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One-Step Synthesis of Donor−Acceptor type Conjugated Polymers from Ferrocene-Containing Poly(aryleneethynylene)s

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Introduction. Ferrocene-containing conjugated polymers have attracted much attention because of the combination of the optoelectronic properties of conjugated polymers and the redox activities of the ferrocene moieties.[1] Inspired by the famous polyacetylene studies,[2] chemical doping has been examined for the initially reported polyferrocenes, poly(1,1′-ferrocene) and poly(ferrocenylacetylene), and the electric conductivities of some polymers indeed increased to the order of 10^{-2} S cm^{-1}.[3] However, doping always produces chemically unstable open shell species, which dramatically decreases the material's durability.

Recently, it was found that some cyano-containing doping reagents, such as tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and their derivatives, undergo a [2 + 2] cycloaddition reaction with electron-rich alkynes to form the cyclobutene ring, which spontaneously opens to give the corresponding donor−acceptor chromophores in a remarkably high yield.[4] The reactivity significantly depends on the electron density of the alkyne groups and the steric factor of the substances. Among the already reported donors, the dialkylaniline groups often provide the desired donor−acceptor products in a quantitative yield.[5] Very recently, we employed this reaction and reported the quantitative addition reaction of TCNE to the aromatic polyamines bearing electron-rich alkynes as a side chain.[6] To expand the generality of this reaction, we decided to investigate other effective donor groups and applicable polymer structures. In this communication, we report (i) that ferrocene is also an effective donor group for this reaction, and (ii) the first addition reaction of TCNE to the alkyne moieties of poly(aryleneethynylene)s containing ferrocene in the main chain.[7] In sharp contrast to chemical doping, the resulting polymers are chemically stable because of their closed shell structures. This will be a new synthetic method for donor−acceptor type conjugated polymers.

Results and Discussion. First, the reactivity of the alkyne groups activated by ferrocene was studied for the model monomer **1**.[8] The addition of 1 equiv of TCNE to a CH_2Cl_2 solution of **1** lead to an immediate color change from orange to green at room temperature, quantitatively yielding a donor−acceptor molecule **2** via the cyclobutene intermediate (Scheme 1). The chemical structure of **2** was characterized by NMR, IR, elemental analysis, and an X-ray crystal structure analysis. The crystal structure revealed the efficient charge transfer from the ferrocene donor to the tetracyanobutadiene (TCBD) acceptor (Figure 1SI). However, the addition of an excess amount of TCNE and heating did not provide the double adduct. This result suggests that the ethynylferrocene moiety substituted with the TCBD acceptor cannot further react with TCNE. In other words, the ferrocene moiety can activate only one alkyne group for the reaction with TCNE.

On the basis of the monomer study, the reaction was applied to the poly(aryleneethynylene)s. Precursor polymers were prepared by the Sonogashira cross-coupling reaction of 1,1′-diiodoferrocene and the diethynylbenzene monomer. The molecular weight of the obtained poly(aryleneethynylene)s is sufficiently high (M_w = 41100 and M_n = 8100 for **3** and M_w = 16200 and M_n = 7000 for **5**). They were then subjected to the reaction with TCNE. Unexpectedly, the reaction did not proceed in CH_2Cl_2 at room temperature and, therefore, heating was necessary. The poor reactivity of the alkyne groups in the poly(aryleneethynylene)s, as compared to the model monomer, might reflect the steric factor and/or slow diffusion of the polymers. The reaction at 50 °C in 1,2-dichloroethane slowly changed the solution color from orange to green. Higher temperatures lead to a faster reaction and a higher yield. However, the temperature must be lower than the onset decomposition temperatures of the ferrocene polymers. Thus, the solvent and the reaction temperature were carefully optimized on the basis of a thermogravimetric analysis (TGA) of the resulting polymers (Figure 2SI). The optimized conditions (120 °C for 3 h in 1,2-dichlorobenzene) yielded **4** with the TCNE addition yield (x) of 0.75 and **6** with an x of 0.62. It should be noted that an excess amount of TCNE did not produce any side reactions at this temperature and could readily be removed by sublimation. Thus, the reaction yields were simply estimated by the gravimetric analyses, which were consistent with the results of the elemental analyses. The addition reaction of TCNE was confirmed by the IR spectra (Figure 3SI). The monomer **2** showed a new cyano vibrational peak at 2222 cm^{-1}, which does not exist in **1**. This is also true for the polymers. After the TCNE addition reaction, **4** and **6** showed a new cyano vibrational peak at 2222 cm^{-1}. Since the polymers do not display the peak characteristic of TCNE at 2257 cm^{-1}, the products are not a mixture of **4**/**6** and unreacted TCNE. Furthermore, it was found that this addition reaction can improve the glass transition temperature (T_g) of the polymers (Table 1). The T_g values of the precursor polymers increased by 6−12 °C after the TCNE addition. This enhancement is expected to be more significant with the increasing amount of added TCNE.[6]

