

# Band-gap tuning of carbazole-containing donor–acceptor type conjugated polymers by acceptor moieties and $\pi$ -spacer groups

Tsuyoshi Michinobu<sup>a,b,\*</sup>, Kensuke Okoshi<sup>a</sup>, Haruka Osako<sup>a</sup>,  
Hiroe Kumazawa<sup>a</sup>, Kiyotaka Shigehara<sup>a,b,\*\*</sup>

<sup>a</sup> Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

<sup>b</sup> Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received 31 August 2007; received in revised form 24 October 2007; accepted 12 November 2007

Available online 17 November 2007

## Abstract

Carbazole-containing donor–acceptor type conjugated polymers were prepared by Sonogashira cross-coupling reaction of 3,6-diethynyl-9-hexadecylcarbazole and arylene dibromides, and the optical and electrochemical properties were extensively investigated. Copolymerization with 4,7-dibromo-2,1,3-benzothiadiazole furnished the orange-colored polymer with a charge-transfer band at 440 nm in  $\text{CH}_2\text{Cl}_2$ , indicating efficient intramolecular donor–acceptor interactions. On the other hand, the color of the copolymer with 2,5-dibromopyridine was ochre and the longest wavelength absorption band was 381 nm in  $\text{CH}_2\text{Cl}_2$ , suggesting almost negligible donor–acceptor interactions. This difference was also reflected by the emission spectra, solvatochromic behaviors, and electrochemical redox potentials. Comparison of the ethynylene spacer between the donor and acceptor moieties to other  $\pi$ -spacers revealed that the ethynylene spacer serves as a more efficient  $\pi$ -spacer than vinylene and direct connection (without spacer) for strong donor–acceptor coupling in this polymer system.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Carbazole; Conjugated polymers; Donor-acceptor systems

## 1. Introduction

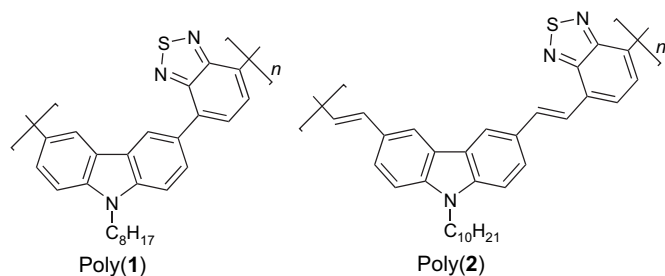
Donor–acceptor (D–A) type conjugated polymers have attracted increasing attention since they can serve as efficient nonlinear optical (NLO) and electrochromic materials as well as low-band-gap polymers with high intrinsic conductivity in the neutral state [1–11]. The NLO effects and the electronic properties are highly dependent on the polymer band gaps associated with intramolecular D–A interactions. Carbazole is known not only as an efficient short wavelength emitter

but also as a strong electron-donating chromophore. The conjugative coupling with electron-accepting moieties through a  $\pi$ -spacer results in a charge-transfer band caused by the intramolecular D–A interactions. The strength of D–A interactions is determined by acceptor groups and  $\pi$ -conjugated spacers. Strong electron-accepting groups and short spacers generally enhance the D–A interactions, whereas weak electron-accepting groups and long spacers lower the D–A strength. To utilize these characteristics in practical optoelectronic materials, many conjugated carbazole polymers have been prepared and the properties were extensively investigated [12–17]. One of the most common approaches to conjugated carbazole polymers is the connection at 3,6-positions through  $\pi$ -conjugated spacers [18–30]. For example, some alternating copolymers, poly(1) and poly(2), of electron-donating carbazole and electron-accepting benzothiadiazole groups via direct connection and through a vinylene spacer, respectively, have been prepared, and they were revealed to show excellent electrochromic and electroluminescent properties based on

\* Corresponding author. Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. Tel.: +81 42 388 7406; fax: +81 42 381 8175.

\*\* Corresponding author. Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. Tel.: +81 42 388 7502; fax: +81 42 381 8175.

E-mail addresses: [tmichi@cc.tuat.ac.jp](mailto:tmichi@cc.tuat.ac.jp) (T. Michinobu), [jun@cc.tuat.ac.jp](mailto:jun@cc.tuat.ac.jp) (K. Shigehara).



Scheme 1.

the D–A interactions (Scheme 1) [31–34]. However, another advantageous  $\pi$ -spacer of ethynylene group has never been applied to the alternating conjugated polymer composed of the same donor and acceptor combination [35]. An ethynylene spacer is an important class of  $\pi$ -spacers for efficient electronic communication of  $\pi$ -chromophores and for construction of poly(arylene ethynylene)s by Sonogashira cross-coupling reaction [36,37].

In this paper we report the preparation of novel carbazole-containing D–A type conjugated polymers by Sonogashira cross-coupling reaction. Efficiency of D–A strength in the polymers was characterized by optical absorption and emission spectroscopy as well as electrochemistry. The D–A type polymers showed significant solvent-dependence of optical absorption and emission spectra. Especially for the polymer with benzothiadiazole acceptors, the intensity of the charge-transfer band can be controlled by addition of trifluoroacetic acid (TFA) or methanol.

## 2. Experimental section

### 2.1. Measurements

$^1\text{H}$  NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from  $\text{SiMe}_4$ , using the solvent's residual signal as an internal reference. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV–vis spectra were recorded on a JASCO V-550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP6500 spectrophotometer. Gel permeation chromatography (GPC) was measured on a JASCO system (PU-980, CO-965, RI-930, UV-970, and AS-950) equipped with polystyrene gel columns using THF as an eluent at a flow rate of  $1.0 \text{ ml min}^{-1}$  after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was carried out on a Rigaku Thermoplus TG 8120, at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  between 20 °C and 500 °C. Differential scanning calorimetry (DSC) measurements were carried out on a Rigaku Thermoplus DSC 8230 equipped with  $\text{LN}_2$  controller. Electrochemistry measurements were carried out at 20 °C in a classical three-electrode cell. The working and auxiliary electrodes were a glassy carbon disk electrode ( $0.07 \text{ cm}^2$ ) and Pt, respectively. The reference electrode was  $\text{Ag}/\text{Ag}^+/\text{CH}_3\text{CN}/n\text{Bu}_4\text{NClO}_4$  for both solution and thin film measurements. Polymer thin films on a glassy carbon

disk electrode were prepared by casting the  $\text{CH}_2\text{Cl}_2$  solution followed by drying under air.

