

Supplementary Information

Red-light sensitized hole-conducting polymer for energy conversion

Bianca Seidler,^{ab} Ruri A. Wahyuono,^c Pascal Wintergerst,^d Johannes Ahner,^{ef} Martin D. Hager,^{ef} Sven Rau,^d Ulrich S. Schubert,^{ef} Benjamin Dietzek,^{abf*}

^a Institute of Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany.

^b Leibniz Institute of Photonic Technology Jena (Leibniz-IPHT), Albert-Einstein-Str. 9, 07745 Jena, Germany.

^c Department of Engineering Physics, Institut Teknologi Sepuluh Nopember (ITS) Surabaya, Jl. Arif Raham Hakim, 60111 Surabaya, Indonesia.

^d Institute of Inorganic Chemistry, University Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany.

^e Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Helmholtzweg 10, 07743 Jena, Germany.

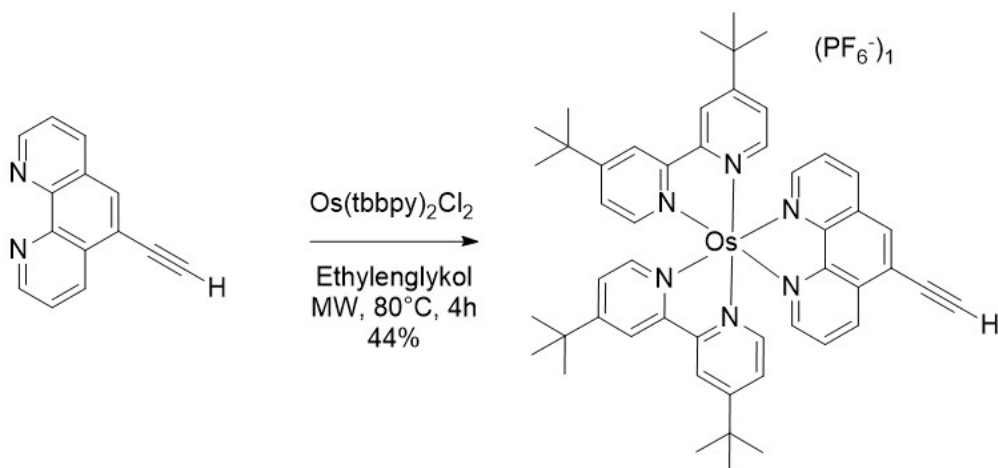
^f Centre for Energy and Environmental Chemistry Jena (CEEC-Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany.

*Corresponding authors: benjamin.dietzek@leibniz-ipht.de

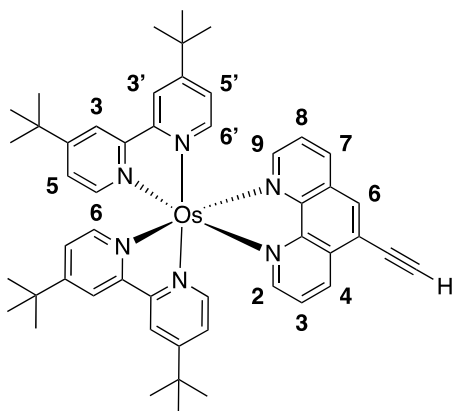
Supporting Information

Table of Content

1	Synthesis	3
2	Ground state absorption properties	9
2.1	Gibbs Energy for Charge Injection	9
2.2	CLV experiments	10
2.3	EIS experiments	12
2.4	References.....	20

1 Synthesis**(tbbpy)₂Os(5-ethynyl-1,10-phenanthroline)**

Os(tbbpy)₂Cl₂ (66 mg, 83 μmol) and 5-ethynyl-1,10-phenanthroline (17 mg, 83 μmol) were dissolved in 10 mL of ethylene glycol. The mixture was heated in the microwave to 80 °C with a maximum power of 150 W. An excess of NH₄PF₆ dissolved in water was added and the precipitate was collected by filtration and washed with large amounts of water and diethyl ether. The dark solid was purified first by size exclusion chromatography (Sephadex, methanol) and then by diffusion crystallization (MeCN, MeOH, Et₂O) to obtain the pure product as a black solid (44 %, 44 mg, 36 μmol).



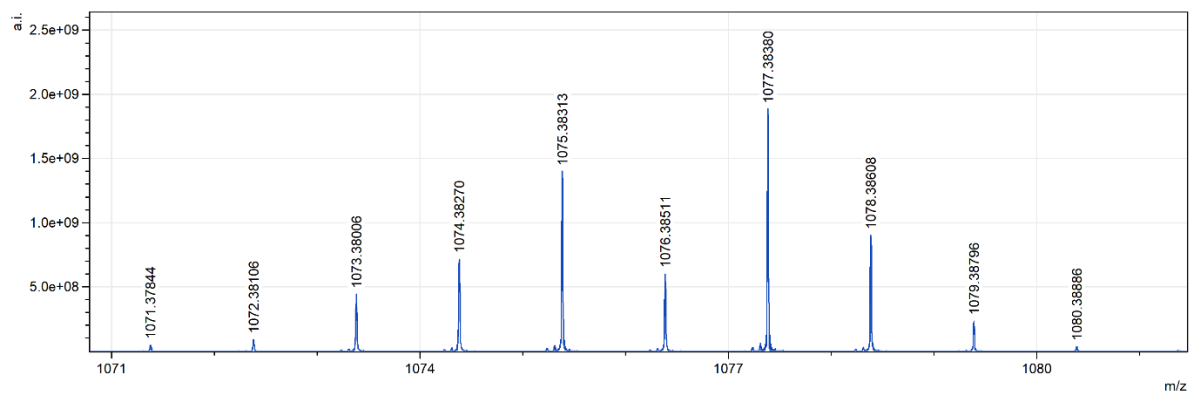
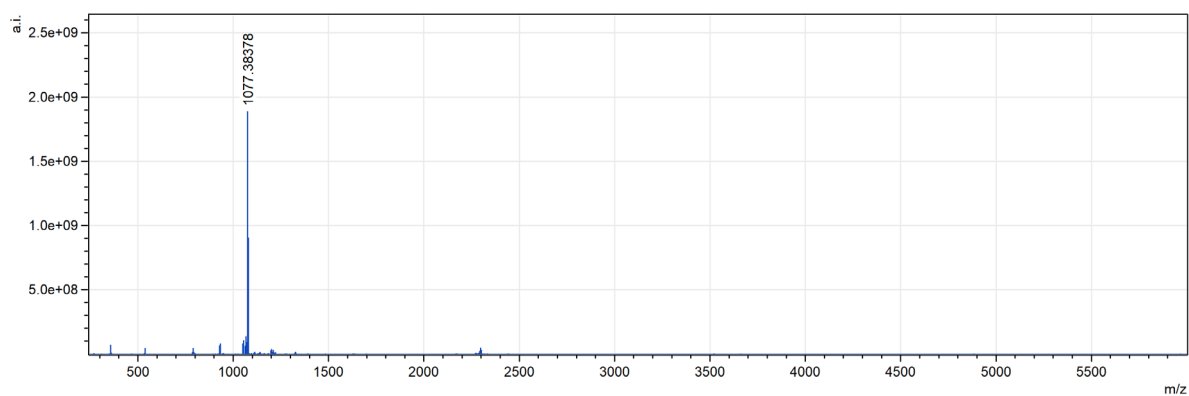
¹H NMR (400 MHz, CD₃CN) δ [ppm] = 8.59 (dd, J = 8.3, 1.1 Hz, 1H, H₄), 8.52 – 8.42 (m, 3H, H₇, H_{bpy-3}), 8.45 – 8.40 (m, 2H, H_{bpy-3'}), 8.30 (dd, J = 8.4, 1.1 Hz, 1H, H₂), 8.01 (dd, J = 5.4, 1.2 Hz, 1H, H₉), 7.99 (dd, J = 5.4, 1.1 Hz, 1H, H₂), 7.72 (dd, J = 8.4, 5.4 Hz, 1H, H₃), 7.65 (dd, J = 8.2, 5.4 Hz, 1H, H₈), 7.58 (d, J = 6.1 Hz, 2H, H_{bpy-6}), 7.37 (dd, J = 6.2, 2.2, 0.7 Hz, 2H, H_{bpy-6'}), 7.27 (ddd, J = 10.1, 6.2,

