

Novel Redox-Switching Systems Composed of Conjugated Bimetallic Complexes

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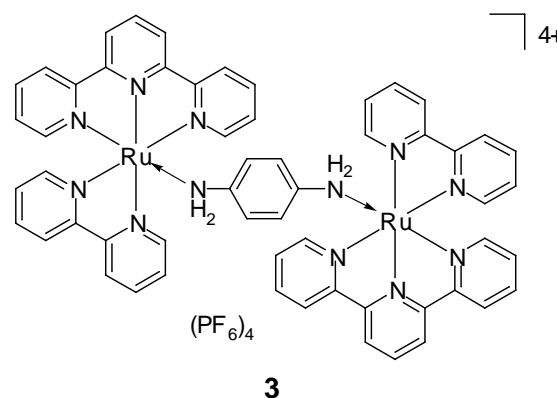
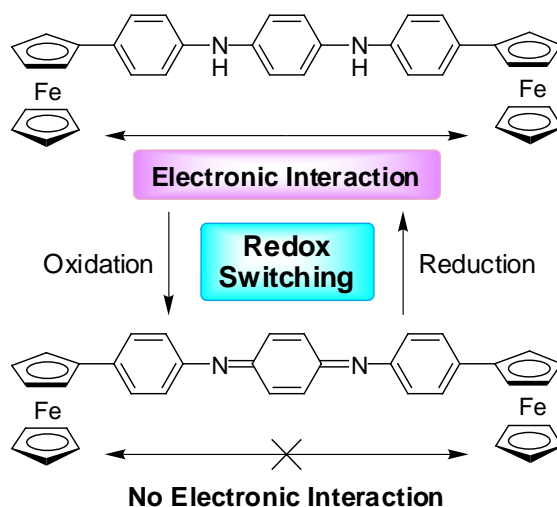
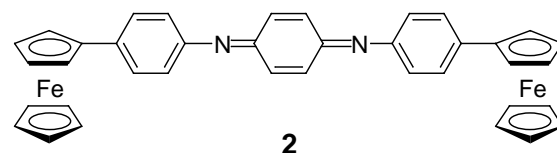
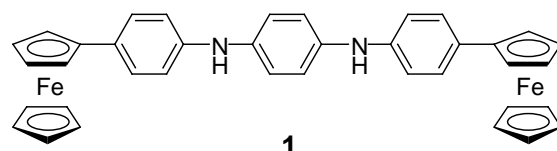
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The redox forms including the neutral phenylenediamines, the partially oxidized phenylenediamine radical cations, and the oxidized quinonediimines are recognized as the molecular redox unit of polyanilines. In a previous paper, the controlled complexation with the oxidized quinonediimine unit has been demonstrated to afford the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex depending on the coordination mode.¹ We herein report the introduction of terminal redox-active transition metals into the *p*-phenylenediamine bridging spacer to provide novel redox-switching systems.

The *p*-phenylenediamine derivative **1** bearing terminal ferrocene units was synthesized by Pd₂(dba)₃/(±)-BINAP catalyzed amination of 4-bromophenylferrocene with *p*-phenylenediamine in 26% yield. The *p*-phenylenediamine derivative **1** was readily oxidized with PhIO to give the quinonediimine derivative **2** as an oxidized form.

The redox properties of **1** and **2** were investigated by cyclic voltammetry. The *p*-phenylenediamine derivative **1** in CH₂Cl₂ exhibited four one-electron redox waves ($E_{1/2} = -0.13, -0.03, 0.16,$ and 0.49 V vs Fc/Fc⁺). The waves at -0.13 and -0.03 V are assigned to the successive one-electron oxidation of the ferrocene moieties. It should be noted that electronic communication is observed through the *p*-phenylenediamine bridging spacer. The extent of the ferrocenyl-ferrocenyl interaction is estimated from the wave splitting, $\Delta E_{1/2} = 0.10$ V. The corresponding equilibrium constant (K_c) for the comproportionation reaction ($[\text{Fc-Fc}] + [\text{Fc}^+ - \text{Fc}^+] = 2[\text{Fc}^+ - \text{Fc}]$) is 49. The waves at 0.16 and 0.49 V are assigned to one-electron oxidation processes of the *p*-phenylenediamine moiety. This result is in sharp contrast to the redox behavior of **2** in CH₂Cl₂, in which the redox of the quinonediimine moiety and ferrocene ones were observed as an irreversible reduction wave at -1.66 V and simultaneous one-electron redox wave at 0.05 V, respectively. In the case of the oxidized form **2**, electronic communication between the terminal ferrocene moieties was not observed. These results indicate that a redox switching of the electronic communication through the redox-active *p*-phenylenediamine bridging spacer was found to be achieved in this system.

The ruthenium dinuclear complex **3** with *p*-phenylenediamine bridging spacer was also synthesized. A redox switching of the electronic communication and emission properties through the redox-active *p*-phenylenediamine bridging spacer was also described.



Reference

1. a) T. Moriuchi, S. Bandoh, M. Miyaishi, and T. Hirao, *Eur. J. Inorg. Chem.*, **2001**, 651. b) T. Moriuchi, M. Miyaishi and T. Hirao, *Angew. Chem. Int. Ed.*, **40**, 3042 (2001). c) T. Moriuchi, M. Kamikawa, S. Bandoh, and T. Hirao, *Chem. Commun.*, **2002**, 1476.