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Studies of photoluminescence of *p*-phenylenevinylene oligomer and its polymer blends

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Abstract

A *p*-phenylenevinylene oligomer, 1,4-bis(3′-methyl-6′-octyloxystyryl)benzene was synthesized using Wittig's reaction. The oligomer was isomerized to all *trans* structure by refluxing in toluene with a catalytic amount of iodine. The oligomer was characterized by using ^{1}H NMR, UV–VIS, differential scanning calorimetry and fluorescence techniques. Polymer blends of the oligomer with PMMA and two short conjugation length polymers were studied for their photoluminescence (PL) properties. The blends with short conjugation length polymers showed significant increase in PL intensity, suggesting the occurrence of excitonic migration from oligomer to these polymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photoluminescence; *p*-Phenylenevinylene oligomer; Polymer blends; Excitonic migration

1. Introduction

The main driving force for the continued interests in conjugated polymers is the discovery that they can be used as the light-emitting diodes (LEDs) [1]. The luminescence is obtained by the recombination of electrons injected at the negative electrode and holes injected at the positive electrode in polymer thin films. The holes and electrons recombine in the polymer thin film, forming excited carriers (singlet excitons) which decay radiatively [2–5]. LEDs using conjugated or nonconjugated polymers as the active luminescent layer are a promising application for semiconducting polymers. The polymer LEDs have many advantages compared with inorganic LEDs. One of the important advantages for the polymers lies in the ability for the fabrication of flexible polymer LEDs. Other advantages include the ability to produce colours spanning through the visible spectrum by altering the π–π* energy gap. The quantum efficiency however are generally lower compared with their inorganic counterparts. Efforts have been made to increase the quantum efficiency of the polymer LEDs, such as using high work function polymer (polyaniline) as hole injecting electrode [6] and low work function metal (Ca) as an electron injection electrode [7]; fabrication of multilayer LEDs with electron-transporting layer placed between the luminescent layer and the negative electrode, which enhances the electroluminescent efficiency through charge carrier confinement [8,9]; blending of electron- or hole-transporting molecules with luminescent polymers to reduce the energy barrier between the electrodes and the luminescent polymers [10–12] and blending of fully conjugated polymer with confined conjugated polymer [13].

In this paper, the synthesis of 1,4-bis(3′-methyl-6′-octyloxystyryl)benzene, the properties if its blends with an inert polymer binder and that with short conjugation length polymers will be discussed.

2. Experimental

2.1. Synthesis

Scheme 1 shows the structures of the short conjugation length polymers, 01cp and 28cp used in the polymer

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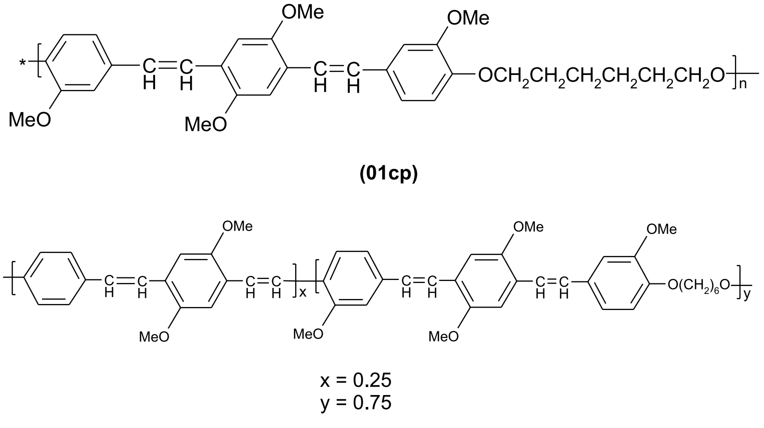


(01cp)

x = 0.25
y = 0.75

(28cp)

Scheme 1. Structures of 01cp and 28cp.

blend. The detail of the polymer preparation have been reported [14,15].

The synthesis route of 1,4-bis(3′-methyl-6′-octyloxystyryl)benzene is shown in Scheme 2.

