Synthesis and Characterization of a Cyclic Polyacetonitril Oligomer and its Application on Solid Polymer Electrolyte

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Here we introduce a new synthetic approach to grow polyacetonitrile (PACN) oligomer via electrochemical method, and the polymerization degree of PACN oligomer is investigated completely by mass spectrum. The PACN oligomer with well-defined polymerization degree is obtained in this work, which shows an excellent heat resistance till 400 °C. Particularly, the PACN oligomer is successfully applied as an additive of the solid polymer electrolyte for lithium batteries. By adding 3 wt. % PACN oligomer, the ionic conductivity of the PEO-based SPE grows by two orders of magnitude and reaches 2.59×10$^{-5}$ S/cm at 30 °C. Furthermore, the electrochemical stability window and mechanical processing property of SPE are also enhanced greatly by adding of PACN oligomer. The PACN oligomer is proved to be a promising additive for SPE.

Keywords: polyacetonitril oligomer; electrochemical synthesis; solid polymer electrolyte; electrochemical stability; lithium ion battery

1. INTRODUCTION

The π-conjugated organic polymers played prominent roles in the development of polymer chemistry and laid the solid foundation of the polymerization of organic polymers. These carbon-carbon π-conjugated organic polymers, such as polyacetylene, polyphenylacetylene and polydicyclopentadiene, have been known for many years as advanced materials for electronic and photonic applications.
applications[1-4]. Subsequently, the system of π-conjugated polymers with O, N and S atoms, such as polypyrrole[5], had been developed rapidly[3,6]. The conjugated system with the N atoms participated would have more intrinsic properties than the carbon-carbon π-conjugated system, since the polarity of the N atom is greater than the C atom. Meanwhile, the lone pair electrons of nitrogen atoms also attend the conjugation and delocalization[7], which makes the electron delocalization degree of whole molecule system increased and may lead to more superior performance than other conjugated polymer in some aspects. Polyanionitrile (PACN), a polymer with alternate carbon-nitrogen π-conjugated sequence structure, has shown high polarizability of the π-conjugated structure and excellent potential performance [8,9]. However, there are fewer reports about aggregation of acetonitrile due to two obstacles [10]. On the one hand, the stable carbon-nitrogen triple bond in acetonitrile makes it difficult to polymerize. Because under the traditional equilibrium condition, the enthalpy is small and entropy change is a negative value for this polymerization, resulting in the increase of the Gibbs free energy based on the equation ∆G=ΔH-TΔS[11]. On the other hand, the majority of acetonitrile polymerized products are always cross-linked and insoluble [11-13], which makes it difficult for structural characterization and performance testing. Therefore, it is very important to make a breakthrough on preparation of PACN. Considering the inherent stability of acetonitrile, some previous studies employed various methods to promote the polymerization reactions of acetonitrile including chemical complexation[11], alkaline initiator, plasma[14] and electrochemical polymerization[15,16]. For instance, Kabanov[11] and Oikawa[8,9] etc. have successfully synthesized the polypropionitride, polybenzonitrile and polyanionitrile using chemical complexation method by introducing some metal halides in 1960s. However, the synthetic route was extremely complicated and the characteristic results of the products were quite few due to the limitation of early synthetic conditions and deficiency of characterization methods [13-17]. Concerning the research of polymerized nitriles, further developing a new and efficient synthetic approach and more comprehensive characterization are highly desired.

Organic electrochemical synthesis had been proved to be a highly efficient method for the polymerization of organic materials[18,19]. Using this method, numerous novel materials can be easily synthesized at low cost and low temperature with high purity and environmental friendliness[20,21]. Electrochemical synthesis can easily provide a non-equilibrium environment, such as a relatively high voltage, under which the stable carbon and nitrogen triple bond can react and polymerize easily. Furthermore, compared with traditional chemical methods, a more purified product can be obtained in the electrochemical synthesis process. Therefore, electrochemical synthesis would be an efficient method to prepare PACN.

