Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information (ESI)

Methylene spacer regulated variation in supramolecular assembly of zinc(II) dicyanamide complexes with reduced Schiff base ligands: Synthesis, structure and DFT study

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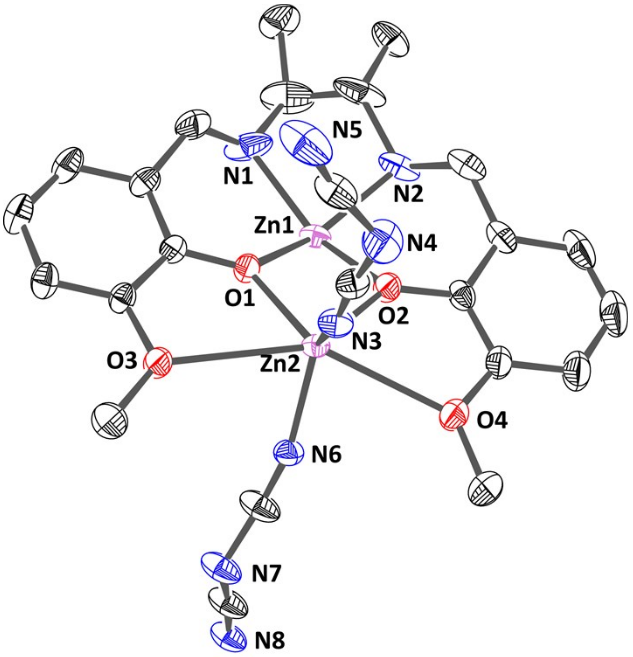

Fig. S1 ORTEP plot (with 40% ellipsoid probability) of the asymmetric unit of complex **1** with selective atom numbering scheme. Hydrogen atoms have been removed for clarity.

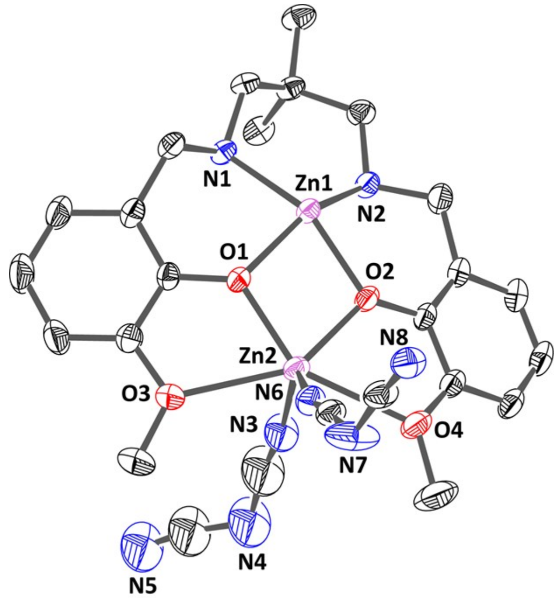

Fig. S2 ORTEP plot (with 40% ellipsoid probability) of the asymmetric unit of complex **2** with selective atom numbering scheme. Hydrogen atoms have been removed for clarity.

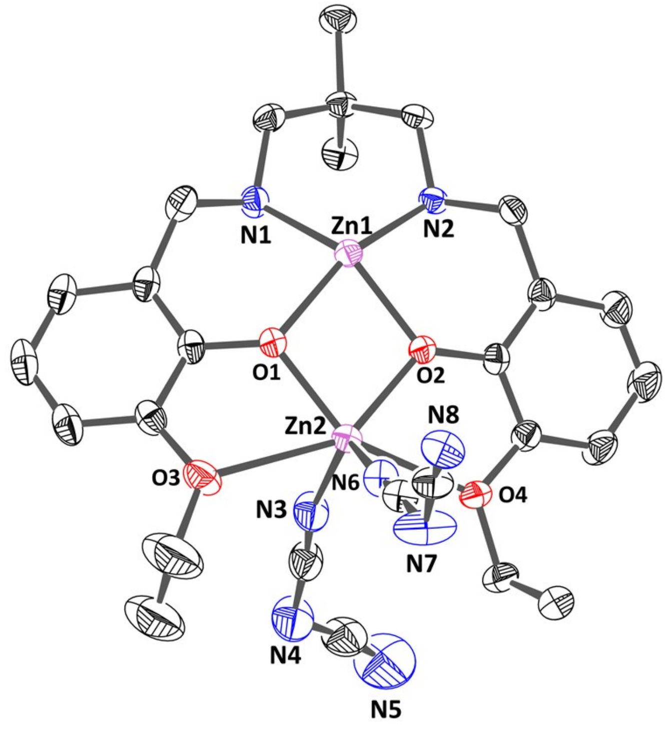

Fig. S3 ORTEP plot (with 40% ellipsoid probability) of the asymmetric unit of complex **3** with selective atom numbering scheme. Hydrogen atoms have been removed for clarity.

