



## Synthesis and electronic properties of ferrocene-containing organic dyads



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### ABSTRACT

Novel ferrocene–oligothiophenylene–cyanoacrylic acid in the form of donor–spacer–acceptor dyads was synthesized. The compound with a single unit of thiophenylene showed the lowest energy transition in neutral state. For radical cations, the lowest energy transition appears red-shifted along with the increased number of thiophenylene units. These results suggested that the electronic structure of radical cations is significantly different from that of neutral molecules.

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Donor–spacer–acceptor dyads in the forms of both discrete molecules and polymers have been used for the design of a variety of opt-electronic devices such as molecular wires,<sup>1a</sup> field effect transistors,<sup>1b</sup> sensors,<sup>1c</sup> organic light emitting diodes,<sup>1d</sup> and dye-sensitized solar cells (DSSCs).<sup>2,3</sup> For example, in the application of DSSC, the polypyridylruthenium(II) complexes such as N719<sup>2</sup> has displayed remarkable power conversion efficiency. Since then, many efforts have been devoted to further enhance the efficiency and to reduce the cost of rare metals. One of promising strategies is to replace the ruthenium complexes by metal free organic donor–spacer–acceptor dyads. A wide variety of organic dyes have been reported in the literature. For example, the donors may consist of coumarin, triphenyl amine, merocyanine, phenothiadine, carbazole, and fluorine, and for the spacers are thienylene-vinylene, phenylene–vinylene, oligophenyl, oligothiophene, etc. The acceptor of the dyads is mostly either cyanoacrylic acid or acetic acid.<sup>3</sup> The spacer groups are usually a  $\pi$ -conjugated chromophore, which can broaden the absorption range and reduce the HOMO–LUMO band gap. This line of strategy has successfully enhanced the power conversion efficiency to ~13% in the case of porphyrin type dyes.<sup>4</sup>

Among many kinds of donor groups, ferrocene and its derivatives have been extensively studied for the applications on molecular wire<sup>5</sup> and non-linear optical materials.<sup>6</sup> The mechanism of  $\pi$ -delocalizing between ferrocene and the acceptor moiety via spacer is a key issue to understand the long range charge transport phenomenon, which includes metal-to-ligand transfer and ligand-to-metal transfer. The structure of  $\pi$ -conjugated spacer also plays an important factor in the charge transport process. Many kinds of ferrocene dyads have been reported, but very few were using them as dye-sensitizers. The reason is due to a strong electron donating ability of ferrocene, that renders it difficult to regain an electron after oxidation from the redox mediator such as iodine. Chauhan et al. have reported that ferrocene–imine dyads with a lower level of HOMO (the highest occupied molecular orbital) were able to induce an effective charge flow in dye-sensitized solar cells.<sup>7</sup> In our recent works, we have prepared many metal-free dyes with a cyanoacrylic acid moiety as an acceptor to apply them on dye-sensitized solar cells,<sup>8</sup> dye-sensitized water splitting cells,<sup>9</sup> and sensing systems.<sup>10</sup> Here we report the preparation of a new series of dyes in the form of vinylferrocene–oligothiophene–cyanoacrylic acid. Their electrochemical and photochemical properties are analyzed in both neutral and radical cation states. When the size of thiophenylene spacer is elongated, the metal to ligand

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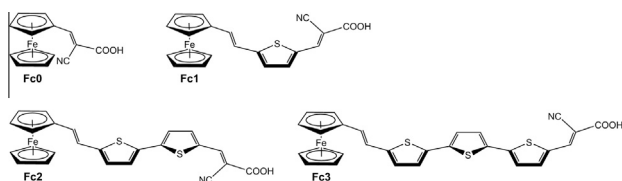
charge transfer (MLCT) character is reduced and therefore leads to the reduction of electron donating ability (Figs. 1–3).

