



Crystal structure and luminescence property of novel three-dimensional network of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$

M. Wang^{a,*}, J. Xia^a, L. Jin^a, G. Cai^b, S. Lu^c

^aDepartment of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

^bChemical Defense Institute, PLA, Beijing 102205, People's Republic of China

^cLaboratory of Excited State Processes, Chinese Academy of Science, Changchun 130021, People's Republic of China

Received 3 March 2003; revised 1 May 2003; accepted 14 May 2003

Abstract

The single crystal of a supramolecule, $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ ($p\text{-BDC} = 1,4\text{-benzenedicarboxylate}$), with characteristic luminescence of Eu^{3+} was obtained by means of soft chemistry. The crystal structure determination reveals that each Eu^{3+} ion is coordinated by five oxygen atoms of $p\text{-BDC}$ anions, one oxygen atom from water molecule, and two nitrogen atoms of Phen, respectively, resulting in an eight-coordinated Eu^{3+} center and a distorted square antiprism coordination polyhedron. Four bridges, two carboxylates of $\mu_4\text{-}p\text{-BDC}$ and two of $\mu_3\text{-}p\text{-BDC}$, connect two Eu atoms into a binuclear unit. Moreover, the $\mu_3\text{-}p\text{-BDC}$ integrates the binuclear building blocks at the direction of b axis and the $\mu_4\text{-}p\text{-BDC}$ polymerizes the structure roughly along the direction of the sum vector of axis b and c , respectively, forming two-dimensional layers. Hydrogen bonds between layers make the structure a three-dimensional network. The luminescence spectra measured under 77 K demonstrate the antenna effect of Phen and the ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ energy transfer path within Eu^{3+} ion. Both luminescence spectra and crystal structure lead to the conclusion that the local symmetry around the Eu^{3+} ion is C_1 and that more than one Eu^{3+} ion sites having slight environmental difference are present.

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Keywords: Crystal structure; Luminescence; Europium; $p\text{-Benzenedicarboxylate}$; Coordination polymer

1. Introduction

The increasing interest in metal–organic open frameworks in view of their potential application in catalysis, separation and ion exchange processes [1–3] is one aspect of modern coordination chemistry. Among the various organic ligands, benzenedicarboxylic acid (H_2BDC) has been used to obtain

many extended structures by virtue of exodentate coordination mode [4–10]. Like most of the metal–BDC frameworks, the recently reported three-dimensional networks containing lanthanides [4,5] were obtained under hydrothermal conditions. In both polymers, lanthanide ions are bound to several water molecules and saturate the coordination number.

In the work presented here, we chose BDC as key building block to link metal ions, and a nitrogen-donor Lewis base, 1,10-phenanthroline (Phen), an excellent light-harvester for luminescence of Eu^{3+} ion, to assemble coordination polymers of Eu^{3+} ion with

* Corresponding author. Tel.: +86-10-6220-7838 fax: +86-10-6220-5062.

E-mail address: wangmingzhao976@sohu.com (M. Wang).

characteristic structures and intense luminescence. Furthermore, more moderate synthetic conditions than hydrothermal ones is our additional target. Successfully, single crystals of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ ($p\text{-BDC} = 1,4\text{-benzenedicarboxylate}$), with red-luminescence under UV light were obtained.

2. Experimental

2.1. Preparation of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$

An ethanol–water (3/1 v/v) solution with 0.5 mmol $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and a solution containing 1 mmol $p\text{-H}_2\text{BDC}$, 2 mmol KOH and 0.5 mmol Phen in the same solvent were separately put into both sides of an U-type glass tube filled with agar solution. The tube was sealed. Pale yellow needle crystals were obtained in the agar region after several months.

2.2. Crystal structure determination

The X-ray data collection was carried out by an automated Rigaku AFC7R diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct and heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Texsan crystallographic software package of Molecular Structure Corporation. The crystal data and experimental details are shown in Table 1.

