New Ruthenium Complexes with 4-(1*H*-Pyrrol-1-yl)-Substituted Polypyridine Ligands − Electrochemical and Spectroscopic Properties

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Three new pyrrole-containing ligands and their ruthenium complexes have been prepared. The pyrrole ring bound by nitrogen to pyridine was found to significantly modify photophysical and electrochemical properties compared to parent bi- and terpyridines.

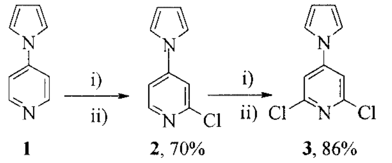
Introduction

The design of new ruthenium(II) complexes that are able to harvest light and turn it into electricity has been the focus of many research works for the development of organic solar cells or luminescence sensors.[1] The nature of the ligands around the metal has been found to play a crucial role during the energy conversion process. Particularly, modification of the classically used bpy and tpy ligands with electron-donor substituents have been found to dramatically improve the absorption in the visible region, which is necessary for sunlight collection. Studies dealing with the effect of several substituents on bipyridines (bpy) in the $Ru(bpy)_3^{2+}$ series revealed that the highest values for $\lambda_{max.}$ were obtained with dimethylamino groups.[2] Moreover, the introduction of a 2-thienyl moieties at the 4′-position in terpyridine (tpy) also led to efficient visible light absorption.[3] From these data, the binding of a nitrogen-containing electron-rich ring such as pyrrole could be expected to tune the photophysical and electrochemical properties of the corresponding complexes. Herein, we report on the preparation of the new homoleptic ruthenium complexes **4a**, **5a** and **7a** from 4-(1*H*-pyrrol-1-yl)pyridine-containing ligands and on the study of their photophysical and electronic properties.

Results and Discussion

Synthesis

We first synthesized the C-2 chlorinated precursors **2** and **3** needed for further organometallic couplings (Scheme 1). The electron-releasing effect of the pyrrole moiety was exploited to selectively direct lithiation at the position alpha to the pyridine nitrogen atom,[4] thus allowing for introduction of the halogens in high yield. An efficient iterative lithiation of compound **2** afforded the expected 2,6-dichloro derivatives **3** (Scheme 1).



Scheme 1. Preparation of **2** and **3**: i) $BuLi/Me_2N(CH_2)_2OLi$ (3 equiv.), toluene, −78 °C, 1 h; ii) C_2Cl_6 (3.5 equiv.), toluene, −78 °C to room temperature

The symmetrical ligand **4** was then prepared efficiently by nickel-catalysed homocoupling of **2**, while **5** and **7** were obtained by Stille cross-coupling of 2-(tributylstannyl)pyridine with **2** and **6**, respectively (Scheme 2).[5] Attempts to obtain **7** by a one-pot coupling remained limited to the formation of compound **6**, and the two-step procedure was preferred for the formation of **7** in an acceptable 50% yield after crystallization in ether.

We then turned our focus to the preparation of the corresponding homoleptic ruthenium complexes **4a**, **5a** and **7a** (Scheme 3). In our first attempts, stoichiometric proportions of the ligands classically reacted overnight with $RuCl_3(H_2O)_x$ in refluxing DMF. Unfortunately, incomplete incorporation of the ligands was observed leading only to complex mixtures. This is assumed to be a result of the pyr-

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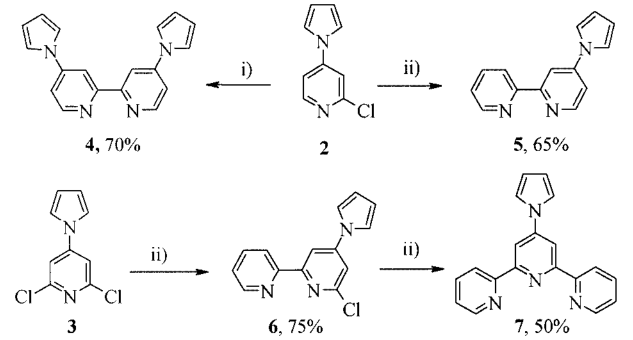
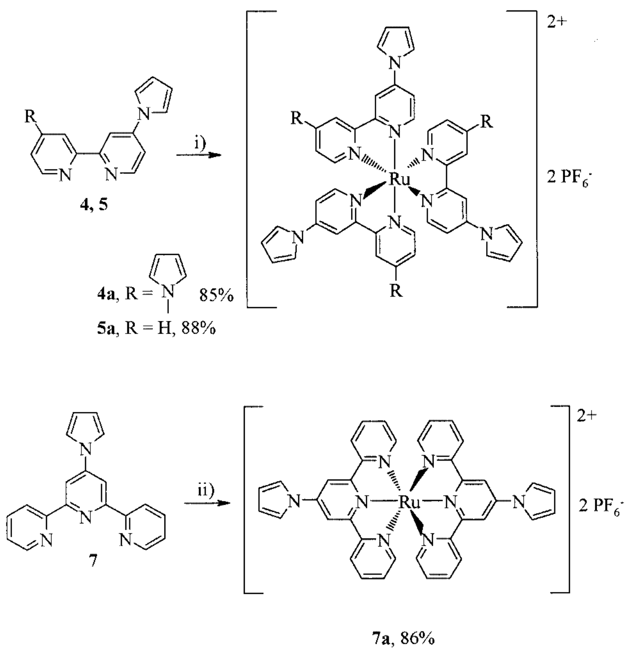


