Araştırma Makalesi *BAUN Fen Bil. Enst. Dergisi, 19(3) Özel Sayı, 7-15, (2017)*

DOI: 10.25092/baunfbed.363733 ***J. BAUN Inst. Sci. Technol., 19(3) Special Issue, 7-15, (2017)***

Synthesis and photophysical properties of new Eu(III) complex

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Geliş Tarihi (Recived Date): 17.08.2017
Kabul Tarihi (Accepted Date): 19.10.2017

Abstract

*In this study, the new Eu(III) complex was hydrothermally synthesized using oxygen donor ligand and characterized by single crystal X-ray diffraction, elemental analysis, solid UV-Vis spectroscopy, FT-IR and photoluminescence properties. The crystal structure analysis of complex [$C_7H_9EuO_9S$](**1**) indicates that the central lanthanide ions are coordinated by eight oxygen atoms in which* six oxygen *atoms from four ssa$^-$ anionic ligands and two oxygen atoms from a coordinated water molecules. Complex **1** bridged by oxygen atoms from carboxyl and sulfonate groups of the ssa$^-$ ligands are formed in 1D chains. The 1D chains are linked together with ligand ssa$^-$ to form a 2D wave-like layers. All these wave-like layers are further interlinked via strong hydrogen bonding interaction resulting in 3D architecture. Additionally, solid state photoluminescence properties of complex **1** have been investigated in room temperature. The indirect energy transfer mechanism via an Antenna effect in complex **1** has been investigated in detail.*

Keywords: *Eu(III) complex, crystal structure, antenna effect.*

Yeni Eu(III) kompleksinin sentezlenmesi ve fotofiziksel özellikleri

Özet

*Bu çalışmada, oksijen donör ligandı kullanılarak yeni Eu(III) içeren lantanit kompleksi hidrotermal yöntem ile sentezlenmiş ve tek kristal X-ışını kırınımı, element analizi, katı UV-Vis spektroskopisi, FT-IR ve fotolüminesans özellikleri ile karakterize edilmiştir. Eu(III) kompleksinin [$C_7H_9EuO_9S$](**1**) kristal yapısı sekiz oksijen atomu ile koordine olduğunu göstermektedir. Burada altı oksijen atomu ssa$^-$ anyonik ligandından ve iki oksijen atomu ise koordine su moleküllerinden gelmektedir. Kompleks **1**, ssa$^-$ ligandının karboksil ve sülfonat grupları ile köprü kurarak bir-boyutlu zincir oluşturmaktadır. Bir boyutlu zincirler ssa$^-$ ligandları ile birlikte iki-boyutlu dalga benzeri tabakalar oluşturaktadır. Tüm bu dalga benzeri tabakalar güçlü hidrojen bağı etkileşimleri üç-boyutlu mimari ile sonuçlanmıştır. Buna ek olarak, kompleks (**1**)' in katı durum fotolüminesans özellikleri oda sıcaklığında araştırılmıştır. Kompleks için anten etkisi ile dolaylı enerji transfer mekanizması detaylı olarak araştırılmıştır.*

Anahtar kelimeler: *Eu(III) kompleksi, kristal yapı, anten etkisi.*

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1. Introduction

In recent years, the construction of coordination polymers has been a field of rapid growth not only for their intriguing topologies and diverse structures but also for their interesting chemical and physical properties, such as magnetism, luminescence, gas storage, sorption, separation, catalysis, non-linear optical properties, *etc* [1–6]. Intense research has resulted in a great number of coordination polymers with new structures and interesting luminescence and magnetic properties. In particular, lanthanide ions are interlinked by organic H_3ssa and 2-stp and/or carboxylate groups to form many diversity structures [6–9]. Moreover, these ions with special luminescent resulting from 4f electrons, which illustrate the coordination polymers are intriguing and remarkable suitable for the development of technological devices [10]. Furthermore, Eu(III) compounds shows strong yellow luminescence in the visible region, making them to be good candidates for fluoroimmunuassays and structural and biological probes [11,12]. Due to the lanthanide ions have poor absorption coefficient, the emission intensities are very low. Using the suitable chromophore (antenna ligand or sensitizer), which is absorbed as a strongly in the UV-visible region and transfer its energy to the excited states Ln(III) ions. Therefore, the choice of appropriate ligand is very important [13,14].

Aromatic carboxylic ligands are good luminescent chromophores, resulting in the intense luminescence of lanthanide ions. An important example of a chromorphic carboxylate ligand is the 5-sulfosalicylic acid (H_3ssa). The choice of 5-sulfosalicylic acid (H_3ssa) can be attributed to the following properties: 5-sulfosalicylic acid (H_3ssa) has interesting biological activities, such as anti-microbial, anti-fungal and anti-inflammatory activities. The H_3ssa ligand involves three functional groups, $–SO_3H$, –COOH and –OH, which can be partly or fully deprotonated in different forms, fabricating many novel architectures [15].

In this work, Eu^{III} ion is aimed to gain luminescence properties by antenna effect. After ligand-mediated excitation of the complex, it shows the characteristic visible and/or near infrared (NIR) luminescence of the corresponding Ln^{III} ion. This is attributed to efficient energy transfer from the ligands to the central Ln^{III} ion (antenna effect). In this context, we report the synthesis, structural characterization and photophysical properties of novel Lanthanide-salicylate organometallic complex, $\{[Eu(ssa)(H_2O)_2].H_2O\}_n$ (**1**). The crystal structure of complex **1** were previously reported at room temperature [16,17]. Herein, the crystal structure of complex **1** have been re-determined by the single crystal X-ray diffraction analysis and by FT-IR, UV-Vis and photoluminescence properties this complex will report in this work .

