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Synthesis, characterization, electrochemical and theoretical study of substituted phenyl-terpyridine and pyridinequinoline based mixed chelate ruthenium complexes

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ABSTRACT

In the present work, we report two methoxy-substituted phenyl-terpyridine ruthenium complexes with pyridine carboxyquinoline and NCS as ancillary ligands, [Ru(OMePhtpy)(pcqH)(NCS)](PF_e) (1) and [Ru(tri-OMePhtpy)(pcqH)(NCS)](PF₆) (**2**) (where OMePhtpy = (4'-(4-methoxy) phenyl-2,2':6',2"-terpyridine, triOMePhtpy = (4'-(3,4,5-trimethoxy))phenyl-2,2':6',2''-terpyridine and pcgH = pyridine-carboxyguinoline). Both complexes have been characterized by spectroscopic techniques e.g., mass, ¹H-NMR and FTIR. UV-vis spectrophotometric and electrochemical studies for both complexes have been performed. The substitution pattern of the –OMe groups have been successfully utilized to tune the redox potential of the metal complexes. On the anodic side of cyclic voltammogram, 1 and 2 show an irreversible wave corresponding to Ru^{II/III} couple at 0.95 and 0.85 V, respectively. The lower Ru^{II/III} oxidation potential for **2** may be attributed to increased electron density on ruthenium due to three (+R) methoxy-groups appended to the phenyl moiety of triOMePhtpy. DFT optimization of structure and energy calculation reveals that in both complexes, HOMO is metal- and thiocyanate-based, whereas the LUMO is based on pcqH. Correlation of TDDFT results with experimental electronic spectrum indicates that bands at 502 nm (1) and 528 nm (2) are of MLLCT character from ruthenium-thiocyanate to pcqH.

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1. Introduction

Polypyridine-based ruthenium complexes attract attention as photosensitizers [1] with applications in DSSCs [2–18], artificial photosynthesis [19], photodynamic therapy [20] and molecular electronics [21]. [Ru(bpy),]⁺² is the most-established photosensitizer due to its excellent photophysical properties (an excited state lifetime of 1100 ns) [22], structural robustness and close proximity of the Ru^{II/III} oxidation to that of Photosystem-II [23]. However, for the [Ru(II)(bpy)] systems with substituted bpy ligands, the Ru-centered inherent stereogenicity produces stereoisomers which are difficult to separate [24]. In [Ru(terpy)₂]⁺² type complexes, although there is no such synthetic complexity, they are photophysically less meritorious due to the very low excited-state lifetime (for $[Ru(terpy)_2]^{+2}$, $\tau = 0.25$ ns) at room temperature [25]. The reason behind this shortcoming is the rigid tridentate moiety of terpyridine that results in a distorted octahedral geometry in the corresponding Ru(II) complexes. In coordinated terpyridine, the N-Ru-N trans angles are ~158.6° whereas it is 173.0° in the analogous [Ru(II)(bpy)] complexes [26]. This, in turn, weakens the ligand-field strength, reducing the energy of the d-d metal-centered triplet state (${}^{3}MC$) [27]. Consequently, the energy gap between the ³MLCT and ³MC states decreases and, thus, the ³MC state becomes thermally accessible from the ³MLCT state, causing easy non-radiative decay back to the ground state. In [Ru(terpy),]⁺² complexes, terpyridines with substituted electron donating and withdrawing groups have varied results [28]. In a number of systems substitution of the 4'-position of terpyridine with a phenyl group stabilizes the ³MLCT state more than the ¹MLCT [29]. In the ground state, the phenyl ring twists away from the central pyridine ring due to repulsive steric effect of the hydrogens at the 3'- and 5'-positions of the terpyridine whereas in the excited state, the dihedral angle between the phenyl ring and the central pyridine ring changes to give a coplanar arrangement. Consequently, the ³MLCT excited state is more



Complex 1: $R_1=R_3=H$ $R_2=OMe$ Complex 2: $R_1=R_2=R_3=OMe$

Figure 1. Labeled diagram for 1 and 2.

