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Reversal of Regioselectivity during Photodimerization of 2-Anthracenecarboxylic Acid in a Water-Soluble Organic Cavitand

Xueqin Wei,[†,‡] A. Mohan Raj,[§] Jiecheng Ji,[‡] Wanhua Wu,[‡] Giri Babu Veerakanellore,[§] Cheng Yang,[*,‡] and Vaidhyanathan Ramamurthy[*,§]

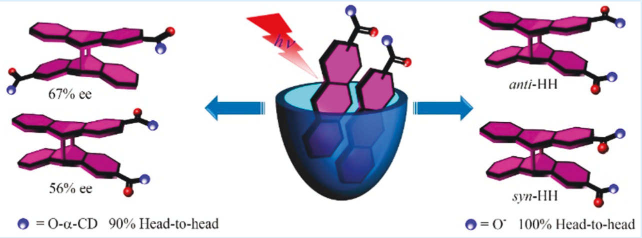
[†] School of Pharmacy, Guangxi Medical University, Nanning 530021, China

[‡] Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, State Key Laboratory of Biotherapy, and Healthy Food Evaluation Research Center, Sichuan University, Chengdu 610064, China

[§] Department of Chemistry, University of Miami, Coral Cables, Florida 33124, , United States

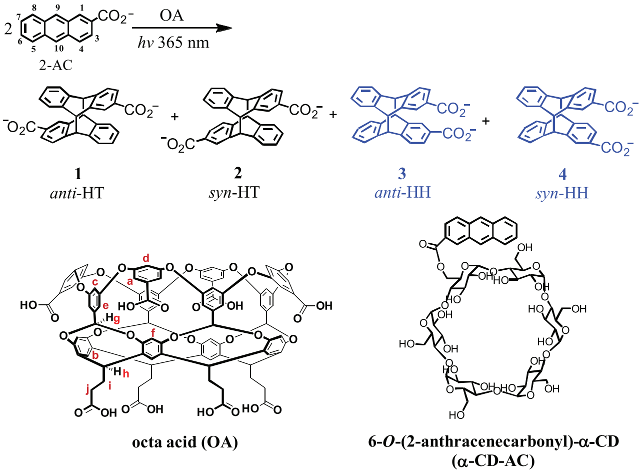
Supporting Information

ABSTRACT: The value of octa acid (OA) as a reaction vessel in steering a photoreaction toward a less favored product was established. Photodimerization of 2-anthracenecarboxylic acid within OA yields exclusively *head-to-head* dimers, while in media such as solution, cyclodextrins (CD) and related hosts yield predominantly *head-to-tail* dimers. Further, OA enhances the chiral selectivity on the product dimers. The difference between OA and CD is attributed to the variation in the dimensions of their entry ports.



In recent years, supramolecular hosts such as micelles, cyclodextrins (CD), crystals, zeolites, and synthetic organic and organometallic cavitands have been employed to steer photodimerization reactions.[1] Herein, we identify an organic host that functions in a complementary fashion to cyclodextrins and steer reactions quantitatively to products that are different from that in solution, in cyclodextrins and related supramolecular hosts. In this study, we have identified the uniqueness of the host octa acid (OA, Scheme 1)[2] as a reaction vessel by exploring the photodimerization of 2-anthracenecarboxylic acid (2-AC; Scheme 1). The choice of the system is dictated by our earlier observation in which OA reversed the well-known excited state behavior of anthracene in solution by forming a capsuleplex.[3] In addition, photodimerization of 2-AC has been extensively investigated as a benchmark supramolecular photoreaction in the context of regio- and stereoselectivities by Tamaki,[4] Ueno,[5] and Inoue.[1f,6] In various media thus far investigated, *head-to-tail* (HT) dimers **1** and **2** predominated the product mixture (Scheme 1) with varying amounts of enantiomeric excess (ee) in **2**. Based on literature reports,[7] we visualized 2-AC to orient with the head (COOH) facing water and the body (aryl ring) buried within the hydrophobic OA cavity favoring a *head-to-head* (HH) dimer unlike the usual HT dimer within γ-CD. The results presented below establish that OA includes guest molecules to form an open cavitandplex and favors exclusively regioselective HH dimers. In addition, by employing guests appended with chiral auxiliary (α-CD−AC; Scheme 1) we find that achiral OA can enforce diastereoselectivity on photoproducts.