2.2. Synthesis of 4-octyloxytoluene (OT)

Into a 250 ml round-bottom flask fitted with a condenser, 10.8 g (0.1 mol) of *p*-cresol, 17.27 ml (0.1 mol) of *n*-bromooctane, 13.82 g (0.1 mol) of anhydrous potassium carbonate and 50 ml of dried reagent grade acetone were added. The mixture was refluxed at 70°C with constant magnetic stirring for 8 h. The mixture was then poured into 300 ml of water. The organic layer floating on top was separated. The aqueous layer was then extracted with three 15 ml portions of ether. The organic layer and the ether extracts were then combined and washed with three 10 ml portions of 2 M sodium hydroxide solution, followed by drying over anhydrous sodium carbonate. The ether was removed with a rotary evaporator and the residue was vacuum distilled. The product, OT was collected at 150–155°C. The yield was 11.2 g (50.9%). Elemental Analysis: C: 82.54; H: 11.42%. Calculated: C: 81.8%; H: 10.9%. ^{1}H NMR: δ 1.06 [t, 3H, $-O(CH_2)_7CH_3$], 1.48 [m, 10H, $-OCH_2CH_2(CH_2)_5CH_3$], 1.919 [t, 3H, $-OCH_2CH_2(CH_2)_5CH_3$], 2.43 [s, 3H, $-CH_3$], 4.05 [t, H, $-OCH_2(CH_2)_6CH_3$], 6.95 [d, 2H, H_a], 7.2 [d, 2H, H_b].

2.3. Synthesis of 3-chloromethyl-4-octyloxytoluene (cl-OT)

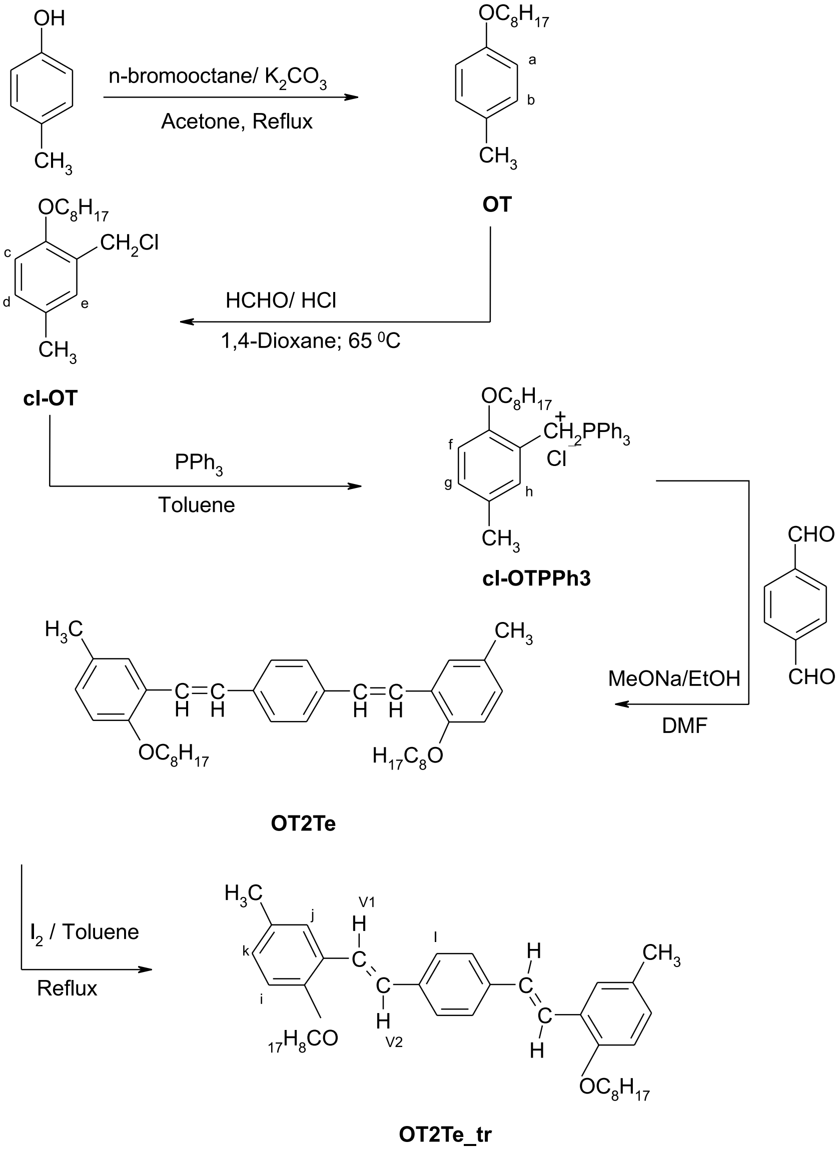
4-Octyloxytoluene, 9.0 g (40.9 mmol) was dissolved in 30 ml of 1,4-dioxane a 100 ml three-neck round-bottom flask. The solution was maintained at 65°C while dried HCl gas (generated by adding concentrated H_2SO_4 into concentrated HCl acid) was bubbled into the flask for 6 h and formaldehyde (81.8 mmol) was added into the flask. At the end of the reaction, two layers were formed. The top layer was separated. The solvent, 1,4-dioxane, was removed by rotary evaporation under reduced pressure. The yield was 8.88 g (80.9%). Elemental analysis: C: 72.5%; H: 9.85%. Calculated: C 71.5%; H: 9.3%. ^{1}H NMR: δ 0.88 [t, 3H, $-O(CH_2)_7CH_3$], 1.31 [m, 10H, $-OCH_2CH_2(CH_2)_5CH_3$], 1.78 [t, 3H, $-OCH_2CH_2(CH_2)_5CH_3$], 2.24 [s, 3H, $-CH_3$], 3.93 [t, H, $-OCH_2(CH_2)_6CH_3$], 4.59 [s, 2H, $-CH_2Cl$], 6.71 [d, 1H, H_c], 7.03 [d, 1H, H_d], 7.11 [s, 1H, H_e].

