Electronic Supporting Information for

Adsorption Studies of a Phosphonic Acid on ITO: Film Coverage, Purity, and Induced Electronic Structure Changes

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S1. Materials and methods

2,3,4,5,6-pentafluorobenzylphosphonic acid (PFBPA) was prepared as previously reported.[1] ITO substrates (Colorado Concepts, 9-15 Ω/□, RMS ~ 3 nm) were detergent / solvent cleaned (DSC) by scrubbing with cloth soaked with Triton X-100 in water, followed by 10 min successive sonications in diluted Triton X-100, deionized water and ethanol. AFM scans for surface roughness measurements were obtained using an Agilent 5600ls in AC mode with a 100 µm scanner head using Tip B from MikroMasch NCS35/No Al (typical resonant frequency 315 kHz, spring constant 14 N/m) at 0.5 lines/s.

For Section 1 (*comparison of coverage at room temperature, varying concentrations*), O_2 plasma treatment was done in a Plasma Preen II at 100% power for 3 min. For Section 2 (*coverage comparison when using high temperature vs. room temperature deposition for 10 mM PFBPA)*, a PE-50 etcher (Plasma Etch, Inc., Carson City, NV) at 50% power fed with O_2 was used for 3 min. For phosphonic acid depositions, 10 mM ethanolic solutions were placed in round bottom flasks, or vials and the slides immersed and removed according to the scheduled immersion times, then immediately rinsed with fresh ethanol, dipped in ethanol and finally placed in 5% triethylamine solution in ethanol to sonicate for 30 min, time after which they were rinsed again with ethanol and blown dried. The samples were kept under N_2 and the time between preparation and XPS analysis minimized as much as possible, never exceeding more than a day. XPS was performed in a Thermo K-Alpha with monochromated X-rays (12 kV, 6 mA) with a spot size of 400 µm and a take off angle of 90° relative to the surface.

For Section 3 (*tracking monolayer purity and work function changes with coverage*), the plasma cleaning was done in a Harrick plasma cleaner PDC-001 at high power for 3 min, typically at a pressure of 200 mTorr. PA modifications were done as above but sonication in 5% triethylamine was for 10 min. Loosely-capped amber bottles were used for high temperature deposition. A Kratos Axis Ultra^{DLD} XPS/UPS system was used for analysis of samples. All samples were in electronic equilibrium with the spectrometer via a metallic clip on the sample and characterizations were performed at normal take-off angle. XPS using monochromatic Al Kα line was run at a base pressure of 10^{-9} Torr with the Fermi level calibrated using atomically clean silver. Spot size was *ca.* 700 μm. Survey XPS scans were run at 160 eV pass energy and high resolution scans typically at 20 eV pass energy and 100 meV steps, while UPS was acquired at 5 eV pass energy and 0.05 eV step size with the aperture and iris set to 55 μm. XPS peak fits were done with Vision Processing Software 2.2.8 using mixed Gaussian/Lorentzian distributions to minimize χ^2. At least three spots were measured per sample.

A dry air-purged Digilab FTS-600 FT-IR instrument equipped with an MCT detector was used for measuring IR spectra. A grazing-angle accessory (80° angle of incidence, Pike) was employed in the IRRAS studies. The light was p-polarized with a gold grid polarizer from Perkin-Elmer. The resolution was 2 cm^{-1} and the mirror speed used was 1.28 cm/s. 4000-6000 scans were collected for each sample.

S2. Correction of F/In ratios for substrate signal attenuation

The F1s/In3$p_{3/2}$ area ratio is converted to F/In ratio after correcting for instrumental and sensitivity factors. For Al Kα radiation, electrons emerging from the In3$p_{3/2}$ orbitals (*ca.* 666 eV binding energy) will have a kinetic energy of *ca.* 816 eV. This energy determines the inelastic mean free path (λ) for the photoelectrons being scattered as they emerge. One λ_M^{CL} is, by definition, the average distance electrons ejected from a given core level (*CL*) can travel through a material *M* before 1-1/e (63%) are inelastically scattered: hence, only a 1/e fraction of all the electrons at a depth of λ from the surface will be detected without energy loss.

