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Periodic Functionalization of Surface-Confined Pores in a Two-Dimensional Porous Network Using a Tailored Molecular Building Block

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ABSTRACT. We present here the periodic functionalization of a two-dimensional (2D) porous molecular network using a tailored molecular building block. For this purpose, a dehydrobenzo[12]annulene (DBA) derivative, **1-isoDBA**, having an isophthalic acid unit connected by an azobenzene linker to a C₁₂ alkyl chain and five C₁₄ chains was designed and synthesized. After the optimization of monolayer preparation conditions at the 1,2,4-trichlorobenzene (TCB)/graphite interface, scanning tunneling microscopy (STM) observation of the self-assembled monolayer of **1-isoDBA** revealed the formation of extended domains of a porous honeycomb type molecular network, which consists of periodically located nanowells each functionalized by a cyclic hexamer of hydrogen-bonded isophthalic acid units and those without functional groups. This result demonstrates that the present strategy based on precise molecular design is a viable route to site-specific functionalization of surface-confined nanowells. The nanowells of different size can be used for guest coadsorption of different guests, coronene **COR** and hexakis[4-(phenylethynyl)phenylethynyl]benzene **HPEPEB** whose size and shape match the respective nanowells. STM observation of a ternary mixture (**1-isoDBA/COR/HPEPEB**) at the TCB/graphite interface revealed the site-selective immobilization of the two different guest molecules at the respective nanowells, producing a highly ordered three-component 2D structure.

INTRODUCTION

Two-dimensional (2D) molecular networks formed by self-assembly of organic molecules on solid surfaces are a subject of keen interest because of the perspectives in the field of nanoscience and nanotechnology.^{1–4} In particular, 2D porous molecular networks have attracted a great deal of attention due to the ability to form multi-component 2D nanostructures by the accommodation of guest molecule(s) in surface-confined pores (also called nanowells) of these networks.^{5–14} Main driving forces for these phenomena are vertical van der Waals interactions between a guest and the solid substrate surface and lateral van der Waals interactions between a guest and the surrounding host matrix of the molecular network. Consequently, for the lateral interactions, shape and size complementarity between the guest and the nanowell play an important role. According to these criteria, various types of guest molecules having different shape and size were immobilized in nanowells.^{15–17} Moreover, in the recent past, the modification of the chemical environment in the interior space of the nanowells has been reported, in which the functionalized nanowells showed characteristic binding abilities to specific guest molecules.^{11,18–22} One of the remaining challenges in this field is periodic functionalization of the 2D porous molecular network. Such periodically functionalized porous networks offer the potential to produce controlled multi-component 2D architectures of higher complexity by selective coadsorption of different kinds of guest molecules at differently sized or shaped pores. Scanning tunneling microscopy (STM) is a powerful tool to characterize such 2D structures in molecular scale precision under ultrahigh vacuum (UHV) conditions or at a liquid/solid interface, when such molecular systems are adsorbed on atomically flat and conductive substrates.

Over the past decade, we studied the self-assembly of alkoxy-substituted dehydrobenzo[12]annulene (DBA) derivatives **DBA-OCns** ($n = 4–20$) at the liquid/solid interface

(Figure 1). For example, **DBA-OCns** form honeycomb type porous structures at the 1,2,4-trichlorobenzene (TCB)/graphite interface.^{23,24} The main driving force for the formation of the surface-confined honeycomb patterns, i.e. a regular array of hexagonal nanowells, is van der Waals interactions between the interdigitated alkyl chains of the DBA derivatives (Figure 1). A variety of guest molecules was immobilized in the nanowells in the DBA networks to form multi-component 2D structures.^{25–27} Moreover, the environment of the nanowell can be modified through the introduction of functional groups at the end of three of the six alkoxy chains of a DBA molecule in an alternating fashion. For instance, DBA derivative **3-isoDBA** having isophthalic acid units connected to the end of three alkoxy chains through *trans*-azobenzene linkers forms a honeycomb structure in which each nanowell contains a cyclic hexamer of the isophthalic acid units (Figure 1). The size of this nanowell was altered reversibly by irradiation with light of different wavelengths as revealed by the change of the number of coadsorbed guest molecules.²¹ Moreover, we recently reported the construction of a fluorinated nanowell having perfluoroalkane groups around the perimeter.²² A fluorinated guest molecule was preferentially accommodated at the fluorinated nanowell by fluorophilicity.

