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

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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

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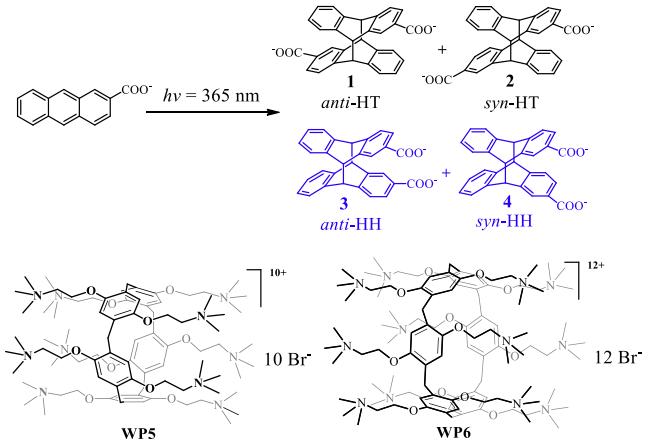

Scheme 1. Photocyclodimerization of AC with water-soluble pillararenes **WP5** and **WP6**.

γ-CD has a large cavity that can simultaneously 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

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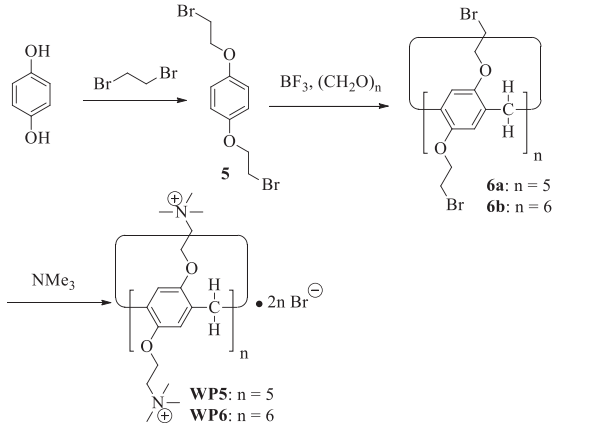


Scheme 2. The synthesis of the cationic pillararenes **WP5** and **WP6**.

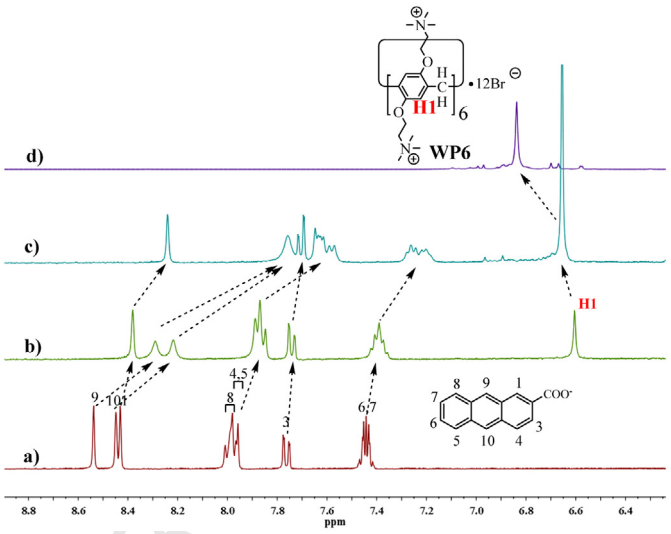


Fig. 1. Partial ^{1}H NMR of a) 0.2 mmol/L AC, b) 0.2 mmol/L AC + 0.2 mmol/L **WP6**, c) 0.2 mmol/L AC + 1.0 mmol/L **WP6** and d) **WP6** in pD = 9.0 D_2O solutions.

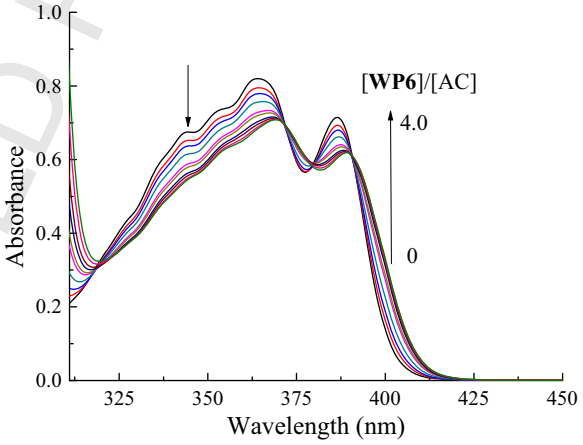
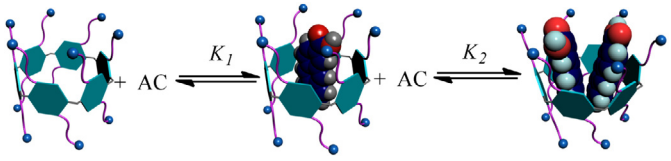


Fig. 2. UV–vis spectral changes of AC upon increasing the concentration of **WP6** measured in aqueous solution at 25 °C.

of a large amount of ammonium groups. In view of the hydrophobicity of hydroquinone ether units, we deduced that **WP5** and **WP6** can accommodate AC molecules in aqueous solution mainly through the hydrophobic interactions. The framework of pillararenes, with benzene rings linked by methylene group, are relatively rigid. The tethers grafted on the rims form a flexible hydrophobic wall, which should jointly function in complexation. On the other hand, the electrostatic interaction between ammonium cations and carboxylate anion of AC should also play an important role for the complexation. To understand the binding behavior between cationic pillararenes and AC, UV–vis, ^{1}H NMR spectroscopies and Isothermal titration calorimetry (ITC) were carried out (Scheme 3).

