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The synthesis and redox-induced off–on PL properties of poly(3,4-bisphenyl-*N*-methylferrocene-pyrrole-2,5-dione)

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Abstract

A novel π-conjugated polymer containing a ferrocene group was designed and synthesized from 3,4-bis(4-bromophenyl)-*N*-methylferrocene-pyrrole-2,5-dione by dehalogenation polycondensation with the zerovalent nickel complexes (a Yamamoto reaction). The polymer was characterized by FT-IR, ^{1}H NMR, gel permeation chromatography, UV, cyclic voltammetry and Fluorescence spectroscopy. The polymer has the M_w of 2620 and polydispersity index of 1.5. Also this polymer showed high solubility in common organic solvents, good film formability on the glass substrate and redox property. The fluorescence of the model compound and polymer with a diphenylmaleimide moiety is almost quenched due to the ferrocene group because of the intramolecular electron transfer. However, the model compound and the polymer showed a recovered fluorescence when a ferrocene group of them was oxidized chemically and electrochemically. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Yamamoto method; Diphenylmaleimide; Ferrocene

1. Introduction

Recently, conjugated polymers and oligomers containing organometallic groups in the backbone or pendant of the chains have attracted attention in the last several years because of their promising electronic and optical properties arising from interactions between the organometallic groups and π-conjugated structure [1,2]. Many attempts have made to introduce a ferrocene unit as one of the most common organometallic chemicals into the main chain of the π-conjugated polymer or luminescent molecules. It has been well known as a good electron donor and quasi-reversible redox center. Also it has been widely used as a luminescence quencher in intermolecular processes taking place in solution. Luminescence quenching led to numerous applications in the areas of analytical chemistry and biology [3,4].

Also many researches to the combination of redox and luminescent property have been studied in naphthalimide [5], anthracene [6], pyrene [7]. But those were reported only on the luminescent phenomena for organic compounds by chemical oxidation. Up to now, it has been not reported on the luminescence property of polymer by electrochemical and chemical oxidation.

In this article, the new π-conjugated polymer containing a ferrocenyl group, was designed and synthesized, it's luminescent switching effect was investigated by electrochemical and chemical oxidation.

2. Experimental

2.1. Materials

All chemical reagents were purchased from Aldrich, Acros, Merck and TCI. 2,2′-Bipyridyl (bpy) was used after recrystallization from *n*-hexane and then ethanol. 3,4-Bis(4-bromophenyl)-2,5-furanedione [8], 3,4-bisphenyl-2,5-furanedione [9] and ferrocenylmethylamine [10,11] were prepared according to the previously reported procedure. Other reagents were used without further purification.

2.2. Synthesis

2.2.1. 3,4-Bisphenyl-N-methylferrocene-pyrrole-2,5-dione (1)

The mixture of ferrocenylmethylamine (0.25 g, 1.2 mmol),

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3,4-bisphenyl-2,5-furanedione (0.32 g, 1.2 mmol) and triethylamine (Et_3N) (catalytic amount) in toluene (40 ml) was refluxed for 24 h. Water was removed using a Dean stark trap. Then, toluene was removed under reduced pressure. The product was obtained after recrystallization from ethanol. Yield: 0.47 g (78%). ^{1}H NMR ($CDCl_3$): $\delta = 4.13$ (2H, Cp), 4.20 (5H, Cp), 4.37 (2H, Cp), 4.58 (2H, $-CH_2-$), 7.35 (6H, aromatic CH), 7.42 (4H, aromatic CH). IR (KBr): 1759 and 1693 cm^{-1} (C=O), 1421 cm^{-1} (C–N).

2.2.2. *3,4-Bis(4-bromophenyl)-N-methylferrocene-pyrrole-2,5-dione (**2**)*

The mixture of ferrocenylmethylamine (0.37 g, 1.7 mmol) and 3,4-bis(4-bromophenyl)-2,5-furanedione (0.7 g, 1.7 mmol) according to the same procedure for the preparation of compound **1** gave a glittering yellow crystal. Yield: 0.92 g (89%). ^{1}H NMR ($CDCl_3$): $\delta = 4.13$ (2H, Cp), 4.20 (5H, Cp), 4.36 (2H, Cp), 4.57 (2H, $-CH_2-$), 7.30 (4H, aromatic CH), 7.48 (4H, aromatic CH). IR (KBr): 1764 and 1698 cm^{-1} (C=O), 1431 cm^{-1} (C–N), 1250 cm^{-1} (C–Br).

