Synthesis, Characterization, Luminescence Properties, and Electrochemical Behaviour of Ruthenium(II) Complexes with Two New Bi- and Tri-dentate 2-Pyridylquinoline Ligands

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Two new ligands, 4-phenyl-2-(2'-pyridyl)quinoline (ppq) and 2,6-bis(4'-phenyl-2'-quinolyl)pyridine (bpqpy) and their ruthenium(II) complexes $[Ru(bipy)_2(ppq)][PF_6]_2$ (bipy = 2,2'-bipyridine) **1** and $[Ru(bpqpy)_2][PF_6]_2$ **2** have been synthesized and characterized by conventional techniques. The IR, fast atom bombardment mass and UV–VIS spectra of the ligands and their complexes are briefly discussed. A study of the luminescence properties and electrochemical behaviour of the complexes has shown that **1** is a good candidate as a luminescent and redox-active species to be incorporated in a polymer polyquinoline-based backbone.

The photophysics and photochemistry of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) and of $[Ru(terpy)_2]^{2+}$ (terpy = 2,2':6',2''-terpyridine) have been the subject of extensive research.[1] Ruthenium(II) polypyridine complexes have found widespread use as homogeneous catalysts for the photodecomposition of water,[2] as sensitizers for photoinduced electron injection on semiconductors,[3] in photoelectrochemical cells for the production of dihydrogen,[4] and as sensitizers for the photocleavage of DNA.[5]

Lately many researchers have shown that it may be preferable to incorporate the ruthenium polypyridine complexes in polymer matrices that may offer: (*i*) more rigidity of the system, slowing down radiationless-decay processes;[1] (*ii*) the presence of multiple binding sites that, when complexed, allow multi-electron transfer (a behaviour that can or could be essential for obtaining some valuable functions);[1b,6,7] (*iii*) the opportunity of a variety of chromophore–quencher combinations within the same molecular framework.[8]

Some of us have been interested in the synthesis of polyquinolines,[9] which are known for their thermal stabilities, chemical resistance and cross-linking ability.[10] Since the polyquinoline backbone possesses nitrogen atoms as potential binding sites for Ru^{II}, we have designed copolymers containing in the main backbone, and not as a pendant group, bidentate (Scheme 1, **a**) and tridentate (Scheme 1, **b**) chelating units, which closely mimic the co-ordination of bipy and terpy at each ruthenium(II) centre.

This paper describes the synthesis and characterization of two new ligands, 4-phenyl-2-(2'-pyridyl)quinoline (ppq) and 2,6-bis(4'-phenyl-2'-quinolyl)pyridine (bpqpy) (Scheme 2), and of their ruthenium(II) complexes $[Ru(bipy)_2(ppq)][PF_6]_2$ **1** and $[Ru(bpqpy)_2][PF_6]_2$ **2**, respectively, along with their photochemical and electrochemical properties, as models for related polymeric polyquinoline ruthenium(II) complexes.

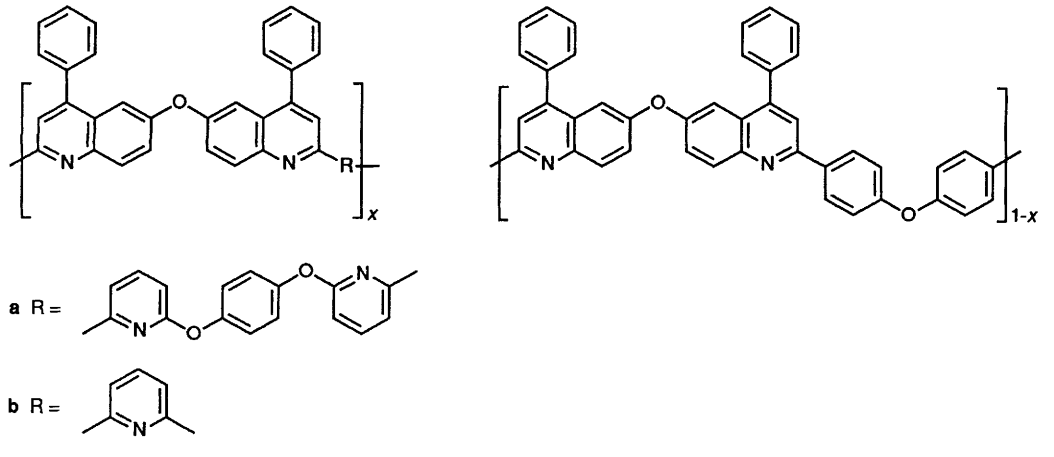
Experimental

Materials.—The complex $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ was prepared by the literature procedure.[11] All the reactions were performed under an inert atmosphere of nitrogen, and the solvents were dried and stored under nitrogen and over 4A molecular sieves. Melting points are uncorrected. Elemental analyses were performed commercially. The compounds $RuCl_3\cdot 3H_2O$ and $K_2[RuCl_5(H_2O)]$ were purchased from Aldrich. All other reagents were reagent grade.

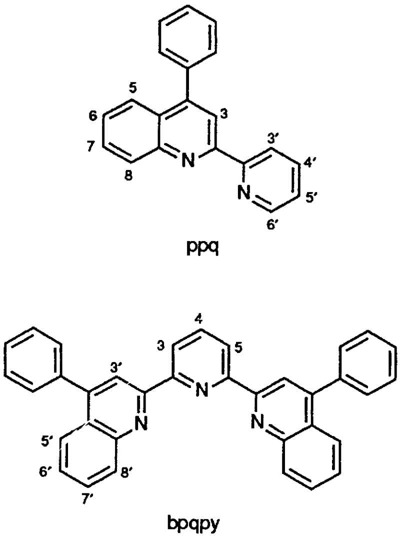
Physical Measurements.—Proton NMR spectra were taken on a Bruker AC 250 instrument using $SiMe_4$ as internal reference, IR spectra (KBr disks) on a Perkin-Elmer 684 spectrophotometer. Positive-ion fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS 50 S double-focusing mass spectrometer equipped with a standard FAB source, using 3-nitrobenzyl alcohol as a matrix.

