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**STUDIES ON THE CHARACTERIZATION OF NOVEL  
Eu(III) COMPLEXES WITH  $\beta$ -DIKETONES AND DIAZA-18-  
CROWN-6**

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**ABSTRACT**

Three kinds of novel luminescent complexes of Eu(III) with mixed ligands of  $\beta$ -diketone and diaza-18-crown-6 ([2,2]) were synthesized:  $H_2[Eu(TTA)_4]_2 \cdot [2,2]$  (**A**),  $[Eu(TTA)_3]_2 \cdot [2,2]$  (**B**) and  $[Eu(DBM)_3]_2 \cdot [2,2]$  (**C**) (HTTA = thenoyltrifluoroacetone, HDBM = dibenzoylmethane and [2,2] = diaza-18-crown-6). Their observed fluorescence intensities are greater than those of the complexes  $Eu(TTA)_3 \cdot 2H_2O$  (**D**) and  $Eu(DBM)_3 \cdot 2H_2O$  (**E**), respectively, with the relative intensity ratios being **A** : **B** : **D** = 13.7 : 3.7 : 1 and **C** : **E** = 11.6 : 1. The monochromaticity of fluorescence of these complexes was also found to be improved in **A**, **B** and **C**, presumably because the macrocycle was introduced into the complexes. A possible mechanism of

fluorescence enhancement is proposed. The properties of these complexes were determined by TG and DTA methods as well as FT-IR and FT-Raman spectroscopy.

## INTRODUCTION

The importance of lanthanide ion fluorescence is related to its unique characteristics, including long lifetimes and fluorescent monochromaticity. The complexes of rare earth ions with  $\beta$ -diketones are one of the examples of traditional lanthanide luminescent compounds. For example,  $[\text{Eu}(\text{TTA})_3]_2 \cdot \text{H}_2\text{O}$  (see Fig. 1 for ligand structure) can strongly fluoresce when excited at 254 nm<sup>1</sup>. Mixed-ligand complexes with  $\beta$ -diketones and other organic ligands, such as ethylpyridinium bromide, are used not only to enhance the efficiency of intermolecular energy transfer from ligand to lanthanide ions, but also to avoid fluorescence quenching from coordinated water<sup>1-4</sup>. Lehn<sup>5</sup> pointed out that some macrocyclic molecules could absorb energy and transfer it efficiently to rare earth ions, which is known as "antenna effect". The objective of this work is to report the novel fluorescent complexes of Eu(III) with  $\beta$ -diketones [HTTA or HDBM] and diaza-18-crown-6 ([2,2], 1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane, as shown in Fig. 1). These complexes may be excited by UV light and then strongly fluoresce. The properties of these complexes were studied by TG and DTA as well as FT-IR and FT-Raman spectroscopy. A possible mechanism of fluorescence enhancement is proposed based on these spectral studies.

## EXPERIMENTAL

### Chemical Reagents

Chloroform, thenoyltrifluoroacetone (HTTA) and dibenzoylmethane (HDBM), A.R., were obtained from the Beijing Chemical Industrial Works.

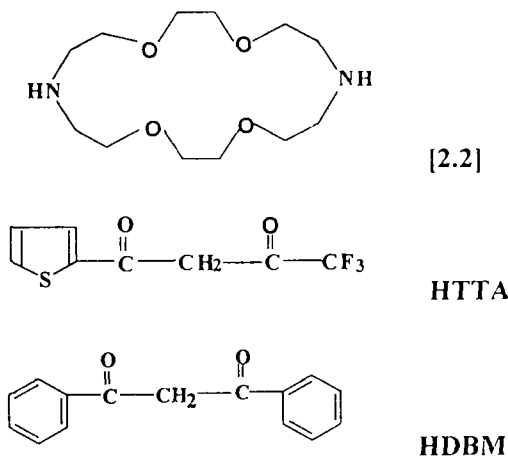


Fig. 1. The Structures of Diaza-18-Crown-6 ([2,2]), HTTA and HDBM

HTTA and HDBM were recrystallized from cyclohexane/benzene (V/V = 1/1). Diaza-18-crown-6 was synthesized by a literature method<sup>6,7</sup> as white plates, m.p.: 110.5° C (lit.<sup>6</sup> : 115-116° C). C<sub>12</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> (MW 262, Calc. (Found)) (%): C, 54.94 (54.80); H, 9.99 (10.25); N, 10.68 (10.74). IR (cm<sup>-1</sup>): 3334 (NH stretching vibration), 1100-1130 (C-O-C, C-N-C); <sup>1</sup>H NMR, δ (D<sub>2</sub>O): 3.10 (8H, t, N-CH<sub>2</sub>), 3.68 (8H, t, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.55 (8H, s, -CH<sub>2</sub>-CH<sub>2</sub>-O).

