# 基于3,4′,5-联苯三羧酸构筑的钕配合物的 合成、结构、荧光、光催化及磁性质

# 郑欢焦媛冯思思\*

(山西大学分子科学研究所,化学生物学与分子工程教育部重点实验室,太原 030006)

摘要:采用 NdCl<sub>3</sub>·6H<sub>2</sub>O和3,4',5-联苯三羧酸(H<sub>3</sub>bpt)为原料在 DMF/H<sub>2</sub>O 混合溶剂热条件下合成得到一个三维钕配合物 {[Nd(bpt)(DMF)(H<sub>2</sub>O)]·2H<sub>2</sub>O},(1),并通过红外光谱、元素分析、单晶及粉末 X 射线衍射表征了配合物1的结构。单晶衍射结果表 明,配合物1具有(5,5)-连接的三维结构,拓扑符号为(4<sup>4</sup>·6<sup>3</sup>·8<sup>3</sup>)(4<sup>8</sup> 6<sup>2</sup>)。此外,对配合物1的热稳定性、荧光性质、光催化降解染 料及磁性质进行了详细研究。

关键词: 钕金属有机框架; 3,4',5-联苯三羧酸; 晶体结构; 荧光; 光催化; 磁性质
中图分类号: 0614.33<sup>+5</sup>
文献标识码: A 文章编号: 1001-4861(2021)09-1691-09
DOI: 10.11862/CJIC.2021.193

# Synthesis, Structure, Luminescence, Photocatalytic and Magnetic Properties of a Neodymium Complex Constructed from Biphenyl-3,4',5-tricarboxylic Acid

ZHENG Huan JIAO Yuan FENG Si-Si\*

(Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University, Taiyuan 030006, China)

**Abstract:** A Nd<sup>3+</sup> MOF, namely {[Nd(bpt)(DMF)(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub> (1) (H<sub>3</sub>bpt=biphenyl-3,4',5-tricarboxylic acid, DMF= N,N-dimethylformamide), has been obtained by the self-assemble reaction of NdCl<sub>3</sub>·6H<sub>2</sub>O and H<sub>3</sub>bpt ligand under solvothermal conditions (DMF/H<sub>2</sub>O). Complex **1** was characterized by means of elemental analysis, infrared spectroscopy, powder X-ray diffraction and single-crystal X-ray diffraction analyses. Single-crystal X-ray structural analysis reveals that complex **1** displays three-dimensional frameworks featuring a (5,5)-connected topological network with the point symbol of  $(4^4 \cdot 6^3 \cdot 8^3)(4^8 6^2)$ . In addition, the thermal stability, luminescent properties, photocatalytic behaviour, and magnetic property of complex **1** were also investigated in detail in the solid state. CCDC: 2074972.

Keywords: Nd3+ metal-organic framework; biphenyl-3,4',5-tricarboxylic acid; crystal structure; luminescence; photocatalysis; magnetism

## **0** Introduction

Metal-organic frameworks (MOFs) constructed by coordination bonds between metal ions and organic ligands have attracted much attention not only because of their diverse striking structural topologies, but also for their wide range of potential applications, such as gas adsorption and separation, catalysis, luminescence, magnetism, chemical sensing, drug delivery<sup>[1-5]</sup>. In recent years, novel photocatalytic materials based on MOFs have been extensively studied due to their adjustable porosity, high crystallinity and semiconductor properties, which are largely driven by the need for green degradation of organic pollutants<sup>[6-7]</sup>. These appli-

\*通信联系人。E-mail:ssfeng@sxu.edu.cn

收稿日期:2021-02-19。收修改稿日期:2021-07-15。

国家自然科学基金(No.21671124)、山西省1331工程重点创新研究团队和山西省自然科学基金(No.201701D121039)资助。

cations make MOFs important functional materials. More significantly, these applications can be combined and integrated into individual framework to form multifunctional MOFs<sup>[8-10]</sup>.

Lanthanide metal-organic frameworks (Ln-MOFs) are well known for their combination of both photoluminescent centers and magnetic properties because of the characteristic of central cations, making them attractive candidates for the development of novel multifunctional materials<sup>[11-14]</sup>. Moreover, proper organic bridging linkers are also significant for assembling the required MOFs materials. As is well - known, multicarboxylate ligands are commonly used in the architectures of Ln-MOFs due to their powerful topological and structural diversity capabilities<sup>[15-17]</sup>. Moreover, multicarboxylate ligands are good candidates for H-bonded acceptors and donors which serve as an effective building block for the formation of supramolecular skeleton<sup>[18]</sup>.

