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A novel, conjugated polymer containing fluorene, pyridine and unsymmetric carbazole moieties: Synthesis, protonation and electrochemical properties

Der-Jang Liaw [a,*], Kun-Li Wang [b], Sidharam Pundlik Pujari [a], Ying-Chi Huang [a], Bo-Cheng Tao [a], Min-Hung Chen [a], Kueir-Rarn Lee [c], Juin-Yih Lai [c]

[a] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*
[b] *Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan*
[c] *R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung-Li 32023, Taiwan*

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ABSTRACT

An optically active, conjugated polymer bearing unsymmetric pendant carbazole chromophores was prepared *via* the Suzuki coupling of 9,9-dioctylfluorene-2,7-diboronic acid and a novel pyridine-containing compound. The polymer had a T_g of 192 °C and T_{d10} at 437 °C under a nitrogen atmosphere and exhibited absorption bands at 320–400 nm and displayed an additional absorption bands at 380–480 nm after protonation with aq. HCl solution. The photoluminescence of the polymer shifted from 360–460 nm to 460–560 nm after protonation and the photoluminescence quantum yield of the polymer in THF solution was 0.88. The emission color of the polymer film changed from blue (439 nm) to yellow (551 nm) under an applied bias voltage of 2.5 V.

1. Introduction

Over the past decade, much research has focused on π-conjugated polymers, which offer potential applications both in optoelectronics and photonics owing to their unique electronic properties [1]. In particular, fluorene and its derivatives have attracted much attention because of their wide energy gap and high luminescent efficiency [2].

In terms of high thermal stability, *n*-type heterocyclic compounds, pyridine has been the subject of much interest owing to its high thermal and chemical stability [3–12]. In addition, polymers which contain a pyridine moiety display electron-transporting abilities and can undergo modification of their optical properties, via protonation, because of the localized, lone pair of sp^2 orbital electrons of the nitrogen atom [7–9]. Moreover, Koleva's group observed a relationship between structure and spectroscopic properties of some pyridinium compounds [13–16]. Recently, Liu et al. showed that a conjugated polymer containing pyridine in the main chain exhibited potential applications in polymeric memory materials [17].

In contrast, the carbazole substituent is an interesting functional group for incorporation into a polymer backbone owing to its high thermal stability, good solubility, extended glassy state and moderately high oxidation potential [18]; in this context, an unsymmetrical pendant structure shows higher solubility than comparable symmetrical architecture [19–21]. Carbazole is also a conjugated group that is of interest in terms of both optical and electronic applications such as photoconductivity, photorefractivity and high charge mobility [22,23].

This work concerns the design and synthesis of novel diiodo compounds containing pyridine and unsymmetric carbazole moieties incorporated within a conjugated polymer having high thermal stability and good solubility. In this paper, the novel, conjugated polymer (**PyCzPF8**) containing fluorene, pyridine and unsymmetric carbazole moieties is reported and its optical, electrochemical and electrochromic properties were investigated using fluorescence spectroscopy and cyclic voltammetry (CV) and its thermal stability was determined.

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[*] Corresponding author. Tel.: +886 2 27376638/35050; fax: +886 2 23781441/7376644.
E-mail addresses: liawdj@mail.ntust.edu.tw, liaw6565@yahoo.com.tw (D.-J. Liaw).

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2. Experimental

2.1. Materials

4-Iodoacetophenone and ammonium acetate were purchased from Merck, acetophenone from BDH Chemicals Ltd and 9-ethyl-3-carbazolecarboxaldehyde, 9,9-dioctylfluorene-2,7-diboronic acid from Aldrich. The catalyst, tetrakis-(triphenylphosphine) palladium ($Pd(PPh_3)_4$), was purchased from Acros Organics and was used as received. THF (Merck) was distilled from sodium/benzophenone under nitrogen; DMSO, hydrochloric acid (Acros Organics), methanesulfonic acid (MSA; Fluka), *p*-toluene sulfonic acid (PTS; TCI) and glacial acetic acid (Aldrich) were used as received.

2.2. Measurements

IR spectra were recorded in the range 400–4000 cm^{-1} for the synthesized monomer and polymer in a KBr disk (Bio-Rad Digilab FTS-3500). Elemental analysis was made on a Perkin–Elmer 2400 instrument. NMR spectra were recorded using a BRUKER AVANCE 500 NMR (^{1}H at 500 MHz and ^{13}C at 125 MHz). Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns (300 × 7.5 mm, guard, 10^5, 10^4, 10^3, and 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF; 1 mL min^{-1}) as the eluent. The eluents were monitored with a UV detector (JMST Systems, VUV-24, USA) at 254 nm. Polystyrene was used as the standard. Thermogravimetric data were obtained on a TA instrument Dynamic TGA 2950 under nitrogen flowing condition at a rate of 30 $cm^3\,min^{-1}$ and at a heating rate of 10 °C min^{-1}. Differential scanning calorimetric analysis was performed on a differential scanning calorimeter (TA instrument TA 910) under nitrogen flowing condition at a rate of 30 $cm^3\,min^{-1}$ and at a heating rate of 10 °C min^{-1}. UV–vis spectra of the polymer films or solutions were recorded on a JASCO V-550 spectrophotometer at room temperature in air. The fluorescence spectra were recorded by a Shimadzu RF-5031 spectrophotometer. Photoluminescence (PL) was observed by HORIBA JOBIN FluoroMax-3. Electrochemical properties were measured by Cyclic Voltammeter (CV) CH Instrument Electrochemical Analyzer with a standard three-electrode electrochemical cell in acetonitrile solution containing 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF6) at a scan rate of 0.1 V s^{-1} at room temperature under the protection of argon. For the measurement of electrochromic behavior, polymer was deposited on ITO glasses by casting from polymer solution of 10 mg mL^{-1} in chloroform.

