Hybrid nanocomposites for optical applications

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ABSTRACT

Incorporating inorganic particles into conjugated polymer matrices is an area of current interest in the fields of optoelectronics and solar energy. The hybrid nanocomposites exhibit interesting physical properties thanks to good optical properties of polymers and to high carrier mobility of inorganic semiconductors. A judicious combination of organic/inorganic can therefore provide materials of low cost, ease processing, high stability, with specific electrical and optical properties.

In the present study, we briefly review the composite materials that have been successfully utilized in the field of optoelectronics and photovoltaic conversion. We shall describe in particular a family of nanocomposites using polyhedral oligomeric silsesquioxane (POSS) of general formula $(RSiO_{3/2})n$ where R is an organic group as a core. The composites are made by grafting functional polymer groups to the core, which allows the control of their optical properties. Such composites have high mechanical resistance and stability because of the special structure of the core. For illustration, we present a study of polyfluorene (PF)/POSS materials used as an active layer in organic light emitting diodes, with improved performance as compared to those using polymer only, and we discuss the role of the particles in the transport and emission processes in the devices studied.

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1. Introduction

Hybrid organic–inorganic nanocomposites are a new class of materials, which has promising potential applications in optoelectronic and photovoltaic fields. Indeed, the inorganic part contributes to the stability of materials while the organic part – usually polymers – is chosen for its functional chemical properties. The combination of their characteristics can provide high performance materials, which further can be used as active components in devices by exploiting the specific properties of the composites. For optical applications, such materials have been used in numerous fields of applications. The most recent developments in organic semiconductors have encouraged researchers to incorporate nanocomposites in devices because of their good electrical and optical properties, which contribute to improve the performance of devices studied. The choice of the components depends on the properties, which are intentionally favored for the applications. As organic semiconductors are developed for electronic devices such as light emitting diodes (LEDs) and photovoltaic cells, which have low weight and low cost, most of them are conjugated polymers, whose optical gap can be controlled by synthesis. They display interesting optoelectronic properties, which will be principally used for applications. Inorganic materials are generally conventional semiconductors or oxides. Nanocomposites are obtained either by dispersing inorganic nanoparticles in a polymer matrix (organic–inorganic or OI systems) or by confining the polymer in an inorganic template (inorganic–organic or IO systems) [1]. In both cases, the optical properties of the polymer are expected to be changed, and will be exploited for applications.

In this paper, we are mainly interested on nanocomposites, which are used for optoelectronic applications, and are made by incorporating nanoparticles in a conjugated polymer matrix. First, we shortly review the different materials used for such composites, their fabrication process, and their general properties. Next, we consider nanocomposites using polyhedral oligomeric silsesquioxanes (POSS) of general formula $(RSiO_{3/2})n$ where R is an organic group. For illustration, we present results obtained in devices made of POSS and a polyfluorene (PF) derivative, and we discuss the possible roles of the nanoparticles in the improvement of performance of the devices in comparison to those using the polymer alone.

2. Hybrid conjugated polymer–inorganic composites

Conjugated polymers are widely used in organic electronic devices because of their semiconducting properties. Indeed, the

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conjugated structure with alternating single and double bonds provides a conducting pathway along the backbone through the π orbital overlapping, and the electrical conductivity of conjugated polymers is comparable to that of undoped conventional semi-conductors. Although it is possible to dope these polymers in a similar way to that used in silicon technology to obtain high and controllable conductivity, these polymers are rarely used when doped because of their instability upon doping. Instead, when they are deposited as very thin films (of ∼100 nm thick) in devices, a reasonable applied voltage can produce a current of several mAs, which is enough to run these devices. Processable conjugated polymers found numerous applications including non-linear optical devices [2,3], transistors [4,5], photovoltaic cells [6,7], and light emitting diodes [8,9]. The most studied conjugated polymers are poly(phenylene vinylene) or PPV, poly(*p*-phenylene) or PPP, and polythiophene or PT and their derivatives. These polymers are used for light emitting applications (green for PPV, blue for PPP and red for PT). By using a combination of smart device design and well-controlled synthesis, polymer light emitting diodes (PLEDs) with good color-tunability have been fabricated and several applications such as small display screens have been successfully commercialized. More recently, developments in solution-processed polymer blend cells lead to solar power conversion efficiency of about 3%, making the organic photovoltaic cells very promising for the near future.

