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Homoleptic and Heteroleptic Ruthenium(II) Complexes based on 2,6-bis(quinolin-2-yl)pyridine Ligands: Multiple Charged State Modules for Potential Density Memory Storage


Abstract: The two ligands 2,6-bis(4-methylquinolin-2-yl)pyridine (L₁) and diethyl 2,2′-(pyridine-2,6-diyl)bis(quinolone-4-carboxylate) (L₂) were used to prepare the homoleptic [Ru(L₂)₂](PF₆)₂ (RU1) and heteroleptic [Ru(L₁)L₂](PF₆)₂ (RU2) complexes. DFT calculations (B3PW91, 3-21G**) performed on both RU1 and RU2 revealed that redox at the ruthenium site for RU2 is less positive by around 110 mV. The corollary is that one-electron ligand-based reduction for RU2 is more cathodic by 80 mV. Electrochemistry experiments confirmed that the prediction is qualitatively correct and that the complexes can each hold up to five electrons reversibly.

Introduction
Poly(pyridyl ligands [e.g. 2,2′-bipyridine (bipy), 2,2′:6′,2′′-terpyridine (terpy)] and their complexes with metal ions such as ruthenium(II), osmium(II) and iridium(III) hold an especially prominent place in the development side of photoactive and redox-active supramolecular systems.[11] In distinctive cases the metal complex is the focal photoactive segment to instigate cascade energy and electron transfer processes, and in other situations it is the essential "glue" to hold together large arrays.[2]

By precise choice of metal and ligands the redox behavior is manipulated to facilitate charge migration in unique directions.[3] The past three decades have witnessed great efforts to design new ligands, especially those which are tridentate, to circumvent the poor photochemistry observed for [Ru(terpy)₂]²⁺ complexes.[4] It is recognized that the poor bite angle for the terpy ligands in [Ru(terpy)₂]²⁺ means that the e₃⁻ orbitals are close in energy to the occupied π⁻ ligand orbital of the triplet metal-to-ligand charge transfer state (³MLCT).[5] As a consequence thermally activated depopulation of the ³MLCT state is highly efficient and the luminescence lifetime is sub-ns.

Modification of the basic terpyridine structure has certainly been extremely popular and the exchange of the two outer pyridines for quinolone groups has produced the most dramatic and contrasting results. Early work concentrated on 2,6-di(quinolino-2-yl)pyridine, DQ₂P (Figure 1), and its ruthenium(II) complex which showed no improvement in excited state lifetime performance at room temperature.[6] In complete contrast the later reported ruthenium(II) complex of the ligand 2,6-di(quinolin-8-yl)pyridine, DQ₈P (Figure 1), is highly luminescent and the excited state lifetime is several microseconds.[7] Considering the failure of DQ₂P and its analogues to improve the photophysical properties of transition metal ion complexes, not surprisingly the ligands have received less attention. However, one slightly overlooked and notable feature of bis-DQ₂P ruthenium(II) complexes is their electrochemistry, and in particular the reduction portion of cyclic voltammograms.[8] Four closely spaced reversible waves were reported, essentially meaning that complexes are not only proficient at multi-electron storage but may be applicable to high density memory storage.[9] Here the concept is to access multiple-charged states at distinct voltages reversibly; the ferrocene molecule is a prime example consisting of two states: the neutral and the mono-positive (ferroconium) state.[10] In contrast, a bis-DQ₂P ruthenium(II) complex would be considered a five-state system, starting neutral and adding in sequentially four electrons. However, when re-examining the electrochemistry for two derivatives of DQ₂P we noticed that upon reduction at least one more redox state is readily accessible. An interesting conundrum arises because of this observation; namely, where does the fifth electron reside, considering that tri-anion formation is necessary if the final electron addition is solely ligand-based[21]

![Figure 1](image_url)

Figure 1. Examples of quinolone-based tridentate ligands, showing the subtle difference in chelate ring arrangement by alteration in N-atom positions. Note: the drawings do not represent the energy-minimized conformations but those required for tridentate ligation.

