Supporting Information

Organobismuth Molecular Crystals for Organic Topological Insulators

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Contents of Supporting Information:

1: General Experimental Information

All reagents were purchased from Tokyo chemical industry (TCI) and used without further purification. TGA spectra were obtained to confirm the vaporization temperature of organobismuth molecules using a thermogravimetric analyzer (TGA, SCINCO model no.1000) Also, the morphologies of the product crystals were characterized by SEM (JSM-7410F, JEOL) at National Institute for Nanomaterials Technology (NINT) in Pohang. The PL images and signals were obtained using a fluorescence microscope (Olympus microscope) and spectrometer (SpectraPro, Prineton Instruments) equipped with a filter set (Exciter BP 330 – 380 nm; beam splitter 400 nm; Emitter LP 410 nm, Semrock).

2: Syntheses

Synthesis of organobismuth (TPB, o-TTB, p-TTB) crystals using PVT method : A small amount of organobismuth precursor powder was located at the center of a heating furnace with a protection quartz tube, and a piece of SiO_2/Si substrate was attached at the end of furnace to collect resulting crystals. the quartz tube was flushed using pure argon gas (99.999 %) at a flow rate of 100 sccm for 30 min. Under argon atmosphere, the temperature was gradually increased from room temperature to 150 ^oC, 170 ^oC , 145 ^oC for **TPB**, **o-TTB** and **p-TTB**, respectively. During the crystallization, the flow rate of argon gas was maintained as 50 sccm. After 1 h, big, white and wire-shaped crystals were obtained on the SiO_2/Si substrate.

Synthesis of organobismuth (TPB, o-TTB, p-TTB) crystals in solution phase:

(1) Drop-drying method : Acetonitrile was used as a slovent to disolve **TPB**, **p-TTB** and **o-TTB** precursors respectively. The concentration was controlled to be 1 mg/mL. After 10

minute sonication, a small aliquot of the final solution was dropped on SiO_2/Si substrate and dried under ambient condition.

(2) Solvent-vapor annealing method : 10 mL of aeetonitrile was added in the 70 mL vial. To avoid contact between precursor solutions and pre-loaded acetonitrile solvent, pillar was placed inside the 70 mL vial on which precursor solution which are identical with that of drop-drying method was dropped on a SiO_2/Si substrate, respectively. After 12 h, fully dried the samples were carefully taken out of the vial.

3: Single crystal X-ray structure determination

The X-ray diffraction data for **TPB**, **p-TTB** and **o-TTB** were recorded on an ADSC Q210 CCD area detector with a synchrotron radiation (l = 0.63000 Å) at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000.[1] Absorption correction was performed by using the program PLATON.[2] The structure was solved by ShelXT[3] using Intrinsic Phasing and refined by ShelXL.[4] All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions.

Triphenyl bismuth (**TPB** C18H15Bi1, Mr = 440.28, crystal dimensions 0.36 × 0.05 × 0.01 mm3 , monoclinic, C2/C, a =27.486(6) Å, b =5.7130(11) Å, c =20.248(4) Å, β = 114.25(3)° V = 2898.9(12) Å3, T = −173 °C, Z = 8, rcalcd= 1.852 g cm−3, m = 8.89 mm−1, 5559 unique reflections out of 5435 with I>2s(I), 172 parameters, 1.44º< θ <29.85º, R1= 0.0287, wR2= 0.0999, GOF = 0.918. (Reported CCDC deposit number: 111762)

Tri-p-tolyl-bismuthine (**p-TTB**): $C_{21}H_{21}Bi_1$, Mr = 481.35, crystal dimensions 0.50 × 0.10 × 0.05 mm^3, triclinic, *P-1*, a = 6.3570(13) Å, b = 10.463(2) Å, c = 13.921(3) Å, α= 91.70(3) ° β= 91.54(3) ° γ =107.56(3) °, V = 881.8(3) $Å^3$, T = −173 °C, Z = 2, r_{calcd}= 1.813 g cm^{-3}, m = 7.31 mm^{-1}, 6081

unique reflections out of 5164 with $I>2s(I)$, 202 parameters, 2.18º<θ<29.87º, R_1= 0.0541, wR_2= 0.1363, GOF = 0.967. (Reported CCDC deposit number: 1115925)

