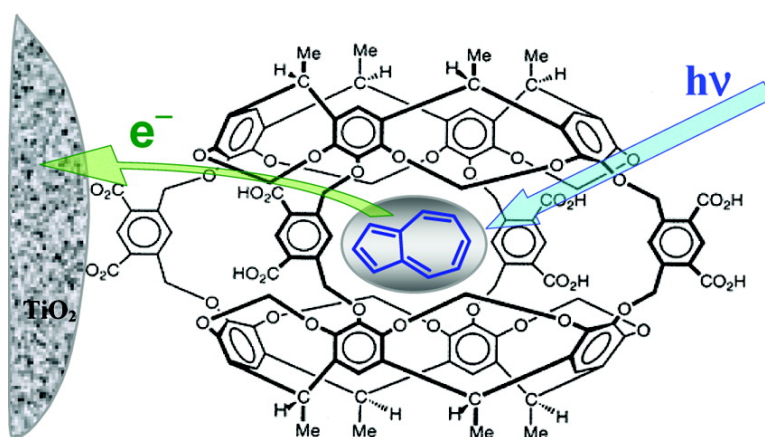


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J. Am. Chem. Soc., **2004**, 126 (32), 9888-9889 • DOI: 10.1021/ja0475252 • Publication Date (Web): 22 July 2004

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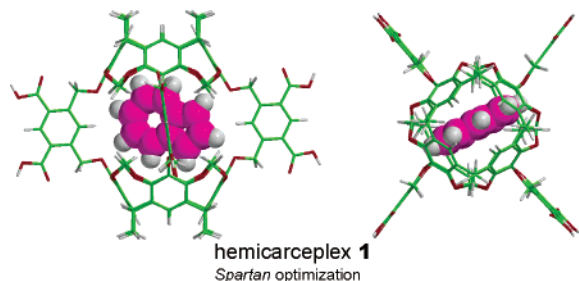
Hybrid Photoactive Assemblies: Electron Injection from Host–Guest Complexes into Semiconductor Nanoparticles

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One of the most promising applications of supramolecular chemistry has been the selective binding, transport, and detection of molecular and ionic species.^{1,2} Cyclodextrins, calixarenes, cryptands, and crown ethers received the bulk of attention, while the chemistry of fully encapsulating molecular containers (hemicarcerands)³ remains little explored in this context. Cram-type encapsulating host–guest complexes (hemicarceplexes) were used in the past to study fundamental aspects of electron and excitation transfer processes,^{4–8} as well as to isolate reactive intermediates.⁹ Hemicarceplexes made it possible to map out the Marcus inverted region in triplet energy transfer and to analyze the dependence of energy transfer on the internal reorganization energy, λ_{int} , of the donor and the acceptor.⁸ In a separate study the dependence of the transfer rate on the size of the molecular container was investigated.¹⁰ As a result of these studies electron and excitation transfer between encapsulated chromophores and partners on the outside of the hemicarcerand are understood in a quantitative manner.



In this report we describe a novel hybrid system consisting of amphiphilic host–guest complex (hemicarceplex) **1** bound to the surface of metal oxide nanoparticles. The presence of eight carboxylic groups on the periphery of the molecular container (hemicarcerand)¹¹ serves a dual function: (1) renders it water-soluble under pH from 7.5 upward and (2) enables attachment to metal oxides such as the wide band gap semiconductor TiO₂. The water-soluble host encapsulates a hydrophobic guest in a highly size-selective manner and delivers it to the surface of a semiconductor nanoparticle. Azulene was selected as the guest chromophore because of its compatibility with the size of the molecular container and favorable photoredox properties (strong S₀–S₂ absorption in the near-UV and low oxidation potential). The formation of the complete ternary assembly and the presence of the encapsulated guest were sensed by electron transfer (ET) fluorescence quenching. In aqueous solution the insertion of the hydrophobic guest into the lipophilic cavity of the host is spontaneous and occurs within

