

Supporting Information

In-situ PTCDI-aided Lateral Crystallization of Benzothieno-benzothiophene Derivative for Photoresponsive Organic Ambipolar Devices

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Device fabrication

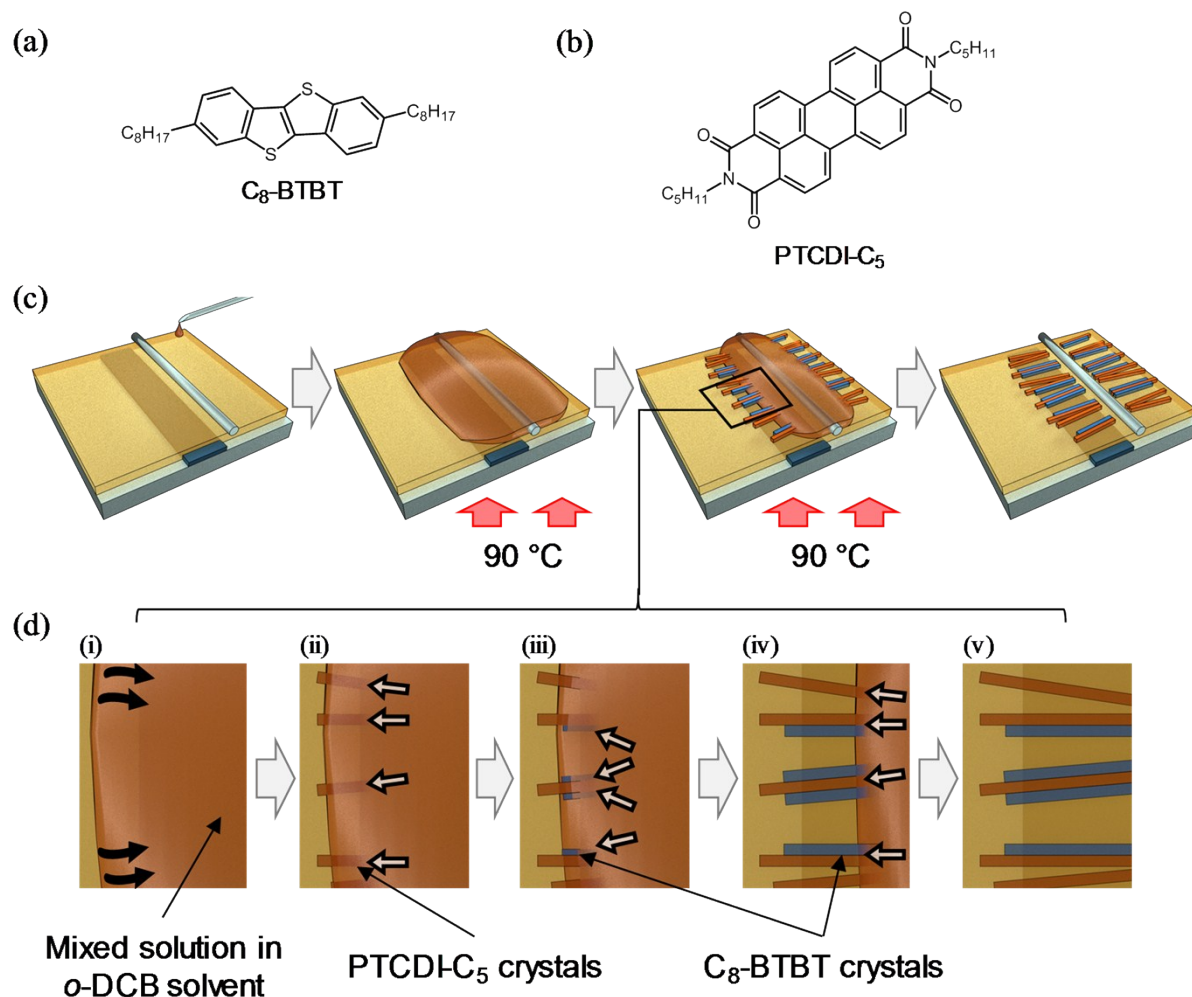


Figure S1. The chemical structure of (a) C₈-BTBT and (b) PTCDI-C₅, (c) schematics for the crystal deposition process, (d) detailed diagram of the crystal formation showing the direction of the retreating meniscus (black arrows), and the crystal growth direction (white arrows).

