*Electronic Supplementary Information for Chem. Commun.*

# Unique $Zn^{II}$ coordination entanglement networks with a flexible fluorinated bis-pyridinecarboxamide tecton and benzenedicarboxylates

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## Experimental section

### General methods

With the exception of the ligand $H_2$tfpbbp, which was prepared according to the literature procedure,[1] all reagents and solvents for synthesis and analysis were commercially available and used as received. Infrared spectra were recorded on a Nicole ESP 460 FT-IR spectrometer (KBr pellets) in the range of 4000–600 $cm^{-1}$. C, H and N analyses were performed on a PE-2400 II (Perkin-Elmer) analyzer. Luminescent spectra in the solid state were recorded on a Varian Cary Eclipse spectrometer. Thermogravimetric analysis (TGA) experiments were performed by using a Dupont thermal analyzer from room temperature to 800 °C under a $N_2$ atmosphere at a heating rate of 10 °C /min. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku D/max-2500 diffractometer at 60 kV and 300 mA for Cu Kα radiation (λ= 1.5406 Å), with a scan speed of 2°/min and a step size of 0.02° in a 2$\theta$ range of 3.00–50.00°.

### Synthesis

Complexes **1**–**4** were similarly synthesized by a typical procedure as described below.

Preparation of **1**: A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (22.0 mg, 0.1 mmol), $H_2$tfpbbp (41.8 mg, 0.1 mmol), $H_2$ip (16.6 mg, 0.1 mmol), and water (7 mL) was placed into a Teflon-lined stainless steel vessel (20 mL), which was heated to 160 °C for 24 h and subsequently cooled to room temperature at a rate of 2 °C/h. Colorless block crystals of **1** were obtained.

**$[Zn_2(H_2tfpbbp)(ip)_2(H_2O)_2]_n$ (1)**. Yield: 20.6 mg (45%, based on $Zn^{II}$). Anal. Calcd for $C_{18}H_{13}F_2N_2O_6Zn$: C, 47.34; H, 2.87; N, 6.13%. Found: C, 47.30; H, 2.83; N, 6.15%. IR ($cm^{-1}$): 3313s, 1646vs, 1595w, 1542s, 1492s, 1448m, 1408m, 1374m, 1315s, 1290m, 1236w, 1066s, 1026s, 845w, 687s.

**$[Zn_2(H_2tfpbbp)(mip)_2(H_2O)_2]_n$ (2).** Yield: 23.5 mg (50%, based on $Zn^{II}$). Anal. Calcd for $C_{19}H_{15}F_2N_2O_6Zn$: C, 48.48; H, 3.21; N, 5.95%. Found: C, 48.43; H, 3.21; N, 5.99%. IR ($cm^{-1}$): 3313s, 1646vs, 1543s, 1494s, 1446m, 1409w, 1370m, 1314s, 1233w, 1064s, 1028s, 756w, 727w, 685s.

**$\{[Zn(H_2tfpbbp)(fip)]\cdot H_2O\}_n$ (3).** Yield: 30.8 mg (45%). Anal. Calcd for $C_{28}H_{19}F_5N_4O_7Zn$: C, 49.18; H, 2.80; N, 8.19%. Found: C, 49.15; H, 2.85; N, 8.33%. IR ($cm^{-1}$): 3446s, 3282s, 3091m, 1670vs, 1630s, 1587w, 1554s, 1490s, 1421w, 1376m, 1310vs, 1238w, 1064s, 1031w, 959w, 853w, 770w, 733m, 689s.

**$\{[Zn_2(H_2tfpbbp)_2(nip)_2]\cdot H_2O\}_n$ (4).** Yield: 25.3 mg (36%). Anal. Calcd for $C_{56}H_{36}F_8N_{10}O_{17}Zn_2$: C, 47.91; H, 2.58; N, 9.98%. Found: C, 47.94; H, 2.56; N, 9.97%. IR ($cm^{-1}$): 3449w, 3306s, 3065m, 1647vs, 1539s, 1487s, 1411w, 1342w, 1308vs, 1170w, 1064s, 1014w, 849w, 764w, 730m, 687m.