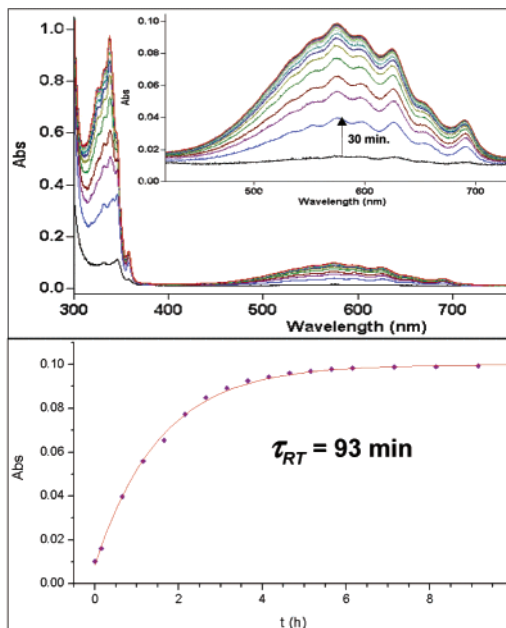


Figure 1. Kinetics of “incarceration” of azulene and formation of hemicarceplex **1** monitored by UV–vis spectroscopy at 20 °C.

minutes to hours, indicating the presence of a high activation barrier associated with the ingress and egress from the cage. The thermodynamic stability of **1** is determined by the hydrophobicity of the guest and its size. For large nonpolar guests such as naphthalene, ferrocene, and azulene that match well the $\sim 200 \text{ \AA}^3$ internal volume of the host, the binding constants exceed $1 \times 10^8 \text{ M}^{-1}$, with the corresponding free energies in excess of -12 kcal/mol .¹² ¹H NMR and UV–vis spectroscopy show that upon addition of solid azulene to aqueous solution of empty octacarboxyhemicarcerand, the normally insoluble azulene enters the hydrophobic interior of the cage to form a 1:1 host–guest complex **1**. The kinetics of the encapsulation process has been fully characterized (Figure 1).

Upon photoexcitation at 345 nm hemicarceplex **1** exhibits the characteristic S₂–S₀ fluorescence of azulene (Figure 2a). When a $2 \times 10^{-4} \text{ M}$ solution of **1** is mixed with a 1 g/L solution of TiO₂ nanoparticles with average radius of 10 nm, nearly total (90%) quenching of emission takes place, indicating that efficient photoinduced electron transfer from the S₂ state of encapsulated azulene to the conduction band of TiO₂ takes place. Similar behavior is observed when 1-carboxy- or 2-carboxyazulene is directly bound to the surface of colloidal TiO₂ (Figure 2b). Considering the 1.3 ns lifetime of the S₂ state of azulene,¹³ this reduction of emission yield corresponds to the electron injection taking place with a time constant of 140 ps. While this rate of transferring an electron across

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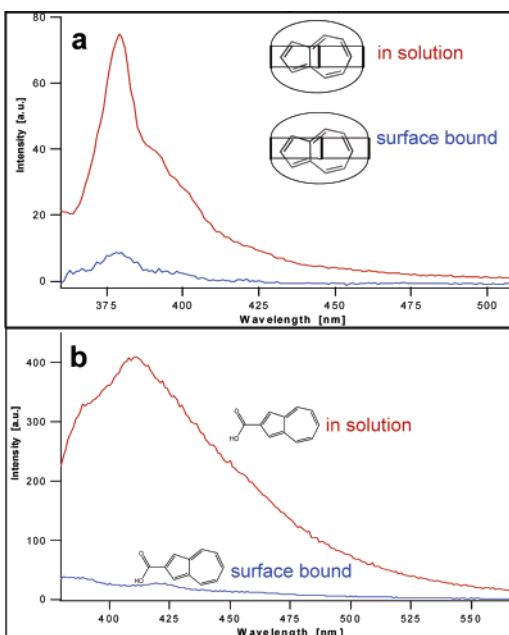


Figure 2. (a) Electron-transfer quenching of the S_2 - S_0 fluorescence of azulene encapsulated within the octacarboxyhemicarcerand upon binding to TiO_2 ; (b) corresponding quenching of the S_2 - S_0 fluorescence of 2-carboxyazulene directly bound TiO_2 nanoparticles. Excitation at 345 nm, $\epsilon_{\text{azulene}} = 5 \times 10^3 \text{ M}^{-1} \text{ L}^{-1}$, emission intensities corrected for light scattering and absorption by TiO_2 .