2. Material and method

2.1. Materials and measurements

All chemical reagents and solvents were purchased from Aldrich and used without further purification. Elemental (C, H, N) analyses were carried out by standard methods with a LECO, CHNS–932 analyzer. FT-IR spectra were measured with a Perkin-Elmer Spectrum 65 instrument in the range of 4000 – 600 cm^{-1}. Powder X-ray measurements were performed using Cu Kα radiation ($\lambda_{K\alpha}$ = 1.5418 Å) on a Bruker-AXS D8-Advance diffractometer equipped with a secondary monochromator. The data were collected in the range 5º < 2h < 60º in θ – θ mode with a step time of ns (5 s < n < 10 s) and step width of 0.02º. Solid state luminescence spectra in the visible and NIR region were measured at room temperature with an ANDOR SR500i-BL Photoluminescence Spectrometer, equipped with a triple grating and used an air-cooled CCD camera as detector. The measurements were done by using the excitation source (349 nm) of a Spectra-physics Nd:YLF laser with a 5 ns pulse width and 1.3 mJ of energy per pulse as the source.

2.2. Preparation of $\{[Eu(ssa^-)(H_2O)_2](H_2O)\}(1)$

Complex **1** were prepared under hydrothermal condition. A mixture of $Eu(NO_3)_3.(H_2O)_5$ (0.0428 g, 0.1 mmol) and H_3ssa (0.0254 g, 0.1 mmol) in 20 ml of distilled water was sealed into a bomb equipped with a Teflon liner (45 ml) and then heated 140 °C for 5 days. The final pH values of these reactions media are close to 4.0. Crystals of complex **1** (yellow) was collected and washed distilled water. Anal. Calcd (%) for $C_7H_9EuO_9S$: C, 19.96; H, 2.15; Found: C, 19.92; H, 2.14.

2.3. X-ray structure determination

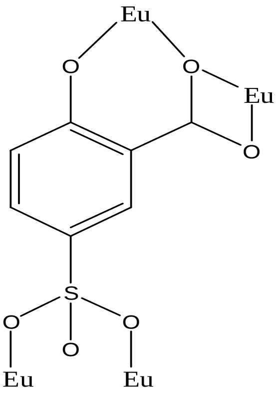
X-ray single crystal data for complex **1** were collected on a Xcalibur, Eos diffractometer using MoKα radiation at room temperature (293 K). The data were collected for Lorentz, polarization and absorption effects using the analytical numeric absorption correction technique [18]. Using OLEX2 [19], the structure was solved by direct methods using SHELXS [20] and refined by full-matrix least-squares based on $|F_{obs}|^2$ using SHELXL [20]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, generated using idealized geometry, were made to “ride” on their parent atoms and used in the structure factor calculations. Detail of the supramolecular π-interactions were calculated PLATON 1.17 program [21].

3. Result and discussion

3.1. Structural description of complex 1

The crystal data and structure refinement details for complex **1** are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. Possible hydrogen bond geometry (Å, °) and distance between ring centroids [Å] are also given in Table 3. Representative structural diagrams of complex **1** are shown in Figure 1, while packing diagrams are given in Figures 2, 3 and 4. The X-ray crystal structure analysis reveals that complex **1** consists of a Eu(III) ion, one ssa^- ligand, two coordinated water molecules and one free water molecules in the asymmetric unit. The eight-coordinated environment around each Eu(III) centre is completed by six oxygen atoms from four ssa^- ligands and two oxygen atoms from a coordinated water molecule with Eu–O bond lengths in the range of 2.257(10) – 2.657(10) Å (Figure 1). All bond distances and angles are comparable to similar structures [16,17,22].

The ssa^- ligand serves as μ_4-bridge linking four Eu(III) ions by a bidentate bridging mode of the sulfonate, a bidentate chelating-bridging mode of the carboxylate, and a monodentate mode of hydroxyl group (see Scheme 1). Eu(III) ions are bridged by oxygen atoms of carboxyl and sulfonate groups, forming 1D chains. The neighbouring Eu···Eu distance is 4.654 Å. The adjacent phenyl rings of ssa ligands are parallel with the vertical distance of 3.71 Å, which shows there exist strong π–π interactions in the 1D chains (Figure 2). Moreover, the 1D chains are linked together with ligand ssa to form a 2D wave-like layers (Figure 3). All these wave-like layers are further interlinked via strong hydrogen bonding interaction resulting in 3D architecture (Figure 4).



Scheme 1. The coordination mode of ssa ligand of complex (**1**).

