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Accepted 00th January 20xx DOI: 10.1039/x0xx00000x Self-Enhanced Multicolor Electrochemiluminescence by Competitive Intra- vs Inter-molecular Electron-transfer Processes

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Controlling the electrochemiluminescence (ECL) color(s) is crucial for many applications ranging from multiplexed bioassays to ECL microscopy. This can only be achieved through the fundamental understanding of high-energy electron-transfer processes in complex and competitive reaction schemes. Recently, this field has generated huge interest, but the effective implementation of multicolor ECL is constrained by the limited number of ECL-active organometallic dyes. Herein, the first self-enhanced organic ECL dye, a chiral red-emitting cationic diaza [4]helicene connected to a dimethylamino moiety by a short linker, is reported. This molecular system integrates bifunctional ECL features (i.e. luminophore and coreactant) and each function may be operated either separately or simultaneously. This unique level of control is enabled by integrating but decoupling both molecular functions in a single molecule. Through this dual molecular reactivity, concomitant multicolor ECL emission from red to blue with tunable intensity is readily obtained in aqueous media. This is done through competitive intra- and inter-molecular electron-transfer processes between the helicene and a ruthenium or iridium dye. Such competitive paths lead also to an intriguing heretofore unreported situation where ECL emission resulting from purely intermolecular electron-transfer reaction is more efficient than the one from the intramolecular processes. The reported approach provides a general methodology to extend to other coreactant/luminophore systems, opening enticing perspectives for spectrally distinct detection of several analytes, and original analytical and imaging strategies.

Introduction

Electrochemiluminescence (ECL) is the light emission resulting from an initial electron-transfer reaction occurring at the electrode surface.^{1, 2} The discovery of ECL emission in aqueous solution with an efficient 'coreactant' reagent has led to successfully commercialized bioassays for the detection of clinical biomarkers, biological warfare agents and foodborne pathogens.³⁻⁵ The coreactant is a sacrificial molecule that is added to the solution containing the luminophore. In the classic ECL mechanistic pathway, both molecules, the luminophore and the coreactant, have specific and separate functions. The coreactant that is either oxidized or reduced is consumed irreversibly due to a bond-breaking reaction whereas the luminophore is regenerated during the ECL process.^{4, 6} The function of the coreactant is to provide sufficiently energetic radicals to undergo exergonic intermolecular electron-transfer with the luminophore in order to reach the electronicallyexcited state.⁷⁻¹⁰ Tri-*n*-propylamine (TPrA) and several closely related tertiary amines are the most efficient coreactants to

^{a.} University of Bordeaux, Bordeaux INP, ISM, UMR CNRS 5255. 33607 Pessac, France. E-mail: <u>neso.sojic@enscbp.fr</u> enhance ECL intensity in aqueous solution.^{9, 10} On the other hand, the role of the luminophore is solely to emit *in fine* light. Thus, electron-transfer is at the core of the ECL phenomenon. A thorough understanding of the underlying principles of the associated inter- and intra-molecular electron-transfer reactions and reactivity is necessary to propose novel ECL strategies.

Since light is the final output of ECL, original concepts and applications have been developed exploiting the different properties of light, such as surface plasmon resonance ECL,¹¹ circularly-polarized ECL,¹² light-emitting devices,^{13, 14} photoinduced ECL,¹⁵ and ECL interferometry.¹⁶ Recently, ECL has been used as a microscopy technique to image latent fingerprints,¹⁷ single micro- and nano-particles,¹⁸⁻²² cells,^{23, 24} cellular membranes,²⁵ and membrane proteins.^{26, 27} Most of these applications rely on the use of ruthenium(II) polypyridyl complexes as luminophores, especially ruthenium(II) tris(bipyridine), and more recently on ortho-metalated or heteroleptic cationic iridium complexes.²⁸⁻³⁵ Indeed, the emission of such iridium(III) complexes is tunable at more hypsochromic wavelengths compared to the typical orange/red color resulting from the ruthenium complexes.^{31-34, 36} The ability to tune the emission color(s) has generated recently a wide interest due to potential applications ranging from multiplexed bioassays to ECL microscopy.^{28-31, 37-42} However, the effective implementation of such strategies is constrained by the limited number of luminophores that combine water solubility and a

