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Supporting Information

Interfacial Electron Transfer in Photoanodes based on Phosphorus(V) Porphyrin Sensitizers Co-deposited on SnO_2 with the Ir(III)Cp* Water Oxidation Precatalyst

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Methods.

NMR and Mass Spectroscopy. NMR spectra were recorded with Bruker Avance 300 MHz and 600 MHz Digital NMR spectrometers using CD_3CN or $CDCl_3$ as the solvent. HR-FAB mass spectra were recorded on a Kratos Concept 1S High Resolution E/B mass spectrometer.

Electrochemistry. Cyclic and differential pulse voltammetry experiments (CH_3CN, 0.1 M tetrabutylammonium hexafluorophosphate, $(TBA)PF_6$) were performed on a BAS Epsilon electrochemical analyzer (working electrode: glassy carbon, auxiliary electrodes: Pt wire, reference electrode: Ag wire). The Fc^+/Fc (Fc = ferrocene, $E_{1/2}(Fc^+/Fc) = 0.40$ V *vs* SCE in CH_3CN, 0.1 M $(TBA)PF_6$)[1] couple was used to calibrate the redox potentials and they were reported against NHE (NHE = SCE + 0.240 V). Sample concentrations were held at ~ 0.5 mM.

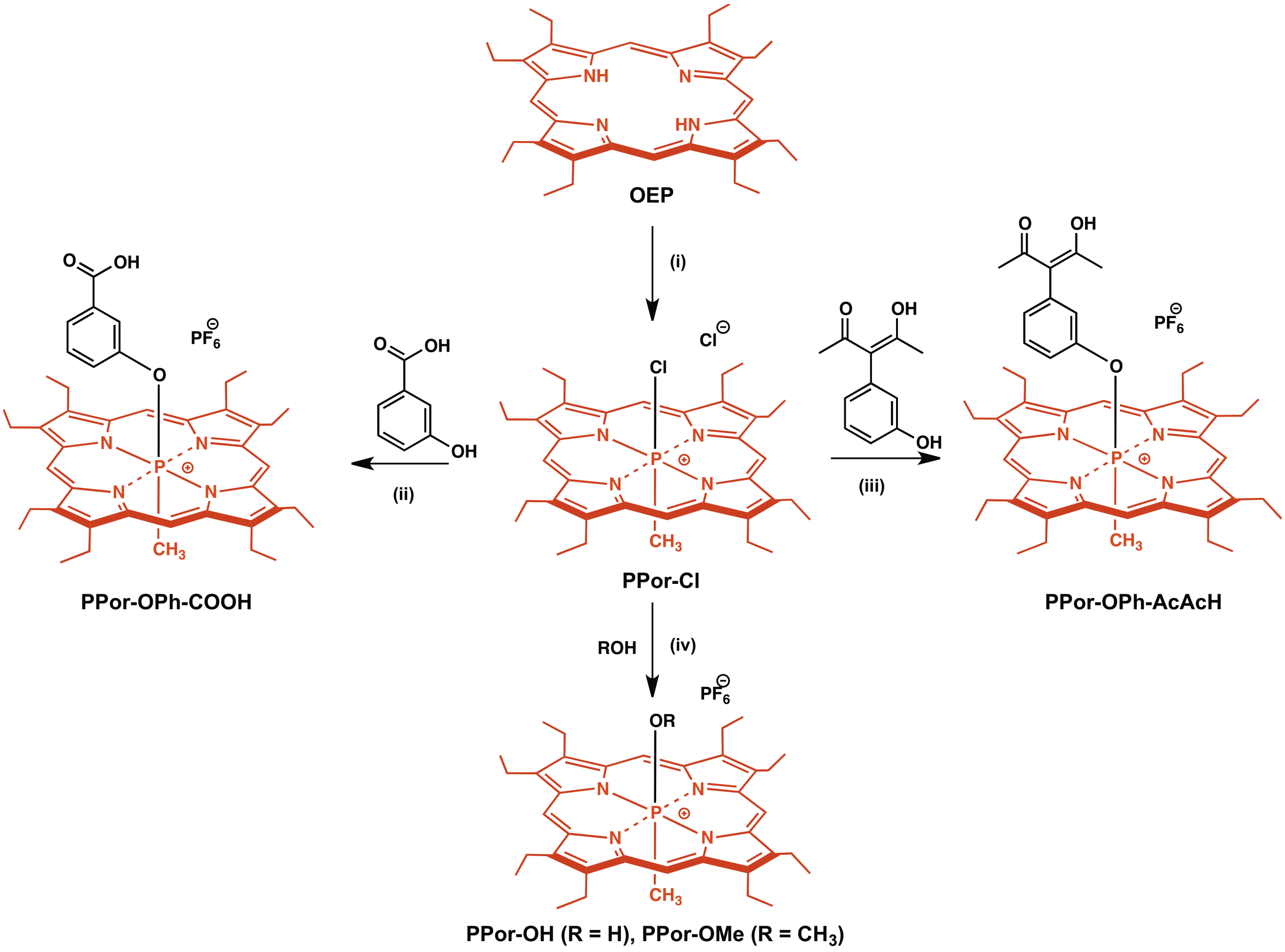
Absorption Spectroscopy. Solution UV-visible absorption spectra were recorded with a ThermoSpectronic/Unicam UV-4 UV-VIS spectrometer. The concentration of the samples used for these measurements ranged from 10^{-6} M (porphyrin Soret I band) to 10^{-5} M (Q-bands and Soret II bands) solutions. Surface-bound solid-state UV-visible absorption spectra (Diffuse-Reflectance Spectroscopy) were taken on a Varian Cary 3 spectrophotometer with an integrating sphere attachment. For comparison between solid and solution state spectra, the %absorptance was converted into absorbance.

Fluorescence Spectroscopy. Steady-state fluorescence spectra were recorded using a Photon Technologies International (London, Ontario) Quanta Master Model QM-2001 L-format, equipped with double-grating monochromators, a 150 W xenon lamp, and running Felix 32 software. An excitation wavelength of 550 nm, which corresponds to an exclusively porphyrin-based transition, was used and the concentrations were held constant at 0.1 mM for all the compounds.

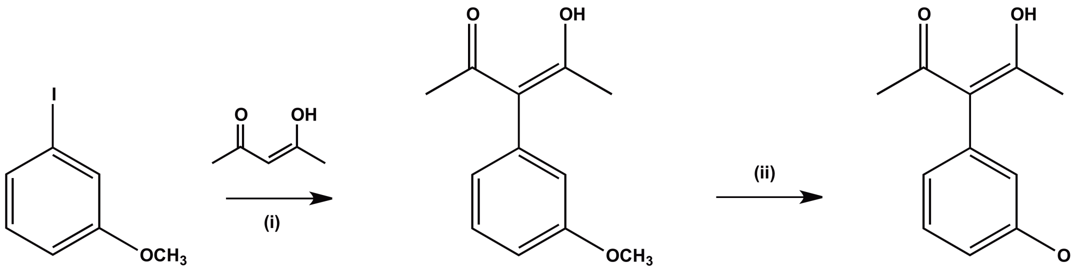
Synthesis

General. All chemicals used in this study were purchased from either Sigma-Aldrich or Alfa Aesar. Octaethylporphyrin (OEP) and the chromatography material Al_2O_3 (neutral AW 3) were obtained from Sigma-Aldrich. The precursor PPor-Cl and reference porphyrins PPor-OH and PPor-OMe were synthesized from OEP by previously established methods.[1] Synthesis of 3-(3-hydroxyphenyl)-acetylacetone (HO-Ph-AcAcH) was carried out according to the reported procedures, Scheme S2.[2] By NMR, we observed that over time one of the acetyl (Ac) groups is lost from the molecule. However, after linking HO-Ph-AcAcH to the PPor in the axial position, the acetyl group appears to be stabilized and decomposition is no longer observed. As shown in

Scheme S1, the porphyrins were prepared initially as their chloride salts. Counter ion exchange was performed by dissolving the chloride salt in ethanol and then precipitating as PF_6 salt by addition of saturated aqueous NH_4PF_6.



Scheme S1. Synthesis of PPor-Cl, PPor-OPh-COOH and PPor-OPh-AcAcH derivatives. Reaction conditions: (i) CH_3PCl_2, 2,6-lutidine, dry dichloromethane, reflux for 2 days under nitrogen. (ii, iii and iv) dry acetonitrile, stirring under nitrogen at room temperature for 2-6 h.



Scheme S2. Synthesis of 3-(3-hydroxyphenyl)-acetylacetone (HO-Ph-AcAcH). Reaction conditions: (i) 10 mol% CuI, 20 mol% L-proline, K_2CO_3, DMSO, 90°C, 20 h. (ii) BBr_3, DCM, room temperature, 3 h.

Preparation of [PPor-Cl]Cl: A solution of OEP (50 mg, 0.093 mmol), CH_3PCl_2 (30 µL, 0.33 mmol) and 2,6-lutidine (50 µL, 0.43 mmol) in dry dichloromethane (10 mL) was refluxed for 48 h under nitrogen. The solvent was evaporated, and the crude product was dried under vacuum and then washed with dry hexane under an inert atmosphere to remove traces of 2,6-lutidine and OEP. The product was used for surface binding studies without further purification. Yield = 50 mg (83%). NMR (CD_3CN, δ ppm) ^1H (300 MHz): 9.90 (s, 4H), 4.10 (m, 16H), 1.86 (t, 24H), −5.87 (d, 3H, $J = 15.6$ Hz); ^{31}P(121 MHz): −194.42 (s).

