Synthesis and Properties of Conjugated Copolymer Having Alternate Structure of Diphenylanthracene and Allene

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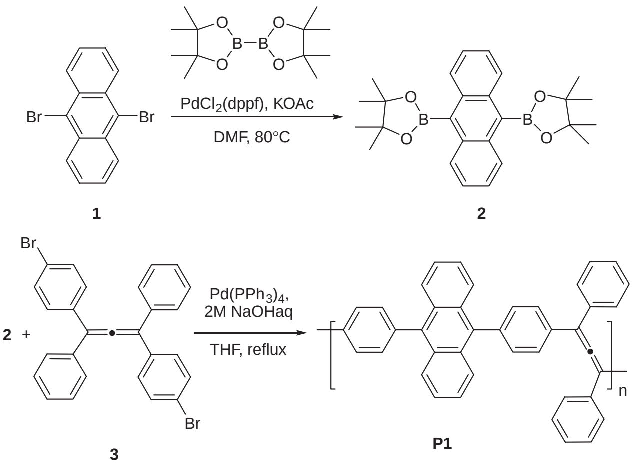
A conjugated copolymer having an alternate structure of 9,10-diphenylanthracene and 1,3-diphenylallene was synthesized by the Suzuki–Miyaura cross-coupling reaction with 9,10-dibororanylanthracene and 1,3-bis(4-bromophenyl)-1,3-diphenylallene. The diphenylanthracene moiety worked as an absorptive and emissive center unit in the polymer. The twisted allene moiety not only controlled conjugation length of the polymer but also suppressed formation of excimers, which realized intense pure blue fluorescence with high quantum efficiency ($\Phi_f \approx 1.0$) in $CHCl_3$ solution.

A variety of polymer containing anthracene moieties has been synthesized and researched of interest in electronic and optical applications of anthracene functions. An outstanding direction of the research is development of emissive conjugated polymers having anthracene moieties, whose instances are poly(arylene)s,[1] poly(arylenevinylene)s,[2] and random copolymers of dialkylfluorenes.[3] However, the conjugated anthracene polymers, reported so far, exhibit little original emissive characteristics of anthracene, frequently leading to self-quenching of excitons, unexpected red-shift, and broadened photoluminescence (PL) spectrum. In order to develop a conjugated polymer having original characteristics of anthracene, the polymer must have i) a controlled dimension of conjugation with a simple regular structure, ii) an appropriate steric hindrance so as not to form excimers, and to say nothing of iii) a good solubility in organic solvents for characterizations and materials processing.

In this paper, we propose a conjugated copolymer alternately consisting of diphenylanthracene and allene (**P1**) as the target polymer. Special features of **P1** must be that 1) the 9,10-diphenylanthracene (DPhA) unit becomes an emissive center, 2) the regular alternate structure of the twisted allene brings steric hindrance in some degree and controls dimension of π-conjugation,[4] and 3) the twisted allene unit reduces intermolecular interactions between polymer chains.[4]

P1 was synthesized by the Suzuki–Miyaura cross-coupling reaction as shown in Scheme 1. 9,10-bis(4,4,5,5-tetramethyl-[1.3.2]dioxaborolan-2-yl)anthracene (**2**), was prepared by the cross-coupling reaction of bis(pinacolato)diboron with 9,10-dibromoanthracene in the presence of KOAc as a base and $PdCl_2(dppf)$-CH_2Cl_2 complex as a catalyst.[5,6] The structure of **2** was confirmed by IR and NMR spectroscopies and elemental analysis.[6] Anthracene diboronic ester **2** was thermally stable as easy to handle in air and considerably soluble in THF. 1,3-bis(4-bromophenyl)-1,3-diphenylallene (**3**) was previously synthesized by the modified dehydrohalogenative route.[4a] The $Pd(PPh_3)_4$ catalyzed copolymerization with **2** and **3** was carried out in THF/aq NaOH, affording **P1** in excellent yield (91%).[7,8]



Scheme 1. Synthesis of **P1**.

