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Synthesis and light absorption/emission properties of novel squarylium dimers bearing a ferrocene spacer

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Abstract

The squarylium (SQ) dimer **1** bearing a ferrocene spacer was synthesized, and its electronic absorption and fluorescence properties were investigated. The dimer **1a**, in which the ferrocene moiety and each SQ chromophore are separated by an ethylenoxycarbonyl liking unit, exhibited an electronic absorption band with a large half-bandwidth compared to an analogous monomeric SQ dye, indicating that the two squarylium chromophores in **1a** electronically perturb each other. On the other hand, the dimer **1c**, bearing the longer undecamethylenoxycarbonyl linking unit than **1a**, did not exhibit any significant interaction between the SQ chromophores. Significant fluorescence quenching was observed in the dimer **1a** as well as the ferrocene-SQ dyad **2a** bearing the same linking unit as that in **1a**, compared to **1c** and the reference SQ dye **3**. This result indicated that photoinduced electron transfer from the ferrocene moiety to the SQ chromophore occurs. In particular, the fluorescence emission of **1a** was quenched more effectively than that of **2a**, and thus, intramolecular chromophoric interaction in **1a** facilitates ferrocene-SQ photoinduced electron transfer.

Keywords: Squarylium dimer; Ferrocene; Electronic absorption; Fluorescence emission; Fluorescence lifetime; Photoinduced electron transfer

1. Introduction

The squarylium (SQ) chromophoric system provides many well-established functional dyes, which have so far contributed greatly to various areas of optoelectronics fields, such as xerography [1], optical recording [2], non-linear optics [3], solar cells [4], and electroluminescence devices [5]. Although SQ dyes are often regarded as substituted cyanine dyes in terms of their donor–acceptor polymethine structures, their π-conjugation system contains a central four-membered ring, which affords unique physicochemical properties; e.g., sharp and intense light absorption band, intense fluorescence emission, photoconductivity, and so on. As the photochemical properties of SQ dyes may also contribute further to the development of various molecular optoelctronics devices, it is of much importance to investigate photochemistry of SQ dyes involving electron and/or energy transfer reactions. However,

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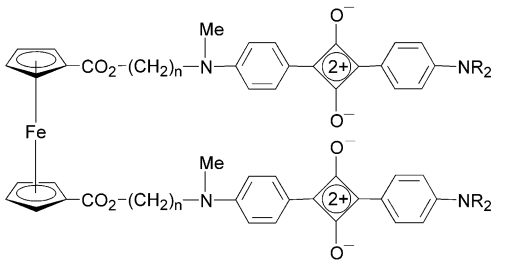
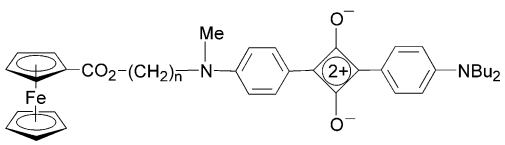
few examples are known about photochemical properties of multi-chromophoric systems consisting of SQ and other photochemically and electrochemically active components. One of the reasons would be that the restricted methods for preparation of SQ dyes [6] prevent us from constructing the suitable model systems.

Recently, synthetic methods for unsymmetrical SQ dyes were independently reported [7–9], and then, promoted us to design the SQ dimer **1** in which two SQ chromophores are linked by a ferrocene spacer. Although ferrocene has often been employed as an electron donor in artificial photosynthetic systems [10], nothing is reported about photochemical features in the covalently linked ferrocene-SQ system. In the present paper, we show the synthesis of the SQ dimer **1** (Fig. 1) and its photochemical properties, especially focusing on photoinduced electron transfer from the ferrocene moiety to the SQ chromophores.



1a: R = Bu, n = 2
1b: R = -CH_3, -$C_{18}H_{37}$, n = 2
1c: R = Bu, n = 11



2a: n = 2
2b: n = 11

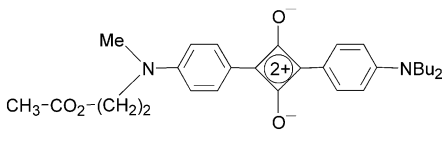


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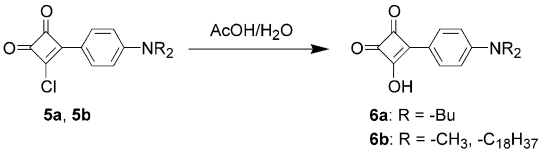
Fig. 1. The structures of the ferrocene-linked squarylium dimer **1**, the ferrocene-squarylium dyad **2**, and the squarylium dye **3**.

