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Luminescent Coordination Polymers Based on Self-Assembled Cadmium Dipyrrin Complexes

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Abstract: A series of novel Cd^{II} complexes based on α,β-unsubstituted dipyrrin ligands (dpm) has been prepared and characterised both in solution and in the solid state. These compounds are of the $[Cd(dpm)_2]$ type, with the coordination sphere of the metal centre occupied by two dpm chelates. Interestingly, in contrast to what has been reported for the Zn^{II} analogues, in the presence of a pyridyl- or imidazolyl-appended dpm ligand, the coordination number of the Cd^{II} cation can be increased to six, leading to an octahedral coordination sphere. As a consequence, the formation of 1-, 2-, and 3D coordination polymers by self-assembly is observed. Photophysical investigations of the discrete complexes and self-assembled networks have demonstrated that both types of compounds are luminescent in the solid state.

Keywords: cadmium · coordination polymers · dipyrrin · luminescence · self-assembly

Introduction

Over the past two decades, the field of coordination networks, also called coordination polymers (CPs) or metal–organic frameworks (MOFs), has been the subject of intense research activity fuelled by their applications in gas storage, sensing, separation, catalysis, and magnetism, among others.[1] MOFs are also appealing as novel luminescent materials.[2] Indeed, in these species, resulting from the self-assembly of metal centres and organic tectons,[3] the emission properties can be generated by either the inorganic or organic components, as well as by metal–ligand charge-transfer processes or by the presence of guest molecules in the frameworks. The majority of the reported luminescent CPs are based on Zn^{II}, Cd^{II}, Ag^{I}, or lanthanide ions assembled with polycarboxylate- or pyridyl-based tectons.[2] Interestingly, to the best of our knowledge, no luminescent infinite crystalline architectures based on dipyrrins (dpms)[4] have hitherto been described. This is surprising, considering that several discrete luminescent dpm complexes have been reported, most of which are Zn^{II}-based species,[5–8] along with bispyrrolic-based homo- and heterometallic CPs.[9–12] Heterometallic dpm-based networks result from the association of metallatectons bearing coordinating groups at the periphery of the dpm moieties with other metal centres, in particular Ag^{I}.[10,11] As regards homometallic analogues, the metallatectons are based on metal complexes bearing self-complementary hydrogen-bonding groups[12] or [Cu(acac-R)(dpm-R′)] species (acac-R = functionalised acetylacetonate derivative) with functionalised monodipyrrin ligands capable of self-assembly to form extended architectures by coordination.[11] Although one example of a luminescent nanoscale architecture derived from the combination of Zn^{II} cations with divergent bisdpms has been reported,[5d] no self-assembled Zn-based networks with monodpm have hitherto been described. This may be related to the fact that, unlike what is observed for Zn porphyrins, the metal cation in $[Zn(dpm)_2]$-type complexes has not been reported with a coordination number greater than four (Figure 1).[6] For example, Zn complexes of dpms **1**–**4** (Scheme 1) were found to crystallise as discrete complexes with or without a peripheral coordinating group (Figure 1 b).[6,13] Furthermore, upon addition of excess pyridine or 1-methylimidazole to $[Zn(\mathbf{1})_2]$, no binding of these ligands to the Zn^{II} centre could be detected by NMR spectroscopy in $CDCl_3$ (Figure 1 a).[6] In contrast, the chemistry of dpm-based Cd^{II} complexes is almost unexplored, and some of the few reported examples of such species incorporating α-substituted dpms show a coordination number higher than four for the cadmium cation.[14] This suggests that, unlike for $[Zn(dpm)_2]$ compounds, the Cd^{II} centre in $[Cd(dpm)_2]$ species may be capable of penta- or hexacoordination in the presence of additional coordinating groups (Figure 1). It is worth noting that the latter can be introduced either independently, leading to discrete species (Figure 1 a) or at the periphery of the dpm moiety, thus promoting self-assembly into infinite architectures (Figure 1 b). In addition, in light of the reported photophysical properties of the Zn compounds,[5,6] luminescence can be anticipated for the Cd analogues.

We report herein the synthesis and characterisation in solution and in the solid state of α,β-unsubstituted dipyrrin

