

## **Supporting Information**

### **Photodimerization of Acenaphthylene within a Nanocapsule: Excited state lifetime dependent dimer selectivity**

Lakshmi S. Kaanumalle and V. Ramamurthy\*

#### **Supporting Information (4 pages)**

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\*- Department of Chemistry, University of Miami, Coral Gables, Florida, 33155, USA.

Fax: +1 305 284 4571; Tel: +1 305 284 1534; E-mail: murthy1@miami.edu

## Experimental Details

### Materials

Host **1** was synthesized and characterized following the literature procedure. Sodium tetraborate and acenaphthylene were purchased from Sigma-Aldrich. Acenaphthylene was vacuum sublimated thrice prior to use.

### General Protocol for Binding Studies and NMR Characterization

Six hundred mL of a D<sub>2</sub>O stock solution of host **1** (1 mM) and sodium borate buffer (10 mM) was added to a NMR tube. The resulting NMR **1** is shown in Figure 1a. To this was added aliquots of guest such that 0.25 equivalents were added at each addition (5  $\mu$ l of a 30 mM solution in DMSO-*d*<sub>6</sub>). The complexation was achieved by shaking the NMR tube. Spectra were recorded after ca. 5 minutes. Each sample was also examined 24 hours later. No changes in the spectra were observed. Spectra were recorded at room temperature under aerated conditions on a Bruker 500 MHz NMR at 25°C. Full complexation was observed after 1 equivalent of acenaphthylene was added. The addition of excess guest led to turbid solutions and NMR spectra demonstrated the presence of free guest in addition to the capsular complex.

### Inclusion and Photolysis of Substrates within Host **1**:

#### Direct Irradiation:

A 1mM stock solution of host **1** was prepared in 10m M sodium borate buffer (15.5 mg in 8.96 mL of 10 mM buffer solution, H<sub>2</sub>O). A volume of solutions corresponding to 1 mg of the substrates was pipetted into a test tube. The solution was purged with air to remove the organic solvent. Two equivalents of the host **1** stock solution were added and the solution was stirred for 10 min. The clear solution was purged with dry N<sub>2</sub> for 20 min., and irradiated using a 450 W medium pressure Hg lamp for 3 h s in a Pyrex test tube with 340 nm cut off filter. Almost 100% conversion to product dimer was achieved in 3 hours.

#### Sensitized Irradiation:

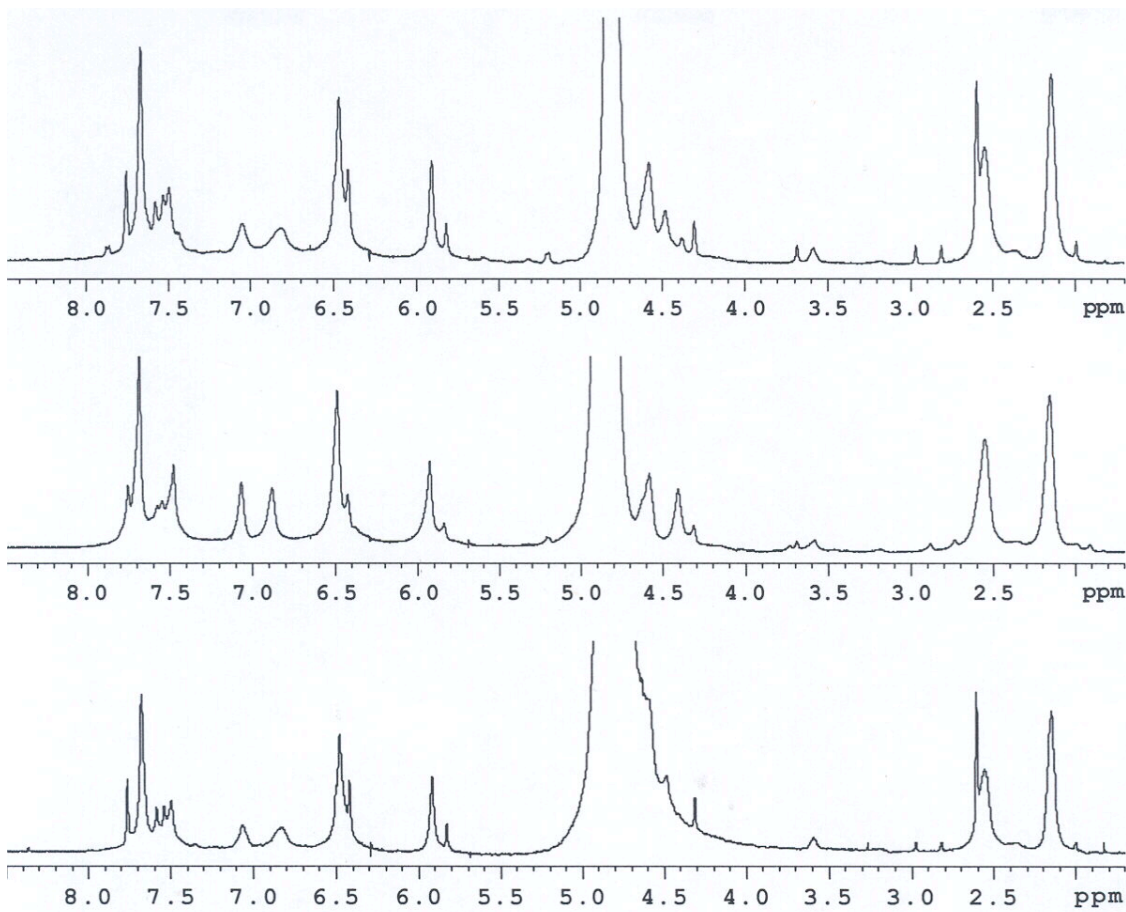
A 1mM stock solution of host **1** was prepared in 10m M sodium borate buffer. A volume of solutions corresponding to 1 mg of the substrates was pipetted into a test tube. The solution was purged with air to remove the organic solvent. Two equivalents of the host **1** stock solution was added and the solution was stirred for 10 min. To the clear solution, 0.1 ml of eosin Y-triplet sensitizer in water was added (2mg/ml). The resulting coloured solution was irradiated using a 450 W medium pressure Hg lamp for 3 h s with 500 nm cut off filter.

### Extraction and Analysis of Photoproducts from Host **1**:

After photolysis, reactants and products were extracted from the aqueous host solution using an ethyl acetate and acetonitrile (6:4) solvent mixture, dried over anhydrous MgSO<sub>4</sub>, concentrated and analyzed on an HP-5890 series II gas chromatograph fitted with an SE-30 capillary column. Products were identified by NMR and GCMS.

### Isolation of photoproducts:

*Syn* and *Anti* dimers of acenaphthylene were isolated from the direct and sensitized irradiation of benzene solution. For the direct irradiation, continuous stream of oxygen was purged into the solution during irradiation. *Syn* dimer was formed in 90% yield. The resulting *syn* dimer was purified by column chromatography using hexane-ethyl acetate eluent mixture. For sensitized irradiation, Rosebengal was used as sensitizer and irradiation was carried out in methanol solution. *Anti* dimer was formed in 65% yield, further purification by column chromatography



**Figure S1.** Top- <sup>1</sup>H NMR of Irradiated acenaphthylene in Octa acid. Middle- <sup>1</sup>H NMR of encapsulated *syn*-dimer of acenaphthylene in octa acid. Bottom- <sup>1</sup>H NMR of Irradiated d<sub>8</sub>-acenaphthylene in Octa acid.