Photoinduced electron transfer in covalent ruthenium-anthraquinone dyads: Relative importance of driving-force, solvent polarity, and donor-bridge energy gap

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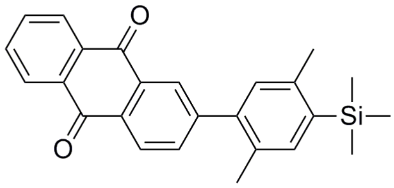
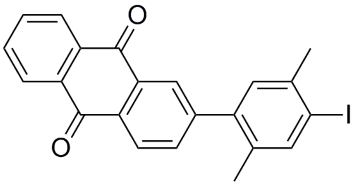
Molecule **4a**



2-bromoanthraquinone (**3**) (5.00 g, 17.4 mmol), 4-trimethylsilyl-2,5-dimethylphenylboronic acid (**2a**) [1] (4.64 g, 0.02 mol) and a solution of Na_2CO_3 (5.53 g, 52.2 mmol) in de-ionized water were added to a solvent mixture comprised of 30 ml toluene and 5 ml ethanol. The reaction mixture was deoxygenated for 30 minutes before adding the $Pd(PPh_3)_4$ catalyst and heating to reflux overnight. The product **4a** 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).

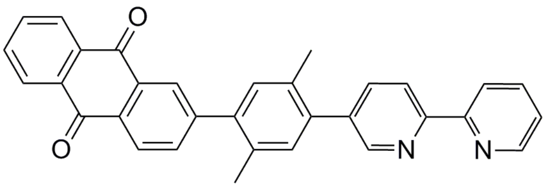
Molecule **5a**



Molecule **4a** (4.47 g, 0.011 mol) was dissolved in dichloromethane (20 ml). To this solution, ICl (3.78 g, 0.023 mol) in acetonitrile (80 ml) was added dropwise under nitrogen at 0°C. After stirring at room temperature overnight, the mixture was washed with an aqueous solution of $Na_2S_2O_3$ (5%, 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).

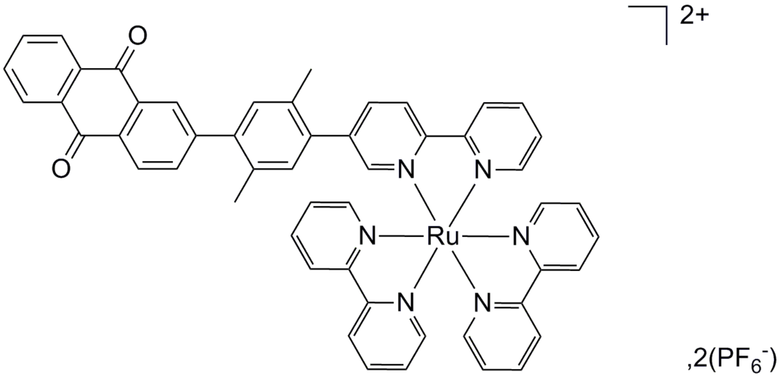
Ligand **6a**



$Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) was added under inert atmosphere to a stirred and deoxygenated suspension of molecule **5a** (0.30 g, 0.68 mmol) and 5-(tri-*n*-butylstannyl)-2,2'-bipyridine [2] (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,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).

