

Synthesis, structure and luminescence properties of zinc and cadmium linear-chain compounds with anionic monoalkoxy-tetracyanopropenes bridged by 4,4'-bipyridines

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ABSTRACT

The synthesis, characterization and 3D structure determination of Zinc and Cadmium compounds are reported, containing the non-chelating bidentate ligand 4,4'-bipyridine and the anions 1,1,3,3-tetracyano-2-propoxy-propenide (tcnopr) or 1,1,3,3-tetracyano-2-ethoxy-propenide (tcnoet). The structures consist of linear chains (1D) built from metal ions and 4,4'-bipyridine, where the octahedral coordination around the metals is completed by two trans anions tcnoet (or tcnopr), and two trans-oriented water molecules. Weak interchain interactions are present, based on hydrogen bonds between the water ligands (both hydrogens are involved) and two CN groups of two nearby other chains. Metal-ligand distances appear as uneventful. For the same anion, the Zn and Cd compounds are isomorphous. Possible decomposition of the compounds has been investigated in the temperature range 30–800 °C in a static air atmosphere. Thermal analysis studies (TG, DTG, DTA) show that the axial water ligands for all three compounds are gradually lost upon heating above 60 °C to about 170 °C. Luminescence properties, recorded as powders, are reported as well, and these appear as strong for the Cd compound **I**, when irradiated at 390 nm, extremely weak for the Cd compound **II**, when irradiated at wavelengths from 300–400 nm, and moderately weak for the Zn compound **III** when irradiated at 385 nm.

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1. Introduction

In recent years d¹⁰ metal coordination compounds comprising zinc(II) and cadmium(II) with a variety of poly-pyridyl ligands, have attracted increasing attention due to their interesting luminescence properties [1–7].

The use of polynitrile anions as ligands, either alone or in combination with neutral co-ligands, is a very versatile and effective strategy for developing molecular architectures with different topologies and dimensionalities, as a result of their geometric flex-

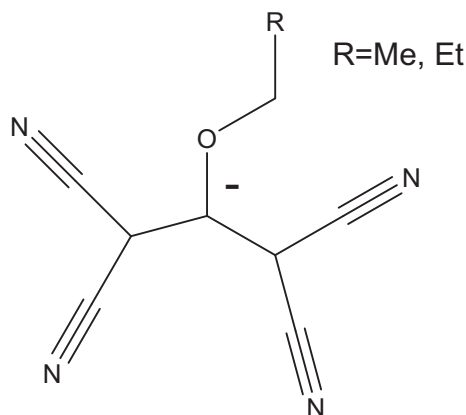
ibility and ability to coordinate and bridge metal ions in many different ways [8–14]. The presence of other potential donor groups such as –OH, –SH or –NH₂, together with their rigidity and their high electronic delocalization, can lead to the synthesis of new magnetic [15–21] and luminescent [22–24] coordination polymers with transition-metal ions. Apart from coordination on the nitrile groups, they can also accept hydrogen bonds, e.g. from coordinated or lattice water. Schematic structures of the anionic ligands are depicted in Scheme 1.

Given the crucial role of these anionic ligands, we became interested in using them in combination with other chelating or bridging neutral co-ligands in order to design and generate new luminescent coordination polymeric materials.

We report here the synthesis, characterization, structure determination, thermal stability and luminescent properties of the first 3 compounds.

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Scheme 1. Schematic structure of the used anionic ligands tcnopr, and tcnobet.

2. Experimental

2.1. Materials and physical measurements

The starting materials and solvents were purchased from commercial sources (analytical reagent grade) and used without further purification. The two cyanocarbanion salts, i.e. K(tcnobet) and K(tcnopr), have been prepared following the known recipes [25,26].

Elemental analyses of the obtained compounds (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. Infrared spectra were recorded in the range 4000–500 cm^{-1} on a FT-IR Bruker ATR Vertex 70 Spectrometer. The TG, DTA and DTG measurements were carried out using a Perkin-Elmer Diamond TG/DTA Thermal Analysis Instrument under static air at a heating rate of 10 K min^{-1} from 30 to 800 $^{\circ}\text{C}$ using platinum crucibles. The excitation and emission spectra were performed at room temperature by using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a Shimadzu solid-state sample holder.