2.2.3. *Poly(3,4-bisphenyl-N-methylferrocene-pyrrole-2,5-dione) (**3**)*

In a 20 ml sealed tube were placed $Ni(COD)_2$ (0.331 g, 1.2 mmol), bpy (0.187 g, 1.2 mmol) and compound **2** (0.61 g, 1.0 mmol) under an argon atmosphere. Dry DMF (10 ml) and 1,5-cyclooctadiene (COD) (2.3 mmol, 0.29 ml) were added using a syringe through a rubber septum. The mixture was stirred at 60 °C for 40 h under a nitrogen atmosphere. The resultant mixture was poured into aqueous ammonia (200 ml). The precipitated dark yellow polymer **3** was collected, washed with warm methanol, a hot aqueous solution of *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetate (EDTA) (pH 3.8), a hot aqueous solution of disodium EDTA (pH 9), warm water and then methanol in order and dried in vacuo. Yield: 0.45 g. ^{1}H NMR ($CDCl_3$): $\delta = 4.13$ (2H, Cp), 4.21 (5H, Cp), 4.39 (2H, Cp), 4.60 (2H, $-CH_2-$), 7.53 (8H, aromatic CH). IR (KBr): 1760 and 1701 cm^{-1} (C=O), 1431 cm^{-1} (C–N).

2.2.4. *Oxidation of the compound **1** (**4**)*

A 0.1 g (0.21 mmol) amount of compound **1** was dissolved in 10 ml of concentrated sulfuric acid. The solution was stirred 1 h at ambient temperature and was poured into 200 ml of water. The dilute solution was filtered to remove sulfur, etc. and an aqueous solution of $NaPF_6$ was added. The resulting dark green precipitate was filtered, washed several times with water, and dried in vacuo. Yield: 0.05 g (38%). IR (KBr): 1769 and 1672 cm^{-1} (C=O), 1430 cm^{-1} (C–N), 834 cm^{-1} (PF_6).

2.2.5. *Oxidation of the polymer **3** (**5**)*

A 0.05 g amount of polymer **3** according to the same procedure for the preparation of compound **5** gave a dark greenish yellow solid. Yield: 0.02 g (32%). IR (KBr): 1765 and 1702 cm^{-1} (C=O), 801 cm^{-1} (PF_6).

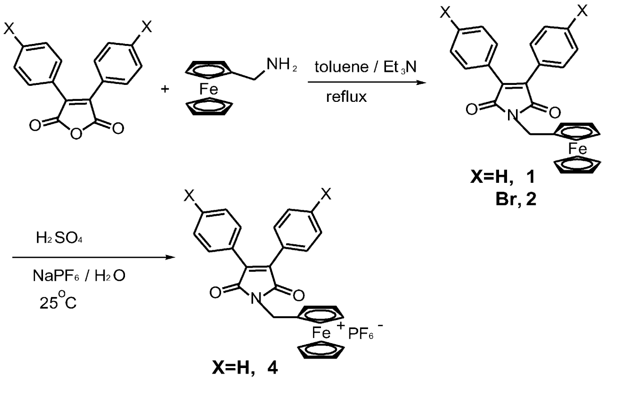
2.3. *Measurements*

Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. ^{1}H NMR spectra were obtained using a Varian VXR-300 and referenced to tetramethylsilane. IR spectra were recorded on a Nicolet Avatar 360 FT-IR ESP. Elemental analysis was carried out using an Elementar Analysensysteme GmbH Vario EL. The molecular weight was measured by gel permeation chromatography (GPC) using THF as an eluent and polystyrene standards as a reference. The measurement of cyclic voltammetry (CV) was conducted with the CV cell composed of a working electrode (platinum plate), a reference electrode (Ag/AgCl), a counter electrode (platinum plate), and two supporting electrolytes (0.1 M $[NBu_4]$-BF_4/acetonitrile and 0.1 M $LiClO_4$/tetra (ethylene glycol) dimethyl ether) with using a Potentiostat/Galvanostat Model 273 (EG & G Instrument Inc.). UV–visible absorption spectra and fluorescence spectra were recorded on a Sinco UVS-2100 and a Shimadzu RF 5301PC Spectrofluorophotometer, respectively.

