



## Investigation of the optical properties of polyfluorene/ZnO nanocomposites

J.P. Zou<sup>a,b</sup>, P. Le Rendu<sup>a</sup>, I. Musa<sup>a</sup>, S.H. Yang<sup>c</sup>, Y. Dan<sup>b</sup>, C. Ton That<sup>d</sup>, T.P. Nguyen<sup>a,\*</sup>

<sup>a</sup> Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, BP32229, 44322 Nantes, France

<sup>b</sup> State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University, Chengdu, 610065, China

<sup>c</sup> Institute of Lighting and Energy Photonics, National Chiao Tung University, Tainan County 71150, Taiwan

<sup>d</sup> Department of Physics and Advanced Materials, University of Technology Sydney, PO Box 123, NSW 2007, Australia

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### ABSTRACT

Polyfluorene (PF) and its derivatives are very promising candidates for organic light emitting diodes (OLEDs) in lighting applications because of their high photoluminescence and electroluminescence efficiencies. Recent investigations of potential materials for OLEDs have shown that introducing n-type inorganic nanoparticles into conjugated polymers is efficient to produce stable and high performance devices. In this study, composite thin films made by incorporation of zinc oxide (ZnO) nanoparticles into a PF derivative have been prepared and their optical properties have been investigated.

The prepared thin films were stored in different media (in air, in vacuum, in the dark or exposed to light) in order to study environmental influences on the material stability. Analysis of spectral data obtained from infrared (IR), Raman, UV–vis, and photoluminescence (PL) measurements shows a large enhancement in luminescence for polymer nanocomposites while using high nanoparticle concentrations (within a limit of 10% ZnO). Time-resolved PL performed on those nanocomposite films corroborated the above result: it indicated that the light-emission enhancement can be explained by efficient energy transfer from nanoparticles to the polymer chains and increase of the chain separation distance. In addition, the nanocomposites were found to be more stable than pristine polymer films whatever the storage conditions were used. It was confirmed by IR analysis that incorporation of nanoparticles into polymers prohibited the formation of fluorenyl groups in PF chains, which was identified as the main cause of the degradation of the polymer under photo-oxidation.

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### 1. Introduction

The possibility of employing organic light emitting diodes (OLEDs) has triggered an ever-increasing number of studies aimed at synthesizing  $\pi$ -conjugated polymers that are able to emit light in the visible region and are endowed with long-term spectral stability. Among the wide bandgap  $\pi$ -conjugated polymers, polyfluorene (PF) derivatives can be considered as one of the most promising materials, owing to their high photoluminescence quantum yields [1–3], good hole mobility [4,5], and ease of functionalization at the C-9 position with two alkyl groups that generally warrants good solubility and processability of the corresponding macromolecules. Moreover, the tetrahedral structure of the C-9 atom guarantees efficient polymer backbone isolation in the solid state by forcing the functional groups to assume an orthogonal disposition with respect to the fluorene plane.

However, the degradation of polyfluorene derivatives limits their device lifetime. Many efforts have been made to impede the degradation of polymers, such as surface coating or addition of organic

