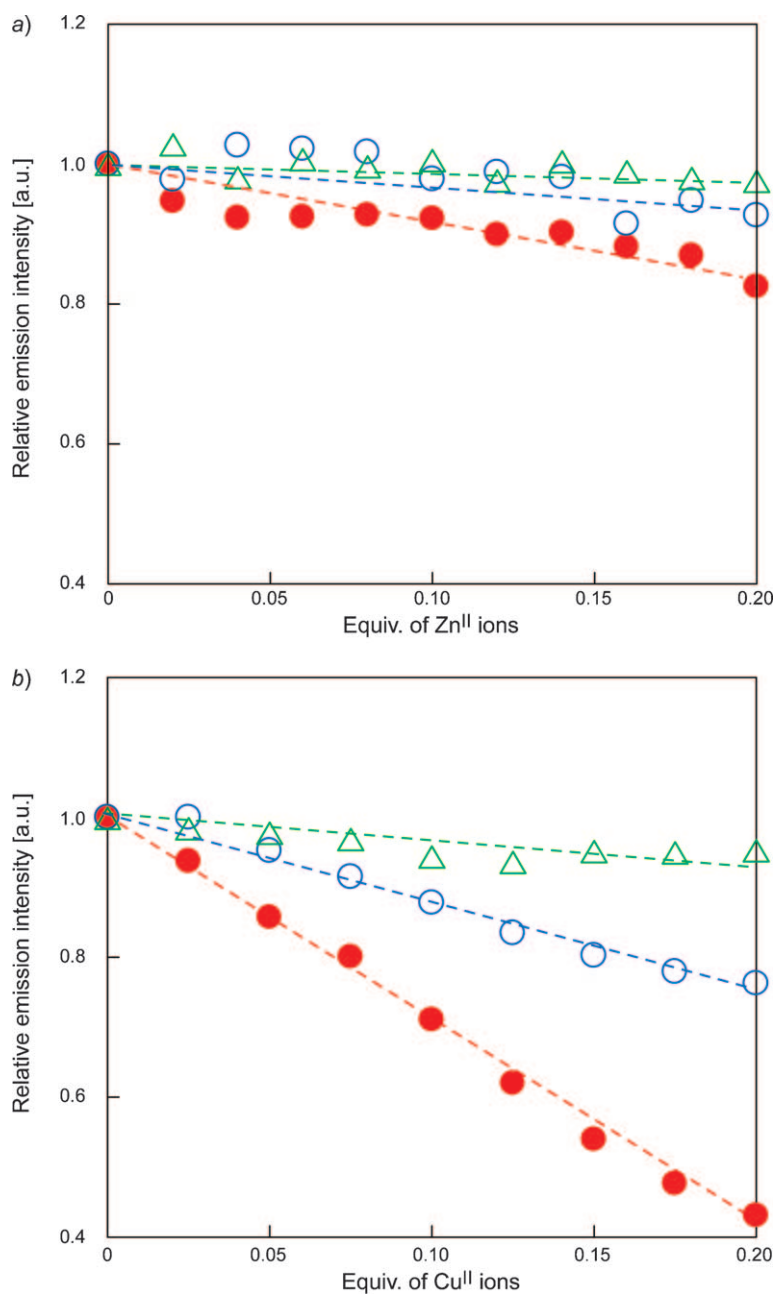


Fig. 5. Emission-intensity profiles of  $[Eu(hfa)_3(BIPYPO)]$  (1 mM; red dots),  $[Eu(hfa)_3(Me-BIPYPO)]$  (1 mM; blue circles), and  $[Eu(hfa)_3(BIPHEPO)]$  (1 mM; green triangles) in the presence of  $Zn^{II}$  and  $Cu^{II}$  ions in ( $D_6$ )acetone excited at 465 nm

decrease of the emission intensity of  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  on addition of  $\text{Zn}(\text{II})$  and  $\text{Cu}(\text{II})$  ions; however, the decrease ratios of the emission intensity of  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  were smaller than those of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$ . We consider that formation of  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  with attached  $\text{Zn}^{\text{II}}$  or  $\text{Cu}^{\text{II}}$  ions may be partially prevented by steric hindrance of the Me groups at the bipyridine moiety. The effective decrease of the emission intensities of  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  in the presence of  $\text{Zn}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  ions was not observed. From these results, we propose that the BIPYPO is the most useful ligand for luminescent lanthanide complexes having high emission quantum yields and effective chemosensing properties.

