# Quasi-solid-state dye-sensitized solar cells with cyanoacrylate as electrolyte matrix

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## Abstract

A quasi-solid-state dye-sensitized solar cells (DSSCs) employing a commercial glue ("SuperGlue®") as electrolyte matrix was fabricated. The cyano groups of the cyanoacrylate can form a supramolecular complex with tetrapropylammonium cations. This immobilizes the cations and therefore might lead to a favored anionic charge transport necessary for a good performance of the iodide/triiodide electrolytic conductor. Obtaining energy conversion efficiencies of more than 4% under $100 \, mW/cm^2$ of simulated A.M. 1.5 illumination, the cyanoacrylate quasi-solid-state electrolyte is an ordinary and low-cost compound which has fast drying property and offers significant advantages in the fabrication of solar cells and modules as it is in itself is a very good laminating agent. The influences of different porous layer thicknesses of titanium oxide and various kinds of cations on DSSC performance and long-term stability are presented.
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## 1. Introduction

Since 1991 [1], dye-sensitized nanocrystalline titanium oxide solar cells (DSSCs) using a liquid electrolyte as ionic conductor have received considerable attention because of their high solar energy conversion efficiencies up to 10% [2] and because of the prospective of a low production costs. However, the liquid electrolyte has some major technological disadvantages as it requires very advanced sealing and breakage protection to avoid leakage or evaporation losses lowering the performance as well as posing a threat to the environment. Therefore, large efforts have been made into replacing the liquid electrolyte by inorganic and organic semiconductors [3–6] or solid polymer electrolytes [7–10].

Unfortunately, photoelectrochemical cells based on solid polymer electrolyte have low conversion efficiency compared to the liquid versions, because of the high recombination rate at the $TiO_2$/solid-state-electrolyte interface and the low conductivity of the solid-state-electrolyte itself [11].

An alternative approach to retain the good device properties of the liquid electrolytes while drastically reducing these problems is the use of quasi-solid electrolytic materials. Polymer gel electrolytes can exhibit as high ionic conductivities as liquid electrolytes, and the gelation mitigates the potential instability against solvent leakage. In 2003, 6% solar energy conversion efficiency was reported in quasi-solid-state DSSCs based on poly(vinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) matrix showing stable performance under both thermal stress and light soaking, matching the durability criteria applied to silicon solar cells for outdoor applications [12]. In 2006, Biancardo et al. reported that quasi-solid-state DSSCs based on poly(methyl-methacrylate) (PMMA) polymer

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matrix were fabricated to be a large area solar module composed of a master plate of $25\,cm \times 25\,cm$ with 23 cells (active area of $12.5\,cm^2$ per cell) connected in series, which allows power extraction up to $\sim 100\,mW$ with an $I_{sc}$ of $25.1\,mA$ and a $V_{oc}$ of $10.65\,V$ under A.M. 1.5, $100\,mW/cm^2$ standard conditions presenting solar cells application in building elements like windows, facades and semitransparent roofs [13]. Other groups have used polymers or oligomers bearing reactive groups that can form a three-dimensional molecular network as solid matrix in which the charge-carrying ions can move. Very high efficiencies have been reported from three such approaches using different chemistry to achieve a network [14–16].

In this paper, we present a quasi-solid-state DSSCs utilizing a molecular network formed by a cyanoacrylate compound in which an iodide/triiodide redox couple performs the charge transport. Cyanoacrylate, the so-called "SuperGlue®", is a reactive monomer that can be easily polymerized under ambient humidity, forming a high molecular weight polymer. The gluing process responsible for the bonding between the two glass plates of the solar cell is based on the polymerization described in Scheme 1. From a technology point of view, this is very desirable, as it provides excellent mechanical stability by keeping the substrates together. Obtaining energy conversion efficiencies of more than 4% under $100\,mW/cm^2$ of simulated A.M. 1.5 illumination, the cyanoacrylate quasi-solid electrolyte is an ordinary and low-cost compound which has fast drying property and offers significant advantages in the fabrication of solar cells and modules as it is in itself a very good laminating agent.

## 2. Experimental

Titanium isopropoxide (TIP, 99.99%), tetrapropylammonium iodide (TPAI), 4-*tert*-butylpyridine (TBP), iodine, ethylene carbonate (EC), acetonitrile (ACN), all from Aldrich, were used as received. The titanium oxide paste (Ti-nanoxide HT) and the Ru dye (RuL2 (NCS) 2:2TBA, L: 2,2′-bipyridyl-4,4′-dicarboxylic acid, TBA: tetrabutylammonium, N-719) were bought from Solaronix. Cyanoacrylate was purchased as "SuperGlue®"(Ropid 100 Sekundenkleber from Conrad Elektronikversand, €3.59 per 20 g).