2. Results and discussion

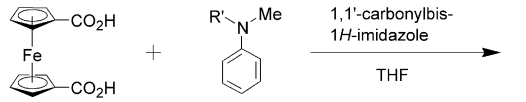
2.1. Synthesis of the ferrocene-linked SQ dimer *1*

The ferrocene-linked SQ dimers **1a–c** were prepared according to the synthetic protocol as shown in Scheme 1. First, the dye precursors **4a** and **4b** were obtained by condensation of 2 equivalents of *N*-(2-hydroxyethyl)- and *N*-(11-hydroxyundecyl)-*N*-methylanilines **9a** and **9b** with ferrocenedicarboxylic acid **8a** in the presence of 1,1′-carbonylbis-1*H*-imidazole in 77 and 42% yields, respectively. Then, **4a** reacted with the monosubstituted squaric acids **6a** and **6b** [9] in 2-propanol in the presence of triethyl orthoformate to yield the SQ dimers **1a** and **1b** in 52 and 9% yields, respectively. The dimer **1c**, in which the SQ chromophores and ferrocene moiety are spaced by the long alkyl chains, was prepared in the same manner: the reaction of **4b** with **6a** afforded **1c** in 11% yield. As reference compounds, the ferrocene-SQ dyads **2a** and **2b** and the SQ monomer **3** were employed. The dyads **2a** and **2b**, which involve ethylene and undecamethylene linking units, respectively, were prepared by condensation



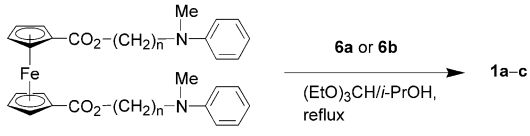
5a, **5b**

6a: R = -Bu
6b: R = -CH_3, -$C_{18}H_{37}$



8a

9a: R' = -CH_2CH_2OH
9b: R' = -$(CH_2)_{11}OH$



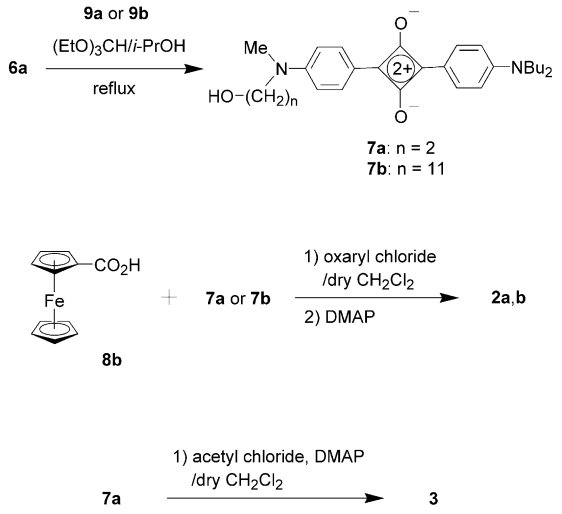
4a: n = 2
4b: n = 11

Scheme 1.

of ferrocenecarboxylic acid with the corresponding SQ derivatives, as shown in Scheme 2. The SQ dimers **1a–c** and the reference compounds **2a–b** and **3** were characterized by ^{1}H NMR, ^{13}C NMR and FAB mass spectra as well as elemental analysis.

2.2. Electronic absorption spectra of the ferrocene-linked SQ dimers

The electronic absorption spectral data of **1**, **2**, and **3** are summarized in Table 1. In Fig. 2 are shown the electronic absorption spectra of **1a** and **2a** in $CHCl_3$ at 298 K, where the concentration of the SQ chromophore in each solution was adjusted to 5.0 μmol/l. The absorbance of **1a** at λ_{max} was two thirds as large as that of **2a**, although the spectra of **2a** resembled that of the SQ monomer **3**. In addition, the dimer **1a** showed a broader half-bandwidth of the spectra than those of **2a** and **3**. These significant differences indicate that the SQ chomophores in **1a** electronically interact with each other due to linkage by the ferrocene spacer: indeed, the distance between cyclopentadienyl rings in a ferrocene is ca. 3.3–3.5 Å, corresponding to the face-to-face distance in π– π stacking, so the ferrocene spacer can act not only as a scaffold to bring two SQ chromophores within close distance but also as a module unit to induce intramolecular exciton interaction [11]. On the other hand, the dimer **1c** exhibited a relatively large absorbance and a narrow half-bandwidth in comparison with **1a**, indicating that the intramolecular electronic interaction between the two SQ chromophores was suppressed by the long and flexible undecamethylene chains. The dimer **1b** exhibited a similar spectral profile to **1a**, showing that introduction of long alkyl (octadecyl) chains at the ends of the SQ components did not interfere with the intramolecular exciton interaction. Although one may expect that the absorption spectral profiles of **1a** and **1b** could be caused by inter- or intramolecular aggregation of the SQ chromophores, the half-bandwidths of the absorption bands of **1a** and **1b** were independent of the dye concentrations in the range from 0.2 μmol/l to 4 mmol/l as well as the temperature from 253 to 293 K, indicating that the



Scheme 2.