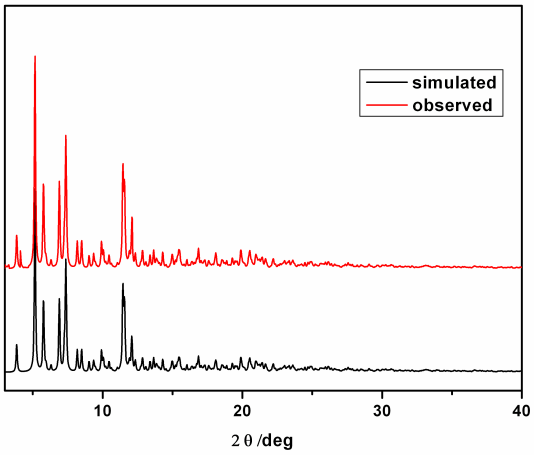
**Luminescence study**

To explore the potential applications as luminescent materials, solid-state fluorescent properties for **1**–**4** and the free $H_2$tfpbbp ligand (Fig. S6) were studied at room temperature. The $H_2$tfpbbp ligand displays emissions in the range of 415–525 nm peaking at *ca.* 435 and 500 nm (upon excitation at 335 nm). The $Zn^{II}$ complexes **1**–**3** show the broad emission bands (from 360 to 550 nm) with shoulder peaks, upon excitation at 335–337 nm (Fig. S7), indi-

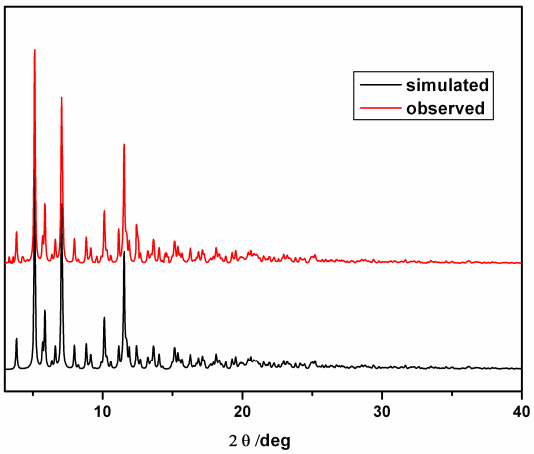
cating the blue shifts comparing with that of $H_2$tfpbbp. Luminescence quench is observed for **4**. Complex **1** has a very broad blue emission band with $\lambda_{max}$ of 470 nm, which is similar to that of the free ligand. While the maximum emissions of **2** and **3** are similarly observed at 440 and 418 nm, respectively, which are in the blue region and result in visible luminescence.

**Reference:**

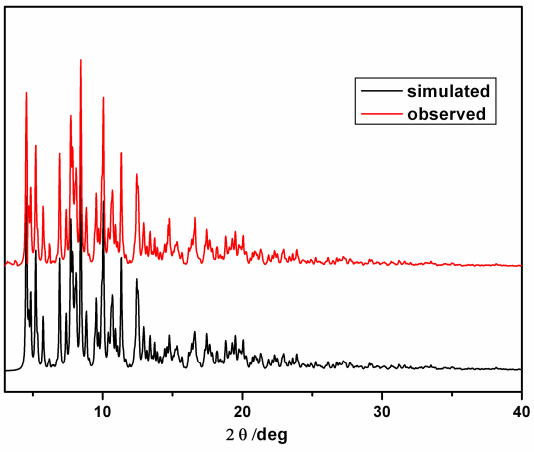
1 S.-C. Chen, M.-Y. He, K. Yan, Q. Chen, Y. Guo and Y.-F. Zhang, *Inorg. Chem. Commun.*, 2007, **10**, 451.


