

Electronic Supplementary Information

Microporous sensor: gas sorption, guest exchange and guest-dependant luminescence of metal-organic framework

Sergey A. Sapchenko, Denis G. Samsonenko*, Danil N. Dybtsev, Maxim S. Melgunov, and Vladimir P. Fedin

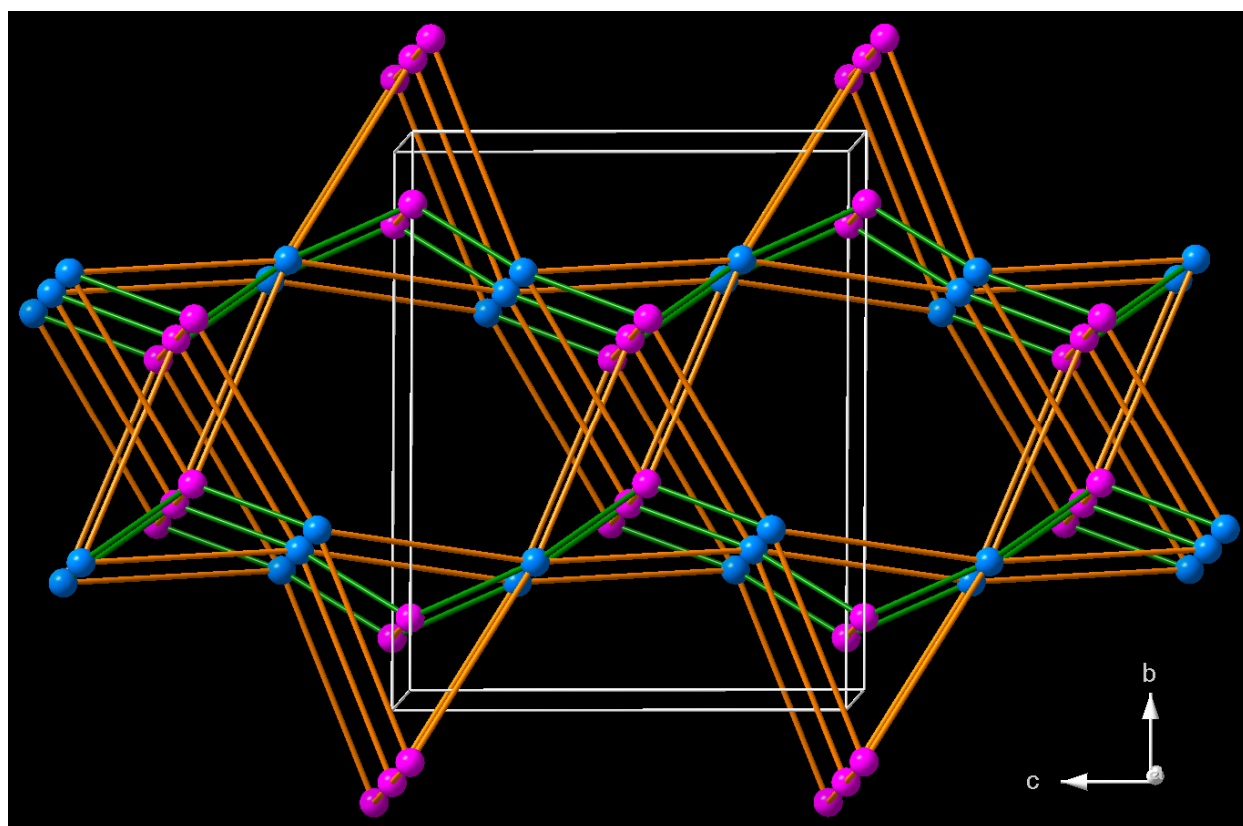


Fig. S1. Simplified topology of the coordination network in **1** (view along *a* axis). Type A building units are blue, type B are purple, ndc^{2-} linkers are brown, urotropin linkers are green. The unit cell is white.

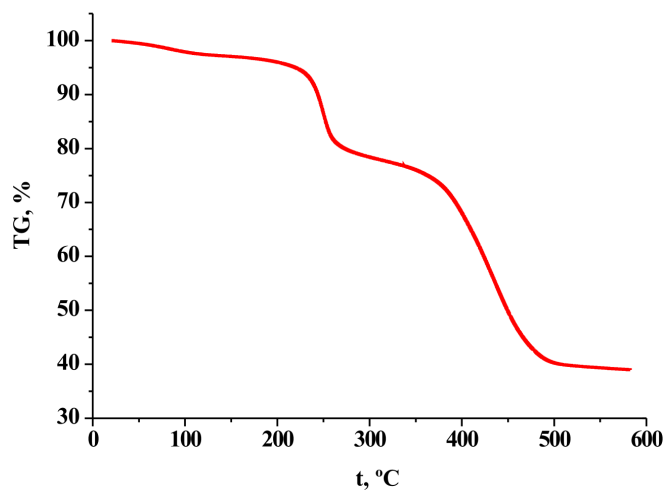


Fig. S2. TG curve of compound **1** at a heating rate of 10 K min⁻¹.