Preparation of [PPor-OPh-COOH]PF$_6$: A solution of OEP (50 mg, 0.093 mmol), CH_3PCl_2 (30 µL, 0.33 mmol) and 2,6-lutidine (50 µL, 0.43 mmol) in dry dichloromethane (10 mL) was refluxed for 48 h under nitrogen. The solvent was evaporated and the crude product was dissolved in 5 mL dry acetonitrile. This was added to 5 mL of 3-hydroxybenzoic acid (HO-Ph-COOH, 20 mg, 0.14 mmol in dry acetonitrile) solution in three portions over a period of 30 minutes under nitrogen. The resulting solution was stirred at room temperature for 6 h. The solvent was evaporated and the crude product was dissolved in ethanol and precipitated as the PF_6 salt by addition of saturated aqueous NH_4PF_6. The precipitate was collected by filtration and washed with water and air-dried. The product was purified by silica gel column chromatography. Initially, the column was eluted with dichloromethane:ethylacetate (90:10) to remove less polar impurities (OEP and PPor-OH). The solvent polarity was then increased to dichloromethane:methanol (90:10) to collect the pure desired compound as the PF_6 salt. The sample was stored in a desiccator with freshly prepared $CaCl_2$ to remove the traces of water. Yield = 32 mg (40%). HR-FAB MS: *m/z* 715.34418 for $[M{-}PF_6]^+$, calculated 715.37715 for $C_{44}H_{52}N_4O_3P$. NMR (CD_3CN, δ ppm), ^1H (300 MHz): 9.90 (s, 4H), 6.52 (d, 1H, $J = 6.6$ Hz), 5.75 (t, 1H), 4.09 (m, 16H), 1.96 (d, 1H), 1.79 (t, 1H+24H), −5.70 (d, 3H, $J = 13.8$ Hz); ^{13}C (150 MHz): 164.88, 148.36, 144.92, 138.14, 127.0, 123.0, 120.74, 115.88, 95.30, 29.36, 18.98, 17.34. ^{31}P (121 MHz): −195.18 (s), −144.67 (sept, $J = 706$ Hz).

***Preparation of [PPor-OPh-AcAcH](PF$_6$)*:** A solution of OEP (50 mg, 0.093 mmol), CH_3PCl_2 (30 µL, 0.33 mmol), and 2,6-lutidine (50 µL, 0.43 mmol) in dry dichloromethane (10 mL) was refluxed for 48 h under nitrogen. The solvent was evaporated and the crude product was added to 10 mL of a solution of 3-(3-hydroxyphenyl)-acetylacetone (HO-Ph-AcAcH, 19 mg, 0.099 mmol in acetonitrile). The resulting solution was stirred at room temperature for 6 h under nitrogen. The reaction mixture was directly loaded onto a silica gel column and eluted with dichloromethane:acetonitrile:methanol (80:10:10). The low polarity fractions of the eluent were discarded, and the desired compound was obtained as the high polarity band in the form of the chloride salt. The solvent was evaporated and the compound was dissolved in ethanol and precipitated as the PF_6 salt using saturated aqueous NH_4PF_6. The obtained precipitate was collected by filtration, washed with water, and dried in air. The sample was stored in a desiccator over freshly prepared $CaCl_2$ to remove traces of water. Yield = 75 mg (88%). HR-FAB MS: *m/z* 769.39014 for $[M{-}PF_6]^+$, calculated 769.4241 for $C_{48}H_{58}N_4O_3P$. NMR (CD_3CN, δ ppm), ^1H (300 MHz, keto (20%) – enol (80%)): 16.31 (s, 1H), 9.93 (s, 4H, enol form), 9.89 (s, 4H, keto form), 5.73 (m, 2H), 4.09 (m, 16H), 1.97 (d, 1H), 1.79 (t, 24H), 1.14 (s, 6H), 0.76 (s, 1H), −5.75 (d, 3H, J = 13.6 Hz); ^{13}C (150 MHz): 189.90, 148.41, 144.91, 144.42, 138.15, 137.61, 135.34, 127.35, 124.64, 115.60, 113.61, 95.29, 94.25, 54.34, 29.91, 28.95, 22.89, 18.97, 17.35; ^{31}P (121 MHz): −196.11 (s), −195.09 (s), −144.67 (sept, J = 706 Hz).

Reaction Yields and Purification. The observed yields were moderate in the case of PPor-OPh-COOH and high for PPor-OPh-AcAcH. The moderate yield of PPor-OPh-COOH is the result of competition between the desired elimination reaction of the P–Cl moiety with the ring -OH group of hydroxybenozoic acid to form the P–OR bond and the unwanted substitution reaction between P–Cl and the OH group of the carboxylic acid to give the acid chloride and P–OH. Purification of these compounds by chromatographic methods is not particularly convenient because they bind irreversibly to the stationary phase (alumina or silica gel). However, this process is sufficiently slow to allow purification by flash column chromatography if silica gel is used as the stationary phase. After final purification, the compounds were stored in a desiccator over freshly prepared $CaCl_2$ to remove traces of water.

Structural Characterization. The ^1H NMR spectra of PPor-OPh-COOH and the reference components 3-hydroxybenzoic acid and PPor-Cl (Figure S1) are shown in Figure S4, Figure S3 and Figure S1, respectively. Shielding effects are apparent for the protons on the axial Ph-COOH subunit. For example, resonances due to the protons H_a and H_d, which appear at 7.42 and 7.07 ppm in the isolated 3-hydroxybenzoic acid, are strongly shifted upfield to 1.79 and 1.96 ppm due to the ring current effect of the porphyrin macrocycle. Similarly, resonances due to the protons H_b and H_c are shifted upfield, but by a smaller amount because they are further away from the porphyrin ring. Analogously, the axial methyl proton signal is shifted upfield by −5.70 ppm and is also split into a doublet by coupling to phosphorus. Similar shielding effects were observed in the case of PPor-OPh-AcAcH (Figure S7) in comparison with free 3-(3-hydroxyphenyl)-acetylacetone (Figure S6). The AcAcH group can exist in different keto-enol tautomers and the observed peak at 16.31 ppm was assigned to the enol hydroxyl group proton. The ^{31}P signals due to the central phosphorus atoms in PPor-OPh-COOH and PPor-OPh-AcAcH appear at −195.18 and −195.06 ppm, respectively and are slightly upfield than that of PPor-Cl (−194.42 ppm). In addition, a septet from the counter ion PF_6 was also observed at −144.67 ppm for both PPor-OPh-COOH and PPor-Ph-AcAcH samples.

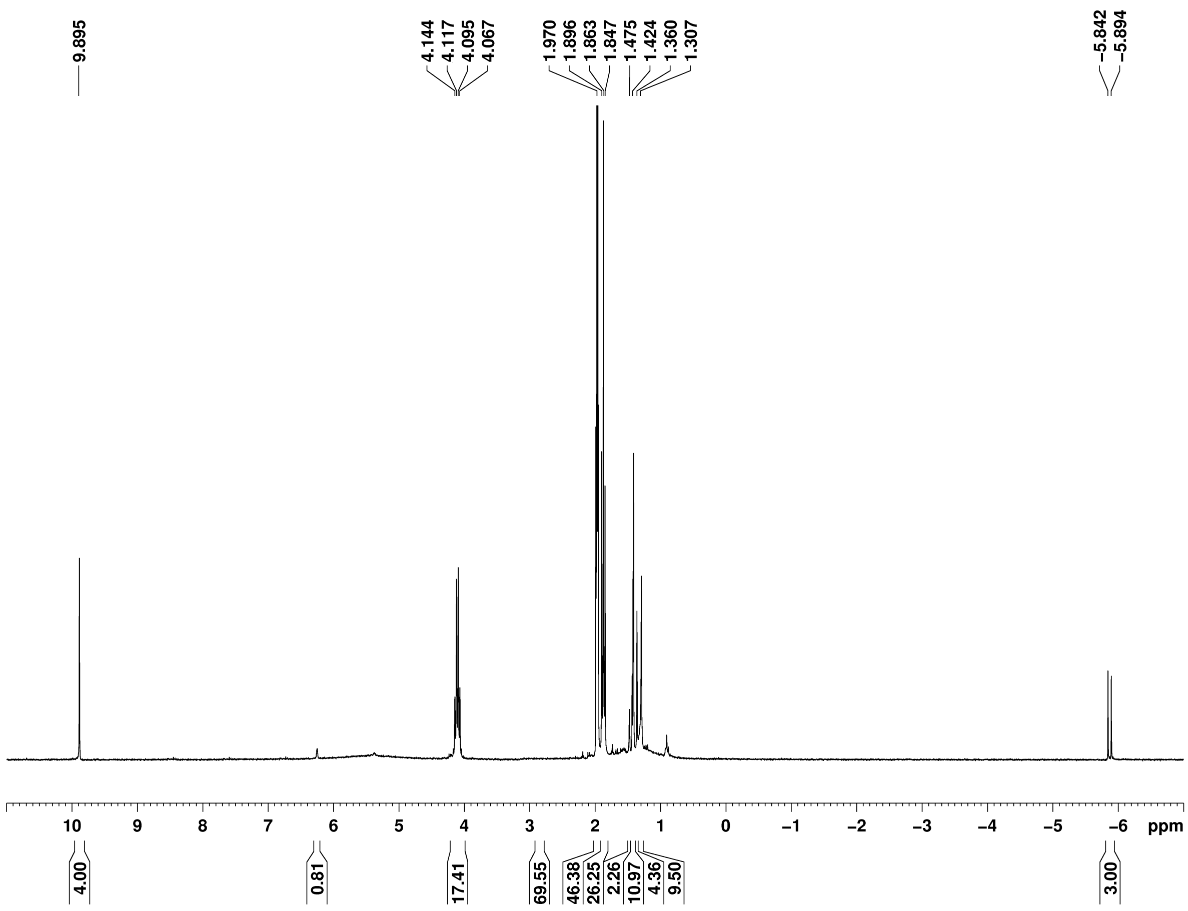


Figure S1. ^{1}H NMR (300 MHz) spectrum of (PPor-Cl)Cl in CD_3CN. Note that this is a crude product and peaks between 1.0 – 1.6 ppm are due to impurities.