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high ECL efficiency in aqueous media. In this context, multicolor ECL emission has been reported using a combination of different organometallic ruthenium(II) and iridium(III) luminophores, mainly in organic media.^{28-30, 41} The concomitant ECL emissions of several luminophores has been described by controlling the energetics of the luminophore.^{30, 43, 44} Ding and coworkers have explored a different approach with a specifically designed iridium complex emitting at three wavelengths in acetonitrile.45 Nanoparticles have also been used for this purpose.³⁹ For example, a hybrid system consisting of PbS nanocrystals and a BODIPY capping ligand was proposed to generate highly efficient dual emissions.⁴⁶ However, organic molecules offer a promising alternative due to their structural versatility that allows to tune precisely the optical and electronic properties. A large variety of such organic molecules have been designed and prepared to investigate their ECL properties, almost exclusively in organic solvents.⁴⁷⁻⁵⁴

In this work, we demonstrate that the integration of both functions (i.e. the coreactant, which generates energetic radicals and the luminophore, which is thus "electro-excited" and emits light) can be decoupled and accomplished sequentially in a single molecule in order to control multicolor ECL emissions. Herein, we report the first self-enhanced organic ECL dye that integrates successfully both coreactant and luminophore functions. The molecular scaffold is based on a cationic diaza [4]helicene (Fig. 1a). With the goal of obtaining multicolor ECL emission, we selected the archetypical [Ru(bpy)₃]²⁺ complex and also two iridium(III) luminophores that emit at shorter wavelengths to avoid Förster resonance energy transfer (Fig. 1b). Hence, we investigate competitive highly exergonic intra- and inter-molecular electron-transfer reactions between different luminophores (Fig. 1). Finally, we demonstrate that concomitant multicolor ECL emission ranging from red to blue with tunable intensity can be obtained by intermolecular electron-transfer processes between the electron-donor helicene radicals and all three electron-acceptor organometallic complexes.

Results and discussion

Cationic helicenes are ortho-fused polyaromatics that combine the main properties of triarylcarbenium ions with the structural features of (chiral) helicenes.^{55, 56} These dyes and luminophores are readily prepared,⁵⁶ and can be further functionalized via versatile late stage synthetic strategies that allow the regioselective introduction of various functional groups at the periphery of the helical core.57-61 We selected this family of luminophores because it allows fine-tuning not only the photophysical and redox properties of the luminophores but also its solubility in aqueous media.56, 62 More specifically, a diaza [4]helicene bearing a tertiary dimethylamino-terminated group, noted [HEL-AMH]⁺, was designed and prepared. In this dual molecule, HEL and AMH refer to the [4]diaza core and to the dimethylamino moiety, respectively. It was foreseen that the core helical structure would (i) remain a red-emitter distinct from the emission of model ruthenium and iridium complexes,57



Fig. 1 a) Molecular structures and b) photoluminescence emission spectra of the ECL luminophores. From left to right: $[Ir(df-ppy)_2(pt-R)]^*$ (blue curve/emitter), $[Ir(ppy)_2(pt-R)]^*$ (green curve/emitter), $[Ru(bpy)_3]^{2*}$ (orange curve/emitter) and the dual helicene noted [HEL-AMH]* (red curve/emitter). R = TOxT-Sq (a trioxatridecane chain with squarate amide ethyl ester).

(ii) integrate easily the coreactant function as a substituent,^{58, 60} and (iii) exhibit also reasonable solubility in aqueous media. In terms of synthesis, the central helical core was functionalized at position 6 with an ester functional group featuring a dimethylamino moiety as its terminal end. Previously, the synthesis of the diaza [4]helicene carboxylic acid was reported (Scheme 1).⁶³ Herein, this compound was converted to the corresponding acyl chloride with CO_2CI_2 and subjected to a nucleophilic substitution reaction at 0 °C by slow addition of an excess of *N*,*N*-dimethylethanol. The corresponding ester [HEL-AMH]⁺ was isolated after purification by flash column chromatography in 74% yield.



Scheme 1 Synthesis of water soluble diaza [4]helicene [HEL-AMH]*.

