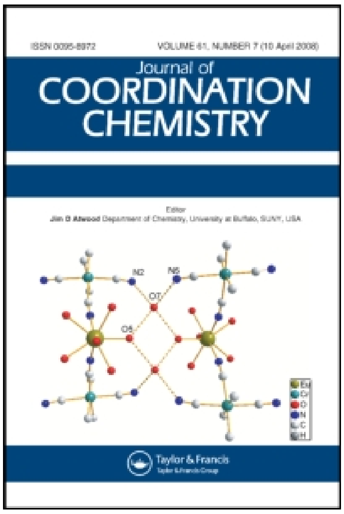

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CRYSTAL STRUCTURE AND LUMINESCENCE OF (4, 4' -DIMETHYL-2, 2' -BIPYRIDINE)-TRIS(BENZOATE)EUROPIUM(III)

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CRYSTAL STRUCTURE AND LUMINESCENCE OF (4,4′-DIMETHYL-2,2′-BIPYRIDINE)-TRIS(BENZOATE)EUROPIUM(III)

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A mixed ligand europium complex, $[Eu(BA)_3dmbpy]_2$, has been prepared, where BA = benzoate and dmbpy = 4,4′-dimethyl-2,2′-bipyridine. The complex crystallizes in the triclinic system, space group $P\bar{1}$. Its structure has been determined using X-ray diffraction methods. The two europium ions in the molecule are held together by four carboxylate groups of benzoic acid and each europium ion is further bonded to one bidentate carboxylate group and one 4,4′-dimethyl-2,2′-bipyridine molecule. Excitation and luminescence spectra observed at 77 K show that the europium site in the crystal has low symmetry and changes of the chemical surroundings of the europium ion in the molecule depend mainly on the flexibility of 4,4′-dimethyl-2,2′-bibyridine.

Keywords: Europium; benzoic acid; 4,4′-dimethyl-2,2′-bipyridine; crystal structure; luminescence

INTRODUCTION

Structural studies of lanthanide carboxylate complexes have shown that the rare earth atoms have several types of coordination, usually with coordination number of eight or nine. The carboxylate group of organic acids may act in different ways in coordinating to lanthanide ions. When the

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carboxylate group is of a bidentate chelating or monodentate character, monomeric complexes are formed. A great number of lanthanide carboxylate complexes is found to be dimeric or polymeric. This depends on not only the nature of the organic acid, but also on characteristics of the central metal ion. Europium carboxylate hydrates luminesce weakly because of the quenching effect of coordinated water molecules. However, ternary europium carboxylate complexes with bipyridine or 1,10-phenanthroline result in strong emission of a red colour. The number and intensities of the peaks which arise from $^5D_0 \rightarrow {}^7F_J$ ($J = 0–6$) transitions of the europium ion are sensitive to the chemical environments of the ion,[1] especially $^5D_0 \rightarrow {}^7F_2$. This hypersensitivity can be used to probe environmental changes of the central metal ion. X-ray diffraction analysis combined with site-selective excitation spectroscopy provides more information of molecular structures and metal ion sites. As part of our continuing study of europium carboxylate complexes with nitrogen-containing ligands we have synthesized and studied a number of europium benzoate (or its derivatives) complexes with bipyridine or 1,10-phenanthroline.[2–8] The present paper reports the crystal structure and luminescence of (4,4′-dimethyl-2,2′-bipyridine)tris-(benzoate)europium(III).

EXPERIMENTAL

Preparation

A stoichiometric amount of benzoic acid and 4,4′-dimethyl-2,2′-bipyridine was dissolved in 95% C_2H_5OH. The pH of the solution was adjusted to ~6.5 with 1 M NaOH solution, and the mixture was added dropwise to an ethanolic $EuCl_3$ solution. The mixture was heated under reflux with stirring for a few hours, when a white precipitate formed. Crystals of $Eu(BA)_3dmbpy$ suitable for X-ray analysis were obtained from the mother liqour after a month. *Anal.* Calcd.(%): C, 56.66; H, 3.89; N, 4.01. Found: C, 56.41; H, 3.68; N, 3.73.

