Supporting Information for:

Anion-Dependent Spin State Switching Properties of $[(H_2bip)_2Fe(6\text{-}Mebpy)]X_2$

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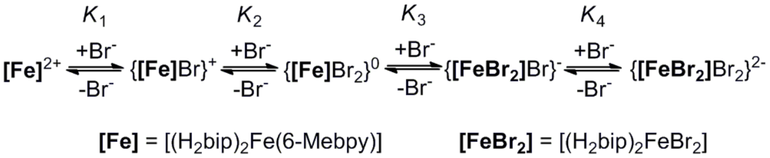

Calculations of Equilibrium Constants. The "4K" model used to rationalise binding between **2** and Br^- is based on the scheme shown at right, which was previously (and successfully) used to model behavior in similar complexes.[1] Titration data (Figure S5) were fit to equations S1 and S2:

$$\Delta A = \frac{[H_t]\{\Delta\varepsilon_1 K_1[G] + \Delta\varepsilon_2 K_1 * K_2[G]^2 + \Delta\varepsilon_3 K_1 * K_2 * K_3[G]^3 + \Delta\varepsilon_4 K_1 * K_2 * K_3 * K_4[G]^4\}}{1 + K_1[G] + K_1 * K_2[G]^2 + K_1 * K_2 * K_3[G]^3 + K_1 * K_2 * K_3 * K_4[G]^4} \tag{S1}$$

$$G_t = [G] + \frac{[H_t]\{K_1[G] + 2K_1 * K_2[G]^2 + 3K_1 * K_2 * K_3[G]^3 + 4K_1 * K_2 * K_3 * K_4[G]^4\}}{1 + K_1[G] + K_1 * K_2[G]^2 + K_1 * K_2 * K_3[G]^3 + K_1 * K_2 * K_3 * K_4[G]^4} \tag{S2}$$

Here, K_n is the stepwise binding constants, $[H_t]$ denotes the total concentration of host and [G] corresponds to the concentration of free guest in solution. $\Delta\varepsilon_n$ indicates the difference in molar absorptivities between the complex HG_n and the host. For plots of binding isotherms, the *x* axis is the total concentration of guest, $[G_t]$, and the *y* axis is the change in absorbance, ΔA.[2] All spectrophotometric titration curves were fitted with the 1stOpt 3.0 program.[3] The Global Levenberg-Marquardt method was used for the non-linear regression. Binding constants were obtained from a simultaneous fit of the electronic absorption spectral changes at four selected wavelengths in the range 430–500 nm. Wavelengths were selected in the 430-500 nm region because of the large difference in molar absorptivities for **1** and **2**. Data in the range of 550-750 may contain contributions from ligand dissociation products, including (but not limited to) $[Fe(H_2bip)_3]^{2+}$ and $[(H_2bip)Fe(6\text{-}Mebpy)_2]^{2+}$. Also, we note that the spectrum of **2** with 2 eq Br^- is not identical to that recorded for **1** in the range of 550-750 nm. Perhaps not unsurprising, unsatisfactory fits were obtained when longer wavelength data was included. Binding constants determined are 6.8, 3.9, 0.9 and 1.4 corresponding to log K_{1-4}, respectively, with estimated error of ±13 % based on analogy with data collected for similar complexes.[1] Based on the complex mixture encountered in this system, the binding constants presented above should be regarded as approximate.

References

1 Z. Ni, A. M. McDaniel and M. P. Shores, *Chem. Sci.*, 2010, DOI:10.1039/C1030SC00303D.
2 K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, John Wiley and Sons, New York, 1987.
3 *1stOpt 3.0; 7D-Soft High Technology Inc., Beijing, China, 2009.*