For the electrochemical measurements a three-electrode cell was used, which was thermostatted at 25 °C by circulating water: working electrode, platinum microsphere; counter electrode, platinum foil; pseudo-reference electrode, silver wire calibrated internally through the ferrocene–ferrocenium couple; potential scan rate in differential pulse voltammetry (DPV) experiments, 5 mV s^{-1}. Voltammetry studies were carried out using a PAR 273 apparatus, driven by an IBM AT personal computer, through dedicated software. Acetonitrile was distilled twice over CaH_2; NBu_4ClO_4 (Carlo Erba, polarographic grade) was used without further purification. Dinitrogen, presaturated in MeCN, flowed into the cell during voltammetric experiments.

Ultraviolet-visible absorption spectra were recorded on a Perkin-Elmer 330 double-beam spectrophotometer using 1 cm quartz cells at room temperature, emission spectra with a Perkin-Elmer 650–40 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 phototube. Emission lifetime measurements were made with a JK System 2000 neodymium YAG DPLY4 laser (λ_{ex} = 355 nm, pulse width 20 ns) and a Tektronix 7612 digitizer for data acquisition. Emission quantum yields were measured by the optically dilute method,[12] the fluorimeter being calibrated with a standard lamp, and the emission spectra corrected for photomultiplier response. The ion $[Ru(bipy)_3]^{2+}$ in aqueous aerated solution was used as a quantum-yield standard, assuming a value of 0.028.[13] When necessary, the solutions were deaerated with bubbling nitrogen.



Scheme 1



Scheme 2

Preparations.—*4-Phenyl-2-(2′-pyridyl)quinoline*. A mixture of *m*-cresol (40 cm^3) and phosphorus pentaoxide (1.63 g) was stirred at 150 °C for 2 h to afford a homogeneous solution. After cooling, 2-aminobenzophenone (4 g, 20.3 mmol) and 2-acetylpyridine (2.45 g, 20.3 mmol) were added with *m*-cresol (10 cm^3) to rinse the powder funnel. The reaction mixture was heated at 130–135 °C overnight. The dark solution was poured into ethanol (200 cm^3) containing triethylamine (20 cm^3). After 30% of solvent was distilled off under reduced pressure, a white-yellow precipitate was collected by filtration, recrystallised from ethanol plus 10% triethylamine to give 4 g (70%) of ppq as off-white needles, m.p. 152–154 °C. ^1H NMR [$(CD_3)_2CO$]: δ 8.77 (br, 1 H, J = 7.5, $H^{3'}$ of pyridine), 8.73 (br, 1 H, J = 4.9, $H^{6'}$ of pyridine), 8.60 (s, 1 H, H^3 of quinoline), 8.25 (br, 1 H, J = 8.5 Hz, H^8 of quinoline), and 8.1–7.6 (m, 10 H, aromatic and heteroaromatic H). Mass spectrum: *m/z* 282 ($M^{\cdot+}$, 86%) (Found: C, 85.00; H, 5.05; N, 10.00. Calc. for $C_{20}H_{14}N_2$: C, 85.05; H, 5.00; N, 9.90%).

2,6-Bis(4′-phenyl-2′-quinolyl)pyridine. A mixture of *m*-cresol (60 cm^3) and phosphorus pentaoxide (2.62 g) was stirred at 150 °C for 2 h to afford a homogeneous solution. After cooling, 2-aminobenzophenone (6.31 g, 32.0 mmol) and 2,6-diacetylpyridine (2.61 g, 16.0 mmol) were added, with *m*-cresol (20 cm^3) to rinse the powder funnel. The reaction mixture was heated at 145 °C overnight. After cooling, the dark solution was poured into ethanol (350 cm^3) containing triethylamine (35 cm^3). The yellow precipitate was collected by filtration and recrystallised from toluene to give 6 g (78%) of bpqpy as white needles, m.p. 277–279 °C. ^1H NMR ($CDCl_3$): δ 8.80 (d, 2 H, J = 7.9 Hz, $H^{3,5}$ of pyridine), 8.70 (s, 2 H, $H^{3'}$ of quinoline), and 8.3–7.5 (m, 19 H, aromatic and heteroaromatic H). Mass spectrum: *m/z* 485 ($M^{\cdot+}$, 40%) (Found: C, 86.30; H, 4.85; N, 8.70. Calc. for $C_{35}H_{23}N_3$: C, 86.55; H, 4.75; N, 8.65%).

[$Ru(bipy)_2(ppq)$][PF_6]$_2\cdot H_2O$ **1**. To a refluxing solution of [$Ru(bipy)_2Cl_2$]$\cdot 2H_2O$ (0.156 g, 0.3 mmol) in ethanol (20 cm^3) was added dropwise a solution of ppq (0.1 g, 0.35 mmol) in EtOH (20 cm^3), and the mixture was allowed to reflux for 8 h. After concentration and addition of water (15 cm^3) the mixture was refluxed for 5 min and filtered while hot. The complex was precipitated as the hexafluorophosphate by dropwise addition of a 20% water solution of NH_4PF_6 (5 cm^3). The red-orange product was collected, washed with cold water and Et_2O, and purified by gel filtration on a column of Sephadex LH-20 in EtOH followed by recrystallisation from acetone–Et_2O, to give 0.22 g (72%) of **1** as red-orange crystals. ^1H NMR [$(CD_3)_2CO$]: δ 9.18 (d, 1 H, $H^{3'}$ of pyridine, J = 8.14 Hz), 8.95 (m, 2 H, $H^{3,3'}$ of bipy), 8.78 (s, 1 H, H^3 of quinoline), and 8.7–7.3 (m, 26 H, aromatic and heteroaromatic H) (Found: C, 47.75; H, 3.05; N, 8.40. Calc. for $C_{40}H_{32}F_{12}N_6OP_2Ru$: C, 47.85; H, 3.20; N, 8.35%).