Tri-o-tolyl-bismuthine (**o-TTB**): $C_{21}H_{20}Bi_1$, *M*r = 482.36, crystal dimensions 0.18 × 0.01 × 0.007 mm^3, triclinic, *P-1*, *a* = 5.111(1) Å, *b* = 10.198(2) Å, *c* = 16.588(3) Å, α= 91.16(3) ° β = 95.53(3) ° γ =95.27(3) °, *V* = 856.6(3) Å^3, *T* = −173 °C, *Z* = 2, r_{calcd}= 1.870 g cm^{-3}, *m* = 9.831 mm^{-1}, 4686 unique reflections out of 4473 with $I>2s(I)$, 202 parameters, 1.12º<θ<29.93º, R_1= 0.0525, wR_2= 0.1478, GOF = 0.947. (Reported CCDC deposit number: 1005303)

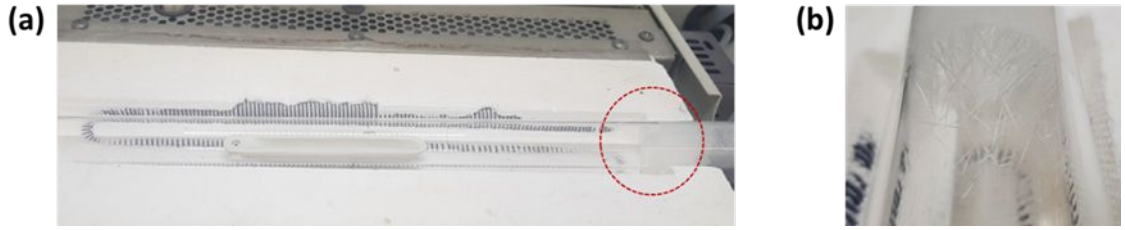


Figure S1. Photographs of obtained **TPB** crystals without SiO_2/Si substrate. (a) overall experimental setup after finishing the reaction (b) magnified view of the region where **TPB** crystals are grown in the quartz tube.

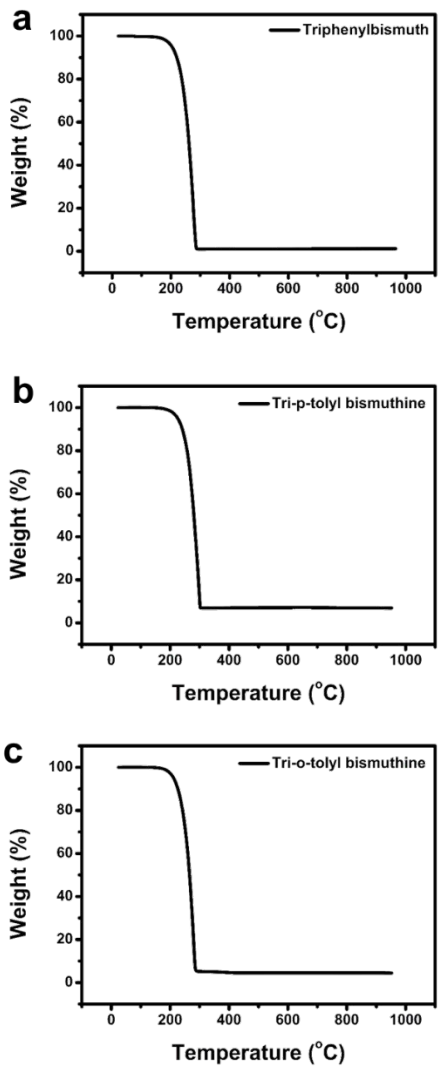


Figure S2. TGA results for **TPB** (a), **p-TTB** (b), and **o-TTB** (c) powder.

