Supplementary information for

Spin-crossover in iron(II) complexes of N,N'-disubstituted 2,6-bis(pyrazol-3-yl)pyridines: an effect of a distal substituent in the 2,6-dibromophenyl group

by

Igor A. Nikovskiy,[a] Alexander V. Polezhaev,[ab] Valentin V. Novikov,[ac] Dmitry Yu. Aleshin,[ad] Rinat R. Aysin,[ac] Elizaveta K. Melnikova,[ae] Luca M. Carrella,[f] Eva Rentschler,[f] Yulia V. Nelyubina*[abc]

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

[b]Bauman Moscow State Technical University, 105005, 2nd Baumanskaya Str., 5, Moscow, Russia

[c]Moscow Institute of Physics and Technology, 141700, Institutskiy per., 9, Dolgoprudny, Moscow Region, Russia

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

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

[f]Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

Supplementary Figures

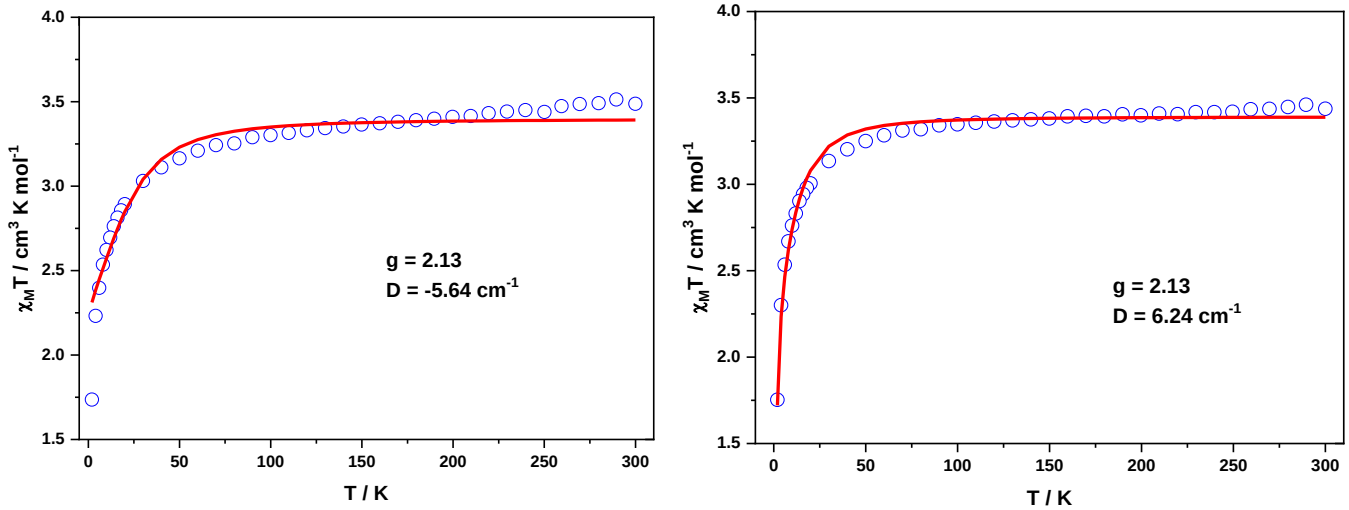

Figure S1. Variable-temperature magnetic susceptibility data for fine-crystalline samples of $[Fe(\mathbf{L^{Br}})_2](ClO_4)_2$ (left) and $[Fe(\mathbf{L^{Me}})_2](ClO_4)_2$ (right) according to the *dc*-magnetometry; the red lines represent the fits.

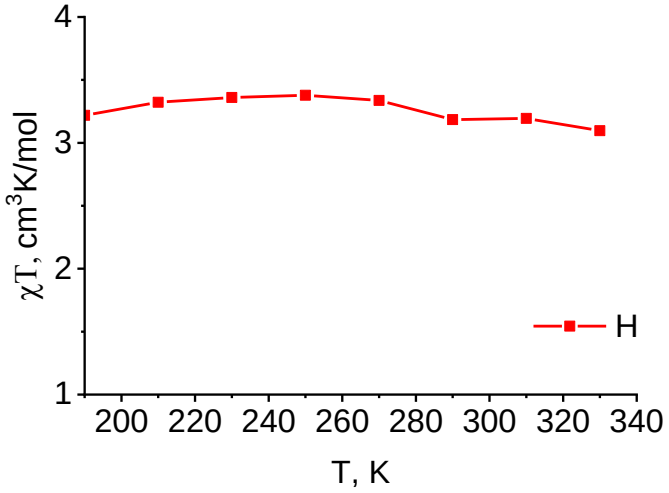

Figure S2. Variable-temperature magnetic susceptibility data for the solution of $[Fe(\mathbf{L^{H}})_2](ClO_4)_2$ in methanol-d_4 according to the Evans method.

