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Methodology for Functionalization of Water Oxidation Catalyst IrO_x Nanoparticles with Hydrophobic and Multi-Functionalized Chromophores

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SUPPORTING INFORMATION

Table of contents :

1 – Experimental Section

1.1 – Materials

All chemicals were purchased from Aldrich, Alfa Aesar, Acros and Fluka and were used without further purification unless otherwise noted. Solvents were obtained from EM Science and were used as received unless otherwise noted. Water used in the IrOx-NP synthesis and dialysis, as well as in the preparation of the KNO_3 and PBS solutions, was purified using a NANOpure purification system. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography was carried out using Silicycle silica gel 60 with 230-400 mesh. Purification by dialysis was carried out using Dialysis membrane Spectra/Por® 6 MWCO (molecular weight cut-off) 2000 with 38 mm flat width, purchased from SpectrumLabs and used as received. About 10 cm of dialysis membrane were cut and the aqueous solution containing the NPs was added into the dialysis bag, which was capped and then placed in a beaker containing 1L of water. The dialysis bag was gently stirred for 5 hours at room temperature, after which the exterior water was replaced with 1 L of fresh water. Six washing cycles of 5 hours each were carried out, totalizing 30 hours of dialysis purification for each batch of NPs.

1.2 – Spectroscopic and Electrochemical Measurements

1.2.1 - Nuclear Magnetic Resonance: The ^{1}H-NMR spectra were recorded on a Varian spectrometer at 400 MHz or 500 MHz. NMR samples were prepared in deuterated solvents used as received and with tetramethylsilane as an internal reference using a Wilmad 528-PP 5 mm NMR tube.

1.2.2 - Mass Spectrometry: Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF), using (1E, 3E)-1,4-diphenylbuta-1,3-diene (DPB), cyano-4-hydroxycinnamic acid (CCA), terthiophene or trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (t-BPM) as a matrix. The reported mass is of the most abundant isotopic species observed. To facilitate comparison, calculated values for the most abundant isotopic ratio expected are listed after the experimental result.

1.2.3 - Ultraviolet-Visible Spectroscopy: UV-Vis absorption measurements were carried out on a Shimadzu UV2100U UV-visible spectrometer, using a 1 cm quartz cuvette.

Spectra of **2** were obtained in aqueous solution after purification of the nanoparticles by dialysis. Spectra of compound **1** and IrOx-NPs **4** were obtained in a water/methanol (9:1, v/v) solvent mixture; the use of methanol as co-solvent was necessary due to the low solubility of **1** in water. For comparison reasons, the same amount of methanol was added to the aqueous suspension of **4**.

1.2.4 - Infrared Spectroscopy: The IR spectra were measured in a Thermo Scientific Smart iTR ultra-high-performance sampling accessory, equipped with a versatile Attenuated Total Reflectance (ATR) diamond Crystal, coupled to a UV-3101PC UV-Vis-NIR spectrometer. A few drops of the suitable compound solution were deposited on the ATR diamond crystal, and allowed to dry under air at room temperature for 2 h. The IR spectra reported are averages of 64 scans.

1.2.5 - Cyclic Voltammetry: Cyclic voltammograms were measured using a CH Instruments 760D potentiostat. Five milliliters of the suitable IrOx-NPs were introduced in a single glass cell and degased with argon for 5 minutes before each run. The working electrode was cleaned between runs by polishing with alumina slurry, followed by sonication in water for 5 minutes. Working electrode: glassy carbon; reference electrode: SCE; counter electrode: platinum wire; support electrolyte: 0.1 M KNO_3; buffer: 0.1 M PBS pH 7.4.

1.2.6 - Oxygen Evolution Experiments: The amount of oxygen produced by the IrOx-NPs catalysts was measured using a Neofox Optical Oxygen Sensor (from *Ocean Optics*). The experiments were carried out in a two-compartment electrochemical glass cell separated by a Nafion membrane. Seven milliliters of the proper IrOx-NPs were introduced in compartment 1 together with support electrolyte (0.1 M KNO_3) and PBS buffer (0.1 M, pH 7.4). The working (glassy carbon) and reference (SCE) electrodes as well as the Neofox Oxygen probe and the temperature sensor were immersed in compartment 1, and the solution was purged by bubbling argon until the O_2 concentration was below 5 $\mu mol.L^{-1}$. In compartment 2, the counter electrode (platinum wire) was immersed in 3 mL of support electrolyte (0.1 M KNO_3) and PBS buffer (0.1 M, pH 7.4) solution. After reading a stable concentration of oxygen below 5 $\mu mol.L^{-1}$ for 5 minutes, the amperometry experiment was initiated by applying steady potential of 1.50 V *vs* SCE.

1.3 – Spectroscopic and Electrochemical Data Mentioned in the Manuscript

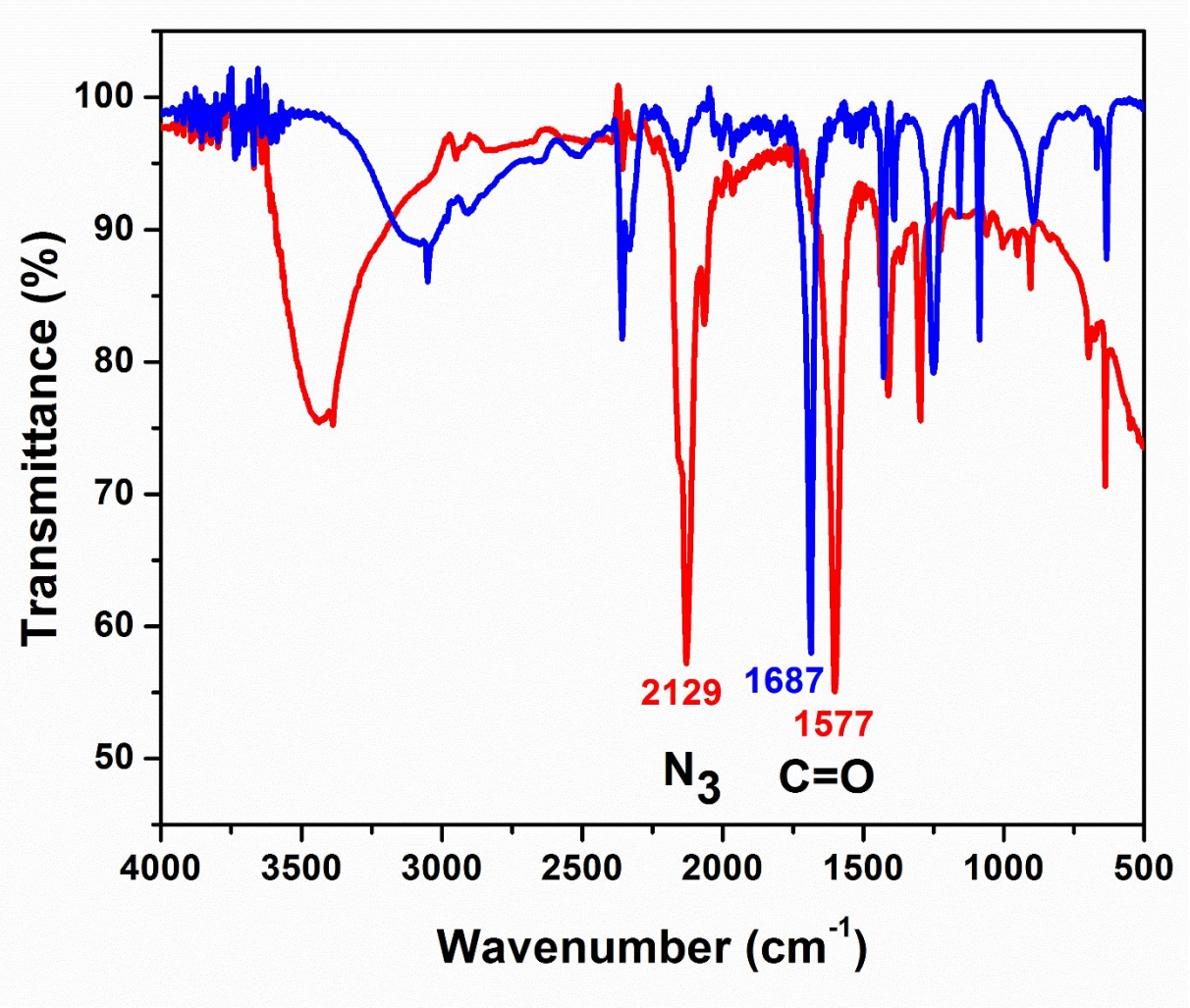


Figure S1. FTIR spectra of iodoacetic acid (blue), and IrO_x-NPs **2** (red).