Dyad **Ru-xy-AQ**



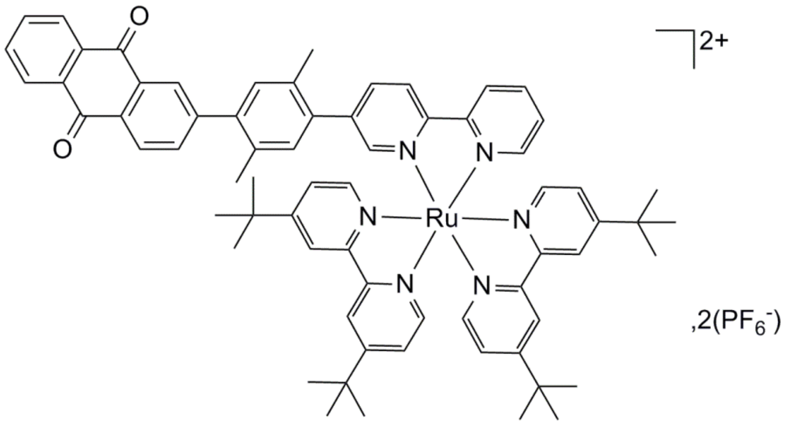
A suspension of ligand **6a** (0.05 g, 0.1mmol) and $Ru(bpy)_2Cl_2$ (0.058 g, 0.1 mmol) in a mixture of $CHCl_3$/EtOH (3/10) was heated to reflux under nitrogen atmosphere overnight. The resulting red-orange solution was evaporated using a rotary evaporator. The remaining dark solid was purified by column 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, 0.8 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 = 440.105 (calculated 440.104 for $C_{52}H_{38}N_6O_2Ru^{2+}$).

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

Dyad **Ru(^{t}Bu)-xy-AQ**



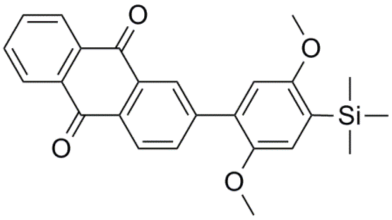
The same synthetic procedure as described for the Ru-xy-AQ dyad was followed. Ru(^{t}Bu)-xy-AQ was obtained in 72% yield, by using (Ru(^{t}Bu-bpy)$_2$Cl$_2$) [^{t}Bu-bpy = 4,4'-di(*t*-butyl)-2,2'-bipyridine] instead of Ru(bpy)$_2$Cl$_2$ as a starting material.

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 1.40 (m, 36 H, ^{t}Bu), 1.99 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 7.10 (s, 1 H, xy), 7.22 (s, 1 H, xy), 7.46 (m, 1 H), 7.50 (m, 1 H), 7.54 (m, 2 H), 7.63 (m, 2 H), 7.72 (m, 5 H), 7.82 (m, 2 H), 7.96 (td, *J* = 8.0 Hz, 1.3 Hz, 1 H), 8.07 (dd, *J* = 8.0 Hz, 2.0 Hz, 1 H), 8.19 (m, 4 H), 8.24 (m, 2 H), 8.32 (m, 3 H), 8.46 (m, 1 H), 8.55 (m, 1 H).

ES-MS m/z = 552.229 (calculated 552.229 for $C_{68}H_{70}N_6O_2Ru^{2+}$).

Anal. Calcd. for $C_{68}H_{70}N_6O_2RuP_2F_{12}$ · $2H_2O$: C 57.10, H 5.21, N 5.88. Found: C 57.02, H 5.24, N 5.65.

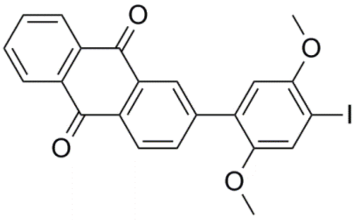
Molecule **4b**



2-Bromoanthraquinone (**3**) (5.00 g, 0.017 mol), 4-trimethylsilyl-2,5-dimethoxyphenylboronic acid (**2b**) [3] (5.31 g, 0.02 mol) were dissolved in 120 ml toluene and 20 ml ethanol. A saturated solution of Na_2CO_3 (5.53 g, 0.05 mol) in de-ionized water was added. The mixture was deoxygenated by bubbling nitrogen gas during 30 minutes, then, $Pd(PPh_3)_4$ (1.00 g, 0.8 mmol) was added, and the reaction was carried out at 90°C overnight. The product was extracted with CH_2Cl_2 and purified by silica gel column chromatography using an eluent mixture comprised of 1:1 pentane/dichoromethane. This gave an orange solid (6.7 g, 92% yield).

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 0.33 (s, 9 H, TMS), 3.81 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.90 (s, 1 H, dmb), 7.06 (s, 1 H, dmb), 7.80 (m, 2 H, AQ), 8.01 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H, AQ), 8.32 (m, 3 H, AQ), 8.48 (d, *J* = 1.6 Hz, 1 H, AQ).

