Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 5884–5889

polymer

www.elsevier.com/locate/polymer

Novel π-conjugated cyclophane polymers containing phenylamine moieties with strong blue-light emission

Y. Morisaki, N. Wada, Y. Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received 15 April 2005; received in revised form 17 May 2005; accepted 18 May 2005
Available online 14 June 2005

Abstract

Novel through-space conjugated polymers based on poly(*p*-phenylene-ethynylene) (PPE) containing alternate [2.2]paracyclophane and phenylamine moieties in the main chain were synthesized by the Sonogashira coupling reaction. Polymers were soluble in common organic solvents, and transparent and uniform thin films of the polymers were obtained easily by casting or spin-coating from toluene solution. According to the UV–vis absorption spectra, π-electrons of the polymer were delocalized via the through-space interaction between the two benzene rings in the cyclophane unit. The polymer exhibited strong blue emission in solution and in the solid state.

Keywords: Conjugated polymers; Through-space interaction; Blue emission

1. Introduction

The organic light emitting diode (OLED) has recently gained great importance as a flat panel display due to the realization of its quick response, efficient luminance, and wide varieties of colors, as compared to the conventional liquid crystal [1]. Organic light-emitting polymers are promising materials in terms of the feasibility in fine-tuning their luminescent properties by manipulation of their chemical structures. In addition, facile printing processes for large-area flat-panel displays by spin-coating or by the inkjet method are desirable. Although polymer-based light emitting diodes (PLEDs) that produce all three primary colors (red, green, and blue) have been developed, the green and orange PLEDs currently satisfy the requirements of commercial use. Therefore, various polymers for the intense blue LED, such as polymers containing fluorene [2–6] and biphenyl [7,8], have been synthesized and investigated.

In order to improve the efficiency of PLEDs, several layers have been intercalated between two electrodes, e.g. emitting-layer, charge-transporting layer, charge-injection layer, hole-blocking layer, and so on [9–12]. Among them, the emitting- and charge-transporting layers are intrinsically the most important building block, since effective transportation of the hole or the electron is crucial to achieve high quantum efficiency. Nitrogen atom-containing polymers are well known as emitting- and/or charge-transporting materials, such as polyvinylcarbazoles, which are now used for the photosensitive drum of a copy machine [13,14]. Due to their photoactivity, a number of polymers containing nitrogen atoms have been synthesized, and their applications in optoelectronic devices, such as electro-photography, light-emitting diodes, charge-transporting materials, photo-refractive materials, and photo-voltaic devices, have been investigated [15].

On the other hand, [2.2]paracyclophane has a unique structure in which two benzene rings closely face each other. A number of [2.2]paracyclophane derivatives have been prepared, and their structural and electronic properties resulting from characteristic interactions between the two co-facial π-electron systems have been investigated in detail [16–20]. However, only a few reports on conjugated polymers containing cyclophane currently exist [21–27]. We recently reported the synthesis of well-defined conjugated polymers containing a cyclophane skeleton in their polymer backbone [28–39]. We found that the obtained polymers exhibited an extension of π-delocalization via the through-space interaction, and they also exhibited intense photo- or electroluminescence.

---

* Corresponding author. Tel.: +81 75 383 2604; fax: +81 75 383 2605.
E-mail address: chujo@chujo.synchem.kyoto-u.ac.jp (Y. Chujo).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.05.063

In this paper, we report on the successful synthesis of novel [2.2]paracyclophane polymers having phenylamine units as well as their emitting properties. The obtained polymers exhibited a strong blue photoluminescence in solution and in the solid state.

2. Experimental section

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX400 spectrometer. All samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. FT-IR spectra were obtained on a Perkin–Elmer 1600 spectrometer. UV–vis measurements were carried out on JASCO V-530 spectrophotometer at room temperature. Photoluminescence spectra were recorded on a Perkin–Elmer LS50B luminescence spectrometer at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Purification of the obtained polymers was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd, Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

2.2. Materials

THF was distilled from sodium benzophenone ketyl, and triethylamine (TEA) was distilled from KOH. Phenylacetylene was fractionated and stored in nitrogen atmosphere. $Pd(PPh_3)_2Cl_2$, CuI, and PPh_3 were obtained commercially, and used without further purification. 4,16-Diethynyl[2.2]paracyclophane **1** [33] and 4,4′-diiododiphenylamine **2a** [40] were prepared as described in the literature. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 silica gel. All reactions were performed under N_2 atmosphere using standard Schlenk techniques.

