Electronic supporting information

Unexpected Disruption of the Dimensionality-driven Two-Photon Absorption Enhancement within a Multipolar Polypyridyl Ruthenium Complexes Series.

Nicolas Durand [1], Rana Mhanna [2], Paul Savel [1], Huriye Akdas-Kiliç [1,3], Jean-Pierre Malval*[2], Olivier Soppera[2], Jean-Luc Fillaut*[1].

[1] Université Rennes, Institut des Sciences Chimiques de Rennes CNRS UMR 6226, F-35000 Rennes.

[2] Institut de Science des Matériaux de Mulhouse CNRS-UMR 7361, Université de Haute Alsace, 15 rue Jean Starcky, 68057, Mulhouse, France.

[3] Yildiz Technical University, Department of Chemistry, 34220 Esenler, Istanbul, Turkey.

E-Mails: jean-luc.fillaut@ univ-rennes1.fr and jean-pierre.malval@uha.fr

CONTENTS

1. Figures and Tables.

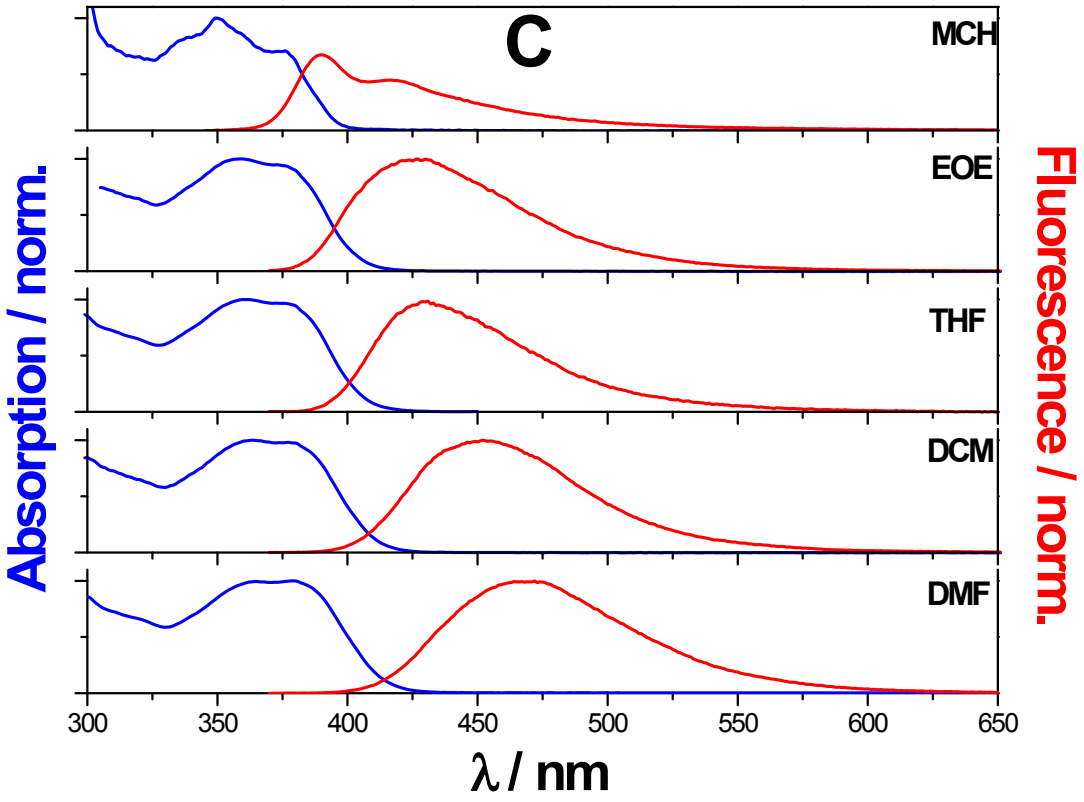


Figure S1. Normalized absorption and fluorescence spectra of **C** in various solvents of increasing polarity (**MCH**: methylcyclohexane, **EOE**: ethyl ether, **THF**: tetrahydrofuran, **DCM**: dichloromethane, **DMF**: N,N' dimethylformamide).

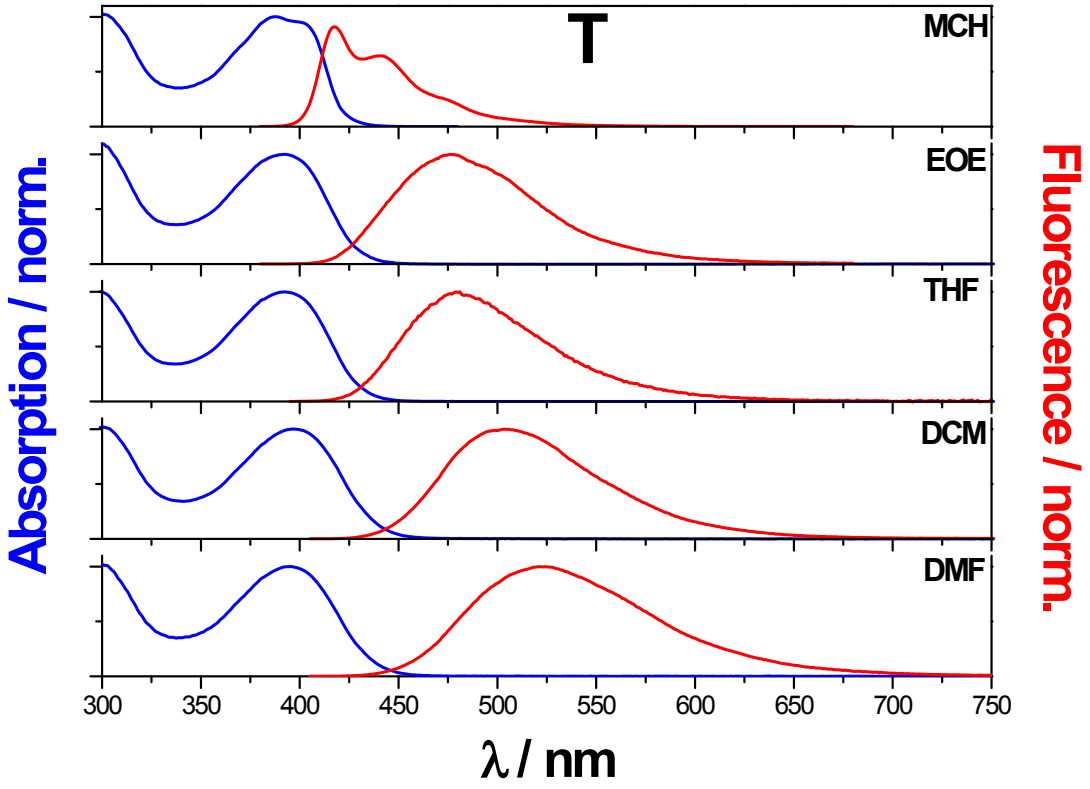


Figure S2. Normalized absorption and fluorescence spectra of **T** in various solvents of increasing polarity (**MCH**: methylcyclohexane, **EOE**: ethyl ether, **THF**: tetrahydrofuran, **DCM**: dichloromethane, **DMF**: N,N' dimethylformamide).

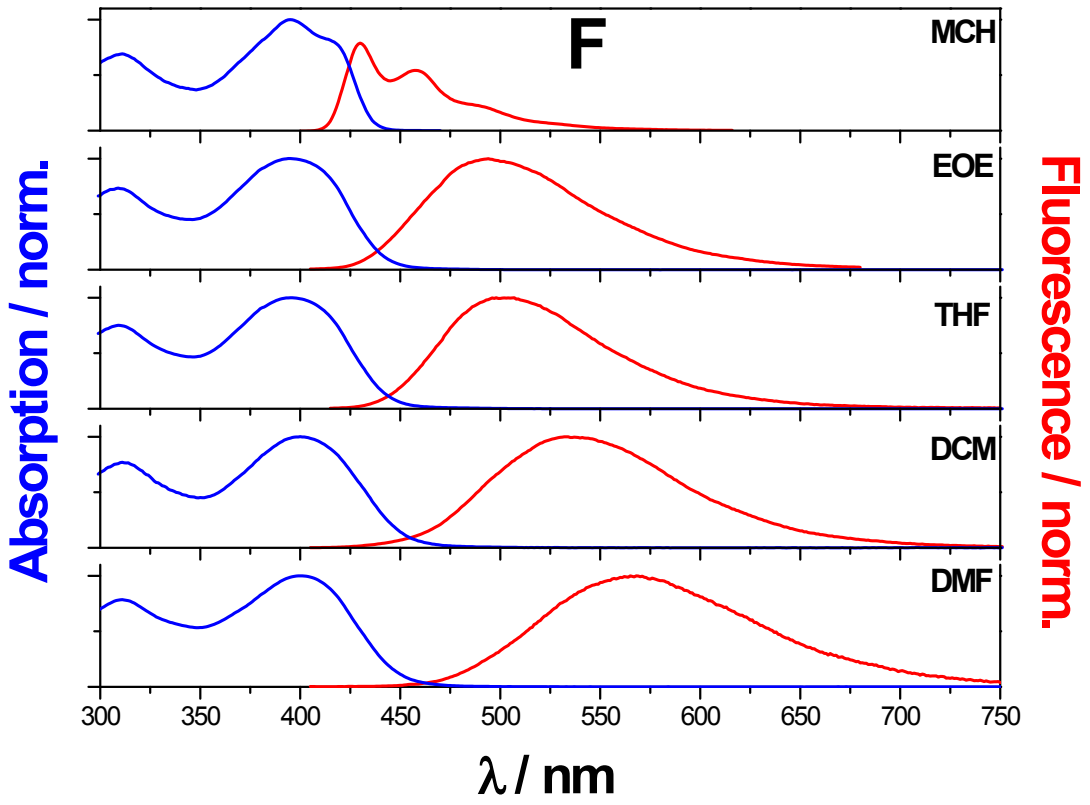


Figure S3. Normalized absorption and fluorescence spectra of **F** in various solvents of increasing polarity (**MCH**: methylcyclohexane, **EOE**: ethyl ether, **THF**: tetrahydrofuran, **DCM**: dichloromethane, **DMF**: N,N' dimethylformamide).

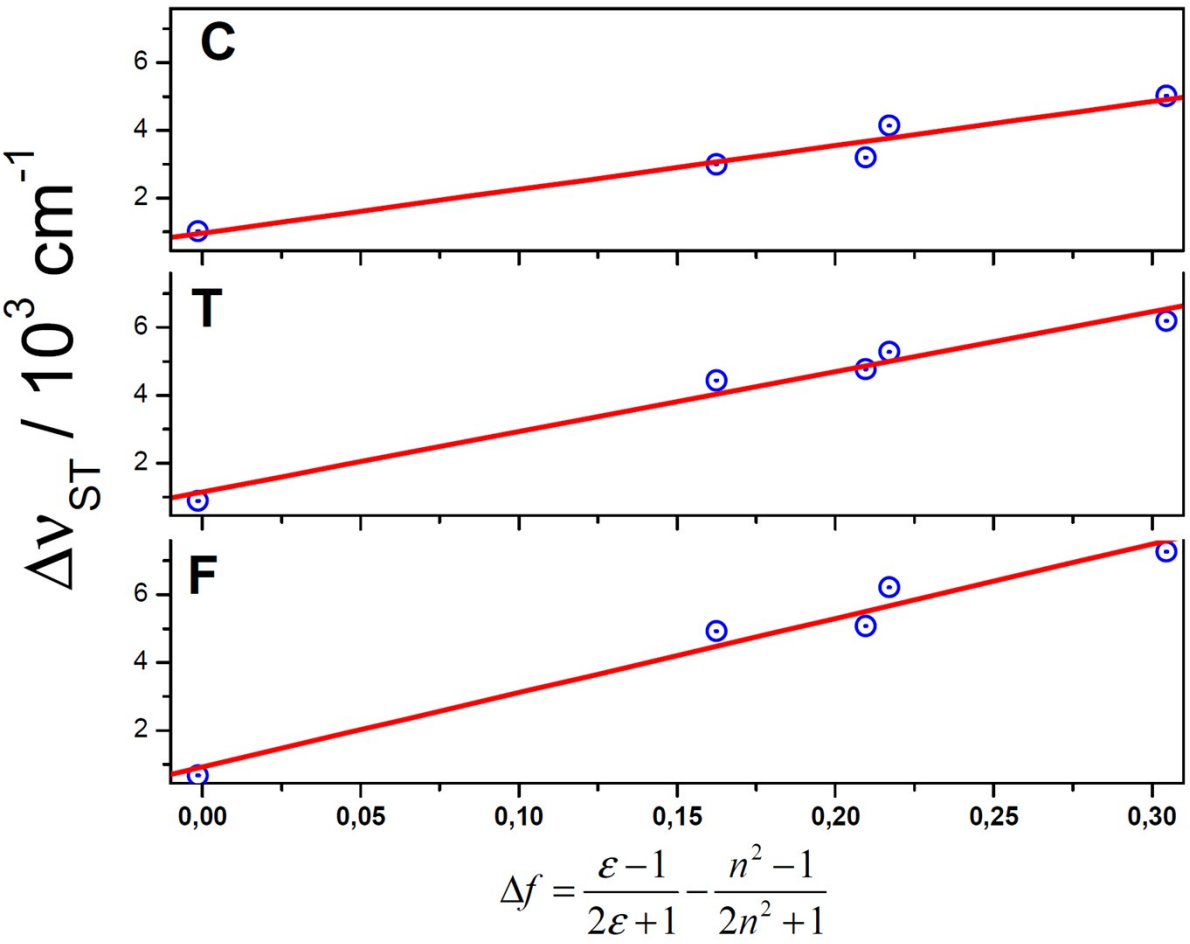


Figure S4. Solvatochromic plots of the Stokes shift ($\Delta\nu_{ST}$) measurements for all the ligands as function of the Lippert-Mataga solvent polarity function, f (ε,n).

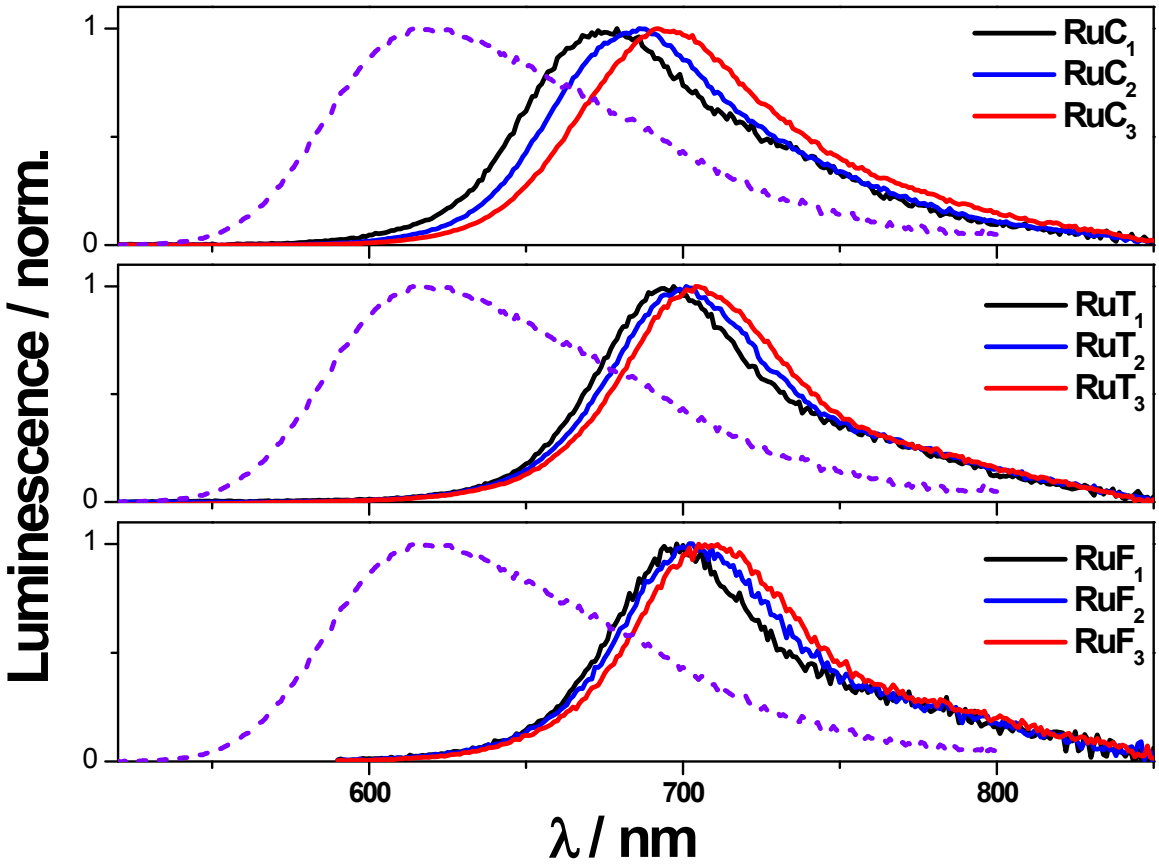


Figure S5. Normalized luminescence spectra of the Ru-complexes in THF. Dashed lines: Luminescence spectrum of $Ru(bpy)_3^{2+}, 2PF_6^-$ in acetonitrile.