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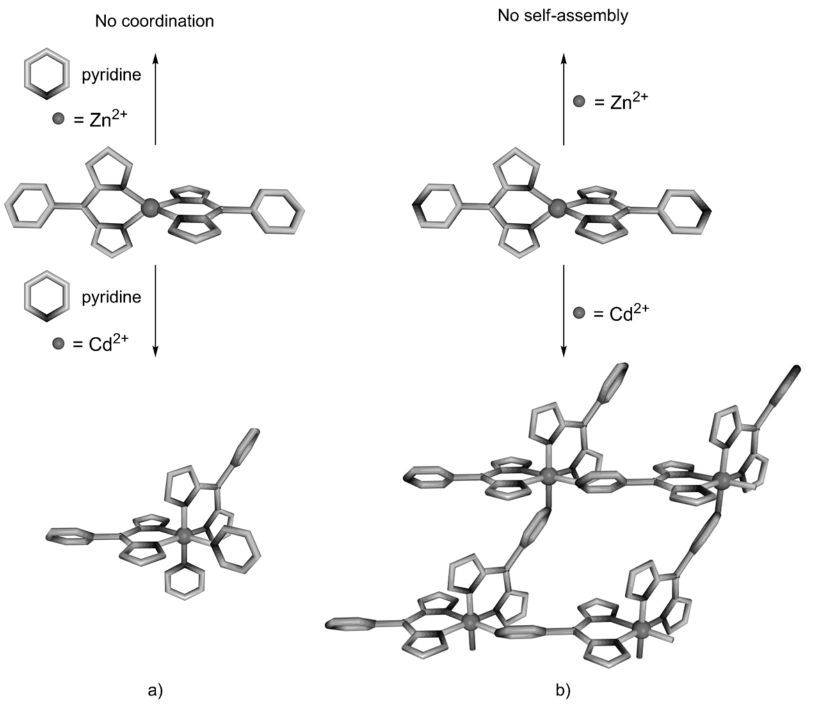
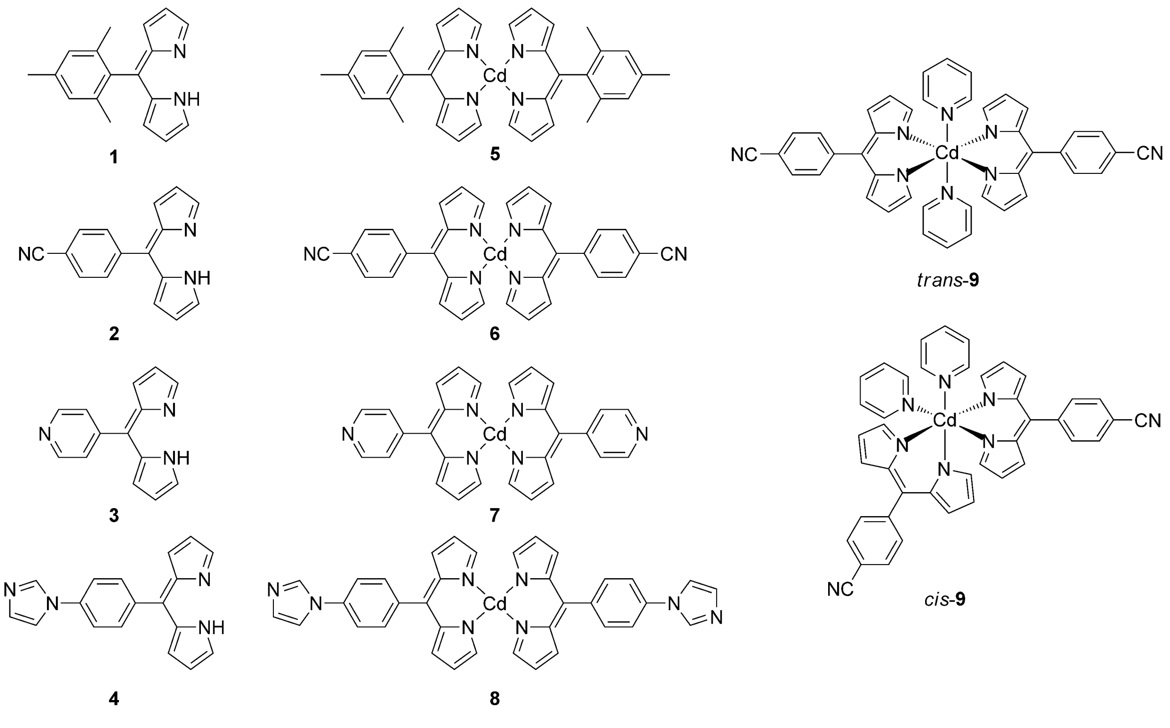


Figure 1. Schematic representation of the effects of the presence of additional coordinating units either a) as an external ligand or b) at the periphery of the dpm as reported previously[6] for $[Zn(dpm)_2]$ complexes and as expected for $[Cd(dpm)_2]$ derivatives.

Cd^{II} complexes, with a particular emphasis on the use of these compounds as metallatectons for the preparation of luminescent coordination polymers.

Results and Discussion

Design: Dipyrrins **1–4** (Scheme 1) were chosen as ligands for the synthesis of $[Cd(dpm)_2]$ complexes. Derivative **1** consists of a dpm chelate and a mesityl peripheral group. Although this latter moiety is not a coordinating unit, it has been shown that the presence of methyl groups in the *ortho* positions hinders rotation of the peripheral group with respect to the chelate, which disfavours non-radiative deactivation pathways, thus enhancing the emissive properties of such complexes.[8] Ligands **2–4** are based on a dpm core appended with peripheral coordinating groups, namely cyanophenyl, pyridyl, and phenylimidazolyl groups. The coordinating ability of the cyano group is expected to be weaker than those of the other two peripheral units. Furthermore, in ligand **4**, the imidazolyl group can rotate about a C–N bond, offering more orientational possibilities compared to **2** or **3**. As a consequence, one might anticipate that complexes **5** and **6** will be less



Scheme 1. Representations and compound numbers of the dipyrrin ligands and their Cd complexes.

prone to self-assembly into CPs than **7** and **8** bearing stronger binding moieties at their periphery.

Synthesis and characterisation in solution: Dipyrrins **1**–**4** were prepared as described previously[8b,15] and reacted with $Cd(OAc)_2$ in the presence of NEt_3 to afford complexes **5**–**8** in yields of 48–88%. Although complexes **5** and **6** proved to be soluble in common organic solvents, compounds **7** and **8** were found to be only sparingly soluble in MeOH, DMF, and DMSO, suggesting the formation of oligomeric species by self-assembly through coordination of the peripheral pyridyl or imidazolyl groups.

Crystallisation of **6** by Et_2O vapour diffusion into a solution of the complex in pyridine afforded large single crystals of the pyridyl adduct $[(Py)_2(\mathbf{6})]$, **9**. Interestingly, both the *cis* and *trans* isomers of **9** could be isolated (see below).

