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A Fiber Optic Sensor for Determination of 2,4-Dichlorophenol Based on Oxygen Oxidation Catalyzed by Iron(III) Tetrasulfophthalocyanine

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A new fiber optical sensor was developed for the determination of 2,4-dichlorophenol (DCP). The sensor was based on DCP oxidation by oxygen with the catalysis of iron(III) tetrasulfophthalocyanine (Fe(III)PcTs). The optical oxygen sensing film with $Ru(bpy)_3Cl_2$ as the fluorescence indicator was used to determine the consumption of oxygen in solution. A lock-in amplifier was used for detecting the lifetime of the oxygen sensing film by measuring the phase delay change of the sensor head. The different variables affecting the sensor performance were evaluated and optimized. Under the optimal conditions (*i.e.* pH 6.0, 25 ºC, Fe(III)PcTs concentration of 0.62 mg/mL), the linear detection range and response time of the sensor are 1.0×10^{-6}-9.0×10^{-6} mol/L and 250 s, respectively. The sensor displays high selectivity, good repeatability and stability, and can be used as an effective tool in analyzing DCP concentration in practical samples.

Key Words : 2,4-Dichlorophenol, Iron(III) tetrasulfophthalocyanine, Fiber optic sensor, Phase delay

Introduction

Chlorinated phenols are pervasive environmental pollutants because they are widely used in the production of several herbicides, pesticides, preservatives, plant growth regulators and formed in the environment as a result of the degradation and metabolism of these agricultural and food chemicals.[1-4] 2,4-Dichlorophenol (DCP) is of perticular interest since it is a precursor for the synthesis of carcinogenic endocrine, 2,4-dichlorophenoxyacetic acid, which is the active ingredient of more than 1500 herbicides. The toxicity linked to DCP exposure has been shown to cause endocrine related cancers and chronic conditions such as chloracne and porphyria in humans.[3,4] It was regarded as the toxic organic substance to be specially controlled.[5] Therefore, the detection of DCP concentration is of crucial importance to environmental protection and human health. Although there are several methods for the determination of DCP, such as gas chromatography (GC),[6,7] flow injection analysis (FIA),[8] HPLC,[9,10] electrode,[11,12] electrochemical sensor,[1,2,13,14] these methods have many disadvantages, including time-consuming, high cost, complicated sample preparation, signal disturbance by electric and magnetic field.

Fiber optic sensors have many advantages such as high precision, fast response, strong ability to resist disturbance, possibility of on-line and real time detection.[15] Fiber optic sensors based on DCP oxidation catalyzed by enzyme supply the preferred way for DCP detection. However, the application of the natural enzymes has been limited because of their poor stability, very limited source, and difficult extraction and purification. Therefore, the biomimetic enzymes have been studied and developed as an effective alternative to the nature ones. Metallophthalocyanines (MPc), which have a perfect symmetrical 18-electron aromatic macrocycle, are easily accessible, very stable to degradation and cost effective, and have been developed as an effective replacement for the nature enzymes.

In this work, iron(III) tetrasulfophthalocyanine (Fe(III)PcTs) had been used as a biomimetic enzyme to catalyze the oxidation of DCP and the influence factors such as pH, temperature, catalyst concentration to this oxidation had been studied. A novel fiber optic sensor based on the DCP oxidation by oxygen with the catalysis of Fe(III)PcTs had been designed and fabricated and the performance of the sensor was investigated. To the best of our knowledge, there has been no report on this kind of work. The linear detection range, detection limit and response time of this sensor are 1.0×10^{-6}-9.0×10^{-6} mol/L, 2.3×10^{-7} mol/L, 250 s, respectively. It shows good repeatability, selectivity and stability, and the prospect of its practical application is promising.

Experimental

Reagents and Apparatus. 4-Sulfophthalic acid ($C_8H_6O_7S$), urea ($CO(NH_2)_2$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 6H_2O$), ammonium chloride ($NH_4Cl$), ferrous sulfate ($Fe_2(SO_4)_3$), DCP, cellulose acetate and 4-aminoantipytine (4-AAP) were obtained from Shanghai Chemical Reagent Company. Fluorescence indicator tris(2,2'-bipyridyl) dichloro-ruthenium(II) hexahydrate ($Ru(bpy)_3Cl_2\cdot 6H_2O$) was purchased from Sigma-Aldrich. All the reagents were of analytical grade and used without further purification. Fe(III)PcTs was synthesized

and purified according to the literature.[16]

The absorption spectra were determined using a UV-2450 spectrophotometer (Shimadzu, Japan). A lock-in amplifier (SR830, Standford Research Systems, U. S. A) was used for measuring the phase delay of the sensor head.

