

Charge Injection and Photooxidation of Single Conjugated Polymer Molecules

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Oxidative damage of organic conjugated materials is a serious problem for organic electronic devices, such as solar cells, optical sensors, thin-film phototransistors and organic light-emitting diodes (OLEDs).¹ The molecular-level mechanism of oxidative damage remains poorly understood due to a complex set of chemical interactions among a large number of diverse chemical species. These species include excited states (excitons), charge carriers (polarons), and atmospheric impurities, e.g., molecular oxygen and water. Photooxidation, the most common form of oxidative damage, involves photochemical damage of organic materials, e.g., oxidized double bonds. It is usually associated with singlet oxygen chemistry involving the formation of endoperoxides and dioxetanes.^{2,3} Photooxidation has also been reported to lead to decreases in the fluorescence yield of organic devices (i.e., photobleaching) due to the generation of fluorescence-quenching sites of unknown structure.^{4–8} Photobleaching can be especially detrimental to devices whose function is based on fluorescence, such as OLEDs and fluorescence-based sensors.

This communication presents a new technique for the investigation of photooxidation that combines single-molecule spectroscopy with charge injection through a charge-transporting layer. This approach allows for the first *direct correlation of photobleaching and charge carrier effects* for the same nanometer-scale region (i.e. isolated single molecule) of a conjugated polymer. It is applied in this report in the investigation of the photooxidation mechanism of the prototypical conjugated polymer, poly[2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylene-vinylene] (MEH-PPV).

As shown in Figure 1, the experiments employed a large area (1 cm²), multilayer structure comprising (bottom-up) a transparent indium tin oxide (ITO) electrode, a thick charge-blocking layer of silicon dioxide, a poly(methyl methacrylate) (PMMA) spacer layer, another PMMA layer in which MEH-PPV single molecules (M_n : 450,000) were contained at high dilution, a charge-transport layer of *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD), and finally the Au top electrode. The layers were prepared in sequence by e-beam evaporation (SiO₂), spin coating (PMMA and PMMA/MEH-PPV), and thermal evaporation (Au and TPD). Previous results demonstrated that single-MEH-PPV molecules in spin-coated PMMA exist as folded 10–20-nm-sized nanoparticles.⁹ The thickness of the PMMA/MEH-PPV layer was adjusted to be about 10 nm, accordingly, allowing for electrical contact between the MEH-PPV molecules and the TPD charge-transport layer.

For zero bias ($V = 0$), the MEH-PPV fluorescence (photoluminescence) is indistinguishable from that previously reported for isolated MEH-PPV single molecules in PMMA simple thin films⁸ (i.e. without a transport layer or electrodes). As a consequence of reversible photobleaching, discrete and large amplitude jumps to lower fluorescence intensity levels are observed for periods of 10 s or more in the fluorescence vs time traces (e.g., Figure 1). This behavior, which is known as “fluorescence flickering”, is relatively rare in freshly prepared (oxygen-depleted) samples but becomes

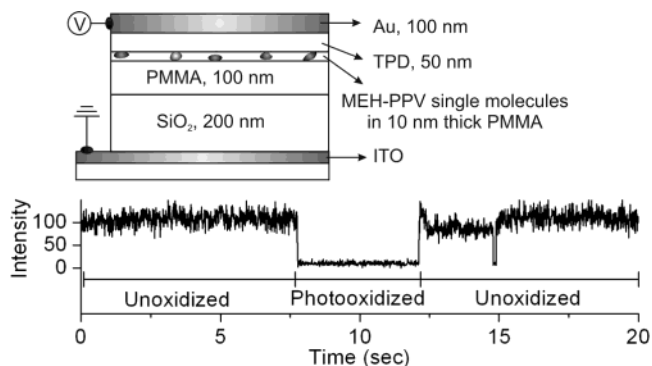


Figure 1. Configuration of the single-molecule charging device and single-MEH-PPV molecule fluorescence intensity vs time trace at zero bias. The single-molecule spectroscopy experimental methods were similar to that described elsewhere.⁸

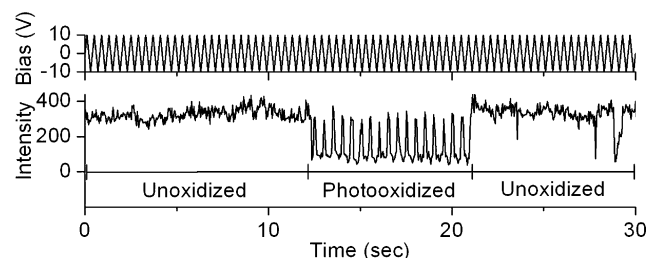


Figure 2. Fluorescence modulation of a single-MEH-PPV molecule by photooxidation and an electrical bias. A triangle voltage sequence was repeatedly applied to the device (upper trace) while collecting fluorescence transients (lower trace).

more common as the sample ages in ambient conditions, i.e. allowing for oxygen diffusion through pinholes in the Au electrode. Fluorescence flickering in single-conjugated polymer molecules has been attributed to efficient energy funneling to a reversibly formed, long-lived quencher site, involving some type of local photooxidation of MEH-PPV. A single-MEH-PPV molecule, in this study, has ~1500 repeat units, corresponding to ~100 coupled chromophores.

