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Synthesis and photophysics of new highly luminescent poly(alkylthiophene) derivatives with pyridine in the backbone

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Abstract

Starting from 2,6-bis-(3-octylthiophene-2yl)-pyridine, two new poly(alkylthiophene) derivatives, POTPyOT and POTPy, containing pyridine in the backbone were prepared from nickel(0)-mediated Stille coupling or by palladium-catalyzed Yamamoto coupling. These polymers exhibited good solubility in common organic solvents, thermal stability up to 400 °C, and facile film formation. They were amorphous and give strong luminescence both in $CHCl_3$ solution and solid state film. The polymers emitted blue light in solution with photoluminescence (PL) emission maximum at 420–484 nm and green light with PL emission maximum at 500–514 nm in thin films. These polymers showed a reversible redox reaction at potential from 0 to 1.3 V (vs. SCE). Nevertheless, the reduced form of the polymer was very unstable; it decomposed in the presence of oxygen or water. The emission and UV–vis absorption of the polymer were influenced by the solvent polarity, protonation, and acid–base treatment. These may be the results of the stabilization of the polar excited state by solvation and the change of the conformation in polymer backbone. Electroluminescence (EL) was achieved from a single-layer PLED with the configuration of ITO/POTPyOT/Al. The turn-on voltage of the device is 10 V and the λ_{max} (550 nm) of the EL is voltage independent.

Keywords: Polythiophenes; Yamamoto coupling; Copolymer

1. Introduction

Since the first report of light emitting diodes based on PPV [1], conjugated polymers have shown their great potential for the new generation of display technology [2]. In PLED investigations, tunability of the emission spectrum to any desired color including white still presents interesting challenges. Various methods have been reported for tuning the emission of the polymer LED. Such as changing the main chain molecular structure [3], changing the side chain molecular structure [4], blending an electroluminescent polymer with a second active polymer [5] or with low molecular weight organic or inorganic molecules [6], through heterojunctions of two EL polymers [7] and doping [8]. To date, a variety of conjugated polymers and/or copolymers have been found whose emission colors cover all the visible spectra. However, searching for materials with improved processibility, mechanical properties, and stability is still a continuing research challenge.

Amongst conjugated polymers, processable polythiophene derivatives occupy an important position [9]. In comparison with other conjugated polymers, polythiophenes have many attractive characteristics, such as unique electro-optical properties, good environmental stability, and structure versatility, for application in polymeric light emitting diodes (PLEDs) [10]. Nevertheless, compared with other electroluminescent polymers, such as PPVs and PPPs, the poor electroluminescence quantum yields (typically $\sim 10^{-4}\%$) limits their application as the active materials in PLEDs [11]. Much work has been devoted to improve the PL and EL efficiencies of processable polythiophenes [12]. For example, Pei et al. [13] had mentioned that introduction of phenyl ring either as the side chain or as part of the main chain of polythiophenes has an obvious effect on the improvement of PL quantum yields of the polymers.

The application of pyridine as the π-deficient moiety in the backbone of conjugated polymers is driven by the consideration that its homopolymer (Ppy) has been used in blue emitting devices [14] and that other pyridine-containing

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copolymers have been demonstrated to be highly luminescence [15]. In addition, introduction of the pyridinyl moiety in the polymer backbone not only have the electron-accepting ability but also are reactive for N-protonation, N-oxidation, and quaternization with RX, which can modify their optical and electrical properties [16]. Furthermore, as compared to phenylene-based analogues, one of the most important features of the pyridine-based polymers is the higher electron affinity. As a consequence, the polymer shows better electron transport properties. The capability of using relatively stable metals, such as Al or even ITO, as an efficient electron injecting contact and eliminating the use of low work-function metals make the pyridine based polymers the excellent candidates for polymer light-emitting devices.

Herein we report the syntheses and properties of two soluble luminescent polymers containing the pyridine and thiophene units. The synthetic approaches, photophysics, and chemsensing properties were investigated. A single layer ITO/polymer/Al device based on these polymers has also demonstrated.

2. Experimental section

2.1. Chemicals

Dibromopyridine, 3-bromothiophene, and other chemicals used in this study were obtained from commercial resource and used as received. Solvents were dried over sodium and distilled before use. ITO glass was purchased from the Merck Display Technologies Ltd with ITO thickness of 100 nm and surface resistance of ~20 Ω/sq.

2.2. General procedure for polymer preparation

2,6-Bis-(3-octylthiophene-2yl)-pyridine (OTPyOT) was prepared with the methods modified from the literature [17] and identified with ^{1}H NMR. Poly-2,6-bis-(3-octylthiophene-2yl)-pyridine (POTPyOT) was obtained from the bromination of OTPyOT followed by Yamamoto coupling catalyzed with $NiCl_2$. Poly-2-(3-octylthiophene-2yl)-pyridine (POTPy) was prepared by first stannylation of OTPyOT followed by reacting it with 2,6-dimromopyidine via Stille coupling reaction. All the reactions were carried out in dry Ar atmosphere using solvent dried over Na. The crude polymers were dissolved in THF, separated from the solid impurity by filtration, and precipitated from methanol. Polymer powders were collected by centrifugation and then washed with methanol and hexane for one week respectively using a Soxhlet apparatus. POTPyOT is a yellowish green powder. ^{1}H NMR (200 MHz, $CDCl_3$) are δ: 7–8 (m, 5H), 3.0 (s (broad), 4H), 0.4–1.8 (m, 30H). Elemental analyses calculate for $(C_{29}H_{39}NS_2)_{16}Br_2$: C, 73.26%; H, 8.21%; N, 2.94%; S, 13.47%. Found: C, 71.79%; H, 7.85%, N, 2.93%; S, 11.72%. The color of POTPy powder is greenish yellow and ^{1}H NMR (200MHz, $CDCl_3$) are δ: 7–8 (m, 5H), 3.0 (s (broad), 4H), 0.4–1.8 (m, 30H). Elemental analyses calculate for $(C_{17}H_{21}NS)_{22}(SnMe_3)_2$: C, 72.34%; H, 7.68%; N, 4.88%; S, 11.17%. Found: C, 63.18%; H, 6.94%, N, 4.34%; S, 10.70%. POTPy is a very thermal stable polymer; there is a large amount of carbon residue left after heating up to 1150 °C.

