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Research paper

Nitrobenzene-detection cadmium thiophenedicarboxylate coordination polymers with flexible dipyridylamide ligands and diverse topologies

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ARTICLE INFO	A B S T R A C T
Keywords: Coordination polymer X-ray diffraction Self-penetration Cadmium Nitrobenzene detection	Hydrothermal reaction of cadmium nitrate, 2,5-thiophenedicarboxylic acid (H ₂ tdc) and one of the con- formationally flexible dipyridylamide ligands <i>N</i> , <i>N</i> '-(heptane-1,7-diyl)dinicotinamide (hdn), <i>N</i> , <i>N</i> '-(hexane-1,6- diyl)diisonicotinamide (hdin), <i>N</i> , <i>N</i> '-(hexane-1,6-diyl)dinicotinamide (hdn), <i>N</i> , <i>N</i> '-(propane-1,3-diyl)dinicotina- mide (pdn), <i>N</i> , <i>N</i> '-(propane-1,3-diyl)diisonicotinamide (pdin) produced five new coordination polymers which were structurally characterized by single-crystal X-ray diffraction. {[Cd(tdc)(hedn)(H ₂ O)]·3H ₂ O} _{<i>n</i>} (1) manifests looped (4,4) grid motifs with two-fold parallel interpenetration. {[Cd(tdc)(hdin)(H ₂ O)]·H ₂ O} _{<i>n</i>} (2) shows stacked (4,4) grid motifs. {[Cd ₂ (tdc) ₂ (hdn)(H ₂ O) ₄]·H ₂ O} _{<i>n</i>} (3) exhibits herringbone (6,3) grid motifs. In contrast to the 2D topologies seen in 1–3, {[Cd ₂ (tdc) ₂ (pdn)(H ₂ O) ₂]·4H ₂ O} _{<i>n</i>} (4) displays a 3D self-penetrated net with 6 ⁴ 8 ² nbo topology and [Cd(tdc)(pdin)] _{<i>n</i>} (5) shows a 1D ribbon structure constructed from staple-conformation pdin li- grands and (Cd O) dimer containing [Cd(tdc)]

properties of these five new materials are discussed.

1. Introduction

Basic research efforts towards the design, preparation, and structural characterization of crystalline coordination polymers have continued over the past two decades, remaining a focus of coordination chemists worldwide. Coordination polymers manifest diverse applications in hydrogen storage [1], selective separations [2], drug delivery [3], heterogeneous catalysis [4], non-linear optics [5], and more recently, in trace detection of nitroaromatic explosive compounds [6]. The near infinite combination of divalent metal ions, anionic dicarboxylate ligands, and ancillary neutral dipyridyl ligands as precursor mixtures provides a limitless ability for exploratory synthesis. Coordination polymers remain under intense study not only due to their efficacious properties, but also because of the striking aesthetics of their underlying molecular structures and topologies [7].

A common choice for the construction of coordination polymers is the isophthalate (ip, 1,3-benzenedicarboxylate) ligand. Its rigid structure and multiple possible carboxylate binding modes can afford coordination polymers with a plethora of diverse topologies, especially used in tandem with an ancillary dipyridyl ligand. Guo and coworkers reported the (4,4) grid structure and strong fluorescence of [Zn(ip) (bpy)(H₂O)]·1.5H₂O₃ [8], using the rigid rod bpy (4,4'-bipyridine) ligand, which has been called "the C–C bond of crystal engineering" due to its common and efficacious utility [9]. Two coordination polymers with formulation $\{[Zn(ip)(bpe)]$ -solvent $\}_n$ were obtained by employing more flexible ligand 1,2-bis(4-pyridyl)ethane (bpe), depending on the solvent system used during self-assembly [9]. One isomer had a standard (4,4) grid topology, while the other displayed a rare non-diamondoid 6^{58} **dmp** 4-connected net [10]. $\{[Zn(ip)(bpmp)] \cdot H_2O\}_n$ (bpmp = bis(4-pyridylmethyl)piperazine presented a five-fold interpenetrated 6^6 **dia** diamondoid topology [11]. Therefore it can be seen that employing progressively longer and more flexible dipyridyl-type ligands can provide access to wide structural diversity in a similar system of coordination polymers.

The aromatic ligand 2,5-thiophenedicarboxylate (tdc, Scheme 1) is similar to isophthalate, but the five-membered thiophene ring orients the carboxylate groups ~144° apart, as opposed to the 120° disposition of the *meta* carboxylate groups in isophthalate. Because of this significant difference in the angle between the carboxylate groups, dual ligand coordination polymers containing fdc or tdc ligands can present widely different structures from their isophthalate analogs. For example, $[Co(ip)(bpy)]_n$ shows a decorated (4,4) grid structure via bpy pillaring of $[Co(ip)]_n$ dimer-based chains [12]. Instead, $[Co(tdc)(bpy)]_n$ manifests a two-fold interpenetrated $4^{12}6^3$ **pcu** net built from pillaring of 2-D $[Co(tdc)]_n$ layer motifs [13]. In some other cases, the ip and tdc coordination polymer analogs possessed the same structural topology.

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Scheme 1. Ligands used in this study.

For instance, {[Cu(ip)(dpa)]- $0.5H_2O$ }_n (dpa = 4,4'-dipyridylamine) and [Cu(tdc)(dpa)]_n both show {Cu₂(OCO)₂} dimer-based copper dicarboxylate chains linked into non-interpenetrated 4-connected 6⁵8 **cds** nets [14]. On account of these precedents, it is not possible to predict in advance whether ip- or tdc-containing coordination polymers will manifest different structural topologies, even if the divalent metal ions and dipyridyl coligands are the same.

