Supplementary Material (ESI) for Analyst
This journal is (C) The Royal Society of Chemistry 2010

Electronic Supplementary Information to:

meso-Tetraarylporpholactones as High pH Sensors

Gamal E. Khalil,* Pedro Daddario, Kimberly S. F. Lau, Sayed Imtiaz, Michelle King, Martin Gouterman, Alexey Sidelev, Narissa Puran, Masoud Ghandehari and Christian Brückner*

Department of Chemistry, University of Connecticut, Unit 3060, Storrs, CT 06269-3060.
Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700.
Department of Civil and Environmental Engineering, Polytechnic Institute of New York University, Six MetroTech Center, Brooklyn, NY 11201.

* Authors to whom correspondence should be addressed. (GK) gamalk@u.washington.edu; (CB) Fax: +01-860-486-2981, phone: +01-860-486-2743, c.bruckner@uconn.edu

SI Table of Contents

SI Figures

SI Tables

Experimental

Instruments and Materials.

Instruments. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer in the solvents indicated. IR spectra were recorded on Perkins Elmer 1600 Series or Thermo Nicolet Nexus 670 FTIR spectrometers. UV-vis spectra were recorded either on a Hewlett-Packard 8452A Diode array or on a Cary 50 (Varian) spectrometer. For the optical fiber instrumental set-up, see below.

Materials. All solvents and reagents were used as received. Chremophor EL® was purchased from Acros. *meso*-Tetraphenylporphyrin (**TPP**),[1] [*meso*-tetraphenylporphyrinato]Pt(II) (**TPPPt**),[2] *meso*-tetra(pentafluorophenyl)porphyrin (**T^{F}PP**),[3] [*meso*-tetra(pentafluorophenyl)porphyrinato]Pt(II) (**T^{F}PPPt**),[3] *meso*-tetraphenylporpholactone (**TPL**)[4], and [*meso*-tetraphenylporpholactonato]Pt(II) (**TPLPt**)[5] were prepared as described in the literature. Free base *meso*-tetra(pentafluorophenyl)porpholactone (**T^{F}PL**)[6] and its Pt(II) complex **T^{F}PLPt** were either prepared by direct oxidation of **T^{F}PP**,[3] followed by insertion of Pt(II) using standard conditions,[2] stepwise oxidation of **T^{F}PP/T^{F}PPPt** as described in the SI, or purchased from Frontier Science, Inc., Logan, UT, USA, and used after plate chromatographic purification.

Analytical TLC plates (aluminum backed, silica gel 60, 250 μm thickness), preparative TLC plates (20 × 20 cm, glass backed, silica gel, 500 or 1000 μm thickness), and the flash column silica gel (premium grade, 60 Å, 40-75 μm) used were provided by Sorbent Technologies, Atlanta, GA.

VWR clear pH buffers from pH 7.0, pH 9.0, pH 11.0 and pH 13.0 were used.

Poly(methyl methacrylate)/methylenebis-acrylamide-methacrylamido-propyl trimethylammonium chloride co-polymer (PMMA/MAPTAC) (95:5 polymer ratio) was provided by the Polymer Research Institute at Polytechnic Institute of NYU.

---

1. Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
2. Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, p 389-483.
3. Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *19*, 386-391.
4. McCarthy, J. R.; Jenkins, H. A.; Brückner, C. *Org. Lett.* **2003**, *5*, 19-22.
5. Dean, M. L.; Schmink, J. R.; Leadbeater, N. E.; Brückner, C. *Dalton Trans.* **2008**, 1341-1345.
6. Gouterman, M.; Hall, R. J.; Khalil, G.-E.; Martin, P. C.; Shankland, E. G.; Cerny, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 3702-3707.

Titanium dioxide powder (Grade CR-828, Lot. number: G8281334) was obtained from TRONOX.

Synthesis of [*meso*-tetra(pentafluorophenyl)porpholactonato]Pt(II) (T^FPLPt).

To a solution of *meso*-tetra(pentafluorophenyl)porphyrinato]Pt(II) **T^FPPt** (1.33 g, 1.65 mmol) in 30% pyridine ethanol-stabilized $CHCl_3$, 1.0 g OsO_4 (1.1 equiv) was added. The solution was stirred at room temperature for 24 h, shielded from light. The solution was filtered through a plug of Celite® (diatomaceous earth) and washed with $CHCl_3$ until the filtrate was colorless. The filtrate was concentrated to dryness under vacuum, then redissolved in CH_2Cl_2 and purified by column chromatography (0.5% MeOH in CH_2Cl_2). The first burgundy fraction was collected and reduced to dryness to provide the [*meso*-tetra(pentafluorophenyl)chlorinato]Pt(II) osmate ester bispyridine adduct[7] in 55% yield (MW = 1580.03, 1.43 g, 0.91 mmol). For the ^{1}H NMR of this product, see Figure ESI-1. This product was dissolved in CH_2Cl_2 until the solution became translucent (ca. 1 L of solvent for every 250 mg of chlorin). To this solution were added 6 equiv of cetyltrimethylammonium permanganate (CTAP) in two parts over 30 min at ambient temperature and shielded from light (aluminum foil). When TLC control revealed the complete consumption of the starting material, the solution was filtered through a short plug Celite (in a glass frit M) to remove the precipitated brown-black and pasty manganese salts. The filter was washed with CH_2Cl_2 until the filtrate was colorless. The combined filtrates were evaporated to dryness by rotary evaporation to afford [*meso*-tetrakis(pentafluorophenyl)porpholactonato]Pt(II) (**T^FPLPt**) as a red powdery solid in essentially quantitative yields. The material proved to be identical to that described before:[8] R_f = 0.88 (silica, 30% petroleum ether 30-60 in CH_2Cl_2); UV-vis (CH_2Cl_2) λ_{max} (log ε): 396 (5.26), 536 (4.22), 574 (4.82) nm; UV-vis (CH_2Cl_2, xs DBU) λ_{max} (log ε): 432 (5.18), 702 (4.94) nm; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.0-8.8 (m) ppm; ^{1}H NMR (400 MHz, xs DBU, δ): 7.6-7.2 (m); ^{13}C NMR (100 MHz, $CDCl_3$, D1 = 2.5 s, δ): 163.2, 148.7, 146.7, 142.7, 141.0, 139.9, 139.3, 138.7, 133.9, 131.6, 130.3, 130.0, 129.9, 129.0, 118.7, 112.0, 108.4, 105.9, 88.0; ^{13}C NMR (100 MHz, xs DBU, D1 = 2.5 s, δ): 178.9, 171.4, 165.9, 152.2, 146.65, 146.62, 144.4, 139.7, 133.8, 131.3, 130.3, 127.0, 125.2, 121.4, 111.3, 98.0, 96.7, 96.3; ^{19}F NMR (376.5 MHz, $CDCl_3$, D1 = 3.0 s, δ): –136.4 to –136.8 (m, 6F_{ortho}), –138.1 to –138.3 (m, 2F_{ortho}), –

---

[7] The bispyridine adducts of ß,ß'-diolchlorins are described in further detail in: (a) Brückner, C. Ph.D. Thesis, University of British Columbia, Canada, 1996. (b) Samankumara, L. P.; Zeller, M.; Krause, J. A.; Brückner, C. *Org. Biomol. Chem.* **2010**, accepted for publication.

[8] Khalil, G.; Gouterman, M.; Ching, S.; Costin, C.; Coyle, L.; Gouin, S.; Green, E.; Sadilek, M.; Wan, R.; Yearyean, J.; Zelelow, B. *J. Porphyrins Phthalocyanines* **2002**, *6*, 135-145.

150.1 to –150.35 (m, $3F_{para}$), –150.8 to –151.0 (m, $1F_{para}$), –160.3 to –160.7 (m, $6F_{meta}$), –161.1 to –161.3 (m, $2F_{meta}$); ^{19}F NMR (376.5 MHz, xs DBU, D1 = 3.0 s, δ): –137.9 (d, *J* = 22 Hz, $2F_{ortho}$), –138.7 to –139.3 (m, $6F_{ortho}$), –153.6 (t, *J* = 21 Hz, $1F_{para}$), –154.1 (t, *J* = 21 Hz, $1F_{para}$), –156.4 (t, *J* = 21 Hz, $1F_{para}$), –157.9 (t, *J* = 21 Hz, $1F_{para}$), –162.0 to –162.3 (dt, $4F_{meta}$), –164.2 to –164.7 (dt, $4F_{meta}$); IR (Teflon card, xs NaOMe) ν_{max}: 1766 cm^{-1}. For select spectra, see below.

Preparation of Planar Optode

A solution of polymer (100 mg) and **T^{F}PL** (2 mg) in CH_2Cl_2 (4 mL) was prepared. A 100 µL aliquot of this solution was spin-coated onto a 1 × 2 cm transparent polycarbonate coupon, forming an optical clear red film. The dried film was fitted into an optical cell filled with aqueous buffer solutions.

Preparation of High pH Fiber Optics Chemical Sensor

meso-tetra(pentafluorophenyl)porpholactone (**T^{F}PL**) (20 mg, 2.0×10^{-5} mol) were dissolved in 25% PMMA/MAPTAC copolymer in chloroform ($CHCl_3$, 4 mL). Titanium dioxide (TiO_2, 1.0 g) was added to the mixture that was stirred for 1.5 h.

Optical glass fiber (Thorlabs, Inc. BFL600, 600 µm silica core and coated by a fluoro-polymer cladding) was cut into 30 cm sections. 0.25 cm of the fluoropolymer cladding was removed from the fiber tips and the tips were polished (diamond paste). Then the tips were washed with acetone. The fibers were dip-coated with the PMMA/MAPTAC/**T^{F}PL**/TiO_2/$CHCl_3$ solution twice, with a 30 min drying time between coatings. This process was monitored using a Bodelin Proscope Microscope (50 x). After fibers were coated, they were cured for 24 h at 70 °C and then hydrated for 1.5 hours in distilled water.

The optical fibers were coupled into an optical fiber beam splitter. Ocean Optics USB2000 UV-vis Spectrometer and an Ocean Optics LS1 White light source were used to collect spectral data (450-800 nm). Media changes were accomplished by pipetting media in and out of a test tube without disturbing the position of the probe.