2.4. Synthesis of 3-methyl, 6-octyloxybenzyl triphenylphosphonium chloride (cl-OTPPh3)

The chloromethyl compound, cl-OT (6.71 g, 35.3 mmol) and triphenylphosphine (6.5 g, 24.8 mmol) were dissolved in 50 ml of toluene. The reaction mixture was heated to 110°C for 12 h. The product, cl-OTPPh3 formed a white hygroscopic precipitate when cooled to room temperature. It was separated and washed with toluene and dried in vacuum. Yield: 11.3 g (86.4%). ^{1}H NMR: δ 0.9 [t, 3H, $-O(CH_2)_7CH_3$], 1.3 [m, 12H, $-OCH_2(CH_2)_6CH_3$], 2.1 [s, 3H, $-CH_3$], 3.3 [t, H, $-O\,CH_2(CH_2)_6CH_3$], 5.1 [d, 2H, $-CH_2-$], 6.5 [d, 2H, H_f], 7.2 [m, 2H, H_g, H_h]. 7.6–7.8 [m, 15H,$-P(C_6H_5)_3$].

2.5. Synthesis of 1,4-bis(3-methyl, 6-octyloxystyryl)benzene (OT2Te)

The phosphonium salt, cl-OTPPh3 (12.6 g, 23.1 mmol) and terephtaldehyde (1.55 g, 11.55 mmol) were placed in a 250 ml three-necked round bottom flask equipped with a stirrer, a nitrogen gas inlet tube, and a dropping funnel with a pressure equalizing side arm. It was then dissolved in 50 ml of dimethylformamide (DMF). A slow stream of nitrogen gas was bubbled



Scheme 2. Schematic routes for the synthesis of OT2Te_tr.

through the mixture, at room temperature. Approximately 100 ml of freshly prepared solution of sodium methoxide in ethanol (0.3 M) was added dropwise so that the coloured ylide was consumed in between successive additions. After the complete addition of sodium methoxide, the reaction mixture was left to react at room temperature for 12 h. It was then quenched by the addition of an equal volume of water. The mixture was extracted with diethyl ether three times. The ether extract was washed with water several times and dried over sodium sulphate, and the solvent removed. The product was separated by column chromatography using silica gel (230–400 mesh ASTM) with chloroform as eluent. The first fraction gave pure compound, OT2Te ($Rf \approx 0.9$) on evaporation. Elemental analysis: C: 84.77%; H: 9.98%. Calculated: C: 84.81%; H: 9.54%. Yield: 1.3 g (24.3%). ^{1}H NMR: δ 0.8 [m, 6H, $-O(CH_2)_7CH_3$], 1.3 [m, 20 H, $-OCH_2CH_2(CH_2)_5CH_3$], 1.6 [m, 4H, Ar–CH_3], 3.9 [m, 4H, $-OCH_2(CH_2)_6CH_3$], 6.5–7.4 [m, 14H, phenylene and vinylene protons]. m.p. = 100.29°C.

