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Molecular engineering leading to better processability of conjugated chromophores: The optical properties of new soluble copolymers containing alternative oligo-octylthiophene and oligo-methylene blocks

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ABSTRACT

A series of conjugated/non-conjugated copolymers and their corresponding oligomers were prepared and their optical and physical properties were investigated for understanding the merit of blocking the conjugated chromophores with non-conjugated spacers. It was found that compared to the oligomers, copolymers have the advantages of amorphous nature, high thermal stability, and good thin film processability without sacrificing the quantum efficiency and purity of the emission color. Furthermore, based on the optical data of these copolymers and oligomers, the conjugation length of the polyoctylthiophene was estimated to be extended over 23–31 octylthiophene rings.

1. Introduction

Conjugated polymers have shown a great potential for the new generation of display technology [1]. They have been considered potential candidates for large area flat-panel displays, due to the good processability. Therefore since the first report of the light emitting diodes based on PPV [2], much work has been carried out with the objective of tuning the emission color and improving quantum efficiency, processability, and stability [3]. Nevertheless, tuning the emission spectrum to any desired color including white still presents a challenge. Several methods have been reported for tuning the emission properties of the conjugated polymers, such as changing the main chain molecular structure [4], changing the side chain molecular structure [5], blending an electroluminescent polymer with a second active polymer [6] or with low molecular weight organic or inorganic molecules [7], doping [8], and using multiplayer device architecture [9]. Although there has been a rapid progress, searching for materials with improved luminescence efficiency, processability, mechanical properties, and stability is still a continuing research effort.

Amongst the luminescent conjugated polymers, processable polythiophene derivatives play an important role [10]. In comparison with other conjugated polymers, polythiophenes have many attractive characteristics in searching the proper materials for the polymeric light emitting diodes (PLEDs), such as unique electro-optical properties, good environmental stability, structure versatility [11], and ease in preparation although the electroluminescence quantum yields (typically $\sim 10^{-4}\%$) is very low [12]. It was also conceivable that shortening the effective conjugation length of polythiophenes would be one of the effective means of shifting the emission spectrum from red to green or blue. One of the best ways to shorten the conjugation length of the polymer is to cape the polymer backbone with non-conjugated spacers to form conjugated/non-conjugated block copolymer [13,14]. The merits of such an approach are the improvement of processability of the polymers and the control of π-conjugation length, resulting in polymers with well-defined lumophores. Further-

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more, copolymer containing alternating rigid and flexible blocks in which the rigid blocks of specified and uniform conjugation lengths determines the light emitting spectrum, whereas, the flexible blocks contribute to the solubility and film-forming properties of the polymer. The advantages of such a copolymer over a small molecule/inert polymeric matrix blend lie in its homogeneity and the prevention of recrystallization or elution of the small molecules within the matrix.

There are several examples to isolate the chromophores in a polymer backbone with a non-conjugated segment. For instance: Yang et al. [15] reported the insertion of ether in-between phenylene-vinylene oligomers to obtain a copolymer with λ_{EM} of 470 nm, which is much shorter than that of polyphenylene-vinylene. Morisaki et al. [16] prepared poly(*p*-phenylene-vinylene)s with a paracyclophane skeleton in the main chain and found that paracyclophane spacer cannot block the conjugating amongst the conjugated segments. The polymer showed an extension of π-delocalization via the through-space π–π stacking. Wang et al. [17] synthesized a series of PBO–octane–PBO block copolymers and found that the luminescent efficiency was dependent of the mole ratio of octane in the copolymer. Tang et al. [18] prepared PBPV-*co*-PS copolymers and found that the photoluminescence (PL) spectra showed a clear blue shift as the amount of styrene added in the copolymerization increased, which indicates that the average conjugating length of PBPV segment in the copolymer is adjustable. A remarkable progress has been made, nevertheless, the systematic study on fixing the conjugated blocks with non-conjugated moieties is not found. The present study is focused on finding an optimal way to confine the chromophore to tailor the luminescence color of a conjugated/non-conjugated copolymer using oligo-alkylthiophenes as model compounds. By comparing closely the optical and physical properties of the copolymers with their corresponding oligomers, the strategy for defining the chromophore of a polymer by inserting non-conjugated spacers into the polymer backbone can be closely evaluated. Furthermore, by studying the optical properties of the isolated oligomers with systematically increased conjugation length, information regarding to the extension of the π-electrons in a conjugated backbone can be obtained.

2. Experimental

2.1. Chemicals

3-Bromothiophene, dibromoalkanes, $Pd(PPh_3)_4$, Me_3SnCl, LAH, $AlCl_3$, *n*-BuLi, $NiCl_2$(dppp), NBS, and silica gel were obtained from commercial resources and used as received. All solvents used were purified with the literature methods [19] and distilled right before use.