stabilized by extended electron delocalization than the ground state [30]. In our previous publications, we have reported heteroleptic ruthenium complexes with electron withdrawing p-fluoro substituted phenyl-terpyridine and extended electron delocalizing p-(9-anthranyl) terpyridine [31]. In the present work, we report two -OMe substituted phenyl-terpyridine mixed-chelate complexes with pyridinecarboxyquinoline and NCS as ancillary ligands, [Ru(OMePhtpy)(pcqH)(NCS)](PF₆) (1) and [Ru(triOMePhtpy)(pcqH)(NCS)](PF₆) (2), where OMePhtpy = (4'-(4-methoxy)phenyl-2,2':6',2"-terpyridine and triOMePhtpy = (4'-(3,4,5-trimethoxy)phenyl-2,2':6',2"-terpyridine (figure 1). Both complexes have been structurally characterized by MS, NMR and FTIR spectroscopic techniques. The spectrophotometric and electrochemical studies for both complexes have been performed. A detailed Time Dependent Density Functional Theory (TDDFT) analysis of 1 and 2 has been performed to reveal the electronic transitions behind the experimental absorption spectra.

2. Experimental

4-Methoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, tetrabutylammonium bromide and silver nitrate were purchased from Merck. Ammonium hexafluorophosphate was purchased from Sigma Aldrich and ruthenium chloride was obtained from Arora Mathey India Limited. Ethanol and DMF were HPLC grade, whereas methanol was dried according to literature procedure [32]. Tetrabutylammonium perchlorate (TBAP) was synthesized according to the literature [33].

Infrared spectra were recorded as KBr pellets on a Shimadzu IR-Prestige21 spectrometer. UV-vis spectra were recorded using a Perkin Elmer Lambda 750 spectrophotometer. Cyclic voltammograms and differential pulse voltammograms were recorded in a CHI6003E potentiostat, either in DMF or DMF-water solutions, containing 0.1 M TBAP as supporting electrolyte, glassy carbon as working electrode, Pt wire as a counter electrode and Ag/Ag⁺ non aqueous reference electrode. The ferrocene/ferrocenium couple was observed at E⁰ (ΔEp) = 0.4 V (100 mV) under these experimental conditions. ¹H NMR spectra and ¹³C NMR spectra were recorded with a JNM-ECZ400S/L1 spectrometer. ESI-MS spectra of the samples were recorded on a JEOL JMS 600 instrument.

2.1. Computational methods

The quantum chemical calculations were performed using density functional theory (DFT) implemented in GAUSSIAN 09 [34]. A split basis set was used for optimization of the complex using the B3LYP hybrid functional and 6–31 g (d) basis set for hydrogen, carbon, oxygen, nitrogen and fluorine and the LANL2DZ basis set for ruthenium. The absorption spectra were simulated using TD-DFT. All computational studies were carried out in DMSO using the Polarizable Continuum Model (PCM) implemented in GAUSSIAN 09. The orbital contribution was calculated by GaussSum [35].

2.2. Synthesis

2.2.1. Preparation of ligands

2.2.1.1. 4'-(4-Methoxyphenyl)-2,2':6',2"-terpyridine (OMePhtpy) (L1). The terpyridyl ligand was synthesized by the reported procedure [36]. 4-Methoxybenzaldehyde (0.680 g, 5 mmol) and 2-acetylpyridine (1.21 g, 10 mmol) were dissolved in ethanol. KOH (0.77 g, 10 mmol) was added and the mixture was vigorously stirred. After the potassium hydroxide pellets completely dissolved, ammonia (excess, *ca.* 20 mL) was added and the mixture was stirred at room temperature for 16 h under N₂. The resulting solution was filtered under vacuum and washed with ethanol to give a very light blue fluffy solid (yield: 0.678 g, 40%). The crude product was recrystallized from methanol. Mass spectrum (ESI + ve) (*m*/*z*): observed 340.2 (M + 1); Calcd 339 (M). ¹H NMR (CDCl₃, δ): 8.72 (4H, d, H_{A,K}), 8.66 (2H, s, H_G), 7.85–7.89 (4H, m, H_{D,J}), 7.36 (2H, m, H_C), 7.07 (2H, dd, H_B), 3.846 (3H, s, H_N). ¹³C NMR (CDCl₃, δ): 160.54 C_P 155.63 C_E, 155.27 C_A, 149.03 C_H, 148.61 C_K, 137.33 C_C, 130.41 C_L, 128.54 C_P, 123.85 C_B, 121.58 C_{D'} 118.48 C_G, 114.30 C_{J'} 56.56 C_N.