The essence of the donor−acceptor chromophores is the appearance of charge-transfer (CT) bands in the visible absorption region and the redox activities in both the anodic and cathodic directions. The precursor monomer **1** displayed the π−π* transition at 307 nm and d−d transition at 453 nm in $CHCl_3$, whereas a well-defined CT band appeared at 618 nm for **2** (Table 1 and Figure 4SI). Similarly, the donor−acceptor polymers **4** and **6** displayed the broad CT band in the entire visible region and the end absorption reached ~850 nm in the near-IR region, suggesting the corresponding low band gap of ~1.46 eV (Figure 1). The *m*-phenylene-linked polymer **6** showed a peak profile similar

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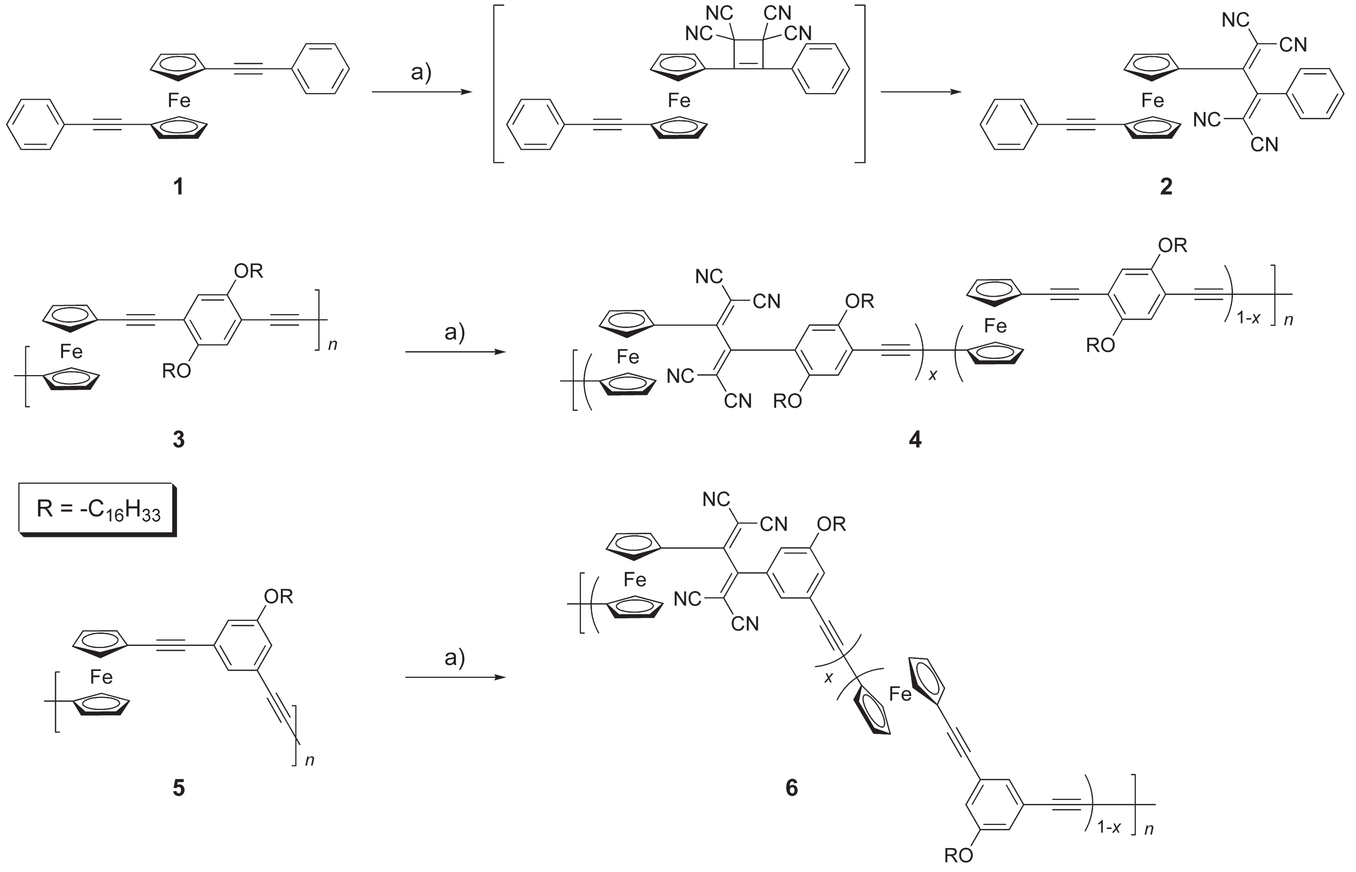
Scheme 1. Addition Reaction of TCNE to Ferrocene-Substituted Ethynylene Derivatives: (a) TCNE, CH_2Cl_2 or 1,2-Dichloroethane or 1,2-Dichlorobenzene, 20 °C or Δ



