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Optical Gain from Polyfluorene Keto Defects in a Liquid Crystal Mixture

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By means of confocal photoluminescence measurements and fs pump-probe spectroscopy, we observe the optical properties of the phase separation in a mixture of polyfluorene and Liquid Crystals (LC). The boundaries of LC-rich micro-domains display a large polarized gain region from keto defects stemming from the single-chain nature of this defect.

Semiconducting polymers are a class of materials characterized by low cost processability and easy-tailored optical properties. In the last years great interest has been shown for their use as active layers in organic light-emitting diodes (OLEDs) [1] thanks to the high fluorescence efficiency and carrier mobility [2], and as gain medium in photonic devices such as lasers or amplifiers [3] given their intense and long-lasting optical gain.

Unfortunately, their performances as photonic devices are limited by two important factors: the creation of free charges or polaron pairs after pump excitation [4] and easy degradation in air [5]. In polymeric samples, the photo-induced charges, due to inter-chain interactions, produce self-absorption in the material since their absorption band partially overlaps with the emission and gain spectral region of the excitons [6].

Different approaches have been explored to quench photoinduced charges in organic materials, such as tailored synthesis of molecules [7] or dispersion of the polymer in an inert matrix [8]. In particular, it has been shown that the dispersion of the most studied polyfluorenes derivative, Poly(9,9-dioctylfluorene) (PFO), in an inert matrix allows to isolate the PFO chains, preventing the formation of inter-chain photoinduced charges and therefore allowing the formation of a large stimulated emission (SE) [6,9]. However, the poor miscibility of these two compounds is responsible for a large sample inhomogeneity [8]. Furthermore PFO easily reacts with oxygen creating a defect along its polymeric chain, the so-called keto defect (also known as “fluorenone”) [10], which

degrades the colour purity of the emission band and decreases the device efficiency and stability [11].

Photoluminescence (PL) and Electroluminescence (EL) studies indicates that Förster energy transfer to and charge carrier trapping on fluorenone defects (with subsequent fluorenone emission) are responsible for the colour degradation [12] i.e. the characteristic blue emission is replaced by a green-whitish one [13]. This process is so efficient to be significant at a very low fluorenone fraction [14].

Whether the green emission from this defect is due to a single-chain defect [13,14] or to an aggregation effect [15] has been the subject of a long debate. In any case, the presence of high transient charge concentrations in degraded polyfluorene makes it difficult to obtain optical gain (stimulated emission), hindering applications of this material in photonic devices such as optical amplifiers or lasers.

In this work we show, by means of confocal PL measurements and fs pump-probe spectroscopy, that a large polarized SE band from isolated polyfluorene keto defects is obtained in a mixture of polyfluorene with a nematic low molecular weight Liquid Crystal (LC), shedding new light on the single-chain nature of the keto defect. In this blend a peculiar phase separation generates an ordered network of LC-rich micro-domains with most of the polyfluorene chains placed isolated on the boundaries of the micro-domains.

Mixtures of organic compounds and LCs are highly promising for devices requiring electrically switchable polarized fluorescence [16] or optical gain. In particular lasing and random lasing were demonstrated in such mixtures [17], with potential applications for illumination and imaging [18].

The LC used is the 6CHBT (4-(trans-4'-n-hexylcyclohexyl)-isothiocyanatobenzene; Military University of Technology, Warsaw, Mw: 301, synthesis details [19]), which presents a nematic phase at room temperature: the molecules move freely in space maintaining a mean preferential orientation (called director). Our samples consist in 9- μm thick cells (LC2-9.0, Instec) composed by two polyamide-coated plates rubbed to force the alignment of the director along the

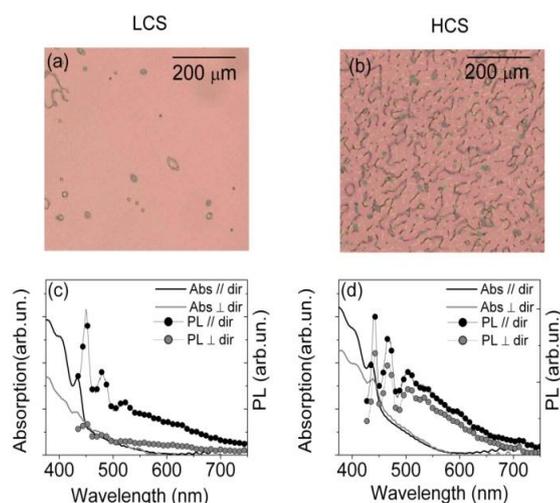


Fig. 1: Images under cross-polarized light microscope of the LCS (a) and the HCS (b). The absorption and the emission parallel and orthogonal to the LC director (after Savitzky-Golay filtering and the subtraction of the constant background) for the LCS (c) and the HCS (d).

rubbing direction and to induce a macroscopic optical anisotropy of the LC molecules.