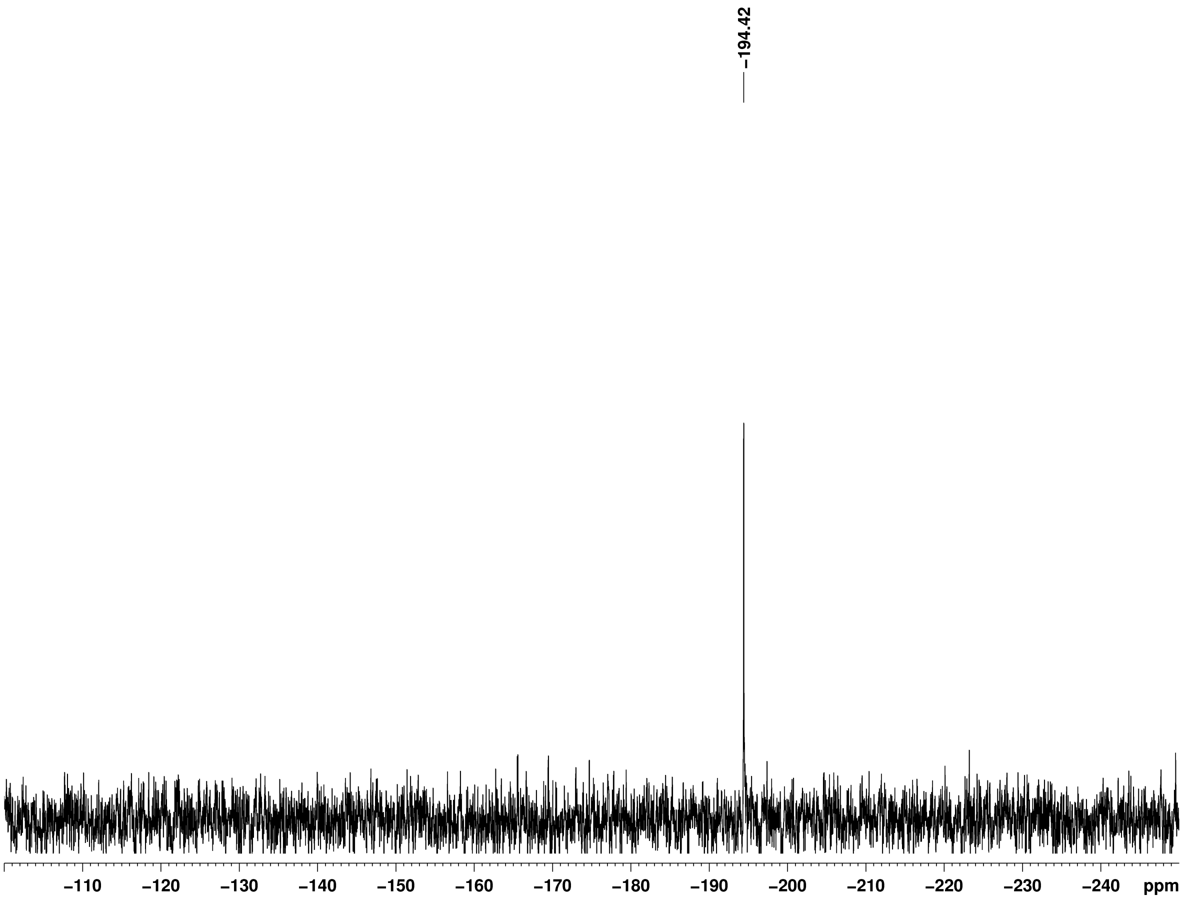


Figure S2. ^{31}P NMR (121 MHz) spectrum of (PPor-Cl)Cl in CD_3CN.

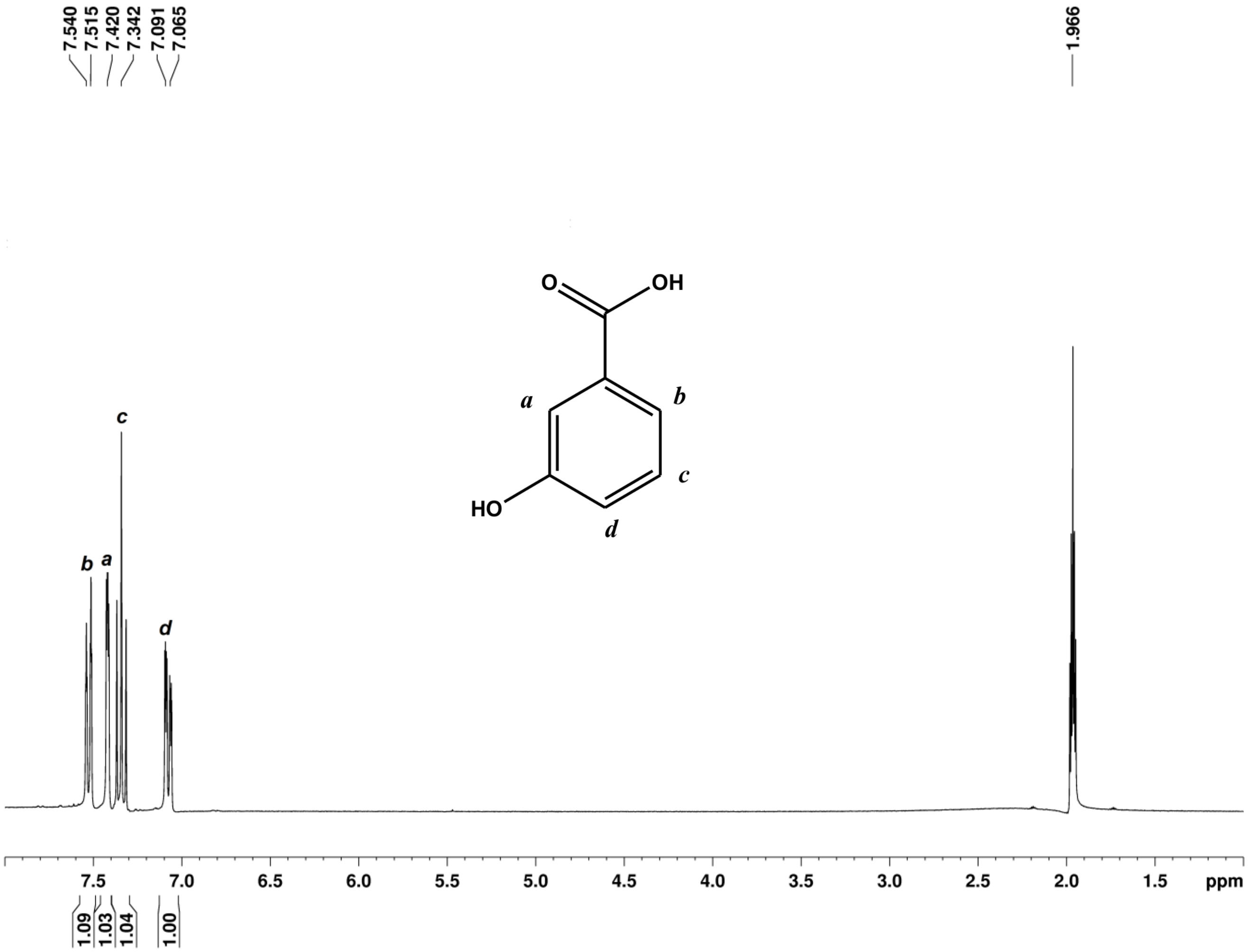


Figure S3. ^{1}H NMR (300 MHz) spectrum of 3-hydroxybenzoicacid in CD_3CN.

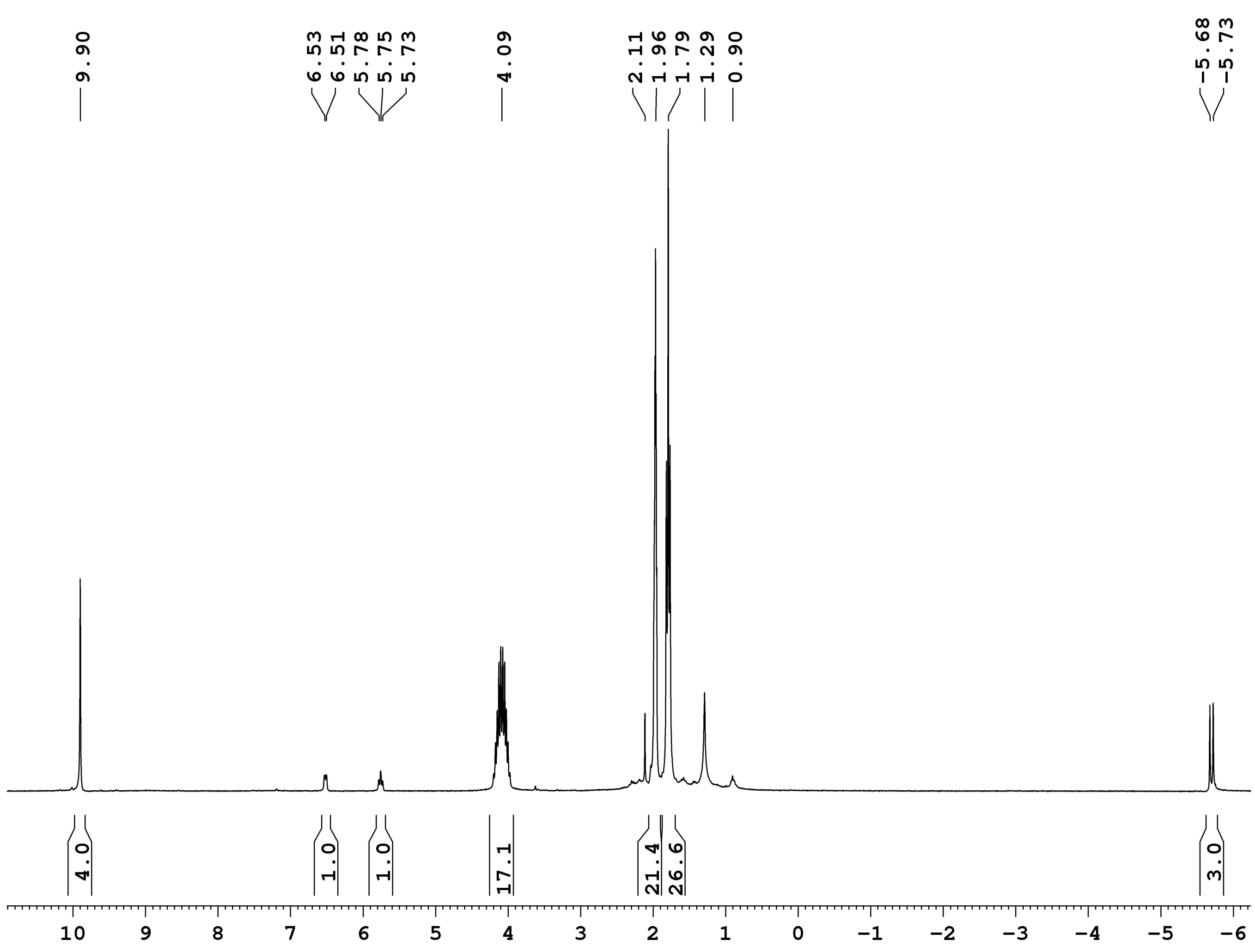


Figure S4. ^{1}H NMR (300 MHz) spectrum of (PPor-OPh-COOH)(PF_6) in CD_3CN. Note that the peaks at 0.90, 1.29 and 2.11 are solvent impurities.

