Incorporation by coordination and release of the iron chelator drug deferiprone from zinc-based metal-organic frameworks†

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Supplementary information

1. General experimental details

Chemicals were purchased from Sigma-Aldrich or Acros Organics and used without further purification. Reactions were carried out in glass 10 cm^3 vials (Biotage) in a Sanyo drying oven.

Powder X-ray diffraction (PXRD) was carried out on a Bruker axs D8 Advance diffractometer with a Super Speed detector, using copper K_α radiation, with wavelength, λ = 1.5406 Å, at 298 K and with a beam slit set to 1 mm, detector slit set to 0.2 mm and anti-scattering slit set to 1 mm. The scan speed was 1 s per step with a step size (2θ) of 0.02°.

Synthesised MOF samples for NMR studies were dried in an oven for 1 h at 100 °C, then digested in 0.4 cm^3 DMSO-d_6 and 0.2 cm^3 stock DCl solution (0.1 cm^3 35% DCl/D_2O, in 3 cm^3 DMSO-d_6). Spectra were recorded at 298 K on a Bruker Avance 300 MHz Ultrashield NMR spectrometer. ^1H NMR spectra were referenced to the residual *protio* peaks at δ 2.50 ppm for DMSO-d_6.

Mass spectra were recorded on a micrOTOF (ESI-TOF) spectrometer. LCMS data were recorded on a Waters 2695 HPLC (see Section 4 below). Single crystal X-ray diffraction data were collected either on a Nonius KappaCCD diffractometer (**1**, **3**) or at Diamond Light Source (**2**, **5**). Crystal structures were solved using SHELXS-97 and refined with SHELXL-97.[S1]

2. Synthesis of dfp-containing MOFs

*(a) Synthesis of [$Zn_3(bdc)_2(dfp)_2$]·2DMF **1***

$Zn(NO_3)_2\cdot6H_2O$ (0.0889 g, 0.30 mmol), H_2bdc (0.0499 g, 0.30 mmol) and Hdfp (0.0419 g, 0.30 mmol) were dissolved in DMF (6 cm^3) in a glass vial. The vial was sealed and placed in an oven at 100°C for 24 hours after which time block-shaped colourless crystals of **1** were observed. Yield 0.0728 g (77%). The powder X-ray diffraction pattern of the bulk sample showed a good correlation with that calculated from the crystal structure (Figure S1) whereas the ^1H NMR spectrum of **1** digested in DCl/D_2O and DMSO-d_6 confirmed the 1:1 ratio of ligands (Figure S2). Reactions carried out in a DMF-water mixture generally yielded mixtures of **1** and **2**.

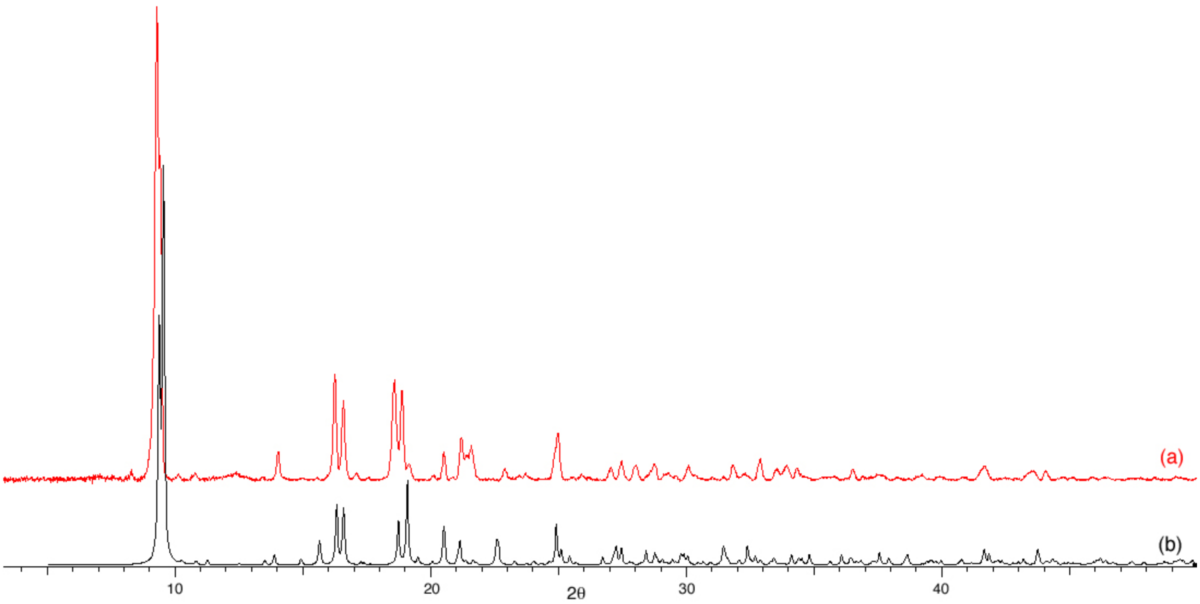

Figure S1. Powder X-ray diffraction pattern for **1**, showing (a) the observed diffraction pattern and (b) the diffraction pattern calculated from the X-ray single crystal structure.

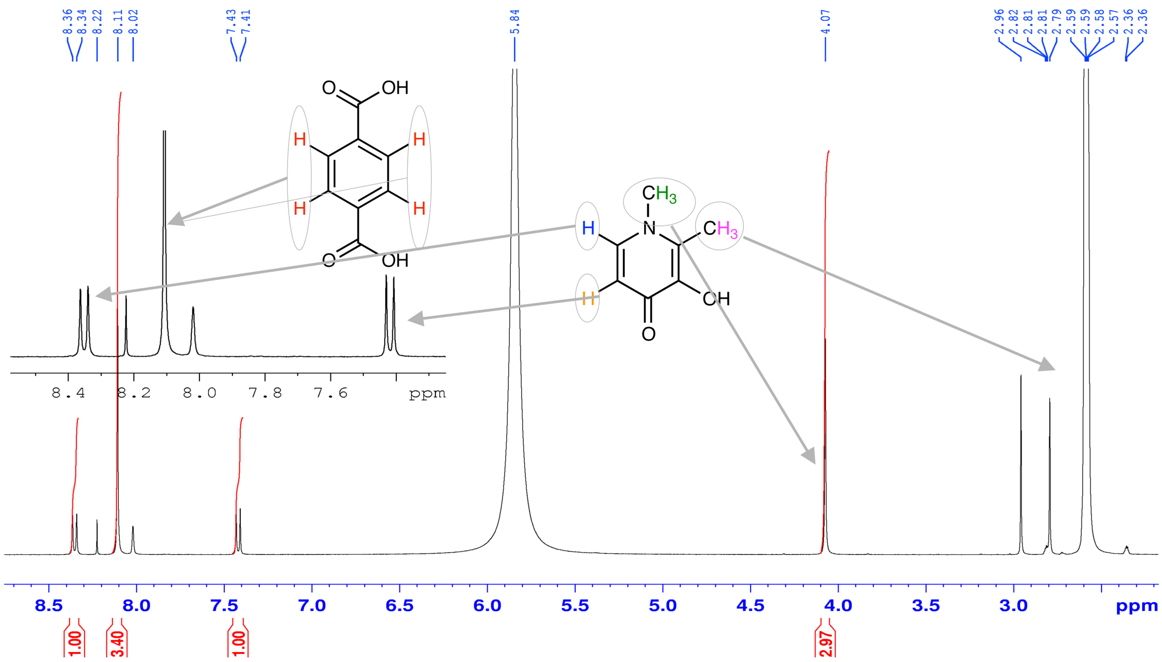

Figure S2. [1]H NMR spectrum of **1** following digestion in DCl/D_2O and DMSO-d_6 confirming the 1:1 ratio between bdc and dfp.

(b) Synthesis of [$Zn_3(bdc)_2(dfp)_2(H_2O)_2$] ***2***

$Zn(NO_3)_2 \cdot 6H_2O$ (0.0893 g, 0.30mmol), H_2bdc (0.0499 g, 0.30 mmol) and Hdfp (0.0419 g, 0.30mmol) were added to a glass vial. Ethanol (5 cm^3) and distilled water (1 cm^3) were added and the solution was left to stir for 30 min. after which time most of the reactants had dissolved. The glass vial was sealed and placed in an oven at 95°C for 24 hours. Colourless rhomboid-shaped crystals emerged as the products of this reaction. Yield 0.0687 g (82%). The powder X-ray diffraction pattern of the bulk sample showed a good correlation with that calculated from the crystal structure (Figure S3).

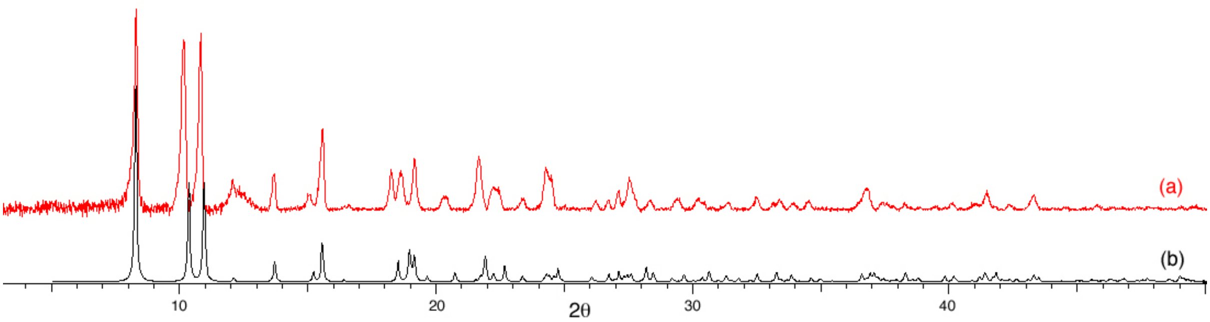

Figure S3. Powder X-ray diffraction pattern for **2**, showing (a) the observed diffraction pattern and (b) the diffraction pattern calculated from the X-ray single crystal structure.

(c) Synthesis of [$Zn_3(bdc\text{-}NH_2)_2(dfp)_2$]·DMF ***3*** *and [$Zn_3(bdc\text{-}NH_2)_2(dfp)_2(H_2O)_2$]* ***4***

$Zn(NO_3)_2 \cdot 6H_2O$ (0.134 g, 0.45 mmol), H_2bdc-NH_2 (0.054 g, 0.30 mmol) and Hdfp (0.042 g, 0.30 mmol) were added to a glass vials along with DMF (5 cm^3) and water (1 cm^3). The solution was agitated until all of the reactants had dissolved, then the vial was sealed and placed in an oven at 100 °C for 24 hours. Upon observation of the product under a microscope, it was apparent that the sample contained two crystalline compounds. Yield 0.0693 g (48%, assuming sample is **3**). The presence of two products was verified powder X-ray diffraction (Figure S4), which showed that the mixture consisted of **3** and a compound isostructural to **2**.

