

Supporting information for

## Microsecond charge recombination in a linear triarylamine-Ru(bpy)<sub>3</sub><sup>2+</sup>-anthraquinone triad

Jihane Hankache, Oliver S. Wenger\*

*Georg-August-Universität Göttingen*

*Institut für Anorganische Chemie*

*Tammannstrasse 4*

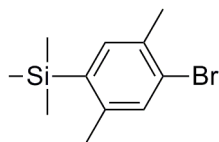
*D-37077 Göttingen, Germany*

*oliver.wenger@chemie.uni-goettingen.de*

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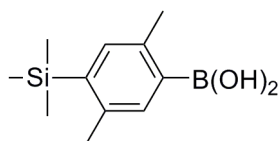
### Synthetic protocols and product characterization data



#### **TMS-xy-Br**

1,4-dibromo-*p*-xylene (10.00 g, 38 mmol) was dissolved in dry THF (70 ml) under inert atmosphere. 28.4 ml of *n*-BuLi (1.6 M in hexane) was added dropwise at -78°C. This temperature was maintained for 1 hour, and trimethylsilyl chloride (5.74 ml) was added slowly. After stirring overnight at room temperature, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over MgSO<sub>4</sub>. The combined organic solvents were removed to afford the desired compound as a colorless oil (9.78 g, 100 %).

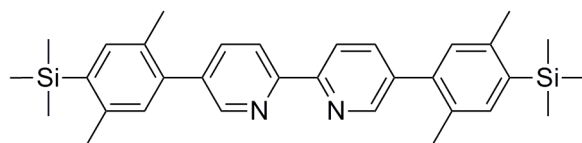
<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>, 25°C): δ [ppm] = 0.31 (s, 9 H, TMS), 2.36 (s, 3 H, CH<sub>3</sub>), 2.39 (s, 3 H, CH<sub>3</sub>), 7.27 (s, 1 H, xy), 7.34 (s, 1 H, xy).



#### **TMS-xy-B(OH)<sub>2</sub>**

Grains of magnesium (1.017 g, 42 mmol) were suspended in dry THF (10 ml). A solution of TMS-xy-Br (9.78 g, 38 mmol) in the same solvent (40 ml) was added very slowly to the suspension of magnesium under inert atmosphere at 60°C. The mixture was heated to reflux for 1 hour, then cooled to room temperature and finally to -78°C. Then B(OCH<sub>3</sub>)<sub>3</sub> (4.34 g, 42 mmol) was added, and the reaction mixture was stirred at room temperature overnight. Aqueous HCl solution (2 M, 50 ml) was added slowly with stirring for 10 minutes. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the solvents were removed under vacuum. This gave the product as a white solid (7.5 g, 89 %).

<sup>1</sup>H NMR: (400 MHz, acetone-*d*<sub>6</sub>/D<sub>2</sub>O (3/1), 25°C): δ [ppm] = 0.16 (s, 9 H, TMS), 2.36 (s, 3 H, CH<sub>3</sub>), 2.39 (s, 3 H, CH<sub>3</sub>), 7.06 (s, 1 H, xy), 7.23 (s, 1 H, xy)

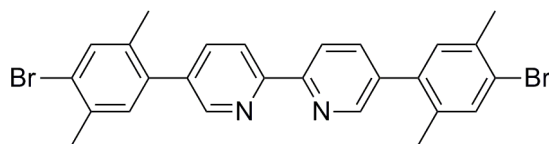


#### **TMS-xy-bpy-xy-TMS**

In a 250 ml double neck flask, 5,5'-Dibromo-2,2'-bipyridine (3.10 g, 9.87 mmol) was coupled to TMS-xy-B(OH)<sub>2</sub> (4.82 g, 21.7 mmol) in presence of 15.00 g Na<sub>2</sub>CO<sub>3</sub> in 80 ml THF and 60 ml de-ionized water. The biphasic solution was deoxygenated by bubbling nitrogen gas for 30 minutes, and the Pd(PPh<sub>3</sub>)<sub>4</sub> (0.57 g, 0.49 mmol) was added, and the solution was deoxygenated for another 15 minutes. The reaction mixture was refluxed overnight, and the workup was

done by extracting the organic phase with  $\text{CH}_2\text{Cl}_2$ , drying with anhydrous  $\text{MgSO}_4$ , and evaporation of the solvents. The resulting solid was recrystallized from pentane to yield 78% of white product.

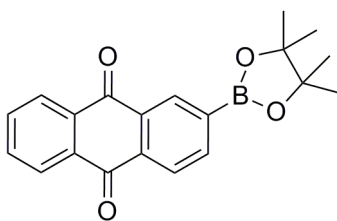
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 0.40 (s, 18 H, TMS), 2.32 (s, 6 H,  $\text{CH}_3$ ), 2.49 (s, 6 H,  $\text{CH}_3$ ), 7.11 (s, 2 H, xy), 7.40 (s, 2 H, xy), 7.82 (dd,  $J = 8.1$  Hz, 2.2 Hz, 2 H, bpy), 8.48 (dd,  $J = 8.1$  Hz, 0.7 Hz, 2 H, bpy), 8.70 (dd,  $J = 2.1$  Hz, 1.4 Hz, 2 H, bpy).