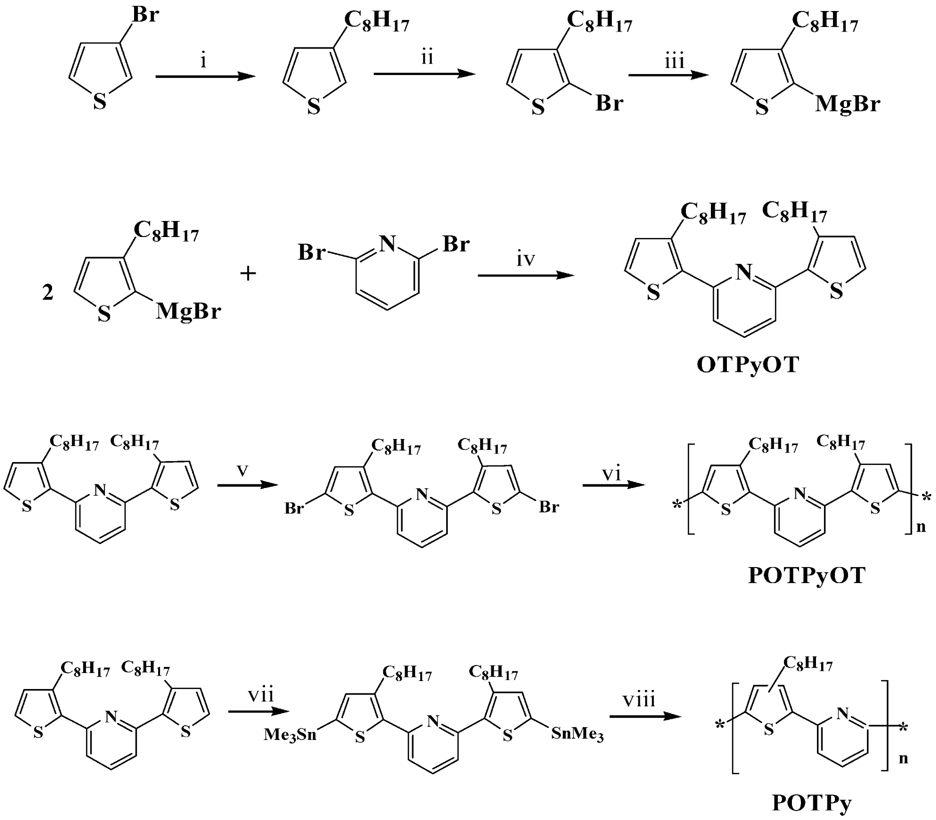
2.3. Physicochemical measurements

^{1}H NMR spectra were recorded with a Bruker DRX-200 NMR spectrometer in $CDCl_3$. Elemental analyses were carried out with a Heraeus CHN–O–S Rapid-F002 analysis system. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7 thermal analysis system using dry nitrogen (or oxygen) as a carrier gas at a flow rate of 100 ml/s X-ray photoelectron spectroscopy studies were carried out on a Perkin–Elmer PHI-590AM ESCA/XPS spectrometer system with a Cylindrical Mirror Electron (CMA) energy analyzer. The X-ray sources were Al K_α at 600 W and Mg K_α at 400 W. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters-2487 instrument calibrated using THF as an eluent and polystyrene as standards. Scanning electron micrographs (SEM) were recorded with a Hitachi S-800 at 15 kV. The samples (film on ITO glass) for SEM imaging were mounted on metal stubs with a piece of conducting tape then coated with a thin layer of gold film to avoid charging. Photoluminescence spectra (both in $CHCl_3$ solution and spin-coated films) were obtained using Hitachi F-4500 spectrophotometer in the laboratory atmosphere at room temperature. Variable temperature UV/vis/NIR spectra were recorded with a Cary 5E spectrometer equipped a hot plate in the sample compartment. The polymer film on glass was mounted on the hot plate; the spectra were recoded from 30 to 150 °C with 20 °C increment. Cyclic voltammograms of the polymer films (dip-coated onto Pt disk) were recorded using a Model 263 electrochemical instrument of EG&G PAR potentiostat/galvanostat. The electrochemical was put inside the sample compartment of the UV/vis spectrometer, therefore the UV/vis spectra can be taken simultaneously. The experiments were carried out in air at room temperature using a solution of $LiClO_4$ (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A Pt wire was used as the counter electrode and an Ag/Ag^+ electrode as the reference electrode. Single layer PLED devices were fabricated by first spinning coated polymer on ITO glass and then Al metal was deposited on top of the polymer film in high vacuum ($<10^{-6}$ Torr). The active area of the device was approximately 12 mm^2 and the measurements were curried out under DC-biased condition in ambient atmosphere. The voltage-current and voltage-luminance characteristics were recorded on a current-voltage source (Keithley 2400) and a luminescence detector (Newport 1835-C). EL spectra were obtained with a Hitachi F-4500 spectrophotometer. The thickness and surface roughness of polymer films were measured with a Dektak ST surface profile measuring system. The scan length is 10 mm and the thickness and surface roughness were calculated from the average values of the scanned length.