2.2. Synthesis

2.2.1. Synthesis of *catena*-[Cd(H₂O)₂(4,4'-bpy)(tcnoet)₂] (I)

Compound (I) was synthesized solvothermally under autogenous pressure from a mixture of Cd(OAc)₂·2H₂O (54 mg, 0.2 mmol), 4,4'-bipyridyl (16 mg, 0.1 mmol) and Ktcnoet (90 mg, 0.4 mmol) in water-methanol (4:1 v/v, 20 mL). This mixture was sealed in a Teflon-lined autoclave and heated at 130 $^{\circ}\text{C}$ for 2 days. After cooling to room temperature at a rate of 10 $^{\circ}\text{C h}^{-1}$, colorless crystals were obtained containing I, and some impurities that could be manually separated. A powder profile of the Cd compound (I) is shown in Fig. S1. Elemental analysis and IR data for hand-picked crystals: *Anal. Calc.* for C₂₈H₂₂CdN₁₀O₄ (674.6 g/mol): C, 49.81; H, 3.29; N, 20.76. Found: C, 49.79; H, 3.41; N, 20.54%. Main IR band (ATR-IR, cm^{-1}): $\nu_{(\text{CN})}$: 2194(s).

2.2.2. Synthesis of *catena*-[Cd(H₂O)₂(4,4'-bpy)(tcnopr)₂] (II)

To mixture containing Cd(OAc)₂·2H₂O (54 mg, 0.2 mmol) and 4,4'-bipyridyl (16 mg, 0.1 mmol) dissolved in water-methanol (1:1 v/v, 10 mL), an aqueous solution of Ktcnopr (80 mg, 0.4 mmol) in 5 mL H₂O was added. The resulting solution was heated to 90 $^{\circ}\text{C}$ for 10 min, filtered and then allowed to crystallize at room temperature. After two weeks, yellow crystals of II appeared which were washed with the mother liquid and dried. *Anal. Calc.* for C₃₀H₂₆CdN₁₀O₄ (702.6 g/mol): C, 51.24; H, 3.73; N, 19.93. Found: C, 50.97; H, 3.69; N, 19.69%. Main IR band (ATR-IR, cm^{-1}): $\nu_{(\text{CN})}$: 2187(s).

2.2.3. Synthesis of *catena*-[Zn(H₂O)₂(4,4'-bpy)(tcnopr)₂] (III)

The compound was synthesized following a procedure similar to that of compound (II), except that Zn(OAc)₂·2H₂O (44 mg, 0.2 mmol), was used instead of Cd(OAc)₂·2H₂O. Yellow colored crystals were obtained containing III. The powder profile of the Zn compound (III) is shown in Fig. S3. *Anal. Calc.* for C₃₀H₂₆ZnN₁₀O₄ (655.6 g/mol): C, 54.91; H, 4.00; N, 21.36. Found: C, 54.52; H, 3.97; N, 21.14%. Main IR band (ATR-IR, cm^{-1}): $\nu_{(\text{CN})}$: 2195(s).

2.3. X-ray crystallography

For the compound I suitable single crystals were selected and measured around 95 K on a four-circle diffractometer Supernova of Rigaku Oxford Diffraction using Cu K α radiation from a microfocus source and a mirror collimator, and a CCD detector Atlas S2. Suitable single crystals of II and III were measured around 120 K with a four-circle CCD diffractometer, Gemini of Oxford Diffraction, using Mo K α radiation from a classical sealed tube monochromated by graphite and collimated by fibre-optics Enhance collimator. As a detector the CCD detector Atlas S2 was used. Data of all compounds were processed with the CrysAlis software [27]. Crystal structures were easily solved by charge flipping with program SUPERFLIP package [28] and refined with the Jana2006 program [29] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by using Diamond [30] and Mercury [31] software. According to common practice, H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å, while H atoms bonded to O were refined. For all hydrogen atoms we kept $U_{\text{iso}}(\text{H})$ equal to 1.2 $U_{\text{eq}}(\text{C/N})$. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Powder samples were measured with an Empyrean diffractometer of PANalytical with Cu K α radiation and a Nickel beta filter in the 2θ range of 4.5–80 $^{\circ}$. Profile parameters were refined with Jana2006 [29]. X-ray powder patterns for each compound are added in supplementary (Figs. S1–S3). The profile matching of compound II and III show a pure composition contrary to the compound I, where impurities appear to be present in the powder.

