

Luminescence of Organic Materials: Metal Induced Quenching and Its Revival

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Abstract

Organic light-emitting devices (OLED) have demonstrated to have the necessary attributes to be competitive for flat panel displays. In a typical OLED, metallic electrodes are used to inject charge carriers into the organic electroluminescent (EL) medium. We report here severe photoluminescence (PL) quenching of organic thin films comprising of some of the most useful materials, namely tris-(8-hydroxyquinoline) aluminum and 1,4-bis[4-(3,5-di-tert-butylstyryl)styryl]-benzene (4PV), upon sub-monolayer deposition of Al, Ag, and Ca in an ultra high vacuum environment. The quenching can greatly affect the EL device performance. For example, a sub-monolayer coverage of the various metals on a 300 Å 4PV thin film can reduce the PL by as much as 50%. An exciton diffusion length of 200 Å can be estimated from the quenching data. The quenched PL is also observed to be revived partially by oxidation of the Ca overlayer. Valence level photoemission spectra showed that the Ca induced gap states vanishes upon oxidation of the Ca overlayer. These results are discussed in terms of PL quenching by Ca-induced gap states and their removal by oxidation. We also discuss the implications of our results in the performance of optoelectronic devices.

Introduction

The use of organic materials electronic applications, such as light emitting diodes (LEDs), has been gaining momentum in recent years.¹⁻⁵ One of the key issues for the organic semiconductors to be useful is the understanding of interfaces, since organic devices consists of thin film structures with typical effective thicknesses of 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.^{6,7} Injection electroluminescence (EL) has been demonstrated in numerous organic materials ranging from tris-(8-hydroxyquinoline) aluminum (Alq₃),^{6,8} a sublimable compound, to

poly(p-phenylene vinylene) (PPV),⁹ a conjugated polymer. The device structure generally consists of, in sequence, an indium tin oxide (ITO) covered glass as the anode, a thin layer (or multiple layers) of organic materials, and an evaporated metal film as the cathode.

The efficiency of these EL devices has been found to be highly dependent on the injection behaviors of the contacts,¹⁰⁻¹² limited primarily by the electron injection efficiency of the cathode.¹³⁻¹⁶ The role of the metal electrode as merely an agent for charge injection has been challenged by our recent observation¹⁷ that the photo-luminescence (PL) of 1,4-bis[4-(3,5-di-t-butylstyryl)styryl]-benzene (4PV, Figure 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, particularly for PPV based LEDs due to the hole conducting nature of PPV.

At a metal/organic interface, charge transfer from the metal to the organic material may induce gap states associated with lattice deformation of the organic material.^{18,19} The effect of these states on the luminescence properties of organic materials has not been explored. In this paper, we report our systematic investigation to characterize the luminescence quenching phenomenon using Ca, Al, and Ag on 4PV in an ultra high vacuum (UHV) environment. We observed that deposition of all three metals on the 4PV layer produced dramatic luminescence quenching even at sub-monolayer coverages, suggesting that metal quenching may critically affect the efficiency of organic EL devices. Similar quenching processes are also observed for Alq₃, which is one of the most representative light emitting organic molecule. We also present evidence that the formation of gap states upon Ca deposition is responsible for the observed PL quenching in 4PV. The recovery of the PL upon removal of these states will also be discussed.

Experimental

The synthesis and basic photophysical properties of 4PV are described in detail elsewhere.²⁰⁻²² We used ultraviolet photoelectron spectroscopy (UPS) to probe the valence electronic structure of Ca/4PV. The PL and UPS experiments were performed in a UHV chamber with the base pressure of 1×10^{-10} Torr. The thickness of the 4PV films was 300 Å. The films for the UPS experiments were deposited on Au coated Si substrates while those for PL were deposited on ITO coated substrates through thermal evaporation in UHV. The evaporated sample was then transferred to the analysis chamber *in situ* for PL and UPS data acquisition as well as Ca deposition. The deposition rates were monitored by a quartz crystal microbalance. No detectable impurity was found for the deposited 4PV films as observed by x-ray photoemission spectroscopy (XPS). An Oriel 77501 fiberoptic 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 used was 400 nm, since it produced the highest level of luminescence for 4PV. The PL data was 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 (99.999 %) oxygen gas 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.²³

