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Cd(II) coordination polymers based on expanded N,N'-heteroaromatic donor ligands

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ABSTRACT

The isomeric N donor linkers bis(pyridin-4-ylmethylene)naphthalene-1,5-diamine (**L1**) and bis(pyridin-3-ylmethylene)naphthalene-1,5-diamine (**L2**) have been used with acetate and iodide as co-ligands to generate four new cadmium(II) coordination polymers. [Cd**L1**(OAc)₂]_n (**1**), [Cd**L1**(I)₂]_n (**2**), [Cd**L2**(OAc)₂]_n (**3**) and [Cd**L2**(I)₂]_n (**4**) were characterized by elemental analysis, X-ray powder diffraction, IR spectroscopy, thermal analysis and single crystal X-ray diffraction. In line with the concept of crystal engineering, their structures share common motifs: the heteroaromatic linkers generate chains, subtending Cd...Cd distances consistent with their N donor arrangement. The co-ligands control the coordination number of the Cd(II) cations and interchain connectivity: The acetate moieties either adopt bridging and chelating or exclusively bridging modes and crosslink essentially linear chains based on octahedral metal centers; in the former case, the ladder-like one-dimensional ribbon **1** is generated, whereas the latter connectivity results in the two-dimensional layer structure **3**. In contrast, iodide acts as terminal ligand towards tetrahedral Cd(II), and hence **2** and **4** are single-stranded 1D zig-zag polymers. In comparison to the uncoordinated heteroaromatic **L1** and **L2**, the Cd coordination polymers show slightly red-shifted luminescence spectra of significantly higher intensity due to the more rigid arrangement of the π systems.

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1. Introduction

Coordination polymers continue to attract enormous interest not only because of their intriguing variety of architectures and topologies but also for applications in the fields of magnetism [1,2], nonlinear optics [3], luminescence [4,5], conductivity [6–8] and heterogeneous catalysis [9].

The topology of a coordination polymer depends on various factors such as the chemical constitution and stoichiometry of the ligands, the metal center and its oxidation state, and crystallization parameters, e.g. temperature and solvent polarity [10–13]. It may be affected by weak non-covalent supramolecular interactions, for example by hydrogen bonding or π - π interactions [14,15]. Crystal engineering attempts to control the assembly of target frameworks by combining the plethora of organic ligands with

suitable metal cations. In this context, the specific features of the organic ligands and their structural consequences must be taken into account: their flexibility and length as a space as well as the disposition and type of potential donor atoms play vital roles for the target structures [16–18]. Neutral aromatic N donor ligands allow to construct diverse coordination polymers with interesting one, two and three-dimensional structures [19–21]. Bipyridyl Schiff base ligands with tunable spacers between the pyridine functionalities are even more versatile and lead to the formation of a wide range of coordination networks with different structures and interesting topologies [22,23]. Two among these bidentate N-donor ligands, namely bis(pyridin-4-ylmethylene)naphthalene-1,5-diamine (**L1**) and its isomer bis(pyridin-3-ylmethylene)naphthalene-1,5-diamine (**L2**) are depicted in Scheme 1.

L1 and **L2** attracted our attention because their π -conjugation, rod shape and limited conformational freedom makes them suitable spacers; both can easily be synthesized and have not been used very frequently for the design of extended structures. Their structural chemistry started with the Co(II) and Cd(II) derivatives

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Scheme 1. Expanded N,N'-heteroaromatic linkers used in this work.

of **L1**; nitrate anions acted as co-ligands. These self-assembly reactions resulted in a 1-D ladder-shaped coordination polymer $[\text{Co}_2\text{L1}_3(\text{NO}_3)_4]_n$ and the more complex 3D network $[\text{Cd}_2\text{L1}_3(\text{NO}_3)_4]_n$; the latter adopts a rare fourfold interlocked topology [24]. Soon after, Liu et al. published the crystal structure of un-coordinated **L1** [25]. Lee et al. [26] devoted a comprehensive study to both isomeric ligands **L1** and **L2**; 1-D zigzag chains $[\text{Zn}(\text{Lx})(\text{NO}_3)_2]_n$ ($x = 1, 2$) and also $[\text{CdL1}_{1.5}(\text{NO}_3)_2]_n$ 1-D ladder coordination polymer could be addressed. The same authors reported 3D diamondoid frameworks [27] obtained from **L1** and Ag(I) salts of weakly coordinating anions such as PF_6^- , SbF_6^- and BF_4^- . This was followed by investigations concerning two and three dimensional mixed-ligand polymers with 4,4'-bipyridine and biphenyl-4,4'-dicarboxylic acid as co-ligands in the presence of Co(II) cations [28]. More recent contributions by Kepert and co-workers [29] targeted 1-D and 2-D solids in which **L1** coordinates to Fe(II). We have recently reported three new compounds based on **L1**, namely the 2-D layer structure $[\text{PbL1}(\mu\text{-Br})_2]_n$ and the chain polymers $[\text{CuL1}(\text{acac})_2]_n$ and $[\text{Cu}_2\text{L1}(\text{OAc})_4]_n$ [30]. As for **L2**, we mention the 2D derivative $[\text{CdL2}_2(\text{NO}_3)_2]_n$ and the double-bridged chain polymer $[\text{CoL2}_2(\text{NO}_3)_2]_n$ [31]. Finally, we wish to highlight the 2-D coordination polymer $[\text{Cd}_2\text{L2L1}(\text{NO}_3)_4]_n$ [32] which incorporates both isomeric ligands **L1** and **L2** in the same solid. In total, the CSD data base [33] contains 18 structurally characterized derivatives of ligand **L1** and seven of **L2**, and we will compare these earlier structures to our results below.