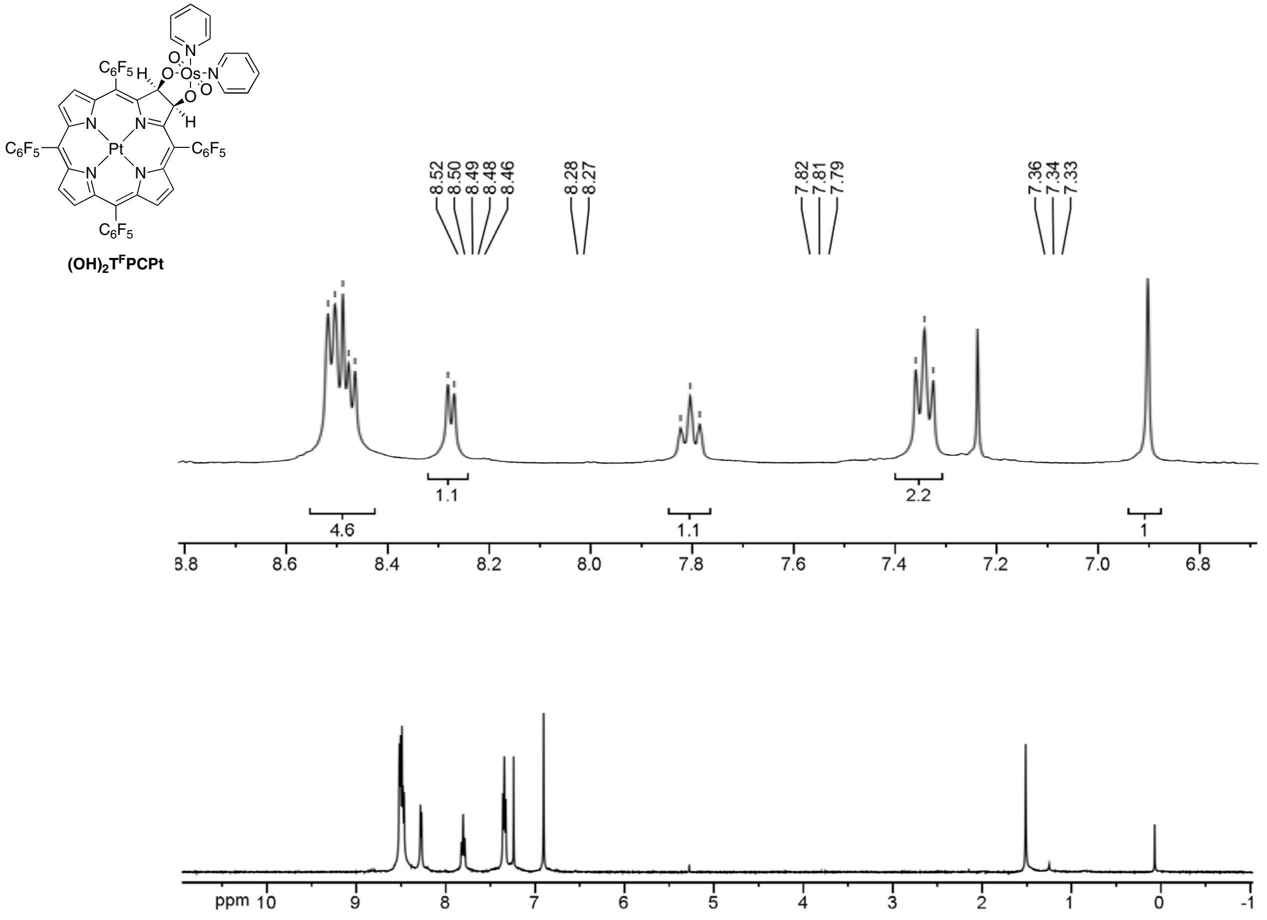
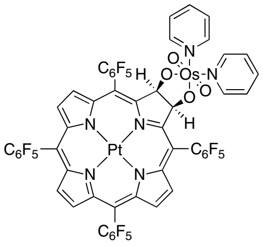


Figure ESI - 1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **(OH)$_2$T^{F}PCPt** osmate ester bispyridine adduct.



(OH)$_2$T^{F}PCPt

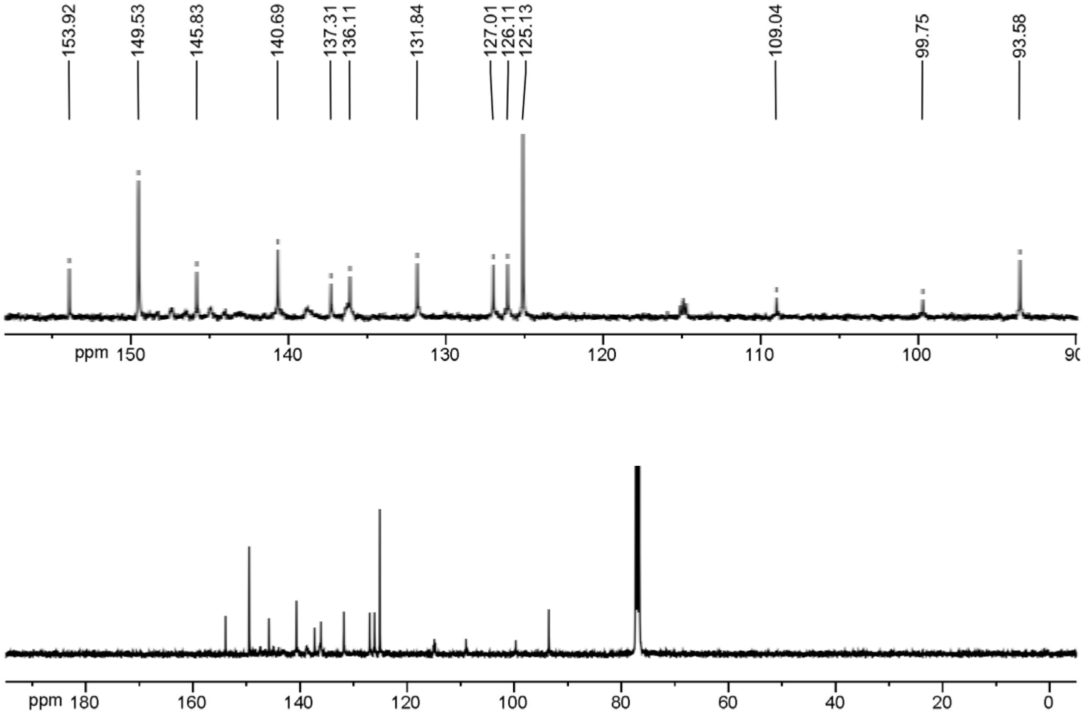
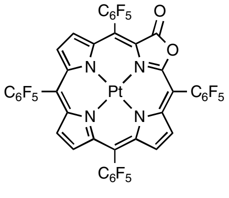


Figure ESI - 2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **(OH)$_2$T^{F}PCPt** osmate ester bispyridine adduct.



T^{F}PLPt

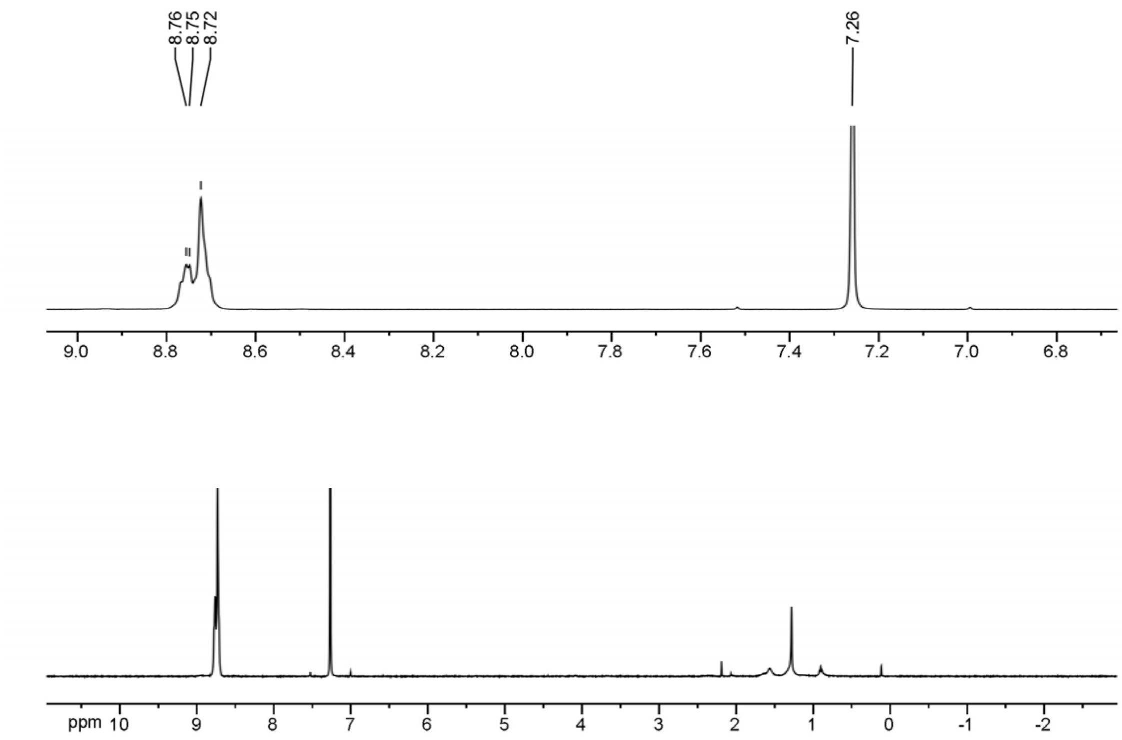
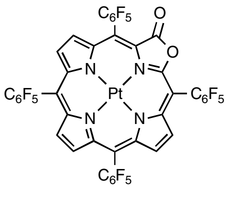


Figure ESI - 3. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of **T^{F}PLPt**.



T^FPLPt

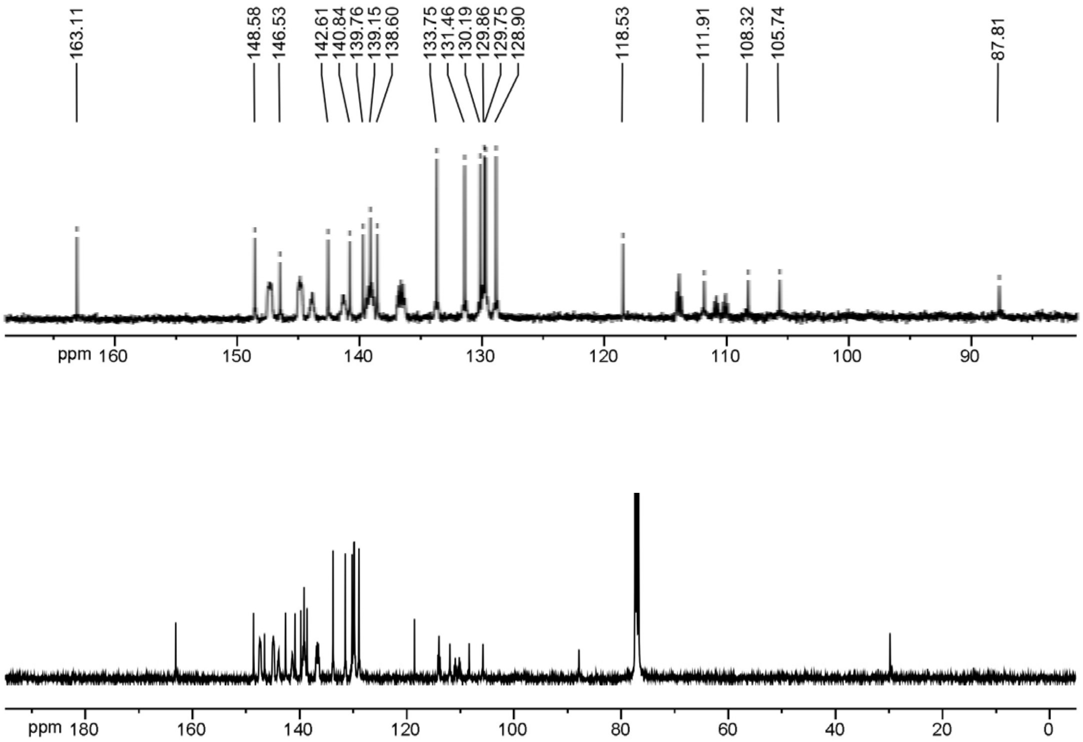


Figure ESI - 4. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 25 °C) of **T^FPLPt**.

