Supplementary information for

"Spin state behavior of a spin-crossover iron(II) complex with N,N'-disubstituted 2,6-bis(pyrazol-3-yl)pyridine: a combined study by X-ray diffraction and NMR spectroscopy"

by

Elizaveta K. Melnikova,[ab] Dmitry Yu. Aleshin,[ac] Igor Nikovskiy,[a] Gleb L. Denisov,[a] Yulia V. Nelyubina*[a]

[a]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991, Vavilova Str., 28, Moscow, Russia, e-mail: unelya@ineos.ac.ru

[b]Lomonosov Moscow State University, 119991, Leninskiye Gory, 1-3, Moscow, Russia

[c]Mendeleev University of Chemical Technology of Russia, 125047, Miusskaya pl., 9, Moscow, Russia

Supplementary Figures

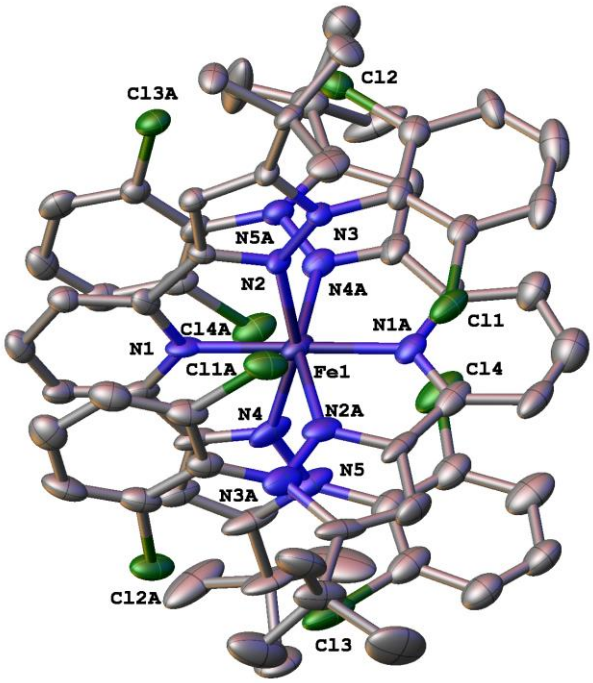

Figure S1. General view of the cation $[Fe(\mathbf{L})_2]^{2+}$ in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (red) from X-ray diffraction at 120 K. Hydrogen atoms and a minor components of the disordered t-butyl group are omitted for clarity, non-hydrogen atoms are shown as thermal ellipsoids (p = 25%), and only labels of the heteroatoms in an asymmetric part of the unit cell are given.