2.6. *Trans-isomerization of OT2Te*

OT2Te, 2 g was isomerized into all-*trans* configuration by refluxing for 4 h in toluene in the presence of a catalytic amount of iodine (~0.1 g) [16]. After removal of the toluene, the product was dissolved in 10 ml of chloroform. The solution was slowly added to 200 ml of ethanol for precipitation. The solid was dried in a vacuum oven at 40°C for two days to give 1.5 g (75%) of the product, OT2Te_tr. Elemental analysis: Calculated: C: 84.81%; H: 9.54%. Found: C: 84.94%; H: 9.59%. ^{1}H NMR: δ 0.93 [t, 6H, $-O(CH_2)_7CH_3$], 1.31 [m, 16H, $-OCH_2CH_2CH_2(CH_2)_4CH_3$], 1.57 [t, 4H, $-OCH_2CH_2CH_2(CH_2)_4CH_3$], 1.87 [t, 4H, $-OCH_2CH_2CH_2(CH_2)_4CH_3$], 2.36 (s, 6H, $-CH_3$), 4.04 [t, 4H, $-OCH_2(CH_2)_6CH_3$], 6.82 [d, 2H, H (V1)], 7.05 [d, 2H, H (V2)], 7.18 [d, 2H, H_i], 7.28 [s, 2H, H_j], 7.48 [d, 2H, H_k], 7.55 [s, 4H, H_l]. m.p. = 100.85°C.

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were performed to detect the presence of phase separation in the polymer/oligomer blend matrixes. Solid samples of pure oligomer (OT2Te and OT2Te_tr) and the PMMA/OT2Te, PMMA/OT2Te_tr, 01cp/OT2Te_tr films were scanned from 5°C to 250°C at the scan rate of 20 K/min under the N_2 atmosphere.

3. Results and discussion

3.1. Substitution reaction

It was found that the substituted phenylene ring became resistant to any further electrophilic substitution after the substitution of one chloromethylene ($-CH_2Cl$) group despite the HCHO:OT ratio being raised to 2.5:1. This suggests that after the introduction of the first electron-withdrawing group, the phenylene group has become too electron deficient to facilitate further electron donation to any other electrophile.

3.2. Absorption and photoluminescence

A broad structureless absorption spectrum is observed for OT2Te and the all *trans*-isomer OT2Te_tr solutions with λ_{max} at 362 nm. The PL spectrum of OT2Te solution shows two emission maxima at 420 and 440 nm and so is the PL spectrum for OT2Te_tr (Fig. 1). The emission properties of these molecules in PMMA blends were also studied. This was done by dissolving the PMMA and the compounds in $CHCl_3$ to make a 1% (w/v) polymer solution, after which it was spin coated on a glass substrate to form a thin film. The characteristics of the PMMA and the oligomer blend matrices are summarized in Table 1.

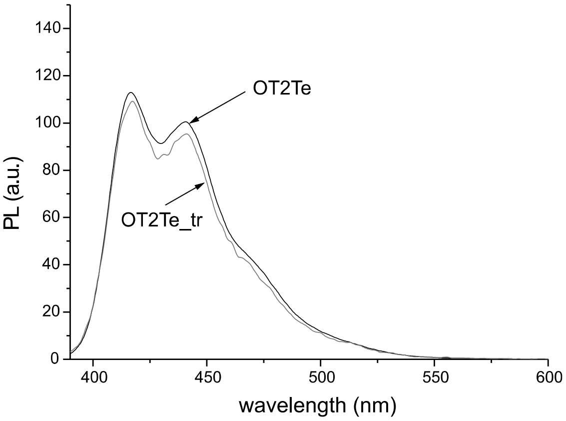


Fig. 1. PL (excited at 358 nm) spectra of OT2Te and OT2Te_tr solution.

