Efficient and Selective Photochemical Labilization of a Given Bidentate Ligand in Mixed Ruthenium(II) Complexes of the $Ru(phen)_2L^{2+}$ and $Ru(bipy)_2L^{2+}$ Family (L = Sterically Hindering Chelate)

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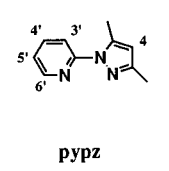
Mixed ruthenium(II) complexes containing 1,10-phenanthroline (or 2,2′-bipyridine) and a sterically congested bidentate ligand such as 2,9-diphenyl-1,10-phenanthroline, 6,6′-dimethyl- or 6,6′-diphenyl-2,2′-bipyridine, or 1-(2′-pyridyl)-3,5-dimethylpyrazole undergo clean and selective ligand substitution under irradiation with visible light. For instance, $Ru(phen)_2(dmbp)^{2+}$ in CH_3CN is quantitatively converted to $Ru(phen)_2(CH_3CN)_2{}^{2+}$ in a photochemical reaction accompanied by expulsion of the sterically hindering chelate dmbp (phen = 1,10-phenanthroline; dmbp = 6,6′-dimethyl-2,2′-bipyridine). Interestingly, 2,2′-bipyridine was found to be photochemically ejected in one case, probably as a consequence of its greater flexibility.

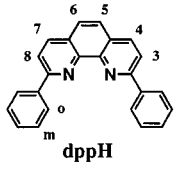
The development of new molecular devices relying on electronic and photonic processes is an attractive challenge. Signal processing and information storage at the molecular level could be based on molecules able to exist in two stable states,[1] with the interconversion between these states having to be fast and quantitative.

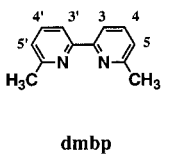
Ruthenium(II) complexes display photochemical properties that permit their use as photoactive electron- or energy-transfer components,[2] photochemical stability of the complex being an essential requirement. On the other hand, *the photolabilization of a ligand followed by its recoordination in the dark could be the key steps in the construction of photoswitchable molecular devices.* Interesting photochemically labile ruthenium(II) complexes have been reported, some of which are capable of clean photo-expulsion of a given ligand with a high quantum efficiency.[3]

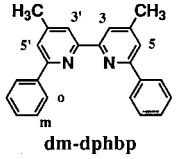
Herein, we describe the quantitative photosubstitution reactions that occur in four tris-chelated ruthenium(II) complexes. These complexes (**1**, **2**, **5**, **6**), incorporating two identical bidentate ligands (bipy or phen; bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) and a suitable third ligand, are shown in Scheme 1.

The choice of the third ligand was made with the help of models, which predicted that photolabilization would be most likely to occur on the weakest ligand field axis.[4] Hindering bidentate ligands such as dppH, dmbp, and dm-dphbp (dppH = 2,9-diphenyl-1,10-phenanthroline; dmbp = 6,6′-dimethyl-2,2′-bipyridine; dm-dphbp = 4,4′-dimethyl-6,6′-diphenyl-2,2′-bipyridine) or disymmetrical ligands with poor σ-donor character such as pypz [pypz = 1-(2′-pyridyl)-3,5-dimethylpyrazole] are considered to decrease the ligand field. Excitation in the MLCT region leads to a charge-transfer excited state, allowing the thermal









$Ru(bipy)_2(pypz)(PF_6)_2$	**1**
$Ru(bipy)_2(dppH)(PF_6)_2$	**2**
$Ru(bipy)(dppH)(CH_3CN)_2(PF_6)_2$	**3**
$Ru(bipy)(dpp)(CH_3CN)(PF_6)$	**4**
$Ru(phen)_2(dmbp)(PF_6)_2$	**5**
$Ru(phen)_2(dm\text{-}dphbp)(PF_6)_2$	**6**

Scheme 1. The various ligands used and the ruthenium(II) complexes made and studied

population of low-lying dissociative d-d states.[5] As expected, visible (300 nm ≤ λ ≤ 800 nm) light irradiation of **1**, **2**, **5**, and **6** in degassed acetonitrile led very selectively to a substitution of one bidentate ligand by two molecules of solvent (reactions 1, 2, and 3 in Scheme 2). The photoproduct was unambiguously identified as $[Ru(bipy)_2(CH_3CN)_2](PF_6)_2$ or $[Ru(phen)_2(CH_3CN)_2](PF_6)_2$ depending on the starting complex.