Table 1
Electronic absorption and fluorescence emission spectral data of **1**, **2**, and **3**[a]

Compound	Electronic absorption		Fluorescence emission	
	λ_{max}[b]/nm(log ϵ)	Half-bandwidth/nm	F_{max}[c]/nm (relative intensity)	Fluorescence lifetime[d]/ns
1a	638 (5.59)	40	646 (6)	0.7
1b	635 (5.48)	41	646 (16)	0.8
1c	637 (5.64)	31	651 (85)	2.1
2a	633 (5.51)	28	652 (32)	0.4
2b	638 (5.53)	28	653 (89)	2.1
3	632 (5.56)	30	646 (100)	2.1

[a] Obtained in $CHCl_3$ at 298 K.
[b] The wavelength at which the absorption maximum was observed.
[c] The wavelength at which the fluorescence emission maximum was observed.
[d] The errors are within 0.1 ns.

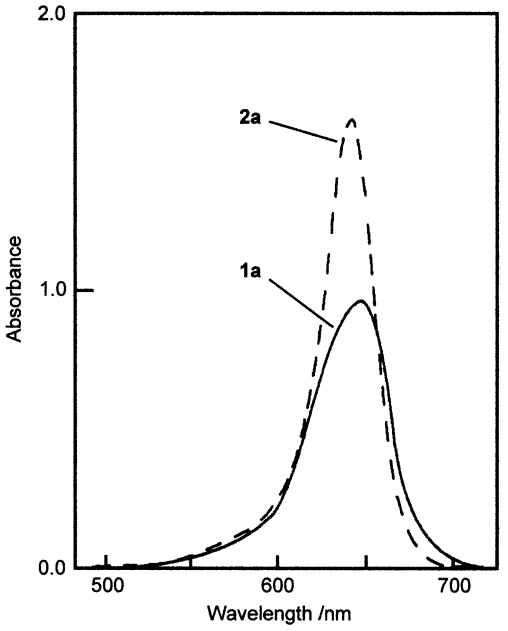


Fig. 2. Electronic absorption spectra of **1a** (2.5 μM) and **2a** (5.0 μM) in $CHCl_3$ at 298 K.

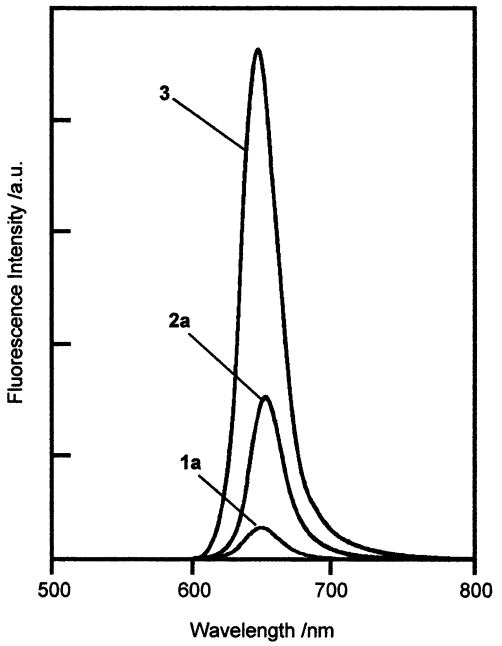


Fig. 3. Fluorescence emission spectra of **1a** (0.3 μM), **2a** (0.6 μM), and **3** (0.6 μM) in $CHCl_3$ at 298 K.

effect of intermolecular aggregate formation on the spectral properties of **1a** and **1b** is negligible.