2.3. Monomer synthesis

2.3.1. 4,4′-Diiodo-N-octyldiphenylamine 2b

This was synthesized according to the modified procedure as described in the literature [41]. To a solution of tetrabutylammonium iodide (3.69 g, 10 mmol) in dry toluene (25 ml), potassium hydroxide (2.25 g, 40 mmol), diphenylamine (1.69 g, 10 mmol), and 1-bromooctane (1.93 g, 10 mmol) were added. The mixture was treated with an ultrasonic technique (IWAKI ultrasonic cleaning bath containing an aqueous detergent solution) for 3 h. After the reaction, water was added followed by usual isolation procedures. The crude products were purified by Kugelrohr to give *N*-octyldiphenylamine (yield 42%). This compound was then iodized at 4,4′-positions by benzyltrimethylammonium dichloroiodate (BTMA-ICl_2). To a solution of *N*-octyldiphenylamine (422 mg, 1.5 mmol) in dichloromethane–methanol (15–6 ml) were added BTMA-ICl_2 (1.04 g, 3.0 mmol) and calcium carbonate (210 mg). The mixture was stirred for 24 h at room temperature. Excess amount of calcium carbonate was filtered, and the filtrate was condensed. To the obtained residue was added aqueous $NaHSO_3$ solution. The mixture was extracted with ether, dried with Na_2SO_4, and concentrated under vacuum. The crude product was purified on SiO_2 column with eluent hexane ($R_f=0.26$) to give 4,4′-diiodo-*N*-octyldiphenylamine **2b** in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$); δ 0.89 (t, $J=6.4$ Hz, 3H), 1.26 (m, 10H), 1.66 (m, 2H), 3.72 (t, $J=7.6$ Hz, 2H), 6.98 (d, $J=8.0$ Hz, 4H), 7.32 (m, 6H), 7.42 (d, $J=8.0$ Hz, 4H), 7.51(d, $J=7.2$ Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.1, 22.6, 27.0, 27.4, 29.2, 29.3, 31.7, 52.2, 88.5, 89.6, 115.6, 120.5, 123.5, 127.8, 128.2, 131.3, 132.7, 147.2. Anal. Calcd for $C_{20}H_{25}I_2N$: C 45.05, H 4.73, N 2.63, I 47.65; found C 45.29, H 4.76, N 2.62, I 47.49. HRMS (FAB): calcd for $C_{20}H_{25}I_2N$, 533.0077; found, 533.0075.