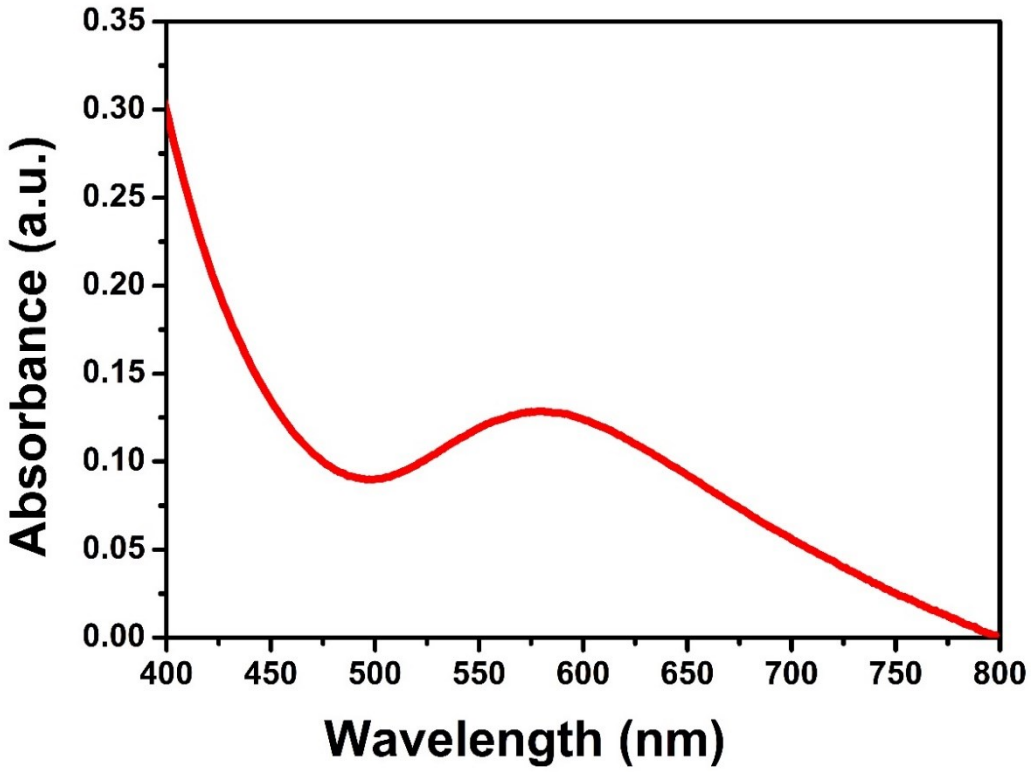
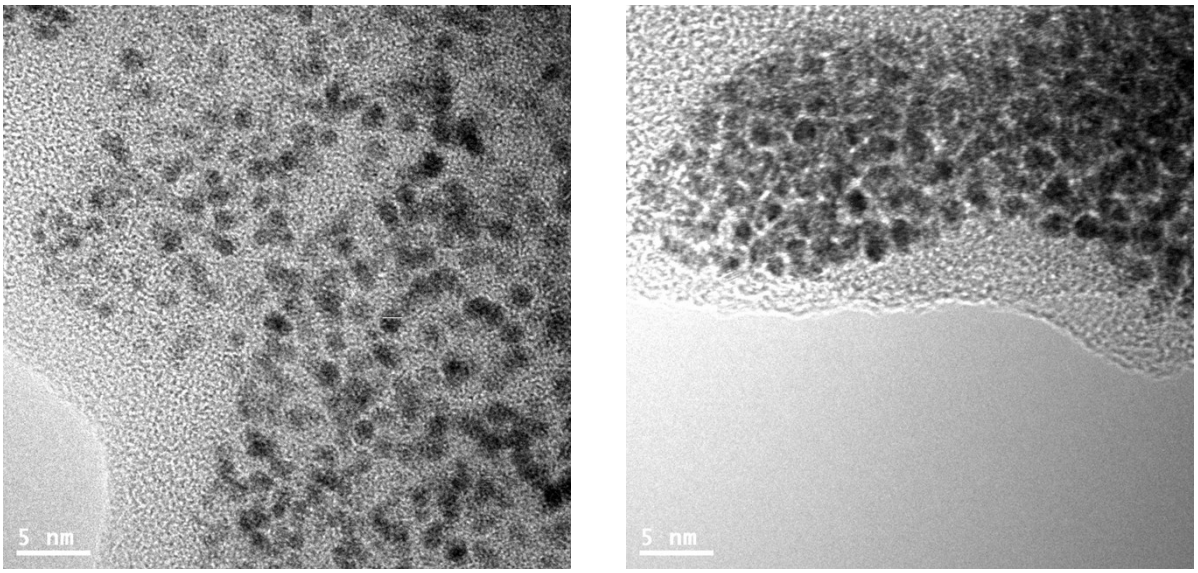


Figure S2. Ground state UV-Vis absorption spectrum of the IrO_x-NP **2** in water, [Ir] ~ 1.0 mM (prepared from dilution of 1.22 mM suspension), room temperature. a.u. = arbitrary unit.



(a) **(b)**

Figure S3. Transmission Electron Microscopy images of the IrO_x-NPs **2** (a) and IrO_x-NPs **4** (b).

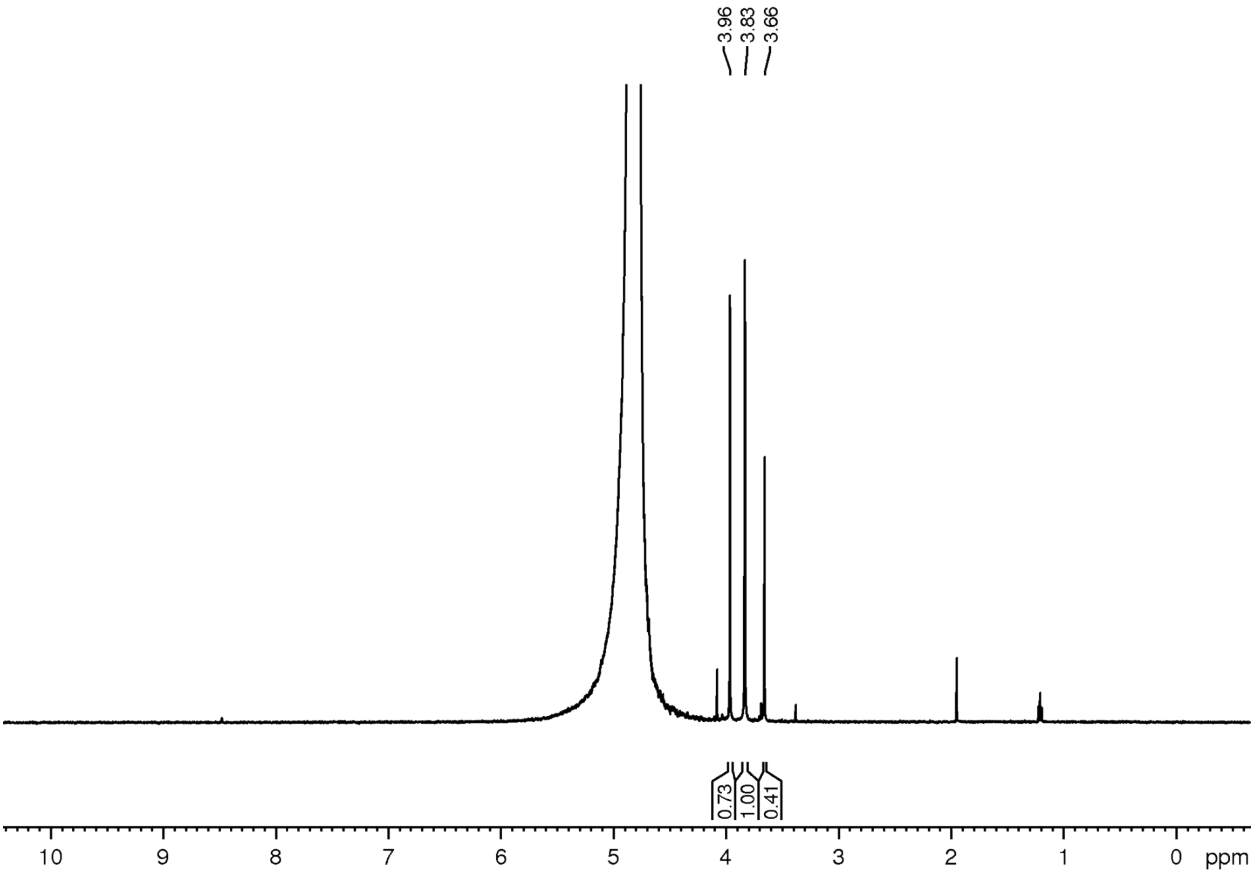


Figure S4. ^{1}H NMR spectrum of the IrOx-NP **2** (500 MHz, D_2O, 298K).

Some of the iodomethyl functionalities underwent nucleophilic substitution reactions with the excess of hydroxyl ions present in the reaction medium during the synthesis of **2**. Therefore, the IrOx-NPs' surfaces are partially and randomly decorated with hydroxymethyl groups. Accordingly, this side reaction deactivates some of the iodomethyl groups, thus precluding complete (100% yield) decoration of the IrOx-NPs' surfaces with azide functionalities. By comparing the relative intensities of the signals at 3.66, 3.83 and 3.96 ppm, which correspond to the resonances of the methylene groups in –C$\underline{H_2}$–I, –C$\underline{H_2}$–N_3 and –C$\underline{H_2}$–OH moieties, respectively, we roughly estimated that the surface of the IrO_xNP **2** is randomly decorated with about 47% –CH_2–N_3, 19% –CH_2–I and 34% –CH_2–OH functionalities. As the hydroxymethyl and iodomethyl groups are unreactive under the "click" conditions that afford IrOx-NP **4** and assuming 100% yield for the "click" reaction (no free compound **1** was detected by UV-Vis spectroscopy in the dichloromethane fractions afforded from the washing of IrOx-NP **4** before purification by dialysis), the theoretical yield for the attachment of compound **1** to IrOx-NP **2** is about 47%.

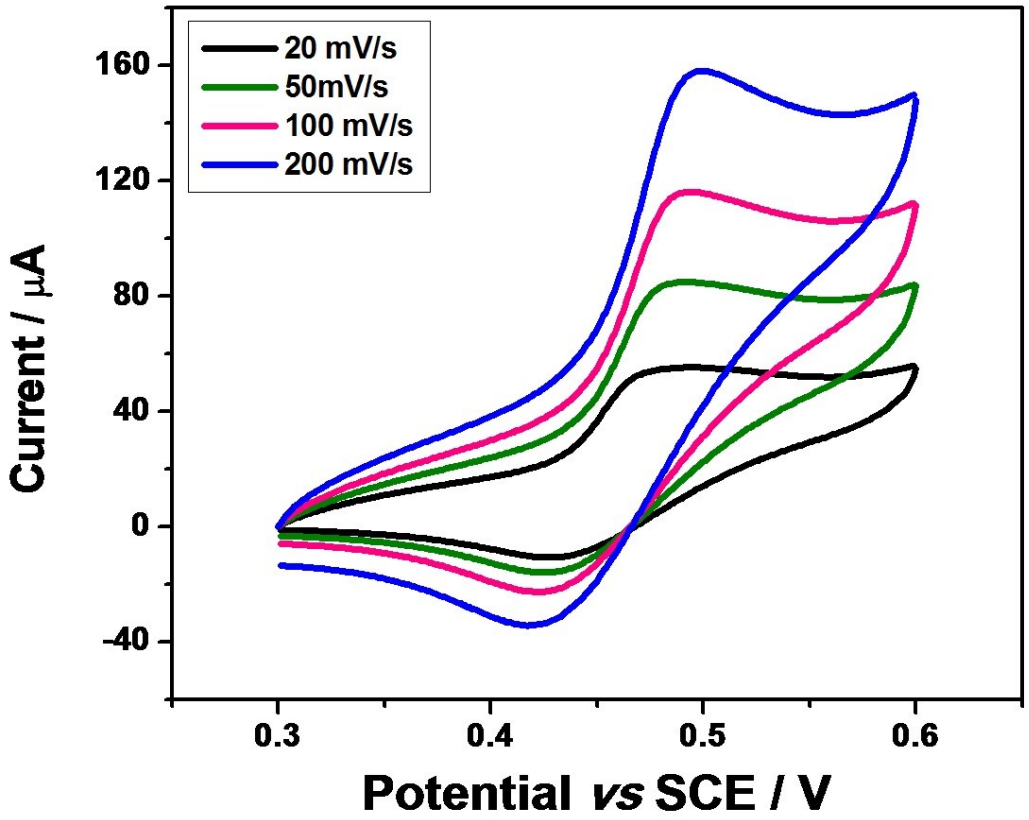


Figure S5. Cyclic voltammetry of IrOx-NP **2** ([Ir] = 1.22 mM) at several scan rates in the potential range for the $Ir^{V/IV}$ redox pair (working electrode: glassy carbon; reference electrode: SCE; counter electrode: platinum wire; support electrolyte: 0.1 M KNO_3; buffer: 0.1 M PBS pH 7.4).