2.3. Synthesis of monomer (*$\mathbf{M_1}$*) and model compound (*$\mathbf{M_2}$*)

2.3.1. 4-(9-Ethyl-3-carbazole)-2,6-bis(4-iodophenyl)pyridine (*$\mathbf{M_1}$*)

The diiodo monomer of 4-(9-ethyl-3-carbazole)-2,6-bis(4-iodophenyl)pyridine ($\mathbf{M_1}$) was synthesized from 9-ethyl-3-carbazolecarboxaldehyde and 4-iodoacetophenone *via* the Chichibabin reaction in the presence of ammonium acetate and acetic acid according to Refs. [7–9]. The crude product of $\mathbf{M_1}$ was recrystallized five times from DMSO to obtain light yellow particles with 30% yield. M.P. = 141 °C. FTIR (KBr, cm^{-1}) Ar–H, 3050; C–H, 2971; C–H, 2932; C=N, 1597 for C–N of pyridine group; C=C, 1480; Ar–I, 1001.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.39 (s, 1H), 8.18–8.17 (d, J = 8.2 Hz, 1H), 7.91–7.90 (m, 6H), 7.82–7.81 (d, J = 7.8 Hz, 4H), 7.78–7.76 (m, 1H), 7.53–7.50 (d, J = 7.5 Hz, 1H), 7.48–7.46 (d, J = 7.5 Hz, 1H), 7.45–7.43 (d, J = 7.43 Hz, 1H), 7.30–7.27 (m, 1H), 4.41–4.36 (m, 2H), 1.47–1.44 (t, J = 1.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 156.27, 151.24, 140.48, 140.42, 139.03, 137.75, 129.13, 128.80, 126.26, 124.73, 123.63, 122.83, 120.59, 119.37, 119.05, 117.02, 108.98, 108.82, 95.31, 37.72, 13.81.

Elemental Analysis (%): $C_{31}H_{22}I_2N_2$ Calcd.: C, 55.05; H, 3.28; I, 37.53; N, 4.14; found: C, 54.98; H, 3.38; N, 3.92.

2.3.1.1. Synthesis of model compound, 4-(9-ethyl-3-carbazole)-2,6-biphenyl pyridine (*$\mathbf{M_2}$*).

The model compound $\mathbf{M_2}$ was prepared in the similar procedure with the monomer $\mathbf{M_1}$ except using acetophenone instead of 4-iodoacetophenone.

In a round-bottomed flask equipped with a reflux condenser, a mixture of 9-ethyl-3-carbazolecarboxaldehyde (10 g, 44.8 mmol), acetophenone (10.44 mL, 89.6 mmol), ammonium acetate (60 g, 0.67 mol) and glacial acetic acid (214 mL) was refluxed for 72 h. Upon cooling, the ensuing viscous oil was separated and washed with hot ethanol and then purified by column separation from toluene to afford a light yellow colored, solid product (M.P. = 120 °C by DSC).

FTIR (KBr; cm^{-1}) Ar–H, 3039; C–H, 2970; C–H, 2926; C=N, 1597; C–N, 1226 for C–N of pyridine group; C=C, 1479.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.58–8.57 (d, J = 1.6 Hz, 1H), 8.45–8.43 (t, J = 8.4 Hz, 4H), 8.34–8.32 (dd, 1H), 8.13 (s, 2H), 7.91–7.89 (m, 1H), 7.71–7.68 (m, 4H), 7.65–7.60 (m, 3H), 7.53–7.50 (t, J = 18.2 Hz, 2H), 7.45–7.42 (m, 1H), 4.38–4.34 (q, 2H), 1.52–1.49 (t, J = 14.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 157.13, 150.70, 140.29, 140.17, 139.73, 129.34, 128.78, 128.53, 127.05, 126.02, 124.66, 123.42, 122.77, 120.48, 119.15, 118.89, 116.85, 108.77, 116.85, 37.40, 13.62.

Elemental Analysis (%): $C_{31}H_{24}N_2$ Calcd.: C, 87.70; H, 5.70; N, 6.60; found: C, 87.80; H, 5.67; N, 6.76.

2.3.2. Synthesis of the conjugated polymer, ***PyCzPF8***

In a 50 mL round flask fitted with a thermometer and a condenser were added 0.621 g (0.92 mmol) of $\mathbf{M_1}$, 0.439 g (0.92 mmol) of 9,9-dioctylfluorene-2,7-diboronic acid ($\mathbf{M_3}$), and 9.18 mL of K_2CO_3 (2 M in H_2O) in 20 mL of THF under nitrogen atmosphere. Then, $Pd(PPh_3)_4$ (0.6 mol%) was added, and the mixture was allowed to reflux at 60 °C for another 24 h. The polymer was precipitated in 1 L of acetone/MeOH (v/v = 1:1) and filtered. The precipitate was washed with a large amount of water. The polymer was reprecipitated three times. The polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues and was dried under reduced pressure at 150 °C with a high yield of 92%. FTIR (KBr; cm^{-1}) Ar–H, 3031; C–H, 2927; C–H, 2853; C=N, 1596; C=C, 1489.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.59 (s, 1H), 8.48–8.46 (d, J = 8.5 Hz, 4H), 8.30–8.29 (d, J = 8.3 Hz, 1H), 8.15 (s, 2H), 7.97–7.87 (m, 7H), 7.80 (s, 2H), 7.77–7.73 (t, J = 7.7 Hz, 2H), 7.60–7.57 (t, J = 7.5 Hz, 2H), 7.52–7.50 (d, J = 7.5 Hz, 1H), 7.38–7.35 (t, J = 7.4 Hz, 1H), 4.46–4.45 (m, 2H), 2.19 (m, 4H), 1.54–1.51 (t, J = 1.5 Hz, 3H), 2.28–1.19 (m, 20H), 0.89–0.76 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 157.03, 151.86, 151.05, 142.16, 140.51, 140.40, 140.28, 139.63, 138.64, 129.77, 127.59, 127.42, 126.21, 126.09, 124.90, 123.68, 122.95, 121.52, 120.63, 120.15, 119.35, 119.16, 117.03, 109.01, 108.80, 55.35, 40.40, 37.72, 31.78, 30.05, 29.24, 29.21, 23.93, 22.60, 14.06, 13.82.

