

Study of the Structure and the Luminescence Properties of the Tb Compound

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Abstract: A lanthanide-organic frameworks Tb (C₂O₄)(HCOO) (1) is synthesized via hydrothermal methods (autogenous pressure) at temperature around 200°C over a period of a week. Obtained single crystals are characterized by Elemental Analysis (EA), Single Crystal Powder X-Ray Diffraction SCPXRD as well as optical measurements were categorized by Photoluminescence (PL) experiments. The results showed crystals are pure and they exhibit the peak of crystalline orthorhombic Pnma group space. The PL emission spectrum has been monitored at 325 nm (pulsed laser He-Cd). Resulted green luminescence spectrum for the green luminescence emission for compound 1 was located at 544 nm attributed to (⁵D₄•⁷F₅) electronic transition. The noticeable emission intensity for the compound 1 indicated that the lanthanide organic frameworks are good candidate materials for electro-optical devices, Field Emission Displays (FEDs) and they have a potential application in solid-state light.

Key words: Lanthanide organic framework, photoluminescence, hydrothermal method, single crystal, rare earth, solid-state light

INTRODUCTION

Lanthanide-Organic Frameworks (LOFs) are certain types of materials which have a potential application in the fields of sensitive devices, biology, chemistry, medicine and optoelectronics like optical displays panels and Light-Emitting Diodes (LEDs) due to their special chemical and physical properties (Zhang *et al.*, 2008, 2011; Feng *et al.*, 2010; Dai *et al.*, 2010; Klein *et al.*, 2009; Zhu *et al.*, 2007; Mahata *et al.*, 2007; Maspoeh *et al.*, 2007; Zhao *et al.*, 2009; Cheng *et al.*, 2007). The hybrid frameworks are composed by an organic ligand and a metal ion within a porous structure establishing an extensive range of emissive phenomena, for instance linker-based luminescence (Du *et al.*, 2007; Lan *et al.*, 2007; Lu *et al.*, 2007; Wang *et al.*, 2007) metal-based emission (Sonnauer *et al.*, 2007; Gandara *et al.*, 2007; Serre *et al.*, 2004) or antennae effects (De Lill *et al.*, 2017; McManus *et al.*, 2007; Chen *et al.*, 2006; Wagner *et al.*, 2002). Both the inorganic and the organic moieties can provide the platforms to produce luminescence, typically the origin of luminescence emission widely observed in lanthanide MOFs via the so-called (antenna effect) which is often referred to as (LMCT), since, the strongly absorbing ligand acts as a receiving antenna for the bond metal ion. In addition, the cooperative functionalities of permanent porosity and luminescence property qualified

luminescent MOFs as a very attractive new class of sensing materials (Hatanaka *et al.*, 2017; Rossin *et al.*, 2012).

Trivalent lanthanide Ln (•••) ions produce attractive optical properties. Recently the luminance studies of rare earths metals that are synthesized with various organic ligands have been conducted. Ln (•••) chelates provide narrow band emissions and very pure luminescence using UV/VIS excitation (Latva *et al.*, 1997). This sensitized luminescence of the lanthanide compounds are commonly used for the optical materials, biological applications, electroluminescent devices, optical amplifier or laser and sensors (Bunzli and Piguet, 2005; Cui *et al.*, 2014).

Luminescence of compound Terbium (Tb³⁺) take the tending due to the narrow f-f transitions have attracted a lot of attention because of their good sensitization luminescence that can be carried out through the antenna effect as well as the line of emission spectra look mostly sharp as it depends on the crystal field around the metal ions. Furthermore, a great attention has been paid to the luminescence of Tb³⁺ ions owing to the ability of acting as phosphors and progress of materials (Vicentini *et al.*, 2000). It is well-known that Rare Earth Organic Frameworks (REOFs) have attracted comprehensive interest over the past few years because not only their interesting applications but also their luminescence which originated from intra 4f or 4f-5d transitions (Robin and

