

The Stability of Electro-opto-active Organics

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ABSTRACT

The marketing of OLED/PLED urges for long-life electro-active organic materials. Through collaborative works with UCSB (Dr. Alan Heeger's group), McGill University (Dr. Ishiang Shin's group), Technion Institute (Dr. Nir Tessler's group) and SCUT of China (Dr. Yong Cao's group), we found the keto defect in polyfluorenes is catalyzed by the presence of calcium. We also found that the high molecular weight polymers yield to high charge mobility, and that the introduction of bulky inorganic groups like POSS, improves the stability and efficiency of PLED, as well as increases the charge mobility of TFT device.

INTRODUCTION

From light emitting diodes, solar cells, sensors, to transistors, semi-conductive organic materials, conjugated polymers in particular, have been emerging as potential challengers to inorganic silicon and gallium arsenide as the backbones of the semiconductor industry.

Although the ability of chemists to construct organic structures is unlimited, electronic devices made from these organic materials still suffer from short operation life. Among various causes found for device degradations, some are materials related such as: photo-oxidation[1], singlet oxygen and chain scissions[2], carbonyl group and other destructive species[3], recrystallization and aggregation[4], excimer formation, impurities and charge trappers, photo-bleach, etc. However, some are not directly associated with materials such as "dark spots", reactive metal contacts, electron injection, hole injection, oxygen migration from ITO, encapsulation, etc. Certainly, to have long lifetime electro-active organic materials is not for chemists only. From the synthesis and characterization, upto device construction and evaluation, chemists, physicists and engineers are collaborating closely to

better understanding the structure-properties relationship of such materials.

The results reported herein are abstracted from collaboration works between ADS, UCSB, SCUT, McGill, and Technion. We will discuss the oxidation of polyfluorenes, different approaches to prevent this degradation and the effect of molecular weight on the charge mobility.

TEXT

Photo-oxidation Study Figure 1 presents PFO films on glass prepared by spin coating, which were exposed to UV-irradiation in air for different period. As experienced by others[1], a green emission with a peak ~520 nm appeared upon UV-exposure and its intensity increased with the exposure time. Sealing these films in glass tubes under different atmospheres before UV-irradiation leads us to find that the green emission could only be observed in the presence of air (Figure 2.). Figure 3 suggests that in the presence of oxygen, PFO films will exhibit a more pronounced oxidization effect than in the presence of water vapor. Furthermore, such oxidation can also be catalyzed by heat as show in Figure 4. Certainly, we can conclude that this green emission is oxygen associated.

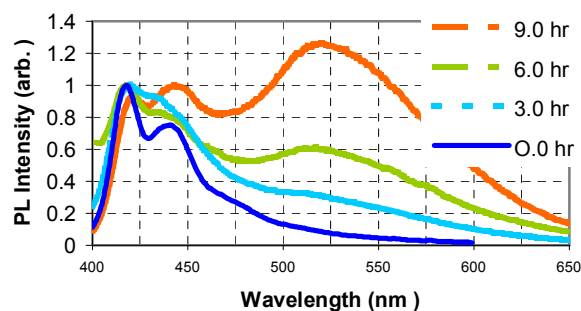


Figure 1. PL spectra of PFO films after UV-exposure in air for different hours.

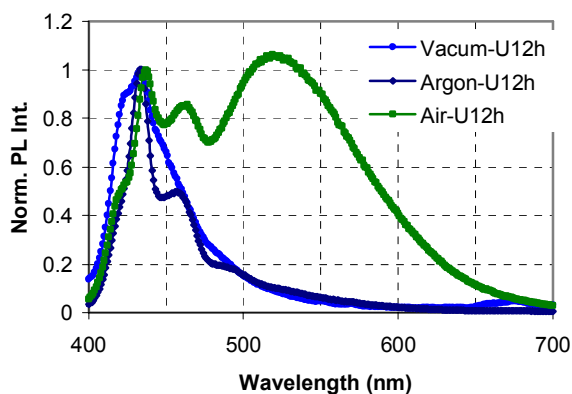


Figure 2. PL spectra of PFO films after UV-exposure in different atmospheres for 12 hours.

