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Synthesis of a new polypyridinic highly conjugated ligand with electron-acceptor properties

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Abstract—A new acceptor polypyridinic ligand functionalized with a quinone fragment is reported. The ligand, dipyrido[3,2-*a*:2′,3′-*c*]-benzo[3,4]-phenazine-11,16-quinone, Nqphen, was synthesized by condensation of 1,10-phenanthroline-5,6-dione and 2,3-diamino-1,4-naphthoquinone. The syntheses of two rhenium complexes with this ligand are also reported. © 2001 Elsevier Science Ltd. All rights reserved.

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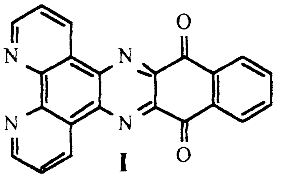
1. Introduction

The development of artificial systems able to transform solar energy in a form of usable energy is one of the present big challenges of many research groups.[1] In this context, d^6 transition metal complexes with bidentate (*N*,*N*) type ligands as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), and monodentate ligands as pyridine (py) or their derivatives, have been amply studied. The interest in these types of complexes relies on their capacity to absorb visible light and thereby to access to excited states by means of metal-to-ligand charge-transfer (MLCT) processes.[2] The electron promoted to a ligand orbital in the excited state can be injected into the conducting band of the electrode oxide, starting in this way the conversion of light into electricity. Similar studies with porphirine as ligand have been reported.[3] In order to favor photoinduced electron transfer, carotenoid units were covalently linked to the porphirinic entity, as well as quinonic residues. This latter type of function plays an important role as acceptor moieties in natural photosynthetic systems.[4]

In an attempt to combine these two properties—the ability to generate MLCT by (*N*,*N*) coordination to metal and the presence of a quinonic acceptor group—the ligand dipyrido[3,2-*a*:2′,3′-*c*]-benzo[3,4]-phenazine-11,16-quinone, Nqphen (I), was designed and prepared.



I

The quinone moiety had also been incorporated to previously reported ligands as Aqphen[5,6] and bpy-AQ,[7] although Nqphen has the advantage of being more rigid and linear, favoring in this way the electron transfer to the quinone.

2. Results and discussion

The synthesis of Nqphen, **I**, was conducted by the condensation of 1,10-phenanthroline-5,6-dione (phendione) and 2,3-diamino-1,4-naphthoquinone chlorhidrate (**V**).

This latter reagent was synthesized starting from 2,3-dicloro-1,4-naphthoquinone (Aldrich), by successive substitutions of the chlorine atoms by amino groups, as shown in Scheme 1. The synthesis of the intermediate compounds **II**, **III**, and **IV** was made according to published procedures.[8,9] Compound **V** was synthesized by acid hydrolysis of **IV** in methanol.

In regard to the characterization of the new ligand Nqphen **I**, an important feature in its IR spectrum is the disappearance of the (NH) stretching of 2,3-diamino-1,4-naphthoquinone (**V**), (3477 and 3364 cm^{-1}), verifying in this way the condensation reaction to form **I**. The ν (C=O) of the quinonic fragment of this

