

Model Aluminum–Poly(*p*-phenylenevinylene) Interfaces Studied by Surface Raman Spectroscopy

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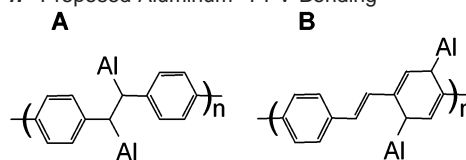
Polymeric organic light-emitting diodes (OLEDs) have emerged as inexpensive and versatile alternatives to traditional inorganic-based display technologies.^{1,2} Their synthetically tunable emission wavelengths, low-cost processability, and flexible physical properties are commercially desirable with numerous applications on the horizon. The advancement of this field is dependent on extending device lifetimes and improving electroluminescence efficiencies, both of which strongly depend on the integrity and charge injection efficiencies of the electrode/organic contacts.^{3–6} The critical nature of these interfaces has generated widespread interest in determining the electronic and chemical states, and molecular structure and packing within these interfacial regions.^{7–17}

A typical OLED consists of an electron-transport layer (ETL) and a hole-transport layer (HTL) sandwiched between a transparent anode and a vacuum-deposited low-work function metal cathode such as Na, Ca, or Al. During the initial stages of cathode deposition, the metal atoms can either physically interact with the ETL polymer chains as dopants or chemically react with unsaturated carbon–carbon bonds and other chemical functionalities along the polymer backbone. Previous studies of these interfaces have been restricted to traditional ultrahigh vacuum (UHV) surface techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), and near-edge X-ray adsorption fine structure (NEXAFS).⁷ The effects of metal deposition on interfacial electronic energy levels and chemical states have been thoroughly examined by these methods. However, most of our understanding of metal–polymer bonding during cathode formation comes from theoretical calculations and modeling fits to XPS and UPS data.^{8–13} In this report, we introduce a new experimental approach for studying the cathode/ETL interface that yields unique, bond-specific, vibrational information for the direct determination of interfacial metal–polymer chemical structures.

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have been widely used as emitting ETLs in OLEDs.^{2,18} Therefore, reactions between low-work function metals and PPV have been the focus of multiple investigations. Joint experimental and theoretical studies have predicted that Al preferentially reacts with PPV at the vinylene carbons (Scheme 1, **A**) as opposed to the benzene carbons (Scheme 1, **B**).^{3,5,8–11} In an attempt to experimentally observe Al–PPV bonding, we demonstrate the use of surface Raman spectroscopy to determine the vibrational signature of the products of Al deposited on ultrathin films of *trans*-stilbene, a PPV model.¹⁹

Ultrathin (50–200 Å) films of *trans*-stilbene were vacuum-deposited by thermal evaporation onto cooled (77 K), gently sputtered Ag(111) surfaces.²⁰ Al was then deposited onto this assembly from an aluminum oxide-coated tungsten boat at a rate of 1 Å/s as determined by QCM monitoring. Prior to deposition, the base pressure of the UHV system was below 3.0×10^{-10} Torr, and only trace amounts of water and oxygen were detected by mass spectrometry. Raman spectra were acquired after deposition of 0, 1, 2, 3, 4, 5, and 10 Å Al (mass thickness) on three separate *trans*-

Scheme 1. Proposed Aluminum–PPV Bonding



stilbene/Ag(111) surfaces using a Raman system described elsewhere.²¹

Figure 1 shows three representative spectra for pristine *trans*-stilbene on Ag(111) and *trans*-stilbene/Ag(111) with 1 and 5 Å of Al. The spectrum of *trans*-stilbene on Ag is essentially identical to that of crystalline *trans*-stilbene. The major vibrational modes of *trans*-stilbene in this spectral region are the in-plane (ip) ring-breathing mode at 997 cm^{-1} , the $\delta(\text{C–H})$ mode at 1183 cm^{-1} , the $\nu(\text{C–phenyl})$ mode at 1192 cm^{-1} , the ip ring $\delta(\text{C–H})$ mode at 1593 cm^{-1} , and the vinylene $\nu(\text{C=C})$ mode at 1635 cm^{-1} .²² The latter two modes are useful for an initial assessment of whether structure **A** or **B** in Scheme 1 is formed. If **A** is the product as predicted, the 1635 cm^{-1} mode should decrease relative to the 1593 cm^{-1} band as the reaction proceeds.

After deposition of only 1 Å of Al, significant spectral changes are observed between 400 and 1200 cm^{-1} (Figure 1b). Several new bands appear at 485, 586, 625, 753, 839, 948, and 1091 cm^{-1} . The intensities of these modes relative to the *trans*-stilbene modes increased upon deposition of more Al (Figure 1c). A quantitative treatment of the *trans*-stilbene and new product modes as a function of Al coverage is shown in Figure 2.

