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Synthesis, structure, and luminescence properties of arylpyridine-substituted terpyridine Zn(II) and Cd(II) complexes

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Dedicated to the memory of Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

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ABSTRACT

Two terpyridine derivatives, 4'-(4-(pyridin-4-yl)phenyl)-[2,2':6',2"]terpyridine (L1) and 4'-(4'-(pyridin-4-yl)-[1,1'-biphenyl]-4-yl)-[2,2':6',2"]terpyridine (L2) have been synthesized by palladium-catalyzed cross-coupling reactions, and their metal complexes $[Zn(L1)_2](ClO_4)_2$ ·2MeOH·CHCl₃ (1) and $[Cd(L2)_2]$ ($ClO_4)_2$ ·DMF·2.8H₂O (2) characterized by single crystal X-ray crystallography and spectroscopic methods including electronic absorption and emission measurements. In the crystalline materials, both metal ions have the expected pseudo-octahedral N₆ coordination environment and the lattice structures appear to be influenced by aromatic–aromatic interactions involving the heteroaryl tails and the pyridyl rings of the terpyridine units. In solution and in the solid state, the complexes display blue emission attributed to an intramolecular charge transfer transition.

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1. Introduction

Of the extraordinarily numerous derivatives of 2,2':6',2"-terpyridine synthesized to endow both the ligand and its metal complexes with novel properties, those involving heteroaromatic substituents, notably (poly)pyridyl, have been prominent [1–3]. Most commonly, substituents have been introduced on the 4'-position of terpyridine, so that a pyridyl unit introduced there can provide a metal ion coordination site which is divergent from that defined by the N-donor atoms of the original terpyridine chelate site, thus facilitating the formation of various heterometallic, oligomeric complexes, some of which have been shown to have exceptional electronic, magnetic and electrochemical properties [4]. In our earlier work on polymeric Co(II) complexes of 4'-(4-pyridyl)-2,2':6',2"-terpyridine, for example, an abrupt spin transition was found to be inducible by the mere change of lattice solvent [5]. Coordination complexes of pyridyl-substituted terpyridine deriva-

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tives have been used, however, not only in this way as building blocks to construct, as further examples, luminescent coordination polymers [6], heteronuclear photocatalysts [7] and organized monolayers [8], but also as antennae to promote lanthanide luminescence [9], and as reagents for the photocleavage of biomolecules [10]. Of further interest with a pyridyl substituent is the fact that it expands the heteroaromatic ligand core and thus enhances its capacity for involvement in weak interactions that may modulate the reactivity of the system [11]. Further still, it is a nucleophilic site that can be alkylated to give complexes of the cationic ligand which can be used as luminescent anion sensors [12] and constituents of electrochromic materials [13], while the reaction of alkylation itself can be used to form metallamacrocycles [14] and mechanically interlocked molecules [15].

In extension of our studies of pyridyl-appended terpyridines, we have now investigated the consequences of introducing unsubstituted aromatic substituents between the terpyridine and pyridine units by synthesizing the ligands 4'-(4-(pyridin-4-yl) phenyl)-[2,2':6',2"]terpyridine (**L1**; previously known [9]) and 4'-(4'-(pyridin-4-yl)-[1,1'-biphenyl]-4-yl)-[2,2':6',2"]terpyridine (**L2**) and conducting a preliminary structural and spectroscopic characterization of their complexes with Zn(II) and Cd(II), two metal ions expected to give luminescent species.



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2. Experimental

2.1. General

Elemental analyses for C, H and N were carried out at the Instrumental Analysis Center of Kumamoto University. ¹H NMR spectra were measured on a JEOL (500-ECX) instrument (500 MHz) using deuterated solvents with TMS as internal reference. UV–vis and fluorescence spectra were recorded with a Shimadzu UV-3600 spectrophotometer and a Perkin-Elmer LS55 spectrofluorimeter, respectively. Infrared spectra were recorded on a Shimadzu FT-IR 8700 instrument. Mass spectral data were collected on a JEOL JMS-BU-20GC-mate spectrometer operating in positive ion fast atom bombardment mode (FAB⁺) with an NBA matrix.

