

Effect of strong coupling on photodegradation of the semiconducting polymer P3HT

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Photonic structures are commonly designed to manipulate scattered or emitted light. However, in recent years, they were demonstrated to affect a variety of phenomena, including chemical reactions, which lie outside the traditional electrodynamics domain. In this work, we have studied the effect of a Fabry–Perot cavity on the chemical reaction of practical importance—photodegradation of the semiconducting polymer 2,5-poly(3-hexylthiophene) (P3HT), which is the material of choice in organic photovoltaics. Experimentally, Fabry–Perot cavities, composed of two silver mirrors and filled with P3HT polymer, were photoexposed over tens of hours, and the concentration of the remaining thiophene rings (composing P3HT) was studied as a function of time. It has been found that in the regime of strong coupling with the cavity, characterized by one of the largest values of the Rabi splitting reported in the literature (1.0 eV), the normalized rate of photodegradation is reduced threefold, substantially larger than in the weak coupling regime reported in our recent study. This result adds to the toolbox of strong coupling phenomena and paves the road towards long-range control of chemical reactions and catalysis. © 2019 Optical Society of America under the terms of the

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1. INTRODUCTION

The vicinity to plasmonic structures, lamellar metal/dielectric metamaterials, and simple metallic surfaces can control scores of physical phenomena, including spontaneous and stimulated emission [1–3], Förster energy transfer [4–6], van der Waals interactions [7], and chemical reactions [8–10]. Many of these processes occur in the regime of weak light–matter interaction, which affects transitions' rates but not the energy eigenvalues of interacting systems.

Even stronger effects can be observed at *strong coupling* between, e.g., ensembles of highly concentrated dye molecules and resonant plasmonic structures or cavities. In the latter regime, the eigen-energies of the hybridized system are modified, leading to the avoided crossing behavior and the Rabi (or normal mode) splitting of the dispersion curves [11–13]. Strong coupling involving surface plasmon polaritons, Fabry–Perot cavities, and excitons has been demonstrated in recent Ref. [14]. When large ensembles of dye molecules couple to surface plasmons or resonant cavities, the splitting can be on the order of ~ 1 eV (!) [9,10,13,15,16], comparable to eigen-energies of non-interacting constituents. The record-high Rabi splitting of ~ 1.12 eV has been experimentally demonstrated in organic semiconductors coupled to cavity modes [17].

The latter regime, realized in our study reported below, is known as ultra-strong coupling. Strong and, in particular,

ultra-strong coupling have been reported to modify surface potential [18], electrical conductivity [19], exciton transport [20,21], Raman scattering [22–24], and energy transfer beyond the Förster regime [25]. Of particular interest to this study is the effect of strong coupling on chemical reactions. Thus, control of a photoisomerization reaction with strong coupling to a Fabry–Perot cavity and reversible all-optical switching between two isomers, spiropyran and merocyanine, have been demonstrated in the pioneering studies [9,10]. A more recent example of the effect of strong coupling of J-aggregated TDBC [26] organic dye molecules with triangular silver nanoprisms, resulting in hundredfold reduction of the photodegradation rate, has been reported in Ref. [27]. The effect of strong coupling on photochemical reactions (the type of reaction researched in the present study) was explained in the literature in terms of altered landscapes of electronic excited and ground states [10,28], modification and creation of avoided crossing energy gaps [28,29], and increase of relaxation rates of hybridized states [27]. Strong coupling of a coherent molecular ensemble to a cavity mode was also shown to trigger many-molecule reactions with a single photon [30].

Furthermore, strong coupling of a cavity with an electronic transition was predicted to decouple collective electronic and nuclear degrees of freedom in a molecular ensemble, leading to enhancement or suppression of intramolecular electron transfer by