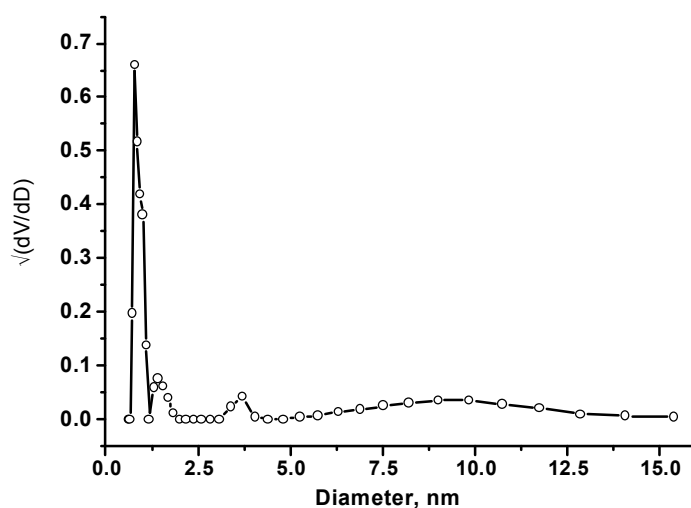
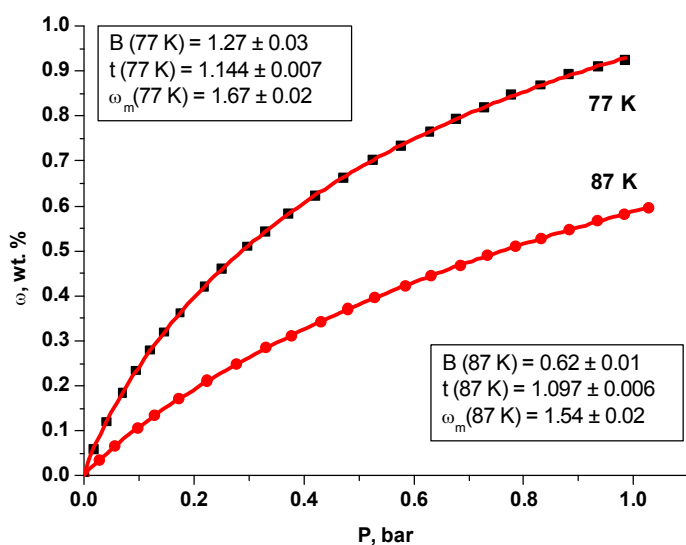


Fig. S3. Channels size distribution diagram for **2**.



$$\frac{\omega}{\omega_m} = \frac{BP^{1/t}}{1 + BP^{1/t}}$$

$$P = \left(\frac{\frac{\omega}{\omega_m}}{B - B \frac{\omega}{\omega_m}} \right)^t$$

ω – amount adsorbed (wt. %),
ω_m – amount adsorbed (wt. %) at saturation,
P – pressure,
B and t – constants

Fig. S4. Langmuir-Freundlich fit.

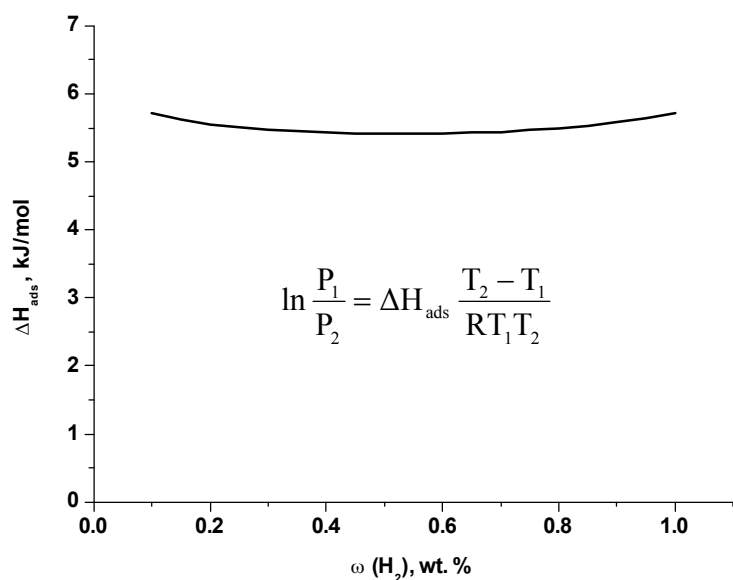


Fig. S5. A function of enthalpy of adsorption from amount of hydrogen adsorbed.

