Supporting Information

Photoelectric Conversion at a $[Ru(bpy)_3]^{2+}$- Based Metallic Triad Anchored on ITO Surface.

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Materials and Methods.

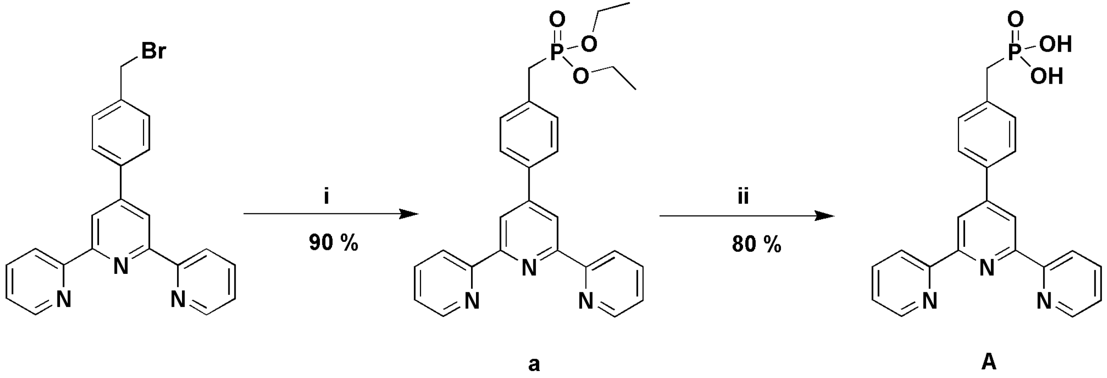
General method.

Acetonitrile (CH_3CN, Rathburn, HPLC grade), ethylene glycol ($C_2H_6O_2$, Prolab), chloroform ($CHCl_3$, Carlo Erba, HPLC grade), diethyl ether ($C_4H_{10}O$, Aldrich, 99.8%), hexane (C_6H_{14}, Acros, 95%) were purchased and used as received. Tetra-n-butyl-ammonium perchlorate ($[Bu_4N]ClO_4$, Fluka), triethanol amine ($C_6H_{15}NO_3$, Aldrich) were used as received and stored under an argon atmosphere. All the chemical reagents used in the synthetic route were obtained from commercial sources as guaranteed-grade reagents and used without further purification, except for the 2-bromopyridine which was distilled before use. The 4'-(4-hydroxyphenyl)-2,2':6',2"-terpyridine,[1] 4'-(4-bromomethylphenyl)-2,2':6',2"-terpyridine,[1] 4'-(4-tolyl)-2,2':6',2"-terpyridine,[2] 4'-(4-bromomethylphenyl)-2,2':6',2"-terpyrdine,[2] and 5,5'-dibromopyridine[3] were prepared according to previously described procedures.

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded at room temperature on Bruker Avance 400 MHz spectrometers. ^1H chemical shifts were referenced to residual solvent peaks. Coupling constants value (J) are given in hertz and chemical shift (δ) in ppm. The abbreviations used are: s = singlet, d = doublet, dd = doublet of doublet, t = triplet and m = multiplet. The electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a triple quadrupole mass spectrometer Quattro II (microlass, Altrincham, UK). The ESI source was heated to 80 °C. The sampling cone voltage was set within the range 14-18 V. Complex in solution (1-2 mg.mL^{-1} in CH_3CN) were injected using a syringe pump at a flow rate in the range of 5 μL.min^{-1}. The electrospray probe (capillary voltage was optimized in the range 2.9 – 3.30 kV for positive ion electrospray.

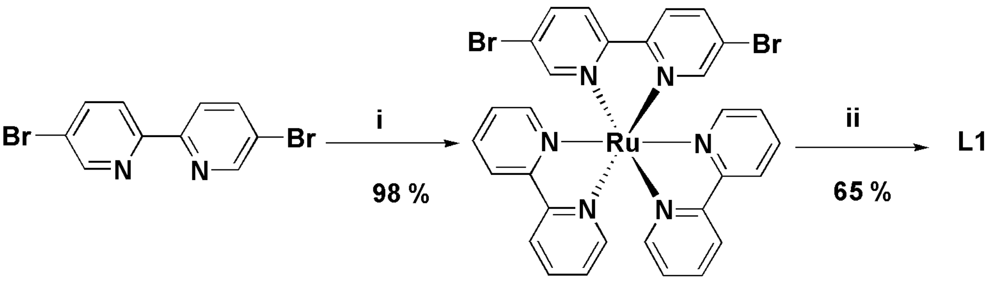
Synthesis.

