

Supplementary Information

A Charge Transfer State Induced by Strong Exciton Coupling in a Cofacial μ -Oxo-bridged Porphyrin Heterodimer

Niloofar Zarrabi,^a Brandon J. Bayard,^a Sairaman Seetharaman,^b Noah Holzer,^a Paul Karr,^c Susanna Ciuti,^d Antonio Barbon,^d Marilena Di Valentin,^d Art van der Est,^{e,} Francis D'Souza,^{b,*} Prashanth K. Poddutoori^{a,*}*

^aDepartment of Chemistry & Biochemistry, University of Minnesota Duluth, 1039 University Drive, Duluth, Minnesota 55812, USA. ^bDepartment of Chemistry, University of North Texas, 1155 Union Circle, # 305070, Denton, Texas 76203-5017, USA. ^cDepartment of Physical Sciences and Mathematics, Wayne State College, 111 Main Street, Wayne, Nebraska, 68787, USA. ^dDipartimento di Scienze Chimiche, Università degli studi di Padova, Via Marzolo 1, 35131 Padova, Italy. ^eDepartment of Chemistry, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, ON, L2S 3A1, Canada.

Experimental Section.

Synthesis. All the chemicals, solvents and chromatographic materials were obtained from Aldrich Chemicals, Fisher Chemicals or Alfa Aesar and were used as received.

Synthesis of PPor-OH.PF₆: A solution of OEP (50 mg, 0.093 mmol), CH₃PCL₂ (50 μ L, 0.57 mmol) and 2,6-Lutidine (50 μ L, 0.43 mmol) in dry CH₂Cl₂ (10 mL) was refluxed for 36 h under nitrogen. The solvent was evaporated and the solute was dried under vacuum. The obtained crude PPor-Cl was dissolved in CH₃CN (5 mL) and H₂O (5 mL) was added. The resulting solution was stirred at room temperature for 3-4 h. The solvent was evaporated and the crude product was purified on a neutral alumina column. The column was eluted with C₆H₆:CH₃OH (= 95:5) to remove the low polarity impurities and collect the desired compound as the chloride salt, PPor-OH.Cl. To exchange the counter-ion, the chloride salt was dissolved in 10 mL of ethanol and precipitated with a saturated aqueous solution of NH₄PF₆. The precipitate was collected by filtration and washed with water and air dried. At this point, the minor impurities found in the crude product were separated by silica gel column chromatography using CH₂Cl₂:EtOAc (= 95:5) as the eluent. The polarity was then increased to CH₂Cl₂:CH₃OH (= 98:2) to elute the desired product PPor-OH.PF₆ in pure form. Yield = 55 mg (80 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.61 (s, 4H), 4.03 (m, 16H), 1.91 (t, 24H), -5.38 (d, 3H, J = 12.8 Hz).

Synthesis of AlPor-CH₃ and AlPor-OH: To a solution of OEP (50 mg, 0.093 mmol) in dry toluene (5 mL) was added AlMe₃ (0.047 mL, 2.0 M in hexane, 0.093 mmol) under nitrogen atmosphere. The resulting reaction solution was stirred for 24 h under dry and inert atmosphere. The compound was purified by flash column chromatography using neutral alumina and toluene as an eluant. The first red colored fraction was collected as AlPor-CH₃. During the column purification some of the AlPor-CH₃ was converted to AlPor-OH, and was collected separately as a second band. AlPor-CH₃: Yield = 30 mg (56%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.35 (s, 4H), 4.00 (m, 16H), 1.82 (t, 26), -6.53 (s, 3H). AlPor-OH: Yield = 20 mg (37%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.31 (s, 4H), 4.17 (m, 16H), 1.97 (t, 24).