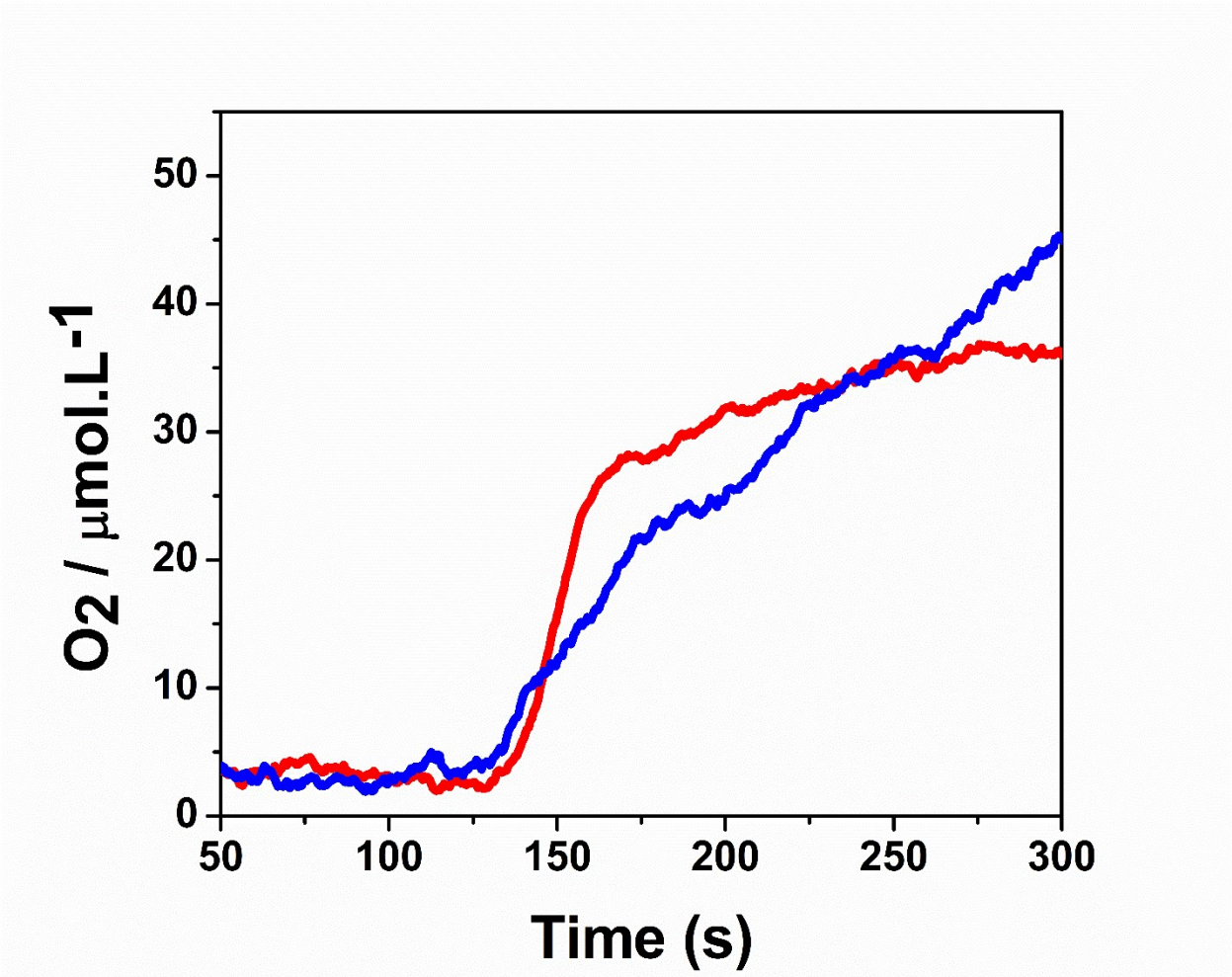
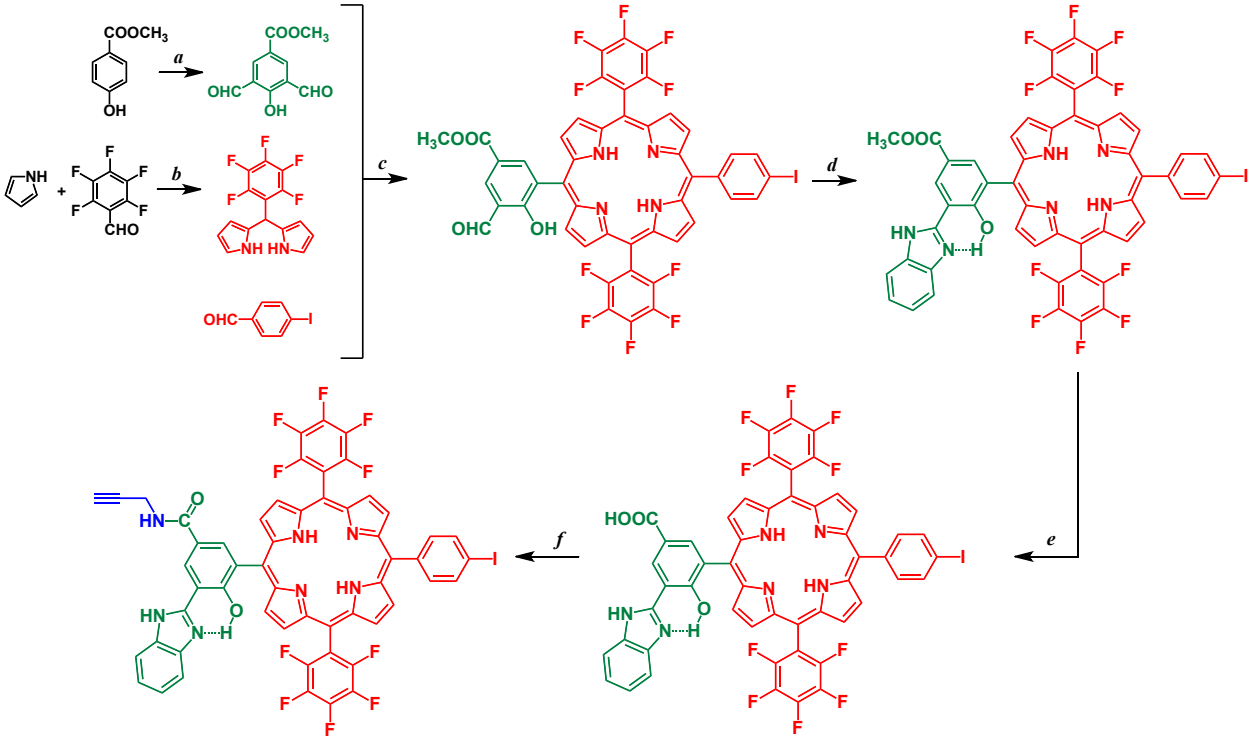


Figure S6. Oxygen evolution detected on a solution of IrOx-NP **2** ([Ir] = 1.22 mM) (blue trace) and IrOx-NP **4** ([Ir] = 1.22 mM) (red trace) upon applying a steady potential of 1.5 V vs SCE from 125 s. This experiment demonstrates that functionalized IrOx-NPs **2** and **4** are catalytically active in the water oxidation reaction.

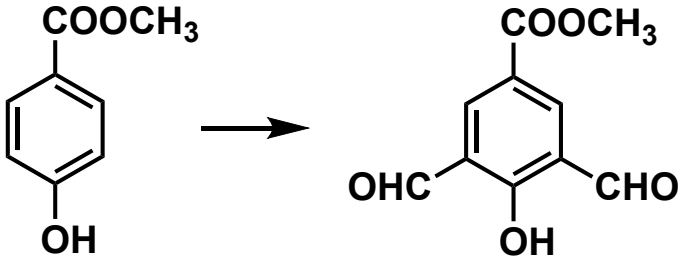
1.4 – Synthesis [S1-S3]

Scheme 1. Overview of the synthetic strategy used for the preparation of compound **1**.



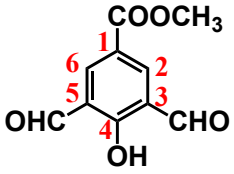
a) hexamethylenetetramine, trifluoroacetic acid, reflux, 24 h; *b)* trifluoroacetic acid, room temperature, 30 min; *c) i)* BF_3OEt_2, chloroform, room temperature, 2 h; *ii)* 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), room temperature for 24 h, and then in toluene at reflux for 2 h; *d)* orthophenylenediamine, nitrobenzene, reflux, 8 h; *e)* hydrochloric acid/trifluoroacetic acid mixture (2:1, v/v), reflux, 24 h; *f)* dichloromethane, propargyl amine, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 4-dimethylaminopyridine (DMAP), room temperature, 20 h.