Figure 1. Chemical structures of **DBA-OCn**, **3-isoDBA**, **1-isoDBA**, coronene (**COR**), and hexakis[(phenylethynyl)phenylethynyl]benzene (**HPEPEB**).

In this context, we herein delineate the construction of a 2D porous molecular network where functionalized nanowells are periodically located over a whole porous network using a tailored molecular building block. Our strategy is based on the use of a DBA derivative having one functionalized alkoxy chain and five simple alkoxy chains as a molecular building block. We envisioned that two possible patterns, A and B, would be formed. In pattern A, the functional groups are randomly placed in the nanowells (Figure 2). In contrast, if thanks to non-covalent

interactions the functional groups are directed to cluster together in the same nanowell, the functional groups would be periodically distributed in the network forming the pattern B. As a result, the functionalized nanowells would be located periodically in the honeycomb network in such a manner as they are surrounded by six unfunctionalized nanowells.

On the basis of this hypothesis, we designed DBA derivative **1-isoDBA** having an isophthalic acid unit at the end of the one alkoxy chain connected with an azobenzene linker (Figure 1). Taking into account the self-assembling behavior of **3-isoDBA** mentioned above,²¹ six isophthalic acid units of **1-isoDBA** molecules may assemble in a nanowell to form a hydrogen bonded cyclic hexamer, if its formation is thermodynamically favorable and in absence of kinetic constraints. As a result, nanowells of different size would be periodically arranged wherein different guest molecules may be coadsorbed to form a periodically ordered multi-component pattern.⁵⁻¹⁷

To this end, we synthesized **1-isoDBA** by the alkyne metathesis reaction of an unsymmetrical precursor catalyzed by a Mo nitride complex. STM observations of monolayers formed by **1-isoDBA** at the TCB/graphite interface revealed the formation of a honeycomb structure in which the functionalized and unfunctionalized hexagonal nanowells are arranged periodically. Moreover, to explore the guest co-adsorption in the periodically functionalized porous network, coronene **COR** and hexakis[4-(phenylethynyl)phenylethynyl]benzene **HPEPEB** were chosen as guest molecules because these molecules match in terms of both shape and size with the functionalized and unfunctionalized hexagonal nanowells, respectively (Figure 1). STM observations of self-assembly prepared from the ternary mixture showed that these guest molecules were immobilized at the respective nanowells to form a highly ordered three-component structure.

Figure 2. Schematic drawings representing the formation of a porous molecular network of **1-isoDBA** (patterns A and B) and the coadsorption of guest molecules at the respective nanowells.

RESULTS AND DISCUSSION

For the synthesis of an unsymmetrical **1-isoDBA**, we prepared compound **1** by the stepwise connection of unsymmetrical ethynylbenzene units by the Sonogashira coupling reactions (See Supporting Information). Dehydrobenzoannulene **2** was obtained by the alkyne metathesis reaction of **1** catalyzed by a Mo nitride complex (Scheme 1).^{28–30} Removal of the (methoxy)methyl (MOM) group of **2**, followed by attachment of the last alkyl group having an azobenzene diacid diethyl ester unit and hydrolysis afforded **1-isoDBA**.

Scheme 1. Synthesis of 1-isoDBA.

Self-assembled monolayers were prepared by dropping a solution of (a) compound(s) in TCB onto a graphite surface. All STM observations of the monolayers were performed at the interface between TCB and graphite at room temperature. The low vapor pressure of TCB leads to negligible evaporation during the course of the experiment. The solute concentration of the DBA was set to less than 2.1×10^{-6} M to ensure the formation of the porous honeycomb structures.³¹ Mixtures of DBA and appropriate guest molecule(s) in TCB were used to study guest coadsorption at the nanowells. Concentrations of each component are described in the Figure captions. When annealing treatment was performed, ca. 100 μ L of a sample solution was placed into a liquid cell attached to the graphite substrate, and these setups were annealed in an oven before carrying out the STM imaging. During the annealing treatment, the liquid cell was wrapped in an aluminum foil to minimize concentration change by solvent evaporation. STM images were recorded in the constant current mode. This means that while scanning the sample, the vertical position of the STM tip is continuously adjusted to maintain a constant tunneling current. This gives rise to a so-

called topography image where the contrast reflects changes in the vertical position of the STM tip.

