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Syntheses and Luminescence of Three Lanthanide Complexes Constructed by Flexible Carboxylate Ligand[1]

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Abstract—Three new complexes, namely $\{[\mathrm{Ln(L)_3(2,2'\text{-}Bipy)}]_n \cdot \mathrm{H_2O}\}$ (Ln = Pr (**I**), Sm (**II**), and Nd (**III**)) (HL = 3-(2-hydroxyphenyl)propanoic acid), have been synthesized and structurally characterized. The structural determinations indicated (CIF files CCDC nos. 1472729 (**I**), 1472730 (**II**), 1472734 (**III**)) that **I**–**III** have similar dinuclear structures, which can be further linked into 2D sheet via the hydrogen bond interactions. Furthermore, the luminescent properties of **I**–**III** show the strong emissive power and feature.

Keywords: carboxylic acid, supramolecular interaction, photoluminescence

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INTRODUCTION

Lanthanide luminescence attracts a special status in photonics due to the unique spectroscopic features of lanthanide ions, including long lifetime, large Stokes shift, and narrow band [1–3]. In recent decades, the number of photonic applications of lanthanides has been explored, extending from sensing to biomedical analyses, imaging, lighting and displays [4–9]. Moreover, the search for new lanthanide materials with controlled and tunable luminescent properties for applications in thermometry and white light emission is currently a very active field.

On the other hand, the ligand-based strategy realized for new luminescent MOFs is used [10–16]. As a building block, 3-(2-hydroxyphenyl)propanoic acid (HL) can be multidentate and is an excellent candidate for construction of lanthanide coordination polymers. With the above in mind, we chose HL as ligand to construct MOFs based on the following considerations: (1) HL, as a derivative of the *p*-hydroxybenzoic acid ligand, is a good spacer and has been rarely used in the assembly of coordination polymers; (2) the carboxylic group may have different coordinative mode due to the flexible chain, which may induce higher metal cluster [17]. Up to now, construction of new lanthanide coordination polymers based on HL is not reported, especially involving chelating N-donor ligand. Taking account of the above, we tried to synthesize and explore new complexes with HL and lanthanide ions. Herein, three new Ln coordination complexes based on HL ligand, namely, $\{[\mathrm{Ln(L)_3(2,2'\text{-}Bipy)}]_n \cdot \mathrm{H_2O}\}$ (Ln = Pr (**I**), Sm (**II**) and Nd (**III**)), have been synthesized and characterized. Compounds **I**–**III** display strong photoluminescent property and high thermal stability.

EXPERIMENTAL

Materials and physical measurements. All the reagents and solvents for synthesis and analysis were commercially available and used directly. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 $\mathrm{cm^{-1}}$) were recorded by using KBr pellet on an AVATAR-370 IR spectrometer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized $\mathrm{Mo}K_\alpha$ radiation. Thermogravimetric (TG) analyses were carried out with a Metter–Toledo TA 50 in dry dinitrogen (60 mL $\mathrm{min^{-1}}$) at a heating rate of 5 K/min. X-ray power diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA for $\mathrm{Cu}K_\alpha$ radiation ($\lambda = 1.5406$ Å), with a scan speed of 2 K/min and a step size of 0.02° in 2θ. Luminescence spectra for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter.

Synthesis of I. A solution of $\mathrm{Pr(NO3)_3 \cdot 4H_2O}$ (0.15 mmol) in water was added to a solution containing HL (0.1 mmol) in a mixture of $\mathrm{H_2O}$ (10 mL) and $\mathrm{CH_3OH}$ (5 mL) at 60°C. The pH of the resulting solution was adjusted to 6 using dilute NaOH (0.1 mol/L) and kept at room temperature to prepare compound **I**.

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[1] The article is published in the original.

From that solution, crystals suitable for X-ray measurements were obtained. The yield was 50% based on Pr.

For $C_{37}H_{37}N_2O_{10}Pr$ ($M = 810.60$)

anal. calcd., %:	C, 54.82;	N, 3.46;	H, 4.60.
Found, %:	C, 54.80;	N, 3.43;	H, 4.61.

IR (KBr; ν, cm^{-1}): 3391 v, 2929 m, 1577 v.s, 1455 v.s, 1249 v.s, 1170 m, 1087 v, 743 v.s.

Compound **II** was synthesized by a method similar to that of **I**, except that $Pr(NO_3)_3 \cdot 6H_2O$ was replaced by $Sm(NO_3)_3 \cdot 6H_2O$ accordingly. The yield was 45%.