Equation S1 describes the decay in signal from electrons originating at a distance *t* from the surface.[2]

Equation S1

$$\boldsymbol{I = I_S \exp\left(-\frac{t}{\lambda cos\theta}\right)}$$

where I_S is the unscattered intensity and θ the detection angle relative to the surface normal. Since all data discussed here was acquired at normal angle detection, $cos\theta$ is 1. Figure S1 shows the decrease in intensity for a given distance from a surface.

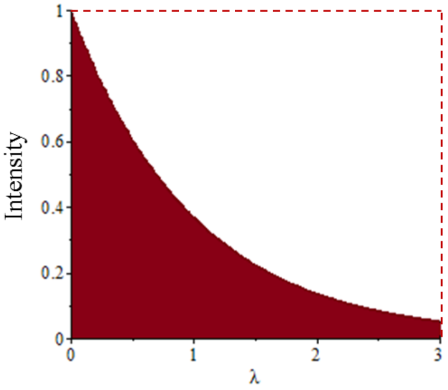

Figure S1. Signal intensity as a function of distance from surface in units of λ for normal angle detection.

Integration of Equation S1 from 0 to 3λ will give the total intensity for electrons coming from right at the surface to those 3λ deep into the sample (information depth is 3λ). This evaluates to 0.95λ, which translates into 95% of the signal coming from within 3λ. It can be seen from Figure S1 that if there were no attenuation ($I = I_S$), the integration would be merely the area of a rectangle 1 × 3λ = 3λ (shown in dashed lines). Hence, it is possible to correct for the scattering attenuation by dividing the expected F/In ratio by the factor 3.16 (= 3λ / 0.95λ), or multiplying the observed XPS F/In by 3.16. For the In $3p_{3/2}$ line in ITO, $\lambda_{ITO}^{In3p_{3/2}}$ = 27.4 Å using the inelastic mean free path curve for inorganic materials.[2]

The unit cell area of the 222 crystalline face of ITO is composed of 28 In and 4 Sn atoms per layer.[3] Each layer is separared from the next by 3.32 Å. The value of 3λ for In $3p_{3/2}$ is 8.2 nm, which can fit 24.8 layers of ITO. Considering PFBPA on top of one of these layers, the footprint of each PA is 22.62 $Å^2$.[4] This corresponds to a maximum coverage of 4.4×10^{14} molecules cm^{-2}. Each 22.6 $Å^2$ can hold 1.78 In atoms, so in 3λ there will be a total of 44 In atoms. This gives an expected PFBPA / In ratio of 1/44 = 5 F atoms per 44 In atoms = 0.11 F/In ratio. Hence, a close-packed monolayer of PFBPA on smooth ITO would have a ratio of 0.11 F/In, considering an information depth of 3λ. If this hypothetical structure was measured by XPS, the In signal would be attenuated as discussed in the previous paragraph, so the expected measured F / In would be 0.11 × 3.16 = 0.36.

S3. AFM images and roughness for various samples

Selected samples from the batches prepared with 1, 10 and 100 mM at r.t. as well as 10 mM PFBPA at 75 °C were observed by atomic force microscopy (AFM) to check for etching or roughness changes. Representative images are compared in Figure S2. The topography features are the same, even for the harsher treatments. As Table S1 shows, for samples treated in 10 mM PFBPA for 15 s at r.t. or several days at 75 °C, a roughness close to 3.2 nm was determined. Even in the case of 0.1 mM treated samples, the roughness was still 3.3 nm. It is concluded that the acidities and temperatures used during these treatments are not appreciatively affecting the surface roughness, nor etching the ITO.

