

Supplementary Information

Colorimetric Visualization of Acid-Base Equilibria in Non-Polar Solvent

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Contents

| | |
|--|-----|
| 1. Materials and general experimental..... | S2 |
| 2. UV-vis titration of DBU with MA in the presence of OxP | S3 |
| 3. ¹ H-NMR titration of DBU with MA | S4 |
| 4. ¹ H-NMR titration of OxP with DBU | S5 |
| 5. Solution state FTIR spectra | S6 |
| 6. ¹ H-NMR titration of OxP with TFA..... | S7 |
| 7. ¹ H-NMR spectra of OxP in the presence of excess TFA- <i>d</i> | S8 |
| 8. Solid state detection of acid (TFA) vapor by OxP-polymer film | S9 |
| 9. Summary of OxP colorimetric response in solution..... | S10 |

1. Materials and general experimental.

OxP, 5,10,15,20-(3,5-di-*t*-butyl-4-oxocyclohexa-2,5-dienylidene)porphyrinogen, was synthesized according to Milgrom¹ and purified by column chromatography and recrystallization prior to use. Organic reagents used as acids and bases were obtained from Tokyo Kasei Chemical Co., Wako Chemical Co., Nacalai Tesque Chemical Co. or Aldrich Chemical Co. and used without further purification. Dehydrated dichloromethane obtained from Wako Chemical Co. was used for UV-vis spectroscopic measurements. Solvents for NMR spectroscopy were obtained from Cambridge Isotope Ltd. and were used as received. For fabrication of the polymer film containing OxP, 2-nitrophenyl octyl ether (NPOE) and polyvinyl chloride (PVC) with a number-average molecular weight of 99,000 were purchased from Wako Chemical Co. and Aldrich Chemical Co., respectively, and used as received.

Electronic absorption spectra (UV-vis) were measured using a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. NMR spectra were obtained using a JEOL AL300BX spectrometer operating at a frequency of 300.4 MHz for ¹H nuclei. FT-infrared spectra were obtained from solutions using a Thermo-Nicolet Nexus 670 FT-IR spectrometer.

References

1. L. R. Milgrom, *Tetrahedron*, 1983, **39**, 3895.

2. UV-vis titration of DBU with MA in the presence of OxP

DBU was dissolved into a CH_2Cl_2 solution of OxP (10^{-5} M). Concentration of DBU was varied at 10^{-4} , 2×10^{-4} , 3×10^{-4} and 4×10^{-4} M. Solutions of 3 mL volume were placed in a 10 mm pathlength quartz cell. CH_2Cl_2 solution of MA (0.03 M) was added into the DBU solution by using a microsyringe (0 – 300 μl) and UV-vis spectra were recorded at 25 °C after each addition and mixing.

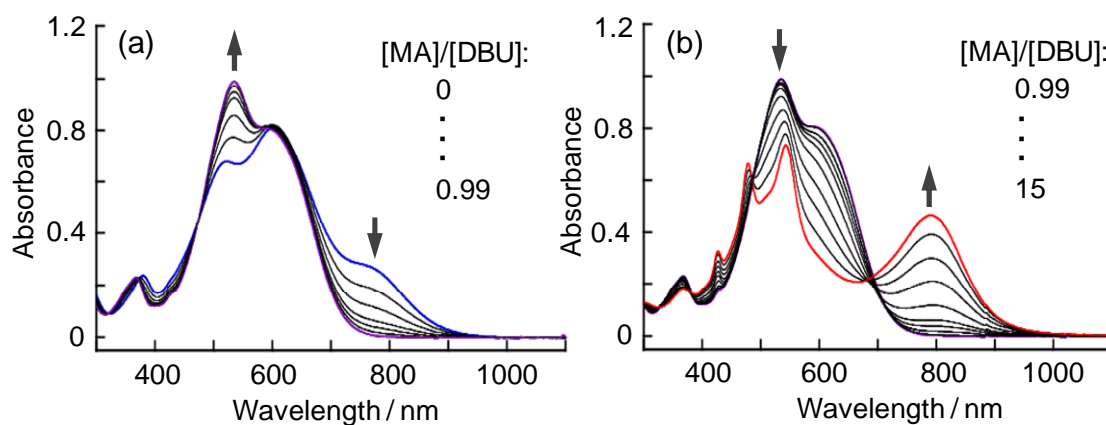


Figure S1 Changes in electronic absorption spectra observed during titration of DBU with MA in the presence of OxP.