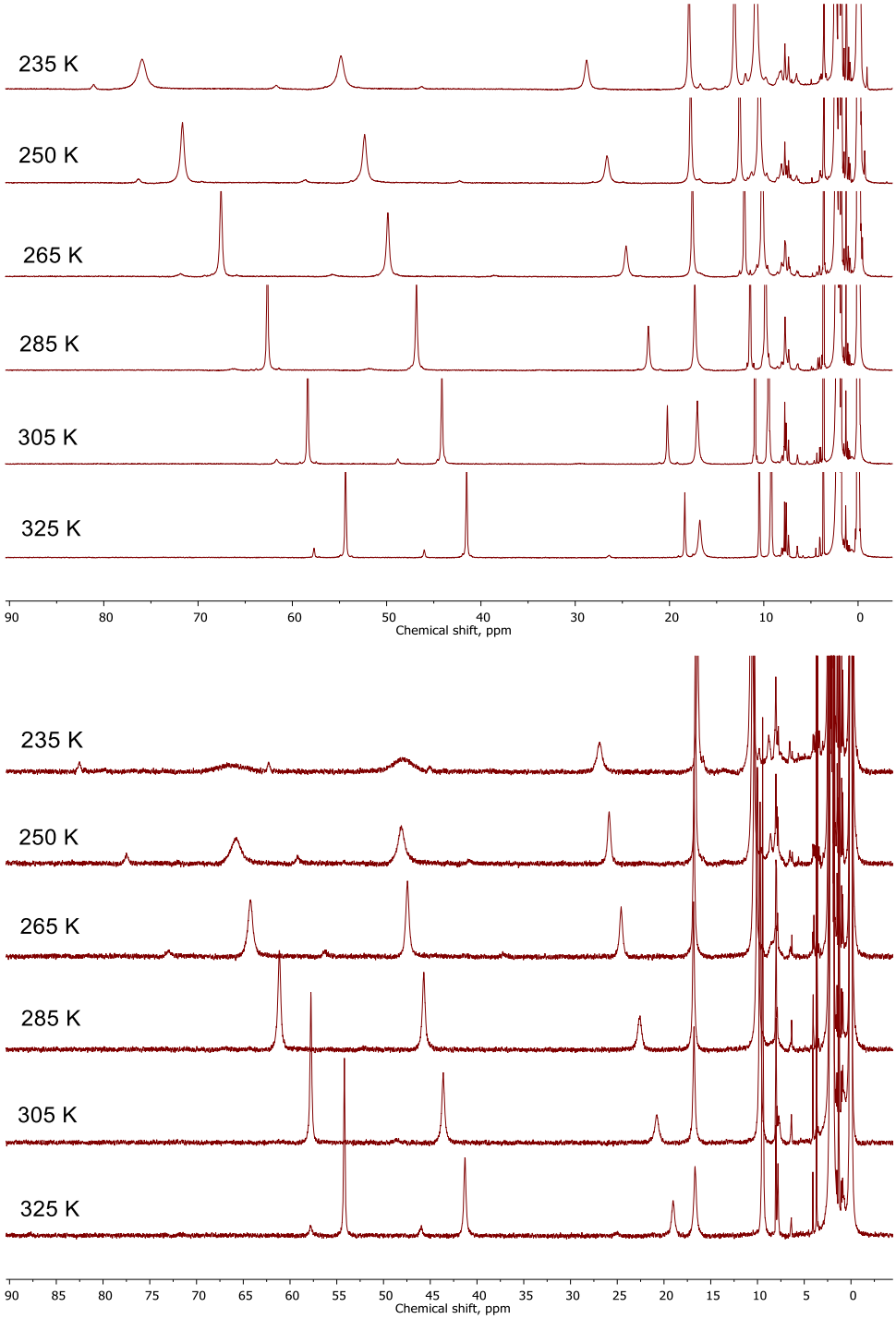

Figure S3. Variable-temperature ^{1}H NMR spectra for $[Fe(\mathbf{L^{H}})_2](ClO_4)_2$ (top) and $[Fe(\mathbf{L^{Br}})_2](ClO_4)_2$ (bottom) in an acetonitrile-d_3 solution.

