Synthesis and optical properties of the [2.2]paracyclophane-containing \(\pi\)-conjugated polymer with a diacetylene unit

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Summary

Novel through-space \(\pi\)-conjugated polymer based on poly(p-phenylene-ethynylene)/poly(p-phenylenebutadiynylene) hybrids containing a [2.2]paracyclophane unit in the main chain was synthesized by copper-catalyzed alkyne coupling reaction. The structure of the polymer was supported by \(^1\)H NMR and IR spectra. The obtained polymer was soluble in common organic solvents such as THF, \(\mathrm{CH}_2\mathrm{Cl}_2\), \(\mathrm{CHCl}_3\) and toluene. The number-average of molecular weight of the polymer was estimated to be 63000 by GPC. The polymer emitted a bluish green light in solution and in the solid state.

Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel \(\pi\)-conjugated polymers [1], because of their unique properties such as electrical conductivity [2], electroluminescence [3], liquid crystallinity [4], third-order nonlinear optical properties [5], and chemical sensing [6]. During the last decade, ever since the first demonstration of a light-emitting diode (LED) based on poly(p-phenylenevinylene) (PPV) in 1990 [7], a number of \(\pi\)-conjugated polymers with efficient luminescence have been synthesized, and are being applied to photoluminescence (PL) and/or electroluminescence (EL) materials. Current research interest in conjugated polymers has focused on the tuning of their spectral and electrical properties. The extended strategy toward the appropriate design of \(\pi\)-conjugated polymers involves varying the arylene building block and the strategy to bind arylene units, i.e., binding directly (\(-\mathrm{Ar}\cdots\mathrm{Ar}\)), with a carbon-carbon double bond (\(-\mathrm{Ar}\cdots\mathrm{C}\cdots\mathrm{C}\cdots\mathrm{Ar}\)), with a triple bond (\(-\mathrm{Ar}\cdots\mathrm{C}=\mathrm{C}\cdots\mathrm{Ar}\)), and so on. While polyarylenes, poly(arylenevinylene)s, and poly(arylene-ethynylene)s have played increasingly important roles as organic semiconductors, a few attempts have been made to synthesize the polymers which have a diacetylene moiety (\(-\mathrm{Ar}\cdots\mathrm{C}=\mathrm{C}=\mathrm{C}\cdots\mathrm{Ar}\)) in the polymer backbone [8].

On the other hand, [2.2]paracyclophane is a very attractive molecule, because the two
benzene rings face close together. A number of [2.2]paracyclophane derivatives have been prepared to date, and their physical properties have been investigated in detail, due to their characteristic interactions between the two co-facial \(\pi\)-electron systems [9]. In addition, several non-conjugated polymers, which have a paracyclophane skeleton in the main chain [10] or in the side chain [11], have been synthesized. However, few \(\pi\)-conjugated polymers using the longitudinal \(\pi\)-\(\pi\) interactions of cyclophane as a repeating unit have been reported so far [12-13]. In 1985, Mizogami and Yoshimura reported the first synthesis of polymetacyclophane achieved by a polycondensation reaction using an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane, which exhibited a conductivity of 0.25 S cm\(^{-1}\) by doping with H\(_2\)SO\(_4\) vapor [14]. Recently, we reported the synthesis and physical properties of the first well-defined [2.2]paracyclophane-containing \(\pi\)-conjugated polymers based on poly(\(\pi\)-phenylene-ethynylene)s (PPEs) and PPVs. In these studies, we demonstrated that the polymers obtained were capable of extended \(\pi\)-delocalization, via the through-space, with a \(\pi\)-\(\pi\) stacking of a [2.2]paracyclophane moiety [13a, 13b]. In the present study, we report the synthesis and optical properties of the [2.2]paracyclophane-containing \(\pi\)-conjugated polymer having a diacetylene unit, with the aim of controlling the optical properties.

**Experimental**

**General**

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. Samples were analyzed in CDCl\(_3\), and the chemical shift values were expressed relative to Me\(_4\)Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl\(_3\) at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in CHCl\(_3\) at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using chloroform as an eluent after calibration with standard polystyrene.

**Materials**

THF was distilled from sodium benzophenone ketyl under nitrogen. Et\(_3\)N and N,N,N',N'-tetramethylethylenediamine (TMEDA) were distilled from KOH. Chlorobenzene and CHCl\(_3\) were distilled from CaCl\(_2\). PPh\(_3\), PdCl\(_2\)(PPh\(_3\))\(_2\), CuI, CuCl, [2.2]paracyclophane (I), trimethylsilylacetylene, Bu\(^n\)\(_4\)NF (1.0 M solution in THF) were obtained commercially, and used without further purification. 4,16-Dibromo[2.2]paracyclophane (2) [15] and 2,5-didodecyloxy-1,4-diiodobenzene (5) [16] were prepared as described in the literature. All new compounds are characterized below.

4,16-Bis[(trimethylsilyl)ethynyl][2.2]paracyclophane (3).

4,16-Dibromo[2.2]-paracyclophane (2) (3.5 g, 9.7 mmol), trimethylsilylacetylene (10 mL), PdCl\(_2\)(PPh\(_3\))\(_2\) (0.70 g, 1.0 mmol), PPh\(_3\) (0.52 g, 2.0 mmol), and CuI (0.20 g, 1.0 mmol) were