2.3. Fluorescence emission properties of the ferrocene-linked SQ dimers

Bridging SQ chromophores with a ferrocene spacer gave rise to a significant difference in fluorescence emission properties from the normal SQ dye. As shown in Fig. 3 and Table 1, fluorescence emission intensities of **1a** and **2a** were extremely weak compared to that of **3**: the ferrocene moieties quenched the fluorescence emission of the SQ chromophores. Separating the ferrocene and SQ moieties by the undecamethylene chains suppressed the quenching of the fluorescence emission, as seen in the emission spectra of **1c** and **2b**. These results indicate that the fluorescence emission in ferrocene-appended SQ derivatives **1a**, **1b** and **2a** was quenched through photoinduced electron transfer from the ferrocene unit to the SQ chromophore. Indeed, the oxidation and reduction at +0.43 and −0.85 V (reference electrode, Ag/AgCl; electrolyte, Bu_4N^+-ClO_4^-), corresponding to E_{ox} of ferrocene and E_{red} of the SQ chromophore, respectively, were observed for a solution of a mixture of ferrocene and **3** in acetonitrile, indicating that electronic interaction existed between the ferrocene and SQ moieties. The effective fluorescence quenching in the dimers **1a** and **1b** in comparison with **2a** is presumably due to the intramolecular chromophoric interaction, although experimental evidence for the detailed mechanism has not yet been obtained. Investigation of the fluorescence lifetimes, as summarized in Table 1, also supported the mechanism of fluorescence quenching: the lifetimes of **1a**, **1b** and **2a** were much shorter (< 1 ns) than that of the typical SQ dye**3** (2.1 ns). Furthermore, the undecamethylene-spaced ferrocene-SQ systems **1c** and **2b** exhibited the same values of the lifetime as **3**, clearly showing that the electron transfer was inhibited by keeping the ferrocene and SQ moieties away from each other.

3. Conclusions

In the present study, we described the synthesis of the novel SQ dimers **1a–c** in which the SQ chromophores are linked by a ferrocene spacer,

and discussed their light absorption and fluorescence emission properties. As demonstrated in the electronic absorption spectra of **1a** and **1b**, the ferrocene moiety acts as a spacer which facilitates intramolecular electronic interaction between the SQ chromophores, when the alkyl linking units are relatively short and increase the proximity of the SQ and ferrocene units. Photoinduced electron transfer from the ferrocene to the SQ chromophore was also indicated by the derease in fluorescence emission and fluorescence lifetime studies. The intramolecular chromophoric interactions in **1a** and **1b** improved the efficiency of the electron transfer, compared to that in the ferrocene-SQ dyad **2a**. As SQ dyes possess intense absorption bands in the visible region, the conjugation of electron donors and acceptors with SQs should allow us to construct the photoinduced charge separation systems. Therefore, the ferrocene-SQ system demonstrated here are potentially applicable to the photoreceptor-electron donor unit of application in dye-sensitized solar cells.

4. Experimental

4.1. General remarks

Ferrocenecarboxylic acid **8a** and ferrocenedicarboxylic acid **8b** were prepared by the reported procedure [12]. The dye precursor **6a** was obtained according to the reported procedure [9]. ^{1}H and ^{13}C NMR spectra were taken on a Jeol JNM-GX270 spectrometer. IR spectra were recorded on a Horiba FT-200 spectrometer in KBr pellets. The electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. The fluorescence emission and excitation spectra were recorded on a Shimadzu RF-5000 spectrometer. The fluorescence lifetime analysis was carried out on a Horiba NAES-550 nanosecond fluorometer. The solvent used for electronic absorption and fluorescence emission spectra was of spectroscopic grade. Elemental analysis was recorded on a Yanaco CHN Corder MT-3 recorder. Melting points were measured by a Yanaco MP-21 apparatus. EI mass spectra were recorded on a Shimadzu QP-5000 mass spectromrter. FAB mass spectra were recorded on a Finnigan mat mass spectrometer using 3-nitrobenzylalchohol as a matrix. Cyclic boltammograms were obtained on a Yanaco VMA-010 cyclic boltammetric analyzer, using a Ag/AgCl referential electrode (scan rate, 50 mV/s), where $Bu_4N^+ClO_4^-$ was used as an electrolyte.

4.2. Sample preparation

4.2.1. 2-(N-methyl-N-phenylamino)ethanol **9a**

A mixture of 2-anilinoethanol (41.5 g, 303 mmol) and iodomethane (35.9 g, 253 mmol) in benzene was stirred at 50 °C for 6 h, and then, Et_3N (10 ml) was added to the reaction mixture. The mixture was stirred at 50 °C for additional 20 h, and the solvent was removed on a rotary evaporator. The residue was poured into water, and then, extracted with AcOEt. The organic layer was dried over K_2CO_3, and the solvent was evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2 as eluent) to afford **9a** as a pale yellow oil (22.8 g, 151 mmol, 60% yield): ^{1}H NMR ($CDCl_3$) δ 3.00 (s, 3H), 3.26 (t, J = 6.9 Hz, 2H), 3.64 (t, J = 6.9 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 38.69, 55.24, 59.84, 112.75, 116.88, 128.97, 148.70; EI MS m/z (relative intensity) 120 ($[M-C_2H_5O]^+$, 100%), 151 (M^+, 15%); this compound was used for the syntheses of **4a** and **7** without further purification.

