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Short communication

Synthesis of novel dyes containing ferrocene

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Abstract

The synthesis of some novel dyad dyes containing ferrocene (Fc) is described. By incorporating the Fc moiety, the triplet-state of the dyad dyes could be effectively quenched, thus enhancing photostability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ferrocene; Dyad dyes; Photostability; Naphthalimide; Intramolecular electron-transfer

1. Introduction

It is known that singlet oxygen plays an important role in the photodegradation of organic dyes [1]. In this regard, singlet oxygen arising from the interaction between the triplet-state of dyes and molecular oxygen would be instrumental in the dye degradation process. Therefore, singlet oxygen quenchers have been employed as additives during dye application, to enhance photostability. Another approach to increasing dye photostability involves blocking triplet state formation using quenching agents. Both approaches are intermolecular methods for quenching the triplet-state and it is clear that they are not applicable to all end-use applications.

Ferrocene (Fc), a well-known organometallic compound, is a good electron donor that can be reversibly oxidized and there have been several reports of Fc-substituted multicomponent molecules [2,3]. For dyads based on a naphthalimide–Fc assembly, Fc effectively quenched fluorecsence from the naphthalimide (NP) chromophore [2]. Since Fc has an oxidation potential of +0.50 V (SCE), intramolecular electron transfer from Fe to NP occurs to quench fluorescence of the latter. When Fc is oxidized electrochemically or chemically, intramolecular electron transfer from the oxidized ferrocene species (Fc^+) is inhibited and the fluorescence of the NP moiety recovers. This type of dyad would be important in the development of an electrochemical controlled molecular switch or molecular sensor. Due to the low absorption properties of the Fc chromophore ($\lambda_{abs} = 440$ nm, $\varepsilon = 90$ M^{-1} cm^{-1}), the absorption spectra of NP-Fc dyads are nearly identical to that of NP alone and a 1:1 physical mixture (i.e. NP+Fc). No additional bands were produced from the charge transfer process.

Recently, a series of covalent linked fullerene–Fc dyads were studied to demonstrate that the ferrocenyl center reduces the excited singlet states of fullerene via intramolecular electron transfer [3]. Since Fc is an effective singlet oxygen and triplet state quencher [4], it is anticipated that the

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introduction of Fc into dye systems would improve photostability without significantly affecting color and intensity. Therefore, we have synthesised the novel dyad dyes shown in Fig. 1 and studied their excited states. The triplet-state quenching of dye chromophores by the Fc unit in NP–Fc-1, AN–Fc-1 and K–Fc-1 dyad systems was also evaluated in the light of previous results [5,6].

2. Experimental

2.1. General

^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. The mass spectra were recorded on either a Hitachi M80 or Finnigan MAT 8430 spectrometer. Elemental analyses were obtained using a Carolo Erba MOD 1106 instrument (Italy). Chemical reactions were monitored by thin-layer chromatography on silica gel. All solvents were distilled prior to use.

2.2. Syntheses

2.2.1. NP–Fc dyads

2-Ferrocenyl-ethylamine was prepared according to a published method [7]. 4-Pyrrolidino-1,8-naphthyl anhydride and its 4-substituted analogs were also prepared according to prior methods [8,9]. To make the analogs, 4-bromo-1,8-naphthyl anhydride and excess amines such as pyrrolidine were stirred under reflux in 2-methoxyethanol for 2–4 h under nitrogen. After cooling, the deposited solids were recrystallised several times from chlorobenzene to give orange to deep yellow needles.

To prepare the dyads, a mixture of 4-substituted 1,8-naphthyl anhydride (1 mmol) and 2-ferrocenyl-ethylamine (1 mmol) was stirred under reflux in pyridine (15 ml) for 3 h. The reaction was monitored by TLC (silica gel, using methylene chloride:acetone/ 30:1 as the eluent) and showed the formation of a product component at $R_f = 0.65$. The solvent was evaporated and the product was purified by chromatography (silica gel) eluting with methylene chloride: acetone (30:1) to afford a bright yellow solid.

