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A Supramolecular Strategy for Enhancing Photochirogenic Performance through Host/Guest Modification: Dicationic γ-Cyclodextrin-Mediated Photocyclodimerization of 2,6-Anthracenedicarboxylate

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Cite This: *Org. Lett.* 2020, 22, 9757–9761 Read Online

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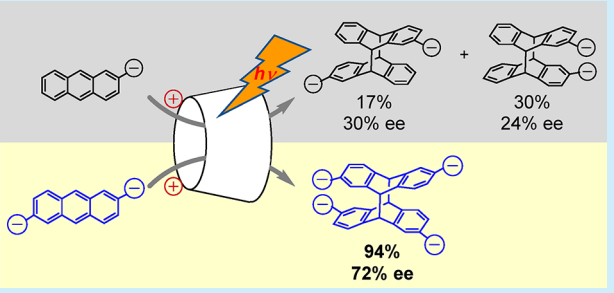
ABSTRACT: Possessing an extra anionic handle for chiral supramolecular interactions, 2,6-anthracenedicarboxylate exhibited greater photochirogenic performance than 2-anthracenecarboxylate to afford the *anti*-cyclodimer in up to 94% yield and −72% enantiomeric excess upon photoirradiation with dicationic γ-cyclodextrins.



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Chiral photochemistry has attracted significant attention of chemists in recent years by virtue of its ability to succinctly construct optically active polycyclic and constrained skeletons that are inaccessible or tedious to build up through thermal reactions.[1] Nevertheless, precisely controlling the stereochemical course of enantiodifferentiating photoreaction remains a significant challenge due to the inherently weak and short-lived interactions available for substrates in the excited state.[2] Several methodologies have hitherto been invented for enhancing the stereochemical outcomes of various photochirogenic reactions by optimizing the internal (structural and electronic) factors of the substrate, chiral auxiliary, and sensitizer[3] and also by manipulating the external variants (temperature,[4] solvent,[5] pressure,[6] irradiation wavelength,[7] etc.) to achieve substantial successes.[2f]

For bimolecular photochirogenic reactions, chiral supramolecular hosts have been exploited as mediators for simultaneously boosting the reaction rate and selectivity through the enantiotopic face-selective ground-state complexation of multiple guest substrates and the subsequent diastereodifferentiating photoreaction expedited by confining the substrates in a chiral host cavity.[8] The enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate (AC) to four *anti*/*syn*- and *head-to-tail*/*head-to-head*-isomeric cyclodimers, mediated by chiral hosts and templates,[3a,9] has been intensively investigated since 2003, and is now considered as a benchmark photochirogenic system with well-established mechanistic details and tools for enhancing stereoselectivities, although their general validity and expandability to other substrates remains less explored.

By introducing an additional carboxylate group to AC at its 6-position, we obtain symmetrically substituted 2,6-anthracenedicarboxylate (AD). As a guest substrate for the supramolecular photochirogenesis via 1:2 complexation with a chiral host, such as γ-cyclodextrin (γ-CD), dianionic AD is expected to augment the steric and electrostatic host−guest and interguest interactions than monoanionic AC, leading to an enhancement of stereodifferentiation. An extra benefit of using AD is the number of produced regioisomeric cyclodimers, which is four for AC but mere two for AD. Thus, the photoirradiation of AD yields chiral *anti*- and achiral *syn*-cyclodimers (*anti* and *syn*), as shown in Scheme 1.[10] Bach, Inoue, and coworkers have recently reported that the enantiodifferentiating photocyclodimerization of AD mediated by C_2-symmetric hydrogen-bonding template affords *anti* in modest chemical and optical yields of up to 76% yield and 55% enantiomeric excess (ee).[10c]

In this proof-of-the-concept study, we wanted to elucidate how and to what extent the regio- and enantioselectivities of the photocyclodimerization are manipulable by introducing an extra carboxylate to AC and further to develop a reliable strategy for enhancing the performance of supramolecular photochirogenesis. For this purpose, we chose AD as a

