[2.2]Paracyclophane-Based Through-Space Conjugated Polymers with Fluorescence Quenchers

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ABSTRACT: New [2.2]paracyclophane-based through-space conjugated polymers containing fluorescence quenchers such as anthraquinone and ferrocene units at the polymer termini were designed and synthesized. Their optical properties were investigated in detail. Fluorescence emission from the stacked π -electron systems was effectively quenched by the stacked π -electron systems at the polymer termini due to the energy

and electron transfer through a single polymer chain; thus, the polymers acted as the molecular wire. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 51: 334–339, 2013

KEYWORDS: conjugated polymers; copolymerization; fluorescence; molecular wire; [2.2]paracyclophane

INTRODUCTION Since the discovery of conductive polyacetylenes three decades ago,¹⁻³ there has been considerable interest in the design and synthesis of new conjugated polymers. Further, various π -electron systems such as poly(*p*-arylene-ethynylene),^{4,5} poly(*p*-arylenevinylene),^{6,7} and poly(*p*-arylene)^{8,9} have been synthesized.^{10–12} Although most of such polymers comprise a through-bond conjugation system composed of sp or sp² carbon frameworks, there are very few studies on through-space conjugated polymers with stacked π -electron systems.

Introduction of a π -stacked structure into the conjugated polymer backbone would allow for effective energy and charge transfer in a single polymer chain. As a representative example, Nakano et al. reported the synthesis of poly(dibenzofulvene)s consisting of π -stacked fluorene rings^{13–15} that showed higher hole mobility than the through-bond conjugated polymers.¹⁵ Recently, we have focused on the π -stacked structure of [2.2]paracyclophane¹⁶⁻¹⁸ and synthesized through-space conjugated polymers by incorporating [2.2] paracyclophane, which has a π -stacked structure, into the conjugated polymer backbone.¹⁹⁻²⁹ Because of throughspace conjugation, the conjugation length of the resulting polymers increased with an increase in the number of stacked π -electron systems.²⁴ In addition, end-capping of the through-space conjugated polymers by anthracene-containing π -electron systems allowed for fluorescence resonance energy transfer from the stacked π -electron systems to the end-capping π -electron systems, because of the efficient overlap between the emission of the layered π -electron systems and the absorption of the end-capping anthracene moiety.²⁴ In this article, we report the synthesis and properties of [2.2]paracyclophane-based through-space conjugated polymers with fluorescence quenchers at the polymer termini; they are responsible for photo-excited energy transfer from the staked π -electron systems to the stacked terminal units. These polymers give rise to a new class of single molecular wires comprising stacked π -electron systems, in which energy and/or charge transfer occurs via through-space interactions among the stacked π -electron systems.

EXPERIMENTAL

General

¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz, respectively. The chemical shift values were expressed relative to Me₄Si as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Analytical thin-layer chromatography was performed with silica gel 60 Merck F₂₅₄ plates. Column chromatography was performed with Wakogel C-300 silica gel. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using CHCl₃ as an eluent after calibration with standard polystyrene samples. Recyclable preparative high-performance liquid chromatography was performed on a Japan Analytical Industry LC-9204 (JAIGEL-2.5H and 3H columns) using CHCl₃ as an eluent. UV-vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer. Photoluminescence spectra were

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SCHEME 1 Synthesis of polymers P1-P3.

obtained on a Horiba FluoroMax-4 luminescence spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

Tetrahydrofuran (THF) and Et₃N were purchased and purified by passage through purification column under Ar pressure.³⁰ Pd(PPh₃)₄, CuI, ethynylferrocene (**3**), and 2,5-dimethylphenylacetylene (**5**) were obtained commercially, and used without further purification. Pseudo-*p*-diethynyl[2.2]paracyclophane (**1**),³¹ 1,4-diiodo-2,5-didodecyloxybenzene (**2**),^{32,33} 1-ethynylanthraquinone (**4**),³⁴ and 1,4-bis(2,5-dimethylphenylethynyl)-2,5-didodecyloxybenzene (**7**)³⁵ were prepared as described in the literature. All reactions were performed under Ar atmosphere.