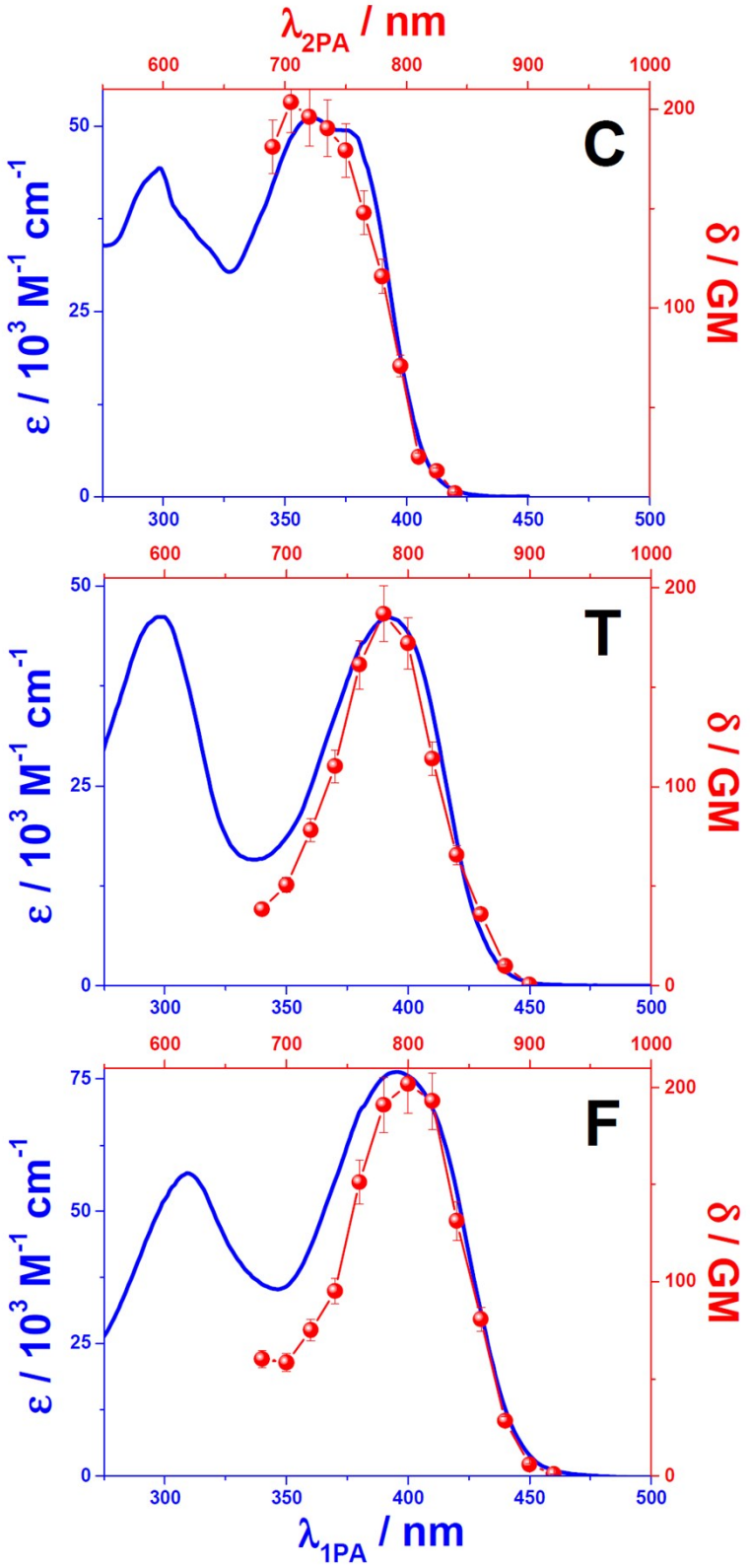


Figure S6. 1PA (full lines) and 2PA (symbols) of the ligands in THF.

	m / cm^{-1}	a_0 [a] / Å	$\Delta\mu_{01}$ / D
C	12950 ± 1500	5.5	13.6 ± 1.6
T	17710 ± 1700	5.8	18.5 ± 1.8
F	21900 ± 2300	7.1	27.9 ± 3.0

[a] Onsager radius : 40% of the longest axis[1] of the molecular synthon fully optimized by the AM1 method[2].

Table S1. Slopes of the solvatochromic plots and dipole moment differences between ground and excited states for all the ligands.

	λ_{abs} / nm	$\lambda_{em.}$ / nm	Φ_L	E_{S1} [b] / eV	E_{T1} [c] / eV
C	362	433	0.11	3.15	-
RuC_1	415	675	0.0034 (0.017) [a]	-	1.84
RuC_2	415	685	0.0057 (0.047) [a]	-	1.81
RuC_3	420	695	0.0063 (0.056) [a]	-	1.79
T	392	480	0.80	2.88	-
RuT_1	455	695	0.0013 (0.014) [a]	-	1.79
RuT_2	445	700	0.0021 (0.031) [a]	-	1.77
RuT_3	437	705	0.0032 (0.041) [a]	-	1.76
F	395	480	0.78	2.86	-
RuF_1	450	695	0.0012 (0.011) [a]	-	1.79
RuF_2	426	700	0.0018 (0.017) [a]	-	1.77
RuF_3	429	705	0.0028 (0.029) [a]	-	1.76

[a] N_2-saturated THF, [b] $E_{S1} \approx ½\ hc(\nu_{abs} + \nu_{fluo})$, [b] $E_{T1} \approx hc\nu_{phos.}$

Table S2. Photophysical data of the ligands and their corresponding Ru-complexes in THF.

2. Materials and General Characterization Methods.

Materials and general methods.

Materials. All the solvents employed were Aldrich spectroscopic grade. The absorption and fluorescence of all solvents were checked for impurities and have been subtracted from the sample spectra. Tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate was purchased from Aldrich.

Steady-state absorption and luminescence spectra. The absorption measurements were carried out with a Perkin Elmer Lambda 2 spectrometer. The extinction coefficients and λ_{abs} were measured using UV-Visible absorption methods. More precisely, the extinction coefficients were calculated on the basis of Beer-Lambert law using various THF solutions with dye in the μM concentration range. No spectral effect was observed with the concentration change excluding thereby any aggregation of the dyes. Steady-state fluorescence spectra in solution were collected from a FluoroMax-4 spectrofluorometer. Emission spectra are spectrally corrected, and luminescence quantum yields include the correction due to solvent refractive index and were determined relative to quinine bisulfate in 0.05 molar sulfuric acid ($\Phi_{fluo} = 0.52$)[3] for all the ligands and relative to $Ru(bpy)_3^{2+}$, $2PF6^-$ in aerated ACN ($\Phi_L = 0.018$)[4] for all the Ru-complexes.

Solvatochromic measurements. The difference between the dipole moments of the ground (S_0) and the relaxed singlet excited state (S_1) can be estimated using the Lippert–Mataga equation[1, 5]:

$$\Delta\nu_{ST} = \nu_{abs} - \nu_{abs} = \frac{2\Delta\mu_{01}^2}{hca_0^3}\left[\frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{n^2 - 1}{2n^2 - 1}\right]$$

In this dielectric continuum model, ε is the relative permittivity, n is the refractive index of the solvent, h is the Planck constant and c is the speed of light. The Onsager radius a_0 which corresponds to the solvent shell around the molecule was approximated, following Lippert's suggestion[1] for non-spherical chromophores, as 40% of the longest axis of each linear stilbenoid synthon whose geometry was fully optimized using the AM1 method[2]. The solvatochromic plots of Stokes shifts are shown in **Figure S4** and the corresponding slopes as well as the values for $\Delta\mu_{01}$ are gathered in **Table S1**.

Two-photon excited luminescence measurements. The two-photon absorption (2PA) measurements were performed with femtosecond mode-locked laser pulse using a Ti: Sapphire laser (Coherent, Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz; wavelength range: 680-1040 nm). A relative two-photon excited luminescence (2PEL) method[6] was employed to measure the two-photon absorption cross-sections, δ. This well-established method consists in recording the luminescence signal of the excited dyes upon two-photon absorption by tightly focusing a *fs*-pulse excitation laser into an optical cell containing a solution with the chromophore. The luminescence signal whose intensity displays a quadratic dependence with the laser excitation power was typically collected at a perpendicular direction from the laser excitation beam. The measurements of 2PA cross-sections were performed relative to a set of three reference molecules (*r*) : fluorescein[6, 7] in water at pH = 11, Rhodamine 6G[8, 9] in methanol and Coumarin 153[8, 9] in DMSO. The value of δ for a sample (*s*) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r c_r}{S_r \Phi_S \eta_S c_S} . \delta_r$$

Where S is the detected two-photon excited fluorescence integral area, c the concentration of the chromophores, and Φ is the fluorescence quantum yield of the chromophores. η is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were conducted in a regime where the luminescence signal showed a quadratic dependence on the intensity of the excitation beam. As a representative example, **Figure S7** shows various two-photon induced luminescence spectra of **RuF_3** in N_2-saturared THF recorded at various excitation powers ($\lambda_{exc.}$ = 850 nm). The inset in **Figure S7** shows the quadratic dependence correlation between the luminescence intensity at λ_{MAX} and the incident excitation power. For the calibration of the two-photon absorption spectra, the two-photon excited luminescence signal of each compound was recorded at the same excitation wavelength as that used for standards. The laser intensity was in the range of 0.2-2 x 10^9 W/cm^2. The experimental error on the reported cross section is 15 %.

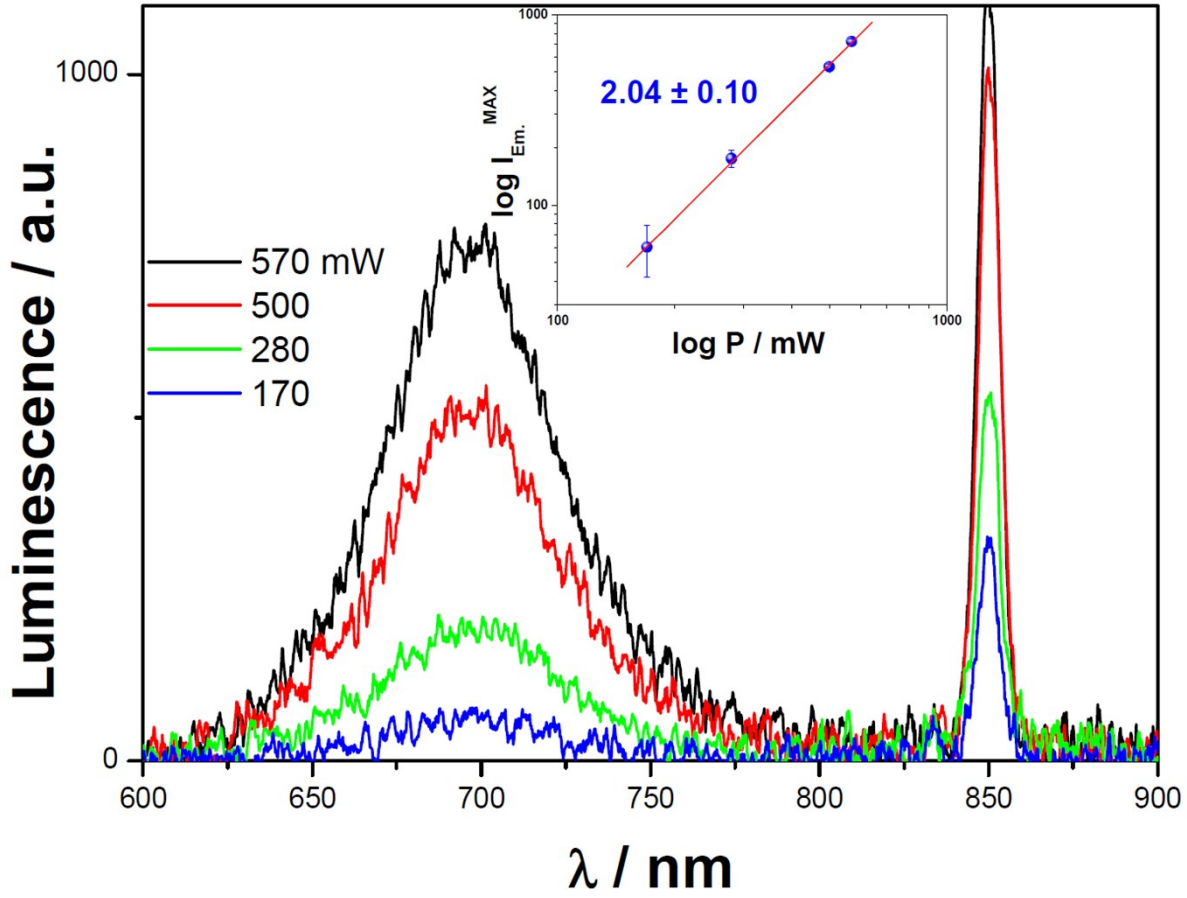
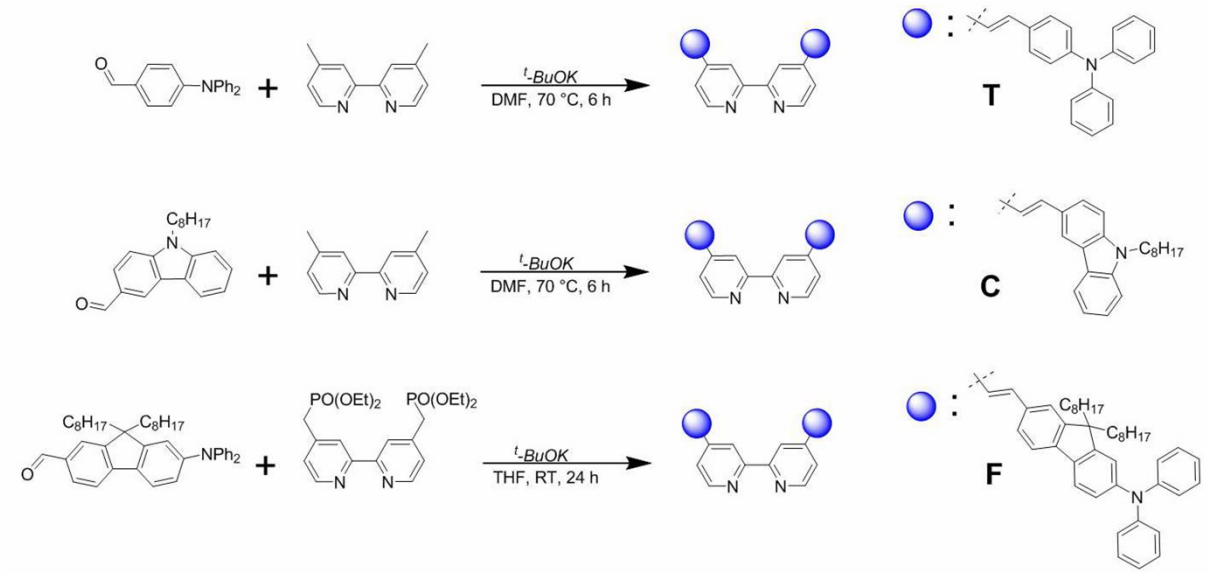


Figure S7. Two-photon induced emission spectra of **RuF_3** (3.10^{-4} M) in N_2-saturated THF as function of the incident laser excitation power at 850 nm. Inset: Plots of log $I_{Lum.}^{MAX}$ *vs.* log [excitation power].

3. Synthesis of chromophores.

3.1 General synthetic procedure for the ligands.

The bipyridyl ligands **C**, **T** and **F** were synthesized according to the procedures reported by Bourgault *et al*.[10]. The synthetic route can be schematized as follows:



Scheme S1. Synthetic routes for the ligands.

First Method (Ligands C and T). In a Schlenk tube under an argon atmosphere, 4,4'-dimethyl-2,2'-bipyridine (300 mg, 1.6 mmol) and potassium *tert*-butoxide (1.1 g, 9.8 mmol) were dissolved in freshly distillated dimethylformamide (8 mL). The mixture was heated at 70 °C for 1 h and the corresponding aldehyde (3.6 mmol) was added as a solid at 70°C and stirred for 6 h. The mixture was cooled down to room temperature and water (150 mL) was added. Then, the precipitate was collected by filtration and washed with water and diethylether (10 mL).

Second Method (Ligand F). In a Schlenk tube under an argon atmosphere, 4,4'-(diethylphosphonomethyl)-2,2'-bipyridine (300 mg, 0.7 mmol) and the corresponding aldehyde (1.4 mmol) were dissolved in freshly distillated tetrahydrofuran (15 mL). In a second Schlenk tube and under argon, potassium *tert*-butoxide (443 mg, 3.9 mmol) was dissolved in freshly distillated tetrahydrofuran (8 mL) and was added to the first mixture which was stirred at room temperature for 24 h. Then, the product was extracted with ethyl acetate (3 x 80 mL) and the solvent was removed under reduced pressure to give the product as a solid.