Recently, there has been an increasing interest in solid polymer electrolytes (SPEs) due to their outstanding properties compared with liquid electrolytes currently in use, such as high energy density, light weight, high safety, flexible shapes and long cycle life [22-27]. The most commonly studied SPE is polyethylene oxide (PEO) based polymer electrolyte, which has an ionic conductivity of 10^{-7} or 10^{-8} S/cm at ambient temperature [28,29]. It suffered from the low ionic conductivity and poor mechanical strength, which restricted its practical application [23-30]. Recently, our group found that cyano resin-based gel polymer electrolyte demonstrated an excellent performance in lithium-ion batteries[31], which indicates that the cyano is a good additive for SPE.
In this work, a conjugated PAcN oligomer was successfully prepared by electrochemical synthesis and the polymerization degree defined by mass spectrum is 17. It is interesting found that 3 wt. % of PAcN oligomer strongly improves the ionic conductivity, electrochemical stability window and mechanical processing property of PEO-based SPE. This PAcN oligomer synthesized by electrochemical approach would tremendously promote the development of the polynitriles and application as a promising additive for SPE.

2. EXPERIMENTAL

2.1 Synthesis of PAcN oligomer

The electrochemical synthetic process of PAcN oligomer was shown in Figure 1. The experimental device includes two silicon electrodes and is separated into cathode and anode rooms by a perfluorinated ion membrane. The silicon electrode was cut into pieces of 80 mm ×16 mm ×4 mm and polished with abrasive papers from #400 to #1600, followed by rinsed with deionized water and then cleaned ultrasonically in acetone. Electropolymerization of PAcN was carried out on a DYY-4 electrophoresis apparatus by constant current (100 mA) at room temperature in 0.50 mol L⁻¹ iodide lithium and 19.0 mol L⁻¹ acetonitrile monomer in dimethyl sulfoxide (DMSO) on the silicon electrodes. After two days electrifying, the orange flocculent product (shown in Figure 1 inserted) was obtained in the cathode room (especially on the silicon cathode). Subsequently, the product was dissolved in DMSO and purified by recrystallization with DMSO/ethyl acetate solution (1/5 for volume ratio). The final product was obtained after a 12 hours drying in a 100°C vacuum oven. It should be noted that all the raw materials are waterless and the whole process should avoid introducing water [32].

![Figure 1. Schematic representation of experimental device and photograph of PAcN oligomer (insert).](image-url)
2.2 Preparation of polymer electrolyte film

Appropriate PEO (Molecular weight =3.0 \times 10^5 , Alfa Aesar) and LiClO$_4$ (J & K Chemical Technology) were dissolved in acetonitrile to get a precursor solution. The PEO and LiClO$_4$ concentration was fixed to [EO]:[Li]=16:1 in mole ratio [33]. Different mass percents of PAcN oligomer (1 wt.%, 3 wt.% and 5 wt.%) were added into the precursor solution followed by stirring at room temperature for 12 h to get a homogeneous and viscous mixture. Then, the mixture was cast on Teflon plates and then excess solvent was evaporated in an argon-filled box for 1 day. After that, the electrolyte films were taken off and dried in a vacuum oven at 60 °C for 12 h to completely remove residual solvents. Finally, the dried films were punched into small wafers (about 150μm in thickness) for testing. All procedures for the polymer electrolyte films preparation were carried out in an argon-filled glove box at the moisture and oxygen level below 1 ppm.

2.3 Characterization

The fourier transform infrared (FTIR) spectrum was taken on Nicolet NEXUS 670 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were carried out on JAM-ECA 600 Spectrometer (600 MHz) at 298 K. Coupling constants (J) and chemical shifts (δ) were denoted in Hz and ppm, respectively. The mass spectrometry (MS) analysis was recorded on Thermo Electron, LCQ Deca XP Plus mass spectrometer. UV–vis spectrum was recorded on a TU-1901 UV-Vis Spectrophotometer with a quartz cuvette (path length = 1 cm) at room temperature. The Thermo-gravimetric (TG) experiments were carried out on TGA Q5000 analyzer in the temperature range of 25-900 °C under N$_2$ atmosphere at a heating rate of 20 °C/min.

