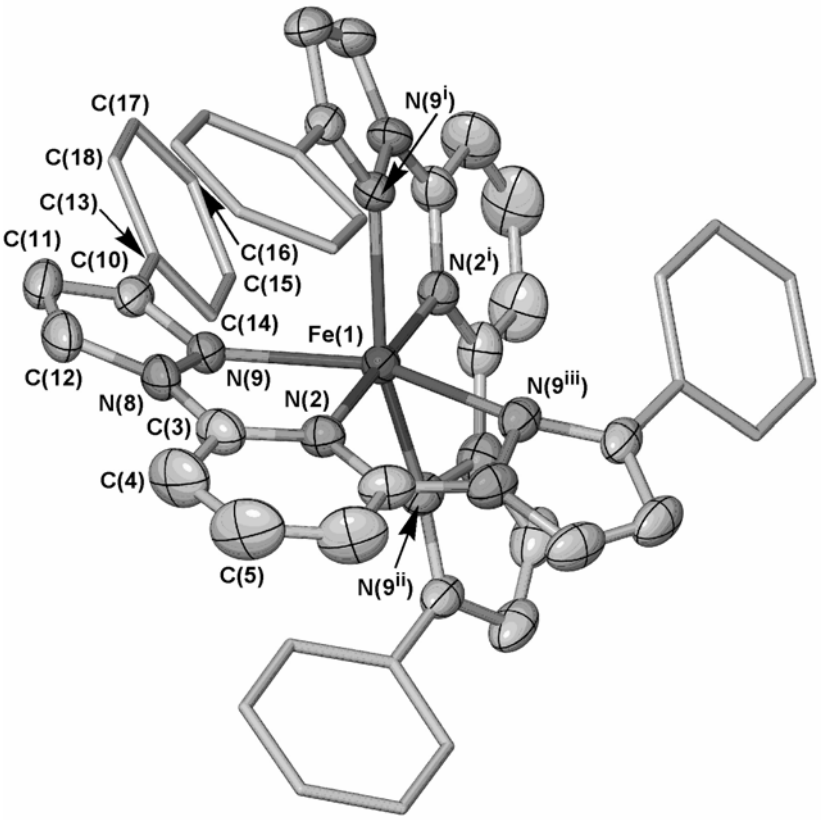


Fig. S1. View of the complex dication in the crystal structure of β-$[Fe(L^2)_2][BF_4]_2$ (β-**2[BF_4]$_2$**). Thermal ellipsoids are at the 35% probability level, except for the L^2 phenyl substituents which have arbitrary atomic radii. All H atoms have been removed for clarity. The non-sequential atom numbering scheme has been chosen to correspond with the numbering used in the α-polymorph of the same compound. Symmetry codes: (i) $-x+¼, -y+¼, z$; (ii) $x, -y+¼, -z+¼$; (iii) $-x+¼, y, -z+¼$.

