Electronic Supplementary Information (ESI)

New Journal of Chemistry

Bis(picolinato) complexes of vanadium and zinc as potential antidiabetic agents: synthesis, structural elucidation and *in vitro* insulin-mimetic activity study

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Supplementary material

Crystallographic data: **Figs. S1–S9 and Tables S1–S10**

Table S1: Selected crystallographic data for $NH_4[VO_2(picFF)_2]\cdot 1.6H_2O$ (**3**·1.6H_2O) and $NH_4[VO_2(Hhypic)_2]\cdot H_2O$ (**4**·H_2O), $[Zn(picFF)_2(H_2O)_2]$ (**5**), $[Zn(picFF)_2(py)_2]\cdot py$ (**6**·py), $[Zn(picFF)_2(DMAP)_2]\cdot \frac{2}{3}H_2O$ (**7**·⅔H_2O), $[Zn(picFF)_2(phen)]\cdot CHCl_3$ (**8**·$CHCl_3$), $[Zn(Hhypic)_2(MeOH)_2]$ (**10**), $[Zn(Hhypic)_2(DMAP)(H_2O)]$ (**11**) and $[Zn(Hhypic)_2(phen)]$ (**12**).

	3·1.6H_2O	**4**·H_2O	**5**	**6**·py	**7**·⅔H_2O	**8**·$CHCl_3$
Formula	$C_{12}H_{11.2}F_4N_3O_{7.6}V$	$C_{12}H_{14}N_3O_9V$	$C_{12}H_8F_4N_2O_6Zn$	$C_{27}H_{19}F_4N_5O_4Zn$	$C_{78}H_{76}F_{12}N_{18}O_{14}Zn_3$	$C_{26}H_{14}Cl_6F_4N_4O_4Zn$
M_r	445.98	395.20	417.57	618.84	1913.67	800.48
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P4_2/n$	$C2/c$	$P\bar{1}$	$P2_1/c$	$Pbca$	$C2/c$
a (Å)	21.5080(5)	8.0697(3)	6.5421(3)	18.0287(4)	26.2936(3)	12.9576(8)
b (Å)	21.5080(5)	13.0146(5)	6.9212(3)	10.3166(2)	24.3520(3)	28.0951(7)
c (Å)	7.9027(3)	15.4733(6)	8.7493(4)	14.9805(3)	26.5498(3)	10.7178(5)
α (°)	90.00	90.00	97.521(3)	90.00	90.00	90.00
β (°)	90.00	104.392(2)	101.906(2)	106.0220(10)	90.00	126.182(8)
γ (°)	90.00	90.00	114.749(3)	90.00	90.00	90.00
Volume (Å^3)	3655.7(2)	1574.07(10)	341.35(3)	2678.06(10)	16999.9(3)	3149.3(3)
Z	8	4	1	4	8	4
D_c (g/cm^3)	1.621	1.668	2.031	1.535	1.492	1.688
μ (mm^{-1})	0.620	0.686	1.888	0.988	0.939	1.353
Reflections collected	24513	3471	2783	11360	25088	14737
Reflections unique (R_{int})	4192 (0.0968)	1781 (0.0178)	1551 (0.0154)	6124 (0.0218)	13040 (0.0314)	3602 (0.0319)
Parameters	286	126	121	370	1138	232
R, wR_2 [I>2σ(I)][a]	0.0938, 0.2439	0,0714, 0,1905	0.0268, 0.0698	0.0420, 0.1038	0.0486, 0.1178	0.0521, 0.1220
R, wR_2 (all data)[a]	0.1361, 0.2729	0,0766, 0,1929	0.0277, 0.0704	0.0685, 0.1180	0.0955, 0.1409	0.0699, 0.1335
GOF, S[b]	1.024	1.170	1.133	1.020	1.006	1.053

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S1: continuation.

	10	**11**	**12**
Formula	$C_{14}H_{16}N_2O_8Zn$	$C_{19}H_{20}N_4O_7Zn$	$C_{24}H_{16}N_4O_6Zn$
M_r	405.66	481.76	521.78
T (K)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2/*c*	*Pnna*	$P2_1/c$
a (Å)	19.6242(9)	7.9159(4)	14.0406(2)
b (Å)	6.4863(2)	18.3331(10)	10.5121(2)
c (Å)	15.5404(6)	13.4273(7)	13.9610(2)
α (°)	90.00	90,00	90.00
β (°)	126.316(6)	90,00	92.8360(10)
γ (°)	90.00	90,00	90.00
Volume (Å^3)	1593.89(15)	1948.61(18)	2058.07(6)
Z	4	4	4
D_c (g/cm^3)	1.690	1.642	1.684
μ (mm^{-1})	2.594	1.313	2.133
Reflections collected	3853	7918	17368
Reflections unique (R_{int})	1613 (0.0125)	2238 (0. 0278)	4199 (0.0272)
Parameters	121	149	318
R, wR_2 [I>2σ(I)][a]	0.0274, 0.0757	0.0278, 0.0735	0.0265, 0.0683
R, wR_2 (all data)[a]	0.0283, 0.0763	0.0353, 0.0790	0.0300, 0.0709
GOF, S[b]	1.073	1.045	1.033