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Supporting information for this article is given via a link at the end of the document.
**Results and Discussion**

**Synthesis**

Prior work has shown that ligands based on the DQ2P unit are prepared by applying a one-pot Pfitzinger reaction. Therefore, using established procedures the two ligands L₁ and L₂ were synthesized by this method and fully characterized. Crystal structures for both ligands (see Supporting Information) confirm the anti-anti arrangement of the nitrogen atoms. Our interest was to prepare both homoleptic and heteroleptic ruthenium(II) complexes based on these two ligands, and so the first step was to prepare a mono-ligand ruthenium(III) synthon. Thus, reaction of L₂ with RuCl₃ proceeded smoothly to produce the adduct RuL₂ as a dark green solid in 79% yield. A very strong band at 1715 cm⁻¹ in the IR spectrum confirmed that the ethyl ester remained intact during complexation. To facilitate attachment of a second ligand to RuL₂ the chloro ligands were removed by reaction with AgBF₄, changing the color of the solution from green to purple. The in-situ generated solvated complex was reacted under reflux in n-BuOH with either L₁ or L₂ to produce the heteroleptic complex RU₂ or homoleptic complex RU₁, respectively.

![Scheme 1](image)

**Scheme 1:** Reagents and Conditions: (i) RuCl₃, EtOH, reflux, L₂ (ii) AgBF₄, acetone, n-BuOH, reflux, L₁ or L₂. Note: each asterisk marks the 8-hydrogen atom on a quinoline.

The identity of the final complexes was confirmed by ¹H and ¹³C NMR spectroscopy as well as mass spectrometry. Given that clean NMR spectroscopic data could be collected it is safe to assume that the complexes are diamagnetic and each contains a low-spin d⁶ (Ru⁷⁺) ion. It was possible to obtain very small but good quality single crystals for the nitrate salt of RU₁, collect synchrotron X-ray diffraction data, and solve the structure (Figure 2). Selected bond lengths and angles are collected in Table 1. The first point to note is that only two counter-ions are evident and so the oxidation state of the ruthenium is again confirmed to be +2. From inspection of the bond angles it is evident that the metal ion coordination is best described as a distorted octahedron. The N₅–Ru–N₂ bond angle is close to the ideal 180°, but the other two trans bond angles are ca. 24° away from this value. As observed in previous [Ru(terpy)₂]⁺ structures the Ru–N bond lengths to the central pyridine are shorter than the other two Ru–N bond lengths. A major contribution to distortion of the structure is caused by the presence of quinoline rings in each of the ligands. The 8-hydrogen atom for both quinolines points toward the central pyridine of the complementary ligand. The four hydrogen-to-pyridine centroid distances are between 2.49 Å and 2.79 Å (see Supporting Information). The outcome is a severe twist to the ligand, which is best viewed as two planes created using each quinoline ring (see Supporting Information). The degree of twist for each ligand is somewhat different (32.3° and 12.7°). An additional contribution to distortion for the structure is likely triggered by packing effects, since there is a clear π-stacking motif in the unit cell (see Supporting Information): two quinoline groups for adjacent cations are aligned in a "slipped" parallel configuration at a centroid-to-centroid distance of 3.72 Å. An additional packing effect is seen for one of the ester groups. Near coplanarity of a carbonyl and aryl is expected because of the beneficial increase in π-conjugation. Whereas torsion angles for three of the esters are modest (13.1°, 16.1° and 24.4°) the final angle of 48.9° certainly suggests decoupling of the two groups and there must be a loss in stabilization energy. The reason for this difference is not obvious from the crystal packing diagram (see Supporting Information). As discussed later for computer-calculated structures the result is an anomaly.

![Figure 2](image)

**Figure 2.** Structure of the cation of RU₁. H atoms, solvent molecules and nitrate anions are omitted for clarity.
Table 1. Selected bond lengths and angles in the crystal structure of RU1.

