

Preparation of MEH-PPV/Nanosized Titania Hybrids Via *In Situ* Sol–Gel Reaction of Titanium Alkoxide: Optical Property

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ABSTRACT: Homogenously dispersed organic (MEH-PPV)/inorganic (nanosized titania) hybrids were successfully synthesized. The method of preparation was based on a simple one-step *in situ* sol–gel technique using titanium isopropoxide (TIP) as the precursor. The key benefit of this preparation was that TIP interacted with both 2-chlorophenol and MEH-PPV, so that the degree of aggregation and phase separation could be kept to a minimum with a suitable recipe. MEH-PPV/TIP/H₂O/2-chlorophenol of various weight ratios were synthesized to examine the morphology as well as optical properties of the MEH-PPV/TIP(titania) hybrid. The observation of MEH-PPV gelation and Fourier transform infrared results verified the interaction existing between MEH-PPV and TIP. SEM photographs showed that TIP(titania) were homogenously dispersed in the MEH-PPV film if the hybrid solution was clear from the use of a suitable recipe. UV–vis absorption measurements showed that the addition of TIP decreased the conjugation length of MEH-PPV. A redshift in the photoluminescence (PL) emission was observed in almost all the hybrids in the solution state, because of the aggregation of MEH-PPV. However, it was found that spinning destroyed the aggregation of MEH-PPV, resulting in a blueshift in the PL emission of the hybrids. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 515–529, 2008

Keywords: composites; conjugated polymer; phase separation

INTRODUCTION

Today, the preparation of nanosized materials is taking on an increasingly prominent role in the forefront of research, and especially so for organic/nanosized–inorganic hybrid materials. By combining the advantages of organic and inor-

ganic materials, organic/nanosized–inorganic hybrid materials open up a myriad of possibilities for application. Hence, depending on the exact demands and specifications of a particular device, the composite material structure can be precisely tailored to suit the type of application. Materials of different characteristics can be chosen, combined, and have their miscellaneous functions elaborated in such a way as to complement one another to yield vastly superior performances. Ever since the discovery of poly(*p*-phenylene vinylene) (PPV) by the Friend

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group at Cambridge in 1990,¹ organic materials have remained the focus of intense interests over the years, with a view to finding further novel application of this new class of material, either by itself or in conjunction with other materials. This movement gathered further momentum when the Wudl group became the first group to synthesize a soluble PPV derivative through the alkyl and alkoxy side chain on the phenylene ring, poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV),² because this novel conjugated polymer makes processing vastly easier. Among inorganic materials, titania has been exhaustively studied over the past several decades and widely used in catalyst application because of its highly catalytic property, nontoxicity, and relatively low price.^{3,4} It is common knowledge that MEH-PPV is a good electron donor while titania is a good electron acceptor.⁵⁻⁸ Hence, an organic/inorganic hybrid based on MEH-PPV and titania will very likely exhibit some interesting properties. For example, in organic solar cell applications, where the diffusion length of the photoinduced excitons is generally smaller than 15 nm,⁹ a bicontinuous MEH-PPV/titania hybrid would lead to much higher photoinduced electron transfer efficiency.

The major issue in synthesizing organic/inorganic hybrid is overcoming the original incompatibility of the organic and inorganic materials. The chemical natures of organic and inorganic materials are fundamentally different. In general, there are three different kinds of methods to prepare the organic/inorganic hybrid materials. The first and simplest method is to select a suitable cosolvent, that is a bifavorable solvent, for each of the constituents. In the case where an appropriate cosolvent could not be found, the alternative is to modify the surface structure of the inorganic particles so that they can be dispersed in the organic solvent effectively.¹⁰⁻¹² The second method involves the use of a coupling agent. Usually, the nanosized-inorganic particles will aggregate easily due to their high surface energy. The coupling agent can link the organic and inorganic components by covalent bonding, hydrogen bonding, or simply physical interaction to prevent the phase separation.¹³⁻¹⁶ The third method is *in situ* sol-gel reaction. If there exist interactions between the inorganic particles and polymer, the *in situ* sol-gel reaction of the metal alkoxide in different kinds of polymer solutions will most likely disperse the titania nanoparticles evenly in the polymer solu-

tions. This method enhances the electrical-optical, mechanical, thermal, or coating properties of the resulting hybrids.¹⁷⁻²⁰

In the preparation of the organic/inorganic hybrid, by whichever method, a homogenous organic/titania hybrid is relatively more difficult to synthesize than an organic/silica hybrid because of the high reactivity of titanium alkoxide.²¹ Janssen and coworkers reported an air sol-gel process to form a bulk-heterojunction hybrid material of MDMO-PPV/TiO₂.²² However, this particular sol-gel process proceeded based on the humidity of air, which was difficult to control. Here, a different process to prepare the MEH-PPV/titania hybrid is presented. It makes use of the *in situ* sol-gel reaction of titanium alkoxide in a polymer solution. This process requires just one single step. The synthesized hybrid solution is then cast to form a hybrid film. In this study, the effects of the different synthesizing conditions on the optical properties of MEH-PPV/titania hybrid were investigated.

EXPERIMENTAL

Materials

Titanium (IV) isopropoxide (TIP) and 2-chlorophenol (2-CP) were used as received. The water used in the sol-gel reaction was purified using a Millipore Milli-Q system. The weight-average molecular weight (M_w) of MEH-PPV was ~600,000 as determined by gel permeation chromatography, which was calibrated using a polystyrene (PS) standard. The MEH-PPV was stored in the dark when not in use.

Preparation of MEH-PPV/Titania(TIP) Hybrid

Explanation of the Notation

Table 1 shows the reagents and the corresponding proportion used in the preparation of the MEH-PPV/titania(TIP) hybrids. The notation was explained by using "W2-T85-C5" as an example. The first term W2 is a measure of the effect of the amount of water used, and 2 indicates that the molar ratio of water to TIP was 2. The second term examines the effect of the TIP content on the hybrid performances and 85 means that the weight percent of TiO₂ in the hybrid was 85% if the conversion of TIP to TiO₂ was 100%. For the purpose of 85 wt % of titania in hybrid, the real wt % of TIP participating in

Table 1. Composition and Appearance of the MEH-PPV/TIP Hybrid Solution

	H ₂ O/TIP (mole ratio)	Titania (TIP)/Hybrid (wt %)	Concentration (mg/mL)	Appearance
W0 -T85-C5	0	85 (95.2)	5	Clear
W2 -T85-C5	2	85 (95.2)	5	Clear
W4 -T85-C5	4	85 (95.2)	5	Turbid
W4- T85 -C5	4	85 (95.2)	5	Turbid
W4- T70 -C5	4	70 (89.2)	5	Clear
W4- T50 -C5	4	50 (77.8)	5	Clear
W4- T30 -C5	4	30 (60.3)	5	Clear
W4-T85- C5	4	85 (95.2)	5	Turbid
W4-T85- C3	4	85 (95.2)	3	Turbid
W4-T85- C1	4	85 (95.2)	1	Clear

Note: The bold word in the different parts mean that it is the variable.

the *in situ* sol-gel reaction was 95.2 wt %. As for the last term, it is a gauge of the effect of the solution concentration on the *in situ* sol-gel reaction and 5 implies that the concentration of MEH-PPV was 5 mg/mL (0.5% w/v) in 2-CP solution.

In Situ Sol-Gel Reaction

A 100-mL round-bottom flask equipped with a stirrer and condenser was used. In a typical procedure, the desired amount of TIP was fully dissolved in a premixed solution containing MEH-PPV and 2-CP. When TIP was added to the MEH-PPV solution, an instantaneous change in the color of the solution from orange to dark brown was observed. It could thus be inferred that the reaction between TIP and 2-CP was extremely fast. After 30 min of stirring, the calculated amount of water was added to the MEH-PPV/TIP solution dropwise. During the addition of water, the solution was stirred vigorously to avoid local aggregation. The sol-gel reaction was carried out first at room temperature for 30 min and then reacted at 90 °C for 10 h. The appearance of the final MEH-PPV/titania(TIP) hybrid solution was described in Table 1.

