

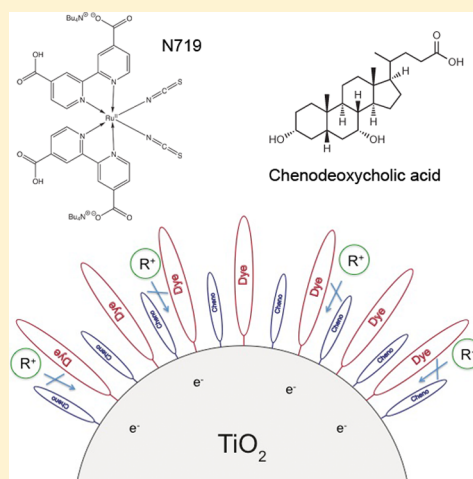
Dye Regeneration Dynamics by Electron Donors on Mesoscopic TiO₂ Films

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ABSTRACT: The influence of different redox mediators and electrolyte constituents on charge transfer processes in dye-sensitized solar cells (DSC) was studied by contactless transient photoconductance (TPC) measurements. Device subsets without FTO (Fluorine-doped tin oxide) contacts were prepared to increase the reliability and sensitivity of the TPC measurements. Results revealed a decrease of electron decay rate with increasing concentration of the redox couple ([Co(III/II)(bpy)₃](PF₆)_{3/2}) which was attributed to an improvement of the reduction of the dye cation (dye regeneration). Furthermore, the presence of the electrolyte additives 4-*tert*-butylpyridine (TBP) and chenodeoxycholic acid was found to decrease the electron decay rate, which was attributed to blocking of interfacial charge recombination. The use of other redox couples (quinone/hydroquinone and ferrocene/ferrocenium) with these electrolyte additives displayed a significant improvement for ferrocene/ferrocenium, while the electron lifetime for quinone/hydroquinone appeared unaffected. Prospects for a further optimization of DSC's redox couples are discussed.



1. INTRODUCTION

Alternatives to the commonly used tri-iodide/iodide redox couple in dye-sensitized solar cells (DSC) are needed to reduce the energetic mismatch between the oxidation potential of the dye and the redox couple as well as its corrosive properties toward sealants and metal interconnects. The iodide/tri-iodide system has been successful due to the slow recombination kinetics between electrons in the TiO₂ with the oxidized dye and the oxidized state of this redox system, which minimizes recombination losses in the DSC. One of the main drawbacks, however, is the large energetic mismatch between the redox potential of the dye and that of the iodine redox system. This leads to voltage losses of several hundreds of meV limiting the open circuit voltage (V_{OC}) to 0.7–0.8 V, and thus the overall cell efficiency.¹ However, this slow and complicated reaction kinetics involving two electrons may also decrease the electron recombination probability and so improve the efficiency of this system for solar energy conversion.

Single-electron redox couples based on cobalt and ferrocene have more positive redox potentials, therefore reducing the potential loss (Figure 1). They are less colorful^{2,3} than tri-iodide and lead to higher J_{sc} 's. Furthermore, their redox potential can be further tuned using different ligands with different electron donating or withdrawing groups closer to the oxidation potential of the dye to minimize energy loss in the dye regeneration step to obtain a higher V_{OC} .

Cobalt polypyridine complexes are promising candidates due to their favorable redox potential enabling open-circuit voltages

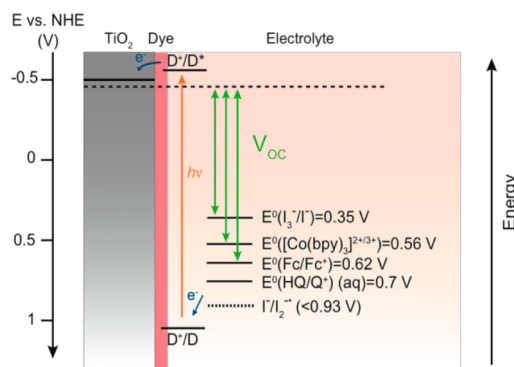


Figure 1. Schematic energy diagram for several redox couples in a dye-sensitized solar cell. This schema should give some hint of the redox potentials, although the real redox potentials for our device arrangement cannot be determined.