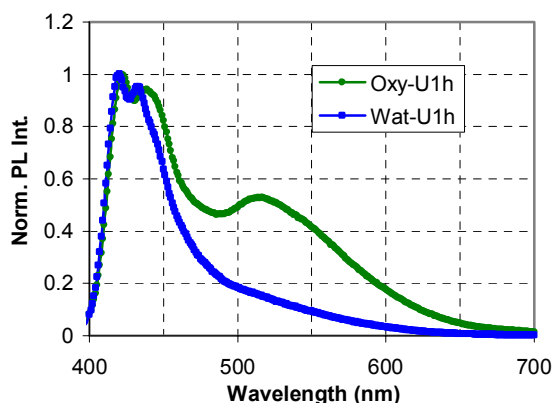


Figure 3. PL spectra of PFO films after UV-exposure in oxygen or in water vapor for 1 hour.

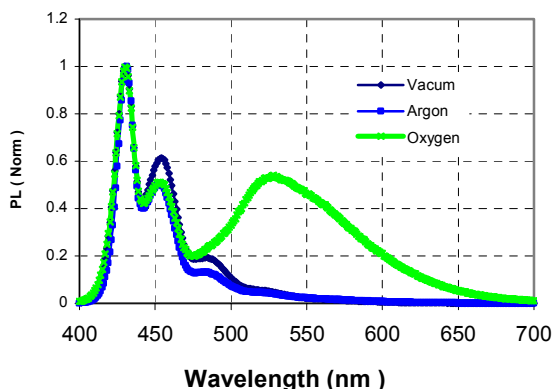


Figure 4. PL spectra of PFO films after heating for 4 hours at 140°C in different atmosphere.

However, the green emission was not observed from a toluene solution made by stripping polymer from the UV-irradiated film, which had already exhibited a pronounced green emission (Figure 5). This suggested that the emissive behavior of PFO in irradiated film was different from that of PFO in striped solution.

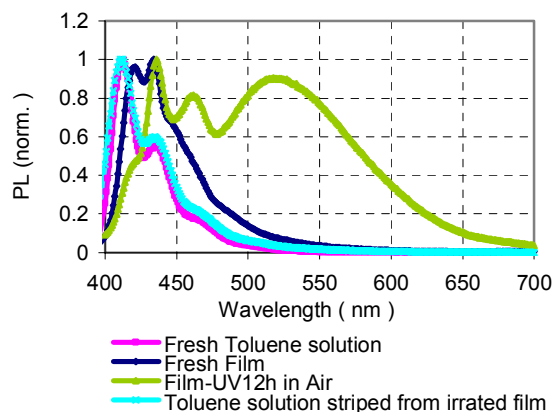
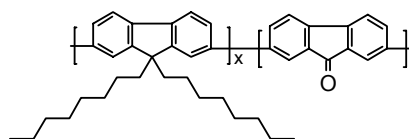


Figure 5. PL spectra of PFO in various environments

The green emission peak at 520nm corresponding to a low energy emission band at 2.2-2.4 eV from polyfluorenes was presumed to a result of aggregation and/or excimer formation in the material[5]. Recently, results from the same research group have identified this strong low-energy emission band at 2.2-2.3 eV as the emission from exciton-and/or charge-trapping keto defect sites[1,6]. In order to compare the results with a known structure, we have synthesized a co-polymer containing 1% 9-fluorenone (scheme 1).



Scheme 1. Structure of PFO co-polymer with keto in the backbone.

The co-polymer exhibited a clear keto ($>C=O$) stretching mode at 1720 cm^{-1} in IR transmission spectra, and the film casting from its toluene solution exhibited a pronounced green emission in the PL spectra. But, this green emission was not observed in polymer solution until the concentration reached 500 ppm. In addition, the PL intensity was remarkably reduced after at higher concentrations. Such observations may indicate that the energy transfer from blue-emission sites to green emission sites can only be facilitated when the two sites close enough one to another. This also explains the results presented in Figure 5, where a green emission could be detected from an irradiated film but not from its low concentration stripped solution. This phenomenon tends to show that the green emission could be prevented if the two sites (blue emission sites from the pristine polymer and the green emission sites from keto defect) can be spaced apart. This may also apply for the films.