Ionic conductivity of the polymer electrolyte was determined by electrochemical impedance spectroscopy using Chenhua CHI760B Electrochemical Workstation. The electrochemical impedance spectra in the frequency range of 1Hz to 1MHz at temperature range between -10 and 80 °C were recorded [33]. A stainless steel /SPE/ stainless steel test cell was assembled in an Ar-filled glove box at the moisture and oxygen concentration below 1 ppm by sandwiching the polymer electrolyte film between two stainless steel plates as blocking electrodes. The assembled cell was and was kept 30 min at each measuring temperature to ensure thermal equilibration before measurement. The conductivities were calculated from the bulk resistance, i.e. Rb, obtained by the intercepts of the typical impedance curves for various temperatures (Figure S3). The ionic conductivity was calculated using the following equation[33]:

$$\sigma = \frac{L}{R_b \cdot S}$$

where L, S and R$_b$ are thickness (cm), effective area (cm$^2$) and bulk resistance (ohm) of polymer electrolyte, respectively.

The electrochemical stabilities of the polymer electrolyte films were studied by cyclic voltammetry (CV). The stainless steel /SPE/ Li test cell assembly was accomplished in an argon-filled glove box. Stainless steel blocking electrode was used as the working electrode while a lithium foil was used as the counter and the reference electrode in this system[30]. The CV was conducted in a
Shanghai Chenhua CHI760B Electrochemical Workstation between −0.5 to 6 V versus Li/Li⁺ at 80 °C with a scanning rate of 1 mV s⁻¹. Stress-strain tests for the polymer electrolyte films were performed by using a CMT6104 tensile testing machine with a tensile speed of 10mm min⁻¹ at room temperature (25°C).

3. RESULTS AND DISCUSSION

3.1 Characterization and analysis of PAcN oligomer

The molecular structure of the product is characterized by nuclear magnetic resonance spectrum (NMR, ¹H and ¹³C), mass spectrometry (MS), Fourier transform infrared spectroscopy (FTIR) and ultraviolet visible (UV-Vis) spectrum, respectively. The ¹H NMR spectrum of the product is shown in Figure 2a. The strongest signals at δ 1.63 (s) demonstrate the existence of the protons on methyl of the chain structure in prepared product. Other signals appear at 3.43, 2.54, 2.50 are assigned to small amount of adsorption of water, the DMSO residuary in the reaction process and solvent peak of DMSO, respectively. The ¹³C NMR spectrum (Figure 2b) of the product displays two singlets at 26.42 and 175.45ppm, which illustrate the existence of carbon atoms of methyl and unsaturated carbon in the chain structure, respectively. The peak with relatively strong intensity at 40 ppm is attributed to the carbon atom in solvent DMSO. On the basis of the results of NMR characterization, it can be obtained that the PAcN oligomer was formed according to the molecular formula as shown in Figure 1.

![Figure 2. The structure information of PAcN oligomer](image)

The investigation of FTIR provides further support for the formation of PAcN oligomer from the perspective of chemical bonds. In the FTIR spectrum (Figure3a), two sharp absorption peaks appear at 1585 cm⁻¹ and 1419 cm⁻¹, which indicate the presence of C=N bonds and C-H of methyl in
aliphatic, respectively[34]. However, the intensity of peaks around 2200 cm\(^{-1}\) belonging to C≡N bonds of raw materials weakened, indicating the reactions of opening C≡N bonds occurs and materials with C≡N bonds is formed[35], which unambiguously demonstrate that the PAcN is synthesized through electrochemical polymerization of acetonitrile. Moreover, the analysis of ultraviolet-visible (UV-Vis) absorption spectrum was carried for PAcN (Figure 3b). The maximum absorption band is formed at 238nm, which is attributed to the \(\pi\rightarrow\pi^*\) transitions of the conjugated backbone. The second band appearing at 286 can be assigned to the \(n\rightarrow\pi^*\) transitions of C≡N bond. Meanwhile, some absorption appears in the visible light region from violet to green light. That is the reason why the product color appears orange. According to the above characterization results, it clearly shows that the PAcN was successfully prepared by electrochemical approach.

![Figure 3](image)

**Figure 3.** Spectral characteristic of PAcN oligomer (a) FTIR spectrum (b) UV-Vis spectrum (in DMSO solution, \(\lambda=238, 286, 358\text{nm}\)).