Received: November 20, 2020
Published: December 7, 2020

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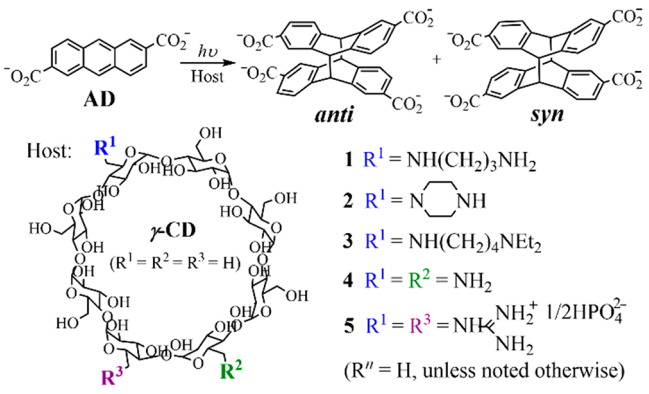
https://dx.doi.org/10.1021/acs.orglett.0c03848
Org. Lett. 2020, 22, 9757–9761

Scheme 1. Supramolecular Photocyclodimerization of AD Mediated by Native and Dicationic γ-CD Hosts 1−5



dianionic guest substrate and a series of native and dicationically modified γ-CDs **1**−**5** (Scheme 1) as chiral hosts capable of forming 1:2 complexes with AD to multidimensionally and more efficiently control the stereochemical outcomes through the increased steric conflicts as well as the attractive host−guest and repulsive guest−guest electrostatic interactions under a variety of conditions.

Prior to the photochemical investigations, we examined the complexation behavior of AD with the γ-CD derivatives by UV−vis, circular dichroism, and fluorescence spectroscopy. Upon UV−vis spectral titration of AD with γ-CD host **1** (Figure 1a), a new band emerged at longer wavelengths (420−450 nm) at the expense of the low-energy (^1L_a and ^1L_b) bands (320−420 nm) with accompanying apparent isosbestic point at 408 nm, indicating a smooth conversion of free AD to an energetically stabilized species, the complexation stoichiometry of which was confirmed by UV−vis spectral Job analysis, see Figure S11 in the Supporting Information.

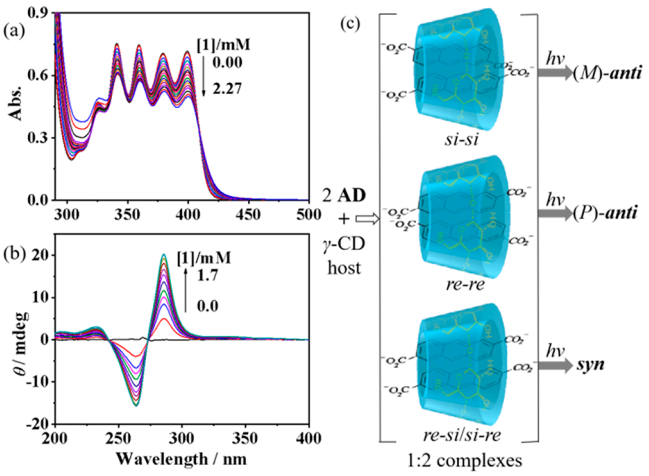


Figure 1. (a) UV−vis spectral titration of AD (0.2 mM) with host **1** (0−2.27 mM) in a pH 9 phosphate buffer at 25 °C (10 mm path length). (b) Circular dichroism spectral titration of AD (0.2 mM) with **1** (0−1.72 mM) under the same conditions as above (1 mm path length). (c) A plausible mechanism for the 1:2 complexation to give diastereomeric *si-si*, *re-re*, and *re-si/si-re* complexes, which then photocyclodimerize to (*M*)- and (*P*)-*anti* and achiral *syn*.