### Br-xy-bpy-xy-Br

Bromine (0.88 ml, 17.13 mmol) was added dropwise to a stirred and ice-cooled suspension of TMS-xy-bpy-xy-TMS (2.18 g, 4.28 mmol) and NaOAc (0.70 g, 8.56 mmol) in THF (40 ml) in the dark. After 5 minutes, the ice bath was removed and the reaction mixture was stirred for 2 hours at room temperature.  $\text{Et}_3\text{N}$  (4.77 ml, 34.27 mmol) was added and the excess of bromine was destroyed by addition of a saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The two resulting phases were separated, and the organic phase was dried over  $\text{MgSO}_4$  and filtered. The solvent was evaporated and the residue purified by chromatography on silica gel, using a mixture of pentane/diethylether (1:1) as the eluent, to give a pure white solid (1.76 g, 79%).

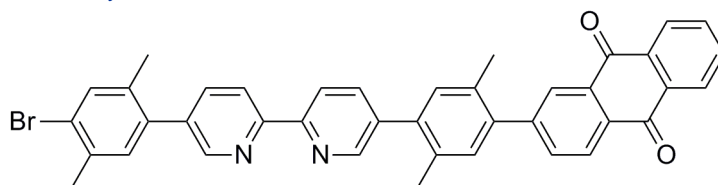
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 2.27 (s, 6 H,  $\text{CH}_3$ ), 2.42 (s, 6 H,  $\text{CH}_3$ ), 7.15 (s, 2 H, xy), 7.50 (s, 2 H, xy), 7.77 (dd,  $J = 8.1$  Hz, 2.2 Hz, 2 H, bpy), 8.48 (dd,  $J = 8.1$  Hz, 0.7 Hz, 2 H, bpy), 8.64 (dd,  $J = 2.2$  Hz, 0.7 Hz, 2 H, bpy).



### AQ-boronic ester

2-bromoanthraquinone (1.00 g, 3.48 mmol), bis(pinacolate)diboron (1.06 g, 4.17 mmol),  $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$  (dppf = 1,1'-Bis(diphenylphosphino)ferrocene) (0.14 g, 0.17 mmol), KOAc (1.02 g, 10.00 mmol), and 30 ml of anhydrous DMSO were added to a dried 100 ml double neck flask. The reaction mixture was stirred at  $80^\circ\text{C}$  for 2 days; afterwards a saturated aqueous  $\text{NH}_4\text{Cl}$  solution was added. The organic phase was extracted with EtOAc, dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. Recrystallization of the crude product from pentane leads to a yellow solid (0.56 g, 48%).

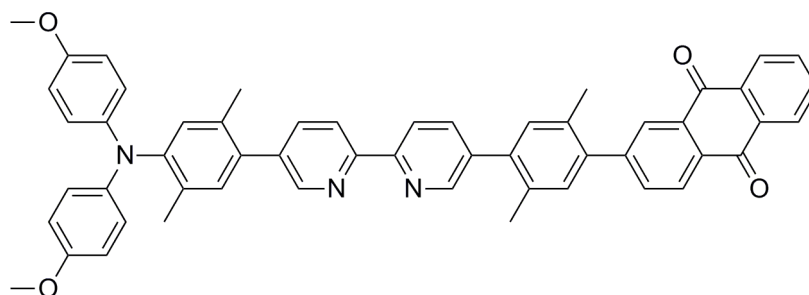
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 1.38 (s, 12 H,  $\text{CH}_3$ ), 7.80 (m, 2 H, AQ), 8.20 (dd,  $J = 7.5$  Hz, 1.1 Hz, 1 H, AQ), 8.31 (m, 3 H, AQ), 8.75 (d,  $J = 0.5$  Hz, 1 H, AQ).



### Br-xy-bpy-xy-AQ

$\text{Pd}(\text{PPh}_3)_4$  (0.13 g, 0.19 mmol) was added under inert atmosphere to a stirred and deoxygenated suspension of AQ-boronic ester (0.40 g, 1.19 mmol), Br-xy-bpy-xy-Br (1.56 g, 2.99 mmol), and 5 g of  $\text{Na}_2\text{CO}_3$  in a 1:1 mixture of THF and de-ionized water (20 ml:20 ml). After refluxing overnight, the product was extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$ , filtered and the solvents were removed under reduced pressure. A yellow solid (0.56 g, 72%) was obtained by recrystallization from pentane.

