Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

A Filled Organic Crystal as a Hybrid Large-Bandwidth Optical Waveguide

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Contents

List of Supporting Schemes

List of Supporting Figures

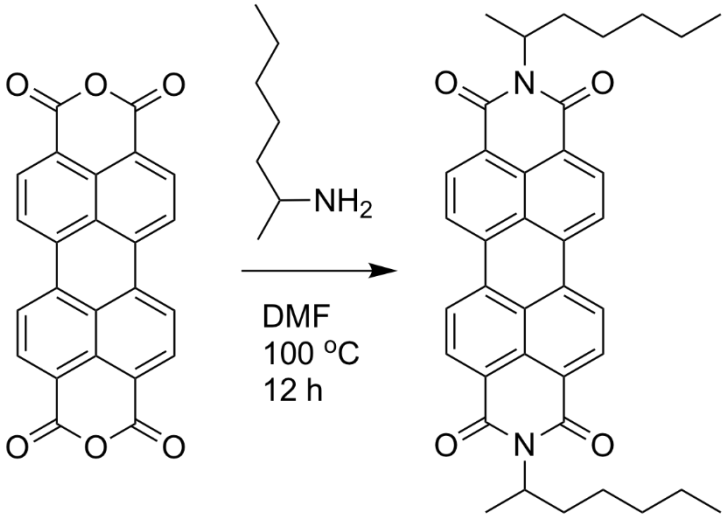
S1. General information

All reagents and solvents were purchased from Sigma-Aldrich and used without further purification. 9,10-dicyanoanthracene (DCA) was purchased from Sigma-Aldrich (CAS number: 1217-45-4) and used without further purification. Slow diffusion of diethyl ether in saturated solution of DCA in toluene afforded a mixture of hollow and regular crystals.

S2. X-Ray diffraction analysis

The unit cell of the hollow crystals of DCA was determined by using MoK_α radiation on a Bruker KAPPA APEX II diffractometer at room temperature (a = 3.88 Å, b = 8.52 Å, c = 9.21 Å, α = 71.60°, β = 78.59 °, γ = 90.84°) and it was identical with the previously reported structure (CCDC number 1865362).

S3. Synthesis of the PDI derivative and preparation of the crystalline fibrils



Scheme S1. Synthesis of the PDI derivative.

Perylenetetracarboxylic dianhydride (1 g, 1.27 mmol) was added to a solution of *N*,*N*-dimethylformamide (5 mL). 2-aminoheptane (1.6 mL, 12.7 mmol) was added to the suspension and heated with reflux for 12 hours. The reaction was cooled to room temperature and partitioned between dichloromethane (50 mL) and 1 M HCl (50 mL). The organic phase was washed with water, brine, dried with magnesium sulfate and concentrated on a rotary evaporator. The resulting residue was purified using silica column with 100% dichloromethane to yield 100 mg (13% yield) of PDI as bright red powder.

Characterization: m.p.: decomposes above 282 °C. IR (solid, ATR, cm^{-1}): 2935, 2914, 2847, 1655, 1646, 1590, 1451, 1402, 1335, 1253, 1176, 1093, 1030, 972, 951, 813, 806, 744, 620. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.68 (d, J = 8.0 Hz, 4H), 8.62 (d, J = 8.0 Hz, 4H), 5.35 (sextet, J = 7.0 Hz, 2H), 2.24 (m, 2H), 1.97 (m, 2H), 1.64 (d, J = 7.0 1 Hz, 6H) 1.32 (m, 12H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ/ppm: 163.8, 134.31, 134.25, 129.4, 126.3, 123.7, 122.9, 50.1, 33.5, 31.7, 26.8, 22.6, 18.3, 14.0. HRMS (MALDI-TOF) calculated for $C_{38}H_{38}N_2O_4$ $[M+H]^+$ m/z = 586.2832, found: 586.2871.