First self-assembly of **1-isoDBA** was investigated at room temperature. Whereas **1-isoDBA** formed small domains of a honeycomb structure (Figures 3a,b), any cyclic hexamer of the isophthalic acid units was not observed. We considered that the system did not reach a thermodynamic equilibrium state. To promote the monolayer formation, annealing treatment was performed under conditions of various annealing temperature and time.^{32,33} After annealing at 100 °C for 11 h, the domain size of the honeycomb structure increased (Figures 3c,d). We found that, by annealing treatment at 100 °C for 11 h, very large domains of the monolayer were formed at the TCB/graphite interface (Figure 3e). There are no domain boundaries in 9 large area images (120 nm × 120 nm). Figure 4a displays enlarged STM image of the 2D molecular network consisting of **1-isoDBA** obtained after annealing.³⁴ In the image, the triangular bright features correspond to the π -conjugated cores of the DBA derivative while the darker parts are composed of four interdigitated alkyl chains,³⁵ showing the formation of a honeycomb structure. The orientations of the four interdigitated alkyl chains are parallel to the main symmetry axes of the underlying graphite surface. Six dim spokes in certain nanowells correspond to the azobenzene units, indicating the formation of hydrogen bonded cyclic hexamers of the isophthalic acid units. Notably, the locations of such functionalized nanowells are periodically arranged within the honeycomb lattice. Namely, the functionalized nanowells with small pore space were surrounded by large unfunctionalized nanowells exhibiting a long range periodicity. The unit cell contains six **1-isoDBA** molecules and its parameters are $a = b = 8.6 \pm 0.1$ nm and $\gamma = 60 \pm 1^\circ$. This unit cell is significantly larger than that of parent **DBA-OC14** ($a = b = 5.0$ nm, $\gamma = 60^\circ$ and two molecules per the unit cell). A network model of the periodically functionalized porous network is shown in

Figure 4b. Dim fuzzy features in the functionalized small hexagonal nanowells (white arrows in Figure 4a) are attributed to coadsorbed TCB molecules. The fuzzy appearance is due to its lateral or rotational dynamics in the nanowell.³⁶ In addition, we noticed that bright fuzzy features occasionally occupied the unfunctionalized nanowells (blue arrows in Figure 4a). We consider that these fuzzy features are most probably because of coadsorbed **1-isoDBA** or TCB molecules which are also mobile. Our working hypothesis for construction of a periodic functionalization of the porous molecular network was thus experimentally verified.

Figure 3. STM images of monolayers consisting of **1-isoDBA** at the interface between 1,2,4-trichlorobenzene (TCB) and graphite (a, b) at room temperature (concentration; 2.0×10^{-6} M, tunneling parameters; $I_{\text{set}} = 0.05$ nA, $V_{\text{set}} = -0.99$ V), (c, d) after annealing treatment at 100 °C for

1 h (concentration; 1.7×10^{-6} M, tunneling parameters; $I_{\text{set}} = 0.05$ nA, $V_{\text{set}} = -0.65$ V), and (e) after annealing treatment at 100 °C for 1 h (concentration; 1.6×10^{-6} M, tunneling parameters; $I_{\text{set}} = 0.05$ nA, $V_{\text{bias}} = -0.99$ V). White lines and letters “h” in images (b, d) indicate isolated hexagonal structures or small domains of the honeycomb structure. While the domain size of the honeycomb structure becomes larger after the annealing treatment (c, d), there remain defects and domain boundaries as seen in large area image. In the image (e), no domain boundary was observed.

