



HAL
open science

Photoinduced electron transfer in supramolecular ruthenium-porphyrin assemblies

Diego Rota Martir, Mattia Averardi, Daniel Escudero, Denis Jacquemin, Eli Zysman-Colman

► **To cite this version:**

Diego Rota Martir, Mattia Averardi, Daniel Escudero, Denis Jacquemin, Eli Zysman-Colman. Photoinduced electron transfer in supramolecular ruthenium-porphyrin assemblies. Dalton Transactions, 2017, 46 (7), pp.2255-2262. 10.1039/c6dt04414j . hal-02141301

HAL Id: hal-02141301

<https://hal.science/hal-02141301>

Submitted on 4 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Photoinduced Electron Transfer in Supramolecular Ruthenium-Porphyrin Assemblies.

*Diego Rota Martir,^a Mattia Averardi, Daniel Escudero,^b Denis Jacquemin^{b,c} and Eli Zysman-
Colman^{a*}*

^a Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK, Fax: +44-1334 463808; Tel: +44-1334 463826; E-mail: eli.zysman-colman@st-andrews.ac.uk;

URL: <http://www.zysman-colman.com>

^b CEISAM UMR CNRS 6230, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

^c Institut Universitaire de France, 1, rue Descartes, 75005 Paris Cedex 5, France

SUPPORTING INFORMATION

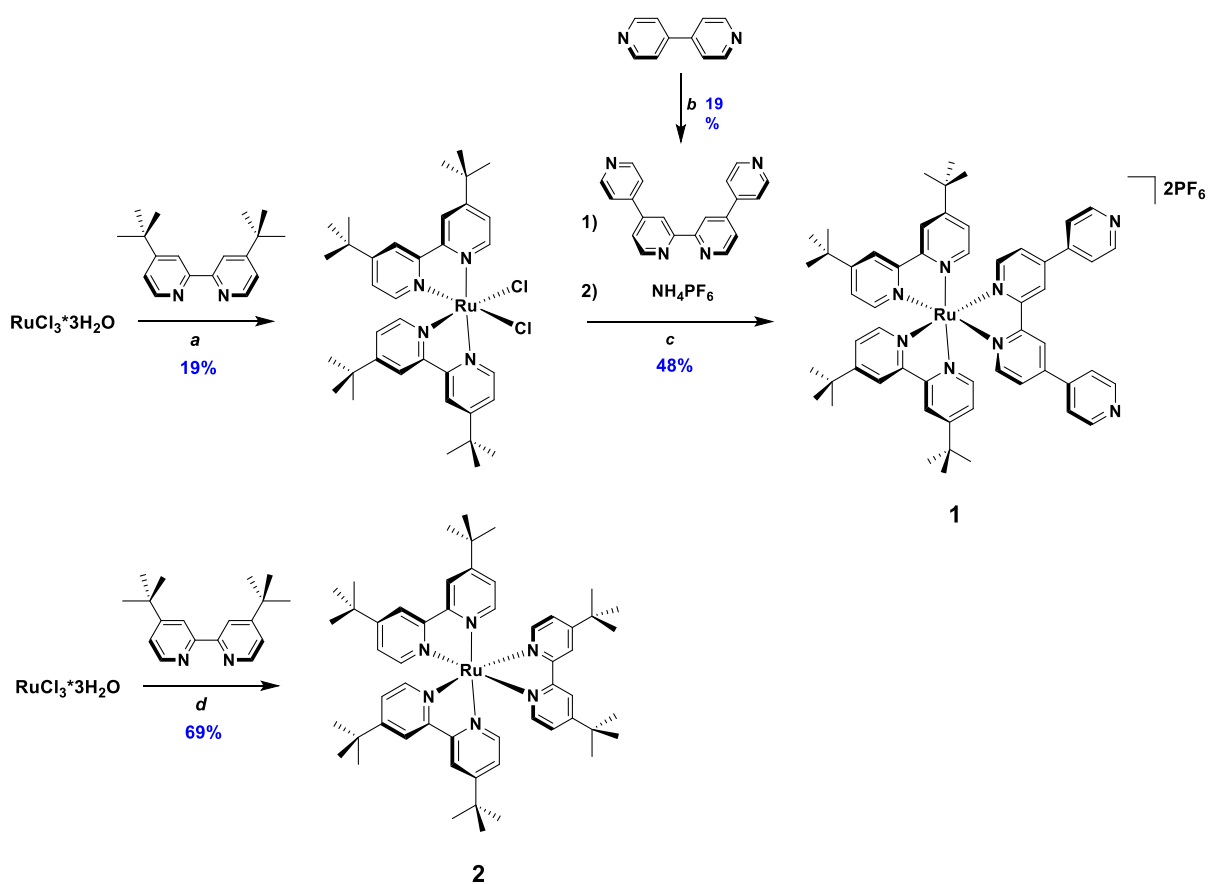
Table of Contents:

| | Pages |
|--|--------------|
| Experimental section | S2 |
| Characterization of complexes | S7 |
| Determination of association constants of 1a and 1b | S14 |
| Control ¹ H NMR spectrum of the “non assembly” 2a | S15 |
| Supplementary optoelectronic characterization for complexes 1 , 2 , ZnTPP, assemblies 1a , 1b , and “non-assembly” 2a | S16 |
| Computational details | S25 |
| References | S26 |

Experimental section.

General Synthetic Procedures. Commercial chemicals were used as supplied. All reactions were performed using standard Schlenk techniques under inert (N₂) atmosphere with reagent-grade solvents. Flash column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63 µm). Analytical thin layer chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with indicator F-254). Compounds were visualized under UV light. ¹H, ¹³C and ¹⁹F solution-phase NMR spectra were recorded on a BrukerAvance spectrometer operating at 11.7 T (Larmor frequencies of 500, 126 and 471 MHz, respectively). The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet and “br” for broad. The solvent was CD₂Cl₂. Melting points (Mps) were recorded using open-ended capillaries on an Electrothermal melting point apparatus and are uncorrected. High-resolution mass spectra were recorded at the EPSRC UK National Mass Spectrometry Facility at Swansea University on a quadrupole time-of-flight (ESI-Q-TOF), modelABSciex 5600 Triple TOF in positive electrospray ionization mode and spectra were recorded using sodium formate solution as the calibrant.

Synthesis of complexes 1 and 2.



Scheme S1. Synthesis of complexes $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})]_2\text{PF}_6$, **1** and $[\text{Ru}(\text{dtBubpy})_3]_2\text{PF}_6$, **2**. Reagents and conditions. ^a 4.0 equiv. LiCl, N_2 , dark, DMF, 140 °C, 6 h; ^b DMF, 10 mol% Pd/C, 165°C, 48h, ^c i. ethylene glycol, 160 °C, 1 h, N_2 ; ii. Excess solid NH_4PF_6 ; ^d ethylene glycol, 160 °C, 1 h, N_2 .

Synthesis of bis-(4,4'-di-tert-butyl-2,2'-bipyridine)-dichloro ruthenium(II), $\text{Ru}(\text{dtBubpy})_2\text{Cl}_2$.

The synthesis of this complex is by a modified method to that previously reported.¹

RuCl₃·xH₂O (207 mg, 0.792 mmol, 1 equiv.), 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (400 mg, 1.490 mmol, 2 eq) and LiCl (126.3 mg, 2.98 mmol, 4 equiv.) were added to a round bottom flask containing 15 mL of DMF. The mixture was refluxed under nitrogen atmosphere and in absence of light for 6 hours and then cooled to room temperature. Most of the solvent was removed by evaporation under reduced pressure, diethyl ether was added and the resultant solution was cooled at -25°C overnight. Filtering the resulting mixture yielded a red to red-violet filtrate and a nearly black microcrystalline product. The solid was washed well with several portions of cold water, followed by several portions of diethyl ether. **Yield** 19.0 %. **¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm):** 9.83 (d, *J* = 2.0 Hz, 2H), 8.63 (d, *J* = 2.0 Hz, 2H), 8.47 (d, *J* = 2.1 Hz, 2H), 7.77 (dd, *J* = 6.1, 2.1 Hz, 2H), 7.38 (d, *J* = 6.2 Hz, 2H), 7.14 (dd, *J* = 6.2, 2.1 Hz, 2H), 1.51 (s, 18H), 1.28 (s, 18H). The characterisation matches that reported.²

Synthesis of 4,4':2',2'':4'',4'''-quaterpyridine (qpy).

The synthesis of this ligand followed that previously reported.³

4,4'-Bipyridine (5.0 g, 0.032 mol), Pd/C (0.70 g, 10% weight Pd) and DMF (50 mL) were added to a dry round bottomed flask, and the reaction mixture was sonicated and oxygenated by bubbling air through the solution. The mixture was refluxed at 165° for 48 h, cooled to room temperature and the solvent was removed using high vacuum rotary evaporator. The crude product was dissolved in CHCl₃ (50 mL) and the catalyst was filtered. A bright yellow solution was obtained and CHCl₃ was distilled under vacuum to obtain a brown solid (7.5 g). The crude was purified by flash chromatography (5% methanol / dichloromethane). To give 0.9 g as pure compound as a white solid. **Yield:** 15%. **R_f:** 0.40 (5% MeOH/DCM on silica). **¹H NMR (500 MHz, CDCl₃) δ (ppm):** 8.86 (d, *J* = 5.4 Hz, 2H), 8.82 – 8.79 (m, 6H), 7.71 (d, *J* = 5.1 Hz, 4H), 7.64 (d, *J* = 5.5, 2H). **¹³C NMR (126 MHz, CDCl₃) δ (ppm):** 156.6, 150.7, 150.1, 146.7, 145.6, 121.7, 121.5, 119.1. The characterization matches that reported.³

Synthesis of bis-(4,4'-di-*tert*-butyl-2,2'-bipyridine)ruthenium(II) 4,4':2',2'':4'',4''' quaterpyridine hexafluorophosphate [Ru(dtBubpy)₂(qpy)](PF₆)₂.

The synthesis of this complex is by a modified method to that previously reported.⁴

Ru(dtBubpy)₂Cl₂ (91 mg, 0.129 mmol, 1 equiv.) and 4,4':2',2'':4'',4'''-quaterpyridine (40 mg, 0.129 mmol, 1 equiv.) were added to a round bottom flask containing 13 mL of ethylene glycol. The mixture was refluxed

under nitrogen atmosphere for 1 hour and then cooled to room temperature and filtered. A saturated, aqueous NH_4PF_6 solution was added to the filtrate and a red precipitate was filtered off and washed with water and diethyl ether. The crude product was purified by silica flash chromatography (silica, acetone : acetonitrile 1:1 with NH_4PF_6 0.3 M); after an initial orange fraction was removed, the major red fraction was evaporated to dryness, washed with water and dried to yield an orange solid. **Yield:** 47.5%. **Rf:** 0.4 (acetone/acetonitrile, 1 : 1 with NH_4PF_6 0.3 M on silica). **^1H NMR (500 MHz, CD_2Cl_2) δ (ppm):** 8.86 (d, $J = 1.9$ Hz, 2H, H_a), 8.71 (m, 4H, H_b), 8.31 (d, $J = 2.0$ Hz, 2H, H_c), 8.29 (d, $J = 2.0$ Hz, 2H, H_d), 8.05 (m, 4H, H_e), 7.89 (d, $J = 6.0$ Hz, 2H, H_f), 7.77 (dd, $J = 6.0, 1.9$ Hz, 2H, H_g), 7.71 (d, $J = 6.1$ Hz, 1H, H_h), 7.62 (d, $J = 6.0$ Hz, 2H, H_i), 7.48 (m, 4H, H_j), 1.43 (s, 9H, H_k), 1.39 (s, 9H, H_l). **^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm):** 163.3, 158.1, 156.8, 156.6, 152.5, 151.4, 150.9, 147.8, 147.7, 147.4, 145.7, 126.2, 125.9, 123.7, 123.7, 122.6, 121.2, 121.2, 121.2, 121.2, 35.9, 35.9, 30.4, 30.4, 30.4, 30.3, 30.3, 30.3. **FT NSI+ MS:** $[\text{M} - 2\text{PF}_6]^{2+}$ Calculated ($\text{C}_{56}\text{H}_{62}\text{N}_8\text{Ru}$): 474.2070; Found: 474.2060.

Synthesis of tris-(4,4'-di-*tert*-butyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate, $[\text{Ru}(\text{dtBubpy})_3](\text{PF}_6)_2$.

The synthesis of this complex is by a modified method to that previously reported.⁵

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (55 mg, 0.210 mmol, 1 equiv.) and 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (198 mg, 0.736 mmol, 3.5 equiv.) were added to a round bottom flask containing 25 mL of ethylene glycol. The mixture was refluxed under nitrogen atmosphere for 1 hour and then cooled to room temperature. A saturated, aqueous NH_4PF_6 solution was added to the filtrate and an orange precipitate was filtered off and washed with water, diethyl ether and hexane. **Yield:** 68.7%. **^1H NMR (400 MHz, CD_2Cl_2) δ (ppm):** 8.25 (d, $J = 2.0$ Hz, 6H), 7.57 (d, $J = 6.0$ Hz, 6H), 7.45 (dd, $J = 6.0, 2.0$ Hz, 6H), 1.42 (s, 54H). **FT NSI+ MS:** $[\text{M} - 2\text{PF}_6]^{2+}$ Calculated ($\text{C}_{54}\text{H}_{72}\text{N}_6\text{Ru}$): 453.2429; Found: 453.2415. The characterisation matches that reported.⁶

Synthesis of zinc tetraphenylporphyrin, (ZnTPP).