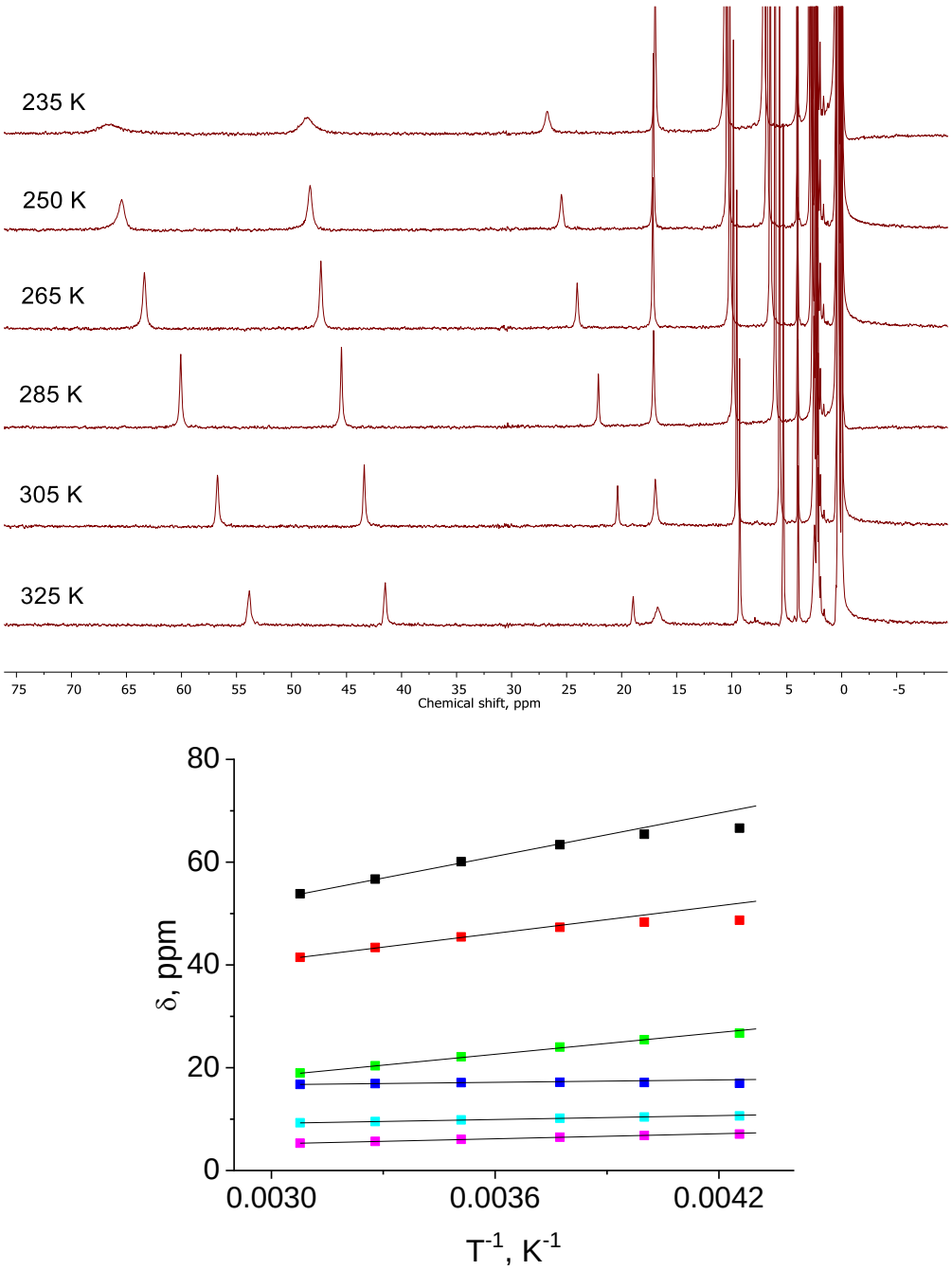

Figure S4. Variable-temperature ^{1}H NMR spectra for $[Fe(\mathbf{L^{Me}})_2](ClO_4)_2$ in an acetonitrile-d_3 solution (top) and its chemical shifts plotted versus *1/T* (bottom). Solid lines represent the linear fit over the temperature range 285 – 325 K; each color indicates a specific type of the protons that are the same between the complexes.

