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ORIGINAL PAPER

Through-space conjugated polymer containing [2.2]paracyclophane and dithiafulvene units in the main chain

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Abstract A new through-space conjugated polymer containing alternate [2.2]paracyclophane and dithiafulvene units was synthesized by cycloaddition polymerization of aldothioketene derived from 4,16-diethynyl[2.2]paracyclophane. The obtained polymer was soluble in common organic solvents and could form thin films. UV–vis absorption spectrum of the polymer revealed that its conjugation length increased due to the through-space interaction of the [2.2]paracyclophane units. The polymer formed a charge transfer (CT) complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in DMSO.

Keywords Through-space conjugation · [2.2]Paracyclophane · Dithiafulvene · Charge transfer complex

Introduction

Conjugated polymers are one of the most promising functional materials, because they can be used in the fabrication of conducting devices [1–6], light-emitting diodes [7, 8], field effect transistors [5, 6], etc. Their optical and electronic properties can be easily tuned by changing the components of their backbones and modifying their structures. A number of aromatic compounds have been incorporated into conjugated polymers, and their physical properties have been studied.

[2.2]Paracyclophane is a fascinating molecule comprising two benzene rings closely linked (a distance of approximately 2.8–3.1 Å) by two ethylene bridges.

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Since the first preparation of [2.2]paracyclophane in 1949 [9], cyclophane chemistry has attracted significant attention. As the two benzene rings are very close to each other, [2.2]paracyclophane and its derivatives exhibit a transannular π–π interaction, which leads to a unique extended through-space π-conjugation [10–20]. A variety of [2.2]paracyclophane derivatives have been prepared so far, and their structural features and physical properties have been investigated in detail [10–13]. There are several reports on the synthesis of polymers containing [*m.n*]paracyclophane ($m \leq 3$, $n \leq 3$) by chain polymerization [21–31] and polycondensation techniques [32–35]. However, despite the fact that conjugated polymers have an impressive conjugation system, a few studies have been conducted on the synthesis of conjugated polymers with [2.2]paracyclophane in the polymer main chain [36–39]. Recently, we focused on the synthesis of through-space conjugated polymers with [2.2]paracyclophane as the repeating unit in the polymer main chain [40–55]. We found that their conjugation length increased via the through-space interaction of the benzene rings. In addition, they exhibited intense blue–orange fluorescence emissions, irrespective of their π-stacked structures in the polymer main chain.

Cycloaddition of aldothioketene proceeds smoothly under a mild reaction condition, producing a dithiafulvene skeleton [56–58]. In our previous studies, we prepared a series of conjugated polymers containing a dithiafulvene unit by cycloaddition polymerization [59–61]. This method enables the incorporation of a variety of aromatic compounds in the conjugated polymer backbone containing dithiafulvene. In this study, we demonstrated the cycloaddition polymerization of a 4,16-diethynyl[2.2]paracyclophane monomer in order to expand the substrate scope of the cycloaddition polymerization of cyclophane compounds as well as to elucidate the electrochemical behaviors of the [2.2]paracyclophane-containing conjugated polymer by exploiting the through-space interaction.

Experimental

General

^{1}H and ^{13}C NMR were recorded on a JEOL 400 instrument at 400 and 100 MHz, respectively. All samples were analyzed in $CDCl_3$ or DMSO-d_6, and chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV–vis measurements were carried out on a JASCO V-530 spectrophotometer at room temperature. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer at room temperature. Gel permeation chromatography (GPC) was carried out on a UV-8020 and RI-8020 (TSK-GEL α-3000) using DMF containing 10 mM LiBr as an eluent after calibration with standard polystyrene. For cyclic voltammetry (CV), a polymer thin film was obtained from a DMSO solution on an indium-tin-oxide (ITO) coated glass electrode. CV was carried out on a BAS CV-50W electrochemical analyzer in CH_3CN containing 0.1 M Et_4NBF_4 with a Pt counter electrode and an Ag/Ag^+ pseudo-reference electrode at a scan rate of 100 mV s^{-1}. Electrical conductivity of a thin film was measured at room temperature with a four-probe technique using a Loresta-EP MCP-T360 (Mitsubishi Chemical Corp.). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Elemental analysis was carried out on a vario MICRO elemental analyzer (Elementar Analysensysteme GmbH).

Materials

THF was purified by passage through solvent purification columns under Ar pressure [62]. Dehydrated DMSO and DMF were purchased from Wako Pure Chemicals Industries and used without further purification. *n*-BuLi (1.6 M in hexane) was purchased from Kanto Chemical Co., Inc. Dioctylamine and S_8 were purchased from Wako Pure Chemicals Industries, Ltd. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was purchased from Tokyo Chemical Industry Co., Ltd. 4,16-Diethynyl[2.2]paracyclophane **1** was synthesized according to the literature [47].

