SUPPLEMENTAL INFORMATION

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

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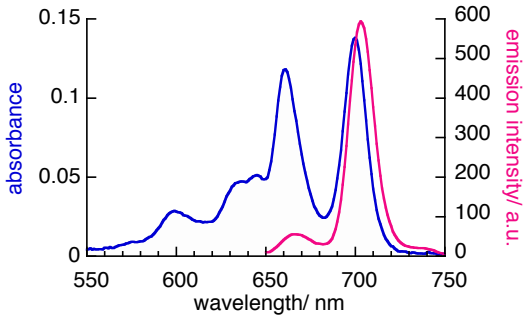
Contents

S1. Chemical Material and Instrument

Free-base phthalocyanines, **H_2Pc** and **H_2Pc8** 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 **H_2Pc** was performed by Gaussian 09/Gauss View5.

S2. UV-vis absorption and fluorescent spectrum of H_2Pc8



FigureS1. Absorption (optical path length: 10 mm) and emission spectra (excitation wavelength: 638 nm) of **H_2Pc8** 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.

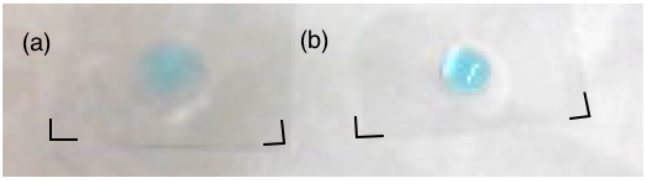


Figure S2. Photographs of (a) cleaned glass substrate (**bare glass**) and (b) octadecyl groups modified glass substrate (**C18-glass**). Colored water (Milli-Q, 10 μL) was dropped on the surface to confirm water-repellency.

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 (**H_2Pc or H_2Pc8**, 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 $\mu W \mu m^{-2}$ 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).

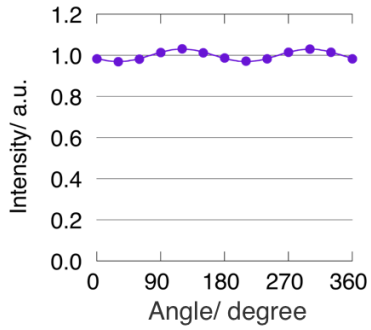
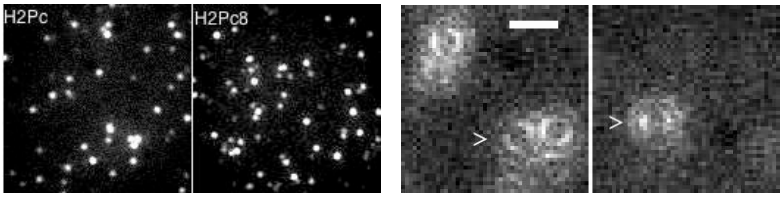


Figure S3. Polarization degree of the illumination of a 638 nm-laser. Intensity was measured using rotation polarizer at sample plane level. Amplitude of the wave is 2.9%, small.

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_2Pc** and **H_2Pc8** 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 “>”.