The anions play an important role in engineering coordination polymers with desirable structures and properties, well beyond simple charge balancing. They may remain uncoordinated or act as either terminal or bridging co-ligands, thus influencing the stereochemistry at the cations and the dimensionality of the extended structures. Our group has systematically investigated the structural chemistry of halide-bridged polymers with substituted pyridines [34–36], but in general halides have received less attention as potential co-ligands. In this contribution, we combine the expanded donor ligands **L1** and **L2** with Cd(II) cations and two anions of presumably different functionalities: acetate often represents a bridging moiety, whereas iodide mostly acts as a terminal ligand [37]. Scheme 2 summarizes our results.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were commercially available and used without further purification. Elemental analyses were performed with a Heraeus CHNO-Rapid VarioEL. FT-IR spectra were obtained by a Bruker Tensor 27 Perkin–Elmer FT-IR and on a Nicolet Avatar 360 E.S.P. spectrometer. NMR spectra were recorded on a Bruker Avance II Ultrashield Plus 400. TG and SDTA analyses were performed in air with a heating rate of 5 K min^{-1} in the temperature range 25–800 °C on a Mettler Toledo TGA/SDTA 851e instrument. Photoluminescence spectra were recorded on an Andor-Shamrock spectrophotometer (SR-303i-B). X-ray powder diffraction patterns were obtained at ambient temperature on flat samples with a Stoe Imageplate Detector IP-PSD with $\text{Cu K}\alpha_1$ radiation.

2.2. Synthesis of the spacer ligands **L1** and **L2**

2.2.1. Synthesis of **L1**

We used a modified synthesis adapted from Ref. [26]: An ethanol (10 ml) solution of 4-pyridine carboxaldehyde (1.88 ml, 20.0 mmol) was added dropwise to an ethanol solution (10 ml) of 1,5-diaminonaphthalene (1.58 g, 10.0 mmol), and the mixture was refluxed for 3 h. The resulting yellow crystalline solid was washed with ethanol ($3 \times 5 \text{ ml}$) and hexane ($3 \times 5 \text{ ml}$) and crystallized from CH_2Cl_2 –hexane to give the pure ligand. Yield: 83%. m.p.: 239–241 °C. ^1H NMR (400 MHz, CDCl_3) δ : 8.84 (d, 4H), 8.61 (s, 2H), 8.29 (d, 2H), 7.90 (d, 4H), 7.56 (m, 2H), 7.18 (d, 2H). IR (KBr, cm^{-1}): 3025(w), 1622 (s), 1590 (s), 1405 (s), 1316 (m), 1229 (m), 977 (m), 923 (m), 788 (s), 648 (w). Anal. Calc. for $\text{C}_{22}\text{H}_{16}\text{N}_4$: C, 78.5; H, 4.7; N, 16.6. Found: C, 79.2; H, 4.8; N, 16.5%.

2.2.2. Synthesis of **L2**

The preparation was analogous to **L1**, except that the isomeric 3-pyridine carboxaldehyde was used instead of the 4-pyridine carboxaldehyde. Yield: 77%. m.p.: 201–203 °C. ^1H NMR (400 MHz, CDCl_3) δ : 9.15 (s, 2H), 8.73 (d, 2H), 8.62 (s, 2H), 8.41 (m, 4H), 8.24 (d, 2H), 7.53–7.44 (m, 4H), 7.14 (d, 2H). IR (KBr, cm^{-1}): 3053 (w), 1623 (s), 1569 (s), 1407 (s), 1319 (m), 1225 (m), 927 (s), 791 (s), 711 (s), 665 (s). Anal. Calc. for $\text{C}_{22}\text{H}_{16}\text{N}_4$: C, 78.5; H, 4.7; N, 16.6. Found: C, 78.1; H, 4.5; N, 16.9%.