As expected, the dimethylamino group improved drastically the aqueous solubility of the luminophore (Fig. S9 and S10) and its role as coreactant was tested. The electrochemical

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characterization of the helicene shows two irreversible oxidation waves in PBS (Fig. 2). The first wave occurs at 0.8 V, which can be attributed to the oxidation of the dimethylamino AMH moiety (reaction 1). Indeed, the irreversible oxidation of TPrA has been reported previously at the same potential in aqueous media and we can assume a mechanism similar to the one described for TPrA.⁶⁴ The oxidation of the deprotonated dimethylamino group generates the dication radical [HEL- $AMH^{\bullet}]^{2+}$ (reaction 1). The latter deprotonates rapidly to form locally the monocation radical [HEL-AM•]+, which is a strong reductant (reaction 2). The second irreversible wave peaking at 1.33 V corresponds to the oxidation of the diaza core. To confirm this assignment, another water soluble diaza [4]helicene [HEL-SO₃H]⁺ was also prepared (79% from the carboxylic acid precursor, see Supporting Information). In that case, the sulfonic group is electro-inactive in the investigated potential window and only the oxidation of the diaza core is visible at 1.3 V (Fig. S13). Through a simple comparison of the voltammetric behavior of both [4]diaza complexes, we can therefore assign without ambiguity the two oxidation waves of [HEL-AMH]⁺: the first and second correspond to the oxidation of the dimethylamino group and of the diaza core (reaction 3), respectively. In acetonitrile, the oxidation of helicene [4]diaza complexes is reversible and it means that the resulting electrogenerated cation is stable in such an organic solvent. In PBS, the oxidation wave of the diaza core is irreversible, indicating that the oxidized radical of the diaza core is not stable over the timescale of the voltammetric experiments. In addition, since the same oxidation potential of the diaza core is obtained with and without the dimethylamino group, it implies that the electronic communication between these groups is negligible. This is further supported by the near identical oxidation potential of TPrA and the dimethyl amino moiety of [HEL-AMH]⁺. In brief, the two parts of the luminophorecoreactant molecule behave independently from an electrochemical point of view. This decoupling is an essential prerequisite for the ECL mechanism, which involves reactions intermolecular electron-transfer with the organometallic complexes to enable multicolor ECL emission (vide infra).



Fig. 2 Voltammetric (black curve) and ECL (blue curve) signals of 10-4 M [HEL-AMH]+ in PBS on a glassy carbon (GC) electrode. Scan rate: 0.1 V s⁻¹.

At an applied potential above 1.3 V, both parts of the molecules are oxidized and the resulting trication [HEL--AMH[•]]³⁺ intermediate is probably formed (reaction 3) and may deprotonate to form [HEL•-AM•]²⁺ (reaction 4). We can assume that the coreactant mechanism for the amino moiety is analogous to that of the model TPrA reagent (see the detailed structures of the amino radicals in Scheme S1).64,65

$[\text{HEL-AMH}]^+ - e^- \rightarrow [\text{HEL-AMH}^\bullet]^{2+}$	(1)
$[\text{HEL-AMH}^{\bullet}]^{2+} \rightarrow [\text{HEL-AM}^{\bullet}]^{+} + \text{H}^{+}$	(2)
$[\text{HEL-AMH}]^+ - 2 \text{ e}^- \rightarrow [\text{HEL}^\bullet-\text{AMH}^\bullet]^{3+}$	(3)
$[HEL^{\bullet}-AMH^{\bullet}]^{3+} \rightarrow [HEL^{\bullet}-AM^{\bullet}]^{2+} + H^{+}$	(4)

