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A Three-Dimensional Porous Metal-Organic Framework Based on 9,9-Dimethylfluorene-2,7-Dicarboxylic Acid (H_2MFDA): $\{[Tb_2(MFDA)_3(DMF)_2(H_2O)_3] \cdot (H_2O)_3(DMF)_6\}_n$[1]

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Abstract—The title metal-organic framework, $[Tb_2(MFDA)_3(DMF)_2(H_2O)_3] \cdot (H_2O)_3(DMF)_6\}_n$ (**I**) (H_2MFDA = 9,9-dimethylfluorene-2,7-dicarboxylic acid, DMF = *N*,*N*-dimethylformamide), has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction (CIF file CCDC no. 995892). Complex **I** crystallizes in triclinic space group $P\bar{1}$ with $a = 13.0022(3)$, $b = 13.3793(3)$, $c = 25.8929(4)$ Å, $\alpha = 84.060(2)°$, $\beta = 88.104(2)°$, $\gamma = 66.361(2)°$, $V = 4104.05(15)$ Å^3, $C_{75}H_{104}N_8O_{26}Tb_2$, $M = 1851.50$, $\rho_c = 1.498$ g/cm^3, $\mu(MoK_\alpha) = 1.790$ mm^{-1}, $F(000) = 1896$, GOF = 1.055, $Z = 2$, the final $R_1 = 0.0522$ and $wR_2 = 0.1380$ for $I > 2\sigma(I)$. In MOF I, the Tb_2 dinuclear units double-bridged by two carboxylate groups are connected together by MFDA ligands to give rise to a 3D architecture that consists in two types of 1D open channels along the *y* axis with about 6 × 8 and 9 × 12 Å^2 dimensions. The solvent accessible space for the desolvated **I** is 53.4% of the total volume. The 3D structure can also be rationalized as a six-connected ($3.4^{11}.5^2.6$) topological network by considering the Tb_2 dinuclear units as six-connected nodes and MFDA ligands as linkers, respectively.

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INTRODUCTION

Metal-organic frameworks (MOFs), also called as coordination polymers, have attracted much interest because of their intriguing structural topologies and interesting applications as functional materials in catalysis, optics, magnetism, molecular architectures, and materials chemistry, etc. [1–5].

Reports about MOFs based trivalent lanthanides (LnMOFs) gradually increased in recent years, but still much less compared with the transition metal-organic frameworks, due to the inherently flexible coordination geometry of the trivalent lanthanide ions resulting in their structures with less predictability. Lanthanide ions possess excellent optical, electrical and magnetic properties and have been extensively contained in various materials [6–10]. For our group, the research interests are focused on the optical properties of complexes containing lanthanide ions, especially LnMOFs [11–15]. However, the lanthanide-based luminescence emission is typically weak due to low light-absorption efficiency, so it requires an antenna molecule in the framework for energy transfer. The fluorene molecule was considered as a good chromophore for developing lanthanide complexes due to its chemical, structural and optical properties. In this work, based on the 9,9-dimethylfluorene-2,7-dicarboxylic acid (H_2MFDA), we synthesize a three dimensional porous lanthanide metal-organic framework **I**, $\{[Tb_2(MFDA)_3(DMF)_2(H_2O)_3] \cdot (H_2O)_3(DMF)_6\}_n$ and describe its structure in detail.

EXPERIMENTAL

The terbium(III) nitrate was converted from its oxide by nitric acid. Other reagents and solvents were purchased from commercial sources and used as received. H_2MFDA was synthesized according to the literature [16]. Elemental analyses for C, H, and N were performed on a PerkinElmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. The crystal structure was determined by single-crystal X-ray diffraction and using SHELXS-97, SHELXL-97 software for structure solution and refinement correspondingly.

