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Polynitrile-bridged two-dimensional crystal: Eu(III) complex with strong fluorescence emission and NLO property

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The first polynitrile coordinated lanthanide complex $\{[Eu(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ (cda = carbamyldicyanomethanide anion) has been synthesized and the two-dimensional structure coordination polymer exhibits strong fluorescence emission and strong powder second harmonic generation efficiency (16.8 times that of urea).

Polynitrile compounds, such as tricyanomethanide, dicyanamide, 1,2,4,5-tetracyanobenzene and tetracyanoethene display versatile bridging behavior and many coordination polymers with useful properties have been constructed from such polynitriles and metal ions.[1] In the published work on polynitrile coordination complexes the coordinated metal ions are mainly transition metal ions and no lanthanide complexes have been reported. In terms of physical properties the focal point is on the magnetic interaction between polynitrile-bridged metal ions with only limited studies dealing with electrical conductance[2] and optical properties.[3] For the latter no fluorescence and NLO properties have been reported. Owing to its chemical structure the polynitrile ligand cda should be a very useful bridging ligand and can be used to construct coordination polymers with new structures and physical properties. Although complexes[4] of cda with Zn(II), Co(II), Ni(II), Cu(II) have been published, the crystal structures and physical properties of these complexes have not been reported.

The complex $\{[Eu(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ was obtained in about 85% yield by treating $Eu(ClO_4)_3\cdot 6H_2O$ and Na(cda) in H_2O.† The IR spectrum shows characteristic sharp peaks of the –CN groups at 2200, 2150 and 2145 cm^{-1} and bands due to $–CO(NH_2)$ appear at about 3350, 1620, 1535 and 1440 cm^{-1}. The complex crystallizes in the monoclinic space group *Cc*.‡ The Eu(III) ion is coordinated by three nitrogen atoms and five oxygen atoms; the three nitrogen atoms are from nitrile groups while of the five oxygen atoms three are from H_2O molecules and two are from amide groups. Generally speaking amide-oxygen atoms rarely takes part in coordination and the amide-oxygen atom coordination indicates that there is a strong conjugation in cda. The coordinated bond lengths range from 2.263(4) to 2.550(7) Å and the associated angles range from 69.10(18) to 147.68(19)°. These bonds lengths and angles indicate that the Eu(III) ion lies in a distorted dodecahedral environment (Fig. 1). In the crystal two types of coordination occur for cda. Two out of three cda ligands bridge Eu centers *via* nitrile-nitrogen and amide-oxygen while the remaining cda coordinates Eu(III) as a unidentate ligand *via* its nitrile-nitrogen atom. Coordination of μ_2-cda to Eu(III) leads to the formation of a two-dimensional sheet in the *ab* plane. Hydrogen bonding interactions lead to the sheets piling up along the *c* axis in a parallel manner to form a three-dimensional crystal structure.

The fluorescence spectra for Na(cda) and the complex were measured at room temperature in the solid state and in H_2O solution. In the solid state the maximum excited wavelengths are 464 nm for Na(cda) and 484 nm for the complex while the maximum emission bands are located at about 640 and 690 nm for Na(cda) and 660 and 726 nm for the complex as shown in Fig. 2. Fig. 3 shows the fluorescence spectra in H_2O solution, in which the maximum excited wavelength is 360 nm for both Na(cda) (1.5×10^{-3} mol L^{-1}) and the complex (5.6×10^{-4} mol L^{-1}), while the maximum emission peak is at 409 nm for Na(cda) and 408 nm for the complex. The peak shapes and the peak position of Na(cda) and the complex are very similar, both in H_2O solution and in the solid state, which implies that the fluorescence emission of the complex arises from cda. The chemical structures of organic fluorescing compounds[5] generally contain aromatic rings, fused aromatic rings or other conjugated ring systems along with fluorophores, such as =C=O, –N=O, –N=N–, >C=S, whereas cda dose not possess a conjugated ring structure and contains a fluorochromic group, –C≡N, which generally serves to decrease fluorescence in-

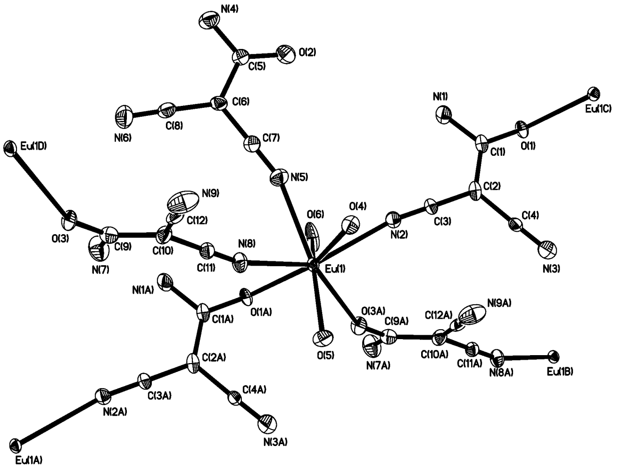

Fig. 1 An ORTEP drawing of $\{[Eu(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ with atom numbering scheme.