2.3.2. 4,4′-Diiodo-4″-pentyltriphenylamine 2c

This was synthesized according to the modified procedure as described in the literature [42]. A dried round-bottomed flask equipped with condenser and magnetic stirring bar was charged with $Pd(OAc)_2$ (89.8 mg, 0.40 mmol), NaO-*t*-Bu (577 mg, 6.0 mmol), 2,8,9-trisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (274 mg, 0.80 mmol), diphenylamine (676 mg, 4.0 mmol), 1-iodo-4-pentylbenzene (1.10 g, 4.0 mmol) and dry toluene (40 ml) under N_2 atmosphere. The mixture was then stirred at 80 °C for 24 h. After the reaction mixture was cooled to room temperature, the crude solution was plugged through the Celite column. The crude brown product was purified by column chromatography on SiO_2 with eluent hexane ($R_f=0.14$) to give 4-pentyltriphenylamine in 71% yield. To a solution of 4-pentyltriphenylamine (734 mg, 2.3 mmol) in dichloromethane–methanol (24–9 ml) were added BTMA-ICl_2 (1.64 g, 4.7 mmol) and calcium carbonate (326 mg). The mixture was stirred for 24 h at room temperature. Excess amount of calcium carbonate was filtered and the filtrate was condensed. To the obtained residue was added aqueous $NaHSO_3$ solution. The mixture was extracted with ether, dried with Na_2SO_4, and concentrated under vacuum. The crude product was purified on SiO_2 column with eluent hexane ($R_f=0.29$) to give 4,4′-diiodo-4″-pentyltriphenylamine **2c** in 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$); δ 0.89 (t, $J=6.4$ Hz, 3H), 1.26 (m, 10H), 1.66 (m, 2H), 3.72 (t, $J=7.6$ Hz, 2H), 6.98 (d, $J=8.0$ Hz, 4H), 7.32 (m, 6H), 7.42 (d, $J=8.0$ Hz, 4H), 7.51(d, $J=7.2$ Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.1, 22.6, 27.0, 27.4, 29.2, 29.3, 31.7, 52.2, 88.5, 89.6, 115.6, 120.5, 123.5, 127.8, 128.2, 131.3, 132.7, 147.2. Anal. Calcd for $C_{23}H_{23}I_2N$: C 48.70, H 4.09, N 2.47, I 44.74; found C 48.78, H 4.17, N 2.33, I 44.52. HRMS (FAB): calcd for $C_{23}H_{23}I_2N$, 566.9920; found, 566.9921.

2.4. Polymerization

A typical procedure is as follows [43]. A mixture of monomers **1** (51 mg, 0.20 mmol), **2** (0.20 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.020 mmol), CuI (3.8 mg, 0.020 mmol), PPh_3 (11 mg, 0.040 mmol), TEA (0.30 ml), and THF (2.0 ml) was placed in the Schlenk tube equipped with a magnetic stirring bar and a reflux condenser under N_2 atmosphere. The mixture was stirred over 48 h at reflux temperature. After the reaction mixture was cooled to room temperature, ammonium salts were removed through Celite and washed with THF several times. The filtrate was condensed and poured into a large amount of MeOH to precipitate the crude brown colored polymer. The crude product was dissolved in $CHCl_3$, washed with 10 wt% aqueous NH_3 in order to remove inorganic species, followed by drying over Na_2SO_4. After removal of Na_2SO_4, the solvent was condensed under reduced pressure. Finally, the condensed liquid residue was poured into a large amount of MeOH to give the yellow powder. Further purification was carried out by recyclable preparative HPLC. After drying under reduced pressure, polymer **3** was obtained as a yellow powder.

3a. Yield: 37%. ^{1}H NMR (400 MHz, $CDCl_3$); δ 3.23 (m, 8H), 6.02 (s, 1H), 6.54 (m, 2H), 6.59 (s, 2H), 7.05 (m, 2H), 7.15 (m, 4H), 7.53 (m, 4H). IR (film) 2201 cm^{-1}.

3b. Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.30 (m, 15H), 3.23 (m, 8H), 3.78 (m, 2H), 6.52 (d, $J=7.6$ Hz, 2H), 6.59 (s, 2H), 7.06 (m, 6H), 7.52 (d, $J=7.6$ Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.2, 22.7, 27.1, 29.3, 31.8, 34.0, 34.2, 50.9, 52.3, 89.0, 93.0, 116.3, 120.7, 124.9, 129.1, 132.6, 133.2, 137.0, 138.0, 139.4, 141.2, 147.2. IR (film) 2201 cm^{-1}.

3c. Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.30 (m, 9H), 2.60 (m, 2H), 3.21 (m, 8H), 6.51 (d, $J=7.6$ Hz, 2H), 6.58 (s, 2H), 7.03 (d, $J=7.6$ Hz, 2H), 7.11 (m, 8H), 7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.2, 22.7, 31.3, 31.7, 34.0, 34.2, 35.5, 89.3, 92.9, 117.2, 123.0, 124.8, 125.6, 129.4, 130.0, 132.3, 133.1, 137.0, 139.2, 139.4, 141.8, 144.0, 147.2. IR (film) 2202 cm^{-1}.