ITO-coated glass substrates were cleaned by ultrasonication in acetone and isopropanol. A ca. 100 nm thick layer of dense titanium oxide [17] measured by the Surface profilometer (Tencor Alpha-500) was coated by spin-coating, a mixture of TIP:ethanol:acetic acid in a volume ratio of 1:9:0.1 at 8000 rpm and subsequently sintering at 450 °C for 30 min. On these substrates, a porous layer of titanium oxide was deposited by spreading the titanium oxide paste with a glass rod. Scotch "Magic" tape® from 3M was used to determine the thickness. By changing the amount of paste and the layers of Scotch tape®, we can roughly vary the thickness of the porous layer. After sintering at 450 °C for 30 min and subsequently cooling to 80 °C, the titanium oxide electrodes were immersed into 0.4 mM solution of the N-719 Ru dye in ethanol in dry atmosphere at room temperature for 12 h.

The electrolyte solution is prepared by dissolving TPAI (0.5 M), iodine (0.1 M) and TBP (0.5 M) in a solvent mixture 4:1 of EC:ACN. Approximately 10wt% of
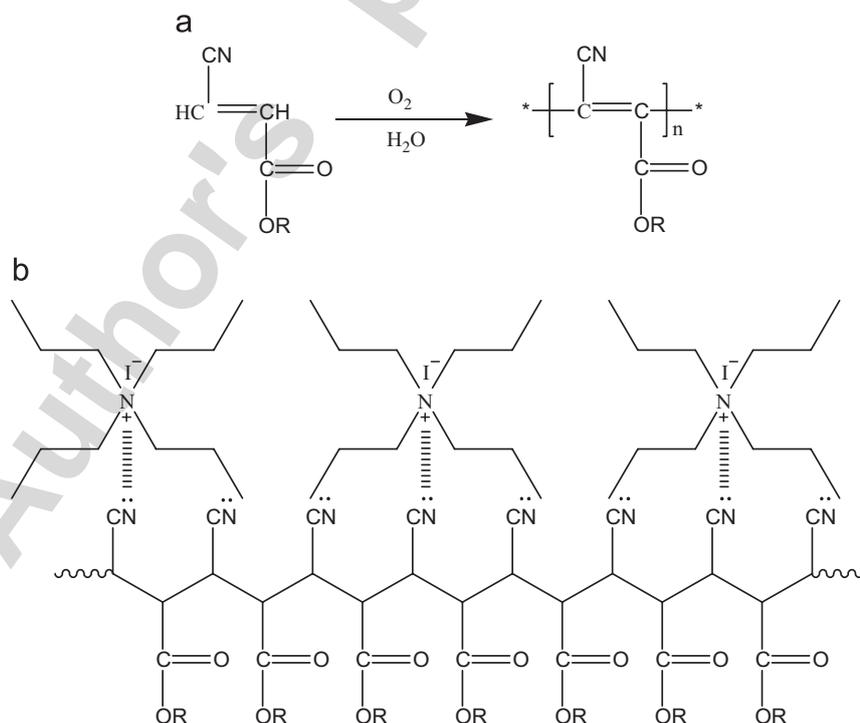


Scheme 1. (a) Chemical structure of cyanoacrylate and polymerization reaction; R indicates a short alkyl chain. (b) Proposed interaction mechanism between the tetrabutylammonium cation and the polymerized cyanoacrylate matrix.

cyanoacrylate was mixed into the solution directly before processing. One drop of this mixture was put on the sensitized titanium oxide electrode, which was immediately pressed together with a glass slide on which a ca. 200 nm thick layer of Pt was thermally evaporated. After about 1 min, depending on ambient humidity, the two glass slides were laminated together by the cyanoacrylate polymerization and were therefore mechanically rigid. To provide further stability, the slides were covered with standard "SuperGlue®". The active area of the cells was about 0.1 cm$^2$ determined by the cross section of Pt electrode and titanium oxide photoanode.

The cross-sectional images were taken with a JSM6400 scanning electron microscope (SEM). The current–voltage characteristics of the solar cells were measured using a Keithley 286 SMU. Simulated 100 mW/cm$^2$, A.M. 1.5 illumination was provided by a KHS Steuernagel solar simulator.

