

Electronic Interactions in Hybrid Organic-Nanoparticle Materials

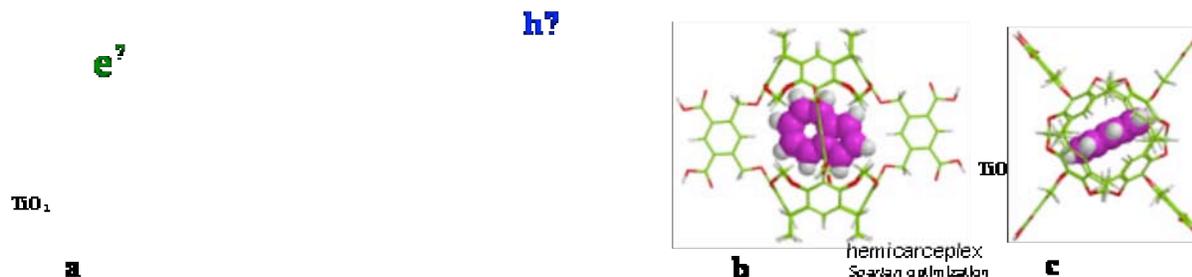
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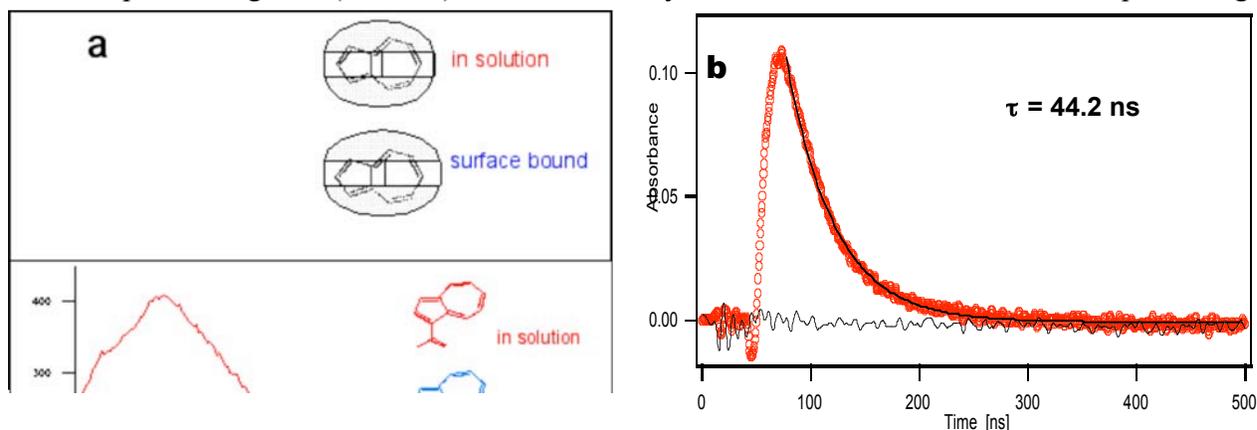
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The progress in three areas of our collaborative research aimed at the understanding of interactions in heterogeneous materials consisting of semiconductor nanoparticles and molecular components that are also of nanometer size is reported. The long term goal of these efforts is to achieve a similar degree of control over electronic interactions at interfaces between molecules and nanoparticles as is already possible in purely molecular synthetic systems. Specific objectives include ultrafast long-range transduction of signals through organic bridges ('molecular wires') and the design of nanometers sized sensor and molecular transporters.

1. Host-Guest Complexes bound to Semiconductor Nanoparticles: Towards Size Selective Nanosensors: Novel hybrid system consisting of amphiphilic host-guest complexes (hemicarceplexes) bound to metal oxide nanoparticles were prepared. The presence of carboxylic



groups on the periphery of the molecular container serves dual function: (1) renders it water-soluble; (2) enables attachment to metal oxides. The water soluble host encapsulates a hydrophobic guest in a highly size selective manner and binds it to the surface of a semiconductor nanoparticle. The formation of the complete ternary assembly and the presence of the encapsulated guest (azulene) were sensed by electron transfer fluorescence quenching