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

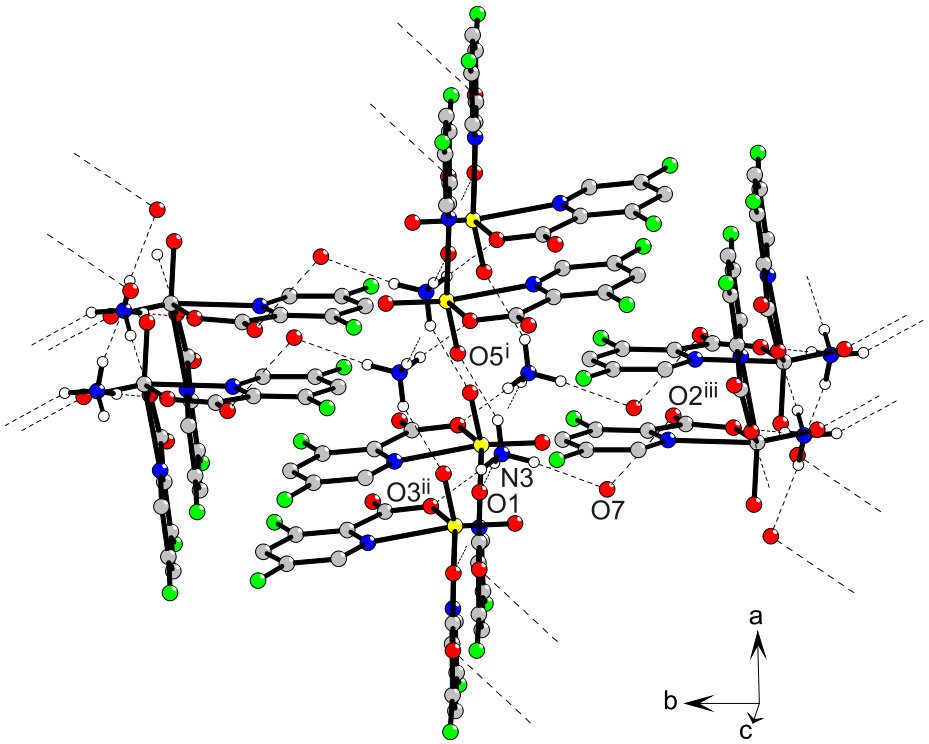

Figure S1: Hydrogen-bonding network in **3**·1.6H_2O. Dashed lines indicate N–H···O and O–H···O bonds. Symmetry codes: (i) −*x* + 1, −*y* + 1, −z + 1; (ii) *x*, *y*, *z* − 1; (iii) *y*, –*x* + ½, –*z* + 1½.

Table S2: Hydrogen bonds and other weak intermolecular interactions in **3**·1.6H_2O.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*D*H*A*)	Symmetry transformation of the acceptor
N3–H3*A*···O7	0.882(19)	2.05(3)	2.892(12)	160(5)	*x*, *y*, *z*
N3–H3*B*···O5	0.89(2)	2.05(3)	2.892(7)	158(5)	−*x* + 1, −*y* + 1, −z + 1
N3–H3*C*···O3	0.881(19)	1.95(2)	2.831(6)	174(5)	*x*, *y*, *z* − 1
N3–H3*D*···O1	0.880(19)	1.97(2)	2.848(6)	174(5)	*x*, *y*, *z*
C4–H4···O5	0.93	2.39	3.274(7)	158.0	–*y* + ½, *x*, –*z* + ½
C6–H6···O2	0.93	2.50	3.340(8)	149.5	*x*, *y*, *z* − 1
C10–H10···O4	0.93	2.53	3.353(8)	147.0	–*y* + 1, *x* + ½, *z* + ½
C12–H12···O4	0.93	2.48	3.321(7)	151.2	*x*, *y*, *z* + 1

