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Investigation on Critical Aggregation Concentration of Carbosiloxane Dendrimer in Dilute Solution Probed by Rhodamine B

Mei-Ling Zheng,[†,‡] Wei-Qiang Chen,*[,†,§] and Xuan-Ming Duan*[,†,§]

Laboratory of Organic NanoPhotonics and, Laboratory of Optoelectronic Functional Materials and Molecular Engineering, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, and Graduate School of Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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We propose a novel method for probing aggregation of dendrimers by investigating the isomerization equilibrium between pink zwitterionic form (Z-form) and colorless lactonic form (L-form) of rhodamine B (RhB) molecules in dilute solution. Investigation using carbosiloxane dendrimers (CSiO-D) with different generations as the model dendrimer molecules showed that the equilibrium constant of isomerization of RhB increased dramatically at the critical aggregation concentration (CAC) of dendrimers. The redox potential differences between isomers of RhB indicated that aggregation of CSiO-D accelerated the isomerization of RhB and stabilized the L-form of RhB. The data on Gibbs energy and electrolytic conductivity provided further evidence for confirming the CAC of dendrimers in dilute solution and showed good agreement with our other experimental results. The proposed method is effective in estimating the CAC of dendrimers in dilute solution.

Introduction

Dendrimers are considered as a new category of hyperstructured macromolecular materials with well-defined structure, a treelike configuration, and a high degree order.[1–3] It has been proven that dendrimers are useful in diagnostics as a component of thin layers and in catalysis as well as in nanosciences.[4–7] Dendrimers are being applied in the optical and electrooptic fields as host materials because they can change the microenvironment around the guest molecules.[8–10] This is the result of the site-isolation effect due to their particular branching architecture and specific inner space. The morphology of dendrimers in dilute solution has been intensively investigated both experimentally and theoretically using polyamine (PAM) as a model molecule.[11,12] The aggregates of amphiphilic polystyrene−PAM dendrimers were well-understood. The morphology of this type of dendrimer was reported as spheres and became branches and micelle structures beyond the critical micelle concentration in the biphase system.[11] Although the critical aggregation concentration (CAC) of amphiphilic polystyrene−PAM dendrimers are well-studied, studies on aggregation concentration are rarely extended to other heteroatom-containing dendrimers, such as silicon-based dendrimers. The CAC of dendrimers could give information on their further applications.

Silicon-based dendrimers, which have organic and inorganic structures, are attractive materials for many chemical applications due to their unique flexible configuration and good biocompatibility.[13–17] In our previous study on the optical gain enhancement of carbosiloxane dendrimer (CSiO-D) in dilute rhodamine B (RhB) methanol solution, emission quenching was observed when the concentration of CSiO-D reached a certain level, which resulted from the change of microenvironment around RhB molecules. [18] The conversion of RhB's isomers—cation (C-form), zwitterion (Z-form), and lactone (L-form)—is known to be sensitive to the chemical microenvironment, such as the solution pH, the solvent polarity, the temperature, and the concentration.[19–26] Usually, RhB exists as conformations of both pink Z-form and colorless L-form in aprotic solvent.[21,27,28] The solvent polarity causes the solvatochromic shift in the UV−vis absorption and also intensely influences the isomerization equilibrium between the Z-form and the L-form due to the environment change around RhB. Therefore, the phenomenon of fluorescence quenching or color fading may be used as a simple probing method for confirming the aggregation or conformation change of dendrimers in dilute solution.

Since the aggregation of dendrimers becomes a spontaneous process beyond the CAC, the chemical potential of CSiO-D should change. This can contribute to the change of Gibbs energy and can provide the energy for driving the isomerization equilibrium shift of RhB in acetone. In this respect, the RhB can act as a probe for the aggregation of CSiO-D dendrimers. Here, we study the aggregation of CSiO-D dendrimers in dilute acetone solution through the color fading phenomenon of RhB. We measure redox potentials and electrolytic conductivities of the RhB dilute solutions with and without CSiO-D dendrimers. The results showed that the isomerization equilibrium of RhB shifted from the pink Z-form to the colorless L-form RhB while the aggregation of CSiO-D dendrimers occurred with the addition of CSiO-D dendrimers. UV−vis spectra of RhB in acetone solution clearly showed a dramatic shift in the isomerization equilibrium of RhB which occurred at a certain concentration of CSiO-D dendrimers. The sudden decline in Gibbs energy of this system confirmed the existence of a CAC of CSiO-D dendrimers. This simple method could provide a facile and useful way to estimate the aggregation of dendrimers in dilute solution.

