

Electron and excitation transfer in hetero-supramolecular assemblies and at molecule–nanoparticle interfaces*

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Abstract: Encapsulation of chromophores within Cram-type hemicarcerands allowed the investigation of fundamental photophysical phenomena, such as long-range triplet energy transfer, electron transfer, and the remote heavy atom effect. Furthermore, novel water-soluble hemicarcerands are being used to develop unique hybrid materials composed of semiconductor nanoparticles and host–guest assemblies. Photoinduced charge injection from the “incarcerated” guest into the conduction band of the semiconductor has been demonstrated.

INTRODUCTION

Host–guest complexes (hemicarceplexes) [1] consisting of chromophores imprisoned within hemicarcerand “molecular containers” (Figs. 1 and 3) were used to study the propagation of the donor–acceptor electronic coupling across the intervening wall of the molecular cage. Using these systems, it was possible to demonstrate the existence of the Marcus “inverted region” in triplet energy transfer [2–6] and to analyze in unprecedented detail the strong dependence of electronic energy-transfer processes on the internal reorganization energy of the donor and the acceptor [7]. In a separate study, the dependence of the energy-transfer rate, and hence the magnitude of the donor–acceptor electronic interaction, on the size of the molecular cage was investigated [8]. As expected, reducing the size of the molecular cage has a similar effect to decreasing the donor–acceptor distance in linked systems: it increases the donor–acceptor coupling.

In the second part of this report, we describe how these concepts are being applied toward the development of size-selective sensors based on hybrid materials composed of host–guest assemblies (hemicarceplexes) covalently bound to nanoparticles of a wide-band semiconductor, TiO₂. Water-soluble hemicarcerands are used to efficiently trap appropriately sized hydrophobic chromophores whose presence within the molecular container is subsequently detected by fluorescence quenching accompanied by rapid photoinduced electron injection from the chromophore into the conduction band of the semiconductor.

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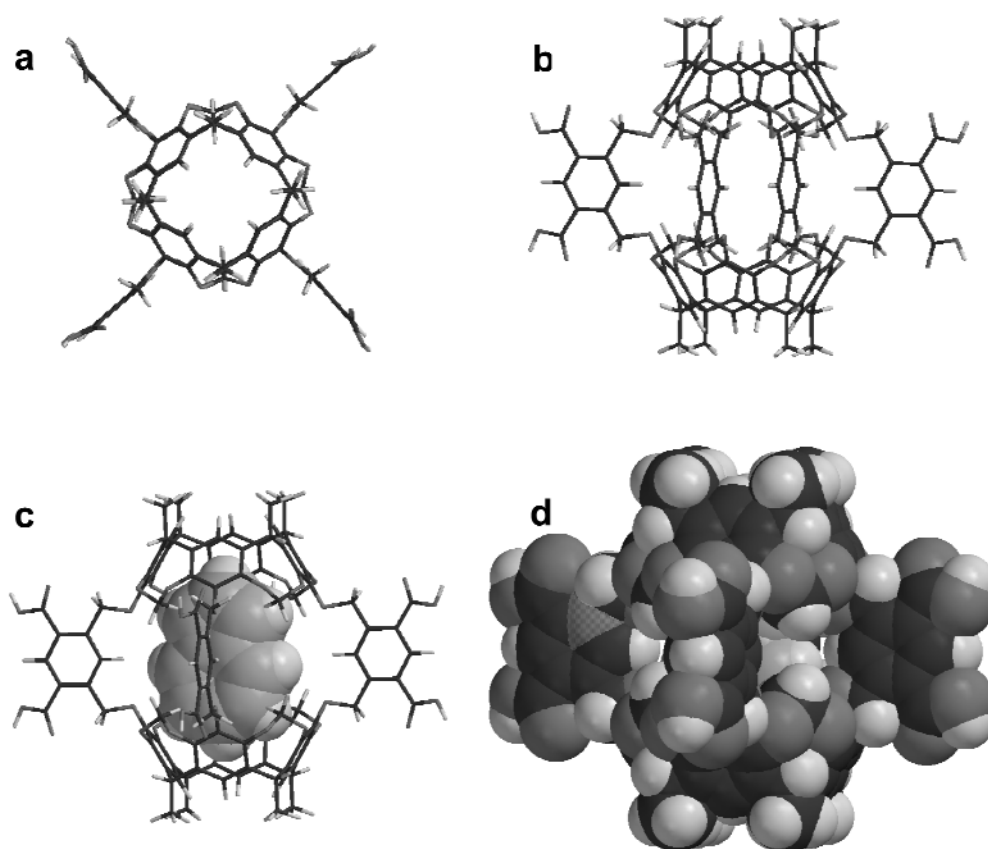


Fig. 1 Two views of the water-soluble octacarboxyhemicarcerand cage molecule (a,b). The hemicarcerand host with the encapsulated azulene guest (c,d). AM1 optimization, PC Spartan Pro, Wavefunction, Inc.

