Supporting Information

Reversible Light-induced Magnetization Change in an Azobenzene-attached Pyridylbenzimidazole Complex of Iron(II) at Room Temperature

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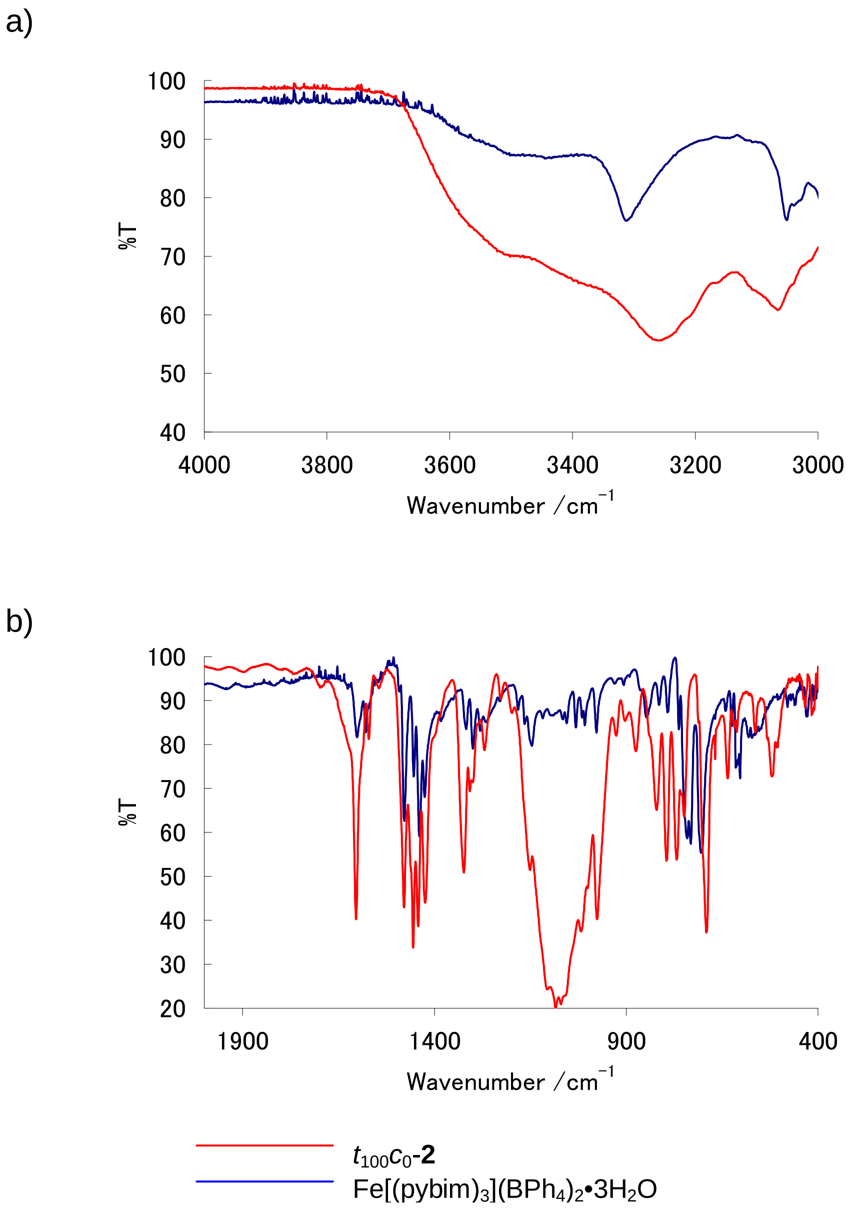
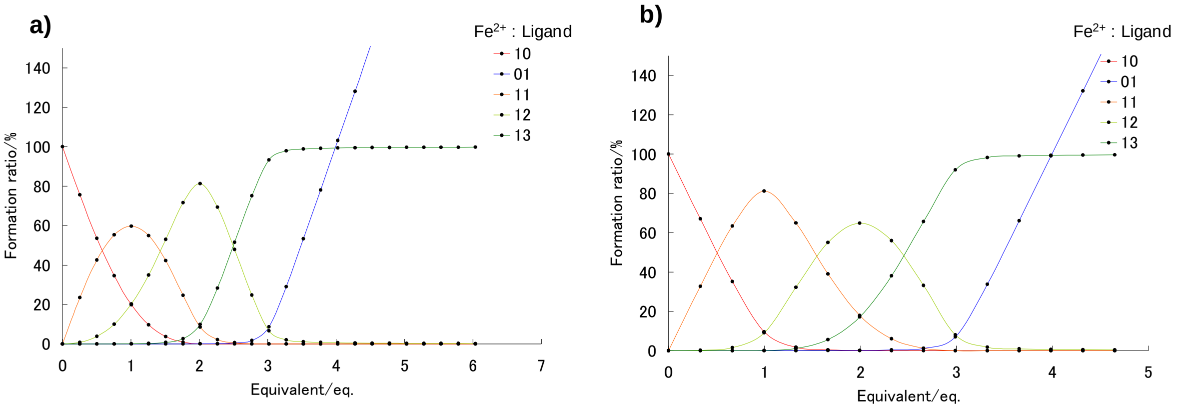


