Hydrogen-bond strengthening upon photoinduced electron transfer in ruthenium-anthraquinone dyads interacting with hexafluoroisopropanol or water

Supporting Information

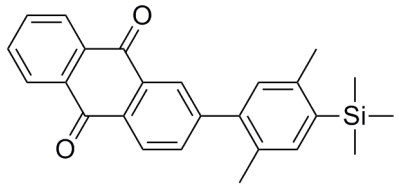
Jihane Hankache, David Hanss, and Oliver S. Wenger*

Georg-August Universität Göttingen, Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany. E-mail: oliver.wenger@chemie.uni-goettingen.de

Contents

Synthetic protocols and product characterization data – organic ligands

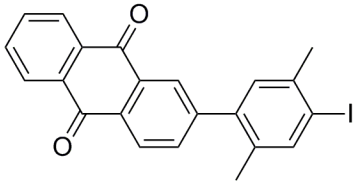
TMS-xy_1-AQ



2-bromoanthraquinone (5.00 g, 17.4 mmol), 4-trimethylsilyl-2,5-dimethylphenylboronic acid (TMS-xy_1-$B(OH)_2$) [2] (4.64 g, 0.02 mol) and a solution of Na_2CO_3 (5.53 g, 52.2 mmol) in de-ionized water were dissolved in a solvent mixture comprised of 30 ml toluene and 5 ml ethanol. The solution was deoxygenated for 30 minutes before adding the $Pd(PPh_3)_4$ catalyst and heating to reflux overnight. The product was extracted with CH_2Cl_2 and purified by silica gel column chromatography. The eluent was a 1:1 pentane/dichloromethane mixture. A yellow solid was obtained (6.45 g, 96% yield).

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 0.38 (s, 9 H, TMS), 2.30 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 7.11 (s, 1 H, xy), 7.4 (s, 1 H, xy), 7.82 (m, 3 H, AQ), 8.35 (m, 4 H, AQ).

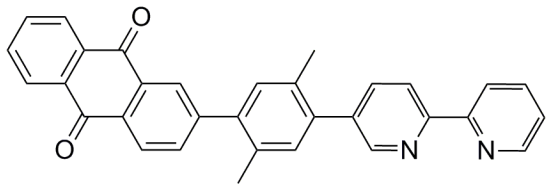
I-xy_1-AQ



TMS-xy_1-AQ (4.47 g, 0.011 mol) was dissolved in dichloromethane (20 ml). ICl (3.78 g, 0.023 mol) in an acetonitrile solution (80 ml) was added dropwise under nitrogen at 0°C to the dichloromethane solution. After stirring at room temperature overnight, the mixture was washed with an aqueous solution of $Na_2S_2O_3$ (5% in water, 250 ml). The two resulting phases were separated. Afterwards, the yellow organic phase was dried over $MgSO_4$ and filtered. The solvent was evaporated, and the desired product was obtained as a yellow powder in essentially quantitative yield.

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 2.23 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 7.14 (s, 1 H, xy), 7.73 (dd, *J* = 8.0 Hz, 2.0 Hz, 1 H, AQ), 7.79 (s, 1 H, AQ), 7,83 (m, 2 H, AQ), 8.25 (d, *J* = 1.6 Hz, 1 H, xy), 8.35 (m, 3 H, AQ).

bpy-xy$_1$-AQ

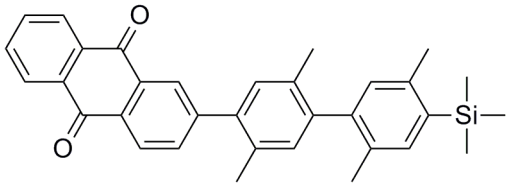


$Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) was added under inert atmosphere to a stirred and deoxygenated suspension of I-xy$_1$-AQ (0.30 g, 0.68 mmol) and 5-(tri-*n*-butylstannyl)-2,2'-bipyridine (0.40 g, 0.90 mmol) in *m*-xylene (30 ml). The yellow suspension was deoxygenated for an additional 10 minutes, and then the reaction was carried out at reflux during 48 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The dark brown remaining solid was purified by three consecutive silica gel column chromatographies, using a mixture of CH_2Cl_2/CH_3OH (9/1) to give the product as a yellow solid (0.12 g, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 2.35 (m, 6 H, *J* = 3.2 Hz, CH_3), 7.27 (s, 1 H, xy), 7.34 (ddd, *J* = 4.8 Hz, 1.2 Hz, 0.8 Hz, 1 H, xy), 7.85 (m, 5 H, AQ), 8.35 (m, 3 H), 8.40 (d, *J* = 8.0 Hz, 1 H, bpy), 8.46 (td, *J* = 8.0 Hz, 0.8 Hz, 1 H, bpy), 8.5 (dd, *J* = 8.0 Hz, 0.8 Hz, 1 H, AQ), 8.72 (m, 2 H, bpy).

