Supporting Information for

A Covalently Linked Nickel(II) Porphyrin – Ruthenium(II) Tris(bipyridyl) Dyad for Efficient Photocatalytic Water Oxidation

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General methods

The chemicals were used as received unless otherwise indicated. All the moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. The synthesis of bpy-COOH[1] and bpy(COOMe)$_2$[2] intermediates as well as NiP,[3] TPP-NH$_2$,[4] and Ru-bpy-COOH[5] reference compounds were performed following already published procedures. The identity and purity of the synthesized molecules were verified by ^{1}H and ^{13}C NMR as well as COSY, HMBC and HSQC 2D NMR spectroscopy experiments, conducted on Bruker DPX-300 MHz and Bruker AVANCE III-500 MHz spectrometers. The following chemical shifts are given in ppm. The multiplicities are given as: s (singlet), d (doublet), m (multiplet), and the coupling constants, J, are given in Hz. Mass spectra were recorded on a Bruker UltrafleXtreme matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix.

The UV-visible spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right-angle detection method was used. Differential pulse and cyclic voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer using a three-electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas.

Spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised of a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt Gauze working electrode. Spectra were recorded by applying a potential 80 mV past the potential of a given oxidation or reduction process and continued until no additional changes were observed.

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectroscopy experiments were performed using an ultrafast femtosecond laser source (Libra) by Coherent incorporating a diode-pumped, modelocked Ti:sapphire laser (Vitesse) and a diode-pumped intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with a femtosecond harmonics generator, both provided by Ultrafast Systems LLC, was used. The sources for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz; 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with a 290−2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of a white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is ±10%.

Photocatalytic and photoelectrocatalytic experiments

In the photocatalytic experiments a 450 W Xenon lamp equipped with a 400 nm cut-off filter was used. For the detection of O_2 during photocatalysis a NeoFox optical oxygen sensor[6] purchased from Ocean Optics was used. In detail the reaction solvent was DMF containing 4% of water while the final volume was 3 mL. In all examined cases the concentration of Methyl Viologen (sacrificial electron acceptor) was 50 mM. The turn-over-number was obtained from the following equation:

$$TON = \frac{mol\ O_2}{mol\ catalyst}$$

The photoelectrocatalytic experiments were performed using a VersaSTAT 4 Potentiostat and a three-electrode electrochemical cell with the NiP-Ru-COOH/TiO_2/FTO working electrode, a platinum mesh as the counter electrode, and the Ag/AgCl (3 M NaCl aqueous solution) reference electrode. The photocurrent was measured at 0 V vs. Ag/AgCl without stirring. 450 W Xenon lamp equipped with a

400 nm cut-off filter was used. In order to prepare the NiP-Ru-COOH/TiO_2/FTO working electrode we incubated the TiO_2/FTO glass in a 0.5mM solution of NiP-Ru-COOH ($CHCl_3$:EtOH 1:1) for 4 hours and let it dry in the air.

Synthetic procedures

Synthesis of **5-[4-(4-methyl-2,2′-bipyridine-4′-carboxyamidyl)phenyl]-10,15,20-triphenyl porphyrin: TPP-bpy**

A solution of 4-methyl-2,2′-bipyridine-4′-carboxylic acid, **bpy-COOH** (153 mg, 0.715 mmol) in 15 mL thionyl chloride ($SOCl_2$) was heated at reflux under an Ar atmosphere for 2 h. The excess thionyl chloride was removed *in vacuo* and the yellow residue was dried under vacuum. A solution of **TPP-NH$_2$** (150 g, 0.24 mmol) in dry THF (30 mL,) and dry triethylamine (330 μL) were added and the mixture was stirred at 50 °C under argon overnight. The solvents were removed *in vacuo* and the product was purified by column chromatography (silica gel, DCM:MeOH 97:3 v/v) to yield the title compound, **TPP-bpy** (157 mg, 0.19 mmol, 80%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.90 (m, 10H), 8.68 (s, 1H), 8.62 (d, J = 4.8 Hz, 1H), 8.37 (bs, 1H), 8.26 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 6.3 Hz, 6H), 8.13 (d, J = 8.3 Hz, 2H), 8.02 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 1H), 7.76 (m, 9H), 7.24 (bs, 1H), 2.51 (s, 3H), -2.75 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 164.3, 157.4, 155.2, 150.7, 149.2, 148.9, 143.2, 142.3, 139.1, 137.4, 135.4, 134.7, 131.2, 127.9, 126.8, 125.6, 122.5, 122.2, 120.4, 119.4, 118.8, 117.5, 21.4.

Synthesis of **Ru(bpy(COOMe$_2$))$_2$**

Dimethyl [2,2'-bipyridine]-4,4'-dicarboxylate **Bpy(COOMe)$_2$** (50 mg, 0.184 mmol) was dissolved in 2 mL of dry MeOH and $RuCl_3$ (19 mg, 0.092 mmol) was added. The solution was refluxed in a schlenk tube under argon atmosphere overnight. After the completion of the reaction the solution was cooled to 0 °C, the crude product was precipitated and filtered. The title compound was purified by column chromatography (silica gel, DCM:MeOH 97:5 v/v) (27 mg, 41%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 10.44 (d, J = 5.0 Hz, 2H), 8.84 (s, 2H), 8.68 (s, 2H), 8.17 (d, J = 5.0 Hz, 2H), 7.69 (d, J = 5.5 Hz, 2H), 7.49 (d, J = 5.5 Hz, 2H), 4.11

(s, 6H), 3.97 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 164.8, 164.2, 160.6, 158.1, 155.4, 152.8, 136.1, 134.9, 125.2, 124.6, 122.0, 121.8, 53.5, 53.4.

Synthesis of **H_2P-Ru**

In a two-neck round flask **TPP-bpy** (52.4 mg, 0.0636 mmol) was dissolved in 38 mL of CH_3COOH. The solution was degassed with N_2 for 15 minutes, then **Ru(bpy(COOMe$_2$))$_2$** (91 mg, 0.127 mmol) was added and the reaction mixture was refluxed at 118 °C overnight under N_2. Subsequently the solvent was evaporated and the solid residue was washed with Et_2O. The title compound was purified by column chromatography (silica gel, polarity changed from DCM/MeOH 97/3 v/v to MeCN/H_2O/$KNO_{3(\text{saturated in water})}$ 30/2/1 v/v/v). Precipitation followed by dissolving the compound in minimum amount of MeCN, adding MeOH saturated with PF_6^- and final adding water. After filtration **H_2P-Ru** was obtained (19 mg, 20%).

^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.24 (bs, 1H), 8.89 (m, 13H), 8.20 (m, 12H), 7.97 (m, 8H), 7.74 (m, 11H), 7.33 (bs, 1H), 3.91 (m, 12H), 2.57 (bs, 3H), -2.79 (bs, 2H). *UV-Vis* (DMF): λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 419.0 (308.6), 513.0 (23.1), 550.0 (14.1), 591.0 (10.7), 646.5 (6.2).

Synthesis of **NiP-Ru**

For the metalation reaction, **H_2P-Ru** (50 mg, 0.034 mmol) was dissolved in 10 mL $CHCl_3$ and heated to 55 °C. Excess of $Ni(CH_3COO)_2{\cdot}4H_2O$ salt (85 mg, 0.34 mmol) were dissolved in 10 mL EtOH, heated to 55 °C and then inserted to the porphyrin-ruthenium solution. Heating the two solutions before mixing was important so that **H_2P-Ru** will remain soluble after the addition of ethanol. The reaction mixture was stirred for 24 hours at 58 °C. The organic solvents were evaporated and then the solid residue was washed with water in order to remove the excess of nickel salt. The title compound was purified by column chromatography (silica gel, MeCN/H_2O/$KNO_{3(\text{saturated in water})}$ 30/2/1 v/v/v). Precipitation followed by dissolving the compound in minimum amount of MeCN, adding MeOH saturated with PF_6^- and final adding water. After filtration **NiP-Ru** was obtained (44 mg, 85%).

^1H NMR (DMSO-d_6, 500 MHz): δ (ppm) 11.18 (bs, 1H), 9.40 (bs, 4H), 9.04 (bs, 2H), 8.75 (bs, 8H), 8.05 (m, 18H), 7.80 (m, 12H), 7.46(m, 1H), 4.01 (bs, 12H), 2.61 (bs, 3H). *MS-(MALDI-TOF)*: m/z calc. for $C_{84}H_{61}N_{11}NiO_9Ru$ $[M]^+$: 1527.31, found

1527.35. *UV-Vis* (DMF): λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 308.0 (86.5), 415.0 (282.6), 527.0 (29.1).