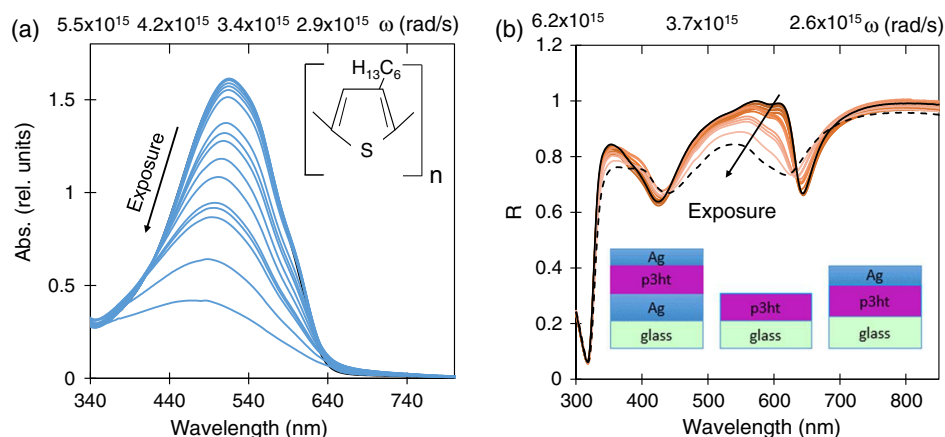


Fig. 1. (a) Transformation of the absorption spectrum of P3HT deposited on glass under tungsten lamp illumination in the presence of ambient oxygen. (b) Same for the reflectance spectrum of the P3HT filled cavity. Inset in Fig. 1(a): chemical formula of P3HT. Inset in Fig. 1(b): schematic of the experimental samples: P3HT in the cavity, P3HT on glass, P3HT on glass covered by a thin semitransparent Ag film.

orders of magnitude in comparison with free space [31]. As photochemical reactivity critically depends on strong coupling involving excited molecular electronic states, a much larger class of ground state reactions can be controlled by vibrational coupling to the vacuum electromagnetic field in a cavity [32–34]. Thus, the ground-state deprotection of a simple alkynyl-silane has shown fivefold reduction of the reaction rate when the Si-C vibrational stretching modes of the reactant were strongly coupled to the resonant IR cavity [34]. Progress and trends in the polariton chemistry are reviewed in recent Ref. [35].

In this paper, we show that strong coupling of the regioregular 2,5-poly (3-hexylthiophene) (P3HT) semiconducting polymer [the material of choice for organic photovoltaics, inset in Fig. 1(a)] with a resonant cavity slows down the polymer's photo-degradation approximately threefold.

According to the literature, there are two processes that lead to photodegradation of P3HT. One mechanism is ignited by the formation of radicals caused by exposure to ultraviolet (UV) light. In this reaction path, the oxygen-based radical attacks the α -carbon of the hexyl side chain, which leads to chain scission and photobleaching [36,37]. In the second mechanism, the polymer backbone is attacked by singlet oxygen (formed at direct photo-excitation of the thiophene rings in the visible part of the spectrum), leading to the polymer's destruction [36,38]. Both mechanisms result in reduction of the P3HT absorption band and its blue shift caused by shortening of the polymer chains. The latter effect is particularly strong at random chain scission of the polymer backbone, taking place in the case of the singlet oxygen photodegradation mechanism [Fig. 1(a)]. As we have shown in Ref. [8], photodegradation of P3HT is inhibited in the vicinity of metallic films and lamellar metal/dielectric meta-materials 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). Control of the photodegradation of P3HT by its strong coupling with a resonant cavity is discussed below.

2. EXPERIMENTAL SAMPLES

The experimental samples in our photodegradation studies included:

(i) Fabry–Perot cavities formed by a highly reflecting silver back mirror (~ 90 nm), P3HT film of the targeted thickness (ranging between 34 nm and 162 nm), and a semi-transparent top silver mirror (~ 30 nm); see Section 6 (Methods). The cavities were designed to be resonant or not resonant with the strong P3HT absorption band, which has a maximum at ~ 0.55 μm , as discussed below;

(ii) similar cavities filled with undoped poly(methyl methacrylate) (PMMA) polymer, which does not have any absorption bands in the spectral range of interest;

(iii) P3HT films on glass; and

(iv) P3HT films on glass, covered by a semi-transparent silver mirror (~ 30 nm).

The fabrication procedure is described in Section 6 (Methods).

3. CAVITY DESIGN: NUMERICAL SOLUTIONS OF THE MAXWELL EQUATIONS

Maxwell equations were solved with the commercial finite-element-method (FEM) solver, COMSOL Multiphysics. In the first series of simulations, we modeled reflection spectra of the cavities formed by a thick (~ 90 nm) film of Ag deposited on glass, the film of P3HT of varied thickness, and thin semi-transparent Ag film. The spectra of real and imaginary parts of the dielectric permittivity of Ag were taken from Ref. [39], and those of P3HT were determined in our earlier study [8]. By varying the thickness of the P3HT film, we found one (~ 100 nm), at which two dips in the reflectance spectra (signifying strong exciton–cavity coupling) had about the same magnitude [Fig. 2(a)], and the spectral distance between them was close to minimal [Fig. 2(b)]. Therefore, the 100 nm cavity size was concluded to be (nearly) optimal for the strong coupling regime. The color map of the light intensity distribution ($\propto |E|^2$) within the P3HT film and surrounding layers, showing the $\lambda/2$ standing wave resonance, is depicted in Fig. 2(c) for $\lambda = 632$ nm (corresponding to one of the dips in the reflectance spectrum of the cavity). The values $|E|^2$, integrated over the thickness of the P3HT layer (in the cavity, on top of glass and on top of Ag), were plotted as the function of frequency, resulting in the $|E|^2(\omega)$ spectra shown in Figs. 3 and S1.