2.2.1.2. 4'-(3,4,5-Trimethoxyphenyl)-2,2':6',2"-terpyridine (triOMePhtpy) (L2). The terpyridyl ligand was synthesized by the reported procedure [36]. 345-Trimethoxybenzaldehyde (0.620 g, 5 mmol) and 2-acetylpyridine (1.21 g, 10 mmol) were dissolved in ethanol. KOH (0.77 g, 10 mmol) was added and the mixture was vigorously stirred. After the potassium hydroxide pellets completely dissolved, ammonia (excess, *ca.* 20 mL) was added and the mixture was stirred at room temperature for 16 h under N₂. The resulting solution was filtered under vacuum and washed with ethanol to give a very light blue fluffy solid (yield: 0.656 g, 40%). The crude product was recrystallized from methanol. Mass spectrum (ESI + ve) (m/z):

observed 399.20 (M); Calcd 399.44 (M). ¹H NMR (CDCl₃, δ): 8.74 (2H, d, H_A), 8.66 (4H, s, H_{G,J}), 7.86 (2H, t, H_D), 7.36 (2H, m, H_C), 7.07 (2H, dd, H_B), 3.99 (6H, s, H_M), 3.93 (3H, s, H_N). ¹³C NMR (CDCl₃, δ): 156.24 C_P, 155.90 C_E, 153.64 C_A, 150.56 C_H, 149.17 C_K, 139.00 C_C, 136.94 C_L, 134.55 C_I, 123.89 C_B, 121.47 C_D, 118.99 C_G, 104.69 C_I, 61.02 C_N, 56.56 C_M.

2.2.1.3. 2-(2-Pyridyl)-4-carboxyquinoline (pcqH). The ligand was prepared according to literature method [37]. 18 g (0.12 mol) of 23-indolinedione was crushed to powder and mixed with 15 g (0.12 mol) of 2-acetylpyridine for ~30 min. 60 g (~60 mL) of 33% NaOH were added at 5 °C with stirring. The solution was stirred continuously for 30 min when the temperature rises to ~50 °C. Ice flakes were added to the mixture. Stirring the mixture with a glass rod produced a purple red solid. The solid was filtered, washed with water followed by cold acetone. The crude product was recrystallized from water to give a light purple crystal (yield: 18 g, 67%). Mass spectrum (ESI + ve) (m/z): base peak: 295 (M + 23 + 23) 23 = mass of Na⁺.

2.2.1.4. [$Ru(L1)Cl_3$]. L1 (1.5 mmol) and RuCl₃ (0.40 g, 1.5 mmol) were dissolved in 20 mL of dry methanol and heated to reflux under N₂ for 3 h. The resulting deep brown solution was allowed to cool at room temperature, after which the solution was cooled in an ice-bath for 0.5 h. The brown solid was collected by vacuum filtration and washed with cold methanol until the filtrate was colorless and then washed with Et₂O and air-dried. The product (yield: 0.662 g, 72%) was used without further purification.