The synthesis of ZnTPP followed that previously reported.³

Tetraphenylporphyrin TPP (0.1 g, 0.162 mmol) was dissolved in 25 mL of chloroform. The solution was purged with nitrogen for 10 min. Zinc acetate (0.073 g, 0.33 mmol) was dissolved in ~ 5 mL methanol and then added to the porphyrin solution. The mixture was stirred under nitrogen overnight at room temperature.

All solvents were removed under reduced pressure leaving, a purple solid. The solid was dissolved in DCM and washed with 3×20 mL portions of 5 % w/v aqueous sodium bicarbonate, followed by 3×20 mL portions of water. The organic layer dried over MgSO_4 and the solvent was removed under reduced pressure. The zinc porphyrin was purified by flash column chromatography on a silica gel using 100% chloroform as the eluent. **Yield:** 90%. **R_f:** 0.65 (CHCl_3). **¹H NMR (500 MHz, CDCl_3) δ (ppm):** 8.88 (s, 8H), 8.15 (dd, $J = 7.4, 1.6$ Hz, 8H), 7.69 (m, 12H). **¹³C NMR (126 MHz, CDCl_3) δ (ppm):** 150.2, 142.8, 134.4, 131.9, 127.5, 126.6, 121.1. FT NSI+ MS: [M + H]⁺ Calculated ($\text{C}_{44}\text{H}_{29}\text{N}_4\text{Zn}$): 677.1684; Found: 677.1683. The characterization matches that reported.³

General procedure for the synthesis of 1a and 1b. The synthesis of the assemblies **1a** and **1b** followed that previously reported.³ In a dry 2 mL vial, complex **1** and ZnTPP (1 or 2 equiv.) were dissolved in CD_2Cl_2 (1 mL) to give a concentration of the iridium complex of approximately 0.05 M. The solution was sonicated for few seconds and subsequently transferred to an NMR tube for characterization.

Photophysical measurements. All samples were prepared in HPLC grade dichloromethane with varying concentrations in the order of $10^{-3} - 10^{-5}$ M. Absorption spectra were recorded at room temperature using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least four independent solutions at varying concentrations with absorbance ranging from 6.05×10^{-5} to 2.07×10^{-5} M.

The sample solutions for the emission spectra were prepared in HPLC-grade DCM and degassed *via* three freeze-pump-thaw cycles using a quartz cuvette designed in-house. Steady-state emission and excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. All samples for steady-state measurements were excited at 420, 500 and 550 nm, while samples for time-resolved measurements were excited at 378 nm. Emission quantum yields were determined using the optically dilute method.⁷ A stock solution with absorbance of *ca.* 0.5 was prepared and then four dilutions were prepared with dilution factors between 2 and 20 to obtain solutions with absorbances of *ca.* 0.095, 0.065, 0.05 and 0.018, respectively. The Beer-Lambert law was found to be linear at the concentrations of

these solutions. The emission spectra were then measured after the solutions were rigorously degassed *via* three freeze-pump-thaw cycles prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (R^2) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)$ was used to calculate the relative quantum yield of each of the sample, where Φ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in aerated H_2O at 298 K ($\Phi_r = 4\%$) were used as external references.⁸

Electrochemistry measurements. Cyclic voltammetry measurements were performed on an Electrochemical Analyzer potentiostat model 600D from CH Instruments. Solutions for cyclic voltammetry were prepared in DCM and degassed with DCM-saturated nitrogen by bubbling for about 10 min prior to scanning. Tetra(*n*-butyl)ammonium hexafluorophosphate (TBAPF₆; *ca.* 0.1 M in ACN) was used as the supporting electrolyte. A Ag/Ag⁺ electrode (silver wire in a solution of 0.1 M KCl in H₂O) was used as the pseudoreference electrode; a Pt electrode was used for the working electrode and a Pt electrode was used as the counter electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) electrode with a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal reference (0.46 V *vs.* SCE).⁹

Characterization of complexes.

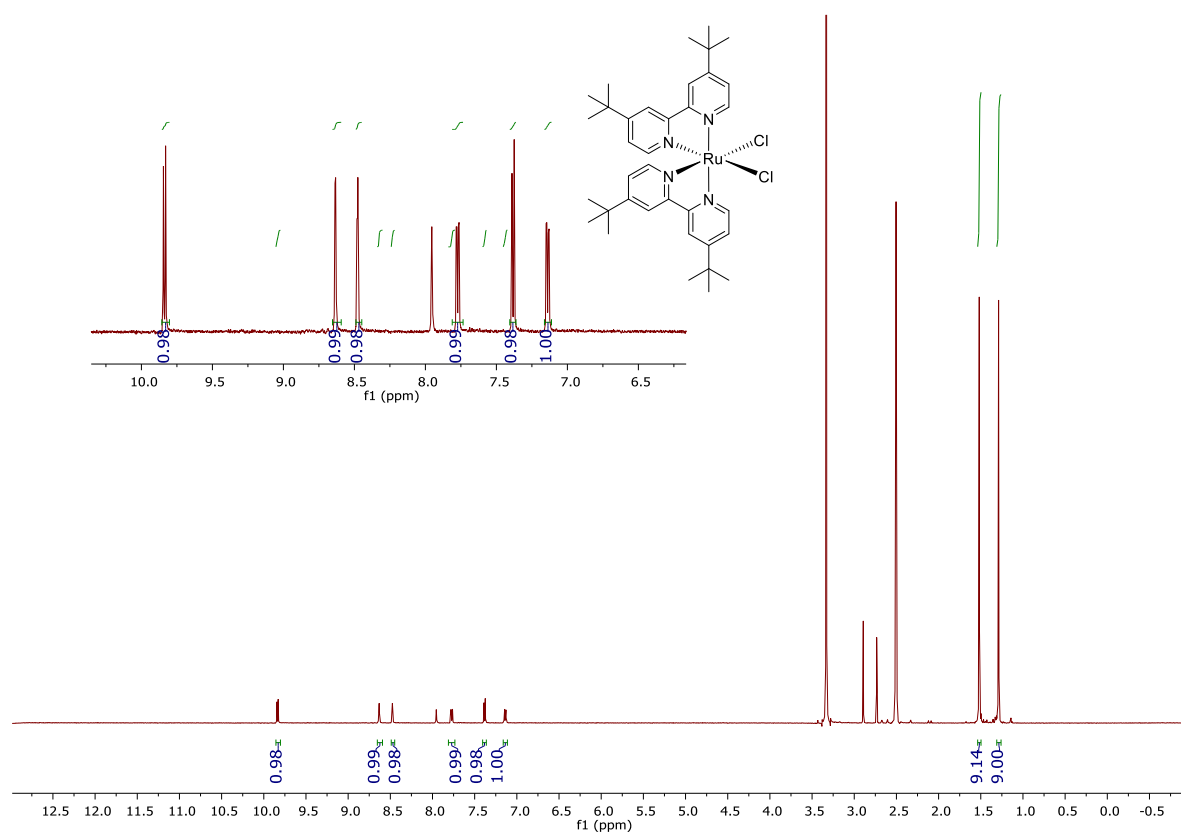


Figure S1. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of $\text{Ru}(\text{dtBubpy})_2\text{Cl}_2$.

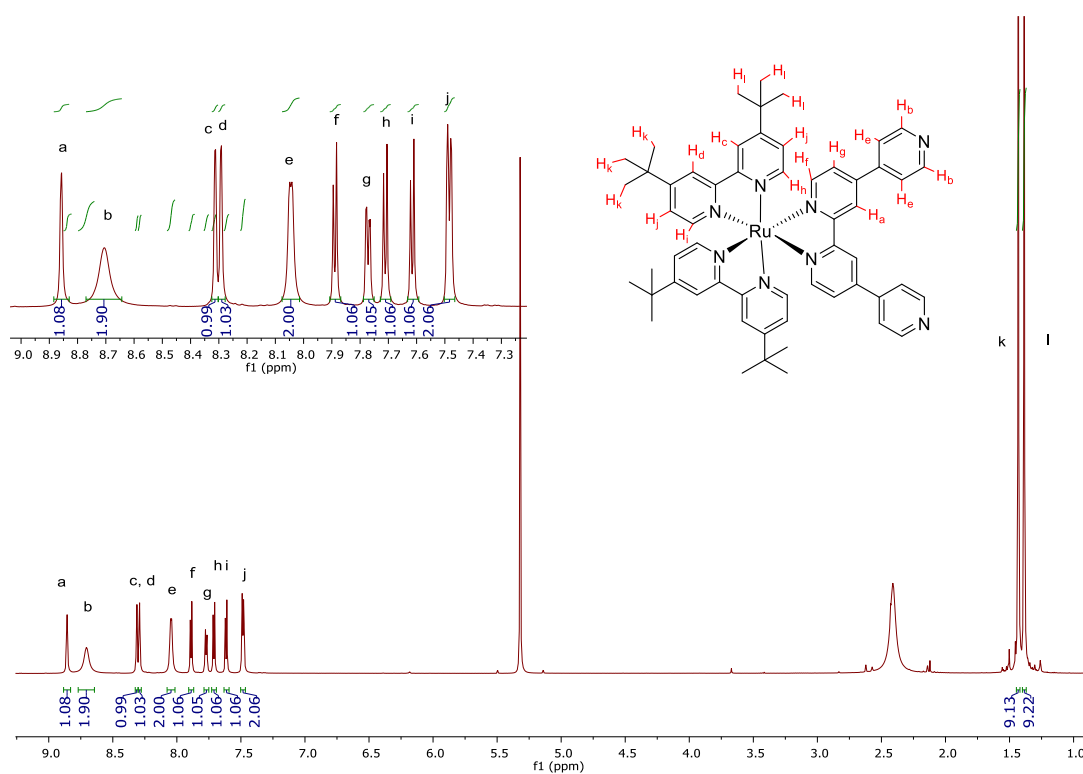


Figure S2. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})](\text{PF}_6)_2$, **1**.

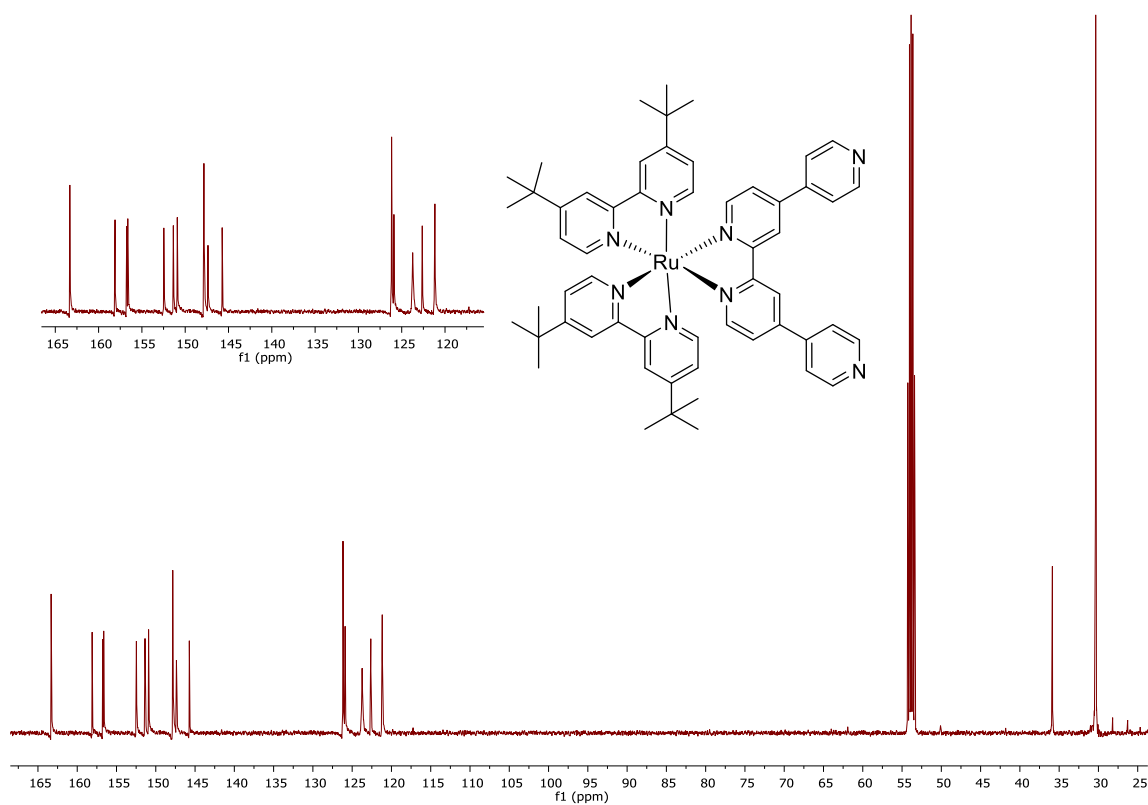


Figure S3. ^{13}C NMR spectrum (126 MHz, CD_2Cl_2) $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})](\text{PF}_6)_2$, **1**.

