Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information

for:

Synthesis, X-ray characterization, DFT calculations and Hirshfeld surface analysis of Zn(II) and Cd(II) complexes based on isonicotinoylhydrazone ligand

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Table S1. Selected bond distances (Å) and angles (°) for compound **1**.

Zn-N(1)	2.2189(19)	Zn-N(5)	2.1815(18)
Zn-N(2)	2.0627(18)	Zn-N(6)	2.0787(18)
Zn-O(1)	2.1514(16)	Zn-O(2)	2.1166(15)
N(2)-Zn-N(6)	173.79(7)	O(2)-Zn-N(5)	149.97(6)
N(2)-Zn-O(2)	110.58(6)	O(1)-Zn-N(5)	93.15(6)
N(6)-Zn-O(2)	74.88(6)	N(2)-Zn-N(1)	74.72(7)
N(2)-Zn-O(1)	75.28(6)	N(6)-Zn-N(1)	101.98(7)
N(6)-Zn-O(1)	107.70(6)	O(2)-Zn-N(1)	97.40(7)
O(2)-Zn-O(1)	94.83(6)	O(1)-Zn-N(1)	149.94(6)
N(2)-Zn-N(5)	99.45(7)	N(5)-Zn-N(1)	89.85(7)
N(6)-Zn-N(5)	75.11(7)		

Table S2. Selected bond distances (Å) and angles (°) for compounds **2** and **3.**

	2, X=Br		**3**, X=I
Zn-N(1)	2.237(2)	Zn-N(1)	2.2307(18)
Zn-N(2)	2.053(2)	Zn-N(2)	2.0495(19)
Zn-O(1)	2.1791(17)	Zn-O(1)	2.1643(17)
Zn-X(1)	2.4094(5)	Zn-X(1)	2.6055(3)
Zn-X(2)	2.4293(5)	Zn-X(2)	2.6287(3)
N(2)-Zn-O(1)	74.80(7)	N(2)-Zn-O(1)	74.97(7)
N(2)-Zn-N(1)	74.06(8)	N(2)-Zn-N(1)	74.26(7)
O(1)-Zn-N(1)	147.90(7)	O(1)-Zn-N(1)	148.52(7)
N(2)-Zn-X(1)	131.83(6)	N(2)-Zn-X(1)	131.45(5)
O(1)-Zn-X(1)	98.40(5)	O(1)-Zn-X(1)	98.49(5)
N(1)-Zn-X(1)	96.50(5)	N(1)-Zn-X(1)	96.80(5)
N(2)-Zn-X(2)	111.19(6)	N(2)-Zn-X(2)	113.63(5)
O(1)-Zn-X(2)	101.26(5)	O(1)-Zn-X(2)	101.07(5)
N(1)-Zn-X(2)	97.04(5)	N(1)-Zn-X(2)	97.17(5)
X(1)-Zn-X(2)	116.858(14)	X(1)-Zn-X(2)	114.821(11)

Table S3. Selected bond distances (Å) and angles (°) for compound **4.**

Zn-N(1)	2.1894(18)	Zn-N(5)	1.9747(19)
Zn-N(2)	2.0516(18)	Zn-N(6)	1.9960(19)
Zn-O(1)	2.1101(15)		
N(5)-Zn-N(6)	102.72(8)	N(2)-Zn-O(1)	75.66(6)
N(5)-Zn-N(2)	133.97(7)	N(5)-Zn-N(1)	98.53(7)
N(6)-Zn-N(2)	123.31(7)	N(6)-Zn-N(1)	98.65(7)

N(5)-Zn-O(1)	100.51(7)	N(2)-Zn-N(1)	75.52(7)
N(6)-Zn-O(1)	98.06(7)	O(1)-Zn-N(1)	151.16(6)