Absolute peak intensities for 1183, 1192, 1593, and 1635 cm^{-1} were normalized to the peak intensity sum of these four bands. The average normalized peak intensities are plotted as a function of Al coverage in Figure 2. The normalized ring $\delta(\text{C–H})$ (1593 cm^{-1}) and $\nu(\text{C–phenyl})$ (1192 cm^{-1}) modes are stable with increasing Al coverage, whereas the 1183 cm^{-1} mode increases concomitant with a decrease in the $\nu(\text{C=C})$ (1635 cm^{-1}) mode. The 1593 mode is expected to remain intense in, and hence is an indicator of, **A**. Conversely, the 1635 cm^{-1} mode is expected to remain intense and therefore is a signature for **B**. On the basis of the stable intensity of the 1593 cm^{-1} mode, Figure 2 provides compelling evidence for the formation of **A**. If structure **B** were formed, the 1593 cm^{-1} band would be expected to diminish or disappear.

The increase in peak intensity at 1183 cm^{-1} is not thought to represent a change in $\delta(\text{C–H})$ but rather a coincidental overlap with a peak of the reaction product. An intensity increase in the $\delta(\text{C–H})$ mode would not be predicted for either structure **A** or structure **B**. A more likely explanation for the intensity increase in this band is a shift to lower frequency of the 1192 cm^{-1} mode following Al–C bonding. The increase in the 1183 cm^{-1} intensity is also directly correlated to growth of the more prominent bands at 625, 839, and 948 cm^{-1} . These peak intensities were normalized

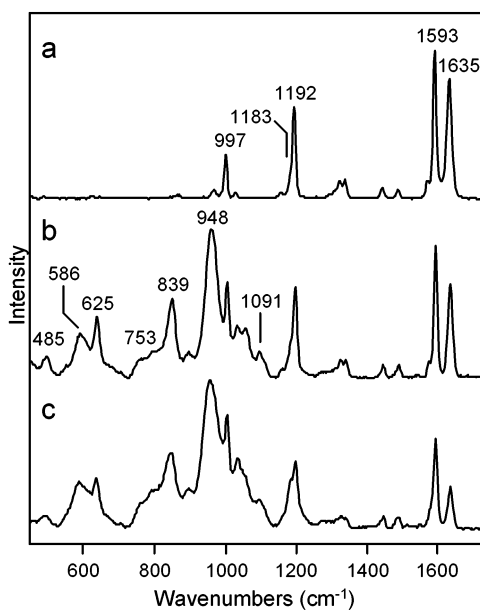


Figure 1. Raman spectra of *trans*-stilbene on Ag(111) at 77 K (a) pristine, (b) with 1 Å of Al deposited, and (c) with 5 Å of Al deposited.

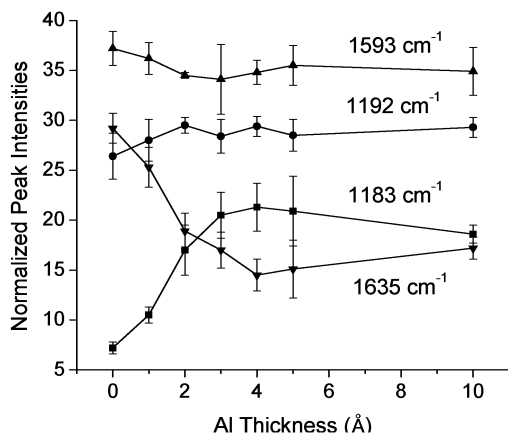


Figure 2. Normalized peak intensities for 1183, 1192, 1593, and 1635 cm^{-1} modes as a function of Al thickness.

in the same way as in Figure 2 and exhibit no changes in intensity, suggesting that all four are derived from the same species.

The 948 cm^{-1} mode is tentatively assigned to the ip combination ring mode of the monosubstituted aromatic product. The large shift to lower frequency is rationalized as an Al-ring π interaction in the solid product to stabilize the electrophilic Al.

Additional evidence for covalent Al addition to the vinylene group comes from studies on organoaluminum compounds and from theoretical calculations. Gas-phase Raman spectra of trimethylaluminum exhibit several $\nu(\text{Al}-\text{C})$ bands in the low-frequency range including those at 530 and 760 cm^{-1} .²³ Moreover, Brédas and co-workers have predicted several modes below 1000 cm^{-1} for a number of Al-*trans*-polyacetylene complexes including a $\nu(\text{Al}-\text{C})$ band at 486 cm^{-1} .^{12,13} The 485 cm^{-1} band in Figure 1b is identical in frequency to this predicted value, and its intensity is relatively weak as would be expected for a $\nu(\text{metal}-\text{C})$ mode.