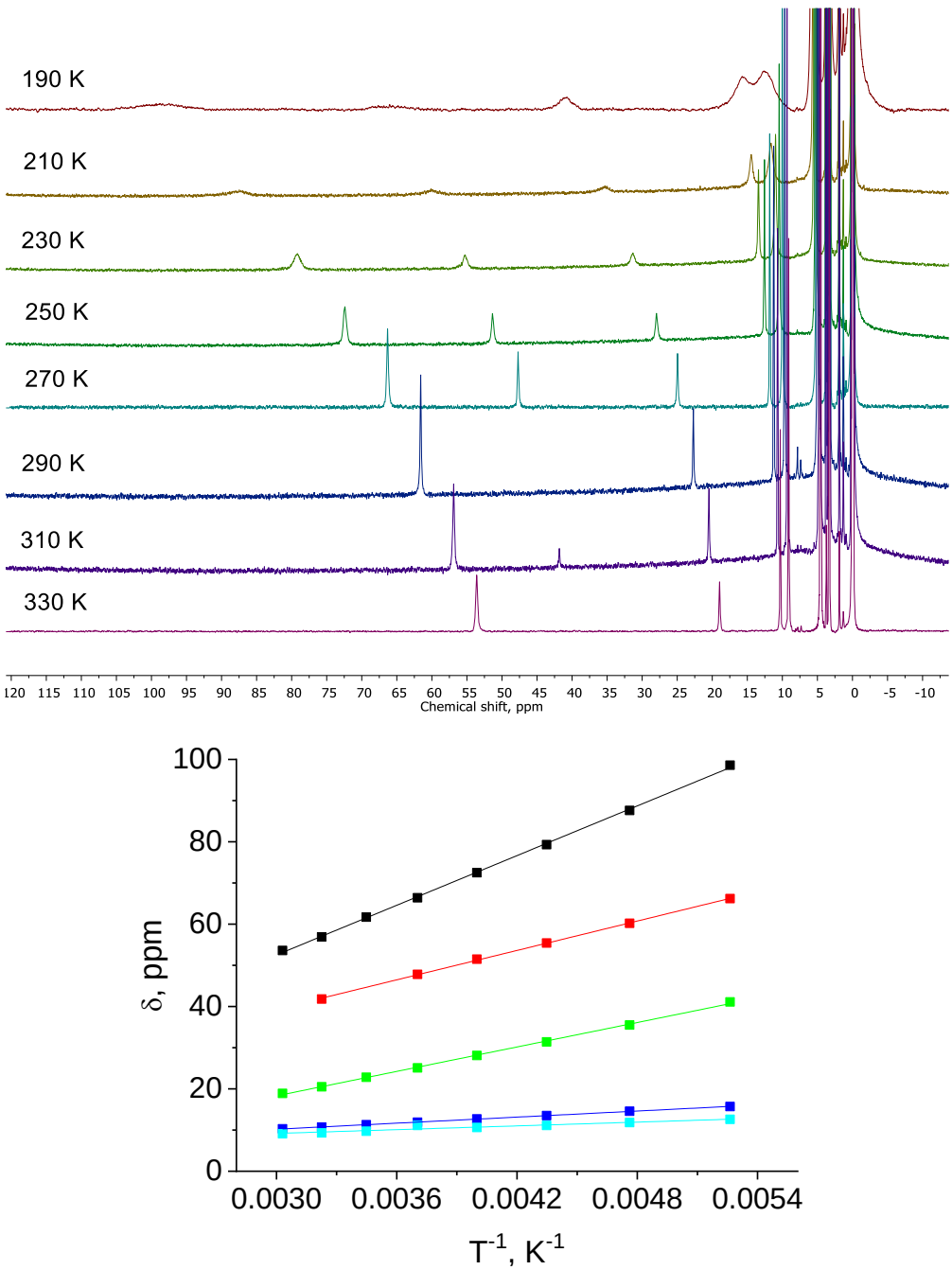

Figure S5. Variable-temperature ^{1}H NMR spectra for $[Fe(\mathbf{L^{H}})_2](ClO_4)_2$ in a methanol-d_4 solution (top) and its chemical shifts plotted versus *1/T* (bottom)./ Solid lines represent the linear fit over the entire temperature range; each color indicates a specific type of the protons that are the same between the complexes.

