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ORIGINAL PAPER

Aromatic ring-layered polymer containing 2,7-linked carbazole on xanthene

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Abstract New aromatic ring-layered polymer comprising the 2,7-linked carbazole and xanthene units was synthesized by the Sonogashira coupling reaction. The structure and optical properties of the 2,7-linked carbazole-layered polymer were compared with those of the 3,6-linked carbazole-layered polymer by using their model compounds.

Keywords Aromatic ring-layered polymer · Conjugated polymer · Carbazole · Xanthene

Introduction

The design and synthesis of new conjugation systems are important in polymer chemistry in order to discover new functionalities and unique properties. A large number of conjugated polymers with various conjugation systems have been synthesized to exploit their intriguing properties such as electrical conductivity [1–4], electroluminescence [5–9], chemical sensing [10–12], etc. Versatile chemical modifications of their main chain and side chain allow them to tune physical properties, chain structures, and higher-ordered structures. Most conjugated polymers reported to date are through-bond conjugated polymers comprising sp or sp^2 carbon frameworks. Few studies have focused on the synthesis of through-

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space conjugated polymers consisting of layered π-electron systems in a single polymer chain [13–47].

Recently, we have developed the construction of layered π-electron structures in the main chain of a polymer by incorporating a [2.2]paracyclophane unit into the polymer chain as the key component [13–16, 32–42]. The synthesized [2.2]paracyclophane-containing polymers exhibited through-space conjugation via π–π interaction. In addition, we have developed a new synthetic strategy for creating aromatic ring-layered structures in the polymer main chain by using xanthene as scaffold and [2.2]paracyclophane as the layered aromatic ring [43–46]. Using this approach, it is possible to incorporate and layer various aromatic rings in a single polymer chain. Thus, we synthesized oligophenylene- [47], oligothiophene- [48], and 3,6-linked carbazole-layered polymers [49], which transfer the photo-excited energy from the layered aromatic rings to the terminal aromatic rings. These results suggest that this class of polymers have the potential to be used as a single molecular wire. The expansion of the substrate scope of the newly developed aromatic ring-layered polymers is important, and the investigation of their properties is necessary for making advances in the field of the conjugated polymers. In this paper, we describe the synthesis and properties of the 2,7-linked carbazole-layered polymer. The carbazole unit can be linked at the 3- and 6-position as well as 2- and 7-position [50–52] to yield the corresponding carbazole-containing conjugated polymers [53, 54]. Conformation and optical properties of the 2,7-linked carbazole-layered polymer are compared with those of the 3,6-linked carbazole-layered polymer.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz, respectively. The chemical shift values were expressed relative to Me_4Si as an internal standard. FTIR spectra were obtained on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. 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. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry LC-918R (JAIGEL 1H and 2H columns) or LC-9204 (JAIGEL 2.5H and 3H columns) instrument using $CHCl_3$ as an eluent. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel α-3000 column) instrument using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. UV–Vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer. Photoluminescence spectra were obtained on a Perkin-Elmer LS50B luminescence spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an Applied Biosystems Voyager Elite spectrometer using

2,5-dihydroxybenzoic acid (DBH) as a matrix. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

X-ray crystal structure analysis

Intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at −180 °C. The structures were solved by direct method (SIR97) [55] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97) [56].

Materials

NEt_3 was purified by passage through solvent purification columns under Ar pressure [57]. Dehydrated toluene was purchased and used without further purification. $Pd(PPh_3)_4$ and CuI were purchased and used without further purification. 2,7-Di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) [49], 2,7-diiodo-9-octylcarbazole (**2a**) [52], 3,6-diiodo-9-octylcarbazole (**2b**) [58], 4,5-diethynyl-9,9-dimethylxanthene (**3**) [59], 2-bromo-9-methylcarbazole (**4a**) [60, 61], and 3-iodo-9-methylcarbazole (**4b**) [58] were synthesized according to the literature.

