

Supporting Information for

The role of intermolecular interactions in [Fe(X-salEen)₂]ClO₄ spin crossover complexes

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1. FTIR Spectroscopy

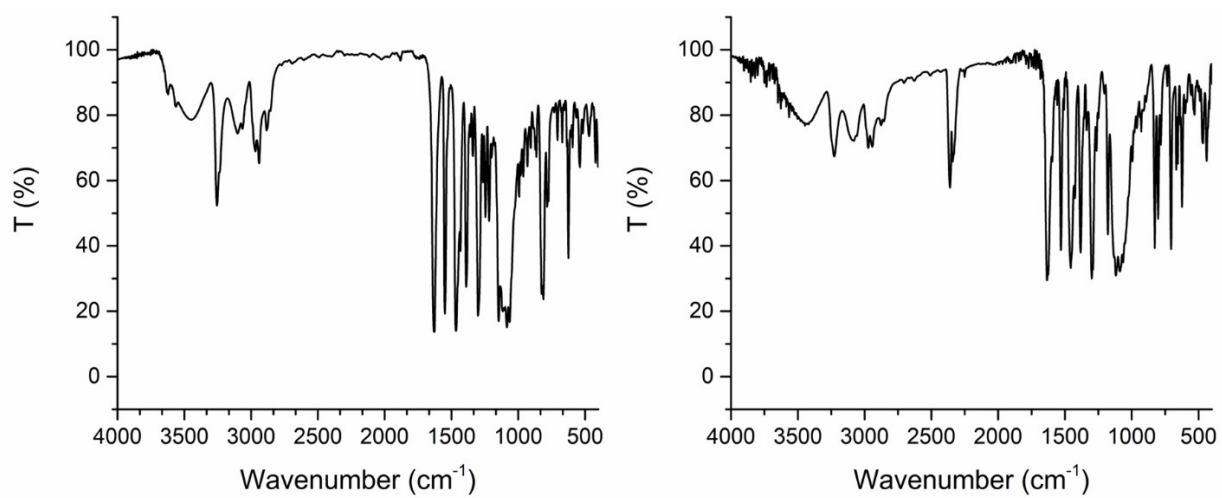


Figure S1. FTIR spectrum of **1** (left) and **2** (right) in KBr

2. X-ray diffraction

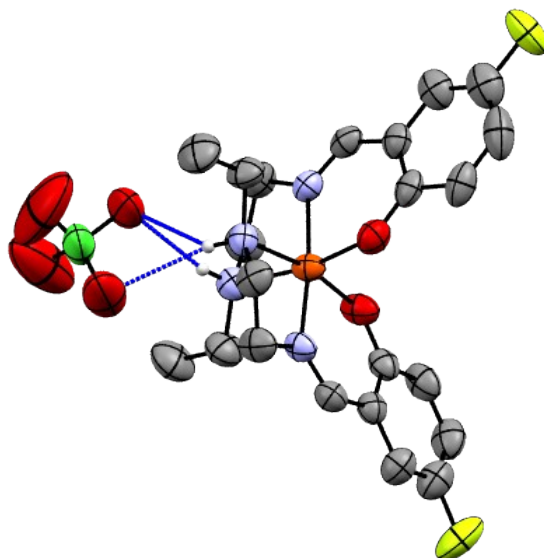


Figure S2. ORTEP view of compound **1** at 300 K, represented with 50% probability level ellipsoids. All hydrogen atoms, with exception of those involved in hydrogen bonding with the anion, were omitted for clarity. Atom colours: Carbon: grey, hydrogen: white, nitrogen: blue, oxygen: red, chlorine green, fluorine: yellow, iron: orange. N–H...O hydrogen bonds represented in blue dashed lines.

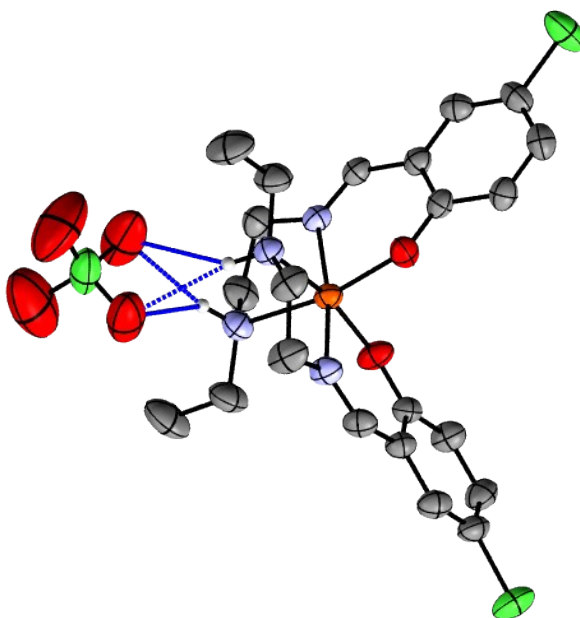


Figure S3. ORTEP view of compound **2** at 300 K, represented with 50% probability level ellipsoids. All hydrogen atoms with exception of those involved in hydrogen bonding with the anion, were omitted for clarity. Atom colours: Carbon: grey, hydrogen: white, nitrogen: blue, oxygen: red, chlorine green, fluorine: yellow, iron: orange. N–H...O hydrogen bonds represented in blue dashed lines.

Table S1. Selected angles for **1**, **1-110K**, **2** and **2-110K** [°].

	1	1-110K	2	2-110K
<i>bond angles</i>				
N1–Fe1–N3	174.13(13)	178.61(9)	171.75(8)	178.17(8)
O1–Fe1–N2	168.29(14)	175.86(9)	165.30(9)	177.48(7)
O2–Fe1–N4	167.49(13)	177.43(8)	165.55(9)	176.41(7)
N1–Fe1–O2	95.67(13)	86.01(8)	97.60(9)	88.23(7)
N3–Fe1–O2	89.18(13)	93.59(8)	87.15(8)	93.59(7)
N1–Fe1–N4	95.81(13)	96.45(9)	96.51(10)	94.96(8)
N3–Fe1–N4	79.09(13)	83.93(9)	78.48(9)	83.22(8)

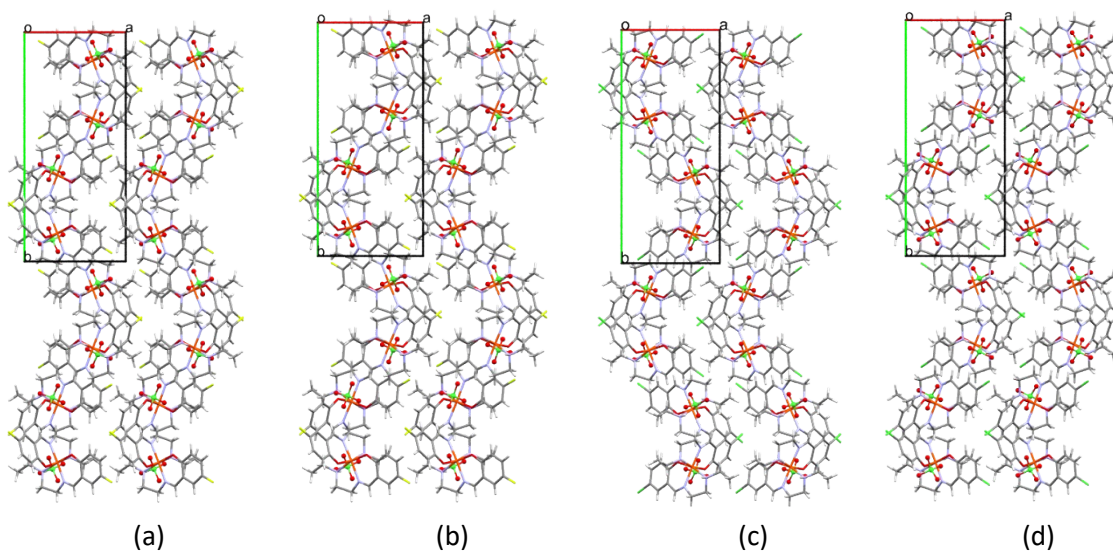


Figure S4. Supramolecular arrangement in complexes (a) **1**, (b) **1-110K**, (c) **2** and (d) **2-110K**, viewed along the *c* axis. The Fe(III) cations and the ClO₄⁻ anions are represented in capped sticks and ball and stick styles, respectively.

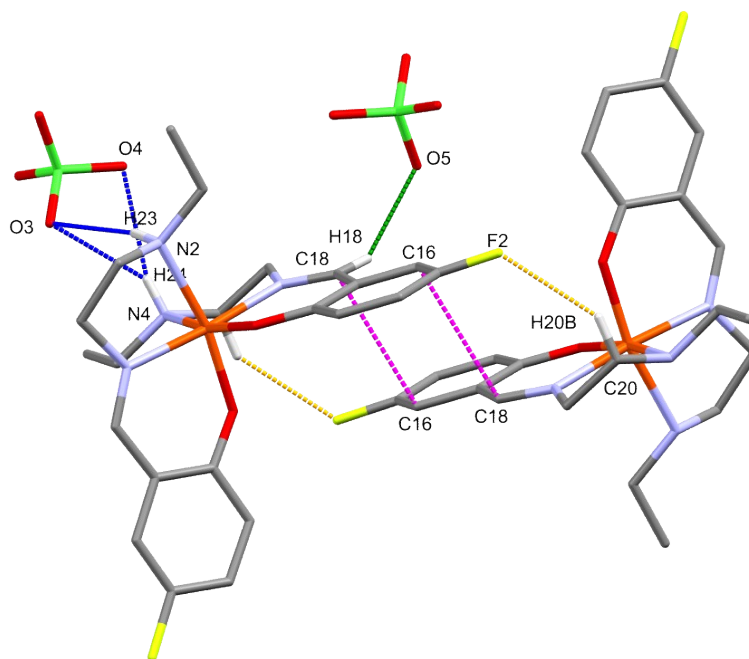


Figure S5. Intermolecular interactions observed in the crystal packing of complex **1** at 300 K: classical H-bonds [N–H...O (blue)], non-classical H-bonds [C–H...O (green)], halogen bonds [C–H...F (orange)], and π ... π (magenta) bonds, represented as dashed lines.