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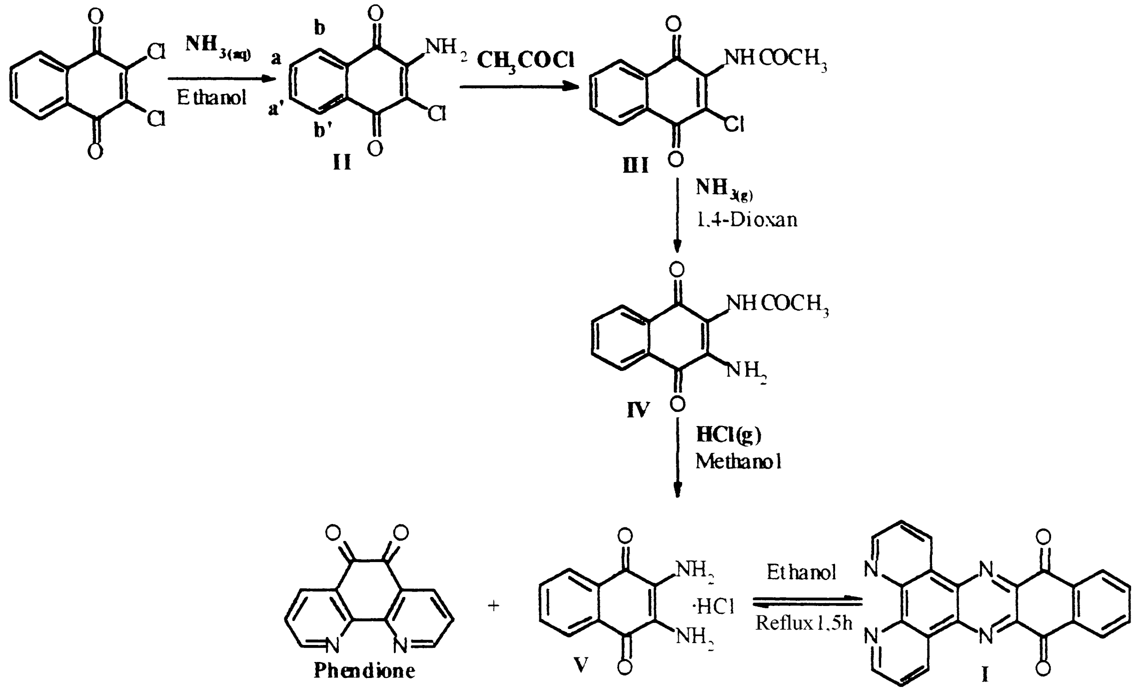


Scheme 1.

ligand appears at 1686 cm^{-1}, slightly displaced to higher energy in regard to the corresponding position in precursor **V** (1682 cm^{-1}).

Ligand **I** showed low solubility in most common solvents. The better solubility in $CDCl_3$ permits to record the ^1H NMR spectrum (Fig. 1A). The effect on the NMR pattern of metal coordination to the ligand was checked by synthesizing the complexes (Nqphen)Re(CO)$_3$Cl (**VI**) and (Nqphen)Re(CO)$_3$(OTf) (**VII**), (OTf = trifluoromethanesulfonate anion). These complexes are more soluble than the free ligand. Fig. 1B shows the ^1H NMR pattern for **VII** in CD_3CN. The simplicity of the pattern spectra denotes the magnetic equivalence of the phenanthroline protons fragment as well as the quinonic protons fragment due to ring planarity and molecular symmetry. This is also reflected by an integral relation 1:1 in both protons fragment and 2:1 between phenanthroline protons and quinonic protons. The main effect observed due to coordination

