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Photochemical Reaction Containers as Energy and Electron-Transfer Agents

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ABSTRACT

Two deep cavity cavitands, octa acid and resorcinol-capped octa acid, have been established to be good triplet energy donors in the excited state and electron donors in the ground state to excited acceptors. This property endows them the capacity to be "active" reaction containers. The above recognition provides opportunities to investigate the excited state chemistry of host-encapsulated guests without the use of secondary triplet energy and electron donors.

In recent years, supramolecular assemblies have become a tool to control and manipulate reactions, stabilize and store reactive intermediates, and generate materials with unusual properties.[1−3] In this context, hosts such as micelles, cyclodextrins, calixarenes, cucurbiturils, larger cavitands, and inorganic assemblies have been extensively explored in aqueous solution.[4−9] Of these, larger cavitands and inorganic assemblies constructed with aromatic rings have been demonstrated to show great promise.[6,10] However, in contrast to conventional micelles, cyclodextrins, calixarenes, cucurbiturils that possess "passive" reaction cavities, larger cavitands, and inorganic assemblies with absorption extending to the UV−vis region could be considered to have "active" reaction cavities.[11−13] This requires one to understand the excited-state properties of the host itself. During the last 8 years, the value of a deep cavity cavitand commonly known as octa acid (**1** in Scheme 1) has been established to be a valuable reaction vessel to manipulate photoreactions.[10,14−21] To further explore its value as a photochemical reaction vessel, we felt it to be important to understand the energy and electron-donor/acceptor properties of **1**. In this paper, we present results that establish that two related deep cavity

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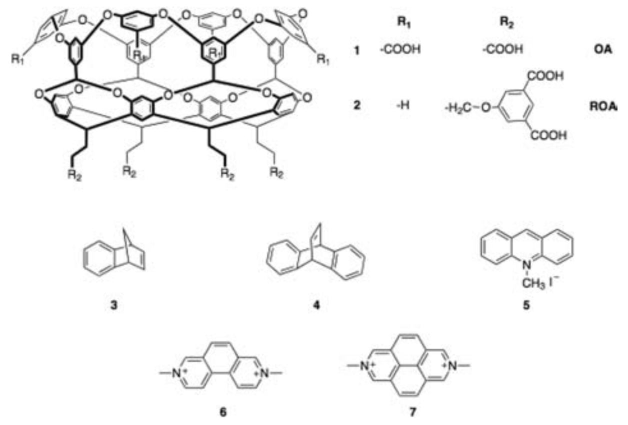
cavitands, commonly known as octa acid (OA, **1**)[14] and resorcinol-capped octa acid (ROA, **2** in Scheme 1),[22] are not inert and in fact can serve as triplet energy donors in the excited state to ground state guest molecules and as electron donors in the ground state to excited acceptors.

Scheme 1. Structure of Hosts, Guests and Electron Acceptors



As shown in Figure S1 in the Supporting Information, hosts **1** and **2** absorb up to 320 nm. This is in contrast to the absorption properties of cyclodextrins and cucurbutrils that absorb below 220 nm. Excitation of **1** and **2** at 280 nm resulted in weak fluorescence in the region 320 to 420 nm (Figure 1). Remarkable overlap between absorption and excitation spectra and mirror symmetric relationship between emission and absorption spectra suggested the observed emission to be from first excited singlet state of the hosts. Based on the above spectra, we believe that the S_1 of **1** and **2** has an approximate energy of 88 kcal mol^{-1}. We believed that the presence of carbonyl groups in the host would favor intersystem crossing and a triplet would be formed upon direct excitation of the host.[23] Since no phosphorescence could be detected, as outlined below we probed the possible triplet generation by carrying out classical triplet-sensitized photoreactions.

