Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting Information

Crystal Engineering Principles Applied to Solution Photochemistry: Controlling the Photodimerization of Stilbazolium Salts within γ-Cyclodextrin and Cucurbituril[8] in Water

Raja Kaliappan, Murthy V. S. N. Maddipatla, Lakshmi. S. Kaanumalle and V. Ramamurthy*

Supporting Information (14 pages)

Figure S6. Nonlinear curve fitting according to equation 3 for the complex of **4a**.HCl@γ-CD

4. Effect of host (γ-CD) concentration on the photodimerization of 4a.HCl.

5. References

* Department of Chemistry, University of Miami, Coral Gables, Florida, 33146, USA.

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

Experimental

General methods

The solvents used were reagent grade and were purified by distillation before use. Irradiations were carried out in NMR tubes using a medium pressure 450W mercury lamp. ^{1}H NMR spectra were recorded on a 400MHz or a 300 MHz spectrometer in $CDCl_3$, CD_2Cl_2 and D_2O solvents.

Materials

The hosts α-CD, β-CD and γ-CD were procured from Wacker Biochem Corp. and used as such. The hosts CB[7] and CB[8] were synthesized by following procedure reported by Day et al.[1] The guests **1a**-**5a** were synthesized by following literature procedure.[2] The ^{1}H NMR spectral data for the stilbazoles are provided below.

1a. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.03 (1H, d, *J* = 17 Hz), 7.32 – 7.47 (6H, m), 7.56 (2H, d, 6.6 Hz), 8.59 (2H, d, *J* = 5.8 Hz).

2a. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31 (3H, s), 6.85 (1H, d, *J* = 16 Hz), 7.21 (2H, d, *J* = 8Hz), 7.32 (2H, d, *J* = 16 Hz), 7.41 (2H, d, *J* = 4 Hz), 7.46 (2H, d, *J* = 8 Hz), 8.51 (2H, d, *J* = 5.2 Hz).

3a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (3H, s), 6.89 (1H, d, *J* = 16.4 Hz), 6.93 (2H, d, *J* = 8.6 Hz), 7.27 (1H, d, *J* = 16.4 Hz), 7.35 (2H, d, *J* = 4.8 Hz), 7.49 (2H, d, *J* = 8.4 Hz), 8.55 (2H, d, *J* = 5.5 Hz).

4a. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.03 (1H, d, *J* = 16.4 Hz), 7.33 (1H, d, *J* = 16.4 Hz), 7.38 (2H, d, *J* = 8.6 Hz), 7.47 -7.53 (4H, m), 8.60 (2H, d, *J* = 5.8 Hz).

5a. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.09 (1H, d, *J* = 16.4 Hz), 7.34 (1H, dd, *J* = 2 Hz), 7.50 (1H, d, *J* = 2 Hz), 7.67 (1H, d, *J* = 8 Hz), 7.75 (2H, d, *J* = 6.6 Hz), 7.86 (1H, d, *J* = 16 Hz), 8.60 (2H, d, *J* = 6 Hz).

General procedure for complexation, irradiation, extraction and analysis

Complexation(γ- CD complexes)

Calculated volume of the standard stock solution of the guest (**1a-5a**.HCl) corresponding to 3.36 mM of the guest was pipetted into a NMR tube and purged with air to remove the solvent. To the dried guest sample in the NMR tube the host γ-CD was added in small increments, sonicated for 5 minutes and the ^{1}H NMR spectrum was recorded after each addition. Averaged NMR signals for the complexed and uncomplexd guest was observed suggesting that the complexed and uncomplexed guest is undergoing fast exchange in the NMR time scale (300 MHz). Also, continuous upfield shift of the guest proton signals was observed with the addition of the host suggesting that excess host drives the complexation equilibrium to the complexed state of the guest .