2.2.1.5. [Ru(L1)(pcqH)NCS](PF,) (1). [Ru(L1)Cl₃] (0.5 mmol) and pcqH (0.125 g, 0.5 mmol) were taken in a round-bottomed flask in 25 mL DMF and refluxed for 6 h under N₂. The reaction mixture was then reduced in a rotatory evaporator to 5 mL and a saturated aqueous solution of NH₄PF₆ was added to the solution. On addition of more water, precipitate appeared which was collected by filtration in a G4 sintered glass filter. The product was purified by column chromatography using silica as the stationary phase and DCM as mobile phase, eluted with 1:1 DCM/CH₃OH eluent. This chloro-complex (101 mg, 0.104 mmol) was further reacted with ammonium thiocyanate (279 mg (excess)) in 20 mL DMF and refluxed for 5 h to give a reddish solution which was reduced in a rotatory evaporator to 5 mL and then saturated aq. solution of NH₄PF₆ was added to the solution to give reddish precipitate. The precipitate was washed with water, dried, washed with ether and collected by filtration in a G4 sintered glass filter. Crude weight: 95 mg. The product was purified by column chromatography using silica as the stationary phase and DCM as mobile phase. The deep red product (26 mg, 0.031 mmol, yield 29.5%) is eluted with 1 : 1 DCM/CH₃OH eluent (scheme 1). FTIR (cm⁻¹): 3383 (broad), 2102, 1600, 1400, 1200, 786. Mass spectrum (ESI + ve): observed 749 (M + 1); Calcd: 748 (M). ¹H NMR (d₆-DMSO, δ): 9.6–9.4 (1H, d, H_a), 9.212 (2H, s, H_G), 8.99–8.91 (3H, d, H_{Am}), 8.79 (1H, s, H_a), 8.4–8.3 (3H, t, H_{B,d}), 8.1–8.0 (3H, m, H_{Lki}), 7.83–7.80 (2H, d, H_D), 7.66–7.61 (2H, m, H_C), 7.40 (2H, m, H₁), 7.26 (2H, m, H_c), 7.2–7.1 (2H, m, H_k), 3.82 (3H, s, OMe-C₁).

2.2.1.6. [*Ru*(*L2*)(*pcqH*)*NCS*](*PF*₆) (2). Complex **2** was prepared in the same method as **1** (Yield: 28.5%). FTIR (cm⁻¹): 3000 (broad), 2098, 1600, 1400, 1265, 844, 786. Mass spectrum (ESI + ve): observed 809.72 (M + 1); Calcd 808 (M). ¹H NMR (d₆-DMSO, δ): 9.4 (1H, d, H_a), 9.13 (2H, s, H_G), 8.96 (2H, d, H_A), 8.92 (1H, d, H_m), 8.81 (1H, d, H_d), 8.79 (1H, s, H_g), 8.1 (2H, t, H_B), 7.84 (3H, m, H_{1,k,j}), 7.64 (2H, d, H_D), 7.57 (2H, m, H_c), 7.4 (2H, m, H_J), 7.2 (1H, m, H_c), 4.02 (6H, s, OMe-C_k), 3.945 (3H, s, OMe-C₁).



Scheme 1. Scheme for synthesis of 1 and 2.

3. Results and discussion

3.1. Synthesis

Syntheses of **1** and **2**, the corresponding terpyridines L1 and L2 and pcqH are outlined in the generalized scheme 1.

The complexes were obtained by firstly reacting the corresponding terpyridine with RuCl₃ in dry methanol for 3 h and then after subsequent washing with cold methanol and filtration, the product [Ru(tpy)Cl₃] was obtained which was further reacted with pcqH in DMF for 6 h. The product was precipitated by treating the reduced volume of the reaction mixture with excess saturated aqueous solution of NH₄PF₆. The so-obtained solid was filtered and dried under vacuum, purified by column chromatography in silica, eluting the desired product by 40–50% methanol in dichloromethane. The solid product was further refluxed in DMF with excess ammonium thiocyanate for 5 h and then precipitated by addition of excess NH₄PF₆ and water to a reduced volume of the DMF mixture. The red solid was filtered, dried, and purified by column chromatography in silica to elute the bright red band with 25% methanol in dichloromethane. Evaporation of the solvent in vacuum provided the desired reddish-violet solid product. IR spectra of both complexes show an intense absorbance around 2100 cm⁻¹ (NC stretch) and 780 cm⁻¹ (CS stretch), which confirms the N-coordination of NCS [38].



Figure 2. UV-vis spectra of (a) 1 and (b) 2.

3.2. Absorption spectra

Complex **1** shows appreciable light harvesting capacity as evident from its absorption spectrum with a broad MLCT band at 502 nm extending to 700 nm with significant absorptivity (figure 2). In **2**, this broad band is centered at 527 nm. Analysis of this band in both complexes by TDDFT shows a Ru- and Ru-NCS-to-pcqH MLCT transition responsible for the maxima, whereas the trail of the band spanning 600 nm is due to a Ru-to-terpyridine transition. Moving toward the UV region, both complexes show major bands at 330 and 280 nm. The former band is due to a high-energy Ru-to-pcqH charge-transfer transition with a considerable contribution of intraligand transition based on terpyridine. The latter band has the highest contribution from terpyridine-based intraligand transitions. An interesting feature is **2** has a considerably higher molar extinction coefficient than **1**. This is in conformity with literature where the presence of –OMe groups increases absorptivity [39]. The presence of three –OMe groups in **2** increases the absorptivity in comparison to **1** which has one –OMe group.