To test the possibility of the host itself acting as a triplet sensitizer for a guest molecule, we examined the photochemistry of two aromatic molecules **3** and **4** (Scheme 1) that give distinctly different products from S_1 and T_1 (Scheme 2). Conveniently, both molecules absorb at shorter wavelengths than the host (Figure S2, Supporting Information). Photochemistry of **3** and **4** has been well investigated in solution and acetophenone sensitization of **3**, and acetone sensitization of **4** yielded **9** and **11** respectively.[24−28] The complex of guest **3** with host **1** was prepared by stirring equivalent amounts (1 mM) of host and guest in aqueous sodium tetraborate buffer solution (for details, see the Supporting Information). In the case of guest **4**, 0.5 mM of guest and 1 mM of host were used. ^{1}H NMR titration experiments established that the guest **3** formed 2:2 (host−guest) complexes with hosts **1** and **2**. Support for inclusion of **3** within hosts **1** (Figure 2) and **2** (Figure S3, Supporting Information) came from the expected upfield shift in the ^{1}H NMR signals of the protons attached to the saturated carbons of the guest and from DOSY experimental data.[29,30] The diffusion constants estimated by DOSY ($\sim$1.22 × 10^{-6} cm^2 s^{-1}) were consistent with what has been reported in the literature for OA capsular assemblies.[29,30] Similar ^{1}H NMR experiments with **4** as guest and **1** and **2** as hosts established that **4** formed 2:1 host−guest capsular assemblies with these hosts. Based on variable-temperature ^{1}H NMR studies, we concluded that the guest **4** formed a weaker complex with host **1** (Figure S4, Supporting Information). Unlike in the case of guest **3**, upfield shifted signals due to the guest **4** could not be clearly identified upon its complexation with hosts **1** and **2**. However, inclusion was suggested by the changes in the signals due to the hosts (Figures S5 and S6, Supporting Information).

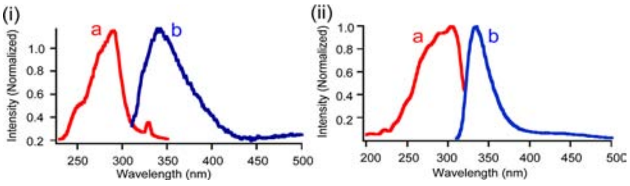
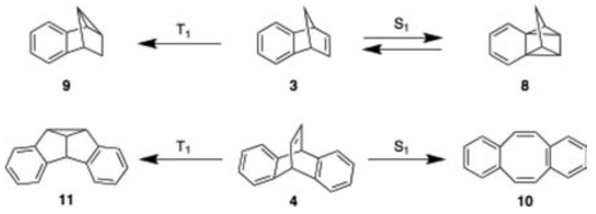


Figure 1. (i) (a) Excitation and (b) emission spectra of **1** (λ_{ex} = 280 nm). (ii) (a) Excitation and (b) emission spectra of **2** (λ_{ex} = 280 nm). ([**1**] = [**2**] = 5 × 10^{-5} M in 10 mM $Na_2B_4O_7$ buffer solution).

Scheme 2. Photochemistry of **3** and **4** in Solution



Irradiation (450 W medium pressure mercury lamp) of $3_2@1_2$ (two molecules of **3** included within two molecules of **1**) dissolved in borate D_2O buffer solution in Pyrex

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NMR tube resulted in quantitative conversion of **3** to **9**. As illustrated in Figure 2, following 30 min of irradiation there were changes, especially in the region below δ 1.0, in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of the complex of independently synthesized **9** and **1** gave identical ^{1}H NMR spectrum to the 30 min irradiated sample (Figure 2). This is consistent with the conclusion that irradiation of $\mathbf{3}_2@\mathbf{1}_2$ where the light was absorbed mainly by the host resulted in quantitative conversion of $\mathbf{3}_2@\mathbf{1}_2$ to $\mathbf{9}_2@\mathbf{1}_2$. Spectral comparison of the product extracted with chloroform with independently synthesized **9** confirmed the formation of the triplet product **9** upon irradiation of $\mathbf{3}_2@\mathbf{1}_2$. Similar irradiation of $\mathbf{3}_2@\mathbf{2}_2$ in borate buffer solution gave **9** in quantitative yield (Figure S3, Supporting Information). However, in this case the reaction was slow and required 12 h of irradiation to obtain quantitative conversion to **9**. With both hosts the conversion of **3** to the triplet product **9** was clean and quantitative. This was possible only if the hosts **1** and **2** reached the T$_1$ state via intersystem crossing from S$_1$ and transferred the energy to the guest. To further probe the possibility of triplet−triplet energy transfer from excited host to the included guest molecule we investigated an additional example namely $\mathbf{4}@\mathbf{1}_2$ (one molecule of **4** included within two molecules of **1**). Irradiation of $\mathbf{4}@\mathbf{1}_2$ and $\mathbf{4}@\mathbf{2}_2$ under conditions detailed above gave the expected triplet product **11** in quantitative yield. Formation of **11** in the above experiments was confirmed by comparing the spectral data of the product with independently synthesized **11**.

