Supporting Information

Three is not a crowd: Efficient sensitization of TiO_2 by a bulky trichromic trisheteroleptic cycloruthenated dye

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1. Experimental

All manipulations were performed using solvents passed through an MBraun solvent purification system prior to use; chloroform ($CHCl_3$) and tetrahydrofuran (THF) solvents were analytical grade (without stabilizer). All reagents were purchased from Aldrich unless otherwise stated. 1-bromo-2,4-bis(trifluoromethyl)benzene was purchased from Oakwood Chemical and $Pd(PPh_3)_4$ from the Pressure Chemical Company. 4,4'-diethylester-2,2'-bipyridine (deeb), 4,4'-dicarboxy-2,2'-bipyridine (dcbpy), 4,4'-dibromo-2-2'-bipyridine, 1-butyl-3-methylimidazolium iodide, $[Ru(bpy)(deeb)(ppy)]PF_6$ and compounds **P1** and **P4** were prepared as previously reported.[1-3] Purification by column chromatography was carried out using silica (Silicycle: Ultrapure Flash Silica) and Sephadex L-20. Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets pre-coated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany). ^{1}H NMR chemical shifts (d) are reported in parts per million (ppm) from low to high field and referenced to residual non-deuterated solvent. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. Labeling scheme for ^{1}H NMR assignments for all compounds follows Fig. S5. Elemental analysis (EA) and electrospray ionization (ESI) mass spectrometry data were collected at the University of Calgary.

N-(4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)phenyl)-4-(hexyloxy)-N-(4-(hexyloxy)phenyl)benzenamine (P2) – A degassed THF solution (75 mL) containing **P1** (785 mg, 1.29 mmol) was cooled to -78 °C at which point n-butyllithium (0.62 mL, 1.6 mmol) was added dropwise while maintaining the temperature at -78 °C. After stirring the reaction for 45 minutes, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.40 mL, 2.0 mmol) was added. The dark green reaction was warmed to 25 °C and stirred for 18 h to produce a light orange solution. The addition of MeOH (mL) turned the solution orange in colour. The solvent was removed in vacuo and the residual product redissolved in DCM and washed with H_2O (3 × 20 mL), then dried with $MgSO_4$ and filtered. The resultant product was preadsorbed on SiO_2 and purified using column chromatography [SiO_2; CH_2Cl_2/Hexanes, 4:1, *v*:*v*) to remove impurities followed by EtOAc to obtain the product]. The product could not be isolated pure. The resultant mixture was used as is in subsequent reaction steps.

4,4'-di(N-(4-(5-thiophen-2-yl)phenyl)-4-(hexyloxy)-N-(4-(hexyloxy)phenyl)benzenamine)-2,2'-bipyridine (P3) – A degassed THF/H_2O (9:1, *v*:*v*, 50 mL) solution containing **P2** (520 mg, 0.795 mmol), 4,4'-dibromo-2,2'-bipyridine (101 mg, 0.322 mmol), K_2CO_3 (554 mg, 4.00 mmol) and $Pd(PPh_3)_4$ (45 mg, 0.039 mmol) was heated at reflux for 24 h upon which a half equivalent of $Pd(PPh_3)_4$ (22 mg,

0.019 mmol) was added to the reaction. The reaction was heated at reflux for another 16 h and then the solvent removed in vacuo. The resultant solid was redissolved in DCM and washed with H_2O (3 × 20 mL), then dried with $MgSO_4$ and filtered. Hexanes were added to the filtrate to precipitate the desired product. Filtration yielded 350 mg (95.0%) of a yellow/green solid. ^{1}H NMR ($CDCl_3$): δ 8.67 (d, 2H, ^3J = 5.3 Hz, H_a), 8.65 (d, 2H, ^4J = 1.7 Hz, H_c), 7.62 (d, 2H, ^3J = 3.8 Hz, H_d), 7.51 (dd, 2H, ^3J = 5.2 Hz, ^4J = 1.8 Hz, H_b), 7.45 (d, 4H, ^3J = 8.7, H_f), 7.23 (d, 2H, ^3J = 3.8 Hz, H_e), 7.09 (d, 8H, ^3J = 8.9 Hz, H_h), 6.93 (d, 4H, ^3J = 8.7 Hz, H_i), 6.85 (d, 8H, ^3J = 8.9 Hz, H_g), 3.95 (t, 8H, ^3J = 6.6 Hz, H_j), 1.79 (m, 8H, H_k), 1.48 (m, 8H, H_l), 1.35 (m, 16H, $H_{m,n}$), 0.92 (m, 12H, H_o). ^{13}C NMR ($CDCl_3$): 156.1, 149.2, 140.4, 132.4, 132.3, 132.1, 132.1, 128.8, 128.7, 127.1, 126.7, 125.7, 123.1, 120.2, 119.8, 117.3, 115.6, 68.5, 31.8, 29.6, 26.0, 22.8, 14.2. HRMS (ESI): *m/z* = 1207.61370 [$(M+H)^+$] (calcd for $[C_{78}H_{87}N_4O_4S_2]$+: *m/z* = 1207.61687).

[Ru(L1)(deeb)(ppy(CF$_3$)$_2$)]PF$_6$ (P5) – To a 3:1 ABS EtOH/$CHCl_3$ mixture containing deeb (77.6 mg, 0.259 mmol) and **P3** (312 mg, 0.259) was added **P4** (181 mg, 0.259 mmol). The reaction mixture was heated at reflux for 1.5 h to produce a dark brown solution. After solvent removal *in vacuo* the resultant solid was purified by column chromatography [SiO_2; DCM/MeCN (96:4); Rf = 0.6] and isolated to afford 267 mg (52.5%) of a brown solid. ^{1}H NMR ($CDCl_3$): δ 9.00 (s, 1H, H_t), 8.93 (s, 1H, H_s), 8.35 (m, 3H, $H_{e,l,m}$), 8.11 (d, 1H, ^3J = 6.1 Hz, H_q), 8.03 (d, 1H, ^3J = 5.6 Hz, H_v), 7.83 (m, 2H, $H_{f,u}$), 7.71 (dd, 1H, ^3J = 5.7 Hz, ^4J = 1.1 Hz, H_h), 7.65 (m, 3H, $H_{r,w,y}$), 7.55 (s, 1H, H_c), 7.47 (d, 1H, ^3J = 6.2 Hz, H_i), 7.43 (d, 1H, ^3J = 6.1 Hz, H_p), 7.30 (m, 6H, $H_{j,o,a',a''}$), 7.18 (m, 3H, $H_{a,x,z}$), 7.06 (ddd, 1H, ^3J = 7.8 Hz, 5.9 Hz, ^4J = 1.0 Hz, H_g), 6.93 (d, 4H, ^3J = 8.9 Hz, $H_{d' or d''}$), 6.92 (d, 4H, ^3J = 8.9 Hz, $H_{d' or d''}$), 6.77 (d, 4H, ^3J = 8.9 Hz, $H_{c' or c''}$), 6.76 (d, 4H, ^3J = 8.9 Hz, $H_{c' or c''}$), 6.67 (d, 2H, ^3J = 8.5 Hz, $H_{b' or b''}$), 6.65 (d, 2H, ^3J = 8.6 Hz, $H_{b' or b''}$), 4.43 (m, 2H, ^3J = 7.1 Hz, $H_{k' or k''}$), 4.41 (m, 2H, ^3J = 7.1 Hz, $H_{k' or k''}$), 3.83 (t, 8H, ^3J = 6.5 Hz, $H_{e',e''}$), 1.64 (quintet, 8H, ^3J = 5.3 Hz, $H_{f',f''}$), 1.37 (m, 14H, $H_{g',g'',l',l''}$), 1.25 (m, 16H, $H_{h',h'',i',i''}$), 0.83 (m, 12H, $H_{j',j''}$). MS (ESI): *m/z* = 1898.4 [M^+] (calcd for $[RuC_{107}H_{108}F_6N_7O_8S_2]^+$: *m/z* = 1898.6). Anal. calcd. for $RuC_{107}H_{108}F_{12}N_7O_8S_2P$: C, 62.87; H, 5.33; N, 4.80. Found: C, 62.93; H, 5.21; N, 4.64.