Ligand C. Yield: 755 mg, 67%, first method. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.71 (d, *J* = 5.1 Hz, 2H, *6,6'*), 8.68 (d, *J* = 1.6 Hz, 2H, *3,3'*), 8.37 (d, *J* = 1.6 Hz, 2H, H_{Cbz}), 8.20 (d, *J* = 7.7 Hz, 2H, H_{Cbz}), 7.80 (dd, *J* = 8.6, 1.7 Hz, 2H, *5,5'*), 7.74 (d, *J* = 16.3 Hz, 2H, *CH=CH*), 7.54 – 7.48 (m, 8H, H_{Cbz}), 7.32 (d, *J* = 8.0 Hz, 2H, H_{Cbz}), 7.27 (d, *J* = 16.4 Hz, 2H, *CH=CH*), 4.36 (t, *J* = 7.3 Hz, 4H), 1.92 (q, *J* = 7.1 Hz, 4H), 1.48 – 1.22 (m, 20H), 0.90 (d, *J* = 7.0 Hz, 6H).^{13}C NMR (101 MHz, CD_2Cl_2) 157.42, 157.34, 157.30, 151.81, 151.81, 151.61, 151.19, 147.70, 141.43, 141.11, 137.97, 137.92, 127.91, 127.84, 126.92, 126.31, 125.41, 124.39, 123.87, 123.31, 122.65, 120.99, 120.56, 120.31, 120.21, 119.52, 109.71, 109.59, 109.43, 42.78, 31.59, 29.7, 29.5, 29.1, 26.90, 22.34, 13.41. MALDI-TOF-MS: calc. for ($C_{54}H_{58}N_4$) *m/z* = 762.466, found *m/z* = 763.046. Anal. Calcd. For $C_{54}H_{58}N_4$: C, 85.00; H, 7.66; N, 7.34. Found: C, 84.15; H, 7.49; N, 7.33.

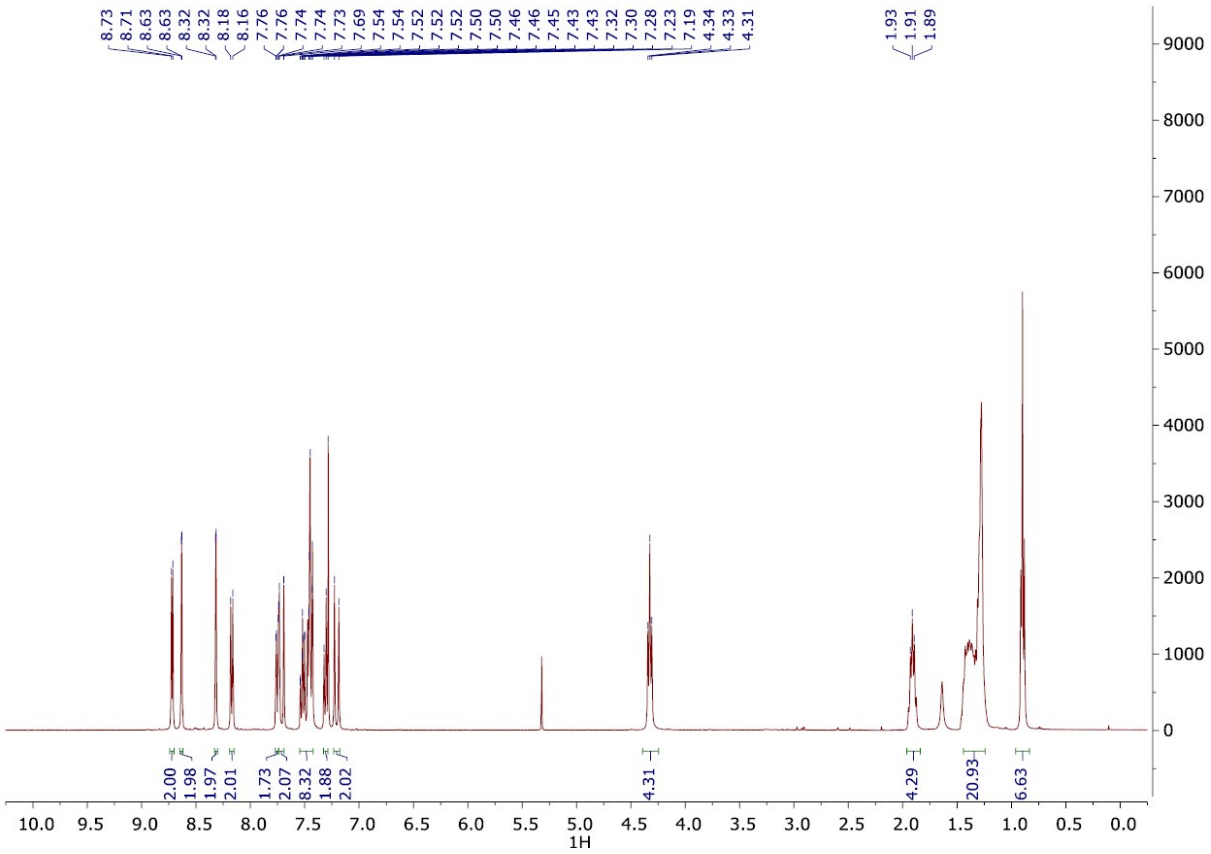


Figure S8. ^{1}H NMR spectrum of **Ligand C** in CD_2Cl_2, 400 MHz.

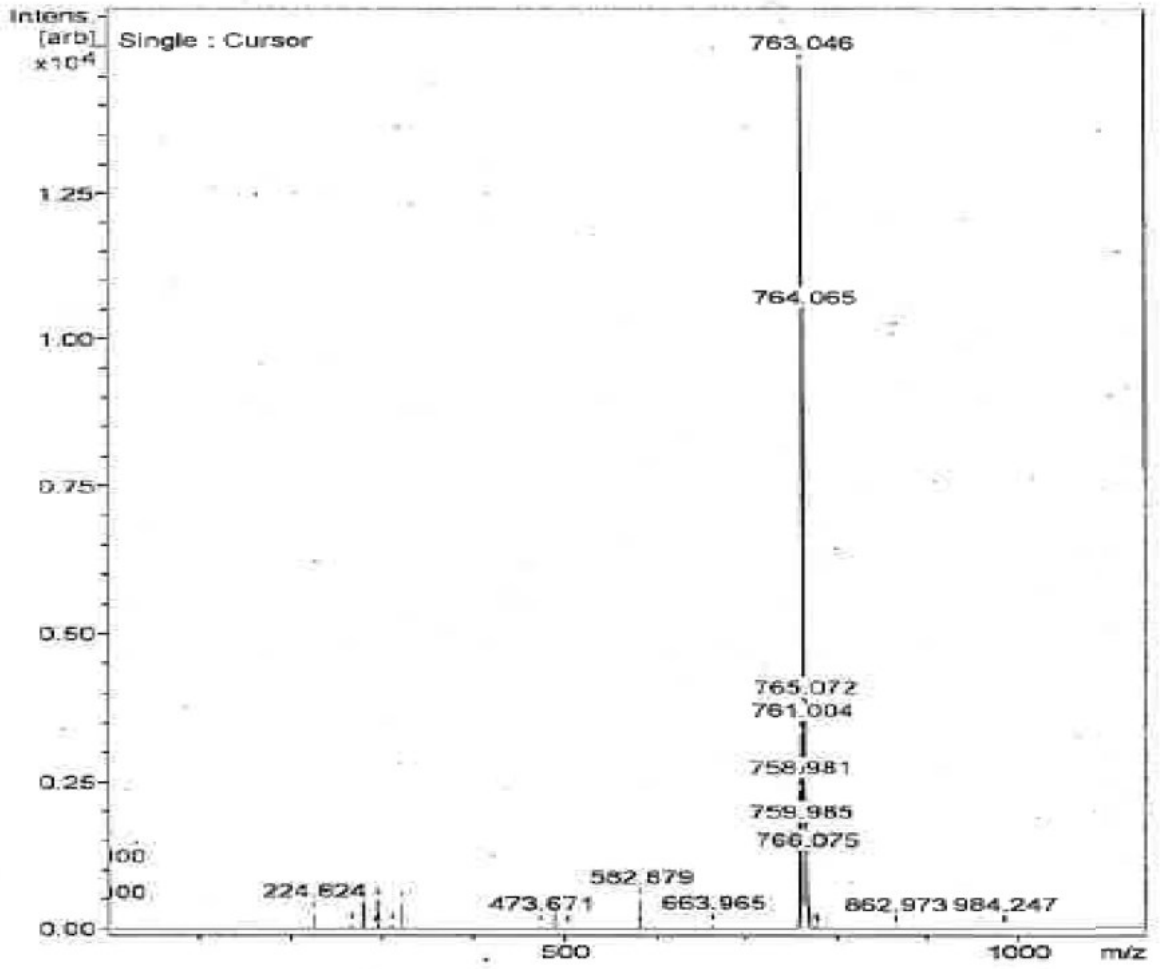


Figure S9. Maldi-TOF-MS spectrum of **Ligand C**.

Ligand T. Yield: 748 mg, 69 %, first method. ^{1}H NMR (400 MHz, CD_3Cl) δ 8.62 (d, 2H, *6,6'*), 8.49 (s, 2H, *3,3'*), 7.44 – 6.95 (m, 34H, *5,5'* + H_{Ar}).^{13}C NMR (101 MHz, CD_3Cl) δ 156.5, 149.4, 148.4, 147.3, 146.1, 132.8, 130.0, 129.3, 128.0, 124.9, 124.1, 123.4, 122.8, 120.8, 118.0. MALDI-TOF-MS: calc. for ($C_{50}H_{38}N_4$) *m/z* = 694.3096, found *m/z* =694.824. Anal. Calcd. For $C_{50}H_{38}N_4$: C, 86.42; H, 5.51; N, 8.06. Found: C, 85.13; H, 5.43; N, 8.15.

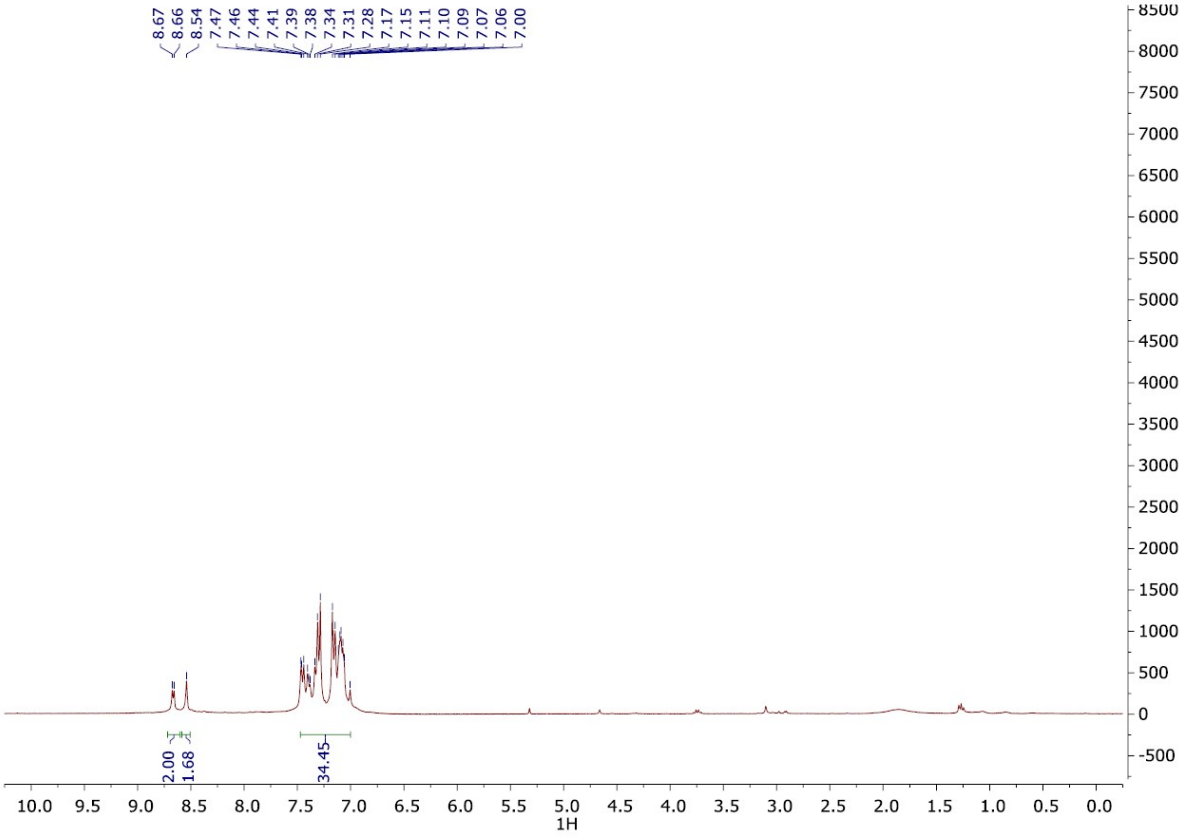


Figure S10. ^{1}H NMR spectrum of **Ligand T** in CD_3Cl, 400 MHz.

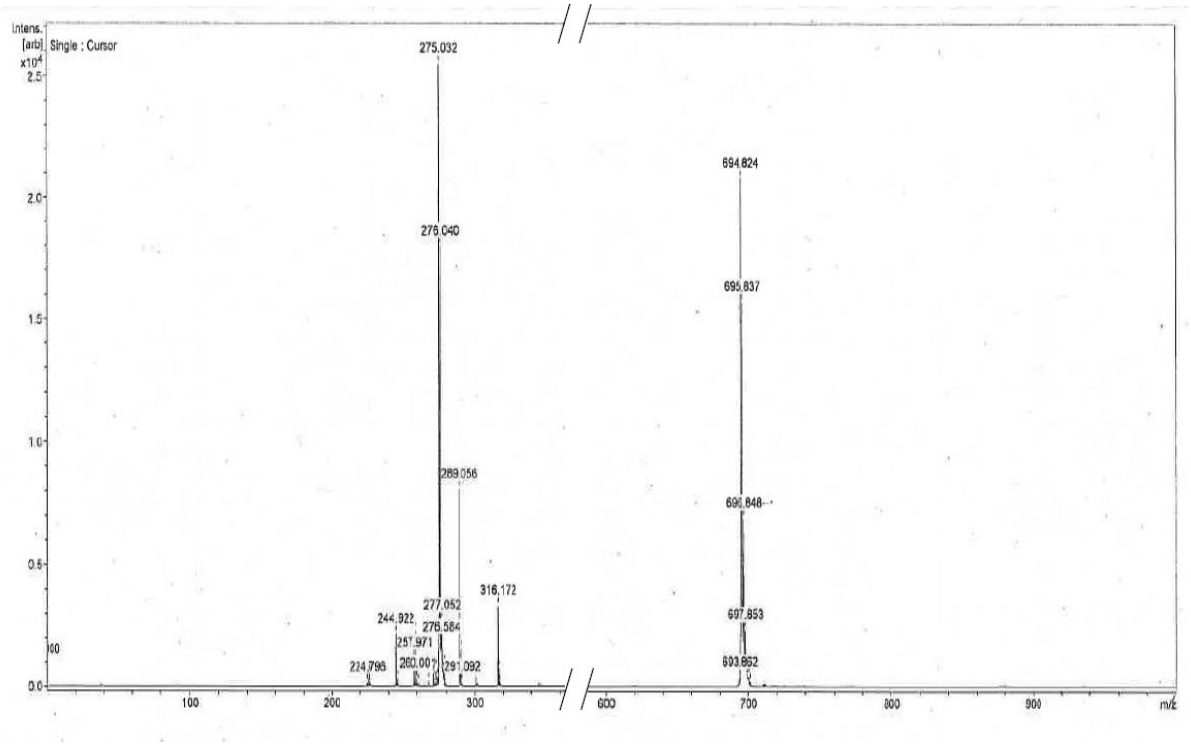


Figure S11. Maldi-TOF-MS spectrum of **Ligand T**.

Ligand F. Yield: 748 mg, 65%, second method. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.66 (d, *J* = 5.1 Hz, 2H, *6,6'*), 8.63 (s, 2H, *3,3'*), 7.67 (d, J = 15.8 Hz, 2H, *CH=CH*), 7.52 (m, 8H, *5,5'* + H_{Fluo}), 7.46 (dd, *J* = 5.1, 1.7 Hz, 2H, H_{Fluo}), 7.26 (dd, *J* = 8.6, 7.1 Hz, 10H, *CH=CH* + H_{Fluo}), 7.11 (d, *J* = 7.6 Hz, 10H, H_{Ar} + H_{Fluo}), 7.02 (t, *J* = 7.4 Hz, 6H, H_{Ar} + H_{Fluo}), 2.02 – 1.81 (m, 8H), 1.25 – 1.03 (m, 40H), 0.83 (t, *J* = 6.9 Hz, 12H), 0.68 (s, 8H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.5, 152.6, 151.3, 149.5, 147.9, 147.6, 145.9, 141.9, 135.6, 134.5, 133.7, 129.2, 126.5, 125.0, 123.9, 123.3, 122.6, 121.2, 120.7, 120.5, 119.3, 119.2, 117.9, 55.0, 40.2, 31.8, 30.0, 29.3, 29.2, 23.9, 22.6, 13.9. MALDI-TOF-MS: calc. for ($C_{96}H_{110}N_4$) *m/z* = 1319.876, found *m/z* = 1320.836. Anal. Calcd. For $C_{96}H_{110}N_4$: C, 87.36; H, 8.40; N, 4.24. Found: C, 87.35; H, 8.47; N, 4.18.

