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B. Muthuraaman<sup>a</sup>; Thiyagarajan Shanmugam<sup>b</sup>; P. Maruthamuthu<sup>a</sup>; A. Sultan Nasar<sup>b</sup>

<sup>a</sup> Department of Energy, University of Madras, Chennai, India <sup>b</sup> Department of Polymer Science, University of Madras, Chennai, India

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# Dye-Sensitized Solar Cell Based on a Blend of Hyperbranched Poly(aryl-ether-urethane) Electrolyte with TiO<sub>2</sub> Nanoparticles

B. MUTHURAAMAN<sup>1</sup>, THIYAGARAJAN SHANMUGAM<sup>2</sup>, P. MARUTHAMUTHU<sup>1,\*</sup> and A. SULTAN NASAR,<sup>2,\*\*</sup>

<sup>1</sup>Department of Energy, University of Madras, Guindy campus, Chennai, India

<sup>2</sup>Department of Polymer Science, University of Madras, Guindy campus, Chennai, India

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Hyperbranched poly(aryl-ether-urethane) is reported in this work as an efficient polymer electrolyte for photovoltaic application. Along with KI and I<sub>2</sub> as redox carriers in nanocrystalline dye-sensitized solar cell (DSC), this polymer yielded an overall conversion efficiency of 4.1%, upon illumination with visible light. The fabricated cell results in stable device performing under thermal stress maintaining about 70% of its initial value for 2 days in the direct atmosphere without sealing.

**Keywords:** Polymer solar cell, hyperbranched poly(aryl-ether-urethane), nanocrystalline dye-sensitized solar cell

## 1 Introduction

Dye-sensitized solar cells (DSC) are currently under investigation as potential low-cost devices for sustainable solar energy conversion. The originally developed DSC device utilizes an iodine-iodide redox mediator dissolved in acetonitrile to transport holes (1). Although the efficiency of light conversion was very impressive, one limitation of this liquid electrolyte-based DSC is the use of low viscosity and highly volatile solvents impedes commercialization. Recently, polymer electrolytes gained much importance in replacing the liquid electrolyte and many investigations have been reported. In this present study, for the first time we envisaged the successful use of hyperbranched polymer based electrolyte in DSC. Great efforts have been devoted to the synthesis and property investigation of hyperbranched polymers (HBPs) prepared from AB<sub>x</sub>-type monomer (where  $x \geq 2$ ). Their nonlinear architecture with numerous cavities, plenty of peripheral functional groups, solubility, melt and solution viscosity, amorphous nature are attractive scaffolds that can be suitably tailored to produce more fascinating materials. Hence, HBPs are potentially useful in the areas of nanoscience

and technology, polymer electrolytes, optical materials, electronic and magnetic materials and chemical sensors etc. (2).

Literature studies on hyperbranched polyurethanes have revealed the existence of a polymer with alkyl-ether-alkyl connectivity (3), whereas a polymer with aryl-ether-aryl connectivity has not been reported until 2007. Very recently, we have reported hyperbranched polyurethane with aryl-ether-aryl connectivity (4). The importance of aryl-ether-aryl connectivity lies in the fact that this hyperbranched poly(aryl-ether-urethane) is expected to have conducting properties similar to ion-conducting polymers and this property has been exploited in this report by utilizing it as a potential polymer electrolyte in nanocrystalline dye-sensitized solar cell.

## 2 Experimental

Hyperbranched poly(aryl-ether-urethane) was prepared according to our earlier report (4). The polymer electrolyte was prepared by dissolving 0.2 g of the synthesized polymer, 0.03 g of KI and 0.006 g of I<sub>2</sub> in 25 ml of N, N – Dimethyl formamide (DMF) at 80°C. Thin polymer electrolyte films were made by a solution casting technique and were used for characterization studies.