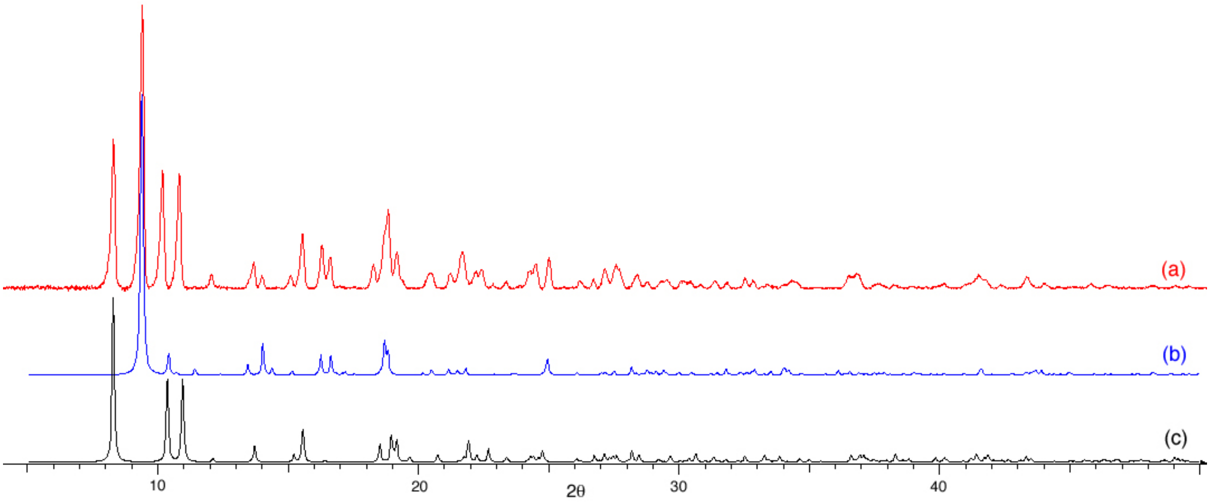

Figure S4. Powder X-ray diffraction pattern for a mixture of **3** and **4**, showing (a) the observed diffraction pattern, (b) the diffraction pattern for **3** calculated from the X-ray single crystal structure, and (c) the diffraction pattern for **2** calculated from the X-ray single crystal structure.

(d) Synthesis of [Zn$_3${bdc-(OH)$_2$}$_2$(dfp)$_2$(H$_2$O)$_2$]·2DMF ***5***

$Zn(NO_3)_2 \cdot 6H_2O$ (0.140 g, 0.47 mmol), H_2bdc-(OH)$_2$ (0.032 g, 0.16 mmol) and Hdfp (0.077 g, 0.55 mmol) were dissolved in DMF (6 cm^3) with stirring. Water (0.3 cm^3) was added to the solution, then the vial was sealed and placed in an oven at 100 °C for 20 hours. The colourless crystals obtained were collected by filtration and washed with THF. Yield 0.0885 g (54%). The powder X-ray diffraction pattern of the bulk sample showed a good correlation with that calculated from the crystal structure (Figure S5) whereas the ^{1}H NMR spectrum of **5** digested in DCl/D_2O and DMSO-d_6 confirmed the 1:1 ratio of ligands (Figure S6).

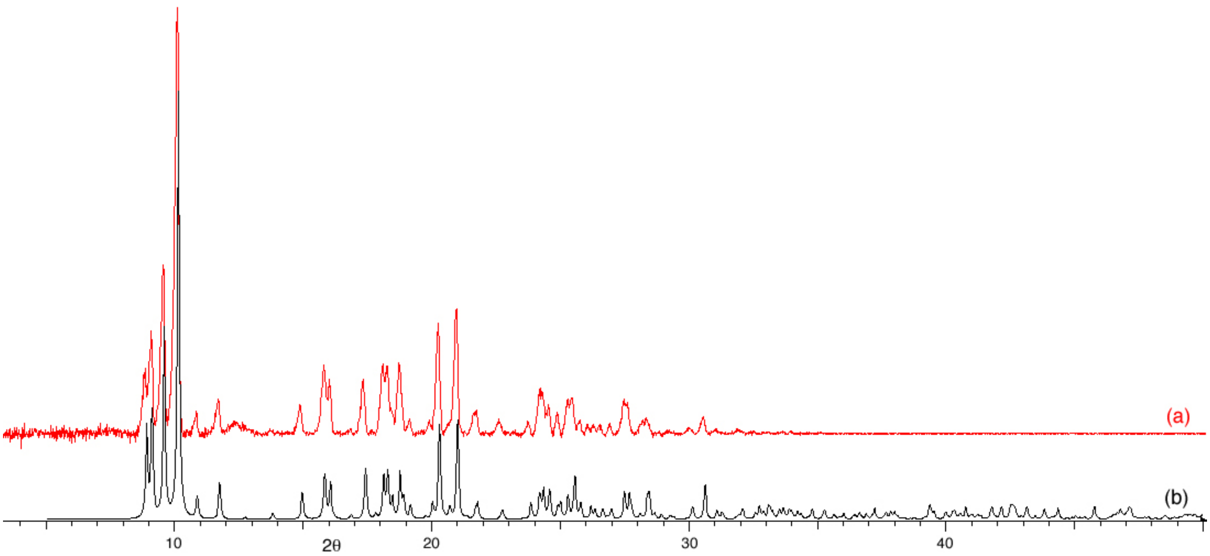

Figure S5. Powder X-ray diffraction pattern for **5**, showing (a) the observed diffraction pattern and (b) the diffraction pattern calculated from the X-ray single crystal structure.

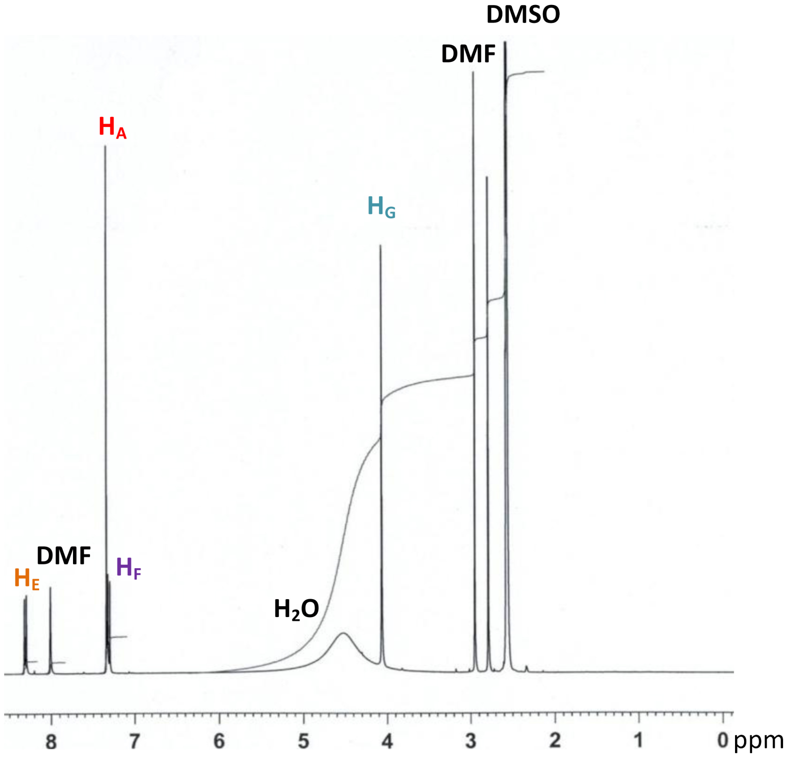

Figure S6. ^{1}H NMR spectrum of **5** following digestion in DCl/D_2O and DMSO-d_6 confirming the 1:1 ratio between bdc-$(OH)_2$ (H_A, 2H) and dfp (H_E, H_F, 1H each).

3. Reactions with [Fe(acac)$_3$]

(a) Addition of deferiprone to a solution of [Fe(acac)$_3$]

[Fe(acac)$_3$] (0.0704 g, 0.2 mmol) and Hdfp (0.0832 g, 0.6 mmol) were dissolved in ethanol (10 cm^3). The solution was stirred and heated at 40 °C for 48 hours. The resultant deep red solution was diluted by a factor of a thousand in ethanol for analysis by mass spectrometry (Figure S7). *m/z* 471.1096 (Fe(dfp)$_3$ + H$^+$, calc. 471.1093), 493.0940 (Fe(dfp)$_3$ + Na$^+$, calc. 493.0912). Similar results were observed using DMF in place of ethanol.

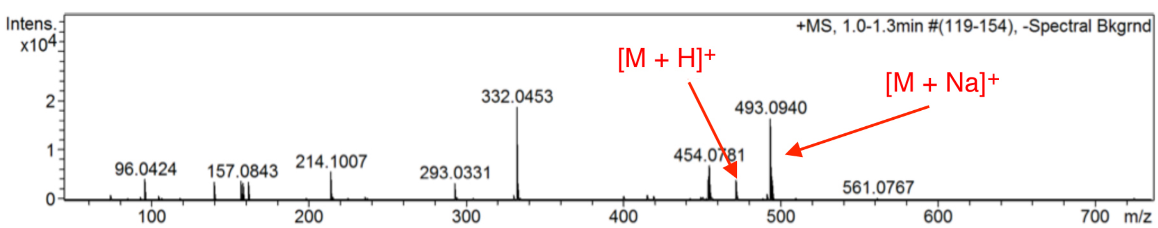

Figure S7. ESI mass spectrum of [Fe(acac)$_3$] and Hdfp, showing the presence of the iron deferiprone complex [Fe(dfp)$_3$].

*(b) Addition of **1** to a solution of [Fe(acac)$_3$]*

[Fe(acac)$_3$] (0.020 g, 0.043 mmol) and **1** (0.060 g, 0.13 mmol) were combined in a glass vial and DMF (6 cm^3) was added. The vial was sealed and heated at 40 °C for 48 hours. After this time, crystals were observed in the vial. An aliquot of the solution was taken and diluted by a factor of a thousand in ethanol for analysis by mass spectrometry (Figure S8). No peaks containing dfp or [Fe(dfp)$_3$] were identified in the mass spectrum.

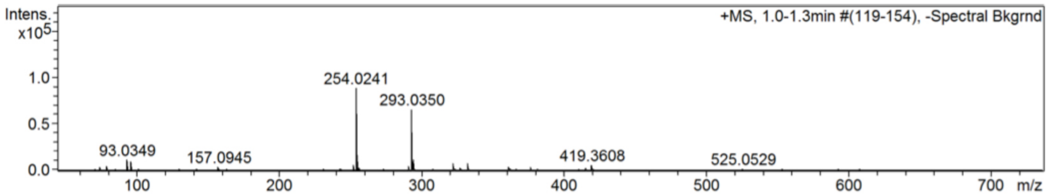

Figure S8. ESI mass spectrum of [Fe(acac)$_3$] and **1**, showing no evidence for the iron deferiprone complex [Fe(dfp)$_3$].

*(c) Addition of **1** to a solution of [Fe(acac)$_3$] in the presence of HCl*

[Fe(acac)$_3$] (0.011 g, 0.030 mmol) and **1** (0.031 g, 0.065 mmol) were combined in a glass vial and DMF (6 cm^3) followed by hydrochloric acid (10.8 M, 0.2 cm^3) were added. pH paper indicated an approximate value of pH 2 for the solution. The vial was sealed and heated at 40 °C for 48 hours. After this time there were no crystals present, and the solution had become pale orange. An aliquot of the solution was taken and diluted by a factor of a thousand in ethanol for analysis by mass spectrometry (Figure S9). *m/z* 471.1085 (Fe(dfp)$_3$ + H$^+$, calc. 471.1093).

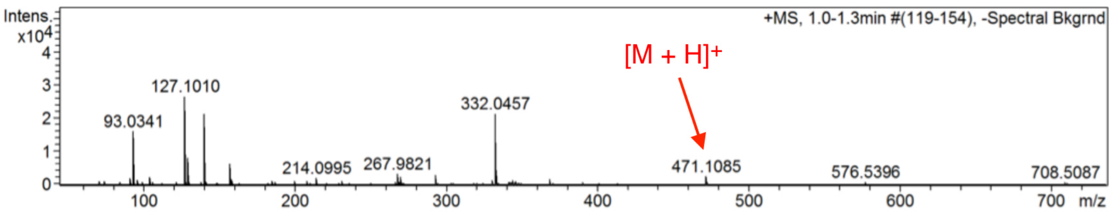

Figure S9. ESI mass spectrum of [Fe(acac)$_3$] and **1** in the presence of hydrochloric acid, showing the presence of the iron deferiprone complex [Fe(dfp)$_3$].