<table>
<thead>
<tr>
<th>Bond Length / Å</th>
<th>Bond Length / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru–N1</td>
<td>2.150(2)</td>
</tr>
<tr>
<td>(2.150)</td>
<td>(2.162(2))</td>
</tr>
<tr>
<td>Ru–N2</td>
<td>1.986(2)</td>
</tr>
<tr>
<td>(2.006)</td>
<td>(2.007)</td>
</tr>
<tr>
<td>Ru–N3</td>
<td>2.151(2)</td>
</tr>
<tr>
<td>(2.161)</td>
<td>(2.162)</td>
</tr>
<tr>
<td>N5–Ru–N2</td>
<td>177.38(9)</td>
</tr>
<tr>
<td>(179.75)</td>
<td>(155.52)</td>
</tr>
<tr>
<td>N3–Ru–N1</td>
<td>155.69(9)</td>
</tr>
<tr>
<td>(155.59)</td>
<td></td>
</tr>
</tbody>
</table>

[a] DFT calculated value using B3PW91 and a 3.21G** basis set is given in parentheses below the crystallographically determined value.

Figure 3. Room-temperature normalised absorption spectra for RU1 (black) and RU2 (red) in MeCN.

Absorption/Emission Spectroscopy

The electronic absorption spectra for the two ligands L1 and L2 display typically intense bands below 400 nm and are associated with n–π* transitions (see Supporting Information). The two ester groups attached to L2 help push the absorption envelope toward slightly lower energy, and the overall band shape is broader and has less defined peaks compared to L1. It is conceivable that n–π* transitions may contribute to the absorption profile for L2. The absorption spectra collected from dilute MeCN solutions when the ligands are complexed in RU1 and RU2 are shown in Figure 3. Besides the ligand-based absorptions below 400 nm, the characteristic metal-to-ligand charge-transfer (MLCT) bands are observed up to around 700 nm. The broad feature for RU1 actually comprises four peaks at 621 nm, 566 nm, 525 nm and 483 nm. There is compelling evidence to suggest that the multiple band feature is partly a result of interchromophore coupling.[13] Even though RU1 does not exhibit pure O₃ symmetry there is definite loss of symmetry in moving to the heteroleptic complex RU2. In addition, the electron affinity of the two ligands is different and, as a consequence, several MLCT states slightly different in energy are feasible. These two factors contribute to the alteration in appearance of the MLCT profile for RU2. The main peak is observed at 512 nm and the shoulders either side are less discernible. In solution at room temperature no emission from either RU1 or RU2 was observed. Certainly this observation is consistent with previous work on similar derivatives and is explained by the efficient thermally activated non-radiative route via the eπ* orbitals. Time-resolved pump-probe experiments (see Supporting Information) confirmed that the excited state lifetime for RU1 in MeCN is only 144 ps.

Figure 4. Cyclic voltammogram for RU1 in MeCN containing 0.1 M TBATFB background electrolyte at a glassy carbon working electrode. Scan rate = 50 mV s⁻¹. * = artefact possibly from deposition of material on the electrode.

Electrochemistry

Prior work by Campagna et al.[8] reported the electrochemical behavior of ruthenium(II) complexes of 2,6-bis(4′-phenyl-2′-quinolyl)pyridine. Although up to four ligand-based reductions were reported we found that an additional wave may have been previously overlooked. Cyclic voltammograms were recorded from MeCN solution using 0.1 M N-tetrabutylammonium tetrfluoroborate (TBATFB) background electrolyte. The cyclic voltammogram for RU1 is shown in Figure 4 and data are collected in Table 2. Upon scanning to positive potentials a clear quasi-reversible wave is observed at +1.28 V vs Fc/Fc and is readily assigned to redox at the ruthenium center. The scan within the negative potential window is far more detailed and consists of five one-electron reversible waves; observation of the first four waves is in agreement with previous findings.[8] It was not possible to push the scan any further negative because of solvent cut-off. The differences in the half-wave potentials E₁–E₂, E₂–E₃ and E₃–E₄ are very similar (average = 220 mV), but there is a large increase in the difference for the final two couples (E₄–E₅ = 500 mV). The consistency observed in the first three energy gaps is an outcome of the two ligands being identical for RU1. The addition of the fifth electron must be to a species that formally has a –2 charge, and the large final energy gap is a
result of the electrostatic penalty. The first four reduction waves can be assigned to sequential addition of an electron to the two ligands. The cyclic voltammogram for RU2 (see Supporting Information) contains overall the same basic features as those seen in Figure 4: ruthenium-based redox and five one-electron reductions. The most prominent disparity is observed for the five reduction waves, which appear closer together. The differences in the half-wave potentials E2−E1, E3−E2, E4−E3 and E5−E4 are 280, 370, 390 and 270 mV; the effect is a result of the complex containing two dissimilar ligands and the difference in their electron affinic nature. At first it may appear that addition of the fifth electron does not encounter as large an electrostatic penalty when compared to complex RU1. However, it is clear that sequential electron additions to RU2, at least up to four electrons, become progressively more difficult, as illustrated by the steady increase in ΔE as highlighted in Table 2. The final reduction is still some 210 mV more cathodic for RU2 when compared to RU1. A couple of points are worth noting; namely, the more easily oxidized complex at the ruthenium center is RU2 and the more easily reduced complex at the ligand centers is RU1. Clearly, the main conundrum is this: to which part of the complex does the fifth electron go, considering that after addition of four electrons each ligand would be formally a dianion? The electrochemistry of the “free” ligands was extremely poor, affording no real insight into what may occur in the complexes. Our attention turned to calculations to try to shed light on the problem.

