Sonication-assisted supramolecular nanorods of *meso*-diaryl-substituted porphyrins

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Experimental Section

Preparation of porphyrin nanoassembly. The synthesis of H_2DBuPP, H_2TBuPP and H_2DPP has been performed in accordance with the reported literatures.[9] H_2TPP was purchased from Aldrich. The porphyrin nanorod was prepared by the following procedure. First, 3.5 mmol dm^{-3} porphyrin solution was prepared in toluene. Then, the toluene solution is simply mixed with 9 times volume of acetonitrile. The final concentration is 0.35 mmol dm^{-3} in a poor/good solvent (acetonitrile/toluene) = 9/1, v/v. With regard to the sonication system for preparation of self-assembled porphyrins, we set up an original system composed of an ultrasonic generator (AS-ONE VS-100 III) and a temperature control circulator for external open system (Yamato Scientific Co., Ltd. Cool-Line CLS 300). The solution was sonicated (45 or 28 kHz) for 30 min at 15 ºC to form macroscopic self-assembled porphyrins such as rod-like structures. In all experiments, we maintained the final concentration (0.35 mmol dm^{-3}) and temperature (15ºC). It should be noted that no formation of rod-like structure is observed without sonication, and all measurements for analysis of the structures were performed quickly before occurrence of the precipitation.

Fig S1. Pictures of 0.35 mmol dm^{-3} H_2DBuPP solutions (acetonitrile/toluene = 9/1, v/v) before and after sonication.

Steady-state absorption & fluorescence and microscope measurements. The UV-visible spectra were recorded on a Perkin Elmer LAMDA 750 spectrophotometer equipped with an integrating sphere. Fluorescence spectra were measured on Perkin Elmer LS 55 fluorescence spectrometer. TEM images were recorded using a Hitachi H-7100 transmission electron microscope. SEM images of porphyrin assemblies were

also recorded using a Hitachi S-4100 scanning electron microscope. Optical and fluorescence images were recorded using KEYENCE BZ-8000.

Fluorescence lifetime measurement. The time-resolved fluorescence spectra were measured by single photon counting method using a streakscope (Hamamatsu Photonics, C5680) as a detector and the laser light (Hamamatsu Photonics M10306, laser diode head, 408 nm) as an excitation source. Lifetimes were evaluated with a software attached to the equipments.

X-ray diffraction measurement. X-ray diffraction (XRD) measurement was carried out with a BRUKER-axs M18XHF-SRA using filtered Cu K_α radiation. The sample for XRD analysis was prepared by drying suspension liquid over a glass substrate in air.

Preparation of porphyrin-deposited films. Porphyrin films were simply prepared by drop-cast method. ~1 mL of 0.35 mmol dm^{-3} porphyrin nanorod in acetonitrile/toluene = 9/1, v/v or 0.35 mmol dm^{-3} porphyrin in toluene were dropped onto substrates (ITO, quartz plate etc, surface area: 10 mm x 35 mm), and then dried in air.

Measurement of photoelectrochemical solar cells. An optically transparent electrode (OTE) was prepared by casting SnO_2 colloidal solution (Alfa Chemicals) onto an ITO film (Sanyo Vacuum Industires Co., Ltd.) The detail procedure was reported.[4,18] Photoelectrochemical measurements were carried out in a standard two-compartment cell consisting of a working electrode and a Pt wire gauze counter electrode in the electrolyte. The electrolyte is 0.5 M LiI and 0.01 M I_2 in acetonitrile. μAutolab III was used for recording photocurrent generation response and IPCE action spectrum. A collimated light beam from a 500 W Xenon lamp with a AM 1.5 filter was used for excitation of porphyrin assembly film deposited on optically transparent electrode. In the case of measurement of IPCE spectra, a monochromator (JASCO CT-25C) was introduced into the path of the excitation beam for the selected wavelength. The schematic illustration is shown in Fig. 3A for clarify.