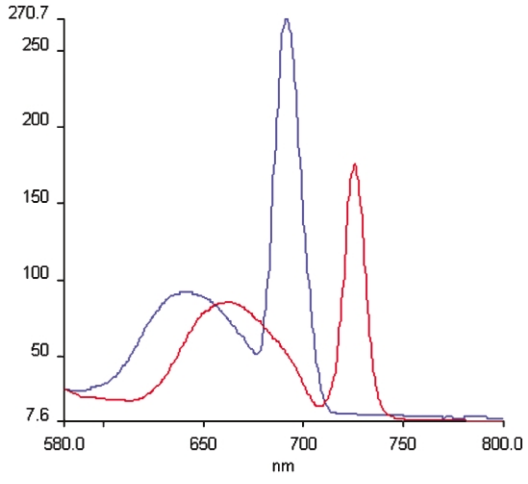

Fig. 2 The fluorescence spectra for Na(cda) (blue) and $\{[Eu(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ (red) in the solid state.

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tensity or quenches fluorescence emission. In order to understand the fluorescence emission mechanism of cda, *ab initio* Cis/6-31G(d, p) calculations with the Gaussian 94 program were conducted under the condition of the absence of a potential field around cda. The calculation results indicate that there is a rigid conjugated planar structure in cda both in the ground and excited state. The calculation results also indicate that there exists a transition peak at 458.80 nm assignable to a $\pi \rightarrow \pi^*$ transition and may be the reason why cda exhibits the property of fluorescence emission. Figs. 2 and 3 also show that the peak shapes and the peak position will change with a change of the environment around cda. For cda and the complex in H_2O solution the fluorescence signal is observed as a single peak but in the solid state double peaks are observed and the excited and emission signals are found at longer wavelengths than in H_2O solution. This result implies that the potential field around cda has an important influence on the fluorescence spectra of cda. Very similar experimental phenomena were observed for other complexes[6] with cda as ligand. The two emission peaks in the solid state obviously indicate that there are two stable excited states which may arise from π–π stacking interactions[7] among cda anions, and the energy band may be formed in solid Na(cda) or the solid complex through such π–π stacking interaction. It seems that the orderly arrangement of cda in the crystal lowers the $\pi \rightarrow \pi^*$ transition energy and increases the emission wavelengths.

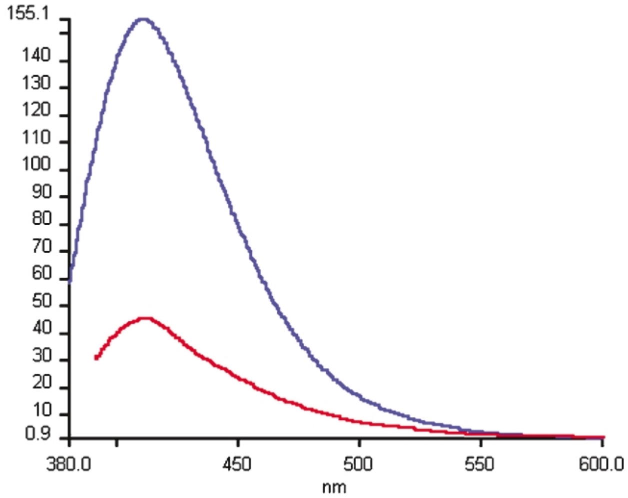

Fig. 3 The fluorescence spectra for Na(cda) (blue) and $\{[Eu(cda)_3(H_2O)_3]\cdot H_2O\}_\infty$ (red) in H_2O solution.

According to the principles proposed by Kurtz and Perry[8] the strength of the second harmonic generation (SHG) efficiency of the complex was tested by measuring the microcrystalline powder of the complex.§ The SHG efficiency of the complex is 16.8 times that of urea and the strong SHG effect may arise from the large π conjugated system in the *ab* plane of the crystal. This is the first example of SHG in polynitrile complexes.

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Notes and references

† *Preparation*: a solution of Na(cda) (0.4140 g, 3.16 mmol) was added to a solution of $Eu(ClO_4)_3\cdot 6H_2O$ (0.5895 g, 1.05 mmol) and the mixed solution was stirred for a few min. Yellowish single crystals were obtained after the mixed solution was allowed to stand for two months at room temperature. Elemental analysis: found: Eu: 28.15; C, 26.62; H, 2.89; N, 23.40; calc. for $C_{12}H_{14}EuN_9O_7$: Eu: 27.72; C, 26.28; H, 2.57; N, 23.00%.

Thermogravimetric analysis: the experiment was carried out under flowing argon at a heating rate of 10 °C min^{-1} and the experimental result indicates that the uncoordinated H_2O and coordinated H_2O molecules are lost from 115 to 168 °C.

‡ *Crystal data*: $(C_{12}H_{14}EuN_9O_7)_\infty$, M = 548.28, monoclinic, space group *Cc*, a = 15.949(3), b = 8.2517(15), c = 15.587(3) Å, β = 113.713(2)°, V = 1878.2(6) Å^3, Z = 4, T = 301(2) K, D_c = 1.939 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ = 3.397 mm^{-1}, $R1$ = 0.0247, $wR2$ = 0.0625 for $I > 2\sigma(I)$, GOF = 1.031. CCDC reference number 171168. See http://www.rsc.org/suppdata/cc/b2/b200894g/ for crystallographic data in CIF or other electronic format.

§ *SGH experiment*: the experimental set up included a high-power mode-locked Nd-YAG laser system with a selected wavelength of 1064 nm as incident beam. The laser beam is split into two parts: one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference urea powder.

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