**Conclusion.** – We successfully synthesized novel  $\text{Eu}^{\text{III}}$  complexes with bidentate phosphine oxide ligands containing a bipyridine framework,  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  and  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$ . Their high emission quantum yields and effective metal-ion sensing properties were achieved by the coordination of the low-vibrational phosphine oxide bearing the chemosensing unit.  $\text{Eu}^{\text{III}}$  Complexes with strong luminescence and effective metal-ion-sensing properties would open up new fields for luminescent chemosensors.

### Experimental Part

*General.* IR Spectra: *Jasco-FT/IR-420* spectrometer; ATR = attenuated total reflection; in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  Spectra: *Jeol-AL300* spectrometer (300 MHz); chemical shifts  $\delta$  in ppm rel. to  $\text{Me}_4\text{Si}$  as an internal standard,  $J$  in Hz. EI- and ESI-MS: *Jeol-JMS-700-M* station; in  $m/z$ .

*Optical Measurements.* Absorption spectra of  $\text{Eu}^{\text{III}}$  complexes in acetone (1.0 mm) were measured at r.t. with a *Jasco-V-660* spectrophotometer. Emission spectra of  $\text{Eu}^{\text{III}}$  complexes in acetone (1.0 mm) were measured at r.t. with a *Hitachi-F-4500* spectrophotometer. The samples were excited at 465 nm. The emission lifetime of  $\text{Eu}^{\text{III}}$  complexes were determined with a Q-switched Nd:YAG laser (*Spectra Physics INDI-50*,  $\text{fwhm} = 5$  ns,  $\lambda = 1064$  nm). Samples were excited by the third harmonic (355 nm) of the fundamental nanosecond pulse. Emission decays were monitored with a digital oscilloscope (*Sony Tektronix, TDS3052B*) synchronized to single-pulse excitation. The emission quantum yields of  $[\text{Eu}(\text{hfa})_3(\text{BIPYPO})]$  and  $[\text{Eu}(\text{hfa})_3(\text{Me-BIPYPO})]$  were evaluated by utilizing  $[\text{Eu}(\text{hfa})_3(\text{BIPHEPO})]$  as the standard of  $\Phi_{\text{em}} = 0.60$  [18].

*[2,2'-Bipyridine]-3,3'-diol.* The *[2,2'-bipyridine]-3,3'-diol* was obtained by the same method as previously reported [19].  $\text{NiCl}_2$  (3.9 g, 30 mmol), Zn powder (5.9 g, 90 mmol), and  $\text{Ph}_3\text{P}$  (32 g, 120 mmol) were dissolved in anh. DMF (150 ml), and the mixture was heated to  $50^\circ$ . After 1 h, 2-bromopyridin-3-ol (5.2 g, 90 mmol) in anh. DMF (100 ml) was added, and the mixture was kept for another 20 h at  $50^\circ$ . The warm mixture was poured into 10N aq. NaOH (100 ml) and vigorously stirred for 30 min. The precipitated  $\text{Ph}_3\text{P}$  was filtered and the filtrate again poured into 10N aq. NaOH (50 ml). The product was precipitated by the addition of conc. HCl soln. to the combined NaOH soln. (pH 4) and stirring for 30 min. The solid was immediately filtered, washed with distilled  $\text{H}_2\text{O}$ , and dried in a desiccator. The residue was purified by CC ( $\text{SiO}_2$ ): *[2,2'-bipyridine]-3,3'-diol* (0.70 g, 25%). Yellow solid.  $R_f$  ( $\text{CHCl}_3$ ) 0.7.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 8.06 (d,  $J = 4.5$ , 2 H); 7.43 (d,  $J = 7.5$ , 2 H); 7.30 (dd,  $J = 4.8$ , 4.8, 2 H). EI-MS: 188.0586 ( $M^+$ ).

