Asian Journal of Chemistry; *Vol. 27, No. 7 (2015), 2555-2558*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18018

Synthesis, Photophysical and Electrochemical Properties of Two Novel Heterobinuclear Ru(II)/Fe(II) Complexes

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Received: 16 May 2014; *Accepted*: 7 August 2014; *Published online*: 30 March 2015; AJC-17078

Two polypyridyl ligands namely 5-(2-ferrocenylethynyl)-2,2'-bipyridine (L^1) and 3-(2-ferrocenylethynyl)-1,10-phenanthroline (L^2) and corresponding Ru(II) complexes $[(bpy)_2Ru(L^{1-2})](PF_6)_2$ (Ru-L^1, Ru-L^2) (bpy = 2,2'-bipyridine) have been synthesized and characterized. Both ligands were synthesized by cross-coupling reactions of ethynyl ferrocene with 5-bromo-2,2'-bipyridine and 3-bromo-1,10-phenanthroline, respectively, in the presence of $(PPh_3)_2PdCl_2$, CuI and Et_3N under nitrogen atmosphere. The Ru(II) complexes, $[(bpy)_2Ru(L^1)](PF_6)_2$ and $[(bpy)_2Ru(L^2)](PF_6)_2$, have been obtained by refluxing $Ru(bpy)_2Cl_2{\cdot}2H_2O$ with each ligand in ethanol under nitrogen atmosphere. The spectroscopic behaviour of both heterobinuclear complexes was investigated with UV/visible absorption and emission spectroscopy. Both complexes exhibit metal-to-ligand charge transfer (MLCT) absorption at around 450 nm. Complex Ru-L^1 is non-emissive and Ru-L^2 exhibits weak fluorescence in CH_3CN solution at room temperature. In 4:1 EtOH:MeOH glassy matrix at 77 K, both complexes display weak fluorescence. Electrochemical studies of the two complexes display two metal-centered and three ligand-centered redox couples.

Keywords: Ru(II)/Fe(II) Complex, UV/visible Absorption, Emission, Electrochemistry, Energy Transfer.

INTRODUCTION

Covalently linked oligometallic complexes are of great interest in the study of photoinduced energy and electron transfer. Particular interest has been focused on complexes containing Ru(II) polypyridyl components because of their outstanding electrochemical and photophysical properties and their extensive use in luminescence, pH switching, *etc.*[1]. Photo-induced energy and electron transfer processes have drawn increasing attention due to their potential applications in fields as diverse as artificial photosynthesis, photocatalysis and molecular informatics, *etc.*[2]. In the design of such Ru(II) systems, the bridging ligands that are used to link two or more metal polypyridine subunits are crucial because the interactions between the bridged units and thereby the ground- and excited-state properties of the polynuclear complex, are strongly dependent on the size, shape and electronic nature of the bridging ligands[3]. Thus, the judicious choice of an appropriate bridging ligand is the most important factor in realizing molecular devices bases on polynuclear Ru(II) complexes. Much effort has been devoted to the design and synthesis of polypyridyl ligands that lead to Ru(II) complexes with interesting photophysical and electrochemical properties. A wide range of bridging ligands have been used in recent years, among the kinds of polypyridyl ligands, 2,2'-bipyridine ligands substituted at the 5,5' positions and 1,10-phenanthroline ligands substituted at the 3,8 positions exhibit intense electronic transitions along the strategic long axis of the molecules[4] and acetylenic linkages are attractive candidates to promise effective vectorial energy and electron transfer over long distances[5]. Meanwhile, ferrocene has rich optical and redox properties. Herein, we report the synthesis of two Ru(II)/Fe(II) binuclear complexes and the spectroscopic and electrochemical properties of both complexes.

EXPERIMENTAL

2,2'-Bipyridine, 1,10-phenanthroline, NH_4PF_6, hydrated ruthenium trichloride, ethyl acetate, petroleum ether, toluene, $(PPh_3)_2PdCl_2$, $CHCl_3$, CuI, Et_3N, EtOH, MeOH, MeCN, Et_2O and DMF were purchased from the Tianjin Chemical Reagent Factory. Solvents and raw materials were of analytical grade and used as received, apart from CH_3CN, which was filtered through activated alumina and distilled from P_2O_5 immediately prior to use. Ethynylferrocene[6], 5-bromo-2,2'-bipyridine[7], 3-bromo-1,10-phenanthroline[8], tetrabutylammonium perchlorate (TBAP)[9] and $Ru(bpy)_2Cl_2{\cdot}2H_2O$[10] were prepared according to literature procedures.