Scheme 2. Preparation of ligands **4**−**7**: i) $NiCl_2$ (1.1 equiv.), PPh_3 (4.4 equiv.), Zn (1.1 equiv.), degassed DMF, 50 °C, 1.5 h, ii) 2-(tributylstannyl)pyridine (1.1 equiv.), $[PdCl_2(PPh_3)_2]$ (5 mol %), PPh_3 (10 mol %), degassed xylene, reflux, 24 h



Scheme 3. Preparation of ruthenium complexes: i) $RuCl_3(H_2O)_x$ (0.33 equiv.), *N*-ethylmorpholine (2 drops), ethylene glycol, microwave irradiation, 200 °C, 5 min, ii) $RuCl_3(H_2O)_x$ (0.5 equiv.), *N*-ethylmorpholine (2 drops), ethylene glycol, microwave irradiation, 200 °C, 5 min

role-induced lower π-accepting power of the ligands. Indeed, the corresponding unsubstituted bpys and tpy are known to react smoothly under the same conditions leading to $[Rubpy_3]^{2+}$ and $[Rutpy_2]^{3+}$ complexes, respectively.[5] Complexation under microwave irradiation was then attempted (see Exp. Sect.). We were pleased to observe the formation of the target complexes **4a**, **5a** and **7a** in high yields after 3 min at 200 °C in ethylene glycol (Scheme 3).

Properties

Electrochemical and photophysical data of **4a**, **5a** and **7a** are reported in Table 1 and are compared with those of the corresponding parent complexes.

All complexes display a reversible Ru^{II} to Ru^{III} oxidation wave. No ligand reduction waves are detected for **7a**. This may be attributed to the formation of a nonconducting layer by adsorption at the electrode surface.[3b] An irreversible oxidation wave of the pyrrole moiety is distinctively observed only with complex **7a** at 0.8V, while overlap with the Ru^{III}/Ru^{II} oxidation wave is observed for **4a** and **5a**. The oxidation of pyrrole-containing complexes is observed at a less positive voltage than those of $[Rubpy_3]^{2+}$ and $[Rutpy_2]^{3+}$.

Comparison of the values obtained for **4a** and **5a** show that the introduction of a second pyrrole unit on the bpy ligand has a much lower effect than the introduction of the first unit. All these results indicate a significant destabilisation of the metal d orbital due to the electron-donor effect induced by the pyrrole substituent bound by the nitrogen atom to the pyridine ring. This property is also clearly evidenced by electronic transition spectra in acetonitrile. Indeed, all the MLCT absorptions in the visible region are red-shifted. Values for $\lambda_{max.}$ from 465 to 490 nm are observed; the larger effect is observed for complex **4a** bearing ligands with two pyrrole units. Electron-donor groups like pyrrol-1-yl destabilise the HOMO (π t_{2g}) metal orbital more than the LUMO (π*) ligand orbital.[8] Consequently, both absorption and emission maxima of **4a**, **5a** and **7a** are shifted to longer wavelengths than those of $[Ru(bpy)_3]^{2+}$and $[Ru(terpy)_2]^{2+}$. For the same reasons the oxidation processes on **4a**, **5a** and **7a** occur with greater ease than those on their parent complexes. A consequence of the electron-donor effect is a $^3MLCT \rightarrow {}^3MC$ energy gap decrease,[9] and thus, the following order is obtained for quantum yields $\Phi_{5a} < \Phi_{4a} < \Phi_{[Ru(bpy)_3]^{2+}}$.