Measurements

Fourier Transform Infrared Measurement

The functional groups as well as the complex behaviors of the MEH-PPV, TIP, 2-CP, and

hybrids were analyzed by a Fourier transform infrared spectrophotometer (FTIR) (Bio-Rad, FTS-3000). The specimens were prepared by coating the hybrid solution on potassium bromide (KBr) pellet and drying out the solvent. The absorption spectra were recorded with 16 scans at a resolution of 4 cm⁻¹ between 1800 cm⁻¹ and 400 cm⁻¹.

UV-Vis Measurement

The UV-vis absorptions of all hybrids were performed by using the UV-vis spectrometer (Thermo Spectronic gamma series). All the hybrid solutions used for UV-vis spectrometer, with the exception of W0-T85-C5 and W2-T85-C5, were diluted to 1×10^{-3} of the original concentrations and measured in a 1-cm path length cuvette. As for W0-T85-C5 and W2-T85-C5, they were diluted to 1×10^{-4} of the original concentrations. The preparation for film measurement was performed by spin coating at a spin rate of 3000 rpm.

Photoluminescence Measurement

Photoluminescence (PL) studies were recorded on a Fluorolog-Tau-3 spectrometer (Jobin Yvon) using a xenon lamp as the excitation source, with the photoexcitation at 502 nm. The concentration of all the hybrids solutions used for the measurement of PL in the solution state was original concentration. The preparation for film measurement was performed by spin coating at a spin rate of 3000 rpm.

RESULTS AND DISCUSSION

Observation of MEH-PPV Gelation

In order to investigate the interaction between MEH-PPV and TIP, a comparison experiment was conducted. Fifty milligrams of MEH-PPV and PS were dissolved in 10 mL of 2-CP in two different round-bottom flasks respectively. After full dissolution, 50 mg TIP was added to each flask and the reaction was carried out at 90 °C for 10 h. For the MEH-PPV system, after cooling to room temperature, the viscosity of solution gradually increased until a gel was formed after 3 days. In the case of the PS system, it remained in the solution state even after 1 month. One can therefore come to a preliminary conclusion that there was indeed interaction between the MEH-PPV and TIP. From the literature, the most likely source of interaction appeared to be the coordination of the O atom of MEH-PPV and the Ti atom of TIP.²³ For further characterization of this interaction, the FTIR analysis will be presented as follows. This additional experiment on the MEH-PPV/TIP hybrid gel was designed to prove beyond any doubt that interaction did occur between the MEH-PPV and TIP. The hybrids under discussion either did not gel at all or took more than 2 weeks to do so.

FTIR Analysis

The Interaction of MEH-PPV and TIP

The FTIR spectra of MEH-PPV, TIP, 2-CP, MEH-PPV/TIP hybrid, and TIP in 2-CP were shown in Figure 1. From Figure 1(a,b), it can be seen that the (RO)—CH₂ asymmetric vibration at 1460 cm⁻¹ of MEH-PPV²⁴ had disappeared and two new bands at 910 cm⁻¹ and 830 cm⁻¹ were generated. One can conclude that the interaction between MEH-PPV and TIP occurred at the O atom of the 2-ethyl hexyloxy side chain. As for the O atom of MEH-PPV on the other side, the methoxy side chain, it always contributed to the aggregation of MEH-PPV chains and did not have enough space to coordinate with Ti atom.^{25,26}

Complex Reaction of TIP and 2-CP

Comparison of Figure 1(c–e) revealed that a new band at 1278 cm⁻¹ was formed when TIP reacted with 2-CP. The disappearance of the bands of O—H bending and deformation at 1338

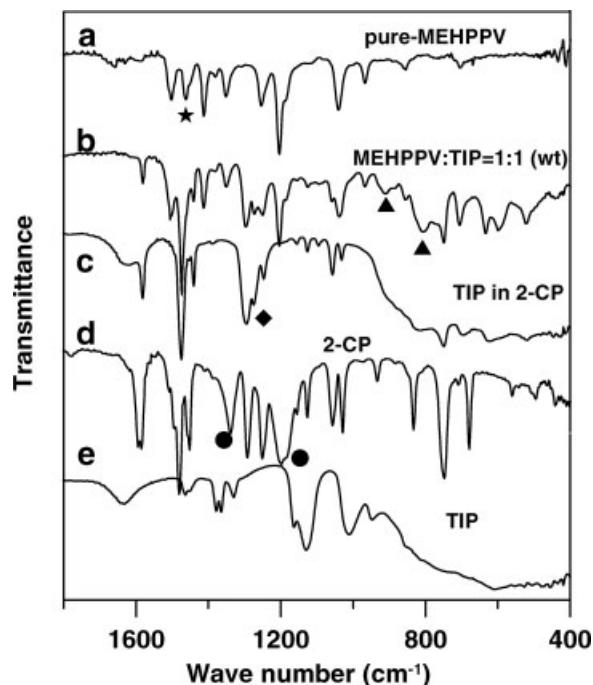
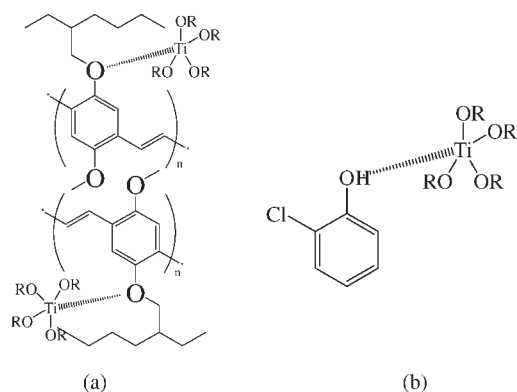


Figure 1. FTIR spectra of (a): pure-MEHPPV, (b): MEH-PPV/TIP hybrid with 1:1 weight ratio, (c): TIP dissolved in 2-CP, (d): 2-CP, and (e): TIP. ★: disappeared band of MEH-PPV when interacting with TIP, ▲: generated bands of MEH-PPV when interacting with TIP, ◆: new band when TIP reacted with 2-CP, ●: O—H bending and deformation of 2-CP.

and 1198 cm⁻¹ indicated that 2-CP reacted with TIP.²⁷ Figure 1(c) indicated that TIP and 2-CP took on a complex form through oxygen bonding. The new band at 1278 cm⁻¹ was used to identify that the complex reaction occurred between TIP and 2-CP. As can be seen from Figure 1(c), the 2-CP served not only as a solvent but also as a complex reagent to slow down the hydrolysis and condensation reaction rate of TIP. When adding TIP to the MEH-PPV solution, the partial 2-CP would undergo complex reactions with the TIP immediately. Therefore, the hydrolysis and condensation reaction rate of TIP could be well controlled. A moderate sol–gel reaction played a key role in preventing significant phase separation. Based on the results of FTIR, both of the schematic interaction between (a) MEH-PPV and TIP, and (b) 2-CP and TIP were depicted in Scheme 1.

SEM Morphology

The particle size and distribution of TIP(titania) in the MEH-PPV/TIP(titania) hybrid can be



Scheme 1. (a) The proposed function of oxygen of MEH-PPV on different side chain, 2-ethyl hexyloxy or methoxy, in the hybrid without water addition; (b) the proposed interaction between 2-CP and TIP.

deduced from SEM photographs. Figure 2 shows the SEM morphology of W4-T85-C5 and W4-T30-C5 with different magnifications, 50,000 and 1000, respectively. From Figure 2(b,b*), it can be seen that the TIP(titania) were homogeneously dispersed in the MEH-PPV film if the hybrid solution was clear from the use of a suitable recipe. On the contrary, an apparent phase separation could be observed if the hybrid solution was treated with the wrong recipe, as shown in Figure 2(a,a*). Figure 2(b,b*) was a direct proof that attaining full dissolution remained the major hurdle in synthesizing organic/inorganic hybrid, a manifestation of the original incompatibility of organic and inorganic materials.