P1 was obtained as a light-brown powder and the structure was confirmed by IR and NMR spectroscopy and elemental analysis.[8] The number-average molecular weight (M_n) of **P1** was 4300, which was determined by gel permeation chromatography vs polystyrene standard. The molecular weight distribution (M_w/M_n) of **P1** was 1.5 and the degree of polymerization (D.P.) estimated from M_n was 8. **P1** had good solubility in common organic solvents such as THF, $CHCl_3$, and toluene and also had a good processability for thin films.

UV–vis absorption and PL spectra of **P1** are shown in Figure 1 and the data are summarized in Table 1. **P1** had absorption λ_{max} at 398 nm in $CHCl_3$ solution and 400 nm in the thin-film state, respectively. Little difference in the absorption spectra suggests that **P1** takes similar conformations both in the solution and in the solid state. Surprisingly the both spectra closely resemble to that of DPhA in $CHCl_3$, except for the shoulder from 280 to 320 nm due to the tetraarylallene moiety. As shown in Table 1, the absorption λ_{max} and the molar extinction coefficient (ε_0) for **P1** are almost same to those for DPhA. These results suggest that the polymerization successfully produces the DPhA unit, whose conjugation length is strictly controlled by the twisted allene moiety. The absorption band covers a wide region from 200 to 450 nm, which contributes to efficient photoexcitation of **P1**.

P1 in $CHCl_3$ solution showed an intense blue fluorescence by irradiation of UV with an emission λ_{max} at 430 nm, whose PL spectrum was as narrow as DPhA (Figure 1). The thin film also showed a moderate light-blue fluorescence with an emission λ_{max} at 442 nm, in which some red-shift and broadening of the PL peak were recognized in comparison with those in solution. In both cases, excimeric radiative processes are practically suppressed by the twisted conformation of **P1**. In addition, the excitation spectrum was almost same to the absorption spectra, which suggested that **P1** fluoresced via a simple excitation–emission process. The Stokes' shift in $CHCl_3$ was 32 nm, which

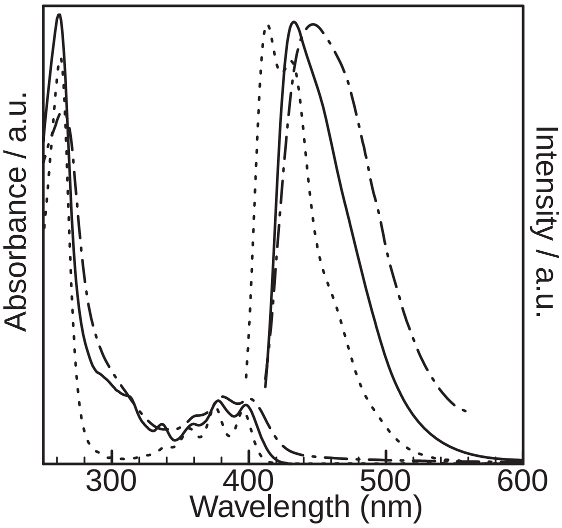


Figure 1. UV–vis absorption and PL spectra (excited at 274 nm) of **P1** in CHCl$_3$ (—), in the solid thin-film state (–·–), and DPhA in CHCl$_3$ (···).

Table 1. UV–vis and Photo physical data of **P1**

	Abs.[a]	PL	
	λ_{max}/nm (ε_0)	ex. λ/nm[b]	em. λ_{max}/nm[c]
DPhA		252	
	263 (84200)	272	
	338 (3300, sh[d])	339 (sh[e])	413
	357 (7600)	356	430
	375 (12400)	374	
	396 (11600)	394	
P1		255	
	262 (84500)[e]	278	
	337 (7700)[e]	341 (sh[e])	430
	359 (8500)[e]	360 (sh[e])	
	378 (12800)[e]	376	
	398 (11900)[e]	396	

[a] Measured in CHCl$_3$. [b] Excitation spectrum for emission at 430 nm in CHCl$_3$ (3×10^{-5} mol dm^{-3}). [c] Emission excited at 274 nm in CHCl$_3$ (3×10^{-5} mol dm^{-3}). [d] Shoulder. [e] Molar absorptivity per monomer unit.

was very small in comparison with oligophenylenes.[9] The fluorescence quantum yield (Φ_f) was $\approx$1.0 relative to DPhA ($\Phi_f = 0.9$) in cyclohexane. The enhanced quantum efficiency might be due to an extended π-conjugation effect through the polymer main chain by an electronic interaction at the allene portion.