Polymerization

2,7-Di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) (57 mg, 0.15 mmol), diiodo-9-octylcarbazole (**2**) (86 mg, 0.17 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol), and CuI (33.7 mg, 0.17 mmol) were placed in a 10 mL Pyrex tube equipped with a magnetic stirrer and a reflux condenser. The equipment was purged with Ar, followed by adding toluene (3.0 mL) and NEt_3 (1.5 mL). The reaction was carried out at 100 °C for 48 h. After cooling, the reaction mixture was filtered. The filtrate was diluted with $CHCl_3$, and washed twice with aqueous NH_4OH (25%, 50 mL) and twice with water (50 mL). The organic layer was dried over $MgSO_4$. The organic layer was concentrated and reprecipitated from a large amount of methanol. Then, the obtained polymer was purified by recycling preparative HPLC to afford the polymer as a brown solid.

P1. Yield: 63%. ^{1}H NMR (in CD_2Cl_2) δ 0.83 (br), 1.38 (br), 1.70 (br), 3.70 (br), 7.50 (br) ppm; ^{13}C NMR (in CD_2Cl_2) δ 13.1, 21.8, 26.5, 28.4, 30.4, 33.6, 42.1, 84.8, 94.1, 110.2, 119.4, 121.7, 122.8, 128.1, 131.0, 139.9, 144.9, 147.5 ppm.

P2. Yield: 62%. ^{1}H NMR (in CD_2Cl_2) δ 0.88 (br), 1.27 (br), 1.42 (br), 1.72 (br), 4.00 (br), 7.51 (m) ppm; ^{13}C NMR (in CD_2Cl_2) δ 26.6, 28.6, 30.0, 31.6, 108.6, 120.4, 126.2, 126.9, 142.8, 145.3 ppm.

9,9-Dimethyl-4,5-bis(9-methyl-2-carbazolyl)xanthene **M1**

A mixture of **1** (130 mg, 0.50 mmol), 2-bromo-9-methylcarbazole (**4a**) (520 mg, 2.0 mmol), $Pd(PPh_3)_4$ (180 mg, 0.16 mmol), and CuI (144 mg, 0.75 mmol) in toluene (4.0 mL) and NEt_3 (2.0 mL) was reacted at 100 °C for 48 h under Ar atmosphere. The reaction mixture was filtered with Celite, and the filtrate was washed with NH_4OH (25%, 30 mL), brine (30 mL), and water (30 mL). The organic layer was dried over $MgSO_4$. The solution was evaporated under reduced pressure, and the residue was purified by column chromatography on SiO_2 with hexane–CH_2Cl_2 (v/v = 5:2, $R_f = 0.2$) as an eluent. Then, the obtained compound was purified by recycling preparative HPLC and recrystallization from CH_2Cl_2 to afford **M1** as a white crystal (31 mg, 0.05 mmol, 10%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.69 (s, 6H), 3.18 (s, 6H), 6.88 (d, $J = 8.4$ Hz, 2H), 7.02 (t, $J = 7.6$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 2H), 7.22 (m, 6H), 7.51 (m, 6H), 7.58 (d, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 28.4, 32.4, 34.3, 84.3, 95.5, 108.3, 112.0, 112.1, 118.9, 119.4, 119.5, 119.9, 121.7, 122.3, 123.2, 126.0, 126.5, 130.5, 131.9, 140.0, 141.2, 150.4 ppm. HRMS (EI): *m/z* calcd for $C_{45}H_{32}ON_2$ (M^+): 616.2515. Found: 616.2517. Anal. calcd for $C_{45}H_{32}ON_2$: C, 87.63; H, 5.23; N, 4.54. Found: C, 87.42; H, 5.19; N, 4.60.