Elemental Analysis (%): Calcd.: $(C_{60}H_{62}N_2)_n$: C, 88.84; H, 7.70; N, 3.45; found: C, 88.11; H, 7.67; N, 3.19.

2.4. Preparation of protonated polymer solutions

The protonation of the polymer was carried out by MSA, *p*-toluene sulfonic acid (PTS) and HCl solutions. For example, the polymer solution of 10^{-7} mg mL^{-1} with 1 M HCl was prepared by combining equal volume of a polymer solution of 2×10^{-7} mg mL^{-1} in THF and a 2 M HCl and THF solution. Then, the UV–vis and PL spectra of the polymer solution were recorded.

3. Results and discussion

3.1. Monomer synthesis

The diiodo compound, 4-(9-ethyl-3-carbazole)-2,6-bis(4-iodophenyl)pyridine (**M$_1$**), and model compound, 4-(9-ethyl-3-carbazole)-2,6-diphenyl pyridine (**M$_2$**), containing pyridine and carbazole groups were synthesized *via* facile Chichibabin reaction from 4-iodoacetophenone and acetophenone, respectively, with 9-ethyl-3-carbazolecarboxaldehyde as shown in Fig. 1. The structures were confirmed by elemental analysis, IR and NMR spectra. The characteristic band for the pyridine group in **M$_1$** and **M$_2$** monomers was observed at 1597 cm^{-1} in the FTIR spectrum. Fig. 2 shows the ^{1}H NMR (Fig. 2A) and ^{13}C NMR (Fig. 2B) spectra as well as two-dimensional spectra including COSY (Fig. 2C) and HMQC (Fig. 2D) of the model compound (**M$_2$**). The ethyl protons attached on the carbazole group appeared at 1.50 and 4.36 ppm in ^{1}H NMR spectrum (Fig. 2A). The signals appeared at 157.1, 150.7 and 116.9 ppm in ^{13}C NMR spectrum (Fig. 2B) confirmed the formation of heterocyclic pyridine ring. The assignments of the proton and the carbon peaks are assisted by the integral of proton peaks and the two-dimensional COSY (Fig. 2C) and HMQC (Fig. 2D) techniques. The basic COSY and HMQC procedures give two-dimensional spectra from which almost all of the ^{1}H–^{1}H and ^{1}H–^{13}C connectivity can be determined. Elemental analysis, IR and NMR spectra clearly confirm that the monomer compound (**M$_1$**) and model compound (**M$_2$**) synthesized herein are consistent with the proposed structure.

3.2. Polymerization

The synthesis of the conjugated polymer **PyCzPF8** containing pyridine and fluorene groups in the main chain and carbazole moiety in the side chain is depicted in Fig. 3. The conjugated polymer was prepared from the diiodo monomer (**M$_1$**) and 9,9-dioctylfluorene-2,7-diboronic acid (**M$_3$**) *via* Suzuki coupling reaction, which was carried out in a mixture of tetrahydrofuran (THF) and aqueous potassium carbonate solution (2 M) containing 0.6 mol% Pd(PPh$_3$)$_4$ under vigorous stirring at 60 °C for 24 h. After purification and drying, the polymer **PyCzPF8** was obtained as white color in good yield of 92%. The chemical structure of the polymer was verified by FTIR, elemental analyses and NMR spectra. The ^{1}H NMR and ^{13}C NMR in *d*-chloroform as well as peak assignments of polymer **PyCzPF8** were confirmed by the assistance of two-dimensional NMR spectra of **PyCzPF8**, such as COSY, HMQC, HMBC (Supplementary Fig. S1). The peaks of hydrogen in fluorene alkyl chain appear at 0–2 ppm. The integral of the hydrogen in ^{1}H NMR is consistent with the proposed polymer structure. The proton resonance signal of pyridine appeared at 7.90, 8.13 and 8.15 ppm for **M$_1$**, **M$_2$** and **PyCzPF8**, respectively. This means the electronic environment of model compound (**M$_2$**) is more similar to that of corresponding structure in **PyCzPF8** than that of monomer compound (**M$_1$**). In ^{13}C NMR spectrum, there are 26 well-resolved signals for the aromatic carbons which appeared in the range of 100–160 ppm and the peaks for the octyl carbon appeared in the range of 14–40 ppm. In addition, the carbon at 9-position of fluorene appeared at 55.3 ppm. All the results suggest that the conjugated polymer was successfully prepared.

3.3. Physical properties

The molecular weight of the polymer was determined by gel permeation chromatography (GPC) using the polystyrene as the standard and is summarized in Table 1. The number-average molecular weight of the prepared polymer was as high as 2.28×10^4 and the polydispersity index of **PyCzPF8** was 1.38. The polymer was soluble in common organic solvents, such as *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), dichloromethane (DCM), chloroform, toluene, 1,4-dioxane, xylene, 1,2-dichlorobenzene, anisole and benzene at room temperature.