However, contrasting behavior between the various complexes could also be observed. Since the tris complex $Ru(pypz)_3{}^{2+}$, previously studied by Marzin et al.,[6] undergoes photosubstitution in acetonitrile to produce $Ru(pypz)_2(CH_3CN)_2{}^{2+}$,[7] it was not unexpected that irradiation of **1** led efficiently to $Ru(bipy)_2(CH_3CN)_2{}^{2+}$. On the contrary,

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$$Ru(bipy)_2(pypz)^{2+} \xrightarrow[CH_3CN]{h\nu} Ru(bipy)_2(CH_3CN)_2{}^{2+} + pypz \quad (1)$$

$$Ru(bipy)_2(dppH)^{2+} \xrightarrow[CH_3CN]{h\nu} Ru(bipy)(dppH)(CH_3CN)_2{}^{2+} + bipy \quad (2)$$

$$Ru(phen)_2(L)^{2+} \xrightarrow[CH_3CN]{h\nu} Ru(phen)_2(CH_3CN)_2{}^{2+} + L \quad (3)$$

L = dmbp or dm-dphbp

Scheme 2. Photochemical subtitution of a given bidentate chelate by CH_3CN

compound **2** formed from the same $Ru(bipy)_2$ core and disubstituted 1,10-phenanthroline (dppH) displayed unexpected behavior. In this case, a bipyridine was photolabilized rather than the hindering dppH ligand. This finding may be related to the distorted structure of the complex. Indeed, the coordination of dppH in this complex may be quite normal in terms of Ru−N distances and the N−Ru−N angle. On the other hand, strong steric interactions between the phenyl groups and the bipy ligands could result in extension of the Ru−N(bipy) distances or to a twisting of the pyridine moieties. Such a distortion has been found in the solid state for the closely analogous complex $Ru(phen)_2(dmp)^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline).[8] An alternative argument hinges on the different rigidities of the bipyridine and phenanthroline ligands. Intuitively, the decoordination of phenanthroline must be more difficult than that of bipyridine, since after the first Ru−N bond breaking, the pyridine ring can rotate about the $C^2-C^{2'}$ bond in the case of bipy, whereas the aromatic plane of phen is almost impossible to distort. Indeed, intermediates with η^1-bipyridine ligands have been previously postulated[3a,5b] and recently identified[9] in the photosubstitution of $Ru(bipy)_2(3,3'\text{-dmbp})^{2+}$ in acidic media (3,3′-dmbp = 3,3′-dimethyl-2,2′-bipyridine). Unfortunately, complex **2** does not fulfil the requirements of reversibility because the photoproduct $Ru(bipy)(dppH)(CH_3CN)_2{}^{2+}$ is highly base-sensitive. During its attempted purification on an alumina column or in the presence of a trace of base, an orthometallation reaction takes place at one phenyl group leading to the very stable $Ru(bipy)(dpp)(CH_3CN)^+$ complex. This complex was fully characterized by ^{1}H NMR, FAB MS, and cyclic voltammetry. In order to avoid this reaction, and in view of the behavior of the disubstituted phenanthroline in complex **2**, complexes **5** and **6**, based on the $Ru(phen)_2$ core and incorporating a disubstituted bipyridine (dmbp or dm-dphbp), were prepared and irradiated in acetonitrile. These two systems were found to undergo very efficient photolabilization of the hindering bipyridine ($t_{1/2}$ = 28 and 390 s for **5** and **6**, respectively). As illustrated in Figure 1, after 140 s of irradiation, the electronic spectrum of a degassed acetonitrile solution of **5** is transformed to the characteristic spectrum of the $Ru(phen)_2(CH_3CN)_2{}^{2+}$ species.[10]

The presence of marked isosbestic points at 342 and 404 nm demonstrates the selectivity of the photosubstitution.