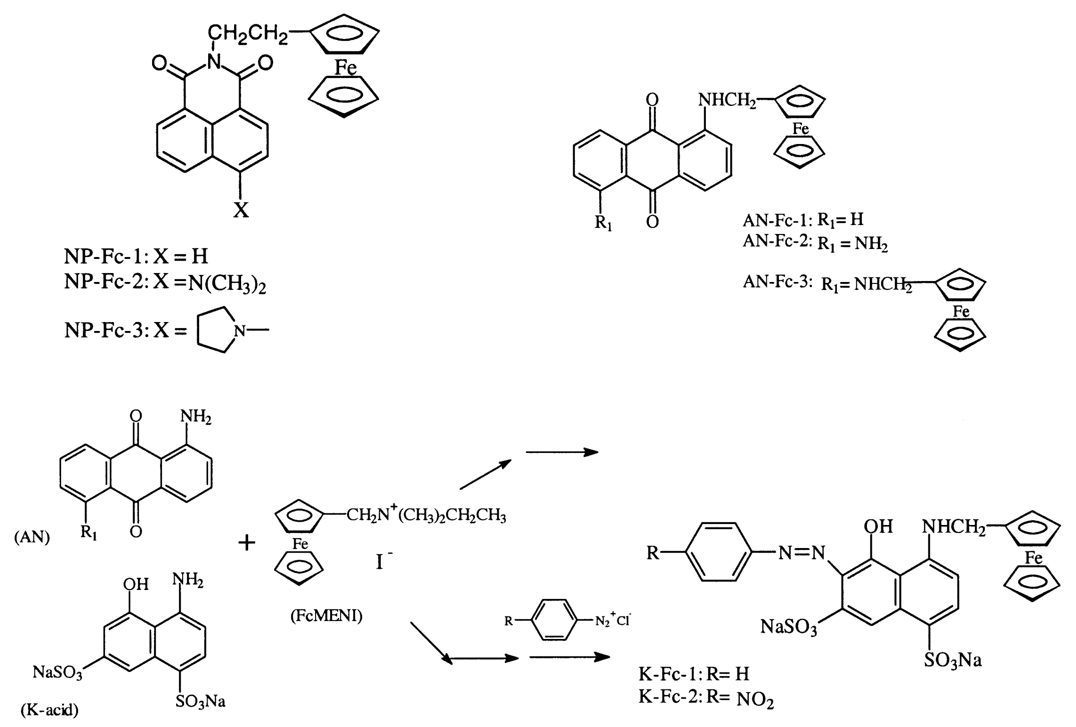

Fig. 1. Synthetic routes and chemical structures of the dyad dyes containing ferrocene.

2.2.1.1. NP–Fc-1. Yield = 41%. ^{1}H NMR ($CDCl_3$): 2.70 (m, 2H, $FcCH_2$), 4.09 (s, 2H, cyclopentadiene), 4.19 (s, 7H, cyclopentadiene), 4.33 (m, 2H, NCH_2), 7.75 (t, 2H), 8.21 (d, J = 2.20 Hz, 2H), 8.60 (d, J = 2.17 Hz, 2H) (naphthalene ring). MS (EI, 70 eV): 408 (M^+, 42%). Anal. calcd for $C_{24}H_{19}FeNO_2$: C, 70.41; H, 4.64; N, 3.42. Found: C, 70.30; H, 4.56; N, 3.26%. Absorption spectrum (CH_3CN) λ_{max}(nm) ($\epsilon \times 10^4$(M^{-1} cm^{-1})) = 331 (1.239).

2.2.1.2. NP–Fc-2. Yield = 38%. ^{1}H NMR ($CDCl_3$): 2.69 (m, 2H, $FcCH_2$), 3.10 (s, 6H, $N(CH_3)_2$), 4.10 (s, 2H, cyclopentadiene), 4.18 (s, 7H, cyclopentadiene), 4.32 (m, 2H, NCH_2), 7.13 (d, J = 1.95 Hz, 1H), 7.65 (m, 1H), 8.48 (m, 3H) (naphthalene ring). MS (EI, 70 eV): 452 (M, 57%). Anal. calcd for $C_{26}H_{24}FeN_2O_2$: C, 69.05; H, 5.31; N, 6.20. Found: C, 69.07; H, 5.26; N, 6.17%. Absorption spectrum (CH_3CN) λ_{max}(nm) ($\epsilon \times 10^4$(M^{-1} cm^{-1})) = 416 (1.355).