In recent years, biphenyl-3,4',5-tricarboxylic acid ( $H_3$ bpt), a planar rigid ligand with three carboxylate groups, has attracted extensive attention<sup>[19-24]</sup>. The tricarboxyl oxygen-donor linker with a variety of bridg-ing/chelating functions could have diverse coordination

modes to produce fascinating structures, while the coexistence of two benzene rings can make H<sub>3</sub>bpt a highly conjugated organic linker, resulting in the formed MOFs with potential optical properties<sup>[25-29]</sup>. We focused on the design and synthesis of MOFs containing different aromatic multicarboxylate ligands, and reported some novel MOFs with luminescent, magnetic and photocatalytic functions in our previous work<sup>[30-33]</sup>. In this study, a Nd-MOF (1) with the chemical formula  $\{[Nd(bpt)(DMF)(H_2O)] \cdot 2H_2O\}_n$  (DMF=N,N-dimethylformamide) was synthesized from the Y-shaped aromatic tricarboxylic ligand H<sub>3</sub>bpt under solvothermal condition (Scheme 1). The complex was characterized by elemental analysis (EA), infrared (IR) spectroscopy, thermogravimetric (TG) and X - ray diffraction analyses. Crystal structure analysis shows that complex 1 consists of one-dimensional (1D) binuclear secondary building unit along a axis which is connected into a three -dimensional (3D) framework by bpt<sup>3-</sup> ligands. In addition, the fluorescence, magnetic properties and photocatalytic degradation of dyes of 1 have also been explored.



Scheme 1 Synthesis route of complex 1

### **1** Experimental

#### 1.1 Materials and measurements

H<sub>3</sub>bpt ligand was bought from Jinan Henghua Sci. & Technol. Co., Ltd., and used directly without further purification. All solvents and reagents were of standard commercial grade and used directly without further purification. The sample for EA was dried under vacuum and performed with a CHN-O-Rapid instrument. IR spectra were obtained on KBr pellet by a BRUKER TENSOR27 spectrometer. Powder X-ray diffractions (PXRD) patterns were collected on a Bruker D8 Advance X - ray diffractometer employing Cu K $\alpha$  radiation ( $\lambda$  = 0.154 18 nm) with a 2 $\theta$  range of 5°~50°. The operating voltage and current were 40 kV and 25 mA, respectively. TG analysis was performed on a Dupont thermal analyzer under a nitrogen atmosphere with a heating rate of 10  $\degree$ C ·min<sup>-1</sup>. Luminescence analyses were performed on a Fluoromax-4 spectrofluorometer with a xenon arc lamp as the light source. UV-visible spectra were obtained with a JASCO V-570 spectrophotometer. Magnetic susceptibility measurements data were obtained with a SQUID magnetometer (QuantumMPMS) in a temperature range of 2.0~300 K by using an applied field of 1 000 Oe.

#### **1.2** Preparation of complex 1

A mixture of H<sub>3</sub>bpt (21.5 mg, 0.075 mmol) and

NdCl<sub>3</sub>·6H<sub>2</sub>O (71.7 mg, 0.2 mmol) in H<sub>2</sub>O/DMF (4 mL, 1 : 1, *V/V*) was heated at 393 K for 72 h under autogenous pressure in a sealed 23 mL Teflon-lined stainlesssteel vessel. Purple block - shaped crystals of **1** were obtained after cooling to room temperature. The crystalline samples were collected by filtration, washed with H<sub>2</sub>O and dried under vacuum overnight (Yield: 40%, based on H<sub>3</sub>bpt). Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>10</sub>Nd(%): C 38.97, H 3.61, N 2.53; Found(%): C 39.01, H 3.69, N 2.56. IR (KBr, cm<sup>-1</sup>): 3 410w, 2 932w, 1 666s, 1 624s, 1 583s, 1 533s, 1 405s, 1 252m, 1 107m, 1 062m, 1 017w, 871m, 777s, 720s, 676s, 469w.