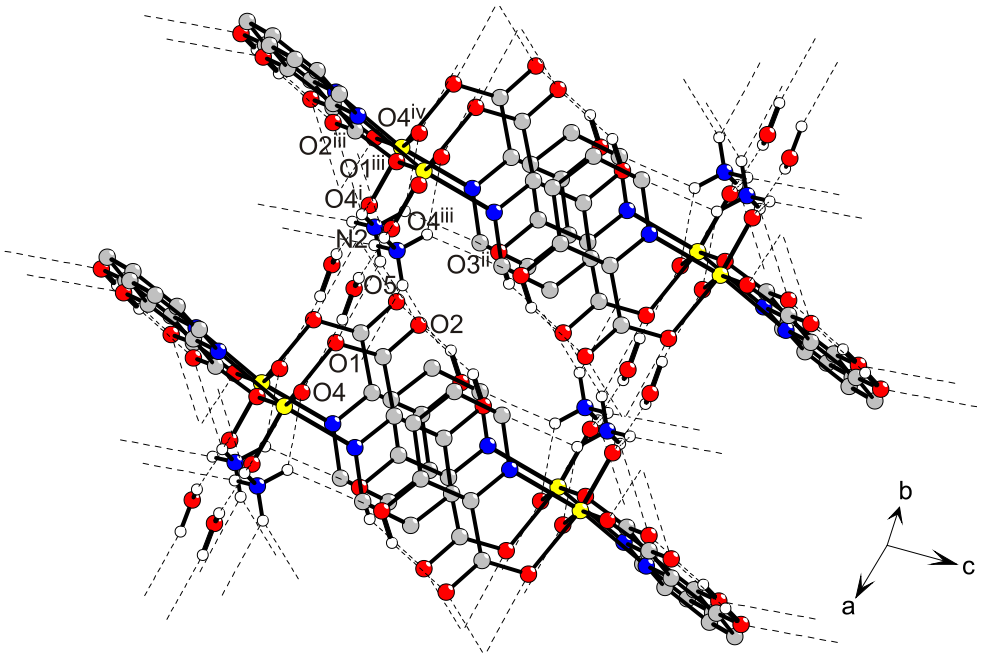

Figure S2: Hydrogen-bonding network in **4**·H_2O. Dashed lines indicate N–H···O and O–H···O bonds. Symmetry codes: (i) $-x + ½, y + ½, -z + ½$; (ii) $-x + ½, -y + ½, -z + 1$; (iii) $–x, y, –z + ½$; (iv) $x – ½, y + ½, z$.

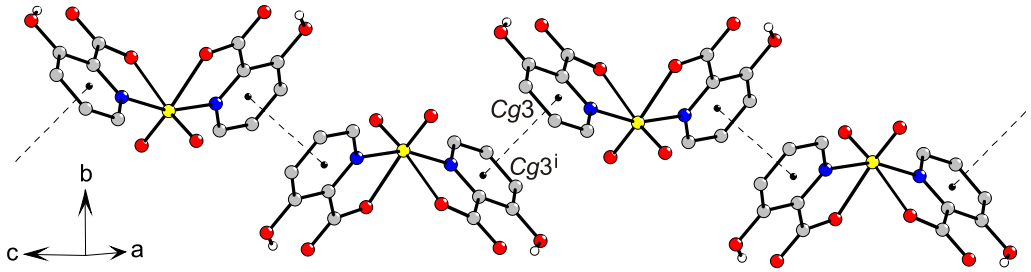

Figure S3: A chain of $[VO_2(Hhypic)_2]^-$ anions in crystal structure of **4**·H_2O connected by π···π interactions. Dashed lines indicate centroid-to-centroid distances. Symmetry code: (i) $-x + 1, –y, –z + 1$.

Table S3: Hydrogen bonds and other weak intermolecular interactions in **4**·H_2O.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
O3–H3···O2	0.82	1.87	2.593(6)	147.1	*x*, *y*, *z*
O5–H5A···O4	0.83(2)	2.160(16)	2.942(4)	158(4)	*x*, *y*, *z*
N2–H2A···O1	0.870(16)	2.40(3)	3.067(4)	134(4)	*x*, *y*, *z*
N2–H2A···O2	0.870(16)	2.415(14)	3.029(4)	128.0(14)	*x*, *y*, *z*
N2–H2B···O3	0.861(16)	2.57(3)	3.124(4)	123(3)	$x - ½, -y + ½, z - ½$
N2–H2B···O4	0.861(16)	2.34(2)	2.963(7)	129(2)	$-x + ½, y + ½, -z + ½$
C4–H4···O4	0.93	2.53	3.094(6)	119.8	$–x + 1, –y, –z + 1$
C6–H6···O2	0.93	2.45	3.285(7)	150.1	$x + ½, y – ½, z$

Table S4: Geometrical parameters (Å, °) for π···π stacking interactions in **4**·H_2O.

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Ring Slippage	Symmetry transformation of the acceptor
*Cg*3···*Cg*3	3.736(3)	0	2.46	–3.732(2)	0.160	$-x + 1, –y, -z + 1$

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring C*g*J. *Cg*3 is N1/C2–C6 ring centroid.