simulated
observed
10
20
30
40
2 θ /deg

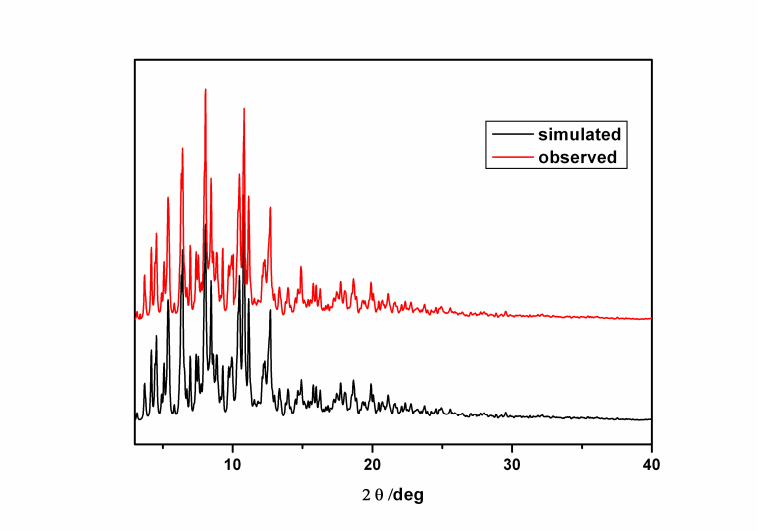
**(a)**


simulated
observed
10
20
30
40
2 θ /deg

**(b)**

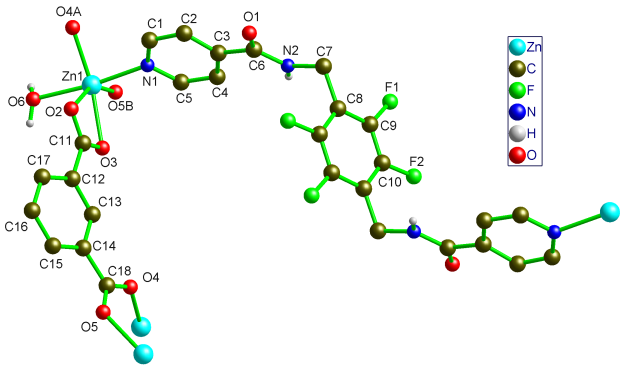

simulated
observed
10
20
30
40
2 θ /deg

**(c)**

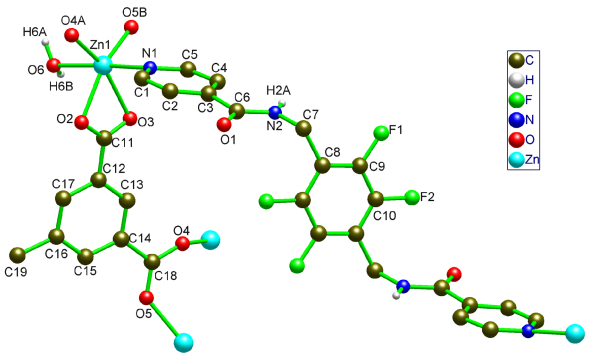



**(d)**

**Fig. S1** Powder X-ray diffraction (PXRD) patterns for complexes **1**–**4** (**a**–**d**).

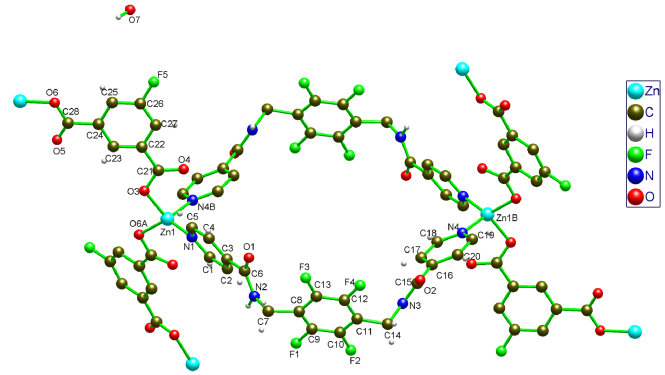



**(a)**

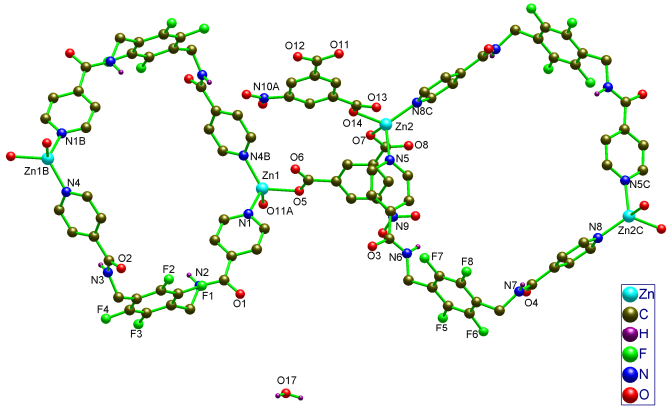



**(b)**

**Fig. S2** A portion view of **1** (a) and **2** (b) with labeling of the asymmetric atoms. Symmetry codes: A = $x - 1, -y - 1/2, z + 3/2$; B = $-x + 1, y + 1/2, -z + 3/2$.