3. Results and discussion

3.1. Synthesis and characterization

The starting salts K(tcnobet) and K(tcnopr) were synthesized and characterized as before [19,23,25,26], and further used in the synthesis of the three new compounds. The elemental analysis and infrared spectra of compound I was performed on a pure phase, manually separated under a binocular microscope. The impurities in the bulk sample, mentioned above, are ascribed to products that resulted from partial decomposition of the polynitrile anions under the solvothermal conditions [21]. The three derivatives exhibit quite similar infrared spectra patterns, especially in the range 2250–2150 cm^{-1} which can be attributed to the CN bonds vibrations, i.e. a strong broad band at 2194 cm^{-1} for I, 2187 cm^{-1} for II and 2195 cm^{-1} for III. These features do not allow any discussion about the coordination of the CN groups in these derivatives, since the three absorption bands are similar to those observed for the starting potassium salts of both anions (Ktcnoet: 2196(s) cm^{-1} and Ktcnopr: 2198(s) cm^{-1}) in which the interaction between the CN groups and the potassium ions do not affect significantly the absorption bands of the nitrile groups. So, for further characterization of the 3 new compounds, in addition to the elemental analysis and IR spectra, X-ray diffraction, thermal analysis and luminescence studies were performed, which will be described below. No pure Zn compound with the tcnobet anion could be isolated.

Table 1
Crystal data and structure refinement parameters for compounds **I**, **II** and **III**.

	Compound I	Compound II	Compound III
Crystal data			
Chemical formula	C ₂₈ H ₂₂ CdN ₁₀ O ₄	C ₃₀ H ₂₆ CdN ₁₀ O ₄	C ₃₀ H ₂₆ ZnN ₁₀ O ₄
Formula weight	674.6	702.6	655.6
Temperature (K)	95(1)	120(1)	120(1)
Wavelength (Å)	1.54184	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	C2/c	Fdd2	Fdd2
Unit cell dimensions			
a (Å)	12.1556(5)	11.8248(9)	12.1413(11)
b (Å)	11.7067(5)	45.6858(3)	44.9388(4)
c (Å)	21.3875(9)	11.7875(3)	11.4963(3)
β (°)	99.867(3)		
V (Å ³)	2998.5(2)	6367.9(5)	6272.6(6)
Z	4	8	8
D _{calc} (g/cm ³)	1.495	1.467	1.389
Absorption coefficient (mm ⁻¹)	6.27	0.74	0.84
F(0 0 0)	1360	2848	2704
Index ranges	-14 ≤ h ≤ 13 -13 ≤ k ≤ 9 -25 ≤ l ≤ 25	-16 ≤ h ≤ 15 -61 ≤ k ≤ 61 -16 ≤ l ≤ 16	-16 ≤ h ≤ 16 -56 ≤ k ≤ 60 -15 ≤ l ≤ 15
Reflections collected	4496	25 556	26 136
Independent reflections	2656 [R _{int} = 0.022]	4177 [R _{int} = 0.085]	4074 [R _{int} = 0.062]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	2656/0/203	4177/1/213	4074/1/213
Goodness-of-fit (GoF) on F ²	1.75	1.088	1.01
Final R indices [I > 3σ(I)]	R ₁ = 0.039, wR ₂ = 0.104	R ₁ = 0.038, wR ₂ = 0.065	R ₁ = 0.036, wR ₂ = 0.077
Largest difference peak and hole (e Å ⁻³)	1.63 and -1.14	0.95 and -0.83	0.67 and -0.37

3.2. Description of the crystal structures

The compounds [Cd(H₂O)₂(4,4'-bpy)(*tcnoet*)₂] (**I**) and [Cd(H₂O)₂(4,4'-bpy)(*tcnopr*)₂] (**II**) are closely related from the chemical point of view, the single difference being the functional group for the alkoxyoxy site of the polynitrile ligand, i.e. an oxyethyl group in **I** and an oxypropyl group in **II**. Although both compounds share many structural features, they crystallize with different crystal symmetry, i.e. monoclinic for **I** and orthorhombic for **II**. The Zn compound (**III**) has also been characterized, while using *tcnopr* (Table 1) and appears as isomorphous with compound **II**.