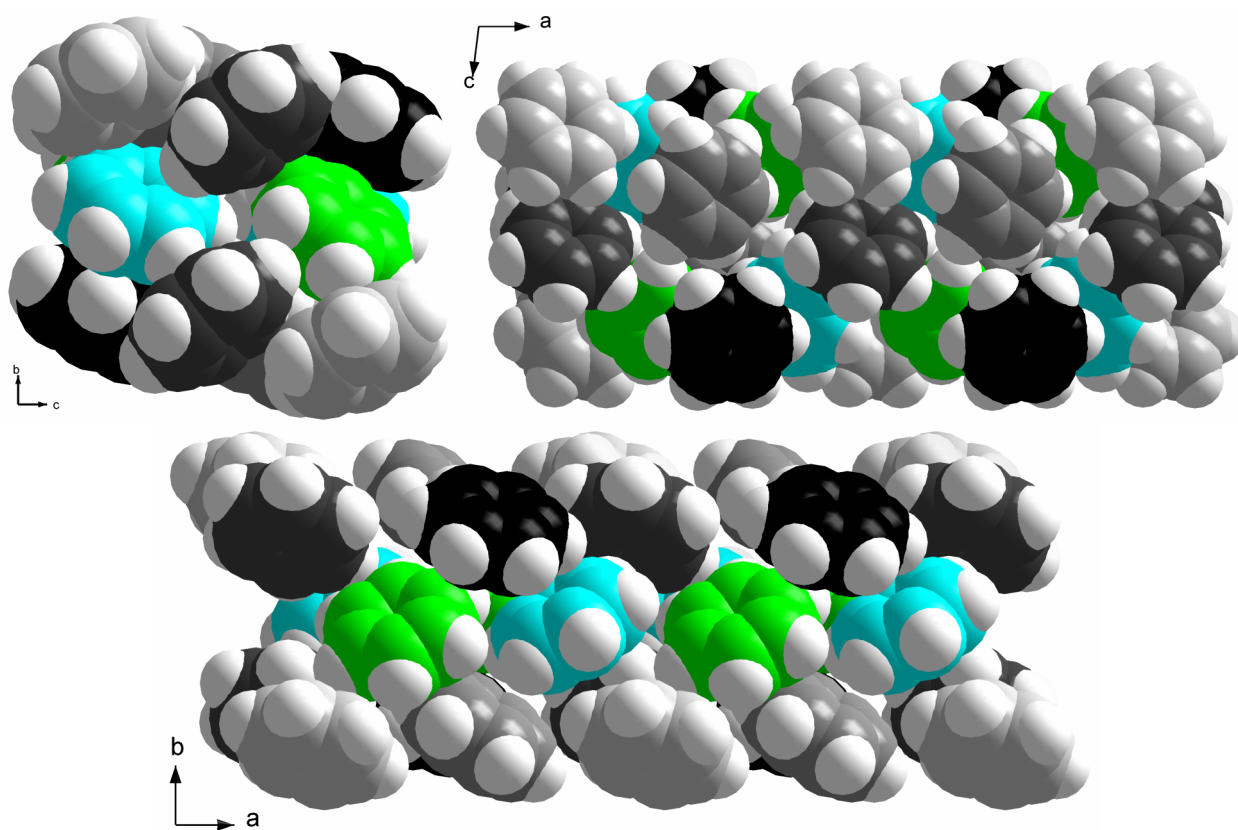


Fig. S6. Packing of benzene molecules inside the channels of **3**.

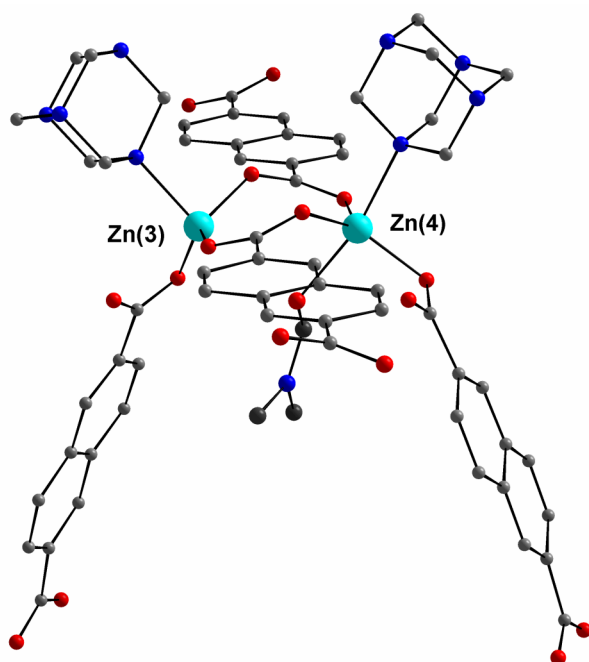


Fig. S7. Structure of secondary building unit $\{Zn_2(dmf)(COO)_4\}^{2-}$ in **4**. Zn atoms are shown cyan, O – red, N – blue, C (ndc) – grey, C (dmf) – dark grey. Hydrogen atoms are omitted for clarity.