3. ^1H -NMR titration of DBU with MA

DBU was dissolved into deuteriodichloromethane (CD_2Cl_2) in an NMR tube. MA was added directly as a solid into the solution because of its low solubility in pure CD_2Cl_2 . ^1H NMR spectra were recorded at 25 °C following each addition/dissolution of the aliquot.

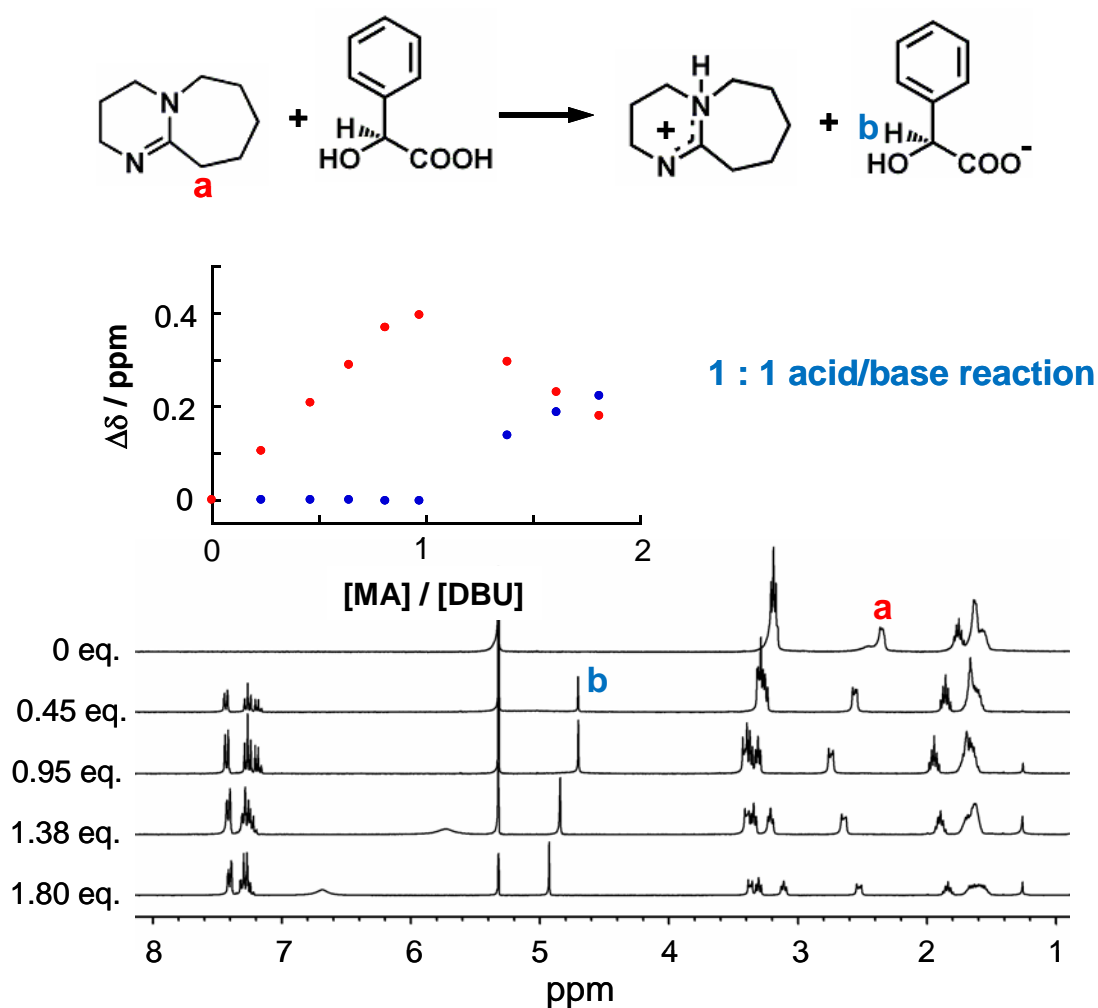


Figure S2 ^1H -NMR titration of DBU with MA in CD_2Cl_2 at 25 °C.

4. ^1H -NMR titration of OxP with DBU

OxP was dissolved in CD_2Cl_2 (1.4 mM) in an NMR tube. CD_2Cl_2 solution of DBU (0.46 M) was added into the OxP solution by using a microsyringe. ^1H NMR spectra were recorded at 25 °C following each addition/dissolution of the aliquot.