For $C_{37}H_{37}N_2O_{10}Sm$ ($M = 820.05$)

anal. calcd., %:	C, 54.19;	N, 3.42;	H, 4.55.
Found, %:	C, 54.11;	N, 3.38;	H, 4.41.

IR (KBr; ν, cm^{-1}): 3395 v, 2927 m, 1575 v.s, 1450 v.s, 1246 v.s, 1170 m, 1081 v, 745 v.s.

Compound **III** was synthesized by a method similar to that of **I**, except that $Pr(NO_3)_3 \cdot 6H_2O$ was replaced by $Nd(NO_3)_3 \cdot 6H_2O$ accordingly. The yield was 40%.

For $C_{37}H_{37}N_2O_{10}Nd$ ($M = 813.93$):

anal. calcd., %:	C, 54.60;	N, 3.44;	H, 4.58.
Found, %:	C, 54.50;	N, 3.40;	H, 4.56.

IR (KBr; ν, cm^{-}): 3390 v, 2920 m, 1580 v.s, 1435 v.s; 1240 v.s, 1165 m, 1083 v, 740 v.s.

X-ray crystallography. Single crystal X-ray diffraction analyses of the compounds were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan techniques; all structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [18]. Absorption corrections were applied by using multi-scan program SADABS. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The not good data of **III** were observed, which may be attributed to the small measurable crystals and the relatively bad quality of data. The water hydrogen atoms were refined with isotropic thermal parameters 1.5 times those of their carrier atoms. The H atoms of free water molecule were not located in a difference Fourier map. Table 1 shows crystallographic data of **I**–**III**. Selected bond distances and bond angles are listed in Table 2. Some H-bonded parameters are listed in Table 3.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1472729 (**I**), 1472730 (**II**), 1472734 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Compounds **I**–**III** are isostructural, herein, only the structure of **I** will be discussed in detailed as a representation. The asymmetric unit of **I** contains one Pr^{3+} ion, three ligands L, one 2,2'-Bipy, one lattice water molecule. As shown in Fig. 1, Pr^{3+} ion is nine-coordinated by four oxygen atoms from two η^1-η^1-μ_1 carboxylate groups of ligands L [19], two oxygen atoms from η^1-η^1-μ_2 carboxylate groups of ligands L, three oxygen atoms from η^1-η^2-μ_2 carboxylate groups of ligands L, and two nitrogen atoms from 2,2'-Bipy molecules. The ligands L show three different coordinative modes, resulting in a dinuclear unit with the separations between two neighboring Pr(III) being 4.0 Å. In addition, careful analysis reveals that the hydrogen bonded interaction association of solvent water molecules, phenolic groups and carboxylate groups in **I** leads to the formation of 2D supramolecular network. The O(3) from hydroxyl group taking as donor involves in O(1*w*) into a 1D chain, which are cross-lined by other H-bonded interactions between phenolic groups and free water molecules. It should be noted that there is not any packing interaction between rings from adjacent 2,2'-Bipy molecules, as shown in Fig. 2.

As to FT-IR spectra, both compounds show a broad band centered around 3390 cm^{-1} attributable to the O–H stretching frequency of the water molecule in **I**–**III**. Specifically, asymmetric stretching vibration ν(COO$^-$) appear around 1580 cm^{-1} for **I**–**III**, and the symmetric stretching vibration ν (COO$^-$) are observed 1450 cm^{-1} for **I**–**III**. For two complexes, the difference between the asymmetric and symmetric stretches, $\Delta\ \nu_{as}(COO^-) - \nu_s(COO^-)$, are on the order of 160 cm^{-1} indicating that carboxyl groups are coordinated to the metal in a bidentate modes [20], consistent with the observed X-ray crystal structures of **I**–**III**.

To study the stability of the polymers, TG analyses of complexes **I**–**III** were performed (Fig. 3). The TGA results of **I**–**III** show the same weight loss steps. Only weight loss character of the compound **I** was discussed. The first weight loss began at 38°C and completed at 135°C. The observed weight loss of 2.1% is corresponding to the loss of coordinated water molecules (calcd. 2.2%). After 165°C, the elimination of organic ligands was observed.