Synthesis of **Ru-bpy**

Ru(bpy(COOMe$_2$))$_2$ (32 mg, 0.045 mmol) was dissolved in 10 mL EtOH and 2,2'-bipyridine (10.5 mg, 0.067 mmol) was added. The reaction mixture was refluxed at 90 ^{o}C overnight and then the solvents were removed under vacuum. Purification was conducted via column chromatography (silica gel, MeCN/H_2O/$KNO_{3(saturated\ in\ water)}$ 30/2/1 v/v/v) to yield the title compound (20 mg, 55%).

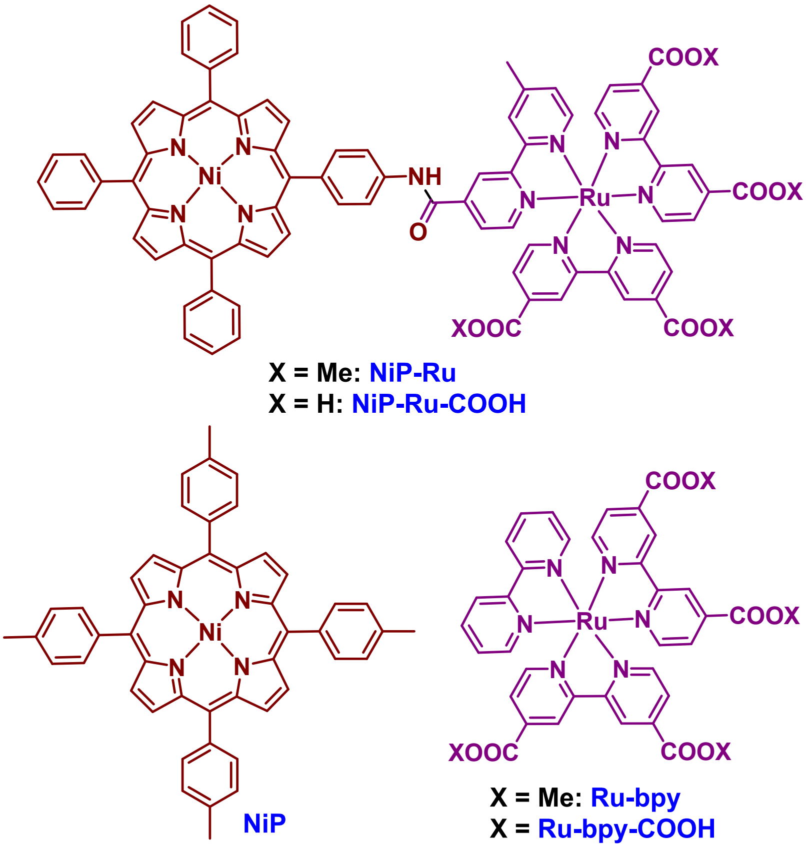
^{1}H NMR (CD_3CN, 300 MHz): δ (ppm) 9.05 (s, 4H), 8.52 (d, *J* = 8.1 Hz, 2H), 8.10 (t, *J* = 7.5 Hz, 2H), 7.87 (m, 8H), 7.65 (d, *J* = 5.3 Hz, 2H), 7.41 (t, *J* = 6.3 Hz, 2H), 4.46 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 164.3, 158.4, 158.3, 157.4, 154.0, 153.7, 152.7, 140.2, 139.6, 128.8, 127.6, 127.5, 125.5, 124.7, 63.7. *UV-Vis* (DMF): λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 304.0 (85.1), 469.0 (23.6).

Synthesis of **NiP-Ru-COOH**

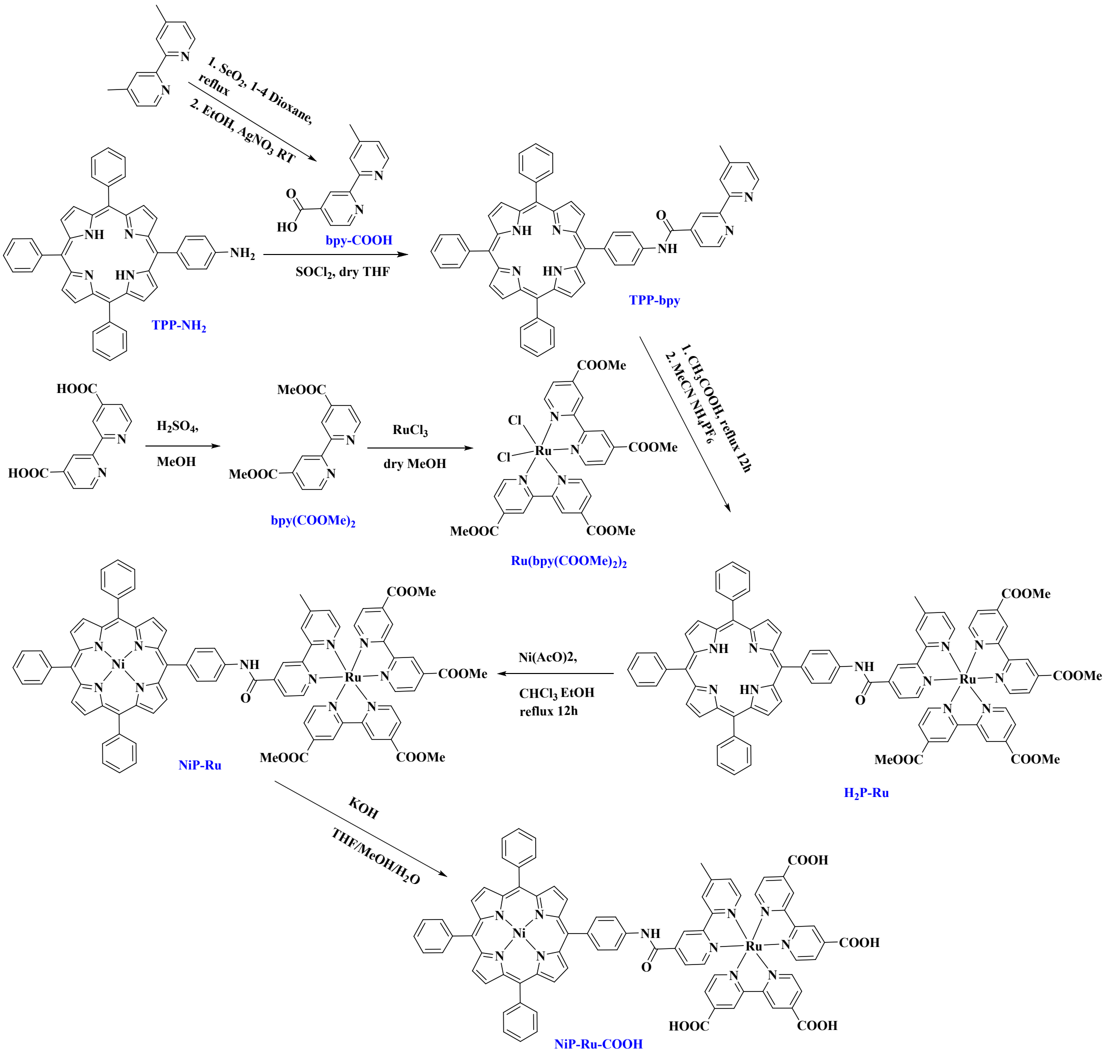
NiP-Ru (56 mg, 0.036 mmol) was dissolved in 24 mL of a THF/MeOH mixture (2 : 1), followed by the addition of an aqueous solution (9 mL) of KOH (525 mg, 9.4 mmol) and the reaction was left under stirring at room temperature overnight. The organic solvents were evaporated under reduced pressure, and then a solution of 1 M HCl (aq) was added dropwise for the acidification of the mixture till pH = 5, resulting to the precipitation of the desired product. Finally, after the dyad was filtered, washed with H_2O and dried under vacuum 45 mg of NiP-Ru-COOH were isolated (yield: 83%). ^{1}H NMR and ^{13}C NMR spectra could not be recorded due to solubility reasons. *MS-(MALDI-TOF)*: m/z calcd for $C_{80}H_{53}N_{11}NiO_9Ru$ $[M]^+$: 1471.24, found 1471.28. *UV-Vis* (DMF): λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 309.0 (53.5), 416.0 (190.9), 526.5 (19.5).