Nanoporous TiO<sub>2</sub> semiconductor thin films, which were approximately 15–17 μm thick, on FTO (fluorine doped tin oxide [F: SnO<sub>2</sub>]) conducting glasses of sheet resistance

\*Address Correspondence to: P. Maruthamuthu, Department of Energy, University of Madras, Guindy campus, Chennai 600025, India. Tel: +9144 22202780; Fax: +9144 22352494; E-mail: pmaruthu@yahoo.com

\*\*E-mail: drasultannasar@yahoo.com

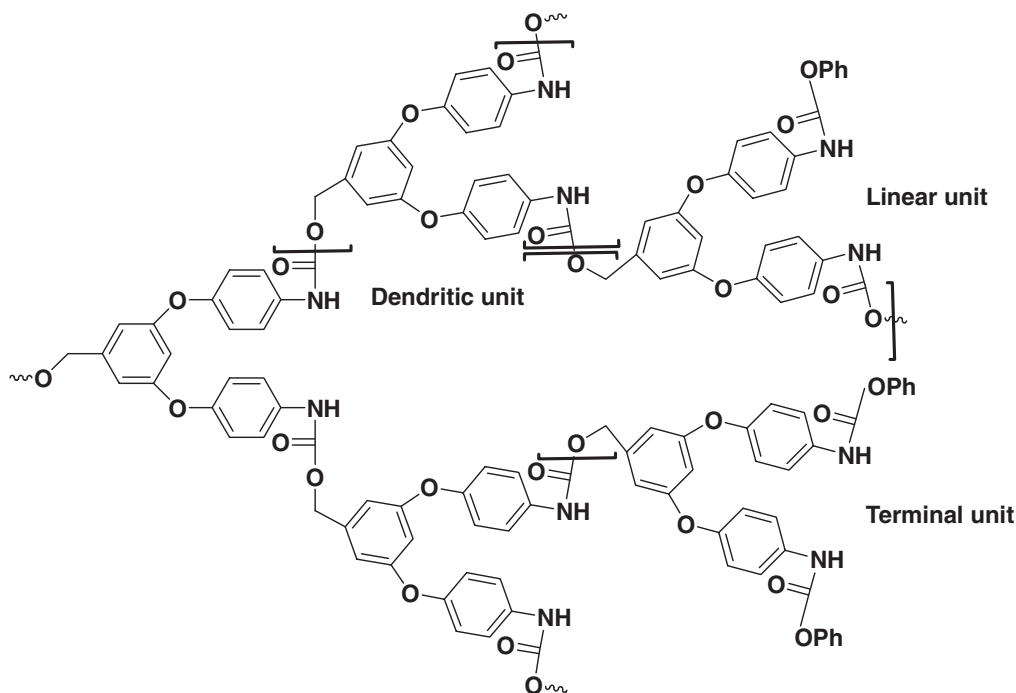


Fig. 1. Structure of hyperbranched poly(aryl-ether-urethane).

10  $\Omega$ /sq.cm [BHEL, India] were prepared according to our earlier reports (5). For the fabrication of solar cell in the present work, the dye [cis-dithiocyanato-*N*, *N*-bis (2,2' bipyridyl-4, 4' dicarboxylic acid)ruthenium(II)] dihydrate (N3 dye) adsorbed TiO<sub>2</sub> nanoparticles coated on the FTO conducting glasses were used as anode and the platinum coated FTO [coated by sputtering technique] was used as photocathode. On the surface of the photoanode, the polymer electrolyte solution ( $\leq 500 \mu\text{L}$ ) was cast and evaporated to dryness in a hot plate at 160°C. This was placed on the face of the cathode (after just wetting the photoanode again with the electrolyte in a very minute quantity of approximately  $< 150 \mu\text{L}$ ) by the way such that the polymer electrolyte was sandwiched between the two electrodes ( $2 \times 2 \text{ cm}^2$ ) and they were held tightly together by alligator clips.

A BAS-100A electrochemical analyzer was used to perform Linear Sweep Voltammetry to measure the current-voltage (IV) characteristics, under an illumination of area 1.27 sq.cm with tungsten halogen lamp (OSRAM, Germany) of intensity 40 mW/cm<sup>2</sup> [EXTECH - 33, Light meter with memory] by masking the remaining area with Teflon.