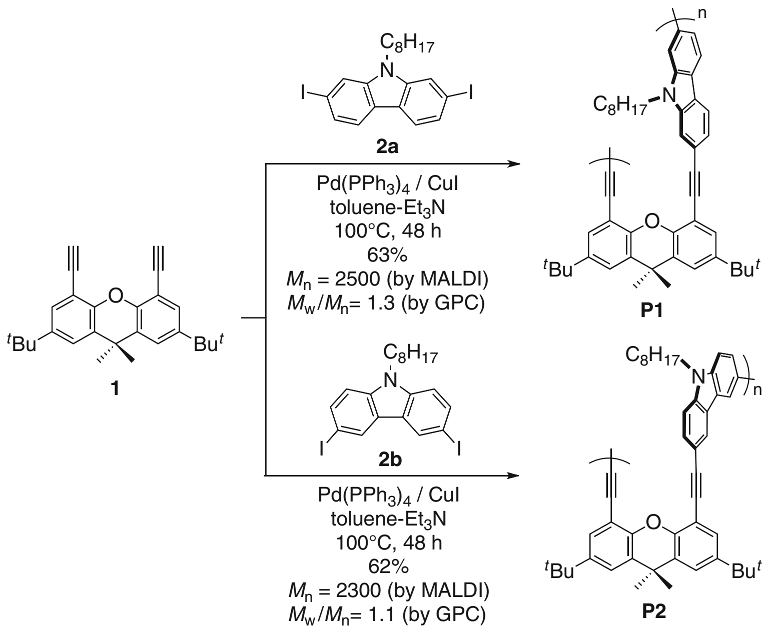
9,9-Dimethyl-4,5-bis(9-methyl-3-carbazolyl)xanthene **M2**

A mixture of **1** (130 mg, 0.50 mmol), 3-iodo-9-methylcarbazole (**4b**) (614 mg, 2.0 mmol), $Pd(PPh_3)_4$ (180 mg, 0.16 mmol), and CuI (144 mg, 0.75 mmol) in toluene (4.0 mL) and NEt_3 (2.0 mL) was reacted at 100 °C for 48 h under Ar atmosphere. The reaction mixture was filtered with Celite, and the filtrate was washed with NH_4OH (25%, 30 mL), brine (30 mL), and water (30 mL). The organic layer was dried over $MgSO_4$. The solution was evaporated under reduced pressure, and the residue was purified by column chromatography on SiO_2 with hexane–CH_2Cl_2 (v/v = 2:1, $R_f = 0.3$) as an eluent. Then, the obtained compound was purified by recycling preparative HPLC and recrystallization from CH_2Cl_2 to afford **M2** as a white crystal (174 mg, 0.28 mmol, 56%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.70 (s, 6H), 3.20 (s, 6H), 6.71 (d, $J = 8.4$ Hz, 2H), 6.99 (t, $J = 6.8$ Hz, 2H), 7.13 (m, 4H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.49 (m, 8H), 7.87 (s, 2H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 28.3, 32.3, 34.3, 82.9, 95.8, 108.0, 108.1, 112.6, 112.7, 118.7, 120.2, 121.9, 122.2, 123.2, 123.8, 125.6, 126.1, 129.3, 130.4, 131.7, 140.1, 140.8, 150.4 ppm. HRMS (EI): *m/z* calcd for $C_{45}H_{32}ON_2$ (M^+): 616.2515. Found: 616.2512. Anal. calcd for $C_{45}H_{32}ON_2$: C, 87.63; H, 5.23; N, 4.54. Found: C, 86.89; H, 5.16; N, 4.37.

Results and discussion

The synthetic route for the preparation of aromatic ring-layered polymers containing 2,7-linked carbazole and 3,6-linked carbazole is shown in Scheme 1. Polymerization was carried out by the Sonogashira–Hagihara coupling reaction of 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) with 2,7-diiodo-9-octylcarbazole (**2a**) or 3,6-diiodo-9-octylcarbazole (**2b**). The treatment of **1** and **2** in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI yielded a crude polymer, which was purified by reprecipitation from a large amount of MeOH and by recycling preparative HPLC to obtain polymers **P1** and **P2** in 63 and 62% isolated yields, respectively.



Scheme 1 Synthesis of polymers **P1** and **P2**

Molecular weight measurements were performed by using a MALDI-TOF mass spectrometer as well as by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards. The number-average molecular weights (M_n) of **P1** and **P2** calculated from the MALDI-TOF mass spectra (Figures S7 and S8 in Supporting Information) were 2500 and 2300, respectively. This result indicates that degrees of polymerization of **P1** and **P2** are 4.0 and 3.6, respectively. Polymer **P1** exhibited a major series of peaks that were regularly separated by the molar mass of a repeating unit (*m*/*z* 645). Polydispersity indices (M_w/M_n) of **P1** and **P2** estimated using GPC were found to be 1.3 and 1.1, respectively (Table 1).

