Research paper

Diverse stacked and entangled topologies in cadmium tricarballylate coordination polymers with nitrobenzene detection capability

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Hydrothermal reaction of cadmium salts, tricarballylic acid (H_3tca) and dipyridyl ligands resulted in generation of four coordination polymers that were characterized by single-crystal X-ray diffraction. The nature of the ancillary dipyridyl ligand plays a primary role in enforcing differing structural topologies across the series of new phases. $[Cd_2(tcaH)_2(dpe)_2]_n$ (**1**, dpe = 1,2-di(4-pyridyl)ethane) displays a 2-fold interpenetrated 3D $4^{12}6^3$ **pcu** net based on 6-connected $\{Cd_2(O)(OCO)\}$ cluster nodes. $[Cd(tcaH)(dpp)(H_2O)]_n$ (**2**, dpp = 1,2-di(4-pyridyl)propane) manifests a 1D + 1D → 3D interlocked system of loop-containing perpendicular ribbon motifs. $\{[Cd_4(tca)_2(Htca)(bpmp)_5(H_2O)_2]\cdot27H_2O\}_n$ (**3**, bpmp = bis(4-pyridylmethyl)piperazine) has intersecting $[Cd_4(tca)_2(Htca)(H_2O)_2]_n$ layer, $[Cd(bpmp)(H_2O)]_n$ chain, and $[Cd_2(bpmp)_3]_n$ ladder submotifs and forms a complicated 3,4,5-connected trinodal 3D self-penetrated network with $(6.9^2)(4^26^38)(4^26^38.9^310)$ topology. $\{[Cd(tcaH)(Hbpmp)](ClO_4)\cdot5.5H_2O\}_n$ (**4**) exhibits stacked cationic bilayer (4,4) grid slabs. All compounds showed potential as potential detectors for nitrobenzene in ethanol suspension via luminescence quenching, with **1** showing the highest uptake of analyte.

1. Introduction

Crystalline coordination polymers remain an important research focus, as due to their significant capabilities in gas storage [1], shape-selective separations [2], ion exchange [3], catalysis [4], and detection of nitroaromatic explosives traces [5]. Additional impetus for exploratory synthesis in this subgenre of chemistry is offered by the aesthetic beauty of their molecular networks [6], including interpenetrated [7] or self-penetrated topologies [8]. One of the most efficacious anionic ligand choices for the construction of functional coordination polymers is 1,3,5-benzenetricarboxylate (btc), which has afforded the classic and well-studied absorbent metal-organic framework material $[Cu_3(btc)_2]_n$ [9]. Inclusion of dipyridyl-type coligands and use of different metal atoms has expanded the structural scope and utility of this class of materials [10–13], such as extensive gas absorption and bright luminescence in a zinc 1,3,5-benzenetraicarboxylate coordination polymer incorporating a dipyridyl derivatized BODIPY-type ligand [10].

Less commonly employed have been aliphatic tricarboxylate ligands, which can induce greater degrees of conformational freedom due to their flexible C—C σ bonds. A series of 2D and 3D gadolinium and europium coordination polymers based on the methanetriacetate ligand has been reported by Ruiz-Pérez and coworkers [14,15]. The tricarballylate ligand (1,2,3-propanetricarboxylate, tca) has been found to regulate the biomineralization of calcite [16] and can also act as a carbon source for the growth of the fungus *Exophiala spinifera* [17]. Although the use of tricarballylate in the generation of coordination polymers has been infrequent, its derivatives can show extremely intriguing interlocked and self-penetrated topologies due to its conformational flexibility and multifarious possible binding and bridging modes [17–22]. $\{[Zn_3(tca)_2(bpmp)(Hbpmp)_2](ClO_4)_2\cdot5H_2O\}_n$ (bpmp = bis(4-pyridylmethyl)piperazine) possessed a unique self-penetrated 2-D layered topology with threaded-loop type linkages, while the oxoanion-free phase $\{[Zn_3(H_2O)_4(tca)_2(bpmp)_2]\cdot8H_2O\}_n$ manifested a three-fold interpenetrated $(6^3)(6^58)$ 3,4-connected 3-D binodal network [18]. $\{[Cd_2(tca)_2(Hdpa)_2]\cdot7H_2O\}_n$ (dpa = 4,4′-dipyridylamine) exhibited 1-D ribbon motifs with pendant $Hdpa^+$ ligands. $\{[Zn_3(tca)_2(dpa)_2]\cdot2H_2O\}_n$ displayed a new 4,4-connected binodal $(4^26^28^2)_4(6^28^4)$ topology, while the copper derivative $[Cu(Htca)(dpa)]_n$ manifested a 3,5-connected binodal net with rare $(4.6^2)(4.6^68^3)$ topology [19]. To the best of our knowledge, no tricarballylate-containing coordination polymers have as yet been prepared using the simple dipyridyl linkers 1,2-di(4-pyridyl)ethane (dpe) and 1,3-di(4-pyridyl)propane (dpp).