3. Results and discussion

3.1. Synthesis

The synthetic routes of the key monomer, OTPyOT, and target polymers were outlined in Scheme 1. The palladium(0)-catalyzed Yamamoto-coupling of 2,6-bis-(5-bromo-3-octylthiophene-2yl)-pyridine, which is prepared from the bromination of OTPyOT by *N*-bromosuccinimide (NBS), was used to prepare POTPyOT. Oxidative polymerization is the general method to synthesize conjugated polymers. However, when ferric chloride is employed as the oxidant for polymerization, the main drawback comes from the difficulty in removing the trace amount of ferric ions from the resulting polymers. The ferric impurity level affects the photo-physics of the polymer and therefore the PLED device performance. Chemical coupling polymerization reactions, such as Yamamoto coupling, can also produce deserved conjugated polymers. This type of reactions not only avoids using oxidant but also affords the desired polymer without irregular coupling or branching sometimes seen in conventional electrochemical and oxidative polymerization [18]. Therefore, POTPyOT studied in this article was synthesized via a Yamamoto coupling reaction. The attempt to prepare POTPy from the oxidative polymerization of 2-(3-octylthiophene-2yl)-pyridine has failed and the bromination of 2-(3-octylthiophene-2yl)-pyridine with NBS in DMF was also not successful. The high electronegative nitrogen atom in the pyridine ring made the carbon atom more positive, therefore more difficult to be oxidized, compared to thiophene ring. Therefore, POTPy was prepared by Stille coupling of 2,6-bis-(3-octyl-5-trimethylstannanyl-thiophene-2-yl)pyridine (which was prepared by lithiation of 2-(3-octylthiophene-2yl)-pyridine followed by treating the resulting product with trimethyltin chloride) and then with 2,6-dibromopyridine (Scheme 1). Chemical coupling polymerization, such as Stille coupling (Scheme 1), also provided a proper way to prepare new conjugated polymer. The palladium cross-coupling and metathesis methods provide access to a large variety of polymers with different moieties in the repeating units. They could facilitate the generation of pyridine-containing copolymer with many different building blocks selected to enhance properties such as solubility, photo-physics, charge transport, and intramolecular charge transfer [19]. Nevertheless, the trimethyltin terminal group on the polymer backbone may affect the photo-physics and the applications of the polymer. Fortunately, the



Scheme 1. Synthesis of (poly(2,(3-octylthiophene-2yl)-pyridine (POTPy) and poly-2,6-bis-(3-octylthiophene-2yl)-pyridine (POTPyOT).

trimethyltin can be removed by passing the polymer solution (in toluene) through the silicon-gel column or washing the polymer with acidic aqueous solution. The structure and purity of the polymers were characterized using ^{1}H NMR and elemental analysis (reported in the Section 2).

3.2. Characterization of the polymers

The physical data of POTPyOT and POTPy are summarized in Table 1. The obtained polymers showed good solubility in common organic solvents such as chloroform, THF, and toluene. As shown in Table 1, the weight-average molecular weights (M_w) of these polymers are estimated to be 6000–7000 (polystyrene standards) with the polydispersity index (M_w/M_n) of ~1.6 by GPC measurement. These results agree with the data obtained from the elemental and ESCA analysis. Both polymers showed good thermal stability under N_2. The first major weight loss started around 360–400 °C, and a residual weight of about 20–60% was detected at 850 °C. Data of the 5% weight loss temperatures (T_d) of the polymers are up to 400 °C. Fig. 1 depicts the ^{1}H NMR spectra of POTPyOT, POTPy and the corresponding monomer in $CDCl_3$. The chemical shifts of the pyridinyl protons were revealed at d 7.78, 7.45, 7.25 ppm whilst thiopheneyl proton appeared at ~7.0 ppm. The remaining resonance at 3.0 and 0.5–2.0 ppm corresponded to the C_β-proton and other protons of the *n*-octyl pendant chains. The chemical shifts of the polymers (Fig. 1(b)) are similar to those of the corresponding monomers but the peak is broader and not well resolved. This is consistent with what had observed in conjugated polymer and its corresponding monomer reported in the literature [20]. IR spectra of the polymer films showed two different aromatic ring stretchings at 1558, and 1434 cm^{-1}, respectively. IR spectra of the polymers resembled those of the monomers; except a weak absorption peak at near 1100 cm^{-1} (ν(C–Br)) was observed in POTPyOT. This peak comes from the terminal C–Br bond of the polymer chain. No peak at 1100 cm^{-1} was detected in POTPy since its terminal group is trimethyl tin ($SnMe_3$). X-ray diffraction study showed that the polymer films are amorphous in nature. Non-ordered structure is considered to be advantageous in the application in light emitting diode devices [21]. Fig. 2 shows the cyclic voltammogram (CV) for a cast film of POTPyOT on a Pt plate in an acetonitrile solution of $LiClO_4$ (0.10 M). In the oxidative region, a peak is observed at $E_{ox} = 1.2$ V (vs. Ag^+/Ag), which is assigned to oxidation (p-doping) of the thiophene ring and a reversible reduction (p-dedoping) peak appeared at 0.7 V. The electrochemical p-doping/p-dedoping process is very reversible. There is no obvious change in the features of the CV diagrams during the repeated scanning. However, when the potential was scanned up to 2.0 V, no p-dedoping occurs between 2.0–0 V (vs. Ag^+/Ag). On the other hand, during the cathodic scan, a reduction (n-doping) starts at about −1.8 V (overlap with the reduction of H_2O, as displayed in Fig. 2). Nevertheless, the n-doped POTPyOT is not quite stable; it decomposed in the presence of H_2O or oxygen. Therefore, no corresponding oxidation (n-dedoping) peak was observed at the reverse scan. The electrochemical redox data of the polymers are also summarized in Table 1.