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* To whom correspondence should be addressed. E-mail: chenwq7315@mail.ipc.ac.cn (W.-Q.C.); xmduan@mail.ipc.ac.cn (X.-M.D.).

[†] Laboratory of Organic NanoPhotonics, Chinese Academy of Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

[§] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences.

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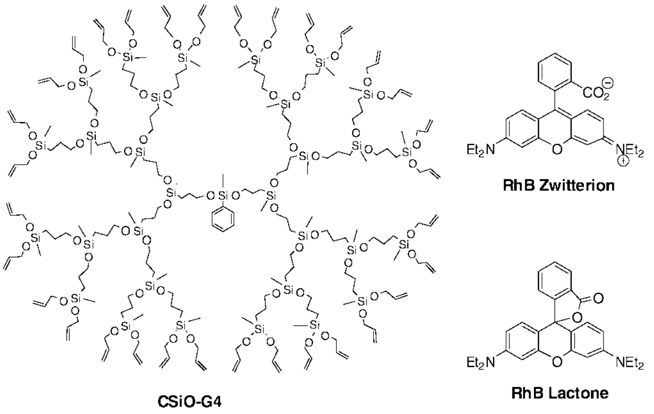
SCHEME 1: Molecular Structures of Carbosiloxane Dendrimers G4 (CSiO-G4), RhB's Zwitterion and Lactone Forms



CSiO-G4

RhB Zwitterion

RhB Lactone

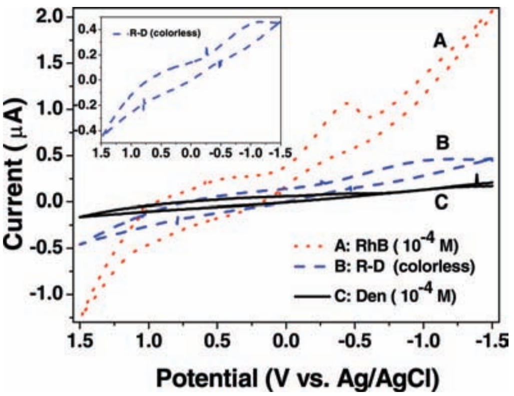


Figure 1. Cyclic voltammograms of RhB solution (A, red dotted line), colorless dendrimer/RhB solution (B, blue dashed line), and the CSiO-G4 solution (C, black line) obtained at Pt electrodes. The inset shows the amplified cyclic voltammogram curve of the colorless L-form. Scan rate: 100 mV·s^{-1}.

Experimental Section

Materials. Carbosiloxane dendrimers G0−G4 (CSiO-G0 to CSiO-G4) were synthesized according to ref 18. The chemical structures of CSiO-G4 and both isomerization forms of RhB molecule, Z-form and L-form, are shown in Scheme 1. The CSiO-D/RhB solutions for the evaluations were prepared by adding a CSiO-D acetone solution at a concentration of 1.0×10^{-4} M to a RhB solution in acetone at the concentration of 1.0×10^{-5} M. In this process, it was assumed that only the Z-form existed in the acetone solution of RhB.

Measurements. Cyclic voltammograms were recorded on a potentiostat/galvanostat (Princeton 263A) with Pt electrode as working electrode, Pt electrode as counter electrode, and standard Ag/AgCl/KCl (3 M) as reference electrode. The scan speed is 100 mV·s^{-1}. RhB solution at the concentration of 1.0×10^{-4} M, the CSiO-G4 solution at the concentration of 1.0×10^{-4} M, and the colorless CSiO-G4/RhB solution with RhB concentration at 6.7×10^{-5} M were used for the measurement. All solutions were purged with nitrogen for 10 min before the measurement. All UV−vis spectra of CSiO-D/RhB solutions studied in this paper were recorded on a Shimadzu UV-2500 spectrophotometer. The electrolytic conductivities of CSiO-G4/RhB solutions were measured on an electrometer/high resistance meter (KEITHLEY, 6517A) with the CSiO-G4 concentrations varying from 1.0×10^{-6} to 5.6×10^{-5} M.

