Supplementary Material

Crystal Structure, Hirshfeld Surface Analysis and Energy Framework Calculations of Different Metal Complexes of a Biphenol-based Ligand: Role of Solvent and Transition Metal Ion

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Table S1. Distances (Å) and angles (°) involving the Pd(II) ion and dihedral angles in compound **6**.

Pd-X (Å)	
Pd1-N1	2.02(1)
Pd1-N2	2.02(1)
Pd1-O1	2.01(1)
Pd1-O3	2.026(9)
Pd-N (CSD)	1.997-2.105 (mean value: 2.044)
Pd-O (CSD)	1.968-2.095 (mean value: 2.014)
X-Pd-Y (°)	
N1-Pd1-N2	87.4(5)
N1-Pd1-O1	93.5(5)
N1-Pd1-O3	176.1(4)
N2-Pd1-O1	174.4(5)
N2-Pd1-O3	88.8(4)
O1-Pd1-O3	90.3(4)
Dihedral angles (°)	
C3-C2-C1-N1 (τ1)	56(2) +sc
C2-C1-N1-C15 (τ2)	-180(1) ap
C1-N1-C15-C16 (τ3)	166(1) ap
N1-C15-C16-N2 (τ4)	-53(2) -sc
C15-C16-N2-C18 (τ5)	-82(2) -sc
C16-N2-C18-C19 (τ6)	-178(1) ap
N2-C18-C19-C20 (τ7)	-34(2) -sc

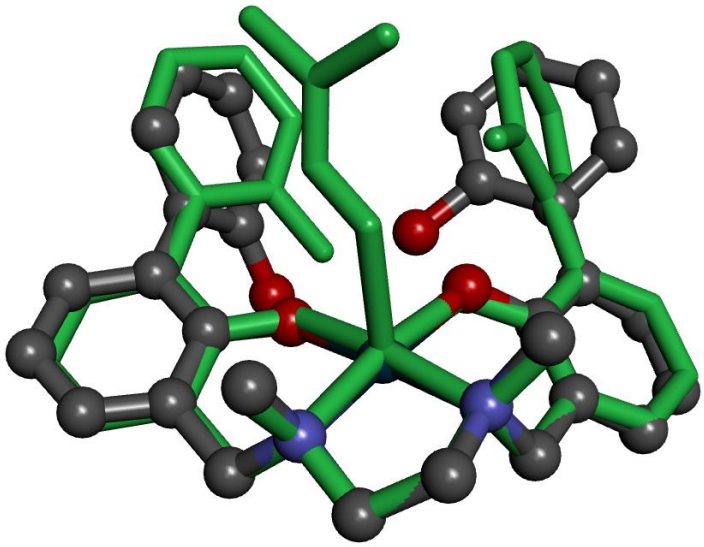


Figure S1. Superimposition of the [Pd(H$_{-2}$**L**)] complex (**6**) (ball and stick) and OTIYEX (**4**) (stick, green).

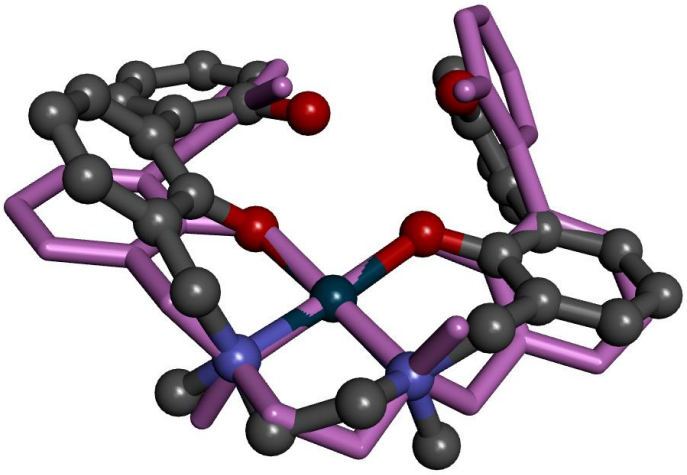


Figure S2. Superimposition of the [Pd(H$_{-2}$**L**)] complex (**6**) (ball and stick) and OTIYIB (**5**) (stick, pink).