Supporting Information

0.6 Hz, 2H, H_{bpy-5}), 7.15 – 7.05 (m, 2H, H_{bpy-5'}), 4.12 (s, 1H, H_{CCH}), 1.43 (s, 9H, H_{tBu}), 1.43 (s, 9H, H_{tBu}), 1.34 (s, 9H, H_{tBu}), 1.34 (s, 9H, H_{tBu}).

¹³C NMR (126 MHz, CD₃CN) δ [ppm] = 159.97, 159.79, 153.44, 153.31, 151.68, 151.64, 151.53, 151.47, 151.32, 136.86, 135.36, 134.07, 132.33, 131.68, 128.00, 127.92, 126.22, 126.19, 126.16, 126.10, 126.08, 126.03, 122.92, 122.88, 122.84, 122.80, 122.78, 122.76, 122.01, 87.75, 87.72, 79.14, 36.36, 36.29, 30.83, 30.73.

HR-MALDI-MS: m/z calculated for [C₆₂H₆₂F₆N₈PRu]⁺: m/z = 1077.38285 found: m/z = 1077.38380
[M + PF₆]⁺



Supporting Information

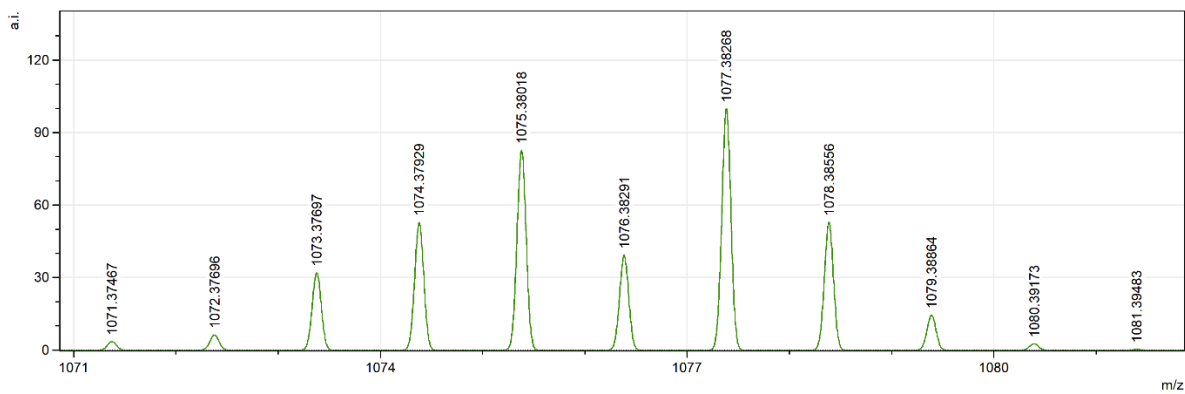


Figure S1 MALDI-HRMS-spectrum of *(tbbpy)2Os(5-ethynyl-1,10-phenanthroline)* (top, middle) and simulated spectrum (bottom).

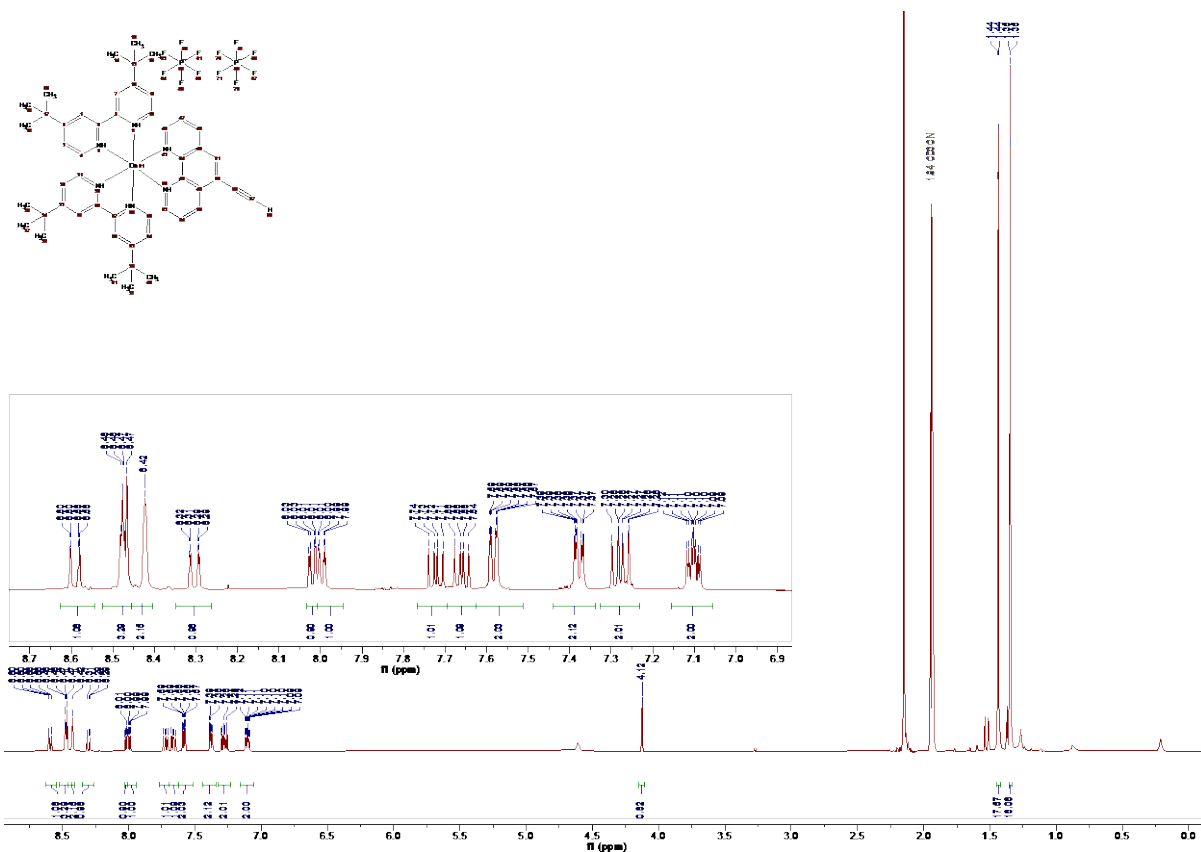


Figure S2 $^1\text{H-NMR}$ spectrum of *(tbbpy)2Os(5-ethynyl-1,10-phenanthroline)* in CD_3CN .