Proposed mechanism of water oxidation with Ni(II) porphyrin

In the system presented in this work, the ruthenium complex acts as PS absorbing a photon and undergoes an intramolecular reductive electron transfer from the NiP and an intermolecular electron transfer towards the electron acceptor MV^{2+}. After the oxidation of the Ni(II) porphyrin a water molecule binds to the Ni(II) metal center generating $\text{Por}^{\cdot+}$–Ni(II)–OH_2. The coordinated water molecule gets deprotonated through proton and electron transfer reactions with simultaneous oxidation of the Ni(II) center to give the hydroxide bound species, $\text{Por}^{\cdot+}$–Ni(III)–OH. Afterwards an intramolecular electron transfer from the hydroxide to the porphyrin ring coupled with a proton abstraction produces Por–Ni(III)–$\text{O}^{\cdot}$. The O–O bond is formed utilizing a second H_2O molecule and via a proton release, the peroxide bound species, Por-Ni(II)-OOH, is generated. The latter undergoes a proton-coupled electron transfer reaction to produce Por-Ni(II)-$\text{OO}^{\cdot}$. The final oxidation step involves the release of O_2 and the regeneration of the Ni(II) porphyrin catalytic moiety.[7, 8]



Scheme S1. Structures of **NiP-Ru** dyad, nickel tetra-toulylporphyrin, **NiP**, and ruthenium complex, **Ru-bpy** controls.



Scheme S2. Synthetic procedure followed for the preparation of **NiP-Ru** dyad.

^{1}H and ^{13}C NMR spectra

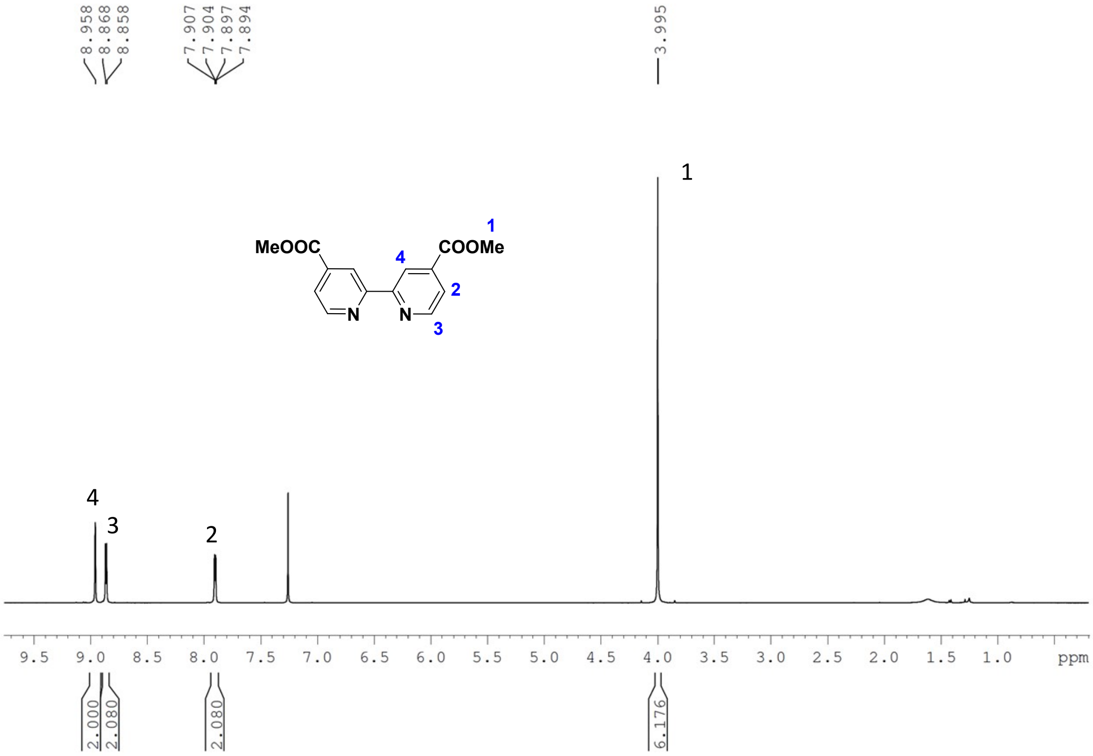


Figure S1. ^{1}H NMR spectrum of compound **bpy(COOMe)$_2$** in CDCl$_3$.

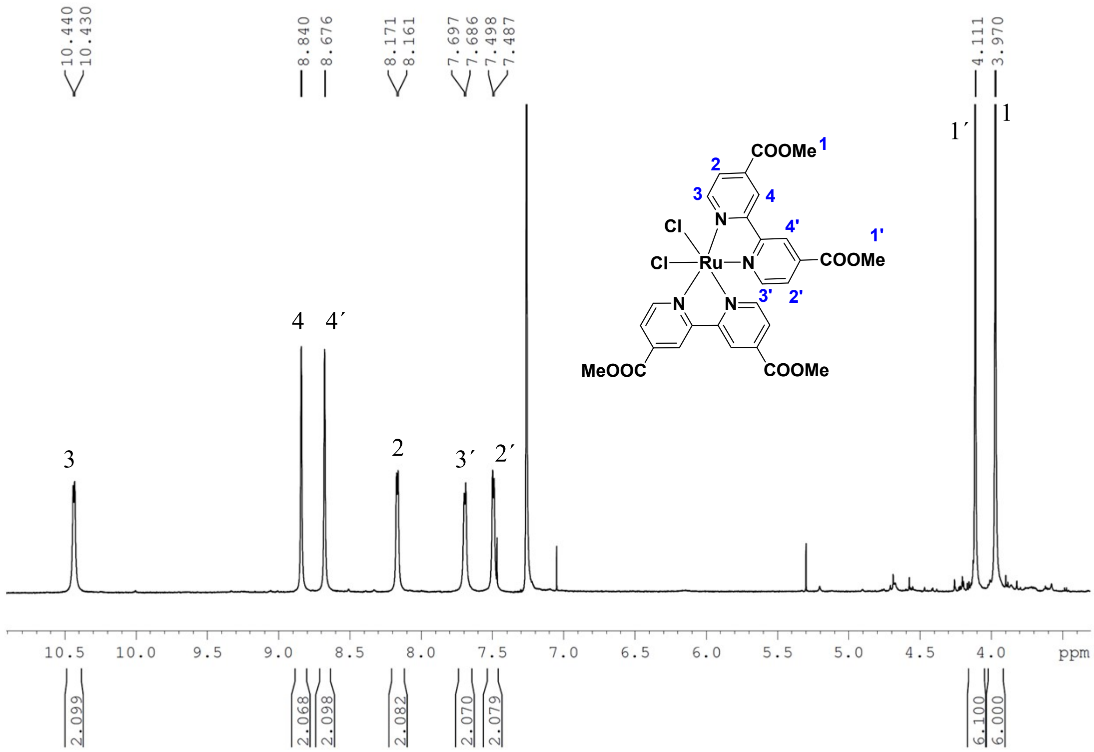


Figure S2. ^{1}H NMR spectrum of compound **Ru(bpy(COOMe)$_2$)$_2$** in CDCl$_3$.

