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Photocatalytic Supramolecular Enantiodifferentiating Dimerization of 2-Anthracenecarboxylic Acid through Triplet−Triplet Annihilation

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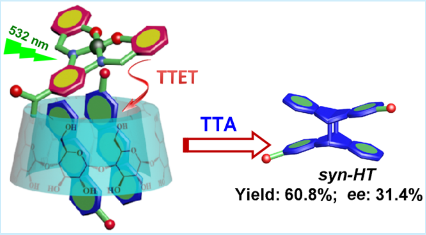
Supporting Information

ABSTRACT: Visible-light-driven enantiodifferentiating photodimerization of 2-anthracenecarboxylic acid (AC) sensitized by Schiff base Pt(II) complex-grafted γ-cyclodextrins leads the first triplet−triplet annihilation-based catalytic photochirogenesis. The *syn-head-to-tail* (HT) photodimer **2** was achieved in up to 31.4% ee at 61.0% conversion in the presence of 0.5% equiv of the photocatalyst.

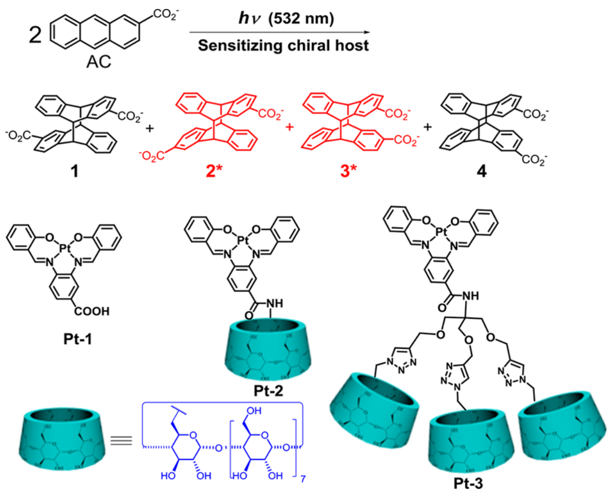


Supramolecular photochirogenesis has recently received much interest because supramolecular complexation provides relatively long-lasting and strong interaction toward photosubstrates and, therefore, represents a promising solution to address the short-lived, highly reactive, and weak interactive weaknesses of electronically excited photosubstrates.[1] Chiral molecular hosts, such as cyclodextrins (CD),[2] chirally modified zeolites,[3] chiral templates,[4] and biomacromolecules[5] have been explored for conducting chiral photoreactions. In most cases, an excess amount of chiral host is demanded for the purpose to inhibit the racemic photoproduct arising from photoreaction of unbound photosubstrates. This significantly limits the application of the supramolecular photochirogenesis, especially considering that chiral hosts are often not readily accessible. Catalytic photoreactions[6] have been realized by strategies, such as triplet sensitization,[7] photoinduced electron transfer,[8] selective photoexcitation of complexes,[9] and photoredox catalysis.[10] However, very few have been applied to supramolecular photochirogenesis.

Triplet−triplet annihilation (TTA) is a process whereby two triplet excited state molecules interact to form a singlet excited state molecule. TTA upconversion has attracted extensive attention for potential applications in fields, such as bioimaging, photocatalysis, and photovoltaics due to the low-power, incoherent excitation and high upconversion efficiency.[11] However, a TTA-based chiral photochemical reaction has not yet been reported. Herein, we describe a TTA-based chiral photocatalysis in the supramolecular photocyclodimerization of 2-anthracenecarboxylic acid (AC).

Photodimerization of AC generally affords four [4 + 4] cyclodimers **1**−**4** (Scheme 1), in which the *syn-head-to-tail* (HT) dimer **2** and *anti-head-to-head* (HH) dimer **3** are chiral.[12a] The enantiodifferentiating photodimerization of AC has been studied with CDs,[12] liquid crystals,[13] chiral templates,[14] biomolecules,[15] and chiral aggregations.[16] In most cases, excess amounts of chiral inductors are indispensable to reduce the photoreaction from unbound AC.[17]

Scheme 1. [4 + 4] Photocyclodimerization of AC Mediated by Photosensitizers Pt-1, Pt-2, and Pt-3



To realize the supramolecular TTA sensitization, we synthesized sensitizing chiral hosts **Pt-2** and **Pt-3** by grafting Schiff base Pt(II) complexes **Pt-1** onto γ-CD. **Pt-2** and **Pt-3** show moderate visible absorption and intensive red phosphorescence in deaerated solution (Table 1). The triplet energies of both sensitiers are higher than that of AC, guaranteeing an efficient energy transfer to AC. All photosensitizers show large thermally induced Stokes shifts (ΔE_S) and structured emission spectra (Figure S27),[18] suggesting a ^{3}MLCT feature of the triplet excited state.[19]