Table S5: Hydrogen bonds and other weak intermolecular interactions in **5**.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
O3–H3A···O2	0.816(10)	2.052(12)	2.8486(18)	165(3)	$-x + 1, -y + 2, -z + 1$
O3–H3A···F1	0.816(10)	2.44(2)	2.9389(19)	120(2)	$-x + 1, -y + 2, -z + 1$
O3–H3B···O2	0.818(10)	1.963(12)	2.7674(19)	168(3)	$x - 1, y, z$
C4–H4···F1	0.93	2.53	3.297(3)	140	$-x + 1, -y + 2, -z$
C6–H6···F2	0.93	2.41	3.237(3)	148	$-x – 1, -y + 1, -z$

Table S6: Geometrical parameters (Å, °) for π···π stacking interactions in **5**.

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Ring Slippage	Symmetry transformation of the acceptor
*Cg*3···*Cg*3	3.6302(10)	0	23.20	-3.3366(7)	1.430	$–x, –y + 1, –z$

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring C*g*J. *Cg*3 is N1/C2–C6 ring centroid.

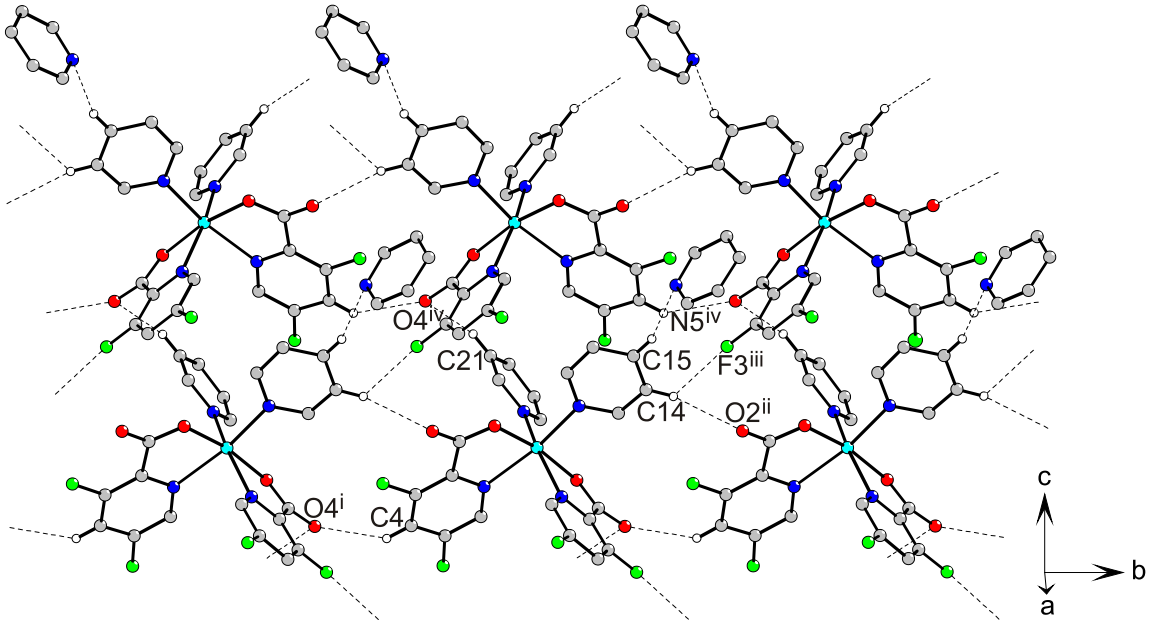

Figure S4: Formation of hydrogen-bonded layer in **6**·py. Dashed lines indicate C–H···O/N/F interactions. Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x*, *y* + 1, *z*; (iii) *x*, –*y* + 2½, *z* + ½; (iv) *x*, –*y* + 1½, *z* + ½.

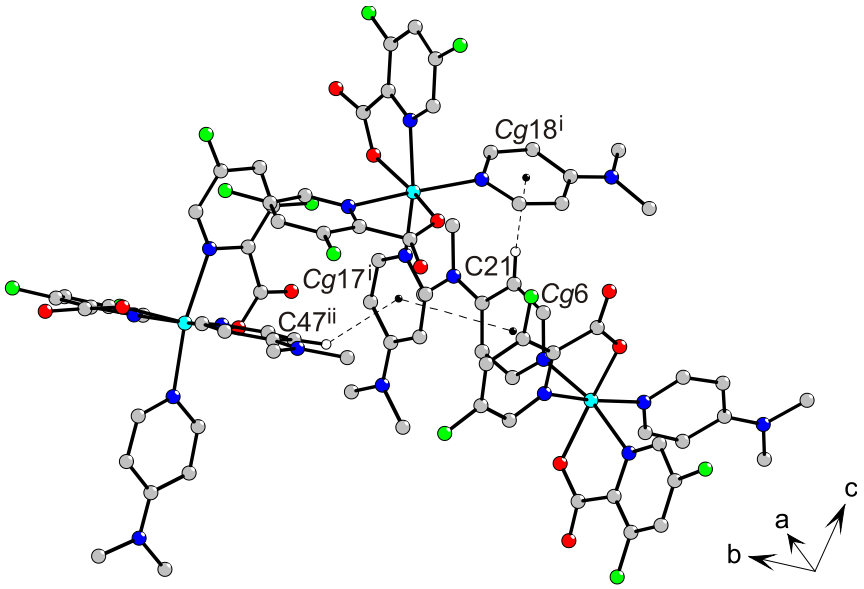

Figure S5: Interactions between three adjacent molecules in **7**·⅔H_2O. Dashed lines indicate weak C–H··· π and π ··· π interactions. Symmetry codes: (i) *x*, –*y* + 1½, *z* + ½; (ii) –*x* + ½, *y* + ½, *z*.