The polymer-LC mixture is obtained by first dissolving PFO (Mw: 40000 -120000, commercial American Dye Source) in toluene (10 mg/ml) and then adding the LC. The solvent is evaporated by heating the solution at about 110°C then the cells are filled with this mixture at a constant temperature of 70°C. Two samples with different PFO concentrations are investigated: Low Concentration Sample (LCS, 0.26% wt of PFO) and High Concentration Sample (HCS, 0.61% wt of PFO).

Figs. 1a and 1b show the bright-field microscope images of, respectively, LCS and HCS between crossed polarizers. The first cell (LCS) shows a homogeneous texture (Fig. 1a) indicating a good dispersion of the polymer in the LC matrix and a pronounced anisotropy in the absorption and PL spectra (Fig. 1c). These last ones are recorded with a 400 nm pump excitation polarized along the LC director (the LC matrix is transparent at this wavelength [20]). Differently, the HCS shows a much more complex structure extended all over the cell (Fig. 1b). In fact, long filaments (structures of tens of microns) are dispersed in the homogeneous LC matrix. The sample displays a less pronounced anisotropy in the absorption and in the PL spectra (Fig. 1d) with respect to the LCS. Moreover, the PL spectrum indicates a higher intensity emission from keto defects (band centered at 550 nm) if compared to the LCS. It is important to note that the concentration of keto defects in polyfluorene chains is still very low, as the blue emission from the polyfluorene backbone is quite intense and not completely depleted by the efficient energy transfer to the keto defect.

To better understand the complex microscopic organization in the HCS we recorded diffraction-limited confocal PL maps (shared objective numerical aperture NA = 0.8). This is achieved by exciting the sample with a circularly-polarized 405 nm diode laser and recording the total PL intensity-maps, with linear polarizations both parallel (I_p) and orthogonal (I_o) to the LC director.

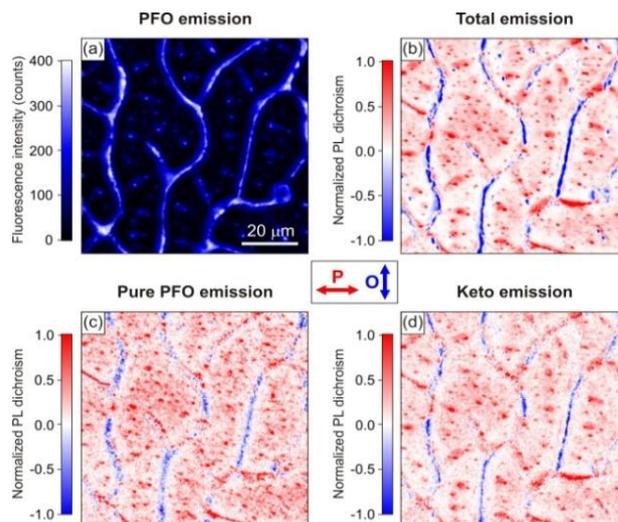


Fig. 2: Confocal fluorescence maps. Total PFO fluorescence emission (a), normalized linear dichroism (D) of the total PL from PFO (b) both collected with a long pass colour filter cutting wavelengths below 455 nm. Normalised D from the defect-free PFO collected with a 10 nm band pass filter centred at 440 nm (c) and from the keto defect collected with a 10 nm band pass filter centred at 560 nm (d).

Fig. 2 shows four confocal PL maps ($80 \mu\text{m} \times 80 \mu\text{m}$). The first one (Fig. 2a) displays the total emission intensity collected from the sample and shows that most of the photoluminescence intensity comes from the boundaries of the micro-domains, while elsewhere just a few emitting spots are detected. The other three maps instead, show the normalized linear PL dichroism defined as the difference between the two polarization maps: $D = (I_p - I_o)$. Fig. 2b represents the map of the parameter D obtained by taking into account the overall fluorescence emission from the sample, while Fig. 2c and 2d show the isolated contributions from the defect-free PFO and from the keto defect, respectively.