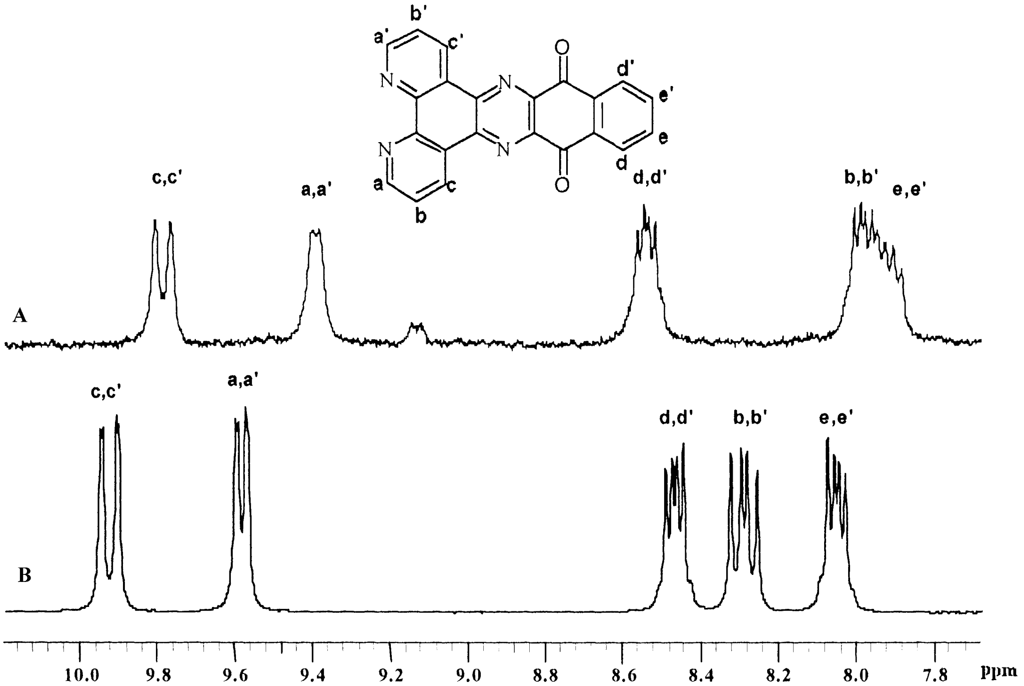
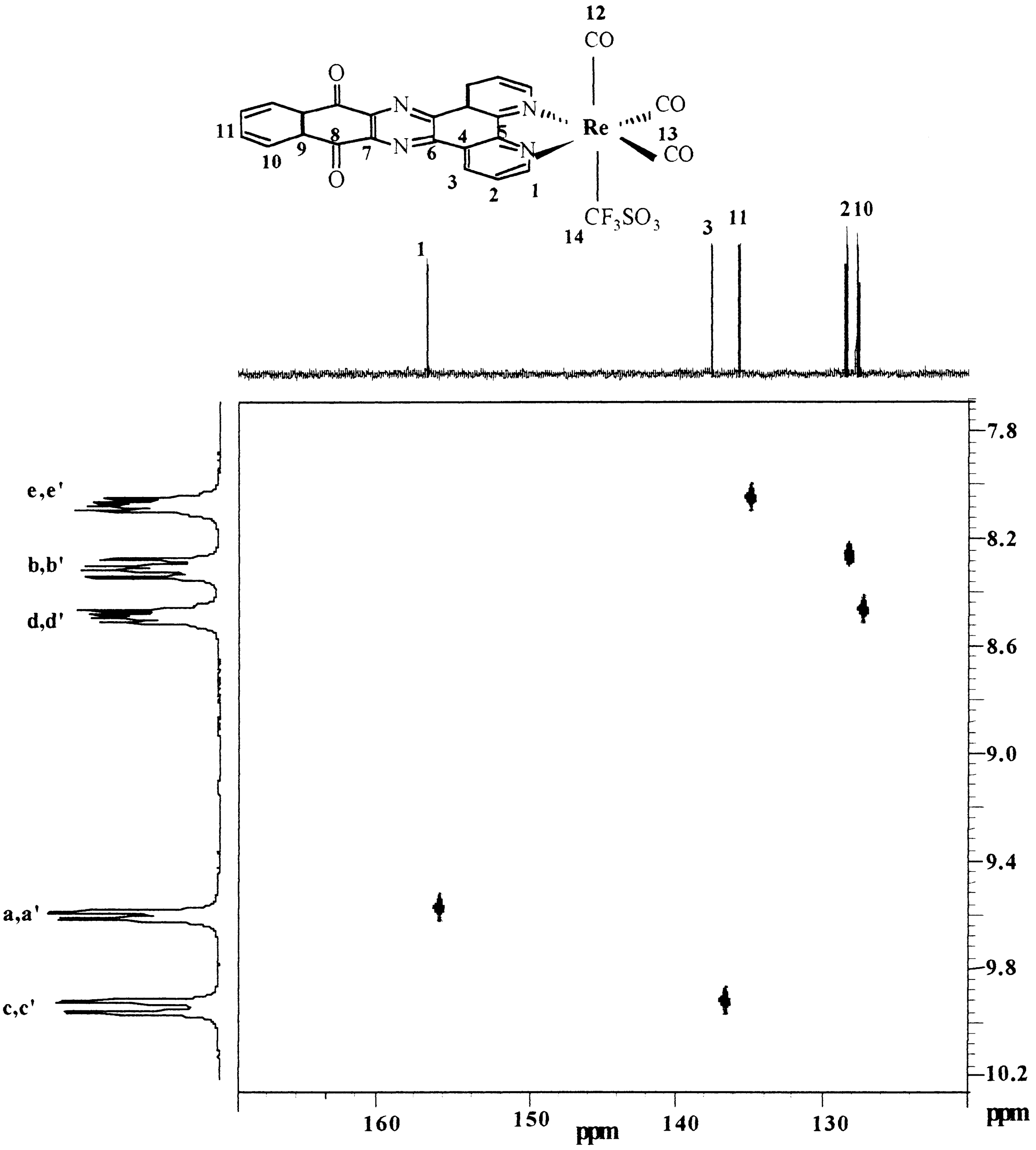