The thermal properties of the polymer were measured by DSC and TGA, and the results are summarized in Table 2. The glass transition temperature of **PyCzPF8** was 192 °C (Fig. 4), which is much higher than that of poly-(9,9-dioctylfluorene) (POF) (POF; $T_g = 75$ °C) [24,25] due to the rigid heterocyclic pyridine groups [7–9] in the main chain and unsymmetric carbazole groups in the

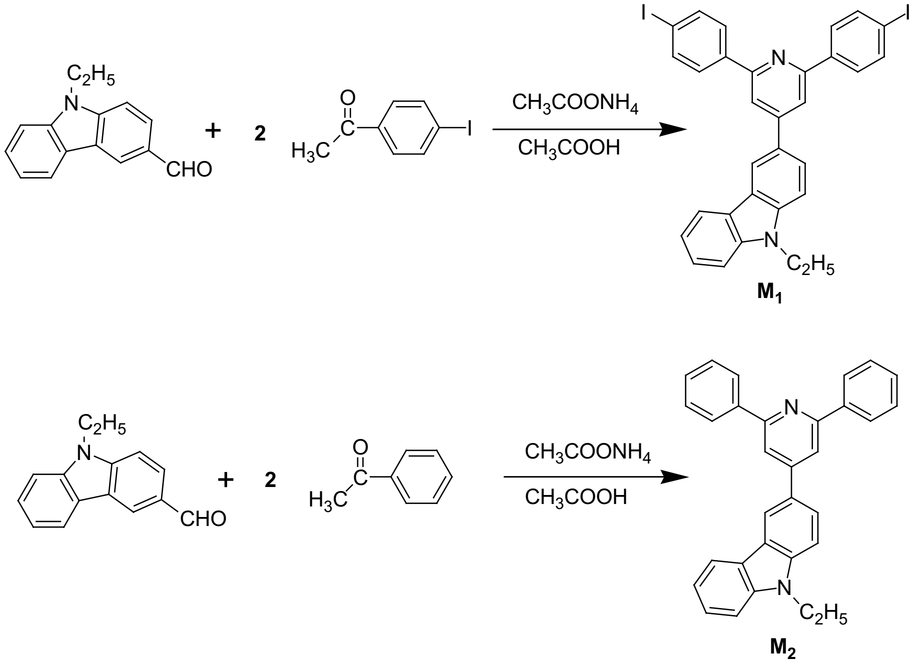

Fig. 1. Synthesis of monomer (**M$_1$**) and model compound (**M$_2$**).

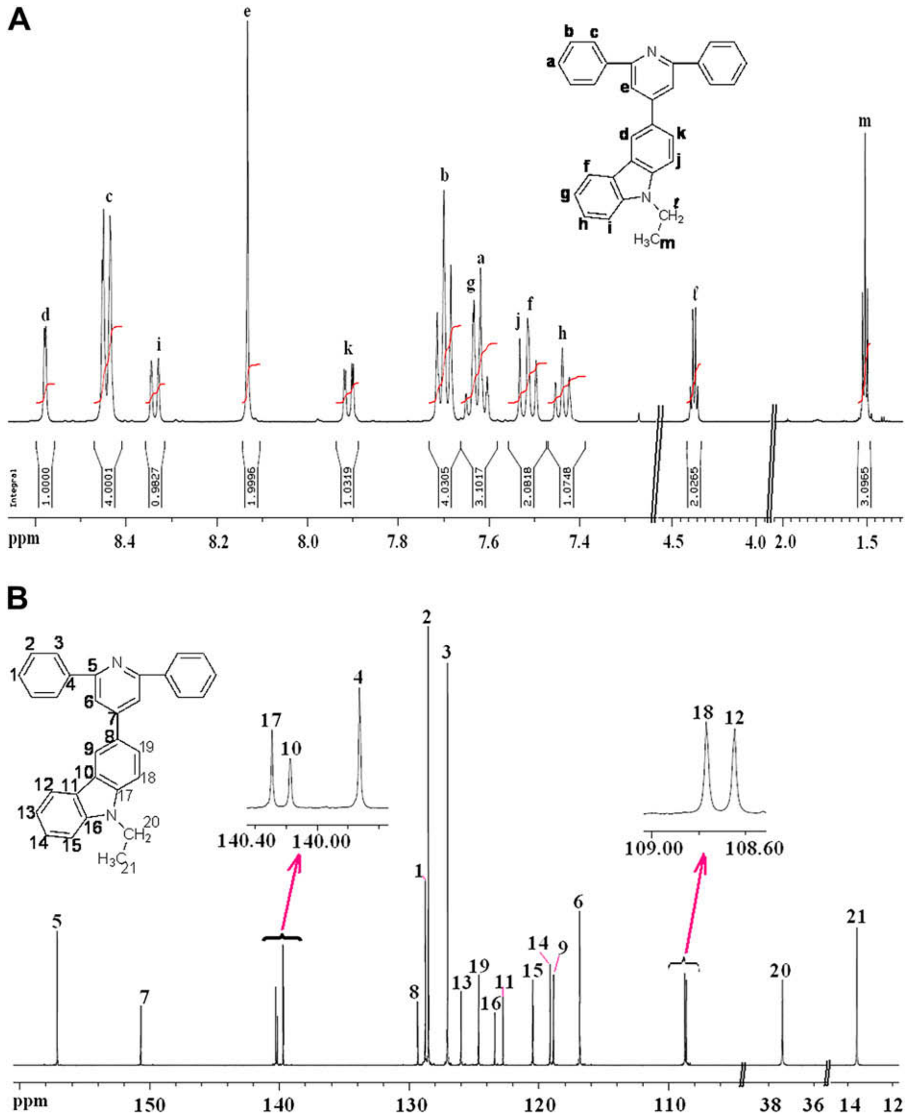

Fig. 2. (A) ^{1}H NMR, (B) ^{13}C NMR, (C) COSY and (D) HMQC spectra of model compound **M_2** in $CDCl_3$.

side chain [14,18]. The relatively high glass transition temperature has the thermal advantage for the application of electronic materials [15]. The thermal stability of the polymer was measured by TGA in nitrogen and air atmospheres as shown in Fig. 5. Two-step degradation was observed in the TGA spectrum in air atmosphere. The 1st degradation begins at about 401 °C and the 2nd at about 482 °C. The weight loss of **PyCzPF8** at 1st stage is 26.9%, which is also consistent with the content (28.0%) of alkyl chain in the polymer. This result suggested that the 1st degradation was due to the decomposition of the weak alkyl groups attached on fluorene. The result showed that the T_{d10} was 437 °C in nitrogen atmosphere.