Table 1
The physical data of POTPyOT and POTPy

Polymer	POTPyOT[d]	POTPy
Color	Yellow green	Brownish yellow
M_w[a]	7316	6040
PDI	1.6	1.6
T_d[b] (°C)	350	407
Eox (V vs. SCE)[c]	1.2	1.3

[a] M_w: weight average molecular weight determined by GPC (polystyrene standard).

[b] 5% weight-loss temperature measured by TGA under N2 with a heating rate of 10 °C min^{-1}.

[c] Peak potential.

[d] Prepared from the oxidation polymerization of OTPyOT.

3.3. Photophysics of the polymers

Fig. 3 depicts the UV–vis absorption spectra of POTPyOT and POTPy both in $CHCl_3$ and film states. POTPyOT solution exhibits the absorption peak (λ_{max}) due to π–π^* absorption at 399 nm at solution and at 420 nm in film. The λ_{max} position is comparable to those of poly(fluorene)s [22] but is shifted by about 130 nm to a shorter wavelength compared with that of POTTOT (its thiophene analogue, prepared by our Lab.). Comparing with the similar polymers prepared by Ng [23] (and others) and other polythiophene derivatives containing only thiophene rings [24], introducing the pyridine ring which has meta-linkage in thiophene backbone do show blue-shifted absorption. Polymer chain with a meta-linkage pyridine ring has less extended π-electron delocalization, therefore, has shorter π-conjugation length. The absorption maxima of POTPy in $CHCl_3$ solution and film state are 353 and 370 nm, even more blue-shifted compared to POTPyOT. This might be attributed to the more meta-linked pyridine ring per unit mass of the polymer in POTPy. It was worth noting that the absorption maximum of POTPy in $CHCl_3$ is only 20 nm shorter than that in the film state. The similar absorption maximum of POTPy in $CHCl_3$ solution and solid state indicated that the interaction between polymer chains is negligible in the film state. Weak interaction between polymer chains can avoid aggregation quench and thus may be the reason that why the quantum efficient of POTPy film is relatively high (vide infra). We also measured the optical properties of these polymers in CF_3COOH solutions and films cast from CF_3COOH solutions. As expect, the absorption and emission of these polymers occur at a longer wavelength in CF_3COOH solution compared to those in $CHCl_3$ solution and at the same time the luminescent intensity decreased. These phenomena were also observed

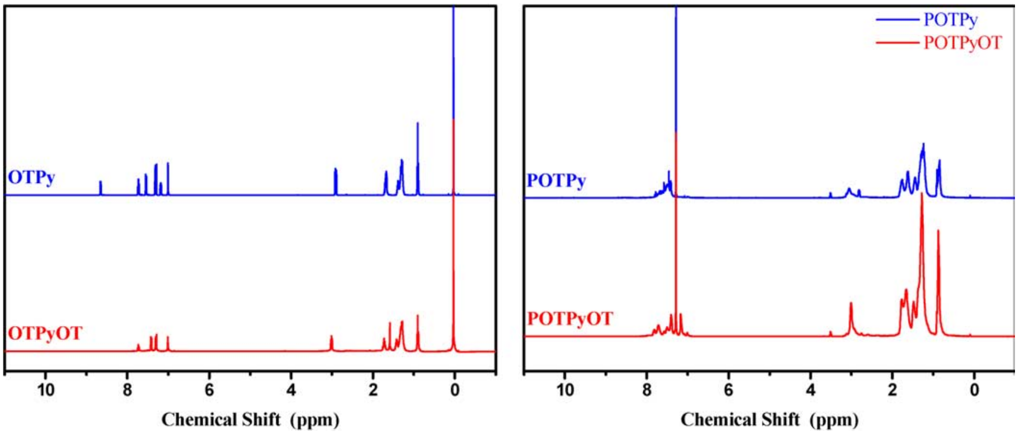


Fig. 1. ^1H NMR spectra of OTPy, OTPyOT, POTPy, and POTPyOT.

in other pyridinyl- [24] or quinoline- [25] containing conjugated polymers. The optical properties of POTPy and POTPyOT in solution and film states were summarized in Table 2. Variable temperature UV/vis spectra of POTPyOT and POTPy films were shown in Fig. 4. The $\lambda_{\max}$ of the POTPy and POTPyOT films shift from 370 and 420 nm at room temperature to 360 and 400 nm, respectively at 150 °C and the changes were reversible.