Polymerization

To a solution of 4,16-diethynyl[2.2]paracyclophane **1** (120 mg, 0.47 mmol) in THF (5.0 mL), *n*-BuLi in hexane (1.6 M, 0.75 mL, 1.2 mmol) was added dropwise at 0 °C. After stirring for 1 h, the powder of S_8 (34 mg, 1.1 mmol) was added to the solution. The reaction mixture was stirred for 2 h. The reaction mixture was cooled to −78 °C, and water (17 μL) was carefully added. Then the mixture was allowed to warm to room temperature and the reaction mixture was stirred for 2 h. Finally, to the mixture was added dioctylamine (0.15 mL) and stirred for 13 h. The mixture was then poured into a large amount of Et_2O. The obtained precipitate was washed with Et_2O and THF for several times to remove the unreacted dioctylamine, followed by washing with water to remove inorganic salts. After drying the polymer under reduced pressure, an orange powder was obtained.

Yield: 57%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.8 (br s, –Me), 1.0–2.0 (br m, $-(CH_2)_2-$), 2.7–3.8 (br m, bridged $-(CH_2)_2-$ of [2.2]paracyclophane and $N-CH_2-$), 5.9 (m, C=C–H), 6.2–7.0 (br, Ar–H of [2.2]cyclophane and dibenzofulvene ring). IR (KBr): 1610, 1505, 1495, 1195.

2-Ethynyl-*p*-xylene **3**

2-Ethynyl-*p*-xylene **3** was synthesized by the standard Sonogashira coupling reaction and deprotection. 2-Bromo-*p*-xylene (2.6 g, 14.3 mmol), trimethylsilylacetylene (14.3 mL), $PdCl_2(PPh_3)_2$ (0.67 g, 0.96 mmol), PPh_3 (0.74 g 2.86 mmol), CuI (0.29 g, 1.43 mmol) were dissolved in THF (27 mL) and NEt_3 (18 mL). The reaction mixture was stirred at 75 °C for 19 h under Ar. Precipitated ammonium salts were filtered, and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography on SiO_2 with hexane to obtain 2-trimethylsilylethynyl-*p*-xylene as a white solid (1.9 g, 9.6 mmol, 67%). To a solution of 2-trimethylsilylethynyl-*p*-xylene (1.9 g, 9.6 mmol) in THF (35 mL) was added Bu_4NF (10 ml, 1.0 M in THF). The reaction mixture was stirred at room temperature overnight under Ar. The solution was evaporated under reduced pressure, and the residue was purified by HPLC to afford **3** as a white solid (0.82 g, 6.3 mmol, 66%). The analysis data agree with the literature's values [63].

Model compound **4**

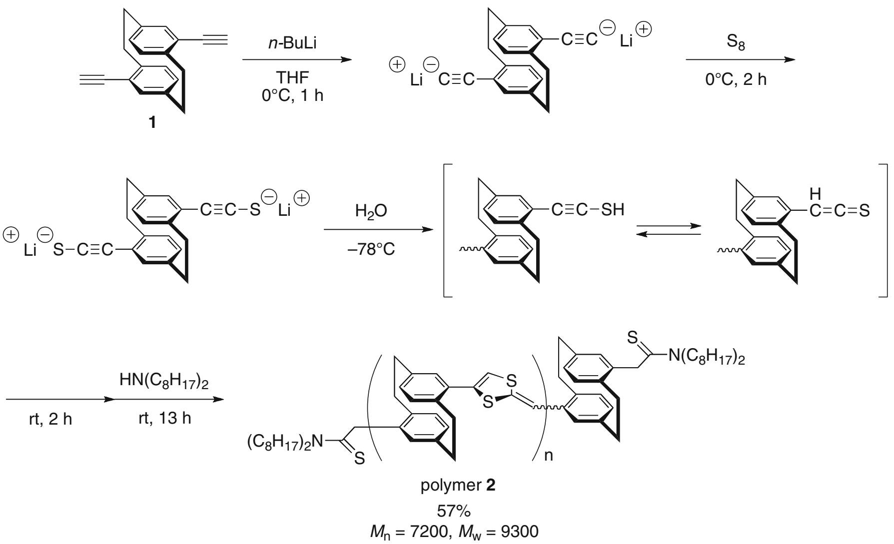
To a solution of 2-ethynyl-*p*-xylene **3** (0.13 g, 1.0 mmol) in Et_2O (2.0 mL), *n*-BuLi in hexane (1.6 M, 1.0 mL, 1.6 mmol) was added at 0 °C. After stirring for 1.5 h, the powder of S_8 (50 mg, 1.1 mmol) was added to the solution. The reaction mixture was stirred for 2 h, and cooled to −78 °C. Water (30 µL) was carefully added. The mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was extracted with Et_2O, followed by washing with saturated NaCl aq. The organic layer was dried over Na_2SO_4, and then, the solvent was dried in vacuo. The residue was subjected to column chromatography on SiO_2 with hexane to afford **4** as a yellow solid.