[Ru(P3)(dcbpy)(ppy-(CF$_3$)$_2$)]PF$_6$ (3) – A 3:1:1 DMF/H_2O/NEt_3 mixture containing **P5** (240 mg, 0.118 mmol) was heated at reflux for 18 h to produce a dark brown solution. After solvent removal *in vacuo* the resultant solid was purified by column chromatography [Sephadex; Acetone] and isolated to afford 140 mg (62.7%) of a brown solid. MS (ESI): *m/z* = 1842.7 [M^+] (calcd for $[RuC_{103}H_{100}F_6N_7O_8S_2]^+$: *m/z* = 1842.6). Anal. calcd. for $RuC_{103}H_{100}F_{12}N_7O_8S_2P$: C, 62.23; H, 5.32; N, 5.00. Found: C, 62.75; H, 5.07; N, 4.93.

Physical Methods. 1D and 2D ^{1}H and ^{13}C spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature unless otherwise stated. Electrochemical measurements were performed under anaerobic conditions with a Princeton Applied Research VersaStat 3 potentiostat using dry solvents, Pt working and counter electrodes, a Ag pseudoreference electrode, and 0.1 M NBu_4BF_4 supporting electrolyte. Electronic spectroscopic data were collected on DMF solutions using a Cary 5000 UV-vis spectrophotometer (Varian). Steady-state emission spectra were obtained at room temperature using an Edinburgh Instruments FLS920 Spectrometer equipped with a Xe900 450W steady state xenon arc lamp, TMS300-X excitation monochromator, TMS300-M emission monochromator, Hamamatsu R2658P PMT detector and corrected for detector response. Lifetime measurements were obtained at room temperature using an Edinburgh Instruments FLS920 Spectrometer equipped with Fianium SC400 Super Continuum White Light Source, Hamamatsu R3809U-50 Multi Channel Plate detector and data were analyzed with Edinbrugh Instruments F900 software. Curve fitting of the data was performed using a non-linear least squares procedure in the F900 software.

Cell Fabrication. Photoanodes were prefabricated by Dyesol, Inc. (Australia) with a screen-printable TiO_2 pastes (18-NRT and WER4-O, Dyesol™). The active area of the TiO_2 electrode is 0.28 cm^2 with a thickness of 12 μm (18-NRT) and 3 μm (WER4-O) on fluorine-doped tin-oxide (FTO; TEC8 (8 Ω cm^{-2})). TiO_2 substrates were treated with $TiCl_{4(aq)}$ (0.05 M) at 70 °C for 30 min and subsequently rinsed with H_2O and dried prior to heating. The electrodes were heated to 450 °C for 20 min under ambient atmosphere and allowed to cool to 80 °C before dipping into the dye solution. The anode was soaked overnight for 16 h in an ABS EtOH solution containg dye (~0.25 mM) and chenodeoxycholic acid (~2.5 mM). The stained films were rinsed copiously with ABS EtOH and dried. The cells were fabricated using Pt-coated counter-electrode (FTO TEC-15 (15 Ω cm^{-2})) and sealed with a 30 μm Surlyn (Dupont) gasket by resistive heating. An acetonitrile based electrolyte solution: (0.6M butylmethylimidazolium iodide, 0.06M I_2, 0.1M sodium iodide, 0.1M guanidinium thiocyanate and 0.5M *tert*-butylpyridine in acetonitrile) was introduced to the void via vacuum backfilling through a hole in the counter electrode. The hole was sealed with an aluminum-backed Bynel foil (Dyesol™). After sealing, silver bus bars were added to all cells.

