

Radiation-induced photoluminescence quenching of phenylene vinylene oligomer thin films

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We have studied the radiation-induced photoluminescence (PL) quenching and the associated electronic structure modification of a light-emitting conjugated oligomer, namely, 1,4-bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene (4PV), in the absence of oxygen. We found that a short period of exposure to the radiation sources used in UV or x-ray photoelectron spectroscopies (UPS or XPS) resulted in total PL quenching in 4PV. Although there was no detectable change in the XPS C 1s core-level spectra UPS valence spectra indicated the disappearance of the vinylene peak upon exposure to UV radiation. This suggests the destruction of the vinylene groups, and the possible creation of radical species, which may serve as PL quenching sites. We also found that the modification in the electronic structure by Ca deposition masks that by radiation, although both quenches the PL effectively. [S0163-1829(97)08024-7]

Organic light-emitting materials ranging from tris-(8-hydroxyquinoline) aluminum (Alq₃),¹ a sublimable compound, to poly(*p*-phenylene vinylene) (PPV),² a conjugated polymer, have recently attracted much interest due to their intriguing physical properties and potential applications in light emitting devices and flat panel displays.³⁻⁵ Extensive studies using surface analytical tools on these materials have generated important information on the electronic structures and interface properties.^{6,7} However, the relation between the modification of the luminescence and the electronic structure of the material has not been reported. The clarification of such a relationship may provide valuable insights into the understanding of the organic electroluminescence phenomenon.

It has been established that the same excited species is responsible for both photoluminescence (PL) and electroluminescence in PPV.⁸ PL studies have generated important information on the properties of organic materials, such as metal-induced⁹ and photo-oxidation¹⁰ quenching. In this paper, we report the observation of radiation induced quenching of the PL and the associated electronic structure modification of 1,4-bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene (4PV), an oligomer of PPV. The use of 4PV enabled us to prepare thin films in an ultrahigh vacuum (UHV) environment, yielding films free of impurities. This in turn inhibits the occurrence of degradation processes, such as photooxidation, a process known to quench the luminescence of PPV.¹⁰ The radiation sources are commonly used in x-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) with photon energies of 1253.6 eV (Mg K α) and 21.2 eV (He I discharge), respectively. We found that both x-ray and ultraviolet (UV) radiations quenched the PL completely in a time scale of the order of 30 min. The UPS spectra revealed the breaking of the vinylene double bonds which was confirmed by the PL and absorption spectra. We also found that the

modification in the electronic structure by Ca deposition masks that by radiation, although both quench the PL effectively.

The experiment was done in an UHV main chamber¹¹ with a base pressure of 1×10^{-10} Torr. The chamber was equipped with metal deposition sources, a He discharge lamp, an angle-resolved electron energy analyzer, and a Mg K α x-ray source. The overall energy resolutions of XPS and UPS were about 1.2 and 0.2 eV, respectively. The synthesis of 4PV was described elsewhere.¹² The 4PV film (300 Å) was deposited onto an indium tin oxide (ITO) substrate by thermal evaporation in a separate UHV chamber. Film thickness was monitored by a quartz-crystal microbalance, and the deposition rate was about 2.0 Å/min. The evaporated sample was then transferred into the main chamber *in situ* through a gate valve for PL data acquisition. No detectable impurities were found for the evaporated 4PV films as observed by XPS. An Oriel 77501 fiber optic light source with regulated lamp was used to produce the excitation light for PL. The PL spectra obtained immediately after the light source was turned on, and 5 h later, were identical in both shape and intensity, affirming the stability of the light source as well as the 4PV film in the UHV environment. A Carl Zeiss M40III prism monochromator with variable entrance and exit slits was used to obtain an excitation wavelength of 380 nm. PL was monitored with a Photo-Research Spectra-Scan 650 photo colorimeter. The absorption and PL spectra of a pristine and a UV-exposed sample were also done in ambient atmosphere using a Perkin-Elmer Lambda9 spectrophotometer, and a Spex Fluorolog-2 fluorometer equipped with a DM3000F spectroscopy computer where the samples were positioned such that the emission was detected at 22.5° from the incident beam. The UPS lamp discharge area was 30 cm away from the sample, and the UV light was incident on the sample at 52.2° from the surface normal. The center