POTPy in $CHCl_3$ has the emission maximum of 420 nm and the PL $\lambda_{\max}$ of POTPyOT/$CHCl_3$ solution is 489 nm, both are blue luminescence. POTPy is highly photoluminescent both in solution and film state. The photoluminescence quantum yield of the polymer in $CHCl_3$ solution relative to quinine sulfate in 0.1 N H_2SO_4 solution was determined according to the method described in the literatures [26]. The quantum yield of POTPy in $CHCl_3$ solution is not as good as that of the quinine sulfate, however, the PL quantum efficiency of the POTPy film is three times better than that of MEH-PPV film [27] at the similar thickness. The PL peak (the position of λ_{EM}) of the polymers in $CHCl_3$ agreed with the onset position of the absorption band; this was usually observed with π-conjugated polymers in organic solvents. The Stokes shift of POTPy solution is similar to that of POTPyOT solution, suggesting that both polymers can be well-dispersed in $CHCl_3$, although POTPy is less soluble in $CHCl_3$ than POTPyOT. The higher luminescence of POTPy compared to POTPyOT in $CHCl_3$ is due to that the former has more highly luminescent pyridine rings per unit mass. It is interesting to note that the PL behavior of POTPyOT was quite different from that of POTPy. The difference of λ_{EM} for POTPyOT in film and $CHCl_3$ solution are only 25 nm. Nevertheless, the λ_{EM} of POTPy in film shifts by about 80 nm toward longer wavelength compared to those in solution and there is also a large Stokes shift (130 nm) of POTPy film (Table 2). This may be due to the aggregation of POTPy chains or the formation of the excimer-like adducts between the photoexcited POTPy and POTPy in the ground state. We did not know the conformation of POTPy and POTPyOT chains. However, computer simulation of the corresponding dimers showed that the pyridine ring and thiophene ring was not coplanar (due to pyridine is metalinked to thiphene); the torsion angle of POTPy dimer is bigger than that of POTPyOT dimer. We can expect that POTPy film has more aggregated chains. Jenekhe et al. [28] had proposed that the rather large Stokes shift and broad emission band in the solid state suggested that the dominant emitting species are intermolecular in nature, namely aggregates and excimers. The formation of aggregates or excimers may be one of the possible non-radiative mechanisms in the solid state. However, POTPy film revealed high PL quantum efficiency compared to other luminescent conjugated polymers, such as MEH-PPV [27]. The results may suggest that the photo absorption and excitons recombination process in pyridine-based polymer may different from that in other conjugated polymers.

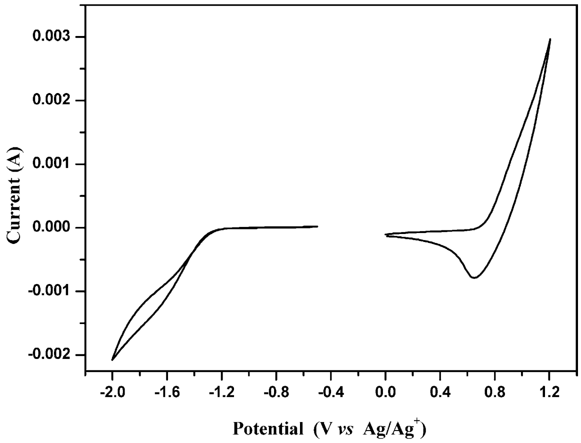


Fig. 2. The cyclic voltammogram (CV) for a cast film of POTPyOT on a Pt plate in an acetonitrile solution of $LiClO_4$ (0.10 M).

The absorption coefficient in $CHCl_3$ solution and the lifetime of the excitons (obtained from the time-resolved PL spectra [29]) for POTPyOT and POTPy were listed in Table 3. Comparing to the thiophene analogues [30], pyridine-containing polyalkylthiophenes have a lower absorption

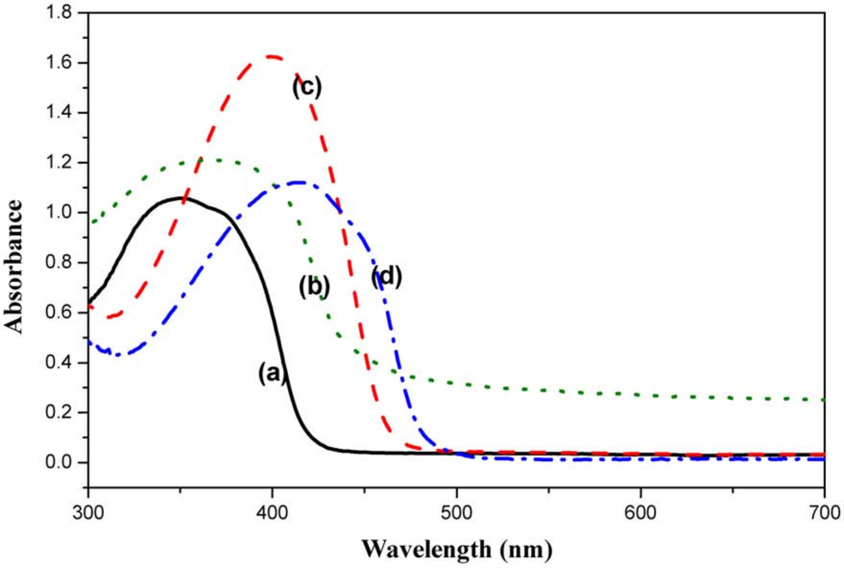


Fig. 3. UV/vis spectra of (a) POTPy in $CHCl_3$ (b) POTPy film (c) POTPyOT in $CHCl_3$ (d) POTPyOT film (the concentration of polymer solution is 5×10^{-5} M).

coefficient and longer exciton lifetime. The longer lifetime of the excitons may be the reason that POTPy showed high quantum efficiency. Interestingly, the exciton lifetime of POTPyOT film is close to that of POTPy film, nevertheless, POTPyOT in $CHCl_3$ has a lifetime much shorter than POTPy but similar to its thiophene analogue in $CHCl_3$. These results indicated that the exciton relaxation in pyridine ring is different from that of thiophene ring. The detailed studies of the luminescent mechanism of these pyridine containing polymers will be reported elsewhere [29].