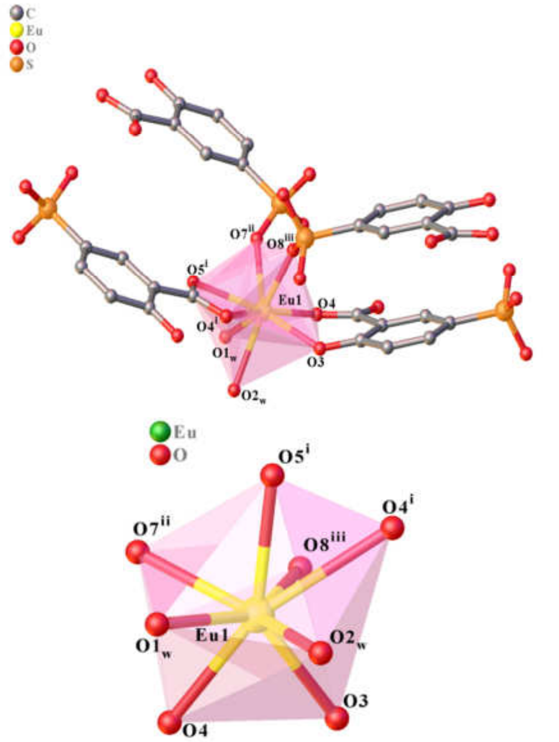


Figure 1. (a) Perspective view of the coordination environment of Eu(III) ions of *complex* **1**. Lattice water molecule and hydrogen atoms are omitted for clarity. (b) the trigonal dodecahedron coordination polyhedron of Eu(III) atom in complex **1**.

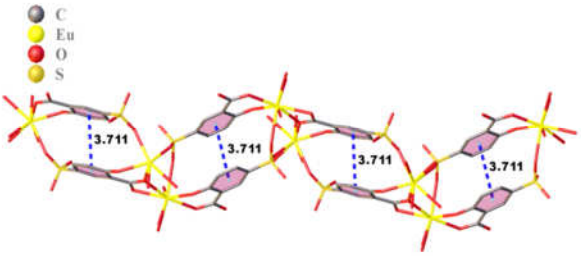


Figure 2. A view of π-π interaction in the 1D infinite chains.

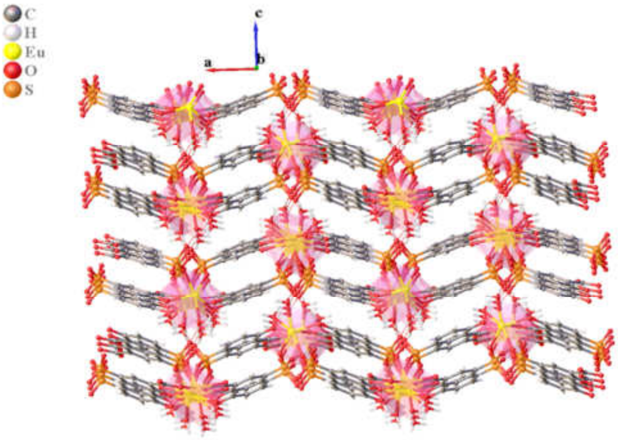


Figure 3. The 2D wave-like layers in the *ab*-plane.

Table 1. Crystallographic data and refinement parameters of compound **1**.

	Eu(1)
Chemical Formula	$C_7H_9EuO_9S$
M_w	421.16
Crystal System	Orthorhombic
Space Group	Pbcn
a/Å	15.8832(13)
b/Å	9.1963(6)
c/Å	14.9987(11)
α, β, γ	90, 90, 90
V/Å^3	2190.8(3)
T/K	293(2)
Z	8
ρ_{calc}/g.cm^{-3}	2.554
μ/mm^{-1}	5.956
Reflections Collected	5878
Independent Reflections	2232 (R_{int}=0.068)
R_1 [I>2σ(I)]	0.0709
wR_2 (all data)	0.1980
S	1.015

Table 2. Selected bond length (Å), and bond angles (°).

Eu1 – O1	2.397(9)	Eu1 – O4^i	2.657(10)
Eu1 – O2	2.388(10)	Eu1 – O5^i	2.426(10)
Eu1 – O3	2.257(10)	Eu1 – O7^{ii}	2.400(9)
Eu1 – O4	2.373(10)	Eu1 – O8^{iii}	2.377(10)
O1 – Eu1 – O2	69.6(3)	O3 – Eu1 – O4^i	87.6(3)
O1 – Eu1 – O3	125.3(4)	O3 – Eu1 – O5^i	138.3(4)
O1 – Eu1 – O4	76.2(3)	O3 – Eu1 – O7^{ii}	131.9(3)
O1 – Eu1 – O4^i	120.5(3)	O3 – Eu1 – O8^{iii}	77.4(4)
O1 – Eu1 – O5^i	84.0(4)	O4 – Eu1 – O4^i	159.55(17)
O1 – Eu1 – O7^{ii}	76.4(3)	O4 – Eu1 – O5^i	149.0(4)
O1 – Eu1 – O8^{iii}	151.7(3)	O4 – Eu1 – O7^{ii}	73.3(3)
O2 – Eu1 – O3	79.8(4)	O4 – Eu1 – O8^{iii}	98.5(3)
O2 – Eu1 – O4	109.0(4)	O4^i – Eu1 – O5^i	50.7(3)
O2 – Eu1 – O4^i	70.3(3)	O4^i – Eu1 – O7^{ii}	120.0(3)
O2 – Eu1 – O5^i	85.4(4)	O4^i – Eu1 – O8^{iii}	72.3(3)
O2 – Eu1 – O7^{ii}	143.9(4)	O5^i – Eu1 – O7^{ii}	79.1(4)
O2 – Eu1 – O8^{iii}	136.6(3)	O5^i – Eu1 – O8^{iii}	87.7(4)
O3 – Eu1 – O4	72.4(3)	O7^{ii} – Eu1 – O8^{iii}	75.4(3)

Symmetry transformations used to generate equivalent atoms for complex1: (i)1/2-x,1/2+y,+z, (ii) -1/2+x, ½-y, 1-z, (iii) 1-x, 1-y, 1-z.