2.2. Synthesis

All chemicals and solvents were used as received without further purification. 4'-(4'-(Pyridin-4-yl)-phenyl)-[2,2':6',2'']ter-pyridine (L1) [9] and 4'-(4'-bromo-biphenyl-4-yl)-[2,2':6',2'']ter-pyridine (Brbptpy) [16] were prepared according to literature procedures.

2.2.1. Synthesis of 4'-(4'-pyridin-4-yl-biphenyl-4-yl)-[2,2':6',2"]terpyridine (**L2**)

An oven-dried three-neck round-bottom flask was charged with Brbptpy (0.20 g, 0.43 mmol), 4-pyridinyl-boronic acid (0.15 g, 1.2 mmol), and $Pd(PPh_3)_4$ (0.1 g, 0.086 mmol), and then filled with argon gas. After successive additions of DME (30 mL) and degassed aqueous Na₂CO₃ (2 M, 15 mL), the mixture was heated at reflux for 24 h under argon. The solvent was evaporated off under reduced pressure and the residue dissolved in dichloromethane. A black solid and Na₂CO₃ salt were filtered out through Celite and the filter bed washed with dichloromethane. The filtrate was taken to dryness under vacuum and the residue purified by column chromatography on silica gel with ethyl acetate/hexane (1:1). Yield: 0.18 g (91 %). MS (FAB⁺): m/z = 463.21 [M+H]. ¹H NMR (500 MHz, CDCl₃): δ = 8.74 (s, 2H, PyH^{3',5'}), 8.69 (d, 2H, PyH^{6,6''}), 8.64–8.62 (m, 4H, PyH^{2,6'',2'',6'''}), 7.98 (d, 2H, PyH^{3''',5'''}), 7.85 (t, 2H, PyH^{5,3''}), 7.75–7.69 (m, 6H, ArH), 7.54 (d, 2H, ArH^{3,5}), 7.32 (t, 2H, PyH^{4,4"}), UV spectrum in CH₃CN: λ_{max} (ϵ_{max} (× 10⁴ M⁻¹ cm⁻¹)) = 258 nm (sh, 1.91), 296 nm (3.57).

2.2.2. Synthesis of $[Zn(L1)_2](ClO_4)_2 \cdot 2MeOH \cdot CHCl_3(1)$

To a solution of **L1** (0.03 g, 0.078 mmol) in MeOH/CHCl₃ (10 mL, v/v = 1:1), Zn(ClO₄)₂·6H₂O (0.014 g, 0.039 mmol) in MeOH (10 mL) was added. The mixture was stirred for 2 h at room temperature and then the solvent volume was reduced under vacuum to ~5 mL. The white precipitate formed was collected by filtration, washed with methanol and dried in vacuo (Yield: 0.04 g). Crystals suitable for a structure determination were obtained by liquid diffusion of methanolic Zn(ClO₄)₂·6H₂O into a chloroform solution of **L1**. *Anal.* Calc. for C₅₅H₄₅Cl₅N₈O₈Zn: C, 54.12; H, 3.72; N, 9.18. Found: C, 54.42; H, 3.74; N, 9.27 %. ESI–MS: *m/z* = 418.58 [Zn(**L1**)₂]²⁺. UV spectrum in CH₃CN: λ_{max} (ε_{max} (× 10⁴ M⁻¹ - cm⁻¹)) = 236 nm (4.44), 269 nm (sh, 4.95), 287 nm (6.60), 315 nm (6.17). IR spectrum (KBr disc, cm⁻¹) 3076 (Ar C–H), 1089 (ClO₄⁻).