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Table 1. Photophysical Properties of the Sensitizers and AC[a]

	E_S[b] (nm)	ε[c]	E_T[d] (nm)	Φ_P[e]	K_{SV} (10^4 M^{-1})	k_q (10^9 M^{-1} s^{-1})
Pt-1	529	5396	599	0.13	1.28	6.46
Pt-2	533	6267	611	0.20	2.29	5.65
Pt-3	534	6384	610	0.38	2.97	4.67
AC	365	5492	680[f]	n[g]	n[g]	n[g]

[a] In DMF at 5×10^{-5} M. [b] Singlet energy derive from the lowest absorption band. [c] Molar absorption coefficient at the absorption maxima. [d] Triplet energy derive from phosphorescence emission maxima. [e] Phosphorescence quantum yield was measured in deaerated water at 25 °C. [f] Literature data.[11d] [g] Not determined.

The circular dichroism spectrum of **Pt-2** shows negative signals at the π−π* transition of the Schiff base (245−330 nm) and a weak positive signal at the MLCT transition (500−580 nm). According to the "sector rule" proposed by Kajitar,[20] we conclude that the sensitizer's square-coordinated plane reclines on the primary rim of γ-CD and partially inserting into γ-CD cavity. Adding AC into the solution of 0.2 mM **Pt-2** slightly reduced the circular dichroism intensity of **Pt-2** in the range 400−565 nm, implying a complexation-induced orientational change of the sensitizer. An apparent circular dichroism inversion was observed at 280 nm (Figure 1a). This is consistent with the positive exciton coupling circular dichroism of a 1:2 complex of AC and γ-CD.[12a] The stepwise 1:1 (K_1) and 1:2 (K_2) association constants were determined by isothermal titration calorimeter (ITC) studies (Figure 1b). **Pt-2** showed a much larger apparent association constant K_1 (10 400 M^{-1}) than K_2 (719 M^{-1}), which is opposite to the smaller K_1 (182 M^{-1}) than K_2 (56 700 M^{-1}) observed with native γ-CD.[12a] This result implies that the attached sensitizer serves as a co-including guest to facilitate the complexation of the first AC molecule, but prevent the access of the second AC. The overall association constant K_1K_2 (7.48×10^6 M^{-2}) for **Pt-2** is comparable to that of native γ-CD (1.03×10^6 M^{-2}), indicating that **Pt-2** remains strongly binding toward AC.

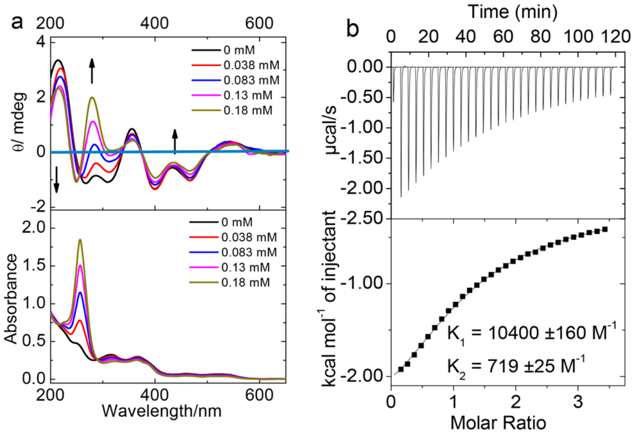

Figure 1. (a) Circular dichroism (upper panel) and UV−vis (lower panel) spectra of **Pt-2** (0.2 mM) in a pH 9.0 borate buffer in the presence of various concentration of AC at 20 °C. (b) ITC titration profile of 0.2 mM AC with 3.0 mM **Pt-2** in a pH 9.0 borate buffer at 25 °C.

Stronger red emissions for **Pt-2** (Φ = 0.20) and **Pt-3** (Φ = 0.38) than **Pt-1** (Φ = 0.13) were observed in aqueous solution, which is presumably due to the protection of sensitizer from solvent collision by CD complexation. Adding AC led to a progressive decrease of the phosphorescence intensity of all sensitizers (Figure S28),[18] for which the TTET from the sensitizers to AC should be responsible. The Stern−Volmer analysis of the emission quenching data shows an apparent linear relationship (Figure S29),[18] from which the Stern−Volmer constants K_{SV} were derived. **Pt-2** and **Pt-3** show K_{SV} values of 2.29×10^4 and 2.97×10^4 M^{-1} (Table 1),[18] respectively, which is apparently larger than that of **Pt-1** (1.28×10^4 M^{-1}). This demonstrates that the complexation of AC with γ-CD improves the TTET efficiency.