Fig. S1 IR spectrum of $t_{100}c_0$-**2** (red line) and [Fe(pybim)$_3$](BPh$_4$)$_2$·3H$_2$O (blue line) in the 4000-3000 cm^{-1} region (a) and 2000-400 cm^{-1} region (b).



log β_{11}	8.5(2)	log β_{11}	8.9(5)
log β_{12}	16.0(3)	log β_{12}	15.9(6)
log β_{13}	21.7(3)	log β_{13}	21.7(6)

Fig. S2 Formation ratio versus equivalent of the ligand and formation constant of $t_{100}c_{0}$-**1** (a) and $t_{6}c_{94}$-**1** (b) toward $Fe(ClO_4)_2 \cdot 6H_2O$. The initial concentration of $Fe(ClO_4)_2 \cdot 6H_2O$ and concentration of added ligand was 5.00×10^{-4} mol dm^{-3} and 3.78 mol dm^{-3} for (a), and 2.51×10^{-4} mol dm^{-3} and 4.70×10^{-3} mol dm^{-3} for (b). Data analysis and the determination of formation constants with respect to the formation of iron(II) complexes were carried out by the program SPECFIT/32; this procedure is based on factor analysis and a least-squares method.

Detail description for Evans ^{1}H NMR method

The paramagnetic molar susceptibility $\chi_M{}^P$ of the paramagnetic compound is given by eq. (1), and the value $(d_0 - d_s)/m^P$ takes between –1 and 0 (eq. (2)).

$$\chi_M{}^P = 3\delta\upsilon^P M^P/4\pi\upsilon_0 m^P + \chi_0(M^p + M^p(d_0 - d_s{}^P)/m^P) - \chi_M{}^{dia} \tag{1}$$

$$-1 < (d_0 - d_s)/m^P < 0 \tag{2}$$

υ_0 is the operating frequency of the NMR spectrometer, $\delta\upsilon^P$ is the shifts in frequency (Hz), M^p is the molecular mass of the dissolved paramagnetic compound (g mol^{-1}), m^P is the concentration of the paramagnetic solute (g cm^{-3}), d_0 and d_s are the densities of the pure solvent and solution, $\chi_M{}^{dia}$ is the diamagnetic contribution of the compound. When M^p is large, $\chi_M{}^{dia}$ gives large contribution toward $\chi_M{}^P$. Moreover, although less error will be introduced by eliminating the second term in $\chi_M{}^P$ when M^p is small, these solvent effects should be considered when M^p is large. Because M^p (M^p = 1181.5) of $t_{100}c_0$-**2** is rather large, the effects of diamagnetic contribution and solvent effects should be considered. Alhough an excellent way to cancel these effects is the use of corresponding diamagnetic complex, we could not use this way, because [Zn(**1**)$_3$]$^{2+}$ was not isolated yet. As an alternative way, we conducted Evans method using a reference solution that contains the same quantity of the ligand (C. Piguet, *J. Educ. Chem.*, **1995**, *74*, 815). This method leads to reduce the contributions derived from (a) solvent correction and (b) diamagnetic contribution as follows.

(a) Solvent correction

In general, $\chi_M{}^P$ estimated by neglecting the term of solvent correction, the second term of eq (1), takes higher value than the actual paramagnetic molar susceptibility (eq. (2)). When pure solvent is used as a reference solution, HS percentage obtained by neglecting the second term is estimated 5% higher at a maximum than the actual paramagnetic molar susceptibility in the case of our complex (M^p = 1181.5, $\chi_0 = -5.85 \times 10^{-7}$ cm^3/g).

In our study, a reference solution that contains the same quantity of the ligand (eq. (3)) was used to modify the second term. Diamagnetic susceptibility of the ligand ($\chi_M{}^{dia(L)}$) shifts in frequency, $\delta\upsilon^L$, toward virtual pure solvent is shown by eq. (4), and measurable shifts in frequency, $\delta\upsilon^{obs}$, is given by eq. (5).

$$M^L/m^L = 3M^P/m^P \tag{3}$$

$$\chi_M{}^{dia(L)} = 3\delta\upsilon^L M^L/4\pi\upsilon_0 m^L + \chi_0(M^L + M^L(d_0 - d_s)/m^L) \tag{4}$$

$$\delta\upsilon^{obs} = \delta\upsilon^P - \delta\upsilon^L \tag{5}$$

Using eq. (3-5), eq. (1) gives eq. (7) under the assumption that diamagnetic contribution can be described as a summation of diamagnetic susceptibility of three ligand ($3\chi_M{}^{dia(L)}$), one iron(II) ($\chi_M{}^{dia(Fe)}$), two tetrafluoroborate ($2\chi_M{}^{dia(BF4)}$), and three water crystalline molecule ($\chi_M{}^{dia(H2O)}$) (eq. (6)).