Synthesis of complex I. A mixture of H_2MFDA (0.1 mmol, 28.2 mg), $Tb(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 43.5 mg), DMF (6 mL) and H_2O (3 mL) was sealed in a 15 mL Teflon-lined bomb and heated at 80°C for 3 days. The reaction mixture was slowly cooled to room temperature. Colorless rod-like crystals of **I** suit-

[1] The article is published in the original

Table 1. Crystal data and structure refinement for complex **I**

Parameter	Value
Fw	1851.50
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	13.0022(3)
b, Å	13.3793(3)
c, Å	25.8929(4)
α, deg	84.060(2)
β, deg	88.104(2)
γ, deg	66.361(2)
V, Å^3	4104.05(15)
ρ_{calcd}, g cm^{-3}	1.498
T, K	120(2)
μ, mm^{-1}	1.790
F(000)	1896
Reflections collected	43865
Unique reflections, R_{int}	16102 (0.0324)
GOF (F^2)	1.055
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0522, 0.1380
R_1, wR_2 (all data)*	0.0629, 0.1459

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$.

able for X-ray diffraction analysis were isolated in about 15% yield.

For $C_{75}H_{104}N_8O_{26}Tb_2$ (**I**)

anal. calcd., %:	C, 48.65;	H, 5.66;	N, 6.05.
Found, %:	C, 48.42;	H, 5.79,	N, 6.14.

X-ray structure determination. A colorless single crystal of **I** with dimensions of 0.10 × 0.11 × 0.12 mm was mounted on a Bruker Smart Apex CCD area detector diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) using the ω–θ scan mode in the range 2.83° ≤ θ ≤ 26.00° at 120(2) K. A total of 43865 reflections were collected and 16102 were independent with R_{int} = 0.0324, of which 13569 were observed with $I > 2\sigma(I)$. Raw frame data were integrated with the SAINT program [17]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [18]. An empirical absorption correction was applied with the program SADABS [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding mode, with C–H = 0.93 Å for sp^2 hybridizated carbon atom, 0.96 Å for sp^3 hybridizated carbon atom, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the water molecules were located in calculated positions and refined as riding mode with O–H = 0.85 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The final $R_1 = 0.0522$ and $wR_2 = 0.1380$ for 13569 observed reflections $I > 2\sigma(I)$ ($w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 34.0506P]$ where $P = (F_o^2 + 2F_c^2)/3$). $(\Delta\rho)_{max} = 3.085$ *e*/Å^3, $(\Delta\rho)_{min} = -2.986$ *e*/Å^3 and $(\Delta/\sigma)_{max} = 0.030$. Crystallographic details for **I** have been summarized in Table 1. Selected bond lengths and angles for **I** are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (no. 995892; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) or can be obtained from the authors.

RESULTS AND DISCUSSION

The asymmetric unit of **I** contains two crystallographically independent terbium(III) ions, three MFDA ligands (the dihedral angles between two benzene rings of which are 3.585°, 4.061°, and 7.374°, respectively), two coordinated DMF molecules, three coordinated water molecules, six lattice DMF molecules and three lattice water molecules (Fig. 1). The Tb(1) ion is eight-coordinated by eight oxygen atoms, five of which from four MFDA ligands (O(3), O(4), O(5), O(11)^i, and O(12)^{ii}), two from two water molecules (O(13) and O(14)) and last one from DMF (O(15)) with a distorted bicapped trigonal-prism geometry. The Tb(2) ion is also eight-coordinated by

