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Journal of Organometallic Chemistry 645 (2002) 168–175

Journal of Organometallic Chemistry

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Synthesis and luminescence properties of novel ferrocene–naphthalimides dyads

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Received 9 August 2001; received in revised form 11 October 2001; accepted 13 October 2001

Abstract

Ferrocene derivatives containing 4-amino-1,8-naphthalimide linked on the 4-position of the naphthalimide ring have been synthesized. The electrochemical data and the free energy of charge separation (ΔGcs) showed that photo-induced electron transfer (PET) from the ferrocenyl unit to the naphthalimide moiety is thermodynamically feasible for these ferrocene derivatives. Their absorption spectra show that the electronic interaction between the ferrocenyl unit and the naphthalimide moiety are very different for these ferrocene derivatives. We attribute these differences due to different spacers used to link the ferrocenyl unit and the naphthalimide moiety. Measurements of the fluorescence spectrum and the fluorescence lifetime confirmed that the fluorescence of the naphthalimide is strongly quenched by the effective PET from the ferrocenyl units to the naphthalimide moieties. The PET path in 6-[4-(2-oxo-2-ferrocenyl-ethyl)-piperazin-1-yl]-benzo[*de*]isoquinoline-1,3-diones can be switched off by both the oxidation of the ferrocene unit and the protonation of the alkylated amine group. These kind of dyads can be employed as dual-mode chemical (protons)/electrochromic molecular switches.

Keywords: Ferrocene; Naphthalimide; Luminescent properties; Synthesis

1. Introduction

Owing to its remarkable electrochemical properties, ferrocene has found widespread application as an electron-active building-block for elaborating switching molecular aggregates [1], redox-active receptors [2], redox-active polymeric ionomers [3] and conducting and magnetic materials [4]. Ferrocene has a low-lying triplet excited state and is known to be an effective triplet quencher [5]. Ferrocene is also known to be a good electron donor [6,7]; rapid electron tunneling from the ferrocene unit to the acceptor through the oligophenylenevinylene bridges was described by Sikes [8]. It has been reported that the ferrocene center can serve as an electron donor to the lowest excited state of Cr(2,2′-bipyridine)$_3^{3+}$ [9] and can quench excited Ru(II)polypyidyls by both electron donation and energy transfer [10].

Recently, naphthalimide derivatives have been used as supramolecular moieties for the study of photo-induced electron transfer (PET) [11,12]. A repulsive electric field existing in the naphthalimide was described by de Silva [13]. When an electron donor such as alkylated amine is linked with spacer on the *N*-imide atom of the 1,8-naphthalimide, the PET path is inhibited by the repulsive electric field and the fluorescence quenching of the 1,8-naphthalimide is not observed. The preparation of some imide–ferrocene with isoquinoline substituents on the naphthalimide ring has been reported [14,15]. Though fluorescence quenching of the naphthalimide fluorophore was observed, a node at the *N*-imide atom acting as an insulator of the *N*-ferrocenyl redox switch from the naphthalimide fluorophore was described [15]. The effect of the node is the same as that of the repulsive electric field, which inhibits the electron transfer from the ferrocene electron donor linking with the imide moiety to the 1,8-naphthalimide fluorophore.

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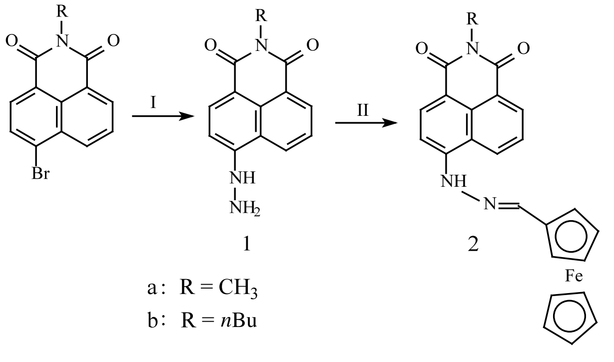
0022-328X/02/$ - see front matter
PII: S0022-328X(01)01416-4

In this paper, we report synthesis and studies of novel ferrocene–naphthalimide dyads, in which the ferrocenyl unit and the naphthalimide fluorophore are linked with different spacers on the 4-position of the naphthalimide ring. The node at the *N*-imide atom, which blocks PET from electron donor to the *N*-imide, is avoided. The synthesis and structures of the dyads are shown in Schemes 1 and 2. For the two kinds of ferrocene–naphthalimide dyads, the fluorescence of the naphthalimide fluorophore is strongly quenched by the ferrocenyl units via the PET. The electrochemical data were obtained by cyclic voltammetry. Their fluorescence spectral properties and their UV–vis absorption spectral properties were investigated.