Results and Discussion

The PL intensities of 4PV plotted as a function of coverage, Θ , of Ca, Al and Ag on 300 Å 4PV films are shown in Figure 1. The shape of the PL spectra and the position of the peaks are consistent with those obtained by Woo *et al.*²² The behavior of the PL as a function of coverage is similar for all three metals even though their workfunctions differ by as much as 2 eV. This suggests that the quenching is relatively insensitive to the details of the energetics of the particular metal used. For the rest of the paper, we will focus our work on Ca. The observed PL quenching is very severe as indicated by the fact that even the deposition of 1/30th of a monolayer of Ca reduces the PL intensity by 50%. However, there is no noticeable change in the spectral shape. Further deposition of Ca continues to quench the PL although the effect is more gradual.

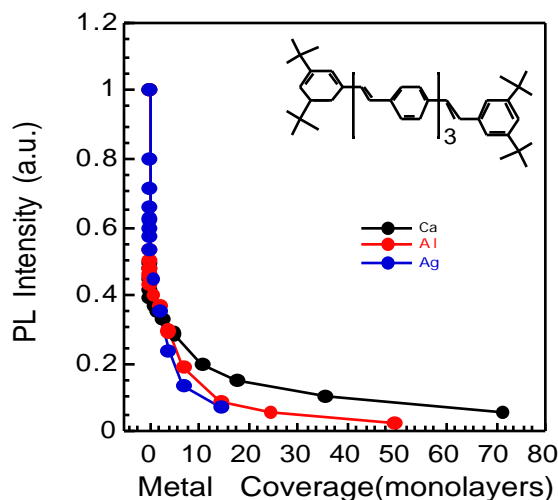


Figure 1: PL intensities plotted as a function of coverage, Θ , of Ca, Al and Ag on 300 Å 4PV films. The inset shows the molecular structure of 4PV.

At least three possible mechanisms are responsible for the dramatic PL quenching. First, this decrease could be due to Ca induced energy level bending which splits the excitons apart, resulting in lower yields. Second, a strong chemical reaction between Ca and 4PV may have occurred, yielding products which effectively quenches the luminescent species. Third, the Ca atoms provide nonradiative decay routes. Our previous XPS studies²⁴ of the interface formation between Ca and 5PV have shown that the Ca induced energy level bending is completed at a much larger value of Θ than 1 \AA , and since the same XPS studies did not show any evidence of a strong chemical reaction between Ca and 5PV, mechanism (1) and (2) can be ruled out. Therefore, we attribute the initial drop in intensity to mechanism (3), nonradiative decay channels created by the deposited Ca. The charge injection from the Ca atom into 4PV may induce the formation of radical anions or polarons, acting as dissociating centers for photoinduced excitons.²⁵

After the initial drop, the effect of PL quenching by Ca atoms is reduced, as indicated by a slower rate of PL quenching. This can be explained by a rather simple argument. Consider a surface with several Ca atoms. Each Ca atom has a certain "quenching radius" defined by the exciton diffusion length within which any exciton created will be quenched. Therefore, any additional Ca atoms added within the quenching radius of an existing Ca atom will have a lesser effect than it would have if it were deposited on a clean surface. This picture may be complicated by the fact that Ca may diffuse into the near surface region of 4PV just as has been reported for poly(2,5-dihexyl-1,4-phenylenevinylene) (DH-PPV),²⁶ and by the possibility of contributions from the Ca induced energy level bending process. However, if Ca diffuses extensively into 4PV, we would expect its density inside 4PV to be linearly

proportional to the amount of Ca deposited, leading to total quenching of the PL at $\Theta = 0.2 \text{ \AA}$.