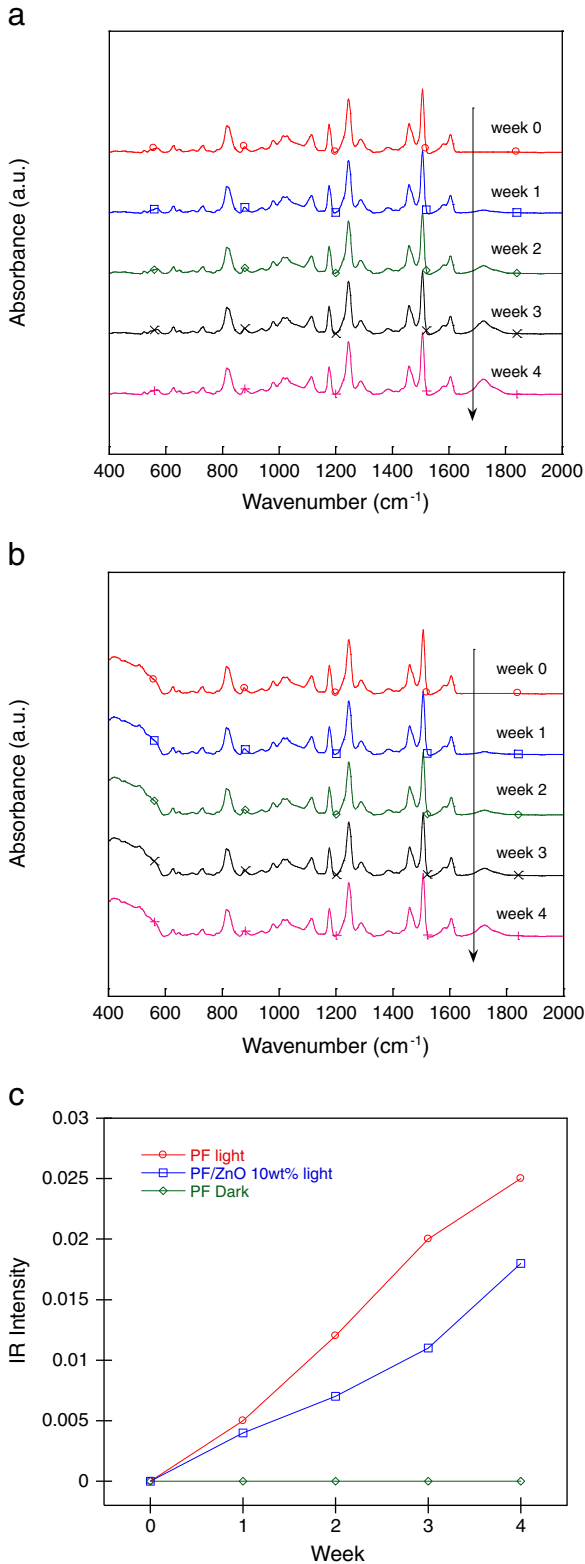
and inorganic stabilizers [6–11]. Organic stabilizer additives are easy to lose and less effective for polymer matrix. Some of the surface coatings are easily peeled off and hence lose their protective effects. On the other hand, incorporating inorganic nanoparticles into conjugated polymer matrices might solve the problems. One can take advantages of the beneficial properties of both materials: good optoelectronic properties of conjugated polymers and high electron mobility of inorganic semiconductors [12]. Optical properties can be changed after incorporating inorganic nanoparticles into conjugated polymers [13–17]. It is proved that introducing the n-type inorganic nanoparticles into conjugated polymers is an effective way to develop polymer-based photovoltaic devices with high efficiency [18–20].

Zinc oxide (ZnO), a well-known n-type inorganic material, possesses strong absorption ability of UV light. It is considered to stabilize polymer matrix from environmental degradation, to increase the mechanical property, and to prolong the lifetime of materials [21,22]. In this paper, optical properties of PF/ZnO nanocomposites as well as their photo and air oxidation process were investigated. The composite thin films were stored under four different conditions; in the dark under air/vacuum, and in the light under air/vacuum. Many spectroscopic techniques, such as the Raman, infrared (IR), photoluminescence (PL), time-resolved photoluminescence (TRPL), and

\* Corresponding author.

E-mail address: [nguyen@cnrs-ilmn.fr](mailto:nguyen@cnrs-ilmn.fr) (T.P. Nguyen).





**Fig. 3.** IR spectra of (a) PF-oxe and (b) PF-oxe/ZnO (10 wt.%) exposed to light in air during different times, (c) variation of IR band intensity at 1730 cm<sup>-1</sup> as a function of time.

band around 1600 cm<sup>-1</sup>. The variation of band intensity at 1730 cm<sup>-1</sup> as a function of time was depicted in Fig. 3c. It means that ZnO possesses capability to prohibit the formation of C=O groups. On the other hand, no apparent C=O band could be found for PF-oxe in the dark after 4 weeks, as shown in Fig. 3c. The above results indicate that

air oxidation (without light exposure) of PF-oxe is not observable, while photo-oxidation of PF-oxe is more significant. Furthermore, ZnO may play a key role of shielding light exposure that prevents photo-oxidation of conjugated polymers in the organic/inorganic hybrid nanocomposites.