The structures of **P1** and **P2** were confirmed by ^1H and ^{13}C NMR spectra. The spectra of **P1** in CD_2Cl_2 are shown in Fig. 1. Signals between 0.8 and 1.6 ppm denote overlapping peaks of *tert*-butyl and octyl chains. The signals of $–CH_3$ groups at the 9-position of xanthene appear at around 1.7 ppm. Peaks of the aromatic

Table 1 Results of polymerization

Polymer	Yield[a] (%)	M_n^b	M_n^c	DP[b,d]	M_w/M_n^c
P1	63	2500	2000	4.0	1.3
P2	62	2300	2500	3.6	1.1

[a] Isolated yield after reprecipitation and HPLC

[b] Calculated by MALDI-TOF mass spectra, polystyrene standards

[c] Calculated by GPC ($CHCl_3$), polystyrene standards

[d] Degree of polymerization

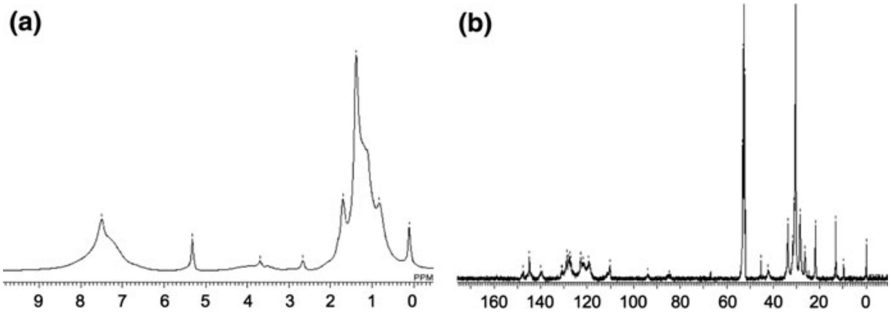
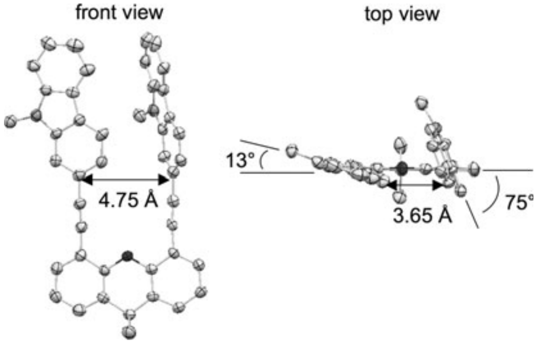


Fig. 1 (*a*) ^{1}H NMR and (*b*) ^{13}C NMR spectra of **P1** in CD_2Cl_2

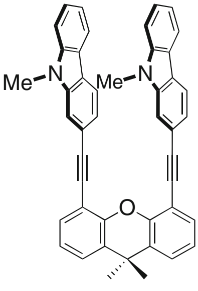
protons of carbazole and xanthene units were observed around 7.0–8.0 ppm as broad signal. The ^{13}C NMR spectrum of **P1** exhibits signals of the carbon–carbon triple bond at 84.8 and 94.1 ppm. The NMR spectra of **P1** were similar to those of **P2**, which were previously reported by us [49].

In order to evaluate the structures and optical properties of the polymers, we designed and prepared model compounds **M1** and **M2** by reacting 4,5-diethynyl-9,9-dimethylxanthene (**3**) with 2-bromo-9-methylcarbazole (**4a**) and 3-iodo-9-methylcarbazole (**4b**), respectively. A single crystal of **M1** was successfully obtained from its CH_2Cl_2 solution, and the structure was confirmed by X-ray crystallography [62], as shown in Fig. 2. As can be seen in the front and top views of **M1**, two carbazoles are twisted, and the torsion angles of the carbazole and xanthene rings are 13° and 75°, respectively. Distance between two carbazoles is 4.75 Å (front view in Fig. 2), and the shortest distance between the carbazole rings is 3.65 Å (top view in Fig. 2). To gain further insight on the layered structure, we performed density functional theory (DFT) calculations at the B3LYP/6-31G* level for **M1** and **M2**. As shown in Figure S10 in Supporting Information, the frontier orbital of **M2** showed a significant overlap, while the electron density of LUMO in **M1** was delocalized in one layer. The results of X-ray crystallography and DFT calculations suggest that the carbazole layer of **M1** favors conjugation with the xanthene ring. The steric hindrance prevents the carbazole unit in **M2** from forming a π-conjugation with the xanthene ring, which results in the twisted and layered