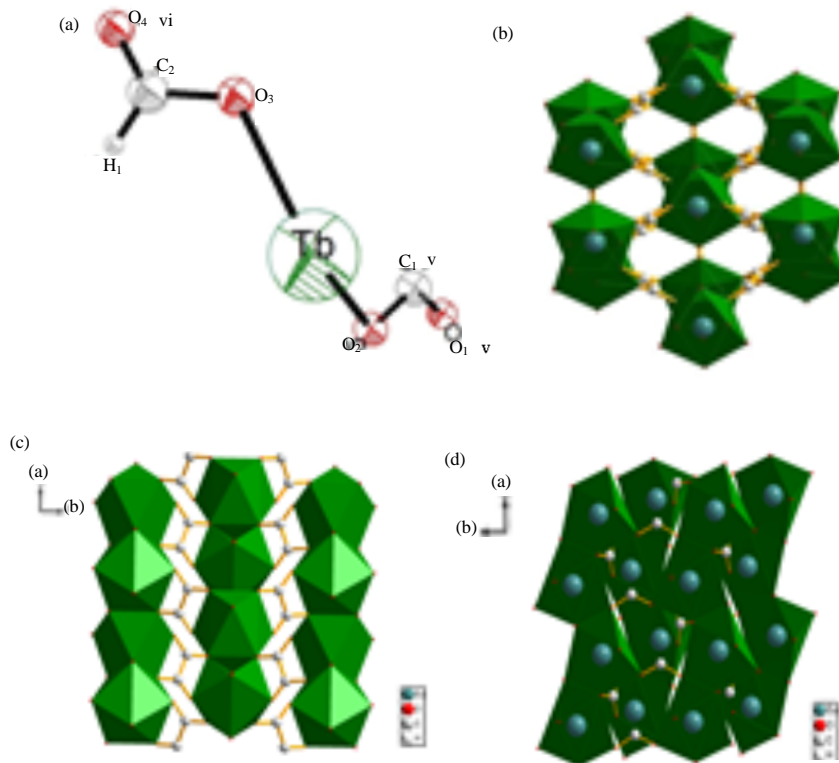


Fig. 1: Illustration of the crystal structure of the $\text{Tb}(\text{C}_2\text{O}_4)(\text{HCOO})$ 1 hybrid framework with asymmetric unit: a) Typical single crystal morphology (habit) and its low index face and b-d) Views perpendicular to the (100), (010) and (001) planes, respectively, hydrogen atoms have been deleted for clarity

Fromm, 2006; Chandler *et al.*, 2016; Pretsch *et al.*, 2006; Yeung *et al.*, 2006; Gu and Xue, 2016; Sun *et al.*, 2006; Gheorghe *et al.*, 2006; Zhu *et al.*, 2007; Huang *et al.*, 2007; Gandara *et al.*, 2007; Zimmermann *et al.*, 2007; Shi *et al.*, 2008; Pompidor *et al.*, 2008; Lunstroot *et al.*, 2009). This specific luminescence is characterized by high luminescence quantum yield, narrow bandwidth, long life time, large Stokes shifts and ligand dependent luminescence sensitization (Shang *et al.*, 2012, Sun *et al.*, 2007).

Here in, we show crystalline framework materials incorporated both inorganic and organic moieties are attracting candidates because of their wide chemical and structural variety that propose opportunities for making many technologically relevant properties (Cheetham *et al.*, 2006; Rao *et al.*, 2008; Kurmoo, 2009; Allendorf *et al.*, 2009; Jain *et al.*, 2008). Notably, the dense hybrid systems usually incorporated with infinite inorganic connectivity, like Metal-Oxygen-Metal (M-O-M) arrays that present the topological characteristics desired for certain types of physical properties (Rao *et al.*, 2004). The synthesized compound 1 was first successfully synthesized by hydrothermal method where compound 1

and 2 consist of lanthanide organic frameworks with an orthorhombic crystal structure, as previously prepared by Romero *et al.* (1996). In Fig. 1, we illustrated the crystal structure of compound 1, we can notice that the three basic building blocks are the inorganic M-O-M chains and the two organic bridging ligands, namely the oxalate ($\text{C}_2\text{O}_4^{2-}$) and the formate (HCOO) ions which are effectively oriented perpendicular to one another as well, it is also known that oxalate is structurally more rigid than formate.

In the present research, compound 1 is successfully prepared by hydrothermal method, the crystal structure and the optical properties have been described in details. The results showed that compound 1 exhibited strong green luminescence the characteristics luminescence of Tb^{3+} ions indicating that the compound 1 are a perfect experimental probe of the crystalline environment.