Crystal **I** belongs to space group C2/c, and the asymmetric unit contains half the formula, since both the metal center and the 4,4'-bpy ligand lie on the twofold axis. On the other hand, the symmetric 4,4'-bpy ligand is bidentate, and has resulted in a polymerization direction along this twofold axis, in the [0 1 0] direction. As a result, the Cd²⁺ ion displays an almost perfect octahedral coordination geometry, with two *trans* 4,4'-bpy ligands, two *trans* monodentate *tcnoet* anionic ligands bonding through one cyano functionality, and two *trans* water molecules (Fig. 1).

Coordination bond lengths span a short range: 2.297(4)–2.347(3) Å. Regarding the ligand conformations, the 4,4'-bpy molecule

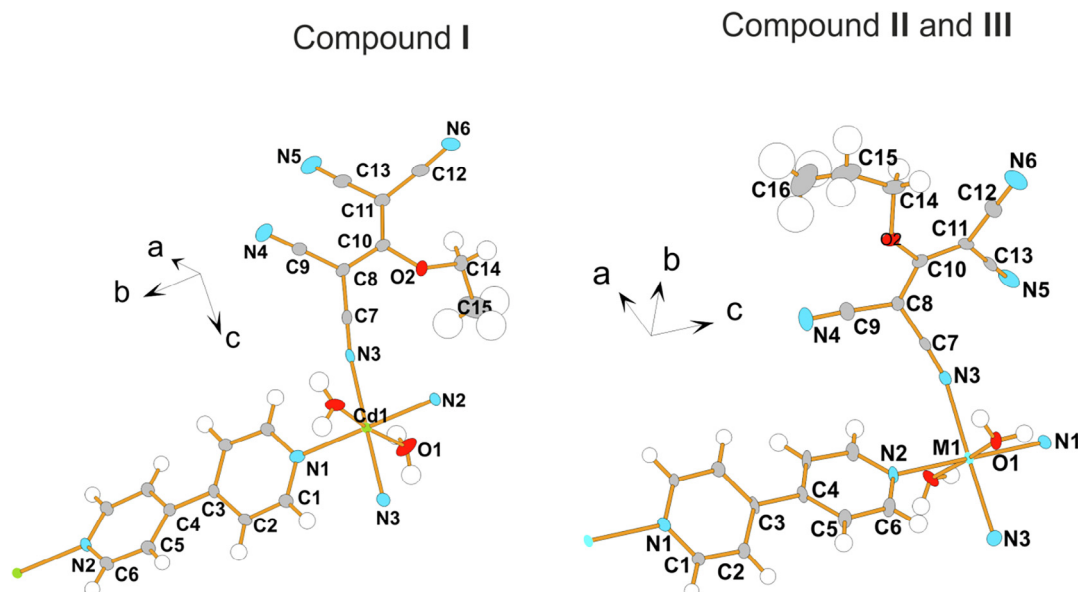


Fig. 1. Coordination environments of Cd and Zn for part of the polymeric structures in compound **I** (left) and for that of compounds **II** and **III** (right). The molecules are drawn using the ellipsoid definition of the anisotropic's atomic displacement models (50% probability ellipsoids).