2.2.1.3. NP–Fc-3. Yield = 45%. ^{1}H NMR ($CDCl_3$): 2.15 (m, 4H, pyrrolidine, $NCH_2\underline{CH_2}$), 2.72 (m, 2H, $FcCH_2$), 3.83 (m, 4H, pyrrolidine, NCH_2), 4.08 (s, 2H), 4.18 (s, 7H), 4.36 (m, 2H, NCH_2), 6.89 (d, J = 2.05 Hz, 1H), 7.57 (m, 1H), 8.47 (m, 1H), 8.63 (m, 2H) (naphthalene ring). MS (EI, 70 eV): 478 (M, 52%). Anal. calcd for $C_{28}H_{26}FeN_2O_2$: C, 70.31; H, 5.44; N, 5.86. Found: C, 70.25; H, 5.39; N, 5.79%. Absorption spectrum (CH_3CN) λ_{max}(nm) ($\epsilon \times 10^4$ (M^{-1} cm^{-1})) = 444 (1.366).

2.2.2. AN–Fc dyads

Ferrocenemethyl-dimethylethylammonium iodide (FcMENI) was prepared according to previously reported methods [10,11]. Product formation is based on an established reaction between an ammonium compound and an arylamine [12].

The general procedure used to prepare the target dyads was as follows: A mixture of FcMENI (1.6 g) and 1,5-diaminoanthraquinone or 1-aminoanthraquinone (1 g) was stirred under reflux in ethanol (30 ml) for 4 h. The reaction was monitored by TLC (silica gel, using methylene chloride as the eluent) and showed the formation of a product component at $R_f = 0.7$. The solvent was evaporated and the product was purified by chromatography (silica gel) eluting with methylene chloride, to afford a violet-red solid.

2.2.2.1. AN–Fc-1. Yield = 45%. ^{1}H NMR ($CDCl_3$): 4.15–4.30 (m, 11H, cyclopentadiene and $NH\mathit{CH_2}$), 7.09 (d, J = 1.66 Hz, 1H), 7.44 (m, 1H), 7.54 (d, J = 1.44 Hz, 1H), 7.66 (m, 2H), 8.22 (d, J = 1.52 Hz, 1H), 8.32 (d, J = 1.52 Hz, 1H). MS (EI, 70 eV): 421 (M, 90%). Anal. calcd for $C_{25}H_{19}FeNO_2$: C, 71.28; H, 4.51; N, 3.33. Found: C, 71.24; H, 4.48; N, 3.29 %. Absorption spectrum (ethanol) λ_{max}(nm) = 490.5.

2.2.2.2. AN–Fc-2. At the end of the reaction between FcMENI and 1,5-diaminoanthraquinone, the second component obtained from the column was AN–Fc-2 (45%). ^{1}H NMR ($CDCl_3$): 4.15–4.30 (m, 11H, cyclopentadiene and $NH\underline{CH_2}$), 6.92 (m, 2H), 7.50–8.0 (m, 4H). MS (EI, 70 eV): 436 (M, 85%). Absorption spectrum (ethanol) λ_{max}(nm) = 495.4.

2.2.2.3. AN–Fc-3. This synthesis required FcMENI (4.8 g) and 1,5-diaminoanthraquinone (1 g), and the first component from the column was AN–Fc-3 (50%). ^{1}H-NMR ($CDCl_3$): 4.15–4.30 (m, 22H, cyclopentadiene and $NH\underline{CH_2}$), 6.92 (m, 2H), 7.50–8.0 (m, 4H). MS (EI, 70 eV): 634 (M, 12%). Absorption spectrum (ethanol) λ_{max}(nm) = 510.6.