The MS of the purified product (Figure 4) indicates that the product is not a polymer accorded with normal distribution of molecular weight, but an oligomer with certain molecular weight and polymerization degree. In the mass spectra, the peaks mainly appear at \(m/z = 327.40, 370.41\) and 721.13, which are attributed to PAcN oligomer with polymerization degree \(n= 8, 9\) and 17, respectively. The peak intensity at polymerization degree of 17 is significantly higher than other peaks. And the polymerization degree 8 and 9 could be considered as the broken parts of 17. Therefore, the polymerization degree of obtained product mainly is 17.

Combining the characterizations of the product, this oligomer may have a linear alternate carbon-nitrogen \(\pi\)-conjugated sequence structure. From the mass spectrum, it can be inferred that the PAcN oligomer has the defined polymerization degree of 17. But why the product with polymerization degree of 17 is more stable in this system? For linear alternate carbon-nitrogen \(\pi\)-conjugated PAcN, two possible polymer structures, including trans-form and cis-form structure, may exist. As the stabilization of the total energy at its lowest minimum, trans-form structure will be stable in the PAcN system[36].
Figure 4. Mass spectrometry and analysis on polymerization degree of PAcN oligomer.

Figure 5. Molecular models of circular PAcN oligomer. Perspective (a) From the top, (b) From the front, (c) From arbitrary direction.
However, in terms of the trans-formed chain structure of PAcN, the chain structure will bend under repulsive interaction force of the same side methyl because of the repellent action and stereo-hindrance effect among the methyls. With the increase of the polymerization degree, the bending degree of the PAcN oligomer chain increases[10]. Here we speculate that a circular PAcN oligomer with polymerization degree of 17 may be formed in our experimental system. The circular simulation structure of PAcN oligomer with polymerization degree n=17 have been built by Gauss View, as shown in Figure 5. Moreover, the $^{13}$C NMR spectrum demonstrates that only two kinds of carbon atoms exist while the $^1$H NMR spectrum demonstrates only one kind of hydrogen atom exist, which is well in consistent with the circular structure.

The thermal stability of the PAcN oligomer has been investigated by thermo gravimetric (TG) under nitrogen atmosphere (Figure 6). It is seen that the sample exhibits a gradual weight loss of about 3% at 320 °C, which is considered as the loss of residual solvent in PAcN oligomer. The weight loss mainly occurs between 400 to 550 °C with a weight loss of 34%, resulting from the decomposition of PAcN oligomer structure. The final stage of weight loss occurs between 550 to 900°C indicating the skeleton structure of PAcN gradually damaged. At 900°C, about 52 wt. % weight of the sample is left. According to the TG curve result, it demonstrates that the PAcN oligomer material has excellent heat resistance.

![Figure 6. TG analysis of PAcN oligomer under nitrogen atmosphere.](image)

3.2 Application in polymer electrolyte

After investigation of the structure and heat resistance of PAcN oligomer, the electrochemical performance test was carried. A small amount of the circular PAcN oligomer is added into the PEO based SPE for lithium batteries. The dependence of ionic conductivities of these polymer electrolyte films on temperature are shown in Figure 7. The ionic conductivity of these films increases with temperature in the range of -10–80°C, and a flat inflection appears at around 60 °C(PEO crystalline-to-
amorphous transition)[22]. Lithium ion (Li\(^+\)) transport depends on local relaxation and segmental motion of the PEO chains which can only be obtained in amorphous state, that is, above 60 °C [23]. For PEO-based SPEs with different ratio of PAcN oligomer doping, the basic feature is similar to PEO based SPEs. The ionic conductivity for the PAcN oligomer-free sample is only \(9.15 \times 10^{-7}\) S cm\(^{-1}\) at 30°C, as shown in Figure 7. As a small amount of PAcN oligomer doping, the ionic conductivities enhance greatly. By adding 3 wt. % PAcN oligomer, the ionic conductivity increases by more than 28 times and reach \(2.59 \times 10^{-5}\) S cm\(^{-1}\) at 30°C. However, when adding a higher amount (5 wt. %) of PAcN oligomer, the conductivity drops to \(1.48 \times 10^{-5}\) S cm\(^{-1}\) at 30°C, which mainly due to the incompletely dissolution of PAcN oligomer in PEO based electrolyte (Figure S2). In general, small amount of PAcN oligomer greatly improves the low-temperature conductivity of PEO based SPE.