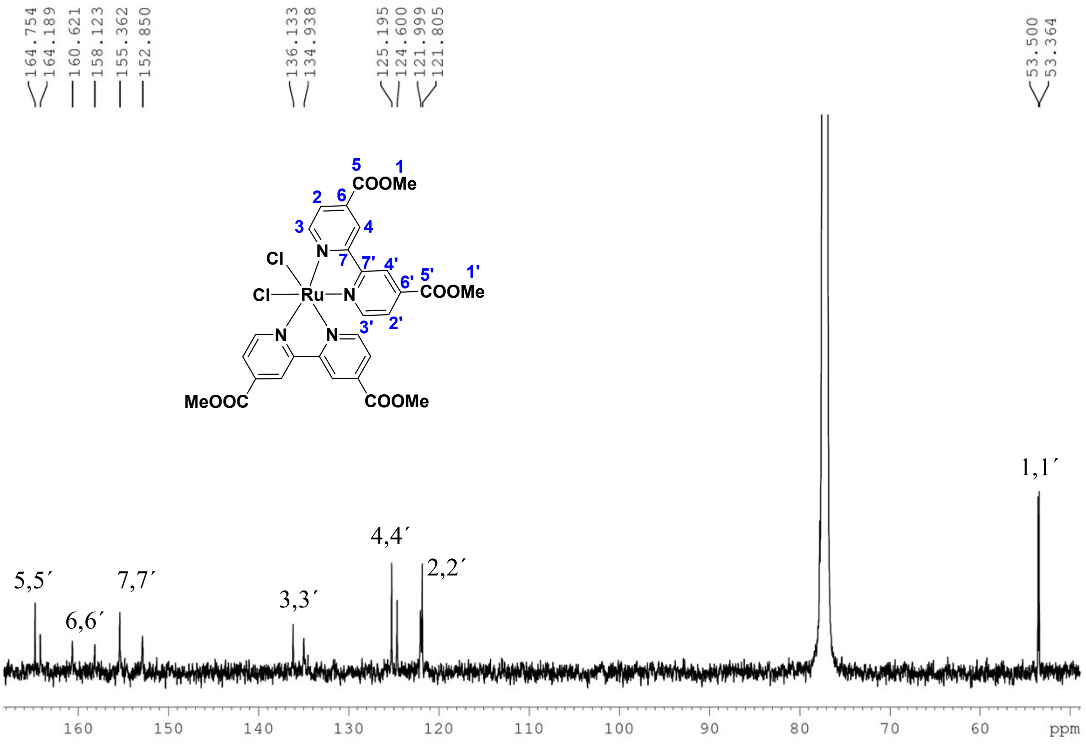


Figure S3. ^{13}C NMR spectrum of compound **Ru(bpy(COOMe)$_2$)$_2$** in CDCl$_3$.

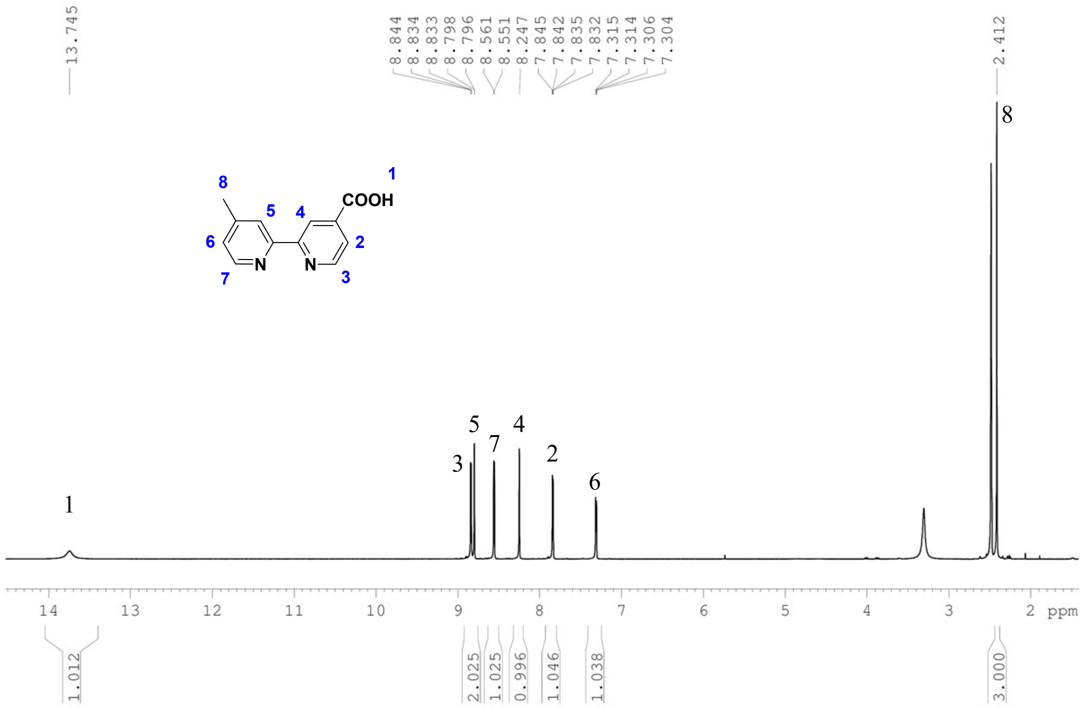


Figure S4. ^{1}H NMR spectrum of compound 4'-methyl-[2,2'-bipyridine]-4-carboxylic acid **bpy-COOH** in DMSO- d$_6$.

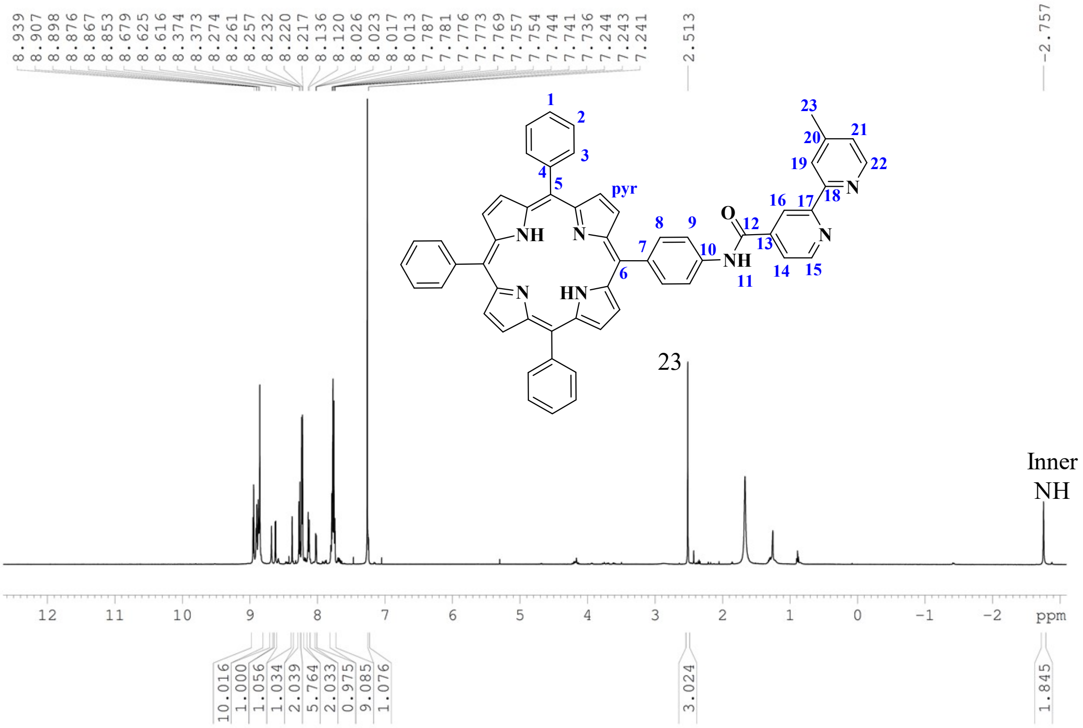


Figure S5. ^{1}H NMR spectrum of **TPP-bpy** in $CDCl_3$.

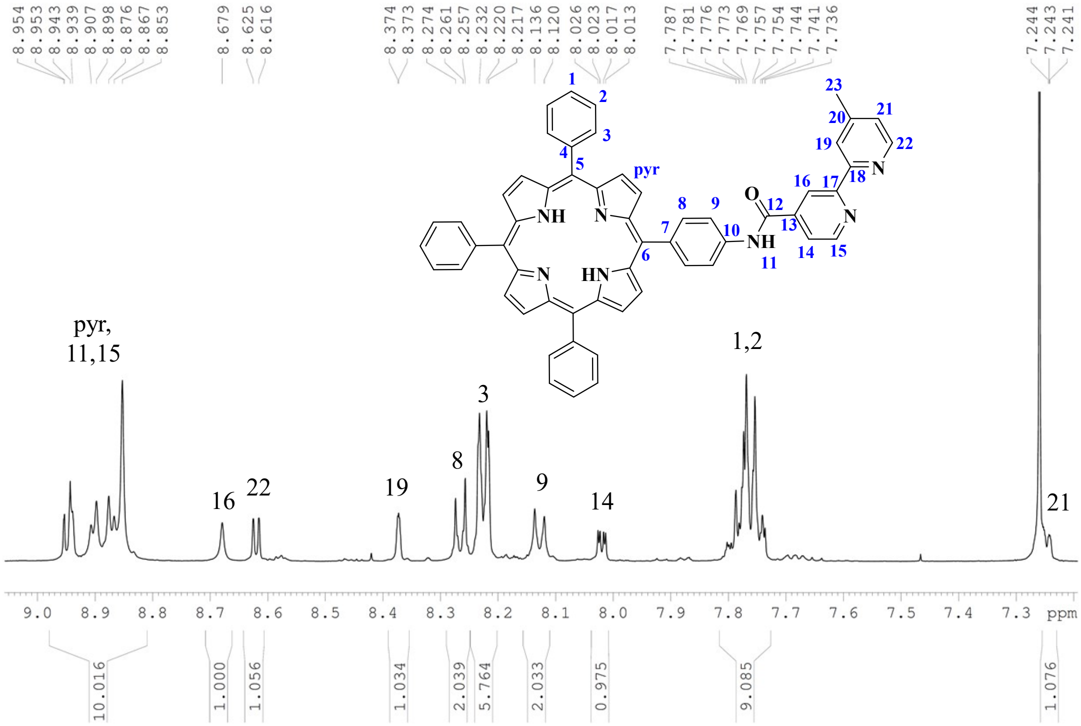


Figure S6. Aromatic region of ^{1}H NMR spectrum of **TPP-bpy** in $CDCl_3$.