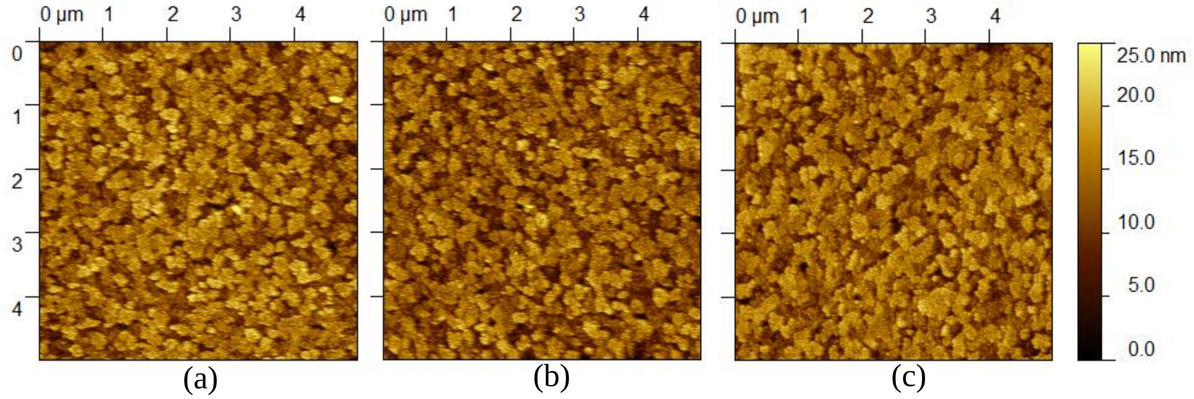

Figure S2. Typical AFM micrographs: (a) 75 °C 10 mM treatment for 4 days, (b) 18 h in 100 mM at r.t. and (c) 15 s in 10 mM r.t.

Table S1. Roughness determined from 5 × 5 micron AFM images.

Sample	RMS / nm
Plasma	3.2
15 s / 10 mM rt	3.2
10 in / 10 mM rt	3.4
1 h / 10 mM rt	3.4
18 / 100 mM rt	3.3
4-7 days / 10 mM 75 °C (average)	3.2

S4. UPS for tracking electronic structure changes

ITO is such a heavily doped semiconductor that, in the bulk, the Fermi level resides in the conduction band. Given the imbalance in charge neutrality close to the surface, there is an upward band bending so that for the top layers, the Fermi level lies in the band gap (Figure S3). UPS is a surface-sensitive technique (λ = 2-10 nm depending on kinetic energy[2]), so the electronic structure measured is that at the surface. While the independent variable in the raw UPS data is kinetic energy, it can easily be converted into binding energy by measurement of a clean metal with a visible Fermi edge ($E_F = 0$). The UP spectrum shows an abrupt cutoff, the secondary electron edge (SEE), determined by the radiation used and the work function of the material. Subtracting the width of the spectrum (the difference between the SEE binding energy and the Fermi edge) from the radiation used affords the local work function of the film in question ($\Phi = h\nu - \mathrm{SEE}$).

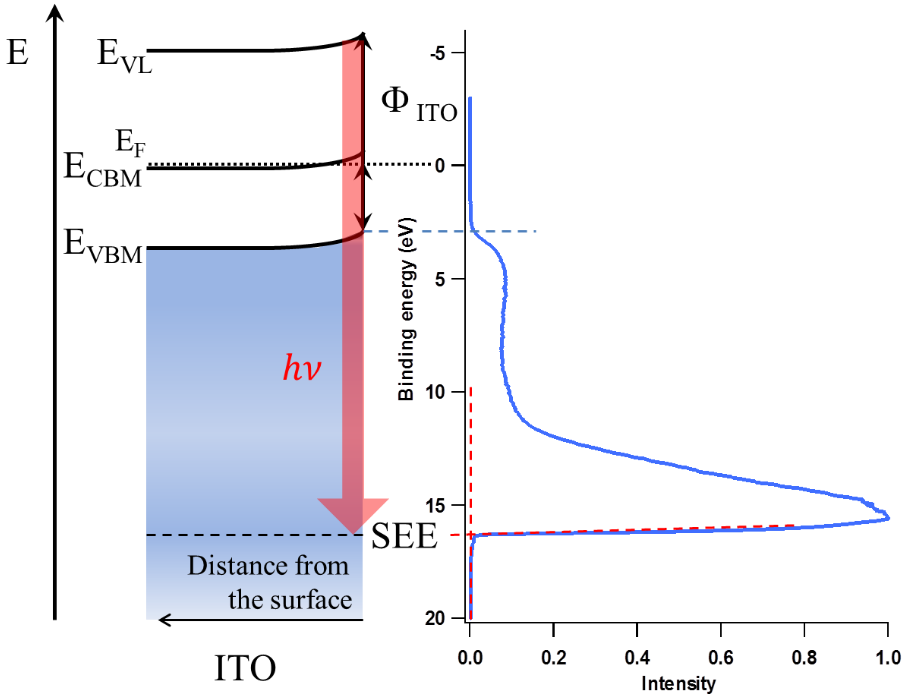

Figure S3. Tracking work function and valence band maximum by UPS: on the left, the electronic structure of ITO, with its corresponding energy levels onsets (VBM = valence band maximum, CBM = conduction band minimum) and their bending in the depletion layer near the surface. The work function (Φ) and UV radiation energy (hν) are also marked.