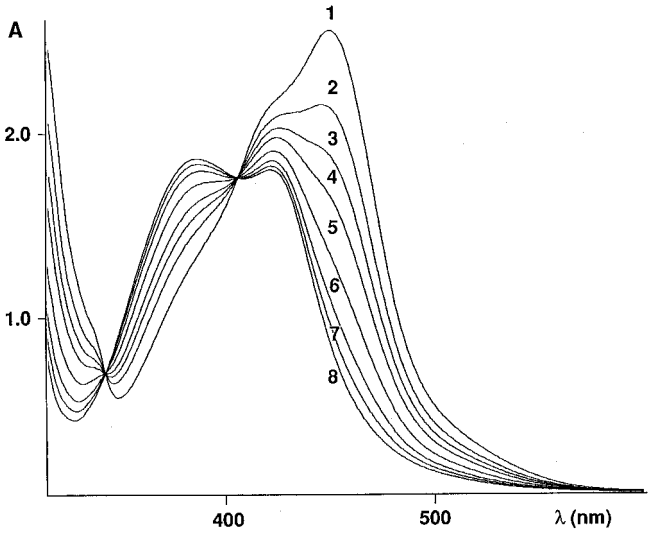

Figure 1. Visible spectra of a CH_3CN solution of **5** (1-cm cell; [**5**] = $2.4\cdot10^{-4}$ molL^{-1}) after various irradiation times: 0 s (1), 15 s (2), 25 s (3), 35 s (4), 55 s (5), 80 s (6), 105 s (7), 140 s (8)

The same result was also obtained by ^{1}H-NMR spectroscopy with direct light irradiation of the NMR tube. As suggested by the behavior of **2** and confirmed in the case of **5** and **6**, phenanthrolines are seen to be much more difficult to photolabilize than bipyridine ligands, regardless of which type of ligand is the hindering one. This conclusion can be related to the different quantum yields of photoanation found for $Ru(bipy)_3Cl_2$ and $Ru(phen)_3Cl_2$ (0.1 and 0.014, respectively) in CH_2Cl_2, which differ almost by one order of magnitude.[5b]

In conclusion, we have shown that by combining ligands with precisely defined electronic and steric properties in the same ruthenium(II) complex, it is possible to prepare photochemically active compounds that undergo quantitative and selective decoordination of a given ligand under light irradiation. Work currently in progress is concerned with the use of the present photolabile complexes as building blocks and their incorporation into multi-component systems. Preliminary experiments demonstrate that the recoordination reaction of dmbp onto the ruthenium centre, starting from $Ru(phen)_2(CH_3CN)_2{}^{2+}$ is indeed quantitative.

Experimental Section

Physical Measurements: ^{1}H NMR: Bruker WP200 SY (200 MHz) and Bruker AM 400 (400 MHz) instruments; the reported chemical shifts are referenced to Me_4Si as an internal standard. − UV/Vis: Kontron Uvikon 860. − MS: VG ZAB-HF, Thomson THN 208. − Irradiation: Hanimex slide projector (150-W halogen lamp). − Cyclic voltammetry: PAR model 273A potentiostat, Pt disc as working electrode, CH_3CN solution, 0.1 M Bu_4NBF_4 as supporting electrolyte, Pt wire as auxiliary electrode, SCE as reference electrode.

Photolysis Experiments − Representative Photolysis of 1: In a round-bottomed Pyrex Schlenk flask, 30 mg (0.034 mmol) of **1** was dissolved in 50 mL of CH_3CN. The resulting solution was stirred under argon and irradiated for 8 h. In order to obtain a crystalline

