



Design and characterization of ferrocene–peptide–oligoaniline conjugates

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ABSTRACT

Ferrocene–peptide–oligoaniline conjugates were designed by the introduction of two ferrocene–peptide conjugates into a π -conjugated phenylenediamine spacer to demonstrate the luminescent switching by changing the redox states of the π -conjugated phenylenediamine moiety, wherein the self-aggregation of the π -conjugated moiety was achieved in a higher concentration to induce the chirality organization with a red shift of the maximum emission wavelength.

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Architectural control of molecular arrangement of π -conjugated systems has gained increasing interest due to their potential applications as advanced molecular devices based on defined functional properties.¹ The utilization of molecular self-organization is one of the most important strategies for the development of functional materials.² Control of hydrogen bonding³ has attracted much attention in the design of various molecular assemblies by virtue of the directionality and specificity.⁴ The utilization of self-assembling properties of amino acids, which possess chiral centers and hydrogen bonding sites, is considered to be a convenient approach to highly ordered molecular assemblies. Recently, we have embarked upon the introduction of peptides or amino acids into molecular scaffold to induce chirality organization through the chirality of amino acids and the intramolecular interchain hydrogen bonding.^{5–7} In previous Letters, the introduction of one dipeptide chain (-Ala-Pro-) into the ferrocene scaffold was demonstrated to permit well-defined chirality organization through multiple hydrogen-bonded network.^{5b,f,j,l,n,o,8} On the other hand, the redox-active phenylenediamine, which exists in three redox forms: the reduced phenylenediamine, the partially oxidized phenylenediamine radical cation, and the oxidized quinonediimine, is a molecular unit of poly-anilines as π -conjugated polymers. The redox switching of the emission properties of Ru(II) dipyridyl complexes bearing the phenylenediamine moieties by changing the redox states of the phenylenediamine moiety has already been demonstrated in previous Letters.⁹ The utilization of self-assembling properties of ferrocene–peptide conjugates is envisioned to regulate the molecular arrangement of π -conjugated systems. From these points of view, we herein report the design and characterization of ferrocene–peptide–oligoaniline conjugates.

Our design is based on the symmetrical introduction of two ferrocene–peptide conjugates (Fc-CO-L-Ala-L-Pro-) into a π -conjugated

phenylenediamine spacer as shown in Figure 1. The advantage in the use of the -alanyl-proline sequence as a dipeptide chain depends on a hydrogen bonding alanyl moiety and a sterically constrained proline as a well-known turn inducer in proteins. The ferrocene–peptide–phenylenediamine conjugate **1red** was synthesized from (chlorocarbonyl)ferrocene and the corresponding dipeptidyl oligoaniline **2red** in 66% yield. The redox properties of **1red** were investigated by cyclic voltammetry. The ferrocene–peptide–phenylenediamine conjugate **1red** in dichloromethane exhibited two oxidation waves at 0.30 and 0.67 V versus Fc/Fc⁺ as shown Figure 2. The peak with threefold height at 0.30 V might be assignable to the one-electron oxidation processes of two ferrocene moieties and one-electron oxidation of the phenylenediamine moiety. The wave at 0.67 V is assumed to be attributable to the one-electron oxidation of the partially oxidized phenylenediamine radical cation to the oxidized quinonediimine. The ferrocene–peptide–phenylenediamine conjugate **1red** was easily oxidized into the ferrocene–peptide–quinonediimine conjugate **1ox** by treatment with lead(IV) acetate as an oxidant in 80% yield. The oxidized form **1ox** could be again reduced to **1red** with hydrazine monohydrate (Fig. 3). These ferrocene–peptide–oligoaniline conjugates were fully characterized by spectral data and elemental analyses.