Supporting Information

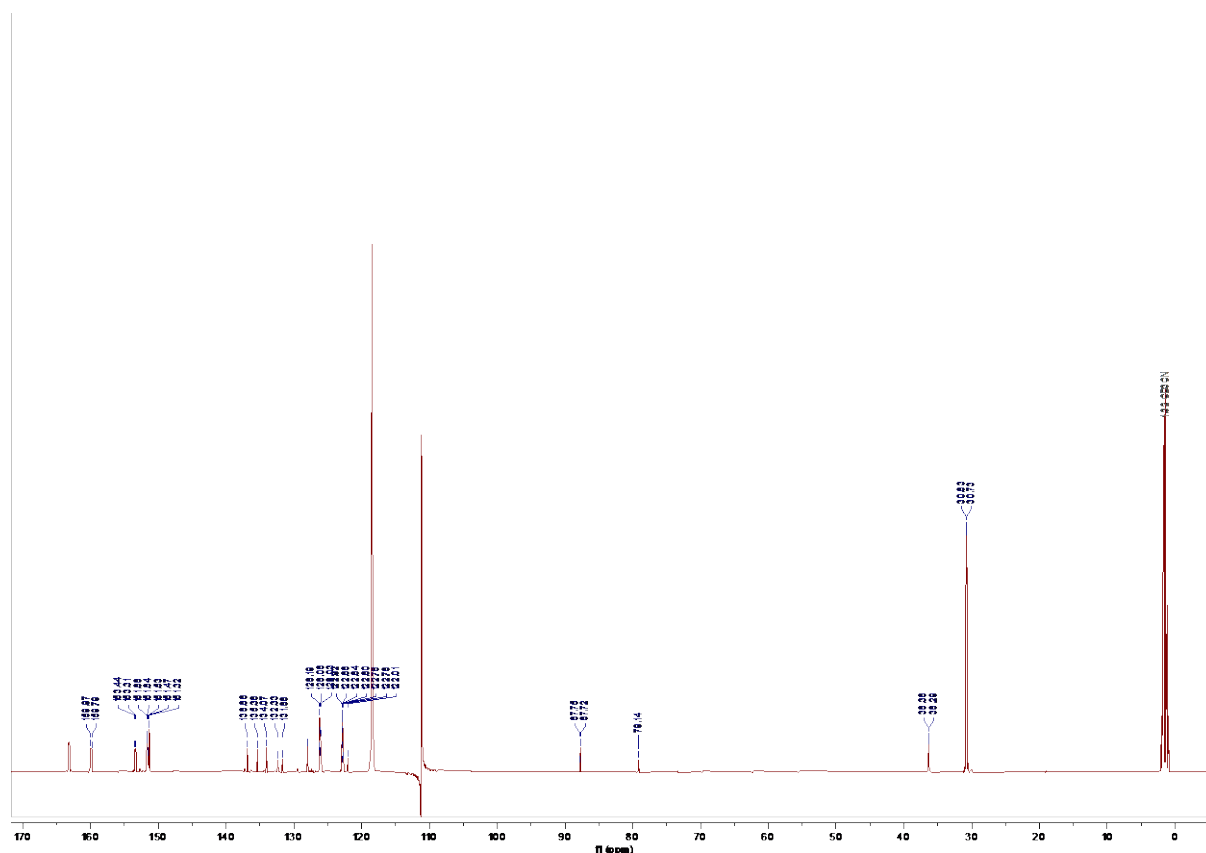


Figure S3 ^{13}C -NMR spectrum of $(\text{tbbpy})_2\text{Os}(5\text{-ethynyl-}1,10\text{-phenanthroline})$ in CD_3CN .

NMR spectra were recorded on a Bruker Avance III HD 400 or 500 at 293 K and processed with MestReNova software (Version 12.0.0). The chemical shifts are reported in parts per million (ppm). ^1H NMR and ^{13}C NMR shifts are referenced according to the applied deuterated solvent as internal standard. Constants J are presented as absolute values in Hz. For the characterization of the NMR signals the following abbreviations are used: s = singlet, d = doublet, m = multiplet and dd = doublet of doublets. High resolution mass spectrometry (HRMS) was performed on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as a matrix.

Synthesis of azide-functionalized PPV

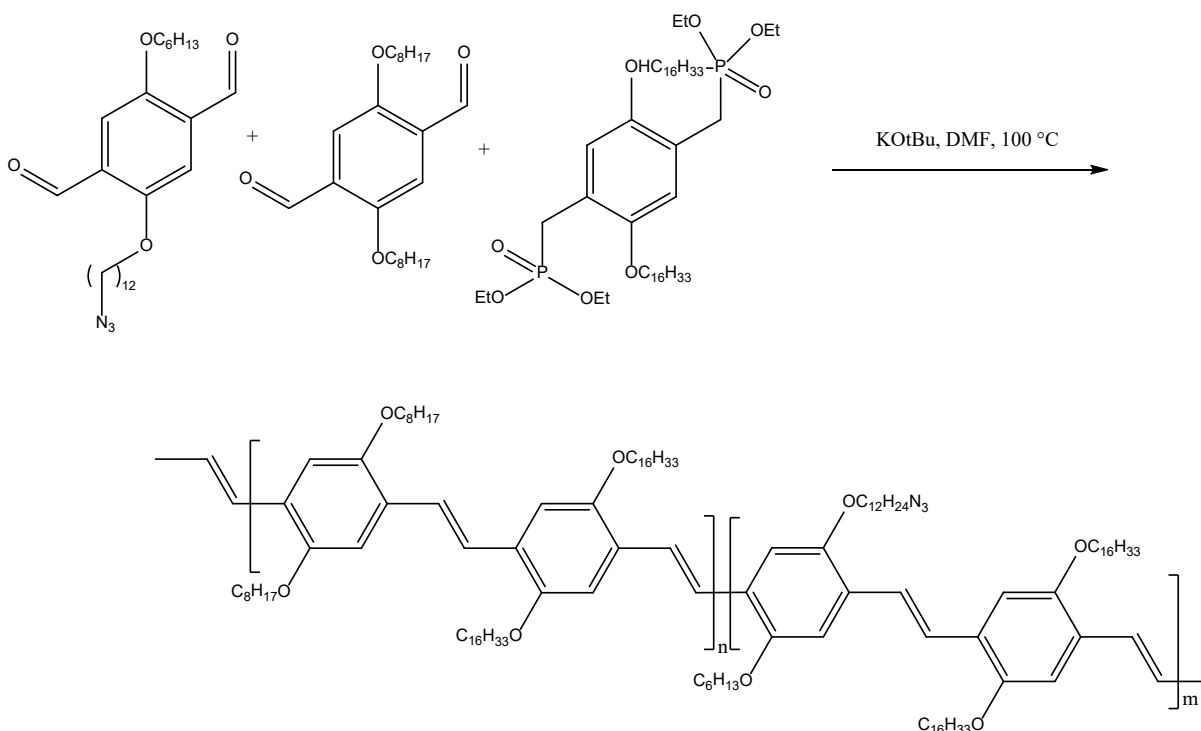


Figure S4 Synthetic route yielding in azide-functionalized PPV.

