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7, 11- diphenyl-8*H*- acenaphth[1, 2- f] isoindole- 8, 10 (9*H*) - Dione functionalized polysiloxane with aggregation-induced emission: Synthesis and highly sensitive detection for Fe³⁺

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ABSTRACT

Fluorescent silicone polymers have attracted much attention owing to their strong fluorescence and high stabilities. However, most of these silicone polymers have suffered from fluorescence quenching caused by aggregation in high concentrations. In this work, 7, 11-diphenyl-8*H*- acenaphth[1, 2- *f*] isoindole-8, 10 (9*H*) - dione functionalized polysiloxane (PMDF) with strong blue fluorescence was successfully synthesized via Diels-Alder reaction. Besides high thermal stability, PMDF showed unique aggregation-induced emission enhancement in high concentrations, indicating it is an excellent fluorescent silicone polymer in both disperse and aggregate state. Moreover, the product polymer showed highly sensitive fluorescence response to Fe³⁺, with low detection limit to 0.895 ppm and a high selectivity in the present of other metal ions. This work may open a new window for exploring fluorescent polymers as ideal probe for Fe³⁺.

1. Introduction

Silicon-containing fluorescent materials, including small molecules and polymers, have received vast attention in many fields owing to their outstanding properties, such as facile preparation, high chemical stabilities, excellent fluorescent properties, and good biocompatibility [1, 2]. In our group's previous work, Wang et al. [3-6] prepared various silicon-cored small molecules and revealed that silicon-cored structure can enhance fluorescence emission intensity and adjust emission colors, which is called "silicon-cored effect". Besides, Zuo et al. [7-9] synthesized several fluorescent silicone polymers with excellent thermal stability and fluorescent emission, and attributed the reason to enormous bond energy and wide range of bond angles of Si-O-Si moiety. However, these silicon-containing materials, particularly silicone polymers, have still suffered fluorescence quenching which caused by the aggregation in high concentrations until now. It seriously limited the application of fluorescent silicone polymers. Exploring fluorescent materials with aggregation-induced emission is well known to be the key to address fluorescence quenching caused by aggregation. However, only few examples of silicone polymers with aggregation-induced emission have been reported to date [10].

Iron is one of the most essential transition metal trace elements in

human body and plays an indispensable role in metabolism [11-13]. Ferric iron (Fe³⁺) deficiency could lead to anemia, and recent studies report that it may cause Parkinson's and Alzheimer's diseases [14-16]. Meanwhile, excess Fe³⁺ ions can cause some types of cancers and deterioration of organs, such as heart, pancreas, and lungs [17]. Thus, quantitative determination of Ferric iron concentration became an essential research topic. Many analytical techniques have been used for detection of Fe³⁺ and can provide good limit of detection (LOD) and wide linear ranges, such as atomic absorption spectrometry, atomic fluorescence spectrometry, ion-coupled plasma-mass spectroscopy, total reflection X-ray fluorimetry, and anodic stripping voltammetry [18–23]. However, these methods are not easily conducted and usually require expensive and sophisticated equipment and tedious sample preparation steps [24,25]. Compared with these methods, fluorescent probe, which is easily performed with low cost, high detection sensitivity and non-sample-destroying, has become the most potential detection method to Fe^{3+} [26,27].

In this work, we demonstrated the facile synthesis of 7, 11- diphenyl-8*H*- acenaphth[1, 2- *f*] isoindole- 8, 10 (9*H*) - dione functionalized polysiloxane (PMDF) by one-step Diels–Alder reaction (see Scheme 1). The structure of product polymer was determined through proton nuclear magnetic resonance (¹H NMR) spectroscopy. Optical properties of

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PMDF were further investigated by UV–vis and fluorescence spectroscopy. PMDF exhibited unique aggregation-induced emission besides high thermal stability. Moreover, PMDF was used as fluorescent probe to detect Fe^{3+} and showed higher sensitivity and selectivity. The detection performance of PMDF in different PH and solid films was also studied.

