Synthesis of three series of ruthenium tris-diimine complexes containing acridine-based \( \pi \)-extended ligands using an efficient “chemistry on the complex” approach.

Supplementary information

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**General information**

Chemicals and solvents (analytical grade) were purchased from Sigma-Aldrich, Alfa Aesar or Fisher Scientific and used without further purification. Silica gel 60 was purchased from Sigma-Aldrich. Silica gel 100 C18 – Reversed phase was purchased from Fluka. Some purification were carried out on a puriflash 450 using prepacked columns (Interchim). 2-ethoxy-5,6-diaminoacridone was prepared according to a slightly modified (reaction at 60°C instead of room temperature) previously reported procedure\(^1\). The complexes \([\text{Ru(bpy)}_2(\text{phendione})](\text{PF}_6)_2\), \([\text{Ru(phen)}_2(\text{phendione})](\text{PF}_6)_2\), \([\text{Ru(TAP)}_2(\text{phendione})](\text{PF}_6)_2\), \([\text{Ru(phen)}_2(\text{phendione})](\text{PF}_6)_2\), \([\text{Ru(TAP)}_2(\text{phendione})](\text{PF}_6)_2\), \([\text{Ru(TAP)}_2(\text{phendione})](\text{PF}_6)_2\), and \([\text{Ru(TAP)}_2(\text{phendione})](\text{PF}_6)_2\) were prepared according to reported procedures.

NMR spectra were recorded at room temperature in 5 mm tubes on a Bruker AC 300 or Avance 400 MHz spectrometer equipped with a QNP probehead and on a Bruker Avance 300 equipped with a BBO probehead, operating respectively at 300.0 MHz, 400.0 MHz and 500.0 MHz. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual non-deuterated solvent relative to Me$_4$Si (δ = 1.94 ppm for acetonitrile). Standard abbreviations for multiplicity were used as follows: s = singlet; d = doublet; t = triplet; m = multiplet.

UV-vis spectra were recorded with a Cary 60 UV-vis (Agilent Technologies) spectrophotometer or a PerkinElmer Lambda 40 UV-vis spectrophotometer in quartz Schlenk cells. High resolution mass spectrometry (HRMS) was carried out on a Bruker UHR-Q-TOF MaXis-ETD (Time of Flight) mass spectrometer using ElectroSpray Ionisation (ESI) in Institut de Chimie Organique et Analytique (CBM-ICOA) in Orleans (France) and MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer at UMONS (Belgium). The MALDI source is constituted of a Nd-YAG laser, operating at 355 nm with a maximum pulse energy of 104.1 μJ delivered to the sample at 50 Hz repeating rate. All samples were prepared using α-cyano-4-hydroxycinnamic acid as the matrix (saturated solution in acetonitrile, CH$_3$CN).
Synthetic procedures

Complex 1 – [Ru\(^{II}\)(bpy)\(_2\)(oxo-dpqp)](PF\(_6\))\(_2\)

[Ru\(^{II}\)(bpy)\(_2\)(phendione)](PF\(_6\))\(_2\) (0.244 g, 2.67x10\(^{-4}\) mol) and 5,6-diamino-2-ethoxyacridin-9-one (0.078 g, 2.90x10\(^{-4}\) mol) were loaded in a Schlenk tube, purged with argon and dissolved in a mixture ethanol (EtOH)/CH\(_3\)CN (7/7 mL). The solution was then heated in microwave conditions at 90°C for 45 minutes. The mixture was concentrated and the product was precipitated by adding diethyl ether (Et\(_2\)O) to the residue. The solid was filtered, washed with Et\(_2\)O and dried to afford 290 mg of crude [Ru\(^{II}\)(bpy)\(_2\)(oxo-dpqp)](PF\(_6\))\(_2\) as an orange solid in 95% yield. The crude product was pure enough for further synthesis.

\(^1\)H NMR (CD\(_3\)CN, 25°C, 300 MHz, 5x10\(^{-3}\) mol x L\(^{-1}\)): δ 10.59 (br s, 1H), 9.92 (d, J = 8.1 Hz, 1H), 9.08 (d, J = 5.1 Hz, 1H), 8.64 (d, J = 8.2 Hz, 2H), 8.58 (d, J = 8.1 Hz, 1H), 8.54 (d, J = 8.3 Hz, 1H), 8.38 (br d, J = 5.4 Hz, 1H), 8.31 (d, J = 5.1 Hz, 1H), 8.24 (dd, J = 5.3 and 1.0 Hz, 1H), 8.18 (t, J = 8.1 Hz, 1H), 8.17 (t, J = 8.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 8.02 (td, J = 8.3 and 1.0 Hz, 1H), 7.99 (dd, J = 8.1 and 5.1 Hz, 1H), 7.92 (d, J = 5.4 Hz, 1H), 7.89 (d, J = 4.1 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.76 (dd, J = 8.3 and 5.3 Hz, 1H), 7.71 (d, J = 5.5 Hz, 1H), 7.60-7.46 (m, 3H), 7.26 (td, J = 5.5 and 1.0 Hz, 1H), 7.09 (dd, J = 9.2 and 2.5 Hz, 1H), 6.32 (s, 1H), 3.38-3.24 (m, 1H), 3.14-2.99 (m, 1H), 1.16 (t, J = 6.9 Hz, 3H) ppm.

\(^{13}\)C NMR (CD\(_3\)CN, 25°C, 75 MHz, 2.3x10\(^{-2}\) mol x L\(^{-1}\)): δ 174.68, 158.19, 158.04, 157.99, 157.97, 157.90, 157.44, 155.30, 154.62, 153.19, 153.15, 152.98, 152.86, 151.27, 150.78, 144.73, 141.17, 139.21, 139.06, 137.71, 136.90, 136.27, 135.44, 134.44, 133.90, 133.76, 130.78, 130.52, 129.77, 129.11, 128.83, 128.73, 128.62, 128.12, 127.81, 125.45, 125.42, 125.30, 125.18, 124.50, 123.75, 121.46, 121.30, 116.88, 104.55, 63.62, 14.64 ppm. UV-vis (CH\(_3\)CN): \(\lambda_{max}\) (ε): 248 nm (58500 L x mol\(^{-1}\) x cm\(^{-1}\)), 285 (96000), 301 (sh 70500), 338 (32500), 413 (20500), 448 (20200), 519 (sh 8500). HRMS (ESI\(^{+}\)): calcd for C\(_{47}\)H\(_{31}\)N\(_6\)O\(_2\)\(^{102}\)Ru: m/z 428.5901, found: m/z 428.5903 ([M]\(^{+2}\)); calcd for C\(_{48}\)H\(_{55}\)N\(_{18}\)O\(_{10}\)\(^{102}\)Ru\(_2\): m/z 571.1182, found: m/z 571.1186 ([2M - H]\(^{+3}\)). Elem. An.: calcd for C\(_{47}\)H\(_{31}\)F\(_3\)N\(_6\)O\(_2\)P\(_2\)Ru • 0.2 NH\(_4\)PF\(_6\): N 10.93, C 47.86, H 2.89; found: N 10.61, C 47.41, H 2.98.
Complex 1(Cl) – [Ru\textsuperscript{II}(bpy)(oxo-dpqp)](Cl)\textsubscript{2}

\[
\text{[Ru}^{\text{II}}(\text{bpy})_{2}(\text{oxo-dpqp})]^{2+} \text{ (0.04 g, 3.5x10}^{-5}\text{ mol)}
\]
was dissolved in a mixture methanol (MeOH)/CH\textsubscript{3}CN (1/1 mL). The complex solution was deposited on a small pad of Dowex previously packed with MeOH. The column was slowly eluted with MeOH until the solution was colorless. The solution collected was concentrated and the product was precipitated by adding Et\textsubscript{2}O to the residue. The solid was filtered, washed with Et\textsubscript{2}O and dried to afford 32 mg of [Ru\textsuperscript{II}(bpy)\textsubscript{2}(oxo-dpqp)](Cl)\textsubscript{2} as an orange solid in quantitative yield.

