# Destruction of amplified spontaneous emission via chemical doping at low-work-function metal/conjugated polymer interfaces

Bertrand Tremolet de Villers and Benjamin J. Schwartz[a)]
*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569*

The authors investigate how the use of different metal electrodes affects the ability of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) films to undergo amplified spontaneous emission (ASE). High-work-function metals such as Ag or Au have little effect on the ASE threshold, but low-work-function metals such as Ca or Al completely shut off ASE. ASE is restored when a thin spacer layer, such as a few nanometers of polystyrene or oxidized Ca, is introduced between the MEH-PPV film and the Ca or Al electrode. This suggests that low-work-function metals chemically dope the polymer, creating polarons that destroy ASE not only by lowering the gain through emission quenching but primarily by increasing the loss via optical absorption. Thus, the exponential sensitivity of ASE to optical losses provides a spectroscopic probe of conjugated polymer/metal interfaces. © 2007 American Institute of Physics.
[DOI: 10.1063/1.2710188]

It has been over a decade since amplified spontaneous emission[1] (ASE) and optically pumped lasing[2,3] were observed in films of semiconducting polymers, yet in the intervening years, no one has produced an electrically pumped polymer-based diode laser. Although there are several possible explanations as to why electrically pumped lasing has been so difficult to achieve, here we focus on the nature of the metal electrodes used in fabricating conjugated polymer-based optoelectronic devices. In particular, we show that the use of low-work-function metal electrodes, which are critical to high current injection in conjugated polymer-based diodes, leads to chemical doping of the polymer and that the resulting polarons introduce enough optical loss to destroy the ability of the polymer film to undergo ASE or lasing. Thus, because of its exponential sensitivity to optical loss, ASE can be used as an indicator of chemical interactions at polymer/metal interfaces.

To investigate how different electrode metals affect the ability of conjugated polymer films to undergo lasing and ASE, we prepared samples of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), one of the most well-studied semiconducting polymers. We synthesized MEH-PPV by following method b of Neef and Ferraris,[4] except that we halved the concentrations of potassium $t$-butoxide and monomer and we performed the recrystallization from methylene chloride instead of tetrahydrofuran. In an inert atmosphere, we spun 1% w/v solutions of MEH-PPV in chlorobenzene onto precleaned glass substrates at ∼2000 rpm to produce films with thicknesses ranging from 150 to 200 nm (optical densities of 1.5–1.9 at the 500 nm absorption maximum); the films were baked at ∼50 °C for ∼1 h to drive off any excess solvent. We then prepared samples in two basic configurations: glass/MEH-PPV/$M$ or glass/MEH-PPV/spacer/$M$, where $M$=Ag, Al, Ca, or Au and "spacer" is a thin layer of either polystyrene or oxidized Ca, as discussed further below. The metals were thermally evaporated under a vacuum of $10^{-8}$ bar at evaporation rates of 0.1–1.5 nm/s to give a total metal layer thickness of ∼100 nm. The ability of our samples to undergo ASE was investigated by exciting them from their nonmetallated side with ∼100 fs pulses of 490 nm light whose energy was controlled between ∼10 and 800 nJ; the details of our laser setup are described elsewhere.[5,6] Emission was collected ∼50°–55° from the sample normal and analyzed using a fiber optic spectrometer.

Figure 1 shows the emission collected from a ∼150-nm-thick film of MEH-PPV with no top layer as a function of the 490 nm excitation energy. It is clear that once the excitation energy becomes large enough, the emission spectrum changes from the characteristically broad fluorescence spectrum associated with the continuous-wave excitation of MEH-PPV to a much narrower emission dominated by a single peak near 620 nm. This turn on of line narrowing above a well-defined threshold is the classic signature of ASE.[1,3] To characterize the ASE threshold, we integrated the intensity of the ASE peak in each spectrum after subtracting the below-threshold broad fluorescence, whose shape is independent of excitation energy. The ASE threshold of ∼22 nJ/pulse was then determined as the intersection of least-squares fit lines to the low- and high-energy portions of the integrated spectral data, as shown in the inset of Fig. 1. The ASE thresholds determined this way for all of our samples are reported in Table I.