Figure 1. ^1H NMR for (A) Nqphen in $CDCl_3$, and (B) (Nqphen)Re(CO)$_3$(OTf) in CD_3CN.



* H atoms labeled according to Figure 1. C atoms labeled according to Figure 2.

Figure 2. ^1H–^{13}C-hetero COSY for **VII** in CD_3CN.

of Nqphen to Re(I) is the enhanced deshielding of the protons of the phenanthrolinic fragment of the ligand, which are the ones most affected by the presence of the metal.

^{13}C NMR† and ^1H–^{13}C-hetero COSY spectra were recorded in order to confirm the proton assignment for the ^1H NMR. Fig. 2 shows the ^1H–^{13}C-hetero COSY spectrum for **VII** in acetonitrile. The most deshielded C(1) belongs to the phenanthroline fragment, adjacent to the nitrogen atom that lost charge density by its coordination to the metal. This carbon atom is bound to $H_{a,a'}$ (9.63 ppm.). The protons in *para*-position $H_{c,c'}$ in addition to being affected by the coordination are also affected by the anisotropie of the pyrazine nitrogen. That is the cause of a great chemical shift to low field (9.94 ppm). Table 1 summarizes the final assignment of the ^1H NMR spectra, done by using the ^1H–^{13}C-hetero COSY information.

The UV–vis spectra of **I** recorded in chloroform presents three bands at 241 (ε=8.3x10^4), 274 (ε=6.5x10^4)

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† ^{13}C NMR spectra data for **VII** (in CD_3CN): C(1), 157.10; C(2), 128.36; C(3), 137.57; C(4), 122.81; C(5), 129.66; C(6), 133.79; C(7), 145.34; C(8), 149.96; C(9), 141.61; C(10), 127.65; C(11), 135.64; C(12), 189.98; C(13), 180.49; C(14), 193.18.

Table 1. ^{1}H NMR signals for ligand **I**, and compounds **VI** and **VII**

Compound	Chemical shifts (in ppm) (see Fig. 1)				
	H(a), H(a′)	H(b), H(b′)	H(c), H(c′)	H(d), H(d′)	H(e), H(e′)
Nqphen[a]	9.41 (d) $J_{ab}=4.18$	7.92 (dd) $J_{ba}=4.18$ $J_{bc}=8.12$	9.80 (d) $J_{cb}=8.12$	8.54 (dd) $J_{de}=5.66$ $J_{de'}=3.44$	7.98 (dd) $J_{ed}=5.66$ $J_{ed'}=3.44$
[Nqphen Re(CO)$_3$Cl][a]	9.58 (dd) $J_{ab}=5.16$ $J_{ac}=1.47$	8.14 (dd) $J_{ba}=5.16$ $J_{bc}=8.23$	10.00 (dd) $J_{cb}=8.12$ $J_{ca}=1.47$	8.58 (dd) $J_{de}=5.91$ $J_{de'}=3.45$	8.03 (dd) $J_{ed}=5.91$ $J_{ed'}=3.45$
[Nqphen Re(CO)$_3$(OTf)][b]	9.59 (dd) $J_{ab}=5.41$ $J_{ac}=1.23$	8.29 (dd) $J_{ba}=5.41$ $J_{bc}=8.37$	9.94 (dd) $J_{cb}=8.37$ $J_{ca}=1.23$	8.47 (dd) $J_{de}=5.91$ $J_{de'}=3.44$	8.05 (dd) $J_{ed}=5.91$ $J_{ed'}=3.44$