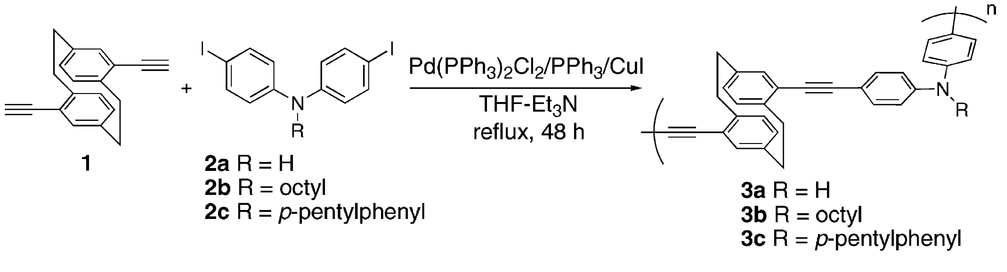
2.5. Synthesis of model compound 4

A mixture of phenylacetylene (102 mg, 1.0 mmol), **2b** (213 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.040 mmol), CuI (7.6 mg, 0.040 mmol), PPh_3 (21 mg, 0.080 mmol), TEA (1.0 ml), and THF (4.0 ml) was placed in the Schlenk tube equipped with a magnetic stirring bar and a reflux condenser under N_2 atmosphere. The mixture was stirred for 12 h at reflux temperature. After the reaction mixture was cooled to room temperature, ammonium salts were removed through Celite and washed with THF several times. The filtrate was condensed and purified on SiO_2 column with eluent hexane/$CHCl_3=3/1$ ($R_f=0.57$). Further purification was carried out by recyclable preparative HPLC. After drying under reduced pressure, model compound **4** was obtained as a brown oil in a yield of 33%.

^{1}H NMR (400 MHz, $CDCl_3$); δ 0.89 (t, $J=6.4$ Hz, 3H), 1.26 (m, 10H), 1.66 (m, 2H), 3.72 (t, $J=7.6$ Hz, 2H), 6.98 (d, $J=8.0$ Hz, 4H), 7.32 (m, 6H), 7.42 (d, $J=8.0$ Hz, 4H), 7.51(d, $J=7.2$ Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.1, 22.6, 27.0, 27.4, 29.2, 29.3, 31.7, 52.2, 88.5, 89.6, 115.6, 120.5, 123.5, 127.8, 128.2, 131.3, 132.7, 147.2. Anal. Calcd for $C_{36}H_{35}N$: C 89.55, H 7.33, N 2.84; found C 89.77, H 7.33, N 2.90. HRMS (FAB): calcd for $C_{36}H_{35}N$, 481.2770; found, 481.2771.

3. Results and discussion

As shown in Scheme 1, according to the standard Sonogashira coupling method [43], monomers **1** and **2a–c** can be easily polymerized to their corresponding polymers **3a–c** in the presence of a catalytic amount of $Pd(PPH_3)_2Cl_2$/PPh_3/CuI in THF–TEA at reflux temperature for 48 h. After the reaction, the inorganic salts were filtered, and the filtrate was reprecipitated into a large amount of MeOH to obtain crude polymers **3a–c**. The polymers were then dissolved in $CHCl_3$ and washed three times with aqueous NH_3 in order to remove the metal species. Finally, low molecular weight compounds including oligomers were completely removed



Scheme 1.

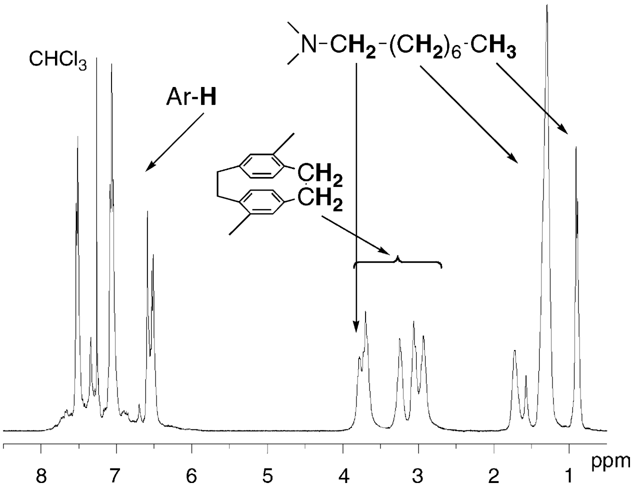


Fig. 1. ^{1}H NMR spectrum of polymer **3b** in CDCl$_3$.

