Supporting Information

Selective Encapsulation and Controlled Diastereoselectivity at Alkene-Geometry: *E-Z* Photoisomerization of Oxazolidinone-Functionalized Enecarbamates within Hydrophobic *Nano*-Cavities

Hideaki Saito,[†,‡] J. Sivaguru,[†] Steffen Jockusch,[†] Joanne Dyer,[†] Yoshihisa Inoue,[‡,§] Waldemar Adam,[#] and Nicholas J. Turro[*,†,Ψ]

[†]*The Department of Chemistry, Columbia University, 3000 Broadway, Mail Code 3119, New York, NY 10027.*

[‡]*The Department of Molecular Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan*

[§]*Entropy Control Project, ICORP, JST, 4-6-3 Kamishinden, Toyonaka 560-0085, Japan*

[#]*Institute für Organische Chemie, Universität Würzburg, 97074 Würzburg, Germany, and the Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931*

[Ψ] *The Department of Chemical Engineering, Columbia University, 3000 Broadway, Mail Code 3119, New York, NY 10027.*

E-mail: njt3@columbia.edu

Contents:

1) Materials and Methods

2) Complexation of *Z*-enecarbamates (**1*Z***) with γ-Cyclodextrin:

   a) *In D_2O/CD_3OD*

   b) *In Solid State*

3) CD spectra of various cyclodextrin-complexes.

4) Photoreactions

   a) *In D_2O/CD_3OD*

   b) *In Solid State*

5) Gas Chromatographic characterization of **1*E***.

6) NMR characterization.

7) Phosphorescence lifetime measurements.

1) Materials and Methods: Deuterated solvents obtained from Cambridge Isotope Labs were used as received. The *Z*- and *E*-enecarbamates were synthesized as previously described.[S1] γ-Cyclodextrin was purchased from Aldrich and used as received. Product ratios and diastereoselectivities were determined by ^{1}H NMR (300MHz, Bruker). The DRIFTS spectra were recorded using a ThermoNicolet Nexos870FT-IR fitted with a DRIFTS accessory (Smart Collector). Steady-state luminescence spectra were recorded on a SPEX Fluorolog-3 spectrometer FL3-22 (J. Y. Horiba, Edison, NJ) at 77 K using 3 mm suprasil quartz tubes in conjunction with a liquid nitrogen dewar. Time-resolved phosphorescence measurements were performed by multi-channel scaling on an OB900 fluorimeter (Edinburgh Analytical Instruments) using a pulsed xenon lamp μF 900 for excitation.

2) Complexation of *Z*-enecarbamates (1*Z*) with γ-Cyclodextrin:

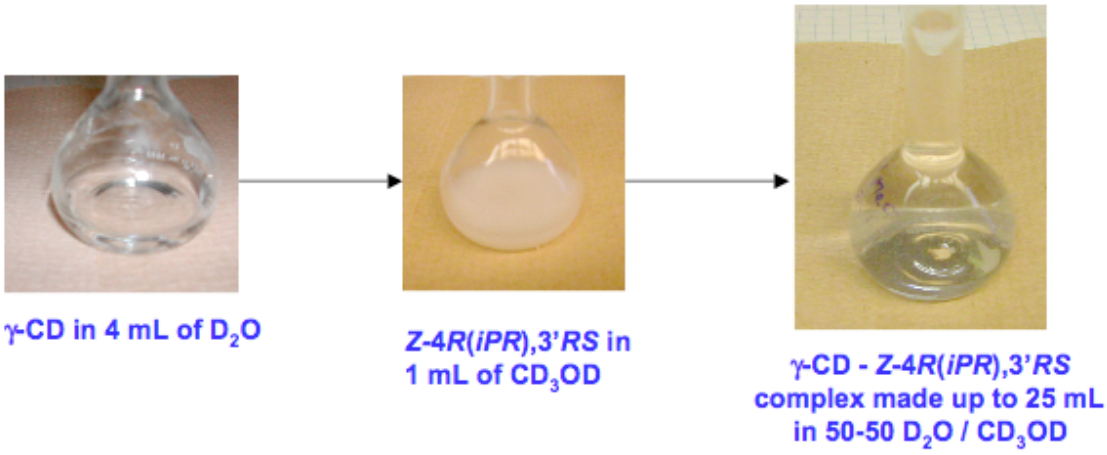

Figure S1: Complexation of *Z*-enecarbamates (1*Z*) with γ-Cyclodextrin in 1:1 D_2O/CD_3OD.

a) In D_2O/CD_3OD:

4 mL of D_2O was added to a 25 mL standard flask with 0.03 mmol of γ-Cyclodextrin. **1*Z*** (0.03 mmol) was dissolved separately in a test tube in 1 mL of CD_3OD and added to the standard flask (Figure S1). A white precipitate formed immediately (Figure S1) and the precipitate was then dissolved in a mixture of 8.5 mL D_2O and 11.5 mL CD_3OD to give a clear solution of γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD.