Complexation(CB[8] complexes)

About 0.8mg of guest (**1a-5a.**HCl) was dissolved in 0.6mL of D_2O in NMR tube. The ^{1}H NMR spectrum of the guest alone was recorded. To the guest solution, finely powdered CB[8] was added in fractions from 0.1 equivalent to 1 equivalent. After adding every 0.1 equivalent of the host, the solution was sonicated in a water bath and ^{1}H NMR was recorded for the host-guest complex. Continuous and prominent upfield shifts in guest proton signals were observed until the host:guest stoichimetry was 1:2. Upon adding excess host beyond this stoichiometry, no further upfield shift in the guest proton signals was observed suggesting the 1:2 H:G complex formation of the host (CB[8]) with the guests (**1a-5a.**HCl).

Irradiation, extraction and analysis

The complexes were prepared by following the procedure described above. The concentration of the guest (**1a-5a**.HCl) used was 5.6 x 10^{-3} M. In the case of CD complexes, an excess host (G:H = 1:2 mixing ratio) was used to avoid reaction from uncomplexed guest, while in the case of CB complexes a G:H = 2:1 mixing ratio was used. This solution was irradiated for 3 hours using a 450W medium pressure mercury lamp(pyrex cut off). The conversion obtained for the CD complexes were 80-85%, while for the CB complexes 90-95% conversion was obtained. Following irradiation the pH of the solution was brought to ~ 9 by the addition of NaOD. The white solid precipitated after neutralization was extracted into $CDCl_3$. The ^{1}H NMR spectra of the $CDCl_3$ layer

and the D_2O layer were recorded to identify the formed photoproducts and to ensure the complete extraction of the photoproducts respectively

Characterization of the dimers of stilbazoles 1a–5a:

All products have been characterized previously in the literaure and the data reported below are consistent with the literature reports.[3-6]

Anti HT dimer of **1a**:

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.48 (4H, m), 7.08 – 7.4 (14H, m), 8.35 (4H, d, J = 4.0 Hz).

Anti HT dimer of **2a**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (6H, s), 4.36 (2H, m), 4.45 (2H, m), 6.95 – 7.25 (12H, m), 8.36 (4H, d, J = 6.0 Hz).

Anti HT dimer of **3a**:

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.74 (6H, s), 4.45 (4H, m), 6.74 (4H, d, J = 8.0 Hz), 7.0 (4H, d, J = 8.0 Hz), 7.14 (4H, d), 8.41 (4H, d, J = 4.8 Hz).

Anti HT dimer of **4a**:

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.37 (2H, m), 4.46 (2H, m), 6.95 – 7.04 (8H, m), 7.16 (4H, d, J = 6 Hz), 8.4 (4H, d, J = 6 Hz).

Anti HT dimer of **5a**:

δ 4.52 (2H, t), 4.76 (2H, t), 7.1 – 7.26 (10H, m), 8.41 (4H, d, J = 6 Hz).

Syn HH dimer of **1a**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.46 (4H), 6.97 – 7.21 (14H, m), 8.39 (4H, d, J = 4.0 Hz).

Syn HH dimer of **2a**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 6H), 4.40 (4H), 6.92 – 7.05 (14H, m), 8.37 (4H, d, J = 6.0 Hz).

Syn HH dimer of **4a**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.40 (4H, d, J = 2Hz), 6.98 (8H, d, J = 6Hz), 7.15-7.19 (4H, m), 8.39 (4H, d, J = 4.0 Hz).

Syn HH dimer of **5a**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.35 (2H, d, 6Hz), 4.89 (2H, d, 6Hz), 6.98-7.35 (10H, m), 8.42 (4H, d, J = 4.0 Hz).