Recently we reported some intriguing topologies in coordination polymers containing the tdc ligand and conformationally flexible dipyridylamide ligands. { $[Cd(tdc)(bpfp)(H_2O)] \cdot 2H_2O_n$ (bpfp = bis(4pyridylformyl)piperazine) exhibits (4,4) sawtooth coordination polymer layer motifs that engage in relatively uncommon $2D + 2D \rightarrow$ 3D parallel interpenetration [15a]. Use of the related bis(4-pyridylformyl)homopiperazine ligands (bpfh) shows different layer topologies and chirality among a series of three coordination polymers [15b]. {[Cd(tdc)(bpfh)(H₂O)]·3H₂O}_n (1) shows a two-fold parallel interpenetrated centrosymmetric (4,4) layered grid structure. {[Zn(tdc) (bpfh)]·H₂O}_n exhibits a similar system of two-fold interpenetrated (4,4) grid-like layers, but in contrast to the cadmium derivative, it crystallizes acentric group. in an space $\{[Ni_2(tdc)_2(bpfh)_2(H_2O)] \cdot 2H_2O\}_n$ possesses antiferromagnetically coupled {Ni2(µ-H2O)(OCO)2} dimeric units connected into a doubled layer motif by the full span of the tdc and bpfh ligands. [Co(tdc)(4-ppbp) (4-ppbp = propane-1,3-diylbis(piperidine-4,1-diyl))bis(pyr- $(H_2O)]_n$ idin-4-ylmethanone) shows a 1-D tubular structure that engages in very rare $1D + 1D \rightarrow 2D$ parallel interpenetration, while [Ni(tdc)(4ppbp)₂(H₂O)]_n possesses a unique looped system of $2D + 2D \rightarrow 2D$ interpenetrated layers, derived from an edge-crossed (4,4) net [16].

We therefore endeavored to undertake exploratory synthetic experiments towards the preparation of nitrobenzene-detecting cadmium tdc coordination polymers containing the long-spanning dipyridylamide ligands *N*,*N*'-(heptane-1,7-diyl)dinicotinamide (hedn. Scheme 1), N,N'-(hexane-1,6-divl)diisonicotinamide (hdin, Scheme 1), N,N'-(hexane-1,6-diyl)dinicotinamide (hdn, Scheme 1), N,N'-(propane-1,3-diyl)dinicotinamide (pdn, Scheme 1), N,N'-(propane-1,3-diyl)diisonicotinamide (pdin, Scheme 1). By varying the aliphatic tether length and the geometric disposition of the terminal pyridyl nitrogen atom within the dipyridylamide component, we hoped to uncover a system with diverse topologies. In this contribution we report the synthesis, single crystal structures, topological features, thermal properties, and nitrobenzene detection properties of five new cadmium 2,5-thiophenedicarboxylate coordination polymer solids: {[Cd(tdc)(hedn) (H_2O)]·3H₂O}_n (1), {[Cd(tdc)(hdin)(H₂O)]·H₂O}_n (2), {[Cd₂(tdc)₂(hdn) $(H_2O)_4] \cdot H_2O_n$ (3) { $[Cd_2(tdc)_2(pdn)(H_2O)_2] \cdot 4H_2O_n$ (4), and [Cd(tdc)(pdin)]_n (5).

2. Experimental section

2.1. General considerations

Cadmium nitrate and 2,5-thiophenedicarboxylic acid were purchased commercially. The hedn ligand was prepared via condensation of two molar equivalents of nicotinoyl chloride hydrochloride and one

molar equivalent of 1,7-diaminoheptane in dry pyridine solvent, followed by quenching with water, basicification with NaOH, extraction with methylene chloride, drying over sodium sulfate, and removal of solvent in vacuo [17]. The hdin ligand was prepared similarly via condensation of two molar equivalents of isonicotinoyl chloride hydrochloride and one molar equivalent of 1,6-diaminohexane. The hdn ligand was prepared via condensation of two molar equivalents of nicotinoyl chloride hydrochloride and one molar equivalent of 1,6-diaminohexane. The pdn ligand was prepared via condensation of two molar equivalents of nicotinoyl chloride hydrochloride and one molar equivalent of 1,3-diaminopropane. The pdin ligand was prepared via condensation of two molar equivalents of isonicotinovl chloride hydrochloride and one molar equivalent of 1.3-diaminopropane. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. Thermogravimetric analysis was performed under flowing N2 on a TA Instruments TGA Q50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. The luminescence spectra were obtained with a Hitachi F-4500 Fluorescence Spectrometer.

2.2. Preparation of $\{ [Cd(tdc)(hedn)(H_2O)] \cdot 3H_2O \}_n$ (1)

Cd(NO₃)₂·4H₂O (113 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (63 mg, 0.37 mmol) and hedn (124 mg, 0.37 mmol) and 0.75 mL of a 1.0 *M* NaOH solution were placed into 10 mL distilled H₂O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2 d, and then cooled slowly to 25 °C. Colorless crystals of **1** (170 mg, 65% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{25}H_{34}CdN_4O_{10}S$ **1**: C, 43.20; H, 4.93; N, 8.06% Found: C, 42.68; H, 5.03; N, 7.84%. IR (cm⁻¹): 3230 (w), 2938 (w), 1638 (m), 1600 (w), 1542 (s), 1525 (s), 1476 (m), 1427 (w), 1374 (s), 1330 (m), 1315 (s), 1291 (m), 1198 (w), 1163 (w), 1137 (w), 1054 (w), 1033 (w), 941 (w), 828 (m), 820 (m), 775 (s), 695 (s).

2.3. Preparation of $\{[Cd(tdc)(hdin)(H_2O)] \cdot H_2O\}_n$ (2)

Cd(NO₃)₂·4H₂O (113 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (63 mg, 0.37 mmol) and hdin (119 mg, 0.37 mmol) and 0.75 mL of a 1.0 *M* NaOH solution were placed into 10 mL distilled H₂O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2 d, and then cooled slowly to 25 °C. Colorless crystals of **2** (170 mg, 71% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for C₂₄H₂₈CdN₄O₈S **2**: C, 44.69; H, 4.38; N, 8.69% Found: C, 44.33; H, 4.55; N, 8.56%. IR (cm⁻¹): 3000(w), 1654 (m), 1553 (s), 1527 (s), 1469 (w), 1418 (w), 1360 (s), 1308 (s), 1226 (w), 1181 (w), 1066 (w), 1020 (w), 852 (s), 810 (s), 770 (s), 674 (s).