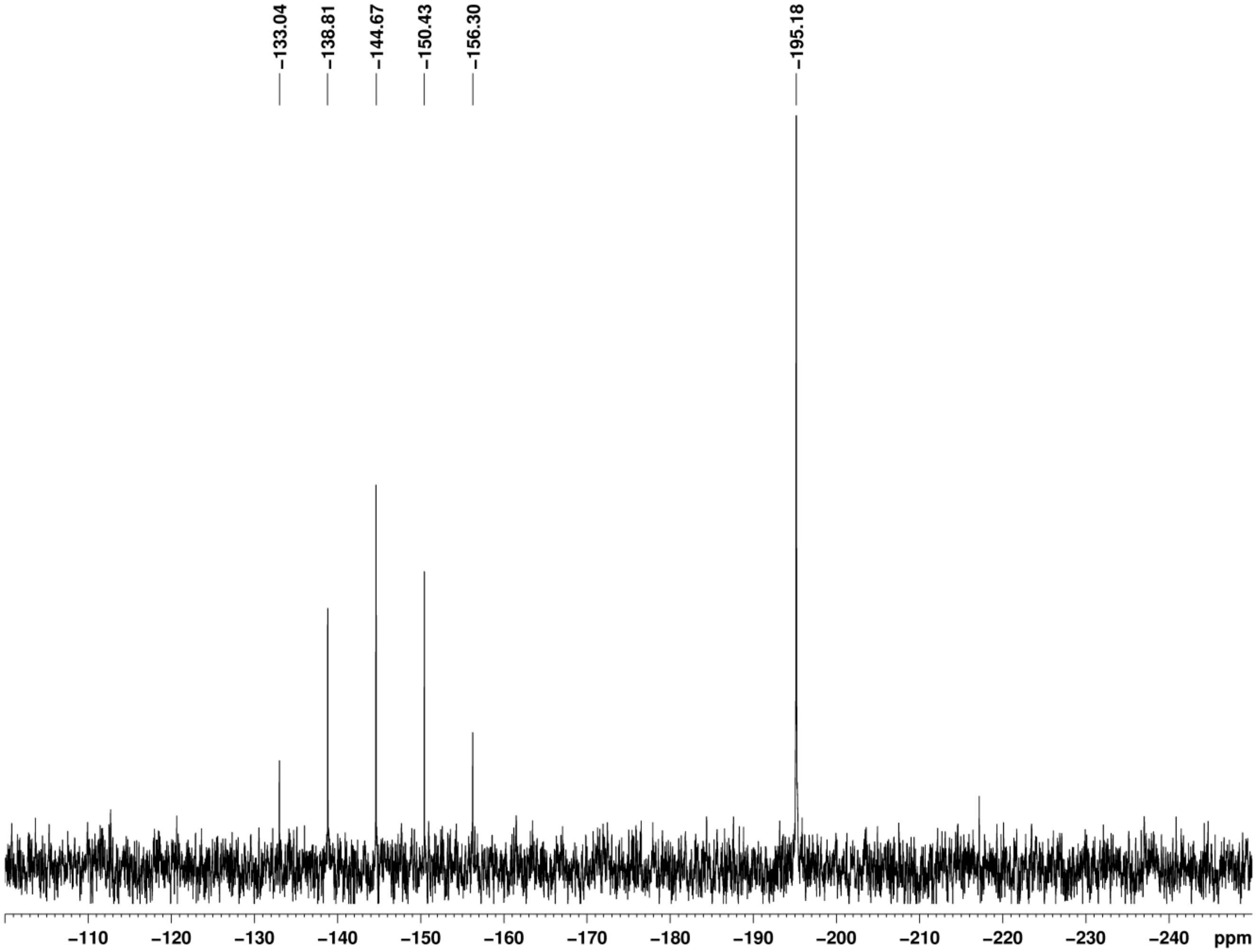


Figure S5. ^{31}P NMR (121 MHz) spectrum of (PPor-OPh-COOH)(PF_6) in CD_3CN.

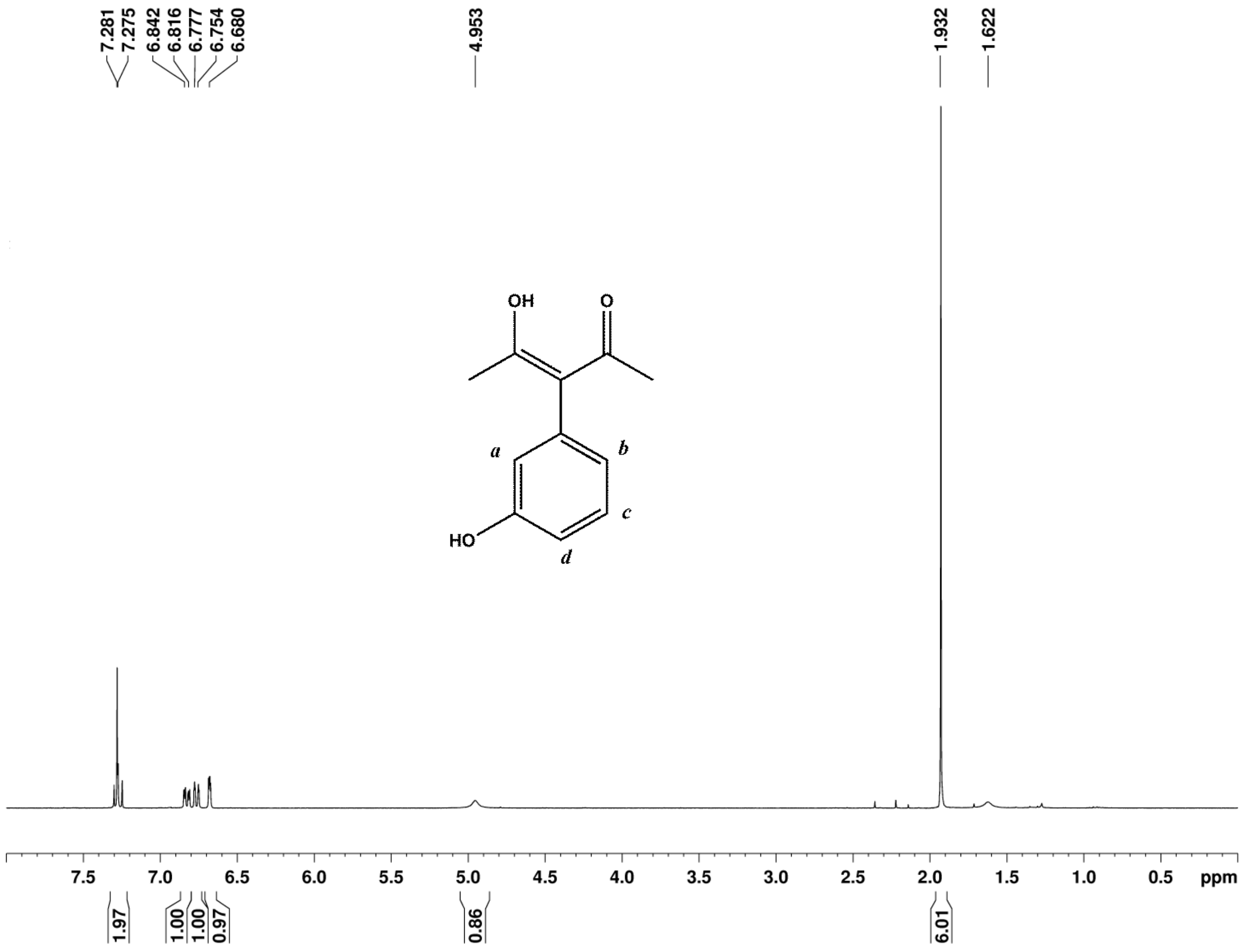


Figure S6. ^{1}H NMR (300 MHz) spectrum of 3-(3-hydroxyphenyl)-acetylacetone in CDCl$_3$.