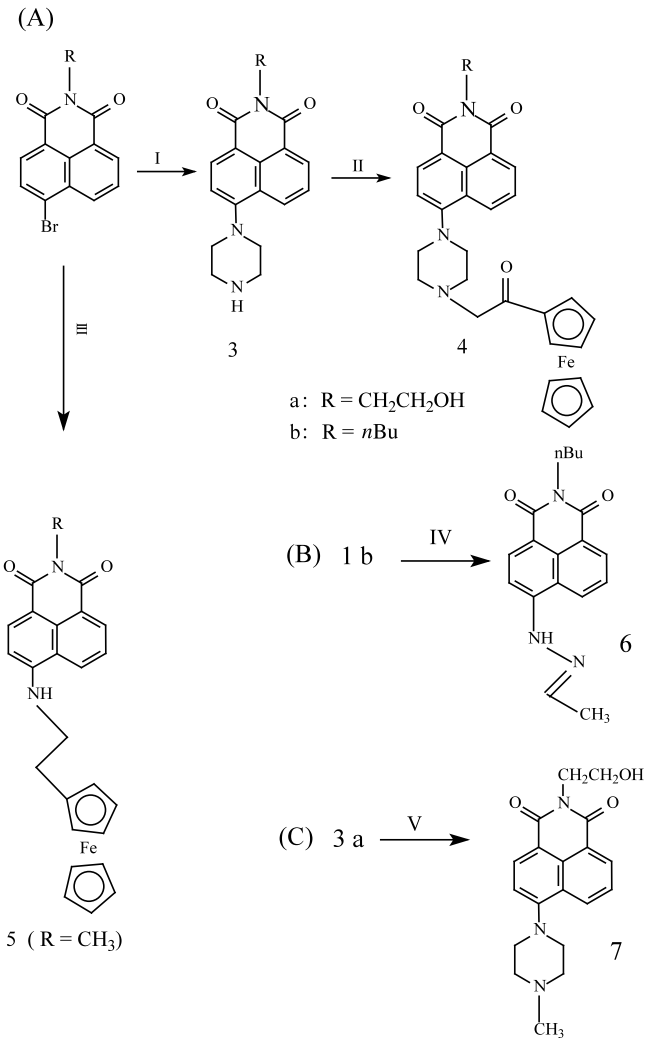
2. Experimental

2.1. General

Melting points were measured on a X4 Micro-melting point apparatus and were not corrected. ^{1}H-NMR spectra were obtained using a Bruker AM 500 spectrometer operating at 500.131 MHz. Mass spectra (MS) were recorded on a MA1212 instrument using standard conditions (EI, 70 eV). UV–vis spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were recorded on a Hitachi-850 spectrophotometer. Cyclic voltammetry was performed with a ZF-3 potentiostat and a ZF-4 programmer, using a platinum working electrode, and a saturated calomel reference electrode (SCE), data were recorded on a ZF-10 data collector, solutions were 10^{-4} M in electroactive material and 0.1 M in supporting electrolyte (NBu_4BF_4). The transient photoluminescence spectra and the decay kinetics were measured by pumping with a pulsed laser (titanium: sapphire, pulse width less than 2 ps) and recorded on a streak camera. The experimental methodology was described elsewhere [16].



Scheme 1. The synthesis route of 6-(*N*-ferrocenylmethylidene-hydrazino)-benzo[*de*]isoquinoline-1,3-diones (**2a**–**b**). The reaction conditions: I: hydrazine hydrate/methoxyl ethanol, II: formylferrocene and glacial acetic acid/ethanol.



Scheme 2. (A) The synthesis route of 6-[4-(2-oxo-2-ferrocenyl-ethyl)-piperazin-1-yl]-benzo[*de*]isoquinoline-1,3-diones (**4a**–**b**). (B) The synthesis route of the reference compound **6**. (C) The synthesis route of the reference compound **7**. The reaction conditions: I: piperazine hydrate/methoxyl ethanol, II: sodium iodide, chloroacetyl ferrocene and potassium carbonate/acetone. III: 2-ferrocenylethylamine/dimethyl sulphoxide. IV: acetaldehyde (40%)/ethanol. V: paraaldehyde and formic acid.

2.2. Syntheses

All the compounds were derived from 6-bromo-2-methyl, 2-butyl or 2-(2-hydroxyl-ethyl)benzo[*de*]isoquinoline-1,3-diones which were prepared by a known method. Chloroacetyl ferrocene, formylferrocene and 2-ferrocenylethylamine were prepared as described by Schlölgl [17], Sato [18] and Osgerby [19], respectively.

2.2.1. Preparation of 6-hydrazino-benzo[de]isoquinoline-1,3-diones (1a–b)

A typical preparation, that of **1a**, follows. 6-Bromo-2-methyl-benzo[*de*]isoquinoline-1,3-dione (5 g, 18.2 mmol) and 2 ml 80% hydrazine hydrate in 20 ml methoxyl ethanol were heated under reflux for 3 h. After cooling to room temperature (r.t.), the precipitated product was filtered, washed with EtOH and dried to afford 4 g yellow crystals with a yield of 97%. m.p. $>$ 300 °C. Anal. Found: C, 64.95; H, 4.72; N, 17.84. Calc. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42%.

1b: from 6-bromo-2-butyl-benzo[*de*]isoquinoline-1,3-dione/hydrazine hydrate, recrystallization from EtOH to afford golden yellow crystals, 85%. m.p. 220–222 °C. Anal. Found: C, 67.96; H, 6.12; N, 15.08. Calc. for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83%.