2.4. Preparation of $\{ [Cd_2(tdc)_2(hdn)(H_2O)_4] \cdot H_2O \}_n$ (3)

Cd(NO₃)₂4H₂O (113 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (63 mg, 0.37 mmol) and hdn (119 mg, 0.37 mmol) and 0.75 mL of a 1.0 *M* NaOH solution were placed into 10 mL distilled H₂O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2 d, and then cooled slowly to 25 °C. Colorless crystals of **3** (155 mg, 85% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{30}H_{36}Cd_2N_4O_{15}S_2$ **3**: C, 36.71; H, 3.70; N, 5.71% Found: C, 36.48; H, 3.89; N, 5.65%. IR (cm⁻¹): 3221 (w), 1645 (m), 1542 (s), 1524 (s), 1422 (w), 1373 (s), 1314 (m), 1199 (w), 1032 (w), 822 (m), 766 (s), 699 (s).

2.5. Preparation of $\{ [Cd_2(tdc)_2(pdn)(H_2O)_2] \cdot 4H_2O \}_n$ (4)

 $Cd(NO_3)_2$ '4H₂O (113 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (63 mg, 0.37 mmol) and pdn (104 mg, 0.37 mmol) and 0.75 mL of

Table 1

Crystal and Structure Refinement Data for 1-5.

Data	1	2	3	4	5
Empirical Formula Formula Weight Crystal system Space group	$C_{25}H_{34}CdN_4O_{10}S$ 708.27 Monoclinic $P2_{1/c}$	C ₂₄ H ₂₈ CdN ₄ O ₈ S 644.96 Monoclinic <i>P</i> 2./ <i>n</i>	C ₃₀ H ₃₆ Cd ₂ N ₄ O ₁₅ S ₂ 981.55 Monoclinic C2/c	C ₂₇ H ₃₂ Cd ₂ N ₄ O ₁₆ S ₂ 957.48 Monoclinic P2 ₁ /c	C ₂₁ H ₁₈ CdN ₄ O ₆ S 566.85 Triclinic
$a (\hat{A})$ $b (\hat{A})$ $c (\hat{A})$ $a (^{\circ})$ $\beta (^{\circ})$ $\gamma (^{\circ})$ $V (\hat{A} ^{3})$ Z $D_{calc} (g cm^{-3})$ $\mu (mm^{-1})$ Min./max. trans. $hkl ranges$	9.1418(15) 19.601(3) 16.160(3) 90 94.114(2) 90 2888.3(8) 4 1.598 0.890 0.8968 $-10 \le h \le 11,$ $-23 \le k \le 23,$	$10.2461(7)$ $17.8182(11)$ $14.6857(9)$ 90 $101.213(1)$ 90 $2629.9(3)$ 4 1.629 0.965 0.8900 $-12 \le h \le 32,$ $-12 \le k \le 25,$	14.632(2) 13.025(2) 19.761(3) 90 99.580(4) 90 3713.6(10) 4 1.756 1.331 0.9147 $-17 \le h \le 17,$ $-15 \le k \le 15,$	$13.9650(14)$ $12.5870(13)$ $20.273(2)$ 90 $109.178(2)$ 90 $3365.7(6)$ 4 1.890 1.468 0.8685 $-16 \le h \le 16,$ $-15 \le k \le 15,$	P1 9.4291(14) 10.5051(16) 12.452(2) 102.834(5) 98.727(5) 105.691(4) 1128.0(3) 2 1.669 1.106 0.8853 $-11 \le h \le 11,$ $-12 \le k \le 12,$
Total reflections Unique reflections R(int) Parameters R_1 (all data) R_1 ($I > 2\sigma$ (I)) wR_2 (all data) wR_2 ($I > 2\sigma$ (I)) Max/min residual ($e^-/Å^3$) G.O.F.	$-19 \le l \le 19$ 17,728 5289 0.0388 386 0.0419 0.0345 0.0905 0.0846 0.947/-0.529 1.054	$-21 \le l \le 21$ 21,979 5019 0.0455 347 0.0482 0.0379 0.0978 0.0898 1.554/-0.488 1.052	$-23 \le l \le 23$ 14983 3406 0.0605 245 0.0497 0.0338 0.0665 0.0617 1.148/-0.480 0.908	$-23 \le l \le 24$ 23502 6171 0.0313 474 0.0384 0.0328 0.0908 0.0852 1.541/-0.704 1.065	$-15 \le l \le 15$ 14759 4143 0.0327 298 0.0370 0.0325 0.0811 0.0777 1.388/-0.489 1.101

a 1.0 *M* NaOH solution were placed into 10 mL distilled H₂O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2 d, and then cooled slowly to 25 °C. Colorless crystals of 4 (123 mg, 69% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{27}H_{32}Cd_2N_4O_{16}S_2$ 4: C, 33.87; H, 3.37; N, 5.85% Found: C, 33.45; H, 3.51; N, 5.69%. IR (cm⁻¹): 3200 (w, br) 1625 (m), 1544 (s), 1374 (s), 1319 (m), 1200 (w), 1032 (w), 831 (m), 767 (s), 730 (m), 697 (s).

2.6. Preparation of $[Cd(tdc)(pdin)]_n$ (5)

Cd(NO₃)₂·4H₂O (113 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (63 mg, 0.37 mmol) and pdin (104 mg, 0.37 mmol) and 0.75 mL of a 1.0 *M* NaOH solution were placed into 10 mL distilled H₂O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2 d, and then cooled slowly to 25 °C. Colorless crystals of **5** (113 mg, 54% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{21}H_{18}CdN_4O_6S$ **5**: C, 44.49; H, 3.20; N, 9.88% Found: C, 44.78; H, 3.20; N, 9.12%. IR (cm⁻¹): 3296 (w), 3072 (w), 1676 (w), 1643 (m), 1550 (s), 1521 (s), 1452 (w), 1437 (w), 1421 (w), 1371 (s), 1315 (s), 1226 (m), 1124 (w), 1069 (m), 1049 (w), 1019 (m), 968 (w), 856 (m), 820 (m), 810 (m), 780 (s), 759 (s), 681 (s), 666 (s).

2.7. Nitrobenzene detection studies

Suspensions of 10 mg finely ground samples of coordination polymers 1–5 were made in 10 mL ethanol in volumetric flasks, with immersion in an ultrasonic bath for 60 s to ensure an even dispersion. The fluorescence spectra of 1–5 in suspension were recorded with an excitation wavelength selected to optimize emission at 400 nm. Aliquots of a stock solution of nitrobenzene and *m*-nitrophenol $(1 \times 10^{-4} M)$ in dimethyl sulfoxide were added sequentially to the ethanol suspensions of 1–5 in quartz cuvettes with sonication for 30 s after each addition. The emission spectra were then measured after each aliquot of analyte solution.