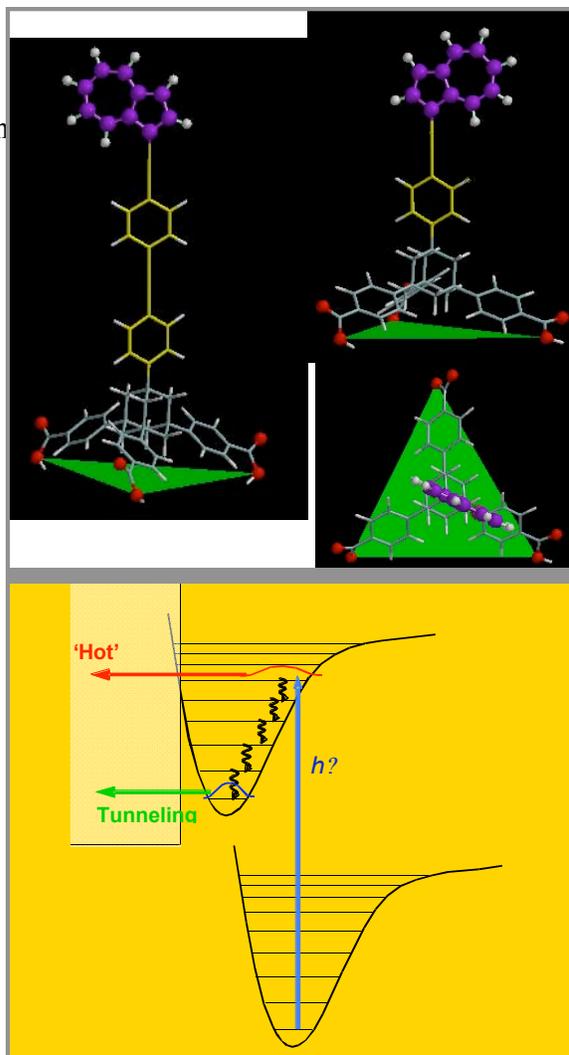


(above, left).² The formation of encapsulated azulene radical cations resulting from the electron injection from host-guest complex into TiO_2 was confirmed by transient absorption measurements. Encapsulation within the hemicarceplex dramatically slows down the recombination and extends the lifetime of the guest radical cation (above, right). The

recombination kinetics is well reproduced by a single exponential with $\tau = 44.2$ ns. This is in contrast with any other recombination processes on TiO_2 which exhibit complex behavior. The homogeneous kinetics suggests that the quantum mechanical tunneling of the electron through the wall of the hemispherical and back to the radical cation of the guest is the rate limiting step of the process. To summarize, at this early stage of the project we have demonstrated that water soluble hemispherical dendrimers can be used to intercept hydrophobic molecules and bind them to the surface of TiO_2 nanoparticles. The presence of the incarcerated chromophore can be detected by fluorescence quenching. Hemispherical dendrimers can also be bound to films of TiO_2 on solid support, e.g. conducting glass. In this case, the sensing of the sequestered guest can be accomplished via the measurement of the generated photocurrent. This approach is currently explored.

2. Long-range Electron Injection from 'Molecular Tripods' into TiO_2 Nanoparticles:

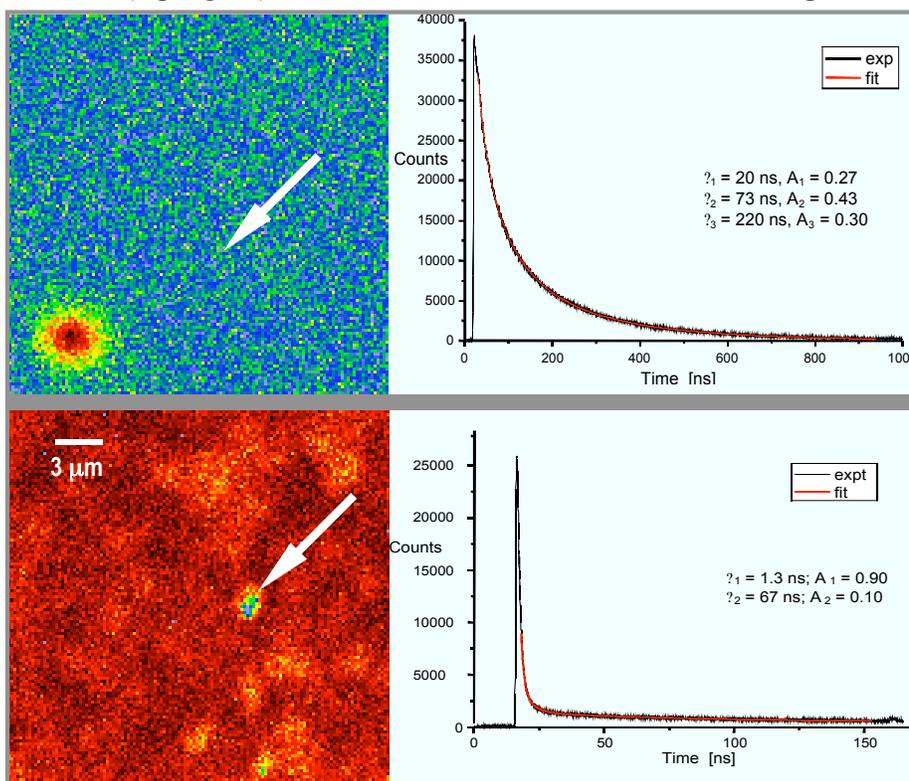
Molecular tripods have a tetrahedral core made of tetraphenylmethane or tetraphenyladamantane, three $-\text{COOH}$ binding groups and a rigid bridging unit carrying the chromophore. This design provides a stable, 3-point attachment to the surface of metal oxide nanoparticles and a well-defined position and orientation of the chromophore on nanoparticle surfaces (on the right, top). The second type of linker is a "rigid-rod" that provides continuous π -conjugation between the chromophore and the binding groups. Aromatic chromophores, with their well-defined spin states and vibronic structures were selected to provide detailed insights that are difficult to obtain from the more commonly studied inorganic sensitizers. Azulene, with its long-lived emissive S_2 state and the extremely short-lived S_1 provides a unique "molecular clock". We have already demonstrated that charge injection from the S_2 states of 1-carboxy and 2-carboxyazulene bound to TiO_2 is complete within 100 fs. Because of the short lifetimes azulene is exceptionally well suited for the study of charge injection from short-lived vibrationally "hot states" (on the right, bottom). Pyrene's unusually long-lived S_1 state (190 ns in polar and 650 ns in nonpolar media) coupled with the favorable redox potentials makes it a frequent choice for photoinduced ET experiments. The long excited state lifetime is an assurance that the charge injection will occur even at the largest distances between the chromophore and the nanoparticle. Indeed, efficient ET from pyrene attached to TiO_2 surface by the "rigid rod" linker has been already demonstrated.³ Detailed ultrafast spectroscopy measurements on the pyrene and azulene systems await the installation of a set of two noncollinear optical parametric amplifiers (NOPAs) in December 2005. Lastly, 2-photon photoelectron spectroscopy experiments on perylene bearing 'molecular tripods' bound to monocrystalline rutile were performed in



