Synthesis of three series of ruthenium tris-diimine complexes containing acridine-based π-extended ligands using an efficient "chemistry on the complex" approach.

Supplementary information

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General information

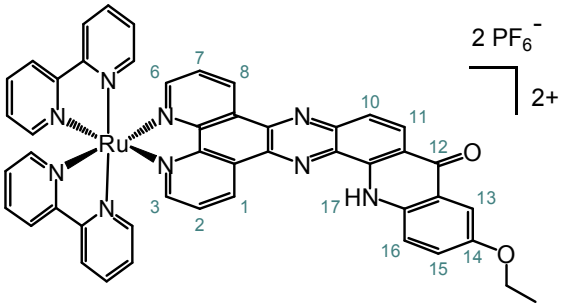
Chemicals and solvents (analytical grade) were purchased from Sigma-Aldrich, Alfa Aesar or Fisher Scientific and used without further purification. Silica gel 60 was purchased from Sigma-Aldrich. Silica gel 100 C18 – Reversed phase was purchased from Fluka. Some purification were carried out on a puriflash 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 $[Ru(bpy)_2(phendione)](PF_6)_2$,[2] $[Ru(phen)_2(phendione)](PF_6)_2$,[3] and $[Ru(TAP)_2(phendione)](PF_6)_2$,[4] 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_4Si (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_3CN).

Synthetic procedures

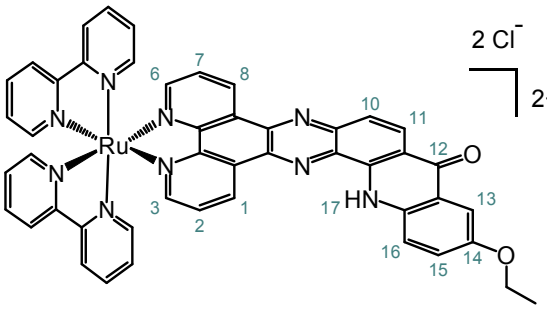
Complex 1 – $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(bpy)_2(phendione)](PF_6)_2$ (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_3CN (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_2O) to the residue. The solid was filtered, washed with Et_2O and dried to afford 290 mg of crude $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ **1** as an orange solid in 95% yield. The crude product was pure enough for further synthesis.

^{1}H NMR (CD_3CN, 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* = 8.3 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_3CN, 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_3CN):** λ_{max} (ε): 248 nm (58500 L x mol^{-1} x cm^{-1}), 285 (96000), 301 (sh 70500), 338 (32500), 352 (35500), 413 (20500), 448 (20200), 519 (sh 8500). **HRMS (ESI^+):** calcd for $C_{47}H_{33}N_9O_2{}^{102}Ru$: *m/z* 428.5901, found: *m/z* 428.5903 ($[M]^{2+}$); calcd for $C_{94}H_{65}N_{18}O_4{}^{102}Ru_2$: *m/z* 571.1182, found: *m/z* 571.1186 ($[2M - H]^{3+}$). **Elem. An.:** calcd for $C_{47}H_{33}F_{12}N_9O_2P_2Ru$ • 0,2 NH_4PF_6: N 10.93, C 47.86, H 2.89; found: N 10.61, C 47.41, H 2.98.

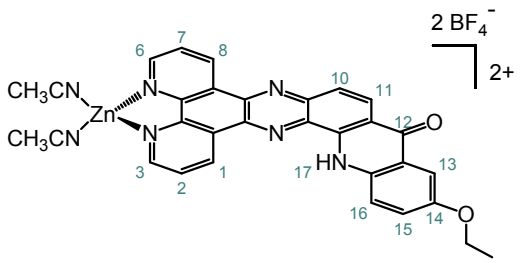
Complex 1(Cl) – $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](Cl)_2$



$[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ **1** (0.04 g, $3.5x10^{-5}$ mol) was dissolved in a mixture methanol (MeOH)/CH_3CN (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_2O to the residue. The solid was filtered, washed with Et_2O and dried to afford 32 mg of $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](Cl)_2$ **1(Cl)** as an orange solid in quantitative yield.

^{1}H NMR (CD_3CN + 10% D_2O, 25°C, 300 MHz, 10^{-3} mol x L $^{-1}$): δ 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* = 7.3 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_2O):** λ_{max} (ε): 253 nm (49100 L x mol^{-1} x cm^{-1}), 284 (75500), 305 (sh 47000), 338 (sh 23500), 422 (sh 16500), 446 (17700).

Complex $[Zn^{II}(oxo\text{-}dpqp)](BF_4)_2$

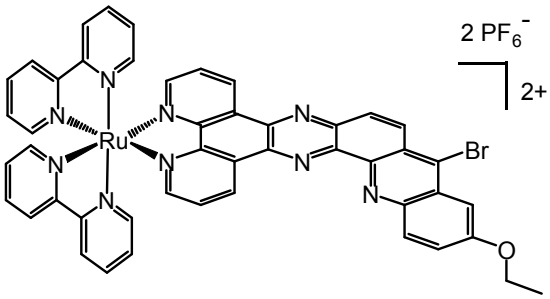


Oxo-dpqp (0,19 mg, $4.28x10^{-7}$ mol) was suspended in CH_3CN (5 mL). Zinc(II) tetrafluoroborate $Zn(BF_4)_2$ (10.2 mg, $4.27x10^{-5}$ mol, 100 eq.) was solubilised in CH_3CN (5 mL) and added to the suspension. The mixture was stirred overnight in a sealed flask in the dark. After filtration, the solution was directly used for UV-vis absorption spectroscopy measurement and ESI MS characterization.

UV-vis (CH_3CN): λ_{max} (ε): 247 nm (35300 L x mol^{-1} x cm^{-1}), 277 (42200), 302 (37250), 343 (sh 21500), 357 (22500), 409 (5700), 486 (br 5100).

ESI MS: *m/z* 526.2 $[M - 2\ CH_3CN + F]^+$ (the fluoride coming from partial decomposition of BF_4 anions), *m/z* 294.5 $[M]^{2+}$, *m/z* 253.5 $[M - 2\ CH_3CN]^{2+}$.

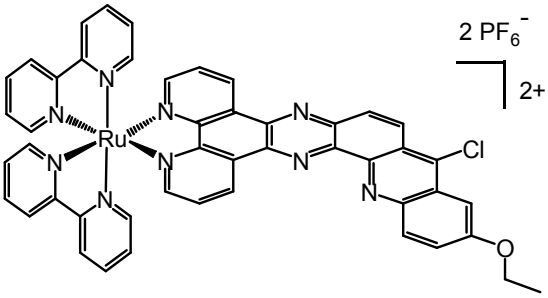
Complex 2 - $[Ru^{II}(bpy)_2(Br\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ **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 (NH_4PF_6), filtered, washed with H_2O and dried. The solid solubilised in CH_3CN was purified by column chromatography on silica gel using a gradient of aqueous 10% KNO_3 solution in CH_3CN as eluent (0 to 20%). The product was precipitated by adding NH_4PF_6 in the aqueous residue, filtered, washed with H_2O and dried. The solid was solubilised in a small amount of CH_3CN and precipitated by adding Et_2O. Filtration, washings with Et_2O and drying afforded 105 mg of pure $[Ru^{II}(bpy)_2(Br\text{-}dpqp)](PF_6)_2$ **2** as an orange solid in 64% yield.

^{1}H NMR (CD_3CN, 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), 8.01-7.96 (m, 1H), 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. **^{13}C NMR (CD_3CN, 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, 127.88, 126.97, 125.94, 125.48, 105.03, 64.96, 14.70 ppm. **UV-vis (CH_3CN):** 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^+):** calcd for $C_{47}H_{32}BrN_9O^{102}Ru$: *m/z* 459.5477, found: *m/z* 459.5480 ($[M]^{2+}$); calcd for $C_{47}H_{33}BrN_9O^{102}Ru$: *m/z* 306.7009, found: *m/z* 306.7010 ($[M + H]^{3+}$); calcd for $C_{47}H_{32}BrF_6N_9OP^{102}Ru$: 1064.0600, found: 1064.0597 ($[M + PF_6]^+$). **Elem. An.:** calcd for $C_{47}H_{32}BrF_{12}N_9OP_2Ru$ • 0,7 NH_4PF_6: N 10.26, C 42.64, H 2.65; found: N 10.05, C 42.29, H 2.67.

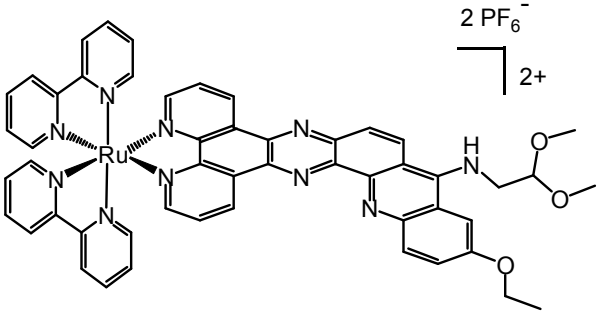
Complex 3 - $[Ru^{II}(bpy)_2(Cl\text{-}dpqp)](PF_6)_2$



Crude $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ **1** (0.28 g, $2.40x10^{-4}$ mol) was loaded in a round bottom flask and dissolved in phosphorus oxychloride ($POCl_3$, 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_2CO_3) until neutral pH. CH_3CN was added until the solution was clear. The product was then precipitated by adding aqueous NH_4PF_6, filtered, washed with H_2O and dried. The solid was solubilised in a small amount of acetonitrile and reprecipitated by adding Et_2O. Filtration, washings with Et_2O and drying afforded 270 mg of pure $[Ru^{II}(bpy)_2(Cl\text{-}dpqp)](PF_6)_2$ **3** as an orange solid in 95% yield.