*[2,2'-Bipyridine]-3,3'-diyl Bis(trifluoromethanesulfonate).* To a soln. of *[2,2'-bipyridine]-3,3'-diol* (0.57 g, 3.0 mmol) in anh.  $\text{CH}_2\text{Cl}_2$  (25 ml) under  $\text{N}_2$  at r.t. pyridine (1.6 ml, 18 mmol) was added. Then, trifluoromethanesulfonic anhydride (1.5 ml, 9.0 mmol) was added dropwise (yellow  $\rightarrow$  red and white fume). The mixture was stirred at r.t. for 17 h.  $\text{H}_2\text{O}$  was added into the soln. and the mixture extracted with  $\text{CH}_2\text{Cl}_2$ . The combined org. phase was washed with  $\text{H}_2\text{O}$  and brine, dried ( $\text{MgSO}_4$ ), and concentrated and the residue purified by CC ( $\text{SiO}_2$ ): *[2,2'-bipyridine]-3,3'-diyl bis(trifluoromethanesulfonate)* (1.3 g, 94%). White solid.  $R_f$  0.4 (hexane/AcOEt 3:1). FT-IR (ATR): 1587 (pyridine C=C,



C=N), 1424 (pyridine C=C, C=N), 1270–1170 (br., S=O), 1260–1070 (br., C–F). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.79 (*d*, *J* = 4.5, 2 H); 7.82 (*d*, *J* = 8.4, 2 H); 7.58 (*dd*, *J* = 4.5, 4.8, 2 H). EI-MS: 451.9570 (*M*<sup>+</sup>).

*3,3'-Bis(diphenylphosphoryl)-2,2'-bipyridine* (BIPYPO). Diphenylphosphine (1.8 ml, 10 mmol) was added to a stirred soln. of [2,2'-bipyridine]-3,3'-diyl bis(trifluoromethanesulfonate) (1.5 g, 3.4 mmol), Et<sub>3</sub>N (1.2 ml), and [Pd(OAc)<sub>2</sub>] (0.31 g, 1.4 mmol) in dry DMF (20 ml) (→ instantly red soln.). The soln. was heated at 90° under N<sub>2</sub> for 24 h. H<sub>2</sub>O was added and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined org. phase was washed with H<sub>2</sub>O and brine, dried (MgSO<sub>4</sub>), and concentrated and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The soln. was cooled to 0°, and then 30% H<sub>2</sub>O<sub>2</sub> soln. (7.0 ml) was added. The mixture was stirred for 12 h and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined org. phase was washed with H<sub>2</sub>O and brine, dried (MgSO<sub>4</sub>), and concentrated and the residue purified by CC (SiO<sub>2</sub>): *3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine* (0.71 g, 38%). Yellow solid. *R*<sub>f</sub> 0.1 (THF). FT-IR (ATR): 1647, 1580–1540 (pyridine, C=C, C=N), 1460–1360 (pyridine, C=C, C=N), 1210–1160 (br., P=O), 1140–1000. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.26 (*td*, *J* = 2.4, 2.4, 2 H); 7.75–7.68 (*m*, 10 H); 7.46–7.37 (*m*, 12 H); 7.11 (*dd*, *J* = 4.8, 4.8, 2 H). EI-MS: 556.1470 (*M*<sup>+</sup>).

