

# Supporting Information

## Structural features that modulate the sharpness of the spin crossover transition in $[\text{Fe}^{\text{III}}(5\text{-X-qsal})_2]^+$ based salts

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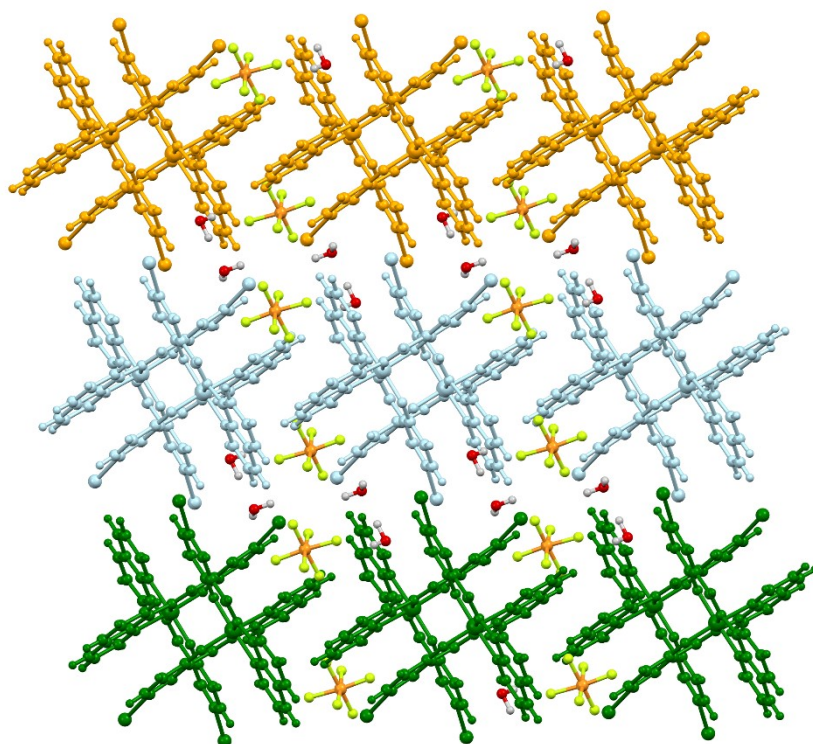
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**Fig. S1:** Chain Layers supramolecular structure in **4.PF<sub>6</sub>.1.5H<sub>2</sub>O**. Cations belonging to the same layer share the same color: top layer orange cations, middle layer light blue cations and bottom layer green cations.

