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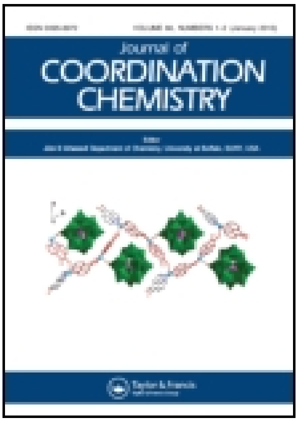

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Two M(II)-1,5-NDS-dafo supramolecular architectures (M=Cu, Cd): syntheses, structures, and photoluminescence properties

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Two M(II)-1,5-NDS-dafo supramolecular architectures (M = Cu, Cd): syntheses, structures, and photoluminescence properties

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Under hydrothermal conditions, reaction of Cu(II)/Cd(II) salts with 1,5-naphthalenedisulfonate (1,5-NDS) and 4,5-diazafluoren-9-one (dafo) afforded $[Cu(dafo)_2(1,5\text{-}NDS)]_n$ (**1**) and $[Cd(dafo)_2(1,5\text{-}NDS)]_n$ (**2**), respectively. The compounds were characterized by elemental analysis, IR, PXRD, TG-DSC, and single-crystal X-ray diffraction. Both **1** and **2**, which are the first M(II)-1,5-NDS-dafo systems, exhibit 3-D supramolecular structures generated by 1-D chains via C–H···O hydrogen bonds and π–π interactions. Solid-state photoluminescence properties of both **1** and **2** were investigated with emission bands at 426–496 nm (λ_{ex} = 280, 270 nm for **1** and **2**, respectively).

Keywords: Naphthalenedisulfonate; Hydrothermal condition; Supramolecule; Photoluminescence property

1. Introduction

There has been significant interest in the construction of supramolecular architectures owing to topologies and potential applications in catalysis, luminescence, and gas storage [1–5]. The selection of ligands as linkers and metal ions as connected centers is the main factor to manipulate structures and properties of supramolecular architectures [6–8]. Current efforts on the synthesis of supramolecular architectures mostly use polycarboxylates [9–11] and phosphonates [12–14]. Fewer studies are dedicated to the coordination chemistry of organosulfonates because of the weak coordination strength of sulfonates [15–18]. Nevertheless, organosulfonates are important ligands, as they are not only used in diverse supramolecular architectures, but also have fascinating properties of metal organosulfonate materials [6, 17–19]. Among organosulfonates, arenedisulfonate ligands, for example 1,5-naphthalenedisulfonate (1,5-NDS), are useful to construct supramolecular architectures as linkers due to the following reasons: (1) arenedisulfonates with rigid spacers provide a variety of potential binding sites to show multiple coordination and

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*Corresponding author. Email: yulanzhu2008@126.com construct coordination polymers with various topologies [15, 20–22] and (2) the six oxygens of sulfonate groups can take part in hydrogen bond interactions as acceptors, giving multi-dimensional supramolecular architectures [6, 13]. The coordination strength of sulfonates is tunable through the introduction of other ligands as auxiliaries, which can alter the structures and properties of compounds [6, 16, 20].

The phen derivative, 4,5-diazafluoren-9-one (dafo) as a co-ligand with a large conjugate plane [23], can provide an uncommon coordination environment to yield numerous coordination compounds because of the larger bite distance (2.99 Å) between two coordination nitrogens [24]. M(II)-1,5-NDS-dafo system has never been reported. We report Cu(II)/Cd(II) compounds with 1,5-NDS and dafo, respectively. In this article, two 3-D supramolecular compounds, $[Cu(dafo)_2(1,5\text{-}NDS)]_n$ (**1**) and $[Cd(dafo)_2(1,5\text{-}NDS)]_n$ (**2**), were synthesized and characterized. In addition, photoluminescence properties for **1** and **2** were also investigated.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased from commercial sources and used without purification. 4,5-Diazafluoren-9-one (dafo) was prepared by following the literature method [25]. Elemental analyses were performed on a Perkin-Elmer 2400LS elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} with a Nicolet AVATAR360 instrument. Thermal gravimetric analyses (TGA) were carried out with a TGA/SDTA851e differential thermal analyzer with a rate of 10 °C min^{-1} under flowing air. Powder X-ray diffraction patterns were performed on an ARLX'TRA diffractometer using Cu Kα radiation. Emission spectra in the solid state at room temperature were taken on a Perkin-Elmer LS-55 fluorescence spectrophotometer.