[*3,3'-Bis(diphenylphosphoryl)-κO*]-2,2'-bipyridine]tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κO,κO)europium(III) ([Eu(hfa)<sub>3</sub>(BIPYPO)]). [Eu(hfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (0.49 g, 0.60 mmol) and *3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine* (0.28 g, 0.50 mmol) were dissolved in MeOH (100 ml). The soln. was refluxed and stirred for 12 h and then concentrated. The residue was washed with CHCl<sub>3</sub> and Et<sub>2</sub>O several times: [Eu(hfa)<sub>3</sub>(BIPYPO)] (0.43 g, 62%) as a white solid. Recrystallization from acetone/H<sub>2</sub>O gave a colorless crystal. FT-IR (ATR): 1680–1630 (*s*, C=O), 1580–1430 (pyridine, C=C, C=N), 1210–1180 (P=O), 1170–1040 (br., C–F). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.77 (br., 4 H); 8.37 (br., 2 H); 8.13 (*dd*, *J* = 7.8, 8.4, 2 H); 7.80 (br., 6 H); 7.50 (br., 4 H); 6.76 (br., 4 H); 5.79 (br., 4 H). ESI-MS: 1123.0358 ([*M* – (hfa)]<sup>+</sup>). Anal. calc. for C<sub>49</sub>H<sub>29</sub>EuF<sub>18</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>: C 44.26, H 2.20, N 2.11; found: C 44.13, H 1.85, N 2.11.

*2-Bromo-6-methylpyridin-3-ol*. The 2-bromo-6-methylpyridin-3-ol was obtained by the same method as previously reported [20]. Bromine (14 ml, 270 mmol) was slowly added to a soln. of 6-methylpyridin-3-ol (25 g, 230 mmol) in pyridine (300 ml) at 0°. The mixture was stirred for additional 20 h at r.t. H<sub>2</sub>O was added into the soln., and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined org. phase was washed with H<sub>2</sub>O and brine, dried (MgSO<sub>4</sub>), and concentrated and the residue purified by CC (SiO<sub>2</sub>): *2-bromo-6-methylpyridin-3-ol* (19 g, 43%). White solid. *R*<sub>f</sub> 0.2 (CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.19 (*d*, *J* = 8.1, 1 H); 7.02 (*d*, *J* = 8.1, 1 H); 2.47 (*s*, 3 H). EI-MS: 186.9633 (*M*<sup>+</sup>).

*6,6'-Dimethyl[2,2'-bipyridine]-3,3'-diol*. As described above for [2,2'-bipyridine]-3,3'-diol, with NiCl<sub>2</sub> (6.4 g, 49 mmol), Zn powder (9.8 g, 150 mmol), Ph<sub>3</sub>P (51 g, 200 mmol), DMF (200 ml), 2-bromo-6-methylpyridin-3-ol (9.2 g, 49 mmol), and DMF (100 ml). Workup with 10*N* NaOH (200 and 50 ml): *6,6'-dimethyl[2,2'-bipyridine]-3,3'-diol* (1.2 g, 23%). Yellow solid. *R*<sub>f</sub> 0.7 (CHCl<sub>3</sub>). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 14.75 (*s*, 2 H); 7.32 (*d*, *J* = 8.4, 2 H); 7.12 (*d*, *J* = 8.4, 2 H); 2.52 (*s*, 6 H). EI-MS: 216.0899 (*M*<sup>+</sup>).