[$Ru(bpqpy)_2$][PF_6]$_2\cdot H_2O$ **2**. To a blue hot (*ca*. 160 °C) solution of $K_2[RuCl_5(H_2O)]$ (0.15 g, 0.4 mmol) in glycerol (20 cm^3) was added dropwise a solution of bpqpy (0.431 g, 0.88 mmol) in glycerol–EtOH (1:1 v/v, 60 cm^3). After removal of ethanol, the mixture was stirred at 210 °C for 24 h, diluted with water (80 cm^3), refluxed again for 10 min and filtered while hot. The filtrate was heated to about 100 °C and a hot aqueous ammonium hexafluorophosphate solution (20%, 10 cm^3) was added. The dark purple powder formed was collected, washed with cold water and Et_2O, and purified by gel filtration on a column of Sephadex LH-20 in acetonitrile followed by recrystallisation from acetonitrile–Et_2O to give 0.312 g (57%) of complex **2** as dark purple crystals. ^1H NMR (CD_3CN): δ 9.20 (d, 4 H, J = 7.9, $H^{3,5}$ of pyridine), 8.81 (t, 2 H, J = 7.9 Hz, H^4 of pyridine), 8.36 (s, 4 H, $H^{3'}$ of quinoline), 7.8–7.3 (m, 32 H, aromatic and heteroaromatic H) and 6.69 (m, 4 H, $H^{8'}$ of quinoline) (Found: C, 60.70; H, 3.40; N, 6.35. Calc. for $C_{35}H_{25}F_{12}N_6OP_2Ru$: C, 60.90; H, 3.50; N, 6.10%).

Results and Discussion

Synthesis.—The Friedlander reaction has been used to afford, by using appropriate reagents, the ligands ppq and bpqpy in good yields. The synthesis of ruthenium(II) complexes with these bidentate and tridentate ligands parallels the synthetic procedure for the preparation of similar ruthenium(II) complexes.[14]

NMR, mass, IR, and UV–VIS spectral data support the formulation of the synthesized compounds. The ligands and their ruthenium(II) complexes show very complicated ^1H NMR spectra. A complete NMR analysis and stereochemical studies

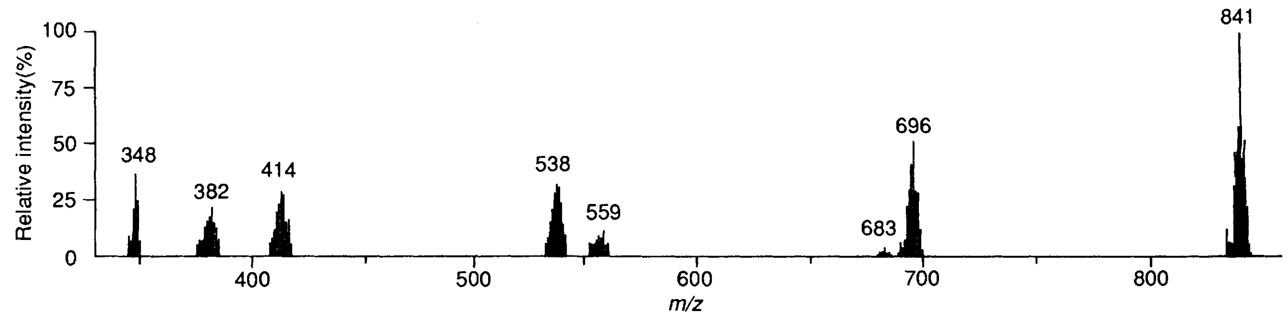


Fig. 1 Positive-ion FAB mass spectrum of $[Ru(bipy)_2(ppq)][PF_6]_2$ complex

Table 1 Selected IR (KBr disks) bands (cm^{-1}) of the synthesized compounds

Compound	$C \overset{\cdots}{-} C/C \overset{\cdots}{-} N$ ring stretching (1600–1360 cm^{-1})	Aromatic C–H out-of-plane bending (900–560 cm^{-1})
ppq	1590s, 1575m, 1550ms, 1490m, 1475m, 1440mw 1410m, 1360m	890w, 800s, 780s, 760s, 710ms, 680m, 625mw, 620m, 595m
bpqpy	1590s, 1580m, 1555s, 1497ms, 1485w, 1450mw, 1420mw, 1360m	900m, 825ms, 780s, 765s, 710ms, 675w, 620w, 585w
$[Ru(bipy)_2(ppq)]^{2+}$	1610mw, 1590mw, 1540w, 1470m, 1450m, 1380w	840s, 770m, 735w, 705w, 560ms
$[Ru(bpqpy)_2]^{2+}$	1590m, 1535mw, 1485w, 1450w, 1415w, 1375w	840s, 810w, 770m, 705mw, 560m

s = Strong, m = medium, w = weak.

of the ligands and complexes will be reported elsewhere. It is worth noting that the aromatic proton in the 3 position of the pyridine moiety in the ruthenium(II) complexes displays a remarkable deshielding of *ca.* 0.4 ppm, as compared to the free ligands, which is considered diagnostic for their formation.

Mass Spectroscopy.—The ligands are very stable to electron-impact (EI) decomposition, as reflected by very strong molecular ion intensities, by the presence of relatively intense peaks associated with doubly charged molecular ions, and by a negligible fragmentation pattern.

The mass spectrum of ppq is dominated by peaks at *m/z* 282 ($M^{\bullet +}$, relative intensity 86%) and 281 ($[M - H]^+$, base peak), the latter arising from a metastable supported loss of $H^\bullet$ from the molecular ion. The most intense peak in the spectrum of bpqpy is due to the molecular ion at *m/z* 485. The second most intense peak at *m/z* 242.5 (relative intensity 25%) results from a doubly charged molecular ion. The molecular ion undergoes α fission relative to the central pyridine to generate complementary ions at *m/z* 281 (3) and 204 (12.4%). The positive charge is mainly retained on the quinoline fragment.