2.2. *Syntheses*

2.2.1. $[Cu(dafo)_2(1,5\text{-}NDS)]_n$ (1). An aqueous water solution (14 mL) of $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.2 mM), 1,5-NDS (0.066 g, 0.2 mM), and dafo (0.036 g, 0.2 mM) was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 120 °C. After keeping in these conditions for 3 days, the reaction vessel was cooled to room temperature. Blue columnar crystals of **1** were obtained. Yield: 43%. Anal. Calcd for $C_{32}H_{18}CuN_4O_8S_2$ (%): C, 53.77; H, 2.52; N, 7.84. Found: C, 53.72; H, 2.49; N, 7.82. IR (KBr, cm^{-1}): 3448 (w), 3095 (w), 1733 (s), 1667 (w), 1621 (w), 1590 (m), 1568 (s), 1463 (w), 1406 (m), 1273 (s), 1236 (w), 1202 (w), 1173 (s), 1146 (s), 1116 (m), 1054 (m), 1009 (s), 915 (w), 842 (w), 803 (w), 762 (s), 614 (s), 581 (w), 518 (w), 479 (w).

2.2.2. $[Cd(dafo)_2(1,5\text{-}NDS)]_n$ (2). An aqueous water solution (14 mL) of $Cd(OAc)_2 \cdot 2H_2O$ (0.053 g, 0.2 mM), 1,5-NDS (0.066 g, 0.2 mM), and dafo (0.073 g, 0.4 mM) was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 120 °C. After keeping in these conditions for 3 days, the reaction vessel was cooled to room temperature, giving yellow acicular crystals of **2**. Yield: 47%. Anal. Calcd for $C_{32}H_{18}CdN_4O_8S_2$ (%): C, 50.32; H, 2.36; N, 7.34. Found: C, 50.28; H, 2.32; N, 7.31. IR (KBr, cm^{-1}): 3421 (w), 3085 (w), 1738 (s), 1661 (w), 1591 (m), 1569 (s), 1469 (w), 1414 (s), 1339 (w), 1296 (w), 1257 (s), 1226 (m), 1173 (s), 1151 (s), 1107 (m), 1021 (s), 913 (w), 844 (w), 805 (w), 763 (m), 733 (w), 611 (m), 573 (w), 472 (w).

2.3. *X-ray crystallography*

Single crystals of **1** and **2** were mounted on Bruker Smart CCD using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at room temperature. The structures were solved by direct methods and successive Fourier difference syntheses, and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using *SHELXS-97* [26] and *SHELXL-97* [27], respectively. Hydrogens of the ligands were located geometrically. Details of the crystal structures and refinements are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure analyses*

3.1.1. Crystal structure of [Cu(dafo)$_2$(1,5-NDS)]$_n$ (1). **1** crystallizes in the monoclinic system with $P2_1/c$ space group. Structure determination reveals that **1** is a 3-D supramolecular structure generated by 1-D chains through hydrogen bonds and the π–π interactions. As shown in figure 1, Cu(II) shows an octahedral geometry with N1, N2, N1A, and N2A from two dafo and O2, and O2A of two sulfonates from different 1,5-NDS ligands. Bond distances and angles are given in table 2. The Cu–O length is 2.000(2) Å, and two distinct

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

	1	**2**
Empirical formula	$C_{32}H_{18}CuN_4O_8S_2$	$C_{32}H_{18}CdN_4O_8S_2$
Formula weight (g mol^{-1})	714.19	763.05
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	9.8105(2)	10.339(2)
b	9.7959(2)	9.684(2)
c	14.503(3)	14.569(3)
α	90.00	90.00
β	95.226(2)	96.381(3)
γ	90.00	90.00
Volume (Å^3), Z	1388.0(4), 2	1449.6(6), 2
Calculated density (mg m^{-3})	1.709	1.748
Absorption coefficient (mm^{-1})	1.003	0.960
θ range for data collection (°)	2.08–26.00	1.98–26.00
Reflection collected	10,089	8544
Independent reflection	2695 [R(int) = 0.0687]	2791 [R(int) = 0.0398]
Paramaters	214	214
$F(0\,0\,0)$	726	764
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0451, 0.0935	0.0352, 0.0840
Final R_1, wR_2 [all data]	0.0749, 0.1035	0.0515, 0.1052
Goodness of fit on F^2	0.997	1.067
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.358, −0.361	0.357, −0.501