S5. XPS/UPS data summary for AP-treated ITO modified at room temperature with PFBPA

Figure S4a summarizes the changes induced on ITO after air plasma treatment, as probed by XPS/UPS and IRRAS, as discussed in the main text.

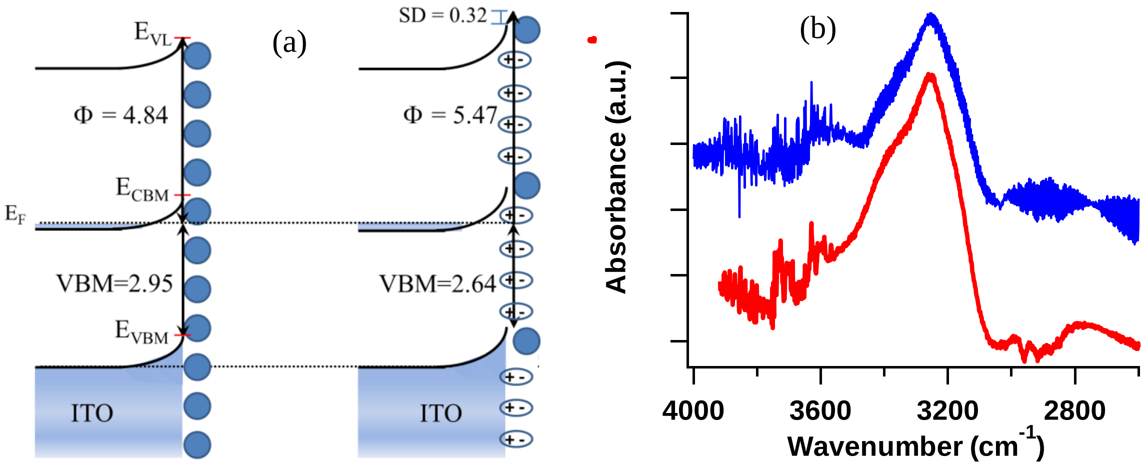

Figure S4. (a) Comparison of electronic structure for detergent/solvent cleaned ITO and after plasma treatment. Blue circles represent adventitious carbon. All energies are in eV. (b) IRRAS spectrum in the region of νO-H for air plasma (blue) and O_2 plasma (red) treated ITO using DSC ITO as background.

Figure S5 shows the result of the treatments on the electronic structure of plasma cleaned ITO; the work function decreases with immersion on the phosphonic acid solution and only after 7 days recovers slightly. This decrease of the work function can be traced back to a decrease in the surface dipole contribution that was gained from the plasma treatment, lost upon immersion in the phosphonic acid solution in the early stages of phosphonate deposition. When the plasma sample is immersed in the PFBPA solution, after only 10 seconds the C/In ratio increases to 0.27 and the F/In goes from 0 to 0.10 (Figure S6). However, the F/C deviates from the expected stoichiometry (0.39 *vs.* 0.71), which suggests that there is a mixture of phosphonic acid and adventitious carbon. There is a significant valence band shift (+0.20 eV) relative to the bare plasma sample. This implies band bending or geometry rearrangement. This shift would normally cause an increase in the work function, but the surface dipole obtained through plasma treatment is lost after 10 s immersion. This is likely due to the pillow effect from the adsorbed, disordered phosphonic acid and additional contaminants not present on the air plasma sample before immersion. A control experiment where the plasma ITO is immersed in pure ethanol for 10 s leaves the work function intact but shifts the valence band maximum closer to E_F, in the same range as the 10 s immersion in 10 mM PFBPA solution does; hence, both the phosphonic acid and the ethanol, or whatever contaminants adhere to the ITO in this period, are responsible for the decrease in the intrinsic surface dipole of ITO. After 7 days the molecular dipole contribution from the phosphonate film is comparable with that of the bare plasma-cleaned ITO. The work function after such an immersion time is lower due to a shift in the valence band further from the Fermi level than that of plasma-clean ITO; again this can be due to geometry rearrangement or decrease of the band bending to its pre-plasma configuration.