4.2.2. 11-(N-methyl-N-phenylamino)undecanol **9b**

This compound was obtained by the similar method to the preparation of **9a**, using 11-bromoundecanol as a starting material (90% yield, pale yellow oil) : ^{1}H NMR ($CDCl_3$) δ 1.20 (m, 12H), 1.53–1.58 (m, 4H), 2.76–2.95 (m, 5H), 3.26 (t, J = 6.9 Hz, 2H), 3.64 (t, J = 6.9 Hz, 2H), 6.80 (m, 3H), 7.15–7.24 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.78, 26.68, 27.23, 29.46, 29.57, 29.59, 29.62, 29.66, 32.83, 38.30, 52.83, 61.09, 111.96, 112.30, 115.65, 128.98, 149.19, 162.36; this compound was used for the synthesis of **4b** without further purification.

4.2.3. Di[2-(N-methyl-N-phenylamino)ethyl] ferrocecedicarboxylate **4a**

A mixture of **8a** (2.20 g, 8.03 mmol) and 1,1′-carbonylbis-1*H*-imidazole (5.20 g, 32.1 mmol) in

dry THF (50 ml) was heated at reflux for 30 min under nitrogen, followed by addition of **9a** (4.85 g, 32.1 mmol). The mixture was heated at reflux for 56 h, and after cooling, the solvent was removed on a rotary evaporator. The residue was poured into water, and then, extracted with CH_2Cl_2. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by silica gel column chromatography (CH_2Cl_2 as eluent) to afford a crude product, which was dissolved in 3 ml of CH_2Cl_2 and reprecipitated into MeOH to afford **4a** as an orange solid (416 mg, 0.770 mmol, 77% yield): mp 84–88 °C; ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 6H), 3.68 (t, $J=5.9$ Hz, 4H), 4.31 (t, $J=1.8$ Hz, 4H), 4.37 (t, $J=5.9$ Hz, 4H), 4.73 (t, $J=1.8$ Hz, 4H), 6.73 (t, $J=7.3$ Hz, 4H), 6.84 (d, $J=7.3$ Hz, 4H), 7.26 (t, $J=7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 38.58, 51.05, 61.68, 61.87, 71.49, 71.64, 72.43, 72.54, 72.79, 112.04, 112.51, 116.44, 116.54, 129.07, 148.79, 170.10, 170.55; IR (KBr) 1707, 1279 cm^{-1}; FAB MS m/z 541 ($[M+1]^+$); this compound was used for the syntheses of **1a** and **1b** without further purification.

4.2.4. *Di[11-(N-methyl-N-phenylamino)undecyl] ferrocecedicarboxylate* ***4b***

This compound was synthesized by the similar method to the preparation of **4a**, using **9b** as a starting material (42% yield, orange oil): ^{1}H NMR ($CDCl_3$) δ 1.29 (m, 28H), 1.56 (m, 4H), 1.72 (m, 4H), 2.91 (s, 6H), 3.28 (t, $J=7.3$ Hz, 4H), 4.19 (t, $J=7.3$ Hz, 4H), 4.38 (t, $J=1.8$ Hz, 4H), 4.82 (t, $J=1.8$ Hz, 4H), 6.60–6.70 (m, 6H), 7.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.06, 26.67, 27.21, 28.87, 29.32, 29.57, 29.64, 38.26, 52.77, 64.54, 71.37, 72.74, 73.04, 111.92, 112.23, 115.62, 128.94, 128.99, 149.14, 170.23; FAB MS m/z 793 ($[M+1]^+$); this compound was used for the synthesis of **1c** without further purification.