The optical properties of the polymer were investigated by UV–vis and PL spectroscopy in solid state and in THF. The UV–vis and PL spectra of the polymer are shown in Fig. 6. The absorption and emission spectra of the polymer in THF solution as well as the model compound **M_2** and carbazole are shown in Fig. 6A. The photophysical properties of the polymer as well as the monomer and carbazole are summarized in Table 3. In THF solution, a major absorption at around 355 nm and a minor absorption at 306 nm were observed. By comparing with the absorption spectra of **M_2** and carbazole, we ascribe the minor absorption at 306 nm to π–π^* transition of pendant carbazole groups. From the result of the maximum absorption peak for poly-(9,9-dioctylfluorene) (POF) at 391 nm [24], the major absorption to π–π^* transition was ascribed to the conjugated polymer backbone. The polymer emits blue fluorescence in THF solution with a major emission at 399 nm and a minor emission at 418 nm. As comparing to emission peak of poly-(9,9-dioctylfluorene) (POF) [24], it is clear that the major emission originated from the fluorene structure. The emission peak of carbazole is overlapped by the absorption of the polymer. Therefore, the minor peak at 418 nm may be due to the Förster energy transfer as a consequence of good spectral overlap between the emission spectrum of carbazole and the absorption spectrum of the polymer backbone [26]. The fluorescence quantum yield (Φ_F) of the polymer in THF was estimated by comparing with the standard of 9,10-diphenylanthracene (*ca.* 1×10^{-5} M solution). The fluorescent quantum yield for **PyCzPF8** was 88% in THF solution. The choice of pyridine moiety as a comonomer for blue emission was motivated by their electron-deficient character, which generally leads to good electron transport properties. The absorption and PL spectra in solid state shown in Fig. 6B are similar to those in THF solution. The UV absorption peaks of the solid film were observed

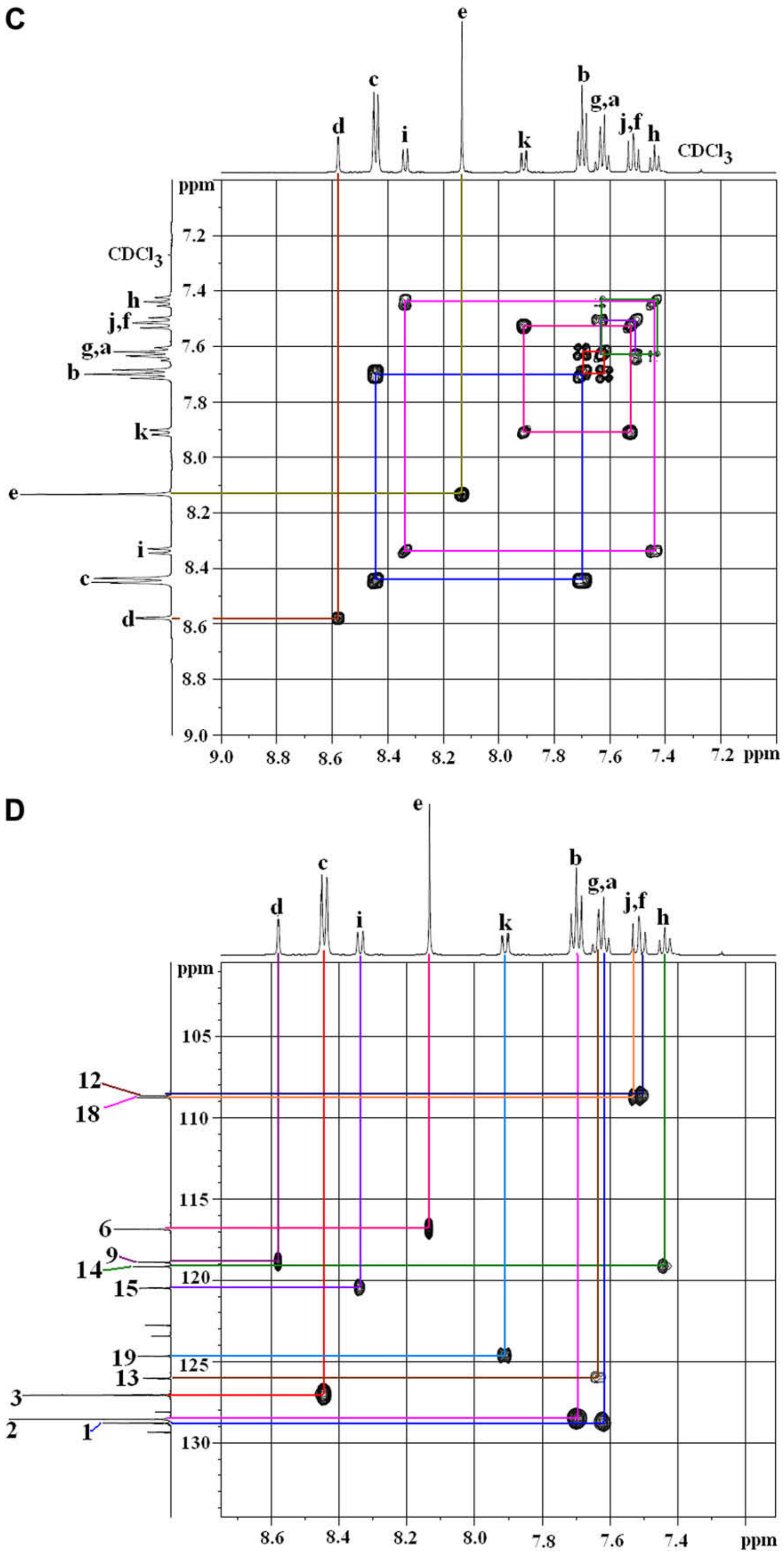

Fig. 2. (*continued*).