product, the solution was first concentrated to half of its original volume, 30 mL of toluene was added, and then the remaining CH_3CN was evaporated with the temperature not exceeding 40°C. Orange crystals were obtained, which were filtered off on a porosity grade 4 glass frit and washed with diethyl ether. The product was dried in vacuo to give 26 mg of $[Ru(bipy)_2(CH_3CN)_2](PF_6)_2$ (96%). The remaining 4% was accounted for by recovered starting material **1**. − UV/Vis (CH_3CN): λ_{max} (ε) = 425 nm (8460 $Lmol^{-1}cm^{-1}$). − ^1H NMR ([D_6]acetone, 200 MHz): δ = 9.7 (d, *J* = 5.05 Hz, 2 H, 6-H), 8.9 (d, *J* = 7.88 Hz, 2 H, 6′-H), 8.76 (d, *J* = 7.87 Hz, 2 H, 3-H), 8.51 (td, *J* = 7.93, 1.55 Hz, 2 H, 5-H), 8.19 (td, *J* = 7.87, 1.48 Hz, 2 H, 4-H), 8.07 (td, *J* = 6.58, 1.35 Hz, 2 H, 5′-H), 7.96 (d, *J* = 4.92 Hz, 2 H, 3′-H), 7.52 (td, *J* = 6.64, 1.47 Hz, 2 H, 4′-H), 2.59 (s, 6 H, 2 CH_3CN). − The photolysis of **2** was performed following the same method (yield 81%). The photolyses of **5** and **6** were realized in a Schlenk cell on an analytical scale.

Synthesis of Ligands and Complexes: The ligands dppH,[11] pypz,[6] dmbp,[12] and dm-dphbp,[13] and the complexes *cis*-$Ru(L)_2Cl_2$ (L = bipy or phen),[14] were prepared according to literature procedures.

$[Ru(bipy)_2(pypz)](PF_6)_2$ (1): The complex *cis*-$Ru(bipy)_2Cl_2$ (145 mg, 0.3 mmol) was dissolved in 20 mL of EtOH/H_2O (3:1) and the resulting solution was refluxed for 1 h. The ligand pypz (52 mg, 0.3 mmol) was then slowly added and refluxing was continued for a further 4 h, in the course of which the colour of the solution changed from purple-red to orange-red. The mixture was then filtered, the filtrate was concentrated to dryness, and the residue was redissolved in water (20 mL). The complex was precipitated as the hexafluorophosphate by the dropwise addition of concentrated KPF_6 solution. The product was filtered off (grade 4 glass frit) and recrystallized from EtOH/H_2O to give an orange-red microcrystalline powder (210 mg), yield 80%. − UV/Vis (CH_3CN): λ_{max} (ε) = 449 nm (9200 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_3CN, 200 MHz): δ = 8.45 (m, 4 H), 8.2−7.9 (m, 7 H), 7.77 (m, 2 H), 7.60 (d, *J* = 5.42 Hz, 1 H), 7.53−7.28 (m, 5 H), 7.22−7.14 (m, 1 H), 6.35 (s, 4-H), 2.82 (s, 5-CH_3), 1.48 (s, 3-CH_3).

$[Ru(bipy)_2(dppH)](PF_6)_2$ (2): In a 100-mL round-bottomed flask fitted with a reflux condenser, a mixture of 145 mg (0.3 mmol) of *cis*-$Ru(bipy)_2Cl_2$ and 120 mg (0.36 mmol) of dppH in 25 mL of ethylene glycol was heated under reflux for 3 h. After cooling to room temperature, the orange solution was filtered through a porosity grade 4 glass frit. Then, at 100°C, the filtrate was treated dropwise with a saturated aqueous solution of KPF_6. The resulting solution was allowed to cool and left to stand overnight at 0°C, whereupon the complex crystallized. It was filtered off, washed with a copious amount of water, and air-dried. The crude red product was purified by chromatography on silica gel, eluting with acetonitrile/water/saturated aqueous KNO_3 (100:5:0.5). After anion exchange, 243 mg (76%) of **2** was obtained. − UV/Vis (CH_3CN): λ_{max} (ε) = 451 nm (13300 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_3CN, 400 MHz): δ = 8.66 (d, *J* = 8.04 Hz, 4-H, 7-H), 8.34 (s, 5-H, 6-H), 8.24 (d, *J* = 7.76 Hz, 2 H), 8.05 (td, *J* = 7.88, 1.53 Hz, 2 H), 7.89 (d, *J* = 5.08 Hz, 2 H), 7.84 (d, *J* = 7.76 Hz, 2 H), 7.54 (d, *J* = 8.28 Hz, 3-H, 8-H), 7.45 (t, *J* = 7.9 Hz, 2 H), 7.34 (t, *J* = 6.44 Hz, 2 H), 7.13 (br. s, 2 H, *o*-H), 7.02 (t, *J* = 7.5 Hz, 2 H, *p*-H), 6.86 (br. s, 2 H, *o*-H), 6.74 (br. s, 2 H, *m*-H), 6.66 (d, *J* = 5.64 Hz, 2 H), 6.56 (td, *J* = 6.68, 1.5 Hz, 2 H), 6.12 (br. s, 2 H, *m*-H). − Redox potential (V vs. SCE): $E°(Ru^{III/II})$ = 1.3 V, $E°(Ru^{II/I})$ = −1.3 V, irreversible wave.