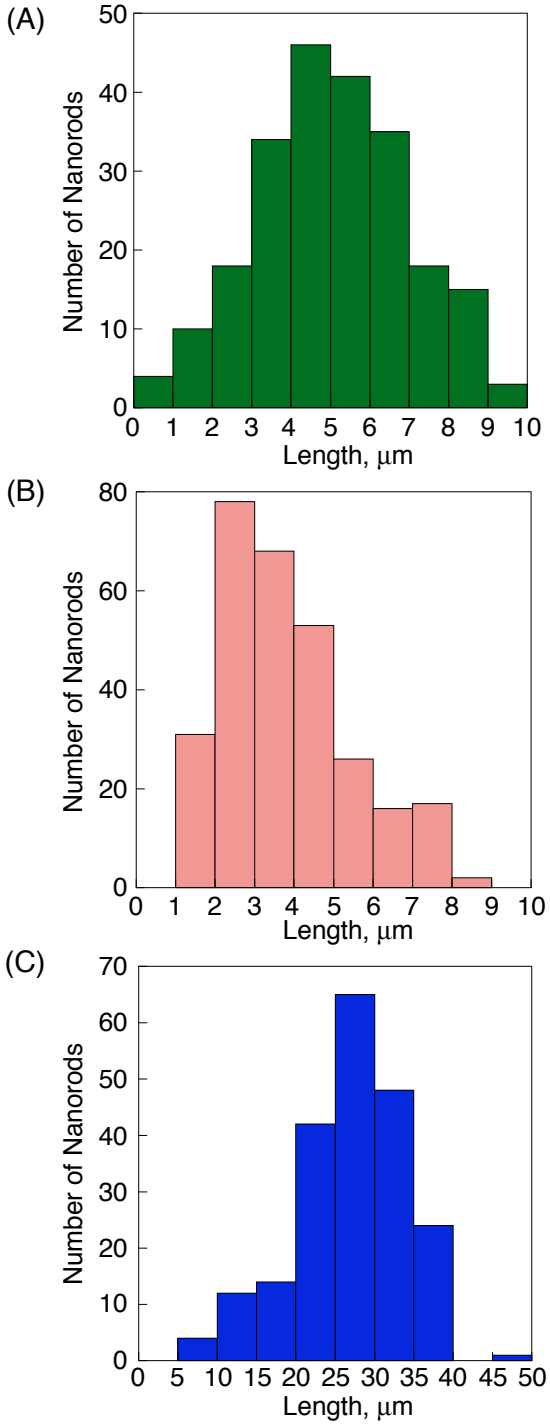

Fig. S2 Length-distributions of (A) H_2DBuPP nanorods (5.02 ± 1.94 μm), (b) H_2DPP nanorods (3.77 ± 1.63 μm) and (c) H_2DBuPP fibers (27.2 ± 6.9 μm).