Scheme 1. Photocyclodimerization of 2-AC and the Structures of the Host (OA) and the Chiral Guest Molecule (α-CD−AC) Used in This Study



Inclusion of 2-AC within OA was established by recording absorption, emission, and ^{1}H NMR spectra. Changes in emission (Figure 1a) and absorption spectra (Figure 1b), in line with what is known with γ-CD as the host,[8] were observed upon addition of OA to 2-AC in borate or phosphate buffer solution. ^{1}H NMR spectra (Figure 2 and Figures S1−4) of 2-AC and OA were recorded by titrating the host into the guest and vice versa. Addition of OA to a solution of 2-AC resulted in an upfield shift and broadening of the guest signals due to

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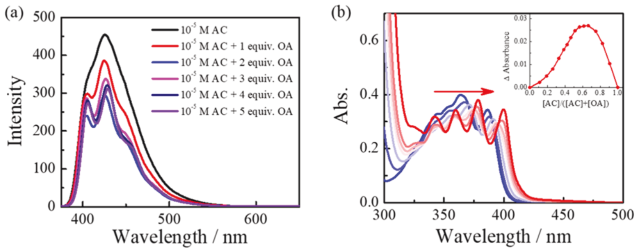

Figure 1. (a) Fluorescence spectra of 2-AC (1×10^{-5} M) upon addition of OA at room temperature in phosphate buffer (pH 9) solution, λ_{ex} = 360 nm. (b) UV spectral changes of 2-AC (0.2 mM) upon addition of OA in phosphate buffer (pH 9.0) at 25 °C and (inset) Job plot of the changes in the UV−vis spectra showing the stoichiometry of OA with AC.

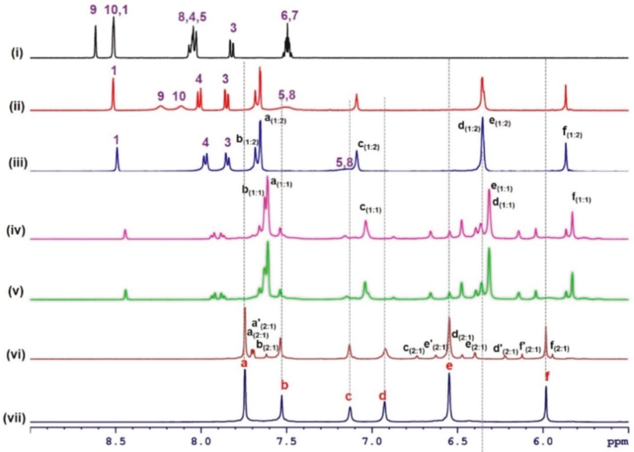

Figure 2. ^{1}H NMR (500 MHz) spectra of aromatic region: (i) 2-AC (1 mM) in D_2O buffer; (ii) 2-AC + OA (1:0.25 equiv); (iii) 2-AC + OA (1:0.5 equiv); (iv) 2-AC + OA (1:1 equiv); (v) OA + 2-AC (1:1 equiv); (vi) reverse addition OA + 2-AC (1:0.2 equiv); (vii) OA (1 mM) in D_2O buffer.

H-5−10 (Scheme 1), while that due to H-1, -3, and -4 remained sharp with little shift (Figure 2i−iii and Figures S1−S3). The continuous shift in signals due to H-5−10 with added OA suggested an exchange between the free and the bound 2-AC. The above changes suggested inclusion of one or two molecules of 2-AC within the host OA (acting as a cavitand and not as a capsule) with the hydrophilic COOH-substituted aryl ring exposed to water.