In contrast, the fluorescence of AD was monotonically quenched upon gradual addition of host **1** without affording any appreciable new emission at longer wavelengths, implying that the 1:2 complex species observed in the UV−vis spectra is nonfluorescent due to the spontaneous cyclodimerization upon excitation; see Figure S14 and the relevant discussion in the Supporting Information.

Circular dichroism spectral titration revealed more dramatic changes. As shown in Figure 1b, the addition of host **1** to an aqueous solution of AD induced a strong positive exciton couplet at the main (^1B_b) band, while the CD signals were extremely weak at the ^1L_a and ^1L_b bands.

All of these spectral behaviors, resembling those reported for AC,[3a,9a,b] as well as the similar host/guest dimensions allow us to postulate essentially the same complexation and photocyclodimerization mechanisms for AD. Thus, the enantiodifferentiating photocyclodimerization of AD mediated by γ-CD derivative is deduced to proceed through the diastereomeric *si-si*, *re-re*, and *re-si/si-re* termolecular (1:2) complexes, which are the precursors to (*M*)- and (*P*)-*anti* and *syn*, respectively, as illustrated in Figure 1c; the *re/si* definition is for the enantiotopic face of AD confronting to each other.

Assuming the stepwise 1:2 complexation, we analyzed the UV−vis spectral titration data obtained for **1** (Figures 1a and S12) to obtain the first and second association constants: K_1 = 190 M^{-1} and K_2 = 10 200 M^{-1} at 25 °C. This means that, when the concentrations of AD and **1** are set to those for photoirradiation (i.e., [AD] = 0.4 mM and [**1**] = 2 mM), free AD, 1:1, and 1:2 complexes populate in a 52:18:30 ratio (Table S1).

It is to note that, although the 1:1 complex is a single species, the 1:2 complex is actually a mixture of three diastereomeric isomers of different thermodynamic and spectroscopic properties (Figure 1c), which enable us to manipulate the photochirogenic consequences by various external variants.

We first examined the effects of irradiation wavelength (λ) on the photochirogenic behavior of AD in aqueous buffer solution at 0.5 °C using parent γ-CD as a host. As shown in Figure S17 and Table S2 (entries 1−14), the chemical yield of *anti* turned out to be a critical function of λ, fluctuating between 50 and 60% at 254−400 nm but abruptly increasing at λ > 400 nm to 84% at 440 nm, while the ee of *anti* was modest and less λ-dependent, affording a maximum value of −18% at 313 nm.

These results indicate that the three stereoisomeric precursor complexes significantly differ in absorption spectrum and the *anti*-stacked (*re-re* and *si-si*) complexes suffer larger spectral red-shifts than the *syn*-stacked (*re-si/si-re*) complex, which also means that the former complexes are more stabilized than the latter, probably for the steric and electrostatic reasons. On the other hand, the low ee observed indicates that discriminating the *re-re* from the *si-si* complex by the spectral or energy difference is a harder task for the chiral cavity of unmodified γ-CD.

Crucially, the absolute configuration of the preferentially obtained chiral cyclodimer, i.e. (*P*)-*anti*, agrees with the *P*-helical arrangement of two AD chromophores in *re-re* precursor complex (Figure 1c), which is deduced from the positive exciton coupling observed in the CD spectra using the exciton chirality theory.[10b,11]

For a better control of the complexation and photochirogenic behaviors of dianionic AD, we prepared a series of single- and double-armed dicationic γ-CD hosts **1**−**5** (Scheme 1), in which single diamino-substituent or dual amino- or guanidino-substituents are attached to the primary rim of CD

https://dx.doi.org/10.1021/acs.orglett.0c03848
Org. Lett. 2020, 22, 9757−9761

Table 1. Supramolecular Photocyclodimerization of AD Mediated by Native and Modified γ-CD Hosts 1−5[a]