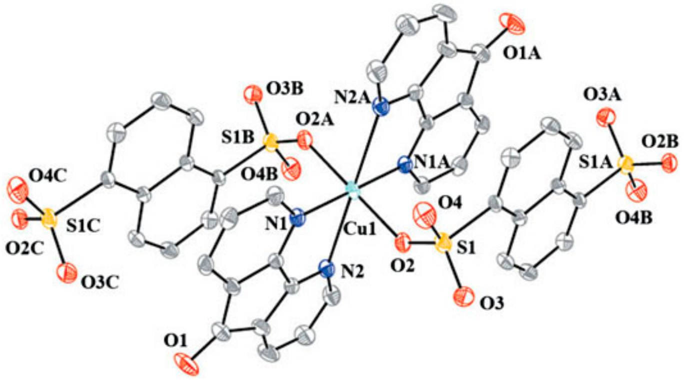


Figure 1. Coordination environment of Cu(II) in **1** with 30% probability displacement ellipsoids (hydrogens of ligands are omitted for clarity).

Cu–N distances are observed (Cu–N1 = 1.976(2) Å; Cu–N2 = 2.595(3) Å), which are similar to those reported previously [28]. In **1**, dafo coordinates to Cu(II) as an asymmetric bidentate ligand. The compounds containing dafo have a general feature that is "long and short" Cu–N distances [29, 30]. Some Cu(II) complexes with unsymmetric chelation to dafo have been reported previously [23, 28–34]. The N···N distance is 2.65 Å in 1,10-phenanthroline and 2.62 Å in 2,2′-bipyridine (planar conformation), while it is 2.972 Å in dafo of **1**. The bite angle N–Cu–N (for symmetric chelation) decreases from 84° in 1,10-phenanthroline (82° in 2,2′-bipyridine) to 79.86(1)° in dafo for a Cu–N1 distance of 1.976(2) Å. The strain imposed by the five-membered ring in dafo results in the large bite based on close examination of the dafo structure. The larger bite implies a much greater misalignment of Cu–N bonds with the lone pair orbitals in a symmetrical chelate [33]. Improved overlap between the lone pairs of N and the metal orbitals is a consequence of the unsymmetrical coordination [29].

In **1**, each sulfonate coordinates monodentate to $[Cu(dafo)_2]^{2+}$, and the naphthalenedisulfonate is a bifunctional spacer, which positions the cations into a 1-D chain. The chain propagates in a ladder-like fashion, in which the $[Cu(dafo)_2]^{2+}$ units are sandwiched between two 1,5-NDS ligands and located at different sides of the aromatic plane of 1,5-NDS along the *a* direction (figure 2(a)). The coordination mode of 1,5-NDS in **1** is the same as that of some Cu(II) compounds [15, 35]. In a 1-D chain, the aromatic plane of dafo and that of 1,5-NDS are almost parallel, resulting in π–π interactions (centroid–centroid distances are 3.409(2)–3.7590(2) Å; dihedral angles are 1.49–5.73°) which stabilize the 1-D chain. The compound exhibits a rectangular grid 2-D layer structure via hydrogen bonds (C16–H16···O1#2, 3.339(5) Å, 166°) (table 3) and π–π interactions with the centroid–centroid distance of 3.834(2) Å and a dihedral angle of 0° between aromatic rings of dafo ([N2, C9, C8, C7, C6, C10]···[N2, C9, C8, C7, C6, C10]#4) (table 4) of adjacent 1-D chains along the *ab* plane, as shown in figure 2(a). The supramolecular 3-D framework is constructed by inversion-related 2-D layers via hydrogen bonds (C2–H2···O1#1, 3.258(4) Å, 143°) (figure 2(b)).