Results and Discussion

Cyclic Voltammograms Curve. Experimentally, the color of RhB solution in acetone at the concentration of 1.0×10^{-5} M changed rapidly from pink to colorless when CSiO-G4 was added. The redox potentials of RhB molecules in the solutions with and without CSiO-G4 were evaluated to confirm the effect of CSiO-G4 dendrimers on isomerization of RhB molecules in dilute solution. As shown in Figure 1, RhB obviously showed a redox potential of −0.45 V in pink acetone solution and the redox process was irreversible. The colorless solution of RhB, which resulted from the addition of CSiO-G4, exhibited a redox potential of approximately −1.0 V with an unrecognizable peak in the cyclic voltammetry curve. From the redox potential differences, we can estimate the Gibbs energy ($\Delta G = -n\Delta E\, F = -53.1$ kJ/mol) from the pink Z-form of RhB to the colorless L-form with CSiO-G4. The result demonstrates that the isomerization of RhB in acetone solution became a spontaneous process when CSiO-G4 was added. It also indicates that CSiO-G4 stabilized the neutral L-form of the RhB molecule.

UV−vis Spectra. The isomerization of RhB molecules between the Z-form and the L-form leads to the color fading phenomenon of RhB, which can be easily evaluated by simple measurement of UV−vis absorption spectra. Figure 2a shows that the maximum absorbance peak at 555 nm of RhB in acetone declined with increasing concentration of CSiO-G4. The absorption changed with varying concentration of the Z-form since the L-form of RhB is colorless and shows no absorption in the region of 400−600 nm. It indicates that the microenvironment around RhB changed when dendrimer CSiO-G4 was added. Figure 2b presents the dependence of absorption variation on the dendrimers concentration for different generations of CSiO-D. The CSiO-G0 showed a slight absorption change in all generations of CSiO-D studied here. The CSiO-G3 and CSiO-G4 almost exhibited the same influence on the absorption variation, which were much stronger than CSiO-G1 and CSiO-G2. When the concentration of CSiO-G3 or CSiO-G4 was increased to 4.5×10^{-5} M, the RhB solution became colorless, which indicates the almost complete conversion of the isomerization of RhB from Z-form to L-form. It is well-known that the isomerization equilibrium between Z-form and L-form of RhB changes with solvent polarity. However, the CSiO-D dendrimers contributed little change to the solvent polarity in this study, since the concentration of CSiO-D dendrimers was lower than 1.0×10^{-4} M. Therefore, the results provide clear evidence that the isomerization of RhB molecules could be influenced by the interaction between the L-form of RhB and CSiO-D dendrimers due to the change of the microenvironment around RhB in acetone solution. These experimental results also clearly show that higher generation dendrimers are more effective on the conversion of isomerization for RhB molecules than lower generation. Thus, CSiO-D dendrimers participate and play an important role in the isomerization equilibrium shift.

Isomerization Equilibrium with CSiO-D. We investigated the isomerization equilibrium of RhB molecules in dilute solution with CSiO-D dendrimers by analyzing the kinetics parameters obtained from the UV−vis absorption results. The equilibrium can be defined by

$$\mathrm{Z} + x(\mathrm{Den}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{L} \cdot x\mathrm{Den} \qquad (1)$$

The L·xDen is the formed cluster of the L-form with dendrimers in solution, x represents the aggregation number of dendrimers in the solution, and k_1 and k_{-1} denote the forward and backward rate constants. Since L·xDen does not show any