3.3. Electrochemistry

Complexes **1** and **2** are characterized electrochemically by cyclic voltammetry and differential pulse voltammetry (figure 3). Complex **1**, in the anodic scan, shows an irreversible wave at 0.95 V corresponding to Ru^{II/III} couple, whereas **2** shows an irreversible wave at 0.85 V, clearly showing more electron density on Ru in **2** with three (+R) –OMe groups. In a reported complex with a terpyridine motif similar to **2** but coordinated to 4,4'-bipyridine-dicarboxylic acid in place of pcqH, the E₀ value of the Ru^{II/III} redox couple is 0.70 V [40]. The higher E_0 value of **2** may be due to the greater withdrawing nature of pcqH [41]. The cathodic wave shows a first reduction peak at –1.46 V for **1** and –1.43 V for **2** and a second reduction wave at –1.83 V for both complexes. Cyclic voltammetry of free terpyridine and pcqH show similar reduction processes (SM 19): triOMePhtpy (–1.42 V) and pcqH (–1.01 V, –1.74 V). Hence, the first reduction wave is a terpyridine-based process and the second reduction peak is assigned to pcqH-based in both complexes, indicating higher electron density of pcqH than triOMePhtpy. On comparing the reduction takes place at –1.16 V, it can be concluded that pcqH has more electron density than 4,4'-bipyridine-dicarboxylic acid analog, where the reduction takes place at –1.16 V, it can be concluded that pcqH has more

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3.4. DFT studies

A theoretical study using DFT with the B3LYP hybrid functional was performed to get optimized structures of **1** and **2** in DMSO for a better understanding of their electronic structures (figure 4). The metrical parameters are displayed in Table 1 while the compositions and energies of the frontier molecular orbitals of the complexes are given in SM 15 (for **1**) and SM 16 (for **2**). Complex **1** adopts a distorted octahedral geometry where the *cis* angles vary from 77.32 to 102.44° and the *trans* angles are 157.79–177.44°. Complex **2** also adopts a distorted octahedral geometry with *cis* angles 77.27–102.82° and *trans* angles 157.91– 177.96°. Due to its rigidity, the terpyridine ligand in **1** is expected to coordinate to the metal center in a meridional fashion, which is also observed in our optimized structures. The bond length for Ru–Npy_(central) is shorter (1.99 Å) than that of Ru-Npy_(terminal), in accord with the literature [42]. The other basal coordination is satisfied by quinoline-N of the anchoring ligand, whereas the axial sides are coordinated by pyridine-N and thiocyanate. The complex



Figure 3. Cyclic voltammogram and differential pulse voltammogram of (a) 1 (anodic scan), (b) 1 (cathodic scan), (c) 2 (anodic scan) and (d) 2 (cathodic scan).



Figure 4. DFT-optimized structure of (a) 1 and (b) 2.

Complex 1				
Bond	Distance (Å)	Bond	Distance (Å)	
Ru1–N2	1.9960	Ru1–N5	2.19828	
Ru1–N3	2.11945	Ru1–N6	2.08388	
Ru1–N4	2.13066	Ru1–N74	2.10022	
Angle	Degree (°)	Angle	Degree (°)	
N6-Ru1-N2	95.959	N2-Ru1-N3	78.96	
N6-Ru1-N3	92.413	N3-Ru1-N4	157.788	
N6-Ru1-N4	89.905	N4-Ru1-N5	99.631	
N6-Ru1-N5	77.328	N5-Ru1-N2	173.157	
N74-Ru1-N2	84.204	N6-Ru1-N74	177.443	
N74-Ru1-N3	90.123	N2-Ru1-N4	78.829	
N74-Ru1-N4	87.622	N3-Ru1-N5	102.431	
	Com	olex 2		
Bond	Distance (Å)	Bond	Distance (Å)	
Ru1–N2	1.99447	Ru1–N5	2.20521	
Ru1–N3	2.11977	Ru1–N6	2.08403	
Ru1–N4	2.12938	Ru1–N82	2.10229	
Angle	Degree (°)	Angle	Degree (°)	
N6–Ru1–N2	95.995	N2-Ru1-N3	78.994	
N6-Ru1-N3	92.070	N3-Ru1-N4	157.905	
N6-Ru1-N4	90.073	N4-Ru1-N5	99.726	
N6-Ru1-N5	77.276	N5-Ru1-N2	173.171	
N82-Ru1-N2	83.867	N6-Ru1-N82	177.958	
N82-Ru1-N3	89.904	N2-Ru1-N4	78.911	
N82-Ru1-N4	87.902	N3-Ru1-N5	102.197	
N82-Ru1-N5	102.815			