\textsuperscript{1}H NMR (CD\textsubscript{3}CN + 10% D\textsubscript{2}O, 25°C, 300 MHz, 10\textsuperscript{-3} mol x L\textsuperscript{-1}): \(\delta\) 10.14 (d, \(J = 7.3\) Hz, 1H), 9.36 (d, \(J = 8.2\) Hz, 1H), 8.65-8.59 (m, 2H), 8.59 (d, \(J = 8.3\) Hz, 1H), 8.54 (d, \(J = 8.0\) Hz, 1H), 8.48 (d, \(J = 9.3\) Hz, 1H), 8.27 (dd, \(J = 5.0\) and 0.9 Hz, 1H), 8.22 (dd, \(J = 5.4\) and 1.2 Hz, 1H), 8.18-8.05 (m, 5H), 8.01 (br d, \(J = 8.2\) Hz, 1H), 8.02-7.97 (m, 1H), 7.94 (d, \(J = 9.3\) Hz, 1H), 7.89 (br dd, \(J = 5.0\) and 0.9 Hz, 1H), 7.86 (br d, \(J = 6.7\) Hz, 1H), 7.83 (dd, \(J = 8.3\) and 5.4 Hz, 1H), 7.68 (d, \(J = 5.7\) Hz, 1H), 7.54-7.46 (syst AB, 2H), 7.40 (m, 1H), 7.33-7.27 (m, 1H), 7.27-7.21 (m, 1H), 7.02 (br s, 1H), 3.76-3.63 (m, 1H), 3.61-3.48 (m, 1H), 1.26 (t, \(J = 6.9\) Hz, 3H) ppm.

UV-vis (H\textsubscript{2}O): \(\lambda_{\text{max}}(\varepsilon)\): 253 nm (49100 L x mol\textsuperscript{-1} x cm\textsuperscript{-1}), 284 (75500), 305 (sh 47000), 338 (sh 23500), 422 (sh 16500), 446 (17700).

Complex \[\text{Zn}^{\text{II}}(\text{oxo-dpqp})]\(\text{BF}_4\)\textsubscript{2}

Oxo-dpqp (0.19 mg, 4.28x10\textsuperscript{-7} mol) was suspended in CH\textsubscript{3}CN (5 mL). Zinc(II) tetrafluoroborate Zn(BF\textsubscript{4})\textsubscript{2} (10.2 mg, 4.27x10\textsuperscript{-5} mol, 100 eq.) was solubilised in CH\textsubscript{3}CN (5 mL) and added to the suspension. The mixture was stirred overnight in a sealed flask in the dark. After filtration, the solution was directly used for UV-vis absorption spectroscopy measurement and ESI MS characterization.

\textbf{UV-vis (CH\textsubscript{3}CN):} \(\lambda_{\text{max}}(\varepsilon)\): 247 nm (35300 L x mol\textsuperscript{-1} x cm\textsuperscript{-1}), 277 (42200), 302 (37250), 343 (sh 21500), 357 (22500), 409 (5700), 486 (br 5100).

\textbf{ESI MS:} \(m/z\) 526.2 [M – 2 CH\textsubscript{3}CN + F]\textsuperscript{-} (the fluoride coming from partial decomposition of BF\textsubscript{4} anions), \(m/z\) 294.5 [M]\textsuperscript{2+}, \(m/z\) 253.5 [M – 2 CH\textsubscript{3}CN]\textsuperscript{2+}. 
Complex 2 - [Ru^{II}(bpy)_2(Br-dpqp)](PF_6)_2

[Ru^{II}(bpy)_2(oxo-dpqp)](PF_6)_2 1 (0.155 g, 1.35x10^{-4} mol) was loaded in an argon purged round bottom flask and dissolved in dry N,N-dimethylformamide DMF (6 mL). The mixture was cooled in an ice bath and phosphorus tribromide PBr_3 (0.08mL, 8.42x10^{-4} mol, 6.4 eq.) was slowly added by syringe. The cooled solution was then stirred for one hour and left to warm to room temperature over one hour under argon (the solution become thick and need sometimes adding of more DMF to allow the stirring). The mixture was poured onto ice and neutralized by adding ammonia. The product was precipitated by adding ammonium hexafluorophosphate (NH₄PF₆), filtered, washed with H₂O and dried. The solid solubilised in CH₃CN was purified by column chromatography on silica gel using a gradient of aqueous 10% KNO₃ solution in CH₃CN as eluent (0 to 20%). The product was precipitated by adding NH₄PF₆ in the aqueous residue, filtered, washed with H₂O and dried. The solid was solubilised in a small amount of CH₃CN and precipitated by adding Et₂O. Filtration, washings with Et₂O and drying afforded 105 mg of pure [Ru^{II}(bpy)_2(Br-dpqp)](PF_6)_2 2 as an orange solid in 64% yield.

¹H NMR (CD₃CN, 25°C, 300 MHz, 2.5x10^{-3} mol x L⁻¹): δ 9.91 (d, J = 8.0 Hz, 1H), 9.66 (d, J = 8.5 Hz, 1H), 8.77 (d, J = 9.6 Hz, 1H), 8.58 (d, J = 8.9 Hz, 2H), 8.55 (d, J = 9.0 Hz, 2H), 8.38 (d, J = 9.4 Hz, 1H), 8.28 (d, J = 9.6 Hz, 1H), 8.25 (t, J = 5.1 Hz, 2H), 8.14 (t, J = 8.0 Hz, 2H), 8.04 (t, J = 6.6 Hz, 2H), 7.95-7.89 (m, 1H), 7.89 (d, J = 5.1 Hz, 2H), 7.77 (t, J = 5.1 Hz, 2H), 7.65 (s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.54-7.45 (m, 2H), 7.29 (t, J = 6.6 Hz, 2H), 4.27 (q, J = 6.9 Hz, 1H), 4.26 (q, J = 6.9 Hz, 1H), 1.49 (t, J = 6.9 Hz, 3H) ppm. ¹³C NMR (CD₃CN, 25°C, 75 MHz, 2.7x10⁻² mol x L⁻¹): δ 159.90, 158.17, 158.09, 154.85, 154.72, 153.39, 153.10, 153.02, 152.97, 150.62, 150.33, 145.25, 144.57, 143.53, 142.26, 139.71, 139.20, 138.81, 134.45, 133.82, 133.22, 133.03, 131.43, 130.49, 129.38, 128.97, 128.82, 128.79, 128.38, 128.28, 126.97, 125.94, 125.48, 105.03, 64.96, 14.70 ppm. UV-vis (CH₃CN): λ_max (ε): 241 nm (46000 L x mol⁻¹ x cm⁻¹), 249 (sh 45400), 283 (75000), 343 (47600), 393 (sh 18200), 430 (21500), 443 (sh 20600). HRMS (ESI⁺): ccaled for C₄₇H₃₂BrN₉O₁₀²Ru: m/z 459.5477, found: m/z 459.5480 ([M]²⁺); calted for C₄₇H₃₂BrN₉O₁₀²Ru : m/z 306.7009, found: m/z 306.7010 ([M + H]³⁺); calced for C₄₇H₃₂BrF₁₂N₉O₁₀²Ru: 1064.0600, found: 1064.0597 ([M + PF₆]⁺). Elem. An.: calced for C₄₇H₃₂BrF₁₂N₉O₁₀²Ru • 0.7 NH₄PF₆: N 10.26, C 42.64, H 2.65; found: N 10.05, C 42.29, H 2.67.
Complex 3 - [Ru\textsuperscript{II}(bpy)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2}