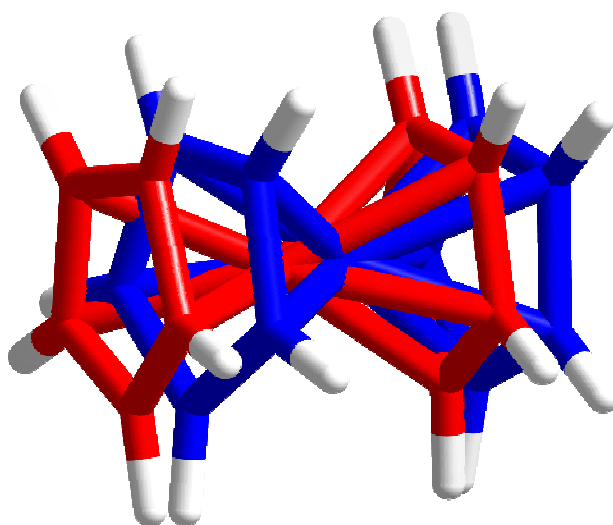


Fig. S8. Guest ferrocene molecule disorder over two positions (shown red and blue) in **4**.

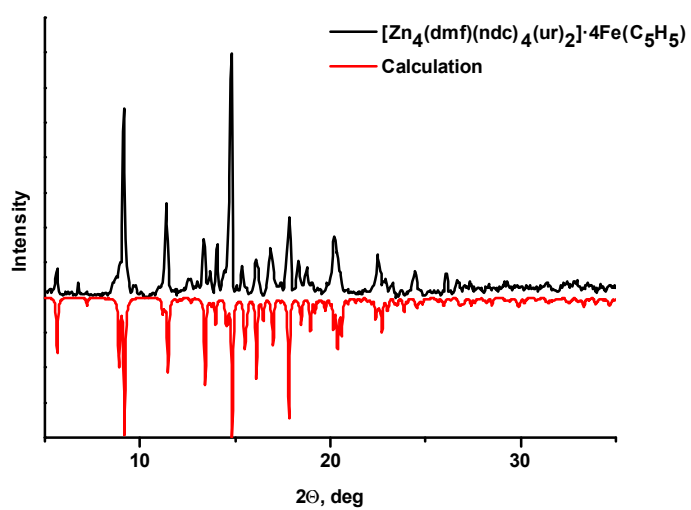
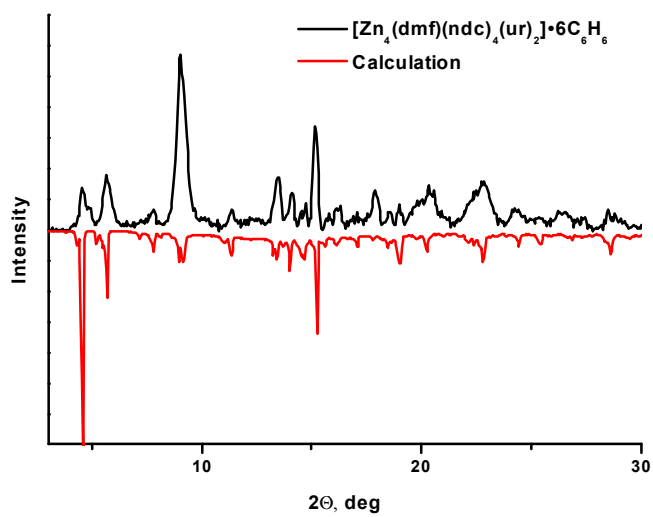
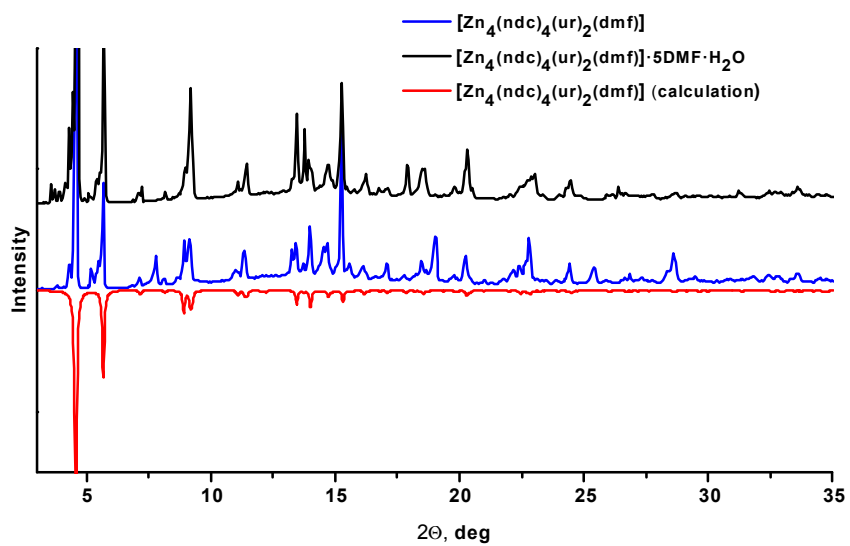


Fig. S9. XRD plots for 1–4.