Figure 4. STM image (a) and molecular models (b) of a monolayer consisting of **1-isoDBA** at the 1,2,4-trichlorobenzene (TCB)/graphite interface after annealing treatment at 100 °C for 11 h (concentration; 2.1×10^{-6} M, tunneling parameters; $I_{\text{set}} = 0.05$ nA, $V_{\text{set}} = -0.71$ V). Functionalized nanowells were arranged periodically in the honeycomb structure of **1-isoDBA**. Unit cell parameters are $a = b = 8.6 \pm 0.2$ nm, and $\gamma = 60 \pm 1^\circ$. White and blue arrows indicate fuzzy features at the small and large hexagonal nanowells, respectively.

Next, we investigated guest coadsorption in the porous network of **1-isoDBA**. Because the size and shape of **COR** molecule fit the nanowell formed by the isophthalic acid cyclic hexamer,^{12,13,26} we expected that one **COR** molecule will be immobilized in the small hexagonal nanowell. Indeed, the investigation of self-assembly of a mixture of **1-isoDBA** and **COR** at the TCB/graphite interface revealed that **COR** molecule was immobilized selectively in the small hexagonal nanowell (See Supporting Information, Figures S1 and S2).²⁵ On the other hand, as a guest molecule for the large hexagonal nanowell, we designed and synthesized **HPEPEB**. STM observation using a mixture of **1-isoDBA** and **HPEPEB** showed that **HPEPEB** molecule was accommodated only at the large hexagonal nanowell as well (See Supporting Information, Figures S3–S7).

With the above results on the selective coadsorption of the individual guest in hand, we investigated coadsorption of two guest molecules, **COR** and **HPEPEB**, in the porous network of **1-isoDBA**. The solute concentrations of each component were set to 1.7×10^{-6} M for **1-isoDBA**, 7.7×10^{-6} M for **HPEPEB**, and 7.7×10^{-6} M for **COR**, respectively, based on the results of the bicomponent mixtures. Figures 5a and S8 show STM images of the monolayers prepared from the mixture at the TCB/graphite interface after annealing treatment at 100 °C for 11 h. In the large area images (Figure S8), there are large domains of a honeycomb structure. In the enlarged image (Figure 5a), bright disks were imaged at the center of the bright spoke containing pores and asterisks consisting of dim dots were clearly visible at the large hexagonal nanowells. Obviously, small functionalized nanowells each containing a **COR** molecule are surrounded by large unfunctionalized nanowells each accommodating a **HPEPEB** molecule. Close inspections of the large nanowells revealed coadsorption of a TCB molecule at each space between the “spokes” of radial **HPEPEB** molecule (Figure 5a inset), though it was not discernible in two-component

system of **1-isoDBA** and **HPEPEB** (Figure S4) due to low resolution. The coadsorption of TCB molecules contributes significantly to stabilization of the network structure as described later. These observations reveal the formation of a highly ordered three-component network by selective coadsorption of two different guest molecules at the respective nanowells in the periodically functionalized porous network (Figure 5b).

Figure 5. STM image (a) and molecular models (b) of a monolayer consisting of **1-isoDBA**, **COR**, and **HPEPEB** at the TCB/graphite interface after annealing treatment at 100 °C for 11 h

(concentration; 1.7×10^{-6} M for **1-isoDBA**, 7.7×10^{-5} M for **COR**, and 7.5×10^{-6} M for **HPEPEB**, tunneling parameters; $I_{\text{set}} = 0.15$ nA, $V_{\text{set}} = -0.31$ V). Inset in (a) is a digital zoom of the large pore. Unit cell parameters are $a = b = 8.6 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. In the model, **COR** and **HPEPEB** are colored in orange and yellow, respectively.

