Electronic Supplementary Information

Two Modes of Photoinduced Twisted Intramolecular Charge Transfer in *meso*-Arylaminated Subporphyrins

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Experimental Details

Sample preparaion : The details in synthesis, characterization, and X-ray crystallographic analysis of 1, 2 and 3 are described elsewhere.⁵ All reagents and solvent were of the commercial reagent grade and were used without further purification.

Steady-state Absorption and Emission Measurements : Steady-state absorption spectra were obtained with an UV-VIS-NIR spectrometer (Varian, Cary5000) and steady-state fluorescence spectra were measured on a Hitachi model F-2500 fluorescence spectrophotometer and a Scinco model FS-2. For the observation of steady-state emission spectra in near-infrared (NIR) region, a photomultiplier tube (Hamamatsu, R5108), a lock-in amplifier (EG&G, 5210) combined with a chopper and a CW He-Cd laser (Melles Griot, Omnichrome 74) for the 442 nm excitation were used.

Picosecond Time-resolved Emission : Time-resolved fluorescence decays were obtained by using a time-correlated single-photon counting (TCSPC) technique. A mode-locked Ti:sapphire oscillator (MaiTai-BB, Spectra Physics) were used as a excitation light source, which provide a fwhm (full width at half maximun) of 80 fs with a high repetition rate of 80 MHz. In order to minimize artifacts such as thermal lensing and accumulation effect, repetition rate was reduced down to 800 kHz using a home-made acousto-optic pulse selector. The picked fundamental pulses were frequency doubled by a 1 mm of thickness of BBO nonlinear crystal (Eksma). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, R3809U-51, Hamamatsu) with a thermoelectric cooler (C4878, Hamamatsu). Time-resolved fluorescence signals were calculated by a TCSPC board (SPC-130, Becker & Hickel GmbH). The overall instrumental response function (IRF) was determined to be less than 30 ps (fwhm) in all spectral regions.

Femtosecond Transient Absorption Measurements : The femtosecond time-resolved transient absorption (TA) spectrometer consisted of Palitra (optical parametric amplifier (OPA), Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C, Quantronix) operating at 1 kHz repetition rate and an optical detection system. The generated visible pulses by OPA had a pulse width of ~ 100 fs and an average power of 1 - 30 mW in the range 460-800 nm which were used as pump pulses. White light continuum (WLC) probe

pulses were generated using a sapphire window (3 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering to the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by miniature spectrograph (USB2000+, OceanOptics). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses excite samples to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used. After fluorescence and TA experiments, we carefully checked absorption spectra of all compounds to avoid artifact from degradation and photo-oxidation of samples. The HPLC grade solvents were used in all steady-state and time-resolved spectroscopic studies.

Computational Methods. Quantum mechanical calculations were performed with the Gaussian 09 program suite. All calculations were carried out by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP), employing the 6-31G(d) basis set. The X-ray crystallographic structures were used as initial geometries for geometry optimization.



Figure S1. Temperature dependent steady-state absorption and fluorescence spectra of **1** in m-THF.



Figure S2. (A) Steady-state absorption spectra of **1** (black/gray), **2** (blue/sky-blue) and **3** (red/pink) in toluene/paraffin oil. (B) Fluorescence spectra of **1** (black), **2** (blue) and **3** (red) in paraffin oil. (C) Fluorescence quantum yields of **1**, **2** and **3** in toluene, ACN and paraffin oil.



Figure S3. Transient absorption spectra of **1** in toluene were obtained by using the excitation wavelength of 520 nm.



Figure S4. Fluorescence decay profile of **1** in toluene was measured by TCSPC using the excitation wavelength of absorption band maximum.



Figure S5. Decay-associated spectra obtained from global multiexponential analysis of the TA spectra measured with **2** in toluene.



Figure S6. Cyclic voltammograms of **1**, **2**, and **3** (in V vs. ferrocene/ferrocenium cation). Measuring conditions; solvent: distilled CH_2Cl_2 , supporting electrolyte: 0.10 M tetrabutylammonium hexafluorophosphate, working electrode: glassy carbon rod, counter electrode: platinum wire, reference electrode: Ag/0.01 M AgClO₄.



Figure S7. Absorption spectra of **1** in DCM with 0.10 M Bu4NPF6 upon titration with a solution of NOSbF6 in DCM/acetonitrile (1:1).



Figure S8. Transient absorption spectra of **2** (A) and **3** (B) in paraffin oil/toluene (100:1) were obtained by using the excitation wavelength of 520 nm.