2.2. Preparing of octylthiophene oligomers

3,4’-dioctyl-[2,2’]-bithiophene (2OT), 3,4’,4”-trioctyl-[2,2’;5’,2”]-terthiophene (3OT), 4’,4”,4”’-tetraoctyl-[2,2’;5’,2”;5”,2”’]-quar-terthiophene (4OT), 3,4’,4”,4”’,4””,4””’-hexaoctyl-[2,2’;5’,2”;5”,2”’;5”’,2””;5””,2””’]-sexi-thiophene (6OT) and 3,4’,4”,4”’,4””,4””’,4”””,4”””’-octaoctyl-[2,2’;5’,2”;5”,2”’; 5”’,2””;5””,2””’;5””’,2”””]-octathiophene (8OT) were synthesized with a Stille coupling method. The synthetic procedures were illustrated in Scheme 1 and the detailed preparation conditions and structure characterization with ^{1}H NMR can be found in the Supporting information. All the reactions were carried out in dry Ar atmosphere using solvents dried over Na.

2.3. Preparing copolymer with methylene spacer (PM3OT)

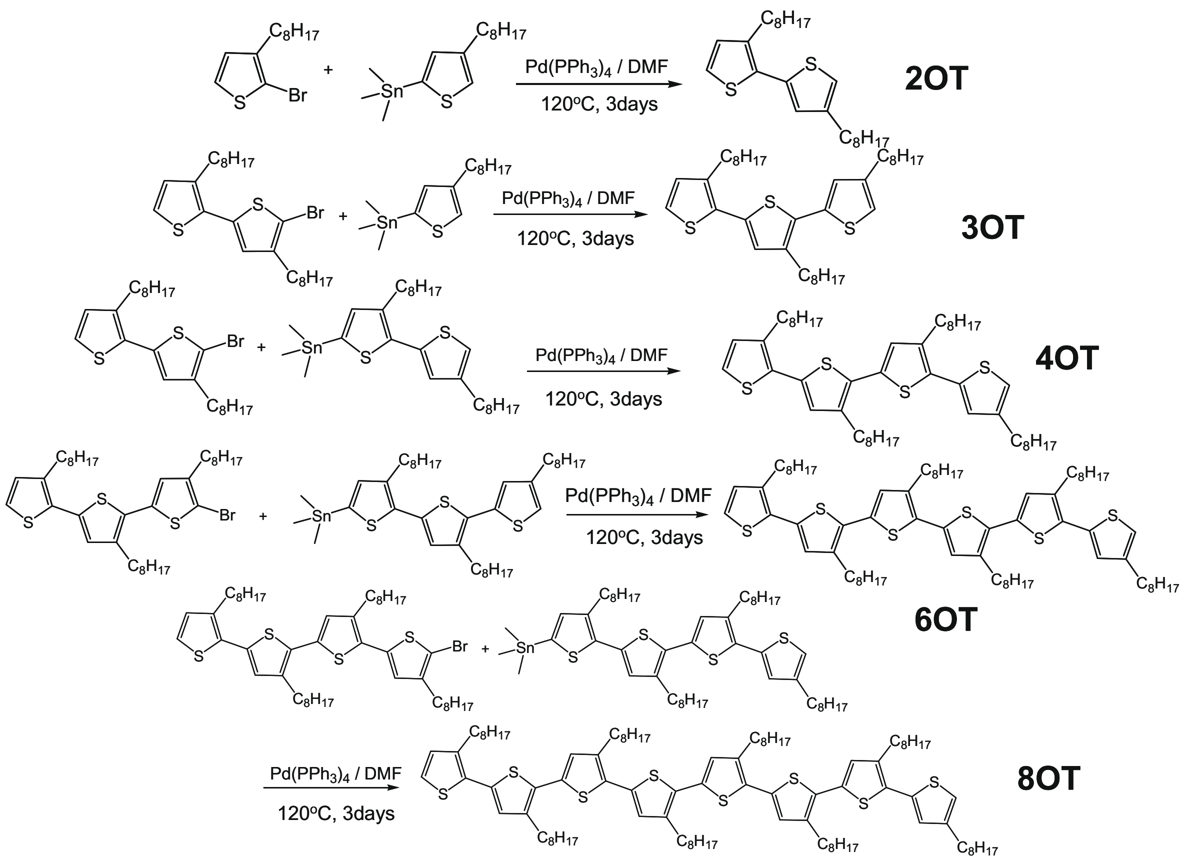
poly(4,4′,4″-trioctyl-5-methyl-[2,2′;5′2″]-terthiophene, PM3OT was synthesized by Stille coupling between DTMSnM2OT (which was prepared by Stannylation of 1.5 g (3.7 mmol) M2OT (Bis(3-octylthiophen-2-yl)methane) with 1.84 g (9.3 mmol) trimethylzin chloride) and 2,5-dibromo-3-octylthiophene. M2OT was prepared with the methods modified from the literature [20] and the synthetic conditions were displayed in Scheme 2. The copolymer obtained was dissolved in CH_2Cl_2, extracted the impurity with saturated $NaHCO_3$(aq), H_2O, and NaCl(aq). After removing the solvent (CH_2Cl_2), the polymer was washed with methanol for 1 week using a Soxhlet apparatus then using $CHCl_3$ to extract the soluble portion. A dark red solid was obtained after $CHCl_3$ was removed by vacuum with a yield of 90%. The structure of the polymer was characterized using ^{1}H NMR. ^{1}H NMR (200 MHz, δ_H/ppm in $CDCl_3$): 6.88 (s, 4H), 4.12 (s, 2H), 2.70 (m, 4H), 2.54 (m, 4H), 1.62 (m, 8H), 1.26 (m, 40H), 0.87 (m, 12H). Elemental analysis calcd. for $(C_{37}H_{56}S_3)_{10}Br$ (PM3OT): C, 73.51%; H, 9.27%; S, 15.89%. Found: C, 73.64%; H, 9.40%; S, 15.97%.