Computer Calculations
As a starting point we focused on the two ligands, L1 and L2, and in particular mapping electron density distributions as electrons were added sequentially. DFT calculations were performed for the gas phase using the B3LYP correlation function and 6-311G basis set with Gaussian03. The electron density maps shown in Figure 5 help to illustrate in which parts of the ligands electrons may reside after their addition. The starting density distributions for both neutral ligands are in agreement with the electron-donating (methyl group) and -withdrawing (carboxylic ester) effects. The addition of one electron to L1 places negative density on the central pyridine group, thus avoiding build-up of charge on the quinolone subunits. Addition of two more electrons leads to severe charge accumulation focused on the pyridine. One-electron addition to L2 does not result in localization of negative charge on any specific aromatic ring. Even after three-electron reduction the negative charge is evenly distributed on the ligand backbone. In view of the calculations it would appear that tri-anion formation, as may be required in the complex, is more favorable for L2.  

Table 2. Redox potentials measured for the two complexes in dry MeCN and referenced to ferrocene.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E1[II]/V e2+/1</th>
<th>E2[II]/V e1+/0</th>
<th>E3[II]/V e0/-1</th>
<th>E4[II]/V e-1/-2</th>
<th>E5[II]/V e-2/-3</th>
<th>Ee[III]/V Ru3+/Ru2+</th>
</tr>
</thead>
<tbody>
<tr>
<td>RU1</td>
<td>-1.00 (70)</td>
<td>-1.21 (70)</td>
<td>-1.44 (70)</td>
<td>-1.66 (70)</td>
<td>-2.16 (70)</td>
<td>1.28 (130)</td>
</tr>
<tr>
<td>RU2</td>
<td>-1.06 (70)</td>
<td>-1.34 (70)</td>
<td>-1.71 (70)</td>
<td>-2.10 (70)</td>
<td>-2.37 (70)</td>
<td>1.10 (90)</td>
</tr>
<tr>
<td>ΔE[II]/mV</td>
<td>60 (80)d</td>
<td>130</td>
<td>270</td>
<td>440</td>
<td>210</td>
<td>180 (110)d</td>
</tr>
</tbody>
</table>

[a] Peak separation Eo−Ee measured to be 70 mV for the ferrocene couple. [b] Half-wave potential (Eo/1) and peak separation (Eo−Ee) in parentheses. [c] Modulus of the difference between the half-wave potentials RU2−RU1. [d] Value calculated from DFT results.

Figure 5. Electron density maps created for the two ligands using Gaussian 03 (B3LYP) and a 6-311G basis set. Blue = low electron density, red = high electron density. Note: to simplify the calculations the methyl ester was used.

