Chinese Chemical Letters 27 (2016) 1017–1021

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Enhanced head-to-head photodimers in the photocyclodimerization of anthracenecarboxylic acid with a cationic pillar[6]arene

Jian-Chang Gui [a,1], Zhi-Qiang Yan [a,1], Yuan Peng [b], Ji-Gao Yi [a], Da-Yang Zhou [c], Dan Su [a], Zhi-Hui Zhong [a], Guo-Wei Gao [a], Wan-Hua Wu [a], Cheng Yang [a,*]

[a] *Key Laboratory of Green Chemistry & Technology, College of Chemistry, State Key Laboratory of Biotherapy, West China Medical Center and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China*
[b] *Chengdu Environmental Monitoring Center, Chengdu 610042, China*
[c] *Comprehensive Analysis Center, ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 5670047, Japan*

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 7 April 2016
Accepted 14 April 2016
Available online 11 May 2016

Keywords:
Pillar[6]arene
Photocyclodimerization
Anthracenecarboxylic acid
Supramolecular complexation

ABSTRACT

The complexation behaviors of anthracenecarboxylic acid and water-soluble cationic pillararenes have been investigated by ^{1}H NMR, UV–vis and ITC methods. The cationic pillar[6]arene was found to stepwise form 1:1 and 1:2 complexes, having a large K_1 and a relatively small K_2 values. Photocyclodimerization of AC within the pillar[6]arene improved the yield of the head-to-head photodimers. Up to 4.97 HH/HT ratio has been reached by optimizing the reaction conditions.

1. Introduction

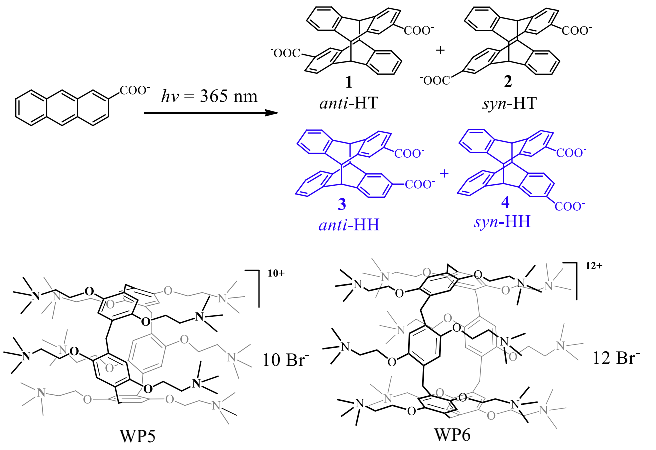
Manipulating the chemo- and regio-selectivity of photochemical reactions through supramolecular complexation is an intriguing topic of current photochemistry. Photosubstrates at the electronic excited state are featured by high reactivity and short lifetime, which makes it difficult to control the selectivity of photoreactions [1]. Supramolecular complexation could orientate substrates in confined spaces, make reaction centre spatially close to the catalytic site and stabilize their high-energy transition states. Photosubstrates complexed in the cavity of molecular host often show switched photophysical and photochemical properties [2]. Consequentially, supramolecular complexation provides a promising strategy to affect the rate and selectivity of photoreactions. Intermolecular photochemical reactions demand suitable size and reasonable driving force of binding site of the host to arrange two photosubstrates together. In this context, controlling the reaction selectivity of photodimerization are more challenging [3]. Molecular hosts bearing a large cavity suitable for accommodating two photosubstrates, such as γ-cyclodextrins (CD) [4–7], crown ethers [4], coordinated cages [8,9], cucurbiturils [10–12], templates [13] and biomolecules [14], have been employed as host molecules for conducting photodimerizations. Recently, pillar[n]arenes, a new family of macrocyclic compounds composed by several 1,4-disubstituted hydroquinone ethers, have attracted significant attention from chemists [15]. Their cavities are possible to accommodate organic guest mainly through electrostatic dipole interactions in organic solvent [16–21]. Up to now, pillar[n]arenes comprising 5–15 hydroquinone ether units have been explored [22–24]. This makes pillar[n]arenes versatile hosts capable of binding guest molecules of different sizes. On the other hand, water-soluble pillar[n]arenes, synthesized by suitable chemical modification on the rims of pillar[n]arenes, make the intriguing host molecules possible to complex a wide range of organic guests through hydrophobic interaction [25,26].