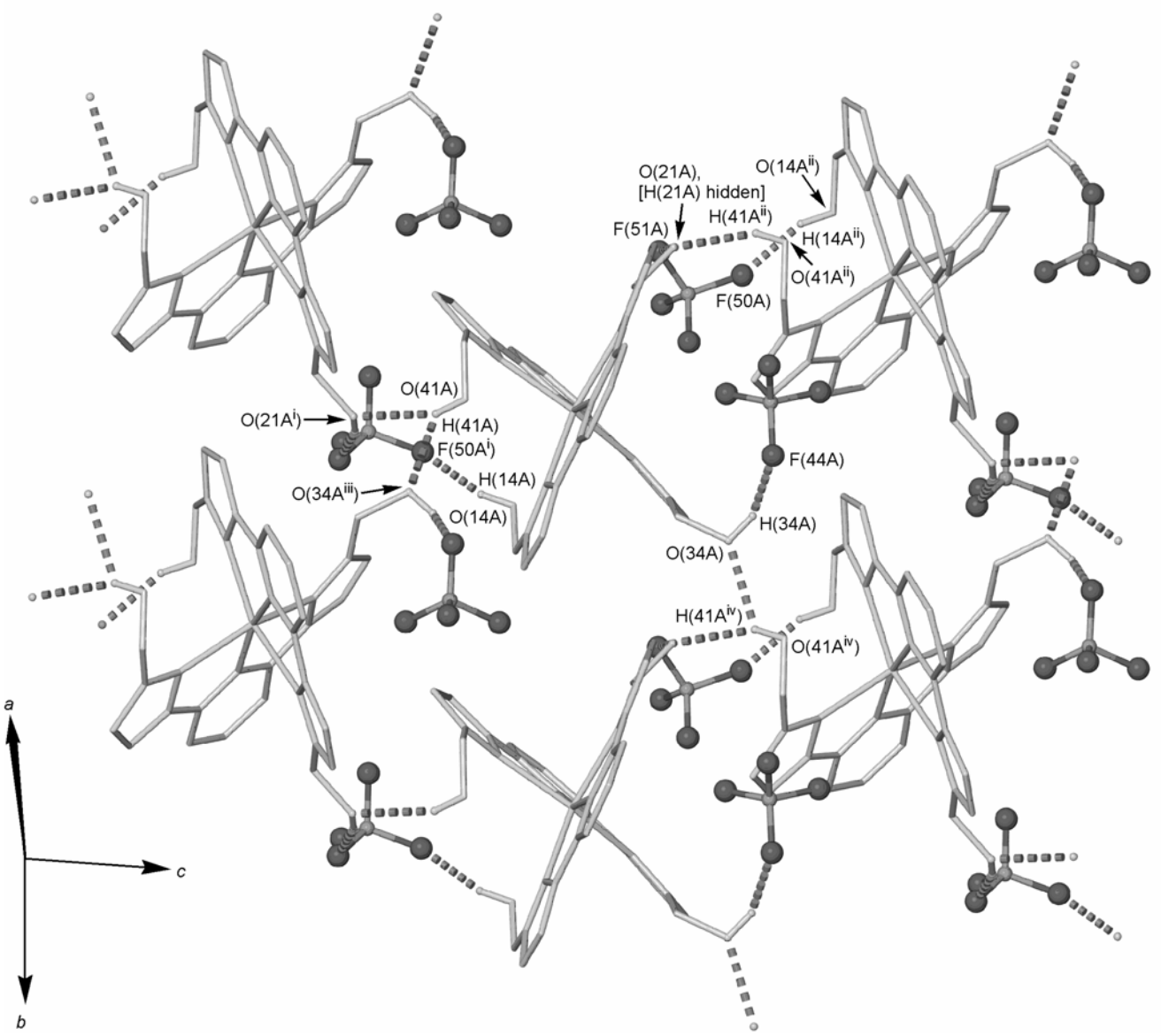


Fig. S1. Partial packing diagram of the major cation and anion disorder orientation of **5[BF_4]$_2$**, showing the association of the complex molecules into hydrogen-bonded zig-zag chains running parallel to the crystallographic *c*-axis, which are in turn linked into 2-D sheets parallel to the crystallographic [100] plane by the O(41A)–H(41A)…O(34A^{iii}) interaction. All C-bound H atoms are omitted for clarity, and all atoms have arbitrary radii. Symmetry codes: (i) *x*, ½–*y*, –½+*z;* (ii) *x*, ½–*y*, ½+*z;* (iii) *x*, $^{3}/_{2}$–*y*, –½+*z;* (iv) *x*, $^{3}/_{2}$–*y*, ½+*z*.

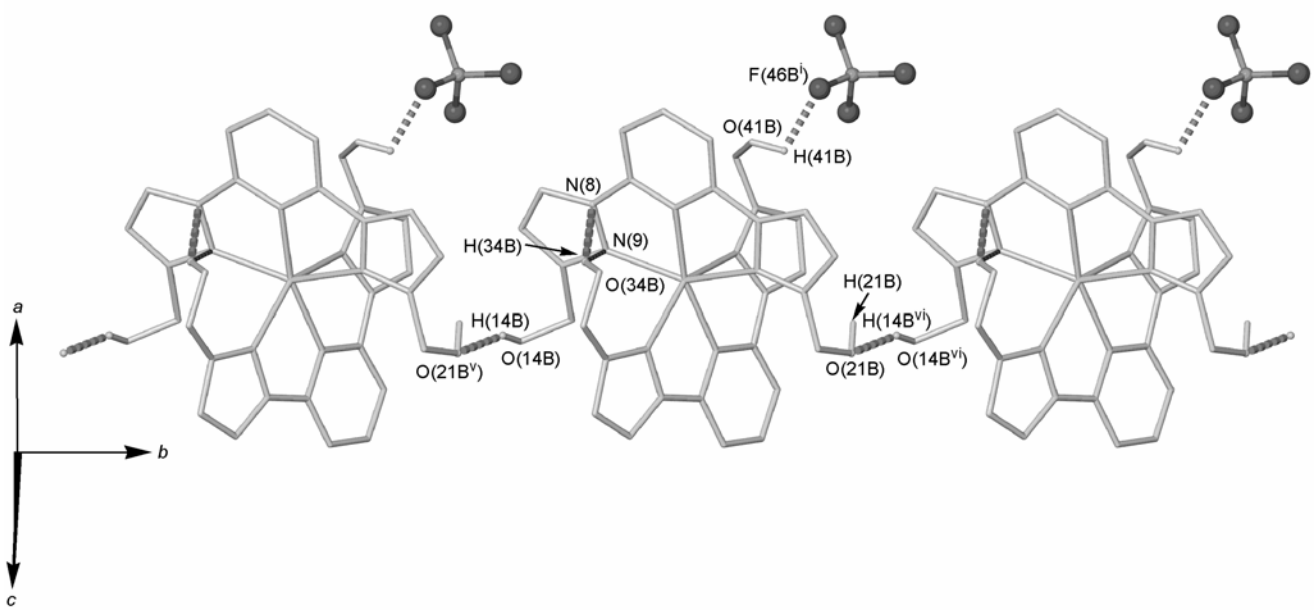
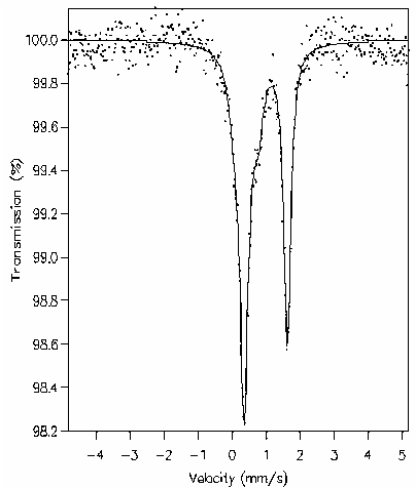
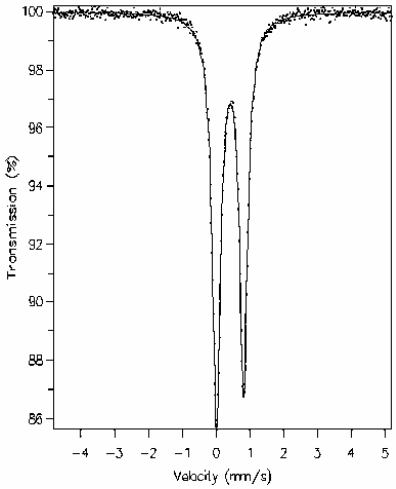