### 3.3. Time-resolved photoluminescence spectra

To verify the possible energy transfer from ZnO to PF-oxe, time-resolved PL and the PL decay of composite films were performed at room temperature using an excitation wavelength of 267 nm from a femto-second pulse laser (100 fs, 1 kHz). Indeed, using such a short wavelength, we are able to excite the ZnO nanoparticles since they exhibit optical absorption band at 362 nm (see below). The time-resolved spectra were recorded by a streak camera. Fig. 4 shows the time-resolved PL spectra of pristine PF-oxe and its composites with 1 wt.%, 2 wt.%, 10 wt.%, and 15 wt.% of ZnO nanoparticles. It is seen that PL emission is significantly enhanced by adding ZnO nanoparticles into PF-oxe polymer matrix, and a maximum PL emission intensity is reached by adding 10 wt.% of ZnO. By increasing ZnO with a concentration higher than 15%, the PL emission is somewhat quenched and PL intensity is decreased.

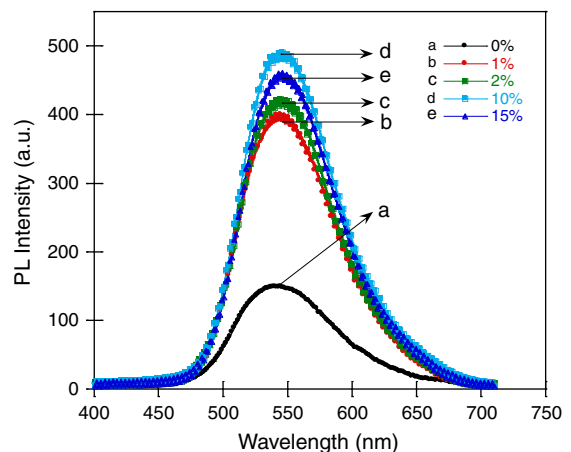
The PL decay curves of the previous films are shown in Fig. 5. The PL decay time could be fitted using a bi-exponential decay function. The fitting curves (solid lines) in Fig. 5 are consistent with the experimental decay curves in the range 0–1 ns. The decaying photoexcited population ( $n$ ) can be expressed by:

$$n = n_1 + n_2$$

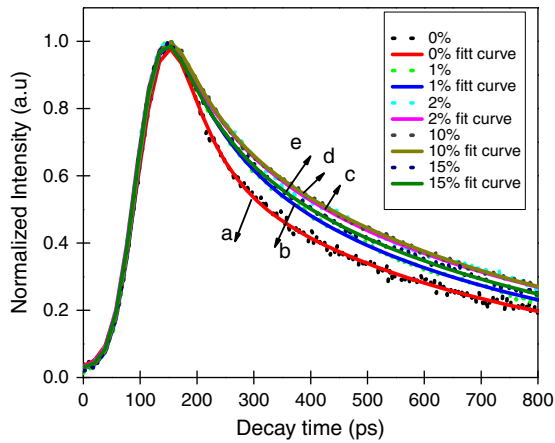
with  $n_1 = A_1 e^{-t/\tau_1}$  and  $n_2 = A_2 e^{-t/\tau_2}$  where  $n_1$  and  $n_2$  are the photoexcited populations,  $A_1$ ,  $A_2$  are the pre-exponential factors proportional to  $n_1$  and  $n_2$  and  $\tau_1$ ,  $\tau_2$  are the decay time constants. The decay time  $\tau_2$  for the pristine PF-oxe and the composite containing 1, 2, 10 and 15 wt.% ZnO are 490, 535, 583, 569, and 549 ps, respectively. Longer PL decay is observed for PF-oxe/ZnO composites compared with pristine PF-oxe, implying stronger PL emission for composite films. The result is in accordance with time-resolved PL experiments.