A rapid structural characterisation of the ruthenium(II) complexes was achieved by FAB mass spectroscopy. The positive-ion FAB mass spectrum of $[Ru(bipy)_2(ppq)][PF_6]_2$ is reported in Fig. 1. It shows a diagnostically important peak at *m/z* 841 (base peak), corresponding to $[Ru(bipy)_2(ppq)(PF_6)]^+$, which displays the expected isotopic pattern for a Ru atom. The loss of a PF_6 group from this ion generates the ion at *m/z* 696, $[Ru(bipy)_2(ppq)]^{\bullet +}$, which is the second largest peak in the spectrum (relative intensity 53%). The third most intense peak at *m/z* 348 (37%) is due to the doubly charged $[Ru(bipy)_2(ppq)]^{2+}$. Less-intense fragments at *m/z* 559 (11.8%), $[Ru(bipy)_2(PF_6)]^{2+}$, and 414 (28%) $[Ru(bipy)_2]^+$, are also present, due to the sequential loss of ppq and PF_6 groups from the ion at *m/z* 841. The low-intensity peak at *m/z* 683 (4.6%) may be associated with a dehydrogenated $[Ru(bipy)(ppq)(PF_6)]^+$ species. This fragment ion undergoes sequential loss of PF_6 and bipy groups to generate dehydrogenated $[Ru(bipy)(ppq)]^{\bullet +}$ and $[Ru(ppq)]^{\bullet +}$ species at *m/z* 538 (32) and 382 (22%) respectively.

The positive-ion FAB mass spectrum of $[Ru(bpqpy)_2][PF_6]_2$ shows spectral features similar to those of $[Ru(bipy)_2(ppq)][PF_6]_2$. Thus, the highest observable set of peaks centred at *m/z* 1217 (41%) is due to $[Ru(bpqpy)_2(PF_6)]^+$. This ion decomposes by loss of a PF_6 group to give the fragment $[Ru(bpqpy)_2]^{\bullet +}$ at *m/z* 1072, which is the base peak in the spectrum. Other intense sets of peaks centred at *m/z* 536 (49) and 585 (48%) are due to the doubly charged $[Ru(bpqpy)_2]^{2+}$ ion, and to the dehydrogenated $[Ru(bpqpy)]^{\bullet +}$ fragment, respectively.

Infrared Spectra.—The IR spectra of the ligands ppq and bpqpy are similar (Table 1). They are characterised by aromatic C–H stretching bands between 3080 and 3010 cm^{-1} and by a series of overtone bands between 2000 and 1650 cm^{-1} due to the presence of monosubstituted benzene and/or pyridine derivatives.[15]

The spectral region 1600–1360 cm^{-1} is complicated by quinoline and pyridine vibrations, but a series of six, strong or medium, bands between 1600 and 1450 cm^{-1} along with two others between 1420 and 1360 cm^{-1} can be assigned to quinoline breathing vibrations.[16] Finally, well resolved absorption bands are present at lower frequencies which can be ascribed to the in-plane and out-of-plane ring deformations.[17,18]

The IR spectra of complexes **1** and **2** are quite different from those of the free ligands (Table 1), and show (*i*) a changed 1600–1360 cm^{-1} spectral region with the disappearance or shift to higher frequencies of the eight characteristic bands assigned to the quinoline breathing vibrations of the free ligands, (*ii*) in the 900–700 cm^{-1} spectral region only two main bands at 770 and 705 cm^{-1} that can be assigned to the aromatic C–H out-of-plane bending of the co-ordinated quinoline and pyridine rings. The complex $[Ru(bipy)_2(ppq)][PF_6]_2$ shows in this spectral region a third band at 735 cm^{-1} that is characteristic of a co-ordinated bipy ring; two strong and medium, respectively, bands at 840 and 560 cm^{-1} are characteristic of a PF_6^- anion.[19] Assignments of metal–ligand modes are hampered by a lack of data.

Electronic Spectra.—The UV electronic spectra of the ppq and bpqpy ligands in methanol are shown in Fig. 2, while their maxima and absorption coefficients are summarised in Tables 2

Table 2 Ultraviolet–visible spectral data for bidentate ligands and related mixed-ligand ruthenium(II) complexes[a]

Compound	$d_\pi \longrightarrow \pi^*$ (pq or ppq)	$d_\pi \longrightarrow \pi^*$ (bipy)	$\pi \longrightarrow \pi^*$[b]
pq[c]			247 (34.0)
ppq			334sh, 320sh, 302sh, 273 (16.1), 253 (26.5)
$[Ru(bipy)_2(pq)]^{2+}$[d]	476sh	452 (10.5)	289 (51.6), 275 (49.7), 247 (35.8)
$[Ru(bipy)_2(ppq)]^{2+}$	473sh	452 (15.3)	340sh, 323sh, 310sh, 290 (84.3), 282sh, 247 (43.6)

[a] λ_{max} in nm, error ±1 nm; ε values in parentheses, in $dm^3 mol^{-1} cm^{-1} \times 10^{-3}$. Spectra were recorded in methanol solution at room temperature. [b] Transitions for both bidentate ligands and bipyridine ligands are superimposed. [c] Calculated data from ref. 21. [d] From ref. 22.

Table 3 Ultraviolet–visible spectral data for tridentate ligands and related ruthenium(II) complexes[a]

Compound	$d\pi \longrightarrow \pi^*$	$\pi \longrightarrow \pi^*$
bqpy[b]		340 (17.1), 320 (31.0), 310 (30.2), 250 (78.7)
bpqpy		338sh, 320sh, 313 (33.1), 253 (75.7)
$[Ru(bqpy)_2]^{2+}$[b]	613sh, 562sh, 510 (9.0), 45 (7.0)	373 (53.9), 354 (36.5), 329sh, 309 (53.0), 257sh, 249 (83.7)
$[Ru(bpqpy)_2]^{2+}$	610sh, 560sh, 518 (11.5), 473sh	376 (47.3), 357sh, 340 (54.4), 312 (53.5), 258 (73.2)

[a] λ_{max} in nm, error ±1 nm; ε values in parentheses, in $dm^3 mol^{-1} cm^{-1} \times 10^{-3}$. Spectra were recorded in methanol solution at room temperature. [b] From ref. 23.