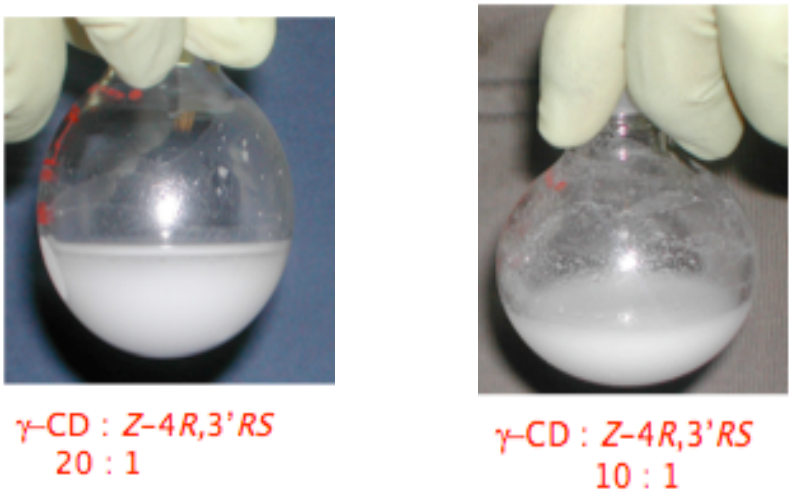

Figure S2: Complexation of *Z*-enecarbamates (1*Z*) with γ-Cyclodextrin with Ether/Water for solid-state studies.

b) In Solid State:

The complexation of γ-CD and **1*Z*** was achieved by adding **1*Z*** (1.5×10^{-5} mol) in 5 mL ether to 1.5×10^{-4} mol of γ-CD in 10 mL deionized water, that gave a white precipitate of γ-CD/**1*Z*** complex (Figure S2). [s2] This complex was labeled 10:1 based on the starting molar ratio. Similarly a 20:1 γ-CD/**1*Z*** complex was prepared. The complexes thus prepared were filtered and washed thoroughly with ether. The residue was dried by vacuum overnight.

Figure S3: *Z*-enecarbamates (**1*Z***) crashes out from water without cyclodextrin in 1:1 D_2O / CD_3OD (center); but is completely soluble in CD_3OD (left) and in the presence of γ-Cyclodextrin in 1:1 D_2O / CD_3OD (right).

3) Circular Dichroism Spectra of *Z*-enecarbamates with γ-Cyclodextrin:

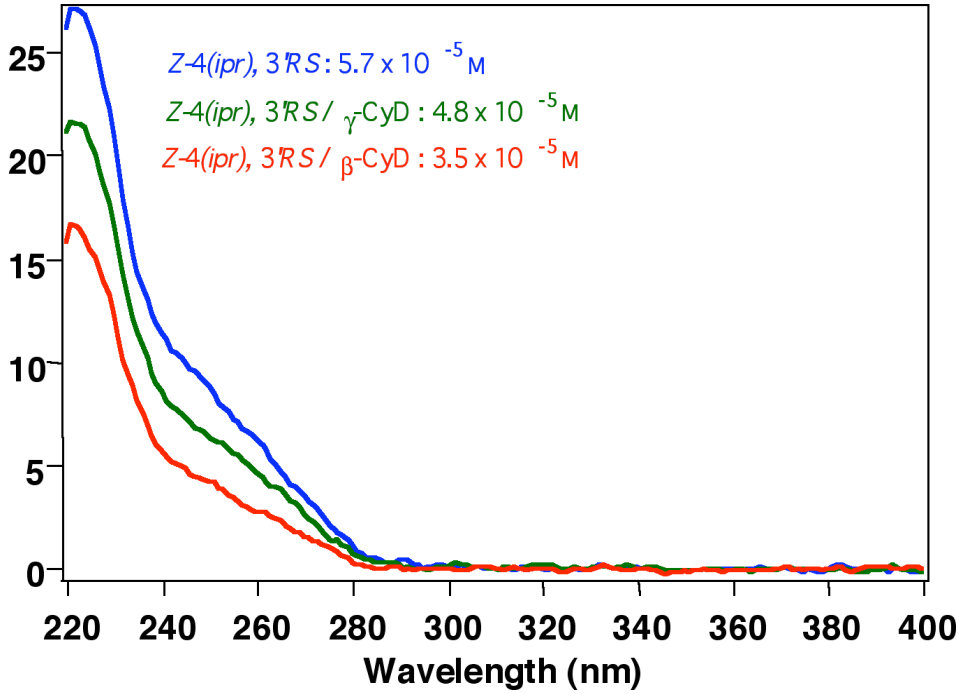

Figure S4: Circular dichroism spectra of **1*Z*** with/without CDs; [**1*Z***] = 5.7 x 10^{-5} M (blue), [**1*Z***] = [γ-CD] = 4.8 x 10^{-5} M (green), and [**1*Z***] = [β-CD] = 3.5 x 10^{-5} M (red).