Finally, before proceeding to the photoluminescence characterization, we note that PXRD patterns for bulk microcrystalline sample of **1** were consistent with the exclusive presence of the phase identified in the single crystal experiment (Figure 5).

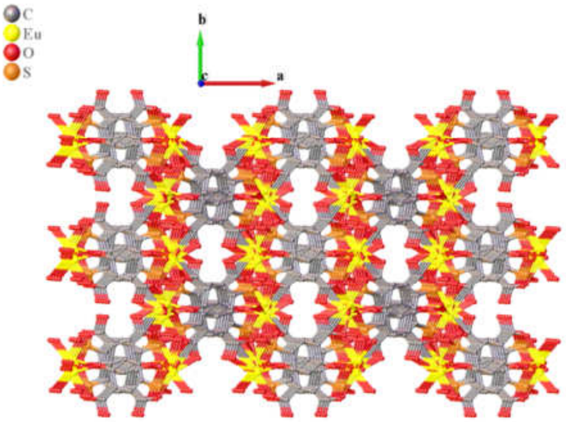


Figure 4. A view of 3D framework stabilized by hydrogen bonding interactions between different layers in *ac* plane (Hydrogen atoms have been omitted for clarity).

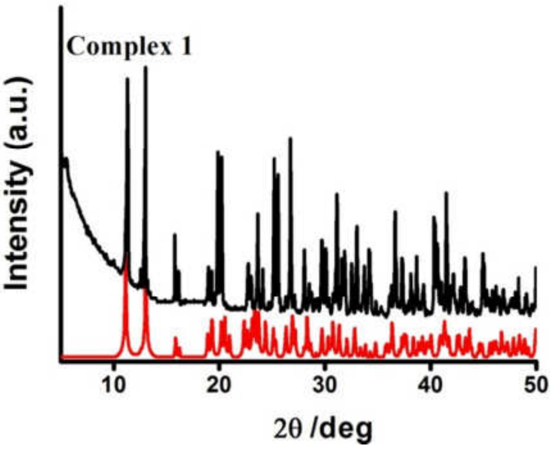


Figure 5. X-ray powder diffraction pattern of complex **1** (Red-simulated CIF, Black-experimental)

Table 3. Hydrogen bond geometry (Å, °) and distance between ring centroids (Å) for complex **1**.

D–H…A*	**D–H**	**H…A**	**D…A**	**D–H…A**	**Symmetry Code**
O1–H1A…O9	0.90	2.37	2.93(2)	120	
O1–H1B…O6	0.90	2.28	3.130(13)	156	1-x,y,3/2-z
O2–H2A…O6	0.89	2.05	2.913(15)	165	1-x,y,3/2-z
O2–H2B…O9	0.89	2.46	2.97(2)	118	
O9–H9A…O2	0.85	2.52	2.97(2)	115	
O9–H9B…O1	0.85	2.38	2.93(2)	123	
Cg(I)…Cg(J)					
Cg(1)…Cg(1)			4.167(7)		1-x,y,3/2-z
Cg(1)…Cg(1)			3.711(7)		1-x,1-y,1-z

D: Donor, A: Acceptor, Cg(I): Plane number I (=ring number in () above), Cg(1): C2-C3-C4- C5-C6-C7.

3.2. FT-IR spectra and UV-Vis analysis

The FT-IR and solid state UV-Vis spectra of complex **1**were shown in comparison with that of its free ligand H_3ssa (Figures 6 and 7). As seen from Figure 6, the broad peak at 3337 cm^{-1} indicates the presence of ν(O–H) vibration associated with coordinated water molecules [23]. The carboxyl band of the free ligand H_3ssa is found at 1657 cm^{-1}. The absence of this band indicates that H_3ssa are completely deprotonated in the form of ssa$^-$ anions upon reaction with the metal ions [10]. For complex **1,** two medium bands are at 1606 and 1379 cm^{-1} corresponding to the stretching vibrations of asymmetric and symmetric carboxyl groups. The difference of asymmetric and symmetric vibration bands is about 227 cm^{-1}, which indicating carboxylic groups are coordinated to Eu^{III} in chelating mode [23]. The two peaks at 1468 and 1434 cm^{-1} were assigned to the skeletal vibration of benzene ring bonds. The band at 1330 and 1255 cm^{-1} resulted from asymmetric stretching vibration, whereas the bands at 1139 and 1043 cm^{-1} were caused by the symmetric stretching vibrations of the sulfonate groups in ssa$^-$ [7]. The medium bands at 911 and 832 cm$^{\mathbf{-1}}$ are ascribed to O−Eu−O stretching and the strong band at 670 cm^{-1} and the weak band at 809 cm^{-1} are characteristic of Eu−O stretching vibration [24]. To obtained results are in agreement with data from the single crystal X-ray analysis.

