

# Thermochromism of the disproportionation equilibrium of $\pi$ -dimer radical anion complexes bridged by scandium ions

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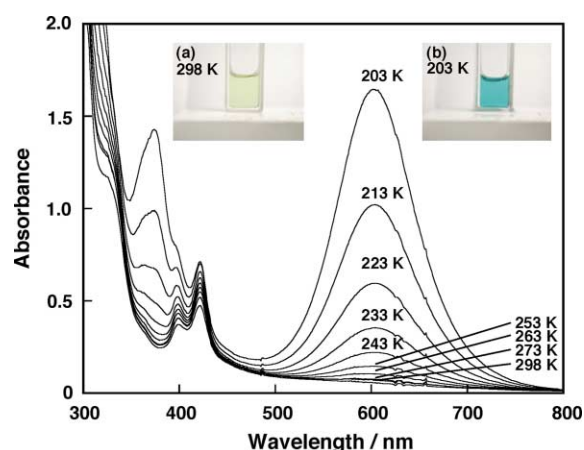
Semiquinone radical anion ( $Q^{\cdot-}$ ) forms a stable  $\pi$ -dimer with neutral *p*-benzoquinone (Q), bridged by two or three scandium ions ( $Sc^{3+}$ ) to afford  $Q^{\cdot-}-nSc^{3+}-Q$  ( $n = 2,3$ ), which is in disproportionation equilibrium with Q and hydroquinone ( $QH_2$ ). The number of binding scandium ions changes depending on temperature, causing a remarkable color change associated with the change in the ESR spectra.

The complex formation between acceptor radical anion ( $A^{\cdot-}$ ) and metal ion ( $M^{n+}$ ) with strong Lewis acidity induces a large acceleration of electron transfer.<sup>1,2</sup> In this context, we have recently reported unusually high kinetic order in scandium ion ( $Sc^{3+}$ )-promoted electron transfer from iridium complex to *p*-benzoquinone (Q) due to the formation of  $\pi$ -dimer radical anion complexes of Q bridged by two or three scandium triflates [ $Sc(OTf)_3$ ] ( $Q^{\cdot-}-nSc^{3+}-Q$ ,  $n = 2,3$ ).<sup>3</sup> The number of binding scandium ions is expected to be changed by temperature, inducing drastic color change of the  $\pi$ -dimer radical anion complexes.<sup>3</sup> However, the complex formed between  $A^{\cdot-}$  and  $M^{n+}$  ( $A^{\cdot-}-M^{n+}$ ) is usually too unstable to examine the temperature dependent change in spectroscopic properties.<sup>1-3</sup> Such temperature induced color change has been known as thermochromism for a long time.<sup>4</sup> A search for new thermochromic systems has attracted increased attention to the design of a molecular switch, *i.e.*, an efficient interconversion between two accessible states at ambient temperature.<sup>5-14</sup> Thermochromism results from many types of thermally driven changes in the energy of electronic excitations such as: proton tautomerization of organic compounds involving different proton accepting moieties,<sup>5,6</sup> valence tautomerism of metal complexes involving a redox active metal center,<sup>7-10</sup> conformational change of the polymer backbone,<sup>11,12</sup> and formation of supramolecular complexes or aggregates.<sup>13</sup> Although most thermochromic compounds so far reported are diamagnetic and paramagnetic thermochromic systems containing a redox active metal center,<sup>7-10</sup> organic radical ions normally possess low-lying excited states and the resulting color is highly susceptible to environmental change.<sup>1-3</sup> In this context, tetracyanoethylene (TCNE) a stable radical anion has recently been reported to exhibit thermochromism.<sup>14</sup> In this case, however, the color change is caused by an equilibrium between the paramagnetic monomer radical anion and the dimer dianion, which is diamagnetic.

We report herein a novel type of thermochromism involving  $\pi$ -dimer radical anion complexes of *p*-benzoquinone and naphthoquinone bridged by scandium triflates [ $Sc(OTf)_3$ ]. Semiquinone radical anions exist in a disproportionation equilibrium. The number of binding scandium ions is shown to change depending on temperature, causing a remarkable color change, which is associated with the change in the ESR spectra.

Addition of a high concentration of  $Sc(OTf)_3$  ( $5.4 \times 10^{-1}$  mol  $dm^{-3}$ ) to a deaerated propionitrile solution of hydroquinone ( $QH_2$ ) ( $1.2 \times 10^{-3}$  mol  $dm^{-3}$ ) and *p*-benzoquinone (Q) ( $3.9 \times 10^{-3}$  mol  $dm^{-3}$ ) affords a yellow solution at 298 K (inset

of Fig. 1a). When the temperature is lowered to 203 K, the color turns blue (inset of Fig. 1b). The color change depending on temperature is completely reversible and it can be repeated many times.