to monomer **2** and the peak top value was observed at 603 nm. This is because of the cross-conjugated *m*-phenylene spacer, which interrupts the efficient electronic communication between the repeat units. On the other hand, the CT band of the *p*-phenylene-linked polymer **4** was very broadened and no clear peak top was detected. This result means that the donor−acceptor chromophores interact with each other through the *π*-conjugated main chain, resulting in several CT transitions with different strengths.

Table 1. Summary of Thermal, Optical, and Electrochemical Properties of the Ferrocene Monomers and Polymers

			potential (V vs Fc/Fc^+)[c]			
	T_g (°C)[a]	λ_{CT} (nm)[b]	$E_{1/2}^{red}(2)$	$E_{1/2}^{red}(1)$	$E_{1/2}^{ox}(1)$	$E_{1/2}^{ox}(2)$
1					0.22	
2		618	−1.30	−0.93	0.53	
3	32				0.26	
4	38	[d]	[d]	−0.86[e]	0.30	0.55
5	51				0.25	
6	63	603	−1.24[e]	−0.90[e]	0.29	0.64

[a] Determined by DSC. [b] CT band in $CHCl_3$. [c] Measured with a glassy carbon disk electrode as a working electrode in CH_2Cl_2 containing 0.1 M $(nC_4H_9)_4NClO_4$ at 20 °C, at a scanning rate of 0.1 V s^{-1}. [d] Could not be determined due to the broad peak. [e] Quasi-reversible peak.