Methyl-3,5-diformyl-4-hydroxybenzoate **S1**:



S1

Commercially available methyl-4-hydroxybenzoate (1.52 g, 10 mmol, 1 equiv.), hexamethylenetetramine (3.50 g, 25 mmol, 2.5 equiv.) and trifluoroacetic acid (10 mL) was heated at reflux for 24 h. The reaction was quenched while hot with water (5 mL) and the resulting mixture was allowed to cool to room temperature with stirring. The crude product was extracted with diethyl ether (3 × 15 mL), and the extract was neutralized with a saturated aqueous solution of sodium bicarbonate and finally washed with water (3 × 50 mL). The organic phase was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. The crude product was taken up in dichloromethane and the white precipitated was filtered off through paper. The filtrate was concentrated and final purification was achieved by column chromatography (SiO_2), using dichloromethane/ethyl acetate as eluent to afford the title compound **S1** as a white solid in 45% yield (0.93 g).



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 12.05 (s, 1H, OH); 10.28 (s, 2H, CHO); 8.65 (s, 2H, $H_{4,6}$); 5.30 (s, residual CH_2Cl_2); 3.96 (s, 3H, $COOCH_3$); 2.17 (s, residual acetone); 1.54 (s, residual water in the deuterated solvent).

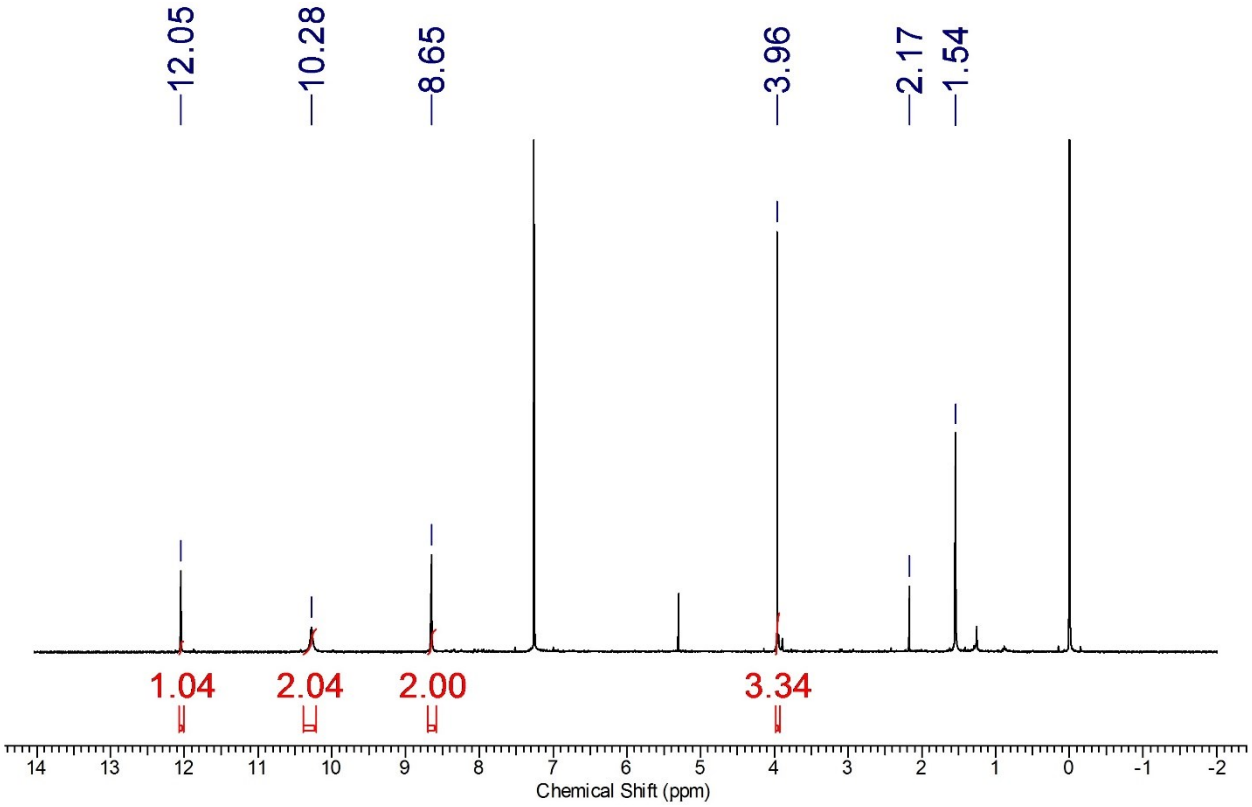
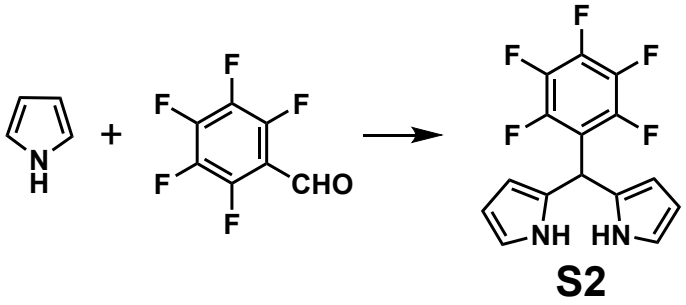


Figure S7. ^{1}H NMR spectrum of compound **S1**, 400 MHz, $CDCl_3$, 25 °C.

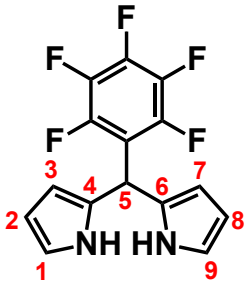
5-(Pentafluorophenyl)dipyrromethane **S2**:



S2

A solution of pentafluorobenzaldehyde (2.0 mL, 16.2 mmol, 1 equiv.) in freshly distilled pyrrole (50 mL, 720 mmol, 44.45 equiv.) was degassed with a stream of argon for 10 min before adding trifluoroacetic acid (0.12 mL, 1.62 mmol, 0.1 equiv.). The mixture was stirred for 30 min at room temperature, diluted with CH_2Cl_2 (400 mL), and then washed with 0.1 M NaOH (400 mL). The organic phase was washed with water (400 mL) and dried over Na_2SO_4. Evaporation of the solvent at reduced pressure gave a brown oil. Unreacted pyrrole was removed under high vacuum at room temp, yielding a tacky solid that was purified by flash chromatography on a column of silica using a mixture of hexanes/ethyl

acetate/triethylamine (80:20:1) as the eluent. The product was recrystallized from dichloromethane/hexanes to yield 3.29 g of 5-(pentafluorophenyl)dipyrromethane **S2** as a white powder in 65% yield (3.28 g).



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.11 (2H, brs, N$\underline{H}$), 6.73 (2H, m, C$\underline{H}_1$ and C$\underline{H}_9$), 6.16 (2H, m, C$\underline{H}_2$ and C$\underline{H}_8$), 6.02 (2H, brs, C$\underline{H}_3$ and C$\underline{H}_7$), 5.89 (1H, brs, C$\underline{H}_5$), 5.29 (residual solvent C$\underline{H}_2Cl_2$), 1.54 (residual water in the deuterated solvent).

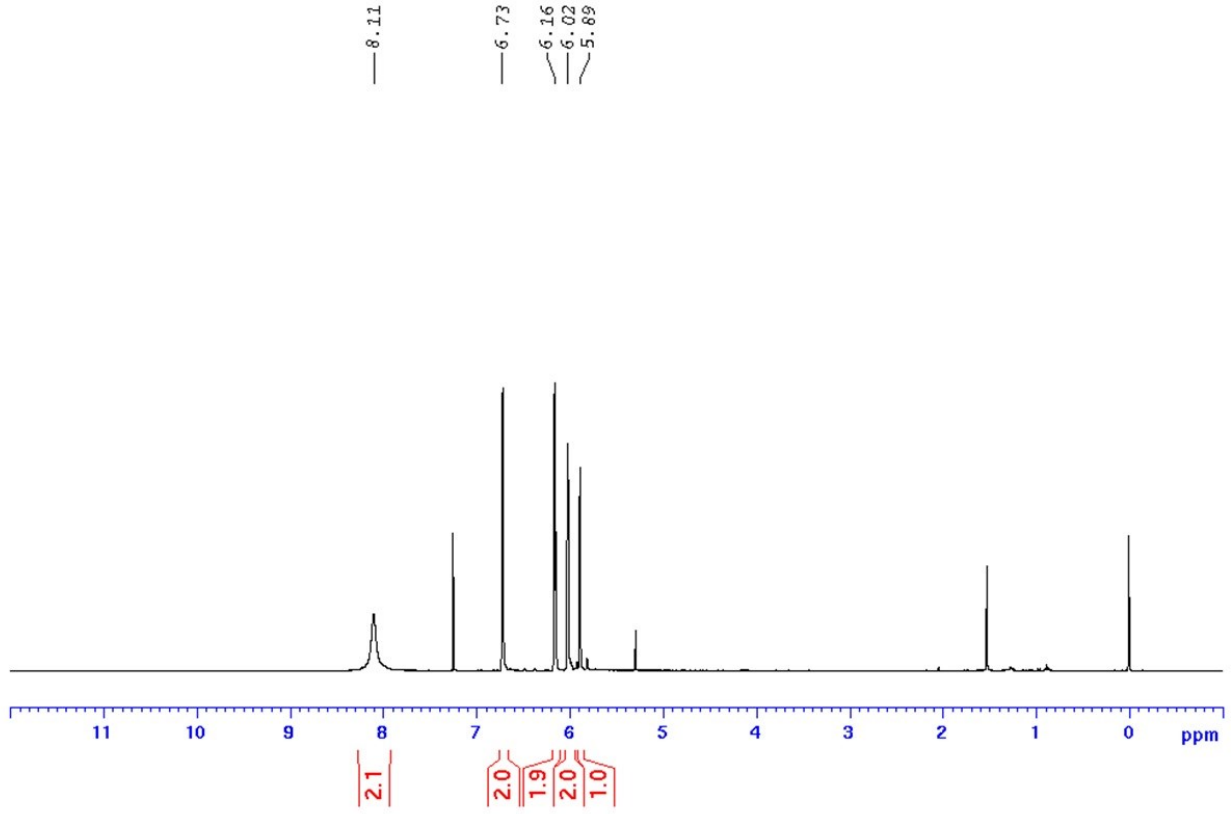
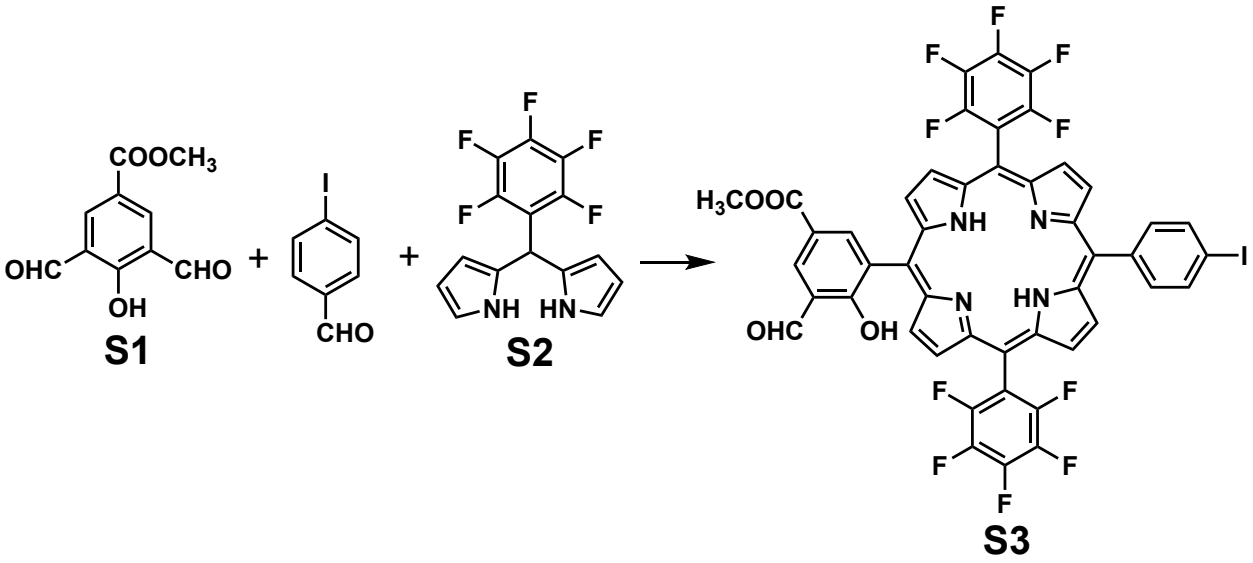
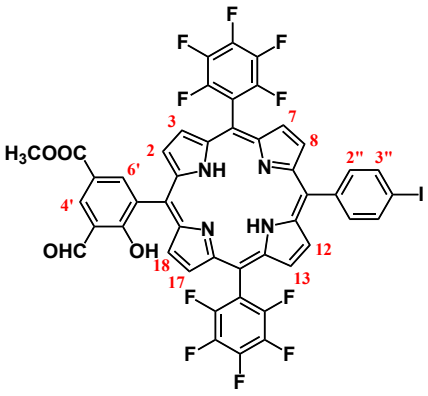