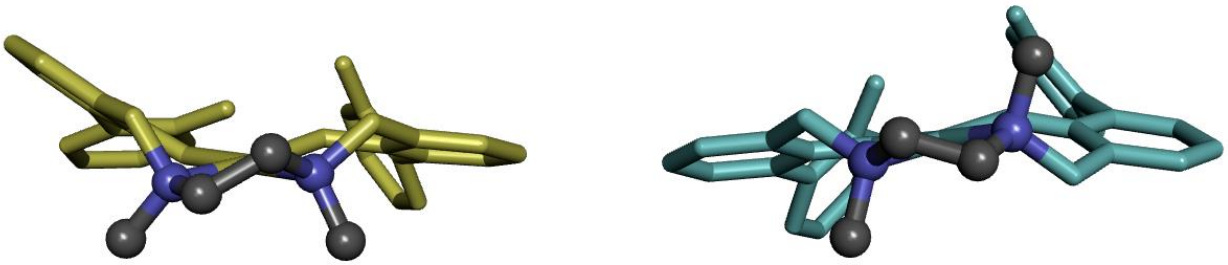


Figure S3. Disposition of the two methyl groups in [Pd(H$_{-2}$**L**)] (**6**) (left, yellow) and OTIYIB (**5**) (right, pale blue).

Table S2. Selected interactions within the crystal packing of **6**.

D*-H···*A	***D*···*A* (Å)**	**H···*A* (Å)**	**∠ *D*-H···*A* (°)**
C1-H1A···Pd1[a]	3.59	2.61	167
C15-H15A···C26[a]	3.42	2.79	122
C18-H18B···C30[a]	3.57	2.80	134
C17-H17C···C19[a]	3.54	2.80	133
C28-H28···C26[b]	3.64	2.87	139
C15-H15A···O3[a]	3.54	2.56	169
C18-H18A···O3[a]	3.64	2.66	175
C14-H14C···O2[a]	3.45	2.50	164
C28-H28···O4[b]	3.50	2.61	156
C11-H11···O2[b]	3.32	2.47	148

[a] -1/2+x,y,1.5-z; [b] -1/2+x,y,1/2-z

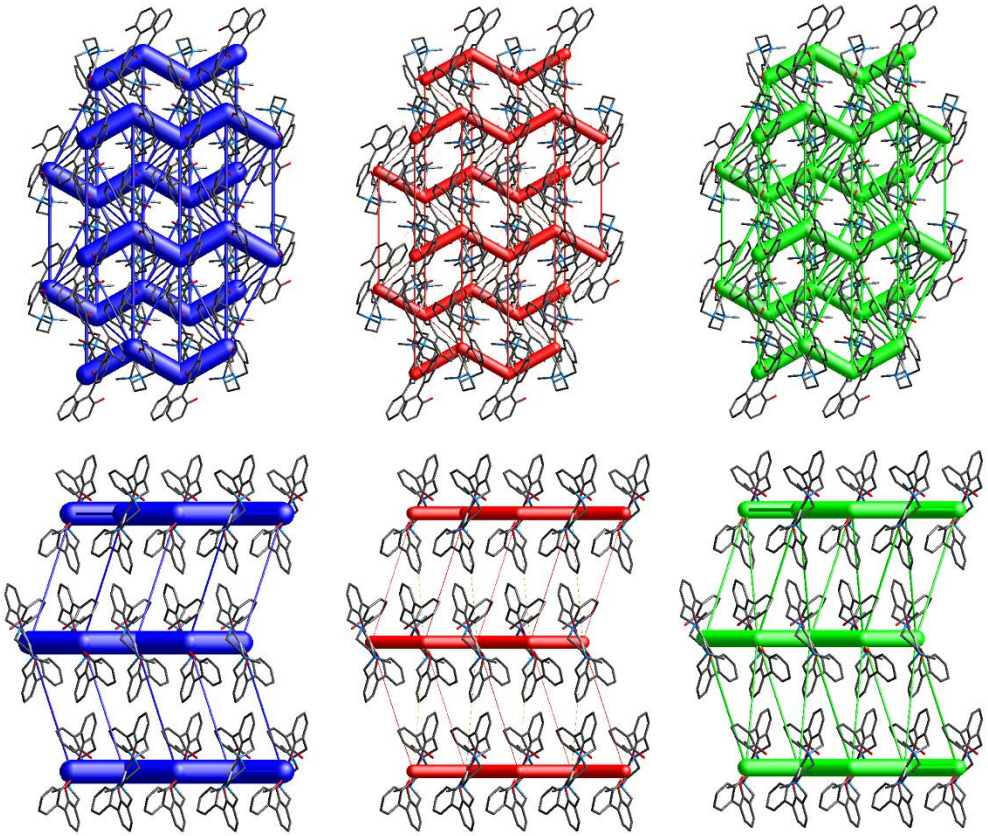


Figure S4. Energy frameworks of **6** (view along the *b* (top) and *c* (bottom) axes). Total energy as blue cylinders, Coulomb energy as red cylinders, dispersion energy as green cylinders.