3.1.2. Crystal structure of $[Cd(dafo)_2(1,5\text{-NDS})]_n$ (2).

2 crystallizes in the monoclinic system with $P2_1/c$ space group. Structure determination reveals that **2** is a 3-D supramolecular structure generated by 1-D chains through hydrogen bond interactions. The asymmetric

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

1			
Cu1–O2	2.000(2)	Cu1–N1	1.976(2)
Cu1–N2	2.595(3)		
O2–Cu1–N1	89.98(9)	O2–Cu1–N2	79.07(8)
O2–Cu1–O2#1	180.00	O2–Cu1–N1#1	90.02(9)
O2–Cu1–N2#1	100.93(8)	N1–Cu1–N2	79.86(1)
N1–Cu1–N2#1	100.14(1)	O2#1–Cu1–N2	100.93(8)
O2#1–Cu1–N1	90.02(9)	N1–Cu1–N1#1	180.00
N2–Cu1–N2#1	180.00		
2			
Cd1–O3	2.309(3)	Cd1–N2	2.323(3)
Cd1–N1	2.410(3)		
O3–Cd1–N1	78.74(1)	O3–Cd1–N2	94.59(1)
O3–Cd1–O3#1	180.00	O3–Cd1–N1#1	101.26(1)
O3–Cd1–N2#1	85.41(1)	N1–Cd1–N2	77.67(1)
N1–Cd1–N2#1	102.33(1)		

Symmetry codes: for **1**, #1 $-x$, $-y$, $-z$; for **2**, #1 $-x$, $-y$, $2-z$.

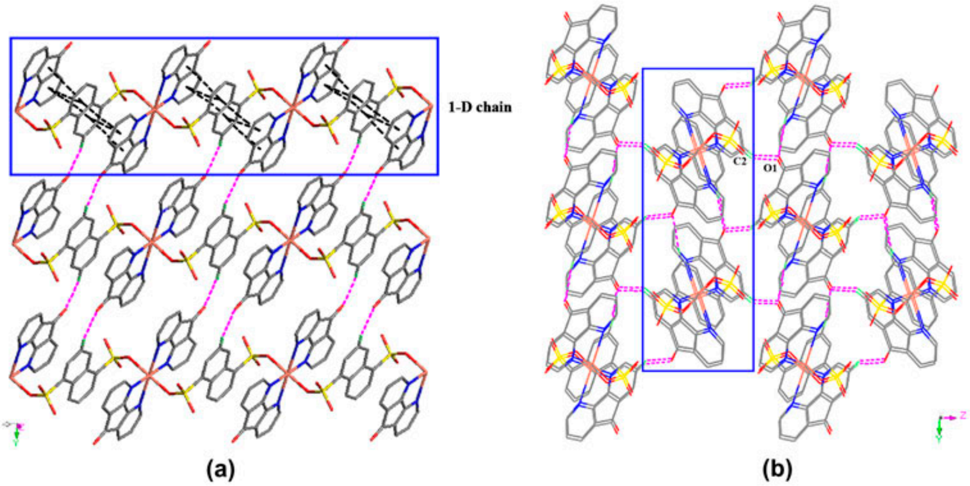


Figure 2. (a) 2-D layer of **1** parallel to the *ab* plane through hydrogen bonds (pink) and *π*–*π* interactions (black), (b) 3-D supramolecular framework of **1** through hydrogen bonds (pink) (see http://dx.doi.org/10.1080/00958972.2013.813938 for color version).

unit of **2** is built of one Cd(II), one dafo, and one 1,5-NDS. Cd(II) is six-coordinate, surrounded by two dafo ligands and two sulfonates of two different 1,5-NDS ligands (Supplementary material). The coordination polyhedron is best described as octahedral with N1, N2, N1A, and N2A as equatorial ligands and O3 and O3A in axial positions. The Cd–N/O bond lengths (Cd–N = 2.323(3)–2.410(3) Å; Cd–O = 2.309(3) Å) are similar to those reported previously [36]. Selected bond lengths and angles for **2** are listed in table 2.

In **2**, 1,5-NDS adopts the same coordination mode as that of **1**. Thus, a 1-D ladder-like chain is formed by $[Cd(dafo)_2]^{2+}$ units via 1,5-NDS along the *a* direction like **1** (figure 3 (a)). The coordination mode of 1,5-NDS in **2** has been observed in some Cd(II) complexes [16, 37]. In a 1-D chain, there are *π*–*π* interactions between nearly parallel aromatic rings of dafo ligands and 1,5-NDS ligands and between rings ([Cd1, N1, C11, C10 and N2])

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1** and **2**.