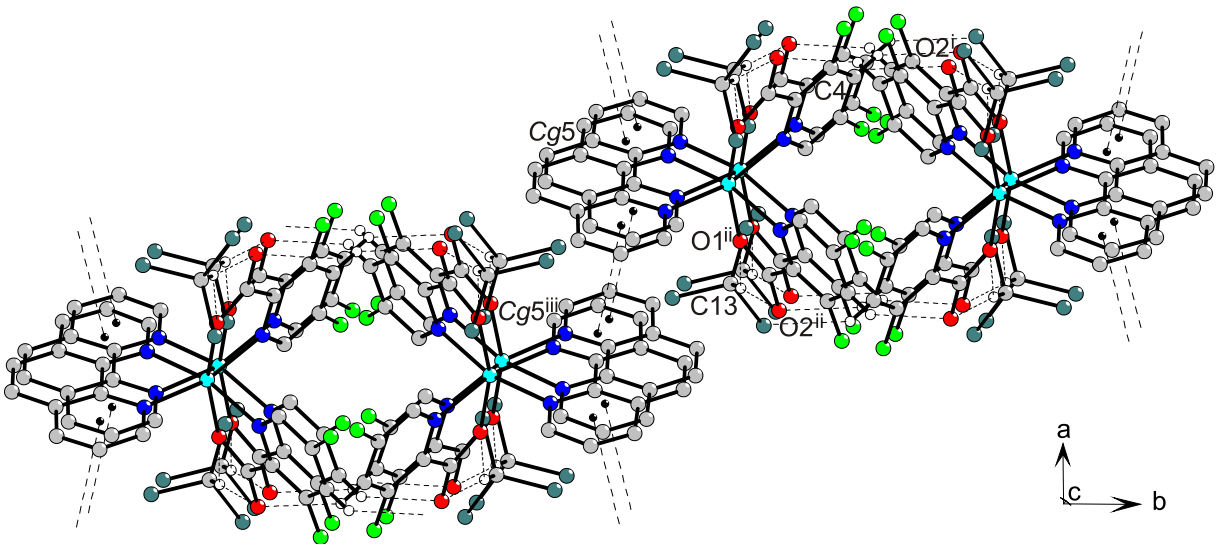

Figure S6: Crystal packing in **8**·2CHCl$_3$. Dashed lines indicate of C–H···O and π ··· π interactions Symmetry codes: (i) *x*, –*y* + 2, *z* + ½; (ii) −*x* + 2, *y*, −*z* + ½; (iii) −*x* + 1½, –*y* + 1½, –*z*.

Table S7: Hydrogen bonds and other weak intermolecular interactions in [Zn(picFF)$_2$(py)$_2$]·py (**6**·py), [Zn(picFF)$_2$(DMAP)$_2$]·⅔H$_2$O (**7**·⅔H$_2$O), [Zn(picFF)$_2$(phen)]·2CHCl$_3$ (**8**·2CHCl$_3$).

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
6·py					
C4–H4···O4	0.93	2.43	3.212(3)	142.3	*x*, *y* − 1, *z*
C14–H14···O2	0.93	2.59	3.500(4)	165.2	*x*, *y* + 1, *z*
C14–H14···F3	0.93	2.53	3.128(4)	121.9	*x*, –*y* + 2½, *z* + ½
C15–H15···N5	0.93	2.57	3.446(7)	157	*x*, –*y* + 1½, *z* + ½
C21–H21···O4	0.93	2.50	3.291(3)	142.8	*x*, –*y* + 1½, *z* + ½
7·⅔H$_2$O					
C10–H10···O8	0.93	2.44	3.269(6)	148.1	*x* – ½, –*y* + 1½, –*z* + 1
C14–H14···O12	0.93	2.45	3.312(6)	154.7	–*x*, –*y* + 1, –*z* + 1
C18–H18B···O13	0.96	2.60	3.529(8)	163.9	*x*, *y*, *z*
C23–H23···O8	0.93	2.49	3.391(5)	162.1	*x*, *y*, *z*
C26–H26A···F3	0.96	2.49	3.053(6)	117.0	*x* + ½, –*y* + 1½, –*z* + 1
C56–H56···O6	0.93	2.41	3.218(7)	145.1	*x*, *y*, *z*
C62–H62···O13	0.93	2.53	3.374(9)	151.9	*x*, –*y* + ½, *z* – ½
C73–H73···O2	0.93	2.52	3.344(5)	147.9	*x*, –*y* + 1½, *z* – ½
C21–H21···*Cg*18	0.93	2.90	3.701(5)	146	*x*, –*y* + 1½, *z* + ½
C47–H47···*Cg*17	0.93	2.98	3.667(5)	132	–*x* + ½, –*y* + 1, *z* + ½
8·2CHCl$_3$					
C4–H4···O2	0.93	2.56	3.351(5)	143.5	*x*, –*y* + 2, *z* + ½
C13–H13···O1	0.98	2.57	3.388(5)	141.1	−*x* + 2, *y*, −*z* + ½
C13–H13···O2	0.98	2.27	3.217(5)	162.8	−*x* + 2, *y*, −*z* + ½

