

Transient photophysics of phenothiazine–thiophene/furan copolymers in solvents

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ARTICLE INFO

Article history:

Received 6 January 2009

Received in revised form

10 November 2009

Accepted 11 December 2009

Available online 23 December 2009

Keywords:

Picosecond

Polymer

Phenothiazine

TICT

ABSTRACT

The steady-state and transient photophysics of a series of newly synthesized phenothiazine-based conjugated polymers and copolymers with thiophene and furan moieties in solvents were investigated. Positive solvatochromism in emission spectra was observed in polar solvents due to excited-state intramolecular charge-transfer. The picosecond time-resolved spectra using streak camera revealed fast chain twisting motion at ~ 10 ps, verified by solvent viscosity dependency. A non-radiative de-activate pathway is assigned to the non-planar conformation at excited state. This reveals a possible way for intramolecular energy loss in new polymer design for applications.

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1. Introduction

π -conjugated polymers and oligomers attracted many attentions in the past few decades for their great potential applications in organic light emitting diodes (OLEDs) [1–4], photovoltaic devices [5–6], field effect transistors [7] and biosensors [8]. Phenothiazine, bearing electron-rich sulfur and nitrogen atoms, is a well-known pharmaceutical class of six-member hetero-cycles compound. It is a strong electron-donating group due to its low oxidation potentials ($E_{1/2}^{OX} = 0.59$ V vs. SCE) [9]. Besides, phenothiazine ring favors a butterfly conformation in the ground state since the centre six-member ring bents with a dihedral angle (153°) in C–N–C (140.0°) and C–S–C (141.9°), which is different from carbazole and fluorene [1,4,10–12]. This special structure significantly reduces the hydrodynamic volume of the oligomers [13] and the π -stacking aggregation, which might be greatly beneficial to its optical properties in solid films. For example, high-performance electro-luminance (EL) devices with phenothiazine as the donor and phenylquinoline as the acceptor were manufactured [1,14–17]; conjugated dendrimers consisting of phenothiazine peripheral moieties with good photo-luminance (PL) and EL properties were synthesized [10,18]. The photophysics of phenothiazine-based dyads or triads with pyrene [19–21] and flavin [22,23] were studied

by Daub and Shirdel, respectively. Some newly synthesized phenothiazine dyads/triads and oligomers reported by Müller's group show interesting electronic properties, such as unique electronic communication in the excited state, pronounced fluorescence, and distinct reversible redox behaviors [24–27].

Recently, several groups present theoretical calculations on structural and correspondent electronic states of conjugated polymer chains such as thiophene [28,29], furan [30], phenothiazine [31], and carbazole/fluorene-based polymers with thiophene and furan moieties [32–37]. The conformation relaxation seems to be an immediate result at excited state right after the excitation. This is an interesting topic for polymer applications since the polymer chains are buried in solid matrix after the solution is spin-coated on substrates. However, limited experimental investigations were carried out. The dynamic study is essential to analyze this mechanism and finally help to enhance the performance of the devices. In this paper, we report the steady-state photophysics together with picosecond time-resolved fluorescence spectra of a series of 3,7-phenothiazinevinylene derivatives [38] in solvents with various viscosities to clarify the role of conformational relaxation coupled to the excited-state charge-transfer.

2. Materials and methods

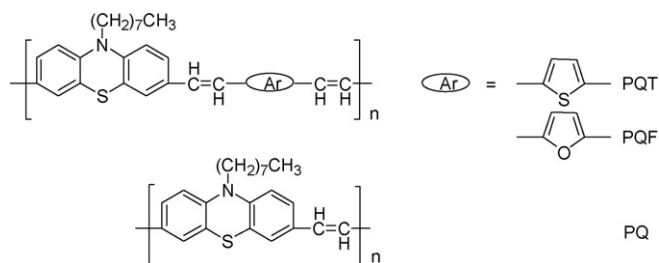
2.1. Materials

The samples in this work are phenothiazine-based conjugated polymers and copolymers with thiophene and furan moieties, namely PQ, PQT and PQF, synthesized by Knoevenagel or Wittig

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Scheme 1. Chemical structures of PQ, PQT and PQF.

condensations method [38]. Their molecular structures with 6–8 repeat units are shown in Scheme 1. Conjugation and electron-transfer along the chain backbone is proposed.

