A Zinc(II) Coordination Polymer with Tetraiodoterephthalate: Synthesis, Crystal Structure, and Luminescence

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A new coordination polymer {[Zn(BDC-I$_4$)-(DMSO)$_2$]·(DMSO)$_2$(H$_2$O)$_4$}$_n$ (**1**) was prepared from the reaction of Zn(II) nitrate with 2,3,5,6-tetraiodo-1,4-benzenedicarboxylic acid (H$_2$BDC-I$_4$) in DMSO/water and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Complex **1** crystallizes in the orthorhombic space group *Pnma* and shows a zigzag chain coordination structure, which is assembled into a 2D network through weak C–H···O and C–H···π interactions. The thermal and photoluminescence properties of complex **1** in the solid state are also reported.

Key words: Coordination Polymer, Zn(II) Tetraiodoterephthalate, Crystal Structure, Luminescence

Introduction

In recent years, the design and construction of new polymeric metal carboxylates have been the focus of increasing attention because of the diverse architectures of these complexes and their potential applications as functional solid materials [1 – 6]. In general, the extended network structures of such crystalline materials primarily depend on the coordination tendency of the metal ions and the interconnecting function of organic ligands. Among various carboxylate ligands, 1,4-benzenedicarboxylic acid (1,4-H$_2$BDC) has been widely employed for the synthesis of diverse coordination networks [7 – 10]. Because of their in-teresting structural motifs, many 1,4-H$_2$BDC derivatives decorated by electron-donating or -accepting substituents such as methyl [11], methylthio [12], fluoro [13], chloro [14], and bromo [15] groups have been used for the construction of functional coordination polymers. We have been focusing our studies on the coordination chemistry of polyhalogen substituted benzenedicarboxylate ligands such as tetrachloro- (H$_2$BDC-Cl$_4$) [14, 16, 17], tetrafluoro-terephthalic acid (H$_2$BDC-F$_4$) [18, 19], and tetrafluorophthalic acid (1,2-H$_2$BDC-F$_4$) [20, 21], due to their unique linking modes and potential ligand-metal interactions. Meaningfully, Cu(II) or Zn(II) polymers based on 2,3,5,6-tetraiodo-1,4-benzenedicarboxylic acid (H$_2$BDC-I$_4$) have been synthesized and applied for nanoparticle materials in computer tomography (CT) contrast enhancement [22]. In this context, we selected H$_2$BDC-I$_4$ as a building block, considering its following characteristics: (a) the bulky *ortho* iodine groups can significantly affect the relative orientation of the carboxylate groups, (b) the four large iodine atoms can preclude interpenetration and (c) there are potiential applications for CT contrast agents. Herein, we wish to report the synthesis and crystal structure of {[Zn(BDC-I$_4$)(DMSO)$_2$]·(DMSO)$_2$(H$_2$O)$_4$}$_n$ (**1**), obtained from H$_2$BDC-I$_4$ with Zn(II) nitrate in DMSO/H$_2$O solvents. In addition, the IR spectrum, thermal stability, and luminescence property of **1** are also discussed.

Results and Discussion

Synthesis and general characterization

The ligand H$_2$BDC-I$_4$ is insoluble in water and soluble in common polar organic solvents, such as MeOH, EtOH, DMF, and DMSO. Complex **1** was synthesized in a mixed solvent system (DMSO/H$_2$O) through assembly of Zn(NO$_3$)$_2$ · 6H$_2$O and H$_2$BDC-I$_4$ under ambient conditions. When Zn(OAc)$_2$ and Zn(ClO$_4$)$_2$ were used, complex **1** could also be isolated by the same procedure (confirmed by IR spectra and X-ray structure analysis), which suggests that the final products are independent of the counterions in such solvent systems. **1** is air-stable and was characterized by elemental analysis and IR spectroscopy. In the IR spectrum of **1**, the absence of the characteristic band at ~ 1705 cm^{-1}

for the free H_2BDC-I_4 molecule indicates the complete deprotonation of the carboxyl groups. As a result, the antisymmetric and symmetric carboxylate stretching vibrations are found in the range of 1590–1610 and 1390–1440 cm^{-1}, respectively. The band at $\sim$ 1026 cm^{-1} can be attributed to the S=O stretching absorption, indicating the presence of DMSO molecules.