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Tb(1)–O(3)	2.497(4)	Tb(1)–O(4)	2.391(4)	Tb(1)–O(5)	2.332(4)
Tb(1)–O(11)^{i}	2.288(4)	Tb(1)–O(12)^{ii}	2.317(4)	Tb(1)–O(13)	2.475(4)
Tb(1)–O(14)	2.422(5)	Tb(1)–O(15)	2.372(5)		
Tb(2)–O(1)^{iii}	2.410(4)	Tb(2)–O(2)^{iii}	2.418(4)	Tb(2)–O(7)	2.447(4)
Tb(2)–O(8)	2.430(4)	Tb(2)–O(9)	2.314(4)	Tb(2)–O(10)^{iv}	2.290(4)
Tb(2)–O(16)	2.403(5)	Tb(2)–O(17)	2.336(7)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(11)^{i}Tb(1)O(12)^{ii}	108.73(17)	O(11)^{i}Tb(1)O(5)	144.31(17)	O(12)^{ii}Tb(1)O(5)	74.66(16)
O(11)^{i}Tb(1)O(15)	141.64(19)	O(12)^{ii}Tb(1)O(15)	85.44(19)	O(5)Tb(1)O(15)	73.14(19)
O(11)^{i}Tb(1)O(4)	87.08(16)	O(12)^{ii}Tb(1)O(4)	150.63(17)	O(5)Tb(1)O(4)	78.24(15)
O(15)Tb(1)O(4)	97.40(17)	O(11)^{i}Tb(1)O(14)	74.96(16)	O(12)^{ii}Tb(1)O(14)	75.95(17)
O(5)Tb(1)O(14)	137.37(16)	O(15)Tb(1)O(14)	74.38(17)	O(4)Tb(1)O(14)	133.05(15)
O(11)^{i}Tb(1)O(13)	71.75(15)	O(12)^{ii}Tb(1)O(13)	80.41(16)	O(5)Tb(1)O(13)	73.99(15)
O(15)Tb(1)O(13)	146.61(17)	O(4)Tb(1)O(13)	81.48(14)	O(14)Tb(1)O(13)	129.79(14)
O(11)^{i}Tb(1)O(3)	76.46(16)	O(12)^{ii}Tb(1)O(3)	152.59(17)	O(5)Tb(1)O(3)	117.41(15)
O(15)Tb(1)O(3)	75.89(18)	O(4)Tb(1)O(3)	53.73(14)	O(14)Tb(1)O(3)	79.75(15)
O(13)Tb(1)O(3)	125.68(14)	O(10)^{iv}Tb(2)O(9)	110.28(19)	O(10)^{iv}Tb(2)O(17)	152.5(2)
O(9)Tb(2)O(17)	83.4(2)	O(10)^{iv}Tb(2)O(16)	79.00(18)	O(9)Tb(2)O(16)	77.00(17)
O(17)Tb(2)O(16)	81.3(2)	O(10)^{iv}Tb(2)O(1)^{iii}	80.27(18)	O(9)Tb(2)O(1)^{iii}	152.39(17)
O(17)Tb(2)O(1)^{iii}	98.6(2)	O(16)Tb(2)O(1)^{iii}	130.59(15)	O(10)^{iv}Tb(2)O(2)^{iii}	81.32(18)
O(9)Tb(2)O(2)^{iii}	150.09(18)	O(17)Tb(2)O(2)^{iii}	76.12(19)	O(16)Tb(2)O(2)^{iii}	78.50(15)
O(1)^{iii}Tb(2)O(2)^{iii}	54.26(15)	O(10)^{iv}Tb(2)O(8)	125.04(17)	O(9)Tb(2)O(8)	75.90(17)
O(17)Tb(2)O(8)	80.6(2)	O(16)Tb(2)O(8)	148.87(16)	O(1)^{iii}Tb(2)O(8)	77.29(15)
O(2)^{iii}Tb(2)O(8)	120.94(15)	O(10)^{iv}Tb(2)O(7)	74.90(16)	O(9)Tb(2)O(7)	74.30(18)
O(17)Tb(2)O(7)	132.51(19)	O(16)Tb(2)O(7)	130.96(16)	O(1)^{iii}Tb(2)O(7)	84.63(15)
O(2)^{iii}Tb(2)O(7)	135.49(16)	O(8)Tb(2)O(7)	53.67(14)		

* Symmetry codes: ^{i} $-x+1, -y+2, -z+1$; ^{ii} $x, y+1, z$; ^{iii} $x, y, z+1$; ^{iv} $-x+2, -y+1, -z+2$.

