



Communication Molecular Cage Promoted Aerobic Oxidation or Photo-Induced Rearrangement of Spiroepoxy Naphthalenone

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Abstract: Herein, we report a Pd_4L_2 -type molecular cage (1) and catalyzed reactions of spiroepoxy naphthalenone (2) in water, where selective formation of 2-(hydroxymethyl)naphthalene-1,4-dione (3) via aerobic oxidation, or 1-hydroxy-2-naphthaldehyde (4) via photo-induced rearrangement under N_2 have been accomplished. Encapsulation of four molecules of guest 2 within cage 1, i.e., (2)₄ \subset 1, has been confirmed by NMR, and a final host-guest complex of 3 \subset 1 has also been determined by single crystal X-Ray diffraction study. While the photo-induced ring-opening isomerization from 2 to 4 are known, appearance of charge-transfer absorption on the host-guest complex of (2)₄ \subset 1 allows low-power blue LEDs irradiation to promote this process.

Keywords: supramolecular catalysis; host-guest chemistry; aerobic oxidation; rearrangement

1. Introduction

Artificial supramolecular architectures constructed via self-assembly with metal ions and organic ligands have attached tremendous attentions due to aesthetic structural diversity [1–12] and bio-mimic catalysis [13,14]. Among them, coordination molecular cages have been extensively studied as artificial enzyme-mimics to promote various reactions of the contained molecules within the confined space [15–19]. Cage catalyzed reactions can be classified into three pathways [20]: (1) cage promoted reactions directly; (2) modified cage to improve catalysis performance; (3) cooperation with other catalysts. For the cage promoted reactions, it is generally accepted that enhanced effective concentration and the pre-organization effect imposed to the guest molecules by the cage cavity contribute to the accelerated reaction rate and the improved product selectivity. To date, cage promoted cycloaddition [21,22], rearrangement [23,24], photocatalysis reactions [25–27], oxidation or reduction [28-32], nucleophilic addition [33,34], elimination [35] and acid or base-catalyzed addition [36–38] have been reported, and a part of works exhibit rate enhancement, amazing selectivity and wide substrate scope. Moreover, highly-charged molecular cages can perform catalysis in water, like enzymes do in nature. Recently, we have developed a redox-active coordination-assembled cage 1 (Scheme 1) based on bridged pyridinium ligands, which has been employed as a water-soluble bio-mimic catalyst [39]. The large hydrophobic cavity of cage 1 allows a variety of guests to be encapsulated, and the big apertures on the cage favor the product turn-over during catalysis [40].

Spiroepoxy-cyclohexdienones, one type of vinyl epoxides [41,42], are important building blocks for organic synthesis due to their highly reactive nature toward self-coupling Diels-Alder reactions [43]. We anticipate that new reaction pathways may be discovered if spiroepoxy-cyclohexdienones are entrapped within molecular cages. Herein, we report that cage 1 promoted aerobic oxidation and photo-induced isomerization reactions in water from spiroepoxy naphthalenone 2. In the presence of cage 1, both naphthoquinone 3 and



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). aldehyde **4** can be selectively obtained by regulating the reaction conditions. It is worth to note that as a typical spiroepoxy-cyclohexdienones compound, reactivity of **2** has seldom been studied, with only one type of acid mediated rearrangement reaction being reported previously [44].



Scheme 1. Cage 1 promoted selective transformation from 2 to 3 or 4.

2. Results and Discussion

Cage 1 and substrate 2 were synthesized according to the previous reports [40,44]. We started from the investigation of their host-guest chemistry. After excess amount of guest 2 was added to cage 1 in D₂O, the formation of a 1:4 host-guest complex was indicated by ¹H NMR spectra. Compared to the signals of free 2 (Figure 1a) and empty cage 1 (Figure 1b), the host-guest complex shows significant changes. Obvious up-field shifts for the aromatic signals on 2 from 8.1–5.9 ppm to 6.4–4.5 ppm, and the methylene signals from 3.4–3.1 ppm to 2.0–2.2 ppm were observed in ¹H NMR spectrum (Figure 1c), which indicates the efficient guest encapsulation within the hydrophobic cavity of cage 1. Moreover, integral ratio (Figure S3) confirms that four molecules of 2 could be encapsulated by 1. Diffusion-ordered ¹H NMR spectroscopy (¹H DOSY, Figure S4) also confirmed the formation of a single host-guest species with a diameter of 1.70 nm estimated from the Stokes–Einstein equation. The optimized host-guest complex model indicates that four molecules of 2 completely occupied the space of cavity within the cage 1 (Figure 2a).