However, for **4a** and **5a** the reduction potentials are shifted to higher values than for $[Rubpy_3]^{2+}$. The corresponding stabilization of the LUMO (π*) ligand orbital

Table 1. Electrochemical and photophysical data for ruthenium complexes

Complex[a]	$E_{1/2,ox}$ (V)[b] R^{III}/Ru^{II} (ΔEp/mV)	Ligand processes (V)	λ_{abs} (nm)	ε × 10^{-3} (M^{-1} cm^{-1})	λ_{em} (nm)[c]	φem (%)
$Ru(bpy)_3(PF_6)_2$	1.27 (90)[d]	−1.31 (rev.)/−1.50 (rev.)/−1.77 (rev.)	451[d]	14.0[d]	615[e]	0.059[f]
4a	1.12(90)	−1.20 (rev.)/−1.32 (rev.)/−1.52 (rev.)	480	22.2	630	0.044
5a	1.16 (90)	−1.21 (rev.)/−1.37 (rev.)/−1.60 (rev.)	465	8.6	650	0.022
$[Ru(tpy)_2]$ $(PF_6)_2$ [g]	1.30 (100)	−1.24 (rev.)/−1.49 (rev.)	474	10.4	629	$<5 \times 10^{-6}$
7a	1.18 (100)	n.d.	490	38.5	n.d.	n.d.

[a] All measurements performed in degassed acetonitrile solutions at 298 K. [b] First potential standardised with Fc as internal standard and converted into SCE scale by adding 0.38 V [$E_{1/2}$ (Fc^+/Fc)]. Recorded at 100mV/s with $LiClO_4$ as supporting electrolyte. [c] DO < 0.1. [d] See ref.[6]. [e] See ref.[7]. [f] See ref.[8]. [g] See ref.[9].

does not correspond to an electron-donor effect. A possible explanation may be based on the fact that the observed electronic transitions involve the HOMO and the SLUMO (second lowest unoccupied MO) centred on the pyridine ring, whereas the electrochemical reduction processes involve the LUMO localised on the remote *N*-pyrrolyl group. Such an anomalous electrochemical and/or spectroscopic behaviour has been observed in the case of $[\mathrm{Ru(taphen)_3}]^{2+}$(taphen = dipyrido[3,2-*c*:2′,3′-*e*]pyridazine).[10] On the taphen ligand, the LUMO is strongly localised on the −N=N− bridge between the two pyridine rings.

Also of high interest is the dramatic increase in the ε values induced by incorporation of the pyrrole units on the ligands in complexes **4a** and **7a**, while a surprising decrease is observed with **5a**. In the latter case, dissymmetry of ligand **5** allows for the formation of the *fac*- and *mer*-isomers of complex **5a**.[11] The expected strongly different dipole moments of the two isomers may be responsible for the decrease in the ε value. The incorporation of a second pyrrole on the bpy ligand induces a huge increase from 8600 in **5a** to 22200 $\mathrm{M^{-1}cm^{-1}}$ in **4a**. For **7a**, the value (38400 $\mathrm{M^{-1}cm^{-1}}$) is similar to that obtained with the complex $[\mathrm{Ru(tsite)_2}]^{2+}$ (tsite = 4,4′,4′′-triphenyl-2,2′,2′′-terpyridine), which displays one of the highest known ε values (38400 $\mathrm{M^{-1}cm^{-1}}$) in terpy complex series.[12]

Conclusion

In summary, we have prepared new homoleptic ruthenium complexes from bpy and tpy pyrrole-containing ligands. The electron-donor effect of the pyrrole moiety was clearly demonstrated by the lower $\mathrm{Ru^{II}/Ru^{III}}$ oxidation potential and by the significant red-shifted MLCT absorption and emission maxima relative to those of the unsubstituted ligands. The use of bpy ligands bearing two pyrrole units leads to a high ε value. These new complexes are promising for developing novel solar harvesting devices. Work is now in progress to investigate the electropolymerisation of the pyrrole moiety for preparation of new photosensitising materials.