### 3.4. PL spectra

Fig. 6 shows the PL spectra of pristine PF-oxe and PF-oxe/ZnO nanocomposites with different ZnO concentrations. The spectra were recorded using an excitation wavelength of 400 nm. The main emission band of PF-oxe is located at 554 nm, referring to green emission. Compared to the spectra obtained in Fig. 4, the enhancement

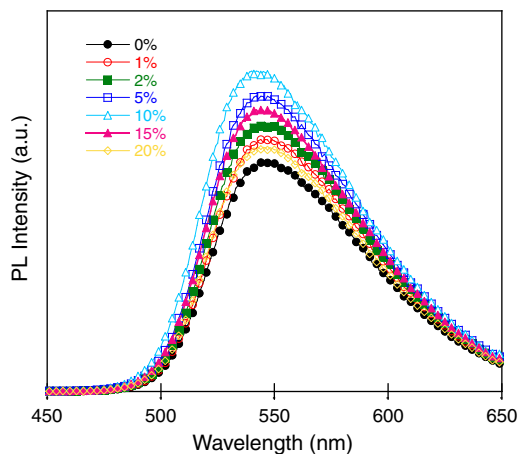


**Fig. 4.** Time-resolved PL spectra of PF-oxe/ZnO with different ZnO concentrations (excited at 267 nm).

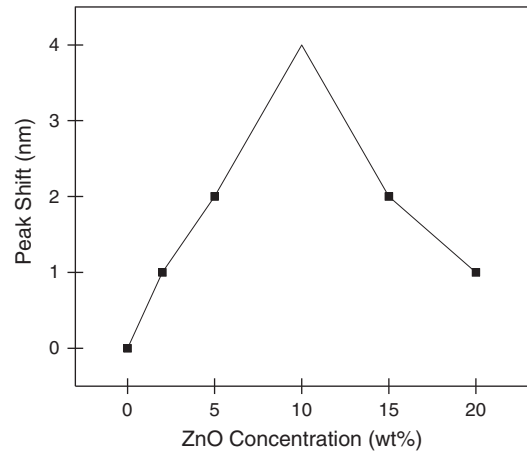


**Fig. 5.** PL decay time of PF-oxe/ZnO with different ZnO concentrations. The analyzed samples are the same as in Fig. 4. The solid lines depict the result of fitting curves using bi-exponential function.

in intensity of composite spectra is lower since ZnO nanoparticles would be weakly involved, and the energy transfer from these particles to the polymer matrix is low. It can be seen that the main emission band is gradually enhanced and blue shifted as ZnO concentration is increased. A maximum emission is found for PF-oxe/ZnO nanocomposite with 10 wt.% of ZnO. The change in PL emissive behavior can be interpreted in two ways: charge trapping effect and chain separation. The n-type character of ZnO suggests that the material can trap electrons and allows more holes to recombine through the interface of PF-oxe and ZnO. The probability of exciton formation inside composite layer is increased and thus enhanced luminescent properties. A maximum PL emission is reached with the addition of 10 wt.% ZnO nanoparticles. By adding too much ZnO, most electrons are mainly blocked around the surface of ZnO and restricted the recombination population for the PF-oxe/ZnO composite system. On the other hand, the blue shift in the luminescence spectrum is associated with changes in the conjugation length [27]. When ZnO is incorporated into PF-oxe, these ZnO nanoparticles would insert into polymer matrix and thus PF-oxe polymer chains will be segregated. As a consequence, the conjugation length of PF-oxe is reduced and a blue shift in PL spectra is observed. Fig. 7 depicts the variation of peak shift in PL spectrum as a function of ZnO concentration. It is seen that a maximum blue shift is observed with adding 10 wt.% of ZnO nanoparticles. The blue shift of the composite is decreased when adding more ZnO (>10 wt.%) to the polymer film, and this can be