^{1}H NMR (CD_3CN, 25°C, 400 MHz, $6x10^{-3}$ mol x L^{-1}): δ 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* = 8.8 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, 2H), 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 (d, *J* = 5.4 Hz, 1H), 7.54-7.47 (m, 4H), 7.36-7.29 (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. **^{13}C NMR (CD_3CN, 25°C, 75 MHz, $2.5x10^{-2}$ mol x L^{-1}):** δ 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_3CN):** λ_{max} (ε): 243 nm (60250 L x mol^{-1} x cm^{-1}), 253 (sh 58150), 284 (94950), 344 (58500), 361 (sh 33400), 390 (21200), 431 (25350), 452 (sh 23050). **HRMS (ESI$^+$):** calcd for $C_{47}H_{33}ClN_9O^{102}Ru$: *m/z* 292.0511, found: *m/z* 292.0514 $([M + H]^{3+})$; calcd for $C_{47}H_{32}ClN_9O^{102}Ru$: *m/z* 437.5730, found: *m/z* 437.5733 $([M]^{2+})$; calcd for $C_{47}H_{32}ClF_6N_9OP^{102}Ru$: 1020.1107, found: 1020.1095 $([M + PF_6]^+)$.

Complex 4 - $[Ru^{II}(bpy)_2(DMEA\text{-}dpqp)](PF_6)_2$

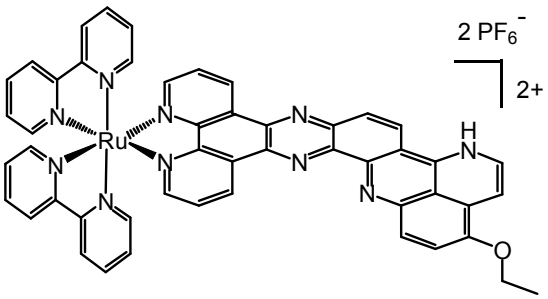


$[Ru^{II}(bpy)_2(Cl\text{-}dpqp)](PF_6)_2$ **3** (0.15 g, $1.22x10^{-4}$ mol) was loaded in a microwave oven reactor and dissolved in DMF (4 mL) with 2,2'-dimethoxyethylamine DMEA (0.3 mL, $2.75x10^{-3}$ mol, 22.5 eq.). The mixture was heated at 110°C for 1.5 hours in a microwave oven. After cooling of the reaction, a small amount of aqueous K_2CO_3

was added to neutralize the mixture. Aqueous NH_4PF_6 was added to precipitate the product. The solid was filtered, washed with H_2O and dried. The solid was then solubilised with CH_3CN through the fritted glass funnel, the solvent was concentrated and Et_2O was added to precipitate again the product. Filtration, washings with Et_2O and drying afforded 145 mg of $[Ru^{II}(bpy)_2(DMEA\text{-}dpqp)](PF_6)_2$ **4** as a red solid in 91% yield.

^{1}H NMR (CD_3CN, 25°C, 400 MHz, 5x10^{-3} mol x L^{-1}): δ 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), 8.05 (d, *J* = 4.8 Hz, 1H), 8.01 (td, *J* = 8.1 and 1.4 Hz, 1H), 7.92 (d, *J* = 4.8 Hz, 1H), 7.91 (d, *J* = 9.7 Hz, 1H), 7.87 (d, *J* = 5.2 Hz, 1H), 7.70 (d, *J* = 5.2 Hz, 1H), 7.65 (dd, *J* = 8.1 and 5.4 Hz, 1H), 7.58-7.47 (m, 5H), 7.41 (dd, *J* = 8.9 and 1.9 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, 2H), 3.38 (s, 6H), 1.48 (t, 6.9 Hz, 3H) ppm. **^{13}C NMR (CD_3CN, 25°C, 75 MHz, 2x10^{-2} mol x L^{-1}):** δ 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 (CH_3CN):** λ_{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 $C_{50}H_{39}N_{10}O_2{}^{102}Ru$: *m/z* 304.4099, found: *m/z* 304.4102 ($[M - OCH_3]^{3+}$); calcd for $C_{51}H_{43}N_{10}O_3{}^{102}Ru$: *m/z* 315.0853, found: *m/z* 315.0856 ($[M + H]^{3+}$); calcd for $C_{51}H_{42}N_{10}O_3{}^{102}Ru$: 472.1244, found: 472.1247 ($[M]^{2+}$).

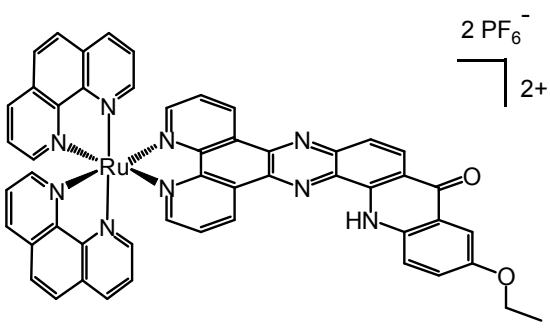
Complex 5 - $[Ru^{II}(bpy)_2(dppqp)](PF_6)_2$



$[Ru^{II}(bpy)_2(DMEA\text{-}dpqp)](PF_6)_2$ **4** (0.1 g, 8.10x10^{-5} mol) was dissolved in trifluoroacetic acid (2 mL) and stirred for 4 hours at room temperature in the dark. The mixture was then poured onto ice and neutralized with saturated aqueous K_2CO_3. CH_3CN was added to the suspension to obtain a clear solution. Aqueous NH_4PF_6 was then added to precipitate the product. The solid was filtered, washed with H_2O and dried. The crude product was purified by column chromatography on silica gel using a gradient of 10% aqueous KNO_3 solution in CH_3CN as eluent. The product was precipitated by adding NH_4PF_6 in the aqueous residue, filtered, washed with H_2O and dried. The solid was then solubilized with CH_3CN through the frit funnel, the solvent was concentrated and Et_2O was added to precipitate again the product. Filtration, washings with Et_2O and drying afforded 70 mg of $[Ru^{II}(bpy)_2(dppqp)](PF_6)_2$ **5** as a dark red solid in 73% yield.

^{1}H NMR (CD_3CN, 25°C, 300 MHz, 2.5x10^{-3} mol x L^{-1}): δ 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), 7.34 (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_3CN, 25°C, 100 MHz, 10^{-2} mol x L^{-1}):** δ 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_3CN):** λ_{max} (ε): 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 - $[Ru^{II}(phen)_2(oxo\text{-}dpqp)](PF_6)_2$ (procedure modified compared to already reported method)[5]



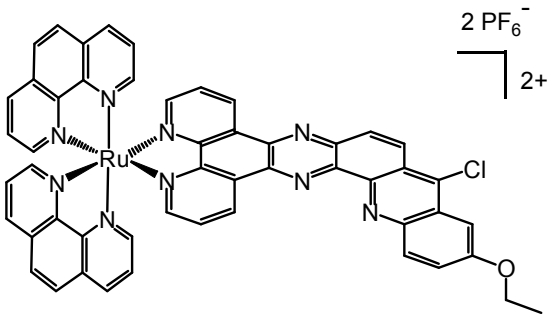
$[Ru^{II}(phen)_2phendione](PF_6)_2$ (192 mg, 2x10^{-4} mol) and 5,6-diamino-2-ethoxyacridin-9-one were dissolved in 6 mL of CH_3CN/EtOH (3/1). The mixture was heated under argon upon microwave irradiation at 90 °C for 60 minutes. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel using CH_3CN/EtOAc (70:30 to 100:0) as eluent. $[Ru^{II}(phen)_2(oxo\text{-}dpqp)](PF_6)_2$ **6** (177 mg) was obtained as an orange solid with 74% yield.

Characterizations are in accordance to previously published.[5]

^{1}H NMR (CD_3CN, 25 °C, 400 MHz, 10^{-2} mol x L^{-1}) : δ 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_3CN, 25°C, 125 MHz, 10^{-2}mol x L^{-1}):** δ 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_3CN):** λ_{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 $C_{51}H_{33}N_9O_2{}^{96}Ru$: *m/z* 899.1833, found: *m/z* 899.1857 ($[M]^+$). *At UMONS, we perform exact mass measurements on the lightest Ru isotope (i.e. ^{96}Ru) 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*

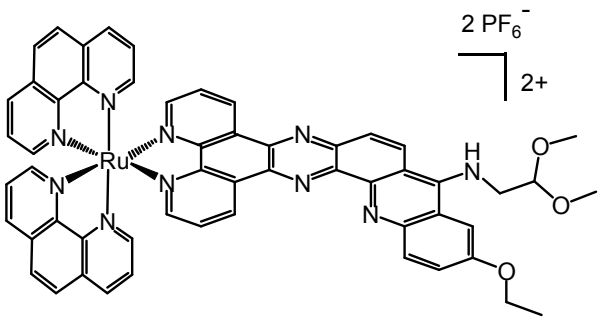
Complex 7 - $[Ru^{II}(phen)_2(Cl\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(phen)_2(oxo\text{-}dpqp)](PF_6)_2$ (120 mg, 10^{-4} mol) was carefully added to 3 mL of $POCl_3$ 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 H_2O. It was redissolved in a minimum amount of CH_3CN and precipitated with Et_2O. $[Ru^{II}(phen)_2(Cl\text{-}dpqp)](PF_6)_2$ **7** (114 mg) was obtained as an orange solid with 94% yield.

^{1}H NMR (CD_3CN, 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. **^{13}C NMR (CD_3CN, 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 (CH_3CN):** 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 $C_{51}H_{32}ClN_9O^{96}Ru$: *m/z* 917.1494, found: *m/z* 917.1497 ($[M]^+$).

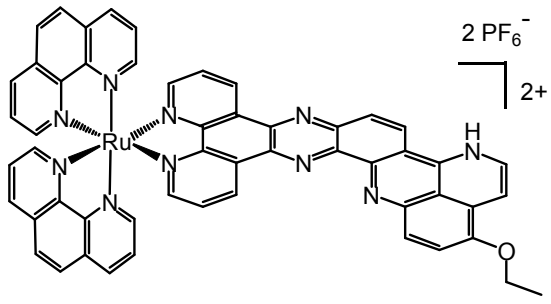
Complex 8 - $[Ru^{II}(phen)_2(DMEA\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(phen)_2(Cl\text{-}dpqp)](PF_6)_2$ (100 mg, $8x10^{-5}$ mol) was dissolved in anhydrous DMF (4 mL) with DMEA (0.17 mL, $1.6x10^{-3}$ 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_6, filtered and washed with H_2O. The product was purified by column chromatography on C18 with a CH_3CN/H_2O gradient (20% to 40%). $[Ru^{II}(phen)_2(DMEA\text{-}dpqp)](PF_6)_2$ **8** (87 mg) was obtained as a red solid with 85% yield.