Synthesis of AlPor-O-PPor.PF₆: To a solution of OEP (50 mg, 0.093 mmol) in dry toluene (5 mL) was added AlMe₃ (0.047 mL, 0.093 mmol) under nitrogen atmosphere. The resulting reaction solution was stirred for 24 h under dry and inert atmosphere. To this PPor-OH.Cl (80 mg, 0.126 mmol) was added and the reaction was further stirred for 24 h. After this time, the reaction was purified by neutral alumina chromatography. For solubility reasons the minimum amount of CH₂Cl₂ needed to completely dissolve the crude product was added to the reaction solution before it was loaded on the column. The column was eluted initially with benzene followed by a 95:5 benzene: methanol mixture to remove the low polarity impurities. The desired heterodimer was collected by increasing the solvent polarity to an 80:20 benzene:methanol mixture. To exchange the counter-ion, the chloride salt was dissolved in 20 mL of methanol and precipitated with NH₄PF₆ (500 mg). The precipitate was collected by filtration and washed with cold methanol and water and air dried. Yield = 85 mg (75 %). HR ESI MS: *m/z* 1153.6362 for [M-PF₆]⁺ calculated 1153.6869 for C₇₃H₉₁AlN₈OP⁺. ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.08 (s, 4H), 8.45 (s, 4H), 4.19 (m, 8H), 4.05 (m, 8H), 3.93 (m, 16H), 1.84 (t, 26), 1.69 (t, 24H), -7.93 (d, 3H, *J* = 16 Hz); ³¹P NMR (162 MHz, CDCl₃, δ ppm): -191 (s), -144 (sept, *J* = 712 Hz).

Methods.

NMR and mass spectroscopy. NMR spectra were recorded with Bruker 400 MHz NMR spectrometer using CDCl₃ as the solvent. ESI mass spectra were recorded on a Bruker MicroTOF-III mass spectrometer.

Electrochemistry. Cyclic and differential pulse voltammetric experiments (CH₂Cl₂, 0.1 M tetrabutylammonium perchlorate, (TBAP)) were performed on a BAS Epsilon electrochemical analyzer (working electrode: glassy carbon, auxiliary electrodes: Pt wire, reference electrode: Ag wire). The ferrocene couple (*E*_{1/2} (Fc⁺/Fc) = 0.48 V in DCM, 0.1M TBAP under our experimental conditions) was used to calibrate the redox potential values.

Absorption spectroscopy. Steady-state UV-visible absorption spectra were recorded with a Cary 100 UV-VIS spectrometer. The concentrations of the samples used for these measurements ranged from 10^{-6} M (porphyrin Soret band) to 10^{-5} M (Q-bands bands) solutions.

Fluorescence spectroscopy. Steady-state fluorescence spectra were recorded using a Photon Technologies International Quanta Master 8075-11 spectrofluorometer, equipped with a 75 W xenon lamp, running FelixGX software. An excitation wavelength 550 nm, exclusively porphyrin, was used and the concentrations were held constant at 0.1 mM for all the compounds. The fluorescence lifetimes were evaluated by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right-angle detection method was used.

Transient absorption spectroscopy. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating a diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.5 W. For optical detection, a Helios transient absorption spectrometer provided by Ultrafast Systems LLC coupled with an optical parametric amplifier (OPA) provided by Light Conversion was used. The source for the pump and probe pulses were derived from the fundamental output of the Libra laser (Compressed output 1.5 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into the OPA, while the rest of the output was used for generation of the white light continuum. In the present study, the maximum absorption wavelength for each compound was used in all the experiments. 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.

TR-EPR spectroscopy. TR-EPR spectra were recorded at X-band on a Bruker Elexsys E580 spectrometer equipped with a dielectric cavity and a CF935 cryostat. The microwave power used for the TR-EPR experiments was about 0.2 mW. Experiments were performed at a temperature of 80K using cold nitrogen gas as the cryogen and an Oxford ITC503 temperature controller to regulate the temperature. TR-EPR spectra were recorded in direct detection mode without field modulation; the signal was sampled with a LeCroy 9361 oscilloscope (20 ns per point). The time resolution of the spectrometer has been estimated to be about 2.0 μ s. Photoexcitation was performed using a Nd:YAG laser (Quantel Rainbow) equipped with an optical parametric oscillator (OPOTECH) pumped by the third harmonic module, operating at a 10Hz repetition rate. Laser pulses were 5 ns long, with energies of about 3 mJ and a wavelength of 575 nm. To avoid magnetophotoselection effects the data were collected with the polarization of the laser parallel and perpendicular to the magnetic field. Spectra from the two

measurements were then added in the ratio $I_{||}+2I_{\perp}$ to obtain the spectrum corresponding to isotropic excitation. The polarization of the light with respect to the magnetic field was controlled through a half-wave plate and a polarizing filter near the optical window of the cavity.