NMR studies, elemental analysis, and structural investigations (see below) unambiguously demonstrated the formation of the $[Cd(dpm)_2]$ complexes. For example, in the millimolar range, distinct ^{1}H NMR spectra were obtained for the free dipyrrins **1** and **2** compared to those of the corresponding Cd complexes **5** and **6** in $CDCl_3$ (Figures S1 and S3 in the Supporting Information). Furthermore, DOSY NMR experiments performed in $[D_8]$toluene on the free ligands **1** and **2** and the Cd^{II} complexes **5** and **6** clearly demonstrated the presence of a single species in solution in all four cases. The observed spectra were clearly different for the free ligands and the corresponding complexes (Figures S2 and S4 in the Supporting Information). It is nevertheless worth noting that Lindsey et al., on the basis of UV/Vis spectroscopic data, concluded that the reaction of 5-phenyldipyrrin with $Cd(OAc)_2$ in the presence of NEt_3 in MeOH does not afford the expected Cd^{II} complex.[5a] This statement was substantiated by the similarity of the UV/Vis spectra of the reaction mixture and the free dpm ligand. In the micromolar range, as usually used for UV/Vis studies, we found that the prepared $[Cd(dpm)_2]$ complexes dissociated upon standing in toluene. Indeed, the spectra of freshly prepared solutions of the complexes, obtained by dissolving single crystals, initially featured two strong absorption bands at 463 and 483 nm (Figure 2 and Figure S5 in the Supporting Information) corresponding to π–π* transitions, as observed for other dipyrrin metal complexes.[5–12] However, as shown in Figure 2 for complex **5**, over the course of 24 h, these two bands vanished and were replaced by a band at around 430 nm corresponding to the absorption of the free dpm ligand **1**. The conversion of the complex into the free ligand gives rise to spectral changes with isosbestic points. The same holds for complex **6** (Figure S5 in the Supporting Information). These observations clearly indicate either dissociation of the $[Cd(dpm)_2]$ complexes or their transformation into other species in toluene. Considering the non-coordinating and apolar nature of this solvent, the observed phenomenon is surprising. However, a possible explanation may be the presence of traces of water.

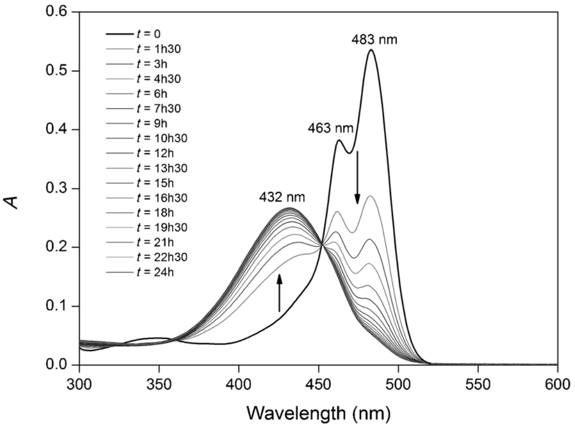


Figure 2. Evolution of the absorption spectrum of complex **5** in a 4.9×10^{-5} M solution in toluene at room temperature over 24 h.

Crystal structure: Crystals of **5** were obtained by slow evaporation of the solvent from a solution of the complex in Et_2O. It crystallises in the triclinic space group $P\bar{1}$ with one molecule in a general position and a disordered Et_2O solvate molecule at an inversion centre. The cadmium cation is in a distorted tetrahedral coordination environment with an angle of 75.4° between the planes of the two dpm chelates (Figure 3a), similar to the reported structure of the zinc analogue.[6] As observed for other complexes bearing peripheral mesityl groups, the latter are almost perpendicular to the bispyrrolic system (78.6 and 87.4°).[8] The Cd–N bond lengths (Table 1) are similar to those reported for dipyrrin and tripyrrin complexes of Cd^{II}.[14,16]

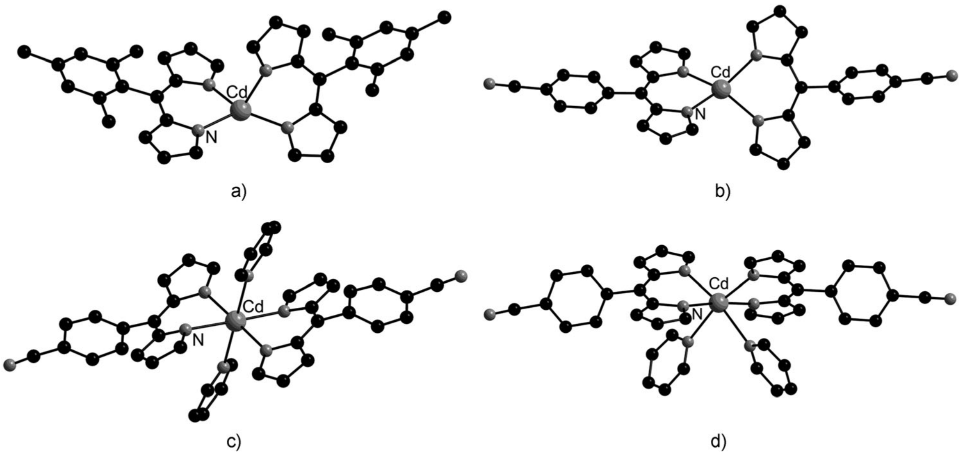


Figure 3. Crystal structures of complexes a) **5**, b) **6**, c) *trans*-**9**, and d) Δ-*cis*-**9**. Hydrogen atoms and solvent molecules have been omitted for clarity. For bond lengths, see Table 1.