^{1}H NMR (CD_3CN, 25 °C, 400 MHz, $5x10^{-3}$ mol x L^{-1}): δ 13.98 (br s, 1H), 10.17 (d, *J* = 8.0, 1H), 9.68 (d, *J* = 7.9 Hz, 1H), 8.73-8.67 (m, 4H), 8.33 (m, 6H), 8.28-8.26 (m, 2H), 8.23 (d, *J* = 9.7 Hz, 1H), 8.18 (d, *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, *J* = 4.6 Hz, 1H), 4.34 (m, 2H), 4.01 (m, 2H), 3.57 (s, 6H), 1.19 (m, 3H) ppm. **^{13}C NMR (CD_3CN, 25°C, 125 MHz, $5x10^{-3}$ mol x L^{-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, 143.47, 139.91, 138.14, 138.09, 138.03, 138.01, 135.39, 134.95, 134.73, 134.45, 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. **UV-vis (CH_3CN):** λ_{max} (ε): 223 nm (57000 L x mol^{-1} x cm^{-1}), 265 (69000), 300 (sh 32000), 330 (30000), 347 (30000), 423 (21000). **HRMS (MALDI-TOF):** calcd for $C_{55}H_{42}N_{10}O_3{}^{96}Ru$: *m/z* 986.2517, found: *m/z* 986.2520 ($[M]^+$).

Complex 9 - $[Ru^{II}(phen)_2(dppqp)](PF_6)_2$

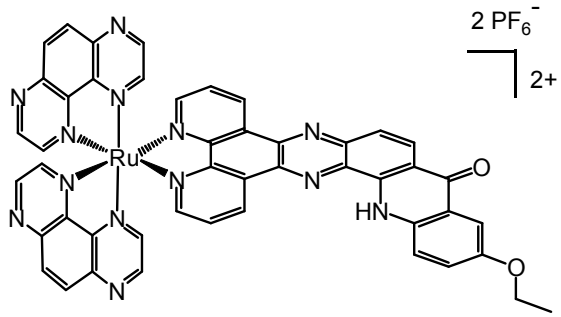


$[Ru^{II}(phen)_2(DMEA\text{-}dpqp)](PF_6)_2$ (50 mg, $4x10^{-5}$ mol) was dissolved in pure TFA (2 mL) and the solution was stirred for 4 hours at room temperature in the dark. The mixture was then poured onto ice and neutralized with NaOH (1M). The solid was filtered and washed with H_2O before purification by column chromatography on C18 with a CH_3CN/H_2O gradient (15% to 30%). $[Ru^{II}(phen)_2(dppqp)](PF_6)_2$ **9** (36 mg) was obtained as a dark red solid with 74% yield.

^{1}H NMR (CD_3CN, 25 °C, 400 MHz, $8x10^{-3}$ mol x L^{-1}): δ 9.75 (d, J = 7.2 Hz, 1H), 8.85 (br s, 1H), 8.72-8.63 (m, 4H), 8.39 (d, J = 5.2 Hz, 1H), 8.30 (syst AB, 4H), 8.23 (d, J = 5.1 Hz, 1H), 8.19 (d, 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. **^{13}C NMR (CD_3CN, 25°C, 125 MHz, $2x10^{-2}$**

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, 128.11, 128.02, 127.07, 127.05, 127.03, 127.00, 111.82, 108.84, 64.85, 14.94 ppm. **UV-vis (CH_3CN):** λ_{max} (ε): 221 nm (78000 L x mol^{-1} x cm^{-1}), 261 (97000), 288 (60000), 303 (sh 52000), 368 (27000), 381 (29000), 456 (22000)**. HRMS (MALDI-TOF):** calcd for $C_{53}H_{34}N_{10}O^{96}Ru$: *m/z* 922.1993, found: *m/z* 922.2021 ([M]$^+$).

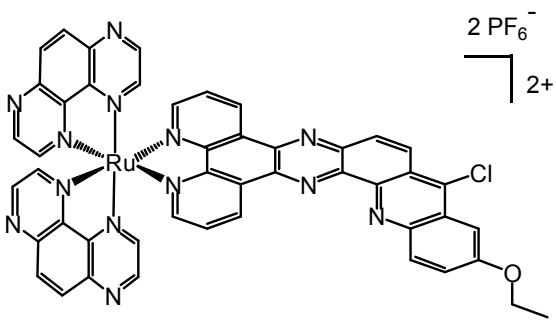
Complex 10 - $[Ru^{II}(TAP)_2(oxo\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(TAP)_2phendione](PF_6)_2$ (192 mg, 2x10^{-4} mol) and 5,6-diamino-2-ethoxyacridin-9-one were dissolved in 6 mL of CH_3CN/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_3CN/EtOAc (80:20 to 100:0) as eluent. $[Ru^{II}(TAP)_2(oxo\text{-}dpqp)](PF_6)_2$ **10** (201 mg) was obtained as an orange solid with 84% yield.

^{1}H NMR (CD_3CN, 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}C NMR (CD_3CN, 25°C, 125 MHz, 5x10^{-3} mol x L^{-1}):** δ 156.11, 156.06, 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 (CH_3CN):** λ_{max} (ε): 232 nm (73000 L x mol^{-1} x cm^{-1}), 248 (59000), 277 (100000), 302 (86000), 348 (sh 2.5.10^4), 411 (22000), 457 (16000), 512 (sh 7300). **HRMS (MALDI-TOF):** calcd for $C_{47}H_{29}N_{13}O_2{}^{96}Ru$: *m/z* 903.1643, found: *m/z* 903.1661 ([M]$^+$).

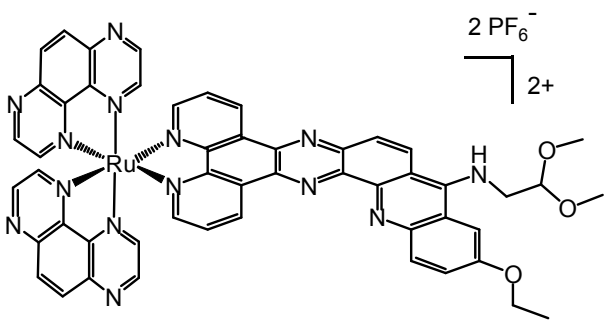
Complex 11 - $[Ru^{II}(TAP)_2(Cl\text{-}dpqp)](PF_6)_2$



$[Ru^{II}(TAP)_2(oxo\text{-}dpqp)](PF_6)_2$ (120 mg, 10^{-4} mol) was carefully added to 3 mL of$POCl_3$ 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_2O. It was redissolved in a minimum amount of CH_3CN and precipitated with Et_2O. $[Ru^{II}(TAP)_2(Cl\text{-}dpqp)](PF_6)_2$ **11** (118 mg) was obtained as an orange solid with 97% yield.

^{1}H NMR (CD_3CN, 25 °C, 400 MHz, 5x10^{-3} mol x L^{-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. **^{13}C NMR (CD_3CN, 25°C, 125 MHz, 5x10^{-3} mol x L^{-1}):** δ 160.61, 156.42, 156.20, 150.68, 150.53, 150.39, 150.37, 150.18, 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, 128.48, 127.84, 125.82, 102.82, 65.68, 14.79 ppm. **UV-vis (CH_3CN):** λ_{max} (ε): 227 nm (58000 L x mol^{-1} x cm^{-1}), 253 (sh 46000), 277 (81000), 343 (43000), 368 (26000), 393 (23000), 417 (24000), 440 (28000). **HRMS (MALDI-TOF):** calcd for $C_{47}H_{28}ClN_{13}O^{96}Ru$: *m/z* 921.1304, found: *m/z* 921.1321 ($[M]^+$).

Complex 12 - $[Ru^{II}(TAP)_2(DMEA\text{-}dpqp)](PF_6)_2$

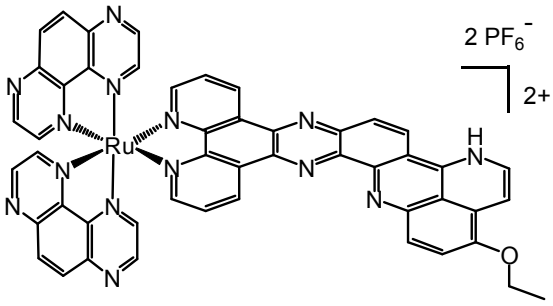


$[Ru^{II}(TAP)_2(Cl\text{-}dpqp)](PF_6)_2$ (20 mg, 1.5x10^{-5} mol) was dissolved in anhydrous DMF (3 mL) with DMEA (80 µL, 8x10^{-4} mol, 50 eq.). The mixture was heated in a microwave oven at 140 °C for 15 minutes. The solid was then precipitated upon addition of a saturated solution of KPF_6 and washed with H_2O. The product was purified by column chromatography on C18 with a CH_3CN/H_2O gradient (20% to 40%). $[Ru^{II}(TAP)_2(DMEA\text{-}dpqp)](PF_6)_2$ **12** (5 mg) was obtained as a red solid with 24% yield.

^{1}H NMR (CD_3CN, 25 °C, 400 MHz, 5x10^{-3} mol x L^{-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),

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. **^{13}C NMR (CD_3CN, 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 (CH_3CN)**: 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 $C_{51}H_{38}N_{14}O_3{}^{96}Ru$: *m/z* 990.2327, found: *m/z* 990.2346 ([M]$^+$).

Complex 13 - $[Ru^{II}(TAP)_2(dppqp)](PF_6)_2$



$[Ru^{II}(TAP)_2(DMEA\text{-}dpqp)](PF_6)_2$ (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 CH_3CN and precipitated upon addition of a saturated aqueous solution of KPF_6. It was washed with H_2O and purified by column chromatography on C18 with a CH_3CN/H_2O gradient (15% to 30%). $[Ru^{II}(TAP)_2(dppqp)](PF_6)_2$ **13** (31 mg) was obtained as a dark red solid with 84% yield.

^{1}H NMR (CD_3CN, 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. **^{13}C NMR (CD_3CN, 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 (CH_3CN):** 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 $C_{49}H_{30}N_{14}O^{96}Ru$: *m/z* 926.1803, found: *m/z* 926.1800 ([M]$^+$).