1-Anchoring Ligand **A**:



Synthesis of the diethyl 4-([2,2':6',2"-terpyridine]-4'-yl)benzylphosphonate **(a)**:
4'-(4-bromomethyl phenyl)-2,2':6',2"-terpyridine (163 mg, 0.405 mmol) was dissolved in 3 mL of triethyl phosphite and heated at 160 °C overnight. The reaction mixture was cooled down, and triethyl phosphite was removed under vacuum. The beige powder was then triturated in n-hexane to afford the desired product pure (90%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 8.78(s, 2H), 8.76 (d, $^{4}J = 3.85$ Hz, 2H), 8.71 (d, $^{3}J = 7.83$ Hz, 2H), 7.96-7.89 (m, 4H), 7.45 (dd, $^{3}J = 8.42$ Hz, $^{4}J = 2.54$ Hz, 2H), 7.40 (t, $^{3}J = 6.35$ Hz, 2H), 4.06 (m, 4H), 3. (d, $J =$ 22.10 Hz, 2H), 1.29 (t, $^{3}J = 7.15$ Hz , 6H). ^{31}P NMR: (400 MHz, $CDCl_3$) δ (ppm): 25.76.
Synthesis of the (4-([2,2':6',2"-terpyridine]-4'-yl)benzyl)phosphonic acid **(A)**:
4-ethylphosphonate-2,2':6',2"-terpyridine (170 mg, 0.371 mmol) was dissolved in 3 mL of dry dichloromethane. TMSBr (227 mg, 1.48 mmol) was added dropwise under Ar and the reaction mixture was stirred overnight. After evaporation, the brown solid was stirred in 15 mL of methanol for 2 hr. The precipitate was filtered, washed with acetone to afford the desired product as a white powder (80%). ^{1}H NMR: (400 MHz, D_2O) δ (ppm) : 8.39 (d, $^{4}J =$ 4.25 Hz, 2H), 8.14 (m , 2H), 8.04 (m, 2H), 7.68 (m, 4H), 7.68 (t, $^{3}J = 5.93$ Hz, 2H), 7.60 (s, 2H), 7.04 (d, $^{3}J = 7.88$ Hz, 2H), 6.90 (d, $^{3}J = 7.31$ Hz, 2H), 2.90 (d, $^{3}J = 21.4$ Hz, 2H). ^{31}P NMR: (400 MHz, D_2O) δ (ppm): 19.45. ESI-MS: m/z = 404.1 ([M+H]$^{+}$).

2-Ditopic metallo-ligand **L1**:



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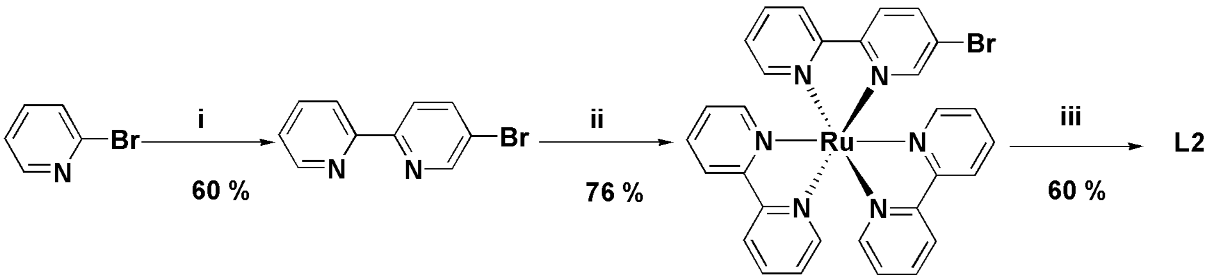
Synthesis of [Ru(bpy)$_2$(5,5'-(Br)$_2$-bpy)].2(PF$_6$) **(1)**:
5,5'-bromopyridine (150 mg, 0.481 mmol), and [Ru(bpy)$_2$Cl$_2$].2H$_2$O (192 mg, 0.370 mmol) were dissolved in the minimum amount of ethylene glycol and refluxed for 90 min at 120 °C. The reaction mixture was cooled down and precipitated with a saturated solution of KPF_6. The solution was filtered over a cotton, and the precipitate was dissolved in acetone, evaporated to dryness and submitted to a chromatography on a silica using $CH_3CN/H_2O/KNO_3$sat (100:20:2) affording the desired compound as a red powder (98%). ^{1}H NMR: (400 MHz, acetone-d$_6$) δ□(ppm): 8.82 (d, $^{3}J = 8$ Hz, 4H), 8.76 (d, $^{3}J = 8.8$ Hz, 2H), 8.29 (d.d, $^{3}J = 8.6$ Hz, 2H), 8.26-8.17 (m, 6H), 8.10 (d, $^{3}J = 8.06$, 2H), 8.02 (d, $^{3}J = 6$ Hz, 2H), 7.61-7.56 (m, 4H).
Synthesis of [Ru(bpy)$_2$(5,5'-(O-ttpy)$_2$-bpy)].2(PF$_6$) (**L1**):
[Ru(bpy)$_2$(5,5'-(Br)$_2$-bpy)].2(PF$_6$) (150 mg, 0.147 mmol), 4'-(4-hydroxyphenyl)-2,2':6',2"-terpyridine (106 mg, 0.325 mmol), and K_2CO_3 (150 mg, 1.09 mmol) were dissolved in 75 mL of acetonitrile and refluxed for 48 h under argon. The reaction mixture was concentrated to 10 mL and precipitated with a saturated solution of KPF_6. The solution was filtered over a cotton,

and the precipitate was dissolved in acetone, evaporated to dryness and submitted to a chromatography on a silica using $CH_3CN/H_2O/KNO_3$sat (100:5:0.5) affording the desired compound **(L1)** as an orange powder (65%). ^{1}H NMR: (400 MHz, CD_3CN) δ (ppm): 8.71 (d, $^4J = 4$ Hz, 2H), 8.66 (m, 10H), 8.45 (d, $^3J = 8$ Hz, 2H), 8.36 (d, $^3J = 9$ Hz, 2H),8.28 (d, $^3J = 8$ Hz, 2H), 8.09 (t.d, $^3J = 8$ Hz $^4J = 1.09$ Hz, 2H), 7.98 (t.d, $^3J = 7.5$ Hz $^4J = 1.57$ Hz , 2H), 7.84(d, $^3J = 5.3$ Hz, 2H), 7.82-7.77 (m, 6H), 7. 71(d.d, $^3J = 9$ Hz $^4J = 2.5$ Hz, 6H), 7.54 (d, $^3J = 5.38$ Hz, 2H), 7.52 (m, 2H), 7.45 (m, 4H), 7.19 (m, 2H), 7.08 (d, $^3J = 8.7$ Hz, 4H), 7.00 (d, $^4J = 2.7$ Hz, 2H). ^{13}C NMR: (400 MHz, CD_3CN) δ (ppm):157.38, 157.34, 157.30, 157.23, 156.88, 156.20, 155.28, 152.50, 152.23, 151.68, 149.98, 149.52, 139.75, 138.65, 138.39, 137.80, 137.95, 136.73, 129.91, 129.02 128.32, 127.87, 126.98, 125.33, 125.01, 124.88, 124.60, 121.69, 121.65, 116.63, 119.11. ESI-MS: m/z = 1361.3 ($[M-PF_6]^+$), 608.3 ($M-2PF_6]^{2+}$).

3-Mono-fonctionalised metallo-ligand **L2**:



1'

2'

Synthesis of 5-bromobipyridine **(1')**:

Freshly distilled 2-bromopyridine (0.61 mL, 6.3 mmol) was added to 30 mL of dry diethyl ether and maintained at -78°C under argon, followed by a dropwise addition of *n*BuLi (3.45 mL, 2M, 6.93 mmol) over a period of 15 min. The mixture turned immediately red, and was stirred for 2 hr at -78°C. After warming up to room temperature, $ClSnMe_3$ (1.51g, 7.6 mmol) in toluene (5 mL) was carefully added and the reaction was stirred for an additional hour at -78 °C, and overnight at room temperature. The solution was then concentrated under vacuum, redissolved in 5 mL of n-hexane, where non soluble products were filtered off and the filtrate was evaporated to dryness. The resulting yellow oil and 5-bromo-2-iodo pyridine (1.23 g, 4.35 mmol) were dissolved in 35 mL dry toluene. The solution was degassed for 1 hour, $[Pd(PPh_3)_4]$ (502 mg, 0.345 mmol) was added and the solution was refluxed overnight. Pd was filtered off and the solvent was evaporated to dryness. The resulting solid was submitted to chromatography on deactivated silica using ethyl acetate: pentane (6:4) as an eluent to afford 3-bromopyridine as a beige solid (60 %).

