Tuning of spin crossover equilibrium in catecholatoiron(III) complexes by supporting ligands†

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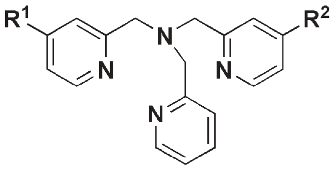
Introduction of electron-withdrawing groups on co-ligands effectively raises the spin crossover temperature of catecholatoiron(III) complexes and induces a significant amount of the low spin species in solution even at around room temperature.

The spin crossover phenomenon has been studied very intensely during the last decade, in relation to their potential applications in molecular electronics.[1] Chemical tuning of spin crossover behavior would offer the possibility of designing spin transition complexes, which can be useful for technical and/or scientific applications at ambient temperature. A variety of transition metal compounds exhibiting spin crossover between high-spin and low-spin states have been reported.[2] Recently, Girerd's and our groups separately reported spin crossover behavior between high-spin and low-spin states in catecholatoiron(III) complexes $[Fe^{III}(TPA)(cat)]^+$ (TPA = tris(pyridin-2-ylmethyl)amine, cat = catecholate dianion),[3,4] whose 3,5-di-*tert*-butylcatecholate analogue was prepared first by Que *et al.*[5] These studies demonstrated that substituent groups on the catecholate ligands greatly influence the spin crossover behavior. Compared with spin crossover temperatures in the solid state, however, those in solution are extremely low and not greatly altered.[3,6] This suggests that there are additional influences arising from intermolecular interactions between the complexes in the solid state. In this study, we report that introduction of electron-withdrawing groups on the TPA ligand greatly increases the spin crossover temperature of catecholatoiron(III) complexes, which results in a significant amount of the low-spin species in solution even at room temperature.



	R^1=	R^2=
for **1**	MeO	MeO
for **2**	H	H
for **3**	Cl	Cl
for **4**	NO_2	H
for **5**	NO_2	NO_2

4-Chlorocatecholatoiron(III) complexes (**1**–**5**)‡ having substituted TPA ligands have been synthesized.[7] The EPR spectra of frozen solutions of **1**–**5** at 123 K (Fig. 1) clearly show that electron-withdrawing R-groups effectively shift spin equilibrium to the low-spin state. Spin crossover transition can be observed for **4** and **5** in non-frozen solution; *i.e.*, the effective magnetic moments in acetonitrile decrease from 5.5 to 5.3 μ_B for **4** and from 5.0 to 4.6 μ_B for **5** in CH_3CN on lowering the temperature from 303 K to 243 K (Fig. S1, see ESI†). In contrast, **1**–**3** show constant magnetic moments of about 5.5 μ_B in the same temperature range, indicating that they retain the high-spin ferric center. Assuming the magnetic moments of 5.5 μ_B for high-spin and 1.7 μ_B for low-spin, the extent of the high-spin species is estimated to be 100% (**1**–**3**), 92% (**4**), and 67% (**5**) at 243 K.

The complexes **1**–**5** show two intense bands in the visible-NIR region (Table 1), which are assignable to charge transfer bands (LMCT) from the catecholate ligand to the high-spin iron(III) center.[8,9] As R-groups become electron-withdrawing, the LMCT bands are shifted to longer wavelengths. This indicates a decrease in the d-orbital energy of the ferric center,[8] which parallels the result of reduction potentials of the iron center of **1**–**5** (Table 1). Interestingly, the intensity of the lower LMCT band of **5** is *ca.* 60% of those of the others. The unique features of **5** become more

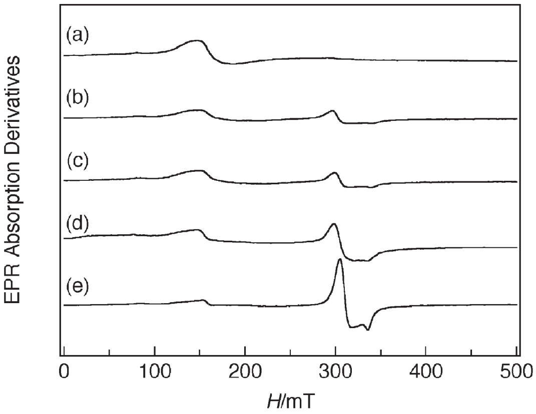


Fig. 1 X-band EPR spectra of **1**–**5** in frozen CH_3CN at 123 K. **1** (a), **2** (b), **3** (c), **4** (d), and **5** (e).