Crude [Ru\textsuperscript{II}(bpy)\textsubscript{2}(oxo-dpqp)](PF\textsubscript{6})\textsubscript{2} \textit{I} (0.28 g, 2.40x10\textsuperscript{-4} mol) was loaded in a round bottom flask and dissolved in phosphorus oxychloride (POCl\textsubscript{3}, 6 mL). The mixture was heated to 120°C overnight. The solution was cooled to room temperature and poured very slowly and carefully onto ice. The acidic solution was then neutralized with aqueous potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) until neutral pH. CH\textsubscript{3}CN was added until the solution was clear. The product was then precipitated by adding aqueous NH\textsubscript{4}PF\textsubscript{6}, filtered, washed with H\textsubscript{2}O and dried. The solid was solubilised in a small amount of acetonitrile and reprecipitated by adding Et\textsubscript{2}O. Filtration, washings with Et\textsubscript{2}O and drying afforded 270 mg of pure [Ru\textsuperscript{II}(bpy)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2} \textit{II} as an orange solid in 95% yield.

\textsuperscript{1}H NMR (CD\textsubscript{3}CN, 25°C, 400 MHz, 6x10\textsuperscript{-3} mol x L\textsuperscript{-1}): \(\delta\) 9.78 (d, \(J = 8.0\) Hz, 1H), 9.51 (d, \(J = 7.9\) Hz, 1H), 8.69 (d, \(J = 9.7\) Hz, 1H), 8.59 (d, \(J = 9.8\) Hz, 2H), 8.56 (d, \(J = 9.8\) Hz, 2H), 8.26 (d, \(J = 9.8\) Hz, 1H), 8.26-8.23 (m, 1H), 8.21 (dd, \(J = 5.4\) and 1.2 Hz, 1H), 8.18 (d, \(J = 9.7\) Hz, 1H), 8.15 (t, \(J = 8.2\) Hz, 1H), 8.05 (td, \(J = 8.0\) and 1.2 Hz, 1H), 8.04 (td, \(J = 7.9\) and 1.2 Hz, 1H), 7.95 (dd, \(J = 8.2\) and 5.4 Hz, 1H), 7.89 (d, \(J = 5.4\) Hz, 2H), 7.86-7.81 (m, 2H), 7.80 (td, \(J = 7.9\) and 1.2 Hz, 1H), 7.76-7.72 (m, 2H), 4.18 (q, \(J = 6.9\) Hz, 1H), 4.16 (q, \(J = 6.9\) Hz, 1H), 1.43 (t, \(J = 6.9\) Hz, 3H) ppm.

\textsuperscript{13}C NMR (CD\textsubscript{3}CN, 25°C, 75 MHz, 2.5x10\textsuperscript{-2} mol x L\textsuperscript{-1}): \(\delta\) 159.83, 158.15, 154.83, 154.77, 153.45, 153.10, 153.00, 150.71, 150.43, 145.52, 144.90, 143.69, 142.53, 139.93, 139.16, 139.07, 138.96, 134.36, 133.90, 133.05, 131.44, 130.59, 130.16, 129.16, 128.78, 128.36, 127.93, 127.34, 126.31, 125.46, 125.09, 102.22, 65.17, 14.73 ppm.

UV-vis (CH\textsubscript{3}CN): \(\lambda_{\text{max}}\) (\(\varepsilon\)): 243 nm (60250 L x mol\textsuperscript{-1} x cm\textsuperscript{-1}), 253 (sh 58150), 284 (94950), 344 (58500), 361 (sh 33400), 390 (21200), 431 (25350), 452 (sh 23050).

HRMS (ESI\textsuperscript{+}): caleld for C\textsubscript{47}H\textsubscript{33}ClN\textsubscript{9}O\textsubscript{10}Ru: m/z 292.0511, found: m/z 292.0514 ([M + H]\textsuperscript{3+}); caleld for C\textsubscript{47}H\textsubscript{32}ClN\textsubscript{9}O\textsubscript{10}Ru: m/z 437.5730, found: m/z 437.5733 ([M]\textsuperscript{2+}); caleld for C\textsubscript{47}H\textsubscript{32}ClF\textsubscript{6}N\textsubscript{9}O\textsubscript{10}Ru: 1020.1107, found: 1020.1095 ([M + PF\textsubscript{6}]\textsuperscript{+}).

Complex 4 - [Ru\textsuperscript{II}(bpy)\textsubscript{2}(DMEA-dpqp)](PF\textsubscript{6})\textsubscript{2}

[Ru\textsuperscript{II}(bpy)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2} \textit{II} (0.15 g, 1.22x10\textsuperscript{-4} mol) was loaded in a microwave oven reactor and dissolved in DMF (4 mL) with 2,2’-dimethoxyethylamine DMEA (0.3 mL, 2.75x10\textsuperscript{-3} mol, 22.5 eq.). The mixture was heated at 110°C for 1.5 hours in a microwave oven. After cooling of the reaction, a small amount of aqueous K\textsubscript{2}CO\textsubscript{3}
was added to neutralize the mixture. Aqueous NH₄PF₆ was added to precipitate the product. The solid was filtered, washed with H₂O and dried. The solid was then solubilised with CH₃CN through the fritted glass funnel, the solvent was concentrated and Et₂O was added to precipitate again the product. Filtration, washings with Et₂O and drying afforded 145 mg of [Ru(II)(bpy)₂(DMEA-dpqp)](PF₆)₂ as a red solid in 91% yield.