In the ¹H NMR spectra of **1red** in CDCl₃ (5.0 × 10⁻⁴ M), the NH resonances of the central phenylenediamine moiety were hardly perturbed by the addition of aliquots of DMSO-*d*₆ to CDCl₃ (CDCl₃: 8.74 ppm, CDCl₃/DMSO-*d*₆ (9:1): 8.71 ppm). On the contrary, a down-field shift was observed with the Ala and C-terminal amide NH resonances (CDCl₃: 6.48 and 9.09 ppm, CDCl₃/DMSO-*d*₆ (9:1): 7.10 and 9.56 ppm, respectively). These results indicate the formation of intramolecular hydrogen bonds between the NH of the central phenylenediamine moiety and the CO of the ethyl ester moiety although the Ala and C-terminal amide NHs do not participate in intramolecular hydrogen bonding in solution. In the case of **1ox**, the Ala and C-terminal amide NH resonances were perturbed by the addition of aliquots of DMSO-*d*₆ to CDCl₃ (CDCl₃: 6.45 and 9.33 ppm, CDCl₃/DMSO-*d*₆ (9:1): 6.89 and 9.78 ppm, respectively),

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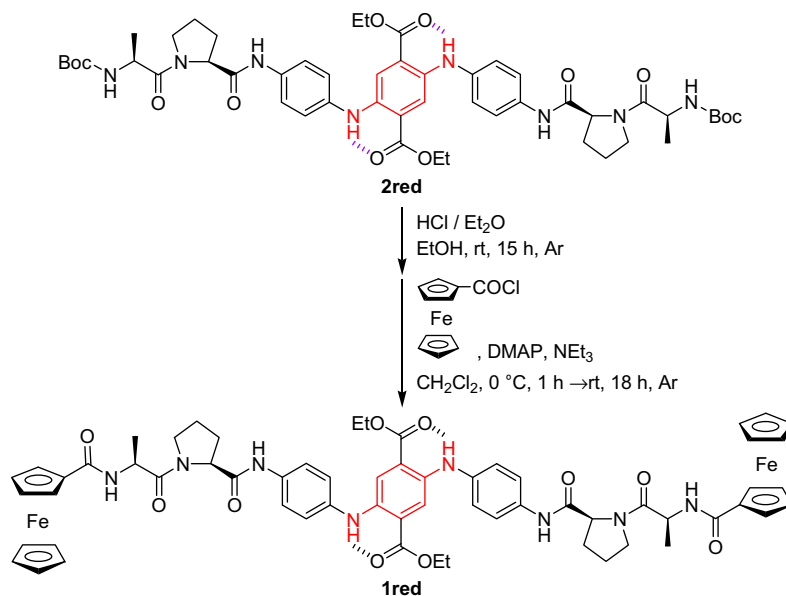


Figure 1. Synthesis of ferrocene-peptide-phenylenediamine conjugate **1red**.

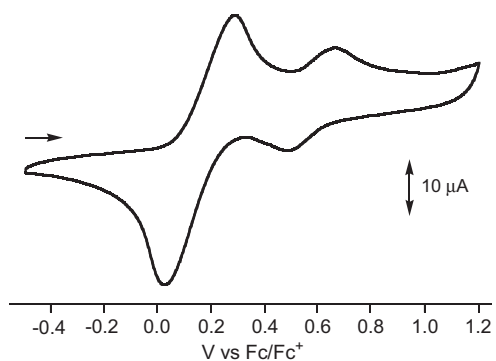


Figure 2. Cyclic voltammogram of **1red** in dichloromethane (5.0×10^{-4} M) containing 0.1 M Bu₄NClO₄ at a glassy carbon working electrode with scan rate 100 mVs⁻¹ under an atmosphere of argon.

indicating the absence of intramolecular hydrogen bonds in a solution state.

The UV-vis spectra of the reduced form **1red** and the oxidized form **1ox** in dichloromethane showed a broad absorption at around 400–550 and 400–650 nm, respectively, which are probably due to a low-energy charge-transfer transition of the π -conjugation moiety (Fig. 4a). The reduced form **1red** exhibited luminescence at 593 nm (Fig. 4b). It is noteworthy to mention that weak luminescence was observed with the oxidized form **1ox**. These findings indicate that the redox switching of the luminescent properties is achieved by changing the redox states of the π -conjugated moiety.