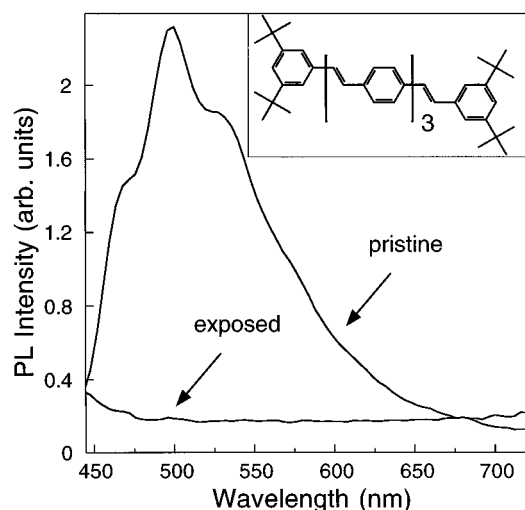


FIG. 1. PL spectra of 300-Å 4PV film before and after a 30-min exposure to UV radiation of the magnitude needed for UPS, 21.2 eV. Exposure to UV effectively quenches the PL.

of the end of the x-ray source is 1 cm from the sample surface, also at an angle of 52.2° from the surface normal. For our setup, it is difficult to estimate the photon flux in both cases. However, in the following paragraph we have endeavored to include a rough estimate of the photon flux using the photocurrent.

The PL of 4PV, measured in UHV, before and after a 30-min exposure to 21.2-eV UV radiation of the magnitude typical for UPS, are shown in Fig. 1. The structure of 4PV is shown in the inset of Fig. 1. The PL spectrum before UV exposure is identical to that presented by Woo *et al.*,¹³ UV exposure for 30 min results in a total quenching of PL. Noting that the photocurrent generated by our UV source was 40 nA, and that 1000 photons typically produce one photoelectron, we could estimate that there are 2.5×10^{14} photons per second hitting the sample. Given that the size of the UV spot is approximately 0.79 mm^2 , this is equivalent to a photon flux of 3.2×10^{20} photons/ m^2 . This is only a crude estimate since secondary electrons also contribute to the photocurrent. Nevertheless, it gives a basis for comparison if similar investigations were to be conducted. A similar PL quenching behavior was observed after exposure to an unmonochromatized Mg $K\alpha$ x-ray radiation at a power setting of 14.0 kV $\times$ 20.0 mA for 10 min. It is difficult, however, to estimate the x-ray photon flux at the sample surface since the radiation is not focused, and the photocurrent measured may have contributions other than from the sample.

Figure 2 shows the evolution of the valence band spectrum taken with a 21.2-eV He I UV source as a function of UV exposure time t . For the unexposed 4PV, $t=0$, features similar to those of pristine PPV (Ref. 14) and 5PV (Ref. 15) are well resolved. The highest occupied molecular orbital (HOMO) feature, which has been attributed to the delocalized π orbitals of the vinylene groups,^{14,15} starts at about binding energy 1.9 eV and peaks at 2.8 eV, with respect to the Fermi level. The Fermi level was obtained by evaporating Ag on the organic layer and locating the Fermi edge. The peak observed at about 4.3 eV is due to the π orbitals localized in the phenylene rings. As the exposure times increased,

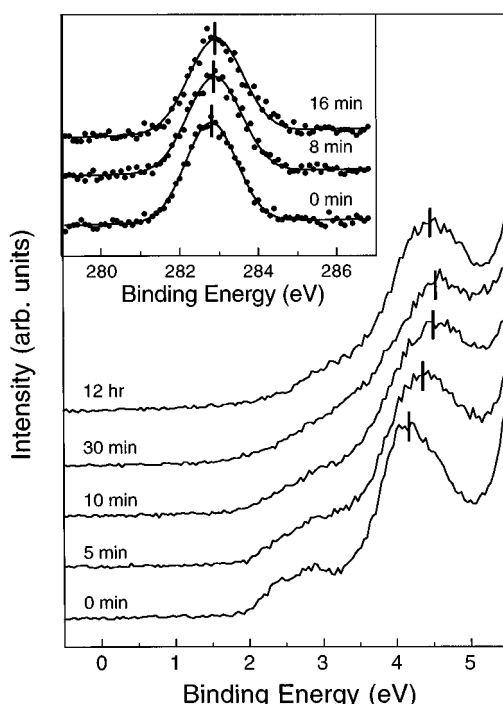
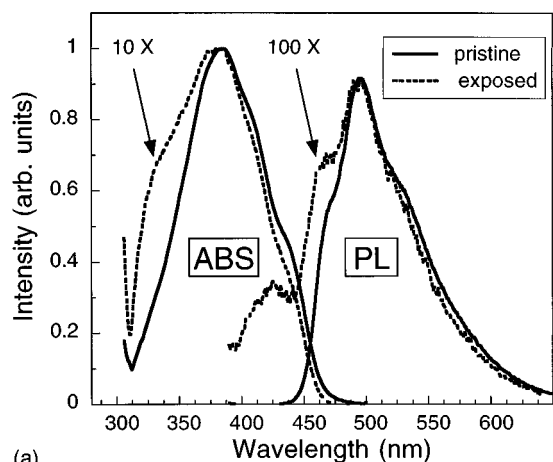