Table S4. Selected bond distances (Å) and angles (°) for compound **5.**

Cd-N(1)	2.365(2)	Cd-N(5)	2.361(2)
Cd-N(2)	2.2621(17)	Cd-N(6)	2.2716(19)
Cd-O(1)	2.306(2)	Cd-O(2)	2.313(2)
N(2)-Cd-N(6)	170.90(9)	O(1)-Cd-N(5)	95.18(8)
N(2)-Cd-O(1)	69.36(8)	O(2)-Cd-N(5)	139.17(7)
N(6)-Cd-O(1)	111.11(8)	N(2)-Cd-N(1)	70.10(8)
N(2)-Cd-O(2)	101.89(7)	N(6)-Cd-N(1)	110.42(8)
N(6)-Cd-O(2)	69.02(7)	O(1)-Cd-N(1)	138.38(7)
O(1)-Cd-O(2)	101.03(11)	O(2)-Cd-N(1)	96.06(9)
N(2)-Cd-N(5)	118.90(8)	N(5)-Cd-N(1)	96.12(9)
N(6)-Cd-N(5)	70.20(7)		

Table S5. Selected bond distances (Å) and angles (°) for compounds **6** and **7.**

	6, X=Br	**7**, X=I
Cd-N(1)	2.3838(17)	2.369(2)
Cd-N(2)	2.2816(16)	2.349(2)
Cd-O(1)	2.3041(14)	2.395(2)
Cd-X(1)	2.5625(3)	2.7268(8)
Cd-X(2)	2.6035(3)	2.7459(11)

N(2)-Cd-N(1)	69.28(6)	67.85(8)
N(2)-Cd-O(1)	69.70(5)	66.39(7)
O(1)-Cd-N(1)	138.97(5)	128.81(7)
N(1)-Cd-X(1)	100.05(4)	96.09(6)
N(2)-Cd-X(1)	126.38(4)	140.55(6)
O(1)-Cd-X(1)	104.66(4)	104.82(5)
N(1)-Cd-X(2)	97.28(4)	116.33(6)
N(2)-Cd-X(2)	122.35(4)	102.77(6)
O(1)-Cd-X(2)	103.63(4)	95.16(5)
X(1)-Cd-X(2)	110.946(9)	116.52(3)

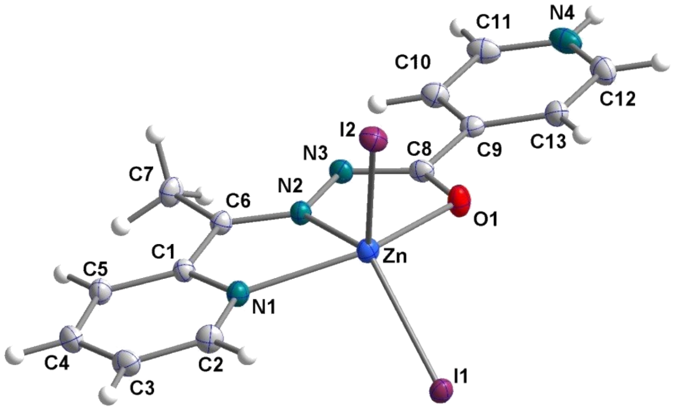


Fig. S1. ORTEP view of the molecular structure of complex **3**.

Hirshfeld surface

Hirshfeld surfaces (HS) divide the crystal space into smooth non-overlapping molecular volumes and give a unique information about each molecule in a crystal. This enables a convenient analysis of intermolecular interactions in a crystal. The normalized contact distance d_{norm}, is a parameter that includes the distances of any surface point to the nearest nucleus internal to the surface (d_{i}) and the nearest nucleus external to the surface (d_{e}) and the van der Waals radii of atoms (r^{vdW}),[1] given by the equation (1).

$$d_{norm} = \frac{d_i - r_i^{\mathrm{vdW}}}{r_i^{\mathrm{vdW}}} + \frac{d_e - r_e^{\mathrm{vdW}}}{r_e^{\mathrm{vdW}}} \tag{1}$$