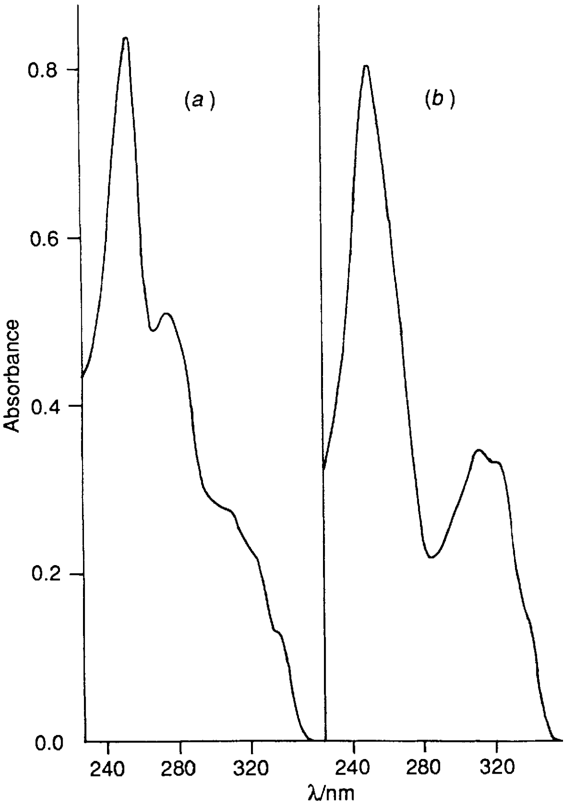


Fig. 2 Absorption spectra of the ppq (*a*) and bpqpy (*b*) free ligands in methanol solution; $c = 3.17 \times 10^{-5}$ and 1.47×10^{-5} mol dm^{-3}, respectively

and 3, respectively. It is apparent that phenyl substitution on 2-(2′-pyridyl)quinoline (pq) and 2,6-bis(2′-quinolyl)pyridine (bqpy) to produce ppq and bpqpy, respectively, results in a small red shift of the energy of the π → π* transition.[20,21]

The absorption spectrum of $[Ru(bipy)_2(ppq)]^{2+}$ ion [Fig. 3(*a*)] shows an intense transition at 452 nm with a low-energy shoulder at 473 nm and a strong absorption at 290 nm. On the basis of the similarity in energy and molar absorption coefficient (Table 2) with previously reported complexes such as $[Ru(bipy)_2(pq)]^{2+}$ and $[Ru(bipy)_3]^{2+}$, the former absorptions are most likely d ⟶ π* metal-to-ligand charge-transfer (m.l.c.t.) transitions. The highest absorption at 290 nm is assigned as an intraligand transition.[22,24]

For the above reasons and in agreement with literature data,[25–27] the two m.l.c.t. transitions at 473 and 452 nm, the intensities of which are weighted by the numbers of each ligand in the complex, can be assigned to the Ru ⟶ ppq and Ru ⟶ bipy c.t. transition, respectively. The UV–VIS spectrum of the $[Ru(bpqpy)_2]^{2+}$ ion [Fig. 3(*b*)] shows an intense transition at 518 nm with two low-energy shoulders at 560 and 610 nm, while the ultraviolet region exhibits several strong bands with absorption coefficients between 47 300 and 73 200 $dm^3 mol^{-1} cm^{-1}$ (Table 3).

Similarities in the absorption spectra of the bpqpy complex compared to that of bqpy,[20] and correlation between electronic spectra and electrochemistry (see below), allow the conclusion that the maximum at 518 nm can be associated to a Ru ⟶ bpqpy c.t. transition. The absorption tail towards the red, with shoulders at 560 and 610 nm, already noted for other quinoline-containing complexes,[6b,20,28] is likely due to interchromophoric coupling, as pointed out by De Armond and coworkers;[29] indeed the highest absorptions at 376, 340, 312 and 258 nm can be assigned as intraligand transitions.

The phenyl substitution on pq to give ppq does not seem to produce any appreciable effect on the visible region of the absorption spectrum of the mixed-ligand complex $[Ru(bipy)_2(ppq)]^{2+}$ with respect to $[Ru(bipy)_2(pq)]^{2+}$.[21] On the contrary, in the case of the homoligand ruthenium(II) complex **2**, the phenyl substitution on bqpy to produce bpqpy causes a bathochromic (510 *versus* 518 nm) and hyperchromic (ε 9000 *versus* 11 500 $dm^3 mol^{-1} cm^{-1}$) effect on the absorption spectrum of $[Ru(bpqpy)_2]^{2+}$ with respect to $[Ru(bqpy)_2]^{2+}$ (Table 3).[20,23] It can be probably explained by the greater electronegativity of the phenylated ligand and by the presence of resonance interactions.[28]

Electrochemistry.—Differential pulse voltammetry (DPV) curves in MeCN are shown in Fig. 4, and electrochemical data for $[Ru(bipy)_2(ppq)]^{2+}$ and $[Ru(bpqpy)_2]^{2+}$ complexes are summarised in Table 4. For comparison the complex $[Ru(bipy)_3]^{2+}$ was also studied under identical experimental conditions. For the last complex one oxidation and three monoelectronic reduction waves, reflecting the addition of electrons to the three bipyridyl ligands, are observed. The electrochemical data obtained (Table 4) are in accord with the values of other similar compounds.[1]