ELECTRONIC INTERACTIONS MEDIATED BY THE WALLS OF HEMICARCERANDS

Dependence of triplet energy-transfer rates on the driving force, ΔG^0 , and the reorganization energy, λ

Because of the encapsulation, the magnitude of the electronic coupling $|V_{DA}|$ between the incarcerated triplet donor and acceptors in solution is greatly reduced. Consequently, triplet energy-transfer rates fall well below the “normal” diffusion-controlled limit of $\sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$ even though the diffusion rate of the acceptor molecules remains unchanged (Fig. 2d). This reduction of $|V|$ allows one to map out the entire Marcus dependence of the transfer rate on the driving force ΔG^0 [3,7].

Hemicarcerand with *o*-xylyl linkers shown in Fig. 3b was used to encapsulate the molecule of biacetyl, which served as triplet energy donor. Biacetyl exhibits a long-lived room-temperature phosphorescence ($\tau \sim 1 \text{ ms}$) and can be readily excited at 450–470 nm, i.e., at wavelengths much longer than the absorption of the hemicarcerand cage ($\sim 300 \text{ nm}$). Triplet energy acceptors corresponding to 17 different values of the driving force were introduced into the solution, and Stern–Volmer analysis of the phosphorescence quenching was performed. The fastest transfer rate constant of $2.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ was observed when pyrene was the acceptor, thus showing that the optimum Frank–Condon factors, $\Delta G^0 = \lambda$, are attained at a fairly low driving force, $\Delta G^0 = 9.3 \text{ kcal/mol}$. For comparison, the triplet of free biacetyl in solution is quenched by pyrene at a nearly diffusion-controlled rate of $6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. In accordance with the Marcus–Jortner equation, the measured transfer rates from encapsulated biacetyl fell off

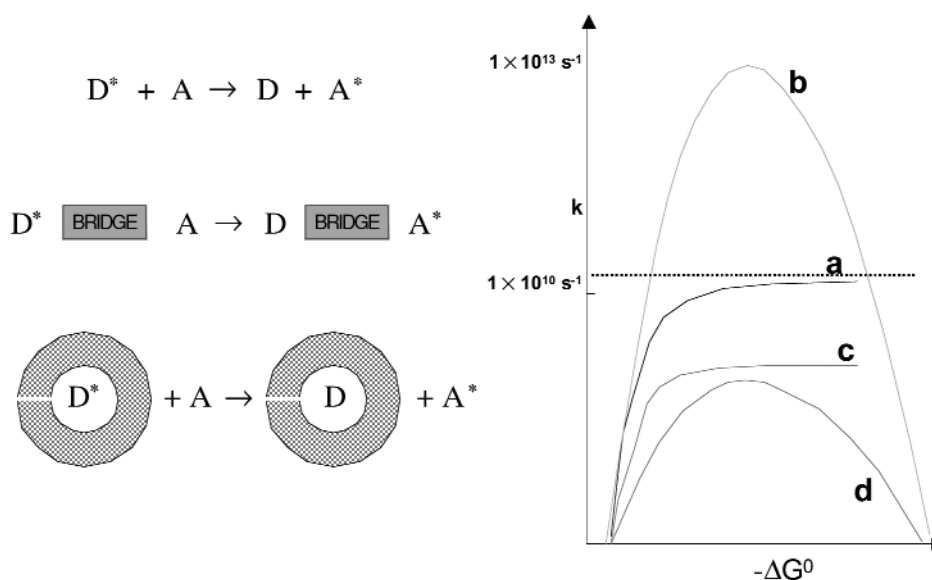


Fig. 2 Limiting cases of the ΔG^0 dependence of triplet excitation transfer: (a) diffusion-controlled limit for free donors and acceptors in nonviscous solvents; (b) Marcus dependence observed for rigidly linked donors and acceptors or frozen glasses; (c) diffusion-controlled limit in viscous media; (d) complete Marcus dependence observed when the donor is encapsulated within a molecular cage.

steeply for both lower and higher values of ΔG^0 , illustrating the existence of “normal” and “inverted” regions in excitation transfer. To our knowledge, this is the only clear example of the “inverted region” in a system in which the donor–acceptor distance is not fixed. For all acceptors spanning a broad ΔG^0 range of 26 kcal/mol, the rates of triplet transfer from the encapsulated biacetyl were more than two orders of magnitude slower than the corresponding rates reported for free biacetyl. This slowing of rates translates into an approximately 20–30-fold reduction of the donor–acceptor electronic coupling caused by the presence of the intervening hemispherical wall.