#### 1.3.1 X-ray crystallography

Single-crystal X-ray diffraction data for complex **1** were collected at 100(2) K in a Beijing Synchrotron Radiation Facility (BSRF) beam-line 3W1A, which was equipped with a MARCCD-165 detector ( $\lambda$  =0.072 00 nm) with the storage ring working at 2.5×10° eV. The data were collected by a MARCCD diffractometer and

processed by using HKL 2000<sup>[34]</sup>. The structures were solved by the direct method and refined by the fullmatrix least squares method on  $F^2$  using the SHELXTL<sup>[35]</sup>. All the non-H atoms were refined anisotropically. Hydrogen atoms attached to C and N atoms were placed geometrically and refined by using a riding model. Hydrogen atoms in hydroxyl and water molecules were located from difference Fourier maps and refined using their global  $U_{iso}$  value with the length of O-H being 0.082 nm. In the refinement of 1, the SQUEEZE routine of PLATON<sup>[36]</sup> was used to remove the contributions of disordered solvent molecules in the structure factors. EA and TGA results matched with the formula C<sub>18</sub>H<sub>20</sub>NO<sub>10</sub>Nd, corresponding to [Nd(bpt)  $(DMF)(H_2O)] \cdot 2H_2O$ . A summary of the crystallographic data as well as the data collection and refinement parameters for complex 1 is provided in Table 1. Selected bond lengths and angles for 1 are provided in Table 2.

CCDC: 2074972.

Table 1 Crystal data and structure refinement for c	complex	1
---	---------	---

Formula	$\mathrm{C}_{18}\mathrm{H}_{20}\mathrm{NO}_{10}\mathrm{Nd}$	F(000)	2 200
Crystal system	Monoclinic	$D_{\rm c}$ / (Mg • m <sup>-3</sup> )	1.563
Space group	C2/c	$\mu$ / mm <sup>-1</sup>	2.251
<i>a</i> / nm	2.489 2(5)	Reflection collected	7 283
<i>b</i> / nm	1.272 1(3)	Independent reflection	6 421
<i>c</i> / nm	1.497 5(3)	$R_{ m int}$	0
β / (°)	96.32(3)	GOF	1.088
$V / \text{nm}^3$	4.713 1(16)	$R_1, wR_2 [I > 2\sigma(I)]$	0.040 2, 0.111 7
Т / К	100	$R_1, w R_2$ (all data)	0.044 3, 0.114 0
Ζ	8		

Table 2	Selected	hand	longthe	(nm	) and	angles	(°)	for	1
r able 2	Selected	Dolla	rengtils	(IIIII)	) and	angles	U	101	1

Nd1—O3 <sup>i</sup>	0.241 1(2)	Nd1-02	0.243 4(2)	Nd1—O1 <sup>ii</sup>	0.244 5(2)
Nd1-08	0.246 6(3)	Nd1—O4 <sup>iii</sup>	0.248 9(2)	Nd1-07	0.2500(3)
$Nd1-05^{iv}$	0.251 4(3)	Nd1—O6 <sup>iv</sup>	0.254 2(2)	Nd1—O3 <sup>iii</sup>	0.272 5(2)
03 <sup>i</sup> —Nd1—02	73.95(8)	O3 <sup>i</sup> —Nd1—O1 <sup>ii</sup>	79.91(8)	02—Nd1—O1 <sup>ii</sup>	132.62(8)
03 <sup>i</sup> —Nd1—08	85.04(12)	02—Nd1—08	140.51(11)	01 <sup>ii</sup> —Nd1—08	73.14(11)
03 <sup>i</sup> —Nd1—O4 <sup>iii</sup>	122.57(8)	02—Nd1—O4 <sup>iii</sup>	70.84(9)	01 <sup>ii</sup> —Nd1—O4 <sup>iii</sup>	92.21(9)
08—Nd1—O4 <sup>iii</sup>	146.61(12)	03 <sup>i</sup> —Nd1—07	151.77(11)	02—Nd1—07	133.63(12)
01 <sup>ii</sup> —Nd1—07	75.38(10)	08—Nd1—07	74.96(15)	04 <sup>iii</sup> —Nd1—07	72.31(13)
$03^{i}$ Md1 $-05^{iv}$	129.54(8)	$02$ —Nd1— $05^{iv}$	75.43(9)	01 <sup>ii</sup> —Nd1—O5 <sup>iv</sup>	147.72(9)
$08$ —Nd1— $05^{iv}$	94.26(11)	$O4^{iii}$ -Nd1- $O5^{iv}$	82.27(9)	$07$ —Nd1— $05^{iv}$	72.63(11)
$03^{i}$ Md1 $-06^{iv}$	80.84(8)	$02$ —Nd1— $06^{iv}$	72.12(9)	01 <sup>ii</sup> —Nd1—O6 <sup>iv</sup>	141.09(9)
$08$ —Nd1— $06^{iv}$	71.76(11)	$04^{iii}$ -Nd1- $06^{iv}$	126.58(8)	$07$ —Nd1— $06^{iv}$	110.57(11)

