Blue luminescent zinc(II) complexes with polypyridylamine ligands: crystal structures and luminescence properties

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A series of blue luminescent zinc(II) complexes, [Zn(dpa)X$_2$] [dpa = di-2-pyridylamine, X = OAc **1a**, Cl **1b**, CN **1c** or 4-MeC$_6$H$_4$S **1d**], [Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$ **2**, [Zn(tpda)X$_2$] [tpda = 2,6-bis(2-pyridylamino)pyridine, X = OAc **3a** or Cl **3b**] and [Zn(tpda)(CF$_3$SO$_3$)$_2$] **4** has been prepared. Their molecular structures, except complex **4**, have been established by X-ray crystallography. In the crystal lattice of **2** the [Zn(dpa)$_2$]$^{2+}$ cations and CF$_3$SO$_3^-$ anions are disposed in pairs *via* intermolecular hydrogen bonds [N(2)···O(2) 2.865(4) Å]. The crystal packing of [Zn(dpa)(OAc)$_2$] **1a** revealed that two adjacent molecules associate in pairs through intermolecular hydrogen bonding [N(2)···O(4′) 2.816(3) Å]. However, the crystal lattice of its tpda derivative **3a** shows that the molecules are linked by extensive intermolecular hydrogen bonding between the amino groups and the acetate ligands [N(2)···O(2′) 2.805(3) and N(4)···O(4′) 2.860(3) Å] resulting in an interlocking hydrogen bond network. Polymeric one-dimensional tapes are generated through extended π–π stacking interactions between the molecules of [Zn(dpa)(4-MeC$_6$H$_4$S)$_2$] **1d**, and the thiolate groups are aligned in an all-*anti* conformation along the metal chain. In the case of [Zn(dpa)(CN)$_2$] **1c**, co-operative intermolecular hydrogen bonds and aromatic π–π interactions in its solid state lead to a supramolecular two-dimensional sheet. All the zinc(II) complexes display high energy intraligand ^{1}(π–π*) fluorescence in degassed MeOH at 298 K, and intraligand ^{3}(π–π*) phosphorescence in a glassy solution (MeOH–EtOH 1:2 at 77 K). An emission band observed for **1c** (418 nm) and **1d** (481 nm) in their solid state emission spectra is ascribed to excimeric emission due to aromatic π–π interactions.

Introduction

The search for blue luminous materials for applications in blue light-emitting devices (LEDs) remains an ongoing interest in materials sciences.[1–5] The first realization of blue electroluminescence using poly(9,9-dihexylfluorene)[4a,b] and poly(*para*-phenylene)[4c] had triggered an intensive research in this area.[4d] Thus far, the studies have mainly been focused on the use of aromatic organic molecules or conjugated organic polymers as the light emitting materials.[1] Blue luminescent inorganic and organometallic compounds have limited precedents;[3,5] a notable example is the [Zn$_4$O(AID)$_6$] (AID = 7-Azaindolate) complex which has successfully been applied to the construction of a blue LED device.[5a,b] Prompted by the recent reports on blue photoluminescence from organoaluminum(III) complexes[6] of di-2-pyridylamine and the formation of an intermolecular hydrogen bonded metal chain in its cobalt derivative,[7] the use of this and related ligands as structural motifs have received our attention for developing new blue luminous materials with a polymeric supramolecular structure.[8] Self-assembly of molecular components based on hydrogen bonding and aromatic π–π stacking interactions has been widely investigated, and these intermolecular forces are readily harnessed to provide an effective approach to generate a diversity of superstructures from properly designed structural elements.[9]

We herein describe a full account on the preparation and structural characterization of a series of zinc(II) complexes containing di-2-pyridylamine (dpa) and 2,6-bis(2-pyridylamino)pyridine (tpda) ligands, which were found to exhibit blue photoluminescence. In general, these complexes show self-assembled supramolecular structures in the solid state *via* co-operative hydrogen bonds and/or aromatic π–π interactions to generate pairs, chains or networks. Part of this work has been reported in a communication.[5c]

Experimental

All the starting materials were used as received and solvents purified according to the literature methods.[10] Di-2-pyridylamine was obtained commercially, whereas 2,6-bis(2-pyridylamino)pyridine was prepared by the coupling reaction between 2,6-diaminopyridine and 2-bromopyridine.[8b] The UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer, emission spectra on a SPEX Fluorolog-2 Model F11 fluorescence spectrophotometer. Emission lifetimes of the zinc complexes were measured with a Quanta Ray DCR-3 Nd-YAG laser as the excitation light source (pulse output 266 nm, 8 ns). The ^{1}H NMR spectra were recorded on a DPX-300 Bruker FT spectrometer with chemical shifts (in ppm) relative to tetramethylsilane. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, UK.