The electrochemical behaviors were analyzed by cyclic voltammograms (CVs) (Table 1). All precursors, **1**, **3**, and **5**, displayed a reversible single oxidation step at 0.22, 0.26, and 0.25 V, respectively, which is attributable to the ferrocene moiety. The slight anodic shift in terms of the ethynyl substitution is consistent with previous reports.[1d,1h,9] After the reaction with TCNE, monomer **2** showed a further anodically shifted ferrocene redox at 0.53 V as well as several new reduction steps (Figure 5SI). Thus, two well-resolved reversible reduction steps at −0.93 and −1.30 V are ascribed to the TCBD moiety and the irreversible third reduction step occurs at the phenylethynyl center. In the case of the TCNE-adducted polymers, two reversible ferrocene-centered oxidations appeared due to the incomplete reaction of TCNE (Figure 2). Judging from the redox behaviors of the model monomers, the first oxidation potential originates from the diethynylferrocene moieties and the second one from the TCBD-substituted ferrocenes. The reduction potentials of polymers **4** and **6** appeared at almost the same potentials as monomer **2**. Unfortunately, the electrochemical responses were poor and the observed reduction peaks were quasi-reversible. The conventional electrochemical band gaps, calculated from the first oxidation and the first reduction potentials, are 1.16 V for **4** and 1.19 V for **6**. However, it should be noted that the electrochemical band gaps, which are correlated with the optical band gaps, are 1.41 V for **4** and 1.54 V for **6**, values that were calculated from the second oxidation and the first reduction potentials. Polymer **4** showed a lower band gap than **6**, which reflects the difference in the linear and cross-conjugated connectivities.

Conclusions. A high-yielding addition reaction between electron-rich alkynes and TCNE was employed to prepare donor−acceptor type conjugated polymers. Ferrocene was found to be an efficient donor group for this reaction, and the optimization of the reaction conditions enabled the incorporation of the TCBD moiety up to 75% in the repeat unit of the poly(aryleneethynylene)s. The low energy in the CT bands and the associated electrochemical band gaps were demonstrated. Donor−acceptor type conjugated polymers are promising materials for semiconductors in organic

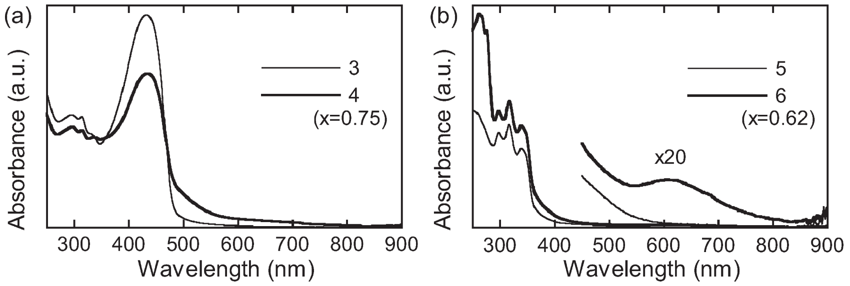


Figure 1. UV−vis spectra of (a) *p*-phenylene-linked ferrocene polymers and (b) *m*-phenylene-linked ferrocene polymers in $CHCl_3$ at 20 °C.

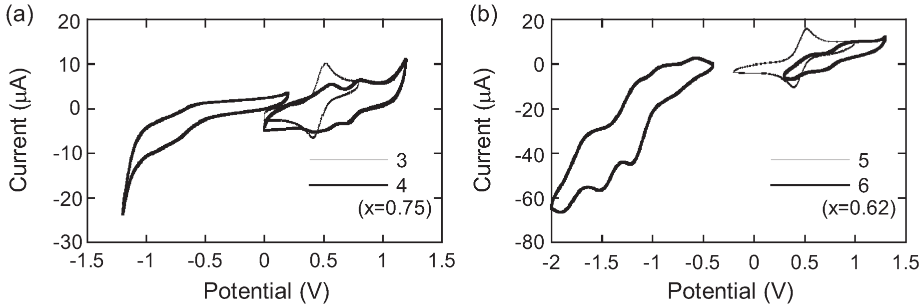


Figure 2. Cyclic voltammograms of (a) *p*-phenylene-linked ferrocene polymers (4 mM/repeat unit) and (b) *m*-phenylene-linked ferrocene polymers (4 mM/repeat unit) in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NClO_4$ at 20 °C, at a scanning rate of 0.1 V s^{-1}.

photovoltaic devices as well as nonlinear optical applications. These properties are now being characterized in our laboratory.