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) : 8.64 (d, $^4J = 2.11$ Hz, 1H), 8.58 (d, $^4J = 4.87$ Hz, 1H), 8.29 (d, $^3J = 8.06$ Hz, 1H), 8.24 (d, $^3J = 8.39$ Hz, 1H), 7.84 (dd, $^3J = 8.52$ Hz, $^4J = 2.48$ Hz, 1H), 7.72 (dt, $^3J = 7.81$ Hz, $^4J = 1.33$ Hz, 1H), 7.26-7.21 (m, 1H).

Synthesis of $[Ru(bpy)_2(5\text{-}Br\text{-}bpy)].2(PF_6)$ **(2')**:

5-bromopyridine (100 mg, 0.427 mmol), and $[Ru(bpy)_2Cl_2].2H_2O$ (185 mg, 0.356 mmol) were dissolved in the minimum amount of ethylene glycol and refluxed for 90 min at 120 °C.

The reaction mixture was cooled down and precipitated with a saturated solution of KPF_6. The solution was filtered over a cotton, and the precipitate was dissolved in acetone, evaporated to dryness and submitted to a chromatography on a silica using $CH_3CN/H_2O/KNO_3$sat (100:10:1) affording the desired compound **(1)** as a red powder (76%). ^{1}H NMR: (400 MHz, acetone-d_6) δ (ppm): 8.84 (m, 5H), 8.77 (d, ^3J = 8.6 Hz, 1H), 8.29 (d, ^3J = 8.06 Hz, 1H), 8.41 (dd, ^3J = 8.55 Hz, ^4J = 2.10 Hz, 1H), 8.26-8.20 (m, 6H), 8.11 (d, ^4J = 2.00 Hz, 1H), 8.09-8.00 (m, 4H), 7.61-7.56 (m, 5H).

Synthesis of $[Ru(bpy)_2(5\text{-}O\text{-}ttpy\text{-}bpy)].2(PF_6)$ (**L2**):

$[Ru(bpy)_2(5\text{-}Br\text{-}bpy)].2(PF_6)$ (183 mg, 0.195 mmol), 4’-(4-hydroxyphenyl)-2,2’:6’,2”-terpyridine (84 mg, 0.256 mmol), and K_2CO_3 (71 mg, 0.512 mmol) were dissolved in 100 mL of acetonitrile and refluxed overnight under argon. The reaction mixture was concentrated to 10 mL and precipitated with a saturated solution of KPF_6. The solution was filtered over a cotton and the precipitate was dissolved in acetone, evaporated to dryness and submitted to a chromatography on a silica using $CH_3CN/H_2O/KNO_3$sat (100:5:0.5) affording the desired compound **(L2)** as an orange powder (60%). ^{1}H NMR: (400 MHz, CD_3CN) δ (ppm): 8.77-7.73 (m, 6H), 8.48 (m, 4H), 8.41 (d, ^3J = 8.17 Hz, 1H), 8.36 (d, ^4J = 8.02 Hz, 1H), 8.12-7.98 (m, 6H), 7.89-7.83 (m, 4H), 7.79-7.67 (m, 4H), 7.57(d, ^3J = 5.58 Hz, 1H), 7.49-7.34 (m, 6H), 7.22 (t, ^3J = 6.45 Hz, 1H), 7.13 (d, ^3J = 8.53 Hz, 2H), 7.07 (d, ^4J = 2.37 Hz, 1H). ^{13}C NMR: (400 MHz, CD_3CN) δ (ppm): 157.85, 157.52, 157.47, 157.37, 157.22, 156.96, 156.25, 155.16, 152.45, 152.33, 152.19, 152.05, 151.93, 150.02, 149.55, 139.95, 138.58, 139.42, 138.38, 137.94, 136.88, 129.96, 128.29, 128.18, 128.11, 127.93, 127.50, 126.79, 125.98, 125.01, 124.92, 124.85, 124.63, 124.23, 121.72, 121.68, 119.12. ESI-MS: m/z = 1038.3 ($[M\text{-}PF_6]^{+}$), 446.8 ($[M\text{-}2PF_6]^{2+}$).