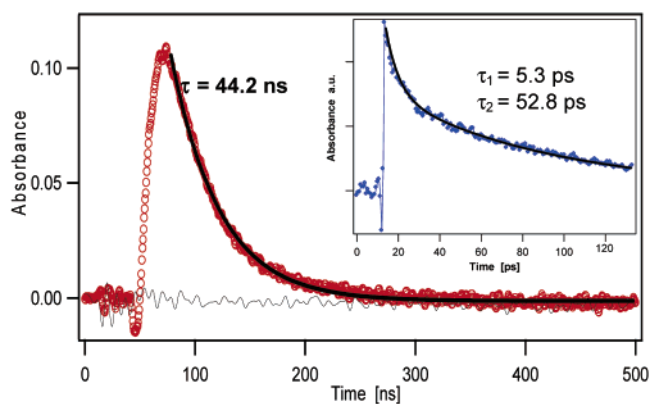


Figure 3. Monoexponential charge recombination in hemicarceplex **1** bound to TiO_2 monitored at 750 nm, $k = 2.3 \times 10^7 \text{ s}^{-1}$ (circles and solid fit). Inset: Early portion of the inhomogeneous charge recombination in 1-carboxyazulene bound to TiO_2 , $k_1 = 1.9 \times 10^{11} \text{ s}^{-1}$, $k_2 = 1.9 \times 10^{10} \text{ s}^{-1}$.

the wall of the cage and the cage–nanoparticle interface may appear fast, the corresponding injection in the 1-carboxy- and 2-carboxyazulene/ TiO_2 system, for which ultrafast transient absorption measurements were possible, is complete within 110 fs, i.e. it is ~ 1000 -times faster.¹⁴

The formation of encapsulated azulene radical cations resulting from the electron injection from **1** into TiO_2 was confirmed by nanosecond transient absorption measurements (Figure 3 and Supporting Information). Excitation of **1** in absence of TiO_2 does not produce the azulene radical cation (Figure 3, thin line). Encapsulation within the hemicarcerand dramatically slows down the recombination rate and extends the lifetime of the azulene radical cation. Interestingly, the recombination kinetics is very well

reproduced by a single exponential (Figure 3) with $\tau = 44.2 \text{ ns} \pm 5\%$. This is in sharp contrast with any other charge recombination processes on TiO_2 which exhibit complex multiexponential behavior.¹⁵ For example, in the case of 1-carboxy- and 2-carboxyazulene bound directly to the surface of TiO_2 the recombination has major components ranging from a few picoseconds to tens and hundreds of picoseconds (Figure 3, inset). The homogeneous recombination kinetics strongly suggests that the tunneling of the electron through the wall of the hemicarcerand back to the radical cation of azulene is the rate-limiting step of the process. The slow tunneling through the wall appears to average out the wide distribution of rates that normally results from inhomogeneity of binding and the presence of surface traps. While the precise binding geometry of **1** on TiO_2 cannot be readily determined, the three-dimensional (3D) arrangement of the eight $-\text{COOH}$ groups on its periphery suggests that from one to four of them can be involved in binding to a nanoparticle. The possible distribution in the number of surface linkages is not reflected in the monoexponential recombination kinetics, reinforcing the notion that tunneling through the cage material is indeed the rate-limiting step in the return of the electron.

In summary, we have demonstrated that water-soluble hemicarcerands can be used to intercept hydrophobic molecules and bind them to the surface of semiconductor nanoparticles. The presence of the incarcerated chromophore can be detected by fluorescence quenching. Hemicarceplexes similar to **1** can also be bound to thin films of TiO_2 on solid support, e.g., conducting glass. In this case, the sensing of the sequestered guest can be accomplished through the measurement of the generated photocurrent, in a fashion analogous to the dye-sensitized Grätzel cell.¹⁵ This approach is currently being explored.

Acknowledgment. Support by an NSF-NIRT Grant 0303829 is gratefully acknowledged. We thank Dr. Lazaros Kakalis for the assistance with the collection of the NMR spectra.

Supporting Information Available: ^1H NMR encapsulation kinetics of azulene and additional time-resolved spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0475252