The ferrocene-peptide-phenylenediamine conjugate **1red** is expected to self-assemble through contribution of all available hydrogen bonding donors of the Ala and C-terminal amide moieties in a high concentration to change the luminescent properties. Circular dichroism (CD) spectrometry is a useful tool to determine

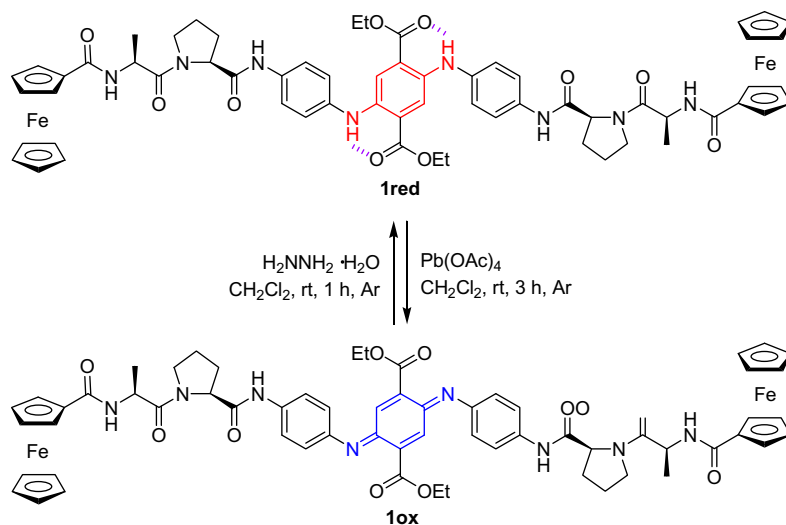


Figure 3. Redox interconversion between **1red** and **1ox**.

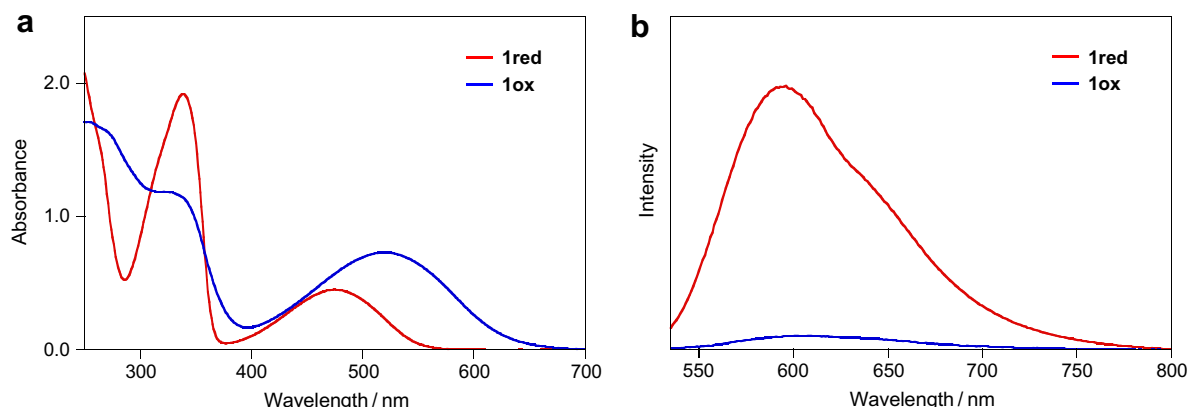


Figure 4. (a) Electronic spectra of **1red** and **1ox** in dichloromethane (5.0×10^{-5} M). (b) Emission spectra of **1red** ($\lambda_{\text{exc}} = 475$ nm, 5.0×10^{-5} M, 298 K) and **1ox** ($\lambda_{\text{exc}} = 517$ nm, 5.0×10^{-5} M, 298 K) in dichloromethane.