Description of the crystal structure

Complex **1** crystallizes in the space group *Pnma* with $Z = 4$. The molecular structure consists of one Zn(II) ion located on a crystallographic mirror plane, one BDC-I_4 dianion with crystallographically imposed centrosymmetry, two coordinated DMSO ligands, four water and two DMSO solvate molecules. Each Zn(II) ion is tetrahedrally coordinated by two oxygen atoms from two BDC-I_4 ligands and two oxygen atoms from two DMSO molecules (Fig. 1a). The Zn–O bond lengths vary from 1.926(4) to 1.997(6) Å, and the O–Zn–O bond angles range from 95.5(3) to 118.0(3)°. Each BDC-I_4 dianion bridges two Zn(II) ions in a bis-monodentate fashion to form a zigzag chain (Fig. 1b). Within each chain, the distance between successive Zn(II) ions is 10.967(1) Å, and the closest Zn···Zn separation between the neighboring strands is 7.633(1) Å. The two carboxylate groups within the BDC-I_4 ligand are almost perpendicular to the tetraiodobenzene plane

with dihedral angles of 89.7(3)°, which is similar to that of other carboxylate compounds with a polyiodinated core [22 – 24].

Notably, although complex **1** shows a 1-D coordination array similar to the previously reported $\{[Zn(BDC-I_4)(EtOH)_2]\cdot(EtOH)_2\}_n$ [22], the replacement of the solvent ethanol by a mixed solvent of H_2O and DMSO leads to the formation of a distinct supramolecular framework. Intramolecular C6–H6A···O1 interactions (further hydrogen bond parameters are listed in Table 1) have been found to stabilize the 1-D coordination motifs. Moreover, each coordinated DMSO ligand also forms a weak intermolecular hydrogen bond (C6–H6C···O5^i, with distances: 2.26/3.145(1) Å, angle: 153°, $i = -x + 1/2, y + 1/2, z + 1/2$) with a solvate DMSO moiety. No strong hydrogen-bonding interactions have been detected because of the disorder of the lattice water molecules. Edge-to-face C–H···π [C7–H7B···Cg1^{ii} (Cg1 = C1–C3, C1A–C3A): H7B···Cg1, 2.61(1) Å; C10···Cg1, 3.521(1) Å; ii = $x, y, z - 1$] inter-chain interactions lead to a 3-D supramolecular architecture (Fig. 2).

Thermal stability

To investigate the thermal stability of **1**, a thermogravimetric analysis (TGA) was carried out from room temperature to 800 °C. The corresponding curve
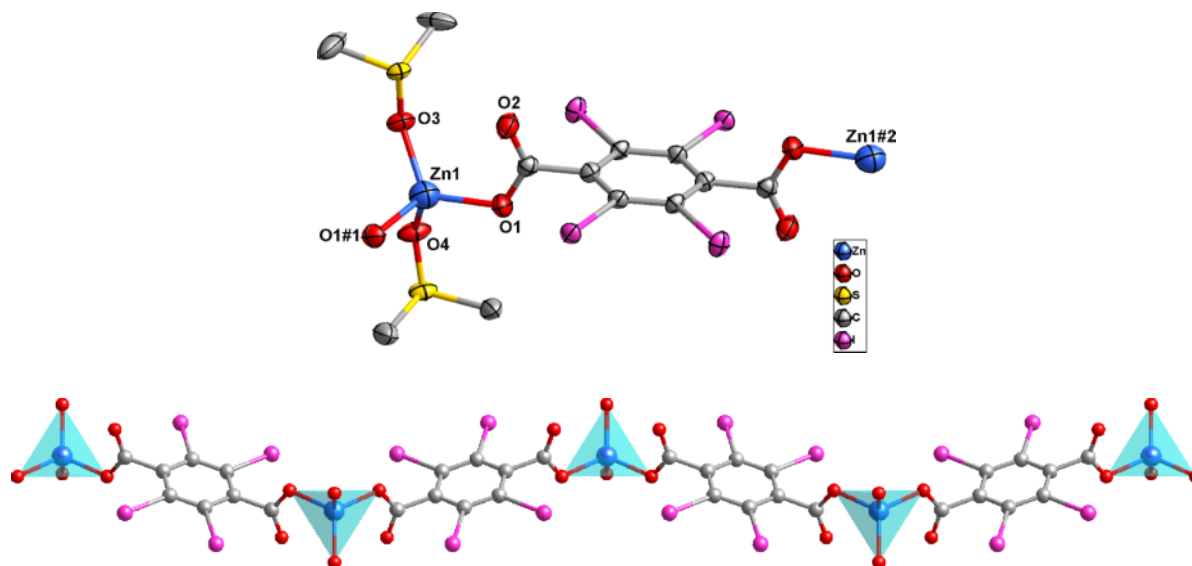