$$\chi_M{}^{dia} = 3\chi_M{}^{dia(L)} + \chi_M{}^{dia(Fe)} + 2\chi_M{}^{dia(BF4)} + 3\chi_M{}^{dia(H2O)} \tag{6}$$

$$\chi_M{}^P = 3\delta\upsilon^{obs} M^P/4\pi\upsilon_0 m^P + \chi_0(M^p + M^p(d_0 - d_s{}^P)/m^P - 3(M^L + M^L(d_0 - d_s{}^L)/m^L)) - \chi_M{}^{dia(Fe)} - 2\chi_M{}^{dia(BF4)} - 3\chi_M{}^{dia(H2O)} \tag{7}$$

The second term in eq. (7) is the term of modified solvent correction. The term within parentheses of the second term takes positive value, because eq. (2) can be also applied to the reference solution. The modification of this term using eq. (3) again leads to eq. (8)

$$0 < (M^p - 3\,M^L) + M^p(d_s{}^L - d_s{}^P)/m^P \tag{8}$$

Here, $d_s^L - d_s^P$ should be negative, because mass concentration of the paramagnetic molecule is larger than that of ligand in reference solution, and density of the paramagnetic molecule is also larger (D. H. Grant, *J. Educ. Chem.*, **1995**, *72*, 39.). Thus, eq. (8) is led to eq. (9).

$$0 < (M^p - 3\,M^L) + M^p(d_s^L - d_s^P)/m^P < (M^p - 3\,M^L) \qquad (9)$$

As $M^p - 3\,M^L$ is much smaller than M^p ($M^p = 1181.5$, $(M^p - 3\,M^L) = 283.5$), the second term in eq. (7) only can affect 1% toward HS percentage at a maximum. Now that the second term modified by this method is found to less affect total magnetic susceptibility and also thermodynamic parameters on spin crossover behaviour that we discusses, we treated the effect of solvent correction as negligible.

(a) Diamagnetic contribution

As is already appeared in eq. (7), diamagnetic contribution of the ligand is experimentally corrected. The other diamagnetic contribution is corrected using Pascal's constant ($\chi_M^{\mathrm{dia(Fe)}}$, $\chi_M^{\mathrm{dia(BF4)}}$, and $\chi_M^{\mathrm{dia(H2O)}}$ are –13, –39,and –13 × 10^{-6} cm^3 mol^{-1}, respectively).

Another considerable effect is the degree of change in diamagnetic contribution before and after photoisomerization, *i.e.*, between $[\mathrm{Fe}(t_{100}c_{0}\text{-}\mathbf{1})_3]^{2+}$ and $[\mathrm{Fe}(t_{67}c_{33}\text{-}\mathbf{1})_3]^{2+}$, because changes in HS ratio between two states (3%) is rather small. Here, molar susceptibility of diamagnetic contribution, χ_M^{dia}, can be roughly estimated using molecular weight of the molecule, M (O. Kahn, *Molecular Magnetism*; VCH: New York–Weinheim–Cambridge, 1993.).

$$\chi_M^{\mathrm{dia}} = -nM \times 10^{-6} \; (n = 0.4\text{-}0.5) \qquad (10)$$

n takes smaller value when the molecule is aromatic due to its constitutive correction. Actually, χ_M^{dia} of $[\mathrm{Fe}(t_{100}c_{0}\text{-}\mathbf{1})_3]^{2+}$, which is aromatic molecule, is estimated to be –369 × 10^{-6} cm^3 mol^{-1} using Pascal's constant, corresponding to the case of $n \approx 0.4$. As far as we consider Pascal's constant, $[\mathrm{Fe}(t_{67}c_{33}\text{-}\mathbf{1})_3]^{2+}$ takes the same value, because such structual change affects no change toward its constitutive correction. Moreover, if we consider that $[\mathrm{Fe}(t_{67}c_{33}\text{-}\mathbf{1})_3]^{2+}$ takes $n = 0.5$ in eq. (10), the changes of diamagnetic contribution only can affect 0.3% toward HS percentage at a maximum. As $n = 0.5$ can be applied in the case with aliphatic molecule, actual diamagnetic contribution would change less than 0.3% because $[\mathrm{Fe}(t_{67}c_{33}\text{-}\mathbf{1})_3]^{2+}$ is still aromatic molecule. Thus, changes in diamagnetic contribution between $[\mathrm{Fe}(t_{67}c_{33}\text{-}\mathbf{2})_3]^{2+}$ and $[\mathrm{Fe}(t_{100}c_{0}\text{-}\mathbf{1})_3]^{2+}$ is far lower than observed magnetization change (3% change in HS percentage), confirming that observed magnetization changes are derived from changes in spin-equilibrium state induced by photoisomerization.