The matrix was homogeneous when the composition of oligomer in the blend was small. However, as the oligomer content increased, phase separation became increasingly apparent.

The emission spectra for the OT2Te and OT2Te_tr dispersed in the PMMA film are shown in Figs. 2 and 3 respectively. It is noticed that the spectra are red shifted about 40 nm compared to their dilute solution counterpart. This is attributed to the chain extension in the solid state. The all *trans*-isomer exhibits two emission peaks at 420 and 440 nm. The emission intensity is highest when excited at 362 nm. For the OT2Te/PMMA

Table 1
Characteristics of PMMA–oligomer matrices at different PMMA:oligomer ratio

Oligomer	PMMA:oligomer ratio	Visual observation	DSC
OT2Te	1:5	Strong phase separation	Phase separation
	1:1	Phase separation	Phase separation
	1:0.4	Phase separation	Phase separation
	1:0.2	Clear	Phase separation
	1:0.1	Clear	$T_g = 110.7$°C
OT2Te_tr	1:5	Strong phase separation	Phase separation
	1:1	Phase separation	Phase separation
	1:0.4	Phase separation	Phase separation
	1:0.2	Clear	Phase separation
	1:0.1	Clear	$T_g = 111.2$°C

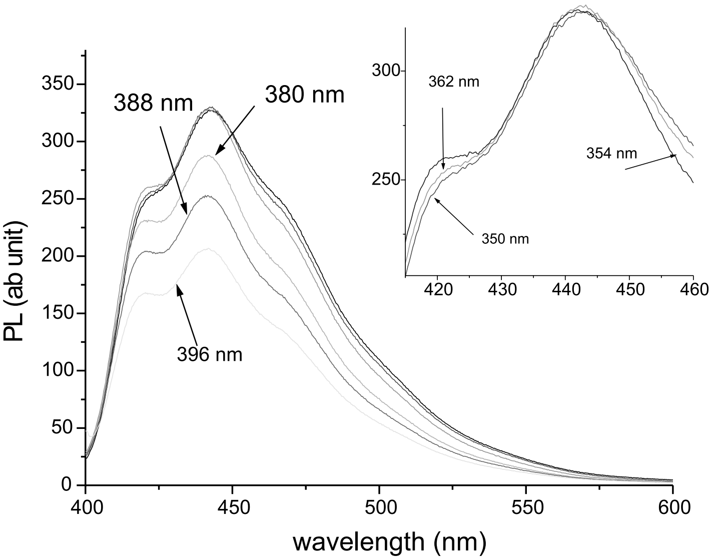


Fig. 2. PL spectra of the PMMA/OT2Te (1:0.1) film at different excitation wavelengths. Inset: enlargement of the top three unlabeled spectra.

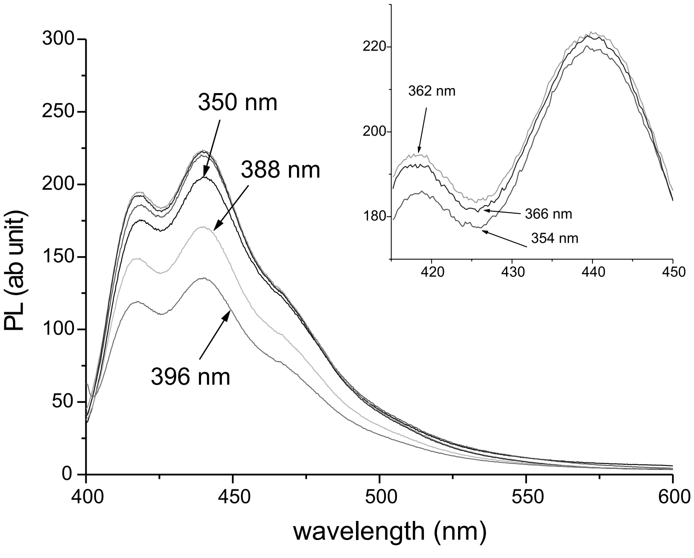


Fig. 3. PL spectra of the PMMA/OT2Te_tr (1:0.1) film at different excitation wavelengths. Inset: enlargement of the top three unlabeled spectra.

film, when excited at 350, 354 and 362 nm, a crossover in the PL intensity can be observed at 420 and 440 nm peaks. However, the PL spectra of PMMA/OT2Te_tr film show no crossover in the PL intensity at these peaks. The phenomena clearly show that the various isomers in OT2Te have different emission spectral pattern and the λ_{exc} that contribute to the PL intensity of the individual isomers are also different.