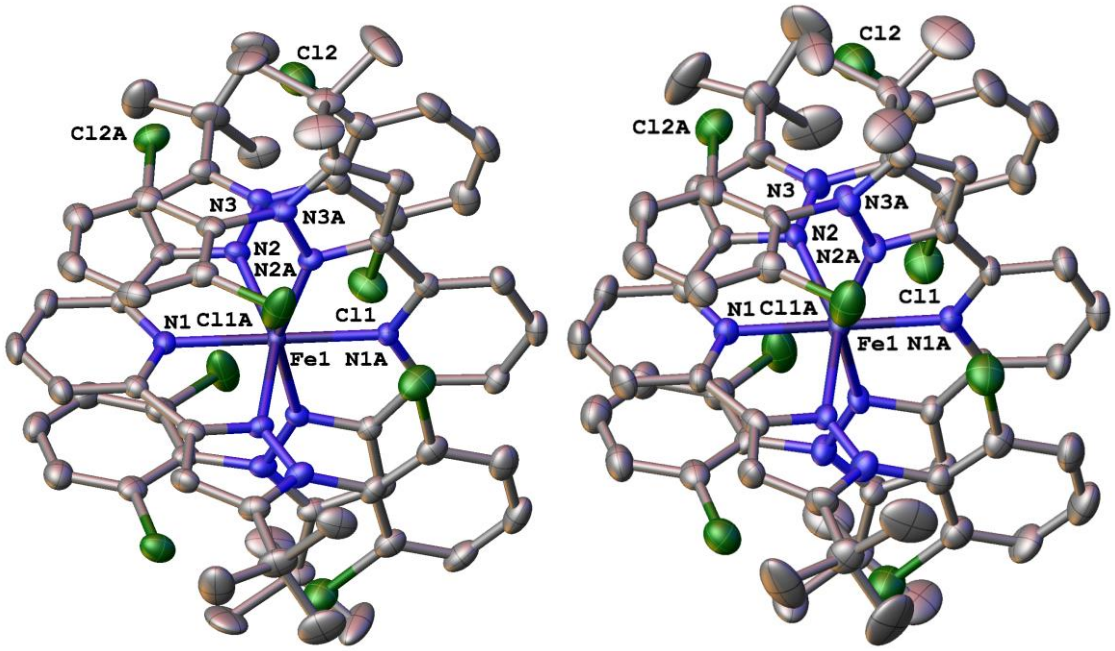

Figure S2. General view of the cation $[Fe(\mathbf{L})_2]^{2+}$ in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (yellow) from X-ray diffraction at 120 K (left) and 293 K (right). Hydrogen atoms and a minor components of the four disordered t-butyl groups are omitted for clarity, non-hydrogen atoms are shown as thermal ellipsoids (p = 50 and 30%, respectively), and only labels of the heteroatoms in an asymmetric part of the unit cell are given, as the complex occupies a special position, a two-fold axis that passes through the metal ion along the line N_{Py}-M-N_{Py}.

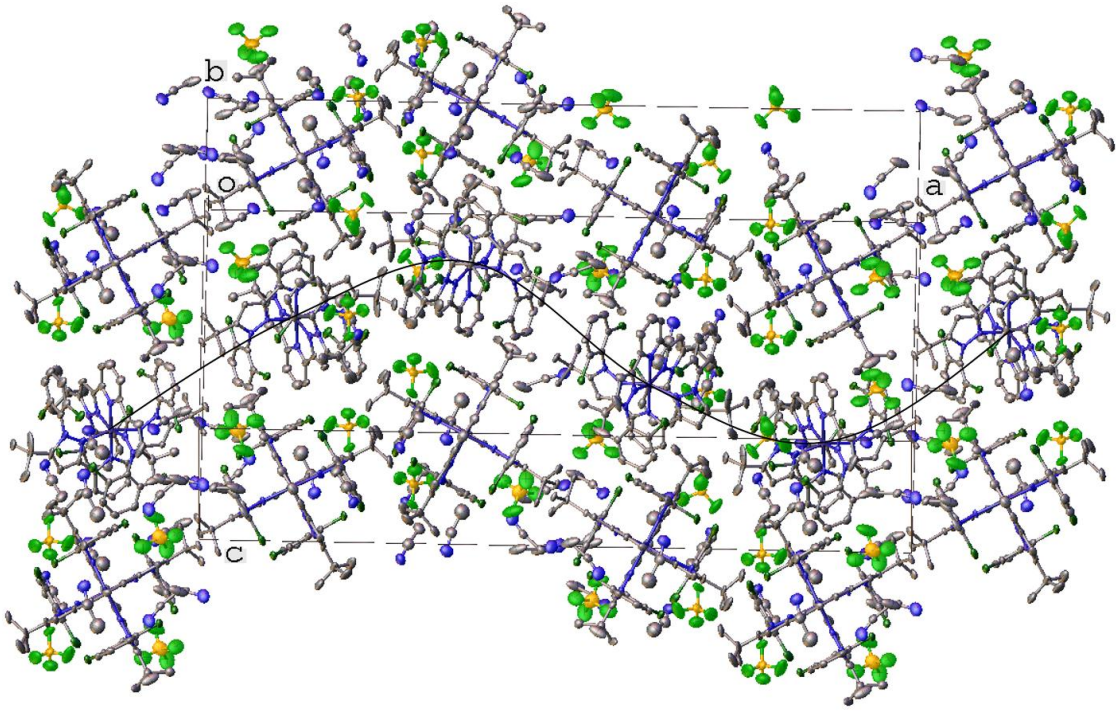

Figure S3. A fragment of the crystal packing in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (red).