Table 1 Data for **1**–**5**

Complex	$E_{pc}{}^{a}$/mV	LMCT bands^{b}/nm (ε/$M^{-1}cm^{-1}$)	$k_{obs}{}^{c}$/10^{-4} s^{-1}
1	−903	474 (2010), 767 (3040)	0.18
2	−828	483 (1930), 787 (2970)	0.67
3	−748	496 (1920), 805 (2950)	1.6
4	−731	498 (2040), 815 (2670)	2.1
5	−641	509 (2400), 839 (1820)	2.9

[a] Cathodic peak potential *vs.* Fc/Fc^+ couple, in CH_3CN containing 0.1 M *n*-Bu_4NClO_4. Scan rate 100 mV s^{-1}. [b] In CH_3CN at 298 K. [c] In CH_3CN under 1 atom O_2 at 243 K.

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† Electronic supplementary information (ESI) available: Magnetic moments in solution and solid states, ^1H NMR and variable-temperature UV-Vis-NIR spectra. See http://www.rsc.org/suppdata/cc/b4/b418678h/

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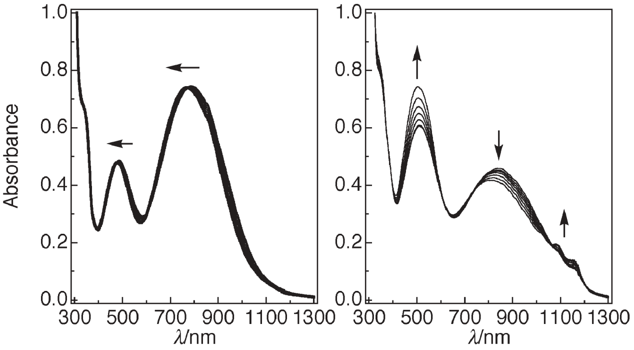

Fig. 2 Variable temperature UV-Vis-NIR spectra of **2** (left) and **5** (right) in CH_3CN. The arrows indicate the changes as the temperature is lowered from 303 to 243 K.

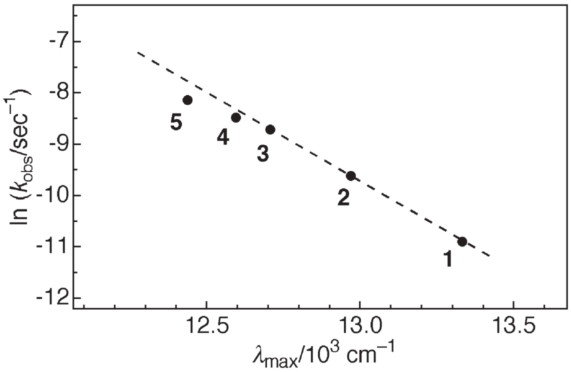

Fig. 3 Correlation between the logarithm of the reaction rate constant (k_{obs},) and the lower energy of the LMCT bands (λ_{max}) at 243 K.

prominent in the variable-temperature UV-Vis-NIR spectra. As the temperature is lowered, the absorption band at around 856 nm decreases in its intensity accompanying a blue shift, and those at around 509 and 1100 nm increase in their intensities (Fig. 2 right). The complex **4** shows the similar but less significant spectral changes. The complexes **1–3**, on the other hand, exhibit only blue shifts while retaining the intensities (Fig. 2 left, Fig. S2, see ESI†). When considered with the results of the effective magnetic moment, the spectral changes observed for **4** and **5** must reflect the spin crossover transition in these complexes. Therefore, we tentatively assign the new peaks at around 1100 nm to the LMCT band for the low-spin species.