					yield (ee)[d]/%			
entry	host	solvent[b]	T/°C	λ[c]/nm	*anti*		*syn*	*anti*/*syn*
1[e]	none	B[e]	25	>320	50	(0)	50	1.0
2	γ-CD	B[b]	0.5	313	55	(−18)	45	1.2
3				380	58	(−11)	42	1.4
4				440	84	(−10)	17	5.1
5	**1**	B[b]	0.5	313	41	(−21)	59	0.7
6				380	50	(−20)	50	1.0
7				440	73	(−16)	27	2.7
8	**2**	B[b]	0.5	313	49	(−23)	51	1.0
9				380	55	(−19)	45	1.2
10				440	81	(−10)	19	4.4
11	**3**	B[b]	0.5	313	47	(−21)	53	0.9
12				390	55	(−20)	45	1.2
13				440	79	(−15)	21	3.9
14	**4**	B[b]	0.5	313	29	(−31)	71	0.4
15		M[b]	−50	313	63	(−71)	37	1.7
16				360	58	(−72)	42	1.4
17				450	58	(−53)	42	1.4
18	**5**	M[b]	−40	313	63	(−39)	37	1.7
19				380	64	(−31)	36	1.8
20				440	87	(−22)	13	6.5
21		A[b]	0.5	313	64	(−46)	36	1.8
22				360	66	(−45)	34	2.0
23				440	88	(−45)	12	7.7
24			−60	313	64	(−61)	36	1.8
25				360	67	(−61)	33	2.1
26				440	84	(−59)	16	5.2
27				450	94	(−69)	6	15.1

[a][AD] = 0.4 mM; [host] = 2 mM. [b]Solvent B: pH 9 phosphate buffer; solvent M: a 1:1 mixture of phosphate buffer (pH 9) and methanol; solvent A: 28% aqueous ammonia. [c]Irradiation wavelength. [d]Chemical yield and enantiomeric excess (in the parentheses) determined by chiral HPLC. Negative ee value indicates the preferential formation of the second-eluted (*P*)-enantiomer of *anti* under the HPLC conditions employed (see Supporting Information); the error in ee < 1%. [e]Ref 10b, where the photoreaction was performed in a pH 7 buffer solution at 25 °C.

as built-in handle(s) to dictate the spatial arrangement of an AD pair accommodated in chiral CD cavity through the electrostatic interactions. The photocyclodimerization of AD mediated by **1**−**5** was carried out at various λ values under the same condition as above for native γ-CD to give the results shown in Table 1 (entries 5−14); see also Table S2.

Somewhat unexpectedly, the single-armed dicationic γ-CD hosts **1**−**3** did not appreciably improve the chemical or optical yield of *anti*, affording the comparable maximum yields of 73−81% upon irradiation at 440 nm and the ee values of −21 to −23% upon irradiation at 313 nm (Table 1, entries 5−13), revealing the relatively poor stereocontrol by the single dicationic side arms.

On the contrary, double-aminated γ-CD **4** gave a noticeably higher ee of −31% at 313 nm under the same condition (Table 1, entry 14). We therefore changed the solvent to a 1:1 mixture of the phosphate buffer and methanol to lower the solvent polarity, where stronger electrostatic (attractive host−guest and repulsive guest−guest) interactions are expected to operate upon complexation. Indeed, the ee of *anti* was enhanced up to −71 and −72% upon irradiation at 313 and 360 nm, respectively, while the chemical yield stayed modest at 58−63% (entries 15 and 16). The use of double-guanidinated γ-CD **5** further enhanced the chemical yield up to 87% in aqueous methanol at −40 °C (entry 20) and to 94% and the ee to −69% upon irradiation at 450 nm in aqueous ammonia at −60 °C (entry 27). The enhanced stereoselectivity would be ascribed to the more intimate (stereodifferentiating) attractive host−guest interactions between the guanidine and carboxylic acid moieties and the repulsive guest−guest interactions at the other ends of included ADs (see Figure S18), both of which are expected to be intensified upon addition of less polar, more basic cosolvent ammonia to the aqueous solution.[4c] The *anti*/*syn* ratio of 15.1 and the 72% ee achieved for AD by using hosts **5** and **4**, respectively, are much higher than the corresponding best values (the *anti*/*syn* ratio of 4.8 and 44% ee) reported for the photocyclodimerization of AC mediated by all the possible primary-side diaminated and diguanidinated γ-CDs, including **4** and **5**, under the comparable conditions (i.e., 30% aqueous ammonia at temperatures ranging from −40 to −70 °C).[4c]