above 1 V.^{2,4} The previously observed fast recombination rates (at least an order of magnitude higher) when compared to the tri-iodide/iodide system⁵ were reduced by designing new organic dyes with bulky groups without affecting the electron transfer rate.⁶ Recently, this approach was applied to the donor-

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Table 1. Composition of Cobalt Bipyridine Based Electrolyte Solutions with Acetonitrile (ACN) as Solvent

| electrolyte name ⁺ constituents ↓ | Co ²⁺ /Co ³⁺ concentration/mol·L ⁻¹ | (50%) Co concentration/mol·L ⁻¹ | (10%) Co concentration/mol·L ⁻¹ | Co ²⁺ /Co ³⁺ /50% (LiClO ₄ /TBP) concentration/mol·L ⁻¹ |
|---|--|--|--|---|
| [Co(II)(bpy) ₃](PF ₆) ₂ | 0.22 | 0.11 | 0.022 | 0.22 |
| [Co(III)(bpy) ₃](PF ₆) ₃ | 0.03 | 0.015 | 0.003 | 0.03 |
| 4- <i>tert</i> -butylpyridine | 0.2 | 0.2 | 0.2 | 0.1 |
| lithiumperchlorate | 0.1 | 0.1 | 0.1 | 0.05 |
| chenodeoxycholic acid | 0; 0.1 (as indicated) | | | |

Table 2. Composition of Electrolyte Solutions with Ethanol As Solvent

| electrolyte name ⁺ constituents ↓ | I ₃ ⁻ /I ⁻ concentration/mol·L ⁻¹ | I ₃ ⁻ /I ⁻ /TBP concentration/mol·L ⁻¹ | Fc/Fc ⁺ concentration/mol·L ⁻¹ | HQ/Q ⁺ concentration/mol·L ⁻¹ |
|---|---|--|--|---|
| lithiumiodide | 5 | 5 | | |
| iodine | 0.05 | 0.05 | | |
| 4- <i>tert</i> -butylpyridine | | 0.05 | | |
| ferrocene | | | 0.01 | |
| ferrocenium | | | 0.001 | |
| hydroquinone | | | | 1 |
| benzoquinone | | | | 0.01 |
| chenodeoxycholic acid | | | 0; 0.05; 0.5; 1 (as indicated) | 0.1 (as indicated) |

π -acceptor dye YD2-o-C8, and a world record efficiency of 12.3% under AM1.5 illumination conditions was obtained.⁷

Significant progress has also been achieved in the application of single-electron redox couples based on ferrocene/ferrocenium. The exclusion of oxygen as well as the use of certain electrolyte additives reduced recombination losses and led to efficiencies of 7.5%.⁸ Recently, a study of several ferrocene derivatives revealed that for efficient dye regeneration, the difference between the redox energy of the electrolyte and HOMO level of the sensitizer should be in the range of 0.36 V, which gives the flexibility to increase the device V_{OC} by selecting appropriate dye and redox electrolyte combinations.⁹

In this work, the kinetics of interfacial electron transfer on mesoscopic TiO₂ films sensitized with N719 is investigated by contactless transient photoconductance (TPC) measurements.^{10,11} These measurements do not permit the investigation of the transport of the positive charge to the counter electrode. Consequently, it is not possible to judge the device's overall power conversion efficiency of the systems investigated. However, the information obtained can be attributed unambiguously to electron transfer kinetics at the photoanode and is not perturbed by the influence of electrode processes at the counterelectrode.

Previous work¹² has shown that the application of this technique to subsystems of dye-sensitized solar cells (DSC) without FTO back contacts and counter electrode yields detailed information on the charge exchange between semiconductor, dye cation, and redox couple. We prepared the same type of samples for the investigation presented here but in addition to the standard tri-iodide/iodide (I₃⁻/I⁻) redox couple electrolyte used in ref 12, we also investigated the influence of ferrocene/ferrocenium (Fc/Fc⁺), quinone/hydroquinone (HQ/Q⁺), and cobalt bipyridine (Co²⁺/Co³⁺) based redox systems on charge carrier kinetics in TiO₂ sensitized with N719. Furthermore, the influence of the addition of 4-*tert*-butylpyridine (TBP) and chenodeoxycholic acid (cheno) on charge carrier kinetics in these systems was investigated.

