Effect of Strong Coupling on Photodegradation of the p3ht Semiconducting Polymer

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Abstract: We have studied photodegradation of the semiconducting polymer p3ht in the resonant cavity and the control samples. The nearly three-fold reduction of the reaction rate is attributed to the strong polymer-cavity coupling.

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The vicinity to plasmonic structures, lamellar metal/dielectric metamaterials and simple metallic surfaces can control scores of physical phenomena, including spontaneous emission, Förster energy transfer, van der Waals interactions, and chemical reactions. Even stronger effects can be observed in the regime of *strong coupling* between *e.g.* ensembles of highly concentrated dye molecules and resonant plasmonics structures or cavities.

At this time, we study the effect of strong coupling on photodegradation of the regioregular 2,5-poly(3-hexylthiophene) (p3ht) semiconducting polymer (inset of Fig. 1) – the material of choice for organic photovoltaics. This polymer, as well as many other semiconducting polymers, is prone to photodegradation in presence of oxygen. Two known reactions paths include (i) singlet oxygen mechanism, facilitated by visible (~0.45 μm - 0.6 μm) light absorption by thiophene rings and (ii) free radical mechanism activated by the UV light. The former reaction can be efficiently triggered by a tungsten lamp (≥ 0.33 μm), while the latter mechanism becomes predominant at excitation with UV-enhanced xenon lamp (≥0.22 μm). As we have shown in Ref. [1], photodegradation of p3ht is inhibited in vicinity of metallic films and metal/dielectric stacks separated from p3ht by a thin MgF_2 spacer (effect of non-local dielectric environment) and accelerated at direct contact of p3ht with metal (presumably, catalytic effect).

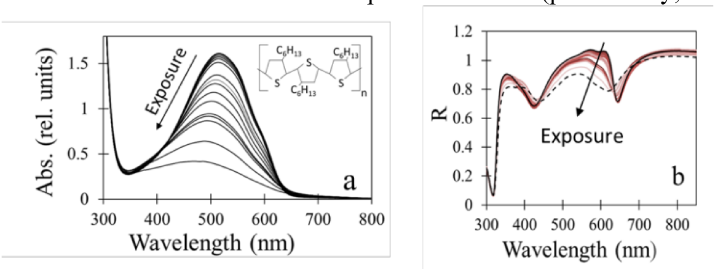

Figure 1. (a) Transformation of the absorption spectrum of p3ht under light illumination in the presence of oxygen. (b) same for the reflectance spectrum of p3ht filled cavity. Inset: chemical formula of p3ht.

The experimental samples in our study were (i) resonant cavities formed by a highly reflecting (~80 nm) Ag mirror, 104 nm thick p3ht film, and semi-transparent (~30 nm) Ag mirror, (ii) ~95 nm thick p3ht films on glass, covered by the semi-transparent (~30 nm) Ag mirror, and (iii) 110 thick p3ht films on glass. The cavity was designed to be resonant with the strong p3ht absorption band, which has a maximum at ~0.55 μm. The strong coupling of the polymer and the cavity was manifested by the splitting of the dip in the reflectance spectra, whose magnitude (~0.18 μm) was comparable with the resonances of the cavity or p3ht taken separately, Fig. 1b.

In the first series of experiments, the cavity sample and the p3ht film on glass were exposed to radiation of the tungsten lamp for several tens of hours. Multiple number of times, the photo-exposure was paused, the reflectance spectra of the cavity samples and the absorbance spectra of the p3ht films on glass have been measured, after which the photo-exposure was resumed. The series of the absorbance spectra of the p3ht films on glass demonstrated the expected reduction of the absorption strength and blue shift of the absorption (Fig. 1a), characteristic of destruction of thiophene rings and shortening of the polymer chains [2]. The reflectance spectra of the cavity samples changed too, although the alteration was less significant, Fig. 1b.

In another particular experiment, the reflectance and transmittance spectra of p3ht on glass have been measured and fitted with the model approximating the spectrum of dielectric permittivity with the combination of three

Lorentzian bands. This allowed us to model the spectrum of dielectric permittivity of partly degraded p3ht (with reduced concentration of thiophene rings). We further calculated the reflectance spectra of the cavities with partly degraded p3ht (COMSOL) and related the concentration of remaining p3ht rings to the spectral distance between the dips in the reflectance spectra – the quantity, which can be easily determined experimentally.