2.3. Preparation of coordination compounds

2.3.1. $[\text{CdL1}(\text{OAc})_2]_n$ (**1**)

A dichloromethane solution (6 ml) of **L1** (33.6 mg, 0.10 mmol) was allowed to diffuse slowly into a methanol solution (6 ml) of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.6 mg, 0.10 mmol) through an intermediate layer of methanol/dichloromethane (1:1, 4 ml). Yellow needle-shaped crystals formed within 5 days, yield 63%. IR (KBr, cm^{-1}): 3040(w), 1608(s), 1565(vs), 1415(vs), 1366(w), 1321(w), 1235 (w), 1062(m), 827 (m), 786 (m). Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Cd}$: C, 55.1; H, 3.9; N, 9.9. Found: C, 55.4; H, 3.6; N, 9.7%.

2.3.2. $[\text{CdL1}(\text{I})_2]_n$ (**2**)

KI (33.2 mg, 0.20 mmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.8 mg, 0.10 mmol) were dissolved in methanol (6 ml) and stirred for 15 min. Similar as in the reaction above, a dichloromethane solution (7 ml) of **L1** (33.6 mg, 0.10 mmol) was allowed to diffuse slowly into this mixture through an intermediate layer of methanol/dichloromethane (1:1, 5 ml). A few brown block-shaped single crystals suitable for X-ray diffraction were obtained after one week. IR (KBr, cm^{-1}): 3036 (w), 1607 (s), 1556 (m), 1475 (m), 1419(m), 1384 (s), 1315(w), 1282 (m), 1242(w), 1061(m), 818 (m), 775 (s). We note that in contrast to 1, 3 and 4, only isolated crystals and no appreciable quantity of the target compound could be obtained; no data from elemental and thermal analysis are available.

2.3.3. $[\text{CdL2}(\text{OAc})_2]_n$ (**3**)

A solution of **L2** (16.5 mg, 0.05 mmol) in tetrahydrofuran (THF, 6 ml) was carefully layered with a mixture of CH_3OH and THF (1:1, 4 ml). A solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (13.3 mg, 0.05 mmol) in methanol (6 ml) was introduced as a third layer. Yellow block-shaped crystals of **3** formed within 3 days, yield 52%. IR (KBr, cm^{-1}): 3040 (w), 1599 (s), 1563 (vs), 1419 (vs), 1319 (w), 1223 (w), 1069(m), 926(m), 873(m), 786 (s). Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Cd}$: C, 55.1; H, 3.9; N, 9.9. Found: C, 55.0; H, 3.7; N, 9.7%.

2.3.4. $[\text{CdL2}(\text{I})_2]_n$ (**4**)

The method as in the synthesis of **2** was used, except that **L1** was replaced by **L2** (33.6 mg, 0.1 mmol). Brown block-shaped

Scheme 2. Summary of the coordination polymers synthesized and structurally characterized in this work.

X-ray quality crystals formed after 7 days, yield 38%. IR (KBr, cm^{-1}): 2923(w), 1617(s), 1575(w), 1499(w), 1429(s), 1373(m), 1315(w), 1295 (w), 1202(m), 1051(m), 791 (s), 699 (s). *Anal. Calc.* for $\text{C}_{22}\text{H}_{17}\text{N}_4\text{I}_2\text{Cd}$: C, 37.5; H, 2.4; N, 8.0. Found: C, 36.9; H, 2.3; N, 8.4%. We are aware of the fact that the discrepancies between calculated and experimentally observed elemental composition slightly exceed general standards, and we therefore explicitly refer to the X-ray powder pattern of the bulk material (Fig. S4); it supports our idea that the bulk of **4** shares the composition suggested by the single crystal diffraction experiment.

2.4. Single crystal X-ray diffraction

Intensity data for **1** were collected at 100 K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, focusing multilayer optics) on a Bruker D8 Venture equipped with a Photon100 area detector at the Zernike Institute for Advanced Materials, University of Groningen. Data for **3** and **4** were obtained at 100 K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, Incoatec microsource with multilayer optics) on a Bruker D8 goniometer equipped with an APEX area detector at the Institute of Inorganic Chemistry, RWTH Aachen University. The data sets for **1**, **3** and **4** were integrated with SAINT [38] and corrected for absorption by multi-scan methods [39]. The data collection for **2** was performed at 293 K with Mo $K\alpha$ radiation ($\lambda = 0.71019 \text{ \AA}$) on an Xcalibur four-circle diffractometer equipped with an EOS CCD detector at the Faculty of Arts and Sciences, Ondokuz Mayıs University. The CrysAlisPro software [40] was used for data collection, cell refinement and data reduction. All structures were solved by direct methods (SHELXS-97) [41] and refined by full matrix least squares procedures based on F^2 as implemented in SHELXL-97 [42] or SHELXL-2014 [43]. Non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms bonded to C were positioned geometrically and refined using a riding model with $\text{C-H} = 0.98 \text{ \AA}$, $\text{Uiso(H)} = 1.5 \text{ Ueq(C)}$ for methylene and $\text{C-H} = 0.95 \text{ \AA}$, $\text{Uiso(H)} = 1.2 \text{ Ueq(C)}$ for aryl H atoms. Crystal data, parameters for intensity data collection and refinement details are given in Table 1.