4. Stability evaluation of $[Zn_3(bdc)_2(dfp)_2]\cdot 2DMF$ 1 under acidic media

The release of deferiprone from $[Zn_3(bdc)_2(dfp)_2]\cdot 2DMF$ **1** was monitored by LCMS. The LCMS data were recorded on a Waters 2695 HPLC using a Waters 2487 UV detector and a Thermo LCQ ESI-MS. The samples were eluted through a Phenomenex Lunar 3μ C18 50 mm × 4.6 mm column, using water and acetonitrile acidified by 0.1% formic acid at 1 cm^3 min^{-1} and detected at 254 nm. The gradient employed is summarised in Table S1.

Table S1. Gradient employed in LCMS studies.

Time (minutes)	% Water + 0.1% formic acid	% MeCN + 0.1% formic acid
0.0	70	30
5.0	10	90
6.0	10	90
6.5	70	30
7.0	70	30

(a) Reference samples and MOF stability

(i) The LCMS trace for H_2bdc (0.002 g) in DMSO/water (8/2) (1 cm^3) is shown in Figure S10.

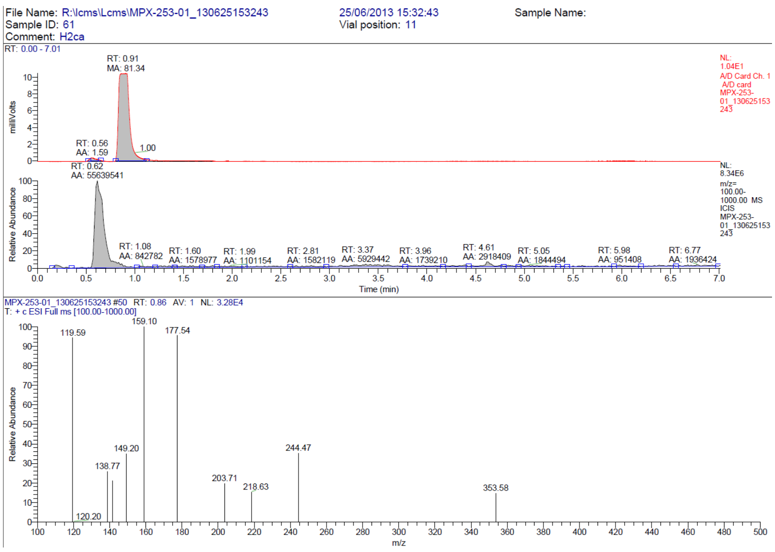

Figure S10. LCMS for H_2bdc in DMSO/water (R_t = 0.69 min, *m/z* 166.87).

(ii) The LCMS trace for Hdfp (0.002 g) in DMSO/water (8/2) (1 cm^3) is shown in Figure S11.

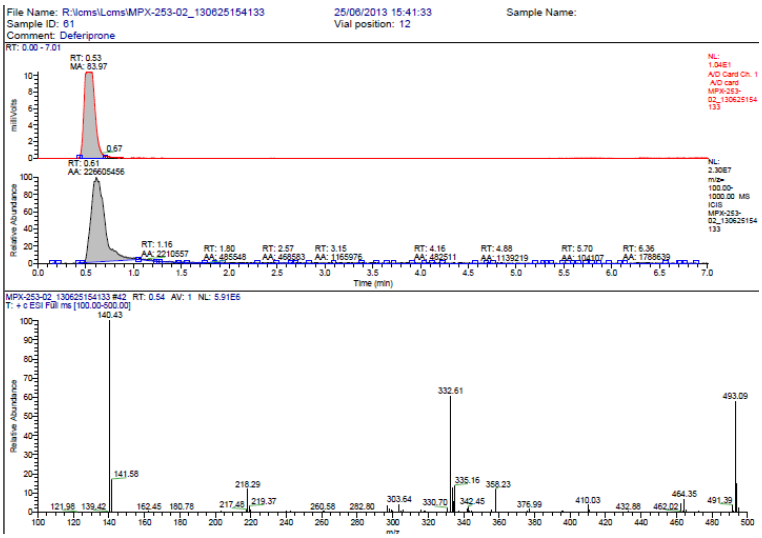

Figure S11. LCMS for Hdfp in DMSO/water (R_t = 0.52 min, *m/z* 140.30).

(iii) The LCMS trace for **1** (0.002 g) in DMSO (1 cm^3) after 10 min is shown in Figure S12. No sign of release of Hdfp was observed.

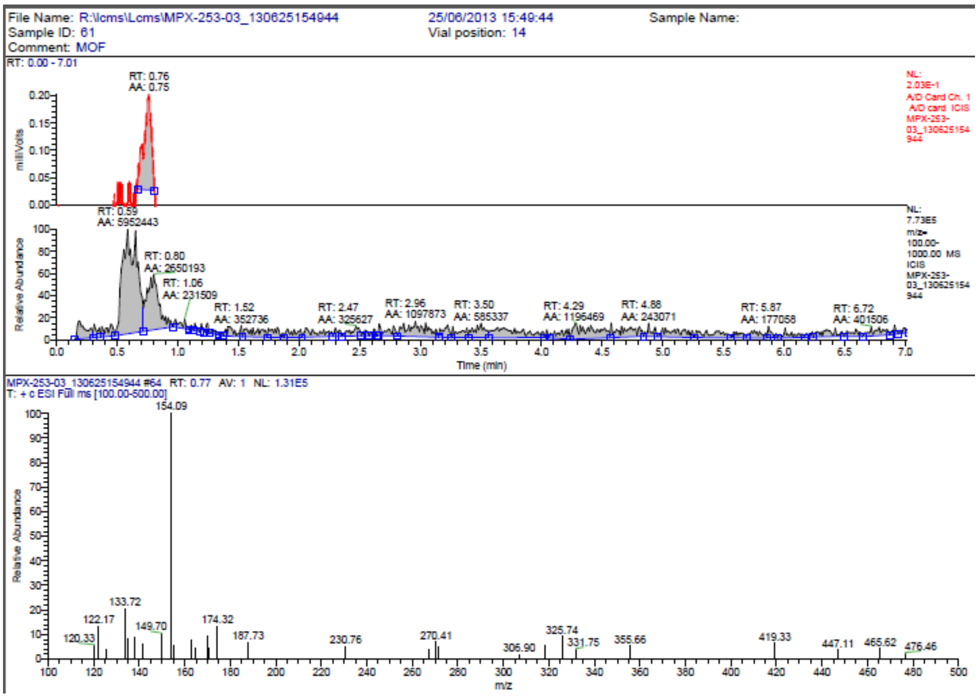

Figure S12. LCMS for **1** in DMSO.

(iv) The LCMS trace for **1** (0.002 g) in methanol (1 cm^3) after 10 min is shown in Figure S13. No sign of release of Hdfp was observed.

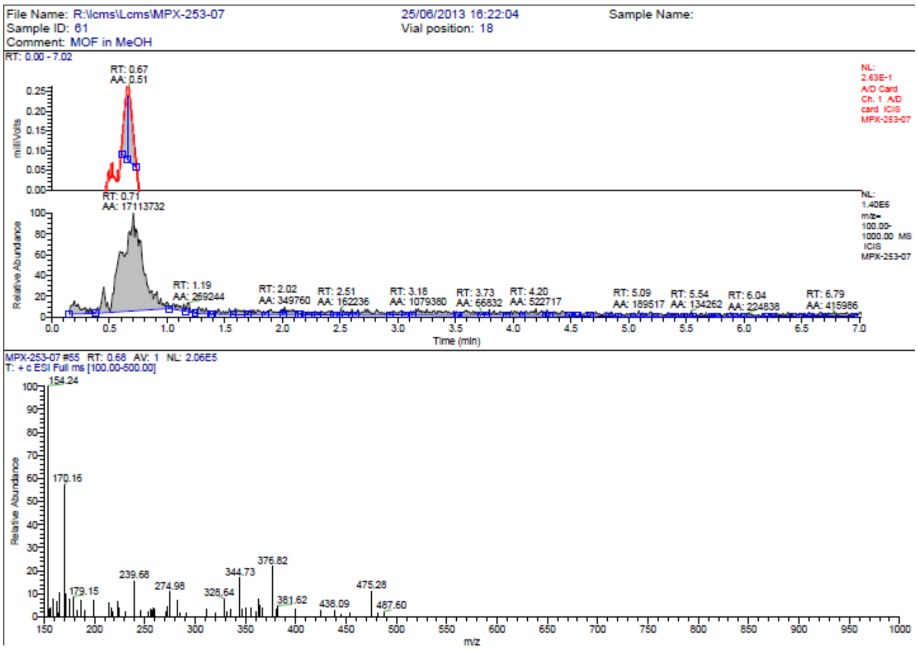

Figure S13. LCMS for **1** in methanol.

(b) Release under acidic conditions

(i) A sample of **1** was suspended in 1 N hydrochloric acid (1 cm^3). An aliquot of the solution was taken immediately after the addition and injected onto the LCMS. The results are shown in Figure S14.

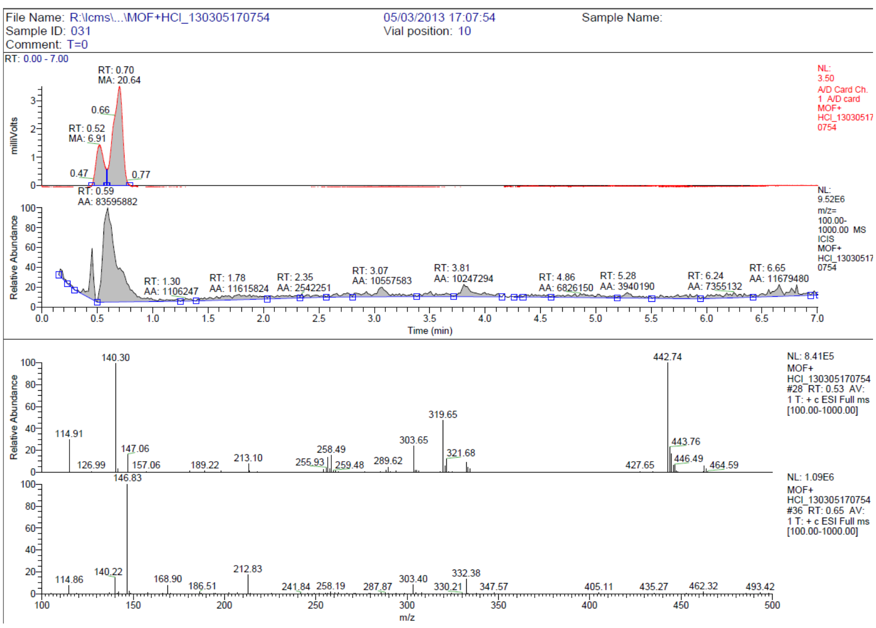

Figure S14. LCMS showing release of Hdfp from **1** in the presence of 1 N HCl.

(ii) A sample of **1** was suspended in a saturated citric acid solution (1 cm^3). An aliquot of the solution was taken immediately after the addition and injected onto the LCMS. The results are shown in Figure S15.