Anal. Calcd. for $C_{32}H_{22}N_2O_2 \cdot 0.6\ CH_3OH$: C 80.61, H 5.06, N 5.77. Found C 80.25, H 4.70, N 5.77.

TMS-xy$_2$-AQ

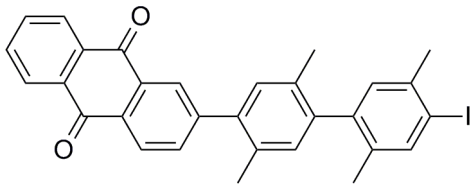


I-xy-AQ (3.00 g, 6.84 mmol) and TMS-xy-$B(OH)_2$ [2] (1.67 g, 7.55 mmol) were dissolved together in toluene (100 ml). Then, a solution of Na_2CO_3 (2.18 g, 0.02 mol) in de-ionized water (20 ml) was added.

The yellow mixture was deoxygenated by bubbling nitrogen gas during 30 minutes. After addition of the $Pd(PPh_3)_4$ catalyst (0.395 g, 0.14 mmol), the reaction mixture was heated to 90°C overnight under nitrogen atmosphere. After cooling to room temperature, the organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure. A yellow solid was obtained, and the raw product was purified by silica gel column chromatography using an 80% pentane / 20% dichloromethane eluent mixture (3.18 g, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 0.37 (s, 9 H, TMS), 2.11 (s, 6 H, CH_3), 2.30 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 6.96 (s, 1 H, xy), 7.07 (s, 1 H, xy), 7.55 (s, 1 H, xy), 7.35 (s, 1 H, xy), 7.82 (m, 3 H, AQ), 8.35 (m, 4 H, AQ).

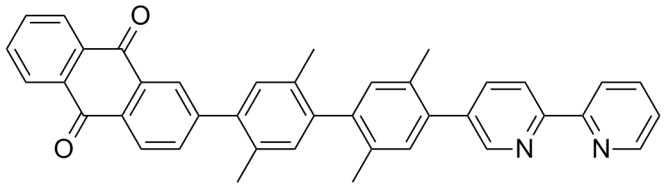
I-xy$_2$-AQ



TMS-xy$_2$-AQ (3.18 g, 6.51 mmol) was dissolved in dichloromethane (80 ml). ICl (2.11 g, 0.013 mol) in an acetonitrile solution (60 ml) was added dropwise under inert atmosphere at 0°C. After stirring for one night at room temperature, excess iodine monochloride was destroyed by adding an aqueous saturated solution of $Na_2S_2O_3$. The organic phase was extracted with CH_2Cl_2, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to give a yellow powder (3.1 g, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 2.05 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 7.02 (s, 2 H, xy), 7.19 (s, 1 H, xy), 7.75 (s, 1 H, xy), 7.83 (m, 3 H, AQ), 8.36 (m, 4 H, AQ).

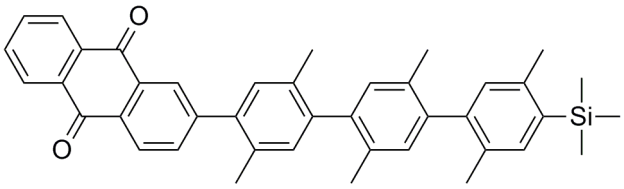
bpy-xy$_2$-AQ



For the Stille coupling reaction, I-xy$_2$-AQ (0.31 g, 0.57 mmol) was dissolved in *m*-xylene (30 ml) with 5-(tri-*n*-butylstannyl)-2,2'-bipyridine [1] (0.33 g, 0.74 mmol). The Pd(PPh$_3$)$_4$ catalyst (0.066 g, 0.057 mmol) was added once the mixture was deoxygenated by bubbling nitrogen gas for 15 minutes. Afterwards, an additional deoxgenation was carried out, and the solution was heated to reflux under nitrogen during 2 days. The solvent was evaporated, and the resulting black solid was chromatographed on silica gel using a 99:1 dichloromethane/methanol eluent mixture affording a light yellow solid (0.11 g, 35% yield).

