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Self-assembled coordination cage as a reaction vessel: triplet sensitized [2+2] photodimerization of acenaphthylene, and [4+4] photodimerization of 9-anthraldehyde

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Abstract—Inner cavity of Pd-nanocage has been used as a reaction vessel for performing triplet sensitized [2+2] photodimerization of acenaphthylene using water soluble xanthene dyes (Eosin Y and Rose Bengal) as sensitizers, and [4+4] photodimerization of 9-anthraldehyde. Although the [4+4] photodimerization of 9-anthraldehyde gave similar results to solution reaction, the xanthene dye sensitized [2+2] triplet state photodimerization of acenaphthylene encapsulated within Pd-nanocage yielded the *syn* dimer in quantitative yield. The results obtained from the triplet state [2+2] photodimerization of acenaphthylene within Pd-nanocage is remarkable given the fact that the photodimerization reaction when performed in methanol in the presence of Eosin Y and Rose Bengal gave the *syn* and *anti* dimers in the ratio 0.5 and 0.6, respectively. Preaggregation of molecules encapsulated inside Pd-nanocage in a *syn* fashion seems to be the governing factor for such a behavior.

Self-assemblies based on hydrogen bonding, metal organic coordination networks, π–π stacking, van der Waal forces and hydrophobic–hydrophilic interactions have been designed to mimic enzymes.[1] The focus of the present communication is to explore the use of one such supramolecular assembly as a reaction vessel in aqueous medium for performing photochemical transformations. The host used for this purpose, a self-assembly of six metal ions and four tridendate ligands (the Pd-nanocage shown in Fig. 1) was originally designed and utilized by Fujita et al. for performing highly regioselective homo and hetero [2+2] photodimerization of acenaphthylenes.[2] We have used this assembly that is commercially available as a reaction vessel to perform [4+4] photodimerization of anthracene derivatives from their excited singlet states and [2+2] photodimerization of acenaphthylene from its triplet state.

Our interest in this cage derives from our long range goal of achieving selectivity in photochemical reactions using confined media. We have explored previously photoreactions in micelles, cyclodextrins, dendrimers, zeolites, and in crystals.[3] Our recent studies have included the use of water soluble hosts such as octa acids, calixarenes, and cucurbiturils.[4] These organic hosts have dimensions similar to the Pd-nanocage that is commercially available. We were particularly attracted to the report in which Fujita and co-workers demonstrated that acenaphthylene undergoes dimerization upon direct excitation to a single dimer (*syn*) within the Pd-nanocage.[6] Since acenaphthylene in solution in the absence of the cage yields the *syn* dimer as the major product

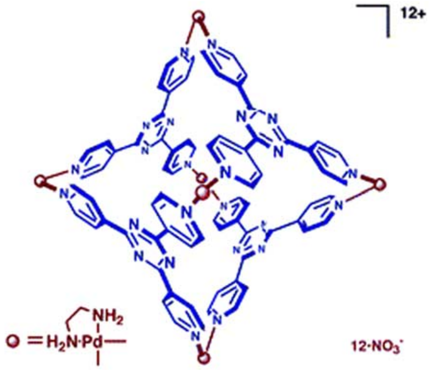

Figure 1. Structure of Pd-nanocage.

Keywords: Pd-nanocage; Regioselectivity; Photodimerization; Acenaphthylene; 9-Anthraldehyde.

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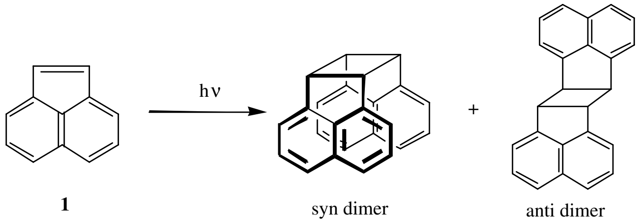


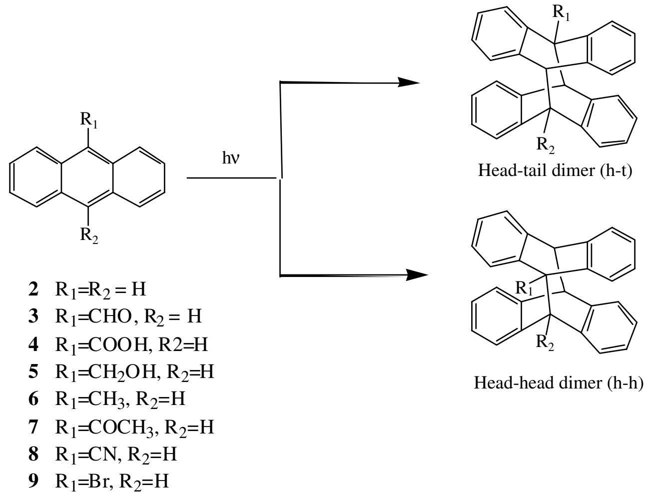
Scheme 1.

from the excited singlet state, formation of the *syn* dimer within the cage did not fully demonstrate the ability of the cage to orient molecules. Further it was not clear whether the Pd-nanocage could be useful to perform selective dimerization of other molecules. Ready commercial availability of the Pd-nanocage and our interest in exploring chemistry in confined media prompted us to explore the Pd-nanocage as a reaction vessel. We find that the cage has limited potential as a reaction vessel.

