Supporting Information

Experimental

Materials

1,4-Bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene, **1**, (CCDC deposition no. 1847366) was synthesized by previous procedure.[18] Solvents (Water content < 10 ppm; Kanto chemicals) for crystallization were used as received. The crystals were fabricated by crystallization in solution as follows. 50 mg of 1,4-bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene in a test tube (φ = 1 cm) was dissolved in chloroform (2 mL), and then 20 mL of methanol was carefully loaded on the chloroform solution. The procedure gave two organic phases. Slow evaporation of the solvents below 20 °C was carried out for 2 days. The crystals were collected by decantation, and then washed with pure methanol (< 20 °C), giving large crystals. Space Group: P 21/c (14), Cell: *a* 10.306(3)Å, *b* 4.3965(11)Å, *c* 15.490(4)Å, *α* 90°, *β* 92.080(3)°, *γ* 90°.

Measurements

UV-vis absorption spectra were obtained on an Ocean Optics USB4000-XR1 fiber spectrometer with DH2000-BAL tungsten halogen light source. The spectra of the crystal were measured form the method illustrated in Fig. S1. Fluorescence spectra were obtained on an Ocean Optics USB4000 fiber spectrometer with a LED light source (365 nm). Fluorescence spectra of each face were measured by USB4000 fiber spectrometer with a 365 nm LED light source (perpendicular to the samples) see Fig. S2. The samples were also mounted in a micro-photoluminescence (μ-PL) measurement setup equipped with a long-distance 5 x objective. The crystal was excited on the circumference by a He-Ne laser (OptoSigma) with a 405 nm wavelength with the power and spot size of 3.5 mW and 2x1 mm, respectively. The photoluminescence was detected by a flame spectrometer (OceanOptics, 1.5 nm resolution). Absolute quantum yield was obtained by Hamamatsu C9920-02. The value of the crystal and fibers was measured form the method illustrated in Fig. S3. Powder 1D XRD analysis of the crystals and the fibers was performed by JEOL JDX-3530 X-ray diffractometer system. Crystal images and video were obtained by optical microscope, Olympus FV1000 and KEYENCE VH-Z500R. The single crystal X-ray diffraction data for single crystals were collected at room temperature using SMART APEX II (Bruker AXS) with a CCD detector. The crystal structures were solved by the direct method and refined by full matrix least-squares using SHELXTL.

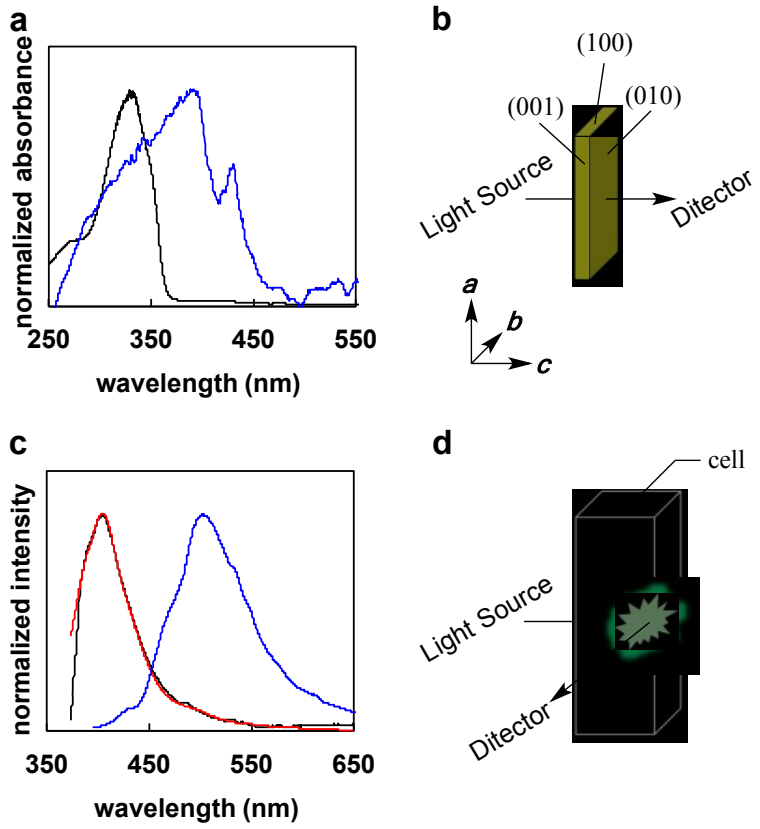

Figure S1. (a) UV-vis absorption spectra of **1** in tetrahydrofuran (black line) and crystal (blue line). (b) Schematic illustration of UV-vis absorption spectrum measurement of the crystal **1**. (c) Fluorescence spectra of **1** in tetrahydrofuran (black line: 1.0 x 10^{-6} M, red line: 1.0 x 10^{-2} M) and the crystal (blue line). (d) Schematic illustration of normal fluorescence spectrum measurement of the crystal.