We have comprehensively investigated the photocyclodimerization of anthracenecarboxylic acid (AC) by using γ-cyclodextrin (CD) [27–31], bio-macromolecules [32], chiral templates [33,34] as well as coordinated cages [35] as host molecules. Photocyclodimerization of AC affords *anti*- and *syn*-head-to-tail (HT) photodimers **1** and **2** (Scheme 1) accompanying by the *anti*- and *syn*-head-to-head (HH) photodimers **3** and **4**. Among different types of host molecules, γ-CD derivatives have been most extensively employed, because γ-CD has a large cavity that can simultaneously

---

[*] Corresponding author.
E-mail address: yangchengyc@scu.edu.cn (C. Yang).
[1] ‡*These Authors contributed equally to this work.*

http://dx.doi.org/10.1016/j.cclet.2016.04.021
1001-8417/



Scheme 1. Photocyclodimerization of AC with water-soluble pillararenes WP5 and WP6.

accommodate two AC molecules. The photocyclodimerization of AC is thus accelerated by a factor of 10 to show reaction selectivity significantly different from those observed in homogeneous solution [5]. γ-CD determines the photoreaction outcome through the formation of 1:2 complexes, and AC pairs of different stacking pattern in the 1:2 complexes lead to corresponding photodimers upon photoexcitation [36–38]. Photocyclodimerization of AC has become a model photochemical reaction for evaluating the supramolecular complexation between AC and host molecule, which provides the detailed stacking model of AC pairs in the host cavity through the analyses of the population of photodimers. Photocyclodimerization of AC in aqueous solution usually prefers the HT photodimers **1** and **2** due to the electrostatic repulsion for HH photodimers. Complexation with γ-CD led to an enhancement of the HT photodimers, and the HH photodimers were given in poor yield of $< 15\%$. Therefore, to improve the yield of HH photodimers **3** and **4** are more challenging. It occurred to us that introduction of cationic groups on the two rims of a pillararene will make pillararenes water-soluble, and thus extend the ability of pillararenes to complex a wide range organic guest through hydrophobic interaction. More importantly, the presence of cationic groups will improve the electrostatic attraction and consequently reduce the electrostatic repulsion between carboxylate anions of HH-stacked AC pairs. In this study, we report our efforts to improve the HH photodimers of AC by using the water-soluble pillar[6]arene (WP6).

2. Experimental

2.1. Materials and instruments

2-Anthracenecarboxylic acid (AC) was purchased from TCI (China) and used as received. Doubly distilled water and HPLC grade solvents were used for photoreactions and spectral measurements. Other solvents were purchased from Wako Pure Chemical Industries, Ltd. ^{1}H NMR and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively, on a Bruker DRX-400 instrument. HR-MS were obtained by using the Shimadzu LCMS-IT TOF (ESI) spectrometer. UV–visible spectra were recorded on a JASCO V650 spectrophotometer. Fluorescence measurements were carried out by using a JASCO-FP 8500 spectrofluorimeter. Photoproducts were analyzed by using a Shimadzu LC Prominence 20 HPLC instrument equipped with UV–vis and fluorescence detectors.

2.2. General preparation procedure and characterization for target compounds

Compound **5**: Hydroquinone (10.0 g, 91 mmol), 1,2-dibromoethane (35 mL, 0.41 mol) and potassium carbonate (40 g, 0.29 mol) were added into acetone (150 mL), the mixture was refluxed for 24 h under N_2. After the reaction mixture was cooled down to room temperature, precipitate was removed by filtration. The solvent was removed under reduced pressure and the product was purified by column chromatography (eluent: hexane: dichloromethane = 1:1). A white solid was obtained (6.3 g, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 4H), 4.24 (t, 4H, J = 6.3 Hz), 3.61 (t, 4H, J = 6.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.81, 116.07, 77.36, 77.04, 76.72, 68.69, 29.30.