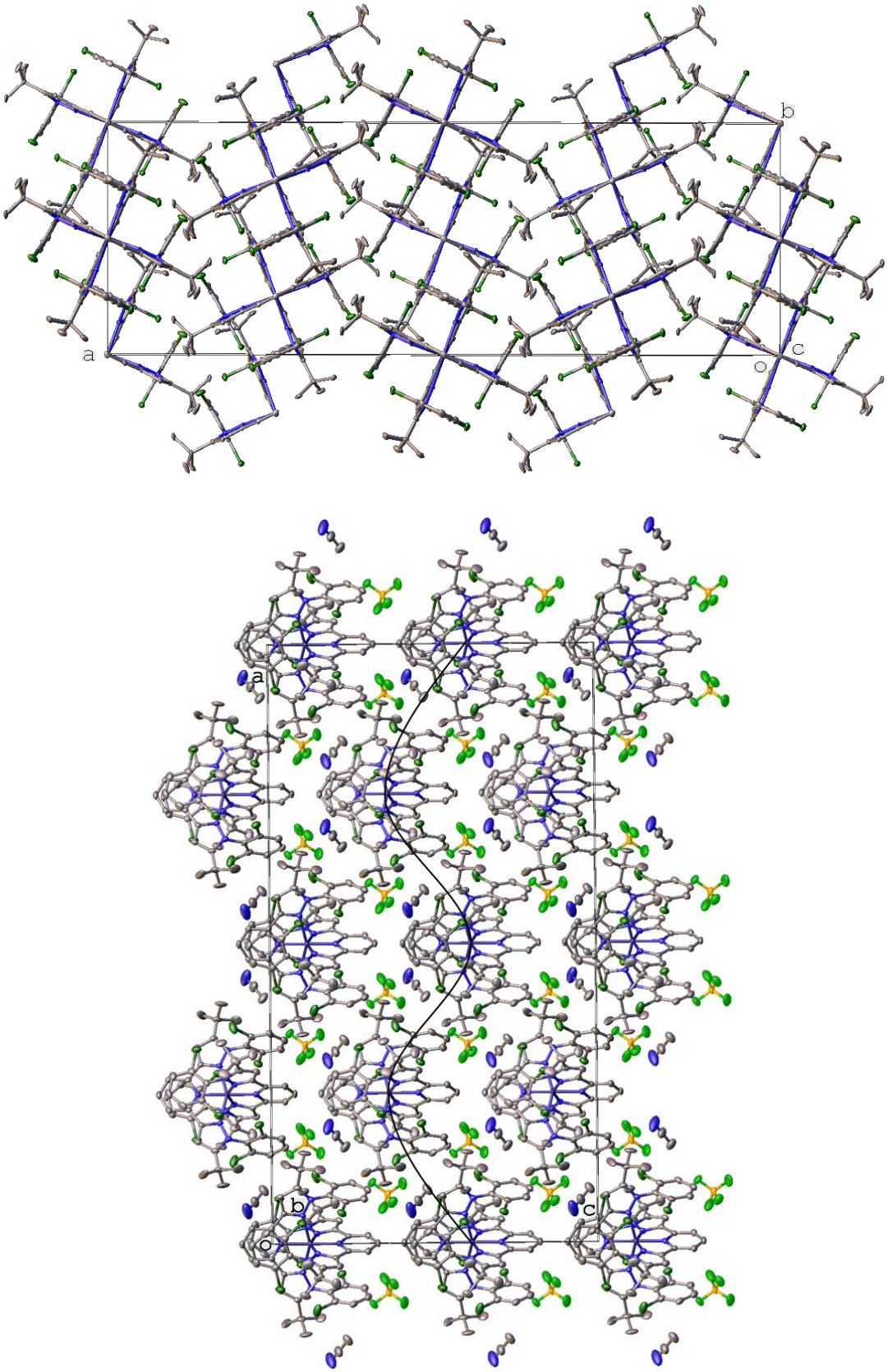

Figure S4. 'Terpyridine-embrace'-like (top) and spiral-like (bottom) packing of the cations $[Fe(\mathbf{L})_2]^{2+}$ in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (yellow).