Table 1. Bond parameters (distances and angles) of the optimized structures of 1 and 2.

in the present study shows a trend in Ru–Npy and Ru–N_(quinoline) bond distances similar to the tris-chelate Ru complex of 2-(2-pyridyl)-4-carboxyquinoline) ligand [43]. Literature values for the two bonds are 2.06 and 2.15 Å, whereas for the present molecule those values are 2.08 and 2.19 Å, respectively. Complex **2** follows the same trends as **1** with minor differences in bond lengths and angles. Compositions of the frontier molecular orbitals for **1** and **2** show that HOMO and HOMO-1 are essentially ruthenium- and thiocyanate-based, whereas HOMO-2 has maximum contributions from terpyridine and HOMO-4 has substantial contributions from ruthenium, thiocyanate and terpyridine ligands. LUMO and LUMO + 3 are rich with 2-(2-pyridyl)-4-carboxyquinoline ligand.

3.5. TDDFT studies

The theoretical spectrum generated from TDDFT calculations (figure 5) matches well with the experimental absorption spectrum. In **1**, the experimental spectrum shows a broad band at 502 nm corresponding to theoretical absorptions at 542 nm (f = 0.013) and 507 nm (f = 0.2). Here, the absorption corresponds to the metal- and metal-ligand-to-ligand charge-transfer (MLCT and MLLCT) transition from Ru and Ru-thiocyanate to pcqH. The observed shoulder at 337 nm corresponds to contributions from both calculated bands at 389 nm (f = 0.26) and at 328 nm (f = 0.27). The former is a terpyridine-based intraligand transition and the latter is a pcqH-based transition. The experimental band at 313 nm comprises intra- and inter-ligand transitions within terpyridine and from terpyridine-to-pcqH corresponding to a theoretical band at 309 nm with high oscillator strengths (f = 0.39). The band



Figure 5. Electronic transitions assigned to the major absorption bands for (a) 1 and (b) 2. Theoretical absorption spectra of (c) 1 and d) 2.

positions with their oscillator strengths and assignment are represented in SM 17. In **2**, the experimental band at 527 nm corresponds to a theoretical MLLCT charge transfer from Ru -NCS to pcqH at 508 nm (f = 0.14) and at 486 nm (f = 0.12). The broad hump at 455 nm is also depicted in the theoretical spectrum at 486 nm (f = 0.12). The experimental band at 317 nm is best correlated to the theoretical band at 309 nm (f = 0.21) which is an intra-ligand transition from mostly terpyridine- and pcqH-based occupied orbitals to terpyridine-based vacant orbitals. The band at 277 nm arises from a similar transition. SM 18 shows the band positions with their oscillator strength and character assignment.

4. Conclusion

We have synthesized two ruthenium complexes with terpyridine and 2-(2-pyridyl)4-carboxyquinoline as ligands and thiocyanate as an ancillary co-ligand. With the increase in +R donating groups (–OMe) substituted over the phenyl-moiety of the terpyridine ligand, the redox potential for the Ru^{II/III} process is reduced as expected. The complexes have efficient light harvesting capabilities as evident from their high absorptivity.

Supplementary data

All the structural characterization data, namely mass, ¹H and ¹³C NMR data, DFT-optimized molecular orbital diagrams of the complexes can be found in the Supporting Information.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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