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Supporting Information Available: Text giving experimental details on synthesis (with structures), measurements, and crystal data, figures showing the ORTEP plot of **2**, TGA curves of **4** and **6**, IR spectra of monomers and polymers, UV−vis spectra of **1** and **2** and cyclic voltammograms of **1** and **2**, and a cif file for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (b) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Polym. J.* **1981**, *13*, 255. (c) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S. *Macromolecules* **1995**, *28*, 8713. (d) Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390. (e) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (f) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **2000**, *33*, 6965. (g) Park, P.; Lough, A. J.; Foucher, D. A. *Macromolecules* **2002**, *35*, 3810. (h) Morisaki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 9319. (i) Shi, J.; Tong, B.; Li, Z.; Shen, J.; Zhao, W.; Fu, H.; Zhi, J.; Dong, Y.; Haussler, M.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2007**, *40*, 8195. (j) Masson, G.; Lough, A. J.; Manners, I. *Macromolecules* **2008**, *41*, 539.

(2) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

(3) (a) Cowan, D. O.; Park, J.; Pittman, C. U.Jr; Sasaki, Y.; Mukherjee, T. K.; Diamond, N. A. *J. Am. Chem. Soc.* **1972**, *94*, 5110. (b) Pittman, C. U.Jr.; Surynarayanan, B. *J. Am. Chem. Soc.* **1974**, *96*, 7916. (c) Pittman, C. U.Jr.; Sasaki, Y. *Chem. Lett.* **1975**, 383. (d) Yamamoto, T.; Sanechika, K.-I.; Yamamoto, A. *Inorg. Chim. Acta* **1983**, *73*, 75.

(4) (a) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, 737. (b) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem.—Eur. J.* **2006**, *12*, 1889. (c) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4731. (d) Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235.

(5) (a) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 6357. (b) Alonso-Gómez, J. L.; Schanen, P.; Rivera-Fuentes, P.; Seiler, P.; Diederich, F. *Chem.—Eur. J.* **2008**, *14*, 10564. (c) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Enko, B.; Seiler, P.; Muller, I. B.; Langer, N.; Jarowski, P. D.; Gescheidt, G.; Diederich, F. *Chem.—Eur. J.* **2009**, *15*, 4111.

(6) Michinobu, T. *J. Am. Chem. Soc.* **2008**, *130*, 14074.

(7) For some reported reactions of alkynes in poly(aryleneethynylene)s, see: (a) Marshall, A. R.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 4688. (b) Beck, J. B.; Kokil, A.; Ray, D.; Rowan, S. J.; Weder, C. *Macromolecules* **2002**, *35*, 590. (c) Ricks, H. L.; Choudry, U. H.; Marshall, A. R.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 1424. (d) Scholz, S.; Leech, P. J.; Englert, B. C.; Sommer, W.; Weck, M.; Bunz, U. H. F. *Adv. Mater.* **2005**, *17*, 1052.

(8) For the previous report on the reaction of TCNE with ethynylferrocene derivatives, see: Mochida, T.; Yamazaki, S. *J. Chem. Soc., Dalton Trans.* **2002**, 3559.

(9) (a) Morikita, T.; Maruyama, T.; Yamamoto, T.; Kubota, K.; Katada, M. *Inorganic. Chim. Acta* **1998**, *269*, 310. (b) Plenio, H.; Hermann, J.; Sehring, A. *Chem.—Eur. J.* **2000**, *6*, 1820. (c) Morikita, T.; Yamamoto, T. *J. Organomet. Chem.* **2001**, *637−639*, 809.