Photolyses of AC with hosts/sensitizers were carried out by using a diode pumped solid state laser (532 nm) in a borate buffer solution (pH 9.0) at 20 °C to give results listed in Table 2. In the presence of a photosensitizer, photoirradiation with the 532 nm laser smoothly triggered photochemical conversion of AC, as demonstrated by the decrease of the UV−vis absorption of AC (Figures S31, S32).[18] The sensitizers' MLCT absorption bands remained essentially intact with the irradiation, indicating the good photochemical stability of the sensitizers. In contrast, 532-nm-laser photoirradiation of the AC and γ-CD mixture in the absence of any sensitizer afforded completely no photoproduct (Table 2). Photosensitization with **Pt-1** gave the sterically and electrostatically favored HT dimers in 74% combined relative yield at a conversion of 53.1% (Table 2). This result demonstrates a TTA-based photodimerization, because a triplet anthracene does not directly react with a ground anthracene[21] but can undergo dimerization through TTA process.[22]

Photosensitization of 0.2 mM AC with 0.05 mM **Pt-2** or **Pt-3** for 2.0 h led to >90% conversions, much higher than that obtained with **Pt-1** (53.1%), further confirming the improved TTET efficiency due to the supramolecular complexation. The relative yields and enantioselectivities for photodimer **2** were evidently improved in the photosensitization by **Pt-2** or **Pt-3**. For instance, 532 nm photoirradiation of 0.2 mM AC in the presence of 0.01 mM **Pt-2** gave **2** in 58.3% relatively yield and 27.7% enantiomeric excess (ee). Meanwhile, 365 nm photoirradiation of the same solution with a 2.0-W LED lamp gave dimers **2** and **3** in only 4.1% and −7.2% ee, respectively (Table 2). Based on the K_1 and K_2 values, the population of free AC, a 1:1 complex, and a 1:2 complex in an aqueous solution containing 0.2 mM AC and 0.01 mM **Pt-2** was calculated to be 96.1:3.1:0.8 (Table S1). The poor enantioselectivity obtained in direct photoexcitation of AC is therefore ascribed to the small population of the 1:2 complex, even though the 1:2 complex usually has a higher reaction efficiency.[12a] The 1:1 complex will prevent the photodimerization (Figure S35).[18] Increasing the concentration of **Pt-2** will increase the 1:2 complex and consequentially improve the stereoselectivity. Indeed, 365 nm photoirradiation of the aqueous solution containing 0.20 mM **Pt-2** and 0.20 mM AC, in which the ratios of the 1:2 complex and free AC are 6.3% and 46.2%, respectively, afforded **2** in 21.5% ee and **3** in −14.2% ee (Table 2). These results are in good agreement with the previous conclusion that excess chiral sources are indispensable in traditional supramolecular photochirogenesis. On the other hand, ee's of **3** obtained under 365 nm photoirradiation are higher than in the case of TTA-based photodimerization under similar reaction conditions (Table 2). This interesting result implies that the chirality transfer of the TTA-based photoreaction could also be different from that of direct irradiation of AC (Figure S35).[18] The complexation of triplet AC may differ from that of ground state AC, which could

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Table 2. Photocyclodimerization of AC in the Presence of a Sensitizer/Host[a]

			relative yield (%)[c]				ee %[c]	
host/sen.	[sen.] (mM)[b]	conv (%)[c]	1	2	3	4	2	3
γ-CD[d]	0	0	n[e]	n[e]	n[e]	n[e]	n[e]	n[e]
Pt-1	0.05	53.1	37.3	36.7	15.9	10.1	0	0
Pt-1/γ-CD[d]	0.05	30.6	32.2	45.7	15.9	6.2	8.5	7.4
Pt-2	0.001[f]	61.0	29.9	60.8	6.1	3.1	31.4	−0.5
	0.005	40.1	35.1	58.1	4.6	2.3	31.1	−0.2
	0.01	74.2	34.0	58.3	4.9	2.8	27.7	−1.8
	0.05	91.6	31.3	52.0	10.5	6.2	22.5	−6.8
	0.01[g]	70.1	42.6	40.9	9.8	6.8	4.1	−7.2
	0.20[g]	97.2	32.9	34.1	19.0	14.0	21.5	−14.2
Pt-3	0.001[f]	63.0	32.6	49.5	11.9	6.0	26.4	1.0
	0.005	44.2	31.4	47.7	13.8	7.2	25.4	7.9
	0.01	76.2	31.0	47.4	13.9	7.7	24.3	9.6
	0.05	91.0	31.7	48.0	13.2	7.2	21.3	14.1