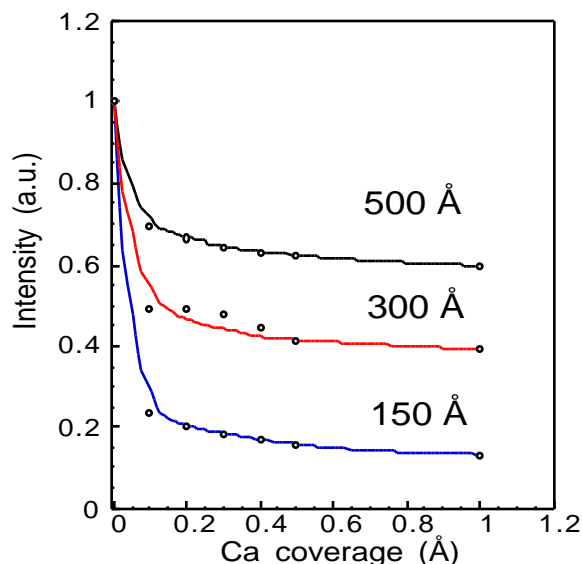


Figure 2: The PL intensity of 4PV samples with different 4PV layer thicknesses plotted as a function of Ca coverages, Θ .

The PL intensity of 4PV samples with different 4PV layer thicknesses plotted as a function of Θ , shown in Figure 2, confirms that Ca indiffusion is limited in the time frame of our experiment. If Ca indiffusion was extensive, it would be reasonable to expect that the percentage of the quenched PL intensity to be independent of the thickness of the sample. However, this is not the case as shown in Figure 2. Given that Ca indiffusion is limited, and neglecting the quenching effect of the ITO substrate, it can be estimated from the 65% reduction of the PL intensity of the 300 Å thick sample that the light emitting species within the top 200 Å of the film has been quenched. Similarly, we find that the apparent quenching thickness, Δ , is 200 Å and 127 Å for the 500 Å and 150 Å films, respectively. The fact that $\Delta_{Ca} = 200 \text{ \AA}$ for both the 300 Å and 500 Å films proves that the Ca indiffusion is limited. This indiffusion process can be explained by substrate disruption due to the release of condensation energy when Ca impacts the organic film. We believe that PL quenching by the ITO substrate is negligible, since we were able to observe PL for a 20 Å 4PV layer on ITO. The quenching thickness of 200 Å can therefore be attributed to the exciton migration distance, which is much greater than the size of a 4PV molecule ($2 \times 8 \times 40 \text{ \AA}$). For the 150 Å 4PV film, intuitively, one would expect its luminescence to be completely quenched from the Δ obtained from analysis of the 300 Å and 500 Å films. However, luminescence was still observed in the 150 Å film. Several factors may have contributed to this. One factor is the roughness of the glass substrate. Such roughness may noticeably alter the local thickness for the 150 Å film. The morphology of the 150 Å

film may also be affected by the substrate to a greater degree than that of the thicker films. Furthermore, although the average exciton migration distance is 200 Å, it is reasonable to expect that some excitons will recombine radiatively before traveling that distance.