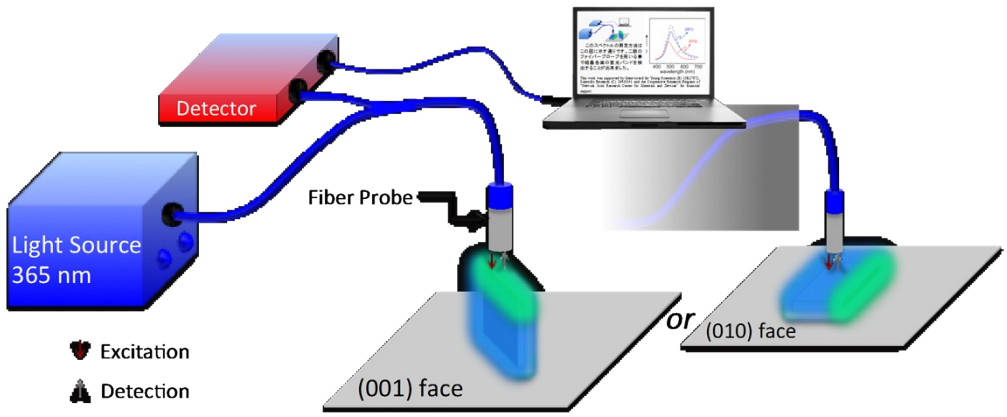

Figure S2. How to measure. Schematic illustration of the determination of the fluorescence spectra from the crystal at each face. Measurements at the (010) and (001) faces of the crystals were performed using a 20 μm fiber probe.

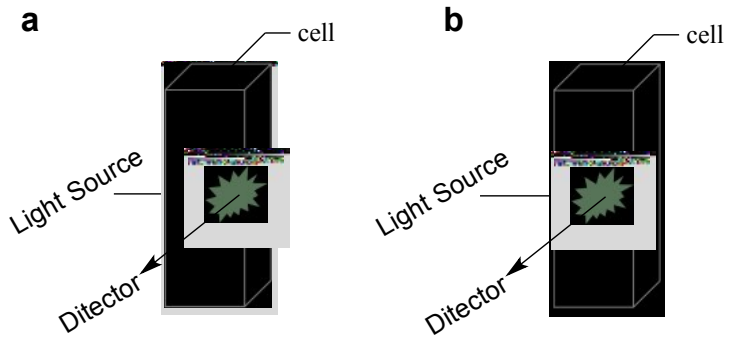

Figure S3. How to measurement. Normal fluorescence spectral measurements of large-scale single crystal and disassembled crystal.

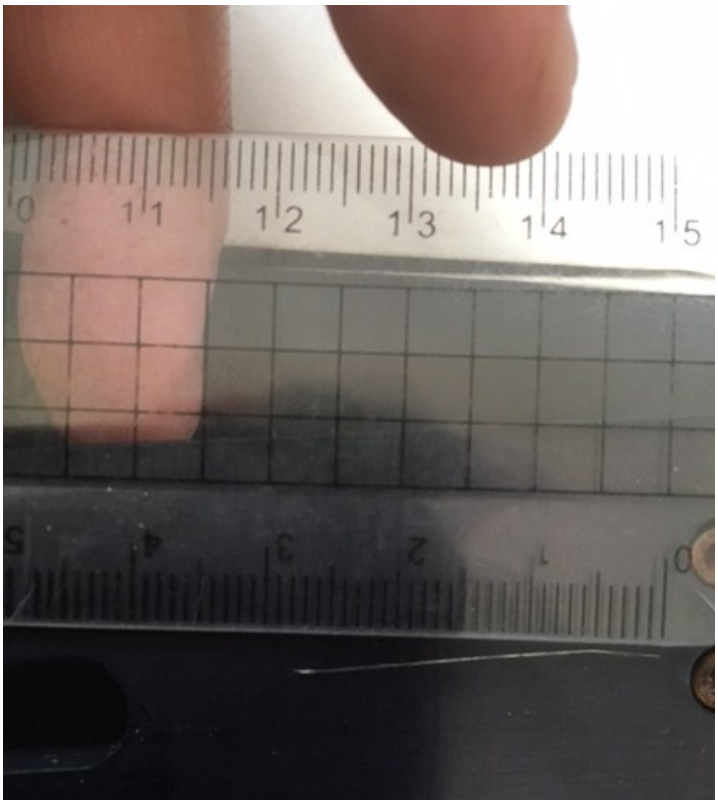

Figure S4. Photograph of long and fine fiber.