2.2.3. Synthesis of $[Cd(L2)_2](ClO_4)_2 \cdot DMF \cdot 2.8H_2O(2)$

To a solution of **L2** (0.030 g, 0.065 mmol) in DMF (15 mL), Cd(ClO₄)₂·6H₂O (0.014 g, 0.033 mmol) in DMF (5 mL) was added. The mixture was stirred for 2 h at 100 °C. The solvent was removed under reduced pressure. The solid residue was washed with MeOH and the white product was collected by filtration and dried in vacuo. Yield: 0.03 g. Crystals suitable for a structure determination were obtained by vapor diffusion of methanol into a DMF solution of the product. *Anal.* Calc. for C₆₇H_{56.6}CdCl₂N₉O_{11.8}: C, 59.17; H, 4.20; N, 9.27. Found: C, 59.00; H, 4.21; N, 9.24%. ESI–MS: *m*/ *z* = 519.33 [Cd(**L2**)₂]²⁺. UV spectrum in CH₃CN: λ_{max} (ε_{max} (× 10⁴ M⁻¹ cm⁻¹)) = 236 nm (sh, 4.62), 287 nm (6.97), 332 nm (8.35). IR spectrum (KBr disc, cm⁻¹), 3066 (Ar C-H), 1089 (ClO₄⁻⁻).

2.3. Crystal structure determinations

X-ray structural analyses for **1** and **2** were carried out using RIG-AKU Saturn CCD diffractometer with a confocal mirror using graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å) at 100 K. The structures were solved by direct methods (SHELXL-97 [17]) for **1** and by heavy-atom Patterson methods (DIRDIF99 PATTY) for **2**, and refined by full-matrix least-squares method on F^2 (SHELXL-97).

2.3.1. Crystal data for 1

 $C_{55}H_{45}Cl_5N_8O_{10}Zn$, M = 1276.09, triclinic, space group $P\bar{1}$, a = 12.5578(6), b = 14.4664(5), c = 14.7705(7)Å, $\alpha = 89.702(2)$, $\beta = 79.220(2)$, $\gamma = 88.108(2)^\circ$, V = 2634.5Å³, Z = 2, $D_{calc} = 1.609$ g cm⁻³, μ (Mo K α) = 7.912 cm⁻¹, T = 100 K, 26051 reflections collected. Refinement of 12071 reflections (712 parameters) with $I > 2\sigma(I)$ converged to a final $R_1 = 0.0797$, $wR_2 = 0.2349$. Goodness-of-fit (GOF) = 1.080.

2.3.2. Crystal data for 2

C₆₇H_{56.6}CdCl₂N₉O_{11.8}, *M* = 1359.95, triclinic, space group *P*Ī, *a* = 14.896(2), *b* = 15.260(1), *c* = 15.358(2) Å, *α* = 80.168(2), *β* = 64.542 (2), *γ* = 83.140(2)°, *V* = 3101.7(4) Å³, *Z* = 2, *D*_{calc} = 1.456 g cm⁻³, *μ*(Mo K*α*) = 5.098 cm⁻¹, *T* = 100 K, 22436 reflections collected. Refinement of 12703 reflections (804 parameters) with *I* > 2*σ*(*I*) converged to a final *R*₁ = 0.1093, *wR*₂ = 0.2894. Goodness-of-fit (GOF) = 1.054.

3. Results and discussion

3.1. Synthesis and structure

Both heteroaryl-substituted terpyridine ligands **L1** (previously known [9]) and **L2**, possessing phenylpyridine and biphenylpyridine moieties, respectively, were obtained in good yield through Pd-catalyzed Suzuki cross-coupling reactions [9], as depicted in Scheme 1. The intermediate Brbptpy was prepared by using (see Section 2) our previously reported synthetic procedures [16]. **L2** was obtained as a white solid by coupling Brbptpy with 4-pyridinylboronic acid. The bis(ligand) complexes of Zn(II) with **L1** (1) and of Cd(II) with **L2** (2) were obtained by reacting stoichiometric quantities of the ligands and the metal perchlorates in mixed solvents.



Scheme 1. Ligand syntheses via Suzuki cross-coupling reactions.