2. Experimental section

2.1. Materials and methods

All reagents and solvents were purchased from a commercial source and used without further purification, unless otherwise specified. Tetrahydrofuran, dichloromethane, methanol, and ethanol were purchased from Tianjin Fuyu Chemical Co. Ltd. 1,3-bis(aminopropyl) tetramethyldisiloxane was purchased from Hangzhou Dadi Chemical Co. Ltd. Acenaphthenequinone and 1,3-diphenyl-propan-2-one were purchased from Shanghai Chemical Reagent Company. Inorganic salt, FeCl₃·6H₂O, was purchased from Guangfu Chemical Industry Research Institute. CuCl₂·2H₂O, CrCl₃·6H₂O, CoCl₂·6H₂O, ZnCl₂, CaCl₂, MgCl₂, KCl, NaCl, ZnCl₂, Fe₂SO₄·7H₂O, Fe₂(SO₄)₃, and Fe(NO₃)₃ were purchased from Aladdin Industrial Company.

¹H and ¹³C were recorded on a Bruker Avance-300 NMR spectrometer. The UV–vis and fluorescence spectra were recorded on a TU-1901 double-beam UV–visible spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively. Absorption and emission measurements were conducted on samples in 1 cm \times 1 cm quartz cuvettes. All experiments were conducted at room temperature (~25 °C) unless otherwise specified. Thermal gravimetric analyses (TGA) were performed with a Mettler Toledo SDTA-854 TGA system in nitrogen at a heating rate of 10 °C min⁻¹.

2.2. Synthesis of α, ω -bis(aminopropyl)polydimethylsilioxane (AMP)

A mixture of tetramethylammonium hydroxide (1.55 g) and octamethylcyclotetrasiloxane (D4) (80 g, 270 mmol) was added into 250 ml three-neck round-bottom flask with mechanical raking at 60 °C. Water in D4 and system was removed under vacuum, and system atmosphere was replaced with nitrogen. After dissolution of siloxanolate catalyst, mixture was heated to 80 °C. End-capping agent (1,3-bis(aminopropyl) tetramethyldisiloxane) (2.48 g, 1 mmol) was dissolved in D4 (10 g, 34 mmol) when the viscosity of mixture increased. After 3 h, the mixture was heated to 135 °C for 1 h to destroy siloxanolate catalyst. After cooling down to 55 °C, the mixture was distilled under vacuum to remove low-boiling components while temperature was slowly increased to 150 °C. A transparent oily liquid was obtained with 74% yield. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 0.5–0.56 (t, J = 8.5 Hz, 2H, Si-CH₂), 1.31-1.36 (m, 2H, Si-CH₂-CH₂), 1.90 (s, 2H, NH₂), 2.64-2.69 $(t, J = 6.9 \text{ Hz}, 2H, \text{Si}-CH_2-CH_2-CH_2)$. ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 44.29, 26.48, 14.55, 0.13.

Mn = 3150 (PDI = 1.2).



PMDF

Scheme 1. The synthesis process of PMDF.

2.3. Synthesis of PM

AMP (5 g, 1.79 mmol) and glacial AcOH (20 ml) were mixed in 100 ml round-bottom flask. Maleic anhydride (0.5 g, 5.1 mmol) was dissolved in glacial AcOH (5 ml) and dropped into the mixture. Then the mixture was heated to 160 °C for 6 h with magnetic stirring [28]. After cooling down to room temperature, glacial AcOH was removed by rotary evaporator. Crude product was redissolved in CH₂Cl₂ (50 ml) and washed with saturated sodium chloride aqueous solution (150 mL, thrice). Organic layer was dried with anhydrous sodium sulfate for 3 h and then filtered. The solvent was removed to obtain the desired product, which is brown viscous oily liquid with 90% yield. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 0.43–0.57 (t, J = 8.5 Hz, 2H, Si–CH₂),1.54–1.65 (m, 2H, Si–CH₂–CH₂), 3.47–3.52 (t, J = 7.3 Hz, 2H, Si–CH₂–CH₂–CH₂), 6.67–6.68 (s, 2H, -CH=CH- in maleimade). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 169.81, 132.99, 40.92, 34.71, 21.53, 14.22, 0.10. Mn = 3310 (PDI = 1.2).