Study of π–π stacking by ^{1}H NMR spectroscopy

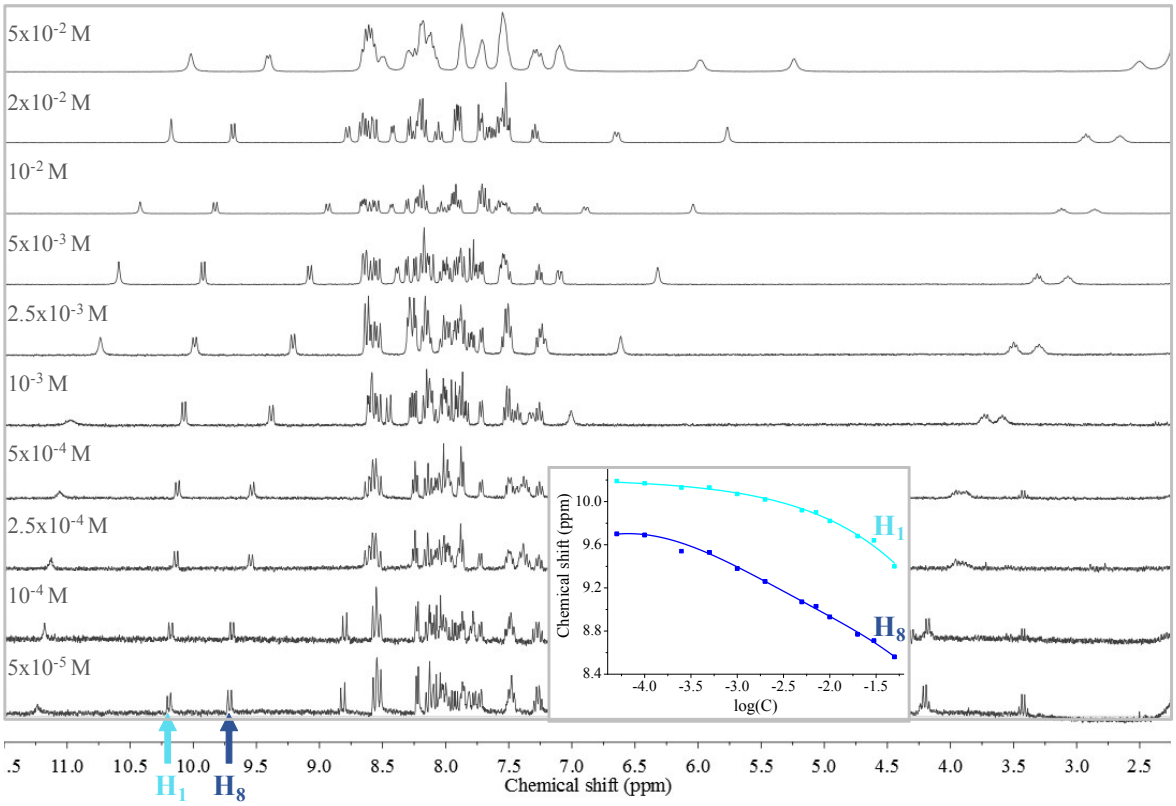


Figure S1 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ in CD_3CN at different concentrations (inset : δ = f(log(C))).

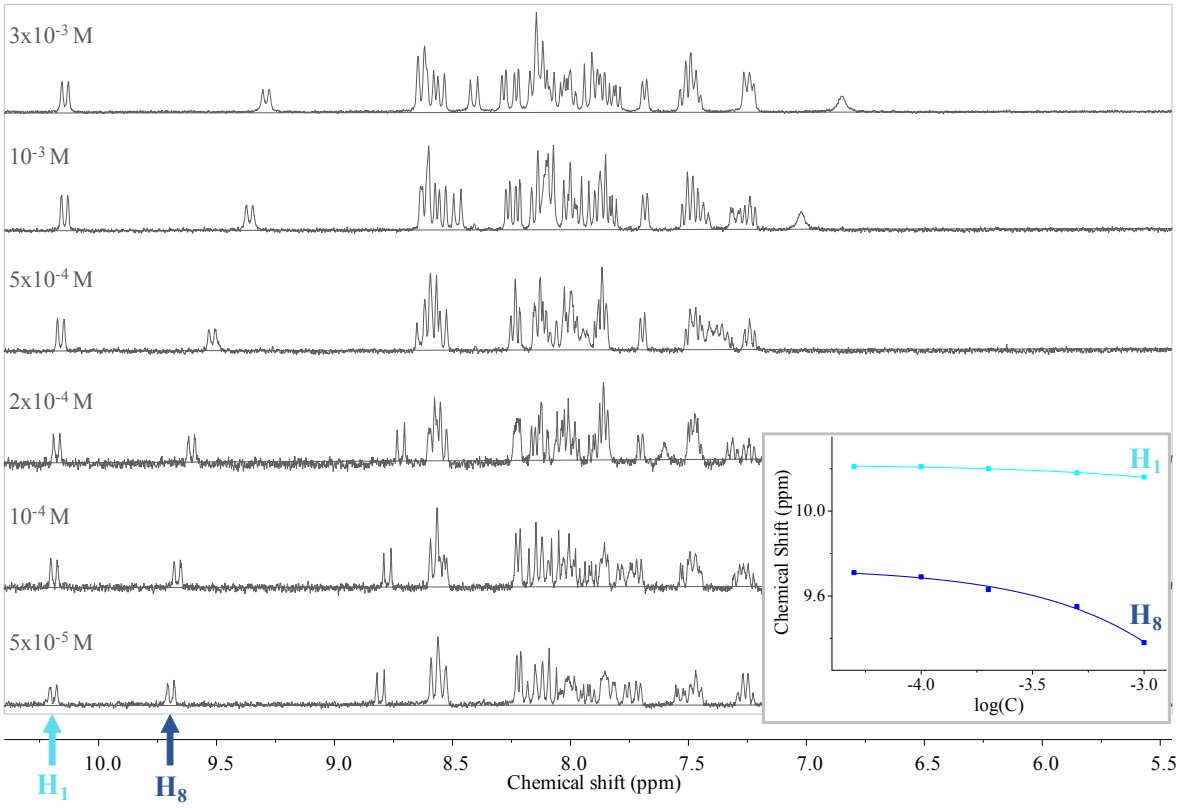


Figure S2 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](Cl)_2$ in CD3CN + 10% D_2O at different concentrations (inset : δ = f(log(C))).

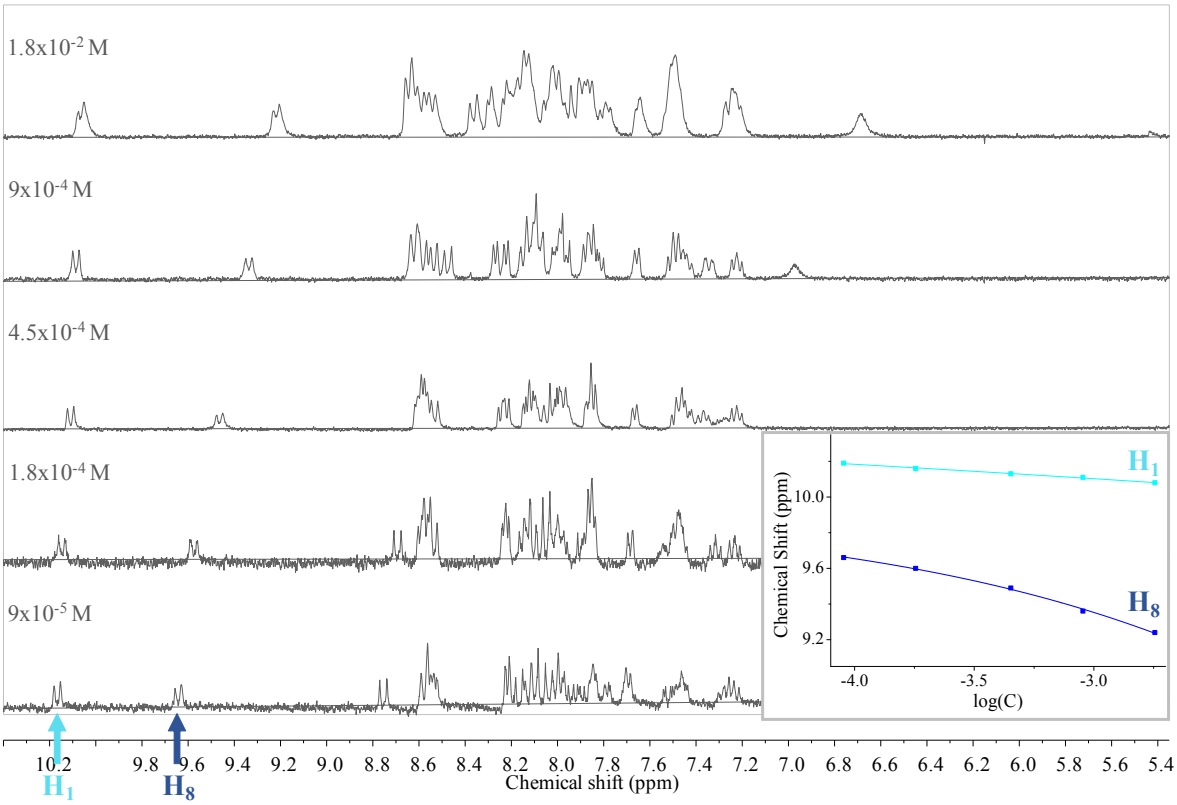


Figure S3 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)](Cl)_2$ in CD_3CN + 20% D_2O at different concentrations (inset : δ = f(log(C))).