$Ru(bipy)(dppH)(CH_3CN)_2(PF_6)_2$ (3): In a round-bottomed Schlenk flask, 20 mg (0.019 mmol) of **2** was dissolved in 30 mL of acetonitrile and the resulting orange-red solution was stirred under argon and irradiated for 8 h. The yellow solution thus obtained was chromatographed on a silica gel column, eluting with acetonitrile/water/saturated aqueous KNO_3 (100:5:0.5). After anion exchange, 0.15 g of **2** (81%) was obtained. − UV/Vis (CH_3CN): λ_{max} (ε) = 401 nm (4720 $Lmol^{-1}cm^{-1}$), 424 nm (4690 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_2Cl_2, 200 MHz): δ = 8.80 (d, *J* = 8.36 Hz, 7-H or 4-H), 8.37 (d, *J* = 8.36 Hz, 4-H or 7-H), 8.27 (d, *J* = 8.62 Hz, 5-H or 6-H), 8.25 (d, *J* = 6.4 Hz, 1 H), 8.10 (t, *J* = 8.12, 8.36 Hz, 3-H or 8-H, 6-H or 5-H), 8.02 (d, 7.88 Hz, 1 H), 7.92 (d, *J* = 7.62 Hz, 1 H), 7.83−7.71 (m, 4 H), 7.58 (m, 4 H), 7.44 (d, *J* = 8.36 Hz, 8-H or 3-H), 7.36 (td, *J* = 3.66, 1.47 Hz, 2 H), 7.14 (td, *J* = 6.64, 1.48 Hz, 2 H), 7.05 (td, *J* = 6.4, 1.48 Hz, 1 H), 6.95 (t, *J* = 7.62 Hz, 1 H), 6.70 (d, *J* = 5.66 Hz, 1 H), 6.44 (d, *J* = 7.62 Hz, 1 H), 2.77 (s, 3 H, CH_3CN), 1.50 (s, 3 H, CH_3CN). − Redox potential (V vs. SCE): $E°(Ru^{III/II})$ = 1.49 V, $E°(Ru^{II/I})$ = −1.3 V, irreversible wave.

$Ru(bipy)(dpp)(CH_3CN)(PF_6)$ (4): 40 mg (0.039 mmol) of **3** was subjected to chromatography on 5 successive alumina columns, eluting with CH_2Cl_2/MeOH (99.3:0.7), to give 25.5 mg of **4** (85%). − UV/Vis (CH_3CN): λ_{max} (ε) = 458 nm (7900 $Lmol^{-1}cm^{-1}$), 520 (9681 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_3CN, 200 MHz): δ = 8.99 (d, *J* = 6.4 Hz, 1 H), 8.47 (d, *J* = 8.38 Hz, dpp-H), 8.40 (d, *J* = 8.86 Hz, dpp-H), 8.28 (d, *J* = 8.86 Hz, dpp-H), 8.15 (d, *J* = 8.86 Hz, dpp-H), 8.07 (d, *J* = 8.84 Hz, dpp-H), 8.03 (t, *J* = 7.12, 7.64 Hz, 2 H), 7.89 (m, 1 H), 7.85 (dd, *J* = 7.74, 1.35 Hz, 1 H), 7.76 (td, *J* = 7.75, 1.48 Hz, 1 H), 7.61 (d, *J* = 8.36 Hz, dpp-H), 7.54 (td, *J* = 7.5, 1.48 Hz, 1 H), 7.36 (m, 2 H), 7.20 (d, *J* = 4.92 Hz, 1 H), 7.01 (m, 3 H), 6.87−6.62 (m, 4 H), 5.95 (d, *J* = 6.4 Hz, 1 H), 1.99 (s, 3 H, CH_3CN). − FAB-MS; *m*/*z*: 589 [M^+ − bipy], 630.1 [M^+ − bipy + CH_3CN]. − Redox potential (V vs. SCE): $E°(Ru^{III/II})$ = 0.5 V, $E°(Ru^{II/I})$ = −1.68 V.