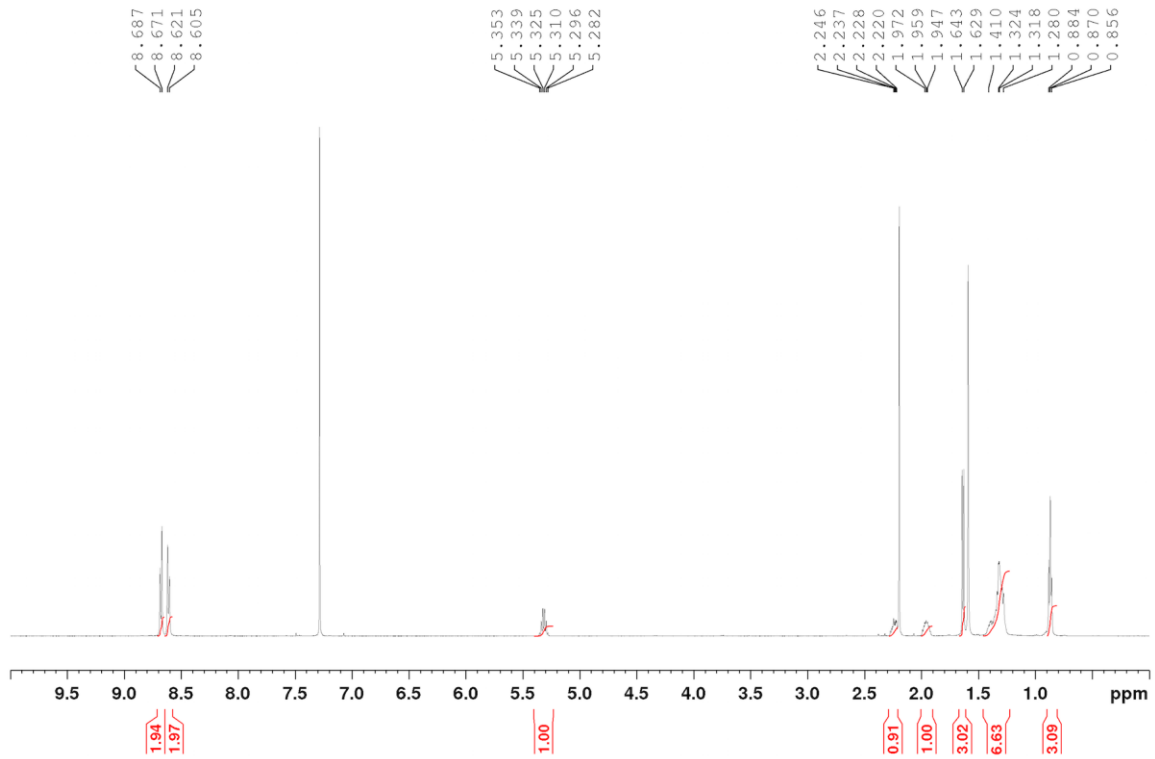


Figure S1. ^{1}H NMR (500 MHz) of PDI in $CDCl_3$.