Preparation of Oxygen Sensing Film. The oxygen sensitive membrane was prepared by using $Ru(bpy)_3Cl_2·6H_2O$ as the fluorescence indicator and cellulose acetate as the matrix according to our previously work.[17] Briefly, 0.1 g cellulose acetate was added into 3.0 mL acetone and stirred at room temperature for 2 h. A certain amount of $Ru(bpy)_3Cl_2$ water solution was added in the mixture and it was stirred at room temperature for 6 h to form an uniform solution. The solution was dipped onto a glass culture dish with the diameter of 6 cm and made it well-distributed. The cellulose acetate membrane embedded with fluorescent indicator was obtained after the acetone and water were volatilized.

Preparation and Principle of Fiber Optic Sensor. The detecting system consisted of a lock-in amplifier, a LED with the excitation wavelength of 416 nm as the light source, a sensor head with a oxygen sensing membrane and a computer for data processing (see Fig. 1).

The principle of the sensor was based on the fluorescence quenching and consumption of oxygen.[17] The change of oxygen concentration was detected by measuring fluorescence of $Ru(bpy)_3Cl_2$ quenched by oxygen. Since a lock-in amplifier was used, the quchening could be described as

$$\frac{\tan\varphi_0}{\tan\varphi} = 1 + K_{sv}[Q] \quad (1)$$

Where φ_0 and φ were the phase delay change of the sensor in the absence and presence of the oxygen quencher, respectively, and K_{sv} was the Stern-Volmer constant. $[Q]$ was oxygen concentration. Since φ was very small (*i.e.* $< 5^o$) in the experiment, $\tan\varphi \approx \varphi$. By collecting the data of phase delay φ the quantification of DCP was achieved.

Measurements. The catalytic oxidation of DCP assisted with 4-AAP using Fe(III)PcTs as catalyst was performed as follows: A 40 mL of deionized water, 5 mL of 4-AAP aqueous solution (1.0×10^{-3} mol/L) and 5 mL of DCP (1.0×10^{-3} mol/L) were added into a 80 mL glass beaker with magnetic stirring. The catalytic reaction was initiated by addition of 31.0 mg of Fe(III)PcTs powder followed by the ultrasonic treatment for 1 min to make it dissolved in the mixture. The mixture was stirred magnetically at 25 °C and was detected with UV-Vis spectrophotometer at regular intervals in the catalytic process. The catalytic reaction was performed in different conditions to investigate the influencing factors to the catalytic efficiency of Fe(III)PcTs.

For the detection of DCP concentration, measurements were performed with the setup shown schematically in Figure 1. The sensor head was placed into a tiny reaction cell which was available for a small quantity of sample. The reaction cell contained DCP buffer solution and a certain amount of Fe(III)PcTs was dissolved in it. In order to eliminate the interference of oxygen from the open air, an entire airtight reaction cell was introduced. All the measurements were carried out at 25 °C under continuous and constant stirring. The fluorescence signal was collected by PIN and guided to the lock-in amplifier through the output bundle, and then transferred to phase-delay collected by the computer. The following measurement could be performed after a simple washing of the sensor head with buffer solution and adding Fe(III)PcTs into the reaction cell containing DCP buffer solution.

All the measurements were performed in triplicate.

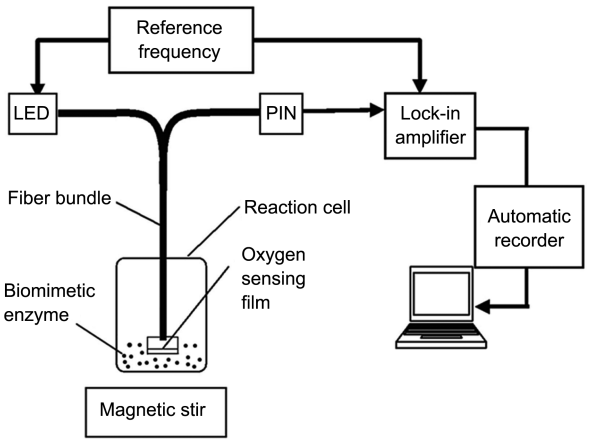

Figure 1. Schematic diagram of the detecting system.