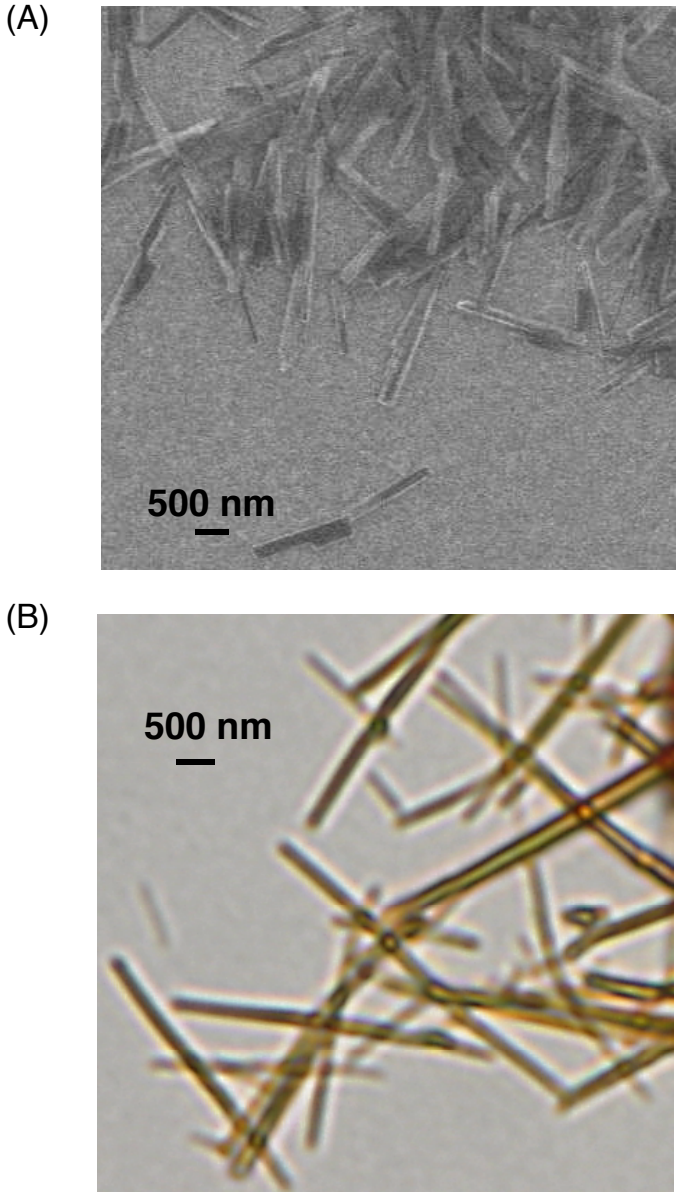

Fig. S3 H_2DBuPP nanorod structures. (A) SEM image on an ITO plate and (B) optical microscope image on a quartz plate.