3. X-ray crystallography

Single crystal X-ray diffraction on crystals of 1–5 was performed using a Bruker-AXS ApexII CCD instrument at 173 K. Reflection data were acquired using graphite–monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data was integrated via SAINT [18]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [19]. The structures were solved using direct methods and refined on F^2 using SHELXTL [20] within the OLEX2 crystallographic software suite [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. Relevant crystallographic data for 1–5 are listed in Table 1.

4. Results and discussion

4.1. Synthesis and spectral characterization

Compounds 1-5 were prepared by hydrothermal reaction of cadmium nitrate, 2,5-thiophenedicarboxylic acid acid, and the requisite dipyridylamide ligand. Their infrared spectra were consistent with structural components determined by single-crystal X-ray diffraction. Intense, slightly broadened asymmetric and symmetric carboxylate C-O stretching bands for the dicarboxylate ligands were observed at 1542 and 1374 cm^{-1} for 1, 1553 and 1360 cm^{-1} for 2, 1542 and 1374 cm^{-1} for **3**, 1544 and 1374 cm⁻¹ for **4**, and 1550 and 1371 cm⁻¹ for 5. Sharp and medium intensity bands in the range of $\,\sim\!1600\,\text{cm}^{-1}$ to $\sim 1300 \text{ cm}^{-1}$ were attributed to stretching mode of the pyridyl rings of the dipyridylamide ligands and the thiophene rings in 1-5. Broad weak spectral bands in the vicinity of $\sim 3000 \text{ cm}^{-1}$ to $\sim 3500 \text{ cm}^{-1}$ indicate the presence of N-H bonds within the pyridylamide ligands in 1-5 and bound and unbound water molecules in 1-4. The C=O stretching band of the carbonyl groups of the dipyridylamide ligands in **1–5** are seen at 1638 cm^{-1} , 1654 cm^{-1} , 1645 cm^{-1} , 1625 cm^{-1} , $1643 \, \mathrm{cm}^{-1}$.



Fig. 1. Coordination environment of 1, with thermal ellipsoids at 50% probability and partial atom numbering scheme. The symmetry codes are as in Table 2.

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

Cd1-O1	2.487(2)	O4 ^{#1} -Cd1-O1	165.89(7)
Cd1-02	2.338(2)	O5-Cd1-O1	86.21(8)
Cd1-03 ^{#1}	2.386(2)	O5-Cd1-O2	140.39(8)
Cd1-O4#1	2.438(2)	O5-Cd1-O3#1	134.07(8)
Cd1-O5	2.310(2)	O5-Cd1-O4#1	80.55(8)
Cd1-N1	2.340(3)	O5-Cd1-N1	90.86(8)
Cd1-N4 ^{#2}	2.334(3)	O5-Cd1-N4#2	83.06(8)
O2-Cd1-O1	54.19(7)	N1-Cd1-O1	92.68(7)
O2-Cd1-O3#1	85.44(8)	N1-Cd1-O3#1	92.28(8)
O2-Cd1-O4#1	138.73(8)	N1-Cd1-O4#1	82.73(8)
O2-Cd1-N1	90.08(8)	N4 ^{#2} -Cd1-O1	84.17(8)
O3 ^{#1} -Cd1-O1	139.30(7)	N4 ^{#2} -Cd1-O2	92.83(8)
O3 ^{#1} -Cd1-O4 ^{#1}	54.53(8)	N4 ^{#2} -Cd1-O3 ^{#1}	93.94(8)
N4 ^{#2} -Cd1-N1	173.32(9)	N4 ^{#2} -Cd1-O4 ^{#1}	98.94(8)

Symmetry transformations: #1 -x, y + 1/2, -z + 3/2; #2 -x + 2, y - 1/2, -z + 3/2.

4.2. Structural description of $\{ [Cd(tdc)(hedn)(H_2O)] \cdot 3H_2O \}_n$ (1)

The asymmetric unit of compound 1 contains a divalent cadmium atom, a tdc ligand, an hedn ligand ligand, an aqua ligand, and three water molecules of crystallization. The coordination environment at cadmium (Fig. 1) is a $\{CdO_5N_2\}$ distorted pentagonal bipyramid, with trans pyridyl nitrogen donor atoms from two hedn ligands in the axial positions. The equatorial plane is comprised of a bound water molecule and chelating carboxylate groups from two tdc ligands. Bond lengths and angles within the coordination environment are listed in Table 2.

Bis(chelating) tdc ligands form $[Cd(tdc)(H_2O)]_n$ chain motifs that are arranged parallel to the *b* crystal direction, with a Cd···Cd internuclear distance of 10.566(2) Å. These are connected into 2D [Cd(tdc)(hedn)(H₂O)]_n coordination polymer (4,4) grid layer motifs by pillaring hedn ligands that span a Cd···Cd internuclear distance measuring 17.372(3) Å. The central seven-carbon aliphatic tethers within the hedn ligands have an *anti-anti-anti* conformation (torsion angles = 169°, 164, 177, 172°). The large apertures within the grid as measured by through-space Cd…Cd distances of 18.3 by 19.6 Å, and the looping hedn ligands allow parallel interpenetration of another [Cd(tdc)(hedn) (H₂O)]_n layer (Fig. 2a). A side view of the 2-fold interpenetration of [Cd (tdc)(hedn)(H₂O)]_n layers is shown in Fig. 2b. Hydrogen bonding patterns (Table S1) mediated by water molecules of crystallization conjoin the N–H moieties within the hedn ligands in one layer to tdc carboxylate oxygen atoms in the other interpenetrating layer. Adjacent layer pairs aggregate by means of hydrogen bonding between bound water molecules of crystallization occupy small pockets comprising 11.9% of the unit cell volume according to PLATON [22].