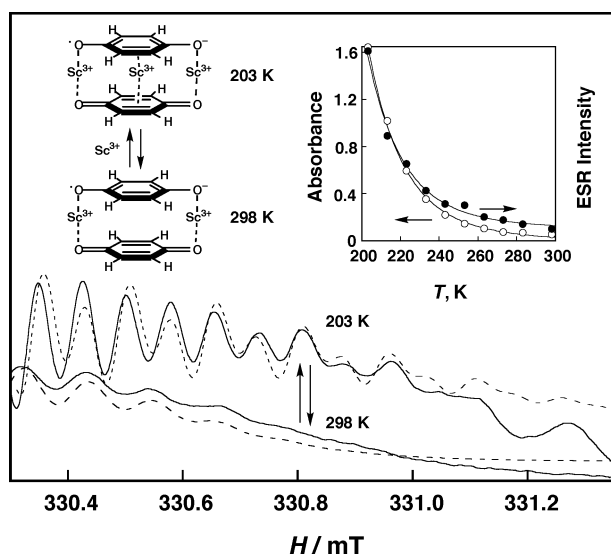


**Fig. 1** Absorption spectral changes of a deaerated propionitrile solution of  $QH_2$  ( $3.2 \times 10^{-3}$  mol  $dm^{-3}$ ) and Q ( $1.8 \times 10^{-2}$  mol  $dm^{-3}$ ) in the presence of  $Sc(OTf)_3$  ( $3.2 \times 10^{-1}$  mol  $dm^{-3}$ ) at various temperatures (1 mm path length). Inset: visible color change of a deaerated propionitrile solution of  $QH_2$  ( $1.2 \times 10^{-3}$  mol  $dm^{-3}$ ) and Q ( $3.9 \times 10^{-3}$  mol  $dm^{-3}$ ) in the presence of  $Sc(OTf)_3$  ( $5.4 \times 10^{-1}$  mol  $dm^{-3}$ ) at (a) 298 K and (b) 203 K.

Such a visible spectral change of the solution depending on temperature is shown in Fig. 1. New absorption bands ( $\lambda_{max} = 374$  and 604 nm) appear and the absorbance increases with decreasing temperature. There is no isosbestic point observed because the absorbance increases in the whole spectral region in Fig. 1. However, the reverse process is observed when temperature is increased and the absorbance change depending on temperature is completely reversible. Virtually the same spectral change depending on temperature is observed when  $QH_2$  and Q are replaced by hydronaphthoquinone ( $NQH_2$ ) and 1,4-naphthoquinone (NQ), respectively.

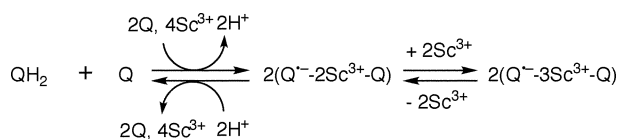
In order to confirm the species responsible for the color change depending on temperature, the ESR spectra of a propionitrile solution of  $QH_2$  ( $3.2 \times 10^{-3}$  mol  $dm^{-3}$ ), Q ( $1.8 \times 10^{-2}$  mol  $dm^{-3}$ ) and  $Sc(OTf)_3$  ( $3.2 \times 10^{-1}$  mol  $dm^{-3}$ ) were measured at 298 K and 203 K. The ESR spectrum observed at 298 K with hyperfine splitting due to eight equivalent protons [ $a(8H) = 0.112$  mT] and superhyperfine splitting due to two equivalent  $Sc^{3+}$  ions [ $a(2Sc^{3+}) = 0.112$  mT] agrees with that of the  $\pi$ -dimer formed between  $Q^{\cdot-}$  and Q, which is bridged by two equivalent  $Sc^{3+}$  ions ( $Q^{\cdot-}-2Sc^{3+}-Q$ ) as reported in  $Sc^{3+}$ -promoted electron transfer from iridium complexes to Q.<sup>3</sup> When the temperature is lowered to 203 K, the ESR spectrum is changed to exhibit further superhyperfine splitting due to an additional  $Sc^{3+}$  ion [ $a(Sc^{3+}) = 0.075$  mT]. The ESR spectrum agrees with that of  $Q^{\cdot-}-3Sc^{3+}-Q$ , in which additional  $Sc^{3+}$  is placed between the

$\pi$ -planes of  $(Q)_2^{\cdot-}$  to produce  $Q^{\cdot-}-3Sc^{3+}-Q$  (Fig. 2).<sup>3</sup> The change in the ESR spectrum between  $Q^{\cdot-}-2Sc^{3+}-Q$  and  $Q^{\cdot-}-3Sc^{3+}-Q$  was reversible as in the case of the color change in Fig. 1. The decrease in the number of binding  $Sc^{3+}$  ions from three to two is clearly identified as the disappearance of the ESR signal at the lowest or highest magnetic field region due to the loss of additional superhyperfine splitting due to one  $Sc^{3+}$  ion with increasing temperature (Fig. 2), where the change in the ESR spectra (solid line) at the higher magnetic field region is shown together with the computer simulation spectra (broken line) under the same experimental conditions as employed for the color change in Fig. 1. The decrease in the ESR signal intensity with temperature agrees largely with the accompanied decrease in absorbance at 604 nm (inset of Fig. 2).<sup>15</sup>