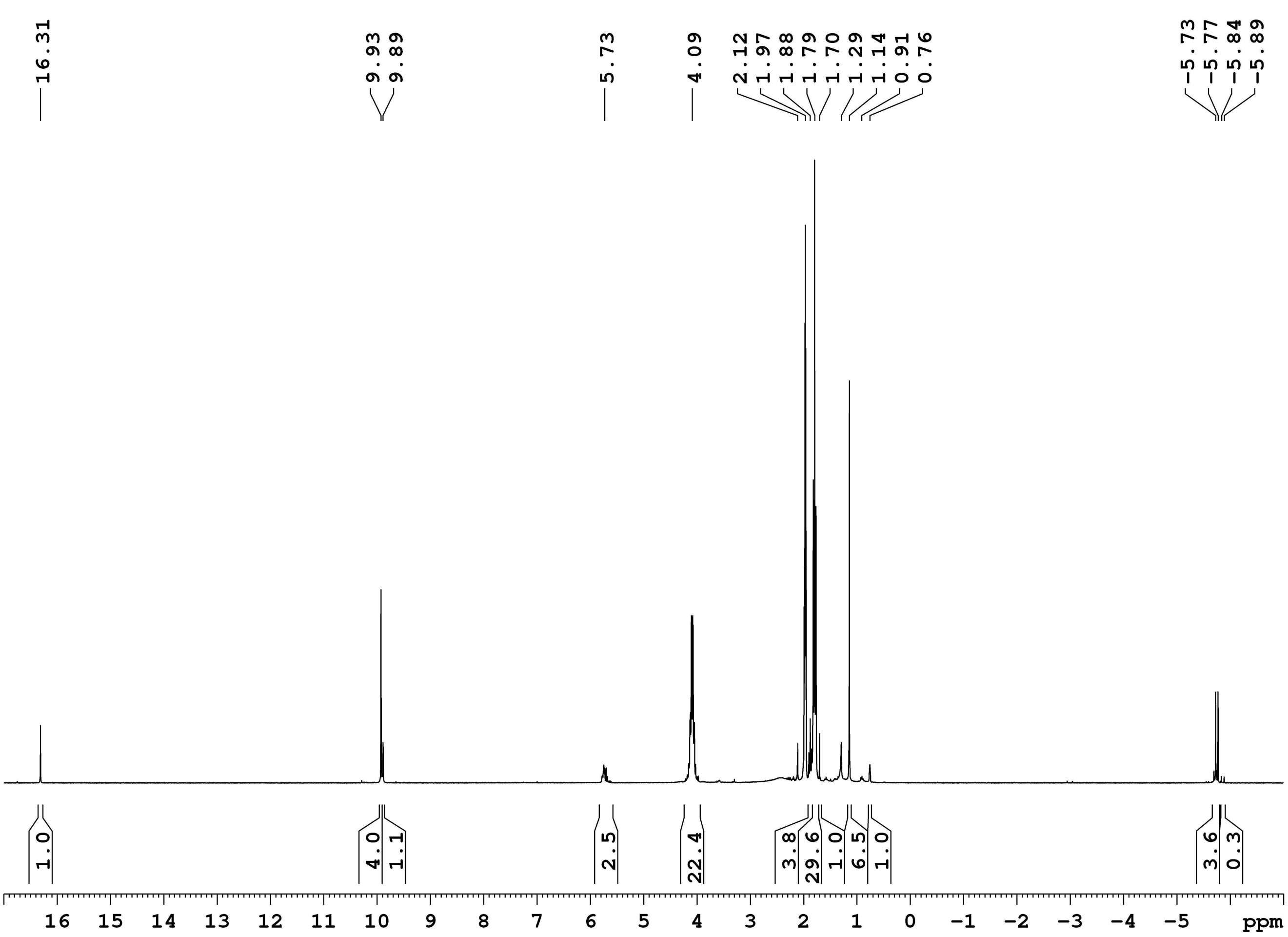


Figure S7. ^{1}H NMR (300 MHz) spectrum of (PPor-OPh-AcAcH)(PF_6) in CD_3CN. Note that the peaks at 0.91, 1.29, 1.70 and 2.12 are solvent impurities.

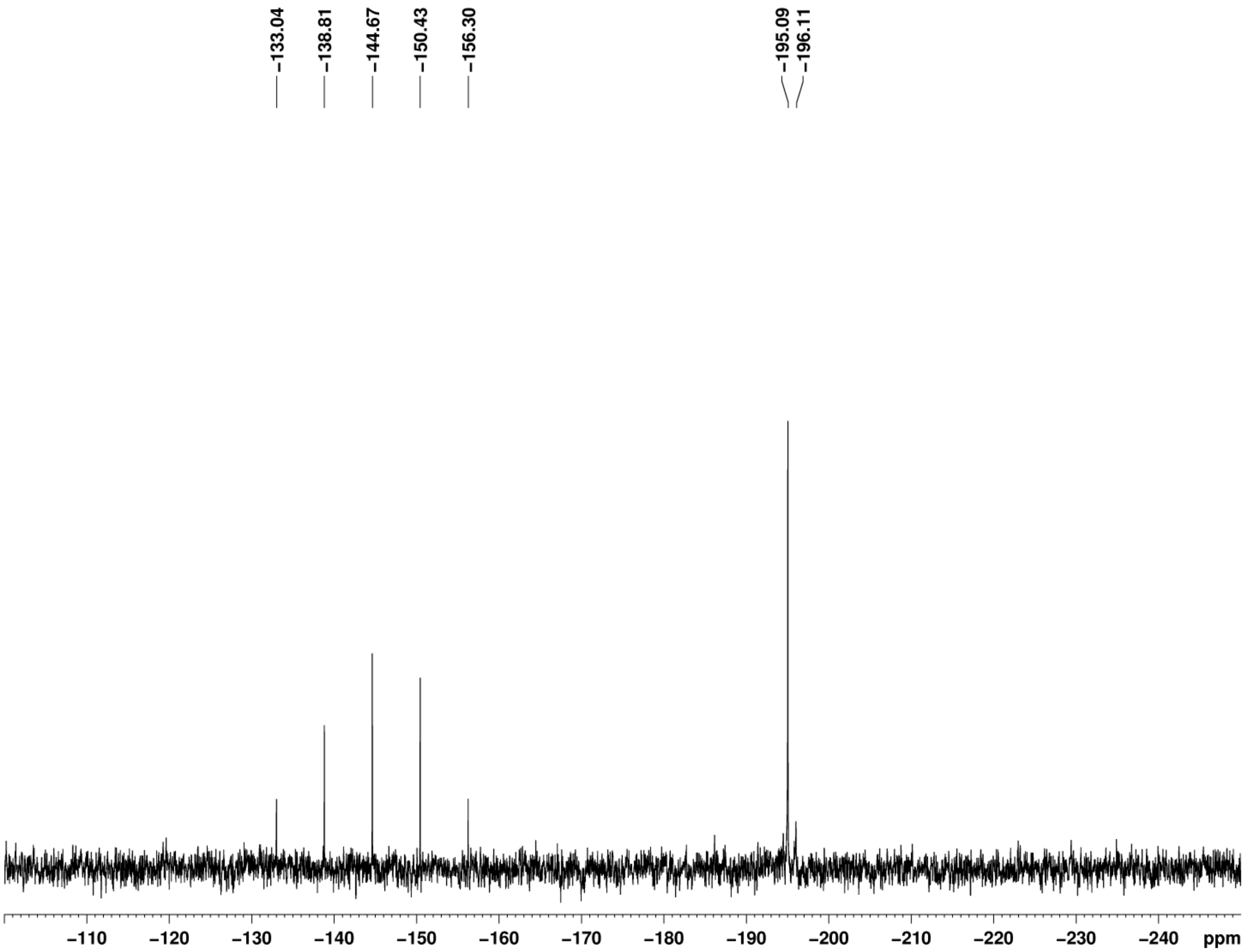


Figure S8. ^{31}P NMR (121 MHz) spectrum of (PPor-OPh-AcAcH)(PF$_6$) in CD$_3$CN.

Cyclic Voltammetry. Figure S9 shows the cyclic voltammograms of the compounds in acetonitrile with 0.1 M TBAPF$_6$ supporting electrolyte. During the anodic scan of PPor-OPh-COOH (Figure S9c), a one-electron quasi-reversible oxidation process was observed. Comparing the voltammogram with those of the reference compounds PPor-OMe (Figure S9b) and 3-hydroxybenzoic acid (data not shown), the observed quasi-reversible oxidation process for PPor-OPh-COOH can be assigned to the first oxidation of the porphyrin.[1] In the cathodic scan, two one-electron reversible reduction processes were observed and are ascribed to the successive first and second reductions of the porphyrin. Similar results were observed for PPor-OPh-AcAcH (Figure S9d). The cyclic voltammogram of the water-oxidation precatalyst IrCp*-COOH (Figure S9a) shows quasi-reversible and irreversible peaks corresponding to the first and second oxidations of the complex.