\(^1\)H NMR (CD₃CN, 25°C, 400 MHz, 5x10⁻³ mol x L⁻¹): \(\delta\) 9.42 (d, \(J = 8.1\) Hz, 1H), 9.31 (d, \(J = 8.0\) Hz, 1H), 8.62 (d, \(J = 9.7\) Hz, 1H), 8.60 (d, \(J = 8.4\) Hz, 2H), 8.56 (d, \(J = 8.1\) Hz, 1H), 8.52 (d, \(J = 8.1\) Hz, 1H), 8.18-8.07 (m, 6H), 7.92 (d, \(J = 8.1\) and 5.4 Hz, 1H), 7.87 (d, \(J = 8.1\) Hz, 1H), 7.85 (d, \(J = 8.0\) Hz, 1H), 7.81 (dd, \(J = 8.9\) and 1.9 Hz, 1H), 7.78-7.70 (m, 5H), 7.58-7.47 (m, 5H), 7.41 (dd, \(J = 8.1\) and 5.4 Hz, 1H), 7.28-7.23 (m, 1H), 5.61 (br s, 1H), 4.63 (t, \(J = 5.2\) Hz, 1H), 4.26 (q, \(J = 6.9\) Hz, 2H), 3.89 (t, \(J = 5.2\) Hz, 1H), 3.38 (s, 6H), 1.48 (t, \(J = 6.9\) Hz, 3H) ppm. \(^{13}\)C NMR (CD₃CN, 25°C, 75 MHz, 2x10⁻² mol x L⁻¹): \(\delta\) 158.24, 158.21, 158.13, 157.94, 157.83, 154.39, 154.21, 154.13, 153.09, 152.97, 152.88, 151.82, 150.39, 150.09, 146.55, 139.58, 139.27, 139.08, 138.98, 137.99, 133.58, 132.55, 131.48, 131.20, 130.71, 129.21, 128.74, 128.69, 128.61, 128.40, 127.75, 127.41, 125.55, 125.47, 125.42, 125.30, 125.10, 124.92, 124.25, 122.59, 117.58, 104.80, 102.03, 65.03, 55.28, 55.15, 53.10, 14.93 ppm. UV-vis (CH₃CN): \(\lambda_{\text{max}}\) (ε): 237 nm (47840 L x mol⁻¹ x cm⁻¹), 255 (61400), 287 (86600), 329 (42700), 352 (34700), 427 (sh 21800), 462 (23500). HRMS (ESI⁺): calcd for C₅₀H₃₉N₁₀O₁₂Ru: m/z 304.4099, found: m/z 304.4102 ([M - OCH₃]⁺); calcd for C₅₁H₄₃N₁₀O₁₂Ru: m/z 315.0853, found: m/z 315.0856 ([M + H]⁺); calcd for C₅₁H₄₂N₁₀O₃₁₂Ru: 472.1244, found: 472.1247 ([M]²⁺).

Complex 5 - [Ru(II)(bpy)₂(dpqpp)](PF₆)₂

NH₄PF₆ was then added to precipitate the product. The solid was filtered, washed with H₂O and dried. The crude product was purified by column chromatography on silica gel using a gradient of 10% aqueous KNO₃ solution in CH₃CN as eluent. The product was precipitated by adding NH₄PF₆ in the aqueous residue, filtered, washed with H₂O and dried. The solid was then solubilised with CH₃CN through the frit funnel, the solvent was concentrated and Et₂O was added to precipitate again the product. Filtration, washings with Et₂O and drying afforded 70 mg of [Ru(II)(bpy)₂(dpqpp)](PF₆)₂ as a dark red solid in 73% yield.
$^1$H NMR (CD$_3$CN, 25°C, 300 MHz, $2.5 \times 10^{-3}$ mol x L$^{-1}$): $\delta$ 9.86 (d, $J = 8.1$ Hz, 1H), 9.39 (d, $J = 8.5$ Hz, 1H), 8.60 (d, $J = 7.9$ Hz, 2H), 8.58 (d, $J = 7.6$ Hz, 2H), 8.52 (d, $J = 9.1$ Hz, 1H), 8.20 (d, $J = 5.5$ Hz, 2H), 8.19-8.12 (m, 2H), 8.07 (tt, $J = 7.9$ and 1.6 Hz, 2H), 7.94-7.83 (m, 2H and 2H), 7.82 (d, $J = 5.3$ Hz, 1H), 7.58 (d, $J = 9.1$ Hz, 1H), 7.58 (d, $J = 4.6$ Hz, 1H), 7.55-7.47 (m, 2H), 7.39 (dd, syst AB, $J = 7.6$ and 1.1 Hz, 1H), 7.19-7.10 (m, 1H), 6.95 (br d, $J = 8.4$ Hz, 1H), 6.67 (d, $J = 6.3$ Hz, 1H), 3.87 (q, $J = 6.9$ Hz, 1H), 3.85 (q, $J = 6.9$ Hz, 1H), 1.21 (t, $J = 6.9$ Hz, 3H) ppm.

$^{13}$C NMR (CD$_3$CN, 25°C, 100 MHz, $10^{-2}$ mol x L$^{-1}$): $\delta$ 158.20, 154.89, 154.51, 153.05, 152.97, 151.49, 151.20, 150.66, 145.35, 144.87, 141.19, 139.14, 138.18, 138.11, 135.11, 134.21, 133.35, 132.74, 131.22, 131.16, 129.04, 128.78, 128.69, 128.65, 128.29, 128.16, 125.44, 122.40, 120.44, 111.43, 64.64, 15.05 ppm.

UV-vis (CH$_3$CN): $\lambda_{\text{max}}$ ($\varepsilon$): 240 nm (sh 51900 L x mol$^{-1}$ x cm$^{-1}$), 255 (sh 58700), 287 (112700), 365 (32700), 380 (32000), 455 (23750).

HRMS (ESI$^+$): calcd for C$_{49}$H$_{35}$N$_{10}$O$_{102}$Ru: m/z 293.7345, found: m/z 293.7348 ([M + H]$^+$3+); calcd for C$_{49}$H$_{34}$N$_{10}$O$_{102}$Ru: m/z 440.0981, found: m/z 440.0976 ([M]$^2+$).

Complex 6 - [Ru$^{II}$](phen)$_2$(oxo-dpqp)](PF$_6$)$_2$ (procedure modified compared to already reported method)$^5$

[Ru$^{II}$](phen)$_2$phendione](PF$_6$)$_2$ (192 mg, 2x10$^{-4}$ mol) and 5,6-diamino-2-ethoxyacridin-9-one were dissolved in 6 mL of CH$_3$CN/EtOH (3/1). The mixture was heated under argon upon microwave irradiation at 90 °C for 60 minutes. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel using CH$_3$CN/EtOAc (70:30 to 100:0) as eluent. [Ru$^{II}$](phen)$_2$(oxo-dpqp)](PF$_6$)$_2$ 6 (177 mg) was obtained as an orange solid with 74% yield.

Characterizations are in accordance to previously published.$^5$

$^1$H NMR (CD$_3$CN, 25 °C, 400 MHz, $10^{-2}$ mol x L$^{-1}$): $\delta$ 11.11 (s, 1H), 9.80 (d, $J = 7.9$ Hz, 1H), 8.98 (br s, 1H), 8.88-8.82 (m, 2H), 8.68-8.62 (m, 3H), 8.36 (syst AB, 2H), 8.33–8.26 (m, 2H), 8.22 (d, $J = 5.0$ Hz, 1H), 8.18 (d, $J = 4.6$ Hz, 1H), 8.15 (d, $J = 4.9$ Hz, 1H), 8.08-8.01 (m, 3H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.80 (dd, $J = 7.4$ Hz and 5.6 Hz, 1H), 7.72–7.55 (m, 6H), 6.54 (br s, 1H), 5.76 (br s, 1H), 2.63 (m, 2H), 0.48 (m, 3H) ppm. $^{13}$C NMR (CD$_3$CN, 25°C, 125 MHz, $10^{-2}$mol x L$^{-1}$): $\delta$ 174.61, 155.83, 155.10, 155.00, 154.93, 154.19, 154.15, 153.94, 151.60, 151.04, 148.81, 148.74, 148.70, 148.60, 144.88, 141.07, 138.07, 137.99, 137.96, 137.77, 136.63, 135.41, 134.76, 134.14, 133.79, 132.05, 132.00, 131.97, 130.94, 130.44, 129.87, 129.26, 129.10, 129.07, 127.98, 127.56, 127.51, 127.05, 127.02, 124.22, 123.59, 121.76, 121.34, 117.00, 104.05, 62.98, 14.31 ppm. UV-vis (CH$_3$CN): $\lambda_{\text{max}}$
(ε): 265 nm (sh 85000 L x mol⁻¹ x cm⁻¹), 340 (sh 23000), 353 (26000), 416 (19000), 445 (18000), 514 (800). **HRMS (MALDI-TOF):** calcd for C₅₁H₃₃N₉O₂⁹⁶Ru: m/z 899.1833, found: m/z 899.1857 ([M⁺]).