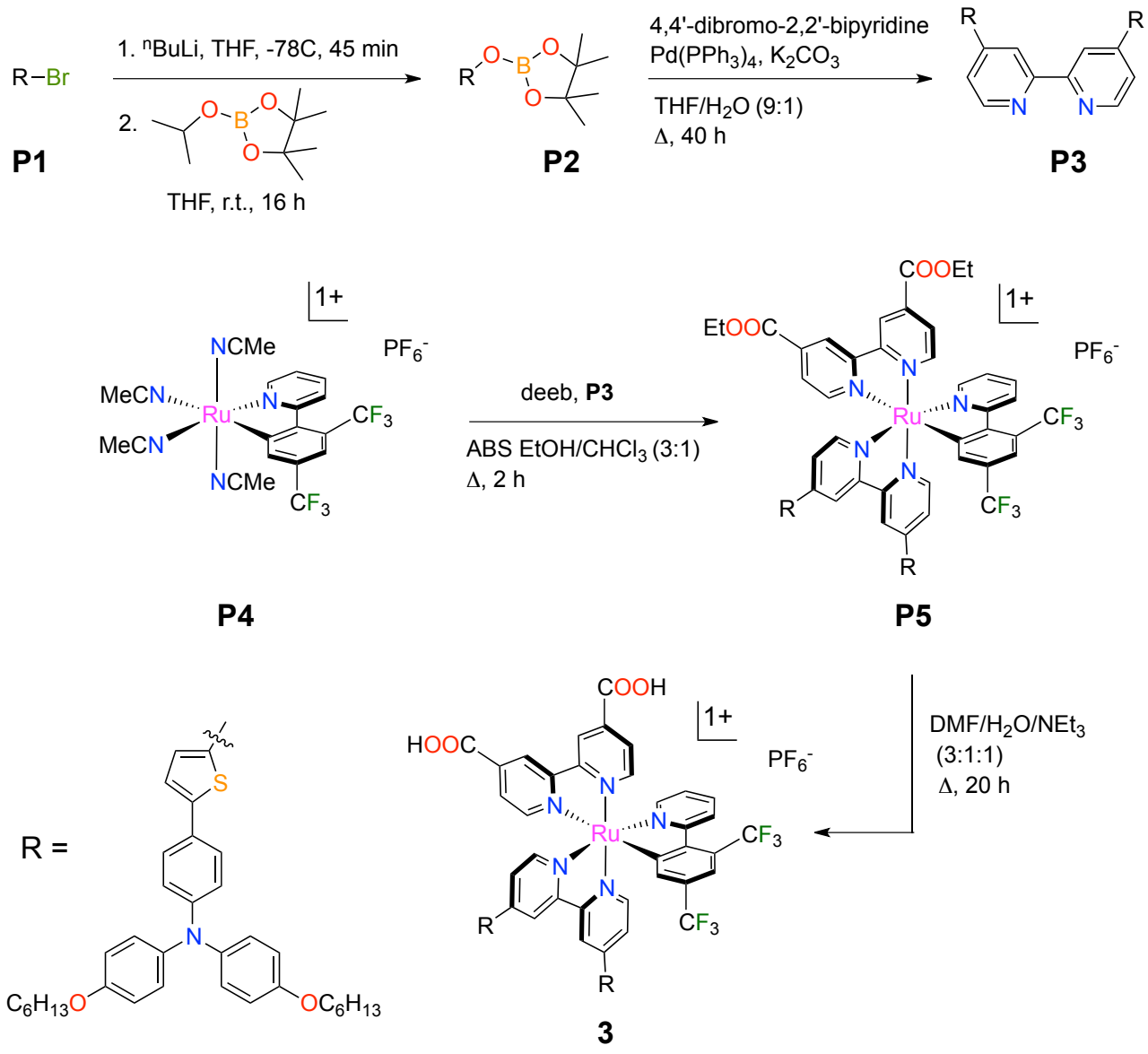
Dye Desorption Studies. Photoanodes containing dyes **2** and **3** were prepared according to the method described in the cell fabrication section. The dye soaked films were desorbed with 0.1 M NBu_4OH in ABS EtOH (**1**) or DMF (**2**). Calibration curves were constructed in the respective solvents and used to determine the amount of dye loading.

Cell Characterization. Photovoltaic measurements were recorded with a Newport Oriel solar simulator (Model 9225A1) equipped with a class A 150 W xenon light source powered by a Newport power supply (Model 69907). The light output (area = 5 cm × 5 cm) was calibrated to AM 1.5 using a Newport Oriel correction filter to reduce the spectral mismatch in the region of 350-700 nm to less than 1.5%. The power output of the lamp was measured to 1 Sun (100 mW cm^{-2}) using a certified Si reference cell. The current-voltage (*I–V*) characteristic of each cell was obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (Model 2400). All cells were measured with a mask size of 0.28 cm^2 or 0.13 cm^2. IPCE measurements were performed on a QEX7 Solar Cell Spectral Response Measurement System from PV Instruments, Inc. The system was calibrated with a photodiode that was calibrated against NIST standard I755 with transfer uncertainty less than 0.5% between 400-1000 nm and less than 1% at all other wavelengths. All measurements were made in AC mode at 4 Hz chopping frequency under a bias light between 0.01 to 0.1 sun. The system was calibrated and operated in Beam Power mode. Electrochemical impedance spectroscopy (EIS) was measured on a Gamry EIS300 potentiostat. All EIS measurements were performed in the dark and scanned a frequency range from 100 kHz to 0.5 Hz with a 10mV voltage modulation applied to the bias.

Single crystal X-ray diffraction data. A dark purple, block shaped, crystal of $[Ru(bpy)(deeb)(ppy)]PF_6$ was grown in a crystallization tube from a layered mixture of MeOH/Hexanes. The crystal was then coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_α radiation. Details of crystal data, data collection[4,5] and structure refinement have been provided in Table S1. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan methods[1]. The structure was solved by the direct methods[6] and expanded using Fourier techniques[7]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[8] converged with unweighted and weighted agreement factors, R = 0.0817 and wR = 0.1949 (all data), respectively, and goodness of fit, S = 1.049. The weighting scheme was based on counting

statistics and the final difference map had no chemically significant features. The C33-C34 bond distance was fixed to match that of the analogous C36-C37 bond distance due to disorder in the ethyl pedant group in one of the ester moieties. Attempts to partition "PART" the PF_6 had no influence on the agreement factors since more than two positions were made available due to disorder on the counter anion moiety of the molecule. The PLATON/SQUEEZE program[9] was employed to deal with disordered and partial occupancy MeOH/hexane molecules of solvation.

3. Figures, Schemes and Tables



Scheme S1 – Synthesis of **3**.