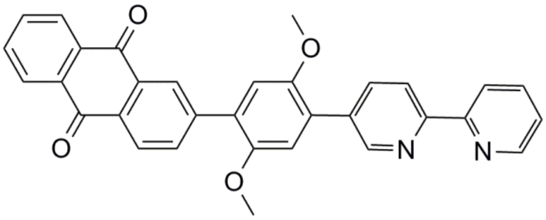
Molecule **5b**



Molecule **4b** (3.05 g, 7.3 mmol) was dissolved in CH_2Cl_2 (20 ml). Under nitrogen atmosphere, a solution of ICl (2.38 g, 14.6 mmol) in acetonitrile (70 ml) was added dropwise at 0°C. After stirring for 2 days at room temperature, the mixture was washed with an aqueous solution of sodium meta-bisulfite (5% in water, 20 ml). The organic phase was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. A yellow powder was obtained (3.44 g, 82% yield).

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 3.80 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 6.87 (s, 1 H, dmb), 7.43 (s, 1 H, dmb), 7.82 (m, 2 H, AQ), 7.97 (dd, *J* = 8.0 Hz, 2.0 Hz, 1 H, AQ), 8.34 (m, 3 H, AQ), 8.43 (d, *J* = 1.6 Hz, 1 H, AQ).

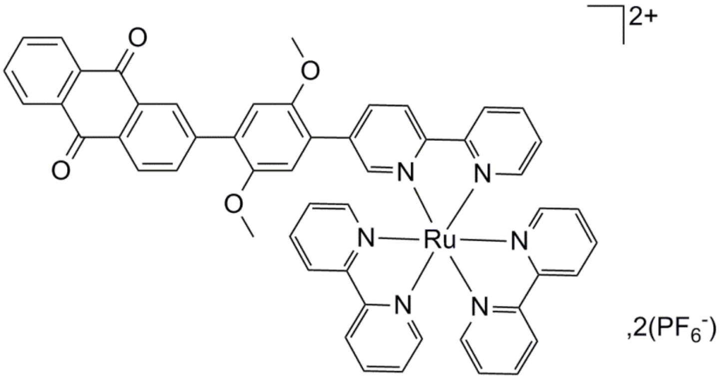
Ligand **6b**



In a double-neck flask, molecule **5b** (0.25 g, 0.53 mmol) and 5-(tri-*n*-butylstannyl)-2,2'-bipyridine [1] (0.30 g, 0.69 mmol) were dissolved in *m*-xylene (30 ml). The mixture was deoxygenated for 30 minutes by bubbling nitrogen gas, and then the $Pd(PPh_3)_4$ catalyst (0.06 g, 0.053 mmol) was added. The reaction mixture was heated to reflux for 48 hours. After cooling to room temperature, the solvent was evaporated. A red-orange solid was obtained, and this substance was purified by silica gel column chromatography using a CH_2Cl_2/CH_3OH/triethylamine (98:1:1) eluent mixture (0.18 g, 69% yield).

^1H NMR: (400 MHz, $CDCl_3$, 25°C): δ ppm = 3.86 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 7.08 (s, 1 H, dmb), 7.09 (s, 1 H, dmb), 7.34 (ddd, *J* = 8.0 Hz, 4.8 Hz, 1.2 Hz, 1 H, AQ), 7.83 (m, 3 H, AQ), 8.07 (m, 2 H, AQ), 8.35 (m, 3 H, AQ/bpy), 8.48 (m, 2 H, bpy), 8.53 (d, *J* = 1.6 Hz, 1 H, bpy), 8.71 (m, 1 H, bpy), 8.93 (d, *J* = 1.6 Hz, 1 H, bpy).