On the other hand, the reverse addition (2-AC to OA) disclosed the presence of a capsule. Examination of Figure 2vi and Figures S2 and S3 reveals the presence of weak signals due to complexed OA in addition to the strong ones due to uncomplexed OA. It is important to note that in Figure S3b (magnified spectrum) the signals due to H-a, -e, and -f from complexed OA are split into two, indicative of a capsule with two magnetically nonequivalent halves resulting from inclusion of the unsymmetric guest 2-AC within OA capsule.[7b,9] The signals due to the guest (starred peaks in Figure S3b) as identified by COSY spectra (Figures S7−8) clearly showing them to be spread between δ 5.1 and 7.7 ppm without any signals above δ 7.75 ppm is interpreted as the entire guest molecule to be within the host, possibly from a capsule formed by two molecules of OA.[10] Perusal of Figure 2 from top-down as well as from bottom-up and Figures S1−S3 unambiguously suggests that the nature of the complex formed at the initial stages depends on the mode of addition. The formation of capsuleplex appears to be preferred over cavitandplex at the initial stage of the addition of 2-AC to OA. Interestingly, at a host−guest ratio of 1:1, independent of the mode of addition, signals indicative of both the cavitand and capsule are obtained (Figure 2iv,v). Based on the spectra shown in Figure 2 and Figures S1−S3, we conclude the coexistence of at least three kinds of 2-AC supramolecular complexes, 1:1 and 1:2 cavitandplexes and 2:1 capsuleplex (Figure 3a), in equilibrium and further supported by the Job plot (Figure 1b inset) generated from the absorption changes during titration of OA to 2-AC in buffer. The observed plateau in the region of OA/AC ratios between 0.55 and 0.65 (Figure 1b inset and Figure S5) is consistent with the conclusion that the solution contains a mixture of 1:2[5b] and 1:1 host−guest complexes. Diffusion constants measured by ^{1}H NMR DOSY experiments (Figure S6) also favor the presence of cavitandplex in solution. The k_d for free 2-AC, OA, and the OA−2-AC mixture were found to be 5.81, 1.80, and 1.61 $\times$ 10^{-6} cm^2/s. Had it been a capsuleplex, the value would be in the range of 1.3−1.4 $\times$ 10^{-6} cm^2/s.[7b] To further probe the nature of the complexes, we performed isothermal titration calorimetric studies of AC with OA. As shown in Figure S9, OA and AC form 1:1 and 1:2 complexes with K_1 and K_2 values of 14400 and 104000 M^{-1}, respectively. Further experiments are planned to fully uncover the nature of the equilibrium that apparently contains both a capsuleplex and a cavitandplex.

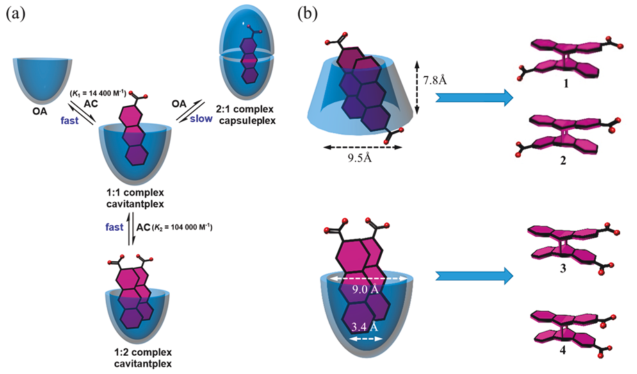

Figure 3. (a) Diagrammatic representation of interaction of 2-AC and types of possible complexes with OA. (b) Complexation of 2-AC and the subsequent products of photocyclodimerization in the γ-CD (top) and OA cavity (bottom).