MATERIALS AND METHODS

Materials and measurements: All starting materials and solvents are reagent grade commercially available the

Table 1: Crystallographic data of compound 1

Variables	Values
Compound	1
Formula sum	C ₃ H ₄ O ₈ Tb ₁
Formula weight	291.96 g/mole
Crystal system	Orthorhombic
Space-group	Pnma
Cell parameters	a = 7.0138(3) Å b = 10.6077(4) Å c = 6.66021(6) Å
•	90
•	90
•	90
V(Å ³)	491.198
D _c (g cm ⁻³)	3.948
Z	4

Table 2: Atomic parameters of compound 1

Atom	x/a	y/b	z/c
Tb1	0.20372(4)	0.13266(4)	0.25000(4)
O1	-0.0863(5)	0.1464(4)	0.1234(3)
O2	0.2361(5)	-0.0205(6)	0.4562(3)

materials provided by Aldrich. All materials were used as received without further purification. PXRD patterns for complex 1 was collected on (Empyrean, PANalytical V. V., 40 kV, 40 mA) diffractometer, using (Cu-Kα) (1.540598Å) radiation in the angular range 2θ = 5-80°. Single crystal X-ray data of 1 were collected at room temperature using OXFORD diffraction Rigaku. XtalABmin™ diffractometer. EA test was performed using an Elementar Vario Micro Cube EL *** elemental analyzer. Optical measurements were performed using pulsed laser He-Cd (325 nm) (Horiba Jobin Yvon) at room temperature.

Synthesis of Tb (C₂O₄)(HCOO): We prepared the title compounds was carried out in a Pyrex-lined steel bomb (autogenous pressure) at the temperature around 200 coover a period for a week, single crystals were obtained by heating an aqueous suspension of Tb oxalate decahydrate Tb₂(C₂O₄) 10 H₂O, 0.5 mmol of Tb oxalate decahydrate and 15 mmol of acid oxalic dihydrate in 10 mL of water for a week. By varying the heating time less or more than 7 days, it has been observed that no single crystals were developed. The final product, consisting of single crystals of compound 1 were recovered by filtration, washed with water and ethanol and then dried in air.

Structure determination: Table 1 and 2 present a summary of the crystal data, data collection and refinement parameters for the compound 1. Figure 2 shows the XRD pattern of the as-formed samples through hydrothermal method. Crystallographic data were collected with oxford diffraction Rigaku. XtalABmin™ diffractometer and all data indicates that the compounds Tb(C₂O₄)(HCOO) are pure and exhibited

Table 3: Selected geometric information of compound 1

Atoms	U ₁₁	U ₂₂	U ₃₃
Tb1	0.00933(16)	0.00875(14)	0.00791(16)
O1	0.0160(15)	0.0158(13)	0.0098(14)
O2	0.0164(15)	0.0294(18)	0.0162(17)
Atoms 1,2	d 1,2 [Å]	Atoms 1, 2	d 1,2 [Å]
Tb1-O ₁	2.465(3)	Tb1-O ₃	2.493(4)
Tb1-O ₁ ⁱ	2.491(3)	Tb1-O ₃ ⁱ	2.442(5)
Tb1-O ₁ ⁱⁱ	2.465(3)	Tb1-O ₄	2.472(5)
Tb1-O ₁ ⁱⁱⁱ	2.491(3)	O1-C ₂	1.274(5)
Tb1-O ₂ ⁱⁱ	2.436(3)	O2-C ₂ ^v	1.238(5)
Tb1-O ₂	2.436(3)	C2-C ₂ ^{iv}	1.545(8)
Tb1-C ₂ ^{iv}	3.230(4)	O3-C ₃	1.293(7)
Tb1-C ₂ ^v	3.230(4)	C3-O ₄ ^{vi}	1.216(8)