^{1}H NMR spectra were obtained with a Mercury Plus 400 spectrometer using TMS as internal standard. ESI-HRMS spectra were obtained with a Bruker Daltonics APEXII47e mass spectrometer. Elemental analyses were obtained with a Perkin-Elmer 240C analytical instrument. Absorption spectra were obtained with a Varian Cary-100 UV/visible spectrophotometer and emission spectra with a Hitachi F-4500 spectrophotometer. The emission quantum yields were calculated relative to $Ru(bpy)_3^{2+}$ (Φstd = 0.062) in deoxygenated CH_3CN solution at room temperature and relative to $Ru(bpy)_3^{2+}$ (Φstd = 0.376) in EtOH/MeOH (4:1,v/v) glassy matrix[11]. Electrochemical measurements were carried out at room temperature using a CHI 660B electrochemical workstation. Cyclic voltammetry and differential pulse voltammetry were performed in CH_3CN solutions using a micro cell equipped with a platinum disk working electrode, a platinum auxiliary electrode and a saturated potassium chloride calomel reference electrode with 0.1 mol L^{-1} TBAP as supporting electrolyte. All samples were purged with nitrogen prior to measurement.

Synthesis of 5-(2-ferrocenylethynyl)-2,2'-bipyridine (L^1): A mixture of 5-bromo-2,2'-bipyridine (92 mg, 0.39 mmol), ethynylferrocene (85 mg, 0.40 mmol), $(PPh_3)_2PdCl_2$ (8 mg), CuI (6 mg) and Et_3N (1 mL) in benzene (30 mL) and methanol (5 mL) was heated to reflux for 12 h under nitrogen atmosphere. Then the solvent was evaporated under reduced pressure, the residue was purified by column chromatography on silica, being eluted with ethyl acetate-petroleum ether (5:1, v/v) to afford the desired product as an orange solid. Yield: 71 mg (50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (s, 5H), 4.31 (s, 2H), 4.56 (s, 2H), 7.37 (s, 1H), 7.90 (t, *J* = 8.4 Hz, 2H), 8.45 (d, *J* = 7.6 Hz, 2H), 8.72 (d, *J* = 4.0 Hz, 1H), 8.77 (s, 1 H). ESI-HRMS: *m/z* 364.0662 (M^+).