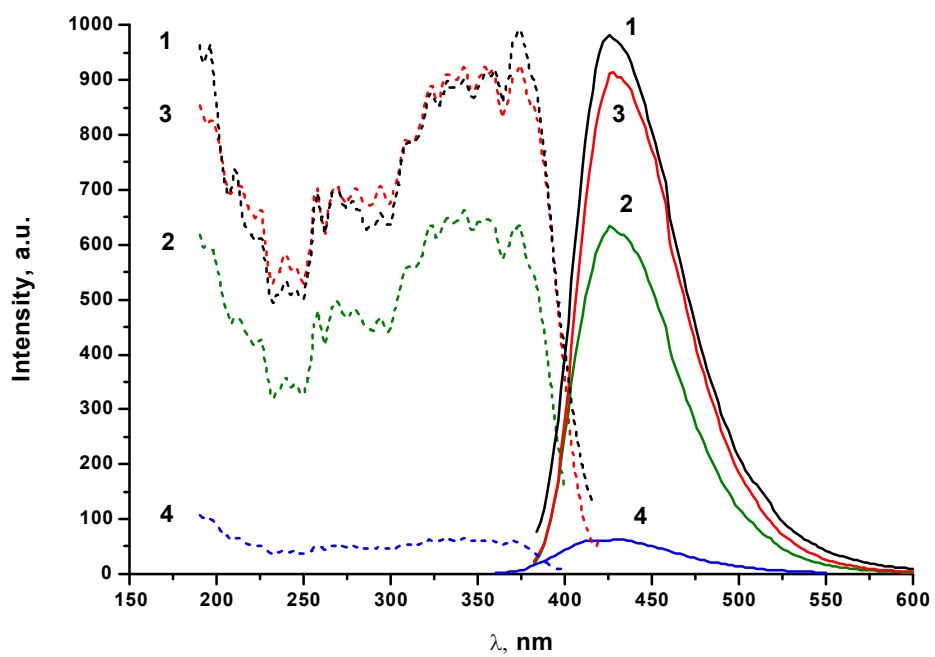


Fig. S10. The solid-state fluorescent spectra of **1** (black), **2** (green), **3** (red) and **4** (blue) recorded at room temperature (dashed lines — excitation spectra, solid lines — emission spectra)