X-ray Structure Determination

Crystal Data

$Eu_2C_{66}H_{54}N_4O_{12}$, M = 1399.09, triclinic, space group $P\bar{1}$, $a = 11.505(3)$, $b = 12.949(4)$, $c = 11.350(5)$ Å, $\alpha = 104.63$, $\beta = 100.02(3)$, $\gamma = 64.09(2)°$, $V = 1467.7(9)$ Å^3, $Z = 1$, $Dc = 1.583$ g cm^{-3}, $\lambda(MoK_\alpha) = 0.71069$ Å. $\mu = 21.80$ cm^{-1}, $F(000) = 700$.

A colourless prismatic crystal with dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre. Intensity data were measured on a Rigaku AFC-7R diffractometer at 20 ± 1°C using the ω–2θ scan technique to a maximum 2θ value of 50°. Data were corrected for Lorentz and polarization effects. Empirical absorption corrections were used. Of the 4536 reflections collected, 4254 were unique ($R_{int} = 0.0019$).

The structure was solved by the Patterson method[9] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Reliability factors are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$. All calculations were performed using TEXSAN crystallographic software package.[10] The final R and R_w values were 0.020 and 0.026, respectively. Details of X-ray data collection, structure solution and refinement, and complete F_c and F_o tables and thermal parameter, H atom positions and full lists of bond lengths and angles are available from Linpei Jin upon request.

Excitation and Luminescence Measurements

Excitation and luminescence spectra of the title complex were recorded as described previously.[11]

RESULTS AND DISCUSSION

Structure of $[Eu(BA)_3dmbpy]_2$

The structure of (4,4′-dimethyl-2,2′-bipyridine)tris(benzoate)europium(III) is shown in the Figure 1. The structure consists of centrosymmetric dimers in which europium(III) ions are connected by four ligands through the carboxylate groups. The carboxylate groups of the four molecules of benzoic acid are bidentate bridging and terdentate, chelating-bridging. Two of the four carboxylate groups simultaneously bridge two europium(III) ions and the other two carboxylate groups chelate one europium ion and at the same time bridge two europium(III) ions. Each europium(III) ion is further coordinated to one chelating carboxylate group and one 4,4′-dimethyl-2,2′-bipyridine molecule to form nine-coordinated metal ions.

Final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are given in Table I, and bond lengths and angles in Tables II and III, respectively.

The Eu–Eu distance is 4.000 Å and is similar to that in (2,2′-bipyridine)-tris(p-chlorobenzoate)europium(III), 4.048 Å. The latter complex has a

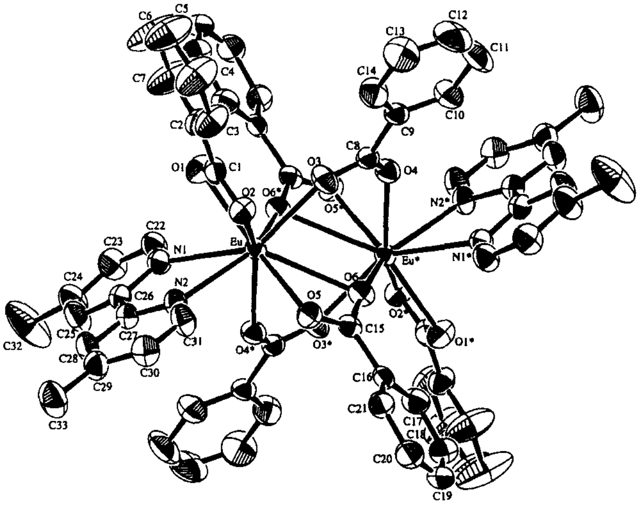

FIGURE 1 The molecular structure of the dimer of (4,4′-dimethyl-2,2′-bipyridine)-tris(benzoate)europium(III).