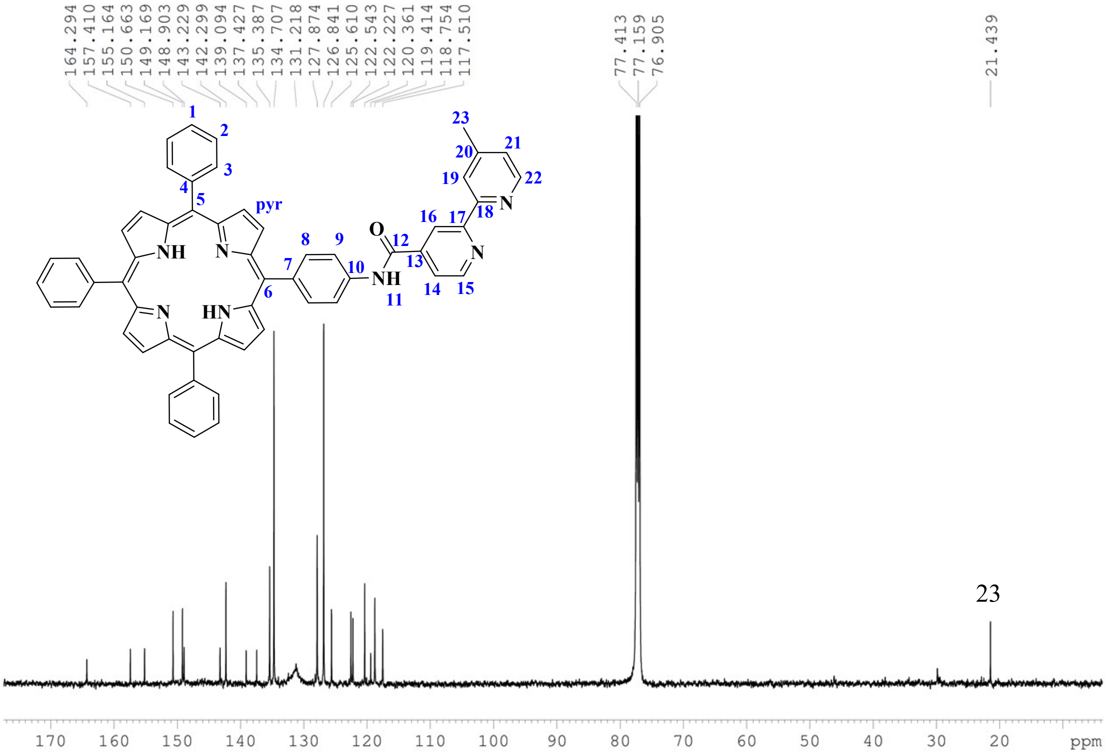


Figure S7. ^{13}C NMR spectrum of **TPP-bpy** in $CDCl_3$.

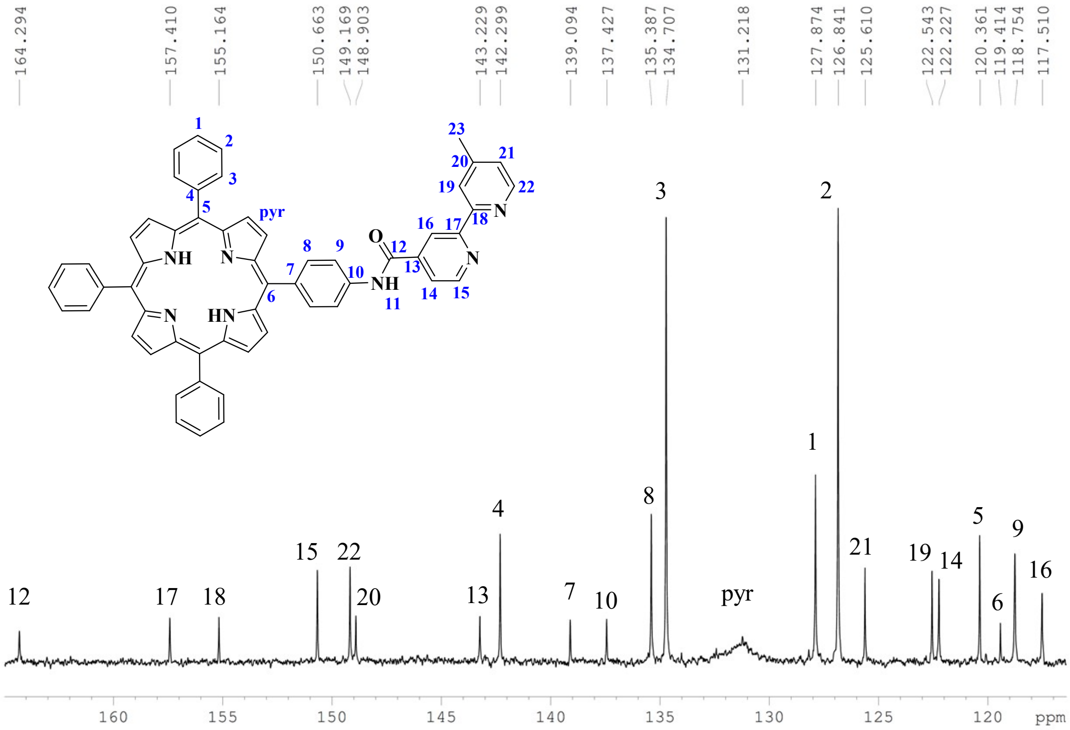


Figure S8. Aromatic region of ^{13}C NMR spectrum of **TPP-bpy** in $CDCl_3$.

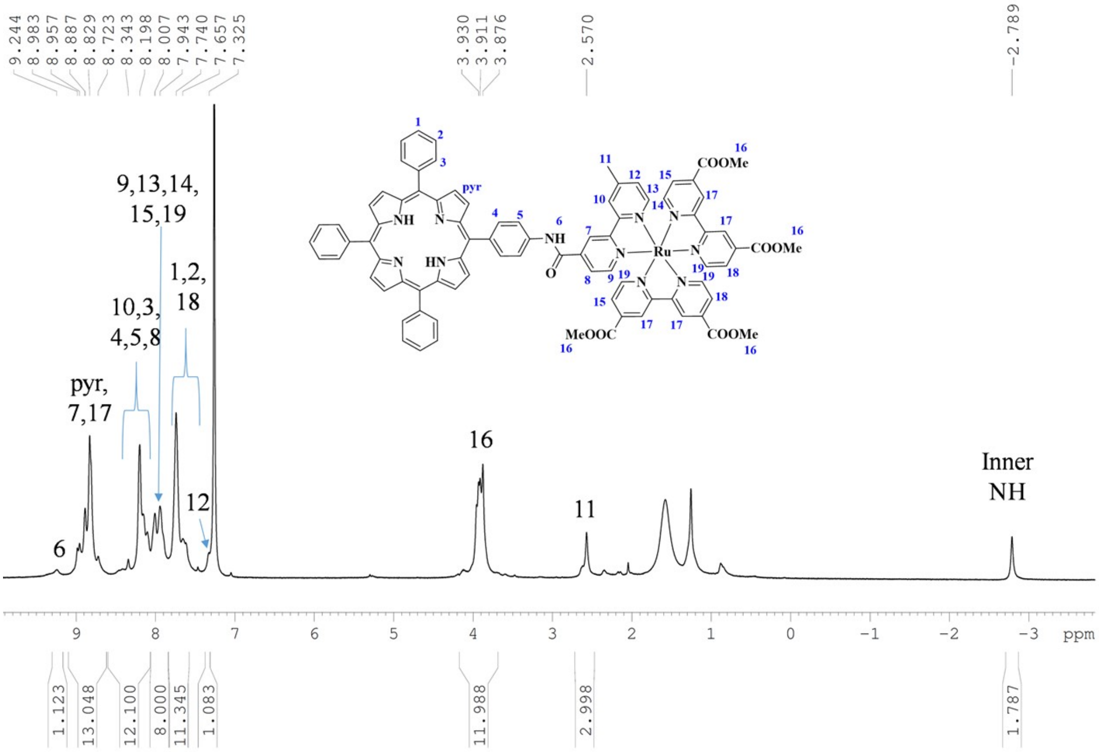


Figure S9. ^{1}H NMR spectrum of **H_2P-Ru** in $CDCl_3$.