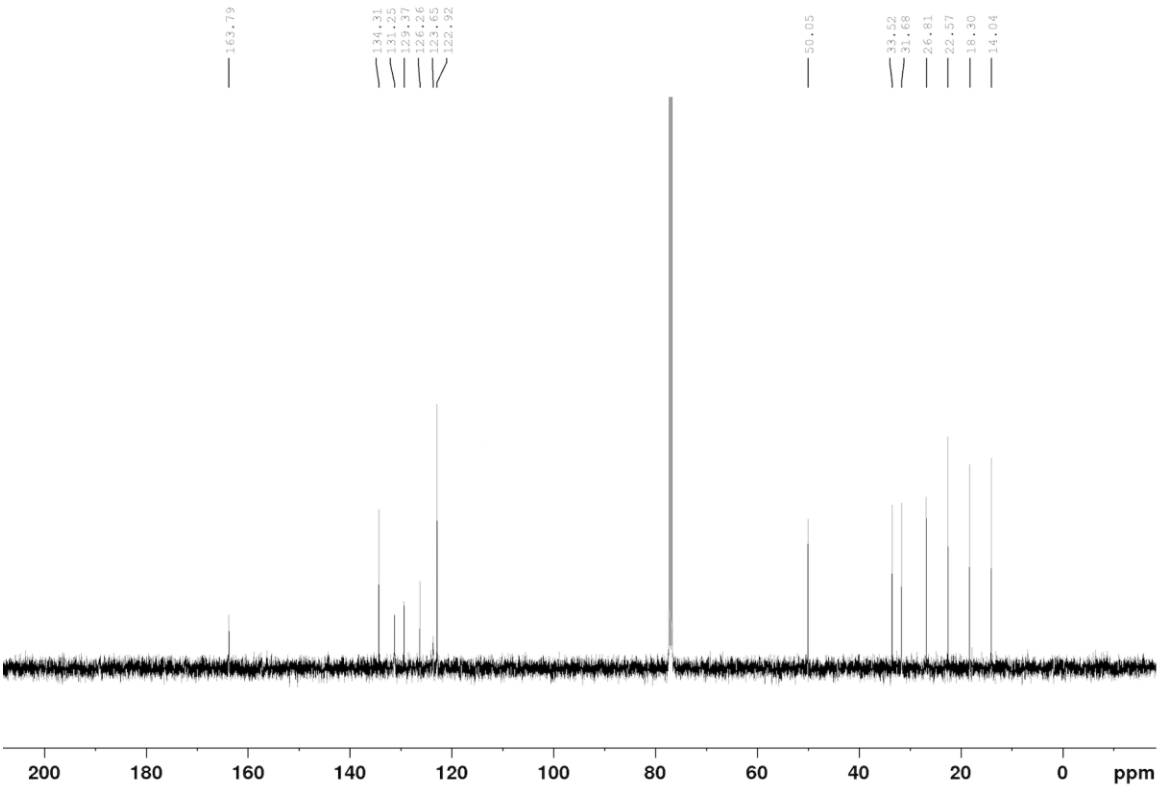


Figure S2. ^{13}C NMR (125 MHz) of PDI in $CDCl_3$.

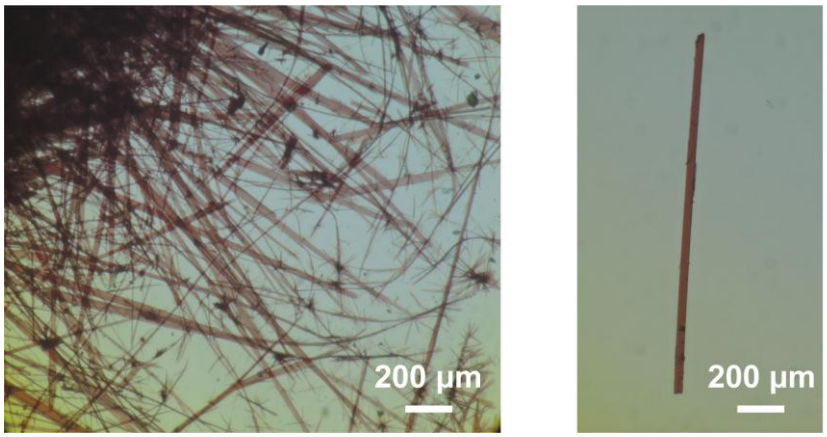


Figure S3. Microscopic images of typical PDI crystals.

To obtain the crystalline fibrils, PDI powders were dissolved in nitrobenzene at room temperature in a glass jar, which was left open to allow slow evaporation of the solvent. The crystals shown in Figure S3 were obtained after one week.

S4. Optical spectroscopy

All solid-state fluorescence spectra were recorded on a FP8500 spectrofluorometer (Jasco) equipped with an ILFC-847S cooled integration sphere and ESC-842 reference light source for the quantum yield and low-temperature measurements. The solid-state absorbance measurements were carried out on the same instrument by using a FUV-803 absorbance measurement cell.

The confocal fluorescence measurements were performed on Leica TCS SP8 using a PicoQuant PDL 880-B 40 MHz pulsed 405 nm diode laser as excitation source. The fluorescence spectra were recorded with ±7 nm resolution. The measured lifetime of DCA was uniformly distributed across the PDI fibers (Figure S4).