### Physical Measurements

A Carlo-Erba MOD 1102 elemental analyzer was used to establish the C, H and N contents of the complexes. The Eu(III) contents were obtained by complexometric titration with EDTA after the complexes were carbonized and transformed into chlorides.

The fluorescence spectra of the complexes were measured on a Hitachi 850 fluorophotometer. The complexes were excited at 254 nm, and the relative

intensities of the fluorescence bands were determined on the strongest emission bands. The fluorescence lifetimes were measured on a SLM 4800s Multi-frequency Fluorescence Analytical Instrument. [RF (Reference Frequency): 0.3 K-1 K, Ref. (Reference): glycogen, Ex (Excitation): 280 nm, Longpass filter: 580 nm].

Thermogravimetric measurements were performed on a DTA-TG analyzer (Beijing Analytical Instrument Works) equipped with a LCT-1 balance made at the Beijing Balance Works. Samples (10 mg) were heated in flowing argon under atmospheric pressure. The heating rate was 2° C /min.

FT-IR spectra were recorded using KBr pellets in the region from 400 to 4000  $\text{cm}^{-1}$  on a Nicolet Magna 750 FT-IR spectrometer at 4  $\text{cm}^{-1}$  resolution, and in CsI pellets in the region from 100 to 500  $\text{cm}^{-1}$  on a Bio-rad FTS-65A FT-IR spectrometer at 4  $\text{cm}^{-1}$  resolution. The variable temperature FT-IR spectra (VTFS) of the complexes **A**, **B** were recorded from 20° C (room temperature) to 140° C in 5° C increments, then cooled to 70° C. Their VTFS spectra were recorded after the temperature of each complex was constant for 5 min. FT-Raman spectra were recorded in the region from 100 to 3600  $\text{cm}^{-1}$  on a Nicolet 910 FT-Raman spectrometer. Samples in 5 mm NMR tubes were excited by a NdYVO<sub>4</sub> laser (1064 nm, about 500 mW, resolution 4  $\text{cm}^{-1}$ ), and their spectra were obtained from the average of 200 scans.

### Synthesis of Complexes

**H<sub>2</sub>[Eu(TTA)<sub>4</sub>]<sub>2</sub>·[2,2] (A)**. A quantity of 5 mL of an aqueous solution containing 0.169 g Eu(NO<sub>3</sub>)<sub>3</sub> (0.500 mmol) was added dropwise with stirring to 17 mL of a toluene solution containing 0.533 g HTTA (2.40 mmol) and 0.314 g diaza-18-crown-6 (1.20 mmol). The organic phase was separated after 30 min and added to 20 mL of cyclohexane when precipitation occurred. The

precipitate was collected and recrystallized from a mixture of toluene and cyclohexane (V/V = 1:1). Finally, the resulting white, rod-like crystals were dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> for 5 h and 0.362 g of product was obtained (62%).