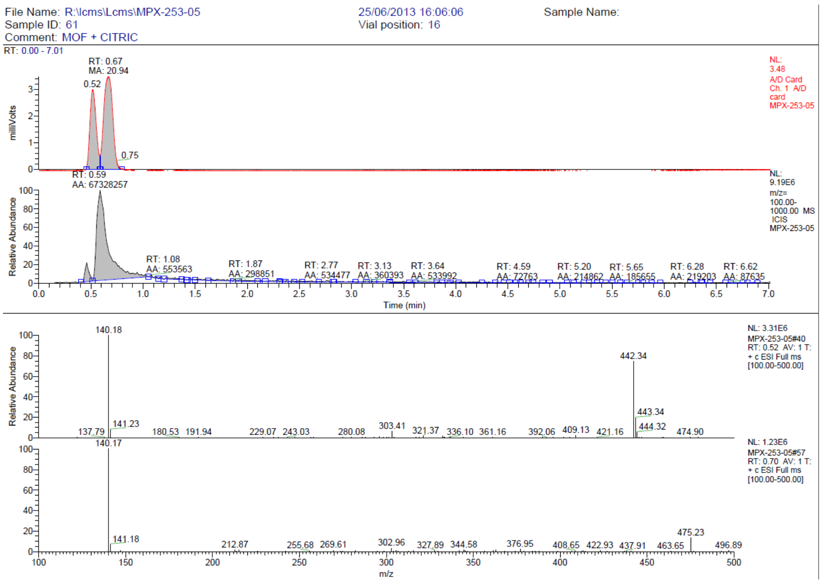

Figure S15. LCMS showing release of Hdfp from **1** in the presence of citric acid.

(iii) A sample of **1** was suspended in a methanol (0.5 cm^3) / ethanoic acid (0.5 cm^3) mixture. An aliquot of the solution was taken immediately after the addition and injected into the LCMS. The LCMS trace (Figure S16) only shows traces of Hdfp detected (R_t = 0.50 min). Although, the LCMS is not calibrated with any internal standard that would show a concentration, the very weak signal (0.2 mV) is indicative that release of Hdfp is not as rapid as with either HCl or citric acid.

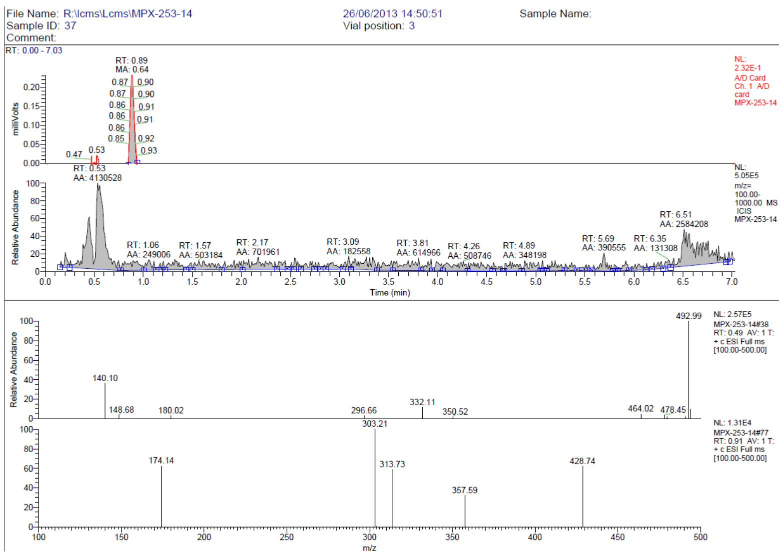

Figure S16. LCMS showing minimal release of Hdfp from **1** in the presence of methanol/ethanoic acid immediately after injection.

(iv) A further aliquot of the sample suspended in methanol / ethanoic acid was injected into the LCMS after 20 min from adding the ethanoic acid solution and the trace is shown in Figure S17. The UV intensity of Hdfp detected has significantly increased from that shown in Figure S16, removing any ambiguity associated with potential lack of sensitivity from the sample.

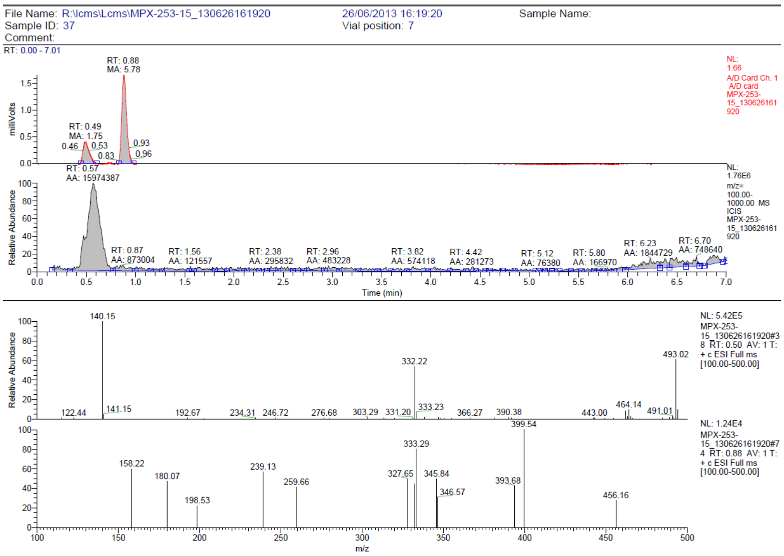

Figure S17. LCMS showing release of Hdfp from **1** in the presence of methanol/ethanoic acid 20 minutes after injection.

(v) A further aliquot of the sample suspended in methanol / ethanoic acid was injected into the LCMS after 55 min from adding the ethanoic acid solution (Figure S18). The UV intensity of Hdfp detected has further increased.

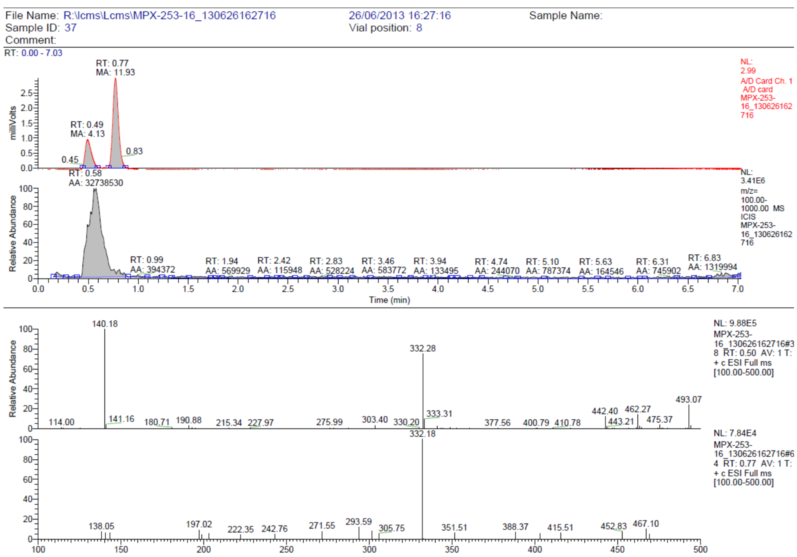

Figure S18. LCMS showing release of Hdfp from **1** in the presence of methanol/ethanoic acid 55 minutes after injection.

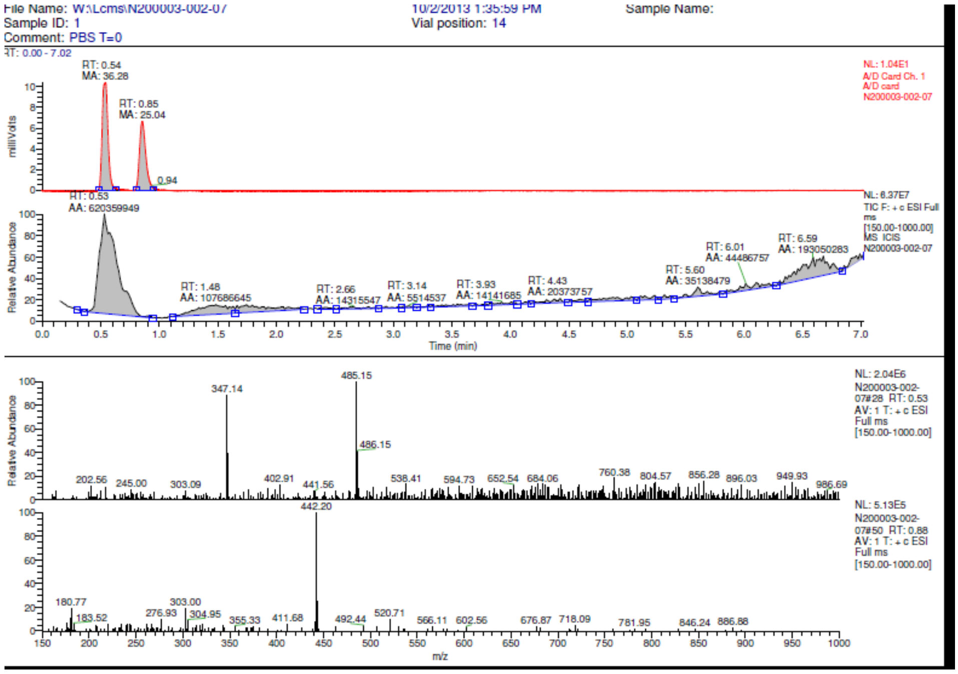

Figure S19. LCMS showing immediate release of Hdfp from **1** in the presence of PBS 5 minutes after injection.

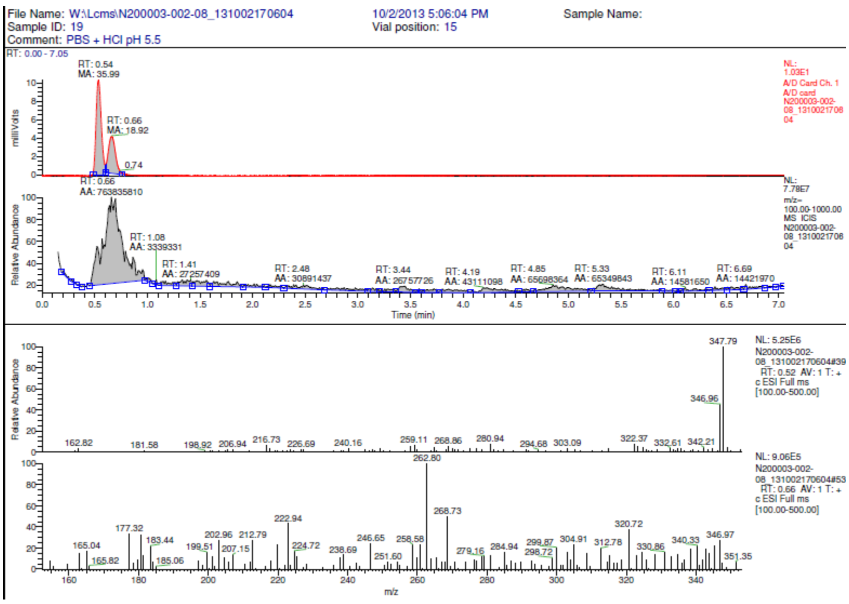

Figure S20. LCMS showing immediate release of Hdfp from **1** in the presence of PBS/HCl (pH=5.5) 5 minutes after injection.

5. Crystallography

*(a) Crystal structure of [$Zn_3(bdc)_2(dfp)_2$]·2DMF **1***

Crystal data for **1** were collected on a Nonius KappaCCD diffractometer. The asymmetric unit comprises one and a half zinc centres, one bdc ligand, one deprotonated deferiprone and one uncoordinated DMF molecule. Details of the crystal data and structure refinement are given in Table S2 and bond length and bond angles are given in Table S3. The asymmetric unit for **1** is shown in Figure S21.

Table S2. Crystal data and structure refinement for [$Zn_3(bdc)_2(dfp)_2$]·2DMF **1**.