**(a)**




**(b)**

**Fig. S3** A portion view of **3** (a) and **4** (b) with labeling of the asymmetric atoms. Symmetry codes: A = $x$, $-y + 1/2$, $z - 1/2$; B = $-x + 1$, $-y + 2$, $-z + 1$ for **3**. A = $x$, $y - 1$, $z$; B = $-x + 2$, $-y$, $-z + 2$; C = $-x - 1$, $-y + 1$, $-z + 2$ for **4**.

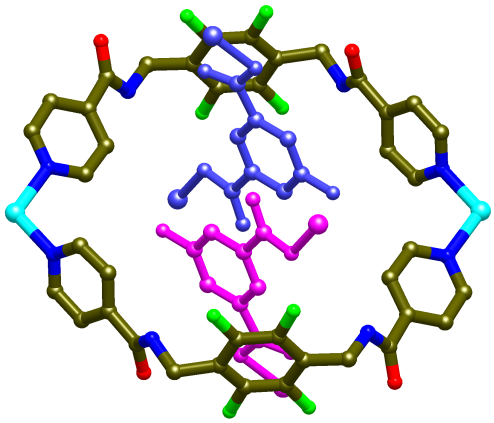


**Fig. S4** View of **3** showing the threading of two fip spacers into the $Zn_2(H_2tfpbbp)_2$ loop.

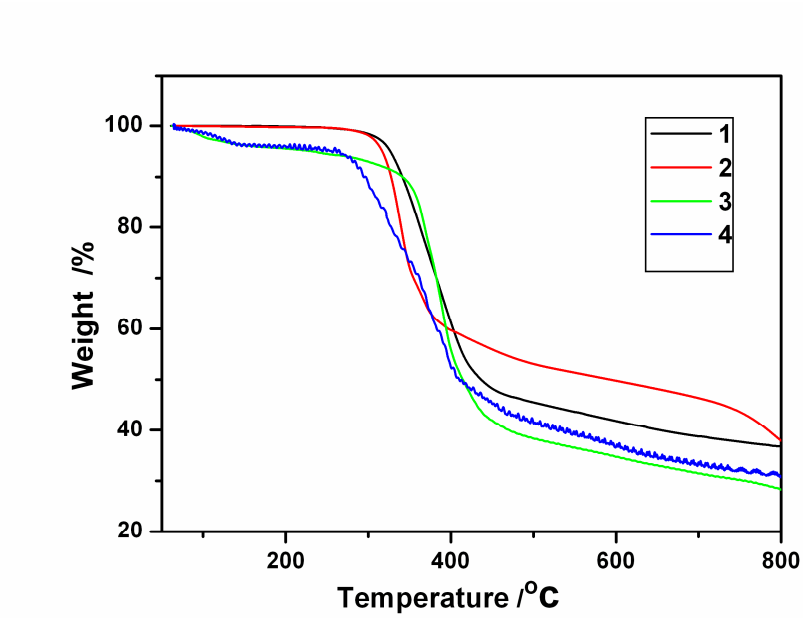



**Fig. S5** TGA curves of complexes **1**–**4**.

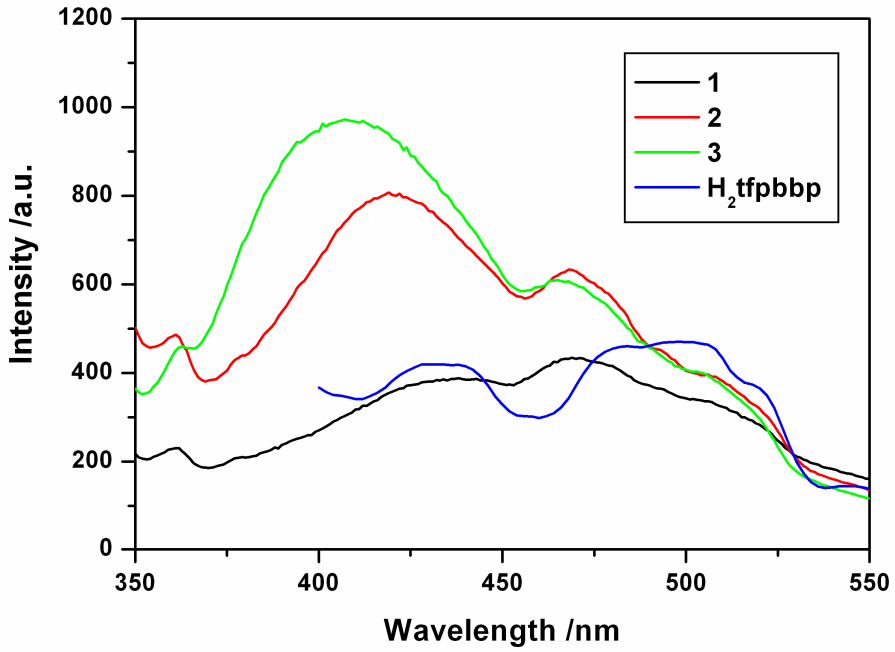



**Fig. S6** Solid state emission spectra of **1**–**3** and $H_2$tfpbbp.

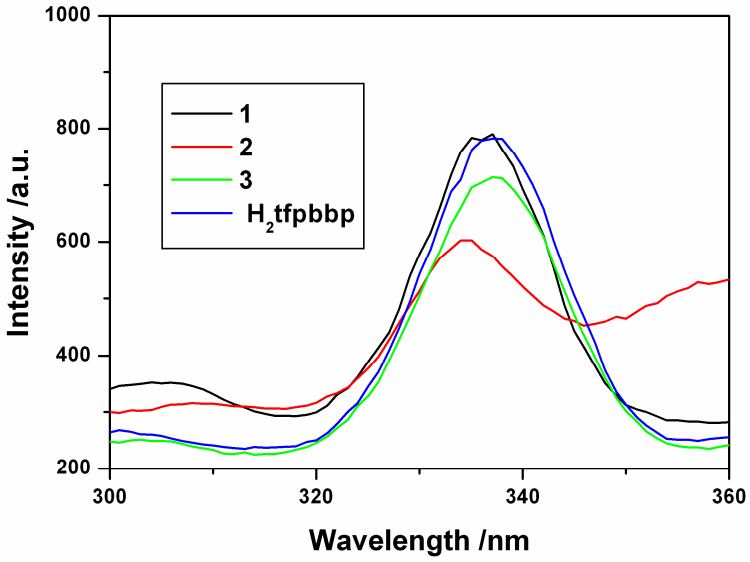



**Fig. S7** Solid state excitation spectra of **1**–**4** and the free $H_2$tfpbbp ligand.

**Table S1** Crystallographic data and structure refinement for complexes **1**–**4**.

| Complex | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| formula | $C_{18}H_{13}F_2N_2O_6Zn$ | $C_{19}H_{15}F_2N_2O_6Zn$ | $C_{28}H_{19}F_5N_4O_7Zn$ | $C_{56}H_{36}F_8N_{10}O_{17}Zn_2$ |
| *Mr* | 456.69 | 470.70 | 683.84 | 1403.69 |