Synthesis of *meso*-tetra(pentafluorophenyl)porpholactone (T^FPL).

Prepared in 60% yield from *meso*-tetrakis(pentafluorophenyl)porphyrin (**T^FPP**) according to the procedure delineated for **T^FPLPt**. The material proved to be identical to that described before.[8,9]

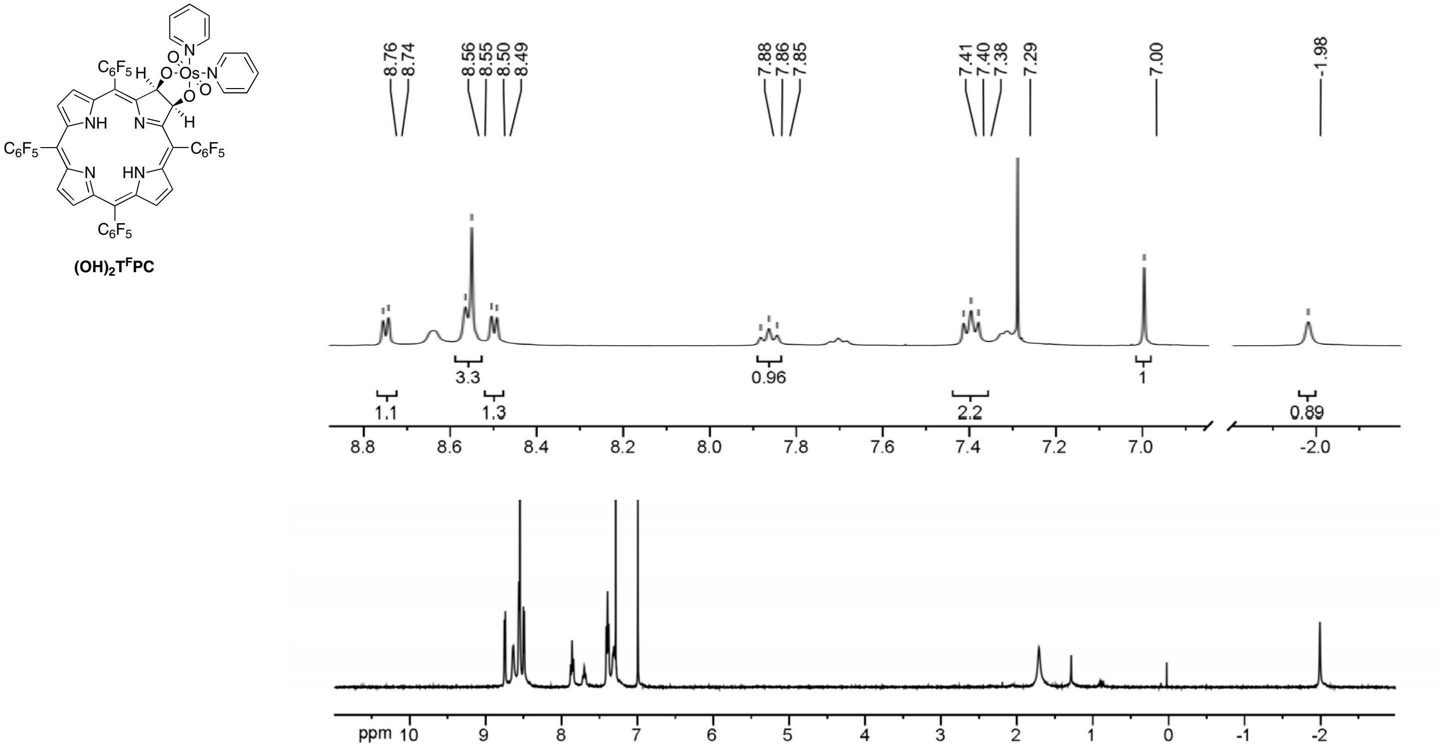
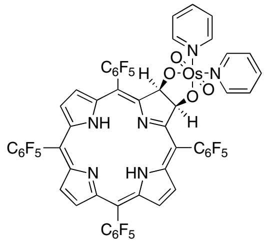


Figure ESI - 5. ^1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **$(OH)_2T^FPC$** osmate ester bispyridine adduct.

---

[9] Gouterman, M.; Hall, R. J.; Khalil, G.-E.; Martin, P. C.; Shankland, E. G.; Cerny, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 3702-3707.



(OH)$_2$T^{F}PC

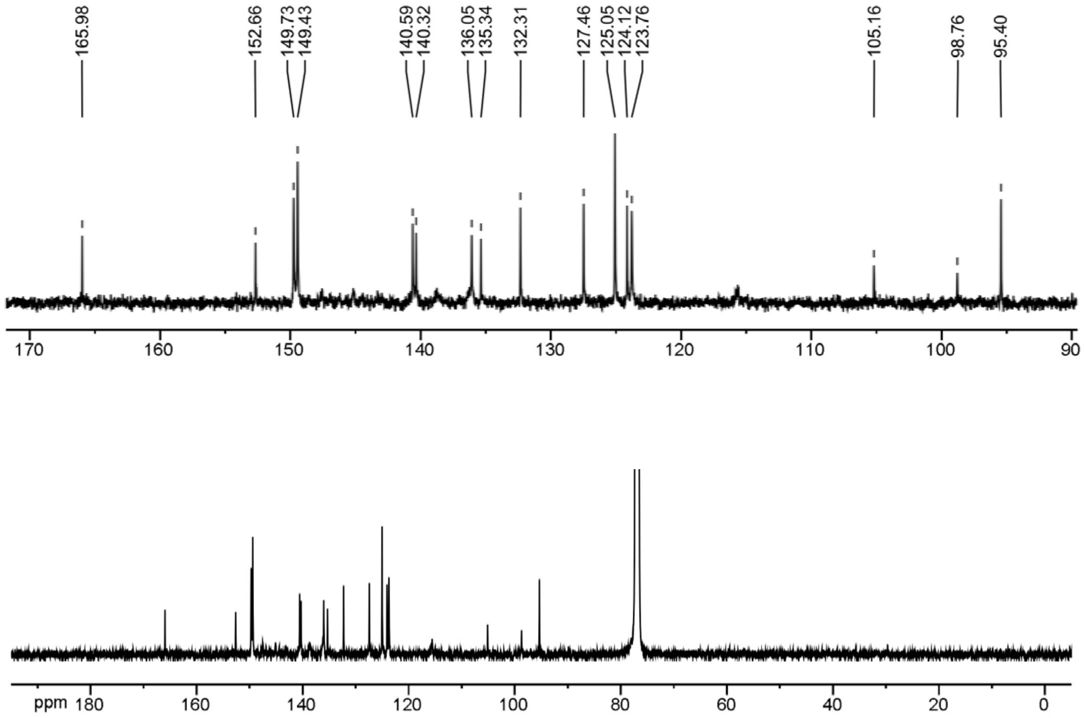
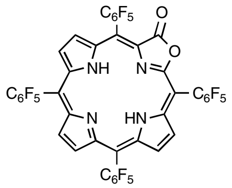


Figure ESI - 6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25°C) of **(OH)$_2$T^{F}PC** osmate ester bispyridine adduct.



T^{F}PPL

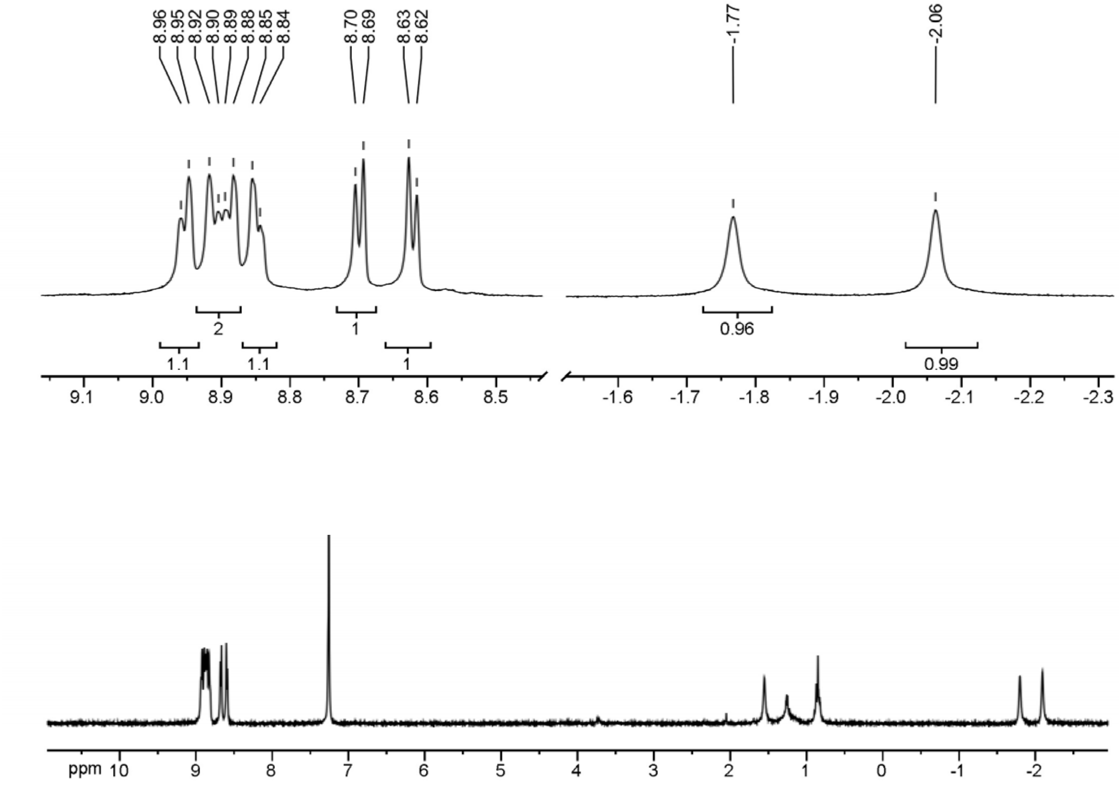
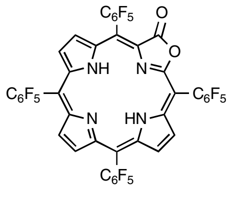


Figure ESI - 7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of **T^{F}PL**.