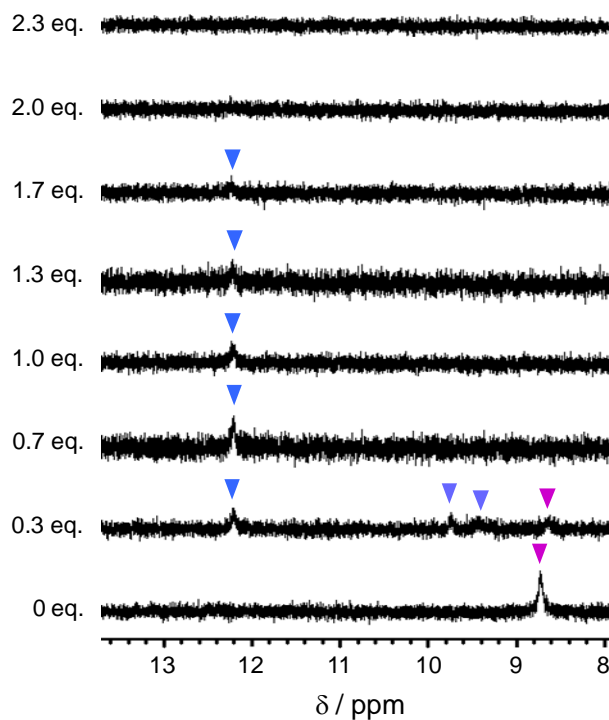


Figure S3 Partial ^1H -NMR spectra obtained by titration of OxP with DBU in CD_2Cl_2 at 25 °C.

5. Solution state FTIR spectra

The sample solution was sandwiched between ZnSe windows separated by a 100- μm -thick Teflon spacer. This sample assembly was then mounted in a temperature-controlled cell (Harrick Scientific Co., TFC-M25). The IR spectra were recorded using an MCT/A detector, operating at a resolution of 4 cm^{-1} with 100 scans collected from the sample at $0\text{ }^\circ\text{C}$.