2.4. General procedure for preparing copolymers with propylene and hexylene spacer

The key intermediate for synthesizing copolymers with propylene spacer is 1,3-di-(3-octylthiophene)propane (P2OT) which was prepared by reacting of the octylthiophene with 1,3-dibromopropane. Various copolymers with propylene spacer were then synthesized by Stille coupling of Bis(5-trimethylstannyl-3-octylthiophen-2yl)propane (which was prepared by stannylation of P2OT by trimethylzin chloride) and 2,5-dibromo-oligo-3-octylthiophene which were prepared followed the literature report with slightly modification [21]. The preparation procedures for poly(4,4′,4″-trioctyl-5-hexyl-[2,2′;5′,2″]terthiophene (PH3OT) is the same as those for poly-(4,4′,4″-trioctyl-5-propyl-[2,2′;5′,2″]terthiophene (PP3OT) except using 1,6-dibromohexane instead of 1,3-dibromopropane. The synthetic steps were also listed in Scheme 2 and the detailed preparation conditions and structure characterization with ^{1}H NMR can be found in the Supporting information.

2.5. General procedures for purification of the copolymers

In the preparation of the copolymer, Stille coupling reaction was quenched with a saturated NH_4Cl(aq) then extracted the polymer with CH_2Cl_2. The impurity in the polymer/CH_2Cl_2 solution was extracted with $NaHCO_3$(aq), H_2O, and NaCl(aq), respectively, dried the polymer solution with $MgSO_4$. CH_2Cl_2 was removed with an evaporator and



Scheme 1. The preparation of oligo-octylthiophenes.

the crude powder was washed with methanol for one week using a Soxhlet apparatus then using $CHCl_3$ to extract the soluble portion. Gel-type copolymers with various colors were obtained after removing the solvent.

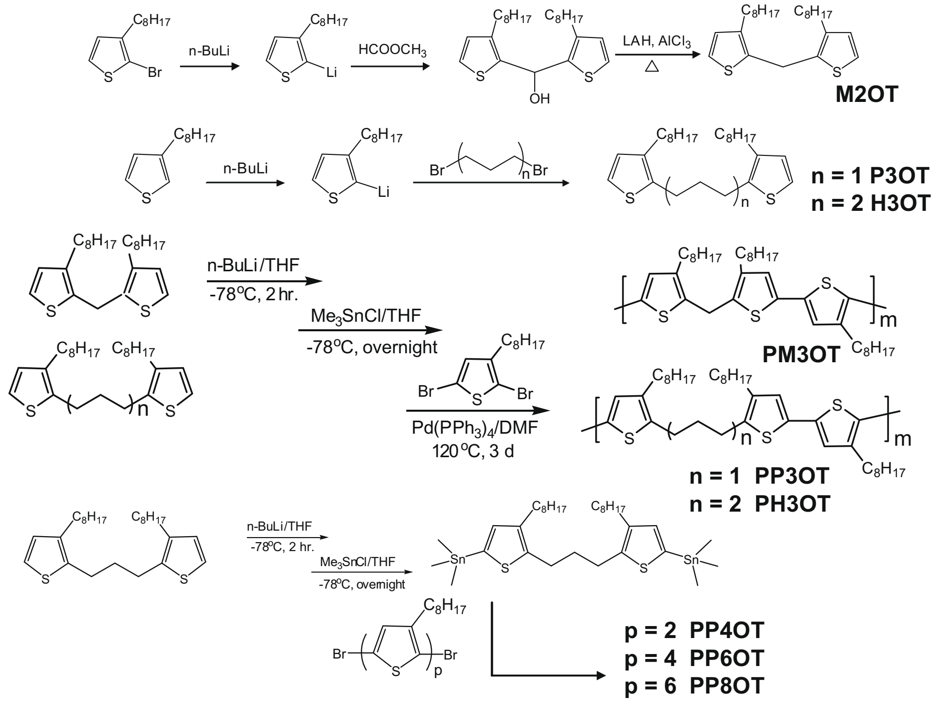
2.6. Physicochemical measurements

^1H NMR spectra were recorded with a Bruker DRX-200 NMR spectrometer in $CDCl_3$. The molecular weights of the copolymers were determined by gel permeation chromatography (GPC) on a Waters-2487 instrument calibrated using THF as an eluent and polystyrene as the standard. UV/Vis absorption and photoluminescence spectra (both in $CHCl_3$ solution and spin-coated films) were obtained using Cary 5E spectrometer and Hitachi F-4500 spectrophotometer, respectively, in the laboratory atmosphere at room temperature. The PL quantum yield calculated by comparing with that of quinine sulfate. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen as a carrier gas at a flow rate of 100 ml/sec. The TGA experiments were conducted from 25 to 900 °C with a linear heating rate of 10 °C/min. Differential Scanning Calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 822^e apparatus. Samples were heated from room temperature to 150 °C at a heating rate of 10 °C/min and then cooled to −40 °C. Three heating–cooling cycles were recorded. Melting point (T_m) and melting enthalpy (ΔH_m) were determined from the DSC endothermic peaks on both the first and the second heating runs. Glass transition temperatures (T_g) were estimated as the mean value between onset and endset temperature of the process.