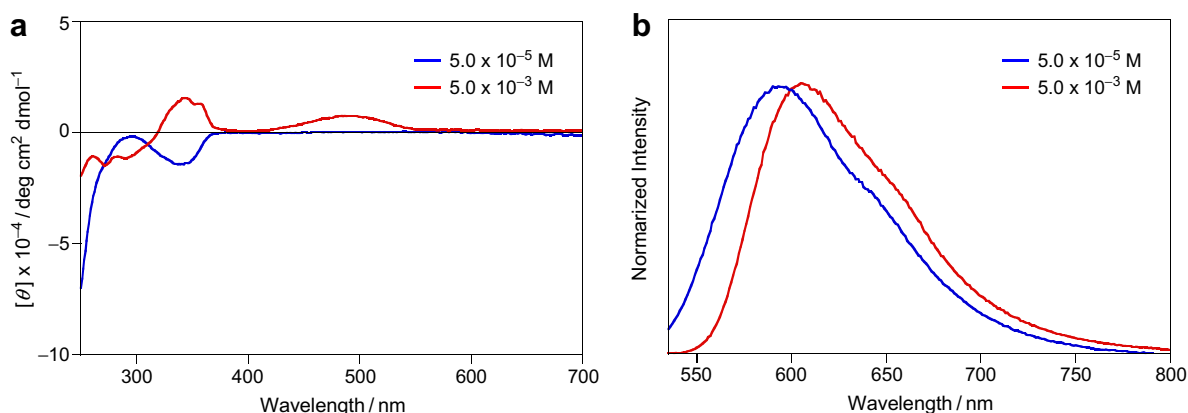


Figure 5. (a) CD spectra of **1red** in 5.0×10^{-5} M and 5.0×10^{-3} M dichloromethane solution. (b) Emission spectra of **1red** in 5.0×10^{-5} M and 5.0×10^{-3} M dichloromethane solution ($\lambda_{\text{exc}} = 475$ nm, 298 K).

an ordered structure in solution. Interestingly, an induced circular dichroism (ICD) at the absorbance region of the π -conjugated moiety was observed in the CD spectrum of **1red** in a high concentration dichloromethane solution (5.0×10^{-3} M) although such ICD was not detected in a dilute dichloromethane solution (5.0×10^{-5} M) as shown in Figure 5a. The ferrocene–peptide conjugates bearing one dipeptide chain (-L-Ala-L-Pro-) have been demonstrated to induce well-defined chirality organization through multiple hydrogen-bonded network in the crystal packing.^{5b,f,o} Chirality organization of the π -conjugated moiety of **1red** might be achieved by self-assembly through intermolecular hydrogen bondings. Although luminescence was observed at 593 nm in a dilute dichloromethane solution of **1red** (5.0×10^{-5} M), **1red** exhibited luminescence at 609 nm in a high concentration dichloromethane solution (5.0×10^{-3} M) (Fig. 5b). A red shift of the luminescence suggests π - π interaction based on the intermolecular aggregation with increasing concentration. This self-aggregation is consistent with the result of the CD spectrum in a high concentration.

In conclusion, ferrocene–peptide–oligoaniline conjugates were designed to demonstrate the luminescent switching by changing the redox states of the π -conjugated phenylenediamine moiety. The introduction of the ferrocene–peptide conjugates (Fc-CO-L-Ala-L-Pro-) into the π -conjugated phenylenediamine spacer was found to induce the self-aggregation of the π -conjugated moiety, resulting in the chirality organization with a red shift of the maximum emission wavelength. Further investigation including structural characterization of nanostructure of self-aggregates and tuning of the color is now in progress.

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Supplementary data

Supplementary data (general information and experimental details for syntheses and characterization of **1red** and **1ox**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.101.

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