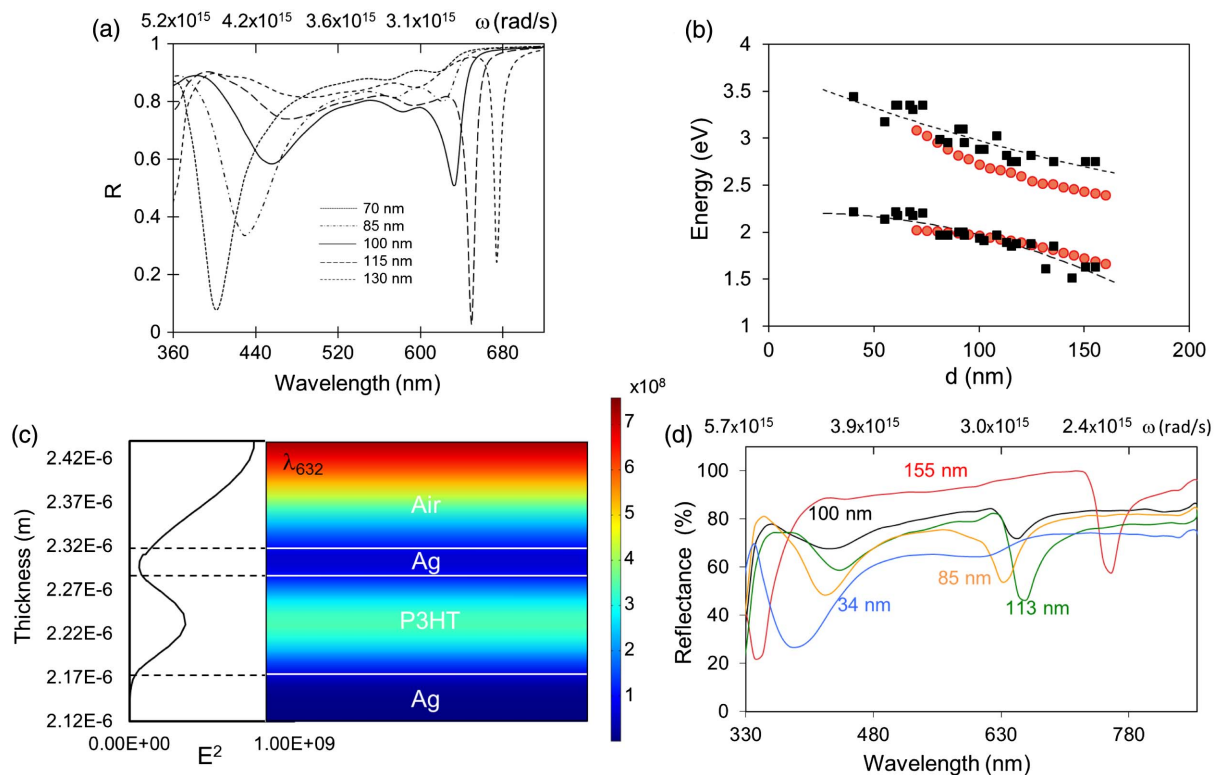


Fig. 2. (a) Reflectance spectra calculated for several cavities of different sizes. Two dips in the spectra are characteristic of strong coupling of P3HT and the cavity. (b) Dependence of the spectral positions of the dips on the cavity size d . Red circles, calculations; black squares, experiment. (c) Light intensity ($|E|^2$) distribution in the 100 nm cavity calculated at $\lambda = 632$ nm, position of the dip in the reflectance spectrum (left, plot; right, color map). (d) Experimental reflectance spectra of the cavities.