Table 1
Crystal and Structure Refinement Data for **1–4**.

Data	1	2
Empirical Formula	$C_{36}H_{36}Cd_2N_4O_{12}$	$C_{19}H_{22}CdN_2O_7$
Formula Weight	941.49	502.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	13.9255(10)	18.8260(14)
b (Å)	12.7541(9)	14.6412(11)
c (Å)	20.0983(14)	15.4657(11)
β(°)	96.4030(10)	112.5690(10)
V (Å^3)	3547.3(4)	3936.4(5)
Z	4	8
D_{calc} (g cm^{-3})	1.763	1.697
μ(mm^{-1})	1.270	1.154
Min./max. trans.	0.8170	0.8968
hkl ranges	$-16 \leq h \leq 16$	$-10 \leq h \leq 10$
	$-13 \leq k \leq 15$	$-15 \leq k \leq 15$
	$-24 \leq l \leq 24$	$-16 \leq l \leq 16$
Total reflections	21,732	33,712
Unique reflections	6541	4830
R(int)	0.0288	0.0454
Parameters	493	271
R_1 (all data)	0.0298	0.0369
R_1 ($I > 2\sigma$ (I))	0.0241	0.0257
wR_2 (all data)	0.0598	0.0588
wR_2 ($I > 2\sigma$ (I))	0.0568	0.0544
Max/min residual (e$^-$/Å^3)	0.496/$-$0.412	0.472/$-$0.303
G.O.F.	1.027	1.041

Data	3	4
Empirical Formula	$C_{98}H_{174}Cd_4N_{20}O_{47}$	$C_{22}H_{38}CdClN_4O_{16}$
Formula Weight	2834.18	762.41
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	12.3556(10)	17.1148(13)
b (Å)	12.0599(10)	20.5960(16)
c (Å)	40.705(3)	8.7252(7)
β(°)	90.5390(10)	98.8400(10)
V (Å^3)	6065.1(9)	3039.1(4)
Z	2	4
D_{calc} (g cm^{-3})	1.551	1.666
μ(mm^{-1})	0.787	0.886
Min./max. trans.	0.8846	0.6920
hkl ranges	$-14 \leq h \leq 14$	$-20 \leq h \leq 20$
	$0 \leq k \leq 14$	$-24 \leq k \leq 24$
	$0 \leq l \leq 49$	$-10 \leq l \leq 10$
Total reflections	137,985	24,378
Unique reflections	11,266	5540
R(int)	0.0702	0.0360
Parameters	974	435
R_1 (all data)	0.0640	0.0612
R_1 ($I > 2\sigma$ (I))	0.0531	0.0538
wR_2 (all data)	0.1264	0.1613
wR_2 ($I > 2\sigma(I)$)	0.1217	0.1530
Max/min residual (e$^-$/Å^3)	1.600/$-$1.245	1.871/$-$2.140
G.O.F.	1.098	1.071

Table 2
Selected Bond distance (Å) and angle (°) data for **1**.

Cd1–O7	2.2337(16)	N2$^{\#2}$–Cd1–O1	85.41(7)
Cd1–O12$^{\#1}$	2.2810(16)	N1–Cd1–O1	97.83(7)
Cd1–N2$^{\#2}$	2.3029(19)	O2–Cd1–O1	54.96(6)
Cd1–N1	2.3085(19)	O8–Cd2–N4$^{\#2}$	88.34(7)
Cd1–O2	2.3451(18)	O8–Cd2–N3	88.39(7)
Cd1–O1	2.4310(18)	N4$^{\#2}$–Cd2–N3	176.32(7)
Cd2–O8	2.3262(17)	O8–Cd2–O3$^{\#3}$	85.49(6)
Cd2–N4$^{\#2}$	2.330(2)	N4$^{\#2}$–Cd2–O3$^{\#3}$	95.54(7)
Cd2–N3	2.3367(19)	N3–Cd2–O3$^{\#3}$	85.87(7)
Cd2–O3$^{\#3}$	2.3439(18)	O8–Cd2–O11$^{\#1}$	137.87(7)
Cd2–O11$^{\#1}$	2.3554(16)	N4$^{\#2}$–Cd2–O11$^{\#1}$	89.49(7)
Cd2–O4$^{\#3}$	2.5023(18)	N3–Cd2–O11$^{\#1}$	91.81(6)
Cd2–O12$^{\#1}$	2.5746(18)	O3$^{\#3}$–Cd2–O11$^{\#1}$	136.56(6)
O7–Cd1–O12$^{\#1}$	111.03(6)	O8–Cd2–O4$^{\#3}$	138.01(6)
O7–Cd1–N2$^{\#2}$	95.41(7)	N4$^{\#2}$–Cd2–O4$^{\#3}$	85.40(7)
O12–Cd1–N2$^{\#2}$	85.19(7)	N3–Cd2–O4$^{\#3}$	98.17(7)
O7–Cd1–N1	86.71(7)	O3$^{\#3}$–Cd2–O4$^{\#3}$	54.03(6)
O12$^{\#1}$–Cd1–N1	90.91(7)	O11$^{\#1}$–Cd2–O4$^{\#3}$	83.61(6)
N2$^{\#2}$–Cd1–N1	176.02(7)	O8–Cd2–O12$^{\#1}$	86.18(6)
O7–Cd1–O2	146.16(6)	N4$^{\#2}$–Cd2–O12$^{\#1}$	98.45(6)
O12$^{\#1}$–Cd1–O2	102.01(6)	N3–Cd2–O12$^{\#1}$	79.65(6)
N2$^{\#2}$–Cd1–O2	94.39(7)	O3$^{\#3}$–Cd2–O12$^{\#1}$	163.47(6)
N1–Cd1–O2	85.64(7)	O11$^{\#1}$–Cd2–O12$^{\#1}$	52.62(5)
O7–Cd1–O1	93.70(6)	O4$^{\#3}$–Cd2–O12$^{\#1}$	135.81(5)
O12$^{\#1}$–Cd1–O1	154.24(6)		