The redox potentials of such charge mediating systems are normally determined in solvents like water, acetonitrile, or ionic liquids with respect to the NHE (normal hydrogen electrode)

or as an internal reference to the ferrocene redox couple. Obviously in our arrangement such direct conversion of the redox potentials cannot be made. Still one can expect that in all cases used here, the redox capabilities of the different redox couples can be used to probe charge transfer and quenching reactions. This is also true for the quinone/hydroquinone system.^{13,14} It was shown that this redox system can also operate in aprotic solvents by the formation of quinhydrone radical as an intermediate step and, upon further oxidation, to finally form the quinone.^{13–16}

2. EXPERIMENTAL SECTION

2.1. Materials. All solvents and reagents were used as received. TiO₂ paste DSL18NR-T (approximately 20 nm average particle size, transparent), Ruthenium dye N719 was purchased from Dyesol. Ethanol, acetonitrile (99.8%, anhydrous), 4-*tert*-butylpyridine (99%), iodine (99.99%, metals basis), chenodeoxycholic acid, ferrocene (98%), ferrocenium tetrafluoroborate, hydroquinone ($\geq 99\%$), and benzoquinone ($\geq 98\%$) were provided by Sigma-Aldrich. Lithium iodide (anhydrous) and *t*-butanol ($\geq 98.5\%$) were purchased from Fluka. Lithium perchlorate (99.5%, anhydrous) was purchased from Ventron-Alfa. RBS 50 concentrate (Carl Roth) was diluted to 3% v/v in water. Milli-Q (Millipore) grade water was used in all experiments.

The synthesis of the cobalt (III/II) tris-bipyridyl redox system, ([Co(III/II)(bpy)₃](PF₆)_{3/2}), was performed as previously described.²

2.2. Sample Preparation. TiO₂ films were prepared via screen-printing. A TiO₂ paste (DSL 18 NR-T) was screen-printed (SEFAR 61–64W screen mesh) on glass substrates (Corning 7059, $d = 0.5$ mm). Surface profiles revealed a layer thickness of about 12.5 μm . The layers were sintered at 520 °C for 30 min, followed by a cooling under ambient atmosphere. At about 60 °C, samples were immersed in a 0.3 mM dye solution (N719 in *tert*-butanol/acetonitrile) overnight for typically 16–20 h. After sensitization, the area surrounding the sensitized TiO₂ was masked by means of an adhesive PTFE tape (Polytetrafluoroethylene, CT-6571, Chem-Tec) and 3 μL of the electrolyte solution was deposited on the sensitized TiO₂

area, and the solvent was let to evaporate in a procedure that is called "treatment" below. The composition of the different electrolytes is given in Tables 1 and 2 below.

2.3. Methods. Transient photoconductance measurements (TPC) in the microwave frequency range were performed by using a K_a -band (28–40 GHz) apparatus as previously described.^{10,11} The excitation occurred by 10 ns (fwhm) pulses of an Nd:YAG laser at wavelengths of 532 nm with a diameter of about 3 mm. The excitation intensity was adjusted by the use of calibrated filters. The TPC signal ($\Delta P/P$), is the relative change of the microwave power reflected by the sample induced by a photogenerated change of the conductance ($\Delta S(t)$).¹¹ The TPC signal is proportional to this photo-generated change of the conductance:^{11,17,18}

$$\frac{\Delta P(t)}{P} = A \Delta S(t)$$

where A is a sensitivity factor depending on the experimental configuration and the electrical parameters of the sample and $\Delta S(t)$ refers to electrons at the bottom of the conduction band and holes at the top of the valence band,^{10,11,18,19}

$$\frac{\Delta P(t)}{P} = A \{ \Delta n(t) \mu_e + \Delta p(t) \mu_p \} e$$

with $\Delta n(t)$ ($\Delta p(t)$) the total number of excess electrons (holes) with mobility μ_e (μ_p) at time t in cm^{-2} referring to an integration of the excess carrier concentration over the thickness of the sample. For the experiments on DSC device subsets presented here, only electrons are generated in TiO_2 after light excitation of the dye. Therefore, the TPC signal can be written as follows:

$$\frac{\Delta P(t)}{P} = A \Delta n(t) \mu_e e$$

3. RESULTS AND DISCUSSION

Figure 2 compares the TPC signal of a N719 sensitized TiO_2 layer on a glass substrate to samples treated with the standard tri-iodide/iodide and the Fc/Fc^+ redox electrolyte.