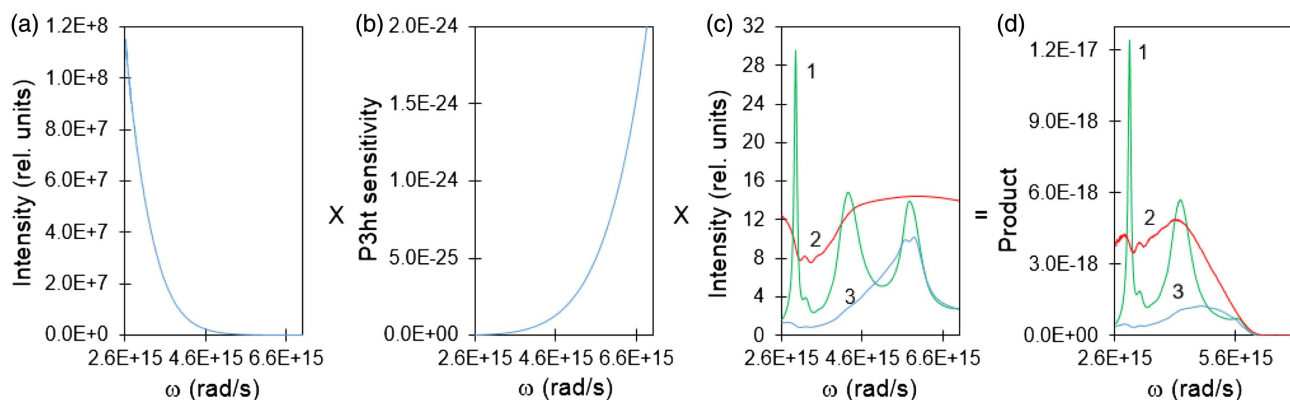


Fig. 3. Spectra of (a) tungsten lamp emissivity, (b) sensitivity of P3HT to photoexposure, and (c) value $|E|^2$ integrated over thickness of the P3HT layer in the cavity (trace 1) on top of a glass substrate (trace 2), and in the P3HT film covered by a thin semitransparent silver film (trace 3). (d) Product of the three spectra depicted in Figs. 3(a)–3(c) was used to calculate the “action” integrals $\int_c$ (trace 1), $\int_g$ (trace 2), and $\int_{Ag}$ (trace 3).

4. MEASUREMENTS

We started our experiments with measurements of reflectance spectra of the cavities filled with PMMA and found a reasonably good agreement between the experimental and the theoretically predicted [40] wavelength positions of the reflectance dips (Supplement 1, Fig. S2). This gave us confidence that our fabrication procedure and thickness evaluation were adequate. The small discrepancy between the experiment and the calculation is the subject of a separate study to be published elsewhere.

The transmission spectra of the P3HT films on glass, with and without the semi-transparent silver mirror, and the reflection spectra of the cavities have been studied in the spectrophotometer setup (see Methods).

The strong coupling of the polymer and the cavity was manifested by two dips in the reflectance spectra [Fig. 1(b)], corresponding to the upper and lower branches of the polariton dispersion curve [13,41]. By analyzing the energy positions of the dips in multiple cavities of varied sizes (see Methods), we found the minimal distance between the polariton branches to

be equal to 1.0 eV, $\sim 44\%$ of the resonance energies of the cavity and P3HT taken separately, 2.26 eV (~ 550 nm). This is one of the largest Rabi (or normal mode) splittings observed experimentally at (ultra) strong coupling of excitonic media with resonant Fabry–Perot cavities reported in the literature [13,15,16,41].

A. Photodegradation of P3HT Under Tungsten Lamp Illumination

In the first series of experiments, the cavity sample and P3HT film on glass were exposed to radiation of the tungsten lamp for several tens of hours (see Methods). This lamp did not radiate much UV light, Fig. 3(a), and its visible emission directly excited P3HT rings (the singlet oxygen mechanism of photodegradation [36]). At multiple times, the photo-exposure was paused, and the reflectance spectra of the cavity samples and absorbance spectra of the P3HT films on glass were measured, after which the photo-exposure was resumed. The series of absorbance spectra of the P3HT films on glass demonstrated the expected reduction of absorption strength and the blue shift of absorption maximum [Fig. 1(a)], which is characteristic of destruction of thiophene rings and shortening of polymer chains [42]. The reflectance spectra of the cavity samples changed too, although the alteration was less significant [Fig. 1(b)].

B. Correspondence Between the Concentration of Remaining P3HT Rings and the Spectral Distance Between the Dips in the Reflectance Spectra of the Cavities

The experimental absorbance spectra of P3HT on glass (at varied photo-exposures) were fitted with the model approximating the spectrum of dielectric permittivity with the combination of three Lorentzian bands, whose intensities were proportional to the concentration of remaining thiophene rings and whose spectral positions were tuned to model the blue shift of the absorption band observed experimentally [Fig. 4(a)]. Knowing the spectra of dielectric permittivities of P3HT at different exposures, we further calculated the reflectance spectra of the cavities with partially degraded P3HT and related the concentration of remaining P3HT rings to the spectral distance $\Delta\omega$ between the dips in the reflectance spectra, Fig. 4(b).

