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Water-soluble octa acid capsule as a reaction container: Templated photodimerization of indene in water



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ABSTRACT

In the context of green chemistry, identifying strategies to carry out organic reactions in aqueous medium in the absence of organic and inorganic reagents is important. We show below that octa acid (OA), a water-soluble cavitand, is capable of solubilizing water insoluble reactant in water and yielding selective product by confining the reactants and intermediates during a light initiated reaction. By employing indene as the substrate we have observed that the OA capsule upon irradiation facilitates the formation of *anti-head-tail* dimer, the isomer that is generally not obtained upon direct excitation and triplet and electron transfer sensitizations in isotropic organic solvents.

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1. Introduction

Conducting photochemical reactions within confined spaces has been an important strategy to control the reactivity of reactants and intermediates and channelize photoreactions to obtain high product selectivity [1]. For this purpose, various media such as zeolites, clays, crystals, cyclodextrins, cucurbiturils, calixarenes, micelles, dendrimers, polymers, host-guest complexes and natural proteins have been successfully explored during the last few decades [2–17]. These studies have clearly shown that the confinement and weak interactions provided by a host can steer reactivity of guest molecules resulting in highly selective reactions that are otherwise challenging in isotropic media. Reactions of a guest molecule in confined spaces could be visualized to occur within a ‘reaction cavity’ with a defined boundary and some amount of ‘free space’ surrounding the reactant within the cavity [18]. The extent of selectivity within such a reaction cavity depends on this free space, flexibility (hard or soft) of the boundary and weak interactions that hold the guest within the host. It is important to note that confined hosts offer an environment that is more free than solids but more restricted than isotropic solutions.

Herein, we report photo-dimerization of indene molecules held together within the inner cavity of a water-soluble host, octa acid (indene₂@OA₂, Scheme 1). Cavitand OA is known to self-assemble

into a dimeric capsule in presence of appropriate hydrophobic guest molecules [11,19,20]. In spite of being water soluble, polarity of OA capsules’ interior resembles that of organic solvents. Thus guest encapsulation by OA makes it possible to conduct organic reactions in aqueous medium yet in completely non-polar organic solvent-like microenvironment [21–23]. Results of our studies presented here further strengthen our postulate that free space around the guest molecule along with weak non-covalent guest–host interactions can significantly influence the outcome of photodimerization of encapsulated olefin molecules. Indene molecules encapsulated within OA capsule upon photoexcitation yields *anti-head-tail* dimer, the dimer that has not been obtained through conventional photochemical techniques such as direct excitation and energy and electron transfer sensitizations. The results described below bring out the uniqueness of the OA capsule as a reaction container.

2. Experimental

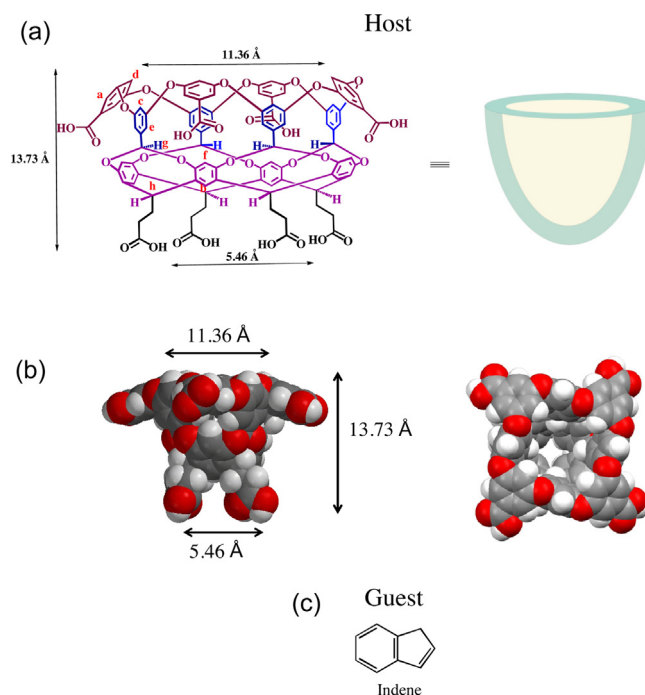
Indene was procured from Aldrich and used as such. All ¹H NMR spectra were recorded using a Bruker 500 MHz NMR at 27 °C. OA was synthesized as per the reported procedure and was dissolved in sodium borate buffer. The borate buffer OA solution was used for NMR and photochemical experiments.

