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Supporting Information for

Spatial distribution of triplet excitons formed from charge transfer states at donor/acceptor interface

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OLED fabrication

The OLED devices were fabricated on indium tin oxide (ITO)-coated glass substrates (ITO thickness: 150 nm; sheet resistance: 10.3 Ω sq^{-1}; Techno Print). Rubrene (sublimed, Tokyo Chemical Industry) were purified by single-crystal sublimation. PTCDI (sublimed, Lumtec), CuPc (sublimed, Lumtec) and DBP (sublimed, Lumtec) were used without further purification. The MoO_3 hole-transporting layer (10 nm, 0.01 nm s^{-1}), rubrene donor layer (110 or 210 nm, 0.1 nm s^{-1}), PTCDI

acceptor layer (50 nm, 0.1 nm s^{-1}), LiF electron-injection layer (0.2 nm, 0.01 nm s^{-1}), MoO_3 layer (0.3 nm, 0.01 nm s^{-1}) and Al electrodes (70 nm, 0.1 nm s^{-1}) were deposited by thermal evaporation under high vacuum (~10^{-5} Pa) in a vacuum evaporation system (VTS-350M, ULVAC) housed in a glove box (DSO-1.5S MS3-P, Miwa). CuPc and DBP were introduced into the rubrene layer via the codeposition technique. The CuPc and DBP concentration were 1% and 0.5% that are described as the volume percent relative to the rubrene volume in the film. The devices were encapsulated in the glove box by a glass substrate and epoxy resin. The active area of the devices was 0.065 cm^2.

OLED characterization

The *J–V* and *L–V* curves of the OLEDs were measured using a source/measure unit (B2902A, Keysight Technologies Inc.) and a luminance meter (BM-9, TOPCON Ltd.). A fiber optic spectrometer (Avaspec-UV/VIS/NIR, Avantes) was used to measure the absolute EL spectra of the OLEDs. The fiber spectrometer consists of an Si detector at the visible region and an InGaAs detector at the near-infrared region. The Si detector was used with a sensitivity of 470 kcounts/μW/ms and a S/N ratio of 300/1. The InGaAs detector was used in high sensitivity mode, with a sensitivity of 1,300 kcounts/μW/ms and a S/N ratio of 2000/1. Absolute EL spectra were measured when a constant current was applied; these spectra were collected by a cosine collector (CC-VIS/NIR, Avantes) attached to the end of an optical fiber to cover all the emission region of the device. EL decay was measured by a hand-made system composed of a digital oscilloscope (T3DSO1302A, Teledyne Lecroy), a Si-photodiode (FDS100, Thorlabs) and a transimpedance amplifier (AMP140, Thorlabs)

when the function generator (WF1974, NF Corp.) was applied a square voltage of 100 Hz to the OLEDs. EL decay waveforms were measured using oversampling at a rate of 2 GS/s and smoothing by a moving average of 100 times.

PUC film fabrication

ITIC-Cl (Ossila) was used without further purification. Chloroform solution containing 2.5 g L^{-1} of ITIC-Cl was spin-coated onto a quartz substrate at a spinning rate of 1000 rpm for 30 s in a N_2-filled glove box (UNICO). The thicknesses of the layers were approximately 23 nm. Rubrene layer (100 nm, 0.1 nm s^{-1}) was deposited by thermal evaporation under high vacuum (~10^{-5} Pa) in a vacuum evaporation system (VTS-350M, ULVAC), housed inside a N_2-filled glove box (DSO-1.5S MS3-P, Miwa). The film surface was encapsulated by an evaporated Al thin film (70 nm).

PUC characterization

PL spectra were measured on a spectrofluorometer (Fluorolog, Horiba). The films were illuminated by single-color LEDs (LED750L, THORLABS) with a constant current flow controlled by a source meter (2450, Keithley). The bandwidth of LED750L was 23 nm. The LED light was focused on the sample by an aspheric lens. The incident light shape was measured by a beam profiler and the beam diameter was defined as $1/e^2$ width. The measured beam diameters of the light from LED750L at the sample positions were 4.01 mm. The incident light power from the LED on the sample was measured by a power meter (3A-P, Ophir Photonics).