^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ [ppm] = 2.16 (s, 6 H, CH$_3$), 2.33 (d, *J* = 3 Hz, 6 H, CH$_3$), 7.12 (s, 2 H, CH$_3$, xy), 7.22 (d, *J* = 3 Hz, 2 H, xy), 7.33 (ddd, *J* = 3 Hz, 6 Hz, 9 Hz, 1 H, bpy), 7.85 (m, 5 H), 8.36 (m, 4 H), 8.47 (m, 2 H, bpy), 8.72 (ddd, *J* = 0.87 Hz, 1.7 Hz, 4.8 Hz, 1 H, bpy), 8.75 (dd, *J* = 0.72 Hz, 2.2 Hz, 1 H, bpy).

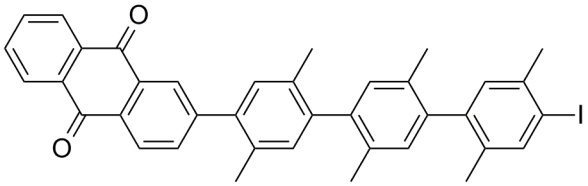
TMS-xy$_3$-AQ



I-xy$_2$-AQ (2.80 g, 5.16 mmol) and TMS-xy-B(OH)$_2$ [2] (1.26 g, 5.68 mmol) were dissolved in toluene (100 ml) and ethanol (20 ml). A solution of Na$_2$CO$_3$ (1.64 g, 0.015 mol) in de-ionized water (20 ml) was added, and the yellow solution was deoxygenated by bubbling nitrogen gas during 30 minutes. Pd(PPh$_3$)$_4$ catalyst (0.30 g, 0.26 mmol) was added, followed by heating the mixture to 90°C overnight. After cooling to room temperature, the organic layer was extracted with CH$_2$Cl$_2$, dried over MgSO$_4$, and filtered. The solvent was removed under reduced pressure. A yellow solid was obtained. This raw product was purified by silica gel column chromatography using a mixture of pentane/dichloromethane (first 8:2 and then 1:1) to give the pure product (2.40 g, 78% yield).

1H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 0.37 (s, 9 H, TMS), 2.08 (s, 3 H, CH_3), 2.11 (m, 6 H, CH_3), 2.15 (d, *J* = 5.2 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 6.99 (s, 1 H, xy), 7.03 (t, *J* = 5.2 Hz, 2 H, xy), 7.15 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.35 (s, 1 H, xy), 7.84 (m, 3 H, AQ), 8.37 (m, 4 H, AQ).

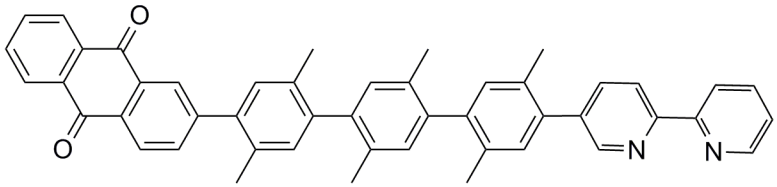
I-xy$_3$-AQ



To a solution of TMS-xy$_3$-AQ (1.25 g, 2.10 mmol) in dichloromethane (80 ml), ICl (0.69 g, 4.21 mmol) dissolved in acetonitrile (60 ml) was added dropwise under inert atmosphere at 0°C. After stirring at room temperature overnight, an aqueous saturated solution of $Na_2S_2O_3$ was added. The organic layer was extracted with CH_2Cl_2, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure. This yielded a yellow powder (1.18 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 0.37 (s, 9 H, TMS), 2.11 (s, 6 H, CH_3), 2.30 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 6.96 (s, 1 H, xy), 7.07 (s, 1 H, xy), 7.55 (s, 1 H, xy), 7.35 (s, 1 H, xy), 7.82 (m, 3 H, AQ), 8.35 (m, 4 H, AQ).