### 2.2. Materials

Chemicals and dehydrated solvents were purchased from Kanto, Tokyo Kasei, and Wako, and used as received. 3,6-Diethynyl-9-hexadecylcarbazole was prepared according to the literature procedure from 9-hexadecylcarbazole by iodination followed by Sonogashira cross-coupling reaction with trimethylsilylacetylene and the deprotection of the silyl group [38]. 4,7-Dibromo-2,1,3-benzothiadiazole was prepared by bromination of commercially available 2,1,3-benzothiadiazole [39].

### 2.3. Polymerization

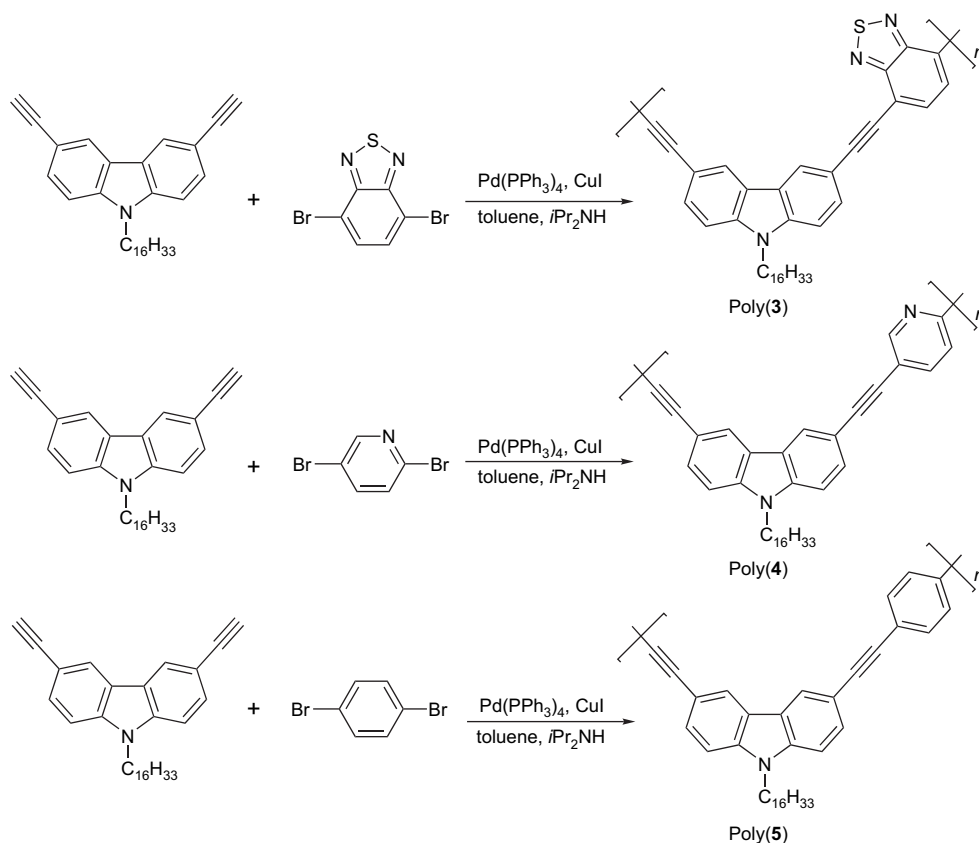
All the polymerizations were carried out by Sonogashira cross-coupling reaction of the two monomers in an inert atmosphere. In a glove box 3,6-diethynyl-9-hexadecylcarbazole (100 mg, 0.227 mmol), arylene dibromide (0.227 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (10.5 mg, 9.72  $\mu\text{mol}$ ), and  $\text{CuI}$  (1.7 mg, 9.0  $\mu\text{mol}$ ) were placed in a Schlenk tube. After addition of deoxygenated toluene (3.0 ml) and diisopropylamine (1.5 ml), the tube was removed from the glove box and then heated to 60 °C for 24 h. After cooling to room temperature, the polymerization mixture was poured into a large amount of methanol to precipitate a polymer, which was collected by filtration followed by drying in vacuo at room temperature.

Poly(3):  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.90\text{--}0.92$  (*br*,  $-\text{CH}_3$ ), 1.10–1.34 (*br*,  $-\text{CH}_2-$ ), 3.57 (*br s*,  $\text{N}-\text{CH}_2-$ ), 6.83–8.40 ppm (*br*, ArH); IR (KBr):  $\nu = 2923, 2851, 2203, 2140, 1623, 1595, 1483, 1383, 1350, 1286, 1236, 1149, 1132, 882, 841, 806, 723, 653, 590 \text{ cm}^{-1}$ . Poly(4):  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.90\text{--}0.92$  (*br*,  $-\text{CH}_3$ ), 1.10–1.34 (*br*,  $-\text{CH}_2-$ ), 3.54–3.56 (*br*,  $\text{N}-\text{CH}_2-$ ), 6.82–9.11 ppm (*br*, ArH); IR (KBr):  $\nu = 2923, 2852, 2209, 2140, 1627, 1595, 1564, 1540, 1485, 1467, 1383, 1351, 1286, 1235, 1149, 1132, 1089, 1002, 880, 832, 806, 742, 727 \text{ cm}^{-1}$ . Poly(5):  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 0.92$  (*br s*,  $-\text{CH}_3$ ), 1.07–1.32 (*br*,  $-\text{CH}_2-$ ), 3.49–3.62 (*br*,  $\text{N}-\text{CH}_2-$ ), 6.81–8.32 ppm (*br*, ArH); IR (KBr):  $\nu = 2923, 2852, 2208, 2139, 1628, 1596, 1483, 1467, 1383, 1351, 1286, 1236, 1149, 1132, 1069, 1022, 1010, 882, 805, 723, 653, 590 \text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Polymer synthesis and characterization