3. Results and discussion

3.1. *Synthesis and characterization of the monomer and the polymer*

The thermal imidizations of 3,4-bis(4-bromophenyl)-2,5-furanedione and 3,4-bisphenyl-2,5-furanedione with the ferrocenylmethylamine in toluene provided the 1,2-diphenylmaleimide-based model compound and monomer, 3,4-bisphenyl-*N*-methylferrocene-pyrrole-2,5-dione (**1**) and 3,4-bis(4-bromophenyl)-*N*-methylferrocene-pyrrole-2,5-dione (**2**), respectively (Scheme 1). Fig. 1 showed the ^{1}H NMR spectrum of the imides, which was well in accordance with the expected chemical structures. The methylene proton peaks of the imides were shifted to 4.57 and 4.58 ppm downfield, which compared with that of its amine's peak ($\delta = 3.55$). Fig. 2 represented FT-IR spectrum of the imides, compounds **1** and **2**, showed the characteristic



Scheme 1. Synthesis and chemical oxidation of the monomer and the model compound.

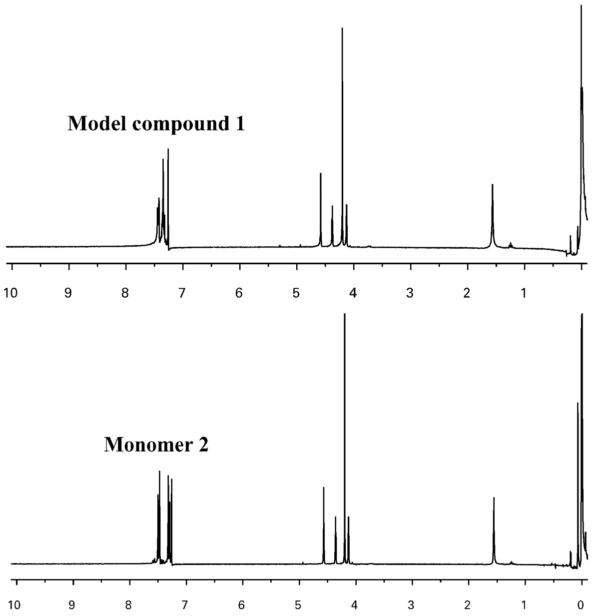


Fig. 1. ^{1}H NMR spectra of the compounds **1** and **2**.

imide group absorption bands of C=O stretching bands at 1759, 1693 cm^{-1} (**1**) and 1764, 1698 cm^{-1} (**2**). C–N stretching bands at 1421 cm^{-1} (**1**) and 1431 cm^{-1} (**2**).

Dehalogenation polycondensation of the compound **2** by the use of a zerovalent nickel complex gave the π-conjugated polymer **3**. The coupling catalyst Ni(COD)$_2$ was used as a nickel(0) complex, COD and bpy as ligands and DMF as a solvent as described in the Yamamoto coupling method (Scheme 2) [12,13]. The ^{1}H NMR spectrum (Fig. 3) of the polymer **3** showed that the polymer had the well-defined as the expected structure. The methylene proton peak between the ferrocene and an imide moiety appeared at 4.60 ppm, which was similar to that of monomer **2**. The substituted ferrocene proton peaks appeared between 4.13 and 4.39 ppm. Aromatic proton peaks near 7.53 ppm came under the protons at biphenyl groups in the main chain, formed by the carbon–carbon coupling reaction. The GPC result of the polymer **3** showed M_n and M_w of 1744 and 2620, respectively. The polymer **3** showed good solubility in most common organic solvents such as chloroform, THF, toluene and DMF. The film property of the resulting polymer was very good in above solutions by a spin-casting technique. We could not obtain a ^{1}H NMR spectrum for the [(diphenylmaleimide–FeCP$_2$)]$^+$ as expected [14].