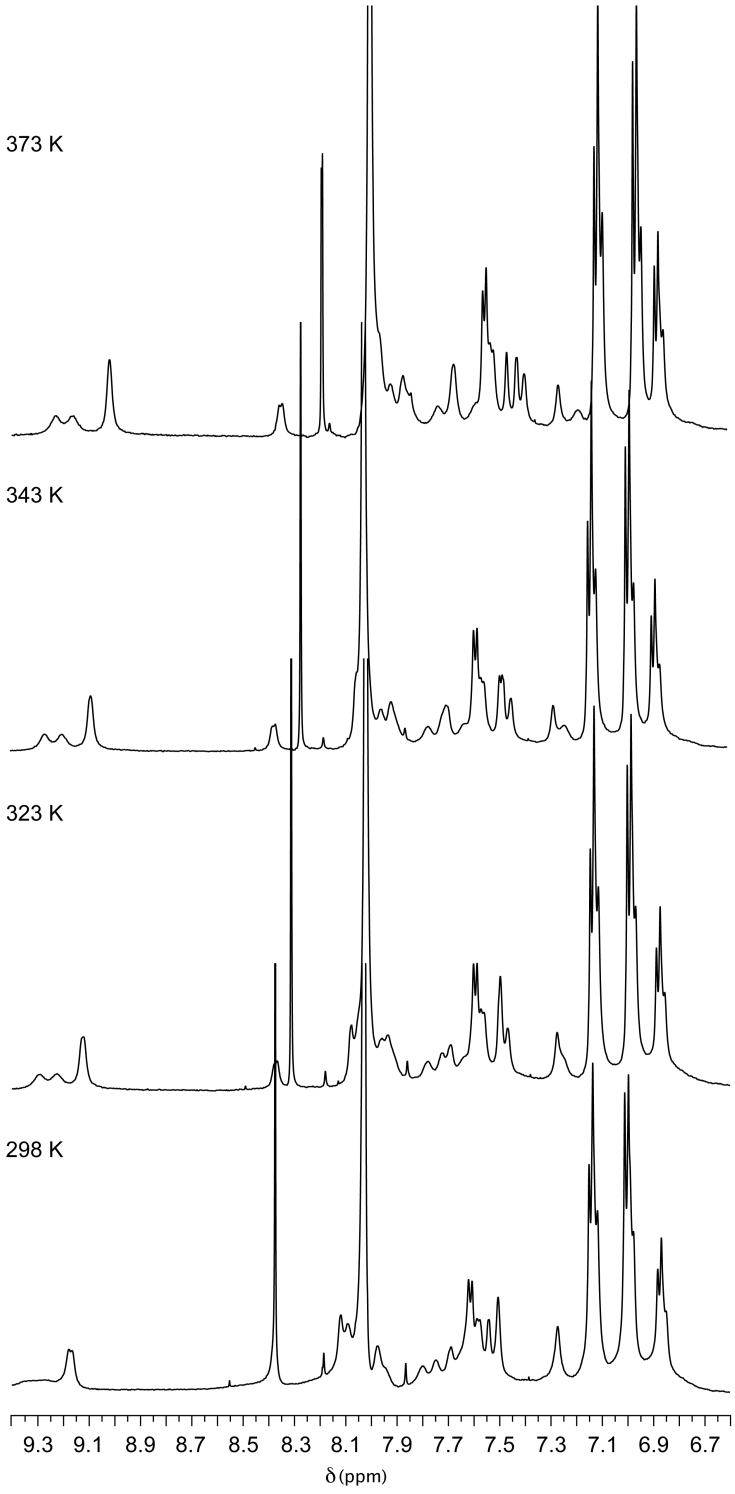


Fig. S1 – ^{1}H NMR spectra of **3** in d_8-DMF recorded at the specified temperatures.

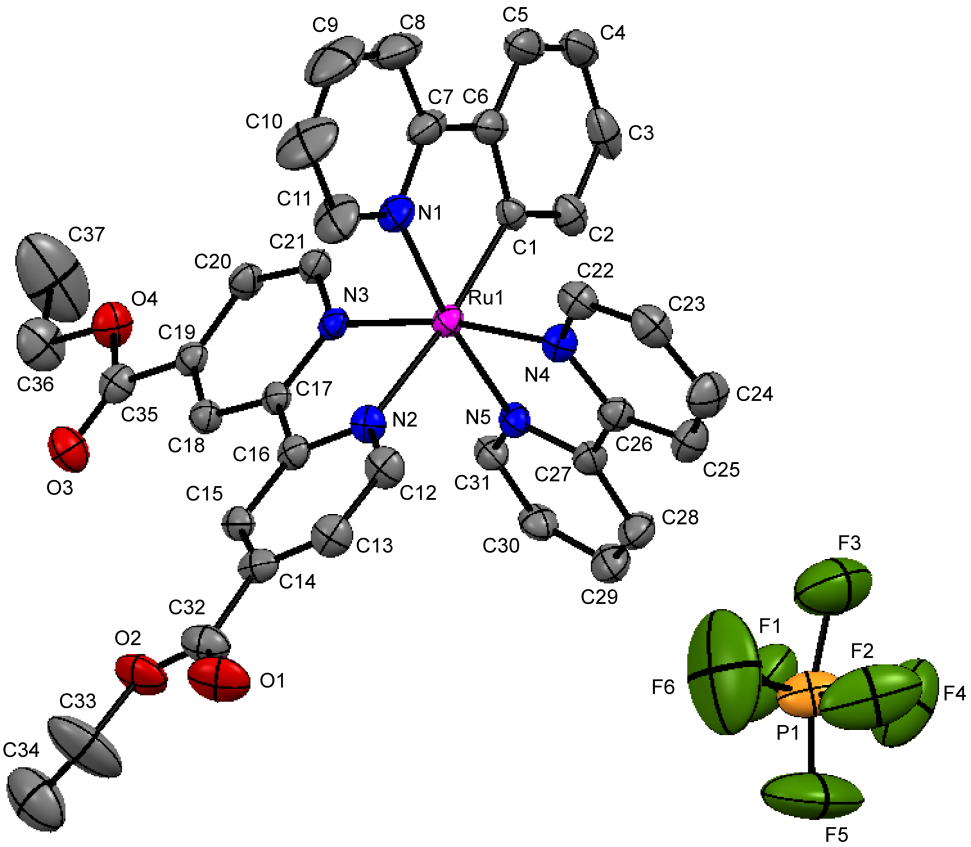


Fig. S2 – ORTEP plot of [Ru(bpy)(deeb)(ppy)]PF_6. Ellipsoids presented at 30% probability level. We assign the isomer depicted in Figure 1 according to this crystal structure. Note that we had inferred a different structural isomer in prior reports of related compounds based on the order of the ligation steps.