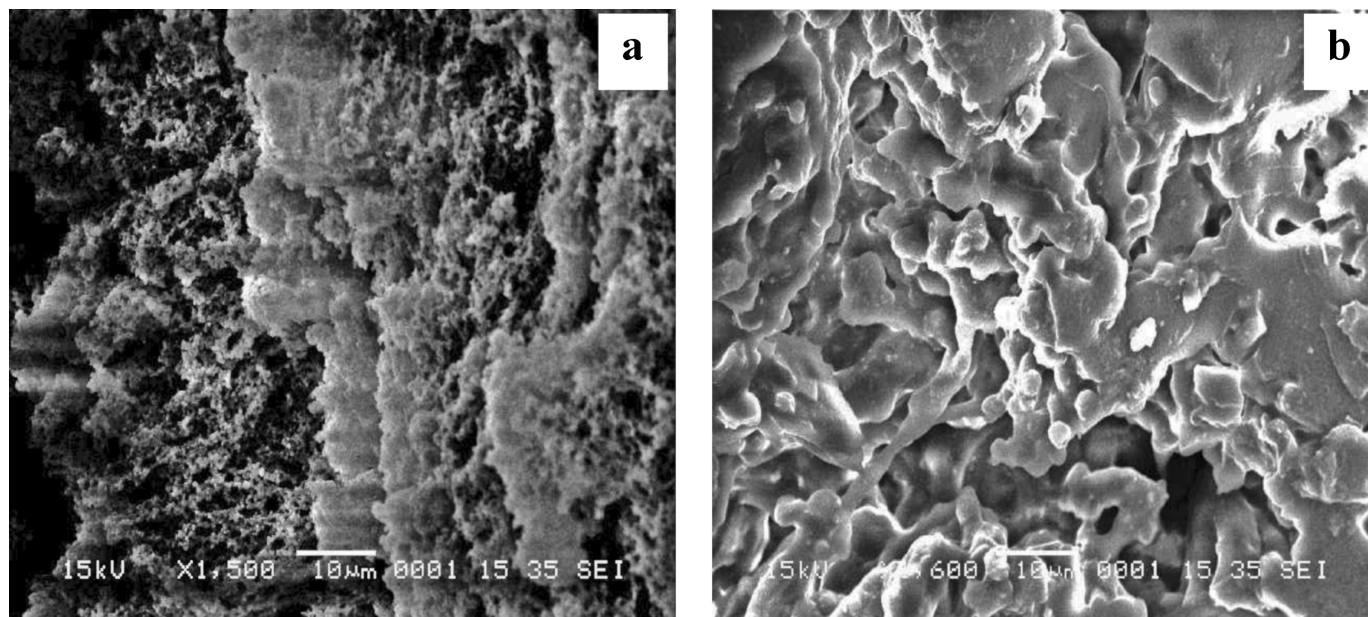
The SEM pictures were taken by a JEOL JSM 6362 Model. Electrical conductivities of the synthesized polymer electrolytes were evaluated from the complex impedance data obtained in the frequency range of 20 Hz to 1 MHz using Hewlett Packard 4284A Precision LCR Meter. The X-ray diffraction was taken using Siefert Model SF 60 (X-ray diffraction system with Cu-K <sub>$\alpha$</sub> 1 radiation).

### 3 Results and Discussion

The conducting property of hyperbranched polyurethane was first described by Hong et al. (6). This paved the way to synthesize a novel hyperbranched poly(aryl-ether-urethane) and the structure of this polymer is given in Figure 1. Molecular weight of the polymer was determined by GPC with polystyrene standards; the molecular mass ( $M_w$ ) was found to be  $3.1 \times 10^5$  and the dispersity was found to be 1.5. The glass transition temperature ( $T_g$ ) of the polymer was determined using DSC. The curve shown  $T_g$  at 190°C and does not show any decomposition up to 250°C. This observation indicates that the polymer chains are flexible at temperatures substantially below the decomposition temperature.

The SEM micrographs show vivid picture of the morphology of this polymer electrolyte. Figure 2a shows flake-like formation, which is a characteristic nature for high molecular weight polymers. The Figure 2b depicts the micrograph picture of the doped polymer (polymer + KI + I<sub>2</sub>) film that clearly reveals distributed amorphous layers. Such a feature is also confirmed by XRD studies. This polymer electrolyte when cast on the surface of the dye coated nanocrystalline TiO<sub>2</sub>, forms interconnected structures that fits well into the pores (Figure 3).