## 3. Results and discussion

The photoelectrochemical power conversion in a DSSC occurs at the titanium oxide–dye-electrolyte interface. After excitation, a very efficient photo-induced electron
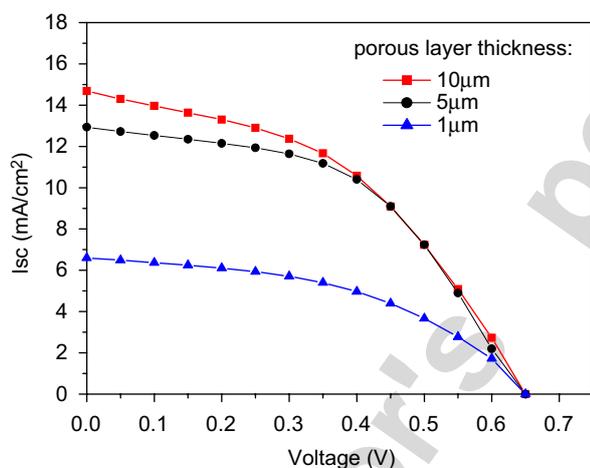


Fig. 1. Photovoltaic performance for DSSC with different porous titanium oxide layer thicknesses (100 mW/cm$^2$, A.M. 1.5; active area: 0.1 cm$^2$).

transfer from the excited dye molecules to the titanium oxide takes place, and then the electrons migrate through the titanium oxide until they reach the ITO electrode. The electric current thus produced is passed into an external circuit to perform electrical work. Electrons reenter the cell through the Pt counter electrode and are transferred to the electrolyte via a reduction reaction in which $I_3^-$ (triiodide) is converted to $I^-$ (iodide). The iodide ions transport electrons to the oxidized dyes on the titanium oxide where they are transferred to the dye molecules thus completing the electrical circuit. Therefore, the electrolytic conductor has to exhibit a good contact to the titanium oxide–dye interface as well as a high ionic conductivity.

As depicted in the lower part of Scheme 1, the cyano groups of the cyanoacrylate can form a supramolecular complex with tetrapropylammonium cations. This immobilizes the cations and therefore might lead to a favored anionic charge transport [10] necessary for a good performance of the iodide/triiodide electrolytic conductor. The small size of the cyanoacrylate monomer as well as its low viscosity allows an easy penetration into the titanium oxide electrode pores, which enlarges the interface area between the dye and the electrolyte resulting in efficient photoelectrochemical reactivity occurring and then suppressing the possible back electron transfer, finally resulting in an efficient charge collection at the dye–titanium oxide interface.

The thickness of the porous titanium oxide layer plays a crucial role for the conversion efficiency of the solar cell. A very thick porous layer provides a large surface area for dye adsorption, leading to a strong light absorption and therefore a large photocurrent. Fig. 1 shows the performance of solar cells with porous layer thicknesses of 1, 5 and 10 μm as determined under 100 mW/cm$^2$ of simulated A.M. 1.5 illumination. The corresponding power conversion efficiencies are around 2.0% (1 μm), 4.1% (5 μm) and 4.2% (10 μm). As expected, the current increases with the thickness of the layer. The decrease in the fill factor (FF) of the cell with the largest thickness can be attributed to the series resistance of the charge conducting layers. Thus, in this configuration the optimal porous layer thickness seems to be limited to about 5–10 μm, a common value for liquid electrolyte cells [1].
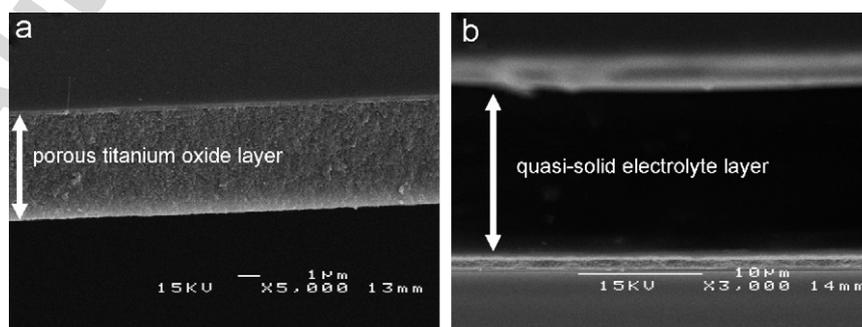


Fig. 2. Scanning electron microscopy images of cross sections of (a) the porous titanium oxide layer used in the determination of the layer thicknesses and (b) the laminated cell.