4) Photoreactions

a) In D_2O/CD_3OD:

The γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD was placed into a quartz cell and then irradiated using an excimer laser at 308 nm; 20 Hz, 100 mJ/Pulse (2 Watts). The complex was then analyzed by ^{1}H-NMR spectroscopy and then by Gas chromatography.

b) Solid State:

Irradiations in solid state were performed with the well-grounded samples sandwiched between two quartz plates for the specified time intervals (Figure S5). The

complex was then dissolved in water and extracted (5 x 5 mL) with dichloromethane and dried over $MgSO_4$. The dichloromethane layer was concentrated and then submitted to ^{1}H-NMR spectroscopy (CD_3CN as solvent) followed by Gas chromatographic analysis.

Figure S5: Samples for solid-state irradiation. The γ-Cyclodextrin-**1*Z*** complex sandwiched between quartz plates were irradiated within a Rayonet reactor at 254 nm.

5) Gas Chromatographic analysis

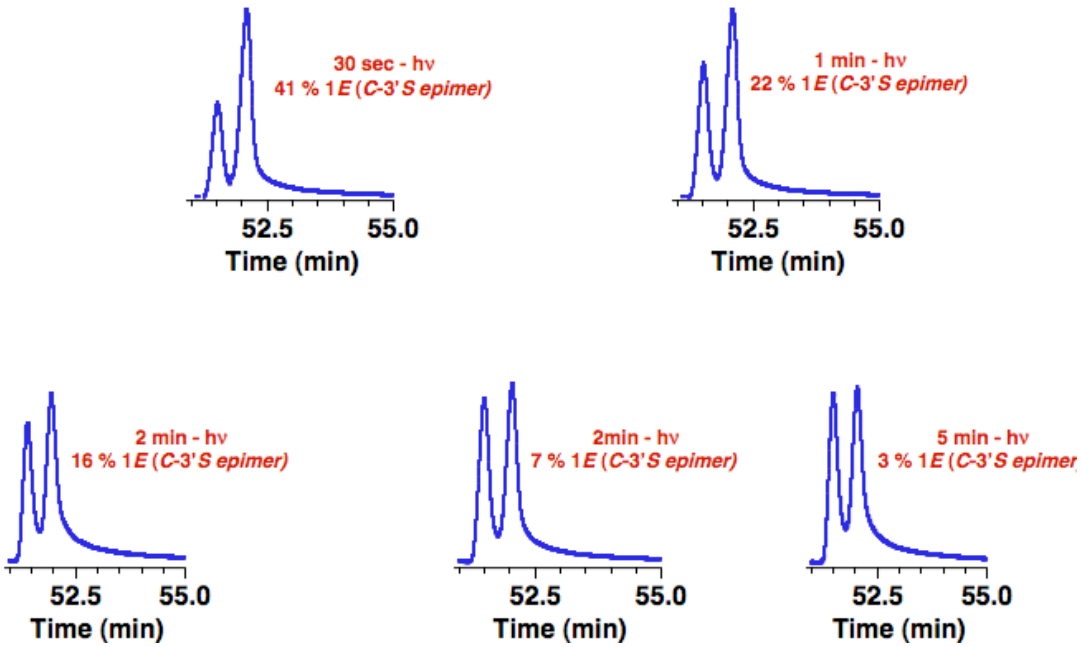

Figure S6: Gas Chromatographic analysis showing the diastereomeric *E*-enecarbamate peaks upon irradiation of the γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD.