Table S1. Selected bond lengths and angles for **1**.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–N(11)	2.067(6)	Zn(3)–N(12) ^b	2.111(7)
Zn(1)–O(12)	2.006(5)	Zn(3)–O(34) ^c	1.899(9)
Zn(1)–O(13) ^a	2.024(6)	Zn(3)–O(42)	1.974(6)
Zn(1)–O(22)	2.053(6)	Zn(3)–O(43) ^d	1.962(6)
Zn(1)–O(32)	2.041(6)	Zn(4)–N(22)	2.143(7)
Zn(2)–N(21)	2.065(6)	Zn(4)–O(23) ^e	2.161(16)
Zn(2)–O(11)	2.069(6)	Zn(4)–O(24) ^e	2.367(13)
Zn(2)–O(14) ^a	2.038(6)	Zn(4)–O(41)	1.982(7)
Zn(2)–O(21)	2.013(6)	Zn(4)–O(44) ^d	1.997(6)
Zn(2)–O(31)	2.021(6)	Zn(4)–O(1D)	2.297(11)
Angle	ω, deg.	Angle	ω, deg.
O(12)–Zn(1)–N(11)	103.9(2)	O(34) ^c –Zn(3)–O(42)	97.4(4)
O(12)–Zn(1)–O(13) ^a	159.1(2)	O(34) ^c –Zn(3)–O(43) ^d	120.7(4)
O(12)–Zn(1)–O(22)	88.7(3)	O(42)–Zn(3)–N(12) ^b	92.1(3)
O(12)–Zn(1)–O(32)	87.6(3)	O(43) ^d –Zn(3)–N(12) ^b	96.7(3)
O(13) ^a –Zn(1)–N(11)	97.0(2)	O(43) ^d –Zn(3)–O(42)	130.5(3)
O(13) ^a –Zn(1)–O(22)	86.9(3)	N(22)–Zn(4)–O(23) ^e	102.0(5)
O(13) ^a –Zn(1)–O(32)	89.5(3)	N(22)–Zn(4)–O(24) ^e	92.3(4)
O(22)–Zn(1)–N(11)	99.4(2)	N(22)–Zn(4)–O(1D)	172.0(4)
O(32)–Zn(1)–N(11)	100.6(3)	O(23) ^e –Zn(4)–O(24) ^e	57.6(4)
O(32)–Zn(1)–O(22)	160.0(3)	O(23) ^e –Zn(4)–O(1D)	83.9(5)
N(21)–Zn(2)–O(11)	95.4(2)	O(41)–Zn(4)–N(22)	94.9(3)
O(14) ^a –Zn(2)–N(21)	104.3(3)	O(41)–Zn(4)–O(23) ^e	139.9(4)
O(14) ^a –Zn(2)–O(11)	160.2(2)	O(41)–Zn(4)–O(24) ^e	85.9(4)
O(21)–Zn(2)–N(21)	98.6(3)	O(41)–Zn(4)–O(44) ^d	124.8(3)
O(21)–Zn(2)–O(11)	87.9(3)	O(41)–Zn(4)–O(1D)	83.8(4)
O(21)–Zn(2)–O(14) ^a	87.5(3)	O(44) ^d –Zn(4)–N(22)	90.4(3)
O(21)–Zn(2)–O(31)	159.1(3)	O(44) ^d –Zn(4)–O(23) ^e	91.5(4)
O(31)–Zn(2)–N(21)	102.1(3)	O(44) ^d –Zn(4)–O(24) ^e	148.8(4)
O(31)–Zn(2)–O(11)	86.8(3)	O(44) ^d –Zn(4)–O(1D)	84.0(3)
O(31)–Zn(2)–O(14) ^a	90.7(3)	O(1D)–Zn(4)–O(24) ^e	95.5(4)
O(34) ^c –Zn(3)–N(12) ^b	116.9(4)		

Symmetry transformations used to generate equivalent atoms: ^a $x-1/2, -y+1/2, z-1/2$;

^b $x-1/2, -y+1/2, z+1/2$; ^c $-x+1, -y+1, -z+1$; ^d $x-1, y, z$; ^e $-x+1/2, y+1/2, -z+1/2$.

Table S2. Selected bond lengths and angles for **2**.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–N(11)	2.073(3)	Zn(3)–N(12)	2.150(3)
Zn(1)–O(11)	2.033(3)	Zn(3)–O(24) ^b	1.934(3)
Zn(1)–O(14) ^a	2.055(2)	Zn(3)–O(42)	1.982(2)
Zn(1)–O(21)	2.020(2)	Zn(3)–O(43) ^b	1.949(2)
Zn(1)–O(31)	2.031(2)	Zn(4)–O(1)	2.282(4)
Zn(2)–N(21)	2.067(3)	Zn(4)–N(22) ^d	2.184(3)
Zn(2)–O(12)	2.039(3)	Zn(4)–O(41)	1.993(2)
Zn(2)–O(13) ^a	2.040(3)	Zn(4)–O(44) ^c	2.002(2)
Zn(2)–O(22)	2.011(2)	Zn(4)–O(33) ^e	2.259(4)
Zn(2)–O(32)	2.029(2)	Zn(4)–O(34) ^e	2.118(3)
Angle	ω, deg.	Angle	ω, deg.
O(11)–Zn(1)–N(11)	102.20(11)	O(24) ^b –Zn(3)–O(42)	97.40(13)
O(11)–Zn(1)–O(14) ^a	162.21(11)	O(24) ^b –Zn(3)–O(43) ^c	127.92(13)
O(14) ^a –Zn(1)–N(11)	95.58(11)	O(42)–Zn(3)–N(12)	90.36(10)
O(21)–Zn(1)–N(11)	100.01(10)	O(43) ^c –Zn(3)–N(12)	94.05(10)
O(21)–Zn(1)–O(11)	89.33(12)	O(43) ^c –Zn(3)–O(42)	128.12(11)
O(21)–Zn(1)–O(14) ^a	87.56(11)	N(22) ^d –Zn(4)–O(1)	170.44(13)
O(21)–Zn(1)–O(31)	161.76(10)	N(22) ^d –Zn(4)–O(33) ^e	101.12(12)
O(31)–Zn(1)–N(11)	98.23(10)	O(41)–Zn(4)–O(1)	84.27(13)
O(31)–Zn(1)–O(11)	86.84(12)	O(41)–Zn(4)–N(22) ^d	91.87(10)
O(12)–Zn(2)–N(21)	96.93(11)	O(41)–Zn(4)–O(44) ^c	120.47(11)
O(12)–Zn(2)–O(13) ^a	161.61(11)	O(41)–Zn(4)–O(33) ^e	149.70(12)
O(13) ^a –Zn(2)–N(21)	101.45(10)	O(41)–Zn(4)–O(34) ^e	92.04(12)
O(22)–Zn(2)–N(21)	100.19(11)	O(44) ^c –Zn(4)–O(1)	86.15(11)
O(22)–Zn(2)–O(12)	88.95(12)	O(44) ^c –Zn(4)–N(22) ^d	88.29(10)
O(22)–Zn(2)–O(13) ^a	87.51(13)	O(44) ^c –Zn(4)–O(33) ^e	87.48(11)
O(22)–Zn(2)–O(32)	161.55(11)	O(44) ^c –Zn(4)–O(34) ^e	146.73(12)
O(32)–Zn(2)–N(21)	98.23(10)	O(33) ^e –Zn(4)–O(1)	86.41(15)
O(32)–Zn(2)–O(12)	87.60(11)	O(34) ^e –Zn(4)–O(1)	90.66(13)
O(32)–Zn(2)–O(13) ^a	90.07(12)	O(34) ^e –Zn(4)–N(22) ^d	98.23(12)
O(24) ^b –Zn(3)–N(12)	111.49(12)	O(34) ^e –Zn(4)–O(33) ^e	59.26(12)