4.3. Structural description of $\{[Cd(tdc)(hdin)(H_2O)] : H_2O\}_n$ (2)

The asymmetric unit of compound **2** contains a divalent cadmium atom, a tdc ligand, an hdin ligand, a water molecule of crystallization and a water molecule of crystallization. A distorted {CdN₂O₄} octahedral coordination environment is observed at the cadmium atom (Fig. 3), with *trans* pyridyl nitrogen donor atoms from two hdin ligands defining the nominal axial positions. The nominal equatorial plane contains a chelating carboxylate group from a tdc ligand, and a single oxygen donor atom from a second tdc ligand and a bound water molecule in *cis* positions. Bond lengths and angles within the coordination sphere are listed in Table 3.

Chelating/monodentate tdc ligands construct $[Cd(tdc)(H_2O)]_n$ chain motifs that are arranged parallel to the *b* crystal direction, with a Cd···Cd internuclear distance of 10.153(2) Å. The chain motifs are pillared into (4,4) grid $[Cd(tdc)(hdin)(H_2O)]_n$ coordination polymer motifs (Fig. 4) by hdin ligands with a *gauche-anti-gauche* conformation of their central 6-carbon aliphatic tethers (torsion angles = 78°, 170°, 62°). The hdin ligands in **2** span a Cd···Cd internuclear distance of 22.772(3) Å. The Cd···Cd angles of 67.8° and 112.2° within the layer motifs promote a flat rhomboid grid topology. The lack of highly looped dipyridylamide



Fig. 2. Interpenetrated $[Cd(tdc)(hedn)(H_2O)]_n$ 2D (4,4) grid motifs in 1. a) Face view. b) Side view.



Fig. 3. Coordination environment of 2, with thermal ellipsoids at 50% probability and partial atom numbering scheme. The symmetry codes are as in Table 3.

 Table 3

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

Cd1-01	2.238(2)	O3 ^{#1} -Cd1-O4 ^{#1}	54.15(8)
Cd1-O3 ^{#1}	2.345(2)	O3 ^{#1} -Cd1-N4 ^{#2}	80.99(9)
Cd104 ^{#1}	2.528(2)	O5-Cd1-O3#1	103.15(10)
Cd1-05	2.278(3)	O5-Cd1-O4#1	152.33(10)
Cd1-N1	2.315(3)	O5-Cd1-N1	85.90(10)
Cd1-N4#2	2.394(3)	O5-Cd1-N4#2	85.52(9)
O1-Cd1-O3 ^{#1}	132.09(9)	N1-Cd1-O3#1	92.69(9)
O1-Cd1-O4 ^{#1}	77.99(8)	N1-Cd1-O4#1	108.66(9)
O1-Cd1-O5	123.17(10)	N1-Cd1-N4#2	167.90(10)
O1-Cd1-N1	101.45(9)	N4#2-Cd1-O4#1	76.01(9)
01-Cd1-N4#2	90.38(9)		

Symmetry transformations: #1 -x - 1/2, y - 1/2, -z - 1/2; #2 x - 2, y, z - 1.

ligands in 2 prevent any interpenetration. Individual $[Cd(tdc)(hdin) (H_2O)]_n$ layers stack and interdigitate by means of hydrogen bonding (Table S1) between N–H moieties in the hdin ligands in one layer to the C=O carbonyl groups within the hdin ligands in a neighboring layer (Fig. S1). The water molecules of crystallization occupy small pockets comprising minimal volume, and are anchored to the coordination polymer layers by donating hydrogen bonding to tdc carboxylate oxygen atoms and to hdin carbonyl oxygen atoms.

4.4. Structural description of $\{ [Cd_2(tdc)_2(hdn)(H_2O)_4] \cdot H_2O \}_n$ (3)

The asymmetric unit of compound **3** contains a divalent cadmium atom, a fully deprotonated tdc ligand, half of an hdn ligand whose central C–C σ bond is sited over a crystallographic inversion center, two bound water molecules and a water molecule of crystallization

sited on a two-fold rotation axis. The cadmium atoms display a {CdNO₆} pentagonal bipyramidal geometry (Fig. 5a) with trans aqua ligands in the axial positions. Chelating carboxylate groups from two tdc ligands and a pyridyl nitrogen donor atom from an hdn ligand occupy the equatorial plane. Bond lengths and angles within the pentagonal bipyramidal coordination environment are listed in Table 4.

Bis(chelating) tdc ligands connect $[Cd(H_2O)_2]^{2+}$ coordination fragments into $[Cd(tdc)(H_2O)_2]_n$ coordination polymer chains arranged along the c crystal direction (Fig. 5b), with a Cd…Cd distance of 10.528(2) Å. Parallel sets of chain motifs are pillared by hdn ligands into $[Cd_2(tdc)_2(hdn)(H_2O)_4]_n$ coordination polymer layers oriented along the bc crystal planes (Fig. 6). The hdn ligands span a Cd-Cd distance of 17.620(3) Å, and have an anti-anti-anti conformation of their hexamethylene tethers (torsion angles = 175°, 180°, 175°). Each Cd atom connects to three others within the layer motif, providing a (6,3) herringbone type topology (Fig. 7). Adjacent layer motifs stack along the a crystal direction in an ABAB pattern mediated by hydrogen bonding patterns (Table S1) involving the water molecules of crystallization and hdn N-H moieties in neighboring layers (Fig. S2). The isolated water molecules of crystallization occupy small cavities in the interlamellar regions comprising minimal volume. They are anchored to the coordination polymer layers by means of hydrogen bonding donation to ligating tdc carboxylate oxygen atoms (Table S1).

4.5. Structural description of $\{ [Cd_2(tdc)_2(pdn)(H_2O)_2] \cdot 4H_2O \}_n$ (4)

The asymmetric unit of compound 4 contains two crystallographically distinct divalent cadmium atoms (Cd1, Cd2), two fully deprotonated tdc ligands (tdc-A, tdc-B), a pdn molecule, two bound water molecules and four water molecules of crystallization. The Cd1 cadmium atoms display a {CdNO₆} pentagonal bipyramidal coordination environment with the axial positions taken up by a bound water molecule and an oxygen atom belonging to a C=O moiety within the amide functional group of a pdn ligand. Its equatorial plane contains chelating carboxylate groups from two tdc-A ligands and a pyridyl nitrogen donor atom from a pdn ligand. In contrast the Cd2 cadmium atoms display a trigonal bipyramidal {CdNO₄} coordination environment, with the axial positions taken up by a bound water molecule and an oxygen atom belonging to a C=O moiety within the amide functional group of a pdn ligand. The equatorial plane at Cd2 contains single carboxylate oxygen atom donors from two tdc-B ligands and a pyridyl nitrogen donor atom from a pdn ligand (Fig. 8).