Fig. 1 (color online). Views of (a) the coordination environment of the Zn(II) center in **1**. Symmetry codes: #1 $x, -y + 1/2, z$; #2 $-x, y - 1/2, -z + 2$; (b) the coordination chain arrangement of **1**.
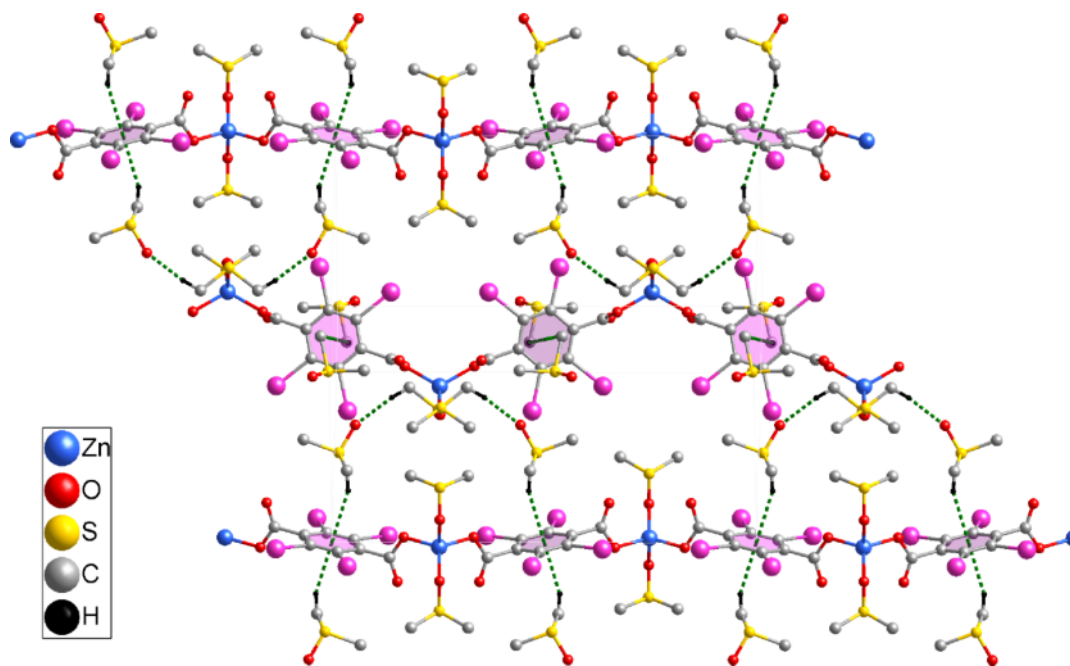
Fig. 2 (color online). The 3-D supramolecular architecture showing the weak hydrogen bonding interactions between adjacent chains. Irrelevant atoms are omitted for clarity.

Table 1. Hydrogen bonds in the crystal structure of **1**.

D–H⋯A	H⋯A (Å)	D⋯A (Å)	D–H⋯A (deg)	Symmetry code for A
O3–H3⋯O4	1.86	2.639(6)	151	
O4–H4⋯O1	1.93	2.736(6)	159	$x+1/2, y+1/2, z$
C6–H6A⋯O1	2.57	3.277(13)	130	$x, -y+1/2, z$
C6–H6C⋯O5	2.26	3.145(15)	153	$-x+1/2, y+1/2, z+1/2$
C7–H7B⋯Cg1[a]	2.61	3.521(15)	159	$x, y, z-1$

[a] Cg1 = C1–C3, C1A–C3A.

is depicted in Fig. 3 and shows the first weight loss of 36.3% (calculated: 36.1%), occurring from 65 °C to 210 °C, corresponding to the release of lattice water and solvate DMSO as well as coordinated DMSO molecules. The remaining framework is decomposed through three consecutive weight losses beginning at 240 °C.