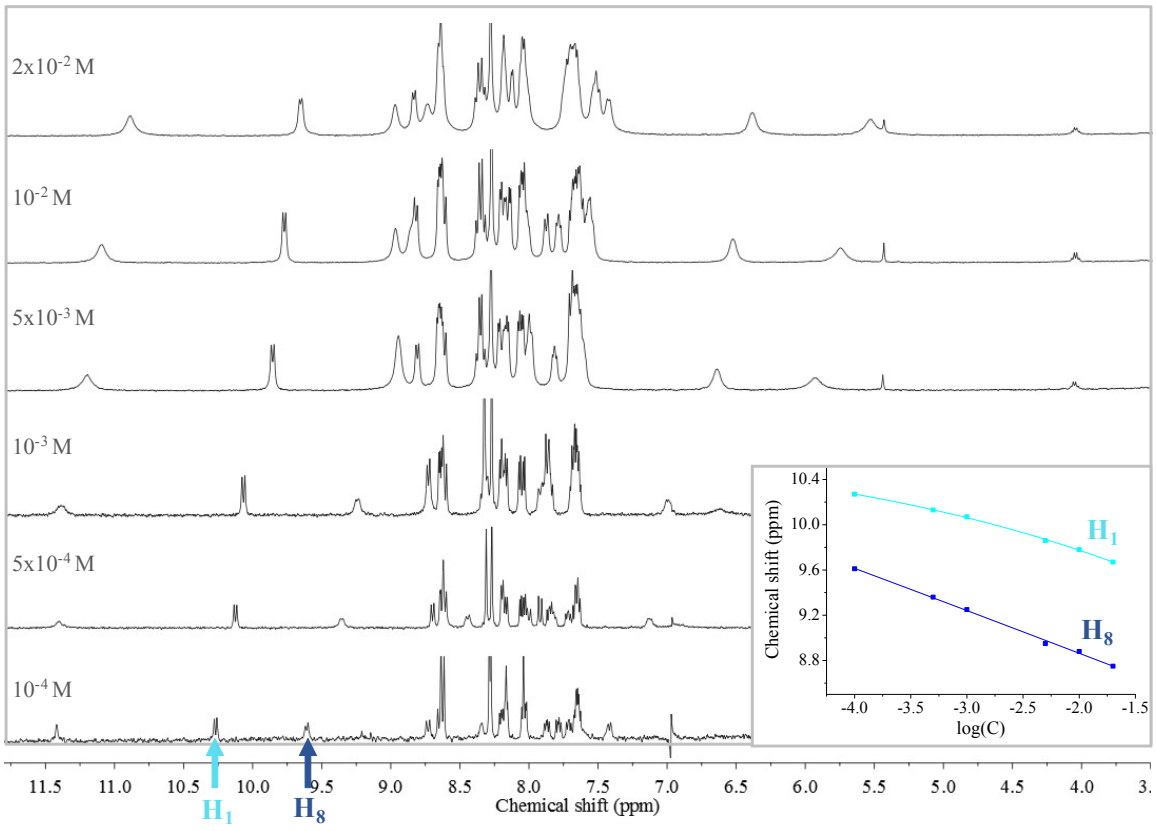


Figure S4 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(phen)_2(oxo\text{-}dpqp)](PF_6)_2$ in CD_3CN at different concentrations **(inset : δ = f(log(C))).**

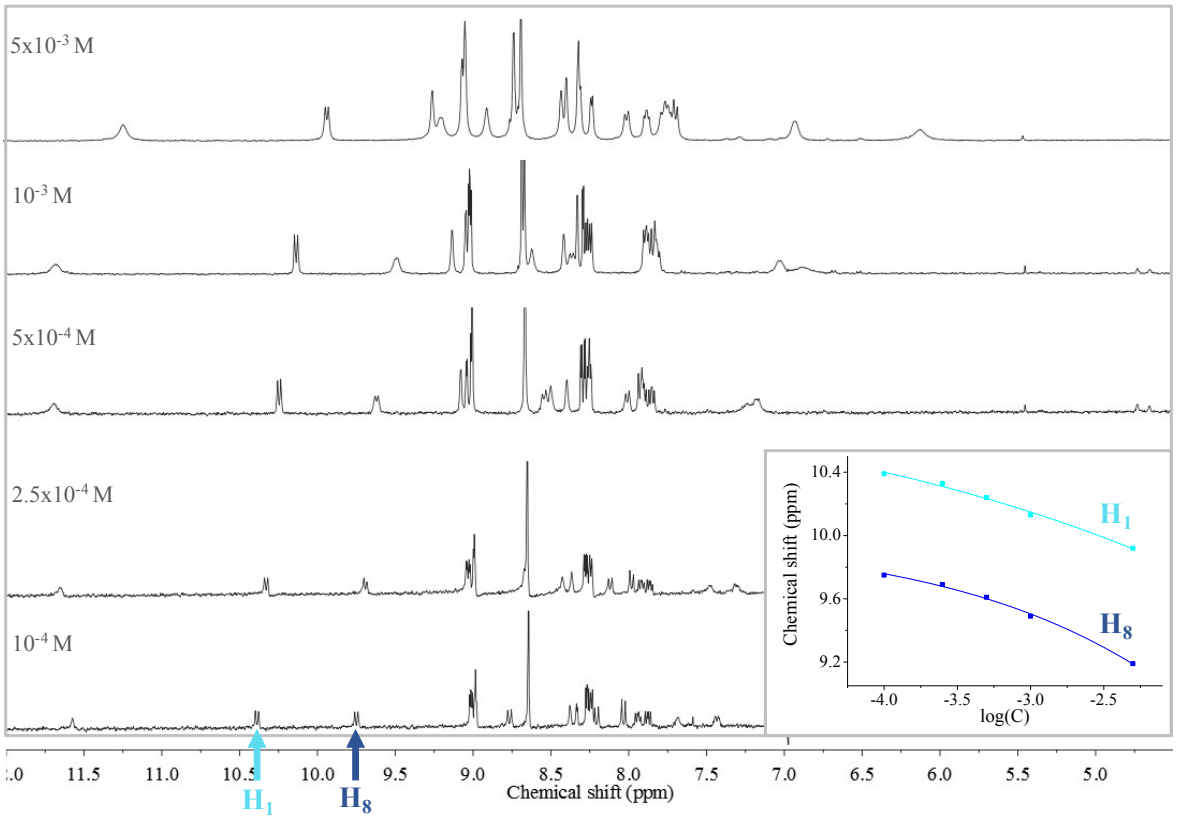


Figure S5 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(TAP)_2(oxo\text{-}dpqp)](PF_6)_2$ in CD_3CN at different concentrations **(inset : δ = f(log(C))).**

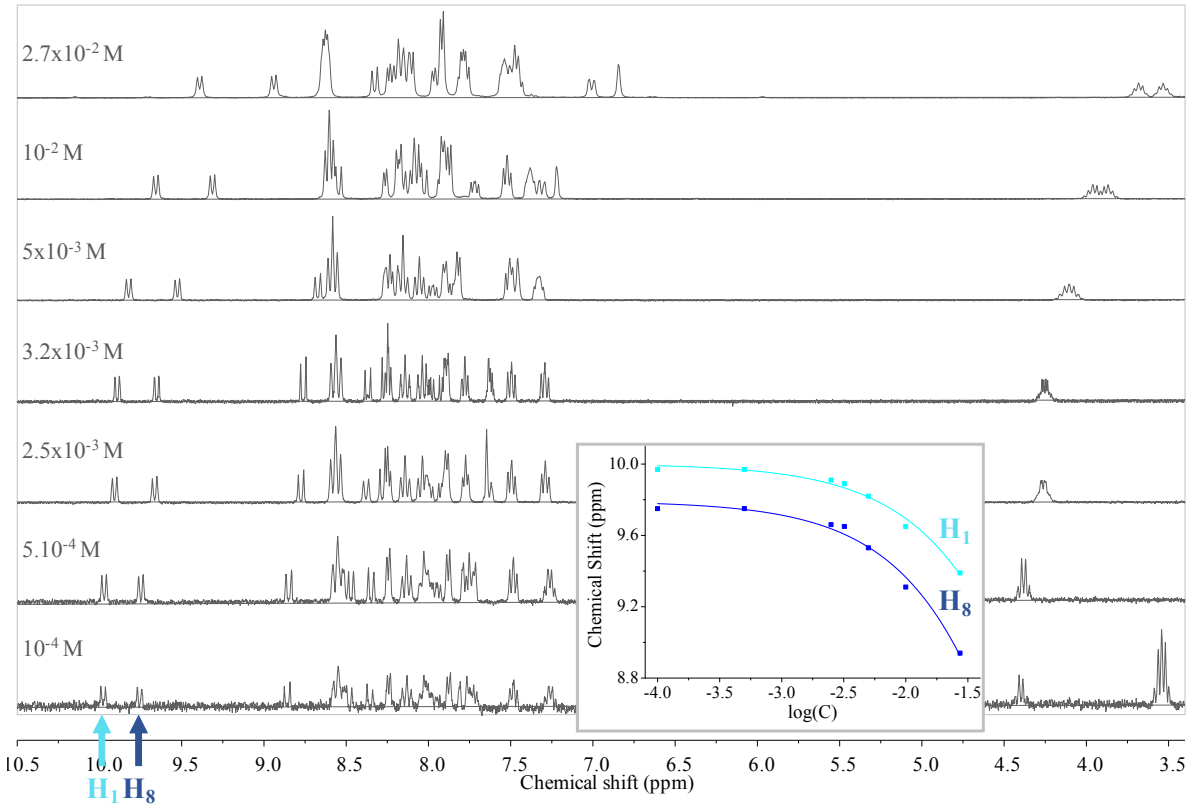


Figure S6 - ^{1}H NMR study of the π-π stacking of $[Ru^{II}(bpy)_2(Br\text{-}dpqp)](PF_6)_2$ in CD_3CN at different concentrations (inset : δ = f(log(C))).