To support the experimental observation of site-selective coadsorption, the strength of noncovalent intermolecular interactions was evaluated by molecular mechanics (MM) simulations using the COMPASS force field for models of the network structures placed on a graphene bilayer which represents graphite. Since the unit cell parameters of the periodically functionalized porous network of **1-isoDBA** are large, the unit cell parameters of parent honeycomb structure of **DBA-OC14** are used as periodic boundary conditions ($a = b = 5.02$ nm and $\gamma = 60^\circ$) for all systems in order to reduce computational costs.³¹ Models of a small nanowell, formed by **3-isoDBA** with three azobenzenedicarboxylic acid units, with a TCB or **COR** molecule and a large nanowell, formed by **DBA-OC14**, containing a cluster of seven **COR** molecules, single **HPEPEB**, or **HPEPEB** plus six TCB molecules were optimized. The optimized geometries are displayed in Figure 6 and the calculated intermolecular interactions and internal energies are summarized in Table 1. In Table 1, E_{total} stands for the interaction energy of the entire system consisting of the molecular network of the model DBAs, guest molecules, and the graphite sheet including all intramolecular, intermolecular, and molecule-substrate interactions. E_{host} consists of two kinds of interaction energies of the molecular network of the DBAs on the graphite sheet, one is for non-bonding interaction energies of the host network (without substrate) including both intra- and intermolecular interactions and the other for host-substrate interactions. E_{guest} is the sum of two kinds of interaction energies, intramolecular non-bonding interactions of the guest molecule in itself without substrate and the interactions between the guest and substrate. From these values,

the interaction energies between the host network and guest molecule, $E_{\text{host-guest}} = -(E_{\text{total}} - E_{\text{host}} - E_{\text{guest}})$, were calculated, which are included in Table 1. For the small nanowells, both E_{guest} and $E_{\text{host-guest}}$ of **COR** are larger than those of TCB, being consistent with the experimental observation of a **COR** occupation in the small nanowell. On the other hand, the large nanowell can be filled with seven molecules of **COR** as we proposed previously.²⁵ The MM simulations predict the interaction energy ($E_{\text{host-guest}}$) of 25.2 kcal/mol for this cluster. Though the estimated intermolecular host-guest interaction energy is much larger than that for single **HPEPEB** molecule (11.7 kcal/mol), confinement of seven **COR** molecules in 2D space from solution should pay a significant toll to entropy. Moreover, the vacant space between the “spokes” of **HPEPEB** is filled by six molecules of TCB, as experimentally observed in the three component system (inset in Figure 5a). This significantly increases the interaction energy to 29.4 kcal/mol, thereby favoring selective coadsorption of **HPEPEB**. Note that the entropy penalty for solvent TCB molecules may not be significant as we reported previously.³³

Figure 6. Optimized models of (a) a small nanowell/TCB system, (b) a small nanowell/**COR** system, (c) a large nanowell/**HPEPEB** system, (d) a large nanowell/seven **CORs** system, and (e) a large nanowell/**HPEPEB**/TCB system on a bilayered graphene sheet by molecular mechanics simulations (COMPASS force field) using the experimental unit cell parameters of a **DBA-OC14** network as periodic boundary condition ($a = b = 5.02$ nm and $\gamma = 60^\circ$).

Table 1. Intermolecular Energies for Host-Guest Systems on Bilayered Graphene Sheet Calculated by MM Simulations Using COMPASS Force Field.

nano-well	guest	intermolecular energy (kcal/mol) ^a			interaction energies between the host and guest molecule ($E_{\text{host-guest}}$) ^d
		whole system (E_{total}) ^a	host network (E_{host}) ^b	guest molecule (E_{guest}) ^c	
small nano-well	TCB	−840.1	−820.3	−16.6	5.2
	COR	−851.2	−820.2	−19.3	11.8
large nano-well	7 COR	−583.2	−413.1	−144.9	25.2
	HPEPEB	−520.8	−414.1	−95.0	11.7
	HPEPEB + 6 TCB	−659.9	−414.8	−215.7	29.4

^a Sum of the intermolecular and molecule-substrate interaction energy. ^b E_{host} s were obtained by single point energy calculations for the host-guest systems in their optimized geometries which do not contain the guest molecules. ^c E_{guest} s consist of the non-bonding interactions without substrate and the host-substrate interactions. ^d E_{guest} s were obtained by single point energy calculations for the host-guest systems in their optimized geometries which do not contain the host networks. E_{guest} s consist of the non-bonding interactions without substrate and the host-substrate interactions. ^d Calculated by the following equation, $E_{\text{host-guest}} = -(E_{\text{total}} - E_{\text{host}} - E_{\text{guest}})$.