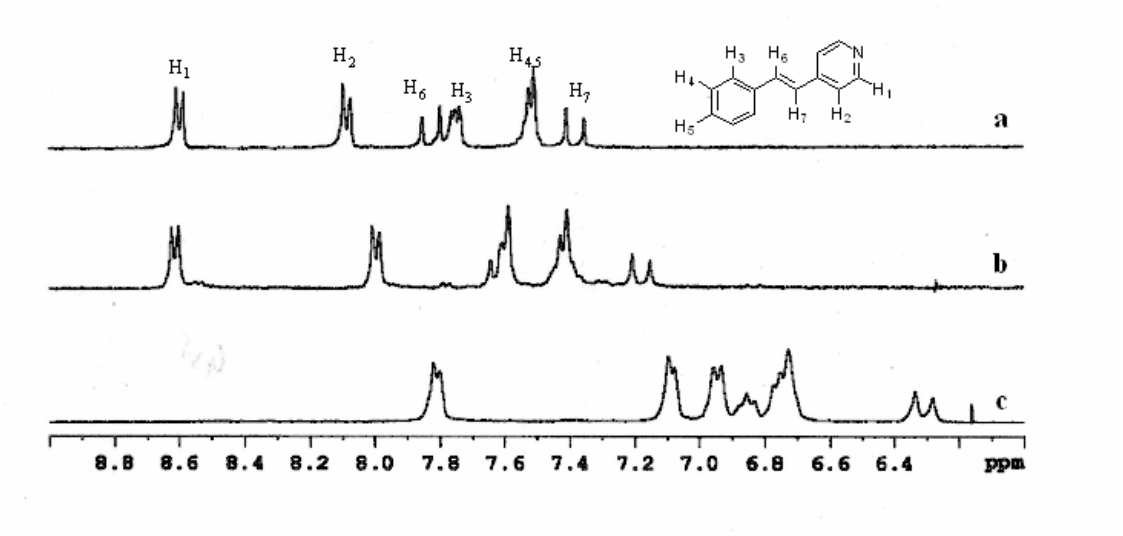

Figure S1. ^{1}H NMR of (a) **1a**.HCl in D_2O, (b) 1:2 complex of **1a**.HCl with γ-CD in D_2O. (c) 1:2 complex of **1a**.HCl with CB[8] in D_2O. ([**1a**.HCl] = 5.6 x 10^{-3}M, [γ-CD] = 1.12 x 10^{-2}M, [CB[8]] = 2.8 x 10^{-3}M)

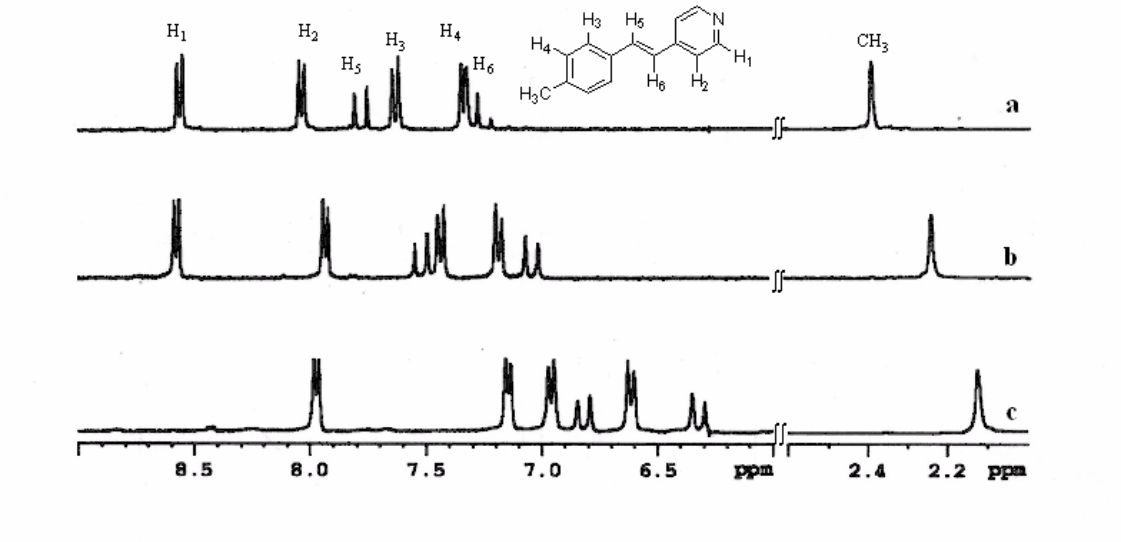

Figure S2. ^{1}H NMR of (a) **2a**.HCl in D_2O, (b) 1:2 complex of **2a**.HCl with γ-CD in D_2O. (c) 1:2 complex of **2a**.HCl with CB[8] in D_2O. ([**2a**.HCl] = 5.6 x 10^{-3}M, [γ-CD] = 1.12 x 10^{-2}M, [CB[8]] = 2.8 x 10^{-3}M)