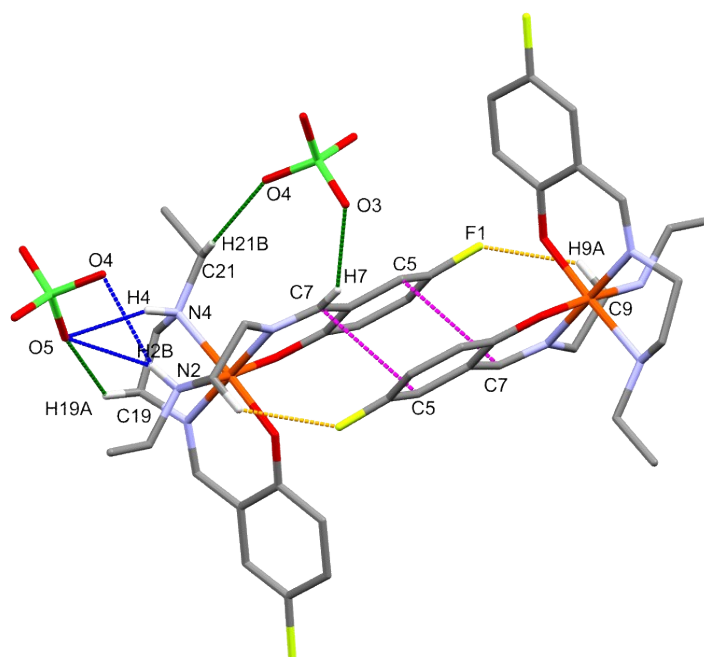


Figure S6. Intermolecular interactions observed in the crystal packing of complex **1** at 110 K: classical H-bonds [N–H...O (blue)], non-classical H-bonds [C–H...O (green)], halogen bonds [C–H...F (orange)], and π ... π (magenta) bonds, represented as dashed lines.

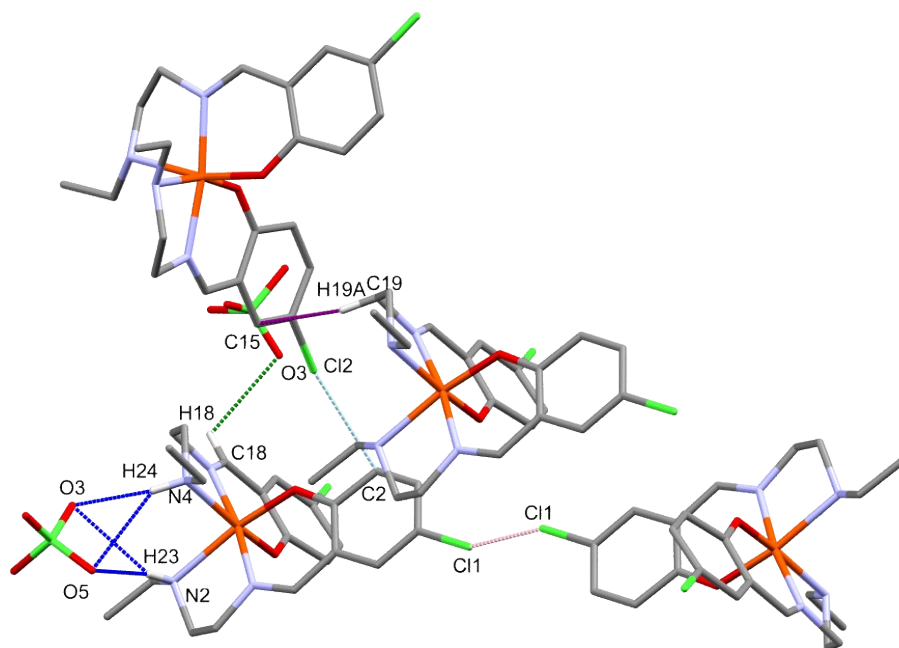


Figure S7. Intermolecular interactions observed in the crystal packing of complex **2** at 300 K: classical H-bonds [N–H...O (blue)], non-classical H-bonds [C–H...O (green)], and halogen bonds [π ...Cl (light blue), Cl...Cl (pink)], represented as dashed lines.

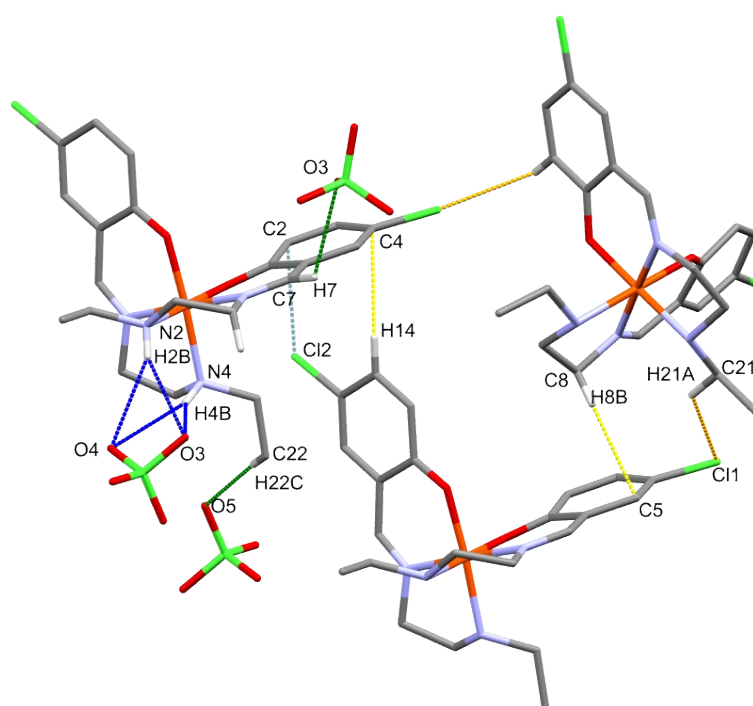


Figure S8. Intermolecular interactions observed in the crystal packing of complex **2** at 110 K: classical H-bonds [N–H...O (blue)], non-classical H-bonds [C–H...O (green)], and halogen bonds [π ...Cl (light blue), C–H...Cl (orange)], and C–H... π (yellow), represented as dashed lines.

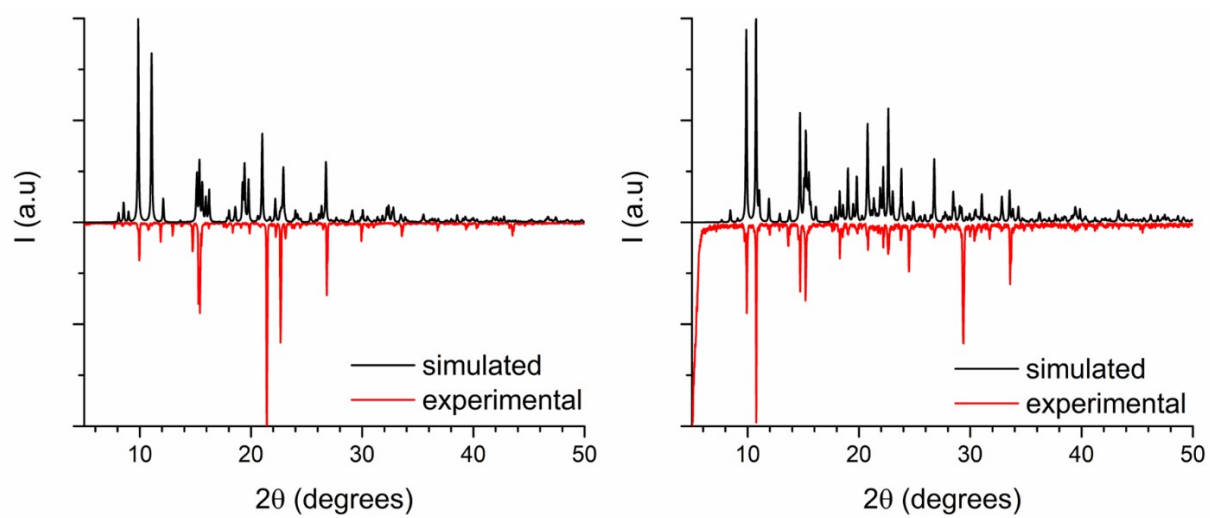
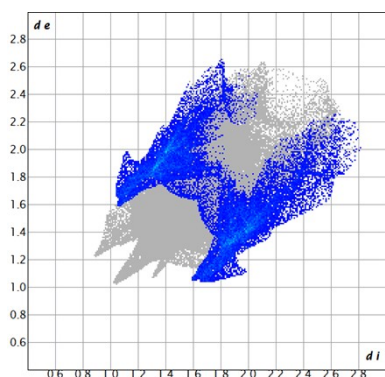
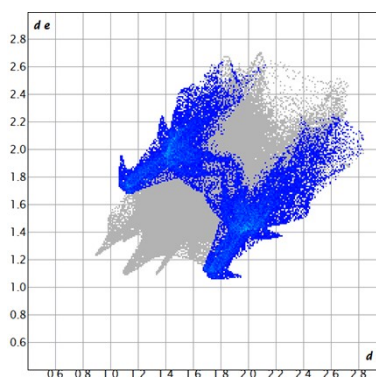