The ^{1}H NMR titration of AC with **WP6** clearly demonstrates the formation of the host–guest complex between AC and **WP6**. As shown in Fig. 1, adding **WP6** into the aqueous solution of AC led to an evident upfield shift of the proton signals of AC. The largest change was seen for the protons at the 9′-H and 10′-H of the central nucleus of AC, exhibiting a shift larger than 0.7 ppm (Fig. 1), accompanied by a broadening of 9′-H and 10′-H protons. This could be reasonably rationalized by the shielding effect from the aromatic rings of **WP6**. On the other hand, the singlet aromatic proton of **WP6** presents a downfield shift with the concentration of **WP6**, demonstrating that the wall of **WP6** is suffering the shielding effect from AC rings.

The complexation between cationic pillararenes and AC was also confirmed by the UV–vis spectral studies. As exemplified in Fig. 2, UV–vis spectral change in the wavelength range of 310–450 nm were carried out by keeping the concentration of AC constant and varying the concentration of **WP6** in aqueous solution at 25 °C. Increasing the concentration of **WP6** resulted in an apparent bathochromic shift and the band broadening of the ^1L_a transition. Such a UV–vis spectral variation is similar to that observed in the complexation between AC and γ-CD, where the significant change of ^1L_a band is ascribed to the formation of the 1:2 complex between γ-CD and AC [5]. Relatively smaller bathochromic shift without band broadening was seen in the UV–vis titration with **WP5**, which has a smaller cavity and is expected to accommodate only one AC molecule.



Scheme 3. Stepwise 1:1 and 1:2 complexation between **WP6** and AC.

ITC titration of AC with **WP5** based on 1:1 complexation model at 25 °C showed a K_1 value of 5.47×10^3 L·mol^{-1} (Fig. S13 in Supporting information). This is a typical binding affinity commonly observed by artificial host–guest complexation driven mainly by hydrophobic interaction. The binding is an enthalpy- and entropy-favored process, showing a ΔH value of −13.3 kJ·L·mol^{-1} and ΔS of 27.0 J·K^{-1}·L·mol^{-1}. On the other hand, ITC titration of AC with **WP6** on the basis of 1:1 and 1:2 complexation model offered stepwise binding constants $K_1 = 1.21 \times 10^4$ L·mol^{-1} and $K_2 = 94$ L·mol^{-1} (Fig. 3). This result remarkably differs from the complexation of AC with γ-CD, which shows a much smaller K_1 with an overwhelmingly higher K_2 value [5]. While the ΔS_1 (27.1 J·K^{-1}·L·mol^{-1}) value is comparable with the ΔS value of **WP5**, The ΔH_1 (−15.2 kJ·L·mol^{-1}) is relatively higher than the ΔH value of **WP5**, for which more active water molecules released from the cavity of **WP6** is possibly responsible. We deduce that the small K_2 value observed with **WP6** is due to that the cavity of **WP6** is relatively crowd for accommodating the second AC molecule, and the secondly-coming AC may position mainly in the hydrophobic environment formed by flexible tethers. The inclusion of the second AC molecule in the cavity of **WP6** should cause significant loss of rotational and motional freedom of

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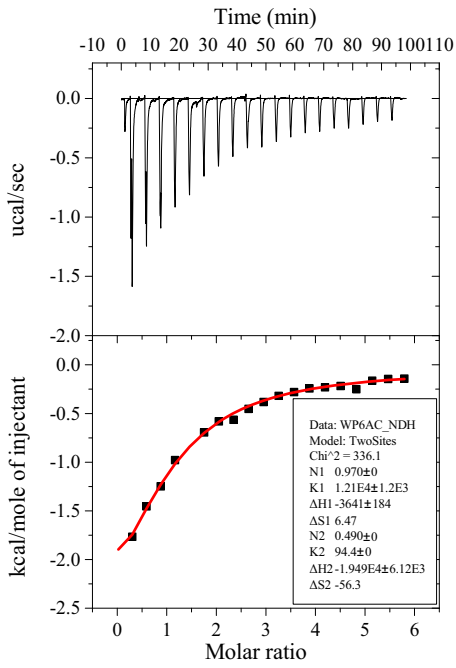

Fig. 3. ITC titration of **WP6** into the aqueous solution of AC.

