Gap-State Induced Photoluminescence Quenching of Phenylene Vinylene Oligomer and Its Recovery by Oxidation

Y. Park,[1] V.-E. Choong,[1] B. R. Hsieh,[2] C. W. Tang,[3] and Y. Gao[1]

[1]*Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627*
[2]*Xerox Corporation, 114-39D, 800 Phillips Road, Webster, New York 14580*
[3]*Eastman Kodak Company, Rochester, New York 14650*
(Received 18 October 1996)

We demonstrate that the gap states at the interface of Ca and a phenylene vinylene oligomer thin film are responsible for the dramatic quenching of its photoluminescence (PL). Upon oxidation of the Ca layer, the midgap states are removed, and the PL intensity recovers. From the cumulative Ca deposition and oxidation study, a 30 Å Ca oxide layer between the oligomer and the Ca metal prevents PL quenching due to metal induced midgap states. The implications of these results in the design and operation of organic light-emitting devices are discussed. [S0031-9007(97)03206-7]

The discovery of electroluminescence (EL) in conjugated polymers such as poly(p -phenylene vinylene) (PPV) has stimulated intensive research on the photophysics and device physics of organic materials [1]. One of the key issues for organic semiconductors is the understanding of interfaces, since organic devices are characterized by thin film structures of typical effective thicknesses on the order of 100 nm. Thus, the distinction between the bulk and the interface is blurred. The demonstration that a multilayer structure is critical to the improvement of device performance further emphasizes the importance of interfaces [2]. In a typical organic light-emitting device (LED), a metal layer is used as the electrode to inject charge carriers into the organic materials. The radiative recombination of electrons and holes produces the EL. The role of the metal electrode as merely an agent for charge injection has been challenged by our recent observation [3] that the photoluminescence (PL) of 1,4-bis[4-(3,5-di-t-butylstyryl)styryl]benzene (4PV, Fig. 1 inset) can be severely quenched by the deposition of Ca, a metal known as a superior cathode for PPV based EL devices due to its low work function. The fact that the measured spectra for both EL and PL are basically identical implies that both processes are due to the same emissive species. Consequently, the observation of metal-induced PL quenching may be important for single-layer LEDs. This quenching mechanism is particularly significant for PPV based LEDs since the recombination region is near the metal cathode.

At a metal/organic interface, charge transfer from the metal to the organic materials may induce gap states associated with lattice deformation of the organic material [4]. The formation of gap states, of which polaron and bipolaron states are examples, have been experimentally observed in polymers with similar chemical structures [4–7]. However, the effect of these states on the luminescence properties of organic materials has not been explored. In this Letter, we present for the first time strong evidence that the formation of gap states upon Ca deposition is responsible for the observed PL quench-

ing in 4PV. We demonstrate that the removal of such states, accomplished by exposure to oxygen, recovers the PL. This observation therefore presents a new aspect of metal/organic interaction, and may shed light on the direction to significantly improve the organic LED efficiency. We estimate that a proper oxidation of Ca at the Ca/4PV interface could significantly improve the efficiency of a single-layer EL device. We chose 4PV as a model system since it can be sublimed to form an impurity-free thin film in an ultrahigh vacuum (UHV) environment, which avoids the screening of physical phenomena by impurities. Also, the size of 4PV is comparable to the typical conjugation length of PPV (5–10 units).

The synthesis and basic photophysical properties of 4PV are described in detail elsewhere [8]. The thickness of the 4PV films were 300 Å. The films were
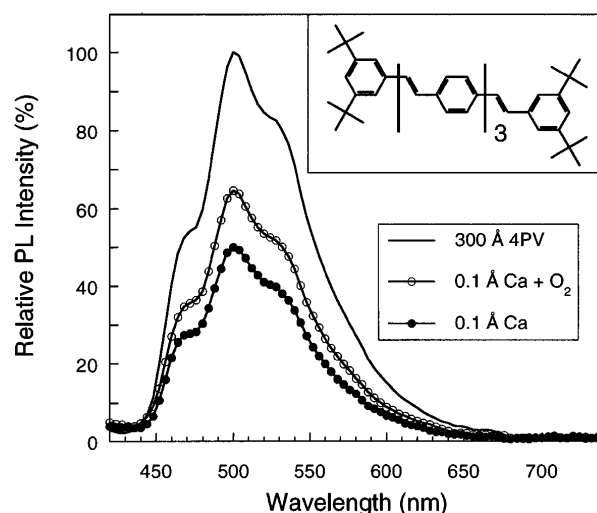