Empirical formula	$C_{18}H_{19}N_2O_7Zn_{1.50}$
Formula weight	473.41
Temperature / K	150(2)
Wavelength / Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.7750(1) Å
	b = 18.9580(2) Å
	c = 11.4690(1) Å
	α = 90°
	β = 111.354(1)°
	γ = 90°
Volume / Å^3	1979.46(3)
Z	4
Density (calculated) / g cm^{-3}	1.589
Absorption coefficient / mm^{-1}	1.874
F(000)	968
Theta range for data collection / °	3.59 to 27.48
Index ranges	$-12 \le h \le 12$; $-24 \le k \le 24$; $-14 \le l \le 14$
Reflections collected	36699
Independent reflections	4533 [R(int) = 0.0384]
Reflections observed (>2σ)	4079
Data Completeness	0.998
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.693 and 0.576
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4533 / 0 / 264
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0248 $wR2$ = 0.0593
R indices (all data)	$R1$ = 0.0288 $wR2$ = 0.0618
Largest diff. peak and hole / eÅ^{-3}	0.575 and –0.621

Table S3. Bond lengths [Å] and angles [°] for $[Zn_3(bdc)_2(dfp)_2]\cdot 2DMF$ **1**.

Zn(1)-O(6)	2.0574(10)	Zn(1)-O(6)#1	2.0575(10)
Zn(1)-O(4)#2	2.0927(10)	Zn(1)-O(4)#3	2.0927(10)
Zn(1)-O(2)#1	2.1105(1	Zn(1)-O(2)	2.1105(10)
Zn(2)-O(3)#3	1.9692(1	Zn(2)-O(1)	1.9820(10)
Zn(2)-O(5)	2.0410(10)	Zn(2)-O(6)	2.0681(10)
Zn(2)-O(5)#4	2.0832(	O(1)-C(1)	1.2712(18)
O(2)-C(1)	1.2482(18)	O(3)-C(8)	1.2721(18)
O(3)-Zn(2)#5	1.9691(	O(4)-C(8)	1.2459(18)
O(4)-Zn(1)#5	2.0927(	O(5)-C(9)	1.3316(18)
O(5)-Zn(2)#4	2.0832(1	O(6)-C(10)	1.2981(17)
O(7)-C(16)	1.222(2)	N(1)-C(12)	1.351(2)
N(1)-C(13)	1.378(2)	N(1)-C(14)	1.4765(19)
N(2)-C(16)	1.328(2)	N(2)-C(17)	1.445(3)
N(2)-C(18)	1.455(2	C(1)-C(2)	1.508(2)
C(2)-C(3)	1.392(2)	C(2)-C(7)	1.395(2)
C(3)-C(4)	1.388(2)	C(4)-C(5)	1.395(2)
C(5)-C(6)	1.394(2)	C(5)-C(8)	1.509(2)
C(6)-C(7)	1.390(2)	C(9)-C(13)	1.385(2)
C(9)-C(10)	1.439(2)	C(10)-C(11)	1.401(2)
C(11)-C(12)	1.367(2)	C(13)-C(15)	1.499(2)
O(6)-Zn(1)-O(6)#1	180.0	O(6)-Zn(1)-O(4)#2	90.97(4)
O(6)#1-Zn(1)-O(4)#2	89.03(4)	O(6)-Zn(1)-O(4)#3	89.02(4)
O(6)#1-Zn(1)-O(4)#3	90.97(4)	O(4)#2-Zn(1)-O(4)#3	180.0
O(6)-Zn(1)-O(2)#1	91.56(4)	O(6)#1-Zn(1)-O(2)#1	88.44(4)
O(4)#2-Zn(1)-O(2)#1	94.10(4)	O(4)#3-Zn(1)-O(2)#1	85.90(4)
O(6)-Zn(1)-O(2)	88.44(4)	O(6)#1-Zn(1)-O(2)	91.56(4)
O(4)#2-Zn(1)-O(2)	85.90(4)	O(4)#3-Zn(1)-O(2)	94.11(4)
O(2)#1-Zn(1)-O(2)	180.00(5)	O(3)#3-Zn(2)-O(1)	119.44(5)
O(3)#3-Zn(2)-O(5)	121.91(4)	O(1)-Zn(2)-O(5)	118.59(4)
O(3)#3-Zn(2)-O(6)	99.77(4)	O(1)-Zn(2)-O(6)	93.41(4)
O(5)-Zn(2)-O(6)	79.18(4)	O(3)#3-Zn(2)-O(5)#4	95.70(4)
O(1)-Zn(2)-O(5)#4	93.41(4)	O(5)-Zn(2)-O(5)#4	78.48(4)
O(6)-Zn(2)-O(5)#4	157.24(4)	C(1)-O(1)-Zn(2)	122.97(9)
C(1)-O(2)-Zn(1)	133.61(9)	C(8)-O(3)-Zn(2)#5	126.62(10)
C(8)-O(4)-Zn(1)#5	139.48(10)	C(9)-O(5)-Zn(2)	113.57(9)
C(9)-O(5)-Zn(2)#4	143.48(9)	Zn(2)-O(5)-Zn(2)#4	101.51(4)
C(10)-O(6)-Zn(1)	135.01(9)	C(10)-O(6)-Zn(2)	113.39(9)
Zn(1)-O(6)-Zn(2)	111.57(5)	C(12)-N(1)-C(13)	121.82(13)
C(12)-N(1)-C(14)	117.99(13)	C(13)-N(1)-C(14)	120.12(13)
C(16)-N(2)-C(17)	120.45(16)	C(16)-N(2)-C(18)	121.38(16)
C(17)-N(2)-C(18)	117.83(16)	O(2)-C(1)-O(1)	126.32(13)
O(2)-C(1)-C(2)	118.25(13)	O(1)-C(1)-C(2)	115.43(13)
C(3)-C(2)-C(7)	119.77(14)	C(3)-C(2)-C(1)	120.45(13)
C(7)-C(2)-C(1)	119.78(13)	C(4)-C(3)-C(2)	120.42(14)
C(3)-C(4)-C(5)	120.05(15)	C(6)-C(5)-C(4)	119.39(14)
C(6)-C(5)-C(8)	120.87(13)	C(4)-C(5)-C(8)	119.72(14)
C(7)-C(6)-C(5)	120.68(14)	C(6)-C(7)-C(2)	119.66(14)
O(4)-C(8)-O(3)	126.88(13)	O(4)-C(8)-C(5)	116.99(13)
O(3)-C(8)-C(5)	116.12(13)	O(5)-C(9)-C(13)	124.37(13)
O(5)-C(9)-C(10)	116.18(12)	C(13)-C(9)-C(10)	119.41(13)

O(6)-C(10)-C(11)	124.54(13)	O(6)-C(10)-C(9)	117.13(13)
C(11)-C(10)-C(9)	118.33(13)	C(12)-C(11)-C(10)	119.90(14)
N(1)-C(12)-C(11)	121.19(14)	N(1)-C(13)-C(9)	119.18(13)
N(1)-C(13)-C(15)	118.04(13)	C(9)-C(13)-C(15)	122.77(14)
O(7)-C(16)-N(2)	125.03(19)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1 #2 x-1/2,-y+1/2,z-1/2
#3 -x+1/2,y-1/2,-z+3/2 #4 -x+1,-y,-z+1
#5 -x+1/2,y+1/2,-z+3/2

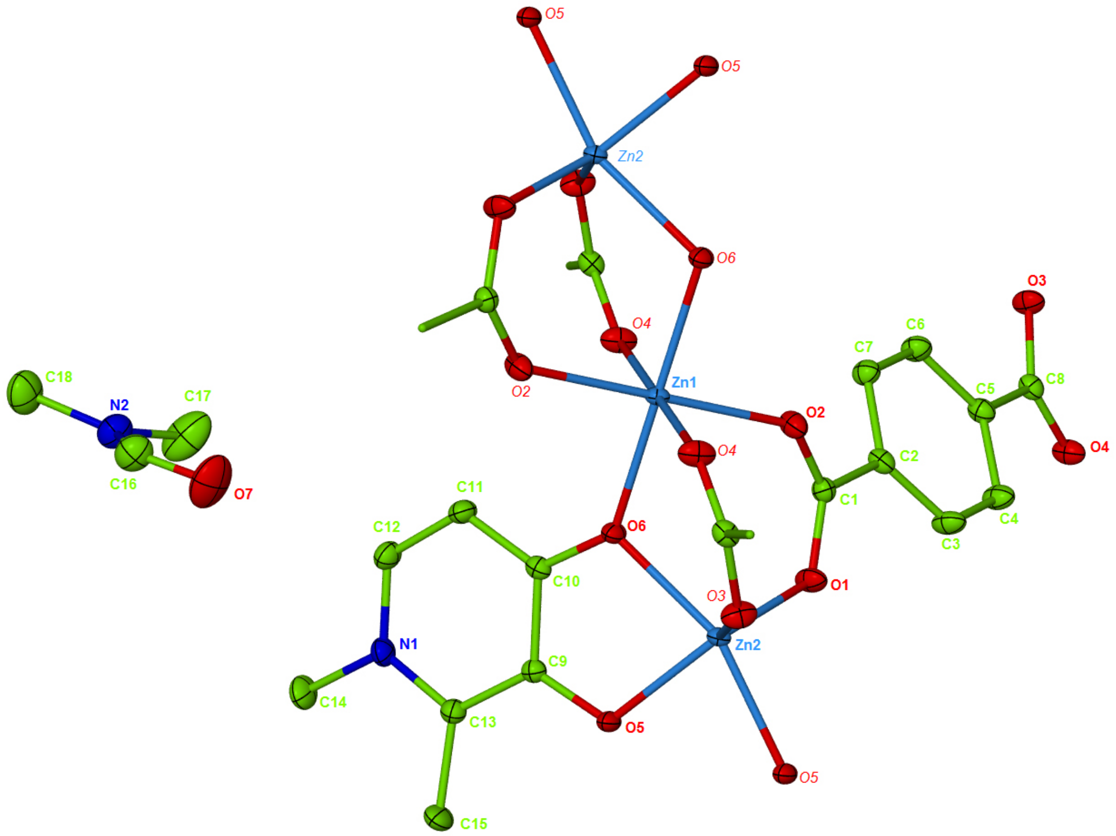

Figure S21. Asymmetric unit for $[Zn_3(bdc)_2(dfp)_2]\cdot 2DMF$ **1**, showing also selected symmetry-related atoms (with italicised labels) *(b) Crystal structure of [$Zn_3(bdc)_2(dfp)_2(H_2O)_2$]* **2**

Crystal data for **2** were collected at Diamond Light Source. The asymmetric unit comprises one and a half zinc centres, two crystallographically independent halves of bdc, one deprotonated deferiprone and one water molecule. The water hydrogen atoms were located and refined subject to some distance restraints to assist convergence. Details of the crystal data and structure refinement are given in Table S4 and bond length and bond angles are given in Table S5. Details of the hydrogen bonding is given in Table S6. The asymmetric unit for **2** is shown in Figure S22.

Table S4. Crystal data and structure refinement for [$Zn_3(bdc)_2(dfp)_2(H_2O)_2$] **2**.