In these PL maps, the red colour represents the emission polarized mainly parallel to the LC director, while the blue colour is associated with the one polarized mainly orthogonal to it (see arrows in Fig. 2). All the four maps show a similar supramolecular structure, as already seen via bright field microscope (Fig. 1b), composed by a matrix of domains separated by rather thick boundaries. Fig. 2c and 2d demonstrate that there are polyfluorene chains with keto defects all over the sample, in particular on the cell boundaries. Moreover, the measured polarized emission reveals that the low energy emission (generated by the keto defects) is polarized along the same axis as the high-energy blue emission, showing that the transition dipole moment of the green emission band lies basically parallel to the chain direction, as previously reported [21]. The orientation of the boundaries defines the polarization of their emission: boundaries orthogonal (parallel) to the LC director display an emission orthogonal (parallel) to the director. In our case the majority of the boundaries is orthogonal to the LC director. Inside the domains few polymeric chains, also containing keto defects and all aligned parallel to the LC director, are responsible for the weak photoluminescence visible in Fig. 2a. The organization of the phase-separated sample closely resembles the network lattice formation observed in mixtures with high-molecular-weight (HMW) polymer

LC [22,23] and low-molecular-weight (LMW) LC. In these systems, phase separation results in a well-ordered honeycomb network structure wherein the LMW-rich phase is accommodated in micro-domains surrounded by walls constituted by the HMW polymer-rich phase. In our case, during the filling procedure of the cell (temperature kept constant at $\approx 70^\circ\text{C}$) the PFO can be considered as a HMW LC, as its glass-transition temperature is around 80°C [24], so phase separation appears. The anchoring effect from the boundary becomes so significant that the polymeric chains are forced to align parallel to its surface [22] despite the LC director orientation, as observed also in our case. Since the presence of this structure depends on the composition of the mixture, we assume that in the LCS the PFO concentration is too low to induce it.

To study the photophysical properties of these samples, we performed polarized transient transmission measurements with a standard pump-probe setup at 1 kHz repetition rate [25]. The pump ($\lambda=390\text{nm}$), and the probe (470-770 nm) beams are focused on the sample with a circular spot (radius $\approx 75\ \mu\text{m}$) and the temporal delay (t) between the two lines is controlled by a delay stage. The collected signal is the differential transmission spectra of the probe defined as $\Delta T/T(\lambda, t)$, with a time resolution of $\approx 250\ \text{fs}$. In order to study the optical anisotropy induced by the LC matrix on the PFO, the polarization of the probe is set either parallel or orthogonal to the LC director. Moreover a polarizer, always parallel to the probe polarization, is put after the sample. We have set the pump polarization orthogonal (excitation density $2.6\ \text{mJ}/\text{cm}^2$) to the LC director, to increase the signal from the PFO chains placed on the boundaries of the micro-domains.

In Fig. 3a and 3c the polarized pump-probe spectra for the LCS are reported. The transient signal appears strongly polarized along the direction parallel to the LC director. The $\Delta T/T$ spectra coincide with those of aggregated PFO, showing a SE band extending up to 500 nm and a photo-induced absorption (PIA) band centred at around 560 nm attributed to the absorption of the inter-chain photo-induced charges [6,26]. The spectra reveal that in the LCS sample the polyfluorene chains are mainly aligned along the LC director, in agreement with Onsager's prediction [27], according to which the LC tends to align the polymer chain along its director. This results in pinning the polarization of the SE and of the charge-induced PIA band. Moreover the absolute value of the anisotropy factor $r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$ stays constant over more than 10 ps (Fig. 3e), meaning that excitons and charges do not experience migration along differently oriented polymeric chains on that time scale [6]. Since the absorption band associated with inter-chain photoexcited charges is typically characterized by a long lifetime [4], similar to the one that we measure on the LCS, our data also demonstrate that the polyfluorene chains are not isolated but packed or aggregated, despite the low concentration.

Fig. 3b and 3d show the transient transmission spectra for the HCS with probe polarization either parallel or orthogonal to the LC director, respectively. When the probe is polarized along the LC director, the HCS shows spectroscopic features similar to one already observed in the LCS. On the other hand, when the probe polarization is rotated by 90° , a completely new feature appears: in the spectral region of the keto defect fluorescence, an intense SE band, which has never been seen before and is not present in the spectra of the LCS.