The azide containing PPV was synthesized according to the literature.^[1]

Clicking with Osmium complex

The Osmium containing polymer was synthesized analogous to the reported click reaction of ruthenium complexes.^[1] In detail, PPV (79 mg, 0,012 mmol azide), osmium complex (23 mg, 0,019 mmol) and iodo(triethyl phosphite)copper(I) (14 mg, 0.037 mmol) were dissolved in 1.5 mL anhydrous chloroform under nitrogen atmosphere. Triethylamine (84 mg) was dissolved in 10 mL dry chloroform. 0.23 mL of this solution were added to the mixture containing the PPV, osmium complex and copper catalyst. The resulting reaction mixture was heated at 60 °C under exclusion of light overnight. After cooling to room temperature, the polymer was precipitated in 60 mL of a mixture of methanol (45 mL) and water (15 mL), which was saturated with sodium hexafluorophosphate. The polymer was filtrated and washed with water (5 · 10 mL), methanol (5 · 10 mL) and acetone (5 · 10 mL). 70 mg of the polymer were obtained.

Supporting Information

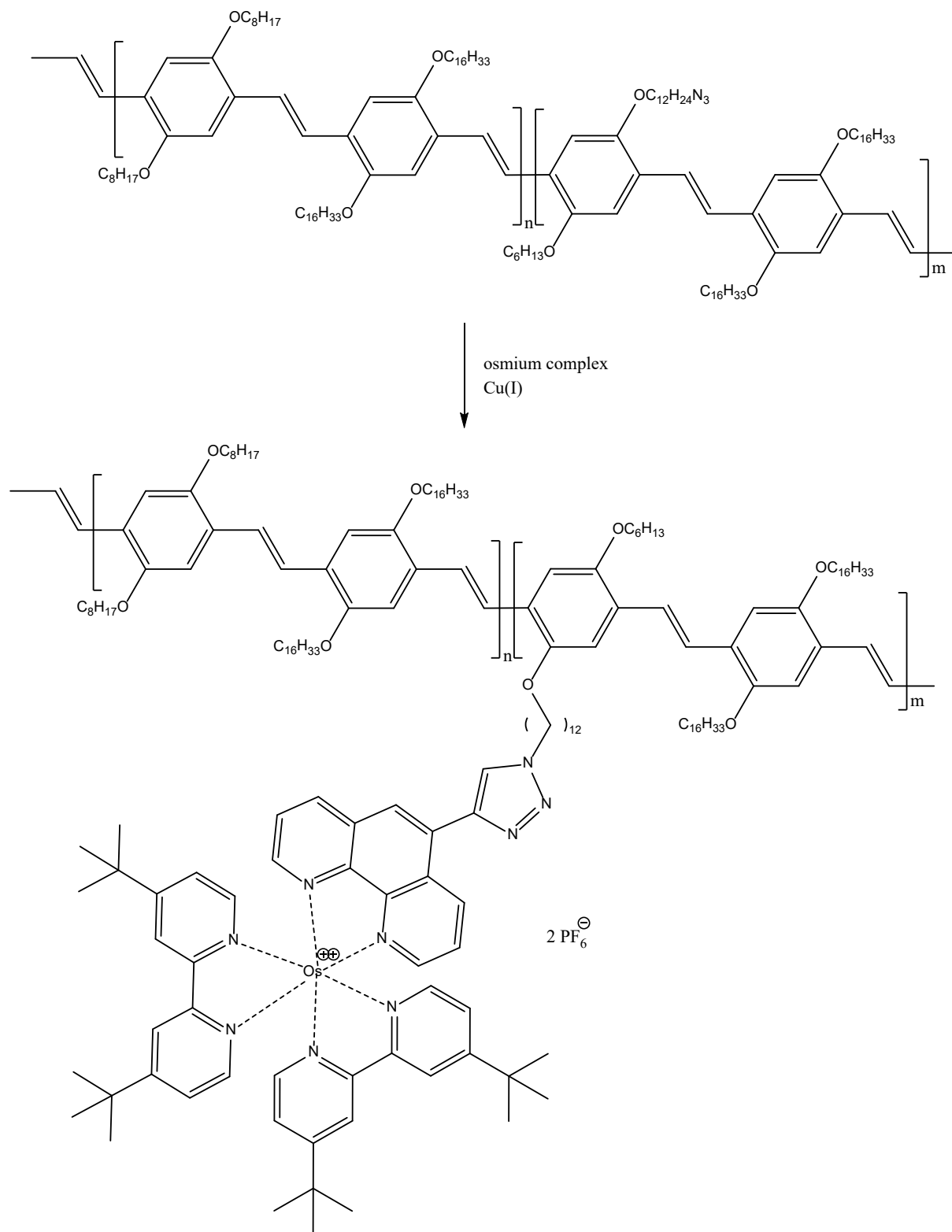


Figure S5 Synthetic route of click chemistry with **Os(II)** and **PPV** resulting in **OsPPV**.

2 Ground state absorption properties

2.1 Gibbs Energy for Charge Injection

The Gibbs energy for electron and hole transfer in **OsPPV** is calculated to see thermodynamically favored or unfavored processes. The Gibbs energy for electron transfer in **OsPPV** was calculated with the following equations for two different cases^[2,3]:

i) only **Os(II)** is excited

$$\Delta G_{inj,e} = e[E(\text{Os}^{+/*}) - E(\text{PPV}^{0/-})] \text{ with } E(\text{Os}^{+/*}) = E(\text{Os}^{+/0}) - E_{0-0}$$

ii) both **Os(II)** and **PPV** are excited

$$\Delta G_{inj,e} = e[E(\text{Os}^{+/*}) - E(\text{PPV}^{* / -})] \text{ with } E(\text{PPV}^{* / -}) = E(\text{PPV}^{0 / -}) + E_{0-0}$$

The Gibbs energy for hole transfer in **OsPPV** was calculated with the following equations for two different cases^[2,3]:

i) only **Os(II)** is excited

$$\Delta G_{inj,h} = e[E(\text{PPV}^{+/0}) - E(\text{Os}^{* / -})] \text{ with } E(\text{Os}^{* / -}) = E(\text{Os}^{0 / -}) + E_{0-0}$$

ii) both **Os(II)** and **PPV** are excited

$$\Delta G_{inj,h} = e[E(\text{PPV}^{+ / *}) - E(\text{Os}^{* / -})] \text{ with } E(\text{PPV}^{+ / *}) = E(\text{PPV}^{+/0}) - E_{0-0}$$

The values taken for the calculation of Gibbs free energy are the following (also shown in Table 1 in the manuscript):

$$E(\text{Os}^{+/0}) = 0.6 \text{ V}, E(\text{Os}^{0/-}) = -1.46 \text{ V}, E_{0-0} = 1.8 \text{ V}$$

$$E(\text{PPV}^{+/0})^* = 0.49 \text{ V}, E(\text{PPV}^{0/-}) = -2.59 \text{ V}, E_{0-0} = 2.34 \text{ V}$$

*: As the oxidation peak of PPV from the CV measurement is broad, the oxidation peaks of PPV from anodic and cathodic scan were determined using derivation techniques of the cyclic voltammetry data.