Symmetry codes: <sup>i</sup> x, -y+1, z-1/2; <sup>ii</sup> -x+1/2, -y+1/2, -z; <sup>iii</sup> -x+1/2, y-1/2, -z+1/2; <sup>iv</sup> -x, y, -z+1/2; <sup>v</sup> -x+1/2, y+1/2, -z+1/2; <sup>vi</sup> x, -y+1, z+1/2.

#### 1.3.2 Photocatalytic activity study

The photocatalytic activity of the sample was evaluated by the degradation of three organic dyes, methyl orange (MO), rhodamine B (RhB) and methylene blue (MB), respectively, in aqueous solution. The experimental operation was similar. Here we took MB as the representative to illustrate. An MB aqueous solution (17  $\mu$ mol·L<sup>-1</sup>, 15 mL) was mixed with complex 1 (2.0 mg), and the mixture was stirred in the dark for 30 min to reach the adsorption-desorption equilibrium, then it was exposed to the illumination. Then, the samples were periodically removed from the reactor and immediately centrifuged to separate any suspended solids. The transparent solution was transferred to trace cuvette and analyzed by a UV-Vis spectrometer. A 300 W medium pressure mercury lamp served as a source of ultraviolet light. The distance between the light and the solution was about 30 cm.

#### 2 Results and discussion

#### 2.1 IR spectrum

IR spectra of  $H_3$  bpt and complex **1** were examined at room temperature (Fig. 1). The main characteristic absorption peaks present the typical stretching vibrations of COO<sup>-</sup> and O-H groups. The broad band in a region of 3 500~3 116 cm<sup>-1</sup> indicates O-H stretching of the coordinated water molecule<sup>[37]</sup>. The strong bands at 1 107 and 1 666 cm<sup>-1</sup> are attributed to the ester C-0 and acyl C=0 stretching vibrations, respectively<sup>[38]</sup>. The characteristic peaks of the asymmetric vibration and the symmetric stretching vibration of the carboxylate groups were at 1 624 and 1 405 cm<sup>-1</sup>, respectively. They were obviously shifted to lower wavenumbers relative to those of free  $H_3$ bpt (1 720 and 1 410 cm<sup>-1</sup>), which suggests that the carboxylate groups in the complex are coordinated to the Nd<sup>3+</sup> ions<sup>[39]</sup>. These structural features are in accord with the results of the



Fig.1 IR spectra of  $H_3$ bpt, complex 1 and the complex after the photocatalytic reaction

X-ray diffraction analysis.

#### 2.2 Crystal structure description

Complex 1 was well characterized by single crystal X-ray diffraction analysis. It crystallizes in the monoclinic system C2/c space group and displays a 3D structure. The asymmetric unit contains one Nd<sup>3+</sup> cation, one bpt<sup>3-</sup> anionic ligand, one coordinated DMF, one coordinated water molecule, and two free water molecules. As shown in Fig.2a, The Nd<sup>3+</sup> cation adopts a nine-coordinated mode, coordinated by nine oxygen atoms from three monodentate (O2, O1<sup>i</sup> and O3<sup>ii</sup>) and two chelating (03<sup>iii</sup>, 04<sup>iii</sup>, 05<sup>iv</sup> and 06<sup>iv</sup>) carboxyl groups from five different bpt3- ligands, one terminal water molecule (O7) and one terminal DMF molecule (O8) (Symmetry codes:  $^{i}$  0.5-x, 0.5-y, -z;  $^{ii}$  x, 1-y, -0.5+z; <sup>iii</sup> 0.5-x, -0.5+y, 0.5-z; <sup>iv</sup> -x, y, 0.5-z). The coordination environment of Nd<sup>3+</sup> cation is a slightly distorted tricapped trigonal prismatic. The Nd-O bond lengths vary from 0.241 1(2) to 0.272 5(2) nm, which correspond to those reported for other lanthanide-bpt3- complexes<sup>[40-42]</sup>. The bpt<sup>3-</sup> ligands adopt three different coordination modes: a bidentate bridging mode (mode I), asymmetric chelating bridging mode (mode II) and a chelating bidentate mode (mode Ⅲ)<sup>[20]</sup> (Fig.2b).