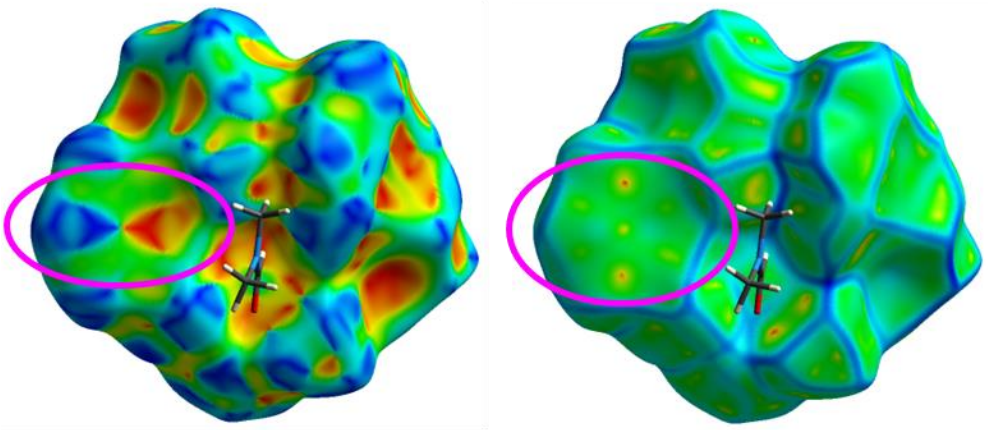
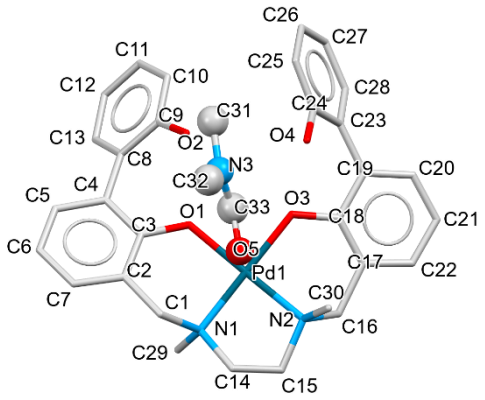


Figure S5. Hirshfeld surface of **5** mapped over shape index (left) and curvedness (right). Magenta ovals refer to π-π stacking interactions.

Table S3. Selected interactions within the crystal packing of **5**.



D-H···*A*	*D*···*A* (Å)	H···*A* (Å)	∠ *D*-H···*A* (°)
C31-H31···O2	3.28	2.45	147
C1-H3···O5	3.58	2.64	158
C16-H16···O5 [a]	3.32	2.37	174
C22-H20···C12 [b]	3.61	2.89	141
C22-H20···C13 [b]	3.58	2.72	166
C14-H12···C23 [b]	3.75	2.96	152
C14-H12···C28 [b]	3.79	2.92	178
C11···C32 [c]	3.30		
C7···C5 [d]	3.56		
C6···C6 [d]	3.58		