Table 4: Selected bond length (Å) and angles (deg.) for compound 1

Atoms 1, 2, 3	Angle 1, 2, 3 [°]	Atoms 1, 2, 3	Angle 1, 2, 3 [°]
O ₁ ⁱⁱ -Tb1-O ₁	66.56(15)	O ₃ -Tb1-O ₁ ⁱ	76.57(11)
O ₁ ⁱⁱ -Tb1-O ₁	100.38(11)	O ₃ -Tb1-O ₂ ⁱⁱ	114.33(9)
O ₁ ⁱⁱ -Tb1-O ₁ ⁱ	100.38(11)	O ₃ ⁱ -Tb1-O ₂ ⁱⁱ	78.52(10)
O ₁ ⁱⁱⁱ -Tb1-O ₁ ⁱ	65.75(15)	O ₃ ⁱ -Tb1-O ₂	78.52(10)
O ₂ ⁱⁱ -Tb1-O ₁	66.32(11)	O ₃ -Tb1-O ₂	114.33(9)
O ₂ -Tb1-O ₁ ⁱ	72.49(12)	O ₃ -Tb1-C ₂ ^{iv}	102.14(9)
O ₂ -Tb1-O ₁ ⁱⁱⁱ	132.86(11)	O ₃ ⁱ -Tb1-C ₂ ^{iv}	97.88(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱⁱⁱ	72.49(12)	O ₃ ⁱ -Tb1-C ₂ ^v	97.88(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱ	132.86(11)	O ₃ -Tb1-C ₂ ^v	102.14(9)
O ₂ -Tb1-O ₁	126.17(12)	O ₄ -Tb1-O ₁	70.70(12)
O ₂ -Tb1-O ₁ ⁱⁱ	66.32(11)	O ₄ -Tb1-O ₁ ⁱⁱⁱ	142.29(9)
O ₂ ⁱⁱ -Tb1-O ₁ ⁱⁱ	126.17(12)	O ₄ -Tb1-O ₁ ⁱⁱ	70.70(12)
O ₂ ⁱⁱ -Tb1-O ₂	129.30(19)	O ₄ -Tb1-O ₁ ⁱ	142.29(9)
O ₃ ⁱ -Tb1-O ₁ ⁱ	64.80(11)	C ₂ ^{iv} -C ₂ -O ₁	115.1(5)
O ₃ ⁱ -Tb1-O ₁ ⁱⁱ	144.72(8)	C ₂ ^{iv} -C ₂ -O ₂ ^{vii}	118.7(5)
O ₃ ⁱ -Tb1-O ₁	144.72(8)	C ₂ -O ₂ -Tb1	122.3(4)
O ₃ -Tb1-O ₁ ⁱⁱ	64.46(10)	C ₃ -O ₃ -Tb1 ^{viii}	134.2(5)
O ₃ -Tb1-O ₁ ⁱⁱⁱ	76.57(11)	O ₄ ^{vi} -C ₃ -O ₃	125.6(7)
O ₃ ⁱ -Tb1-O ₁ ⁱⁱⁱ	64.80(11)	C ₃ ^{iv} -O ₄ -Eu1	129.0(5)
O ₃ -Tb1-O ₁	64.46(10)	-	-

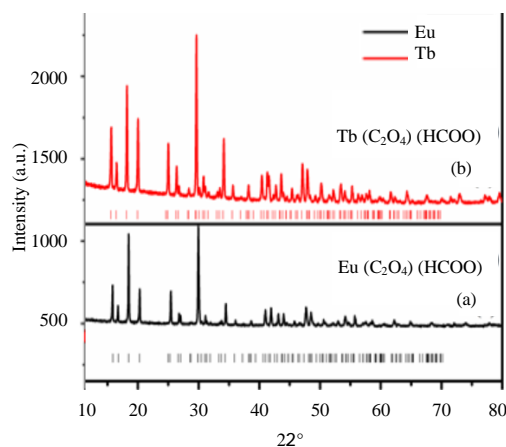


Fig. 2: The PXRD patterns of the as-synthesized Tb(C₂O₄)(HCOO)

the peak of pure crystalline orthorhombic group Pnma (62) which was well consistent with the created CIF file (Xpert HIGH SCORE PLUS) as shown in Fig. 2. Crystallographics and the selected, bond lengths and angles are listed in Table 1-4.

RESULTS AND DISCUSSION

Structure description: In this research, the single crystal X-ray diffraction study revealed that compound 1 have asymmetric unit as illustrated in Fig. 1. It is also, observed that the structure of compound 1 is orthorhombic and it may be described in the following way. The structures of 1 is 3-D hybrid frameworks which are Pnma (62) space group. The dimensionality of its inorganic and organic connectivities are 1 and 2-D, respectively. The 1-D inorganic chains contain of 9 coordinated europium polyhedra that participate their faces to form infinite zigzag chains along the (100) direction. To form the 2-D organic connectivity, europium chains are bridged by formate ligands along the (010) direction to form infinite 2-D layers, nearby layers are subsequently bridged by the oxalate ligands along the (001) direction to make a 3-D framework structure.