6) NMR Characterization

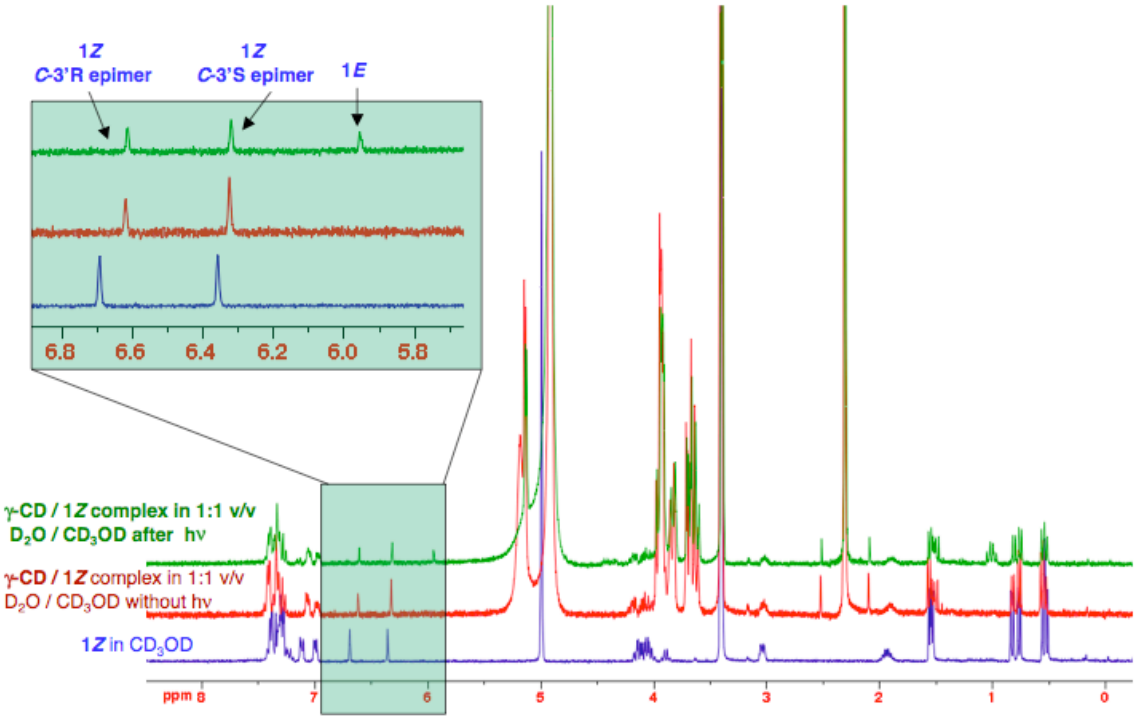

Figure S7: ^{1}H-NMR spectroscopy of a) **1*Z*** in CD_3OD (Blue); (b) γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD before irradiation - Note the shift in the peaks (Red); (c) γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD after irradiation - Note the formation of **1*E*** (Green).

7) Phosphorescence life time measurements

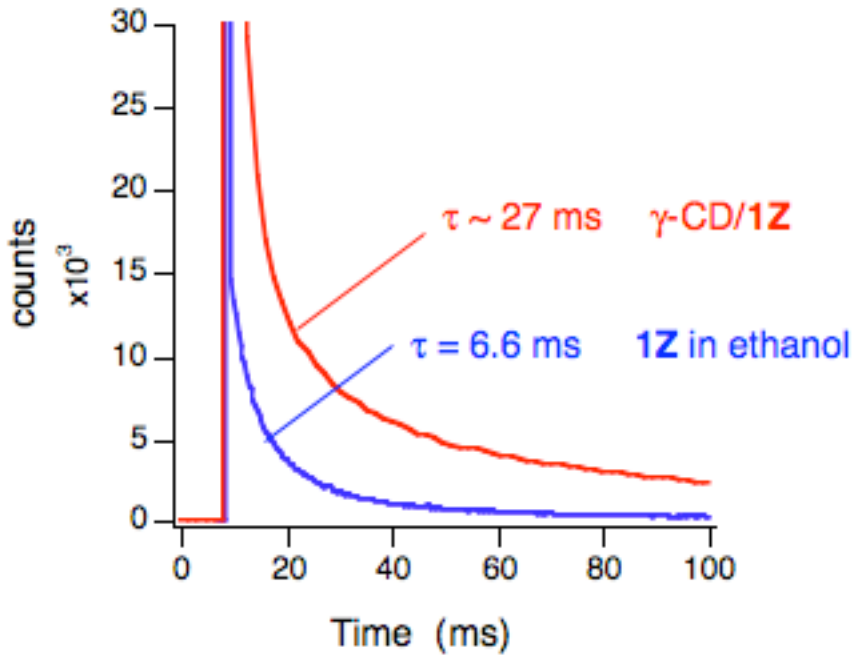

Figure S8: Phosphorescence lifetime measurements multi canal scaling of at 77 K **1*Z*** in ethanol glass (top) and γ-CD/**1*Z*** complex in 1:1 v/v of D_2O/CD_3OD (bottom) (λ_{ex} = 260 nm; λ_{em} = 390 nm).

References

S1 W. Adam, S. G. Bosio, N. J. Turro, and B. T. Wolff, *Journal of Organic Chemistry*, 2004, **69**, 1704.

S2 S. Koodanjeri, J. Sivaguru, A. Pradhan, and V. Ramamurthy, *PINSA-A: Proceedings of the Indian National Science Academy, Part A: Physical Sciences*, 2002, **68**, 453.