Supporting Information

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

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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.\textsuperscript{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 (1Z) with γ-Cyclodextrin:

Figure S1: Complexation of Z-enecarbamates (1Z) with γ-Cyclodextrin in 1:1 D$_2$O/CD$_3$OD.
a) In D$_2$O/CD$_3$OD:

4 mL of D$_2$O was added to a 25 mL standard flask with 0.03 mmol of $\gamma$-Cyclodextrin. 1Z (0.03 mmol) was dissolved separately in a test tube in 1 mL of CD$_3$OD 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$_2$O and 11.5 mL CD$_3$OD to give a clear solution of $\gamma$-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD.

![Figure S2: Complexation of Z-enecarbamates (1Z) with $\gamma$-Cyclodextrin with Ether/Water for solid-state studies.](image)

b) In Solid State:

The complexation of $\gamma$-CD and 1Z was achieved by adding 1Z (1.5 x 10^{-5} mol) in 5 mL ether to 1.5 x 10^{-4} mol of $\gamma$-CD in 10 mL deionized water, that gave a white precipitate of $\gamma$-CD/1Z complex (Figure S2). This complex was labeled 10:1 based on the starting molar ratio. Similarly a 20:1 $\gamma$-CD/1Z 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 (1Z) crashes out from water without cyclodextrin in 1:1 D$_2$O / CD$_3$OD (center); but is completely soluble in CD$_3$OD (left) and in the presence of γ-Cyclodextrin in 1:1 D$_2$O / CD$_3$OD (right).
3) Circular Dichroism Spectra of Z-enecarbamates with γ-Cyclodextrin:

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

4) Photoreactions

a) In D$_2$O/CD$_3$OD:

The γ-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD 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 MgSO₄. The dichloromethane layer was concentrated and then submitted to $^1$H-NMR spectroscopy (CD$_3$CN as solvent) followed by Gas chromatographic analysis.

Figure S5: Samples for solid-state irradiation. The $\gamma$-Cyclodextrin-1Z 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 $\gamma$-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD.
6) NMR Characterization

Figure S7: $^1$H-NMR spectroscopy of a) 1Z in CD$_3$OD (Blue); (b) γ-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD before irradiation - Note the shift in the peaks (Red); (c) γ-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD after irradiation - Note the formation of 1E (Green).
7) Phosphorescence life time measurements

Figure S8: Phosphorescence lifetime measurements multi canal scaling of at 77 K 1Z in ethanol glass (top) and γ-CD/1Z complex in 1:1 v/v of D$_2$O/CD$_3$OD (bottom) ( $\lambda_{ex} = 260$ nm; $\lambda_{em} = 390$ nm).

References