	D–H	H···A	D···A	D–H···A
1				
C2–H2···O1#1	0.93	2.47	3.258(4)	143
C16–H16···O1#2	0.93	2.43	3.339(5)	166
2				
C2–H2···O2#1	0.93	2.56	3.233(6)	130
C7–H7···O4#2	0.93	2.59	3.289(4)	133
C8–H8···O1#3	0.93	2.48	3.333(6)	152
C9–H9···O4#4	0.93	2.60	3.378(5)	142
C15–H15···O1#5	0.93	2.34	3.171(5)	149

Symmetry codes: for **1**, #1 1−*x*, −1/2 + y, 1/2−*z*; #2 −*x*, 1−*y*, −*z*; for **2**, #1 x, 1/2−*y*, 1/2 + z; #2 −1 + *x*, *y*, *z*; #3 −1−*x*, −1/2 + y, 3/2−*z*; #4 −*x*, −1/2 + y, 3/2−*z*; #5 1 + x, −1 + y, z.

Table 4. Aromatic interactions in **1** and **2**.

Ring atoms	Dihedral angle (°)	Distance (Å)
1		
[Cu1, N1, C11, C10, N2]···[C12, C13, C14, C14A, C15A, C16]#1	5.71	3.7590(2)
[Cu1, N1, C11, C10, N2]···[C14, C15, C16A, C12A, C13A, C14A]#2	5.73	3.7587(2)
[Cu1, N1B, C11B, C10B, N2B]···[C12, C13, C14, C14A, C15A, C16]	5.71	3.7590(2)
[Cu1, N1B, C11B, C10B, N2B]···[C14, C15, C16A, C12A, C13A, C14A] #3	5.73	3.7587(2)
[C4, C5, C6, C10, C11]···[C12, C13, C14, C14A, C15A, C16]#1	3.35	3.409(2)
[C4, C5, C6, C10, C11]···[C14, C15, C16A, C12A, C13A, C14A]#2	3.37	3.409(2)
[N1, C1, C2, C3, C4, C11]···[C12, C13, C14, C14A, C15A, C16]#2	1.49	3.6020(2)
[N1, C1, C2, C3, C4, C11]···[C12, C13, C14, C14A, C15A, C16]#1	1.49	3.5396(2)
[N1, C1, C2, C3, C4, C11]···[C14, C15, C16A, C12A, C13A, C14A]#2	1.51	3.5395(2)
[N1, C1, C2, C3, C4, C11]···[C14, C15, C16A, C12A, C13A, C14A]#1	1.51	3.6022(2)
[N2, C9, C8, C7, C6, C10]···[N2, C9, C8, C7, C6, C10]#4	0.00	3.834(2)
2		
[Cd1, N1, C11, C10, N2]···[C12, C13, C13A, C16A, C15, C14]#1	6.24(2)	3.849(2)
[Cd1, N1, C11, C10, N2]···[C13, C16, C15A, C14A, C12A, C13A]#2	6.25(2)	3.849(2)
[Cd1, N1B, C11B, C10B, N2B]···[C12, C13, C13A, C16A, C15, C14]	6.24(2)	3.849(2)
[Cd1, N1B, C11B, C10B, N2B]···[C13, C16, C15A, C14A, C12A, C13A] #3	6.25(2)	3.849(2)
[C4, C5, C6, C10, C11]···[C12, C13, C13A, C16A, C15, C14]#1	4.8(2)	3.478(2)
[C4, C5, C6, C10, C11]···[C13, C16, C15A, C14A, C12A, C13A]#2	4.8(2)	3.478(2)
[N2, C9, C8, C7, C6, C10]···[C12, C13, C13A, C16A, C15, C14]#2	5.41(2)	3.711(2)
[N2, C9, C8, C7, C6, C10]···[C12, C13, C13A, C16A, C15, C14]#1	5.41(2)	3.578(2)
[N2, C9, C8, C7, C6, C10]···[C13, C16, C15A, C14A, C12A, C13A]#2	5.42(2)	3.578(2)
[N2, C9, C8, C7, C6, C10]···[C13, C16, C15A, C14A, C12A, C13A]#1	5.42(2)	3.711(2)

Symmetry codes: for **1**, #1 −*x*, −*y*, −*z*; #2 1 + *x*, *y*, *z*; #3 −1−*x*, −*y*, −*z*; #4 −*x*, 1−*y*, −*z*; for **2**, #1 −*x*, 2−*y*, −*z*; #2 1 + *x*, *y*, *z*; #3 −1−*x*, 2−*y*, −*z*.