Table 1. Selected average bond lengths [Å] for complexes **5**–**9**.

	Cd–N_{dpm}	Cd–N_{py}/Cd–N_{imid}
5	2.180	–
6	2.226	–
trans-**9**	2.307	2.448
Λ-*cis*-**9**	2.273	2.551
Δ-*cis*-**9**	2.275	2.553
7·MeOH	2.250	2.447
7	2.258	2.579
8	2.305	2.438

Crystals of **6** were obtained upon vapour diffusion of *n*-pentane into a solution of the complex in $CHCl_3$. It crystallises in the monoclinic space group *C*2/*c* with a complex on a two-fold axis. The Cd cation is tetracoordinated in a pseudo-tetrahedral environment with an angle of 42.8° between the two chelates (Figure 3b). Interestingly, this arrangement is more similar to the reported structure of [Cu(**2**)$_2$] than that of **5**.[11a] As observed for heteroleptic [Cu(acac)(**2**)], the nitrile group is not coordinated to the metal centre.

Upon slow diffusion of Et_2O vapour into a solution of **6** in pyridine, crystals of **9** were obtained, in which the Cd centre is in an octahedral coordination environment composed of two dipyrrin chelates and two monodentate pyridine ligands. Both the *cis* and *trans* isomers of this compound could be isolated. Complex *trans*-**9** crystallises in the triclinic $P\bar{1}$ space group with one molecule at an inversion centre (Figure 3c). The two bispyrrolic ligands coordinate the Cd cation in a square-planar arrangement, with Cd–N_{dpm} distances longer than those observed in **5** and **6** (Table 1). As observed for square-planar dipyrrin complexes, the pyrrolic rings are not coplanar within the chelate as a result of repulsion between the α-CH hydrogen atoms of the dpm ligands.[8d,12d,e] Two pyridine ligands occupy the axial positions around the metal cation. Unlike the *trans* analogue, the *cis* isomer is chiral. In the analysed crystals, only one enantiomer (either Δ or Λ, see Table 3) was found to be present and the whole batch was a conglomerate. Indeed, the *cis* isomer crystallises in the chiral monoclinic space group $P2_12_12_1$ with one enantiomer of the complex in a general position (Figure 3d). The Cd–N_{dpm} and Cd–N_{py} bond lengths were found to be slightly shorter in the *cis* isomer than in the *trans* isomer (Table 1). It is, however, interesting to note that the Cd–N_{py} bond lengths are longer than those reported for structures of Cd porphyrin complexes with an axially coordinated pyridine ligand.[17]

The structural investigation of these compounds illustrated that the Cd^{II} centre can form complexes with coordination numbers from four to six in the presence of coordinating groups capable of serving as auxiliary ligands, in addition to the dpm chelates. It is striking that the coordination arrangements in **5** and **6** differ in the orientation of the chelates while still retaining similar Cd–N bond lengths. This suggests a rather adaptable coordination sphere of the metal centre in these species. Furthermore, no self-assembly of complex **6** into an extended architecture was observed, despite the presence of the peripheral nitrile groups. This feature has previously been observed for [Cu(acac)(**2**)].[11a] Nevertheless, upon reaction of complex **6** with pyridine, both *cis* and *trans* isomers of **9** could be isolated.

Upon recrystallisation of the as-synthesised complex **7** from hot MeOH, crystals of the methanol solvate (**7**·MeOH) were obtained. It crystallises in the orthorhombic *Fdd*2 space group with one complex and one solvent molecule in general positions. The Cd cation is coordinated by the two dpm chelates and one peripheral pyridyl group of a neighbouring complex (Figure 4). This leads to the formation of a 1D chain along the *c* axis. The Cd–N_{dpm} and Cd–N_{py} distances are similar to those observed in *trans*-**9**. The second pyridyl group forms a hydrogen bond with the methanol solvate molecule (OHN = 149.6°; O–H···N = 2.773(12) Å).

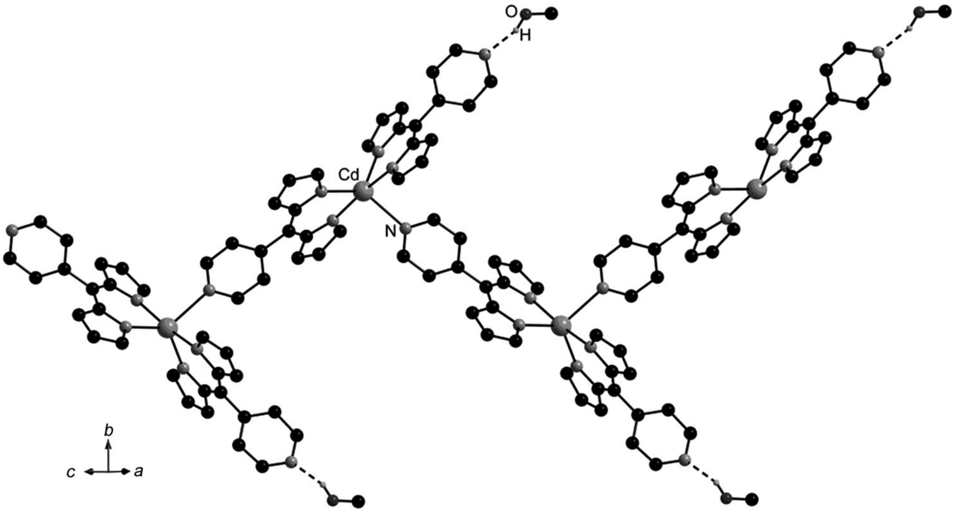


Figure 4. One-dimensional coordination polymer in the structure of **7**·MeOH. For clarity, only the OH hydrogen atoms are presented. For bond lengths, see Table 1 and the text.