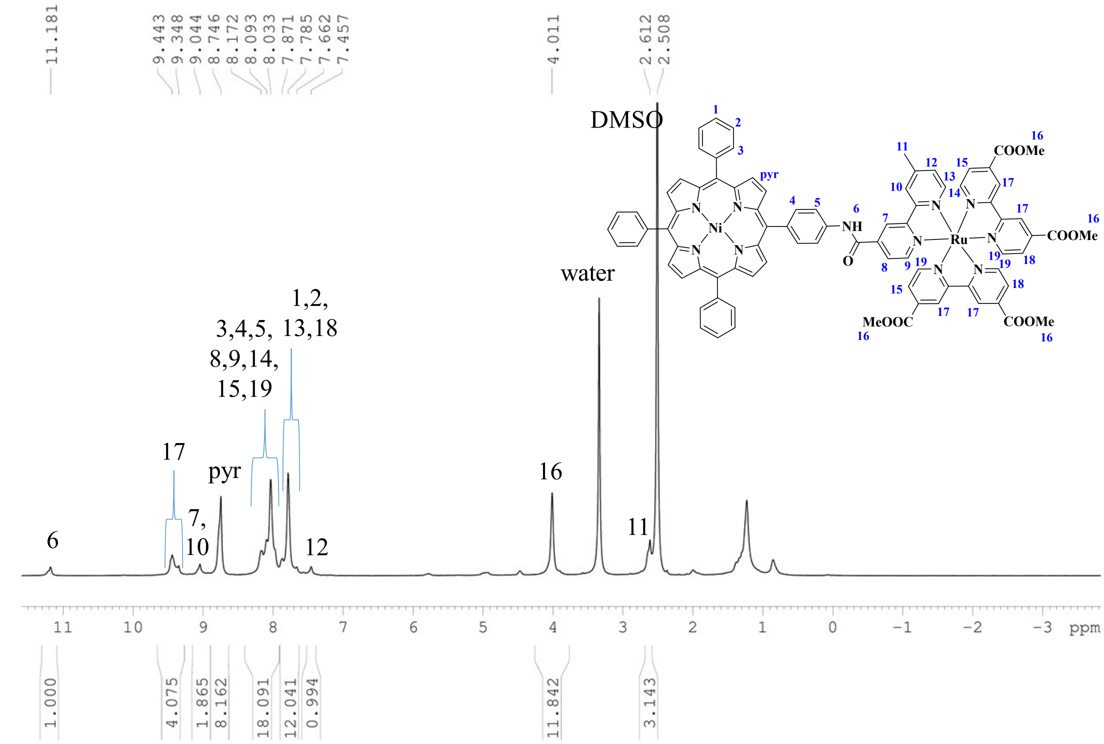


Figure S10. ^{1}H NMR spectrum of **NiP-Ru** in DMSO-d6.

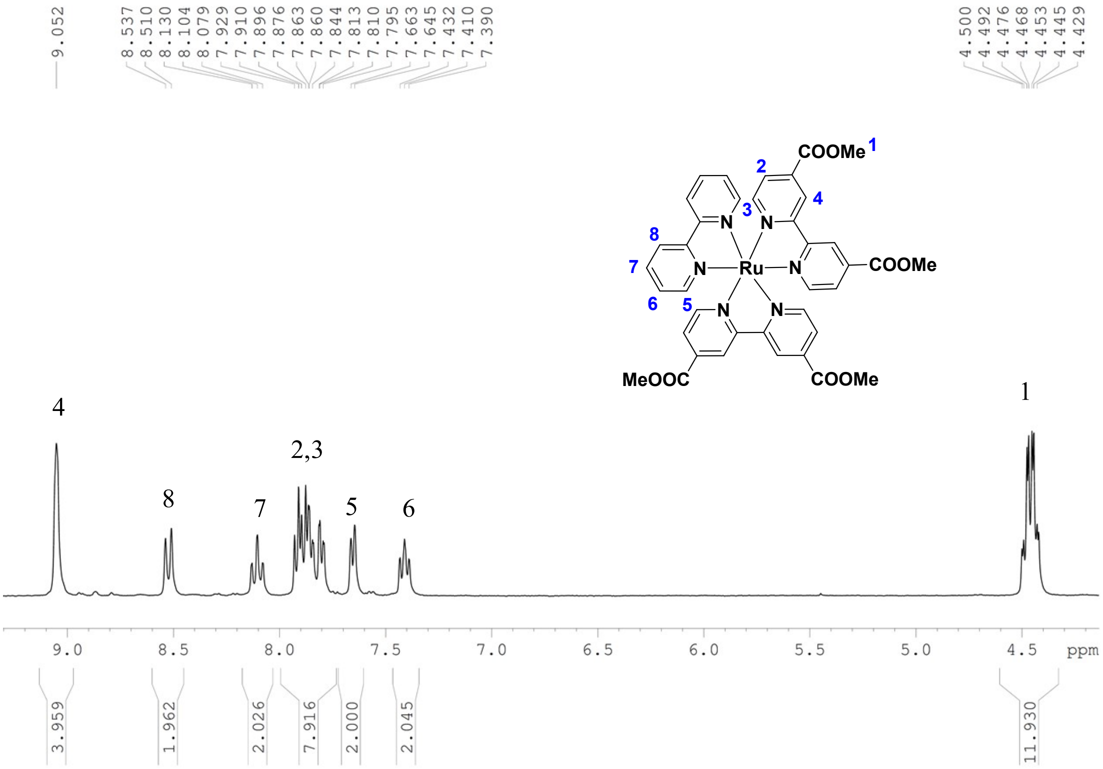


Figure S11. ^{1}H NMR spectrum of **Ru-bpy** in CD_3CN.

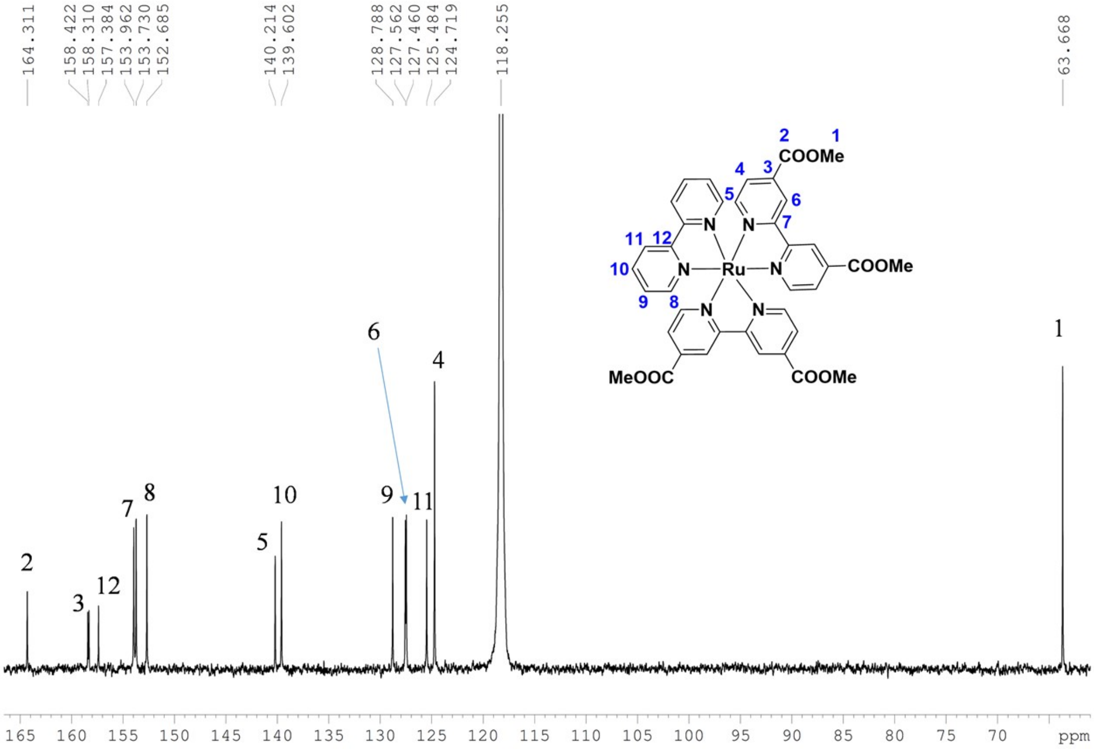


Figure S12. ^{13}C NMR spectrum of **Ru-bpy** in CD_3CN.