T^{F}PPL

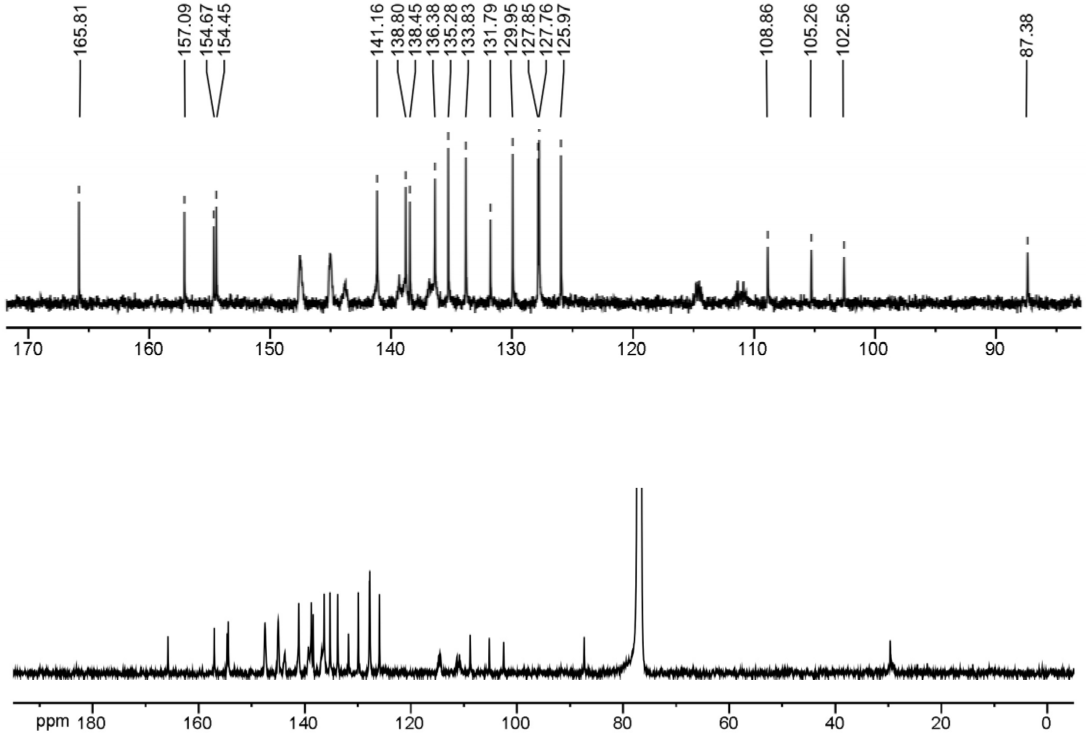


Figure ESI - 8. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 25 °C) of **T^{F}PL**.

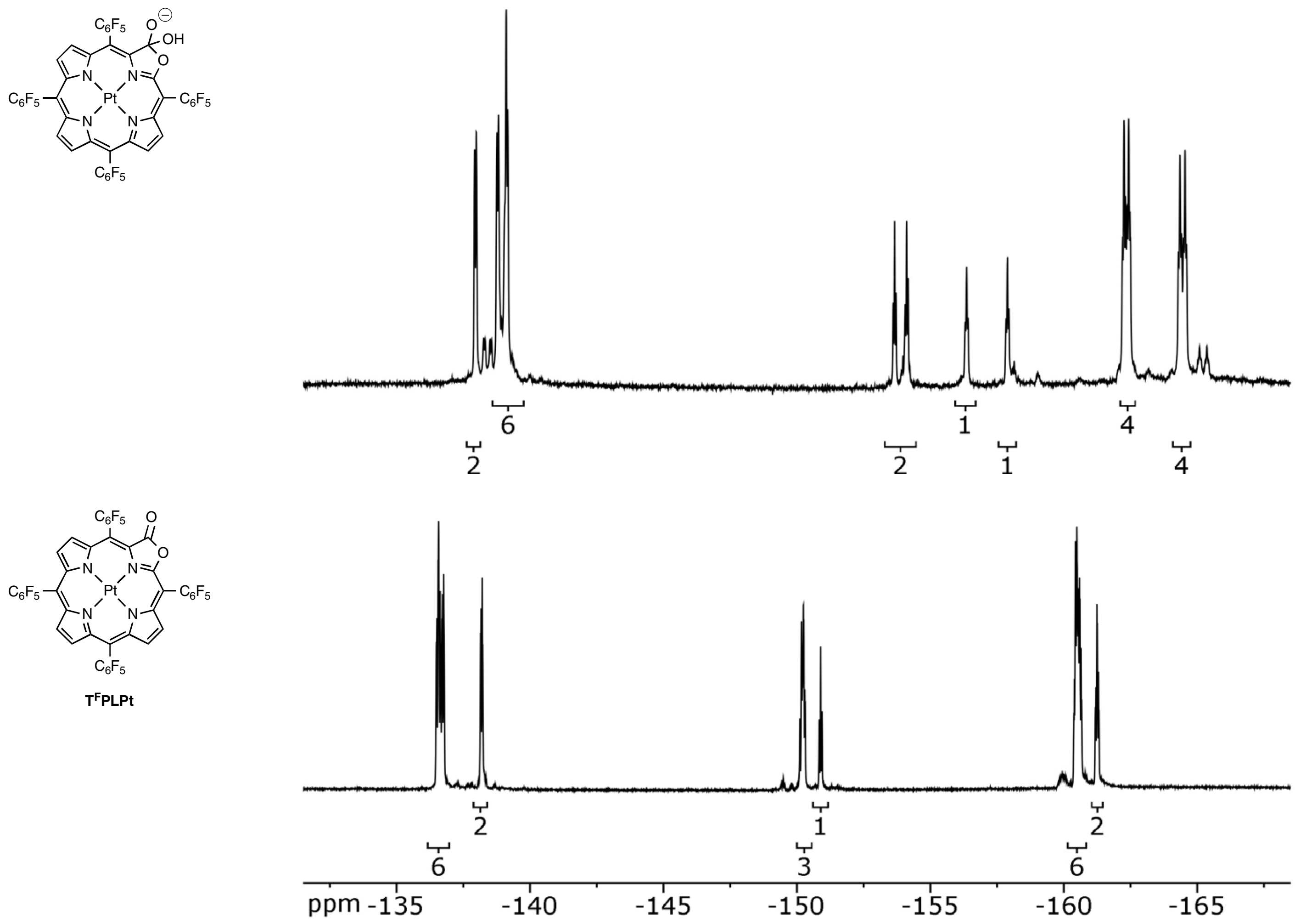
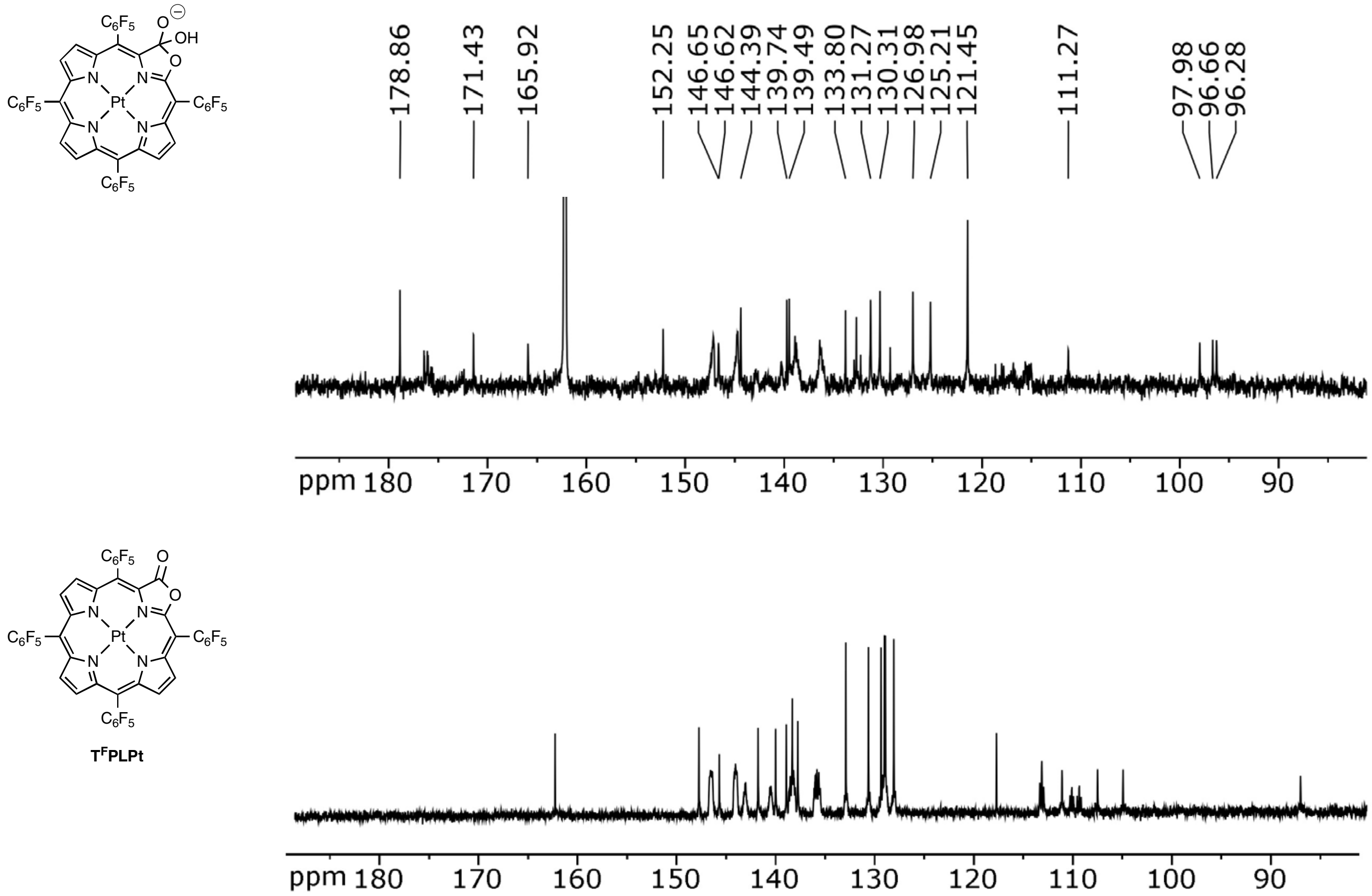


Figure ESI - 9. ^{19}F NMR spectra (376.5 MHz, $CDCl_3$, 25 °C) of **T^{F}PLPt** before (bottom) and after (top) addition of a stoichiometric excess of DBU.



1

3

Figure ESI - 10. ^{13}C NMR spectra (400 MHz, $CDCl_3$, 25 °C) of **T^{F}PLPt** before (bottom) and after (top) addition of a stoichiometric excess of DBU. Peak at 162 ppm corresponds to the protonated DBU imine carbon.