Figure 3 shows the PL intensity as a function of the thickness of the 4PV film, Φ , on two substrates, (a) Ca, and (b) ITO. For the Ca substrate, the PL was not visible until approximately $\Phi = 125 \text{ \AA}$, but was not measurable until $\Phi = 150 \text{ \AA}$. Only after $\Phi = 200 \text{ \AA}$ did the PL increase linearly with Φ . The late onset of the PL is attributed to the quenching of the emitting species in the 4PV layer by Ca. The extrapolation of the linear part of the PL intensity curve to the x-axis yields $\Delta_{Ca} = 145 \text{ \AA}$ (dashed line in Figure 3). By comparing this value for Δ_{Ca} , and our previously estimated value, $\Delta_{Ca} = 200 \text{ \AA}$ (Figure 2.), we can estimate that the deposited Ca disrupts the 4PV layer to a maximum extend of 50 Å. This is consistent with the values previously reported in the literature.²⁶ The situation for the ITO substrate is very different from that for the Ca substrate. The PL was measurable as early as $\Phi = 20 \text{ \AA}$ when ITO was used as the substrate and even at low Φ , the PL was increasing linearly with Φ . Furthermore, an extrapolation of this linear part of the PL intensity curve to the x-axis yields $\Delta_{ITO} = 0 \text{ \AA}$ indicating that ITO does not quench the PL of 4PV. Thus, the PL quenching phenomena does not depend on whether a material is conducting.

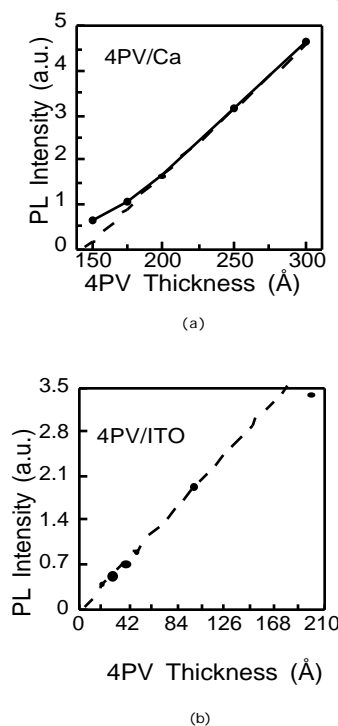


Figure 3: PL intensity as a function of the thickness of the 4PV film, Φ , on two substrates, (a) Ca, and (b) ITO.

We performed repetitive Ca deposition and oxygen exposure cycles up to 50 Å with incremental Ca thickness.

The PL spectra were taken before and after Ca deposition, and after exposure to 5×10^{-6} Torr of O_2 for 5 minutes (1.5×10^3 L), 30 minutes (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). Figure 4 shows the evolution of PL intensity as a function of Ca deposition/oxidation cycles. The horizontal axis indicates the accumulated oxygen exposure in L and the total Ca thickness is indicated in the figure. As reported previously,¹⁷ the dramatic quenching ($\sim 50\%$) of the PL intensity is clearly observed. However, the PL intensity recovers back to about 65% of the pristine 4PV value after the sample was exposed to O_2 for 4.5 hours at 5×10^{-6} Torr (8.1×10^4 L). Also at Ca coverages less than 8 Å, the fresh deposition of Ca still greatly affects the PL even though the previously deposited and oxidized Ca separated the freshly deposited Ca from the 4PV. This indicates that the oxidized Ca underlayer in this thickness regime cannot protect 4PV from Ca-induced PL quenching. However, when the oxidized Ca layer thickness approaches approximately 30 Å, additional Ca deposition does not substantially affect the PL intensity. This indicates that the thicker oxide layer is indeed effectively protecting the 4PV from the PL quenching effect of freshly deposited Ca. The crucial role of the oxidized Ca layer is clearer when we consider that the PL from unoxidized Ca decreases down to around 15% after deposition of 50 Å Ca,¹⁷ a factor of 4 lower than the value of the PL from an oxidized sample. These numbers suggest that a proper oxidation of Ca at the Ca/4PV interface could significantly improve the efficiency of a single layer EL