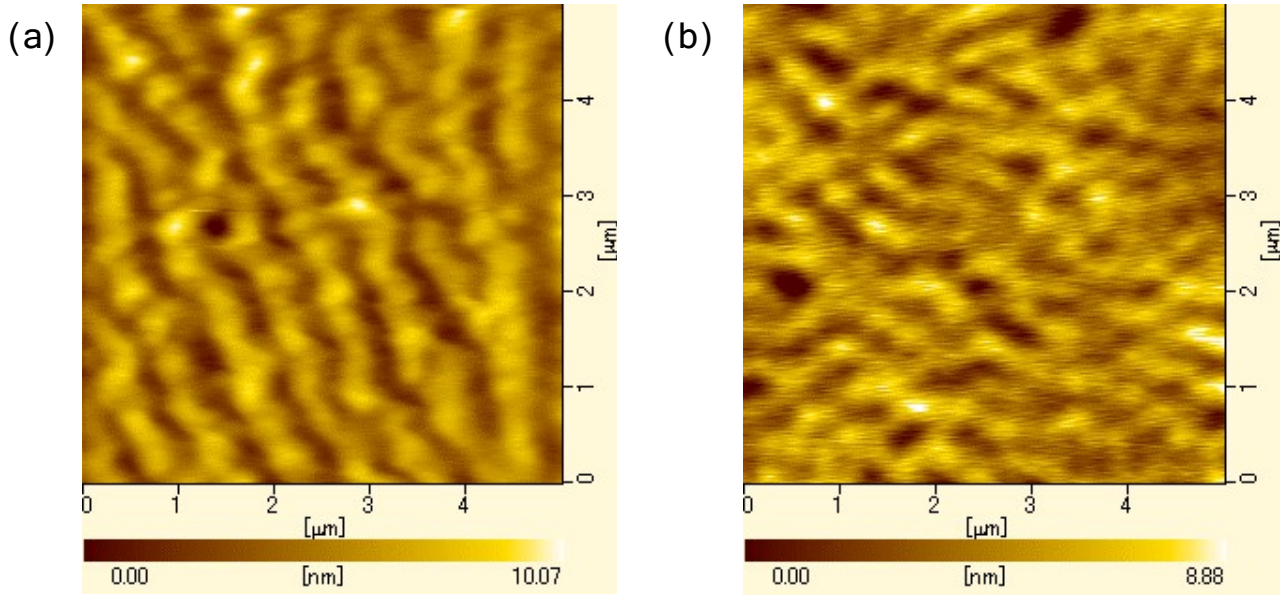

Figure S1. Atomic force microscope (AFM) images for (a) undoped and (b) CuPc-doped rubrene films. The images were measured on a SPI3800 (SII). The arithmetic mean roughness of undoped and doped films are 1.32 and 1.24 nm, respectively.