Then we investigated the ECL properties of this helicene molecule. As shown on Fig. 2, ECL light is only emitted at potentials higher than 1.2 V. When the potential is scanned towards more positive values, ECL emission grew and reached a maximum at 1.32 V. It means that ECL generation requires explicitly the oxidation of the diaza core. ECL is obtained without adding any external coreactant; the dimethylamino moiety acting by itself as a coreactant in the mechanism. In other words, self-enhanced ECL emission is generated by this dual helicene compound. The excited state may be reached by intramolecular (reaction 5) or intermolecular (reaction 6) electron-transfer reactions between the strong radical reductant (denoted -AM[•]) and the oxidized diaza core (HEL[•]). It then deactivates through the emission of a photon at 650 nm (reactions 7 and 8). In this path, ECL generation requires the simultaneous presence of both radicals to form the excited state. Even if the electrogenerated radicals are not stable during the timescale of the voltammetric experiments, the ECL emission is an indirect proof of their formation at the vicinity of the electrode surface. Both inter- and intra-molecular pathways may be postulated and they depend on the radical lifetimes, their reactivity and concentration, amongst other factors. Indeed, self-enhanced ECL of ruthenium tris-bipyridyl and iridium complexes with different amine reductants has been reported based on intra- and inter-molecular interactions.45, 66 Self-enhanced ECL has been also applied for sensing applications.^{42, 67-69} In the present case, the resulting ECL spectrum is identical to the fluorescence spectrum (Fig. S14). Therefore, the same excited state is reached by photoexcitation and by self-enhanced ECL. By assuming that the intramolecular coreactant exhibits the same potential as TPrA• after deprotonation, it is possible to calculate the exergonicity of reactions 5 or 6 ($\Delta G^{\circ} = E^{\circ}_{red}(TPrA^{\bullet}) - E^{\circ}_{ox}(helicene core) \approx -3$ eV with E°_{red} (TPrA•) being reported to be – 1.7 V vs Ag/AgCl ^{64,} ⁷⁰). A direct comparison with the emission wavelength of the [4]helicene core (E_{Fl} = 1239.81 / λ_{max} = 1.9 eV) indicates that the excited state can be directly populated. [HEL*-IM]²⁺ [HEI •_ ^ ^ 12+ (5)

$$[\text{HEL}^{\bullet}-\text{AIVI}^{\bullet}]^{2^{+}} \rightarrow [\text{HEL}^{*}]^{2^{+}}$$

2 $[HEL^{\bullet}-AM^{\bullet}]^{2+} \rightarrow [HEL^{*}-AM^{\bullet}]^{+} + [HEL^{\bullet}-IM]^{3+}$ (6)

 $[\text{HEL*-IM}]^{2+} \rightarrow [\text{HEL-IM}]^{2+} + hv_{red} \text{ (650 nm)}$ (7)

 $[\text{HEL*-AM}^{\bullet}]^{+} \rightarrow [\text{HEL-AM}^{\bullet}]^{+} + hv_{red} (650 \text{ nm})$ (8)

where IM represents the iminium product (see the detailed structures in Scheme S1).64, 71

Annihilation ECL of [Ru(bpy)₃]²⁺ with several iridium(III) complexes has been investigated previously in organic solvents.^{28, 29} In the present work, our goal was to generate

multicolor ECL emission by combining it with self-enhanced ECL. For this purpose, we added first $[Ir(df-ppy)_2(pt-R)]^+$ (Fig. 1a, where R is a trioxatridecane chain (TOXT) and terminal squarate amide ethyl ester (Sq))⁷² to an aqueous solution containing already [HEL-AMH]⁺. The Sq functionality does not change the electrochemical and photophysical properties of the parent luminophore, but provides a convenient attachment point for future works for involving biomolecular labelling and multicolour ECL biodetection. Oxidation of the $[Ir(df-ppy)_2(pt-R)]^+$ complex occurs at a higher potential than the diaza core and the corresponding ECL emission is obtained at 1.5 V (Fig. S15). When both reagents are present, blue and red ECL emissions of $[Ir(df-ppy)_2(pt-R)]^+$ and diaza luminophore are observed



Fig. 3 ECL spectrum recorded in a PBS solution containing 10⁻⁴ M [HEL-AMH]⁺ and 10⁻³ M [Ir(df-ppy)₂(pt-R)]⁺. Applied potential: 1.7 V vs Ag/AgCl/KCl.