Yield: 29%. $R_f = 0.68$ (SiO_2, hexane/CH_2Cl_2, v/v = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (m, 12H, –CH_3), 5.91 (s, 0.45H, (*E*)-C = C–H), 6.02 (s, 0.55H, (*Z*)-C = C–H), 6.51 (s, 0.55H, (*Z*)-dithiafulvene ring proton), 6.54 (s, 0.45H, (*E*)-dibenzofulvene ring proton), 6.86–7.24 (m, 6H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.51, 19.54, 19.83, 19.89, 20.69, 20.71, 21.10, 21.12, 110.58, 110.05, 113.61, 113.63, 125.98, 126.06, 126.72, 126.79, 129.45, 129.48, 129.98, 130.03, 130.29, 130.39, 130.56, 130.61, 131.70, 131.75, 131.87, 132.13, 132.66, 132.99, 133.46, 133.61, 135.17, 135.20, 135.45, 135.48, 135.71, 135.76, 136.75, 137.09. HRMS (EI): m/z calcd for $C_{20}H_{20}S_2$ (M^+): 324.1006. Found: 324.1002. Anal. calcd for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21; S, 19.76. Found: C, 73.67; H, 6.18; S, 19.78.

Results and discussion

4,16-Diethynyl[2.2]paracyclophane **1** can be easily prepared from commercially available [2.2]paracyclophane [47]. Scheme 1 outlines the synthetic procedure of the target polymer **2**. Treatment of **1** with *n*-BuLi and sulfur S_8 at 0 °C in succession afforded diethynethiolate, which was reacted with a small amount of H_2O at −78 °C to produce diethynethiol. Thioketene was formed by tautomerization in situ and reacted with ethynethiol to obtain the polymer containing dithiafulvene units. Finally, octylamine was added to quench the polymerization and to improve the solubility of the polymer. After purification of the crude polymer by washing with Et_2O, THF, and H_2O, polymer **2** was obtained in 57% isolated yield. The molecular weights of the polymers were measured by GPC (eluent: DMF) and calculated by using polystyrene standards. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) were $M_n = 7{,}200$ and $M_w = 9{,}300$, respectively. Polymer **2** could be dissolved in aprotic solvents such as DMSO and DMF. A thin film of **2** could be readily obtained by a casting or spin-coating method.

The structure of polymer **2** was confirmed by ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum of **2** in DMSO-d_6 (400 MHz) is shown in Fig. 1. Signals at 0.8 and



Scheme 1 Synthesis of polymer **2**

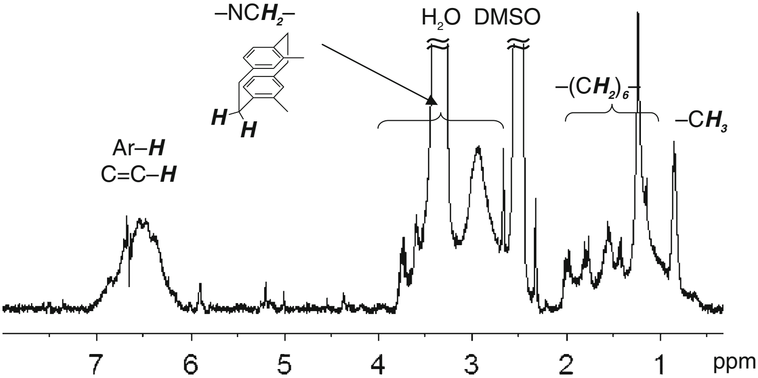


Fig. 1 ^{1}H NMR spectrum of polymer **2** in DMSO-d_6

1.0–2.0 ppm were assigned to –Me and –$(CH_2)_6$– in the alkyl chains of the end-capped dioctylamine moieties, respectively. The signals of –NCH_2– groups overlapped with those of DMSO and bridged methylenes of [2.2]paracyclophane. Peaks of the bridged methylene protons of the [2.2]paracyclophane units were observed at around 2.7–3.8 ppm as broad signals, which overlapped with those of H_2O and DMSO. The benzylidene protons were observed at around 5.9 ppm, which are considered to be a mixture of (*E*)- and (*Z*)-isomers. Signals of the aromatic protons in the [2.2]paracyclophane moieties appeared at 6.2–7.0 ppm due to the ring current effect, which overlapped with the signals of ring protons in the dithiafulvene moieties.