Preparation of 2,6-bis(2-pyridylamino)pyridine

A solution of 2,6-diaminopyridine (2.50 g, 22.9 mmol) in THF (30 cm^3) was added to a suspension of NaH (50%, 3.30 g, 68.7 mmol) in THF (30 cm^3). After stirring for 30 min, 2-bromopyridine (8.7 cm^3, 91.6 mmol) was added to give a greenish grey suspension, which was refluxed for 24 h resulting in a brown solution. After solvent evaporation, the residue was washed successively with brine solution (15 cm^3) and diethyl ether (15 cm^3). The product solid was collected on a frit and air-dried. Yield: 3.50 g, 58%. ^{1}H NMR (270 MHz, dmso-d$_6$): δ 9.37 (2 H, s, NH), 8.21 (2 H, dd, ^4J = 1.3, ^3J = 4.9), 7.84 (2 H, d, ^3J = 8.4), 7.64 (2 H, dt, ^4J = 1.9, ^3J = 7.8), 7.51 (1 H, t, ^3J = 8.0), 7.14 (2 H, d, ^3J = 8.0) and 6.87 (2 H, dt, ^4J = 0.6 Hz, ^3J = 8.0 Hz). EI-MS: *m/z* 270 [M$^+$]. The spectral characterization data are comparable to reported values, see ref. 8(*b*).

Metal complex preparation

[Zn(dpa)(OAc)₂] 1a. A methanolic solution (20 cm³) of dpa (0.17g, 1 mmol) was added to a refluxing solution of Zn(OAc)₂·2H₂O (0.22 g, 1 mmol) in MeOH (30 cm³). The colorless solution was refluxed for 5 h. After cooling to room temperature, the solvent was removed by rotary evaporation and the white residue recrystallized by slow diffusion of diethyl ether into a methanolic solution to afford colorless crystals: yield 0.30 g, 85% (Found: C, 47.25; H, 4.21; N, 11.92. Calc. for $C_{14}H_{15}N_3O_4Zn$: C, 47.41; H, 4.26; N, 11.85%). δ_H (270 MHz; CD₃OD) 8.38 (2 H, dd, $^4J_{HH} = 1.2$, $^3J_{HH} = 5.6$, aryl H), 7.93 (2 H, td, $^4J_{HH} = 1.9$, $^3J_{HH} = 7.9$, aryl H), 7.20 (2 H, d, $^3J_{HH} = 8.6$, aryl H), 7.16 (2 H, td, $^4J_{HH} = 1.0$, $^3J_{HH} = 6.5$ Hz, aryl H) and 1.98 (6 H, s, CH₃). FAB-MS: m/z 294 [M⁺ − OAc].

[Zn(dpa)Cl₂] 1b. The procedure was similar to that for complex **1a** except ZnCl₂ was used and hot DMF for recrystallization: yield 0.25 g, 80% (Found: C, 38.93; H, 2.99; N, 13.75. Calc. for $C_{10}H_9Cl_2N_3Zn$: C, 39.06; H, 2.95; N, 13.67%). δ_H (270 MHz; DMSO-d₆) 8.20 (2 H, d, $^3J_{HH} = 2.6$, aryl H), 7.80 (2 H, m, aryl H), 7.58 (2 H, d, $^3J_{HH} = 8.4$, aryl H) and 7.01 (2 H, t, $^3J_{HH} = 6.3$ Hz, aryl H). FAB-MS: m/z 270 [M⁺ − Cl].

[Zn(dpa)(CN)₂] 1c. A methanolic solution (20 cm³) of dpa (0.17 g, 1 mmol) was added to a refluxing suspension of Zn(CN)₂ (0.12 g, 1 mmol) in MeOH (30 mL). The mixture was refluxed overnight, and the white solid collected by filtration after cooling to room temperature. The product complex was extracted from the white solid into boiling methanol, and pale yellow crystals (yield 0.17 g, 60%) were obtained on cooling of the hot methanolic extract (Found: C, 49.99; H, 3.02; N, 24.41. Calc. for $C_{12}H_9N_5Zn$: C, 49.94; H, 3.14; N, 24.27%). FT-Raman: 2164, 2153, 1619, 1587 and 1436 cm⁻¹. δ_H (270 MHz; CD₃OD) 10.11 (1 H, s, NH), 8.20 (2 H, d, $^3J_{HH} = 4.3$, aryl H), 7.81 (2 H, t, $^3J_{HH} = 7.3$, aryl H), 7.56 (2 H, d, $^3J_{HH} = 7.2$, aryl H) and 7.02 (2 H, t, $^3J_{HH} = 6.0$ Hz, aryl H). FAB-MS: m/z 289 [M]⁺ and 261 [M⁺ − CN].

