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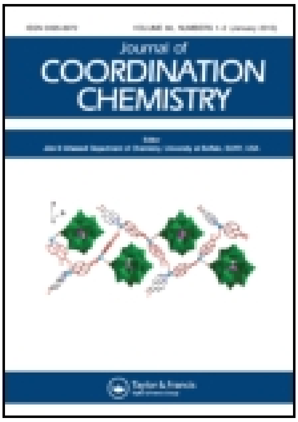

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Influence of solvent on the structures of two copper(II) coordination polymers with tetraiodoterephthalate: syntheses, crystal structures, and properties

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Influence of solvent on the structures of two copper(II) coordination polymers with tetraiodoterephthalate: syntheses, crystal structures, and properties

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Two Cu^{II} coordination polymers $\{[Cu(BDC\text{-}I_4)(MeOH)_4](H_2BDC\text{-}I_4)(MeOH)_2\}_n$ (**1**) and $[Cu(BDC\text{-}I_4)(dioxane)(MeOH)_2]_n$ (**2**) with a rigid periodinated ligand 2,3,5,6-tetraiodo-1,4-benzenedicarboxylic acid ($H_2BDC\text{-}I_4$) have been synthesized and characterized by elemental analysis, IR spectroscopy, and X-ray crystallography. Complex **1** presents a one-dimensional (1-D) linear structure, further assembled to form a two-dimensional (2-D) layer through inter-chain $O–H\cdots I$, $O–H\cdots O$, or $C–I\cdots\pi$ weak interactions. Complex **2** shows a 1-D zigzag structure that is extended into a 2-D supramolecular network by intermolecular $O–H\cdots O$ hydrogen bonds. The Cu^{II} in **1** has a distorted octahedral (CuO_6) coordination sphere, whereas Cu^{II} in **2** displays a nearly ideal square-pyramidal (CuO_5) coordination. The structural differences between **1** and **2** imply that solvent plays an important role in the construction of coordination architectures. In addition, the luminescent properties of $H_2BDC\text{-}I_4$, **1** and **2** in the solid state were investigated.

Keywords: Coordination polymer; Solvent-controlled synthesis; Cu^{II} tetraiodoterephthalate; Crystal structure; Luminescent property

1. Introduction

Syntheses of new functional coordination polymers have attracted a great deal of attention in supramolecular and materials chemistry with captivating structural topologies and potential applications as functional materials [1]. The structural and functional diversification for such crystalline solids depends on the backbone geometry as well as versatile sites for coordination and/or secondary interactions, which are usually directed by external physical or chemical stimuli [2]. Considerable effort has been devoted to syntheses of coordination compounds employing procedures based on reaction variables such as pH [3], solvent [4], and temperature [5]. Reaction solvent is a crucial influence on coordination of ligands as well as crystallization kinetics and thermodynamics [6]. Generally, solvents regulate the self-assembly process in the following ways: (a) solvent as ligand; (b) solvent as guest; (c) solvent as both

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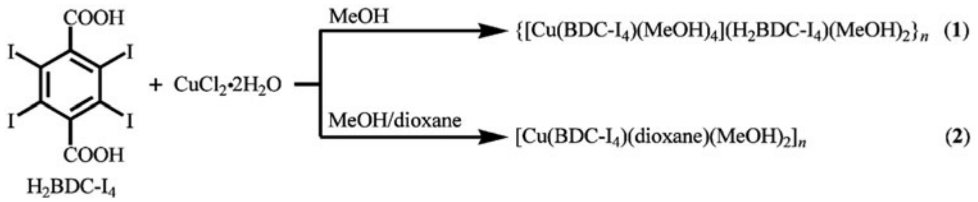

Scheme 1. Solvent-reguated synthesis of 1 and 2.