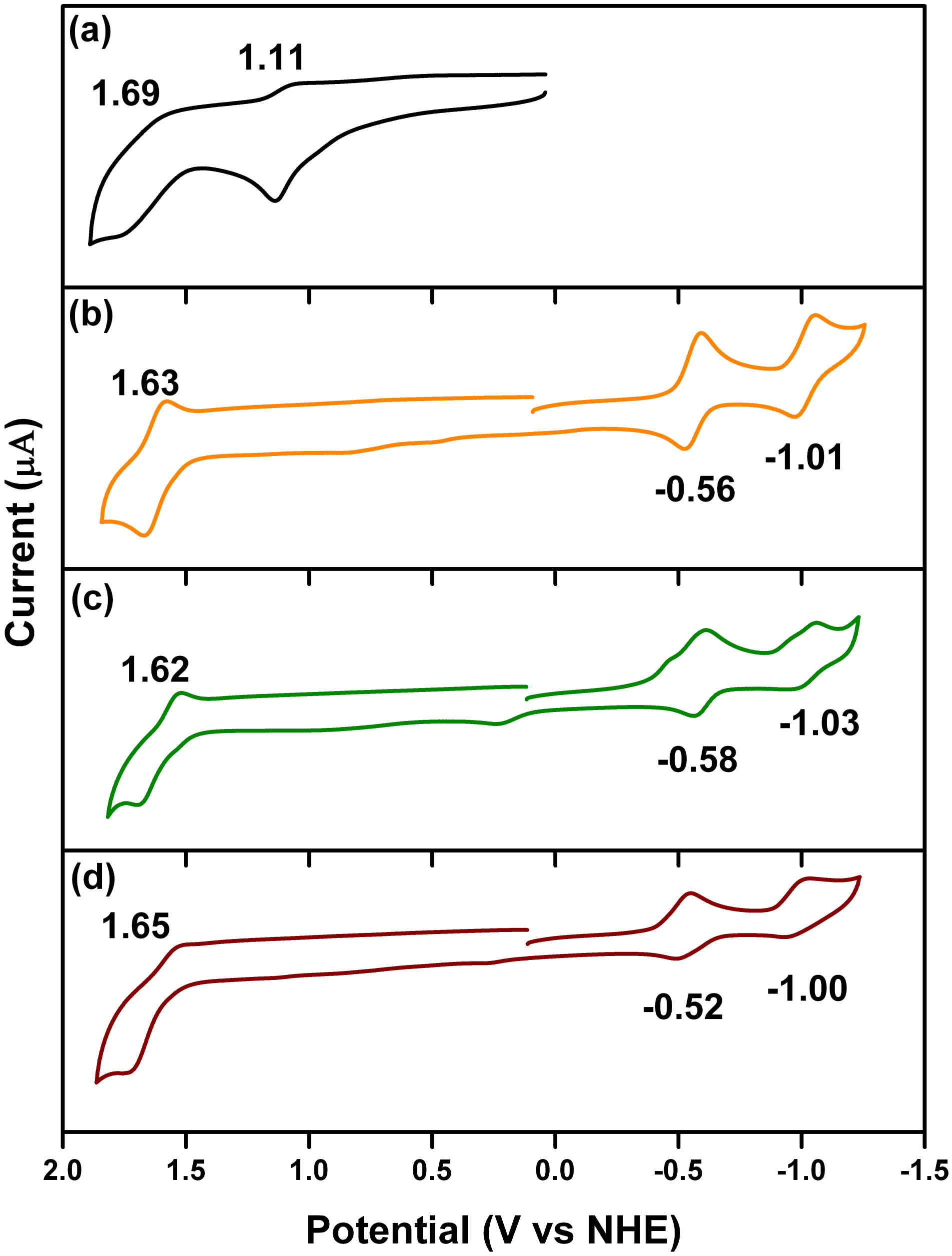


Figure S9. Cyclic voltammograms of (a) IrCp*-COOH (b) PPor-OMe (c) PPor-OPh-COOH and (d) PPor-OPh-AcAcH in 0.1 M TBAPF$_6$ acetonitrile. Scan rate = 100 mV/sec.

UV-Visible Absorption Studies. The UV-visible spectra of the PPor-OPh-COOH and PPor-OPh-AcAcH dyads and their reference compounds PPor-OMe, 3-(3-hydroxyphenyl)-acetylacetone, 3-hydroxybenzoic acid were measured in acetonitrile and are shown in Figure S10. The band positions and extinction coefficients are summarized in Table 1. All of the porphyrin compounds exhibit normal type UV-visible spectra with a Soret band (I) peak in the range of 415-432 nm and two Q-band peaks in the range of 500-630 nm. They also show the relatively weak Soret band (II) peak at 365 nm typical of PPors.[1] The absorption between 250-300 nm observed in the spectrum of PPor-OPh-COOH and PPor-OPh-AcAcH is ascribed to the axially linked 3-

hydroxybenzoicacid and 3-(3-hydroxyphenyl)-acetylacetone subunits, respectively. Based on the absorption data (Table 1) and spectra (Figure S10) it is clear that the absorption spectra of PPor-OPh-COOH and PPor-OPh-AcAcH are the same as that of an equal molar mixture of reference compounds. Thus, we conclude that there is no significant electronic interaction between the axial aromatic subunit and porphyrin. The absorption spectrum of IrCp*-COOH in acetonitrile (Figure S11) shows strong and weak absorption bands between 240-400 nm and 400-480 nm, respectively.

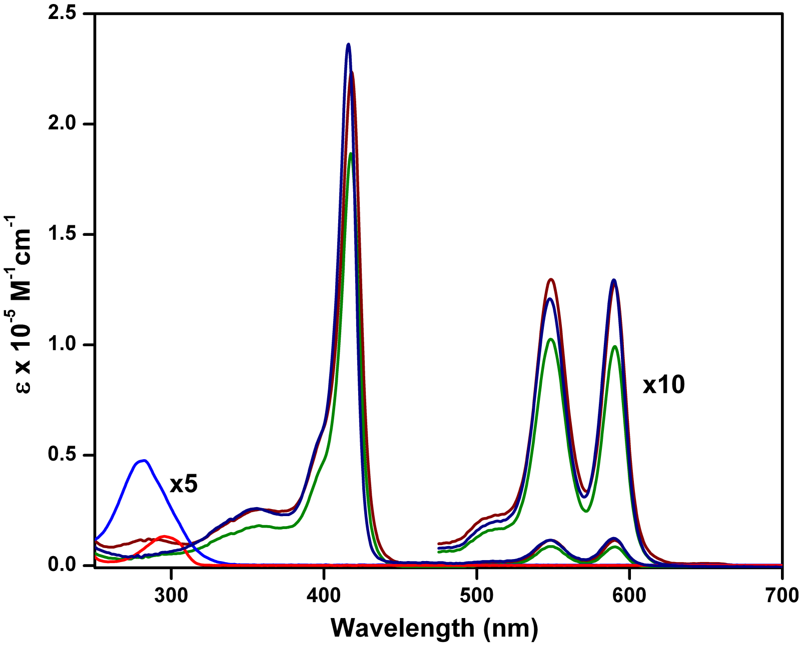


Figure S10. UV-visible absorption spectra of PPor-OMe (navy blue), PPor-OPh-AcAcH (maroon), PPor-OPh-COOH (green), 3-(3-hydroxyphenyl)-acetylacetone (blue), 3-hydroxybenzoic acid (red). Resolution: ε (250-380 nm) × 5 for 3-(3-hydroxyphenyl)-acetylacetone and 3-hydroxybenzoic acid; ε (475-650 nm) × 10 for Q-bands of PPor-OPh-AcAcH and PPor-OPh-COOH.

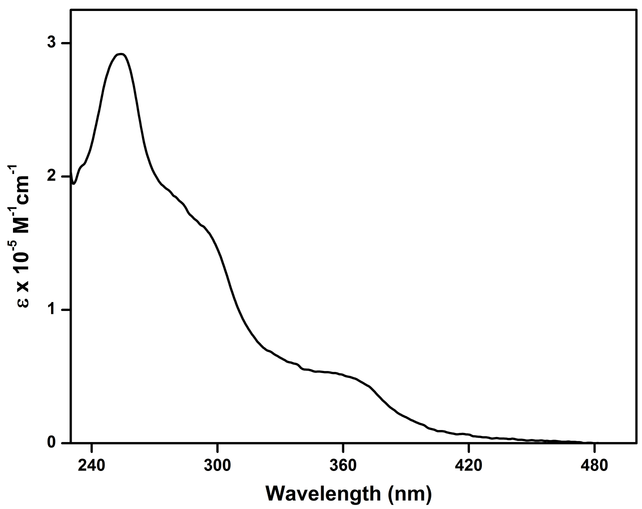


Figure S11. Absorption spectrum of IrCp*-COOH in acetonitrile.

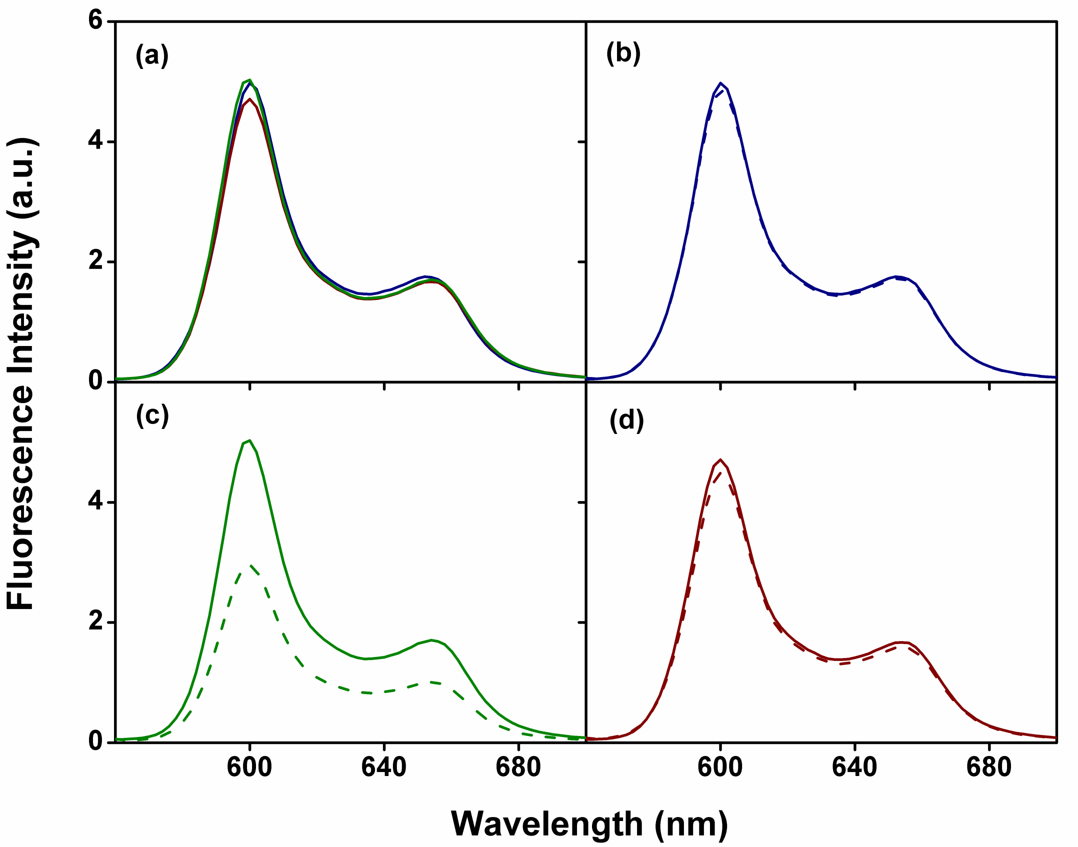


Figure S12. Fluorescence spectra of (a) PPor-OMe (orange), PPor-OPh-COOH (green) and PPor-OPh-AcAcH (maroon) (b) PPor-OMe (solid) and PPor-OMe + IrCp*-COOH (dashed) (c) PPor-OPh-COOH (solid) and PPor-OPh-COOH + IrCp*-COOH (dashed) (d) PPor-OPh-AcAcH (solid) and PPor-OPh-AcAcH + IrCp*-COOH (dashed) in acetonitrile, excitation wavelength 550 nm. PPor and IrCp*-COOH solution concentrations were maintained at 0.1 mM and 0.6 mM, respectively.