[a] 1-x,1/2+y,1/2-z ; [b] x,1/2-y,-1/2+z; [c] x,1+y,z; [d] 1-x,-y,-z

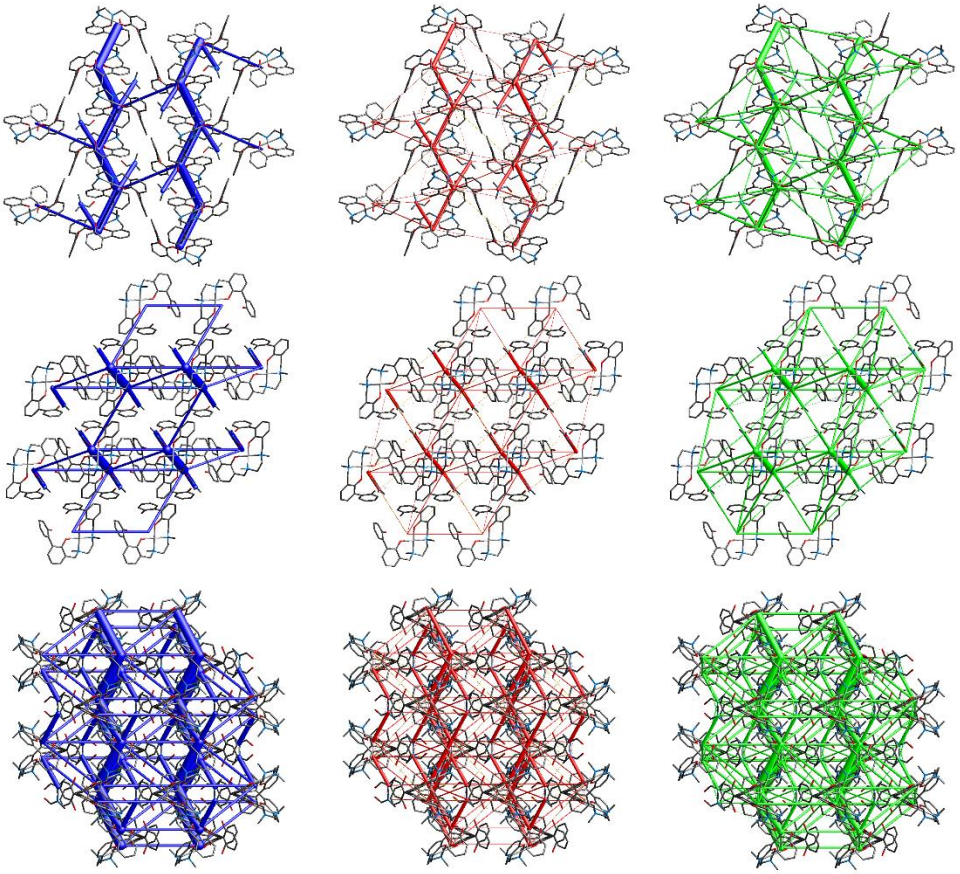


Figure S6. Energy frameworks of **5** (view along the *a* (top), *b* (middle) and *c* (bottom) axes). Total energy as blue cylinders, Coulomb energy as red cylinders, dispersion energy as green cylinders.

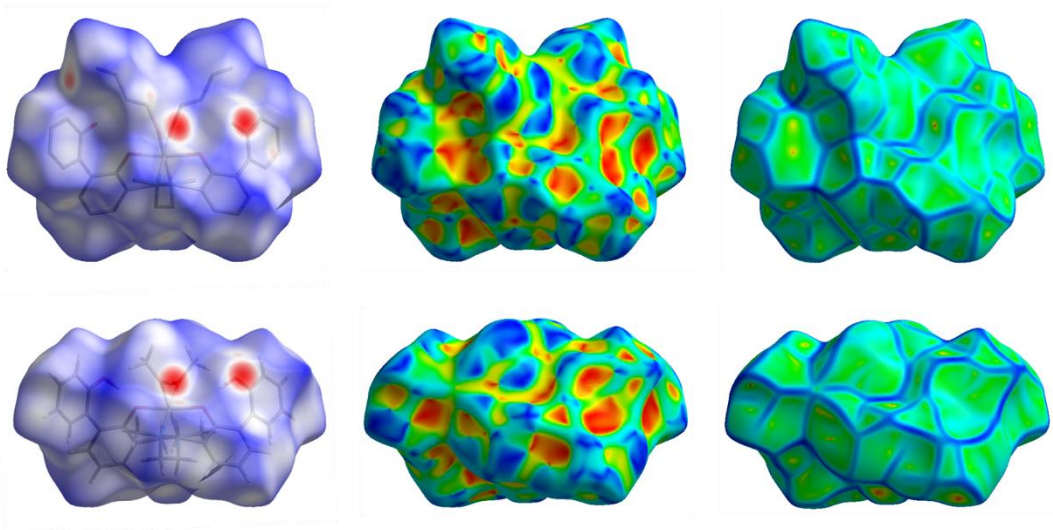


Figure S7. Hirshfeld surfaces mapped over d_{norm} (left), shape index (middle) and curvedness (right) of **1** (top) and **2** (bottom). Globularity: 0.727 (**1**), 0.777 (**2**); asphericity: 0.085 (**1**), 0.136 (**2**).

