Synthesis of Novel Alternating π-Conjugated Copolymers Having [2.2]Paracyclophane and Fluorene Units in the Main Chain Leading to the Blue Light-Emitting Materials

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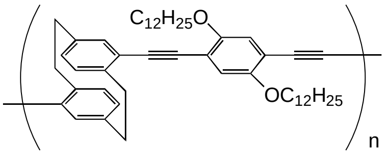
Novel through-space π-conjugated polymers having [2.2]paracyclophane and fluorene units were synthesized by Heck-Sonogashira coupling reaction. The polymers exhibited strong blue fluorescence in solution and in the solid state.

[2.2]Paracyclophane, in which two benzene rings are close to each other and facing, attracts attention to the structure, reactivity, and physical properties.[1] A number of paracyclophane derivatives have been prepared, and their physical properties, especially optical and electronic properties due to the characteristic interactions between the two co-facial π-electron systems, have been investigated.[2] In addition, several non-conjugated polymers having a [2.2]paracyclophane skeleton in the main chain (in the course of developing new processes for crosslinking resins)[3] or in the side chain[4] have been prepared so far. In 1986, Mizogami and a coworker reported the first synthesis of polymetacyclophane, which exhibited a conductivity of $0.25\,\mathrm{S\,cm^{-1}}$ by doping with a H_2SO_4 vapor.[5] However, no π-conjugated polymers using the longitudinal π-π interaction of paracyclophane as a repeating unit have yet been reported, except in our recent study, in which we found that the polymer **1** showed the extension of π-delocalization via the through-space with π-π stacking of [2.2]paracyclophane.[6]



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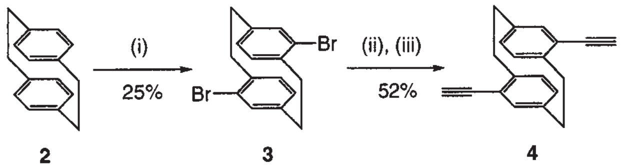
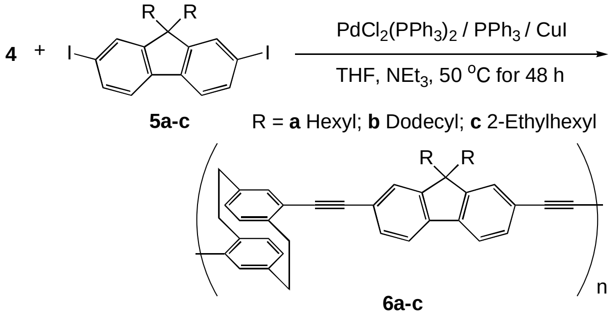
The synthesis of novel π-conjugated polymers has received extensive attention due to their unique optical, electrochemical, and non-linear optical properties.[7] Recent research activity in particular has focused significant interest on the photoluminescence (PL) and electroluminescence (EL) from the first demonstration of the polymer-based light–emitting diode (LED) in 1990.[8] Polyfluorenes have become more important in recent years due to their efficient blue PL and EL properties.[9,10] In the present study, we prepared the novel π-conjugated polymers based on poly(p-phenylene-ethynylene) derivatives having [2.2]paracyclophane and fluorene units in the main chain, and found that the polymers showed strong blue fluorescence in solution and in the solid state.

Monomer **4** was synthesized according to the reaction sequence outlined in Scheme 1, and 2,7-diiodofluorenes **5a-c** were synthesized by diiodination of fluorene and phase transfer alkylation in good yields.[11] The polymers **6a-c** were synthesized by Heck-Sonogashira reaction,[12] as shown in Scheme 2. The polymerization of **4** with **5a-c** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$/PPh_3/CuI in THF-NEt_3 at 50 °C for 48 h under a nitrogen atmosphere proceeded smoothly to give the corresponding polymers **6a-c** in good isolated yields (Table 1). The structure of the polymer was confirmed by ^1H and ^{13}C NMR spectra.[13] All polymers were soluble in common solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene.



Reagents: (i) Br_2, Fe, CH_2Cl_2, CCl_4, reflux for 5 h. (ii) Trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, PPh_3, CuI, THF, NEt_3, reflux for 48 h. (iii) $Bu^n{}_4NF$, THF, r.t. for 20 h.

Scheme 1.



Scheme 2.

The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent $CHCl_3$ using the calibration curve of polystyrene standards, as summarized in Table 1. For example, the polymer **6b** (R = n-dodecyl) had the number average molecular weight (M_n) of 26400, which corresponds to a degree of polymerization of 35, with M_w/M_n of 2.6. The molecular weight of the polymer was highly dependent on the choice of the kind of each monomer. Namely, the treatment of pseudo-p-dibromo[2.2]paracyclophane with 2,7-diethynyl-9,9-didodecylfluorene by the same catalyst system described above under the severer reaction condition, at 85 °C for 72 h, gave **6b** in 60% yield with a degree of polymerization of only 7 (M_n = 5400).

The optical properties of the polymers **6a-c** were examined, and the results are summarized in Table 2. The maxima of the

Table 1. Results of the synthesis of copolymers **6a-c** having [2.2]paracyclophane and fluorene units

Polymer	Yield/%[a]	M_w[b]	M_n[b]	M_w/Mn[b]
6a	76	48000	18500	2.6
6b	76	66800	26400	2.5
6c	85	31000	9800	3.2

[a]Isolated yields after reprecipitation into MeOH. [b]GPC ($CHCl_3$), polystyrene standards.