2.2 CLV experiments

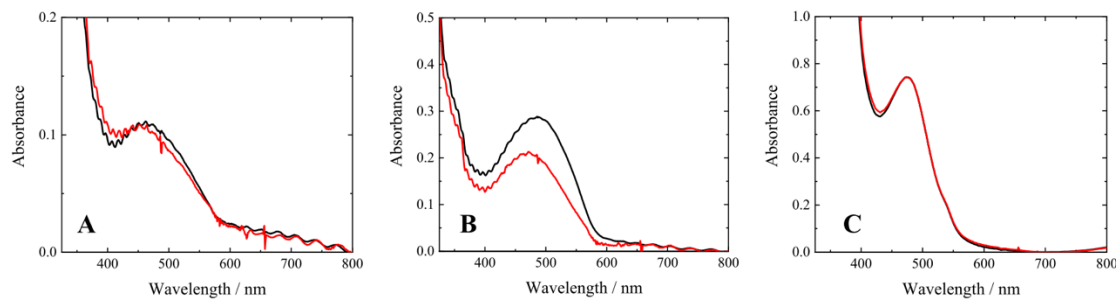


Figure S6: Absorption spectra of (A) **OsPPV**, (B) **PPV** and (C) Co electrolyte solution before (black) and after (red) measuring CLV and LSV upon chopped light illumination of 450 nm.

The (in)stability of the **OsPPV** and **PPV** films upon irradiation of one wavelength as well as the stability of the electrolyte solution is shown in Figure S6. Hereby, under irradiation at 627 nm the degradation of the **OsPPV** film amounts of 11 %, while it amounts of 3 % for the **PPV** film.

Supporting Information

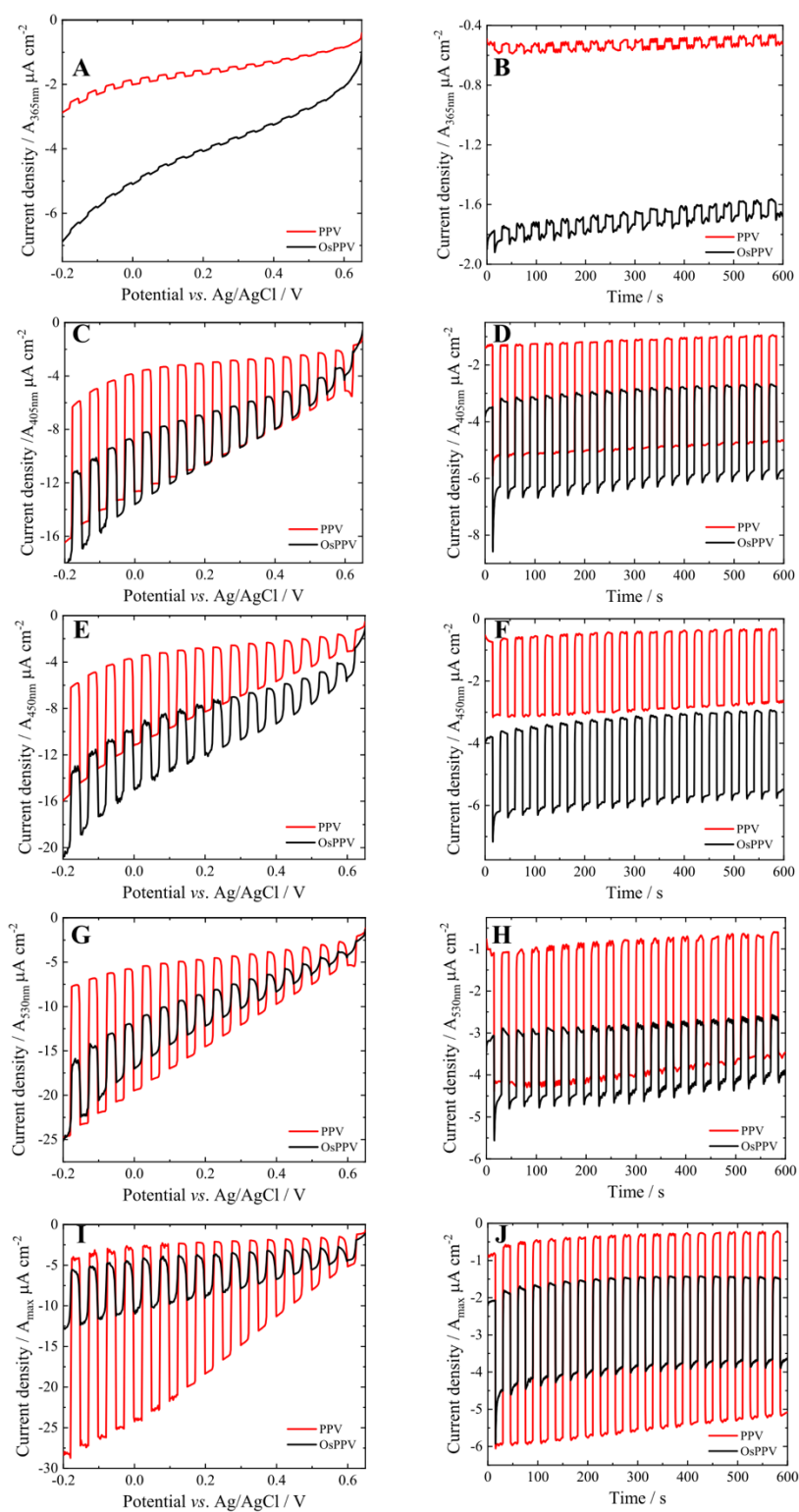


Figure S7: LSV of films of **OsPPV** (black) and **PPV** (red) drop casted on a PETITO substrate working as WE measured in a $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ electrolyte solution in dry ACN with a scan speed of 20 mV/s upon illumination at 365 nm (A), 405 nm (C), 450 nm (E), 530 nm (G), and WL (I). CLV of **OsPPV** (black, concentration 1:1) and **PPV** (red, concentration 1:1) films drop casted

Supporting Information

on a PETITO substrate measured in a $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ electrolyte solution in dry ACN by applying a potential of 0.5 V vs. Ag/AgCl upon illumination at 365 nm (B), 405 nm (D), 450 nm (F), 530 nm (H), and WL (J). The obtained photocurrent was divided by the film area to receive the photocurrent density. Furthermore, the photocurrent density was divided by the absorbance of the film at the specific wavelength accounting for film thickness.

2.3 EIS experiments

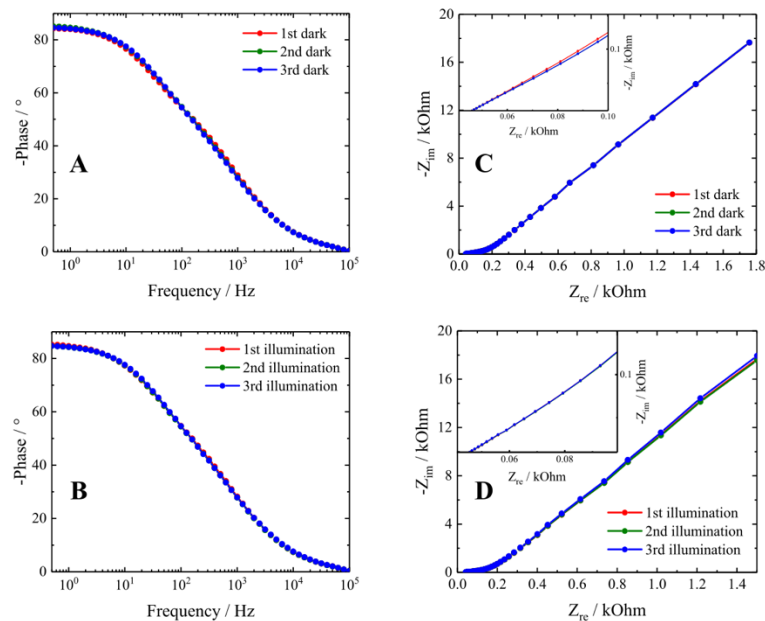


Figure S8: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **OsPPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{\text{LED}} = 365 \text{ nm}$, intensity of 450 W/m^2 FWHM = 137 eV).