By allowing the plasma-cleaned sample to react for 7 days, the F/In ratio increases substantially (from 0.10±0.01 to 0.30±0.02) and the F/C approaches the expected ratio of 0.71 (reaching 0.59±0.03). Interestingly neither the F/In nor F/C seem to reach a plateau at this time, which leads to the next set of experiments at a higher temperature. In comparison with the non-plasma treated set, the coverage and purity obtained for this plasma treated set in one day is similar to that of DSC-only ITO modified for a week (*cf.* Figure 6 in main text).

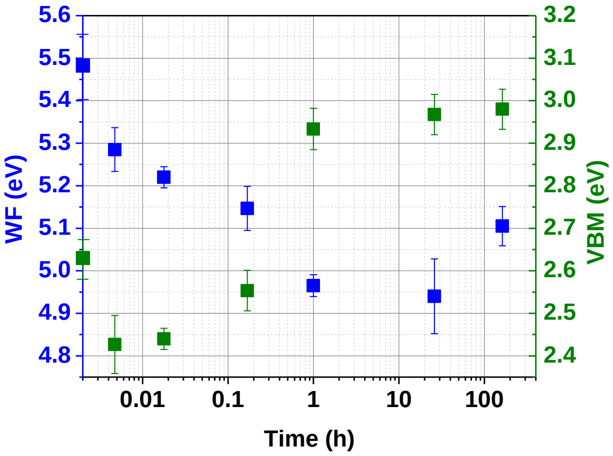

Figure S5. Room temperature, 10 mM PFBPA modification with air plasma pretreatment. The work function (WF, left axis) and valence band maximum (VBM, right axis) as a function of immersion time. The values for bare ITO are on the leftmost side of the plot.

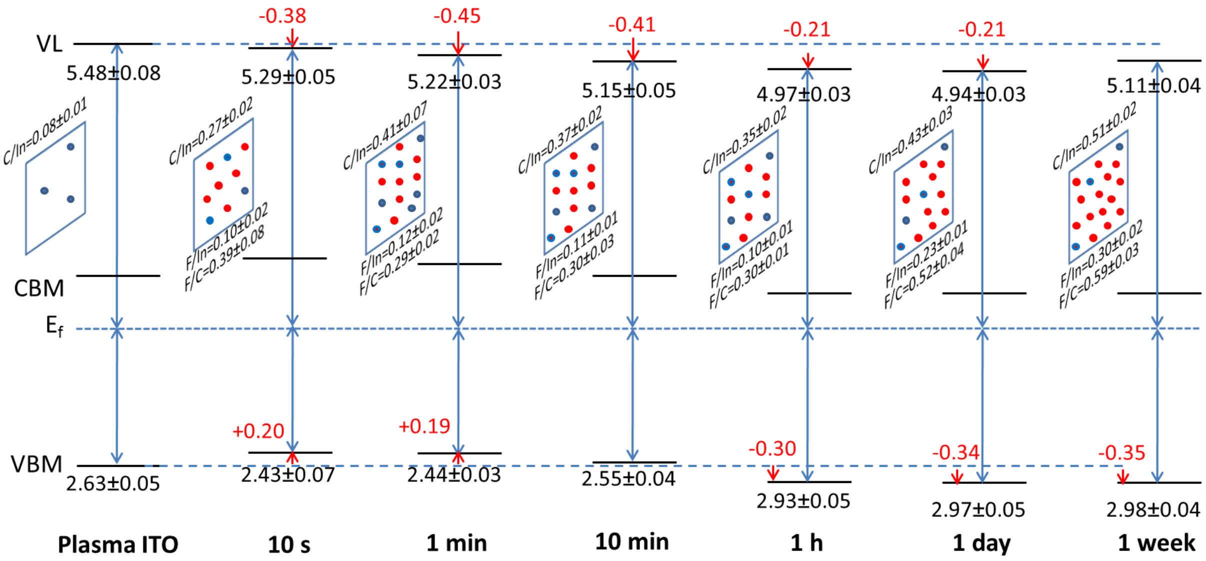

Figure S6. Energy level diagrams constructed from UPS data for plasma treated ITO, and different immersion times in 10 mM PFBPA solution at room temperature. Significant changes in vacuum potential or valence band maximum relative to starting DSC ITO are represented by the small red arrows at the vacuum level. Band gap assumed as 3.6 eV and maintained constant throughout. Blue circles represent adventitious carbon and red circles represent phosphonic acid.

