SUPPLEMENTAL INFORMATION

Real-Time Fluorescence Visualization of Slow Tautomerization of Single Free-Base Phthalocyanines under Ambient Conditions

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S1. Chemical Material and Instrument

Free-base phthalocyanines, H2Pc and H2Pc8 were purchased from ALDRICH (Tokyo, Japan). UV-vis absorption spectra and Fluorescent spectra were recorded with a JASCO V-550 and a FP-6500, respectively. Toluene and o-dichlorobenzene solvent were purchased from Wako Pure Chemical Industries, Ltd (Tokyo, Japan) used as received. DFT calculation for HOMO and LUMO of H2Pc was performed by Gaussian 09/Gauss View5.

S2. UV-vis absorption and fluorescent spectrum of H2Pc8

![Figure S1](image_url). Absorption (optical path length: 10 mm) and emission spectra (excitation wavelength: 638 nm) of H2Pc8 in toluene (1.0 μM) at 298K. Strong peaks/ nm: at 661, 700 for absorption and 703 for emission.
S3. Preparation of Glass substrates

Cleaned glass substrate (Bare glass): Ten pieces of glass slides (32 × 24 mm, Matsunami Glass Ind., Ltd.) were placed on a ceramic stand and washed by bath sonication for 30 min in pure ethanol (200 mL) and then in Milli-Q water (200 mL). The glass slides were dipped in 10 N aqueous KOH and incubated at RT for 16 h, after which they were washed in Milli-Q water (200 mL × 3) by bath sonication for 30 min and dried under a flow of nitrogen gas.

Octadecyl group modified glass substrate (C18-glass): Ten pieces of the bare glass slides were placed on a ceramic stand and dipped in octadecyltrimethoxysilane (ALDRICH, Tokyo, Japan) /toluene solution (100 µL/100mL) at room temperature for 3 h. After which they were washed in ethanol (200 mL) by bath sonication for 30 min and then in Milli-Q water (200 mL), the surface was dried under flow of nitrogen gas.

Figure S2. Photographs of (a) cleaned glass substrate (bare glass) and (b) octadecyl groups modified glass substrate (C18-glass). Colored water (Milli-Q, 10 µL) was dropped on the surface to confirm water-repellency.

S4. Preparation of a sample for microscopic observation

We assembled the slide glass (the bare glass or the C18-glass) and a silicone block (height: ~5 mm) into a slope with the angle of ca. 10°. Ten µL of free-base phthalocyanine/toluene solution (H₂Pc or H₂Pc8, 1.0 µM) was dropped on the slope to bind the glass surface. Then, the glass was dried in vacuo for 30 min.

S5. Optical microscopy setup and image analysis

The glass substrate was placed on an inverted microscope equipped with a 100× oil immersion objective. Fluorescent emission (>650 nm) was imaged using a conventional fluorescent microscope under epi-illumination by a circularly polarized red laser (638 nm, 4.5, 9.0, or 11.6 µW/µm² at the focal plane). Imaging was carried out at an ambient temperature of 22–25 °C. Fluorescent emission was recorded at 5 or 10 fps on a high sensitive digital video camera. The recorded images were analyzed using Moment Calculator (Francois Richard, University of Ottawa) on ImageJ software.

Setup of the optics is as follows:

Microscope: inverted, IX70 (Olympus); Objective lens: UAPON 100XOTIRF, NA: 1.49 (Olympus); Illumination light source: red laser, CUBE635-25C, 638 nm (Coherent Inc.); Beam expander: a couple of lenses; Excitation filter: FF01-638/8 (Semrock); Dichroic mirror: FF660-Di02 (Semrock); Emission filter: BLP01-635R (Semrock); Beam shape: tubular, constructed from an iris diaphragm; Polarization: circularly polarized laser formed by a combination of λ/2 and λ/4 plates; Camera: EMCCD, iXon DV887ECS-BV (Andor).
Figure S3. Polarization degree of the illumination of a 638 nm-laser. Intensity was measured using rotation polarizer at sample plane level. Amplitude of the wave is 2.9%, small.

S6. Legends for Supplemental Movie S1 and S2

Initial frames of Movie S1 (left) and S2 (right) were shown here.

Movie S1. Lateral diffusion of $H_2$Pc and $H_2$Pc8 at the air/C18-glass interface. (recording rate: 5 fps; area: 21×21 µm$^2$; playback rate: ×3)

Movie S2. Switching of the orientation. (recording rate: 5 fps; scale bar: 2 µm; playback rate: ×3). Switched pattern was indicated by a symbol “>”.