[Zn(dpa)(4-MeC₆H₄S)₂] 1d. To a hot methanolic solution (20 cm³) of zinc acetate (0.22 g, 1 mmol) was added 4-methyl-benzenethiol (0.26 g, 2 mmol) in MeOH (10 cm³); the colorless mixture was refluxed for 15 min followed by addition of dpa (0.17 g, 1 mmol) in MeOH (10 cm³). The reaction mixture was refluxed for 15 min. After the solution was cooled to room temperature, solvent was removed by rotary evaporation. The solid residue was recrystallized in MeOH–Et₂O to afford a colorless crystalline solid. Yield: 0.43 g, 90% (Found: C, 59.36; H, 5.01; N, 8.54. Calc. for $C_{24}H_{23}N_3S_2Zn$: C, 59.68; H, 4.80; N, 8.70%). ¹H NMR (270 MHz; dmso-d₆) δ 8.19 (d, 2 H, $^3J = 4.7$), 7.74 (m, 2 H), 7.50 (s, 1 H), 7.07 (m, 4 H), 6.97 (m, 2 H), 6.76 (d, 4 H, $^3J = 7.1$ Hz) and 2.13 (s, 6 H). FAB-MS: m/z 358 [M⁺ − SC₇H₇].

[Zn(dpa)₂][CF₃SO₃]₂ 2. A mixture of complex **1b** (0.31 g, 1 mmol) and Ag(CF₃SO₃) (0.57 g, 2.2 mmol) in MeOH (50 cm³) was refluxed for 2 h. After cooling to room temperature the colorless solution was filtered through Celite and the filtrate was evaporated to dryness. The white residue was recrystallized in MeOH–Et₂O to afford colorless crystals. Yield: 0.29 g, 41% (Found: C, 37.02; H, 2.84; N, 11.84. Calc. for $C_{22}H_{18}F_6N_6O_6S_2Zn$: C, 37.43; H, 2.57; N, 11.91%). ¹H NMR (270 MHz, CD₃OD): δ 10.12 (s, 1 H), 8.20 (d, 2 H, $^3J = 4.9$), 7.81 (t, 2 H, $^3J = 7.2$), 7.56 (d, 2 H, $^3J = 8.2$) and 7.03 (t, 2 H, $^3J = 5.8$ Hz). FAB-MS: m/z 555 [M⁺ − CF₃SO₃] and 384 [M⁺ − CF₃SO₃ − dpa].

[Zn(tpda)(OAc)₂] 3a. A similar procedure was employed as for complex **1a**, except that tpda was used. Yield: 0.36 g,

81% (Found: C, 51.08; H, 4.25; N, 15.61. Calc. for $C_{19}H_{19}N_5O_4Zn$: C, 51.09; H, 4.29; N, 15.67%). ¹H NMR (270 MHz, CD₃OD): δ 8.60 (d, 2 H, $^3J = 4.8$), 8.02 (t, 2 H, $^3J = 7.2$), 7.87 (t, 2 H, $^3J = 7.9$), 7.28 (m, 4 H), 7.00 (m, 1 H) and 6.82 (d, 2 H, $^3J = 8.1$ Hz). FAB-MS: m/z 386 [M⁺ − OAc].

[Zn(tpda)Cl₂] 3b. A similar procedure as for complex **1b** was employed, except that tpda was used. Yield: 0.30 g, 75% (Found: C, 45.20; H, 3.19; N, 17.50. Calc. for $C_{15}H_{13}Cl_2N_5Zn$: C, 45.09; H, 3.28; N, 17.53%). ¹H NMR (270 MHz, dmso-d₆): δ 9.59 (s, 2 H), 8.32 (m, 2 H), 7.73 (m, 5 H) and 6.97 (m, 4 H). FAB-MS: m/z 362 [M⁺ − Cl].

[Zn(tpda)(CF₃SO₃)₂] 4. A similar procedure as for complex **1e** was employed. Yield: 0.41 g, 66% (Found: C, 32.31; H, 2.22; N, 11.25. Calc. for $C_{17}H_{13}F_6N_5O_6S_2Zn$: C, 32.58; H, 2.09; N, 11.17%). ¹H NMR (270 MHz, CD₃OD): δ 7.91 (m, 1 H), 7.77 (m, 4 H) and 6.89 (m, 6 H). FAB-MS: m/z 476 [M⁺ − CF₃SO₃].

Crystal structure determinations

For complex **3b**, a Rigaku AFC7R diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) was employed. The structure was solved by Patterson methods and expanded by Fourier methods (PATTY).[11] The structure was refined by full-matrix least squares using the software package TEXSAN[12] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit contains one formula unit. In the least-squares refinement, 13 non-H atoms were refined anisotropically, the positional parameters of H(1) bonded to N(2) located in a Fourier-difference synthesis were refined, and the H atoms at the calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined.