All the polymers were prepared by Sonogashira cross-coupling reaction between 3,6-diethynyl-9-hexadecylcarbazole and arylene dibromides (Scheme 2). The polymerization results are summarized in Table 1. The carbazole monomer and the arylene dibromides were reacted in toluene/ $i\text{Pr}_2\text{NH}$  (2:1) mixtures at 60 °C for 24 h in the presence of  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{CuI}$  as catalysts. The monomer feed ratio was maintained at  $[\text{C}\equiv\text{CH}]/[\text{Br}] = 1:1$  so as to furnish larger molecular weight



Scheme 2.

polymers. Poly(3) and Poly(4) possessing benzothiadiazole and pyridine electron-accepting moieties, respectively, were obtained as an orange and ochre solid, respectively, reflecting the different intramolecular D–A strength (vide infra). Poly(5) was prepared as a control sample without D–A interactions. As shown in Table 1, all polymers were obtained in moderate yields (61–67%) with reasonable molecular weights, e.g., a number average molecular weight,  $M_n$ , of 6000 for poly(4) determined by GPC (THF eluent, calibrated with polystyrene standards). The polymer structures were characterized by  $^1\text{H}$  NMR and FT-IR spectra. In the  $^1\text{H}$  NMR spectra, the alkyne peak of the carbazole monomer almost completely disappeared after the polymerization (Fig. 1). The IR absorption bands were consistent with the  $^1\text{H}$  NMR results. The  $\text{C}\equiv\text{C}-\text{H}$  and  $\text{C}\equiv\text{C}$  stretching vibrations of the carbazole monomer at 3291 and 2103  $\text{cm}^{-1}$ , respectively, became negligible after the polymerization, and a new peak ascribed to the  $\text{C}\equiv\text{C}$

bond of poly(arylene ethynylene)s appeared at 2203  $\text{cm}^{-1}$  for poly(3), 2209  $\text{cm}^{-1}$  for poly(4), and 2208  $\text{cm}^{-1}$  for poly(5). The polymers are highly soluble in common organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , toluene, and THF, but sparsely soluble in methanol and hexane.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) in the temperature range of 25–500  $^\circ\text{C}$  (Fig. 2). TGA indicated that all polymers were so thermally stable that they did not show any noticeable weight loss at least up to 300  $^\circ\text{C}$ . The 5% weight loss temperatures were determined to be 402  $^\circ\text{C}$  for poly(3), 353  $^\circ\text{C}$  for poly(4), and 386  $^\circ\text{C}$  for poly(5). The values are comparable to those reported for other carbazole-containing conjugated polymers [34].

### 3.2. UV–vis and fluorescence spectra

Optical properties were investigated in various solvents. Fig. 3 shows the UV–vis and fluorescence spectra of poly(3), poly(4), and poly(5) in  $\text{CH}_2\text{Cl}_2$ . Poly(3) displayed a distinct charge-transfer band at 440 nm ascribed to the intramolecular D–A interactions between carbazole donor and benzothiadiazole acceptor moieties, whereas the longest wavelength absorption band of poly(4) was almost the same as that of poly(5) without acceptor moieties. This result indicates that benzothiadiazole moiety is a stronger electron-acceptor than pyridine moiety. The optical band gaps of poly(3) and poly(4), estimated from the end absorptions in  $\text{CH}_2\text{Cl}_2$ , were

Table 1  
Polymerization results<sup>a</sup>

Polymer	Yield <sup>b</sup> (%)	$M_w \times 10^{-3c}$	$M_n \times 10^{-3c}$	$M_w/M_n^c$
Poly(3)	61	7.22	4.73	1.53
Poly(4)	67	15.5	6.00	2.58
Poly(5)	61	26.7	17.2	1.56

<sup>a</sup> All polymerizations were carried out in toluene/ $i\text{Pr}_2\text{NH}$  (2:1) at 60  $^\circ\text{C}$  for 24 h:  $[\text{M}] = 50 \text{ mM}$ ;  $[\text{Pd}(\text{PPh}_3)_4] = [\text{CuI}] = 2 \text{ mM}$ .

<sup>b</sup> After precipitation into methanol.

<sup>c</sup> Determined by GPC (THF eluent, calibrated by polystyrene standard).

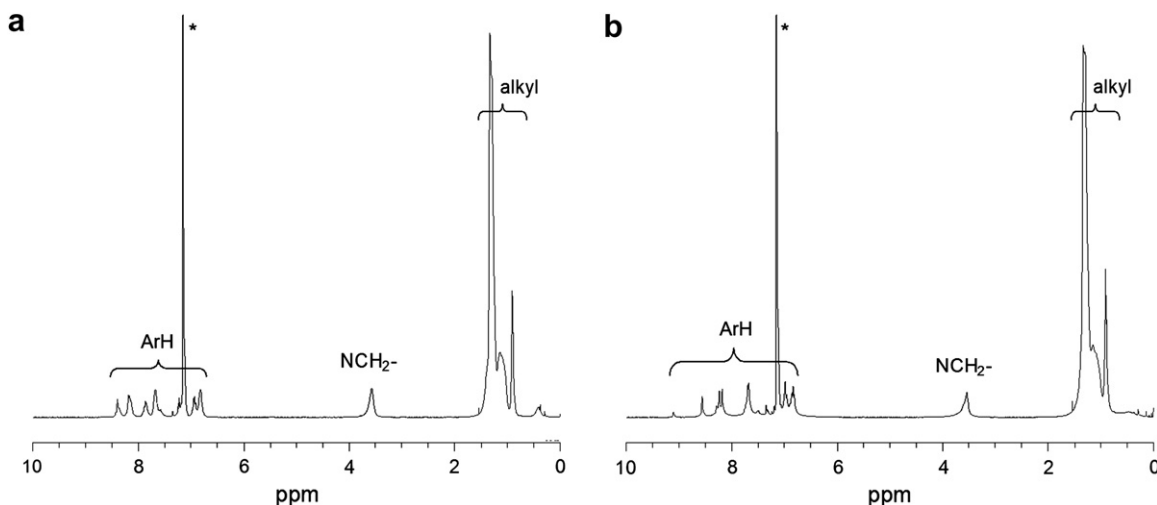


Fig. 1.  $^1\text{H}$  NMR spectra of (a) poly(3) and (b) poly(4) in  $\text{C}_6\text{D}_6$  at  $20^\circ\text{C}$ . The residual solvent peak is marked.

