Synthesis and Light-Emitting Properties of Carbazole-Based Copolymers Bearing Cyano-Substituted Arylenevinylene Chromophore

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ABSTRACT: Two arylenevinylene compounds bearing the cyano group at α -position (6) and β -position (9) from the dialkoxylphenylene unit were synthesized, in which the molecular termini were functionalized with 3-bromocarbazole. The Suzuki coupling copolymerization of these compounds with 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene and 9,9-dihexylfluorene-2,7-bis(boronic acid) was carried out to obtain copolymers (cp67 and cp97) containing the cyano-substituted arylenevinylene fluorophore of 7 mol %. Model compounds (6' and 9') corresponding to the arylenevinylene fluorophore were also prepared. The UV spectra of copolymers resembled that of homopolymer hp with no arylenevinylene segment in both CHCl₃ solution and thin film. The emission maxima of copolymers in CHCl₃ (394 nm) agreed with that of

homopolymer indicating that the emission bands originated from the carbazole-fluorene-carbazole segment. The emission maximum wavelength of copolymer **cp67** in thin film (477 nm) indicated fluorescence from the cyano-substituted arylenevinylene fluorophore because of the occurrence of fluorescence resonance electron transfer. In contrast, copolymer **cp97** showed fluorescence at 528 nm to suggest the formation of a new emissive species such as a charge-transfer complex (exciplex). © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 91–98, 2010

KEYWORDS: carbazole; copolymerization; cyano-substituted arylenevinylene; fluorescence; fluorescence resonance electron transfer; light-emitting diodes

INTRODUCTION Since the discovery of light-emitting properties in the electroluminescent device using poly(*p*-phenylenevinylene),¹ many conjugated polymers including polyfluorene, polyphenylenevinylene, and polythiophene have been developed for the purpose of commercialization of a polymer-based full color display. White-light-emitting diodes have recently drawn much attention as next generation flat panel light sources. Poly(*p*-arylenevinylene)s are regarded as the most important materials in part because the carboncarbon bond formation can occur by several methods (Wessling route, Gilch route, and Wittig-Horner reaction) without using expensive metal complexes. The introduction of appropriate donor and acceptor pairs,² the control of stereochemistry (E or Z) in the vinylene moiety,³ and the intensive reduction of conjugation length with insulating spacers⁴ affect the band gap energy, and thereby the emission color of poly(p-arylenevinylene)s can be tuned. The attachment of an electron-withdrawing cyano group can not only decrease the lowest unoccupied molecular orbital (LUMO) level of materials to impart the electron affinity but also induce the bathochromic shift of photoluminescence and electroluminescence spectra.⁵ Generally, the extension of chain length is a straightforward protocol to obtain longer wavelength emissions. However, the maximum electron delocalization is dominated by the chemical structure in the repeating unit, and the fully conjugated system sometimes brings about problems in the light emission of solid devices. The time-dependent changes of an emission color were observed for conjugated polymers with rigid backbone owing to inevitable structural defects and/or chain aggregations.⁶ From these viewpoints, poly(oligomer)s that join the merits of conjugated oligomer blocks having the minimized structural defect with the long-term morphological stability of polymers are attractive candidates for light-emitting materials.^{4,7} It is known that cyano-substituted arylenevinylene oligomers have potential enough to cover the wide-ranging visible spectrum.⁸

Recently, we have reported the preparation of luminescent poly(oligomer)s containing a carbazole-fluorene-carbazole segment separated by the *p*-xylylene insulating unit and their optical properties.⁹ It is to be emphasized that copolymers carrying a small amount of 2,5-bis(phenylethenyl)-4-decyloxyanisole (PEDA) segment emitted photoluminescence not only from the carbazole-fluorene-carbazole segment but also from the PEDA one through the fluorescence resonance energy transfer (FRET) especially in thin film. A copolymer carrying the PEDA segment of only 5 mol % exhibited the brightest emission among examined copolymers with the PEDA segment ranging from 5 to 50 mol %. This result

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indicates the presence of energy-harvesting phenomenon, namely, the excited energy gained by the carbazole-fluorenecarbazole segment is efficiently concentrated into the PEDA one. In this contribution, we will investigate the utility of cyano-substituted arylenevinylene segments as the energyaccepting and light-emitting fluorophore with the aim of pursuing the possibility of our FRET system.