The ^{1}H NMR spectra of **1–5** at 298 K show very similar broad signals over a wide range of frequencies, which are characteristic of high-spin Fe(III) complexes (Fig. S3, see ESI†). The similarity in the spectra among **5** and the others indicates the rapid spin equilibrium in **5**. As R-groups become electron-withdrawing, the paramagnetic shifts of the TPA ligands decrease and those of the catecholate ligand increase, *e.g.*, the ^{1}H signals of CH_2 of the unsubstituted pyridine arms shift from 130 to 103 ppm, and those of the 4Cl-cat ligand shift from -40.4 to -63.5 ppm. This indicates that the stronger Fe–catecholate interaction becomes, the weaker the Fe–TPA interaction. This result provides the following explanation for the effects of the R-groups on the TPA ligand on the spin equilibrium: the weak coordination of TPA to Fe(III) stabilizes the d-orbital energy of the ferric center, which results in a decrease in the energy difference between the Fe(III) center and the catecholate ligand. The resultant strong catecholate coordination to Fe(III) should stabilize the low-spin state through an increase in the ligand field strength.

Many catecholatoiron(III) complexes have been investigated as functional models for intradiol catechol dioxygenase,[10,11] which catalyzes the oxidative cleavage of the aromatic ring of catechols utilizing molecular oxygen.[10,12] However, the functional models so far investigated were found to contain only a high-spin ferric center at ambient temperatures.[11] Therefore, the oxygen reactivity of **5**, that contains the low-spin state in solution at around room temperature, should provide valuable information on the reaction mechanism.[13] The estimated reaction rate constants of **1–5** (Table 1) were plotted in log units against the energy of the lower LMCT band (See Fig. 3). The complex **5** shows a negative deviation from the linear correlation line for **1–3** . Considering that the linear correlation between the reactivity and the lower LMCT energy is a common feature for the high-spin species,[6] the negative deviation of **5** from the linear correlation indicates that the low-spin state has lower reactivity with O_2 than the high-spin state.

In summary, we found that due to the presence of electron-withdrawing substituents on TPA ligands, the TPA ligand coordinates less efficiently to the Fe(III) center and in turn the catecholate ligand provides more electron density to the Fe(III) center and the low-spin state becomes accessible. Complex **5**, especially, bearing two NO_2-groups gains a significant amount of the low spin fraction in solution even at around room temperature. Reactivity analysis of these novel catecholatoiron(III) complexes first revealed considerable lower reactivity of the low-spin state with O_2 than the high-spin state. The mechanism underlying this new finding is under investigation in our laboratory.

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Notes and references

‡ **1**: Anal. Calc. for $C_{50}H_{45}BClFeN_4O_4$: C 69.18, H 5.23, N 6.45, Cl 4.08; found: C 68.93, H 5.20, N 6.45, Cl 4.07; ESI-MS: *m/z*: 548.1 $[M\text{–}BPh_4]^+$. **2:** Anal. Calc. for $C_{48}H_{41}BClFeN_4O_4$: C 71.35, H 5.11, N 6.93, Cl 4.39; found: C 71.21, H 4.94, N 6.92, Cl 4.15; ESI-MS: *m/z*: 488.1 $[M\text{–}BPh_4]^+$. **3**: Anal. Calc. for $C_{48}H_{39}BCl_3FeN_4O_4$: C 65.75, H 4.48, N 6.39, Cl 12.13; found: C 65.51, H 4.31, N 6.41, Cl 11.87; ESI-MS: *m/z*: 556.2 $[M\text{–}BPh_4]^+$. **4**: Anal. Calc. for $C_{48}H_{39}BClFeN_5O_4\cdot 1.25H_2O$: C 65.85, H 4.89, N 8.00, Cl 4.05; found: C 65.84, H 4.78, N 8.11, Cl 4.28; ESI-MS: *m/z*: 533.3 $[M\text{–}BPh_4]^+$. **5**: Anal. Calc. for $C_{47}H_{39}BClFeN_6O_6\cdot CH_3OH$: C 63.28, H 4.66, N 9.04, Cl 3.81; found: C 63.29, H 4.55, N 9.31, Cl 3.77; ESI-MS: *m/z*: 577.9 $[M\text{–}BPh_4]^+$.

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