Two adjacent Nd<sup>3+</sup> cations are connected by two chelating/bridging and two bis(monodentate) bridging carboxyl groups, forming binuclear  $[Nd_2(COO)_6(H_2O)_2$  $(DMF)_2]$  building units with the Nd1…Nd1<sup>iii</sup> separation of 0.407 0(1) nm, which is further extended into a 1D chain via the bpt<sup>3-</sup> ligand along *a* axis (Fig. 3a). These binuclear building units are further cross-linked by bpt<sup>3-</sup> ligands to form a 3D network with intersected channels<sup>[43]</sup> (Fig. 3b). The solvent accessible volume is  $1.307 9 \text{ nm}^3$  per  $4.713 0 \text{ nm}^3$  unit cell volume (27.8% of the total crystal volume) after the removal of the uncoordinated solvents calculated with PLATON.

Topologically, if each Nd<sup>3+</sup> cation and bpt<sup>3-</sup> ligand are considered as five-connected nodes, respectively, the structure can be considered as a 5,5-connected net with the point symbol of the topology as  $(4^4 \cdot 6^3 \cdot 8^3)(4^8 - 6^2)$  (Fig.4).



Non-hydrogen atoms are represented by thermal ellipsoids drawn at the 30% probability level and coordinated DMF molecules are omitted except O for clarity; Symmetry codes:  $^{i}$  0.5–x, 0.5–y, –z;  $^{ii}$  x, 1–y, –0.5+z;  $^{iii}$  0.5–x, –0.5+y, 0.5–z;  $^{iv}$  –x, y, 0.5–z

Fig.2 (a) Coordination environment of central Nd<sup>3+</sup> cation in 1; (b) Coordination modes for bpt<sup>3-</sup> in 1



H atoms are omitted for clarity

Fig.3 (a) One-dimensional chain and (b) 3D network structure of complex 1



Nd: green, bpt<sup>3-</sup>: magenta

Fig.4 Topological structure of complex 1 with  $Nd^{3+}$  cation and  $bpt^{3-}$  ligand as 5-coonected nodes, respectively

#### 2.3 PXRD pattern and TG curve

To verify the phase purity of the complex, PXRD was performed. The experimental PXRD pattern was in

agreement with the calculated ones based on the X-ray single-crystal data, indicating the high phase purity of complex **1** (Fig. 5a). In order to estimate the thermal stabilities, TG analysis for **1** was performed on bulk samples in a range of 25~800 °C (Fig.5b). As shown in Fig.5b, the weight loss of 23.4% (Calcd. 23.3%) occurring between 25 and 220 °C corresponds to the removal of two free H<sub>2</sub>O molecules and coordinated H<sub>2</sub>O and DMF molecules. After taking off the solvent molecules, with the temperature further heating the skeleton of **1** decomposed gradually without displaying any distinct plateau.



Fig.5 (a) PXRD patterns of complex 1 at room temperature and (b) TG curve of complex 1

#### 2.4 Luminescence property

The solid-state photoluminescent properties of  $H_3$  bpt ligand and complex **1** were investigated at room temperature. It was found that complex 1 showed significant fluorescence enhancement and the strong emission band was observed at 386 nm ( $\lambda_{ex}$ =280 nm) as shown in Fig.6. This band may be due to the emission of H<sub>3</sub>bpt ligand with a slight blue-shift of 12 nm since the free H<sub>3</sub>bpt ligand exhibited emission at 398 nm attributed to the  $\pi$  -  $\pi^*$  transitions ( $\lambda_{ex}$ =280 nm)<sup>[40,44]</sup>. The observed much stronger emission intensity of 1 indicates that the formation of MOF enhances the rigidity of the aromatic backbone of the ligand and maximizes the intramolecular/intermolecular interactions among the organic ligands, which are conducive to energy transfer<sup>[26]</sup>. In addition, there was no obvious characteristic Nd-based emission in the region of 800~1 400 nm<sup>[45]</sup>, indicating an inefficient energy transfer from ligand *p*-excited states to neodymium *f*-excited states.