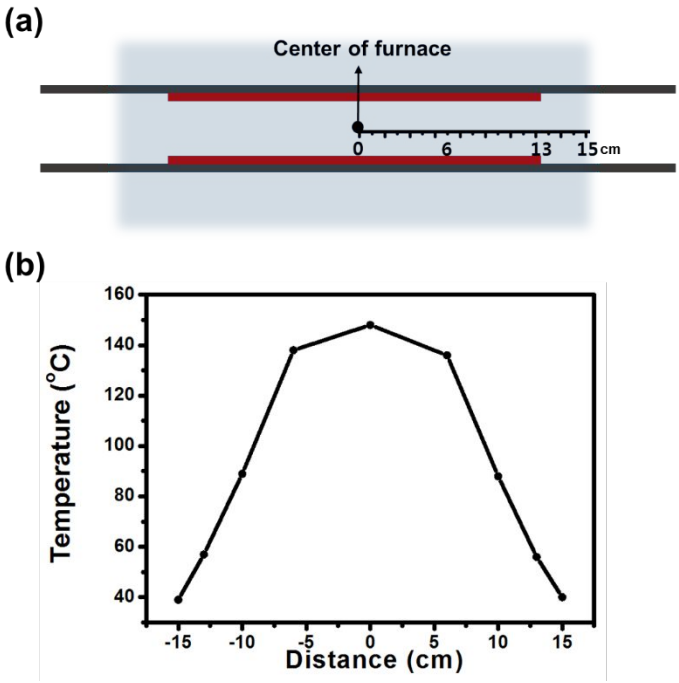
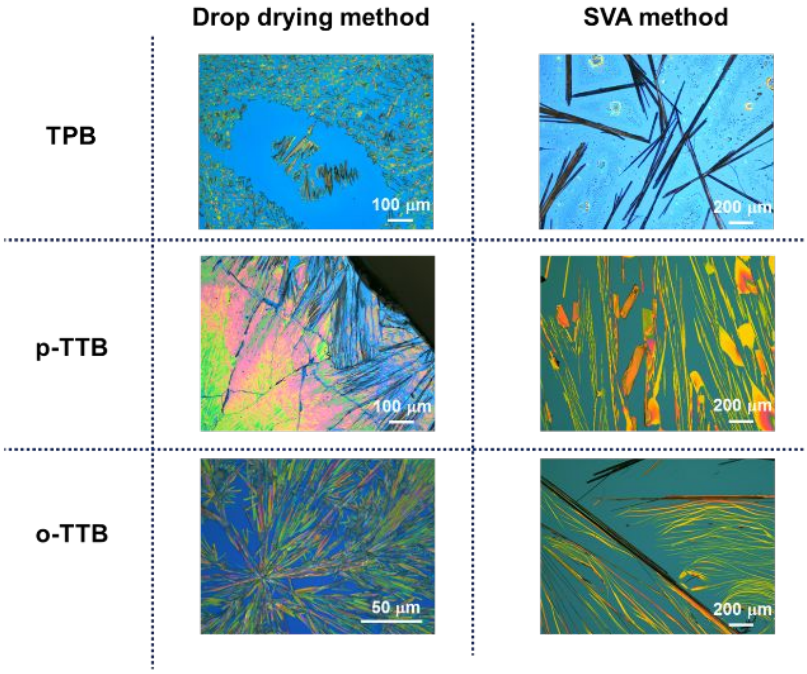


Figure S3. (a) Scheme of the furnace to indicate the distance from the center of furnace (b) measured temperature of each part of the furnace.

(a)



(b)

Unit cell parameter	a	b	c	α	β	γ
SVA **TPB** crystal	27.39(4)	5.702(9)	20.19(3)	90	114.12(4)	90
PVT **TPB** crystal	27.486(6)	5.719(11)	20.248(4)	90	114.25(3)	90
SVA **p-TTB** crystal	6.371(3)	10.473(6)	13.915(9)	91.70(2)	91.50(2)	107.54(4)
PVT **p-TTB** crystal	6.357(13)	10.463(2)	13.921(3)	91.70(3)	91.54(3)	107.56(3)
SVA **o-TTB** crystal	5.121(1)	10.178(2)	16.511(4)	91.02(2)	95.58(3)	95.32(4)
PVT **o-TTB** crystal	5.111(1)	10.198(2)	16.588(3)	91.16(3)	95.53(2)	95.27(3)

Figure S4. (a) Obtained **TPB**, **p-TTB** and **o-TTB** crystals using drop drying and solvent vapor annealing method (b) crystal structure information of **TPB**, **p-TTB** and **o-TTB** crystals grown by SVA and PVT method.