One of the main drawbacks of PLEDs is the lack of stability in long-term use. As polymers are sensitive to chemical reactions, many processes in devices can affect the stability of the films: thermal heating, electrical transport, and photo-oxidation. The most common cause of degradation of conjugated polymers has been identified as the formation of keto groups in the backbone by oxidation, which weakens the structure of the material and reduces its performance by quenching the excitons at the defect sites. To remedy this drawback, several strategies have been proposed [10]. Using chemical methods, better syntheses lead to higher quality polymers, which have improved solubility and less sensitive to defect formation. Using physical methods, the properties of the polymer can be improved by adding inorganic nanoparticles to the host material. Most of the inorganic materials are oxides such as TiO_2 [11], SiO_2 [12], ZnO [13] or others [14]. These materials having size in the range of 1–100 nm, are spherical particles and are dispersed in a polymer matrix for obtaining composite. Several semiconducting and luminescent particles such as CdSe [15] or CdS [16] are also used to fabricate nanocomposites for specific applications. Because of the small size, i.e. from 1 to 20 nm, of these particles, which are called quantum dots (QDs), their electrical and, especially, their optical properties are particularly interesting for applications. Indeed, when the particle size decreases, the semiconductor bandgap increases resulting in quantum confinement of electrons. The emission of semiconducting QDs can cover the entire visible spectrum just by varying the particle size. As a result, white OLEDs can be fabricated by using different sizes of QDs mixed together in a polymer matrix [17].

One special structure called silsesquioxane or POSS is used in composites, which are silicon containing organic polymers [18,19]. In POSS units, each silicon atom is bound to one and a half oxygen atoms and to one hydrocarbon group. Composites with specific optical properties are made by grafting functional polymer groups on the silicon atoms of the POSS units. Such composites have a high thermomechanical stability due to the POSS structure and a controlled optical emission due to the functional polymer group.

In the following section, we shall describe a nanocomposite composed of POSS structure units on which are grafted polymer chains of a polyfluorene derivative, which emits a green light. We compare the electrical and optical performance of devices using a pristine polymer and a composite film and we discuss the role of the POSS units in term of performance of the devices.

3. Experimental

POSS is synthesized by the hydrolytic condensation reaction of trichlorosilane described in Ref. [20]. The fabrication of POSS–PF was processed as follows. The polyfluorene derivative was synthesis by Suzuki coupling. The resulting polymer mixture was refluxed at 85 °C for 5 days under a nitrogen atmosphere. Then POSS core was added and refluxed at the same temperature for 48 h. The weight ratio of POSS:PF was 4%, based upon the results obtained in devices using POSS:MEHPPV composites [21]. In fact, this ratio is expected to provide a high brightness of devices without noticeable decrease of the current intensity. After that, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-ylbenzene was then added as an end-capping agent and refluxed at 70 °C for 24 h. The POSS–PF was obtained by pouring the solution into methanol and the mixture was filtered. The POSS–PF was purified by dissolving it in THF and reprecipitating it from methanol twice. The structure of the POSS–PF is shown in Fig. 1.

The POSS–PF powder was dried at 60 °C under vacuum for 24 h then dissolved in toluene with concentration of 10 mg/ml. Nano-composite thin films were obtained by spin coating the solution onto glass or KBr substrates and dried under nitrogen atmosphere before optical measurements.

Devices using the composite as an active layer were fabricated on indium tin oxide (ITO) substrates, which were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1 volume) mixture, toluene, de-ionized water and acetone. A layer of poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) was spin-coated over the ITO film, forming the hole-injection layer. The substrate with the PEDOT:PSS
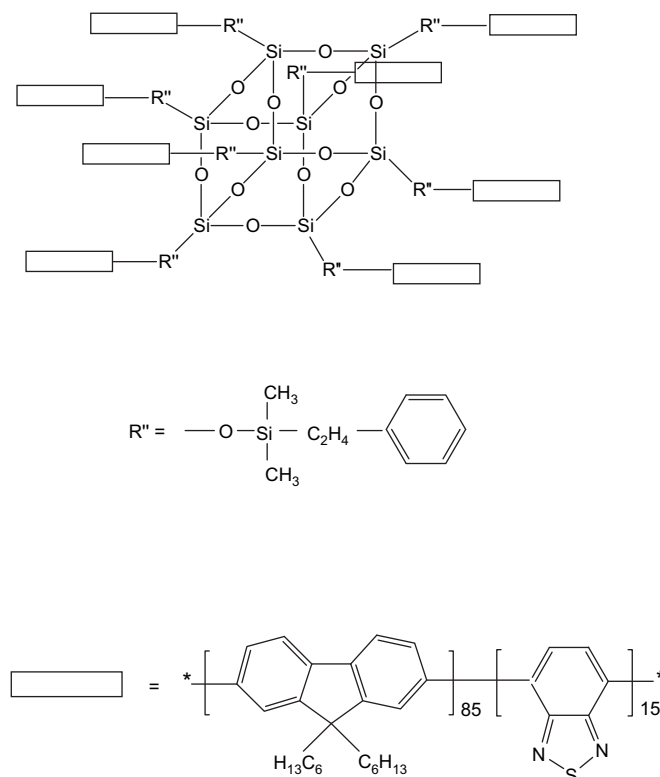