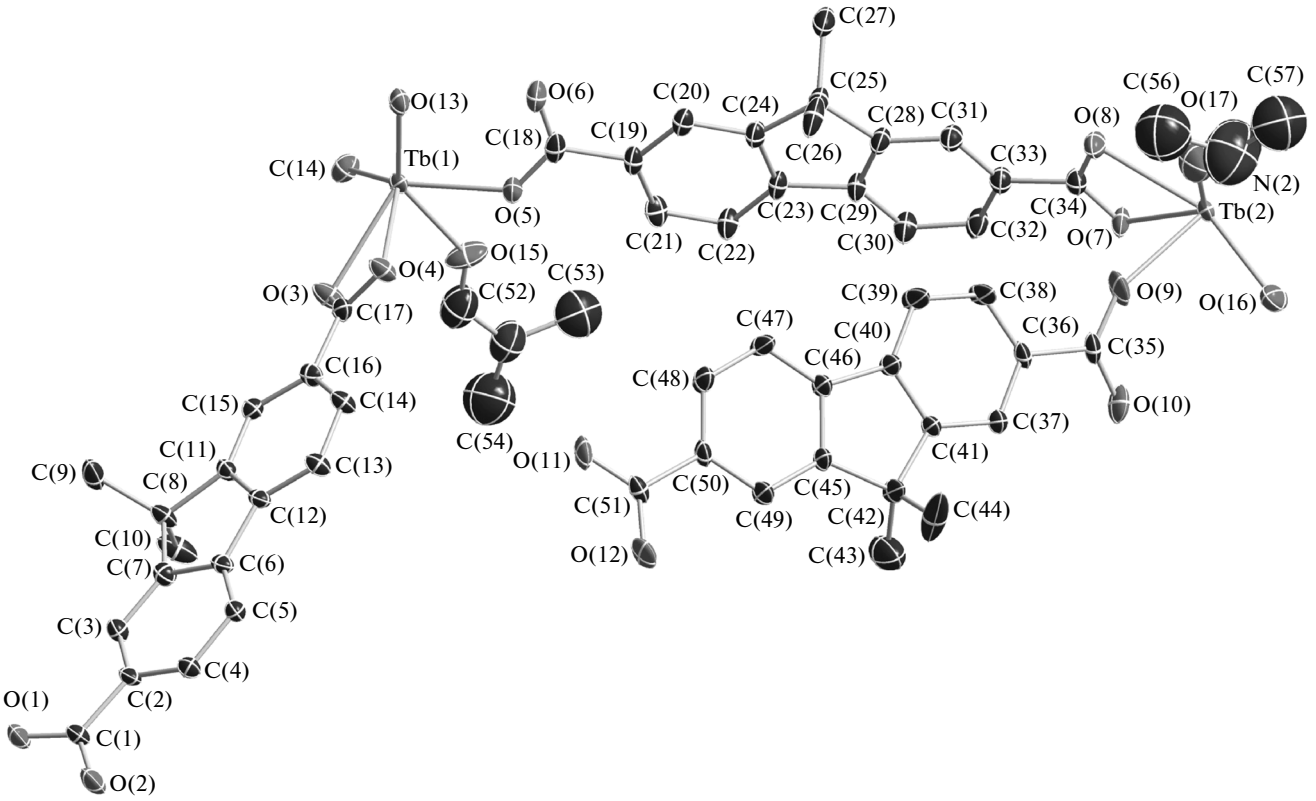

Fig. 1. The structure diagram of **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms, solvated DMF and water molecules have been omitted for clarity.