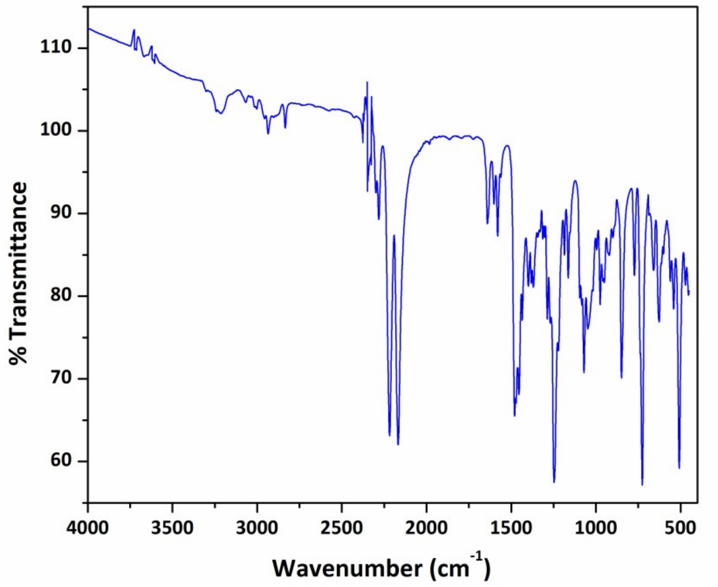

Fig. S4 IR spectrum of complex **1**.

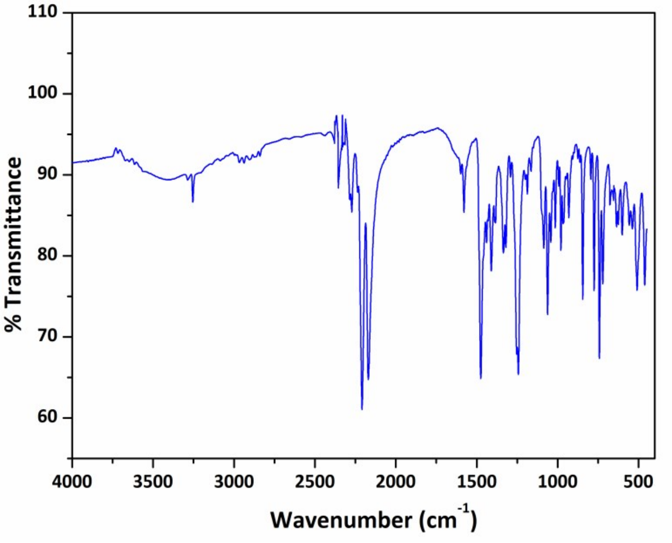

Fig. S5 IR spectrum of complex **2**.

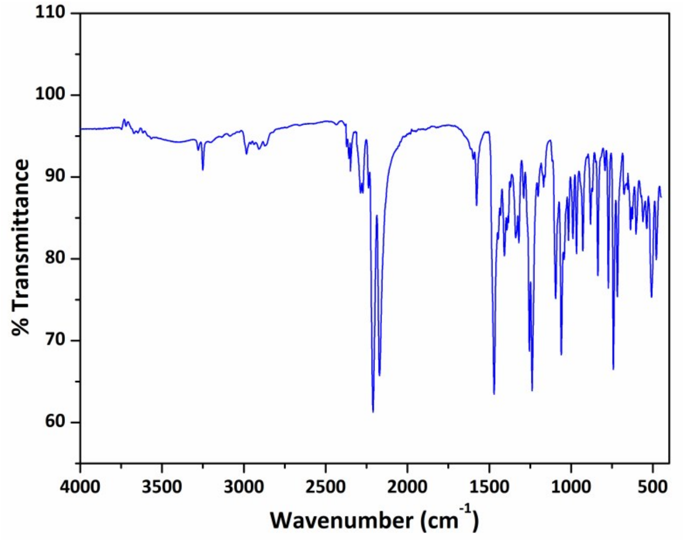

Fig. S6 IR spectrum of complex **3**.