It was known that the conformation and aggregation of polymer chains will affect their photophysics. The effect of chain conformation and aggregation on the optical properties of these polymers was test by dissolving them in solvents with different polarity. The λ_{max}, λ_{EM}, and Φ of POTPy and POTPyOT solutions were not influenced by solvent polarity. Nevertheless, the absorption coefficient (ε) of both polymers varied with solvent polarity as shown in Fig. 5. As seen in Fig. 5, both POTPy and POTPyOT in THF have a highest ε value amongst the solvents used in this study. In other words, polymers may have a largest transition dipole moment in THF. The electronic state of the polymers in the ground state and excited state was affected significantly by the solvent surrounded them. Therefore, we can assume that this solvent effect may be due to the increasing of the dipole moment in the excited state by solvation. Both polymers contain an alternating electron-accepting pyridine unit and an electron-donating alkylthiophene (bisalkylthiophene) unit, and it is considered to have an intramolecular charge transfer (CT) structure at the exciting state. Photoexcitation will cause migration of an electron from the alkylthiophene unit to the pyridine unit to increase the intramolecular polarization, and stabilization of the excited state by the THF accounts for the larger absorption coefficient. This phenomenon was so-called ‘solvent effect’ [31], which has a considerable impact on the luminescence properties of polymers. However, we did not see such solvent effect in luminescence spectra shown in Fig. 5. Therefore, the effect of solvent on the ε of the polymers can be temporarily regarded as the change of the conformation of polymer chains in various solvent and, accidentally, all chain conformation has a similar quantum yield. Detail study of the photophysics of these polymers is undergoing and the results will be reported elsewhere.

POTPyOT and POTPy are considered to react with protic acids. Actually, as reported in previous paragraphs, the polymers were effectively protonated with trifluoroacetic acid (TFA), leads to a considerably large red-shift of the λ_{max} from 353 to 405 nm for POTPy. The PL intensity is, on the other hand, strongly decreased due to the protonation of the imine nitrogen. The pH sensitivity of these polymers was also test by dipping the polymer films in HCl (or NH_4OH) aqueous solution. The absorption and emission spectra of the acid (or base) treated polymer films were showed in Fig. 6. It was surprised to found that without changing the λ_{max} and absorption coefficient, the quantum efficiency of both acid and base treated polymer increased. The enhanced luminescence may be due to the change of the film morphology after reacting with acid or base. A slight increase in the absorption band edge is also observed. This may suggest that there is a conformational change, leading to subtle changes in the electronic structure of the polymer film.

3.4. Electroluminescence properties

To investigate the electroluminescence properties and

Table 2
Optical properties of POTPy and POTPyOT

Polymer	Solution state					Film state			
	In $CHCl_3$ solution			In CF_3COOH solution					
	UV λ_{max} (nm)	λ_{EM} (nm)[a]	Φ (%)[b]	UV λ_{max} (nm)	λ_{EM} (nm)	UV λ_{max} (nm)	λ_{EM} (nm)[c]	Eg (eV)[d]	Φ (%)[e]
POTPy	353	420	31.2	405	533	370	500	2.81	23.3
POTPyOT	399	489	8.5	460	586	420	514	2.57	6.7
MEH-PPV	495	554	7.0	–	–	505	577	2.16	7.0

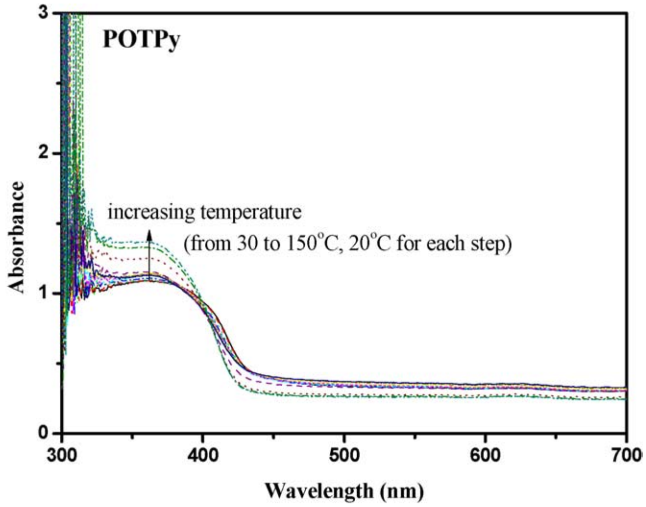
[a] The concentration of polymer is 5×10^{-5} M and the excitation wavelength is 330 nm for POTPy and 360 nm for POTPyOT solution.

[b] PL quantum yield calculated by comparing with the standard of quinine sulfate (ca. 10^{-5} M in 0.1 N H_2SO_4 aqueous solution, having a quantum yield of 55%).

[c] The excitation wavelength is 395 nm for POTPyOT film and 350 nm for POTPy film.

[d] The optical gap, E_g, taken as the absorption onset of the UV/vis spectra of the polymer films.

[e] The quantum yield of polymer films was calculated by comparing with MEH-PPV film which quantum yield was assumed to be the same as that in $CHCl_3$ solution.