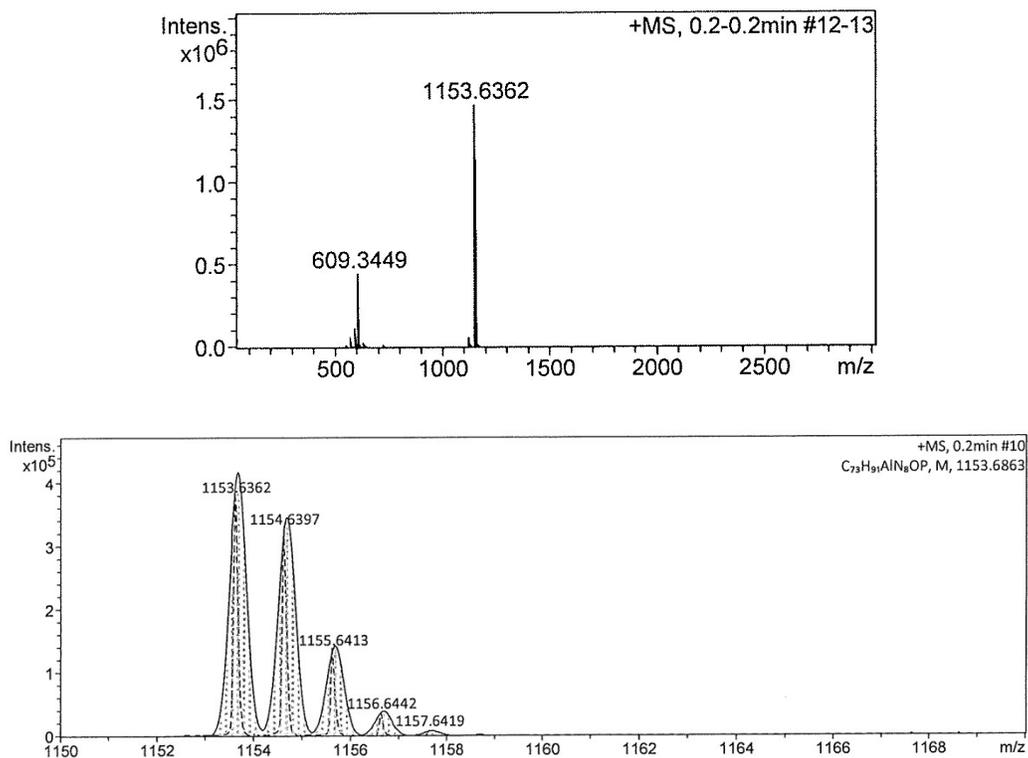


Figure S1. High resolution ESI mass spectra of AlPor-O-PPor.PF₆

