Supporting Information for

Intramolecular Electron Transfer from Axial Ligand to S_2-Excited Sb-Tetraphenylporphyrin

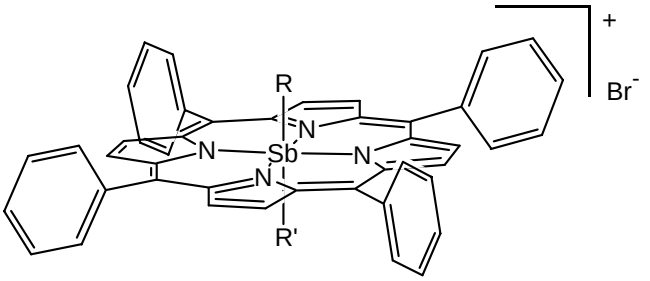
*Mamoru Fujitsuka,[†] Dae Won Cho,[†] Tsutomu Shiragami,[‡] Masahide Yasuda,[‡] and Tetsuro Majima[†]**

Synthesis of SbTPP derivatives.

The synthesis of **1 - 5** (Figure S1) was carried out by the following procedures. Mono-methanolysis of dibromo(tetraphenylporphrinato)antimony(V) bromide ($[SbTPP(Br)_2]^+Br^-$) was performed in MeOH-MeCN (1:1 v/v) to give **7**. An MeCN-pyridine solution (5:1 v/v 50mL) containing **7** (1.1 mmol) and 4-substitutied aniline derivatives was heated for 4h at 80 °C. The solvent was evaporated and the residue was solved in CH_2Cl_2. The CH_2Cl_2 solution was washed three times with 50 mL portions of H_2O. After evaporation, the crude product was chromatographed on silica gel (Fiji Silysia BW-300) using $CHCl_3$-MeOH (10:1 v/v) as an eluent to give **1 - 5**. **6** was synthesized according to a previously reported procedures.[1]

Spectroscopic Data. 4-Methoxyophenylamido(methoxo)tetraphenylporphyrinatoantimony(V) bromide(**1**): Yield 20% from **7**; UV-vis (MeCN) λmax/nm (log ε): 421 (5.51), 557 (4.00), and 599 (3.82); SIMS: m/z 885 (M^+-1); ^{1}H-NMR ($CDCl_3$/ppm) δ -2.31 (3H, s, Sb-OMe), 2.29 (2H, d, *J*= 8.5 Hz, Sb-N-C_6H_4-OMe), 3.35 (3H, s, -OMe), 5.35 (2H, d, *J*= 8.5 Hz, MeO-C_6H_4-N-Sb), 7,85-7.92 (12H, m, Ph), 8.28 (4H, d, *J*= 6.7 Hz, Ph), 8.47 (4H, d, *J*= 6.7 Hz, Ph), 9.41 (8H, S, pyrrole).: 4-Methylphenylamido(methoxo)tetraphenylporphyrinatoantimony(V) bromide(**2**): Yield 20% from **7**; UV-vis (MeCN) λmax/nm (log ε): 421 (5.27), 557 (3.85), and 599 (3.70); SIMS: m/z 869 (M^+-1); ^{1}H-NMR ($CDCl_3$/ppm) δ -2.37 (3H, s, Sb-OMe), 1.17 (3H, s, -OMe), 2.17 (2H, d, *J*= 8.2 Hz, Sb-N-C_6H_4-