2.1. Protocol for complexation of indene with OA

Six hundred microlitres of a D₂O stock solution of host OA (1 mM/10 mM sodium tetraborate) was taken in a NMR tube. Calculated amount of indene stock solution (60 mM solution in

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Scheme 1. (a) Structure and cartoon representation of the host octa acid (OA), (b) CPK models showing the dimensions (left) and OA reaction cavity from top (right), and (c) structure of the guest indene.

DMSO- d_6) was gradually added following which the NMR tube was shaken rigorously to achieve complexation (typically 0.25 equivalents of guest was added during each addition). The NMR spectrum was recorded after *ca* 5 min. The titration was continued until the addition of excess indene did not alter the guest@ host NMR spectrum. In general, the addition of excess guest led to turbid solutions. NMR spectrum was also recorded after 24 h to test the stability of the complex and no change was observed. Spectra

were recorded at room temperature under aerated conditions on Bruker 500 MHz NMR at 25 °C.

2.2. Irradiation of indene included within OA capsule and isolation and analysis of the photoproducts

A 1:1 guest to host complex was made by adding a DMSO- d_6 stock solution of indene (10 μ L of 300 mM solution in DMSO- d_6) to

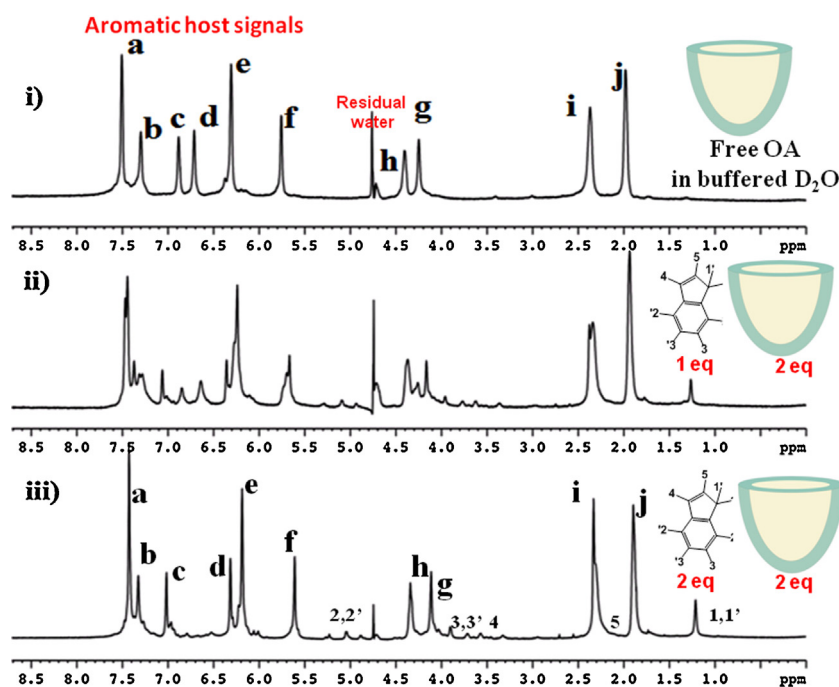


Fig. 1. ^1H NMR showing the formation of 2:2 complex between indene and OA (1 mM) in buffered D₂O (500 MHz). (i) Free OA, (ii) upon addition of 0.5 equivalents of indene to 1 equivalent of OA, and (iii) upon addition of 1 equivalent of indene to 1 equivalent of OA (see Scheme 1 for labeling of OA proton signals).

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