Empirical formula	$C_{30}H_{28}N_2O_{14}Zn_3$
Formula weight	836.65
Temperature / K	150(2)
Wavelength / Å	0.68890
Crystal system	Triclinic
Space group	*P*–1
Unit cell dimensions	a = 8.127(3) Å
	b = 9.909(3) Å
	c = 11.353(4) Å
	α = 107.182(2)°
	β = 90.439(4)°
	γ = 113.787(3)°
Volume / $Å^3$	790.9(5)
Z	1
Density (calculated) / g cm^{-3}	1.757
Absorption coefficient / mm^{-1}	2.331
F(000)	424
Theta range for data collection / °	2.68 to 26.60
Index ranges	$-10 \le h \le 9; -12 \le k \le 12; -14 \le l \le 14$
Reflections collected	7266
Independent reflections	3262 [R(int) = 0.0386]
Reflections observed (>2σ)	2729
Data Completeness	0.896
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.860
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3262 / 5 / 232
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0348 $wR2$ = 0.0986
R indices (all data)	$R1$ = 0.0401 $wR2$ = 0.1010
Largest diff. peak and hole / $eÅ^{-3}$	0.477 and –0.816

Table S5. Bond lengths [Å] and angles [°] for $[Zn_3(bdc)_2(dfp)_2(H_2O)_2]$ **2**.

Zn(1)-O(1)	2.034(2)	Zn(1)-O(1)#1	2.034(2)
Zn(1)-O(5)	2.1198(17)	Zn(1)-O(5)#1	2.1198(17)
Zn(1)-O(7)	2.147(2)	Zn(1)-O(7)#1	2.147(2)
Zn(2)-O(2)	2.0040(18)	Zn(2)-O(5)	2.0537(19)
Zn(2)-O(4)	2.0975(19)	Zn(2)-O(6)#2	2.0985(18)
Zn(2)-O(6)	2.1760(1	Zn(2)-O(3)	2.308(2)
Zn(2)-C(5)	2.528(3)	Zn(2)-Zn(2)#2	3.1590(9)
O(1)-C(1)	1.250(3)	O(2)-C(1)	1.265(3)
O(3)-C(5)	1.248(3)	O(4)-C(5)	1.276(3)
O(5)-C(10)	1.304(3	O(6)-C(9)	1.342(3)
O(6)-Zn(2)#2	2.0985	N(1)-C(12)	1.348(3)
N(1)-C(13)	1.384(3)	N(1)-C(15)	1.482(3)
C(1)-C(2)	1.510(3)	C(2)-C(3)	1.391(4)
C(2)-C(4)	1.399(4)	C(3)-C(4)#3	1.395(4)
C(4)-C(3)#3	1.395(	C(5)-C(6)	1.500(3)
C(6)-C(8)	1.389(4)	C(6)-C(7)	1.388(4)
C(7)-C(8)#4	1.392(4)	C(8)-C(7)#4	1.392(4)
C(9)-C(13)	1.387(3)	C(9)-C(10)	1.430(3)
C(10)-C(11)	1.402(4)	C(11)-C(12)	1.368(4)
C(13)-C(14)	1.499(4)		
O(1)-Zn(1)-O(1)#1	180.0	O(1)-Zn(1)-O(5)	89.94(7)
O(1)#1-Zn(1)-O(5)	90.06(7)	O(1)-Zn(1)-O(5)#1	90.06(7)
O(1)#1-Zn(1)-O(5)#1	89.94(7)	O(5)-Zn(1)-O(5)#1	180.0
O(1)-Zn(1)-O(7)	95.76(8)	O(1)#1-Zn(1)-O(7)	84.24(8)
O(5)-Zn(1)-O(7)	86.69(8)	O(5)#1-Zn(1)-O(7)	93.31(8)
O(1)-Zn(1)-O(7)#1	84.24(8)	O(1)#1-Zn(1)-O(7)#1	95.76(8)
O(5)-Zn(1)-O(7)#1	93.31(8)	O(5)#1-Zn(1)-O(7)#1	86.69(8)
O(7)-Zn(1)-O(7)#1	180.0	O(2)-Zn(2)-O(5)	96.29(8)
O(2)-Zn(2)-O(4)	92.70(8)	O(5)-Zn(2)-O(4)	152.97(7)
O(2)-Zn(2)-O(6)#2	95.42(8)	O(5)-Zn(2)-O(6)#2	103.41(7)
O(4)-Zn(2)-O(6)#2	101.03(7)	O(2)-Zn(2)-O(6)	174.10(7)
O(5)-Zn(2)-O(6)	77.97(7)	O(4)-Zn(2)-O(6)	93.06(7)
O(6)#2-Zn(2)-O(6)	84.72(7)	O(2)-Zn(2)-O(3)	89.28(8)
O(5)-Zn(2)-O(3)	94.94(7)	O(4)-Zn(2)-O(3)	59.66(7)
O(6)#2-Zn(2)-O(3)	160.39(7)	O(6)-Zn(2)-O(3)	92.53(7)
O(2)-Zn(2)-C(5)	89.92(8)	O(5)-Zn(2)-C(5)	124.12(8)
O(4)-Zn(2)-C(5)	30.25(8)	O(6)#2-Zn(2)-C(5)	131.26(8)
O(6)-Zn(2)-C(5)	94.41(7)	O(3)-Zn(2)-C(5)	29.46(8)
O(2)-Zn(2)-Zn(2)#2	138.41(6)	O(5)-Zn(2)-Zn(2)#2	90.60(6)
O(4)-Zn(2)-Zn(2)#2	99.43(6)	O(6)#2-Zn(2)-Zn(2)#2	43.31(5)
O(6)-Zn(2)-Zn(2)#2	41.41(5)	O(3)-Zn(2)-Zn(2)#2	131.01(5)
C(5)-Zn(2)-Zn(2)#2	119.42(6)	C(1)-O(1)-Zn(1)	139.00(17)
C(1)-O(2)-Zn(2)	133.06(17)	C(5)-O(3)-Zn(2)	85.08(15)
C(5)-O(4)-Zn(2)	93.86(15)	C(10)-O(5)-Zn(2)	112.16(15)
C(10)-O(5)-Zn(1)	125.45(15)	Zn(2)-O(5)-Zn(1)	119.12(8)
C(9)-O(6)-Zn(2)#2	121.62(14)	C(9)-O(6)-Zn(2)	107.89(14)
Zn(2)#2-O(6)-Zn(2)	95.28(7)	C(12)-N(1)-C(13)	121.5(2)
C(12)-N(1)-C(15)	118.6(2)	C(13)-N(1)-C(15)	119.9(2)
O(1)-C(1)-O(2)	126.5(2)	O(1)-C(1)-C(2)	117.0(2)
O(2)-C(1)-C(2)	116.4(2)	C(3)-C(2)-C(4)	120.3(2)

C(3)-C(2)-C(1)	120.1(3)	C(4)-C(2)-C(1)	119.6(2)
C(2)-C(3)-C(4)#3	120.0(3)	C(3)#3-C(4)-C(2)	119.7(3)
O(3)-C(5)-O(4)	121.2(2)	O(3)-C(5)-C(6)	120.2(2)
O(4)-C(5)-C(6)	118.5(2)	O(3)-C(5)-Zn(2)	65.46(13)
O(4)-C(5)-Zn(2)	55.89(13)	C(6)-C(5)-Zn(2)	173.37(19)
C(8)-C(6)-C(7)	119.4(2)	C(8)-C(6)-C(5)	119.9(2)
C(7)-C(6)-C(5)	120.8(2)	C(6)-C(7)-C(8)#4	120.2(3)
C(6)-C(8)-C(7)#4	120.4(2)	O(6)-C(9)-C(13)	122.8(2)
O(6)-C(9)-C(10)	116.8(2)	C(13)-C(9)-C(10)	120.3(2)
O(5)-C(10)-C(11)	123.5(2)	O(5)-C(10)-C(9)	118.7(2)
C(11)-C(10)-C(9)	117.8(2)	C(12)-C(11)-C(10)	120.1(2)
N(1)-C(12)-C(11)	121.5(3)	N(1)-C(13)-C(9)	118.8(2)
N(1)-C(13)-C(14)	118.1(2)	C(9)-C(13)-C(14)	123.1(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z   #2 -x,-y+1,-z   #3 -x+1,-y+1,-z+1
#4 -x,-y+2,-z+1

Table S6. Hydrogen bonding present in the crystal structure of $[Zn_3(bdc)_2(dfp)_2(H_2O)_2]$ **2**.

D–H···A	**D···A / Å**	**H···A / Å**	**D–H···A / °**	**Symmetry relating D and A**
O(7)–H(7A)···O(6)	2.719(3)	1.82	151	$-x, -y + 1, -z$
O(7)–H(7B)···O(4)	2.809(3)	1.99	138	$-x, -y + 1, -z$

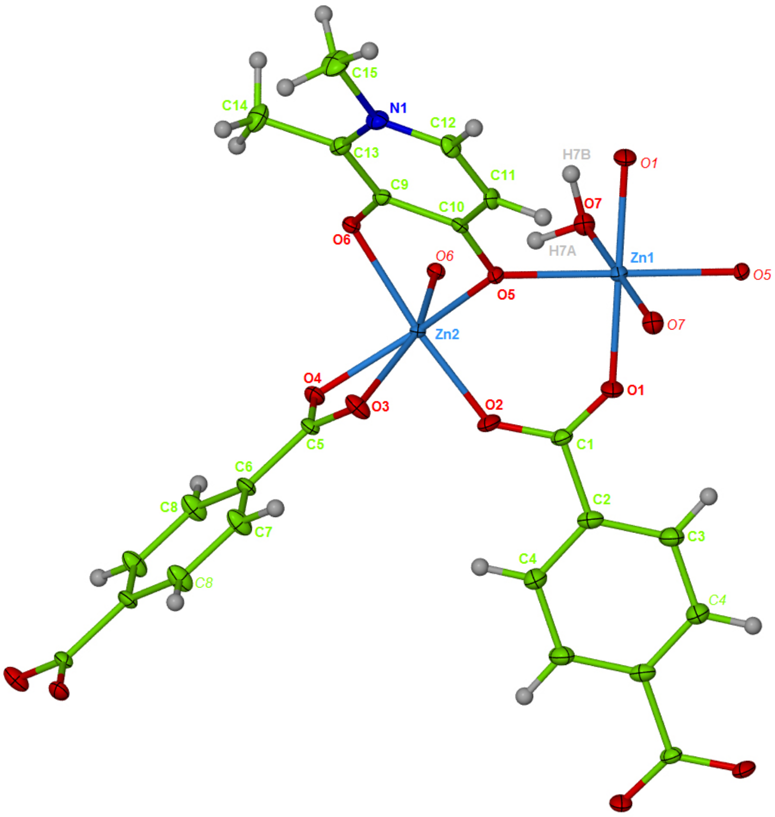

Figure S22. Asymmetric unit for $[Zn_3(bdc)_2(dfp)_2(H_2O)_2]$ **2**, showing also selected symmetry-related atoms *(c) Crystal structure of [Zn_3(bdc-NH_2)$_2$(dfp)$_2$]·DMF* ***3***

Crystal data for **3** were collected on a Nonius KappaCCD diffractometer. The asymmetric unit comprises one and a half zinc centres, one bdc-NH_2 ligand and one deprotonated deferiprone molecule. The amino group on the bdc-NH_2 ligand is disordered over two positions in a 55:45 ratio. Solvent in the lattice was treated using the SQUEEZE algorithm.[S2] Prior to this process, there was evidence for some very disordered DMF in the voids. These moieties were oriented such that the fractional occupancy amino hydrogen from each disordered functionality that is not involved in a framework hydrogen bond, is directed (face on) to a fractional solvent. Details of the crystal data and structure refinement are given in Table S7 and bond length and bond angles are given in Table S8. Details of the hydrogen bonding is given in Table S9. The asymmetric unit for **3** is shown in Figure S23.

Table S7. Crystal data and structure refinement for [Zn_3(bdc-NH_2)$_2$(dfp)$_2$]·DMF **3**.