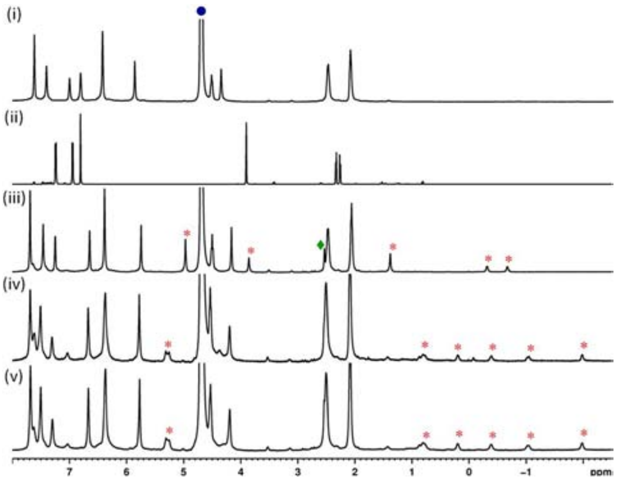

Figure 2. ^{1}H NMR (500 MHz) spectra of (i) **OA** ([**OA**] = 1 mM) in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, (ii) **3** in CDCl$_3$, (iii) (**3**)$_2$@(**OA**)$_2$ in 10 mM Na$_2$B$_4$O$_7$ buffer/D$_2$O, (iv) (**3**)$_2$@(**OA**)$_2$ (after 30 min irradiation) and (v) (synthesized **9**)$_2$@(**OA**)$_2$. Red asterisk represents the bound guest proton peaks. Blue circle and and green diamond represent the residual proton resonance from D$_2$O and DMSO-d_6, respectively.

Once again, the photoreaction with host **1** was much faster (30 min, 98% yield) than with host **2** (8 h, 65% yield). We believe that the benzoate anion part of the cavitand acted as the triplet sensitizer in both hosts. The reason for the difference in efficiencies of triplet sensitization between hosts **1** and **2** most likely is related to the difference in quantum yields of intersystem crossing from S$_1$ to T$_1$ and the distance between the guest molecule (acceptor) residing within the host and the energy transferring mono- (or di-)benzoate anion donor. In **1** the donor benzoate anion is present at the upper rim while in **2** dibenzoate anion is present as a pendant at the bottom (Scheme 1). Based upon the above observed triplet sensitized reactions we believe that the triplet energy of the hosts should be closer to that of acetophenone (73 kcal mol^{-1}),[31] which was used to sensitize the phototransformation of **3** in diethyl ether solution.[27,28] The above results have unequivocally established that the deep cavity cavitands **1** and **2** are photochemically "active", and one must take this feature into consideration while utilizing them as reaction cavities.[11,12]

Having established that the above two hosts are good triplet energy donors, we were interested in examining their electron-donating abilities. For this purpose, we chose three cationic electron acceptors *N*-methylacridinium iodide (**5**), dimethyldiazaphenathrenium iodide (**6**), and dimethyldiazapyrenium iodide (**7**) (Scheme 1).[32−34] The choice was dictated by the fact that these systems (a) are expected to be held closer to the exterior of the anionically charged cavitand through Columbic attraction, (b) absorb light above 350 nm where OA **1** and **2** have no absorption (Figure S7, Supporting Information), (c) show intense fluorescence in aqueous solution, and (d) have low reduction potentials (<-0.5 eV, SCE).[32−34] We have shown previously that cationic molecules remain closer to the exterior of OA **1** capsule and does not get included within the host.[35] In the current study, we noted that when *N*-methylacridinium iodide was added to the host **1** solution there were no changes in the ^{1}H NMR spectrum of the former indicating that it is not included within the cavitand (Figure S8, Supporting Information). As illustrated in Figure 3 (i), (ii) and (iii) fluorescence of all three acceptors was quenched upon gradual addition of host **1**. Similar quenching was noticed upon addition of host **2** to acceptors **5** and **7** (Figure S9, Supporting Information). Although fluorescence was quenched there were no changes in the S$_1$ lifetime of the above three acceptors. In Figure 3 (iv) Stern−Volmer plots with various concentrations of host **1** using steady-state fluorescence intensity (I_0/I) and S$_1$ lifetimes (τ_0/τ) of *N*-methylacridinium iodide are provided. Similar observation was made with host **2** as well (Figure S9, Supporting Information). This suggested that the quenching is static and the rate constant must be beyond the limits of our instrument (in the subnano