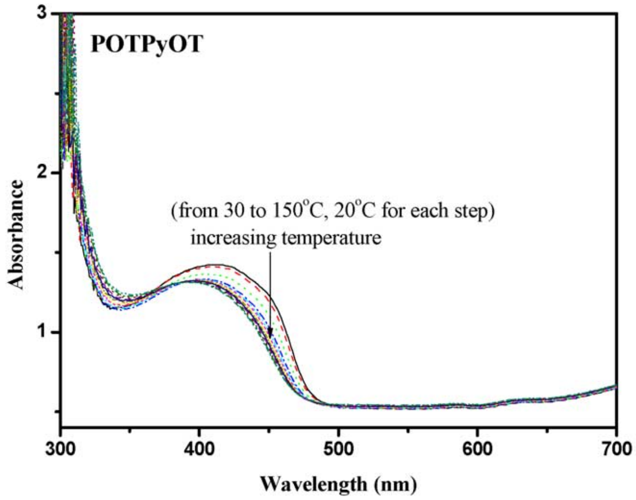


Fig. 4. Variable temperature UV/vis spectra of POTPy and POTPyOT films.

the current–voltage–luminance characteristics of the synthesized polymers, devices with the configuration ITO (100 nm)/polymer (100 nm)/Al (200 nm) were fabricated. The polymer was spin-coated from a 1.0 wt% solution in chloroform onto an ITO substrate then 200 nm of Al was deposited on the polymer via vacuum evaporation. The current density–voltage–luminance characteristics of the device are shown in Fig. 7(a). The turn-on voltage of the diode is ca. 10 V. The corresponding EL spectra, under various operating voltages (10–18 V) revealed a voltage-independent EL colors (CIE: 0.35, 0.58). The EL spectrum together with the absorption and PL spectra of the polymer film were also shown in Fig. 7(b). The EL spectrum of polymer depicted a close correspondence to the PL spectrum, indicating the recombination processes were the same for both cases, as often observed for polymer-based LEDs [32]. It is also of note that tailing in the long wavelength region observed for the electroluminescence

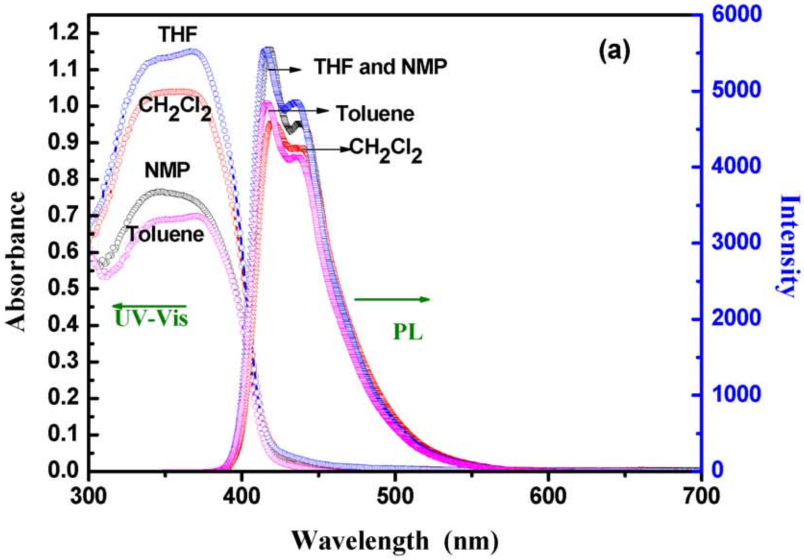
Table 3
The absorption coefficient (ε) and exciton lifetime of POTPy, POTPyOT and their thiophene analogues

Sample	ε (cm^{-1} M^{-1})[c]	Life-time of exciton (ns)[a]	
		In $CHCl_3$	Film
POTPyOT	3.25×10^4	0.62	1.90
POTTOT[a]	3.85×10^4	0.60	0.32
POTPy	2.11×10^4	1.85	2.00
POTT[b]	2.35×10^4	0.60	0.42

[a] Poly(3,3′-dioctyl-2,2′;5′,2′-terthiophene) prepared in our laboratory.

[b] Poly(3′-octyl-2,2′bithiophene) prepared in our laboratory.

[c] The concentration of polymer is 5×10^{-5} M.



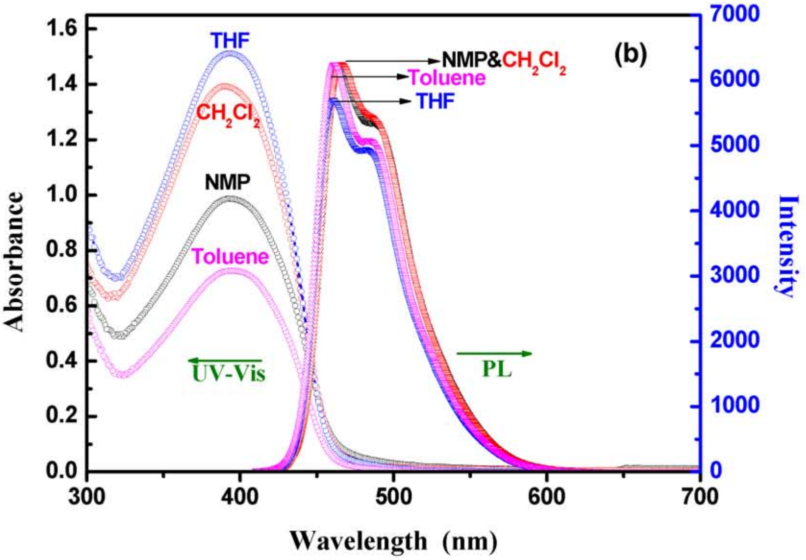


Fig. 5. UV/vis and PL spectra of (a) POTPy (b) POTPyOT in solvent with various polarity (the concentration of polymer solution is 2.5×10^{-5} M. and the exciting wavelength is 330 nm for POTPy and 360 nm for POTPyOT).