Symmetry transformation to generate equivalent atoms: #1 x, $-y + 3/2$, $z - 1/2$; #2 $x + 1$, y, z; #3 x, $y + 1$, z.

2. Experimental section

2.1. General considerations

Cadmium salts, tricarballylic acid, dpe, and dpp were purchased commercially. Bis(4-pyridylmethyl)piperazine was prepared using a published procedure [23]. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. The luminescence spectra were obtained with a Hitachi F-4500 Fluorescence Spectrometer. *CAUTION! Perchlorate compounds can be explosive! While no issues arose during this study, minimum quantities were used and no perchlorate-containing solids were heated above their synthesis temperature.*

2.2. Preparation of $[Cd_2(tcaH)_2(dpe)_2]_n$ (1)

CdSO$_4$·8H$_2$O (63 mg, 0.18 mmol), dpe (68 mg, 0.37 mmol) and tricarballylic acid (33 mg, 0.19 mmol) were placed into 5 mL distilled H$_2$O in a 15 mL screw-cap glass vial. The vial was sealed and heated in an oil bath at 80 °C for 72 hrs, whereupon it was cooled slowly to 25 °C. Colorless blocks of **1** (66 mg, 78% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for C$_{36}$H$_{36}$Cd$_2$N$_4$O$_{12}$ **1**: C, 45.92; H, 3.85; N, 5.95% Found: C, 45.77; H, 3.73; N, 5.89%. IR ($\bar{\nu}$): 3251 (w, br), 1702 (m), 1612 (m), 1579 (s), 1426 (w), 1397 (s), 1312 (w), 1258 (w), 1226 (w), 1098 (w), 1018 (w), 832 (m), 808 (w), 722 (w), 675 (w) cm^{-1}.

2.3. Preparation of $[Cd(tcaH)(dpp)(H_2O)]_n$ (2)

Cd(ClO$_4$)$_2$·6H$_2$O (56 mg, 0.18 mmol), dpp (73 mg, 0.37 mmol) and tricarballylic acid (33 mg, 0.19 mmol) were placed into 5 mL distilled H$_2$O in a 15 mL screw-cap glass vial. The vial was sealed and heated in an oil bath at 80 °C for 72 hrs, whereupon it was cooled slowly to 25 °C. Colorless blocks of **2** (82 mg, 91% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for C$_{19}$H$_{22}$CdN$_2$O$_7$ **2**: C, 45.39; H, 4.41; N, 5.57% Found: C, 45.31; H, 4.36; N, 5.92%. IR ($\bar{\nu}$): 3298 (w, br), 2926 (w), 2500 (w, br), 1717 (s), 1610 (m), 1577 (s), 1560 (s), 1542 (w), 1503 (w), 1450 (m), 1417 (s) 1359 (s), 1314 (m), 1278 (m), 1224 (m), 1193 (s), 1172 (m), 1097 (w),

The zinc and cadmium tricarballylate coordination polymers in these previous studies all exhibited fluorescent behavior upon irradiation with ultraviolet light, due to π–π* transitions within the aromatic dipyridyl coligands, but were not assayed as detectors or sensors. Nevertheless, the visible light spectral window of this class of material could prove beneficial for the detection of nitroaromatics via luminescence quenching. In this contribution we present the synthesis, single-crystal structural determination, and nitrobenzene detection assays for four new cadmium-based coordination polymers containing the tricarballylate ligand: [Cd$_2$(tcaH)$_2$(dpe)$_2$]$_n$ (**1**), [Cd(tcaH)(dpp)(H$_2$O)]$_n$ (**2**), {[Cd$_4$(tca)$_2$(Htca)(bpmp)$_5$(H$_2$O)$_2$]·27H$_2$O}$_n$ (**3**), and {[Cd(tcaH)(Hbpmp)](ClO$_4$)·5.5H$_2$O}$_n$ (**4**). Thermal properties of the non-perchlorate containing materials are also discussed herein.