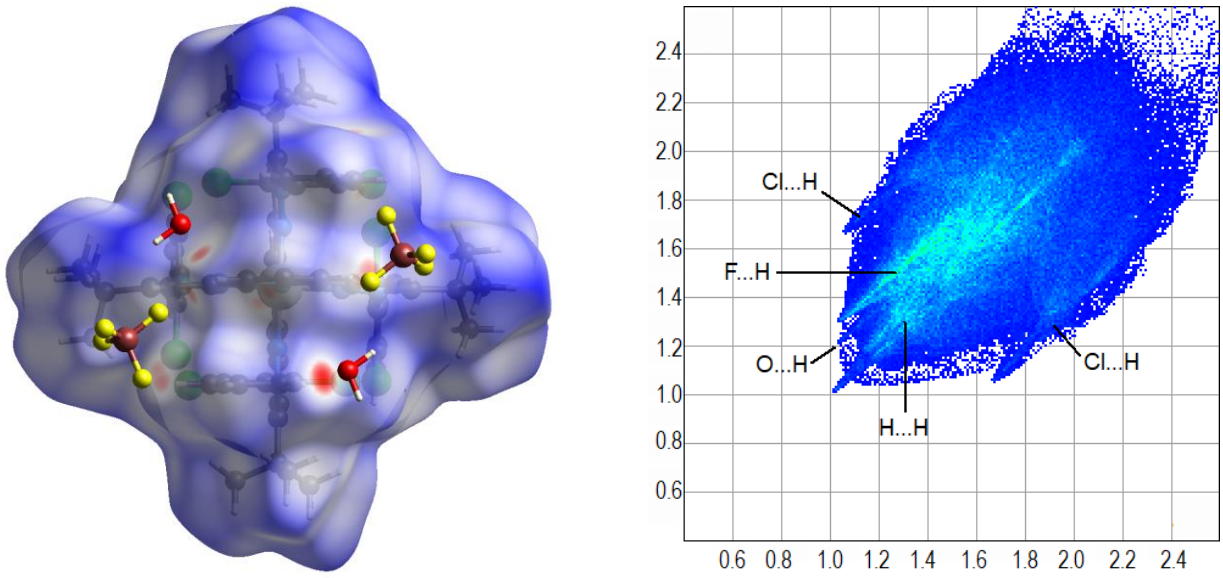

Figure S5. Hirshfeld surface (left) of the cation $[Fe(\mathbf{L})_2]^{2+}$ in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 0.5H_2O$ (red) and a 2D fingerprint plot (right) as generated by *Crystal Explorer*. On the Hirshfeld surfaces (left), intermolecular interactions with interatomic distances below, equal or above a sum of van-der-Waals radii are shown by red, white and blue areas, respectively. Green and blue areas on fingerprint plots (right) stand for higher and lower concentration of points corresponding to (di, de) pairs.

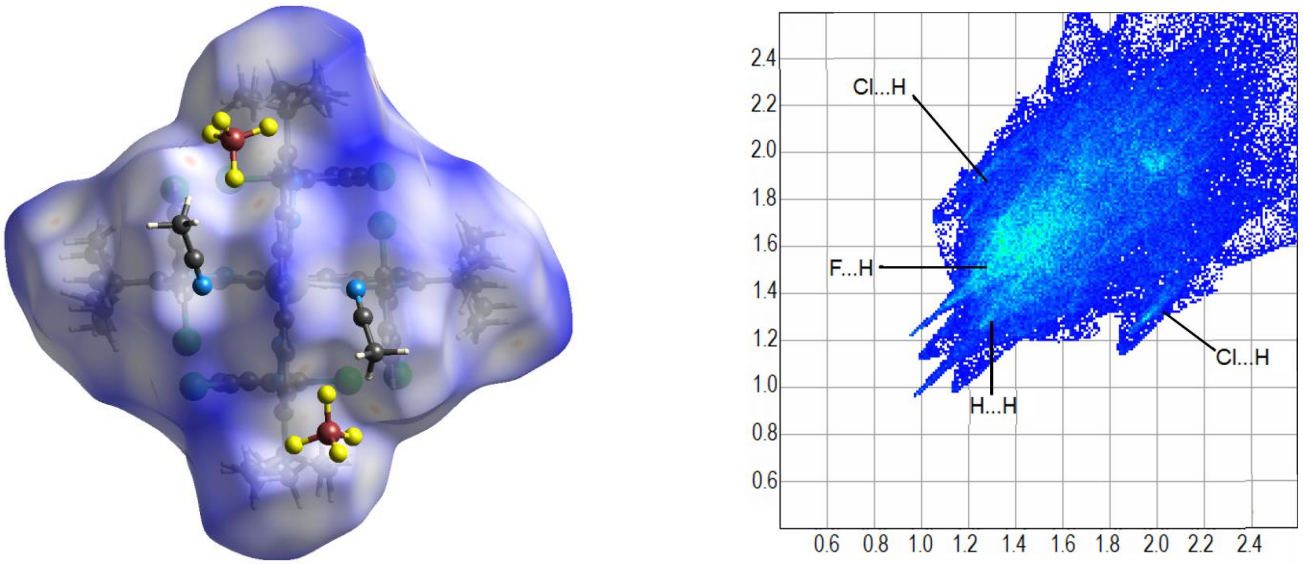

Figure S6. Hirshfeld surface of the cation $[Fe(\mathbf{L})_2]^{2+}$ (left) and its 2D fingerprint plot (right) for $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (yellow) at 293 K. On the Hirshfeld surface, intermolecular interactions with interatomic distances below, equal or above a sum of van-der-Waals radii are shown by red, white and blue areas, respectively. Green and blue areas on the fingerprint plot stand for higher and lower concentration of points corresponding to (di, de) pairs. Contributions of C-H…F, Cl…H and H…H interactions are 16.5%, 11.6% and 60.7%, respectively.