2.30 eV (539 nm) and 2.74 eV (453 nm), respectively. Copolymerization with a stronger electron-accepting monomer reasonably reduces the band gap of the resulting carbazole polymer. Poly(3) showed a strong emission at 566 nm in  $\text{CH}_2\text{Cl}_2$ , indicating complete quenching of the emission from carbazole moiety. On the other hand, poly(4) and poly(5) displayed the emission from carbazole moiety, suggesting negligible D–A interactions in these polymers. In contrast to the absorption spectra, the shape of fluorescence spectra of poly(4) and poly(5) were different. Poly(4) showed a monomodal emission peak similar to that of poly(3), whereas poly(5) displayed multiple shoulders with the end emission reaching 700 nm.

These absorption and emission bands, especially of poly(3), showed a distinct solvatochromism. From  $\text{CH}_2\text{Cl}_2$  ( $\lambda_{\text{max}} = 440$  nm, 2.82 eV;  $\lambda_{\text{em,max}} = 566$  nm, 2.19 eV) to hexane ( $\lambda_{\text{max}} = 421$  nm, 2.95 eV;  $\lambda_{\text{em,max}} = 494$  nm, 2.51 eV), well-defined large shifts of 0.13 and 0.32 eV for absorption and emission spectra, respectively, are observed for poly(3)

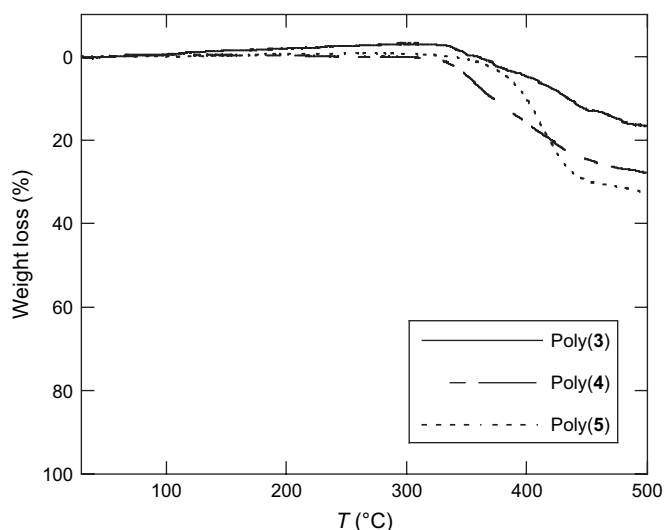


Fig. 2. Thermogravimetric analysis of poly(3), poly(4), and poly(5).

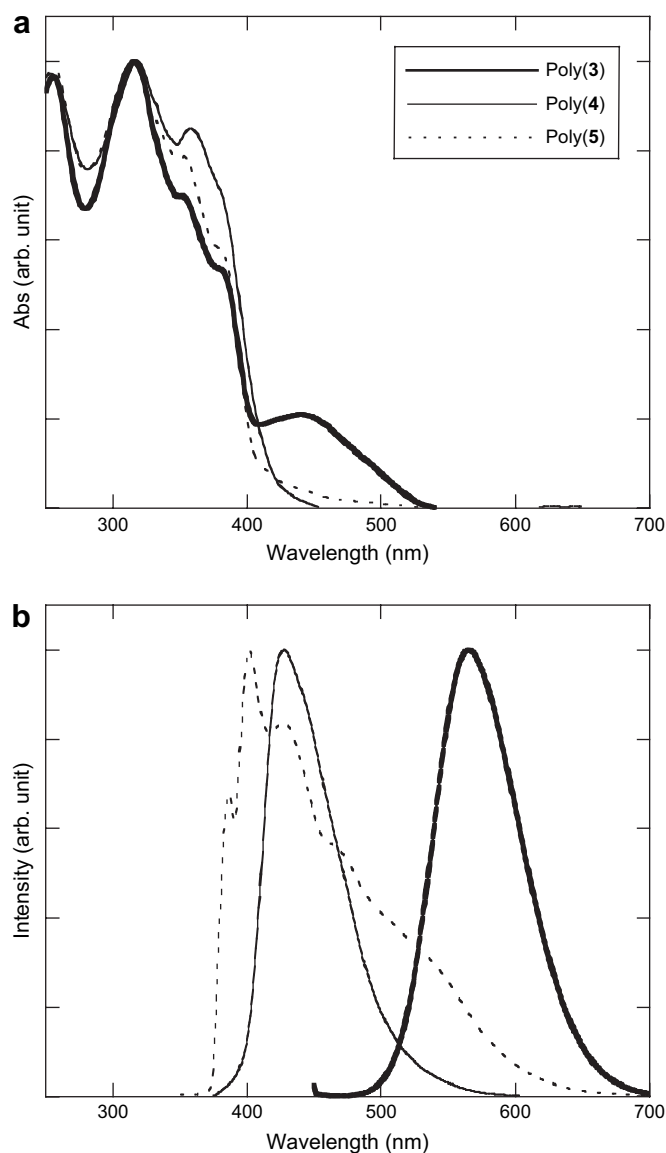


Fig. 3. (a) UV–vis and (b) fluorescence spectra of poly(3), poly(4), and poly(5) in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .

Table 2  
Optical properties of the carbazole polymers

Polymer	Solvent	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{em,max}}$ (nm)	Stoke shift ( $\text{cm}^{-1}$ )
Poly(3)	$\text{CH}_2\text{Cl}_2$	440, 384 <sup>a</sup> , 351 <sup>a</sup> , 316	566	5060
Poly(4)	$\text{CH}_2\text{Cl}_2$	381 <sup>a</sup> , 358, 318	428	2882
Poly(5)	$\text{CH}_2\text{Cl}_2$	382 <sup>a</sup> , 353, 315	537 <sup>a</sup> , 470 <sup>a</sup> , 428, 402	<sup>b</sup>
Poly(3)	Hexane	421, 307	494 <sup>a</sup> , 474	3673
Poly(4)	Hexane	373 <sup>a</sup> , 318	415, 395	2713
Poly(5)	Hexane	372 <sup>a</sup> , 308	418, 404	2958

<sup>a</sup> Shoulder.

<sup>b</sup> Could not be determined due to the uncertainty of  $\lambda_{\text{max}}$  and  $\lambda_{\text{em,max}}$ .

(Table 2). The emission spectra of poly(3) displayed a greater solvatochromic effect than the absorption spectra in the same solvents, and accordingly the large Stokes shift of  $5060 \text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , representing a large transition dipole moment of poly(3), became much smaller in hexane ( $3673 \text{ cm}^{-1}$ ). In contrast, solvatochromic effects of poly(4) and poly(5) are not significant, and the values of the Stokes shift are almost of the same order of magnitude in both  $\text{CH}_2\text{Cl}_2$  and hexane.

The above results clearly demonstrate that the strength of the D–A interactions in the carbazole-containing polymers can be tuned by the acceptor moieties. Copolymerization with the stronger electron-accepting benzothiadiazole moiety results in the larger D–A interactions. However, a larger D–A interaction does not always lead to a smaller band gap [40–42]. In a  $\pi$ -conjugated system, efficient D–A conjugation lowers the HOMO level and elevates the LUMO level, and weaker D–A coupling, in contrast, elevates the HOMO level and lowers the LUMO level. In addition to the combination of donor and acceptor chromophores,  $\pi$ -spacers between them are also known to play an important role in determining D–A coupling strength [43,44]. Therefore, to prove these criteria in polymer systems, we compared the charge-transfer band of poly(3) to the reported values of poly(1) and poly(2) composed of the same donor and acceptor combination but different  $\pi$ -spacer groups. In thin film states poly(3) displayed the charge-transfer band at 453 nm, which is bathochromically shifted relative to those in solutions. The  $\lambda_{\text{max}}$  values of poly(1) and poly(2), in which donor and acceptor moieties are connected directly and through vinylene spacer, respectively, are reported to be 465 and 504 nm in thin film states [31,34]. Previously, an ethynylene spacer inserted between donor and acceptor groups clearly weakened the D–A coupling because of the elongated distance between donor and acceptor moieties [45,46]. However, in this case, insertion of the ethynylene spacer results in a hypsochromic shift of the  $\lambda_{\text{max}}$ , representing an enhanced D–A coupling. This is probably caused by the sterically enforced deconjugation between donor and acceptor groups in poly(1), i.e., the arylene units are twisted with respect to each other. Comparison of the charge-transfer band positions of poly(2) and poly(3) indicates that the ethynylene spacer much more efficiently strengthens the D–A coupling than the vinylene spacer. Consequently, efficiency of the intramolecular charge-transfer in the ground state increases in the order of poly(2) < poly(1) < poly(3).

We also found that intensity of the charge-transfer band of poly(3) can be controlled by addition of trifluoroacetic acid (TFA) or methanol. It is known that TFA undergoes protonation of amine moiety, leading to disappearance of the electron-donating ability. Accordingly, upon protonation of the carbazole moieties with TFA, the solution of poly(3) became almost colorless and the intensity of the charge-transfer band significantly decreased (Fig. 4). The charge-transfer band can be fairly regenerated upon neutralization with triethylamine (TEA). Addition of methanol is known to induce aggregation of  $\pi$ -conjugated polymers and this has been investigated for many poly(arylene ethynylene)s including carbazole-containing polymers [47–50]. As the content of methanol increased, the absorption bands of poly(4) and poly(5) became broader and red-shifted tails as well as slightly blue-shifted absorption maxima were generated (Fig. 5). This result is consistent with the previous report by Leclerc, suggesting that significant excitonic coupling caused such solvatochromic effects [50]. On the other hand, addition of methanol to a  $\text{CH}_2\text{Cl}_2$  solution of poly(3) brings about different chromic behavior. As an increase in methanol content, the intensity of the charge-transfer band of poly(3) decreased and the shoulder peaks at 351 and 384 nm were hypsochromically shifted

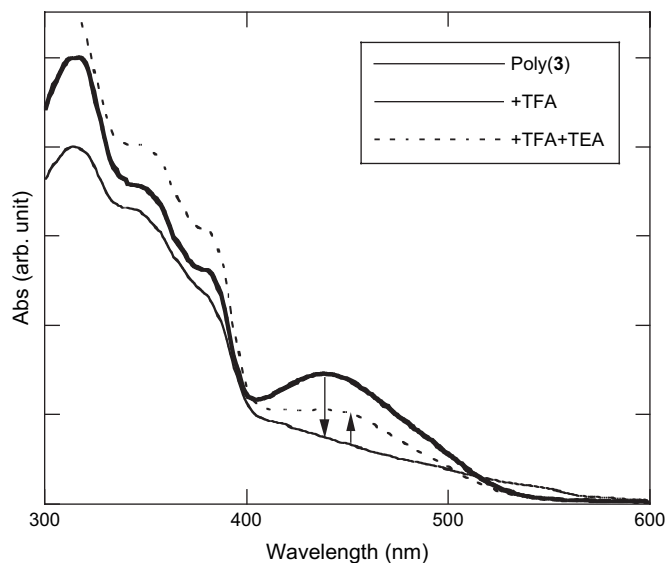


Fig. 4. Intensity shift of the charge-transfer band of poly(3) in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  upon addition of trifluoroacetic acid followed by triethylamine.