Supporting Information

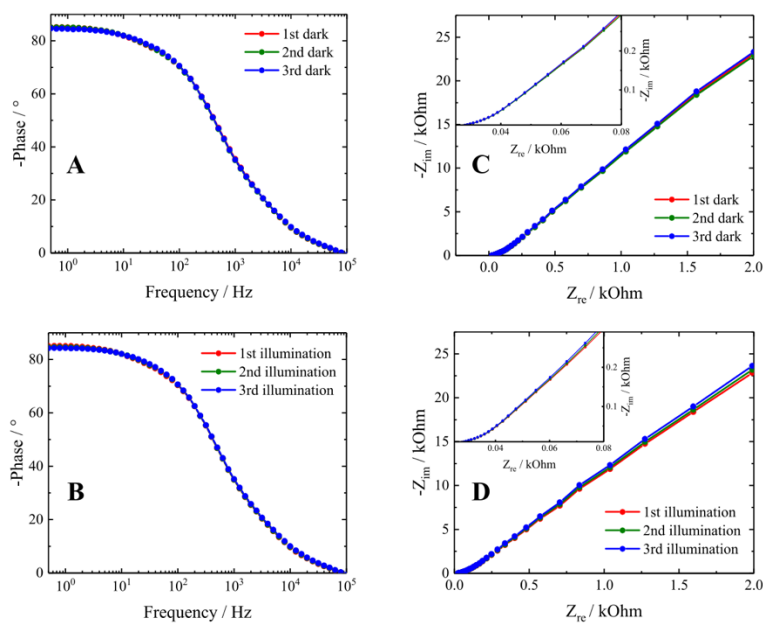


Figure S9: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **OsPPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 405 \text{ nm}$, intensity of 150 W/m^2 FWHM = 85 eV).

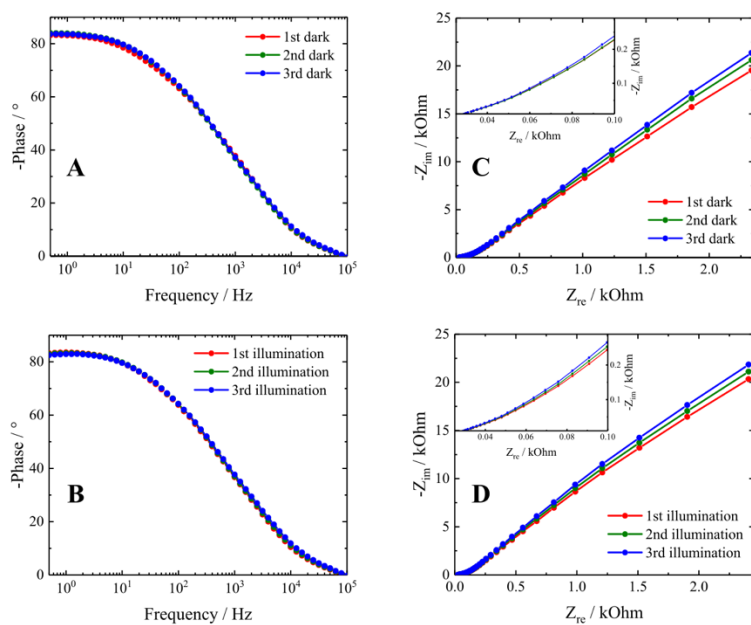


Figure S10: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **OsPPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 450 \text{ nm}$, intensity of 200 W/m^2 FWHM = 60 eV).

Supporting Information

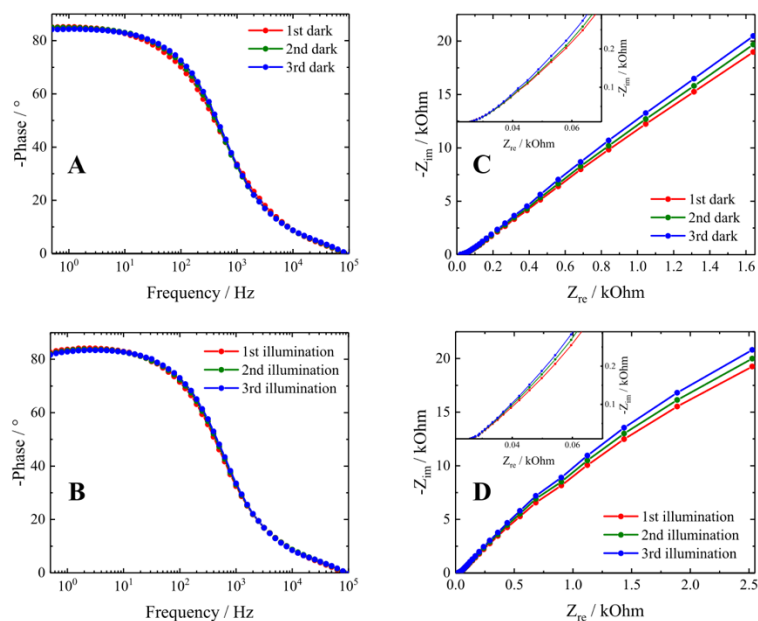


Figure S11: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for OsPPV film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 530$ nm, intensity of 300 W/m^2 FWHM = 41 eV).

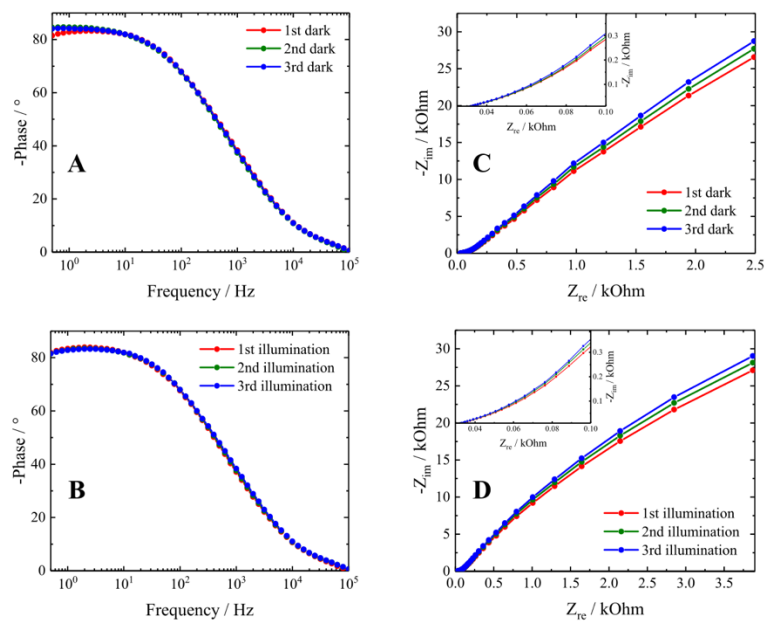


Figure S12: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for OsPPV film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 400-800$ nm, intensity of 1000 W/m^2 FWHM = 9 eV).