The nanoporous TiO<sub>2</sub> semiconductor thin films on FTO (F:SnO<sub>2</sub>) conducting glasses were coated with N3 dye as reported in the literature (5b, 7). The polymer electrolyte solution was cast on the dye plate and evaporated to dryness. The electrolyte solution does not penetrate deeply into TiO<sub>2</sub>



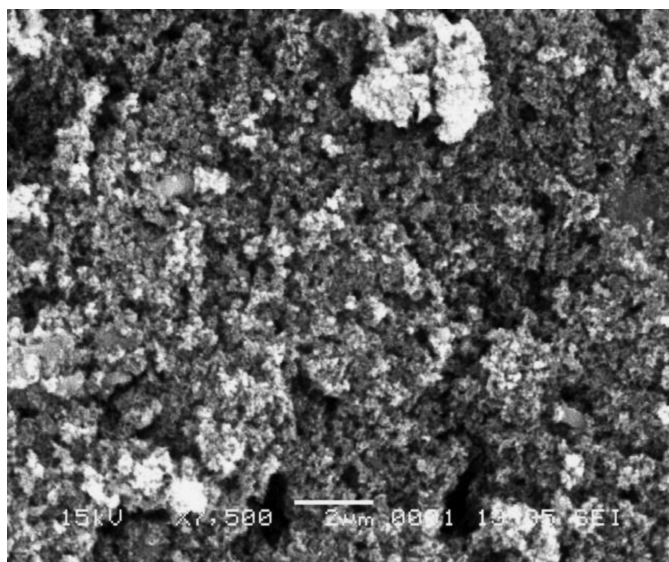
**Fig. 2.** (a) SEM image of pure polymer which shows the flakes like formation and (b) SEM image of doped polymer which shows amorphous layered structure.

film due to its high molecular mass, but spreads uniformly on the dye surface (Figure 3). The amorphous nature of this synthesized polymer electrolyte improves the connectivity between the cavities where the electrolyte is likely to flow freely as in liquid phase enhancing the conduction. The micrograph of the doped polymer electrolyte shows wave-like morphology, which relates to the amorphous layer formation through the interaction between the polymer segments and metal cations. The transport of metal cations

in the polymer electrolytes is coupled with the local relaxation and segmental motion of polymer chains, which can happen only when the polymer is in its amorphous state (8).

Conductivity of this polymer was studied using complex impedance spectroscopy. The skeleton of the polymer was suitably designed in such a way that the lone pair of electrons present in the carbonyl oxygen of urethane group readily interacts with the metal cations added, which also aids in increasing the performance of the DSC. The electrical conductivity ( $\sigma$ ) values of pure and doped polymer electrolytes are  $2.11 \times 10^{-5} \text{ S cm}^{-1}$  and  $3.44 \times 10^{-4} \text{ S cm}^{-1}$ , respectively (Fig. 4a and b). The ionic conductivity is a function of the number of charge carriers in the polymer matrix and it also increases with increasing chain flexibility. The ionic motion is strictly correlated with the segmental motion of the polymer chains. However, the required proportion of salt concentration can maintain the segmental motion of the polymer and may increase the ionic conductivity, which accounts for the high photovoltaic performance (9).

The current-voltage curve measured under illumination is shown in Figure 5. The fabricated cell exhibits a short circuit current ( $I_{sc}$ ) of 6.7 mA and an open circuit voltage ( $V_{oc}$ ) of 720 mV with a fill-factor (ff) of 0.43 under irradiation and the cell has an over-all conversion efficiency ( $\eta$ ) of 4.1% (Table 1). The fabricated cell results in a stable device performing under thermal stress maintaining about 70% of its initial value for 2 days in the direct atmosphere without sealing. The experiment was repeated with three such devices and the results were reproduced within an uncertainty of  $\pm 5\%$ .