We then evaluated the relative concentration of remaining thiophene rings, for each reflectance spectrum taken, and plotted the decay kinetics obtained from the reflectance spectra of the cavities along with those determined from the transmission spectra of P3HT films on glass [Fig. 5(a)]. When the decay kinetics were fitted, in the first approximation, with the exponential functions, the decay rate of P3HT in the cavity γ_c was found to be 4.6 times smaller than that in the P3HT films on glass γ_g . This difference is

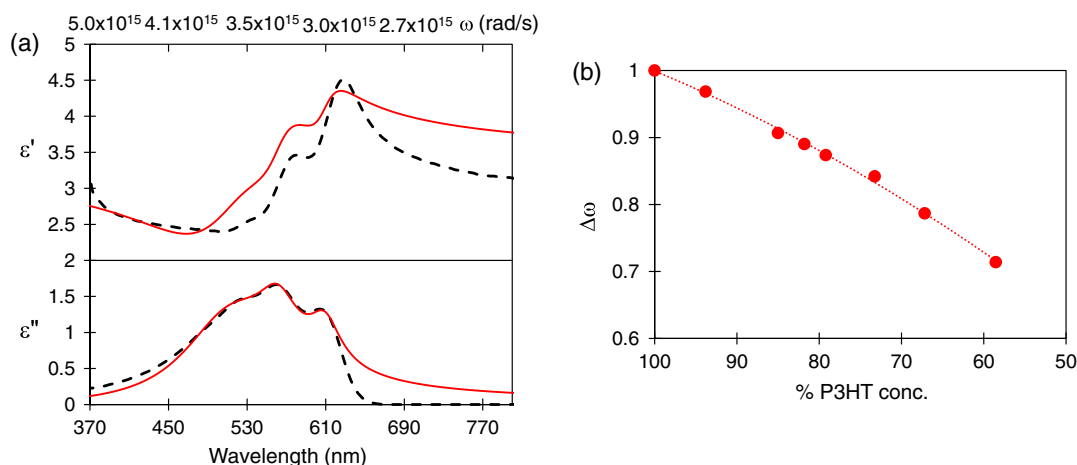


Fig. 4. (a) Fitting the experimental spectra of real ϵ' and imaginary ϵ'' parts of the dielectric permittivity of P3HT (dashed lines) with the sum of three Lorentzian oscillators (solid lines). (b) Calculated correspondence between the concentration of remaining P3HT rings and the spectral distance between the dips in the reflectance spectra of the cavities.

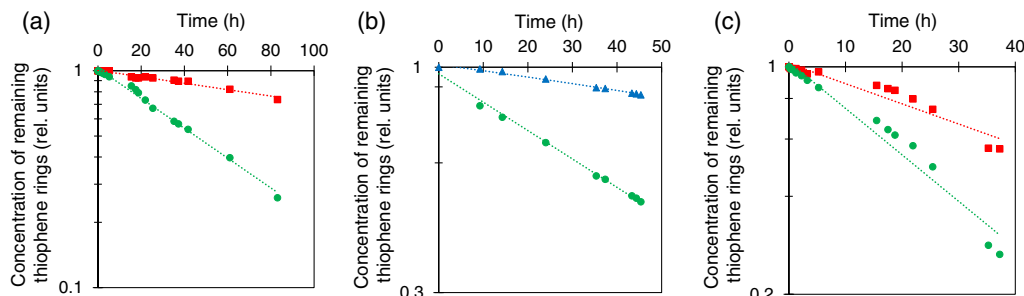


Fig. 5. Photodegradation kinetics of P3HT on glass (circles), on glass with Ag on top (triangles), and in cavity (squares) under illumination with tungsten lamp (a and b) and UV-enhanced xenon lamp (c).

partly due to the fact that the light intensity in the volume of P3HT films in cavities is not the same as that in P3HT films deposited on glass. Therefore, the latter ratio of the decay constants was further normalized by the ratio of the integrals, $\int A(\omega)I(\omega)|E|^2(\omega)d\omega$ [Fig. 3(d) (traces 1 and 2)], taken over the product of (i) the action spectrum of the photodegradation of P3HT $A(\omega)$ [8,36], Fig. 3(b), (ii) the emissivity spectrum of the lamp $I(\omega)$ (see Methods) [Fig. 3(a)], and (iii) the calculated square of the electric field, $|E|^2 = \vec{E}_x \cdot \vec{E}_x + \vec{E}_y \cdot \vec{E}_y + \vec{E}_z \cdot \vec{E}_z$, integrated over the thickness of the P3HT layer [see Methods and Fig. 3(c) (traces 1 and 2)]. The ratio of such “action” integrals, calculated for both P3HT films on glass and in the cavity, was equal to $\int_g/\int_c = 1.4$, and the ratio of the decay rate constants normalized by the ratio of the action integrals was equal to $\frac{\gamma_g/\gamma_c}{\int_g/\int_c} = 3.3$. 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.