It should also be noted that, in this supramolecular photocyclodimerization of AD, all of the γ-CD hosts **1**−**5** afford (*P*)-*anti* as the major enantiomer, and its ee is rather modestly improved by optimizing the irradiation wavelength, temperature, and solvent. In other words, the absolute configuration of the chiral product is governed solely by the host structure, and the external variants only fine-tune the product's ee without affecting the chiral sense. This is in keen contrast to the photochirogenic behavior of AC under the comparable conditions, where the absolute configuration of chiral cyclodimers of AC is not a simple function of the host but is often inverted by altering the irradiation temperature and solvent.[4c] The less important role played by the

https://dx.doi.org/10.1021/acs.orglett.0c03848
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environmental factors in the photocyclodimerization of AD seems reasonable, as the 1:2 complexes derived from the dicationic γ-CD host and the dianionic guests should be more rigid, or in deeper potential wells, due to the generally strengthened attractive host−guest and repulsive guest−guest interactions (Figure S18), leaving little room for the external factors to dynamically modulate the complex structure. The above-mentioned direct correlation between the chiral sense of precursor complex and that of the photoproduct may originate from this structural robustness and further suggests that the subsequent photophysical and photochemical processes do not greatly differ among the three diastereomeric precursor complexes to alter the thermodynamically determined preference upon complexation.

In this study on the supramolecular photochirogenic strategy, we revealed that the guest modification to boost the overall photochirogenic performance through the increased steric and electrostatic interactions upon termolecular complexation is effective indeed in enhancing both the chemical and optical yields of the chiral photoproduct. The strengthened supramolecular interactions enable us to more precisely define the complex structure and strictly control the stereochemical outcomes. On the contrary, the structures of intervening complexes become less flexible to hinder the dynamic modulation of the photochirogenic consequences by external variants. In the present system, the two factors, internal and external, are apparently well-balanced to achieve the excellent overall photochirogenic performance. The basic idea to design a host−guest complex system that is moderately rigid but is still flexible enough to be manipulated by external variants is quite straightforward and versatile and hence expandable to other supramolecular photochirogenic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03848.

Experimental details, characterization of synthesized hosts, ^{1}H and ^{13}C NMR and HRMS spectra of **3**−**5**, determination of the association constants, speculation of the UV−vis spectrum of the 1:2 complex, speculation of the fluorescence spectrum of the 1:1 complex, ^{1}H NMR spectra of AD in the presence/absence of host **1**, Job plot to confirm the complex stoichiometry, chiral HPLC traces of representative photolyzates, wavelength-dependent yield and ee of *anti*, illustrated interactions upon 1:2 complexation of AD with dicationic γ-CD host, population of and light absorption by AD species existing in the solution, and the results of photocyclodimerization of AD with native and modified γ-CDs (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the Natural Science Foundation of Tianjin (18JCQNJC76400, 18JCYBJC89900), the National Natural Science Foundation of China (Nos. 31871811, 21871194, 21971169, 21572142, 92056116, 22001046), the National Key Research and Development Program of China (No. 2017YFA0505903), and the Science & Technology Department of Sichuan Province (2019YJ0160, 2019YJ0090, 2017SZ0021), Fundamental Research Funds for the Central Universities. We thank Prof. Ye Tao and Dr. Yan Huang of BSRF for their assistance during the use of UV light sources.

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https://dx.doi.org/10.1021/acs.orglett.0c03848
Org. Lett. 2020, 22, 9757−9761