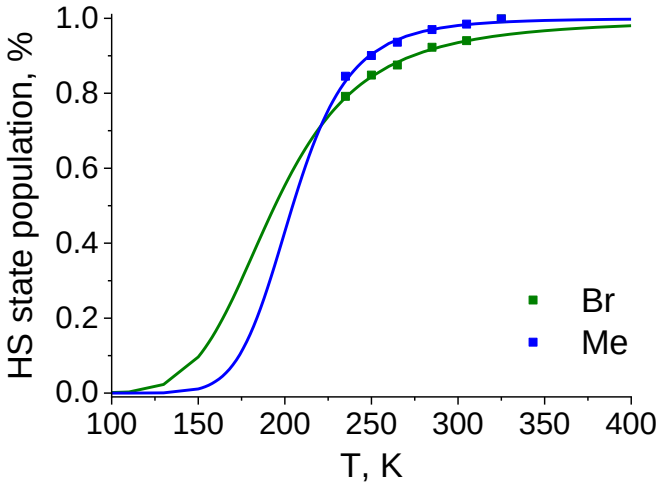

Figure S6. HS state population of $[Fe(\mathbf{L^{Br}})_2](ClO_4)_2$ and $[Fe(\mathbf{L^{Me}})_2](ClO_4)_2$ in acetonitrile-d_3 from the Evans method. The lines correspond to the best fit by a regular solution model [1].