Results and Discussion

It had been reported that phenolic compounds could be oxidized with the catalysis of phthalocyanine metal complex.[18-21] Our previous work documented that tetranitro iron(II) phthalocyanine could catalyze the oxidaton of phenolic compounds by oxygen.[22] Herein the catalytic activity of Fe(III)PcTs was investigated using DCP as the substrate. Figure 2 shows the UV-Vis absorption spectra for chromogenic reaction of DCP with 4-AAP in the presence of Fe(III)PcTs at regular intervals. The absorbance at 510 nm

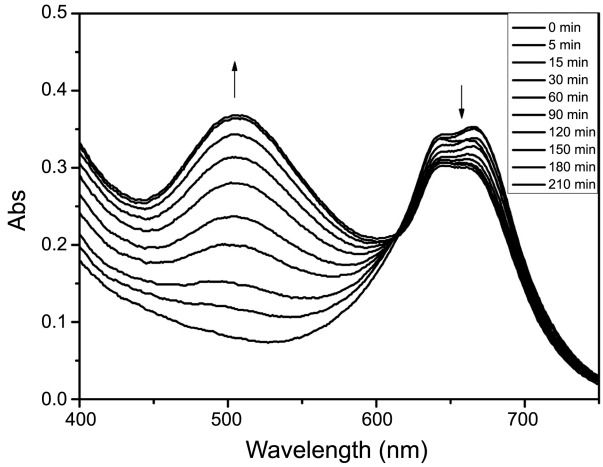

Figure 2. Stacked UV-Vis absorption of catalytic oxidation of DCP with 4-AAP at regular intervals. Conditions: T = 25 °C, pH = 6.0, [DCP] = 1.0×10^{-4} mol/L, [4-AAP] = 1.0×10^{-4} mol/L, [Fe(III)PcTs] = 0.62 mg/mL.

increased during the catalytic oxidation due to the formation of chloro-substituted antipyrilquinoneimine dye.[23] It could be seen that the intensity of characteristic peak of dye at 510 nm gradually increased within 180 min, indicating the continuous transformation of DCP with 4-AAP to dye in the presence of Fe(III)PcTs. However, contrast experiment showed that the auto-oxidation reaction without Fe(III)PcTs was negligible (data not shown). The UV-Vis spectra of this system showed no obvious change after 180 min, demonstrating the completion of catalytic reaction. Since the solution was exposed to air and there were no other oxidants in it, dissolved O_2 was considered to be the possible oxidant for DCP oxidation. To confirm this, the reaction was carried out with continuous nitrogen-bubbling to eliminate the dissolved O_2 in solution. It was found that the dye formation rate was greatly prohibited compared to the system with dissolved O_2 in it, demonstrating that dissolved O_2 was the oxidant for DCP oxidation. We compared the catalytic oxidation of DCP in dark environment with that in the environment with light. No notable differences between them were observed, indicating that light was not necessary to this oxidation of DCP in the presence of Fe(III)PcTs.

The catalytic oxidation of chlorophenols assisted with 4-AAP was closely related to pH because the dominating species of chlorophenol varied with pH of aqueous solution.[22,24] Therefore, pH influence on the DCP oxidation by oxygen with the catalysis of Fe(III)PcTs was investigated in the range of pH 5.0-9.0 by using different buffer. As it could be noticed in Figure 3, a maximal value of absorbance at 510 nm was observed at pH 6.0. This pH was selected for our subsequent investigations.