Figure S8. ^{1}H NMR spectrum of compound **S2**, 400 MHz, $CDCl_3$, 25 °C.

5,15-*bis*(pentafluorophenyl)-10-(4-iodophenyl)-20-(2-hydroxy-3-formyl-5-methoxycarbonylphynyl)porphyrin **S3**:



Compound **S1** (0.183 g, 0.88 mmol, 1 equiv.), 4-iodobenzaldehyde (0.306 g, 1.32 mmol, 1.5 equiv.) and dipyrromethane **S2** (0.690 g, 2.21 mmol, 2.5 equiv.) were dissolved in 350 mL of chloroform containing 2.7 mL (0.75%, v/v) of anhydrous ethanol under a nitrogen atmosphere, to which boron-trifluoride etherate (BF_3OEt_2) was added (0.120 g, 0.106 mL, 0.85 mmol, 1 equiv.), and the reaction mixture was stirred for 2 h at room temperature. The resulting dark red porphyrogenic mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.567 g, 2.50 mmol, 2.8 equiv.) for 24 h at room temperature to yield a black crude mixture that was concentrated under reduced pressure. The crude product was dissolved in 100 mL of toluene and another portion of DDQ (0.567 g, 2.50 mmol, 2.8 equiv.) was added and the resulting black solution was heated at reflux for 2 h to complete the porphyrogen oxidation reaction and to over oxidizing fluorinated byproducts with close R_f values to that of the target porphyrin in order to facilitate the purification process. Filtration through a silica pad to remove tar and polymeric byproducts, followed by concentration under reduced pressure, afforded a deep purple reddish solid. Purification through column chromatography (SiO_2) using a gradient of hexanes/dichloromethane (from 0 to 60 %, v/v) as eluent yielded the target porphyrin **S3** as a purple solid in 9 % yield (0.101 g).



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 11.88 (1H, s, OH); 10.32 (1H, s, CHO); 8.97 (1H, d, J = 2.0 Hz, $H_{4'}$); 8.94 (2H, d, J = 5.0 Hz, H_2 and H_{18}); 8.86 (1H, d, J = 2.0 Hz, $H_{6'}$); 8.82 (6H, br, H_3, H_7, H_8, H_{12}, H_{13} and H_{17}); 8.15 (2H, d, J = 8.0 Hz, $H_{3''}$); 7.95 (2H, t, J = 8.0 Hz, $H_{2''}$); 5.30 (residual dichloromethane); 3.98 (3H, s, $COOCH_3$); 2.17 (residual acetone); 1.54 (residual water in the deuterated solvent); -2.83 (2H, s, internal NH). MALDI-TOF: (*m/z*, positive mode, 1,4-diphenylbutadiene as matrix) 1022.74 $[M]^+$; 1022.0 calculated for $C_{47}H_{21}F_{10}N_4O_4I$.

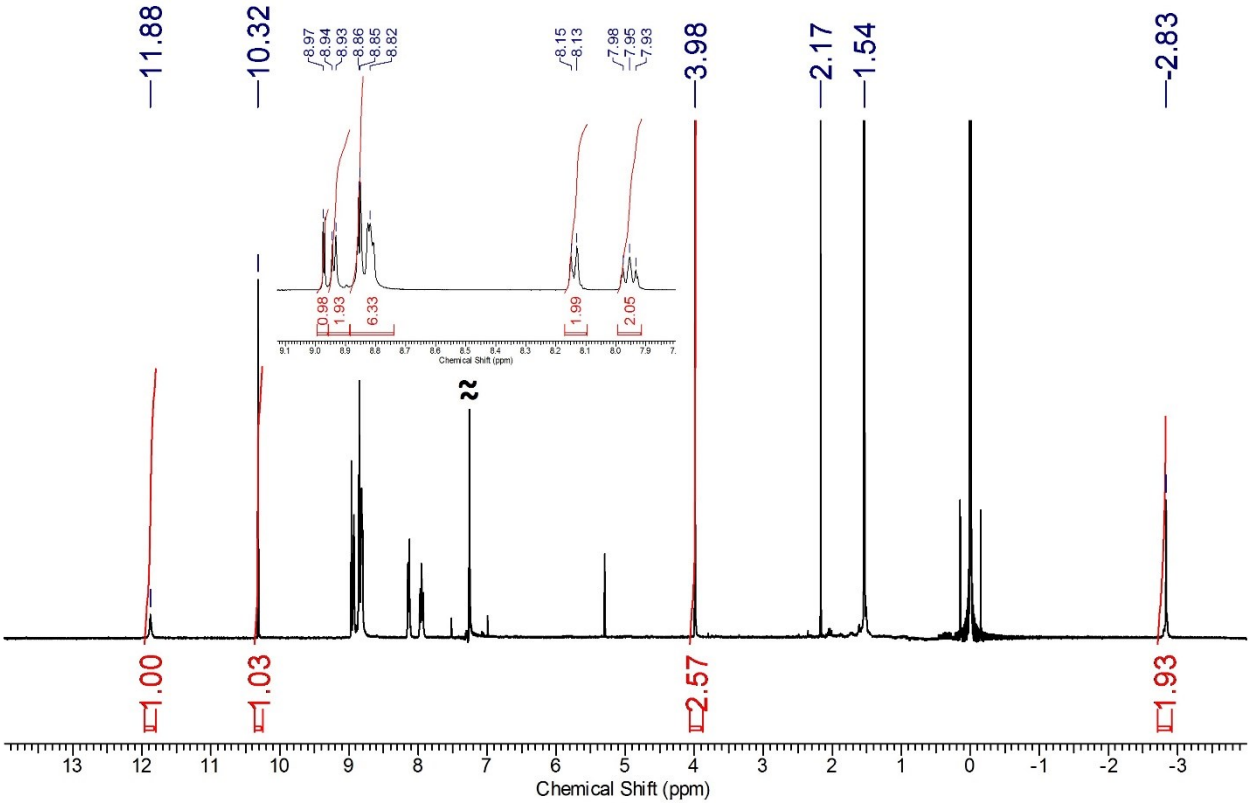
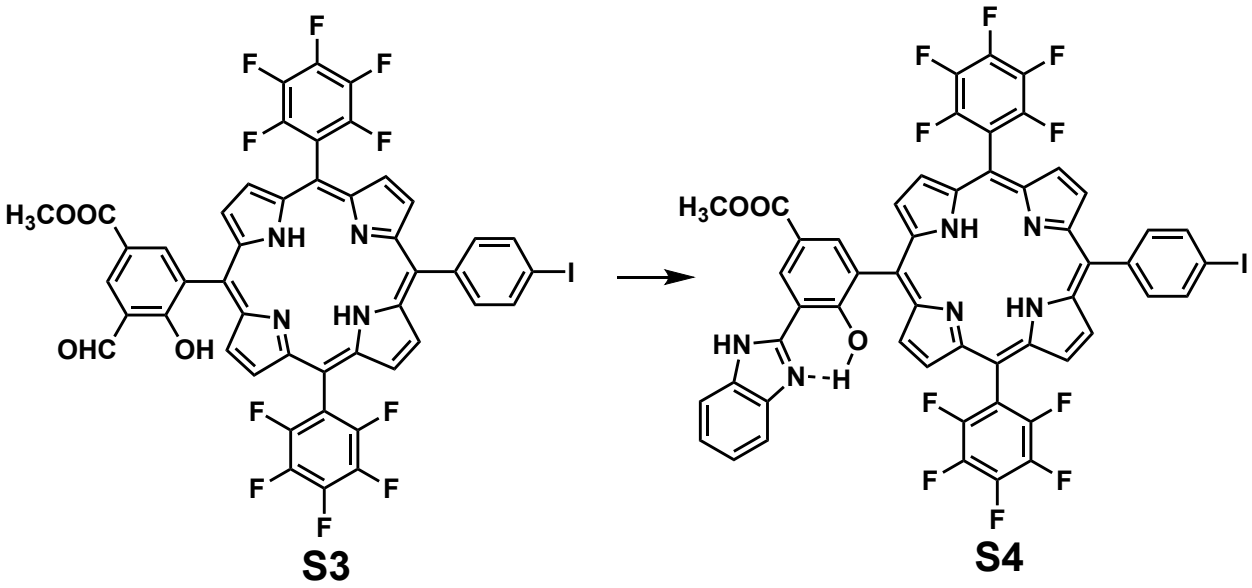
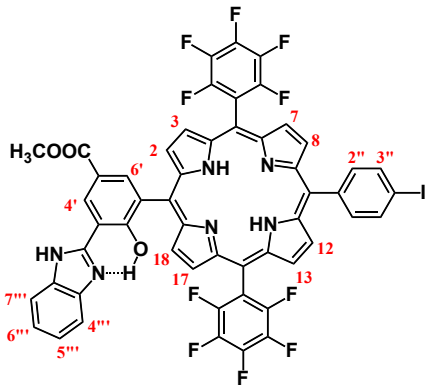


Figure S9. ^{1}H NMR spectrum of porphyrin **S3**, 400 MHz, $CDCl_3$, 25 °C.

