Supporting Information

Unravelling the Spin-state of solvated \([\text{Fe(bpp)}_2]^{2\text{+}}\) Spin-crossover Complexes: Structure-Function Relationship

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**Figure S1:** View of the crystal structure of the hydrated salt \([\text{Fe(bpp)}_2][\text{N(CN)}_2]_2\cdot\text{1H}_2\text{O}\) (2) showing the first and second coordination spheres for the \(\text{Fe}^{2+}\) cation. Carbon, nitrogen and hydrogen atoms are shown as black, blue and light-pink, respectively.

**Figure S2:** (a) A projection of the crystal structure of 2 showing (a) alternating cationic and anionic layers onto the \(zy\) plane and (b) the arrangement of \([\text{Fe(bpp)}_2]^{2\text{+}}\) units onto the \(xz\) plane (yellow lines refer to \(\pi-\pi\) interactions). H atoms are omitted for clarity. Color code for the atoms as it is indicated as follow: carbon, nitrogen, oxygen and hydrogen atoms are shown as black, blue, red and light-pink, respectively.
**Figure S3:** Weigh loss for the deshydration of 1.

**Figure S4:** a) TGA and DSC (curve 1: original sample in the heating mode, curve 2: subsequent temperature cycle in the cooling mode) of compound 2.

**Figure S5:** Temperature dependence of $\chi_m T$ in the temperature range between 2–400K on heating and cooling mode for 2 and the rehydrated sample (2r). Successive temperature cycles (on cooling and heating mode) have been omitted for simplicity, as they all go through the same place.
Figure S6: a) View of the [Fe(bpp)$_2$]$^{2+}$ layer in 1 down the y axis. Fe(1) is shown yellow and Fe(2) blue. Color code for the atoms as it is indicated in Figure S2. H atoms are omitted for clarity. B) Temperature dependence of $\chi_m T$ for compound 1 in the 2–400 K range.

Figure S7: View of the [Fe(bpp)$_2$]$^{2+}$ layer in 2 down the y axis. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S2. B) Temperature dependence of $\chi_m T$ for compound 2 in the 2–400 K range.

Figure S8: View of the [Fe(bpp)$_2$]$^{2+}$ layer in 4 down the y axis. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S2. B) Temperature dependence of $\chi_m T$ for compound 3 in the 2–400 K range.
Figure S9: Composition of the second coordination sphere of the HS and LS Fe$^{2+}$ centers for 5, 7 and 9. The same color has been used for all the atoms for the same crystallographic anion for the sake of clarity.

Figure S10: Supramolecular synthon ([HchtCl]$_{2}^{+}$) found in the crystal structure of 5. Carbon, oxygen and hydrogen atoms are shown as black, red and pink, respectively.
Figure S11: View of the crystal structure of the hydrated salt [Fe(bpp)$_2$]$_2$ [Cr(ox)$_3$]ClO$_4$·5H$_2$O showing the first and second coordination spheres for the two crystallographic independent Fe$^{2+}$ cations, Fe(1) (a) and Fe(2) (b). Carbon, oxygen and nitrogen atoms are shown as black, red and light-blue, respectively. H atoms are omitted for clarity.

Figure S12: View of the [Fe(bpp)$_2$]$^{2+}$ layer in 7. H atoms are omitted for clarity. B) Temperature dependence of $\chi_m T$ for compound 7 in the 2–400 K range.
Figure S13: View of the $[\text{Fe(bpp)}_2]^2^+ \text{ layer in 8 down the } x \text{ axis. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S2. B) Temperature dependence of } \chi_m T \text{ for compound 8 in the } 2–400 \text{ K range.}$

Figure S14: View of the $[\text{Fe(bpp)}_2]^2^+ \text{ layer in 9 down the } x \text{ axis. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S2. B) Temperature dependence of } \chi_m T \text{ for compound 9 in the } 2–400 \text{ K range.}$

Figure S15: View of the $[\text{Fe(bpp)}_2]^2^+ \text{ layer in 9r down the } x \text{ axis. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S4. B) Temperature dependence of } \chi_m T \text{ for compound 9r in the } 2–400 \text{ K range.}$
Figure S16: View of the [Fe(bpp)$_2$]$_2^+$ layer in 10 onto the xy plane. H atoms are omitted for clarity. Color code for the atoms as it is indicated in Figure S2. B) Temperature dependence of $\chi_m T$ for compound 10 in the 2–400 K range.

Figure S17: $\pi-\pi$ stacking interactions between bpy ligands of neighboring [Cr(bpy)(ox)$_3$] anions (3.583(2)–3.742(1) Å) for 8 are shown here in yellow.
Figure S18: π-π stacking interactions between bpy ligands of neighboring [Cr(bpy)(ox)]_2^- anions (3.270(4) Å) and between a bpy ligand and a bpp ligand (3.317(5)–3.341(5) Å) for 6 are shown here in yellow and light-orange, respectively.

Figure S19: Aryl–aryl interactions between [Fe(bpp)]^{2+} complexes (3.204(3) Å) within a 2D layer for 8 are shown here in yellow.