

Delayed Electron Transfer through Interface States in Hybrid ZnO/Organic-Dye Nano-Structures

Christian Strothkämper,[†] Andreas Bartelt,[†] Phillip Sippel,[†] Thomas Hannappel,^{†,‡} Robert Schütz,[†] and Rainer Eichberger[†]

[†]Helmholtz Center Berlin for Materials and Energy, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

[‡]Ilmenau University of Technology, Gustav-Kirchhoff-Straße 5, D-98693 Ilmenau, Germany

Supporting Information

Morphology of the Nanorods

To give the reader an impression of the morphology and the heterogeneity of the nanorods, SEM side and top view pictures are shown in Figure S1.

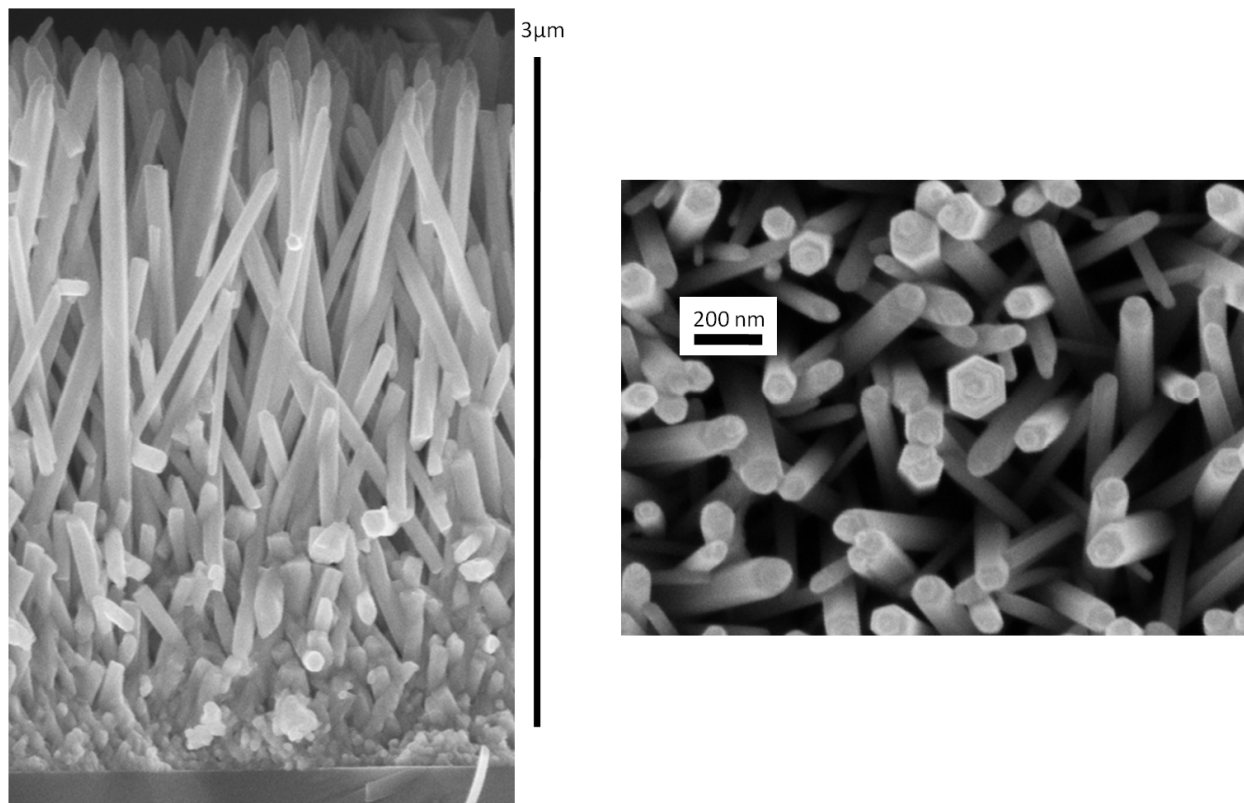


Figure S1 Side (left) and top view (right) pictures of ZnO nanorod sample.