Due to the water soluble nature of xanthene dyes (Eosin Y and Rose Bengal), we envisaged that one could use xanthene dyes as a triplet sensitizer for acenaphthylene present inside the cage. Acenaphthylene **1** dimerizes under both direct and sensitized irradiation conditions to form *syn* and *anti* dimers (Scheme 1).[5] In polar solvents such as methanol, *syn* and *anti* dimers are formed in the ratio 5.7 whereas upon triplet sensitization with xanthene dyes such as Eosin Y ($E_T = 46.8$ kcal/mol) and Rose Bengal ($E_T = 44.6$ kcal/mol), *syn* and *anti* dimers are formed in the ratio 0.5 and 0.6, respectively. Fujita and co-workers have reported that acenaphthylene forms 1:2 host:guest complex with the Pd-nanocage, which on irradiation in aqueous solution, undergoes highly accelerated and regioselective dimerization to form the *syn* dimer.[6] We visualized that if at all the cage can accommodate formation of the *anti* dimer it should happen during triplet senstization under which condition acenaphthylene preferentially yields the *anti* dimer. We were also interested to probe whether a triplet sensitizer present in the aqueous exterior would be able to sensitize a molecule present inside the cage. In this context we have examined the triplet sensitized [2+2] photodimerization of acenaphthylene accommodated within Pd-nanocage in aqueous medium.

On stirring a solution of the host Pd-nanocage (8 mg, 0.003 mM), acenaphthylene (2 mg, 0.013 mM), and Eosin Y (0.5 mg, 0.72 μM) in 1 mL of D_2O, a 1:2 complex of Pd-nanocage:acenaphthylene (examined by ^{1}H NMR) was formed. No complexation took place when Eosin Y was complexed with Pd-nanocage suggesting that Eosin Y prefers the aqueous exterior. Irradiation of this complex under deaerated condition using corning CS 3-69 ($\lambda > 480$ nm) filter for 10 h followed by ^{1}H NMR analysis showed disappearance of acenaphthylene signals and appearance of new signals corresponding to the *syn* dimer. Quantitative formation of the *syn* dimer was confirmed by recording ^{1}H NMR of the product following extraction with $CDCl_3$. Similar results were obtained with the triplet sensitizer Rose Bengal. On stirring a D_2O solution of the host Pd-nanocage (8 mg, 0.003 mM), acenaphthylene (2 mg, 0.013 mM), and Rose Bengal (0.5 mg, 0.72 μM) in 1 mL of D_2O, a 1:2 complex of Pd-nanocage:acenaphthylene (examined by ^{1}H NMR) was formed. As before, the water soluble Rose Bengal preferred the aqueous exterior as compared to the hydrophobic interior. Irradiation of the deaerated aqueous solution of the complex using corning CS 3-69 ($\lambda > 480$ nm) filter for 10 h followed by extraction with $CDCl_3$ and analysis by ^{1}H NMR confirmed the formation of *syn* dimer. These results are remarkable given the fact that sensitized irradiation of acenaphthylene in isotropic solvents yields the *anti* dimer as the major product. Consistent with this when *syn* and *anti* dimers of acenaphthylene were stirred with the host Pd-nanocage, only the *syn* dimer complexed preferentially. We believe that preorientation of the molecules inside the Pd-nanocage along with the compactness of the *syn* dimer (length: 7 Å, width: 8 Å) could be the reason for the preferential formation of the *syn* dimer inside the cage even from the triplet state. Due to space constraints, preorientation of the molecules in the *anti* configuration (molecular dimension of the *anti* dimer length: 14 Å, width: 8 Å) is unlikely within the nano size cavity of Pd-nanocage. Further, absence of the *anti* dimer as a product suggests that the cage does not favor reorientation of the preaggregated acenaphthylene molecules to the *anti* configuration within the lifetime of the triplet state. Thus the Pd-nanocage is able to increase the effective concentration of the reactant molecules and prealign them in a *syn* configuration to yield the *syn* dimer as a single product even from the triplet state.