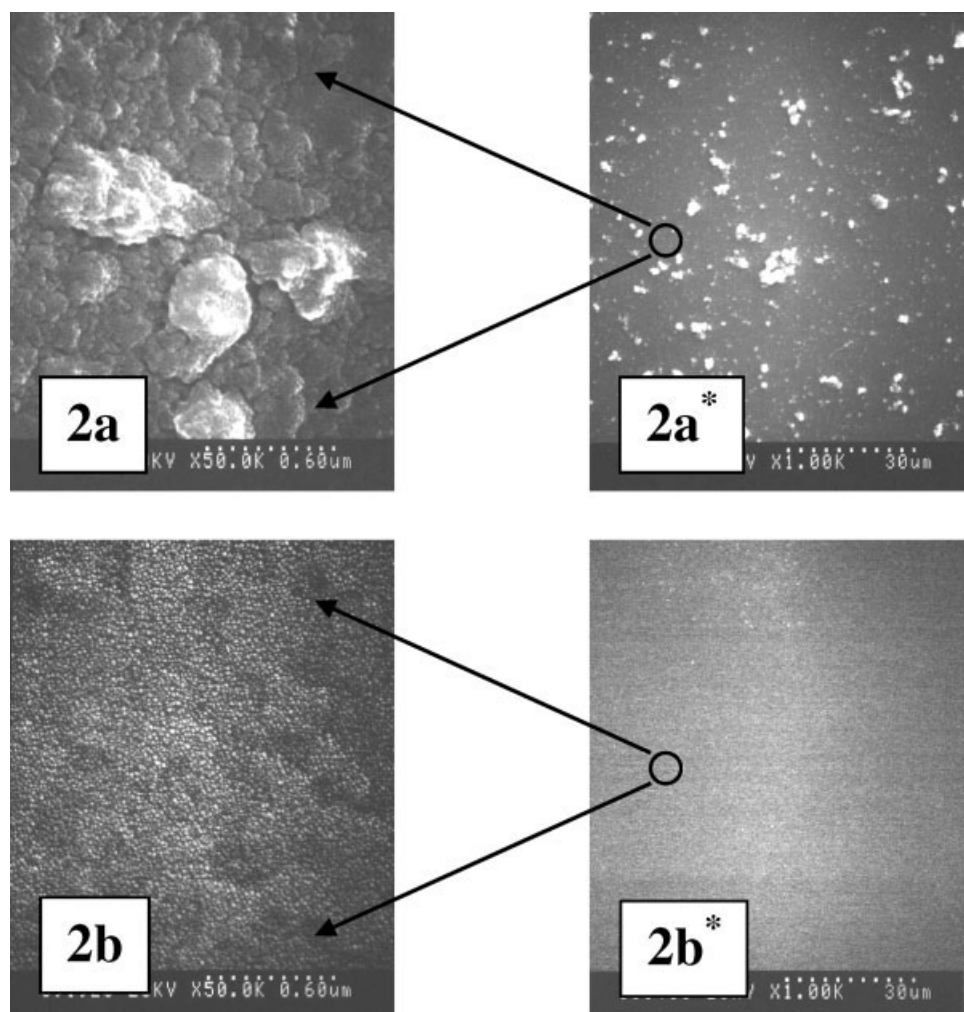


Figure 2. SEM photographs of hybrid W4-T85-C5 and W4-T30-C5 prepared with different amount of TIP. (2a) W4-T85-C5 with 50,000 magnification, (2a*) W4-T85-C5 with 1000 magnification, (2b) W4-T30-C5 with 50,000 magnification, and (2b*) W4-T30-C5 with 1000 magnification.

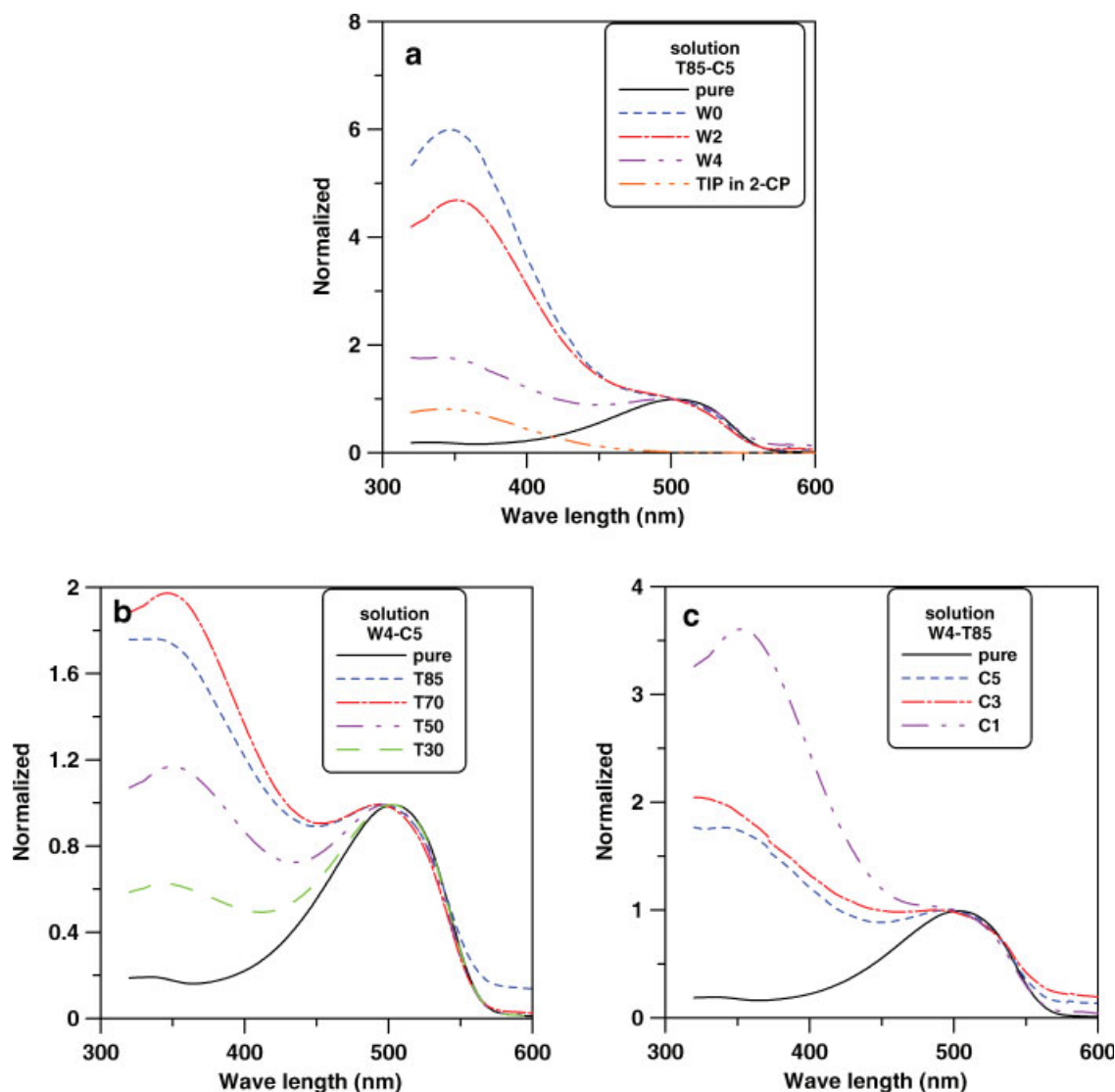


Figure 3. UV-vis absorption of MEH-PPV, TIP in 2-CP, and MEH-PPV/TiO₂ hybrids in solution state. It was normalized based on λ_{\max} of MEH-PPV. Hybrids with different (a) water amount, (b) TIP amount, and (c) concentration.