5,15-*Bis*(pentafluorophenyl)-10-(4-iodophenyl)-20-[2'-(5"-methoxycarbonyl-2"-hydroxyphenyl)benzimidazole]porphyrin **S4**.



A solution of porphyrin **S3** (0.070 g, 0.068 mmol, 1 equiv.) in 6 mL of nitrobenzene was added drop-wise to a 1 mL solution of commercially available 1,2-phenylenediamine (0.008 g, 0.076 mmol, 1.1 equiv.) in nitrobenzene at room temperature and under inert atmosphere. The resulting purple solution was heated at reflux (210 °C) in a sand bath for 8 h. After cooling and without any workup, the crude mixture was transferred to a chromatography column (SiO_2 in hexanes) and nitrobenzene was eluted with a mixture of hexanes/ethyl acetate (98:2, v/v). The remaining purple products were then eluted with hexanes/ethyl acetate (80:20, v/v) and evaporated to dryness. Final purification was achieved by column chromatography (SiO_2) using a gradient mixture of hexanes/dichloromethane/ethyl acetate (5:3:1, v/v) as eluent to yield the target porphyrin **S4** as a purple solid in 85% yield (0.065 g).



^{1}H NMR (400 MHz, CD_3CN, δ ppm): 14.60 (1H, br, OH); 11.65 (1H, s, NH-benzimidazole); 9.11 (1H, d, J = 2.0 Hz, $H_{4'}$); 9.08 (2H, d, J = 5.1 Hz, H_2 and H_{18}); 9.04 (4H, s, H_3, H_7, H_{13} and H_{17}); 8.96 (2H, d, J = 5.1 Hz, H_8 and H_{12}); 8.75 (1H, d, J = 2.0 Hz, $H_{6'}$); 8.12 (2H, m, $H_{5'''}$ and $H_{6'''}$); 7.97 (1H, d, J = 8.3 Hz, $H_{7'''}$); 7.91 (1H, d, J = 8.3 Hz, $H_{4'''}$); 3.94 (3H, s, $COOCH_3$); 2.16 (s, residual water in the

deuterated solvent); 1.93 (residual CH_3CN in the deuterated solvent); -2.94 (2H, s, internal NH). MALDI-TOF: (*m/z*, negative mode, 1,4-diphenylbutadiene as matrix) 1109.87 $[M]^-$; 1110.1 calculated for $C_{53}H_{25}F_{10}N_6O_3I$.

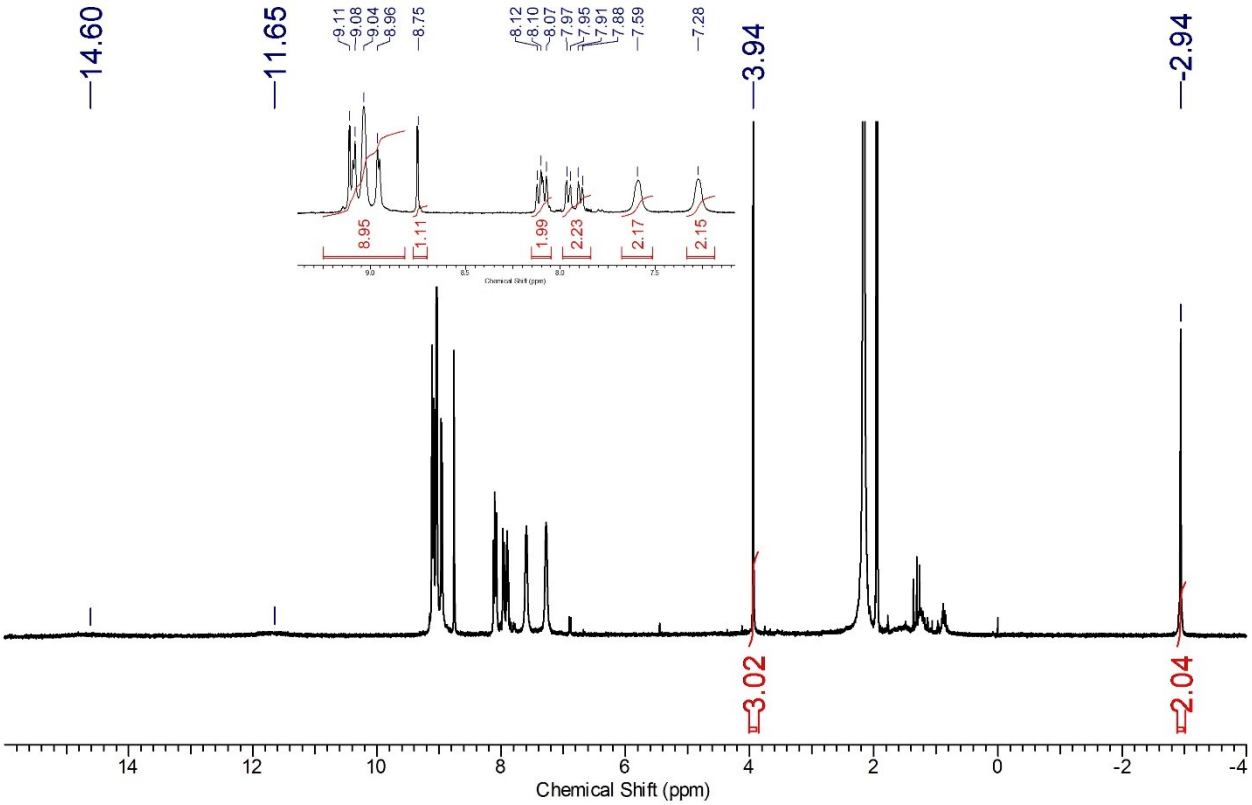


Figure S10. ^1H NMR spectrum of porphyrin **S4**, 400 MHz, CD_3CN, 25 °C.

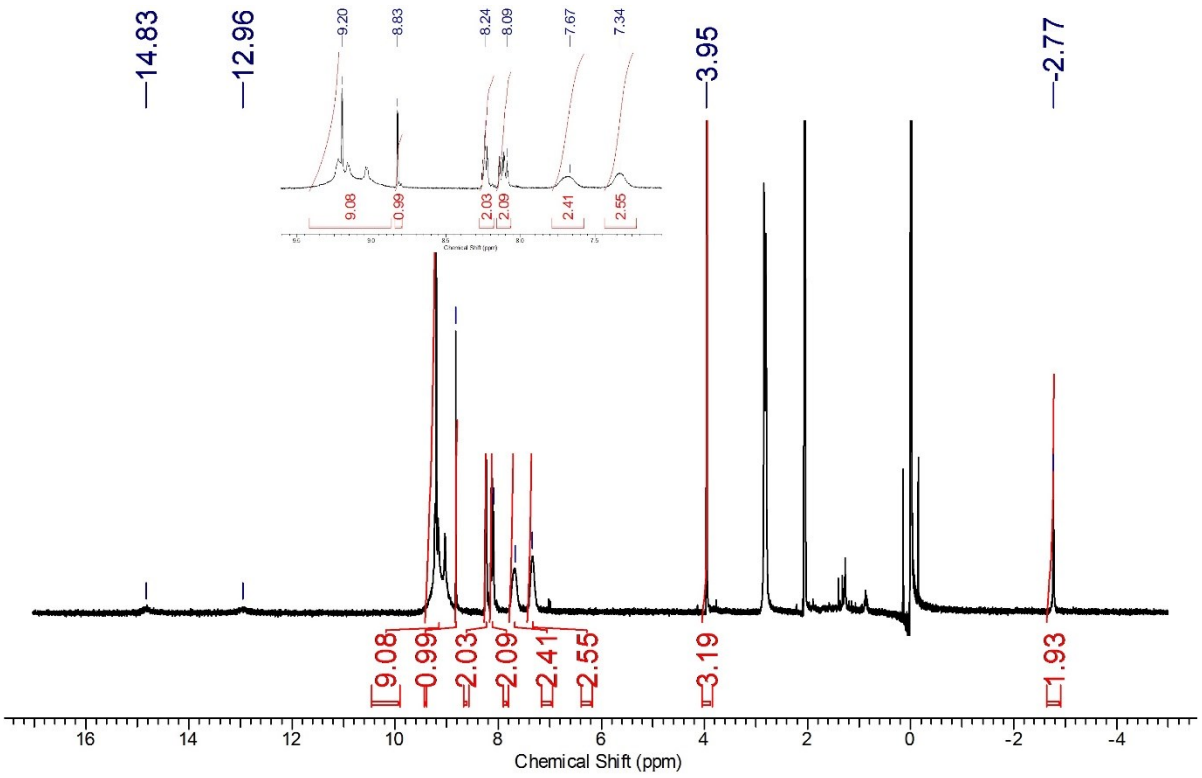


Figure S11. ^{1}H NMR spectrum of porphyrin **S4**, 400 MHz, CD_3COCD_3, 25 °C.