Fig. 1. Synthetic route for POSS–PF.

layer was then dried at 150 °C for 1 h in vacuum to remove all solvent traces. The composite thin film of thickness of 100 nm was then deposited on the PEDOT:PSS film and was dried at 50 °C overnight in vacuum. Finally, 35 nm Ca and 100 nm Al electrodes were deposited through a shadow mask onto the polymer film by thermal evaporation, typically at base pressures in the range of 10^{-8} mbar. The active area of the devices was 4 mm^2.

The UV–vis absorption spectra of the samples were measured with a Cary 5G spectrophotometer and photoluminescence (PL) spectra were obtained with a Fluorolog Horiba spectrophotometer. FT-IR and Raman experiments were performed by using a Bruker Vertex 70 and a Bruker RFS 100 spectrophotometer, respectively. All the measurements were performed at room temperature. Current–voltage characteristics of the diodes were measured using a Keithley 2400 source meter and brightness and efficiency by a Photo Research PR650 spectrometer.

4. Results and discussion

4.1. Optical properties of POSS–PF

Fig. 2 shows the IR spectra of a pristine polymer and a POSS–PF composite thin films. The bands of the polymer have strong intensity and mask those of the POSS, which include the following bands: Si–H stretching (2250 cm^{-1}), Si–O–Si stretching (1120 cm^{-1}) and Si–H bending (860 cm^{-1}) [21]. The onsets of Si–O–Si and Si–C absorption bands, which are usually observed in the range 1000–1080 cm^{-1} and at 1074 cm^{-1}, could not be clearly retrieved. In contrast, we observed the Si–CH$_3$ band at 1253 cm^{-1}, which indicates the presence of POSS–PF bonds via the methyl groups [22,23]. We note also a strong decrease in intensity of the bands at 982, 1120 and 1507 cm^{-1} in the composite film. These bands are assigned to thienyl rings [24] and their changes suggest that the vibrations of the benzothiadiazole monomers could be inhibited by the bulky POSS segments. As these monomers tune the color emission of the PF polymer, and there is no drastic changes in the PL spectra of the composite (see below), we infer that the modifications of the IR components are due to stiffened chain ends caused by the POSS units. Complementary results by Raman scattering spectroscopy are shown in Fig. 3. Only vibrational bands of the polymer could be observed. By comparing the shape and position of the bands in polymer and composite films, we conclude that there is no significant change of the polymer structure upon incorporation of POSS. In particular, the two bands at 1550 cm^{-1}
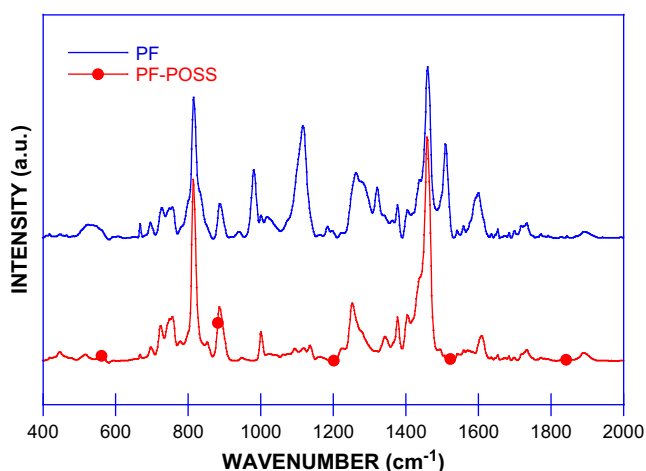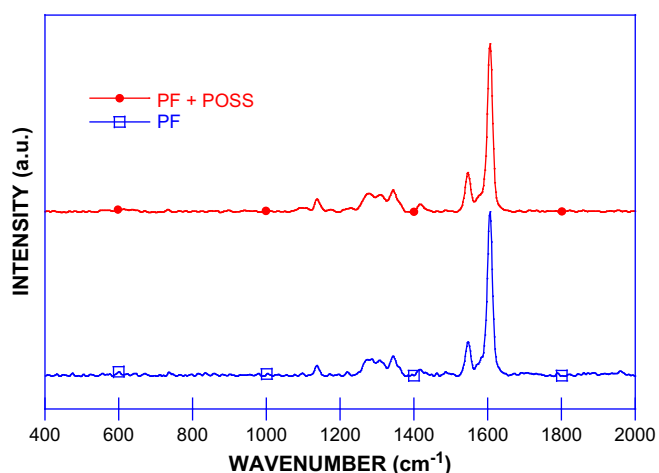