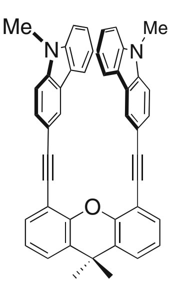
Fig. 2 ORTEP drawings of **M1** with 30% thermal ellipsoids



structure in **M2**. On the other hand, variable-temperature (VT) NMR studies (from 303 to 243 K) were performed for **M1** to investigate the rotation of carbazole units on xanthene; the ^{1}H NMR spectra displayed no coalescence or separation of any signals (Figure S9 in Supporting Information). These results indicate that two carbazoles have sufficient space for rotation and swing in model compound **M1** as well as polymer **P1**.



M1



M2

Optical properties of **P1**, **P2**, **M1**, and **M2** are listed in Table 2. Figure 3 shows the absorption spectra of **P1**, **P2**, **M1**, and **M2** in dilute $CHCl_3$ solutions (1.0×10^{-5} M) at room temperature. The conjugation lengths of **P1** and **M1**, containing carbazole units linked at 2- and 7-position, were longer than those of **P2** and **M2** with 3- and 6-linked carbazole units. This is due to the longer conjugation length of 2,7-carbazole-based compounds as compared to other carbazole derivatives [53], and due to the twisted 3,6-linked carbazole units on xanthene caused by the steric hindrance.

Figure 4 shows the photoluminescence spectra of **P1**, **P2**, **M1**, and **M2** in a diluted $CHCl_3$ (1.0×10^{-7} M) solution excited at each absorption maximum. We confirmed that this concentration (1.0×10^{-7} M) was sufficiently diluted to avoid intermolecular interactions according to the concentration effect of the photoluminescence spectra. Polymers **P1** and **P2** exhibited emission maxima at 431 and 425 nm, respectively, while **M1** and **M2** exhibited emission maxima at 405 and

Table 2 Optical properties of **P1**, **P2**, **M1**, and **M2**

Compound	$\lambda^{a}_{max,abs}$ (nm)		$\lambda^{b}_{max,em}$ (nm)	
	In $CHCl_3$	Film	In $CHCl_3$ (Φ^{c}_{PL})	Film
P1	264, 347	264, 346	431 (0.43)	516
P2	250, 298, 355(sh)	254, 298, 355(sh)	425 (0.11)	425
M1	262, 346	–	405 (0.35)	–
M2	241, 296, 326	–	387 (0.07)	–

[a] Absorption spectra were recorded in $CHCl_3$ (1.0×10^{-5} M)

[b] Photoluminescence spectra were recorded in $CHCl_3$ (1.0×10^{-7} M, excited at each absorption maximum)

[c] Absolute photoluminescence quantum efficiency in $CHCl_3$

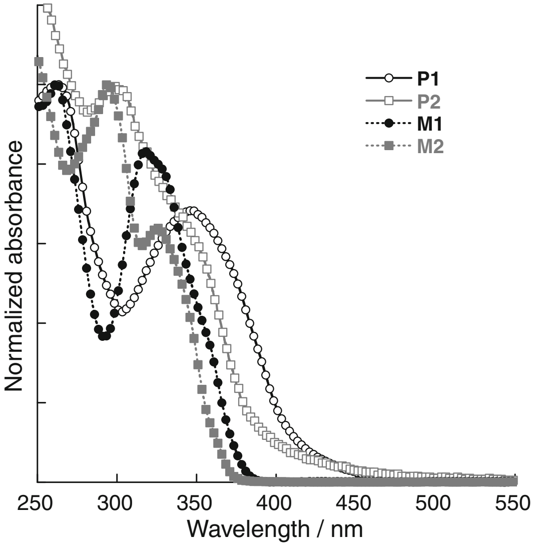


Fig. 3 UV–Vis absorption spectra of **P1**, **P2**, **M1**, and **M2** in $CHCl_3$ (1.0×10^{-5} M)