Such a dual ECL emission is achieved without adding any external coreactant. As already mentioned, Förster resonance energy transfer processes are not possible since the emission of [Ir(df-ppy)₂(pt-R)]⁺ occurs at lower wavelengths than that of the diaza [4]helicene. It is likewise the same energetic configuration for all the three tested organometallic luminophores. The excited states of both luminophores are reached following the reactions occurring between their respective oxidized forms (i.e. [Ir(df-ppy)₂(pt-R)]²⁺ and [HEL[•]-AMH]²⁺) and the radical -AM[•] of the modified helicene (reaction 10). For the iridium complex, it corresponds to an intermolecular electron-transfer reaction with the radical -AM• moiety (reaction 10). The coreactant function of the diaza complex is activated and operates via intermolecular mode for [Ir(df-ppy)₂(pt-R)]²⁺ (reactions 9-10) and/or intramolecular modes for [HEL-AMH]+ (reactions 5 and or 6).

$$\begin{split} & [Ir(df-ppy)_2(pt-R)]^+ - e^- \rightarrow [Ir(df-ppy)_2(pt-R)]^{2+} & (9) \\ & [Ir(df-ppy)_2(pt-R)]^{2+} + [HEL^{\bullet}-AM^{\bullet}]^{2+} \rightarrow [Ir(df-ppy)_2(pt-R)]^{+*} \\ & + [HEL^{\bullet}-IM]^{3+} & (10) \\ & [Ir(df-ppy)_2(pt-R)]^{+*} \rightarrow [Ir(df-ppy)_2(pt-R)]^{+} + hv_{blue} & (11) \end{split}$$

The [HEL-AMH]⁺ molecule, which is a red-emitter, induces also the generation of blue ECL color by $[Ir(df-ppy)_2(pt-R)]^+$ (reaction 11). Even if the final result is reminiscent of an upconversion process, it is not mechanistically the case here. The blue ECL emission results from a very exergonic electrontransfer reaction from the $[HEL^{\bullet}-AM^{\bullet}]^{2+}$ radical to the oxidized $[Ir(df-ppy)_2(pt-R)]^{2+}$. It is not related to an energy-transfer process such as triplet-triplet annihilation. Herein, we solely control and exploit the dual reactivity of the $[HEL-AMH]^+$ molecule.

In the previous example, we showed that ECL can be tuned from red to blue by intermolecular electron-transfer processes. Herein, we investigate the ECL of $[Ru(bpy)_3]^{2+}$ using this original configuration. Indeed, this complex is the model and most widely used ECL luminophore due to its remarkable stability and high ECL efficiency in water. We tested its behavior by increasing its concentration in a solution containing the [HEL-AMH]⁺ compound (Fig. S16). The maximum ECL intensity moved progressively from 650 nm (characteristic of [HEL-AMH]⁺) to 620 nm (Fig. 4), corresponding to the emission of $[Ru(bpy)_3]^{2+}$. This shift is even more striking in the corresponding normalized ECL spectra (Fig. S17). Moreover, one can observe that the $[Ru(bpy)_3]^{2+}$ ECL band increases remarkably. A similar ECL mechanism as that described above for the iridium luminophore (reactions 9-10) can be proposed.



Fig. 4 ECL spectra recorded in a PBS solution containing a constant concentration of 10^{-4} M [HEL-AMH]⁺ and increasing concentrations of [Ru(bpy)₃]²⁺: 0, 1×10^{-5} M, 3×10^{-5} M, 6×10^{-5} M, 1×10^{-4} M and 1×10^{-3} M, as indicated by the arrow. Applied potential: 1.5 V vs Ag/AgCl/KCl.

In a solution containing both luminophores at the same 10⁻⁴ M concentration (green curve, Fig. 4), light intensity is 8-fold higher in comparison to the solution containing only the [HEL-AMH]⁺ (red curve, Fig. 4). When the [Ru(bpy)₃]²⁺ concentration is increased up to 10⁻³ M, ECL intensity is 20.5-fold higher. We checked that addition of $[Ru(bpy)_3]^{2+}$ does not influence the fluorescence of the [HEL-AMH]+ (Fig. S18). Therefore, the enhancement of the [Ru(bpy)₃]²⁺ ECL band is due to the very efficient intermolecular electron-transfer between both species and to the high ECL efficiency of the $[Ru(bpy)_3]^{2+}$ luminophore. Indeed, [HEL-AMH]⁺ was found to have an ECL efficiency of 7.3 % in comparison to [Ru(bpy)₃]²⁺, which accounts for the dramatic increase in ECL intensity. This creates an intriguing situation in which ECL emission resulting from an intermolecular electron-transfer reaction (i.e. with [Ru(bpy)₃]²⁺) is more efficient than that of the intramolecular process (i.e. [HEL-AMH]+).