Table I shows that samples with Ag and Au top layers exhibit ASE thresholds that are approximately twice as large as that of the MEH-PPV film without any metal. This modest ASE threshold increase could result either from the fact that adding a metallic top layer modifies the waveguide that confines the emitted light in the gain region or from the fact that some of the polymer film's emission is likely quenched by image dipoles in the metal,[7] resulting in a slight lowering of the gain. Even though these metals slightly raise the ASE threshold, however, it is clear that the presence of Ag and Au does not destroy the gain behavior of the MEH-PPV films, consistent with other studies in which these metals have been used to create feedback structures for optically pumped conjugated polymer-based lasers.[2,3,8]
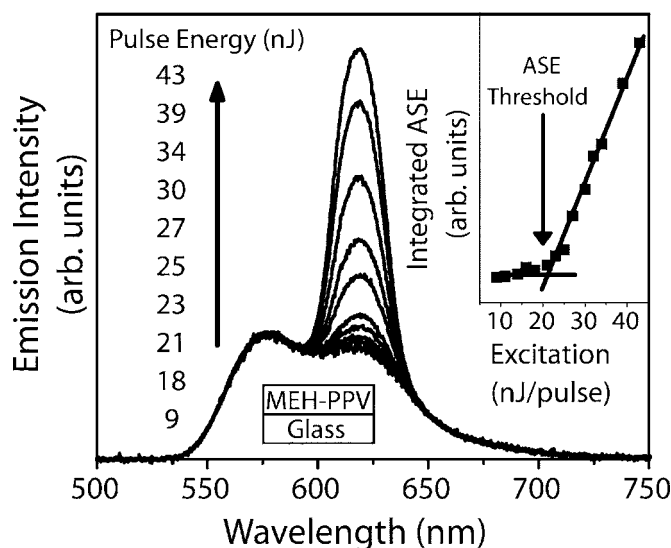
a)Electronic mail: schwartz@chem.ucla.edu

FIG. 1. Normalized emission spectra of a glass/MEH-PPV sample showing the signature line narrowing of ASE as the optical excitation energy is increased. Inset: Integrated intensity of the ASE peak, centered at 620 nm, after subtraction of the below-threshold emission spectrum. The solid lines are least-squares fits to the low- and high-energy portions of the data. The value of the ASE threshold is determined from the intersection of the lines to be ~22 nJ/pulse.
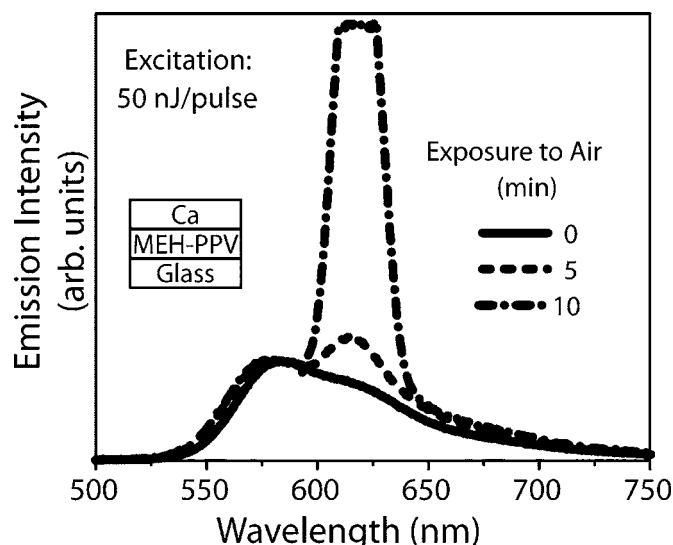


FIG. 2. Normalized emission spectra of an optically excited glass/MEH-PPV/Ca sample that had never been exposed to air (0 min, solid curve) and after 5 min (dashed curve) and 10 min (dot-dashed curve, flat at the top due to saturation of the detector) exposure to air; ASE clearly returns in just a few minutes, showing that doping of the polymer by the metal is oxidatively reversible. The 490 nm excitation energy was ~50 nJ/pulse.