Here we report that the fluorescence intensity of a MEH-PPV single molecule in a device is sensitive to the electrical bias of the device. The electrical bias effect, which is especially apparent for photooxidized single molecules, was observed by recording fluorescence intensity vs time (t) traces while repeatedly applying a triangle wave bias voltage sequence (Figures 2 and 3). To emphasize the effect of bias the single-molecule traces were averaged over many cycles of the bias, and the data were replotted in the form of an intensity vs bias curve as shown in Figure 3.

The observed single-molecule behaviors were diverse with two characteristic effects.¹⁰ First, for unphotooxidized MEH-PPV molecules, fluorescence quenching was observed at positive bias, see Figure 3, A and B. Analogous positive bias-induced quenching

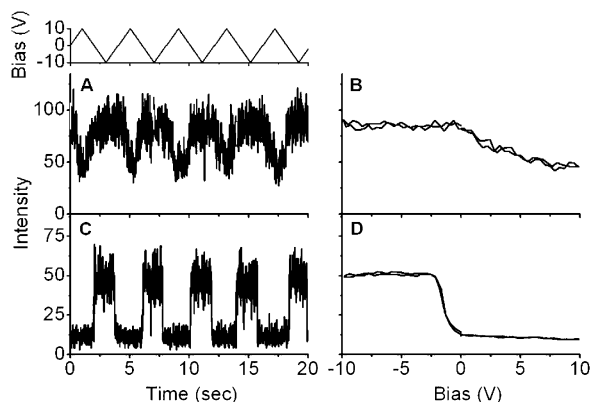


Figure 3. Typical fluorescence modulation by an electrical bias (A–B) of a normal unoxidized MEH-PPV single molecule and (C–D) of a photooxidized molecule. While repeatedly applying a triangle wave voltage sequence (uppermost trace in the left panel) to the device, fluorescence transients were collected (A and C), averaged over many cycles, and replotted as a function of applied voltage (B and D).

has been observed for *neat thin film* MEH-PPV, and assigned to reversible electron transfer between singlet excitons and holes.¹¹ Second, for photooxidized molecules an extraordinary repairing of photobleaching was observed for negative bias. This process fully restores the luminescence to its original value, see Figures 2 and 3, C and D. For example, as the single-MEH-PPV molecule in Figure 2 became photooxidized at $t = 12$ s, the electric bias-induced modulation of the fluorescence significantly increased in magnitude. Correspondingly, when the molecule reverted spontaneously to its unoxidized form at $t = 21$ s, the bias-dependent modulation was diminished.

The discrete sigmoidal behavior in Figure 3D near -1.5 V is indicative of a reversible single-electron transfer event. Experiments on many different molecules demonstrate that the majority of the observed long-lived quencher sites are reversibly oxidized and reduced by the TPD layer at small negative bias. A candidate for the photobleached form of the polymer is a MEH-PPV⁺/anion complex, in which the nearby anion stabilizes the oxidized MEH-PPV.⁸ Such a complex could be formed by photoinduced electron transfer between MEH-PPV and oxygen, forming MEH-PPV⁺/O₂⁻. Photoinduced electron transfer is indeed consistent with well-known, but poorly understood, persistent photoconductivity of conjugated polymers due to exposure to air.^{5,12} As the electrochemical behavior of superoxide in a solid film is different from that in an aqueous solution, the MEH-PPV⁺/O₂⁻ pair is a plausible candidate for the long-lived MEH-PPV⁺/anion complex. Yet another possibility is the formation of a more stable anion such as OH⁻ from the reaction of superoxide with water which is another common impurity in the device.¹³ The reversible oxidation/reneutralization and extraordinary bias-induced repair process apparently excludes typical singlet-oxygen oxidation products such as dioxetanes and endoperoxides, since these latter species would be expected to exhibit nonreversible reduction/oxidation by charge carriers.^{3,14}

The injection of holes at positive bias is consistent with published current–voltage data on OLED-like devices,^{15,16} which demonstrate that holes are injected from gold into TPD at biases of 0–10 V, depending on layer thicknesses and processing conditions. The relatively gradual, i.e., nonsigmoidal, dependence of the quenching

efficiency of unoxidized molecules on bias in Figure 3B, implies that quenching of each molecule is induced by several holes—each with a small quenching efficiency. This suggests that the holes may not fully occupy the MEH-PPV single molecules but, rather, remain in the TPD layer. MEH-PPV hole polarons in bulk MEH-PPV have been reported to be highly efficient (>50%) quenchers.¹¹ The absence of fully occupied MEH-PPV holes at positive bias in the device in Figure 1 is not surprising since there are 10⁶ TPD molecules per MEH-PPV, and TPD and MEH-PPV have comparable HOMO energies. The poor contact between the TPD and PMMA layers can also deter the hole injection. The atomic force microscopy image of thermally evaporated 10-nm TPD layer on PMMA film revealed incomplete coverage, presumably due to unfavorable wetting of TPD on PMMA.

Furthermore, the single-molecule observations reported herein are consistent with published near-field scanning optical microscopy (NSOM) experiments¹⁷ on bulk MEH-PPV which reveal MEH-PPV photoluminescence quenching with a negatively biased NSOM tip (collecting hole polarons in the illumination area) and enhanced photoluminescence by a positive tip (repelling hole polarons).

In summary, reversible and bias-dependent photoluminescence studies on MEH-PPV molecules indicate that the initial photooxidation products of conjugated polymers are charged species, rather than covalent oxidation products, and suggest a strong relationship among photobleaching, charge separation, and persistent photoconductivity of organic conjugated materials.

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