Stepwise anchoring of the assemblies.

Planar ITO substrates were purchased from Solems and cleaned sequentially by sonication in acetone and ethanol. The electrodes were dipped in 10^{-3} M ethanolic solution of ligand **A** (24 hours). For **S1a** and **S1b** the tpy-terminated surface was then immersed in a 10^{-3} M ethanolic solution of $[Fe(BF_4)_2].6H_2O$ or $[Co(BF_4)_2].6H_2O$ at room temperature for 3 hours. After thorough rinsing with ethanol, the electrode is dipped in a 10^{-3}M solution of 4’-(4-tolyl)-2,2’:6’,2”-terpyridine (ttpy) at room temperature for 3 hours. The electrode is then rinsed again and dried under Argon. For **S2**, after addition of $[Co(BF_4)_2].6H_2O$, the electrode is dipped, over night at room temperature, in a 10^{-3}M ethanol/acetone (8:2) solution containing the photosensitizer moiety **L2** that self-assembles on the pending Cobalt center. Finally, **S3** is obtained in a similar strategy as for **S2**, but instead of **L2** the ditopic-metallo ligand **L1** is introduced, followed by dipping in $[Fe(BF_4)_2].6H_2O$ (10^{-3} M in ethanol for 3 hours) and capping with ttpy (10^{-3} M in ethanol for 3 hours). Final rinsing in acetonitrile and ethanol, followed by drying under argon afforded the formation of the desired assemblies in a reproducible pattern.

Absorbance and Emission.

Absorption and emission spectra of **L1** and **L2** were obtained using respectively a Cary 300 UV-visible spectrophotometer (Varian) and a Fluoromax 4 (Horiba). Emission spectra were recorded between 500 and 800 nm after irradiation at 460 nm. Emission quantum yield ϕ_L were determined at 25 °C in deoxygenated acetonitrile solutions using $[Ru(bpy)_3]Cl_2$ in H_2O (ϕ_L = 0.028) as a standard, and a methodology already presented.[4] Emission lifetime were performed after irradiation at 400 nm with a picosecond Nd:YAG laser and using a time-correlated single photon counting detection (PicoHarp 300). The results are presented below (**Table SI1**).

Table SI1: Absorption and Emission properties: Lifetime (τ) and Quantum yields (ϕ_L) of metallo-ligand **L1** and **L2** in deoxygenated CH_3CN solution at 298 K.

Complexes	λ_{abs} [nm] (ε [$cm^{-1}M^{-1}$])	λ_{em} [nm]	ϕ_L	τ [ns]
L1	286 (137000); 445 (13280)	610	0.037	264
L2	286 (88900); 446 (13250)	610	0.048	527

Electrochemistry of L1 and L2 in solution.

Electrochemical measurements were run under argon atmosphere in a dry-glove box at room temperature. Cyclic voltammetry (CV) was performed using an EG&G model 173 potentiostat/galvanostat equipped with a PAR model universal programmer and a PAR model 179 digital coulometer. A standard three-electrode electrochemical cell was used. Potentials were referred to an $Ag/AgNO_3$ (10 mM) reference electrode in CH_3CN + 0.1 M $[Bu_4N]PF_6$. Potentials referred to that system can be converted to the ferrocene/ferricinium couple by subtracting 87 mV, to SCE by adding 298 mV or to NHE reference electrode by adding 548 mV. A vitreous carbon disk (3 mm in diameter) was used as working electrode, and was polished with a 2 µm diamond paste (Mecaprex Presi). The auxiliary electrode was a Pt wire. **Figure SI1** shows the CV of compound **L1** and **L2**. **Table SI2** summarize the potential values of the different systems (Ep_a, anodic peak potential; Ep_c, cathodic peak potential; $E_{1/2} = (Ep_a + Ep_c)/2$; $\Delta Ep = Ep_a - Ep_c$). The CV exhibits in the positive potential region the reversible Ru^{II}/Ru^{III} oxidation process at a similar potential for **L1** and **L2**. In the negative part, 4 successive ligand-based reduction processes are observed. The first three correspond to the reduction of the bipyridine ligands, the most negative one is due to the first reduction of the metal-free terpyridine part. For **L1** the third bipyridine ligand centered reduction process is strongly distorted by some electroprecipitation-redissolution phenomena.