ligand and guest; and (d) solvent as a structure-directing agent. Recently, our interest has focused on solvent-regulated assemblies based on polyhalogen-substituted benzenedicarboxylate derivatives, such as 2,3,5,6-tetrachloro-1,4-benzenedicarboxylic acid [7], 2,3,5,6-tetrafluoro-1,4benzenedicarboxylic acid [8], and 3,4,5,6-tetrachloro-1,2-benzenedicarboxylic acid [9]. We have shown that solvent strongly affects the coordination frameworks with polyhalogen-substituted BDC. As continuation of our research, we report herein the solvent-regulated assembly of two Cu^{II} coordination polymers constructed from a new tetraiodo-substituted benzenedicarboxylate $H_2BDC\text{-}I_4$ (2,3,5,6-tetraiodo-1,4-benzenedicarboxylic acid), $\{[Cu(BDC\text{-}I_4)(MeOH)_4](H_2BDCI_4)(MeOH)_2\}_n$ (**1**) and $[Cu(BDC\text{-}I_4)(dioxane)(MeOH)_2]_n$ (**2**) (see scheme 1). They represent the first reported examples for $BDC\text{-}I_4$ coordination polymers. In addition, the spectroscopic, thermal, and luminescence of both complexes will also be discussed.

2. Experimental

2.1. *Materials and general methods*

All chemicals were commercially available and used as received. Elemental analyses (C and H) were carried out on a PE–2400II (PerkinElmer) analyzer. Infrared spectra were recorded on a Nicolet ESP 460 FT–IR spectrometer with KBr pellets from 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiments were performed on a Dupont thermal analyzer from room temperature to 800 °C (heating rate of 10 °C min^{-1}, nitrogen stream). Fluorescence spectra of solid samples were measured on a Varian Cary Eclipse spectrometer at room temperature.

2.2. *Syntheses of the Cu^{II} complexes*

2.2.1. Synthesis of $\{[Cu(BDC\text{-}I_4)(MeOH)_4](H_2BDC\text{-}I_4)(MeOH)_2\}_n$ (1). In a 25 mL vial, a mixture of $CuCl_2{\cdot}2H_2O$ (17.0 mg, 0.1 mmol) and $H_2BDC\text{-}I_4$ (66.9 mg, 0.1 mmol) was dissolved in MeOH (18 mL) with stirring for 30 min. Then, the resulting solution was filtered and left to stand at room temperature. Blue block single crystals suitable for X-ray analysis were obtained by solvent evaporation after 3 days in ca. 65% yield (51.8 mg, on the basis of $H_2BDC\text{-}I_4$). Anal. Calcd for $C_{22}H_{26}CuI_8O_{14}$ (%): C, 16.59; H, 1.64. Found: C, 16.65; H, 1.61. IR (KBr, cm^{-1}): 3428 bs, 1705 vs 1597 s, 1516 m, 1416 s, 1396 s, 1297 s, 1246 s, 1147 m, 1052 m, 917 w, 767 w, 696 m, 591 m.

2.2.2. Synthesis of $[Cu(BDC\text{-}I_4)(dioxane)(MeOH)_2]_n$ (2). The procedure was the same as that for **1** except that MeOH was replaced with dioxane/MeOH (18 mL, V : V = 1 : 3),

Table 1. Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{22}H_{26}CuI_8O_{14}$	$C_{14}H_{16}CuI_4O_8$
Formula weight	1593.18	883.42
Crystal size (mm^3)	0.26 × 0.24 × 0.22	0.24 × 0.22 × 0.22
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	9.649(2)	9.278(1)
b (Å)	10.005(2)	9.485(1)
c (Å)	10.940(3)	14.019(1)
α (°)	102.357(4)	93.773(2)
β (°)	97.046(4)	91.066(2)
γ (°)	110.698(3)	111.949(2)
V (Å^3)	942.2(3)	1140.66(2)
Z	1	2
ρ_{calcd} (g cm^{-3})	2.808	2.572
μ (cm^{-1})	7.190	6.405
F (0 0 0)	723	810
Range of h, k, l	−11/11, −11/11, −12/8	−11/11, −11/7, −16/16
Total/independent reflections	5230/3261	6356/3951
R_{int}	0.0230	0.0305
R^a, $R_w{}^b$	0.0354, 0.1056	0.0402, 0.1264
GOF^c	1.005	1.011
Residuals (e Å^{-3})	2.653, −2.920	1.719, −1.855