Our pump spot area is almost three times larger than the whole area

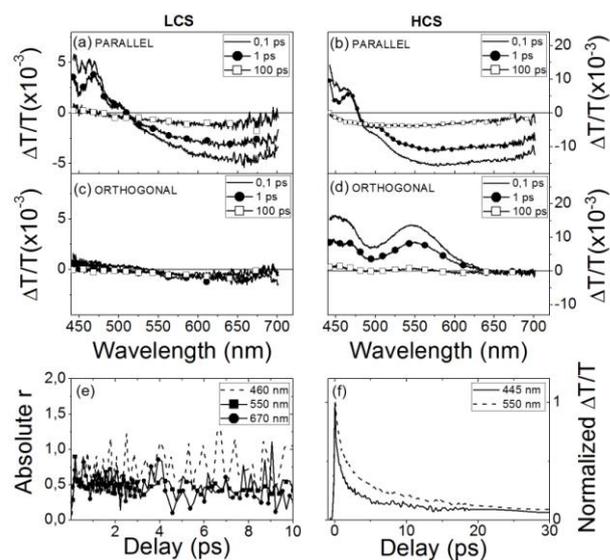


Fig. 3: Transient absorption spectra for the LCS (left panel) and the HCS (right panel). For each sample we distinguish between a probe linear polarization parallel (a,b) or orthogonal (c,d) to the LC director. In (e) we report the temporal dynamics of the absolute value of the anisotropy factor r at different wavelengths for the LCS while in (f) we show the dynamics at two wavelengths for the HCS with probe polarization orthogonal to the LC director.

shown in the confocal images, so our transient $\Delta T/T$ signal is an average of signals coming from many micro-domains comprising homogeneous areas and boundaries. Taking this into account, we assume that the pump-probe signal shown in Fig. 3b, similar to the one of the LCS (Fig. 3a), is due to the few aggregated polymeric chains placed inside the micro-domains and aligned parallel to the LC director. Instead, the micro-domains boundaries, composed mainly of polymeric chains orthogonally aligned with respect to the LC director, are responsible for the signal shown in Fig. 3d. Interestingly, this $\Delta T/T$ signal does not present a PIA band due to inter-chain photoinduced charges, indicating that the polyfluorene chains (with and without keto defects) on the boundaries are mainly isolated. Indeed, the two time decays (see Fig. 3f) at 445 nm (peak of the PFO SE band), and at 550 nm (peak of the keto defect SE band) have an instantaneous rising time and, at least within our time resolution, no competition with an underlying PIA negative signal, as typically observed for isolated chains [9].

The fact that the PFO chains at the domain boundaries are mainly isolated is not surprising since their concentration in the LC matrix is anyway very low. Fig. 3f also shows different decay times at the two wavelengths, confirming that the two bands are originating from different transition dipole moments: one from the defect-free polyfluorene and one from the fluorenone.

To our knowledge this is the first time that optical gain from the fluorenone and its temporal decay are reported. So far, the appearance of the keto defect along the polyfluorene chain has been considered always detrimental for any photonic application, due to the fact that its presence in aggregated films induces a higher concentration of inter-chain photoinduced charges. Conversely, in our system we were able to isolate it and, by reducing inter-chain

interactions, we have been able to detect its transient optical gain. Our results demonstrate that the fluorenone emission originates from a single-chain defect, since sizeable polymer aggregation at the boundaries of the micro-domains can be excluded by the absence of the photo-induced absorption band typically associated with inter-chain photoinduced charges in aggregated samples.

Conclusions

In conclusion, thanks to the LC nature of polyfluorene and by mixing with a low molecular weight nematic LC matrix, we have obtained a supramolecular structure where polyfluorene chains with keto defects are isolated and aligned. The peculiar phase separation between the LC and polyfluorene produces well-defined phase boundaries, with an anchoring effect so strong that the polymeric chains are forced to align parallel to these boundaries regardless of the direction of the nematic LC director induced by the rubbing layers. The isolation and orientation of the polymeric chains open the possibility of obtaining polarized optical gain from keto defects and reveal its nature as single chain defect. We believe that the exploitation of such, so far unknown, gain properties will be fundamental for the development of new photonic applications such as optical amplifiers and lasers based on flexible matrices.

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