Ground State Optical Absorption Spectra

Figure S2 exhibits the optical absorption spectra of C3, C7, and C11 dissolved in methanol and bound to ZnO nanorods. With respect to the molecules in solution the absorption spectrum of the chemisorbed molecules is broadened. This broadening is neither due to lifetime broadening or aggregation but rather due to the heterogeneity of the chemical environment.¹

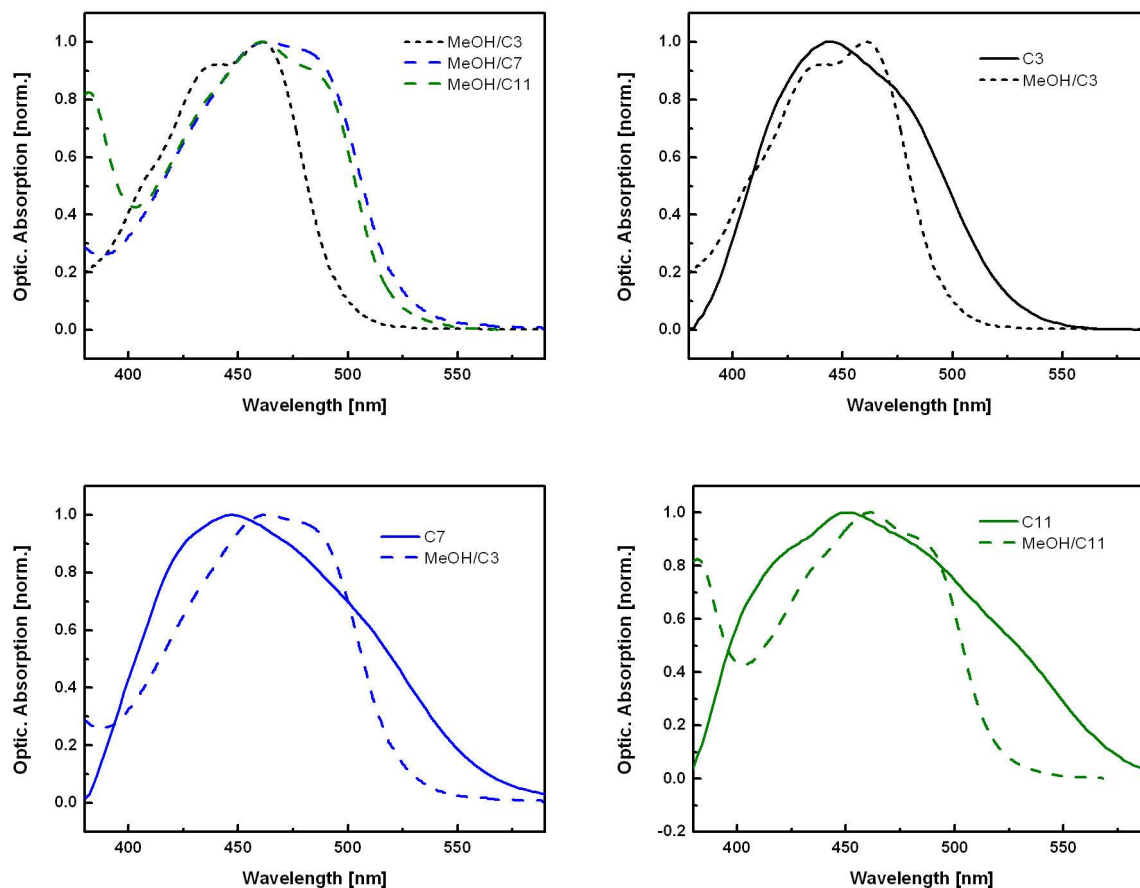


Figure S2 (a) Optical absorption of C3, C7 and C11 dissolved in methanol. (b) Optical absorption of C3 anchored on ZnO and dissolved in methanol. (c) Optical absorption of C7 anchored on ZnO and dissolved in methanol. (d) Optical absorption of C11 anchored on ZnO and dissolved in methanol.

Differential Absorption of the Hybrid Systems

Figure S3 and Figure S4 exhibit the differential absorption of the ZnO hybrid systems consisting of ZnO nanorods and the molecules C5, C7, C9 and C11. Their differential absorption is very similar to that of ZnO/C3, which is shown in ref. ², where the excited state and the cation absorption peak at 710 nm and 590 nm. At short pump-probe delays the differential absorption is dominated by the absorption band of the excited state, which peaks at 650 nm - 720 nm (depending on the dye) and also has significant contributions in the NIR for C9 and C11 (Figure S4). For C5 and C11 an independent measurement of the excited state absorption in methanol yields a maximum at 720 nm and 665 nm, respectively, which is about identical to the adsorbed molecules.³ At longer pump-probe delays the intensity of the excited state absorption band decreases while a new band gains intensity at the blue flank of the excited state absorption (Figure S4).