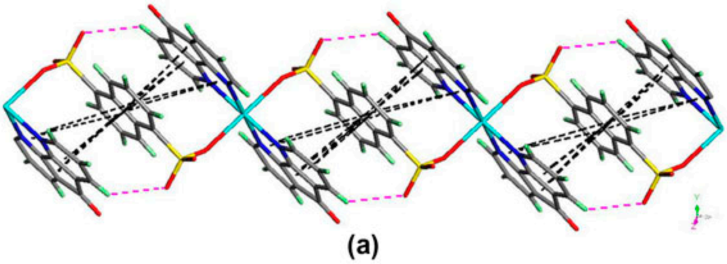
and aromatic rings of 1,5-NDS. The centroid–centroid separations range from 3.478(2) to 3.849(2) Å. The dihedral angles are 4.8(2)–6.25(2)°. The π–π interactions and hydrogen bond (C7–H7···O4#2, 3.289(4) Å, 133°) further stabilize the 1-D chains (table 3 and table 4). In addition, the interchain hydrogen bonds construct rectangular grids. Adjacent grids link via Cd(II) ions along a chain. 1-D chains connect through C15–H15···O1#5 (3.171(5) Å, 149°), resulting in a 2-D layer along the *ab* plane (figure 3(b)). 2-D layers give a supramolecular 3-D framework through C–H···O hydrogen bonds (C2–H2···O2#1, 3.233(6) Å, 130°; C8–H8···O1#3, 3.333(6) Å, 152°; C9–H9···O4#4, 3.378(5) Å, 142°) in the structure of **2**, as shown in figure 3(c).

3.2. *Powder XRD analysis*

PXRD patterns of **1** and **2** are provided in the "Supplementary material" section. Comparative experimental and simulated patterns correspond well, indicating a high level of purity of the compounds. There was difference in reflection intensities between the simulated and experimental patterns because of the variation in preferred orientation of the powder samples during the collection of the experimental data.

3.3. *Thermal analysis*

To estimate the thermal stability of these crystalline materials, TGA experiments were carried out. As shown in the "Supplementary material" section, **1** and **2** have similar TGA curves. There are no lattice and coordination waters in **1** and **2** and, thus, decomposition of the organic components occurs at 300 °C for **1** and 250 °C for **2**. For **1**, the total weight loss of 89.93% (Calcd 91.01%) from 300 to 700 °C corresponds to the loss of organic



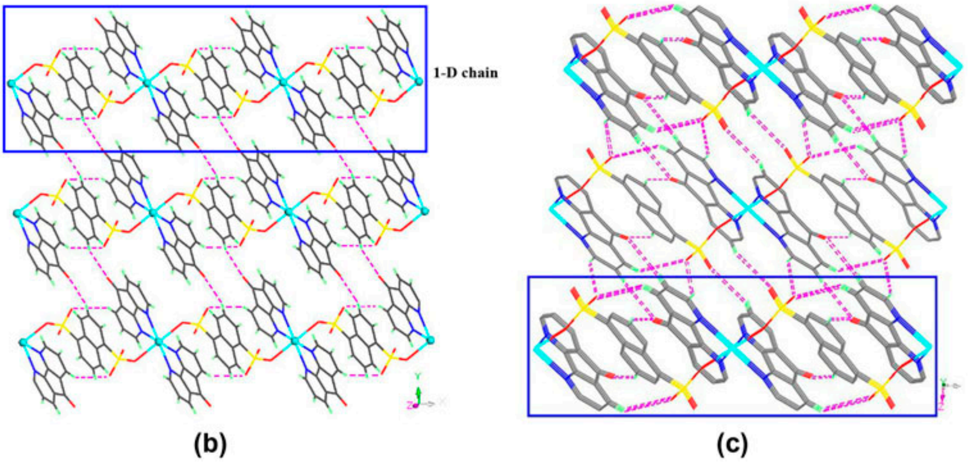


Figure 3. (a) 1-D ladderlike chain in **2** along the *a* direction (hydrogen bonds: pink; π–π interactions: black), (b) 2-D hydrogen-bonded layer of **2** parallel to the *ab* plane (hydrogen bonds: pink), (c) 3-D hydrogen-bonded supramolecular framework of **2** (hydrogen bonds: pink) (see http://dx.doi.org/10.1080/00958972.2013.813938 for color version).