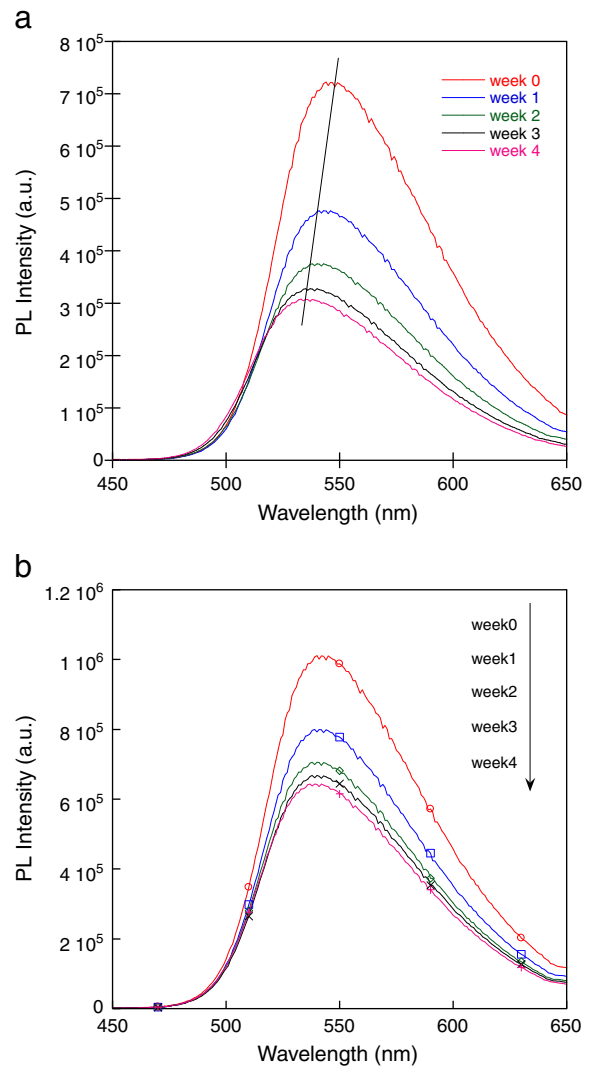
**Fig. 6.** PL spectra of PF-oxe/ZnO with different ZnO concentrations (excited at 400 nm).



**Fig. 7.** Variations of the peak shift of the PL spectrum as a function of ZnO concentration.

explained by the formation of nanoparticle aggregations that polymer chains gather together again. A similar result can be found in the previous literature [17].

Fig. 8a and b shows PL spectra of PF-oxe and PF-oxe/ZnO respectively, under light exposure for different times. Both spectra



**Fig. 8.** PL of (a) PF-oxe and (b) PF-oxe/ZnO (10 wt.%) exposed to light in air during different times.

show a gradual decrease in PL intensity with increasing exposure time. It should be noted that PL of pristine PF-oxe also shows a gradual blue shift with increasing exposure time, while PF-oxe/ZnO nanocomposite does not. Furthermore, PF-oxe/ZnO shows a slower decrease in PL intensity than that of pristine PF-oxe. Here again the incorporation of ZnO nanoparticles prohibits the degradation of polymer chains. In order to explore the degradation process of samples, PL intensity ratio  $L/L_0$  of samples as a function of time in different experimental conditions is estimated and drawn in Fig. 9a, b, and c. Here  $L_0$  represents the original PL intensity of fresh sample, while  $L$  is recorded at a given time. In Fig. 9a,  $L/L_0$  ratio of pure PF-oxe decreases fast in air under light exposure. Furthermore, those PF-oxe/ZnO nanocomposites possess better retention rate of PL intensity than pure PF-oxe. Besides, we noticed that adding too much ZnO with concentration higher than 20% showed no significant effect on suppression of photo-oxidation of PF-oxe. Sims et al. [28] also reported that the PL intensity of PF derivative decreased during photo-oxidation.