FIG. 1. The photoluminescence (PL) spectra for 4PV (top curve), Ca/4PV (bottom curve), and oxidized Ca/4PV (middle curve). Deposition of 0.1 Å Ca reduced PL by 50%. Exposure to oxygen for 4.5 h at 1×10^{-6} Torr (8.1×10^{4} L) results in PL recovery to 65%. The inset shows the molecular structure of 4PV.

deposited on Au coated Si substrates by thermal evaporation in UHV at a rate of approximately 2 Å per minute. The evaporated sample was then transferred to the analysis chamber *in situ* for PL and ultraviolet photoelectron spectroscopy (UPS) data acquisition as well as Ca deposition (the deposition rate was approximately 1.0 Å per minute). We used UPS to probe the valence electronic structure of Ca/4PV. The entire PL and UPS experiments were performed in a UHV chamber with a base pressure of 1×10^{-10} Torr. An Oriel 77501 fiber-optic light source with a regulated lamp was used to produce the excitation light for PL, which went into the UHV chamber through a quartz window. The excitation wavelength was chosen using a Carl Zeiss M4QIII prism monochromator. The excitation wavelength 400 nm produced the highest luminescence intensity for 4PV. The PL data were recorded with a Photo-Research SpectraScan 650 photo colorimeter. The UPS spectra were taken with a 21.2 eV He I discharge lamp and a hemispherical electron energy analyzer. This combination resulted in an overall energy resolution of 0.2 eV. The oxygen exposure was performed by filling the vacuum chamber with pure oxygen gas (99.999%) at the pressure of 5×10^{-6} Torr. The exposure was measured in the unit of Langmuir (L) which is defined as 1×10^{-6} Torr sec. The sample was kept in darkness during the exposure to eliminate possible contributions to the PL quenching due to photo-oxidation and the formation of carbonyl groups in 4PV [9].

The PL quenching due to Ca deposition and its recovery after exposure to oxygen are demonstrated in Fig. 1. The top curve in Fig. 1 is the PL spectrum for a pristine 300 Å 4PV film. The bottom curve is the spectrum taken after 0.1 Å Ca was deposited. As reported previously [3], the dramatic quenching (~50%) of the PL intensity is clearly observed. Since 0.1 Å is not even 1 monolayer of Ca, it is clear that the quenching is not due to the metallic nature of Ca. However, the PL intensity recovered to about 65% of the pristine 4PV value after the sample was exposed to O_2 for 4.5 h at 5×10^{-6} Torr (8.1×10^4 L), shown in the middle curve in Fig. 1. Since the PL quenching and recovery was most prominent at a Ca coverage of 4 Å, we studied the correlation between the PL quenching and recovery with the changes in the electronic structure in a 4 Å Ca/4PV system.

The UPS spectra near the Fermi level for a pristine (300 Å), fresh-Ca/4PV, and oxidized-Ca/4PV (9×10^3 L) are shown in Fig. 2. The spectrum of pristine 4PV exhibits the highest occupied molecular orbital (HOMO) feature near 2.4 eV [7], and is similar to that reported for PPV [10]. Upon deposition of 4 Å of Ca, a broad peak near 1.2 eV was clearly observed. This feature indicates the formation of new states inside the energy gap [5,11]. In the literature, such gap states have been attributed to formation of bipolarons by charge transfer from the metal to the organic materials [5]. Although we were not able to resolve the components of the gap
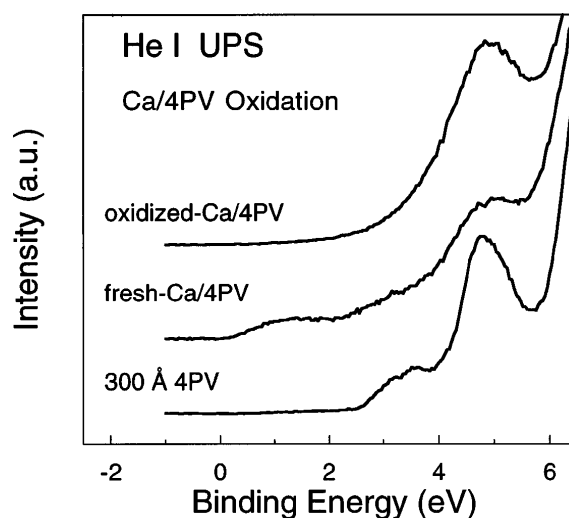
FIG. 2. The changes in UPS spectra upon Ca deposition and oxidation. The bottom curve shows the valence band spectrum of 300 Å pristine 4PV film. The middle curve is when 4 Å of Ca was deposited on the 4PV film. The formation of states in the energy gap region is clearly observed. The top curve shows the same valence band spectrum but after oxidation by 9×10^3 L of exposure.