Notes: $^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$^bR_w = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2]^{1/2}$.
$^c\mathrm{GOF} = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(n-p)\}^{1/2}$.

affording blue block crystals of **2** in ca. 52% yield (46.0 mg, on the basis of H_2BDC-I_4). Anal. Calcd for $C_{14}H_{16}CuI_4O_8$ (%): C, 19.03; H, 1.83. Found: C, 19.12; H, 1.80. IR (KBr, cm^{-1}): 3395 bs, 2967 m, 2913 m, 2885 m, 1589 s, 1450 s, 1399 s, 1297 s, 1273 s, 1253 m, 1213 w, 1114s, 1077 m, 1054 m, 892 m, 867 s, 821 w, 760 w, 612 w, 572 m.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex **1**			
Cu(1)–O(1)	2.002(6)	Cu(1)–O(3)	2.089(1)
Cu(1)–O(4)	2.172(9)		
O(1)–Cu(1)–O(1)#1	180.0(4)	O(1)–Cu(1)–O(3)	89.2(3)
O(1)–Cu(1)–O(3)#1	90.8(3)	O(1)–Cu(1)–O(4)	89.3(3)
O(1)–Cu(1)–O(4)#1	90.7(3)	O(3)–Cu(1)–O(3)#1	180.0(2)
O(3)–Cu(1)–O(4)	88.4(4)	O(3)–Cu(1)–O(4)#1	91.6(4)
O(4)–Cu(1)–O(4)#1	180.0(7)		
Complex **2**			
Cu(1)–O(1)	1.934(6)	Cu(1)–O(3)	1.898(6)
Cu(1)–O(5)	2.262(7)	Cu(1)–O(7)	1.950(7)
Cu(1)–O(8)	1.981(7)		
O(1)–Cu(1)–O(3)	170.7(3)	O(1)–Cu(1)–O(5)	89.7(3)
O(1)–Cu(1)–O(7)	88.8(3)	O(1)–Cu(1)–O(8)	90.6(3)
O(3)–Cu(1)–O(5)	99.6(3)	O(3)–Cu(1)–O(7)	90.5(3)
O(3)–Cu(1)–O(8)	89.1(3)	O(5)–Cu(1)–O(7)	91.9(4)
O(5)–Cu(1)–O(8)	95.1(3)	O(7)–Cu(1)–O(8)	173.0(4)

Note: Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1$, $-y$, $-z$.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction measurements of **1** and **2** were performed on a Bruker Apex II CCD diffractometer at ambient temperature with Mo Kα radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied using *SADABS*, and *SAINT* was used for integration of the diffraction profiles [10]. The structures were solved by direct methods using *SHELXS* of *SHELXTL* packages and refined anisotropically for all non-H atoms by full-matrix least squares on F^2 with *SHELXL* [11]. Hydrogens were located geometrically and allowed to ride during the subsequent refinement. O-bound hydrogens were first located in difference Fourier maps and then fixed geometrically with isotropic temperature factors. Further crystallographic data and structural refinement parameters are summarized in table 1, and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis and general characterization*

$H_2BDC\text{-}I_4$ is insoluble in water and soluble in common polar organic solvents, such as MeOH, EtOH, DMF, and DMSO. Complexes **1** and **2** were synthesized in different solvent systems (MeOH for **1** and dioxane/MeOH for **2**) through assemblies of $H_2BDC\text{-}I_4$ and $CuCl_2 \cdot 2H_2O$ at ambient conditions. When different sources of metal centers such as $Cu(NO_3)_2$, $Cu(OAc)_2$, and $Cu(ClO_4)_2$ were used, **1** and **2** could also be isolated by the same procedure (confirmed by powder X-ray diffraction, see figure S1 in the Supplementary material), which suggests that the final products are independent of counteranion. Both complexes are stable under ambient conditions and insoluble in water and common organic solvents, consistent with their polymeric nature. For IR spectra of **1** and **2**, broad bands centered at 3400 cm^{-1} are O–H stretching frequencies. For **1** and **2**, the antisymmetric and symmetric stretching vibrations of carboxylate are 1580–1600 and 1390–1450 cm^{-1}, respectively. The strong peak at ca. 1705 cm^{-1} in IR spectra of **1** reveals the presence of free $H_2BDC\text{-}I_4$, which is also confirmed by X-ray single-crystal structure analysis.