Device structure and characteristics measurement

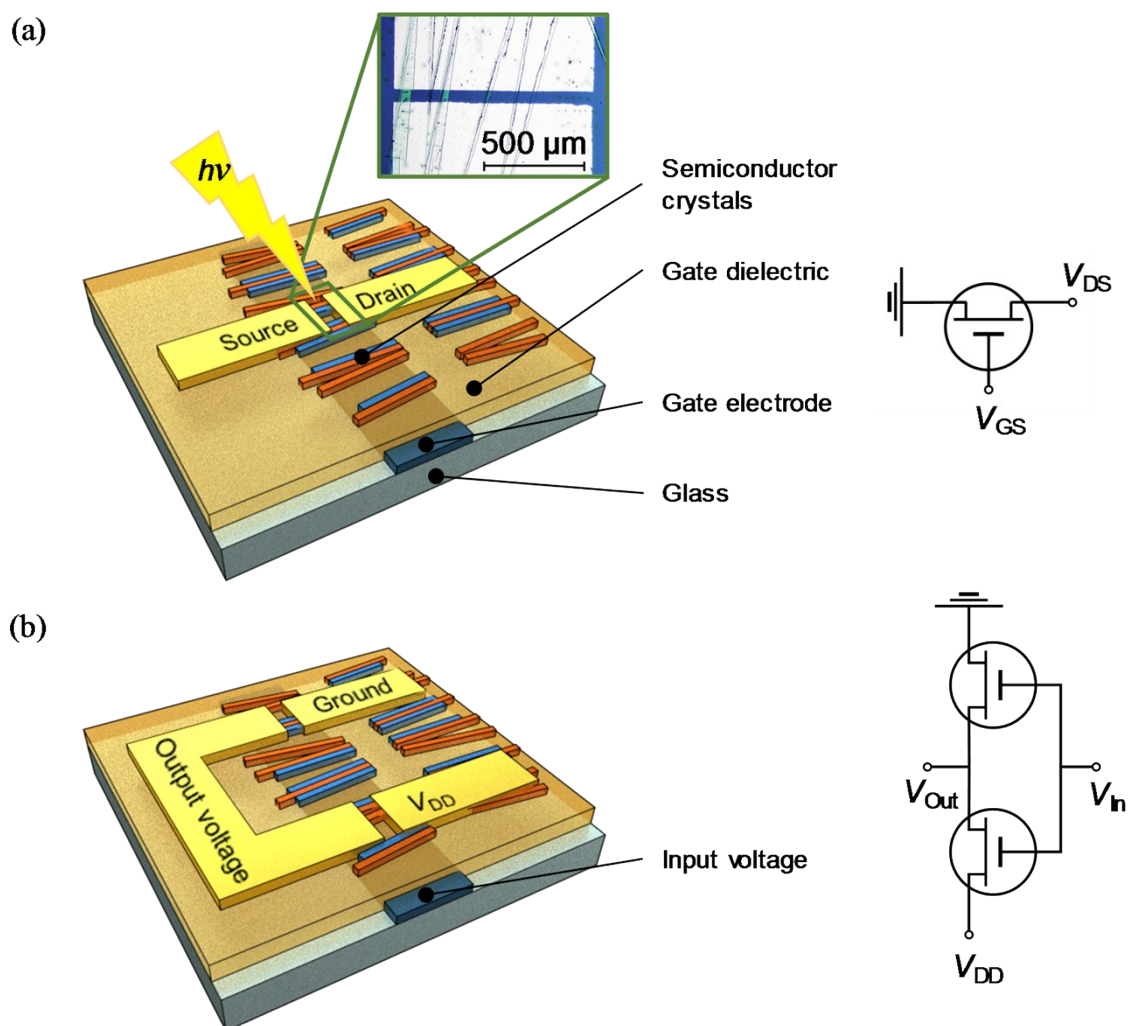


Figure S2. Schematic structure and equivalent circuit of (a) a transistor and (b) an inverter device