In the untreated film, the electron decay observed is clearly due to recombination with the dye cation. The decrease of the

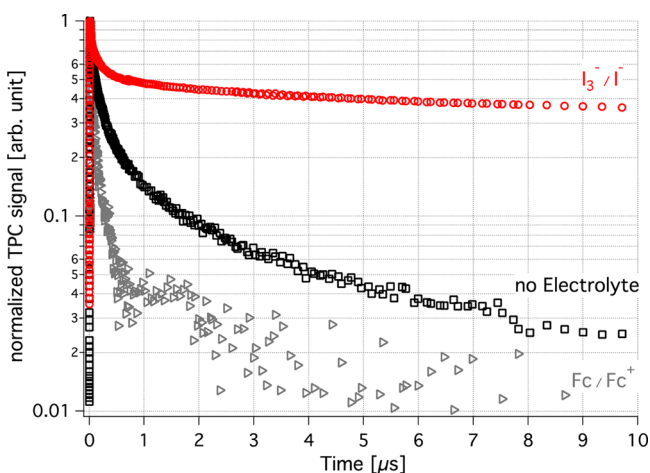


Figure 2. Normalized TPC signals induced by laser pulses at 532 nm of sensitized TiO_2 films on glass substrates with/without redox pair and the Fc/Fc^+ redox pair. Laser intensity: $1.3 \text{ mJ}/\text{cm}^2$.

decay rate in the film treated with the tri-iodide/iodide containing electrolyte was attributed to the decrease of the concentration of dye cations due to transfer of the positive charge from the dye to the tri-iodide/iodide redox couple.¹² This implies evidently that oxidized species of this redox couple have a much lower probability of reacting with the electrons in the TiO_2 than the dye cation. Due to the kinetically slow reduction rates of the oxidized form of the redox couple ($\text{I}_3^{\bullet-}$ or I_3^-), the electron decay rate decreased. In contrast to this behavior, the presence of the kinetically fast one electron charge transfer ferrocene/ferrocenium system led to a dramatic increase of the decay rate (Figure 2). This behavior can be explained by an increased recombination with the ferrocenium ion.

Inspired by the work of Daeneke et al.,⁸ chenodeoxycholic acid (cheno) was added to the ferrocene/ferrocenium electrolyte solution and its effect on electron decay rate investigated. Interestingly, it was observed that by increasing the concentration of cheno in the electrolyte, there is a decrease in decay rate of TPC signals (Figure 3).

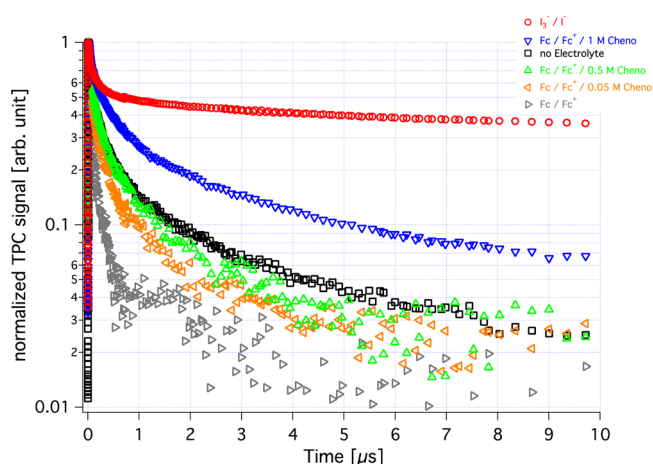


Figure 3. Normalized TPC signals induced by laser pulses at 532 nm of sensitized TiO_2 films on glass substrates with the Fc/Fc^+ redox pair and varied chenodeoxycholic acid concentration. Laser intensity: $1.3 \text{ mJ}/\text{cm}^2$.