3. Results and discussion

3.1. Blocking the conjugated chromophores with non-conjugated segments

It is a straight-forward to think that the non-conjugated segments can be used to block the π-electrons moving from one moiety to another. Therefore, linking the finite conjugational segments with short aliphatic spacers is a good strategy for preparing polymeric luminescence material with a confined conjugation length as proved by several authors [15–18]. Chromophores incorporated into segmented copolymers by linkage with non-conjugated polymethylene chains have the advantage of reducing the undesirable long-wavelength emission bands [22], increasing in PL efficiency by reducing the rate of diffusion of excitons to the quenching sites [23], and provide efficient exciton confinement because of a microphase-separated domain structure [24,25]. Nevertheless, the saturated



Scheme 2. The preparation of oligo-octylthiophene-alkylene copolymers.

spacer between the chromophores may act as a barrier to the injection and mobility of the charge carriers. This leads to high threshold voltage that generally damaged the polymer when the materials were used in OLED. It is worth to find the optimal length of the spacer to achieve the best performance of the luminescence copolymers. Methylene, propylene, and hexylene were used in this study to isolate the oligo-alkylthiophene chromophore.

The effects of the spacer length on the extents of the aggregation and fluorescence can be deduced from the absorption and emission spectra. The UV/Vis and PL spectra of PM3OT, PP3OT, and PH3OT in $CHCl_3$ as well as the corresponding oligomer (alkylthiophene-trimer) were displayed in Fig. 1. It was seen clearly that the λ_{max} of PM3OT is longer than those of 3OT, PP3OT and PH3OT. This result indicates that the methylene spacer cannot totally interrupt the conjugation between chromophores. Nevertheless, when the spacer is longer than three saturated carbon, the transition of π-electron amongst the alkylthiophene-trimer can be totally blocked. Similar result was observed by Hu et al. [26] in the PPV based copolymers. We also found that the propylene spacer can also totally block the π-electron transition when the chromophore segment is octylthiophene-tetramer, octylthiophene-hexamer, and octylthiophene-octamer (*vide infra*).

In the dilute (10^{-5} M) solutions, the PL spectra of all copolymers (Fig. 1b) show an elevated low-energy tail but the oligomer does not have such tail. The low-energy absorption tail comes from the π–π interaction between two/or more octylthiophene-trimer units in a single copolymer chain. In dilute solution. The interaction between oligomer units can be neglected, therefore no extra low absorption band was observed. The λ_{EM} for all copolymers (in $CHCl_3$) is similar to each other but is longer than that of the corresponding oligomer, 3OT. These results also disclose that the aggregates formed in the copolymers are the major emission centers. Nevertheless, the λ_{EM} of 3OT in $CHCl_3$ is only slightly shorter than those of PM3OT, PP3OT, and PH3OT, indicating that only weak π–π stacking exists in the copolymers. The similarity in Stokes shifts of the 3OT and the corresponding copolymers PP3OT and PH3OT also suggests that the degree of aggregation or excimer formation for the oligomer and copolymers is similar. It was shown that the aggregation or π–π stacking of a copolymer will not change significantly by the spin coating process [27], therefore the λ_{EM} of the copolymer films are only slightly red-shifted compared to those of copolymer solutions. The PL data also suggest that increasing the spacer length does not significantly change the intramolecular chromophore interaction or energy-transfer processes. Intramolecular association of the chromophores is an intrinsic property in conjugate/non-conjugated copolymers and it occurs only to a small extent compared to the totally conjugated polymers such as polyalkylthiophene. The excitation spectra of oligomer and all copolymers essentially overlap with their absorption spectra, indicating that the absorbing chromophores are the only significant emitters with high purity. The fluorescence of the copolymer in $CHCl_3$ shows a broadened fine structure which may be associated with a coupled C=C vibronic stretching mode, as suggested by Ranger and Leclerc [28]. More studies on the photo-physics of the copolymers with various conjugated lengths in chromophore moiety will be presented in the following paragraph.

3.2. Synthesis and physical properties of oligo-octylthiophene copolymer with propylene spacers

In order to study systematically the merit of the luminescent copolymers containing conjugated chromophores and saturated spacers in the backbone, a series of octylthiophene-propylene copolymer and the corresponding oligo-octylthiophenes were prepared. The average molecular weights of these copolymers as well as polyoctylthiophene were listed in Table 1. Stille coupling was used here to synthesize the conjugated/non-conjugated copolymers. This type of reaction not only avoids using oxidant but also affords the desired polymer without irregular coupling or branching. Nevertheless, the trimethyltin terminal group on the polymer backbone may affect the photo-physics and therefore the applications of the polymer. Fortunately, we found that the trimethyltin can be removed by passing the polymer solution (in toluene) through the silicon-gel column or washing the polymer with acidic aqueous solution. Moreover, although the molecular weight of the polymer prepared from Stille coupling is rather low (see Table 1), all copolymers showed good thermal stability under N_2. The first major weight loss starts at around 360–400 °C, and a residual weight of about 2–24% is detected after heating at 850 °C. Data of the 5% weight loss temperatures (T_d) of the polymers are up to 350 °C. All copolymers show good solubility in $CHCl_3$.