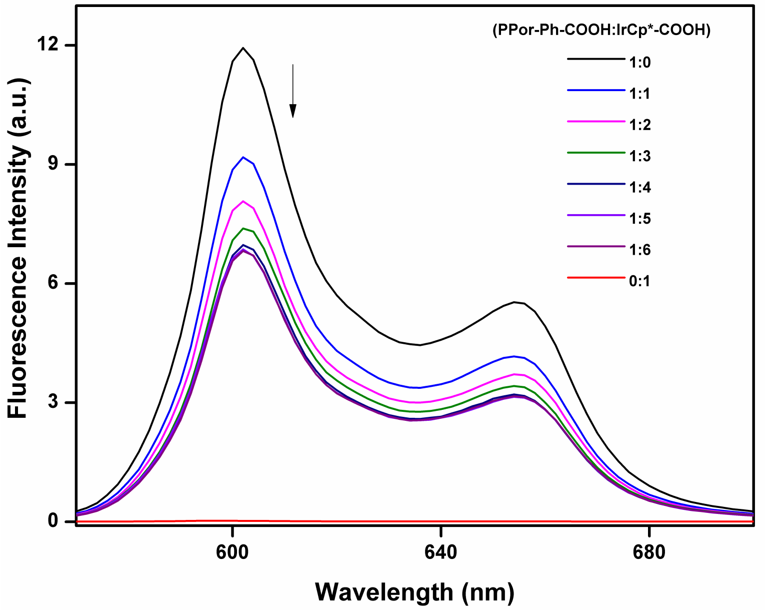


Figure S13. Fluorescence titrations of PPor-OPh-COOH (0.1 mM) in the presence of increasing amounts of IrCp*-COOH (0 to 0.6 mM) in acetonitrile. An excitation wavelength 550 nm.

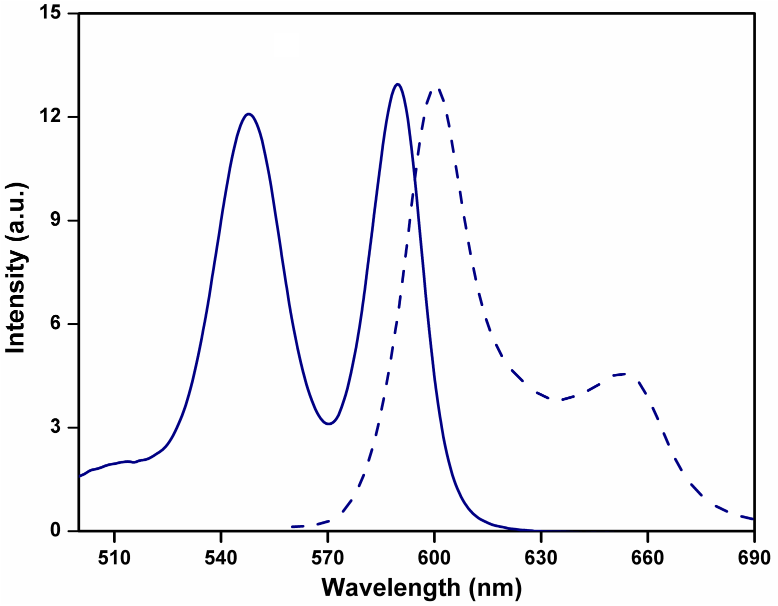


Figure S14. Spectral overlap between absorption (in dichloromethane, solid line) and fluorescence (in acetonitrile, dashed line) spectra of PPor-OMe.

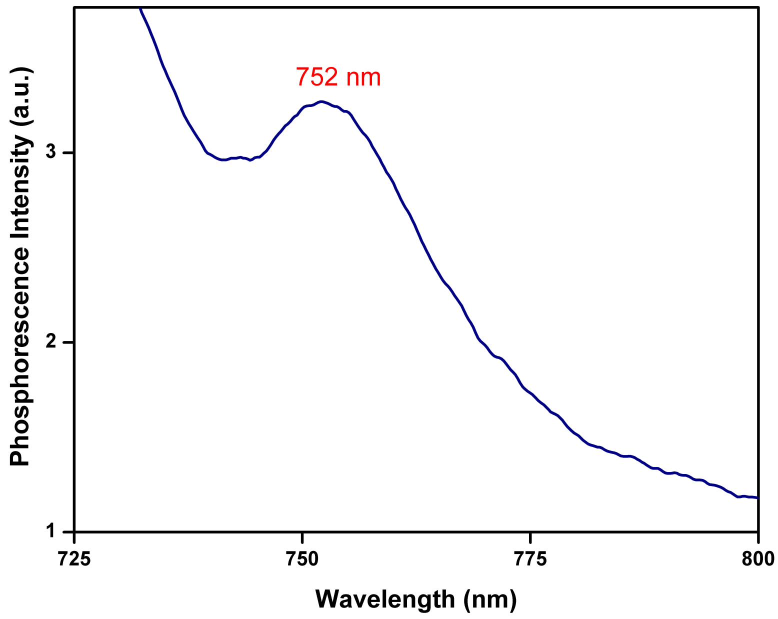


Figure S15. Phosphorescence spectrum of PPor-OMe in acetonitrile at 77 K, excitation wavelength 550 nm.

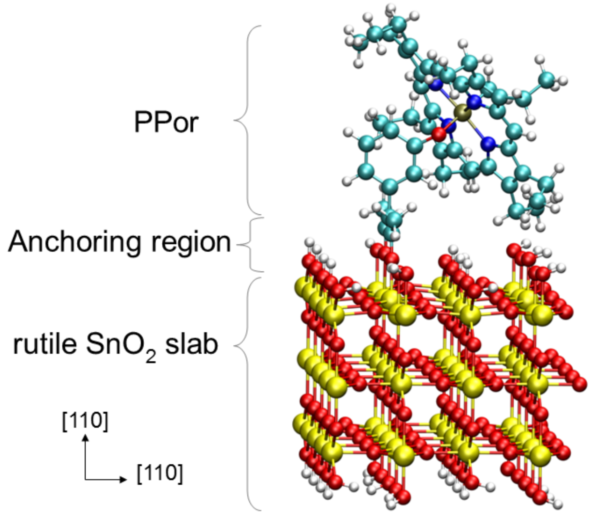
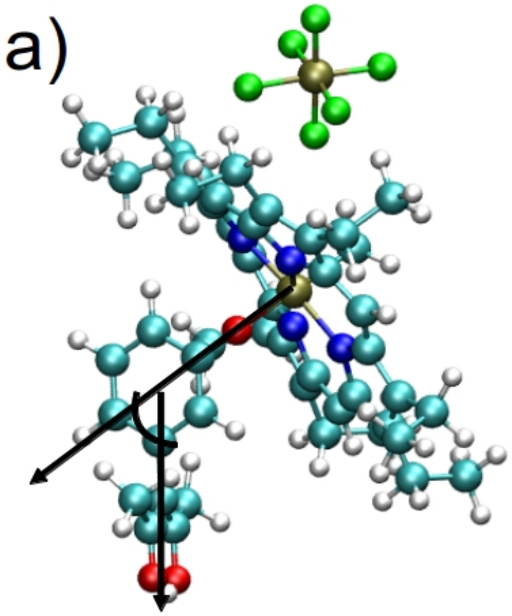


Figure S16. System used for modeling electron injection by PPor-OPh-AcAc on SnO_2.



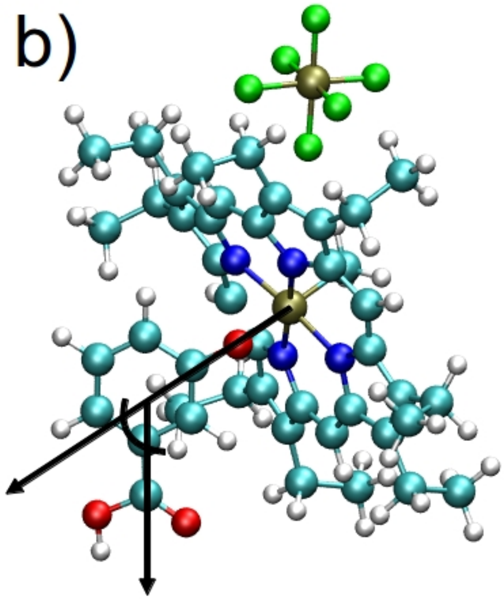


Figure S17. DFT(B3LYP/6-31G) optimized anchoring geometries for the porphyrins a) PPor-OPh-AcAc and b) PPor-OPh-COO^{-}. The arrows show the tilt angle: 57° for PPor-OPh-AcAc and 71° for PPor-OPh-COO^{-}.