2.4. Synthesis of 7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (DCA)

DCA was synthesized through reaction of acenaphthenequinone and 1,3-diphenylpropan-2-one according to literature [29]. Acenaphthenequinone (5.47 g, 0.03 mol) and 1,3-diphenylpropan-2-one (6.3 g, 0.03 mol) were dissolved in ethanol (60 mL) and placed in three-neck 250 mL round-bottom flask equipped with reflux condenser and magnetic stirrer. When the mixture solution was heat to reflux, KOH (0.8 g)which dissolved in ethanol (5 mL) solution was dropwise added via a drop funnel. The mixture immediately turned black. After dropwise addition of KOH ethanol solution completed, the mixture was kept in reflux for 2 h and then cooled down to room temperature. After filtered, black precipitate was obtained. The crude product was washed with ethanol several times to obtain pure product, which is purple-black solid powder with yield of 90%. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.08 (d, J = 7.1 Hz, 2H), 7.86 (m, 6H), 7.62 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 7.6 Hz, 4H), 7.43 (t, J = 7.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 201.7, 154.2, 132.1, 131.5, 131.4, 129.0, 128.6, 128.3, 127.8, 121.7, 120.9. HRMS: m/z calcd. for C₂₇H₁₆O, 357.1235 [M + H]⁺, found: 357.1260 $[M + H]^+$. Melting point: 291 °C.

2.5. Synthesis of PMDF

PM (1 g, 0.33 mmol) and DCA (0.3 g, 0.84 mmol) were mixed in phenyl ether (25 ml). The mixture was heated to 150 °C and kept for 24 h. Crude product was precipitated in methanol, washed three times by water and methanol, and then dried under vacuum to obtain a dark green oily liquid with 74% yield. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 0.47–0.57 (t, J = 8.5 Hz, 2H, Si–CH₂), 1.51–1.56 (m, 2H, Si–CH₂–CH₂), 3.48–3.53 (t, J = 7.4 Hz, 2H, Si–CH₂–CH₂), 7.28–7.92 (16H, Ar*H* in aromatic units). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 164.7, 137.8, 136.6, 134.9, 131.7, 129.4, 128.4, 127.9, 127.3, 127.1, 126.9, 122.8, 122.1, 121.2, 120.4, 45.7, 35.9, 20.1, 0.15. Mn = 3962 (PDI = 1.2).

3. Results and discussion

3.1. Thermal stability

Thermal properties of PMDF were characterized by thermal gravimetric analyzer (TGA) under a nitrogen atmosphere. As shown in Fig. 1, decomposition temperature of PMDF was 363 °C; this value corresponds to a weight loss of 5% at heating rate of 10 °C min⁻¹. The peak decomposition temperature was found to be 480 °C. These high thermal decomposition temperatures suggest PMDF has excellent thermal stability.



Fig. 1. The TGA trace of PMDF recorded at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen atmosphere.

3.2. Structure characterization

¹H NMR spectra were recorded on Bruker 300 (300 MHz) spectrometer without tetramethylsilane as internal reference and shown in Fig. 2. At 0.05, 0.51, and 1.57 ppm, resonance peaks of –Si–CH₃, –Si–CH₂–, and –Si–CH₂–CH₂–, respectively, were easily distinguished in PM (H1, H2, H3, and H4 in Fig. 2A) and PMDF (H7, H8, H9, and H10 in Fig. 2B), thereby confirming presence of alkylsilane groups. Chemical shifts at 6.67 and 6.68 ppm were assigned to double bonds in maleimide groups in PM (H5 and H6 in Fig. 2A). Peak of –CH=CH- of maleimide groups disappeared in PMDF (Fig. 2B), and aromatic hydrogens appeared at 7.28–7.92 ppm. These results indicated that efficient grafting of aromatic groups into polysiloxane chains occurred via Diel-s–Alder reaction.