3.2. *Description of crystal structures*

X-ray diffraction analysis reveals that **1** and **2** crystallize in the triclinic space group $P\bar{1}$ and have one-dimensional (1-D) infinite chain structures (figures 1 and 2). The basic coordination frameworks are similar, consisting of 1-D chains of $[Cu(BDC\text{-}I_4)]_n$, except that the coordinated guest molecules are MeOH in **1** and MeOH/dioxane in **2**. The introduction of dioxane leads to no free guests in **2** but lattice MeOH and free $H_2BDC\text{-}I_4$ in **1** (figures S2 and S3, Supplementary material).

3.2.1. $\{[Cu(BDC\text{-}I_4)(MeOH)_4](H_2BDC\text{-}I_4)(MeOH)_2\}_n$ **(1).** In the asymmetric unit of **1**, there is one Cu^{II}, one completely deprotonated $BDC\text{-}I_4$, four MeOH ligands, one lattice $H_2BDC\text{-}I_4$, and two guest MeOH molecules. As shown in figure 1(a), the octahedral coordination sphere of Cu^{II} is provided by two carboxylate oxygens (O1 and O1A) from two

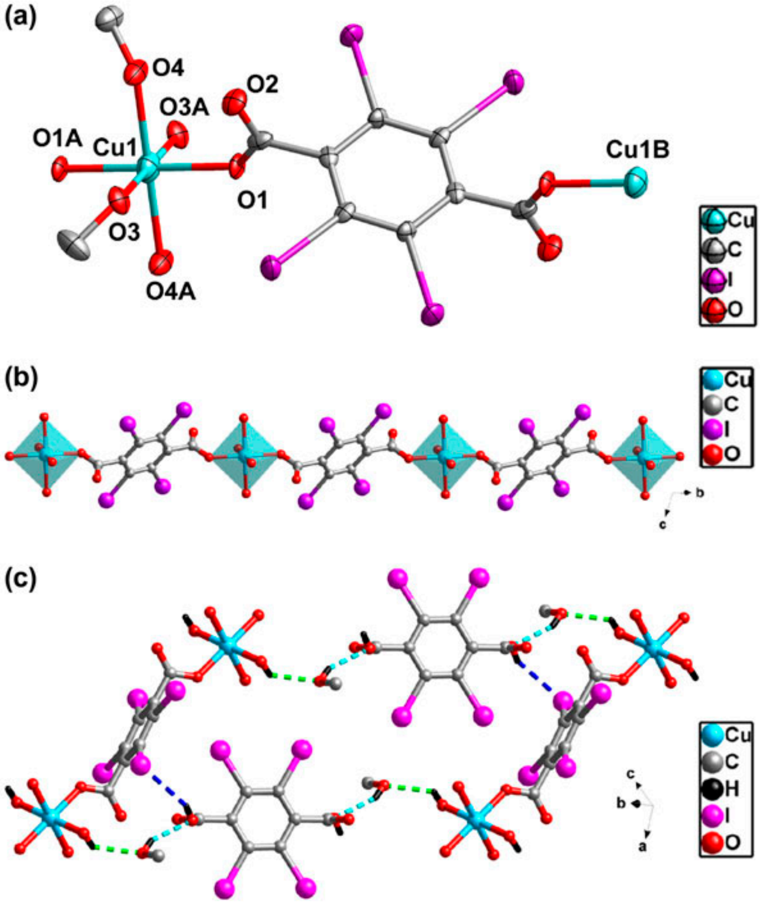

Figure 1. View of (a) the coordination environment of Cu^{II} in **1**. Symmetry codes: (A) $x-1$, $-y$, $-z$; (B) $x+1$, $y+1$, z; (b) the 1-D linear chain of **1**; (c) the hydrogen-bonding layer of **1** along the *ac* plane (irrelevant hydrogens are omitted for clarity).