EXPERIMENTAL

Materials

All reactions were performed under dry nitrogen atmosphere. Dry tetrahydrofuran (THF) was purchased from Kanto Chemical. Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] for the Suzuki coupling polymerization was purchased from TCI. Dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and ethanol (EtOH) were dried and distilled according to the general methods. The synthesis of 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene, 9,9-dihexylfluorene-2,7-bis(boronic acid), 2,5-bis(bromomethyl)-4-decyloxyanisole (1), and 3-bromocarbazole (2) was reported earlier.⁹ The preparation of homopolymer **hp** with no arylenevinylene segment was also described previously.⁹

Instrumentation

¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using tetramethylsilane (δ 0.00) as an internal reference peak. Infrared (IR) spectra were recorded on a JASCO FTIR 460Plus spectrophotometer in the ATR method. Melting points (Mp) were determined on a YANAGIMOTO micro melting point apparatus MP-J3. Elemental analyses (EA) were performed on a Perkin-Elmer PE2400II by the CHN mode. Gel permeation chromatographic (GPC) analyses were performed on a Tosoh DP-8020 using tandem TSK Multipore H_{XL} -M columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with a refractive index detector (RI-8010). Number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined on the basis of a calibration curve made from standard polystyrene samples. Ultraviolet (UV) and photoluminescence (PL) spectra were collected on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using a 1 cm quartz cell or a 1 cm \times 5 cm quartz plate. Fluorescence quantum yields (QYs) of copolymers in solution were determined relative to quinine sulfate in 0.5 M H₂SO₄ having a QY of 0.55. Relative QYs in thin film were calculated by assuming a QY of homopolymer **hp** in thin film to be 1.0.

Monomer Synthesis

2,5-Bis(cyanomethyl)-4-decyloxyanisole (3)

A solution of **1** (3.0 g, 6.7 mmol) and sodium cyanide (0.83 g, 17 mmol) in DMSO (30 mL) was heated at 50 °C for 1 h and then at 85 °C for 0.5 h. The mixture was poured into water and extracted with EtOAc. The organic phase was dried over MgSO₄. After removing solvents, the crude product was washed with MeOH several times and dried *in vacuo* to give colorless solid in 1.4 g (59% yield). Mp. 92–95 °C.

92

¹H NMR (δ , CDCl₃) 6.90 (2H), 3.96 (2H, t, J = 6.5 Hz), 3.83 (3H, s), 3.69 (2H), 3.68 (2H), 1.78 (2H, m), 1.51–1.20 (14H), 0.87 (3H, t, J = 6.6 Hz).

4-[(3'-Bromocarbazole-9'-yl)methylene]benzyl Chloride (4) To a solution of **2** (2.0 g, 8.1 mmol) and *p*-xylylene chloride (3.2 g, 18 mmol) in THF (20 mL) was added NaH (60% oil suspension) (0.39 g, 9.8 mmol), and the mixture was heated at 50 °C for 3 h. The reaction system was filtered to remove inorganic salts and the filtrate was concentrated to dryness. After an EtOAc soluble part was recovered, the crude product was washed with Et₂O and dried *in vacuo* to give colorless solid in 1.6 g (50% yield). Mp. 133–136 °C.

¹H NMR (δ , CDCl₃) 8.20 (1H, d, J = 1.9 Hz), 8.04 (1H, d, J = 7.8 Hz), 7.52–6.99 (9H), 5.44 (2H, s), 4.49 (2H, s).

4-[(3'-Bromocarbazole-9'-yl)methylene]benzaldehyde (5)

A solution of **4** (1.6 g, 4.2 mmol) and sodium periodate (1.3 g, 6.3 mmol) in DMF (40 mL) was heated to reflux for 6 h. The mixture was poured into water and extracted with CH_2Cl_2 . The organic phase was washed with saturated aq. $Na_2S_2O_3$, water, and brine in this order and then dried over MgSO₄. After removing solvents, the crude product was purified by SiO₂ column chromatography (hexane/CH₂Cl₂ = 1:2 in vol %, $R_f = 0.32$) to give colorless solid in 0.50 g (34% yield). Mp. 144–147 °C.