[a] In CDCl$_3$.
[b] In CD$_3$CN.

and 317 ($\varepsilon=5.9\times10^4$) nm. The first two bands are assigned to π–π* intraligand transitions and the third to an n–π* transition. Compounds **VI** and **VII** present the same pattern in the UV region, with some displacement of the bands due to coordination. An additional band, which is assigned to MLCT, appears as a shoulder in the 360–400 nm ($\varepsilon\approx1\times10^4$) region.

The electron-acceptor capacity of Nqphen was checked by cyclic voltammetry, where three irreversible reduction peaks appear: $E_p=-0.708$; −1.340; −1.585 V (versus SCE in CH$_3$CN). The first is assigned to the semiquinone and dianion formation, the second to the pyrazine fragment and the third to the phenanthroline part of Nqphen.

According to the results discussed above, it can be concluded that the Nqphen ligand was obtained in good yield and purity. It shows acceptable coordination capacity, and strong acceptor properties. This makes it a good candidate for the preparation of excited state charge separate systems.

3. Experimental

3.1. Synthesis of 1,10-phenanthroline-5,6-dione (phendione)

This syntheses was carried out according to published procedures.[5,10]

3.2. Synthesis of 2,3-diamino-1,4-naphthoquinone hydrochloride (V)

Compound **IV** (3 g, 11.62 mmol) was suspended in dry methanol (40 ml). This mixture was then cooled in an ice bath and a current of dry hydrogen chloride was passed through it for 2 h. During this time, a yellow solid was formed. The mixture was heated at 60°C for 1 h and then refluxed for 4 h. Yellow needles were obtained by cooling to rt. These were filtered, washed with methanol and diethyl ether. After drying under high vacuum, 2.1 g of dark-yellow product were obtained (yield 77%). Elemental analysis (%) calcd for $C_{10}H_8N_2O_2\cdot HCl$: C, 53.47; H, 4.04; N, 12.47. Found: C, 51.81; H, 4.09; N, 12.59. ^{1}H NMR (CDCl$_3$): 8.08 (dd, H(a), H(a′)); 7.52 (dd, H(b), H(b′)); 5.49 (s, NH$_2$). IR (cm^{-1}) 1682 (ν C=O), 3477.2, 3363.6 (ν N–H), 1645 (δN–H). UV–vis (nm, acetonitrile): 246 ($\varepsilon=1.2\times10^4$), 283 ($\varepsilon=1.3\times10^4$), 510 ($\varepsilon=1.02\times10^3$).

3.3. Synthesis of dipyrido[3,2-*a*:2′,3′-*c*]-benzo[3,4]-phenazine-11,16-quinone (Nqphen) I

Phendione (0.618 g, 2.94 mmol) and **V** (0.660 g, 2.94 mmol) were suspended in dry ethanol (40 ml). The mixture was refluxed for 1.5 h under a N$_2$ atmosphere. A green solid was formed. The mixture was cooled to rt and the solid was filtered, washed with ethanol and diethyl ether. After drying under high vacuum, 0.926 g of Nqphen were obtained as a green powder. Yield 87%; mp 456.25°C. Elemental analysis (%) calcd for $C_{22}H_{10}N_4O_2$: C, 72.93; H, 4.01; N, 12.47. Found: C, 73.21; H, 3.89; N, 12.01.