UV-Vis Absorption Analysis

UV-Vis Absorption in Solution

The UV-vis absorption spectra of MEH-PPV/titania(TiO₂) hybrid solutions prepared with different water content, TIP content, and solution concentration are shown in Figure 3. Figure 3 is the normalized spectra based on the λ_{\max} of MEH-PPV. For ease of comparison, the concentrations of the hybrid solutions were diluted to 5×10^{-4} % (w/v), with the exception of W0-T85-C5 and W2-T85-C5. The concentrations of these two hybrid solutions were further diluted to 5×10^{-5} % (w/v).

From Figure 3, it can be clearly seen that all the hybrids exhibited a slight blueshift in the λ_{\max} of MEH-PPV. This blueshift could probably be attributed to two effects: coiled conformation and aggregation.

We first examine the effects of the coiled conformation. In pure MEH-PPV solution, the polymer chain would be extended in the presence of a good solvent. When TIP and water were added to this solution, the heterogeneous components resulted in the coiled conformation of the MEH-PPV chains. This had the effect of shortening the conjugation length of the MEH-PPV, leading to a blueshift in the absorption. Second, the aggrega-

tion of the polymer chains would affect the UV-vis absorption. Yang and coworkers reported that MEH-PPV chains in dilute solution would be more isolated due to the short-range nature of the interchain interactions.²⁸ The polymer chain became more extended and the effective conjugation length would be longer. As the concentration increased, the polymer chains started to entangle and form the so-called loose aggregation and compact aggregation.^{28–30} When heavy entanglement occurred, the effective conjugation length of the polymer chain would decrease, thus resulting in a blueshift. This was due to the fact that the side chains of the MEH-PPV were not symmetrical, and the π - π stacking of the MEH-PPV backbone was hindered in the ground state because of the bulky 2-ethyl hexyloxy side chain. Therefore, the irregular aggregation of the MEH-PPV chains led to a shortening in the conjugation length.

As stated in the section on MEH-PPV gelation and FTIR analysis, it could be concluded that interaction existed between the MEH-PPV and TIP. During the formation of the MEH-PPV/TIP(titania) hybrid, the aggregation of MEH-PPV occurred mostly in irregular form due to the existence of the heterogeneous point, TIP (titania). Because of the asymmetrical structure of the MEH-PPV and the existence of TIP(titania), the aggregation resulted in a shorter conjugation length for the MEH-PPV and a blueshift in the UV-vis absorption.

UV-Vis Absorption in Film

Figure 4(a–c) show the UV-vis absorption spectra of the MEH-PPV/titania(TIP) hybrids films also prepared with different water content, TIP content, and solution concentration. The spectra were also normalized based on the λ_{\max} of MEH-PPV. Comparing Figures 3 and 4, the blueshifts for the hybrids in the solid state were even more apparent than that in the solution state.

PL Analysis

PL in Solution

Emission Peaks of MEH-PPV. In dilute pure MEH-PPV solution, the PL spectrum generally had three peaks: a yellow emission ($\lambda_{\max} \sim 560$ nm), an orange emission ($\lambda_{\max} \sim 600$ nm), and a red emission ($\lambda_{\max} \sim 650$ nm).^{31,32} These three emissions were commonly attributed to three different morphologies. The first emission came from isolated single chain emission. The second

emission was generally known as loose aggregation emission, and the third was attributed to compact aggregation emission. As mentioned in the section on UV-Vis Analysis, the aggregation would become more and more significant with increasing concentration.

Aggregation of MEH-PPV. Figure 5 shows the PL spectra measured under different variables: the water content, TIP content, and solution concentration. It had been calibrated by using the same amount of MEH-PPV. The intensity obtained in Figure 5 was the original intensity, and it would investigate the effects of the aforementioned variables on the original PL behavior. In order to show the shape of the PL spectrum more clearly for the hybrid with low PL intensity, there were two intensity scales in Figure 5 and the arrows indicated the corresponding intensity for each hybrid. Figure 6 is the normalized PL spectra of Figure 5 based on the λ_{\max} of MEH-PPV. From Figure 6, it can be seen that no isolated single chain emission was observed, and almost all the hybrids, with the sole exception of W4-T85-C1, exhibited a redshift compared to pure MEH-PPV. The reason for the absence of the single chain emission was that the concentrations of all the hybrids used in the PL measurements (0.1–0.5% w/v) were way too high for single chain emission to occur. As a result, loose aggregation emission dominated the spectra. The redshift in the PL emission of the hybrids was also associated with the interchains aggregation.^{33–34}

As expounded in the section on UV-Vis Analysis, the irregular aggregation would shorten the conjugated length of MEH-PPV. Hence, a hybrid with a higher concentration would exhibit a blueshift in the UV-vis absorption. However, for PL emission, a redshift occurred, with respect to pure MEH-PPV. This implied that to some extent, ordered aggregation occurred in the aggregation of coiled MEH-PPV chains in the solution state. It should be noted that there were four different types of MEH-PPV chain in this text: extended chains, free coiled chains, ordered aggregated coiled chains, and irregular aggregated coiled chains. The conjugation length was longer in the case of the ordered aggregated coiled chains, when compared with the free and irregular aggregated coiled chains. And, the most important point was that these ordered aggregated coiled chains served as an intermediate step for energy transfer when free or irregu-