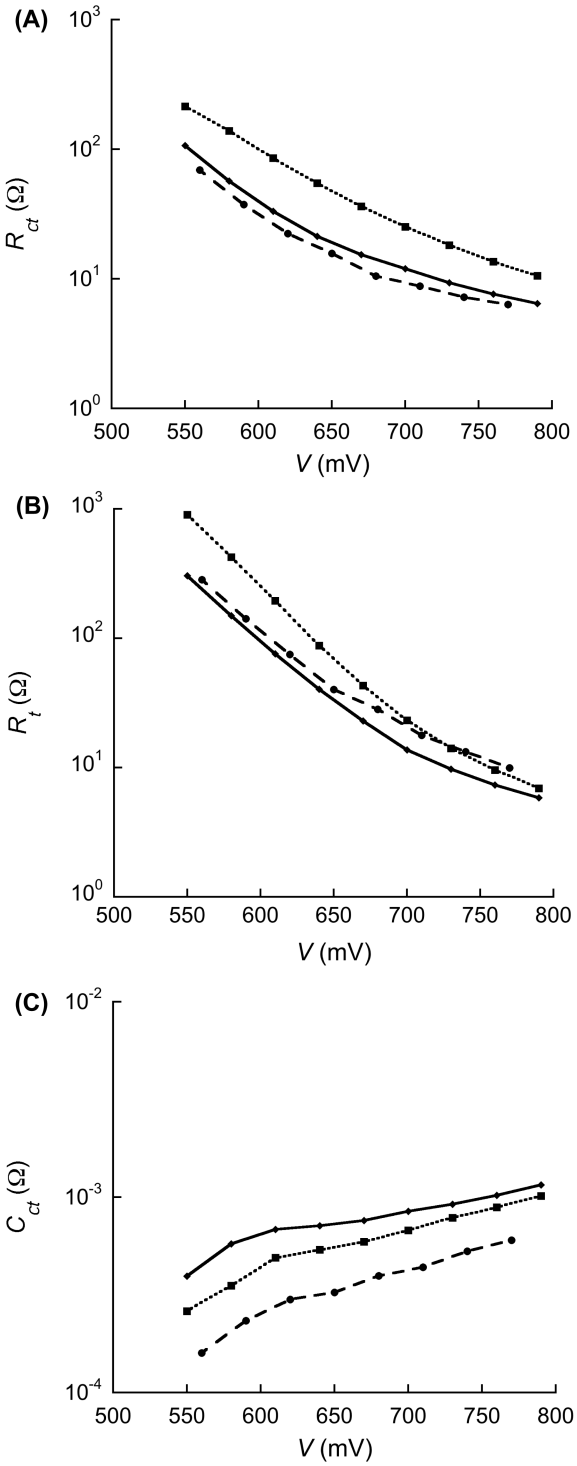


Fig. S3 – Impedance modelling (see Fig. S4) of (A) R_{ct} (B) R_t and (C) C_{ct} vs *V*. Dashed and solid lines represent cells of **3** with and without chenodeoxycholic acid, respectively. Dotted line represents **2** without chenodeoxycholic acid.

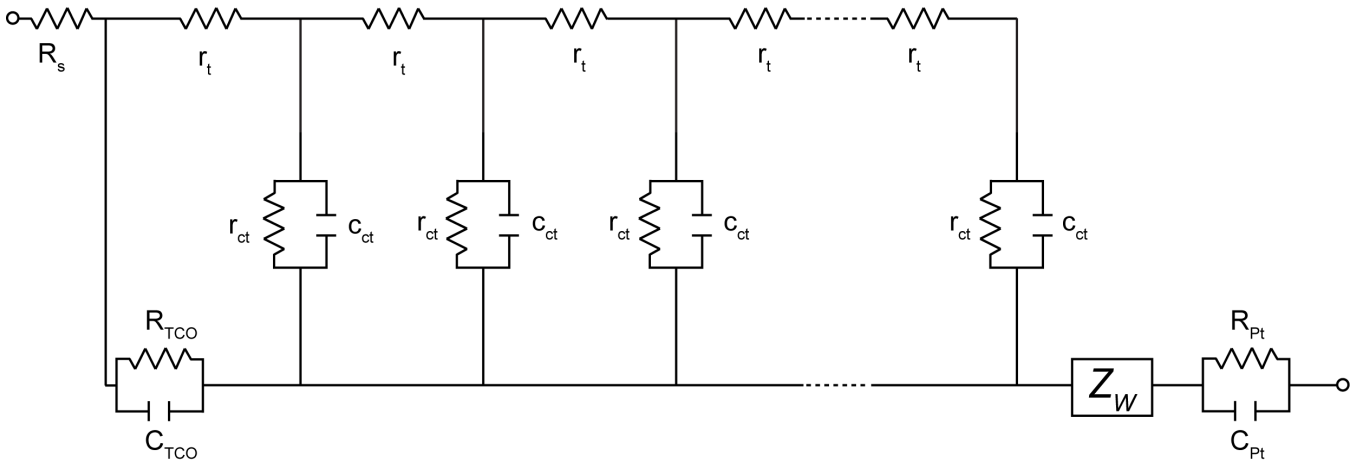


Fig S4 – Transmission line equivalent circuit employed in EIS modeling.[10]

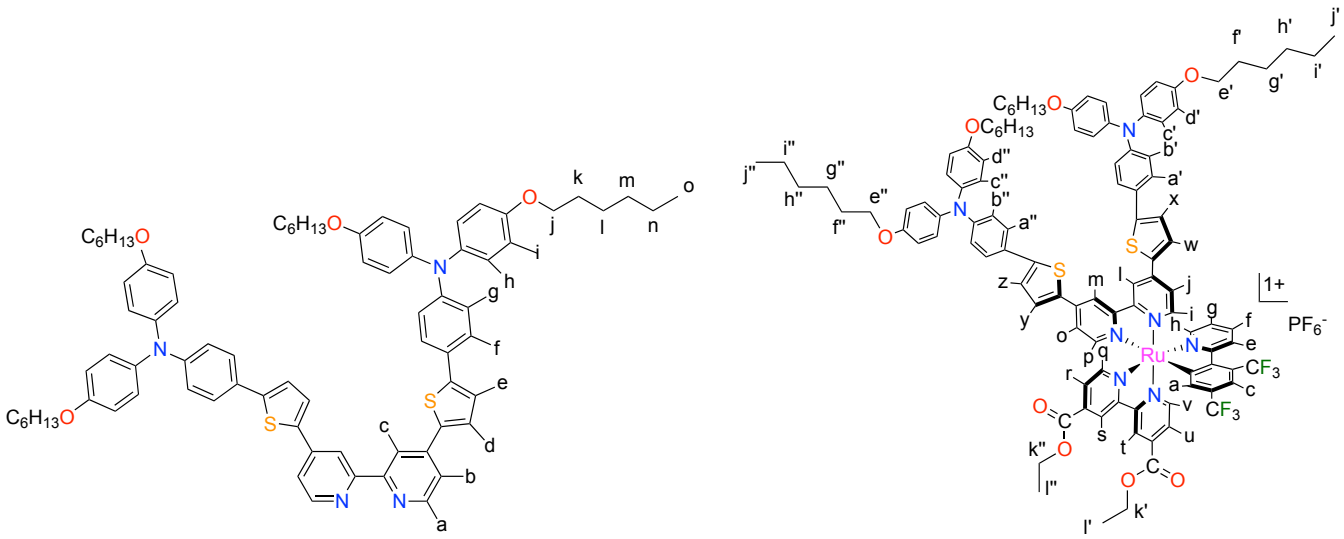


Fig. S5 – ^{1}H NMR labeling scheme for **P3** and **P5**.

Table S1. Crystal data and structure refinement for [Ru(bpy)(deeb)(ppy)]PF_6.