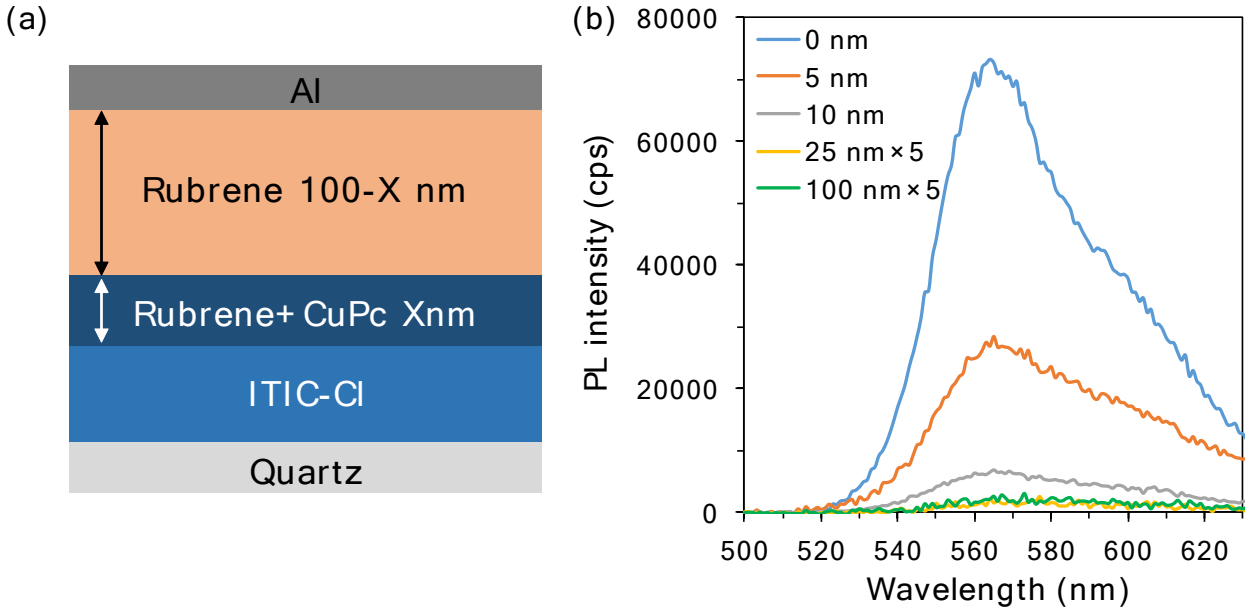

Figure S2. (a) Schematic illustration of rubrene/ITIC-Cl PUC system with CuPc-doped rubrene layer at the D/A interface. (b) PUC emission spectra excited by 750 nm LED light with the intensity of 37 mW/cm^2 for the device with 0 nm (blue), 5 nm (orange), 10 nm (grey), 25 nm (yellow) and 100 nm

(green) of CuPc-doped rubrene layer at the D/A interface. For clarity, the PL intensity of 25 nm and 100 nm was magnified by a factor of 5.

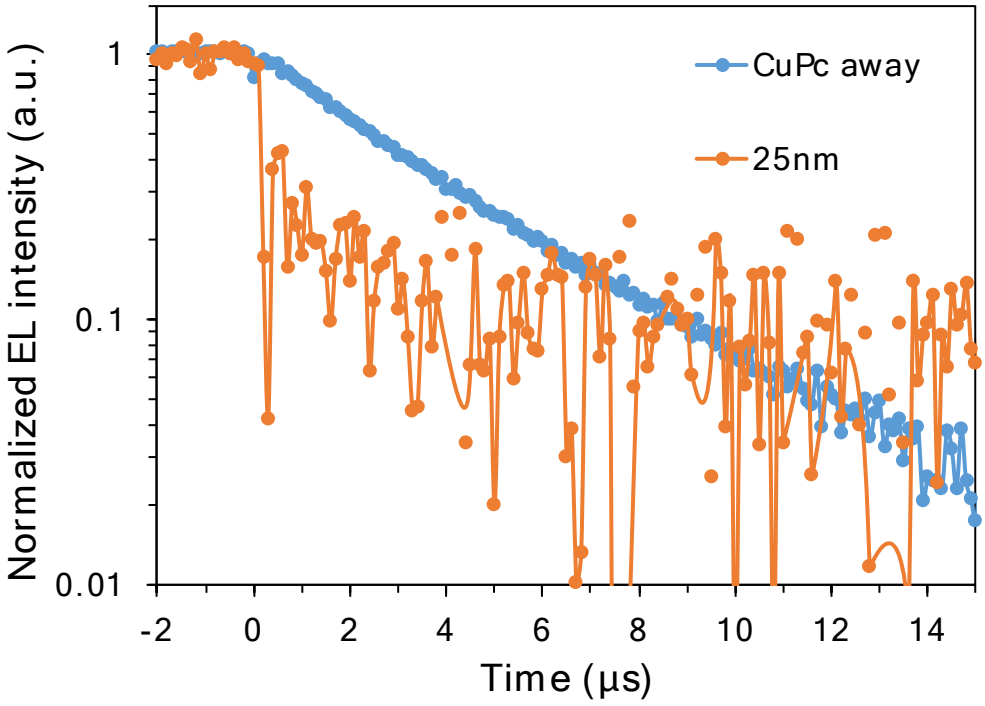

Figure S3. EL decay of the device with CuPc-doped layer away from the D/A interface (blue), and with 25 nm of CuPc-doped layer at the D/A interface (orange). The EL emission was transmitted through NIR cut filter in order to eliminate CuPc emission. Voltages of 6.0 V and 12 V were applied to the devices with CuPc-doped layer away from the interface, and with 25 nm of CuPc-doped layer at the interface, respectively.