In conclusion, we synthesized a novel conjugated anthracene–tetraphenylallene copolymer **P1** by the Suzuki–Miyaura cross-coupling reaction. The success on preparation of 9,10-dibororanylanthracene **2** opened the way to synthesize various alternate conjugated copolymers having 9,10-anthracene unit. The DPhA unit produced by the polycondensation dominated optical properties of **P1** both in absorption and emission. The twisted 1,3-diphenylpropadienylene (allene) unit in **P1** effectively worked to i) control the dimension of π-conjugation, ii) ease the interchain interactions, and iii) bring the steric hindrance, which resulted in pure blue emission, high solubility in organic solvents, and exclusion of excimeric radiative processes, respectively. Additionally, the electronic interaction through polymer main chain contributed enhancing PL quantum efficiency.

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6 Reaction conditions for 9,10-bis[4,4,5,5-tetramethyl(1.3.2)-dioxaborolan-2-yl]anthracene **2**; The mixture of 9,10-dibromoantracene (2.0 mmol), bis(pinacolato)diboron (4.4 mmol), PdCl$_2$-(dppf)-CH$_2$Cl$_2$ complex (6.0 mol %), KOAc (12 mmol) in DMF was stirred at 80 °C for 24 h under Ar. Then water was added, the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO$_4$ and evaporated to a brown solid. After recrystallization from EtOH, **2** was obtained as a fine amber crystal in 74.0% yield. mp > 300 °C. IR (KBr, cm^{-1}): 3060, 2978, 2933, 1515, 1470, 1453, 1415, 1391, 1380, 1372, 1313, 1291, 1241, 1137, 980, 852, 758, 677. UV–vis λ_{max}, (cyclohexane, nm (ε, mol dm^{-3})); 222 (16400), 259 (142000), 351 (5480), 368 (8620), 388 (7850). ^{1}H NMR (270 MHz, CDCl$_3$, ppm); δ 1.57 (s, 24H), 7.45 (dd, 4H, $J = 6.8$, 3.3 Hz), 8.34 (dd, 4H, $J = 6.8$, 3.3 Hz). ^{13}C NMR (67.5 MHz, CDCl$_3$, ppm); δ 25.3, 84.4, 125.0, 128.2, 128.7, 134.8. Anal. Calcd for C$_{26}$H$_{32}$B$_2$O$_4$: C, 72.60; H, 7.50%. Found: C, 72.24; H, 7.33%.

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8 Co-polymerization conditions for **P1**; the mixture of 1,3-bis(4-bromophenyl)-1,3-diphenylallene **3** (0.60 mmol), **2** (0.60 mmol), Pd(PPh$_3$)$_4$ (6.0 mol %) and 2M-NaOHaq (2.4 mmol) in THF was refluxed for 2 days under Ar. Then the polymer was precipitated from HCl–MeOH, NH$_4$OH–MeOH, and washed with MeOH, affording **P1** as a light brown powder in 91% yield. IR (KBr, cm^{-1}): 3057, 3027, 1947, 1920, 1596, 1508, 1491, 1442, 1391, 1276, 1182, 1117, 1072, 942, 828, 764, 696. UV–vis λ_{max}, (CHCl$_3$, nm (ε, mol dm^{-3})); 262 (84500), 359 (8530), 378 (12800), 398 (11900). ^{1}H NMR (270 MHz, CDCl$_3$, ppm); δ 6.90–8.55 (m, 26H). ^{13}C NMR (67.5 MHz, CDCl$_3$, ppm); δ 112.7, 125.0, 126.9, 127.7, 128.2, 128.5, 128.7, 129.8, 131.5, 135.3, 136.3, 136.7, 138.3, 208.7. Anal. Calcd for (C$_{41}$H$_{26}$)$_5$C$_{27}$H$_{18}$Br$_2$: C, 90.02; H, 4.82%. Found: C, 89.99; H, 5.16%.

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