Figure S9. X-ray diffraction pattern of **1** (left) and **2** (right)

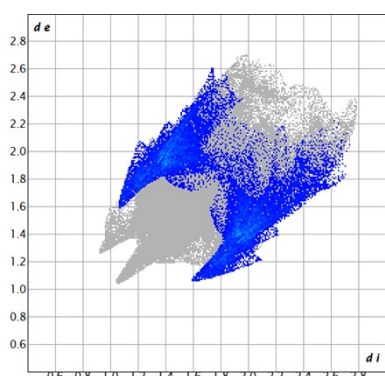
3. Hirshfeld Analysis



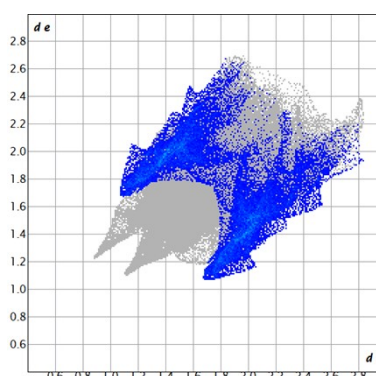
1 (LS state)
***C...H/H...C* 19.7%**



1 (HS state)
***C...H/H...C* 19.1%**

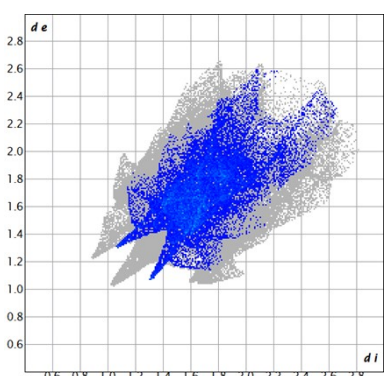


2 (LS state)
***C...H/H...C* 17.8%**

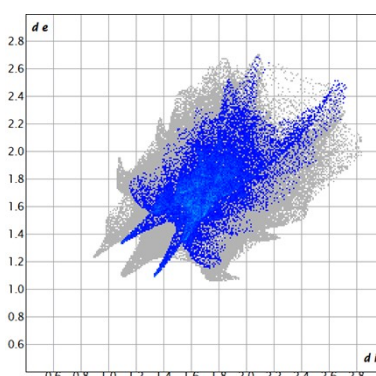


2 (HS state)
***C...H/H...C* 18.1%**

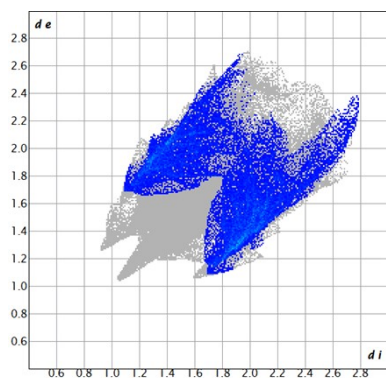
Figure S10. Two-dimensional fingerprint plots for the $H\cdots\pi$ ($H\cdots C$) intermolecular interactions of the metal complexes **1** and **2** in the LS state, on the left, and HS state, on the right.



1 (LS state)
***F...H/H...F* 17.2%**

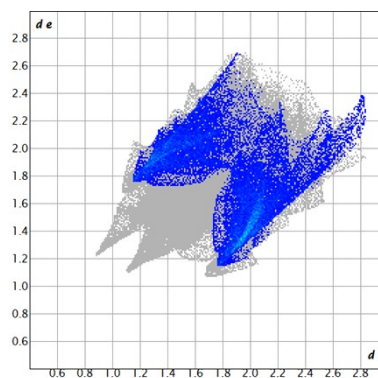


1 (HS state)
***F...H/H...F* 16.2%**



2 (LS state)

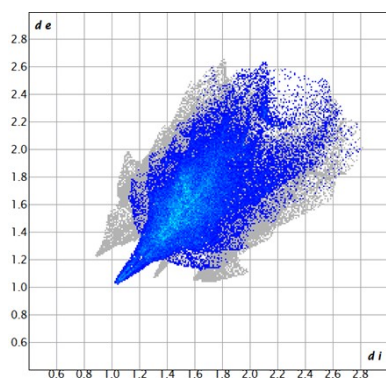
***Cl...H/H...Cl* 19.9%**



2 (HS state)

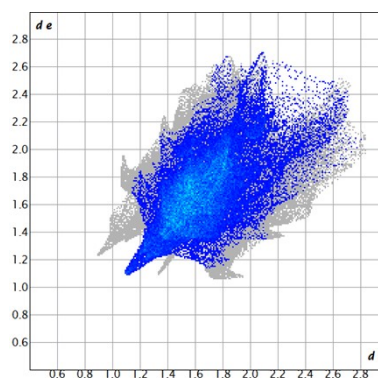
***Cl...H/H...Cl* 18.9%**

Figure S11. Two-dimensional fingerprint plots for the $H\cdots X$ intermolecular interactions of the metal complexes **1** and **2** in the LS state, on the left, and HS state, on the right.



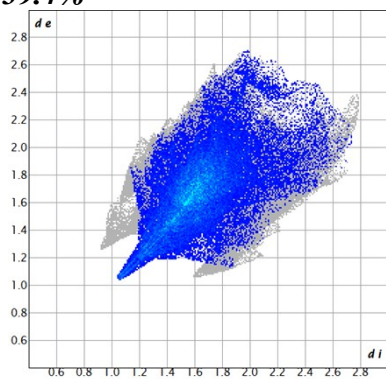
1 (LS state)

***H...H* 39.4%**



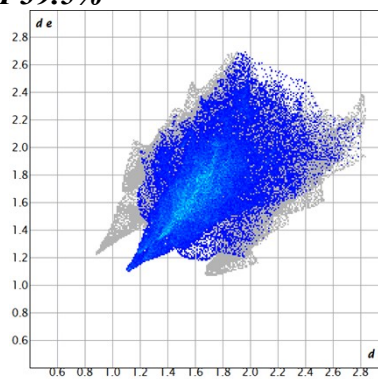
1 (HS state)

***H...H* 39.5%**



2 (LS state)

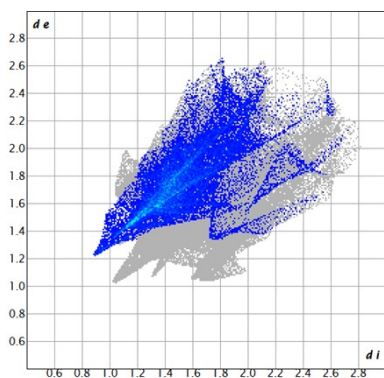
***H...H* 38.3%**



2 (HS state)

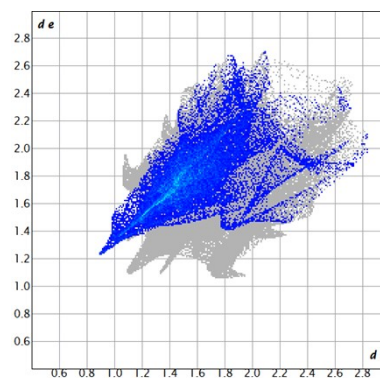
***H...H* 38.0%**

Figure S12. Two-dimensional fingerprint plots for the $H\cdots H$ intermolecular interactions of the metal complexes **1** and **2** in the LS state, on the left, and HS state, on the right.



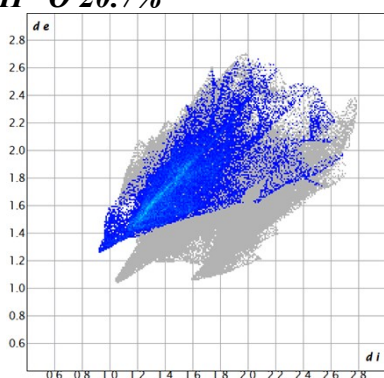
1 (LS state)

***O...H/H...O* 20.7%**



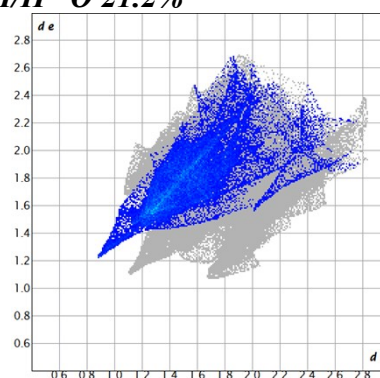
1 (HS state)

***O...H/H...O* 21.2%**



2 (LS state)

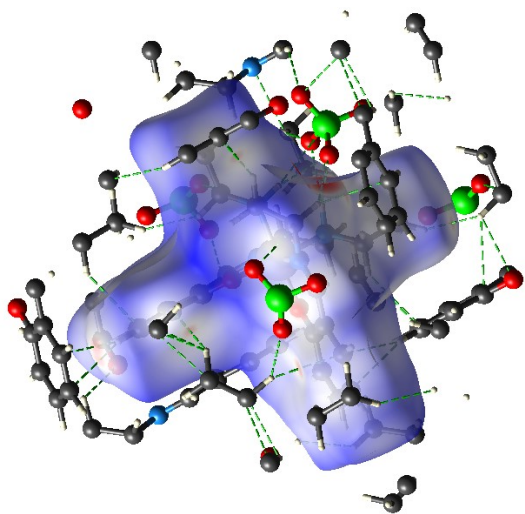
***O...H/H...O* 19.2%**



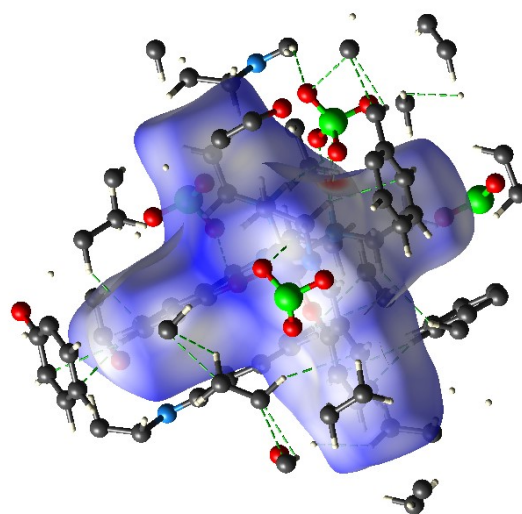
2 (HS state)