Symmetry transformations used to generate equivalent atoms: ^a $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$;

^b $x, -y + 1, z + \frac{1}{2}$; ^c $x, y, z - 1$; ^d $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; ^e $x - \frac{1}{2}, y + \frac{1}{2}, z$.

Table S3. Selected bond lengths and angles for **3**.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–N(11)	2.0775(14)	Zn(3)–N(12) ^b	2.1376(14)
Zn(1)–O(12)	2.0199(12)	Zn(3)–O(34) ^c	1.9441(14)
Zn(1)–O(13) ^a	2.0328(12)	Zn(3)–O(42)	1.9713(12)
Zn(1)–O(22)	2.0635(12)	Zn(3)–O(43) ^d	1.9432(12)
Zn(1)–O(32)	2.0587(12)	Zn(4)–O(1D)	2.2334(16)
Zn(2)–N(21)	2.0634(14)	Zn(4)–N(22)	2.1702(14)
Zn(2)–O(11)	2.0768(12)	Zn(4)–O(23) ^e	2.2102(17)
Zn(2)–O(14) ^a	2.0384(13)	Zn(4)–O(24) ^e	2.1407(15)
Zn(2)–O(21)	2.0286(13)	Zn(4)–O(41)	2.0018(12)
Zn(2)–O(31)	2.0063(12)	Zn(4)–O(44) ^d	2.0163(12)
Angle	ω, deg.	Angle	ω, deg.
O(12)–Zn(1)–N(11)	101.45(5)	O(34) ^c –Zn(3)–O(42)	99.24(6)
O(12)–Zn(1)–O(13) ^a	160.02(5)	O(42)–Zn(3)–N(12) ^b	91.33(5)
O(12)–Zn(1)–O(22)	88.94(5)	O(43) ^d –Zn(3)–N(12) ^b	96.47(5)
O(12)–Zn(1)–O(32)	86.85(5)	O(43) ^d –Zn(3)–O(34) ^c	124.35(6)
O(13) ^a –Zn(1)–N(11)	98.51(5)	O(43) ^d –Zn(3)–O(42)	126.64(5)
O(13) ^a –Zn(1)–O(22)	87.75(5)	N(22)–Zn(4)–O(1D)	169.05(6)
O(13) ^a –Zn(1)–O(32)	90.30(5)	N(22)–Zn(4)–O(23) ^e	100.15(6)
O(22)–Zn(1)–N(11)	97.48(5)	O(23) ^e –Zn(4)–O(1D)	87.83(7)
O(32)–Zn(1)–N(11)	100.36(5)	O(24) ^e –Zn(4)–O(1D)	89.12(6)
O(32)–Zn(1)–O(22)	162.14(5)	O(24) ^e –Zn(4)–N(22)	101.33(6)
N(21)–Zn(2)–O(11)	94.57(5)	O(24) ^e –Zn(4)–O(23) ^e	60.31(6)
O(14) ^a –Zn(2)–N(21)	103.84(5)	O(41)–Zn(4)–O(1D)	85.52(6)
O(14) ^a –Zn(2)–O(11)	161.51(5)	O(41)–Zn(4)–N(22)	91.24(5)
O(21)–Zn(2)–N(21)	99.29(5)	O(41)–Zn(4)–O(23) ^e	149.13(6)
O(21)–Zn(2)–O(11)	88.18(6)	O(41)–Zn(4)–O(24) ^e	89.44(6)
O(21)–Zn(2)–O(14) ^a	87.25(6)	O(41)–Zn(4)–O(44) ^d	118.03(5)
O(31)–Zn(2)–N(21)	101.28(5)	O(44) ^d –Zn(4)–O(1D)	83.54(5)
O(31)–Zn(2)–O(11)	87.50(5)	O(44) ^d –Zn(4)–N(22)	88.79(5)
O(31)–Zn(2)–O(14) ^a	90.47(6)	O(44) ^d –Zn(4)–O(23) ^e	91.02(5)
O(31)–Zn(2)–O(21)	159.25(5)	O(44) ^d –Zn(4)–O(24) ^e	150.72(6)
O(34) ^c –Zn(3)–N(12) ^b	113.89(6)		