The d_{norm} can be negative or positive the sum of d_{i} and d_{e} when intermolecular contacts are shorter or longer than sum of the atoms' van der Waals radii, respectively. HS maps are color-schemed showing red-white-blue areas. This is considered to be a close contact and is coloured red (indicating shorter contacts). A white-coloured region corresponds to weak contacts (around the van der Waals separation). A blue region is considered to be free of significant contacts. The FP are constructed on the d_{e} and d_{i} distances, from the HS to the nearest atom outside – external and inside - internal the surface, respectively. The Hirshfeld surfaces[2] and the related 2D-fingerprint plots[3] were calculated using Crystal Explorer.[4] At the beginning of calculations the bond lengths relative to hydrogen atoms were set to standardized neutron values (O—H = 0.983 Å, N—H = 1.009 Å and C—H = 1.083 Å).

The Hirshfeld surfaces for all structures have been mapped over d_{norm}. The dominant intermolecular interactions are viewed by the bright red area of d_{norm} surface. The Fig. 14 illustrates samples of Hirshfeld surfaces for complexes **1** and **5**. Crystal packing is largely dominated by the common planar components of compounds, leading to interesting stackings involving C–H···π and π···π interactions as well as the close H···H intercontacts. In **1** we also observe a high level of O···H interactions due the hydrogen bonds between solvent molecules with the complex. The Br···H, S···H and I···H interactions are important with ligands containing these atoms.

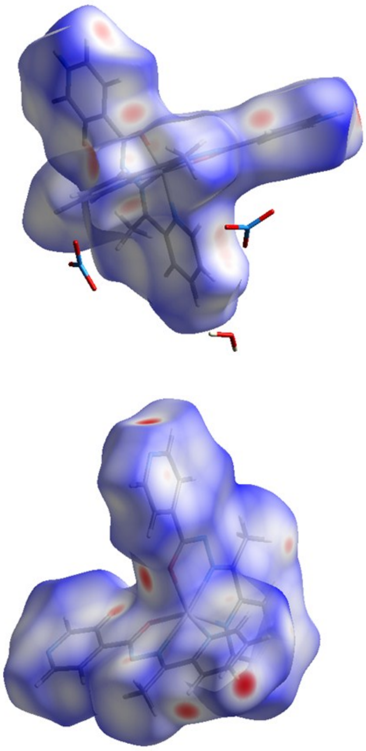
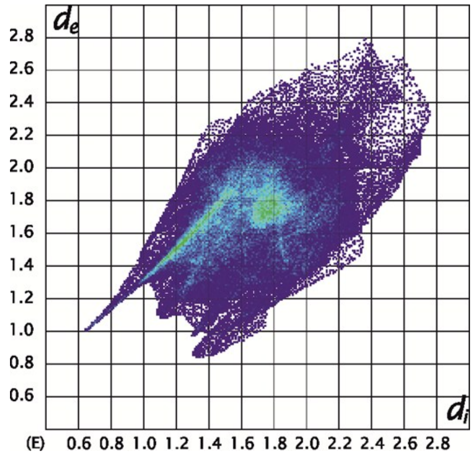


Fig. S2. Views of the Hirshfeld surfaces for complexes **1** (top) and **5** (bottom) mapped with d_{norm}

The 3D Hirshfeld surfaces can also be demonstrated with a 2D representation, the so-called fingerprint plot (FP). Fig. S3 illustrates the two-dimensional fingerprint plots of the HS for complexes **1-5** as selected examples. Generally, the FPs are different and some of them are quite asymmetric. The relevant intermolecular interactions for all structures are presented in Table 2. These data allow to separate the contribution for each interaction, namely H···H, O···H, C···H, C···C, N···C, N···H, O···C, N···N (for all compounds), Br···H, Br···C (in **2** and **6**), I···H, I···C, I···N (in **3** and **7**) and S···H, S···C, S···N (in **4**) which commonly overlap in the full fingerprint plots. The H···H intercontacts contain 35.6, 25.5, 25.0, 18.4, 44.3, 29.1 and 29.0% of HS area in molecules **1–7** respectively, and have almost the higher contribution in all crystal structures relative to the other contacts. The O···H interactions vary from 29.5% for **1** to 5.1% for **4**. The C···H contact represents the C–H···π interactions in the crystals, and the highest values were measured in **5** and **4**. For π···π interactions which correspond to the C···C contacts the highest values were measured in **4** and **7**.



