Supporting information

Facile Synthetic Route for the Morphology-Controlled Formation of Triazine-Based Covalent Organic Nanosheets (CONs)

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Materials and instruments

2,4,6-Tris(5-bromothiophene-2-yl)-1,3,5-triazine and 2,5-bis(trimethylstannyl)thieno-(3,2-b)thiophene were purchased from Luminescence Technology (Lum-Tec). Tetrakis(triphenylphosphine)palladium(0) was purchased from Alfa-Aesar. Mesitylene was obtained from Sigma-Aldrich. All reagents were stored in a glovebox charged with N_2.

Fourier transform infrared (FT-IR) spectra were obtained on a Jasco FT/IR-4100 spectrometer with a 650-4000 cm^{-1} range. UV-vis spectra were obtained on a Shimadzu UV-2600 spectrophotometer (Shimadzu, Japan) using a WI (halogen) lamp and a D2 (deuterium) lamp operating from 220 nm to 850 nm. Powder X-ray diffraction (XRD) patterns were obtained on an Empyrean Series 2 (PANalytical B.V., Netherlands) with Ni-filtered Cu-Kα radiation (λ = 1.5406 Å) with a 5-mm fixed incident beam mask and a 1.60 mm anti-scatter slit. The measurement angle ranged from 3° to 70° with time step increments of 0.0525° and 0.75 s per step. N_2 absorption-desorption isotherm curves were taken with a Belsorp-miniII (Bel Japan Inc.) using N_2 gas at 77 K. Scanning electron microscopy (SEM) images were obtained utilizing a Quanta 250 FEG (FEI Company, Hillsboro, OR). Additionally, the sample surfaces were coated with Au/Pd plasma for 60 s, and the sample images were obtained using a 15 kV electron beam. Transmission electron microscopy (TEM) images were recorded using a JEM-2100F (JEOL) with a voltage of 200 kV. The TEM samples were prepared by drop-casting suspensions on carbon films with 200 mesh copper grids (Electron Microscopy Sciences) after the samples were dispersed in DMF. The suspensions were prepared using a Sonics VCX 130 ultrasonic processor (130 W power output, 20 kHz frequency) with 3 mm homogenizer probe (Standard 630-0422, Vibra-Cell™). The sonicator was run at 20% power using 1 pulse per second with a 2.5 s pulse length for 30 min. Atomic force microscopy(AFM) images were obtained on an NX10 (Park Systems). The AFM images were measured using noncontact mode and a scan rate of 0.5 Hz. The AFM samples were prepared by drop-casting suspensions in DMF on mica discs (V1

disc 10 mm, Probes). The suspensions were prepared using the same method as those for the TEM samples.

Synthetic procedures

1. Synthesis of CON-10.

2,4,6-Tris(5-bromothiophene-2-yl)-1,3,5-triazine (M2) (0.05 g, 8.863×10^{-5} mol), 0.062 g of 2,5-bis(trimethylstannyl)thieno-(3,2-b)thiophene (M1) (1.331×10^{-4} mol), 0.0041 g of tetrakis(triphenylphosphine)palladium(0) (4 mol%) and 3 mL of mesitylene were added to a one-neck flask in a glove box. A reflux condenser was also attached to the flask in the glove box. The solution was heated at 170 °C for 3 days with stirring. The molar ratio of M1 to M2 was 3:2. After the reaction, the solution was poured into methanol, and a red-colored precipitate was collected by filtration. Then, the red powder was purified by Soxhlet extraction with methanol, ethanol, dichloromethane, tetrahydrofuran, methanol, ethanol and acetone for 4 h per step. Finally, the red compound was obtained by vacuum drying for 12 h.

2. Synthesis of CON-16.

The procedures for the synthesis of CON-16 were same as those for CON-10, but all reagents and solvents were placed in an ampule in a glove box. Then, the ampule was flame sealed under vacuum at 77 K after degassing with three freeze-pump-thaw cycles under vacuum at 77 K with liquid N_2 in a dewar and thawing by charging N_2 gas. Then, the resulting mixture was heated in an oven (170 °C) for 3 days without stirring.

3. Solution preparation.

A series of CON suspensions were prepared by dissolving 4 mg of each CON in 1 mL of chlorobenzene with 1-chloronaphtalene, THF, DMF or DMSO with ultrasonication for 30 min, followed by preparing the sample for TEM analysis as described in the materials and instruments section.

4. Film formation

Films were prepared by dropping the suspensions on silicon wafers (2 cm x 2 cm). The wafers were sequentially washed with ethanol and acetone using ultrasonication (20 min

each) and then dried with N_2. The prepared solutions were dropped via a single drop on the Si wafers. Then, the wafers were dried in air at room temperature overnight.