Interestingly, after heating at 50 °C for 2 h, the color of the solution for the initial $(2)_4 \subset 1$ complex changed gradually from yellow to deep red, and the dramatic change in ¹H NMR spectrum (Figure 1d) suggests the formation of a new host-guest complex. Characteristic signals for the encapsulated **2** (methylene signals) disappeared with the evolution of a new set of guest signals. After extraction by CDCl₃, the final product was determined to be 2-(hydroxymethyl)naphthalene-1,4-dione (**3**) by NMR and GC-MS, with an NMR yield of over 99% (Figure 1e and Figures S5–S7). A series of control experiments were carried out to confirm the indispensable role of cage **1** during this reaction. First of all, no such conversion was detected without cage **1**, under N₂, or with ligand L only (entry 2–4). With the Pd salt (TMEDA)Pd(NO₃)₂ as catalyst, product **3** could only be obtained in a 39% yield (entry 5). Considering previous reported work [39,45–50], we propose that redox-active nature of cage **1** plays a key role in this aerobic Wacker oxidation process.

To further confirm that efficient hydrophobic encapsulation is crucial for this conversion, a tetraphenylboron anion (Ph_4B^- , sodium salt) was chosen as a competition inhibitor which is known to strongly bind to cage **1** [40]. Although partial guest **2** can also enter the cavity of cage **1** in the presence of an inhibitor (Figure S8), a lower yield of 36% was observed under the same conditions (entry 6, Figure S9). More importantly, when excess amount of guest **2** (100 equiv.) was added to the solution of cage **1** as a suspension, product **3** was formed in 95% yield after heating for 4 h, leading to a TON of 95 (entry 7).



10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm

Figure 1. ¹H NMR (400 MHz, 298 K) spectra of (a) **2** in CDCl₃; (b) cage **1** in D₂O; (c) host-guest complex of $(2)_4 \subset 1$ in D₂O and $(d) (2)_4 \subset 1$ in D₂O after heating at 50 °C for 2 h; (e) extracted **3** in CDCl₃; (f) $(2)_4 \subset 1$ in D₂O after blue LEDs irradiation under N₂ atmosphere at r.t. for 8 h; (g) extracted **4** in CDCl₃; (**v**: **2**, **a**:**3**, •: cage **1**, **v**: **4**).



Figure 2. (a) Optimized structure of $(2)_4 \subset 1$ based on molecular mechanical simulation; (b) X-ray structure of $3 \subset 1$ host-guest complex. (cage 1 and guests 2 or 3 are displayed with stick and sphere models, respectively. C: wathet blue, N: blue, O: red, Pd: brown. Counterions are omitted for clarity).

DFT calculation indicated that the C2-O2 bond between the naphthalene ring and the epoxy group was longer than the O2-C5 bond, suggesting that the epoxy group tended to undergo ring-opening reaction (Figure 3a). In fact, a previous report [51] revealed that substrate **2** can undergo a photo-induced ring-opening rearrangement to form 1-hydroxy-2-naphthaldehyde **4** by purple LEDs irradiation. UV-vis spectra (Figure 3b) measurements suggest that a new shoulder peak tailing up to visible region appeared for the $(2)_4 \subset 1$ host-guest complex, assignable to host-guest charge transform (CT) absorption. Indeed, under blue LEDs irradiation, cage **1** promoted isomerization reaction of **2** to **4** has been observed in 90% yield after 8 h, which is a significant improvement comparing to that in the absence of cage **1** under the same conditions (Table 1, entry 8 and 9). Considering that conversion from **2** to **3** is a competition pathway under air in the presence of cage **1**, this photo-induced isomerization has to be carried out under N₂ atmosphere. In this case, cage **1** not only plays as a phase transfer catalyst but also facilitates the visible light absorption by the formation of host-guest CT complex.



Figure 3. (a) DFT calculated structure of **2** with selected bond lengths; (b) UV-vis absorption spectra for cage **1**, guest **2** and the (**2**)₄ \subset **1** host-guest complex (1 × 10⁻⁵ M), with their pictures shown.

Table 1. Cage 1 promoted reaction of guest 2 under different conditions *.