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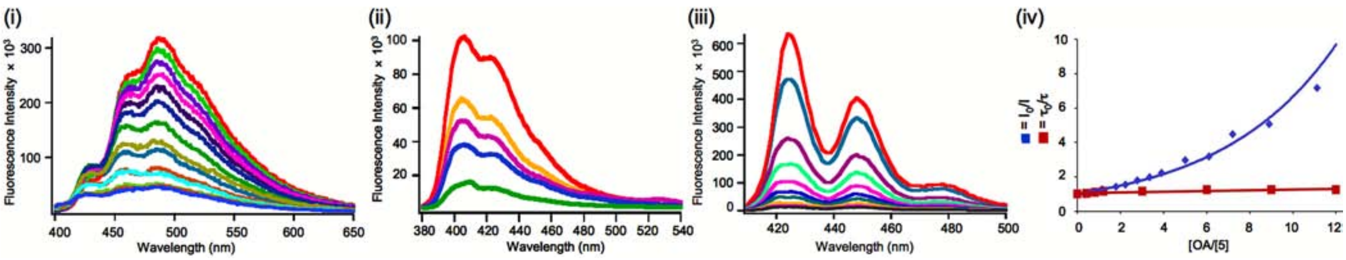

Figure 3. Fluorescence titration spectra of (i) **5** with **1**, [**5**] = 6 × 10^{-6} M (λ_{ex} = 380 nm) and [**1**] = 0 to 7.4 × 10^{-5} M, (ii) **6** with **1**, [**6**] = 6 × 10^{-6} M (λ_{ex} = 360 nm) and [**1**] = 0 to 2.75 × 10^{-6} M, (iii) **7** with **1**, [**7**] = 4 × 10^{-5} M (λ_{ex} = 390 nm) and [**1**] = 0 to 5.66 × 10^{-5} M, (iv) Stern–Volmer plot for the quenching study of **5** with **1**, for lifetime measurements [**5**] = 5 × 10^{-5} M (λ_{em} = 490 nm) and [**1**] = 0 to 5.3 × 10^{-4} M in 10 mM $Na_2B_4O_7$ buffer/H_2O (blue and red squares represent steady-state and fluorescence lifetime data, respectively).

second regime). Note, had the quenching been dynamic, the Stern–Volmer plots based on steady-state fluorescence intensity and lifetime measurements should have fully overlapped, but this was not the case.

On the basis that S_1 energies of **1** and **2** are higher than that of **5**, **6**, and **7** (compare absorption spectra provided in Figure S7, Supporting Information), we ruled out singlet–singlet energy transfer as the cause for fluorescence quenching. For the electron transfer from **1** to S_1 of *N*-methylacridinium iodide to be exothermic the oxidation potential of OA should be lower than 2.31 eV, i.e., the difference in S_1 energy and reduction potential of *N*-methylacridinium iodide (S_1 energy 2.73 eV and reduction potential in acetonitrile −0.42 eV). Although we could not measure the oxidation potential of the two hosts (OA and ROA) in borate buffer, we suspect it to be in the same range as that of an electron-rich benzene, a structure closely similar to the one that form the basic unit of the two hosts (~1.5 eV).[36] On the basis of the above approximation, OA and ROA serving as electron donors to excited **5**, **6**, and **7** is not totally unexpected. Suspecting the methoxybenzoate anion present on the top rim of **1** and appended at the bottom of **2** (Scheme 1) is likely to be the electron donor, we recorded the fluorescence of *N*-methylacridinium iodide in presence of varying amounts of 3,5-dimethoxybenzoic acid in borate buffer (Figure S10, Supporting Information). As expected, the emission was quenched. The studies presented here have unequivocally established that the deep cavity cavitands **1** and **2** possess "active" reaction cavities, and upon absorption of light they undergo intersystem crossing from S_1 to T_1 and transfer triplet energy to the guest molecules included within them.

The results reported here suggest that one should consider the possibility of OA and ROA themselves participating in an electron-transfer process upon excitation of a guest enclosed within a deep cavity cavitand. The recognition that the hosts themselves could serve as energy and electron donors provides opportunities to investigate the excited-state chemistry of host encapsulated guests without the use of secondary triplet energy and electron donors. We are currently exploring such possibilities. Future studies also include sub nanosecond time-resolved experiments to understand the dynamics of electron transfer properties of the supramolecular host–guest systems involving OA and ROA.

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Supporting Information Available. Sample preparation and irradiation procedures, isolation and characterization of products, and additional NMR and absorption spectra and fluorescence quenching data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.