Finally, the structures for the two compounds **1** is built up from Eu, Tb oxalate shared all their oxygen atoms with oxalate and formate ligands, thus take the shape of a 3D framework structure as shown in Fig. 1.

Luminescent property: Photoluminescence experiment results were measured using an excitation wavelength of the pulsed ultraviolet He-Cd laser 325 nm at room temperature. Notably compound 1 show emissions intensity in the range of 300-800 nm as displayed in Fig. 3. The emission spectra of compound 1 gave the characteristics of Tb^{3+} transitions, respectively. The resonance energy levels of terbium ions are presented in Table 5 along with the various luminescence transitions.

Figure 3 illustrates the photoluminescence spectra for compound 1, there are four very strong characteristic emission bands for the Tb^{3+} ion in the visible region. The spectrum is dominated by the major sharp peak at 544 nm due to $^5D_4, ^7F_5$ transition which give strong green emission as well as the other emission bands are: $^5D_4, ^7F_6$ at 486 nm and $^5D_4, ^7F_4$ at 583 nm and $^5D_4, ^7F_3$ at 620 nm, respectively. These transitions which are allowed by Electric Dipole (ED) and supersensitive to surrounding in the vicinity of Tb^{3+} ion, is very intense, emitting strong green luminescence (Bunzli *et al.*, 2007).

Symmetry operators:

$$\begin{aligned} &0.5+x, 0.5-y, 0.5-z, x, y, 0.5-z, 0.5+x, 0.5-y, z \\ &-x, -y, -z, -x, -y, 0.5+z, x, 1+y, z, -x, -y, -0.5+z \\ &-0.5+x, 0.5-y, 0.5-z, x, -1+y, z \end{aligned}$$

The PXRD patterns of the as-synthesized $Tb(C_2O_4)(HCOO)$ was shows in Fig. 2.

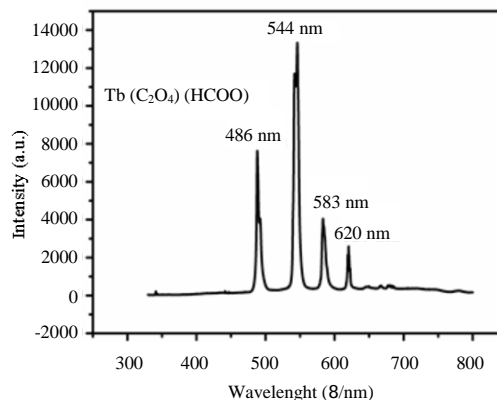


Fig. 3: PL spectra from compound of Tb compound

Table 5: Energy levels and luminescence transition for europium (18 and 19) and terbium (20)

Upper energy levels (energy cm^{-1})	Lower levels	• (nm)
$Tb^{3+}D_3(26250)$	$^7F_6, ^7F_5, ^7F_4, ^7F_3, ^7F_0$	490, 545, 587, 622,
$^5D_4(20500)$	$^7F_6, ^7F_5, ^7F_4$	650, 671, 681

CONCLUSION

In the presented research, 3-D hybrid framework 1 was successfully prepared through hydrothermal method and characterized by SCPXRD. Single crystal structure of compound 1 has asymmetric unit and the spectrum of UV laser induced photoluminescence shows that compound 1 gave a strong strong green emission at 544 nm, respectively. Measurements indicate that the luminescence behavior demonstrates that Rare Earth Organic Framework (REOFs) of compound 1 has excellent potential application in solid state light, Field Emission Displays (FEDs).

REFERENCES

- Allendorf, M.D., C.A. Bauer, R.K. Bhakta and R.J.T. Houk, 2009. Luminescent metal-organic frameworks. *Chem. Soc. Rev.*, 38: 1330-1352.
- Bunzli, J.C.G. and C. Piguet, 2005. Taking advantage of luminescent lanthanide ions. *Chem. Soc. Rev.*, 34: 1048-1077.
- Bunzli, J.C.G., S. Comby, A.S. Chauvin and C.D. Vandevyver, 2007. New opportunities for lanthanide luminescence. *J. Rare Earths*, 25: 257-274.
- Chandler, B.D., D.T. Cramb and G.K. Shimizu, 2016. Microporous metal-organic frameworks formed in a stepwise manner from luminescent building blocks. *J. Am. Chem. Soc.*, 128: 10403-10412.
- Cheetham, A.K., C.N.R. Rao and R.K. Feller, 2006. Structural diversity and chemical trends in hybrid inorganic-organic framework materials. *Chem. Commun.*, 46: 4780-4795.