4.2.5. *3-Chloro-4-[4-(N-methyl-N-octadecylamino) phenyl]cyclobut-3-ene-1,2-dione* ***5b***

This compound was synthesized according to the reported method for the preparation of **5a** [9], using *N*-methyl-*N*-octadecylaniline as a starting material. The purification by silica gel column chromatography was performed using CH_2Cl_2/hexane (1/1, v/v, as eluent) (yield, 38%; orange oil): mp 85–86 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, $J=6.9$ Hz, 3H), 1.24 (m, 32H), 3.09 (s, 3H), 3.43 (t, $J=6.9$ Hz, 2H), 6.73 (d, $J=9.2$ Hz, 2H), 8.11 (d, $J=9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.65, 26.91, 29.31, 29.38, 29.53, 29.65, 31.86, 38.44, 52.43, 111.25, 113.56, 131.27, 153.45, 170.63, 185.34, 189.45, 195.45; FAB MS m/z 473 (M^+), 475 ($[M+2]^+$); IR (KBr) 2918, 2846, 1778 cm^{-1}; this compound was used for the synthesis of **6b** without further purification..

4.2.6. *3-Hydroxy-4-[4-(N-methyl-N-octadecylamino)phenyl]cyclobut-3-ene-1,2-dione* ***6b***

This compound was synthesized according to the reported method for the preparation of **6a** [9], using **5b** as a starting material (89% yield, orange solid): mp 200–201 °C; ^{1}H NMR (DMSO-d_6) δ 0.83 (t, $J=6.9$ Hz, 3H), 1.21 (m, 32H), 2.98 (s, 3H), 3.39 (t, $J=6.9$ Hz, 2H), 6.82 (d, $J=9.2$ Hz, 2H), 7.84 (d, $J=9.2$ Hz, 2H); FAB MS m/z 456 ($[M+1]^+$); IR (KBr) 2916, 2850, 1767, 1751, 1704 cm^{-1}; Anal. calcd for $C_{29}H_{45}NO_3$: C, 76.44; H, 9.95; 3.07. Found: C, 76.55; H, 10.45; 2.99.

4.2.7. *The ferrocene-linked SQ dimer* ***1a***

A mixture of **4a** (0.541 g, 1.00 mmol) and **6a** (0.603 g, 2.00 mmol) in 2-propanol/triethyl orthoformate (12 ml, 5/1, v/v) was heated at reflux for 6 h under nitrogen. To the reaction mixture was added an additional amount of **6a** (0.600 g, 1.99 mmol), and the mixture was heated at reflux for 3 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20/1, v/v, as eluent) followed by recrystallization by the solvent diffusion method from CH_2Cl_2/MeOH to hexane to afford a crystal of **1a** (576 mg, 0.520 mmol, 52%): mp 202–203 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J=7.3$ Hz, 12H), 1.39 (sextet, $J=7.3$ Hz, 8H), 1.63 (m, 8H), 3.20 (s, 6H), 3.44 (t, $J=7.3$ Hz, 8H), 3.87 (t, $J=5.6$ Hz, 4H), 4.31 (t, $J=1.8$ Hz, 4H), 4.41 (t, $J=5.6$ Hz, 4H), 4.64 (t, $J=1.8$ Hz, 4H), 6.71 (d, $J=9.2$ Hz, 4H), 6.89 (d, $J=9.2$ Hz, 4H), 8.36 (d, $J=9.2$ Hz, 4H), 8.38 (d, $J=9.2$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 13.98, 20.30, 29.62, 38.86, 50.75, 51.31, 61.35,

71.53, 71.62, 72.19, 72.77, 77.21, 112.41, 119.31, 120.22, 132.59, 133.60, 153.77, 153.95, 169.85, 183.20, 186.71, 189.06; FAB MS *m/z* 1106 (M^+), 1107 ($[M+1]^+$), 1108 ($[M+2]^+$); Anal. calcd for $C_{66}H_{74}FeN_4O_8 \cdot H_2O$: C, 70.45; H, 6.80; 4.97. Found: C, 70.23; H, 6.74; 5.00.

*4.2.8. The ferrocene-linked SQ dimer **1b***

This compound was synthesized by the similar method to the preparation of **1a**, using **4a** and **6b** as starting materials (9% yield): mp > 240 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J=6.9$ Hz, 6H), 1.26 (m, 60H), 1.64 (m, 4H), 3.15 (s, 6H), 3.22 (s, 6H), 3.47 (m, 4H), 3.86 (br s, 4H), 4.31 (s, 4H), 4.41 (t, $J=5.6$ Hz, 4H), 4.64 (t, $J=1.8$ Hz, 4H), 6.74 (d, $J=8.9$ Hz, 4H), 6.91 (d, $J=8.9$ Hz, 4H), 8.39 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 14.22, 22.80, 27.07, 27.37, 29.46, 29.77, 31.99, 38.90, 39.01, 50.82, 53.01, 61.38, 66.62, 71.62, 72.28, 72.79, 112.42, 112.53, 119.58, 127.87, 132.78, 133.50, 135.43, 163.20, 164.84, 183.16; FAB MS *m/z* 1415 ($[M+1]^+$), 1416 ($[M+2]^+$); Anal. calcd for $C_{88}H_{118}FeN_4O_8 \cdot 2H_2O$: C, 72.80; H, 8.47; 3.52. Found: C, 72.77; H, 8.56; 3.52.