3. Result and discussion

3.1. Synthesis and preliminary characterization

Condensation reactions of 1,5-diaminonaphthalene with the isomeric pyridine carboxyaldehydes afforded the extended spacer ligands **L1** and **L2**. They exhibit two terminal pyridyl groups with their nitrogen atoms in either 4,4' (**L1**) and 3,3' (**L2**) positions. The reaction between these ligands and Cd salts by layer diffusion in a 1:1 M ration gave rise to the less-soluble coordination polymers **1–4**.

Vibrations associated with the imine group of the N-containing ligands are visible in the IR spectra. They show up at ca. 1622 cm^{-1} in the uncoordinated ligands and are shifted to lower frequencies between 1617 and 1599 cm^{-1} in the coordination polymers **1–4**. Consistent with this assignment, C=N stretching frequencies for azomethine are encountered in the range $1600\text{--}1680 \text{ cm}^{-1}$ [44]. Two sharp and strong absorptions in the range $1565\text{--}1563$ and $1419\text{--}1415 \text{ cm}^{-1}$ can be assigned to the asymmetric and symmetric vibrations of the carboxylato groups in **1** and **3**. The differences in wavenumbers between these bands, $\Delta\nu$ ($\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$) amount to 150 and 144 cm^{-1} for **1** and **3**, respectively, indicate bidentate coordination modes for the acetate moieties in **1** and **3** [45].

The results of our single crystal diffraction experiments are supported by microanalytical data, except for compound **2**. Powder diffraction confirms that our samples are phase pure (Figs. S1–S4).

3.2. Crystal structures

3.2.1. $[\text{CdL1}(\text{OAc})_2]_n$, **1**

In **1**, the N donor atoms of two **L1** bridges occupy *trans* positions in a distorted octahedral coordination about Cd. the resulting arrangement is an essentially linear chain in which the **L1** space subtends Cd...Cd separations of $20.4 \text{ \AA}$; next-next intercation distances along the chain amount to $40.8 \text{ \AA}$. One of the acetate co-ligands per cation adopts a *syn-syn* bridging mode about a crystallographic center of inversion whereas the second acetate acts as

Table 1Crystal data and refinement results for compounds **1**, **2**, **3** and **4**.

Compound	1	2	3	4
Chemical formula	C ₂₆ H ₂₂ CdN ₄ O ₄	C ₂₂ H ₁₆ CdI ₂ N ₄	C ₂₆ H ₂₂ CdN ₄ O ₄	C ₂₂ H ₁₆ CdI ₂ N ₄
<i>M_r</i>	566.87	702.59	566.87	702.59
Crystal system, space group	triclinic, <i>P</i> $\bar{1}$	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	triclinic, <i>P</i> $\bar{1}$	orthorhombic, <i>Pnma</i>
<i>T</i> (K)	100	293	100	100
<i>a</i> (Å)	8.7168(7)	9.0694(5)	5.0648(6)	8.6569(13)
<i>b</i> (Å)	9.0671(7)	13.0897(6)	8.9987(11)	22.292(3)
<i>c</i> (Å)	17.0207(13)	19.7733 (10)	12.9073(16)	10.9504(16)
α (°)	84.256(4)		102.359(2)	
β (°)	77.281(3)	98.935(5)	90.901(2)	
γ (°)	65.645(3)		101.225(2)	
<i>V</i> (Å ³)	1195.40 (16)	2318.9 (2)	562.63 (12)	2113.2 (5)
<i>Z</i>	2	4	1	4
μ (mm ^{−1})	0.95	3.62	1.01	3.97
Crystal size (mm)	0.16 × 0.08 × 0.02	0.52 × 0.26 × 0.24	0.34 × 0.16 × 0.13	0.38 × 0.22 × 0.10
Absorption correction	multi-scan	analytical	multi-scan	multi-scan
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.838	0.625	0.721	0.723
<i>R</i> _{int}	0.072	0.024	0.034	0.066
<i>R</i> ₁ , <i>wR</i> ₂ , <i>S</i>	0.047, 0.086, 1.02	0.033, 0.064, 1.01	0.026, 0.061, 1.08	0.042, 0.100, 1.01
No. of reflections	11682	4733	3247	2932
No. of parameters	327	262	161	136
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	1.11, −0.89	0.59, −0.52	0.56, −0.48	1.44, −1.20

Fig. 1. (a) 1D ladder structure of **1** resulting from **L1** bridging in horizontal and acetate bridging in vertical direction. Symmetry operators $i = 1 - x, 1 - y, 1 - z, ii = x - 1, y - 1, z + 1$. (b) Packing in polymer direction along [11-1]. H atoms have been omitted for clarity.

chelating terminal ligand. The Cd···Cd distance in the resulting dinuclear $[\text{Cd}_2(\text{OAc})_4]$ Secondary Building Unit (SBU) amounts to 3.9 Å. Acetate-bridging occurs perpendicular to the chain direction, and hence the overall geometry of **1** corresponds to an infinite ribbon as shown in Fig. 1a.