Interestingly, upon recrystallisation of **7** from hot DMF, crystals of the non-solvated compound were obtained (Figure 5). It crystallises in the monoclinic *C*2/*c* space group with one complex on a two-fold axis. The Cd^{II} centre is in a slightly distorted octahedral environment made up of two dpm chelates and two pyridyl groups, in a *cis* configuration, belonging to neighbouring complexes. This leads to the formation of a 2D sheet. Interestingly, each 2D layer is homochiral containing either the Λ- or Δ-enantiomer (Figure 5).

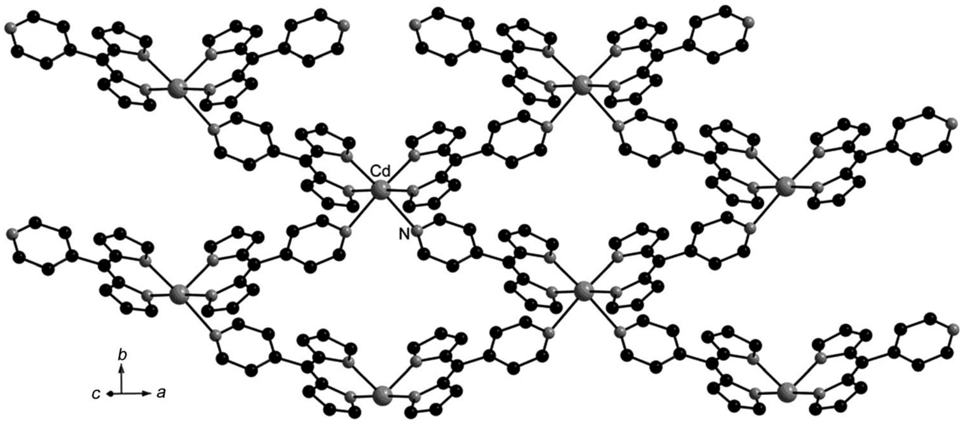


Figure 5. Homochiral 2D arrangement formed by the Λ-enantiomers of **7**. Hydrogen atoms have been omitted for clarity. For bond lengths, see Table 1.

These sheets stack in an alternating ΔΛΔΛ fashion, thus leading to an internal racemate (Figure S6 in the Supporting Information). The Cd–N bond lengths are similar to those observed in *cis*-**9** (Table 1). It is worth noting, however, that the pyridyl groups are tilted away from their expected positions for an octahedral environment.

Crystallisation of the as-synthesised complex **8** from hot DMSO afforded large crystals of the compound. It crystallises in the monoclinic *Cc* space group with one complex in a general position. Several disordered DMSO molecules are present in the crystal. Owing to the high degree of disorder, the SQUEEZE command was applied.[18] As in the structure of **7**, the Cd cation is in an octahedral environment with two dpm chelates and two imidazolyl groups of neighbouring molecules in a *cis* arrangement (Figure 6). This leads to a 3D coordination polymer. The $\mathrm{Cd{-}N_{dpm}}$ bond lengths are analogous to those in **5**–**7** and **9**, whereas the $\mathrm{Cd{-}N_{imid}}$ bond lengths are slightly shorter than the $\mathrm{Cd{-}N_{py}}$ distances in **7** and **9** and shorter than that in the reported structure of a Cd porphyrin with an axially coordinated benzimidazole group.[19] The presence of a phenyl spacer between the dpm chelate and the peripheral imidazolyl group, as well as the possibility of rotation of the latter unit about a C–N bond, seems to alleviate some of the deformation observed in **7** resulting from the unusual positioning of the pyridyl groups.