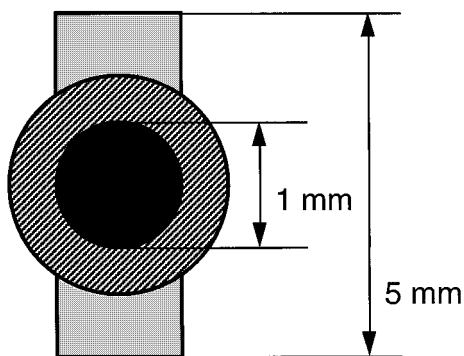
FIG. 2. Evolution of He I ($h\nu = 21.2 \text{ eV}$) UPS spectra for 4PV as a function of UV exposure time t . The vinylene feature, at 2.8 eV, vanishes and the phenylene feature shifts to higher binding energy by $t = 10 \text{ min}$. The inset shows no discernible changes in the position and shape of the XPS C 1s peak for $t = 0$ –16 min.

two distinct changes were observed. First, the 2.8-eV HOMO feature observed in the $t=0$ spectrum started to disappear, indicating the destruction of the vinylene bonds. Second, the 4.3-eV feature was seen to shift to higher binding energies, up to the $t=10 \text{ min}$ spectrum, before stabilizing at roughly 4.5 eV. Although the position of this feature has shifted, the peak shape is largely unaffected,¹⁶ indicating that the phenylene π orbitals are not affected by the UV radiation, and do not directly participate in the UV-induced PL quenching. The inset shows the evolution of XPS C 1s peak obtained for 4PV as a function of x-ray exposure time. No discernible changes were observed in the peak shape and position up to $t = 16 \text{ min}$. Considering that a 10-min exposure was sufficient to quench the PL, it is reasonable to conclude that the core levels are not highly sensitive to the change that causes the PL quenching. Furthermore, our XPS studies on PPV have produced no variation in shape and less than 0.05-eV shift in position in the C 1s XPS spectra even after 4 h of x-ray exposure.

The absorption and PL spectra of 4PV, obtained in ambient atmosphere, taken before and after a 12-h exposure to 21.2-eV UV light, are shown in Fig. 3(a). An excitation wavelength of 380 nm was used to obtain the PL spectra. Since the UV light is focused on an area approximately 0.79 mm^2 , a dark spot is seen in the middle of the UV exposed sample. The darkened area shown in Fig. 3(b) represents the spot hit directly by the UV light, while the surrounding striped region represents a region that is indirectly damaged by the UV light. The latter region still luminesces, but with an intensity much lower than that of pristine 4PV. The rectangle in Fig. 3(b) represents the area sampled by the



(a)



(b)

FIG. 3. (a) The absorption and PL spectra of 4PV before and after exposure to UV, excited by 380-nm light. The absorption and PL of the unexposed 4PV is ten times and 100 times larger than its exposed counterpart, respectively. Components attributed to the formation of oligomers of shorter length were observed. (b) The UV directly illuminated and indirectly illuminated regions are represented by the dark spot and striped area, respectively. The rectangle represents the area sampled by the Spex Fluorolog-2 fluorometer.

Spex Fluorolog-2 fluorometer. The spectra shown in Fig. 3(a) were obtained with the Spex Fluorolog-2 fluorometer, which measures PL from the dotted region. So the PL in Fig. 3(a) was actually a convolution of the small directly illuminated area (darkened spot), surrounding diffusively illuminated area (striped region) and the unaffected 4PV (dotted region), while the PL shown in Fig. 1 was focused fully on the dark spot. Therefore, there is no discrepancy between Figs. 1 and 3(a). The intensity of 4PV absorption spectrum was roughly ten times weaker after UV exposure, while that of PL spectra was approximately 100 times weaker. Woo *et al.*¹³ obtained absorption and PL spectra for oligomers of PPV ranging from 2PV to 6PV. The numbers in the names of the oligomers correspond to the number of vinylene groups. A shift of the absorption curves to lower wavelengths was seen for shorter length oligomers. The shape and position of our absorption and PL spectra are consistent with the 4PV spectra obtained by Woo *et al.*¹³ As is evident from Fig. 3(a), the absorption curve of the UV-exposed film is much broader and has an extra component at a wavelength between 310 and 380 nm. This component, which has a peak at 344 nm, is seen in the 2PV absorption curve obtained by Woo *et al.*,¹³ but not seen in the absorption spectra of the longer oligo-