3.3. 01cp–oligomer blend

Fluorescence studies were carried out for 01cp–OT2Te_tr blends in the both solution and film. The solutions were prepared with 0.3 ppm 01cp containing 10%, 20% and 30% of OT2Te_tr. Whereas, the 01cp–OT2Te_tr films were prepared by spincoating the 1% (w/v) 01cp solution in chloroform which contained 10%,

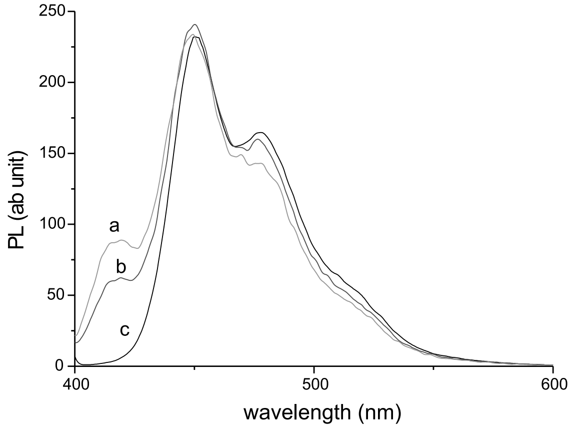


Fig. 4. PL spectra of the 0.3 mg/L 01cp/OT2Te_tr solutions with excitation wavelength at 395 nm. 01cp/OT2Te_tr ratio: (a) 1:0.2; (b) 1:0.1; (c) 1:0.

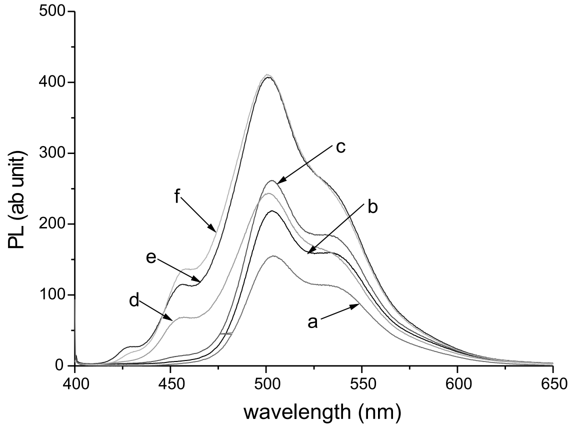


Fig. 5. PL spectra of the 01cp/OT2Te_tr film with $\lambda_{exc} = 397$ nm. 01cp/OT2Te_tr ratio: (a) 1:0; (b) 1:0.1; (c) 1:0.2; (d) 1:0.4; (e) 1:0.8 and (f) 1:1.

Table 2
Characteristics of 01cp–OT2Te_tr matrices at different 01cp: OT2Te_tr ratio

Oligomer	Oligomer:01cp ratio	Visual observation	DSC
OT2-Te_tr	0:1	Clear	$T_g = \sim 73°C$
	0.1:1	Clear	Homogeneous
	0.2:1	Clear	Homogeneous
	0.4:1	Phase separation	Phase separation
	0.8:1	Strong phase separation	Phase separation
	1:1	Strong phase separation	Phase separation

20%, 40%, 80% and 100% OT2Te_tr on glass plates. The thickness of the films was controlled by spincoating the solution mixtures under a constant spin rate of 1000 rpm for a period of 1 min. The spincoated films obtained were then dried in a vacuum desiccator prior to the PL measurement. The standard deviation of the PL intensity for each type of film was found to be within 10%.