It is well-known that the enzyme catalyzed reaction will be significantly influenced by temperature. Therefore, the effect of temperature on the DCP oxidation catalyzed by Fe(III)PcTs was investigated, as shown in Figure 4. It could be seen that as the temperature increased from 5 °C to 25 °C,

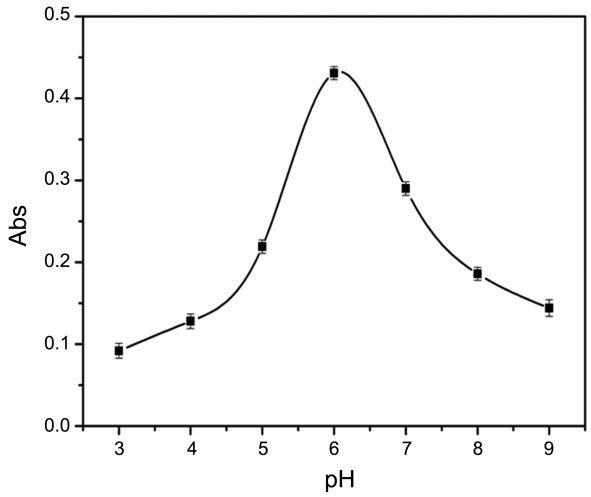

Figure 3. Effect of pH on the oxidation of DCP catalyzed by Fe(III)PcTs. Conditions: T = 25 °C, [Fe(III)PcTs] = 0.62 mg/mL, [DCP] = 1.0×10^{-4} mol/L, [4-AAP] = 1.0×10^{-4} mol/L, t = 120 min, Error bars in the figure show standard deviations calculated with three data points taken from different measurements (n = 3).

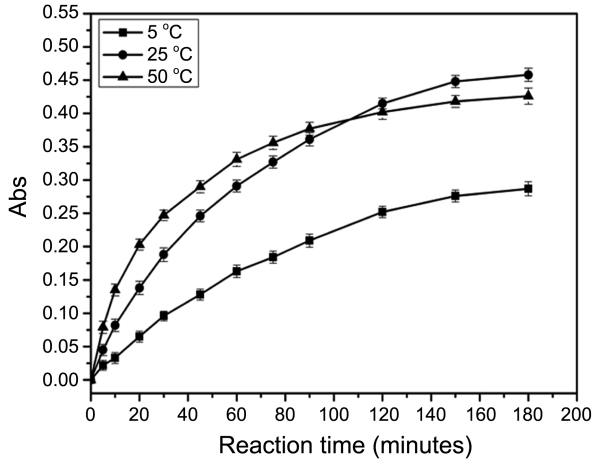

Figure 4. Effect of temperature on the oxidation of DCP catalyzed by Fe(III)PcTs. Conditions: pH = 6.0, [Fe(III)PcTs] = 0.62 mg/mL, [DCP] = 1.0×10^{-4} mol/L, [4-AAP] = 1.0×10^{-4} mol/L, n = 3.

the absorbance of the solution at 510 nm, which indicated the degree of DCP oxidation, increased significantly. When the temperature continued to increase to 50 °C, the absorbance of the solution at 510 nm was greater slightly than that at 25 °C in the first 110 min, and it became smaller than that at 25 °C after 110 min because of the evaporation of DCP at higher temperature. Since the oxygen sensing film would be destroyed when the temperature was higher than 40 °C,[17] in order to prolong the lifetime of the sensor, 25 °C (room temperature) was recommended for our subsequent investigations.

The effect of catalyst concentration on the oxidation of DCP by oxygen catalyzed by Fe(III)PcTs was investigated (Fig. 5). The oxidation rate increased with the increasing amount of Fe(III)PcTs added from 0.09 to 0.62 mg/mL during the time for experiments carried out with a DCP concentration of 0.10 mM. The further increase of Fe(III)PcTs amount could not obviously enhanced the oxidation rate of DCP. Therefore, the concentration of 0.62 mg/mL for the catalyst was recommended for the sensor detection.

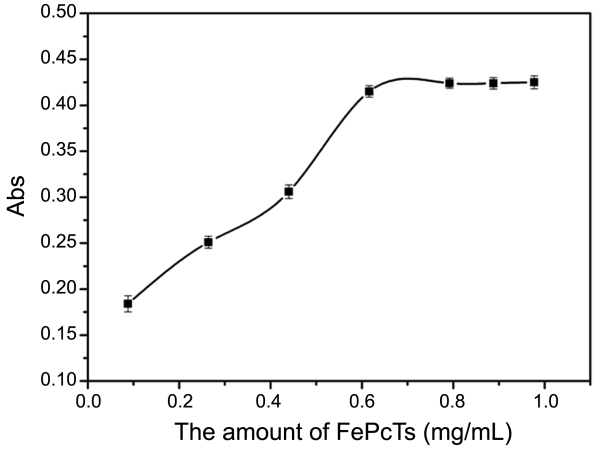

Figure 5. Effect of Fe(III)PcTs concentration on DCP oxidation. Conditions: T = 25 °C, pH = 6.0, [DCP] = 1.0×10^{-4} mol/L, t = 120 min, [4-AAP] = 1.0×10^{-4} mol/L, n = 3.