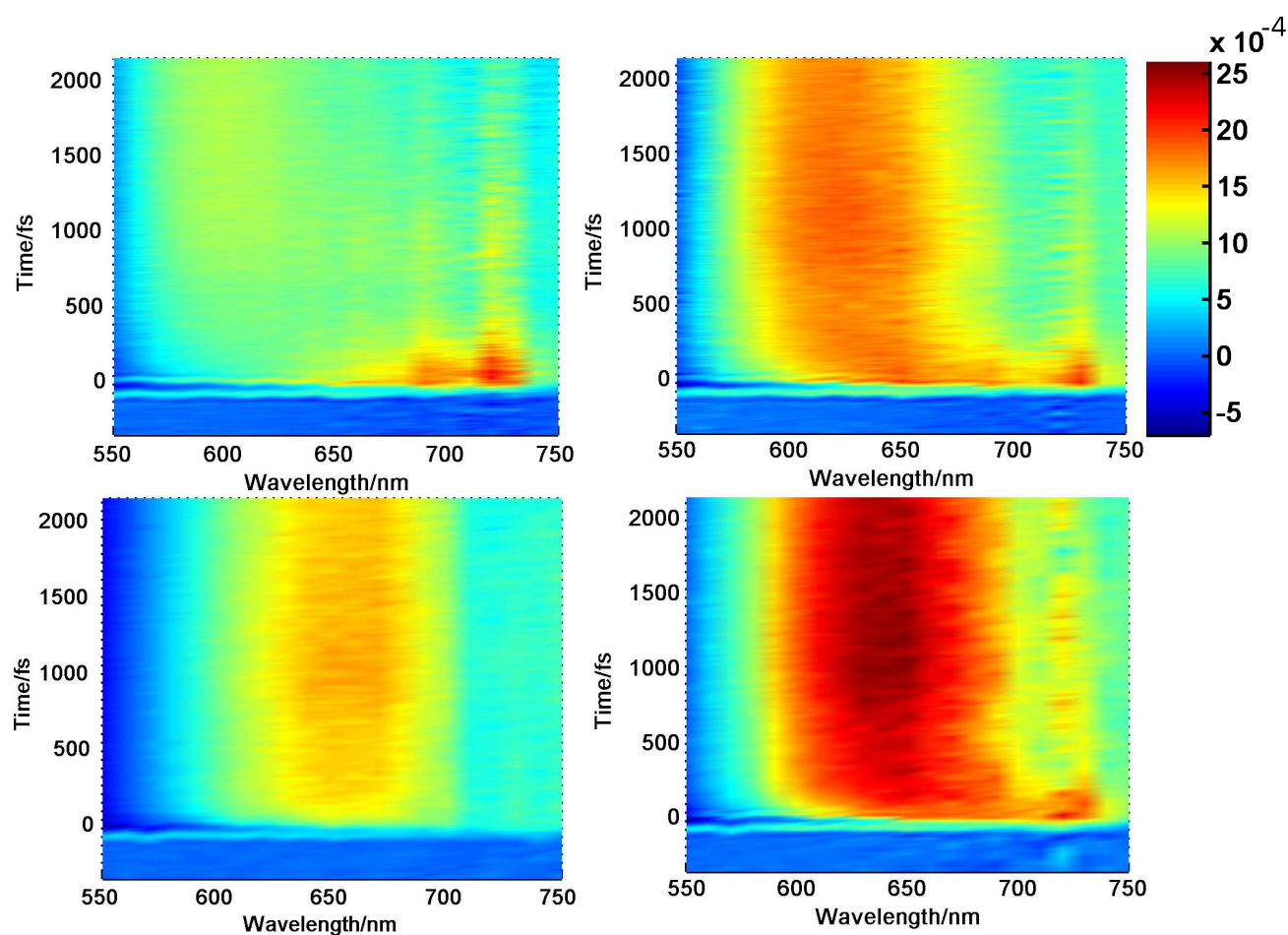


Figure S3 Transient differential absorption of ZnO nanorods with (clockwise, starting top left) C5, C7, C9 and C11 after excitation at 440 nm. The scale bar applies to all graphs. Positive values indicate increased absorption. The increase in differential absorption in the depicted spectral region is attributable to excited and oxidized molecules. The decrease in absorption at the low wavelength side is due to the bleaching of the ground state.