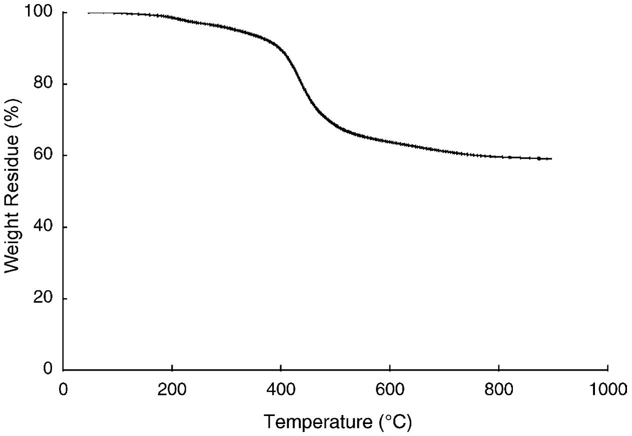


Fig. 2. Thermogravimetric analysis (TGA) of polymer **3b** under N$_2$ (10 °C/min).

using the recycling preparative HPLC to produce target polymers **3a–c** in good yields. The results are summarized in Table 1. In the case of the polymerization of **1** with **2a** (Table 1, run 1), due to the poor solubility of **3a**, the yield was lower than those obtained for **3b** and **3c**. Polymers **3b** and **3c** exhibited good solubility in common organic solvents such as THF, CH$_2$Cl$_2$, CHCl$_3$, and toluene. Polymers **3b** and **3c** could be processed into transparent and uniform thin films by casting or spin-coating from toluene solutions.

The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent CHCl$_3$ using the calibration curve of polystyrene standards, as listed in Table 1. For example, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distribution (M_w/M_n) of polymer **3b** obtained in run 2 were 4300, 13300, and 3.1, respectively, thus providing the estimation of the number-average degree of polymerization as eight.

The structures of the polymers were confirmed by their ^{1}H, ^{13}C NMR, and FT-IR spectra. In the ^{1}H NMR spectrum of **3b** in CDCl$_3$ (Fig. 1), the signals of the alkyl chains were dominant in the region of 0.9–1.7 and 3.8 ppm, and the bridged methylenes of the [2.2]paracyclophane unit appeared in the region of 2.9–3.7 ppm. The peaks between 6.5 and 7.5 ppm were assigned to the aromatic protons. In the ^{13}C NMR spectrum of polymer **3b**, the typical signals for acetylenic carbons appeared at 89 and 94 ppm. A carbon–carbon triple bond was also characterized by the FT-IR spectrum, and the weak stretching vibration mode of the bond was observed at approximately 2200 cm^{-1}.

The thermal stability of polymer **3b** was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere, and the result is shown in Fig. 2. This polymer showed good thermal stability with a 10% weight loss temperature of 390 °C at a heating rate of 10 °C/min. From this TGA result, it is clear that this polymer has sufficient thermal stability to be applied to light emitting materials.

Fig. 3 shows the UV–vis absorption spectrum of polymer **3b**, as a representative polymer, in CHCl$_3$ at room temperature. The absorption maximum of **3b** was observed at 373 nm, which is attributed to the π–π* transition band of the conjugated polymer backbone. Both the absorption maximum and the absorption edge of polymer **3b** were red-shifted ($\lambda_{max}=362$ nm), as compared to those of model compound **4** (Fig. 3), which was synthesized according to Scheme 2. This result indicates that the π-electrons were delocalized along the polymer main chain of **3b**. In other words, the π-electrons were delocalized via the through-space interaction between the two co-facial benzene rings of the [2.2]paracyclophane unit.