Me), 5.53 (2H, d, *J*= 8.2 Hz, Me-C_6H_4-N-Sb), 7,79-7.88 (12H, m, Ph), 8.19 (4H, d, *J*= 6.7 Hz, Ph), 8.34 (4H, d, *J*= 6.7 Hz, Ph), 9.36 (8H, S, pyrrole).: Phenylamido(methoxo)tetraphenylporphyrinatoantimony(V) bromide(**3**): Yield 86% from **7**; UV-vis (MeCN) λmax/nm (log ε): 420 (5.44), 557 (4.11), and 598 (3.98); SIMS: m/z 856 (M^+); ^{1}H-NMR ($CDCl_3$/ppm) δ -2.35 (3H, s, Sb-OMe), 2.27 (2H, d, *J*= 7.4 Hz, Sb-N-C_6H_5), 5.78 (2H, t, *J*= 8.4 Hz, Sb-N-C_6H_5), 6.08 (1H, t, *J*= 7.3 Hz, Sb-N-C_6H_5), 7,82-7.95 (12H, m, Ph), 8.26 (4H, d, *J*= 6.7 Hz, Ph), 8.35 (4H, d, *J*= 6.6 Hz, Ph), 9.39 (8H, S, pyrrole).: 4-Trifluoromethylphenylamido(methoxo)tetraphenylporphyrinatoantimony(V) bromide(**4**): Yield 18% from **7**; UV-vis (MeCN) λmax/nm (log ε): 421 (5.27), 557 (3.85), and 599 (3.70); SIMS: m/z 923 (M^+-1); ^{1}H-NMR ($CDCl_3$/ppm) δ -2.03 (3H, s, Sb-OMe), 6.65 (2H, d, *J*= 8.2 Hz, Sb-N-C_6H_4-CF_3), 7.29 (2H, d, *J*= 8.2 Hz, CF_3-C_6H_4-N-Sb), 7,94-7.98 (12H, m, Ph), 8.31 (4H, d, *J*= 6.7 Hz, Ph), 8.38 (4H, d, *J*= 6.7 Hz, Ph), 9.60 (8H, S, pyrrole).: 4-Cyanophenylamido(methoxo)tetraphenylporphyrinatoantimony(V) bromide(**5**): Yield 18% from **7**; UV-vis (MeCN) λmax/nm (log ε): 420 (5.40), 556 (4.08), and 597 (3.92); SIMS: m/z 880 (M^+-1); ^{1}H-NMR ($CDCl_3$/ppm) δ -2.31 (3H, s, Sb-OMe), 2.58 (2H, d, *J*= 8.5 Hz, Sb-N-C_6H_4-CN), 6.03 (2H, d, *J*= 8.5 Hz, O-C_6H_4-N-Sb), 7,85-7.94 (12H, m, Ph), 8.27 (4H, d, *J*= 7.3 Hz, Ph), 8.49 (4H, d, *J*= 7.3 Hz, Ph), 9.41 (8H, S, pyrrole).



1: R = *p*-CH_3O-C_6H_4-NH-, R' = CH_3O-
2: R = *p*-CH_3-C_6H_4-NH-, R' = CH_3O-
3: R = C_6H_5-NH-, R' = CH_3O-
4: R = *p*-CF_3-C_6H_4-NH-, R' = CH_3O-
5: R = *p*-CN-C_6H_4-NH-, R' = CH_3O-
6: R = R' = HO-
7: R = Br-, R' = CH_3O-

Figure S1. Molecular structures of SbTPP derivatives.

Details of sub-picosecond and steady state spectroscopy and electrochemistry

The fluorescence lifetime in the sub-picosecond regime was measured using fluorescence up-conversion method. The second harmonic oscillation (400 nm) of the output of the femtosecond laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 80 fs, 800 nm) pumped by a diode-pumped solid state laser (Spectra-Physics, Millennia VIIIs) was used to excite the sample in a cell with a 1.0 mm optical path length. The residual fundamental and the fluorescence were focused in a BBO type I crystal to generate a sum-frequency oscillation, which was detected by a photomultiplier tube (Hamamatsu Photonics, H8259) and a photon counter (Stanford Research Systems, SR400) after passing through a monochromator (Nikon G250). The cross correlation time of the apparatus was 200 fs fwhm.

The sub-picosecond transient absorption spectra were measured by the pump and probe method using a regeneratively amplified titanium sapphire laser (Spectra Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra Physics, Empower 15). The seed pulse was generated by the titanium sapphire laser mentioned above. The second harmonic oscillation (400 nm, 130 fs fwhm, 8 μJ $pulse^{-1}$) of the output of the regeneratively amplified titanium sapphire laser was used as the excitation pulse. A white light continuum pulse, which was generated by focusing the residual of the fundamental light to a flowing water cell after a computer-controlled optical delay, was divided into two parts and used as the probe and the reference lights, of which latter was used to compensate the laser fluctuation. The both probe and reference lights were directed to a rotating sample cell with 1.0 mm of optical path and detected with a CCD detector equipped with a polychromator (Solar, MS3504). The pump pulse was chopped by a mechanical chopper synchronized to one half of the laser repetition rate, resulting in a pair of the spectra with and without the pump, from which absorption change induced by the pump pulse was estimated.

The steady state absorption and fluorescence spectra were measured using a Shimadzu UV-3100PC and a Hitachi 850, respectively.

Electrochemical measurements were carried out in a conventional three electrodes cell employing a glassy carbon, platinum, and $Ag/AgNO_3$ electrodes as a working, counter, and reference electrodes, respectively. The potential was scanned at 300 mV s^{-1} using a potentiostat. All electrochemical

measurements were carried out with an acetonitrile solution containing 100 mM of tetraethylammonium tetrafluoroborate after Ar bubbling.

Reference

(1) Shiragami, T.; Matsumoto, J.; Inoue, H.; Yasuda, M. *J. Photochem. Photobio. C. Reviews.* **2005**, *6*, 227.