Dyads **Fc0–Fc3** were synthesized from ferrocene-2-carboxyaldehyde (**1**).<sup>11</sup> The aldehyde moiety of **1** was reduced by NaBH<sub>4</sub> to give alcohol (**2**),<sup>12</sup> which was immediately converted to a Wittig salt with triphenylphosphine hydrobromide (**3**).<sup>13</sup> Donor–acceptor dyad (**Fc0**) was synthesized by Knoevenagel condensation condition with cyanoacetic acid. The oligothiophene spacer groups were introduced via Wittig reactions. The oligothiophene moieties, that is, thiophene-2,5-dicarboxaldehyde, [2,2'-bithiophene]-5,5'-dicarbaldehyde, and [2,2':5',2''-terthiophene]-5,5''-dicarbaldehyde reacted with **3** to afford *cis/trans* isomers, which were readily converted to the pure *trans* form of aldehydes (**4–6**) upon the catalysis of I<sub>2</sub> in CHCl<sub>3</sub> (31–78%). In <sup>1</sup>H NMR spectra, the characteristic aldehyde peaks were confirmed at  $\delta$  10 ppm. Knoevenagel condensation of **4–6** with cyanoacetic acid gave the oligothiophene dyads **Fc1–3** in 10–30%. In <sup>1</sup>H NMR spectra, the aldehyde peaks at around 10 ppm disappeared, while in <sup>13</sup>C NMR spectra, the characteristic peaks of carboxylic acid were appeared at 163–168 ppm. In infrared spectra, the absorption at 2214–2222 cm<sup>-1</sup> was assigned to the stretching of cyanide and that at 1575–1584 cm<sup>-1</sup> was assigned to the vibration of carbonyl moiety of carboxylic acids. The molecular weight of dyads **Fc0–Fc3** was confirmed by using MALDI/MS spectrometry (Scheme 1).

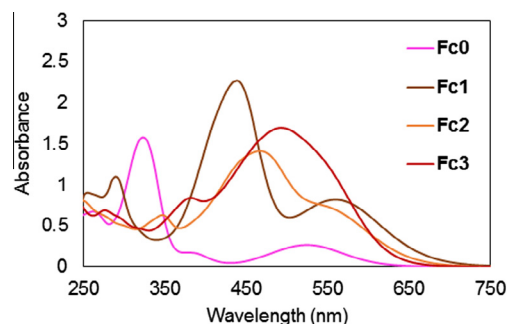
The absorption spectra of ferrocene dyads were measured in CH<sub>2</sub>Cl<sub>2</sub> solutions (10<sup>-4</sup> M). In the spectrum of compound **Fc**, there are three characteristic transitions, that is, two MLCT bands at 456 ( $\epsilon = 2700$ ) and 329 ( $\epsilon = 700$ ) nm and an internal charge-transfer (ICT) band at 245 ( $\epsilon = 88,800$ ) nm (Fig S1a).<sup>14</sup> In the spectrum of **Fc0**, three transition bands are observed with slight shifts: the lowest one appeared as a broad peak at 525 nm ( $\epsilon = 2640$ ) and the other two at 383 (1710) and 323 ( $\epsilon = 15,780$ ) nm with bathochromic shifts. When a thiophene group was inserted between the donor and the acceptor, the lowest energy transition of **Fc1** showed a further bathochromic effect at 560 nm ( $\epsilon = 8170$ ) comparing with that of **Fc0**. The other two peaks of **Fc1** appeared at 439 ( $\epsilon = 22,690$ ) and 290 ( $\epsilon = 10,980$ ) nm. When two and three thiophene groups are inserted, like **Fc2** and **Fc3**, the spectra showed slight blue shifts, with respect to that of **Fc2**, at 556 ( $\epsilon = 7100$ ), 466 ( $\epsilon = 14,110$ ), and 347 ( $\epsilon = 6300$ ) nm, respectively. The corresponding ones of **Fc3** appeared at 552 (sh,  $\epsilon = 12,090$ ), 494 ( $\epsilon = 16,930$ ), and 382 ( $\epsilon = 8390$ ) nm.