2.3. Luminescence spectra measurements

The luminescence spectra were recorded with YAG/Nd³⁺ laser using Spex1403 double grating monochromator. High-resolution spectra were obtained at 77 K using PLT-2000 laser (Rhodamine 6G) pumped by N₂ laser.

3. Results and discussion

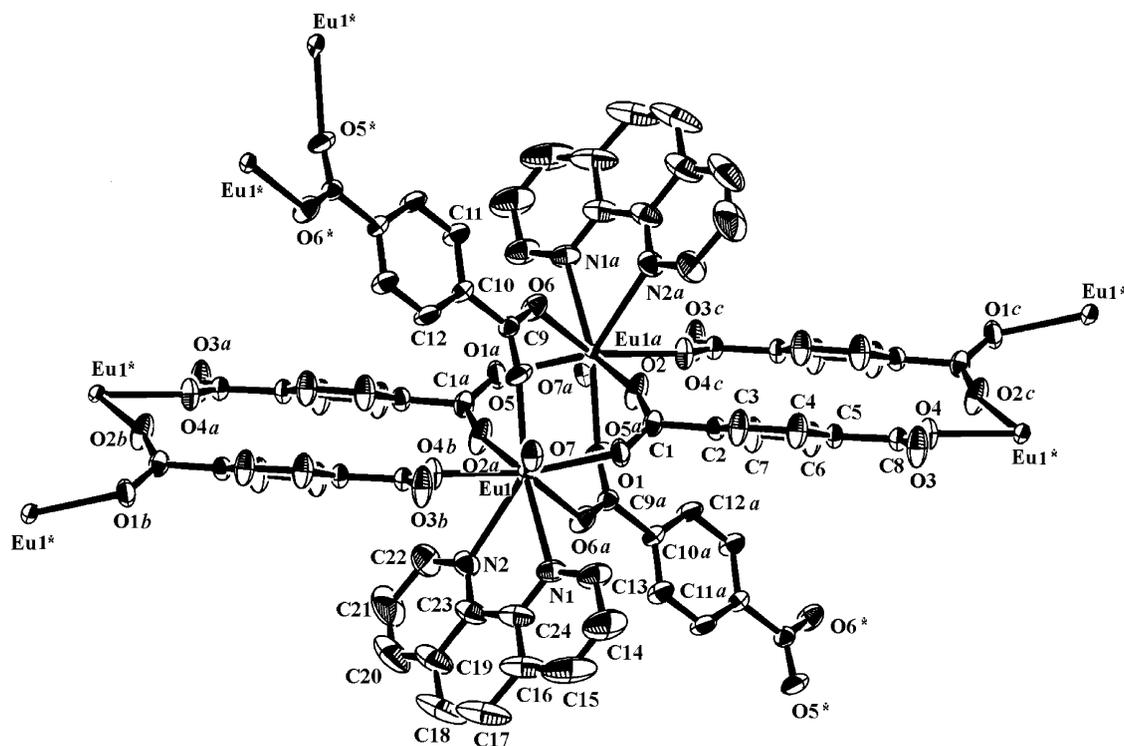
The extended molecular structure and the crystal packing of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ as viewed

Table 1
Crystal data for $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$

Formula weight	1192.72
Temperature	293 K
Radiation	0.71073 \AA
Crystal system	Triclinic
Space group	P_1
Unit cell dimensions	$a = 10.847(2) \text{ \AA}$, $b = 11.367(1) \text{ \AA}$, $c = 10.293(2) \text{ \AA}$, $\alpha = 91.80(1)^\circ$, $\beta = 112.91(1)^\circ$, $\gamma = 107.65(1)^\circ$
Volume	1097.6(3) \AA^3
Z	1
Density (calculated)	1.804 g cm^{-3}
Absorption coefficient	29.00 cm^{-1}
$F(000)$	586.00
Crystal size	0.20 \times 0.20 \times 0.30 mm^3
$2\theta_{\text{max}}$	51°
Index range	$0 \leq h \leq 13$, $-3 \leq k \leq 8$, $-12 \leq l \leq 0$
Reflections collected	4330
Independence reflections	4100
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4100/0/308
Goodness-of-fit on F^2	1.35
Final R indices ($I > 3\sigma(I)$)	$R_1 = 0.020$, $\omega R_2 = 0.028$
Largest differential peak and hole	1.085 and $-0.723 \text{ e \AA}^{-3}$

along the c -axis are presented in Figs. 1 and 2, respectively. The selected bond lengths and bond angles are tabulated in Table 2.