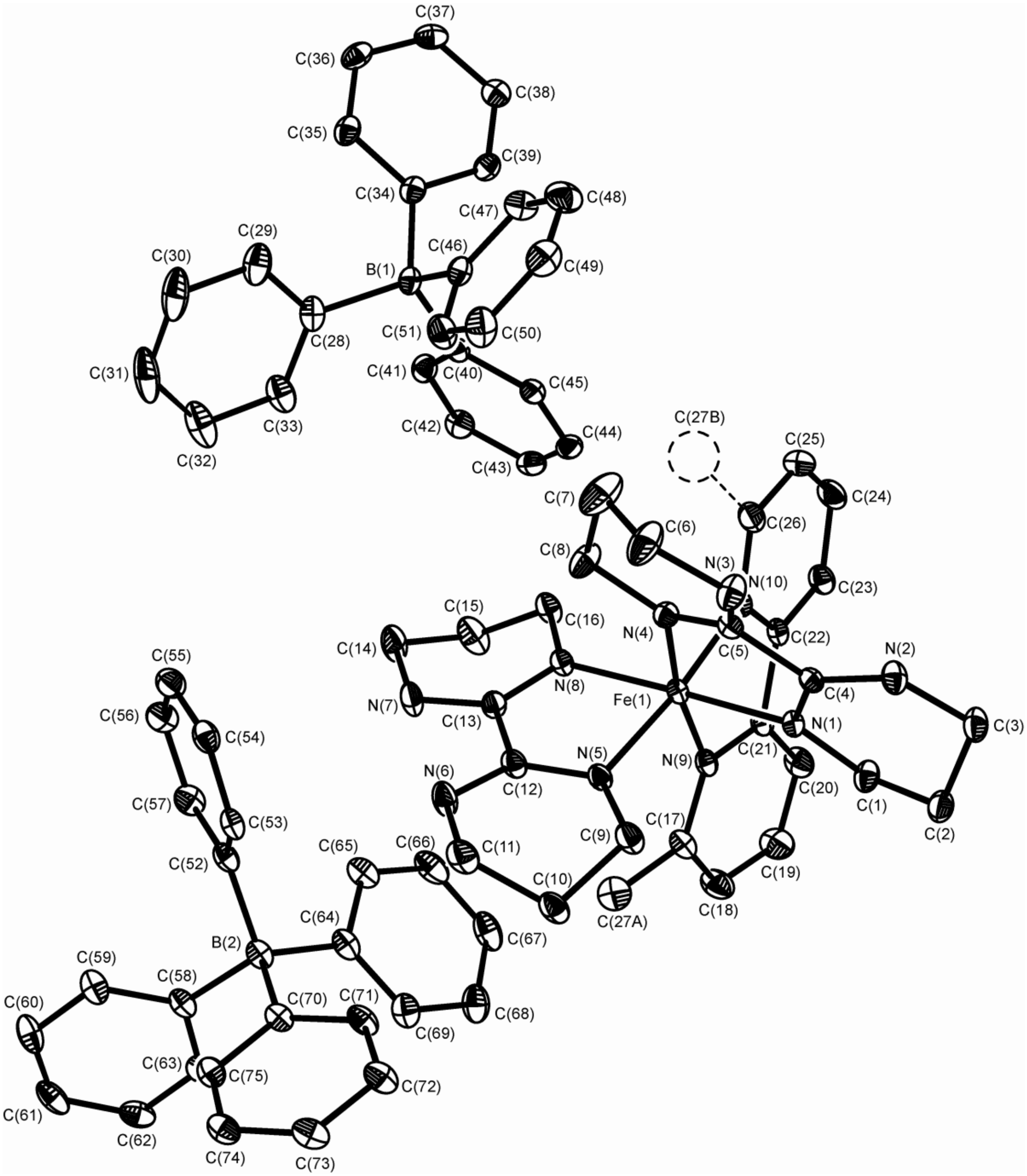

Figure S1. The asymmetric unit in the crystal structure of **2** at 100 K, drawn with 40% probability ellipsoids. Hydrogen atoms bound to C atoms are removed for clarity. The disordered atoms are labeled with suffixes “A” and “B”. Site occupancies for all disordered atoms are included in the respective cif files.