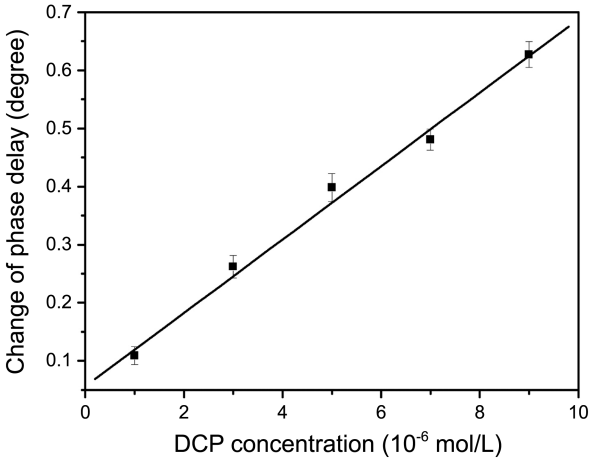

Figure 6. Typical calibration curve of the fiber optic DCP sensor at various concentration of DCP. Conditions: T = 25 °C, [$FePcS_4$] = 0.62 mg/mL, pH = 6.0, n = 3.

The detection of DCP concentration was based on the fluorescence quenching and consumption of oxygen. By detecting the change of phase delay of the sensor head we could detect the DCP concentration. Figure 6 depicts the relationship between the change of phase delay φ and DCP concentration in the concentration range from 1.0×10^{-6} mol/L to 9.0×10^{-6} mol/L (The Integrated Wastewater Discharge Standard of China for DCP is 3.68×10^{-6} mol/L).

There is a good linear relationship between φ and DCP concentration. The linear graph is defined by the equation of $y = 0.0631x + 0.0562$ and $R^2 = 0.976$. φ is defined as the difference between the phase delay of the sensor head with certain DCP concentration and with no DCP in the solution. The response time of the sensor was taken as 250 s because most of the DCP was oxidized in this time. The detection limit was 2.3×10^{-7} mol/L (S/N = 3). For a solution with a certain DCP concentration, it is understandable that the detection is not influenced by the fluctuations of initial dissolved oxygen concentration in samples because the change of oxygen concentration is constant during the detection. Similar results were also reported previously.[25-27]

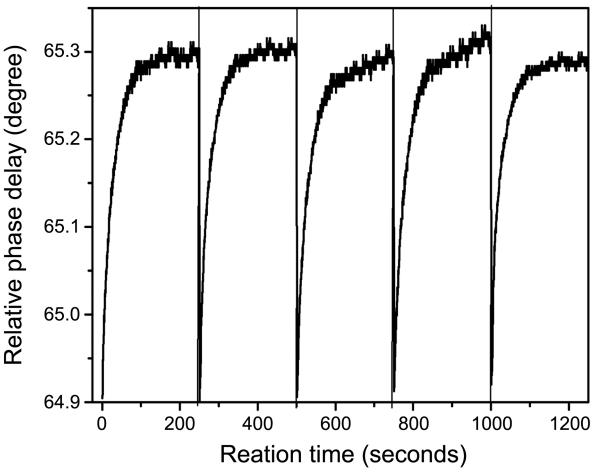

Figure 7. Repeatability and reversibility test on the sensor by exposing the sensor to five cycles of buffer, 5.0×10^{-6} mol/L DCP, respectively. Conditions: T = 25 °C, [$FePcS_4$] = 0.62 mg/mL, pH = 6.0.

The reversibility of the sensor was assessed by exposing the sensor to five cycles of buffer, 5.0×10^{-6} mol/L DCP, respectively. The results in Figure 7 show that it has a highly reproducible and reversible response to DCP. The repeatability of the response of the sensor was also investigated by subjecting the sensor to a 3.0×10^{-6} mol/L DCP solution. The relative standard deviation (R.S.D.) was 4.93% for 10 successive measurements, also indicating the good repeatability of the sensor.