has the aromatic rings forming a dihedral angle of 28.1°, a conformation by far less common than the planar bridging 4,4'-bpy molecule. Also, the *tcnoet* ligand is not planar, with the dicyano moieties making a dihedral angle of 35.2°. However, this anion is known to be highly flexible: for 34 crystal structures containing *tcnoet* deposited so far in the CSD [32–34] the dihedral angle formed by dicyano groups has been observed in the range 9.9–43.9°, with no clear correlation between the stabilized conformation and the role of *tcnoet*, which may be a free anion [35,36], a monodentate ligand [19,37], or a bidentate [25], or tridentate bridging ligand [38]. The bridging ligand 4,4'-bpy is that providing the node for polymerization to form a 1D system for **I**. The other cyano groups in *tcnoet* are not engaged in further polymeric bonds, and this anion thus behaves as a monodentate ligand, despite of having potentially five donor atoms for coordination. Bridging 4,4'-bpy ligands between Cd ions are not new in literature, as learned from a CSD search [34], but only a few are polynuclear [39,40].

Using *tcnopr* instead of *tcnoet* gave a crystal with higher symmetry, *Fdd2* vs. *C2/c*. However, the content for the asymmetric unit is identical in both cases, since the two-fold rotation symmetry is also present in the coordination environment for **II** (see Fig. 1). Both the Cd²⁺ cation and the 4,4'-bpy ligand lie on the twofold axis, as in **I**, and the metal center displays an octahedral geometry with symmetry-related ligands arranged *trans*, with coordination bond lengths in the range 2.307(3)–2.344(8) Å. Even the conformation of ligands is retained, with the dihedral angle for 4,4'-bipy rings being 30.1° and the angle between dicyano groups in *tcnopr* being 36.8°. The bridging 4,4'-bpy ligand forms the 1D polymeric chain in the [0 0 1] direction, along the twofold symmetry axis.

The isotopic compound based on Zn²⁺, [Zn(H₂O)₂(4,4'-bpy)(*tcnopr*)₂] (**III**) has also been characterized, for which Zn–O/N bond lengths range from 2.088(4) to 2.208(4) Å, which agree with a smaller ionic radius for Zn²⁺, compared to Cd²⁺. In that compound, angles characterizing the conformations for ligands are 37.4° (4,4'-bpy) and 36.6° (*tcnopr*). Zinc compounds with bridging 4,4'-bpy ligands between the metal ions are common in literature, as learned from a CSD search [3,41–43], but linear chains quite rare [41].

Inside **I**, **II** and **III** relatively large atomic displacement parameters are observed for the ethyl and propyl part of ligands *tcnoet* and *tcnopr* (see Fig. 1), expressed by large displacement ellipsoids. This large displacement corresponds to a dynamic disorder inside that part of the ligand. The disorder may be due to the absence of hydrogen bonds to stabilize the ligand part. Although the ligands *tcnoet* and *tcnopr* behave as monodentate ligands, and the 4,4'-bpy bidentate node allows the formation of the polymeric 1D structures, different packing structures are to be expected for the *C2/c* crystal and the *Fdd2* crystals. An essential difference is, for example, that the former space group is centrosymmetric while the latter is not.

For compound **I**, polymeric chains are arranged in such a way that rather efficient inter-chain hydrogen bonds are formed. Centrosymmetric $R_2^2(20)$ ring motifs connect the chains, using the coordinating water molecule as donor and uncoordinated cyano groups C13≡N5 and C12≡N6 as acceptor (Fig. 2). The resulting contacts are characterized by short H...N separations and rather flat angles O1–H2o1...N6 = 170, resp. 153° with O...N contact distances of 2.77 and resp. 2.90 Å (Table 2). The other H atom of the water molecule is also involved in other ring motifs including non-coordinating cyano groups, although of much weaker strength. However, it could be inferred from the observed crystal structure that the polymeric nature of the compound is limited to a 1D system as a consequence of the poor coordinating character of the ligand *tcnoet* and the involvement of the water molecules in hydrogen bonding.

