Formation of the Calcium / Poly(3-Hexylthiophene) Interface: Structure and Energetics

Junfa Zhu,[1,2] Fabian Bebensee,[3] Wolfgang Hieringer,[4] Wei Zhao,[1] Jack H. Baricuatro,[2] Jason A. Farmer,[2] Yun Bai,[3] Hans-Peter Steinrück,[3] J. Michael Gottfried,[3] Charles T. Campbell*[2]*

[1]University of Science and Technology of China, National Synchrotron Radiation Laboratory, Hefei 230029, Peoples Republic of China

[2]Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA

[3]Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

[4]Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Supporting Information

1. Sample Optical Absorbency

For a proper calibration of the heat detector signal, the absolute value of sample absorbency must be known, because the calibration is nothing else, but the correlation between the deposited energy – the well known incident laser power multiplied with the pulse length and the reflectivity (in the case of rather massive metal samples the transmission is negligible and therefore reflectivity and absorbency are easily calculated from the other) – and the respective signal. The absorbency of freshly prepared P3HT films was measured ex-situ using an integrating sphere and found to be ~0.3. (For an individual sample, the absorbency was of course determined with a much higher accuracy of ±2%.)

In addition to its importance for the calibration of the heat detector signal, the optical absorbency influences the experiment via the radiation contribution from the hot effusive metal source to the measured signal: although the incident energy per pulse stays constant for this contribution during the whole experiment (the oven temperature is kept constant), the portion of the signal caused by the oven radiation changes with the absorbency. A change in the absorbency caused by metal deposition may be expected and indeed has indeed been observed in previous studies.[1-5] Monitoring the changes in the detector response to a fixed incident power (laser pulses) as a function of Ca coverage gives direct access to the relative changes in the sample absorbency. This method has been successfully applied to this problem before.[5] Figure 5 shows the sample response (normalized to the initial one) to 100 ms pulses of radiation from a He-Ne laser with constant energy as a function of Ca coverage. It remains almost constant when the coverage is less than 1 ML, followed by a decrease to 90% up to 1.5 ML, thereafter it remains almost unchanged.

Thus, the contribution of the oven radiation for every pulse at all coverages can be determined (from the reference data obtained at the beginning and end of every experimental run) and subtracted from the unmodified detector signal in order to give the heat of adsorption.

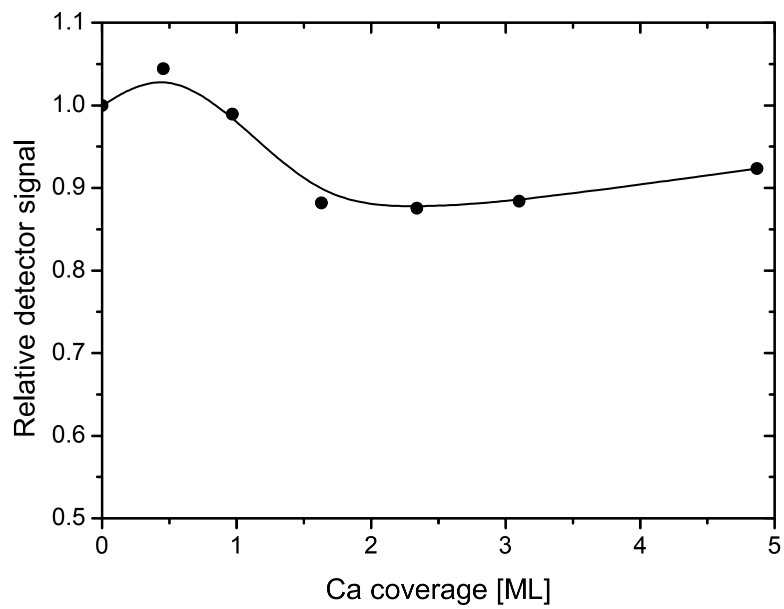

Figure S1. Normalized detector response to pulses of a He-Ne laser of constant energy (0.58 μJ/pulse) as a function of Ca coverage; the solid line is a guide for the eye. The variation of the signal is caused by changes in the optical reflectivity with metal coverage. The detector sensitivity was 450 $V/J_{absorbed}$. All calorimetric signals were corrected for this coverage-dependent change in reflectivity, which influences the measured heats because of absorption of radiation from the source.

References

(1) Starr, D. E. *Microcalorimetric heats of adsorption, surface residence times and stick probabilities of metals on metal-oxide, and silicon substrates.* Ph.D. thesis, University of Washington, Seattle, 2001.

(2) Starr, D. E.; Bald, D. J.; Musgrove, J. E.; Ranney, J. T.; Campbell, C. T. *J. Chem. Phys.* **2001**, *114*, 3752.

(3) Dvorak, J.; Dai, H.L. *J. Chem. Phys.* **2000**, *112*, 923.

(4) Persson, B. N. *Phys. Rev. B* **1991**, *44*, 3277.

(5) Zhu, J.; Goetsch, P.; Ruzycki, N.; Campbell, C. T. *J. Am. Chem. Soc.* **2007**, *129*, 6432-6441.

2. Complete reference 24

(24) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Deglmann, P.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Hättig, C.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Christian; Ochsenfeld; Öhm, H.; Patzelt, H.; Oliver Rubner; Schäfer, A.; Schneider, U.; Sierka, M.; Treutler, O.; Unterreiner, B.; Arnim, M. v.; Weigend, F.; Weis, P.; Weiss, H.; TURBOMOLE version 5.9, University of Karlsruhe.