- Chen, B., Y. Yang, F. Zapata, G. Qian and Y. Luo *et al.*, 2006. Enhanced near-infrared-luminescence in an erbium tetrafluoroterephthalate framework. *Inorg. Chem.*, 45: 8882-8886.
- Cheng, J.W., S.T. Zheng and G.Y. Yang, 2007. Diversity of crystal structure with different lanthanide ions involving in situ oxidation-hydrolysis reaction. *Dalton Trans.*, 36: 4059-4066.
- Cui, Y., B. Chen and G. Qian, 2014. Lanthanide metal-organic frameworks for luminescent sensing and light-emitting applications. *Coord. Chem. Rev.*, 273: 76-86.
- Dai, F., P. Cui, F. Ye and D. Sun, 2010. An open neodymium-organic framework with the NBO structure type based on binuclear SBU involved in situ generated formate. *Cryst. Growth Des.*, 10: 1474-1477.
- De Lill, D.T., A. De Bettencourt-Dias and C.L. Cahill, 2017. Exploring lanthanide luminescence in metal-organic frameworks: Synthesis, structure and guest-sensitized luminescence of a mixed europium/terbium-adipate framework and a terbium-adipate framework. *Inorg. Chem.*, 46: 3960-3965.
- Du, M., X.J. Jiang and X.J. Zhao, 2007. Molecular tectonics of mixed-ligand metal-organic frameworks: Positional isomeric effect, metal-directed assembly and structural diversification. *Inorg. Chem.*, 46: 3984-3995.
- Feng, X., B. Liu, L.Y. Wang, J.S. Zhao and J.G. Wang *et al.*, 2010. A series of lanthanide-organic polymers incorporating nitrogen-heterocyclic and aliphatic carboxylate mixed-ligands: Structures, luminescent and magnetic properties. *Dalton Trans.*, 39: 8038-8049.
- Gandara, F., A. Garcia-Cortes, C. Cascales, B. Gomez-Lor and E. Gutierrez-Puebla *et al.*, 2007. Rare earth arenedisulfonate metal-organic frameworks: An approach toward polyhedral diversity and variety of functional compounds. *Inorg. Chem.*, 46: 3475-3484.
- Gheorghe, R., P. Cucos, M. Andruh, J.P. Costes and B. Donnadieu *et al.*, 2006. Oligonuclear 3d-4f complexes as tectons in designing supramolecular solid-state architectures: Impact of the nature of linkers on the structural diversity. *Chem. A Eur. J.*, 12: 187-203.
- Gu, X. and D. Xue, 2016. Selected controlled synthesis of three-dimensional 4d-4f heterometallic coordination frameworks by lanthanide carboxylate subunits and silver centers. *Cryst. Growth Des.*, 6: 2551-2557.
- Hatanaka, M., Y. Hirai, Y. Kitagawa, T. Nakanishi and Y. Hasegawa *et al.*, 2017. Organic linkers control the thermosensitivity of the emission intensities from Tb (III) and Eu (III) in a chameleon polymer. *Chem. Sci.*, 8: 423-429.
- Huang, Y.G., B.L. Wu, D.Q. Yuan, Y.Q. Xu and F.L. Jiang *et al.*, 2007. New lanthanide hybrid as clustered infinite nanotunnel with 3D Ln-O-Ln framework and (3, 4)-connected net. *Inorg. Chem.*, 46: 1171-1176.
- Jain, P., N.S. Dalal, B.H. Toby, H.W. Kroto and A.K. Cheetham, 2008. Order-disorder antiferroelectric phase transition in a hybrid inorganic-organic framework with the perovskite architecture. *J. Am. Chem. Soc.*, 130: 10450-10451.
- Klein, N., I. Senkowska, K. Gedrich, U. Stoeck and A. Henschel *et al.*, 2009. A mesoporous metal-organic framework. *Angew. Chem. Intl. Ed.*, 48: 9954-9957.
- Kurmoo, M., 2009. Magnetic metal-organic frameworks. *Chem. Soc. Rev.*, 38: 1353-1379.
- Lan, A., L. Han, D. Yuan, F. Jiang and M. Hong, 2007. A blue luminescent inorganic-organic hybrid with infinite $[Cd_3(i_3-OH)_2(i_2-Cl)_2]$ connectivity. *Inorg. Chem. Commun.*, 10: 993-996.
- Latva, M., H. Takalo, V.M. Mukkala, C. Matachescu and J.C. Rodriguez-Ubis *et al.*, 1997. Correlation between the lowest triplet state energy level of the ligand and lanthanide (III) luminescence quantum yield. *J. Lumin.*, 75: 149-169.
- Lu, Z., L. Wen, Z. Ni, Y. Li and H. Zhu *et al.*, 2007. Syntheses, structures and photoluminescent and magnetic studies of metal-organic frameworks assembled with 5-sulfosalicylic acid and 1, 4-Bis(imidazol-1-ylmethyl)-benzene. *Cryst. Growth Des.*, 7: 268-274.
- Lunstrook, K., K. Driesen, P. Nockemann, K.V. Hecke, L.V. Meervelt *et al.*, 2009. Lanthanide-doped luminescent ionogels. *Dalton Trans.*, 2: 298-306.
- Mahata, P., A. Sundaresan and S. Natarajan, 2007. The role of temperature on the structure and dimensionality of MOFs: An illustrative study of the formation of manganese oxy-bis (benzoate) structures. *Chem. Commun.*, 43: 4471-4473.
- Maspoch, D., D. Ruiz-Molina and J. Veciana, 2007. Old materials with new tricks: Multifunctional open-framework materials. *Chem. Soc. Rev.*, 36: 770-818.
- McManus, G.J., J.J. Perry IV, M. Perry, B.D. Wagner and M.J. Zaworotko, 2007. Exciplex fluorescence as a diagnostic probe of structure in coordination polymers of Zn_2^+ and 4, 4'-bipyridine containing intercalated pyrene and enclathrated aromatic solvent guests. *J. Am. Chem. Soc.*, 129: 9094-9101.