*2.2.2. Preparation of 6-(N-ferrocenylmethylidene-hydrazino)-benzo[de]isoquinoline-1,3-diones (**2a–b**)*

A typical preparation, that of **2a**, follows. **1a** 0.5g (2.3 mmol), formylferrocene (0.5 g, 2.5 mmol), 60 ml EtOH and 0.5 ml glacial acetic acid were vigorously stirred and heated to reflux for 5 h under nitrogen. After cooling to r.t., the solid product was filtered. Purification by chromatography (silicon gel column, methylene chloride:acetone = 20:1) to afforded 0.3 g (0.7 mmol) of **2a** as brown powder with a yield of 30%. m.p. 204–206 °C (decomp.). MS-EI: 437(M$^+$) ^{1}H-NMR: (in DMSO-d_6) δ (ppm): 8.78 (d, $J = 8.42$ Hz, 1H), 8.49 (d, $J = 7.21$ Hz, 1H), 8.36 (d, $J = 8.50$ Hz, 1H), 8.31 (–CH=, s, 1H), 7.78 (t, $J = 7.90$ Hz, $J = 7.81$ Hz, 1H), 7.58 (d, $J = 8.52$ Hz, 1H), 4.76 (s, 2H), 4.49 (s, 2H) (substituted cyclopentadiene), 4.26 (s, 5H) (unsubstituted cyclopentadiene), 3.38 (=NCH$_3$, 3H). Anal. Found: C, 65.78; H, 4.42; N, 9.46. Calc. for $C_{24}H_{19}FeN_3O_2$: C, 65.92; H, 4.38; N, 9.61%.

2b: **1b**/formylferrocene, brown crystals, 35%, m.p. 129–131 °C (decomp.). MS-EI: 479 (M$^+$). ^{1}H NMR (in CDCl$_3$) δ (ppm): 8.67 (d, $J = 8.50$ Hz, 1H), 8.52 (d, $J = 7.3$ Hz, 1H), 8.44 (d, $J = 8.50$ Hz, 1H), 8.31 (–CH=, s, 1H), 7.72 (t, $J = 7.29$ Hz, $J = 8.47$ Hz, 2H), 4.76 (t, 2H), 4.46 (t, 2H) (substituted cyclopentadiene), 4.24 (s, 5H) (unsubstituted cyclopentadiene), 4.12 (=NCH$_2$–, t, 2H), 1.69 (–CH$_2$–, m, 2H), 1.32 (–CH$_2$–, m, 2H), 0.97 (–CH$_3$–, t, 3H). Anal. Found: C, 67.43; H, 5.21; N, 8.48. Calc. for $C_{27}H_{25}FeN_3O_2$: C, 67.65; H, 5.26; N, 8.77%.

*2.2.3. Preparation of 6-(piperazin-1-yl)-benzo[de]-isoquinoline-1,3-diones (**3a–b**)*

A typical preparation, that of **3a**, follows. 6-Bromo-2-(2-hydroxyl-ethyl)-benzo[*de*]isoquinoline-1,3-dione (5 g, 15.7 mmol) and piperazine hydrate 5.1g (26.3 mmol) in 20ml methoxyl ethanol were vigorously stirred and heated to reflux for 3 h. The mixture was allowed to stand overnight at r.t. The yellow solid obtained was filtered off. 4 g (75%) pure crystals were obtained by recrystallization from aqueous EtOH with minimum water. m.p. 225–226 °C. ^{1}H-NMR (in DMSO-d_6) δ (ppm): 8.47 (m, 2H), 8.40 (d, $J = 8.10$ Hz, 1H), 7.81 (t, $J = 8.26$ Hz, $J = 7.44$ Hz, 1H), 7.32 (d, $J = 8.25$ Hz, 1H), 4.14 (=NCH$_2$–, d, 2H), 3.60 (–CH$_2$–O–, t, 2H), 3.15 (–N(CH$_2$)$_2$–, 4H), 3.02 (–N(CH$_2$)$_2$–, 4H). Anal. Found: C, 66.63; H, 5.81; N, 12.78. Calc. for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91%.

3b: from 6-bromo-2-butyl-benzo[*de*]isoquinoline-1,3-dione/piperazine hydrate, yellow crystals, 71%, m.p. 130–131 °C. ^{1}H-NMR (in acetone) δ (ppm): 8.51 (m, 2H), 8.44 (d, $J = 8.07$ Hz, 1H), 7.78 (t, $J = 7.96$ Hz, $J = 7.84$ Hz, 1H), 7.33 (d, $J = 8.09$ Hz, 1H), 4.11(=NCH$_2$–, t, 2H), 3.24 (–N(CH$_2$)$_2$–, t, 4H), 3.13 (–N(CH$_2$)$_2$–, t, 4H), 1.68 (–CH$_2$–, m, 2H), 1.41 (–CH$_2$–, m, 2H), 0.97 (–CH$_3$, t, 3H). Anal. Found: C, 71.34; H, 6.91; N, 12.79. Calc. for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45%.