At UMONS, we perform exact mass measurements on the lightest Ru isotope (i.e. ⁹⁶Ru) to avoid isobaric contaminations due to isotope signal overlapping. It is also important to remind that, when measuring MALDI-ToF mass spectra of Ru complexes, singly charged ions are detected and mostly correspond to radical cations generated by one electron reduction upon MALDI.

**Complex 7 - [Ru⁰(phen)₂(Cl-dpqp)](PF₆)₂**

[Ru⁰(phen)₂(oxo-dpqp)](PF₆)₂ (120 mg, 10⁻⁴ mol) was carefully added to 3 mL of POCl₃ and the mixture was heated to 90 °C overnight. The reaction mixture was then cooled to room temperature and the mixture was poured dropwise onto ice. The solution was neutralized with NaOH (1M) and the solid was filtered and washed with H₂O. It was redissolved in a minimum amount of CH₃CN and precipitated with Et₂O. [Ru⁰(phen)₂(Cl-dpqp)](PF₆)₂ 7 (114 mg) was obtained as an orange solid with 94% yield.

**¹H NMR (CD₃CN, 25 °C, 400 MHz, 5x10⁻³ mol x L⁻¹):** δ 9.86 (d, 1H), 9.61 (d, J = 8.2 Hz, 1H), 8.77 (d, J = 9.6 Hz, 1H), 8.65 (d, J = 8.3 Hz, 4H), 8.35 (d, J = 8.7 Hz, 1H), 8.29 (m, 7H), 8.18 (m, 2H), 8.05 (m, 2H), 7.87 (m, 1H), 7.77 (m, 1H), 7.65 (m, 6H), 4.23 (m, 2H), 1.27 (m, 3H) ppm. **¹³C NMR (CD₃CN, 25°C, 125 MHz, 5x10⁻³ mol x L⁻¹):** δ 160.39, 155.40, 155.24, 154.30, 154.20, 154.02, 151.45, 151.28, 148.92, 148.84, 146.34, 145.73, 140.83, 139.84, 139.53, 138.02, 137.95, 134.65, 134.44, 133.44, 132.11, 132.09, 131.79, 131.08, 130.52, 129.51, 129.14, 128.18, 128.06, 127.05, 126.97, 125.72, 102.60, 65.47, 14.82 ppm. **UV-vis (CH₃CN):** λ_max (ε): 226 nm (52000 L x mol⁻¹ x cm⁻¹), 265 (73000), 303 (sh 29000), 347 (32000), 392 (17900), 434 (18500). **HRMS (MALDI-TOF):** calcd for C₅₁H₃₃ClN₉O₂⁹⁶Ru: m/z 917.1494, found: m/z 917.1497 ([M⁺]).
Complex 8 - [Ru\textsuperscript{II}(phen)\textsubscript{2}(DMEA-dpqp)](PF\textsubscript{6})\textsubscript{2}

[\textit{Ru}\textsuperscript{II}(phen)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2} (100 mg, 8\times10^{-5} mol) was dissolved in anhydrous DMF (4 mL) with DMEA (0.17 mL, 1.6\times10^{-3} mol, 20 eq.). The mixture was heated upon microwave irradiation at 130 °C for 90 minutes. The solid was then precipitated upon addition of a saturated aqueous solution of KPF\textsubscript{6}, filtered and washed with H\textsubscript{2}O. The product was purified by column chromatography on C\textsubscript{18} with a CH\textsubscript{3}CN/H\textsubscript{2}O gradient (20% to 40%). [Ru\textsuperscript{II}(phen)\textsubscript{2}(DMEA-dpqp)](PF\textsubscript{6})\textsubscript{2} 8 (87 mg) was obtained as a red solid with 85% yield.

\textbf{1H NMR (CD\textsubscript{3}CN, 25 °C, 400 MHz, 5\times10^{-3} mol x L\textsuperscript{-1})}: δ 13.98 (br s, 1H), 10.17 (d, \textit{J} = 8.0, 1H), 9.68 (d, \textit{J} = 7.9 Hz, 1H), 8.73-8.67 (m, 4H), 8.33 (m, 6H), 8.28-8.26 (m, 2H), 8.23 (d, \textit{J} = 9.7 Hz, 1H), 8.18 (d, \textit{J} = 9.7 Hz, 1H), 7.93-7.90 (m, 3H), 7.78-7.70 (m, 4H), 7.49 (m, 1H), 7.16 (br s, 1H), 4.95 (t, \textit{J} = 4.6 Hz, 1H), 4.34 (m, 2H), 4.01 (m, 2H), 3.57 (s, 6H), 1.19 (m, 3H) ppm.

\textbf{13C NMR (CD\textsubscript{3}CN, 25°C, 125 MHz, 5\times10^{-3} mol x L\textsuperscript{-1})}: δ 157.79, 157.03, 156.28, 155.97, 154.25, 154.16, 154.04, 153.94, 152.18, 151.54, 148.86, 148.82, 148.75, 148.74, 145.18, 145.04, 143.47, 143.45, 132.12, 132.09, 132.08, 131.47, 131.02, 130.65, 129.14, 129.11, 129.07, 129.04, 128.47, 128.45, 128.19, 126.99, 124.48, 123.47, 117.70, 111.40, 103.95, 103.38, 65.59, 55.87, 51.73, 48.54, 14.56 ppm.

\textbf{UV-vis (CH\textsubscript{3}CN)}: \textit{\lambda}_{\text{max}} (\varepsilon): 223 nm (57000 L x mol\textsuperscript{-1} x cm\textsuperscript{-1}), 265 (69000), 300 (sh 32000), 330 (30000), 347 (30000), 423 (21000).

\textbf{HRMS (MALDI-TOF)}: calcd for C\textsubscript{55}H\textsubscript{42}N\textsubscript{10}O\textsubscript{396Ru: m/z 986.2517, found: m/z 986.2520 ([M]+).

The product was purified by column chromatography on C\textsubscript{18} with a CH\textsubscript{3}CN/H\textsubscript{2}O gradient (20% to 40%). [Ru\textsuperscript{II}(phen)\textsubscript{2}(DMEA-dpqp)](PF\textsubscript{6})\textsubscript{2} 8 (87 mg) was obtained as a red solid with 85% yield.