Even though the addition reduced the decay rate, this effect is smaller than the decay reduction observed with the tri-iodide/iodide system.

On the basis of the promising results of the additive cheno on decay rates in ferrocene based redox electrolytes, similar experiments were performed with quinone/hydroquinone and cobalt bipyridine based redox systems. The TPC signals of the N719 sensitized TiO_2 films treated with the $[\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2}$ based redox electrolyte system² show a considerably decreased decay rate compared to the samples treated with the Fc/Fc^+ with and without cheno (Figure 4). Upon the addition of cheno to the cobalt redox system, one can observe a further improvement, i.e., a decrease of the electron decay rate in the system.

The behavior of the redox couple quinone/hydroquinone is again different from that of the $[\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2}$ system: An increase of the decay rate and no effect of the additive cheno was observed (Figure 4), the measurement of the quinone/hydroquinone redox system without cheno is not shown in Figure 4, but is similar to the case with 0.1 M cheno).

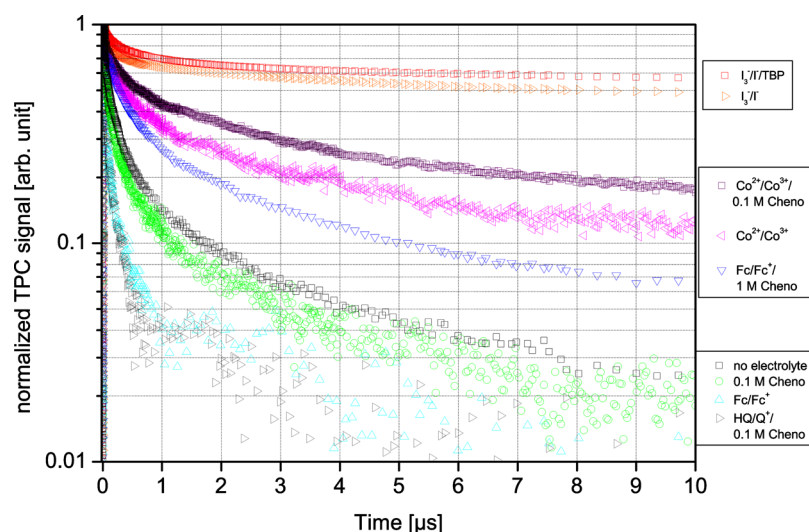


Figure 4. Normalized TPC signals induced by laser pulses at 532 nm of sensitized TiO_2 films on glass substrates with the Fc/Fc^+ , HQ/Q^+ , and $\text{Co}^{2+}/\text{Co}^{3+}$ redox pair and chenodeoxycholic acid additive. Laser intensity: $1.3 \text{ mJ}/\text{cm}^2$.

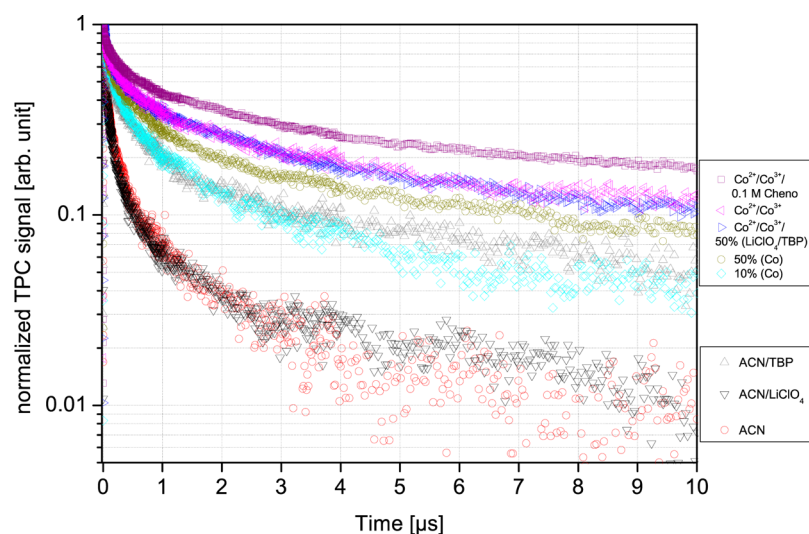


Figure 5. Normalized TPC signals induced by laser pulses at 532 nm of sensitized TiO_2 films on glass substrates: Influence of electrolyte constituents and redox concentration. Laser intensity: $1.3 \text{ mJ}/\text{cm}^2$.

