Supporting Information

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

Gergely Tarsoly, Sunghwi Park and Seungmoon Pyo*

Department of Chemistry, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea

*Corresponding author: pyosm@konkuk.ac.kr (+82-2-450-3397)

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).

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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-C$_5$, C$_8$-BTBT, and the laterally stacked crystals formed from the mixed solution of 0.5 mg/g C$_8$-BTBT and 0.05 mg/g PTCDI-C$_5$ (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-C$_5$ solution in o-DCB and (b) 2.5 µg/g C$_8$-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.
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) C₈-BTBT concentration of the solutions B1 and B5, it is assumed that PTCDI-C₅ crystals form in a highly regular fashion and serve as a crystal template; however, the low amount of C₈-BTBT results in either some spike-like formation along the template (Figure S5a) or small, mostly disconnected C₈-BTBT crystals (Figure S5b), as the low amount of C₈-BTBT gets distributed alongside the relatively high number of PTCDI-C₅ 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 C₈-BTBT can aggregate at the lower number of PTCDI-C₅ template sites. With a higher (1 mg/g) concentration of C₈-BTBT, seemingly independent of the PTCDI-C₅ concentration, the order of the crystal formation seems to change: as the solvent evaporates, C₈-BTBT probably becomes supersaturated before PTCDI-C₅; thus, the formation of C₈-BTBT crystals begin first at the contact line, and the PTCDI-C₅ 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-C₅ crystallizes after C₈-BTBT, the PTCDI-C₅ crystals cannot serve as a crystal template, and rather the previously formed C₈-BTBT crystals disturb the formation of PTCDI-C₅ 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 1.3×10³, in PTCDI-C₅ devices it is 1.9×10³.
Complementary-like inverter

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

V_{DS} = -40 \text{ V} \\
V_{DS} = 40 \text{ V} \\
V_{DD} \\
V_{in} \\
V_{out}