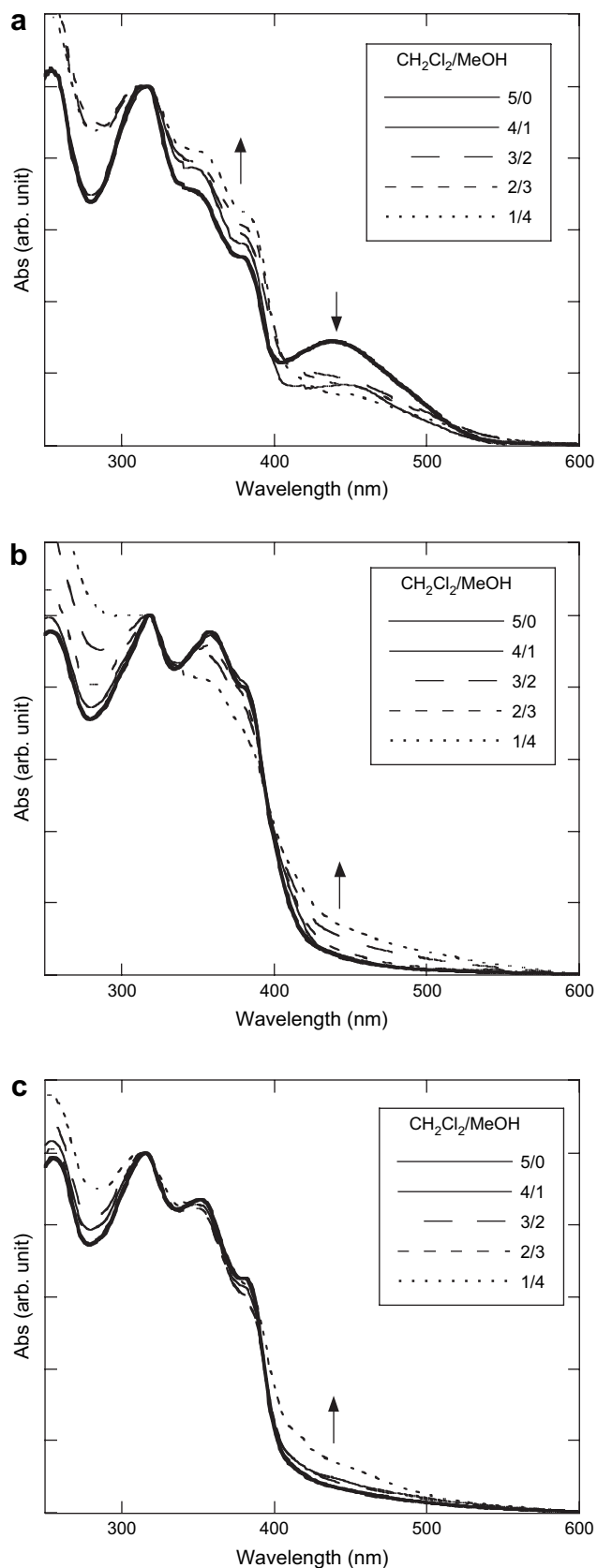


Fig. 5. Solvent dependent UV–vis spectra of (a) poly(3), (b) poly(4), and (c) poly(5) in various  $\text{CH}_2\text{Cl}_2$ /methanol mixtures at 20 °C.

Table 3  
Electrochemical data of the carbazole polymers<sup>a</sup>

Polymer		Cyclic voltammetry		Differential pulse voltammetry
		$E^{\text{od}}$ (V)	$E_{\text{p}}^{\text{c}}$ (V)	$E^{\text{od}}$ (V)
Poly(3)	In solution <sup>b</sup>	0.92, 1.49	1.10, 1.47	0.94, 1.23
Poly(4)	In solution <sup>b</sup>		1.03, 1.17	0.94, 1.07
Poly(5)	In solution <sup>b</sup>			0.93, 1.47
Poly(3)	Film <sup>c</sup>		0.94	0.96, 1.18
Poly(4)	Film <sup>c</sup>		0.91	0.96
Poly(5)	Film <sup>c</sup>		0.90	0.94, 1.20

<sup>a</sup> Potentials vs.  $\text{Ag}/\text{Ag}^+$  couple. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode:  $\text{Ag}/\text{Ag}^+$ .

<sup>b</sup> In  $\text{CH}_2\text{Cl}_2$  (1 mM/repeat unit) with 0.1 M  $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$  at 20 °C. Scanning rate of 0.1  $\text{V s}^{-1}$  for CV.  $\text{Fc}/\text{Fc}^+ = 0.21$  V.

<sup>c</sup> In  $\text{CH}_3\text{CN}$  with 0.1 M  $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$  at 20 °C. Scanning rate of 0.1  $\text{V s}^{-1}$  for CV.  $\text{Fc}/\text{Fc}^+ = 0.08$  V.

<sup>d</sup>  $E^{\text{od}} = (E_{\text{pa}} + E_{\text{pc}})/2$ , in which  $E_{\text{pa}}$  and  $E_{\text{pc}}$  correspond to the anodic and cathodic peak potentials, respectively.

<sup>e</sup>  $E_{\text{p}} =$  Irreversible oxidation peak potential at scanning rate of 0.1  $\text{V s}^{-1}$ .

(Fig. 5). This can be explained by the formation of J-aggregates. We speculate that the aggregation induced the sterically twisted deconjugation between donor and acceptor moieties, leading to insufficient D–A interactions and, consequently, a decrease in the intensity of the charge-transfer band. It should be noted that the cast film of poly(3) possesses the strong charge-transfer band, suggesting the different aggregation behavior in  $\text{CH}_2\text{Cl}_2$ /methanol mixtures.