***O...H/H...O* 19.2%**

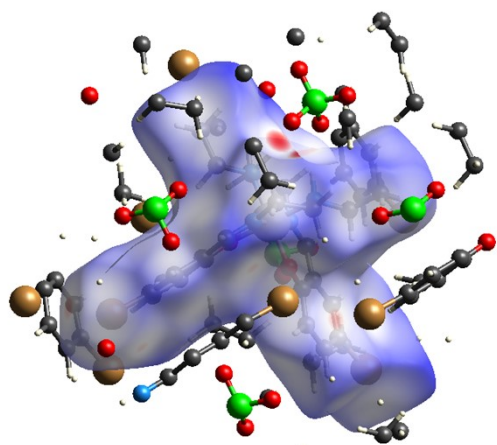
Figure S13 Two-dimensional fingerprint plots for the H...O intermolecular interactions of the metal complexes **1** and **2** in the LS state, on the left, and HS state, on the right.



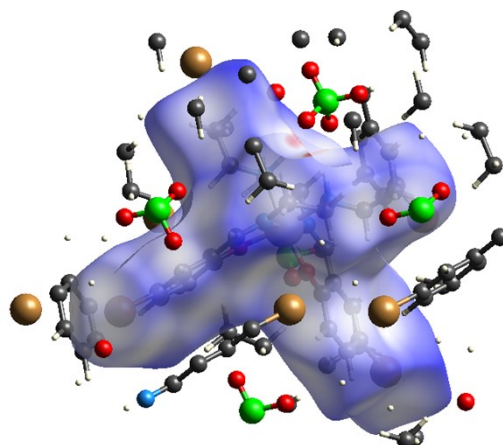
3 (100 K)



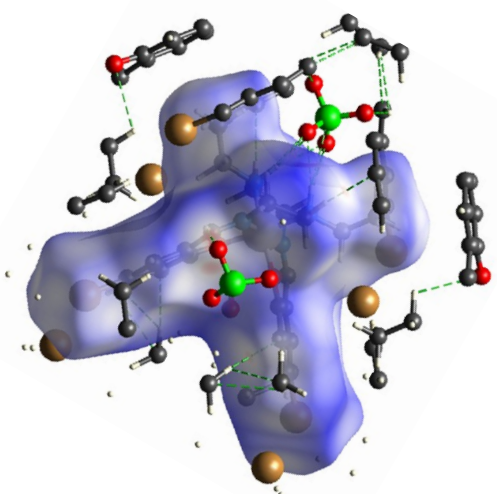
3 (300K)



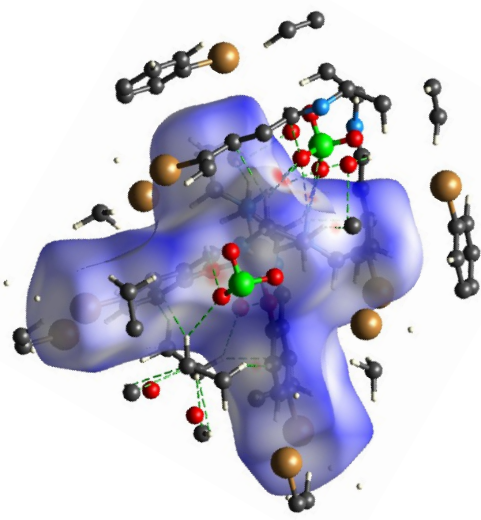
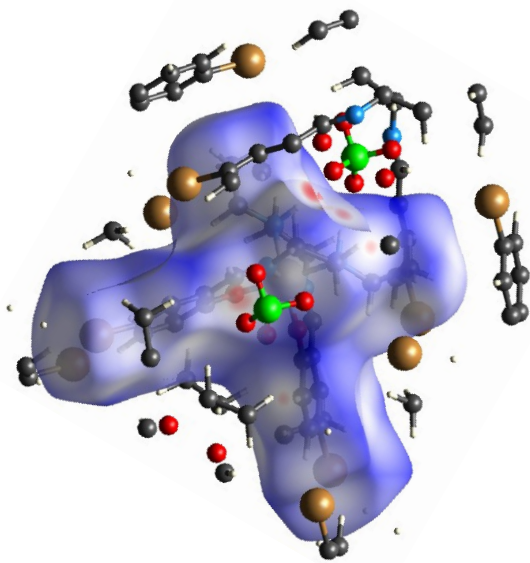
4a (150 K)



4a (300 K)

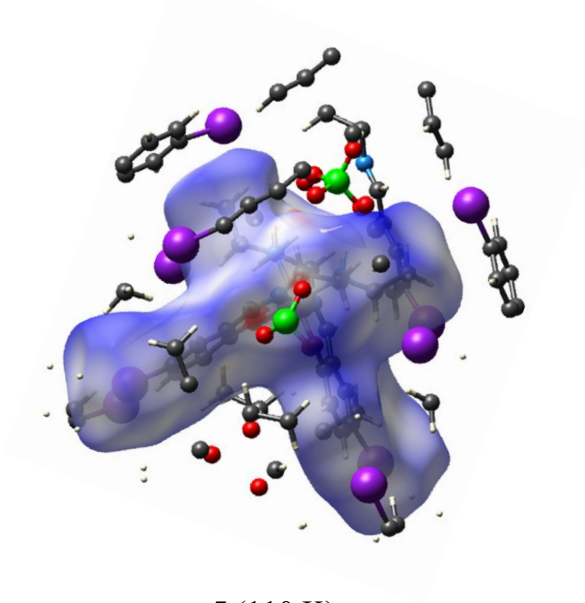


4b (110 K)

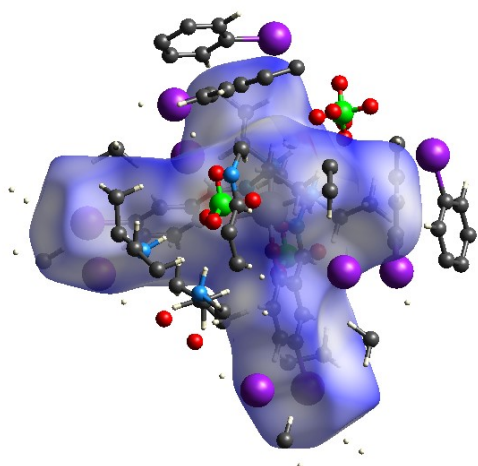


4b (300 K, cooling routine)

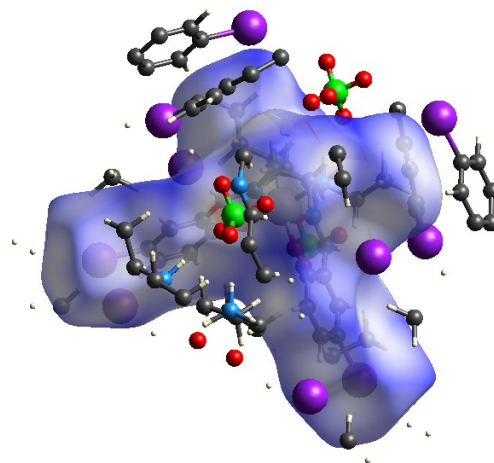
4b (300 K, heating routine)



5 (110 K)

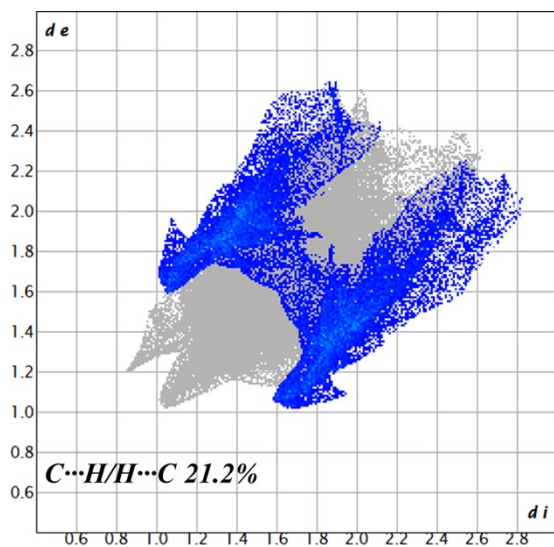


5 (350 K, heating routine)

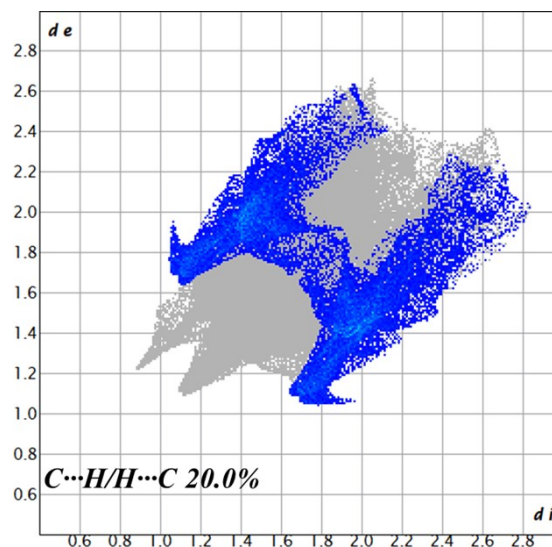


5 (350 K, cooling routine)