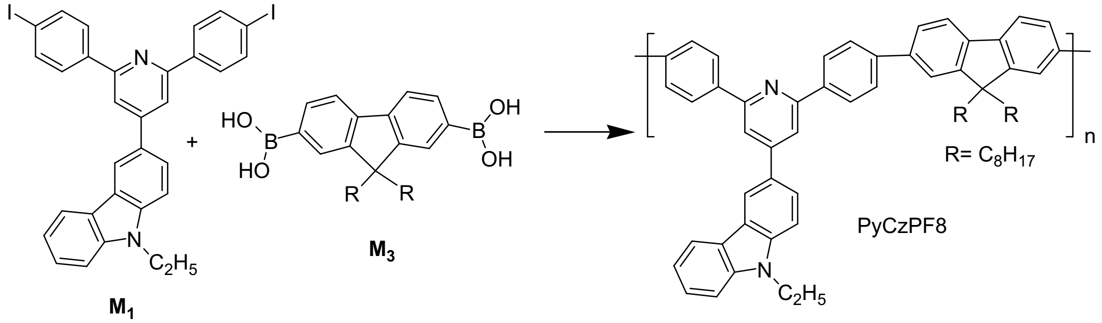

Fig. 3. Preparation of the novel conjugated polymer **PyCzPF8**.

at 304 and 355 nm and the PL spectrum at 414 and 430 nm due to the interchain interaction of the polymer. However, the polymer in solid state has very low fluorescent quantum yield (only about 6%).

The UV–vis absorption of the polymer in dilute solution (*ca.* 10^{-6} M) was investigated in different solutions with increasing solvent polarity including 1,4-dioxane, chloroform, anisole, NMP and mixture of chloroform and methanol (1:1) as shown in Fig. 7. The maximum absorption λ_{max} in above mentioned solvents appeared at 352 nm for less polar solvent like 1,4-dioxane and red-shifted to 382 nm for more polar mixture solvent such as chloroform and methanol (1:1) to 382 nm. It suggests that λ_{max} could increase up to 30 nm with increasing the solvent polarity. Such positive solvatochromism indicates significant intermolecular charge transfer between polar solvent and polymer [27–32].

Compared to benzene ring, pyridine is an electron-deficient aromatic heterocyclic substituent, with localized lone pair electrons in sp^2 orbital on the nitrogen atom. Consequently, the derived polymer offers the possibility of protonation or alkylation of the lone pair as a way of modifying their properties. Herein, the optical properties of the polymers after protonation with *p*-toluene sulfonic acid (PTS), methanesulfonic acid (MSA) and hydrochloric acid (HCl) were also investigated. The absorption spectra of **PyCzPF8** as a function of HCl, MSA and PTS in different concentration (Supplementary Fig. S2A). At low protonated concentration (lower than 0.1 M) the absorption bands are almost the same with pristine polymer. When the acid concentration was increased (higher than 0.1 M), it was apparent that the absorption decreased at around 355 nm and a new absorption band at 411, 412 and 422 nm was formed gradually after protonated by PTS, MSA, HCl, respectively. The new band at 430 nm could be attributed to the protonated form structure of pyridine. At high degree of protonation, the isosbestic point is lost due to repulsion between the charged pyridinium fragments [8]. The emission spectra of protonated polymer with HCl, MSA and PTS in different concentration (Supplementary Fig. S2B). The fluorescence peaks at 400 and 417 nm for the neutral polymer solution decreased and a new fluorescence peak arose at 556, 558 and 542 nm after protonation by PTS, MSA and HCl, respectively. This phenomenon suggests that the protonated structure emits fluorescence at longer wavelength than the unprotonated structure. In addition, the absorption and emission spectra of polymer protonated by PTS and MSA are almost the same, because PTS and MSA have the same structure of sulfonic group. This suggests that the absorption and emission of protonated polymer are relative to the structure of the conjugated base of the acid. Fig. 8 shows the change of emission color from original

Table 1
Molecular weight of the conjugated polymer **PyCzPF8**.

Polymer	M_n[a] ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	PDI	Yield
PyCzPF8	2.28	3.16	1.38	92%

[a] Molecular weight determined in THF.

Table 2
Thermal properties of the conjugated polymer **PyCzPF8**.

Polymer	T_g[a] (°C)	T_{d5}[b] (°C)		T_{d10}[b] (°C)		Char yield[c] (wt%)	
		N_2	Air	N_2	Air	N_2	Air
PyCzPF8	192	417	390	437	431	65	7

[a] Recorded by DSC at a heating rate of 10 °C min^{-1} and a nitrogen-flow rate of 30 cm^3 min^{-1}.

[b] Decomposition temperature, recorded by TGA at a heating rate of 10 °C min^{-1} and a gas-flow rate of 30 cm^3 min^{-1}.

[c] Residual weight percentage at 800 °C.

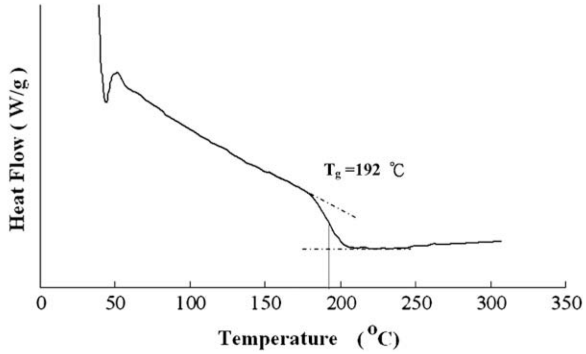

Fig. 4. DSC curve of **PyCzPF8** in nitrogen.