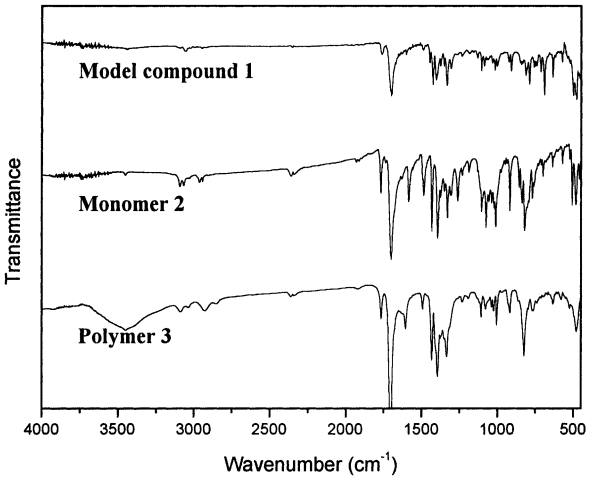
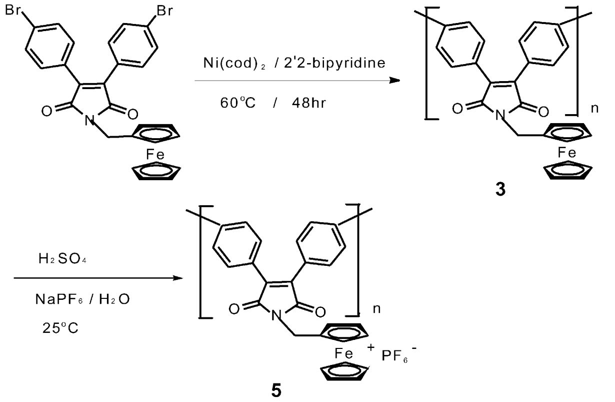


Fig. 2. IR spectra of the compounds **1**, **2**, and **3**.



Scheme 2. Synthesis and chemical oxidation of poly(3,4-bisphenyl-*N*-methylferrocene-pyrrole-2,5-dione).

3.2. Optical characterization

As shown in Figs. 4 and 5, the maximum absorption wavelength (406 nm) of the polymer **3** and oxidized polymer **5** were red-shifted relative to that (379 nm) of the model compound **1** and oxidized model compound **4** due to the extension of π-conjugation. The fluorescence of the model compound **1** and the polymer **3** was almost quenched by a ferrocene group of them, because of intramolecular electron transfer from the excited diphenylmaleimide moiety to the ferrocene group. In chemical oxidation of model compound was observed the photoluminescence spectrum a recovered green fluorescence emission (502 nm) [15] as shown in Figs. 4 and 5. It was suggested the intramolecular electron transfer from the oxidized ferrocene

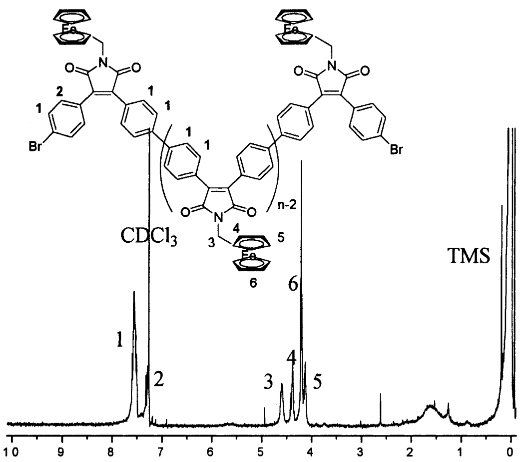


Fig. 3. ^{1}H NMR spectrum of the polymer **3**.

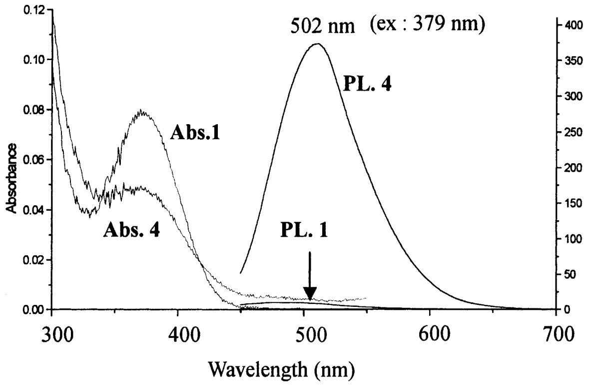


Fig. 4. Absorption and PL spectra of the model compound **1** and chemically oxidized model compound **4** in $CHCl_3$ (1×10^{-5} M).