The bis(chelating) tdc-A ligands link Cd1 atoms into $[Cd(tdc) (H_2O)]_n$ coordination polymer chains with a Cd1…Cd1 internuclear



Fig. 4. [Cd(tdc)(hdin)(H₂O)]_n rhomboid grid coordination polymer layer motif in 2.



Fig. 5. a) Coordination environment of 3, with thermal ellipsoids at 50% probability and partial atom numbering scheme. The symmetry codes are as in Table 4. b) $[Cd(tdc)(H_2O)_2]_n$ coordination polymer chain in 3.

Table 4						
Selected Bond	distance	(Å) and	angle (°)	data	for	3.

Cd1-O1	2.526(3)	O6-Cd1-O1	82.74(9)
Cd1-O2	2.345(2)	O6-Cd1-O2	89.04(9)
Cd1-03#1	2.416(2)	O6-Cd1-O3#1	95.18(9)
Cd1-O4 ^{#1}	2.400(2)	O6-Cd1-O4#1	89.48(9)
Cd1-06	2.260(2)	O6-Cd1-O7	170.02(9)
Cd1-07	2.297(2)	O6-Cd1-N1	93.58(10)
Cd1-N1	2.382(3)	07-Cd1-01	88.46(9)
02-Cd1-01	53.87(8)	07-Cd1-O2	89.57(9)
O2-Cd1-O3#1	167.88(9)	07-Cd1-03#1	88.19(9)
O2-Cd1-O4#1	137.20(9)	07-Cd1-O4#1	84.84(9)
O2-Cd1-N1	83.87(10)	07-Cd1-N1	96.10(9)
03 ^{#1} -Cd1-O1	137.91(8)	N1-Cd1-O1	137.53(9)
04 ^{#1} -Cd1-01	83.53(8)	N1-Cd1-O3#1	84.53(9)
O4 ^{#1} -Cd1-O3 ^{#1}	54.39(8)	N1-Cd1-O4#1	138.90(9)

Symmetry transformation: #1 x, -y + 1, z + 1/2.

Table 5

Sel	ected	Bond	distance	(A)) and	l angl	le (°)) data	for	4	•
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Cd1-O1 Cd1-O2 Cd1-O3 Cd1-O4 ^{#1} Cd1-O5 ^{#1} Cd1-O12 ^{#2} Cd1-N1 Cd2-O6	2.322(2) 2.265(2) 2.613(3) 2.584(3) 2.279(2) 2.370(2) 2.319(3) 2.319(3)	$\begin{array}{c} 05^{\#1}-Cd1-01\\ 05^{\#1}-Cd1-03\\ 05^{\#1}-Cd1-04^{\#1}\\ 05^{\#1}-Cd1-012\\ 05^{\#1}-Cd1-012\\ 05^{\#1}-Cd1-N1\\ 012^{\#2}-Cd1-03\\ 012^{\#2}-Cd1-04^{\#1}\\ 012^{\#1}-Cd1-04^{\#1}\\ 012^{$	93.23(9) 169.22(8) 53.42(9) 91.23(9) 86.27(10) 91.87(8) 86.09(8) 01.72(2)
$\begin{array}{c} Cd2-O6\\ Cd2-O7\\ Cd2-O10^{\#1}\\ Cd2-O11^{\#3}\\ Cd2-N4\\ O1-Cd1-O3\\ O1-Cd1-O4^{\#1}\\ O1-Cd1-O12^{\#2}\\ O2-Cd1-O1\\ O2-Cd1-O3\\ O2-Cd1-O3\\ O2-Cd1-O4^{\#1}\\ \end{array}$	2.318(3) 2.225(3) 2.215(2) 2.380(2) 2.281(3) 84.93(8) 91.34(9) 172.10(8) 86.80(8) 53.09(8) 84.90(8)	$\begin{array}{c} N1-Cd1-O1\\ N1-Cd1-O3\\ N1-Cd1-O4^{\#1}\\ N1-Cd1-O12^{\#2}\\ O6-Cd2-O11^{\#3}\\ O7-Cd2-O6\\ O7-Cd2-O11^{\#3}\\ O7-Cd2-N4\\ O10^{\#1}-Cd2-O6\\ O10^{\#1}-Cd2-O7\\ O10^{\#1}-Cd2-O7\\ O10^{\#1}-Cd2-O7\\ O10^{\#1}-Cd2-O11^{\#3}\\ \end{array}$	91.78(9) 83.17(8) 139.69(9) 95.01(9) 176.76(8) 90.69(10) 87.45(9) 90.91(10) 88.06(9) 135.55(9) 91.41(8)
$\begin{array}{c} 02-Cd1-O5^{\#1}\\ 02-Cd1-O12^{\#2}\\ 02-Cd1-N1\\ 04^{\#1}-Cd1-O3 \end{array}$	137.51(9) 85.50(8) 136.21(9) 137.13(8)	010 ^{#1} -Cd2-N4 N4-Cd2-O6 N4-Cd2-O11 ^{#3}	133.31(10) 86.80(9) 95.88(9)

Symmetry transformations: #1 x, -y + 3/2, z - 1/2; #2 -x + 1, y + 1/2, -z + 1/2; #3 -x + 2, y + 1/2, -z + 3/2.