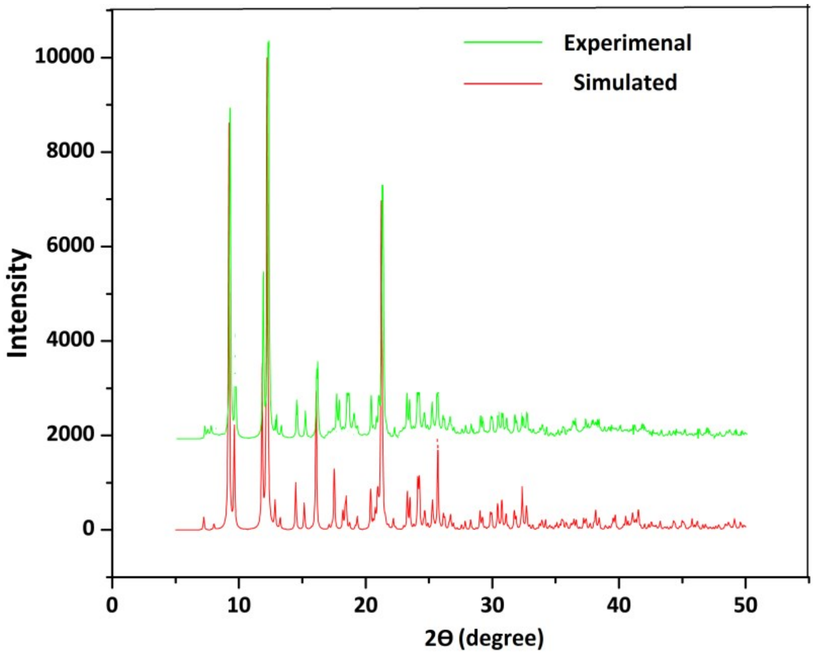

Fig. S7 Simulated and experimental PXRD patterns of complex **1**.

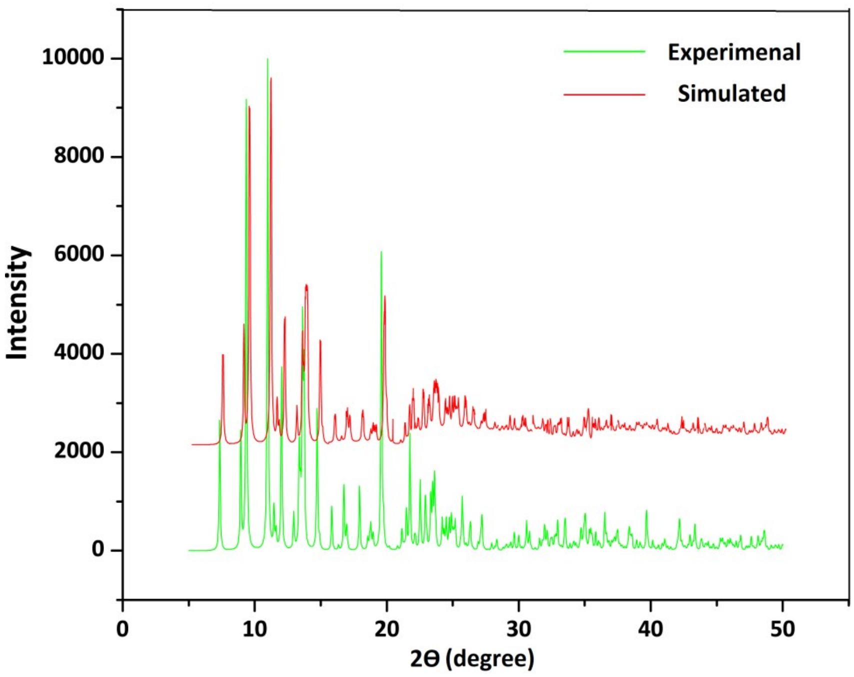

Fig. S8 Simulated and experimental PXRD patterns of complex **2**.