For compound **II**, the crystal structure is also based on ring motifs formed through hydrogen bonds between the water mole-

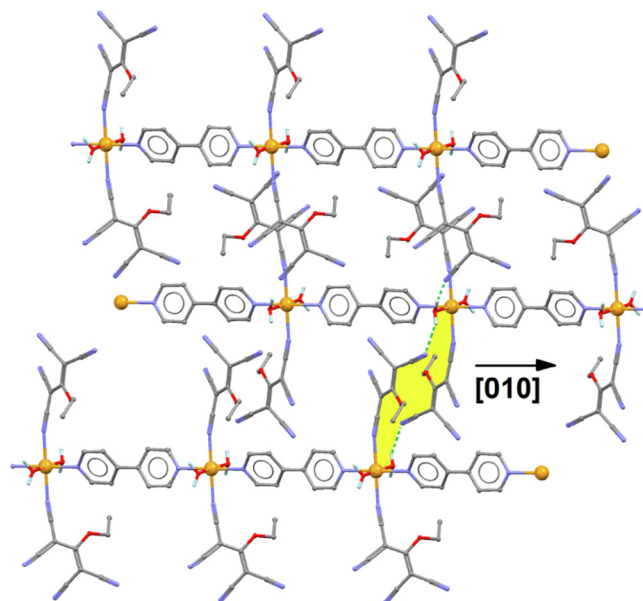


Fig. 2. Part of the crystal structure of compound **I**, showing three parallel chains in the monoclinic cell. Dashed bonds are O–H...N hydrogen bonds, and the yellow cycle corresponds to the smallest ring motif in the crystal structure, $R_2^2(20)$.

cule and non-coordinating cyano groups. In that case, the smallest ring is $R_2^2(25)$, and includes the 4,4'-bpy ligand (Fig. 3). This motif is obviously non-centrosymmetric; however, the strength of the hydrogen bonds O1–H2o1...N6 and O1–H2o2...N4 are similar to those of the main contacts in **I**, with H2o1...N6 = 2.11 Å and O1–H2o1...N6 = 167°, O...N = 2.90 Å and likewise H2o2...N4 = 2.00 Å and O1–H2o2...N6 = 175° and O...N = 2.80 Å (see Table 2). The crystal structure contains the largest ring motifs, all based on an odd number of atoms, for example $R_4^4(49)$. Similar details and distance/angles are found for compound **III** (see Table 2).

3.3. Thermal analysis of the compound

The thermal decomposition behaviors of the three compounds were performed in the temperature range 30–800 °C in static air atmosphere. Thermoanalytical data and thermal decomposition curves of the compounds are given Figs. 4 and S4–S5. The thermal decompositions of the compounds proceeded in three mass loss stages. All of the compounds followed an almost identical decomposition mechanism, i.e. first release of two coordinated water molecules followed by the neutral ligand 4,4'-bpy, and finally decomposition with the loss of anionic ligands (*tcnoet* for **I** and *tcnopr* for **II** and **III**). Compounds **I**, **II** and **III** are all stable upon light heating. Water losses start at 55, 107 and 110 °C, respectively.

In the first stage the compounds started to lose two water ligands between 55 and 154 °C (found 5.56%, calcd. 5.33%) for compound **I**, between 107 and 175 °C (found 5.25% calcd. 5.12%), for compound **II** and between 110 and 166 °C (found 5.46%, calcd. 5.49%) for compound **III**. In the second stage between 154 and 367 °C for compound **I**, between 175 and 427 °C for compound **II** and between 166 and 493 °C for **III** are related to the release of the 4,4'-bpy neutral ligand (DTA_{max} = 229 °C, found 21.85%, calcd. 23.13%, for **I**, DTA_{max} = 242 °C, found 21.85%, calcd. 22.21% for **II** and DTA_{max} = 221 °C, found 21.89%, calcd. 23.80% for **III**), respectively.

In the following stages, the exothermic peaks in the temperature range of 367–601 °C (DTA_{max} = 525 °C, found 53.29%, calcd. 55.16%) for **I**, 427–616 °C (DTA_{max} = 534 °C, found 56.55%, calcd.

Table 2
Selection of H-bond parameters of Compounds **I**, **II** and **III**.