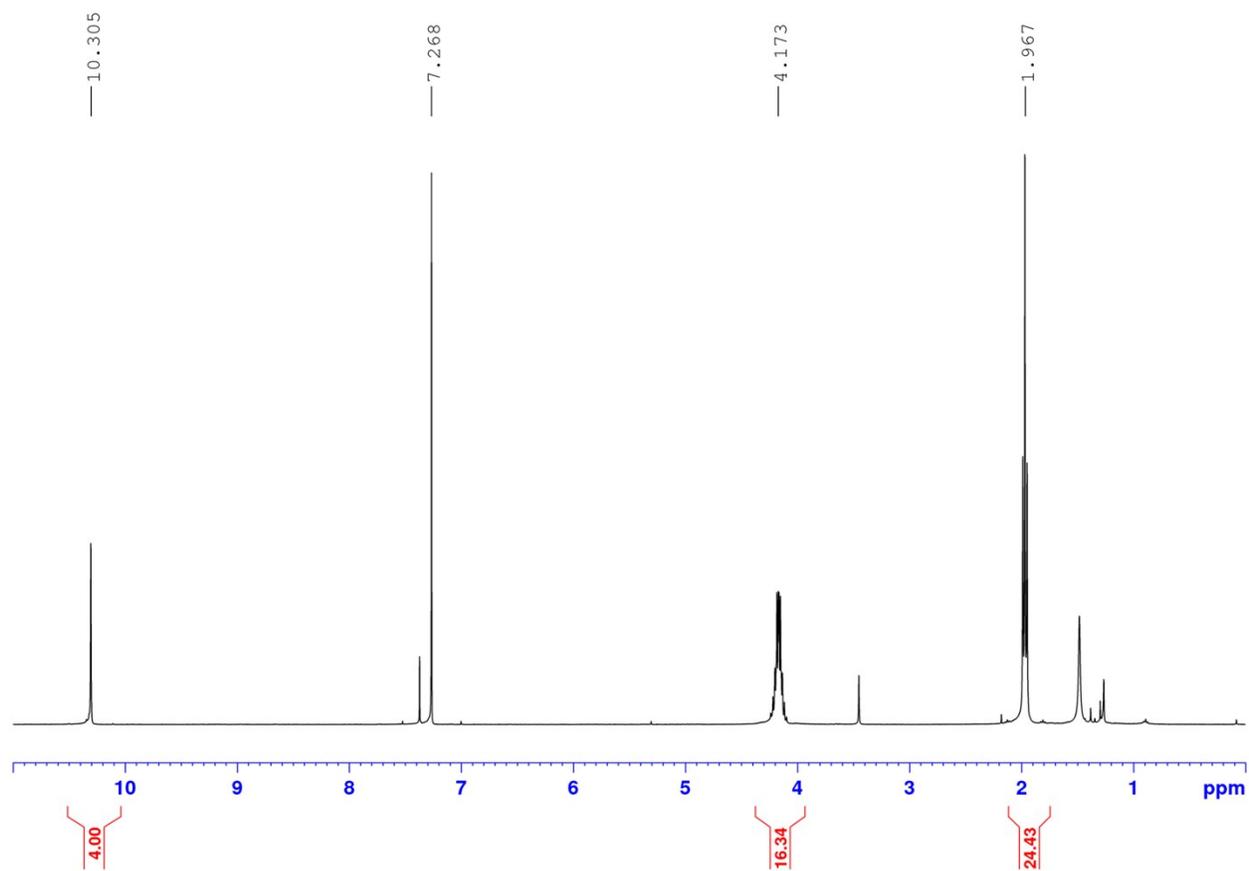


Figure S2. ^1H NMR (400 MHz) spectrum of AlPor-OH in CDCl_3 .