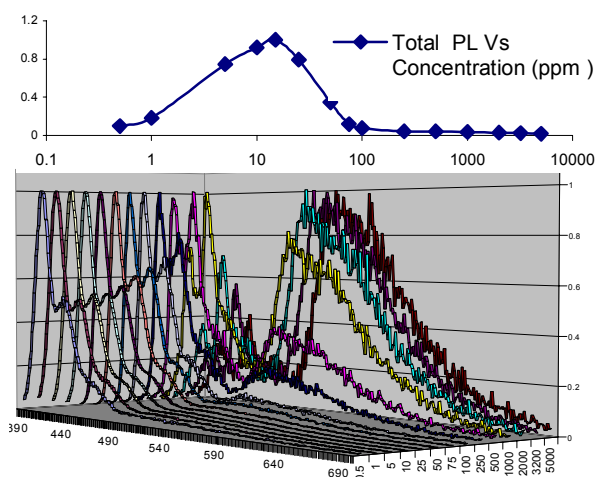


Figure 6. Normalized PL spectra of fluorenone contained PFO solution at different concentration

It is well know that the low energy emission band from PFO is typically more intense in EL than in PL, implying that such defects are also generated during device fabrication. Using XPS, we have investigated the interface of pristine PFO, Ag/Ca/PFO as shown in Figure 7. The thickness of PFO film is about 100nm; that of CA and Ag are each approx. 20nm. Argon ion-milling was used to remove the Ag layer from Ag/Ca/PFO film before scanning the interface of Ca/PFO. For the pristine PFO film, only one C1s core level was seen in the spectrum, and no evidence oxygen contamination was detected. However, evidence of oxygen, through the O1s core level, was detected from Ag/Ca/PFO film. The evolution of the XPS spectrum for O1s indicated that the peak at 529.7 eV resulting from CaO formation, which was further confirmed by Ca2p XPS spectrum. Thus the XPS study suggested that the oxidation of PFO is catalyzed by the presence of calcium, where, the deposited calcium first n-type dopes the polymer, and then the doped polymer is oxidized during device fabrication by the oxygen and generates fluorenone defects.

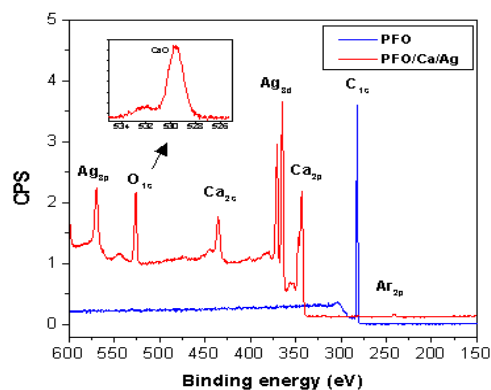


Figure 7. XPS survey scan of the pristine PFO thin film (blue line) and Ag/Ca deposited on the top of PFO film (red line).

Molecular weight Effect on Charge Mobility Different molecular weight of MEH-PPV (Mw = 100K, 1M, 2.8M) have been synthesized via Glitch polymerization, adjusting the reaction conditions. Polymer films were then prepared by spin coating from toluene solutions. Figure 8 shows data collected in a scanning atomic force microscopy operating in the phase mode. Clearly, these scans shows morphological differences. The low molecular weight(Mw~100K) tends to be relatively uniform around the low phase-angles and the highest molecular weight (Mw~2.8M) is again rather uniform but around higher phase-angles (~45°). On the other hand, a more rough and non-uniform surface was imaged for the medium one (Mw~1M), showing a rough mixture of different phases.

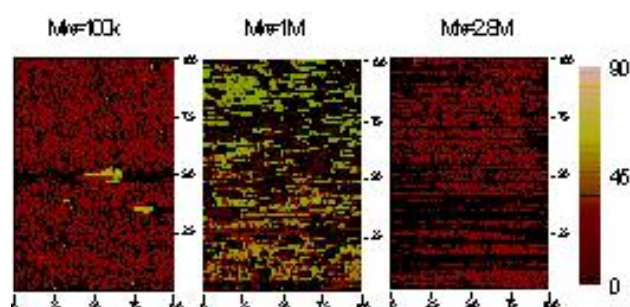


Figure 8. A 10µm x 10µm scan of the three MEH-PPV polymer films span from toluene. The data presented was collected in the phase mode.