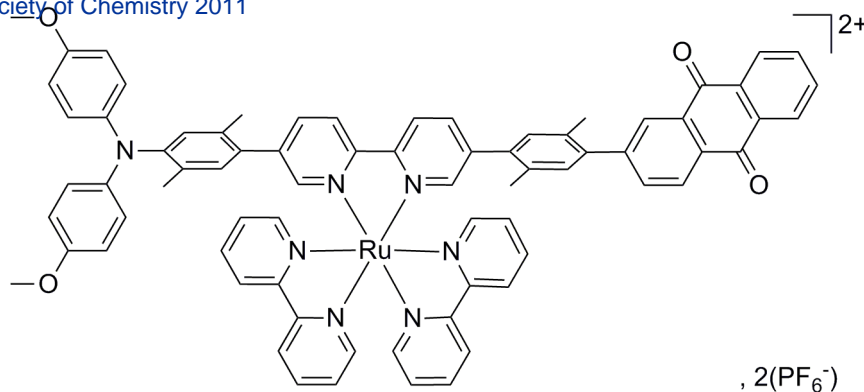
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  [ppm] = 2.28 (s, 3 H,  $\text{CH}_3$ ), 2.36 (s, 3 H,  $\text{CH}_3$ ), 2.37 (s, 3 H,  $\text{CH}_3$ ), 2.43 (s, 3 H,  $\text{CH}_3$ ), 7.16 (s, 1 H, xy), 7.27 (s, 2 H, xy), 7.51 (s, 1 H, xy), 7.81 (m, 4 H, AQ), 7.88 (dd,  $J = 8.1$  Hz, 2.2 Hz, 1 H, bpy), 8.35 (m, 3 H, AQ), 8.40 (d,  $J = 8.0$  Hz, 1 H, bpy), 8.51 (dd,  $J = 8.1$  Hz, 4 Hz, 2 H, bpy), 8.66 (dd,  $J = 2.1$  Hz, 0.5 Hz, 1 H, bpy), 8.75 (dd,  $J = 2.1$  Hz, 0.5 Hz, 1 H, bpy).



### TAA-xy-bpy-xy-AQ

To a dried two-neck flask charged with 4,4'-dimethoxydiphenylamine (0.19 g, 0.86 mmol), AQ-xy-bpy-xy-Br (0.56 g, 0.86 mmol), potassium *tert*-butoxide (0.14 g, 1.29 mmol), and  $\text{Pd}(\text{dibenzylidene-acetone})_2$  (0.02 g, 0.03 mmol), were added freshly distilled toluene (30 ml) and a 1 M solution of tri-*tert*-butylphosphine (0.03 ml, 0.03 mmol) under nitrogen atmosphere. The yellow suspension was heated to 60°C overnight, until all starting material was consumed. The solvent was evaporated and the resulting brown product was purified by column chromatography on a silica gel, using dichloromethane/acetone (9:1) as eluent mixture. This gave a pure solid (0.51 g, 75%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  [ppm] = 2.03 (s, 3 H,  $\text{CH}_3$ ), 2.23 (s, 3 H,  $\text{CH}_3$ ), 2.36 (d,  $J = 3.6$  Hz, 6 H,  $\text{CH}_3$ ), 3.79 (s, 6 H,  $\text{OCH}_3$ ), 6.80 (m, 4 H,  $\text{C}_6\text{H}_4$ ), 6.93 (m, 4 H,  $\text{C}_6\text{H}_4$ ), 6.99 (s, 1 H, xy), 7.13 (s, 1 H, xy), 7.27 (s, 2 H, xy), 7.85 (m, 5 H, AQ/bpy), 8.35 (m, 3 H, AQ), 8.41 (d,  $J = 8.0$  Hz, 1 H, bpy), 8.51 (t,  $J = 8.0$  Hz, 2 H, bpy), 8.68 (dd,  $J = 2.2$  Hz, 0.6 Hz, 1 H, bpy), 8.77 (dd,  $J = 2.2$  Hz, 0.6 Hz, 1 H, bpy).



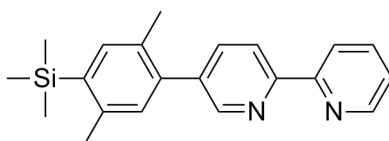
### TAA-Ru<sup>2+</sup>-AQ

Metal complexation occurred by refluxing TAA-xy-bpy-xy-AQ (0.15 g, 0.18 mmol) and Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (0.09 g, 0.18 mmol) in a chloroform/ethanol mixture (6 ml/20 ml) overnight. After removing the solvent, the solid was chromatographed on silica gel using an eluent mixture comprised of 90% acetone, 9% water and 1% aqueous saturated KNO<sub>3</sub> solution. Acetone was evaporated, and the desired complex was precipitated from the remaining aqueous phase by adding an aqueous saturated potassium hexafluorophosphate solution. The orange solid was separated by filtration, and then washed with de-ionized water and diethylether. Finally, it was dried under vacuum (0.21 g, 75%).