Polymers **3a–c** exhibited strong blue-light emission at approximately 410 nm in dilute CHCl$_3$ solution at the excitation wavelength of their absorption maximum (Table 2, Fig. 4). The emission quantum efficiencies of

Table 1
Synthesis of polymers **3a–c**

Run	Polymer	R (monomer)	Yield[a] (%)	M_w[b]	M_n[b]	M_w/M_n[b]
1	**3a**	H (**2a**)	37	4400	2400	1.8
2	**3b**	Octyl (**2b**)	94	13300	4300	3.1
3	**3c**	*p*-Pentylphenyl (**2c**)	99	21000	8000	2.6

Polymerization was carried out at reflux temperature for 48 h under N$_2$.
[a] Isolated yields.
[b] GPC (CHCl$_3$), polystyrene standards.

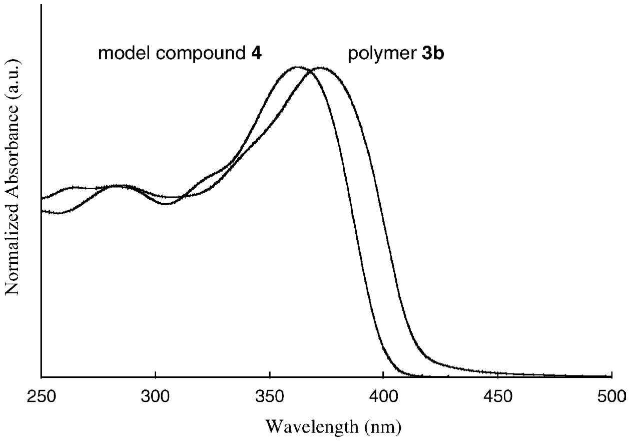


Fig. 3. Absorption spectra of polymer **3b** and model compound **4** in $CHCl_3$ solution.

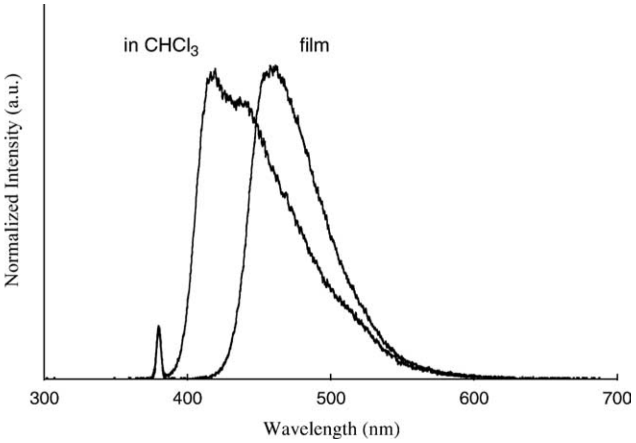


Fig. 4. Fluorescence emission spectra of polymer **3c** in $CHCl_3$ and in the film state, on excitation at the absorption maximum.

Table 2
Summary of the optical properties of polymers **3a–c**

Polymer	UV λ_{max}[a] (nm)		PL λ_{max}[a,b] (nm)		
	Solution	Film	Solution	Film	Φ_{PL}[c]
3a	360	–[d]	406	–[d]	0.18
3b	373	378	410	–[e]	0.65
3c	385	386	416	460	0.70

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solution at room temperature.
[b] Excited at absorption maxima.
[c] PL efficiencies in $CHCl_3$ determined relative to 9-anthracenecarboxylic acid in CH_2Cl_2.
[d] Thin film was not obtained.
[e] No emission was detected.

these polymers are relatively high; for example, the efficiency of **3c** was found to be 0.70 in dilute $CHCl_3$ solution at room temperature using 9-anthracenecarboxylic acid in dilute CH_2Cl_2 solution as a standard ($\Phi = 0.442$) [44]. Because of their bulky structure, strong emission of polymer **3c** was observed at the emission maximum around 460 nm, even in the solid state. The emission spectra in the solid state were red-shifted by approximately 40 nm as compared to those in solution. The emission maximum in dilute $CHCl_3$ solution depended on the concentration and was gradually red-shifted toward that in the film state as the concentration was increased (Fig. 5). This result indicates a relatively strong intermolecular interaction of the conjugated chains in the solid state.