Figure 7 show the UV-vis spectra of the free ligand (H_3ssa) and its Eu(III) complex were recorded in solid state. In the absorption spectra of free ligand, there are two set of broad bands. The high energy band maxima at 306 nm (32680 cm^{-1}) and the other absorption band maxima at 399 nm (25062 cm^{-1}) for (H_3ssa) ligand. The absorption spectra of complex **1** indicated different absorption pattern as compared to its free ligand H_3ssa. The dominated absorption band observed with the maxima at 426 nm (23474 cm^{-1}) in the spectrum of complex **1**, could be assigned to π–π* or n–π* transition of the ligand H_3ssa. The shifthing of absorption band in the spectra of the complex **1** signify the H_3ssa ligand coordination with lanthanide ion [25–27].

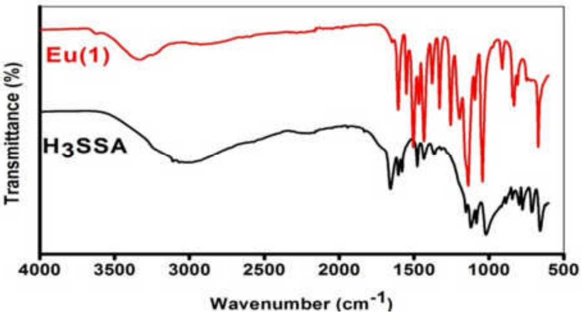


Figure 6. IR spectra of the free ligand H_3ssa and its complex.

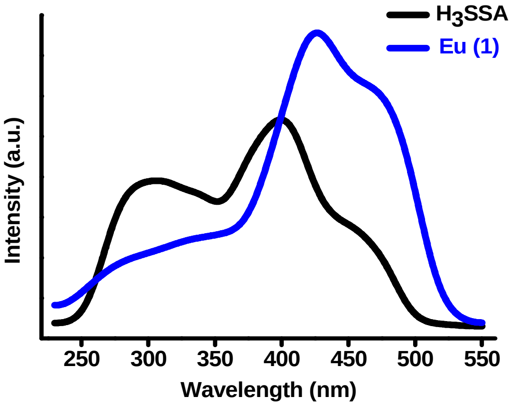


Figure 7. Solid state UV-Vis spectra of the free ligand H_3ssa and its complex.

3.5. Photoluminescence Properties

The solid state luminescent properties of the free ligand H_3ssa and complex **1** were investigated at room temperature in the visible region upon excitation at $\lambda_{exc.}$= 349 nm (Figure 8). The free ligand H_3ssa shows broad emission band at λ_{max}= 465 nm in the blue-region, which may be assigned to the n→π* or π→π* electronic transition intraligand charge transfer (ILCT) [28].

Complex **1** exhibit six characteristic peaks: 523 nm correspond to $^5D_1 \rightarrow {}^7F_0$, 577, 590, 618, 652 and 700 nm originating from the transition of $^5D_0 \rightarrow {}^7F_J$ (J= 0-4) of the Eu^{III} ion, respectively [29–32]. The appearance of the symmetry-forbidden emission band at 577 nm ($^5D_0 \rightarrow {}^7F_0$) indicates that the Eu^{III} ions in complex **1** possess the noncentro-symmetric coordination environment [33]. It is well known that the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition is the most intense emission which leads to yellow luminescence, and hypersensitive transition, whose intensity is very sensitive to site symmetry, while the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is insensitive and hardly varies with the coordination environment [34,35]. The intensity ratio I ($^5D_0 \rightarrow {}^7F_2$) / I ($^5D_0 \rightarrow {}^7F_1$) is equal to ca. 12, indicating that the Eu(III) ions occupy non-inversion symmetry sites, which is in accordance with the results of its single crystal structural [36,37]. On the other hand, the emission spectrum of complex **1** indicates also a broad emission band around 355 to 495 nm with the maximum wavelength of 410 nm. In other words, complex **1** show a broad band, the inefficient quenching of the ligand-centred emission can be further seen from broad bands with low intensity. The spectrum indicates that the energy transfer from the ligand to Eu^{III} ion is moderately efficient [9].

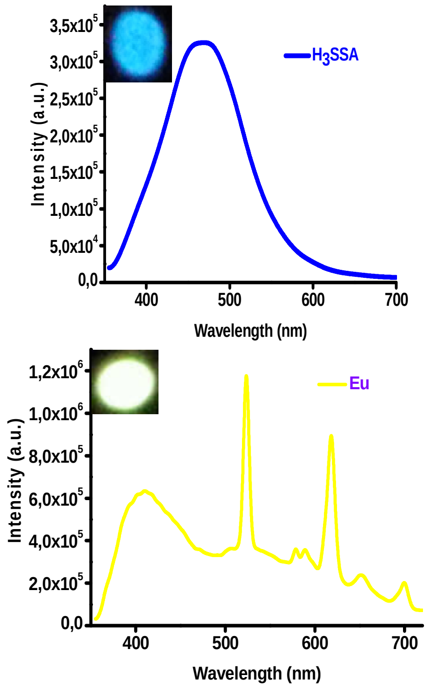


Figure 8. (a) The solid state emission spectrum of the free ligand H_3ssa and (b) complex **1** in the UV-Visible region at room temperature ($\lambda_{exc.}$= 349 nm).