Before jumping to the conclusion that the reduction of photodegradation of P3HT in the cavity is linked to strong coupling, or, more generally, to the effect of nonlocal dielectric environments, one should evaluate two more effects, which are expected to influence the rate of the chemical reaction: (i) reduction of exposure of the P3HT film to ambient oxygen caused by the 30 nm Ag film deposited on top (which should slow the photodegradation down) and (ii) possible catalytic enhancement of the reaction rate by direct contact of P3HT and Ag [43,44]. In order to take these two effects into account, we have studied photodegradation in the P3HT film deposited on glass and in the similar P3HT film covered with the 30 nm Ag layer on top, [Fig. 5(b)]. The morphology of the latter sample partly protected P3HT from exposure to air and enabled its contact with Ag, without providing for any resonant cavity or strong coupling.

We 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 [Fig. 5(b)], the ratio of the corresponding action integrals [Fig. 2(d)] was equal to $\int_g/\int_{Ag} = 4.1$. Thus, in the latter P3HT/Ag sample, the reduction of the air flow and the catalytic enhancement nearly compensated each other and, collectively, practically did not affect the normalized rate of photodegradation. Arguably, the catalytic effect in a cavity, where P3HT film is sandwiched between *two* silver layers, is even stronger than that underneath a single Ag layer. Correspondingly, in the cavity, the catalytic effect (acceleration of the reaction) should prevail over the effect of the reduction of oxygen flow (inhibition of the reaction).

Therefore, in accord with Refs. [9,10], the threefold reduction of the normalized photodegradation rate of P3HT in the cavity, in comparison to that on top of glass, can be attributed to inhibition of a chemical reaction by the strong coupling of P3HT with the resonant cavity.

Note that the effect of the cavity on the photodegradation of P3HT reported here (threefold reduction of the rate) is stronger than that of the Ag/MgF₂ thin film and metamaterial substrates studied in Ref. [8], ~1.5 times reduction. This result manifests that, to no surprise, the control of light–matter interaction in the strong coupling regime is more efficient than that in the weak coupling regime.

C. Photodegradation of P3HT Under Xenon Lamp Illumination

The experiments above have been repeated with a 150 W xenon ozone-free arc lamp. Its emission spectrum extends to the UV range much farther (~220 nm) than that of the tungsten lamp (~350 nm). Therefore, according to Refs. [27,28], the photodegradation of P3HT is arguably dominated by the radical mechanism. The thickness of the P3HT layer in the cavity was still equal to ~100 nm, and a cavity of this size was not in resonance with any notable absorption centers in the UV part of the spectrum. Moreover, the real part of the dielectric permittivity of silver changes to positive at $\lambda = 325$ nm [39]. Therefore, below this wavelength, the reflectance of silver decreases dramatically, and no cavity (with a reasonably high *Q*-factor) formed by two reflectors exists in that spectral range. The only strong coupling (interaction of the cavity with the 0.55 μ m absorption band of P3HT) was observed in the visible part of the spectrum.

Since the photosensitivity of P3HT is much stronger in the UV part of the spectrum than in the visible part of the spectrum [Fig. 3(b)], the photodegradation kinetics of the P3HT film at xenon lamp illumination was much shorter than that at tungsten lamp illumination [compare Figs. 5(a)–5(c)]. Thus, the absorption band of P3HT on glass almost vanished after ~40 h of photoexposure.

The ratio of the rates of photodegradation of P3HT on top of glass and in the cavity, $\gamma_g/\gamma_c = 2.3$, was marginally smaller than the ratio of the corresponding action integrals, $\int_g/\int_c = 2.54$ (see Supplement 1, Fig. S2), which can be interpreted as a slight increase in the normalized rate of photodegradation in the cavity, which was comparable to the error bar of the measurements ($\pm 10\%$).

In contrast to the singlet oxygen mechanism, which requires continuous intake and consumption of oxygen from the atmosphere, the radical mechanism “recycles” and reuses molecular oxygen, which is already present in the volume of the film, and much less depends on the intake of new oxygen [38]. Therefore, in the latter case, the blockage of oxygen should not significantly change the photodegradation rate of P3HT in the cavity, and the catalysis should prevail. This is what we see (marginally) in the Xe lamp photo-exposure experiment. The small magnitude of the effect can be due to low efficiency of the catalytic enhancement or remaining (expectedly small) inhibition of the photodegradation by the cavity.