Photoluminescence properties

The solid-state fluorescence spectra of complex **1** and of the free ligand H_2BDC-I_4 were recorded at room temperature (Fig. 4). Upon excitation at 336 nm, the free ligand exhibits an emission maximum at 474 nm, which can be ascribed to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transitions. For **1**, the maximum emission
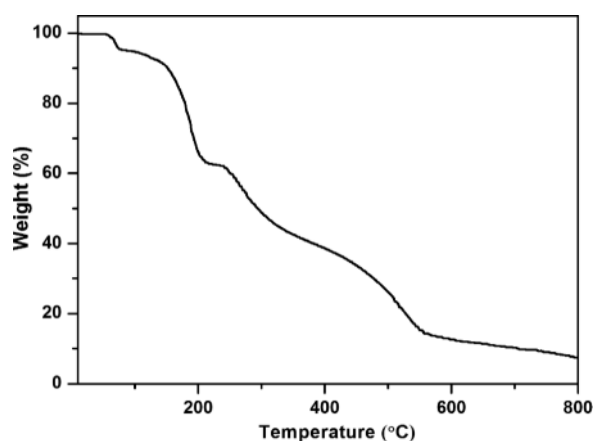
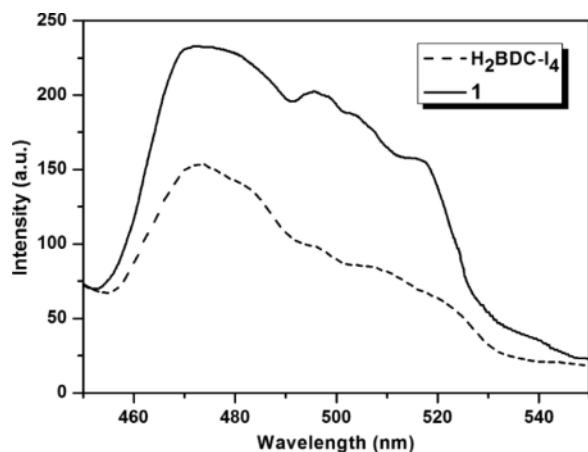

Fig. 3. TGA curve of complex **1**.

Fig. 4. Solid-state fluorescence emission spectra of complex **1** and the free ligand H_2BDC-I_4.

band is similarly observed at 472 nm ($\lambda_{ex} = 336$ nm), which can also be assigned to ligand-centered transitions. The enhancement of the luminescence intensity may be tentatively attributed to the increased rigidity of the deprotonated ligand upon complexation that reduces the non-radiative decay of the intra-ligand ($\pi \rightarrow \pi^*$) excited state [25, 26]. However, no obvious fluorescence was found for {[Zn(BDC-I$_4$)(EtOH)$_2$]·(EtOH)$_2$}$_n$ [22], which is likely due to the quenching effect of the high-energy C–H and O–H oscillators of the coordinated EtOH molecules [13].

Conclusion

In summary, we have synthesized and characterized a Zn(II) coordination polymer based on the deliberate choice of the periodinated benzenedicarboxylate tecton 2,3,5,6-BDC-I$_4$ and the solvent media. Owing to the steric demands of bulky iodine groups, the BDC-I$_4$ dianions serve as bis-monodentate spacers to bridge adjacent metal centers into infinite chains which also feature coordinated DMSO molecules. The chains are expanded to a 3-D supromolecular architecture through C–H···O and C–H···π interactions. This result verifies the fine-tuning of a supramolecular network of similar coordination systems by the choice of solvent and presents a new challenge in the rational design of solvent-regulated polymeric complexes.