Polymerization

Compounds **1** (0.026 g, 0.10 mmol), **2** (0.077 g, 0.11 mmol), Pd(PPh₃)₄ (0.012 g, 0.010 mmol), and CuI (2.3 mg, 0.020 mmol) were placed in a Schlenk flask equipped with a magnetic stirrer bar and a reflux condenser. The equipment was purged with Ar, and THF (4.0 mL) and NEt₃ (2.0 mL) were added. The polymerization was carried out at reflux temperature. After 11 h, mono-acetylenes **3–5** (0.10 mmol) were added to the reaction mixture, and it was stirred overnight. After cooling, the reaction mixture was diluted with CHCl₃, and washed with 0.1 N HCl, 28% aqueous NH₃, water, and brine. The organic layer was dried over MgSO₄. The solvent was concentrated *in vacuo*, and the residue was reprecipitated with MeOH to obtain polymers **P1–P3**.

Polymer **P1**: ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, J = 6.8 Hz), 1.27 (br), 1.59 (br), 1.97 (m), 2.94 (br), 3.05 (br), 3.35 (br), 3.82 (br), 4.08 (m), 4.14 (br), 4.28 (s), 4.54 (s), 6.54 (m), 6.65 (m), 7.0–7.2 (m) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 14.1, 22.7, 26.3, 29.5 (m), 31.9, 34.1, 68.9, 69.4, 70.0, 71.5, 89.6, 95.2, 114.0, 116.1, 116.2, 124.9, 133.3, 137.2, 139.6, 142.2, 153.6 ppm.

Polymer **P2**: ¹H NMR (CDCl₃, 400 MHz): δ 0.89 (s), 1.26 (br), 1.41 (br), 1.61 (br), 1.97 (br), 2.94 (br), 3.05 (br), 3.35 (br), 3.82 (br), 4.14 (br), 6.54 (m), 6.65 (s), 7.09 (m), 7.7–7.9 (m), 8.02 (m), 8.34 (m) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 14.5, 23.1, 26.6, 30 (m), 32.3, 34.4 (m), 69.8, 89.9, 95.5, 114.3, 116.6, 125.2, 133.5, 137.5, 139.9, 142.5, 153.9 ppm.

Polymer **P3**: ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, J = 6.4 Hz), 1.26 (br), 1.59 (br), 1.87 (m), 1.96 (br), 2.33 (s), 3.05 (s), 2.94 (br), 3.05 (br), 3.35 (br), 3.82 (br), 4.14 (m), 6.53 (m), 6.65 (br), 7.05–7.15 (m), 7.36 (br) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 14.1, 20.3, 20.8, 22.7, 26.2, 26.3, 29.5 (m), 32.0, 33.8, 34.1, 69.4, 69.5, 89.6, 91.3, 95.2, 114.0, 116.2, 116.6, 123.1, 125.0, 129.3, 130.6, 132.3, 133.3, 135.0, 137.2, 139.6, 142.3, 153.5, 153.6 ppm.

Synthesis of Compound 6

1-Bromo-4-(2,5-dimethylphenylethynyl)-2,5-didodecyloxybenzene (0.14 g, 0.20 mmol),²⁴ ethynylferrocene (3) (0.063 g, 0.30 mmol), PdCl₂(PPh₃)₂ (4.2 mg, 0.006 mmol), and CuI (2.2 mg, 0.012 mmol) were placed in a 50-mL Pyrex flask equipped with a magnetic stirrer bar and a reflux condenser. The equipment was purged with Ar, followed by adding THF (30 mL) and NEt₃ (15 mL). The reaction was carried out at 50°C for 24 h. After cooling, the reaction mixture was concentrated in vacuo to afford the crude product, which was purified by silica gel column chromatography (hexane/CHCl₃, vol/vol = 4/1 as an eluent) to afford **6** as an orange solid (19 mg, 0.024 mmol, 12%). $R_{\rm f} = 0.15$ (hexane/CHCl₃, vol/ vol = 3/1). ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, I = 6.4 Hz, 6H), 1.2-1.6 (br m, 36H), 1.85 (m, J = 7.2 Hz, 4H), 2.31 (s, 3H), 2.50 (s, 3H), 4.01 (q, J = 7.2 Hz, 4H), 4.24 (d, J = 2.0Hz, 2H), 4.26 (s, 5H), 4.51 (d, J = 2.0 Hz, 2H), 6.95 (s, 1H), 6.98 (s, 1H), 7.03 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.33 (s, 1H); 13 C NMR (CDCl₃, 100 MHz): δ 14.1, 20.2, 20.7, 22.7, 26.10, 26.15, 29.5 (m), 31.9, 68.8, 69.5, 70.0, 71.4, 89.6, 93.7, 93.9, 116.4, 116.9, 129.1, 129.3, 132.2, 134.9, 137.1, 153.4, 153.6. HRMS (ESI) calcd for C₅₂H₇₀FeO₂, 782.4720; found 782.4692 [M]⁺. Anal. calcd for C₅₂H₇₀FeO₂: C 79.77 H 9.01, found: C 79.49 H 8.95.

