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Blue, Green, and Red Light Emission of 1,8-Carbazole-based Conjugated Polymers

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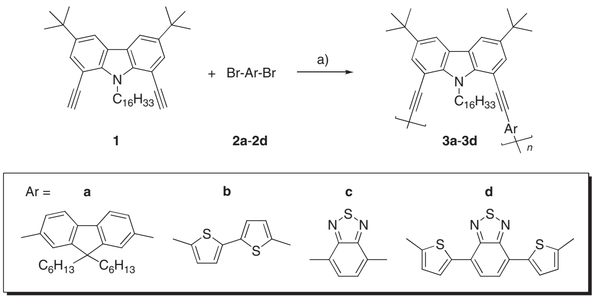
Blue, green, and red light emitting conjugated copolymers based on the 1,8-linked carbazole unit were synthesized by the Sonogashira polycondensation between the 1,8-diethynylcarbazole derivative and arylene dibromide comonomers. The mixture of three polycarbazoles at a suitable molar ratio provided the white light emission in solutions.

Conjugated carbazole polymers are promising candidates for applications in organic electronic devices.[1] It was recently found that a different connectivity of the carbazole unit leads to different polymer properties.[2] For example, the poly(3,6-carbazole) derivatives, in which the highest electron density positions of the carbazole are linked either directly or via π-spacers, are suitable for electrochemical and phosphorescent applications.[3] On the other hand, poly(2,7-carbazole) derivatives usually possess smaller band gaps and accordingly show excellent properties for use in thin film transistors and bulk heterojunction solar cells.[4] We very recently reported successful synthesis and the fundamental properties of the alkyne-linked poly(1,8-carbazole)s.[5] Based on the electron density distribution of the carbazole, the poly(1,8-carbazole) derivatives can be categorized as in the same class of poly(3,6-carbazole)s, but their effective conjugation lengths were found to be comparable to those of the poly(2,7-carbazole) derivatives. This result suggests the high potential of the poly(1,8-carbazole)s for applications in organic electronic devices and therefore we became interested in diversifying the library of this novel class of carbazole polymers. We now report for the first time the synthesis and tunable emission colors of the 1,8-carbazole-based conjugated copolymers.

The conjugated copolymers **3a**–**3d** were synthesized by the Sonogashira polycondensation between the 1,8-diethynylcarbazole derivative and various arylene dibromides **2a**–**2d** (Scheme 1). Taking into account a previous report,[5] the molecular weights and polydispersities are reasonable (Table 1). The difference in the molecular weight might reflect the electronic effects of the dibromide comonomers on the catalytic cycle. Thus, the polymerization with the electron-deficient **2c** provided the highest molecular weight polymer **3c**. The obtained polymers were characterized by ^{1}H NMR and IR spectroscopy (see Supporting Information[10]). In the IR spectra, all polymers show a peak characteristic of the alkyne vibration at 2189–2196 cm^{-1}. Differential scanning calorimetry (DSC) revealed their glass transition temperatures (T_gs), ranging from 50 to 106 °C, depending on the comonomer structure (Table 1). Thermogravimetric analysis (TGA) revealed a sufficiently high thermal stability with the 5% decomposition temperature of >358 °C (Table 1).



Scheme 1. Sonogashira polycondensation of 1,8-diethynylcarbazole derivative **1** and arylene dibromide **2a**–**2d**. (a) $PdCl_2(PPh_3)_2$, CuI, i-Pr_2NH, toluene, 80 °C.

Table 1. Summary of the molecular weight and thermal properties of poly(1,8-carbazole)s **3a**–**3d**

	$M_w/10^{-3}$ [a]	$M_n/10^{-3}$ [a]	M_w/M_n [a]	T_g/°C[b]	$T_{d5\%}$/°C[c]
3a	3.9	3.0	1.3	50	375
3b	4.6	3.5	1.3	70	363
3c	8.6	5.4	1.6	106	370
3d	3.1	2.8	1.1	96	358

[a]Determined by GPC (THF eluent, calibrated by polystyrene standards). [b]Glass transition temperatures determined by DSC. [c]Temperature at which 5% weight loss occurred upon heating.