*Cg*17 and *Cg*18 are N15/C65–C69 and N17/C72–C76 ring centroids, respectively.

Table S8: Geometrical parameters (Å, °) for π···π stacking interactions in $[Zn(picFF)_2(py)_2]\cdot py$ (**6**·py), $[Zn(picFF)_2(DMAP)_2]\cdot ⅔H_2O$ (**7**·⅔H_2O), $[Zn(picFF)_2(phen)]\cdot 2CHCl_3$ (**8**·2$CHCl_3$).

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Ring Slippage	Symmetry transformation of the acceptor
6·py						
*Cg*3···*Cg*5	4.0362(17)	11.82(15)	18.85	–3.6540(12)		*x*, 1½ – *y*, –½ + *z*
*Cg*4···*Cg*7	4.170(3)	12.1(3)	31.47	–3.8915(11)		*x*, 1 + *y*, *z*
7·⅔H_2O						
*Cg*6···*Cg*17	3.917(2)	11.9(2)	23.84	3.5765(18)		*x*, –*y* + 1½, *z* + ½
8·2$CHCl_3$						
*Cg*5···*Cg*5	3.706(3)	0	10.45	–3,645(2)	1.430	−*x* + 1½, –*y* + 1½, –*z*

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring J. In **6**·py *Cg*3, *Cg*4, *Cg*5 and *Cg*7 are N1/C2–C6, N2/C8–C12, N3/C13–C17 and N7/C23–C27 ring centroids, respectively. In **7**·⅔H_2O *Cg*6 and *Cg*17 are N5/C20–C24 and N15/C65–C69 ring centroids, respectively. In **8**·2$CHCl_3$ *Cg*5 is N2/C7–C11 ring centroid.

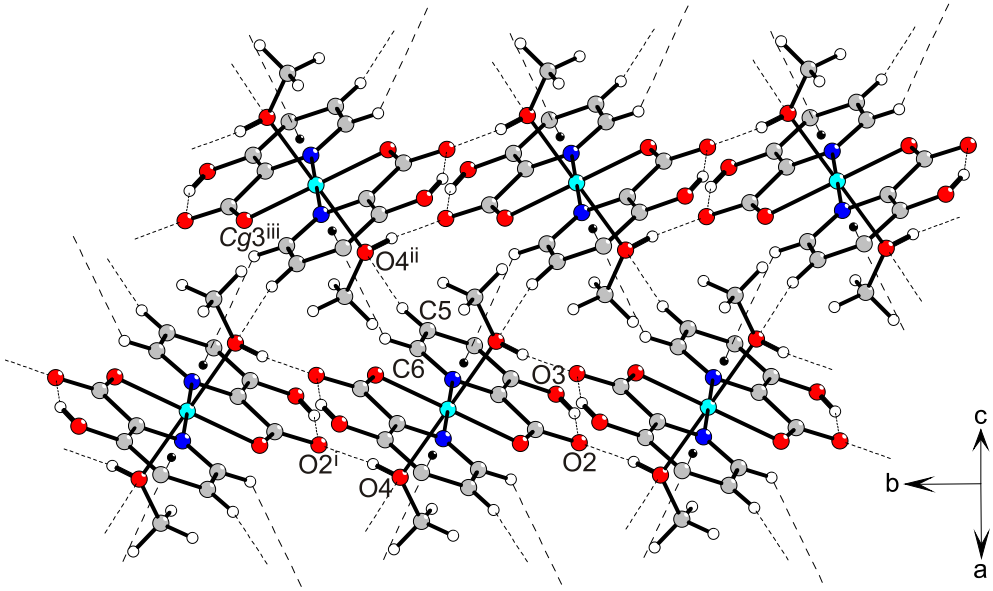

Figure S7: Hydrogen-bonding network in **10**. Dashed lines indicate O–H···O, C–H···O and C–H···π interactions. Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, −*y* + 2, *z* + ½; (iii) −*x* + ½, *y* + ½, −*z* + ½.