| cryst system | monoclinic | monoclinic | monoclinic | triclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ |
| *a* [Å] | 8.0683(8) | 8.2753(9) | 16.511(4) | 11.738(2) |
| *b* [Å] | 15.9656(16) | 16.4858(18) | 11.031(3) | 16.567(3) |
| *c* [Å] | 14.4286(15) | 14.4799(16) | 16.949(4) | 16.799(3) |
| $\alpha$ [°] | 90 | 90 | 90 | 73.420(2) |
| $\beta$ [°] | 101.8500(10) | 106.4530(10) | 112.683(3) | 70.116(2) |
| $\gamma$ [°] | 90 | 90 | 90 | 85.726(2) |
| *V* [Å$^3$] | 1819.0(3) | 1894.5(4) | 2848.4(12) | 2943.3(10) |
| *Z* | 4 | 4 | 4 | 2 |
| $\rho_{calcd}$ [g·cm$^{-3}$] | 1.668 | 1.650 | 1.595 | 1.584 |
| $\mu$ [mm$^{-1}$] | 1.410 | 1.357 | 0.949 | 0.921 |
| *F*(000) | 924 | 956 | 1384 | 1420 |
| total/independent reflns | 15407/4162 | 14768/3719 | 20033/5005 | 22423/10886 |
| parameters | 262 | 272 | 406 | 866 |
| $R_{int}$ | 0.0322 | 0.0529 | 0.0227 | 0.0353 |
| $R^a$, $R_w{}^b$ | 0.0268, 0.0720 | 0.0506, 0.1091 | 0.0266, 0.0698 | 0.0509, 0.1338 |
| GOF | 1.062 | 0.944 | 1.033 | 1.080 |
| residuals [e Å$^{-3}$] | 0.344, –0.511 | 0.327, –0.571 | 0.300, –0.252 | 1.087, –1.374 |

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.