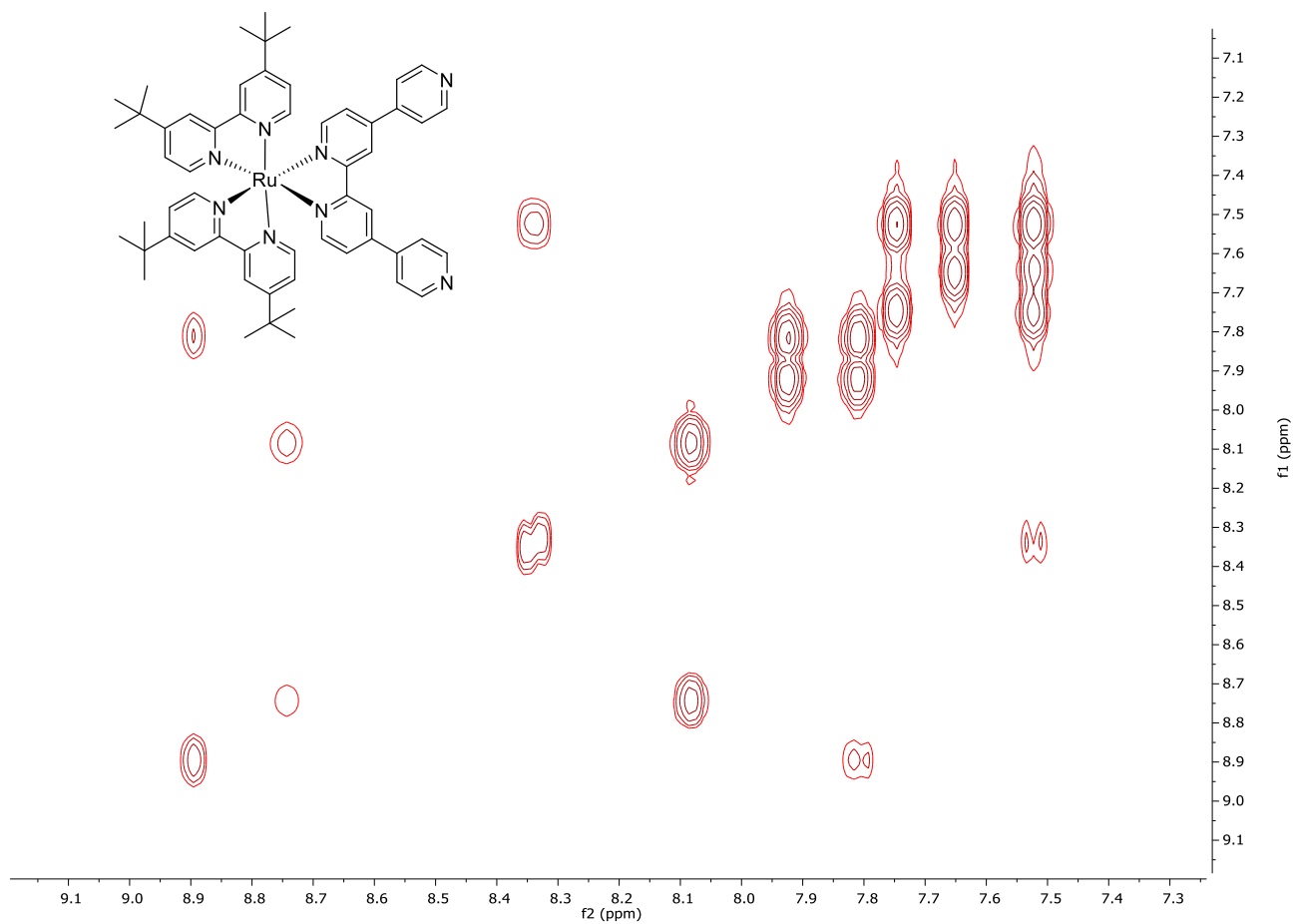


Figure S4. 2D-COSY NMR spectrum (500 MHz, CD_2Cl_2) $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})](\text{PF}_6)_2$, **1**.

STAZYS179-OJ-HNESP #32-44 RT: 0.74-1.04 AV: 12 SM: 7G NL: 6.48E6
T: FTMS + p NSI Full ms [140.00-1935.00]

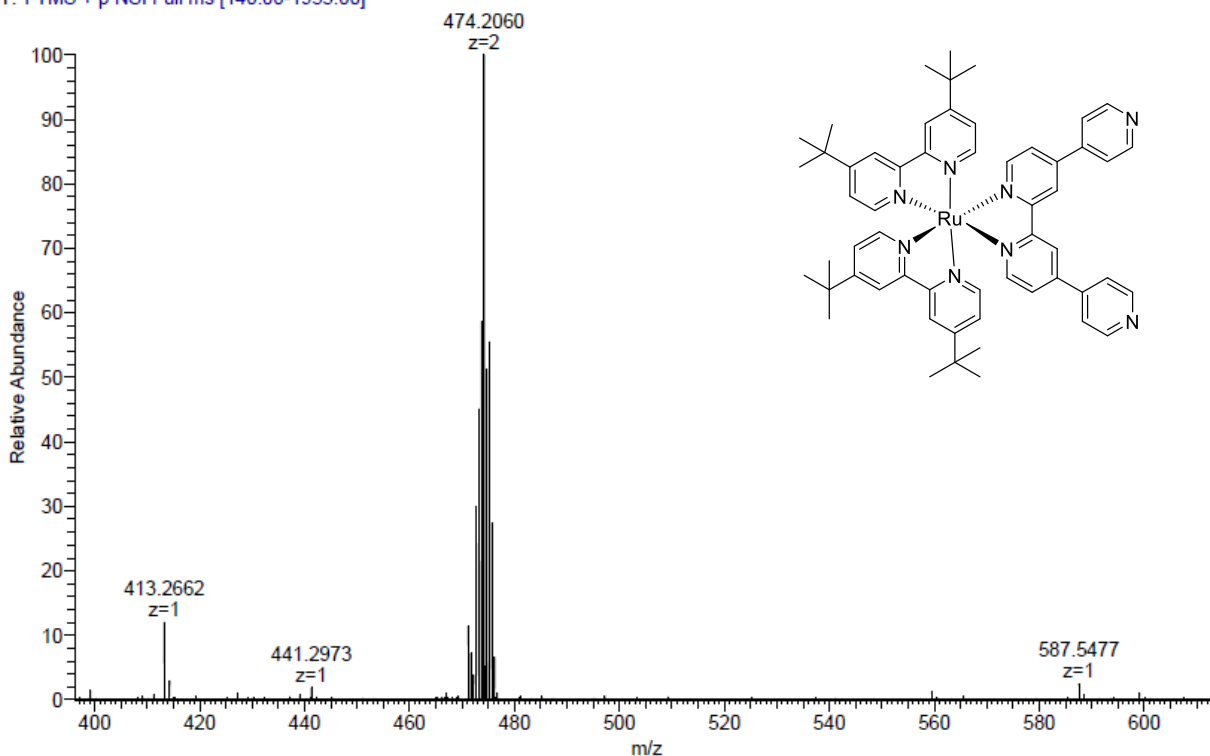


Figure S5. HR-MS spectrum of $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})](\text{PF}_6)_2$, **1**.

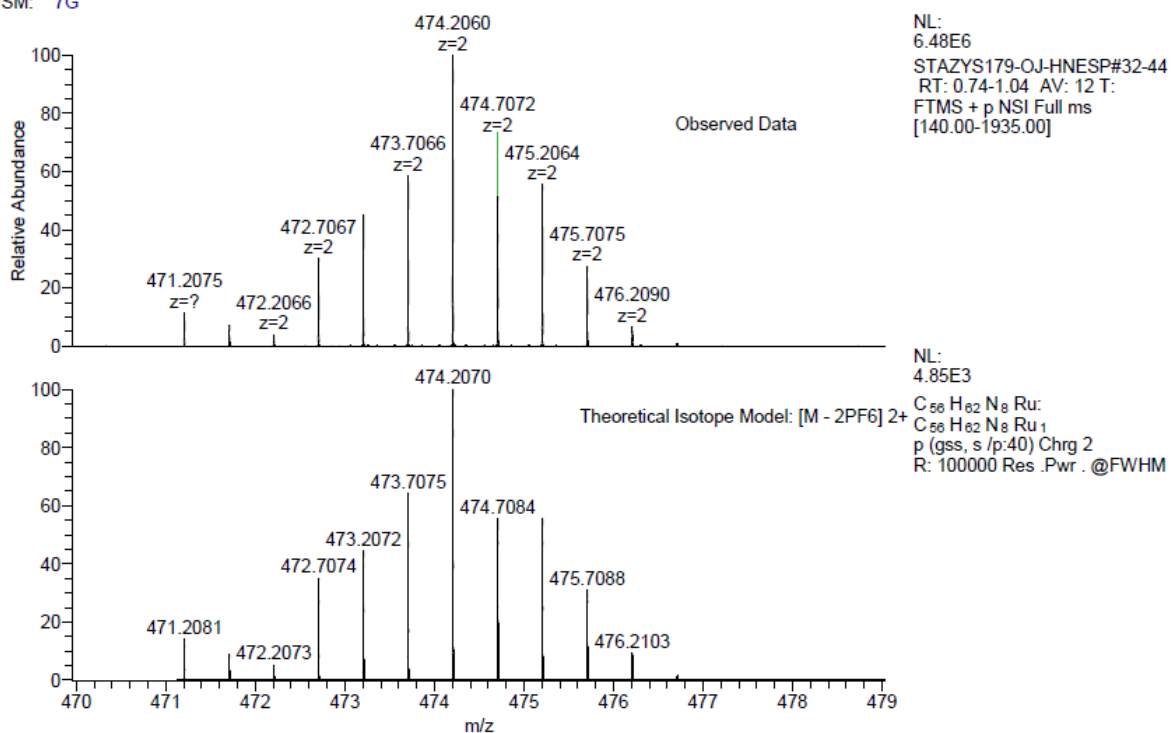


Figure S6. Molecular ion of HR-MS spectrum of $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})](\text{PF}_6)_2$, **1**.

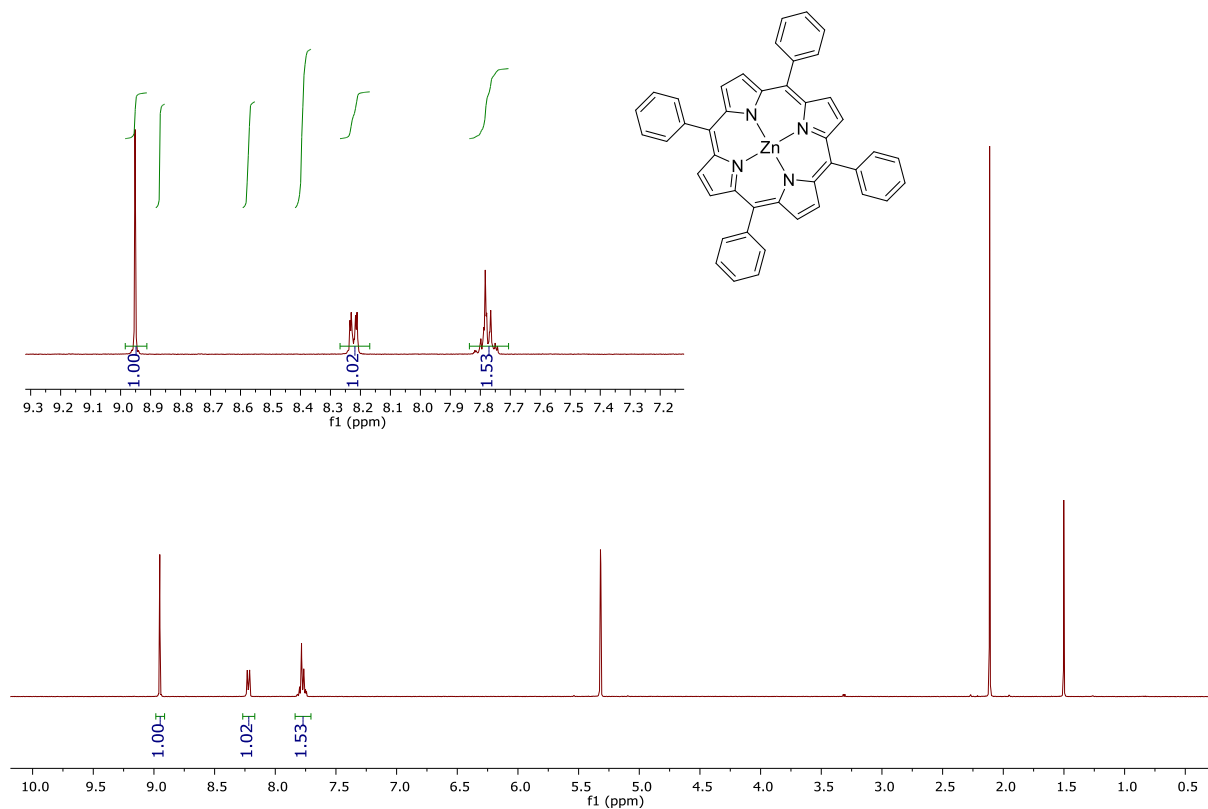


Figure S7. ¹H NMR spectrum (400 MHz, CD₂Cl₂) of ZnTPP.