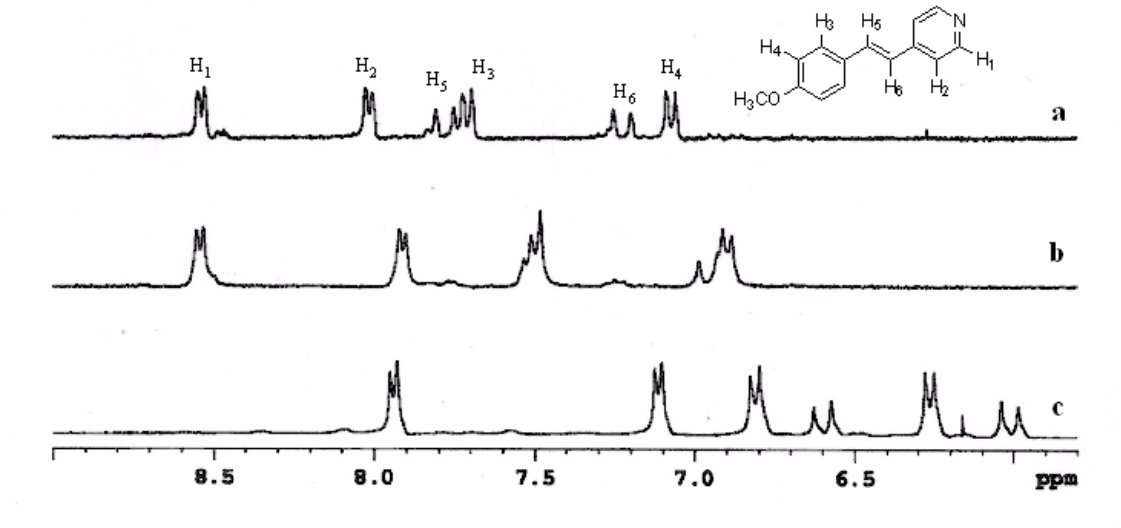

Figure S3. ^{1}H NMR of (a) **3a**.HCl in D_2O, (b) 1:2 complex of **3a**.HCl with γ-CD in D_2O. (c) 1:2 complex of **3a**.HCl with CB[8] in D_2O. ([**3a**.HCl] = 5.6 x 10^{-3}M, [γ-CD] = 1.12 x 10^{-2}M, [CB[8]] = 2.8 x 10^{-3}M)