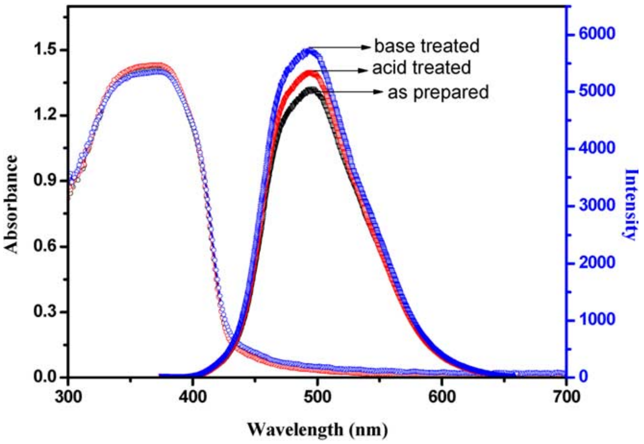


Fig. 6. The UV/vis and PL spectra of the as-prepared and acid or base treated POTPy films.

spectra suggested that emission from some defect states should be taken into consideration.

4. Conclusions

New luminescent polymers consisting of pyridine ring with moderate molecular weights have been synthesized. They are soluble in organic solvents and have high fluorescence quantum yield in both solution and solid state. The quantum efficiency of the POTPy film is 60 times higher than its thiophene analogs. The alternative donor-acceptor architecture of the polymer chains may have an intramolecular charge transfer (CT) structure at the exciting state. Therefore, POTPy showed a substantial solvent effect and high exciton lifetime. Furthermore, the pyridine motif

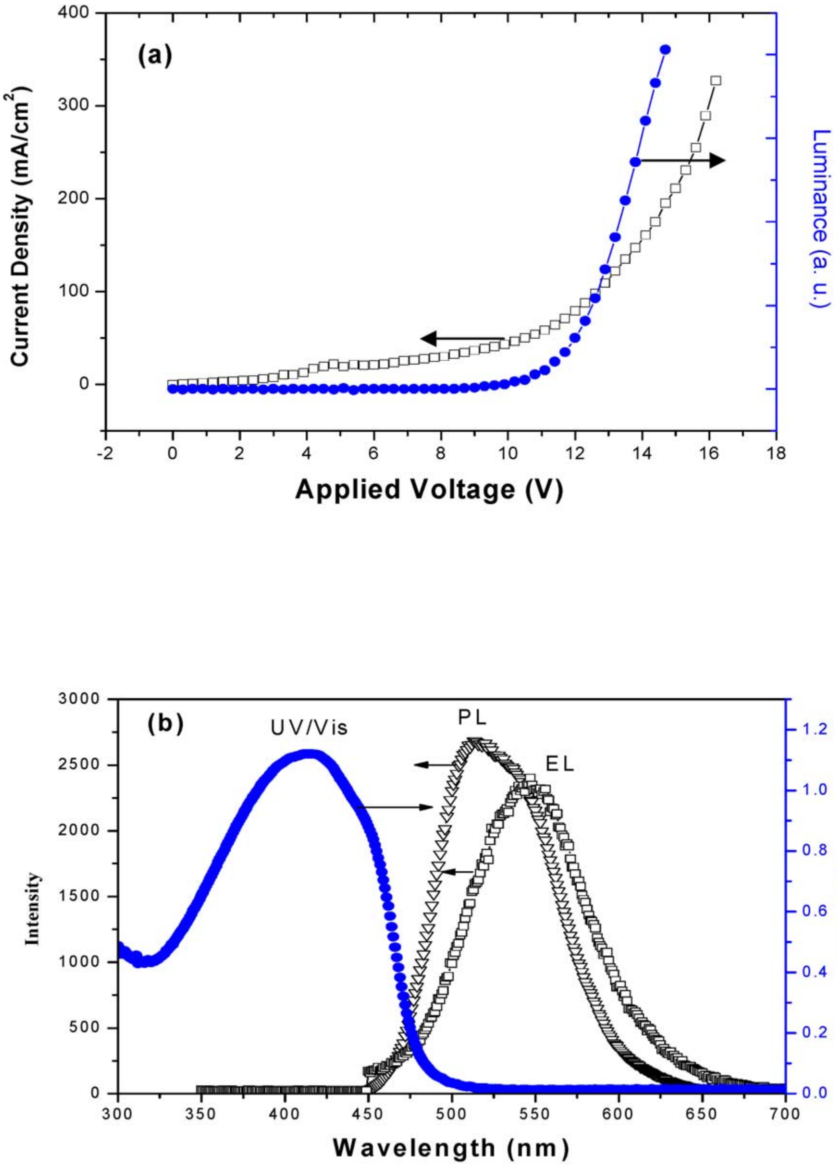


Fig. 7. (a) *I–L–V* curves of ITO/POTPyOT/Al device (b) absorption and fluorescence spectra of POTPyOT.

in the polymer backbone acts as a functional group, which reacts with acids to alter the photophysics of the polymers.

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