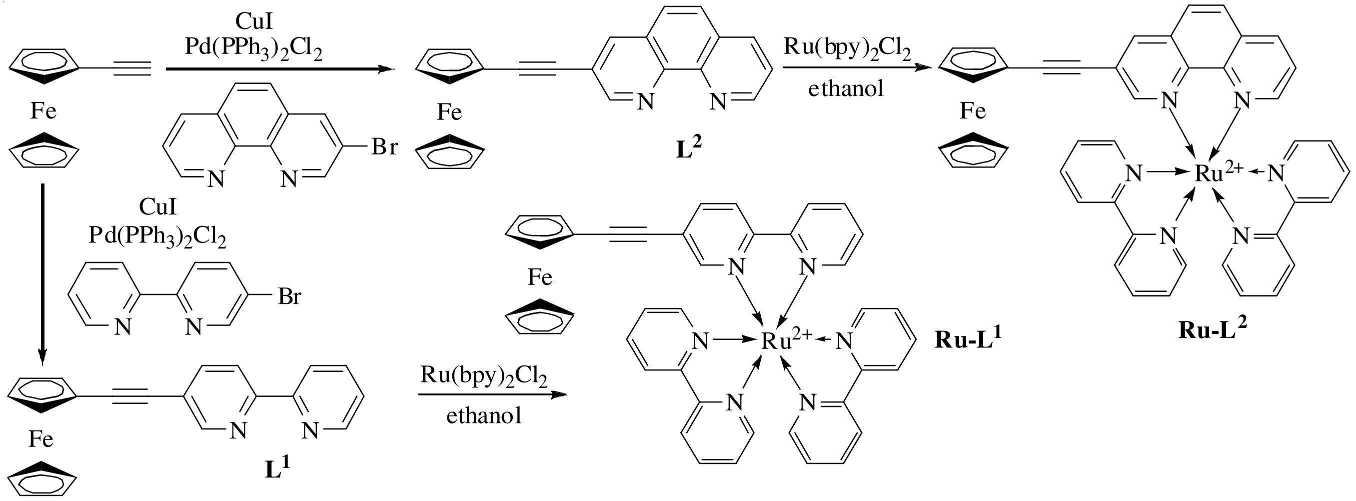
Synthesis of 3-(2-ferrocenylethynyl)-1,10-phenanthroline (L^2): A mixture of 3-bromo-1,10-phenanthroline (120 mg, 0.46 mmol), ethynylferrocene (80 mg, 0.38 mmol), $(PPh_3)_2PdCl_2$ (10 mg), CuI (8 mg) and Et_3N (1 mL) in benzene (30 mL) and methanol (5 mL) was heated to reflux for 12 h under nitrogen atmosphere. Then the solvent was evaporated under reduced pressure, the residue was purified by column chromatography on silica, being eluted with $CHCl_3$ to afford the desired product as an orange solid. Yield: 98 mg (66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (s, 5H), 4.33 (s, 2H), 4.60 (s, 2H), 7.67 (t, *J* = 11.4 Hz, 1H), 7.69-7.86 (m, 2H), 8.26 (d, *J* = 6.8 Hz, 1H), 8.34 (s, 1H), 9.22 (d, *J* = 11.2 Hz, 2H). ESI-HRMS: *m/z* 388.0657 (M^+).

Synthesis of $[(bpy)_2Ru(L^1)](PF_6)_2$ (Ru-L^1): A mixture of ligand L^1 (41 mg, 0.11 mmol) and $Ru(bpy)_2Cl_2\cdot 2H_2O$ (68 mg, 0.13 mmol) in ethanol (20 mL) was refluxed for 8 h under nitrogen atmosphere, then the solvent was evaporated under reduced pressure. The residue was purified twice by column chromatography on alumina, being eluted first with CH_3CN-ethanol (15:1, v/v) to remove impurities, then with CH_3CN-ethanol (5:1, v/v) to afford the complex $[(bpy)_2Ru(L^1)]Cl_2$. This complex was dissolved in the minimum amount of water followed by dropwise addition of saturated aqueous NH_4PF_6 until no more precipitate formed. The precipitate was recrystallized from CH_3CN-Et_2O mixture (vapor diffusion method) to afford a red solid. Yield: 85 mg (71 %). ^{1}H NMR (400 MHz, *d*$_6$-acetone): δ = 4.19 (s, 5H), 4.36 (d, *J* = 2.0 Hz, 2H), 4.46 (d, *J* = 1.6 Hz, 2H), 7.57-7.62 (m, 5 H), 8.01 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 4.0 Hz, 2H), 8.06 (d, *J* = 5.2 Hz, 1H), 8.11-8.24 (m, 7H), 8.79-8.85 (m, 6H). ESI-HRMS: *m/z* 923.0382 ($M-PF_6$)$^+$. Anal. Calcd. For $C_{42}H_{32}F_{12}FeN_6P_2Ru$: C, 47.25; H, 3.02; N, 7.87. Found: C, 47.12; H, 2.92; N, 7.98.

Synthesis of $[(bpy)_2Ru(L^2)](PF_6)_2$ (Ru-L^2): Complex Ru-L^2 was prepared by the same procedure as that described for Ru-L^1, except L^2 (44 mg, 0.11 mmol) was used instead of L^1. Yield: 75 mg (61 %) of a red solid. ^{1}H NMR (400 MHz, *d*$_6$-acetone): δ = 4.23 (s, 5H), 4.38 (d, *J* = 2.0 Hz, 2H), 4.50 (d, *J* = 1.6 Hz, 2H), 7.38-7.44 (m, 2H), 7.62-7.65 (m, 2H), 7.86-7.97 (m, 2H), 8.02-8.07 (m, 2H), 8.11-8.21 (m, 3H), 8.23-8.28 (m, 2H), 8.35-8.49 (m, 4H), 8.81-8.88 (m, 6H). ESI-HRMS: *m/z* 947.0710 ($M-PF_6$)$^+$, 401.0593 ($M-2PF_6$)$^{2+}$. Anal. Calcd. For $C_{44}H_{32}F_{12}FeN_6P_2Ru$: C, 48.41; H, 2.95; N, 7.70. Found: C, 48.20; H, 2.71; N, 7.96.