**Table S2** Selected bond distances (Å) and angles (°) for complexes **1**–**4**.

| **1** | | **2** | |
|---|---|---|---|
| Zn1–O2 | 2.2197(13) | Zn1–O2 | 2.143(3) |
| Zn1–O3 | 2.2147(13) | Zn1–O3 | 2.274(3) |
| Zn1–O6 | 2.1380(13) | Zn1–O6 | 2.179(3) |
| Zn1–N1 | 2.1202(14) | Zn1–N1 | 2.128(3) |
| Zn1–O5$^{i}$ | 2.0395(12) | Zn1–O5$^{i}$ | 2.018(3) |
| Zn1–O4$^{ii}$ | 2.0558(12) | Zn1–O4$^{ii}$ | 2.041(2) |
| O2–Zn1–O3 | 59.01(5) | O2–Zn1–O3 | 59.52(9) |
| O2–Zn1–O6 | 84.50(5) | O2–Zn1–O6 | 81.55(10) |
| O2–Zn1–N1 | 95.26(5) | O2–Zn1–N1 | 95.35(11) |
| O2–Zn1–O5$^{i}$ | 152.01(5) | O2–Zn1–O5$^{i}$ | 151.70(10) |
| O2–Zn1–O4$^{ii}$ | 96.82(5) | O2–Zn1–O4$^{ii}$ | 98.23(10) |
| O3–Zn1–O6 | 90.89(5) | O3–Zn1–O6 | 92.41(10) |
| O3–Zn1–N1 | 94.19(5) | O3–Zn1–N1 | 86.91(10) |
| O3–Zn1–O5$^{i}$ | 93.25(5) | O3–Zn1–O5$^{i}$ | 94.08(10) |

| | | | |
|---|---|---|---|
| O3–Zn1–O4$^{ii}$ | 155.79(5) | O3–Zn1–O4$^{ii}$ | 156.78(10) |
| O6–Zn1–N1 | 173.93(5) | O6–Zn1–N1 | 176.71(11) |
| O5$^{i}$–Zn1–O6 | 92.96(5) | O5$^{i}$–Zn1–O6 | 90.30(10) |
| O4$^{ii}$–Zn1–O6 | 87.77(5) | O4$^{ii}$–Zn1–O6 | 90.45(10) |
| O5$^{i}$–Zn1–N1 | 90.08(5) | O5$^{i}$–Zn1–N1 | 92.95(11) |
| O4$^{ii}$–Zn1–N1 | 86.24(5) | O4$^{ii}$–Zn1–N1 | 88.92(11) |
| O4$^{ii}$–Zn1–O5$^{i}$ | 110.96(5) | O4$^{ii}$–Zn1–O5$^{i}$ | 108.95(10) |
| **3** | | **4** | |
| Zn1–O3 | 1.9598(14) | Zn1–O5/Zn2–O7 | 1.973(4)/1.997(3) |
| Zn1–N1 | 2.0372(17) | Zn1–N1/Zn2–N5 | 2.045(3)/2.047(3) |
| Zn1–N4$^{i}$ | 2.0579(18) | Zn1–O11$^{i}$/Zn2–O14 | 1.978(3)/1.960(4) |
| Zn1–O6$^{ii}$ | 1.9914(14) | Zn1–N4$^{ii}$/Zn2–N8$^{iii}$ | 2.022(3)/2.015(4) |
| Zn1–O5$^{ii}$ | 2.602(2) | Zn1–O12$^{i}$/Zn2–O13 | 2.778(3)/2.695(4) |
| O3–Zn1–N1 | 109.70(6) | O5–Zn1–N1/ O7–Zn2–N5 | 105.33(14)/95.81(13) |
| O3–Zn1–N4$^{i}$ | 109.31(7) | O5–Zn1–N4$^{ii}$/ O7–Zn2–N8$^{iii}$ | 122.44(13)/119.93(14) |
| O3–Zn1–O5$^{ii}$ | 150.40(6) | O5–Zn1–O11$^{i}$/ O7–Zn2–O14 | 91.21(14)/92.24(15) |
| O3–Zn1–O6$^{ii}$ | 97.51(5) | O5–Zn1–O12$^{i}$/ O7–Zn2–O13 | 141.80(11)/145.37(14) |
| N1–Zn1–N4$^{i}$ | 107.73(6) | N1–Zn1–N4$^{ii}$/ N5–Zn2–N8$^{iii}$ | 111.22(14)/116.45(14) |
| O5$^{ii}$–Zn1–N1 | 85.85(6) | O11$^{i}$–Zn1–N1/ O14–Zn2–N5 | 110.04(13)/106.36(17) |
| O6$^{ii}$–Zn1–N1 | 131.31(7) | O12$^{i}$–Zn1–N1/ O13–Zn2–N5 | 81.29(12)/89.28(14) |
| O5$^{ii}$–Zn1–N4$^{i}$ | 88.36(7) | O11$^{i}$–Zn1–N4$^{ii}$/ O14–Zn2–N8$^{iii}$ | 114.71(14)/121.06(16) |
| O6$^{ii}$–Zn1–N4$^{i}$ | 99.72(6) | O12$^{i}$–Zn1–N4$^{ii}$/ O13–Zn2–N8$^{iii}$ | 87.51(12)/87.35(13) |
| O5$^{ii}$–Zn1–O6$^{ii}$ | 55.12(5) | O11$^{i}$–Zn1–O12$^{i}$/ O13–Zn2–O14 | 52.29(11)/53.69(14) |