Experimental Section

General Procedure for Preparation of Complexes 4a, 5a and 7a: The ligand **4** or **5** (0.19 mmol) or **7** (35.9 mg, 0.12 mmol) and $\mathrm{RuCl_3(H_2O)}_x$ (15.7 mg, 0.06 mmol) were dissolved in ethylene glycol (5 mL) and *N*-ethylmorpholine (2 drops) was added. The reaction mixture was then placed into a synthesis microwave oven and irradiated at 200 °C (300 W) for 3 min. After cooling down to room temperature, a saturated aqueous solution of $\mathrm{KPF_6}$ (25 mL) was poured into the glazing orange mixture. The resulting orange precipitate was filtered and washed with diethyl ether and toluene to remove uncomplexed ligands. The filter cake was then dissolved in a minimum amount of acetonitrile and poured into deionised water. After filtration and drying, complexes were obtained in almost quantitative yields. The complexes were characterized by ^{1}H NMR ($\mathrm{CD_3CN}$) and mass spectrometry. Spectral data for complexes: **4a:** ^{1}H NMR (200 MHz, $\mathrm{CD_3CN}$): δ = 8.51−8.74 (m, 6 H), 7.69−8.0 (m, 6 H), 7.53−7.65 (m, 12 H), 7.40−7.54 (m, 6 H), 6.30−6.73 (m, 12 H) ppm. MS (ESI): *m*/*z* = 1105.3 $[\mathrm{M} - \mathrm{PF_6}]^+$, 961.4 $[\mathrm{M} - 2\mathrm{PF_6}]^+$, 480.2 $[\mathrm{M} - 2\mathrm{PF_6}]^{2+}$. UV/Vis ($\mathrm{CH_3CN}$): $\lambda_{\mathrm{max.}}$ ($\varepsilon_{\mathrm{max.}}$, L· $\mathrm{mol^{-1}{\cdot}cm^{-1}}$) = 480 nm (22200). **5a:** ^{1}H NMR (200 MHz, $\mathrm{CD_3CN}$): δ = 8.58−8.82 (m, 3 H), 8.39−8.57 (m, 3 H), 7.98−8.22 (m, 3 H), 7.61−7.96 (m, 6 H), 7.25−7.60 (m, 12 H), 6.25−6.72 (m, 6 H) ppm. MS (ESI): *m*/*z* = 910.2 $[\mathrm{M} - \mathrm{PF_6}]^+$, 764.2 $[\mathrm{M} - 2\mathrm{PF_6}]^+$, 382.6 $[\mathrm{M} - 2\mathrm{PF_6}]^{2+}$. UV/Vis ($\mathrm{CH_3CN}$): $\lambda_{\mathrm{max.}}$ ($\varepsilon_{\mathrm{max.}}$, $\mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}$) = 465 nm (8600). **7a:** ^{1}H NMR (200 MHz, $\mathrm{CD_3CN}$): δ = 8.79−8.97 (m, 4 H), 8.59−8.73 (m, 4 H), 7.92−8.09 (m, 4 H), 7.83−7.92 (m, 4 H), 7.44−7.54 (m, 4 H), 7.15−7.34 (m, 4 H), 6.58−6.78 (m, 4 H) ppm. MS (ESI): *m*/*z* = 985.3 $[\mathrm{M}^+]$, 843.2 $[\mathrm{M} - \mathrm{PF_6}]^+$, 697.2 $[\mathrm{M} - 2\mathrm{PF_6}]^+$, 349.1 $[\mathrm{M} - 2\mathrm{PF_6}]^{2+}$. UV/Vis ($\mathrm{CH_3CN}$): $\lambda_{\mathrm{max.}}$ ($\varepsilon_{\mathrm{max.}}$, $\mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}$) = 490 nm (38500).

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[1] [1a] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85. [1b] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737. [1c] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49. [1d] R. Argazzi, A. Bignozzi, G. M. Hasselmann, G. J. Meyer, *Inorg. Chem.* **1998**, *27*, 4533. [1e] X. Schulze, J. Serin, A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2001**, 1160. [1f] M. I. J. Polson, N. J. Taylor, G. S. Hanan, *Chem. Commun.* **2002**, 1356. [1g] E. Figgemeier, V. Aranyos, E. C. Constable, R. W. Handel, C. E. Housecroft, C. Risinger, A. Hagfeldt, E. Mukhtar, *Inorg. Chem. Commmun.* **2004**, *7*, 117.

[2] M. J. Cook, A. P. Lewis, G. S. McAulife, V. Skarda, A. J. Thomson, *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293.

[3] [3a] J. Hjelm, E. C. Constable, E. Figgemeier, A. Hagfeldt, R. Handel, C. E. Housecroft, E. Mukhtar, E. Chofield, *Chem. Commun.* **2002**, 284. [3b] E. R. Schofield, Ph. D. Dissertation, University of Basel, Switzerland, **1999**.

[4] [4a] Ph. Gros, Y. Fort, *Eur. J. Org. Chem.* **2002**, 3375. [4b] D. Cuperly, Ph. Gros, Y. Fort, *J. Org. Chem.* **2002**, *67*, 238.

[5] Detailed studies on selective lithiation of **1** and coupling reactions will be published in due course.

[6] B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehmann, A. Ludi, *J. Am. Chem. Soc.* **1977**, *99*, 7368.

[7] E. C. Constable, C. E. Housecroft, E. R. Schofield, S. Encinas, N. Armaroli, F. Barigelletti, L. Flamigni, E. Figgenmeier, J. G. Vos, *Chem. Commun.* **1999**, 869.

[8] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1639.

[9] M. Maestri, N. Armaroli, V. Balzani, E. W. Constable, A. M. W. Cargill Thomson, *Inorg. Chem.* **1995**, *34*, 2759.

[10] F. Barigelletti, A. Juris, V. Balzani, P. Belser, A. von Zelewsky, *Inorg. Chem.* **1987**, *26*, 4115

[11] The ^{1}H NMR spectrum of **5a** did not allow to distinguish between the *fac*- and *mer* isomer.

[12] M. L. Stone, G. A. Crosby, *Chem. Phys. Lett.* **1981**, *79*, 169.

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