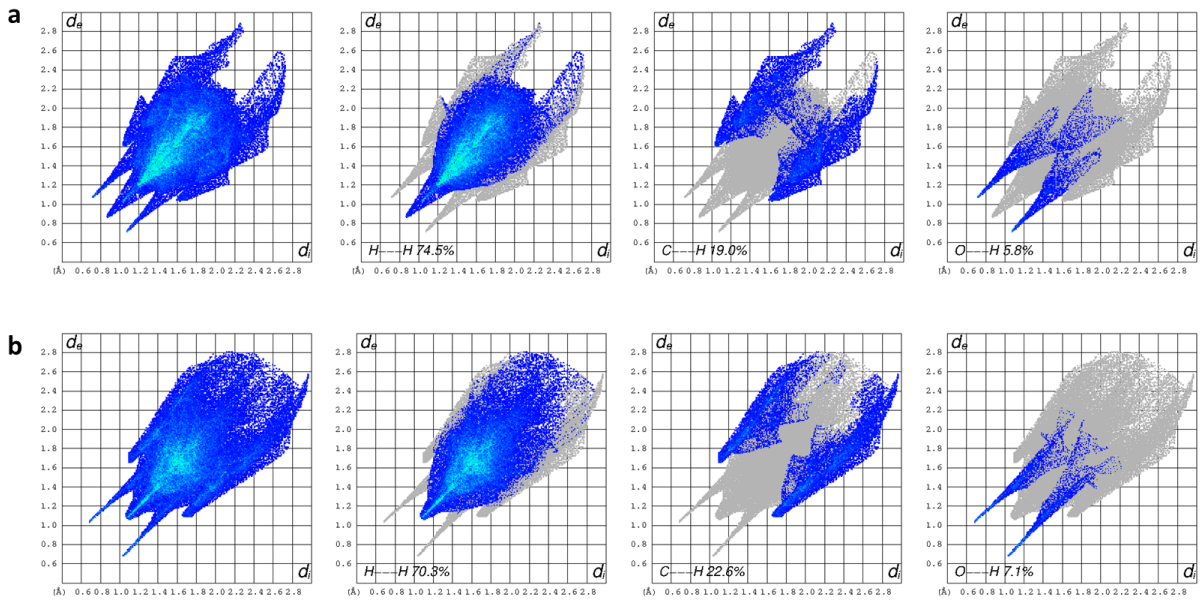
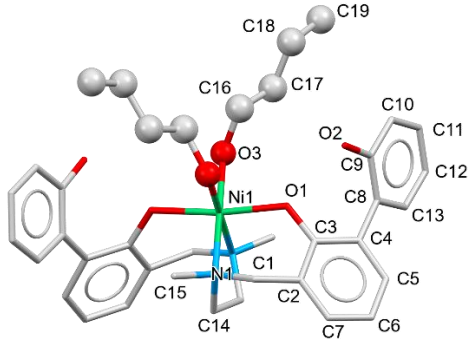
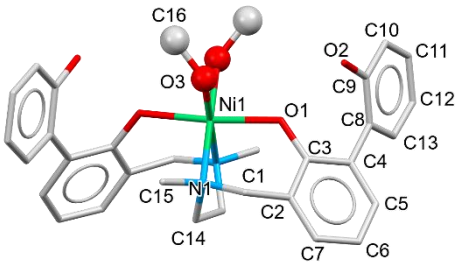


Figure S8. 2D and decomposed fingerprint plots for compounds **1** (**a**) and **2** (**b**).

Table S4. Selected interactions within the crystal packing of **1** and **2**.

	D-H···*A*	*D*···*A* (Å)	H···*A* (Å)	∠ *D*-H···*A* (°)
	O3-H16···O2A [a]	2.77	1.94	169
	C1-H3···O2 [b]	3.56	2.60	157
	C17-H20···C8A [a]	3.63	2.73	148
	C17-H20···C9A [a]	3.68	2.82	143
	O3-H16···C9A [a]	3.31	2.62	140
	C11···C11 [c]	3.43		
	O3-H16···O2A [d]	2.69	1.84	169
	C1-H2···O2 [d]	3.53	2.54	164
	O3-H16···C9 [d]	3.42	2.70	142
	C16-H17···C4 [d]	3.68	2.92	145
	C12-H9···C7A [e]	3.71	2.98	137
	C5···C12 [f]	3.68		

[a] -1/2+x,1.5-y,-1/2+z; [b] 1.5-x,1.5-y,1-z; [c] 1.5-x,1.5-y,2-z; [d] -x,-y,1-z; [e] 1/2+x,1/2-y,1/2+z; [f] 1/2-x,1/2-y,1-z.