RESULTS AND DISCUSSION

The outline of the synthesis of polypyridyl ligands L^1 and L^2 and corresponding complexes $[(bpy)_2Ru(L^1)]$-$(PF_6)_2$ and $[(bpy)_2Ru(L^2)](PF_6)_2$ is presented in **Scheme-I**. L^1 and L^2 were synthesized by cross-coupling reactions of ethynylferrocene with 5-bromo-2,2'-bipyridine and 3-bromo-1,10-phenanthroline,



Scheme-I: Synthesis of polypyridyl ligands and corresponding Ru(II) complexes respectively in the presence of $(PPh_3)_2Pd\text{-}Cl_2$, CuI and Et_3N under nitrogen atmosphere[12]. For each of the ligands, Ru(II) complex was prepared under nitrogen atmosphere by refluxing the starting materials $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and ligand in ethanol under nitrogen atmosphere, then purified twice by column chromatography on alumina and precipitated with saturated aqueous NH_4PF_6. The resulting complexes were characterized by ^1H NMR, ESI-HRMS and elemental analysis.

Absorption spectra: The UV/visible absorption spectra of both complexes in CH_3CN solution (10^{-5} mol L^{-1}) are shown in Fig. 1. The absorption maxima and corresponding molar absorption coefficients are listed in Table-1. Assignments of the absorption bands are made on the basis of the well-documented optical transitions of analogous Ru(II) polypyridyl complexes[13]. Absorption spectra of both complexes comprise four distinct regions. The bands at around 286 and 240 nm are attributed to the 2,2'-bipyridine centered intraligand $\pi \rightarrow \pi^*$ transitions. At higher energy region around 320 and 341 nm, absorption spectra display the characteristic bands of core ligand L^1 and L^2, respectively. The lowest energy band at around 450 nm can be assigned as MLCT, $d\pi \rightarrow \pi^*$ transition[14]. The $d\pi \rightarrow \pi^*$ transition consists of overlapping $d\pi(Ru) \rightarrow \pi^*(bpy)$ and $d\pi(Ru) \rightarrow \pi^*(L)$ components, which results in the appearance of a non-symmetrical MLCT band.

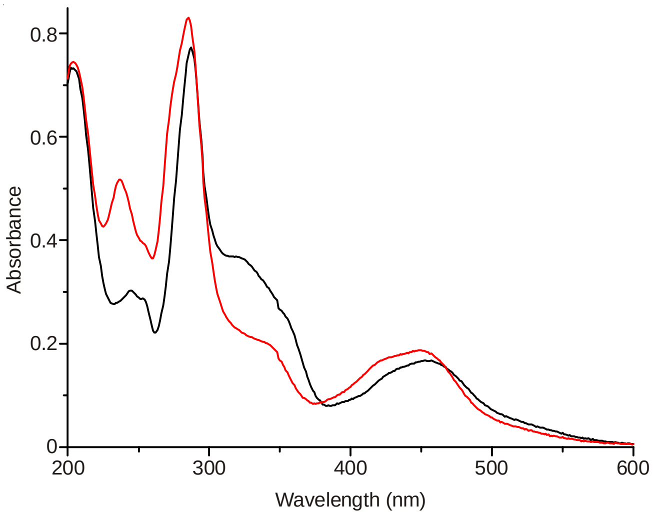


Fig. 1. Absorption spectra of complexes Ru-L^1 (black), and Ru-L^2 (red) in CH_3CN solution at room temperature