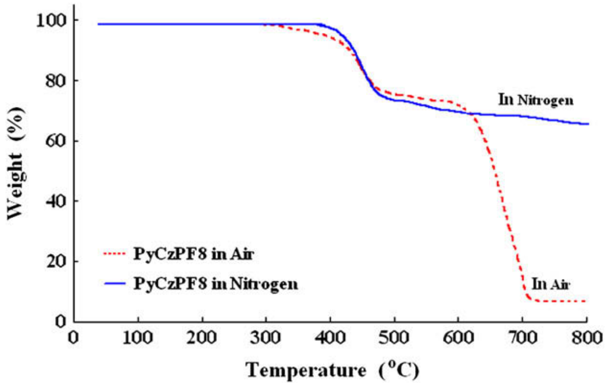

Fig. 5. TGA spectra of **PyCzPF8** in nitrogen and air atmospheres.

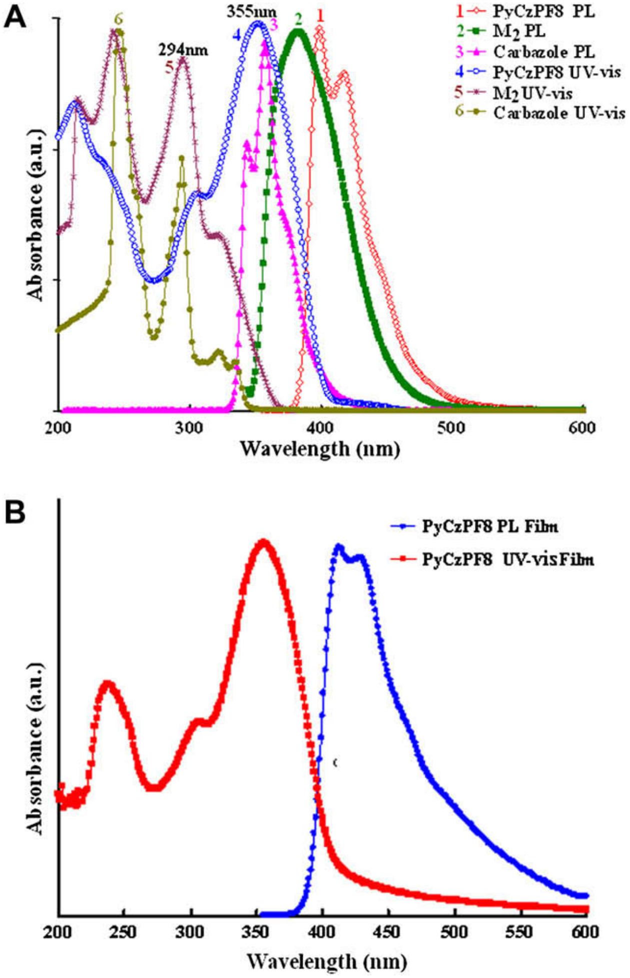

Fig. 6. UV and PL spectra of related compounds and the conjugated polymer **PyCzPF8** in solution (A) and (B) in film state.

blue to yellow in THF solution after protonation by 1 M HCl and MSA.

In order to understand the reversibility of the protonation, the optical properties of protonated polymer solution (protonated by 1 M HCl) was studied by adding additional sodium hydroxide. The reversible absorption and emission spectra are shown in Supplementary Fig. S3. The absorption peak at 420 nm resulted from the quaternized structure decreased and absorption at 355 nm increased as sodium hydroxide was added (Supplementary Fig. S3A). Moreover, the emission peak at 400 nm increased and the

Table 3
Photophysical properties of the monomers and conjugated polymers.

	Solution[a]			Film[b]		
	Abs[c]	PL[c]	Φ_f[d]	Abs[c]	PL[c]	Φ_f[d]
PyCzPF8	[234], [306], 355	399 [418]	0.88	[304], 355	414, [430]	0.06
POF[e] [24,25]	391	418	–	393	425	0.55
Carbazole	246, 294, [322]	[344], 357	–	–	–	–
M$_1$	299, [325]	388, [484]	0.08	–	–	–
M$_2$	241, 294, [322]	384	0.18			

[a] Evaluated in THF.

[b] Prepared by spin coating from a THF solution.

[c] Peaks that appear as shoulders or weak bands are indicated in parentheses.

[d] Determined in THF relative to 9,10-diphenylanthracence in THF ($\Phi_f = 0.9$) with excitation at 346 nm.

[e] POF: poly(9,9-dioctylfluorene).

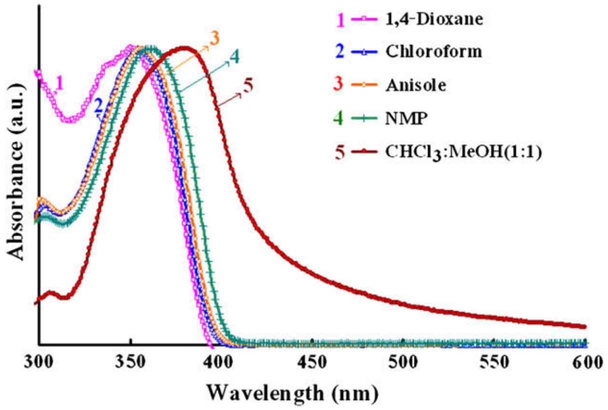

Fig. 7. UV–vis spectra of **PyCzPF8** in different solvents.