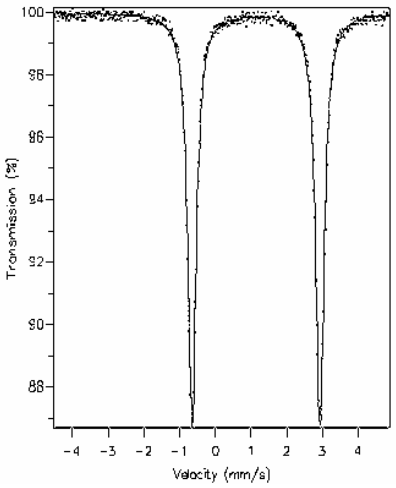
Fig. S2. Partial packing diagram of the minor cation and anion disorder orientation of **5[BF_4]$_2$**, showing the association of the complex molecules into 1-D hydrogen-bonded chains parallel to the crystallographic *b*-axis. Details as for Fig. S1. Symmetry codes: (i) *x*, ½–*y*, –½+*z;* (v) *x*, 1+*y*, *z*; (vi) *x*, –1+*y*, *z*.



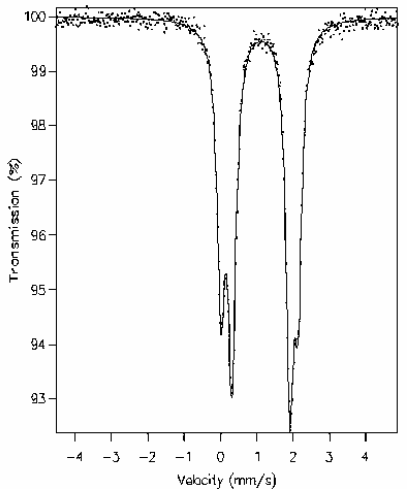
1[BF_4]$_2$ at 298 K



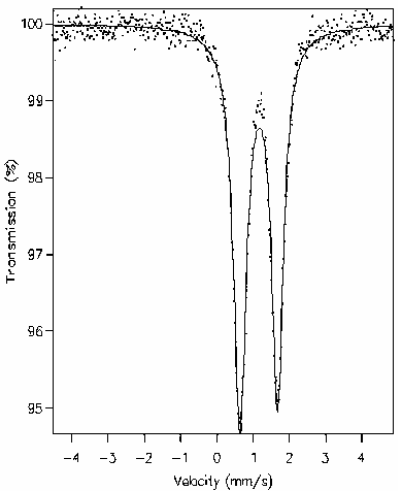
1[BF_4]$_2$ at 80 K



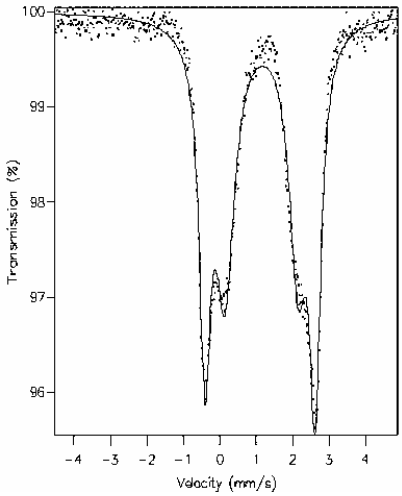
1[ClO_4]$_2$ at 80 K



2[BF_4]$_2$ at 80 K



4[BF_4]$_2$ at 80 K



5[BF_4]$_2$ at 80 K

Fig. S3. Selected Mössbauer spectra from the compounds in this study.