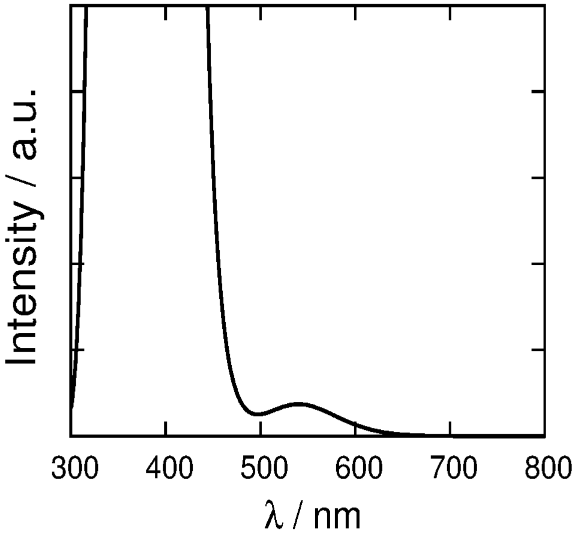
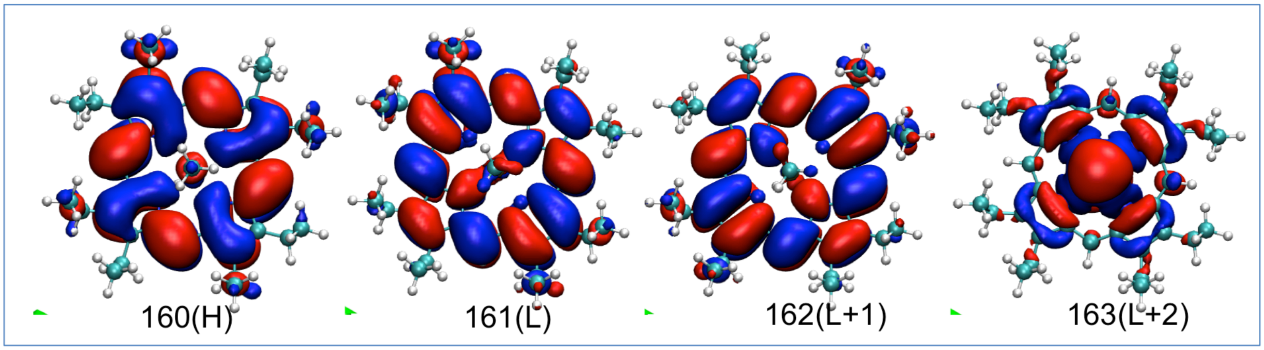


Figure S18. Calculated absorption spectrum of PPor-OH. Time dependent density functional theory (TDDFT) calculations were performed by using GAUSIAN computational package with B3LYP and 631G as functional and basis set, respectively.

DFT B3LYP/631G



EH

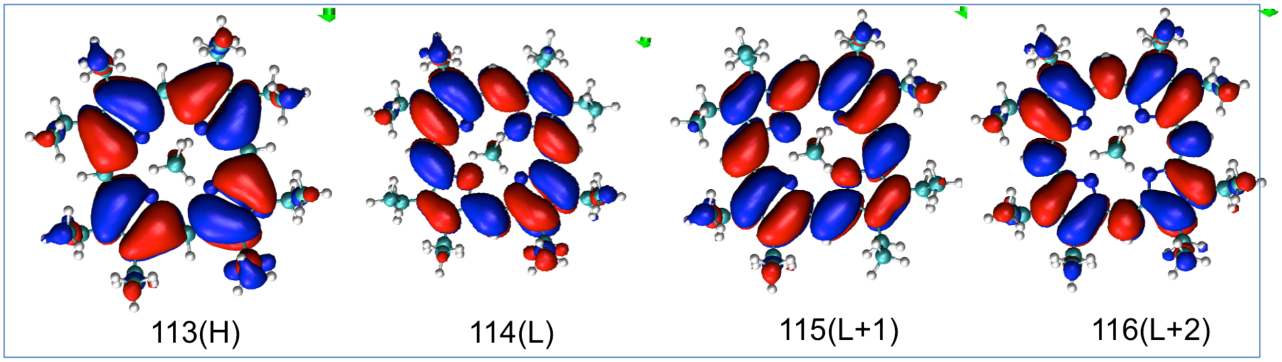


Figure S19. Frontier Molecular Orbitals computed with DFT and EH level of theory, respectively.

Table S1. First seven excitations involved in the UV-visible absorption bands for the free PPor-OH. The strong Soret band composed by the sixth and seventh transitions shows a high participation of the L and L+1 levels. Note here f is the oscillator strength.

Excited State 1: Singlet 2.2746 eV 545.07 nm f = 0.0007

Transition	Probability
159 →161	0.39407
159 ←162	-0.30256
160 →161	0.34303
160 →162	0.36283

Excited State 2: Singlet 2.2964 eV 539.91 nm f = 0.0044

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                    Transition      Probability

                     159 ←161        -0.32497

                       159 ←162        -0.35215

                       160 →161         0.40228

                       160 ←162        -0.32347

Excited State   3:     Singlet      2.8161 eV  440.27 nm  f = 0.0045

                    Transition      Probability

                     160 →163         0.69319

Excited State   4:     Singlet      2.8588 eV  433.69 nm  f = 0.0067

                    Transition      Probability

                     159 →163         0.69277

Excited State   5:     Singlet      3.0783 eV  402.76 nm  f = 0.0684

                    Transition      Probability

                      158 →161         0.65267

                       159 ←161        -0.15619

                       160 →162         0.17367

Excited State   6:     Singlet      3.1481 eV  393.84 nm  f = 0.2936

                    Transition      Probability

                      156 →161         0.14610

                       157 →161         0.45323

                       158 →162         0.12919

                       159 ←161        -0.13031
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159 ←162	-0.34811
160 ←161	-0.27977
160 →162	0.14674

Excited State 7: Singlet 3.1924 eV 388.37 nm f = 0.4258

Transition	Probability
156 ←162	-0.22133
157 →161	0.18439
157 ←162	-0.14550
158 ←161	-0.22088
158 ←162	-0.13990
159 ←161	-0.29480
159 →162	0.25435
160 →161	0.23023
160 →162	0.30715

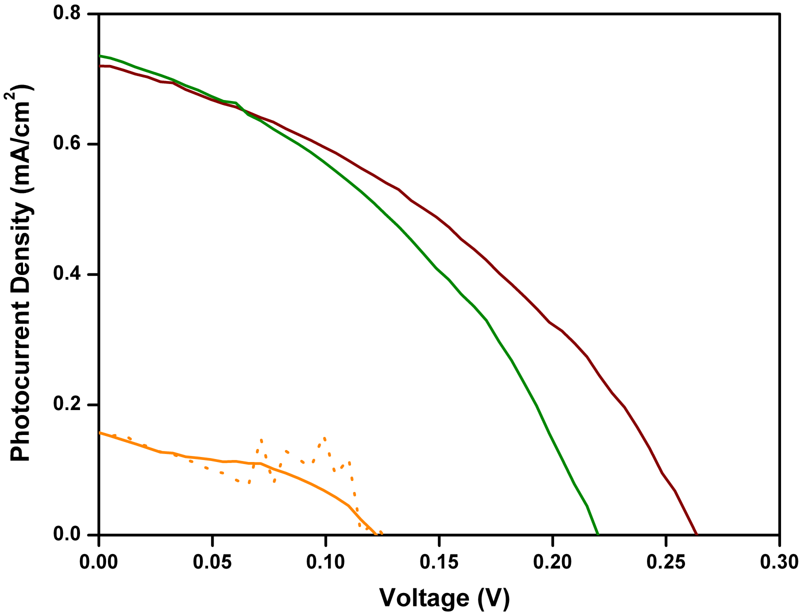

Figure S20. Photocurrent-voltage (*J-V*) scans for DSSCs made using SnO_2 and sensitized with PPor-OPh-COO^- (green), PPor-OPh-AcAc (maroon) and PPor-O^- (orange) in an I_3^-/I^- electrolyte under 100 mW/cm^2 AM 1.5G irradiation. Due to the low efficiency of DSSCs made using the directly bound PPor, which perform worse than even DSSCs incorporating TiO_2 without any dye, *J-V* measurements resulted in substantial noise (dotted orange). In order to accurately determine DSSC parameters, two measurements were taken, then averaged and smoothed (solid orange) using the Adjacent Averaging in OrginPro 8 with 14 points of window and no weighting.

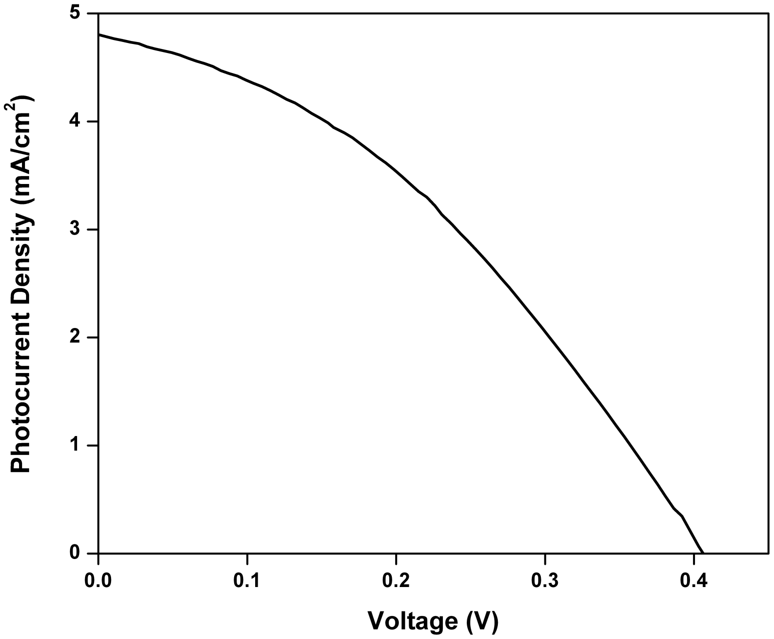

Figure S21. Photocurrent-voltage (*J-V*) scans for DSSCs made using SnO_2 and sensitized with N719 dye in an I_3^-/I^- electrolyte under 100 mW/cm^2 AM 1.5 G irradiation.

1. P. K. Poddutoori, A. Dion, S. J. Yang, M. Pilkington, J. D. Wallis and A. van der Est, *J. Porphyr. Phthalocyanines*, 2010, **14**, 178-187.
2. Y. W. Jiang, N. Wu, H. H. Wu and M. Y. He, *Synlett*, 2005, 2731-2734.