In $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$, each Eu^{3+} ion coordinates to five oxygen atoms of $p\text{-BDC}$ anions in monodentate fashion with a typical $\text{Eu}-\text{O}$ (carboxylate) distance range (2.309(2) ~ 2.401(2) \AA) [11–13], one water molecule with a longer $\text{Eu}-\text{O}$ distance (2.498(2) \AA), and two nitrogen atoms of Phen in chelating fashion with $\text{Eu}-\text{N}$ distances of 2.599(3) and 2.629(3) \AA , respectively, resulting in an eight-coordinated Eu center with a distorted square antiprism coordination polyhedron (Fig. 3). The four oxygen atoms (O1 and O2a from two $\mu_3\text{-}p\text{-BDC}$ s as well as O5 and O6a from two $\mu_4\text{-}p\text{-BDC}$ s) construct a good square plane. The average distance from the plane to the four oxygen atoms is only 0.0345 \AA . However, the other square composed of four different coordination atoms, N1, N2, O4b and O7, is seriously distorted. The rigidity and the bulkiness of the Phen molecule cause the two nitrogen atoms to form the longest coordination bonds and limit the bonding



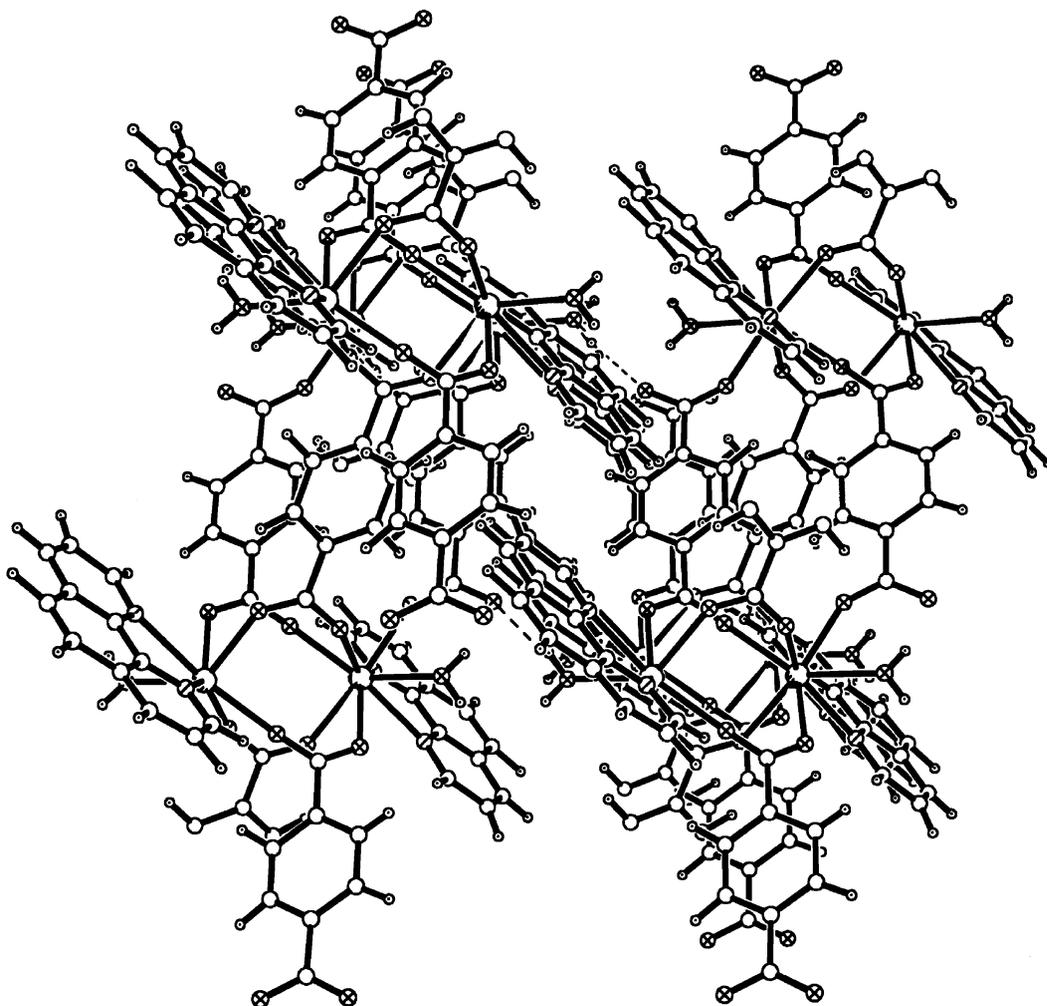


Fig. 2. Crystal packing of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ as viewed along the c -axis.

and very weak one of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ are observed when the delay time is set to 2 μs . As the time delay is increased, ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$ transition bands become weaker and very weak ${}^5\text{D}_1 \rightarrow {}^7\text{F}_2$ transition bands is found at 20 μs . Both bands disappear after 100 μs while the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-2}$ emission bands appear and increase. After 1000 μs , the intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2}$ emission bands decrease evidently. The results show that the lowest triplet state of the ligands and the ${}^5\text{D}_1$ level match well, the energy transfer from the lowest triplet state of the ligands to Eu^{3+} ion is effective, the lifetime of ${}^5\text{D}_1$ is shorter than ${}^5\text{D}_0$ emission level, and the energy transfer path within Eu^{3+} ion is ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ followed by ${}^5\text{D}_0$ emission.