Generally, the lanthanide-based organic complexes, due to the intraconfigurational f←→f transition are parity- forbidden and also Ln ions have low absorption coefficient. Therefore, researchers have proposed the use of organic chromophores in the lanthanide compounds which absorb light in the UV region and transfer the excitation energy from the chromophore to central lanthanide ions via an antenna effect (Figure 9), which can be seen in spectrum as the overlaps between the excitation spectrum of the complex and the absorption spectra of its free ligands (Figure 10) [38–40]. In briefly, Lanthanide-sensitization processing consists of three steps (Figure 9), (i) the ligands absorb the energy and are excited to the singlet (S) excited state, (ii) the energy of the (S) excited state is transferred to its triplet (T) level via intersystem crossing (ISC) and (iii) the energy is transferred to the 4f levels of the Ln(III) ions, resulting in the characteristic emissions of the sensitized Ln(III) ions [40].

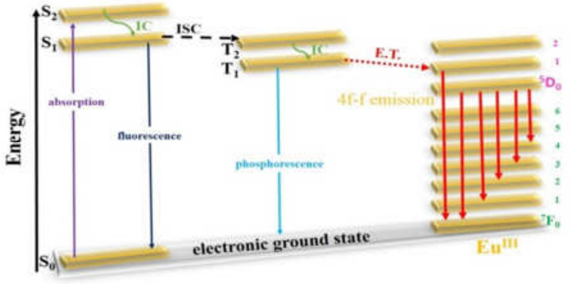


Figure 9. Jablonski diagram showing basic photophysical process (left) and energy level diagrams of Eu^{III} ion (right).

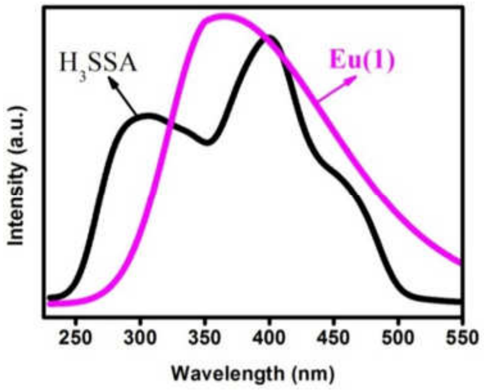


Figure 10. The excitation spectrum for complex **1** and absorption spectra of the free H_3ssa ligand as solid state.

4. Conclusion

The new Eu(III) based coordination polymer has been synthesized successfully under hydrothermal condition with using 5-sulfosalicylic acid (H_3ssa) ligand. The crystal structure of complex **1** has been re-determined by single x-ray diffraction analysis. And also complex characterized by FTIR, UV-Vis spectra, elemental analysis and also as a complementary characterization PXRD. Structural analysis of complex **1** exhibits that each Eu(III) ions is eight coordinated by oxygen atoms of ssa^- ligands and water molecules. The solid state photoluminescence properties have been investigated at room temperature in UV-Visible region for free H_3ssa ligand and its complex **1**. The photoluminescence measurement shows yellow emission for complex **1**, which is attributed to the f-f electronic transitions. Moreover, complex **1** shows a broad band, the inefficient quenching of the ligand-centred emission can be further seen from the broad bands with low intensity around 355-495 nm. The emission spectrum shows that the energy transfer from ligands to complex **1** is moderately efficient. In generally, the coordinated water molecules can quench the emission of Ln(III) ion, but complex **1** indicates intense emission, which also may be accounted for by the sensitization of the ligands and the extensive π system of the polymer structures.

Acknowledgements

The author is grateful to Research Funds of Balikesir University (BAP-2016/131) for the financial support. The author is grateful to Asst. Prof. Muhittin AYGUN and to Dokuz Eylul University for the use of Agilent Xcalibur Eos diffractometer (purchased under University Research Grant No. 2010.KB.FEN.13). The author also acknowledges to Balikesir University, Science and Technology Application and Research Center (BUBTAM) for the use of the Photoluminescence Spectrometer and to Prof. Dr. Hulya KARA SUBASAT for their helpful and constructive suggestion.

References

[1] Oylumluoglu, G., Coban, M.B., Kocak, C., Aygun, M. and Kara, H., 2-and 1-D coordination polymers of Dy(III) and Ho(III) with near infrared and visible luminescence by efficient charge-transfer antenna ligand, **Journal of Molecular Structure**, 1146, 356–364, (2017).

[2] Yahsi, Y., Ozbek, H., Aygun, M. and Kara, H., Crystal structure and photoluminescence properties of a new Cd II coordination polymer catena -poly[bis[4-bromo-2-({[2-(pyrrolidin-1-yl)ethyl]imino}methyl)phenolato-κ 3 N , N ′, O]di-μ 3 -chlorido-di-μ 2 -chlorido-bis(methanol-κ O)tricadmium(II)], **Acta Crystallographica Section C Structural Chemistry**, 72, 426–431, (2016).

[3] Güngör, E., Cu_4O_4 Kübik Formdaki Bakır (II) Kompleksinin Yapısal ve Fotolüminesans Özelliklerinin İncelenmesi, **Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi**, 21, 652-658, (2017).

[4] Gungor, E., 3-D polymeric structure formed by hydrogen bonds of copper (II) complex, **Molecular Crystals and Liquid Crystals**, 642, 21–28 (2017).

[5] Gungor, E., A new stepped tetranuclear copper(II) complex: Synthesis, crystal structure and photoluminescence properties, **Acta Crystallographica Section C Structural Chemistry**, 73, 393–398, (2017).