![Figure 7. Temperature-dependent ionic conductivities of PEO polymer electrolyte with 0 wt. %, 1 wt. %, 3 wt. %, 5 wt. % PAcN oligomer.](image)

A schematic representation illustrating the mechanism that a small amount of PAcN oligomer greatly enhances ionic conductivity in PEO based SPE is provided in Figure 8. The circular PAcN oligomer is simplified as a circle and the blue line with different winding forms represents PEO chain with crystal and amorphous regions. Lithium ions are attracted by oxygen atoms in the PEO chain to form the coordination structure[37]. As the thermal motion of PEO chain, lithium ions realize migration by coordination - dissociation of lithium ion and oxygen groups[38]. Nitriles owns relatively high polarity, which results in promoting the dissociation of lithium salts[43-44]. It continuously provides more lithium ions for PEO chain and results in a higher ionic conductivity. In addition, introduction of PAcN oligomer increases the amorphous regions in the easily crystallized PEO matrix. Previous studies show that lithium ion transport mainly occurred in the amorphous region because PEO chain segment motion is more intense in the amorphous region [22]. For these reasons, a greatly improvement on ionic conductivity is observed when a small amount of PAcN oligomer doped.
Figure 8. Mechanism analysis diagram of conductivity enhanced by introduction of a small amount of PAcN oligomer in PEO polymer electrolyte.

The electrochemical stability of the PEO/PAcN polymer electrolytes are performed by cyclic voltammetry (CV). Figure 9(a) shows the initial CV curves of the polymer electrolyte film tested between -0.5 and 6 V. As can be seen, in the negative scan, a strong current is observed at about 0 V, corresponding to the plating of lithium on the stainless steel electrode. In the positive scan, the stripping of lithium appears at about 0.35 V[39]. The noticeable oxidation current observes at 4.25 V, 4.84 V, 5.16 V and 5.27 V corresponded to the oxidation potential for PEO based polymer electrolytes with 0 wt.% , 1 wt.%, 3 wt.% and 5 wt.% PAcN oligomer, respectively. The increased oxidation potential with addition of PAcN oligomer indicates an enhanced electrochemical stability, which attributed to the exceptional resistance to electrochemical oxidation of nitrile materials[40-41]. These PEO/PAcN polymer electrolytes with a electrochemical stability up to 5.0 V would be applicable for high voltage lithium ion battery.

The stress–strain curves PEO–Li based polymer electrolytes with different PAcN oligomer content are presented in Figure 9b. The maximal stress and strain of the pure PEO based polymer electrolyte is about 5.0 MPa and 37 %. With the addition of 1 wt. % PAcN oligomer, the maximal stress is very close to the pure PEO film (4.9 MPa). However, the elongation-at-break observably rises to 46 %. When 3 wt. % and 5 wt. % PAcN oligomer are added, the maxima stresses of polymer electrolytes slightly decrease to 4.5 MPa and 4.0 MPa, while the maximal strains dramatically increase.
to 54% and 65%, respectively. These increases in maximal strains can be explained by the increase in the amorphous region with the addition of PAcN oligomer[45], and the result is consistent with the increases in ionic conductivity as previously mentioned.

**Figure 9.** Characterizations for PEO polymer electrolyte with 0 wt. %, 1 wt. %, 3 wt. %, 5 wt. % PAcN oligomer (a) Cyclic Voltammogram curves and detail view of CV curves from 3.6V to 5.5V (inserted); (b) Comparison of the tensile stress-strain curves at room temperature.