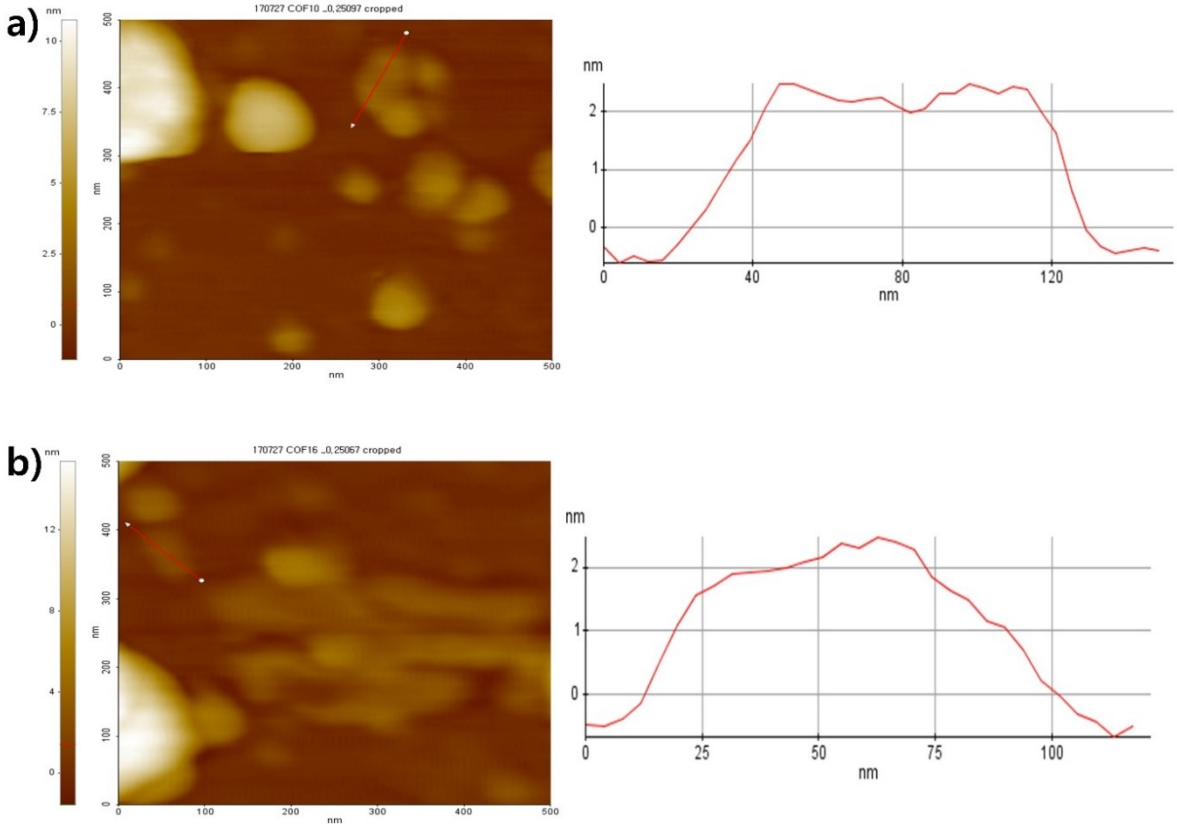

Figure S1. (a) AFM image of CON-10 on a mica surface (left) and the height profile of the primary particles of CON-10 (right); (b) AFM image of CON-16 on a mica surface (left) and the height profile of the primary particles of CON-16 (right).

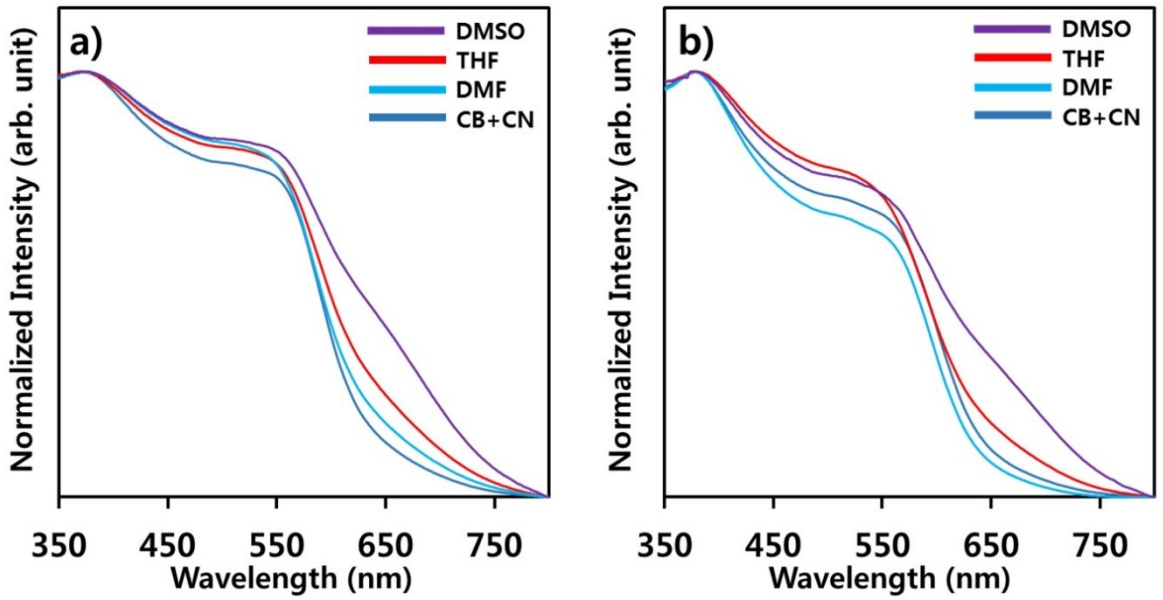

Figure S2. Normalized UV-Vis absorbance spectra of CON-10 (a) and CON-16 (b) films casted from various solvents.