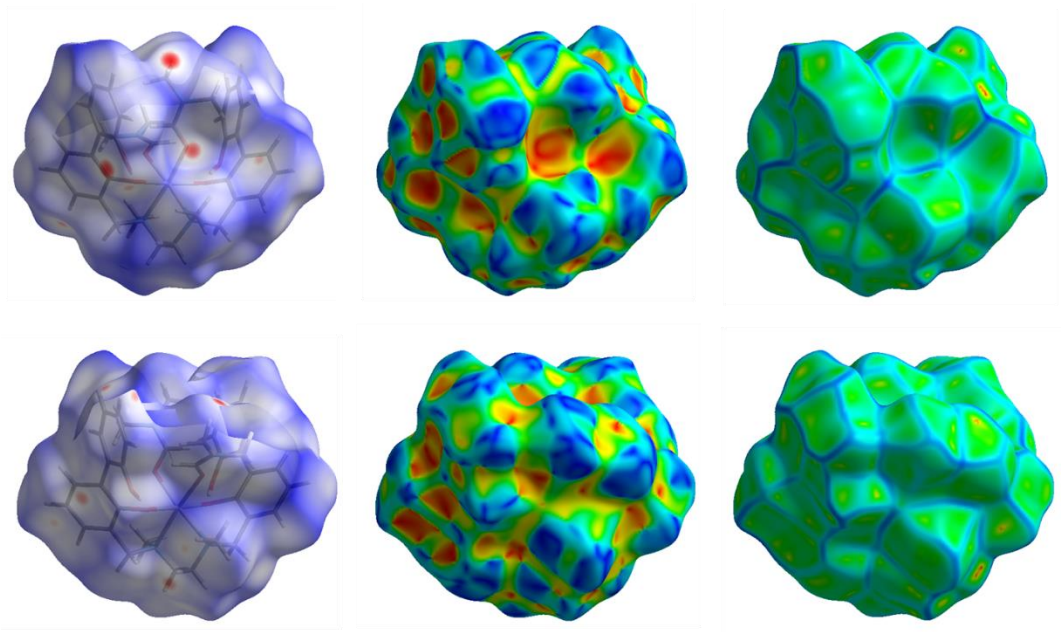


Figure S9. Hirshfeld surfaces mapped over d_{norm} (left), shape index (middle) and curvedness (right) of **3**. Front (top) and back (bottom) views. Globularity: 0.751; asphericity: 0.008.