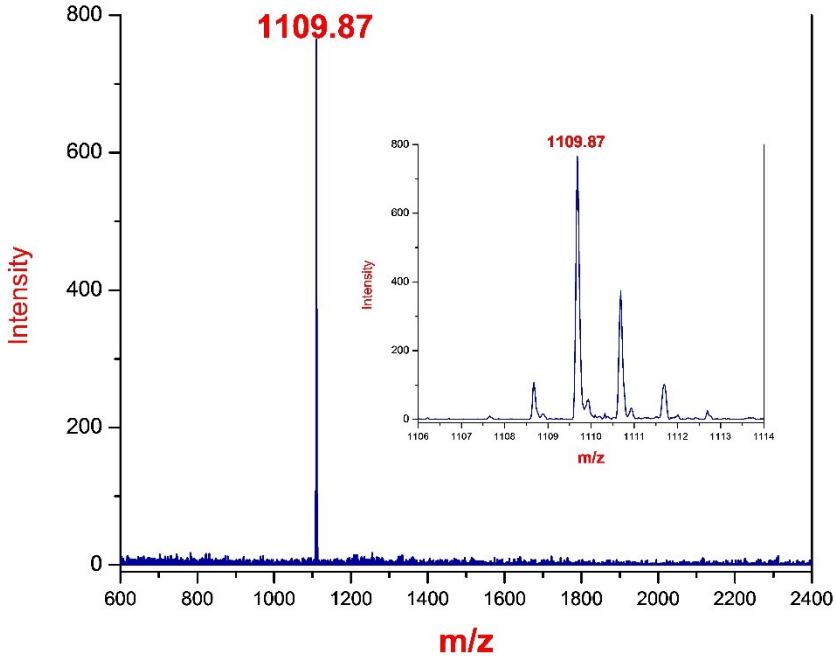
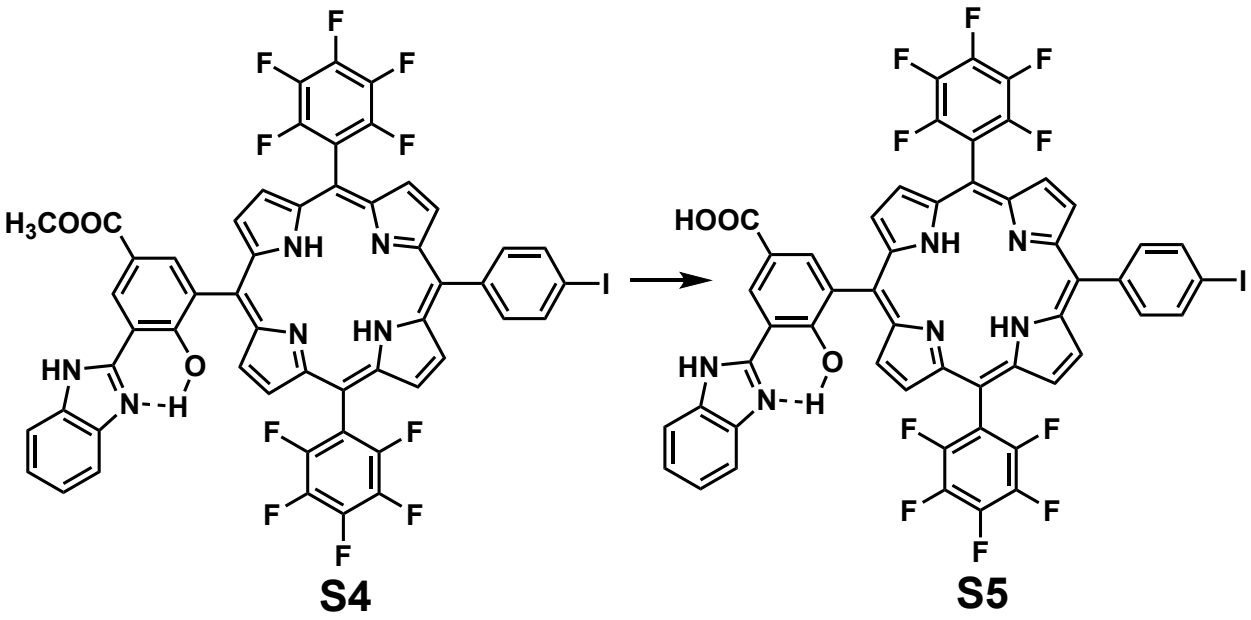


Figure S12. MALDI-TOF spectrum (negative mode, 1,4-diphenylbutadiene as matrix) of porphyrin **S4** and corresponding isotope distribution afforded for $C_{53}H_{25}F_{10}N_6O_3I$.

5,15-*Bis*(pentafluorophenyl)-10-(4-iodophenyl)-20-[2'-(5"-carboxy-2"-hydroxyphenyl)benzimidazole]porphyrin **S5**.



Porphyrin **S4** (0.060 g, 0.054 mmol) was dissolved in 5 mL of trifluoroacetic acid, and 10 mL of concentrated HCl was added. The resulting green mixture was stirred at reflux for 24 h. After cooling, the mixture was taken up in dichloromethane (50 mL), washed with water (50 mL) and then neutralized with a saturated aqueous sodium carbonate solution. The organic phase was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2) using a mixture of dichloromethane/methanol (9:1, v/v) as eluent to afford 0.058 g (98% yield) of the target porphyrin **S5** as a purple solid. MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1096.52 [M]+, calculated 1096.1 for $C_{52}H_{23}F_{10}N_6O_3I$.

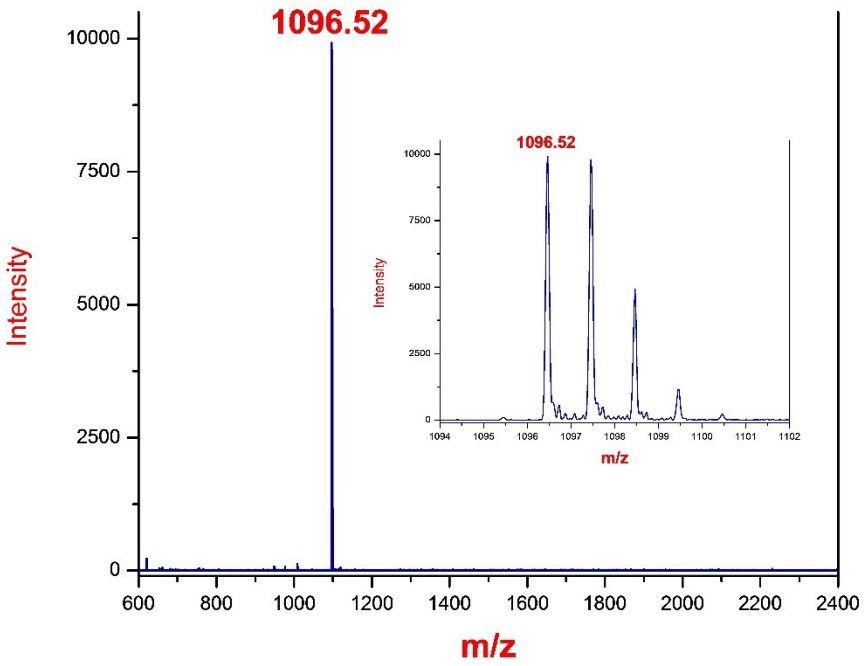
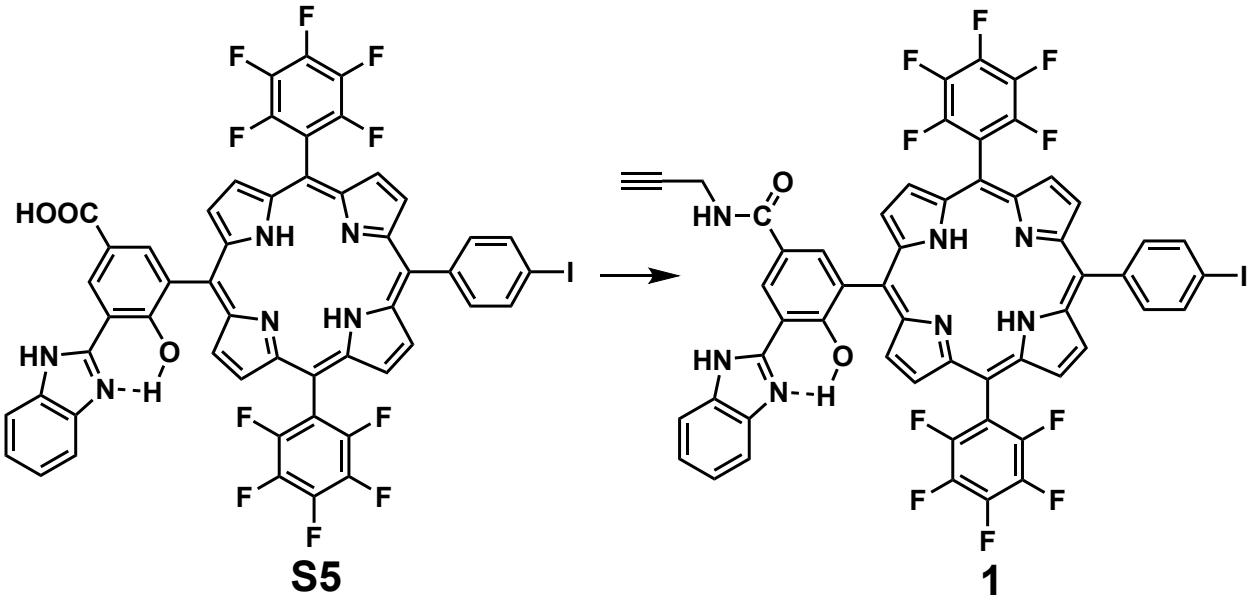


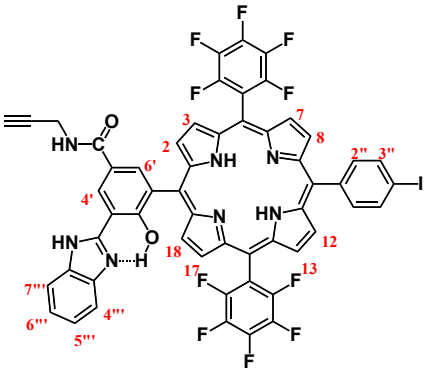
Figure S13. MALDI-TOF spectrum (negative mode, 1,4-diphenylbutadiene as matrix) of porphyrin **S5** and corresponding isotope distribution afforded for $C_{52}H_{23}F_{10}N_6O_3I$.