The formation of porous networks with periodic spacing of two types of nanowells (e.g. Kagomé lattices) and selective co-adsorption of different guest molecules at respective nanowells producing multi-component networks reported in this paper are not unique.^{12,16,37} However, it should be noted that present work is the first ever report on the periodic formation of functionalized and non-

functionalized nanowells. It was achieved by the unprecedented molecular design of building block **1-isoDBA** for site-specific modification of the nanowell size through recognition between the hydrogen bonding sites singly attached in a molecule. The entropic loss due to the formation of a nanowell containing six azobenzene diacid units is roughly estimated to be 3.3 kcal/mol at 300 K on the basis of the number of cases (3^5) for random orientation of the functional group for six molecules of **1-isoDBA** (Pattern A, Figure 2). This is overcome by the enthalpy of the formation of six hydrogen bonds between six isophthalic acid units, which is estimated to be ca. 48 kcal/mol on the basis of the reported enthalpy of 8 kcal/mol for a hydrogen bonded dimer of benzoic acid in benzene.³⁸ Moreover, site-selective guest coadsorption in the functionalized and non-functionalized nanowells demonstrates the effect of the periodic functionalization.

CONCLUSION

In summary, we have designed **1-isoDBA** for the periodic functionalization of the porous molecular network and investigated its 2D self-assembly at the TCB/graphite interface by means of STM. As a result, after optimization of preparation conditions, we observed the formation of large domains of a honeycomb structure in which small functionalized hexagonal nanowells based on the hydrogen-bonded cyclic hexamer of isophthalic acid units appeared in a periodic fashion. To the best of our knowledge, this is the first example of the periodic functionalization of a porous molecular network. Moreover, two different guest molecules, **COR** and **HPEPEB** were successfully immobilized at the functionalized and unfunctionalized hexagonal nanowells, respectively, in the porous network of **1-isoDBA**, producing a highly ordered three-component molecular network. This study provides insight in the construction of complex, hierarchical 2D patterns consisting of multiple components, which is useful in the field of 2D crystal engineering.

METHODS

STM Observations. All experiments were performed at 20–26 °C using a Nanoscope IIIa or IIID (Bruker AXS) with an external pulse/function generator (Agilent 33220A) with negative sample bias. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.25 mm).

Prior to imaging, a compound under investigation was dissolved in commercially available anhydrous 1,2,4-trichlorobenzene (TCB, Aldrich). When more than two components were used, all components were mixed before STM investigations. Concentrations of each component are described in the Figure captions. A drop of this solution (2–5 μL) was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH). When the sample was annealed at high temperature, a homemade liquid cell was employed to minimize effect of solvent evaporation by using a large amount of the sample solution (ca. 100 μL). Moreover, this liquid cell was wrapped in an aluminum foil during annealing in an oven. The proportion of the solvent loss was estimated by weighing the liquid cell system to range from 20% to 30% after annealing at 110 °C for 11 h. Then, all STM observations were performed at the TCB/graphite interface at room temperature. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIPTM software (Scanning Probe Image Processor, SPIPTM, version 5.0.7, December 2009, ImageMetrogyA/S, Hørsholm, Denmark). The white colored axes shown in Figures indicate the direction of main symmetry axes of graphite underneath the molecular layers. The unit cell parameters are determined from more than 30 experimental values of at least two calibrated STM images.

Molecular Mechanics Simulation. Molecular mechanics (MM) simulations were performed with the Materials Studio 5.5 using the Forcite module with COMPASS force field.

Each starting structure of **1-isoDBA**, **COR**, **TCB**, and **HPEPEB** was built from the respective molecular model whose structure was optimized by the semi-empirical PM3 method. Then, the orientation of the alkyl chains of **1-isoDBA** relative to the π -system was adjusted based on that observed in the STM images.

The molecules were placed 0.35 nm above the first layer of a periodic two-layer sheet of graphite (interlayer distance of graphite is also 0.35 nm) and the alkyl chains were adjusted to align parallel to the directions of the graphite symmetry axes. The graphite structure was frozen during the simulations, and a cutoff of 2.0 nm was applied for the van der Waals interactions. All simulations were performed under periodic boundary conditions ($a = b = 5.02$ nm and $\gamma = 60^\circ$)

SUPPORTING INFORMATION

Additional STM images, details of the synthesis of **1-isoDBA** and **HPEPEB**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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