Fig.6 Luminescence spectra of H<sub>3</sub>bpt ligand and complex **1** at 298 K in the solid-state

#### 2.5 Photocatalytic property

Studies have shown that lanthanide complexes may have good photocatalytic activity due to the diverse and stable valence states of lanthanide cations<sup>[6]</sup>. Although a variety of Ln-MOFs based on H<sub>3</sub>bpt have been reported<sup>[20, 22, 29, 40,43]</sup>, their photocatalytic properties have hardly been studied. So, in this research, three organic dyes, MO, RhB and MB, were used as the model pollutant in aqueous media to evaluate the photocatalytic activity of 1. The results showed that complex 1 displayed good specific effect to degradation of MB but little effect to MO and RhB under ultraviolet light irradiation. As shown in Fig. 7a, the variation of UV-visible absorption spectra of MB dye solution in the presence of **1** was measured at each 10 min interval. The characteristic absorption (ca. 665 nm) of MB was selected to monitor the adsorption and photocatalytic degradation process. The photocatalytic activity of 1 was gradually enhanced with time increasing from 0 to 100 min, and nearly 77% of MB was degraded (Fig. 7a). As shown in Fig. 7b, the control experiments as MB without catalyst, and MB with NdCl<sub>3</sub>, H<sub>3</sub>bpt and 1, respectively, were carried out under the same conditions to ensure the results obtained from the photocatalytic experiments were consistent (where  $c_0$  is the initial concentration of MB solution at the beginning of photocatalytic degradation, and c is the concentration of MB solution at each min interval). Under the ultraviolet light, the degradation of MB in the absence of catalysts was negligible, implying that MB was relatively stable under illumination conditions. Furthermore, H<sub>3</sub>bpt ligand showed a certain catalytic degradation rate of MB (about 25%), which indicated that the ligand had certain optical activity. Complex 1 exhibited the best degradation performance for MB. The IR (Fig. 1) and PXRD patterns (Fig. 5a) of complex 1 after the photocatalytic experiment were almost the same as that of the as-prepared complex, which indicates that MB is degraded rather than adsorbed and as a photocatalyst, complex 1 has good stability during the heterogeneous catalytic reaction in the solution.



Fig.7 (a) Variation in UV-Vis absorption spectra of MB solution in the presence of 1 irradiated by visible light;
(b) Photocatalytic degradation rate of MB under ultraviolet light in the absence and presence of NdCl<sub>3</sub>,
H<sub>3</sub>bpt and 1, respectively

#### 2.6 Magnetic property

The magnetic behaviour of complex **1** was studied at a temperature range of 2.0~300 K under a 1 000 Oe direct current magnetic field. The magnetic susceptibilities and products  $\chi_m T$  are presented as functions of the temperature in Fig.8. When the temperature decreased, complex **1** exhibited a regular increase of  $\chi_m$  and a usual decrease of  $\chi_m T$  from 1.51 cm<sup>3</sup>·mol<sup>-1</sup>·K at 300 K to 0.63 cm<sup>3</sup>·mol<sup>-1</sup>·K at 2.0 K. The Curie constant derived from  $\chi_m^{-1}$  vs T plots was 1.74 cm<sup>3</sup>·K·mol<sup>-1</sup>. Such behaviour is a typical isolated Nd<sup>3+</sup> complex<sup>[46]</sup> that matches the structure of complex **1**. Although there are binuclear building units in complex **1**, the Nd····Nd separation is long. For Nd<sup>3+</sup> cations, the spin-orbit coupling is very large; the free-ion ground state is  ${}^{4}I_{9/2}$  and the Zeeman factor  $g_{J}$  is equal to 8/11 which leads to  $\chi_{m}T$  value of 1.64 cm<sup>3</sup>·mol<sup>-1</sup>·K<sup>[47]</sup>. At 300 K, the experimental  $\chi_{m}T$ value of **1** (1.51 cm<sup>3</sup>·mol<sup>-1</sup>·K) was slightly smaller than the expected one for the free Nd<sup>3+</sup> cation, which may be caused by the cumulative effects of crystal field variation, diamagnetic corrections or slight weighing errors. In a range of 50~300 K, the magnetic data obeyed the Curie-Weiss law (Inset in Fig.8). The Weiss constant of -45.5 K agreed with previously reported values<sup>[46-47]</sup>. The susceptibility below 50 K did not conform to the Curie-Weiss law, which may be attributed to the effect of crystal field splitting of  ${}^{4}I_{9/2}$  ground state into five Kramers doublets<sup>[46]</sup>.