3.4. Synthesis of (Nqphen)Re(CO)$_3$Cl (VI)

Compound **I** (0.60 g, 1.66 mmol) and Re(CO)$_5$Cl[‡] (0.60 g, 1.66 mmol) were suspended in 50 ml of dry toluene. The mixture was stirred and refluxed for 2 h under N$_2$. A yellow solid was formed. The reaction mixture was cooled to rt and the solid was filtered, washed with petroleum ether and diethyl ether. After drying under high vacuum, 1.20 g of product was obtained as a yellow powder. Yield 94%; mp 381°C (dec.) Elemental analysis (%) calcd for $C_{25}H_{10}ClN_4O_5Re$: C, 44.95; H, 1.51; N, 8.39. Found: C, 43.85; H, 1.48; N, 8.02.

3.5. Synthesis of (Nqphen)Re(CO)$_3$(OTf) (VII)

Compound **VI** (0.60 g, 0.90 mmol) and silver trifluoromethanesulfonate (AgOTf) (0.231 g, 0.90 mmol) were suspended in 40 ml of dry THF. The mixture was stirred and refluxed for 1 h under N$_2$ in the dark. The

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[‡] Re(CO)$_5$Cl was kindly supplied by Dr. H. Klahn: Klahn, A. H.; Oelckers, B.; Toro, A.; Godoy, F. *J. Organomet. Chem.* **1997**, *548*, 121.

solution was filtered hot to remove the AgCl formed. The filtrate was evaporated to dryness and the yellow residue was dissolved in acetonitrile. The product was reprecipitated by addition of diethyl ether, filtered and finally purified by chromatography on alumina with chloroform/acetonitrile 1:1 (v/v) as eluent. (Nqphen)-Re(CO)$_3$(OTf) was obtained as a yellow powder (0.49 g). Yield 70%; mp 385.56°C (dec.). Elemental analysis (%) calcd for $C_{26}H_{10}F_3N_4O_8ReS$: C, 39.95; H, 1.29; N, 7.16; S, 4.09. Found: C, 38.25; H, 1.09; N, 6.99; S, 3.98.

Acknowledgements

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9. Data for compounds **II**, **III**, and **IV** synthesized in this work.
   2-Amino-3-chloro-1,4-naphthoquinone (II): Yield 74%. Elemental analysis (%): Calcd for $C_{10}H_6NO_2Cl$; C, 57.86; N, 6.75; H, 2.89. Found: C, 57.25; N, 6.58; H, 2.69. ^{1}H NMR (CDCl$_3$): 8.17 (dd, H(a)); 8.07 (dd, H(a′)); 7.75 (td, H(b)); 7.66 (td, H(b′)); 5.50 (s, NH$_2$). IR (cm^{-1}): ν (C=O), 1686; ν (N–H), 3412, 3300. UV–vis (nm): 212, 265, 435.
   2-Acetamido-3-chloro-1,4-naphthoquinone (III): Yield 81%. Elemental analysis (%): Calcd for $C_{12}H_8NO_3Cl$; C, 57.74; N, 5.61; H, 3.21. Found: C, 56.91; N, 5.47; H, 3.05. ^{1}H NMR (CDCl$_3$): 8.17 (dd, H(a)); 8.06 (dd, H(a′)); 7.75 (td, H(b)); 7.65 (td, H(b′)); 2.40 (s, CH$_3$). IR (cm^{-1}): ν (C=O, quinone), 1686; ν (C=O, amide), 1715; ν (N–H), 3310. UV–vis (nm): 346.
   2-Acetamido-3-amino-1,4-naphthoquinone (IV): Yield 73%. Elemental analysis (%): Calcd for $C_{12}H_{10}N_2O_3$; C, 62.60; N, 12.20; H, 4.03. Found: C, 62.10; N, 12.09; H, 3.99. ^{1}H NMR (in ppm): 8.07 (dd, H(a)); 7.95 (dd, H(a′)); 7.65 (td, H(b)); 7.55 (td, H(b′)); 5.52 (s, NH$_2$); 2.24 (s, CH$_3$). IR (cm^{-1}): ν (C=O, quinone), 1657; ν (C=O, amide), 1685; ν (N–H), 3386 and 3296. UV–vis (nm): 254, 278, 461.
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