1 may be compared to related Cd(II) acetate derivatives with 4,4'-bipyridyl- or 4-substituted pyridine ligands. In the chain polymer $[\text{Cd}_2(\mu, \kappa^3\text{-O}, \text{O}':\text{O}-\text{OAc})_2(\kappa^2\text{-O}, \text{O}':\text{O}-\text{OAc})_2(\text{lig})_2]$ [46] (lig = 4'-(4-biphenyl)-4,2':6',4''-terpyridine) and in the binuclear compounds $[\text{Cd}_2(\text{CH}_3\text{COO})_4(4\text{-pyao})_4] \cdot 4\text{H}_2\text{O}$ and $[\text{Cd}_2(\text{CH}_3\text{COO})_4(4\text{-pyamo})_4] \cdot 2\text{DMF}$ (4-pyao = pyridine-4-aldoxime; 4-pyamo = pyridine-4-amidoxime) [47] the Cd(II) cations are seven-coordinated. The $\{\text{O}_5\text{N}_2\}$ coordination polyhedron is a pentagonal bipyramid in which the five equatorial sites are occupied by acetate anions in different coordination modes and two nitrogen atoms of pyridyl ligands occupy the axial positions. The Cd(II) cations in polymeric $[\text{Cd}(\text{O}_2\text{CPh})_2(\text{bpa})_{1.5}]_n$ (bpa = 1,2-bis(4-pyridyl)ethane), [48] and in the mononuclear complexes $[\text{Cd}(\text{CH}_3\text{COO})_2(4\text{-pyao})_3] \cdot 3\text{H}_2\text{O}$ (4-pyao = pyridine-4-aldoxime) [47] and $[\text{Cd}(\kappa^2\text{-OAc})_2(\text{lig})_3] \cdot 2\text{H}_2\text{O}$ (lig = $\text{NC}_5\text{H}_4(\text{NMe}_2)\text{-4}$) [49] adopt a distorted pentagonal bipyramidal $\{\text{N}_3\text{O}_4\}$ coordination with two chelating benzoate and/or acetate anions and three pyridyl N ligands. The coordination polyhedra about Cd(II) in $[\text{Cd}(\kappa^2\text{-OAc})_2(\text{NC}_5\text{H}_4\text{Me-4})_2(\text{H}_2\text{O})]$, $[\text{Cd}(\kappa^2\text{-OAc})_2(\text{H}_2\text{O})_2]$ and in $[\text{Cd}(\kappa^2\text{-OAc})_2(\text{lig})_2(\text{H}_2\text{O})]$ (lig = $\text{NC}_5\text{H}_4(\text{OMe})\text{-4}$ or $\text{NC}_5\text{H}_4\text{tBu-4}$) are best described as distorted pentagonal bipyramids. Their equatorial positions are occupied by two κ^2 chelating acetates and an aqua oxygen; two N donor ligands coordinate via the apical positions [49]. Our comparison suggests that coordination number seven is more frequent for Cd(II) carboxylato complexes than six [50]. Sixfold coordination has, however, been reported for the 1D polymer $[\text{Cd}_2(\mu_2\text{-}\kappa^2:\kappa^1\text{-OAc})_2(\mu_2\text{-}\kappa^1:\kappa^1\text{-OAc})_2(\text{lig})_2]$ (lig = NC_5H_5) [49].

The bond distances of 2.3 Å for Cd–N and the distance range between 2.26 and 2.48 Å for Cd–O encountered in **1** matches the corresponding values in related structures [47,48]. The aromatic rings in the **L1** spacer ligand are not coplanar but subtend dihedral angles of ca. 40°. A projection along the direction of the polymer chain (Fig. 1b) reveals weak C–H···O contacts of ca. 2.4 Å and C–H··· π interactions of ca. 2.8 Å. To the best of our knowledge, the ladder-type topology adopted by **1** is unprecedented among the structurally characterized derivatives of **L1**.