In Fig. 5, the splitting of the ${}^7\text{F}_{1,2}$ sublevels and the appearance of a ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ band suggest a low-symmetry such as C_i , C_s and C_n around the Eu^{3+} ion, according to the rule [14], while the rather big width of halfheight (23.2 cm^{-1}) of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ band as well as the presence of four sublevels for ${}^7\text{F}_1$ and eight for ${}^7\text{F}_2$ indicate more than one Eu^{3+} ion sites in the crystal. The emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, a so-called hypersensitive transition, is bigger than that of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition pointing to non-centrosymmetry of the Eu^{3+} ion sites. We therefore reach the conclusion that the Eu^{3+} ion has a local C_1 symmetry, and that there are more than one kind of metal ion environments in our coordination

Table 2
Selected bond distances (Å) and bond angles (°)

<i>Bond lengths</i>							
Eu–Eu1a	4.3198(6)	Eu–O1	2.385(2)	Eu–O2a	2.354(2)	Eu–O4b	2.350(2)
Eu–O5	2.309(2)	Eu–O6a	2.401(2)	Eu–O7	2.498(2)	Eu–N1	2.599(3)
Eu–N2	2.629(3)						
<i>Bond angles</i>							
O1–Eu–O2a	124.68(8)	O2a–Eu–O4b	85.41(8)	O4b–Eu–O6a	142.59(8)	O5–Eu–N2	142.88(9)
O1–Eu–O4b	139.00(8)	O2a–Eu–O5	73.07(10)	O4b–Eu–O7	70.67(7)	O6a–Eu–O7	135.46(7)
O1–Eu–O5	80.05(8)	O2a–Eu–O6a	81.68(8)	O4b–Eu–N1	92.97(9)	O6a–Eu–N1	75.64(8)
O1–Eu–O6a	75.08(8)	O2a–Eu–O7	140.78(8)	O4b–Eu–N2	68.52(8)	O6a–Eu–N2	74.68(8)
O1–Eu–O7	68.64(7)	O2a–Eu–N1	140.01(9)	O5–Eu–O6a	124.35(8)	O7–Eu–N1	73.76(8)
O1–Eu–N1	80.56(8)	O2a–Eu–N2	79.82(9)	O5–Eu–O7	73.96(9)	O7–Eu–N2	116.86(8)
O1–Eu–N2	136.95(8)	O4b–Eu–O5	84.25(8)	O5–Eu–N1	146.62(9)	N1–Eu–N2	62.72(9)
<i>Intermolecular hydrogen bond</i>							
O3b–H16c	2.006(5)						