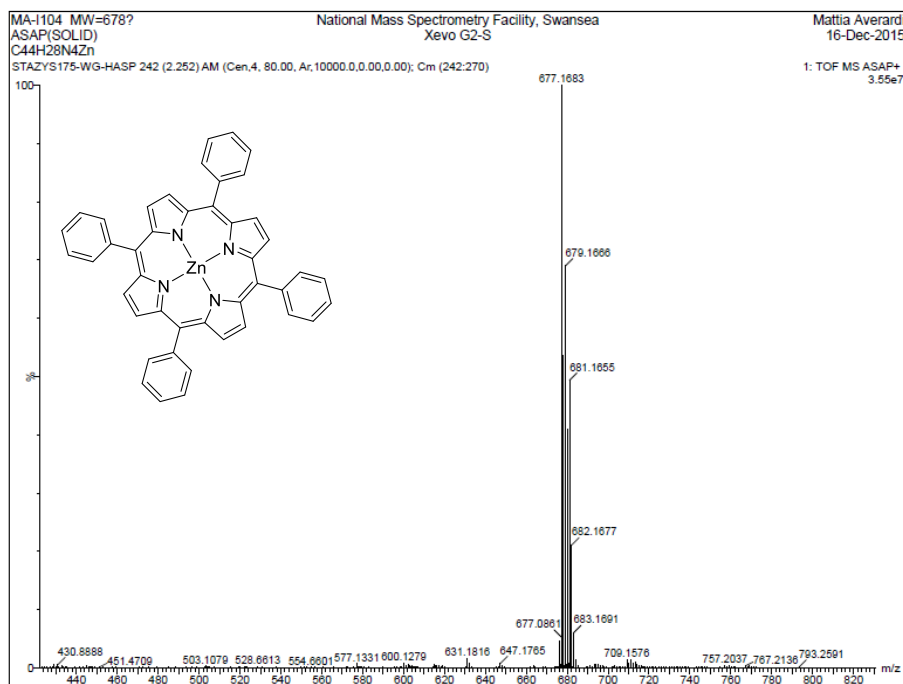


Figure S8. HR-MS spectrum of ZnTPP.

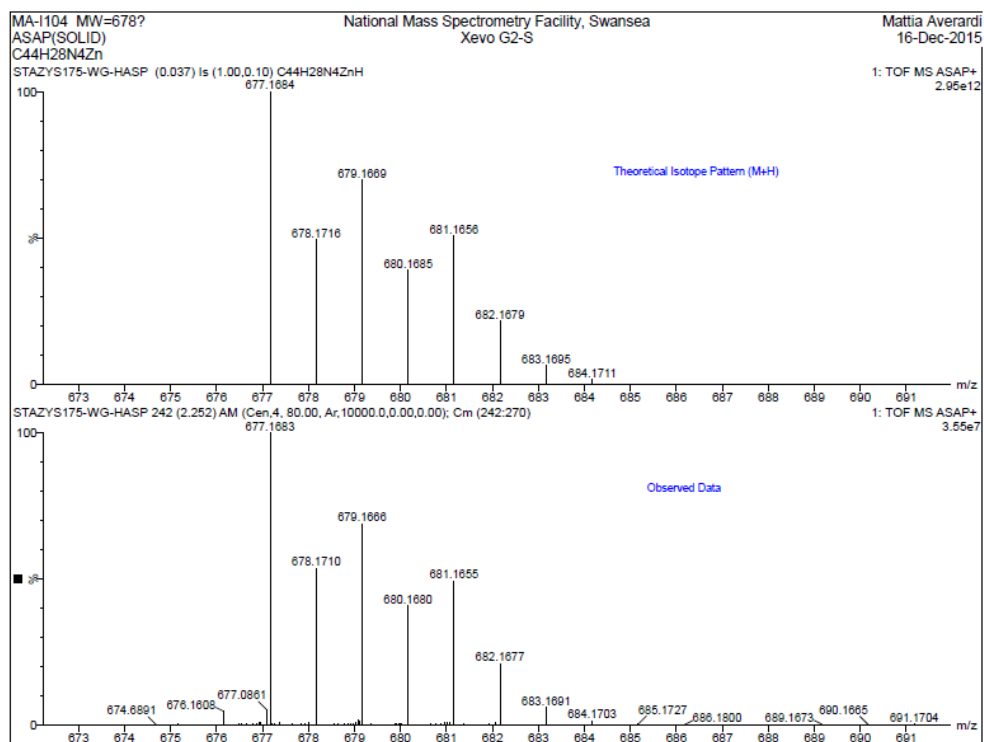


Figure S9. Molecular ion of HR-MS spectrum of ZnTPP.

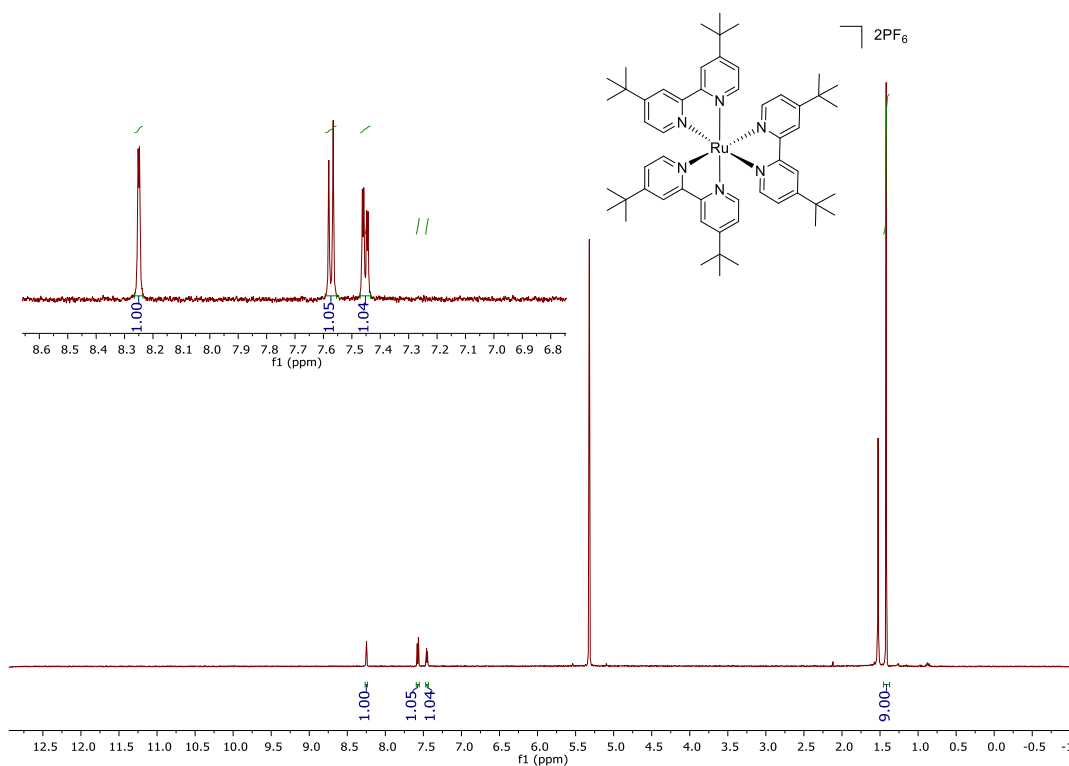


Figure S10. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of $[\text{Ru}(\text{dtBubpy})_3](\text{PF}_6)_2$, **2**.

MA-196 MW=1196?
(DCM)/MeOH
C54H72F12N6P2Ru

EPSRC National Facility Swansea
LTQ Orbitrap XL

Mattia Averardi
16/12/2015 14:25:20

STAZYS178-OJ-HNESP #32-45 RT: 0.72-1.05 AV: 13 SM: 7G NL: 6.86E7
T: FTMS + p NSI Full ms [140.00-1935.00]

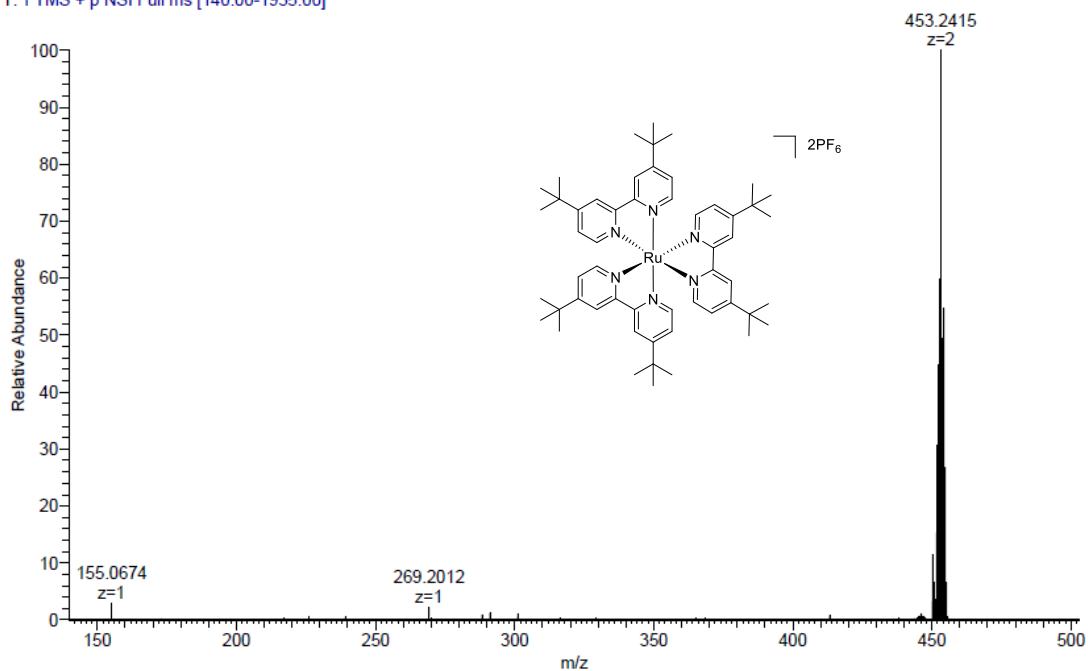


Figure S11. HR-MS spectrum of [Ru(dtBupy)₃](PF₆)₂, **2**.

MA-196 MW=1196?
(DCM)/MeOH
C54H72F12N6P2Ru
SM: 7G

EPSRC National Facility Swansea
LTQ Orbitrap XL

Mattia Averardi
16/12/2015 14:25:20

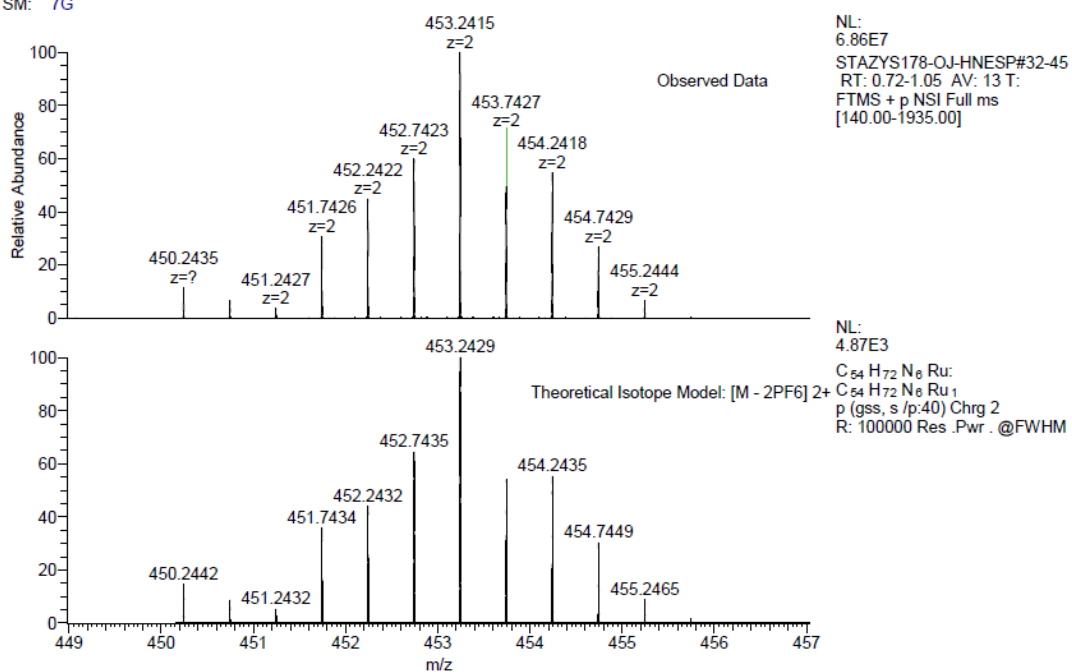
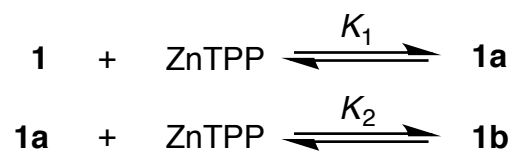


Figure S12. Molecular ion of HR-MS of [Ru(dtBubpy)₃](PF₆)₂, **2**.