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ [ppm] = 1.77 (s, 3 H, CH<sub>3</sub>), 1.87 (s, 3 H, CH<sub>3</sub>), 1.93 (s, 3 H, CH<sub>3</sub>), 2.21 (s, 3 H, CH<sub>3</sub>), 3.69 (s, 6 H, OCH<sub>3</sub>), 6.73 (m, 8 H, C<sub>6</sub>H<sub>4</sub>), 6.95 (s, 1 H, xy), 7.09 (s, 1 H, xy), 7.12 (s, 1 H, xy), 7.49 (m, 2 H, bpy), 7.51 (m, 2 H, bpy), 7.63 (dd, *J* = 6.6 Hz, 1.7 Hz, 2 H, bpy), 7.69 (m, 3 H, bpy), 7.78 (m, 2 H, AQ), 7.84 (m, 2 H, bpy), 8.01 (m, 7 H, AQ/bpy), 8.16 (d, *J* = 1.6 Hz, 1 H, bpy), 8.25 (m, 3 H, AQ/bpy), 8.40 (m, 4 H, bpy), 8.53 (dd, *J* = 8.4 Hz, 4.4 Hz, 2 H, bpy).

ES-MS: *m/z* = 605.684 (calculated 605.685 for C<sub>74</sub>H<sub>59</sub>N<sub>7</sub>O<sub>4</sub>Ru)

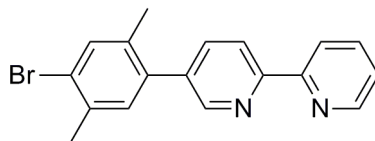
Anal. Calcd. for C<sub>74</sub>H<sub>59</sub>N<sub>7</sub>O<sub>4</sub>RuP<sub>2</sub>F<sub>12</sub> · 4 H<sub>2</sub>O: C 56.41, H 4.29, N 6.23. Found: C 56.48, H 4.17; N 6.16.



### bpy-xy-TMS

Br-bpy (4.44 g, 18.8 mmol)<sup>[1]</sup>, TMS-xy-B(OH)<sub>2</sub> (4.61 g, 20.0 mmol) and Na<sub>2</sub>CO<sub>3</sub> (6.01 g, 56.0 mmol) were dissolved in a mixture of toluene (150 ml), water (50 ml) and ethanol (50 ml). The solution was deoxygenated by three subsequent nitrogen/vacuum cycles, then Pd(PPh<sub>3</sub>)<sub>3</sub> (0.43 g, 0.30 mmol) was added under nitrogen atmosphere. After heating the solution to reflux overnight, the solvents were evaporated and a yellow oil was obtained. The latter was purified by flash chromatography using a mixture of pentane/diethylether (1:1) as the eluent. A colorless oil, which was crystallized upon prolonged standing, was obtained (4.82 g, 76%).

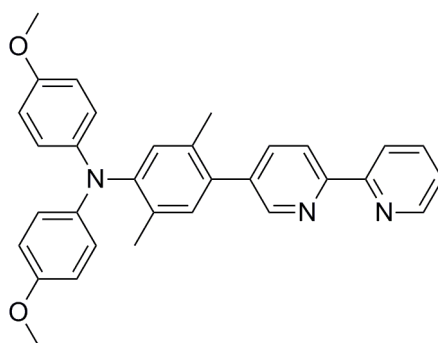
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 0.37 (s, 9 H, TMS), 2.30 (s, 3 H,  $\text{CH}_3$ ), 2.48 (s, 3 H,  $\text{CH}_3$ ), 7.09 (s, 1 H, xy), 7.32 (m, 1 H, bpy), 7.39 (s, 1 H, xy), 7.83 (m, 2 H, bpy), 8.44 (m, 2 H, bpy), 8.70 (m, 2 H, bpy).



### bpy-xy-Br

To an ice-cooled suspension of bpy-xy-TMS (4.81 g, 14.0 mmol) and NaOAc (3.55 g, 43.0 mmol) in 50 ml of THF placed in the dark, bromine (1.49 ml, 29.0 mmol) was added. After stirring for 2 hours at room temperature,  $\text{Et}_3\text{N}$  (16.12 ml, 11.5 mmol) was added, followed by addition of a saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution (50 ml). The organic phase was extracted with  $\text{CH}_2\text{Cl}_2$  and the solvents were removed under vacuum. Silica gel column chromatography was necessary to purify the crude product, using a mixture of pentane/diethylether (1:1) as the eluent. A yellow oil was obtained (3.98 g, 84%).

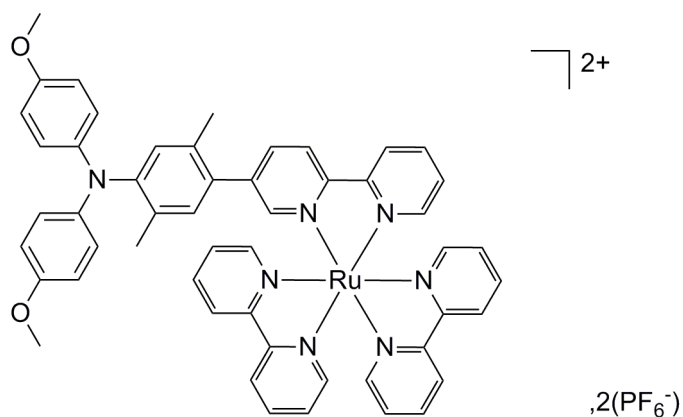
$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 2.25 (s, 3 H,  $\text{CH}_3$ ), 2.41 (s, 3 H,  $\text{CH}_3$ ), 7.13 (s, 1 H, xy), 7.32 (m, 1 H, bpy), 7.49 (s, 1 H, xy), 7.80 (m, 2 H, bpy), 8.44 (m, 2 H, bpy), 8.70 (m, 2 H, bpy).