- Pompidor, G., A. D'Aleo, J. Vicat, L. Toupet and N. Giraud *et al.*, 2008. Protein crystallography through supramolecular interactions between a lanthanide complex and arginine. *Angew. Chemie Intl. Ed.*, 47: 3388-3391.
- Pretsch, T., K.W. Chapman, G.J. Halder and C.J. Kepert, 2006. Dehydration of the nanoporous coordination framework Er III [Co III (CN)₆]₄ (H₂O): Single crystal to single crystal transformation and negative thermal expansion in Er III [Co III (CN)₆]. *Chem. Commun.*, 17: 1857-1859.
- Rao, C.N.R., A.K. Cheetham and A. Thirumurugan, 2008. Hybrid inorganic-organic materials: A new family in condensed matter physics. *J. Phys. Condens. Matter*, 20: 083202-083202.
- Rao, C.N.R., S. Natarajan and R. Vaidhyanathan, 2004. Metal carboxylates with open architectures. *Angew. Chemie Intl. Ed.*, 43: 1466-1496.
- Robin, A.Y. and K.M. Fromm, 2006. Coordination polymer networks with O- and N-donors: What they are why and how they are made. *Coord. Chem. Rev.*, 250: 2127-2157.
- Romero, S., A. Mosset and J.C. Trombe, 1996. Two new families of lanthanide mixed-ligand complexes, oxalate-carbonate and oxalate-formate: Synthesis and structure of [Ce(H₂O)]₂ (C₂O₄)₂(CO₃)• 2.5 H₂O and Ce(C₂O₄)(HCO₂). *J. Solid State Chem.*, 127: 256-266.
- Rossin, A., G. Giambastiani, M. Peruzzini and R. Sessoli, 2012. Amine-templated polymeric lanthanide formates: Synthesis, characterization and applications in luminescence and magnetism. *Inorg. Chem.*, 51: 6962-6968.
- Serre, C., F. Millange, C. Thouvenot, N. Gardant and F. Pelle *et al.*, 2004. Synthesis, characterisation and luminescent properties of a new three-dimensional lanthanide trimesate: M((C₆H₃)-(CO₂)₃) (M= Y, Ln) or MIL-78. *J. Mater. Chem.*, 14: 1540-1543.
- Shang, M., D. Geng, X. Kang, D. Yang and Y. Zhang *et al.*, 2012. Hydrothermal derived LaOF: Ln³⁺ (Ln = Eu, Tb, Sm, Dy, Tm, and/or Ho) nanocrystals with multicolor-tunable emission properties. *Inorg. Chem.*, 51: 11106-11116.
- Shi, F.N., L. Cunha-Silva, R.S. Ferreira, L. Mafra and T. Trindade *et al.*, 2008. Interconvertible modular framework and layered lanthanide (III)-etidronic acid coordination polymers. *J. Am. Chem. Soc.*, 130: 150-167.
- Sonnauer, A., C. Nather, H.A. Hoppe, J. Senker and N. Stock, 2007. Systematic investigation of lanthanide phosphonatoethanesulfonate framework structures by high-throughput methods, Ln(O₃P-C₂H₄SO₃) (H₂O) (Ln = La-Dy). *Inorg. Chem.*, 46: 9968-9974.