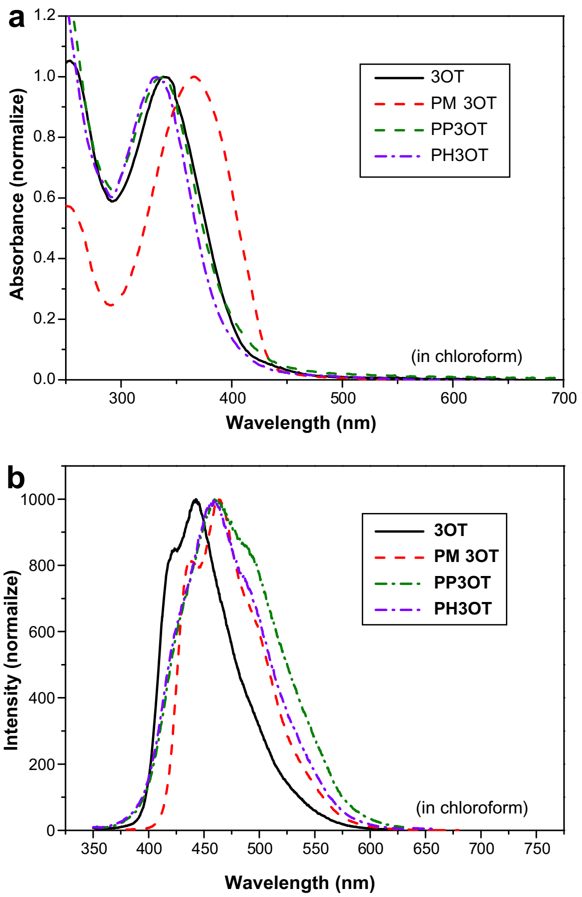


Fig. 1. The (a) UV/Vis and (b) PL spectra of PM3OT, PP3OT, PH3OT and their corresponding oligomer 3OT.

Table 1
Molecular weight and poly-dispersive index of conjugated/non-conjugated copolymers.

Copolymer	Weight average molecular weight	Degree of polymerization	PDI
PM3OT	5900	*ca.* 10	1.8
PP2OT	7590	*ca.* 18	2.0
PP3OT	8460	*ca.* 14	2.2
PP4OT	6060	*ca.* 8	1.9
PP6OT	9730	*ca.* 8	2.4
PP8OT	5830	*ca.* 4	2.3
PH3OT	9450	*ca.* 14	2.3
Ra-POTH[a]	29140	*ca.* 149	2.0

[a] The polymer was prepared by oxidative polymerization of 3-octylthiophene using the method reported in the literature [30].

The UV/Vis and PL spectra of a few conjugated/non-conjugated copolymers are shown in Fig. 2 and the optical data of all copolymers and the corresponding oligomers are displayed in Table 2. It was found that the λ_{max} of the copolymers are very close to those of the corresponding oligo-octylthiophene indicating that propylene is sufficient to interrupt the conjugating between the chromophores with the octylthiophene ring number up to 8. The spectral data shown in Table 2 reveal that the Stoke shift of the oligomers slightly increases as the chain length increases. Nevertheless, the Stoke shift is independent of the chromophore size for all copolymers. Jenekhe and Osaheni had proposed [29] that the excimer emission accounts for the Stoke shift in the conjugated polymers and rod-coil copolymers. Therefore, the most plausible reason for the variation of Stokes shift in oligomers is the variation in the spatial conformation, long chain chromophore has a more coil-like conformation, therefore strong intrachain interactions, resulting in large Stoke shift. In copolymers, the interaction between chromophores may largely depend on the size of the spacer. For the same size of the spacer (such as propylene), the Stoke shifts are similar. The absorption band of all copolymers does not show any resolvable vibronic fine structure suggesting that the polymer chains are relatively flexible in their ground state. Interestingly, both λ_{max} and λ_{EM} for copolymer in $CHCl_3$ and solid film are similar whereas the λ_{max} and λ_{EM} for totally conjugated polyoctylthiophene thin film showed a significant red-shift compared to that in $CHCl_3$. These data reveal that insertion of the saturated spacer in the polymer backbone can reduce the interchain interaction.

3.3. The advantages of linking the finite conjugated segments with short aliphatic spacers

The basic ideal for linking the finite luminescent conjugational segments with short aliphatic spacers is to prepare polymeric materials with well-defined/controllable chromophores. We may expect this type of copolymer will have the advantages of both small molecules (easy to characterize, higher quantum efficiency and pure emission color) and polymer (high thermal stability, amorphous nature and easy process to thin film). The DSC curves (shown in Fig. 3) illustrated that PP8OT is totally amorphous, no endo-thermal or exo-thermal signal was observed. On the other hand, 8OT has an endo-thermal peak at −12 °C and an exo-thermal peak at 53 °C, indicating that 8OT is a crystalline materials. The DSC data demonstrated that linking the conjugated chromophores with aliphatic spacers does able to reduce the crystallinity of the luminescent materials. Low crystallinity of a material is an important characteristic in-turn of the application of the conjugated molecules in the light emitting diode. Then the next question will be: what are the quantum efficiency and emission color of the copolymers compared to those of the corresponding oligomers?