Identification code	[Ru(bpy)(deeb)(ppy)]PF_6 (**3**)	
Empirical formula	C37 H32 F6 N5 O4 P Ru	
Formula weight	856.72	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.1432(6) Å	a= 90°.
	b = 13.2365(5) Å	b= 116.823(2)°.
	c = 22.0134(3) Å	g = 90°.
Volume	3677.6(2) $Å^3$	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	0.547 mm^{-1}	
F(000)	1736	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.95 to 25.00°.	
Index ranges	-16<=h<=16, -12<=k<=15, -26<=l<=26	
Reflections collected	9211	
Independent reflections	6319 [R(int) = 0.0298]	
Completeness to theta = 25.00°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9473 and 0.8984	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6319 / 1 / 487	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0817, wR2 = 0.1949	
R indices (all data)	R1 = 0.0997, wR2 = 0.2070	
Largest diff. peak and hole	0.790 and -0.674 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Ru(bpy)(deeb)(ppy)]PF_6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9752(5)	1749(5)	7365(3)	39(2)
C(2)	10648(6)	2353(6)	7599(4)	53(2)
C(3)	11241(7)	2470(7)	7230(6)	73(3)
C(4)	10892(10)	1970(8)	6606(6)	78(3)
C(5)	10014(10)	1402(8)	6363(5)	72(3)
C(6)	9450(7)	1277(6)	6733(4)	55(2)
C(7)	8512(8)	632(7)	6505(4)	61(2)
C(8)	8050(11)	95(9)	5898(5)	91(4)
C(9)	7161(14)	-503(11)	5746(7)	121(5)
C(10)	6804(11)	-552(11)	6187(7)	116(5)
C(11)	7259(9)	-31(8)	6787(5)	84(3)
C(12)	6963(6)	1192(6)	8195(4)	53(2)
C(13)	6436(6)	837(7)	8532(4)	55(2)
C(14)	6943(6)	136(6)	9041(4)	50(2)
C(15)	7935(6)	-221(6)	9170(4)	44(2)
C(16)	8409(5)	154(5)	8789(4)	41(2)
C(17)	9425(5)	-212(5)	8843(3)	37(2)
C(18)	10056(6)	-922(5)	9319(4)	43(2)
C(19)	10977(6)	-1259(5)	9308(4)	42(2)
C(20)	11233(6)	-908(6)	8811(4)	48(2)
C(21)	10583(6)	-202(5)	8353(4)	46(2)
C(22)	7099(6)	2763(7)	6831(4)	51(2)
C(23)	6489(7)	3633(7)	6644(4)	60(2)
C(24)	6732(8)	4419(7)	7078(5)	71(3)
C(25)	7572(7)	4344(7)	7711(5)	63(2)
C(26)	8180(6)	3466(6)	7895(4)	46(2)
C(27)	9101(6)	3295(6)	8561(4)	48(2)
C(28)	9484(7)	3990(7)	9086(4)	57(2)
C(29)	10389(8)	3785(7)	9673(4)	64(2)
C(30)	10903(7)	2889(6)	9724(4)	53(2)
C(31)	10472(6)	2205(6)	9203(3)	46(2)
C(35)	11643(6)	-1993(6)	9845(4)	50(2)
C(36)	13226(7)	-2948(9)	10309(5)	82(3)

F(1)	7192(7)	5802(8)	9004(5)	168(4)
F(2)	5143(6)	7049(11)	8149(5)	206(6)
F(3)	6296(10)	6304(9)	7931(5)	181(5)
F(4)	6808(8)	7388(8)	8739(6)	195(5)
F(5)	6094(12)	6686(14)	9236(5)	238(7)
F(6)	5529(12)	5418(13)	8388(10)	319(11)
N(1)	8086(6)	566(5)	6954(3)	57(2)
N(2)	7935(4)	872(5)	8302(3)	44(1)
N(3)	9715(4)	178(4)	8373(3)	39(1)
N(4)	7948(4)	2673(5)	7451(3)	45(1)
N(5)	9596(4)	2376(4)	8630(3)	41(1)
O(3)	11417(5)	-2316(5)	10269(3)	66(2)
O(4)	12526(4)	-2235(5)	9799(3)	62(2)
P(1)	6119(2)	6379(3)	8595(2)	99(1)
Ru(1)	8841(1)	1403(1)	7832(1)	37(1)
O(2)	6952(5)	-800(6)	9947(4)	81(2)
O(1)	5479(5)	71(7)	9299(4)	92(2)
C(32)	6366(7)	-191(8)	9424(5)	68(3)
C(37)	14184(11)	-3038(17)	10211(10)	191(10)
C(33)	6329(10)	-1181(16)	10282(7)	152(8)
C(34)	7034(11)	-1560(12)	10966(6)	130(6)

Table S3. Bond lengths [Å] and angles [°] for [Ru(bpy)(deeb)(ppy)]PF_6.

C(1)-C(2)	1.387(11)
C(1)-C(6)	1.404(11)
C(1)-Ru(1)	2.029(7)
C(2)-C(3)	1.413(12)
C(2)-H(2)	0.9500
C(3)-C(4)	1.400(15)
C(3)-H(3)	0.9500
C(4)-C(5)	1.340(15)
C(4)-H(4)	0.9500
C(5)-C(6)	1.383(13)
C(5)-H(5)	0.9500
C(6)-C(7)	1.463(13)
C(7)-N(1)	1.373(11)
C(7)-C(8)	1.389(13)
C(8)-C(9)	1.392(19)
C(8)-H(8)	0.9500
C(9)-C(10)	1.28(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.367(14)
C(10)-H(10)	0.9500
C(11)-N(1)	1.319(12)
C(11)-H(11)	0.9500
C(12)-C(13)	1.352(11)
C(12)-N(2)	1.353(9)
C(12)-H(12)	0.9500
C(13)-C(14)	1.380(12)
C(13)-H(13)	0.9500
C(14)-C(15)	1.384(11)
C(14)-C(32)	1.478(11)
C(15)-C(16)	1.381(10)
C(15)-H(15)	0.9500
C(16)-N(2)	1.361(9)
C(16)-C(17)	1.469(10)
C(17)-N(3)	1.375(9)
C(17)-C(18)	1.389(10)
C(18)-C(19)	1.387(10)

C(18)-H(18)	0.9500
C(19)-C(20)	1.381(10)
C(19)-C(35)	1.491(11)
C(20)-C(21)	1.378(11)
C(20)-H(20)	0.9500
C(21)-N(3)	1.346(9)
C(21)-H(21)	0.9500
C(22)-N(4)	1.356(9)
C(22)-C(23)	1.386(12)
C(22)-H(22)	0.9500
C(23)-C(24)	1.346(13)
C(23)-H(23)	0.9500
C(24)-C(25)	1.367(12)
C(24)-H(24)	0.9500
C(25)-C(26)	1.392(11)
C(25)-H(25)	0.9500
C(26)-N(4)	1.370(9)
C(26)-C(27)	1.474(11)
C(27)-N(5)	1.376(9)
C(27)-C(28)	1.383(11)
C(28)-C(29)	1.374(12)
C(28)-H(28)	0.9500
C(29)-C(30)	1.370(12)
C(29)-H(29)	0.9500
C(30)-C(31)	1.369(10)
C(30)-H(30)	0.9500
C(31)-N(5)	1.330(9)
C(31)-H(31)	0.9500
C(35)-O(3)	1.195(9)
C(35)-O(4)	1.337(9)
C(36)-O(4)	1.459(10)
C(36)-C(37)	1.470(17)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
F(1)-P(1)	1.570(8)
F(2)-P(1)	1.559(10)
F(3)-P(1)	1.594(11)
F(4)-P(1)	1.598(12)