2.2. Steady-state spectra

Ultraviolet–visible (UV–vis) absorption and emission spectra were recorded with an Agilent 8453 UV–vis Spectroscopy System and a Hitachi F-2500 Fluorescence Spectrophotometer at room temperature respectively. The dilute sample solutions of 5×10^{-5} M and 5×10^{-6} M (by repeat unit) are filled in a 1-cm-thick quartz cell for absorption and emission measurement. The emission spectra were collected under 415 nm excitation. Their fluorescence quantum efficiencies (QE) were calculated with Coumarin-152 as the standard reference, whose QE is 21% [39].

2.3. Time-resolved fluorescence spectra

The picosecond time-resolved fluorescence spectra were recorded by a streak camera system. A mode-lock Ti: Sapphire laser (Mira 900F, Coherent) delivered 830 nm, 120 fs pulse train at 76 MHz. The laser beam was focused into a β -BaB₂O₄ (BBO) crystal to generate a second-harmonic (SH) beam. Then the SH beam at 415 nm was used for the excitation of samples, which were filled in a 1 mm thick rotating cell. The fluorescence spectra were collected at magic angle (54.7°) polarization with respect to the excitation beam to avoid the anisotropic effects. Finally, the emissions were collected and focused into a picosecond time-resolved streak camera system (Hamamatsu C5680). Solvents similar in polarity but different for various viscosities (tetrahydrofuran (THF), dichloroethane, and aniline) were chosen for time-resolved analysis.

3. Results and discussion

3.1. Steady-state UV/vis absorption and emission spectra

The UV–vis absorption spectra of PQ, PQT and PQF in THF dilute solution are shown in Fig. 1. The absorption spectra of each copolymer are characterized by two bands: 300–330 nm and 400–440 nm. The low energy bands between 400 nm and 440 nm can be attributed to π – π^* transition (414 nm for PQ, 443 nm for PQT and 402 nm for PQF), due to the π -electron delocalization [12,19]. Study of Qiu [11] reported that the increase of phenothiazine–vinylene units resulted in the decrease of E_g , and the absorption bands of PQ in Fig. 1 is in accordance to the result of 6 repeat units oligomer, which is a proof of the chain length and conjugation mentioned above. Clearly, the absorption bands of PQT and PQF, which extend to the wavelength longer than 500 nm, are broader than that of PQ, possibly due to the n – π^* transition by the non-bonding electrons of the heteroatoms in thiophene (sulfur) and furan (oxygen) moieties [40]. The adding of thiophene and furan moieties reduces the optical band gaps, compared with PQ.

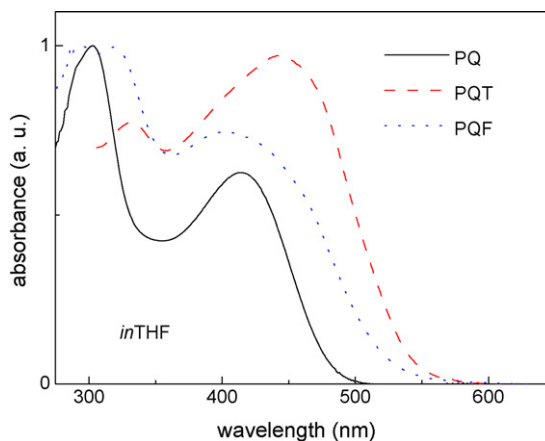


Fig. 1. Normalized UV–vis absorption spectra of PQ, PQT and PQF in THF.

Our experiments revealed that the UV–vis absorption spectra in solvents with different polarities were nearly the same with that in THF as shown in Fig. 2. This indicates that there is no clear intramolecular charge-transfer (ICT) process in the ground state (S_0) of our polymer samples. The emission bands of PQT in different dilute solutions are also shown in Fig. 2. The results for PQF are similar. Compared with PQ, fluorescence of PQT and PQF has a red shift. Different from the UV–vis absorption spectra in the solvents, positive solvatochromism of the emission bands is observed in the polymer solutions, due to the slight increase of the solvent polarity. This reflects the ICT characteristics at their first electronic excited state (S_1) [14], which are not shown in ground state (S_0). The result is similar with that of phenothiazine–phenylquinoline copolymers and donor–acceptor molecules studied by Jenekhe et al. [14,17]. The quantum efficiency in these three solutions decreases against the increase of solvent viscosity. For PQT, the QE are 10.9%, 9.6%, and 1.5%, respectively; for PQF, the QE are 9.7%, 5.9%, and 1.0%, respectively. This indicates that a non-radiative relaxation channel exist correlated to chain structure after the molecule excitation. We figure this non-radiative decay channel correlates with the solvent induced intramolecular charge-transfer and twisting motion, known as twisted intramolecular charge-transfer (TICT).