bpy-xy$_3$-AQ



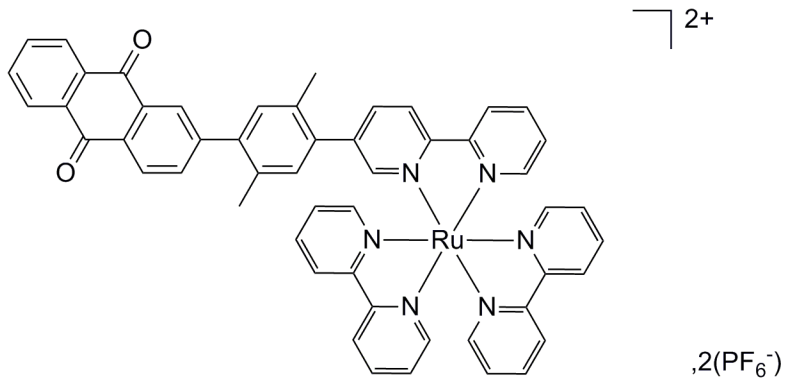
$Pd(PPh_3)_4$ catalyst (0.053 g, 0.04 mmol) was added to a deoxygenated solution of I-xy$_3$-AQ (0.30 g, 0.46 mmol) and 5-(tri-*n*-butylstannyl)-2,2'-bipyridine [1] (0.27 g, 0.60 mmol) in 30 ml of *m*-xylene. The reaction mixture was heated to reflux for 48 hours. The desired yellow compound was obtained after evaporation of the solvent and subsequent purification with silica gel column chromatography using dichloromethane with up to 1% of methanol as the eluent (0.08 g, 26% yield).

^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ [ppm] = 2.13 (s, 6 H, CH_3), 2.16 (m, 6 H, CH_3), 2.34 (s, 6 H, CH_3), 7.07 (m, 2 H, xy), 7.16 (s, 2 H, xy), 7.21 (s, 1 H, xy), 7.23 (s, 1 H, xy), 7.35 (m, 1 H, bpy), 7.85 (m, 5 H), 8.41 (m, 4 H, AQ), 8.47 (m, 2 H, bpy), 8.72 (m, 1 H, bpy), 8.76 (m, 1H, bpy).

Anal. Calcd. for $C_{48}H_{38}N_2O_2 \cdot 0.45\ CH_3OH$: C 84.43, H 5.82, N 4.06. Found C 84.72, H 5.59, N 4.08.

Synthetic protocols and product characterization data – metal complexes

Ru-xy$_1$-AQ



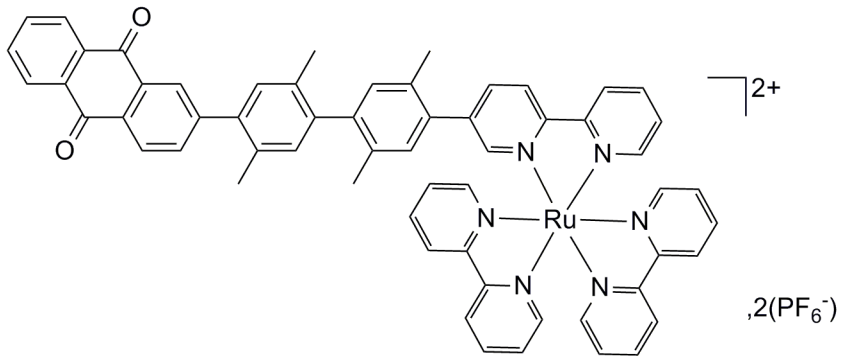
A suspension of bpy-xy$_1$-AQ (0.05 g, 0.1mmol) and $Ru(bpy)_2Cl_2$ (0.058 g, 0.1 mmol) in a mixture of $CHCl_3$/EtOH (3/10) was heated to reflux overnight under nitrogen atmosphere. The resulting red-orange solution was evaporated under reduced pressure. The remaining dark solid was purified by column chromatography on silica gel, using first pure acetone, then a mixture of acetone/H_2O/aqueous saturated KNO_3 (90/10/1) as the eluent. The resulting product was dissolved in minimum of acetone, and a saturated solution of KPF_6 in water was added. The orange precipitate was filtered, washed with water and diethyl ether, and finally dried under vacuum. The yield was 78%.

^{1}H NMR: (400 MHz, CD_3CN, 25°C): δ [ppm] = 2.02 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 7.13 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.44 (m, 5 H), 7.65 (d, *J* = 5.6 Hz, 1 H), 7.76 (d, *J* = 5.6 Hz, 3 H), 7.80 (d, *J* = 5.6 Hz, 1 H), 7.82 (d, *J* = 1.6 Hz, 8 Hz, 1 H), 7.90 (m, 3 H), 8.08 (m, 7 H), 8.19 (d, *J* = 1.6 Hz, 1 H), 8.30 (m, 3 H), 8.56 (m, 8 H).

ES-MS m/z = 440.1056 (calculated 440.1044 for $C_{52}H_{38}O_2N_6Ru^{2+}$).