In contrast to Au and Ag, when either of the common cathode metals Ca or Al is evaporated on top of a MEH-PPV film, Table I shows that ASE is completely shut off: the ASE threshold rises above the optical damage limit of the polymer. To investigate whether the reflectivity of Ca or Al played a role in altering the ASE threshold, we prepared samples in which a ~30-nm-thick spacer layer of polystyrene was spin cast between the MEH-PPV film and the Al or Ca top layer. We found that introduction of the transparent spacer layer restored ASE to the samples with a threshold comparable to that of the neat film (Table I), verifying that the optical properties of these metals are not responsible for the shut off of ASE. Instead, we believe that a chemical interaction of the low-work-function metals with the polymer,[9,10] which does not take place with high-work-function metals such as Ag or Au, causes the quenching of ASE.

One reason that a chemical interaction between a conjugated polymer and a low-work-function metal could destroy the ability of the polymer to undergo ASE is that low-work-function metals are known to quench a polymer's fluores-

TABLE I. ASE thresholds of glass/MEH-PPV/top layer samples.

| Top layer | ASE threshold (nJ/pulse)[a] | Work function Φ (eV) |
|---|---|---|
| No top layer | 22±1 | ... |
| Ca | >800[b] | 2.87 |
| Al | >800[b] | 4.20 |
| Ag | 37±16 | 4.64 |
| Au | 50±12 | 5.47 |
| Polystyrene/Ca | 25±2 | ... |
| Polystyrene/Al | 10±1 | ... |
| Oxidized Ca/Ca | <50[c] | ... |

[a]Quoted errors are one standard deviation.
[b]ASE threshold greater sample's optical damage limit (see text).
[c]Pulse energy for this measurement was fixed at 50 nJ.

cence. For example, Park et al. found that the presence of submonolayers of Ca quenched the emission from a phenylene-vinylene oligomer film,[11] consistent with the idea that doping by Ca produces polarons, which are known to quench polymer emission. Park et al. also found, however, that the effects of quenching by Ca only penetrated ~20 nm into the films.[11] Since the films in our samples are ~150 nm thick, it is difficult to rationalize the complete shutoff of ASE solely on the basis of losing only ~13% of the emissive chromophores. Instead, we believe that the presence of the polarons themselves is responsible for the destruction of ASE. It is well known that polaron absorption in MEH-PPV strongly overlaps the polymer's emission and therefore causes the fluorescence and stimulated emission dynamics of the MEH-PPV films to differ.[6] Even if Ca-created polarons remain within a few nanometers of the metal interface, the fact that they absorb the emitted light introduces loss into the optical waveguide or cavity. Thus, polarons created by doping of a conjugated polymer film by low-work-function metals can shut off the ASE because they both lower the gain by fluorescence quenching[6,11] and increase the loss by optical absorption.[12]

One way to verify that chemical reduction of the polymer by low-work-function metals is responsible for the loss of ASE is to investigate whether the chemistry can be reversed. Figure 2 shows the intensity-dependent emission of a glass/MEH-PPV/Ca sample, both before (solid curve) and after (dashed and dotted curves) a few minutes of exposure to air. The data show that the quenched ASE spontaneously returns after only a few minutes, indicating that the doping of MEH-PPV by Ca is at least partially reversible: enough electron polarons must have reacted with oxygen from the air to restore ASE. Of course, oxidation of the doped polymer film also likely creates carbonyl groups or other chemical defects that can quench the polymer's fluorescence.[13] Thus, the fact that oxidation improves the sample's ability to undergo ASE suggests that optical loss by polaron absorption is the primary mechanism by which ASE is shut off. To confirm that

this chemistry happens only at the polymer/metal interface, we made additional samples in which a very thin layer of Ca ($<2$ nm) was evaporated onto the MEH-PPV film, allowed to oxidize for a few minutes, and then a thick ($\sim100$ nm) layer of Ca was evaporated on top of the thin oxidized layer. ASE is readily observed from such samples (Table I), indicating that just a few nanometers of oxidized Ca (as well as a thin polystyrene spacer, as discussed above) can serve as a blocking layer to protect the polymer from chemical doping.