Electrochemistry: Electrochemical behaviours of both complexes (5×10^{-4} mol L^{-1}) have been studied in CH_3CN solution at room temperature with 0.1 mol L^{-1} TBAP as supporting electrolyte (scan rate = 200 mV/s) and the electrochemical data are given in Table-1. Cyclic voltammetry of complex Ru-L^1 displays two metal-based redox couples, the first one corresponds to the Ru(II)-centered reversible oxidation wave at $E_{1/2}$ = 1.29 V *vs* SCE for the $Ru^{II/III}$ couple and the second one corresponds to the Fe(II)-centered reversible oxidation wave at $E_{1/2}$ = 0.57 V (Fig. 2). Ru(II)-centered oxidation couple is very close to that of parent complex $Ru(bpy)_3^{2+}$ [15], appearing little influence of the strong π-accepting character of ligand L^1. In contrast with the oxidation properties, the first one-electron reduction process shows that Ru-L^1 is better electron acceptor than $Ru(bpy)_3^{2+}$ by about 0.1 V, giving the species $[(bpy)(bpy)Ru^{II}(L^{\bullet-})]^+$. The second reversible reduction process at -1.52 V is located on one of the two 2,2'-bipyridine ligands on Ru(II) metallic terminal, adding electrons to the 2,2'-bipyridine localized LUMO + 1 orbitals yielding the species $[(bpy)(bpy^{\bullet-})Ru^{II}(L^{\bullet-})]$. The third reduction at -1.75 V is reversible and affords the species $[(bpy^{\bullet-})(bpy^{\bullet-})Ru^{II}(L^{\bullet-})]^-$. Electrochemistry behaviour of complex Ru-L^2 is the same as that of Ru-L^1.

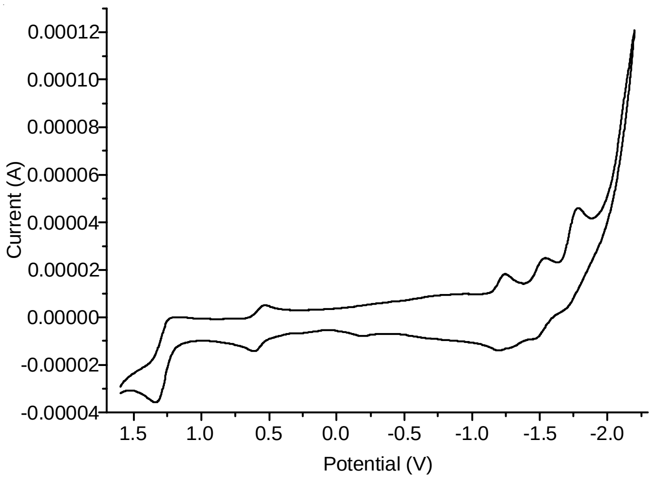


Fig. 2. Cyclic voltammetry of complex Ru-L^1 (5×10^{-4} mol L^{-1}) in CH_3CN (0.1 mol L^{-1} TBAP) solution at room temperature

Emission spectra: Emission band maxima and emission quantum yields of both Ru(II) complexes are summarized in Table-1. Upon excitation into the MLCT band of both

TABLE-1
PHOTOPHYSICAL AND ELECTROCHEMICAL DATA OF BOTH Ru(II) POLYPYRIDYL COMPLEXES

Complex	Absorption[a]	$E_{1/2}$, V (ΔE_p, mV)[b]		Emission[c, d]			
	λ_{max}, nm (10^4 ε, M^{-1} cm^{-1})	Oxidation	Reduction	λ_{max}[c]	ϕ[c]	λ_{max}[d]	ϕ[d]
Ru-L^1	453 (1.67)	1.29 (115)	-1.22 (58)	–	–	577	0.013
	320 (3.68)	0.57 (84)	-1.51 (60)				
	287 (7.72)		-1.75 (69)				
	244 (3.03)						
Ru-L^2	448 (1.87)	1.28 (164)	-1.21 (69)	601	0.012	577	0.206
	341 (2.01)	0.57 (84)	-1.52 (116)				
	285 (8.29)		-1.78 (90)				
	237 (5.17)						