The most important finding that resulted from these experiments is the demonstration of the critical importance of the internal reorganization energy in excitation transfer processes [7]. In all types of electron-transfer processes in condensed media (charge separation, charge recombination or charge shift), the Marcus reorganization energy λ is almost always dominated by the solvent contribution, with the internal component associated with the geometry change of the donor and the acceptor playing a minor role. This is not the case for excitation transfer. Energy-transfer processes do not involve a net shift of charge; as a result, they are weakly coupled to the solvent bath. Consequently, the overall reorganization energy becomes highly dependent on the intramolecular component. While the medium reorganization energy in electron-transfer reactions can be calculated with reasonable accuracy simply on the basis of ionic radii, donor–acceptor separation and solvent polarity, no general recipe for the internal reorganization energy is possible. Therefore, each donor–acceptor pair has to be treated individually. In select cases, the magnitude of the internal reorganization energy can be obtained from Stokes shifts, vibrational progressions of the electronic spectra, or photoacoustic experiments. However, in the case of triplet energy transfer, such detailed spectroscopic data on the relevant $S_0 \rightarrow T_1$ and $T_1 \rightarrow S_0$ transitions of the acceptor and the donor can very rarely be obtained. In the absence of reliable experimental data, MO calculations prove very useful in estimating internal reorganization energies. We have found that while the overall range of the internal reorganization energies for the organic donors and acceptors is very broad, the values for each distinct class of compounds tend to cluster in a quite narrow

distribution. For instance, the average $\lambda_{\text{internal}}$ is 10.2 kcal/mol for the commonly used rigid aromatic chromophores, 19.5 kcal/mol for olefins, 7.6 kcal/mol for ketones, and 1.8 kcal/mol for thioketones. These values can be rationalized in terms of the π - π^* and n - π^* nature of the particular triplet state. The very high value of $\lambda_{\text{internal}}$ for olefins is the result of the dramatic difference in the geometry of the ground state and the fully relaxed biradicaloid triplet state.

The computational predictions agree well with the Marcus–Jortner type analysis of the experimental data. The experimental rate constants of triplet energy transfer from the incarcerated biacetyl to acceptors in solution form two distinct ΔG dependence curves, one for rigid aromatic triplet acceptors and a separate one for olefins. While, as mentioned above, the curve for the aromatics exhibits a well-defined maximum at $\lambda = \Delta G \approx 9.3$ kcal/mol, the curve for the olefins is much broader and reaches its maximum at $\lambda = \Delta G \approx 26$ kcal/mol.

Cage-size dependence of the guest-exterior electronic coupling

The dependence of the magnitude of electronic coupling between the guest and the exterior of the molecular cage on the size of the hemicarcerand cavity was investigated [8]. Three hemicarcerands with different sizes of the internal cavity were prepared (Fig. 3). In the largest and most flexible host molecule, tetramethylene linkers were used to connect the calixarene cups. The intermediate host employed *o*-xylyl groups as linkers, and methylene groups were used in the smallest one. As above, biacetyl was used as the incarcerated chromophore and triplet donor. The host–guest assemblies were dissolved in neat cycloheptatriene, which fulfilled simultaneously the two roles of solvent and triplet energy acceptor. The use of a neat solvent as the acceptor eliminates the diffusion step in the excitation transfer process.