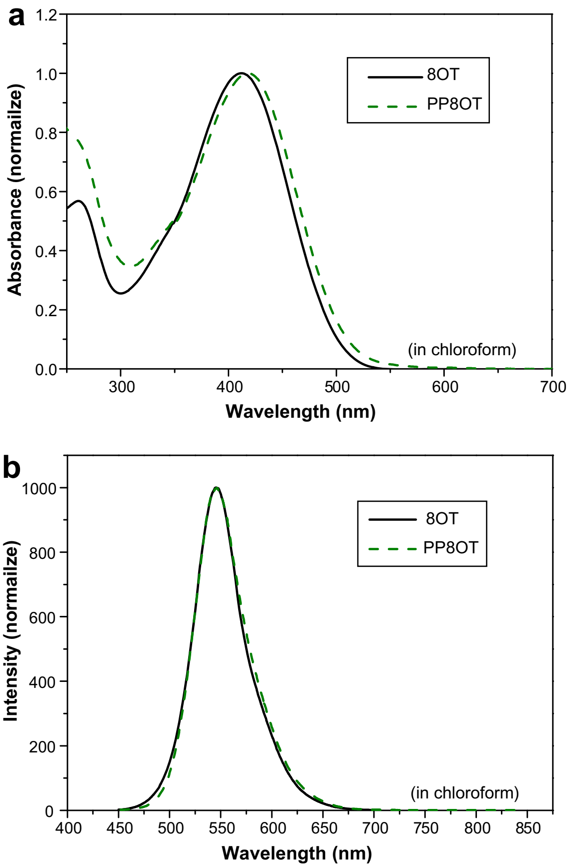


Fig. 2. The (a) UV/Vis and (b) PL spectra of PP8OT and its corresponding oligomer 8OT.

The quantum efficiency (η) and full width at half maximum (FWHM) of all copolymers and their corresponding oligo-octylthiophene in $CHCl_3$ and film state are listed in Table 3. It was shown that except 4OT and 6OT, the quantum efficiency of all copolymer/$CHCl_3$ solutions is similar to those of the oligomers and polyoctylthiophene. Comparing to the oligo-octylthiophene, linking the conjugated chromophores with saturated hydrocarbon spacers does enhance the processibility without significantly decrease the quantum efficiency. Interestingly, the FWHM of the absorption spectra for both copolymers and oligomers in $CHCl_3$ increased as the conjugating length increased. Nevertheless, the FWHM of the PL spectra for both copolymers and oligomers decreased as the increasing of the chromophore size. Furthermore, judging by the bandwidths of the UV/Vis spectra, the distribution of the conformers for the copolymers and their corresponding oligomers at their ground state is similar. One can see from Table 3 that the emission peaks of the copolymers (with the chromophore longer than tetra-octylthiophene) are sharper than their absorption band suggesting the existence of a narrower distribution of the conformers in the excited state. It is worth to note here that when the chain length of the chromophore is higher than hexa-octylthiophene, the FWHM (the color purity of the luminescent light) and quantum efficiency of the copolymers are close to those of the corresponding oligomers. Finally, the PL spectra of all copolymer films were measured and the CIE coordinates were calcu-

Table 2
The optical data of conjugated/non-conjugated copolymers and their corresponding oligomers.

Sample	10^{-5} M in $CHCl_3$		Film state		
	λ_{max} (nm)	λ_{em} (nm)	λ_{max} (nm)	λ_{em} (nm)	E_g (eV)[a][λ_{onset}]
2OT	299	373	–[b]	–[b]	–[b]
3OT	338	443 (424)[c]	–[b]	–[b]	–[b]
4OT	364	468 (490)	–[b]	–[b]	–[b]
6OT	401	523	–[b]	–[b]	–[b]
8OT	413	546	–[b]	–[b]	–[b]
PM3OT	365	463 (437)	369	490	2.81 [440]
PM4OT	383	509 (484)	386	525	2.58 [481]
PP2OT	280	394	283	392	3.39 [366]
PP3OT	337	460	336	490	3.07 [404]
PP4OT	352	494	355	508	2.83 [438]
PP6OT	396	523	404	553	2.47 [502]
PP8OT	418	546	432	564	2.32 [534]
PH3OT	333	457	334	476	3.08 [402]
Ra-POTH	438	561	495	629	1.97 [629]

[a] The onset absorption of the UV/Vis spectra.
[b] Cannot fabricate to film *via* spin coating *t*.
[c] The shoulder of the strongest absorption peak.

lated and displayed in Fig. 4. The color of the copolymer films distributes widely from blue, green to reddish orange.