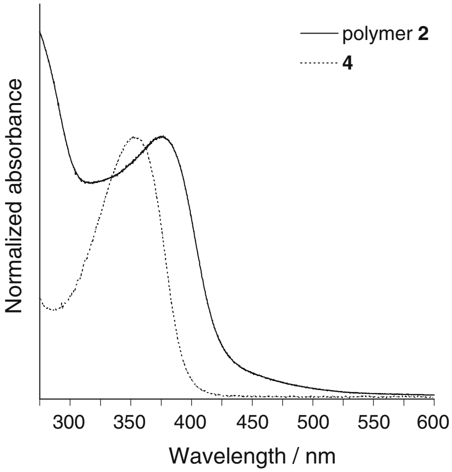


Fig. 2 UV–vis absorption spectra of polymer **2** and compound **4** in DMSO (1.0×10^{-5} M)

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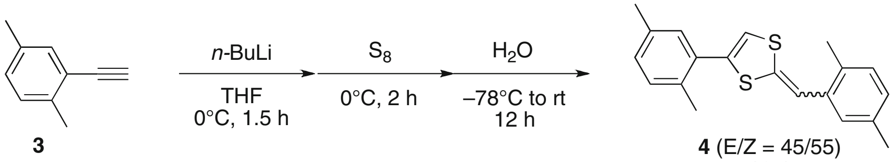


4 (E/Z = 45/55)
13%

Scheme 2 Synthesis of model compound **4**

Figure 2 shows a comparison between the UV–vis absorption spectra of polymer **2** and model compound **4** (*E/Z* = 45/55), which was prepared by dimerization of aldothioketene derived from 2-ethynyl-*p*-xylene **3** (Scheme 2). The absorption maximum of polymer **2** in DMSO was observed at 378 nm. This maximum was attributed to the π–π* transition of the conjugated polymer backbone. The absorption maximum of model compound **4** was observed at 352 nm. The through-space interaction of co-facial benzene rings in the [2.2]paracyclophane moiety resulted in the extension of the π-conjugation length throughout the polymer chain. On the other hand, the absorption maximum of the through-bond conjugated polymer **5** in CH_3CN appears at 398 nm [59, 60]. The through-bond conjugation is more effective for the extension of π-conjugation than the through-space conjugations [40, 41].

The electrochemical behavior of polymer **2** was investigated by CV. The CV measurement of a cast film of **2** was performed in dry CH_3CN with 0.1 M NEt_4BF_4 at room temperature and a scan rate of 100 mV s^{-1}. The cyclic voltammogram is shown in Fig. 3. Polymer **2** exhibited a single broad irreversible oxidation peak at around 0.63 V (vs. Ag/Ag^+). In the previous study, it was found that polymer **5** exhibited an irreversible oxidation peak at 0.61 V (vs. Ag/Ag^+) [60]. The π-stacked structure of **2** did not affect the redox behavior of the dithiafulvene unit [47]; hence, the difference in the peak potential of the dithiafulvene unit between **2** and **5** was small. This result indicates that extension of π-conjugation length of **2** via the through-space interaction would be similar to that of **5** via the through-bond interaction [60].

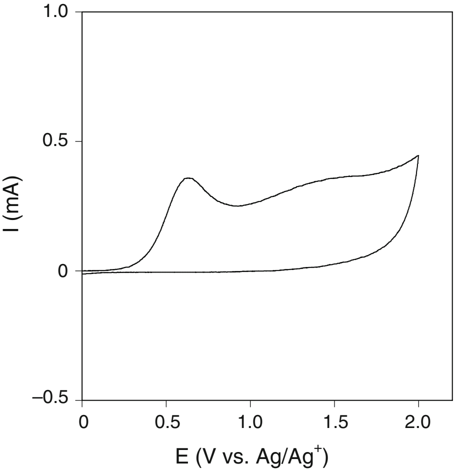
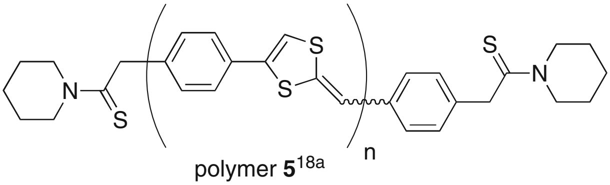