The driving force for triplet energy transfer in these systems depends weakly on the size of the molecular cage and decreases from 16.2 kcal/mol for the largest hemicarcerand to 14.9 kcal/mol for the smallest one. The corresponding triplet energy-transfer rates increase with diminishing size of the hemicarcerand. For the largest cage, a transfer rate, $k = 2.6 \times 10^5 \text{ s}^{-1}$, was found, the intermediate hemicarcerand yielded $k = 3.8 \times 10^5 \text{ s}^{-1}$; finally, the smallest one gave $k = 2.3 \times 10^6 \text{ s}^{-1}$. These rates can be used

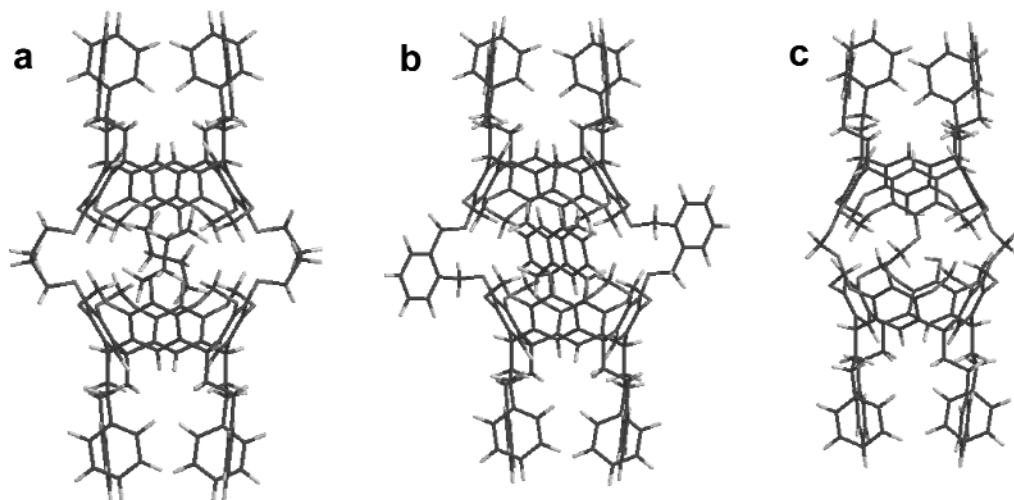


Fig. 3 Hemicarcerands used to study of the dependence of triplet energy-transfer rate on the size of the host cage: (a) the largest host with four $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ linkers connecting the upper and lower calixarene units; (b) intermediate host employing four *o*-xylyl linkers; (c) the smallest host employing three $-\text{CH}_2-$ linkers (AM1 geometry optimization, Spartan PC Pro, Wavefunction, Inc.). The terminal phenyl groups help to solubilize hemicarcerates in organic solvents.

to calculate the magnitudes of electronic coupling, $|V|$, between the triplet state of imprisoned biacetyl and the cycloheptatriene surrounding the molecular cage. The electronic coupling increases from 0.41 cm^{-1} for the largest cage to 1.31 cm^{-1} in the smallest one. To put this in a more familiar perspective, a similar approximately 3-fold increase of electronic coupling would be observed in a covalently linked system if the distance between the triplet donor and the acceptor would be reduced by one carbon-carbon σ bond. Importantly, the triplet transfer rates obtained in neat cycloheptatriene scale linearly to within 5 % with the pseudo-unimolecular triplet transfer rate constants obtained from the Stern-Volmer analysis of phosphorescence quenching in dilute, 0.25–5.0 mM, solutions of cycloheptatriene in dichloromethane. This demonstrates that preassociation or aggregation between the hemicarcerand and the acceptor molecules does not play a significant role in these experiments.

Long-range superexchange-mediated spin-orbit coupling

Encapsulation of the long-lived triplet of biacetyl within the hemicarcerand cage allowed us to provide the perhaps most unequivocal example of a remote intermolecular “heavy atom effect”, i.e., accelerated intersystem crossing (ISC) induced by the spin-orbit coupling with remote atoms carrying large orbital angular momentum [9]. The host-guest complex consisting of biacetyl enclosed within the *o*-xylyl hemicarcerand was dissolved in various halogenated solvents that ranged from dichloromethane to diiodomethane and the lifetime of the biacetyl phosphorescence was monitored. Pronounced acceleration of the decay rate of the T_1 state was observed in solvents with heavy halogen atoms. The phosphorescence lifetime decreased from 1.01 ms in benzene to 950 μs in CH_2Cl_2 to 830 μs in CHBr_3 , finally reaching 134 μs in CH_2I_2 . Since neither electron nor energy transfer are thermodynamically favored in these systems, only the long-range spin-orbit coupling between the T_1 state of the encapsulated biacetyl and the halogenated solvent molecules on the outside of the hemicarcerand can be responsible for this behavior. If one isolates the heavy solvent contribution, k_x , from the overall decay rates, the values of 60 s^{-1} , 220 s^{-1} , and $6.5 \times 10^3 \text{ s}^{-1}$ are found for CH_2Cl_2 , CHBr_3 , and CH_2I_2 , respectively. The results were interpreted using Robinson’s perturbation theory formalism, which involves the virtual open-shell states of the heavy atom solvent molecules [10]. A remarkably good correlation between the experiment and the simple model was found. For instance, the theory predicted a 24-fold increase in the external heavy atom quenching upon transition from CHBr_3 to CH_2I_2 as the solvent, while a 29.5-fold increase was observed experimentally. It is important to emphasize that since the encapsulated chromophore cannot undergo direct contact with the exterior of the molecular cage, all electronic interactions between the guest and the quenchers, including the long range spin-orbit coupling, proceed via the superexchange mechanism and are mediated by the virtual electronic states of the hemicarcerand walls.