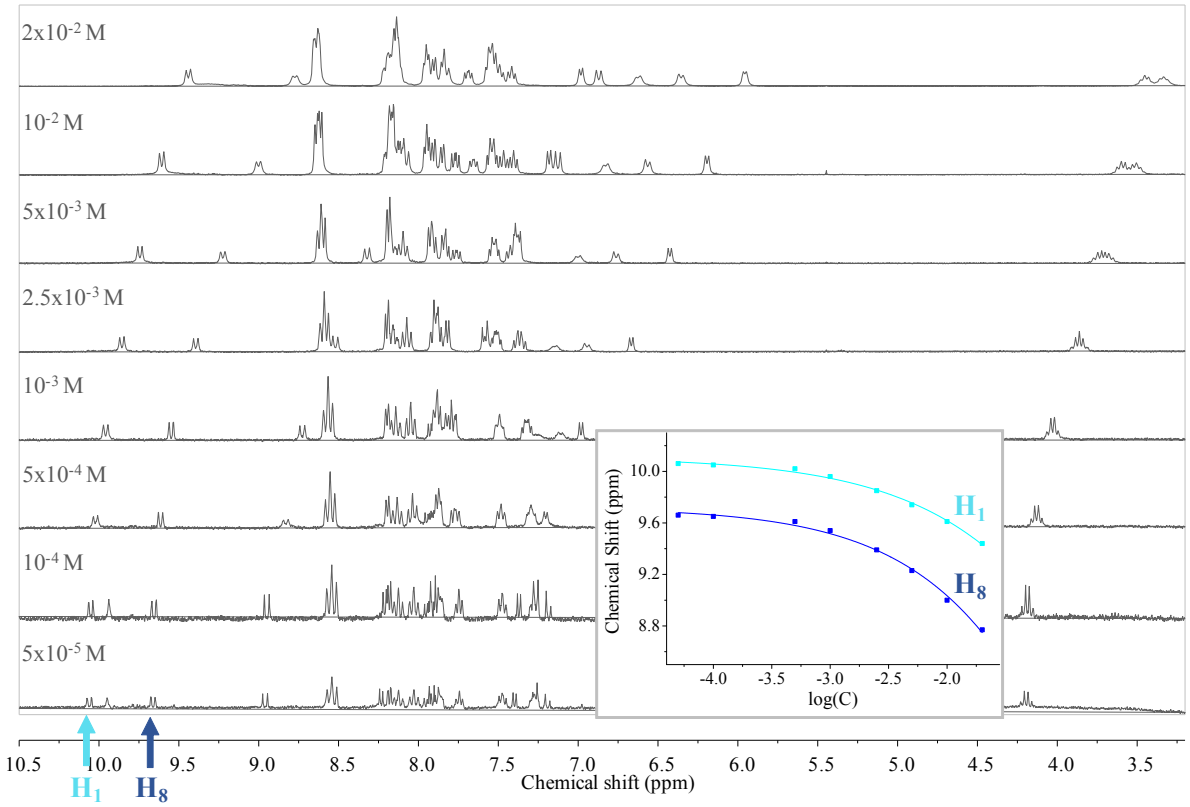


Figure S7 - ^{1}H NMR study of the **π-π** stacking of $[Ru^{II}(bpy)_2(dppqp)](PF_6)_2$ in CD_3CN at different concentrations (inset : δ = f(log(C))).

UV-vis measurements

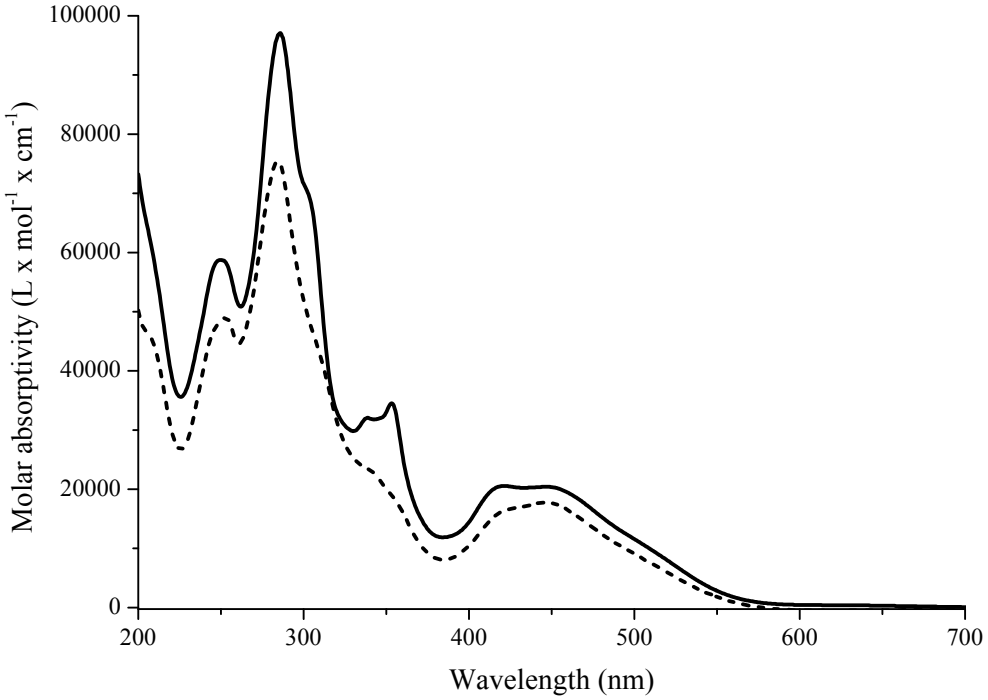


Figure S8 - UV-vis absorption spectra of $[Ru^{II}(bpy)_2(oxo\text{-}dpqp)]X_2$ recorded in CH_3CN (X = PF_6, plain line) and H_2O (X = Cl, dashed line).

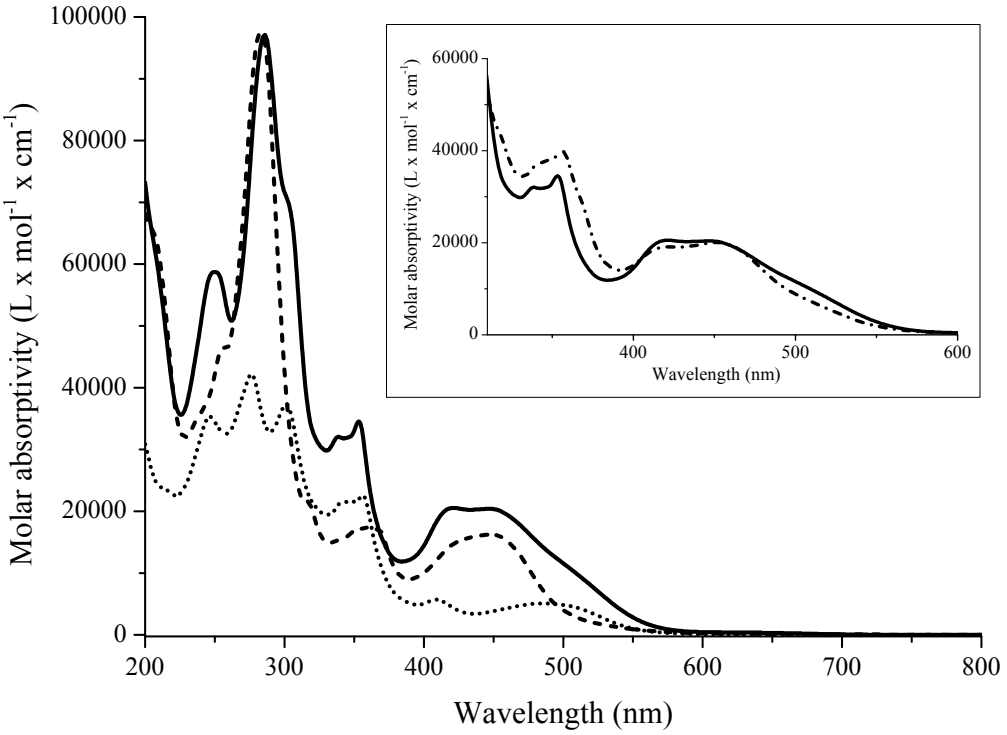


Figure S9 - UV-vis absorption spectra of $[Ru(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ (plain line), $[Ru(bpy)_2(dppz)](PF_6)_2$ (dashed line) and $[Zn(oxo\text{-}dpqp)](BF_4)_2$ (dotted line), recorded in CH_3CN. *Inset*: Superposition of the $[Ru(bpy)_2(oxo\text{-}dpqp)](PF_6)_2$ absorption in the visible region (plain line) with the sum of $[Ru(bpy)_2(dppz)](PF_6)_2$ and $[Zn(oxo\text{-}dpqp)](BF_4)_2$ absorptions (dashed line).

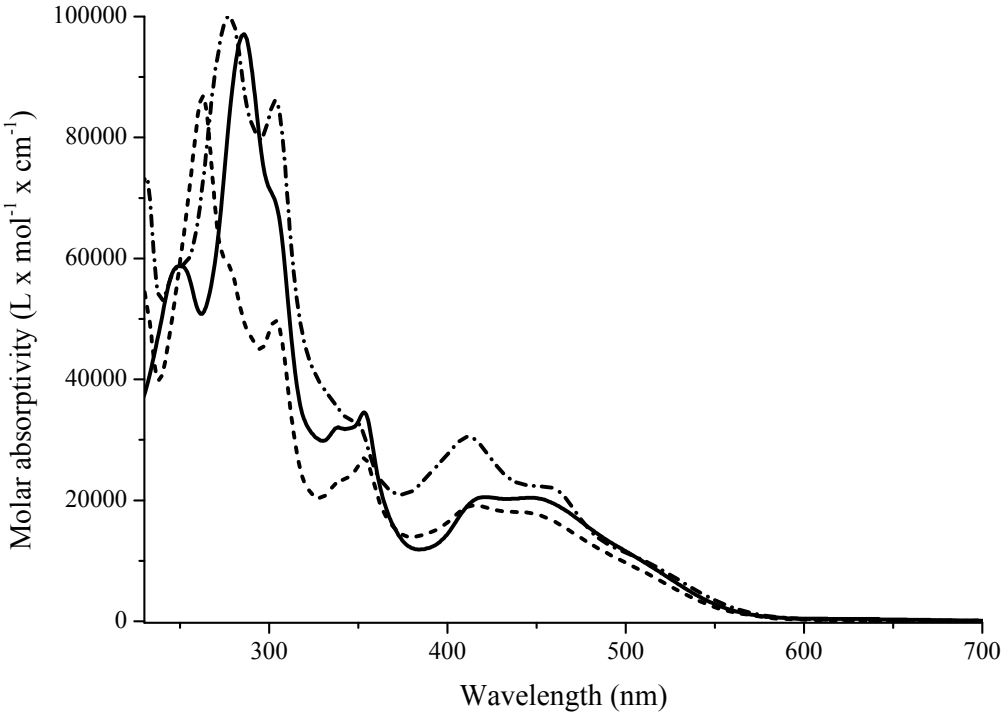


Figure S10 - UV-vis absorption spectra of $[Ru(L)_2(oxo\text{-}dpqp)](PF_6)_2$ (L = bpy in plain line, phen in dashed line or TAP in dashed dotted line), recorded in CH_3CN.