Complex 9 - [Ru\textsuperscript{II}(phen)\textsubscript{2}(dppqp)](PF\textsubscript{6})\textsubscript{2}

[\textit{Ru}\textsuperscript{II}(phen)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2} (50 mg, 4\times10^{-5} mol) was dissolved in pure TFA (2 mL) and the solution was stirred for 4 hours at room temperature in the dark. The mixture was then poured onto ice and neutralized with NaOH (1M). The solid was filtered and washed with H\textsubscript{2}O before purification by column chromatography on C\textsubscript{18} with a CH\textsubscript{3}CN/H\textsubscript{2}O gradient (15% to 30%). [Ru\textsuperscript{II}(phen)\textsubscript{2}(dppqp)](PF\textsubscript{6})\textsubscript{2} 9 (36 mg) was obtained as a dark red solid with 74% yield.

\textbf{1H NMR (CD\textsubscript{3}CN, 25 °C, 400 MHz, 8\times10^{-3} mol x L\textsuperscript{-1})}: δ 9.75 (d, \textit{J} = 7.2 Hz, 1H), 8.85 (br s, 1H), 8.72-8.63 (m, 4H), 8.39 (d, \textit{J} = 5.2 Hz, 1H), 8.30 (syst AB, 4H), 8.23 (d, \textit{J} = 5.1 Hz, 1H), 8.19 (d, \textit{J} = 4.8 Hz, 1H), 8.09-8.02 (m, 4H), 7.85-7.80 (m, 2H), 7.75-7.59 (m, 4H), 7.40 (br s, 1H), 7.25-7.14 (m, 3H), 6.64 (br s, 1H), 3.79 (m, 2H), 1.03 (m, 3H) ppm.

\textbf{13C NMR (CD\textsubscript{3}CN, 25°C, 125 MHz, 2\times10^{-2}}
mol x L⁻¹): δ 155.51, 155.14, 154.16, 154.08, 154.07, 154.04, 151.74, 151.27, 149.00, 148.98, 148.84, 148.82, 145.21, 138.15, 138.03, 138.02, 135.11, 134.29, 133.72, 133.13, 132.20, 132.16, 132.15, 131.22, 131.17, 129.23, 129.15, 129.11, 128.02, 127.07, 127.05, 127.03, 127.00, 111.82, 108.84, 64.85, 14.94 ppm.

UV-vis (CH₃CN): \( \lambda_{\text{max}} (\varepsilon) \): 221 nm (78000 L x mol⁻¹ x cm⁻¹), 261 (97000), 288 (60000), 303 (sh 52000), 368 (27000), 381 (29000), 456 (22000).


Complex 10 - [Ru^{II}(TAP)₂(oxo-dpqp)](PF₆)₂

[N]N[N]N

[Ru^{II}(TAP)₂(phendione)(PF₆)₂ (192 mg, 2x10⁻⁴ mol) and 5,6-diamino-2-ethoxyacridin-9-one were dissolved in 6 mL of CH₃CN/EtOH (3/1). The mixture was heated under argon upon microwave irradiation at 90 °C for 60 minutes. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel using CH₃CN/EtOAc (80:20 to 100:0) as eluent. [Ru^{II}(TAP)₂(oxo-dpqp)](PF₆)₂ 10 (201 mg) was obtained as an orange solid with 84% yield.

\(^{1}\text{H} \text{NMR (CD₃CN, 25 °C, 400 MHz, 5x10⁻³ mol x L}^{-¹})\): δ 11.22 (br s, 1H), 9.92 (d, \( J = 7.9 \) Hz, 1H), 9.24 (br s, 1H), 9.18 (d, \( J = 4.8 \) Hz, 1H), 9.05-9.03 (m, 3H), 9.89 (bs s, 1H), 8.72-8.67 (m, 4H), 8.41-8.38 (m, 4H), 8.22 (d, \( J = 4.8 \) Hz, 1H), 7.99 (d, \( J = 9.1 \) Hz, 1H), 7.87 (dd, \( J = 7.4 \) Hz and 5.9 Hz, 1H), 7.88-7.77 (m, 3H), 6.91 (br s, 1H), 6.11 (br s, 1H), 3.13 (m, 1H), 2.95 (m, 1H), 0.88 (m, 3H). \(^{13}\text{C NMR (CD₃CN, 25°C, 125 MHz, 5x10⁻³ mol x L}^{-¹})\): δ 156.11, 156.06, 156.07, 150.78, 150.69, 150.62, 150.51, 150.40, 150.25, 149.90, 146.62, 146.56, 146.54, 146.46, 145.50, 143.30, 143.18, 143.15, 143.09, 141.30, 137.91, 137.61, 136.64, 135.81, 135.28, 135.17, 133.97, 133.92, 133.86, 131.39, 131.05, 130.51, 128.42, 128.31, 124.79, 124.48, 121.79, 121.38, 117.70, 64.13, 14.77 ppm.

UV-vis (CH₃CN): \( \lambda_{\text{max}} (\varepsilon) \): 232 nm (73000 L x mol⁻¹ x cm⁻¹), 248 (59000), 277 (100000), 302 (86000), 348 (sh 2.5.10⁴), 411 (22000), 457 (16000), 512 (sh 7300).

HRMS (MALDI-TOF): calcd for C₁₉H₂₀N₁₃O₂⁹⁶Ru: m/z 903.1643, found: m/z 903.1661 ([M]+).
Complex 11 - [Ru\textsuperscript{II}(TAP)\textsubscript{2}(Cl-dpqp)](PF\textsubscript{6})\textsubscript{2}

[\textcolor{red}{\text{Ru}^{II}(\text{TAP})\textsubscript{2}[(\text{oxo-dpqp})]PF\textsubscript{6}}\textsubscript{2} (120 mg, 10\textsuperscript{-4} mol) was carefully added to 3 mL of POCl\textsubscript{3} and the mixture was heated to 90 °C overnight. The reaction was then cooled to room temperature and the mixture was poured dropwise onto ice. The solution was neutralized with NaOH (1M) and the solid was filtered and washed with H\textsubscript{2}O. It was redissolved in a minimum amount of CH\textsubscript{3}CN and precipitated with Et\textsubscript{2}O. \textcolor{red}{[Ru}^{II}(\text{TAP})\textsubscript{2}(\text{Cl-dpqp})](PF\textsubscript{6})\textsubscript{2} 11 (118 mg) was obtained as an orange solid with 97% yield.

\textsuperscript{1}H NMR (CD\textsubscript{3}CN, 25 °C, 400 MHz, 5x10\textsuperscript{-3} mol x L\textsuperscript{-1}): δ 10.00 (d, J = 7.7 Hz, 1H), 9.76 (d, J = 8.1 Hz, 1H), 9.04 (d, J = 2.0 Hz, 1H), 9.00 (m, 3H), 8.70 (d, J = 9.7 Hz, 1H), 8.65 (d, J = 3.5 Hz, 1H), 8.38 (d, J = 2.7 Hz, 1H), 8.35 (d, J = 2.6 Hz, 2H), 8.29 (m, 5H), 8.24 (m, 1H), 7.98 (dd, J = 8.0 Hz and 5.6 Hz, 1H), 7.92 (dd, J = 8.2 Hz and 5.4 Hz, 1H), 7.60 (s, 1H), 7.42 (d, J = 8.3 Hz, 1H), 4.23 (q, J = 6.8 Hz, 2H), 0.83 (m, 3H) ppm.