states, Bröms *et al.* were able to resolve the emergence of two new electronic states which they attributed to the formation of bipolarons [10]. However, when the fresh-Ca/4PV sample was exposed to oxygen, the gap states completely disappeared as seen in the top curve of Fig. 2. This is strong evidence that the formation and disappearance of gap states may be responsible for the observed PL quenching and recovery, respectively. One possible scenario for gap-state induced PL quenching is depicted in Fig. 3. The bound electron-hole pairs (excitons or polaron excitons) are excited by external radiation. The exciton diffuses an average distance of approximately 200 Å [3] before recombination occurs. The deposition of Ca creates a region of excess charge at the interface with 4PV. The excess charges from Ca form occupied gap states. When a migrating exciton encounters this region, the hole can jump to the filled gap states and give the excess energy to the electron. This process is similar to the PL quenching observed in acceptor doped conjugated polymers [12–14]. The oxidation of Ca atoms then withdraws the excess charges from 4PV. This removes the gap states in 4PV as seen in Fig. 2, and the PL intensity is observed to recover.

From these experimental results, the PL quenching induced by the deposition of metal can be reversed by oxidation. However, a metal electrode much thicker than 4 Å is typically employed in a real device. Therefore, it is important to investigate how the PL intensity evolves with increasing Ca and Ca-oxide thickness. With this in mind, we performed repetitive Ca deposition (PL quenching) and oxygen exposure (PL recovery) cycles up to 50 Å with incremental Ca thickness. The PL spectra were taken before
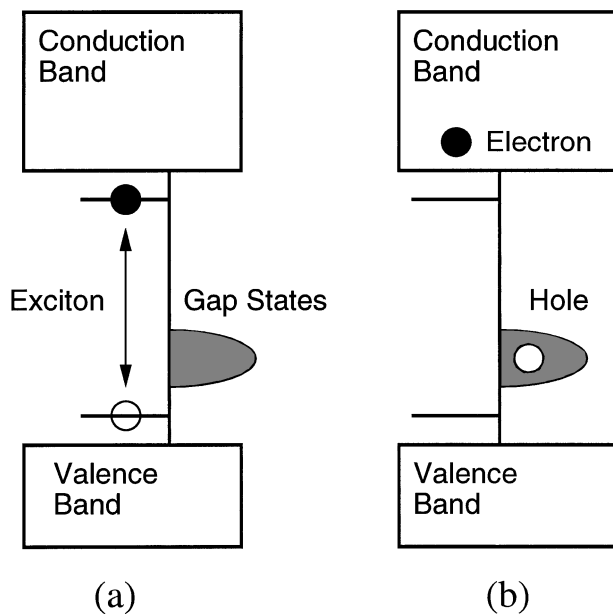
FIG. 3. A simple energy diagram near the Ca/4PV interface depicting the exciton dissociation process in the presence of gap states. (a) The exciton is away from the *doped* region. (b) After the exciton dissociation has occurred, the electron moves to a higher energy states in the conduction band in order to conserve the pair energy [14].

and after Ca deposition. Subsequently similar spectra were taken after exposure to 5×10^{-6} Torr of O_2 for 5 min (1.5×10^3 L), 30 min (1.05×10^4 L), and several hours ($\sim 10^5$ L). This process was repeated on the same sample at several different total Ca thickness (0.1, 1.0, 4.0, 8.0, 15, 30, and 50 Å). The fluctuation of PL intensity during such a cycle is summarized in Fig. 4(a). The horizontal axis indicates the accumulated oxygen exposure in L and the total Ca thickness is indicated in the figure. At initial Ca coverages (<8 Å), fresh deposition of Ca still greatly affects the PL even though previously deposited and oxidized Ca already exists on 4PV. This indicates that the oxidized Ca underlayer in this thickness regime cannot protect 4PV from Ca-induced PL quenching. Also, the recovery of PL after O_2 exposure is more prominent in the initial stages, particularly at 4 Å. However, when the oxidized Ca layer thickness approaches approximately 30 Å, additional Ca deposition does not substantially affect the PL intensity. The thicker oxide layer is effectively protecting the 4PV from the PL quenching effect of freshly deposited Ca.