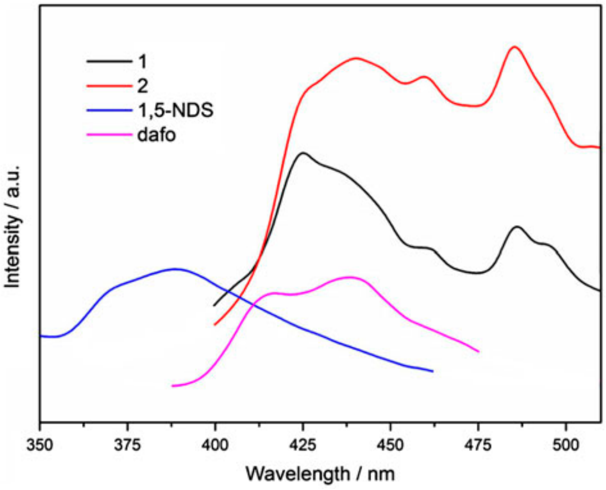


Figure 4. Solid-state emission spectra of **1** and **2**.

ligands. The final residue of **1** corresponds to CuO. For **2**, the observed weight loss from 250 to 425 °C is 24.53% (Calcd 23.85%), which is attributed to the release of one dafo. Then, the weight loss corresponding to release of one 1,5-NDS and one dafo is observed from 425 to 900 °C (exp 61.49%, Calcd 61.33%). The total weight loss of **2** is 86.02% (Calcd 85.18%). The final residue of **2** corresponds to CdO.

3.4. *Photoluminescence properties*

Photoluminescence properties of **1** and **2** were measured in the solid state at room temperature. Free 1,5-NDS displays an emission at 388 nm with a shoulder at 370 nm ($\lambda_{ex} = 320$ nm), and the free dafo exhibits two emission bands at 417 and 439 nm ($\lambda_{ex} = 357$ nm). As shown in figure 4, emission bands are located at 426 nm with shoulders at 441, 461, 487, and 496 nm for **1** ($\lambda_{ex} = 280$ nm), while located at 441 nm with shoulders at 427, 459, 486 nm (a shoulder peak at 495 nm) for **2** ($\lambda_{ex} = 270$ nm). **1** and **2** have similar solid-state emission spectra except that the emission bands of **1** are weaker. The different relative intensities of **1** and **2** may be due to the differences from the metal ions and inter/intramolecular interactions between segments of ligands [38–40]. Compared to free ligands, the emission bands at 426–461 nm of **1** and **2** may be attributed to the combined interaction of intraligand emission from the 1,5-NDS ligand and dafo. Emissions at 486–496 nm of both compounds may originate from the combined interaction of intraligand emission from 1,5-NDS and ligand-to-metal-charge-transfer transitions [41, 42]. The red shift in **1** and **2** may be caused by organic ligand changing its highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels after coordination to metal [43].

4. Conclusion

Two 3-D supramolecular architectures of 1,5-NDS with dafo as co-ligand have been synthesized under hydrothermal conditions. Previous reports show zero-dimensional structures in other transition metal sulfonate compounds containing phen [13, 16, 22, 44–46].

In these compounds, sulfonates are either uncoordinated or coordinated monodentate with M(II). The reported compounds are 1-D chains, in which sulfonates are monodentate bridging. The 1-D coordinated chains of both **1** and **2** form 3-D supramolecular frameworks through hydrogen bonds and π–π interactions. Both compounds display good fluorescence at room temperature. Further syntheses, crystal structures, and properties of metal compounds with arenedisulfonates are also underway in our laboratory.

Supplementary material

CCDC Nos. 872876 and 862902 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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