5,15-*Bis*(pentafluorophenyl)-10-(4-iodophenyl)-20-[3'-(1*H*-benzo[*d*]imidazol-2-yl)-4'-hydroxy-*N*-(prop-2-yn-1-yl)benzamide]porphyrin **1**.



Porphyrin **S5** (0.028 g, 0.025 mmol, 1 equiv.) was dissolved in 10 mL of dry dichloromethane at room temperature and under nitrogen atmosphere. To the resulting

purple solution were added DMAP (0.016 g, 0.125 mmol, 5 equiv.), propargylamine (0.0055 g, 0.1 mmol, 6.5 μL, 4 equiv.) and EDCI (0.01 g, 0.05 mmol, 2 equiv.) in this order and the reaction mixture was stirred at room temperature for 20 h. The crude product was washed with water (3 x 10 mL), dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using a mixture of dichloromethane/methanol (99:1, v/v) as eluent to yield the target porphyrin **1** as a purple solid in 80% yield (0.023 g).



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.37 (1H, s, NH-benzimidazole); 8.98 (2H, d, J = 4.8 Hz, H_2 and H_{18}); 8.93 (2H, d, J = 4.8 Hz, H_8 and H_{12}); 8.81 (4H, m, H_3, H_7, H_{13} and H_{17}); 8.46 (1H, s, CONH); 8.14 (2H, m, $H_{5'''}$ and $H_{6'''}$); 8.01 (1H, s, $H_{4'}$); 7.94 (1H, d, $H_{6'}$); 7.78 (0.3H, d, $H_{4'''}$); 7.56 (2H, br, $H_{3''}$); 7.09 (0.7H, d, $H_{4'''}$); 6.89 (2H, br, $H_{2''}$); 6.73 (0.5H, d, $H_{7'''}$); 6.57 (0.5H, d, $H_{7'''}$); 4.36 (2H, s, CH_2C≡CH); 4.04 (1H, m, C≡CH); 1.54 (residual water in the deuterated solvent); -2.82 (2H, s, internal NH). MALDI-TOF: (*m/z*, positive mode, 1,4-diphenylbutadiene as matrix) 1134.55 $[M + H]^+$; 1133.1 calculated for $C_{55}H_{26}F_{10}N_7O_2I$.

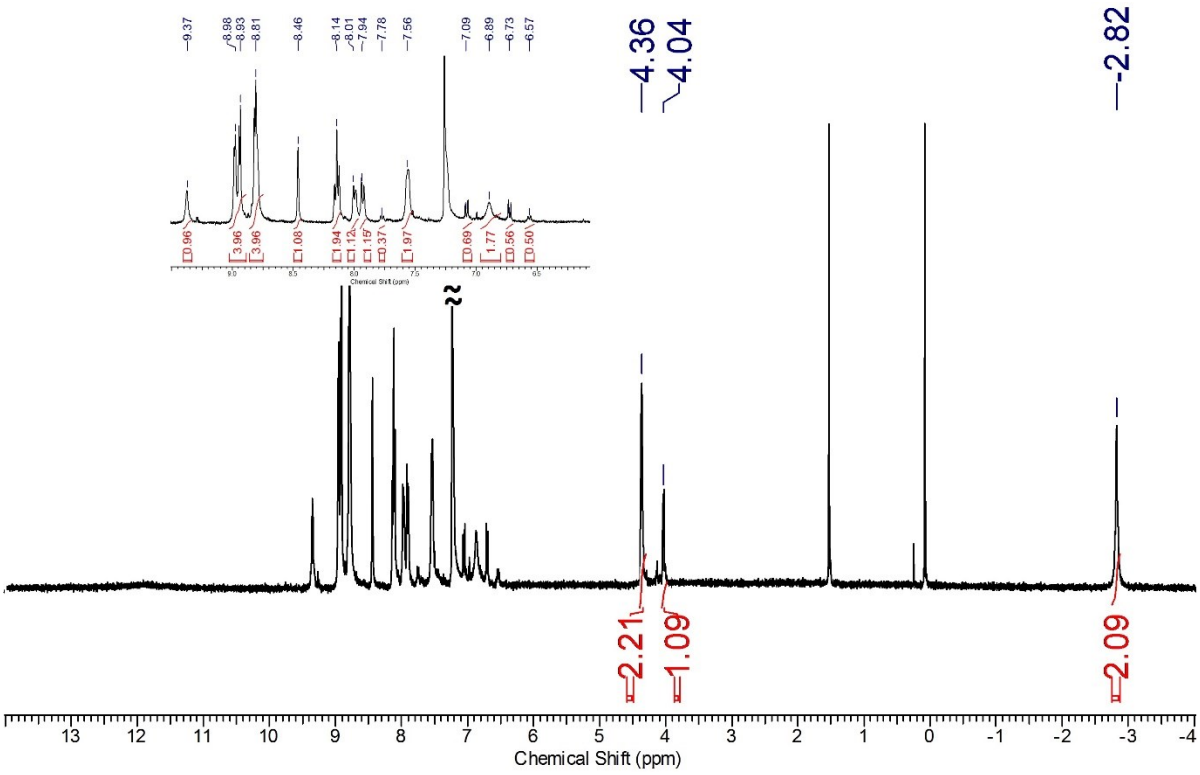


Figure S14. ^{1}H NMR spectrum of compound **1**, 500 MHz, CD_3COCD_3, 25 °C.

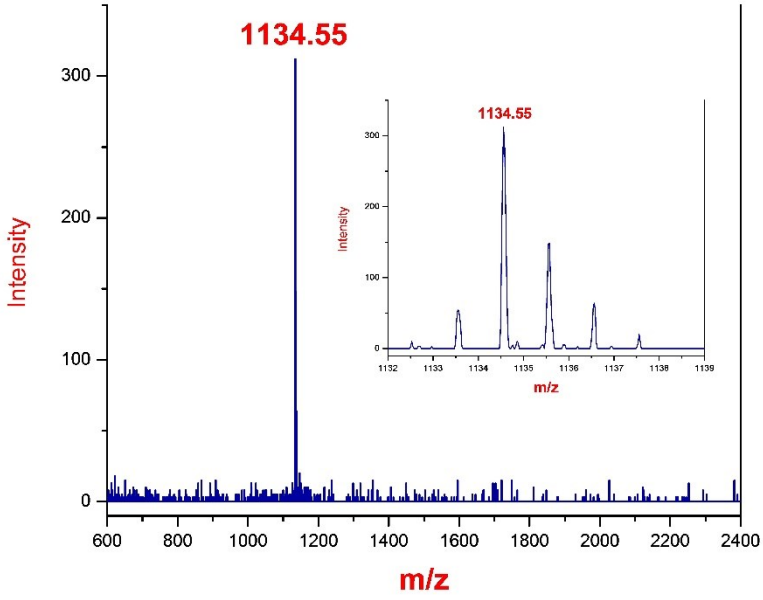


Figure S15. MALDI-TOF spectrum (negative mode, 1,4-diphenylbutadiene as matrix) of compound **1** and corresponding isotope distribution afforded for $C_{55}H_{26}F_{10}N_7O_2I$.

1.5 – Preparation of the "Click" Catalyst.[S4-S7]

In a 20 mL glass vial, copper iodide (0.008 g, 0.042 mmol, 1 equiv.), sodium ascorbate (0.033 g, 0.17 mmol, 4 equiv.) and sulfonated bathophenanthroline (0.045 g, 0.084 mmol, 2 equiv.) were dissolved in 10 mL of a well-degassed solvent mixture composed of ethanol and water (1:1, v/v). The glass vial was tightly closed with a Teflon-coated plastic cap and the resulting pink suspension was heated at reflux for 2 min with a heat gun. The resulting dark red catalytic solution was allowed to cool back to room temperature and was used in the "click" reactions between the iridium oxide nanoparticles and the bio-inspired photosynthetic model without further manipulation.

1.6 – One-Pot Methodology for Preparation of the Iridium Oxide Nanoparticles 2.

In a 20 mL glass vial, iodoacetic acid (0.046 g, 0.25 mmol) was dissolved in 17 mL of water, and K_2IrCl_6 (0.010 g, 0.021 mmol) was added. The pH of the solution was adjusted to 10 using an aqueous solution of NaOH (around 70 μL of a 25% w/w solution). The solution was heated at 90°C in an oil bath for 2h under magnetic stirring (500 rpm). The resulting deep blue solution of IrOx-CH_2I-NPs was cooled to 65°C, and sodium azide (0.033 g, 0.50 mmol) was added to the glass vial and the reaction mixture was stirred for 2h under magnetic stirring (500 rpm). The reaction solution was cooled to r.t. and purified by dialysis against water (MWCO 2000). Assuming a 100% yield with respect to Ir,[S8] the resulting Ir concentration in the NPs' aqueous suspension is about 1.22 mM. The IrOx-NP **2** was characterized by IR, UV-Vis, TEM and CV.

1.7 – Preparation of the Iridium Oxide Nanoparticles 4 using "click" reaction.

For this experiment, we assumed that IrOx-NP **2** with 2 nm in diameter have about 66 Ir atoms per NP considering a rutile lattice for IrOx-NP **2**.[S9] Seventeen mL of IrOx-NP **2** ([Ir] = 1,22 mM, considering 100% yield for formation of IrOx-NP **2** with respect to K_2IrCl_6, [IrOx-NP **2**] = 0.0185 mM, 20.7 μmol of Ir, 0.314 μmol of IrOx-NP **2**, 1 equiv.) were introduced in a 20 mL glass vial, which was capped with a rubber septum. The solution was bubbled with argon for about 10 minutes and 0.46 mL of an THF solution of compound **1** (4 mg/mL) (1.84 mg, 1.62 μmol, 5 equiv.) was added under argon atmosphere, followed by 0.9 mL of the freshly prepared Cu^I "Click" catalyst solution. The

reaction mixture was further bubbled with argon for 2 minutes, and gently stirred magnetically (200 rpm) at room temperature for 24 hours. The aqueous solution containing IrOx-NP **4** was washed with dichloromethane (3 x 5 mL) and purified by dialysis against water following the procedure described in the material section of the present supporting information.

2 – References

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