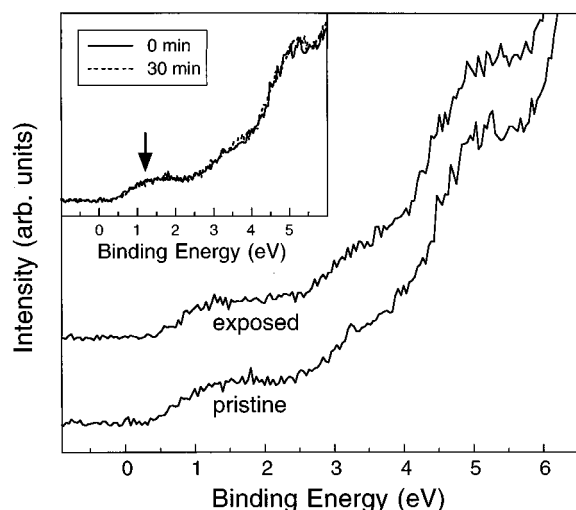


FIG. 4. The UPS spectra of a Ca/4PV/ITO sample for both the dead and fresh spots, taken at $t=30$ min. The inset shows the UPS spectra for the fresh spot taken at $t=0$ and 30 min.

mers. This suggests the formation of oligomers of shorter lengths due to the breaking of some of the vinylene double bonds, as implied by our UPS data. However, the breaking of the vinylene chain not only shortens the conjugation length, it may also cause the formation of radicals.¹⁷ These radicals are very reactive and capable of quenching the PL (Refs. 18 and 19) either acting as exciton traps, or causing cross linking of the chains,²⁰ yielding a nonluminescent product.

The PL spectrum of the unexposed 4PV film has three distinct features at 468, 498, and 530 nm. All three features are also seen in the UV-exposed film, but an extra feature is seen at 438 nm. Again by comparison with the PL obtained by Woo *et al.*¹³ for PPV oligomers, we attribute these changes to the formation of shorter length oligomers. Their PL spectra of 4PV to 6PV showed features similar to our 4PV PL. However, as we go from 4PV to 2PV as the film is exposed to radiation, the features at 495 and 560 nm start to decrease, and eventually vanish. The PL spectra of 2PV had two features, one at 468 nm, and the other at roughly 438 nm. This clearly indicates that our UV irradiated film consists of a mixture of oligomers with four repeat units or less.

We have observed that metal deposition also produces extensive PL quenching.⁹ We therefore investigated and compared the modification of the electronic structure of 4PV due to these two quenching processes. We first irradiated a portion of a 4PV/ITO film with the UV radiation for 35 min, after which we deposited 5 Å of Ca on the entire film. We then took UPS measurements at various exposure times up to $t=30$ min, for both the dead (UV exposed) spot, and a fresh (not exposed) spot. The UPS spectra of the valence region of both the dead and fresh spots, taken at $t=30$ min, are shown in Fig. 4. Due to Ca-induced changes in the valence electronic structure, the feature attributed to the phenylene ring has moved to higher binding energy by about 1.1 eV, which is consistent with our previous work.¹⁵ No discernible differences were seen between the spectra of the fresh and dead spots. The inset of Fig. 4 shows the valence-band spectra for the fresh spot for $t=0$ and 30 min. Again no discernible differences were seen between the two. Since our previous

work have shown that the vinylene feature vanishes upon deposition of Ca,¹⁵ and that the PL of 4PV is quenched by Ca,⁹ it could very well be that the deposited Ca atoms are affecting the 4PV film in a manner similar to the way UV radiation affects it. These results indicate that the metal-induced changes dominate the valence electronic structure and masks the radiation induced ones. Alternatively, the reaction between Ca and 4PV,¹⁵ through charge transfer, for example, may not only lead to PL quenching, but may also stabilize the molecule against radiation damage. This interpretation is also consistent with our previous work,²¹ which shows that Ca disrupts the 4PV layer to a maximum extent of 50 Å.

In summary, we have shown that the PL of 4PV is quenched by exposure to 21.2-eV UV and 1253.6-eV x-ray radiation, even in the absence of oxygen. UPS, PL, and absorption spectra all indicate that the radiation breaks the vinylene double bonds of 4PV, yielding radicals which may, whether directly or indirectly, quench the PL. It is observed that XPS core-level spectra are not sensitive to these radiation-induced changes. In addition, metal-induced spectral changes were seen to dominate radiation-induced ones in UPS.

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