Table 1. Crystallographic data and structure refinement details for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Formula weight	1617.16	1636.04	1623.82
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/n$	$P2/n$	$P2/n$
a, Å	14.051(2)	14.018(3)	13.959(5)
b, Å	16.459(3)	16.366(3)	16.333(6)
c, Å	16.289(3)	16.387(3)	16.172(6)
α, deg	90	90	90
β, deg	110.903(2)	111.252(3)	110.609(5)
γ, deg	90	90	90
V, Å^3	3519.2(11)	3504.0(12)	3451(2)
Z	2	2	2
ρ_{calcd}, g/cm^3	1.526	1.551	1.563
μ, mm^{-1}	1.445	1.736	1.566
F(000)	1640	1652	1644
θ Range, deg	1.6–28.5	2.16–25.10	2.18–25.50
Reflection collected	24809	24409	29823
Unique reflections	8888	8655	7870
Reflections with $I > 2\sigma(I)$	7300	7303	5800
Refined parameters	454	454	454
R_{int}	0.0250	0.0201	0.0735
GOOF	1.04	1.02	0.93
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0272, 0.0656	0.0246, 0.0655	0.0418, 0.1146
R_1, wR_2 (all data)**	0.0382, 0.0724	0.0330, 0.0720	0.0659, 0.1470
Largest diff. peak and hole, e Å^{-3}	–0.73 and 0.99	–0.79 and 0.88	–1.29 and 1.65

* $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, ** $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$.

Additionally, to confirm the phase purity and stability of compounds **I–III**, the original samples were both characterized by XRPD. It can to be considered that the bulk synthesized materials and as-grown crystal are homogeneous for compounds **I–III**.

Metal-organic hybrid coordination polymers with lanthanide metal centers have been widely investigated for their fluorescence properties [21–27]. The lanthanides only exhibit weak emissions under direct excitation due to their low molar absorption. Lanthanide

Table 2. Selected bond distances (Å) and angles (deg) for **I**–**III**

Bond	*d*, Å	Bond	*d*, Å
I			
Pr(1)–O(1)	2.5199(19)	Pr(1)–O(2)	2.7104(18)
Pr(1)–O(4)	2.522(2)	Pr(1)–O(5)	2.5499(19)
Pr(1)–O(8)	2.4423(19)	Pr(1)–N(1)	2.654(2)
Pr(1)–N(2)	2.671(2)		
II			
Sm(1)–O(1)	2.3478(19)	Sm(1)–O(4)	2.3780(19)
Sm(1)–O(7)	2.5124(19)	Sm(1)–O(8)	2.482(2)
Sm(1)–N(1)	2.605(2)	Sm(1)–N(2)	2.627(2)
III			
Nd(1)–O(1)	2.410(3)	Nd(1)–O(4)	2.519(3)
Nd(1)–O(5)	2.487(4)	Nd(2)–O(7)	2.687(3)
Nd(1)–O(8)	2.492(3)	Nd(1)–N(1)	2.614(4)
Nd(1)–N(2)	2.627(5)		
Angle	ω, deg	Angle	ω, deg
I			
O(1)Pr(1)O(2)	49.18(5)	O(1)Pr(1)O(4)	143.68(6)
O(1)Pr(1)O(5)	144.76(6)	O(1)Pr(1)O(8)	82.49(6)
O(1)Pr(1)N(1)	72.59(6)	O(1)Pr(1)N(2)	69.83(6)
O(2)Pr(1)O(4)	149.46(6)	O(2)Pr(1)O(5)	142.46(6)
O(2)Pr(1)N(1)	114.59(6)	O(2)Pr(1)N(2)	112.10(6)
O(4)Pr(1)O(8)	129.36(6)	O(4)Pr(1)N(1)	94.80 (7)
O(4)Pr(1)N(2)	74.32(7)	O(5)Pr(1)N(2)	103.98(6)
II			
O(1)Sm(1)O(4)	74.35(6)	O(1)Sm(1)O(7)	126.32(6)
O(1)Sm(1)O(8)	79.40(6)	O(1)Sm(1)N(1)	139.37(7)
O(1)Sm(1)N(2)	78.36(7)	O(4)Sm(1)O(7)	78.86(6)
O(4)Sm(1)N(1)	145.62(6)	O(7)Sm(1)N(1)	73.72(7)
O(7)Sm(1)N(2)	104.11(7)	O(8)Sm(1)N(1)	94.91(7)
O(8)Sm(1)N(2)	73.76(7)		
III			
O(1)Nd(1)O(4)	79.07(12)	O(1)Nd(1)O(5)	129.58(11)
O(1)Nd(1)O(8)	82.32(10)	O(1)Nd(1)N(1)	78.30(12)
O(1)Nd(1)N(2)	135.79(13)	O(4)Nd(1)O(7)	142.28(11)
O(4)Nd(1)O(8)	144.67(11)	O(4)Nd(1)N(1)	74.26(12)
O(4)Nd(1)N(2)	104.20(13)	O(5)Nd(1)O(7)	149.21(10)
O(5)Nd(1)O(8)	143.71(11)	O(5)Nd(1)N(1)	95.04(12)
O(5)Nd(1)N(2)	74.19(12)		