AC and **WP6**, and therefore results in a large entropic loss ($\Delta S_2 = -235\ J{\cdot}K^{-1}{\cdot}L{\cdot}mol^{-1}$).

Photolyses of AC in the absence and presence of a pillararene have been carried out in aqueous buffer solution (pH 9.0) with an LED lamp at 365 nm. The reaction was monitored by tracing the UV–vis absorption change of AC. Unexpectedly, the photodimerization of AC in the presence of **WP6** is slower than that in the absence of any host molecule. The observed reaction rate constants, by regarding the reaction system as a simple second order reaction, were calculated to be $95\ L{\cdot}mol^{-1}{\cdot}s^{-1}$ and $24\ L{\cdot}mol^{-1}{\cdot}s^{-1}$, respectively, corresponding to the photoreactions in the absence and presence of **WP6**. This result implies that the 1:2 complex does not accelerate but rather inhibit the reaction. Although the reason for this is not yet clear, it is possibly due to the bad matching of the AC's photoreactive 9 and 10 positions in the cavity of **WP6**.

As shown in Table 1, in the absence of any host molecule at 0.5 °C, the HT photodimers **1** and **2** dominate the photocyclodimerization of AC, showing a combined yield of 75.4% (entry 1). Photocyclodimerization of AC with **WP5** offers similar product distribution to that in the absence of any host molecule. This is reasonable because the cavity of **WP5** is too small to include two AC molecules and photocyclodimerization of AC occurs mainly with free AC. The yield ratio of HH photodimers versus HT photodimers (HH/HT ratio) in the absence of host is 0.30 (entry 1). With **WP6**, the yield of HH photodimers was greatly improved, showing a HH/HT ratio of 0.75, for which the reduced electrostatic repulsion due to the interaction from the electrostatic attraction from cationic ammonium should be responsible.

In order to improve the HH photodimers by reducing the electrostatic repulsion between carboxylate of AC, we attempted the strategy of adding salt additive. Indeed, with all salts tried (entries 4, 6 and 10), the yields of HH photodimers are much higher than that obtained in aqueous buffer solution without salt additive. Addition of **WP6** further enhanced the yield of HH photodimers, demonstrating the importance of supramolecular complexation on the photoreaction selectivity. In 1.0 mol/L NH_4Cl aqueous solution at 0.5 °C, the HH/HT ratio was improved to 2.09 (entry 7) by **WP6**. Moreover, raising the temperature lead to further increase of the yield of HH photodimers, and a HH/HT ratio of 4.97 (entry 9) was obtained at 40 °C in 1.0 mol/L NH_4Cl in the presence of **WP6**.

Table 1
Photocyclodimerization of AC mediated by water-soluble pillar[n]arenes.[a]

Entry	Solution	Host	Temp. /°C	Relative yield (%) 1	2*	3*	4	HH/HT[b]	*anti*/*syn* 1/2	3/4
1	Aqu. buffer[c]	No	0.5	37.9	39.3	13.4	9.5	0.30	0.96	1.41
2		**WP5**	0.5	36.2	33.9	17.0	12.9	0.43	1.07	1.31
3		**WP6**	0.5	28.2	29.0	21.5	21.5	0.75	0.97	1.00
4	1.0 mol/L NaCl	No	0.5	32.8	36.1	15.2	16.0	0.45	0.91	0.95
5		**WP6**	0.5	17.6	20.2	28.5	33.7	1.65	0.86	0.85
6	1.0 mol/L NH_4Cl	No	0.5	21.2	23.2	23.6	32.0	1.25	0.91	0.74
7		**WP6**	0.5	15.8	16.5	31.0	36.7	2.09	0.96	0.85
8		**WP6**	25	9.6	9.4	32.8	48.3	4.28	1.02	0.68
9		**WP6**	40	8.5	8.2	32.5	50.8	4.97	1.03	0.64
10	1.0 mol/L CsCl	No	0.5	29.6	27.5	17.8	25.1	0.75	1.08	0.71
11		**WP6**	0.5	21.1	20.0	26.6	32.4	1.44	1.06	0.82

[a] [AC] = 0.2 mmol/L, [**WP5**] = [**WP6**] = 2.0 mmol/L. Irradiation at 365 nm using a LED lamp for 30 min.
[b] [**3**+**4**]/[**1**+**2**].
[c] pH 9.0 phosphate buffer solution (25 mmol/L).

4. Conclusion

In conclusion, we have demonstrated that water-soluble **WP6** can form 1:2 complex with AC. The photocyclodimerization of AC with the water-soluble **WP6** significantly improves the inherently unfavorable HH photodimers. By optimizing the reaction condition, up to 4.97 HH/HT ratio has been reached by using **WP6** as a host. This study opens a window to investigate intermolecular photoreaction using the new host molecule of pillararenes. The mechanism and the detailed effect of salt additive and temperature in this supramolecular photoreaction system are under study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2016.04.021.

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