Determination of association constants in **1a** and **1b**.



Association constants for the 1:1 complex **1a** and the 1:2 complex **1b** were determined by standard NMR spectroscopic titration methods. Small aliquots of ZnTPP were added to a 3.06 mM solution of **1** in CD₂Cl₂ such that the concentration of ZnTPP in the sample carried from 0 mM to 9.44 mM. A ¹H NMR spectrum was recorded on the solution after each addition and the variation of the chemical shift of H^a in **1** with respect to ZnTPP concentration determined from this data. This data was then fitted to the sequential binding model illustrated in Figure S14a using the EQNMR software.¹⁰ The best fit of the binding model to the ¹H NMR data afforded a value for K_1 of $7200 \pm 300 \text{ M}^{-1}$ and a value for K_2 of $2500 \pm 350 \text{ M}^{-1}$. Speciation data, using two scenarios – $[\mathbf{1}]/[\text{ZnTPP}] = 1$ and $[\mathbf{1}]/[\text{ZnTPP}] = 0.5$, were obtained using the parameter scan mode implemented in Gepasi.¹¹

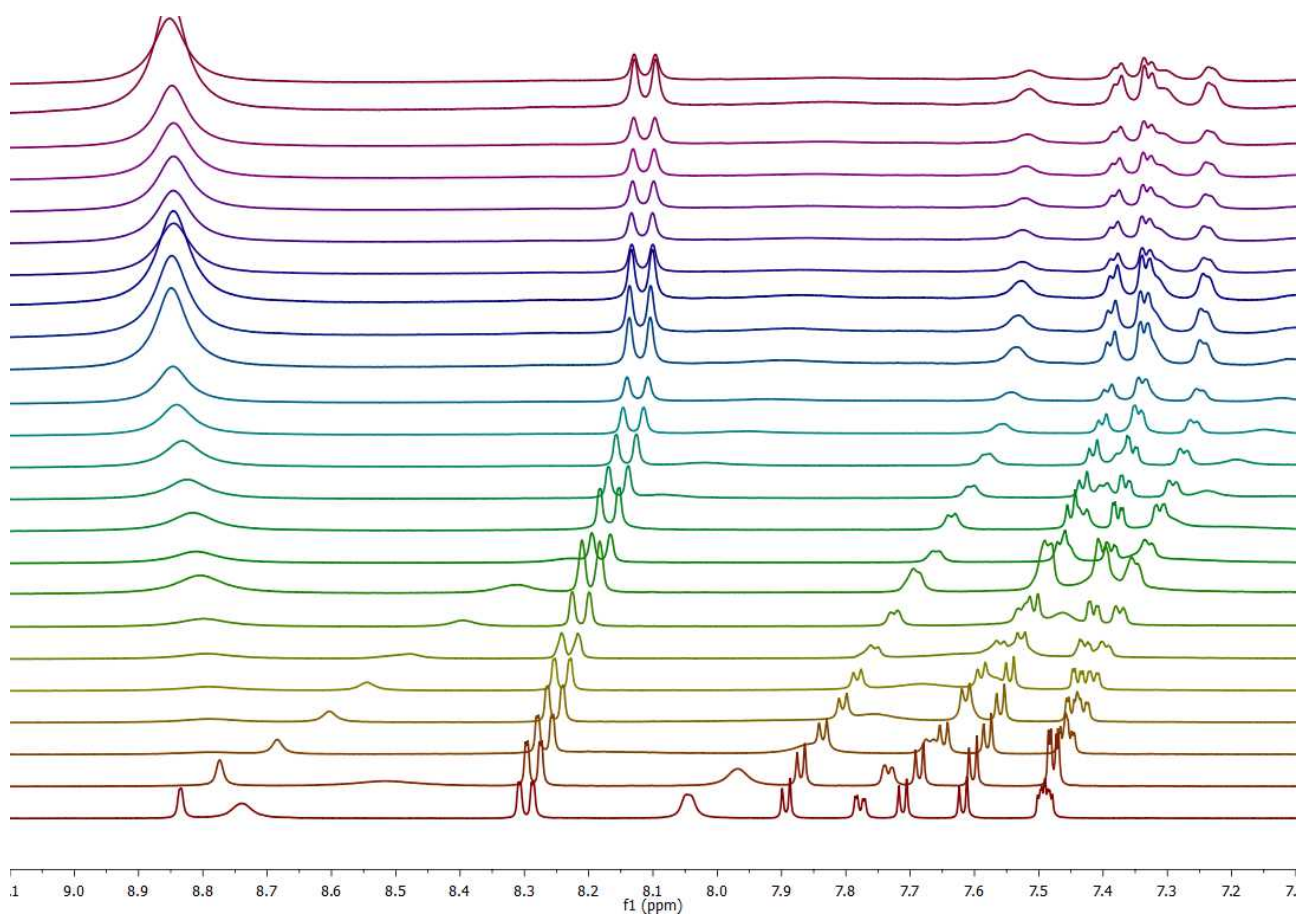


Figure S13. ^1H NMR titration experiments, with spectra collected after gradual addition of ZnTPP (from 0.1 equiv. to 2.5 equiv.) to a solution of 3.06 mM of **1**.

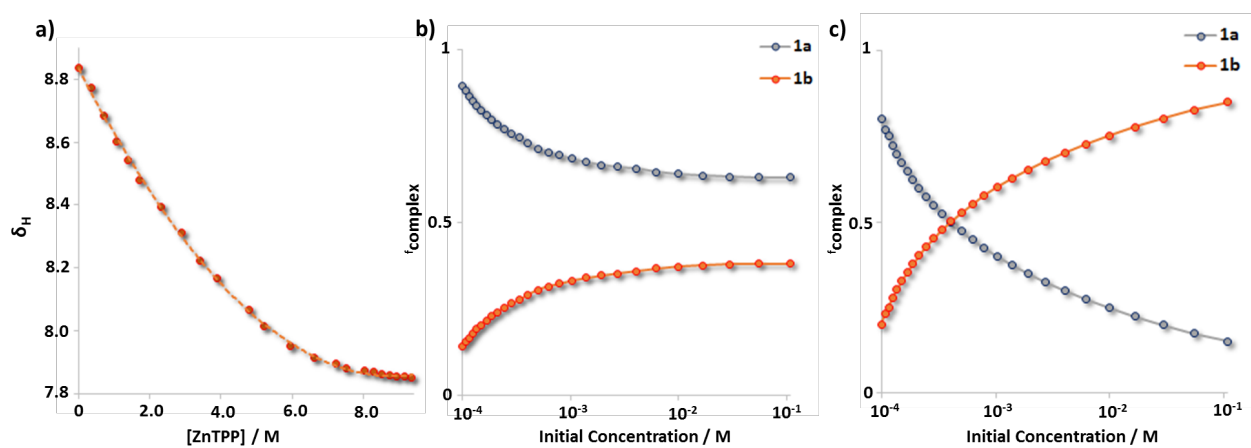


Figure S14. **a)** Chemical shift changes observed in the ^1H NMR spectrum of a 3.06 mM solution of **1** in CD_2Cl_2 on addition of aliquots of ZnTPP (red points) can be fitted (dotted orange line) to a sequential binding model for the formation of **1a** and **1b**. Fractions of 1:1 complex **1a** (blue lines) and 1:2 complex **1b**

(red lines) present in solution as a function of concentration when **(b)** $[\text{ZnTPP}]_{\text{initial}} = [\mathbf{1}]_{\text{initial}}$ and **(c)** $[\text{ZnTPP}]_{\text{initial}} = 2 \times [\mathbf{1}]_{\text{initial}}$.

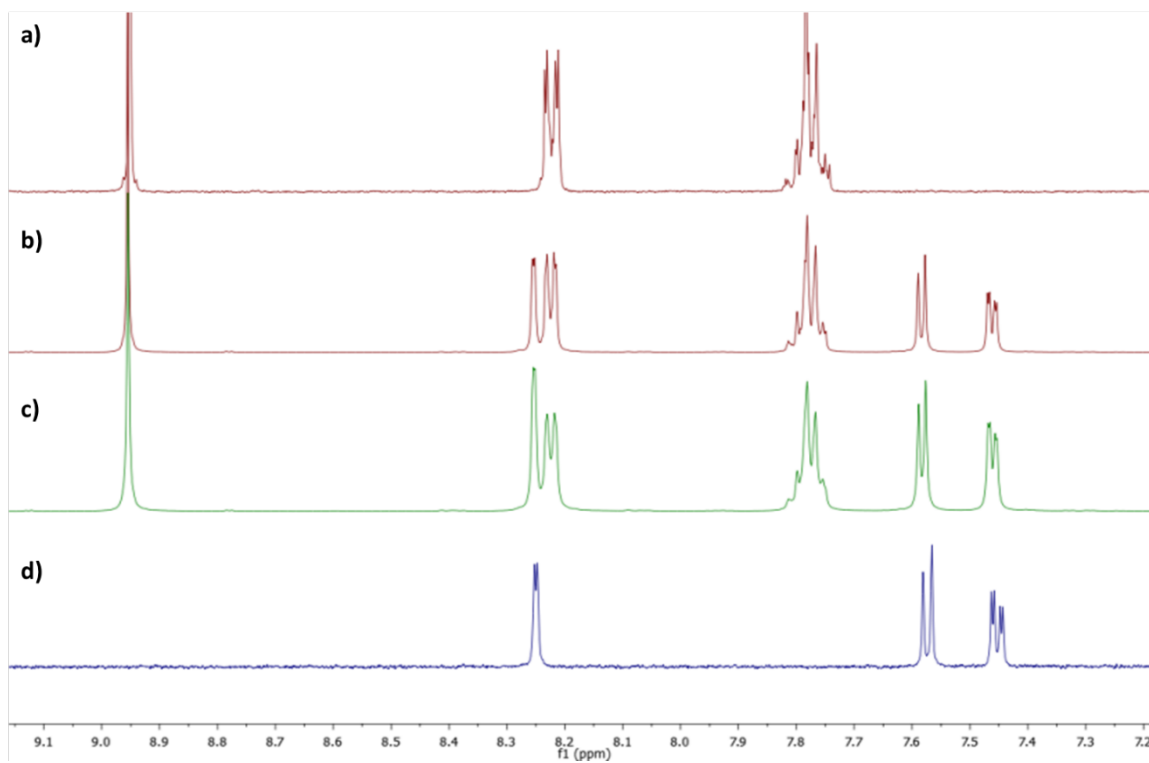


Figure S15. Control ¹H NMR spectra (CD₂Cl₂, 500 MHz, 298 K) of **a)** ZnTPP, **b)** a mixture of complex **2** and 1 equivalent of ZnTPP, **c)** a mixture of **2** and 2 equivalents of ZnTPP and **d)** complex **2**.

Supplementary Optoelectronic Characterization.

UV-Vis spectroscopy.