F(5)-P(1)	1.483(10)
F(6)-P(1)	1.476(14)
N(1)-Ru(1)	2.059(6)
N(2)-Ru(1)	2.100(6)
N(3)-Ru(1)	2.061(6)
N(4)-Ru(1)	2.041(6)
N(5)-Ru(1)	2.047(6)
O(2)-C(32)	1.343(12)
O(2)-C(33)	1.471(13)
O(1)-C(32)	1.207(11)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(33)-C(34)	1.4694(10)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800

C(2)-C(1)-C(6)	116.3(7)
C(2)-C(1)-Ru(1)	128.7(6)
C(6)-C(1)-Ru(1)	115.0(6)
C(1)-C(2)-C(3)	122.0(9)
C(1)-C(2)-H(2)	119.0
C(3)-C(2)-H(2)	119.0
C(4)-C(3)-C(2)	118.3(10)
C(4)-C(3)-H(3)	120.9
C(2)-C(3)-H(3)	120.9
C(5)-C(4)-C(3)	120.7(9)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.6(10)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	122.1(9)
C(5)-C(6)-C(7)	122.9(9)
C(1)-C(6)-C(7)	115.0(7)

N(1)-C(7)-C(8)	119.4(10)
N(1)-C(7)-C(6)	114.5(7)
C(8)-C(7)-C(6)	126.1(10)
C(7)-C(8)-C(9)	120.3(11)
C(7)-C(8)-H(8)	119.9
C(9)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	117.9(12)
C(10)-C(9)-H(9)	121.0
C(8)-C(9)-H(9)	121.0
C(9)-C(10)-C(11)	122.1(14)
C(9)-C(10)-H(10)	119.0
C(11)-C(10)-H(10)	119.0
N(1)-C(11)-C(10)	122.9(12)
N(1)-C(11)-H(11)	118.5
C(10)-C(11)-H(11)	118.5
C(13)-C(12)-N(2)	124.3(8)
C(13)-C(12)-H(12)	117.9
N(2)-C(12)-H(12)	117.9
C(12)-C(13)-C(14)	117.8(7)
C(12)-C(13)-H(13)	121.1
C(14)-C(13)-H(13)	121.1
C(13)-C(14)-C(15)	120.2(7)
C(13)-C(14)-C(32)	116.2(8)
C(15)-C(14)-C(32)	123.6(8)
C(16)-C(15)-C(14)	118.6(7)
C(16)-C(15)-H(15)	120.7
C(14)-C(15)-H(15)	120.7
N(2)-C(16)-C(15)	121.8(7)
N(2)-C(16)-C(17)	114.3(6)
C(15)-C(16)-C(17)	123.8(7)
N(3)-C(17)-C(18)	120.8(6)
N(3)-C(17)-C(16)	115.3(6)
C(18)-C(17)-C(16)	123.8(6)
C(19)-C(18)-C(17)	119.6(7)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(20)-C(19)-C(18)	119.3(7)
C(20)-C(19)-C(35)	123.3(7)

C(18)-C(19)-C(35)	117.3(7)
C(21)-C(20)-C(19)	118.7(7)
C(21)-C(20)-H(20)	120.6
C(19)-C(20)-H(20)	120.6
N(3)-C(21)-C(20)	123.2(7)
N(3)-C(21)-H(21)	118.4
C(20)-C(21)-H(21)	118.4
N(4)-C(22)-C(23)	121.4(8)
N(4)-C(22)-H(22)	119.3
C(23)-C(22)-H(22)	119.3
C(24)-C(23)-C(22)	120.4(8)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	119.6(8)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(24)-C(25)-C(26)	119.7(8)
C(24)-C(25)-H(25)	120.2
C(26)-C(25)-H(25)	120.2
N(4)-C(26)-C(25)	121.0(7)
N(4)-C(26)-C(27)	114.2(6)
C(25)-C(26)-C(27)	124.8(7)
N(5)-C(27)-C(28)	120.5(7)
N(5)-C(27)-C(26)	115.0(6)
C(28)-C(27)-C(26)	124.5(7)
C(29)-C(28)-C(27)	120.2(8)
C(29)-C(28)-H(28)	119.9
C(27)-C(28)-H(28)	119.9
C(30)-C(29)-C(28)	118.8(8)
C(30)-C(29)-H(29)	120.6
C(28)-C(29)-H(29)	120.6
C(31)-C(30)-C(29)	119.0(8)
C(31)-C(30)-H(30)	120.5
C(29)-C(30)-H(30)	120.5
N(5)-C(31)-C(30)	123.6(8)
N(5)-C(31)-H(31)	118.2
C(30)-C(31)-H(31)	118.2
O(3)-C(35)-O(4)	124.2(8)

O(3)-C(35)-C(19)	123.8(7)
O(4)-C(35)-C(19)	112.0(7)
O(4)-C(36)-C(37)	106.8(10)
O(4)-C(36)-H(36A)	110.4
C(37)-C(36)-H(36A)	110.4
O(4)-C(36)-H(36B)	110.4
C(37)-C(36)-H(36B)	110.4
H(36A)-C(36)-H(36B)	108.6
C(11)-N(1)-C(7)	117.3(8)
C(11)-N(1)-Ru(1)	127.1(7)
C(7)-N(1)-Ru(1)	115.5(6)
C(12)-N(2)-C(16)	117.2(6)
C(12)-N(2)-Ru(1)	127.4(5)
C(16)-N(2)-Ru(1)	115.3(4)
C(21)-N(3)-C(17)	118.1(6)
C(21)-N(3)-Ru(1)	126.3(5)
C(17)-N(3)-Ru(1)	115.3(4)
C(22)-N(4)-C(26)	118.0(7)
C(22)-N(4)-Ru(1)	126.0(5)
C(26)-N(4)-Ru(1)	115.7(5)
C(31)-N(5)-C(27)	117.7(6)
C(31)-N(5)-Ru(1)	127.5(5)
C(27)-N(5)-Ru(1)	114.8(5)
C(35)-O(4)-C(36)	115.4(7)
F(6)-P(1)-F(5)	106.0(12)
F(6)-P(1)-F(2)	94.5(8)
F(5)-P(1)-F(2)	92.8(7)
F(6)-P(1)-F(1)	91.3(8)
F(5)-P(1)-F(1)	91.2(7)
F(2)-P(1)-F(1)	171.7(8)
F(6)-P(1)-F(3)	87.9(10)
F(5)-P(1)-F(3)	166.0(10)
F(2)-P(1)-F(3)	85.3(6)
F(1)-P(1)-F(3)	89.0(6)
F(6)-P(1)-F(4)	172.1(11)
F(5)-P(1)-F(4)	81.8(8)
F(2)-P(1)-F(4)	86.4(7)
F(1)-P(1)-F(4)	87.0(6)