Dyad **Ru-dmb-AQ**

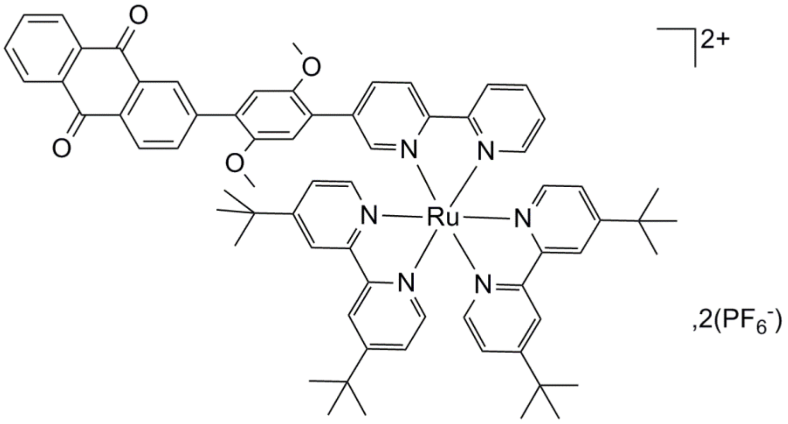


Ligand **6b** (0.05 g, 0.1 mmol) and $Ru(bpy)_2Cl_2$ (0.048 g, 0.1 mmol) were dissolved in a mixture of ethanol and chloroform (10:3). The solution was deoxygenated and heated at reflux for one night. The solvent was evaporated, and the purple solid was purified by silica gel column chromatography using first acetone as the eluent and then a mixture of acetone/H_2O/KNO_3 saturated solution in water (10:1:1). The resulting product was dissolved in minimum of acetone, and a saturated solution of KPF_6 in water was added. The resulting precipitate was filtered and washed with water, then with diethyl ether, and dried under vacuum to give an orange solid (70 mg, 62% yield).

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 3.60 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 7.02 (s, 1 H, dmb), 7.05 (s, 1 H, dmb), 7.44 (m, 5 H), 7.83 (m, 7 H), 8.06 (m, 7 H), 8.26 (m, 3 H), 8.30 (dd, *J* = 8.8 Hz, 2.0 Hz, 1 H), 8.39 (d, *J* = 2.0 Hz, 1 H), 8.58 (m, 6 H).

Anal. Calcd. for $C_{52}H_{38}N_6O_4RuP_2F_{12} \cdot 3H_2O$: C 49.73, H 3.53, N 6.69. Found: C 49.60, H 3.46, N 6.47.

Dyad **Ru(*t*Bu)-dmb-AQ**



Ru(^{t}Bu)-dmb-AQ was prepared following the same protocol as described above, and by replacing $Ru(bpy)_2Cl_2$ with Ru(^{t}Bu-bpy)$_2$Cl$_2$ (79% yield).

^{1}H NMR: (400 MHz, acetone-d_6, 25°C): δ [ppm] = 1.35 (m, 36 H, ^{t}Bu), 3.65 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 7.05 (s, 1 H, dmb), 7.20 (s, 1 H, dmb), 7.52 (m, 2 H), 7.58 (dd, *J* = 6.0 Hz, 2.0 Hz, 2 H), 7.61 (dd, *J* = 6.0 Hz, 2.0 Hz, 1 H), 7.78 (m, 1 H), 7.86 (m, 3 H), 7.92 (m, 2 H), 7.98 (m, 2 H), 8.05 (dd, *J* = 7.0 Hz, 1.0 Hz, 1 H), 8.16 (m, 4 H), 8.29 (d, *J* = 1.7 Hz, 1 H), 8.36 (dd, *J* = 8.5 Hz, 1.8 Hz, 1 H), 8.87 (m, 6 H).

ES-MS m/z = 568.223 (calculated for 568.224 $C_{52}H_{38}N_6O_4Ru^{2+}$).

Anal. Calcd. for $C_{68}H_{70}N_6O_4RuP_2F_{12} \cdot 0.6\ CHCl_3$: C 55.00, H 4.75, N 5.61. Found: C 55.23, H 4.87, N 5.10.

The **$Ru(bpy)_2Cl_2$** / **Ru(^{t}Bu-bpy)$_2$Cl$_2$** complexes and the **$Ru(bpy)_3^{2+}$** / **Ru(^{t}Bu-bpy)$_3^{2+}$** reference complexes were synthesized following a previously published method [4].

References

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[3] M. E. Walther, O. S. Wenger, *ChemPhysChem.* **2009**, *10*, 1203-1206.

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