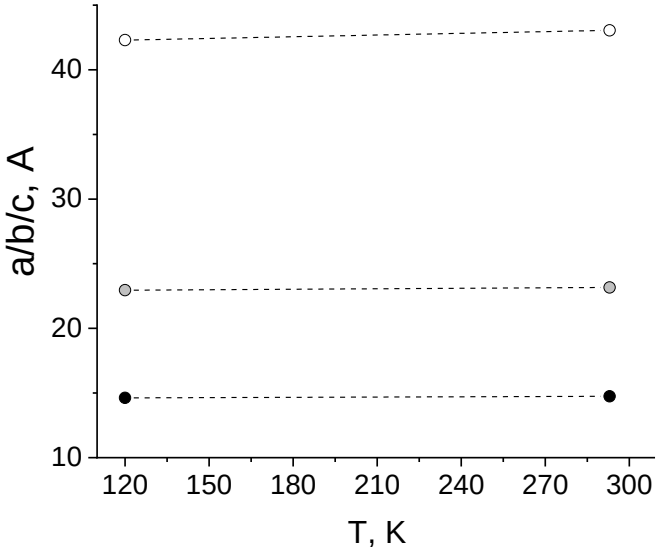

Figure S7. Unit cell parameters ***a*** (open circles), ***b*** (black circles) and ***c*** (grey circles) of $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (yellow) at 120 and 293 K.

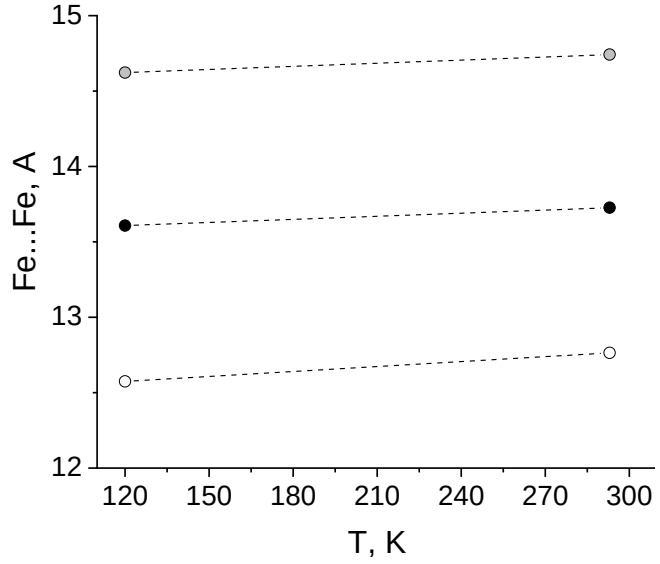

Figure S8. Shorthest distances between the iron(II) ions in (open circles) and between (black and grey circles) the infinite spirals of the cations $[Fe(\mathbf{L})_2]^{2+}$ in $[Fe(\mathbf{L})_2](BF_4)_2 \cdot 2CH_3CN$ (yellow) at 120 and 293 K.