Donor	H	Acceptor	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
I						
C11	H2c11	C14	0.96	2.45	2.943 (6)	111.59
O1	H1o1	N5 ^{iv}	0.87 (5)	1.91 (6)	2.771 (5)	170 (6)
O1	H2o1	N6 ^v	0.81 (6)	2.14 (6)	2.889 (5)	153 (5)
Symmetry codes: (iv) $x + 1/2, -y + 1/2, z + 1/2$; (v) $-x, -y, -z$						
II						
O1	H2o1	N6 ^{iv}	0.80 (4)	2.11 (4)	2.897 (5)	167 (4)
O1	H1o1	N4 ^v	0.80 (3)	2.00 (3)	2.796 (5)	175 (4)
Symmetry codes: (iv) $x - 1/4, -y + 1/4, z - 1/4$; (v) $x - 1/2, y, z + 1/2$						
III						
O1	H2o1	N6 ^{iv}	0.83 (2)	2.04 (2)	2.853 (3)	169 (2)
O1	H1o1	N4 ^v	0.83 (2)	1.93 (2)	2.753 (3)	176 (3)
C1	H1c1	N3	0.96	2.44	3.078 (4)	123.86
Symmetry codes: (v) $x - 1/2, y, z + 1/2$; (vi) $x - 1/4, -y + 1/4, z - 1/4$						

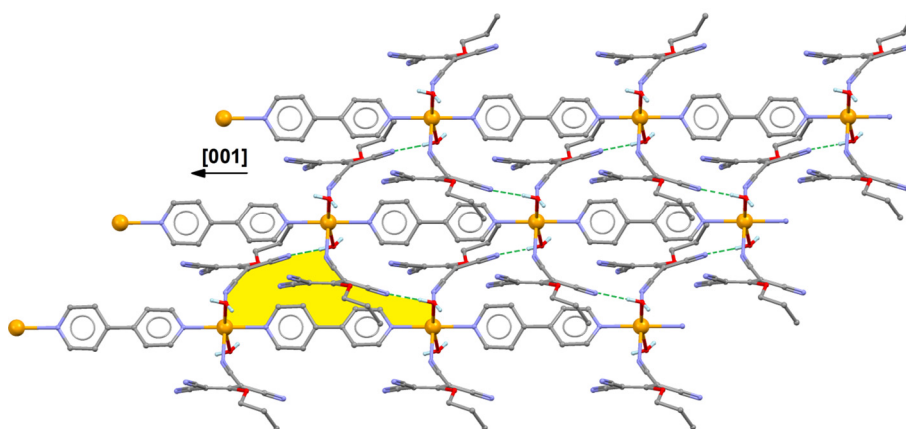


Fig. 3. Part of the crystal structure of compound **II**, showing three parallel chains in the orthorhombic cell. Dashed bonds are O–H...N hydrogen bonds, and the yellow cycle corresponds to the smallest ring motif in the crystal structure, $R_2^2(25)$.

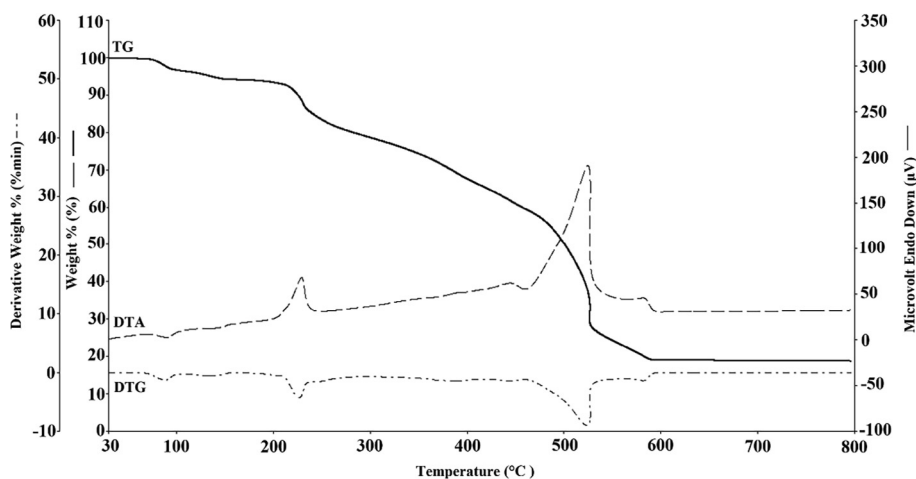


Fig. 4. The TG, DTG and DTA curves of compound **I**.