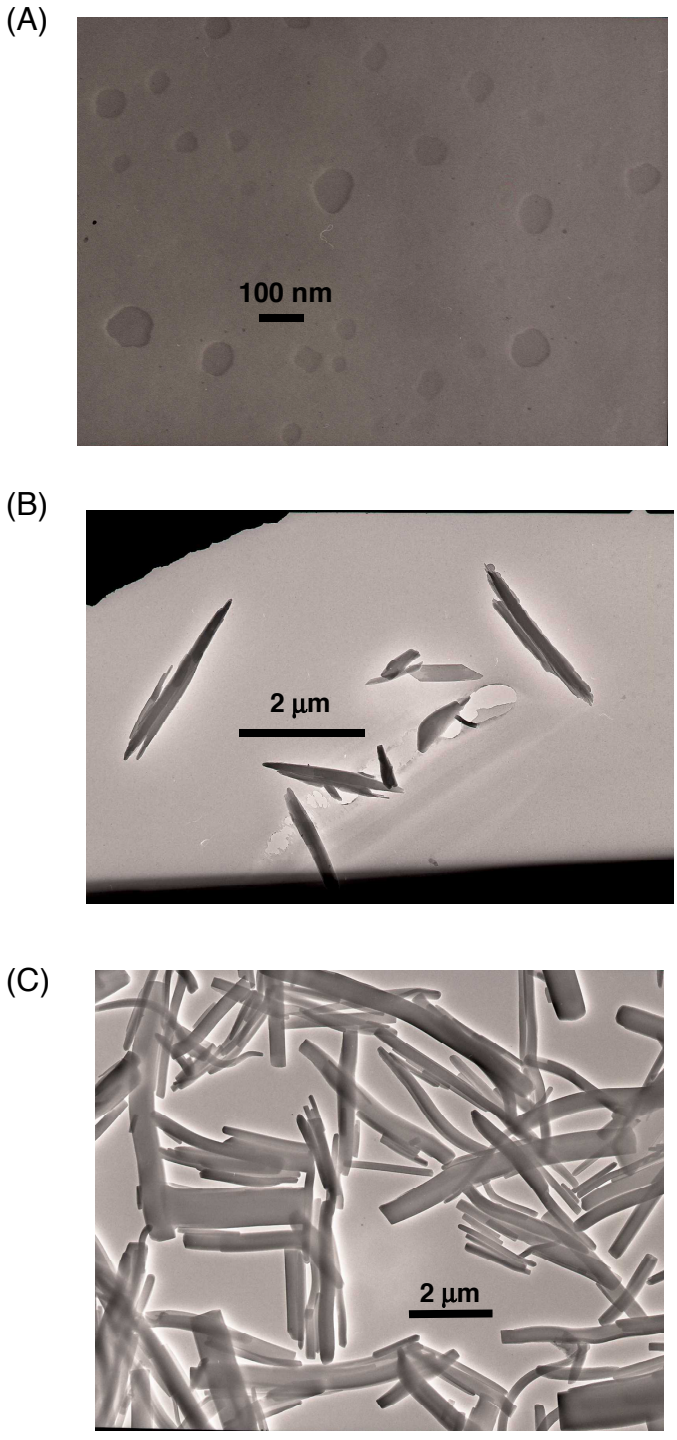

Fig. S4 Sonication time-dependent formation of H_2DBuPP assemblies by TEM analyses. (A) 3 min, (B) 10 min and (C) 20 min.

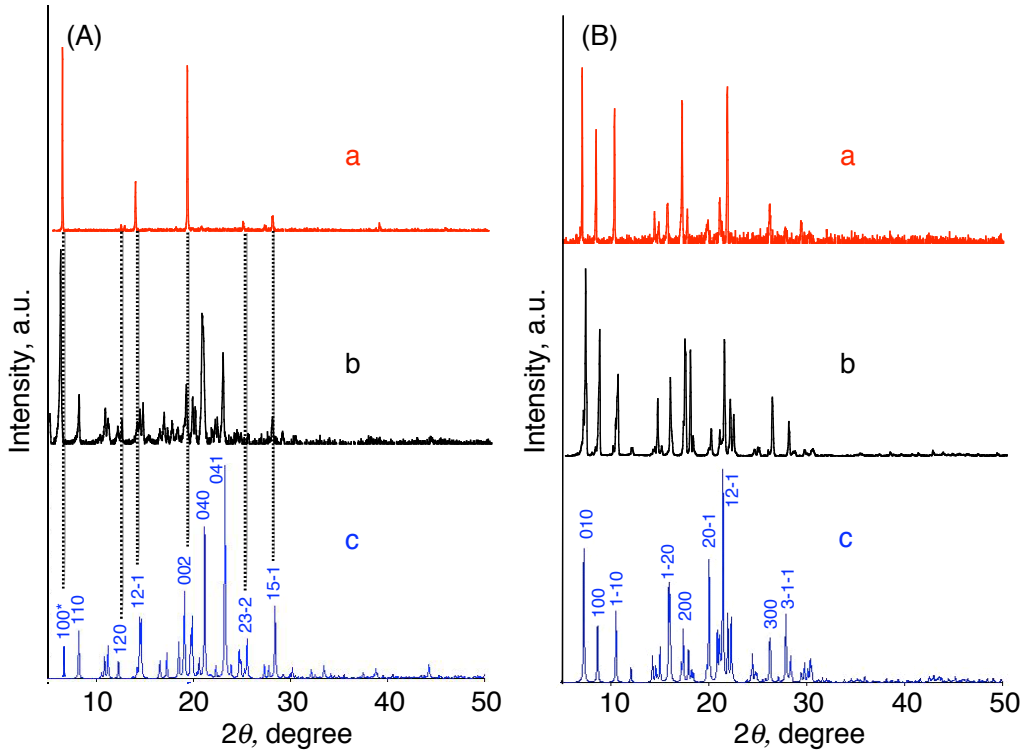

Fig. S5 (A) XRD patterns of (a) H_2DPP nanorod, (b) H_2DPP starting material, and (c) simulated pattern from the crystal structure of H_2DPP. (B) XRD patterns of (a) H_2TPP assembly, (b) H_2TPP starting material, and (c) simulated pattern from the crystal structure of H_2TPP. * x 200 magnification for clarification. The patterns *c* were analyzed by supporting materials of ref. 14 papers.