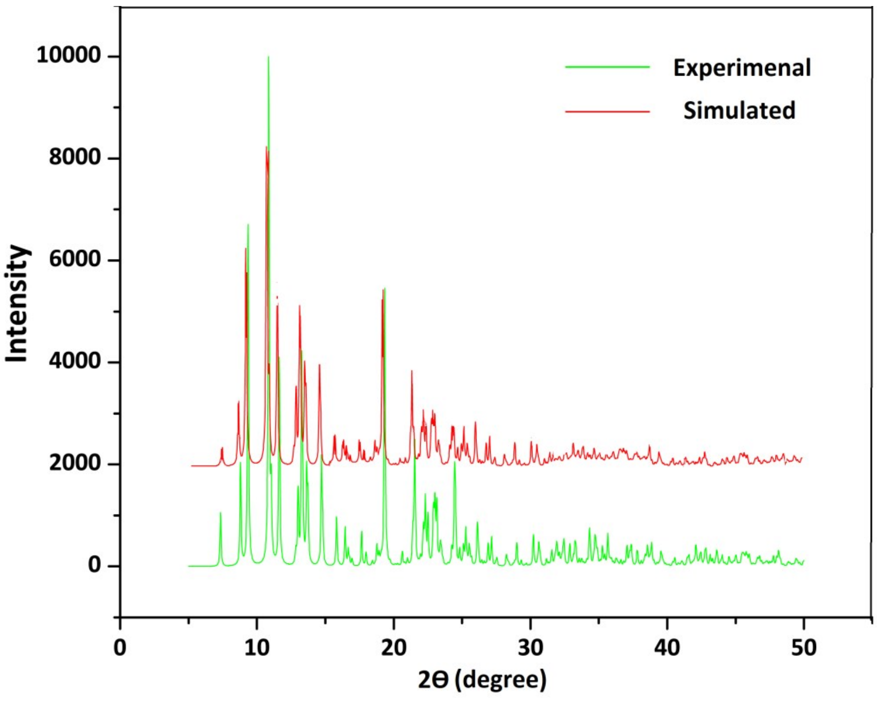

Fig. S9 Simulated and experimental PXRD patterns of complex **3**.

Hirshfeld surfaces analysis

The effort to describe the space occupied by a molecule in a crystal for the purpose of subdividing the crystal electron density into molecular fragments originated the idea of the Hirshfeld surface.[1] The Hirshfeld surface the associated 2D-fingerprint[2] plots of the complexes **1-3** was determined using Crystal Explorer software[3] from the respective CIF files. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld isosurface, two distances d_e, the distance from the point to the nearest nucleus external to the surface and d_i, the distance to the nearest nucleus internal to the surface, were defined. The normalized contact distance (d_{norm}) based on de and d_i was given by-

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vdw}} + \frac{(d_e - r_e^{vdw})}{r_e^{vdw}} \qquad \text{Eq. (S1)}$$

where r_i^{vdw} and r_e^{vdw} were the van der Waals radii of the atoms. The value of d_{norm} was negative or positive depending on intermolecular contacts, being shorter or longer than the van der Waals separations. The parameter d_{norm} displayed a surface with a red-white-blue colour scheme, where bright red spots highlighted shorter contacts, white areas represented contacts around the van der Waals separation, and blue regions were devoid of close contacts.

Hirshfeld surfaces of the complex mapped over d_{norm}, shape index and curveness (range of -0.1 to 1.5 Å) are illustrated in Fig. **S10.** Red spots on these surfaces denote the dominant interactions [N···H/H···N, C···H/H···C and O···H/H···O]. The 2D fingerprint plots revealed that the main intermolecular interactions in the complexes are H···H, O···H/H···O, N···H/H···N or C···H/H···C shown in Fig. **S11.**