Empirical formula	$C_{33}H_{33}N_5O_{13}Zn_3$
Formula weight	903.76
Temperature / K	150(2)
Wavelength / Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.7350(1) Å
	b = 18.8760(3) Å
	c = 11.5940(2) Å
	α = 90°
	β = 108.518(1)°
	γ = 90°
Volume / Å^3	2020.18(5)
Z	2
Density (calculated) / g cm^{-3}	1.486
Absorption coefficient / mm^{-1}	1.832
F(000)	920
Theta range for data collection	3.71 to 27.49°
Index ranges	$-12 \le h \le 11$; $0 \le k \le 24$; $0 \le l \le 15$
Reflections collected	4622
Independent reflections	4622 [R(int) = 0.0000]
Reflections observed (>2σ)	3663
Data Completeness	0.995
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.573 and 0.535
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4622 / 0 / 234
Goodness-of-fit on F^2	1.088
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0355 $wR2$ = 0.1094
R indices (all data)	$R1$ = 0.0479 $wR2$ = 0.1149
Largest diff. peak and hole / eÅ^{-3}	1.029 and –0.613

Table S8. Bond lengths [Å] and angles [°] for $[Zn_3(bdc\text{-}NH_2)_2(dfp)_2]\cdot DMF$ **3**.

Zn(1)-O(6)	2.0671(16)	Zn(1)-O(6)#1	2.0671(16)
Zn(1)-O(4)#2	2.0913(17)	Zn(1)-O(4)#3	2.0913(17)
Zn(1)-O(2)#1	2.1002(1	Zn(1)-O(2)	2.1002(17)
Zn(2)-O(1)	1.9552(17)	Zn(2)-O(3)#2	1.9712(17)
Zn(2)-O(5)	2.0248(17)	Zn(2)-O(6)	2.0642(17)
Zn(2)-O(5)#4	2.0843(18)	Zn(2)-Zn(2)#4	3.1590(5)
O(1)-C(1)	1.278(3)	O(2)-C(1)	1.231(3)
O(3)-C(8)	1.263(3)	O(3)-Zn(2)#5	1.9712(17)
O(4)-C(8)	1.249(3)	O(4)-Zn(1)#5	2.0914(17)
O(5)-C(9)	1.327(3)	O(5)-Zn(2)#4	2.0843(18)
O(6)-C(10)	1.297(3)	N(1)-C(12)	1.336(4)
N(1)-C(13)	1.363(4)	N(1)-C(15)	1.477(4)
N(2)-C(4)	1.409(6)	N(2A)-C(7)	1.391(8)
C(1)-C(2)	1.507(3)	C(2)-C(7)	1.381(4)
C(2)-C(3)	1.385(4)	C(3)-C(4)	1.398(4)
C(4)-C(5)	1.396(4)	C(5)-C(6)	1.367(4)
C(5)-C(8)	1.503(3)	C(6)-C(7)	1.397(4)
C(9)-C(13)	1.381(3)	C(9)-C(10)	1.429(3)
C(10)-C(11)	1.392(4)	C(11)-C(12)	1.373(4)
C(13)-C(14)	1.503(4)		
O(6)-Zn(1)-O(6)#1	180.0	O(6)-Zn(1)-O(4)#2	89.56(7)
O(6)#1-Zn(1)-O(4)#2	90.44(7)	O(6)-Zn(1)-O(4)#3	90.44(7)
O(6)#1-Zn(1)-O(4)#3	89.56(7)	O(4)#2-Zn(1)-O(4)#3	180.0
O(6)-Zn(1)-O(2)#1	90.62(6)	O(6)#1-Zn(1)-O(2)#1	89.38(6)
O(4)#2-Zn(1)-O(2)#1	86.49(8)	O(4)#3-Zn(1)-O(2)#1	93.51(8)
O(6)-Zn(1)-O(2)	89.38(6)	O(6)#1-Zn(1)-O(2)	90.62(6)
O(4)#2-Zn(1)-O(2)	93.51(8)	O(4)#3-Zn(1)-O(2)	86.49(8)
O(2)#1-Zn(1)-O(2)	180.0	O(1)-Zn(2)-O(3)#2	120.41(9)
O(1)-Zn(2)-O(5)	119.56(8)	O(3)#2-Zn(2)-O(5)	119.94(8)
O(1)-Zn(2)-O(6)	99.93(7)	O(3)#2-Zn(2)-O(6)	93.37(7)
O(5)-Zn(2)-O(6)	79.55(7)	O(1)-Zn(2)-O(5)#4	94.75(7)
O(3)#2-Zn(2)-O(5)#4	92.67(7)	O(5)-Zn(2)-O(5)#4	79.52(8)
O(6)-Zn(2)-O(5)#4	158.47(7)	O(1)-Zn(2)-Zn(2)#4	111.76(6)
O(3)#2-Zn(2)-Zn(2)#4	110.53(6)	O(5)-Zn(2)-Zn(2)#4	40.45(5)
O(6)-Zn(2)-Zn(2)#4	119.84(5)	O(5)#4-Zn(2)-Zn(2)#4	39.07(5)
C(1)-O(1)-Zn(2)	125.76(16)	C(1)-O(2)-Zn(1)	140.98(16)
C(8)-O(3)-Zn(2)#5	125.94(16)	C(8)-O(4)-Zn(1)#5	134.79(16)
C(9)-O(5)-Zn(2)	113.57(15)	C(9)-O(5)-Zn(2)#4	144.08(15)
Zn(2)-O(5)-Zn(2)#4	100.48(8)	C(10)-O(6)-Zn(2)	112.42(15)
C(10)-O(6)-Zn(1)	137.09(16)	Zn(2)-O(6)-Zn(1)	110.42(7)
C(12)-N(1)-C(13)	121.4(2)	C(12)-N(1)-C(15)	118.4(3)
C(13)-N(1)-C(15)	120.2(3)	O(2)-C(1)-O(1)	125.9(2)
O(2)-C(1)-C(2)	118.4(2)	O(1)-C(1)-C(2)	115.7(2)
C(7)-C(2)-C(3)	119.6(2)	C(7)-C(2)-C(1)	120.9(2)
C(3)-C(2)-C(1)	119.5(2)	C(2)-C(3)-C(4)	121.4(3)
C(5)-C(4)-C(3)	118.5(2)	C(5)-C(4)-N(2)	123.7(3)
C(3)-C(4)-N(2)	117.5(3)	C(6)-C(5)-C(4)	119.7(2)
C(6)-C(5)-C(8)	119.9(2)	C(4)-C(5)-C(8)	120.4(2)
C(5)-C(6)-C(7)	121.7(3)	C(2)-C(7)-N(2A)	124.3(4)
C(2)-C(7)-C(6)	119.0(3)	N(2A)-C(7)-C(6)	116.6(4)

O(4)-C(8)-O(3)	125.4(2)	O(4)-C(8)-C(5)	118.7(2)
O(3)-C(8)-C(5)	115.8(2)	O(5)-C(9)-C(13)	123.9(2)
O(5)-C(9)-C(10)	116.0(2)	C(13)-C(9)-C(10)	120.0(2)
O(6)-C(10)-C(11)	124.3(2)	O(6)-C(10)-C(9)	117.8(2)
C(11)-C(10)-C(9)	117.9(2)	C(12)-C(11)-C(10)	119.4(3)
N(1)-C(12)-C(11)	121.9(3)	N(1)-C(13)-C(9)	119.2(2)
N(1)-C(13)-C(14)	117.4(2)	C(9)-C(13)-C(14)	123.4(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+2 #2 -x+3/2,y+1/2,-z+3/2
#3 x+1/2,-y-1/2,z+1/2 #4 -x+1,-y,-z+2
#5 -x+3/2,y-1/2,-z+3/2

Table S9. Hydrogen bonding present in the crystal structure of $[Zn_3(bdc\text{-}NH_2)_2(dfp)_2]\cdot DMF$ **3**.

D–H···A	D···A / Å	H···A / Å	D–H···A / °	Symmetry relating D and A
N(2)–H(2A)···O(4)	2.643(7)	2.01	128	–
N(2A)–H(2A1)···O(2)	2.644(8)	2.04	126	–

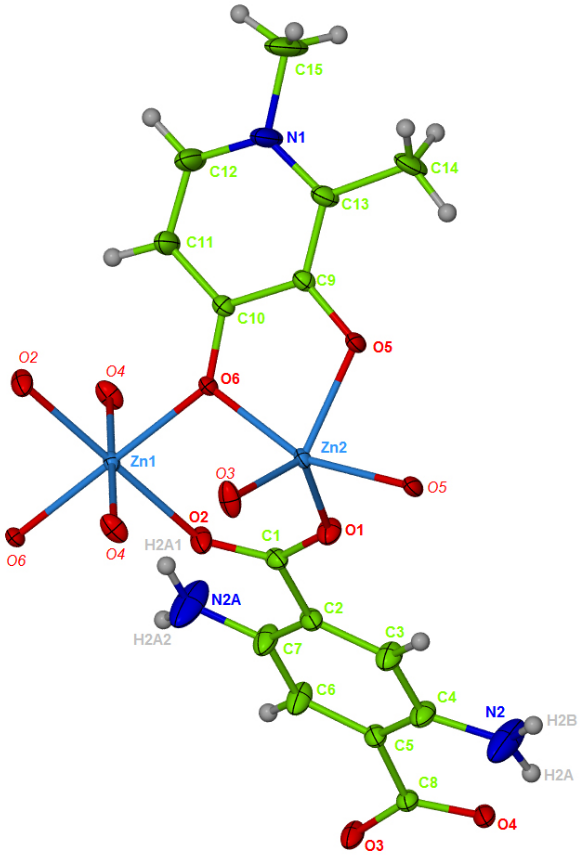

Figure S23. Asymmetric unit for $[Zn_3(bdc\text{-}NH_2)_2(dfp)_2]\cdot DMF$ **3**, showing also selected symmetry-related atoms (with italicised labels) *(d) Crystal structure of [Zn_3{bdc-(OH)}$_2$(dfp)$_2$(H_2O)$_2$]·2DMF* ***5***

Crystal data for **5** were collected at Diamond Light Source. The asymmetric unit comprises one and a half zinc centres, one bdc-$(OH)_2$ ligand, one deprotonated deferiprone molecule, one ligated water and two fragments of uncoordinated DMF molecules. The water hydrogen atoms were located and refined at a distance of 0.98 Å from O(9) and 1.5 Å from each other. In the DMF fragment based on N(3), both the nitrogen atoms and C(18) are located on a 2-fold rotation axis. This necessarily means that O(11) is disordered over two positions and hence has 50% site-occupancy. This disorder precluded inclusion of the hydrogen atom on C(18). The second guest solvent fragment (based on N(2)) also has atoms (N(2) and C(17)) located at a 2-fold rotation axis. Both of these atoms are common to each arrangement of the DMF molecule that straddles this symmetry element.

Details of the crystal data and structure refinement are given in Table S10 and bond length and bond angles are given in Table S11. All oxygen bound water hydrogen atoms are involved in hydrogen bonding, and details of the hydrogen bonds are given in Table S12. The asymmetric unit for **5** is shown in Figure S24.

Table S10. Crystal data and structure refinement for [Zn_3{bdc-(OH)}$_2$(dfp)$_2$(H_2O)$_2$]·2DMF **5**.