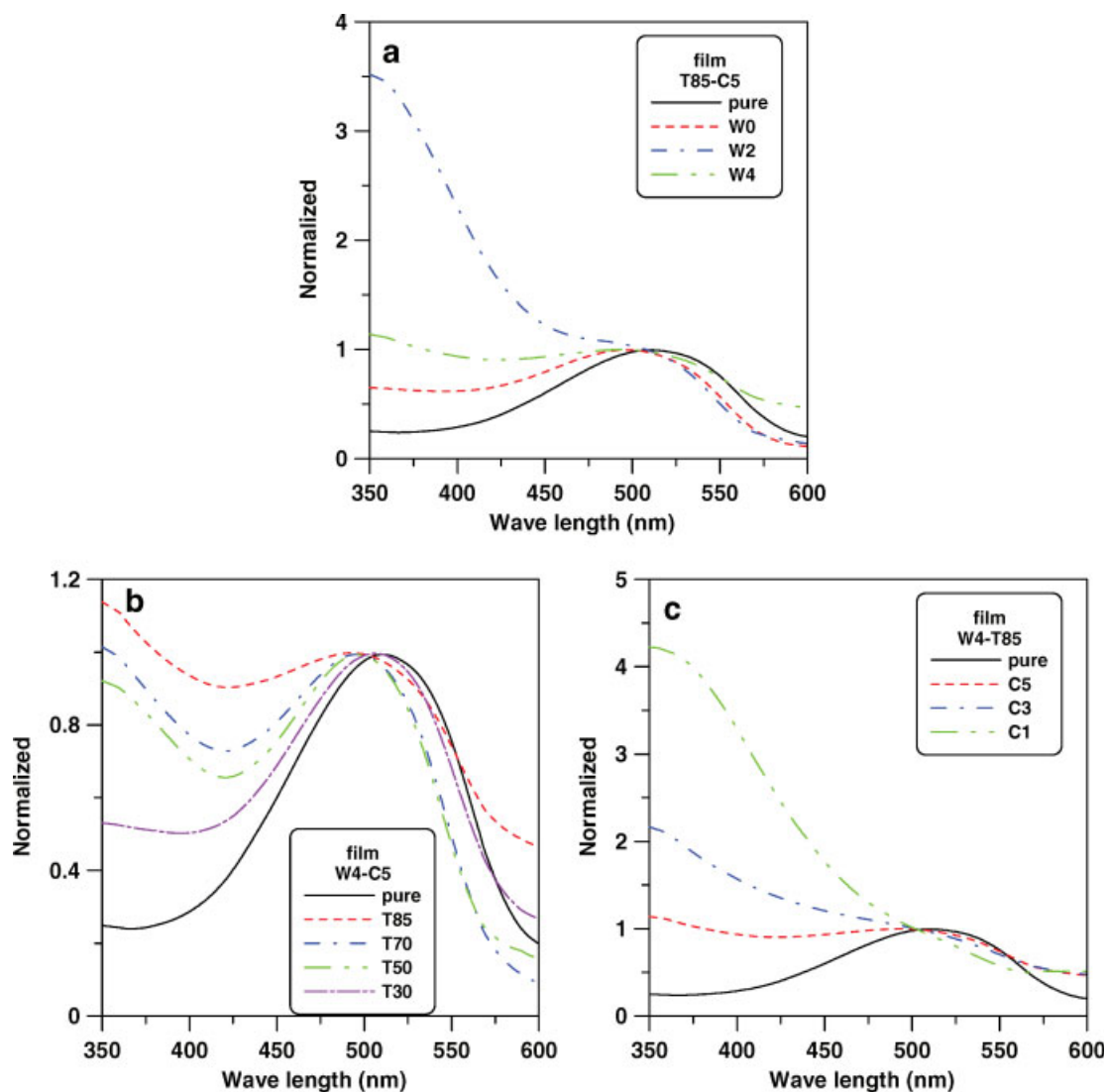


Figure 4. UV-vis absorption of MEH-PPV, TIP in 2-CP, and MEH-PPV/TIP(titania) hybrids in solid state. It was normalized based on λ_{\max} of MEH-PPV. Hybrids with different (a) water amount, (b) TIP amount, and (c) solution concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lar aggregated coiled MEH-PPV chains absorbed energy. Since the energy band gaps of ordered aggregated coiled chains were lower, the absorbed energy from free or irregular aggregated coiled chains had a tendency to be transferred to these lower band gap steps, resulting in lower energy light emission, and thus a redshift. A mechanism had been proposed in which these ordered aggregations worked as funnels for excitation energy by means of a continuous resonance energy transfer from the single-chromophore excitons of disordered chains.³⁵ Although the extent of ordered arrangement was minor, the

funnel effect enhanced the energy transfer and dominated the nature of the PL emission. In another scenario, the emitted energy from the free or irregular aggregated coiled chains was absorbed and then emitted by the ordered aggregated chains. This would also result in a redshift. Therefore, the PL emission of almost all the hybrids in the solution state had a redshift with respect to pure MEH-PPV. The schematic energy band gap diagram of pure MEH-PPV and the hybrid were depicted in Scheme 2.

Effect of the water content: Figure 5(a) shows the PL intensities of hybrids with different

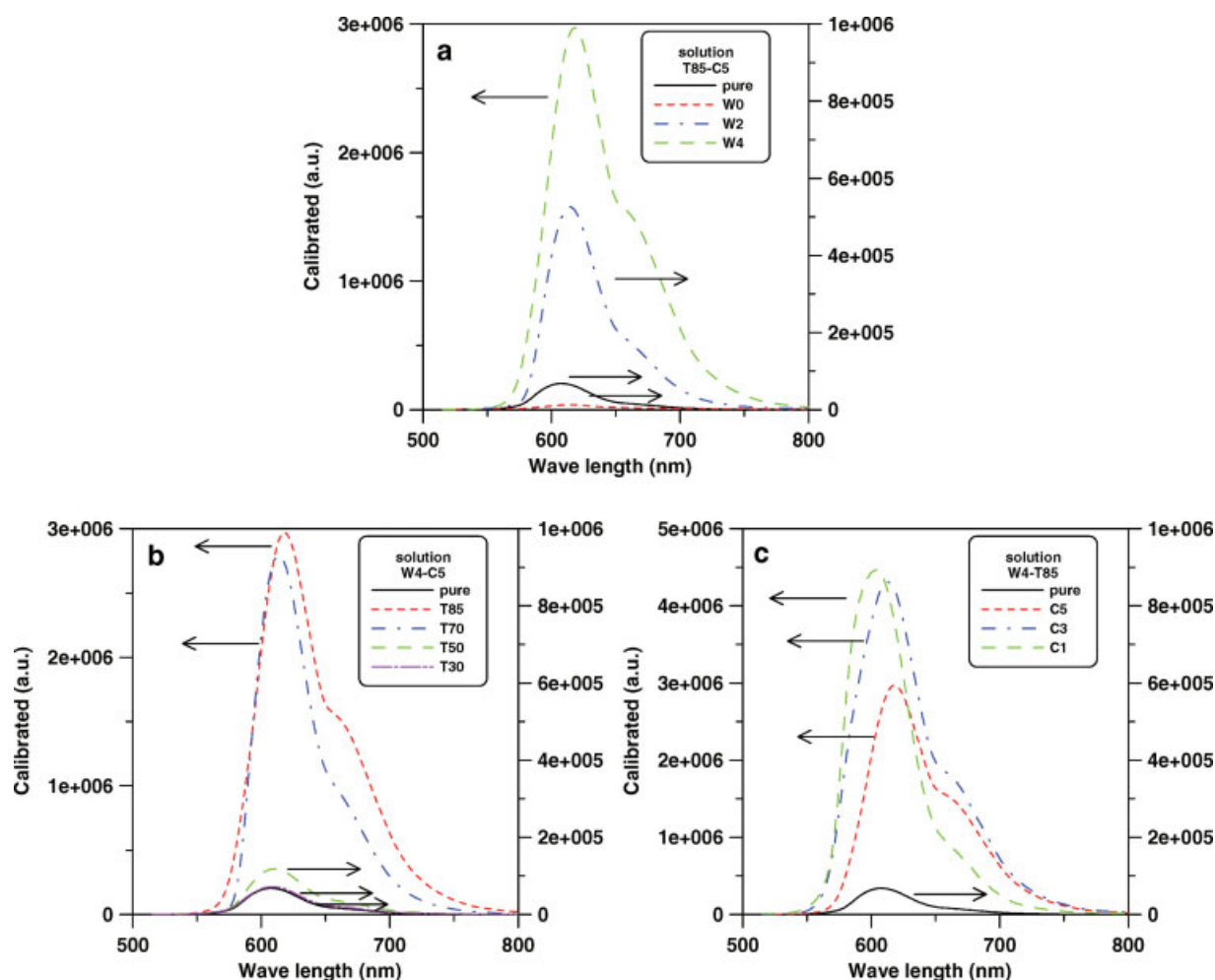


Figure 5. PL emission of MEH-PPV and MEH-PPV/TIP(titania) hybrids in solution state. It had been calibrated based on the same amount of MEH-PPV. Hybrids with different (a) water amount, (b) TIP amount, and (c) solution concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water content. Other than W0-T85-C5, the other three hybrids all had higher PL intensities than pure MEH-PPV. The apparent decrease in the PL intensity of W0-T85-C5 was attributed to three factors. First of all, the electron distribution and conformation of the MEH-PPV had been altered significantly after the interaction with TIP, which caused the emission behavior of MEH-PPV to be changed. Second, the aggregation of the MEH-PPV always had the effect of decreasing the quantum yield.^{33,36–38} Third, the excited electron–hole pairs were mostly separated, with the separated electrons being transferred to the TIP before recombination. The latter two effects are shortcomings when it comes to the application of MEH-PPV in PLED; but, in another aspect, they become advantages when it comes to application in solar cell.