TOWARD HYBRID HETERO-SUPRAMOLECULAR ASSEMBLIES

Most recently, our work on host-guest complexes has led to the preparation of a new class of nanostructures composed of chromophores encapsulated within molecular containers that are covalently attached to the surface of semiconductor nanoparticles (Fig. 4). Photoexcitation of the incarcerated chromophore leads to rapid charge injection into the conduction band of the semiconductor. Hybrid systems of this type can lead to the development of novel, highly size-selective sensors in which the presence of the captured guest can be detected by emission quenching, transient absorption, or ultimately photoelectrochemically. Functionalized hemicarcerands bearing 8 carboxylic groups on their circumference (Fig. 1) are readily soluble in slightly basic water, $\text{pH} \geq 8$. While the exterior of the molecular cage becomes hydrophilic upon this modification, the interior of the cavity remains strongly hydrophobic [11]. As a result, nonpolar and weakly polar molecules that are normally insoluble or weakly soluble in water can enter the interior of the cage provided, naturally, that they are of sufficiently small dimensions. Furthermore, the presence of the carboxylic groups allows strong binding to metal oxide nanoparticles,

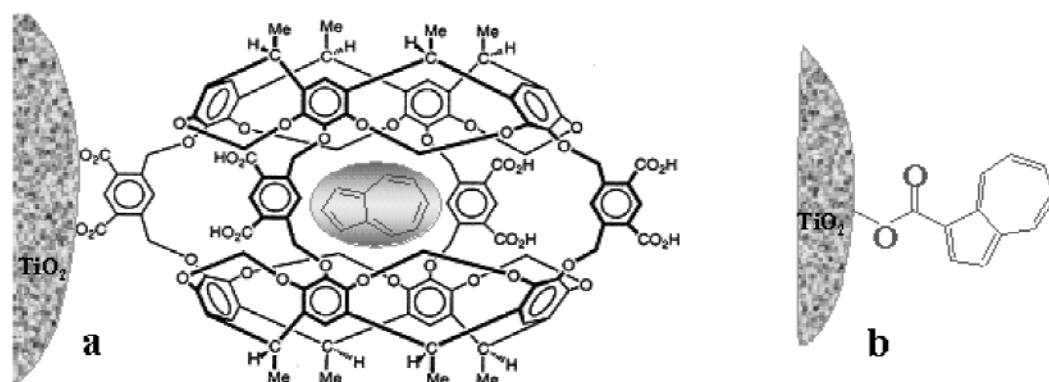


Fig. 4 Schematic representation of the host-guest assembly attached to the surface of colloidal TiO_2 (a) and 1-carboxyazulene directly bound to a nanoparticle (b).

including wide band-gap semiconductors such as TiO_2 and ZnO . The insertion of the hydrophobic guest into the cavity of the host is spontaneous and occurs within minutes to hours. The kinetics of encapsulation has been monitored by UV-vis and ^1H NMR spectroscopy. Depending on the size and polarity of the guest, the driving force for this process can be in excess of 10 kcal/mol. Correspondingly, the host-guest binding constants are as high as $1 \times 10^8 \text{ M}^{-1}$, and the assemblies are indefinitely stable as long as they remain in the aqueous medium [12].

Azulene was selected as the test chromophore because of its favorable spectroscopic properties (strong absorption at wavelengths longer than the absorption of the hemicarcerand and/or TiO_2) and its size, which is compatible with the dimensions of the molecular cage. The similarly sized nonpolar naphthalene and ferrocene, both of which readily enter the cavity of the octacarboxyhemicarcerand, are not as well suited because of the far blue absorption (naphthalene) and the extremely short-lived and nonemissive excited state (ferrocene). The encapsulation process is highly size selective and sensitive to small structural changes of the guest. For instance, our experiments show that 2,7-difluoroazulene is captured at a rate 2–3 times slower the unsubstituted azulene, and anthracene does not enter the cage at all even after prolonged exposure lasting several weeks.