Red solid line represents the best fitting

Fig.8 Plots of  $\chi_m, \chi_m T$  and  $\chi_m^{-1}$  (Inset) as functions of T for **1** 

#### **3** Conclusions

In summary, one 3D Nd<sup>3+</sup>-MOF based on a Y-shaped tricarboxylic ligand (biphenyl-3, 4', 5tricarboxylic acid) was synthesized under solvothermal condition. The crystal structure shows that the framework possesses (5, 5)-connected topological network. The MOF exhibited strong emission in the solid-state at room temperature based on the ligand. The magnetic susceptibility displayed a typical isolated Nd<sup>3+</sup> complex. In addition, the MOF showed high photocatalytic efficiency for the degradation of MB in aqueous solution. This study provides further insights into the rational design of MOF-based multifunctional materials.

#### **References:**

- [1] 刘志强,黄永清,孙为银. 无机化学学报, 2017,33(11):1959-1969
   LIU Z Q, HUANG Y Q, SUN W Y. Chinese J. Inorg. Chem., 2017,33 (11):1959-1969
- [2] Zhou H C, Long J R, Yaghi O M. Chem. Rev., 2012,112:673-674
- [3] Seoane B, Coronas J, Gascon I, Benavides M E, Karvan O, Caro J, Kapteijn F, Gascon J. Chem. Soc. Rev., 2015,44(8):2421-2454
- [4] He C B, Liu D M, Lin W B. Chem. Rev., 2015,115(19):11079-11108
- [5] Wei Y S, Zhang M, Zou R, Xu Q. Chem. Rev., 2020,120(21):12089-12174

- [6] Bai Y T, Zhang S, Feng S S, Zhu M L, Ma S Q. Dalton Trans., 2020, 49:10745-10754
- [7] Rojas S, Horcajada P. Chem. Rev., **2020,120**(16):8378-8415

报

- [8] Zheng M M, Wang Y X, Feng P Y. Catalysts, 2020,10(3):309
- [9] Zhang L L, Guo B B, He H H, Zhang X R, Feng Y, Fan W D, Cao J L, Lu G, Chen Y H, Sun D F, Huang W. *Inorg. Chem.*, **2020**, **59**(1): 695-704
- [10]Li B, Jiang Y Y, Sun Y Y, Wang Y J, Han M L, Wu T P, Li D S. Dalton Trans., 2020,49(42):14854-14862
- [11]Zhao J, Zhu G H, Xie L Q, Wu H L, Zhou A J, Wu Z Y, Wang J, Chen Y C, Tong L. Dalton Trans., 2015,44(32):14424-14435
- [12]Larionov S V, Bryleva Y A, Glinskaya L A, Plyusnin V F, Kupryakov A S, Agafontsev A M, Tkachev A V, Bogomyakov A S, Piryazev D A, Korolkov I V. *Dalton Trans.*, 2017,46(34):11440-11450
- [13]Han M R, Li S D, Ma L, Yao B, Feng S S, Zhu M L. Acta Crystallogr. Sect. C, 2019,C75(9):1220-1227
- [14]Han M R, Zhang H T, Wang J N, Feng S S, Lu L P. RSC Adv., 2019,9 (55):32288-32295
- [15]Shang K X, Jing S, Hu D C, Yao X Q, Zhi L H, Si C D, Liu J C. Cryst. Growth Des., 2018,18(4):2112-2120
- [16]Ma Y L, Du L, Zhao Q H. Inorg. Chem. Commun., 2017,77:1-5
- [17]Wu J W, Zhang H B, Du S W. J. Mater. Chem. C, 2016,4(16):3364-3374
- [18]Lu Y L, Zhao W J, Liu Y, Liu B, Feng S, Tan J T, Li X, Yang X W. J. Solid State Chem., 2012,192:144-152
- [19]Liu Y H, Lu L P, Zhu M L, Su F. Acta Crystallogr. Sect. C, 2016, C72:358-362
- [20]Yan D, Duan Q. Inorg. Chem. Commun., 2013,36:188-191
- [21]Lin Z J, Xu B, Liu T F, Cao M N, Lü J, Cao R. Eur. J. Inorg. Chem., 2010,24:3842-3849
- [22]Han D, Yan X L, Liu J. Z. Anorg. Allg. Chem., 2019,645:422-427
- [23]Wang H J, Cheng F J, Zou C C, Li Q Q, Hua Y Y, Duan J G, Jin W Q. CrystEngComm, 2016,18(30):5639-5646
- [24]Hao Z M, Yang G C, Song X Z, Zhu M, Meng X, Zhao S N, Zhang H J. J. Mater. Chem. A, 2014,2(1):237-244
- [25]Zhao J, Dong W W, Wu Y P, Wang Y N, Wang C, Li D S, Zhang Q C. J. Mater. Chem. A, 2015,3(13):6962-6969
- [26]Li Y L, Zheng L P, Nie H, Wang Y F, Yao L H, Li J, Li J J, Zhou X L, Wang H F, Wang H Y. J. Mol. Struct., 2020,1204:127427
- [27]Li Y L, Zhao Y, Kang Y S, Liu X H, Sun W Y. Cryst. Growth Des., 2016,16(12):7112-7123
- [28]Guo Z Y, Xu H, Su S Q, Cai J F, Dang S, Xiang S C, Qian G D, Zhang H J, O'Keeffe M, Chen B L. Chem. Commun., 2011,47(19): 5551-5553
- [29]Xing S H, Bing Q M, Song L F, Li G H, Liu J Y, Shi Z, Feng S H, Xu R R. Chem. Eur. J., 2016,22(45):16230-16235
- [30]Jia Y Q, Feng S S, Shen M L, Lu L P. CrystEngComm, 2016,18(28): 5344-5352
- [31]Zhang L Y, Lu L P, Zhu M L, Feng S S. CrystEngComm, 2017, 19 (14):1953-1964