The crucial role of the oxidized Ca layer is more clear when we compare the PL intensity evolution with and without the oxidation process, as shown in Fig. 4(b). The bottom curve of Fig. 4(b) is the PL intensity as a function of Ca thickness without the oxidation process, which shows a monotonic intensity decrease [3]. The middle curve is the PL intensity after each fresh deposition of Ca on previously oxidized Ca/4PV. For example the data point at 8 Å is the PL intensity after 4 Å of fresh
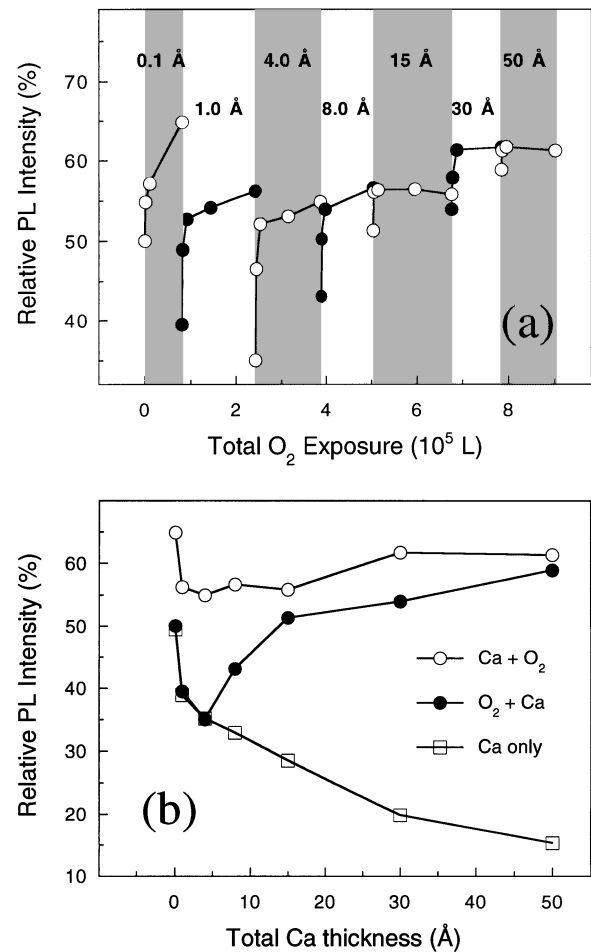

FIG. 4. (a) PL intensity under a sequence of Ca deposition and oxidation cycles. The horizontal axis is the accumulated oxygen exposure. The connected circles indicate the PL recovery process upon oxidation at the Ca thickness indicated. (b) The PL intensity taken with respect to Ca thickness under three different conditions. The bottom curve shows the PL quenching process without the exposure to oxygen. It is clear that the oxide Ca layer protects the 4PV PL intensity at about 30 Å while a monatomic decrease is evident when no oxygen exposure is involved.

Ca was deposited on the 4 Å oxidized-Ca/4PV layer. The middle curve shows how effective a given Ca oxide layer is in protecting 4PV PL from fresh Ca. The top curve in Fig. 4(b) shows the PL intensity at the end of the oxidation process at a given Ca thickness. The top and middle curves are taken from the data shown in Fig. 4(a). In the early stages of Ca deposition (<4 Å), the middle curve is almost identical with the bottom curve indicating that the existence of a very thin (<4 Å) oxidized Ca layer has no effect on the changes in PL upon additional deposition of fresh Ca. However, a thicker Ca oxide layer, about 30 Å, effectively protects the 4PV layer from further PL quenching. From the top curve, the PL intensity of oxidized Ca/4PV remains between 55% and 65% of that of pristine 4PV up to 50 Å of oxidized Ca

layer. On the other hand, the PL from unoxidized Ca decreases down to around 15% after deposition of 50 Å Ca [3]. These numbers suggest that a proper oxidation of Ca at the Ca/4PV interface could significantly improve the efficiency of a single-layer EL device.