¹H NMR (δ , CDCl₃) 9.92 (1H, s), 8.23 (1H, d, J = 1.9 Hz), 8.07 (1H, d, J = 7.4 Hz), 7.76 (2H, d, J = 8.3 Hz), 7.52–7.12 (7H), 5.52 (2H, s).

(E,E')-2,5-Bis[α-cyano-4'-(3"-bromocarbazole-9"-yl) methylene]styryl-4-decyloxyanisole (6)

To a solution of **3** (0.05 g, 0.14 mmol) and **5** (0.11 g, 0.29 mmol) in THF/EtOH (4 mL/2 mL) was added *t*-BuOK (0.04 g, 0.35 mmol), and the mixture was heated to reflux for 4 h. The reaction system was poured into water and an aqueous phase was extracted with EtOAc. The combined organic phase was dried over MgSO₄. After removing solvents, the crude product was washed with acetone several times and dried *in vacuo* to give yellow solid in 0.04 g (24% yield). Mp. 238–241 °C.

¹H NMR (δ, CDCl₃) 8.23 (2H, d, J = 1.8 Hz), 8.07 (2H, d, J = 7.8 Hz), 7.79–7.75 (4H), 7.65–7.12 (16H), 7.05 (1H), 7.03 (1H), 5.54 (4H, s), 4.01 (2H, t, J = 6.4 Hz), 3.87 (3H, s), 1.78 (2H, m), 1.47–1.14 (14H), 0.84 (3H, t, J = 6.4 Hz). IR (cm⁻¹, ATR) 3049, 2923, 2852, 2213, 1596, 1489, 1473, 1456, 1422, 1349, 1331, 1300, 1274, 1227, 1206, 1124, 1034, 912, 857, 802, 789, 764, 738, 718, 656. Found: C, 70.47; H, 5.36%. Calcd for C₆₁H₅₄Br₂N₄O₂: C, 70.79; H, 5.26%.

(*E,E'*)-2,5-Bis(α -cyano-4'-methyl)styryl-4-decyloxyanisole (6') To a solution of **3** (0.10 g, 0.29 mmol) in THF (5 mL) were added sodium amide (0.03 g, 0.73 mmol) and *p*-tolualdehyde (0.09 g, 0.73 mmol), and the mixture was heated to reflux for 2 h. After neutralization with 1 M HCl, an aqueous phase was extracted with Et₂O. The combined organic phase was dried over MgSO₄ and solvents were removed. The crude product was purified by SiO₂ column chromatography (hexane/EtOAc = 4:1 in volume ratio, $R_{\rm f}$ = 0.58) and recrystallization (MeOH/CH $_2$ Cl $_2$) to give a yellow solid in 0.03 g (19% yield). Mp. 113–115.

¹H NMR (δ , CDCl₃) 7.80 (4H, d, J = 8.1 Hz), 7.67 (1H, s), 7.56 (1H, s), 7.28 (4H, d, J = 7.7 Hz), 7.09 (1H, s), 7.06 (1H, s), 4.05 (2H, t, J = 6.4 Hz), 3.92 (3H, s), 2.42 (6H, s), 1.84 (2H, m), 1.52–1.16 (14H), 0.87 (3H, t, J = 6.3 Hz). IR (cm⁻¹, ATR) 3031, 2922, 2852, 2212, 1605, 1513, 1499, 1461, 1410, 1392, 1355, 1278, 1215, 1040, 917, 879, 811, 744. Found: C, 81.02; H, 7.82%. Calcd for C₃₇H₄₂N₂O₂: C, 81.28; H, 7.74%.

2,5-Diformyl-4-decyloxyanisole (7)

A solution of **1** (2.0 g, 4.4 mmol) and sodium periodate (2.9 g, 13 mmol) in DMF (90 mL) was heated to reflux for 6 h. The mixture was poured into water and extracted with CH_2Cl_2 . The organic phase was washed with saturated aq. $Na_2S_2O_3$, water, and brine in this order and then dried over MgSO₄. After removing solvents, the crude product was purified by SiO₂ column chromatography (hexane/CH₂Cl₂ = 1:2 in vol %, $R_f = 0.55$) to give yellow solid in 0.59 g (42% yield). Mp. 88–90 °C.