**Fig. 3.** SEM image of doped polymer electrolyte coated on dye adsorbed  $\text{TiO}_2$ -FTO glass plate.

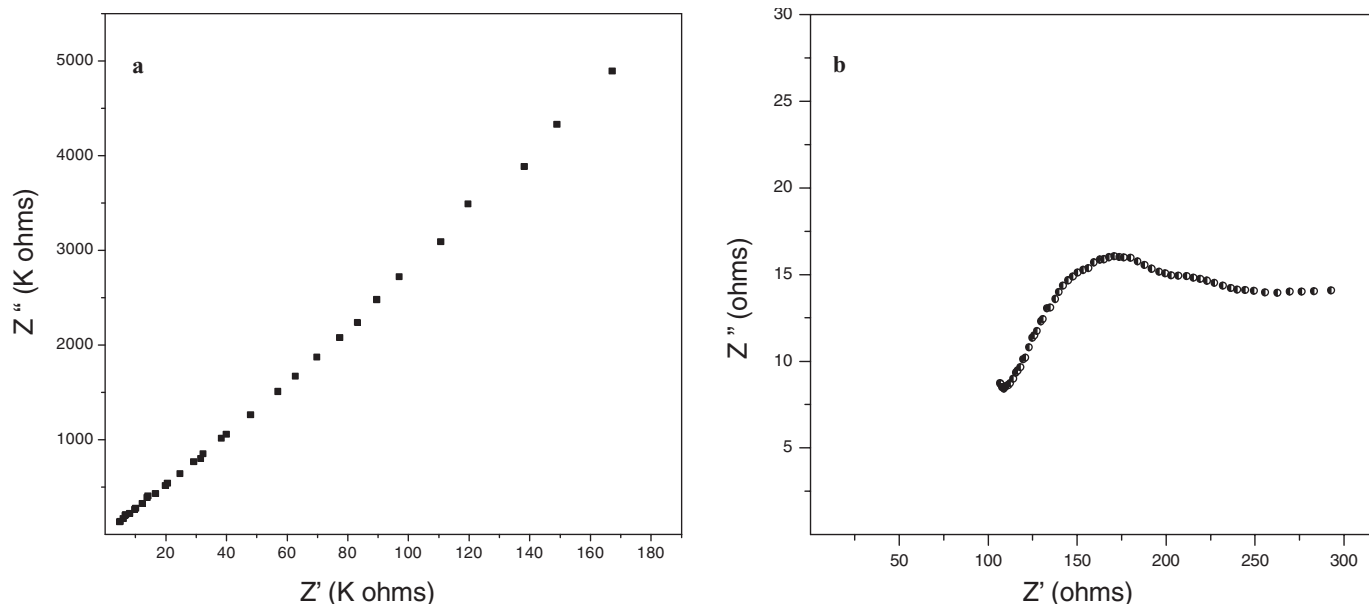


Fig. 4. (a) Complex impedance plot of pure polymer and (b) Complex impedance plot of doped polymer electrolyte.

Recent reports (10,11) indicate that the conversion efficiency obtained in the present case is considerably high. Furthermore, the stability is increased due to the fact that the carbonyl oxygen of urethane moiety forms an effective interaction with the alkali metal cations. These bonds are further stabilized by the presence of a lone pair of electrons in the carbonyl oxygen and also in the ether linkage which is well supported by the nitrogen in the urethane linkage (12). The cell operation mechanism involves absorption of visible light by the chemisorbed dye, and succeeding electron injection from the excited sensitizer into the conduction band of the semiconductor (Fig. 6). The

metal cation coordinated polymer chains are arranged in a three-dimensional mechanically stable network that creates free space and voids into which the  $I^-/I_3^-$  anions can easily migrate (13). The additives in the electrolyte are absorbed onto the surface of the  $TiO_2$  photoelectrode which confers a positive charge thereby increasing the concentration of iodide, which in turn would increase the  $V_{oc}$ . Thus, the use of polymer electrolytes without the addition of any polymeric agents explores the advantages of efficient ionic conduction and also the stability of a solid-state photovoltaic device.

The high efficiency may be attributed as the oxidized dye cations regenerated at an increased rate by electron donation from the redox electrolyte due to the presence of hole transporting materials, enabling efficient charge transport. In addition, the sensitizer plays a vital role as it impairs interfacial charge recombination, and also acts as an insulator in the ground state. The low recombination in the cell are either by the catalytic enhancement of hole transfer to the counter electrode due to platinization or by the presence of mobile ions in the electrolyte to screen photogenerated electrons and holes from each other. Hence, further reduction in the recombination reactions take place, which