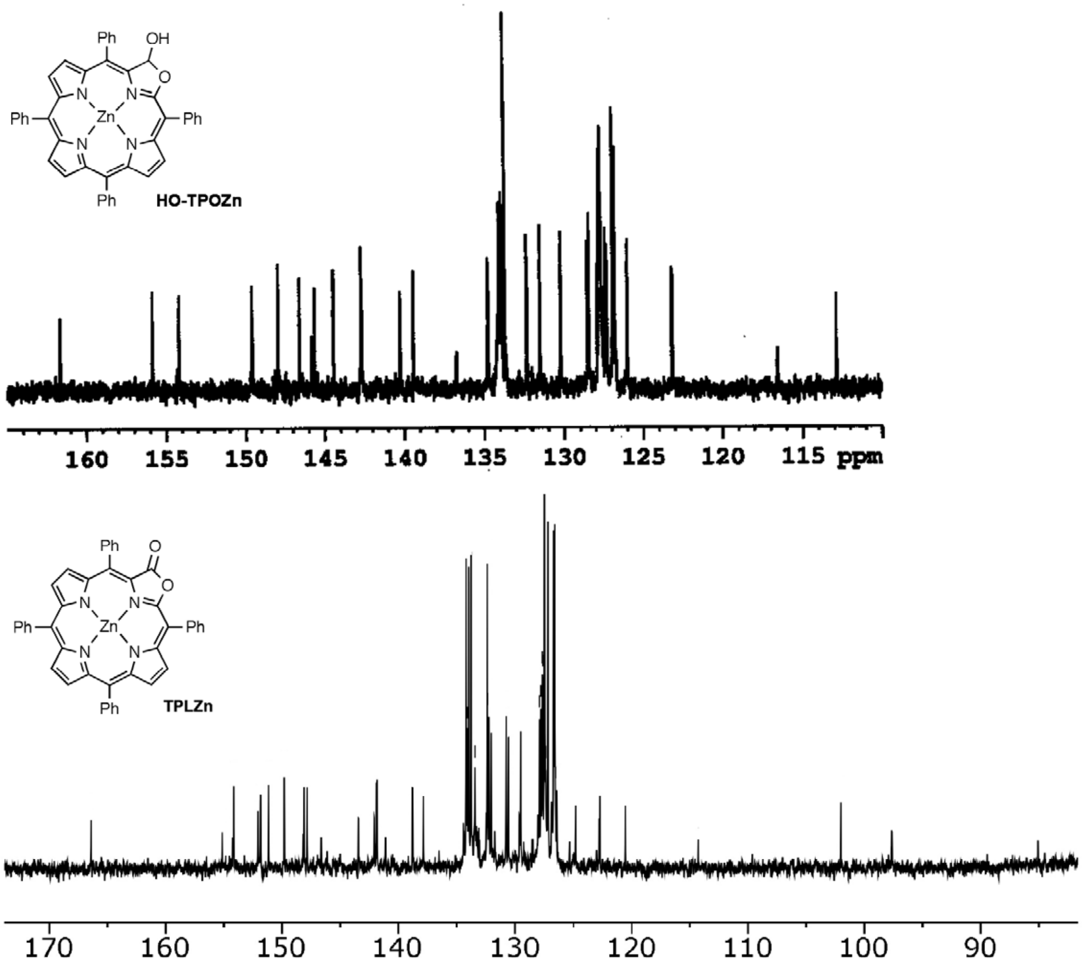
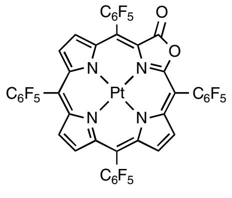


Figure ESI - 11. ^{13}C NMR (100 MHz, $CDCl_3$) comparison of **HO-TPOZn** and **TPLZn**, highlighting their similarities, and the similarity to the **T^{F}PLPt** before and after the addition of a stoichiometric excess of DBU (previous figure).



T^{F}PLPt

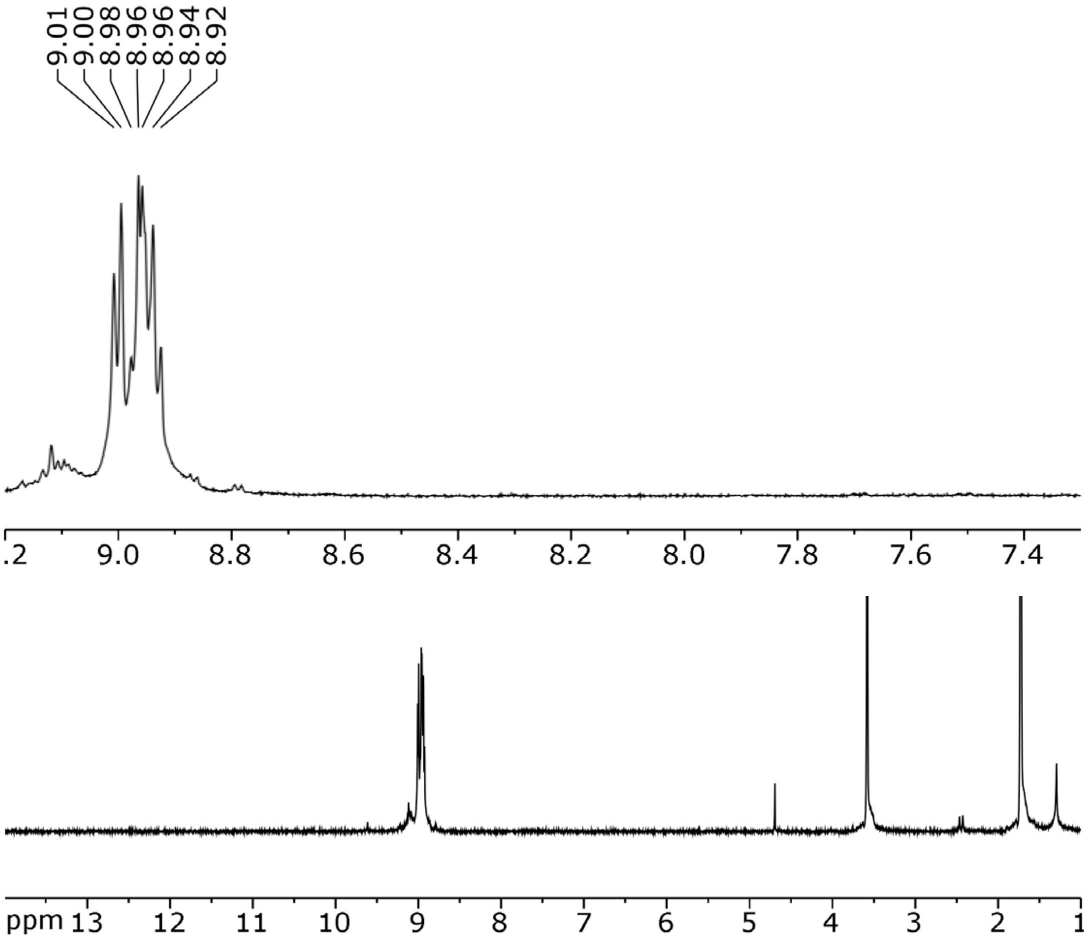


Figure ESI - 12. ^{1}H NMR spectra (400 MHz, CDCl$_3$, 25 °C) of **T^{F}PLPt** before addition of a stoichiometric excess of DBU.

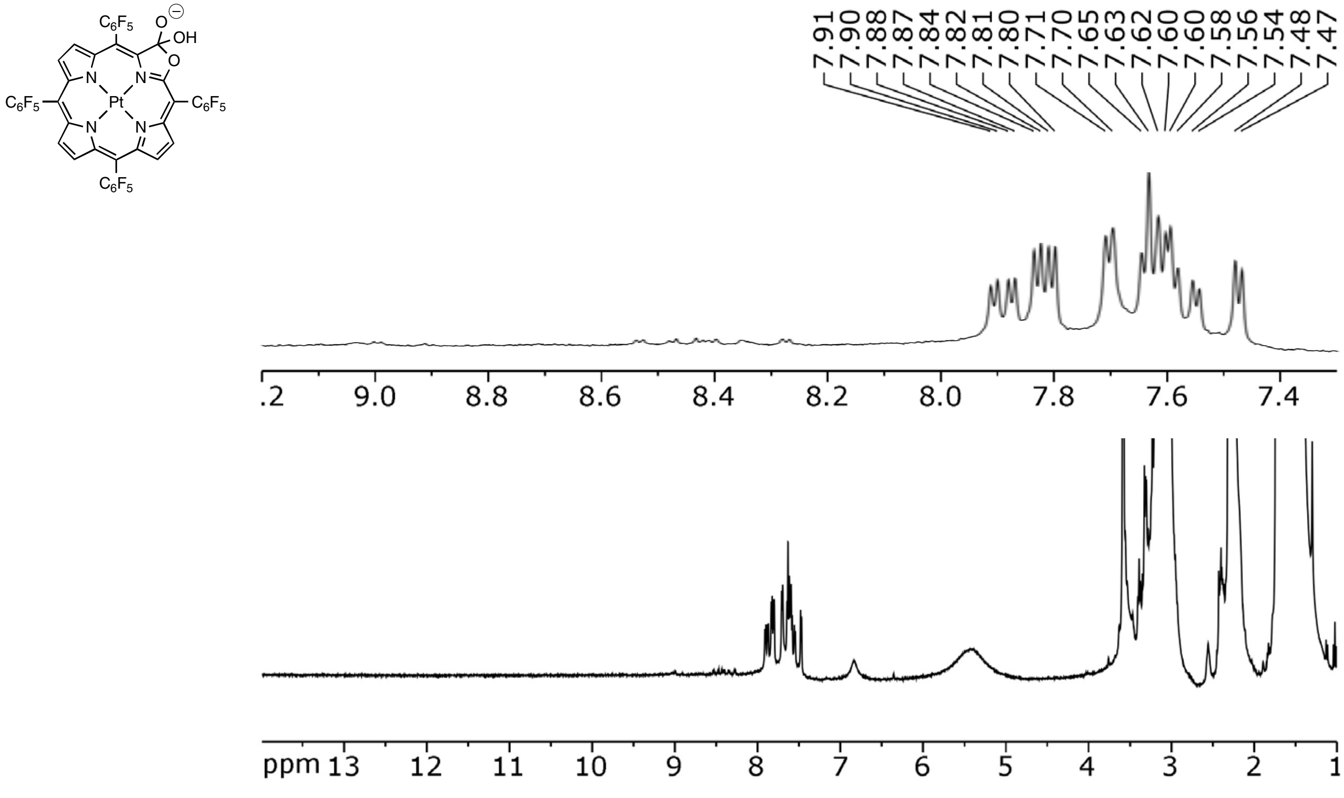


Figure ESI - 13. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of **T^{F}PLPt** after addition of a stoichiometric excess of DBU.

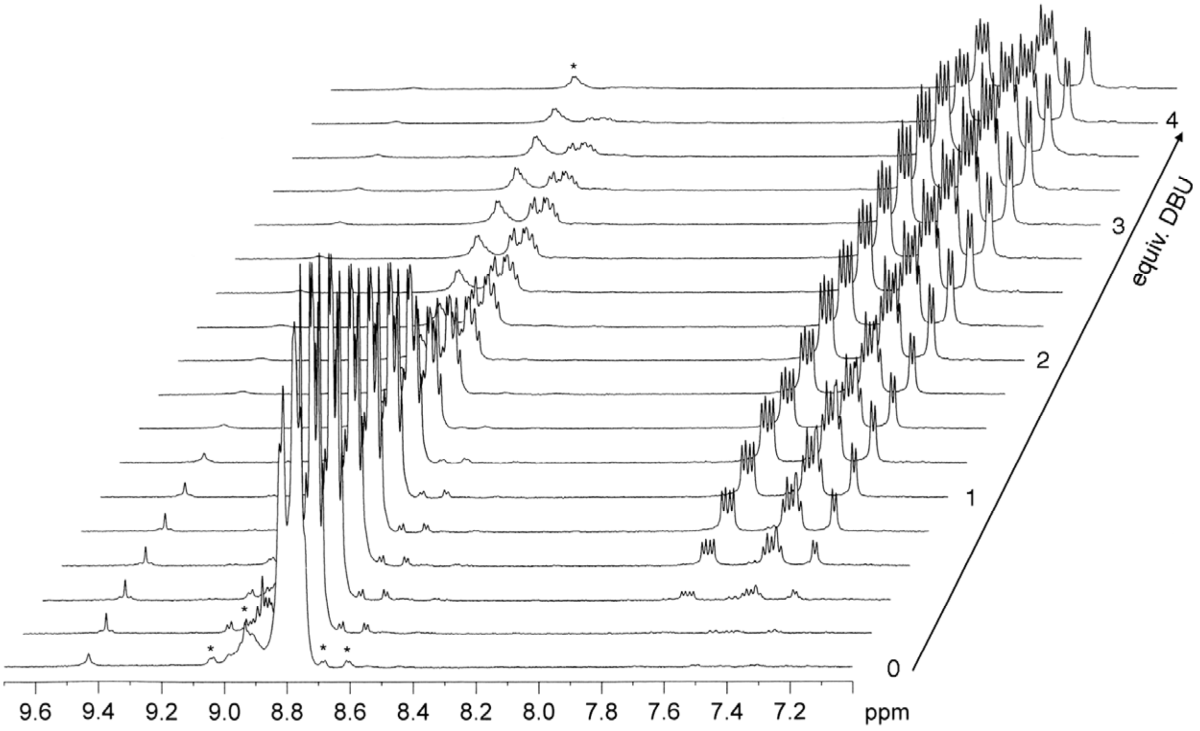


Figure ESI - 14. ^{1}H NMR (THF-d_8, 400 MHz, 22 °C) spectral titration of **T^{F}PLPt** with base (DBU), aromatic (ß-hydrogen) region; * indicates impurity. *Conditions:* 22 mg **T^{F}PLPt** in 500 µL THF-d_8 + 10 µL CH_2Cl_2 as internal integration standard; addition of aliquots (typically 10 µL) of a THF-d_8 solution containing 0.48% (v/v) DBU (50 µL DBU/1.0 mL THF-d_8). For full spectra, see Figures ESI-12 and ESI-13.