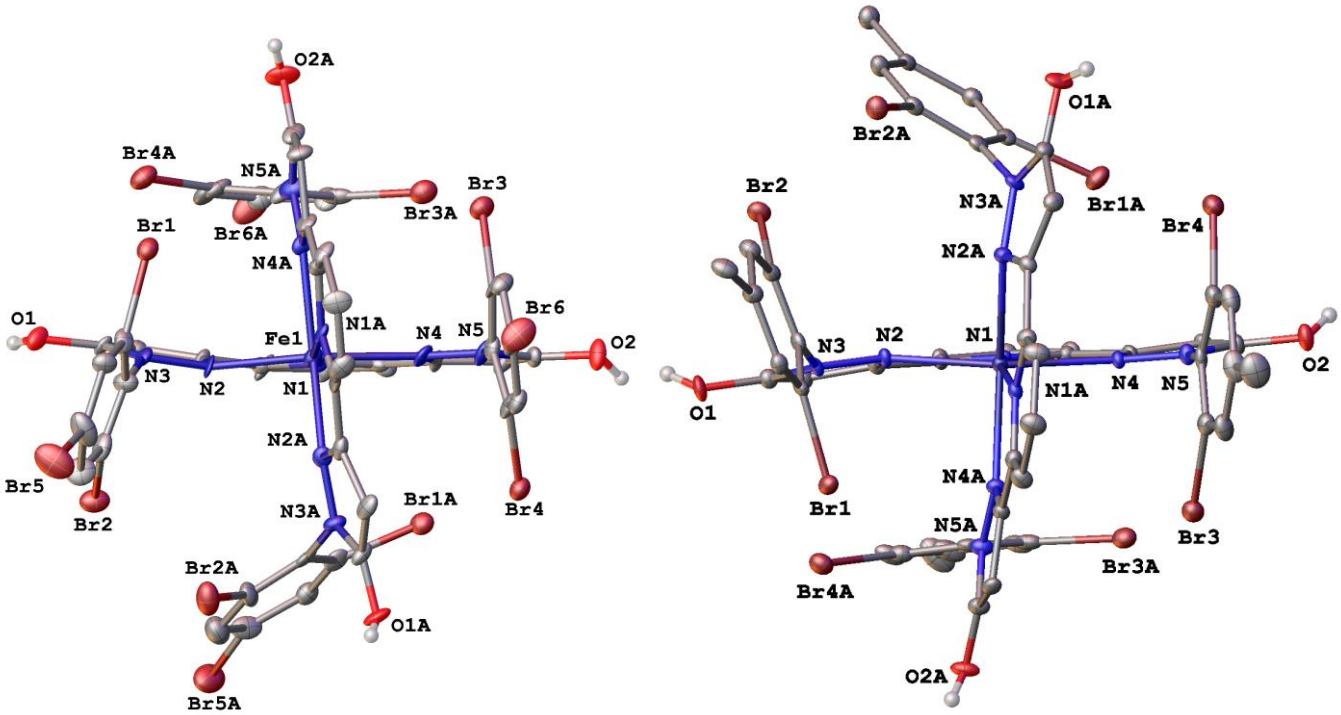

Figure S7. General view of the cations in $[Fe(\mathbf{L^{Br}})]_2(ClO_4)_2$ (left) and $[Fe(\mathbf{L^{Me}})]_2(ClO_4)_2$ (right) as obtained from X-ray diffraction at 120 K. Non-hydrogen atoms are shown as thermal ellipsoids (p = 30%), hydrogen atoms except those of OH groups are omitted for clarity, and only labels of the heteroatoms in an asymmetric part of the unit cell are given.

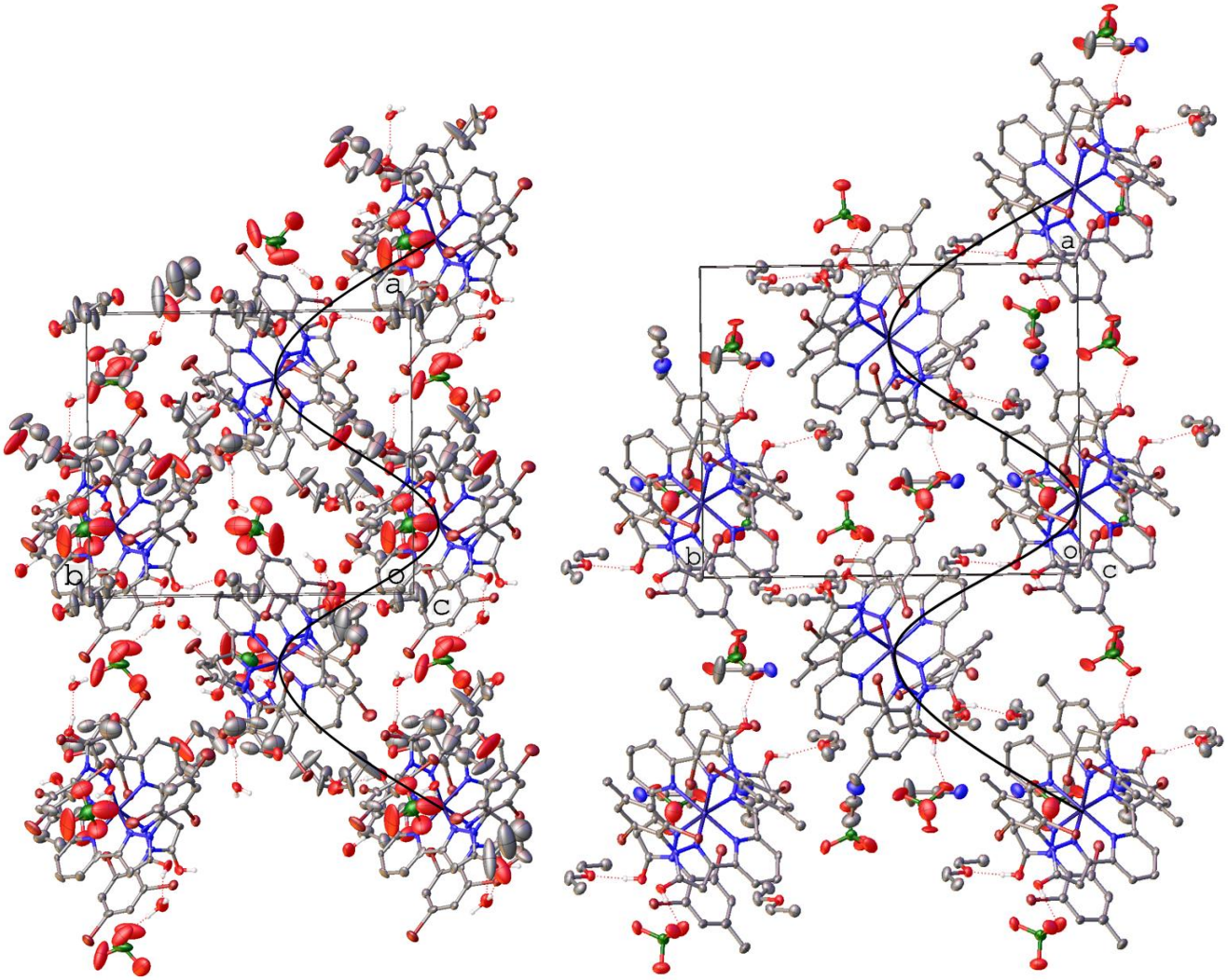

Figure S8. Spiral-like packing of the cations in $[Fe(\mathbf{L^{Br}})]_2(ClO_4)_2$ (left) and $[Fe(\mathbf{L^{Me}})]_2(ClO_4)_2$ (right).