*2.2.4. Preparation of 6-[4-(2-oxo-2-ferrocenyl-ethyl)-piperazin-1-yl]-benzo[de]isoquinoline-1,3-diones (**4a–b**)*

A typical preparation, that of **4a**, follows. **3a** (1 g, 3.1 mmol), sodium iodide (0.5 g, 3.3 mmol), chloroacetyl ferrocene 0.8 g (3.1 mmol) and potassium carbonate 1 g (7.2 mmol) in 60 ml acetone were vigorously stirred and heated to reflux under nitrogen for 7 h. After cooling to r.t., all the solvents was evaporated, 20 ml of EtOH was added. The precipitated product was filtered off. 0.6 g (1.1 mmol) pure red brown crystals were obtained by recrystallization from EtOH with a yield of 36%. m.p.267–269 °C (decomp.). MS-EI: 551(M$^+$). ^{1}H-NMR (in CDCl$_3$) δ (ppm): 8.60 (d, $J = 7.16$ Hz, 1H), 8.54 (d, $J = 8.05$ Hz, 1H), 8.44 (d, $J = 7.74$ Hz, 1H), 7.71 (t, $J = 7.52$ Hz, $J = 8.20$ Hz, 1H), 7.25 (d, $J = 8.18$ Hz, 1H), 4.89 (t, 2H), 4.57 (t, 2H) (substituted cyclopentadiene), 4.46(=NCH$_2$–, 2H), 4.26 (s, 5H) (unsubstituted cyclopentadiene), 3.98 (–CH$_2$–O–, 2H), 3.77 (–CH$_2$–CO–, s, 2H), 3.41 (–N(CH$_2$)$_2$–, 4H), 2.98 (–N(CH$_2$)$_2$–, 4H). Anal. Found: C, 64.97; H, 5.37; N, 7.47. Calc. for $C_{30}H_{29}FeN_3O_4$: C, 65.35; H, 5.30; N, 7.62%.

4b: from **3b**/chloroacetyl ferrocene, red brown crystals, 33%. m.p. 173–174 °C (decomp.). MS-EI: 563 (M$^+$). ^{1}H-NMR (in CDCl$_3$) δ (ppm): 8.59 (d, $J = 7.21$ Hz, 1H), 8.53 (d, $J = 8.03$ Hz, 1H), 8.43 (d, $J = 8.43$ Hz, 1H), 7.70 (t, $J = 7.42$ Hz, $J = 7.41$ Hz, 1H), 7.26 (t, $J = 7.46$ Hz, $J = 8.07$ Hz, 1H). 4.89 (t, 2H), 4.57 (t, 2H) (substituted cyclopentadiene), 4.25 (s, 5H) (unsubstituted cyclopentadiene), 4.17 (=NCH$_2$–, t, 2H), 3.76(–CH$_2$–CO–, s, 2H), 3.39 (–N(CH$_2$)$_2$–, t, 4H), 2.97 (–N(CH$_2$)$_2$–, t, 4H). 1.74–1.41 (–(CH$_2$)$_2$–, m, 4H), 0.97 (–CH$_3$, t, 3H). Anal. Found: C, 68.45; H, 5.88; N, 7.86. Calc. for $C_{32}H_{33}FeN_3O_3$: C, 68.21; H, 5.90; N, 7.46%.

*2.2.5. Preparation of 6-(2-ferrocenylethyl-amino)-2-methyl-benzo[de]isoquinoline-1,3-dione (**5**)*

6-Bromo-2-methyl-benzo[*de*]isoquinoline-1,3-dione (2 g, 7.3 mmol), 2-ferrocenyl ethyl-amine (2 g, 4.4 mmol) and 15 ml dimethyl sulphoxide were vigorously stirred and heated at 70–80 °C under nitrogen. After cooling to r.t., the mixture solvent was pored into 100 ml water, and crude product was filtered. Purification by chromatography (silicon gel column, methylene chloride:acetone = 30:1) to afforded 0.9 g (2.0 mmol) of **5** as yellow powder with a yield of 27%. MS-EI: 438 (M^+) ^{1}H-NMR: (in $CDCl_3$) δ (ppm): 8.78 (d, $J = 7.99$ Hz, 1H), 8.48 (d, $J = 7.21$ Hz, 1H), 8.00 (d, $J = 8.50$ Hz, 1H), 7.61 (t, $J = 7.81$ Hz, $J = 7.90$ Hz, 1H), 6.73 (d, $J = 8.32$ Hz, 1H), 4.20 (m, 9H) (cyclopentadiene), 3.60 (s, 3H, =NCH_3), 2.85 (m, 4H, –$(CH_2)_2$–). Anal. Found: C, 68.68; H, 5.02; N, 6.56. Calc. for $C_{25}H_{22}FeN_2O_2$: C, 68.51; H, 5.06; N, 6.39%.