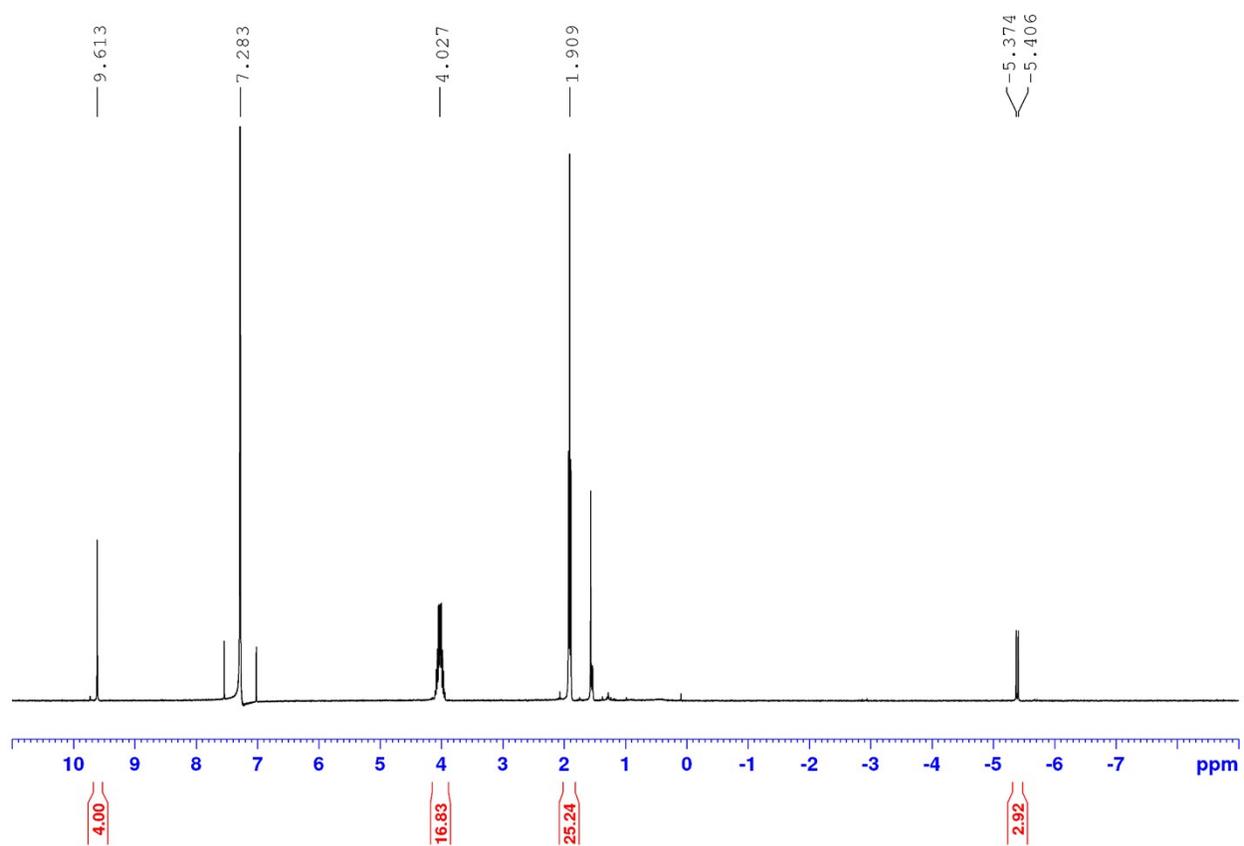


Figure S3. ^1H NMR (400 MHz) spectrum of PPor-OH.PF₆ in CDCl₃.