In comparison with the pure PEO based polymer electrolyte, the addition of PAcN oligomer strongly improves the strain of PEO based polymer electrolyte, which is very useful for the assembly of flexible batteries [42].
4. CONCLUSIONS

PAcN oligomer was firstly prepared via a highly efficient electrochemical synthetic method. An annular structure model with 17 molecules is constructed based on the mass spectrum characterizations. An excellent heat resistance till 400°C was observed via the thermogravimetric analysis. When applied to the PEO based SPE as an additive, the PAcN oligomer strongly enhances the ionic conductivity of the SPE. The ionic conductivity of the SPE increases by more than two orders of magnitude (reached 2.59×10⁻⁵ S/cm at 30 °C) when a relatively low amount of 3 wt. % PAcN oligomer is added. Furthermore, small amount of PAcN oligomer doping greatly improves the electrochemical stability (>5.0 V) and maximal strains of PEO based SPE. The ingenious synthetic method, novel circular structure, and efficient enhancement on ionic conductivity may make such PAcN oligomer potentially as one of the most promising additive materials for next generation polymer electrolytes.

**SUPPLEMENTARY DATA:**

**Optimisation study**

Electropolymerization of PAcN was carried out by constant current (100 mA) at room temperature in 0.50 mol L⁻¹ iodide lithium and 19.0 mol L⁻¹ acetonitrile monomer in dimethyl sulfoxide (DMSO) on the silicon electrodes. With a view to optimize the reaction conditions for maximum yield and purity of this product, we have attempted to explore the influence of several factors such as ionic membrane and electrolytes. We screened several electrolytes like LiI, LiCl and LiClO₄, to our pleasure, LiI is the optimum electrolyte and facilitated the reaction in a relatively high yield. The molar concentration of these electrolytes was kept the same (0.50 mol L⁻¹). From the Table S1, it can be clearly seen that ionic membrane is especially important in the acetonitrile aggregation.

**Table S1 Optimisation study**

<table>
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<th>Entry</th>
<th>Ionic membrane</th>
<th>Electrolyte</th>
<th>Product colour</th>
<th>Yield</th>
<th>Product</th>
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<td>used</td>
<td>LiI</td>
<td>orange</td>
<td>1.0g</td>
<td>L</td>
</tr>
<tr>
<td>2#</td>
<td>none</td>
<td>LiI</td>
<td>black</td>
<td>&gt;100g</td>
<td>H</td>
</tr>
<tr>
<td>3#</td>
<td>used</td>
<td>LiCl</td>
<td>orange</td>
<td>0.5g</td>
<td>L</td>
</tr>
<tr>
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<td>used</td>
<td>LiClO₄</td>
<td>orange</td>
<td>0.6g</td>
<td>L</td>
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</tbody>
</table>

Product L is the product with low degree of polymerization while H is the product with high degree of polymerization. Product H is a black and extremely insoluble solid which is difficult for characterization. And product L is proved to be polyacetonitrile oligomer by mass spectrometry, nuclear magnetic resonance and Fourier transform infrared spectroscopy. Many extremely insoluble black materials which were difficult for
characterized would be produced in the anode room. The ionic membrane successfully separated from the target product and black materials and made the purification process more facile.

Figure S1 The influence of ionic membrane on acetonitrile aggregation. L used ionic membrane and got the polyacetonitrile oligomer, H did not use ionic membrane and got a black and extremely insoluble product.

Solubility study

Figure S2 shows that up to 3 wt. % PAcN oligomer can be totally dissolved in the precursor solution of PEO polymer electrolyte and form a homogeneous and viscous mixture, while in the situation of adding 5 wt. % PAcN oligomer, farthing PAcN oligomer still cannot be dissolved.

Figure S2 Solubility of different mass fraction of PAcN oligomer in the precursor solution of PEO polymer electrolyte.

Electrochemical impedance analysis

Ionic conductivity of the polymer electrolyte was determined by electrochemical impedance spectroscopy using Chenhua CHI760B Electrochemical Workstation. The electrochemical impedance spectra in the frequency range of 1Hz to 1MHz at temperature range between -10 and 80 °C were recorded. The
Electrochemical impedance spectra in Figure S3a clearly shows bulk resistance reduces with the increased temperature, and the addition of small amount of PAcN oligomer greatly reduces the bulk resistance of PEO-based SPE at 30 °C (Figure S3b).

![Figure S3. (a) Electrochemical impedance spectra of PEO based polymer electrolyte with 3 wt. % PAcN oligomer at different temperatures; (b) Electrochemical impedance spectra of PEO based polymer electrolyte with 0 wt. %, 1 wt. %, 3 wt. %, 5 wt. % PAcN oligomer at 30 °C.](image)

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References


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