Though Pd-nanocage is capable of accommodating various organic molecules, the serious limitation of the cage lies in the fact that it has absorption up to 330 nm. Therefore we could not examine the dimerization of cinnamic acids, stilbenes, and stilbazoles, the well known model systems often used in photodimerization reactions.[6] Anthracene and its derivatives have absorption above 330 nm and therefore are ideal candidates for undergoing photodimerization reaction inside the Pd-nanocage. The 9-substituted anthracene derivatives **3**, **4**, **7**, **8**, and **9** on irradiation in isotropic solvents undergo photodimerization to yield head to tail (h–t) photodimer as the only product whereas 9-substituted anthracene derivatives **5** and **6** on irradiation in isotropic solvents yield both head to head (h–h) and head to tail (h–t) photodimers in 25:75 and 40:60 ratios (Scheme 2).[7] Among the eight anthracene derivatives **2**–**9** examined, **3**–**7** formed 1:2 host:guest complex (calculated from NMR) with the Pd-nanocage whereas **2**, **8**, and **9** did not complex with the Pd-nanocage. Like in the acenapthylene case, the complexes of **3**–**7** were easily formed on stirring 1 mL D_2O solution of Pd-nanocage (8 mg, 0.003 mM) and the substrates (3 mg, 0.013 mM) and ^{1}H NMR of the filtered solution confirmed the complexation. Irradiation of Pd nanocage-**3** complex for 4 h followed by ^{1}H NMR analysis showed complete disappearance of signals corresponding to that of **3** (Fig. 2). However, extraction of the aqueous solution with chloroform resulted in a quantitative yield of the head–tail dimer.[8] Clearly, while two anthracene molecules could be accommodated



2 R_1=R_2 = H
3 R_1=CHO, R_2 = H
4 R_1=COOH, R2=H
5 R_1=CH_2OH, R_2=H
6 R_1=CH_3, R_2=H
7 R_1=$COCH_3$, R_2=H
8 R_1=CN, R_2=H
9 R_1=Br, R_2=H

Scheme 2.

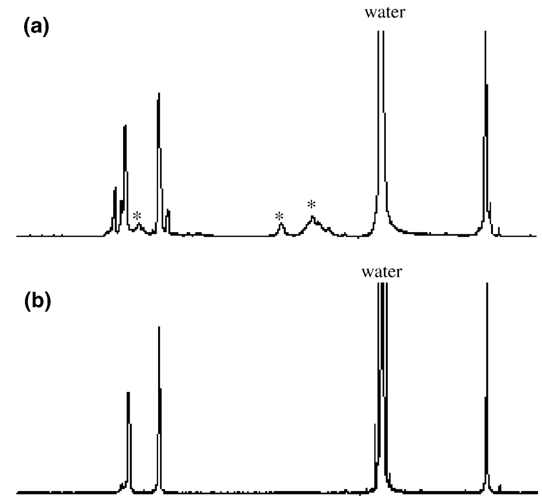


Figure 2. ^{1}H NMR of (a) complexation of **3** with Pd-nanocage. (b) After 4 h of irradiation. Guest peaks are marked by *. Other peaks are of the host.

within the cage in a head–tail sandwich configuration, the head–tail dimer is too large to fit inside. Consistent with this, when pure head to tail (h–t) dimer of **3** was stirred with Pd-nanocage, no complexation took place. Inside the host Pd-nanocage, complete conversion to photoproduct was achieved in 4 h of irradiation whereas in isotropic solvent such as chloroform, for the same time of irradiation (4 h), only 15% conversion was achieved for the same concentration of anthracene. The insolubility of 9-anthraldehyde (**3**) in water does not allow a direct comparison of reaction rates in the same solvent. Hence the Pd-nanocage not only helps to solubilize the insoluble anthracene derivative (**3**) in water, but also enhances the rate of dimerization reaction.

Surprisingly, substrates **4–7** in spite of their long wavelength absorption and their ability to undergo photodimerization in solution, were photoinactive inside the Pd-nanocage. Irradiation of the complexes formed by these substrates with the Pd-nanocage followed by extraction yielded only the starting material. Examination of anthracene derivatives has revealed that lot more need to be understood concerning the rules of the Pd-nanocage templated photodimerization of organic molecules. Also, substrates (**3**, **4**, and **7**) having carbonyl groups formed stronger complexes with the Pd-nanocage when compared to other anthracene derivatives. The evidence for the above observation comes from the ^{1}H NMR studies. For example, stirring **3**, **4**, **5**, and **7** with Pd-nanocage led to selective complexation of **3**, **4**, and **7** with the Pd-nanocage and **5** was left behind in solution.

In conclusion, the nanosized cavity presented by the host Pd-nanocage is useful to tune the outcome of two photochemical reactions namely the xanthene dye sensitized triplet state photodimerization of acenapthylene (**1**) and photodimerization of anthracene derivative (**3**). The encouraging results obtained during triplet state photodimerization of acenaphthylene, water soluble nature of the host and its capacity to solubilize the otherwise insoluble organic molecules in water along with its commercial availability justify further exploration of the host as a reaction vessel for carrying out photochemical reactions. However, there are limitations in the use of Pd-nanocage as the reaction vessel. Its absorption characteristics limit the choice of reactants. It is not clear why only one of five anthracene derivatives reacted within the cage. Clear feeling for the factors that control the inclusion and reactivity of guests by Pd-nanocage is currently lacking. The work presented here forms a part of our continued interest in exploring photoreactions in confined media.[3,4]

Acknowledgements

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8. ^{1}H NMR of the head to tail (h–t) dimer of 9-anthraldehyde: (300 MHz, $CDCl_3$) δ: 10.1 (2H, s), 6.6–7.1 (16H, m), 5.5 (2H, s).