3.2. Time-resolved fluorescence spectra

In order to reveal the conformational relaxation in these polymers in dilute solutions, we measured the picosecond time-

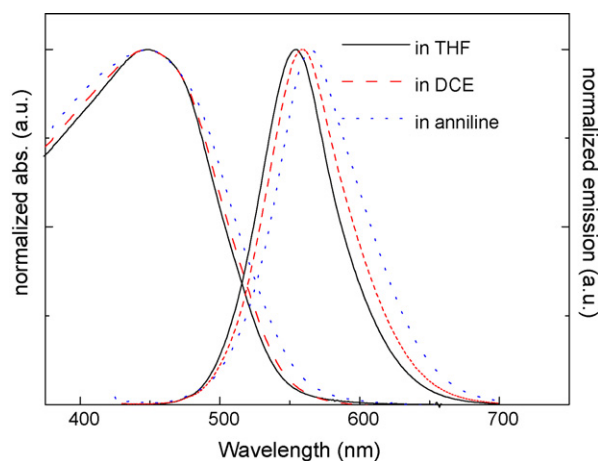


Fig. 2. The UV–vis absorption spectra (solid) and emission spectra (dash, excited at 415 nm) of PQT in solvents.

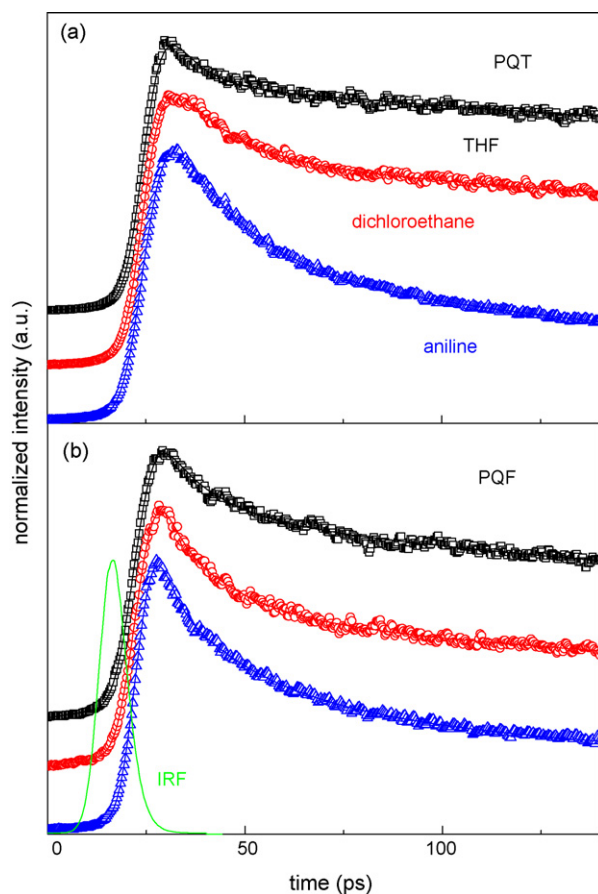


Fig. 3. Fluorescence decay of PQT (a) and PQF (b) in solvents of viscosity series, recorded at fluorescence peaks in 160 ps range together with IRF. The solid lines are fitting curves.

resolved fluorescence spectra using streak camera. The excitation wavelength was 415 nm, and we collected the fluorescence in 2 ns and 160 ps range. Fig. 3 shows the fluorescence decay of PQT and PQF in solvents with various viscosities in concentration of 5×10^{-5} M at the wavelength of their own fluorescence peaks in 160 ps range. The instrumental response function (IRF) gives the time-resolution at ~ 4 ps.

Deconvoluted with the IRF, PQ dissolved in THF presents single exponential lifetime estimated as 1.7 ns, indicating that its excited-state experiences simple radiative decay. However, the time-resolved emissions from PQT and PQF are best fitted with two- or three-exponential components. The time constants and its ratio are listed in Table 1. From the 2 ns range decay results, the excited-state lifetimes of the copolymers in dilute solutions can be obtained as 2–4 ns. A much faster dynamics around 10 ps can be well resolved in 160 ps time window.