XRD patterns of the crystals

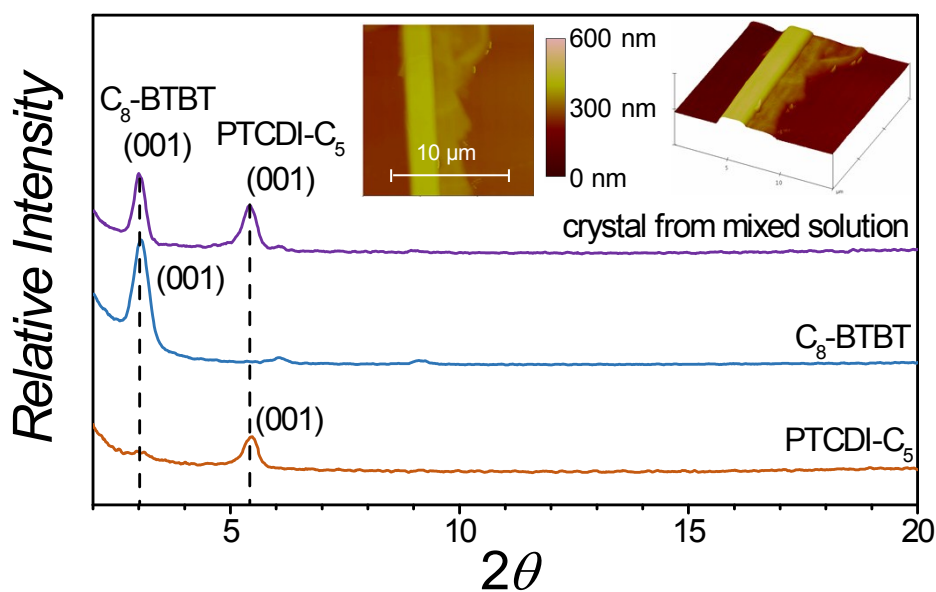


Figure S3. XRD patterns of solution-grown pure PTCDI-C₅, C₈-BTBT, and the laterally stacked crystals formed from the mixed solution of 0.5 mg/g C₈-BTBT and 0.05 mg/g PTCDI-C₅ (B10). Inset: AFM image of the laterally stacked crystal.

Absorbance and fluorescence

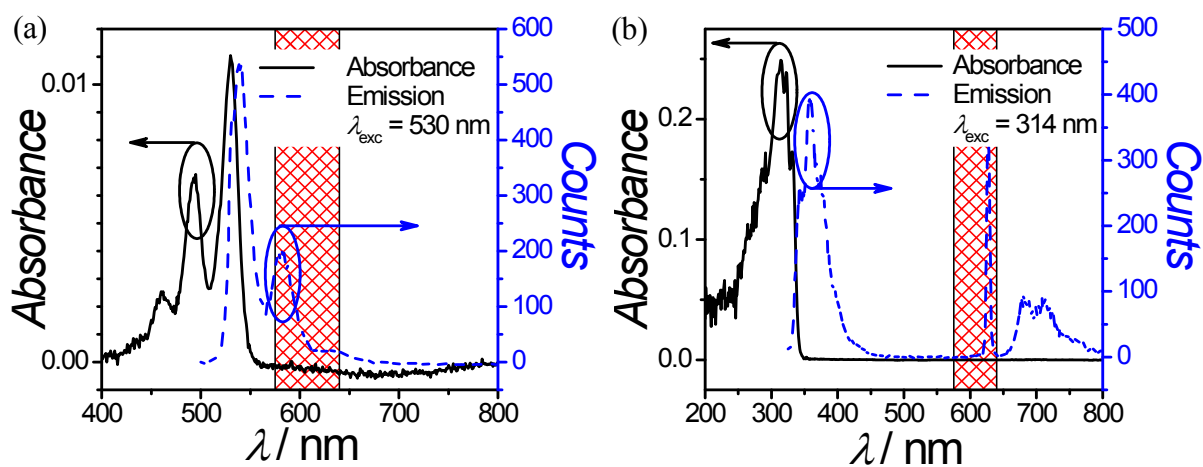


Figure S4. UV-visible absorbance and fluorescent emission spectra of (a) 0.05 μg/g PTCDI-C₅ solution in *o*-DCB and (b) 2.5 μg/g C₈-BTBT solution in *o*-DCB, with the red bar (575–640 nm) showing the detection wavelength using Rhodamine Red-X filter used in fluorescence microscopy. The sharp peak observed at 628 nm of (b) is an artifact at the double of the excitation wavelength due to the monochromator at the light source.