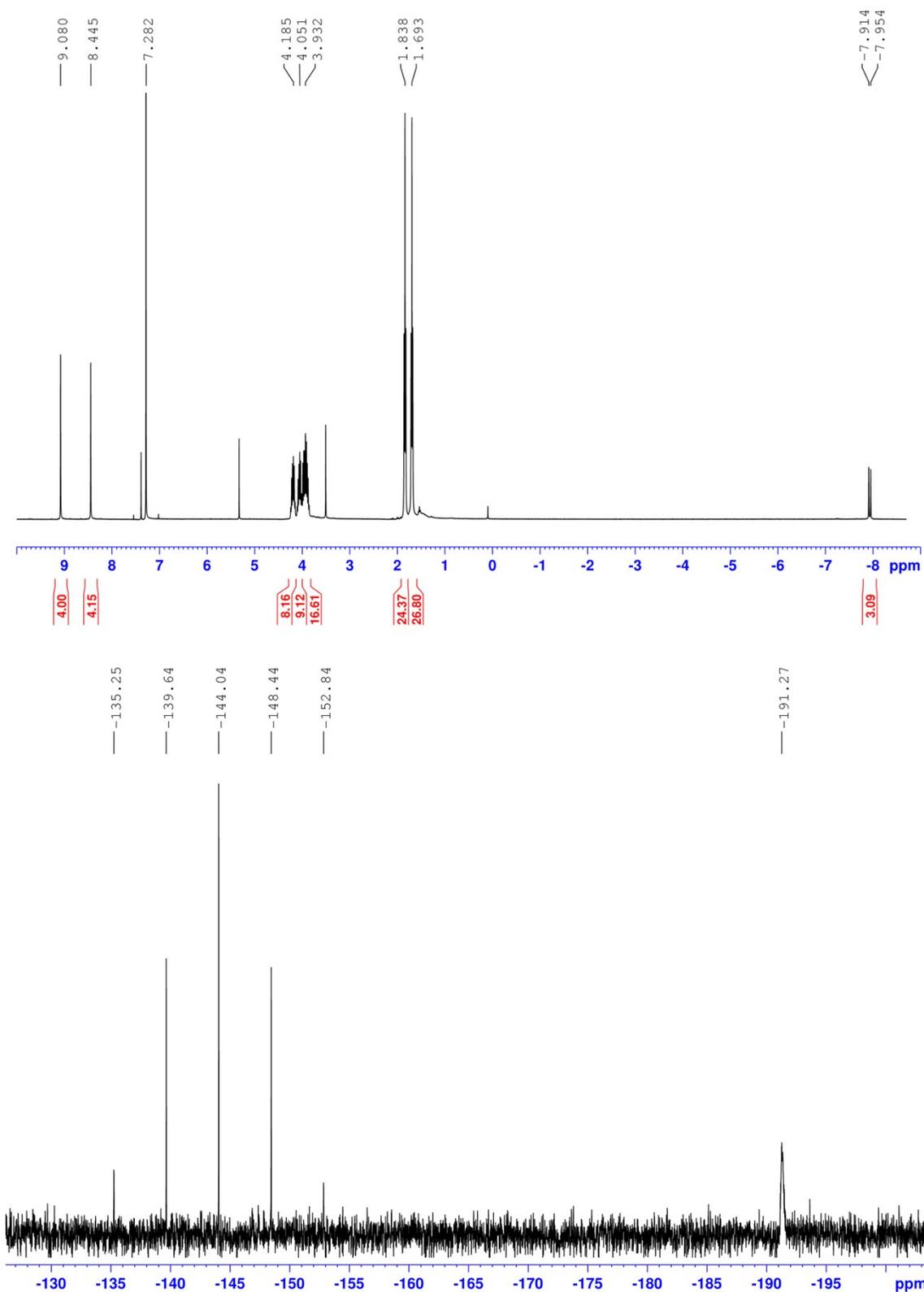


Figure S4. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectrum of AlPor-O-PPor.PF₆ in CDCl₃.

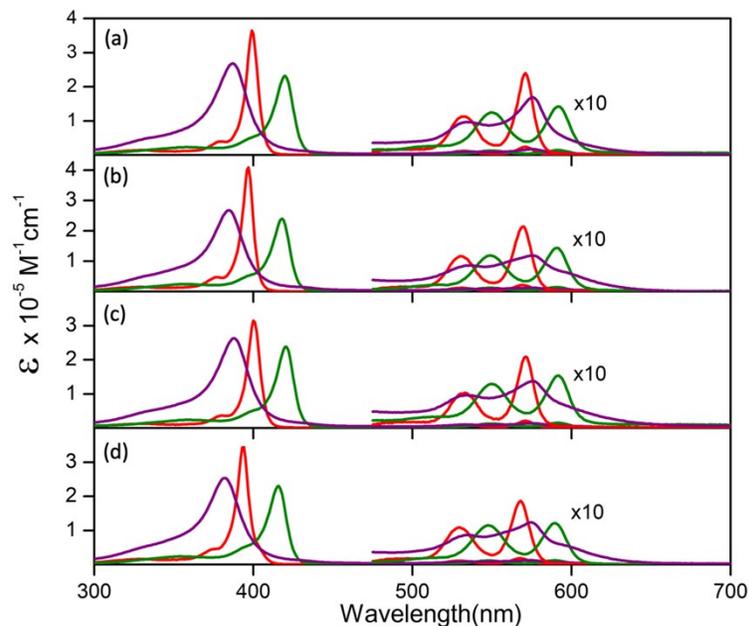


Figure S5. (a) Absorption spectra of AlPor-OH (red), PPor-OMe.PF₆ (green), and AlPor-O-PPor.PF₆ (purple) in (a) toluene, (b) CH₂Cl₂, (c) *o*-DCB and (d) CH₃CN.