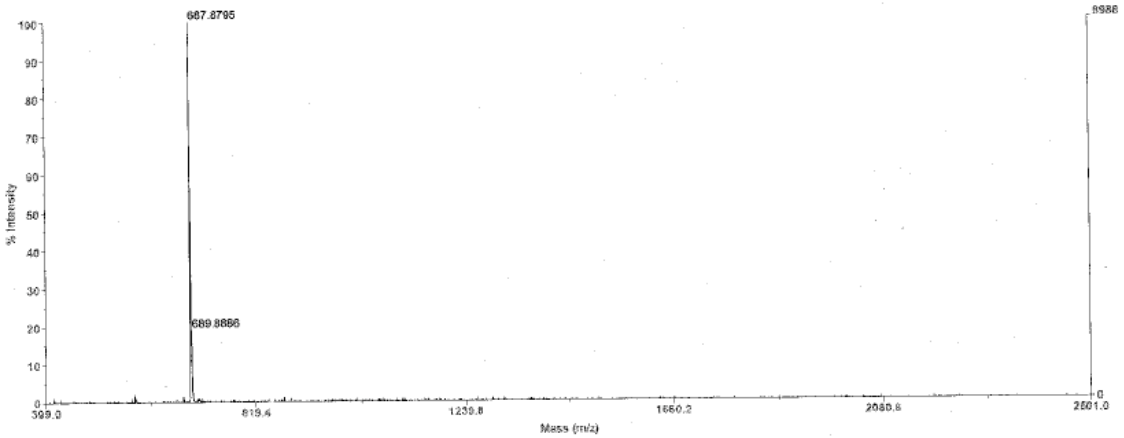

Fig. S6 MULDI/TOF MASS analysis of H_2DPP moiety after diluting H_2DPP nanorods with toluene.