Compound **6a**: A mixture of **5** (3.24 g, 10 mmol) and paraformaldehyde (0.93 g, 30 mmol) in 1,2-dichloroethane (20 mL) was stirred at room temperature for 30 min. $BF_3{\cdot}Et_2O$ (1.25 mL, 10 mmol) was added and the reaction mixture was stirred for additional 30 min. The reaction mixture was washed with water three times, and the organic phase was concentrated and the product was purified by column chromatography (SiO_2; Petroleum ether/CH_2Cl_2/EA, 2:1:0.03) to give a white solid (1.18 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 10H), 4.23 (t, 20H, J = 5.6 Hz), 3.84 (s, 10H), 3.64 (t, 20H, J = 5.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.66, 129.06, 116.09, 77.36, 77.05, 76.73, 68.97, 53.43, 30.75, 29.40.

Compound **6b**: **5** (2 g, 6.17 mmol), paraformaldehyde (926 mg, 30.85 mmol) and $FeCl_3$ (200 mg, 1.24 mmol) were added to $CHCl_3$ (90 mL), and the mixture was heated to 45 °C for 72 h. The mixture was cooled down to room temperature and then washed with water three times, the organic phase was concentrated and subjected to column chromatography (SiO_2; Petroleum ether/CH_2Cl_2/EA, 2:1:0.06). Finally, a white solid was obtained (520 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (s, 12H), 4.17 (t, 24H, J = 5.8 Hz), 3.87 (s, 12H), 3.56 (t, 24H, J = 5.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.19, 128.53, 115.84, 77.37, 77.05, 76.73, 68.97, 30.66, 30.35.

WP5: Trimethylamine (2 mL, 33% in water) was added to 15 mL DMF solution containing **6a** (300 mg, 0.18 mmol), and the resulting mixture was heated to 80 °C for 24 h. After cooling down to room temperature, the solvent was removed and the residue was dissolved in water, and the solution was filtered and applied on a reversed-phase column. After lyophilization, a white solid was obtained (350 mg, 86%). ^{1}H NMR (400 MHz, D_2O): δ 6.93 (s, 10H), 4.44 (s, 20H), 3.91 (s, 10H), 3.80 (s, 20H), 3.23 (d, 90H, J = 15.7 Hz). ^{13}C NMR (101 MHz, D_2O): δ 149.28, 129.84, 116.42, 64.89, 63.41, 59.55, 54.05, 29.51.

WP6: Trimethylamine (0.5 mL, 33% in water) was added to a solution of **6b** (100 mg, 0.05 mmol) in DMF (5 mL), and the resulting mixture was heated to 80 °C for 24 h. After cooling down to room temperature, the solvent was removed under vacuum and the solid was dissolved in water. The resulted solution was membrane-filtered and applied on a reversed-phase column. After lyophilization, a white solid was obtained (115 mg, 85%). ^{1}H NMR (400 MHz, D_2O): δ 6.84 (s, 12H), 4.43 (s, 24H), 3.88 (s, 14H), 3.69 (s, 24H), 3.04 (s, 108H). ^{13}C NMR (101 MHz, D_2O): δ 149.73, 129.02, 116.17, 65.07, 63.36, 59.60, 54.28, 30.13.

3. Results and discussion

The synthesis of the cationic pillararenes WP5 and WP6 was represented in Scheme 2, which were synthesized following a modified procedure given in the previous reports [39–41]. The chemical structures of WP5 and WP6 were identified by HR mass and ^{1}H NMR and ^{13}C NMR spectroscopic examinations. Both WP5 and WP6 are well soluble in aqueous solution due to the presence