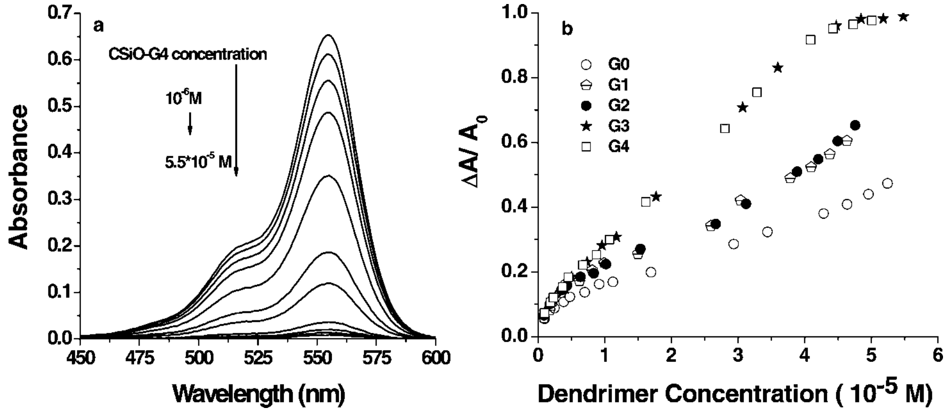


Figure 2. (a) Absorption spectra of RhB upon the concentrations of dendrimer CSiO-G4. (b) Plot of the $\Delta A/A_0$ on the concentrations of CSiO-D.

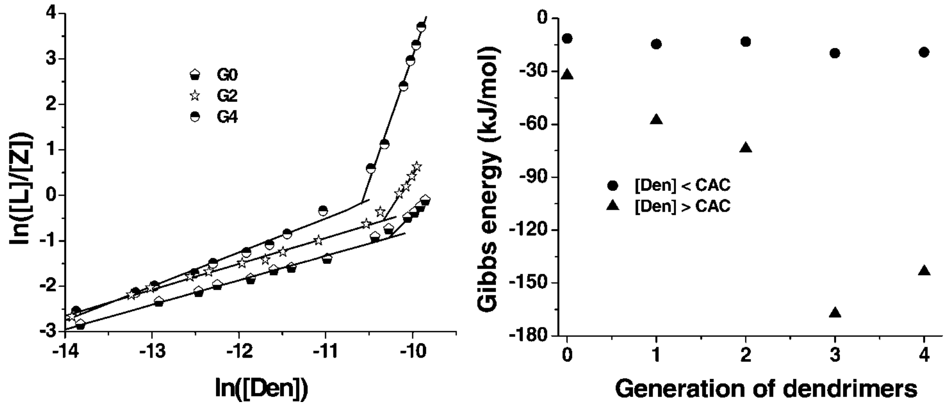


Figure 3. (a) Dependence of [L]/[Z] on the concentration of CSiO-D. (b) Variation of Gibbs energy with different generation dendrimers.

absorption in the range of 400−600 nm, the concentration of L•xDen can be assumed equal to the L-form and can be simply written as [L].

Consequently, the reaction rate r is defined as

$$r = -\frac{\mathrm{d}[Z]}{\mathrm{d}t} = k_1[Z][\mathrm{Den}]^x - k_{-1}[L] \qquad (2)$$

where [Den] is the concentration of dendrimers and, [L] and [Z] denote the concentrations of the L•xDen cluster and the Z-form of RhB, respectively. When the reaction reaches equilibrium, $r = 0$, eq 2 can be written as