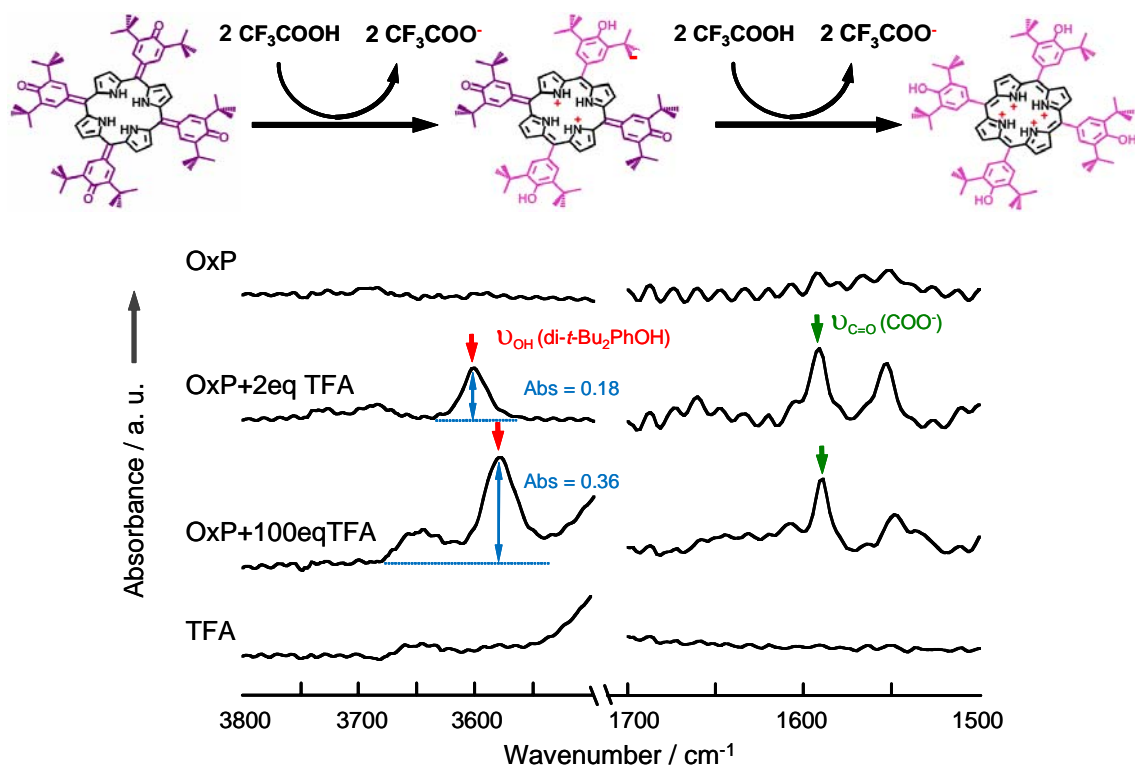


Figure S4. Solution (CH_2Cl_2 , $0\text{ }^\circ\text{C}$) state FTIR spectra of OxP, OxP +2 eq. TFA, OxP +100 eq. TFA, and TFA. Absorbance of the OxP hydroxyl stretching peak is indicated. Appearance of the OH(str) is due to first diprotonation/tautomerization (2 eq. TFA) then further protonation/tautomerization at higher concentration of TFA.

6. ^1H -NMR titration of OxP with TFA

OxP was dissolved in CD_2Cl_2 (1.4 mM) in an NMR tube. A CD_2Cl_2 solution of TFA (0.18 M) or neat TFA was added into the OxP solution by using a microsyringe. ^1H NMR spectra were recorded at 25 °C following each addition/mixing of the aliquot.

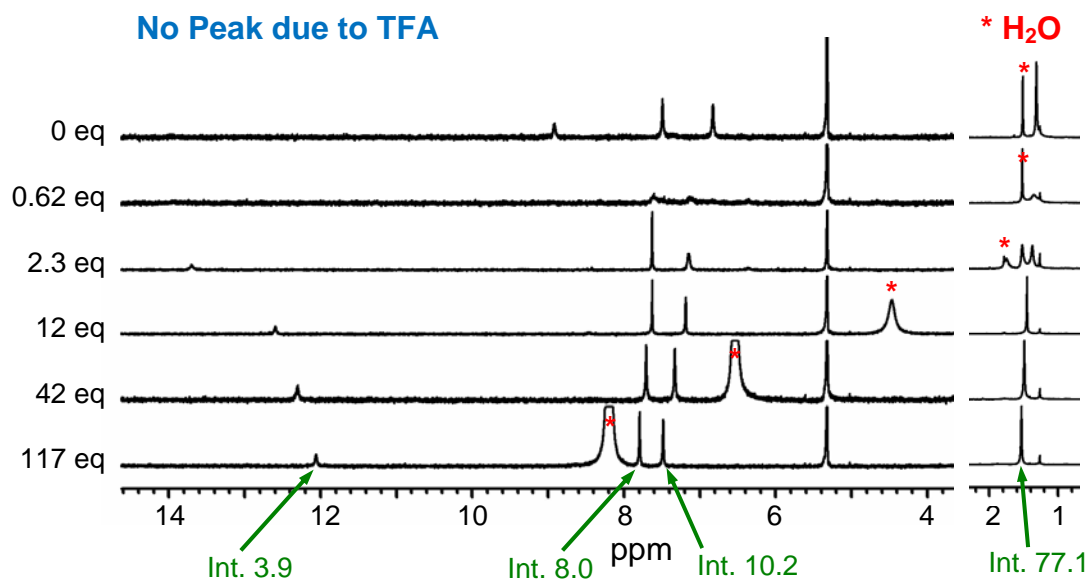


Figure S5 ^1H -NMR titration of OxP with TFA in CD_2Cl_2 at 25 °C. Note at 117 eq. TFA the intensity of the NH peak at 12 ppm corresponds to 4 protons.

7. ^1H -NMR spectra of OxP in the presence of excess TFA-*d*

^1H NMR spectra were recorded at the given temperature (from 25 °C to -85 °C) with 20 min aging before each measurement. After measurement at -85 °C, the sample tube was allowed to stand at 25 °C then the ^1H -NMR spectrum was measured to ensure that the sample had returned to its original state.