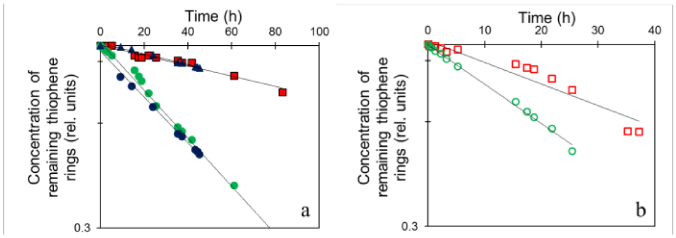

Fig. 2. Photodegradation kinetics of p3ht on glass (circles), Ag on top (triangles), and in cavity (squares) under illumination of Tungsten lamp (a) and UV-enhanced Xenon lamp (b).

We then calculated the relative concentration of thiophene rings for each reflectance spectrum taken, and plotted the decay kinetics of thiophene rings obtained from the reflectance spectra along with those determined from the transmission spectra of p3ht films on glass (Fig. 2a). When the decay kinetics were fitted, in the first approximation, with the exponential functions, the decay rate of p3ht in cavity γ_c was found to be 3.4 times smaller than that in p3ht films on glass γ_g. This ratio was further normalized by the ratio of the integrals taken over the product of the action spectrum of photodegradation of p3ht, $A(\omega)$, [1], the emissivity spectrum of the lamp, $I(\omega)$, and the square of electric field, $E^2(\omega)$, within the p3ht layer. The ratio of such "action" integrals, calculated for both p3ht film on glass and in the cavity, was equal to $\int_g/\int_c=1.44$. Therefore, the cavity slowed down the photodegradation of p3ht much stronger than it could be expected from mere reduction of the light intensity within the volume of the film.

The two straightforward phenomena, which can affect the rate of the p3ht photodegradation, include (i) reduction of exposure of the p3ht film to air by the 30 nm Ag film (which is expected to slow down the reaction) and (ii) catalytic enhancement of the reaction rate at direct contact of p3ht and Ag [3,4]. In order to take these two effects into account, we have studied photodegradation in the sample consisting of the p3ht film deposited on glass and covered with the 30 nm Ag film on top. This sample morphology partly protected p3ht from exposure to air and enabled its direct contact with Ag without providing for any resonant cavity or strong coupling.

We have found that while the ratio of the decay rates in the p3ht film deposited on glass, γ_g, and in the polymer film covered with Ag, γ_{Ag}, was equal to 4.3, the ratio of the corresponding "action" integrals (discussed above) was equal to $\int_g/\int_{Ag}=4.1$. Thus, in the latter sample, the reduction of air flow and the catalytic enhancement nearly compensated each other and, collectively, practically did not affect the rate of the photodegradation. Arguably, these two effects nearly compensated each other in the cavity sample as well. Therefore, the difference between the ratios $\gamma_g/\gamma_c=4.3$ and $\int_g/\int_c=1.65$ in the cavity sample can be attributed, in accord with Ref. [5], to inhibition of a chemical reaction by the strong coupling of p3ht with cavity or, more generally, effect of a nonlocal dielectric environment.

Emission of the Xe lamp extended to the UV range down to 0.22 μm. In this spectral range, the free radical photodegradation mechanism strongly prevails over the singlet oxygen one (direct photo-excitation of thiophene rings) [2]. Correspondingly, the strong coupling occurring at ~0.5 μm, arguably, becomes irrelevant, and no strong coupling of the p3ht polymer with cavity was expected or found at shorter wavelengths. At the Xe lamp photoexposure, the ratio $\gamma_g/\gamma_c=1.82$ was smaller than $\int_g/\int_c=2.54$, suggesting that in the short-wavelength spectral range, the catalytic enhancement prevailed over the reduction of the oxygen flow, leading to effective enhancement of photodegradation in the cavity, normalized by an appropriate "action" integral. The difference between this result and that obtained at photo-exposure with the tungsten lamp is probably due to the fact that the free radical reaction requires less oxygen than the singlet oxygen reaction, making blockage of the oxygen flow less important.

We, thus, observed substantial reduction of the rate of photodegradation of p3ht polymer in a resonant cavity. Following the literature [5,6], we attribute this result to the strong coupling or, more generally, effect of the nonlocal inhomogeneous dielectric environment.

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[1] Peters, V. N., Tumkur, T., Zhu, G., Noginov, M. A. *Scientific Reports* **5**, 14620, 10.1038/srep14620 (2015).
[2] Hintz, Holger et al. *Chemistry of Materials* **23**, 145-154 (2011).
[3] Tian, W. J., Zhang, H. Y. & Shen, J. C. *Surface Review and Letters* **4**, 703–708 (1997).
[4] Bond. G.C. in Homogeneous Catalysis (ed Luberoff, B. J.) Ch. 2, 25-34 (Johnson Matthey and Co. Ltd., 1968).
[5] Hutchinson, J.A. *et al. Angew. Chem. Int. Ed.* **51**, 1592-1596 (2012).
[6] Lee, K.W. *et al.* arXiv:1510.08574 (2015).