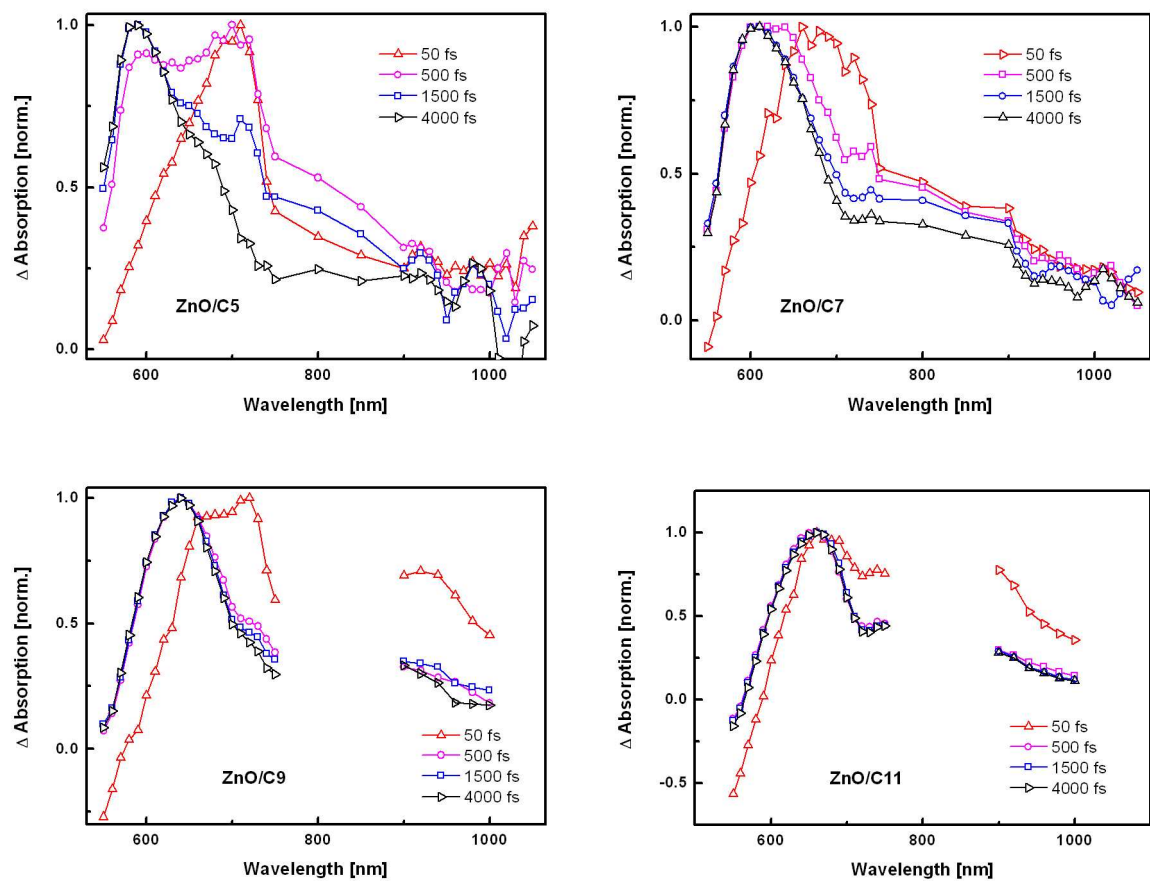


Figure S4 Transient differential absorption spectra at different pump-probe delays.