### TAA-xy-bpy

N-C coupling between bpy-xy-Br (0.28 g, 0.82 mmol) and 4,4-dimethoxydiphenylamine (0.19 g, 0.82 mmol) was performed as follows: To the flask containing the two coupling partners, potassium *tert*-butoxide (0.13 g, 1.23 mmol),  $\text{Pd}(\text{dibenzylidene-acetone})_2$  (0.02 g, 0.03 mmol) and 30 ml of dry toluene was added. After 20 minutes of bubbling nitrogen, tri-*tert*-butylphosphine was added, and the reaction mixture was heated to  $80^\circ\text{C}$  for 2 days. Once the reaction was stopped, the solvent was removed under reduced pressure, and the resulting oil was chromatographed on silica gel, using an eluent mixture of pentane/ethylacetate (9:1). A purple solid was obtained (64.0 mg, 15 %).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  [ppm] = 2.01 (s, 3 H,  $\text{CH}_3$ ), 2.21 (s, 3 H,  $\text{CH}_3$ ), 3.78 (s, 6 H,  $\text{OCH}_3$ ), 6.80 (m, 4 H,  $\text{C}_6\text{H}_4$ ), 6.91 (m, 4 H,  $\text{C}_6\text{H}_4$ ), 6.98 (s, 1 H, xy), 7.10 (s, 1 H, xy), 7.31 (m, 1 H, bpy), 7.83 (m, 2 H, bpy), 8.44 (m, 2 H, bpy), 8.70 (m, 2 H, bpy).



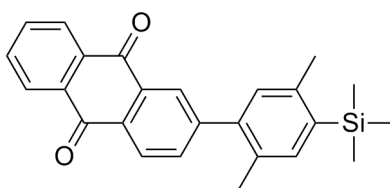
### TAA-Ru<sup>2+</sup>

TAA-xy-bpy (64.0 mg, 0.13 mmol) in 3 ml of CHCl<sub>3</sub> was added to a suspension of Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (69.9 mg, 0.13 mmol) in 10 ml of EtOH. The reaction mixture was refluxed under nitrogen atmosphere overnight. Then, the solvents were removed under reduced pressure, and the crude product was purified by column chromatography on silica gel. The eluent was a mixture of acetone/water/aqueous saturated KNO<sub>3</sub> solution (90/9/1). After acetone removal under reduced pressure, addition of a saturated aqueous solution of potassium hexafluorophosphate induced precipitation of the desired product. The orange solid was filtered, washed with water and diethylether, and dried under vacuum.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ [ppm] = 1.80 (s, 3 H, xy), 1.90 (s, 3 H, xy), 3.73 (s, 6 H, OCH<sub>3</sub>), 6.76 (m, 8 H, C<sub>6</sub>H<sub>4</sub>), 6.95 (s, 1 H), 7.46 (m, 5 H), 7.70 (m, 6 H), 8.05 (m, 7 H), 8.44 (m, 6H).

ES-MS: m/z = 450.634 (calculated 450.635 for C<sub>52</sub>H<sub>47</sub>N<sub>7</sub>O<sub>2</sub>Ru).

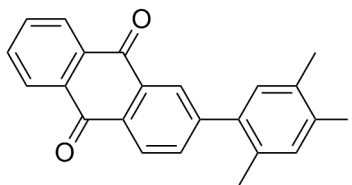
Anal. Calcd. for C<sub>52</sub>H<sub>47</sub>N<sub>7</sub>O<sub>2</sub>RuP<sub>2</sub>F<sub>12</sub> · 0.5H<sub>2</sub>O: C 52.05, H 3.86, N 8.17. Found: C 52.36, H 4.12; N 7.89.



### AQ-xy-TMS

2-bromoanthraquinone (5.00 g, 17.4 mmol), TMS-xy-B(OH)<sub>2</sub> (4.64 g, 0.02 mol) and a solution of Na<sub>2</sub>CO<sub>3</sub> (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<sub>3</sub>)<sub>4</sub> catalyst and heating to reflux overnight. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> 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%).

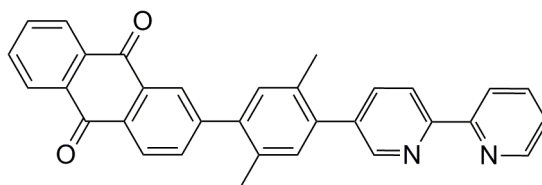
<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>, 25°C): δ [ppm] = 0.38 (s, 9 H, TMS), 2.30 (s, 3 H, CH<sub>3</sub>), 2.49 (s, 3 H, CH<sub>3</sub>), 7.11 (s, 1 H, xy), 7.4 (s, 1 H, xy), 7.82 (m, 3 H, AQ), 8.35 (m, 4 H, AQ).