*Symmetry code *a* : $-x, -y, -z$; *b* : $x + 1, y, z + 1$; *c* : $-x, -y + 1, -z$.

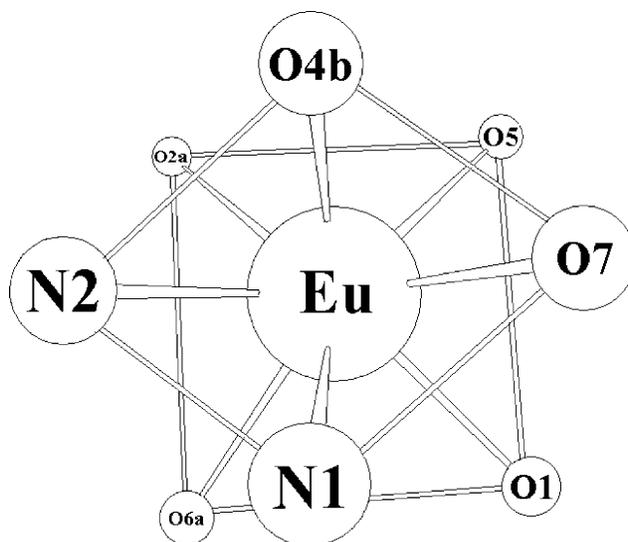


Fig. 3. Coordination polyhedron of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$.

Table 3
Geometric data of the coordination polyhedron of central Eu^{3+} ion

Interior angles of the square (°)				Edge lengths of the square (Å)			
O1–O5–O2a	92.71	O1–O6a–O2a	88.25	O2a–O5	2.78	O1–O5	3.02
O5–O1–O6a	89.13	O5–O2a–O6a	89.90	O1–O6a	2.92	O2–O6a	3.11
N2–N1–O7	98.01	N1–N2–O4b	80.97	O4b–O7	2.81	N1–O7	3.06
N2–O4b–O7	102.05	N1–O7–O4b	75.42	N1–N2	2.72	N2–O4b	2.81

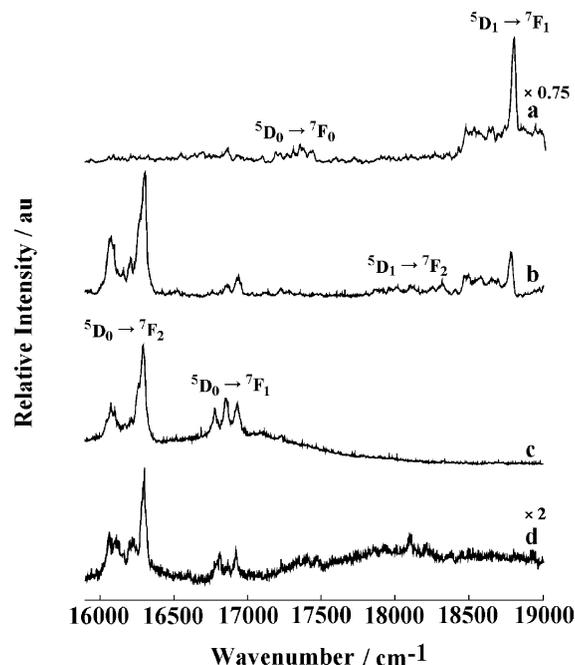


Fig. 4. Time resolved emission spectra of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ (77 K, $\lambda_{\text{ex}} = 355$ nm). Delay time/ μs : a = 2; b = 20; c = 100; d = 1000.

polymer, differing only slightly, which is in agreement with the distorted square antiprism coordination polyhedron and the binuclear coordination center evidenced from the crystal structure analysis.