Supporting Information

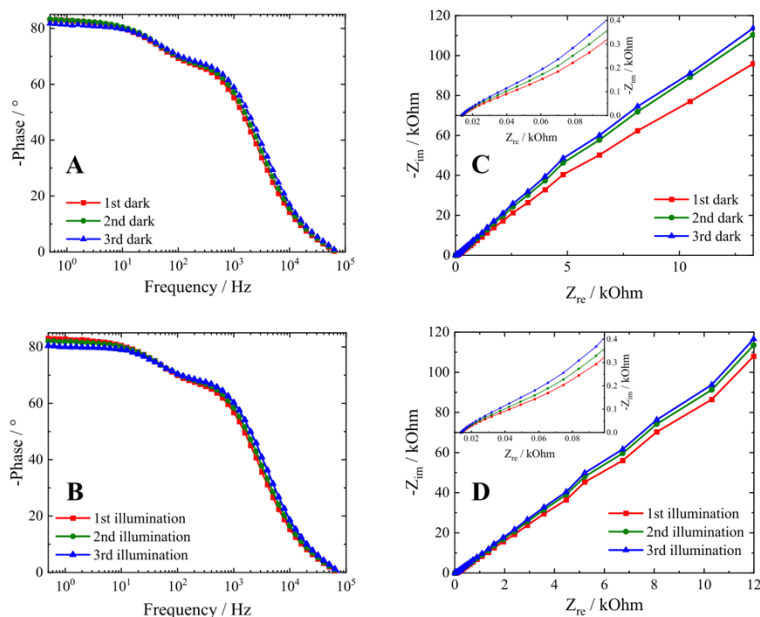


Figure S13: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 365 \text{ nm}$, intensity of 450 W/m^2 FWHM = 137 eV).

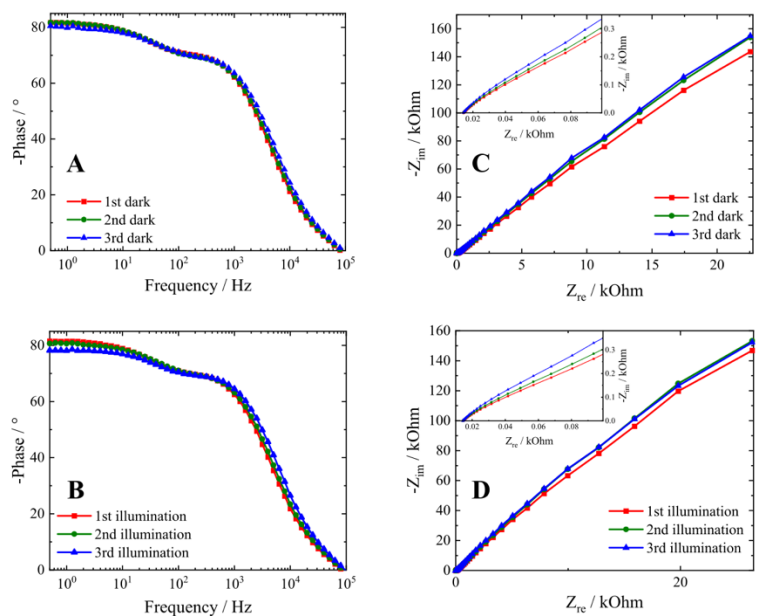


Figure S14: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 405 \text{ nm}$, intensity of 150 W/m^2 FWHM = 85 eV).

Supporting Information

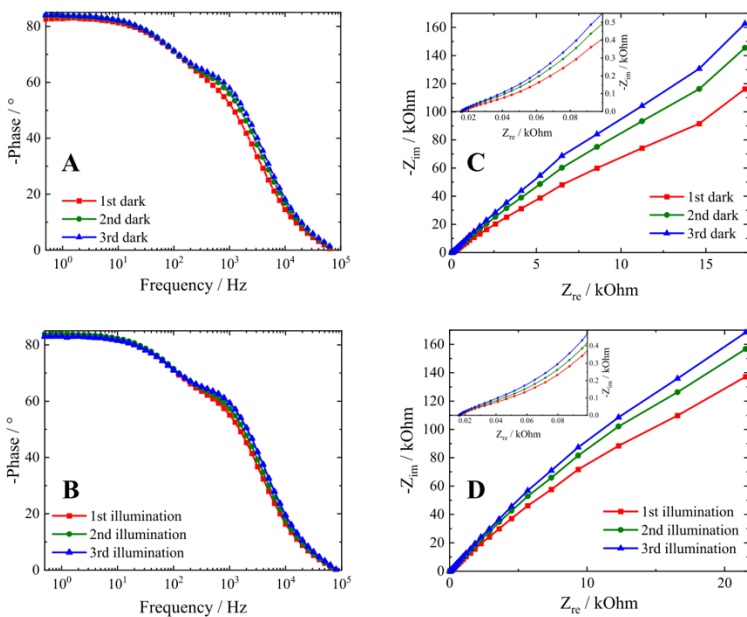


Figure S15: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 450$ nm, intensity of 200 W/m² FWHM = 60 eV).

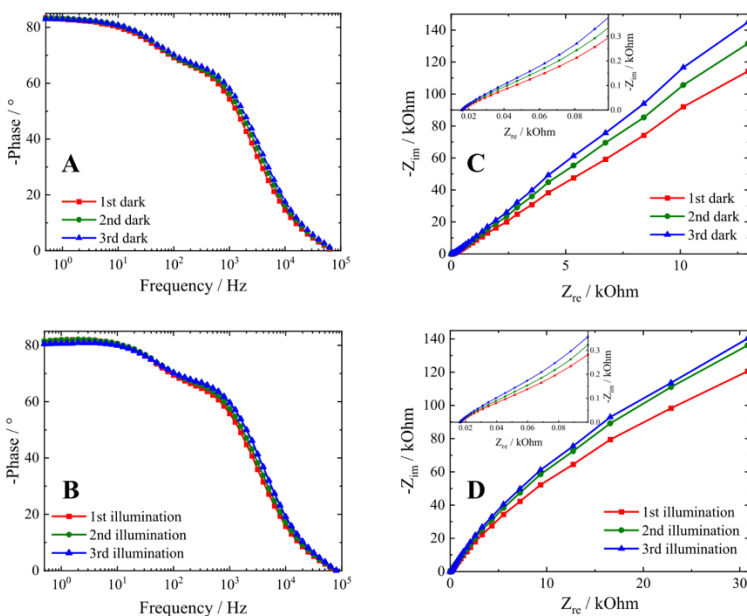


Figure S16: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 530$ nm, intensity of 300 W/m² FWHM = 41 eV).

Supporting Information

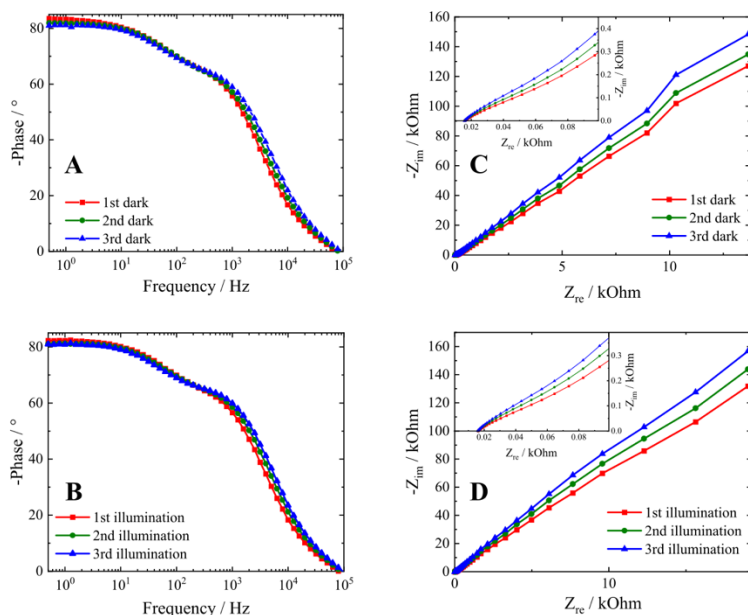


Figure S17: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 627 \text{ nm}$, intensity of 800 W/m^2 FWHM = 86 eV).