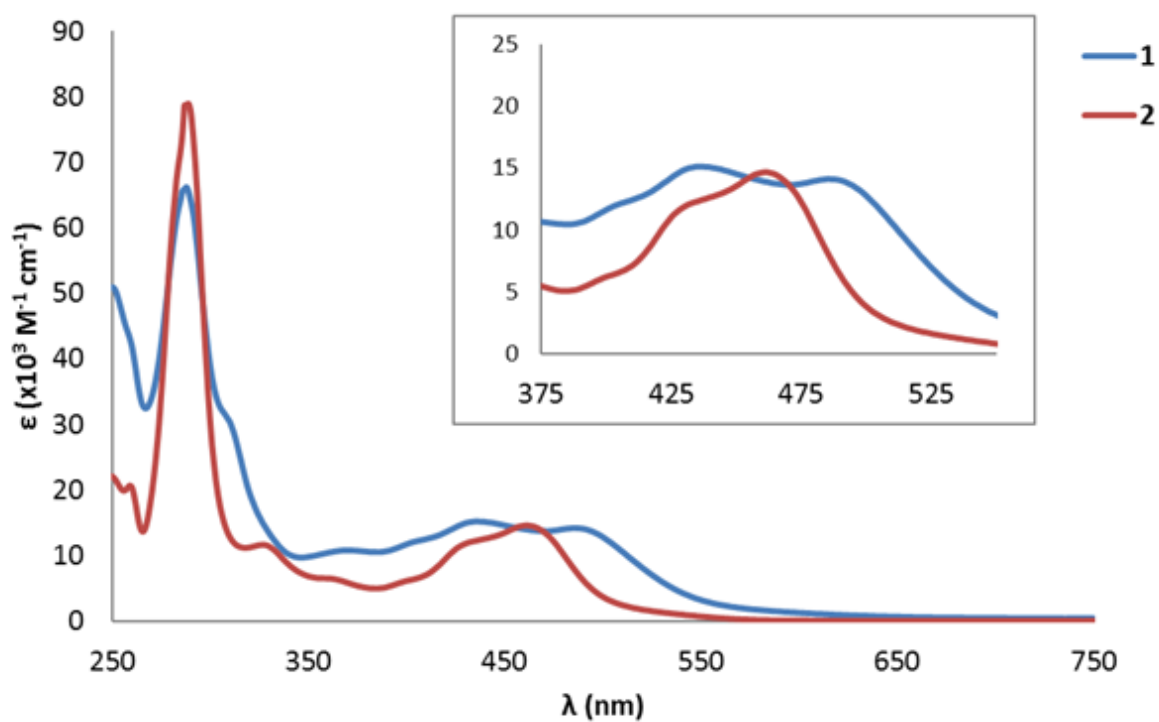


Figure S16. UV-Vis spectra of $[\text{Ru}(\text{dtBubpy})_2(\text{qpy})]_2\text{PF}_6$ (**1**, in blue), $[\text{Ru}(\text{dtBubpy})_3]_2\text{PF}_6$ (**2**, in red) collected in CD_2Cl_2 at 298 K with a concentration on the order of 10^{-6}M .

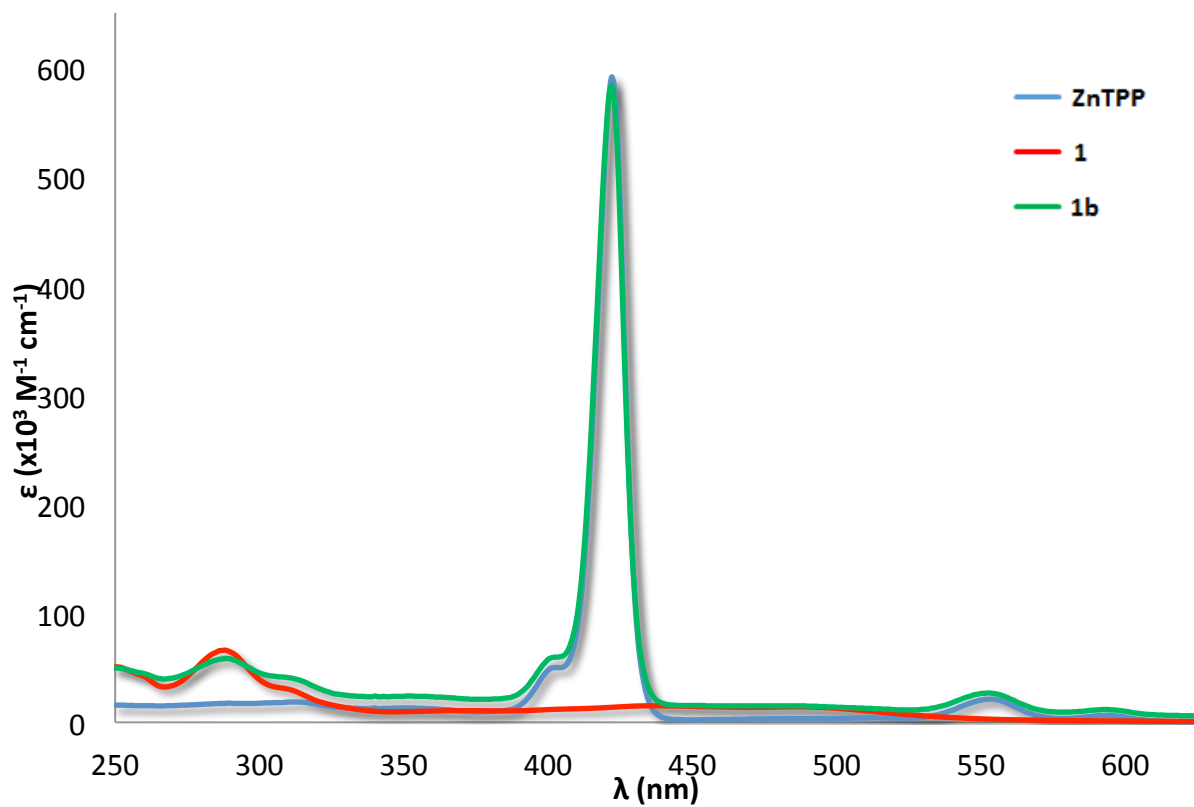


Figure S17. UV-Vis spectra of ZnTPP, (in light-blue), [Ru(dtBubpy)₂(qpy)]2PF₆ (**1**, in red) and assembly **1b** (in green) collected in CD₂Cl₂ at 298 K with a concentration on the order of 10⁻⁶M.

| Compound | $I_{\max}(\text{vis})^a$ [$\epsilon(\times 10^3 \text{ M}^{-1} \text{ cm}^{-1})$] ^b |
|-----------|---|
| ZnTPP | 285 [43.0], 399 [48.5], 422 [598], 480 [1.9], 513 [3.4], 553 [23.0], 595 [5.7] |
| 1 | 289 [65.5], 311 [29.6], 373 [10.7], 437 [15.1], 492 [13.9] |
| 2 | 290 [78.0], 331 [11.2], 369 [6.0], 429 [11.7], 469 [13.7] |
| 1b | 290 [58.0], 311 [39.2], 403 [59.7], 422 [593.2], 554 [26.5], 596 [11.0] |

Table S1. ^a UV-Vis absorption in DCM with a concentration in the order of 10⁻⁶ M collected at 298 K. ^b concentration-independent extinction coefficients.

Cyclic Voltammetry and Differential Pulse Voltammetry.

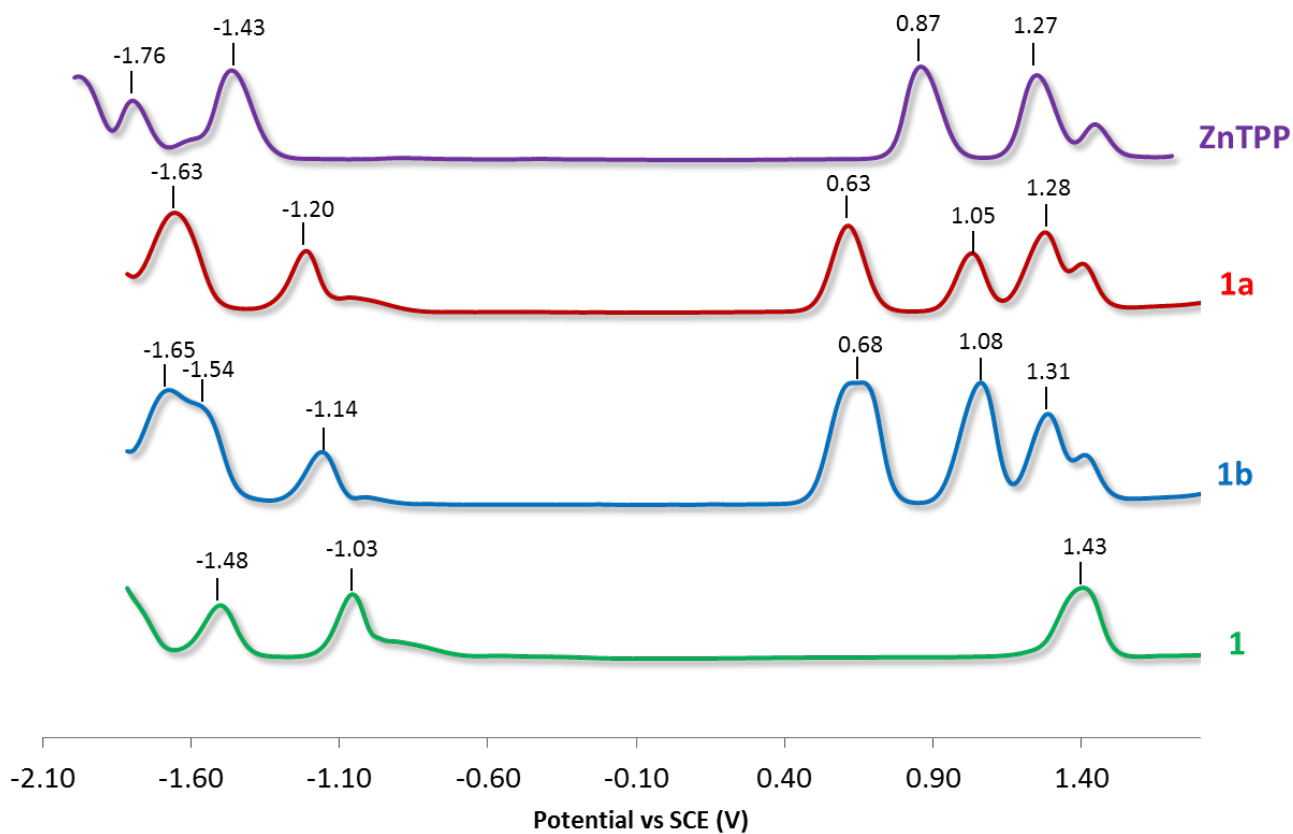


Figure S18. Differential Pulse Voltammograms for complex **1** (green line), assemblies **1a** (red line) and **1b** (light-blue line) and ZnTPP (purple line) recorded at 298 K in deareated DCM solution containing *n*-NBu₄PF₆ as the supporting electrolyte and using Fc/Fc⁺ as an internal standard (Fc/Fc⁺ = 0.46 V in DCM with respect to SCE).

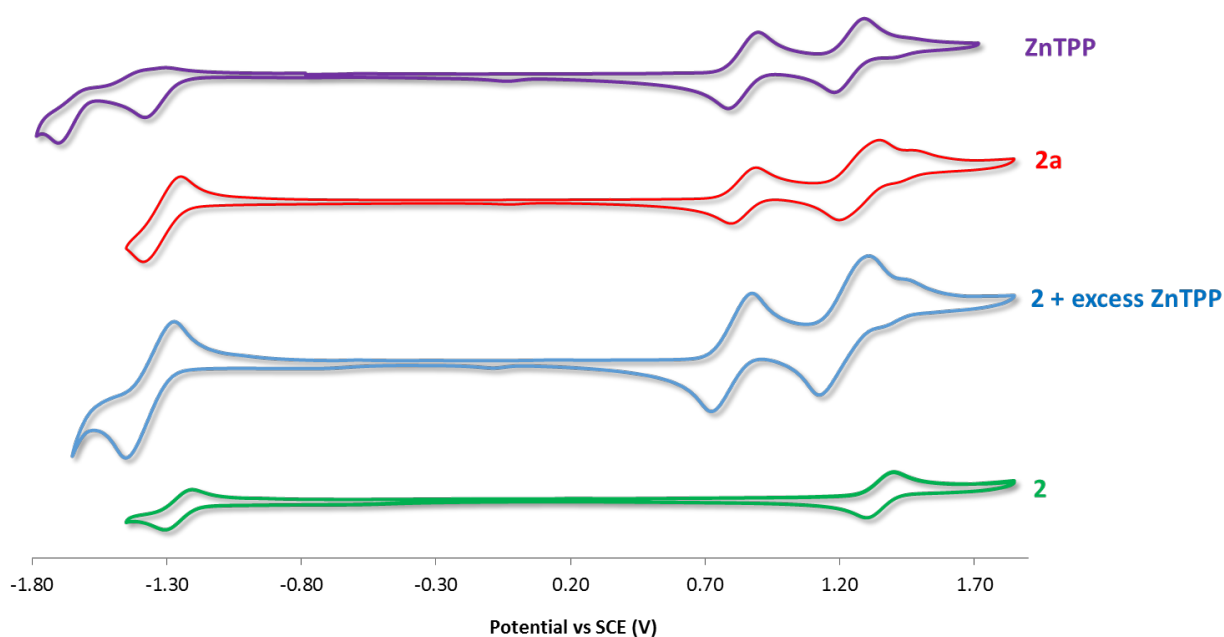


Figure S19. Cyclic Voltammograms for complex **2** (green line), “non-assemblies **2a**” (red line), **2** with an excess of ZnTPP (light-blue line) and ZnTPP (purple line) recorded at 298 K in deaerated DCM solution containing *n*-NBu₄PF₆ as the supporting electrolyte and using Fc/Fc⁺ as an internal standard (Fc/Fc⁺ = 0.46 V in DCM with respect to SCE).