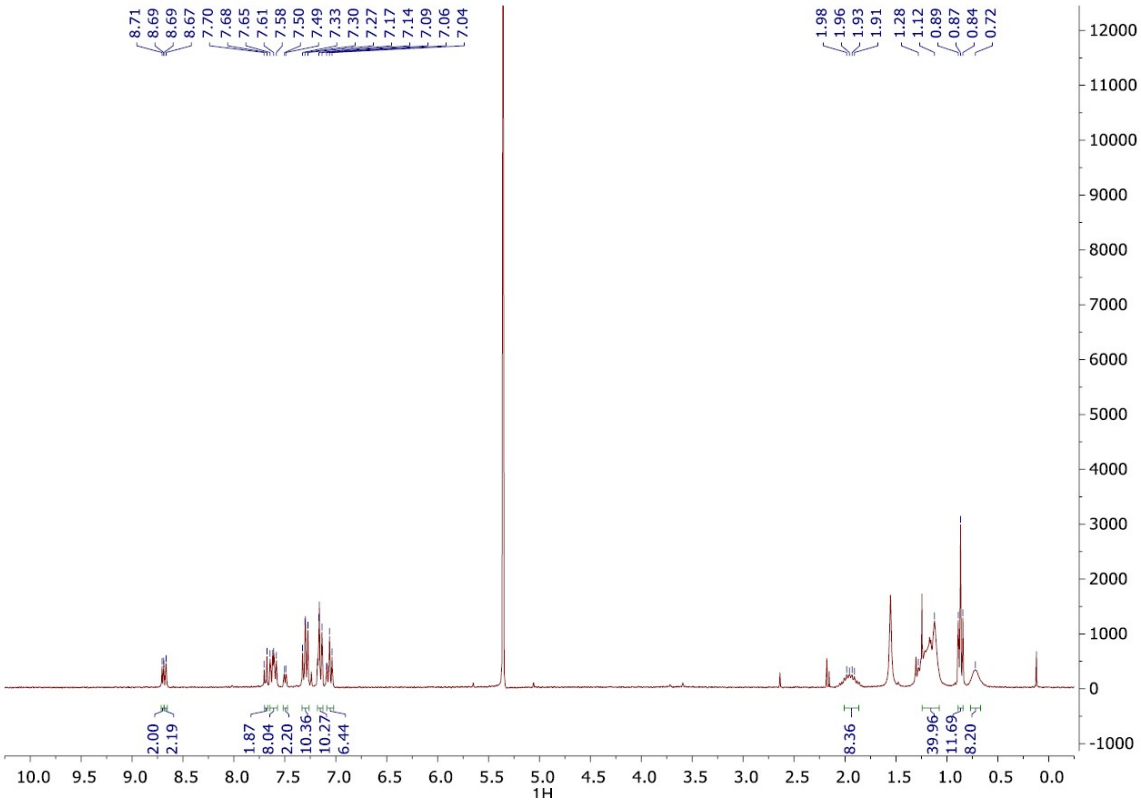


Figure S12. ^{1}H NMR spectrum of **Ligand F** in CD_2Cl_2, 300 MHz.

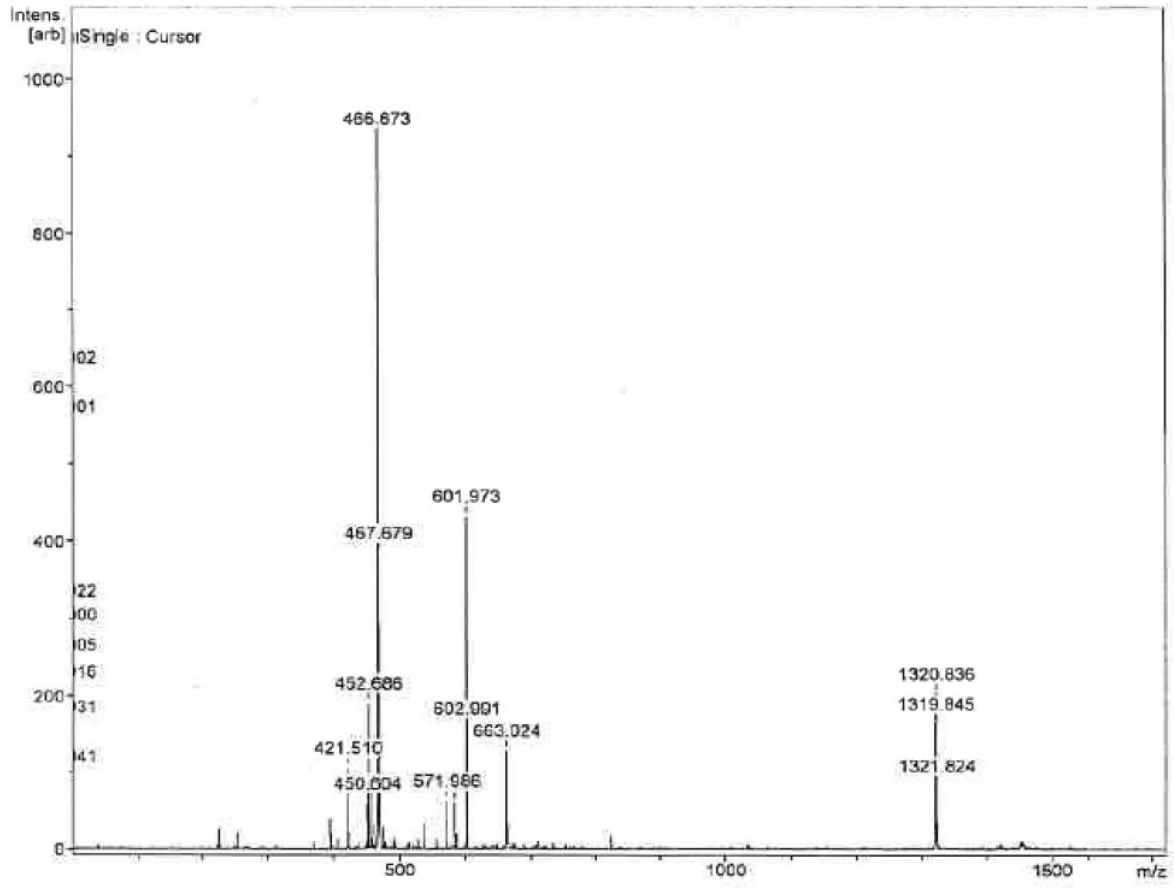
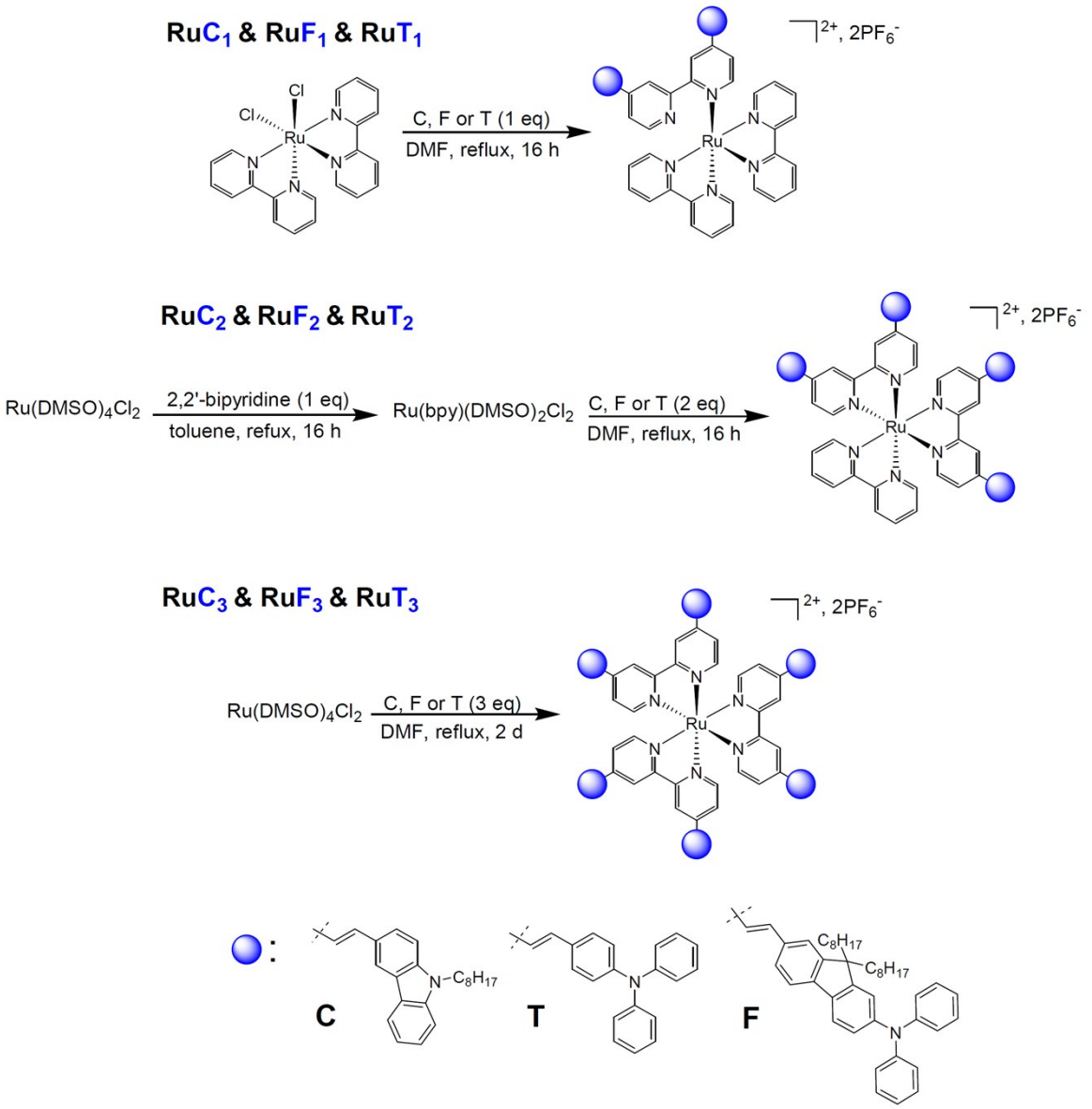


Figure S13. Maldi-TOF-MS spectrum of **Ligand F**.

3.2 General synthetic procedure for the ruthenium complexes.

The general synthetic route for all the ruthenium complexes can be depicted as follows:



Scheme S2. General synthetic route for the Ru-complexes.

Synthetic procedure for the Ru(L)(bpy)$_2$ (PF_6)$_2$ complexes. $Ru(bpy)_2Cl_2$ (48.4 mg, 0.1 mmol) and the bipyridine L (0.1 mmol) were dissolved in degassed ethanol (3 mL) under argon. This solution was heated at 90°C overnight, before being allowed to cool down to room temperature and poured into heptane (150 mL). The products were extracted by chromatography on silica gel using a $(CH_3)_2CO/H_2O/KNO_{3sat}$, 95: 4.5: 0.5 to 90: 9.5: 0.5 mixture as eluant. The product was dissolved in a minimum amount of dimethylformamide (2 mL). A saturated solution of potassium hexafluorophosphate (5 mL) was added and the precipitate collected by filtration and washed with water and diethylether, before being

solubilized in CH_2Cl_2 and dried under vacuum to give the expected products as red-orange powders.

RuC_1. Yield: 144.7 mg, 30 %. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.11 (s, 2H, *3,3'-γ*), 8.88 (d, *J* = 8 Hz, 4H, *3,3'-α, β*), 8.53 (s, 2H, *6,6'- γ*), 8.26 – 8.23 (m, 8H, *4,4'- α, β + 5,5'- γ + H_{Cbz}*), 8.13 (d, *J* = 8 Hz, 2H, *H_{Cbz}*), 8.05 (d, *J* = 16 Hz, 2H, *CH=CH*), 7.95 (d, *J* = 8 Hz, 2H, *H_{Cbz}*), 7.90 (dd, *J* = 4 Hz, 8 Hz, 2H, *H_{Cbz}*), 7.75 – 7.60 (m, 12H, *5,5'- α, β + 6,6'- α, β + H_{Cbz}*), 7.51 (d, *J* = 16 Hz, 2H, *CH=CH*), 7.30 (t, *J* = 8 Hz, 2H, *H_{Cbz}*), 4.53 (t, *J* = 8 Hz, 4H), 1.95 (m, 4H), 1.45 – 1.23 (m, 20H), 0.88 (t, *J* = 8 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d6) δ 157.42, 157.34, 157.30, 151.81, 151.81, 151.61, 151.19, 147.70, 141.43, 141.11, 137.97, 137.92, 127.91, 127.84, 126.92, 126.31, 125.41, 124.39, 123.87, 123.31, 122.65, 120.99, 120.56, 120.31, 120.21, 119.52, 109.71, 109.59, 109.43, 42.78, 31.59, 26.90, 22.34, 13.41.MALDI-TOF-MS: calc. for ([$C_{74}H_{74}N_8F_6PRu$]$^+$) *m/z* = 1321.4722, found *m/z* = 1322.404. Anal. Calcd. For [$C_{74}H_{74}N_8F_{12}P_2Ru$, 0.5$CH_2Cl_2$]: C, 59.28; H, 5.01; N, 7.43. Found: C, 59.32; H, 5.52; N, 7.07.

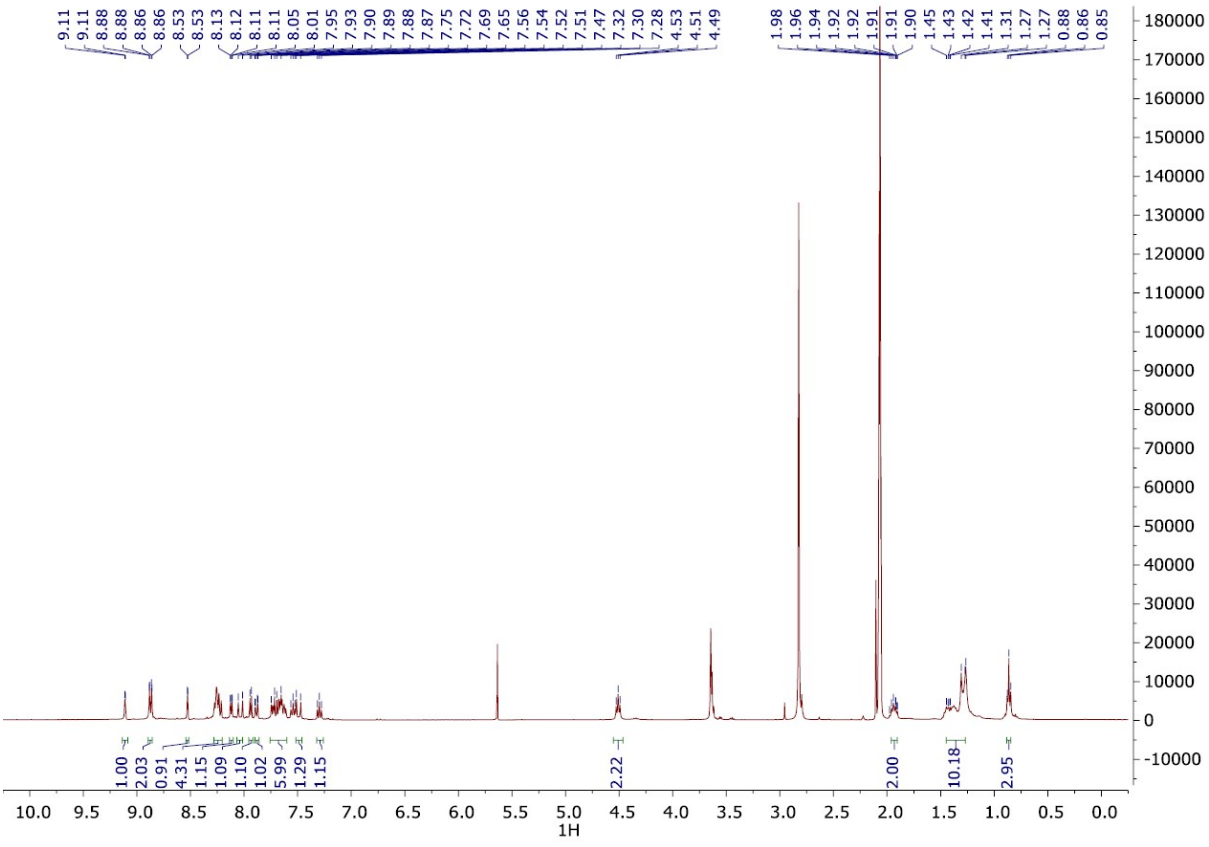


Figure S14. ^{1}H NMR spectrum of **RuC_1** in acetone-d_6, 400 MHz.