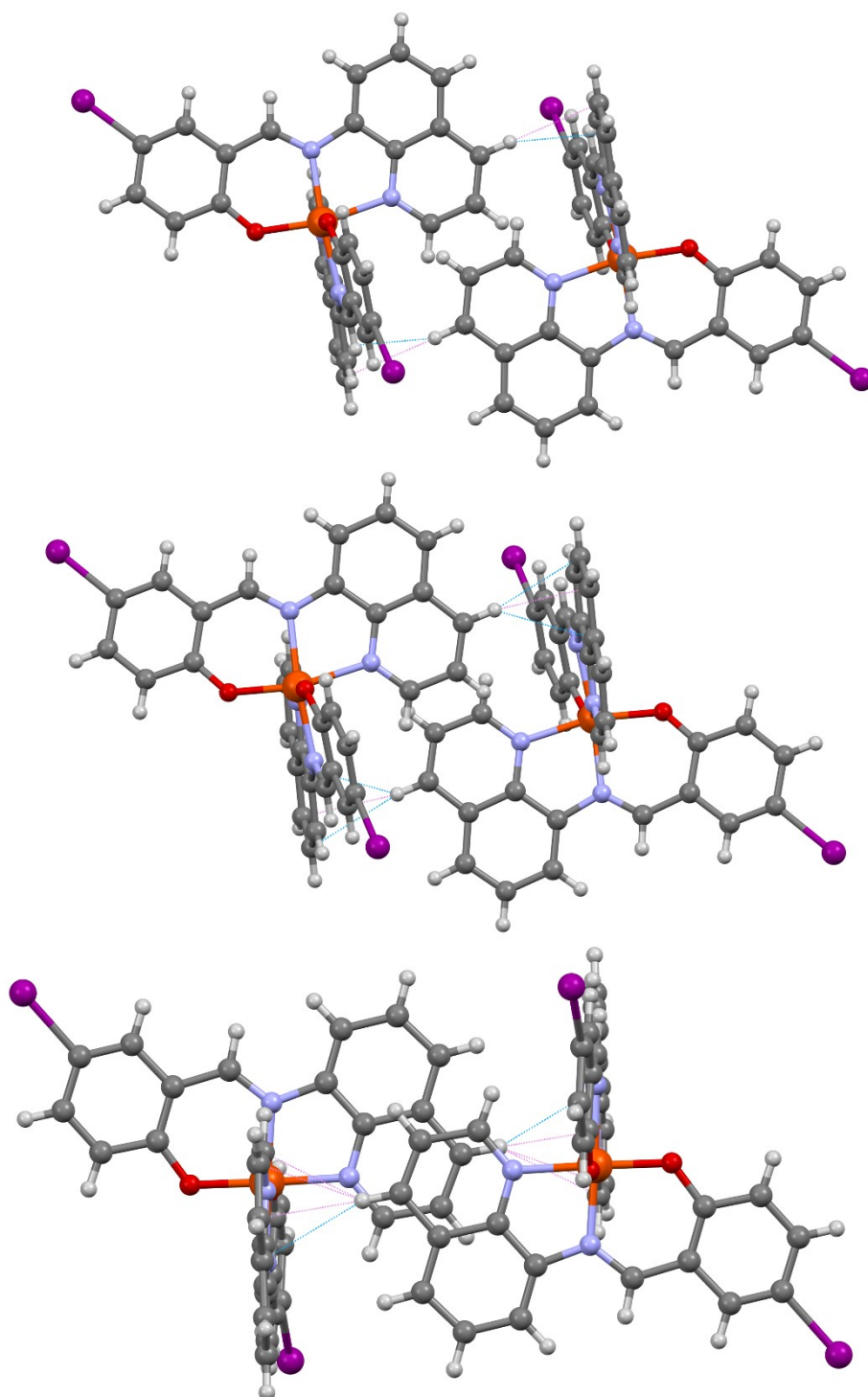
**Fig. S2:** Overlap of the Qn fragments in the interchain connectivity between cations of **4.CF<sub>3</sub>SO<sub>3</sub>.iPrOH** (top), **4.CF<sub>3</sub>SO<sub>3</sub>.nPrOH** (center) and **4.CF<sub>3</sub>SO<sub>3</sub>.MeOH** (bottom). The short contacts colour code corresponds to the difference,  $\Delta$  in Å, between the distance of the contact and the sum of the van der Waals radii of the involved atoms: violet  $\Delta < -0.1$ ; light blue  $\Delta < 0.0$ .

**Fig. S3:** Interlayer DD and DAD connectivity of cations regarding **2.PF<sub>6</sub>.MeCN** (a and d), **3.PF<sub>6</sub>.H<sub>2</sub>O** (b and e) and **5.PF<sub>6</sub>.1.5H<sub>2</sub>O** (c and f). The short contacts colour code corresponds to the difference,  $\Delta$  in Å, between the distance of the contact and the sum of the van der Waals radii of the involved atoms: violet  $\Delta < -0.1$ ; light blue  $\Delta < 0.0$ ; orange  $\Delta < 0.1$ .