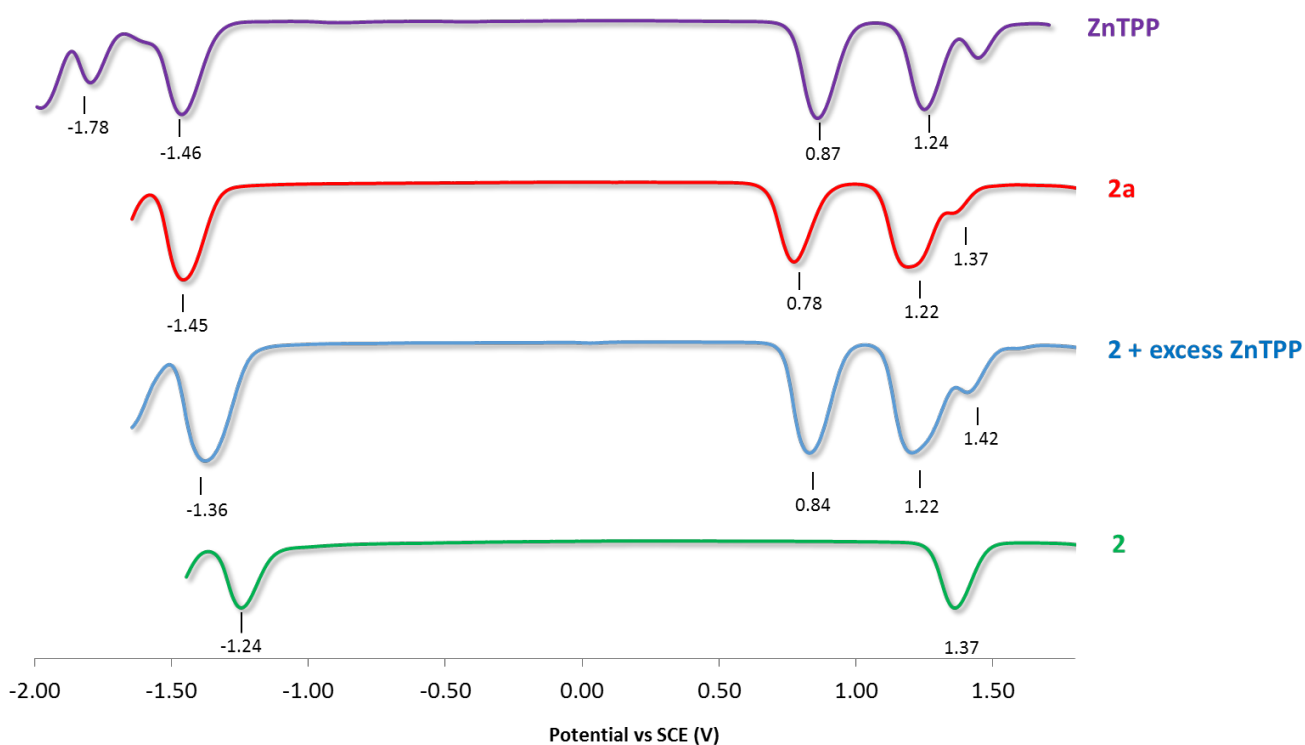


Figure S20. Differential Pulse Voltammograms for complex **2** (green line), “non-assemblies **2a**” (red line), **2** with an excess of ZnTPP (light-blue line) and ZnTPP (purple line) recorded at 298 K in deaerated DCM solution containing *n*-NBu₄PF₆ as the supporting electrolyte and using Fc/Fc⁺ as an internal standard (Fc/Fc⁺ = 0.46 V in DCM with respect to SCE).

Emission studies.

| | λ_{em} (nm) ^{a,b} | | F Φ (%) ^{a,c} | |
|--------------|------------------------------------|--------------------------------|---------------------------------------|---------------------------------------|
| | $\lambda_{exc} = 420$ nm | $\lambda_{exc} = 555$ nm | $\lambda_{exc} = 420$ nm ^c | $\lambda_{exc} = 555$ nm ^c |
| ZnTPP | 605 [0.6], 651 [1], 716 [0.04] | 605 [0.6], 651 [1], 716 [0.04] | 3.7 | 0.8 |

| | | | | |
|-----------|---------------------|---------------------|------------------|------------------|
| 1 | 672 [1] | 672 [1] | - | 7.3 |
| 1a | 601 [0.09], 655 [1] | 601 [0.09], 655 [1] | < 1 ^d | < 1 ^d |
| 1b | 603 [0.19], 655 [1] | 603 [0.19], 655 [1] | < 1 ^d | < 1 ^d |
| 2 | 615 [1] | 615 [1] | - | 9.1 |
| 2a | 599 [0.05], 655 [1] | 599 [0.05], 655 [1] | 1.4 | < 1 ^d |

Table S2. ^a Measurements in deaerated DCM at 298 K at *ca.* 10⁻⁵ M. ^b Relative intensity of principal emission peaks listed in []. ^c Using [Ru(bpy)₃]Cl₂ as the standard ($\Phi_{\text{PL}} = 4\%$ in aerated H₂O at 298 K). ^d Estimated from the reduction of the emission counting compared to neat ZnTPP.

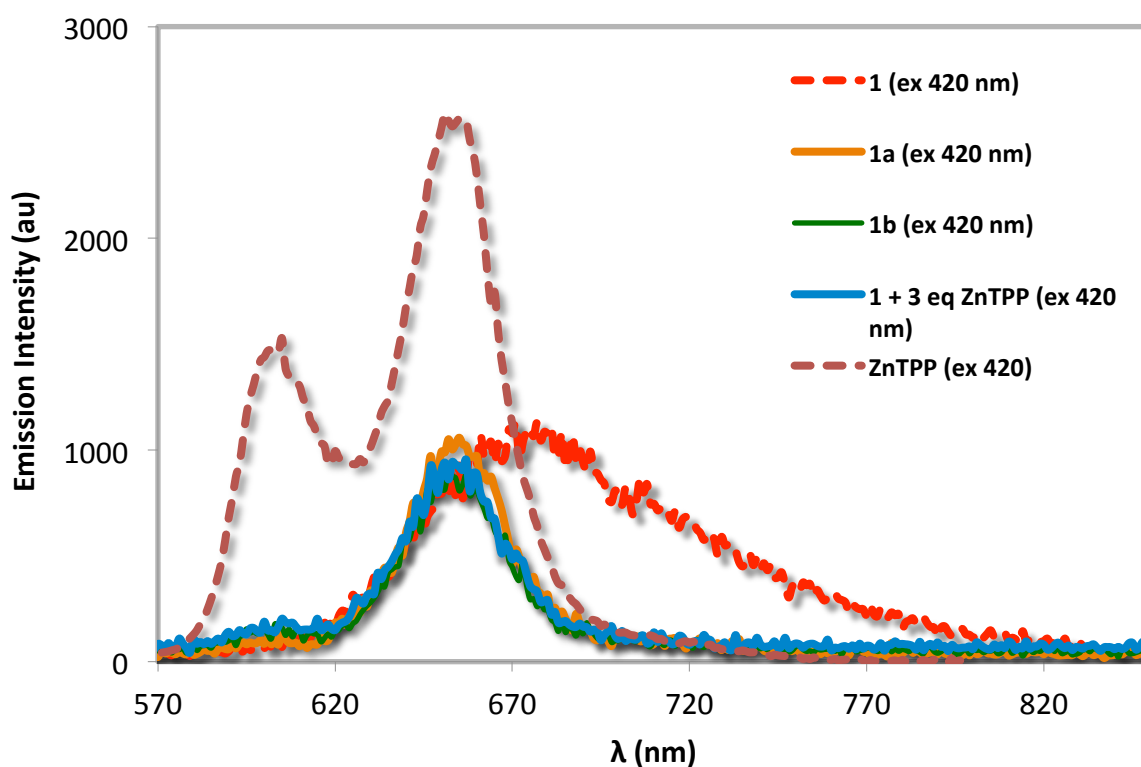


Figure S21. Luminescence spectra of **1** (dotted red line), **1a** (solid orange line), **1b** (solid green line), **1** with an excess of ZnTPP (solid blue line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 420$ nm) with a concentration in the order of 3×10^{-4} M.

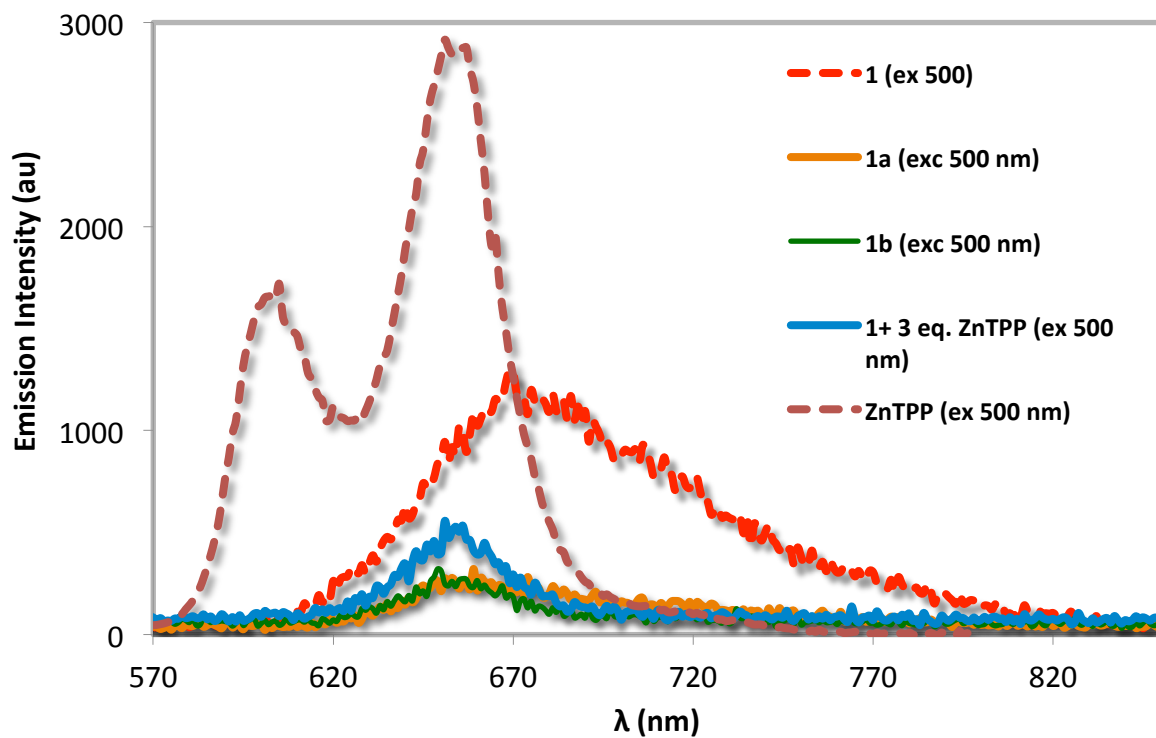


Figure S22. Luminescence spectra of **1** (dotted red line), **1a** (solid orange line), **1b** (solid green line), **1** with an excess of ZnTPP (solid blue line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 500$ nm) with a concentration in the order of 3×10^{-4} M.

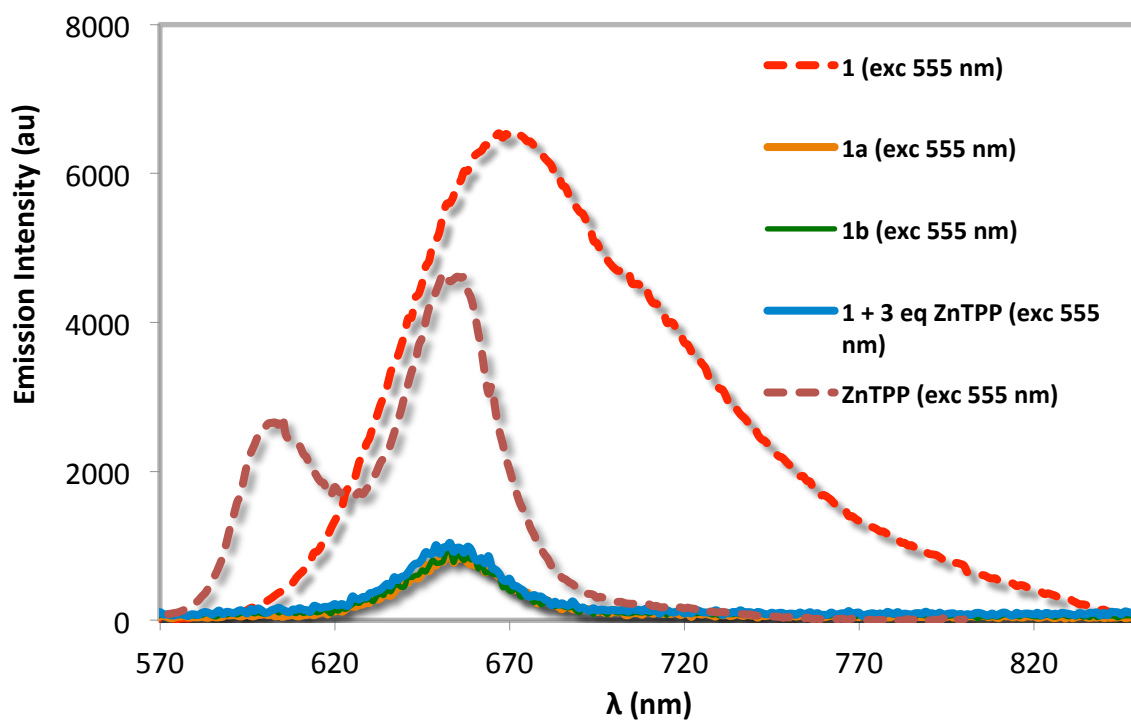


Figure S23. Luminescence spectra of **1** (dotted red line), **1a** (solid orange line), **1b** (solid green line), **1** with an excess of ZnTPP (solid blue line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 550$ nm) with a concentration in the order of 3×10^{-4} M.