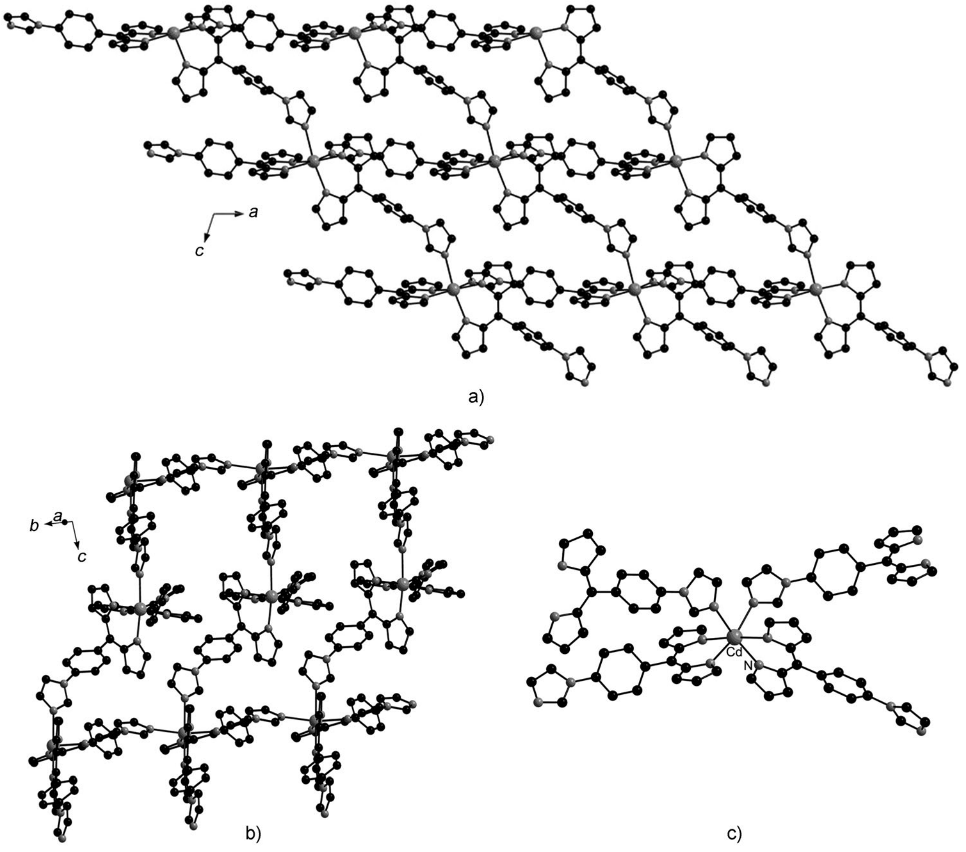


Figure 6. a,b) Two views of the 3D coordination polymer in **8** and c) the coordination environment around the Cd cation. Hydrogen atoms have been omitted for clarity. For bond lengths, see Table 1.

Photophysical properties: The dissociative behaviour observed for complexes **5** and **6** hampered thorough investigation of the emissive properties of these species in solution, since such studies are normally performed under dilute conditions (at concentrations below 10^{-6} M) and require rather long preparation times for degassing of the solutions. Preliminary investigations were performed by examining solutions immediately after their preparation. Upon excitation at 480 nm, both complexes **5** and **6** showed an emission band at 515 nm, distinct from that of the free ligand **1** (500 nm, $\Phi = 0.0026$; Figure S7 in the Supporting Information). This may have been due to the presence of a small amount of an emissive complex in the micromolar range.

In the solid state, the absorption spectra of the coordination polymers **7**, **7**·MeOH, and **8** feature similar bands

Table 2. Photophysical data for compounds **1**, **2** and **5**–**8**.

	λ_{abs} [nm]	λ_{em} [nm]
in toluene at RT		
1	438	500
2	433	no emission
5	463, 483	–
6	463, 483	–
in the solid state		
7·MeOH	403, 491, 556	563, 628
7	427, 494, 530	563, 602
8	427, 494, 536	577, 616

(Table 2, Figure S8 in the Supporting Information). Upon excitation at 430 nm, these compounds display two emission bands (Table 2, Figure 7). Interestingly, complex **5** shows a similar emission spectrum in the crystalline state ($\lambda_{em}=577$, 630 nm; Figure 7). These results suggest that the luminescence is ligand-centred and that the coordination number of the Cd^{II} cation has no effect on the emission given that **7** and **7**·MeOH show similar luminescence properties. Preliminary investigations have indicated that the quantum yield of the luminescence in the solid state is below 1%. However, to the best of our knowledge, these self-assembled Cd^{II} complexes represent the first examples of luminescent monodpm-based crystalline coordination polymers.

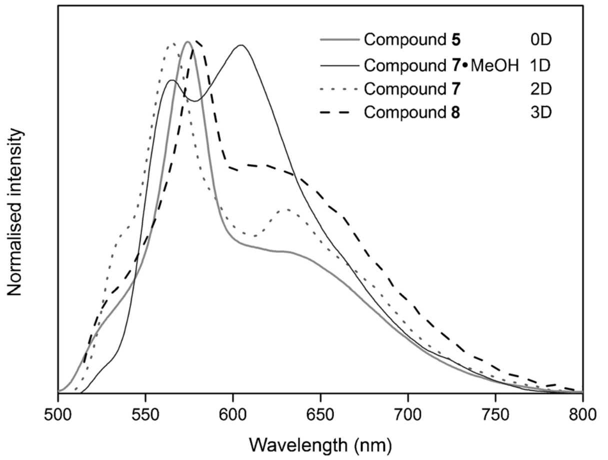


Figure 7. Solid-state emission spectra ($\lambda_{exc}=430$ nm) of compounds **5**, **7**, **7**·MeOH, and **8**.

Conclusion

The first cadmium complexes of the type [Cd(dpm)$_2$] incorporating α,β-unsubstituted dipyrrins have been designed, prepared, and characterised both in solution and in the solid state. Unlike in their Zn analogues, the Cd^{II} cation bound by two dpm chelates adopts a coordination number higher than four in the presence of additional coordinating groups. Indeed, for the cyanophenyl-appended complex **6** and for the mesityl analogue **5**, structural investigation has revealed that the metal centre is in a tetrahedral coordination sphere composed solely of two dpm ligands. However, upon recrystallisation of complex **6** from pyridine, an octahedral environment is observed. Both the *cis* and *trans* isomers of the bispyridyl adduct [(Py)$_2$(**6**)] (complex **9**) have been isolated and characterised by X-ray diffraction analysis. Upon the introduction of additional coordinating units at the periphery of the dpm itself, as in the pyridyl- and imidazolyl-appended derivatives **7** and **8**, respectively, the formation of coordination polymers by self-assembly is observed. Interestingly, although the coordination features of [Cd(dpm)$_2$] complexes differ from those of [Zn(dpm)$_2$] species, these compounds are also luminescent in the crystalline state, regardless of the coordination number of the Cd^{II} cation. To the best of our knowledge, these compounds represent the first luminescent monodpm-based CPs. Future investigations will focus on the use of other dpm ligands and external coordinating groups such as chelates, and other metal centres.