3.2.2. $[\text{CdL1}(\text{I})_2]_n$ (**2**)

In this derivative of spacer ligand **L1** with iodo co-ligands, the Cd(II) cation adopts a distorted tetrahedral coordination (Fig. 2a). The sterically demanding iodo ligands lead to an acute N1–Cd1–N3 angle of only 88°, resulting in a pronounced zig-zag chain extending in [001] direction. After next Cd···Cd distances amount to 23 Å and are only slightly longer than Cd···Cd distances subtended by a single spacer (20.5 Å). **L1** is in a similar conformation as in **1**, with dihedral angles around 40°.

A search in the CSD [33] for CdI_2 derivatives with 4,4'-bipyridyl or 4-pyridyl ligands revealed two compounds which are closely related to **2**: $[\text{CdI}_2(\text{lig})]_n \cdot \text{benzene}$ (lig = 9,10-bis(4-pyridyl)anthracene) [51] and $[\text{Cd}(\text{lig})(\text{I})_2]_n$ (lig = azine-derived ligand) [52] both adopt a 1D zig-zag structure. In these compounds, the Cd–N and Cd–I coordination distances are very similar to those encountered for **2**. In contrast, $[\text{Cd}(\text{dmpt})_2(\text{I})_2] \cdot x\text{S}$ (S = solvent, dmpt = 4'-(3,4-dimethoxyphenyl)-4,2':6',4''-terpyridine) [53], $[\text{Cd}(\text{lig})_2(\text{I})_2]_n$ (lig = azine-derived ligand) [52] and $[\text{Cd}(\text{pyim})_2(\text{I})_2]_n$ (pyim = N-(4-pyridylmethyl)imidazole) [54] are two-dimensional with a distorted octahedral $\{\text{CdN}_4\text{I}_2\}$ environment; the equatorial coordination sites are occupied by four nitrogen atoms of the spacer ligands, and two iodide anions are situated in the axial positions. We finally mention an alternative octahedral Cd(II) coordination by N donor and iodo ligands: chain polymers of composition

Fig. 2. (a) 1D zigzag chain formed by the cadmium atoms and ligands in **2**. Symmetry operators $i = -x + 1, -y + 1, -z$; $ii = -x, -y + 1, -z + 1$. (c) Packing in polymer direction along $[-1-11]$. H atoms have been omitted for clarity.

$[\text{Cd}(\mu\text{-I})_2(\text{lig})_2]$ (lig = pyridine derivative) feature four bridging iodo ligands per cation. This connectivity is rather popular [55–58].

Adjacent chains are π stacked with closest C···C distances of 3.37 Å between neighbouring spacer ligands; in addition, non-classical C–H···I hydrogen bonds of 3.36 Å stabilize the supramolecular assembly (Fig. 2b).

3.2.3. $[\text{CdL2}(\text{OAc})_2]_n$ (**3**)

Similar to the situation in **1**, the coordination sphere about the metal cations in **2** is distorted octahedral. The Cd center is located in a crystallographic center of inversion, and for reasons of symmetry the N donors of two **L2** ligands in *trans* position subtend an angle of 180° (Fig. 3a).

The separation between next-neighbour Cd(II) cations connected by a spacer ligand **L2** amounts to 19.2 Å, shorter than in the case of the **L1** derivatives; the conformation within **L2** is, however, rather similar with interplanar angles of ca. 40°. In contrast to the acetato complex of ligand **L1**, **1**, all acetato co-ligands in **3** adopt a *syn-anti* bridging mode, with Cd···Cd distances corresponding to a lattice parameter *a* (ca 5.1 Å). No chelating acetate moieties terminate the expansion of the polymer in the direction perpendicular to the **L2** spacers dimension, and an overall 2D layer structure based on coordinative bonds is formed (Fig. 3b). Weak non-classical hydrogen bonds between H atoms of the heteroaromatic

Fig. 3. (a) View of the coordination environment of the central Cd(II) atom in **3**. (b) 2D layered structure of **3** resulting from **L2** bridged in horizontal and acetate bridged in vertical direction. Symmetry operators i = $-x, -y, -z + 1$; ii = $-x - 1, -y, -z + 1$; iii = $x + 1, y, z$; v = $x - 1, y, z$. (c) Packing in polymer direction along [1 1 1]. H atoms have been omitted for clarity.

system and acetate oxygen amount to ca. 2.6 Å and lead to stacking of these layers in the third dimension (Fig. 3c).