3.3. Optical properties

UV–vis absorption spectrum of PMDF in THF solution at 1×10^{-6} mol L⁻¹ was shown in Fig. 3a. Absorption peaks at around 226 and 277 nm originated from π - π * transitions of aromatic group. After observing UV–vis absorption spectra, we further investigated optical properties in pure THF solutions at different concentrations.

As shown in Fig. 3b, PMDF was dissolved in THF at concentrations of 1×10^{-3} , 1×10^{-4} , 1×10^{-5} , and 1×10^{-6} mol/L, respectively. As concentration increased, fluorescence emission peak of PMDF exhibited gradual red-shift from 404 nm to 461 nm, and the emission intensity simultaneously increased. The details can be found in Table 1. The emission intensity of solution at high concentration $(1 \times 10^{-3} \text{ mol/L})$ was fifteen times stronger than that of solution at lower concentration $(1 \times 10^{-6} \text{ mol/L})$, indicating PMDF shows aggregation-induced emission (AIE) feature. Furthermore, the emission intensity curve of PMDF in THF mixed with different content of water was measured and shown in Fig. S1a. As the water content increased to 70%, the emission intensity dramatically increased to 135% of the initial value. This emission intensity behavior confirmed that PMDF is an AIE-active polymer. The size distribution of PMDF aggregates was shown in Fig. S1b and the average size was 76 nm. The red-shift of emission peak and the emission intensity enhancement of PMDF could be attributed to the restriction of intramolecular rotation of 7,11-diphenyl-8H-acenaphth[1,2-f] isoindole-8,10 (9H)-dione in PMDF. It can significantly suppress non-radiative path and enhance the molecular rigidity, leading to stronger emission intensity and longer emission wavelength. To further study the effect of siloxane structure, we synthesized PMDF with different MWs of polysiloxane backbone (160, 1500, 3000 and 6000) using a,w-bis(aminopropyl)polydimethylsilioxane with different MWs. The emission



Fig. 2. ¹H NMR spectra of PM (A) and PMDF (B).



Fig. 3. UV–vis absorption spectra (a) of PMDF in THF solutions (PMDF at 1×10^{-4} mol/L) and fluorescence emission spectra (b) PL spectra of PMDF in THF solutions at different concentrations (excitation wavelength is 380 nm, the inset: four solutions under 365 nm UV lamp).

The fluorescence emission and excitation data of PMDF in different concentrations.

Concentration/mol/ L		1×10^{-6}	1×10^{-5}	$1 imes 10^{-4}$	1×10^{-3}
PMDF	λ _{ex} /nm λ _{em} / nm	304 404	310 405	380 461	398 461

intensities of four polymers were shown in Fig. S2. It was found that the emission intensities increased as the MW of polysiloxane backbone increased. While MW of polysiloxane backbone was higher than 3000, the emission intensity almost kept constant. Therefore, the siloxane structure which can suppress the intermolecular π - π stacking of the fluorophores also plays a key role in this process [30,31].

3.4. Selectivity

Table 1

As PMDF showed aggregation-induced emission feature, PMDF was studied as fluorescent probe toward different alkaline earth and transition metal ions. In Fig. 4a and b, among different metal ions, the emission intensity of PMDF was significantly reduced with the addition of Fe^{3+} , while it showed only slight change with the addition of other metal ions. These results indicated that PMDF had high selectivity towards Fe³⁺ among different metal ions. We further investigated the selectivity of PMDF towards Fe³⁺ with the presence of other metal ions. Competitive studies on PMDF with Fe^{3+} (400 µmol) were conducted in presence of other metal cations (400 µmol) in THF solution. It could be clearly seen that the presence or absence of competitive metal ions did not cause any significant variation in fluorescence intensity (Fig. 4c, S3, and S4 in ESI). The selectivity of Fe^{3+} was calculated using selectivity coefficient ($K_{Fe}^{3+} = S_{Fe}^{3+}/S_0$), where S_{Fe}^{3+} is response to Fe^{3+} , and S_0 is response to other cations [32]. Table S1 listed the selectivity coefficients of Fe³⁺ measured against other tested cations. The coefficients clearly indicated better selectivity of sensor PMDF for ${\rm Fe}^{3+}$ than other cations. Thus, PMDF can accurately identify Fe³⁺ in presence of other metal cations. Upon addition of different metal ions (400 µM), UV-vis absorption spectrum of PMDF solution also indicated the high selectivity of PMDF for detection of Fe³⁺ (Fig. S3 in ESI). Absorption of PMDF with Fe³⁺ at high-level curves indicates that PMDF interacts with Fe³⁺ to form larger aggregates [33,34] and thus causes scattering phenomenon [35].