Crystal formation

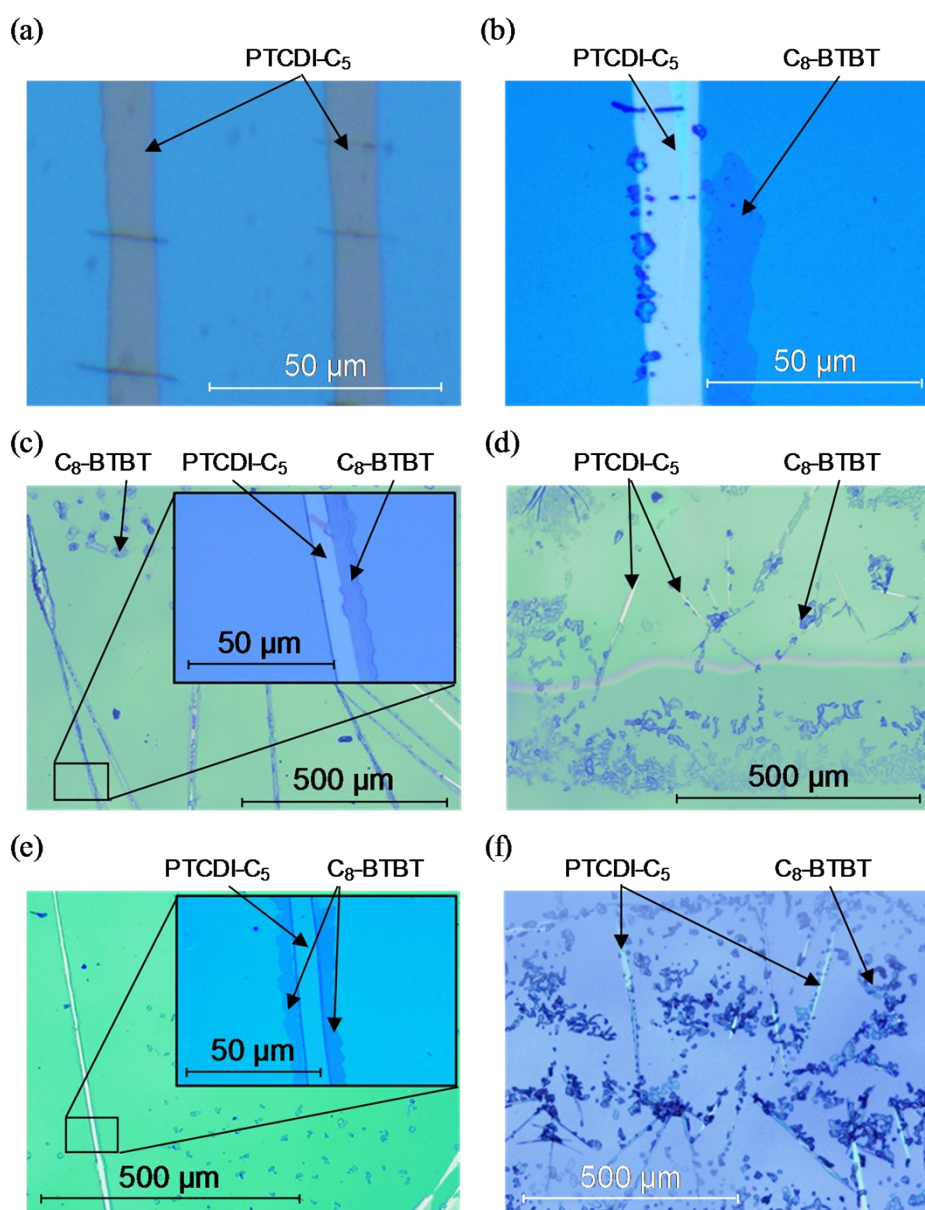


Figure S5. Optical microscope images of the crystals prepared from solutions (a) B1, (b) B5, (c) B10, (d) B20, (e) A10 and (f) C10. The insets of (c) and (e) show magnified images of one crystal.

In the main text, we have described the mechanism for crystal formation from the solution B10. Based on our observations for the crystal formation from various solution compositions, we can also infer a mechanism for the other solutions. In case of the low (0.05 or 0.25 mg/g) C_8 -BTBT concentration of the solutions B1 and B5, it is assumed that PTCDI- C_5 crystals form in a highly regular fashion and serve as a crystal template; however, the low amount of C_8 -BTBT results in either some spike-like formation along the template (Figure S5a) or small, mostly disconnected C_8 -BTBT crystals (Figure S5b), as the low amount of C_8 -BTBT gets distributed alongside the relatively high number of PTCDI- C_5 templates. When both components have a lower concentration as in the solution A10, the mechanism seems to be similar to the B10 case, as the lower amount of C_8 -BTBT can aggregate at the lower number of PTCDI- C_5 template sites. With a higher (1 mg/g) concentration of C_8 -BTBT, seemingly independent of the PTCDI- C_5 concentration, the order of the crystal formation seems to change: as the solvent evaporates, C_8 -BTBT probably becomes supersaturated before PTCDI- C_5 ; thus, the formation of C_8 -BTBT crystals begin first at the contact line, and the PTCDI- C_5 crystals form later. This shows that by changing the concentration of the components sufficiently, it is possible to switch the order in which the crystals nucleate. When PTCDI- C_5 crystallizes after C_8 -BTBT, the PTCDI- C_5 crystals cannot serve as a crystal template, and rather the previously formed C_8 -BTBT crystals disturb the formation of PTCDI- C_5 crystals in both solution B20 or C10 (Figure S5d and f). In our system, the crystal