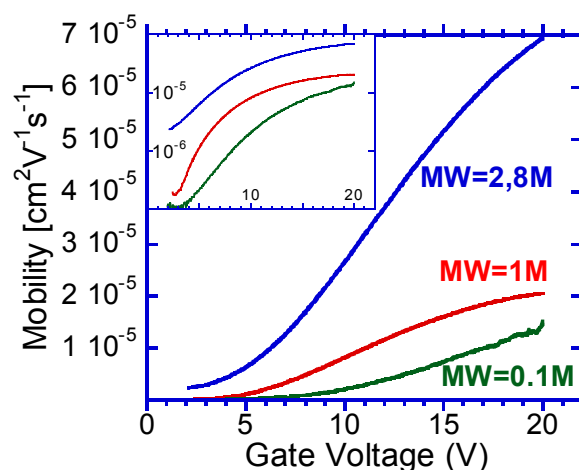
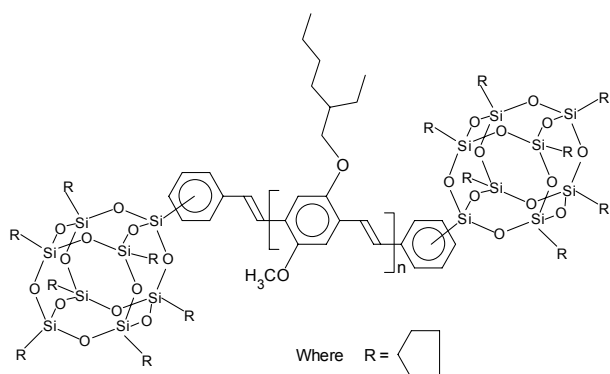


Figure 9. Mobility as a function of gate voltage for different Mw of MEH-PPV.

The Figure 9 shows the mobility value for the different samples (various Mw) of MEH-PPV spin coated films (~100nm thick) from toluene solutions. We noticed a clear increasing trend in the mobility as the Mw is increased from 100K to 2.8M. Referring the morphology results in Figure 8, it is logic to attribute such an increase in charge mobility with molecular weight to the film density, thus, the denser the film, the higher the charge mobility.

Enhance Stability by Inorganic Hybrid We have chemically incorporated polyhedral oligomeric silsesquioxanes (POSS) into conjugated polymers as exemplified in scheme II.



Scheme II. Structure of MEH-PPV-POSS

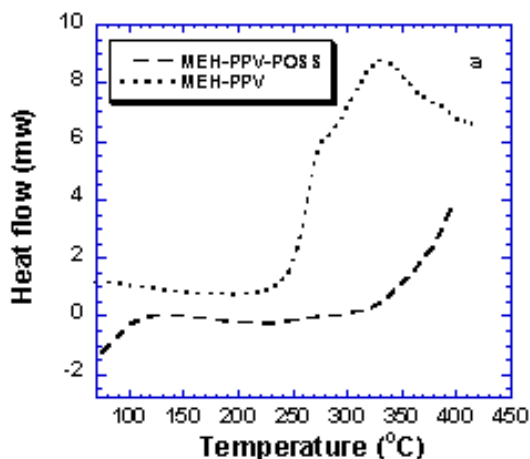


Figure 10. DSC profile of selected polymers

The MEH-PPV-POSS not only exhibited higher thermal stability as evidenced in Figure 10, but also increased the external quantum efficiency from 1.9 to 2.3 Cd/A for PLED constructed in a structure of ITO/PEDOT/Polymer/Ba/Al.

Similarly, we have observed a significant reduction in green emission for the POSS incorporated PFO polymer comparing to PFO polymer, in addition to a 30% increase of external quantum efficiency for PLED configured as ITO/PEDOT/polymer/Ba/Al.

These observations may suggest that the bulky inorganic groups, particularly POSS in this presentation, could space or separate the polymeric chains, thus reducing the aggregation and the energy transfer from the higher energy emission sites to lower energy emission sites.

Interestingly, these bulky inorganic groups like POSS may serve as bridges for charge transporting from one polymeric chain to another, especially for a system where hopping mechanism dominates. Therefore, thin film transistor (TFT) made of POSS incorporated polymers will deliver remarkably higher charge mobility comparing to their parent polymers.

Table-1 Charger mobility ($\text{cm}^2/\text{V.s} \times 10^{-4}$) calculated from TFT devices.

Polymer	Parent Polymer	POSS end-capped
MEH-PPV	2	58
Poly-TPD	21	220

Conclusions Our observations support the argument that the green emission from polyfluorenes resulted from keto defect[1], and the formation of such defect sites is further catalyzed by the presence of calcium in device fabrication.

The stability of conjugated polymers and the efficiency of devices can be improved by incorporating bulky inorganic groups such a POSS to polymeric chains.

We also found that the charge mobility increased with the molecular weight of polymers and can be enhanced also by introduction of bulky inorganic groups like POSS into polymer chains.

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