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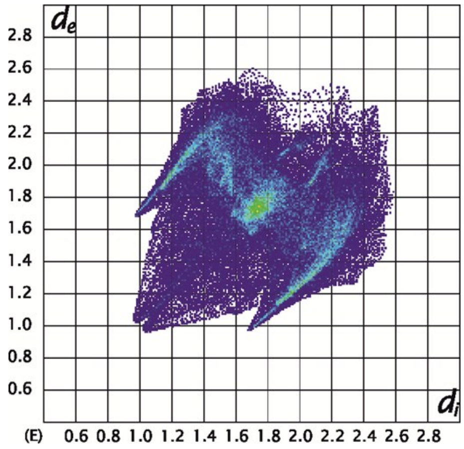

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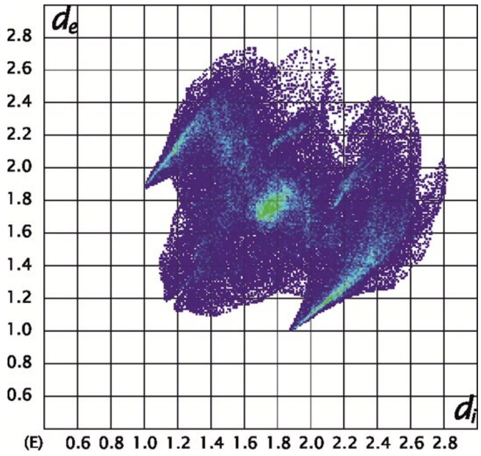

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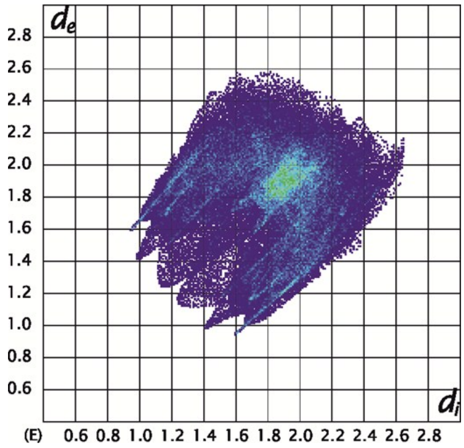