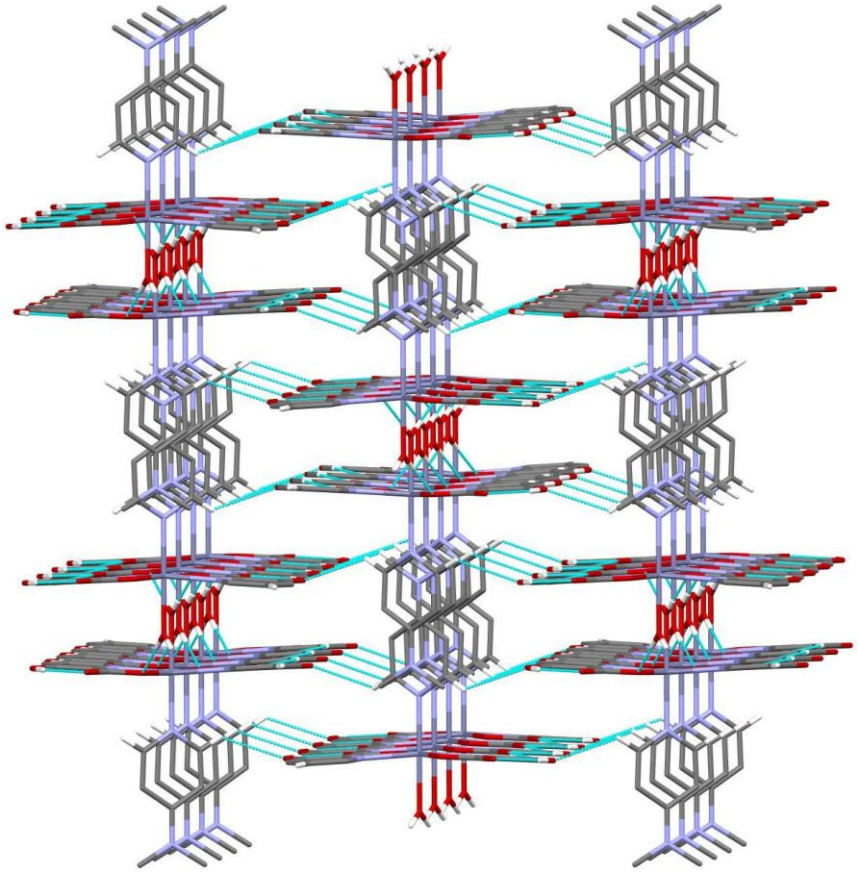

Figure S8: Hydrogen-bonding network in **11**. Dashed lines indicate O–H···O and C–H···O interactions.