4. Conclusion

Because of the introduction of Phen, the BDC anions do not construct a three-dimensional

microporous frameworks as in $\text{Tb}_2(p\text{-BDC})_3\cdot 4\text{H}_2\text{O}$ [4] or in the more sophisticated one found for $\text{Er}_4(p\text{-BDC})_6\cdot 6\text{H}_2\text{O}$ [5], but assemble an unique three-dimensional network. There is one crystallographically independent Eu^{3+} ion in our polymer which is similar to $\text{Tb}_2(p\text{-BDC})_3\cdot 4\text{H}_2\text{O}$ but the local coordination geometry is extremely different. Each Eu^{3+} ion in our polymer coordinates to five oxygen atoms of *p*-BDC anions, one oxygen atom from water molecule, and two nitrogen atoms of Phen, respectively, resulting in an eight-coordinated Eu^{3+} center and a distorted square antiprism coordination polyhedron with C_1 local symmetry. Different from the coordination modes of BDC in the reported two structures, the *p*-BDC uses two bonding modes, bidentate μ_2 - and monodentate μ_1 - carboxylates. The hydrogen bonds that are not found in the two frameworks of Er and Tb exit in our polymer and develop the structure into three-dimensional network.

The luminescence spectra measured under 77 K demonstrate the antenna effect of Phen as expected. The $^5\text{D}_1 \rightarrow ^5\text{D}_0$ energy transfer path within Eu^{3+} ion is revealed by the time resolved emission spectra. The luminescence bands of $^5\text{D}_0 \rightarrow ^7\text{F}_{0-2}$ transitions of Eu^{3+} ion lead to the conclusion of the C_1 local symmetry of Eu^{3+} ion and more than one Eu^{3+} ion sites with slight environmental deference in the polymer which is in agreement with the result of crystal structure analysis.

The results show that the richer and varied coordination polymers with unique photophysical properties could be obtained under various synthetic conditions by means of the careful selection of appropriate ligands.

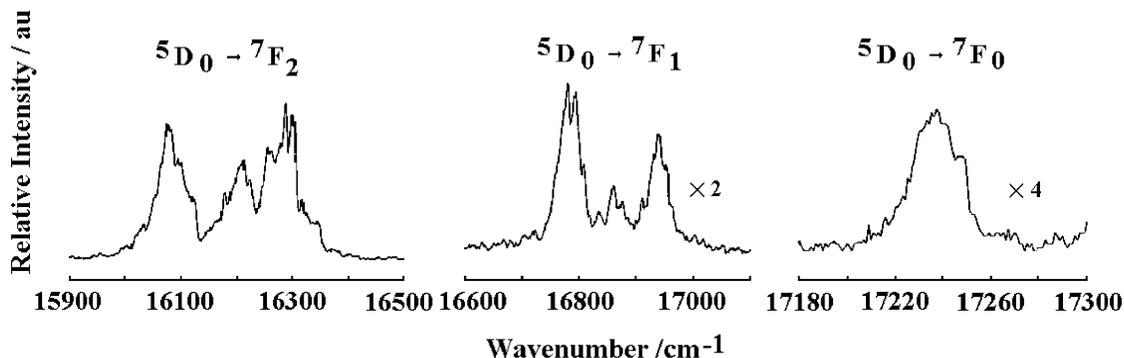


Fig. 5. Luminescence spectra of $\{\text{Eu}_2(p\text{-BDC})_3(\text{Phen})_2(\text{H}_2\text{O})_2\}_n$ (77 K, $\lambda_{\text{ex}} = 355$ nm).

Acknowledgements

We are grateful to State Key Project of Foundational Research of China (G1998061308) and the National Nature Science Foundation of China (G200071004) for support of this research.

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