For complexes **1a**, **1b**, **1d**, **2** and **3a**, a MAR diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) was employed. The structure for **2** was solved by direct methods (SIR 92)[13] and the Patterson method was used for the others. The structures were expanded by Fourier methods (PATTY)[11] and refined by full-matrix least squares using the software package TEXSAN[12] on a Silicon Graphics Indy computer. For **2**, one crystallographic asymmetric unit contains half of the complex cation with the Zn atom at a special position plus one CF₃SO₃⁻ anion. For other complexes, one crystallographic asymmetric unit consists of one molecule. In the least-squares refinement all the non-H atoms were refined anisotropically; the H atoms bonded to the amino groups were located in the Fourier-difference synthesis and their positional parameters refined. The other H atoms at the calculated positions with their thermal parameters equal to 1.3 times those of the attached C atoms were not refined.

CCDC reference number 186/1387.

See http://www.rsc.org/suppdata/dt/1999/1581/ for crystallographic files in .cif format.

Results and discussion

2,6-Bis(2-pyridylamino)pyridine was previously synthesized by Peng and co-workers[8b] using the coupling reaction of 2-bromopyridine and 2,6-diaminopyridine with ᵗBuOK as a base in THF (26% yield). In this work, we employed NaH for the coupling reaction, and a much better product yield of 58% was obtained (Scheme 1). The treatment of Zn(OAc)₂·2H₂O, ZnCl₂ and Zn(CN)₂ with the ligands dpa or tpda in methanol afforded monomeric zinc(II) complexes in high yields. The triflatozinc(II) derivatives were prepared by metathesis of the chlorozinc(II) complexes with silver(I) triflate. All the complexes reported, except [Zn(tpda)(CF₃SO₃)₂] **4**, had their molecular structures determined by X-ray crystallography. The structure
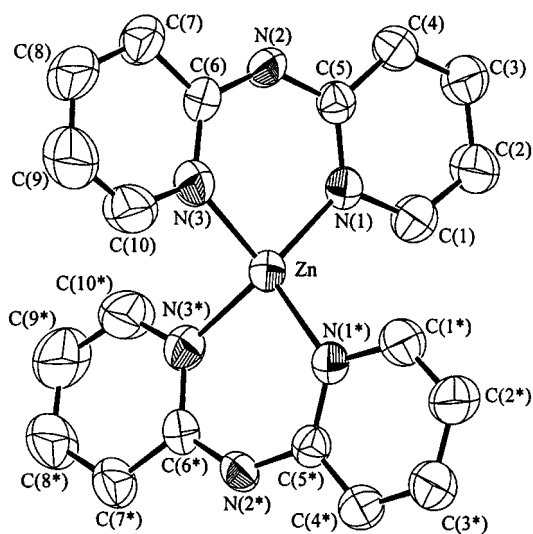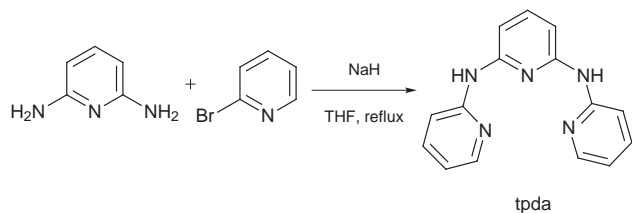
Scheme 1

Fig. 1 Perspective view of [Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$ **2** (50% thermal ellipsoids) and atom-numbering scheme.
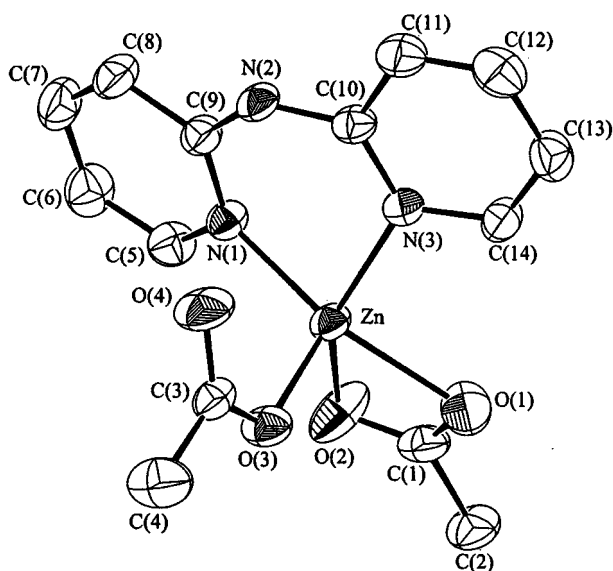
Fig. 2 Perspective view of [Zn(dpa)(OAc)$_2$] **1a**. Details as in Fig. 1.