 ^{1}H and ^{13}C NMR spectra of **P1-P3** and **6** are shown in Supporting Information Figures S1–S8.

RESULTS AND DISCUSSION

As shown in Scheme 1, Sonogashira–Hagihara coupling^{36,37} of pseudo-*p*-diethynyl[2.2]paracyclophane (1) with





TABLE 1 Results of Polymerization

^a Calculated by the ¹H NMR integral ratio.

^b Estimated by GPC (eluent: CHCl₃, polystyrene standards).

1,4-diiodo-2,5-didodecyloxybenzene (2) in the presence of a catalytic amount of $Pd(PPh_3)_4/CuI$ was carried out. The polymerization was monitored by GPC. After reflux for 11 h, monoalkynes were added, and the reaction mixture was stirred overnight to yield [2.2]paracyclophane-based through-space conjugated polymers **P1–P3**. Ferrocene and anthraquinone were employed as end-capping fluorescence quenchers for polymers **P1** and **P2**, respectively. Polymer **P3** containing xylene at the polymer chain ends was also prepared as the reference polymer. When the molar ratio of monomers **1** and **2** was 10:11 (Table 1), the number-average molecular weights (M_n) of polymers **P1**, **P2**, and **P3** were found to be 5500, 7800, and 5400, respectively, according to the ¹H NMR integral ratio (*vide infra*).

Polymers **P1–P3** were readily soluble in common organic solvents such as CH_2Cl_2 , $CHCl_3$, THF, and toluene and hence could be characterized by ¹H and ¹³C NMR spectroscopy in CDCl₃ solution. The ¹H NMR spectrum of **P1** is shown in Figure 1. The signal positions for various groups of protons were as follows: dodecyl protons, 0.9–2.0 ppm; methylene unit ($-OCH_2-$) in the dodecyloxy group, 4.2 ppm; cyclo-





phane bridge methylene protons, 2.9–3.9 ppm; cyclophane and phenylene protons, 6.5–7.2 ppm; ferrocene protons, 4.3 and 4.5 ppm. The M_n value (5500) of **P1**, calculated from the ¹H NMR integral ratio between the ferrocene and cyclophane bridge methylene protons, indicated that an average of six π -electron systems (xylyl–ethynyl–phenylene–ethynyl–xylyl units) were stacked in the primary chain and two ferrocenecontaining π -electron systems (xylyl–ethynyl–phenylene– ethynyl–ferrocenyl units) were stacked at the chain ends.

Optical properties of the through-space conjugated polymers were investigated to identify the potential applications of these polymers as single molecular wires. Figure 2(A) shows the UV-vis absorption spectra of **P1** and **P3** in dilute CHCl₃ solution (1.0×10^{-5} M). The absorption spectrum of **P3** exhibited typical π - π * absorption bands corresponding to the arylene-ethynylene moieties at around 315 and 385 nm. On the other hand, the spectrum of **P1** exhibited broad absorption bands attributable to the metal-to-ligand charge



FIGURE 2 A UV-vis absorption spectra of **P1** and **P3** in CHCl₃ (1.0 \times 10⁻⁵ M/repeating unit), and (B) fluorescence emission spectra of **P1** and **P3** in CHCl₃ (1.0 \times 10⁻⁵ M/repeating unit) excited at 385 nm.

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CHART 1 Structures of compounds 6 and 7

transfer (MLCT) band in the ferrocene-containing π -electron systems at around 450 nm, in addition to the π - π^* absorption peaks. The absorption spectrum of model compound **6** (Chart 1), which corresponds to the ferrocene-containing π -electron system, supported the fact that the broad band was due to the ferrocene unit (Fig. 3).

Fluorescence emission spectra of P1 and P3 in diluted CHCl₂ solution (1.0 \times 10 $^{-5}$ M) are shown in Figure 2(B). It was confirmed that this concentration (1.0 \times 10 $^{-5}$ M) was so low (Supporting Information Fig. S11) that intermolecular interactions were negligible. Both polymers P1 and P3 were excited at 385 nm, and they exhibited almost identical fluorescence spectra with peak maxima at around 415 nm, which was assigned to emission from the stacked π -electron systems, on the basis of the emission spectrum of model compound 7 (Chart 1 and Fig. 3). However, the emission from P1 was guenched, and the peak intensity (relative fluorescence quantum efficiency: $\Phi_{FL} = 0.15$) was significantly lower than that of P3 ($\Phi_{\rm FL}$ = 0.82). Incidentally, emission from P2 was also quenched by the anthraquinone-containing π -electron system at the polymer termini ($\Phi_{\rm FL}=$ 0.26), as shown in Supporting Information Figure S9; UV-vis absorption and fluorescence emission spectra of P2 are shown in Supporting Information Figure S12.