Empirical formula	$C_{36}H_{42}N_4O_{20}Zn_3$
Formula weight	1046.85
Temperature / K	150(2)
Wavelength / Å	0.6889
Crystal system	Hexagonal
Space group	$P6_522$
Unit cell dimensions	a = 11.2503(1) Å
	b = 11.2503(1) Å
	c = 59.7860(11) Å
	α = 90°
	β = 90°
	γ = 120°
Volume / Å^3	6553.27(15)
Z	6
Density (calculated) / g cm^{-3}	1.592
Absorption coefficient / mm^{-1}	1.717
F(000)	3216
Theta range for data collection	2.03 to 26.57°.
Index ranges	$-11 \le h \le 14$; $-14 \le k \le 12$; $-77 \le l \le 77$
Reflections collected	57062
Independent reflections	9997 [R(int) = 0.0838]
Reflections observed (>2σ)	7941
Data Completeness	0.997
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.727
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5022 / 3 / 310
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0345 $wR2$ = 0.0741
R indices (all data)	$R1$ = 0.0381 $wR2$ = 0.0758

Absolute structure parameter	0.055(13)
Largest diff. peak and hole / eÅ^{-3}	0.308 and –0.269

Table S11. Bond lengths [Å] and angles [°] for [Zn_3{bdc-(OH)}$_2$(dfp)$_2$(H_2O)$_2$]·2DMF **5**.

Zn(1)-O(1)	1.998(2)	Zn(1)-O(8)	2.008(2)
Zn(1)-O(3)#1	2.009(2)	Zn(1)-O(9)	2.054(2)
Zn(1)-O(7)	2.083(2)	Zn(2)-O(7)	2.0590(17)
Zn(2)-O(7)#2	2.0590(17)	Zn(2)-O(2)	2.069(2)
Zn(2)-O(2)#2	2.069(2)	Zn(2)-O(6)#1	2.075(2)
Zn(2)-O(6)#3	2.075(2)	O(1)-C(1)	1.260(3)
O(2)-C(1)	1.266(4)	O(3)-C(8)	1.258(3)
O(3)-Zn(1)#4	2.009(2)	O(4)-C(3)	1.362(4)
O(5)-C(6)	1.369(3)	O(6)-C(8)	1.267(4)
O(6)-Zn(2)#5	2.075(2)	O(7)-C(9)	1.313(3)
O(8)-C(10)	1.312(4)	O(10)-C(16)	1.215(6)
O(11)-C(18)	1.211(6)	N(1)-C(12)	1.344(4)
N(1)-C(11)	1.366(4)	N(1)-C(15)	1.477(4)
N(2)-C(16)#6	1.388(4)	N(2)-C(16)	1.388(4)
N(2)-C(17)	1.453(9)	N(3)-C(18)	1.346(9)
N(3)-C(19)#7	1.436(7)	N(3)-C(19)	1.436(7)
C(1)-C(2)	1.484(4)	C(2)-C(7)	1.391(4)
C(2)-C(3)	1.420(4)	C(3)-C(4)	1.375(4)
C(4)-C(5)	1.385(4)	C(5)-C(6)	1.412(4)
C(5)-C(8)	1.495(4)	C(6)-C(7)	1.377(4)
C(9)-C(13)	1.377(4)	C(9)-C(10)	1.443(4)
C(10)-C(11)	1.393(4)	C(11)-C(14)	1.512(4)
C(12)-C(13)	1.377(4)	C(18)-O(11)#7	1.211(6)
O(1)-Zn(1)-O(8)	112.98(9)	O(1)-Zn(1)-O(3)#1	119.22(9)
O(8)-Zn(1)-O(3)#1	127.69(10)	O(1)-Zn(1)-O(9)	88.26(9)
O(8)-Zn(1)-O(9)	94.14(9)	O(3)#1-Zn(1)-O(9)	90.63(10)
O(1)-Zn(1)-O(7)	97.03(8)	O(8)-Zn(1)-O(7)	80.34(8)
O(3)#1-Zn(1)-O(7)	90.08(9)	O(9)-Zn(1)-O(7)	173.51(8)
O(7)-Zn(2)-O(7)#2	176.09(12)	O(7)-Zn(2)-O(2)	94.42(8)
O(7)#2-Zn(2)-O(2)	88.44(8)	O(7)-Zn(2)-O(2)#2	88.44(8)
O(7)#2-Zn(2)-O(2)#2	94.42(8)	O(2)-Zn(2)-O(2)#2	85.69(14)
O(7)-Zn(2)-O(6)#1	87.15(8)	O(7)#2-Zn(2)-O(6)#1	90.06(8)
O(2)-Zn(2)-O(6)#1	92.95(10)	O(2)#2-Zn(2)-O(6)#1	175.27(8)
O(7)-Zn(2)-O(6)#3	90.06(8)	O(7)#2-Zn(2)-O(6)#3	87.14(8)
O(2)-Zn(2)-O(6)#3	175.27(8)	O(2)#2-Zn(2)-O(6)#3	92.95(10)
O(6)#1-Zn(2)-O(6)#3	88.75(14)	C(1)-O(1)-Zn(1)	130.5(2)
C(1)-O(2)-Zn(2)	135.66(19)	C(8)-O(3)-Zn(1)#4	126.4(2)
C(8)-O(6)-Zn(2)#5	136.3(2)	C(9)-O(7)-Zn(2)	133.85(19)
C(9)-O(7)-Zn(1)	112.11(17)	Zn(2)-O(7)-Zn(1)	112.04(9)
C(10)-O(8)-Zn(1)	113.27(16)	C(12)-N(1)-C(11)	121.4(3)
C(12)-N(1)-C(15)	118.0(3)	C(11)-N(1)-C(15)	120.6(3)
C(16)#6-N(2)-C(16)	121.6(5)	C(16)#6-N(2)-C(17)	119.2(3)
C(16)-N(2)-C(17)	119.2(3)	C(18)-N(3)-C(19)#7	121.8(4)
C(18)-N(3)-C(19)	121.8(4)	C(19)#7-N(3)-C(19)	116.4(9)
O(1)-C(1)-O(2)	125.1(3)	O(1)-C(1)-C(2)	118.0(3)

O(2)-C(1)-C(2)	116.9(3)	C(7)-C(2)-C(3)	118.5(3)
C(7)-C(2)-C(1)	119.4(3)	C(3)-C(2)-C(1)	122.0(3)
O(4)-C(3)-C(4)	118.1(3)	O(4)-C(3)-C(2)	122.7(3)
C(4)-C(3)-C(2)	119.2(3)	C(3)-C(4)-C(5)	122.0(3)
C(4)-C(5)-C(6)	119.0(3)	C(4)-C(5)-C(8)	119.4(3)
C(6)-C(5)-C(8)	121.6(3)	O(5)-C(6)-C(7)	117.7(3)
O(5)-C(6)-C(5)	123.0(3)	C(7)-C(6)-C(5)	119.2(3)
C(6)-C(7)-C(2)	122.0(3)	O(3)-C(8)-O(6)	125.1(3)
O(3)-C(8)-C(5)	118.3(3)	O(6)-C(8)-C(5)	116.5(3)
O(7)-C(9)-C(13)	124.8(3)	O(7)-C(9)-C(10)	115.8(3)
C(13)-C(9)-C(10)	119.3(3)	O(8)-C(10)-C(11)	123.7(3)
O(8)-C(10)-C(9)	118.4(3)	C(11)-C(10)-C(9)	117.9(3)
N(1)-C(11)-C(10)	120.3(3)	N(1)-C(11)-C(14)	118.3(3)
C(10)-C(11)-C(14)	121.4(3)	N(1)-C(12)-C(13)	121.2(3)
C(9)-C(13)-C(12)	119.8(3)	O(10)-C(16)-N(2)	124.0(5)
O(11)-C(18)-O(11)#7	116.0(9)	O(11)-C(18)-N(3)	122.0(4)
O(11)#7-C(18)-N(3)	122.0(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,y+1,-z+1/2 #2 -x+y,y,-z+1/2
#3 x,y+1,z #4 -x+y,y-1,-z+1/2 #5 x,y-1,z
#6 -x+y+1,y,-z+1/2 #7 y,x,-z+2/3

Table S12. Hydrogen bonding present in the crystal structure of [Zn_3{bdc-(OH)}$_2$(dfp)$_2$(H_2O)$_2$]·2DMF **5**.

D–H···A	**D···A / Å**	**H···A / Å**	**D–H···A / °**	**Symmetry relating D and A**
O(4)–H(4)···O(2)	2.584(3)	1.85	145	–
O(5)–H(5)···O(6)	2.574(3)	1.90	136	–
O(9)–H(9A)···O(11)	2.724(8)	1.79	160	$-x + y, y, -z + {}^{1}/_{2}$
O(9)–H(9B)···O(8)	2.659(4)	1.69	174	$-x, -x + y, -z + {}^{1}/_{3}$

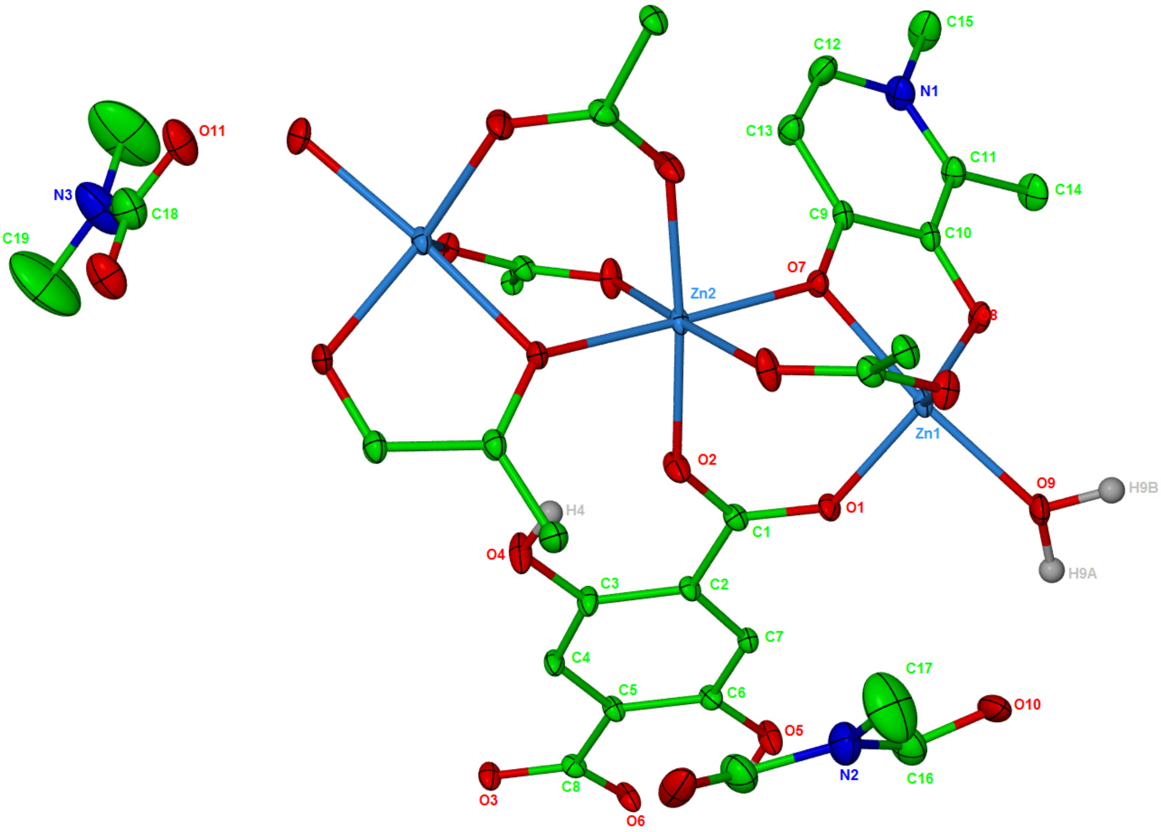

Figure S24. Asymmetric unit for [Zn_3{bdc-(OH)}$_2$(dfp)$_2$(H_2O)$_2$]·2DMF **5**, showing also selected symmetry-related atoms

6. References

S1. G. M. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112.

S2. A. L. Spek, *Acta Cryst. Sect. D*, 2009, **65**, 148.