- Sun, X., Y.W. Zhang, Y.P. Du, Z.G. Yan and R. Si *et al.*, 2007. From trifluoroacetate complex precursors to monodisperse rare-earth fluoride and oxyfluoride nanocrystals with diverse shapes through controlled fluorination in solution phase. *Chem. A Eur. J.*, 13: 2320-2332.
- Sun, Y.Q., J. Zhang and G.Y. Yang, 2006. A series of luminescent lanthanide-cadmium-organic frameworks with helical channels and tubes. *Chem. Commun.*, 45: 4700-4702.
- Vicentini, G., L.B. Zinner, J. Zukerman-Schpector and K. Zinner, 2000. Luminescence and structure of europium compounds. *Coord. Chem. Rev.*, 196: 353-382.
- Wagner, B.D., G.J. McManus, B. Moulton and M.J. Zaworotko, 2002. Exciplex fluorescence of {[Zn (bipy)1.5 (NO₃)₂]}[CH₃OH]_{0.5} pyrene} n: A coordination polymer containing intercalated pyrene molecules (bipy= 4, 4'-bipyridine). *Chem. Commun.*, 18: 2176-2177.
- Wang, X.L., Y.F. Bi, H.Y. Lin and G.C. Liu, 2007. Three Novel Cd (II) metal-organic frameworks constructed from mixed ligands of dipyrido [3, 2-d: 2', 3'-f] quinoxaline and Benzene-dicarboxylate: From a 1-D ribbon, 2-D layered network, to a 3-D architecture. *Cryst. Growth Des.*, 7: 1086-1091.
- Yeung, W.F., T.C. Lau, X.Y. Wang, S. Gao and L. Szeto *et al.*, 2006. 2D LnIII RuIII₂ compounds constructed from trans-[Ru(acac)₂ (CN)₂]-Syntheses, structures and magnetic properties. *Inorg. Chem.*, 45: 6756-6760.
- Zhang, H.J., X.Z. Wang, D.R. Zhu, Y. Song and Y. Xu *et al.*, 2011. Novel 3D lanthanide-organic frameworks with an unusual infinite nanosized ribbon [Ln₃(i₃-OH)₂ (-CO₂)₆]ⁿ⁺ (Ln = Eu, Gd, Dy): Syntheses, structures, luminescence and magnetic properties. *Cryst Eng. Comm.*, 13: 2586-2592.
- Zhang, J.Y., Y. Ma, A.L. Cheng, Q. Yue and Q. Sun *et al.*, 2008. A manganese (II) coordination polymer with mixed pyrimidine-2-carboxylate and oxalate bridges: Synthesis, structure and magnetism. *Dalton Trans.*, 15: 2061-2066.
- Zhao, B., X.Y. Chen, Z. Chen, W. Shi and P. Cheng *et al.*, 2009. A porous 3D heterometal-organic framework containing both lanthanide and high-spin Fe (II) ions. *Chem. Commun.*, 21: 3113-3115.
- Zhu, W.H., Z.M. Wang and S. Gao, 2007. Two 3d porous lanthanide-fumarate-oxalate frameworks exhibiting framework dynamics and luminescent change upon reversible de- and rehydration. *Inorg. Chem.*, 46: 1337-1342.
- Zimmermann, M., N. Belai, R.J. Butcher, M.T. Pope and E.V. Chubarova *et al.*, 2007. New lanthanide-containing polytungstates derived from the cyclic P8W48 anion: {Ln₄(H₂O)₂₈ [K₂P₈W₄₈O₁₈₄ (H₄W₄O₁₂)₂Ln₂ (H₂O)₁₀]¹³⁻} x, Ln = La, Ce, Pr, Nd. *Inorg. Chem.*, 46: 1737-1740.