[a]Irradiation at 532 nm in pH 9.0 borate buffer solution using a 50 mW laser for 2.0 h at 20 °C, [AC] = 0.2 mM. [b]Concentration of the sensitizers. [c]Relative yield and *ee* were determined by HPLC analyses. [d][γ-CD] = 4.0 mM. [e]Not determined. [f]Irradiation at 532 nm for 10.0 h. [g]Irradiation with a medium pressure mercury lamp at 365 nm.

also be responsible for the different stereoselectivity obtained with the TTA-based photoreaction.

Pt-2- or **Pt-3**-sensitized TTA dimerization of AC affords higher enantioselectivity for **2** in the presence of catalytic amounts of chiral hosts. **Pt-2** gives **3** in small negative ee's (Table 2), which seems in accordance with the poor enantioselectivity for **3** generally observed with γ-CD.[12a] However, **Pt-3** shows higher positive ee's for **3**, suggesting the important role of the tethered group on the enantioselectivity. The relative population and optical yields of **2** are improved by reducing the **Pt-2** amount to give **2** in 60.8% relative yield and 31.4% ee from the solution containing 0.001 mM **Pt-2**. It is noteworthy that the ratio for free AC, the 1:1 complex, and the 1:2 complex under similar conditions is 99.6:0.3:0.1 (Table S1). The good enantioselectivity obtained with such a small amount of the 1:2 complex indicates highly efficient photodimerization in the cavity of **Pt-2**, and photodimerization of free AC is strongly inhibited. We ascribe this to the Dexter TTET mechanism, according to which energy transfer can take place only between a closely spaced sensitizer and acceptor.[23] The TTET to the γ-CD-complexed AC should be much more efficient than to unbound AC in the bulk solution. This is consistent with our previous finding that supramolecular complexion significantly improves the TTET efficiency.[24]

On the other hand, photodimerization of AC in the presence of 0.05 mM **Pt-1** and 4.0 mM γ-CD gives **2** in modest 8.5% ee. This demonstrates the importance of integrating the sensitizer into the chiral host. For the photodimerization mediate by **Pt-1** and γ-CD, the complexed AC molecules were less accessible by **Pt-1** than free AC due to the inhibition of γ-CD. Therefore, TTET and TTA should occur mainly with ACs outside the CD cavity.

With **Pt-3**, chiral dimer **2** was achieved in 49.5% relative yield and up to 26.4% ee in the presence of 0.001 mM **Pt-3**. Slightly unexpectedly, increasing the concentration of both **Pt-2** and **Pt-3** resulted in a decrease of the optical yield of dimer **2**, but an increase of that of dimer **3**. Increasing the concentration of **Pt-2** and **Pt-3** in aqueous solution led to a bathochromic shift of UV−vis spectra (Figure S26),[18] implying aggregations of **Pt-2** and **Pt-3**, which should be jointly driven by solvophobic effect, $\pi-\pi$ stacking, and Pt−Pt interactions.[25] The aggregation is confirmed by the fact that the ^{1}H NMR spectra of **Pt-2** and **Pt-3** display broad signals in D$_2$O solution (Figures S33 and S34).[18] The switched enantioselectivity with the concentration of sensitizers is thus possibly due to the aggregation of sensitizing hosts that changes the chiral environment.

In summary, we have established a new strategy for realizing catalytic supramolecular photochirogenesis through triplet−triplet annihilation. By photoexciting the Schiff base Pt(II) complex grafted on γ-CD, the in situ TTET happens efficiently to the γ-CD-complexed ACs that triggers the TTA-based photodimerization of AC. Photosensitization with 0.5% equiv of **Pt-2** using a 532 nm laser enabled us to achieve the *syn*-HT dimer **2** in up to 31.4% ee and 60.8% relative yield at a conversion of 61%. This work also opens a new potential application for TTA upconversion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00520.

> Experimental procedure, characterization data, and detailed photophysical and photochemical data (PDF)

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Notes

The authors declare no competing financial interest.

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