As can be observed from the SEM images in Fig. 2, the thickness of the electrolyte layer above the porous titanium oxide is in the order of 10–20 μm and varies with the lamination process. Many measurements show that these variations seem to have no significant impact on the solar cell performance.
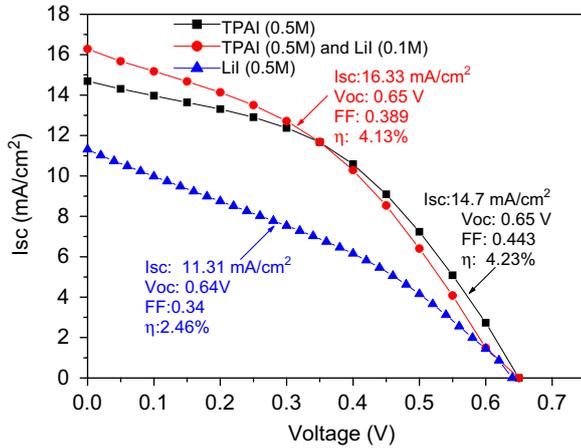


Fig. 3. Influence of different cations on the photovoltaic parameters of DSSC devices (100 mW/cm², A.M. 1.5; active area: 0.1 cm²).

Although the photovoltaic performance is determined by the anionic (triiodide/iodide) conductivity in the electrolyte, a different molecular size and amount of cations can also have an effect. $Li^+$ cations are commonly used in DSSCs, as they can enhance the photocurrent due to $Li^+$ intercalation at the $TiO_2$ surface. This increases the electron diffusion coefficient and induces a shift of the $TiO_2$ conduction band potential, resulting in an increased charge injection yield [18]. It is shown in Fig. 3 that DSSC fabricated only with $Li^+$ (0.5 M) as cations gave $I_{sc}$ of 11.31 mA/cm², $V_{oc}$ of 0.64 V, FF of 0.34 and overall efficiency of 2.46%. Whereas DSSC employing only $TPA^+$ (0.5 M) showed $I_{sc}$ of 14.7 mA/cm², $V_{oc}$ of 0.65 V, FF of 0.443 and overall efficiency of 4.23%. The introduction of a blend of cations ($TPA^+$ 0.5 M and $Li^+$ 0.1 M) as electrolyte mixture gave an increase in short circuit current density reaching 16 mA/cm². Despite the high current, the preferred adsorption of $Li^+$ at the $TiO_2$ surface might decrease the amount of mobile cations [19], resulting in a lower FF (from 0.44 to below 0.4) and leading to a slightly lower overall efficiency. We ascribe the increase in efficiency of the DSSC in presence of $TPA^+$ to the strong interaction between cyano groups and the positive charges on the nitrogen of $TPA^+$. This indicates that the larger