¹H NMR (δ , CDCl₃) 10.53 (1H, s), 10.49 (1H, s), 7.45 (2H, s), 4.09 (2H, t, J = 6.4 Hz), 3.97 (3H, s), 1.84 (2H, m), 1.51–1.22 (14H), 0.88 (3H, t, J = 6.1 Hz).

4-[(3'-Bromocarbazole-9'-yl)methylene]benzyl Cyanide (8) A solution of **4** (0.60 g, 6.7 mmol) and sodium cyanide (0.09 g, 1.9 mmol) in DMSO (20 mL) was heated at 50 °C for 2 h and then at 85 °C for 2 h. The mixture was poured into water and extracted with EtOAc. The organic phase was dried over MgSO₄. After removing solvents, the crude product was purified by SiO₂ column chromatography (the ratio of hexane/CH₂Cl₂ was gradually varied from 2:3 ($R_f = 0.15$) to 0:1 in vol %) to give colorless solid in 0.40 g (68% yield). Mp. 92–95 °C.

¹H NMR (δ , CDCl₃) 8.22 (1H, d, J = 2.0 Hz), 8.06 (1H, d, J = 7.8 Hz), 7.53–7.01 (9H), 5.46 (2H, s), 3.66 (2H, s).

(E,E')-2,5-Bis[β -cyano-4'-(3"-bromocarbazole-9"-yl) methylene]styryl-4-decyloxyanisole (9)

To a solution of 7 (0.06 g, 0.19 mmol) and **8** (0.15 g, 0.40 mmol) in THF/EtOH (6 mL/3 mL) was added *t*-BuOK (0.05 g, 0.48 mmol), and the mixture was heated to reflux for 4 h. The precipitated solid was collected by the filtration that was washed with EtOH and dried *in vacuo* to give orange solid in 0.18 g (91% yield). Mp. 292–295.

¹H NMR (δ, CDCl₃) 8.25 (2H, d, J = 1.8 Hz), 8.09 (2H, d, J = 7.7 Hz), 7.95 (1H, s), 7.90 (1H, s), 7.85 (1H, s), 7.81 (1H, s), 7.64–7.13 (16H), 5.54 (4H, s), 4.06 (2H, t, J = 6.5 Hz), 3.89 (3H, s), 1.78 (2H, m), 1.47–1.15 (14H), 0.86 (3H, t, J = 6.4 Hz). IR (cm⁻¹, ATR) 3053, 2925, 2852, 2206, 1626, 1592, 1513, 1490, 1473, 1455, 1419, 1365, 1342, 1331, 1314, 1296, 1272, 1252, 1216, 1122, 1032, 913, 855, 840, 802, 787, 763, 738, 718, 692, 658, 625. Found: C, 70.61; H, 5.19%. Calcd for C₆₁H₅₄Br₂N₄O₂: C, 70.79; H, 5.26%.

(*E,E'*)-2,5-Bis(β -cyano-4'-methyl)styryl-4-decyloxyanisole (9') To a solution of 7 (0.17 g, 0.54 mmol) and 4-methylbenzyl cyanide (0.15 g, 1.1 mmol) in THF/EtOH (12 mL/6 mL) was added *t*-BuOK (0.15 g, 1.4 mmol), and the mixture was heated to reflux for 4 h. The precipitated solid was collected by the filtration that was washed with EtOH and dried *in vacuo* to give orange solid in 0.21 g (70% yield). Mp. 139–141 $^{\circ}$ C.

¹H NMR (δ, CDCl₃) 8.00 (1H, s), 7.94 (1H, s), 7.90 (1H, s), 7.86 (1H, s), 7.59 (4H, d, J = 7.2 Hz), 7.25 (4H, d, J = 7.2Hz), 4.11 (2H, t, J = 6.4 Hz), 3.95 (3H, s), 2.40 (6H, s), 1.84 (2H, m), 1.56–1.17 (14H), 0.87 (3H, t, J = 6.1 Hz). IR (cm⁻¹, ATR) 3074, 3030, 2920, 2851, 2208, 1612, 1591, 1513, 1496, 1465, 1421, 1393, 1366, 1318, 1296, 1253, 1214, 1129, 1066, 1037, 988, 930, 905, 856, 811, 709, 691, 673. Found: C, 80.97; H, 7.86%. Calcd for C₃₇H₄₂N₂O₂: C, 81.28; H, 7.74%.