Fig. 3. Raman spectra of PF and POSS–PF thin films.

(C=C double bond vibrations) and 1604 cm^{-1} (vinyl group stretching vibration) are not changed in POSS–PF films, indicating that there is no chain scissions due to the POSS units [25]. Comparing the absorption spectra of the polymer and composite thin films (Fig. 4), we note a narrowing of the spectrum of the composite and a small blue shift of the absorption peak. The absorption peak maxima of PF and POSS–PF occur at 378 and 373 nm, respectively. These observations indicate that the polymer chains become more ordered with POSS units incorporated [26]. Fig. 5 shows the photoluminescence spectra of PF and POSS–PF thin films. We note a narrowing of the PL spectrum of the composite film in the high-energy range as compared to that of the polymer. Furthermore, we note a blue shift of ∼10 nm of the peak maximum in the nanocomposite from the PL peak of PF at 552 nm. Such a shift can be assigned either to a reduction of the polymer conjugation chain length or a reduction of the exciton binding energy. From the Raman measurement results, there are obviously no changes in the conjugation length in the composite. Therefore, we attribute the blue shift of the PL spectrum to a possible reduction of the exciton energy in agreement with previous results obtained in Ref. [27].

In summary, when POSS units are incorporated to the PF matrix, the electronic structure of the polymer is not affected but the bulky inorganic parts tend to separate the chains, resulting in a reduction of the exciton binding energy. This reduction hence can increase
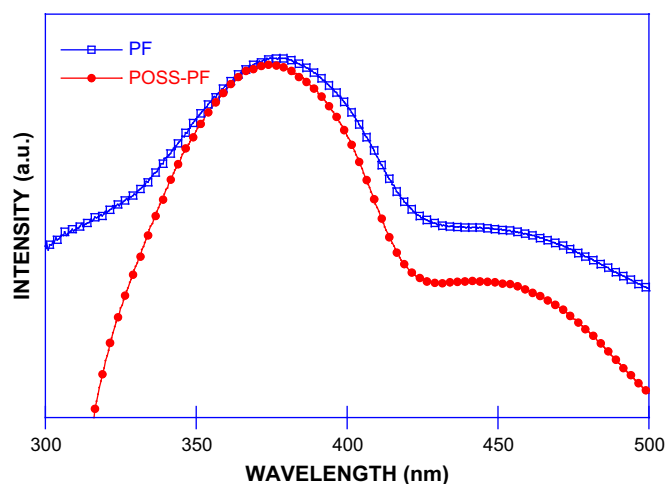

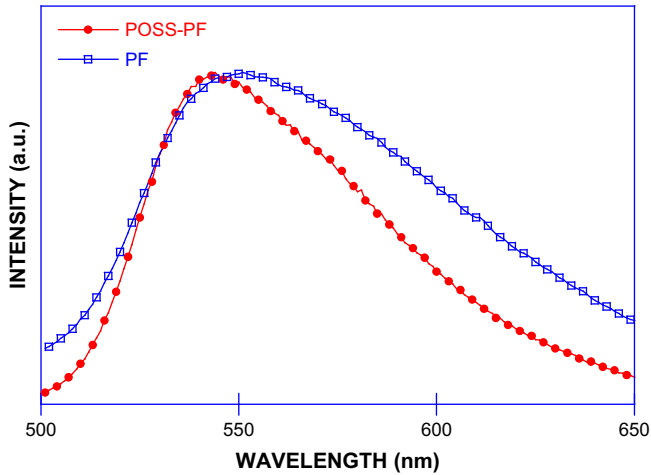**Fig. 2.** FTIR spectra of PF and POSS–PF thin films.