It was noticed that the emission spectra for the solution mixtures showed only an additive phenomenon of the individual PL spectra of OT2Te_tr and 01cp (Fig. 4). No PL intensity enhancement was noticed as a result of the mixing. On the other hand, for the 01cp–OT2-Te_tr blended film, a clear intensity enhancement was observed (Fig. 5). In addition to that, the spectral pattern resembled that of 01cp. Little or no emission was observed at 410 nm $< \lambda_{em} <$ 470 nm region which is part of the emission region of OT2Te_tr. The result suggests that in the condensed form, the chromophores of 01cp and OT2Te_tr were in close proximity for interaction. The interaction gives rise to excitonic migration from higher energy (resulted from OT2Te_tr) to lower energy (resulted from 01cp) level [13,17].

As the composition of OT2Te_tr increased to 40% and above, emission at lower wavelength region attributed to OT2Te_tr started to appear. Interestingly, this coincided with the phase separations of the 01cp–OT2-Te_tr in the blend observed (Table 2). It was found that OT2Te_tr had slightly better miscibility with 01cp than with PMMA.

3.4. 28cp–oligomer blend

In order to ascertain the interchain chromophoric interaction, the PL of 28cp–oligomer blends were also investigated. The blend matrices of OT2Te_tr:28cp ratio = 0.1:1 displayed a homogeneous clear film. The

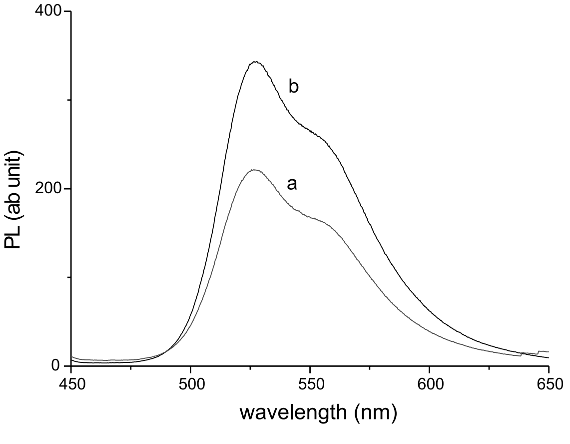


Fig. 6. PL spectra of the 28cp/OT2Te_tr film with $\lambda_{exc} = 420$ nm. 28cp/OT2Te_tr ratio: (a) 1:0 and (b) 1:0.2.

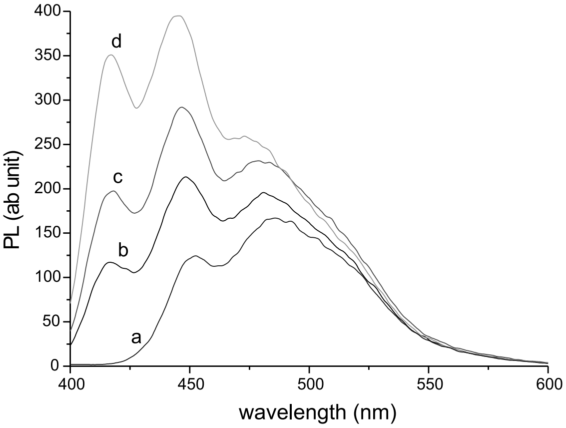


Fig. 7. PL spectra of the 0.3 mg/L 28cp/OT2Te_tr solutions with $\lambda_{exc} = 395$ nm. 28cp/OT2Te_tr ratio: (a) 1:0; (b) 1:0.1; (c) 1:0.2 and (d) 1:0.3.

PL spectral pattern for both the 28cp and OT2Te_tr films are the same (Fig. 6). An intensity enhancement is again evident as a result of the incorporation of OT2Te_tr into the polymer matrix. Again, this is in contrast to the solution PL spectra (Fig. 7) pattern of the two components which show an additive pattern of the emissions from the two components in solution.

4. Conclusion

OT2Te, which consists of various stereo isomers, had been synthesized through Wittig reaction. It could be isomerized into the all *trans* form by refluxing in toluene with a catalytic amount of iodine. PMMA acted as a good inert binder for OT2Te. Homogeneous films of OT2Te_tr blended with the 01cp and 28cp show PL intensity enhancement, suggesting an excitonic migration from OT2Te_tr to 01cp and 28cp.

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