As shown by the voltammetric study, the two moieties of [HEL-AMH]⁺ are electronically decoupled to a large extent. This enables the two functions to be operated either separately or concomitantly by controlling the applied potential and the energetics of the luminophores. The coreactant function of [HEL-AMH]⁺ is activated at 0.8 V where the dimethylamino group is oxidized. The ECL of this molecule, however, requires oxidation of the diaza core at 1.33 V. Therefore, a wide potential window exists between 0.8 V and 1.33 V where another luminophore can be oxidized and generate ECL before the emission of [HEL-AMH]⁺. For this purpose, we used the green emitter, $[Ir(ppy)_2(pt-R)]^+$ (Fig. 1). Oxidation of this iridium complex occurs at 1.14 V (Fig. S19), which in the presence of a suitable coreactant elicits green ECL.



Fig. 5 ECL spectra recorded in a PBS solution containing 10^{-4} M [HEL-AMH]⁺ and 10^{-3} M [Ir(ppy)₂(pt-R)]⁺ when applying either 1.1 V (green curve) or 1.3 V (red curve).

By imposing 1.1 V, we observed predominantly the green ECL emitted by the $[Ir(ppy)_2(pt-R)]^+$ (green curve, Fig. 5). This potential induces the oxidation of $[Ir(ppy)_2(pt-R)]^+$ as well as of the dimethylamino moiety of $[HEL-AMH]^+$, whereas the diaza core is not oxidized, so the red emission of this luminophore was not observed. The oxidized and deprotonated dimethylamino moiety (-AM[•]) acts then only as a coreactant by intermolecular electron-transfer with the oxidized $[Ir(ppy)_2(pt-R)]^{2+}$, as described by the sequence of reactions 1, 2, 12, 13 and 14:

$[Ir(ppy)_2(pt-R)]^+ - e^- \rightarrow [Ir(ppy)_2(pt-R)]^{2+}$	(12)
$[Ir(ppy)_2(pt-R)]^{2+} + [HEL-AM^{\bullet}]^+ \rightarrow [Ir(ppy)_2(pt-R)]^{+*}$	
+ [HEL-IM] ²⁺	(13)
$[Ir(ppy)_2(pt-R)]^{+*} \rightarrow [Ir(ppy)_2(pt-R)]^{+} + hv_{green}$	(14)

Under these conditions, only the coreactant function of the helicene molecule is activated and green ECL emission of $[Ir(ppy)_2(pt-R)]^+$ is solely observed (green curve, Fig. 5). At higher potentials, the red and the green ECL emissions of [HEL-AMH]⁺ and $[Ir(ppy)_2(pt-R)]^+$ are visible concomitantly. The luminescent function of the helicene molecule is activated as well. The helicene molecule acts both as a coreactant and a luminophore. In this potential region, the diaza core is also oxidized and it reacts with the -AM[•] moiety radical to give its characteristic red emission. In brief, single or multicolor ECL emission is obtained by controlling the reactivity of the dual

[HEL-AMH]⁺ luminophore. It is also noteworthy that the resulting color can also be tuned by adjusting the ratio of luminophores dissolved in solution.

Conclusions

In conclusion, self-enhanced ECL emission is demonstrated in aqueous media by integrating bifunctional ECL features in a single molecular system using a red-emitting diaza [4]helicene functionalized with a dimethylamino moiety. The coreactant and the luminescent functions are decoupled and are activated either separately or simultaneously by controlling the applied potential. Self-enhanced multicolor ECL, from red to blue, via orange and green is obtained by intramolecular and intermolecular electron-transfer reactions between the helicene and a series of organometallic iridium or rutheniumbased complexes. Such competitive paths lead to an intriguing heretofore unreported situation where ECL emission resulting from purely intermolecular electron-transfer reaction with [Ru(bpy)₃]²⁺ is more efficient than the one from the intramolecular and intermolecular processes. Single or multicolor emissions with tunable intensity are produced by controlling the dual reactivity of the helicene molecule. This multicolor ECL strategy can be extended to other luminophores and coreactants and has important implications for electrontransfer and energy-transfer processes, multiplexed bioassays and imaging applications.

Conflicts of interest

There are no conflicts to declare.

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