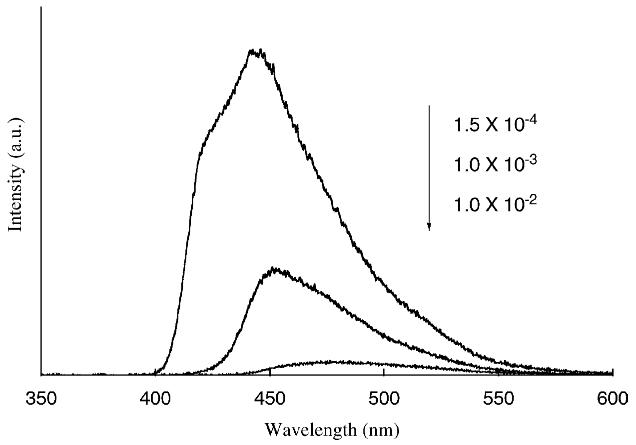
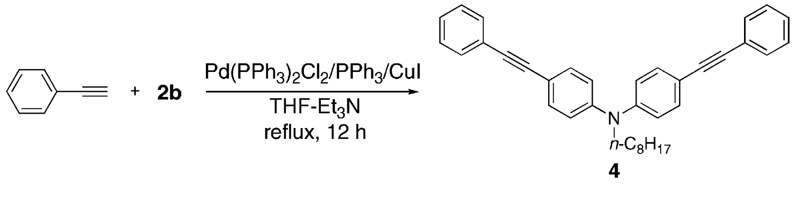


Fig. 5. Dependence on concentration of fluorescence spectra of polymer **3c** in $CHCl_3$ solution on excitation at the absorption maximum.



Scheme 2.

4. Conclusion

Novel conjugated cyclophane polymers combined with phenylamine units based on PPE were prepared according to the Sonogashira coupling reaction. These polymers could be easily processed to obtain uniform thin films with good thermal stability. Polymer **3c** exhibited strong blue photoluminescence in solution and greenish-blue in the solid state. According to the study on the concentration effect of photoluminescence, the aggregation or the intermolecular interaction of the polymer chain would occur in the film state as well as in the concentrated solution. Future work will focus on investigating the contribution of the cyclophane unit for applications in hole-transporting materials and light-emitting materials.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 16750096) from the Ministry of Education, Science, Sports and Culture, Japan. Support from the Mitsubishi Foundation and the Iketani Foundation are also acknowledged.