(Fc^+) group of the model compound would be inhibited and the fluorescence of the model compound was recovered [16]. In the oxidized polymer **5**, similar results were also observed at red-shifted PL spectra (529 nm) in $CHCl_3$ (1×10^{-5} M) (Figs. 5 and 7). PL efficiency of the oxidized model compound **4** was higher than the model compound **1** about 170 times, and the oxidized polymer **5** was higher than the polymer **3** about 11 times by integration of PL spectra in Figs. 4 and 5.

Figs. 6 and 7 showed photoluminescence spectra after electrochemical oxidation of the model compound **1** and the polymer **3**, respectively. Electrochemical oxidation was carried out first (scan of oxidation potential curve as shown in Fig. 8) in the CV; 1×10^{-3} M in CH_3CN using 0.1 M $[NBu_4]BF_4$ as an electrolyte (scan rate: 0.1 mV/s, 0.3–0.6 V). In these Figs. 6 and 7, the PL intensity is increased after electrochemical oxidation of them, but we could not observe decrease of PL intensity when they were reduction by CV. It is not clear, but it was thought that oxidation of the samples may occur at the diffusion layer on the platinum plate in the CV. In conclusion, the maximum wavelength of photoluminescence after chemical and electrochemical oxidation of model compound and polymer exists at the same wavelength, respectively, and the intensity of luminescence at the maximum wavelength is increased.

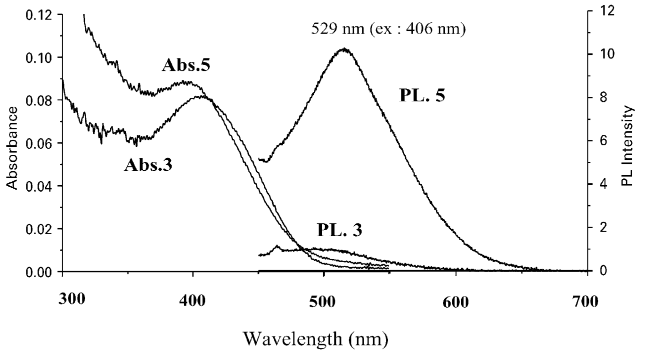


Fig. 5. Absorption and PL spectra of polymer **3** and chemically oxidized polymer **5** in $CHCl_3$ (1×10^{-5} M).

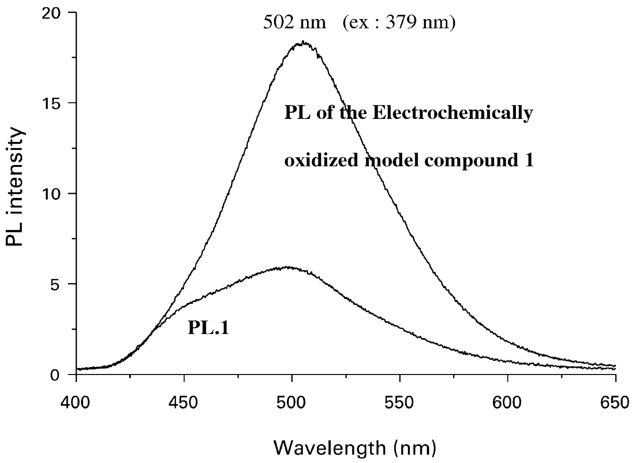


Fig. 6. Photoluminescence spectrum of the model compound **1** and the electrochemically oxidized model compound **1**. (1×10^{-3} M in CH_3CN using 0.1 M $[NBu_4]BF_4$ as an electrolyte) (scan rate: 0.1 mV/s, 0.3–0.6 V).