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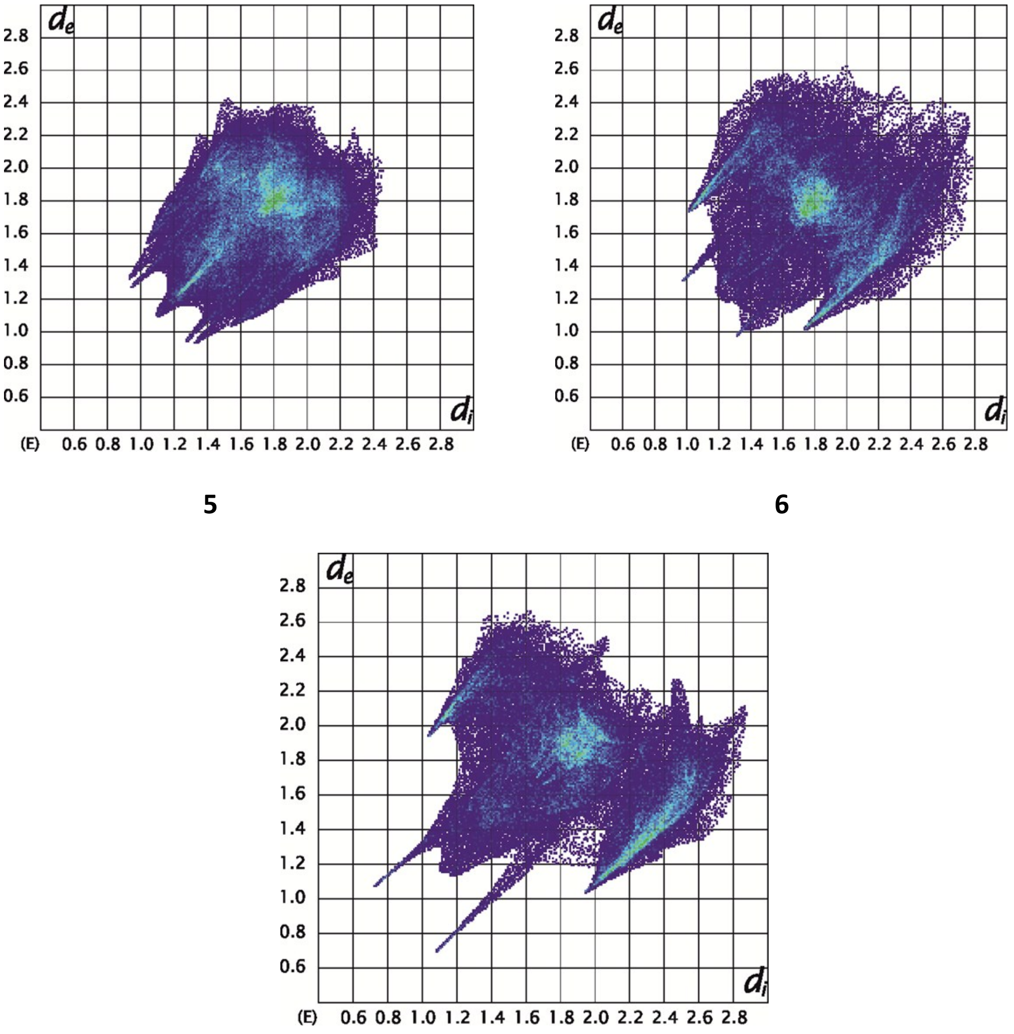

5

6

7

Fig S3. Full fingerprints of compounds **1-7**.

Table S6. Summary of the various contact contributions (in %) in Hirshfeld surface area for all analyzed structures.

Contact type /Structure	**1**	**2**	**3**	**4**	**5**	**6**	**7**
H···H	35.6	25.5	25.0	18.4	44.3	29.1	29.0
O···H/H···O	29.5	6.9	6.5	5.1	8.4	9.2	7.2
C···H/H···C	16.3	10.9	9.2	19.5	23.7	10.9	8.3
C···C	5.7	6.0	5.6	7.6	4.0	4.8	6.2
N···C/C···N	4.0	3.5	3.8	1.5	6.2	3.7	4.0
N···H/H···N	3.9	7.8	7.0	13.9	13.0	2.9	6.3
O···C/C···O	2.6	0.4	0.3	0.4	0.0	0.6	1.0
N···N	1.7	0.3	1.3	1.8	0.5	1.6	0.0
Br···H/H···Br	-	35.3	-	-	-	33.6	-
Br···C/C···Br	-	2.6	-	-	-	1.2	-
I···H/H···I	-	-	30.7	-	-	-	34.4
I···C/C···I	-	-	4.4	-	-	-	0.3
I···N/N···I	-	-	4.1	-	-	-	0.3
S···H/H···S	-	-	-	24.7	-	-	-
S···C/C···S	-	-	-	3.5	-	-	-
S···N/N···S	-	-	-	2.9	-	-	-

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[1] M. A. Spackman, J. J. McKinnon and D. Jayatilaka, *CrystEngComm*, 2008, **10**, 377.

[2] M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19.

[3] M. A. Spackmann and J. J. McKinnon, *CrystEngComm*, 2002, **4**, 378.

[4] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka and M. A. Spackman, CrystalExplorer (Version 3.1), University of Western Australia, 2012.