*6,6'-Dimethyl[2,2'-bipyridine]-3,3'-diyl Bis(trifluoromethanesulfonate)*. As described above for [2,2'-bipyridine]-3,3'-diyl bis(trifluoromethanesulfonate), with *6,6'-dimethyl[2,2'-bipyridine]-3,3'-diol* (1.4 g, 6.2 mmol) CH<sub>2</sub>Cl<sub>2</sub> (40 ml), pyridine (3.5 ml, 42 mmol), and trifluoromethanesulfonic anhydride (3.5 ml, 21 mmol): *6,6'-dimethyl[2,2'-bipyridine]-3,3'-diyl bis(trifluoromethanesulfonate)* (2.9 g, 96%). White solid. *R*<sub>f</sub> 0.5 (hexane/AcOEt 3:1). FT-IR (ATR): 1600–1560 (pyridine, C=C, C=N), 1450–1380 (pyridine, C=C, C=N), 1270–1170 (br., S=O), 1170–1070 (br., C–F), 1145. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.65 (*d*, *J* = 8.7, 2 H); 7.35 (*d*, *J* = 8.4, 2 H); 2.67 (*s*, 6 H). EI-MS: 479.9884 (*M*<sup>+</sup>).

*3,3'-Bis(diphenylphosphoryl)-6,6'-dimethyl-2,2'-bipyridine* (Me-BIPYPO). As described above for *3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine*, with diphenylphosphine (2.7 ml, 16 mmol), *6,6'-dimethyl[2,2'-bipyridine]-3,3'-diyl bis(trifluoromethanesulfonate)* (2.3 g, 5.2 mmol), Et<sub>3</sub>N (1.7 ml), Pd(OAc)<sub>2</sub> (0.47 g, 2.1 mmol), DMF (20 ml), and 30% H<sub>2</sub>O<sub>2</sub> soln. (25 ml; 20 h stirring instead of 12 h). H<sub>2</sub>O was added and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined org. phase was washed with H<sub>2</sub>O and brine, dried (MgSO<sub>4</sub>), and concentrated. The residue was washed with AcOEt, and solid was filtered: *3,3'-bis(diphenylphosphoryl)-6,6'-dimethyl-2,2'-bipyridine* (0.71 g, 23%). Yellow solid. *R*<sub>f</sub> 0.3 (THF). FT-IR (ATR): 1600–1520 (br., pyridine, C=C, C=N), 1450–1400 (br., pyridine, C=C, C=N), 1341, 1200–

1150 (P=O), 1150–1050. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.71–7.64 (*m*, 8 H); 7.55–7.49 (*m*, 2 H); 7.44–7.34 (*m*, 12 H); 6.90 (*d*, *J* = 7.8, 2 H); 2.04 (*s*, 6 H). EI-MS: 583.1704 ([*M* – H]<sup>+</sup>).

[3,3'-Bis(diphenylphosphoryl-κO)-6,6'-dimethyl-2,2'-bipyridine]tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-κO,κO')europium(III) ([Eu(hfa)<sub>3</sub>(Me-BIPYPO)]). As described for [Eu(hfa)<sub>3</sub>(BIPYPO)], with [Eu(hfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (5.9 g, 7.3 mmol), 3,3'-bis(diphenylphosphoryl)-6,6'-dimethyl-2,2'-bipyridine (3.6 g, 6.1 mmol), and MeOH (300 ml): [Eu(hfa)<sub>3</sub>(Me-BIPYPO)] (6.0 g, 73%) as a yellow white solid. Recrystallization from acetone/H<sub>2</sub>O gave a colorless crystal. FT-IR (ATR): 1680–1630 (C=O), 1580–1460 (br., pyridine, C=C, C=N), 1251, 1200–1150 (P=O), 1160–1060 (br., C–F). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 8.22 (br., 4 H); 8.06 (*dd*, *J* = 8.1, 2 H); 7.67 (br., 6 H); 7.52 (*d*, *J* = 7.8, 2 H); 6.96 (br., 4 H); 6.71 (br., 4 H); 5.98 (*s*, 4 H); 2.40 (*s*, 6 H). ESI-MS: 1151.0757 ([*M* – (hfa)]<sup>+</sup>). Anal. calc. for C<sub>51</sub>H<sub>33</sub>EuF<sub>18</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>: C 45.12, H 2.45, N 2.06; found: C 45.09, H 2.19, N 2.06%.

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