formation of the two components are not independent of each other, and no bilayer structures have been observed, which is consistent with both C₈-BTBT and PTCDI-C₅ nucleating at the dielectric-solvent interface.

Mobility of unipolar devices based on one component solutions

For reference, the mobilities of unipolar devices made using the one component solutions have been evaluated. The mean hole mobility in the C₈-BTBT devices is $\mu_h = 3.7 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the mean electron mobility in the PTCDI-C₅ devices is $\mu_e = 5.0 \times 10^{-2} \text{ cm}^2$. The mean on-off ratio in C₈-BTBT devices is 1.3×10^3 , in PTCDI-C₅ devices it is 1.9×10^3 .

Complementary-like inverter

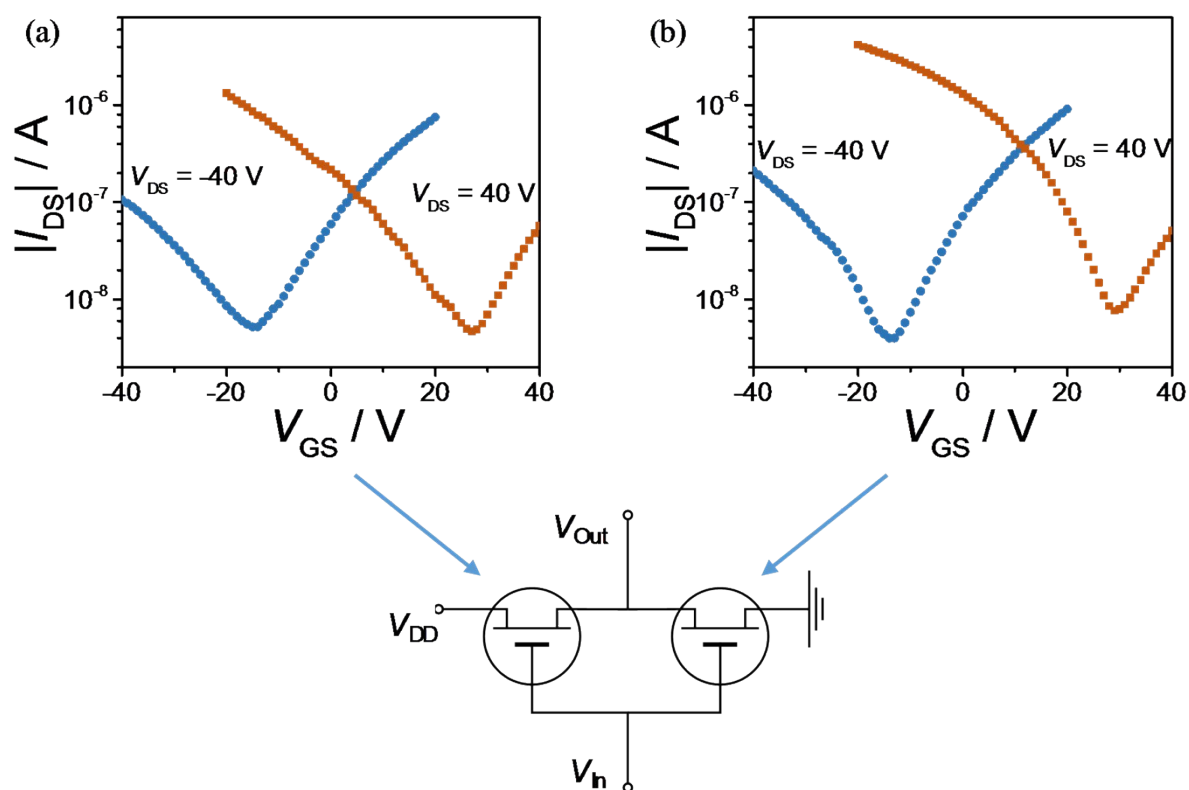


Figure S6. Transfer curves of the transistors used in the inverter as a) pull-up and b) pull-down transistor.