Detailed calculations on the ground-state structures for ruthenium(II) complexes of 6-bis(quinolin-2-yl)pyridine type ligands are limited. For example, Onozawa-Komatsuzaki and co-workers reported frontier molecular orbitals for a ruthenium(II) tris-thiocyanato complex using a ZINDO/1 semi-empirical method. Our interest was firstly to construct a comprehensive picture of the LUMO orbitals and use the results to try to explain the electrochemical findings. In the first iteration the ground-state gas phase structures for RU1 and RU2 were modeled using the semi-empirical AM1 method. The structures were refined further by DFT using the Perdew non-local correlation
function (B3PW91) and a 3-21G** basis set. Confidence that this method works well is evident by comparison of calculated Ru–N bond lengths with those obtained by X-ray crystallography for RU1 (Table 1). The poorest correlation is observed for the Ru–N2 and Ru–N5 bond lengths but the difference is less than 1% and within the standard uncertainty of the crystallographically determined value. The computer-calculated and observed bond angles are again in somewhat good agreement. Calculated structures for both RU1 and RU2 are collected in the Supporting Information along with models displaying the "twist" angles for the two ligands; values appear reasonable and are around 29° (cf. 12.6° and 32.3° for RU1). Recalling that at least one torsion angle for the carbonyl group within RU1 is likely distorted by packing effects, the average torsion angle from calculated structures is only 0.9°.

Figure 6. DFT calculated (B3PW91, 3.21G**) selected frontier molecular orbitals for RU2. The number of the molecular orbital is given in parentheses.

A selection of DFT calculated frontier molecular orbitals for the heteroleptic complex RU2 are collected in Figure 6. For a low-spin Ru^{2+} (d⁶) metal ion in an octahedral field simple crystal field theory predicts the HOMO must be based on the t₂₂ set of orbitals (dₓ²−ᵧ², dₓz, dᵧz). Since for RU2 the coordination sphere is distorted the pure degeneracy of the t₂₂ orbitals is removed and, as shown in Figure 6, the HOMO (233) mainly comprises the dₓz orbital. The LUMO (234) is localized on L₂, which incorporates the two electron-withdrawing ester groups and is quinoline-based. In contrast the LUMO+1 (235) is sited on L₁ but is more biased towards the central pyridine ring. Very close in energy is the LUMO+2 (236) and it is shifted back to reside on L₂. This flipping of spatial location is again observed in moving from LUMO+2 to LUMO+3 (237) and finally LUMO+4 (238), but there is a considerable energy difference (0.85 eV) between these last two orbitals. In contrast, it is noted that the difference in energy from LUMO to LUMO+3 is rather modest (0.38 eV). Calculations were also performed on the singly and doubly reduced forms of RU2 to assess if reduction perturbed the structure to any major extent. We could map any modifications to spatial distributions of the frontier molecular orbitals (see Supporting Information). The sequential addition of an electron to RU2 results as expected in a shortening of the Ru–N bonds as electron density is increased on the ligands. There are small modifications to the N–Ru–N bond angles to accommodate the bond length changes. In addition the “twist” of the two ligands is slightly exaggerated as the angles are increased. If we ignore the anticipated change in orbital energies, the frontier molecular orbitals from 235 to 237 remain relatively close in energy and there is still a significant energy gap between orbitals 237 and 238.

Results of similar ground-state molecular orbital calculations performed on RU1 are collected in the Supporting Information. Overall, the findings are similar, although it is noticed that the HOMO and LUMO for RU1 are lower in energy compared to analogous orbitals for RU2. Consequently, the calculations predict that the ruthenium(II) center for RU2 will be the easier to oxidize of the two complexes (ΔE = 110 mV). In contrast, ligand-based reductions for RU1 will be slightly more facile (ΔE = 80 mV). The two predictions turn out to be remarkably good. Again the good agreement between theory and experiment does suggest that the DFT calculation method is reliable.

Although calculations could not definitively answer the conundrum of the exact location of the fifth electron, the ligand L₂ in the complex is the more likely site. The electron-withdrawing ester groups help stabilize any electron density build up on the ligand and seem to facilitate the spreading out of negative charge.