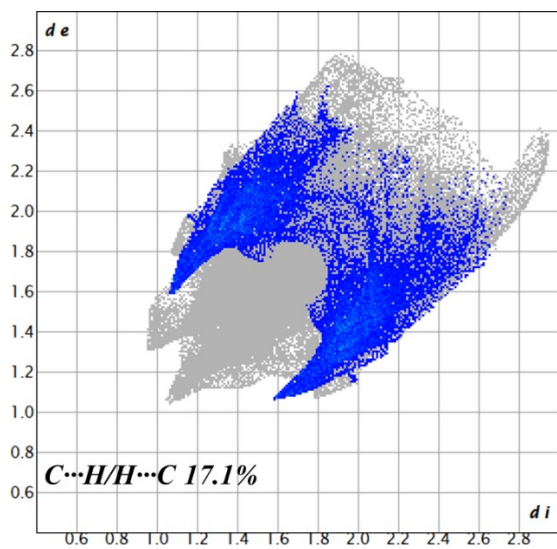
Figure S14. Hirshfeld surfaces within the crystal lattice for the metal complexes without substitution, the metal complexes containing Br and the metal complexes containing I excluding the ClO_4^- counterion from the surface. Low temperature or heating routines are depicted on left, whereas high temperatures or cooling routines are located on right. For these systems, the most strengthened intermolecular interactions are shown in red, which correspond to $\text{H}\cdots\text{O}$, $\text{H}\cdots\pi$, $\text{H}\cdots\text{X}$ and $\text{H}\cdots\text{H}$ interactions.



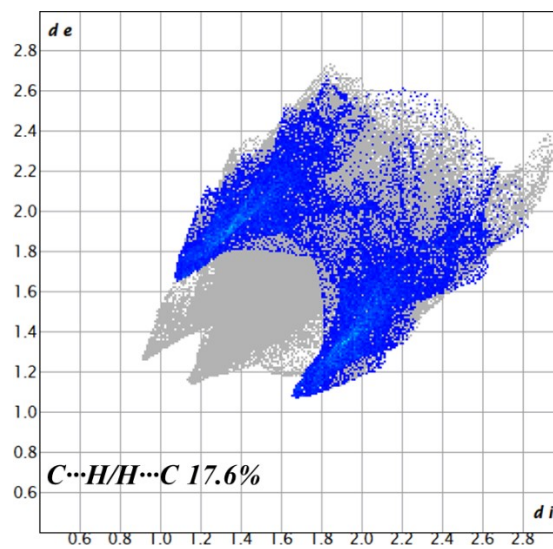
3 (100 K)



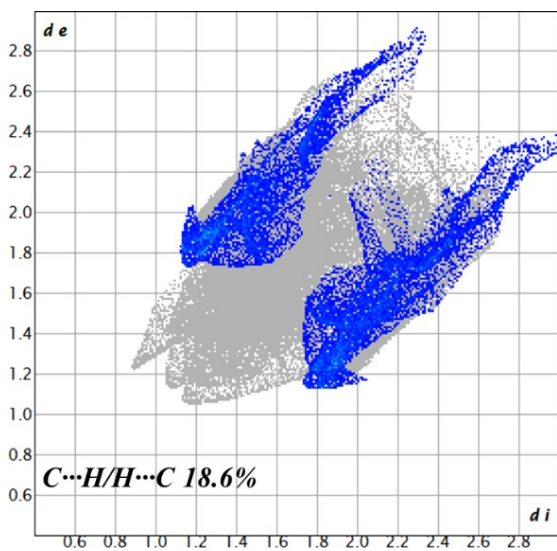
3 (300K)



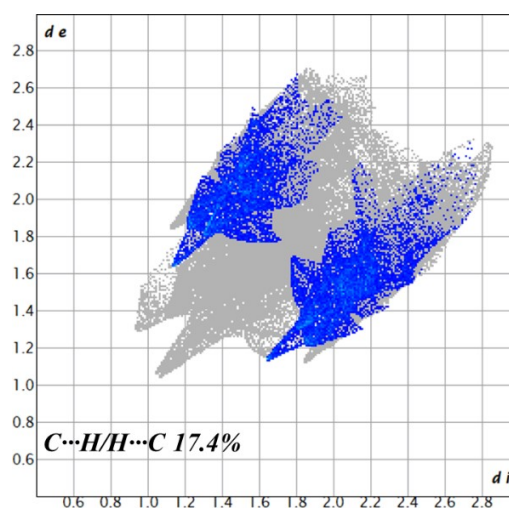
4a (150 K)



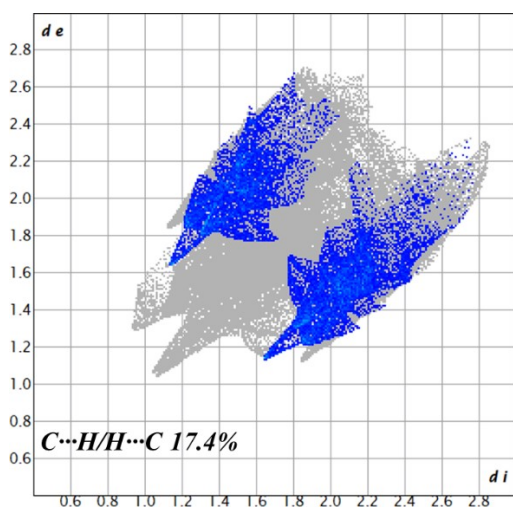
4a (300 K)



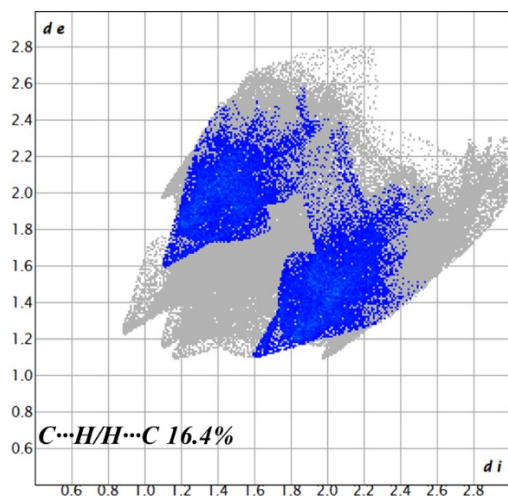
4b (110 K)



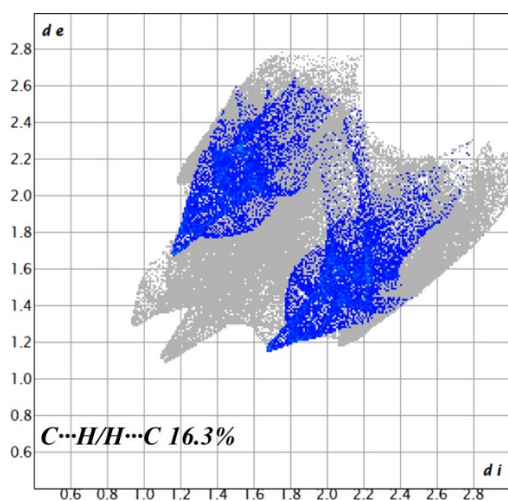
4b (300 K, cooling routine)



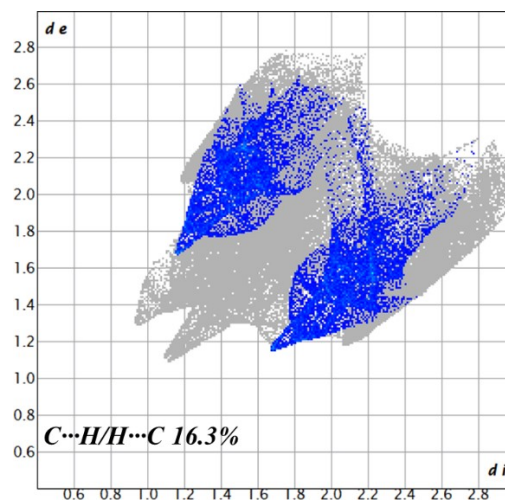
4b (300 K, heating routine)



5 (110 K)

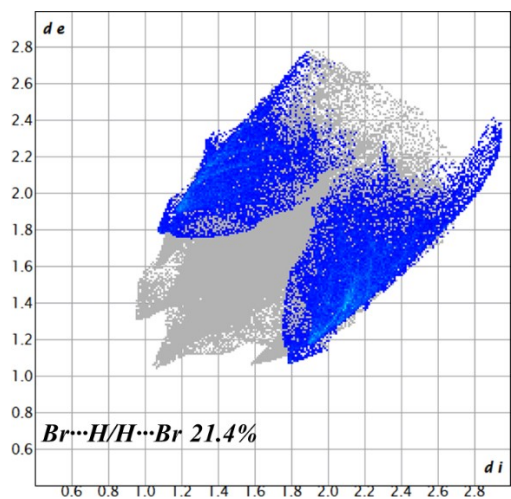


5 (350 K, heating routine)