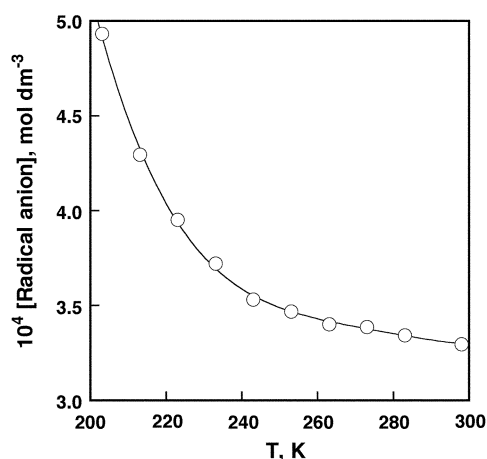


**Fig. 2** ESR spectra of a deaerated propionitrile solution of  $QH_2$  ( $3.2 \times 10^{-3}$  mol  $dm^{-3}$ ) and  $Q$  ( $1.8 \times 10^{-2}$  mol  $dm^{-3}$ ) in the presence of  $Sc(OTf)_3$  ( $3.2 \times 10^{-1}$  mol  $dm^{-3}$ ) in the magnetic range 330.30–331.35 mT at 203 K and 298 K. Broken lines are simulation ESR spectra of  $Q^{\cdot-}-3Sc^{3+}-Q$  [ $a(8H) = a(2Sc^{3+}) = 0.150$  mT,  $a(Sc^{3+}) = 0.075$  mT and  $\Delta H_{msl} = 0.064$  mT] and  $Q^{\cdot-}-2Sc^{3+}-Q$  [ $a(8H) = a(2Sc^{3+}) = 0.112$  mT and  $\Delta H_{msl} = 0.093$  mT]. Inset: dependence of absorbance at 604 nm and ESR intensity at 331.28 mT on temperature.

Thus, the thermochromism associated with the reversible change in the absorption spectrum observed in Fig. 1 is summarized as shown in Scheme 1. There is equilibrium between  $QH_2$  and  $Q$  in the presence of a large concentration of  $Sc^{3+}$ , that is disproportionation equilibrium of  $Q^{\cdot-}-2Sc^{3+}-Q$  and  $Q^{\cdot-}-3Sc^{3+}-Q$ . The total yields of radical anions ( $Q^{\cdot-}-2Sc^{3+}-Q$  and  $Q^{\cdot-}-3Sc^{3+}-Q$ ) based on the concentration of  $QH_2$  were determined by double integration of the ESR signal in reference to that of a known amount of a stable radical, diphenylpicrylhydrazyl (DPPH), at various temperatures as shown in Fig. 3. The yield of the radical anions increases with decreasing temperature. This indicates that the disproportionation equilibrium in Scheme 1 is shifted to the right hand side and formation of the  $Q^{\cdot-}-3Sc^{3+}-Q$  complex is more favored as compared to the  $Q^{\cdot-}-2Sc^{3+}-Q$  complex with decreasing temperature. The change in the number of binding  $Sc^{3+}$  ions causes changes in both the color and the ESR signal depending on temperature. The absence of the isosbestic points in Fig. 1 is ascribed to the involvement of the disproportionation equilibrium with  $QH_2$  and  $Q$  in Scheme 1. The number of binding



**Scheme 1**



**Fig. 3** Plot of the concentration of radical anion in the deaerated propionitrile solution of  $QH_2$  ( $3.2 \times 10^{-3}$  mol  $dm^{-3}$ ) and  $Q$  ( $1.8 \times 10^{-2}$  mol  $dm^{-3}$ ) in the presence of  $Sc(OTf)_3$  ( $3.2 \times 10^{-1}$  mol  $dm^{-3}$ ) at 298 K–203 K.

$Sc^{3+}$  ions is also changed in the case of naphthosemiquinone dimer radical anion  $[(NQ)_2^{\cdot-}]$  from two ( $NQ^{\cdot-}-2Sc^{3+}-NQ$ ) at 298 K to three ( $NQ^{\cdot-}-2Sc^{3+}-NQ$ ) at 243 K.<sup>3</sup>

The absorption band due to the dimer radical anion without  $Sc^{3+}$  ( $Q_2^{\cdot-}$ ) appears at  $\lambda_{max} = 1290$  nm in the NIR (near infrared) region.<sup>16</sup> This is assigned to the transition from the  $\pi$ -bonding orbital of the  $\pi$ -dimer to the  $\pi^*$  orbital.<sup>14</sup> Thus, the  $\lambda_{max}$  value varies depending on the  $\pi$ -bonding strength. The binding of two  $Sc^{3+}$  ions with  $Q_2^{\cdot-}$  results in an increase in the  $\pi$ -bonding strength, leading to a significant blue shift of the absorption band of the  $\pi$ -complex. The additional binding of  $Sc^{3+}$  between the two  $\pi$ -planes of  $Q_2^{\cdot-}$ , which has a coulombic rather than covalent character, may decrease the  $\pi$ -bonding strength, resulting in the red-shift of the absorption band as observed in Fig. 1.

In conclusion, unique thermochromism reported in this study involves a change in the number of scandium ions binding with dimer radical anions in the disproportionation equilibrium depending on temperature, which causes the drastic color change associated with the change in the ESR spectrum.

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