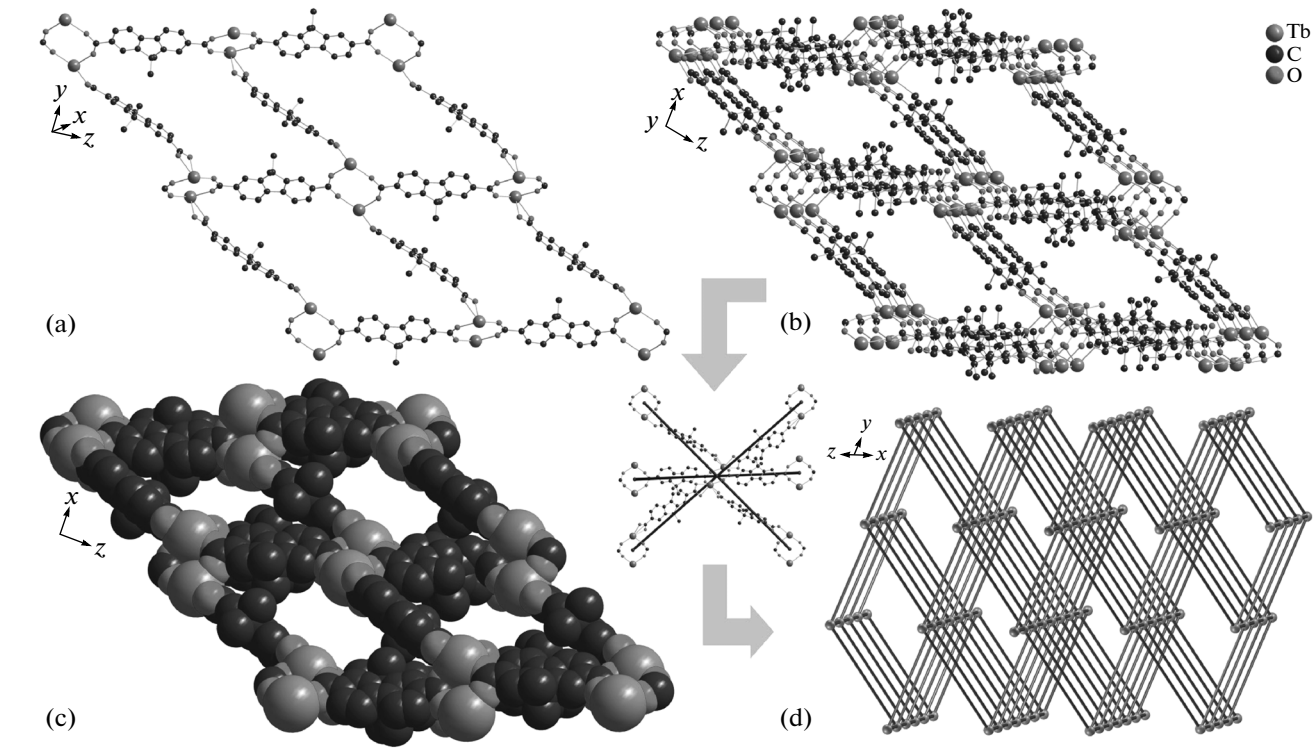

Fig. 2. The (4,4) 2D layer motif (a); the 3D architecture of **I** (b); space filling diagram of crystal structure of **I** (c); topological representation of the structure of **I** (d). H atoms, DMF and water molecules have been omitted for clarity.

six oxygen atoms from four MFDA ligands (O(1)^{iii}, O(2)^{iii}, O(7), O(8), O(9), and O(10)^{iv}), one oxygen atom from a water molecule (O(16)) and one oxygen atom from a terminal DMF molecule (O(17)) with a distorted bicapped trigonal-prism geometry. The Tb–O bond lengths are in the range of 2.288(4)–2.497(4) Å, comparable to those reported for other Tb–O donor complexes [20, 21]. In **I**, the MFDA ligands adopt three coordination modes, namely, μ_2-η^2O,O',η^2O'',O''',μ_2-η^1O,η^2O'',O''', and μ_4-η^1O,η^1O',η^1O'',η^1O''' fashions, respectively. In μ_2-η^2O,O',η^2O'',O''' fashion, the ligand chelates to a Tb(1) and a Tb(2) centers by two carboxylate groups, respectively. In μ_2-η^1O,η^2O'',O''' fashion, the ligand coordinates to a Tb(1) center by a carboxylate oxygen atom and chelates to a Tb(2) center by another a carboxylate group. In μ_4-η^1O,η^1O',η^1O'',η^1O''' fashion, the ligand coordinates to two Tb(1) centers by two oxygen atoms of a carboxylate group and two Tb(2) centers by two oxygen atoms of another a carboxylate group. Two Tb^{3+} ions are double-bridged by two carboxylate groups from two μ_4-η^1O,η^1O',η^1O'',η^1O''' MFDA ligands to form Tb_2 dinuclear unit. The Tb_2 dinuclear units are connected together by μ_2-η^1O,η^2O'',O''' and μ_4-η^1O,η^1O',η^1O'',η^1O''' MFDA ligands to construct the (4,4) two-dimensional (2D) layer motifs resting parallel to the $(10\bar{1})$ crystal plane (Fig. 2a). The μ_2-η^2O,O',η^2O'',O''' MFDA ligands link further the (4,4) 2D layers to lead a 3D architecture with two kinds of 1D channels along the *y* axis having about 6 × 8 and 9 × 12 Å^2 dimensions in which lattice DMF and water molecules reside as guests (Figs. 2b and 2c). The solvent accessible space for the desolvated **I** is 2193.3 Å^3 per unit cell or 53.4% of the total volume, calculated using the PLATON routine [22]. The 3D structure can also be rationalized as a six-connected ($3.4^{11}.5^2.6$) topological network by considering the Tb_2 dinuclear units as six-connected nodes and MFDA ligands as linkers, respectively (Fig. 2d).

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