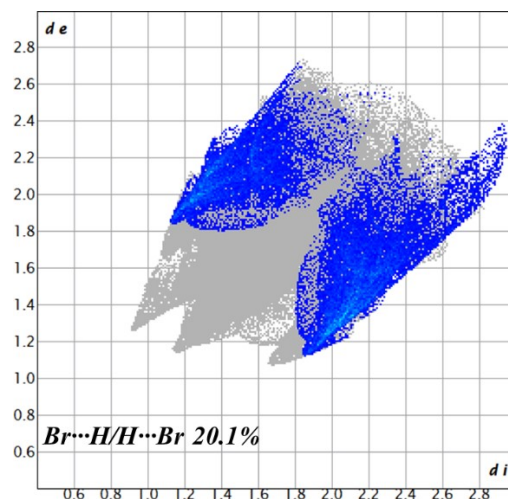


5 (350 K, cooling routine)

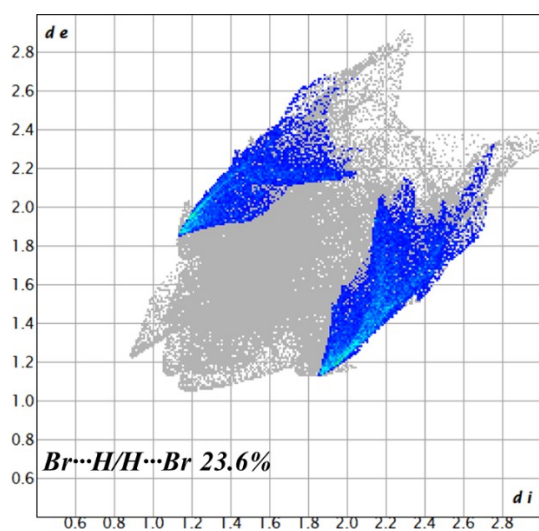
Figure S15. Two-dimensional fingerprint plots for the H $\cdots\pi$ (H \cdots C) intermolecular interactions for the metal complexes without substitution, the metal complexes containing Br and the metal complexes containing I at low temperatures or heating routines on the left and high temperatures or cooling routines are on the right.



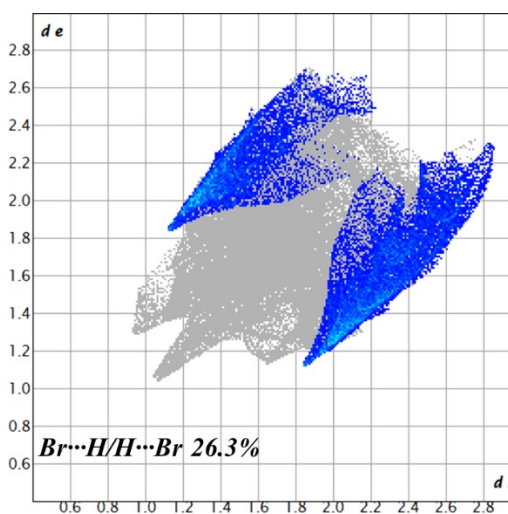
4a (150 K)



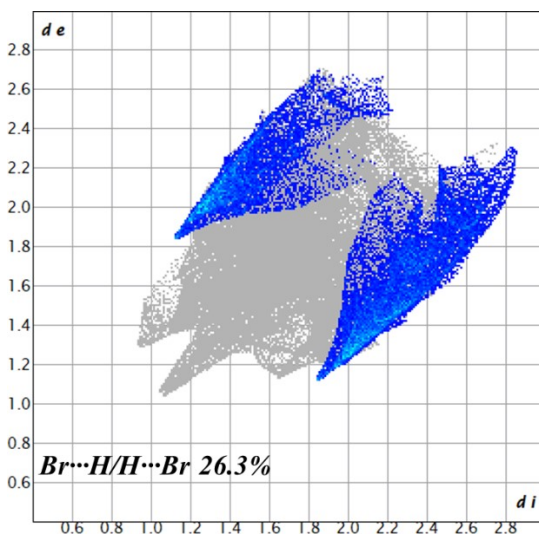
4a (300 K)



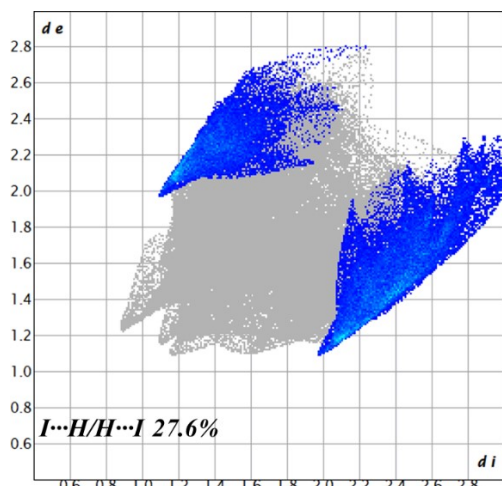
4b (110 K)



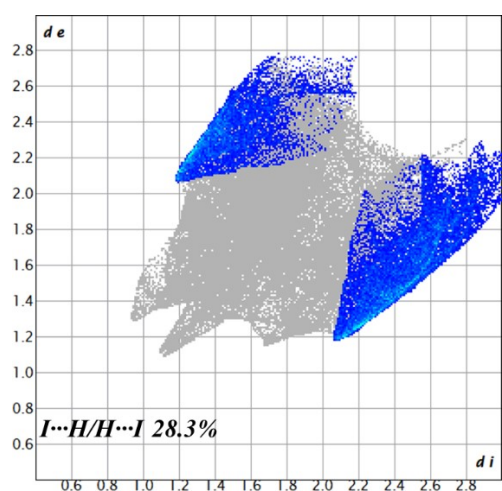
4b (300 K, cooling routine)



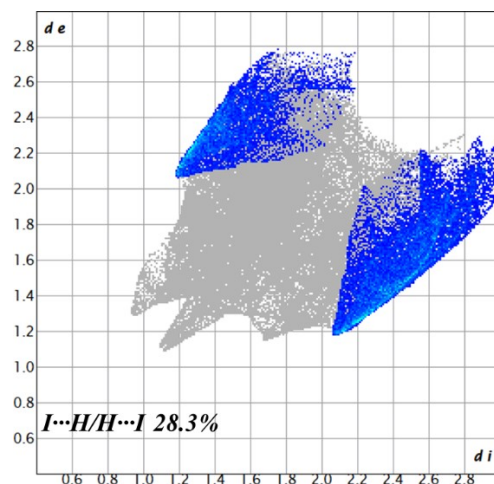
4b (300 K, heating routine)



5 (110 K)

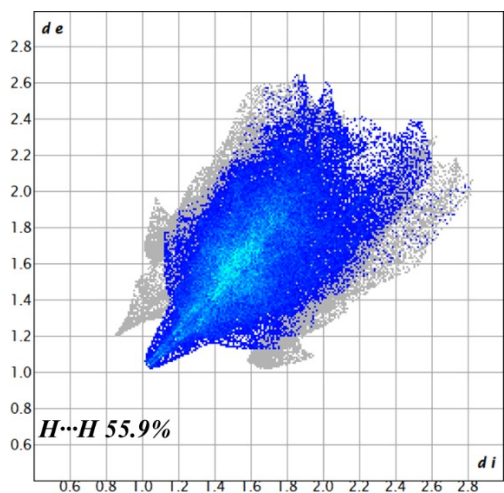


5 (350 K, heating routine)

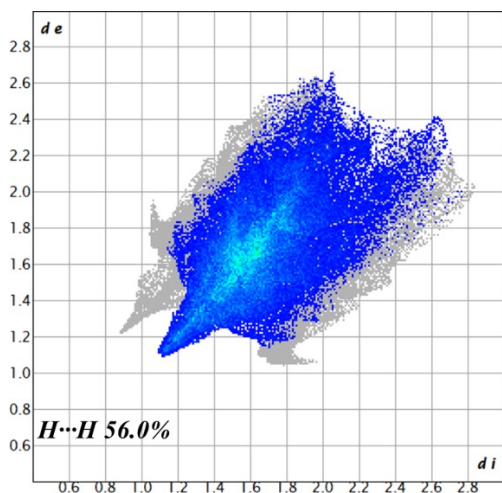


5 (350 K, cooling routine)

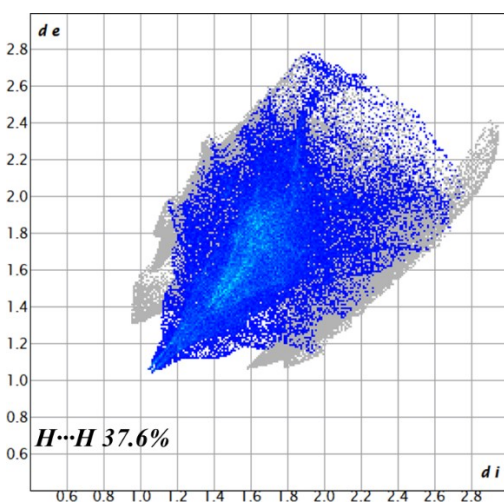
Figure S16. Two-dimensional fingerprint plots for the H \cdots X intermolecular interactions for the metal complexes without substitution, the metal complexes containing Br and the metal complexes containing I at low temperatures or heating routines on the left and high temperatures or cooling routines are on the right.



