

## Spectroelectrochemistry of Single Molecules/Nanoparticles

Caleb Hill and Shanlin Pan

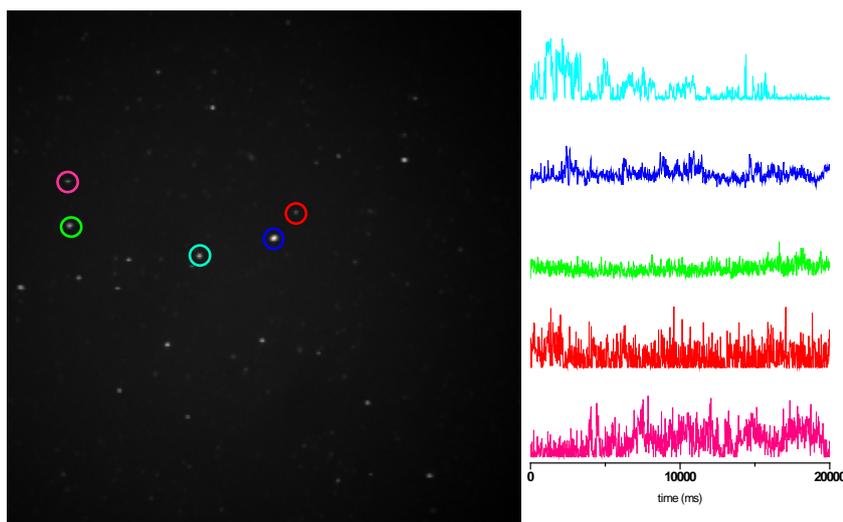
Center for Materials for Information Technology (MINT)

Department of Chemistry

University of Alabama

Tuscaloosa, AL, U.S.A.

Organic photovoltaics (OPV) have been investigated as a possible alternative due to the comparatively low cost of organic materials and the ease with which these cells can be fabricated. Free charge carriers are generated in organic solar cells at the interface of an electron-donating (D) and an electron-accepting (A) material due to high interfacial electric fields and differences in chemical potential. There are a large number of factors that affect the performance of an OPV device. For instance, the efficiency of an OPV can be largely limited by short exciton diffusion lengths and poor carrier transport in organic species. The optimization of one device parameter at a time is a rather daunting task if using overall efficiency as a metric. Resultantly, various analytical techniques have

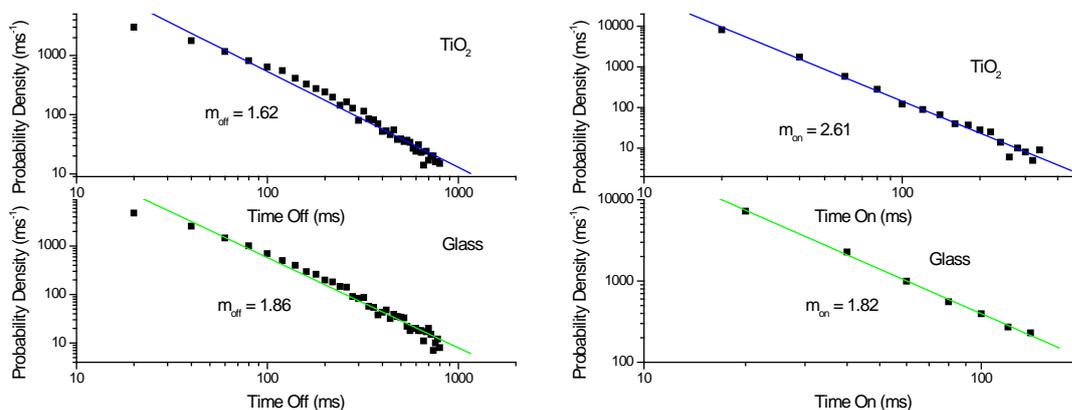


**Figure 1:** Fluorescence image of single CdSe/ZnS core/shell QDs on glass applied by spincoating from a 100 ng/mL solution in toluene (left) and corresponding fluorescence trajectories for individual QDs (right)

been employed to evaluate the potential of a system before attempting to fabricate and optimize a real device. Here, we present single molecule/particle spectroscopic (SMS/SPS) studies of CdSe/ZnS core/shell quantum dots and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) molecules on  $\text{TiO}_2$ , which both represent actual OPV systems of interest. An example SP image can be seen in **Figure 1**.

Both CdSe/ZnS core/shell QDs and single MEH-PPV molecules exhibited typical fluorescence “blinking” behavior which was sensitive to the substrate used; on  $\text{TiO}_2$  both fluorophores exhibited shifts to shorter “on” state durations and longer “off” state durations when compared to measurements

on glass. These distributions were found to exhibit power law behavior, where the probability density,  $P(t)$ , obeys  $P(t) \propto t^{-m}$ ; this behavior is indicative of a high variation in “dark” state creation/annihilation kinetics.<sup>1-4</sup> Examples of these distributions for the CdSe/ZnS QDs can be seen in **Figure 2**. It is our hypothesis that the observed substrate sensitivity is due to electron transfer from the excited states of the individual fluorophores to the conduction band (CB) or surface defect states of TiO<sub>2</sub>.



**Figure 2:** Log-log plots of “on” and “off” time probability densities for QDs on Glass and TiO<sub>2</sub>

## REFERENCES

1. Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. "On"/"off" fluorescence intermittency of single semiconductor quantum dots. *J. Chem. Phys.* **2001**, 115, 1028.
2. Wang, Y.; Wang, X.; Ghosh, S. K.; Lu, H. P. Probing Single-Molecule Interfacial Electron Transfer Dynamics of Porphyrin on TiO<sub>2</sub> Nanoparticles. *J. Am. Chem. Soc.* **2009**, 131, 1479-1487.
3. Hoogenboom, J. P.; van Dijk, Erik M. H. P.; Hernando, J.; van Hulst, N. F.; Garcia-Parajo, M. F. Power-Law-Distributed Dark States are the Main Pathway for Photobleaching of Single Organic Molecules. *Phys. Rev. Lett.* **2005**, 95, 097401.
4. Shimizu, K. T.; Neuhauser, R. G.; Leatherdale, C. A.; Empedocles, S. A.; Woo, W. K.; Bawendi, M. G. Blinking statistics in single semiconductor nanocrystal quantum dots. *Phys. Rev. B* **2001**, 63, 205316.