Conclusions

Despite the poor photochemistry of ruthenium(II) complexes bearing bis(quinolin-2-yl)pyridine ligands, their electrochemistry is more rewarding than initially described. Complexes bearing the electron-withdrawing ester-functionalized ligand are capable of storing reversibly five electrons. The electron storage capacity may be even greater by further modification of the ligand skeleton. Highly electron-withdrawing groups (e.g., CN, CF₃) could facilitate storage to six or even seven electrons by stabilization of the highly charged ligands. Considering the focus of C₆₀ and its multiple-electrons storage capability the metal-based complexes described here may open up new avenues for reversible charge storage.
Experimental Section

All experiments were performed under a nitrogen atmosphere. All solvents, deuterated solvents and starting reagents were purchased from Sigma Aldrich and Alfa Aesar, and were used as received. NMR spectra were recorded on Bruker 300, JEOL 400 or Bruker Ultraspectro 400 plus spectrometers. FT-IR spectra were recorded on a Varian 800FT-IR or a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. MS analyses were performed by the EPSRC National Mass Spectrometry Service Centre, College of Medicine, Swansea University. Ultraviolet–visible (UV–vis) absorption spectra were measured with a Perkin Elmer Lambda 25 spectrometer. Voltammetry studies were carried out using a CH Instruments electrochemical analyzer. Acetonitrile was distilled over CaH₂. TBABF₄ (Sigma Aldrich) was used without further purification.

Dinitrogen presaturated with MeCN flowed into the cell before voltammetric experiments. Computational calculations were performed using a 32-bit version of Gaussian03 on a quadri-core Intel Xeon system with 4GB RAM. The calculations were run in parallel, fully utilizing the multi-core processor. Energy minimization calculations were monitored using Molden and run in parallel with frequency calculations to ensure that optimized geometries represented local minima. Calculations performed on reduced species for both ligands and complexes were run at the singlet and doublet levels only.

Preparation of 2,6-bis(4-methylquinolin-2-yl)pyridine (L₁)

In a small round-bottom flask was placed a saturated solution of C₆H₅OK in EtOH (3 mL). After cooling to 0°C, 2,6-diacetylpyridine (0.344 g, 2.63 mmol) was added and the mixture was stirred until the solution turned yellow. When all the 2,6-diacetylpyridine had dissolved, 2-aminoacetophenone (0.71 g, 5.26 mmol) was added and after 20 h of stirring the mixture was filtered, washed with water (3 x 10 mL) and air-dried, giving a purple/red solid crude product. The solid was washed with water (with a metallic sheen). The suspension was cooled to 5°C, contents hardened (at this point the temperature was approximately 60°C) and 2,6-diacetylpyridine had dissolved, 2,6-bis(4-methylquinolin-2-yl)pyridine, sodium salt (0.571 g, 60%). I₃ [M+H] [130.82, 129.31, 128.66, 126.65, 123.89, 122.30, 119.87, 19.12]; TBABF₄ (0.571 g, 60%). I₃ [M+H] [130.48, 129.06, 126.13, 125.08, 122.77, 119.58, 31.17]; λₘᵦₓ (DMF) = 315 nm.

Preparation of 2,6-bis(4-carboxyquinolin-2-yl)pyridine, sodium salt (I)

In a 100 mL round-bottom flask were thoroughly mixed solid isatin (1g, 6.75mmol) and 2,6-diacetylpyridine (0.55g, 3.375 mmol). The flask was immersed in an ice bath and an ice-cold solution of 33% NaOH (3.75 g) was added with stirring. Stirring and warming was continued until the contents hardened (at this point the temperature was approximately 60°C). Ice water (4 mL) was then added to produce a fine purple/red slurry (with a metallic sheen). The suspension was cooled to 5°C and filtered, giving a purple/red solid crude product. The solid was washed with water (1 mL) and the colored impurities were removed by generous washing with acetone. The solid was allowed to dry, and was recrystallized from a minimum amount of hot water. Activated carbon was added to remove the remaining colored impurities. The crystallization was repeated, until no colored impurities remained, to afford 1 as colorless plates (0.544 g, 34 %). M.p. >300°C. IR (cm⁻¹): 3260 (w), 1602 (s), 1572 (s), 1549 (s), 1506 (m), 1428 (s), 1388 (vs), 1339 (s), 1251 (m), 1150 (m), 1090 (w), 1025 (w), 994 (w), 870 (w), 811 (m), 772 (s), 763 (s), 693(w), 666 (w).