TABLE I Fractional atomic coordinates and equivalent thermal parameters

Atom	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)
Eu	0.10794(1)	−0.17059(1)	−0.00378(1)	2.193(4)
O(1)	0.1725(2)	−0.3285(2)	−0.1768(2)	3.42(5)
O(2)	0.0586(2)	−0.3492(2)	−0.0542(2)	3.19(5)
O(3)	−0.0896(2)	−0.1313(2)	−0.1278(2)	3.51(5)
O(4)	−0.1890(2)	0.0531(2)	−0.1550(2)	2.96(5)
O(5)	−0.0070(2)	−0.1390(2)	0.1706(2)	2.95(5)
O(6)	−0.0889(2)	0.0300(2)	0.1113(2)	2.94(5)
N(1)	0.3572(2)	−0.2218(2)	−0.0179(2)	2.82(6)
N(2)	0.2809(2)	−0.3266(2)	0.1095(2)	2.98(6)
C(1)	0.1102(3)	−0.3805(3)	−0.1522(3)	2.90(7)
C(2)	0.0980(3)	−0.4804(3)	−0.2464(3)	3.32(7)
C(3)	0.0369(4)	−0.5430(3)	−0.2259(4)	4.50(10)
C(4)	0.0268(5)	−0.6349(4)	−0.3142(5)	6.1(1)
C(5)	0.0771(6)	−0.6645(5)	−0.4217(5)	7.2(2)
C(6)	0.1371(8)	−0.6017(6)	−0.4448(5)	9.6(2)
C(7)	0.1485(6)	−0.5098(5)	−0.3569(4)	6.9(1)
C(8)	−0.1797(3)	−0.0497(3)	−0.1706(3)	2.62(7)
C(9)	−0.2868(3)	−0.0776(3)	−0.2467(3)	2.83(7)
C(10)	−0.4007(4)	0.0101(4)	−0.2815(4)	4.10(9)
C(11)	−0.5014(4)	−0.0151(5)	−0.3458(4)	5.7(1)
C(12)	−0.4871(5)	−0.1283(5)	−0.3759(5)	6.3(1)
C(13)	−0.3762(5)	−0.2162(5)	−0.3445(5)	5.9(1)
C(14)	−0.2762(4)	−0.1913(4)	−0.2797(4)	4.14(9)
C(15)	−0.0699(3)	−0.0303(3)	0.1917(3)	2.48(6)
C(16)	−0.1221(3)	0.0308(3)	0.3142(3)	2.54(6)
C(17)	−0.1537(3)	0.1492(3)	0.3568(3)	3.44(8)
C(18)	−0.1938(4)	0.2010(4)	0.4738(3)	4.28(9)
C(19)	−0.2033(3)	0.1374(4)	0.5475(3)	4.21(9)

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)
C(20)	−0.1731(4)	0.0197(4)	0.5058(3)	4.12(9)
C(21)	−0.1323(3)	−0.0333(3)	0.3895(3)	3.33(8)
C(22)	0.3914(3)	−0.1599(3)	−0.0722(3)	3.50(8)
C(23)	0.5127(4)	−0.1586(4)	−0.0554(4)	4.05(9)
C(24)	0.6062(3)	−0.2255(4)	0.0197(4)	4.52(10)
C(25)	0.5725(3)	−0.2917(4)	0.0741(4)	4.17(9)
C(26)	0.4492(3)	−0.2887(3)	0.0548(3)	2.86(7)
C(27)	0.4089(3)	−0.3540(3)	0.1178(3)	2.89(7)
C(28)	0.4961(4)	−0.4372(3)	0.1833(3)	3.67(8)
C(29)	0.4546(3)	−0.4944(3)	0.2438(3)	3.65(8)
C(30)	0.3240(4)	−0.4657(3)	0.2333(4)	3.85(8)
C(31)	0.2430(4)	−0.3845(3)	0.1662(3)	3.65(8)
C(32)	0.7387(6)	−0.2232(9)	0.0456(7)	9.0(2)
C(33)	0.5489(4)	−0.5827(4)	0.3169(5)	5.3(1)