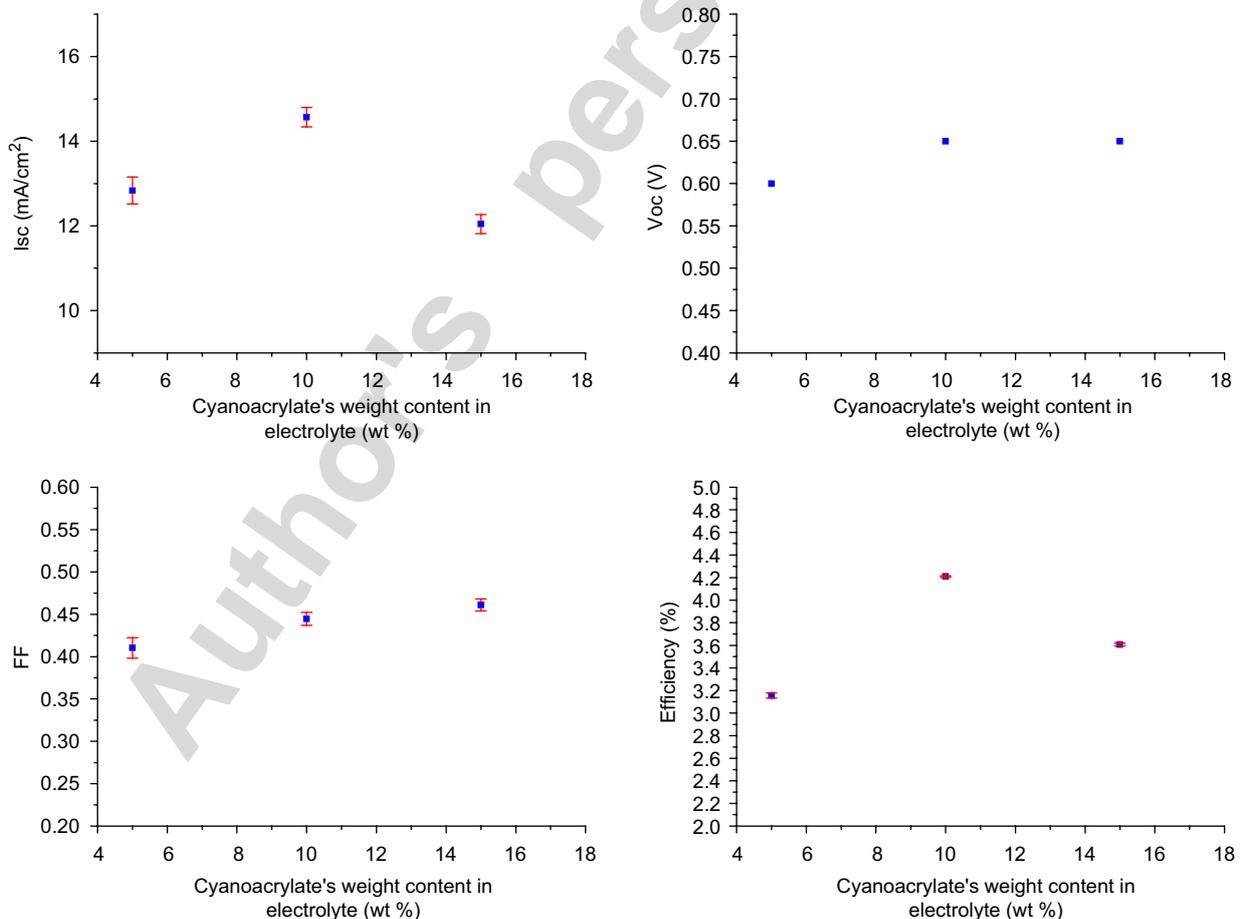Fig. 4. Influence of different cyanoacrylate's weight content (wt%) on the photovoltaic parameters of DSSC devices (100 mW/cm², A.M. 1.5; active area: 0.1 cm²).

TPA$^+$ cations are more likely to be bound to the polymerized cyanoacrylate, providing a better conduction of the iodide ions.

Different weight contents of cyanoacrylate in the electrolyte also affect the performance of the quasi-solid-state DSSC. It can be observed in Fig. 4 that the short circuit current density ($I_{sc}$) is the most influenced parameter, increased from 12.8 to 14.6 mA/cm$^2$ when the weight content of cyanoacrylate was changed from 5% to 10%. The reason for this increase could be due to the formation of the optimized supramolecular complex network between cyanoacrylate and tetrapropylammonium which favors anionic transport. When the weight content of cyanoacrylate is further increased, the viscosity of the electrolyte is increased which makes it difficult for the electrolyte to penetrate into the pores of titanium oxide, resulting in lower values of $I_{sc}$. It is also shown in Fig. 4 that both open-circuit voltage ($V_{oc}$) and FF do not show much change, and the efficiency of DSSC is mostly affected by the changes of $I_{sc}$. As a consequence of our experimental observations, the optimized weight content of cyanoacrylate is 10% presenting 4.2% efficiency.

For the use of our quasi-solid DSSCs, the long-term stability of the devices is essential. Possible degradation mechanisms are either the evaporation of the remaining solvent and precipitation of I$_2$ or dye desorption. This first leads to a decrease of the electrolyte conductivity and therefore an increase in series resistance. The dye desorption leads to a lower light absorption and therefore reduced solar cell current [18].