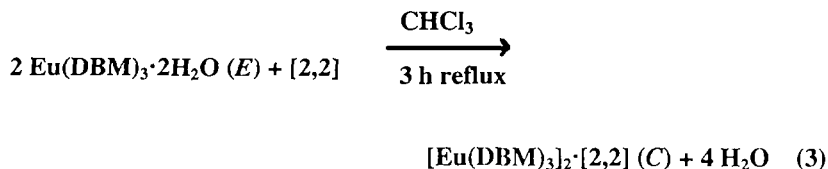
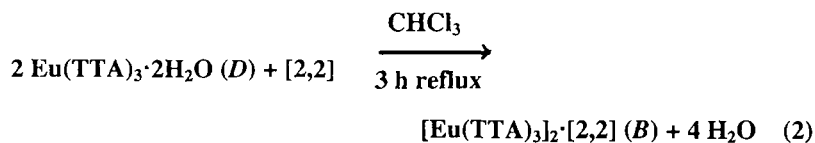
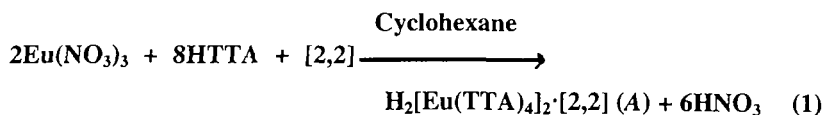
**[Eu(TTA)<sub>3</sub>]<sub>2</sub>·[2,2] (B).** Eu(TTA)<sub>3</sub>·2H<sub>2</sub>O (*D*) and Eu(DBM)<sub>3</sub>·2H<sub>2</sub>O (*E*) were prepared by literature methods<sup>8,9</sup>. A quantity of 0.427 g Eu(TTA)<sub>3</sub>·2H<sub>2</sub>O (*D*) (0.500 mmol) and 0.131 g diaza-18-crown-6 (0.500 mmol) were both dissolved in 20 mL CHCl<sub>3</sub> each, and then the two solutions were mixed and refluxed for 3 h. The solution was then concentrated to 10 mL and yellow crystals formed. These crystals were collected and recrystallized from 10 mL CHCl<sub>3</sub>, washed with ether several times and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> for 5 h and 0.379 g of product was obtained (80%).

**[Eu(DBM)<sub>3</sub>]<sub>2</sub>·[2,2] (C).** A quantity of 0.430 g Eu(DBM)<sub>3</sub>·2H<sub>2</sub>O (*E*) (0.500 mmol) and 0.131 g diaza-18-crown-6 (0.500 mmol) were dissolved in 20 mL CHCl<sub>3</sub> each, and then the two solution were mixed and refluxed for 3 h. The resulting solution was then concentrated to 10 mL and yellow crystals formed. These crystals were collected and recrystallized from 10 mL CHCl<sub>3</sub>, washed with ether several times and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> for 5 h; 0.399 g of product was obtained (71%).

## **RESULTS AND DISCUSSION**

### **The Composition of the Complexes**

The results of the elemental analyses are listed in Table I, which indicate that three kinds of complexes were obtained in this work: H<sub>2</sub>[Eu(TTA)<sub>4</sub>]<sub>2</sub>·[2,2] (*A*), [Eu(TTA)<sub>3</sub>]<sub>2</sub>·[2,2] (*B*) and [Eu(DBM)<sub>3</sub>]<sub>2</sub>·[2,2] (*C*). Their formation equations may be expressed as follows:



According to the elemental analyses (Table I), there are two more HTTA units in **A** than in **B**, and each type of complex contains a diaza-18-crown-6 molecule. The X-ray study of the complex **A** was attempted, however, the crystals decomposed while collecting X-ray data. For the complex **A** obtained by the reaction of eq (1), it was suggested that two  $[\text{Eu}(\text{TTA})_4]^-$  moieties are connected through a diaza-18-crown-6 bridge as shown in Fig. 2. According to Huang<sup>1</sup> and Li<sup>10</sup>, the two  $\text{H}^+$  ions are bound mostly to the two N atoms of diaza-18-crown-6, and connected to the two  $\text{Eu}(\text{TTA})_4^-$  moieties by hydrogen bonds. Based on the reaction of eq (2), the complex **B** can be considered formed by replacement of the two coordinated  $\text{H}_2\text{O}$  molecules in complex **D** by the ligand diaza-18-crown-6 (Fig. 2). The complex **C** has a similar structure as that of complex **B**.