Anal. Calcd. for $C_{52}H_{38}N_6O_2RuP_2F_{12} \cdot H_2O \cdot CH_3COCH_3$: C 53.02, H 3.72, N 6.74. Found: C 53.03, H 3.59, N 6.66.

Ru-xy$_2$-AQ



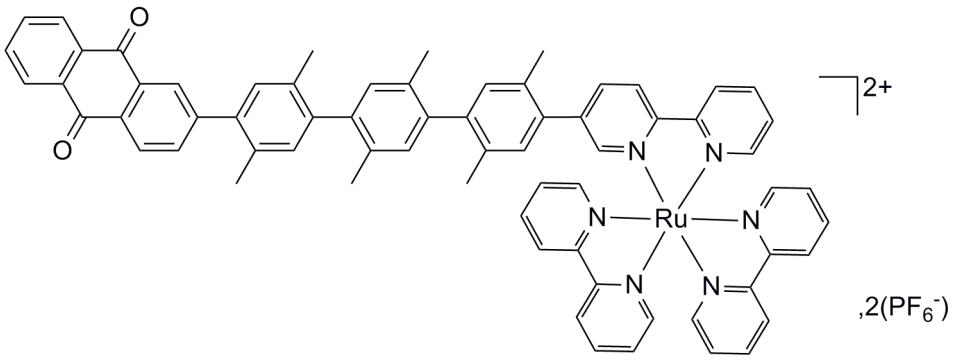
Ru-xy$_2$-AQ was obtained by refluxing bpy-xy$_2$-AQ (0.05 g, 0.087 mmol) and Ru(bpy)$_2$Cl$_2$ (0.04 g, 0.087 mmol) in a chloroform / ethanol mixture (3 ml / 10 ml) overnight. After removal of the solvent, the solid was chromatographed on silica gel using an eluent mixture comprised of 90% acetone, 9% water and 1% saturated aqueous solution of KNO_3. The acetone was evaporated, and the desired complex was precipitated by adding a saturated aqueous KPF_6 solution. The resulting red orange solid was isolated by filtration, washed with water and diethyl ether, and dried under vacuum (0.08 g, 72% yield).

^{1}H NMR (300 MHz, CD3CN, 25°C): δ [ppm] = 1.96 (m, 3 H, CH_3), 2.04 (m, 6 H, CH_3), 2.28 (s, 3 H, CH_3), 7.01 (s, 2 H, xy), 7.09 (d, *J* = 3.5 Hz, 1 H, xy), 7.27 (s, 1 H, xy), 7.44 (m, 5 H), 7.68 (m, 1 H), 7.76 (m, 4 H), 7.89 (m, 4 H), 8.07 (m, 6 H), 8.29 (m, 4 H), 8.52 (m, 5 H), 8.58 (m, 1 H).

ES-MS: m/z = 492.1363 (calculated 492.1363 for $C_{60}H_{46}N_6O_2Ru^{2+}$)$^{\cdot}$.

Anal. Calcd. for $C_{60}H_{46}N_6O_2RuP_2F_{12} \cdot$ xylene: C 59.17, H 4.09, N 6.09. Found: C 58.96, H 4.06, N 6.34.

Ru-xy$_3$-AQ



To a solution of bpy-xy$_3$-AQ (0.04 g, 0.06 mmol) in 3 ml of $CHCl_3$ was added a solution of $Ru(bpy)Cl_2$ (0.029 g, 0.06 mmol) in ethanol. The mixture was deoxygenated by bubbling nitrogen for 15 minutes, and then it was put to reflux overnight. The next day, the solvents were evaporated and the product was chromatographed on silica gel using a mixture of acetone/water/aqueous saturated solution of KNO_3 (80/19/1). After removing acetone, an aqueous saturated solution of KPF_6 was added, leading to an orange precipitate. The latter was filtrated, washed with water and diethyl ether, and dried under vaccum (0.07 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 1.99 (m, 6 H, CH_3), 2.07 (m, 12 H, CH_3), 2.29 (s, 3 H, CH_3), 6.96 (s, 1 H, xy), 7.01 (s, 1 H, xy), 7.07 (m, 2 H, xy), 7.26 (s, 1 H, xy), 7.21 (s, 1 H, xy), 7.45 (m, 5 H), 7.82 (m, 5 H), 7.88 (m, 4 H), 8.08 (m, 6 H), 8.26 (m, 4 H), 8.56 (m, 6 H).