\textsuperscript{13}C NMR (CD\textsubscript{3}CN, 25°C, 125 MHz, 5x10\textsuperscript{-3} mol x L\textsuperscript{-1}): δ 160.61, 156.42, 156.20, 150.68, 150.53, 150.39, 150.37, 149.79, 146.61, 146.58, 146.55, 143.36, 143.34, 143.23, 140.95, 139.75, 136.68, 136.07, 133.88, 133.83, 132.49, 132.20, 132.00, 131.33, 130.54, 129.67, 128.52, 127.84, 125.82, 102.82, 65.68, 14.79 ppm.

UV-vis (CH\textsubscript{3}CN): \lambda_{\text{max}} (\varepsilon): 227 nm (58000 L x mol\textsuperscript{-1} x cm\textsuperscript{-1}), 253 (sh 46000), 277 (81000), 343 (43000), 368 (26000), 393 (23000), 417 (24000), 440 (28000).

HRMS (MALDI-TOF): calcd for C\textsubscript{47}H\textsubscript{28}ClN\textsubscript{13}O\textsubscript{96}Ru: m/z 921.1304, found: m/z 921.1321 ([M]\textsuperscript{+}).

Complex 12 - [Ru\textsuperscript{II}(TAP)\textsubscript{2}(DMEA-dpqp)](PF\textsubscript{6})\textsubscript{2}

[\textcolor{red}{\text{Ru}^{II}(\text{TAP})\textsubscript{2}[(\text{Cl-dpqp})]PF\textsubscript{6}}\textsubscript{2} (20 mg, 1.5x10\textsuperscript{-5} mol) was dissolved in anhydrous DMF (3 mL) with DMEA (80 \textmu L, 8x10\textsuperscript{-4} mol, 50 eq.). The mixture was heated in a microwave oven at 140 °C for 15 minutes. The solid was then precipitated upon addition of a saturated solution of KPF\textsubscript{6} and washed with H\textsubscript{2}O. The product was purified by column chromatography on C18 with a CH\textsubscript{3}CN/H\textsubscript{2}O gradient (20% to 40%). \textcolor{red}{[Ru}^{II}(\text{TAP})\textsubscript{2}(\text{DMEA-dpqp})](PF\textsubscript{6})\textsubscript{2} 12 (5 mg) was obtained as a red solid with 24% yield.

\textsuperscript{1}H NMR (CD\textsubscript{3}CN, 25 °C, 400 MHz, 5x10\textsuperscript{-3} mol x L\textsuperscript{-1}): δ 10.26 (d, J = 8.3 Hz, 1H), 9.77 (d, J = 8.1 Hz, 1H), 9.00 (d, AB syst., 4H), 8.76 (d, J = 9.7 Hz, 1H), 8.62 (d, J = 2.6 Hz, 4H), 8.36 (d, J = 8.7 Hz, 1H), 8.32 (d, J = 2.6 Hz, 2H), 8.27-8.22 (m, 4H), 7.96-7.58 (m, 3H), 7.66 (s, 1H), 7.58 (br s, 1H), 0.83 (m, 3H) ppm.
4.88 (t, J = 4.6 Hz, 1H), 4.30 (m, 2H), 4.21 (q, J = 7.0 Hz, 2H), 3.49 (s, 6H), 1.41 (t, J = 4.8 Hz, 3H) ppm. ¹³C NMR (CD₃CN, 25°C, 100 MHz, 5x10⁻³ mol x L⁻¹): δ 158.34, 157.75, 157.29, 151.39, 150.56, 150.38, 150.13, 149.97, 146.68, 146.61, 145.77, 143.46, 143.38, 143.23, 139.70, 138.58, 136.42, 135.51, 134.51, 133.93, 131.29, 131.17, 128.78, 124.65, 124.42, 123.41, 123.24, 11.65, 104.38, 103.36, 65.84, 55.83, 51.79, 14.87 ppm.

UV-vis (CH₃CN): λ_max (ε): 232 nm (41000 L x mol⁻¹ x cm⁻¹), 279 (60000), 329 (35000), 356 (sh 27000), 419 (23000), 462 (sh 16000).

HRMS (MALDI-TOF): calcd for C₅₁H₃₈N₁₄O₃₉Ru: m/z 990.2327, found: m/z 990.2346 ([M]+).

Complex 13 - [RuII(TAP)₂(dppqp)](PF₆)₂

[RuII(TAP)₂(DMEA-dpqp)](PF₆)₂ (40 mg, 3x10⁻⁵ mol) was dissolved in 4 mL of DCM/TFA (5:1) and the mixture was stirred overnight at room temperature in the dark. The solvent was then evaporated and the resulting solid was redissolved in a minimum of CH₃CN and precipitated upon addition of a saturated aqueous solution of KPF₆. It was washed with H₂O and purified by column chromatography on C18 with a CH₃CN/H₂O gradient (15% to 30%). [RuII(TAP)₂(dppqp)](PF₆)₂ 13 (31 mg) was obtained as a dark red solid with 84% yield.

¹H NMR (CD₃CN, 25 °C, 400 MHz, 5x10⁻³ mol x L⁻¹): δ 12.18 (br s, 1H), 10.21 (d, J = 8.2 Hz, 1H), 9.62 (d, J = 8.2 Hz, 1H), 9.05-9.00 (m, 4H), 8.65 (s, 4H), 8.43 (d, J = 2.6 Hz, 1H), 8.36-8.34 (m, 2H), 8.29-8.28 (m, 3H), 7.94 (dd, J = 8.1 Hz and 5.6 Hz, 1H), 7.89 (dd, J = 8.0 Hz and 5.5 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.6 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.28 (d, J = 7.1 Hz, 1H), 6.94 (d, J = 6.8 Hz, 1H), 4.12 (q, J = 6.8 Hz, 2H), 1.33 (t, J = 6.8 Hz, 3H) ppm. ¹³C NMR (CD₃CN, 25°C, 125 MHz, 5x10⁻³ mol x L⁻¹): δ 157.20, 156.77, 151.43, 150.91, 150.65, 150.63, 150.49, 150.46, 150.25, 150.22, 149.83, 149.79, 149.19, 147.20, 146.66, 146.64, 146.62, 145.89, 143.38, 143.36, 143.29, 143.23, 140.20, 139.70, 137.01, 136.34, 134.51, 133.93, 133.66, 131.34, 131.10, 130.74, 128.78, 128.77, 126.73, 125.86, 123.66, 121.47, 120.52, 113.62, 112.63, 109.69, 66.07, 15.07 ppm. UV-vis (CH₃CN): λ_max (ε): 232 nm (50000 L x mol⁻¹ x cm⁻¹), 280 (66000), 303 (58000), 354 (sh 24000), 416 (22700), 464 (20000), 502 (sh 11000). HRMS (MALDI-TOF): calcd for C₄₉H₃₀N₁₄O₇Ru: m/z 926.1803, found: m/z 926.1800 ([M]+).
Study of $\pi-\pi$ stacking by $^1$H NMR spectroscopy

**Figure S1** - $^1$H NMR study of the $\pi-\pi$ stacking of $[\text{Ru}^{III}(\text{bpy})_2(\text{oxo-dpqp})](\text{PF}_6)_2$ in CD$_3$CN at different concentrations (inset: $\delta = f(\log(C))$).