Crystals of 1 suitable for a structure determination were obtained by slow diffusion over several weeks after layering a methanol solution of $Zn(ClO_4)_2 \cdot 6H_2O$ on a CHCl₃ solution of L1 in a glass tube. A single-crystal X-ray structural determination was successfully carried out at 100 K, the space group being found to be triclinic $P\overline{1}$. Fig. 1 shows the cation present in the lattice of **1** with a partial atomic numbering scheme. Selected bond distances and angles are given in Table 1. The central metal ion is coordinated by six nitrogen donor atoms of two terpyridine units. As usual with terpyridine complexes [2,18], the Zn–N bonds to the central pyridine-N donors (2.067(4)-2.084(4) Å) are significantly shorter than those to the peripheral-ring donors (2.169(5)-2.202(5) Å), giving the ZnN₆ unit a distorted octahedral geometry. The complex cation has very close to a linear, rod-like form (N7...Zn1...N8 177.8°; N7...N8 26.90(3)Å) with, again as usual (see, for example, [6.11.13.14.19.20], the phenyl and pyridyl rings slightly twisted away from coplanarity with one another and the terpyridine head group. This twisting is markedly different for the N8 tail to that of the N7, so that the two tails are clearly inequivalent.

Concerning the lattice of 1, it is apparent that grafting of a pyridylphenyl substituent to terpyridine must be added to the list of factors known to disrupt the "terpyridine embrace" [21], ascribed to aromatic–aromatic interactions, found in the lattices of a large number of complexes of unsubstituted terpyridine (and indeed in some with small substituents such as hydroxyl [22] and even a single pyridyl ring [13]). Obviously, the presence of an aromatic tail, and particularly one containing a polarized aromatic unit (pyridyl),



Fig. 1. Molecular structure of the $[\text{Zn}(\text{L1})_2]^{2+}$ cation in **1** with thermal ellipsoids plotted at the 50 % probability level. For clarity, hydrogen atoms are omitted.

Table 1										
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for 1	and	2.

1		2	
Zn(1)-N(1)	2.178(4)	Cd(1)-N(1)	2.319(7)
Zn(1)-N(2)	2.067(4)	Cd(1)-N(2)	2.308(9)
Zn(1)-N(3)	2.181(4)	Cd(1)-N(3)	2.368(8)
Zn(1)-N(4)	2.169(5)	Cd(1)-N(4)	2.345(8)
Zn(1)-N(5)	2.084(4)	Cd(1)-N(5)	2.297(9)
Zn(1)-N(6)	2.202(5)	Cd(1)-N(6)	2.353(7)
N(1)-Zn(1)-N(2)	75.84(15)	N(1)-Cd(1)-N(2)	70.3(3)
N(1)-Zn(1)-N(3)	151.93(14)	N(1)-Cd(1)-N(3)	139.5(3)
N(1)-Zn(1)-N(4)	95.81(16)	N(1)-Cd(1)-N(4)	97.5(3)
N(1)-Zn(1)-N(5)	106.39(15)	N(1)-Cd(1)-N(5)	126.7(3)
N(1)-Zn(1)-N(6)	90.74(15)	N(1)-Cd(1)-N(6)	100.9(3)
N(2)-Zn(1)-N(3)	76.26(15)	N(2)-Cd(1)-N(3)	69.4(3)
N(2)-Zn(1)-N(4)	103.98(15)	N(2)-Cd1)-N(4)	117.5(3)
N(2)-Zn(1)-N(5)	177.76(15)	N(2)-Cd(1)-N(5)	161.4(3)
N(2)-Zn(1)-N(6)	104.54(16)	N(2)-Cd(1)-N(6)	101.5(3)
N(3)-Zn(1)-N(4)	87.86(16)	N(3)-Cd(1)-N(4)	97.0(3)
N(3)-Zn(1)-N(5)	101.52(15)	N(3)-Cd(1)-N(5)	93.7(3)
N(3)-Zn(1)-N(6)	99.23(15)	N(3)-Cd(1)-N(6)	91.1(3)
N(4)-Zn(1)-N(5)	76.14(15)	N(4)-Cd(1)-N(5)	70.9(3)
N(4)-Zn(1)-N(6)	151.48(14)	N(4)-Cd(1)-N(6)	140.6(3)
N(5)-Zn(1)-N(6)	75.38(16)	N(5)-Cd(1)-N(6)	70.2(3)