[a]UV/visible absorption are measured in CH_3CN solution at room temperature; b. potentials are recorded in 0.1 M TBAP/CH_3CN and were given *vs* SCE; scan rate = 200 mV/s; ΔE_p is the difference between the anodic and cathodic waves. C, d. Luminescence are measured in CH_3CN solution at room temperature and in 4:1 ethanol:methanol glassy matrix, respectively, the uncertainty in quantum yield is 10 %

complexes in CH_3CN solution at room temperature, Ru-L^1 is non-emissive and Ru-L^2 exhibits weak fluorescence comparing with parent complex $Ru(bpy)_3^{2+}$ (Fig. 3). Complexes Ru-L^1 and Ru-L^2 display similar vibrational components to $Ru(bpy)_3^{2+}$ at 77 K in 4:1 EtOH:MeOH glassy matrix (Fig. 4). They exhibit characteristic emission at 577 nm, but the relative fluorescence intensity of $Ru(bpy)_3^{2+}$ is about 30 times stronger than that of complex Ru-L^1 and about 2 times stronger than that of complex Ru-L^2. Fluorescence quenching most likely proceeds *via* intramolecular triplet energy transfer, from parent complex unit $Ru(bpy)_3^{2+}$ to ferrocene unit across ethynyl bridge[16] and energy transfer of Ru-L^1 is more efficient than Ru-L^2.

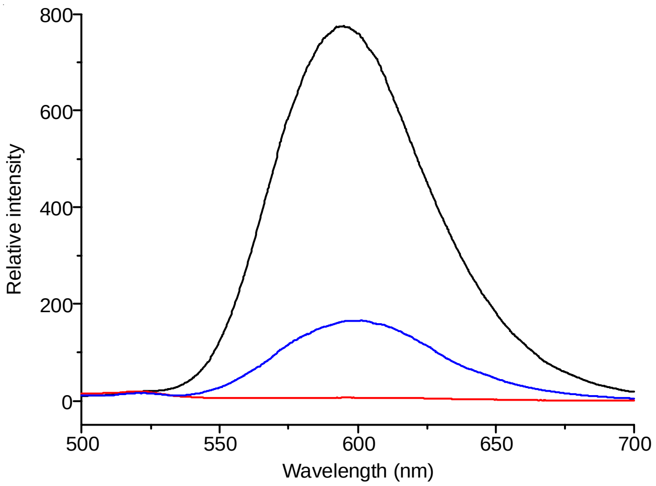


Fig. 3. Fluorescence spectra of Ru-L^1 (red), Ru-L^2 (blue), and $Ru(bpy)_3(PF_6)_2$ (black) in CH_3CN at room temperature

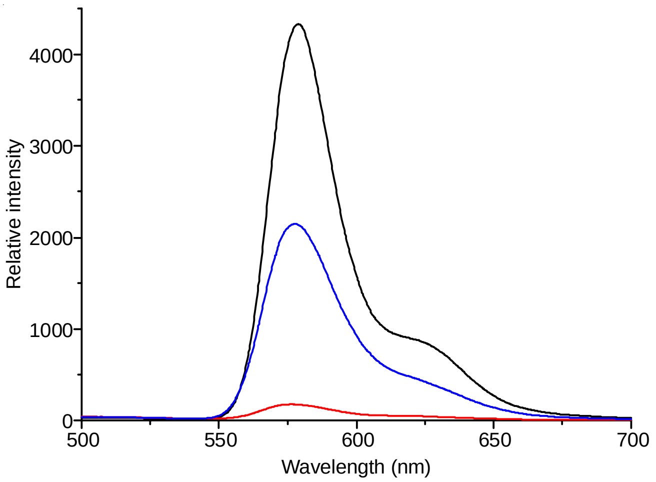


Fig. 4. Fluorescence spectra of Ru-L^1 (red), Ru-L^2 (blue) and $Ru(bpy)_3(PF_6)_2$ (black) in 4:1 EtOH:MeOH glassy matrix at 77 K

Conclusion

In conclusion, two bridging ligands containing ferrocene unit and their corresponding heterobinuclear Ru(II)/Fe(II) complexes were synthesized and characterized. The UV/visible absorption and emission properities of both complexes are dominated by MLCT transitions and excited state. Fluorescence quenching most likely proceeds *via* intramolecular triplet energy transfer from the Ru-based unit to the Fe-based unit. Taking into account the heterobinuclear character of both Ru(II)/Fe(II) complexes, they have potential applications in the research area of intramolecular electron and energy transfer.

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