Fig. 3 Cyclic votammogram of the cast film of polymer **2** in CH_3CN



polymer **5**[18a]
$M_n = 5440$

A charge transfer (CT) complex formation of polymer **2** with TCNQ was examined. It is known that both the dithiafulvene unit [61] and the [2.2]paracyclophane unit [64] form the CT complex. Figure 4 shows the dependence of the UV spectrum of **2** on the TCNQ feed ratio against the [2.2]paracyclophane unit in DMSO. Absorption peaks observed in the range of 600–1,000 nm were derived from the anion radical of TCNQ by CT complexation. Absorbance due to CT complexation with TCNQ increased with the addition of TCNQ. The absorbance in the range of 600–1,000 nm was saturated when the feed ratio, [TCNQ]/[repeating unit], was 2.0. A further increase in the feed ratio of TCNQ did not affect the absorption of the anion radical of TCNQ. The peak intensity ratio of the 400 and 600–1,000 nm band is reported to be approximately 0.50 in the case of simple TCNQ salts [65, 66]. In the present system, the intensity ratio was approximately 0.65 at [TCNQ]/[repeating unit] = 2.0, which implies a formation of TCNQ complex with dithiafulvene as well as [2.2]paracyclophane units in the repeating unit. The absorption peak at around 400 nm increased, and it was almost saturated at [TCNQ]/[repeating unit] = 3.5–4.0. It is considered that excess TCNQ interacts with the conjugated polymer chain.

A thin film of polymer **2** was fabricated by casting from a DMF solution, which had an electrical conductivity of 1×10^{-6} S cm^{-1}. Excess TCNQ on the basis of the repeating unit was added to the solution of **2** to form the CT complex, as mentioned above; after filtration of the remaining TCNQ, a dark green solution was

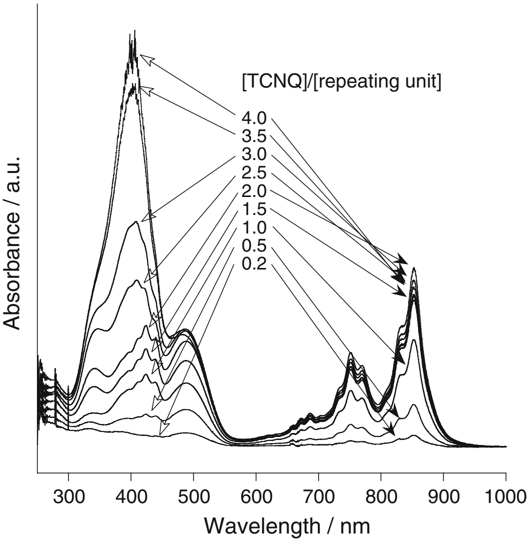


Fig. 4 UV–vis absorption spectra of CT complexes of polymer **2** with TCNQ in DMSO (repeating unit = 1.8×10^{-4} M)

dried on ITO to form the thin film of the CT complex. This thin film had an electrical conductivity of 2×10^{-5} S cm^{-1}, which was higher than that of the undoped polymer thin film. The polymer was doped with an organic acceptor such as TCNQ by the formation of the CT complex [61]. On the other hand, the electrical conductivity measurement of polymer **2** by doping with I_2 vapor was carried out. The oxidized polymer thin film exhibited a conductivity of 3×10^{-6} S cm^{-1} (exposure time: 2 h), 7×10^{-4} S cm^{-1} (exposure time: 24 h), and 2×10^{-3} S cm^{-1} (exposure time: 30 h), which was saturated for an exposure time of 30 h (2×10^{-3} S cm^{-1}, exposure time: 48 h). This value was higher than that obtained by using TCNQ. In addition, the both values of the undoped and doped through-space conjugated polymer **2** were slightly higher than those of the through-bond conjugated polymer **5** we reported previously [60]. Further careful investigations about that enhancement of the conductivity arises from the effect of the π-stacked structure of the through-space conjugated polymer chain are currently in progress.

Conclusion

The cycloaddition polymerization of aldothioketene could be applied to the cyclophane monomer, 4,16-diethynyl[2.2]paracyclophane, to obtain the corresponding through-space conjugated polymer consisting of alternate dithiafulvene and [2.2]paracyclophane units in the main chain. The polymers exhibited an extension of the conjugation length via the through-space interaction of the [2.2]paracyclophane unit. The polymer formed a CT complex with two equivalents of TCNQ based on the repeating unit. A thin film of the through-space conjugated polymer exhibited electrical conductivities of 2×10^{-5} and 2×10^{-3} S cm^{-1} by doping with TCNQ and I_2, respectively, which were higher than those of the through-bond conjugated analogue.

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