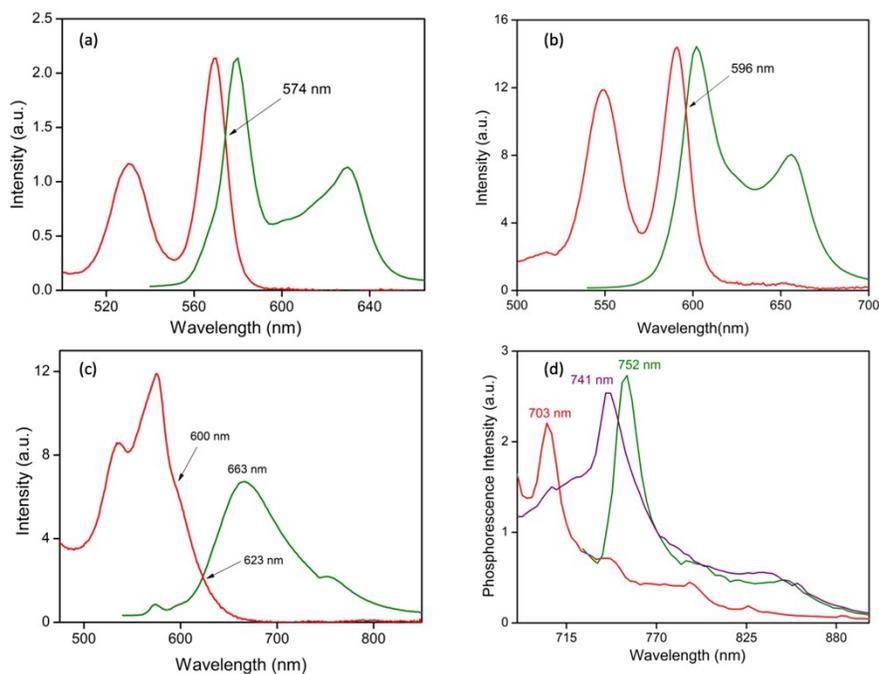


Figure S6. Superposition of the absorption (red) and fluorescence (green) spectra of (a) AlPor-OH, (b) PPor-OMe.PF₆, and (c) AlPor-O-PPor.PF₆ in CH₂Cl₂. (d) Phosphorescence spectra of AlPor-OH (red, excitation at 570 nm), PPor-OMe.PF₆ (green, excitation at 550 nm) and AlPor-O-PPor.PF₆ (purple, excitation at 570 nm) in degassed CH₂Cl₂:THF (=1:3) with few drop of 1,2-dibromoethane mixture at 77K.

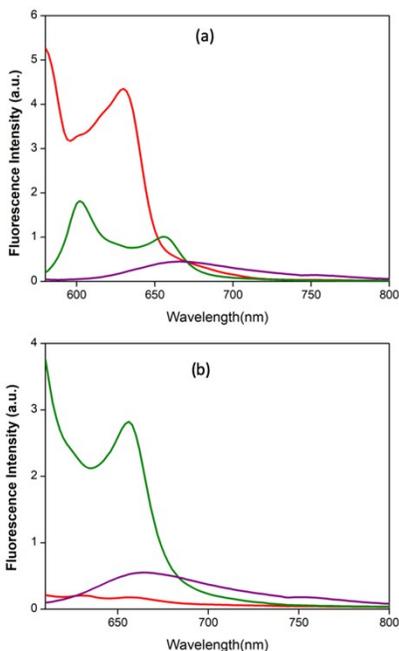


Figure S7. Fluorescence spectra of AlPor-OH (red), PPor-OMe.PF₆ (green) and AlPor-O-PPor.PF₆ (purple) in CH₂Cl₂: (a) excitation at 570 nm and (b) excitation at 600 nm.

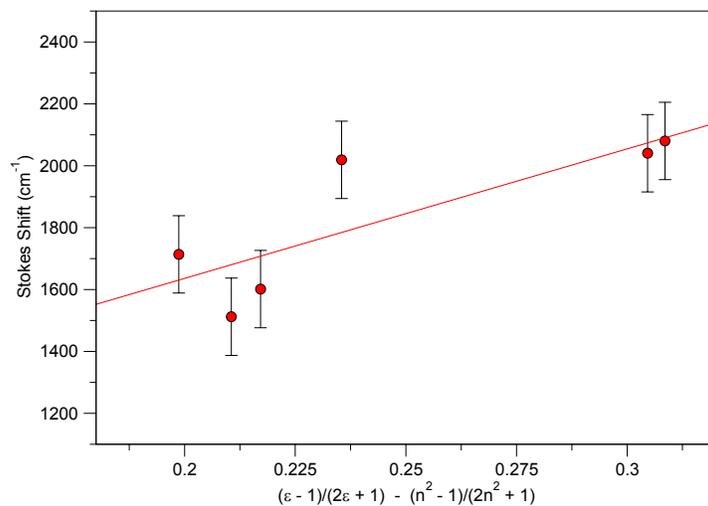


Figure S8. Lippert-Mataga plot of the Stokes shift of AlPor-O-PPor.PF₆ in several solvents (tetrahydrofuran, dichloromethane, o-dichlorobenzene, benzonitrile, methanol, acetonitrile).