What we have observed suggests that an organic LED, employing a hole transporting material as an active layer and a Ca metal layer as the electron injecting electrode, would perform with higher efficiency when 30–50 Å of the metal layer at the Ca/organic interface was simply oxidized before the rest of the electrode was deposited. However, this is contingent on whether such a layer would greatly hinder the carrier injection. From our results, we could expect that an LED based on a 300 Å thick 4PV layer will exhibit nearly 4 times efficiency improvement. There have been several reports that suggest improvement in EL performance by introduction of a foreign layer between the active layer and the electron injecting electrode. Bröms et al. reported [15] that PPV based EL devices with a *dirty* Ca electrode fabricated in 10^{-6} Torr of oxygen partial pressure performed better than the one fabricated in UHV (10^{-10} Torr). Although no correlation between the changes in oxidation-induced electronic structure and enhanced EL performance was suggested in their work, the existence of such a correlation is clear from our results. In addition to suppressing exciton dissociation, the oxide layer (an insulating layer) may facilitate charge carrier confinement in the active layer of EL devices, further enhancing the performance. This was demonstrated by Kim et al., who inserted an insulating layer of poly(methyl methacrylate) (PMMA) between the PPV layer and the Al electrode [16]. They showed that their EL device performed best when the PMMA layer thickness was about 60 Å. Judging from the measured threshold voltage, the PMMA layer of this thickness did not affect the electron tunneling efficiency. Another example is a polymeric LED consisting of multiple bilayers of alternating active and insulating layers [17]. When the multilayer was terminated by the insulating layer on which the metal electrode was deposited, the LED performed better than when the multilayer was terminated with the active layer. In view of these reports, it is clear that a foreign nonmetallic layer at the interface between the metal and the active EL layer enhances the device performance by avoiding metal-induced quenching of excitons.

Finally, PL in our 4PV thin films did not recover to its original value even after prolonged exposure to oxygen. Several possible origins may explain the final PL loss of 35%. One, although extreme care was taken not to expose the sample to light and oxygen at the same time, the oxygen molecule may have adsorbed on the sample and later reacted with 4PV when the light was available. This would create PL quenching centers, such as carbonyl groups. Two, metal deposition could induce structural changes in the organic layers or the deposited Ca could

diffuse further into the 4PV. PL loss due to both of these may not be recovered by exposure to oxygen. The width of Ca-induced gap states is broad (FWHM ≈ 1.0 eV). Therefore, the small difference in the ionization potential between 4PV and PPV (<0.5 eV) should not affect the quenching and recovery mechanisms in both materials.

In summary, we have presented strong evidence that the formation and removal of gap states in Ca/4PV interface may be responsible for the quenching and recovery of its PL. Based on this observation, a simple picture for the gap-state mediated exciton dissociation is proposed. From the PL intensity variation on cumulative Ca deposition/oxidation cycles, it is estimated that approximately 30 Å of oxidized Ca layer can be used as a protective layer against PL quenching due to fresh Ca deposition.

---

[1] J. H. Burroughes et al., Nature (London) **347**, 539 (1990); G. Gustafsson et al., Nature (London) **357**, 447 (1992); J. R. Sheats et al., Science **273**, 884 (1996).

[2] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987); J. Kido, M. Kimura, and K. Nagai, Science **267**, 1332 (1995).

[3] V. Choong et al., Appl. Phys. Lett. **69**, 1492 (1996).

[4] S. A. Brazovskii and N. N. Kirova, Synth. Met. **55-57**, 4385 (1993); P. S. Davids, A. Saxena, and D. L. Smith, J. Appl. Phys. **78**, 4244 (1995).

[5] M. Fahlman et al., Chem. Phys. Lett. **214**, 327 (1993); D. Steinmüller, M. G. Ramsey, and F. P. Netzer, Phys. Rev. B **47**, 13 323 (1993); G. Iucci et al., Chem. Phys. Lett. **244**, 139 (1995).

[6] Y. Park et al., Polym. Preprints **36**, 382 (1995).

[7] Y. Park et al., Appl. Phys. Lett. **69**, 1080 (1996).

[8] R. Schenk et al., J. Chem. Soc., Chem. Commun. **22**, 1673 (1990); J. Am. Chem. Soc. **113**, 2634 (1991); H. S. Woo et al., Synth. Met. **59**, 13 (1993).

[9] M. Yan et al., Phys. Rev. Lett. **73**, 744 (1994).

[10] P. Dannetun et al., Synth. Met. **67**, 133 (1994); J. L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev. B **26**, 5843 (1982).

[11] E. Ettedgui et al., Phys. Rev. Lett. **76**, 299 (1996).

[12] N. S. Sariciftci et al., Science **258**, 1474 (1992); Morita et al., Solid State Commun. **82**, 249 (1992); K. Yoshino et al., Jpn. J. Appl. Phys. **32**, L359 (1993).

[13] H. Antoniadis and B. R. Hsieh, Chem. Phys. Lett. **238**, 301 (1995).

[14] M. J. Rice and Yu. N. Garstein, Phys. Rev. B **53**, 10 764 (1996).

[15] P. Bröms et al., Synth. Met. **74**, 179 (1995).

[16] Y.-E. Kim, H. Park, and J.-J. Kim, Appl. Phys. Lett. **69**, 599 (1996).

[17] A. C. Fou et al., J. Appl. Phys. **79**, 7501 (1996).