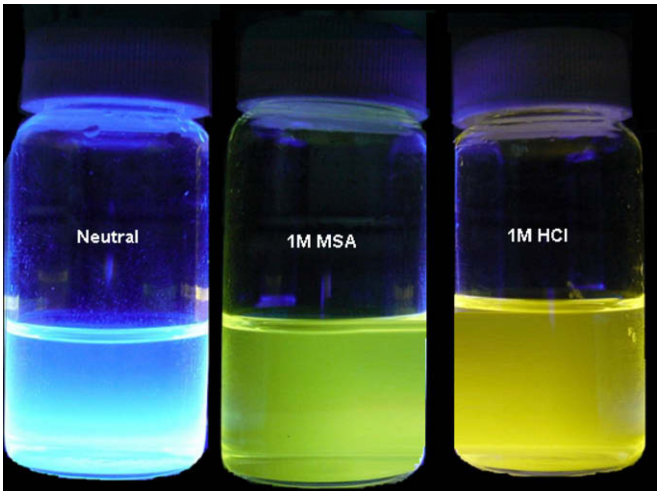

Fig. 8. The color changing of **PyCzPF8** solution from blue (left) to yellow after protonated by 1 M MSA (middle) or HCl (right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

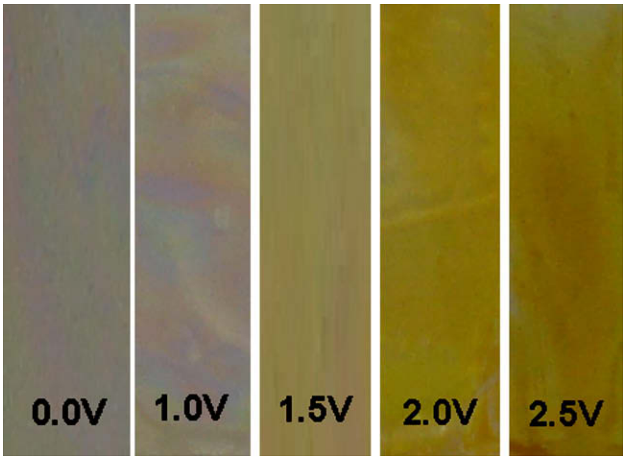

Fig. 9. Color changing of **PyCzPF8** under different applied voltages. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Electrochemical properties of the monomers and the polymer **PyCzPF8**.

Polymer		$\lambda_{\text{onset}}^{\text{abs}}$ (nm)	Band gap[b] (eV)	$E_{\text{onset}}^{\text{ox}}$ [c] (V)	HOMO[d] (eV)	LUMO[d] (eV)
PyCzPF8	Solution[a]	400	3.10	1.48, 0.92	−5.35	−2.25
	Film	409	3.03	1.55, 0.91	−5.97	−2.94
$\mathbf{M_1}$	Solution	370	3.35	1.34, 0.39	−5.21	−1.86
$\mathbf{M_2}$	Solution	365	3.40	0.95, 0.43	−4.85	−1.45

[a] Polymer solution in chloroform.
[b] Calculated from UV absorption spectrum: band gap $= 1240/\lambda_{\text{onset}}^{\text{abs}}$.
[c] The oxidation potential vs Ag/AgCl calculated from CV spectrum using ferrocene as internal standard.
[d] Calculated from the equation: HOMO $= -(E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{Fc}}) - 4.8$, LUMO $=$ HOMO $+$ band gap.

peak at 540 nm resulted from quaternized structure decreased after sodium hydroxide added (Supplementary Fig. S3B). The results suggest that the optical properties of the polymer are reversible under protonation and deprotonation.

The spectroelectrochemical analysis of the polymer was carried out on an ITO-coated glass substrate, and it showed electrochromic behavior when the applied potential was changed. The typical spectroelectrochemical absorption spectra of polymer **PyCzPF8** at various applied potentials are depicted (Supplementary Fig. S4A). When the applied potential was increased positively from 0 to 2.5 V, the peak of characteristic UV absorbance of **PyCzPF8** decreased at 350 nm gradually, while one new shoulder band grew up at 450 nm due to the electron oxidation of pyridine group. The PL emission spectra of the polymer **PyCzPF8** are depicted (Supplementary Fig. S4B). Increasing the voltage from 0 to 2.5 V, the PL peak of characteristic emission of **PyCzPF8** from 417 shifted to 550 nm. The change of the film from white yellow to deep brown with increasing the bias voltage is shown in Fig. 9 due to the oxidation of pyridine group.

The electrochemical behavior of the monomers and the polymer was investigated by cyclic voltammetry (CV) (Supplementary Fig. S5). From the oxidation potential relative to ferrocene/ferrocenium one, which can correspond to 4.8 eV [33] for ferrocene below the vacuum level, we can approximately calculate the HOMO energy level of the conjugated polymer. The LUMO level of the polymer was calculated according to the equation: LUMO $=$ HOMO $+ E_g$. The electrochemical properties of the monomers and polymer are summarized in Table 4. There are two oxidation states for the monomers and the polymer due to the nitrogen in the pyridine and carbazole groups. The HOMO and LUMO values of **PyCzPF8** were calculated to be −5.35 and −2.25 eV in chloroform and to be −5.97 and −2.94 eV for the film state. The energy gap for the polymer is *ca.* 3 eV.

4. Conclusion

A conjugated poly(pyridine–fluorene) polymer was successfully prepared *via* Suzuki coupling reaction from fluorene derivative and novel diiodo monomer containing pyridine with unsymmetric carbazole moieties. The structure of the poly(pyridine–fluorene) having unsymmetric pendant carbazole was well identified. All the optical properties clearly indicate that this new conjugated poly(pyridine–fluorene) exhibited chromic properties for the development of polymeric electrochromic and chemochromic materials. In particular, new poly(pyridine–fluorene) has excellent solubility in common organic solvents, high molecular weight, good thermal stability and high glass transition temperature, which could meet the basic requirements for the development of optoelectronics and photonics.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2008.12.004.

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