Supporting Information

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

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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$_2$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 µl of a 30 mM solution in DMSO-d$_6$). 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$_2$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 N2 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 cosin 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 MgSO4, 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- $^{1}$H NMR of Irradiated acenaphthylene in Octa acid. Middle- $^{1}$H NMR of encapsulated *syn*-dimer of acenaphthylene in octa acid. Bottom- $^{1}$H NMR of Irradiated $^{d8}$-acenaphthylene in Octa acid.