

Structure resembling effect of clay surface on photochemical properties of *meso*-phenyl or pyridyl- substituted monocationic antimony(V) porphyrin derivatives

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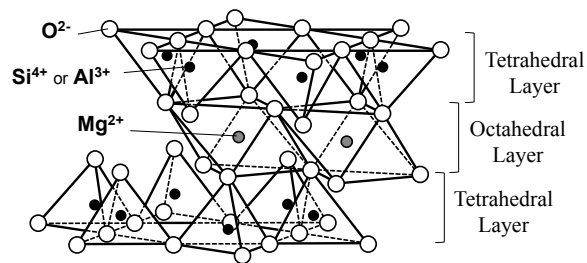


Figure S1. The structure of synthetic saponite, $[(\text{Si}_{7.2}\text{Al}_{0.8})(\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{-0.77}$.

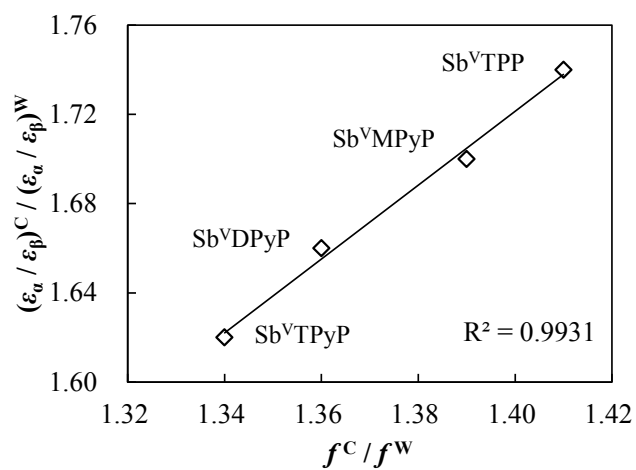


Figure S2. The plot of $(\epsilon_a / \epsilon_b)^c / (\epsilon_a / \epsilon_b)^w$ values against f^c / f^w values for Sb^vPors.

Synthesis of $\text{Sb}^{\text{V}}\text{Por}$

SbCl_5 , 5,10,15,20-tetraphenylporphine (TPP) and 5,10,15,20-tetrakis(4-pyridyl)porphine (TPyP) were purchased from Aldrich, and used without further purification. 5,10,15-triphenyl-20-mono(4-pyridyl)porphine (MPyP) and 5,15-diphenyl-10,20-di(4-pyridyl)porphine (DPyP) was purchased from Frontier Scientific, and used without further purification. All syntheses were carried out under nitrogen atmosphere. ^1H -NMR spectra in D_2O were recorded on a Bruker B-500.

Synthesis of $[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{Cl}$

Dihydroxo(5,10,15,20-tetraphenylporphyrinato)antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{TPP})(\text{OH})_2]\text{Cl}$) was synthesized according to established routes²⁹.

Synthesis of $[\text{Sb}^{\text{V}}(\text{MPyP})(\text{OH})_2]\text{Cl}$

Dihydroxo[5,10,15-triphenyl-20-mono(4-pyridyl)porphyrinato]antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{MPyP})(\text{OH})_2]\text{Cl}$) was synthesized as below. SbCl_5 (1 mL) was added to a solution of MPyP (40.0 mg) in pyridine (30 mL). The reaction mixture was refluxed for 50 hours. H_2O (2 mL) was added to the solution. The solvent was evaporated and the residue was solved in CHCl_3 (100 mL). The CHCl_3 solution was washed three times with 200 mL portions of H_2O and red violet CHCl_3 solution was extracted. After the KCl aqueous solution (1 M, 100 mL) was added to the CHCl_3 solution, the solution was stirred for 21 hours and the CHCl_3 phase was extracted two times and . The CHCl_3 solution was washed two times with 200 mL portions of H_2O and red

violet CHCl_3 solution was extracted. The counter ion (antimony complex anion) was exchanged to Cl^- by the use of ion-exchange resin (Organo, Amberlite Resin IRA-400) to give dihydroxo[5,15-diphenyl-10,20-di(4-pyridyl)porphyrinato]antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{DPyP})(\text{OH})_2]\text{Cl}$) in ca. 11% yield. $^1\text{H-NMR}$ (D_2O /ppm) δ 7.99 (6H, t, *m*-Ph), 8.04 (3H, t, *p*-Ph), 8.44 (6H, d, *o*-Ph), 8.50 (2H, d, *m*-Py), 9.13 (2H, d, *o*-Py), 9.68 (2H, d, β -Pyrr), 9.74 (4H, s, β -Pyrr), 9.76 (2H, s, β -Pyrr).

Synthesis of $[\text{Sb}^{\text{V}}(\text{DPyP})(\text{OH})_2]\text{Cl}$

Dihydroxo[5,15-diphenyl-10,20-di(4-pyridyl)porphyrinato]antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{DPyP})(\text{OH})_2]\text{Cl}$) was synthesized as below. SbCl_5 (1 mL) was added to a solution of DPyP (30.0 mg) in pyridine (30 mL). The reaction mixture was refluxed for 18 hours. H_2O (2 mL) was added to the solution. The solvent was evaporated and the residue was solved in CHCl_3 (100 mL). The CHCl_3 solution was washed two times with 200 mL portions of H_2O and red violet CHCl_3 solution was extracted. After the KCl aqueous solution (1 M, 100 mL) was added to the CHCl_3 solution, the solution was stirred for 24 hours and the CHCl_3 phase was extracted tow times and . The CHCl_3 solution was washed two times with 100 mL portions of H_2O and red violet CHCl_3 solution was extracted and the solvent. The counter ion (antimony complex anion) was exchanged to Cl^- by the use of ion-exchange resin (Organo, Amberlite Resin IRA-400) to give dihydroxo[5,15-diphenyl-10,20-di(4-pyridyl)porphyrinato]antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{DPyP})(\text{OH})_2]\text{Cl}$) in ca. 13% yield. $^1\text{H-NMR}$ (D_2O /ppm) δ 8.00 (4H, t, *m*-Ph), 8.06 (2H, t, *p*-Ph), 8.46 (4H, d, *o*-Ph), 8.52 (4H, d, *m*-Py), 9.14 (4H, d, *o*-Py) , 9.71 (4H, d, β -Pyrr), 9.79 (4H, d, β -Pyrr).

Synthesis of $[\text{Sb}^{\text{V}}(\text{TPyP})(\text{OH})_2]\text{Cl}$

Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]antimony(V) chloride ($[\text{Sb}^{\text{V}}(\text{TPyP})(\text{OH})_2]\text{Cl}$) was synthesized according to established routes²⁹.