*4.2.9. The ferrocene-linked SQ dimer **1c***

This compound was synthesized by the similar method to the preparation of **1a**, using **4b** and **6a** as starting materials (11% yield): mp 164–166 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J=7.3$ Hz, 12H), 1.25–1.46 (m, 36H), 1.65–1.75 (m, 16H), 3.13 (s, 6H), 3.40–3.49 (m, 12H), 4.21 (t, $J=5.6$ Hz, 4H), 4.39 (t, $J=1.8$ Hz, 4H), 4.82 (t, $J=1.8$ Hz, 4H), 6.73 (m, 8H), 8.36 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.81, 20.11, 25.92, 26.83, 27.12, 28.72, 29.18, 29.29, 29.39, 29.43, 29.45, 38.73, 51.40, 52.61, 53.37, 64.40, 71.25, 72.62, 72.89, 111.95, 112.05, 119.10, 119.33, 132.67, 132.94, 153.12, 153.64, 170.10, 183.03; FAB MS *m/z* 1359 (M^+), 1360 ($[M+1]^+$), 1361 ($[M+2]^+$); Anal. calcd for $C_{84}H_{110}FeN_4O_8 \cdot 2H_2O$: C, 72.29; H, 8.23; 4.01. Found: C, 72.51; H, 8.48; 3.74.

*4.2.10. The SQ dye **7a***

A mixture of **9a** (0.605 g, 4.00 mmol) and **6a** (1.20 g, 3.98 mmol) in 2-propanol/triethyl orthoformate (8 ml, 5/1, v/v) was heated at reflux for 12 h under nitrogen. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20/1, v/v, as eluent) followed by recrystallization by the solvent diffusion method from CH_2Cl_2/MeOH to hexane to afford a crystal of **7a** (580 mg, 1.33 mmol, 34%): mp 189–190 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, $J=7.3$ Hz, 6H), 1.37 (sextet, $J=7.3$ Hz, 4H), 1.61 (m, 4H), 3.18 (s, 3H), 3.44 (t, $J=7.3$ Hz, 4H), 3.69 (t, $J=5.9$ Hz, 2H), 3.93 (t, $J=5.9$ Hz, 2H), 6.73 (d, $J=9.2$ Hz, 2H), 6.78 (d, $J=9.2$ Hz, 2H), 8.28 (d, $J=9.2$ Hz, 2H), 8.35 (d, $J=9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.94, 20.32, 29.63, 39.75, 51.28, 54.98, 59.98, 112.32, 112.43, 119.13, 119.64, 132.94, 133.13, 153.35, 154.49, 183.41, 186.15, 186.22; FAB MS *m/z* 435 ($[M+1]^+$); Anal. calcd for $C_{27}H_{34}N_2O_3$: C, 74.62; H, 7.89; 6.45. Found: C, 74.53; H, 8.04; 6.28.

*4.2.11. The SQ dye **7b***

This compound was synthesized by the similar method to the preparation of **7a**, using **9b** and **6a** as starting materials (38% yield): mp 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, $J=7.3$ Hz, 6H), 1.33–1.44 (m, 16H), 1.46–1.68 (m, 10H), 3.14 (s, 3H), 3.40–3.50 (m, 6H), 3.64 (t, $J=6.6$ Hz, 2H), 6.70–6.76 (m, 4H), 8.34 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.95, 20.30, 25.86, 26.78, 27.09, 27.31, 28.56, 29.39, 29.48, 29.65, 32.90, 38.87, 51.24, 52.83, 63.00, 64.12, 112.12, 112.24, 119.34, 119.64, 132.90, 133.27, 153.40, 153.89, 161.05, 183.34, 187.18, 187.62; FAB MS *m/z* 561 ($[M+1]^+$); Anal. Calcd for $C_{36}H_{52}N_2O_3 \cdot H_2O$: C, 74.70; H, 9.40; 4.84. Found: C, 74.39; H, 9.42; 4.51.