### AQ-xy-I

AQ-xy-TMS (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 this solution. After stirring overnight at room temperature, the mixture was washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5% in water, 250 ml). The two resulting phases were separated. Afterwards, the yellow organic phase was dried over MgSO<sub>4</sub> and filtered. The solvent was evaporated, and a yellow powder was obtained in essentially quantitative yield.

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>, 25°C): δ [ppm] = 2.23 (s, 3 H, CH<sub>3</sub>), 2.45 (s, 3 H, CH<sub>3</sub>), 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).

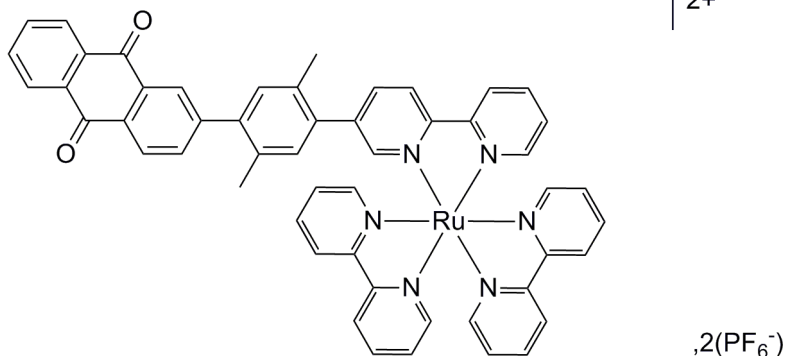


### AQ-xy-bpy

Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 g, 0.03 mmol) was added under inert atmosphere to a stirred and deoxygenated suspension of AQ-xy-I (0.30 g, 0.68 mmol) and 5-(tri-*n*-butylstannyl)-2,2'-bipyridine<sup>[2]</sup> (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<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (9/1) to give the product as a yellow solid (0.12 g, 38%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ [ppm] = 2.35 (m, 6 H, *J* = 3.2 Hz, CH<sub>3</sub>), 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).





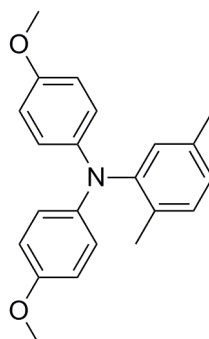
### AQ-Ru<sup>2+</sup>

A suspension of AQ-xy-bpy (0.05 g, 0.1mmol) and Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (0.058 g, 0.1 mmol) in a mixture of CHCl<sub>3</sub>/EtOH (3/10) was heated to reflux overnight under nitrogen atmosphere. The resulting 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<sub>2</sub>O/ aqueous saturated KNO<sub>3</sub> (90/10/1) as the eluent. The resulting product was dissolved in minimum of acetone, and a saturated solution of KPF<sub>6</sub> in water was added. The orange precipitate was filtered, washed with water and diethylether, and finally dried under vacuum. The yield was 78%.

<sup>1</sup>H NMR: (400 MHz, CD<sub>3</sub>CN, 25°C): δ [ppm] = 2.02 (s, 3 H, CH<sub>3</sub>), 2.25 (s, 3 H, CH<sub>3</sub>), 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<sub>52</sub>H<sub>38</sub>O<sub>2</sub>N<sub>6</sub>Ru).

Anal. Calcd. for C<sub>52</sub>H<sub>38</sub>N<sub>6</sub>O<sub>2</sub>RuP<sub>2</sub>F<sub>12</sub> · H<sub>2</sub>O · CH<sub>3</sub>COCH<sub>3</sub>: C 53.02, H 3.72, N 6.74. Found C 53.03, H 3.59, N 6.66.



### TAA-reference

A deoxygenated mixture of 2-bromo-1,4-dimethylbenzene (200 mg, 1.08 mmol), 4,4'-dimethoxydiphenylamine (230 mg, 1.00 mmol), potassium *tert*-butoxide (1.12 g, 10.0 mmol), Pd(dibenzylidene-acetone)<sub>2</sub> (0.025 g, 0.03 mmol), and 15 ml of *m*-xylene was heated to 80°C overnight. The solvent was evaporated under reduced pressure. Then, the crude product was purified by silica gel column chromatography, using a 1:1 pentane/dichloromethane mixture as the eluent. A yellow solid was obtained (305 mg, 92%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C): δ [ppm] = 2.00 (s, 3 H, CH<sub>3</sub>), 2.26 (s, 3 H, CH<sub>3</sub>), 3.80 (s, 6 H, OCH<sub>3</sub>), 6.78 (m, 4 H, C<sub>6</sub>H<sub>4</sub>), 6.89 (m, 4 H, C<sub>6</sub>H<sub>4</sub>), 6.92 (m, 2 H, xy), 7.10 (d, *J* = 7.6 Hz, 1 H, xy).