Polymerization

Typical Example (cp67)

To a ternary mixture of 1,4-bis[(3'-bromocarbazole-9'yl)methylene]-2,5-didecyloxybenzene (79 mg, 87 μ mol), monomer **6** (4.8 mg, 4.6 μ mol), and 9,9-dihexylfluorene-2,7bis(boronic acid) (39 mg, 92 μ mol) in THF (5 mL) were added Pd(PPh₃)₄ (1.1 mg, 0.92 μ mol) and 2 M aq. Na₂CO₃ (0.92 mL). The mixture was heated to reflux for 48 h. After pouring the mixture into water, an aqueous phase was extracted with CH₂Cl₂. The combined organic phase was washed with 1 M HCl and dried over MgSO₄. The concentrated solution was poured into MeOH and the obtained product was dried *in vacuo* to give a yellow powder in 0.09 g (89% yield).

¹H NMR (δ , CDCl₃) 8.44 (2H, bs), 8.24 (2H, d, J = 7.5 Hz), 7.90–7.20 (16H × 0.93 + 26H × 0.07), 7.07 (2H × 0.07, bs), 6.30 (2H × 0.93, bs), 5.62 (4H × 0.07, bs), 5.50 (4H × 0.93, bs), 4.01 (2H × 0.07, bs), 3.88 (3H × 0.07, bs), 3.59 (4H × 0.95, t, J = 6.0 Hz), 2.13 (4H, bs), 1.90–1.74 (2H × 0.07, bs), 1.62–1.00 (32H × 0.93 + 14H × 0.07), 0.96–0.68 (16H × 0.93 + 13H × 0.07). Another copolymer (**cp97**) was likewise synthesized using monomer **9** instead of monomer **6** and the polymer structure was confirmed by the ¹H NMR spectrum.

¹H NMR (δ , CDCl₃) 8.43 (2H, bs), 8.24 (2H, d, J = 7.6 Hz), 7.88–7.19 (16H × 0.93 + 26H × 0.07), 6.85 (2H × 0.07, bs), 6.30 (2H × 0.93, bs), 5.61 (4H × 0.07, bs), 5.50 (4H × 0.93, bs), 4.07 (2H × 0.07, bs), 3.90 (3H × 0.07, bs), 3.59 (4H × 0.93, t, J = 6.0 Hz), 2.13 (4H, bs), 1.90–1.74 (2H × 0.07, bs), 1.67–1.00 (32H × 0.93 + 14H × 0.07), 0.96–0.67 (16H × 0.93 + 13H × 0.07).

RESULTS AND DISCUSSION

Synthesis

The preparation route of monomers bearing a cyano-substituted arylenevinylene core and 3-bromocarbazole terminal groups is shown in Scheme 1. The bromomethyl group in **1** was converted into the cyanomethyl group (**3**) and the formyl group (**7**) by the substitution reaction and the oxidation reaction, respectively. On the other hand, **2** was treated with excess *p*-xylylene chloride to give **4** having the benzyl chloride group that was further transformed into **5** and **8**



SCHEME 1 Synthetic pathway of monomers (6 and 9) carrying cyano-substituted arylenevinylene fluorophore (reagents are omitted for clarity).

having the benzaldehyde group and the benzyl cyanide group, respectively. Finally, the target monomers (**6** and **9**) were obtained by the base-catalyzed Knoevenagel-type condensation using **3**, **5**, **7**, and **8** in combination. The reactions proceeded in a stereoselective manner giving rise to *E*,*E'* products concerning the C=C double bond.^{8(c)} The cyano group was introduced at α -position (**6**) and β -position (**9**) from the dialkoxylphenylene unit. The model fluorophores (**6**' and **9**') replacing 3-bromocarbazole group in monomers (**6** and **9**) with the hydrogen atom were also prepared similarly from **3** with *p*-tolualdehyde and **7** with 4-methylbenzyl cyanide, respectively, (Fig. 1).