The optical properties of the polymers were investigated in CH_2Cl_2. The fluorene and bithiophene copolymers, **3a** and **3b**, showed the longest absorption maximum (λ_{max}) at 404 and 416 nm, respectively, whereas the benzothiadiazole-containing copolymers, **3c** and **3d**, displayed the bathochromically shifted λ_{max} ascribed to the intramolecular charge-transfer (CT) bands at 481 and 494 nm, respectively (Table 2 and Figure 1a). The order of the emission peak positions (λ_{em}) of **3a**–**3d** was consistent with the order of the λ_{max} values (Table 2). Thus, the λ_{em} of **3a**, **3b**, **3c**, and **3d** appeared at 433 (blue), 517 (green), 611 (red), and 683 (red) nm, respectively, covering the entire visible region (Figure 1b). The Stokes shifts also increased in this order, whereas the quantum yields tended to decrease.[6] This significant change in the optical properties from **3a** to **3d** is supposed to reflect the characteristics of the 1,8-carbazole unit. For example, the ethynylene-linked donor–acceptor type polymer **4**, composed of the 3,6-carbazole unit and benzothiadiazole, has previously been reported, and its λ_{max} and λ_{em} values in CH_2Cl_2 were 440 and 566 nm, respectively (Figure 1S).[7] It is generally known that weaker donor–acceptor interactions elevate the HOMO level of the donor moieties and at the same time lower the LUMO level of the acceptor moieties, leading to a smaller band gap of the donor–acceptor type π-conjugated systems.[8] Since both λ_{max} and λ_{em} of **3c** were lower in energy than **4**, the 1,8-carbazole unit is a weaker donor than the 3,6-carbazole unit. To reveal the

Table 2. Summary of the optical properties of **3a**–**3d**[a]

	$\lambda_{\max}$/nm	λ_{em}/nm [λ_{ex}/nm]	Stokes shift/cm^{-1}	$\Phi_{f,sol}$
3a	404	433 [326]	1658	0.60[b]
3b	416	484, 517 [416]	3377	0.31[b]
3c	481	611 [418]	4423	0.16[c]
3d	494	683 [494]	5602	0.36[c]

[a]Measured in CH_2Cl_2. [b]Determined against quinine sulfate in 0.05 M aq. H_2SO_4. [c]Determined against rhodamine 6G in ethanol.

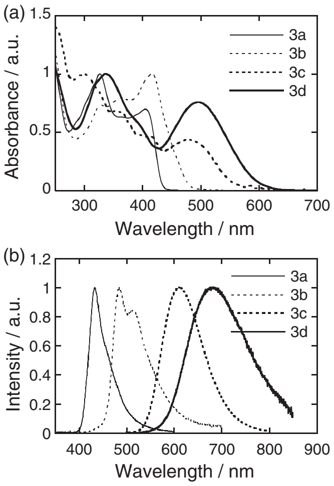


Figure 1. (a) UV–vis and (b) fluorescence spectra of **3a**–**3d** in CH_2Cl_2 at 20 °C.

donor strengths, the cyclic voltammograms (CVs) of **3a**–**3d** were measured in CH_2Cl_2 (+0.1 M *n*-Bu_4NClO_4) at 20 °C (Figure 2S and Table 1S). All polymers showed the reversible carbazole-centered oxidation at ca. 0.80–0.90 V, but the potentials were apparently higher than the homopolymer,[5] suggesting a weaker donor ability. The energy levels of **3a**–**3d** were calculated and summarized (Table 2S). It was revealed that both the HOMO and LUMO levels decreased by copolymerization with the less electron-donating comonomer moieties.

Since we could obtain blue, green, and red color emitting polymers, white light emission was then studied. With the quantum yields in mind, the CH_2Cl_2 solution of **3a** (blue), **3b** (green), and **3d** (red) at the molar ratio of 1:2:2 and 10^{-6} M/repeat unit were prepared. Excitation at 255 nm afforded an efficient emission from the three components and the observed emission color was definitely white (Figure 2).

In conclusion, the 1,8-carbazole unit was found to be a useful donor component for the synthesis of narrow band gap polymers and multicolor emitting polymers. Since the copolymerization can control the component ratio and the energy level of the resulting polymers,[9] single polymer-based white emitting materials are expected. Further studies on organic electronic applications are currently underway.

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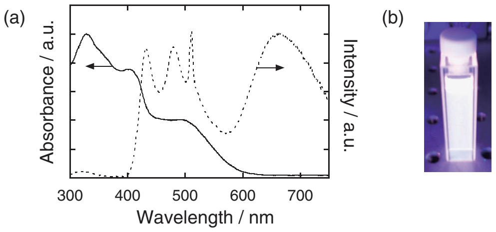

Figure 2. (a) UV–vis and fluorescence spectra of the mixture of **3a**, **3b**, and **3d** (1:2:2) in CH_2Cl_2 at 20 °C and (b) the image of the white light emission.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.