An aqueous solution of 2-AC in the absence of OA at pH 9 was first irradiated at 365 nm with a LED lamp (see the SI). HPLC analysis[8] of the above irradiated mixture (Figure S10) showed that the photodimerization afforded all four dimers **1**, **2**, **3**, and **4** in 42, 36, 14, and 8% yield, respectively (Table 1). Within γ-CD, these dimers were formed in 43, 45, 7, and 5% yields. On the contrary, when 2-AC was irradiated in the presence of OA, **1** and **2** were absent and **3** and **4** were formed in 55 and 45% yield. Upon addition of 1-adamantane carboxylic acid (ACA) as a competitive guest to the OA solution, the nature of the dimer formed was dependent upon the amount of added ACA. While up to 1.0 mM of ACA HH dimers **3** and **4** predominated, their yields were reduced at higher concentrations of 2−50 mM (Table S1). This suggests that the HH dimers are formed from 2-AC present within OA cavity. The ratio of the two products and the conversion

Table 1. Photodimerization of 2-AC (0.2 mM) or α-CD−AC (0.2 mM) in Aqueous Buffer Solutions at pH 9.0 in the Absence and Presence of Host Irradiated at 365 nm[a]

				relative yield (%)				% ee	
guest	host	H/G	CsCl (M)	**1**	**2**	**3**	**4**	**2**	**3**
2-AC	none[b]	0	0	42.0	36.0	13.8	8.2		
	γ-CD[b]	10	0	42.9	44.6	7.3	5.2	32.0	−3.5
	OA	5	0	0	0	57.3	42.7		0
	OA	2	0	0	0	57.8	42.2		0
	OA	1	0	0	0	56.5	43.5		0
	OA	0.5	0	0	0	56.4	43.6		0
	OA	0.33	0	4.7	3.8	54.8	36.7	0	0
	OA	0.25	0	8.7	7.4	47.5	36.4	0	0
	OA	0.2	0	19.4	17.0	38.4	25.2	0	0
	OA	5	6	0	0	49.9	50.1		0
	OA	2	6	0	0	50.1	49.9		0
	OA	1	6	0	0	49.2	50.8		0
	OA	0.5	6	0	0	50.0	50.0		0
	OA	0.2	6	0	0	49.6	50.4		0
α-CD−2-AC	none	0	0	47.7	39.0	11.3	2.0	15.6	−26.0
	none[c]	0	0	34.0	42.0	17.0	7.0	5.0	−16.0
	γ-CD[c]	10	0	35.0	60.0	3.0	2.0	91.0	−2.0
	CB[8][c]	1	0	1.4	1.4	77.1	20.1	17.0	−10.0
	OA	2.5	0	6.1	4.4	52.7	36.8	51.8	−55.7

[a] Solutions were made with 25 mM borate buffer (pH 9) and irradiated under a N_2 atmosphere at 365 nm using a LED lamp for 1 h at 0.5 °C, unless noted otherwise. [b] Reference 8. [c] Reference 11, irradiation temperature 25 °C.

percentage was nearly independent of the excitation wavelength in the region 365−420 nm (Table S2).

To examine whether the reaction is catalytic, irradiation of solutions containing various ratios of host and guest (5:1 to 0.2:1; Table 1) was conducted. Note that to convert all of the guest in solution to a 1:2 host−guest complex a minimum of 0.5 equiv of the host (H/G = 0.5:1) is required. Under all conditions, even when the host was present in smaller amounts (H/G = 0.2:1 of the guest), HH dimers predominated in the product mixture, and the reaction went to completion. Under low H/G ratios (<0.33:1), reaction from the uncomplexed 2-AC also contributed to the product mixture; small amounts of HT dimers were formed. As shown in Table 1, the reaction from free uncomplexed 2-AC can be quenched by the addition of CsCl via heavy-atom induced enhanced singlet−triplet crossing. The ability to drive the photodimerization to an HH dimer with OA less than 25% of guest concentration suggests the catalytic nature of OA. To summarize: (a) OA favors the exclusive formation of HH dimers from 2-AC; (b) OA serves as a cavitand rather than as a capsule in 2-AC dimerization; and (c) OA acts as a catalyst.