$$k_1[Z][\mathrm{Den}]^x - k_{-1}[L] = 0 \qquad (3)$$

Equilibrium constant K can be expressed as

$$K = \frac{k_1}{k_{-1}} = \frac{[L]}{[Z][\mathrm{Den}]^x} \qquad (4)$$

$$\ln K = \ln\left(\frac{[L]}{[Z]}\right) - x \ln\,[\mathrm{Den}] \qquad (5)$$

$$\ln\left(\frac{[L]}{[Z]}\right) = \ln K + x \ln\,[\mathrm{Den}] \qquad (6)$$

According to eq 6, there is a linear relationship between ln([L]/[Z]) and ln [Den]. The plot of ln([L]/[Z]) versus ln [Den] exhibited two linear distinct stages (Figure 3a), which were not observed in the result of absorption variation (Figure 2b). Here, we define the corresponding concentration of dendrimers at the crossing of these two lines as the CAC of the dendrimers. After curve fitting, the parameters x and ln K were obtained for different dendrimer generations. The obtained parameters for the equilibriums are summarized in Table 1. When the concentration was lower than CAC, the influence of dendrimers on the equilibrium by their essential inner space was weak. As the concentration was increased beyond CAC, x values, the aggregation numbers of the dendrimer, in solution were found to be 1.9 for CSiO-G0, 2.9 for CSiO-G2, 6.4 for CSiO-G3, and 5.5 for CSiO-G4. The higher the generation of dendrimers, the higher the molecular density. The maximum aggregation number was obtained in the third generation. From theoretical prediction, the morphology of dendrimers in a dilute solution changes from the structure with stretching end groups to the structure with back-folding end groups.[29] Thus, the structure of CSiO-D might fluctuate with the back-folding end groups of CSiO-D when the concentration was increased beyond the CAC. The fluctuation and aggregation of dendrimers contribute to the form of strong hydrophobic inner space, which resulted in the abrupt shift of RhB equilibrium. In this equilibrium study, the CACs were characterized as 2.66×10^{-5} and 2.51×10^{-5} M for CSiO-G3 and CSiO-G4, respectively. Therefore, RhB could be used as a sensitive probe for effectively detecting the aggregation of dendrimers in the dilute solution.

TABLE 1: Parameter x, ln K, r Factor, and Gibbs Energy for Equilibrium 1

	[Den] < CAC			[Den] > CAC			
	ln K	r	ΔG (kJ/mol)	x	ln K	r	ΔG (kJ/mol)
G0	4.616	0.998	−11.44	1.87	18.33	0.995	−32.31
G1	5.913	0.993	−14.65	2.30	23.38	0.992	−57.93
G2	5.354	0.997	−13.26	2.94	29.85	0.989	−73.96
G3	7.930	0.989	−19.65	6.43	67.60	0.993	−167.48
G4	7.723	0.991	−19.13	5.49	57.98	0.995	−143.65

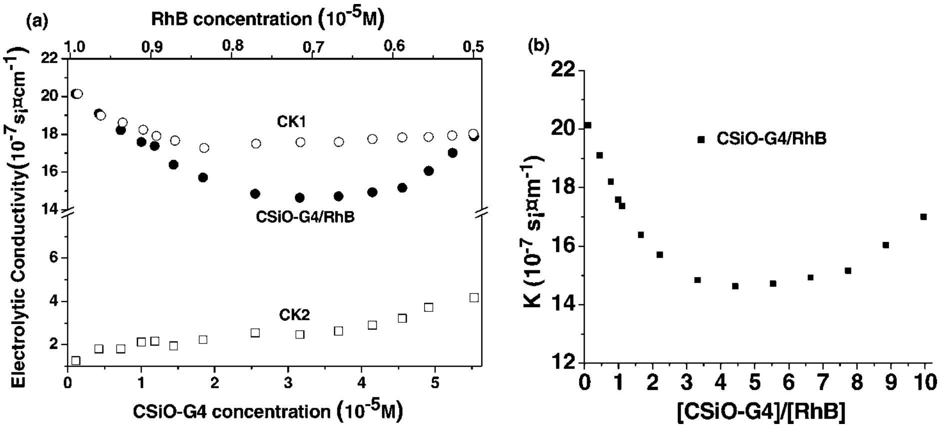


Figure 4. (a) Electrolytic conductivity of RhB solution (open circles, CK1), CSiO-G4/RhB solution (solid circles), and CSiO-G4 solution (squares, CK2). (b) Plot of conductivity of CSiO-G4/RhB in acetone solution with various ratios of [CSiO-G4]/[RhB].

Gibbs Energy. The abrupt shift of isomerization equilibrium can be quantitatively demonstrated by Gibbs energy ΔG, calculated according to