distance of 10.869(2) Å; the bis(monodentate) tdc-B ligands link Cd2 atoms into $[Cd(tdc)(H_2O)]_n$ coordination polymer chains with a longer Cd2…Cd2 internuclear distance of 10.958(2) Å. Both chain motifs are arranged parallel to the *c* crystal direction. The Cd1 and Cd2 atoms in the neighboring chain motifs are linked by *syn*-conformation (N…N…N…N dihedral angle = 94.7°) pbn tethers that span a Cd1…Cd2 distance of 11.379(2) Å, thereby forming 1D $[Cd_2(tdc)_2(pdn)(H_2O)_2]_n$ coordination polymer ribbons (Fig. 9). Furthermore, the carbonyl oxygen atoms within the amide moieties of the pbn ligand also bind to both Cd1 and Cd2 atoms in neighboring ribbon motifs. This exotetradentate ligation mode of the pbin ligand fosters formation of a 3D $[Cd_2(tdc)_2(pdn)(H_2O)_2]_n$ coordination polymer network (Fig. 10). As the Cd1 atoms, Cd2 atoms, and exotetradentate pdn ligands all act as 4-connected nodes, a 3D self-penetrated net with 6^48^2 **nbo** topology can be invoked for 4 (Fig. 11), as determined by TOPOS [23]. The unligated water molecules in 4 are anchored to the 3D coordination polymer network by accepting hydrogen bonds from the N–H moieties of the pdn ligands, and donating hydrogen bonds to tdc-A and tdc-B oxygen atoms. (Table S1). Water molecule trimers and water molecules pairs occupy incipient void space within the structure of 4 comprising 14.8% of the unit cell volume according to PLATON. These are anchored to the 3D coordination polymer network of 4 by donating hydrogen bonding to tdc carboxylate oxygen atoms (Table S1).

4.6. Structural description of $[Cd(tdc)(pdin)]_n$ (5)

The asymmetric unit of compound **5** contains a divalent cadmium atom, a tdc ligand, and a pdin ligand. The coordination environment at cadmium is a highly distorted {CdN₂O₄} octahedron (Fig. 12), with pyridyl nitrogen donor atoms from two pdin ligands in the nominal axial positions. In the nominal equatorial plane are situated a chelating carboxylate group from one tdc ligand, and single carboxylate oxygen atom donor atoms from two other tdc ligands. Bond lengths and angles within the coordination environment in **5** are listed in Table 6.

The tdc ligands adopt an exotridentate μ_3 - κ^3 -O:O,O':O'' binding mode, thereby constructing $[Cd(tdc)]_n$ chains arranged parallel to the b crystal direction (Fig. 13a). Doubly bridging oxygen atom donors within the tdc ligands form embedded {Cd₂O₂} rhomboid units with a Cd-Cd internuclear distance of 3.952(1) Å. These are connected into the $[Cd(tdc)]_n$ chains by the full span of the linking tdc ligands. The $[Cd(tdc)]_n$ chains are decorated by "staple" conformation pdin ligands that connect cadmium atoms within the {Cd₂O₂} rhomboid units to each other, forming $[Cd(tdc)(pdin)]_n$ 1-D coordination polymer ribbons (Fig. 13b). The "staple" conformation of the pdin ligands is enforced by π - π stacking of the pyridyl rings (centroid-to-centroid distance = 3.927(1) Å) and the gauche-gauche conformation of the N-C-C-C central tethers (torsion angles = 76.8° and 62.9°). Dissimilar to 4, the carbonyl groups of the amide moieties of the dipyridylamide ligands do not bind to cadmium, preventing aggregation into higher dimensionality. Adjacent $[Cd(tdc)(pdin)]_n$ ribbons are anchored to each other by N-H-O hydrogen bonding between pdin amide groups and unligated tdc oxygen atoms in neighboring chains along the *a* crystal direction. Additionally, further structural stabilization is provided by N-H-O hydrogen bonding between the N-H moieties of pdin amide groups and the C=O moieties of pdin amide groups in neighboring chains along the c crystal direction. Stacking of adjacent $[Cd(tdc)(pdin)]_n$ ribbons into the full crystal structure of 5 is depicted in Fig. S3.



Fig. 6. $[Cd_2(tdc)_2(hdn)(H_2O)_4]_n$ coordination polymer layer in **3**. The $[Cd(tdc)(H_2O)_2]_n$ chain motifs are drawn in red in the online version of this article. a) Face view. b) Side view. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Schematic perspective of the (6,3) herringbone layer topology of **3**. The Cd atoms are depicted as pink spheres, and the tdc and hdn connectors are shown as red rods and blue rods, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.7. Thermogravimetric analysis

Thermogravimetric analyses were carried out on compounds 1–5 to investigate their degradation behavior. Compound 1 underwent dehydration between 20 and 125 °C, with a mass loss of 10.5% matching very well with the predicted value of 10.2% for four molar equivalents of water. Ligand ejection occurred above 250 °C. Compound 2 underwent dehydration in two steps between 20 and 190 °C, with the total mass loss of 6.2% corresponding well with the calculated value of 5.6% for two molar equivalents of water. Ligand ejection occurred above 270 °C. Compound 3 underwent dehydration between 20 and 150 °C, with an observed mass loss of 9.2% exactly matching the predicted

value for five molar equivalents of water. Ligand combustion occurred above 260 °C. Compound **4** underwent dehydration in two steps between 20 and 150 °C, with a mass loss of 11.5% matching well with the expected value of 11.3% for six molar equivalents of water. Ligand combustion occurred above 265 °C. Compound **5** showed a largely stable mass until 310 °C, whereupon ligand combustion ensued. Thermogravimetric analysis plots for **1–5** are shown in Figs. S4–S8, respectively.

4.8. Nitrobenzene detection

Compounds 1-5 showed capability for detection of nitrobenzene (NB) in ethanol suspension, wherein the nitro functional group is a very well known electron acceptor. The emissive properties of 1-5 under ultraviolet excitation are ascribed to π - π^* molecular orbital transitions within the pyridyl ring systems of the dipyridylamide ligands and the aromatic thiophene ring systems of the tdc ligands [24]. Addition of microliter-level aliquots of nitroaromatics dissolved in DMSO $(1 \times 10^{-4} M)$ resulted in decrease of the emission intensity, with greater decreases upon addition of more nitroaromatic solution, up to 10 µL. A representative graph for detection of NB by compound 1 is shown in Fig. 14; graphs for the detection of NB by 2-5 are shown in Figs. S9-S12, respectively. The loss of emission signal is ascribed to electron transfer from the excited states of the pyridyl or thiophene aromatic molecular orbitals within the coordination polymers, to the lowest unoccupied molecular orbitals of the adsorbed nitrobenzene analyte mediated by the electron withdrawing nitro group [25]. The quenching data for 1-5, in the presence of nitrobenzene analyte, were



Fig. 8. Coordination environments in 4, with thermal ellipsoids at 50% probability and partial atom numbering scheme. Cd1 shows a pentagonal bipyramidal coordination environment while Cd2 displays a trigonal bipyramidal coordination environment. The symmetry codes are as in Table 5.