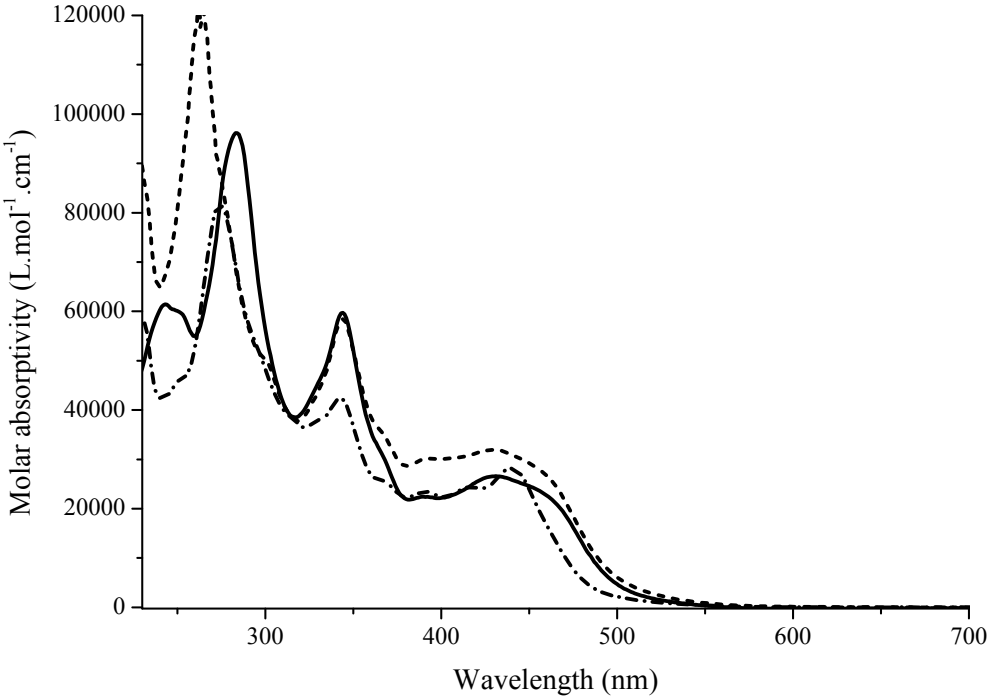


Figure S11 - UV-vis absorption spectra of $[Ru^{II}L_2(Cl\text{-}dpqp)](PF_6)_2$ (L = bpy in plain line, phen in dashed line or TAP in dashed dotted line) recorded in CH_3CN.

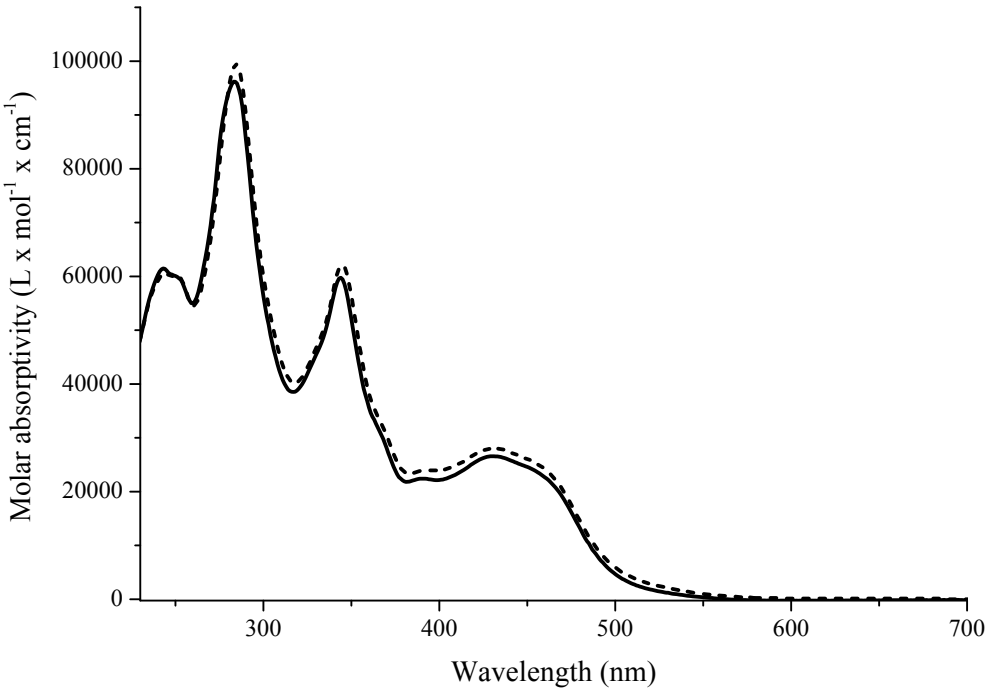


Figure S12 - UV-vis absorption spectra of $[Ru^{II}(bpy)_2(Cl\text{-}dpqp)](PF_6)_2$ (plain line) and $[Ru^{II}(bpy)_2(Br\text{-}dpqp)](PF_6)_2$ (dashed line) recorded in CH_3CN.

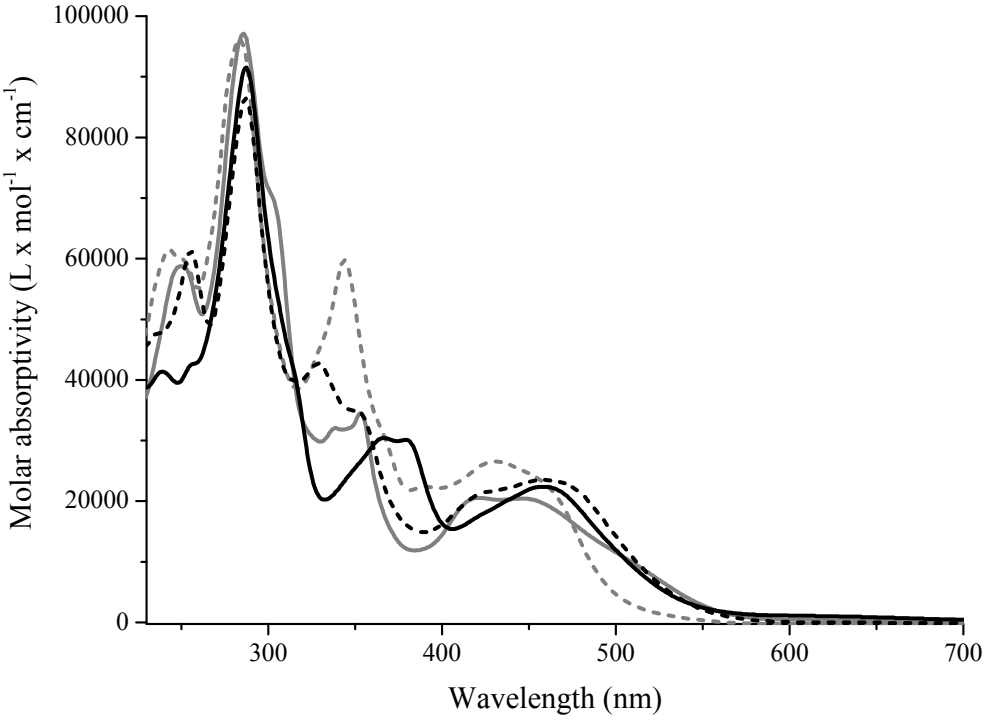


Figure S13 - UV-vis absorption spectra of $[Ru^{II}(bpy)_2L](PF_6)_2$ recorded in CH_3CN (L=oxo-dpqp in plain grey, Cl-dpqp in dashed grey, DMEA-dpqp in dashed black and dppqp in plain black line).

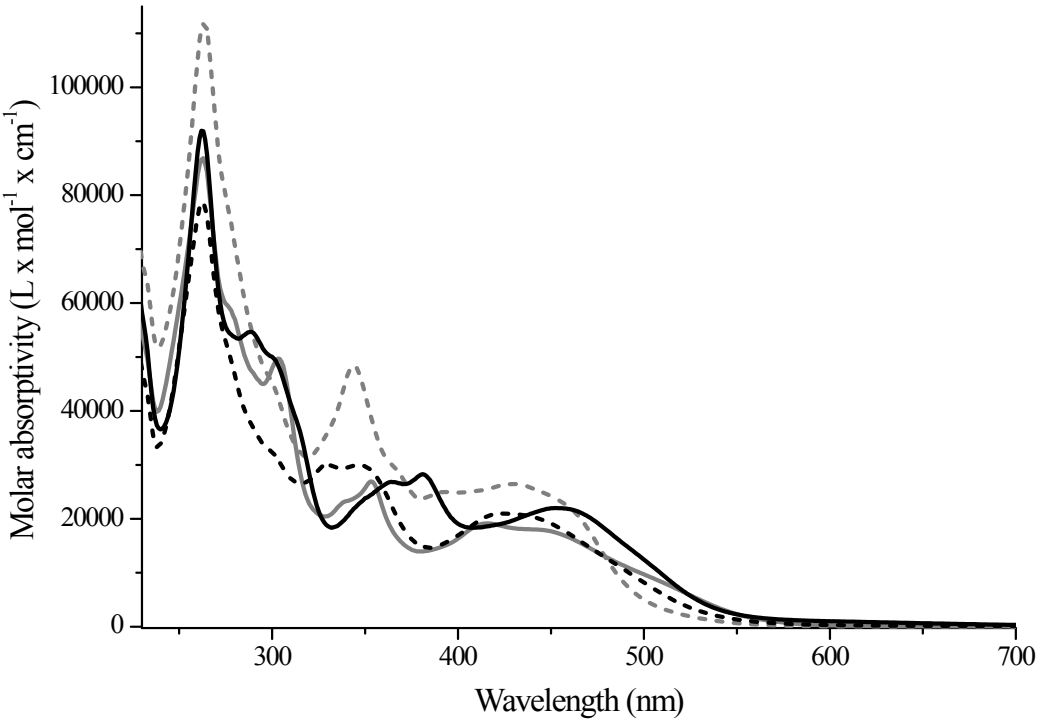


Figure S14 - UV-vis absorption spectra of $[Ru^{II}(phen)_2(L)](PF_6)_2$ recorded in CH_3CN (L=oxo-dpqp in plain grey, Cl-dpqp in dashed grey, DMEA-dpqp in dashed black and dppqp in plain black line).