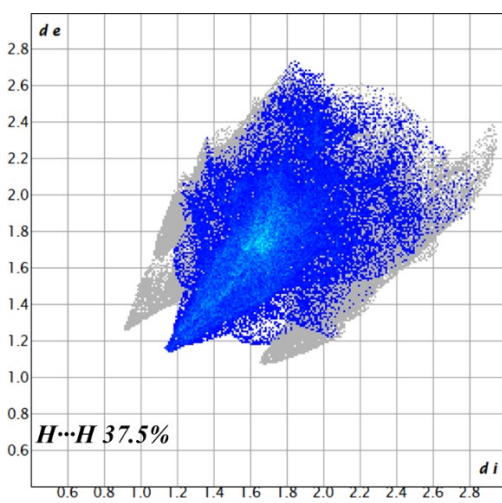
3 (100 K)



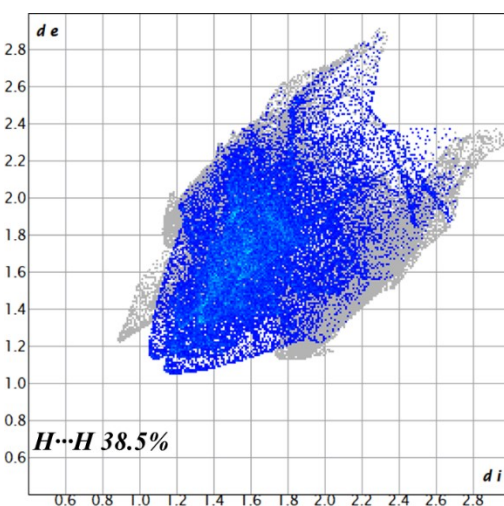
3 (300K)



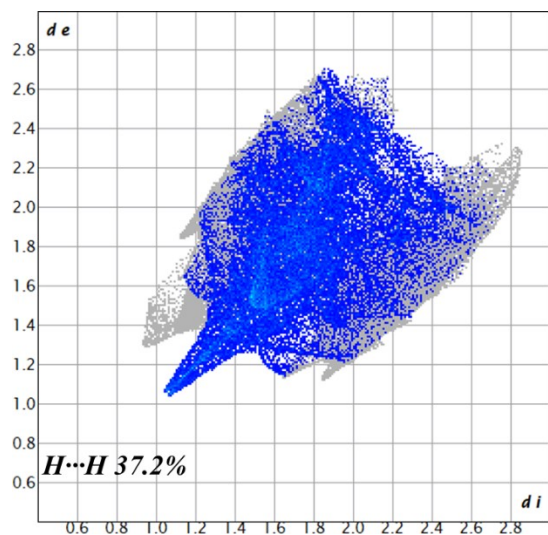
4a (150 K)



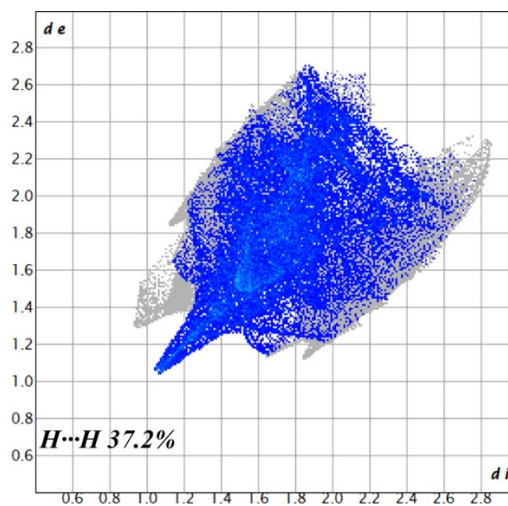
4a (300 K)



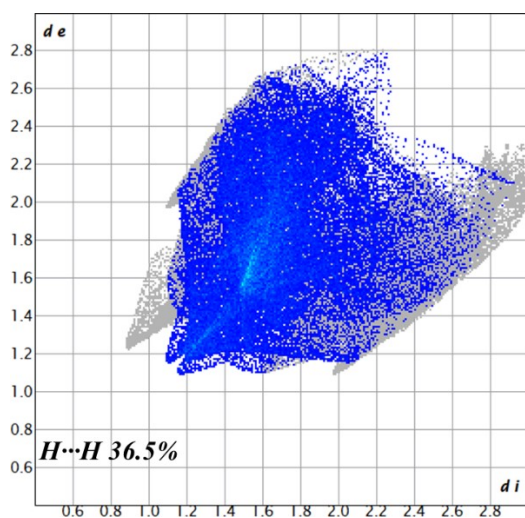
4b (110 K)



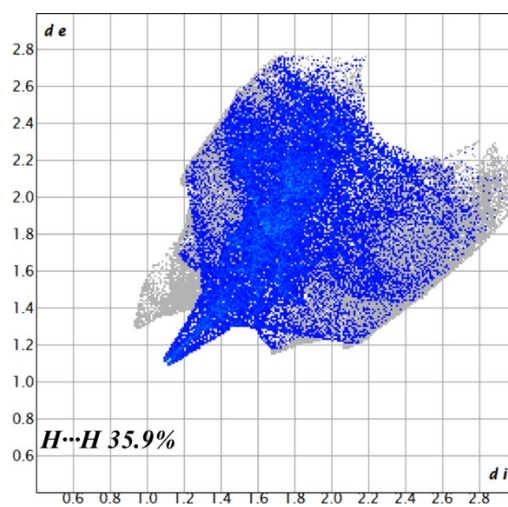
4b (300 K, heating routine)



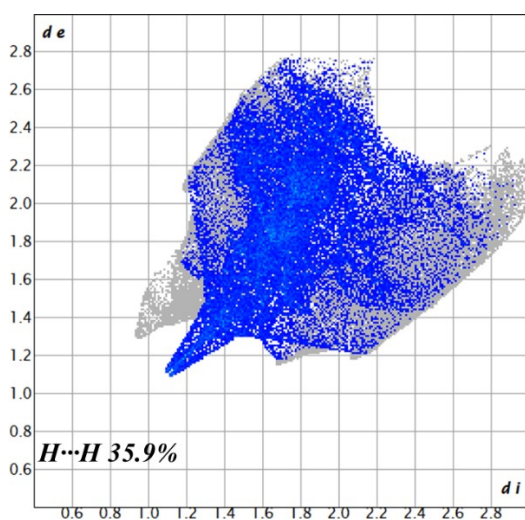
4b (300 K, cooling routine)



5 (110 K)



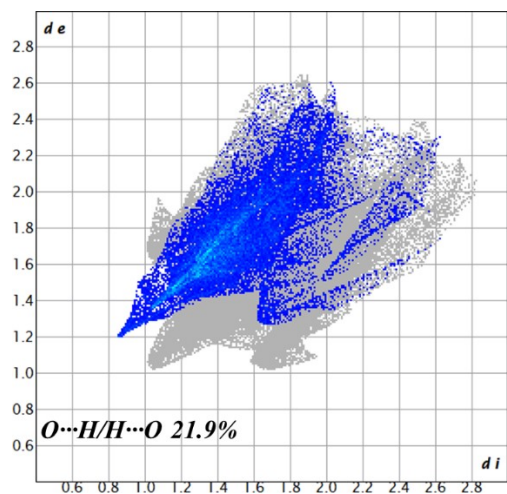
5 (350 K, cooling routine)



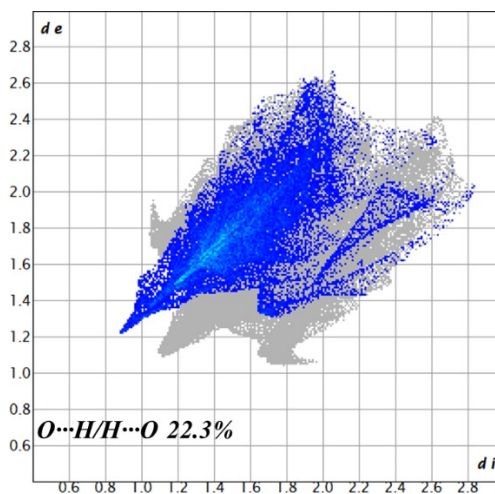
5 (350 K, heating routine)

Figure S17. Two-dimensional fingerprint plots for the H...H intermolecular interactions for the metal complexes without substitution, the metal complexes containing Br and the metal

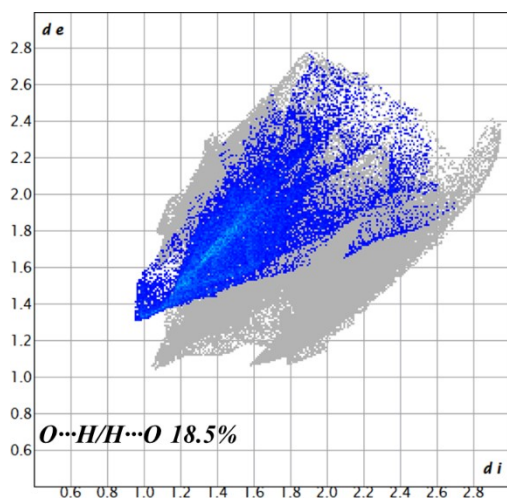
complexes containing I at low temperatures or heating routines on the left and high temperatures or cooling routines are on the right.