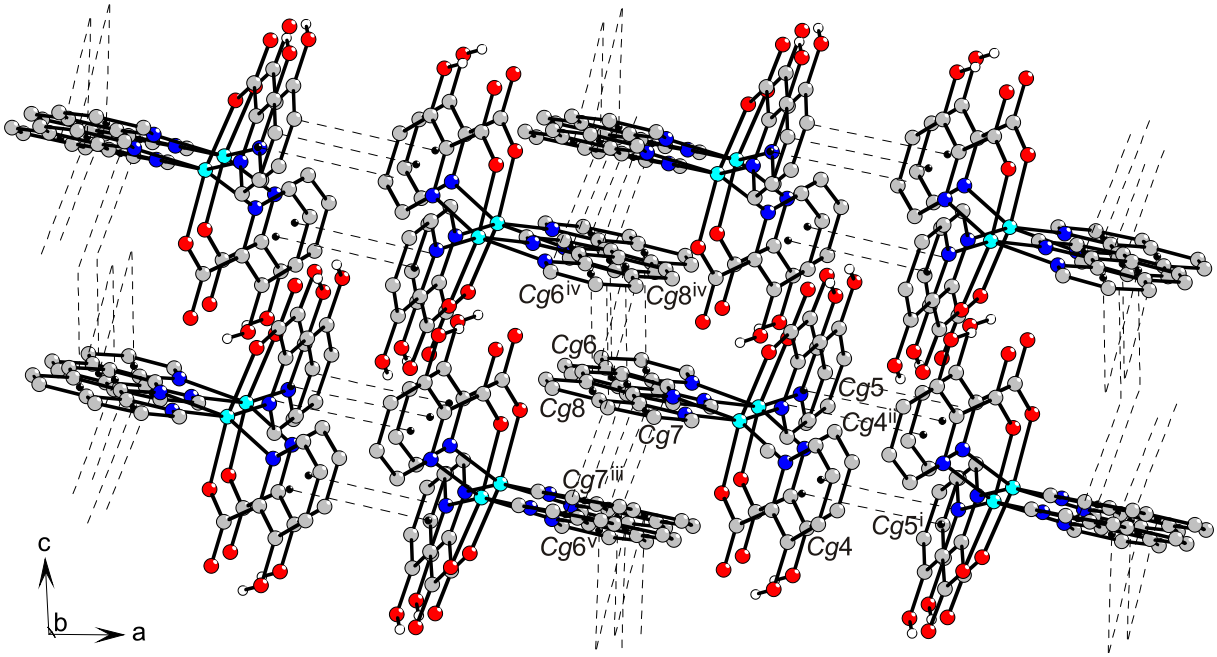

Figure S9: Crystal packing in **12** facilitated by π···π interactions. Dashed lines indicate C–H···O and π ··· π interactions. Symmetry codes: (i) –*x* + 2, *y* – ½, –*z* + ½; (ii) –*x* + 2, *y* + ½, –*z* + ½; (iii) –*x* + 1, *y* + ½, –*z* + ½; (iv) –*x* + 1, –*y*, –*z* + 1; (v) –*x* + 1, *y* – ½, –*z* + ½.

Table S9: Hydrogen bonds and other weak intermolecular interactions in $[Zn(Hhypic)_2(MeOH)_2]$ (**10**), $[Zn(Hhypic)_2(DMAP)(H_2O)]$ (**11**) and $[Zn(Hhypic)_2(phen)]$ (**12**).

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*D*H*A*)	Symmetry transformation of the acceptor
10					
O3–H3···O2	0.84	1.84	2.5772(18)	146.1	*x*, *y*, *z*
O4–H4A···O2	0.849(16)	1.828(16)	2.6658(16)	169(2)	*x*, *y* + 1, *z*
C5–H5···O4	0.95	2.44	3.3390(19)	158.0	*x*, −*y* + 2, *z* + ½
C6–H6···*Cg*3	0.95	3.00	3.653(2)	127	−*x* + ½, *y* + ½, −*z* + ½
11					
O3–H3···O2	0.84	1.80	2.5476(17)	146.7	*x*, *y*, *z*
O4–H4A···O1	0.825(9)	1.907(10)	2.7312(15)	176(2)	*x* + ½, *y*, –*z*
C5–H5···O2	0.95	2.57	3.224(2)	125.8	*x* + 1, *y*, *z*
C7–H7···O3	0.95	2.56	3.245(2)	128.9	*x*, –*y* + 1½, –*z* + ½
C10–H10···*Cg*4	0.95	2.97	3.827(2)	147	1 − *x*, 1 – *y*, 1 − *z*
12					
O3–H3···O2	0.84	1.79	2.5438(19)	147.6	*x*, *y*, *z*
O6–H6···O5	0.84	1.80	2.5438(19)	147.5	*x*, *y*, *z*
C10–H10···O6	0.95	2.48	3.331(2)	148.5	–*x* + 2, –*y* + 1, –*z* + 1
C12–H12···O5	0.95	2.54	3.147(2)	122.1	*x*, –*y* + ½, *z* – ½
C20–H20···O1	0.95	2.33	3.176(2)	148	–*x* + 1, *y* – ½, –*z* + ½
C23–H23···O4	0.95	2.57	3.332(2)	138	–*x* + 1, –*y*, –*z* + 1
C13–H13···*Cg*5	0.95	2.95	3.7459(19)	142	*x*, *y*, *z*
C22–H22···*Cg*4	0.95	2.91	3.6509(18)	135	*x*, *y*, *z*

For **10** and **12**: *Cg*3 and *Cg*4 are N1/C2–C6 ring centroids and *Cg*5 is N2/C8–C12 ring centroid. For **11**: *Cg*4 is N2/C7–C9/C8^{i}/C7^{i} ring centroid.

Table S10: Geometrical parameters (Å, °) for π···π stacking interactions in **12**.

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Ring Slippage	Symmetry transformation of the acceptor
*Cg*4···*Cg*5	3.8969(9)	18.62(8)	36.48	3.7054(6)		–*x* + 2, *y* – ½, –*z* + ½
*Cg*6···*Cg*7	3.6668(9)	11.54(7)	14.67	–3.3233(6)		–*x* + 1, *y* + ½, –*z* + ½
*Cg*6···*Cg*8	3.6168(9)	1.78(7)	19.91	3.3631(6)		–*x* + 1, –*y*, –*z* + 1
*Cg*8···*Cg*8	3.5779(9)	0	18.19	3.3990(6)	1.117	–*x* + 1, –*y*, –*z* + 1

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring C*g*J. *Cg*4, *Cg*5, *Cg*6, *Cg*7 and *Cg*8 are N1/C2–C6, N2/C8–C12, N3/C13–C17, N4/C18–C22 in C16–C19/C24/C23 ring centroids, respectively.