**Figure S2** - $^1$H NMR study of the $\pi-\pi$ stacking of $[\text{Ru}^{III}(\text{bpy})_2(\text{oxo-dpqp})](\text{Cl})_2$ in CD$_3$CN + 10% D$_2$O at different concentrations (inset: $\delta = f(\log(C))$).
Figure S3 - $^1$H NMR study of the $\pi$-$\pi$ stacking of [Ru$^{II}$(bpy)$_2$(oxo-dpqp)][Cl]$_2$ in CD$_3$CN + 20% D$_2$O at different concentrations (inset: $\delta = f(\log(C))$).

Figure S4 - $^1$H NMR study of the $\pi$-$\pi$ stacking of [Ru$^{II}$(phen)$_2$(oxo-dpqp)][PF$_6$]$_2$ in CD$_3$CN at different concentrations (inset: $\delta = f(\log(C))$).
**Figure S5** - $^1$H NMR study of the $\pi$-$\pi$ stacking of [Ru$^{II}$(TAP)$_2$(oxo-dpqp)]($\text{PF}_6$)$_2$ in CD$_3$CN at different concentrations (inset: $\delta = f(\log(C))$).

**Figure S6** - $^1$H NMR study of the $\pi$-$\pi$ stacking of [Ru$^{II}$(bpy)$_2$(Br-dpqp)]($\text{PF}_6$)$_2$ in CD$_3$CN at different concentrations (inset: $\delta = f(\log(C))$).
**Figure S7** - $^1$H NMR study of the $\pi$-$\pi$ stacking of [Ru$^{11}$]+(bpy)$_2$(dppqp)][PF$_6$]$_2$ in CD$_3$CN at different concentrations (inset: $\delta = f$($\log$(C))).

**UV-vis measurements**

**Figure S8** - UV-vis absorption spectra of [Ru$^{11}$]+(bpy)$_2$(oxo-dpqp)][X]$_2$ recorded in CH$_3$CN (X = PF$_6$, plain line) and H$_2$O (X = Cl, dashed line).
**Figure S9** - UV-vis absorption spectra of [Ru(bpy)$_2$(oxo-dpqp)](${PF}_6$)$_2$ (plain line), [Ru(bpy)$_2$(dppz)](${PF}_6$)$_2$ (dashed line) and [Zn(oxo-dpqp)][BF$_4$]$_2$ (dotted line), recorded in CH$_3$CN. *Inset:* Superposition of the [Ru(bpy)$_2$(oxo-dpqp)](${PF}_6$)$_2$ absorption in the visible region (plain line) with the sum of [Ru(bpy)$_2$(dppz)](${PF}_6$)$_2$ and [Zn(oxo-dpqp)][BF$_4$]$_2$ absorptions (dashed line).

**Figure S10** - UV-vis absorption spectra of [Ru(L)$_2$(oxo-dpqp)](${PF}_6$)$_2$ (L = bpy in plain line, phen in dashed line or TAP in dashed dotted line), recorded in CH$_3$CN.
Figure S11 - UV-vis absorption spectra of \([\text{Ru}^\text{II}L_2(\text{Cl-dpqp})](\text{PF}_6)_2\) (\(L = \text{bpy}\) in plain line, \(\text{phen}\) in dashed line or \(\text{TAP}\) in dashed dotted line) recorded in CH\(_3\)CN.

Figure S12 - UV-vis absorption spectra of \([\text{Ru}^\text{II}(\text{bpy})_2(\text{Cl-dpqp})](\text{PF}_6)_2\) (plain line) and \([\text{Ru}^\text{II}(\text{bpy})_2(\text{Br-dpqp})](\text{PF}_6)_2\) (dashed line) recorded in CH\(_3\)CN.
**Figure S13** - UV-vis absorption spectra of [Ru\(^{II}\)(bpy)\(_2\)](PF\(_6\))\(_2\) recorded in CH\(_3\)CN (L=oxo-dpq in plain grey, Cl-dpq in dashed grey, DMEA-dpq in dashed black and dppq in plain black line).

**Figure S14** - UV-vis absorption spectra of [Ru\(^{II}\)(phen)\(_2\)](PF\(_6\))\(_2\) recorded in CH\(_3\)CN (L=oxo-dpq in plain grey, Cl-dpq in dashed grey, DMEA-dpq in dashed black and dppq in plain black line).
Figure S15 - UV-vis absorption spectra of [Ru\(^{II}\)(TAP)\(_2\)](PF\(_6\))\(_2\) recorded in CH\(_3\)CN (L=oxo-dpqp in plain grey, Cl-dpqp in dashed grey, DMEA-dpqp in dashed black and dppqp in plain black line).

**Computational details**

Quantum chemical calculations were performed for the complexes: [Ru(bpy)\(_2\)](oxo-dpqp)]\(^{2+}\), [Ru(bpy)\(_2\)](Br-dpqp)]\(^{2+}\) and [Ru(bpy)\(_2\)](dppqp)]\(^{2+}\) using the Gaussian 09 program\(^6\), while both tautomeric forms of [Ru(bpy)\(_2\)](oxo-dpqp)]\(^{2+}\), namely 12-hydroxyacridine and 12-acridone, were investigated. The fully optimized equilibrium geometries of the four complexes were obtained at the density functional level of theory (DFT) using the \(\omega\)B97X-D\(^7\) XC functional. The 6-31G(d) double-\(\zeta\) basis set\(^8\) was employed for all main group elements. The 28-electron relativistic core potential MWB\(^9\) was applied with its basis set for the ruthenium atom, that is, 4s, 4p, 4d and 5s electrons are treated explicitly, while the first three inner shells are described by the core pseudopotential. A subsequent vibrational analysis carried out for each fully optimized structure verified that the obtained structures correspond to minima of the ground state potential energy surface. The effects of the interaction with a solvent (CH\(_3\)CN, \(\varepsilon = 35.688, n = 1.344\)) on the geometry and vibrational frequencies were taken into account by the integral equation formalism of the polarizable continuum model\(^10\).

Additionally, the possibility of dimerization based on \(\pi-\pi\) stacking interactions was evaluated. Therefore, geometry optimizations and subsequent frequency analyses for [Ru(bpy)\(_2\)](oxo-dpqp)]\(^{2+}\) (only carried out for the more stable 12-acridone tautomer), [Ru(bpy)\(_2\)](Br-dpqp)]\(^{2+}\) and [Ru(bpy)\(_2\)](dppqp)]\(^{2+}\) as well as for the respective head-to-tail
dimers with stacked dpqp/dppqp ligand spheres were obtained using the ωB97X-D\textsuperscript{7} functional. The range-separated ωB97X-D functional incorporates dispersion, which is a crucial parameter in order to accurately describe long-range intermolecular interactions such as π-π stacking. The same basis set, core potential and PCM (CH\textsubscript{3}CN) were utilized as mentioned afore. The bonding energies for the head-to-tail dimers were than approximated by means of the free energies of the dimer and two monomers, respectively.
### Table S1: Fully optimized dimer structures of [Ru(bpy)$_2$(oxo-$\text{dpqp}$)]$_2^{4+}$, [Ru(bpy)$_2$(Br-$\text{dpqp}$)]$_2^{4+}$ and [Ru(bpy)$_2$(dppqp)]$_2^{4+}$, $\pi-\pi$ stacking distances ($d_{\text{stacking}}$) and bonding energies ($E_{\text{dimer}}$).
Table S2: Planarity of the dpqp/dppqp ligand within the optimized equilibrium structures of the monomer and the dimer species described by bending angle $\alpha$ (in red) and dihedral angle $\delta$ (in blue).

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