The DPV curves of the complexes $[Ru(bipy)_2(ppq)]^{2+}$ and

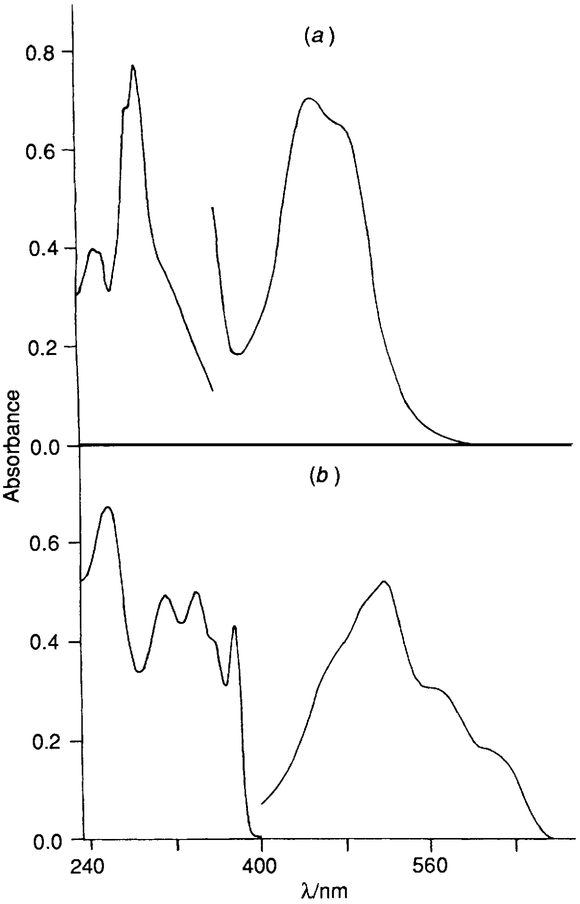


Fig. 3 Ultraviolet–visible spectra of the complexes $[Ru(bipy)_2(ppq)]^{2+}$ (*a*) and $[Ru(bpqpy)_2]^{2+}$ (*b*) in methanol solution; $c = 0.9 \times 10^{-5}$ mol dm^{-3} (five times more concentrated for visible spectra) for both complexes

$[Ru(bpqpy)_2]^{2+}$ show one oxidation and three and four, respectively, reversible monoelectronic waves (Fig. 4).

A comparison of the E_{red} values of complex **1**, with those of $[Ru(bipy)_3]^{2+}$, suggest that for **1**, E_1 reflects the reduction of the ppq ligand and E_2 and E_3 the reduction of the two remaining bipyridyl ligands. The E_2 and E_3 values for **1** are more negative than those of E_1 and E_2 for the complex $[Ru(bipy)_3]^{2+}$ because a negative charge is added to a pre-existing negative $[Ru^{II}\{(bipy)_2(ppq)^-\}]$ species.

Further comparison of E_{red} data for complex **1** with those of $[Ru(bipy)_2(pq)]^{2+}$ and $[Ru(bipy)_3]^{2+}$ shows quite different E_1 values for these complexes (Table 4). A positive shift is observed for the first reduction potential of $[Ru(bipy)_2(ppq)]^{2+}$ (−1.071 V) with respect to $[Ru(bipy)_2(pq)]^{2+}$ and $[Ru(bipy)_3]^{2+}$ (E_1 −1.135 and −1.330 V, respectively). The same positive shift is observed for the E_1 reduction potential of complex **2** (−0.831 V) with respect to the $[Ru(terpy)_2]^{2+}$ (−1.430 V) (Table 4). {No electrochemical data are available in the literature for the $[Ru(bqpy)_2]^{2+}$ complex}. The following waves can be assigned to the first reduction of the second bpqpy (E_2), and to second successive reductions of the polyquinoline ligands (E_3 and E_4). The differences between E_1 and E_3 and E_2 and E_4 ($\approx$0.6 V) are in agreement with this assignment.

This experimental observation confirms that (owing to the presence of a phenyl group) the existence of better resonance interactions favours reduction of the ligand and increase in oxidation potential of the metal (Table 4), and is in accord with the electronic data showing a lowering in energy of the m.l.c.t. state. Furthermore, a plot of the difference between the oxidation potential and the first reduction potential (ΔE), *versus* the absorption maximum of the m.l.c.t. band,[30] for all the complexes reported in Table 4, was roughly linear so confirming the assignments given.

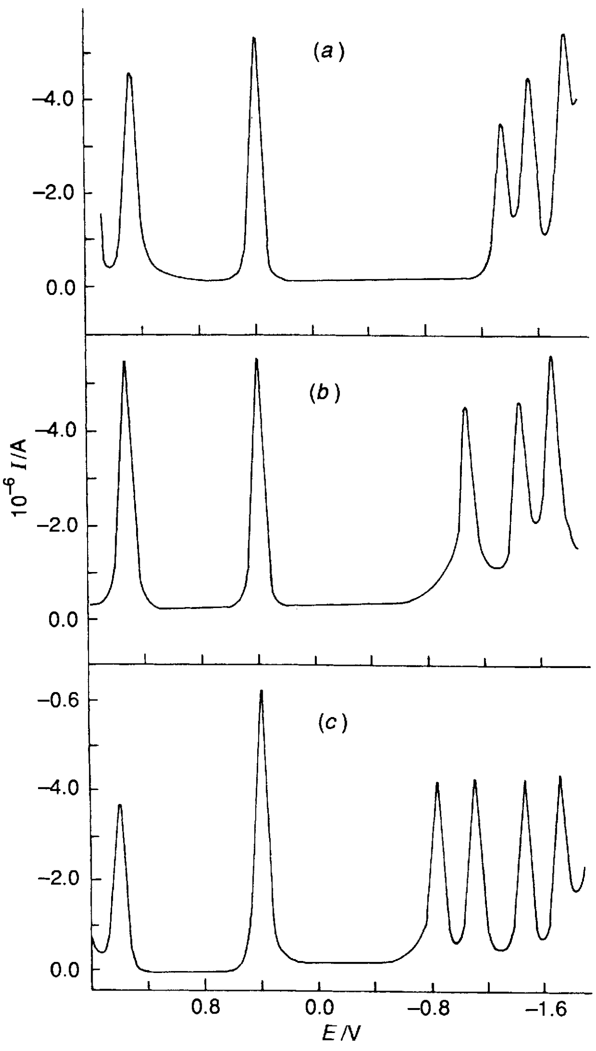


Fig. 4 Differential pulse voltammetry curves for $[Ru(bipy)_3]^{2+}$ (*a*), $[Ru(bipy)_2(ppq)]^{2+}$ (*b*), and $[Ru(bpqpy)_2]^{2+}$ (*c*) complexes in 0.1 mol dm^3 NBu_4ClO_4–MeCN solutions. The signal at 409 mV is due to the ferrocene–ferrocenium couple (see Physical Measurements)