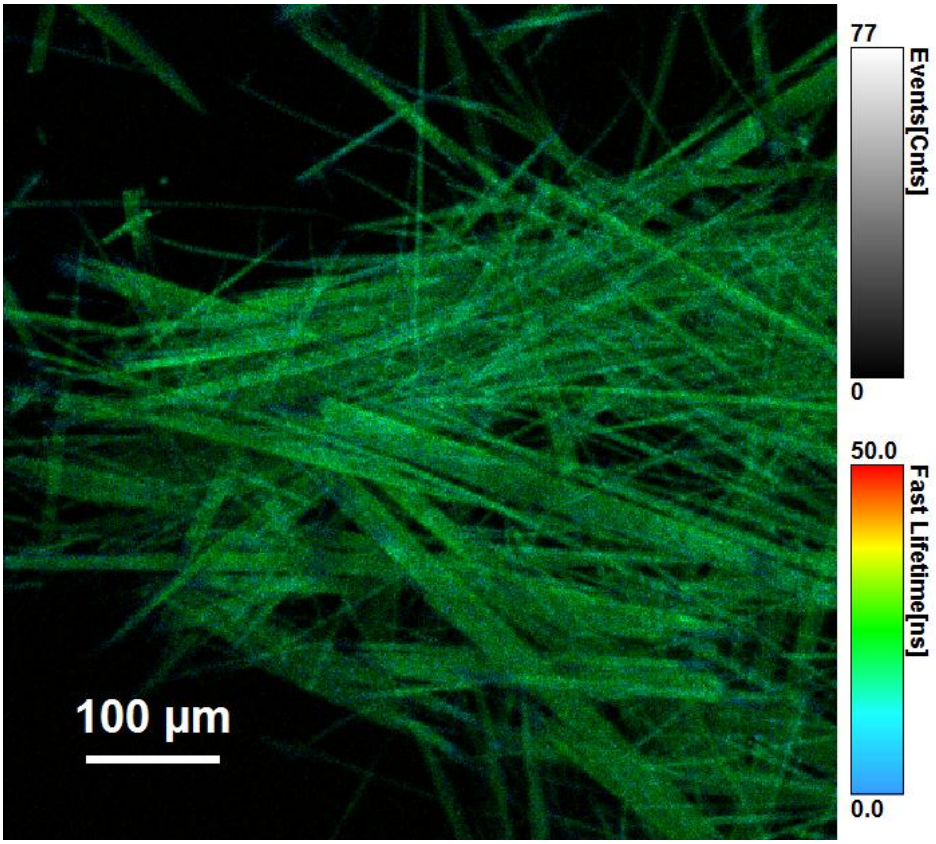


Figure S4. Uniformly distributed fluorescence lifetime of the PDI fibers.

S5. SEM and stereomicroscope imaging

The scanning electron microscopy experiments were carried out in low vacuum mode with a QUANTA FEG 450 electron microscope with a primary electron energy of 1–2 kV.

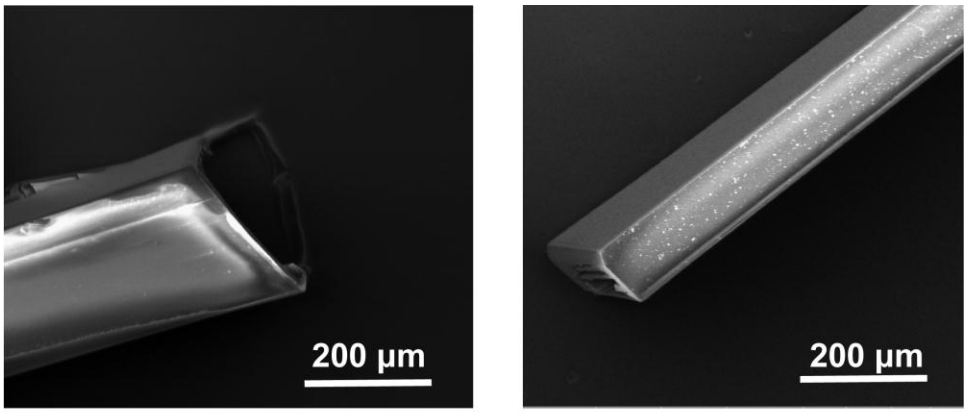


Figure S5. SEM images of representative hollow DCA crystals.