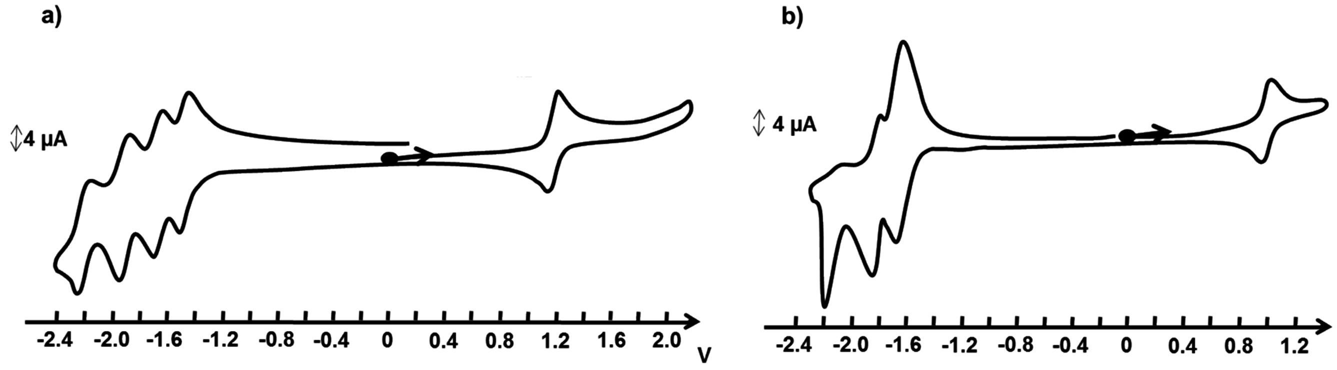


Figure SI1: Cyclic Voltammograms for **L2** (a) and **L1** (b) 10^{-3} M in CH_3CN + 0.1 M $[Bu_4N]PF_6$ *vs* $Ag/AgNO_3$ (10^{-2} M). Scan rate = 100 mV/s.

Table SI2: Redox potentials of **L1** and **L2** in deoxygenated CH_3CN + 0.1 M Bu_4NClO_4 at a scan rate of 100 mV s^{-1}. $E_{1/2}$(V) (ΔEp mV) *vs*. $Ag/AgNO_3$ 10^{-2} M, scan rate = 100 mV/s.

		Reduction processes			
Complexes	Ru^{II}/Ru^{III}	1	2	3	4
L1	1.04 (80)	-1.63 (60)	-1.77 (60)	-2.09 (100) [a]	
L2	1.01 (60)	-1.28 (80)	-1.85 (100)	-2.07 (60)	-2.36 (80)

[a] This value cannot be accurately measured since the wave is strongly distorted by adsorption of the reduction product on the electrode surface.

Electrochemistry of modified electrodes and Photo-Current Generation.

Electrochemical measurements of **S1a,b**, **S2** and **S3** were performed using CHI 621 (CH instrument) potentiostat. Cyclic voltammetry experiments were carried out in a three-electrode electrochemical cell with a flat glass window. The functionalized ITO surfaces were used as working electrode. Potentials were referred to an $Ag/AgNO_3$(10 mM) reference electrode in CH_3CN + 0.1 M $[Bu_4N]PF_6$. The auxiliary electrode was a Pt wire. The distances between the electrodes are small, and ohmic losses can be neglected (**Figure SI2**). For the photocurrent experiments, TEOA (1 M) was added as an electron donor to the solution. The samples were illuminated with a Mercury-Xenon lamp (Hamamatsu L9588) operated at maximum power. The electrochemical cell was held 4 cm above the lamp for every measurement. In these conditions, the radiant power landing on the surface of the electrode is 1.79 W.cm^{-2}. During this experiment, the light was alternatively switched on and off leading to the generation of photocurrent (**Figure SI3**). ICPE values were measured using a diode laser (LD-WL206) (λ = 445 nm, P = 0.33 W.cm^{-2}) as excitation light. Photoaction spectrum was recorded using a monochromator (Jobin Yvon HR250) between the lamp and the electrochemical cell.