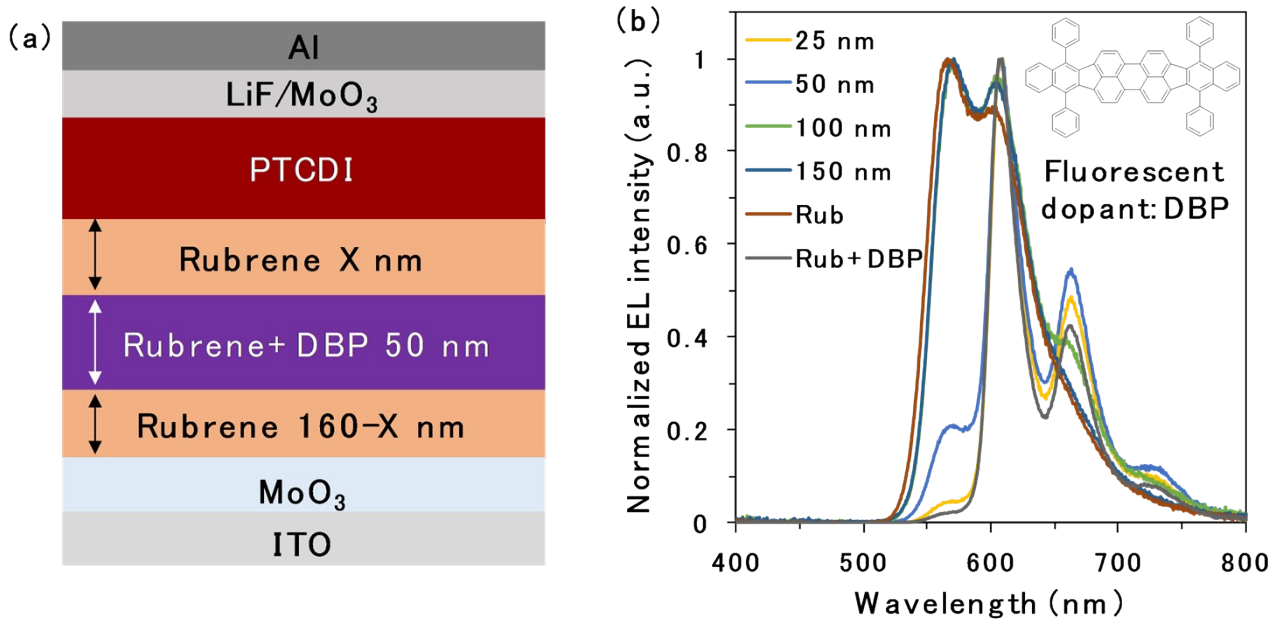

Figure S4. (a) Schematic illustration of the device with DBP-doped rubrene layer away from the D/A interface. (b) EL emission spectra under a constant current flow (10 mA/cm^2) for the device with 50 nm of DBP-doped rubrene layer away from the D/A interface. The thickness of rubrene interlayer at the D/A interface are 25 nm (yellow), 50 nm (sky blue), 100 nm (green) and 150 nm (blue). EL emission spectra for the device without DBP doping (brown), and in which the entire rubrene layer is doped with DBP (grey) at are displayed for the reference. The inset depicts the chemical structure of DBP.

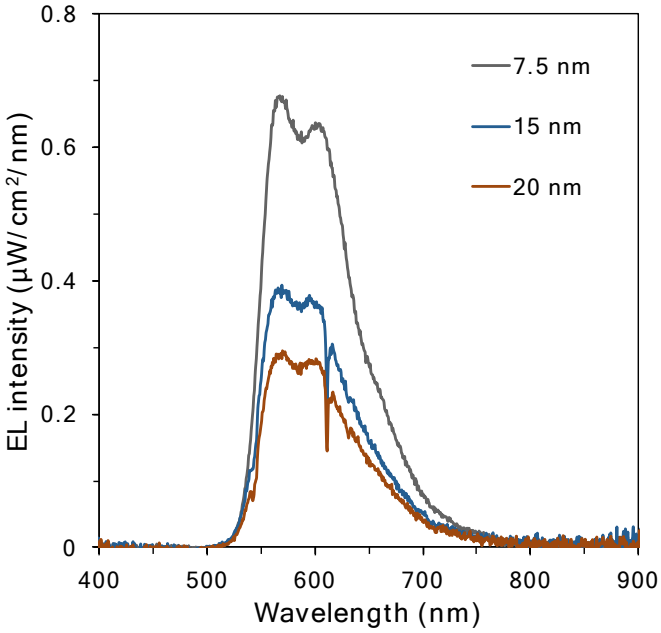

Figure S5. EL emission spectra under a constant current flow (1000 mA/cm^2) for the device with 7.5 nm (grey), 15 nm (blue) and 20 nm (brown) of CuPc-doped rubrene layer at the D/A interface.