gives rise to the possibility of other forms of such interactions [2]. As for other complexes of terpyridines with linear polyaromatic substituents [20], lattice planes can be identified in which the cations form sheets containing these substituents. In 1, these sheets lie parallel to the (10-1) plane and, from the apparent proximity of substituents of adjacent cations, chained polymeric structures can be identified (Fig. 2). The Zn...Zn separations of centrosymmetric pairs within these rods alternate between 19.99(2) and 20.07(2) Å, and for the longer of these two, the intervening pyridylphenyl substituents (involving N7) are arrayed so that the pyridyl of one projects (offset) on the phenyl of the other, with the ring planes being close to parallel and the centroid...centroid separation 3.659(3) Å, with the shortest interatomic contact being C...N of 3.366(8) Å. These parameters are indicative of a significant offset face-to-face (OFF) interaction [21,23]. For the centrosymmetric pair with the slightly shorter Zn...Zn separation of 19.99(2) Å. however, the rings of the overlapping tails do not lie parallel, the centroid ... centroid separation is long at 4.054(3) Å and no interatomic separation is shorter than 3.5 Å. Here, it must be noted that a cation (at Zn...Zn 11.20(1)Å) in an adjacent rod is positioned such that the terminal pyridyl groups of the tails are close to parallel to peripheral pyridyl groups of the terpyridine head groups, with a centroid...centroid separation of 3.672(3) Å and two interatomic contacts <3.5 Å. Further, there is another neighbor (Zn...Zn 11.30(1) Å) for which one of the phenyl groups apparently involved in interactions in the 20.07(2) Å rod-pair lies close to parallel to a peripheral pyridyl of its neighbor's head group, with a centroid...centroid separation of 3.604(3) Å and 4 interatomic contacts at <3.5 Å. In all these situations, there are CH...C contacts <3 Å which may be indicative of edge-to-face CH... π interactions [23-25]. Thus, any analysis of aromatic-aromatic interactions within the lattice of **1** is exceedingly complicated and is rendered even more so by recognizing that there are, of course, other interactions to be considered. Most obvious and probably dominant [21], are cation-anion attractions (which may of course pass through an anion... π pathway [26]) but in the case of the



Fig. 2. A partial view (stick representation) perpendicular to the (01-1) plane of one of the sheets of cations in **1** where the tails lie within the sheet. One of the apparent chains of rod-like cation units is shown in black. For clarity, anions, solvent molecules and hydrogen atoms are not shown (gray = C, blue = N, yellow = Zn).