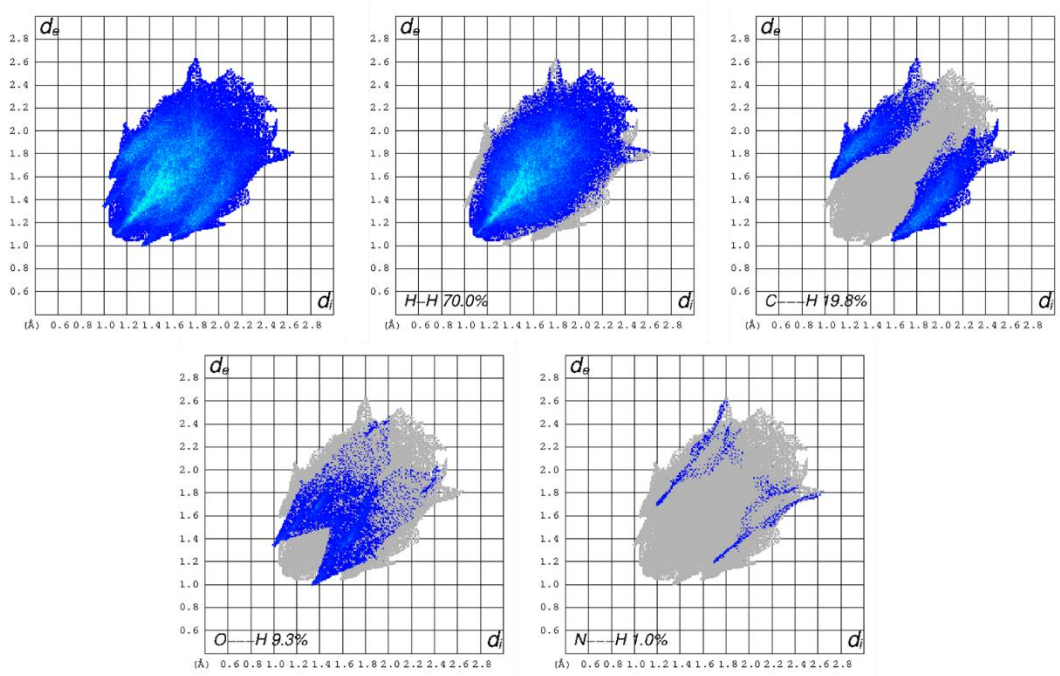


Figure S10. 2D and decomposed fingerprint plots for compound **3**.

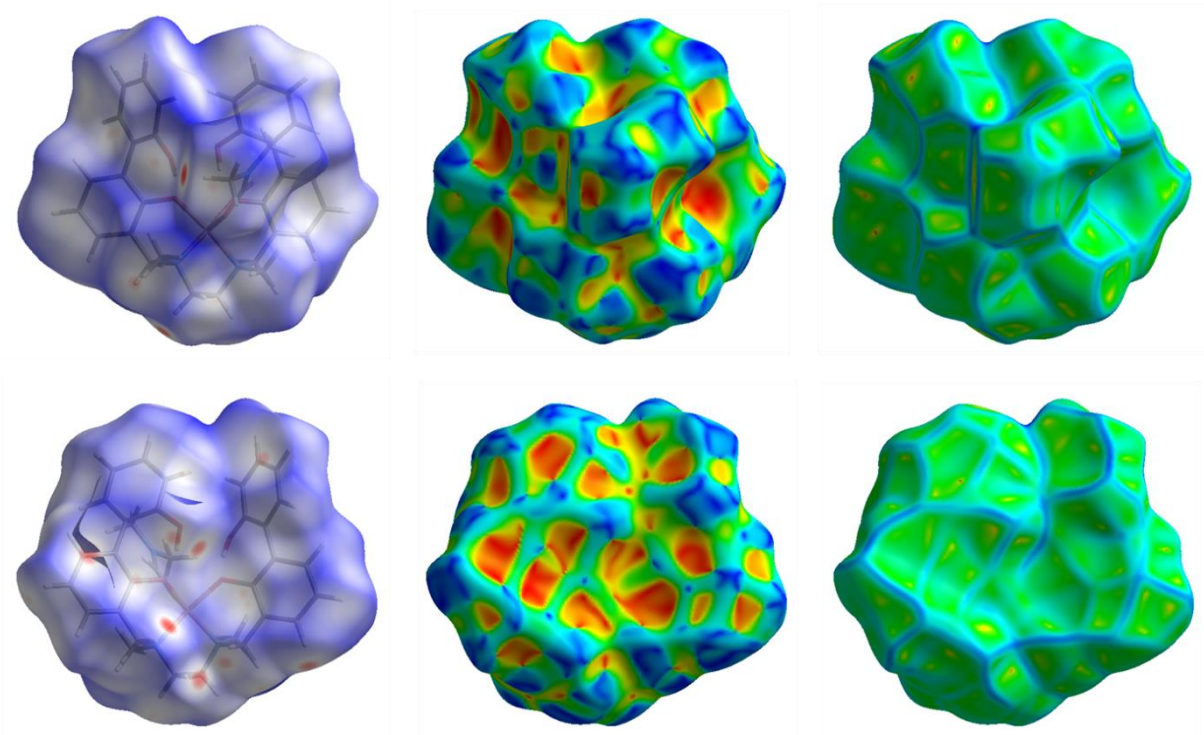


Figure S11. Hirshfeld surfaces mapped over d_{norm} (left), shape index (middle) and curvedness (right) of **4**. Front (top) and back (bottom) views. Globularity: 0.531; asphericity: 0.050.