Table 2. Optical properties of the polymers **6a-c** and **1**

	Absorbance/nm[a]		Emission/nm[a,b]	
Polymer	$CHCl_3$	Film	$CHCl_3$ (Φ_F)	Film
6a	372	370	393, 412 (0.59)	397, 424
6b	370	368	393, 415 (0.58)	397, 418
6c	371	371	393, 415 (0.65)	398, 428
1[c]	319, 384	312, 383	411, 483 (0.30)	523

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [b] Excited at 370 nm (1.0×10^{-5} M). [c] Ref. 6.

absorption spectra of **6a-c** in the $CHCl_3$ solution at room temperature were around 370 nm (Table 2). The absorption and emission spectra of the polymer **6b**, as a typical representative example, are shown in Figure 1. The polymer **6b** showed the absorption peak at 370 nm ($\varepsilon = 39200$) and an onset at 418 nm, which indicates the energy band gap as 2.98 eV. The peak of the absorption spectra of the polymer films was almost the same as in the solution. As shown in Figure 1, the polymer **6b** exhibited strong blue fluorescence with the peak maximum at 415 nm, (a shoulder peak at 425 nm and a weak peak at 393 nm), which was blue-shifted by 68 nm compared to those of the polymer **1** (Table 2). The emission peak maximum was independent on the concentration of the polymer solution, and in the film state the peak maximum at 418 nm was observed in a visible blue region. In contrast, in the case of the polyfluorenes, variation of the emission color (peak maxima at around 430 nm) is possible via the substitution pattern at 9-position of the fluorene unit and/or via the change of a co-monomer.[9,10] In addition, Bunz and co-workers recently reported the synthesis of poly(fluorenylene-ethynylen) by alkyne metathesis and poly(9,9-didodecylfluorenylene-ethynylene) showed emission peaks at 426 and 447 nm in $CHCl_3$ solution.[14] In comparison with these reported fluorene–containing polymers, the titled compounds **6a-c** are one of the polymers, which show an emission peak at the lowest wavelength. Furthermore, the fluorescence quantum yields (Φ_F) of the polymers **6a-c** were determined for highly diluted $CHCl_3$ solutions. **6a-c** showed a quantum yield of around 0.60 using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi_F = 0.442$).

In conclusion, we synthesized alternating copolymers combining [2.2]paracyclophane and fluorene units in the main chain. The photoluminescence spectra of the polymers showed a strong blue light emission in solution and in the solid state, compared with the fluorene-containing polymers reported so far. An appropriate transannular π-π overlap of [2.2]paracyclophane in the polymer backbone is important for efficient transfer of the electronic charge or energy.[2] The polymers obtained are promising candidates for blue light-emitting materials with extreme photoluminescence and electroluminescence.

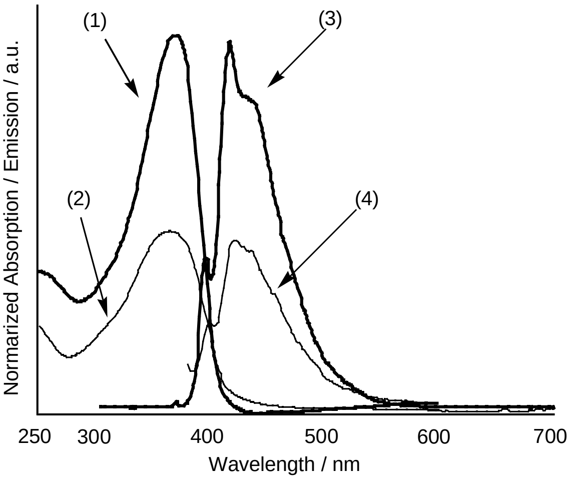


Figure 1. UV-visible spectra of **6b** (1) in $CHCl_3$ solution and (2) in the film state, and fluorescence emission spectra of **6b** (3) in $CHCl_3$ solution (1.0×10^{-5} M) and (4) in the film state, on the excitation at 370 nm.

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13 A typical procedure is as follows. A mixture of **4** (77 mg, 0.30 mmol), **5b** (226 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.030 mmol), PPh_3 (157 mg, 0.060 mmol), CuI (76 mg, 0.040 mol), NEt_3 (2.0 mL), and THF (4.0 mL) was placed in a 50-mL Pyrex flask under nitrogen atmosphere. The reaction was carried out at 50 °C for 48 h with stirring. After the reaction mixture was cooled, ammonium salt was filtered off and washed with THF. The filtrate was concentrated and dried in vacuo. The residue was dissolved in $CHCl_3$ and poured into MeOH (50 mL) twice to precipitate the polymer. The resulting polymer (**6b**) was filtered, washed with MeOH, and dried in vacuo to give 169 mg (0.022 mmol, 76%). ^{1}H NMR (270 MHz, $CDCl_3$); δ 0.69 (br, 4H), 0.85 (br, 6H), 1.20 (m, 36H), 2.02 (br, 4H), 3.00 (m, 4H), 3.32 (br, 2H), 3.77 (br, 2H), 6.58 (m, 2H), 6.69 (m, 2H), 7.09 (m, 2H), 7.38–7.77 (m, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$); δ 14.1, 22.7, 23.8, 29.3, 29.6 (overlapping signals), 30.1, 31.9, 34.2, 40.3, 55.3, 90.1, 93.7, 120.0, 122.4, 124.8, 130.0, 133.1, 134.5, 137.2, 139.6, 140.6, 142.1, 151.2.

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