The pH effect on fluorescence emission of PMDF was further



Fig. 4. (a) and (b) Fluorescence emission of PMDF (1×10^{-4} mol L⁻¹) in THF solutions with different metal iron (400 μ M) (excitation wavelength is 380 nm); (c) Fluorescence response of PMDF upon addition of competitive cations (black bars) and PMDF upon addition of competitive cations (red bars) in THF solution; (d) The effect of pH on the fluorescence intensity of PMDF solution. All data are represented as mean \pm SD (n = 3).

investigated in THF from pH 2–12 (Fig. 4d). All data are represented as mean \pm SD (n = 3). No matter above or below pH = 7, the emission intensity kept almost constant. Moreover, the sensing performance of PMDF toward Fe³⁺ under different pH were also measured and shown in Fig. S5. The sensing performance of PMDF was stable under different pH. This result indicated that stringent control for pH of sample solution is not essential and thus simplified practical application of this

fluorescent probe for detection of Fe³⁺. Detection performance of fluorescent probe is easily disturbed by presence of counter anions. Thus, we further studied fluorescence titrations of PMDF toward Fe³⁺ with different counter-ion salts. We selected ferric nitrate and ferric sulfate salts as contrasts. Amount of ferric nitrate was twice that of ferric sulfate to ensure similar content of iron. Fig. S6 displayed similar quenching efficiency from fluorescence emission spectra. Table S2 showed



Fig. 5. (a) Change in fluorescence of PMDF ($1 \times 10^{-4} \text{ mol L}^{-1}$) upon addition of different amounts of Fe³⁺; (b) Stern–Volmer plot in response to Fe³⁺ ions. The inset figure shows the Stern–Volmer plot obtained at a lower concentration of Fe³⁺ (excitation wavelength is 380 nm).

comparison results of PMDF sensor for detecting Fe^{3+} and other reported fluorescent sensors. These results indicated that PMDF had high selectivity and stable fluorescent response for the detection of Fe^{3+} .

3.5. Fluorescence response in detecting Fe^{3+}

Fluorescence detection experiment was conducted to evaluate detecting ability of PMDF toward Fe^{3+} . As shown in Fig. 5a, PMDF probe emitted fluorescence at 461 nm with excitation wavelength at 380 nm. Fluorescence emission was immediately quenched with the addition increased of Fe^{3+} ions. Fluorescence of PMDF was quenched to 90% of its initial intensity when 500 μ M Fe³⁺ ions were added to the system. Quenching efficiency was studied by using Stern–Volmer equation (Eq. (1)):

$$K_{sv} \times [C] = \frac{I_0}{I} - 1 \tag{1}$$

where I_0 is initial fluorescence intensity of PMDF, I is fluorescence intensity in presence of Fe³⁺ at different concentrations, and K_{sv} and C are quenching constant and concentration of Fe³⁺, respectively.

$$LOD = 3 \times \frac{S_d}{k} \tag{2}$$

where LOD is detection limit, S_d is standard deviation of blank fluorescence intensity of PMDF, and k is slope of calibration curve.