TABLE II Bond lengths (Å) for the complex

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Eu	Eu*	4.000	Eu	O(1)	2.396(2)
Eu	O(2)	2.523(2)	Eu	O(3)	2.375(2)
Eu	O(4)*	2.388(2)	Eu	O(5)	2.421(2)
Eu	O(6)	2.786(2)	Eu	O(6)*	2.352(2)
Eu	N(1)	2.671(3)	Eu	N(2)	2.570(3)
O(1)	C(1)	1.277(4)	O(2)	C(1)	1.243(4)
O(3)	C(8)	1.246(4)	O(4)	C(8)	1.256(4)
O(5)	C(15)	1.250(4)	O(6)	C(15)	1.277(4)
N(1)	C(22)	1.337(4)	N(1)	C(26)	1.345(4)
N(2)	C(27)	1.347(4)	N(2)	C(31)	1.339(4)
C(1)	C(2)	1.498(5)	C(2)	C(3)	1.363(5)
C(2)	C(7)	1.369(5)	C(3)	C(4)	1.382(6)
C(4)	C(5)	1.337(7)	C(5)	C(6)	1.367(7)
C(6)	C(7)	1.385(7)	C(8)	C(9)	1.501(4)
C(9)	C(10)	1.382(5)	C(9)	C(14)	1.380(5)
C(10)	C(11)	1.378(6)	C(11)	C(12)	1.359(7)
C(12)	C(13)	1.352(7)	C(13)	C(14)	1.370(6)
C(15)	C(16)	1.496(4)	C(16)	C(17)	1.384(5)
C(16)	C(21)	1.383(4)	C(17)	C(18)	1.385(5)
C(18)	C(19)	1.359(6)	C(19)	C(20)	1.378(6)
C(20)	C(21)	1.383(5)	C(22)	C(23)	1.382(5)
C(23)	C(24)	1.368(5)	C(24)	C(25)	1.381(5)
C(24)	C(32)	1.513(6)	C(25)	C(26)	1.383(5)
C(26)	C(27)	1.484(4)	C(27)	C(28)	1.385(5)
C(28)	C(29)	1.388(5)	C(29)	C(30)	1.372(5)
C(29)	C(33)	1.502(5)	C(30)	C(31)	1.362(5)

similar bridging structure. The fact that europium ions are bridged by two chelating-bridging carboxylate groups causes a smaller Eu–Eu distance in comparison with other dimeric carboxylate complexes. The main difference between unbound 4,4′-dimethyl-2,2′-bipyridine and the coordinated ligand