In most cases, pure PF-oxe degrades very fast with time. However, it shows a slower decreasing rate in PL intensity when exposed to light under vacuum. The phenomenon can be explained by the photo-oxidation process of polymers. When polymers are exposed to light, the polymer chains would absorb light energy and produce the free radicals, as shown in Scheme 2. The free radicals are highly reactive and break the polymer chains rapidly with the presence of oxygen. In the vacuum condition, much less oxygen molecules exist in the system and photo-oxidation caused by free radicals is decreased. The hypothesis is verified in Fig. 9b and c that shows  $L/L_0$  ratio of PF-oxe/ZnO nanocomposites stored in the dark and under vacuum, respectively. It is seen that PL intensity of PF-oxe/ZnO nanocomposites decreases very little in the dark, and it is almost unchanged under vacuum. Combining the results of PL, FT-IR and UV absorption experiments, we conclude that oxidation of PF-oxe and PF-oxe/ZnO is highly light dependent, while air oxidation is minor. The organic/inorganic nanocomposites are found to be more stable than pristine polymer films whatever the storage conditions are used.

### 3.5. UV-vis spectra

In order to explore the oxidation process, UV-vis absorption spectra of pristine PF-oxe, ZnO particles and PF-oxe/ZnO nanocomposites were examined and analyzed. The absorption spectrum of ZnO in Fig. 10 presents a weak band at 362 nm, the oxide being transparent. Fig. 11a and b shows the UV-vis spectra of pristine PF-oxe film exposed to light and stored in the dark during different times, respectively. The main absorption band located in the range from 350 to 400  $\text{nm}^{-1}$  is attributed to  $\pi$ - $\pi^*$  transition of PF-oxe main chain. As the polymer chain degrades, the effective conjugated length is decreased and its corresponding absorption band becomes blue shifted. Gong et al. demonstrated that oxygen may react with polymer chains and thus interrupt its conjugated [25]. In this case, the degradation of PF-oxe chains is detected by blue shifted and decreased absorption intensity around 370–380  $\text{nm}^{-1}$ . The result is consistent with PL observation that light exposure in air may accelerate photo-oxidation of PF-oxe films. The result can be explained by the formation of fluorenone units in replace of fluorines along the polymer main chain. The shorter conjugation length is observed by blue shifted absorption band in UV-vis spectra [29]. Meanwhile, PF-oxe films, which were stored in the dark, showed almost unchanged absorption maximum wavelength and intensity, indicating a very slow oxidation process in this case. Turning to Fig. 11c, a similar unchanged absorption band is also found for PF-oxe/ZnO nanocomposite film under light exposure during 4 weeks. Here again the incorporation of ZnO into PF-oxe polymer to prohibit photo-oxidation of composite film is deduced.