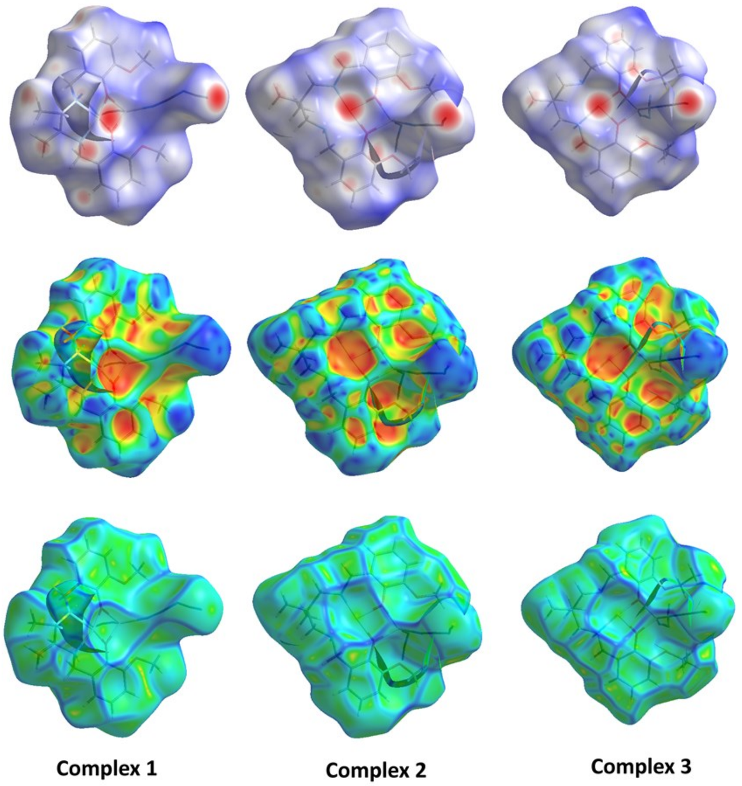

Fig. S10 Hirshfeld surfaces mapped with d_{norm} (up), shape index (middle) and curvedness (down) for complexes **1-3**.

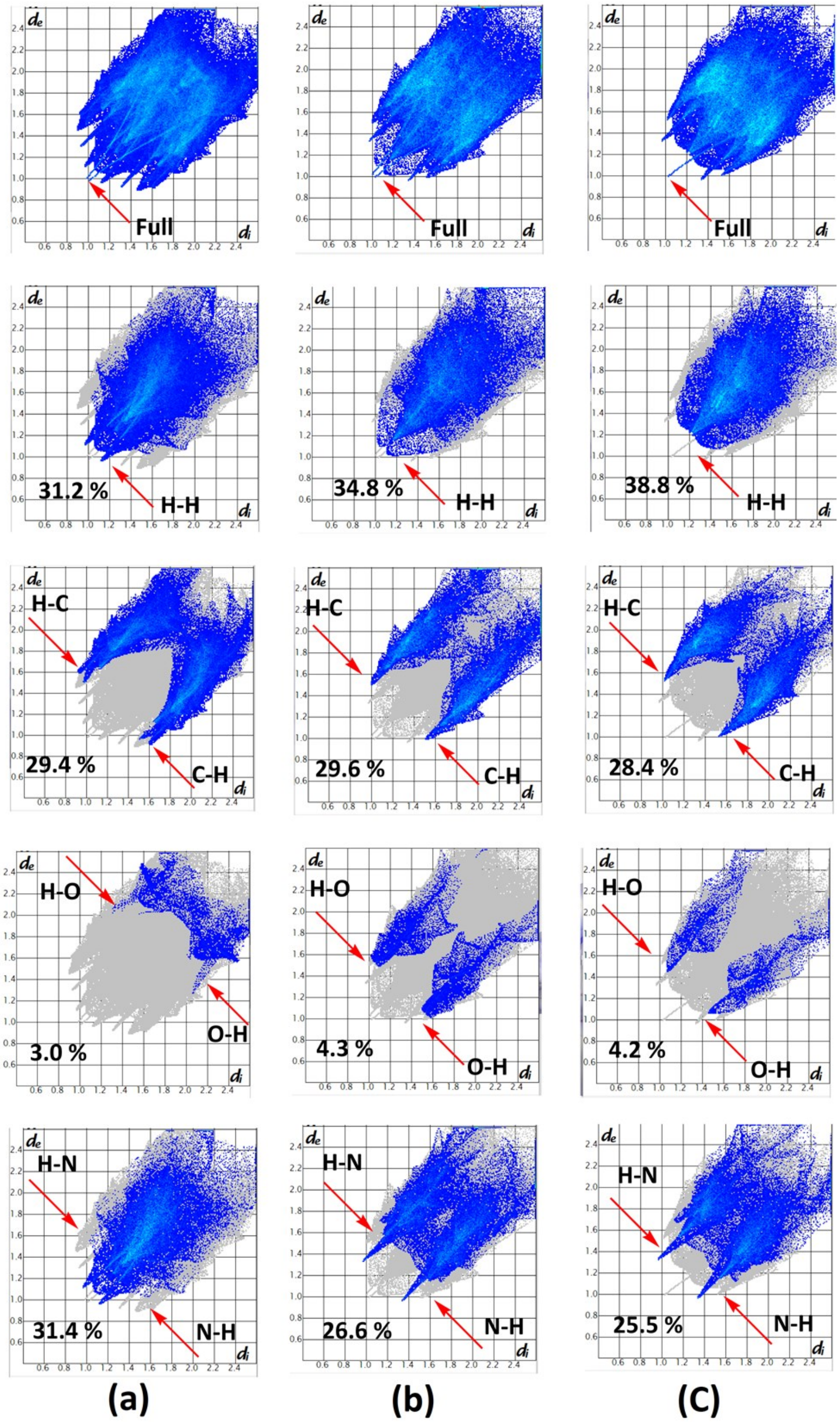

Fig. S11 Fingerprint plot: Different contacts contributed to the total Hirshfeld Surface area of the (a) complex **1**; (b) complex **2** and (c) complex **3.**

References

1 (a) M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, 11, 19; (b) F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, 44, 129-138; (c) H.F. Clausen, M. S. Chevallier, M. A. Spackman and B. B. Iversen, *New J. Chem.*, 2010, 34, 193-199.