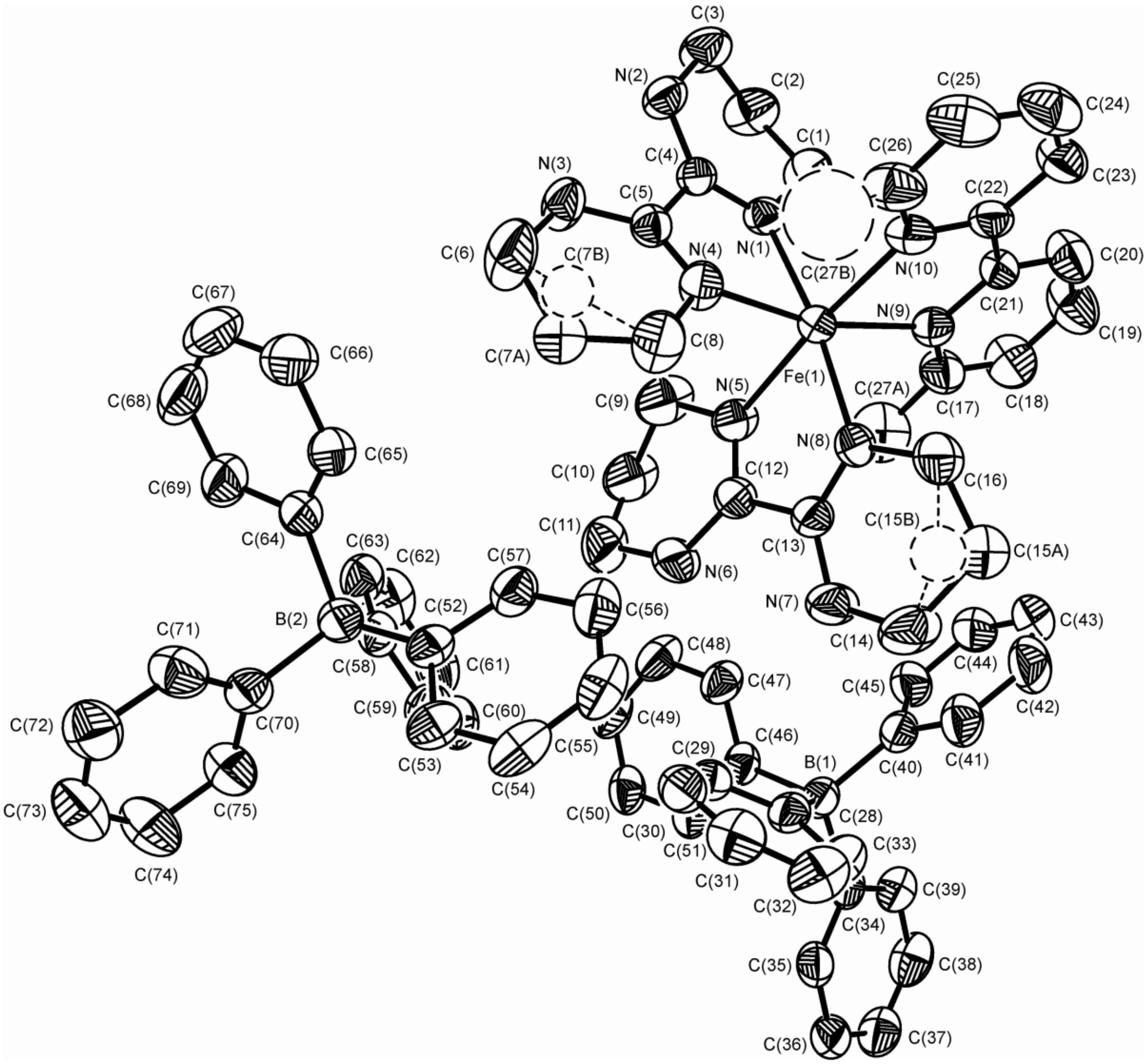

Figure S2. The asymmetric unit in the crystal structure of **2** at 296 K, drawn with 40% probability ellipsoids. Hydrogen atoms bound to C atoms are removed for clarity. The disordered atoms are labeled with suffixes “A” and “B”. Site occupancies for all disordered atoms are included in the respective cif files.