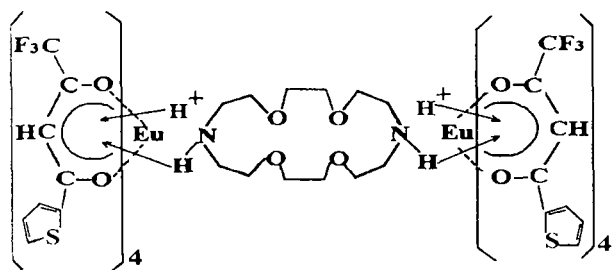
### Thermogravimetric Analysis

The thermogravimetric curves of **A** and **B** (Fig. 3) show that **A** decomposed endothermically at 142° C and lost 18.86% of its mass, which is

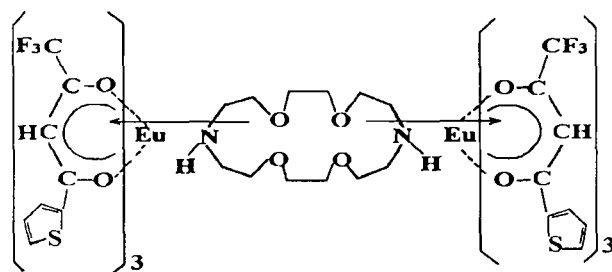
TABLE I. The Results of Elemental Analyses of **A**, **B** and **C**

Complex (Empirical Formula)	Formula Weight	C% (Calcd.)	H% (Calcd.)	N% (Calcd.)	Eu% (Calcd.)	Yield, %	Decomposition Point, °C
$\text{H}_2[\text{Eu}(\text{TTA})_4]_2 \cdot [2,2]$ ( <b>A</b> ) ( $\text{C}_{76}\text{H}_{60}\text{F}_{24}\text{Eu}_2\text{N}_2\text{O}_{20}\text{S}_8$ )	2338	39.64 (39.04)	3.00 (2.59)	1.10 (1.20)	13.10 (13.00)	62	178
$[\text{Eu}(\text{TTA})_3]_2 \cdot [2,2]$ ( <b>B</b> ) ( $\text{C}_{60}\text{H}_{50}\text{F}_{18}\text{Eu}_2\text{N}_2\text{O}_{16}\text{S}_6$ )	1893	37.95 (38.07)	2.70 (2.66)	1.32 (1.48)	16.04 (16.06)	80	185
$[\text{Eu}(\text{DBM})_3]_2 \cdot [2,2]$ ( <b>C</b> ) ( $\text{C}_{102}\text{H}_{92}\text{Eu}_2\text{N}_2\text{O}_{16}$ )	1906	64.48 (64.28)	5.12 (4.87)	1.36 (1.47)	15.60 (15.95)	71	200

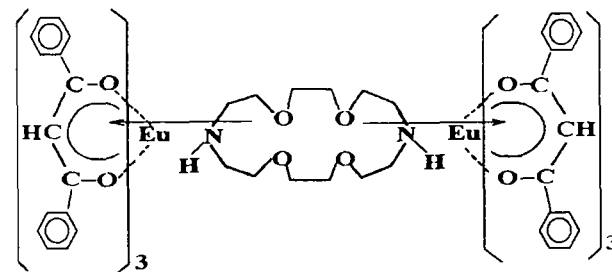




Complex A



Complex B



Complex C

Fig. 2. Suggested Structures of the Novel Complexes A, B and C

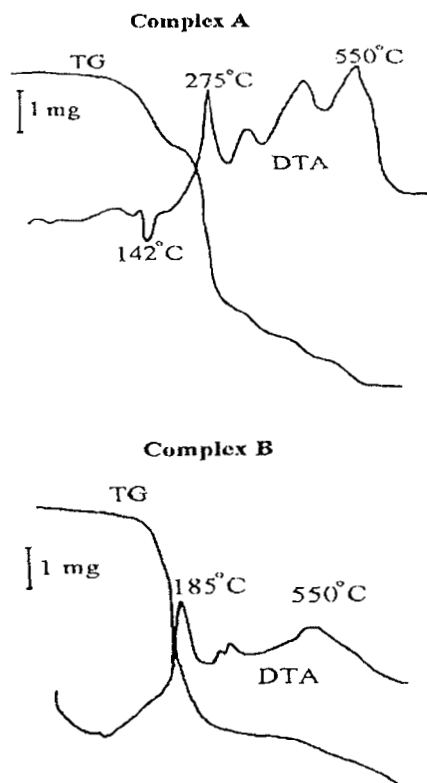


Fig. 3. The Thermogravimetric Curves of Complexes **A** and **B**

close to 19.01% which is the amount calculated for two HTTA units in **A**, indicating that two HTTA units are easily lost at a relatively low temperature (142° C for **A**). This further suggests that two HTTA units are bonded more weakly than the diaza-18-crown-6<sup>11</sup> ligand Fig. 3).