To the same extent as the integrated intensities of the six overlapping doublets corresponding to the six non-equivalent ß-protons in **T^{F}PLPt** (8.7 – 8.9 ppm) are reduced upon addition of DBU, a new species becomes discernible. It is characterized by a high field-shifted spectrum that is spread over a broader shift range (7.6 – 7.2 ppm). The sum of the ß-proton integration of the two species at any stage of the titration corresponds to six hydrogens.

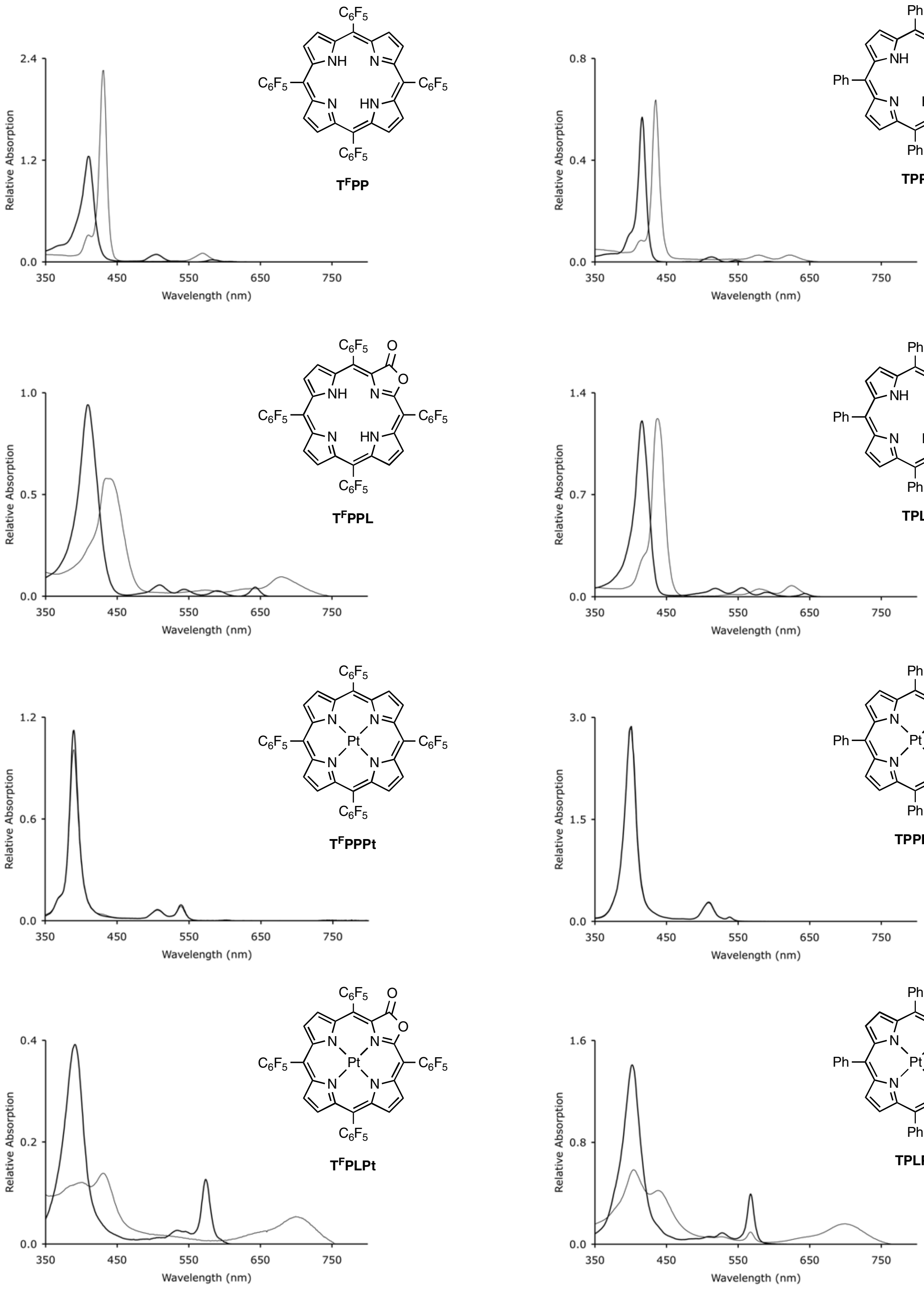


Figure ESI - 15. UV-vis spectra of **T^{F}P** and **TPP** derivatives before (bold) and after (thin line) addition of NaOMe/MeOH (THF, 25 °C).

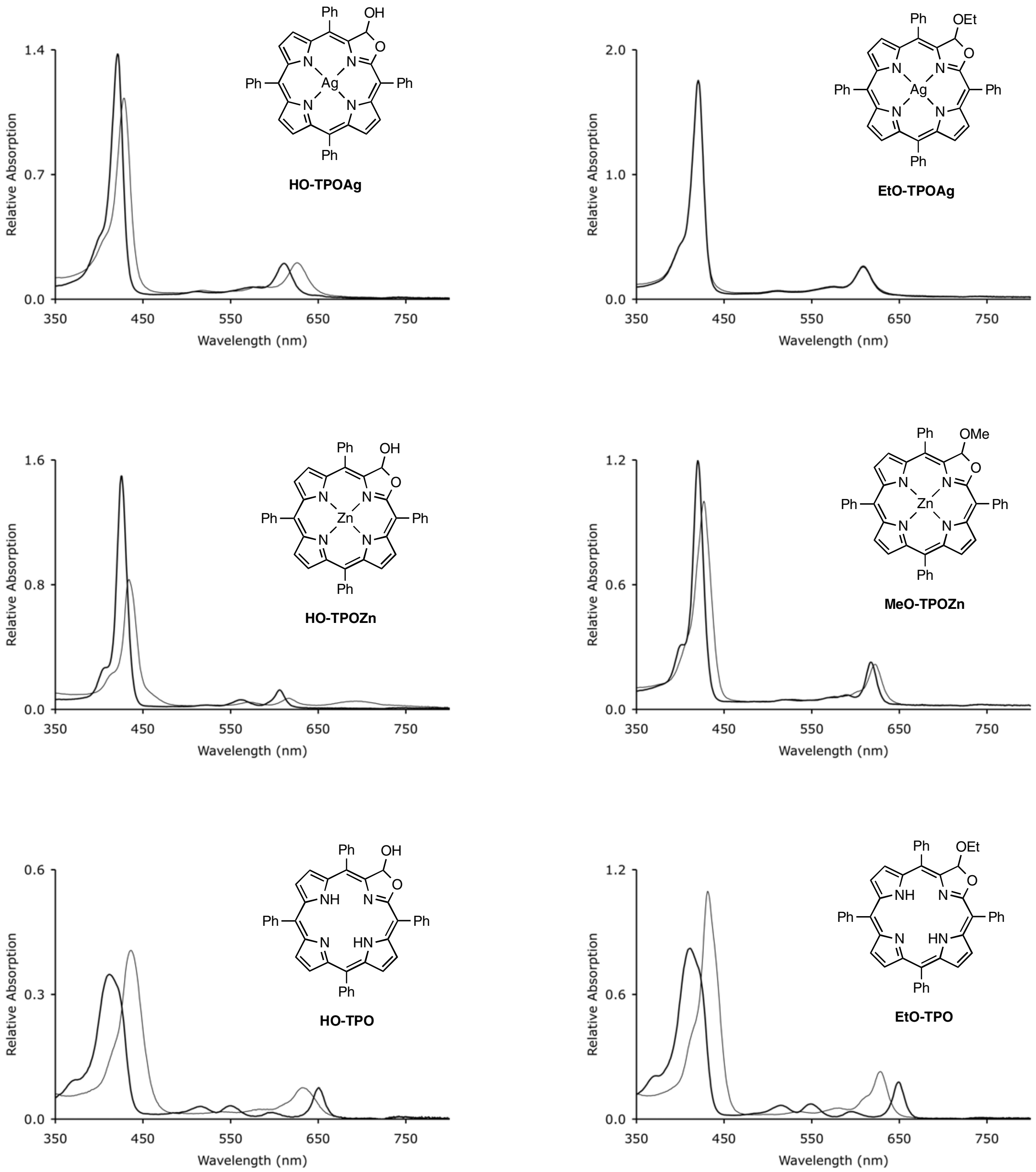


Figure ESI - 16. UV-vis spectra of **HO-TPOM** upon addition of NaOMe/MeOH (THF, 25 °C). The changes observed are interpreted as deprotonation of the alcohol functionality in **HO-TPOAg** and **HO-TPOZn,** but as NH deprotonation in **(OH)TPL** and **EtO-TPO**. The slight change seen in the **MeO-TPOZn** upon reaction with base is possibly due to ligation to the central metal.