In Fig. 5, the evolution of the solar cell parameters over a time of nearly 400 h of storage under ambient atmosphere is shown. Both FF and open-circuit voltage show no significant degradation, while the short circuit current drops by a factor of more than 1.5. The $V_{oc}$ is determined by the difference between the fermi level of the TiO$_2$ and the redox potential of the electrolyte, which is mainly influenced by the molar ratio of triiodide/iodide. It is observed in Fig. 5 that the $V_{oc}$ is slightly decreased, which maybe due to a slight loss of electrolyte resulted in changes of the molar ratio of triiodide/iodide. The FF shows no sign of a severe decrease implying no significant increase in the series resistance. The N-719 Ru dye is hydrophilic and can desorb from the titanium oxide surface under the influence of polar products and water [18]. We ascribe the main degradation parameter to the loss of active dye in the device. In order to improve the stability of such devices, other ionic liquids such as DMPII (1,2-dimethyl-3-propy-limidazolium iodide) should be tested alongside with amphiphilic Ru dyes [12].

## 4. Conclusions

We have fabricated a DSSC that incorporates a novel quasi-solid electrolyte based on cyanoacrylate and a triiodide/iodide redox couple. These materials' combination provides
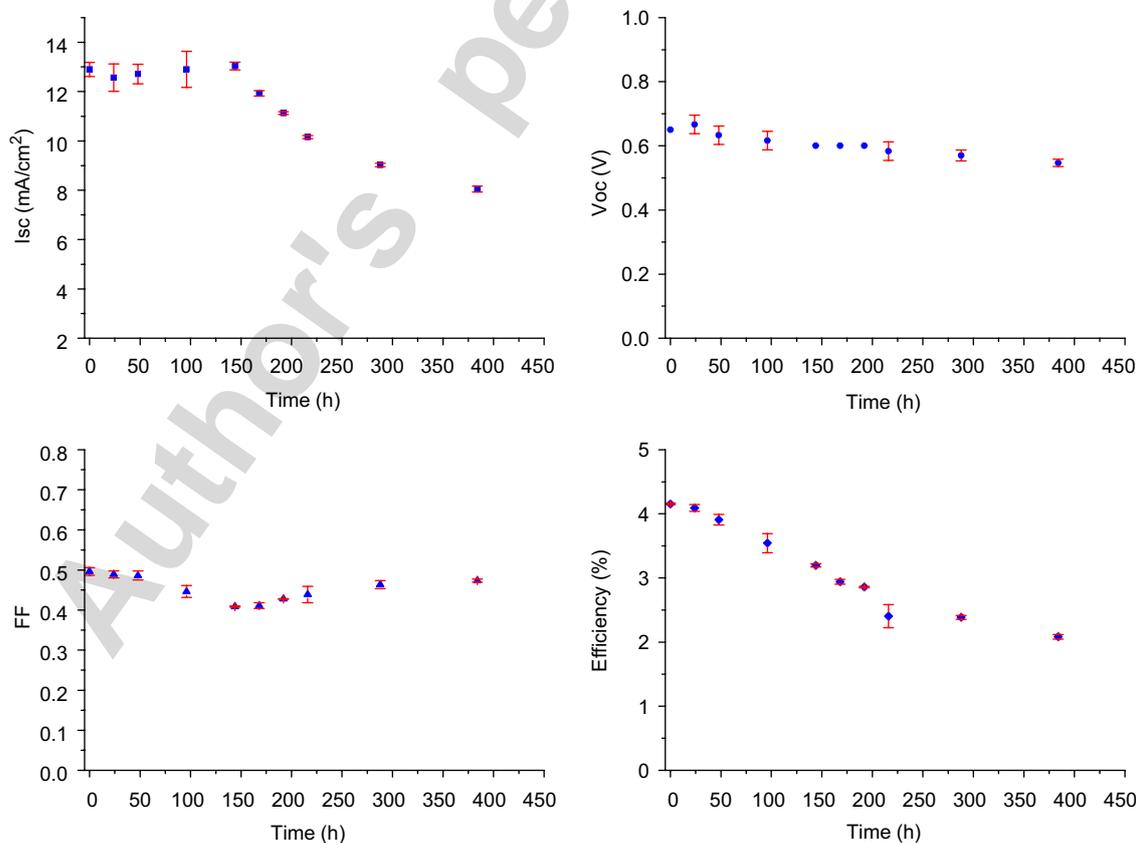


Fig. 5. Evolution of the solar cell parameters over an extended period of time of storage under ambient atmosphere.

solar energy conversion efficiencies of over 4% in combination with extraordinarily low cost and fast drying property. An especially noteworthy advantage is the laminating property of the cyanoacrylate ("SuperGlue$^{®}$") that allows for a very easy production of mechanically stable large area solar cells. Measurements of long-term stability show promising results, which can be further improved by structural engineering of the dyes and salts used.

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