trans BDC-I_4 dianions and four oxygens (O3, O3A, O4, and O4A) from four terminal MeOH molecules with Cu–O distances of 2.002(6)–2.172(9) Å. The O–Cu–O bond angles are from 89.2(3) to 180.0(4)°. The BDC-I_4 dianions, as $\mu_1-\eta^1:\eta^0$-monodentate for each carboxylate, join neighboring Cu^{II} ions into an infinite 1-D linear chain along the [0 1 0] direction, as depicted in figure 1(b), within which the adjacent Cu···Cu separation is 11.180(1) Å and the Cu–Cu–Cu angle is 180°. Owing to steric hindrance of iodines at *ortho* positions of carboxylate, the rotation angle between carboxylate and the tetraiodinated benzene is 82.5(7)° for coordinated BDC-I_4 ligand and 80.5(7)° for lattice H_2BDC-I_4, similar to other carboxylate compounds with polyiodinated backbone [12].

There exist diverse hydrogen-bonding motifs in the crystal lattice of **1**. Intramolecular O4–H4···O2 interactions (further hydrogen bond parameters are listed in table 3) stabilize such 1-D coordination motifs. The uncoordinated H_2BDC-I_4 and methanol work as linkers to fabricate a supramolecular layer by connecting two neighboring parallel coordination chains through O–H···O interactions [O3–H3···O7 and O7–H7···O5, see table 3 and figure 1(c)]. Each I1 of coordinated BDC-I_4 is involved in weak intermolecular hydrogen

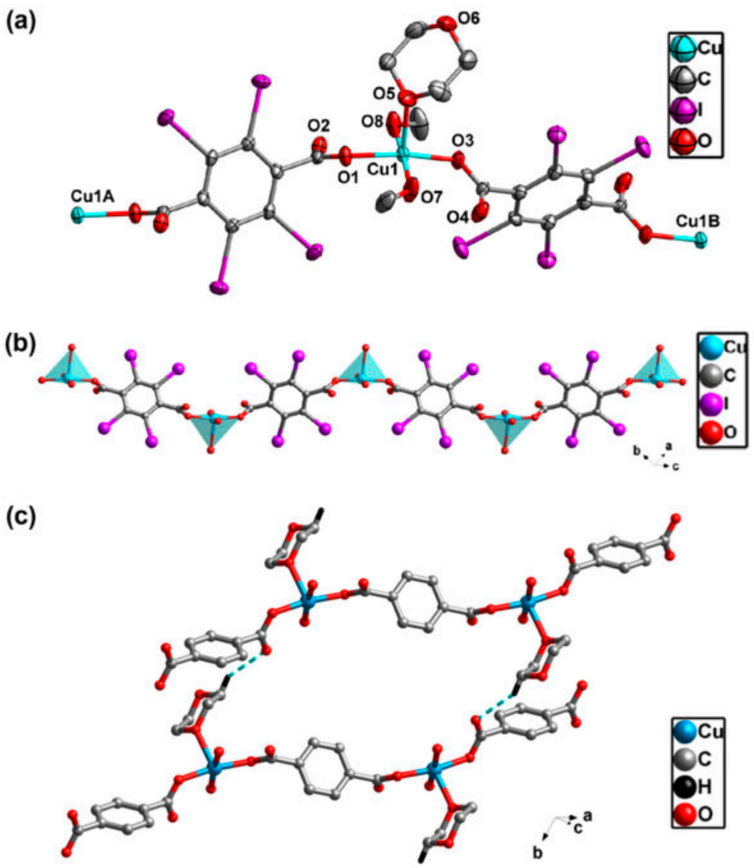

Figure 2. View of (a) the coordination environment of Cu^{II} in **2**. Symmetry codes: (A) $-x+1$, $-y+1$, $-z$; (B) $-x+2$, $-y$, $-z+1$; (b) the 1-D zigzag chain of **2**; (c) the 2-D supramolecular layer of **2** along the *ac* plane (iodines and irrelevant hydrogens are omitted for clarity).