The Suzuki coupling copolymerization using 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene, monomer **6**, and 9,9-dihexylfluorene-2,7-bis(boronic acid) was conducted while keeping the molar balance of bromide and boronic acid to unity. The feed ratio between 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene and monomer **6** was set to 95:5 in mol % to obtain a copolymer having the energy-accepting fluorophore as the minor component and to investigate the energy-harvesting phenomenon. After precipitating into MeOH, copolymer **cp67** containing the arylenevinylene segment having the cyano group



FIGURE 1 Chemical structure of model fluorophores 6' and 9'.

at α -position was obtained. The copolymer had a good solubility in solvents, such as CH₂Cl₂, THF, and toluene, thanks to the nonconjugated methylene spacer on the carbazole nitrogen. The M_n and M_w/M_n determined by GPC analysis in THF were 9700 and 2.4, respectively. The content of cyano-substituted arylenevinylene segment in copolymer cp67 (7 mol %) was calculated by comparing the signal integral ratio of methylene protons adjacent to the arylenevinylene segment [Fig. 2(e)] with those adjacent to the didecyloxyphenylene unit [Fig. 2(f)] in the ¹H NMR spectrum. Likewise, copolymer cp97 containing the arylenevinylene segment having the cyano group at β -position was likewise synthesized using 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene, monomer 9, and 9,9-dihexylfluorene-2,7-bis(boronic acid) in the molar ratio of 95:5:100. The $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ were 7300 and 1.6, respectively. The content of cyano-



FIGURE 2 ¹H NMR spectrum of copolymer cp67 in CDCl₃.



FIGURE 3 Chemical structure of copolymers cp67 and cp97 and that of homopolymer hp.

substituted arylenevinylene segment in copolymer **cp97** was similarly calculated to be 7 mol %. For comparison, homopolymer **hp** with no arylenevinylene fluorophore was synthesized from 1,4-bis[(3'-bromocarbazole-9'-yl)methylene]-2,5-didecyloxybenzene and 9,9-dihexylfluorene-2,7-bis(boronic acid) ($M_n = 7000$, $M_w/M_n = 1.9$). The chemical structures of polymers are illustrated in Figure 3.

Optical Properties

The absorption maxima of copolymers (cp67 and cp97) in CHCl₃ were equally detected at 345 nm (Fig. 4) and that of homopolymer hp was observed at 344 nm (Fig. 4, inset). All these absorption bands could be ascribed to the π - π * transition of the carbazole-fluorene-carbazole segment isolated by the nonconjugated *p*-xylylene spacer. The shape of UV spectra of copolymers and homopolymer resembled each other because copolymers mostly consisted of carbazole-fluorenecarbazole segment. The absorption maximum wavelengths were shorter by a few nanometers than a fluorene trimer interconnected at 2,7-positions (348 nm).¹⁰ The maximum effective conjugation may be limited to the phenylene-fluorene-phenylene sequence in the present case because fluorene is connected to 3-position of carbazole ring. In the UV spectrum of copolymer cp97, an additional small peak originated from the cyano-substituted arylenevinylene segment was also observed at \sim 430 nm, as implicated by the absorption maximum of model fluorophore 9' at 433 nm (vide *infra*). The PL spectra of both copolymers in CHCl₃ had peak maxima at 394 nm when they were irradiated with a light at 345 nm, which would be originated from the carbazole-fluorene-carbazole fluorophore. Similar to our previous report,⁹ the emission maxima of copolymers (cp67 and cp97) blueshifted from that of homopolymer hp (411 nm) by introducing a small amount of arylenevinylene segment into the main chain. The peaks assignable to the vibronic fine structure were also observed at 411 nm in the PL spectra of copolymers. The QYs of copolymers were 0.11 (**cp67**) and 0.13 (**cp97**) being comparable to that of homopolymer **hp** (0.12). On the other hand, the QY of a similar copolymer incorporating PEDA segment of 5 mol % was higher (0.29) than that of homopolymer **hp** because of the occurrence of intramolecular FRET and energy-harvesting phenomenon.⁹

To get information about whether FRET successfully occurs or not in copolymers, the relationship between the emission spectrum of homopolymer **hp** and the absorption spectra of model fluorophores (**6**' and **9**') in $CHCl_3$ is compared in Figure 5. These spectra would correspond to the fluorescence from the carbazole-fluorene-carbazole segment and the



FIGURE 4 UV (open mark) and PL (closed mark) spectra of copolymers **cp67** (circle) and **cp97** (square) in CHCl₃ (10^{-5} M). Excitation wavelengths were 345 nm for both copolymers. Inset shows UV (open triangle) and PL (closed triangle) spectra of homopolymer **hp** in CHCl₃ (10^{-5} M) (excitation wavelength = 344 nm).