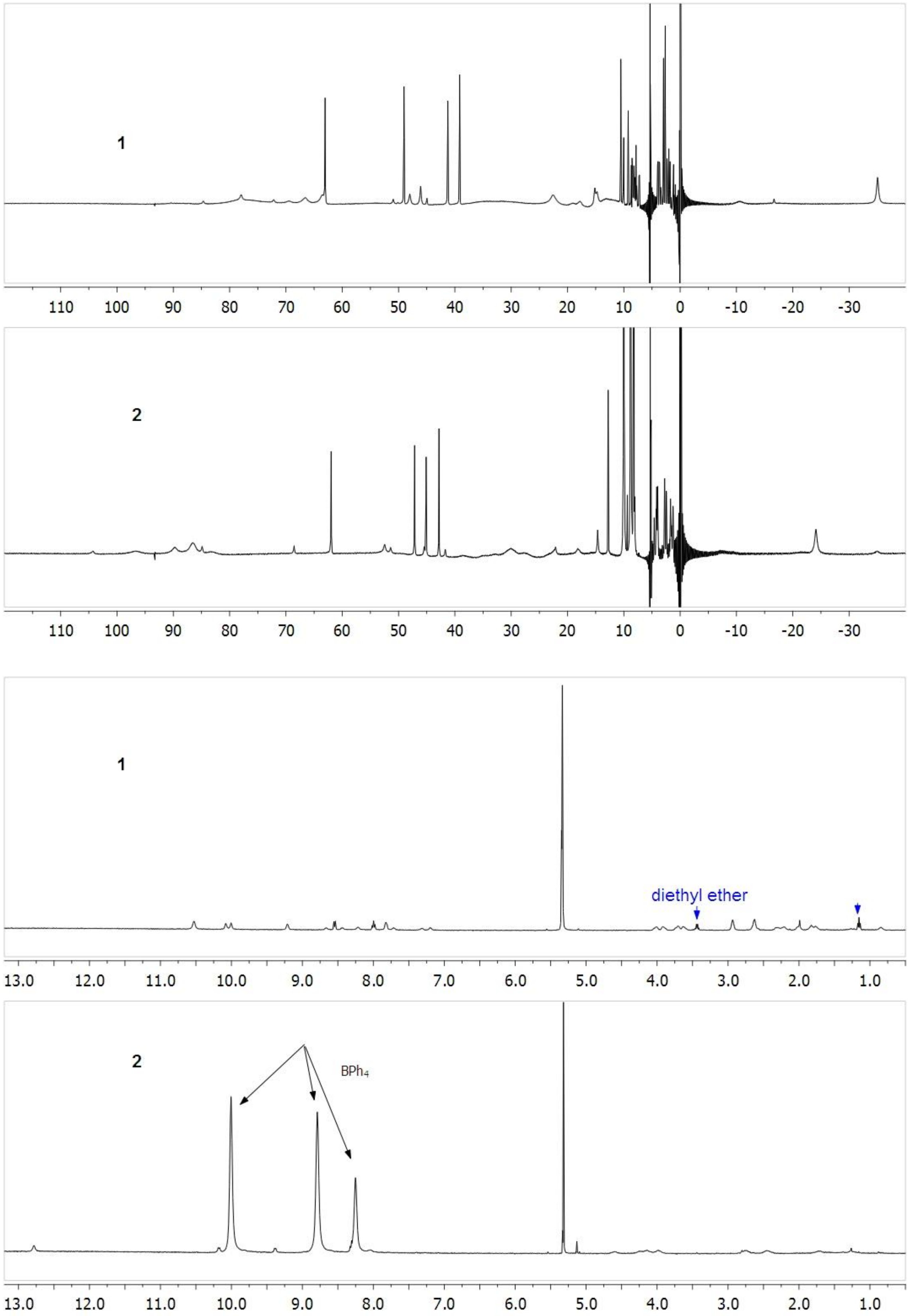

Figure S3. ^{1}H NMR spectra of **1** and **2** at 296 K (400 MHz, CD_2Cl_2).