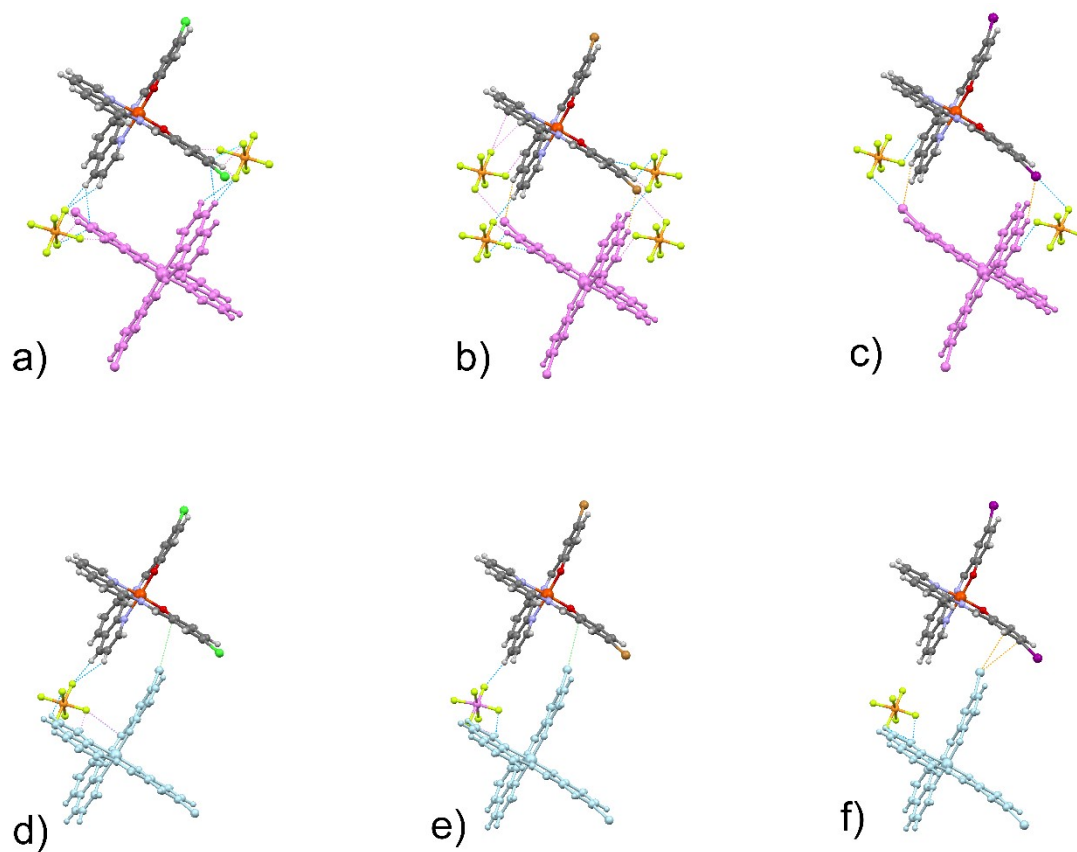
**Fig. S4:** Interlayer DD and DAD contacts in **1.I<sub>3</sub>**. Cations in the same layer have the same color (top layer orange and bottom layer light blue). The short contacts colour code corresponds to the difference,  $\Delta$  in Å, between the distance of the contact and the sum of the van der Waals radii of the involved atoms: violet  $\Delta < -0.1$ ; light blue  $\Delta < 0.0$ . (adapted from Figure S18 of reference [7]).



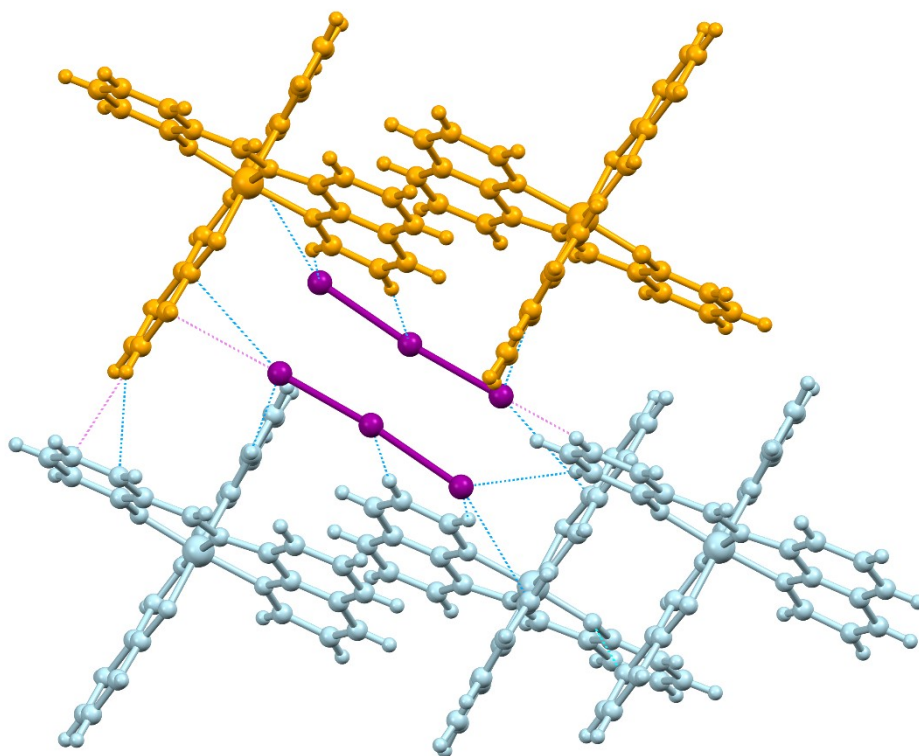
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