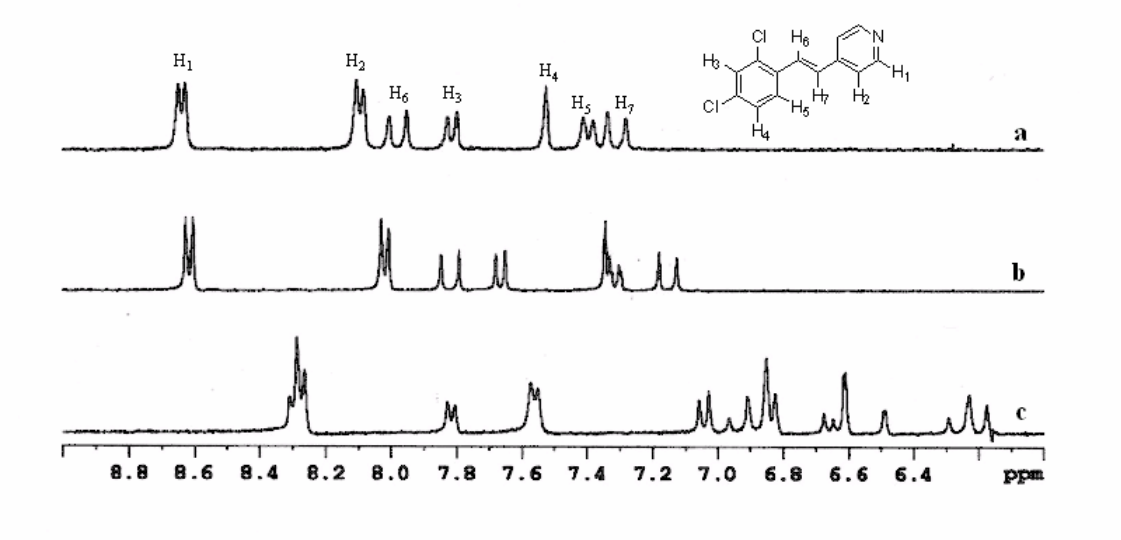

Figure S4. ^{1}H NMR of (a) **5a**.HCl in D_2O, (b) 1:2 complex of **5a**.HCl with γ-CD in D_2O. (c) 1:2 complex of **5a**.HCl with CB[8] in D_2O. ([**5a**.HCl] = 5.6 x 10^{-3}M, [γ-CD] = 1.12 x 10^{-2}M, [CB[8]] = 2.8 x 10^{-3}M)

3. ***Determination of binding constant by UV-Visible titration:***

UV-Visible titration experiments of **4a**.HCl@CB[8] and **4a**.HCl@γ-CD were conducted based on the model depicted in equations 1 and 2.

$$H + G \rightleftharpoons [H.G] \qquad (1)$$

$$[H.G] + G \rightleftharpoons [H.G_2] \qquad (2)$$

The decrease in the absorption band at 320 nm (for γ-CD) and 324nm (for CB[8]) of the guest was monitored as a function of concentration of host (γ-CD or CB[8]) This complexation can be explained by the stepwise mechanism (equations 1 and 2), involving the initial formation of the 1:1 host:guest complex as represented by equation (1), followed by complexation of a second guest to give the 1:2 host: guest complex described in equation (2).

UV-Visible titration results (absorbance v*s.* [host]) of the H:G complex were fit to equation (3) [7] using non-linear least square fitting program Graphpad prism® software.

$$Y = \frac{[(p_0) + (p_1 . K_1)(X) + (p_2 . K_1 . K_2)(X)^2]}{[1 + K_1 . X + K_1 . K_2 (X)^2]} \qquad (3)$$

p_0, p_1, p_2 : Arbitray constants for the non-linear curve fitting iterations

K_1 : Stepwise binding constant for 1:1 H:G complex

K_2: Stepwise binding constant for 1:2 H:G complex

The non-linear nature of the curve (Figure S5 and S6), which was plotted between absorbance and concentration of the host, indicates the presence of higher order inclusion complexes. Fitting yielded an R^2 value of 0.9979 for **4a**.HCl@CB[8] (and 0.986 for **4a**.HCl@γ-CD) indicating that the assumed step-wise equilibrium model fits the

observed experimental trend and is adequately represented by the equilibrium constant expression eqn 3**.**

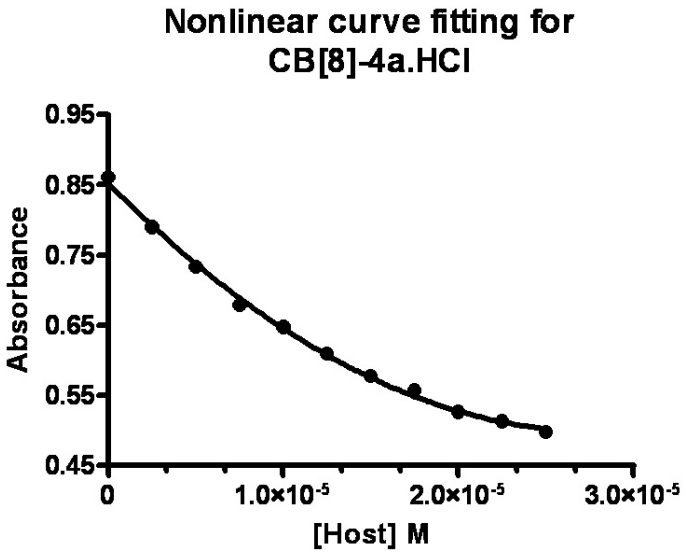

Figure S5. Nonlinear curve fitting according to equation 3 for the complex of **4a**.HCl@CB[8]