### Scientific instrumentation used for experimental investigations

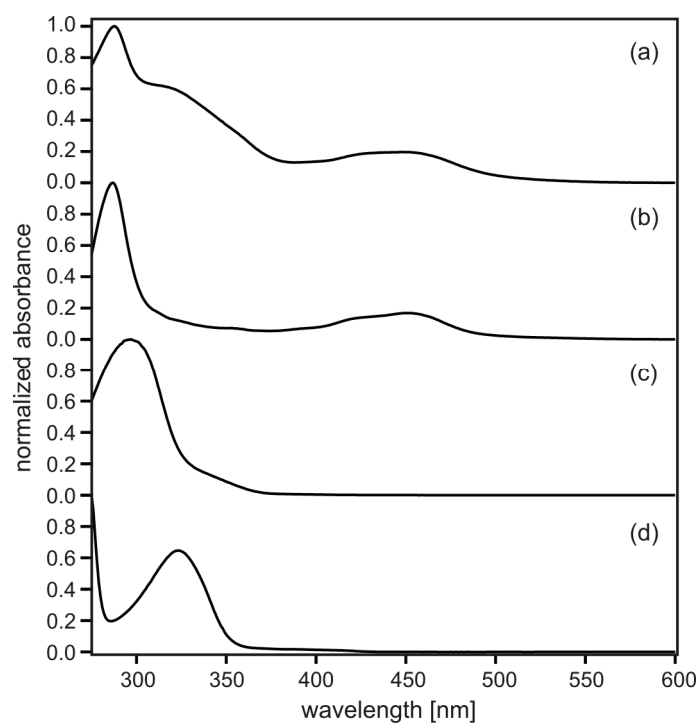
Commercially available chemicals were used as received without further purification. For thin-layer chromatography, Polygram SIL G/UV254 plates from Machery-Nagel were used. Silica Gel 60 from Macherey-Nagel was used for preparative column chromatography.

A Bruker Avance DRX 300 spectrometer was used for all  $^1\text{H}$  NMR experiments. All chemical shifts are reported relative to the tetramethylsilane signal. Electron ionization mass spectrometry (ESI-MS) was performed using a FTCIR-MS APEX IV (Bruker) instrument.

For optical absorption spectroscopy, a Cary 300 instrument from Varian was used. Time-resolved emission and transient absorption spectroscopy was performed using a LP920-KS instrument from Edingburgh Instruments, equipped with a CCD camera from Andor. For these measurements, samples were thoroughly deoxygenated by bubbling nitrogen gas.

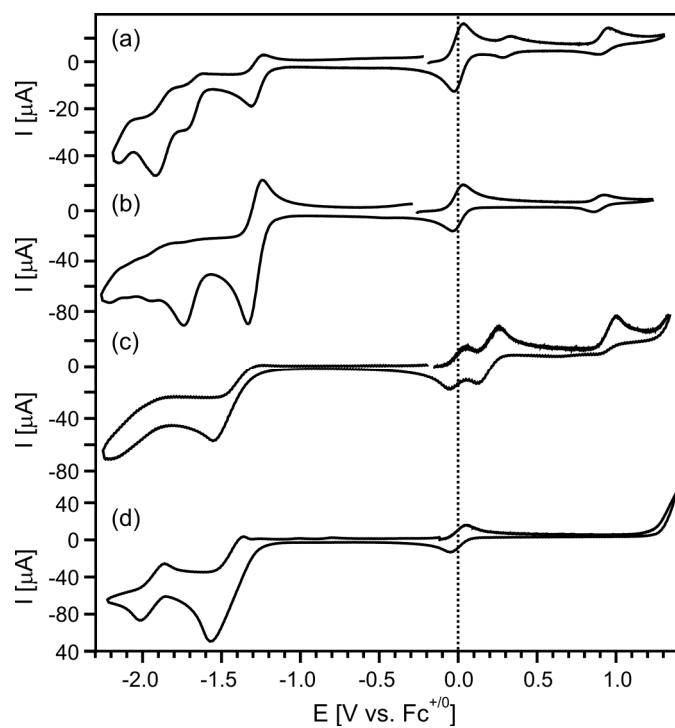
Cyclic voltammetry experiments were performed using a Versastat3-100 potentiostat from Princeton Applied Research equipped with the K0264 Micro-Cell kit. A silver wire served as a quasi-reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. Prior to voltage sweeps, the solution was deoxygenated by bubbling nitrogen gas. The potential scan rate was 200 mV/s. Ferrocene was used as an internal reference.

Figure S1: UV-Vis absorption spectra



**Figure S1.** Normalized optical absorption spectra of (a) TAA-Ru<sup>2+</sup>-AQ; (b) Ru(bpy)<sub>3</sub><sup>2+</sup>; (c) TAA-reference; (d) 9,10-anthraquinone in dichloromethane solution at room temperature.