### 3.3. Electrochemistry

Electrochemical properties of the carbazole-containing polymers were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in solutions and in the cast films. The redox potentials are summarized in Table 3.

Although all the polymers could be oxidized in the reasonable potential range, the first oxidation waves of D–A type polymers were not reversible in the CV time scale. This is because the oxidized arylamine moieties feature a strong electron-acceptor and the conjugative coupling with other electron-accepting groups dramatically lowers the chemical stability. Unlike very broad and featureless CV traces in  $\text{CH}_2\text{Cl}_2$ , those of the cast film on the glassy carbon electrode exhibited well-defined oxidation potentials (Fig. 6). The potential difference reflects the D–A coupling strength in the polymers. Coupling with a stronger electron-acceptor such as benzothiadiazole moiety makes the oxidation of carbazole donor more difficult. On the other hand, a weaker acceptor group does not significantly affect the oxidation potentials. This result is fully consistent with the UV–vis absorption spectra of the polymers (vide supra). The DPV revealed almost the same oxidation potentials for these polymers, indicating the close HOMO levels. Difference in the polymer band gaps was therefore thought to be derived from the difference in the LUMO levels. However, reduction potentials of acceptor

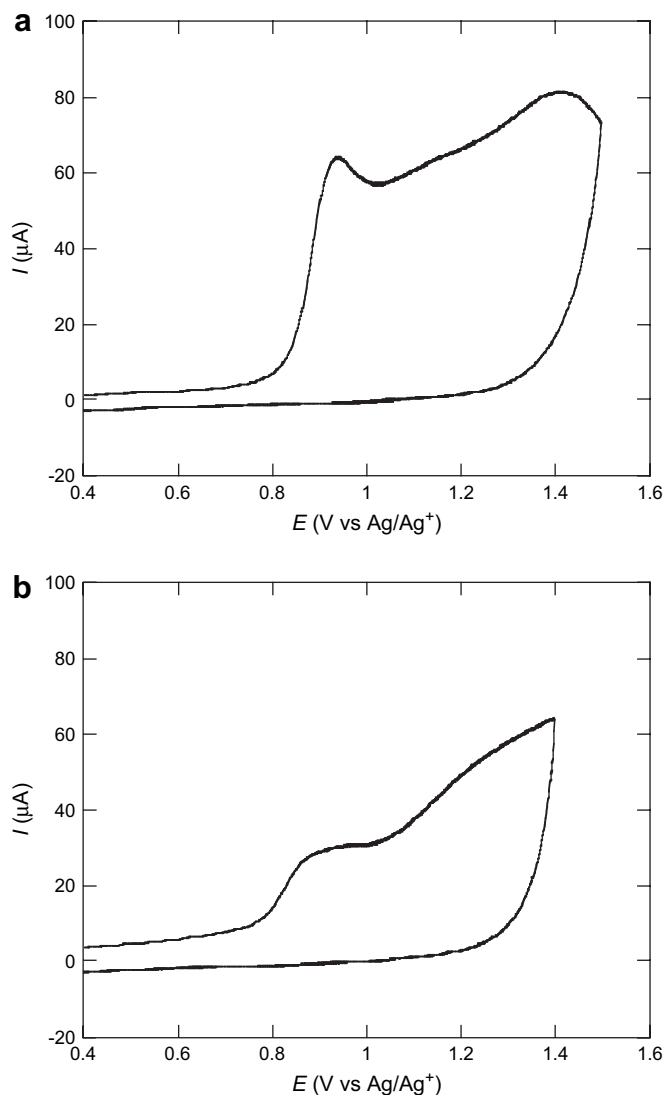


Fig. 6. Cyclic voltammetry of the cast films of (a) poly(3) and (b) poly(4) measured in  $\text{CH}_3\text{CN}$  with 0.1 M  $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$  at 20 °C, at scanning rate of 0.1  $\text{V s}^{-1}$ .

moieties were not observed even for benzothiadiazole moiety, in spite of several trials under different conditions.

#### 4. Conclusion

We have shown the band gap tuning of the D–A type conjugated polymers containing carbazole units in the main chain, prepared by Sonogashira cross-coupling reaction of 3,6-diethyl-nylcarbazole derivative and arylene dibromides. Copolymerization with a stronger electron-acceptor leads to more efficient intramolecular D–A coupling, which was evaluated by the optical absorption spectra of the charge-transfer band as well as the electrochemical oxidation potentials. Appearance of the charge-transfer band and the anodic shift in the oxidation potential of poly(3) with respect to poly(4) clearly demonstrate this. When poly(3) was compared to the previously reported poly(1) and poly(2), the ethynylene spacer was proven to be the most effective  $\pi$ -spacer for strong D–A coupling in this case.

#### Acknowledgements

This work was supported, in part, by a Grant-in-Aids from the Ministry of Education, Science, Sports and Culture, Japan, Iketani Science and Technology Foundation, and Ogasawara Foundation for the Promotion of Science and Engineering. We thank Prof. H. Oike (Tokyo University of Agriculture and Technology) for the assistance in the GPC measurements and Prof. T. Watanabe (Tokyo University of Agriculture and Technology) for the use of the electrochemical setup.