Experimental Section

All chemicals were reagent grade, obtained from commercial sources and used as received without further purifica-

tion. The Fourier transform (FT) IR spectra were recorded on a Nicolet ESP 460 FT-IR spectrometer using KBr pellets. Elemental analysis was performed on a PE-2400II (Perkin-Elmer) analyzer. Thermogravimetric analysis (TGA) was carried out on a Dupont thermal analyzer from room temperature to 800 °C (heating rate: 10 °C min^{-1}, nitrogen stream). Solid-state fluorescence spectra were measured at room temperature on a Varian Cary Eclipse spectrometer.

Synthesis of {[Zn(BDC-I$_4$)(DMSO)$_2$]·(DMSO)$_2$(H$_2$O)$_4$}$_n$ (1)

Complex **1** was prepared by mixing equimolar amount of H_2BDC-I_4 (66.9 mg, 0.10 mmol) and Zn(NO$_3$)$_2$ · 6H$_2$O (29.7 mg, 0.10 mmol) in H$_2$O-DMSO (v/v = 3 : 1, 16 mL). After stirring for *ca.* 15 min, the reaction mixture was filtered and left to stand at room temperature. Colorless block-shaped crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of the filtrate in a yield of 42 % (44.7 mg based on H_2BDC-I_4). – Anal. for C$_{16}$H$_{32}$I$_4$O$_{12}$S$_4$Zn (%): calcd. C 17.32, H 2.18; found C 17.28, H 2.18. – IR (cm^{-1}, KBr pellet): $v = 2937$ (m), 1608 (s), 1496 (s), 1432 (m), 1395 (s), 1337 (s), 1298 (s), 1286 (s), 1237 (m), 1112 (m), 1093 (s), 1026 (s), 925 (m), 862 (w), 760 (w), 727 (w), 663 (s), 650 (s), 611 (w).

X-Ray structure determination

The single-crystal X-ray diffraction measurement was performed on a Bruker Apex II CCD diffractometer at am-

Table 2. Crystal structure data for **1**.

Formula	C$_{16}$H$_{32}$I$_4$O$_{12}$S$_4$Zn
M_r	1117.63
Crystal size, mm^3	$0.28 \times 0.26 \times 0.26$
Crystal system	orthorhombic
Space group	*Pnma*
a, Å	10.4923(9)
b, Å	20.0481(2)
c, Å	17.2999(1)
V, Å^3	3639.0(5)
Z	4
D_{calcd}, g cm^{-3}	2.04
μ (MoK_α), mm^{-1}	4.3
$F(000)$, e	2120
hkl range	$\pm 12, -23 \rightarrow 24, \pm 20$
Refl. measured/unique/R_{int}	19 806/3481/0.033
Param. refined	199
R^a/R_w^b [$I > 2\sigma(I)$]	0.0400/0.1191
R^a/R_w^b (all data)	0.0489/0.1242
GOF (F^2)^c	1.054
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.94/ − 0.77

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GOF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 3. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses[a].

Distances	
Zn(1)–O(1)	1.926(4)
Zn(1)–O(4)	1.998(6)
Zn(1)–O(3)	1.951(6)
Angles	
O(1)–Zn(1)–O(1)#1	118.0(3)
O(1)–Zn(1)–O(4)	101.3(2)
O(1)–Zn(1)–O(3)	117.0(2)
O(3)–Zn(1)–O(4)	95.5(3)

[a] Symmetry code: #1: $x, -y + 1/2, z$.

bient temperature with MoK_{α} radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied using SADABS [27], and the program SAINT [28] was used for integration of the diffraction profiles. The structure was solved by Direct Methods using SHELXS of the SHELXTL program package and refined anisotropically for all non-H atoms by full-matrix least-squares on F^2 with SHELXL [29]. In general, hydrogen atoms were located geometrically and allowed to ride during the subsequent refinement. O-bound H atoms were first located in difference Fourier maps, and then fixed geometrically and refined isotropically. Notably, the S3 atoms of the DMSO solvate molecules in the structure of **1** are disordered over two positions with partial site-occupancies of 0.70 and 0.30. Some hydrogen atoms of the lattice water molecules were not located as the lattice water O atoms are assigned to partial site-occupancies of 0.50. Further crystallographic data and structural refinement parameters are summarized in Table 2, and selected bond lengths and angles are listed in Table 3.

CCDC 879560 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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