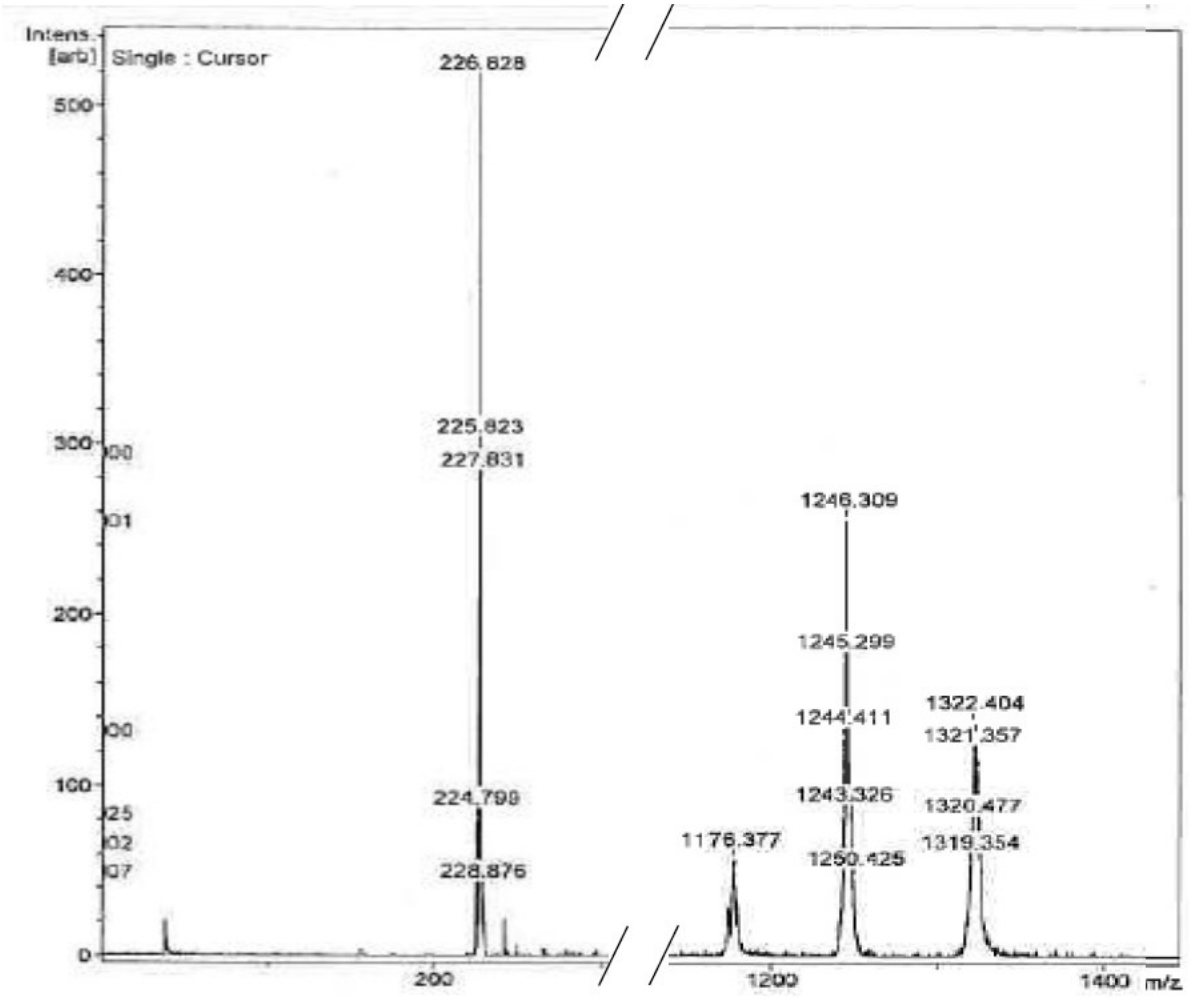


Figure S15. Maldi-TOF-MS spectrum of **RuC_1**.

RuT$_1$. Yield: 73 mg, 36 %. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (s, 2H, *3,3'- γ*), 8.46 (d, *J* = 6 Hz, 4H, *3,3'- α, β*), 8.10 (t, *J* = 7.1 Hz, 4H, *4,4'- α, β*), 7.86 (d, *J* = 5.6 Hz, 2H, *6 or 6'- α, β*), 7.75 (d, *J* = 5.6 Hz, 2H, *6 or 6'- α, β*), 7.59 – 7.48 (m, 14H, *5,5'- α, β + 5,5'- γ + 6,6'- γ + CH=CH + H_{Ar}*) 7.34 (t, *J* = 5.6 Hz, 8H, H_{Ar}), 7.17 – 7.12 (m, 14H, *CH=CH + H_{Ar}*), 7.27 (d, *J* = 5.6 Hz, 4H, H_{Ar}). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.66, 156.49, 151.43, 149.28, 147.54, 146.91, 137.79, 129.48, 128.86, 128.63, 125.26, 123.94, 123.75, 121.92, 121.15.MALDI-TOF-MS: calc. for ($[C_{70}H_{54}N_8F_6PRu]^+$) *m/z* = 1253.3157, found *m/z* = 1254.268 Anal. Calcd. For $[C_{70}H_{54}N_8F_{12}P_2Ru]$: C, 60.13; H, 3.89; N, 8.01. Found: C, 59.77; H, 3.86; N, 7.90.

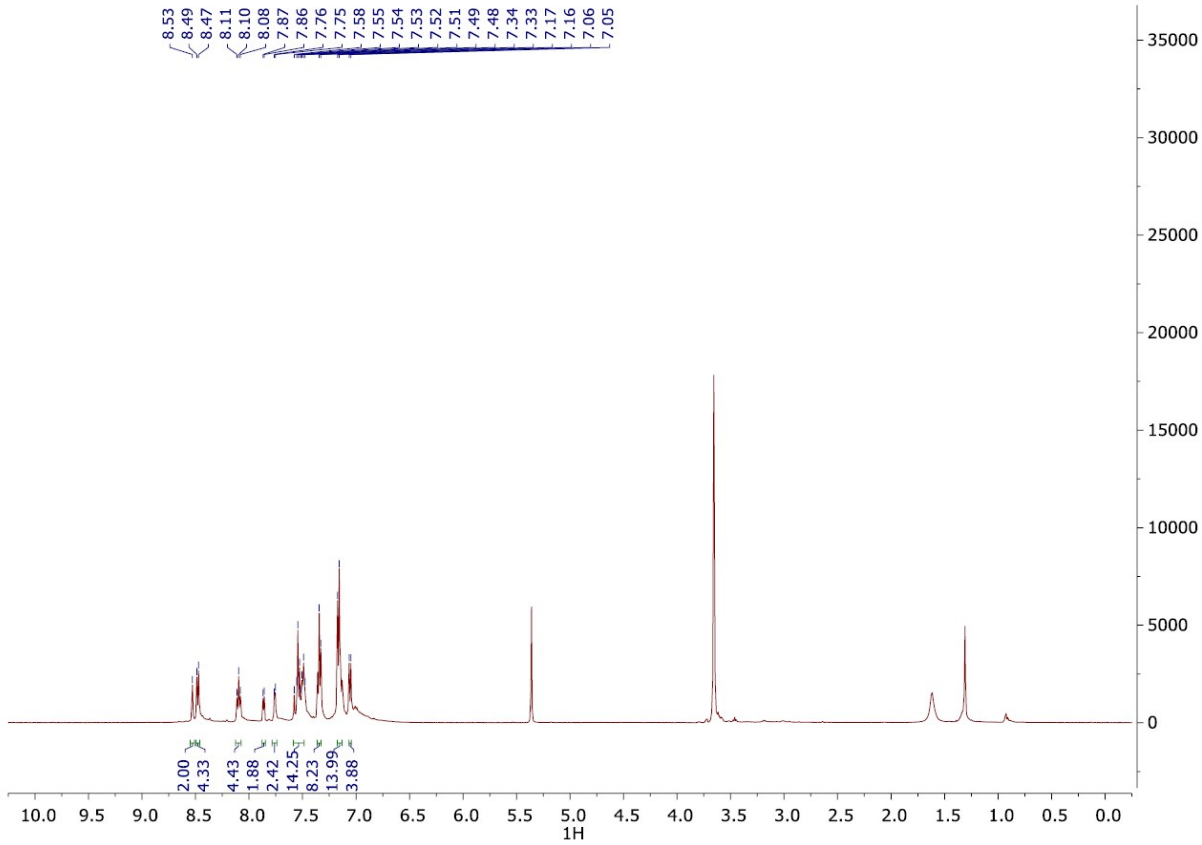


Figure S16. ^{1}H NMR spectrum of **RuT$_1$** in CD_2Cl_2, 400 MHz.

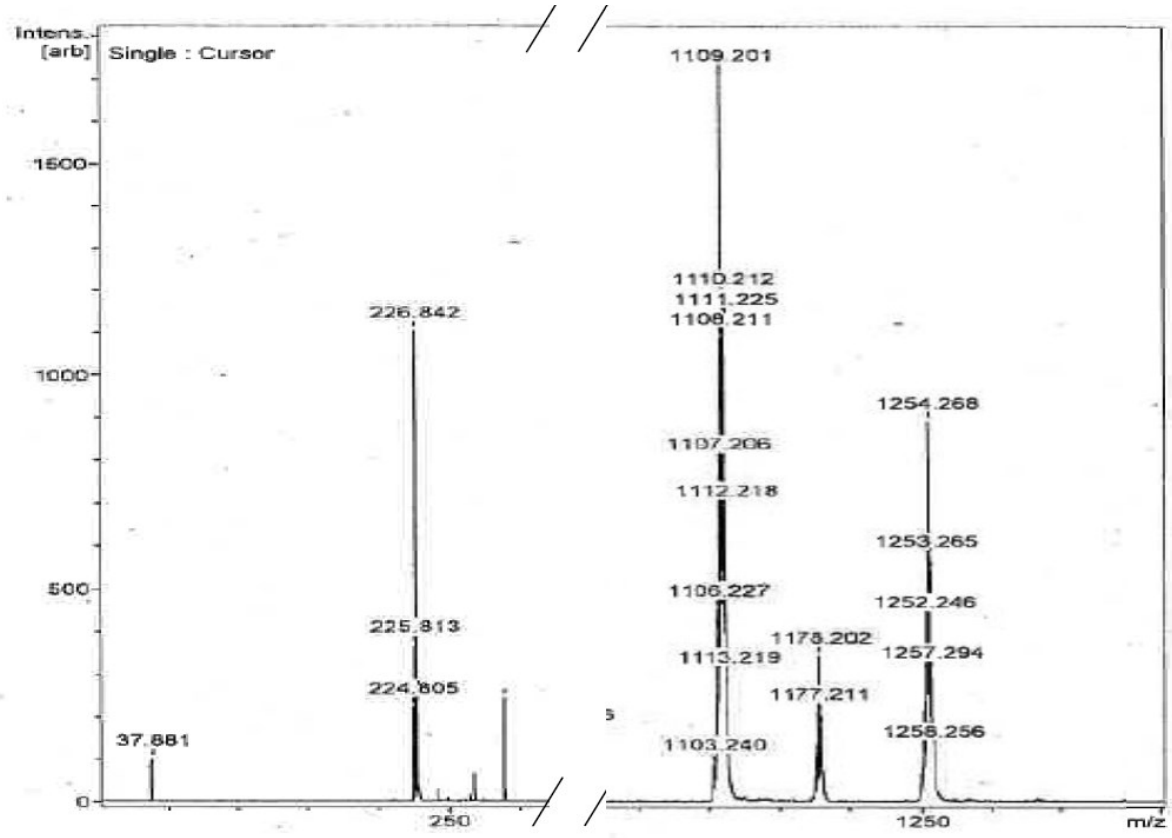


Figure S17. Maldi-TOF-MS spectrum of **RuT$_1$**.

RuF$_1$. Yield: 20 mg, 12 %. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (d, J = 2.0 Hz, 2H, *3,3'- γ*), 8.46 (d, J = 8.2 Hz, 4H, *3,3'- α, β*), 8.08 (t, J = 7.9 Hz, 4H, 4,4'- *α, β*), 7.85 (dd, J = 5.8, 1.3 Hz, 2H, *6 or 6'- α, β*), 7.75 (d, J = 5.6 Hz, 2H, *6 or 6'- α, β*), 7.69 (d, J = 4.3 Hz, 4H, H_{Fluo}), 7.66 – 7.59 (m, 8H, *5,5'- α, β + 6,6'- γ + CH=CH* + H_{Fluo}), 7.54 – 7.47 (m, 10H, 5,5'- *γ* + H_{Ar} + H_{Fluo}), 7.27 (t, J = 7.7 Hz, 10H, *CH=CH* + H_{Ar}), 7.10 (d, 6H, H_{Ar}), 7.03 (m, J = 6.7, 6.1 Hz, 6H, H_{Fluo}), 2.02 – 1.81 (m, 8H), 1.25 – 1.03 (m, 40H), 0.83 (t, J = 6.9 Hz, 12H), 0.68 (s, 8H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.8, 156.8, 156.7, 152.8, 151.5, 151.2, 151.2, 150.7, 148.0, 147.8, 147.8, 147.4, 143.2, 137.9, 137.9, 137.8, 135.1, 133.4, 129.1, 128.0, 127.9, 127.3, 124.1, 124.1, 124.0, 123.1, 122.7, 122.1, 121.7, 120.7, 120.7, 119.4, 118.8, 55.1, 40.1, 31.7, 29.9, 29.3, 29.2, 23.9, 22.6, 13.8. MALDI-TOF-MS: calc. for ([$C_{116}H_{126}N_8F_6PRu$]$^+$) m/z = 1877.8791, found m/z = 1878.795. Anal. Calcd. For [$C_{116}H_{126}N_8F_{12}P_2Ru$], CH_2Cl_2: C, 66.64; H, 6.12; N, 5.32. Found: C, 66.62; H, 5.97; N, 5.21.

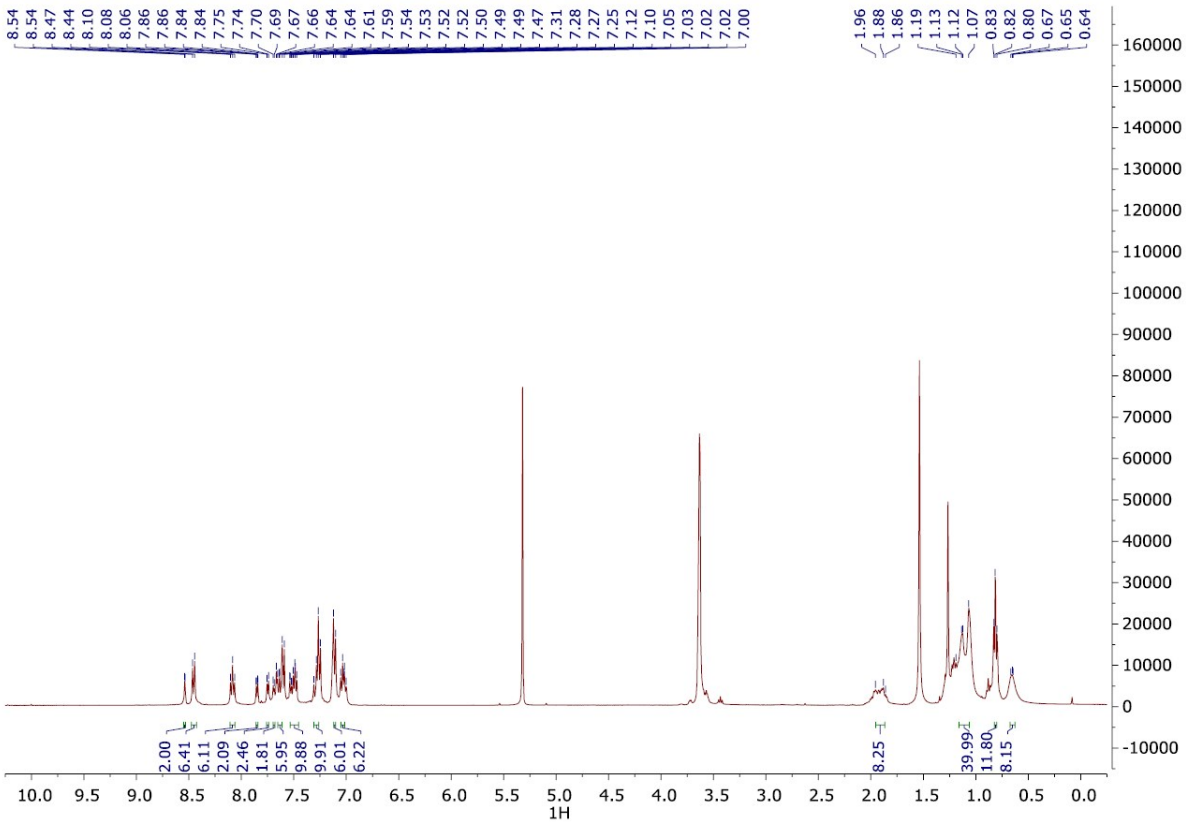


Figure S18. ^{1}H NMR spectrum of **RuF$_1$** in CD_2Cl_2, 400 MHz.