2.2.6. Preparation of 2-butyl-6-(N-ethylidene-hydrazino)benzo[de]isoquinoline-1,3-dione (6)

1b 1.0 g (3.2 mmol) and 1.5 ml 40% acetaldehyde in 15 ml EtOH were vigorously stirred and heated to reflux for 1 h. After cooling to r.t., the precipitated product was filtered. 0.7 g pure compound **6** was obtained by recrystallization from 50% aqueous EtOH with a yield of 64%. m.p. 192–194 °C. MS-EI: 309 (M^+). ^{1}H-NMR (in DMSO-d_6) δ (ppm): 8.73 (d, $J = 8.38$ Hz, 1H), 8.47 (d, $J = 7.23$ Hz, 1H), 8.33 (d, $J = 8.52$ Hz, 1H), 7.8 (–CH=, q, 1H), 7.76 (t, $J = 7.91$ Hz, $J = 7.75$ Hz, 1H), 7.52 (d, $J = 8.50$ Hz, 1H), 4.02 (=NCH_2–, t, 2H), 2.04 (–CH_3, d, 3H), 1.59 (–CH_2–, m, 2H), 1.34 (–CH_2–, m, 2H), 0.92 (–CH_3, t, 3H). Anal. Found: C, 69.46; H, 6.37; N, 13.89. Calc. for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58%.

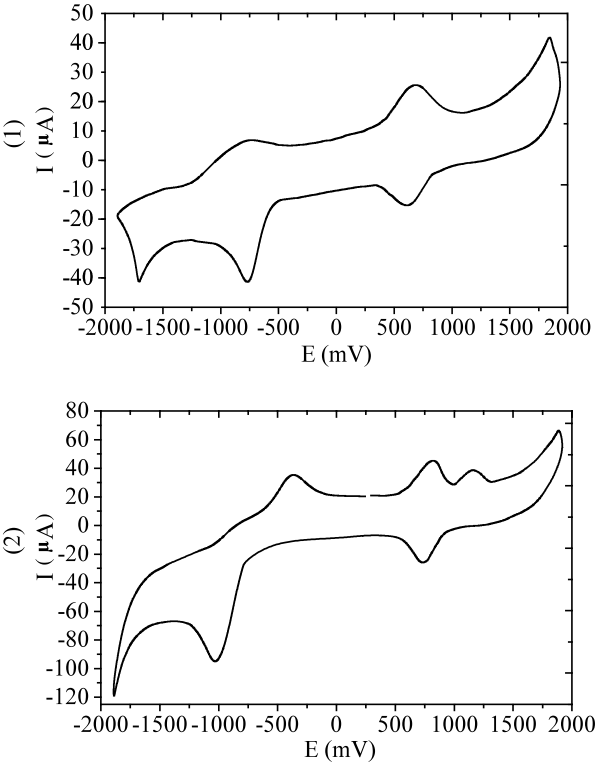


Fig. 1. Cyclic voltammograms (10^{-4} M in CH_3CN, 200 mV s^{-1}, Pt, 20 °C): (1) **2b**; (2) **4b**.

2.2.7. Preparation of 2-(2-hydroxyl-ethyl)-6-(4-methyl-piperazin-1-yl)-benzo[de]isoquinoline-1,3-dione (7)

0.3 g paraaldehyde (amount to 10 mmol formaldehyde) was added to a solution of **3a** (1.5 g, 4.6 mmol) in 10 ml formic acid (88%), with stirring at 80 °C for 20 h. Then all solvent was removed by vacuum, to the residual, 20 ml 3N hydrochloric acid was added, and the solution was refluxed for 1 h. Sodium carbonate powder was added carefully, yellow solid was obtained. 1.2 g pure crystals were obtained by recrystallization from EtOH with a yield of 78%. m.p. 217–219 °C. MS-EI: 339 (M^+). ^{1}H-NMR (in D_2O) δ (ppm): 7.65 (m, 2H), 7.54 (d, $J = 7.98$ Hz, 1H), 7.13 (t, $J = 7.74$ Hz, $J = 7.76$ Hz, 1H), 6.68 (d, $J = 8.04$ Hz, 1H), 3.73 (=NCH_2–, t, 2H), 3.55 (–CH_2O–, t, 2H), 3.08 (–$N(CH_2)_2$ $(CH_2)_2N$–, s, 8H), 2.65 (–CH_3, s, 3H). Anal. Found: C, 67.57; H, 6.41; N, 12.18. Calc. for $C_{19}H_{21}N_3O_3$: C, 67.24; H, 6.24; N, 12.38%.

2.2.8. Preparation of ferrocenium tetrafluoroborate salts

5×10^{-6} mol **2a**–**b**, **4a**–**b** was dissolved in 50 ml MeCN containing 0.1 M of tetrabutylammonium tetrafluoroborate. The solution was placed in the working compartment equipped with a Pt-gauze working electrode. The controlled potential oxidation was performed approximately 200 mV positive of the E_{Ox} for the ferrocene derivatives (according to Fig. 1, no electrochemical process disturbs the controlled potential oxidation for **2b** and **4b**). Current was discontinued after 50% excess of desired number of coulombs had pass through the compartment. The UV–vis absorption spectra and the fluorescence emission spectra of the ferrocenium tetrafluoroborate salts in CH_3CN were determined immediately after the oxidation.