Preparation of 2,2’-(pyridine-2,6-diyldi)quinoxaline-4-carboxylic acid (2)

The sodium salt 1 (0.5 g, 1.19 mmol) was dissolved in water (30 mL). The solution was neutralized with 10% HCl solution. The acid 2 is soluble in acidic solution, and care should be taken not to over-acidify; a pH of 7 is optimum. The free acid 2 is a colorless high melting point solid, and samples obtained at lower pH contain a yellow cast, probably due to the presence of the HCl salt. The solid was filtered, washed with water (3 x 10 mL) and air-dried, giving a light yellow solid (0.44 g, 97 %). M. p. > 300°C. IR (cm⁻¹): 3447 (w), 1696 (vs), 1588 (m), 1553 (m), 1506 (w), 1463 (w), 1415 (m), 1343 (m), 1278 (s), 1238 (s), 1151 (w), 1087 (m), 922 (m), 830 (m), 797 (m), 767 (vs), 737 (s), 669 (w), 686 (m). ¹H NMR (400 MHz, d₆-DMSO) δ 9.15 (s, 2H), 8.77 (dd, J = 7.8 Hz, 3.8 Hz, 4H), 8.29 (t, J = 7.8 Hz, 1H), 8.25 (d, J = 7.9 Hz, 2H), 7.91 (td, J = 1.3, 8.3 Hz, 2H), 7.78 (td, J = 1.3, 7.7 Hz, 2H). ¹³C NMR (101 MHz, d₆- DMSO) δ 168.09, 152.29, 154.81, 148.67, 139.48, 138.02, 130.89, 130.48, 129.06, 126.13, 125.08, 124.05, 121.99, 119.58, 31.17; λₘᵦₓ (DMF) = 315 nm.

Preparation of diethyl 2,2’-(pyridine-2,6-diyldi)quinoxaline-4-carboxylate (L₂)

In a round-bottom flask conc. H₂SO₄ (90 mL) was added carefully with vigorous stirring to EtOH (180 mL). After a few minutes of stirring 2 (0.884g, 2.1 mmol) was added and after 20h of refluxing the transparent solution was cooled to room temperature and diluted with 300 mL of ice. The reaction mixture was neutralized with NaOH (25%) solution to pH 8. The yellow precipitate was filtered off, washed with water (3 x 75 mL) and EtOH (10 mL) and air-dried to give L₂ (0.90 g, 90 %). IR (cm⁻¹): 3058 (w), 2798 (w), 2905 (w), 1736 (s), 1714 (s), 1587 (m), 1555 (m), 1508 (w), 1465 (w), 1451 (w), 1396 (w), 1374 (m), 1342 (w), 1260 (s), 1228 (vs), 1185 (s), 1152 (s), 1092 (m), 1036 (s), 1022 (s), 996 (m), 921 (w), 907 (w), 871 (w), 825 (m), 795 (m), 771 (s), 736 (m), 695 (w), 668 (w). IR (cm⁻¹): 3000 (w), 2950 (w), 2850 (w), 1670 (m), 1560 (s), 1410 (s), 1140 (w), 1025 (w), 958 (m), 905 (m), 837 (s), 810 (w), 762 (m), 738 (s), 635 (s), 570 (m), 530 (s), 471 (s). FTMS [M+H+] calculated for C₂₀H₂₀N₄O₄ (found): 478.1749 (478.1761); λₘᵦₓ (CHCl₃) = 312, 322 nm.

Preparation of RuL₂

To absolute ethanol (30 mL) in a 100 mL round-bottom flask were added RuCl₃·xH₂O (0.11 g (0.42 mmol) and L₁ (0.2 g, 0.42 mmol) under N₂. The mixture was heated at reflux for 20 h in the dark. After this time the reaction mixture was concentrated under vacuum and the green powder was filtered from the solution. The product was washed with EtOH (3 x 15 mL) and Et₂O, until the filtrate became transparent. The solid was air-dried to give the product RuL₂ (0.226 g, 79 %). IR (cm⁻¹): 3069 (w), 2997 (w), 1715 (vs), 1524 (s), 1476 (m), 1431 (m), 1372 (s), 1328 (m), 1255 (vs), 1231 (vs), 1198 (vs), 1152 (s), 1120 (s), 1027 (vs), 952 (w), 905 (w), 859 (m), 767 (vs), 675 (m), 630 (m).