Table 3. Geometric parameters of hydrogen bonds for complexes **I**–**III**

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
O(3)–H(3)···O(1*w*)	0.82	1.83	2.640(6)	172
O(6)–H(6*A*)···O(5)	0.82	1.85	2.665(3)	175
O(9)–H(9)···O(1)	0.82	1.90	2.717(3)	172
		II		
O(3)–H(3)···O(5)	0.82	1.91	2.724(3)	171
O(6)–H(6)···O(1*w*)	0.82	1.83	2.644(6)	171
O(9)–H(9)···O(7)	0.82	1.85	2.661(6)	170
		III		
O(3)–H(3)···O(8)	0.82	1.90	2.703(5)	165
O(6)–H(6)···O(4)	0.82	1.84	2.664(6)	177
O(9)–H(9)···O(1*w*)	0.82	1.84	2.651(11)	171
C(12)–H(12*B*)···O(6)	0.97	2.59	2.929(8)	101

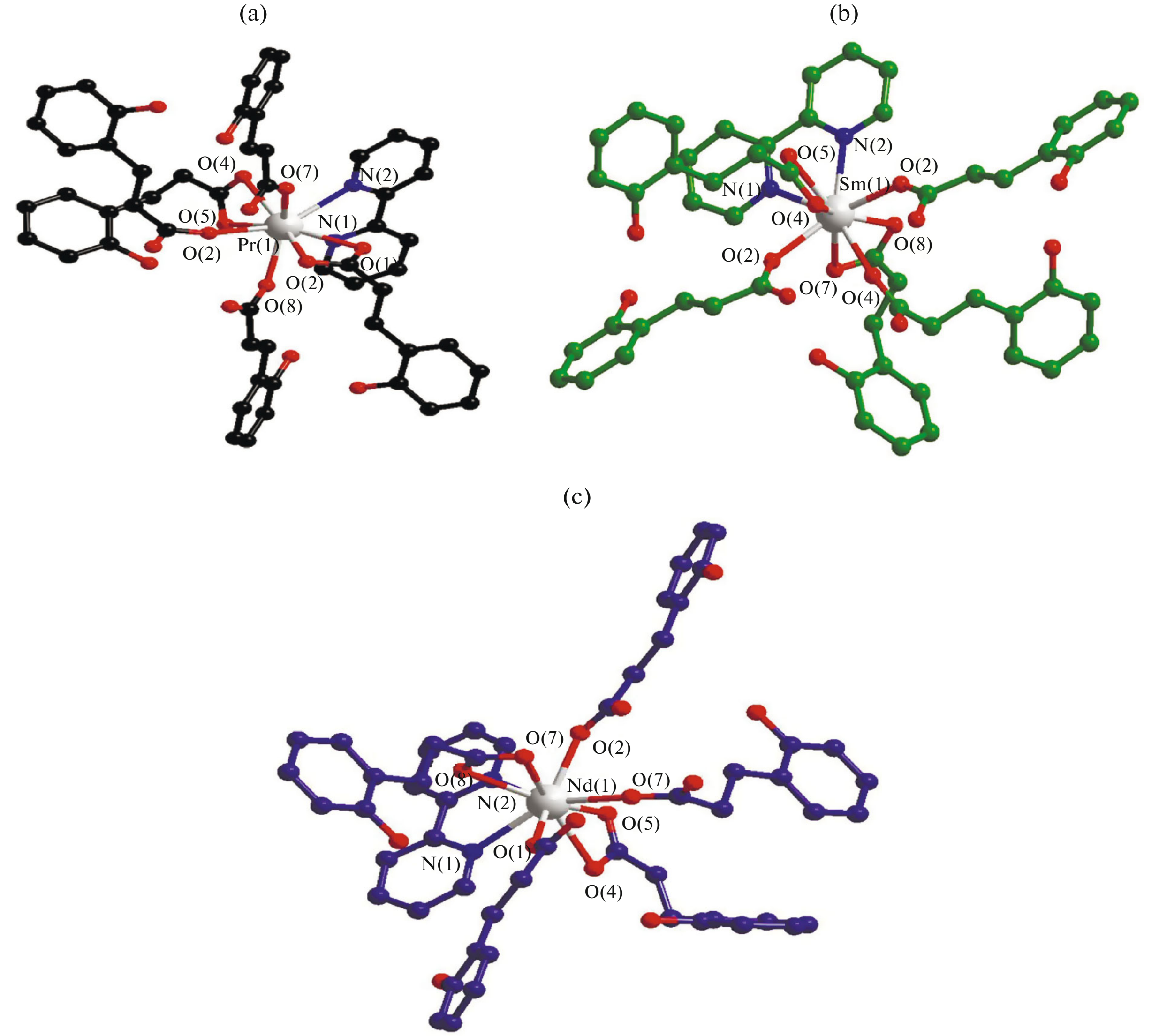

Fig. 1. The coordination geometries of the metal centers and the ligand geometry in **I** (a), **II** (b) and **III** (c). Displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity.

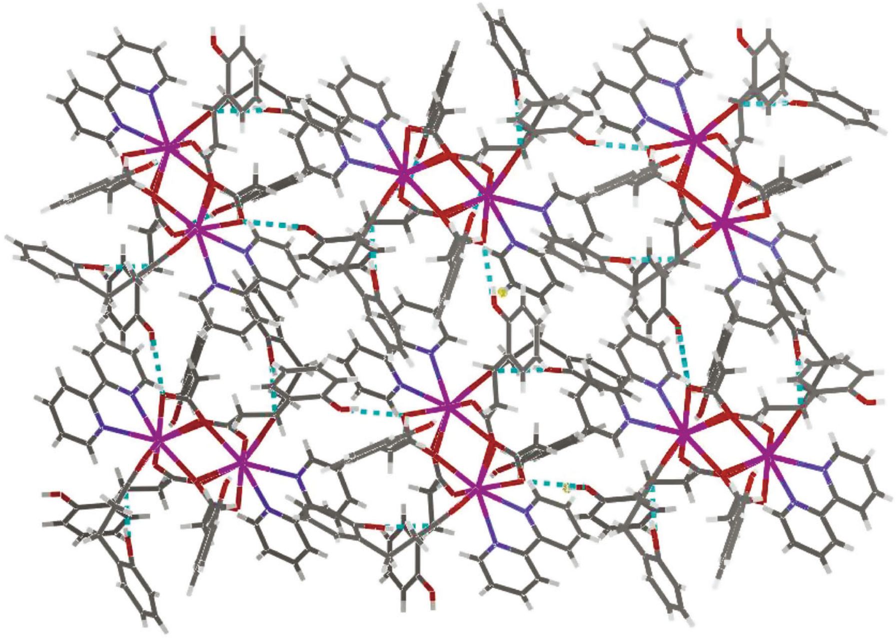

Fig. 2. Viewing of the 2D supramolecular layer along the *xy* plane.

centered emission can be sensitized by coordinating ligands with π-systems, which can efficiently absorb and transfer the energy. The fluorescence behaviors of **I**–**III** were investigated at room temperature under the same excitation wavelength of 380 nm with the same interval of 3 nm, but only compound **III** shows an intense luminescence property. As shown in Fig. 4, emission peaks of **III** at 625 nm can be obtained under the excitation wavelength, which corresponds to $^5D_0 \rightarrow {}^7F_n$ (n = 1–4) transitions of Nd(III), respectively, indicating a moderately efficient ligand-to-metal energy transfer [28]. The observation of the symmetry-forbidden emission $^5D_0 \rightarrow {}^7F_1$ reveals the Nd^{3+} in **III** occupies sites with symmetry and an inversion center. The intensity of the $^5D_0 \rightarrow {}^7F_3$ transition is extremely sensitive to chemical bonds in the vicinity of Nd^{3+}, which increase as the sites symmetry of Nd^{3+} center decrease, while the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition depends only slightly on the nature of the environment of the Nd^{3+} center [29].