$$\Delta G = -RT \ln K \tag{7}$$

Below the CAC of dendrimer, the ΔG value is kept nearly at the same level around −11.44 to −19.65 kJ/mol, as shown in Figure 3b. All changes of Gibbs energies for the equilibrium are summarized in Table 1 with different generation dendrimers. For the CSiO-G3 contained in RhB acetone solution, ΔG decreased from −19.65 to −167.48 kJ/mol, which was much more negative than the change for solutions containing lower generations CSiO-D. The dramatic decrease in Gibbs energy indicates that dendrimers are prone to form aggregates of CSiO-D molecules at higher concentration. In this case, the whole system can be treated as an ideal dilute solution. Before the CAC of dendrimers is reached, the chemical potential and the entropy of dendrimers change during the dilution process, which result in a change in Gibbs energy according to the Gibbs−Duhem equation. Hence, only a slight difference in Gibbs energy was observed for different generation CSiO-D dendrimers in this process. Once the CAC is reached, the chemical potential and the entropy of dendrimers change not only from the dilution process, but also from the conformational change of dendrimers, which contributes to the dramatic change in Gibbs energy. Note that the average aggregation number for CSiO-G4 was obtained as 5.5, less than 6.4 for CSiO-G3; the change of Gibbs energy in the process was −143.65 kJ/mol for CSiO-G4, less negative than −167.48 kJ/mol for CSiO-G3. It is well-known that a higher generation of dendrimers possesses a very tight and rigid structure. Therefore, the bigger molecular size and the stronger molecular interaction in the aggregates of CSiO-G4 as compared to CSiO-G3 contribute to the smaller aggregation number and less negative ΔG value.[11]

Electrolytic Conductivity. Further investigation on electrolytic conductivity also provides the evidence of CSiO-G4 aggregation at critical concentration. The electrolytic conductivity of CSiO-G4 acetone solution varied with concentration, as shown in Figure 4a. The conductivity of the CSiO-G4 acetone solution increased to a planar stage when the concentration of the CSiO-G4 acetone solution was increased from 1.0×10^{-6} to 2.5×10^{-5} M; then a continuous increase was observed when the concentration of CSiO-G4 acetone solution went beyond 3.0×10^{-5} M. When the CSiO-G4 acetone solution was added into the RhB solution, the electrolytic conductivity decreased with an increase of the dendrimer when the concentration was lower than 3.0×10^{-5} M; then it gradually increased when the concentration was beyond 3.0×10^{-5} M. The electrolytic conductivity of RhB solution decreased and drew close to the minimum when we diluted the RhB solution. These results show that with the addition of CSiO-G4, the zwitterion−lactone equilibrium effectively shifted toward the L-form, a neutral molecule contributing to much lower electrolytic conductivity than the Z-form. The plot of conductivity of the RhB solution with addition of CSiO-G4 on the ratio of [CSiO-G4]/[RhB] is shown in Figure 4b; the conductivity showed an inflection at the molar ratio of around 5.5, which is in good agreement with the average aggregation number of 5.5 for CSiO-G4 obtained by dynamic analysis.

Conclusions

In conclusion, we propose and demonstrate a facile method to characterize the aggregation of carbosiloxane dendrimers in dilute acetone solution by using RhB molecules as a probe, which is based on the isomerization equilibrium between the colored Z-form and colorless L-form of RhB molecules. The dendrimers CSiO-D acted as a host and formed a hydrophobic cage in the surrounding microenvironment, which stabilized the L-form of RhB. Moreover, the aggregation of CSiO-D caused a change in the morphology of the CSiO-D, which resulted in a dramatic chemical potential change contributing to the negative Gibbs energy. Thus, the addition of dilute CSiO-D solution caused the equilibrium shift from the Z-form of RhB to its L-form due to a microenvironment change. The study on absorption spectra showed that the conversion of the Z-form to the L-form proceeded rapidly when higher concentrations of CSiO-G3 and CSiO-G4 were used, and the absorption variation was greatly influenced by dendrimer concentration. The kinetic analysis implied that there were two different equilibrium constants with different concentrations of dendrimers. Consequently, the change of the Gibbs energy in the process decreased from −19.65 to −167.48 kJ/mol when CSiO-G3 was used, which provided clear evidence for the existence of a critical aggregation concentration in dilute dendrimer solution. The slightly larger ΔG value of equilibrium using CSiO-G4 indicated a stronger interaction among dendrimer molecules than using CSiO-G3 molecules. The electrolytic conductivity measurements showed further evidence for the dendrimers aggregates formation in the dilute solution. The method proposed here is more effective in estimating the aggregation of dendrimers in dilute solution as compared to other methods which are focused on high-concentration solution.

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