Fig. 4. UV–vis spectra of PF and POSS–PV thin films.

Fig. 5. Photoluminescence spectra of PF and POSS–PV thin films.

Fig. 7. Comparison of the luminance–voltage characteristics of ITO–PEDOT–PF–Ca–Al and ITO–PEDOT–(POSS–PF)–Ca–Al diodes at $T = 300$ K.

the emission efficiency of the composite as compared to that of the polymer.

4.2. Characterization of POSS/PF based PLEDs

To test the performance of the hybrid materials, we have realized polymer light-emitting diodes of single layer structure ITO/PEDOT/POSS–PF/Ca/Al. To prevent the devices from ambient oxidation, an encapsulated glass lid was realized on the devices using a UV cured epoxy. Fig. 6 shows the current–voltage characteristics of diodes having identical geometrical parameters and using PF and POSS–PF, respectively, as an active layer. We can note that the composite based device has a lower turn-on voltage (~3 V as compared to ~4 V of the PF diode). Furthermore, its intensity is higher at higher applied voltages, indicating an improved charge transport. To obtain more information on the electrical characteristics of diodes, we plotted the I–V characteristics in double logarithmic scales as shown in inset of Fig. 6. These plots show typical transport characteristics in organic devices with charge trapping [28]. At high voltages, the current–voltage relation can be described by a relation of the form $I \propto V^2$, indicating a space-charge limited conduction with trap-filled regime. While the composite based diode exhibit a trap-filled behaviour at about 7 V, the PF based device has not reached this regime yet at much higher applied
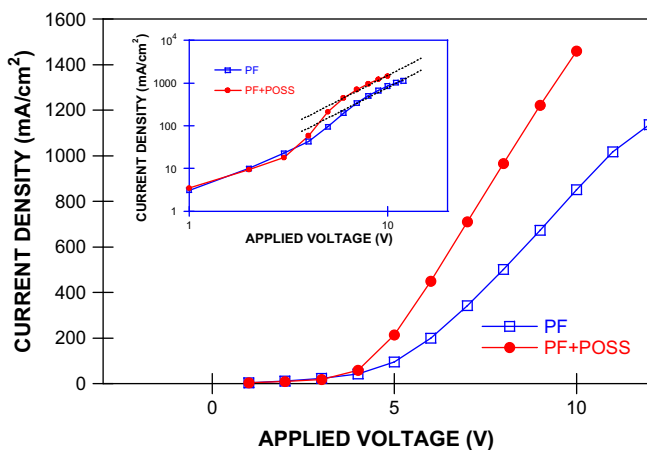
voltage (~10 V). Therefore, we infer that charge carrier trapping in composite based devices is less important than in polymer ones.

The electroluminescent (EL) spectrum of the devices is similar to the PL spectrum, indicating that the light emission originates from the polymer chains. The luminance characteristics of devices operating with PF and PF–POSS are shown in Fig. 7. The maximum of luminance for PF device is 1650 cd/m^2 and that of PF–POSS device is 4250 cd/m^2. On the other hand, the maximum yield of the devices (Fig. 8) using the PF–POSS hybrid material (0.36 cd/A) is also better than that of the polymer based diodes (0.26 cd/A). Therefore, the overall performance of the diodes is increased when using the POSS units in the polymer matrix and with the concentration of the inorganic part used here, there is no changes in the emission of the polymer.

Previous investigations of POSS–MEHPPV based diodes [29] have shown that although there is no significant effect on the electronic structure of the polymer upon introduction of POSS segments, the luminance of the composites is about six times higher than that of the polymer. The improvement in performance was assigned to a higher injection of charge carriers, which would be due to a better electrode/composite interface. On the other hand, the carrier transport in POSS–polymer is believed to be linked to the quality of the composite film because there would not be or less pinhole formation, as compared to pristine polymer film [30]. This