Fig. 3 Perspective view of [Zn(tpda)(OAc)$_2$] **3a**. Details as in Fig. 1.
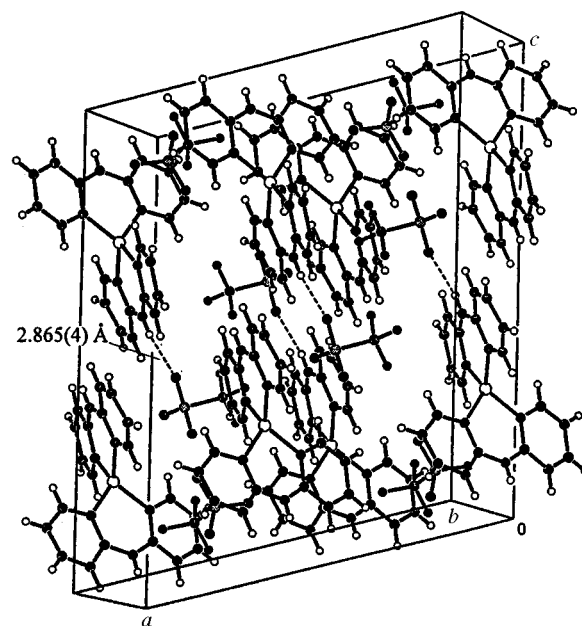
Fig. 4 The crystal packing diagram of [Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$ **2**. Each [Zn(dpa)$_2$]$^{2+}$ cation associates with one molecule of CF$_3$SO$_3^-$ anion through intermolecular hydrogen bonding [N(2)H···O] resulting in ion-pair formation.

of **1c** has previously been communicated.[5c] The crystal data, selected bond lengths and bond angles are in Tables 1 and 2 respectively.

Both dpa and tpda co-ordinate to Zn^{II} *via* the pyridyl nitrogen atoms. For dpa as the ligand, complexes **1b–1d** and **2** are isostructural and the zinc atoms adopt a distorted tetrahedral co-ordination geometry (Fig. 1). The zinc atom of [Zn(dpa)(OAc)$_2$] **1a** is five-co-ordinated, and both η^1 and η^2 co-ordination modes are observed for the two acetate ligands. The Zn–OAc distances are 1.960(2) Å for the η^1-OAc, 2.166(2) and 2.149(2) Å for the η^2-OAc (Fig. 2). The N(1)–Zn–O(1) and N(3)–Zn–O(2) angles are 145.5(1) and 141.0(1)° respectively, whereas the respective O(3)–Zn–N(1) and O(1)–Zn–N(3) angles are 111.72(9) and 95.36(9)°.
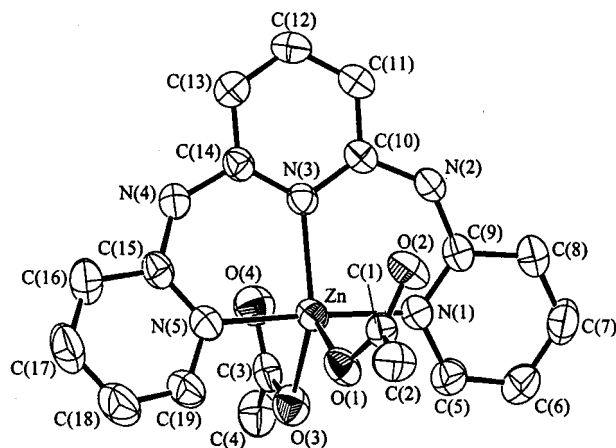
The complexes **3a** and **3b** with tpda are isostructural (Fig. 3), and the zinc atoms adopt a distorted trigonal bipyramidal configuration. The N(1)–Zn–N(5) bond angle of **3a** was found to be 177.00(9)° [the corresponding bond angle for **3b** = 176.98(9)°], while the N(1), Zn atoms and the two auxiliary η^1-OAc ligands are located on the equatorial plane. For all the zinc complexes described in this work the Zn–N (pyridyl) distances are in a 1.972(3)–2.129(2) Å range, comparable to the corresponding distances [2.148(9) and 2.082(9) Å] found for [Zn(L)(dien)](NO$_3$)$_2$ [dien = bis(2-aminoethyl)amine].[14]

Self-assembly of molecular components *via* intermolecular hydrogen bonding and/or π–π stacking interactions has received intense interest in crystal engineering.[9] We found several types of supramolecular structures such as molecular pairing, polymeric tapes and networks in the crystal lattices of the zinc(II) complexes of dpa and tpda ligands *via* these intermolecular interactions.

The crystal packing diagram of [Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$ **2** (Fig. 4) shows that each [Zn(dpa)$_2$]$^{2+}$ cation associates with one CF$_3$SO$_3^-$ anion by hydrogen bonding interaction between the unbound amino group and one of the oxygen atoms of the adjacent triflate anion, resulting in ion pairings [N(2)···O(2′) 2.865(4) Å]. However, no extended intermolecular hydrogen bondings are recognized. Likewise, molecular pairing of the