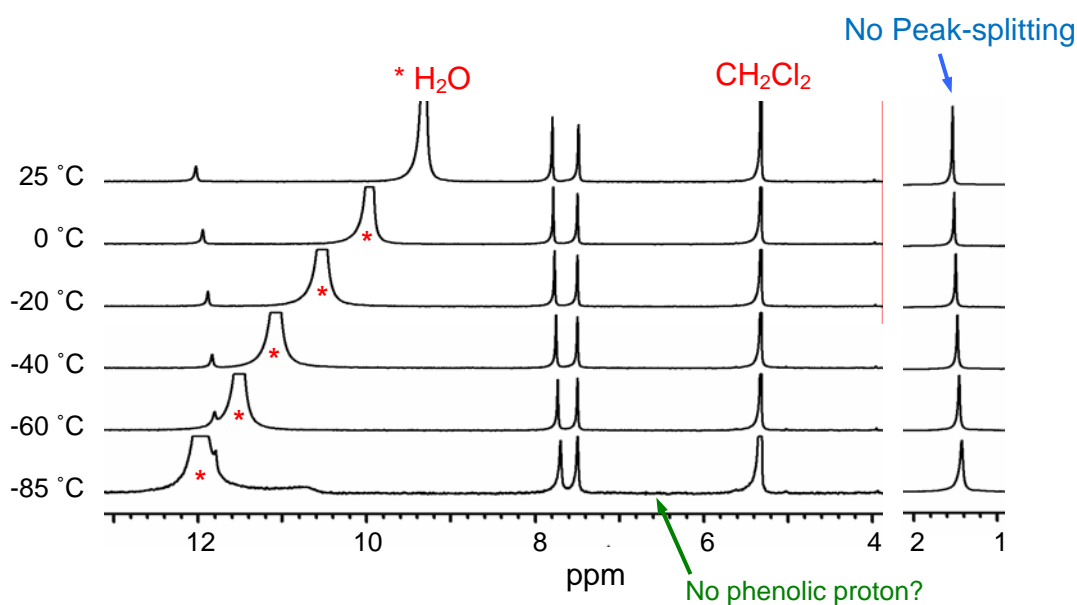


Figure S6 ^1H -NMR spectra of OxP in the presence of ~100 equivalents of TFA-*d* at various temperatures (in CD_2Cl_2). Although the phenolic hydroxyl proton is clearly visible in the FTIR spectra (see Fig. S2), a corresponding resonance is absent here probably due to exchange with monodeuteriotrifluoroacetic acid.

8. Solid state detection of acid (TFA) vapor by OxP-polymer film

A CH_2Cl_2 solution of OxP (4×10^{-4} M) with a volume of 0.5 mL was added into a vial and CH_2Cl_2 was evaporated by using nitrogen gas flow. PVC (30 mg), NPOE (70 mg) and THF (2 mL) were then added into the vial, leading to a mixture of OxP, PVC and NPOE in THF. The polymer film was prepared by casting the mixture on a quartz plate under THF-saturated vapour and then dried under reduced pressure.