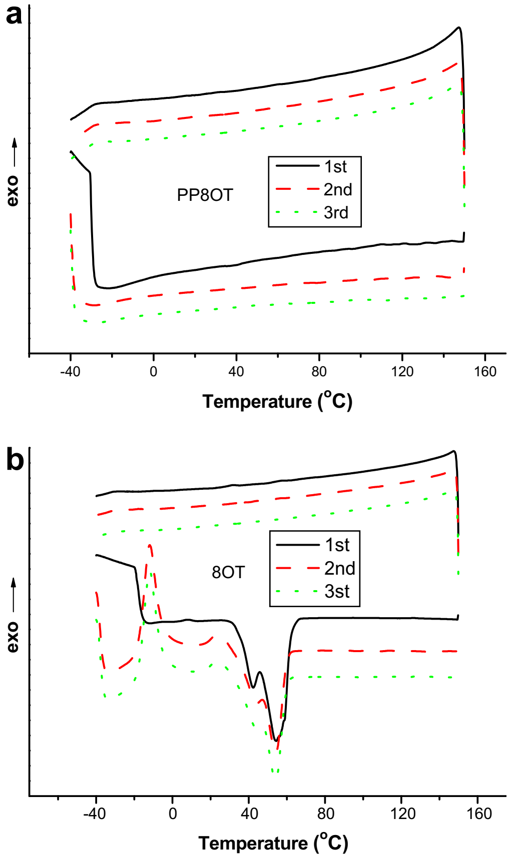


Fig. 3. The DSC curves of (a) PP8OT and (b) 8OT.

3.4. *The delocalization of the π-electrons in a conjugated molecule obtained from the optical data of a series of oligomers and conjugated/non-conjugated copolymers*

How the chain length of conjugated polymers affects the electronic and optical properties of the polymer is an important issue in conducting polymer community. It was known that the λ_{EM} and FWHM of the PL spectra (the emission color) for the conjugated polymers depend on the length and homogeneity of the conjugation as well as the aggregation of the polymer chains. The conjugation length was actually determined by the delocalization of the π-electrons along the polymer chain. Therefore, the degree of conjugation length is not equal to the length of the polymer chain, due to the defect or non-plane conformation of the polymer backbone [30]. Tian et al. [31] reported that the effective conjugated length of poly(*p*-phenylene-vinylene) (PPV) is between 7 and 10 monomers, based on a linear relation between the energy gap and the reciprocal number of monomer units. However, this value is lower than theoretic calculation done by Oelkrug et al. [32]. How far the π-electrons can delocalize in a conjugated polymer backbone is still a contradictory question. We may be able to use the optical data of the copolymers or their corresponding oligomers reported in this article to learn the delocalization length of π-electrons in polyoctylthiophene.

When the curves of the λ_{max} *vs* $1/n$ (n = the number of octylthiophen ring in the chromophore) for oligomers and copolymers solutions was drawn and then use the linear to fit the curves, the approximate equations of the two curves can be obtained as shown in Fig. 5. From the two equations we can find that when the octylthiophene ring is more than 31 and 23 (for oligomers and copolymers, respectively), the λ_{max} of the oligomers or copolymers will be close to that of the totally conjugated polyoctylthiophene. It other words, the π-electrons on the polyoctylthiophene backbone may be able to delocal-

Table 3
The FWHM and quantum yield (η) of oligomers and copolymers.

Molcular	FWHM (nm) of the UV/Vis spectra		FWHM (nm) of the PL spectra		η (%)[a] in $CHCl_3$
	Solution	Film	Solution	Film	
2OT	–[b]	–[c]	61	–[c]	1.7
3OT	83	–[c]	69	–[c]	5.0
4OT	98	–[c]	73	–[c]	6.4
6OT	115	–[c]	63	–[c]	7.2
8OT	117	–[c]	56	–[c]	4.4
PM3OT	85	91	82	91	4.4
PM4OT	106	106	80	63	4.7
PP2OT	–[b]	–[b]	66	144	2.3
PP3OT	83	85	102	106	3.2
PP4OT	100	103	90	90	4.6
PP6OT	117	139	76	70	4.4
PP8OT	119	130	56	78	4.1
PH3OT	77	87	93	95	3.1
Ra-POTH	116	160	51	66	4.0

[a] 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%).

[b] Cannot be determined.

[c] Cannot fabricate to film *via* spin coating.