Compound **D** has two endothermic peaks at 85° C and 95° C, which correspond to two water molecules that are lost in two stages. The weight loss of 4.48% at this endothermic stage is consistent with the loss of the calculated amount of water (4.23%) in **D**.

As shown in Table II, the decomposition temperatures of the four exothermic peaks of *A*, *B* and *D* vary considerably and indicate that there are different coordination environments for the metal ions. It is possible that the arrangement of oxygen atoms bonded to Eu(III) may be distorted from favored or ideal configurations to accommodate crystal packing requirements<sup>12</sup>.

### **FT-IR and FT-Raman Spectra**

The observed IR bands of *A-E* are given in Table III along with their assignments. For *A*, the prominent bands associated with  $\text{NO}_3^-$  are not observed in the IR and Raman spectra, providing strong evidence that  $\text{NO}_3^-$  is not present.

A significant difference between *A* and *B* was observed from variable temperature FTIR spectroscopic (VTFS) measurements. The sharp peak at  $3265\text{ cm}^{-1}$  (NH stretching)<sup>14</sup> in *A* disappeared and a broad band appeared near  $3200\text{ cm}^{-1}$  between 130 and  $140^\circ\text{C}$ . This change could not be restored when the temperature was reduced to  $70^\circ\text{C}$  (Fig. 4). This is in agreement with the result of the TG-DTA experiments in which *A* lost 18.86% of its weight at  $142^\circ\text{C}$ . In contrast, over this temperature range there are only few changes in the VTFS spectrum of *B*.

In Table III it is shown that the C=C stretching vibrations in *A* and *B* (both of them are located at  $1537\text{ cm}^{-1}$ ) are shifted to lower frequencies by  $5\text{ cm}^{-1}$  than that in *D*. These data indicate the degree of conjugation in the chelate rings in *A* and *B* is greater than that in *D*. However, because of overlapping of  $\nu(\text{benzene-ring})$  in the region from  $1595$  to  $1548\text{ cm}^{-1}$ , it is difficult to observe the  $\nu(\text{C=C})$  band in *C* and *E*.

FT-Raman spectroscopy was also used to study *A*, *B* and *D* and some characteristic Raman frequencies are given in Table IV. For *A*, the band

TABLE II. The Temperatures of Exothermic Peaks of *A*, *B* and *D*

Complex	1st Exothermic temperature, °C	2nd Exothermic temperature, °C	3rd Exothermic temperature, °C	4th Exothermic temperature, °C
<i>A</i>	275	375	481	550
<i>B</i>	185	307	330	550
<i>D</i>	268	306	355	550

TABLE III. Some Characteristic FT-IR Frequencies of *A*, *B*, *C*, *D* and *E* ( $\text{cm}^{-1}$ )<sup>9,13,14</sup>

Assignment	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{O})$
<i>A</i>	1631 s, 1607 s	1537 m	185 w
<i>B</i>	1609 s	1537 m	184 w
<i>C</i>	1608 s, a	a	192 w
<i>D</i>	1607 s	1542 m	178 w
<i>E</i>	1595 s, a	a	191 w

a: overlapped by  $\nu(\text{benzene-ring})$  in the region of 1595-1548  $\text{cm}^{-1}$

s: strong; m: medium; w: weak

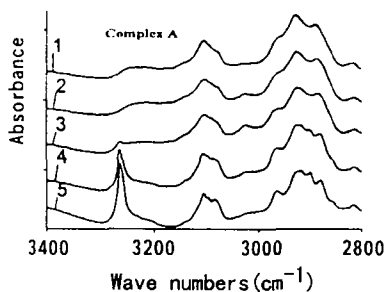


Fig. 4. Variable Temperature FT-IR Spectra of Complex *A* (3400-2800  $\text{cm}^{-1}$ ) (1: cooled to 70 °C; 2: 140 °C; 3: 125 °C; 4: 120 °C; 5: 95 °C)