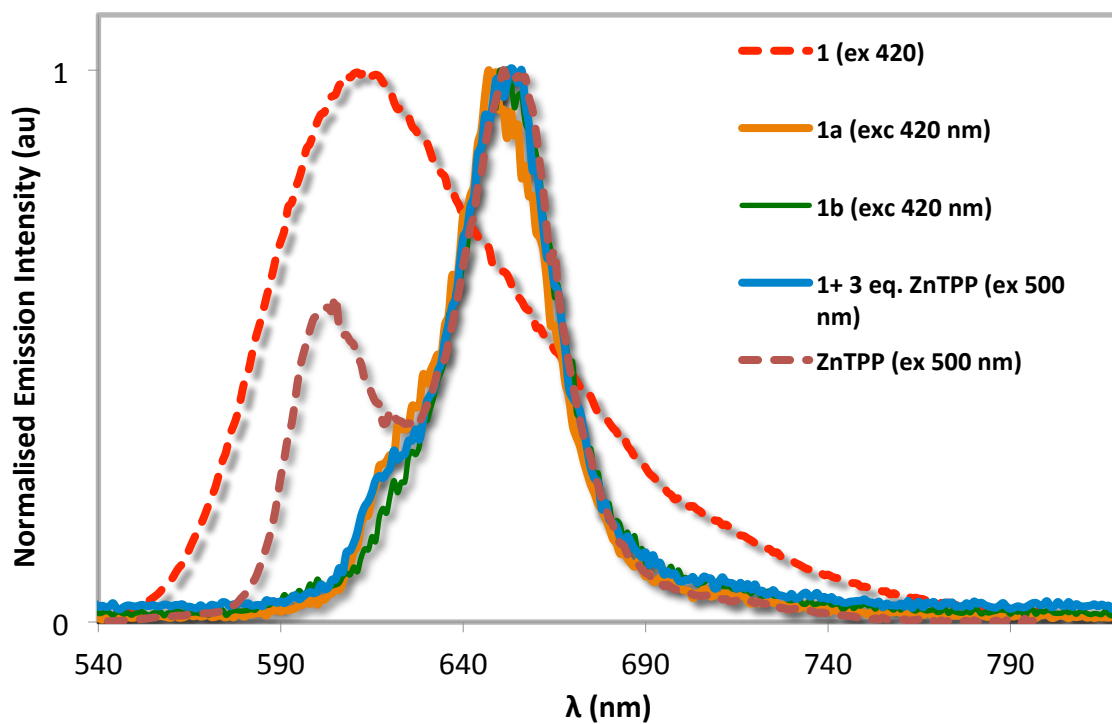


Figure S24. Luminescence spectra of **2** (dotted red line), **2** with 1 equiv. of ZnTPP (solid orange line), **2** with 2 equiv. of ZnTPP (solid green line), **2** with 3 equiv. of ZnTPP (solid blue line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 500$ nm) with a concentration in the order of 3×10^{-4} M.

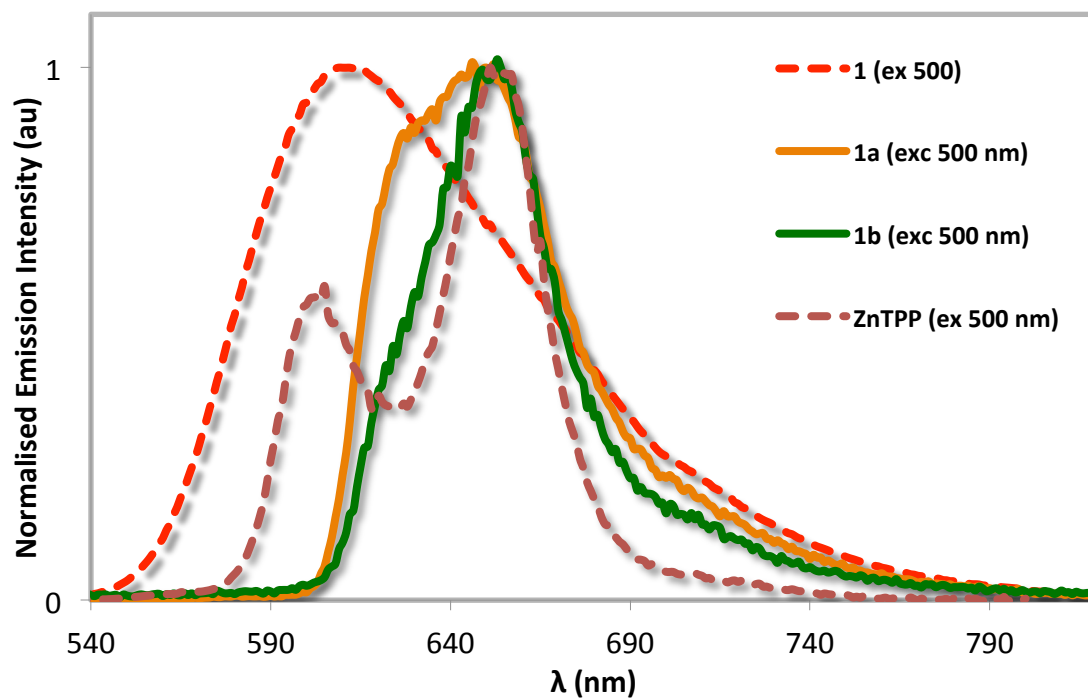


Figure S25. Luminescence spectra of **2** (dotted red line), **2** with 1 equiv. of ZnTPP (solid orange line), **2** with 2 equiv. of ZnTPP (solid green line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 500 \text{ nm}$) with a concentration in the order of $3 \times 10^{-4} \text{ M}$.

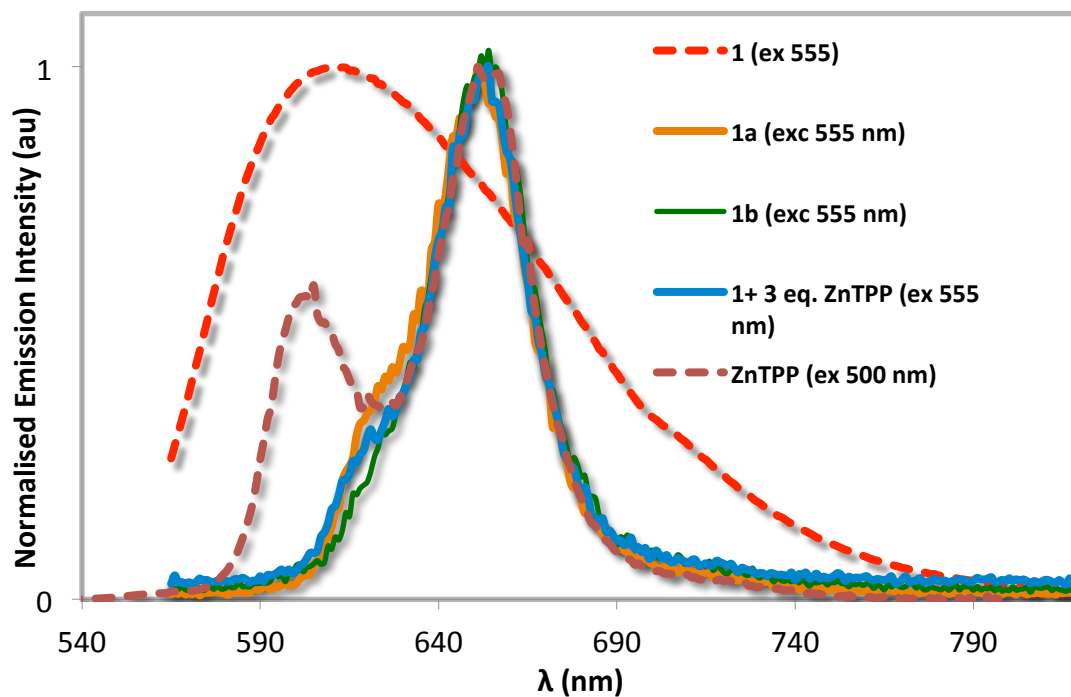


Figure S26. Luminescence spectra of **2** (dotted red line), **2** with 1 equiv. of ZnTPP (solid orange line), **2** with 2 equiv. of ZnTPP (solid green line), **2** with 3 equiv. of ZnTPP (solid blue line) and ZnTPP (dotted brown line) recorded in degassed DCM at 298 K ($\lambda_{\text{ex}} = 550 \text{ nm}$) with a concentration in the order of $3 \times 10^{-4} \text{ M}$.

Computational details.

All calculations use density functional theory (DFT). The geometries of the singlet ground-state (S_0) and the lowest triplet excited-state (T_1) were optimized for complex **1** and the assembly **1a** using the hybrid exchange-correlation functional B3LYP¹² in combination with the def2-SVP atomic basis set under the resolution of the identity (RI) approximation. Scalar relativistic effects were included for the Ru atom by using the ECP-28-mwb Stuttgart/Dresden pseudopotential.¹³ The nature of the stationary points was confirmed by computing the Hessian at the same level of theory. Gas-phase TD-B3LYP vertical singlet energies were obtained at the S_0 geometry using the def2-SVP atomic basis set. Optimizations and TD-DFT calculations were carried out with the Turbomole 6.6 program package.¹⁴

Table S3. Main Vertical (at S_0 geometry) Singlet Electronic Transition Energies (in eV) and Oscillator strengths (in Parentheses) of **1** at the TD-B3LYP/def2-SVP Level of Theory.

| | States | Energy (<i>f</i>) | Character |
|----------|-----------------|---------------------|---|
| 1 | S ₄ | 2.69 (0.036) | ¹ MLCT ($d_{\text{Ru}} \rightarrow \pi_{\text{dtBubpy+qpy}}$) |
| | S ₇ | 2.83 (0.164) | ¹ MLCT ($d_{\text{Ru}} \rightarrow \pi_{\text{dtBubpy+qpy}}$) |
| | S ₈ | 2.86 (0.107) | ¹ MLCT($d_{\text{Ru}} \rightarrow \pi_{\text{dtBubpy+qpy}}$) |
| | S ₄₁ | 3.93 (0.103) | ¹ LC ($\pi_{\text{qpy}} \rightarrow \pi_{\text{dtBubpy+qpy}}$) |

References.

- (1). N. A. F. Al-Rawashdeh, S. Chatterjee, J. A. Krause and W. B. Connick, *Inorg. Chem.*, 2014, **53**, 294-307.
- (2). N. Zabarska, J. G. Vos and S. Rau, *Polyhedron*, 2015, **102**, 173-175.
- (3). D. Rota Martir, G. J. Hedley, D. B. Cordes, A. M. Z. Slawin, D. Escudero, D. Jacquemin, T. Kosikova, D. Philp, D. M. Dawson, S. E. Ashbrook, I. D. W. Samuel and E. Zysman-Colman, *Dalton Trans.*, 2016, **45**, 17195-17205.
- (4). B. J. Coe, E. C. Harper, M. Helliwell and Y. T. Ta, *Polyhedron*, 2011, **30**, 1830-1841.
- (5). H. Huang, B. Yu, P. Zhang, J. Huang, Y. Chen, G. Gasser, L. Ji and H. Chao, *Angew. Chem. Int. Ed.*, 2015, **54**, 14049-14052.
- (6). M. Schwalbe, B. Schäfer, H. Görls, S. Rau, S. Tschierlei, M. Schmitt, J. Popp, G. Vaughan, W. Henry and J. G. Vos, *Eur. J. Inorg. Chem.*, 2008, **2008**, 3310-3319.
- (7). G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991-1024.
- (8). (a) K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys Chem Chem Phys*, 2009, **11**, 9850-9860; (b) A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213-2228.
- (9). N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
- (10). M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311-312.
- (11). (a) P. Mendes, *Computer applications in the biosciences : CABIOS*, 1993, **9**, 563-571; (b) P. Mendes and D. Kell, *Bioinformatics*, 1998, **14**, 869-883.
- (12). (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
- (13). D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theoretica chimica acta*, **77**, 123-141.
- (14). *TURBOMOLE V6.6; a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007; TURBOMOLE GmbH, since 2007. Available from <http://www.turbomole.com>.*, 2014.