2.2.3. K–Fc dyads

The general procedure used to prepare K–Fc dyads was as follows. A mixture of FcMENI (6.4 g) and 1-amino-4,6-disulfo-8-naphthol (4.2 g) was stirred under reflux in ethanol (20 ml) and water (15 ml) for 6 h. The resultant brown solution was cooled to room temperature, whereupon a yellow precipitate formed. The mixture was filtered and the solid was dissolved in water (30 ml) containing Na_2CO_3 (3 g). Coupling with benzenediazomum chloride or 4-nitrobenzenediazonium chloride was carried out in the usual way [13–15], producing a violet dye (56 %). After drying, the crude dye was purified by chromatography (silica gel G), eluting with 3:1:v/v) *n*-butyl alcohol:ethanol:acetone (3:1:1 *n*-butyl alcohol:ethanol:H_2O for K–Fc-2) (v/v) to afford pure red-violet dye.

2.2.3.1. K–Fc-1. ^{1}H NMR (D_2O): 3.70 (s, 2H, $NHCH_2$), 4.20 (m, 9H, cyclopentadiene), 7.20–8.0 (m, 8H). FAB MS, *m/z*: 665 (M, 65 %). Absorption spectrum (H_2O) λ_{max}(nm) = 526.

2.2.3.2. Compound (K–Fc-2). ^{1}H NMR (D_2O): 3.70 (s, 2H, $NHCH_2$), 4.20 (m, 9H, cyclopentadiene), 7.20–8.0 (m, 7H). FAB MS, *m/z*: 781 (10%). Absorption spectrum (H_2O) λ_{max}(nm) = 539.

3. Results and discussion

3.1. Properties offluorescent dyads

It is known that the substituted Fe unit shows a reversible oxidation at a potential relatively close to that of unsubstituted Fc [16]. Similarly, we found that one-electron oxidation of the Fe unit in the present Fc-dyads is chemically and electrochemically reversible in CH_3CN [17,18]. The oxidation potential of the Fc unit is $E^{ox}_{1/2} = 0.75$ V vs SCE. Also, in agreement with the electrochemical properties of 1,8-naphthalimides [19,20], the reduction process for the naphthalimide moiety in the present NP–Fc dyads is a multi-electron, chemically irreversible step.

To illustrate electron transfer involving the NP–Fc dyads, results from NP–Fc-3 are summarised. In this case, fluorescence emission decays via two-exponential kinetics and the fluorescence lifetime of compound NP–Fc-3 is 43 ± 0.7 ps and 161 ± 1.0 ps at 530 nm in a polystyrene matrix [17,18]. This is much shorter than the lifetime of *N*-propyl-1,8-naphthalimide (10.17 ns) at 477 nm in acetonitrile [21], and confirms that the fluorescence of the NP moiety in NP–Fc-3 can be significantly quenched by intramolecular electron transfer from Fe to NP.

Generally, Dexter's mechanism [22] is invoked to explain triplet-triplet energy transfer, while most experimental observations involving singlet–singlet energy transfer are interpreted in terms of Förster's mechanism [23]. The absorption maximum for the Fc moiety (~440 nm) is shorter than the emission maximum for the NP fluorophore in compounds NP–Fc-2 and NP–Fc-3 (~520 nm). This means that singlet–singlet energy transfer from excited NP to the Fc moiety can be ruled out for our NP-Fc dyads. It is more likely that the Fe moiety will quench emission of the NP fluorophore, producing a redox active molecular switch with fluorescence via intramolecular electron transfer.

The triplet absorption of NP–Fc dyads has been measured by nanosecond time resolved pulse photolysis [5]. However, the triplet absorption for the NP unit (~ 490 nm) was not observed for NP–Fc dyads following deaerating with Argon gas for 30 min. These results suggest that Fc effectively quenched the NP triplet-state and that the introduction of Fc into dye systems improves dye photostability by quenching singlet oxygen formation. This is achieved without adversely affecting the color characteristics (including emission peck) of the dyes employed.

3.2. Other dyads

We have also incorporated Fc into the structures of K-acid based monoazo dyes (K–Fc) and anthraquinone (AN–Fc) dyes. The K-acid based monoazo dyes possess good solubility in most common organic solvents and in water and have almost the same dyeing properties as the corresponding azo dyes without Fc substitution. Since the photostability of the K-acid based azo dyes without Fc was generally good, only a minor increase in photostability was observed following Fc substitution. The detailed properties of these novel dyes are summarised elsewhere [14].

Acknowledgements

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