TABLE IV. Some Characteristic FT-Raman Frequencies of *A*, *B*, *C*, *D* and *E* ( $\text{cm}^{-1}$ )<sup>14,15</sup>

Complex	$\nu(\text{aromatic-ring})$	$\nu(\text{C-II of stretching of aromatic-ring})$
<i>A</i>	1464 m, 1448 m, 1431 vs	3097 m
<i>B</i>	1445 m, 1416 vs	3106 m
<i>C</i>	1597 vs	3062 m
<i>D</i>	1442 m, 1414 vs	3105 m
<i>E</i>	1598 vs	3068 m

m: medium; vs: very strong

observed at  $3097\text{ cm}^{-1}$  is the C-H of stretching region of the thenoyl ring, and there is another band in this region at  $2973\text{ cm}^{-1}$ . All of these data suggest that the local symmetry of the thiophene ring of the ligand HTTA in *A* is different from that in *D*.

### Fluorescence Data

When the complexes *A-E* were excited with ultraviolet light, they emit high-intensity orange fluorescence. The spectroscopic data obtained for these complexes are summarized in Table V.

As given in Table V, the emission bands  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ , for the complexes *D* and *E* are split into two bands. If the fluorescence intensity of the bands at 612 nm of *D* is selected as the standard, there exists the intensity relationship for *A*, *B* and *D* as follows:  $A : B : D = 13.3 : 3.7 : 1$ . That is to say, the fluorescent intensity of *A* is 13 times higher than that of *D*. Also, for *C* and *E* the intensity ratio is  $C : E = 11.6 : 1$ . These results show that the fluorescence intensity increases when diaza-18-crown-6 is part of the complex and the fluorescence monochromaticity is also improved by the presence of [2,2]. The characteristic fluorescence of the Eu(III) complex indicates that the organic ligand can absorb energy and transfer it efficiently to Eu(III) through an intermolecular process<sup>17</sup>. In addition, *A* and *B* have different lifetimes. When excited with 280 nm, *A* has a lifetime of 402.7  $\mu\text{s}$ , which is 70  $\mu\text{s}$  longer than that of *B*. The fluorescence intensity of *A* is greater than that of *B*.

### The Relationship between the Structure of the Complexes and Their Fluorescence Spectra

In general, the fluorescence intensities and monochromaticity of rare earth complexes containing R-CO-CH<sub>2</sub>-CO-CF<sub>3</sub> ligands are affected by the

TABLE V. The Fluorescence Data of *A*, *B*, *C*, *D* and *E* ( $^5D_0 \rightarrow ^7F_2$ )

Complex	Excitation (nm)	Emission (nm)	Relative Intensity
<i>A</i>	254	612	763.00
<i>B</i>	254	613	214.00
<i>C</i>	254	613	16.00
<i>D</i>	254	612, 620	50.39, 76.50
<i>E</i>	254	612, 616	185.00, 102.00

efficiencies of intermolecular energy transfers and the local symmetries of the rare earth ion<sup>12</sup>.

(1) For *A* and *B* it is, therefore, possible that the observed results reflect efficient energy transfer between the two  $\text{Eu}(\text{TTA})_n$  ( $n = 3$  or  $4$ ) groups through the diaza-18-crown-6 "bridge". Considering the 'TTA' group, both inductive effects and effects from the conjugation of the chelate ring with the R group could play important roles in transferring intermolecular energy efficiently. The differences of inductive effects among those complexes likely can be ignored. As given in Table III, the IR spectra reveal that the conjugation correlates with energy transfer efficiencies. Moreover, substituting diaza-18-crown-6 for water in *A*, *B* and *C* can eliminate the effects of fluorescence quenching by water, and increases the fluorescence intensities.

(2) Generally speaking<sup>3</sup>, the lower the local symmetry of the central ions, the greater the number the fluorescence peaks for  $\text{Eu}(\text{III})$ . The local symmetries of the metal ions are different because of different coordination environments. There are two  $^5D_0 \rightarrow ^7F_2$  bands in *D* and *E*, and only one in *A*, *B* and *C*, which indicate that the local symmetry of the metal ions becomes higher on adding of diaza-crown-6 molecule.

### ACKNOWLEDGEMENTS

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