Fig. 6. Current density–voltage characteristics of ITO–PEDOT–PF–Ca–Al and ITOPEDOT–(POSS–PF)–Ca–Al diodes at $T = 300$ K. Inset: ln J versus ln V.
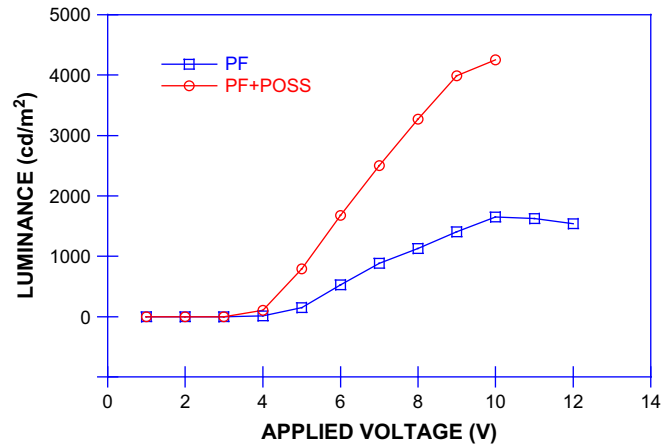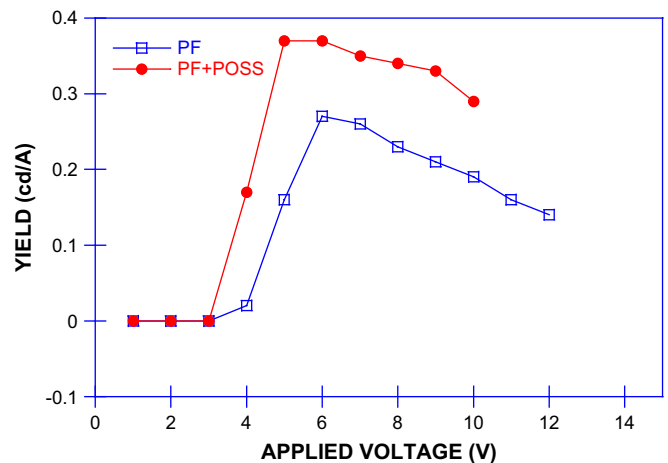

Fig. 8. Comparison of the yield–voltage characteristics of ITO–PEDOT–PF–Ca–Al and ITOPEDOT–(POSS–PF)–Ca–Al diodes at $T = 300$ K.

explanation is consistent with the lower trap density hypothesis in the composites from analysis of the *I–V* characteristic of diodes, which supports the improvement of the charge carrier transport in composites. Furthermore, as POSS units act as chain separators by their steric hindrance, and reduce aggregation effects [31], they contribute to the improvement of exciton recombination by eliminating the excimer formation. This can be seen by the EL spectra measured in the composite based diodes, which show also a narrowing in the high energy range. The effects are similar to those observed in diodes using polymer/clay nanocomposites [32], in which the quantum efficiency was found to be higher to that of the pristine polymer, and was interpreted as a consequence of a better confinement of excitons.

Improvements in recombination process in OLEDs may also result from a more balanced transport of holes and electrons in devices. Indeed, as mobilities of holes and electrons are different in polymers, the transport of fast and low charge carriers results in a low recombination possibility and hence a poor emission efficiency. Therefore, optimized charge balance by modifying the carrier mobility of either holes or electrons in the polymer has been used to increase the recombination of carriers [33]. It was reported in POSS–PPV derivative based devices [21] that the POSS segments may act as hole trap centers, thus equilibrating the density of holes and electrons within the active layer, and increasing the recombination rate. However, we have shown that in POSS–PF devices, the current–voltage characteristic suggests rather a decrease of trapping that may be linked to the isolation of the chains, and avoiding their aggregation. A possible process that can lower the hole mobility is the case of conjugated polymer surrounded partially by insulating POSS segments as observed in POSS–PPV composites [34]. Formation of insulating domains in the polymer matrix can block charge carriers (holes) resulting in a balance of mobilties and then improves the recombinations. Finally, because of the deposition process of thin films, the POSS units can accumulate within the active layer or in the vicinity of the electrodes, forming small insulating areas, which will modify in part, the charge carrier movement. Such a process would result in an increase of the light emission due to a more balance of holes and electrons However, further microscopy work on the interface between the hybrid films and the anode will be needed for understanding the formation and distribution of the POSS units in the polymer matrix.

5. Conclusion

We have shortly reviewed the composites made by incorporation of inorganic nanoparticles into a conjugated polymer matrix in view of their applications in the optical field. When using appropriate materials and inorganic/organic ratios, improved stability and physical properties of the polymer could be obtained for optical applications. We have reported results obtained in organic light emitting devices using a nanocomposite made with an inorganic structure (POSS) and blended with a conjugated polymer (PF). We have found substantial improvements of the device performance by the use of the nanocomposite as an active layer, and we explained the obtained results by the key role of the POSS segments in separating the polymer chains, favoring the carrier transport and their recombinations.

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