Experimental Section

General: Dipyrrins **1**–**4** were prepared as described previously.[8b,11f,15] All solvents were dried according to standard procedures. Other reagents were obtained from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were acquired at 25 °C on Bruker AV 300 (300 MHz), AV 400 (400 MHz), and AV 500 (500 MHz) spectrometers, utilising the deuterated solvent as a lock and residual solvent as an internal reference. NMR chemical shifts are given in ppm and referenced internally to the residual solvent resonance. *J* values are given in Hz. Mass spectrometry was performed at the Service Commun d'Analyses, Université de Strasbourg (France). UV/Vis spectra in solution and in the solid state were recorded on a Perkin–Elmer Lambda 650S spectrophotometer.

Synthesis of 5: A solution of Cd(OAc)$_2$ (127 mg, 0.48 mmol) in MeOH (20 mL) was added to a solution of dipyrrin **1** (250 mg, 0.95 mmol) in CHCl$_3$ (20 mL) and the mixture was heated at reflux for 48 h. After evaporation of the solvents under vacuum, the residue was re-dissolved in CH$_2$Cl$_2$ (150 mL) and the solution was washed with water (3×50 mL). The organic phase was concentrated to afford compound **5** as a dark-red solid (223 mg, 0.35 mmol, 74%). Single crystals were obtained by slow evaporation of the solvent from a solution in Et$_2$O. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): $\delta=2.13$ (s, 12H), 2.37 (s, 6H), 6.36 (dd, $J=1.0$, 4.2 Hz, 4H), 6.55 (d, $J=3.4$ Hz, 4H), 6.93 (s, 4H), 7.55–7.57 ppm (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): $\delta=20.0$, 21.3, 117.3, 127.8, 128.6, 134.5, 136.7, 137.4, 141.0, 142.8, 145.1 ppm; elemental analysis calcd (%) for $C_{78}H_{78}Cd_2N_8O$: C 67.90, H 5.85, N 8.34; found: C 66.95, H 5.61, N 8.31.

Synthesis of 6: A solution of dipyrrin **2** (400 mg, 1.63 mmol) in CHCl$_3$ (40 mL) was mixed with a solution of Cd(OAc)$_2$ (216 mg, 0.82 mmol) in MeOH (40 mL) containing NEt$_3$ (1 mL). The reaction mixture was stirred for 48 h at 70 °C and then the precipitate was separated by centrifugation, washed with methanol and dried under vacuum to afford complex **6** as an orange powder (409.5 mg, 0.68 mmol, 83%). ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): $\delta=6.47$ (dd, $J=1.5$, 4.2 Hz, 4H), 6.55 (dd, $J=0.7$, 4.2 Hz, 4H), 7.62–7.65 (m, 8H), 7.75–7.78 ppm (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): $\delta=112.6$, 117.9, 118.6, 131.2, 131.3, 133.9, 141.1, 144.1, 146.2, 151.9 ppm; elemental analysis calcd (%) for $C_{32}H_{20}CdN_6$: C 63.96, H 3.35, N 13.98; found: C 63.69, H 3.43, N 13.93.

Synthesis of 7: A solution of dipyrrin **3** (294 mg, 1.32 mmol) in CHCl$_3$ (100 mL) was mixed with a solution of Cd(OAc)$_2$ (117 mg, 0.66 mmol) in MeOH (30 mL) containing NEt$_3$ (1 mL). A red precipitate appeared after 10 min. The reaction mixture was stirred for 24 h at room tempera-

Table 3. Crystallographic data for compounds **5**–**9**.

	(**5**)$_2$·Et$_2$O	**6**	**7**·MeOH	**7**	**8**	*trans*-**9**	Λ-*cis*-**9**	Δ-*cis*-**9**
formula	$C_{76}H_{78}Cd_2N_8O$	$C_{32}H_{20}CdN_6$	$C_{29}H_{24}CdN_6O$	$C_{28}H_{20}CdN_6$	$C_{36}H_{26}CdN_8$	$C_{42}H_{30}CdN_8$	$C_{42}H_{30}CdN_8$	$C_{42}H_{30}CdN_8$
M_r [g mol^{-1}]	1343.66	600.97	584.94	552.92	683.05	758.91	759.17	759.17
crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$C2/c$	$Fdd2$	$C2/c$	Cc	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	8.93390(10)	20.3370(5)	19.7582(9)	17.8073(4)	24.6972(5)	8.6261(2)	11.8565(2)	11.8642(2)
b [Å]	11.8931(2)	13.3180(3)	55.481(3)	9.0579(2)	9.6072(2)	10.1861(4)	16.4163(3)	16.4322(3)
c [Å]	16.7197(4)	10.7752(3)	9.2647(4)	16.4457(4)	18.2223(4)	11.4066(2)	17.9239(3)	17.9354(3)
α [°]	103.5330(10)					106.0510(10)		
β [°]	94.8060(10)	120.0620(10)		118.0580(10)	107.7100(10)	110.1300(10)		
γ [°]	106.5020(10)					98.2980(10)		
V [Å^3]	1634.38(5)	2525.86(11)	10155.9(8)	2340.88(9)	4118.72(15)	871.91(4)	3488.71(10)	3496.59(10)
Z	1	4	16	4	4	1	4	4
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
μ [mm^{-1}]	0.702	0.899	0.895	0.962	0.560	0.670	0.669	0.668
refls. coll.	42635	21207	36158	9818	67813	41785	23013	27872
ind. refls. (R_{int})	8671 (0.0399)	3683 (0.0213)	7214 (0.0894)	2676 (0.0211)	11739 (0.0318)	4613 (0.0283)	10173 (0.0238)	8392 (0.0292)
R_1 ($I>2\sigma(I)$)[a]	0.0324	0.0248	0.0599	0.0213	0.0269	0.0199	0.0276	0.0257
wR_2 ($I>2\sigma(I)$)[a]	0.0829	0.0715	0.1159	0.0505	0.0703	0.0515	0.0602	0.0592
R_1 (all data)[a]	0.0401	0.0274	0.0885	0.0235	0.0284	0.0202	0.0375	0.0351
wR_2 (all data)[a]	0.0920	0.0734	0.0516	0.0638	0.0516	0.0749	0.0645	0.0710
GoF	1.107	1.077	1.069	1.034	1.053	1.044	1.035	1.048