3. Results and discussion

The ferrocenyl unit shows a reversible oxidation at a potential comparatively close to unsubstituted ferrocene [20]. One electron oxidation of the ferrocenyl units in **2b** and **4b** are reversible in CH_3CN as shown in Fig. 1. In agreement with the electrochemical data of the 1,8-naphthalimides [15,21], the reduction process of the naphthalimide moieties in these ferrocene–naphthalimide dyads is not a simple step, but a multi-electron, chemically irreversible step. The small wave appeared at $E^{o\prime} = 1.1$ V versus SCE in Fig. 1 (2), was assigned to the oxidation of the alkylated amine in **4b**.

According to the electrochemical data of the ferrocene–naphthalimide dyads (Table 1), the approximate free energy of charge separation (ΔG_{cs}) for the excited singlet states of the ferrocene derivatives can be

Table 1
Electrochemical data of the ferrocene–naphthalimide dyads

Compound	**2a**	**2b**	**4a**	**4b**
Oxidation potentials of the ferrocenyl unit (V vs. SCE)	0.64	0.65	0.75	0.75
Reduction potentials of the naphthalimide moiety (V vs. SCE)	−0.76	−0.76	−1.1	−1.1

given by the following relations [11,22]: $\Delta G_{cs} = E_{Ox} - E_{Red} - e^2/\varepsilon r_{12} - E_S$ where E_{Ox} is the oxidation potential of the donor, E_{Red} is the reduction potential for the electron acceptor, E_S is the potential energy of first excited single state of the electron donor, e is the charge of an electron, ε is the static dielectric constant of the solvent, and r_{12} is the distance between the centers of the donor and the acceptor. When E_S of ferrocene is taken as 2.46 eV [23], ΔG_{CS} for **2b** is calculated to be ca. − 1.08 eV (24.9 kcal mol^{-1}). ΔG_{CS} for **2b** is sufficiently negative for PET between the ferrocenyl unit and the naphthalimide moiety to be thermodynamically feasible. It can be expected that the fluorescence of the naphthalimide fluorophore in these dyads would be obviously quenched by PET from the ferrocenyl units to the naphthalimide moieties.

The absorption spectra data and the fluorescence emission spectra data are listed in Table 2. Since the ferrocene units in derivatives **2** are linked with the 4-amino-1,8-naphthalimide moieties by the –N=CH– group, the two weak absorption bands of the ferrocene unit ($\lambda = 325$ nm, $\varepsilon = 52$; $\lambda = 440$ nm, $\varepsilon = 91$ for unsubstituted ferrocene [24]) are significantly magnified (Fig. 2(A)). This means that there is a significant perturbation of the ferrocene frontier orbital due to the conjugating effect between the 4-amino-1,8-naphthalimide and the ferrocene unit as seen in the delocalization structures II and III [25]. However, for derivatives **4**, the acetylferrocene units are linked on 4-position of the naphthalimide rings through saturated piperazinyl spacers. Both of the two weak absorption bands of the acetylferrocene unit ($\lambda = 335$ nm, $\varepsilon = 1120$; $\lambda = 455$ nm, $\varepsilon = 420$ for unsubstituted acetylferrocene [24]) disappeared or may be hidden in the broad naphthalimide transition band. Comparing with derivatives **3**, there is very small change in the maximum absorption wavelengths of derivatives **4** (Fig. 2 (B) and Table 2).

Table 2
Absorption spectra data and fluorescence emission spectra data (λ^{ab}_{max}/nm, 10^{-4} M in CH_3CN; λ^{flu}_{max}/nm, 10^{-4} M in CH_3CN containing 0.1 M Bu_4NBF_4, excited at the maximum absorption wavelength; room temperature

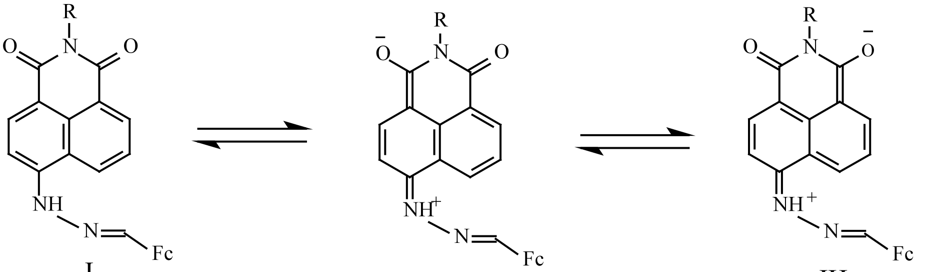
Compound	λ^{ab}_{max} (log ε)	λ^{flu}_{max} (φ_f)
1a	427 (4.07)	525 (0.65)
2a	325 (4.05) 454 (4.15)	567 (0.0039)
2a$^+$	348 (4.02)	564 (0.0052)
1b	425 (4.06)	518 (0.51)
2b	328 (4.05) 455 (4.12)	554 (0.0063)
2b$^+$	347 (3.97) 431 (3.62)	562 (0.0087)
3a	398 (4.08)	517 (0.056)
4a	398 (4.05)	521 (0.0061)
4a$^+$	398 (3.82) 535 (2.84)	521 (0.091)
4a-H+ [a]	373 (4.10)	504 (0.38)
3b	405 (4.07)	515 (0.031)
4b	407 (3.94)	514 (0.0057)
4b$^+$	383 (3.80) 530 (2.79)	516 (0.27)
5	434 (4.19)	530 (0.0068)
6	431 (4.25)	521 (0.90)
7	406 (4.22)	519 (0.092)

Rhodamine B was used as quantum yields standard and its fluorescence quantum yield in CH_3CN was defined as 1.