11.30(2) Å cation pair, for example, they can also be considered to be linked through chains involving H-bonding between terminalpyridine-N, methanol (O(10)...N(7) 2.784(6)Å) and chloroform $(C55...O10 \quad 3.37(1) \text{ Å})$ along with $Cl...\pi$ interactions [27] (Cl3...C46 3.331(7)Å). In addition, this involves but one of the two methanol molecules of the stoichiometric unit; the other is also involved in H-bonding to pyridine-N (O(9)...N(8) 2.899(6) Å) but along with O...HC(aromatic) interactions and without any Hbonding to chloroform (see Fig. 3).X-ray quality, pale violet crystals of **2** were obtained by slowly diffusing methanol vapor into a DMF solution of the complex, the space group again proving to be $P\overline{1}$. The cation present in the lattice of 2 is shown in Fig. 4, and selected bond distances and angles are given in Table 1. Again, the Cd(II) metal ion has a distorted octahedral CdN₆ coordination geometry with, as also in the Zn(II) species, a significant deviation ($\sim 8^{\circ}$) of the mean planes of the terpyridine units from orthogonality. With its longer substituent chains, giving N7...N8 35.79(3) Å, the overall form of the cation is more obviously bent, the angle N7-Cd1-N8 being 166.9°, but the lattice can still be divided into sheets of cations with the tails lying within the sheets, here parallel to the (10-1) plane. Undulating linear arrays, similar to the more strictly linear arrays in the Zn complex lattice, involving overlap in projection of the tail units can be discerned within these sheets (Fig. S1), the Cd...Cd separations alternating between 21.69(2) and 22.11(1) Å. Appearances here are particularly deceptive, however, as for the longer 22.11(1) Å separation, all centroid...centroid distances for the apparently approximately parallel and overlapping rings are >4.5 Å (viz. very long), while for the cations 21.69(2) Å apart, the centroid...centroid distances are shorter (3.941(5), 3.768(5)Å) but still relatively long and no C...C contact shorter than 3.50 Å is evident. The 22.11(1) Å pair may be bridged by CH...N interactions (C15...N8 3.18(2), H...N 2.41 Å) and, if (aromatic)C...O(perchlorate) contacts ≤ 3.40 Å are taken as indicative of interactions, then both pairs of cations are bridged by anions, so no attraction between the aromatic tails need necessarily be postulated. Nonetheless, the two cation pairs just discussed are far from the closest within the lattice and for the closest pair (at 8.98(1) Å), there is even evidence for some degree of retention of the terpyridine embrace in that flanking pyridyl rings of the terpyridine heads have a centroid...centroid separation of 3.619(6) Å and three reciprocal C...C separations well below 3.50 Å. A very similar situation applies for the next-closest pair (at 9.06(1) Å), where the centroid...centroid separation is 3.638(4) Å and two C...C contacts are (just) below 3.50 Å. In fact these two pairs can be considered to form a one-dimensional array along a line parallel to the (111) plane which, especially when viewed in the absence of the tail atoms, resembles very closely a portion of the two-dimensional terpyridine embrace found in simpler complexes (Figs. 5 and S2). Further, for the again centrosymmetric pair found 10.593(7)Å apart, the shortest centroid...centroid separation of all (3.586(4) Å) is found between the first phenyl group of a tail and a peripheral terpyridine pyridyl ring of its neighbor and is associated with one C...C contact as short as 3.29(1) Å. Irrespective of the near pairs considered, all are bridged by anion contacts with C...O \leq 3.40 Å, although any detailed analysis of these interactions is hampered by disorder of the oxygen atom locations. Note that contacts between the cations and anions are concentrated on the bound terpyridine head groups, so that their extension through



Fig. 3. Stick representations of various cation pairs which can be discerned within the lattice of **1**: (a) the pair with Zn. ..Zn 19.99(2) Å; (b) the pair with Zn. ..Zn 20.07(2) Å; (c) the pair with Zn. ..Zn 11.20(1) Å; (d) the pair with Zn. ..Zn 11.30(1) Å. Black spheres define the centroids of aromatic rings in a stacked array, except for (a), where the rings are not parallel. For (a), dashed lines indicate CH...N contacts, while for (d), the dashed lines define links between the cations involving H-bonding and Cl... π interactions (red = 0, green = Cl).



Fig. 4. Molecular structure of $[Cd(L2)_2]^{2+}$ cation in 2 with thermal ellipsoids plotted at the 50% probability level. For clarity, hydrogen atoms are omitted.



Fig. 5. (a) Views of the apparent stacking arrays for (left) the closest cation pairs (8.98(1) Å apart) and (right) the next closest pairs (at 9.06(1) Å) present in the lattice of **2**. Black spheres define the centroids of the stacked rings and C...C contacts <3.5 Å are shown as dashed lines, the separations/Å being indicated. (b) Orthogonal partial views of one of the strands formed by cations in which the Cd...Cd separations alternate between 8.98(1) and 9.06(1) Å. The upper view is that down the perpendicular to the (111) plane. (c) The stacking contacts involving the shortest centroid...centroid distance (3.586(4) Å) of any intercationic aromatic ring pair, occurring for cations 10.593(7) Å apart in the lattice of **2** (violet = Cd).