FIGURE 5 PL spectrum of homopolymer **hp** (closed triangle, excitation wavelength = 344 nm) along with UV spectrum of model fluorophores **6**' (open circle) and **9**' (open square) in CHCl₃ (10^{-5} M).

absorption of the cyano-substituted arylenevinylene segments embedded in copolymers. The absorption spectrum of model fluorophore 6' had two peak maxima at 310 and 366 nm, whereas that of model fluorophore 9' red-shifted to have maxima at 356 and 432 nm indicating the wider conjugation system. Because the absorption spectrum of model fluorophore 6' does not efficiently overlap with the emission spectrum of homopolymer hp, the intramolecular FRET from the carbazole-fluorene-carbazole segment to the cyano-substituted arylenevinylene one is supposed to rarely occur in copolymer **cp67**. Furthermore, 1-cyano-*trans*-1,2-bis(4'-methylbiphenyl)ethylene (CN-MBE) molecule is known to be twisted in solution by the steric interaction of the cyano group introduced at the vinylene moiety.¹¹ Model fluorophore 6' is thus likely to adopt nonplanar conformation and have restricted effective conjugation length resulting in rather low QY (0.006). Accordingly, if the intramolecular FRET occurs to transfer the excited energy from the carbazole-fluorene-carbazole segment to the cyano-substituted arylenevinylene one, photoluminescence from the energyaccepting fluorophore cannot be observed. On the contrary, the absorption spectrum of model fluorophore 9' nicely overlaps with the emission spectrum of homopolymer hp to enable the intramolecular FRET from the carbazole-fluorenecarbazole segment to the cyano-substituted arylenevinylene one. The QY of model fluorophore 9' is large (0.25) enough to detect fluorescence emission at 504 nm (Supporting Information Fig. S10). From the emission spectrum of copolymer cp97 shown in Figure 4, however, no intramolecular FRET seems to occur. It is now speculated that the arrangement of dipole moments of two chromophores is not adequate and/ or the distance between energy-donating and energy-accepting segments is far away for the efficient Förster-type FRET process.

Finally, the UV and PL spectra of copolymers (**cp67** and **cp97**) were measured in thin film obtained by spin-coating a toluene solution of copolymers (ca. 1 mg/mL) in 2000 rpm for 60 s. In both copolymers, the absorption maxima origi-

nated from the π - π ^{*} transition of the carbazole-fluorene-carbazole segment (346 nm) showed ignorable red-shift from those in CHCl₃ (Supporting Information Fig. S11). Owing to the presence of nonconjugated *p*-xylylene spacer, a π - π stacking aggregation between chromophores may be forbidden. The emission maximum of copolymer cp67 was observed at 477 nm that agreed well with that of model fluorophore 6' in CHCl₃ (Fig. 6). The emission from the carbazole-fluorene-carbazole segment having peak maximum at 394 nm was considerably quenched. Although model fluorophore 6' has rather low QY in CHCl₃ because of the nonplanar conformation (vide supra), the QY can be dramatically improved in the frozen state by the aggregation-induced enhanced emission.¹¹ These results would suggest that the excited energy gained by the carbazole-fluorene-carbazole segment is transferred to the cyano-substituted arylenevinylene fluorophore through FRET to give a longer wavelength emission. In the film state, not only the intrachain but also the interchain FRET can take place because polymer chains are close to each other. The emission maximum of copolymer cp67 (477 nm) is close to that of model fluorophore 6' in CHCl₃ (473 nm) rather than in solid state¹² (456 nm) indicating that the cyano-substituted arylenevinylene fluorophores are well dispersed in the polymer matrix. The relative QY of copolymer cp67 in thin film was roughly calculated using homopolymer **hp** as a standard (QY = 1.0). Although the absolute QY cannot be determined, the lightemitting potential of homopolymer **hp** in thin film is probably low as judged from the emission properties in solution (QY = 0.12). If the rate of FRET is slower than that of the nonradiative decay of the carbazole-fluorene-carbazole segment in the excited state, the calculated QY of copolymer cp67 does not exceed 1. In this case, the relative QY of copolymer cp67 was determined to be 1.6 to indicate the fast FRET process. For the efficient energy-harvesting system, the molar balance of energy-donating and energy-accepting