Luminescence Properties.—In fluid solution at room temperature the complex $[Ru(bipy)_2(ppq)]^{2+}$ strongly emits in all the solvents used, whereas no emission was detected for $[Ru(bpqpy)_2]^{2+}$ up to 850 nm. Both complexes were luminescent in a MeOH–EtOH (4:1) rigid matrix at 77 K. Luminescence decays were in all cases strictly monoexponential. The luminescence energy maxima, lifetimes and quantum yields are collected in Table 5.

The emission of complex **1** is attributed to a triplet Ru ⟶ ppq charge-transfer (^{3}m.l.c.t.) excited state, either at room temperature or 77 K, because of: (*i*) the luminescence lifetimes (Table 5);[1] (*ii*) the blue shift of the energy of the emission maximum with decreasing temperature;[1] (*iii*) the quenching of the luminescence lifetimes by dioxygen (Table 5); (*iv*) the fact that the Ru ⟶ ppq c.t. excited state lies at lower energy than that of the corresponding Ru ⟶ bipy state, as suggested by the electrochemical results (see above).

Ruthenium(II) complexes with tridentate polypyridine ligands are usually not luminescent in fluid solution at room temperature, because of the coming into play (by thermal activation from the lowest excited state) of a low-lying metal-centred (^{3}m.c.) excited state, which leads to fast radiationless decay and/or ligand photodissociation.[1,31] The low-energy

Table 4 Electrochemical data for ruthenium(II) complex ions at room temperature[a]

	Half-wave potential, $E_{\frac{1}{2}}$/V					
Complex	+3/+2	+2/+1	+1/0	0/−1	−1/−2	Reference electrode[b]
$[Ru(bipy)_3]^{3+}$[c]	1.290	−1.330	−1.515	−1.770		SCE
$[Ru(bipy)_2(pq)]^{2+}$[d]	1.270	−1.135	−1.500	−1.743		SSCE
$[Ru(bipy)_2(ppq)]^{2+}$[c]	1.334	−1.071	−1.451	−1.681		SCE
$[Ru(terpy)_2]^{2+}$[e]	1.280	−1.430				SCE
$[Ru(bpqpy)_2]^{2+}$[c]	1.406	−0.831	−1.096	−1.474	−1.719	SCE

[a] In MeCN. [b] SCE = Saturated calomel electrode, SSCE = sodium chloride saturated calomel electrode. [c] Containing 0.1 mol dm^{-3} NBu_4ClO_4. [d] From ref. 30. [e] From ref. 1.

Table 5 Luminescence properties of the new complexes

	298 K[a]			77 K[b]	
Complex	λ_{max}/nm	τ/ns	Φ	λ_{max}/nm	τ/μs
$[Ru(bipy)_2(ppq)]^{2+}$	702	430 (234)[c]	0.01	669	2.7
$[Ru(bpqpy)_2]^{2+}$				697	5.8

[a] Deaerated acetonitrile solutions. [b] In MeOH–EtOH (4:1) rigid matrix. [c] Aerated acetonitrile solution.

position of the ^{3}m.c. excited state in ruthenium(II) complexes with tridentate ligands is attributed to the fact that such ligands are not suitable to provide the right octahedral co-ordination site for the Ru^{2+} ion.[32] An exception to such a behaviour is shown by $[Ru(tpterpy)_2]^{2+}$, where tpterpy is 4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine,[23] in which an increased energy gap between the ^{3}m.l.c.t. and ^{3}m.c. excited states, due to mesomeric interactions, has been invoked to justify the room-temperature luminescence.[33] Since in the $[Ru(bpqpy)_2]^{2+}$ complex a lower ^{3}m.l.c.t. excited-state energy with respect to $[Ru(tpterpy)_2]^{2+}$ should be expected, as also confirmed by the low-temperature emission energy (697 and 634 nm,[23] respectively), we hoped that complex **2** would emit at room temperature but this was not the case. This could be due to a lowering in energy of the ^{3}m.c. excited state because of steric hindrance introduced by the quinoline hydrogens of the 8′ position; for this reason no enhanced gain in energy gap between the ^{3}m.l.c.t. and ^{3}m.c. excited states is probably obtained in the studied complex with respect to $[Ru(terpy)_2]^{2+}$, and as a consequence no advantage in room-temperature emission properties is found.

In a rigid matrix at 77 K, thermal activation of the ^{3}m.c. excited state is not possible, and the complex exhibits a strong emission typical of triplet ruthenium → polypyridine c.t. levels. As far as the lifetime of the low-temperature emission is concerned, it should be noted that complex **2** is a longer-lived emitter than **1**, in spite of the expectation based on the energy-gap law.[1] Our results are in agreement with those of Meyer and co-workers[34] concerning the effect on the luminescence lifetime of increasing delocalization in the acceptor ligand of the ^{3}m.l.c.t. excited state.

Conclusion

Two new ruthenium(II) complexes with phenyl-substituted bi- and tri-dentate polypyridine ligands, **1** and **2**, have been synthesised and characterised. The results of an investigation of the luminescence properties and electrochemical behaviour has shown that $[Ru(bipy)_2(ppq)]^{2+}$ is a good candidate as a luminescent and redox-active species to be incorporated in a polymer polyquinoline-based backbone. Although the $[Ru(bpqpy)_2]^{2+}$ complex is not emissive at room temperature, we are currently considering the replacement of one of the two tridentate bpqpy moieties with more suitable ligands, which may eventually lead to mixed-ligand ruthenium(II) complexes with better luminescence characteristics at room temperature. The synthesis and characterization of polyquinoline copolymers and of related ruthenium(II) complexes are underway.