[6] Coban, M.B., Kocak, C., Kara, H., Aygun, M. and Amjad, A., Magnetic properties and sensitized visible and NIR luminescence of Dy III and Eu III coordination polymers by energy transfer antenna ligands, **Molecular Crystals and Liquid Crystals**, 648, 202–215, (2017).

[7] Li, X., Lu, Y., Bing, Y. and Zha, M., Synthesis , Photoluminescent , and Magnetic Properties of Two Lanthanide Sulfosalicylate Complexes, **Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry**, 42, 698–704, (2012).

[8] Zhou, R.-S., Ye, L., Ding, H., Song, J-F., Xu, X-Y. and Xu, J-Q., Syntheses, structures, luminescence, and magnetism of four 3D lanthanide 5-sulfosalicylates, **Journal of Solid State Chemistry**, 181, 567–575, (2008).

[9] Coban, M.B., Amjad, A., Aygun, M. and Kara, H., Sensitization of HoIII and SmIII luminescence by efficient energy transfer from antenna ligands: Magnetic, visible and NIR photoluminescence properties of GdIII, HoIII and SmIII coordination polymers, **Inorganica Chimica Acta**, 455, 25–33, (2017).

[10] Ay, B., Yildiz, E. and Kani, İ., Two novel isostructural and heteroleptic Nd(III) and Dy(III)-organic frameworks constructed by 2,5-pyridinedicarboxylic acid and in situ generated 2-pyridinecarboxylic acid: Hydrothermal synthesis, characterization, photoluminescence properties and hetero, **Polyhedron**, 130, 165–175, (2017).

[11] Allendorf, M.D., Bauer, C.A., Bhakta, R.K. and Houk, R.J.T., Luminescent metal–organic frameworks, **Chemical Society Reviews**, 38, 1330–1352, (2009).

[12] Dang, S., Sun, L-N.,Zhang, H-J., Guo, X-M., Li, Z-F., Feng, J., Guo, H-D. and Guo, Z-Y., Near-Infrared Luminescence from Sol−Gel Materials Doped with Holmium(III) and Thulium(III) Complexes, **The Journal of Physical Chemistry C**, 112, 13240–13247, (2008).

[13] Beeby, A., Botchway, S.W., Clarkson, I.M., Faulkner, S., Parker, A.W., Parker, D. and Williams, J.A.G., Luminescence imaging microscopy and lifetime mapping using kinetically stable lanthanide(III) complexes, **Journal of Photochemistry and Photobiology B: Biology**, 57, 83–89, (2000).

[14] Zhao, J., Zhao, J., Zhu, G-H., Xie, L-Q., Wu, H-L., Zhou, A-J., Wu, Z-Y., Wang, J., Chen, Y-C. and Tong, M-L., Magnetic and luminescent properties of lanthanide coordination polymers with asymmetric biphenyl-3,2′,5′-tricarboxylate, **Dalton Transactions**, 44, 14424–14435, (2015).

[15] Yenikaya, C., Sari, M., Lkimen, H., Bülbül, M. and Büyükgüngör, O., Synthesis and characterization of a novel amino salicylato salt and its Cu(II) complex and their inhibition studies on carbonic anhydrase isoenzymes, **Polyhedron**, 30, 535–541, (2011).

[16] Lu, Z.D., Wen, L.L., Yao, J., Zhu, H.H. and Meng, Q.J., Two types of novel layer framework structures assembled from 5-sulfosalicylic acid and lanthanide ions, **Crystal Engineering Communications**, 8, 847–853, (2006).

[17] Starynowicz, P., Synthesis and crystal structure of europium(II) dihydrogen bis(sulfosalicylate) pentahydrate [Eu(C7H5O6S)2(H2O)5]∞, **Journal of Alloys and Compounds**,305, 117–120, (2000).

[18] Clark, R.C. and Reid, J.S., The analytical calculation of absorption in multifaceted crystals, **Acta Crystallographica Section A Foundations and Advances**, 51, 887–897, (1995).

[19] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. and Puschmann, H., OLEX2: A complete structure solution, refinement and

analysis program, **Journal of Applied Crystallography**, 42, 339–341, (2009).

[20] Sheldrick, G.M., A short history of SHELX, **Acta Crystallographica Section A: Foundations of Crystallography**, 64, 112–122, (2007).

[21] Spek, A.L., Structure validation in chemical crystallography, **Acta Crystallographica Section D: Biological Crystallography**, 65, 148–155, (2009).

[22] Li, X., Xie, Z., Lin, J. and Cao, R., Lanthanide-organic frameworks constructed from multi-functional ligands: Syntheses, structures, near-infrared and visible photoluminescence properties, **Journal of Solid State Chemistry**,182, 2290–2297, (2009).

[23] Coban, M.B., Erkarslan, U., Oylumluoglu, G., Aygun, M. and Kara, H., Hydrothermal synthesis, crystal structure and Photoluminescent properties; 3D Holmium(III) coordination polymer, **Inorganica Chimica Acta**, 447, 87–91, (2016).

[24] Acar, Y., Photoluminescence properties of Gd(III) and Ce(III) lanthanide based metal organic frameworks, **Anadolu University Journal of Science and Technology A - Applied Science and Engineering**,17, 754–754, (2016).

[25] Ilmi, R. and Iftikhar, K., Structure elucidation by sparkle/RM1, effect of lanthanide contraction and photophysical properties of lanthanide(III) trifluoroacetylacetonate complexes with 1,10-phenanthroline, **Journal of Photochemistry and Photobiology A: Chemistry**, 325, 68–82, (2016).