HOMO and LUMO calculations

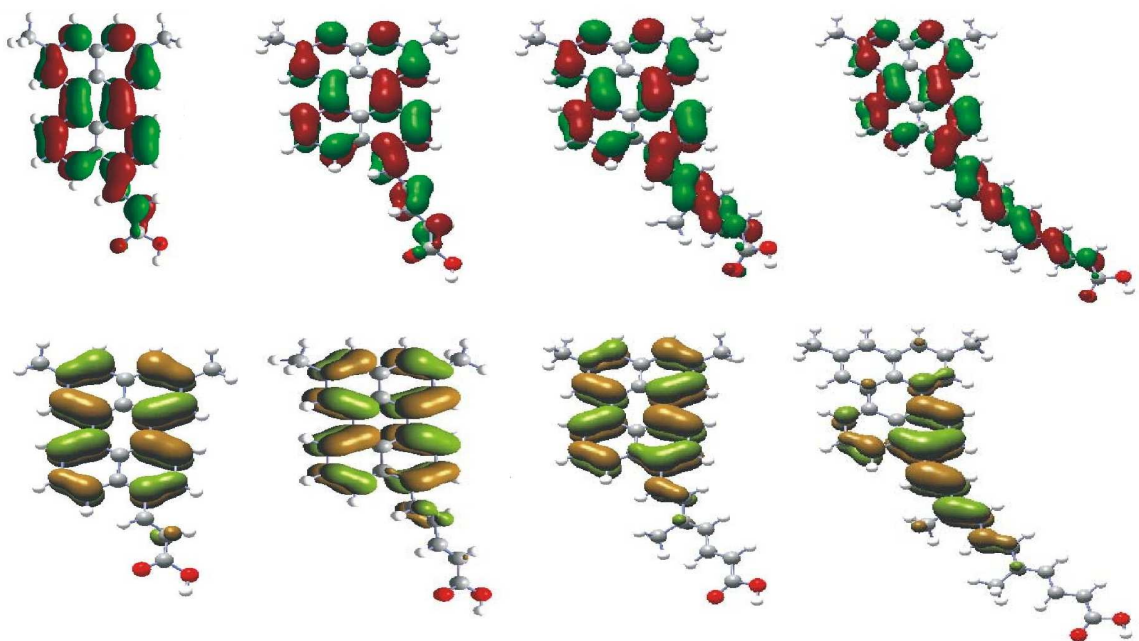


Figure S5 Top: Isodensity plots of the LUMO's of C3, C5, C7 and C11 (left to right). Bottom: Isodensity plots of the LUMO's of oxidized C3, C5, C7 and C11 (left to right). The semiempirical molecular orbital calculations were done using AMPAC with the method AM1. The restricted/unrestricted Hartree-Fock (open/closed shell) method was used for the neutral/oxidized molecule, respectively. Taken with permission from ref. 3.

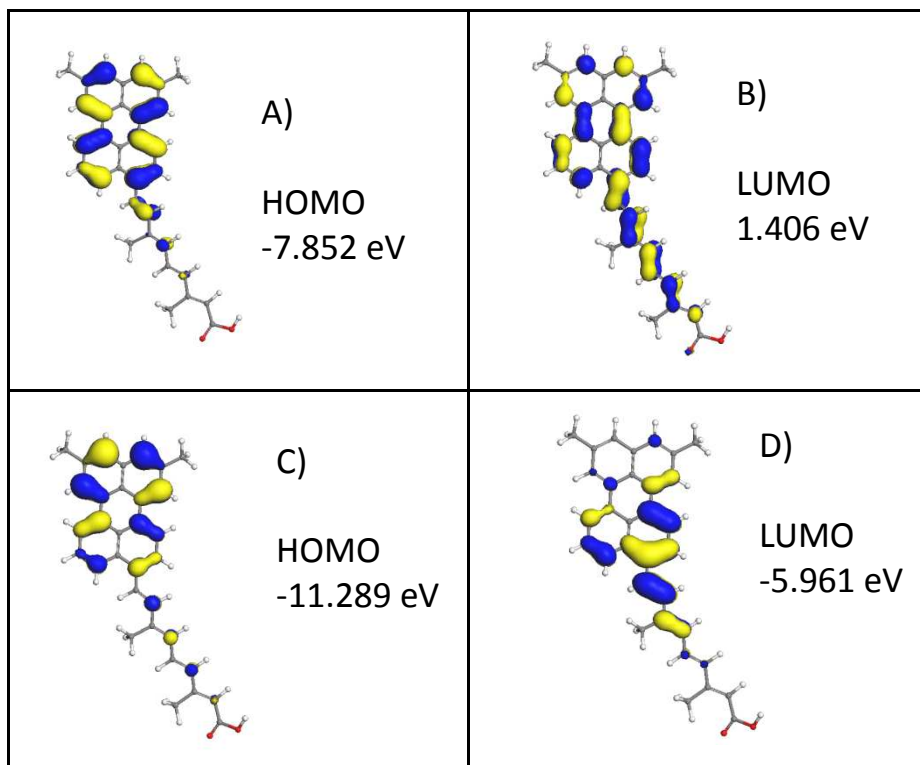


Figure S6 Isodensity plots of different molecular orbitals of the molecule C9. A) HOMO of neutral C9. B) LUMO of neutral C9. C) HOMO of the cation. D) LUMO of the cation. The semiempirical molecular orbital calculations were done using Materials Studio 6.0 (NDDO Hamiltonian, AM1). The restricted/unrestricted Hartree-Fock (open/closed shell) method was used for the neutral/oxidized molecule, respectively.