ES-MS: m/z = 544.1682 (calculated 544.1676 for $C_{68}H_{54}N_6O_2Ru^{2+}$)$^{\cdot}$.

Anal. Calcd. for $C_{68}H_{54}N_6O_2RuP_2F_{12}\cdot 1.5H_2O$: C 58.12, H 4.09, N 5.98. Found: C 58.06, H 4.09, N 5.82.

References

[1] D. Hanss, O. S. Wenger, *Inorg. Chem.* **2009**, *48*, 671-680 and references therein.

[2] J. Hankache, O. S. Wenger, *Chem. Commun*. **2011**, 47, 10145-10147.

Additional cyclic voltammetry data

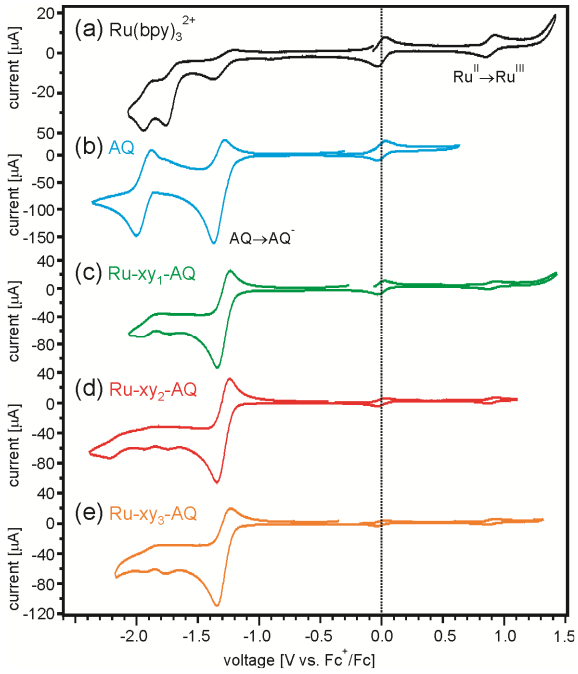


Figure S1. Cyclic voltammograms measured on the $Ru(bpy)_3^{2+}$ reference complex, 9,10-anthraquinone (AQ), and the Ru-xy_n-AQ dyads in dry and deoxygenated CH_3CN in presence of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) electrolyte. Traces of ferrocene (Fc) were added for internal voltage calibration; the wave at 0.0 V is due to the Fc^+/Fc couple.

Additional luminescence lifetime data

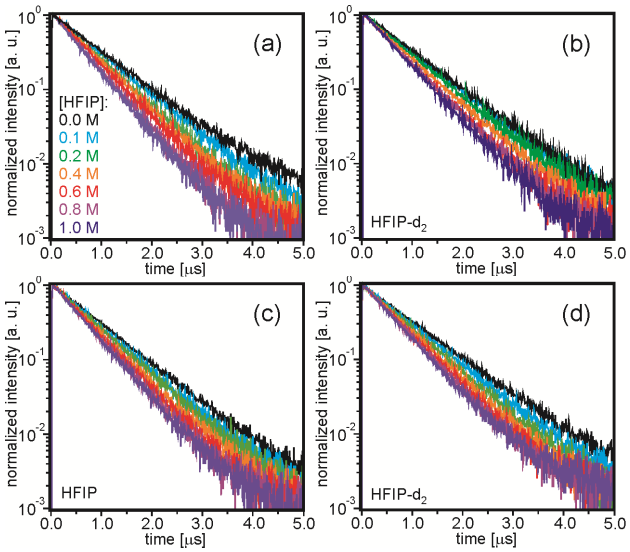


Figure S2. ^{3}MLCT luminescence decays of the $Ru(bpy)_3^{2+}$ unit in two different compounds in deoxygenated CH_2Cl_2 in presence of increasing concentrations of HFIP; the concentration of the emissive compounds was ~10^{-5} M; in all cases the HFIP concentration was as indicated in the legend in panel (a). Excitation occurred at 450 nm with laser pulses of 10 ns width, detection was at 610 nm. The emissive samples were: (a) Ru-xy_2-AQ in presence of ordinary HFIP; (b) Ru-xy_2-AQ in presence of deuterated HFIP (HFIP-d_2); (c) Ru-xy_3-AQ in presence of ordinary HFIP; (c) Ru-xy_3-AQ in presence of deuterated HFIP (HFIP-d_2). In all cases the data was normalized to an initial intensity of 1 (in arbitrary units).