The increase in the decay rate is explained by an additional recombination of the electron with acceptor states associated with the redox couple. A possible explanation for the apparently unaffected decay behavior of the hydroquinone/benzoquinone system in the presence of cheno is due to the formation of stable, hybrid structures between TiO_2 and hydroquinone/benzoquinone^{20,21} that prevents the interaction of cheno with the TiO_2 surface. As a result of the interaction of chenodeoxycholic acid molecules and the TiO_2 surface, the decrease of the electron decay rate observed with the $([\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2})$ and ferrocene/ferrocenium redox system can be interpreted as a blocking or retardation of interfacial charge recombination with the oxidized form of the redox couple.

Further TPC experiments were performed with varying cobalt redox couple concentration (Figure 5). To rule out the influence of the electrolyte constituents like acetonitrile solvent (ACN), LiClO_4 or 4-*tert*-butylpyridine their effect on the TiO_2 was investigated. It was found that there is no influence of ACN and LiClO_4 on the electron decay rate. But as already observed

for the I_3^-/I^- redox couple in ref 12, 4-*tert*-butylpyridine leads to a prolonged electron lifetime.

There is a clear influence of $([\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2})$ redox pair concentration on the electron decay observable (Figure 5). With increasing concentration of the redox couple, a decrease in electron decay rate was observed which can be explained by the faster reduction of the dye cation leaving the recombination with the oxidized form of the redox couple as the main channel.

4. CONCLUSIONS

The measurements presented above show a different behavior for the redox couples absorbed on N719 sensitized TiO_2 surfaces:

- The deposition of the redox couples tri-iodide/iodide¹² and $([\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2})$ on $\text{TiO}_2/\text{N719}$ leads to a decrease of the electron decay rate whereas the deposition of the redox couples Fc/Fc^+ (ferrocene/ferrocenium) and quinone/hydroquinone lead to an increase of the electron decay rate. The decrease of the

electron decay rate for the first two redox couples is explained by the regeneration of dye cations by electron donation from the redox couple while the redox couples themselves have a lower recombination probability with electrons from the TiO_2 . The increase of the electron decay rate for the latter two redox couples is attributed to a faster recombination probability by the redox couple.

- The addition of chenodeoxycholic acid has a greater influence on the Fc/Fc^+ redox couple compared to the HQ/Q^+ . The Fc/Fc^+ redox couple showed a decrease in the electron decay rate with increasing concentration of cheno, while the HQ/Q^+ system did not show dependence on the cheno concentration. These results indicate that the ferrocene/ferrocenium redox couple is a promising candidate for the production of efficient dye sensitized solar cells if the adequate additives are used.

The inactivity of the additives for the quinone/hydroquinone redox system is a strong indication that the effect of retarding the electron decay rate is due to blocking of interfacial charge recombination in view of the hybrid structures between TiO_2 and hydroquinone/benzoquinone reported in the literature.^{20,21}

- The relatively slow electron decay observed with the $([\text{Co}(\text{III}/\text{II})(\text{bpy})_3](\text{PF}_6)_{3/2})$ redox system, which can still be further retarded by addition of cheno, seems to offer promising possibilities for efficient dye sensitized solar cells. However, the real possibilities of this system depend on the efficiency of the transport of the positive charge.

It is important to realize that for electron decay, not only the cross section of the reactive state, but also the distance between electron and the accepting state determine the reaction probability. As the electron resides in TiO_2 , it is clear that states absorbed directly at the TiO_2 surface have the highest reaction probability. This explains perfectly our data on the quinone/hydroquinone redox couple (Figures 4 and 5). The reported formation of stable hybrid structures between TiO_2 and hydroquinone prevents the attachment of cheno at the surface, and so the addition of cheno did not show a significant influence on the electron decay.

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Notes

The authors declare no competing financial interest.

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