bond ($O5\text{-}H5\cdots I1^{i}$, $H\cdots I/O\cdots I$ distances: 2.94/3.707(1) Å, angle: 156°, $i=-x+1$, $-y+1$, $-z+1$) with free carboxylate H5 of lattice $H_2BDC\text{-}I_4$ [figure 1(c)]. Between adjacent chains, weak edge-to-face $C\text{–}I\cdots\pi$ [$C10\text{–}I4B\cdots Cg1^{ii}$ ($Cg1=C2\text{–}C4$, $C2A\text{–}C4A$): $I4\cdots Cg1$, 3.651(4) Å; $C10\cdots Cg1$, 5.341(1) Å; $ii=x-1$, $y-1$, z] intermolecular interactions also stabilize this two-dimensional (2-D) supramolecular network.

Table 3. Possible hydrogen-bonding geometries in the crystal structures of **1** and **2**.

Complex	D–H· · ·A	H· · ·A (Å)	D· · ·A (Å)	D–H· · ·A (°)	Symmetry code
1	O3–H3· · ·O7	2.16	2.707(1)	124	
	C4–H4· · ·O2	2.23	2.771(1)	124	
	O5–H5· · ·I1	2.94	3.707(1)	156	$-x+1$, $-y+1$, $-z+1$
	O7–H7· · ·O5	2.10	2.843(1)	151	$-x+1$, $-y+1$, $-z+1$
2	O7–H7· · ·O4	1.84	2.529(1)	141	
	C10–H10A· · ·O2	2.59	3.422(2)	144	x, $y-1$, z

3.2.2. $[Cu(BDC\text{-}I_4)(dioxane)(MeOH)_2]_n$ (2).

As for **2**, the asymmetric unit contains one Cu^{II}, one fully deprotonated BDC-I_4, one dioxane, and two coordinated MeOH [see figure 2(a)]. Each Cu^{II} is five-coordinate by two oxygens (O1 and O3) from two *trans* BDC-I_4 with Cu–O distances of 1.934(6) and 1.898(6) Å, one oxygen (O5) from one terminal dioxane with Cu–O distance of 2.262(7) Å, and two oxygens (O7 and O8) from two terminal MeOH molecules with Cu–O distances of 1.950(7) and 1.981(7) Å. The O–Cu–O bond angles range from 88.8(3) to 173.0(4)°. Several parameters are used to define the coordination geometry around the five-coordinate metal center with the most common the τ factor defined by Addison *et al.* ($\tau=0$ for a regular square-pyramid and $\tau=1$ for a regular trigonal-bipyramid) [13]. The τ value of 0.04 for Cu1 in **2** indicates a nearly ideal square pyramid. Each BDC-I_4 coordinates $\mu_1-\eta^1:\eta^0$-monodentate for each carboxylate to bridge two adjacent Cu^{II} ions. As a consequence, the Cu^{II} ions are extended by BDC-I_4 spacers to afford a 1-D chain along the [0 1 0] direction [see figure 2(b)], within which the distance between successive Cu^{II} ions is 11.014(1) Å and the Cu–Cu–Cu angle is 149.6(1)°. Similar to **1**, within the BDC-I_4 dianion, two carboxylates are inclined to the tetraiodinated benzene ring with a dihedral angle of 84.5(7)° due to the steric effect. Intramolecular O7–H7···O4 (see table 3) interaction was found between the uncoordinated carboxylate O4 and ligated MeOH to stabilize the resultant coordination structure. Adjacent 1-D arrays are connected through weak intermolecular C–H···O hydrogen-bonding interactions (C10-H10A···O2^i, H···O/C···O distances: 2.59/3.422(2) Å, angle: 144°, i=x, $y-1$, z) between coordinated dioxane and the other uncoordinated carboxylate O2 of BDC-I_4 to afford a 2-D supramolecular layer along the *ac* plane [see figure 2(c)].