5. DISCUSSION AND SUMMARY

To summarize, we have demonstrated that under tungsten lamp illumination, strong coupling of the P3HT semiconducting polymer with a resonant cavity (characterized by the gigantic Rabi splitting of 1.0 eV) causes threefold reduction of the rate of photodegradation (presumably dominated by the singlet oxygen mechanism). The latter value has been normalized by (i) the action spectrum of the P3HT photodegradation, (ii) emissivity spectrum of the lamp, (iii) spectrum of the light intensity integrated over the P3HT film’s thickness, (iv) reduction in the oxygen flow caused by the top silver mirror, and (v) possible effect of chemical catalysis. The reported effect of the resonant cavity (in the strong coupling regime) was larger than that of the Ag/MgF₂ thin film and lamellar metamaterial substrates [8] in the weak coupling regime.

As we have inferred above and in agreement with the commonly occurring mechanism of photobleaching [27], under tungsten lamp illumination, the singlet oxygen mechanism of photodegradation of P3HT is the most plausible reaction path, which is affected by strong coupling with a cavity. This process is depicted in Fig. 6(a), in which we schematically combined the chemical reaction's pathway, adopted from Ref. [36], with the energy levels of ground state polymer P, singlet excited state polymer $^1P^*$, and triplet excited state polymer $^3P^*$. The first two steps of the process, photoexcitation of the polymer, $P \rightarrow ^1P^*$, and intersystem crossing, $^1P^* \rightarrow ^3P^*$, result in populating triplet excited state $^3P^*$ —the reaction's intermediate product, whose concentration determines the rate of photodegradation [27]. The latter is determined by the balance of population and depopulation of both $^1P^*$ and $^3P^*$.

Strong coupling with the cavity causes hybridization of the molecular excited states and the cavity mode [9,10,27–29], resulting in formation of upper (+) and lower (–) polariton branches separated by the Rabi energy $\hbar\Omega$ [Fig. 6(b)]. According to Refs. [27,45], one of the possible factors contributing to deactivation of $^3P^*$ in organic molecules is the reverse intersystem crossing $^3P^* \rightarrow ^1P^*$ [see Fig. 6(b)]. This process, whose rate is proportional to $\exp(-\Delta E_{ST}/kT)$, is negligibly small at large energy gap ΔE_{ST} between the singlet and triplet states and grows as ΔE_{ST} becomes smaller (here, ΔE_{ST} is the energy difference between the singlet and triplet excited states, k is the Boltzmann constant, and T is temperature). As claimed in Ref. [45], strong coupling with the cavity lowers the low polariton branch (–), which is of singlet origin, and does not affect the energy position of triplet state $^3P^*$. Therefore, this process reduces ΔE_{ST} and increases the reverse intersystem crossing, $\sim \exp(-\Delta E_{ST}/kT)$, which depopulates triplet state $^3P^*$.

One can infer that a similar mechanism of depopulation of $^3P^*$ and slowing down photodegradation of P3HT in the cavity took

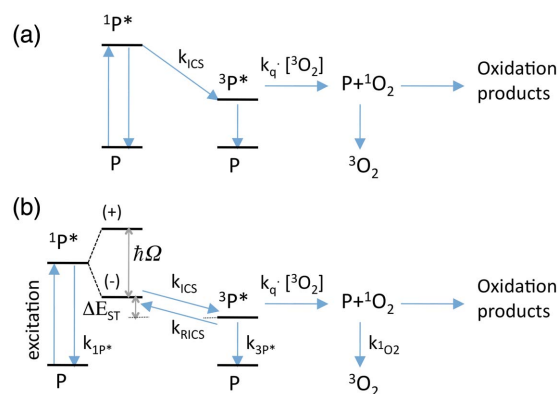


Fig. 6. Scheme of polymer photodegradation by singlet oxygen. (a) P, ground state of the polymer; $^1P^*$, excited singlet polymer state; $^3P^*$, excited singlet polymer state; 3O_2 , ground state oxygen; 1O_2 , singlet oxygen; k_{1P^*} , k_{3P^*} and k_{1O_2} , deactivation constants; k_q , quenching constant; k_r , reaction constant; k_{ISC} , intersystem crossing constant. Horizontal thick black lines represent energy levels. (b) Same as Figure a, but with the excited state $^1P^*$ split into two polariton branches, (+) and (–), due to interaction with the cavity. $\hbar\Omega$, Rabi splitting; k_{RISC} , reverse intersystem crossing constant; ΔE_{ST} , energy difference between excited triplet state of the polymer $^3P^*$ and the lower polariton branch (–) of the excited singlet state of the polymer $^1P^*$.

place in our experiment. In fact, our cavity was resonant with the absorption band of P3HT at ~ 550 nm, which caused the splitting of the dispersion curve, and “pushed” the low polariton branch down, reducing the energy gap ΔE_{ST} . This hand-waving reasoning is in qualitative agreement with our experimental result. At the same time, this is not the only possible model, and a different mechanism of depopulation of the triplet excited state was claimed to be responsible for the hundredfold suppression of photo-oxidation in Ref. [27]. The quantitative examination of possible photodegradation mechanisms, which requires knowledge of several unknown to us system parameters, is the subject of future studies to be published elsewhere.