Orientation of the Molecules on $\text{ZnO}(10\bar{1}0)$

DFT calculations of C9 adsorbed onto the surface of a $(\text{ZnO})_{42}$ cluster were done at the same level of theory as that in ref. ⁴:

“The ZnO and dye@ZnO models have been optimized in vacuo using the BPW91 exchange-correlation functional,⁴⁸ as implemented in the ADF program package.⁴⁹”

(48) A. D. Becke, Phys. Rev. A: At., Mol., Opt. Phys., 1988, **38**, 3098100; (b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Phys. Rev. B, 1992, **46**, 667187.

(49) G. Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, J. Comput. Chem., 2001, **22**, 931–967.

The calculations show that the molecules are oriented upright on $\text{ZnO}(10\bar{1}0)$ even with a prolonged bridge (Figure S7). Thus, the distance of the chromophoric unit to the surface can be controlled by the bridge length.

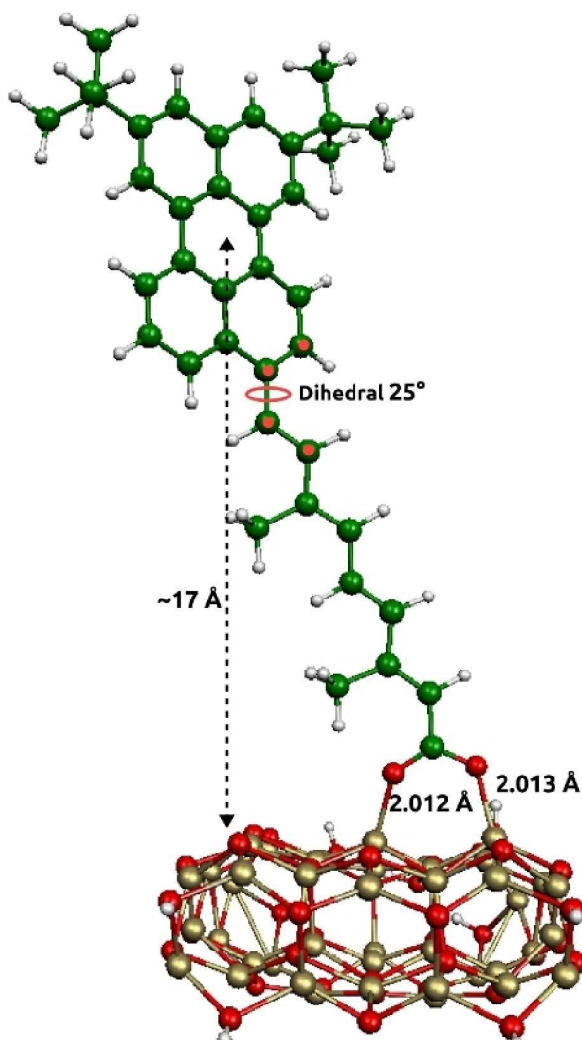


Figure S7 Optimized adsorption geometry of C9 on ZnO.

References

- (1) Neubauer, A.; Szarko, J. M.; Bartelt, A. F.; Eichberger, R.; Hannappel, T. *J. Phys. Chem. C* **2011**, *115*, 5683–5691.
- (2) Szarko, J. M.; Neubauer, A.; Bartelt, A.; Socaciu-Siebert, L.; Birkner, F.; Schwarzburg, K.; Hannappel, T.; Eichberger, R. *J. Phys. Chem. C* **2008**, *112*, 10542–10552.
- (3) Neubauer, A. *Investigation of Ultrafast Electron Transfer Dynamics of Organic/Inorganic Interfaces Employing Femtosecond Spectroscopy in Ultrahigh Vacuum*; Brandenburg University of Technology: Cottbus, 2009.
- (4) Amat, A.; De Angelis, F. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10662–10668.