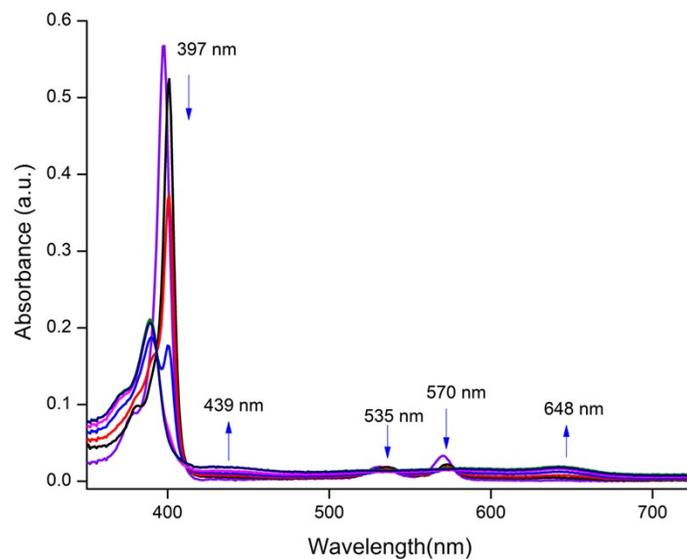


Figure S9. Spectral changes during the oxidation of AlPor-OH with $\text{Fe}(\text{ClO}_4)_3$ in CHCl_3 with 0.2 M TBA. ClO_4 .

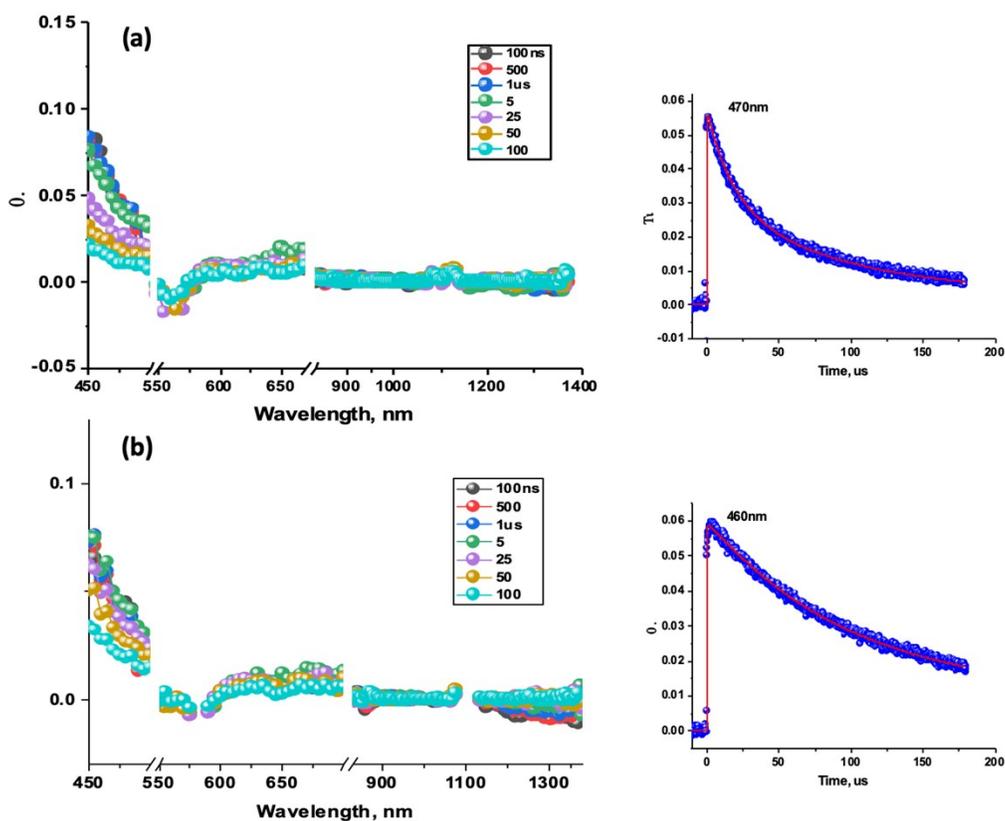


Figure S10. Nanosecond transient absorption spectra of (a) AlPor-OH and (b) PPor-OMe. PF_6 in *o*-DCB at the excitation wavelength of 533 nm.