Entry	Catalyst	C 1111		LED.	Time	Colmant	Yield ^{<i>a</i>}	
		Conc	litions	LEDS	(h)	Solvent -	3	4
1	1	Air	50 °C	-	2 h	D_2O	>99%	-
2	-	Air	50 °C	-	2 h	H_2O	-	-
3	1	N_2	50 °C	-	2 h	D_2O	-	-
4 ^b	L	Air	50 °C	-	2 h	H_2O	-	-
5 ^c	Pd	Air	50 °C	-	2 h	H_2O	39%	-
6	$Ph_4B \subset 1$	Air	50 °C	-	2 h	D_2O	36%	-
7 ^d	1	Air	50 °C	-	4 h	D_2O	95%	-
8	1	N_2	r.t.	blue	8 h	D_2O	-	90%
9	-	Air	r.t.	blue	8 h	H_2O	-	32%

* Unless otherwise stated, all experiments were carried out with 0.01 mmol of **2** and 25% mol of cage **1** in water. The power of LEDs is ca. 6 W.^{*a*}: Yields were determined from ¹H NMR spectra using 1,3,5-trimethoxybenzene as the inner standard. ^{*b*}: 10% mol of ligand was used as catalyst. ^{*c*}: 10% mol of Pd salt [(TMEDA)Pd(NO₃)₂] was used as catalyst. ^{*d*}: 1% mol of cage **1** was used and reaction was carried under suspension condition.

To our delight, dark red crystals were obtained by slow evaporation of the final reaction solution at room temperature over one week. The crystals were of sufficient quality and X-ray crystallography finally established the structure of the new host–guest complex, which contained product **3** and cage **1** (Appendix A). X-ray structure revealed that there was only one molecule of **3** sitting inside in the inner cavity of the cage, along with two molecules of **3** binding to the external panels of the cage (Figure 2b). The external binding of the products explains product replacement of start material observed during the above catalysis.

3. Conclusions

To conclude, we have revealed a condition-controlled supramolecular cage catalyzed reaction for a spiroepoxy-naphthalenone guest molecule, where both quinone product **3** and aldehyde product **4** can be obtained selectively in good yields. Such coordination-cage-promoted selective transformations from one starting material toward different products is still rare in supramolecular catalysis. This approach promised a potential application for cage catalyzed oxidation and photo-isomerization reactions. Further development of catalytic reactions by using cage **1** as an artificial enzyme-mimic is still underway.

4. Materials and Methods

4.1. General

Unless otherwise stated, all chemicals and solvents were purchased from commercial companies (AdamasReagent Ltd., Shanghai, China; J&K Scientific Ltd., Beijing, China, and Sigma-Aldrich LLC., Darmstadt, Germany. etc) and used without further purification. 1D and 2D-NMR were measured on a Bruker Biospin Avance III (400 MHz) spectrometer or JEOL JNM-ECZ600R/S1 (600 MHz) spectrometer. ¹H-NMR chemical shifts were determined with tetramethylsilane (TMS) or respect to residual signals of the deuterated solvents used ($\delta = 4.79$ for D₂O in ¹H NMR). The photoreactors used in this research were bought from Wuhan Geao Instruments Science and Technology Co., Ltd. (Wuhan, China) (Purple LEDs, light intensity = 37.4 mw/cm², λ_{max} = 390 nm; Blue LEDs, λ_{max} = 450 nm; 1 W for every light bulb; every Schlenk tube was irradiated by 6 light bulbs from the side). Gas chromatography mass spectrometry (GC-MS) analyses were performed on a Shimadzu GCMS-QP2010SE instrument. ESI-TOF-MS were recorded on Impact II UHR-TOF from Bruker. Data analysis was conducted with the Bruker Data Analysis software (Version 4.3, Bruker Daltonik GmbH, Bremen, Germany) and simulations were performed with the Bruker Isotope Pattern software. UV-vis adsorption spectra were recorded on UV-2700 UV-visible spectrophotometer from SHIMADZU Corporation.

4.2. Preparation and Catalysis Procedure

The general catalysis procedure and all the characterization data of the products as well as the procedures to prepare are listed in the Supplementary Materials online. The known compounds were recorded in the previous report.

4.3. Computational Methods

Molecular modeling of host-guest complex $(2)_4 \subset 1$ was optimized by force-field calculation carried on Material Studio software by Quasi-Newton Methods which was based on a previously reported cage 1 X-ray structure [39]. Structure optimization of guest 2 which was carried at B3LYP/6-31G level by gaussian software [52].

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/catal11040484/s1. Figures S1–S21: synthesis procedure, catalysis procedure, NMR spectra, ESI-TOF-MS, GC-MS and Single-Crystal information.

Author Contributions: Conceptualization, Q.S. and P.C.; writing—original draft preparation, P.C.; writing—review and editing, Q.S.; P.C. performed most of the experiments and analyzed the data, L.C., D.Y., L.Z. helped with synthesis/characterization and joined the discussion. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All data generated or analyzed during this study are included in this article.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Crystallographic data for the structures of host-guest complex of product **3** and cage **1** have been deposited to the Cambridge Crystallographic Data Centre as supplementary No.: CCDC-2065411.

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