Symmetry codes for **1**: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $x, -y + 3/2, z + 1/2$. For **2**: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $x, -y + 1/2, z - 1/2$. For **3**: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, -y + 1/2, z - 1/2$. For **4**: (i) $x, y - 1, z$; (ii) $-x + 2, -y, -z + 2$; (iii) $-x - 1, -y + 1, -z + 2$.

**Table S3** Possible hydrogen-bonding geometries (Å, °) for complexes **1**–**4**.

| D–H···A | D—H | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| **1** | | | | |
| N2–H2A···O2$^{iii}$ | 0.86 | 2.01 | 2.843(2) | 164 |
| O6–H6A···O1$^{iv}$ | 0.82 | 1.84 | 2.658(2) | 171 |
| O6–H6B···O4$^{i}$ | 0.82 | 2.24 | 2.927(2) | 141 |
| C1–H1···O4$^{ii}$ | 0.93 | 2.52 | 3.016(2) | 114 |
| C4–H4···O2$^{iii}$ | 0.93 | 2.30 | 3.214(2) | 166 |
| C7–H7A···O1 | 0.97 | 2.43 | 2.824(3) | 104 |
| C7–H7B···F1 | 0.97 | 2.48 | 2.875(3) | 104 |
| **2** | | | | |
| N2–H2A···O2$^{iii}$ | 0.86 | 2.05 | 2.871(4) | 160 |
| O6–H6A···O4$^{i}$ | 0.85 | 2.36 | 2.918(4) | 123 |
| O6–H6A···O5$^{ii}$ | 0.85 | 2.55 | 3.123(4) | 125 |
| O6–H6B···O1$^{iv}$ | 0.85 | 1.91 | 2.692(4) | 153 |
| C2–H2···O1 | 0.93 | 2.41 | 2.731(4) | 100 |
| C4–H4···O2$^{iii}$ | 0.93 | 2.55 | 3.450(5) | 162 |
| C7–H7A···O1 | 0.97 | 2.37 | 2.781(5) | 105 |
| C7–H7B···F1 | 0.97 | 2.49 | 2.895(5) | 105 |
| C19–H19A···F2$^{v}$ | 0.96 | 2.49 | 2.880(5) | 105 |
| **3** | | | | |
| O7–H7AA···O2$^{i}$ | 0.82 | 2.01 | 2.828(3) | 174 |
| O7–H7AB···O1$^{ii}$ | 0.82 | 2.58 | 3.398(3) | 179 |
| N2–H2A···O7$^{iii}$ | 0.86 | 2.20 | 3.035(3) | 164 |
| N3–H3A···O6$^{iv}$ | 0.86 | 2.11 | 2.936(2) | 162 |
| C1–H1···O5$^{v}$ | 0.93 | 2.38 | 3.037(3) | 127 |
| C7–H7A···F2$^{vi}$ | 0.97 | 2.53 | 3.485(3) | 166 |
| C7–H7B···F3 | 0.97 | 2.48 | 2.880(3) | 105 |
| C7–H7B···O1 | 0.97 | 2.39 | 2.759(3) | 102 |
| C14–H14A···O2 | 0.97 | 2.48 | 2.839(3) | 102 |
| C14–H14B···F2 | 0.97 | 2.47 | 2.840(3) | 102 |
| C18–H18···F5$^{iii}$ | 0.93 | 2.47 | 3.257(3) | 142 |
| C20–H20···O4$^{vii}$ | 0.93 | 2.42 | 3.137(3) | 133 |
| **4** | | | | |
| N2–H2A···O7$^{i}$ | 0.86 | 2.27 | 3.008(5) | 145 |
| N3–H3···O17$^{ii}$ | 0.86 | 2.06 | 2.879(5) | 158 |
| N6–H6···O5$^{iii}$ | 0.86 | 2.32 | 2.998(6) | 136 |
| N7–H7···O2$^{iv}$ | 0.86 | 2.12 | 2.932(5) | 157 |
| O17–H17A···O8$^{v}$ | 0.82 | 2.00 | 2.813(5) | 172 |
| O17–H17B···O1$^{vi}$ | 0.82 | 2.02 | 2.838(5) | 171 |