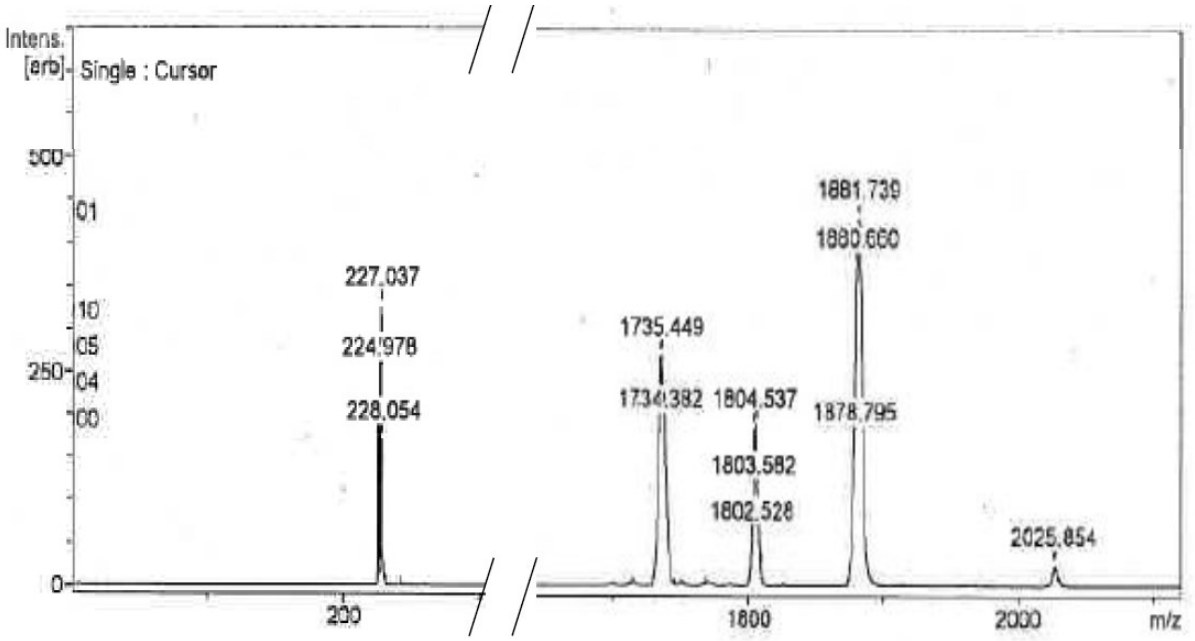


Figure S19. Maldi-TOF-MS spectrum of **RuF$_1$**.

Synthetic procedure for Ru(bpy)(L)$_2$(PF$_6$)$_2$. Ru(bpy)Cl$_2$(DMSO)$_2$ (35 mg, 0.072 mmol) and the bipyridine L (2 eq. , 0.144 mmol) were dissolved in degassed dimethylformamide (3 mL) under argon. The solution was heated at 90°C for two days. The reaction mixture was allowed to cool down to room temperature before being chromatographied on silica gel. The complexes were eluted with a $(CH_3)_2CO/H_2O/KNO_{3sat}$, 95: 4.5: 0.5 to 90: 9.5: 0.5 mixture. The solvents were evaporated and the residue dissolved in dimethylformamide (2 mL). A saturated solution of potassium hexafluorophosphate (5 mL) was added to this solution resulting in a precipitate that was collected by filtration and washed with water and diethylether, before being solubilized in CH_2Cl_2 and dried under vacuum to give the expected products as red powders.

RuC$_2$ Yield: 96 mg, 74 %. ^{1}H NMR (400 MHz, acetone-d$_6$) δ 9.13 (s, 4H, H3, *3,3'- γ, γ'*), 8.90 (d, *J* = 8 Hz, 2H, *3,3'- α*), 8.55 (d, *J* = 8 Hz, 4H, *6,6'- γ, γ'*), 8.29-8.20 (m, 8H, *4,4'- α + 5,5'- γ, γ' + H$_{Cbz}$*), 8.11-8.04 (m, 6H, *CH=CH + H$_{Cbz}$*) 7.97 (d, *J* = 4 Hz, 2H, *H$_{Cbz}$*), 7.92 (t, *J* = 8 Hz, 4H, *H$_{Cbz}$*), 7.79-7.62 (m, 14H, *5,5'- α + 6,6'- α + H$_{Cbz}$*), 7.56-7.48 (m, 8H, *CH=CH +H$_{Cbz}$*), 7.30-7.25 (m, 4H, *H$_{Cbz}$*), 4.53 (m, 8H), 1.94 (m, 8H), 1.42-1.24 (m, 40H), 0.87 (t, *J* = 8 Hz, 12H). ^{13}C NMR (101 MHz, acetone-d6) δ 151.22, 141.44, 141.12, 126.94, 126.32, 125.40, 123.32, 122.63, 121.06, 120.51, 120.29, 119.53, 109.72, 42.78, 31.59, 31.57, 26.91, 22.35, 22.33, 13.42, 13.40. MALDI-TOF-MS: calc. for ([C$_{118}$H$_{124}$N$_{10}$F$_6$PRu]$^+$) *m/z* = 1927.8696, found *m/z* = 1929.502. Anal. Calcd. For [C$_{118}$H$_{124}$N$_{10}$F$_{12}$P$_2$Ru]: C, 68.36; H, 6.03; N, 6.76. Found: C, 67.44; H, 5.86; N, 6.94.

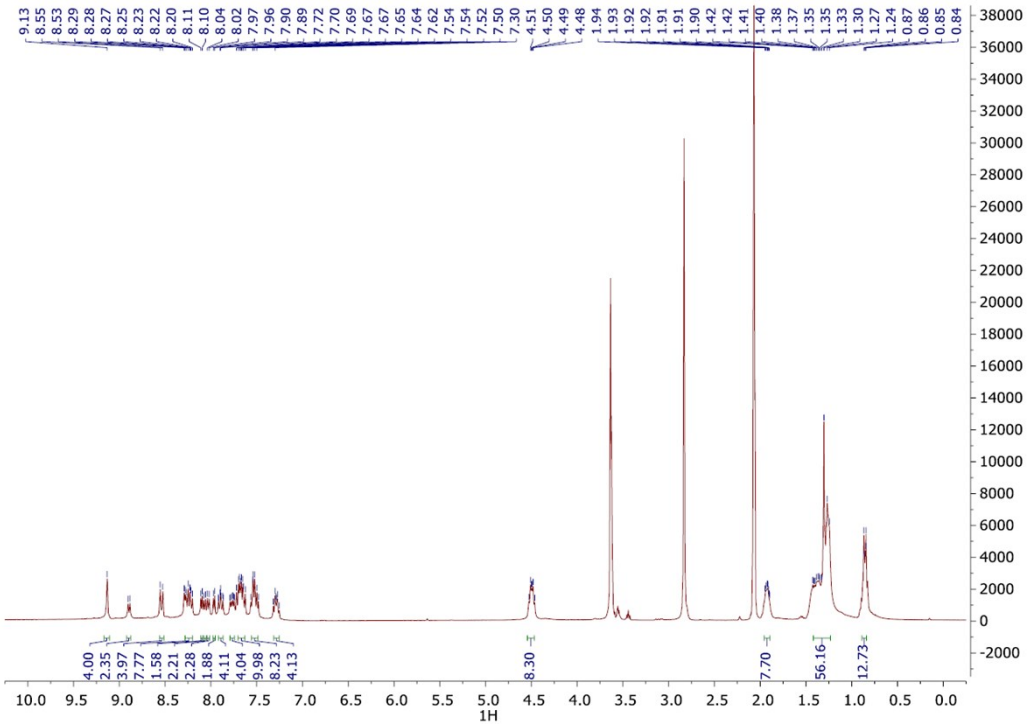


Figure S20. ^{1}H NMR spectrum of **RuC_2** in acetone-d_6, 400 MHz.

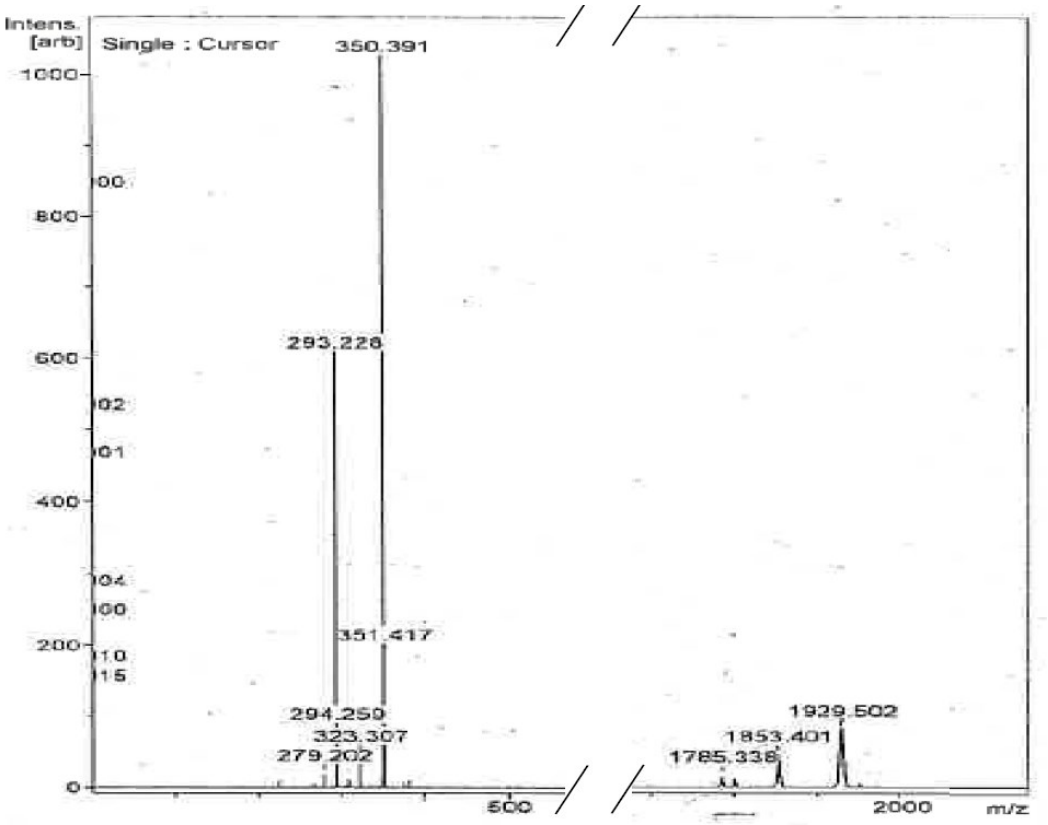


Figure S21. Maldi-TOF-MS spectrum of **RuC_2**.

RuT$_2$. Yield: 45 mg, 68 %. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.42 (s, 4H, *3,3'- γ, γ'*), 8.36 (d, *J* = 8.8 Hz, 2H, *3,3'- α*), 8.10 (t, *J* = 6.8 Hz, 2H, *4,4'- α*), 7.90 (t, *J* = 6.8 Hz, 2H, *6,6'- α*), 7.80 (d, *J* = 6.8 Hz, 2H, *6 or 6'- γ, γ'*), 7.57 (d, *J* = 6.8 Hz, 2H, *6 or 6'- γ, γ'*),7.50 – 7.41 (m, 18H, *5,5'- α + 5,5'- γ, γ' + CH=CH + H_{Ar}*), 7.35 – 7.26 (m, 16H, *H_{Ar}*), 7.28 – 7.23 (m, 28H, *CH=CH + H_{Ar}*), 6.95 (d, *J* = 6.8 Hz, 8H, *H_{Ar}*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 156.78, 149.00, 146.70, 135.62, 129.39, 129.32, 129.32, 128.64, 128.32, 128.32, 125.30, 124.97, 124.97, 123.85, 123.85, 123.53, 121.38, 121.38, 121.28, 119.98. MALDI-TOF-MS: calc. for ($[C_{110}H_{84}N_{10}F_6PRu]^+$) *m/z* = 1791.5166, found *m/z* = 1793.365. Anal. Calcd. For $[C_{110}H_{84}N_{10}F_{12}P_2Ru]$, 1.5 CH_2Cl_2: C, 64.75; H, 4.26; N, 6.81. Found: C, 64.36; H, 4.67; N, 6.83.

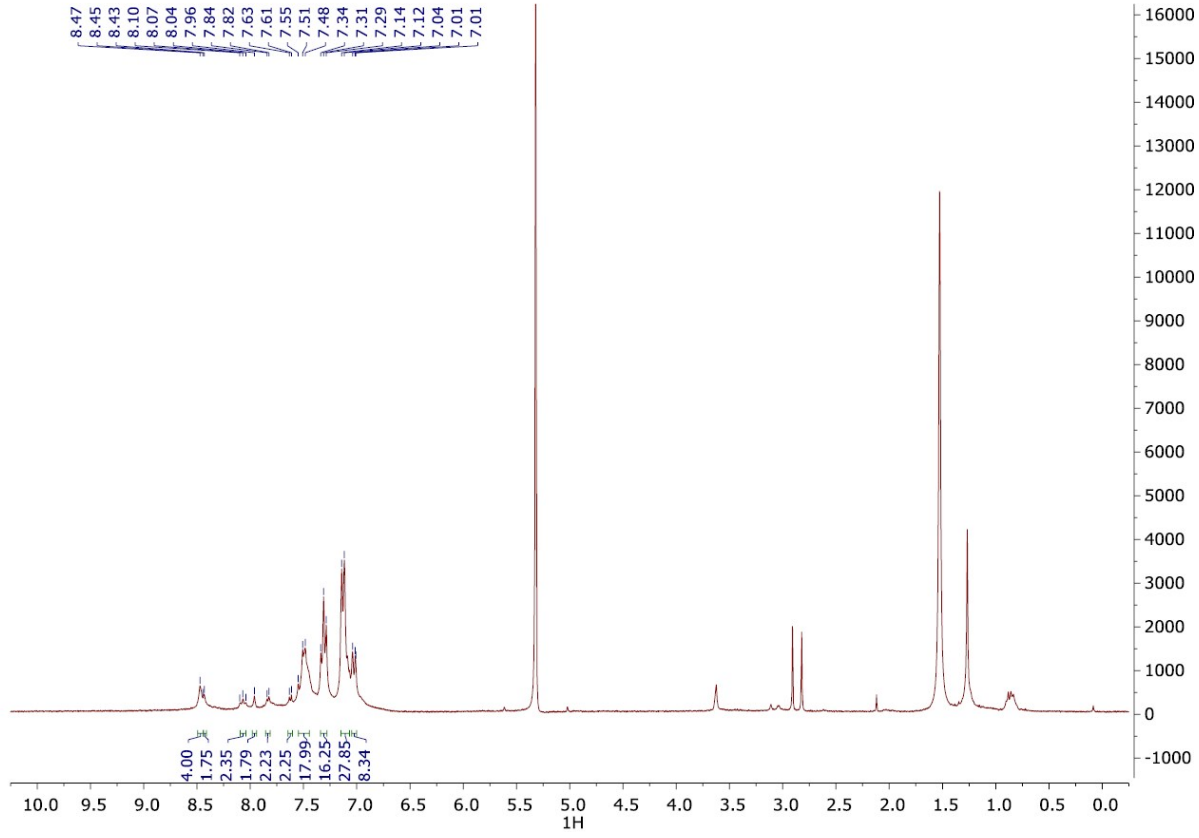


Figure S22. ^{1}H NMR spectrum of **RuT$_2$** in CD_2Cl_2, 300 MHz.