S6. XPS/UPS data summary for DSC-only ITO modified at 75 °C with PFBPA

A summary of the findings for the electronic structure of samples modified using this protocol is shown in Figure S7. Short immersion times (10 s, 1 min) do not change the electronic structure of ITO; it is only after 10 min or more of immersion that significant molecular dipole contributions arise, and the valence band maximum is constant throughout, which means no net contribution from bond dipoles or geometry rearrangements.

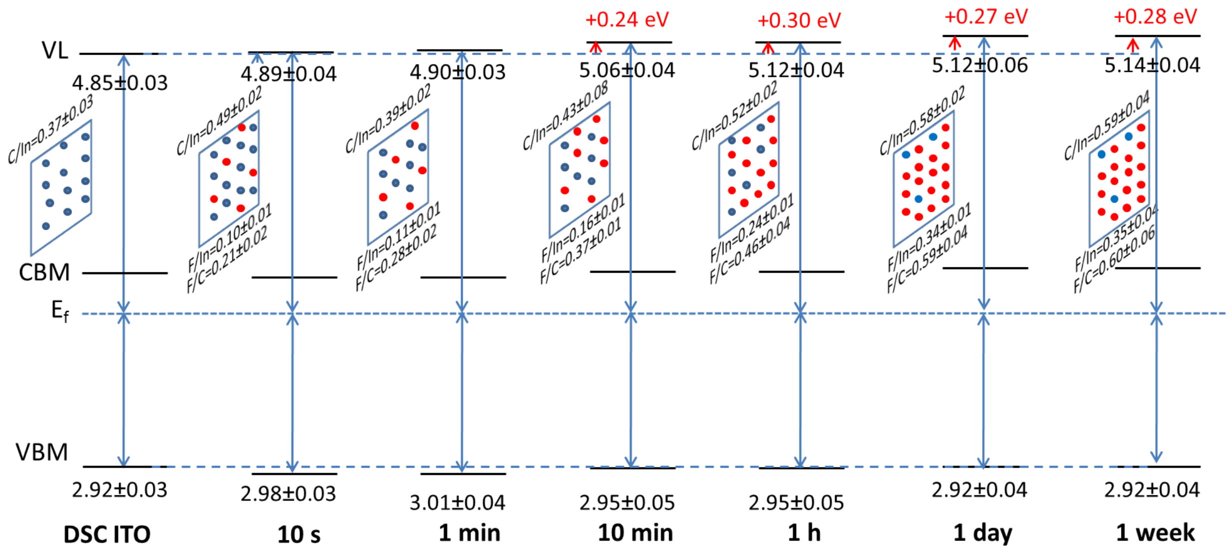

Figure S7. Summary of XPS and UPS results for DSC-only ITO modified with PFBPA 10 mM @ 75 °C. Significant changes in vacuum potential or valence band maximum relative to starting DSC ITO are represented by the small red arrows at the vacuum level. Band gap assumed as 3.6 eV and maintained constant throughout. Blue circles represent adventitious carbon and red circles represent phosphonic acid.

Table S1. Results from Langmuirian fit $\boldsymbol{\Gamma/\Gamma_{max} = A(1-\exp(-k_{ads}ct))}$to adsorption kinetics for 10 mM PFBPA depositions at 75 °C.

Treatment	DSC-only / 75 °C	Plasma / 75 °C
Max. coverage *A*	0.89±0.09	0.93±0.06
k_{ads} /10^2 $M^{-1}h^{-1}$)	4±3	81±27
R^2	0.77	0.90

S8. Supporting Information References

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3 P. B. Paramonov, S. A. Paniagua, P. J. Hotchkiss, S. C. Jones, N. R. Armstrong, S. R. Marder and J. L. Brédas, *Chem. Mater.*, 2008, **20**, 5131.
4 A. J. Giordano, M. Gliboff, A. Hyla, H. Li, K. M. Knesting, D. Nordlund, J. L. Brédas, D. S. Ginger and S. R. Marder, *Manuscript in preparation*.