Figure S2: Cyclic voltammetry data



**Figure S2.** Cyclic voltammograms for (a) TAA-Ru<sup>2+</sup>-AQ; (b) Ru(bpy)<sub>3</sub><sup>2+</sup>; (c) TAA-reference; (d) 9,10-anthraquinone. The solvent was either acetonitrile (a, b) or dichloromethane (c, d).

Figure S3: Luminescence decay of  $\text{Ru}^{2+}$ -AQ

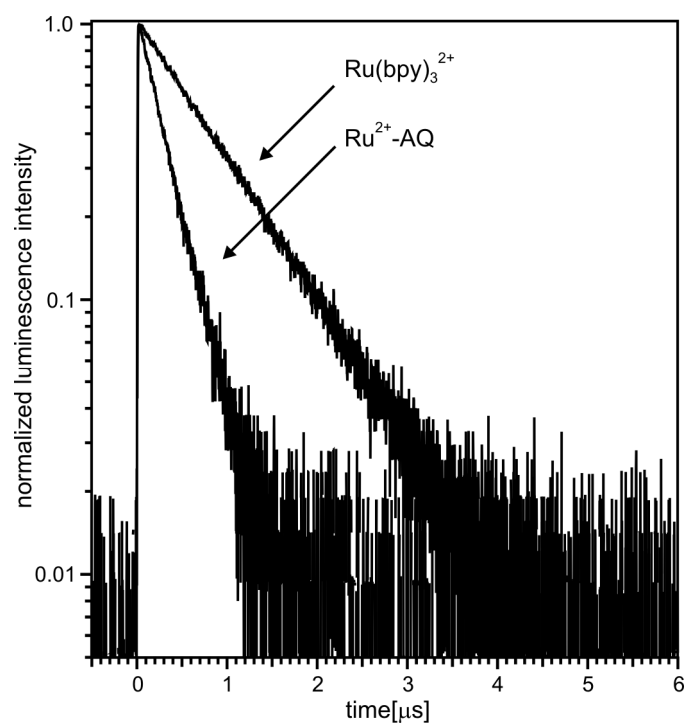


Figure S3. Luminescence decay of dyad  $\text{Ru}^{2+}$ -AQ in deoxygenated acetonitrile solution and luminescence decay of a  $\text{Ru}(\text{bpy})_3^{2+}$  solution under identical conditions.

Figure S4: Transient absorption decay of TAA-Ru<sup>2+</sup>

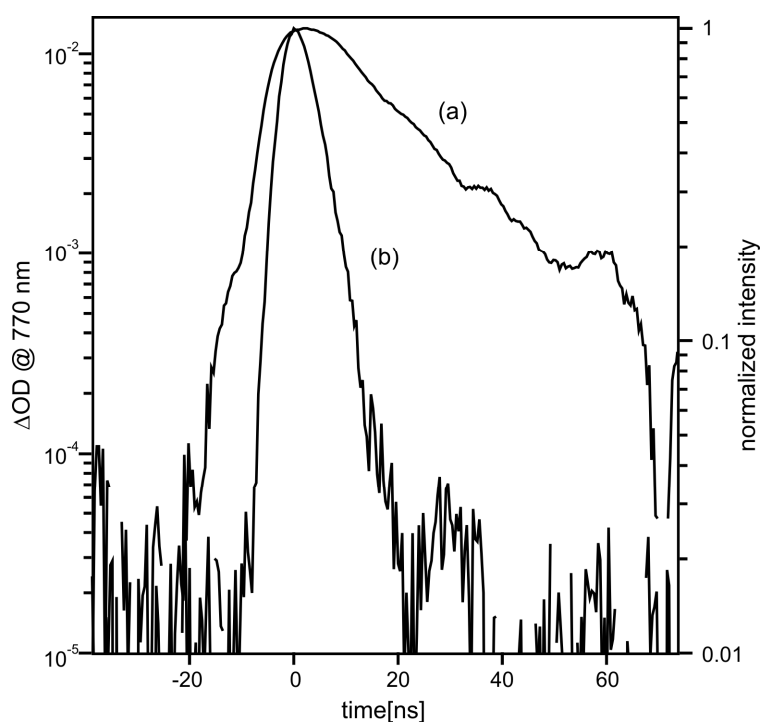


Figure S4. (a) Decay of the transient absorption signal at 770 nm in dyad TAA-Ru<sup>2+</sup> in deoxygenated acetonitrile solution; (b) instrument response function.

## References

- [1] (a) N. Belfrekh, C. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.*, **2001**, *42*, 2779-2781; (b) A. Bouillon, A. S. Voisin, A. Robic, J. C. Lancelot, V. Collot and S. Rault, *J. Org. Chem.* **2003**, *68*, 10178-10180; (c) M. S. Jensen, R. S. Hoerrner, W. J. Li, D. P. Nelson, G. J. Javadi, P. G. Dormer, D. W. Cai, R. D. Larsen, *J. Org. Chem.* **2005**, *70*, 6034-6039; (d) D. Cai, R. D. Larsen, P. J. Reider, *Tetrahedron Lett.* **2002**, *43*, 4285-4287.
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