neutral [Zn(dpa)(OAc)$_2$] **1a** *via* two intermolecular hydrogen bonds between the non-co-ordinating N–H group and the η^1-acetate group of the adjacent molecule is evident. The
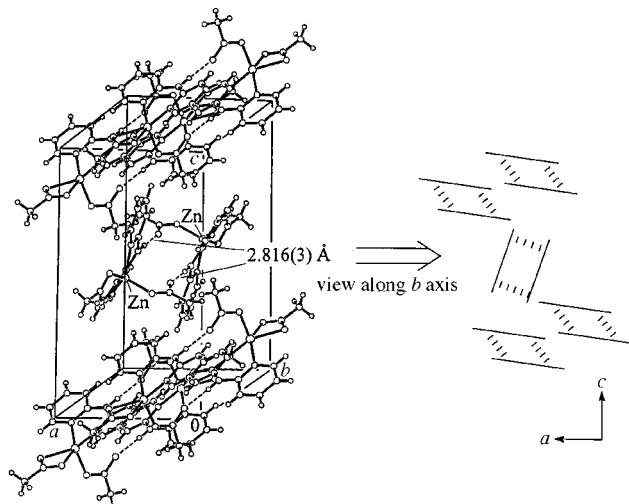

Fig. 5 Herringbone-type crystal packing of [Zn(dpa)(OAc)$_2$] **1a** molecules. The molecular pairing is generated by two intermolecular hydrogen bonds [N(2)H · · · O(4)] between two complexes.
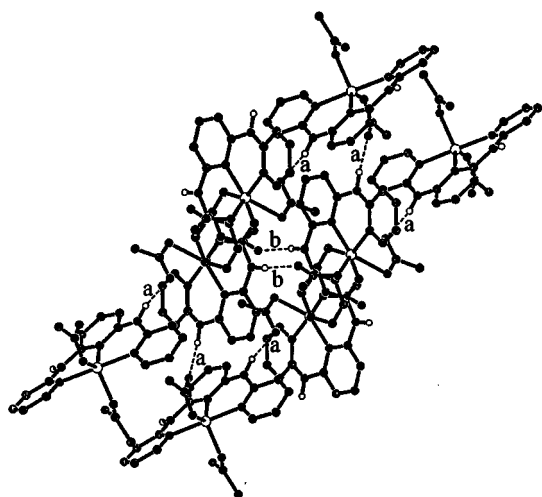

Fig. 6 The crystal packing diagram of [Zn(tpda)(OAc)$_2$] **3a** shows a self-assembled 2-D network structure resulting from two types of extended intermolecular hydrogen bonds [N(2)H · · · O(2) (denoted as a) and N(4)H · · · O(4) (b)].

N(2) · · · O(4′) distance is found to be 2.816(3) Å. As revealed by the crystal packing of **1a** shown in Fig. 5, the molecular pairs are disposed in a herringbone-type pattern.[15]

In the case of [Zn(tpda)(OAc)$_2$] **3a**, there are two non-co-ordinating amino groups [N(4)–H and N(2)–H] available for hydrogen bonding for each tpda ligand. Its crystal packing diagram (Fig. 6) shows that the molecules associate with each other by extensive intermolecular hydrogen bonding interactions between the N(4)–H group and the O(4′) atom of the acetate group of an adjacent molecule [N(4) · · · O(4′) 2.860(3) Å] in a head-to-tail fashion leading to an infinite one-dimensional zigzag chain with an obvious directionality. Each of the chains are cross-linked with neighbouring chains by extensive hydrogen bonds between N(2)–H(1) · · · O(2′) and N(2′)–H(1′) · · · O(2) atoms [N(2) · · · O(2′) distance 2.805(3) Å] along the chains creating a two-dimensional interlocking hydrogen bonding network.

Fig. 7 depicts the crystal lattice packing of [Zn(dpa)-(4-MeC$_6$H$_4$S)$_2$] **1d**. The glide-related molecules self-assemble through aromatic π–π stacking interactions to form an infinite one-dimensional tape with the interplanar distance between the pyridyl rings being 3.5–3.7 Å. The thiolate moieties are aligned in an *anti* conformation along the polymeric chain.
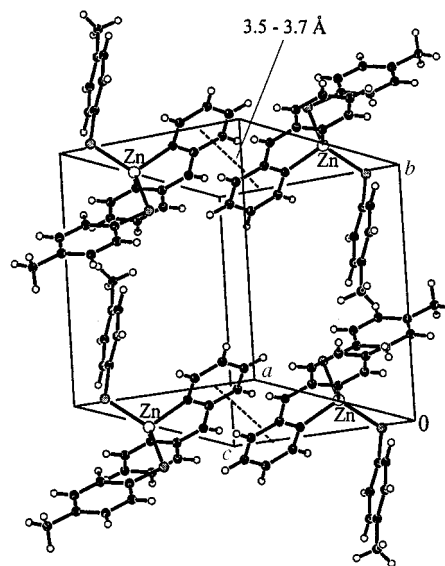

Fig. 7 The crystal packing diagram of [Zn(dpa)(4-MeC$_6$H$_4$S)$_2$] **1d** shows a self-assembled infinite 1-D tape structure generated by extensive aromatic π–π interactions.