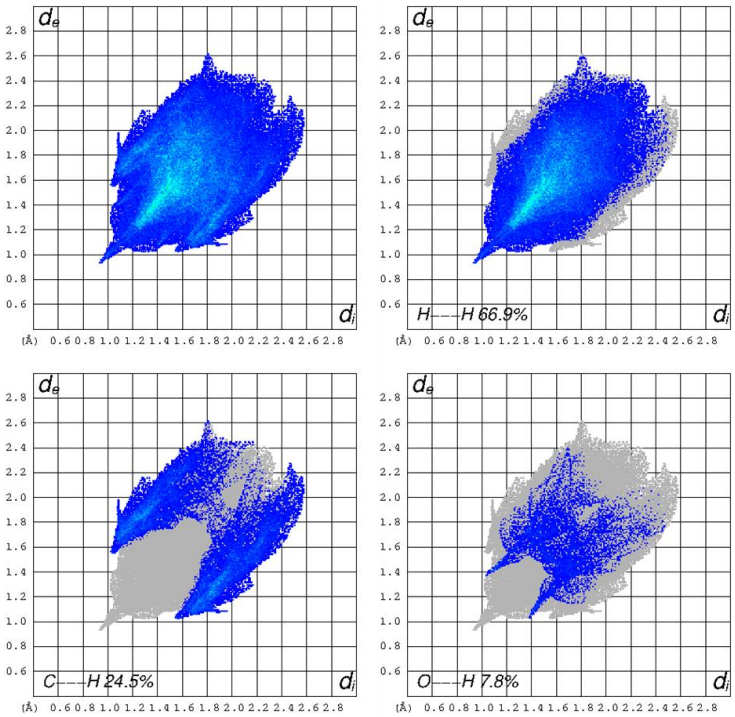
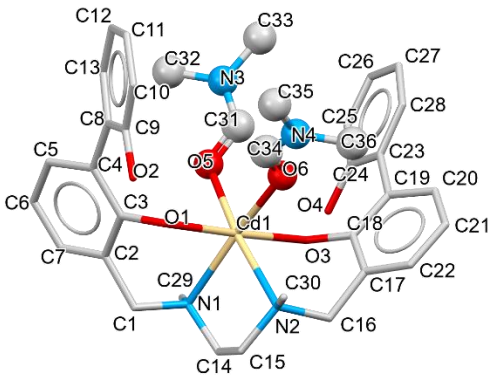
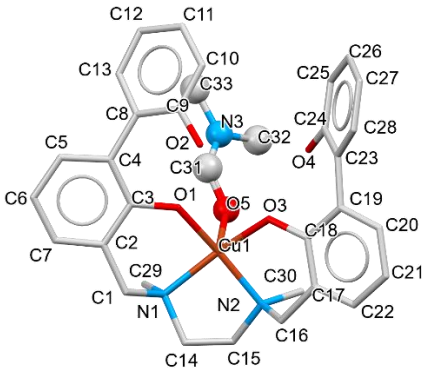


Figure S12. 2D and decomposed fingerprint plots for compound **4**.

Table S5. Selected interactions within the crystal packing of **3** and **4**.

	D*-H···*A	***D*···*A* (Å)**	**H···*A* (Å)**	**∠*D*-H···*A* (°)**
	C33-H34···O4 [a]	3.42	2.46	167
	C35-H39···O5 [b]	3.48	2.53	165
	C15-H12···C4 [c]	3.64	2.74	151
	C30-H28···C6 [c]	3.68	2.82	148
	C32-H30···C22 [d]	3.73	2.78	163
	C35-H37···C28 [e]	3.76	2.92	144
	C36-H40···C27 [e]	3.84	2.95	151
	C36-H41···C6 [b]	3.56	2.78	137
	C14-H13···O2 [f]	3.49	2.53	170
	C16-H17···O2 [f]	3.43	2.58	147
	C12-H10···C6 [g]	3.61	2.93	130
	C14-H12···C17 [f]	3.78	2.86	159
	C14-H12···C18 [f]	3.52	2.81	131
	C15-H15···C10 [h]	3.84	2.87	179
	C16-H16···C3 [f]	3.59	2.81	138
	C22-H20···C5 [f]	3.62	2.72	161
	C22-H20···C6 [f]	3.86	2.94	170
	C25-H21···C26 [i]	3.84	2.98	154
	C30-H30···C27 [h]	3.44	2.74	130

[a] -1/2+x,1/2-y,1-z; [b] 1-x,-1/2+y,1.5-z; [c] -1/2+x,1/2-y,2-z; [d] -1+x,y,z; [e] 1/2-x,-y,-1/2+z; [f] 1.5-x,-1/2+y,1/2-z; [g] 1/2-x,-1/2+y,1/2-z; [h] x,-1+y,z; [i] 1-x,1-y,1-z