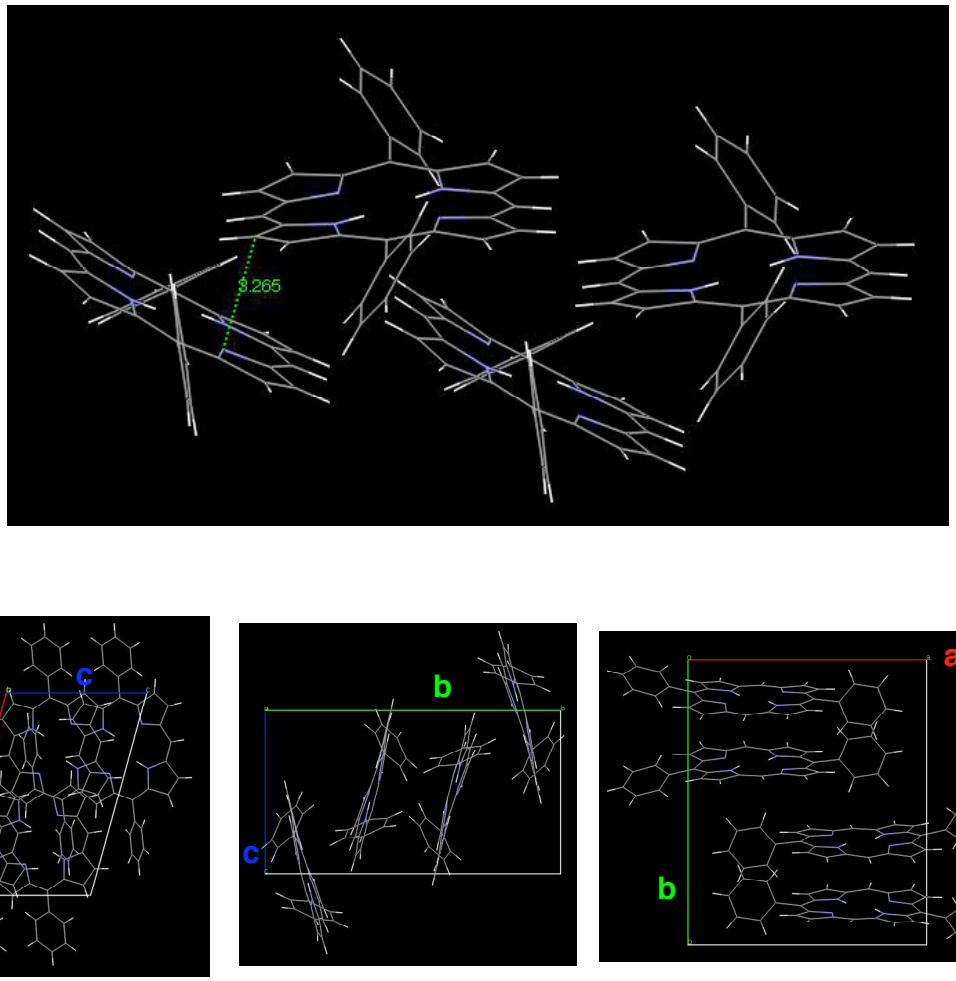

Fig. S7 Crystal structures of H_2DPP. These figures were analyzed by supporting materials of the following papers. H_2DPP: A. D. Bond, N. Feeder, J. E. Redman, S. J. Teat, and J. K. M. Sanders, *Crystal Growth & Design*, 2002, **2**, 27.

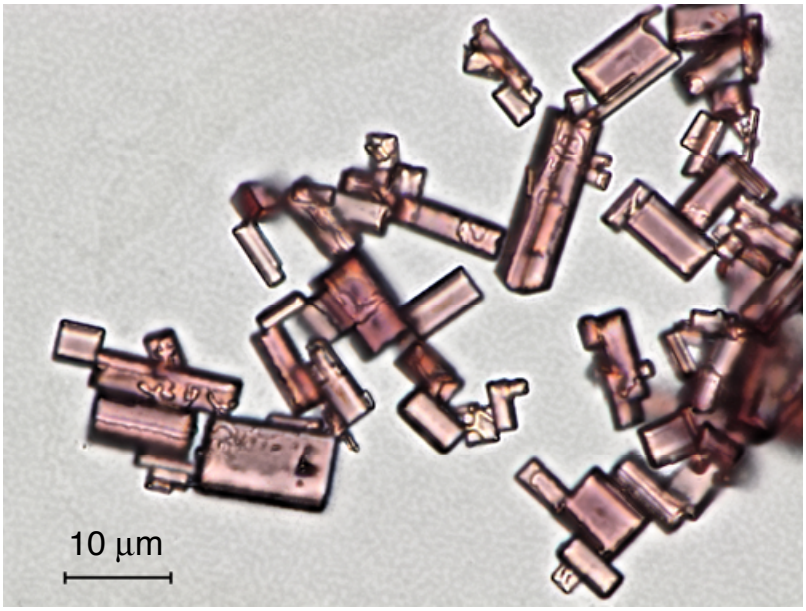

Fig. S8 Optical microscope image of H_2TBuPP assemblies after 6 days of standing.