Determining molecularly specific metal-polymer bonding is critical for the optimization, development, and growth of organic electronics. To date, XPS and UPS data have required theoretical justification for a chemical picture of bonding in these interfacial systems. In this study, Raman spectroscopy provides unique direct insight into chemical bonding in a common cathode/ETL interface. We are currently evaluating additional reactions between metals and functional organic materials by Raman spectroscopy. This work will be coupled with ongoing theoretical work in this Department²⁴ to establish more complete and accurate chemical models for these interfacial regions.

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Supporting Information Available: Additional normalized peak intensities as a function of Al coverage for the reaction product (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Bernius, M. T.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737–1750 and references therein.
- Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428 and references therein.
- Salaneck, W. R.; Stafström, S.; Brédas, J.-L. *Conjugated Polymer Surfaces and Interfaces*; Cambridge University Press: New York, 1996.
- Salaneck, W. R.; Brédas, J.-L. *Adv. Mater.* **1996**, *8*, 48–52.
- Kugler, Th.; Lögdlund, M.; Salaneck, W. R. *IEEE J. Quantum Electron.* **1998**, *4*, 14–23.
- Bharathan, J. M.; Yang, Y. *J. Appl. Phys.* **1998**, *84*, 3207–3221.
- Gao, Y. *Acc. Chem. Res.* **1999**, *32*, 247–255 and references therein.
- Kugler, T.; Lögdlund, M.; Salaneck, W. R. *Acc. Chem. Res.* **1999**, *32*, 225–234.
- Lögdlund, M.; Brédas, J.-L. *J. Chem. Phys.* **1994**, *101*, 4357–4364.
- Fahlman, M.; Brédas, J.-L.; Salaneck, W. R. *Synth. Met.* **1996**, *78*, 237–246.
- Fredriksson, R.; Lazzaroni, R.; Brédas, J.-L.; Dannetun, P.; Lögdlund, M.; Salaneck, W. R. *Synth. Met.* **1993**, *57*, 4632–4637.
- Lazzaroni, R.; Parenté, V.; Fredriksson, C.; Brédas, J.-L. *Synth. Met.* **1996**, *76*, 225–228.
- Parenté, V.; Fredriksson, C.; Selmani, A.; Lazzaroni, R.; Brédas, J.-L. *J. Phys. Chem. B* **1997**, *101*, 4193–4202.
- Nguyen, T. P.; Mansot, J. L. *Thin Solid Films* **1996**, *283*, 135–139.
- Ettedgui, E.; Razafitrimo, H.; Park, K. T.; Gao, Y.; Hsieh, B. R. *J. Appl. Phys.* **1994**, *75*, 7526–7530.
- Konstadinidis, K.; Papadimitrakopoulos, F.; Galvin, M.; Opila, R. L. *J. Appl. Phys.* **1995**, *77*, 5642–5646.
- Dannetun, P.; Lögdlund, M.; Salaneck, W. R.; Fredriksson, C.; Stafström, S.; Holmes, A. B.; Brown, A.; Graham, S.; Friend, R. H.; Lhost, O. *Mol. Cryst. Liq. Cryst.* **1993**, *228*, 43–48.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.
- Nguyen, T. P.; Tran, V. H.; Destruel, P.; Oelkrug, D. *Synth. Met.* **1999**, *101*, 633–634.
- Ag(111) was chemically polished using a slight modification of a procedure described previously.²⁵ The rms roughness of these surfaces as prepared was $1.4 \pm 0.2\text{ nm}$ by AFM. After sputtering, the rms roughness was $1.6 \pm 0.4\text{ nm}$, and these surfaces exhibited surface enhancement factors of ~ 2 for a monolayer of thiophenol as compared to smooth Pt, which was assigned a value of 1.²⁶
- Schoenfish, M. H.; Ross, A. M.; Pemberton, J. E. *Langmuir* **2000**, *16*, 2907–2914.
- Meić, Z.; Güsten, H. *Spectrochim. Acta, Part A* **1977**, *34A*, 101–111.
- O'Brien, R. J.; Ozin, G. A. *J. Chem. Soc. A* **1971**, 1136–1138.
- Crispin X.; Geskin, V.; Crispin, A.; Cornil, J.; Lazzaroni, R.; Salaneck, W. R.; Brédas, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 8131–8141.
- Smolinski, S.; Zelenay, P.; Sobkowski, J. *J. Electroanal. Chem.* **1998**, *442*, 41–47.
- Taylor, C. E.; Pemberton, J. E.; Goodman, G. G.; Schoenfish, M. H. *Appl. Spectrosc.* **1999**, *53*, 1212–1221.

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