Fig. 3(a) shows the fluorescence decay together with exponential fit results of PQT with increasing solvent viscosity at the emission peak wavelength. From the fit results in Table 1, we can

Table 1
Deconvoluted fluorescence decay of the polymers in solutions.

	THF	Dichloroethane	Aniline
PQ	1.7 ns	–	–
PQT	6.7 ps (38%)	14.3 ps (40%)	17.7 ps (55%)
	1.9 ns (62%)	2.0 ns (60%)	1.9 ns (45%)
PQF	2.0 ps (37%)	1.3 ps (72%)	1.2 ps (79%)
	12.4 ps (23%)	15.6 ps (13%)	22.8 ps (10%)
	4.2 ns (40%)	4.5 ns (15%)	2.2 ns (11%)

see that the fast decay increases from 6.7 ps in THF to 14.3 ps in dichloroethane and 17.7 ps in aniline, which indicate that the viscous solvents prevent the motion of the internal bond twisting. Corresponding ratio becomes larger to the increasing viscosity, which means that the slower the internal twisting relaxes, the more possibility the excitation energy vanishes through the non-radiation transition channel. This is the origination of the lower fluorescence quantum efficiency in the more viscous solvents. This reveals a possible path for intramolecular energy loss in organic photovoltaic devices using intrachain donor–acceptor polymerization to lower the band gap and extend solar radiation sensitivity in near infrared region. According to the theoretical study in Refs. [28,29,32–37], polymers or molecules with thiophene moieties favor a non-planar conformation in ground state, possessing a high-torsional flexibilities with rather small energy barrier against planarity (<2.0 kcal/mol), whereas they almost reach planarity in excited state. As discussed that this fast decay around 10 ps presents the dependency to solvent viscosity ensures us to assign this fast decay to the internal twisting relaxation between rings in PQT.

We also discover a similar phenomenon in the fluorescence decay dynamics of PQF shown in Fig. 3(b). There is an increasing twisting time around 10 ps with increasing solvent viscosity: from 12.4 ps in THF to 15.6 ps in dichloroethane and 22.8 ps in aniline. Theoretical studies reveal that furan oligomers [30] or carbazole-based copolymers [35–37] containing furan moieties have planar or near planar structure both in ground and excited state. The contradiction between our experiment and related calculation possibly originates from the vinylene moiety introduced between donor and acceptor, which may cause the photo-isomerization between trans and cis conformation [41]. A very fast component is also found in PQF solution, which should be assigned to a fast non-radiative decay process, such as solvent induced ICT. Due to the limitation of the instrumental response, this component should be further resolved by femtosecond experiment. This fast non-radiative decay and the internal twisting channel both quench the fluorescence of PQF, and make the fluorescence quantum efficiency lower than that of PQT.

On the other aspect, however, the theoretical work of Li [31] reported that poly-phenothiazine possesses bonding and antibonding character between the subunits for excited and ground state, respectively. This implies that the excited state should be more planar than the ground state for poly-phenothiazine. But our experiment results show that PQ in excited state mainly experience simple electronic state radiative decay without twisting, which may also be attributed to the role of vinylene bridge in our samples.

4. Conclusion

We have reported here the steady-state and time-resolved fluorescence spectra of a series of 3,7-phenothiazinevinylene derivatives dissolved in solvents with various viscosities. TICT effect exists in the excited state, while being absent in ground state. The QE varies according to the polarities and viscosities of the solvent. A non-radiative channel is figured out both in static and transient spectra, which stems from the chain conformation and twisting motion. The twisting is verified by the viscosity dependent decay. The slower internal twisting process in more viscous solvents takes higher portion explained the lower QE in dichloroethane and aniline comparing with that in THF. This finding indicates an energy relaxation factor in molecular design for organic photovoltaic applications.

Acknowledgements

This work is supported by National Basic Research Program of China 2009CB930504, 2007CB307001, 2006CB921601,

2006CB806007, the National Natural Science Foundation of China under grant nos. 10504001, 60878019, 10821062, 10934001, 60677002, 10828407, and China Postdoctoral Science Foundation no. 20060400029.

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