Table 1 Crystallographic data for complexes **1a**, **1b**, **1d**, **2**, **3a** and **3b**

	1a	1b	1d	2	3a	3b
Formula	C$_{14}$H$_{15}$N$_3$O$_4$Zn	C$_{10}$H$_9$Cl$_2$N$_3$Zn	C$_{24}$H$_{23}$N$_3$S$_2$Zn	C$_{20}$H$_{18}$N$_6$Zn·2CF$_3$SO$_3$	C$_{19}$H$_{19}$N$_5$O$_4$Zn	C$_{15}$H$_{13}$Cl$_2$N$_5$Zn
M	354.67	307.49	482.97	705.91	446.77	399.59
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	10.310(2)	7.439(2)	8.637(2)	16.393(3)	9.662(2)	7.519(2)
b/Å	8.339(2)	8.669(2)	11.018(2)	8.897	8.016(2)	17.202(2)
c/Å	17.935(3)	9.409(2)	12.138(2)	19.610(3)	24.566(4)	12.869(2)
α/°	—	75.28(2)	86.55(2)	—	—	—
β/°	102.43(2)	89.32(2)	86.59(2)	103.05(2)	92.16(2)	103.96(1)
γ/°	—	86.11(2)	80.74(2)	—	—	—
V/Å^3	1505.8(5)	585.5(2)	1136.5(4)	2786.2(9)	1901.3(6)	1615.4(5)
Z	4	2	2	4	4	4
R_{int}	0.034	0.038	0.038	0.036	0.049	0.018
μ/cm^{-1}	16.52	25.26	12.80	11.21	13.30	18.56
T/K	301	301	301	301	301	301
No. unique data	2929	2512	4950	2573	3749	1656
No. data with $I > 3\sigma(I)$	2326	2291	4108	2097	2791	1367
R	0.036	0.049	0.042	0.054	0.040	0.022
R'	0.056	0.066	0.064	0.082	0.054	0.030

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes **1a**, **1b**, **1d**, **2**, **3a** and **3b**

Complex **1a**

Zn–N(1)	2.055(3)	N(1)–Zn–N(3)	89.78(9)
Zn–O(1)	2.166(2)	N(1)–Zn–O(2)	95.93(9)
Zn–O(3)	1.960(2)	N(3)–Zn–O(1)	95.36(9)
Zn–N(3)	2.039(2)	N(3)–Zn–O(3)	116.21(9)
Zn–O(2)	2.149(2)	O(1)–Zn–O(3)	96.51(1)
		N(1)–Zn–O(1)	145.5(1)
		N(1)–Zn–O(3)	111.72(9)
		N(3)–Zn–O(2)	141.0(1)
		O(1)–Zn–O(2)	59.81(9)
		O(3)–Zn–O(2)	97.3(1)

Complex **1b**

Zn–N(1)	2.023(2)	N(1)–Zn–N(3)	93.08(9)
Zn–Cl(1)	2.2029(9)	N(1)–Zn–Cl(2)	111.79(7)
Zn–N(3)	2.023(2)	N(3)–Zn–Cl(2)	107.56(8)
Zn–Cl(2)	2.243(1)	N(1)–Zn–Cl(1)	113.36(7)
		N(3)–Zn–Cl(1)	116.26(8)

Complex **1d**

Zn–N(1)	2.051(2)	N(1)–Zn–N(3)	89.18(8)
Zn–S(1)	2.2761(8)	N(1)–Zn–S(2)	106.19(7)
Zn–N(3)	2.074(2)	N(1)–Zn–S(1)	114.08(6)
Zn–S(2)	2.2764(8)	S(1)–Zn–S(2)	119.52(3)

Complex **2**

| Zn–N(1) | 1.972(3) | N(1)–Zn–N(1*) | 110.8(2) |
| Zn–N(3) | 2.001(3) | N(1)–Zn–N(3) | 95.8(1) |

Complex **3a**

Zn–N(1)	2.083(2)	N(1)–Zn–N(3)	92.14(9)
Zn–N(5)	2.104(2)	N(1)–Zn–O(1)	93.73(9)
Zn–O(3)	2.144(2)	N(3)–Zn–N(5)	90.37(9)
Zn–N(3)	2.129(2)	N(3)–Zn–O(3)	136.36(9)
Zn–O(1)	2.052(2)	N(5)–Zn–O(3)	89.04(9)
		N(1)–Zn–N(5)	177.00(9)
		N(1)–Zn–O(3)	88.01(9)
		N(3)–Zn–O(1)	121.73(9)
		N(5)–Zn–O(1)	86.34(9)

Complex **3b**

Zn–N(1)	2.099(2)	N(1)–Zn–N(2)	88.49(5)
Zn–Cl(1)	2.3397(6)	Cl(1)–Zn–Cl(1*)	124.18(3)
Zn–N(2)	2.126(2)	N(1)–Zn–Cl(1)	117.91(2)
		N(2)–Zn–N(2*)	176.98(9)
		N(2)–Zn–Cl(1)	92.84(5)
		N(2)–Zn–Cl(1*)	88.57(5)