- [32]An Y Y, Lu L P, Feng S S, Zhu M L. CrystEngComm, 2018,20(14): 2043-2052
- [33]Yang D D, Lu L P, Feng S S, Zhu M L. Dalton Trans., 2020,49(22): 7514-7524
- [34]Otwinowski Z, Minor W. Methods Enzymol., 1997,276:307-326
- [35]Sheldrick G M. Acta Crystallogr. Sect. C: Cryst. Struct. Commun., 2015,C71:3-8
- [36]Spek A L. Acta Crystallogr. Sect. C: Cryst. Struct. Commun., 2015, C71:9-18
- [37]Li D S, Zhao J, Wu Y P, Liu B, Bai L, Zou K, Du M. Inorg. Chem., 2013,52:8091-8098
- [38]Ma X L, Wang Z X, He X, Shao M, Li X M. Inorg. Chem. Commun., 2018,92:131-135
- [39]Li L N, Wang S Y, Chen T L, Sun Z H, Luo J H, Hong M C. Cryst. Growth Des., 2012,12(8):4109-4115
- [40]Xing S H, Zeng G, Liu X M, Yang F, Hao Z Q, Gao W, Yang Y L.

- Wang X R, Li G H, Shi Zhan, Feng S H. *Dalton Trans.*, **2015**, **44**(20): 9588-9595
- [41]Li X Y, Lin Z J, Yang Y Y, Cao R. CrystEngComm, 2014, 16(28): 6425-6432
- [42]Chen Z F, Xue H B, Wu L R, Jin R F. J. Cluster Sci., 2018,29:1269-1274
- [43]Cui P P, Zhao Y, Zhang X D, Wang P, Sun W Y. Dyes Pigm., 2016, 124:241-248
- [44]Chen Y X, Tang K K, Wang X, Chen B Y, Qin G Q, Yang J H. Z. Anorg. Allg. Chem., 2014,640:2292-2295
- [45]Niu W Y, Feng C, Fan N Y, Wang X Y, Yan P F, Sun J W, Li G M. Synth. Met., 2016,221:319-325
- [46]Lhoste J, Campos P A, Henry N, Loiseau T, Rabu P, Abraham F. Dalton Trans., 2011,40(36):9136-9144
- [47]Andruh M, Bakalbassis E, Kahn O, Trombe J C, Porcher P. Inorg. Chem., 1993,32(9):1616-1622