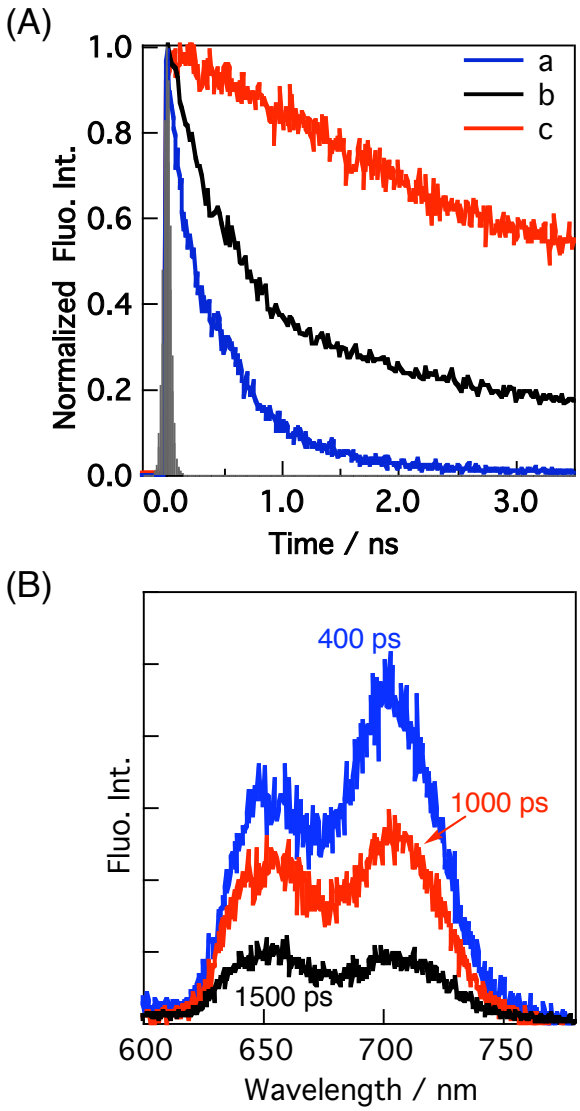

Fig. S9 (A) Fluorescence lifetime decay profiles of (a) H_2DBuPP nanorod film, (b) H_2DBuPP drop-cast film on quartz plates and (c) H_2DBuPP in toluene. Excitation wavelength is 408 nm and collected from 600-750 nm. (B) Time-dependent fluorescence spectra of H_2DBuPP nanorod film.

Comparison of Fluorescence Lifetimes of (a) H_2DBuPP nanorod film, (b) H_2DBuPP drop-cast film on quartz plates and (c) H_2DBuPP in toluene.

	τ_1	τ_2
(a) H_2DBuPP Nanorod film	421 ps (94%)	1854 ps (6%)
(b) H_2DBuPP drop-cast film	750 ps (45%)	6023 ps (55%)
(c) H_2DBuPP in toluene	9700 ps (100%)	

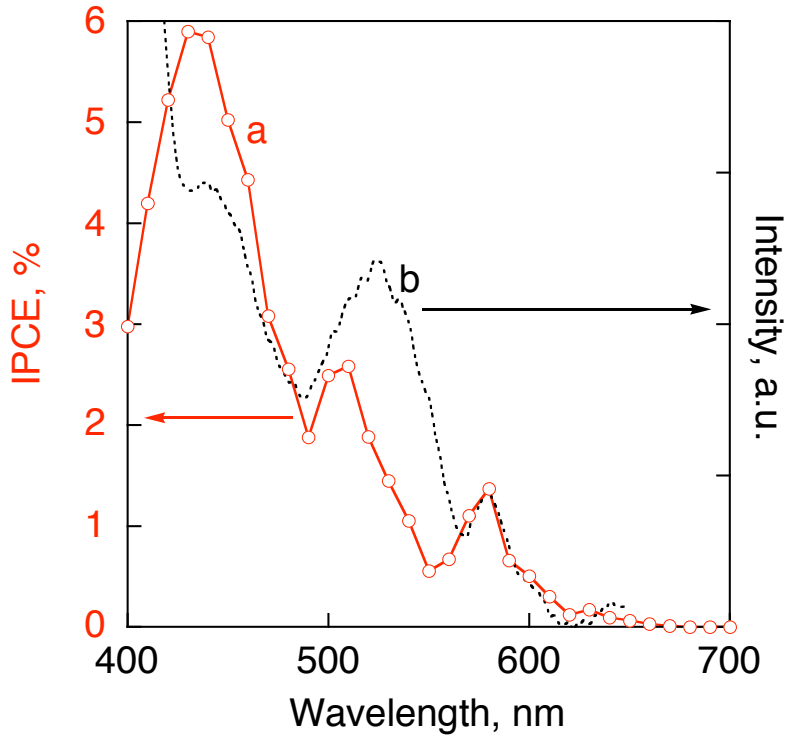

Fig. S10 (a) Photocurrent (IPCE) action spectrum of H_2DBuPP drop-cast film on an OTE. Electrolyte: 0.5 mol dm^{-3} LiI and 0.01 mol dm^{-3} I_2 in acetonitrile. (b) Excitation spectrum of H_2DBuPP drop-cast film on an OTE; Observed at 680 nm.