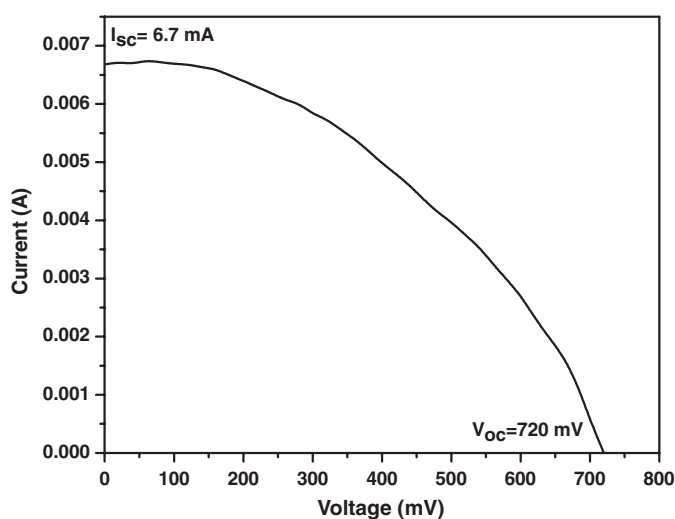


Fig. 5. Current-Voltage curve under illumination at  $40 \text{ mW/cm}^2$  light intensity.

Table 1. Performance parameters of HBP polymer based dye-sensitized solar cell

Type	$V_{oc}$ (mV)	$I_{sc}$ (mA)	FF	$\eta\%$
Hyperbranched Poly (aryl-ether-urethane)	720	6.7	0.43	4.1#

# light intensity  $40 \text{ mW/sq.cm}$ .

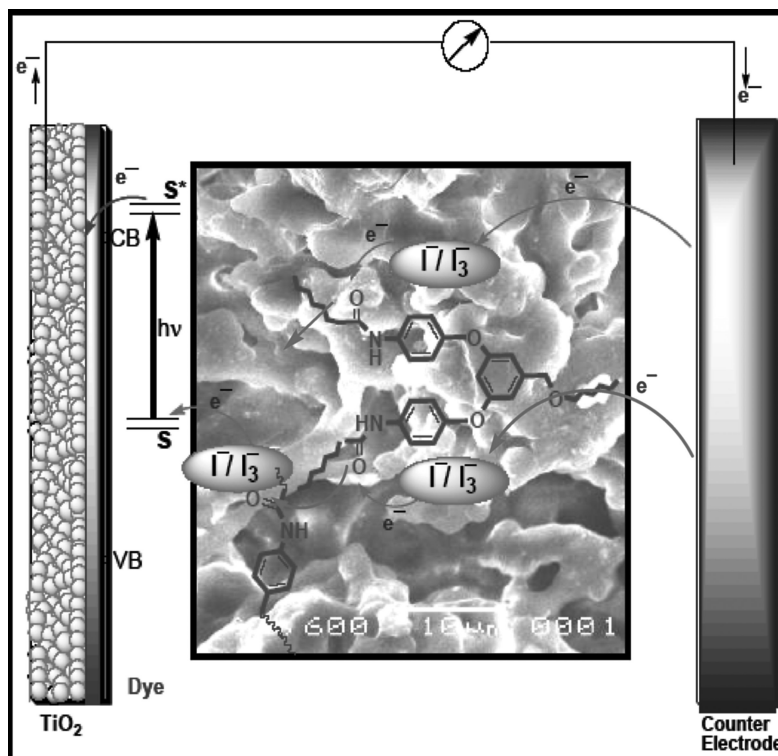


Fig. 6. Schematic representation of the reactions in the DSC with polymer electrolyte.

provides high charge mobility and an enhanced performance of the cell (14).

#### 4 Conclusions

The use of novel poly(aryl-ether-urethane) as an effective polymer electrolyte along with KI and I<sub>2</sub> as redox carriers in nanocrystalline dye-sensitized solar cell was demonstrated. The high conversion efficiency of this device is due to the adsorption of a high concentration of metal cation on the TiO<sub>2</sub> surface that confers a globally positive charge to the surface thereby increasing the local concentration of iodide and hence enhancing the dye regeneration rate and also suppressing the recombination to a considerable extent (15). In spite of its high molecular mass, the polymer electrolyte intercalates well with the nanoporous TiO<sub>2</sub>. The performance of this polymer solar cell can be improved by the enhanced ionic conduction, efficient electron transfer and high charge carrier transport.

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