Coordination polymers constructed from cadmium acetate and 3,3'-bipyridine derived linkers have not yet been reported, but a limited number of cadmium acetate complexes features 3-substituted pyridine ligands. In these complexes, the coordination number of the Cd(II) cations is six or seven, and the acetate moieties show variable binding modes. They may act as monodentate, e.g. in $[(\text{Cd}(\text{OAc})_2(\text{NC}_5\text{H}_3\text{Me}_2\text{-3,4})_2(\text{H}_2\text{O})_2)]$ [49] or $[\text{Cd}(\text{OAc})_2(\text{H}_2\text{O})_2(\text{N,N-diethylnicotinamide})]$ [59], as chelating in $[\text{Cd}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{NO})_2(\text{H}_2\text{O})_2] \cdot 2[\text{Cd}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{NO})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ [60] and as bidentate bridging and/or tridentate chelating and bridging ligand, for example in $[\text{Cd}_2(\mu_2\text{-}\kappa^2\text{:}\kappa^1\text{-OAc})_2(\mu_2\text{-}\kappa^1\text{:}\kappa^1\text{-OAc})_2\text{lig}_2]_n$ (lig = $\text{NC}_5\text{H}_4\text{Me-3}$ or $\text{NC}_5\text{H}_3\text{Me}_2\text{-3,5}$) [49].

3.2.4. $[\text{CdL2}(\text{I})_2]_n$ (**4**)

Chain polymer **4** shows close similarity to **2**, the analogous derivative of spacer ligand **L1**. The iodo ligands subtend the largest angle in the tetrahedral coordination sphere (136°), whereas the N1–Cd1–N2 angle amounts to only 98° . **4** is the only compound reported here in which the aryl rings within the space ligand are almost coplanar (Fig. 4a). This planar conformation of **L2** leads to a significantly longer distance between next-neighbour Cd cations (19.6 Å) than in **3** with its tilt ligand conformation (19.2 Å). Fig. 4b shows a section of the polymer chain. Closest interchain contacts comprise π stacking of aromatic rings with a closest interplanar C...C distance of 3.26 Å and non-classical hydrogen bonds between aryl H and N atoms of the azomethine with 2.63 Å. Cd(II) complexes with 3,3'-bipyridine derived linkers and iodo co-ligands

Fig. 4. (a) 1D zigzag structure of **4** resulting from **L2** bridging. Symmetry operators $i = x, \frac{1}{2} - y, z$; $ii = -x, y + \frac{1}{2}, 1 - z$; $iii = x, y + 1, z$. (b) Packing in polymer direction along $[1-1-1]$. H atoms have been omitted for clarity.

have not yet been reported; we therefore compare the cation coordination in **4** to CdI_2 derivatives with 3-substituted pyridine ligands. These compounds share a tetrahedral $\{\text{N}_2\text{I}_2\}$ coordination environment for the Cd(II) cation in which iodide acts as terminal ligand. We here mention $\text{CdI}_2(\text{C}_{30}\text{H}_{20}\text{N}_4\text{O})\cdot\text{CH}_2\text{Cl}_2$ ($\text{C}_{30}\text{H}_{20}\text{N}_4\text{O} = 2,5\text{-bis-}1,3,4\text{-oxadiazole}$) [61], $[\text{CdI}_2(3\text{-Mepy})_2]$ [35] and $[\text{CdI}_2(2,3\text{-dimethylpy})_2]$ [62].

3.3. Thermal stability

Thermal stability represents an important parameter of inorganic–organic hybrid materials. In order to study this property for **1**, **3** and **4**, thermogravimetric (TGA) and single differential thermal analyses (SDTA) experiments were performed in the temperature range of 25–800 °C in air.

The TGA curve for **1** confirms good thermal stability; no obvious weight loss was observed up to 240 °C. Weight loss above this temperature, in the region of 240–670 °C, occurs in three steps: the first is presumably due to release and decomposition of the naphthalene part of ligand **L1** (found 30.3%, calc 29.4%), and the next steps correspond to the elimination of the remaining part of **L1** and the acetate co-ligand (found 47.2%, calc 48.5%). The residue at 670 °C corresponds to CdO (found 21.9%, calc 22.6%). The SDTA pattern exhibits three exothermic events at 305, 500 and 635 °C (Fig. S5). A comparison with related framework structures derived

from the spacer ligand **L1** suggests intermediate thermal stability for **1**. Our coordination polymer is more stable than $[\text{Cu}(\mu\text{-L1})(\text{acac})_2]_n$ and $[\text{Cu}_2(\mu\text{-L1})(\mu\text{-OAc})_4]_n$ [30] but less stable than $[\text{CdL1}_{1.5}(\text{NO}_3)_2]_n$ [26], $[\text{AgL1}_2]\cdot(\text{PF}_6)$ and $[\text{CoL1}_{1.5}(\text{NO}_3)_2]$ decompose at similar temperatures [27,28] as **1**.