[26] Zhou, X., Zhao X., Wang, Y., Wu, B., Shen, J., Li, L. and Li, Q., Eu(III) and Tb(III) Complexes with the Nonsteroidal Anti-Inflammatory Drug Carprofen: Synthesis, Crystal Structure, and Photophysical Properties, **Inorganic Chemistry**, 53, 12275–12282, (2014).

[27] Shen, H.-Y., Wang, W.-M., Gao, H.-L. and Cui, J.-Z., Near-infrared luminescence and SMM behaviors of a family of dinuclear lanthanide 8-quinolinolate complexes, **The Royal Society of Chemistry Advances**, 6, 34165–34174, (2016).

[28] Feng, X., Feng, Y-Q., Chen, J. J., Ng, S-W., Wang, L-Y. and Guo, J-Z., Reticular three-dimensional 3d–4f frameworks constructed through substituted imidazole-dicarboxylate: syntheses, luminescence and magnetic properties study, **Dalton Transactions**, 44, 804–816, (2015).

[29] Han, Y., Fu, L., Mafra, L. and Shi, F.-N., Hydrothermal synthesis, crystal structures and photoluminescence properties of mixed europium–yttrium organic frameworks, **Journal of Solid State Chemistry**, 186, 165–170, (2012).

[30] Teixeira, J.A., Nunes, W.D.G., Nascimento, A.L.C.S., Colman, T.A.D., Caires, F.J., Galico, D.A. and Ionashiro, M., Synthesis, thermoanalytical, spectroscopic study and pyrolysis of solid rare earth complexes (Eu, Gd, Tb and Dy) with p-aminobenzoic acid, **Journal of Analytical and Applied Pyrolysis**, 121, 267–274, (2016).

[31] Liu, D.D., Chen, Y-G., Zhang, C-J., Meng, H-X., Zhang, Z-C. and Zhang, C-X., Effect of ring coordination of pyridine-3,5-dicarboxylate and metatungstate to Ln ions on metatungstate structure: Synthesis, structure and optical property of four new compounds, **Journal of Solid State Chemistry**, 184, 1355–1360, (2011).

[32] De Moura, A.P., De Oliveira, L.H., Paris, E.C., Li, M.S., Andrés, J., Varela, J. A., Longo, E. and Rosa, I.L.V., Photolumiscent properties of nanorods and nanoplates $Y_2O_3:Eu^{3+}$, **Journal of Fluorescence,** 21, 1431–1438, (2011).

[33] Xu, W., Zhang, C.-J., Wang, H. and Wang, Y., Two Novel Two-Dimensional Lanthanide (III) Coordination Polymers Constructed from Isonicotinic Acid and Iminodiacetic Acid: Synthesis, Structure, and Luminescence Properties, **Journal of Cluster Science**, 28, 2005–2015, (2017).

[34] Liu, C.-B., Li, Q., Wang, X., Che, G.-B. and Zhang, X.-J., A series of lanthanide (III) coordination polymers derived via in situ hydrothermal decarboxylation of quinoline-2,3-dicarboxylic acid, **Inorganic Chemistry Communications**, 39, 56–60, (2014).

[35] Wu, Q-R., Wang, J-J., Hu, H-M., Shangguan, Y-Q., Fu, F., Yang, M-L., Dong, F-X. and Xue, G-L., A series of lanthanide coordination polymers with 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine: Syntheses, crystal structures and luminescence properties, **Inorganic Chemistry Communications**, 14, 484–488, (2011).

[36] Ma, P., Wan, R., Si, Y., Hu, F., Wang, Y., Niu, J. and Wang, J., Double-malate bridging tri-lanthanoid cluster encapsulated arsenotungstates: syntheses, structures, luminescence and magnetic properties, **Dalton Transactions**, 44, 11514–11523, (2015).

[37] Jiao, C-Q., Zhang, J-C., Zhao, Y., Sun, Z-G., Zhu, Y-Y., Dai, L-L., Shi, S-P. and Zhou, W., Lanthanide(III) oxalatophosphonates: syntheses, crystal structures and luminescence properties, **Dalton**

Transactions, 43, 1542–1549, (2014).

[38] Dang, S., Sun, L-N., Song, S-Y., Zhang, H-J., Zheng, G-L., Bi, Y-F., Guo, H-D., Guo, Z-Y. and Feng, J., Syntheses, crystal structures and near-infrared luminescent properties of holmium (Ho) and praseodymium (Pr) ternary complexes, **Inorganic Chemistry Communications**, 11, 531–534, (2008).

[39] Dang, S., Yu, J., Yu, J., Wang, X., Sun, L., Feng, J., Fan, W. and Zhang, H., Novel Holmium (Ho) and Praseodymium (Pr) ternary complexes with fluorinated-ligand and 4,5-diazafluoren-9-one, **Materials Letters**, 65, 1642–1644, (2011).

[40] Dang, S., Yu, J., Wang, X., Sun, L., Deng, R., Feng, J., Fan, W. and Zhang, H., NIR-luminescence from ternary lanthanide [HoIII, Pr III and TmIII] complexes with 1-(2-naphthyl)-4,4,4- trifluoro-1,3-butanedionate, **Journal of Luminescence**, 131, 1857–1863, (2011).

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1565766 for complex **1**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).