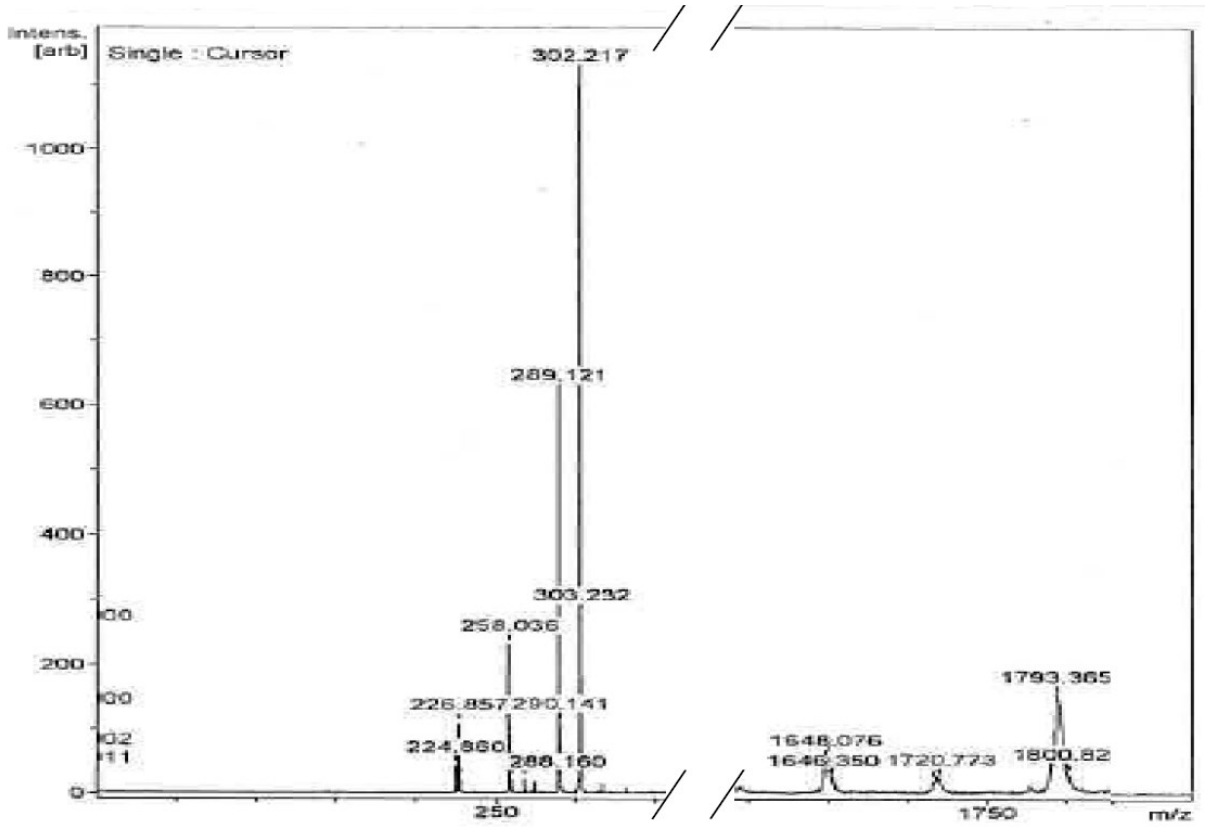


Figure S23. Maldi-TOF-MS spectrum of $\mathbf{RuT_2}$.

RuF_2. Yield: 33 mg, 29 %. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.62 (s, 4H, *3,3'- γ, γ'*), 8.51 (d, *J* = 9 Hz, 2H, *3,3'- α*), 8.14 (t, *J* = 9 Hz, 2H, *4,4'- α*), 7.93 (d, *J* = 6.8 Hz, 2H, *6,6'- α*), 7.77 (d, *J* = 6.8 Hz, 2H, *6 or 6'- γ, γ'*), 7.67 – 7.52 (m, 30H, *5,5'- α + 5,5'- γ, γ' + 6 or 6'- γ, γ' + CH=CH + H_{Fluo}*), 7.38 – 7.27 (m, 20H, *CH=CH + H_{Ar}*), 7.17 (m, 20H, *H_{Ar} + H_{Fluo}*), 7.10 – 7.02 (m, 10H, *H_{Ar} + H_{Fluo}*), 2.02 – 1.81 (m, 16H), 1.25 - 1.03 (m, 80H), 0.83 (t, *J* = 6.9 Hz, 24H), 0.68 (s, 16H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.09, 152.86, 151.51, 150.73, 147.98, 147.88, 143.20, 137.59, 135.24, 133.54, 129.20, 127.30, 124.06, 123.20, 122.77, 120.78, 119.46, 118.93, 40.18, 31.80, 29.97, 29.32, 29.22, 23.92, 22.61, 18.35. MALDI-TOF-MS: calc. for ($[C_{202}H_{228}N_{10}F_6PRu]^+$) *m/z* = 3042.6906, found *m/z* = 3046.996. Anal. Calcd. For $[C_{202}H_{228}N_{10}F_{12}P_2Ru]$, 1.5 CH_2Cl_2: C, 73.73; H, 7.03; N, 4.23. Found: C, 73.18; H, 7.22; N, 4.12.

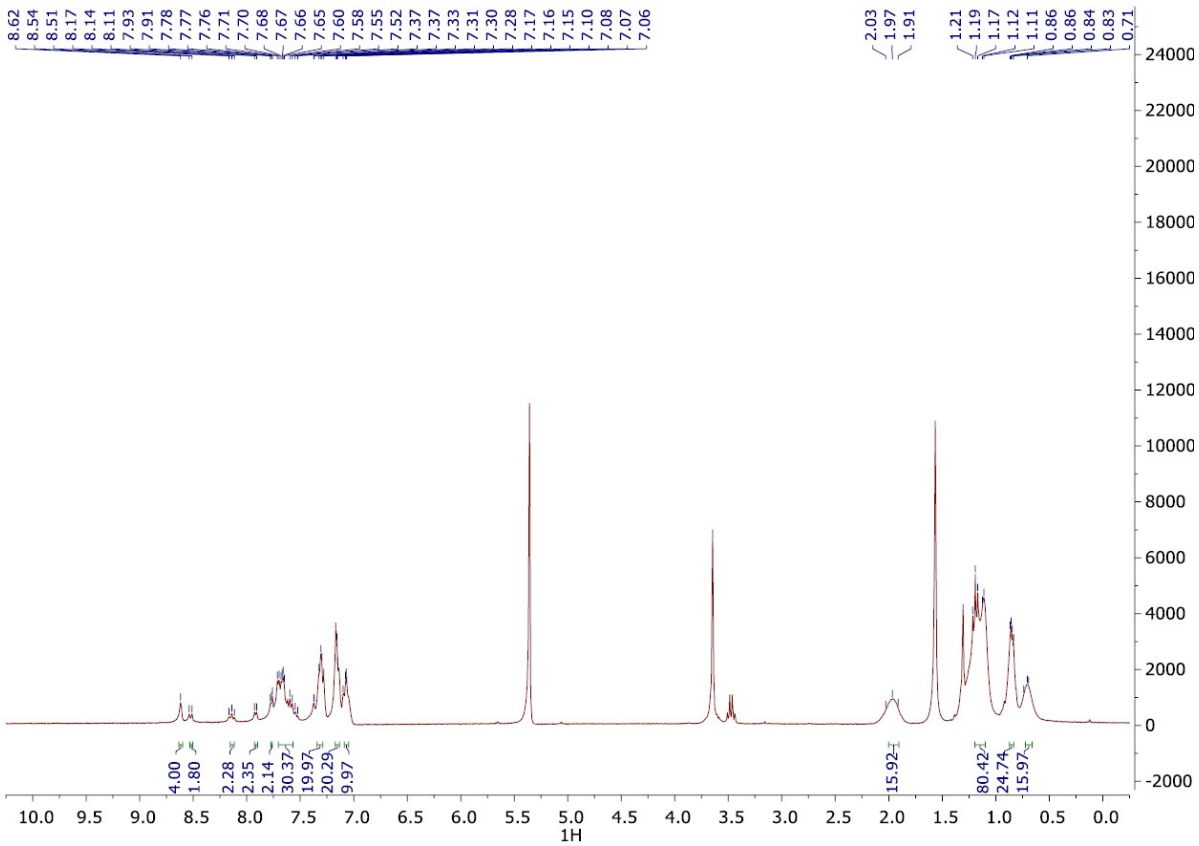


Figure S24. ^{1}H NMR spectrum of **RuF_2** in CD_2Cl_2, 400 MHz.

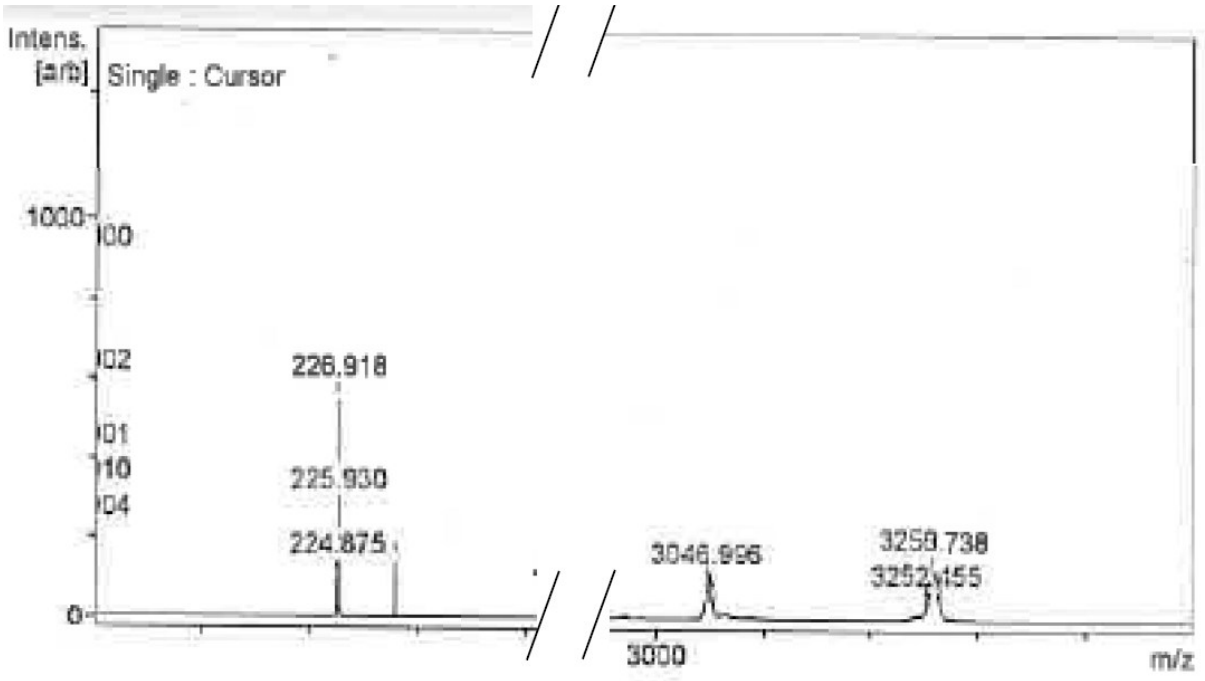


Figure S25. Maldi-TOF-MS spectrum of $\mathbf{RuF_2}$.

Synthetic procedure for the $Ru(L)_3(PF_6)_2$ complexes. $RuCl_2(DMSO)_4$ (20.5 mg, 0.042 mmol) and the bipyridine L (0.131 mmol) were dissolved in 3 mL degassed dimethylformamide, under argon. This mixture was heated at 90°C for one day and 130°C for two days. After the solution was cooled down to room temperature, the mixture was poured into heptane (195 mL) and dichloromethane (5 mL). The expected compounds were chromatographied on silica gel, using $(CH_3)_2CO/H_2O/KNO_{3sat}$, 95: 4.5: 0.5 to 90: 9.5: 0.5 as eluent. The solvents were evaporated and the residue dissolved in dimethylformamide (2 mL). A saturated solution of potassium hexafluorophosphate (5 mL) was added to this solution resulting in a precipitate that was collected by filtration and washed with water and diethylether, before being solubilized in CH_2Cl_2 and dried under vacuum to give the expected products as red powders.

RuC_3. Yield: 68 mg, 60 %. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.20 (s, 6H, *3,3'- γ*), 8.51 (s, 6H, *6,6'- γ*), 8.20 - 17 (dd, *J* = 6 Hz, 10H, *5,5'- γ* + H_{Cbz}), 8.10 (d, *J* = 15 Hz, 6H, *CH=CH*), 7.91 (d, *J* = 9 Hz, 5H, H_{Cbz}), 7.84 (d, *J* = 6 Hz, 7H, H_{Cbz}), 7.73 (d, *J* = 6 Hz, 6H, H_{Cbz}), 7.69 (d, *J* = 9 Hz, 6H, H_{Cbz}), 7.55 (d, *J* = 6 Hz, 7H, H_{Cbz}), 7.53 (d, *J* = 15 Hz, 6H, *CH=CH*), 7.31 (t, *J* = 6 Hz, 7H, H_{Cbz}), 4.53 (t, *J* = 6 Hz, 12H), 1.93 (q, *J* = 7.1 Hz, 12H), 1.48 – 1.22 (m, 60H), 0.90 (d, *J* = 7.0 Hz, 18H). ^{13}C NMR (101 MHz, acetone-d6) δ 147.41, 141.42, 141.10, 127.13, 126.97, 125.37, 123.31, 122.63, 120.28, 119.52, 109.73, 109.61, 42.79, 31.68, 31.58, 26.90, 22.40, 22.34, 13.41, 13.25. MALDI-TOF-MS: calc. for ($[C_{162}H_{174}N_{12}F_6PRu]^+$) *m/z* = 2534.2670, found *m/z* = 2538.8442. Anal. Calcd. For $[C_{162}H_{174}N_{12}F_{12}P_2Ru].2C_7H_{16}.3.5CH_2cl_2$: C, 67.88; H, 6.76; N, 5.30. Found: C, 68.77; H, 6.68; N, 5.28.

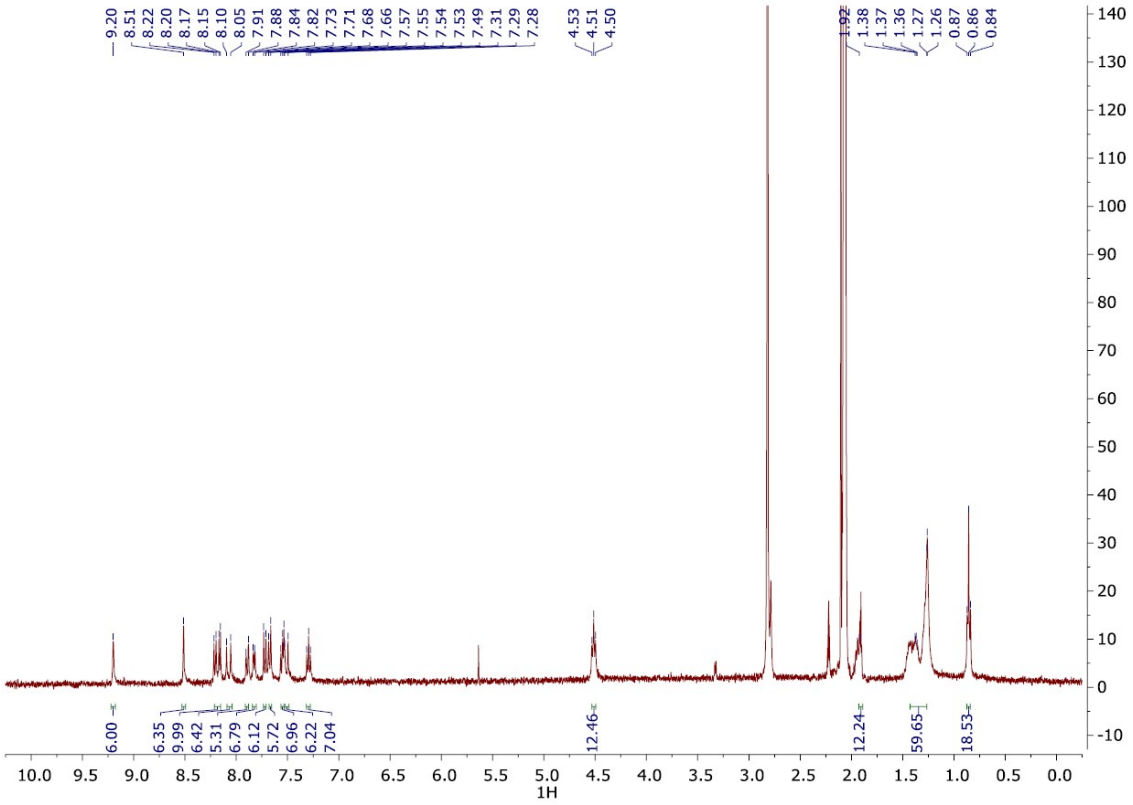


Figure S26. ^{1}H NMR spectrum of **RuC$_3$** in acetone-d$_6$, 400 MHz.