[a] Hydrochloride is the proton source.

For the two kinds of ferrocene–naphthalimide dyads, the node acting as an insulator for the electron transfer from the electron donor linking at the nitrogen atom of the carboximide is avoided. The fluorescence of the naphthalimide fluorophore in derivatives **2** and derivatives **4** is strongly quenched by the ferrocene unit and the acetylferrocene unit, respectively (Table 2 and Fig. 3). These two kinds of ferrocenyl units are effective electron donors.

When **2b** was electrochemically oxidized to its ferrocenium cations, the ferrocene absorption band at



I II III

Fc: ferrocene

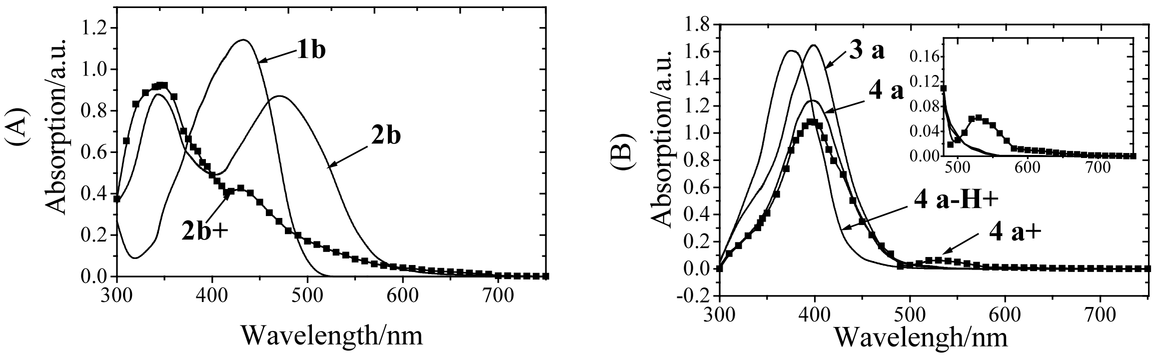


Fig. 2. Absorption spectra of the samples in CH_3CN (10^{-4} M).

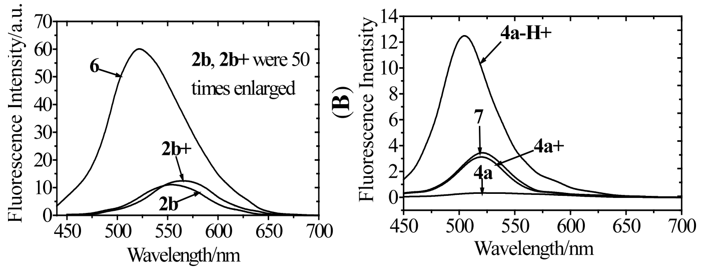


Fig. 3. Fluorescence emission spectra of the samples in CH_3CN (10^{-4} M).

~ 455 nm obviously decreased. The typical unsubstituted ferrocenium absorption band is at ~ 620 nm [24], in $\mathbf{2b}^+$, the ferrocenium unit absorption band is hidden in the broad band. The PET path from the ferrocene unit to the naphthalimide moiety is inhibited by the oxidation of the ferrocene unit, and the fluorescence of the naphthalimide fluorophore should be recovered. However, the fluorescence of $\mathbf{2b}^+$ is 50 times smaller than the fluorescence of reference model compound **6** where a simple methyl group replaces the ferrocene unit of **2b** at the molecular termini (Table 2 and Fig. 3 (A)), and the fluorescence recover is not observed. An energy transfer may occur from the excited naphthalimide moiety to the ferrocenium unit.

When derivatives **4** were oxidized, the PET path from the acetylferrocene unit to the naphthalimide unit was inhibited. Förster transfer of singlet energy from the excited naphthalimide moiety to the ferrocenium unit may be ruled out due to the very small extinction coefficient of the ferrocenium unit and the very small spectral overlap between the emission of the naphthalimide unit and absorption of the ferrocenium unit. The fluorescence of the naphthalimide unit in $\mathbf{4}^+$ is almost completely recovered by the oxidation of the acetylferrocene unit. For $\mathbf{4a}^+$, its fluorescence is almost equal to that of reference model compound **7** where a simple methyl group replaces the acetylferrocene unit of **4a** at the molecular termini (Table 2 and Fig. 3 (B)). The typical absorption band of the ferrocenium is also blue-shifted to ~ 530 nm as described by Prins [26].