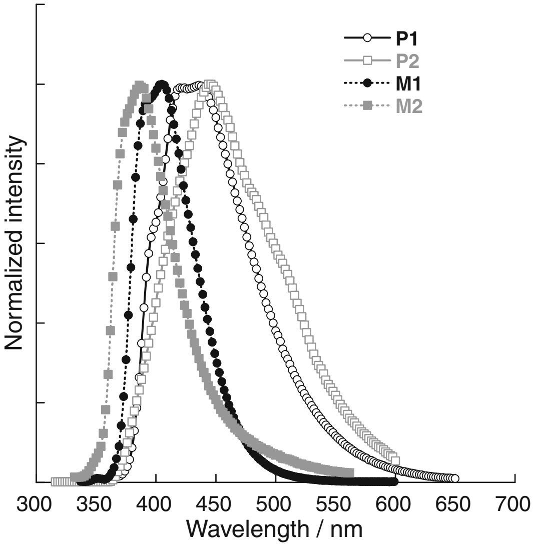


Fig. 4 Photoluminescence spectra of **P1**, **P2**, **M1**, and **M2** in $CHCl_3$ (1.0×10^{-7} M) excited at each absorption maximum

387 nm, respectively. The Stokes shifts of **P2** and **M2** were greater than those of **P1** and **M1** (Table 2). This result suggests that the conformation change from the ground state to the excited state of 3- and 6-linked carbazole are larger than that of 2- and 7-linked carbazole due to the boomerang shape of the 3- and 6-linked carbazole unit.

The absorption and photoluminescence spectra of polymers **P1** and **P2** in the film and in the diluted solution are shown in Fig. 5. The photoluminescence spectrum of the thin film of **P1** exhibited a remarkable red shift (approximately 85 nm) in comparison to that in the diluted solution (Fig. 5a), while the photoluminescence

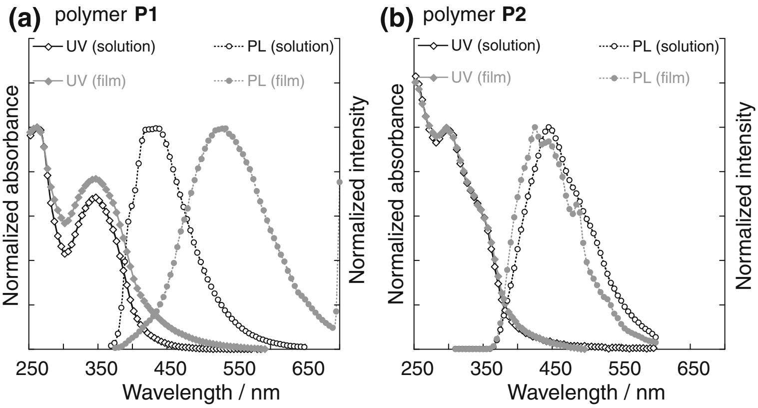


Fig. 5 UV–Vis absorption spectra and photoluminescence spectra in solution and in the film of (a) **P1** and (b) **P2**

spectra of **P2** in both thin film and diluted solution were almost identical (Fig. 5b). In addition, the absorption spectrum of **P1** in the film was broad, and its absorption edge was red-shifted compared to the absorption spectrum in the diluted solution (Fig. 5a). These observations indicate the strong intermolecular interaction of **P1** in the film. In the crystal packing structure of **M1**, as shown in Figure S11 in Supporting Information, the shortest intermolecular distance between carbazole and xanthene units is approximately 3.3 Å; therefore, there is effective π–π stacking between neighboring molecules. Thus, 2,7-linked carbazole leads to intermolecular π–π stacking of the polymer chain in the film of **P1**, while the twisted and boomerang-shaped 3,6-linked carbazole prevents intermolecular interaction in the **P2** film.

Conclusion

In summary, we synthesized the 2,7-linked carbazole-layered polymer using xanthene as the scaffold. Structure and optical properties of the 2,7-linked carbazole-layered polymer were compared to those of the 3,6-linked carbazole-layered polymer by using their model compounds. Differences between 2,7-linked and 3,6-linked carbazole unit, in terms of both their conjugation lengths and shapes, affected the optical properties of the polymers.

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