Fig. 5b shows linear dependence (linear correlation coefficient is 0.9967) of fluorescence intensity ratio (I₀/I) to Fe³⁺concentration at lower concentrations of Fe³⁺ ions. From Eq. (1), Stern–Volmer quenching constant (K_{sv}) is 5.49×10^3 M⁻¹. Curve of plots turned upward as concentrations of Fe³⁺ ions increased. This upward curve

indicated high efficiency of PMDF for ferric detection; detection mechanism differs from collision deactivation [36]. LOD of Fe³⁺ ions was obtained by calculating signal-to-noise ratio based on definition by IUPAC [37] using equation (Eq. (2)); computed value is 15.99 μM (0.895 ppm). Moreover, the sensing properties of PMDF in water were also studied and the results were added in Fig. S7. The Stern–Volmer quenching constant (K_{sv}) is 7.93 \times 10³ M⁻¹ and the LOD of Fe³⁺ in water is 12.32 μM . Therefore, PMDF also exhibited excellent detection performance in water due to the AIE feature, which indicates PMDF can detect iron in biological systems.

3.6. Mechanism of fluorescent response and solid substrate experiments

The mechanism of fluorescence quenching is studied by measuring fluorescence spectra of PMDF-Fe³⁺ system at different temperatures. As shown in Fig. 6a, Stern–Volmer plots are nearly linear, and quenching constants increased with decrease of temperature. Furthermore, the fluorescence lifetimes (Table 2) of PMDF with and without Fe³⁺ were almost same, suggesting that quenching mechanism is static quenching. The FT-IR spectra of PMDF and PMDF with Fe³⁺ were shown in Fig. S8. It could be clearly seen the peak of C=O of PMDF with Fe³⁺ showed

Table 2

Time-resolved fluorescence decay constant ($\tau)$ values of PMDF without and with Fe $^{3+}.$

Sample	$\tau_1(ns)$	$ au_1\%$	$\tau_2(ns)$	$ au_2$ %	τ(ns)	χ^2
PMDF in THF PMDF + Fe ³⁺ in	1.0338 1.2934	24.89 28.28	14.3033 15.9185	75.11 71.72	11.0005 11.7826	1.004 0.995
THF						



Fig. 6. (a) The temperature dependent fluorescence intensity of the PMDF-Fe³⁺ system; (b) mechanism for detection of PMDF upon binding with Fe³⁺; (c) The PMDF solid film and photos under UV lamp at 365 nm.

obvious shift than that of PMDF, indicating PMDF and Fe³⁺ coordinated and formed aggregate. Therefore, we inferred that the quenching mechanism was the interaction of Fe³⁺ with carbonyl groups of aromatic groups in PMDF to form aggregations as shown in Fig. 6b. The electron in the excited state of fluorophore can transfer to the unfilled orbit of Fe³⁺, and lead to nonradiative recombination and fluorescence quenching. The detection performance of PMDF towards Fe³⁺ at solid films was studied and shown in Fig. 6c. PMDF Solution (1×10^{-4} mol/L) was drop-wise placed on silica gel plate. After volatilizing THF solution, the word "Si" was written on the plate by using capillary burette dipped in Fe³⁺ solution. Under UV lamp at 365 nm, obvious fluorescence quenching was observed in gel plate with Fe³⁺-solution engraving. This phenomenon suggested that PMDF can also be used for detection of Fe³⁺ in solid film states.

4. Conclusions

7, 11- diphenyl-8*H*- acenaphth[1, 2- *f*] isoindole- 8, 10 (9*H*) - dione functionalized polysiloxane (PMDF) was successfully prepared through a facile method. Besides high thermal stability, PMDF showed unique aggregation-induced emission enhancement in high concentrations, indicating it is an excellent fluorescent silicone polymer in both disperse and aggregate state. Moreover, the product polymer showed highly sensitive fluorescence response to Fe^{3+} , with low detection limit to 0.895 ppm and a high selectivity in the present of other metal ions. The detection performance was stable in different pH. The mechanism is proposed to be the interaction of Fe^{3+} with carbonyl groups in PMDF to form aggregations. This work can serve as guide for study on fluorescent probe to detect Fe^{3+} and broaden research area of special functional organic silicon materials.

Author statement

Haifeng Lu: Investigation, Formal analysis, Writing - Original Draft, Visualization.

Lichao Xu: Investigation, Writing - Original Draft.

Hua Wang: Validation, Formal analysis.

Shengyu Feng: Writing - Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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