TABLE III Bond angles (°) for the complex

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(1)	Eu	O(2)	53.14(7)	O(1)	Eu	O(3)	78.22(8)
O(1)	Eu	O(4)*	142.30(8)	O(1)	Eu	O(5)	131.88(7)
O(1)	Eu	O(6)	148.21(7)	O(1)	Eu	O(6)*	93.54(8)
O(1)	Eu	N(1)	75.41(8)	O(1)	Eu	N(2)	82.26(8)
O(2)	Eu	O(3)	70.77(8)	O(2)	Eu	O(4)*	143.71(7)
O(2)	Eu	O(5)	78.81(7)	O(2)	Eu	O(6)	113.34(7)
O(2)	Eu	O(6)*	135.20(7)	O(2)	Eu	N(1)	113.21(7)
O(2)	Eu	N(2)	71.26(8)	O(3)	Eu	O(4)*	133.90(7)
O(3)	Eu	O(5)	89.23(8)	O(3)	Eu	O(6)	69.98(7)
O(3)	Eu	O(6)*	73.84(7)	O(3)	Eu	N(1)	140.68(8)
O(3)	Eu	N(2)	141.84(8)	O(4)*	Eu	O(5)	76.08(7)
O(4)	Eu	O(6)	67.34(7)	O(4)	Eu	O(6)*	81.09(7)
O(4)	Eu	N(1)	66.91(8)	O(4)	Eu	N(2)	78.82(8)
O(5)	Eu	O(6)	49.44(7)	O(5)	Eu	O(6)*	127.41(7)
O(5)	Eu	N(1)	130.06(7)	O(5)	Eu	N(2)	79.86(8)
O(6)	Eu	O(6)*	78.10(7)	O(6)	Eu	N(1)	131.27(7)
O(6)	Eu	N(2)	123.42(7)	O(6)*	Eu	N(1)	79.21(7)
O(6)	Eu	N(2)	140.28(8)	O(1)	Eu	N(2)	61.45(8)
Eu	O(1)	C(1)	94.7(2)	Eu	O(2)	C(1)	89.6(2)
Eu	O(3)	C(8)	140.7(2)	Eu	O(5)	C(15)	102.2(2)
Eu	O(6)	Eu*	101.90(7)	Eu	O(6)	C(15)	84.5(2)
Eu	N(1)	C(22)	120.9(2)	Eu	N(1)	C(26)	120.2(2)
Eu	N(2)	C(27)	124.5(2)	Eu	N(2)	C(31)	118.7(2)
C(22)	N(1)	C(26)	116.8(3)	C(27)	N(2)	C(31)	116.8(3)
O(1)	C(1)	O(2)	121.9(3)	O(1)	C(1)	C(2)	118.1(3)
O(2)	C(1)	C(2)	120.0(3)	C(1)	C(2)	C(3)	121.8(3)
C(1)	C(2)	C(7)	119.6(3)	C(3)	C(2)	C(7)	118.5(3)
C(2)	C(3)	C(4)	120.8(4)	C(3)	C(4)	C(5)	120.7(4)
C(4)	C(5)	C(6)	119.3(4)	C(5)	C(6)	C(7)	120.5(5)
C(2)	C(7)	C(6)	120.0(4)	O(3)	C(8)	O(4)	125.8(3)
O(3)	C(8)	C(9)	116.6(3)	O(4)	C(8)	C(9)	117.6(3)
C(8)	C(9)	C(10)	121.1(3)	C(8)	C(9)	C(14)	120.8(3)
C(10)	C(9)	C(14)	118.0(3)	C(9)	C(10)	C(11)	120.9(4)
C(10)	C(11)	C(12)	119.1(4)	C(11)	C(12)	C(13)	121.3(4)
C(12)	C(13)	C(14)	119.8(5)	C(9)	C(14)	C(13)	120.8(4)
O(5)	C(15)	O(6)	121.3(3)	O(5)	C(15)	C(16)	119.5(3)
O(6)	C(15)	C(16)	119.3(3)	C(15)	C(16)	C(17)	121.5(3)
C(15)	C(16)	C(21)	119.4(3)	C(17)	C(16)	C(21)	119.0(3)
C(16)	C(17)	C(18)	119.8(3)	C(17)	C(18)	C(19)	121.0(4)
C(18)	C(19)	C(20)	119.9(3)	C(19)	C(20)	C(21)	119.7(4)
C(16)	C(21)	C(20)	120.6(4)	N(1)	C(22)	C(23)	124.2(3)
C(22)	C(23)	C(24)	119.3(3)	C(23)	C(24)	C(25)	116.9(3)
C(23)	C(24)	C(32)	121.4(4)	C(25)	C(24)	C(32)	121.6(4)
C(24)	C(25)	C(26)	121.3(3)	N(1)	C(26)	C(25)	121.5(3)
N(1)	C(26)	C(27)	116.3(3)	C(25)	C(26)	C(27)	122.1(3)
N(2)	C(27)	C(26)	116.1(3)	N(2)	C(27)	C(28)	121.1(3)
C(26)	C(27)	C(28)	122.8(3)	C(27)	C(28)	C(29)	121.2(3)
C(28)	C(29)	C(30)	116.6(3)	C(28)	C(29)	C(33)	121.1(3)
C(30)	C(29)	C(33)	122.3(3)	C(29)	C(30)	C(31)	119.7(3)
N(2)	C(31)	C(30)	124.5(3)				

lies in its conformation. The former is in the *trans* form[12] and the latter in the *cis* form. Corresponding bond distances in the pyridyl group show little change. C–C distances of the pyridyl groups including the C–C distance linking the two pyridyl groups slightly reduce when coordinated to the europium(III) ion while C–N distances increase.

In the carboxylate groups, C–O distances differ significantly; in the chelating carboxylate groups, coordination causes lengthening of C–O (1.243(4)–1.277(4) Å) for the bidentate-chelating carboxylate group and 1.250(4)–1.277(4) Å for the tridentate-chelating-bridging carboxylate group in comparison to the bidentate bridging carboxylate group (1.246(4)–1.256(4) Å). In the terdentate carboxylate group, one observes longer C–O distances when the oxygen atom coordinates two europium ions compared to when oxygen coordinates only to one europium(III) ion in the dimer. The O_6–O_{15}–O_5 angle in the terdentate chelating-bridging carboxylate group, 121.3(3)°, is approximately the same as the O_1–C_1–O_2 in the bidentate chelating carboxylate group, 121.9(3)°. This is characteristic of chelating carboxylate groups.

Carbon atoms of the dmbpy ring deviate from the average least-squares plane in the range +0.103(4) to −0.141(4) Å and the five atoms of the five-membered chelate ring containing the two nitrogen atoms of dmbpy deviate from the average least-squares plane in the range +0.007(3) to −0.105(3) Å. Therefore, neither the two pyridyl rings nor the pyridyl ring and the five-membered ring are coplanar. This is caused by the flexibility of the dmbpy and is a common feature for lanthanide benzoate complexes with 2,2′-bipyridine or its derivatives.