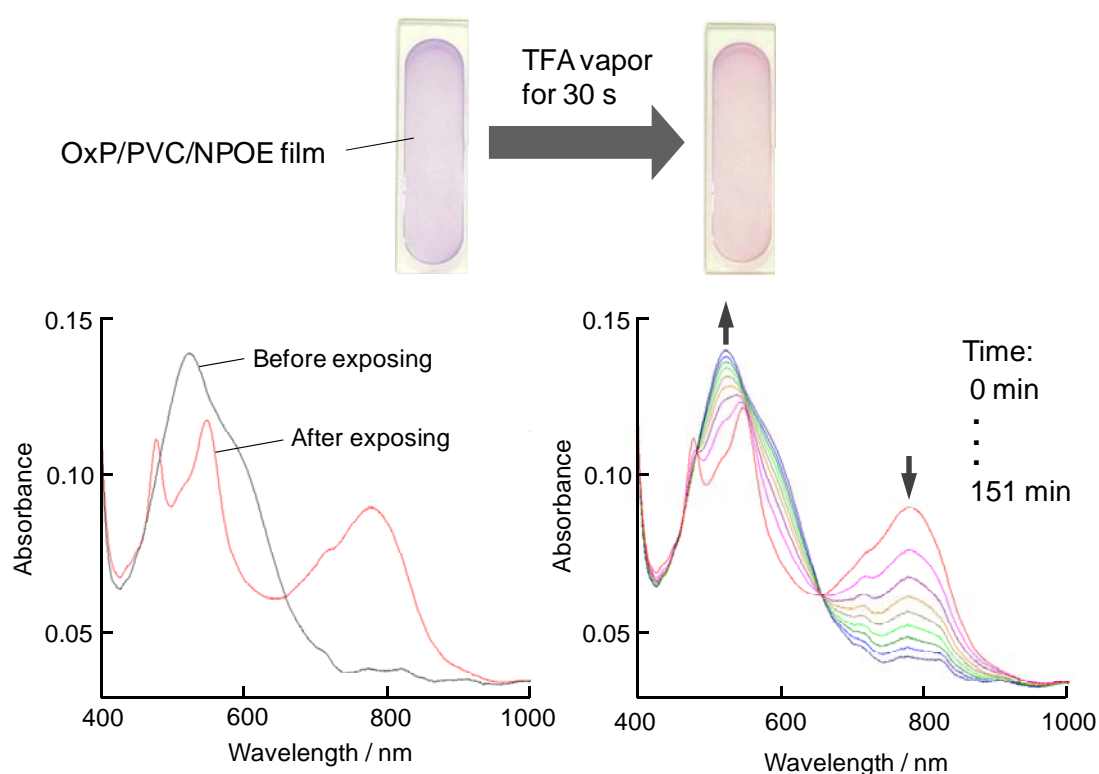


Figure S7. UV-vis spectral changes of OxP/PVC/NPOE cast film upon (a) exposure to TFA vapour for 30 s and (b) subsequently keeping under ambient conditions at room temperature.

9. Summary of OxP colorimetric response in solution illustrating RGB colors

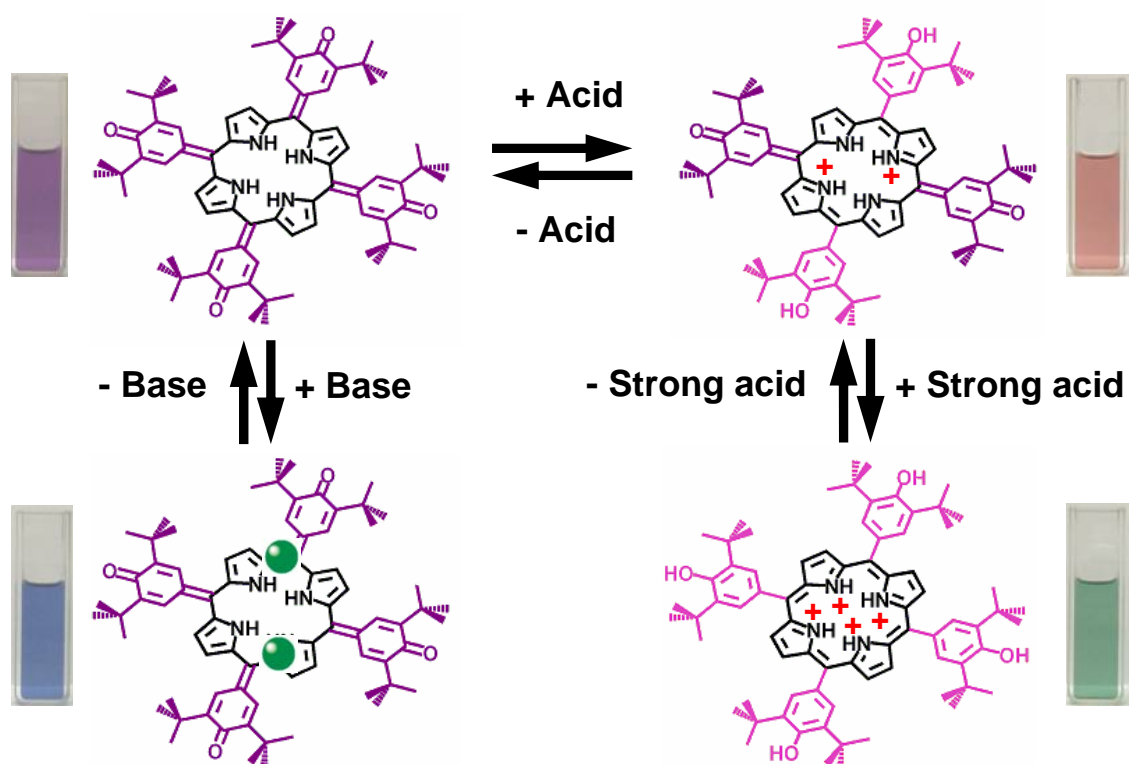


Figure S8. Summary of colorimetric behaviour of OxP in response to base, acid and strong acid.