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References

1 See, for example, (*a*) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; (*b*) T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163.

2 K. Kalyanasundaram, J. Kiwi and M. Gräetzel, *Helv. Chim. Acta*, 1978, **61**, 2720; J. M. Lehn and J. P. Sauvage, *Nouv. J. Chem.*, 1977, **1**, 449; J. M. Lehn, J. P. Sauvage and R. Ziessel, *Nouv. J. Chem.*, 1979, **3**, 423; M. Gräetzel (Editor), *Energy Resources through Photochemistry and Catalysis*, Academic Press, London, 1983.

3 N. Vlachopulos, P. Liska, J. Augustynski and M. Gräetzel, *J. Am. Chem. Soc.*, 1988, **110**, 1216; R. Dabestani, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallonk, S. E. Webber and J. M. White, *J. Phys. Chem.*, 1988, **92**, 1872; R. Amadelli, R. Argazzi, C. A. Bignozzi and F. Scandola, *J. Am. Chem. Soc.*, 1990, **112**, 7099.

4 B. Durham, W. J. Dressick and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1979, 381.

5 J. M. Kelly, D. J. McConnell, C. Ohuigin, A. B. Tossi, F. Kirsch–De Mesmaeker and J. Nasielski, *J. Chem. Soc., Chem. Commun.*, 1987, 1821; A. M. Pyle, J. P. Rehmann, R. Meshoyrer, C. V. Kumar, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc.*, 1989, **11**, 3051; A. B. Tossi and J. M. Kelly, *Photochem. Photobiol.*, 1989, **49**, 545.

6 (*a*) Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Strekas, H. D. Gafney and A. D. Baker, *J. Am. Chem. Soc.*, 1987, **109**, 2691; (*b*) G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 1990, **29**, 4750; (*c*) F. Scandola, M. T. Indelli, C. A. Bignozzi and C. Chiorboli, *Top. Curr. Chem.*, 1990, **158**, 73; (*d*) W. R. Murphy, jun., K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem.*, 1989, **28**, 81; (*e*) K. Kalyanasundaram and Md. K. Nazeeruddin, *J. Chem. Soc., Dalton Trans.*, 1990, 1657; (*f*) V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.

7 J. N. Younathan, S. F. McClanahan and T. J. Meyer, *Macromolecules*, 1989, **22**, 1048.

8 G. F. Strouse, L. A. Worl, J. N. Younathan and T. J. Meyer, *J. Am. Chem. Soc.*, 1989, **111**, 9101; L. A. Worl, G. F. Strouse, J. N. Younathan, S. M. Baxter and T. J. Meyer, *J. Am. Chem. Soc.*, 1990, **112**, 7571.

9 F. A. Bottino, A. Mamo, A. Recca, J. P. Droske and J. K. Stille, *Macromolecules*, 1982, **15**, 227.

10 J. K. Stille, *Macromolecules*, 1981, **14**, 870.

11 P. A. Lay, A. M. Sargeson and H. Taube, *Inorg. Synth.*, 1986, **24**, 291.

12 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

13 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697.

14 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.

15 G. L. Cook and F. M. Church, *J. Phys. Chem.*, 1957, **61**, 458; H. E. Podall, *Anal. Chem.*, 1957, **29**, 1423.

16 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1980.

17 V. Carassiti, A. Seminara and A. Seminara-Musumeci, *Ann. Chim. (Rome)*, 1964, **54**, 1025.

18 N. Neto, M. Muniz-Miranda, L. Angeloni and E. Castellucci, *Spectrochim. Acta, Part A*, 1983, **39**, 97.

19 R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, London, 1971.

20 D. M. Klassen, C. W. Hudson and E. L. Shaddix, *Inorg. Chem.*, 1975, **14**, 2733.

21 D. M. Klassen, *Inorg. Chem.*, 1976, **15**, 3166.

22 D. M. Klassen, *Chem. Phys. Lett.*, 1982, **93**, 383.

23 M. L. Stone and G. A. Crosby, *Chem. Phys. Lett.*, 1981, **79**, 169.

24 M. Maestri and M. Gräetzel, *Ber. Bunsenges. Phys. Chem.*, 1977, **81**, 504.

25 S. Anderson, K. R. Seddon, R. D. Wright and A. T. Cocks, *Chem. Phys. Lett.*, 1980, **71**, 220.

26 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem.*, 1983, **22**, 1617.

27 R. P. Thummel and Y. Decloitre, *Inorg. Chim. Acta*, 1987, **128**, 245.

28 R. P. Thummel, V. Hedge and Y. Jahng, *Inorg. Chem.*, 1989, **28**, 3264.

29 M. L. Myrick, R. L. Blakley and M. K. De Armond, *J. Phys. Chem.*, 1989, **93**, 3936; M. L. Myrick, M. K. De Armond and R. L. Blakley, *Inorg. Chem.*, 1989, **28**, 4077.

30 Y. Ohsawa, K. W. Hanck and M. K. De Armond, *J. Electroanal. Chem., Interfacial Electrochem.*, 1984, **175**, 229.

31 B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4803; J. Van Houten and R. J. Watts, *Inorg. Chem.*, 1978, **17**, 3381; L. De Cola, F. Barigelletti and M. J. Cook, *Helv. Chim. Acta*, 1988, **71**, 733 and refs. therein.

32 F. Barigelletti, L. De Cola, V. Balzani, P. Belser, A. von Zelewsky, F. Vögtle, F. Ebmeyer and S. Grammenudi, *J. Am. Chem. Soc.*, 1989, **111**, 4662.

33 J. R. Kirchhoff, R. McMillin, P. A. Marnot and J. P. Sauvage, *J. Am. Chem. Soc.*, 1985, **107**, 1138.

34 S. Boyde, J. F. Strouse, W. E. Jones, jun. and T. J. Meyer, *J. Am. Chem. Soc.*, 1990, **112**, 7395.

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