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

ture and the orange solid was separated by centrifugation, washed with MeOH and Et_2O, and dried under vacuum to afford **7** (177 mg, 0.53 mmol, 88 %). Crystals of **7** were obtained by concentration of a saturated solution in DMF at 100 °C, whereas crystals of **7**·MeOH were obtained by evaporation of the solvent from a solution in MeOH. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): $\delta=6.32$ (d, $J=3.9$ Hz, 4H), 6.35 (d, $J=3.9$ Hz, 4H), 7.40 (dd, $J=1.6$, 4.3 Hz, 4H), 7.51 (brs, 4H), 8.66 ppm (dd, $J=1.6$, 4.3 Hz, 4H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20 °C): $\delta=116.8$, 124.9, 131.7, 140.2, 144.1, 147.9, 148.5, 150.6 ppm; elemental analysis calcd (%) for $C_{28}H_{20}CdN_6$: C 60.82, H 3.65, N 15.20; found: C 60.44, H 3.80, N 14.98.

Synthesis of 8: A solution of dipyrrin **4** (91.2 mg, 0.32 mmol) in DMF (3 mL) was mixed with a solution of Cd(OAc)$_2$ (42.2 mg, 0.16 mmol) in MeOH (3 mL) and then NEt_3 (1 mL) was added. The reaction mixture was stirred at room temperature. The precipitate obtained was separated by centrifugation, washed with MeOH and dried under vacuum to afford **8** as a dichroic green–orange solid (52.4 mg, 0.08 mmol, 48 %). Single crystals were obtained by slow evaporation of the solvent from a saturated solution of the complex in [D$_6$]DMSO at 80 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): $\delta=6.35$ (dd, $J=0.9$, 4.0 Hz, 4H), 6.42 (d, $J=3.3$ Hz, 4H), 7.16 (s, 2H), 7.49–7.52 (m, 8H), 7.74 (d, $J=8.4$ Hz, 4H), 7.85–7.86 (m, 2H), 8.36–8.38 ppm (m, 2H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20 °C): $\delta=116.4$, 116.8, 117.9, 118.8, 130.0, 131.5, 136.6, 136.5, 138.8, 141.2, 150.1 ppm.

Synthesis of 9: Vapour diffusion of Et_2O into a solution of complex **6** (50 mg, 0.083 mmol) in pyridine (3 mL) afforded crystals of **9** (35 mg, 0.046 mmol, 55 %). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=6.44$ (d, $J=4.1$ Hz, 4H), 6.53 (d, $J=4.1$ Hz, 4H), 7.28–7.31 (m, 4H), 7.57 (s, 4H), 7.63–7.65 (m, 4H), 7.71 (tt, $J=1.9$, 7.6 Hz, 2H), 7.74–7.76 (m, 4H), 8.47–8.49 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=112.3$, 117.6, 118.7, 124.1, 131.3, 131.4, 133.5, 136.7, 141.5, 145.2, 146.1, 150.0, 151.6 ppm; elemental analysis calcd (%) for $C_{43}H_{30}CdN_8$: C 66.45, H 3.98, N 14.76; found: C 66.82, H 4.18, N 14.57.

X-ray diffraction: Data (Table 3) were collected on a Bruker SMART CCD diffractometer by using Mo$_{K\alpha}$ radiation. The structures were solved by using SHELXS-97 and refined by full-matrix least-squares fitting on F^2 using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms.[20] Hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of (**5**)$_2$·Et$_2$O, the diethyl ether solvate molecule is disordered. In the case of the structure of **8**, the SQUEEZE command was applied owing to the presence of highly disordered DMSO solvate molecules.[18] The anomalous dispersion coefficients for ^{48}Cd at the Mo$_{K\alpha}$ wavelength are 1.005 and 1.202 for Δf and $\Delta f'$, respectively. CCDC-899363 ((**5**)$_2$·Et$_2$O)), CCDC-899364 (**6**), CCDC-899365 (**7**·MeOH), CCDC-899366 (**7**), CCDC-899367 (**8**), CCDC-899368 (**8**), CCDC-899369 (*trans*-**9**), CCDC-899370 (Λ-*cis*-**9**), and CCDC-899371 (Δ-*cis*-**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

Steady-state photophysical measurements: Quartz cells and spectrophotometric grade solvents were employed. Degassing was carried out by several freeze–pump–thaw cycles. UV/Vis spectra were recorded on a BioTek Instruments Uvikon XL double-beam UV/Vis spectrophotometer and were baseline-corrected. Steady-state luminescence emission spectra were recorded on a HORIBA Jobin–Yvon FL-3-22 Fluorolog spectrofluorimeter equipped with a 450 W xenon arc lamp. All emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Appropriate cut-off filters were employed to avoid second-order scattering lines from the excitation source. Solid-state measurements were performed on a Perkin–Elmer LS 55 spectrometer.

Quantum yield determination: Based on the method of Crosby and Demas,[21] luminescence quantum yields were measured from optically dilute solutions (absorbance value lower than 0.1 at the excitation wavelength and above) by using fluorescein[22] in 0.1 M NaOH ($\Phi=0.92$) as a standard.

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