With the goal of exploring the value of OA in enforcing selectivity on chiral products, we monitored the enantiomeric excess (ee) on the chiral dimer **3**. Since OA is not chiral, irradiations were performed in the presence of various chiral inductors. The not so encouraging initial results (Table S3), had a pleasant breakthrough with 6-*O*-(2-anthracenecarbonyl)-α-CD (α-CD−AC, Scheme 1) as the guest.[11] Inclusion of this guest within OA was confirmed by absorption and circular dichroism experiments. Addition of OA to an aqueous solution of α-CD−AC (0.1 mM) led to significant bathochromic shifts of α-CD−AC's ^1B_b and ^1L_a bands with isosbestic points at 273, 317, and 409 nm (Figure S11), and in the circular dichroism spectra (Figure 4) the intrinsic weak negative couplet of α-CD−AC gradually shifted to the oppositely signed Cotton effect. This is most likely due to the closeness of the two α-CD−AC units within OA.[11]

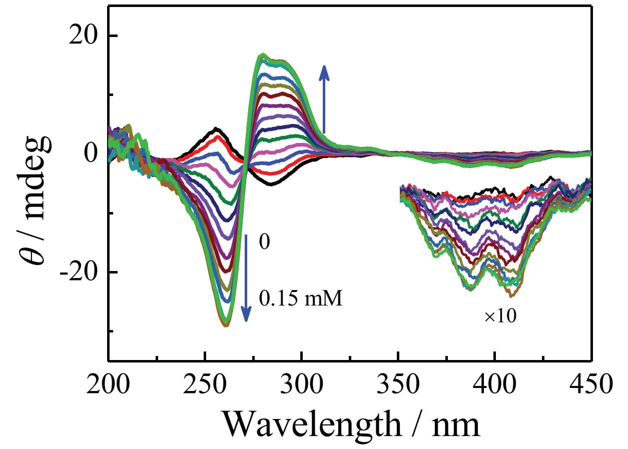

Figure 4. CD spectra of aqueous solutions containing 0.1 mM α-CD−AC and 0 (black) to 0.15 (green) mM OA at 25 °C.

A phosphate buffer solution containing 0.2 mM of α-CD−AC and 0.5 mM of OA was irradiated with 365 nm LED lamp at 0.5 °C. Following irradiation, the products were hydrolyzed in basic solution (see the SI) and analyzed by HPLC. As expected, the major products from α-CD−AC in the presence of OA were the HH dimers (Table 1). The increase in the ee from −26% to −56% in the case of **3** (Table 1) with addition of OA clearly confirms OA's role in asymmetric induction in this photodimerization. It is also important to note that presence of OA increased the ee on the dimer **2** (15.6 to 51.8%). Attempts at further increasing the ee by lowering the temperature, adding CsCl salt to suppress photodimerization in solution and using a mixed solvent (water−methanol) were unsuccessful (Table S4). The observed chiral induction, albeit moderate, establishes OA's ability in serving as a chiral inductor in photoreactions. Further studies are required to develop a predictable model.

In this study employing the photodimerization of 2-AC as a model, we have established the following: (a) OA is a valuable host that can act not only as a capsule but also as a cavitand. (b) As a cavitand with a single large port for guest molecules it can preorient them in a manner different from hosts with dual openings such as CD, cucurbiturils (CB), and calixarenes. (c) OA can enforce product selectivity different from that of CD and CB (Table 1). (d) Despite being an achiral molecule, it can enforce chiral induction through a supramolecular effect. These features of OA revealed for the first time open new avenues in its use as a supramolecular reaction cavitand that we plan to pursue.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02860.

> Experimental details, NMR spectra of host-guest complexes, ITC data, HPLC traces, and the results of UV−vis, fluorescence, and circular dichroism spectral studies (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: murthy1@miami.edu.
*E-mail: yangchengyc@scu.edu.cn.

ORCID

A. Mohan Raj: 0000-0003-3744-7538
Cheng Yang: 0000-0002-2049-1324
Vaidhyanathan Ramamurthy: 0000-0002-3168-2185

Notes

The authors declare no competing financial interest.

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