F(3)-P(1)-F(4)	84.3(7)
C(1)-Ru(1)-N(4)	91.3(3)
C(1)-Ru(1)-N(5)	95.1(3)
N(4)-Ru(1)-N(5)	79.7(2)
C(1)-Ru(1)-N(1)	80.0(3)
N(4)-Ru(1)-N(1)	95.4(3)
N(5)-Ru(1)-N(1)	173.0(3)
C(1)-Ru(1)-N(3)	96.8(2)
N(4)-Ru(1)-N(3)	169.6(2)
N(5)-Ru(1)-N(3)	93.1(2)
N(1)-Ru(1)-N(3)	92.4(2)
C(1)-Ru(1)-N(2)	173.5(3)
N(4)-Ru(1)-N(2)	94.3(2)
N(5)-Ru(1)-N(2)	89.1(2)
N(1)-Ru(1)-N(2)	96.2(3)
N(3)-Ru(1)-N(2)	78.0(2)
C(32)-O(2)-C(33)	111.0(8)
O(1)-C(32)-O(2)	123.0(9)
O(1)-C(32)-C(14)	124.8(10)
O(2)-C(32)-C(14)	112.2(8)
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(34)-C(33)-O(2)	110.3(10)
C(34)-C(33)-H(33A)	109.6
O(2)-C(33)-H(33A)	109.6
C(34)-C(33)-H(33B)	109.6
O(2)-C(33)-H(33B)	109.6
H(33A)-C(33)-H(33B)	108.1
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for [Ru(bpy)(deeb)(ppy)]PF_6. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	38(4)	38(4)	43(4)	8(3)	21(3)	5(3)
C(2)	46(4)	52(5)	60(5)	16(4)	24(4)	11(4)
C(3)	62(6)	62(6)	107(8)	43(6)	49(6)	16(5)
C(4)	122(9)	59(6)	90(7)	31(6)	80(7)	40(6)
C(5)	108(8)	61(6)	64(6)	16(5)	53(6)	32(6)
C(6)	72(5)	49(5)	50(4)	10(4)	32(4)	21(4)
C(7)	75(6)	51(5)	49(4)	-9(4)	22(4)	13(4)
C(8)	122(10)	90(8)	66(6)	-23(6)	46(7)	12(8)
C(9)	146(13)	105(11)	83(9)	-53(8)	25(9)	-3(10)
C(10)	97(9)	120(11)	102(10)	-67(9)	20(8)	-36(8)
C(11)	84(7)	76(7)	72(6)	-27(5)	17(5)	-34(6)
C(12)	34(4)	61(5)	61(5)	-4(4)	18(4)	-9(4)
C(13)	36(4)	62(5)	64(5)	-3(4)	18(4)	-2(4)
C(14)	40(4)	60(5)	56(5)	-22(4)	27(4)	-21(4)
C(15)	46(4)	42(4)	48(4)	-8(3)	25(3)	-15(3)
C(16)	36(4)	40(4)	49(4)	-9(3)	20(3)	-10(3)
C(17)	38(4)	33(4)	44(4)	-7(3)	21(3)	-11(3)
C(18)	45(4)	38(4)	47(4)	-1(3)	22(3)	-2(3)
C(19)	42(4)	36(4)	49(4)	-7(3)	21(3)	-6(3)
C(20)	47(4)	41(4)	65(5)	-1(4)	32(4)	5(3)
C(21)	47(4)	38(4)	62(5)	-5(3)	32(4)	-3(3)
C(22)	42(4)	60(5)	47(4)	2(4)	17(4)	-3(4)
C(23)	48(5)	72(6)	59(5)	15(5)	23(4)	6(4)
C(24)	71(6)	60(6)	75(6)	10(5)	27(5)	29(5)
C(25)	65(5)	48(5)	75(6)	-4(4)	32(5)	6(4)
C(26)	44(4)	47(4)	52(4)	-2(3)	25(3)	0(3)
C(27)	55(5)	42(4)	56(4)	1(3)	33(4)	3(3)
C(28)	69(5)	47(5)	53(5)	-10(4)	24(4)	-3(4)
C(29)	75(6)	56(5)	53(5)	-10(4)	23(5)	-13(4)
C(30)	55(5)	60(5)	36(4)	1(4)	13(3)	-6(4)
C(31)	47(4)	49(4)	38(4)	-2(3)	15(3)	-12(3)
C(35)	41(4)	49(5)	54(5)	-6(4)	16(4)	-4(3)
C(36)	53(5)	97(8)	83(7)	28(6)	19(5)	28(5)

F(1)	108(6)	145(8)	164(8)	-40(7)	-16(6)	35(6)
F(2)	83(5)	336(17)	132(7)	-55(9)	-10(5)	92(8)
F(3)	195(10)	203(12)	142(8)	-14(7)	73(8)	65(9)
F(4)	143(8)	139(9)	203(11)	-29(8)	-12(8)	9(7)
F(5)	254(14)	380(20)	103(7)	0(10)	99(9)	88(14)
F(6)	176(12)	256(18)	390(20)	29(16)	6(13)	-135(13)
N(1)	69(5)	47(4)	50(4)	-11(3)	22(3)	-11(3)
N(2)	31(3)	47(4)	48(3)	-1(3)	14(3)	-4(3)
N(3)	40(3)	31(3)	47(3)	-9(2)	22(3)	-8(2)
N(4)	34(3)	44(3)	53(4)	-1(3)	18(3)	-1(3)
N(5)	40(3)	39(3)	40(3)	-3(3)	15(3)	-11(3)
O(3)	57(4)	73(4)	63(4)	17(3)	22(3)	1(3)
O(4)	44(3)	63(4)	71(4)	10(3)	20(3)	11(3)
P(1)	55(2)	151(3)	68(2)	-26(2)	7(1)	12(2)
Ru(1)	36(1)	36(1)	40(1)	-4(1)	16(1)	-3(1)
O(2)	71(4)	112(6)	82(5)	-5(4)	53(4)	-28(4)
O(1)	44(4)	149(7)	91(5)	-10(5)	39(4)	-13(4)
C(32)	54(5)	93(7)	61(5)	-9(5)	30(4)	-16(5)
C(37)	78(9)	250(20)	250(20)	142(19)	73(12)	80(13)
C(33)	94(10)	260(20)	131(12)	67(14)	73(10)	-4(12)
C(34)	104(10)	161(15)	120(11)	21(10)	44(9)	-45(10)

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