Symmetry transformations used to generate equivalent atoms: ^a $x + 1/2, -y + 3/2, z + 1/2$;

^b $x + 1/2, -y + 3/2, z - 1/2$; ^c $-x + 1, -y + 1, -z + 1$; ^d $x + 1, y, z$; ^e $-x + 3/2, y - 1/2, -z + 3/2$.

Table S4. Selected bond lengths and angles for **4**.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)–N(21)	2.065(3)	Zn(3)–N(14) ^d	2.129(3)
Zn(1)–O(101)	2.022(3)	Zn(3)–O(402)	1.945(3)
Zn(1)–O(201)	2.018(3)	Zn(3)–O(103) ^e	1.956(3)
Zn(1)–O(301)	2.033(3)	Zn(3)–O(404) ^c	1.981(3)
Zn(1)–O(304) ^a	2.051(3)	Zn(4)–O(1D)	2.205(3)
Zn(2)–N(11)	2.068(3)	Zn(4)–N(22)	2.195(3)
Zn(2)–O(102)	2.038(3)	Zn(4)–O(204) ^b	2.027(3)
Zn(2)–O(202)	2.045(3)	Zn(4)–O(401)	1.988(3)
Zn(2)–O(302)	2.049(3)	Zn(4)–O(403) ^c	1.996(3)
Zn(2)–O(303) ^a	2.019(3)		
Angle	ω , deg.	Angle	ω , deg.
O(101)–Zn(1)–N(21)	99.15(12)	O(303) ^a –Zn(2)–O(202)	86.96(12)
O(101)–Zn(1)–O(301)	88.00(12)	O(303) ^a –Zn(2)–O(302)	160.83(12)
O(101)–Zn(1)–O(304) ^a	89.72(11)	O(103) ^e –Zn(3)–N(14) ^d	111.68(12)
O(201)–Zn(1)–N(21)	101.77(12)	O(103) ^e –Zn(3)–O(404) ^c	97.84(12)
O(201)–Zn(1)–O(101)	159.06(12)	O(402)–Zn(3)–N(14) ^d	97.45(12)
O(201)–Zn(1)–O(301)	88.22(12)	O(402)–Zn(3)–O(103) ^e	127.80(12)
O(201)–Zn(1)–O(304) ^a	87.59(12)	O(402)–Zn(3)–O(404) ^c	124.61(11)
O(301)–Zn(1)–N(21)	103.07(12)	O(204) ^b –Zn(4)–O(1D)	89.64(12)
O(301)–Zn(1)–O(304) ^a	162.08(12)	O(204) ^b –Zn(4)–N(22)	102.73(13)
O(304) ^a –Zn(1)–N(21)	94.84(12)	O(404) ^c –Zn(3)–N(14) ^d	91.39(11)
O(102)–Zn(2)–N(11)	96.27(12)	N(22)–Zn(4)–O(1D)	167.58(11)
O(102)–Zn(2)–O(202)	163.37(12)	O(401)–Zn(4)–N(22)	86.01(11)
O(102)–Zn(2)–O(302)	87.70(11)	O(401)–Zn(4)–O(204) ^b	140.70(14)
O(202)–Zn(2)–N(11)	100.35(12)	O(401)–Zn(4)–O(403) ^c	123.74(11)
O(202)–Zn(2)–O(302)	89.51(12)	O(403) ^c –Zn(4)–O(1D)	87.31(11)
O(302)–Zn(2)–N(11)	98.33(12)	O(403) ^c –Zn(4)–N(22)	90.49(11)
O(303) ^a –Zn(2)–N(11)	100.83(12)	O(403) ^c –Zn(4)–O(204) ^b	94.75(14)
O(303) ^a –Zn(2)–O(102)	90.32(12)	O(401)–Zn(4)–O(1D)	85.06(10)

Symmetry transformations used to generate equivalent atoms: ^a $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$;

^b $x, -y + 1, z - \frac{1}{2}$; ^c $x, y, z + 1$; ^d $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; ^e $x + \frac{1}{2}, y - \frac{1}{2}, z$