On the other hand, no emission peak from compound **6** (CHCl₃ solution, excitation wavelength: 315 nm) was detected (Fig. 3), because of MLCT from the iron moiety [highest occupied molecular orbital (HOMO) level: approximately -4.9 eV, estimated by cyclic voltammetry (CV) vs. ferrocene/ferrocenium in Supporting Information Fig. S16(A)] to the aryleneethynylene moiety [HOMO level: approximately -5.6 eV, estimated by CV vs. ferrocene/ferrocenium in Supporting Information Fig. S16(A)] to the aryleneethynylene moiety [HOMO level: approximately -5.6 eV, estimated by CV vs. ferrocene/ferrocenium in Supporting Information Fig. S16(B)]. In **P1**, effective intramolecular energy transfer from the stacked π -electron systems to the terminal π -electron systems and MLCT occurred via through-space interactions; the energy transfer could be explained by the effective overlap between the emission spectrum of **7** ($\Phi_{FL} =$ 0.86) and the MLCT band of **6** (Fig. 3).



FIGURE 3 A UV-vis absorption spectra of **6** and **7** in CHCl₃ (1.0 \times 10⁻⁵ M), and (B) fluorescence emission spectra of **6** and **7** in CHCl₃ (1.0 \times 10⁻⁵ M) excited at 365 nm for **6** and 370 nm for **7**.

Polymer P1 ($M_n = 5800$, $M_w/M_n = 2.0$) was separated into two fractions, polymer **P1a** ($M_n = 3700$, $M_w/M_n = 1.2$) and **P1b** ($M_n = 11400$, $M_w/M_n = 1.5$), by size-exclusion column chromatography. The fluorescence emission spectra of P1, **P1a**, and **P1b** in dilute CHCl₃ solution (1.0 \times 10⁻⁵ M) are shown in Figure 4(A). The shorter the chain length, the greater was the effectiveness of emission quenching, because the quencher concentration of P1a was relatively higher than that of P1 and P1b. The emission spectra of P3 with compound **6** as an additional quencher are shown in Figure 4(B). To the solution of P3, different concentration of 6-0.25, 1, 10, and 100 equiv (/repeating unit)-were added. As expected, the two end-capping ferrocene moieties in P1 effectively quenched the emission from the stacked π -electron systems via through-space interactions. The Stern-Volmer plots of P1 and P3 with additional quenchers are shown in Supporting Information Figure S17. The Stern-Volmer coefficient (K_{sv}) of **P1** was 7.6 \times 10⁶, which was approximately 100 times larger than that of P3 containing

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FIGURE 4 A Fluorescence emission spectra of **P3**, **P1**, **P1a**, and **P1b** in CHCl₃ (1.0 × 10⁻⁵ M/repeating unit) excited at 385 nm, and (B) fluorescence emission spectra of **P3** (1.0 × 10⁻⁵ M/repeating unit in CHCl₃) with 0.25, 1, 10, and 100 equivalents (0.25 × 10⁻⁵, 1.0 × 10⁻⁵, 1.0 × 10⁻⁴, and 1.0 × 10⁻³ M in CHCl₃) of **6** excited at 385 nm.

quencher **6** ($K_{\rm sv} = 5.8 \times 10^4$). A significant polymer concentration effect was observed by the incorporation of ferrocene moieties at the chain ends; thus, effective energy transfer and MLCT occurred from the stacked π -electron systems to the terminal π -electron systems in the through-space conjugated polymer.

In summary, [2.2]paracyclophane-based through-space conjugated polymers containing fluorescence quenchers were synthesized. Fluorescence emission from the stacked π -electron systems was effectively quenched by the stacked π -electron systems at the polymer termini. Our synthesis method allowed for the introduction of various aromatic groups into the polymer chains. Energy and charge transfer along the polymer chain could be controlled by tuning the energy bandgaps and levels of the stacked π -electron systems; hence, this class of polymers can be used as single molecular wires, in which energy and/or charge transfer would occur via through-space interactions among the stacked π -electron systems. Since an electron transfer including MLCT is an important process for the light-induced reduction of proton and/or organic molecules, construction of a photocatalyst system through the electron transfer in the [2.2]paracyclo-phane-based polymers is the next target.

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