3.3. Electrochemical characterization

The redox behaviors of compounds **1**, **3**, and **4** were characterized by CV. 0.1 M $LiClO_4$ in tetra (ethylene glycol) dimethyl ether was used as a supporting electrolyte. Fe(II)–Fe(III) of the ferrocene redox coupled with an oxidation and a reduction peaks appeared at 0.53 and 0.43 V vs Ag/Ag^+ in 0.1 M $[NBu_4]BF_4$/acetonitrile, respectively. However, an oxidation and a reduction peak of ferrocene appeared at 0.32 and 0.02 V vs Ag/Ag^+ by the effects of the solvent and electrolyte [17]. As shown in Fig. 8, the oxidation and the reduction peaks of compounds **1**, **3**, and **4** were similar to that of ferrocene because of being decoupled by the methylene group adjacent to the nitrogen group attached covalently to the ferrocene group as a spacer. It may be the reason why the redox potentials of all samples were same compared with that of ferrocene [18]. And this data were represented at second scan results as shown in Fig. 8, all samples have the reproducibility of redox

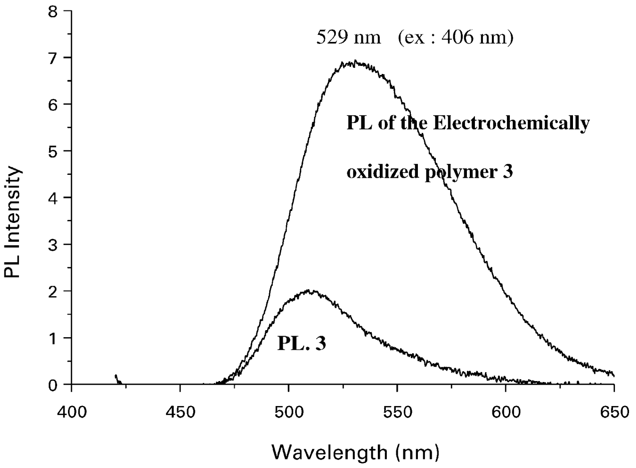


Fig. 7. Photoluminescence spectrum of the polymer **3** and the electrochemically oxidized polymer **3**. (1×10^{-3} M in CH_3CN using 0.1 M $[NBu_4]BF_4$ as an electrolyte) (scan rate: 0.1 mV/s, 0.3–0.6 V).

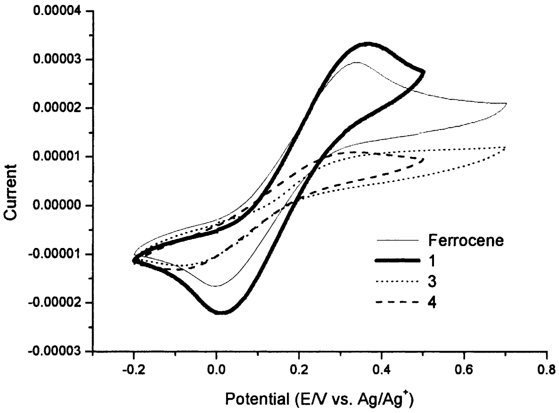


Fig. 8. Cyclic voltammogram of ferrocene, compounds **1**, **3**, and **4**: under the condition of 2×10^{-3} M in tetra (ethylene glycol) dimethyl ether (0.1 M $LiClO_4$; scan rate 0.05 V/s).

behaviors of the resulting compounds including the ferrocene group.

4. Conclusions

A novel *cis*-stilbenoid structured polymer, poly(3,4-bisphenyl-*N*-methylferrocene-pyrrole-2,5-dione), which has a ferrocene group was synthesized by a Yamamoto reaction. The resultant polymer showed good solubility in common organic solvents and good film formability on a glass substrate. But the chemically oxidized polymer showed poor solubility and low fluorescence. The fluorescence of the model compound and the polymer was almost quenched by a ferrocene group. However, the model compound and the polymer have a recovered fluorescence when the ferrocene group was oxidized chemically or electrochemically, the intramolecular electron transfer from the oxidized ferrocene (Fe^+) would be inhibited and then, the greenish yellow fluorescence of the model compound and the polymer was recovered in $CHCl_3$ (1×10^{-5} M). It is expected that the resulting polymer would be used to PL switch.

Acknowledgments

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