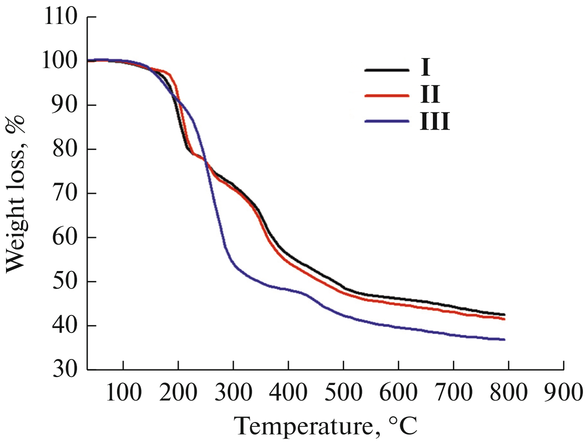

Fig. 3. TG curves for compounds **I**–**III**.

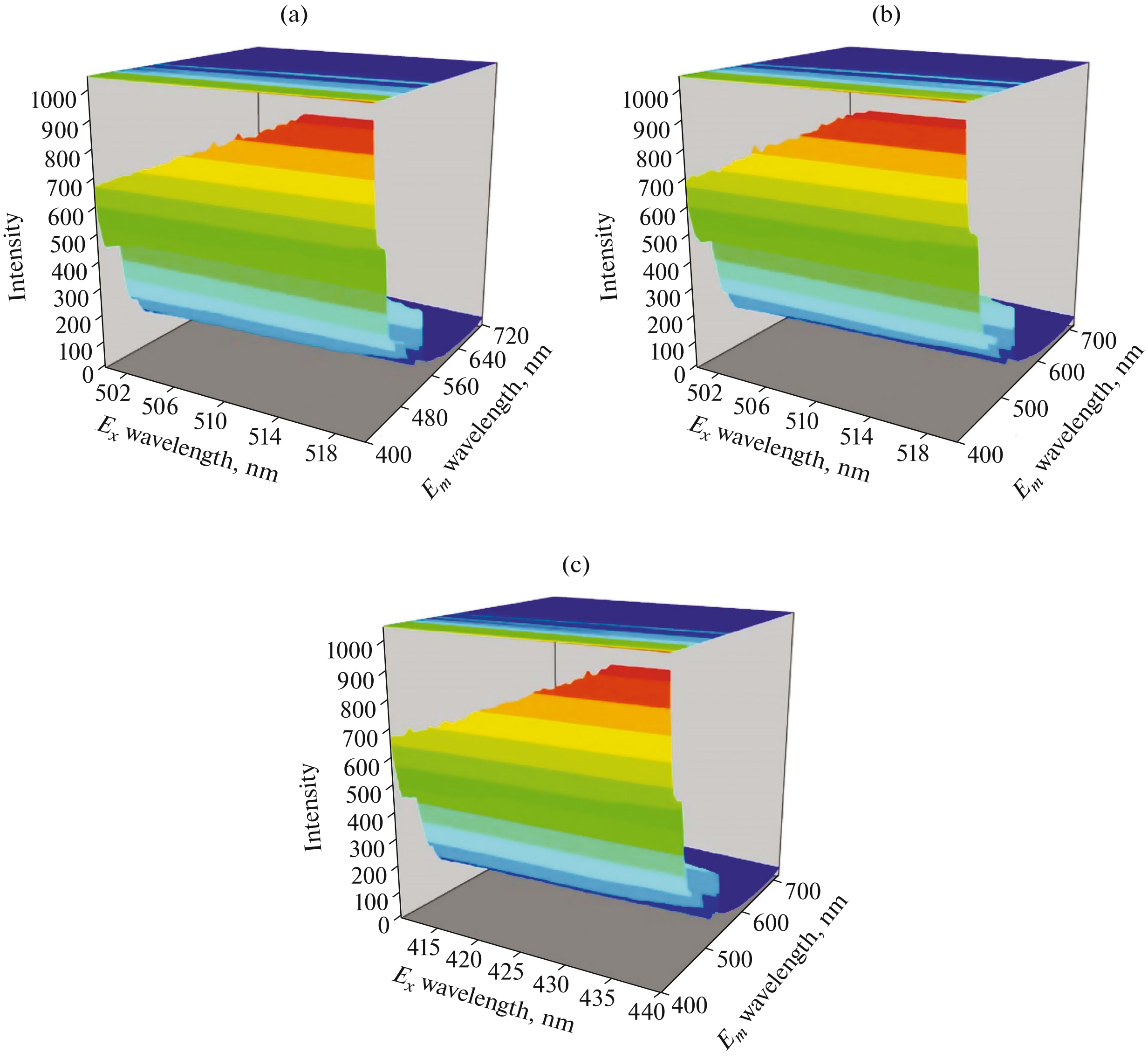

Fig. 4. Emission spectra of compounds **I–III** at room temperature.

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