In summary, we have found that the addition of metal overlayers to MEH-PPV films is detrimental to their ability to undergo ASE. High-work-function metals such as Ag or Au modestly increase the ASE threshold, likely due to changes in the character of the waveguide or due to the small amount of quenching of the polymer's emission by the metal. Low-work-function cathode metals such as Ca and Al, however, completely suppress the ability of the polymer to undergo ASE due to chemical doping of the polymer by the metal. The fact that the use of thin spacer layers can restore ASE in the presence of Ca and Al suggests that it is not fluorescence quenching but rather the absorptive loss introduced by the doped polarons that is primarily responsible for shutting off ASE. It is the fact that ASE is exponentially sensitive to absorptive losses that has allowed us to detect the small number of polarons created by chemical doping at the conjugated polymer/metal interface.

Our results have two important implications. First, the fact that ASE is exponentially sensitive to absorptive loss allows it to serve as a unique optical probe of the chemistry that occurs at conjugated polymer/metal interfaces. The data make it clear that Al is capable of doping MEH-PPV but that Ag is not, effectively bracketing the reduction potential of MEH-PPV between 4.20 and 4.64 eV (Table I).[14] The fact that Al can dope the polymer but Ag cannot also explains why Al is a much better cathode material than Ag even though its work function is not that much lower than Ag: the doping of the polymer by Al creates a more Ohmic contact that greatly enhances current injection. Second, the fact that a small number of polarons introduced by reaction with a low-work-function metal can shut off ASE bodes very poorly for the prospects of producing electrically driven conjugated-polymer-based diode lasers. Even if one avoids the use of low-work-function cathodes, any electrically driven polymer device will always contain a significant number of injected polarons. Thus, even diodes that are bright enough to match the excitation densities achieved in optically pumped lasing experiments[15] likely have enough loss that net gain will not be achievable.

[1] F. Hide, M. A. DiazGarcia, B. J. Schwartz, M. R. Andersson, Q. B. Pei, and A. J. Heeger, Science **273**, 1833 (1996).

[2] N. Tessler, G. J. Denton, and R. H. Friend, Nature (London) **382**, 695 (1996).

[3] M. A. DiazGarcia, F. Hide, B. J. Schwartz, M. D. McGehee, M. R. Andersson, and A. J. Heeger, Appl. Phys. Lett. **70**, 3191 (1997).

[4] C. J. Neef and J. P. Ferraris, Macromolecules **37**, 2671 (2004).

[5] T. Q. Nguyen, I. B. Martini, J. Liu, and B. J. Schwartz, J. Phys. Chem. B **104**, 237 (2000).

[6] I. B. Martini, A. D. Smith, and B. J. Schwartz, Phys. Rev. B **69**, 035204 (2004).

[7] H. Becker, S. E. Burns, and R. H. Friend, Phys. Rev. B **56**, 1893 (1997).

[8] M. Reufer, S. Riechel, J. M. Lupton, J. Feldmann, U. Lemmer, D. Schneider, T. Benstem, T. Dobbertin, W. Kowalsky, A. Gombert, K. Forberich, V. Wittwer, and U. Scherf, Appl. Phys. Lett. **84**, 3262 (2004).

[9] J. Birgerson, M. Fahlman, P. Broms, and W. R. Salaneck, Synth. Met. **80**, 125 (1996).

[10] D. W. Lee, K. Kim, J.-I. Jin, and Y. Park, Synth. Met. **143**, 181 (2004).

[11] Y. Park, V. E. Choong, B. R. Hsieh, C. W. Tang, and Y. Gao, Phys. Rev. Lett. **78**, 3955 (1997).

[12] S. Lattante, F. Romano, A. P. Caricato, M. Martino, and M. Anni, Appl. Phys. Lett. **89**, 031108 (2006).

[13] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).

[14] *CRC Handbook of Chemistry and Physics*, 87th ed., edited by D. R. Lide (Taylor and Francis, Boca Raton, FL, 2007).

[15] N. Tessler, N. T. Harrison, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **10**, 64 (1998).