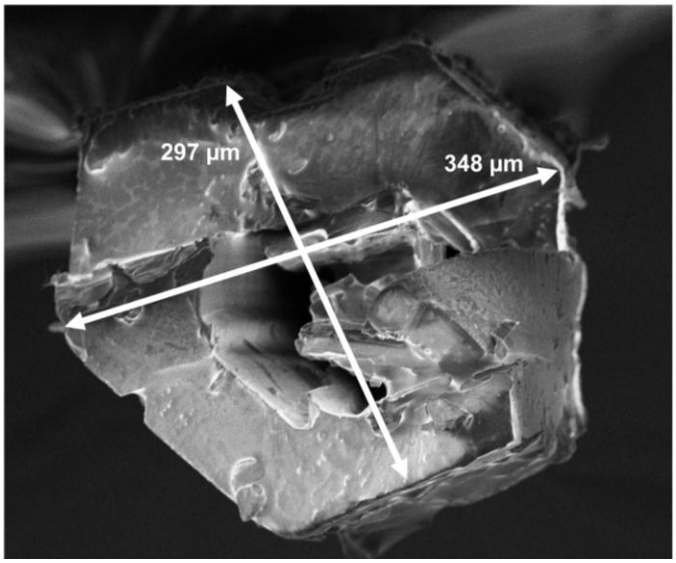


Figure S6. Top-view SEM image of the prototypical optical waveguide filled with PDI fibers and its dimensions.

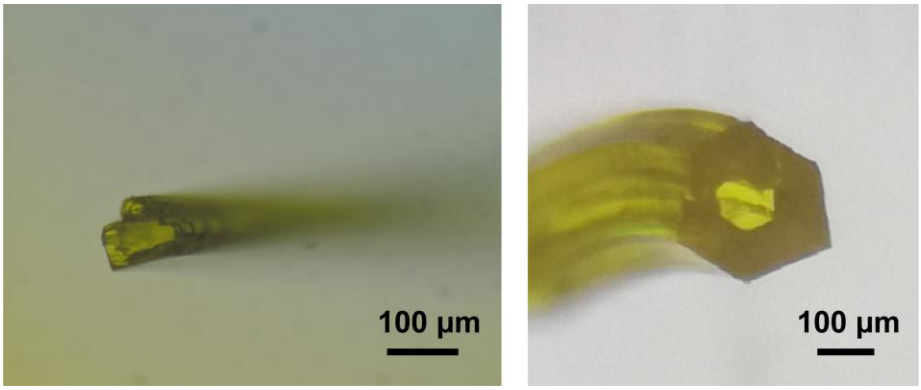


Figure S7. Top-view stereomicroscopic images of representative hollow DCA crystals.

S6. Computed tomography (CT) scan

The 3D CT scans were acquired on an X View CT Scanner, X500 CT. The scans were acquired with a working voltage of 120 kV and 100 A. The crystals were mounted on a molding clay and scanned at a rate of 7.5 frames per second. The images were processed and videos were recorded using X View CT's default software, eFX-view. In the CT images, the difference in density of the material is represented by different colors.

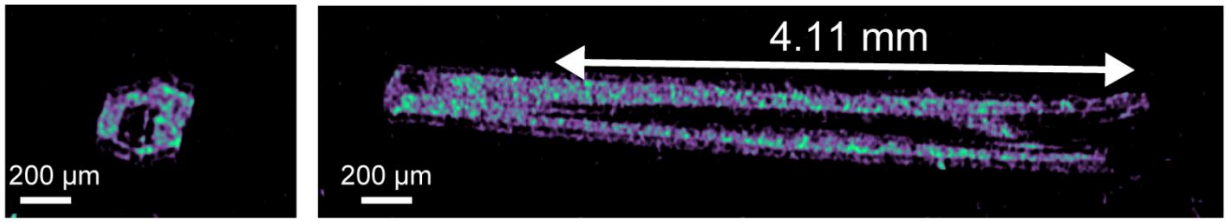


Figure S8. CT scan images of the prototypical fiber. Cross-section is shown on the left and transverse section is shown on the right.