3.3. *Thermal stability*

TGA were performed by heating the corresponding crystalline samples of **1** and **2** (figure S4, Supplementary material). The TGA trace of **1** displays two consecutive steps of weight loss from 40 to 180 °C, indicating exclusion of both lattice and coordinated methanol (calculated, 12.0%; found, 11.1%). The remaining framework is decomposed with a sharp weight loss at 250–310 °C, followed by two weight losses ending at 800 °C. In the case of **2**, the weight loss of 17.6% from 30 to ca. 140 °C corresponds to removal of coordinated dioxane and methanol (calculated, 17.2%). A sharp weight loss at 255–400 °C indicates collapse of the residual framework. Further heating to 800 °C reveals a continuous and slow weight loss. The final residual of 8.5% is close to the calculated 9.0% based on CuO.

3.4. *Photoluminescent property*

The luminescent properties of **1**, **2** and free $H_2BDC\text{-}I_4$ in the solid state were investigated at room temperature (figure 3). Upon excitation at 336 nm, the free ligand exhibits the maximum fluorescent emission band centered at 474 nm, which could be ascribed to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transitions. For **2**, the maximum emission peak is similarly observed at 475 nm, which should be assigned to the ligand-centered transitions. The emission intensity of **2** is evidently weaker than that of the free ligand, and no obvious fluorescence was found for **1** in this case, which is probably related to the quenching effect of high-energy C–H and O–H oscillators from coordinated MeOH [14].

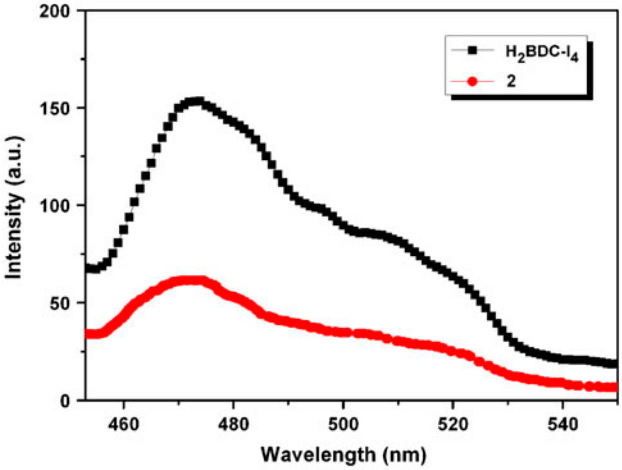

Figure 3. Solid-state fluorescent emission spectra of **2** and free 1,4-H_2BDC-I_4.

4. Conclusion

Assemblies of Cu^{II} with tetraiodo-substituted benzenedicarboxylate BDC-I_4 lead to formation of two new coordination polymers, which can be slightly regulated by choice of solvent. In comparison with Cu^{II} complexes based on terephthalate [2(h,i)], despite the steric demands of bulky iodine forcing formation of 1-D $[Cu(BDC-I_4)]_n$ host coordination chains, the solvents (methanol in **1** and methanol/dioxane in **2**) play significant roles in the finally host-guest supramolecular networks that are also stabilized by intermolecular halogen bonding and related $I\cdots\pi$ interactions. These results prompt us to make a further systemic study on coordination chemistry of halogen-substituent dicarboxylates, which will enrich the scope of crystal engineering for supramolecular hybrid solids.

Supplementary material

Figure S1 is for the powder X-ray diffraction of **1** and **2**, while figures S2 and S3 represent the 3-D packing diagram for **1** and **2**, respectively. Figure S4 shows the TGA curves of **1** and **2**. CCDC 879565 and 879566 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 3360 33; E-mail: deposit@ccdc.cam.ac.uk).

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