Protonation of the alkylated amine group in **4a** drastically alters the electron-donating properties and consequently "switches off" the PET path from the ferrocenyl unit to the 4-amino-1,8-naphthalimide moiety. This results in the fluorescence enhancement of the 4-amino-1,8-naphthalimide fluorophore by more than 50 times and about 15 nm blue-shift of the maximum emission wavelength (Table 2 and Fig. 3 (B)). The naphthalimide absorption bands of **4a-H**+ are blue-shifted about 25 nm compared to those of **4a**, but the shapes are almost unchanged. Since the PET path from the ferrocenyl unit to the 4-amino-1,8-naphthalimide moiety can be switched off by both the oxidation of the ferrocenyl unit and the protonation of the alkylated amine group, **4a** and **4b** could be employed as efficient dual-mode chemical (protons)/electrochromic molecular switches.

Compound **5** was synthesized to investigate PET in the ferrocene–naphthalimides, in which the ferrocenyl unit was linked on the 4-position of the naphthalimide ring through saturated hydrocarbon chain. The fluorescence emission decay according to single exponential kinetics. The fluorescence lifetime of compound **5** was 81 ± 2 ps at 530 nm in the polystyrene matrix (Fig. 4). This confirms that PET from the ferrocenyl unit to the naphthalimide moiety may quench the fluorescence of the naphthalimide in **5** and other process may not perturb the PET path from the ferrocenyl unit to the naphthalimide moiety. Other data of the ferrocene–naphthalimide dyads will be published elsewhere in detail [27].

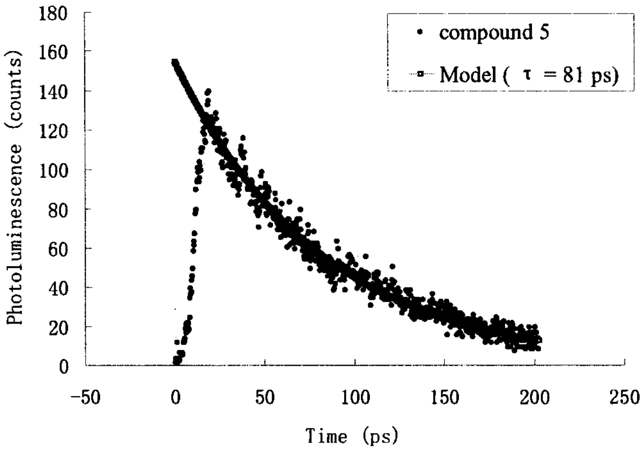


Fig. 4. Fluorescence decay profiles of compound **5** in a polystyrene matrix with the concentration of 1% weight at 530 nm. The solid line is the exponential fits obtained from the analysis.

Energy transfer of singlet excitons is interpreted in terms of the Förster mechanism. Förster transfer is a resonant dipole coupling process that transfers energy between singlet states and conserves the spin state of the donor and the acceptor chromophores. It is dependent on the energetic overlap between the donor emission spectrum and the acceptor absorption spectrum and has an inverse sixth power dependence on the donor–acceptor separation [28–30]. The maximum absorption wavelengths of the ferrocenyl units (at 455 nm) in these ferrocene–naphthalimides are shorter than the maximum emission wavelengths of the naphthalimide fluorophore in both of the two reference compounds (**6** and **7**, at 520 nm). This rules out singlet energy transfer from the excited naphthalimide to the ferrocenyl unit for these ferrocene–naphthalimide dyads.

4. Conclusion

The ferrocene unit in derivatives **2** was linked with the 4-amino-1,8-naphthalimide moiety through –CH=N– spacer, the electronic interaction between the ferrocene group and the naphthalimide moiety was appended. The acetylferrocene units in derivatives **4** were linked with the naphthalimide moiety through saturated piperazinyl spacer; the electronic interaction of the acetylferrocene frontier orbital was relatively weak; this kind of ferrocene–naphthalimide dyads can be approximately considered as supramolecular systems [31,32].

Since the ferrocenyl units were linked on the 4-position of the naphthalimide ring, the node at the carboximide acting as an insulator for electron transfer is avoided. The effective PETs from the ferrocenyl electron donors to the naphthalimide acceptors are not influenced by the decrease of the electronic interactions. When derivatives **2** were oxidized to its ferrocenium cation, the fluorescence of the naphthalimide fluorophore was not recovered whereas the fluorescence of the naphthalimide fluorophore in derivatives **4** was recovered by the oxidation of the acetylferrocene units. Derivatives **4** could be employed as efficient dual-mode chemical (protons)/electrochromic molecular switches because the PET path from the ferrocenyl unit to the 4-amino-1,8-naphthalimide moiety can also be switched off by the protonation of the alkylated amine group in derivatives **4** and the fluorescence enhancement of the 4-amino-1,8-naphthalimide fluorophore was observed.

Acknowledgements

This research was supported by NSFC, China. The transient photoluminescence determination in Sheffield/UK was supported by UK EPSRC (HEFCE JR98SHFX).

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