To evaluate the redox property of dyads **Fc0–Fc3**, cyclic voltammetry was measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M of nBu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. For all dyads the oxidation potential showed quasi-reversible waves. The oxidation potential of **Fc0** is  $E_{1/2}^{ox}(I) = -73$  mV (vs Fc/Fc<sup>+</sup>), suggesting a higher oxidation ability along with the elongation of  $\pi$ -conjugation. However, when thiophene spacers are inserted between ferrocene and 2-cyanobut-3-enoic acid moiety, oxidation abilities were decreased, that is,  $E_{1/2}^{ox}(I) = -49$  mV for **Fc1**,  $E_{1/2}^{ox}(I) = +88$  mV for **Fc2**,  $E_{1/2}^{ox}(I) = +128$  mV for **Fc3**, respectively, (vs Fc/Fc<sup>+</sup>). The energy potentials are summarized in the Figure S3.

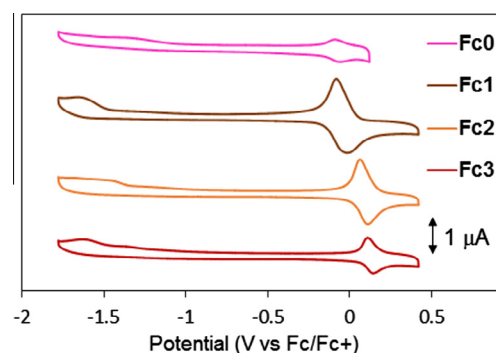
The result of electrochemical measurement of dyads indicated redox property varied with the change of spacer groups. The



**Figure 1.** Ferrocene-containing donor–bridge–acceptor dyads of structures **Fc0–Fc3** in this study.



**Figure 2.** UV/vis spectra of dyads **Fc0–Fc3** in CH<sub>2</sub>Cl<sub>2</sub> solution (1.0 × 10<sup>-4</sup> M).



**Figure 3.** Cyclic voltammogram of dyads **Fc0–Fc3** in 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> of CH<sub>2</sub>Cl<sub>2</sub> solution. Scan rate is 100 mV/s, dyad of concentration is 1.0 × 10<sup>-3</sup> M.

HOMO levels of **Fc0–Fc3** were estimated to be 0.39–0.59 V (vs NHE), which were too close to the oxidation potential of I<sup>-</sup>/I<sup>3-</sup> (0.4 V vs NHE). The charge flow cannot be conducted effectively, so that they cannot be used as workable sensitizers for DSSCs.<sup>15</sup> To further investigate the nature of radical cations after oxidation, electrochemical absorption spectra were recorded. It is reported that the photo-induced radical cation of ferrocene displays the characteristic lowest energy band at 617 nm with very weak intensity in CHCl<sub>3</sub> or CCl<sub>4</sub> solutions.<sup>16</sup> The electrochemically generated radical cation of ferrocene (1.0 × 10<sup>-3</sup> M in 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution) shows a similar position at 616 nm (Fig. S1b). All measurements of dyads were done under a similar condition to that of ferrocene. The characteristic absorption peak of **Fc0** was found at 853 nm with low intensity. In the ground state, the lowest energy bands of dyads **Fc2** and **Fc3** were blue-shifted compared with **Fc1**. In contrast to the ground state, the radical cation of the dyads showed a red-shift with the increased number of thiophene unit, that is, for **Fc1** at 942 nm, for **Fc2** at 1051 nm, and **Fc3** at 1183 nm, respectively.

To confirm the electron coupling in the neutral and radical cation states, time dependent density functional theoretical (TD-DFT) computation was performed at B3LYP/def-TZVPP level by the TURBOMOLE program.<sup>17</sup> The 20 excited states for neutral state and 10 excited states for radical cation state were calculated and the trend agrees well with experimental results (Figs. S2 and S3). Typical examples of selected molecular orbitals for **Fc0** and **Fc3** are illustrated in Figure 4, and those for **Fc2** and **Fc3** in Figure S2. In the absorption spectra, a blue shift was found at the lowest energy band when the thiophenylene moieties were inserted between the donor and acceptor. TD-DFT computation results indicated that the 1st excitation of **Fc0** mainly dominates from HOMO-1 to the second lowest unoccupied molecular orbital (LUMO+1) and LUMO+2, and HOMO to LUMO+1 transition, with HOMO-1 to LUMO, LUMO+2, and LUMO+3 transition, respectively, (Table 1).

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