When the amount of water used in the synthesis was increased, as in the cases of W2-T85-C5 and W4-T85-C5, the titania particles apparently increased in size, with the result that the interaction of TIP and MEH-PPV weakened gradually. Thereafter, it promoted the recovery of electron distribution and conformation of MEH-PPV. Hence, the PL emission of MEH-PPV reappeared. It was even enhanced by the multiple absorptions and emissions in the hybrid solutions. In a turbid solution, the path of light would be lengthened due to the multiple collisions with particles. Also, since the path of the incident light became longer in a solution, it created further opportunities for the multiple light absorption of MEH-PPV. Therefore, the probability for multiple MEH-PPV emission was also increased, significantly enhancing the PL intensity.

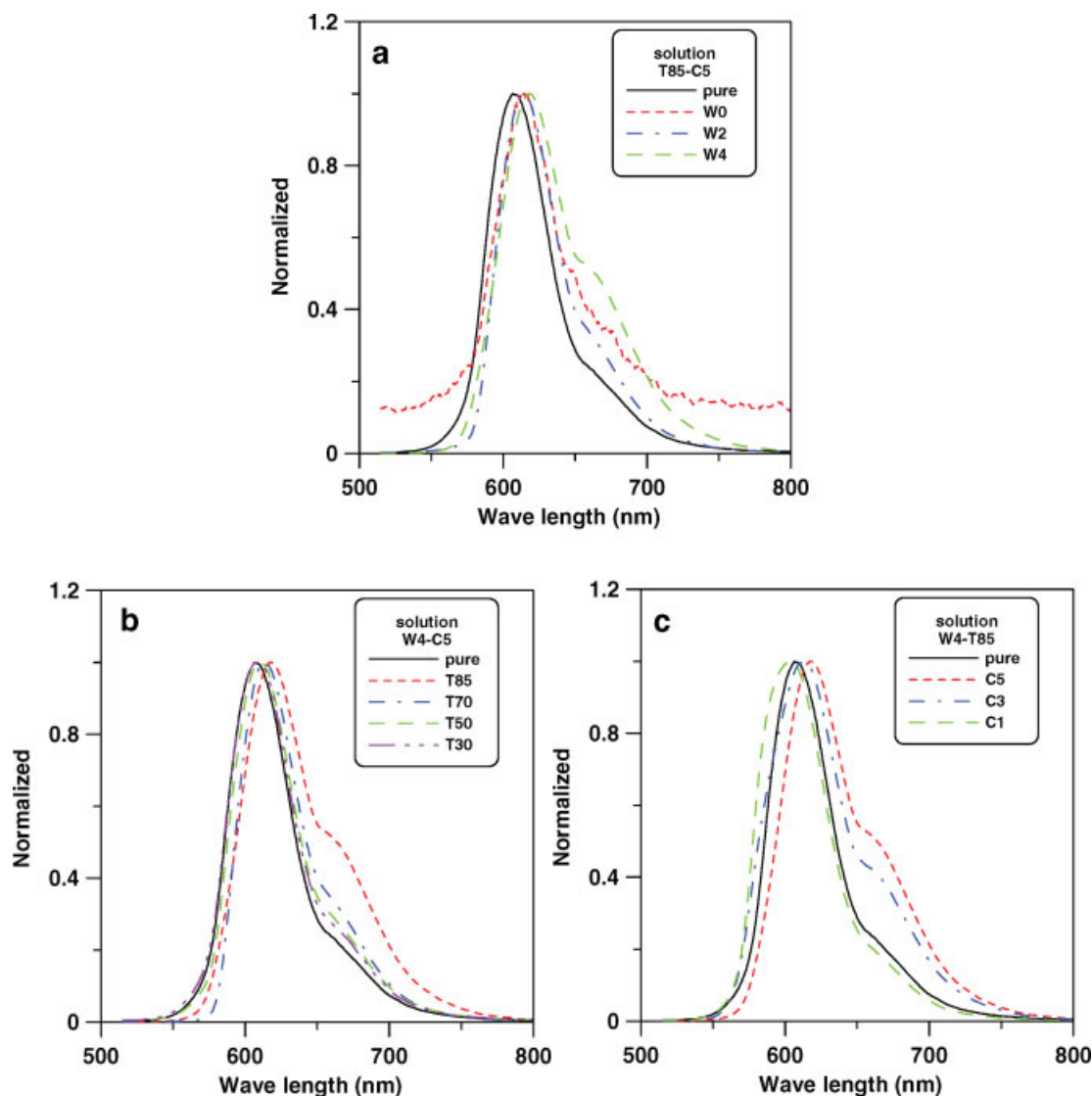
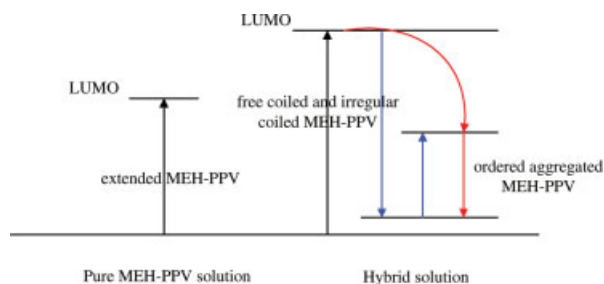


Figure 6. PL emission of MEH-PPV and MEH-PPV/TIP(titania) hybrids in solution state. It was the normalized spectra of Figure 5. Hybrids with different (a) water amount, (b) TIP amount, and (c) solution concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2. The energy band gap diagram of pure MEH-PPV and the hybrid in solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6(a) shows that W4-T85-C5 had higher degree of aggregation of coiled chains than W0-T85-C5 and W2-T85-C5. It seemed to suggest that the larger amount of water promoted the growth of titania and phase separation. The existence of the large amount of titania induced the aggregation of MEH-PPV chains. For all the hybrids, owing to the existence of heterogeneous titania in the MEH-PPV solution, the aggregation of MEH-PPV chains, including irregular (major) and ordered (minor) aggregation, was increased, resulting in a redshift PL compared to pure MEH-PPV.

Effect of the TIP content: Figure 5(b) shows the effect of the TIP content on the PL intensity. The proportion of titania would be higher if more TIP were fed into the hybrid solution. It was thus predictable that the PL intensity would increase as the amount of titania increased, as the effects of multiple absorptions and emissions of MEH-PPV were enhanced.

Figure 6(b) shows the effect of the TIP content on the degree of aggregation of the MEH-PPV coiled chains. As the amount of TIP used was increased, it was believed that the conversion of TIP also increased and that phase separation would occur, which would induce the aggregation of coiled MEH-PPV chains and result in further redshift in the PL emission compared to pure MEH-PPV.

Effect of the solution concentration: Figure 5(c) shows the effect of the solution concentration on the PL intensity. It could be seen that the PL intensity increased with decreasing solution concentration. The loss in quantum yield was more significant for higher concentration hybrids. In other words, the PL intensity for PL polymer was higher in extended form (dilute solution) than in aggregated form (concentrated solution).

Figure 6(c) shows the effect of solution concentration on the degree of aggregation of MEH-PPV coiled chains. It can be seen that the degree of aggregation of coiled chains decreased with decreasing concentration as the degree of redshift diminished with decreasing concentration. For W4-T85-C1, a blueshift was even observed. This seemed to suggest that the MEH-PPV chains were relatively extended at low [0.1% (w/v)] concentration and that the interactions between MEH-PPV and TIP were stronger. Thus, the ordered aggregation of the MEH-PPV chains was hindered by the interacted TIP, and no lower energy band gaps were available as an intermediate step. Therefore, a blueshift in the PL emission relative to pure MEH-PPV resulted. Here, it should be emphasized that while strong interaction between MEH-PPV and TIP would interrupt the ordered aggregation of MEH-PPV, moderate interaction would be beneficial as the MEH-PPV chains were pulled closer together to the heterogeneous points, TIP (or titania).