The hemicarcerand-azulene host-guest assemblies prepared in the above described fashion were subsequently bound to colloidal TiO_2 nanoparticles with typical diameters of 5 to 20 nm as determined by light-scattering measurements. The surface binding occurs via formation of ester linkages. This has been confirmed independently by IR spectroscopy measurements on various carboxylates bound to mesoporous thin films of TiO_2 deposited on solid substrates. The shape of the hemicarcerand permits binding of up to four carboxylic groups to the surface of one TiO_2 nanoparticle, leaving the other carboxylic groups free to bind with other nanoparticles. Light-scattering measurements suggest that this type of aggregation does indeed take place, however, the structure of the resulting aggregates is not yet known.

In solution, azulene and its derivatives exhibit a weak but readily detected fluorescence upon excitation to the S_2 state, with a quantum yield of ~ 0.02 and a lifetime of ~ 1.5 ns. In the case of 1-carboxyazulene, which was used as a reference compound in this study, this emission is almost quantitatively quenched upon binding to colloidal TiO_2 (Fig. 5a). We confirmed by femtosecond transient absorption experiments in the near IR that the quenching is accompanied by the injection of an electron from the S_2 state of azulene into the conduction band of TiO_2 . The injection occurs on subpicosecond time scale, and the minor residual emission seen in Fig. 5a originates most likely from a small fraction of unbound carboxyazulene.

A very similar behavior is observed when azulene is encapsulated within the water-soluble hemicarcerand. In the absence of TiO_2 nanoparticles, the host-guest assembly exhibits typical fluorescence

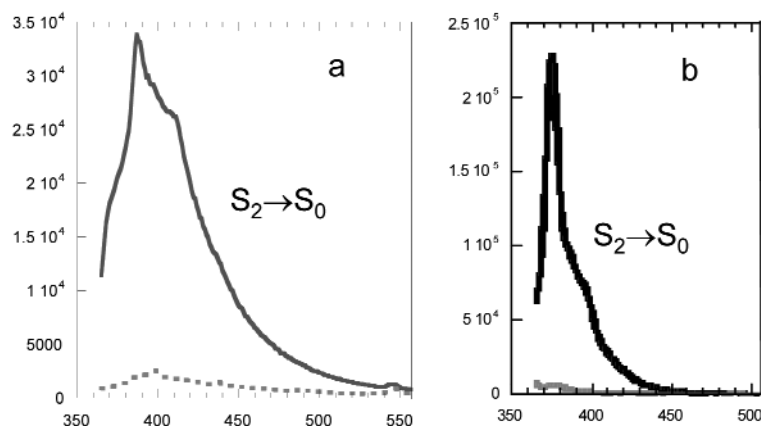


Fig. 5 Emission spectra of: (a) free 2-carboxyazulene in solution (solid line) and bound to TiO_2 nanoparticles (dotted line); (b) azulene incarcerated within the octacarboxyhemicarcerand in aqueous solution (top line) and after binding the host-guest assembly to the surface of TiO_2 (lower line). In both cases, the samples were excited at 360 nm.

of azulene. Upon binding to TiO_2 , the fluorescence is almost completely quenched (Fig. 5b). Considering the short intrinsic lifetime of the S_2 state of azulene, $\tau \sim 1.5$ ns, and the greater than 90 % quenching, we conclude that the injection process is at least as fast as 200 ps. This observation demonstrates that photoinduced electron transfer across the wall of the hemicarcerand can be very rapid and efficient, as well as validates the concept of using the hemicarcerand-semiconductor nanoparticle assemblies as novel sensors. Femtosecond transient absorption measurements on the charge injection dynamics in these systems are in progress.

SUMMARY

Host-guest complexes employing Cram-type hemicarcerands were used in a series of studies on exchange-mediated triplet energy transfer. These unique donor-acceptor systems allowed us to gain new fundamental insights into electronic excitation transfer processes, particularly regarding the importance of internal reorganization energy and the long-distance spin-orbit coupling. This knowledge is now being applied to the design of a new class of “hetero-supramolecular” hybrid materials that are composed host-guest assemblies covalently bound to wide band-gap semiconductor nanoparticles.

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