For **4a**.HCl@CB[8], the best fit presented in Figure S5 was obtained with the parameters p_1= 0.8539, p_2= -103 and p_3= 13.61. The binding constants, K_1 and K_2, were calculated as $2.422x10^2$ M^{-1} and $1.4X10^5$ M^{-1} respectively. The overall binding constant was calculated to be $3.38X10^7$ M^{-2}. The calculated binding constants K_1, K_2 are reasonable and $K_2 > K_1$ means that the formation of 1:2 H:G complex is more favorable.

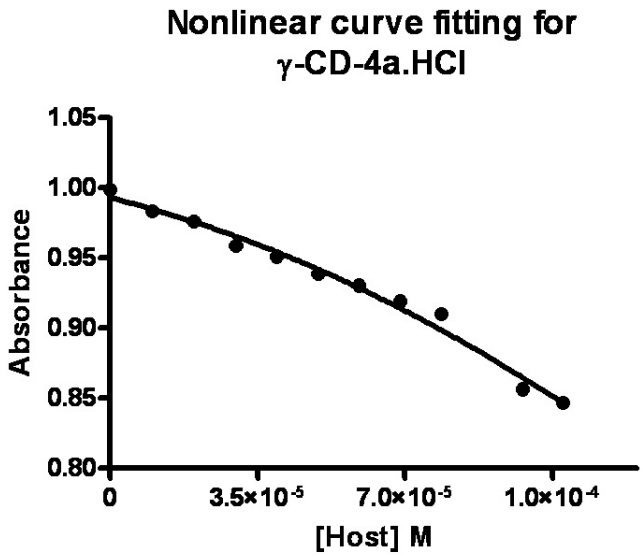

Figure S6. Nonlinear curve fitting according to equation 3 for the complex of 4a.HCl@γ-CD.

For **4a**.HCl@γ-CD, the best fit presented in Figure S6 was obtained with the parameters p_1= 0.9931, p_2= -3.863 and p_3= -56.74. The binding constants, K_1 and K_2, were calculated as 1.545x10^2 M^{-1} and 6.616X10^2 M^{-1} respectively. The overall binding constant was calculated to be 1.02X10^5 M^{-2}. The calculated binding constants K_1, K_2 are reasonable and $K_2 > K_1$ means that the formation of 1:2 H:G complex is more favorable.

4. Effect of host (γ-CD) concentration on the photodimerization of 4a.HCl.

Irradiations were carried out by following the procedure described earlier for γ-CD complexes excepting that the host concentration was varied as required. The optimum G:H ratio was determined to be 1:2 to obtain better yields of the dimer. The results are summarized in the following table (the unreactive *trans* olefin is not taken for calculation purpose).

G : H	% *cis*	% dimer
1 : 0.5	45	55
1 : 1	36	64
1 : 2	29	71
1 : 4	26	74

5. References:

1 A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem*., 2001, **66**, 8094.

2 S. M. N. Efange, R. H. Michelson, R. P. Remmel, R. J. Boudreau, A. K. Dutta, and A. Freshler, *J. Med. Chem.*, 1990, 33, 3133.

3 M. Pattabiraman, A. Natarajan, R. Kaliappan, J. T. Mague and V. Ramamurthy, *Chem. Commun*., 2005, 4542.

4 Q. Chu, D. C. Swenson, and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2005, **44**, 2.

5 R. Kaliappan, L. S. Kaanumalle, A. Natarajan, and V. Ramamurthy, *Photochem. Photobiol. Sci.*, 2006, **5**, 925.

6 F. H. Quina and D. G. Whitten, *J. Am. Chem. Soc.*, 1975, **97**, 1602.

7 S. Nigam, and G. Durocher, *J. Phys. Chem*., 1995, **100**, 7135.