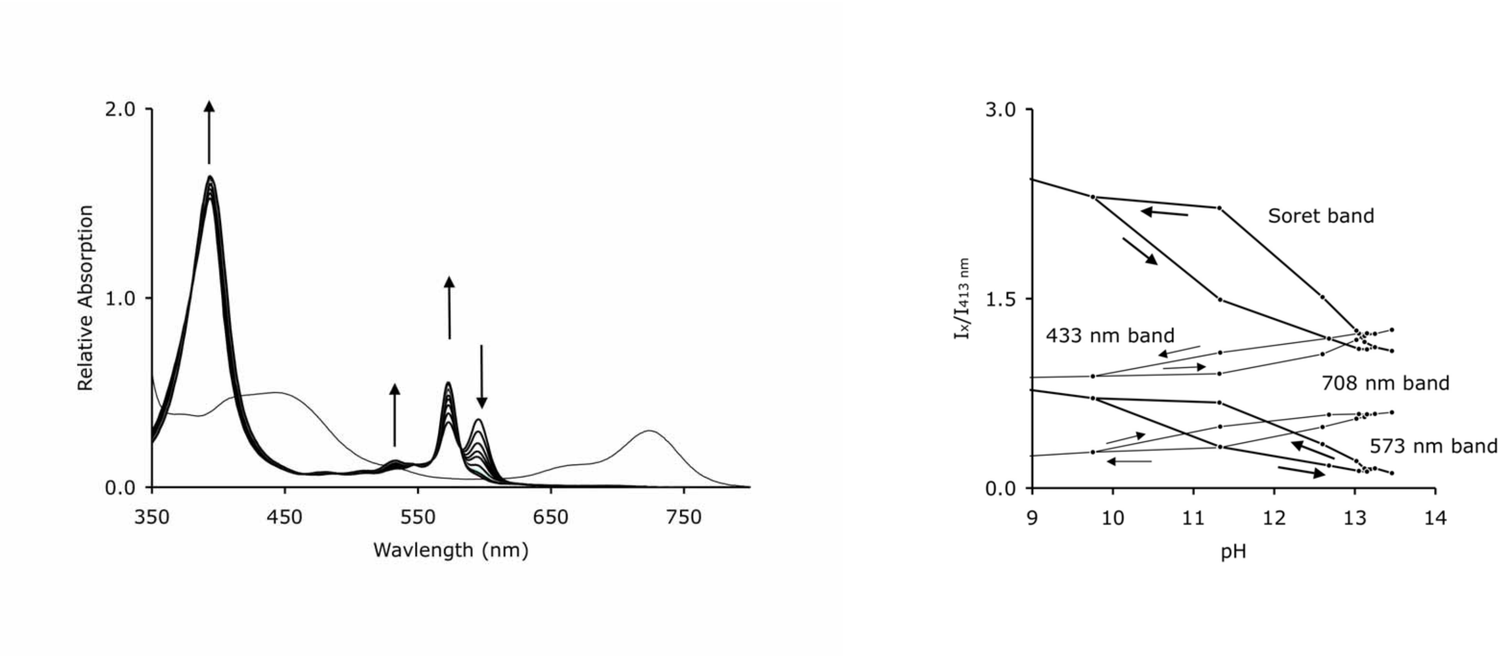


Figure ESI - 17. Hysteresis is observed during the acidification of species formed from **T^{F}PLPt** with base (DBU) (right) back to the starting material. In the presence of water or aqueous basic solutions, we note the appearance of an intermediate species (left), presumably the orthoester, with a band at 593 nm which converts back to the starting material upon further acidification.

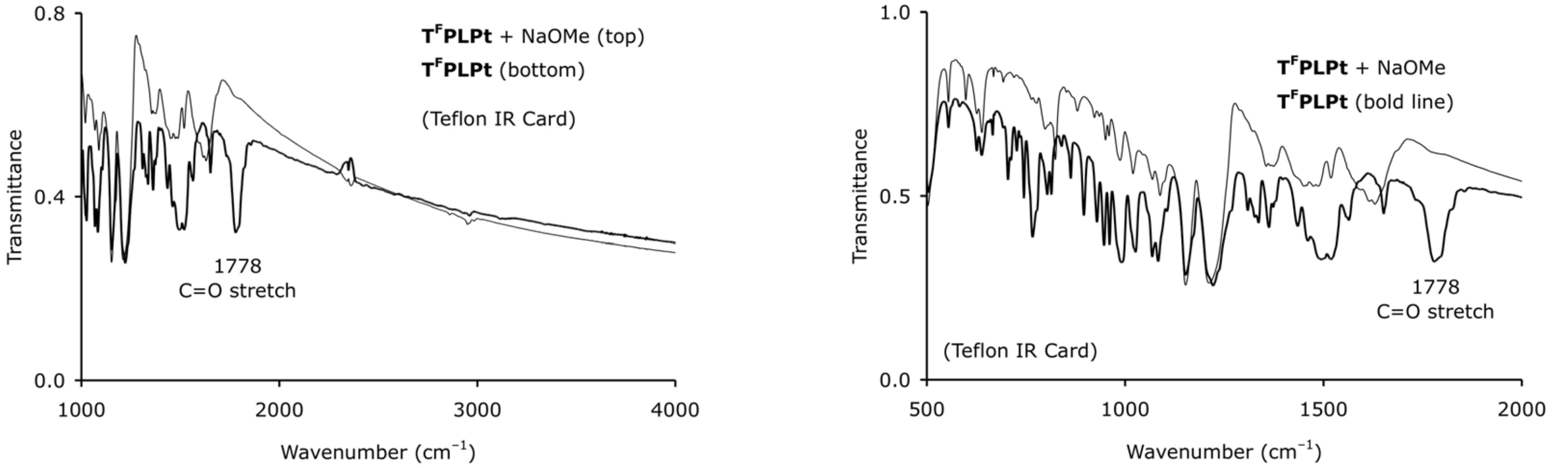


Figure ESI - 18. IR spectra of **T^{F}PLPt** before (bold) and after (thin line) addition of NaOMe/MeOH to a Teflon IR card in full (left) and detail (right). Conditions: ~1.0 µL of a 0.02 M solution of **T^{F}PLPt** in CH_2Cl_2 was deposited on a Teflon IR card and left to dry, and the spectrum recorded. Then ~10 µL of a conc. solution of NaOMe in MeOH was deposited on top of the porphyrinoid and dried. A blank IR card served as reference.

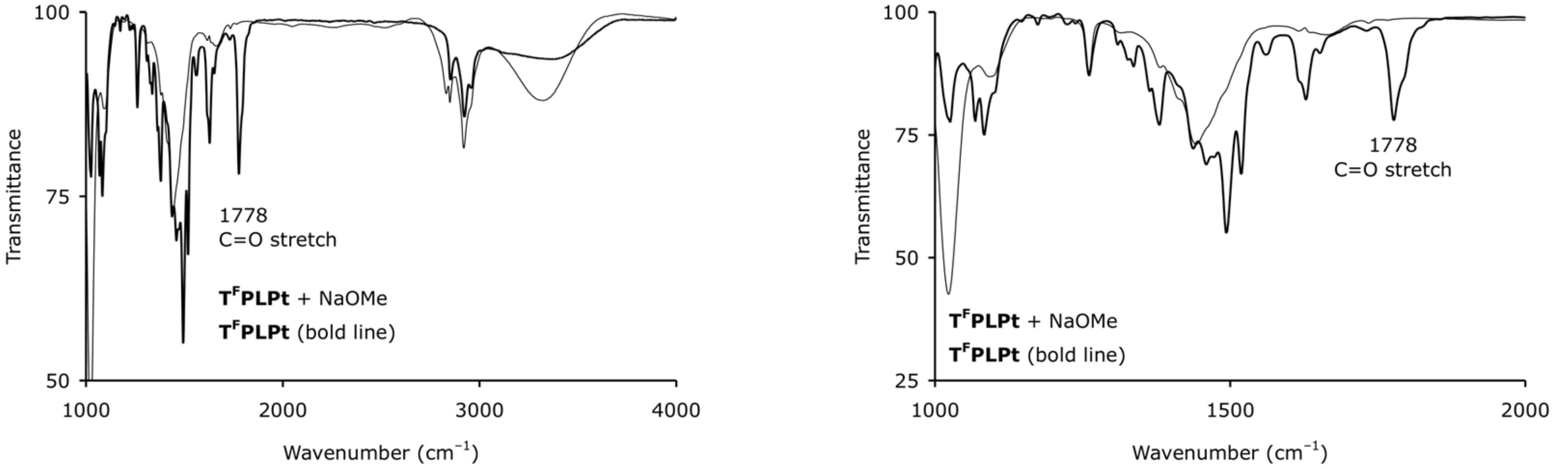


Figure ESI - 19. Diffuse reflectance IR spectrum (neat, between ZnSe windows) of **T^{F}PLPt** before (bold trace) and after (thin trace) the addition of NaOMe/MeOH (after allowing the mixture to dry) in full (left) and detail (right).

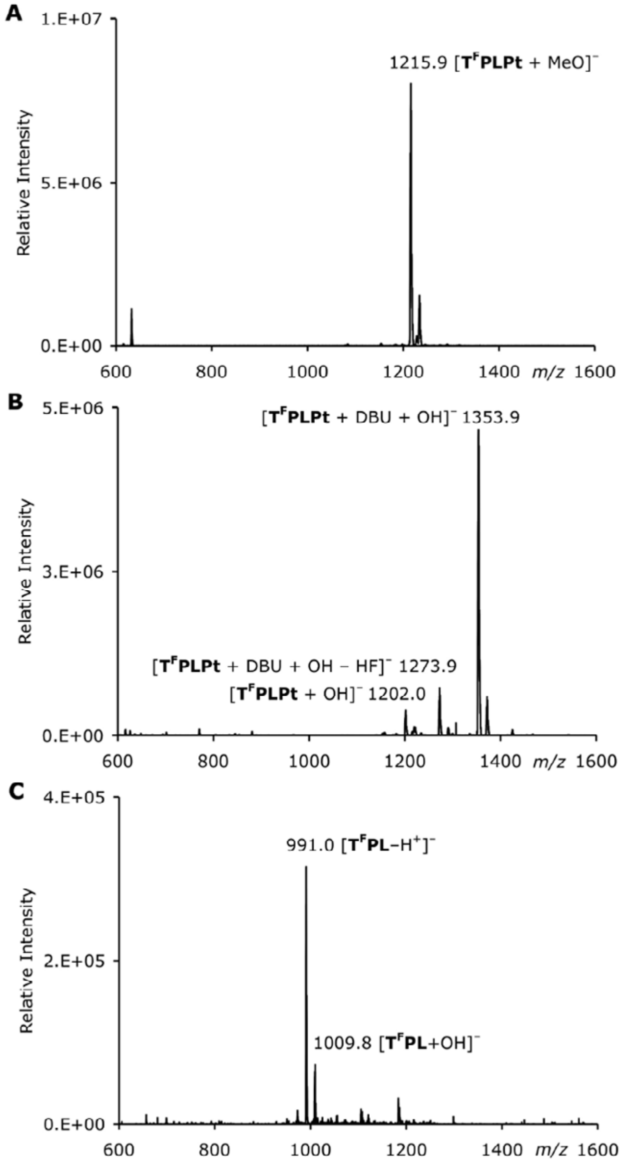


Figure ESI - 20. ESI(–) mass spectra (100% CH_3CN, 30 V cone voltage) of **T^{F}PLPt** in THF in the presence of stoichiometric excess NaOMe/MeOH (A) and DBU (B). The ion at *m/z* 1274 corresponds to the molecular ion ([T^{F}PLPt·OH·DBU]$^-$) –20 amu, representing the well-known HF loss from *meso*-pentafluorophenyl-containing porphyrins under ESI condition.[10–]**.** (C) ESI(–) mass spectra (100% CH_3CN, 30 V cone voltage) of **T^{F}PL** in THF in the presence of stoichiometric excess of DBU. Both NH deprotonation has taken place, as commonly observed for fluorinated porphyrins,[10] as well as the addition of OH^-.