3 and **4** are thermally less stable than **1**. **3** releases a small non-stoichiometric amount of surface-attached methanol in the temperature range between 60 and 180 °C. The polycrystalline sample is thermally stable up to 210 °C, and then an almost continuous weight-loss between 210 and 640 °C occurs. It corresponds to the release of the ligands **L2** and acetate (found 72.54%, calc 73.4%) and finally affords a solid residue of CdO 650 °C (found 21.8%, calc. 21.4%). The SDTA curve displays two exothermic peaks at 500 and 530 °C (Fig. S6). **3** and **4** are similar with respect to thermal stability, but their decomposition modes differ according to their co-ligands. **4** is stable up to 220 °C. The first weight loss in the range between 220 and 425 °C is due to the removal of one iodide (found 17.1%, calc 18.2%), and the step in the range of 425–750 °C can be associated with release of **L2** and the second iodide. However, the slope of the TGA curve (Fig. S7) seems to indicate that this process is not yet complete at 750 °C. The SDTA curve displays two exothermic peaks at 410 and 490 °C. $[\text{ZnL2}(\text{NO}_3)_2]$ [26] represents the only derivative of **L2** for which thermal properties have been reported; it is more stable than **3** and **4**. Our coordination polymers **1** and **3** represent cadmium(II) complexes with acetate co-ligands; they are thermally more stable than similar complexes with substituted pyridine ligands such as $[\text{Cd}_2(\mu_2\text{-}\kappa^2\text{:}\kappa^1\text{-OAc})_2(\mu_2\text{-}\kappa^1\text{:}\kappa^1\text{-OAc})_2\text{lig}]_2$ (lig = NC_5H_5 , $\text{NC}_5\text{H}_4\text{Me-3}$ or $\text{NC}_5\text{H}_3\text{Me2-3,5}$) [49].

3.4. Luminescence properties

Luminescent coordination polymers based on d^{10} metal cations and conjugated linkers have attracted interest because of their potential applications for sensor technologies, photochemistry and electroluminescent displays [63,64].

The presence of Cd(II) metal cations with d^{10} electron configuration and the conjugated π system of the rigid spacer ligands in our compounds suggests to investigate their potential as hybrid luminescent materials. The solid state emission spectra of the uncoordinated ligands **L1** and **L2** and of the coordination polymers **1**, **3** and **4** obtained at room temperature as depicted in Fig. 5. Upon excitation at 380 nm, the ligands **L1** and **L2** display emission peaks with maxima at 595 and 612 nm, respectively. They can be attributed to intraligand $\pi\text{-}\pi^*$ emissions. At the same excitation wavelength their complexes exhibit more intense and broad emission spectra with maxima at 604 nm for **1**, 638 for **3** and 623 nm for **4**. These emissions are only slightly red-shifted in comparison to the uncoordinated ligands; we therefore assume that the luminescence in **1**, **3** and **4** is due to ligand-centered electronic transitions within the aromatic systems. The relative intensity is stronger for the complexes than for the uncoordinated ligands, since metal coordination effectively increases the conformational rigidity of the ligands and hence decreases the non-radiative decay of intraligand excited states [65–67]. Our new coordination polymers represent potential candidates within the wide variety of low-cost electronic and optoelectronic devices which show broad luminescence emission peaks, electron accumulation, conjugated structures and promising stability towards humidity and elevated temperatures [68–70].

4. Conclusions

Four new 1-D and 2-D coordination polymers based on Cd(II) have been successfully prepared by reactant diffusion between two rigid isomeric bifunctional ligands **L1** and **L2** and two

Fig. 5. (a) Solid state luminescence emission spectra for **1** and ligand **L1**. (b) Solid state luminescence emission spectra for **3**, **4** and ligand **L2**.

alternative co-ligands, acetate and iodide. Analysis of the resulting extended structures revealed that these co-ligands and the associated coordination environment about the metal cations rather than the different disposition of the N donor atoms in the isomeric ligands play the pivotal role for the resulting supramolecular architectures. For the acetato complexes **1** and **3**, topologies unprecedented for bis(pyridin-4-ylmethylene)naphthalene-1,5-diamine (**L1**) and 3,3'-bipyridyl-derived organic ligands have been encountered. The coordination polymers are thermally stable up to at least 210 °C, with slightly higher stability for **1** than for **3** and **4**. Differences in the thermal decomposition pathway of **3** and **4** underline the relevance of the co-ligands not only for the crystal structures but also for the properties of these coordination compounds. **1**, **3** and **4** show higher emission intensities at room temperature than the uncoordinated expanded heteroaromatic ligands **L1** and **L2** and thus confirm that the metal cations play a key role for luminescence properties; our compounds appear promising candidates as hybrid organic–inorganic photoactive materials. In summary, the appropriate choice of semi-rigid spacer ligands, metal cations and matching co-ligands allows to synthesize coordination polymers which do not only show interesting solid state structures but also exploitable properties.

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Appendix A. Supplementary data

CCDC 1527447, 1527445, 1527446 and 1527444 contains the supplementary crystallographic data for **1–4**. These data can be obtained free of charge via <http://dx.doi.org/10.1016/j.poly.2017.05.023>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2017.05.023>.

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