Luminescence Studies

The ground state $^7F_0$ and the excited state $^5D_0$ of the europium(III) ion are degenerate and not split by ligand field effects. Each Eu(III) environment may, in theory, give rise to a different peak in an $^7F_0 \rightarrow {}^5D_0$ excitation spectrum,[13] and the number of excitation peaks may reflect the number of Eu(III) species present. The excitation band of $Eu(BA)_3dmbpy$ is resolved into two peaks (580.00 and 580.14 nm) which differ in intensity. Since the $^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to the chemical surroundings of the Eu(III) ion in complexes, luminescence was recorded in the range 605–630 nm, which covers the $^5D_0 \rightarrow {}^7F_2$ emission band of the europium ion of $Eu(BA)_3dmbpy$ in detail. Luminescence spectra obtained upon non-selective and site-selective excitation are shown in Figure 2.

The upper trace (a) is an emission spectrum excited with 337.1 nm N_2 laser energy. The lower traces of (b) and (c) were obtained upon selective

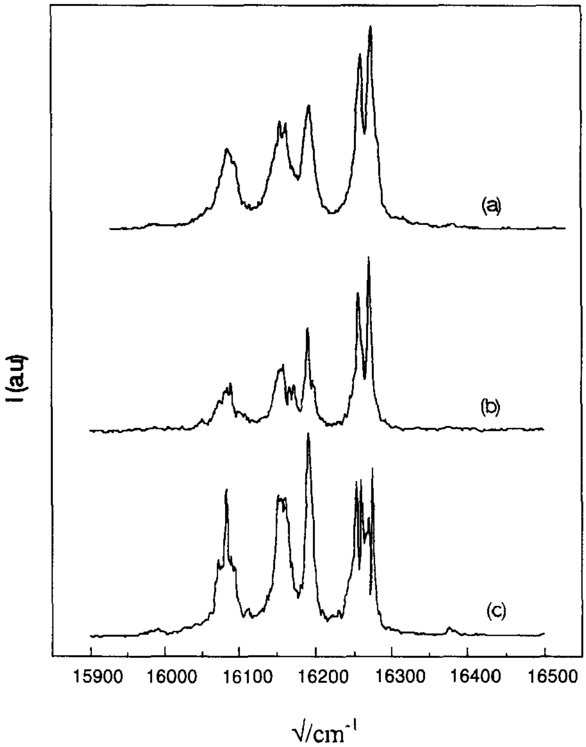

FIGURE 2 Luminescence spectra of Eu(BA)$_3$dmbpy measured at 77K; (a) $\lambda_{exc} = 337.1$ nm; (b) $\lambda_{exc} = 580.00$ nm; (c) $\lambda_{exc} = 580.14$ nm.

excitation at 580.00 and 580.14 nm, respectively. The non-selectively excited emission spectrum (a) shows six separate peaks which are more than $2J+1$ peaks. The selectively excited emission bands (b and c) show fine structure due to J-splitting. They differ from each other in band positions and intensities. Each trace is composed of more than $2J+1$ peaks which may arise from simultaneous excitation of the Eu ions in different surroundings. The fact that ${}^5D_0 \rightarrow {}^7F_0$ emission and $2J+1$ emission peaks in the range of the ${}^5D_0 \rightarrow {}^7F_2$ transition are observed implies that the Eu(III) site is of low symmetry,[1] in agreement with the X-ray analysis. The fact more than $2J+1$ emission peaks with different positions and rather strong intensities arise from the ${}^5D_0 \rightarrow {}^7F_2$ transition also indicates that the Eu(III) sites in the complex differ in chemical environment although this is not pronounced. These slightly different chemical environments are due to the non-rigidity of the dmbpy ligand. Any change in conformation of the complex results in an obvious effect on ${}^5D_0 \rightarrow {}^7F_2$ emission. This may be attributed to different stacking of the molecular components of the Eu(BA)$_3$dmbpy complex in the crystal and a transient perturbation of donor–acceptor interactions caused by rapid conversion of the non-planar geometry of the dmbpy ligand. The latter indicates the impact of non-equilibrium molecular dynamics occurring subsequent to electronic excitation.

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