---

10. (a) R. A. Izquerido, C. M. Barros, M. G. Santana-Marques, A. J. F. Correia, A. M. G. Silva, A. C. Tome, A. Silva, M. G. P. M. S. Neves and J. A. S. Cavaleiro, *Rapid Commun. Mass Spectrom.*, 2004, **18**, 2601. (b) K. S. F. Lau, M. Sadilek, G. E. Khalil, M. Gouterman and C. Brückner, *J. Am. Soc. Mass Spectrom.*, 2006, **17**, 1306.

in H_2O

in H_2O

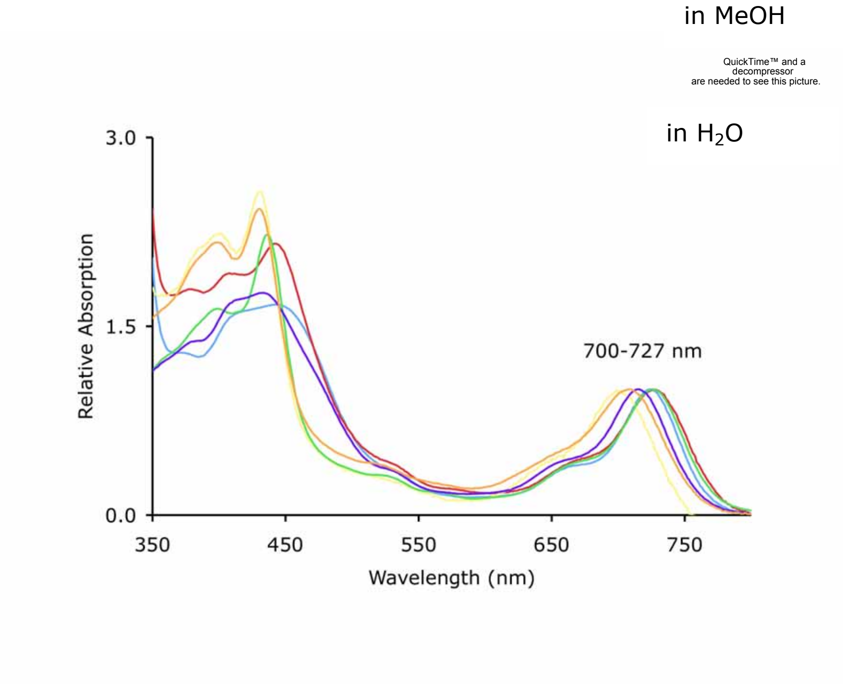


Figure ESI - 21. Solvatochromic effects for **T^{F}PLPt** in THF after addition of stoichiometric excess of the bases/co-solvents indicated. Spectra normalized to λ_{max}. The bases have a much smaller effect on the spectra than the presence of the co-solvents.

Table ESI - 1. The effect of the pentafluorophenyl and lactone moieties on apparent pK_b values (-log[TFA] at half-protonation of porphyrin in CH_2Cl_2), [porphyrin] in the 10^{-5} M range.

Compound	Relative pKb values
TPP	7.2
T^{F}PP	4.8
TPL	5.2
T^{F}PL	2.4

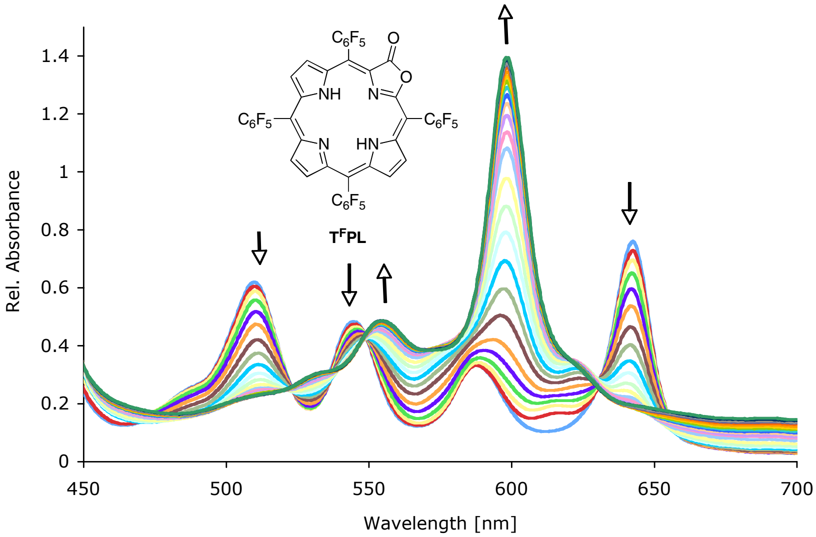


Figure ESI - 22. Representative UV-vis spectral shifts observed during the acid titration of **T^{F}PL** (TFA in CH_2Cl_2).

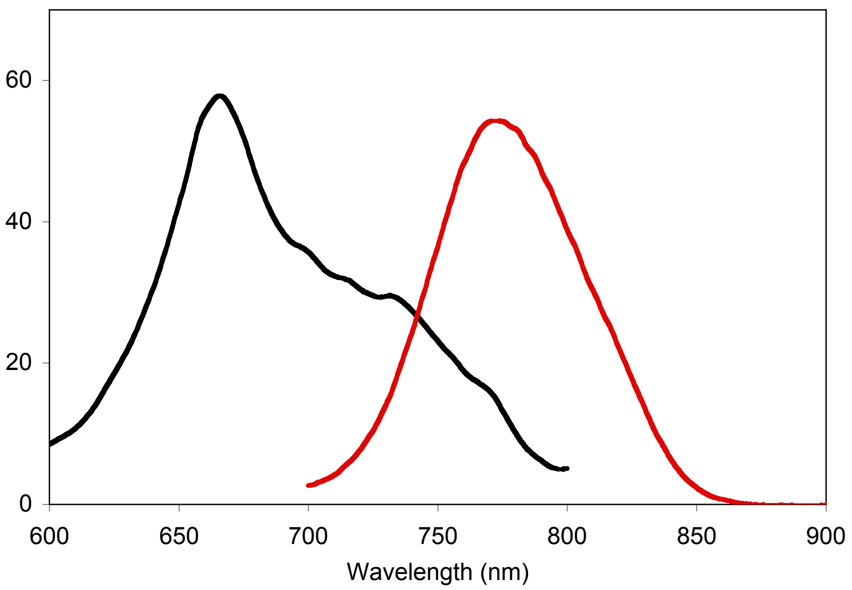


Figure ESI - 23. Fluorescence spectra (CH_2Cl_2) of $\mathbf{T^FPL}$ before (black trace, $\lambda_{excitation}$ = 410 nm) and after (red trace, $\lambda_{excitation}$ = 680 nm) the addition of an excess of MeO^{-}/MeOH.

Table ESI - 2. Luminescence parameters (in 3-MP at 77 K) of tetra(pentafluorophenyl)porpholactones in the absence and presence of NaOMe.

Compound	Emission (nm)		
	Q(0,0)	Q(0,1)	T(0,0)
$\mathbf{T^FPL}$	647	715	
$\mathbf{T^FPL}$ + NaOMe		770	
$\mathbf{T^FPLPt}$			733
$\mathbf{T^FPLPt}$ + NaOMe			1010

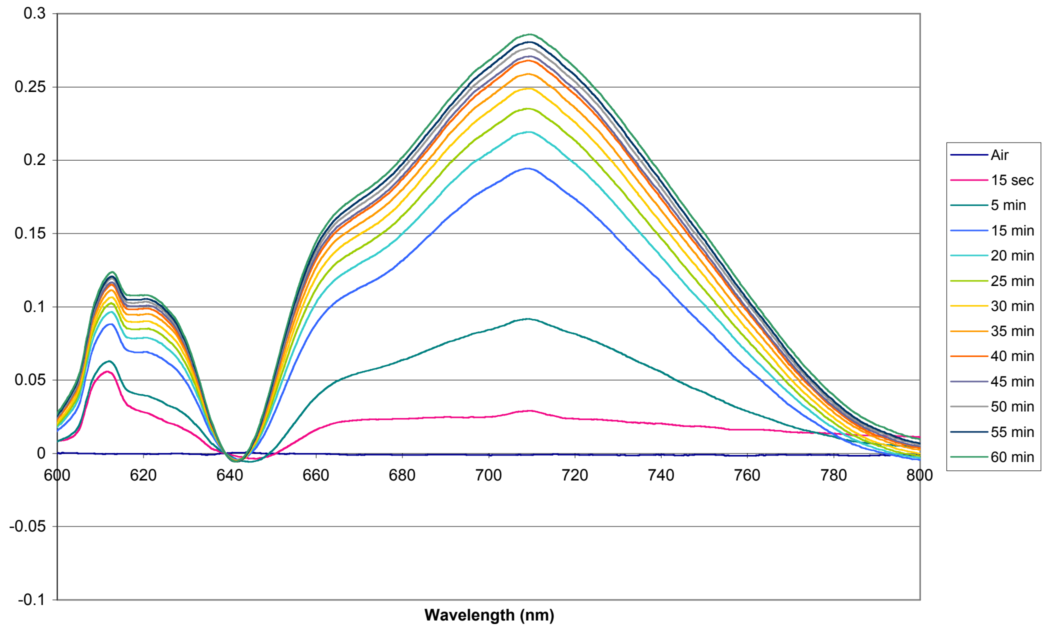


Figure ESI - 24. Absorption spectra of **T^{F}PL**-optode cast in hydrated cement (pH 13).

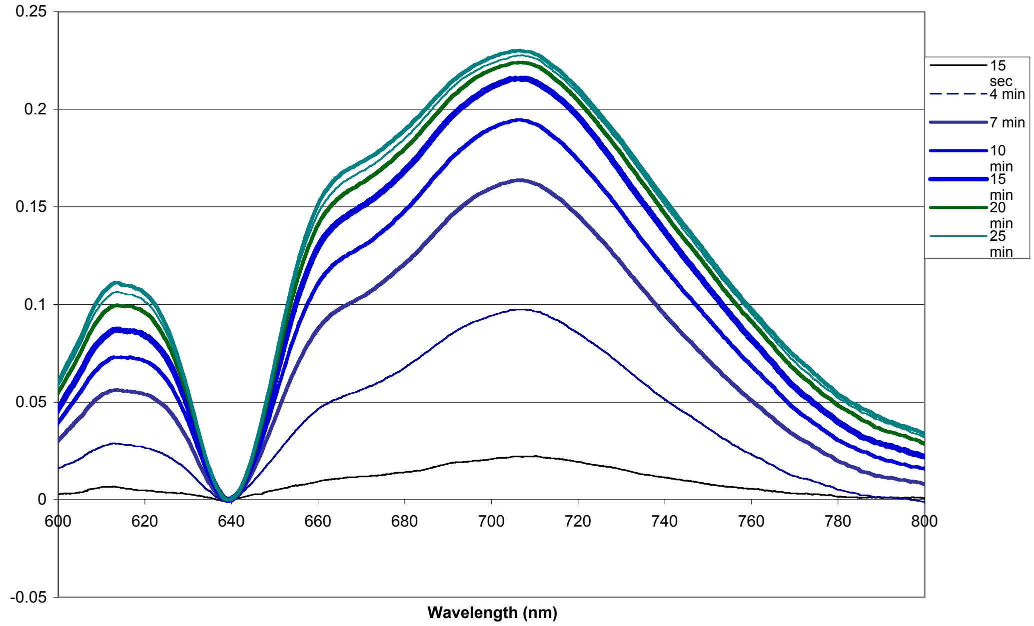


Figure ESI - 25. Absorption spectra of **T^{F}PL**-optode in pH 13 buffer (after equilibration in pH 7 buffer).