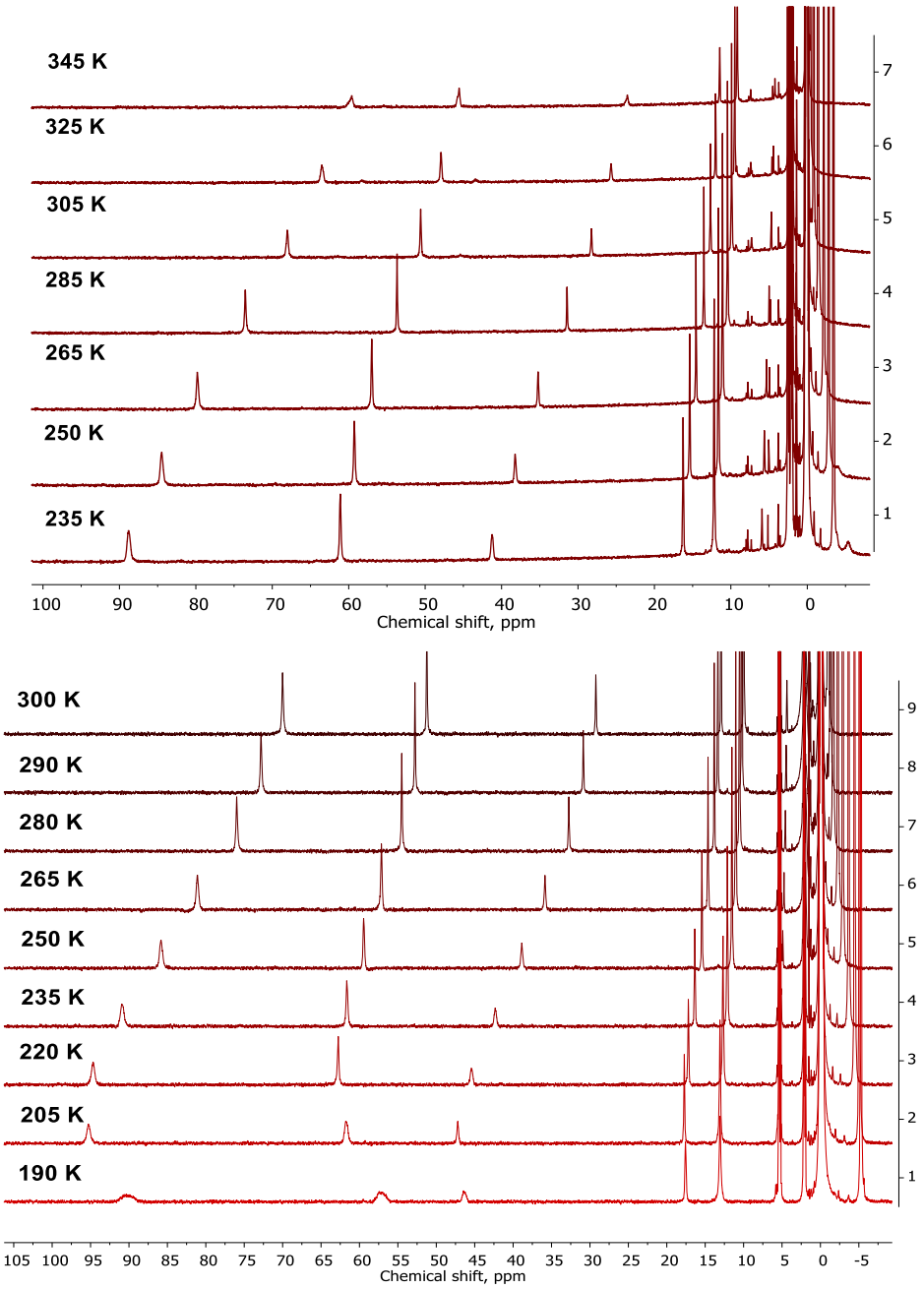

Figure S9. Variable-temperature ^{1}H NMR spectra for [Fe(**L**)$_2$](BF$_4$)$_2$ in acetonitrile-d$_3$ (top) and in methylene-d$_2$ (bottom).

Supplementary Tables

Table S1. Main geometric parameters and continuous symmetry measures as obtained from TPSSh/def2-TZVP calculations of $[Fe(\mathbf{L})_2]^{2+}$ in the LS and the HS state with acetonitrile and water as solvents.[1]

	Acetonitrile		Water	
	LS	HS	LS	HS
Fe-N_{Py}, Å	1.9117–1.9126	2.0462–2.0486	1.9117–1.9126	2.0456–2.0483
Fe-N_{Pz}, Å	2.0609–2.0746	2.2807–2.3133	2.0609–2.0745	2.2835–2.3406
θ,°	89.664	89.206	89.664	89.896
ϕ,°	179.68	179.15	179.68	178.62
γ,°	87.60/87.97/88.06/88.25 av. 87.97	83.01/83.93/84.34/86.98 av. 84.56	87.61/87.97/88.08/88.27 av. 87.98	82.36/84.89/84.98/86.36 av. 84.65
$S(O_h)$	2.202	4.129	2.202	4.122
S(ebcT)	14.174	12.020	14.172	12.045

[1] θ is the 'twist' angle between the two least-squares planes of the 3-bpp ligands; ϕ is the 'rotation' angle N_{Py}-Fe-N_{Py}; γ is the rotation angle of the phenyl group relative to the pyrazol-3-yl plane; $S(O_h)$ and S(ebcT) are octahedral and edge-bicapped tetrahedral symmetry measures, respectively.