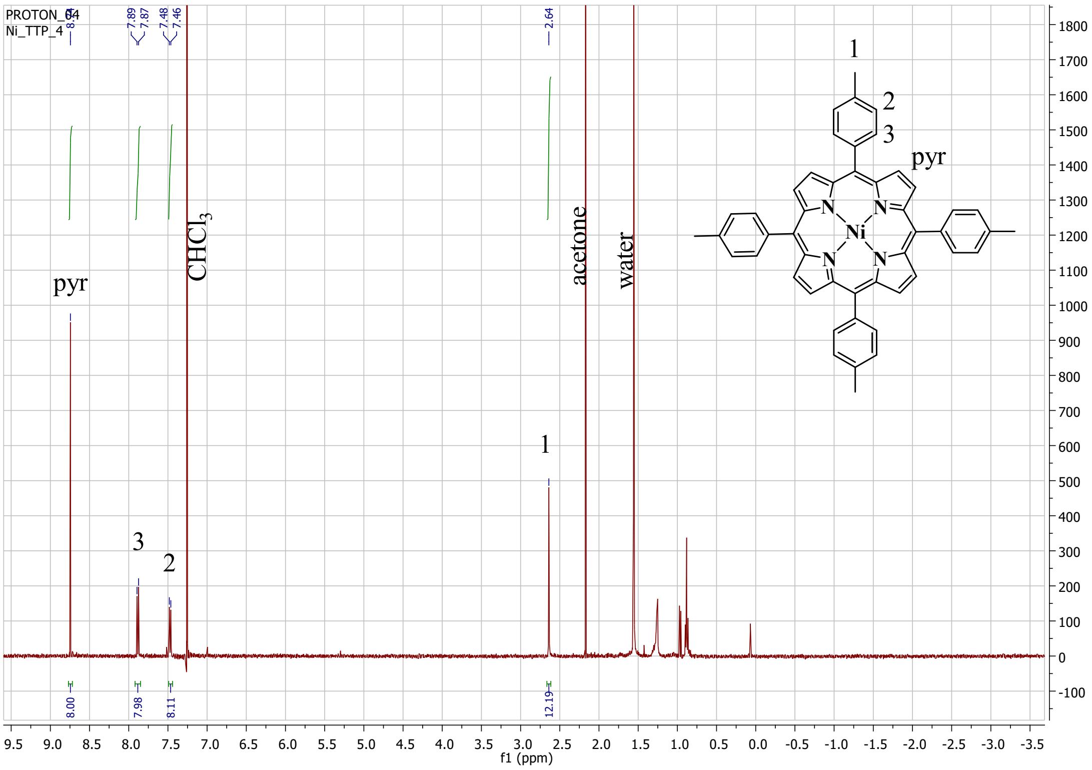


Figure S13. ^{1}H NMR spectrum of **NiP** in $CDCl_3$.

Cyclic and Differential Pulse Voltammograms

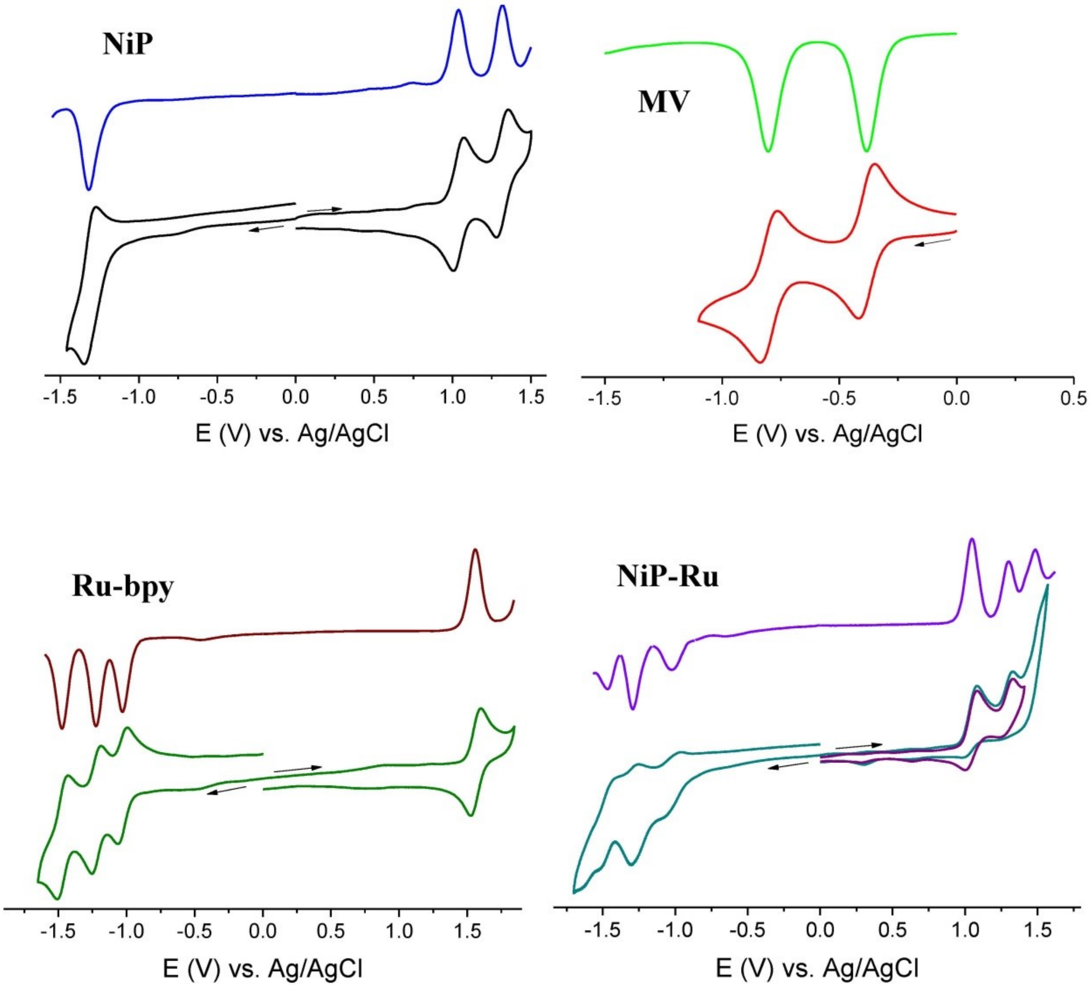


Figure S14. CVs and DPVs of the investigated compounds in benzonitrile, containing 0.1 M (TBA)ClO_4.