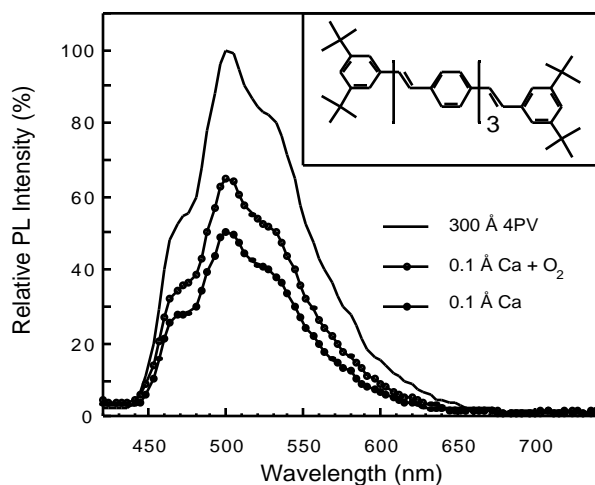


Figure 4: PL intensity under a sequence of Ca deposition and oxidation cycles. The horizontal axis is the accumulated oxygen exposure. The connected circles indicate the PL recovery process upon oxidation at the Ca thickness indicated.

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 Figure 5. The spectrum of the pristine 4PV sample exhibits the highest occupied molecular orbital (HOMO) feature near 2.4 eV,²⁷ and is consistent with that

reported for PPV.²⁸ 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.^{11, 29-31} Such gap states have been attributed to the formation of bipolarons via charge transfer from the metal to the organic material.^{24, 29-31} However, when the fresh-Ca/4PV sample was exposed to oxygen, the gap states completely disappeared as seen in the top curve of Figure 5. This is strong evidence that the formation and disappearance of gap states may be responsible for the observed PL quenching and recovery, respectively.

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 four times efficiency improvement. There have also been several reports that suggest improvement in EL performance by introduction of a foreign layer between the active layer and the electron injecting electrode.³²⁻³⁴ In view of these reports, it is clear that a foreign non-metallic layer at the interface between the metal and the active EL layer enhances the device performance by avoiding metal-induced quenching of excitons. Preliminary work on Alq₃ have also exhibited metal induced PL quenching. However, more work needs to be done before the mechanisms responsible for this quenching in Alq₃ can be explained. Investigations are currently underway to characterize it.

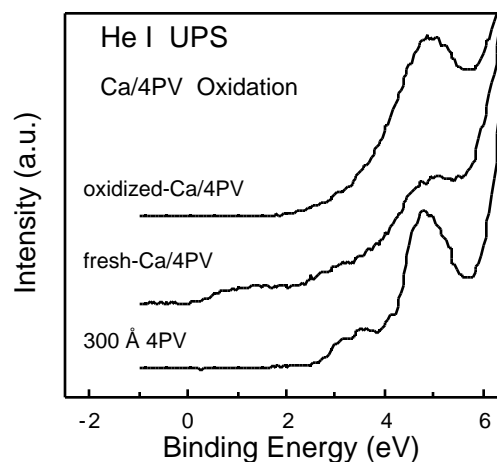


Figure 5: The changes in UPS spectra upon Ca deposition and oxidation. The bottom curve shows the valence band spectrum of 300 Å pristine 4PV film. The middle curve is when 4 Å of Ca was deposited on the 4PV film. The formation of states in the energy gap region is clearly observed. The top curve shows the same valence band spectra but after oxidation by 9.1×10^3 L of exposure.

Summary

We have shown that the very act of depositing Ca, Ag, and Al on 4PV greatly diminishes the PL. Excitons will suffer non-radiative decay if created within the metal atoms quenching radius. The importance of this finding is clear in light of reports that the recombination occurs near the metal cathode.³⁵ Mechanisms which may be responsible for the PL intensity drop were discussed. We have also presented strong evidence that the formation and removal of gap states in the Ca/4PV interface may be responsible for the quenching and recovery of its PL. From the PL intensity variation on cumulative Ca deposition/oxidation cycles, it was estimated that approximately 30 Å of oxidized Ca layer can be used as a protective layer against PL quenching due to fresh Ca deposition. This work improves our understanding of the role of interfaces in device performance, and has obvious ramifications on the LED applications.