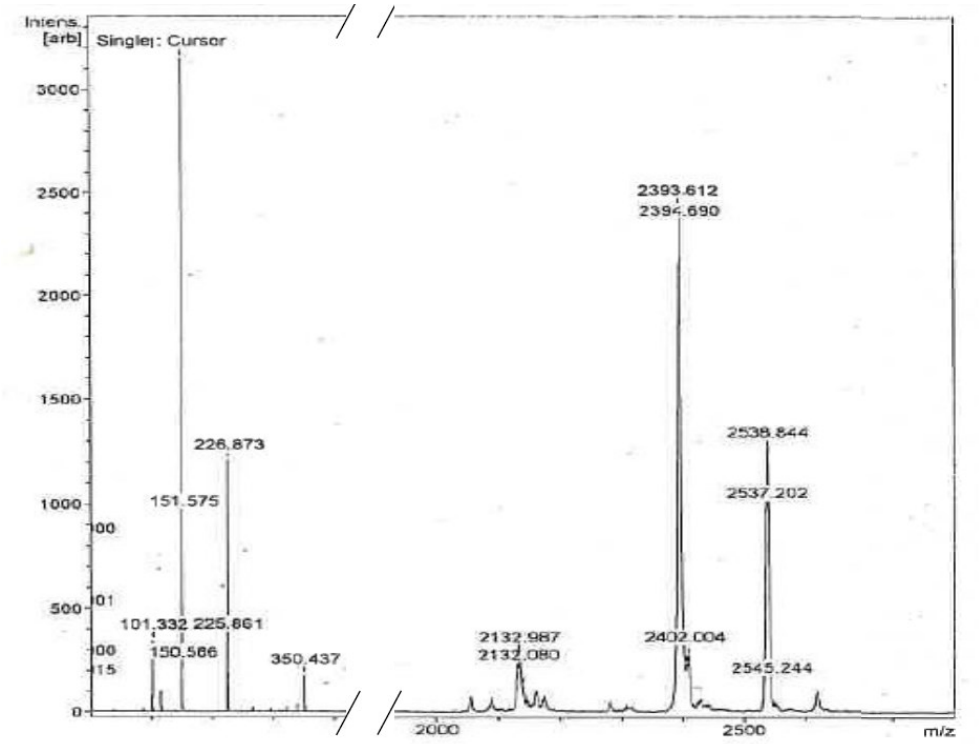


Figure S27. Maldi-TOF-MS spectrum of **RuC$_3$**.

RuT$_3$. Yield: 55 mg, 54 %. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (s, 6H, *3,3'- γ*), 7.66 (d, *J* = 5.8 Hz, 6H, *6,6'- γ*), 7.56 (d, *J* = 16.0 Hz, 6H, *CH=CH*), 7.53 (d, *J* = 7.6 Hz, 12H, H_{Ar}), 7.46 (d, *J* = 5.8 Hz, 6H, *5,5'- γ*), 7.33 (t, J = 7.1 Hz, 24H, H_{Ar}), 7.15 (m, 24H, H_{Ar}), 7.14 (m, 12H, H_{Ar}), 7.13 (d, *J* = 16.0 Hz, 6H, CH=CH), 7.04 (d, *J* = 7.6 Hz, 12H, H_{Ar}). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.99, 150.29, 149.49, 147.20, 146.92, 136.43, 129.45, 128.70, 128.46, 125.38, 124.00, 123.46, 121.73, 121.69, 120.95. MALDI-TOF-MS: calc. for ($[C_{150}H_{114}N_{12}Ru]^+$) *m/z* = 2184.8333, found *m/z* = 2186.331. Anal. Calcd. For $[C_{150}H_{114}N_{12}F_{12}P_2Ru]$, CH_2Cl_2: C, 70.83; H, 4.57; N, 6.56. Found: C, 70.23; H, 4.47; N, 6.74.

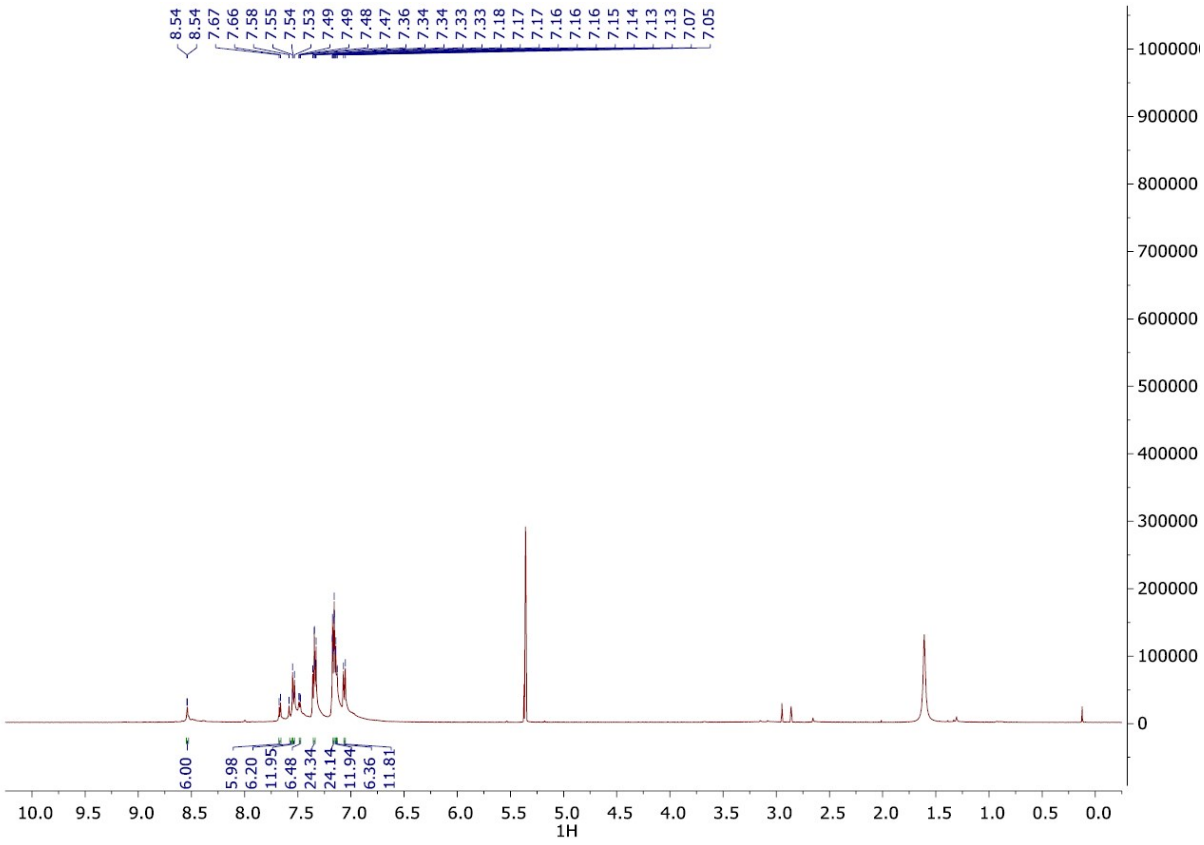


Figure S28. ^{1}H NMR spectrum of **RuT$_3$** in CD_2Cl_2, 400 MHz.

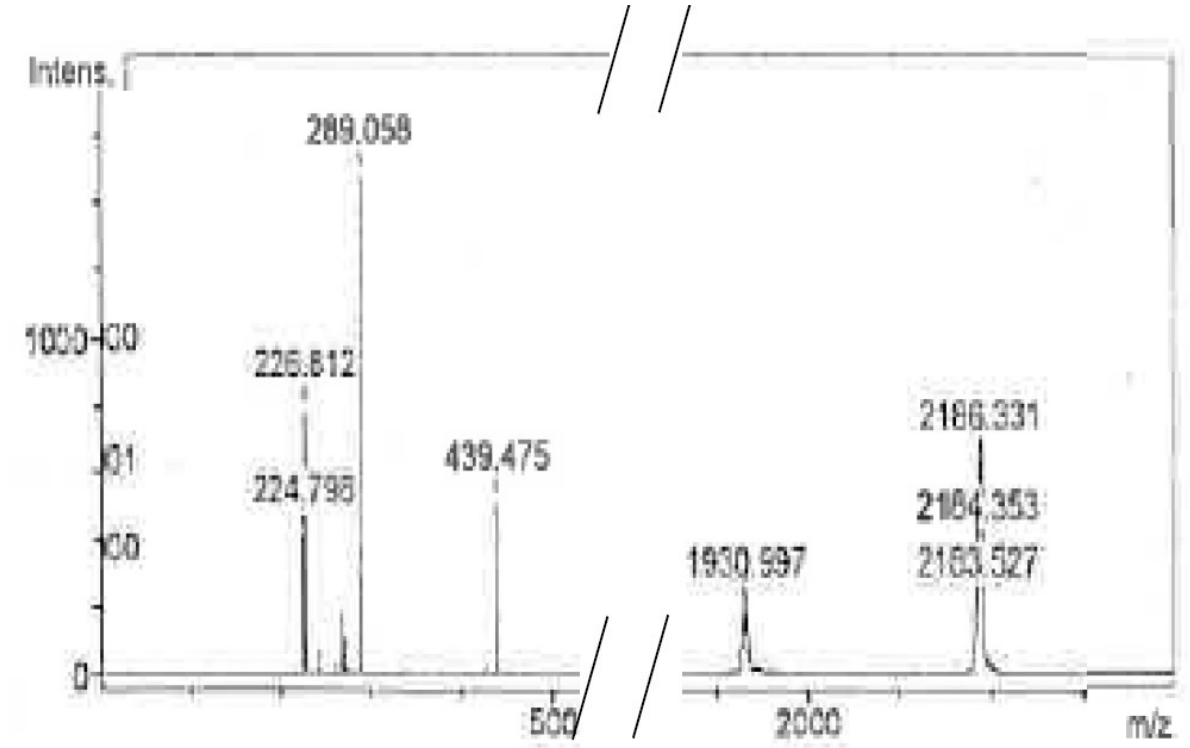


Figure S29. Maldi-TOF-MS spectrum of **RuT_3**.

RuF$_3$. Yield: 41 mg, 38 %. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (s, 6H, *3,3'- γ*), 7.81 – 7.60(m,48H, *5,5'- γ + 6,6'- γ + CH=CH + H$_{Fluo}$*),7.40 – 7.28 (m, 36H, *CH=CH + H$_{Ar}$*), 7.17 – 7.03 (m, 36H, *H$_{Ar}$ + H$_{Fluo}$*), 2.02 – 1.80 (m, 24H), 1.25 - 1.03 (m, 120H), 0.83 (t, *J* = 8 Hz, 36H), 0.68 (s, 24H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.08, 152.89, 151.56, 147.99, 147.88, 147.16, 143.21, 137.60, 135.23, 133.52, 129.20, 127.30, 124.07, 123.93, 123.20, 122.78, 121.77, 120.79, &119.46, 118.93, 40.17, 31.80, 29.97, 29.68, 29.31, 29.21, 23.91, 22.61, 13.85. MALDI-TOF-MS: calc. for ($[C_{288}H_{330}N_{12}Ru]^+$) *m/z* = 4058.5235, found *m/z* = 4059.020. Anal. Calcd. For $[C_{288}H_{330}N_{12}F_{12}P_2Ru]$, 1.5 CH_2Cl_2: C, 77.63; H, 7.50; N, 3.76. Found: C, 77.20; H, 7.80; N, 3.46.

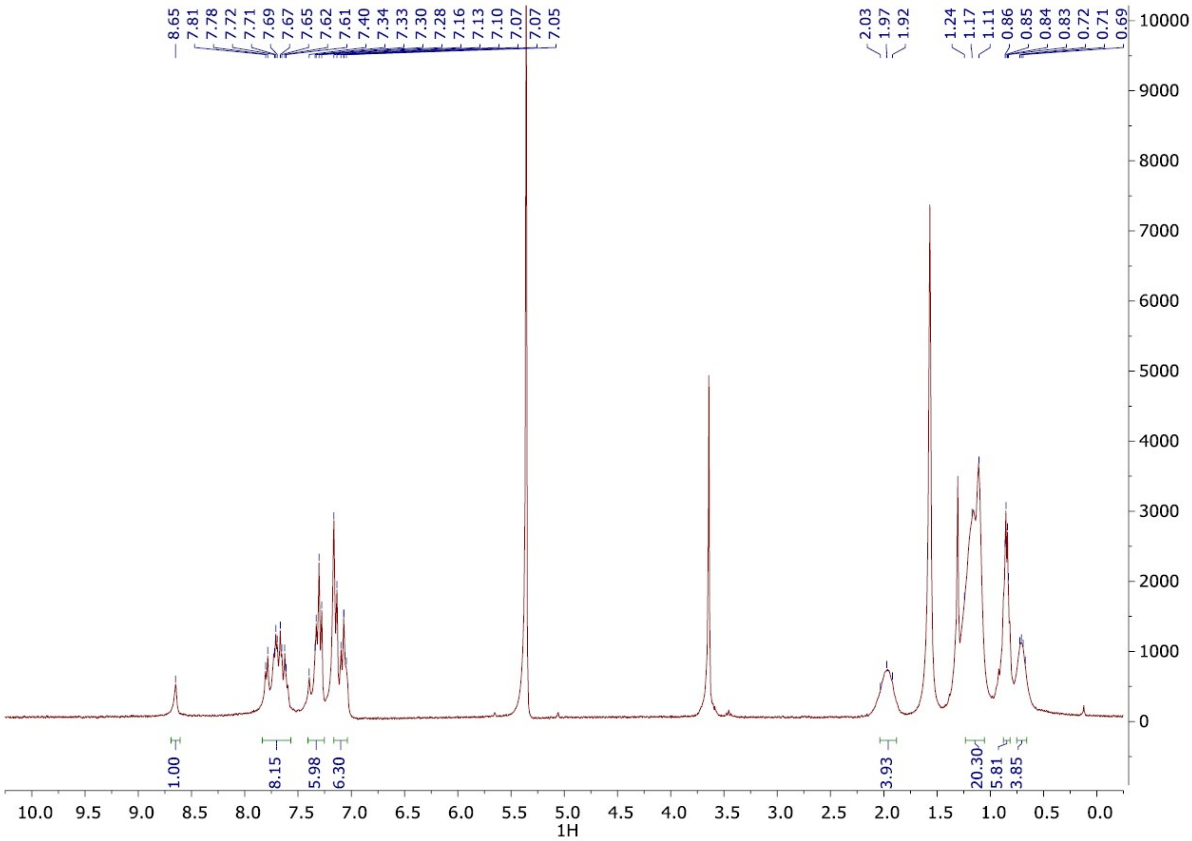


Figure S30. ^{1}H NMR spectrum of **RuF$_3$** in CD_2Cl_2, 400 MHz.

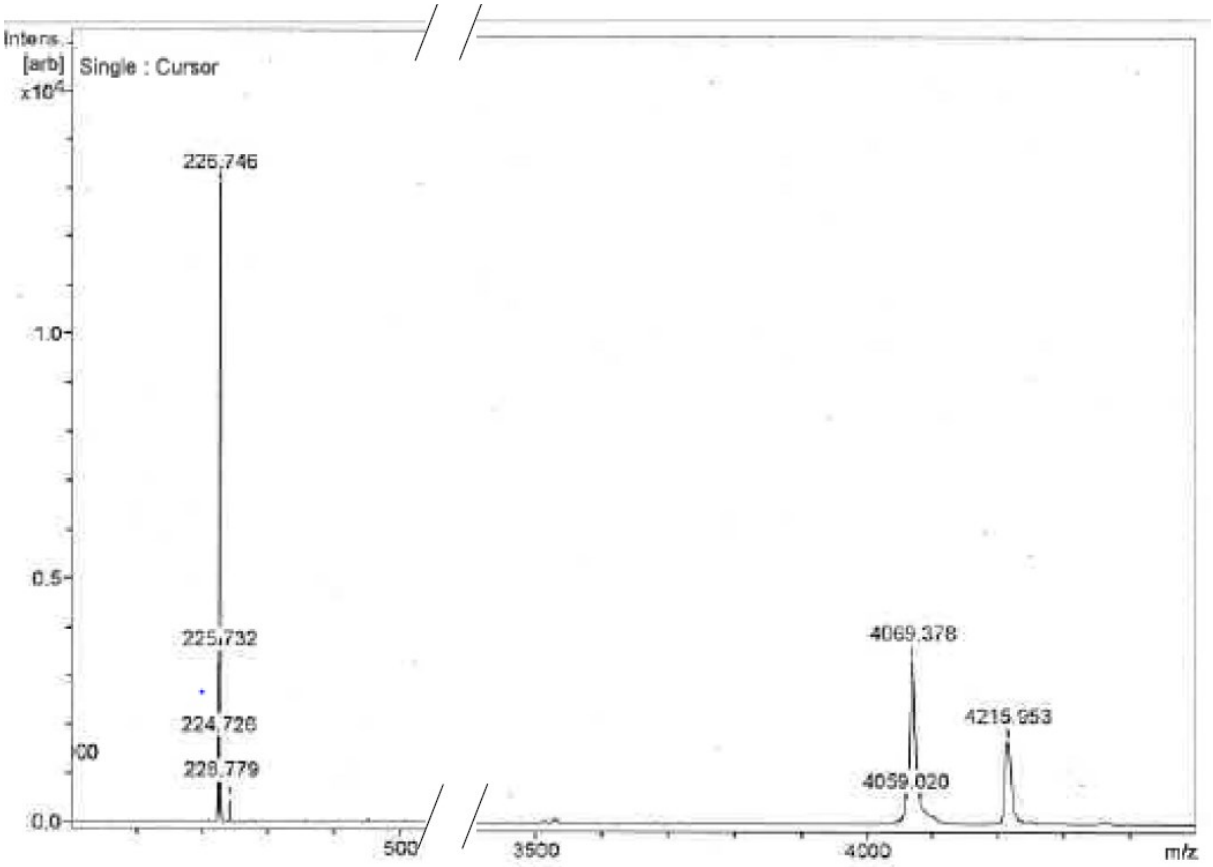


Figure S31. Maldi-TOF-MS spectrum of $\mathbf{RuF_3}$.

4. References

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