Absorbance spectra

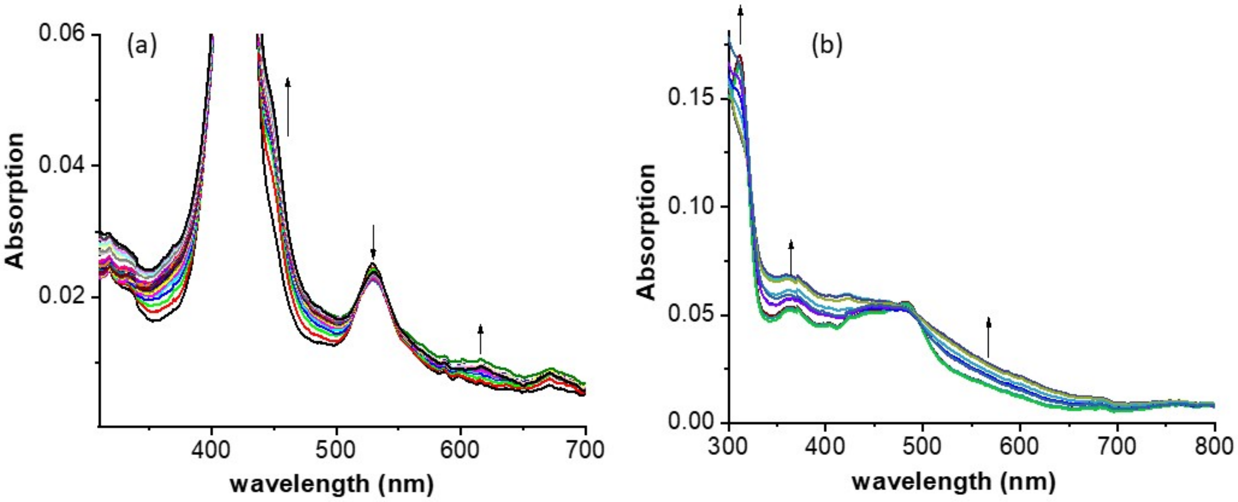


Figure S15. Spectral changes observed during (a) first oxidation of **NiP** and (b) first reduction of **Ru-bpy** in benzonitrile containing 0.2 M (TBA)ClO_4.

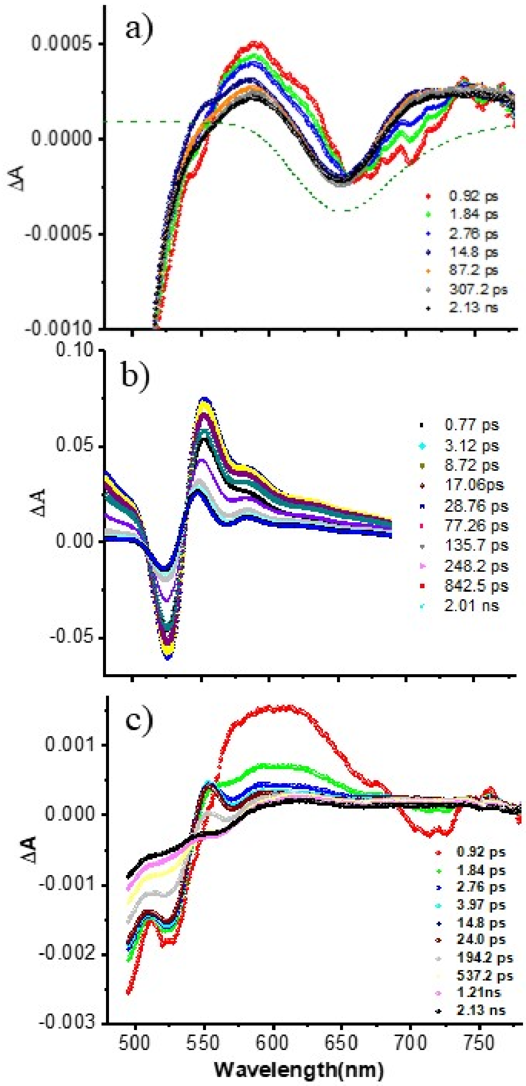


Fig. S16. Femtosecond transient absorption spectra at the indicated delay times of (a) **Ru-bpy** (λ_{ex} = 464 nm), (b) **NiP** (λ_{ex} = 424 nm) and (c) **NiP-Ru** dyad (λ_{ex} = 464 nm) in benzonitrile.

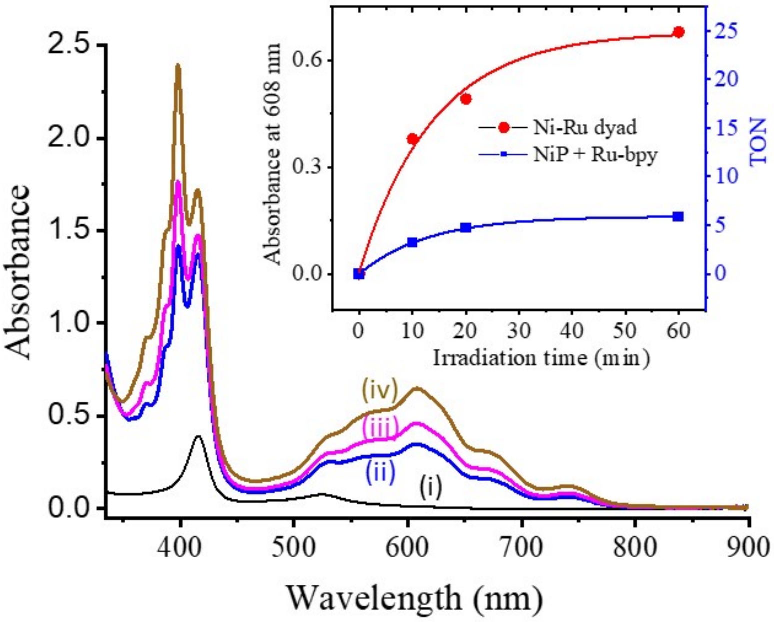


Fig. S17. UV-Vis spectral changes observed during electron pooling experiment. Conditions: 50 mM of Methyl Viologen in DMF and 4% H_2O. **NiP-Ru** dyad containing methyl viologen in DMF as a function of irradiation time (i-0 min, ii-10 min, iii-20 min and iv-60 min) is shown. A 450 W Xe lamp with a 400 nm filter was used. The new peaks in the 400 nm and 550-770 nm range are due to reduced methyl viologen. Figure inset shows changes of the absorption maxima at 608 nm, attributed to MV^+, versus the irradiation time for covalently linked **NiP-Ru** dyad and 1:1 mixture of **NiP** and **Ru-bpy** revealing much improved photocatalytic effect by the dyad.

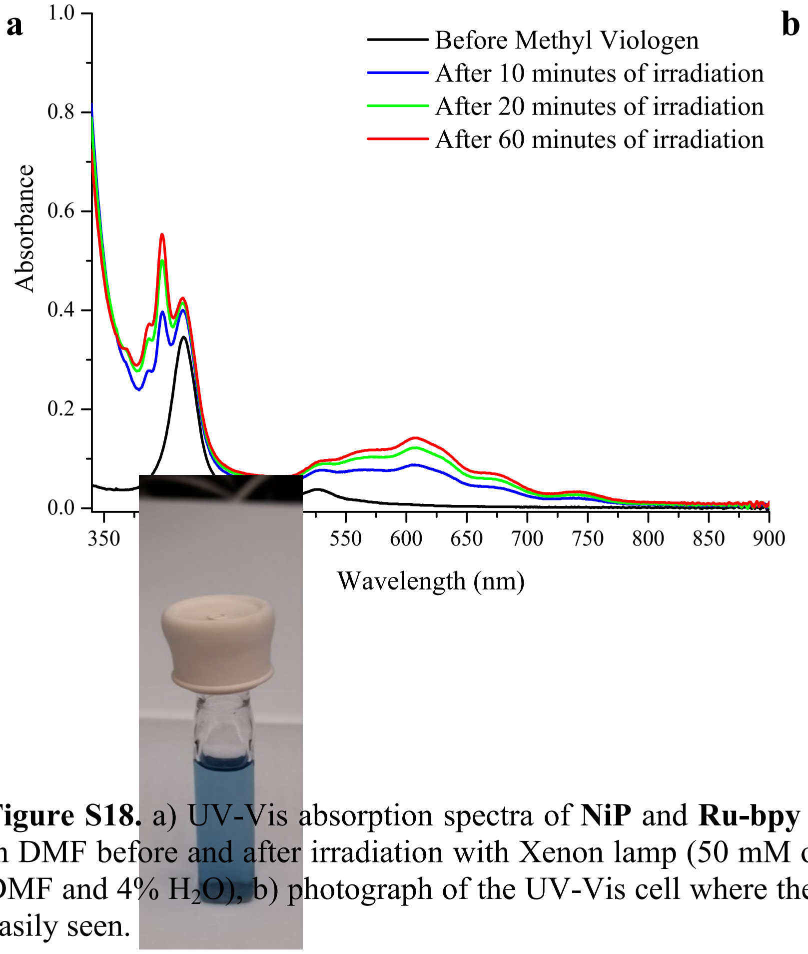


Figure S18. a) UV-Vis absorption spectra of **NiP** and **Ru-bpy** photocatalytic system in DMF before and after irradiation with Xenon lamp (50 mM of Methyl Viologen in DMF and 4% H_2O), b) photograph of the UV-Vis cell where the blue color of MV^+ is easily seen.

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