the lattice may be influenced by differences in the size of Zn(II) and Cd(II) and thus explain some of the differences between the two present structures (other than the obvious difference due to the nature of the tails). If as a measure of the size of the complex core the distances between the C atoms to which the tails are attached (9.68(1) Å for Zn(II), 10.04(2) Å for Cd(II)) and between the two sets

of C atoms *para* to the N-donor atoms of the peripheral rings (9.45(1), 9.46(1) Å for Zn(II); 9.47(2), 9.51(2) Å for Cd(II)) are taken, at least the longitudinal difference can be regarded as significant in terms of a change in any interaction distance but the lateral differences, probably more relevant in relation to anion bridging, are quite small.

3.2. Absorption and emission spectra

The absorption spectra of the ligands and the complexes in CH_3 -CN are shown Fig. S3. Peak wavelengths and their typically high absorption coefficients are given in Table 2. Comparison of the two ligand spectra shows that the lower-energy absorption peak is slightly red-shifted by the extension of the length of the 4' substituent. As expected [19], there is a red-shift induced by coordination of the metal ions.

The emission spectra of the free ligands and their metal complexes in CH₃CN solution and the solid state are shown in Figs. 6

Table 2

Absorption data in CH_3CN (molar absorption coefficient) for the ligands and the complexes.

Molecules	$\lambda_{max}^{abs} nm (\varepsilon_{max} (\times 10^4 \text{M}^{-1} \text{cm}^{-1}))$				
L1	258 (sh, 1.31)	285 (2.22)			
L2	258 (sh, 1.91)	296 (3.57)			
1	236 (4.44), 269 (sh, 4.95)	287 (6.60)	315 (6.17)		
2	236 (sh, 4.62)	287 (6.97)	332 (8.35)		



Fig. 6. Emission spectra of L1 (solid line) and 1 (dotted line) in solution (5 μ M in CH₃CN) and the solid state (inset) as a powder. The excitation wavelengths were 289 (L1) and 291 nm (1).



Fig. 7. Emission spectra of L2 (solid line) and 2 (dotted line) in solution (5 μ M in CH₃CN) and the solid state (inset) for a powder. The samples were excited at 299 (L2) and 331 nm (2).

and 7. The ligand emission bands, found in the near-UV region in both cases, are strongly red-shifted by metal ion coordination. At the concentrations used, it is possible that the complexes were dissociated to some extent and that this may have affected the spectra, although there is close similarity to what is seen in the solid state. Emission from the Cd(II) complex occurs at a considerably lower energy than that from the Zn(II) complex and it is assumed that this is primarily a consequence of the extension of the ligand structure rather than the change in metal ion. Although the presence of the pyridyl substituent in the tails must reduce the overall polarity of the ligand, the characteristics of the emission spectra remain consistent with the emitting excited state being that of an intramolecular charge transfer (ICT) transition [3,28].

4. Conclusions

The grafting of pyridylphenyl and pyridylbiphenyl tails onto the 4' position of terpyridine has the effect on the structure of the Zn(II) and Cd(II) complexes of these ligands of eliminating almost entirely the "terpyridine embrace" typifying the lattices of complexes of terpyridine itself. While evidence for various other forms of aromatic–aromatic interactions is apparent within the lattices, the patterns are quite different in the two cases studied, indicating that these interactions. This is consistent with recent theoretical evidence [29] that π -stacking only becomes a force of greater significance than dispersion interactions when the contact surfaces are quite large, well beyond the confrontation of single aromatic rings.

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Appendix A. Supplementary data

CCDC 879317 and 879318 contain the supplementary crystallographic data for the complexes **1** and **2**. 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.

Fig. S1 – a view, perpendicular to the (10-1) plane of the cation array present in sheets within which the ligands tails lie. One cation chain is identified in black.

Fig. S2 – a view of the same cation array as shown in the upper part of Fig. 5(b) but without the ligand tail atoms being shown. This is compared with the two-dimensional terpyridine embrace array found, for example, in [Co(terpyridine)2]I2·H2O.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.054.

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