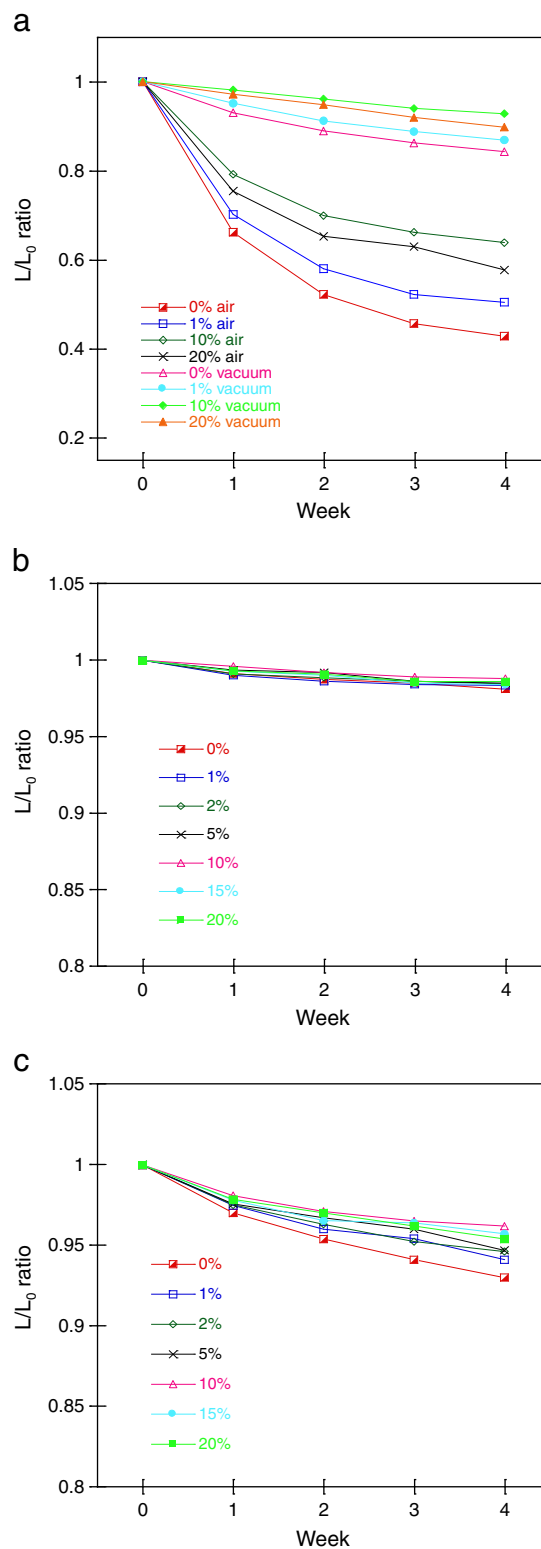


Fig. 9. Variation of PL intensity ratio  $L/L_0$  of PF-oxe/ZnO as a function of time (a) exposed to light, (b) stored in the dark under vacuum, and (c) stored in the dark in air.



Scheme 2. The production of free radical of polymer.

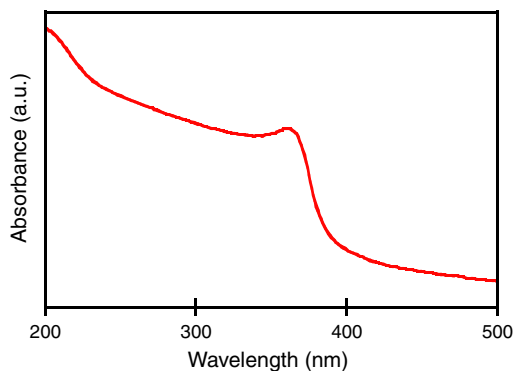


Fig. 10. UV spectrum of ZnO nanoparticles.

### 3.6. Comparison of the stability of PF-oxe/ZnO with other composites

As can be seen in the literature, studies on the degradation of composites made of polymer/inorganic nanoparticles are very limited. Lim et al. reported the degradation of PPV/SiO<sub>2</sub>-Au composite [30]. They found that the rate of photo-oxidation in PPV was drastically reduced by doping films with SiO<sub>2</sub>-Au nanoparticles, while the absorption and photoluminescence spectra varied slightly between pristine PPV and PPV nanocomposite films. They also suggested that the addition of SiO<sub>2</sub>-Au nanoparticles to conjugated polymers-based optoelectronic devices, along with careful processing techniques and device encapsulation, may result in improved lifetimes. Yang et al. reported the UV stability of PPV/TiO<sub>2</sub> and PPV/SiO<sub>2</sub> composites [31]. In their work, little preliminary elimination in nanocomposite precursors could be found during storage and UV irradiation, especially using TiO<sub>2</sub> nanoparticles. They suggested that Ti-OH groups on the surface of hydrophilic TiO<sub>2</sub> nanoparticles interact with tetrahydrothiophene and reduce elimination reaction of tetrahydrothiophene. These results indicate that the insertion of nanoparticles into the PPV precursor can improve the stability of PPV precursors. Yang et al. also studied stability of the PPV/TiO<sub>2</sub> and PPV/SiO<sub>2</sub> and demonstrated a better photo-stability for PPV/SiO<sub>2</sub> nanocomposites [32]. Beside, Guedri et al. reported lifetime improvement of poly(ethylene naphthalate) covered by ZnO adhesive coatings [33]. A good photo-resistance was performed while coating 200 nm of ZnO layer on top of polymer material. In this work, we demonstrate that PF-oxe undergoes photo-oxidation under light exposure in air, resulting in the formation of C=O bond and reduction of effective conjugated length of PF-oxe main chains. In addition, ZnO can act as light-stabilizers that prohibit further photo-oxidation of PF-oxe/ZnO composite films. The above results gather important implications on the enhancement of lifetime for those conjugated polymers-based optoelectronic devices.