*4.2.12. The ferrocene-SQ dyad **2a***

To a solution of **8b** (0.230 g, 1.00 mmol) in dry CH_2Cl_2 (5 ml) was added oxalyl chloride (0.190 g, 1.50 mmol) at 0 °C under nitrogen. Then, the mixture was stirred at ambient temperature for 4 h, followed by addition of 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 0.134 g, 1.10 mmol) and **7a** (0.439 g, 1.01 mmol). The reaction mixture was stirred at ambient temperature for 2 h, and the solvent was removed on a rotary evaporator. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20/1, v/v, as eluent), and recrystallization by the solvent diffusion

method from CH_2Cl_2/MeOH to hexane to afford a crystal of **2a** (0.152 mmol, 15%): mp 171–173 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 6H), 1.40 (sextet, J = 7.3 Hz, 4H), 1.63 (m, 4H), 3.24 (s, 3H), 3.45 (t, J = 7.3 Hz, 4H), 3.87 (t, J = 5.9 Hz, 2H), 4.10 (s, 5H), 4.39 (t, J = 1.8 Hz, 2H), 4.42 (t, J = 5.9 Hz, 2H), 4.73 (t, J = 1.8 Hz, 2H), 6.73 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 8.39 (d, J = 9.2 Hz, 2H), 8.42 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.86, 20.16, 29.51, 38.87, 50.75, 51.19, 61.06, 69.65, 69.97, 70.01, 71.55, 112.21, 112.28, 119.17, 120.18, 132.46, 133.46, 153.62, 153.70, 171.47, 183.01, 186.53, 189.03; FAB MS m/z 647 ($[M+1]^+$); Anal. calcd for $C_{38}H_{42}FeN_2O_4$: C, 70.59; H, 6.55; 4.33. Found: C, 70.35; H, 6.90; 4.33.

*4.2.13. The ferrocene-SQ dyad **2b***

This compound was synthesized by the similar method to the preparation of **2a**, using **7b** as a starting material (65% yield): mp 125–127 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 6H), 1.25–1.46 (m, 20H), 1.59–1.75 (m, 6H), 3.14 (s, 3H), 3.44 (m, 6H), 4.18–4.23 (m, 7H), 4.38 (t, J = 1.8 Hz, 2H), 4.80 (t, J = 1.8 Hz, 2H), 6.73 (m, 4H), 8.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.96, 20.31, 26.13, 27.03, 27.33, 28.98, 29.33, 29.45, 29.54, 29.58, 29.59, 29.65, 38.91, 51.23, 52.84, 64.29, 69.69, 70.08, 70.43, 71.17, 71.52, 112.11, 112.22, 119.40, 119.66, 132.94, 133.25, 153.38, 153.85, 169.06, 171.57, 183.27, 187.33, 187.89; FAB MS m/z 773 ($[M+1]^+$); Anal. calcd for $C_{47}H_{60}FeN_2O_4 \cdot 0.5H_2O$: C, 72.50; H, 7.86; 3.58. Found: C, 72.50; H, 8.15; 3.57.

*4.2.14. The SQ dye **3***

To a solution of **7a** (0.443 g, 1.02 mmol) in dry CH_2Cl_2 (5 ml) was added acetyl chloride (0.160 g, 2.04 mmol) at 0 °C under nitrogen. Then, the mixture was stirred at ambient temperature for 30 min, followed by addition of DMAP (0.123 g, 1.01 mmol). The reaction mixture was stirred at ambient temperature for 24 h, and the solvent was removed on a rotary evaporator. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20/1, v/v, as eluent), and recrystallization by the solvent diffusion method from CH_2Cl_2/MeOH to hexane to afford a crystal of **3** (334 mg, 0.701 mmol, 69%): mp 162–163 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 6H), 1.40 (sextet, J = 7.3 Hz, 4H), 1.63 (m, 4H), 2.01 (s, 3H), 3.17 (s, 3H), 3.45 (t, J = 7.3 Hz, 4H), 3.77 (t, J = 5.6 Hz, 2H), 4.31 (t, J = 5.6 Hz, 2H), 6.74 (d, J = 9.2 Hz, 2H), 6.81 (d, J = 9.2 Hz, 2H), 8.36 (d, J = 9.2 Hz, 2H), 8.40 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.90, 20.22, 29.57, 39.00, 50.72, 51.26, 61.09, 66.17, 112.12, 112.34, 119.20, 120.17, 132.47, 133.57, 153.54, 153.79, 170.56, 183.95, 186.53, 189.15; FAB MS m/z 477 ($[M+1]^+$); Anal. calcd for $C_{29}H_{36}FeN_2O_4 \cdot H_2O$: C, 70.51; H, 7.75; 5.67. Found: C, 70.61; H, 7.96; 5.42.

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