We compare our sensor with HPLC[10] and electrochemical sensor[1] (see Table 1). Although the detection limit of HPLC is very low, the sample preparation for HPLC is much more complicated and the detection is a time-consuming process. The cost of HPLC is rather high, and it can not be used for real-time and on-line detection. Compared with the electrochemical sensor, the detection limit of our sensor is two orders lower than that of the electrochemical sensor,[14] and the response rate is much fast. Since the Integrated Wastewater Discharge Standard of China for DCP is 0.6 mg/L, our sensor has the linear detection range which can meet the need of practical application.

To investigate the lifetime of the sensor, the response value of the oxygen sensing film in contact with 4.0×10^{-6}

Table 1. Comparison of the proposed sensor with HPLC and Electrochemical sensor

Method	Linear detection range	Detection limit	Response time
HPLC[10]	0.05-20.0 (mg/L)	0.76 (μg/L)	
Electrochemical sensor[1]	1.63-48.9 (mg/L)	3.26 (mg/L)	14 min
Proposed sensor	0.16-1.47 (mg/L)	0.037 (mg/L)	4.17 min

Table 2. Interference test of the fiber optic DCP sensor on exposure to various interferents

Interferents	Concentration (mmol/L)	Interference rate ((C-C_0)/C_0 × 100%
K^+	15.0	-3.8
Na^+	15.0	-4.2
Cl^-	15.0	5.2
SO_4^{2-}	15.0	3.6
Br^-	5.0	-3.2
Al^{3+}	5.0	-3.6
Mn^{2+}	5.0	2.4
NH_4^+	5.0	-1.8
Zn^{2+}	5.0	3.0
CO_3^{2-}	5.0	2.4
PO_4^{3-}	5.0	-4.8
CH_3COO^-	5.0	2.6
Ca^{2+}	5.0	2.5
Mg^{2+}	5.0	-3.8

Table 3. Determination of DCP in practical samples using the proposed sensor

Samples	DCP added (10^{-5} mol/L)	DCP found (10^{-5} mol/L)	Recovery (%)
Water in Yangtse River	5.0	5.14 ±0 .07	102.8
Water in East Lake	5.0	4.93 ± 0.09	98.6

mol/L of DCP was recorded after keeping the film in water for two days. The results showed that the change of phase delay of the sensor under optimal conditions only decreased by 3.8%. However, after the oxygen sensing film had been kept in water for one week, a change of phase delay decrease of 9.6% for the film was observed. The indicator leaking from the film might be responsible for the loss of sensitivity. On the other hand, Fe(III)PcTs solid was kept in laboratory (room temperature) for 12 months and there was almost no decrease of its catalysis ability when it was dissolved in water, indicating a outstanding of stability for the catalysis of Fe(III)PcTs.

5.0×10^{-5} mol/L was selected as the actual concentration of DCP, the interference rate in the presence of potential interferents with different concentration were used as indicators for the sensor selectivity. The results are summarized in Table 2. We can see that all the interferents did not cause significant interference on the response of the sensor, demonstrating a good selectivity for this sensor.

The fiber optic DCP sensor was validated by applying it to the determination of DCP in samples from water of East Lake and Yangtse River in Wuhan, China. The DCP concentrations in two samples were determined, in triplicate, using the proposed sensor. The results are shown in Table 3. It can thus be concluded that this sensor is suitable for the determination of DCP in practical samples.

Conclusion

The results reported in this work clearly demonstrate that the biomimetic enzyme Fe(III)PcTs, which has many advantages such as easy preparation, good stability, and low cost, is successfully used for the catalysis of DCP oxidation. The proposed sensor based on the oxidation by oxygen with Fe(III)PcTs catalysis is a precise, low cost, sensitive and highly selective device for the determination of DCP. The sensor is easily prepared, readily regenerated and demonstrated a long lifetime. It is first time to report that this sensor can be used for DCP determination. The sensor shows short response time, appropriate linear calibration curve, good repeatability, selectivity and stability. Finally, the sensor can be successfully applied to detect DCP in real water sample, demonstrating a great application prospect.

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