References

[1] Sheats JR. J Mater Res 2004;19:1974.
[2] Cho NS, Hwang DH, Jung BJ, Oh J, Chu HY, Shima HK. Synth Met 2004;143:277.
[3] Donat-Bouillud A, Lévesque I, Tao Y, Díorio M, Beaupré S, Blondin P, et al. Chem Mater 2000;12:1931.
[4] Guo TF, Chang SC, Yang Y, Kwong RC, Thompson ME. Org Electron 2000;1:15.
[5] Cho NS, Hwang DH, Jung BJ, Lim E, Lee J, Shim HK. Macromolecules 2004;37:5265.
[6] Hou Q, Xu YS, Yang W, Yang RO, Yuan M, Peng JB, et al. Synth Met 2003;135–136:179.
[7] Ding XB, Zheng JG, Jin YD, Heremans PL, Geise HJ, Borghs G. Synth Met 2003;137:1003.
[8] Jin YD, Chen HZ, Heremans PL, Aleksandrzak K, Geise HJ, Borghs G, et al. Synth Met 2002;127:155.
[9] Tang CW, Vanslyke SA. Appl Phys Lett 1987;51:913.
[10] Adachi C, Tokito S, Tsutsui T, Saito S. Jpn J Appl Phys 1988;27:713.
[11] Miyata S, Sakuratani Y, Tao XT. Opt Mat 2003;21:99.
[12] Kulkarni AP, Tonzola CJ, Babel A, Jenekhe SA. Chem Mater 2004; 16:4556.
[13] Moisan JY, Gravey P, Lever R, Bonnel L. Opt Eng 1986;25:151.
[14] Moisan JY, Andre B, Lever R. Chem Phys 1991;153:305.
[15] Grazulevicius JV, Strohriegl P, Pielichowski J, Pielichowski K. Prog Polym Sci 2003;28:1297.
[16] Vögtle F. Cyclophane chemistry. NY, USA: Wiley; 1993.
[17] Bazan GC, Oldham Jr WJ, Lachicotte RJ, Tretiak S, Chernyak V, Mukamel S. J Am Chem Soc 1998;120:9188.
[18] Wang S, Bazan GC, Tretiak S, Mukamel S. J Am Chem Soc 2000; 122:1289.
[19] Zyss J, Ledoux I, Volkov S, Chernyak V, Mukamel S, Bartholomew GP, et al. J Am Chem Soc 2000;122:11956.
[20] Bartholomew GP, Bazan GC. J Am Chem Soc 2002;124:5183.
[21] Mizogami S, Yoshimura S. J Chem Soc Chem Commun 1985;1736.
[22] Guyard L, Audebert P. Electrochem Commun 2001;3:164.
[23] Guyard L, Nguyen Dinh An M, Audebert P. Adv Mater 2001;13:133.
[24] Salhi F, Collard DM. Polym Mater Sci Eng 2002;222.
[25] Salhi F, Collard DM. Adv Mater 2003;15:81.
[26] Wang W, Xu J, Lai Y-H. Org Lett 2003;5:2765.
[27] Wang W, Xu J, Lai Y-H, Wang F. Macromolecules 2004;37:3546.
[28] Morisaki Y, Chujo Y. Macromolecules 2002;35:587.
[29] Morisaki Y, Chujo Y. Chem Lett 2002;194.
[30] Morisaki Y, Ishida T, Chujo Y. Macromolecules 2002;35:7872.
[31] Morisaki Y, Chujo Y. Polym Bull 2002;49:209.
[32] Morisaki Y, Ishida T, Chujo Y. Polym J 2003;35:501.
[33] Morisaki Y, Fujimura F, Chujo Y. Organometallics 2003;22:3553.
[34] Morisaki Y, Chujo Y. Macromolecules 2003;36:9319.
[35] Morisaki Y, Chujo Y. Macromolecules 2004;37:4099.
[36] Morisaki Y, Ishida T, Tanaka H, Chujo Y. J Polym Sci, Part A: Polym Chem 2004;42:5891.
[37] Morisaki Y, Wada N, Chujo Y. Polym Bull 2005;53:73.
[38] Morisaki Y, Chujo Y. Bull Chem Soc Jpn 2005;78:288.
[39] Morisaki Y, Chujo Y. Tetrahedron Lett; in press.
[40] Kajigaeshi S, Kakinami T, Yamasaki H, Fujisaki S, Okamoto T. Bull Chem Soc Jpn 1988;61:600.
[41] Davidson RS, Patel AM, Safder A. Tetrahedron Lett 1983;24:5907.
[42] Urgaonkar S, Nagarajan M, Verkade JG. J Org Chem 2003;68:452.
[43] Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;16: 4467.
[44] The absorbance of each sample was below 0.05 at the excitation wavelength at 350 nm, in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{\mathrm{unk}}=\Phi_{\mathrm{std}}[A_{\mathrm{std}}F_{\mathrm{unk}}/A_{\mathrm{unk}}F_{\mathrm{std}}][n_{\mathrm{D,unk}}/n_{\mathrm{D,std}}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_{D} is the refractive index [CH_2Cl_2 ($n_{\mathrm{D}}=1.424$) and $CHCl_3$ ($n_{\mathrm{D}}=1.446$) were used].