## 4. Conclusion

In this work, optical properties as well as oxidation process of PF-oxe/ZnO nanocomposites were fully investigated. A large luminescent enhancement was obtained for PF-oxe/ZnO nanocomposites when using high nanoparticle concentrations (within a limit of 10% ZnO). The origin of the emission improvement is assigned to the energy transfer from oxide particles to the polymer matrix and its decrease after reaching the limit concentration is explained by the important formation of aggregates. The IR, UV-vis, and PL measurements revealed that the oxidation of PF-oxe highly depends on light exposure. The air oxidation of PF-oxe is slower than its photo-degradation. The composite possesses a better stability than pure PF-oxe whatever the storage conditions used. Among them, the PF-oxe/ZnO (10%) composite films exhibit the best luminescence stability, indicating a potential use for prolonging the lifetime of OLEDs.

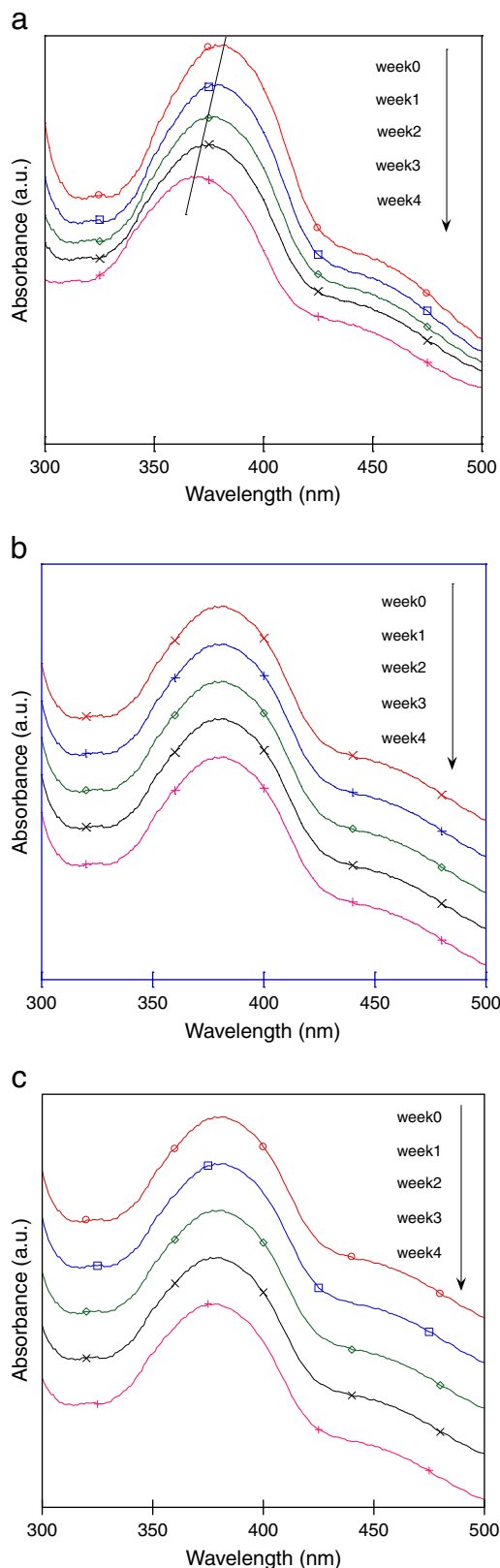


Fig. 11. UV spectra of (a) PF-oxe exposed to light, (b) PF-oxe stored in the dark, and (c) PF-oxe/ZnO (10 wt.%) exposed to light during different times.

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