| | | | | |
|---|---|---|---|---|
| C5–H5···O12$^{vii}$ | 0.93 | 2.54 | 2.993(6) | 111 |
| C7–H7A···O1 | 0.97 | 2.37 | 2.781(6) | 105 |
| C7–H7B···F3 | 0.97 | 2.40 | 2.850(6) | 108 |
| C14–H14A···F4 | 0.97 | 2.45 | 2.860(6) | 105 |
| C14–H14B···O2 | 0.97 | 2.36 | 2.783(6) | 105 |
| C18–H18···O12$^{viii}$ | 0.93 | 2.37 | 3.104(6) | 136 |
| C19–H19···O6$^{ix}$ | 0.93 | 2.29 | 3.087(6) | 144 |
| C21–H21···O15A$^{x}$ | 0.93 | 2.39 | 3.114(14) | 134 |
| C27–H27A···F5 | 0.97 | 2.38 | 2.839(7) | 108 |
| C27–H27B···O3 | 0.97 | 2.40 | 2.806(7) | 104 |
| C34–H34A···O3$^{xi}$ | 0.97 | 2.52 | 3.326(6) | 140 |
| C34–H34B···F6 | 0.97 | 2.42 | 2.866(8) | 107 |
| C37–H37···O2$^{iv}$ | 0.93 | 2.48 | 3.360(6) | 157 |
| C38–H38···O8$^{xii}$ | 0.93 | 2.43 | 3.127(6) | 132 |
| C39–H39···O13$^{xii}$ | 0.93 | 2.21 | 2.982(7) | 140 |
| C40–H40···O3$^{x}$ | 0.93 | 2.57 | 3.358(7) | 143 |
| C40–H40···O4 | 0.93 | 2.42 | 2.738(7) | 100 |

Symmetry codes for **1**: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $x, -y + 3/2, z + 1/2$; (iii) $x + 1, y, z$; (ix) $x - 1, -y + 3/2, z - 1/2$. For **2**: (i) $-x + 1, y + 1/2, -z + 3/2$; (ii) $x, -y + 1/2, z - 1/2$; (iii) $x - 1, y, z$; (iv) $x + 1, -y + 1/2, z + 1/2$; (v) $x + 2, y, z$. For **3**: (i) $-x + 1, y - 3/2, -z + 3/2$; (ii) $x - 1, y - 1$, z; (iii) $-x + 1, y + 1/2, -z + 3/2$; (iv) $x, y + 1, z - 1$; (v) $x, -y + 1/2, z - 1/2$; (vi) $-x + 2, -y + 2, -z + 1$; (vii) $x, -y + 5/2, z - 1/2$. For **4**: (i) $-x + 1, -y, -z + 2$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x, -y, -z + 2$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x + 1, y, z - 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $x, y - 1, z$; (viii) $-x + 2, -y + 1, -z + 2$; (ix) $-x + 2, -y, -z + 2$; (x) $x - 1, y, z$; (xi) $-x, -y + 1, -z + 1$; (xii) $-x - 1, -y + 1, -z + 2$.