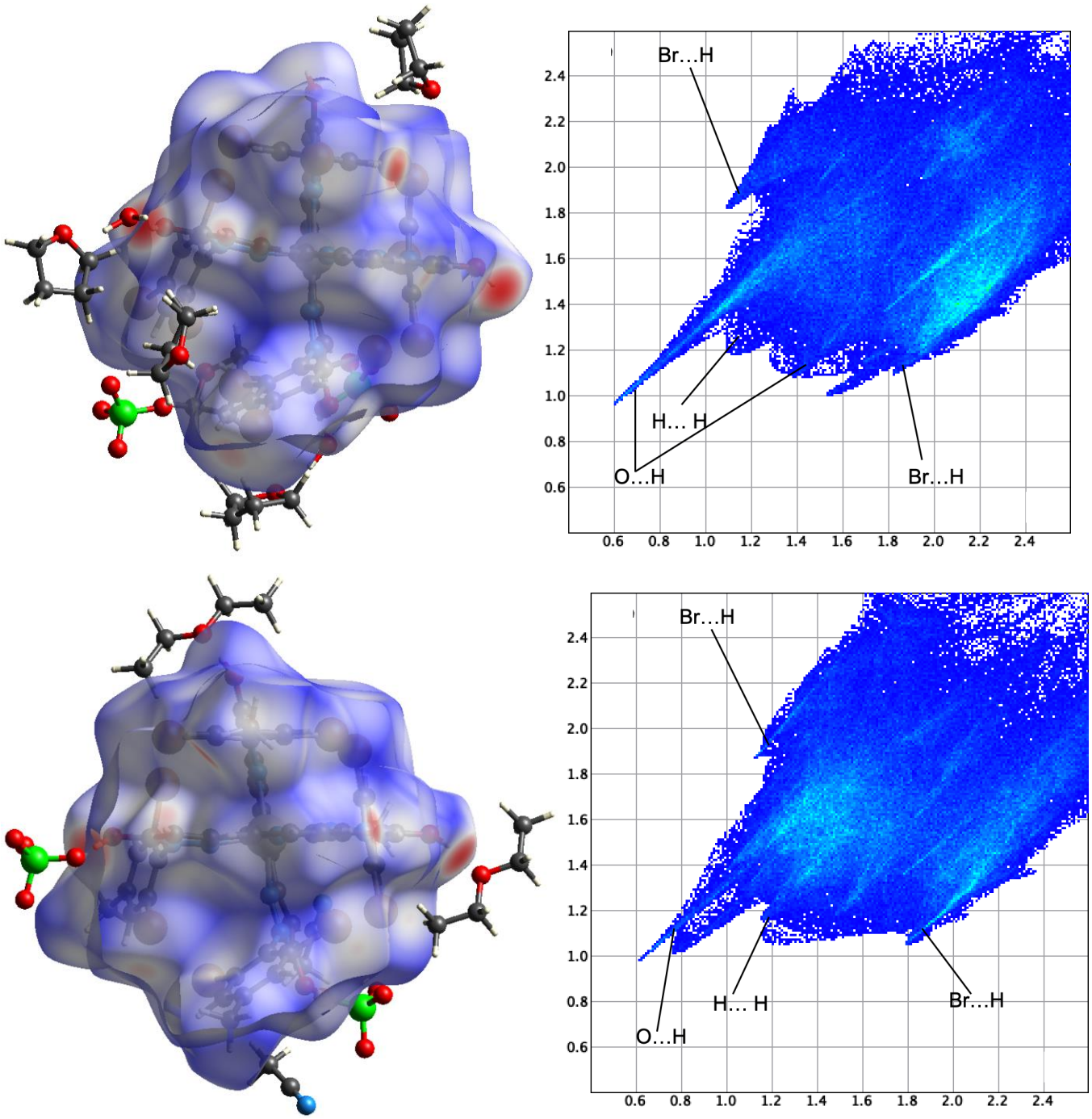

Figure S9. Hirshfeld surfaces (left) of the cations and their 2D fingerprint plots (right) as generated by *Crystal Explorer* [2] in $[Fe(\mathbf{L^{Br}})_2](ClO_4)_2$ (top) and $[Fe(\mathbf{L^{Me}})_2](ClO_4)_2$ (bottom). On the Hirshfeld surfaces (left), intermolecular interactions with interatomic 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.