Under UV-enhanced xenon lamp illumination, the normalized rate of photodegradation (presumably dominated by the radical mechanism) was nearly the same in the cavity and on top of glass. We explain the difference between the tungsten lamp and xenon lamp illumination results by the absence of strong coupling in the UV range of the spectrum and its effect on a chemical reaction.

6. METHODS

A. Experimental Samples

The experimental samples in our study were (i) Fabry–Perot cavities formed by a highly reflecting silver back mirror, P3HT, film of the targeted thickness and a semi-transparent top silver mirror, (ii) similar cavities filled with undoped PMMA polymer, (iii) P3HT films on glass, and (iv) P3HT films on glass, covered by a semi-transparent silver mirror [inset of Fig. 1(b)].

P3HT films were prepared from solutions of 95% regioregular, average 15,000–45,000 M_n , P3HT (from Sigma Aldrich) dissolved in American Chemical Society (ACS) grade chloroform (from Fisher Scientific). Spin coating of the solutions onto Ag and glass substrates resulted in P3HT films, whose thicknesses (determined by the solution's viscosity and spin coating rate) varied from 34 nm to 162 nm. In all samples used in photodegradation experiments, the thickness of P3HT layers was equal to ~ 100 nm.

PMMA polymer was dissolved in dichloromethane (DCM) and spin-coated onto a thick Ag film, as described above, forming a middle layer of a Fabry–Perot cavity.

Thick mirror-like, ~ 90 nm, and thin semi-transparent, ~ 30 nm, silver films were deposited using an Auto 306 thermal deposition evaporator. All film thicknesses were measured using the Bruker Dektak XT profilometer.

B. Transmittance and Reflectance Measurements

The Lambda 900 UV/VIS/IR spectrophotometer with a 150 mm integrating sphere equipped with a photomultiplier (PMT) detector (from Perkin Elmer) was used for both transmittance (absorbance) and reflectance measurements. In the transmittance measurements of P3HT films on glass and P3HT films covered with a semi-transparent Ag layer, the samples were placed in front of the integrating sphere. In reflectance measurements of the cavity samples, the latter were placed in the back of the integrating sphere, with the incidence angle of $\sim 8^\circ$.

C. Evaluation of the Rabi Splitting

We have fabricated over 20 cavity samples, with thicknesses of the P3HT layers ranging from 34 nm to 162 nm, and studied their

near-normal incidence reflectance spectra, which were in fair agreement with those calculated theoretically [compare Figs. 2(d) and 2(a)]. The energies of the observed spectral dips, plotted against the cavity size, resulted in two polariton branches [Fig. 4(b)], manifesting the strong coupling regime. The minimal distance between the two branches was 1.0 eV. This is one of the largest Rabi (or normal mode) splittings reported in the literature.

D. Photo-Exposure

Two photo-exposure light sources used in our experiments were a 250 W quartz tungsten halogen (QTH) lamp and 150 W xenon ozone-free arc lamp, both from Newport. To measure the emissivity of the lamp, the emission spectrum for each lamp was collected using the Oriel MS257 monochromator, and normalized by the Oriel calibration arc lamp. A blackbody fitting of the calibration arc lamp (Model 68831 from ORIEL) extended the normalization spectrum to the deep UV range. The former lamp (W) emitted light at $\lambda \geq 350$ nm, while the emissivity spectrum of the latter one (Xe) started at a much shorter wavelength, $\lambda \geq 220$ nm. The lamp emission was loosely collimated using a combination of the back reflector and the lens, which were a part of the lamp housing, and the samples were mounted ~ 40 cm away from the lamp. Only two samples could fit in the central part of the collimated beam at a time. Therefore, the photo-exposure experiments were done in three sets: (i) P3HT film on glass and P3HT film in a cavity exposed to radiation of the tungsten lamp, (ii) P3HT films on glass, bare and covered by the semi-transparent Ag film, exposed to radiation of the tungsten lamp, and (iii) P3HT film on glass and P3HT film in a cavity exposed to radiation of the xenon lamp. The photo-exposure power densities, measured with the Scientech Astral powermeter, ranged from 190 mW/cm² (xenon lamp) to 285 mW/cm² (tungsten lamp). However, the major contributions to the measured power densities were from the infrared light, which did not play any significant role in photodegradation. (The heating of the samples by the lamps, few degrees, was insignificant).

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See Supplement 1 for supporting content.

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