PL in Film

Figure 7 shows the PL spectra in solid state for all the hybrids. It had been calibrated by using

the same amount of MEH-PPV and the same film thickness. Figure 8 was the normalized PL spectra of Figure 7 based on the λ_{\max} of MEH-PPV. Interestingly, all the hybrids exhibited blueshift and the relative intensity of third emission peak became barely discernible. This implied that the degree of aggregation of coiled chains for all the hybrids had decreased.

Disaggregation of MEH-PPV by Spinning. The films used for the solid state PL measurement were prepared by spinning the hybrid solutions onto cleaned ITO glasses. It was believed that the aggregation of MEH-PPV chains could be destroyed or decreased by the spinning process. The reasoning was that MEH-PPV had interaction with TIP, and the TIP(titania) could be easily spread out by the centrifugal force during the spinning. This would cause the aggregation of coiled MEH-PPV chains to also be spread out evenly on the ITO glasses. In the case where the interaction was low, the aggregation of coiled MEH-PPV chains would also be destroyed or interrupted by the nearby titania. Moreover, the concentrations of all the hybrids were within the range of the loose aggregation region. In this region, the aggregation and morphology depended a lot on the spin rate and could be easily controlled by varying the centrifugal force.²⁸ Therefore, once the aggregation of coiled chains in the hybrids was broken up by spinning, almost no lower energy band gaps remained to serve as a step and the emitting light would be blueshifted. The schematic energy band gap diagram of pure MEH-PPV and the hybrid were shown in Scheme 3:

Effect of the water content: Figure 7(a) shows the PL intensity in film with respect to the amount of water used in the synthesis. Two points should be noted. First, the PL intensities of the hybrid films were much lower than pure MEH-PPV. This indicated that the separation efficiency of electron-hole pairs in the hybrid films was high. In other words, the quenching effect³⁹ was significant in hybrid films. Second, the PL intensity increased with the water content. Looking at the external appearance of the hybrid films, one can see that the hybrids with lower water content, W0-T85-C5 and W2-T85-C5, appeared transparent whereas the hybrids with higher water content, such as W4-T85-C5, appeared turbid. The reason W4-T85-C5 had the largest PL intensity among the hybrids in Figure 7(a) was attributed to the effect of multiple

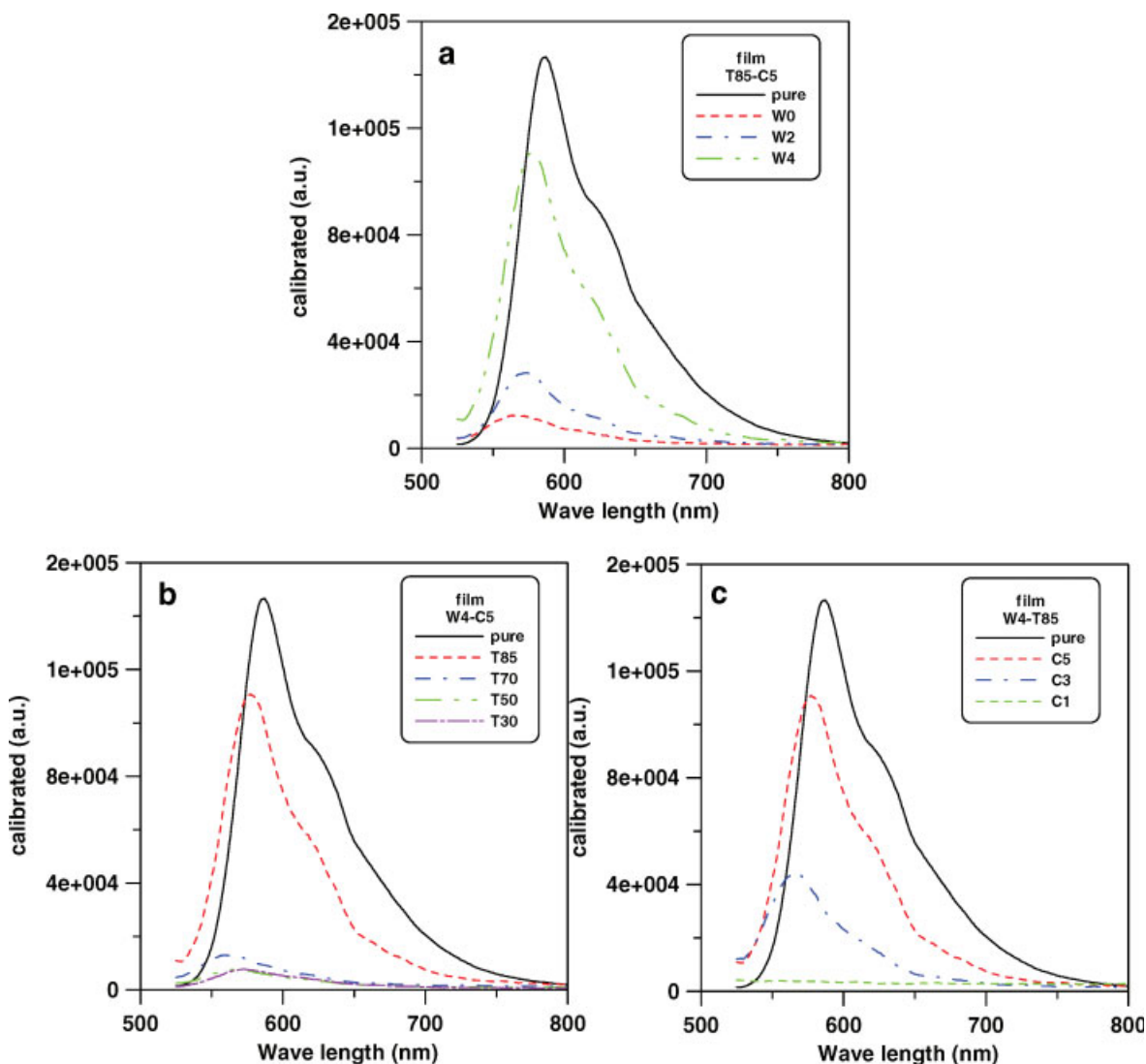


Figure 7. PL emission of MEH-PPV and MEH-PPV/TIP(titania) hybrids in solid state. It had been calibrated based on the same amount of MEH-PPV and film thickness. Hybrids with different (a) water amount, (b) TIP amount, and (c) solution concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

absorptions and emissions of MEH-PPV. Even so, the PL intensity of W4-T85-C5 was lower than pure MEH-PPV. This implied that the PL quenching effect was more significant than the effect of multiple absorptions and emissions of MEH-PPV for W4-T85-C5.

Figure 8(a) shows the effect of water content on the degree of aggregation of MEH-PPV coiled chains. The degree of aggregation of coiled chains was lower than pure MEH-PPV for all the hybrid films. Upon spinning, the possibility of ordered aggregation of MEH-PPV chains diminished significantly in the presence of TIP

(titania). When the water content increased, the degree of phase separation increased and the aggregation of MEH-PPV coiled chains became relatively easier during the spinning. However, the degree of aggregation of coiled chains was still lower than pure MEH-PPV.