$Ru(phen)_2(dmbp)(PF_6)_2$ (5): A mixture of *cis*-$Ru(phen)_2Cl_2$ (0.2 g, 0.38 mmol), dmbp (0.1 g, 0.54 mmol), and degassed ethylene glycol (5 mL) was heated at 160°C under argon for 4 h. After cooling to room temperature, 20 mL of saturated aqueous KPF_6 solution was added. The yellow precipitate thus obtained was collected by filtration, washed with water (30 mL), and redissolved in the minimum volume of CH_3CN. This solution was subjected to column chromatography on silica, using CH_2Cl_2/MeOH (0 to 4%) as eluent. Complex **5** was obtained as a red powder (0.18 g, 51%). − UV/Vis (CH_3CN): λ_{max} (ε) = 449 nm (12200 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_3CN, 200 MHz): δ = 8.71 (dd, *J* = 8.37, 1.23 Hz, 2 H, 2-H), 8.43 (dd, *J* = 7.62 Hz, 1.23 Hz, 2 H, 9-H), 8.40 (dd, *J* = 5.41, 1.23 Hz, 2 H, 4-H), 8.38 (m, 2 H, bipy-H), 8.28 (d, *J* = 8.86 Hz, 2 H, 5-H or 6-H), 8.17 (d, *J* = 8.84 Hz, 2 H, 6-H or 5-H), 7.92 (m, 2 H, bipy-H), 7.88 (dd, *J* = 8.24, 5.3 Hz, 2 H, 8-H or 3-H), 7.58 (dd, *J* = 5.16, 1.22 Hz, 2 H, 7-H), 7.31 (dd, *J* = 8.24, 5.3 Hz, 2 H, 3-H or 8-H), 7.21 (dd, *J* = 7.62, 0.98 Hz, 2 H, bipy-H), 1.46 (s, 6 H, 2 CH_3).

$Ru(phen)_2(dm\text{-}dphbp)(PF_6)_2$ (6): A mixture of *cis*-$Ru(phen)_2Cl_2$ (0.15 g, 0.28 mmol), dm-dphbp (0.93 g, 0.28 mmol), and degassed ethylene glycol (5 mL) was refluxed under argon for 3 h. After cooling, addition of aqueous KPF_6 solution (20 mL) afforded a brown precipitate, which was collected by filtration, washed with water (50 mL) and diethyl ether (50 mL), and finally dried. The product was purified by chromatography (silica gel) using CH_2Cl_2/MeOH (0 to 2%) as eluent, to give a red powder (0.25 g, 81%). − UV/Vis (CH_3CN): λ_{max} (ε) = 454 nm (12100 $Lmol^{-1}cm^{-1}$). − ^1H NMR (CD_3CN, 200 MHz): δ = 8.67 (dd, *J* = 5.29, 1.23 Hz, 2 H, 2-H), 8.70 (dd, *J* = 8.24, 1.12 Hz, 2 H, 4-H), 8.54 (s, 2 H, bipy-H), 8.15 (d, *J* = 8.86 Hz, 5-H), 7.96 (dd, *J* = 8.23, 4.66 Hz, 2 H, 3-H), 7.88 (d, *J* = 8.86 Hz, 2 H, 6-H), 7.87 (dd, *J* = 8.11, 1.23 Hz, 2 H, 7-H), 7.05 (br. s, 2 H, phenyl-H), 6.98 (s, 2 H, bipy-H), 6.64

(m, 4 H, phenyl-H), 6.60 (dd, J = 8.12, 5.42 Hz, 2 H, 8-H), 6.47 (dd, J = 5.29, 1.24 Hz, 2 H, 9-H), 6.11 (br. s, 2 H, phenyl-H), 5.36 (br. s, 2 H, phenyl-H), 2.54 (s, 6 H, 2 CH_3).

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