Table 3 The UV-vis spectral data for complexes **1**–**4** in MeOH at 298 K

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})
[Zn(dpa)(OAc)$_2$]	257 (20000), 315 (18000)
[Zn(dpa)Cl$_2$]	255 (18000), 315 (17000)
[Zn(dpa)(CN)$_2$]	257 (18000), 316 (16000)
[Zn(dpa)(4-MeC$_6$H$_4$S)$_2$]	256 (50000), 317 (16000)
[Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$	258 (35000), 314 (29000)
[Zn(tpda)(OAc)$_2$]	261 (17000), 312 (18000), 345 (12000)
[Zn(tpda)Cl$_2$]	261 (17000), 311 (18000), 342 (13000)
[Zn(tpda)(CF$_3$SO$_3$)$_2$]	261 (32000), 312 (33000), 336 (38000)

Table 4 The emission data and quantum yields (φ) for complexes **1**–**4**

| | Emission λ/nm | | | |
Complex	Degassed MeOH ^{a}	MeOH–EtOH (1:2) ^{b}	Solid state ^{a}	φ
[Zn(dpa)(OAc)$_2$]	359	349, 389	378	0.12
[Zn(dpa)Cl$_2$]	360	348, 390	378	0.12
[Zn(dpa)(CN)$_2$]	359	351, 392	363, 418	0.08
[Zn(dpa)(4-MeC$_6$H$_4$S)$_2$]	354	342, 393	481	0.01
[Zn(dpa)$_2$][CF$_3$SO$_3$]$_2$	360	352, 392	373	0.12
[Zn(tpda)(OAc)$_2$]	394	390, 418	411	0.14
[Zn(tpda)Cl$_2$]	392	387, 447	403	0.14
[Zn(tpda)(CF$_3$SO$_3$)$_2$]	390	388, 450	398	0.15

^{a} At 298 K. ^{b} At 77 K.

The emission spectral data and quantum yields (φ) are summarized in Table 4. For the complexes **1a**–**1d** and **2** the emission energies in MeOH at 298 K are the same (λ_{max} = 359 nm), albeit they contain different auxiliary ligands. The emission is assigned to intraligand fluorescence since a similar emission (λ_{max} = 357 nm) has also been observed for free dpa. Similarly, the emission of complexes **3a**, **3b** and **4** in MeOH at 298 K (λ_{max} = 390 nm) is dominated by the intraligand fluorescence of the tpda ligand. The lifetimes of the fluorescence of these complexes are <10 ns.

In glassy solution (MeOH–EtOH 1:2 at 77 K) both intraligand fluorescence and $^3(\pi–\pi^*)$ phosphorescence have been observed. The low energy emission of all the complexes, except **3b** and **4**, is vibronically structured (ca. 1300 cm^{-1}) with the vibrational progression similar to the skeletal vibrational frequency of the "free" ligand.

In the solid state the Zn–dpa derivatives, except **1d**, show an emission ranging from 363 to 378 nm which arises from the $^1\pi\pi^*$ intraligand excited state. For **1d** which shows π–π aromatic stacking interactions in its solid state, a distinct excimeric emission with λ_{max} = 481 nm was observed. For the complexes with tpda the solid state emission (λ_{max} in 398–403 nm range) is due to the intraligand excited states.

Conclusion

A series of blue photoluminescent zinc(II) complexes with di-2-pyridylamine and 2,6-bis(2-pyridylamino)pyridine have been prepared. Intermolecular hydrogen bonding and aromatic π–π stacking interactions have been observed in the crystal lattice of the complexes, and these interactions generated several types of supramolecular structures.

Acknowledgements

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In this case no intermolecular hydrogen bonding interactions between the free amino group and the sulfur atoms were observed.

All the above complexes display supramolecular structures in the solid state either by intermolecular hydrogen bonding or aromatic π–π interactions. As reported previously, the molecules of [Zn(dpa)(CN)$_2$] **1c** are bound within an infinite two-dimensional supramolecular structure by co-operation of both interactions.[5c]

However, the dichlorozinc(II) complexes **1b** and **3b** do not display a supramolecular structure in their crystal lattices. Their N⋯Cl distances (3.28–3.43 Å) are too long to account for any intermolecular hydrogen bonds, and the shortest intermolecular separations [4.2 (**1b**); 4.7 Å (**3b**)] between two adjacent [Zn(dpa)] moieties are too large to permit aromatic π–π interactions.

The spectroscopic data are listed in Table 3. Complexes with dpa, *i.e.* **1a**–**1d** and **2**, feature two intense absorptions at 257 and 315 nm which are assigned to intraligand π–π^* transitions. For **3a**, **3b** and **4** bearing the tpda ligand, the absorptions with λ_{max} < 345 nm (ε_{max} > 10^4 dm^3 mol^{-1} cm^{-1}) are similarly assigned to intraligand π–π^* transitions.

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Paper 9/00504H