58.10%) for **II** and 493–735 °C ($DTA_{max} = 622$ °C, found 60.95%, calcd. 62.26%) for **III** correspond to the decomposition of the two *tnoet* ligands for **I** and the two *tnopr* ligands for **II** and **III**, respectively. The final decomposition products were identified as CdO for **I** and **II** [found (calcd.) (%) = 19.01 (19.02) for **I** and found (calcd.) (%) = 16.29 (18.26) for **II**] and ZnO for **III**, [found (calcd.) (%) = 12.51 (12.40)].

The differences in thermal behavior, especially the loss of water molecules are quite interesting. For compounds **I** and **II** the slight increase in the size of the anion, should be held responsible for this higher thermal stability. For compounds **II** and **III** the slight decrease in the size of the cation (Cd to Zn), should be held responsible for this higher thermal lattice stability and is reflected by its higher melting point.

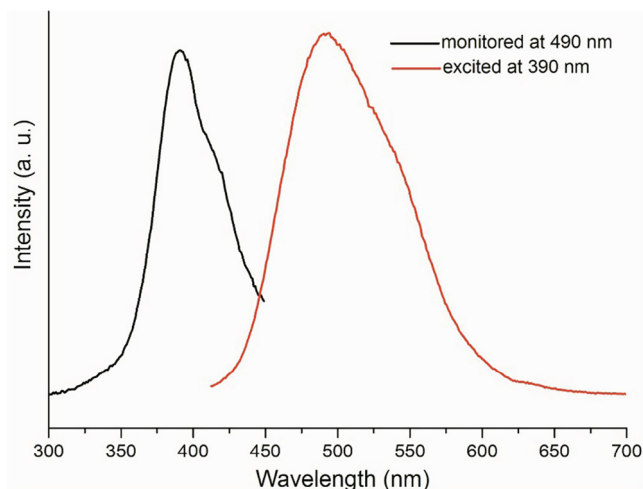


Fig. 5. Room temperature solid-state excitation (black) and emission (red) spectra of compound **I**. Intensities are in arbitrary units (a.u.). (Color online.)

3.4. Emission and excitation spectra

Solid-state emission and excitation spectra of all three compounds have been recorded at room temperature on the pure crystalline phases. The result for compound **I** is depicted in Fig. 5. When excited at 390 nm light, compound **I** shows a single quite strong emission maximum near 490 nm. This band is tentatively ascribed to a ligand $\pi-\pi^*$ transition, as is found in other related cases [23,39,44,45].

Surprisingly, the excitation spectrum of compound **II** having the larger propoxy-containing anion, when studied under several wavelengths (300, 320, 340, 360 and 380 nm) showed no luminescence at all. It remains puzzling why such a small ligand variation results in such a dramatically different luminescence behavior. Perhaps the differences in thermal motion of the OEt and OPPr groups could have an effect on the quenching.

Therefore, it was decided to also study the isomorphous Zn compound (**III**). Often luminescence of Zn and Cd compounds are similar [24]. In this case luminescence was found for the Zn compound, albeit with two relatively weak luminescence bands. Excitations at 385 and 430 nm, resulted in emission maxima at 480 and 510 nm; the diagram is presented in Fig. S6. The origin of the double band is not clear [46].

4. Concluding remarks

The present study has shown that a combination of rigid and bridging ligands, like 4,4'-bipyridine, with Cd and Zn cations and coordination CN-based anions, can yield interesting polynuclear, linear-chain based, structures. In all compounds only one of the CN groups coordinated to the metal. Some of the other CN groups accept hydrogen bonds from water ligand of a neighboring chain. The luminescence, or its quenching are not fully understood, as the isomorphous compounds **II** and **III** have quite different luminescence, suggesting that also the metal plays a role, and not just the ligand $\pi-\pi^*$ transitions.

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Appendix A. Supplementary data

CCDC 1905493, 1905504 and 1905505 contains the supplementary crystallographic data for compounds **I**, **II** and **III**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, 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 to this article can be found online at <https://doi.org/10.1016/j.poly.2019.05.028>.

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