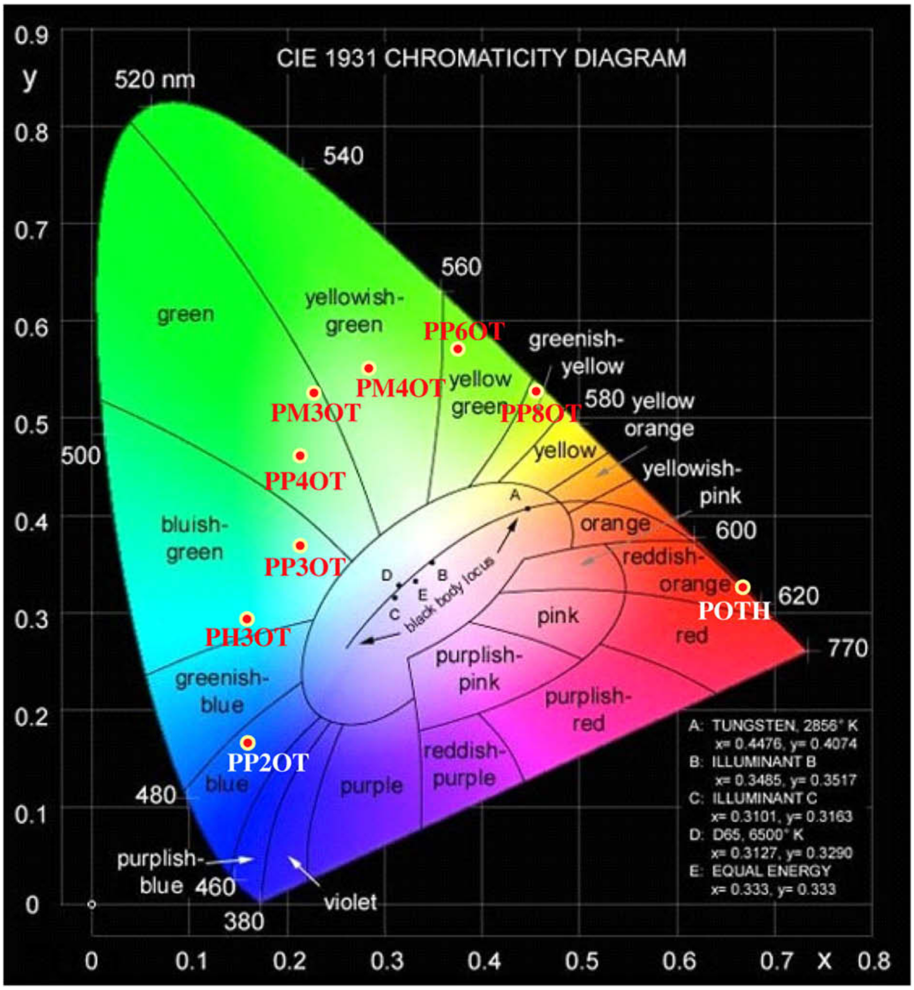


Fig. 4. The luminescence color of the copolymers (in term of the CIE coordination).

ize over 23–31 octylthiophene rings. The π-electrons delocalize in longer distance for polyoctylthiophene compared to PPV [31] may be due to the former contains sulfur atom with un-bonded electrons. The same strategy was used to estimate the delocalization of π-electrons based on the optical data of the copolymer films. Interestingly, it was found that when the chromophore length is infinite, the λ_{max} of the copolymer film is estimated to be 468 nm which is shorter than that (495 nm) of polyoctylthiophene. These results suggested that totally conjugated polyoctylthiophene has a much stronger inter chain interaction compared to the copolymers in the solid state. This is one of the advantages (avoiding the aggregation of the conjugated polymer chains) for confining the chromophores with saturated hydrocarbon spacers. One may inquire that "the polyoctylthiophene we prepared is not defect free, therefore the limitation of the delocalization for π-electron in the polymer backbone is controlled by the defects of polyoctylthiophene. The distance for the delocalization of π-electrons in a defect free conjugated system should be longer (if not much longer) than 31 octylthiophene rings." Nevertheless, polyoctylthiophene is a well-known conjugated polymer and it was prepared according to the literature report [33] with the polymer chain containing more than 150 octylthiophene units (see Table 1). The π-electron delocalized only over 31 octylthiophene rings may not entirely due to the defects of the polymer chains.

4. Conclusion

Capping the conjugated polymer backbone with non-conjugated spacers to confine the conjugated length of the chromophores on a polymer backbone was studied systematically. Propylene chain can block efficiently the π-electron transfer between the chromophores in a polymer backbone. Compared to their corresponding oligomers, the copolymers have the advantages of amorphous nature, better thermal stability and solution processability for thin film but still have the similar quantum efficiency and color purity as those of the oligomers. Furthermore, based on the photo-physical data of

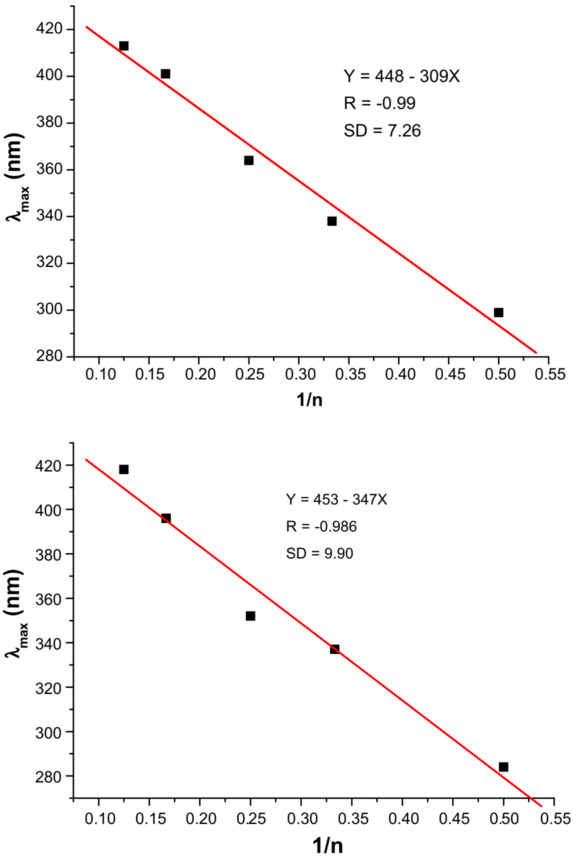


Fig. 5. The $\lambda_{\max}$ *vs* $1/n$ (n is the number of the octylthiophene in the chromophore) of (a) oligo-octylthiophene and (b) copolymer (in $CHCl_3$).

the copolymers and oligomers, the delocalization length of the π-electrons on polyoctylthiophene backbone can be roughly evaluated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj.2008.11.037.

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