FIGURE 6 PL spectrum of homopolymer **hp** (closed triangle) and those of copolymers **cp67** (closed circle) and **cp97** (closed square) in thin film. Excitation wavelengths were 346 nm for all polymers. Inset shows PL spectra of model fluorophores **6'** (open circle, excitation wavelength = 365 nm) and **9'** (open square, excitation wavelength = 433 nm) in CHCl₃ (10⁻⁵ M).

chromophores is one of the most important factors.¹³ In copolymer cp67, one arylenevinylene fluorophore (energy acceptor) is surrounded by many carbazole-fluorene-carbazole chromophores (energy donor) to efficiently collect an excited energy. We have also synthesized another copolymer cp611 containing the arylenevinylene segment having the cyano group at α -position of 11 mol % (not described here), which had decreased relative QY of 0.65 to further support the presence of energy-harvesting phenomenon. In sharp contrast, the emission spectrum of copolymer cp97 showed bimodal peak consisted of 410 and 528 nm. The emission band at 410 nm may be ascribed to fluorescence from the carbazole-fluorene-carbazole segment. The emission maximum observed at 528 nm obviously red-shifted from that of energy-accepting model fluorophore 9' in both CHCl₃ solution (Fig. 6, inset) and thin film (Supporting Information Fig. S12) (504 nm). The relative QY of copolymer cp97 in thin film (0.63) calculated using homopolymer hp as a standard (QY = 1.0) was higher than that in CHCl₃ (0.13) but unexpectedly lower compared with that of copolymer cp67 (1.6), although model fluorophore 9' was a good light emitter $(QY = 0.25 \text{ in CHCl}_3)$. These facts may suggest the generation of a new emissive species such as a charge-transfer complex (exciplex) resulting from the photo-induced electron transfer from the electron-rich carbazole-fluorene-carbazole segment to the electron-poor arylenevinylene one having the cyano group.¹⁴ This hypothesis was supported by the theoretical calculation of reference compounds at HF/31-G* level of theory (Supporting Information). The reference compound corresponding to the model fluorophore 9' (M9') had rather planar structure compared with that of model fluorophore 6'(M6'), namely, the dihedral angle made of central phenylene ring and cyano-substituted vinylene group was 37° in M9', whereas that was 48° in M6' (Supporting Information Fig. S13). These data also agreed with the experimental results in the absorption spectra of model fluorophores 6' and 9'(Fig. 5). The HOMO/LUMO energy levels were determined to be -7.70 eV/1.55 eV and -7.56 eV/1.08 eV for M6' and M9', respectively. The similar theoretical calculation was carried out for the carbazole-fluorene-carbazole segment (MD in Supporting Information Fig. S13), and HOMO/LUMO energy levels were determined to be -6.66 eV/2.37 eV. Accordingly, the energy level of HOMO of MD was closer to that of LUMO of M9' than that of M6' to favor the more efficient orbital interaction (charge transfer).

CONCLUSIONS

Two cyano-substituted arylenevinylene fluorophores (**6** and **9**) sandwiched with 3-bromocarbazole were synthesized, in which the cyano group was introduced at α -position (**6**) and β -position (**9**) from the dialkoxylphenylene unit. The Suzuki coupling copolymerization of these monomers with 1,4-bis[(3-bromocarbazole-9-yl)methylene]-2,5-didecyloxybenzene and 9,9-dihexylfluorene-2,7-bis(boronic acid) gave rise to copolymers (**cp67** and **cp97**) bearing arylenevinylene fluorophores of 7 mol %. Copolymers in CHCl₃ had the absorption and emission maxima originated from the carbazole-fluo-

rene-carbazole segment, which indicated the insufficient FRET and/or the low light-emitting potential of the energyaccepting fluorophore. In thin film, fluorescence from copolymer **cp67** was observed at longer wavelength region through the intramolecular and intermolecular FRET, and the relative QY was improved because of the energy-harvesting phenomenon. The PL spectrum of copolymer **cp97** might suggest a new emissive species such as a charge-transfer complex (exciplex) by the photo-induced electron transfer from electron-rich carbazole-fluorene-carbazole segment to electronpoor arylenevinylene one having the cyano group.

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