collaboration with the group of Dr. Frank Willig at the Hahn-Meitner Institute in Berlin. These measurements are very important as they confirm that the principal axis of the tripod assembly is normal to the surface of the semiconductor substrate.⁴

3. Homogeneity of Binding to TiO₂ Nanoparticles and Mesoporous Films: The critical issue in any interfacial studies is the mode and the homogeneity of binding of the active molecular component to the semiconductor or metallic substrate. Time resolved confocal microscopy measurements reveal a broad range of emission lifetimes in surface modified TiO₂ samples. The inhomogeneity depends strongly on the nature of the semiconductor substrate and the treatment of the sample. Dye sensitized mesoporous films prepared in the standard ‘Graetzel cell’ fashion display the broadest range of lifetimes with the slowest components of the multiexponential decay reaching hundreds of nanoseconds (top figure). In contrast, dilute surface modified nanoparticles

that were extensively dialyzed prior to the measurement exhibit much weaker emission with a dramatically narrower range of lifetimes of only a few nanoseconds (lower figure). This shows that in mesoporous films a fraction of the dye is loosely trapped within the pores and undergoes very slow, diffusional quenching. The origin of residual emission in the dialyzed particles is not clear. It may result from binding to surface defects or from dye molecules that are sufficiently strongly physisorbed to survive the dialysis. The issue of binding homogeneity will continue to be investigated in collaboration with the single molecule spectroscopy group of Dr. Johan Hofkens at the KU Leuven, Belgium.



References:

- [1] For further information about this project contact galoppin@andromeda.rutgers.edu, meyer@jhu.edu or piotr@andromeda.rutgers.edu.
- [2] Hybrid Photoactive Assemblies: Electron Injection from Host-Guest Complexes into Semiconductor Nanoparticles, C. Pagba, G. Zordan, E. Galoppini, E.L. Piatnitski, S. Hore, K. Deshayes, P. Piotrowiak, *J. Am. Chem. Soc.* 2004, 126, 9888
- [3] New Rigid-Rod Linkers for Coupling Molecules to Metal Oxide Nanoparticles, E. Galoppini, D. Wang, W. Guo, P. Piotrowiak, P.G. Hoertz, R.A. Carlisle, G.J. Meyer, *Nanolett.* 2003, 3, 325.
- [4] Ultrafast Heterogeneous Electron Transfer Probed with Photoemission Spectroscopy, Gundlach L., Eichberger R., Zimmermann C., Ernstorfer R., Felber S., Töben L., Galoppini E., Wei Q., Willig F. in *Femtochemistry and Femtobiology*, M.M. Martin and J.T. Hynes Editors, Elsevier, 2004, pp. 539-532.