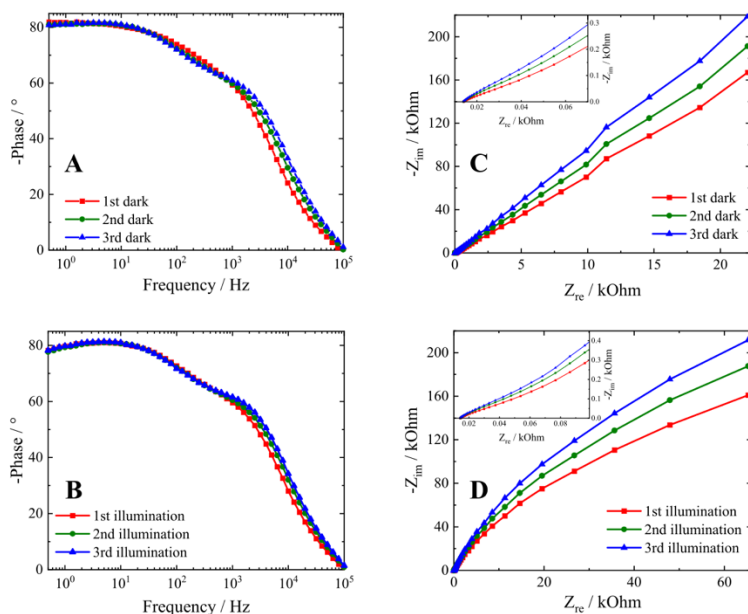
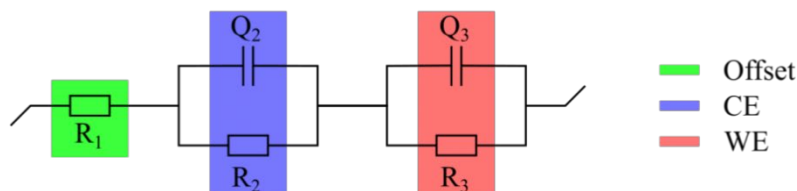


Figure S18: Bode Plot (A,B) and Nyquist Plot (C,D) of EIS experiment for **PPV** film measured in three dark (A,C) and light cycles (B,D) with a LED of UV light ($\lambda_{LED} = 400\text{-}800 \text{ nm}$, intensity of 1000 W/m^2 FWHM = 9 eV).

The recorded frequency for EIS measurements was set between 0.5 Hz to 100 kHz, the AC voltage amplitude amounted to 10 mV. A modified Randle diagram describes the equivalent electric circuit

Supporting Information

used for these measurements. This circuit can describe the electrochemical processes happening in the sample. R_1 is the offset resistance of the conductive substrate of ITO, in this case of the **OsPPV** film dried in CHCl_3 . R_2 and Q_2 describe the process taking place on the CE. R_3 and Q_3 depict the processes occurring on the WE.



Due to the modified Randle diagram, its parameters can be calculated by fitting it into EC-lab program. After the calculation, the parameters in the following equations can be used to obtain values for the hole mobility of **OsPPV** at different LEDs^[4]:

$$\mu = \frac{\delta^2}{V \cdot \tau}$$

$$\tau = (R_3 Q_3)^{\frac{1}{\alpha}}$$

μ describes here the hole mobility, δ is the film thickness (**OsPPV** = 340 nm, **PPV** = 72 nm), V represents the applied voltage of 10 mV and τ is a time constant. This time constant can be calculated by the second equation, which requires the parameters of the Randle diagram received by fitting. In this equation α describes the value of a non-ideal capacitor. The film thickness was received by AFM measurements.

After fitting and calculating the hole mobility, the average values for the three films per wavelength were utilized to represent the hole mobility for a given film, which is depicted in Table S1.

Supporting Information

Table S1: Calculated mean values of hole mobility at the specific wavelengths plus hole mobility of NiO as comparison.

Wavelength LED [nm]	Hole mobility OsPPV [cm ² /Vs]	Hole mobility PPV [cm ² /Vs]	NiO hole mobility ^[5] [cm ² /Vs]
365	5.27·10 ⁻⁵	4.56·10 ⁻⁶	
405	9.07·10 ⁻⁵	5.02·10 ⁻⁶	
450	1.04·10 ⁻³	1.99·10 ⁻⁵	between 1.00·10 ⁻⁴ and 0.29
530	1.16·10 ⁻⁴	7.40·10 ⁻⁶	
627	5.07·10 ⁻⁵	6.22·10 ⁻⁶	
White light	5.85·10 ⁻⁵	1.46·10 ⁻⁵	

The hole mobility is located in the range of 10⁻⁵ for nearly all LEDs. All other LEDs are in the same range. Hereby, the highest hole mobility value occurs for an irradiation at 450 nm, followed by 530 nm. At irradiation at 627 nm only the **Os(II)** in **OsPPV** is excited followed by charge separation and later the charge recombination appears. However, the hole mobility seems to be faster than the charge recombination. For excitation at 450 nm the absorption maximum of **PPV** and **Os(II)** is reached. The hole mobility of **PPV** is located in the range of 10⁻⁶ for nearly all LEDs, the only exception here are also 450 nm as well as WL.

Compared to the hole mobility of NiO one can observe, that 365 and 450 nm show the similar magnitude than the value for NiO. For further use these two wavelengths are the best. However, 627 nm seems to be very interesting due to excitation of **Os(II)** in **OsPPV**. Here the effect of pure **Os(II)** in **OsPPV** can be investigated. The lifetime for the charge transfer is given in Table S2.

Table S2: Summary of lifetime for charge transfer in **OsPPV** and **PPV**, respectively.

λ_{LED} [nm]	OsPPV Lifetime [ms]	PPV Lifetime [ms]
365	2.74	1.40
405	2.39	1.08
450	5.94	0.51
530	1.37	0.75
627	3.16	0.86
White light	2.18	11.50

2.4 References

- (1) Wahyuono, R. A.; Seidler, B.; Bold, S.; Dellith, A.; Dellith, J.; Ahner, J.; Wintergerst, P.; Lowe, G.; Hager, M. D.; Wächtler, M.; Streb, C.; Schubert, U. S.; Rau, S.; Dietzek, B. *Sci. Rep.* **2021**, *11* (1), 1–13.
- (2) Happ, B.; Winter, A.; Hager, M. D.; Schubert, U. S. *Chem. Soc. Rev.* **2012**, *41* (6), 2222–2255.
- (3) Kabatc, J.; Jurek, K. *Polymer (Guildf)*. **2012**, *53* (10), 1973–1980.
- (4) Kokil, A.; Yang, K.; Kumar, J. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (15), 1130–1144.
- (5) Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. *Chem. Soc. Rev.* **2014**, *43* (22), 7501–7519.