#### References

- [1] Yamamoto T, Zhou ZH, Kanbara T, Shimura M, Kizu K, Maruyama T, et al. *J Am Chem Soc* 1996;118:10389.
- [2] Bangcuyo CG, Evans U, Myrick ML, Bunz UHF. *Macromolecules* 2001;34:7592.
- [3] Thomas CA, Zong K, Abboud KA, Steel PJ, Reynolds JR. *J Am Chem Soc* 2004;126:16440.
- [4] Berlin A, Zotti G, Zecchin S, Schiavon G, Vercelli B, Zanelli A. *Chem Mater* 2004;16:3667.
- [5] Yasuda T, Imase T, Nakamura Y, Yamamoto T. *Macromolecules* 2005;38:4687.
- [6] Jiang J, Xu Y, Yang W, Guan R, Liu Z, Zhen H, et al. *Adv Mater* 2006;18:1769.
- [7] Mühlbacher D, Scharber M, Morana M, Zhu Z, Waller D, Gaudiana R, et al. *Adv Mater* 2006;18:2884.
- [8] Edler C, Armstrong PB, Prado KB, Fréchet JMJ. *Chem Commun* 2006:1965.
- [9] Bundgaard E, Krebs FC. *Macromolecules* 2006;39:2823.
- [10] Zhu Y, Chmption RD, Jenekhe SA. *Macromolecules* 2006;39:8712.
- [11] Colladet K, Fourier S, Cleij TJ, Lutsen L, Gelan J, Vanderzande D, et al. *Macromolecules* 2007;40:65.
- [12] Xia C, Advincula RC. *Macromolecules* 2001;34:5854.
- [13] Zhang ZB, Fujiki M, Tang HZ, Motonaga M, Torimitsu K. *Macromolecules* 2002;35:1988.
- [14] Grazulevicius JV, Strohrriegl P, Pielichowski J, Pielichowski K. *Prog Polym Sci* 2003;28:1297.
- [15] Zhang ZB, Motonaga M, Fujiki M, McKenna CE. *Macromolecules* 2003;36:6956.
- [16] Xia C, Advincula RC, Baba A, Knoll W. *Chem Mater* 2004;16:2852.
- [17] Sanda F, Nakai T, Kobayashi N, Masuda T. *Macromolecules* 2004;37:2703.
- [18] Beginn C, Grazulevicius JV, Strohrriegl P, Simmerer J, Haarer D. *Macromol Chem Phys* 1994;195:2353.
- [19] Kanbara T, Ishii T, Hasegawa K, Yamamoto T. *Polym Bull* 1996;36:673.
- [20] Tao XT, Zhang YD, Wada T, Sasabe H, Suzuki H, Watanabe T, et al. *Appl Phys Lett* 1997;71:1921.
- [21] Kanbara T, Ohshima S, Hasegawa K, Takeuchi S. *Polym Bull* 1997;39:453.
- [22] Tao XT, Zhang YD, Wada T, Sasabe H, Suzuki H, Watanabe T, et al. *Adv Mater* 1998;10:226.
- [23] Maruyama S, Tao XT, Hokari H, Noh T, Zhang Y, Wada T, et al. *J Mater Chem* 1999;9:893.
- [24] Maruyama S, Hokari H, Tao XT, Gunji A, Wada T, Sasabe H. *Chem Lett* 1999:731.
- [25] Sakamaki K, Ohshita J, Kuani A, Nakao H, Adachi A, Okita K. *Appl Organomet Chem* 2001;15:604.
- [26] Maruyama S, Hokari H, Wada T, Sasabe H. *Synthesis* 2001:1794.
- [27] Wong WY, Lu GL, Choi KH, Shi JX. *Macromolecules* 2002;35:3506.
- [28] Brizius G, Kroth S, Bunz UHF. *Macromolecules* 2002;35:5317.
- [29] Takihana Y, Shiotsuki M, Sanda F, Masuda T. *Macromolecules* 2004;37:757.
- [30] Liu L, Wong WY, Poon SY, Cheah KW. *J Inorg Organomet Polym Mater* 2006;15:555.

- [31] Huang J, Niu Y, Yang W, Mo Y, Yuan M, Cao Y. *Macromolecules* 2002; 35:6080.
- [32] Huang J, Niu Y, Xu Y, Hou Q, Yang W, Mo Y, et al. *Synth Met* 2003; 135–136:181.
- [33] Witker D, Reynolds JR. *Macromolecules* 2005;38:7636.
- [34] Du J, Fang Q, Chen X, Ren S, Cao A, Xu B. *Polymer* 2005;46: 11927.
- [35] Michinobu T, Okoshi K, Osako H, Kumazawa H, Shigehara K. *J Photopolym Sci Technol* 2007;20:255.
- [36] Voskerician G, Weder C. *Adv Polym Sci* 2005;177:209.
- [37] Chinchilla R, Nájera C. *Chem Rev* 2007;107:874.
- [38] Zhao T, Liu Z, Song Y, Xu W, Zhang D, Zhu D. *J Org Chem* 2006; 71:7422.
- [39] Huang J, Xu Y, Hou Q, Yang W, Yuan M, Cao Y. *Macromol Rapid Commun* 2003;23:709.
- [40] Moonen NNP, Gist R, Boudon C, Gisselbrecht JP, Seiler P, Kawai T, et al. *Org Biomol Chem* 2003;1:2032.
- [41] Moonen NNP, Diederich F. *Org Biomol Chem* 2004;2:2263.
- [42] Moonen NNP, Pomerantz WC, Gist R, Boudon C, Gisselbrecht JP, Kawai T, et al. *Chem Eur J* 2005;11:3325.
- [43] Meier H, Gerold J, Kolshorn H, Baumann W, Bletz M. *Angew Chem Int Ed* 2002;41:292.
- [44] Meier H. *Angew Chem Int Ed* 2005;44:2482.
- [45] Michinobu T, May JC, Lim JH, Boudon C, Gisselbrecht JP, Seiler P, et al. *Chem Commun* 2005:737.
- [46] Michinobu T, Boudon C, Gisselbrecht JP, Seiler P, Frank B, Moonen NNP, et al. *Chem Eur J* 2006;12:1889.
- [47] Halkyard CE, Rampey ME, Kloppenburg L, Studer-Martinez SL, Bunz UHF. *Macromolecules* 1998;31:8655.
- [48] Miteva T, Palmer L, Kloppenburg L, Neher D, Bunz UHF. *Macromolecules* 2000;33:652.
- [49] Pschirer NG, Bunz UHF. *Macromolecules* 2000;33:3961.
- [50] Bouchard J, Belletête M, Durocher G, Leclerc M. *Macromolecules* 2003; 36:4624.