Acknowledgements

This work was supported in part by the National Science Foundation under Grant No. DMR-9612370 and by DARPA DAAL 0196K0086. We would like to thank T. Wehrmeister and K. Müllen for providing the 4PV used in this work

References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
2. J. Kido, M. Kimura, and K. Nagai, *Science* **267**, 1332 (1995).
3. C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
4. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, *et al.*, *Nature* **347**, 539 (1990).
5. E. Etdedgui, H. Razafitrimo, Y. Gao, *et al.*, *Appl. Phys. Lett.* **67**, 2705 (1995).
6. E. Etdedgui, H. Razafitrimo, Y. Gao, *et al.*, *Phys. Rev. Lett.* **76**, 299 (1996).
7. H. Razafitrimo, E. Etdedgui, L.-H. Guo, *et al.*, *Appl. Phys. Lett.* **67**, 2621 (1995).
8. D. D. C. Bradley, *Advance Materials* **4**, 756 (1992).
9. A. R. Brown, D. D. C. Bradley, J. H. Burroughes, *et al.*, *Appl. Phys. Lett.* **61**, 2793 (1992).
10. N. C. Greenham, R. H. Friend, A. R. Brown, *et al.*, *Proceedings of the SPIE* **1910**, 84 (1994).
11. I. D. Parker, *J. Appl. Phys.* **75**, 1656 (1994).
12. V. Choong, Y. Park, Y. Gao, *et al.*, *Appl. Phys. Lett.* **69**, 1492 (1996).
13. S. A. Brazovskii and N. N. Kirova, *Synth. Met.* **55-57**, 4385 (1993).
14. P. S. Davids, A. Saxena, and D. L. Smith, *J. Appl. Phys.* **78**, 4244 (1995).
15. R. Schenk, M. Ehrenfreund, W. Huber, *et al.*, *J. Chem. Soc., Chem. Commun.* **22**, 1673 (1990).
16. R. Schenk, H. Gregorius, K. Meerholz, *et al.*, *J. Am. Chem. Soc.* **113**, 2634 (1991).
17. H. S. Woo, O. Lhost, S. C. Graham, *et al.*, *Synth. Met.* **59**, 13 (1993).
18. M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, *et al.*, *Phys. Rev. Lett.* **73**, 744 (1994).
19. Y. Park, E. Etdedgui, Y. Gao, *et al.*, *Polymer Preprints* **36**, 382 (1995).
20. M. J. Rice and Y. N. Garstein, *Phys. Rev. B* **53**, 10764 (1996).
21. W. R. Salaneck and J. L. Brédas, *Advance Materials* **8**, 48 (1996).
22. Y. Park, V. Choong, E. Etdedgui, *et al.*, *Appl. Phys. Lett.* **69**, 1080 (1996).
23. P. Dannetun, M. Fahlman, C. Fauquet, *et al.*, *Synth. Met.* **67**, 133 (1994).
24. M. Fahlman, D. Beljonne, M. Lögdlund, *et al.*, *Chem. Phys. Lett.* **214**, 327 (1993).
25. D. Steinmüller, M. G. Ramsey, and F. P. Netzer, *Phys. Rev. B* **47**, 13323 (1993).
26. G. Iucci, K. Xing, M. Lögdlund, *et al.*, *Chem. Phys. Lett.* **244**, 139 (1995).
27. Y.-E. Kim, H. Park, and J.-J. Kim, *Appl. Phys. Lett.* **69**, 599 (1996).
28. P. Bröms, J. Birgersson, N. Johansson, *et al.*, *Synth. Met.* **74**, 179 (1995).
29. A. C. Fou, O. Onitsuka, M. Ferreira, *et al.*, *J. Appl. Phys.* **79**, 7501 (1996).
30. U. Lemmer, S. Karg, M. Scheidler, *et al.*, *Synth. Met.* **67**, 169 (1994).