2 (a) A. L. Rohl, M. Moret, W. Kaminsky, K. Claborn, J.J. McKinnon, B. Kahr, *Cryst. Growth Des.*, 2008, 8, 4517-4525; (b) A. Parkin, G. Barr, W. Dong, C.J. Gilmore, D. Jayatilaka, J.J. McKinnon, M.A. Spackman, C. C. Wilson, *CrystEngComm*, 2007, 9, 648-652; (c) M.A. Spackman, J.J. McKinnon, *CrystEngComm*, 2002, 4, 378-392.

3 S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka, M. A. Spackman, Crystal Explorer2.0; University of Western Australia: Perth, Australia, 2007, http://hirshfeldsurfacenet.blogspot.com.

Table S1: Hydrogen bond distance (Å) and angles (º) of complex **1**.

Complex	**D-H···A**	**D-H**	**H···A**	**D···A**	**∠D-H···A**
1	N(2)–H(2)···N(5)^a	0.980(6)	2.261(8)	3.139(10)	158.5(4)

D, donor; H, hydrogen; A, acceptor. Symmetry transformation ^{a} = X,-1+Y, Z

Table S2: Geometric features (distances in Å and angles in °) of the C-H···π interactions obtained for complexes **1-3**.

Complex	C-H···Cg(Ring)	H···Cg	C-H···Cg	C···Cg (Å)
1	C(8)-H(8B)···Cg(6)^b	2.74	169	3.695(9)
2	C(9)-H(9A)···Cg(8)^c	2.86	134	3.608(4)
	C(11)-H(11B)···Cg(2)^d	2.61	139	3.391(5)
3	C(12)-H(12C)···Cg(3)^e	2.78	145	3.610(5)
	C(12)-H(12C)···Cg(8)^e	2.97	120	3.549(5)
	C(14)-H(14B)···Cg(7)^f	2.88	133	3.613(5)

Symmetry transformations: ^{b} = 1-X, 1-Y, 2- Z; ^{c} = -1/2+X, 1/2-Y, 1-Z; ^{d} = 1/2-X, -1/2+Y, Z; ^{e} = 1/2-X, 1/2+Y, Z; ^{f} = -1/2+X, 3/2-Y, 1-Z.

For complex **1**:

Cg(6) = Centre of gravity of the ring [C(2)-C(3)-C(4)-C(5)-C(6)-C(7)]

For complex **2**:

Cg(2)= Centre of gravity of the ring [Zn(2)-O(1)-C(7)-C(2)-C(3)-O(3)] and Cg(8)= Centre of gravity of the ring [C(15)-C(16)-C(17)-C(18)-C(19)-C(20)]

For complex **3**:

Cg(3)= Centre of gravity of the ring [Zn(2)-O(2)-C(21)-C(20)-O(4)], Cg(7)= Centre of gravity of the ring [C(3)-C(4)-C(5)-C(6)-C(7)-C(8)], and Cg(8)= Centre of gravity of the ring [C(16)-C(17)-C(18)-C(19)-C(20)-C(21)]

Table S3: Geometric features (distances in Å and angles in °) of the π···π stacking in complexes **1-3.**

Complex	**Cg(I)···Cg(J)**	**Cg···Cg**	**α**	**Cg(I)···Prep**	**Cg(J)···Prep**	**Slippage**
1	Cg(6)···Cg(7)^{g}	3.936(6)	6.8(4)	3.658(3)	-3. 798(4)	-
	Cg(6)···Cg(7)^{h}	3.936(6)	6.8(4)	-3. 799(4)	3.657(3)	-

Symmetry transformations: ^{g} = 1+X, Y, Z; ^{h} = -1+X, Y, Z.

Cg(6)= Centre of gravity of the ring [C(2)-C(3)-C(4)-C(5)-C(6)-C(7)] and Cg(7)= [C(13)-C(14)-C(15)-C(16)-C(17)-C(18)]