S7. Optical fiber characterization

For UV measurements, the filled DCA crystal was excited in a direction perpendicular to its long axis at two different positions (side A and side B) with a collimated CW 365 nm LED 500 mW (M365LP1 Thorlabs) using an excitation spot with diameter of 1 mm. The light was collected at the tip of the crystal that was manually aligned with a micromanipulator to the end of commercial optical fiber connected to a TE-cooled 1044 × 64-element CCD array detector (Hamamatsu) and OceanOptics QE65 spectrometer.

For the waveguiding measurements using a red-light source, the waveguide was irradiated at a tip orthogonal to its long axis with collimated CW 10 mW 633 nm He-Ne Laser. The diameter of the spot on the crystal was about 1 mm, and the light was collected at the opposite tip of the crystal with a commercial optical fiber connected to a TE-cooled 1044 × 64-element CCD array detector (Hamamatsu) and OceanOptics QE65 Pro spectrometer. FEL0650 filter from Thorlabs with cut-off at 650 nm was used as long-pass filter.

For the waveguiding measurements using an IR source, the waveguide was irradiated at its tip orthogonal to its long axis with collimated CW 500 mW 850 nm LED (M850LP1 Thorlabs). The diameter of the spot on the crystal was about 1 mm, and the light was collected at the opposite tip of the crystal with an optical fiber connected to a TE-cooled 1044 × 64-element CCD array detector (Hamamatsu) and OceanOptics QE65 Pro spectrometer.

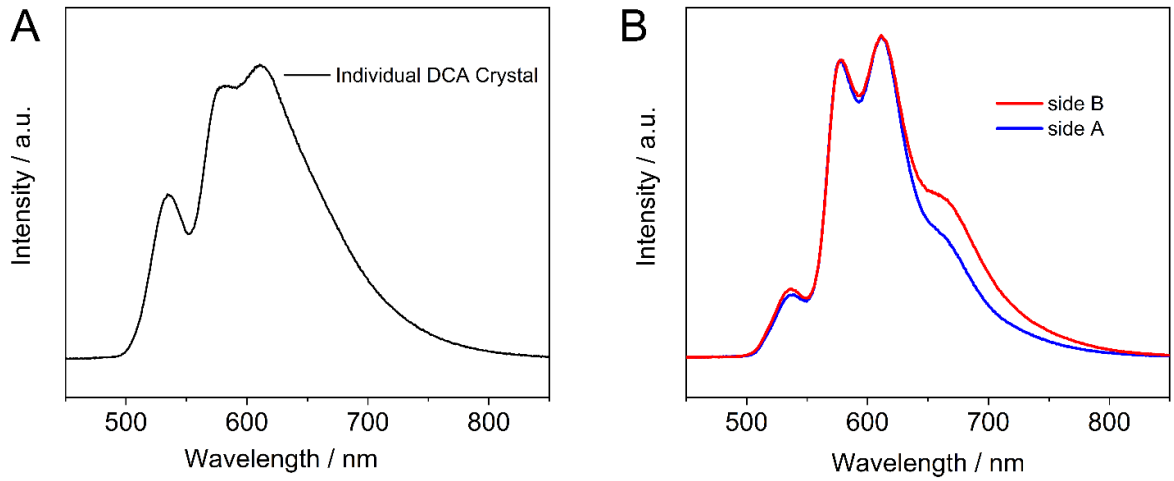


Figure S9. Comparison between (A) the transduced signal coming from a representative DCA crystal without PDI and (B) the output signals from the two sides of the hybrid waveguide reported in the present work upon excitation with 365 nm LED. The peak at ~680 nm in the hybrid originates from PDI fluorescence that is absent in the empty DCA crystal.