Fig. 10. $[Cd_2(tdc)_2(pdn)(H_2O)_2]_n$ 3D coordination polymer network in 4, viewed down *c*. Individual coordination polymer ribbon motifs are drawn in red and blue. These are connected into the 3D network by pdn carbonyl oxygen atom ligation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 11. Schematic representation of the 3D self-penetrated net with 6^48^2 **nbo** topology in **4**. The Cd1 atom nodes, Cd2 atom nodes, and pdn ligand nodes are shown as blue, violet, and black spheres, respectively. The red rods indicate tdc-mediated connections, and the black rods indicate connections through the exotetradentate pdn ligands. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

analyzed using the Stern-Volmer equation [26], $I_0/I = K_{sv}[A] + 1$, where I_0 is the initial emission intensity in the absence of analyte, I is the emission intensity in the presence of analyte, [A] is the molarity of analyte, and K_{sv} is the Stern-Volmer quenching constant in units of M^{-1} . The K_{sv} values for detection of NB by 1–5 are listed in Table 7. Stern-Volmer plots for the uptake of nitrobenzene by solid samples of **Fig.** 9. $[Cd_2(tdc)_2(pdn)(H_2O)_2]_n$ coordination polymer ribbon in 4. The Cd1-based chain motifs are shown in red and the Cd2-based chain motifs are shown in purple. The color legend refers to the online version of this article. a) View down *a*. b) View down *c*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. Coordination environment of 5, with thermal ellipsoids at 50% probability and partial atom numbering scheme. The symmetry codes are as in Table 6.

Table 6 Selected Bond distance (Å) and angle (°) data for 5.

$\begin{array}{c} Cd1{-}O1\\ Cd1{-}O3^{\#1}\\ Cd1{-}O3^{\#2}\\ Cd1{-}O4^{\#2}\\ Cd1{-}N1\\ Cd1{-}N1\\ Cd1{-}N4^{\#3}\\ O1{-}Cd1{-}O3^{\#2} \end{array}$	2.263(2) 2.396(2) 2.561(2) 2.303(2) 2.300(3) 2.307(3) 165.26(8)	$\begin{array}{c} O3^{\#1}-Cd1-O3^{\#2}\\ O4^{\#2}-Cd1-O3^{\#2}\\ O4-Cd1-O3^{\#1}\\ O4^{\#2}-Cd1-N4^{\#3}\\ N1-Cd1-O3^{\#1}\\ N1-Cd1-O3^{\#2}\\ N1-Cd1-O4^{\#2}\\ \end{array}$	74.23(8) 53.56(7) 127.52(8) 95.66(9) 86.83(9) 91.45(9) 89.29(9)
Cd1-04" 2	2.303(2)	O4" ² -Cd1-N4" ³	95.66(9)
Cd1-N1	2.300(3)	N1-Cd1-O3"1	86.83(9)
Cd1-N4 ^{#3}	2.307(3)	N1-Cd1-O3#2	91.45(9)
01-Cd1-O3#2	165.26(8)	N1-Cd1-O4#2	89.29(9)
01-Cd1-O3 ^{#1}	91.03(8)	N1-Cd1-N4 ^{#3}	175.04(9)
01-Cd1-04 ^{#2}	141.07(8)	N4 ^{#3} -Cd1-O3 ^{#1}	90.41(9)
O1-Cd1-N1	87.55(9)	N4 ^{#3} -Cd1-O3 ^{#2}	91.76(9)
01-Cd1-N4 ^{#3}	88.37(9)		

Symmetry transformations: #1 -x + 2, -y + 1, -z + 2; #2 x, y + 1, z; #3 -x + 2, -y + 2, -z + 2.



Fig. 13. a) $[Cd(tdc)]_n$ double chain in 5, showing embedded $\{Cd_2O_2\}$ dimeric units. b) $[Cd(tdc)(pdin)]_n$ ribbon motif in 5, showing "staple" conformation pbin ligands.



Fig. 14. Nitrobenzene detection plot for 1. The volumes represent the total amount of 1.0×10^{-4} M NB solution in DMSO added to 10 mg of 1 suspended in 5 mL ethanol.

Table 7Stern-Volmer constants for the detection of NB by1–5 in ethanol suspension.

Compound	K_{SV} (M ⁻¹)
1 2 3 4 5	$\begin{array}{c} 2.5\times 10^5 \\ 6.4\times 10^5 \\ 8.4\times 10^5 \\ 4.1\times 10^5 \\ 7.4\times 10^5 \end{array}$

1–5 are depicted in Figs. S13–S17, respectively. While all the K_{sv} values were similar in terms of order of magnitude, the K_{sv} value for **3** was the highest in the series. It is plausible that the stacked, non-interpenetrated, non-interdigitated coordination polymer layers of **3** permit the best approach of nitrobenzene to the pyridyl and/or thiophene rings and thereby the optimum excited state electron transfer to the analyte.

5. Conclusions

A series of cadmium coordination polymers featuring the rigid tdc ligand and conformationally flexible dipyridylamide neutral coligands exhibits a wide range of structural topologies. This structural diversity hinges on specific cadmium coordination environments, different tdc binding modes, the dipyridylamide tether length and pyridyl nitrogen donor disposition, and the specific aliphatic tether conformation locked into the respective crystal structures. While all materials in this series acted as "turn-off" sensors for the detection of small quantities of nitrobenzene, optimum detection behavior was achieved by the non-interpenetrated, non-interdigitated stacked layer compound **3**, because it plausibly allowed closest approach of the nitrobenzene analyte to the necessary coordination polymer structural components.

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Appendix A. Supplementary data

Hydrogen bonding information, additional molecular graphics, TGA traces, nitrobenzene detection plots for **2–5**, and Stern-Volmer plots for **2–5**. Crystallographic data (excluding structure factors) for **1–5** have been deposited with the Cambridge Crystallographic Data Centre with Nos. 1839320, 1839321, 1839322, 1839323, and 1865232, respectively. Copies of the data can be obtained free of charge via the Internet at < https://www.ccdc.cam.ac.uk/structures/ > . Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica. 2018.10.039.

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