Effect of TIP content: Figure 7(b) shows the PL intensity in the films with respect to the TIP content. From Figure 7(b), the PL intensities of all the hybrid films were lower than pure MEH-PPV. The intensity of W4-T85-C5 was obviously higher than the other three hybrids. This was due to the fact that the W4-T85-C5 film had

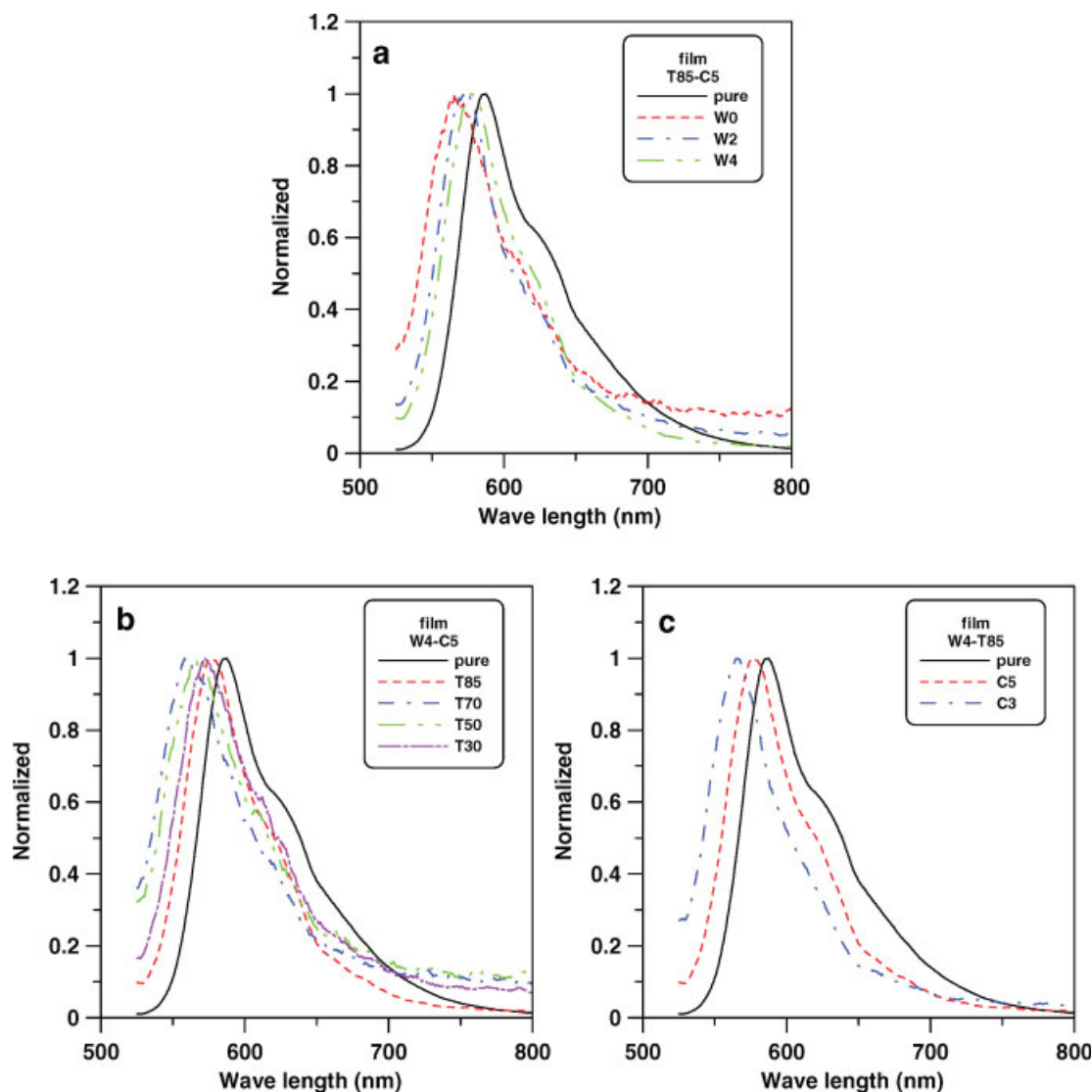
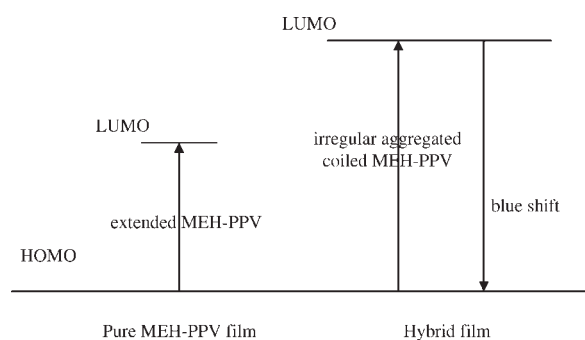


Figure 8. PL emission of MEH-PPV and MEH-PPV/TIP(titania) hybrids in solid state. It was the normalized spectra of Figure 7. Hybrids with different (a) water amount, (b) TIP amount, and (c) solution concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 3. The energy band gap diagram of pure MEH-PPV and the hybrid in film.

visible phase separation but the other three hybrids were transparent films. Certainly, the effect of multiple absorptions and emissions of MEH-PPV had scaled up its intensity.

Figure 8(b) shows the effect of TIP content on the degree of aggregation of MEH-PPV coiled chains. It could be divided into two categories. When the hybrid films were transparent, the degree of aggregation of coiled chains decreased with the increase in TIP content. It was suggested that higher TIP content, up to 89.2 wt %, would hinder the aggregation of MEH-PPV chains more obviously upon spinning as the distribution of tita-

nia in MEH-PPV was homogeneous. On the other hand, once the TIP content reached 95.2 wt %, phase separation occurred. The degree of aggregation of the MEH-PPV coiled chains largely increased. From another point of view, this also indicated that the PL behavior of the hybrid would recover to that of pure MEH-PPV if the hybrid had an apparent phase separation.

Effect of solution concentration: Figure 7(c) shows the influence of different solution concentration on the PL intensity of the films. Figure 7(c) reveals that the PL intensity of the hybrid films decreased with decreasing concentration. This was different from the case of the hybrids in the solution state in Figure 5(c). In solutions, the aggregation phenomenon was dominant and the quantum yield decreased with an increase in the concentration. However, in the case of films, the aggregation phenomenon had a minor or insignificant effect. In this case, the interaction of TIP(titania) and MEH-PPV became important. For lower concentration, the interaction between TIP(titania) and MEH-PPV increased, which confined the PL behavior of MEH-PPV. Hence, the PL intensity decreased with a decrease in concentration.

Figure 8(c) shows the effect of solution concentration on the degree of aggregation of MEH-PPV coiled chains. The characteristic peak of the PL spectrum for W4-T85-C1 could not be observed because its intensity was rather low. Other than the fact that the PL behavior of MEH-PPV was confined by the strong interaction of MEH-PPV and TIP(titania), as mentioned earlier, it could also be due to the fact that the concentration and viscosity of W4-T85-C1 were too low and that the film thickness was too thin at a spin rate of 3000 rpm. As for the other hybrid films, since the interaction of MEH-PPV and TIP(titania) increased with decreasing solution concentration, this indicated that the degree of aggregation of the coiled chains decreased with decreasing solution concentration and the PL peak would shift to a lower wave length (blueshift).

CONCLUSIONS

A simple *in situ* sol-gel reaction for the preparation of MEH-PPV/titania(TIP) hybrid was proposed in this study. The use of a suitable solvent, 2-CP, and the essential existence of

interaction between MEH-PPV and TIP were the keys to the success of this method.

From the results of UV-vis absorption in solutions, it can be seen that almost all the hybrids, except for W4-T30-C5, exhibited a slight blueshift compared to pure MEH-PPV because of the existence of heterogeneous point (TIP or titania), coiled conformation, and irregular aggregation of MEH-PPV. Also, from the absorption in films, the blueshift became more obvious.

The PL behavior of almost all the hybrids, except for W4-T85-C1, exhibited redshift in the solution state compared to pure MEH-PPV. This implied that the presence of some lower energy steps in these hybrids. The lower energy step resulted from the aggregation of coiled MEH-PPV chains. It served as an intermediate step in facilitating the energy transfer. The absorbed higher energy had a tendency to be transferred to a lower energy step, and to be emitted as a redshifted light subsequently. Noticeably, the PL spectra of all the hybrids in solid state exhibited blueshift compared to pure MEH-PPV. This was attributed to the disaggregation of MEH-PPV chains upon spinning. This study provided a new approach to synthesize MEH-PPV/titania nanohybrids with homogenous morphology and adjustable optical properties.

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