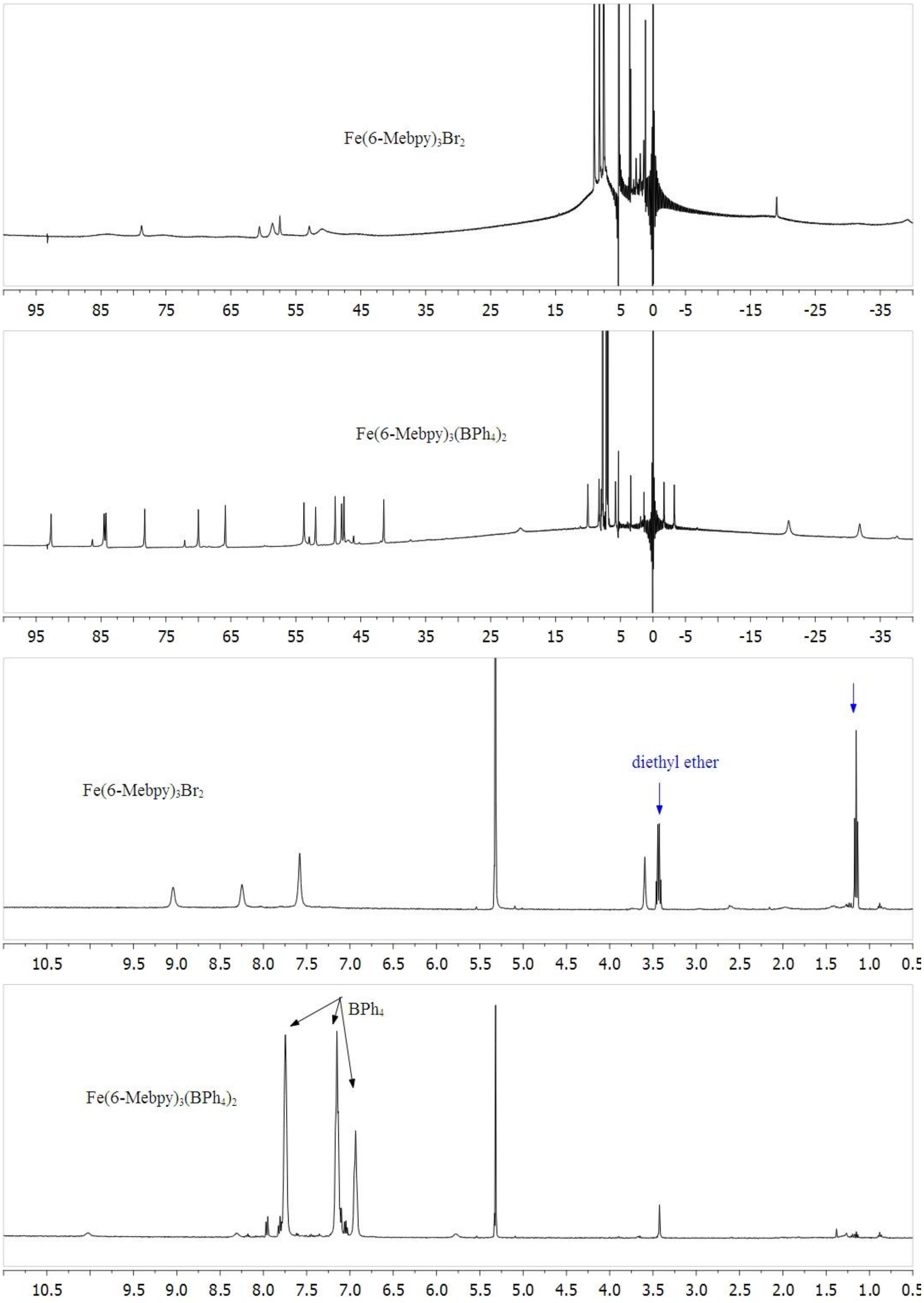

Figure S4. ^{1}H NMR spectra of [Fe(6-Mebpy)$_3$]X$_2$ (X = Br, BPh$_4$) at 296 K (400 MHz, CD$_2$Cl$_2$).

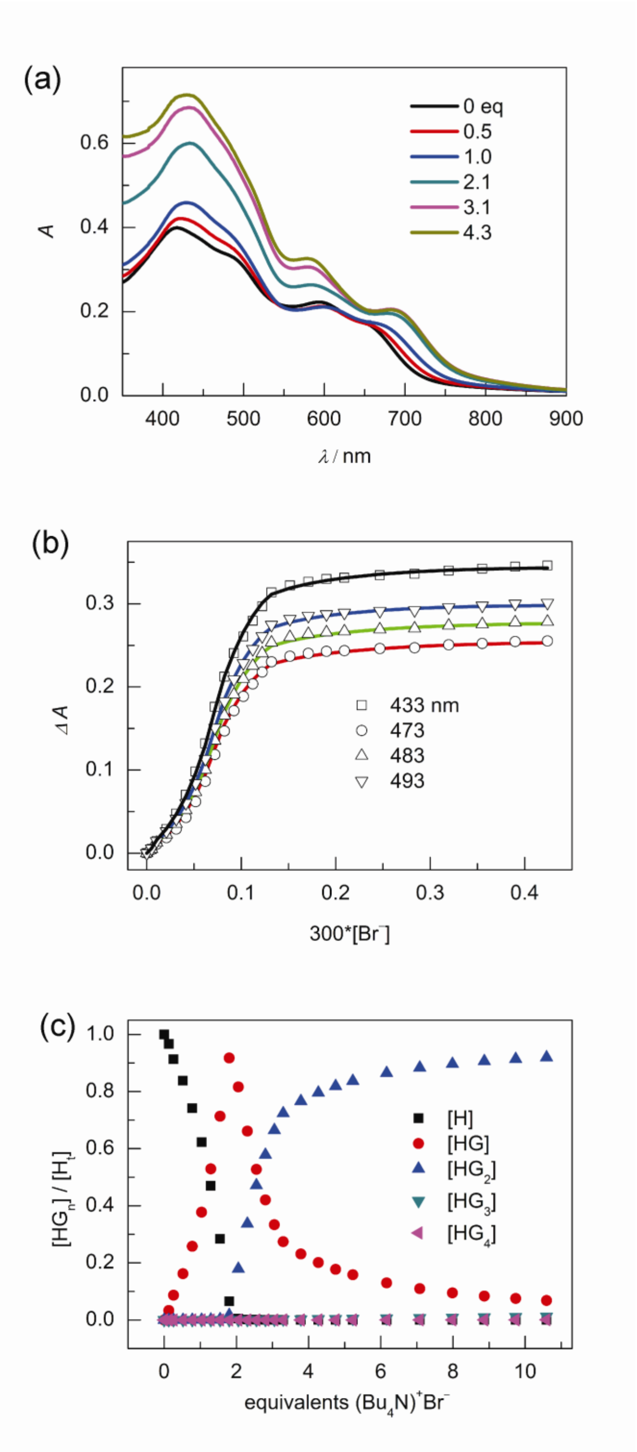

Figure S5. Plots of (a) absorbance changes, (b) binding isotherms with fitted curves and (c) resulting speciation when CH_2Cl_2 solutions of **2** are titrated with Bu_4NBr. As described on p. S1, the quantitative results obtained for the UV-Visible-monitored titration should be regarded as approximate due to complex speciation.