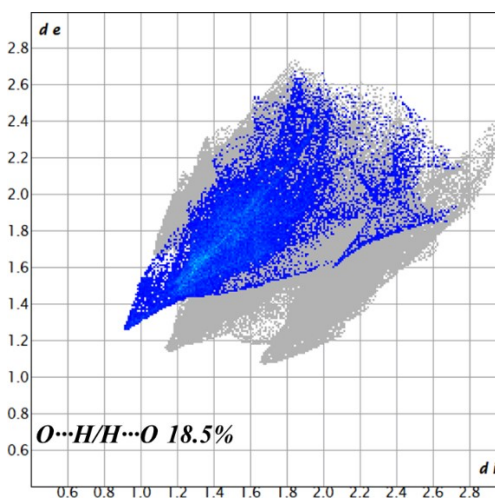
3 (100 K)



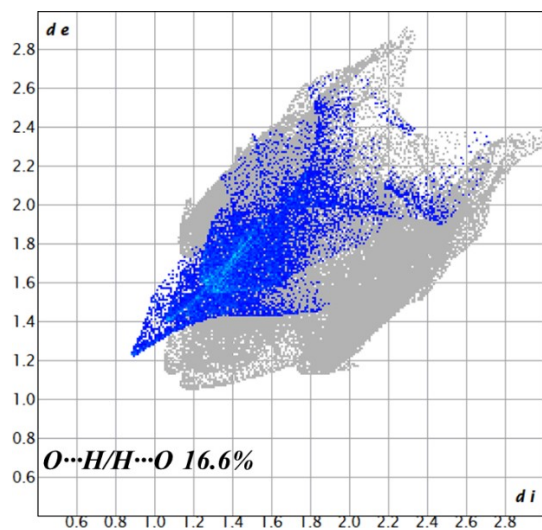
3 (300K)



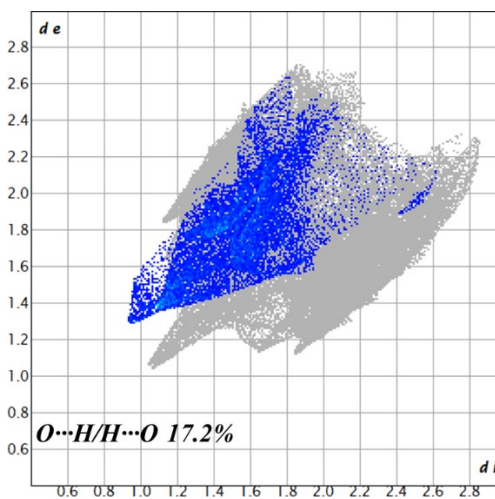
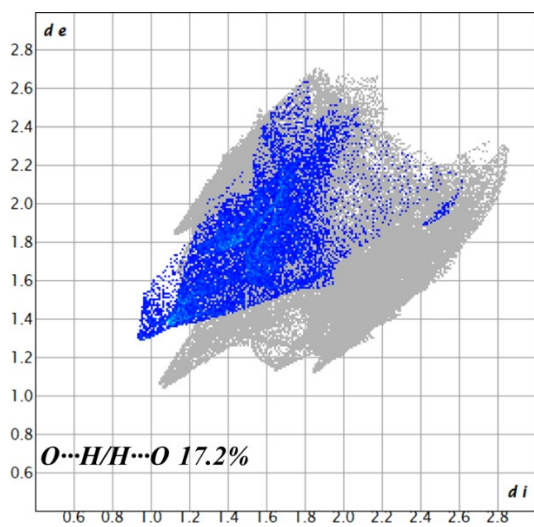
4a (150 K)



4a (300 K)

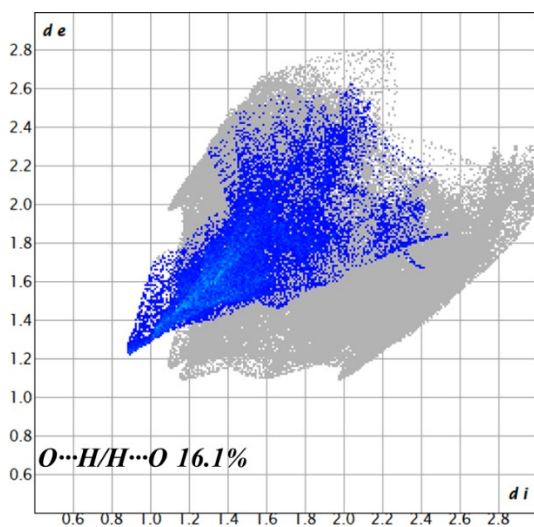


4b (110 K)

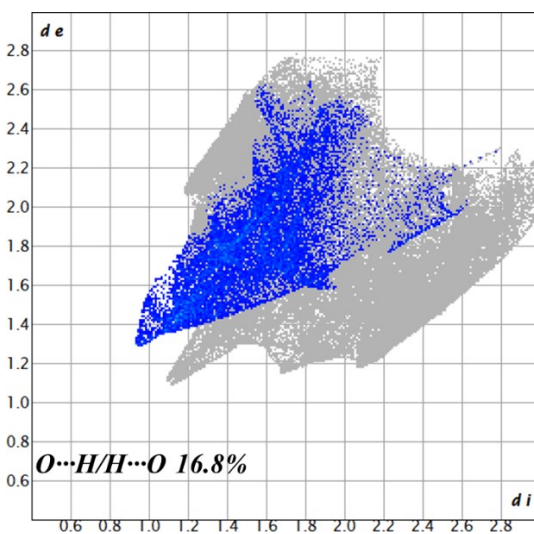


4b (300 K, cooling routine)

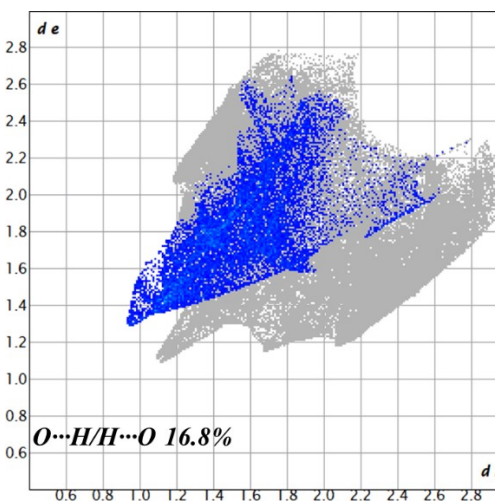
4b (300 K, heating routine)



5 (110 K)



5 (350 K, heating routine)



5 (350 K, cooling routine)

Figure S18. Two-dimensional fingerprint plots for the H \cdots O intermolecular interactions for the metal complexes without substitution, the metal complexes containing Br and the metal complexes containing I at low temperatures or heating routines on the left and high temperatures or cooling routines are on the right.

4. Magnetic and distortion parameters

Table S2. $T_{1/2}$ (K) values for all the compounds studied (1-5).

Compound	$T_{1/2}$ (K)
1	160*
2	195
3	215
4a	172
4b	300*
5	303*

* Apparent $T_{1/2}$ values that were calculated based on the maximum and minimum $\chi_M T$ values obtained for the temperature range studied.

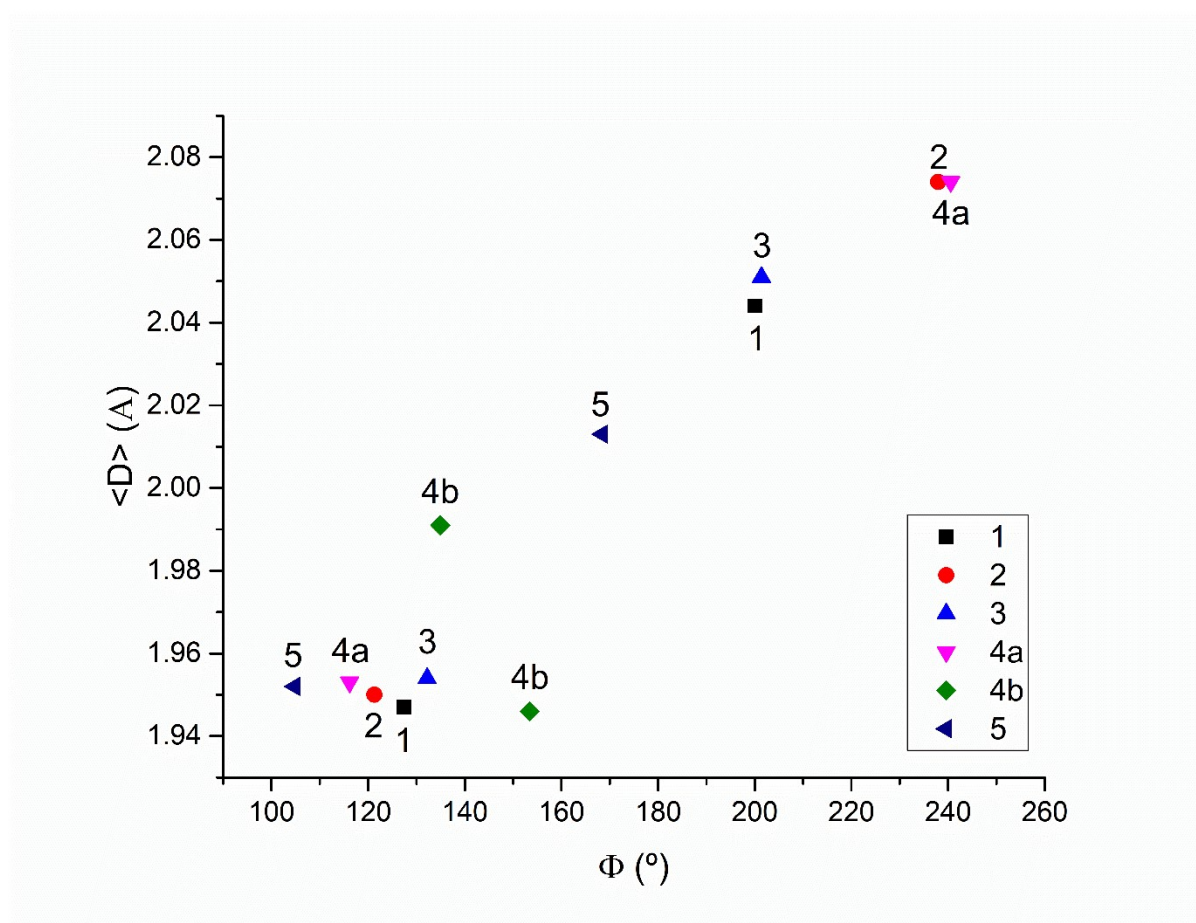


Figure S19. $\langle D \rangle$ vs Θ for compounds 1-5.