Supplementary Tables

Table S1. SCO parameters[1] from the NMR data for acetonitrile-d_3 solutions.

	$\mathbf{L^{Br}}$	$\mathbf{L^{Me}}$
$T_{1/2}$, K	195	205
ΔH, kJ/mol	12.2	20.9
ΔS	62.9	102.5

[1]Thermodynamic parameters are obtained by fitting the Evans data by a regular solution model.

Table S2. Main geometric parameters and continuous symmetry measures[1] as obtained from TPSSh/def2-TZVP calculations of the cations $[Fe(\mathbf{L^R})_2]^{2+}$ in the LS and the HS states.

	$[Fe(\mathbf{L^H})_2]^{2+}$		$[Fe(\mathbf{L^{Br}})_2]^{2+}$		$[Fe(\mathbf{L^{Me}})_2]^{2+}$	
	LS	HS	LS	HS	LS	HS
Fe-N_{Py}, Å	1.921	2.086	1.896	2.089	1.896	2.088
Fe-N_{Pz}, Å	2.064-2.110	2.259-2.387	2.022-2.024	2.254-2.370	2.019-2.024	2.259-2.387
N_{pz}…N_{pz}, Å	4.104/4.105	4.481/4.486	3.991/3.993	4.465/4.466	3.988/3.991	4.485/4.485
N_{pz}…N_{py}, Å	2.555–2.578	2.690–2.692	2.538–2.539	2.684–2.686	2.536–2.539	2.689–2.692
$N_{pz}Np_yN_{pz}$, °	106.2/106.2	112.8/112.9	103.7/103.7	112.5/112.5	103.6/103.7	112.9/112.9
θ,°	84.3	86.4	89.9	85.1	90.0	86.4
ϕ,°	177.8	161.0	179.9	162.5	179.6	160.5
γ,°	87.1/82.0/ 92.0/87.0 av. 87.0	86.0/76.9/85. 9/76.7 av. 81.4	87.4/87.7/ 87.4/87.5 av. 87.5	84.8/78.3/ 78.4/84.7 av. 81.6	87.5/87.7/ 86.6/87.4 av. 87.3	86.0/86.0/ 76.6/76.5 av. 81.3
β,°	3.7/13.2/ 3.7/13.3	1.8/14.8/ 1.7/14.9	5.1/5.3/ 5.3/5.0	1.5/14.2/ 1.6/14.3	4.9/4.2/ 4.7/4.2	2.1/15.0/ 2.1/15.0
S(Oh)	2.454	5.600	1.834	5.438	1.882	5.676
S(ebcT)	13.882	11.711	14.598	11.439	14.489	11.664
Br…Br, Å	3.855/3.942/ 3.498/3.853	3.931/3.960/ 3.823/3.929	3.471/3.475/ 3.468/3.467	3.883/3.8803 .876/3.753	3.460/3.451 3.473/3.479	3.821/3.943/ 3.945/3.987

[1]N_{pz} and N_{py} are the coordinating nitrogen atoms from the pyrazol-3-yl and pyridine moieties; θ is the 'twist' angle between the two least-squares planes of the 3-bpp ligands; ϕ is the 'rotation' angle N_{Py}-M-N_{Py}; γ is the rotation angle of the N-phenyl group relative to the pyrazol-3-yl plane; β is the rotation angle of the pyrazol-3-yl moiety relative to the pyridine plane; S(O_h) and S(ebcT) are octahedral and edge-bicapped tetrahedral symmetry measures, respectively; Br…Br are the distances between the bromine atoms from possible intramolecular Br…Br interactions.

1. Weber, B.; Walker, F.A. Solution NMR studies of iron(II) spin-crossover complexes. *Inorg. Chem.* **2007**, *46*, 6794-6803, doi:10.1021/ic062349e.
2. Wolff, S.K.; Grimwood, D.J.; McKinnon, J.J.; Turner, M.J.; Jayatilaka, D.; Spackman, M.A. *CrystalExplorer (Version 3.1)*, University of Western Australia, Perth, Australia, 2012.