Preparation of RU1

To a green suspension of RuL₂ (0.226 g, 0.316 mmol) in acetone (40 mL) was added AgBF₄ (0.184g, 0.947 mmol) and the mixture was heated
to reflux for 2 h. The resulting purple suspension was filtered to remove precipitated AgCl. The acetone was removed and the residue was dissolved in n-butanol (100 mL); to this was added L2 (0.151 g, 0.316 mmol). The solution was refluxed under N2 in the dark for 24 h. After cooling, the solvent was evaporated and the residue was dissolved in CH3OH (100 mL) and excess KPF6 (0.5 g) in water (50 mL) was added. The red precipitate was collected by filtration, washed with water and air-dried. The crude product (0.450 g) was redissolved in the minimum volume of CH3CN for column chromatography over silica, using CH3CN, water, and saturated aqueous KNO3 (10:1:0.5) as eluent. The pure complex after chromatography was dissolved in CH3OH and excess KPF6 solution was added. The dark purple precipitate was collected, dried and recrystallized from a minimum amount of CH3OH/toluene to afford dark purple crystals (0.224 g, 53%). IR (cm−1): 3097 (w), 1579 (s), 1536 (s), 1436 (m), 1372 (s), 1263 (s), 1209 (m), 1153 (m), 1214 (m), 1208 (m), 835 (vs), 773 (s), 669 (m), 622 (m). 1H NMR (400 MHz, CDCl3) ð 9.21 (d, J = 8.2 Hz, 2H), 9.08 (d, J = 8.2 Hz, 2H), 8.92 (t, J = 8.6 Hz, 2H), 8.68 (s, 2H), 8.43 (d, J = 8.6 Hz, 2H), 8.30 (s, 2H), 7.90 (d, J = 8.4 Hz, 7H), 7.60 (td, J = 1.1, 8.2 Hz, 2H), 7.53 (td, J = 1.1, 8.2 Hz, 2H), 7.28 (td, J = 1.5, 8.6 Hz, 2H), 7.21 (td, J = 1.4, 8.6 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 6.41 (d, J = 8.4 Hz, 2H), 4.45 (q, J = 7.1 Hz, 4H), 2.71 (s, 6H), 1.40 (t, J = 7.1 Hz, 6H). 13C NMR (101 MHz, CD2CN) ð 190.61, 165.17, 161.03, 160.39, 159.49, 159.35, 151.49, 149.55, 139.75, 132.90, 132.58, 131.12, 130.10, 129.67, 127.61, 129.66, 125.33, 121.78, 120.72, 63.83, 49.18, 81.91. FTMS [M-PF6]+ calculated for C54H42Fe2NO6P3Ru2 (found) 1085.9592 (1084.9838).

X-ray crystallography

Data for L1 and L2 were measured on Agilent Technologies diffractometers with MoKα radiation, while the very small crystals of RU1 were examined with synchrotron radiation at beamline I19 of Diamond Light Source. Full details are given in the Supporting Information. CCDC reference numbers are 1035746–1035748.

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Keywords: ruthenium, complex, polypryridine, electrochemistry, X-ray crystallography, DFT calculations


[18] DFT calculations were also performed up to the addition of five electrons to the complex. No further insightful information was obtained from the calculations and addition of electrons appeared to be ligand based. It should be noted that there are many deficiencies in using DFT calculations to map orbital analysis to the redox activity. No account is taken of reorganisation energies following electron additions and reordering of orbitals. Calculations were also only performed at the singlet and doublet levels and any heavy atom effect for the complexes was ignored.

The two ligands diethyl 2,2’-(pyridine-2,6-diyl)bis(quinolone-4-carboxylate) (L₂) and 2,6-bis(4-methylquinolin-2-yl)pyridine (L₁) were used to prepare the homoleptic [Ru(L₁)₂](PF₆)₂ (RU1) and heteroleptic [Ru(L₁)(L₂)](PF₆)₂ (RU2) complexes. Electrochemistry experiments showed that the complexes can hold up to five electrons reversibly.