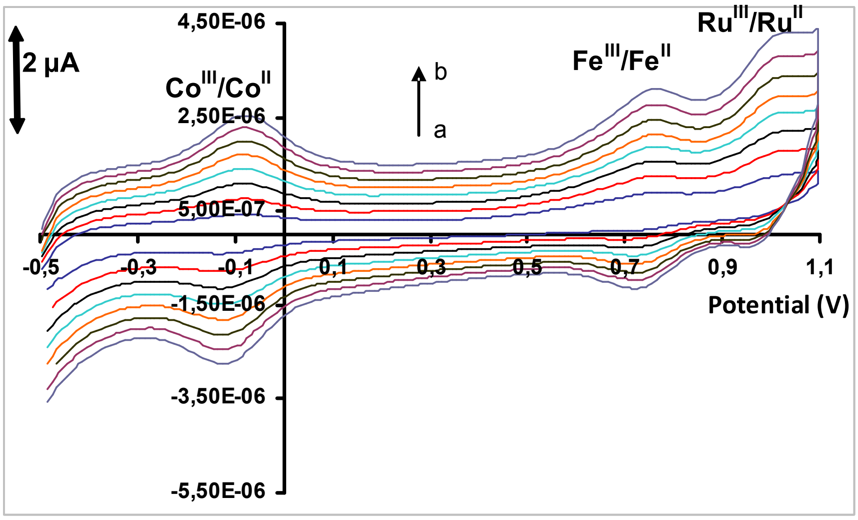


Figure SI2. Cyclic Voltammogram for **S3** in CH_3CN + 0.1 M $[Bu_4N]PF_6$ recorded at different scan rates from 10 mV/s (a) to 80 mV/s (b) (10 mV/s increase at each CV) potentials are referenced versus $Ag/AgNO_3$ (10^{-2} M).

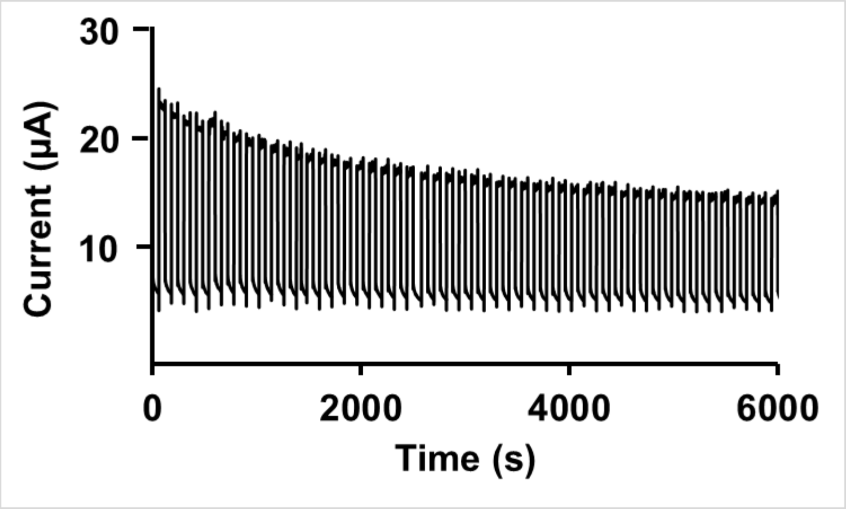


Figure SI3. Anodic photocurrent response of **S3** ($\Gamma = 1 \pm 0.2 \times 10^{-11}$ mol cm^{-2}) *vs* time. Iterative illumination and dark cycles of 20 s.

References:

J.Wang, G. S. Hanan, *Synlett* 2005, **8**, 1251.

2 O. Johansson, M. Borgstrom, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarstrom, L. Sun,B. Akermark, *Inorg. Chem.* 2003**, 42**, 2908.

3 J.-P. Collin, F. Durola, J. Lux, J.-P. Sauvage, *Angew. Chem. Int. Ed.* 2009, **48**, 8532.

4 J. Lombard, J.-C. Lepretre, J. Chauvin, M.-N. Collomb, A. Deronzier, *Dalton Trans.* 2008, 658.