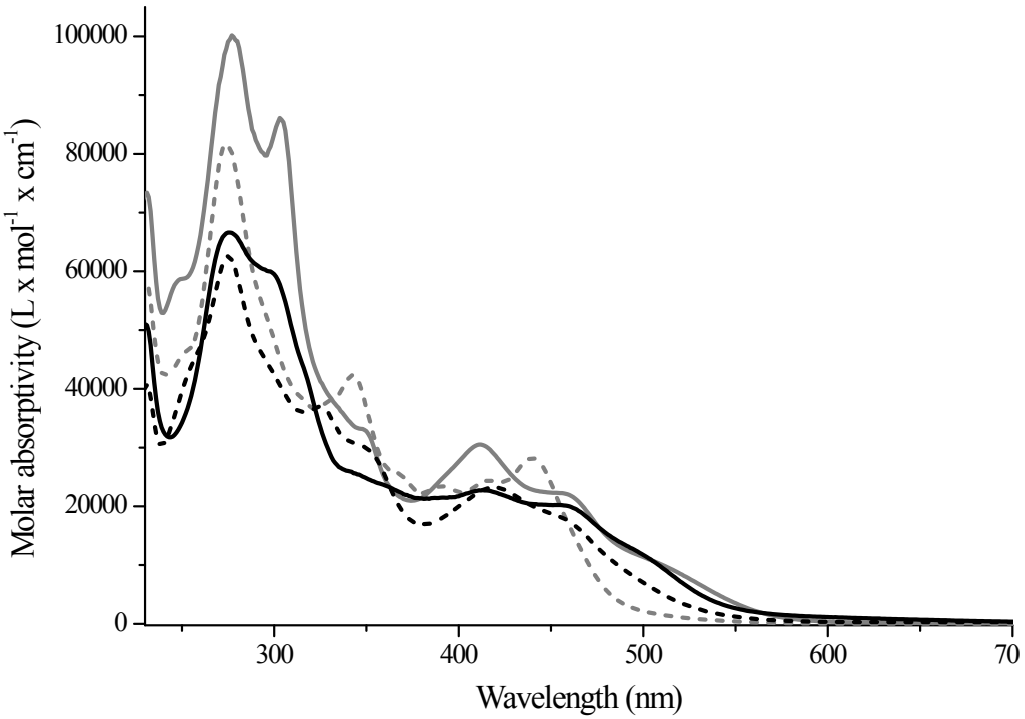


Figure S15 - UV-vis absorption spectra of $[Ru^{II}(TAP)_2L](PF_6)_2$ recorded in CH_3CN (L=oxo-dpqp in plain grey, Cl-dpqp in dashed grey, DMEA-dpqp in dashed black and dppqp in plain black line).

Computational details

Quantum chemical calculations were performed for the complexes: $[Ru(bpy)_2(oxo\text{-}dpqp)]^{2+}$, $[Ru(bpy)_2(Br\text{-}dpqp)]^{2+}$ and $[Ru(bpy)_2(dppqp)]^{2+}$ using the Gaussian 09 program[6], while both tautomeric forms of $[Ru(bpy)_2(oxo\text{-}dpqp)]^{2+}$, 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 ωB97X-D[7] XC functional. The 6-31G(d) double-ζ 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_3CN, $\varepsilon = 35.688$, $n = 1.344$) 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 π-π stacking interactions was evaluated. Therefore, geometry optimizations and subsequent frequency analyses for $[Ru(bpy)_2(oxo\text{-}dpqp)]^{2+}$ (only carried out for the more stable 12-acridone tautomer), $[Ru(bpy)_2(Br\text{-}dpqp)]^{2+}$ 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[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_3CN) 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.

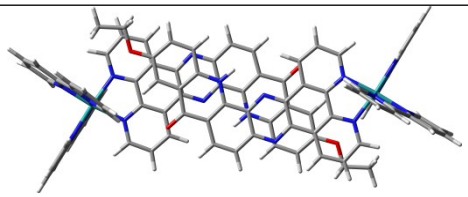
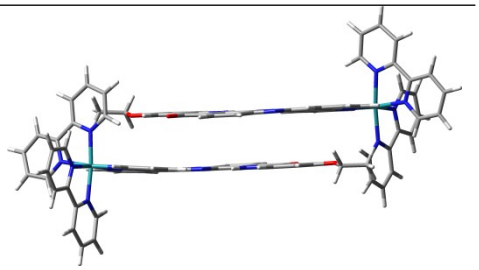
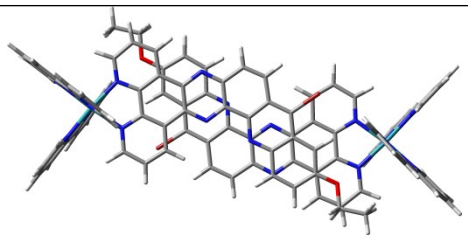
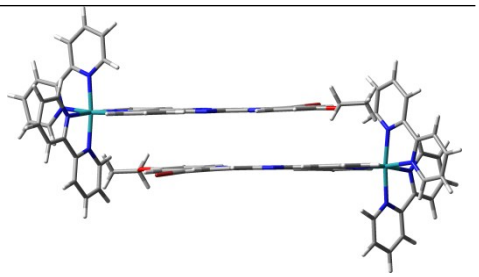
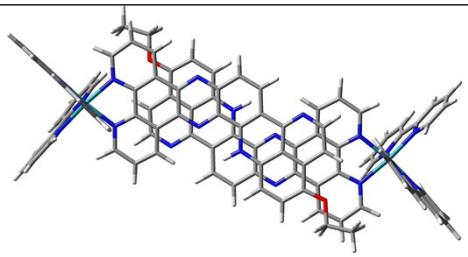
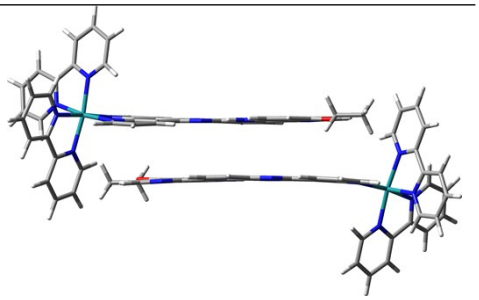
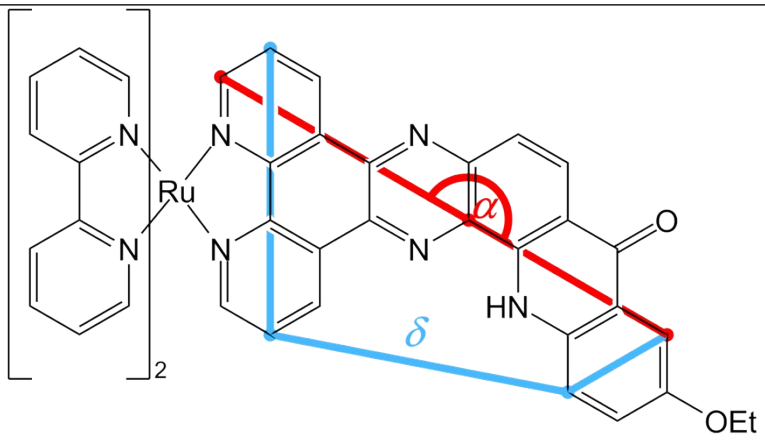
$[Ru(bpy)_2(oxo-dpqp)]^{4+}_2$		
E_{dimer} / kJ/mol (eV)		
112 kJ/mol (1.16 eV)		
$d_{stacking}$ / Å		
3.2-3.3		
$[Ru(bpy)_2(Br-dpqp)]^{4+}_2$		
E_{dimer} / kJ/mol (eV)		
115 kJ/mol (1.19 eV)		
$d_{stacking}$ / Å		
3.2-3.3		
$[Ru(bpy)_2(dppqp)]^{4+}_2$		
E_{dimer} / kJ/mol (eV)		
107 kJ/mol (1.10 eV)		
$d_{stacking}$ / Å		
3.2-3.3		

Table S1: Fully optimized dimer structures of $[Ru(bpy)_2(oxo\text{-}dpqp)]_2^{4+}$, $[Ru(bpy)_2(Br\text{-}dpqp)]_2^{4+}$ and $[Ru(bpy)_2(dppqp)]_2^{4+}$, π–π stacking distances ($d_{stacking}$) and bonding energies (E_{dimer}).



	α / °	δ / °	α / °	δ / °	α / °	δ / °
	$[Ru(bpy)_2(oxo\text{-}dpqp)]^{2+}$		**$[Ru(bpy)_2(Br\text{-}dpqp)]^{2+}$**		**$[Ru(bpy)_2(dppqp)]^{2+}$**	
Monomer	177	1	178	1	178	2
Dimer	177	2	177	1	177	1
	177	4	178	5	177	7

Table S2: Planarity of the dpqp/dppqp ligand within the optimized equilibrium structures of the monomer and the dimer species described by bending angle α (in red) and dihedral angle δ (in blue).

Bibliography

1. R. Dinica, F. Charmantray, M. Demeunynck and P. Dumy, *Tetrahedron Lett.*, 2002, **43**, 7883-7885.
2. C. A. Goss, H. D. Abruna, *Inorg. Chem*. 1985, **24**, 4263-4267.
3. C. Moucheron, A. Kirsch-De Mesmaeker and S. Choua. *Inorg. Chem.* **1997**, 36, 584-592
4. C. Moucheron, A. Kirsch-De Mesmaeker, *J. Phys. Org. Chem.* **1998**, *11*, 577-583.
5. L. Bouffier, M. Demeunynck, P. Dumy, C. Moucheron and A. Kirsch-De Mesmaeker, *Inorg. Chim. Acta*, 2007, **360**, 3162-3168.
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ã. d. n. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, Editon edn., 2009.
7. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620.
8. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.*, 1973, **28**, 213-222.
9. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta.*, 1990, **77**, 123-141.
10. B. Mennucci, C. Cappelli, C. A. Guido, R. Cammi and J. Tomasi, *J. Phys. Chem. A*, 2009, **113**, 3009-3020.