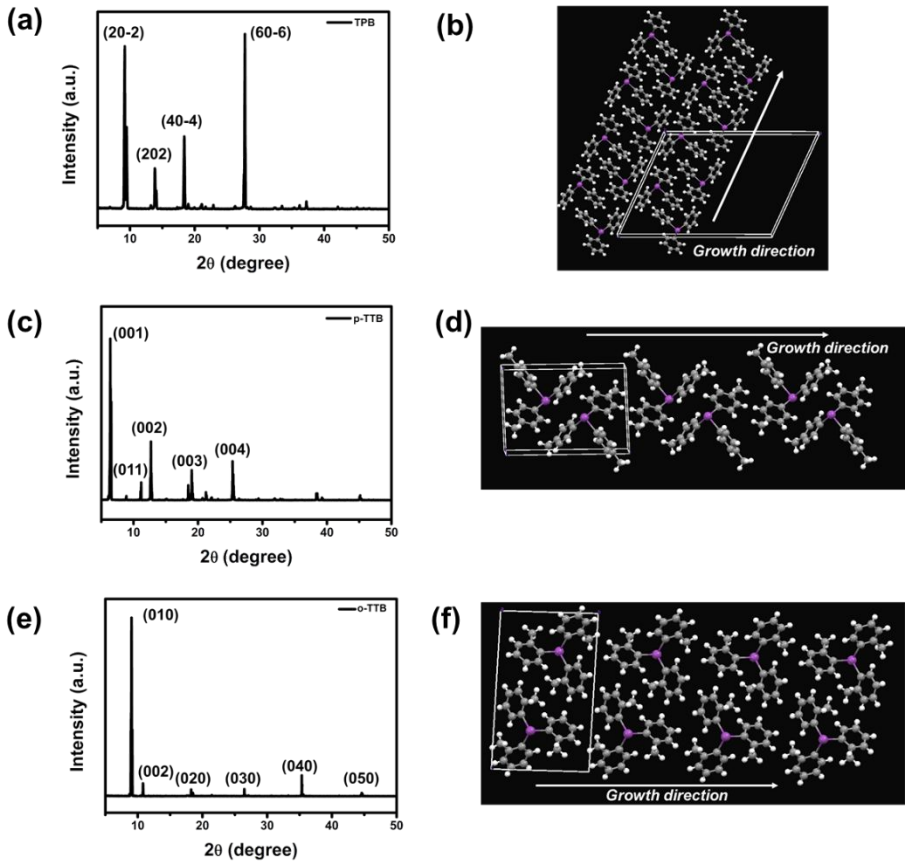


Figure S5. PXRD analysis and molecular packing structure according to the crystal growth direction (a,b) **TPB**, (c,d) **p-TTB** and (e,f) **o-TTB**.

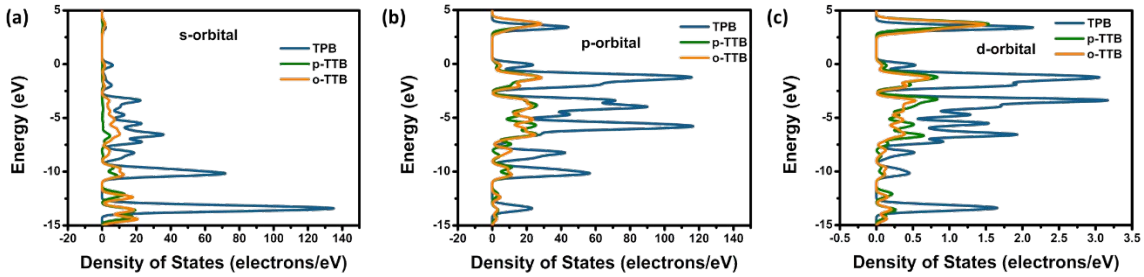


Figure S6. Calculated partial DOS of three organobismuth crystals. (a) s-orbital, (b) p-orbital, and (c) d-orbital contribution in DOS of each crystal.

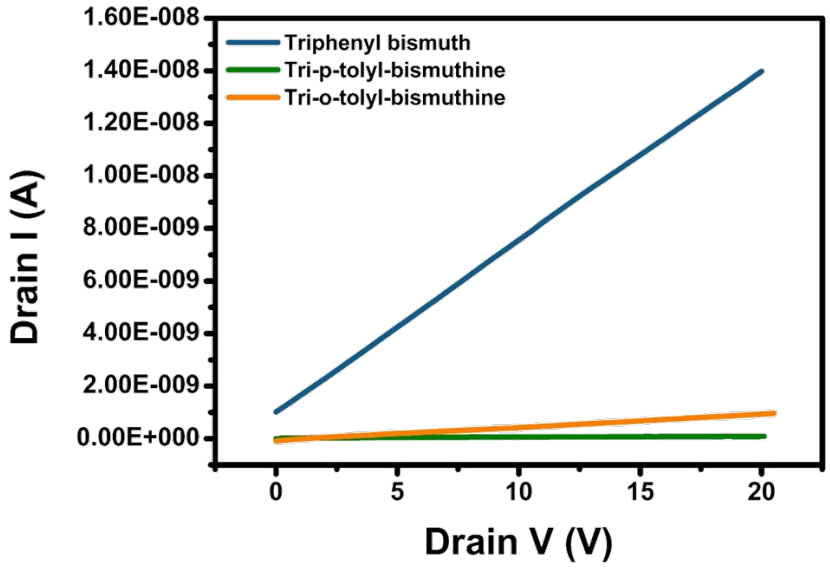


Figure S7. I-V characteristic curves of **TPB** (blue), **p-TTB** (green) and **o-TTB** (orange) crystals grown by PVT process. The devices were prepared on a SiO_2/Si substrate using silver paste as source and drain electrodes.

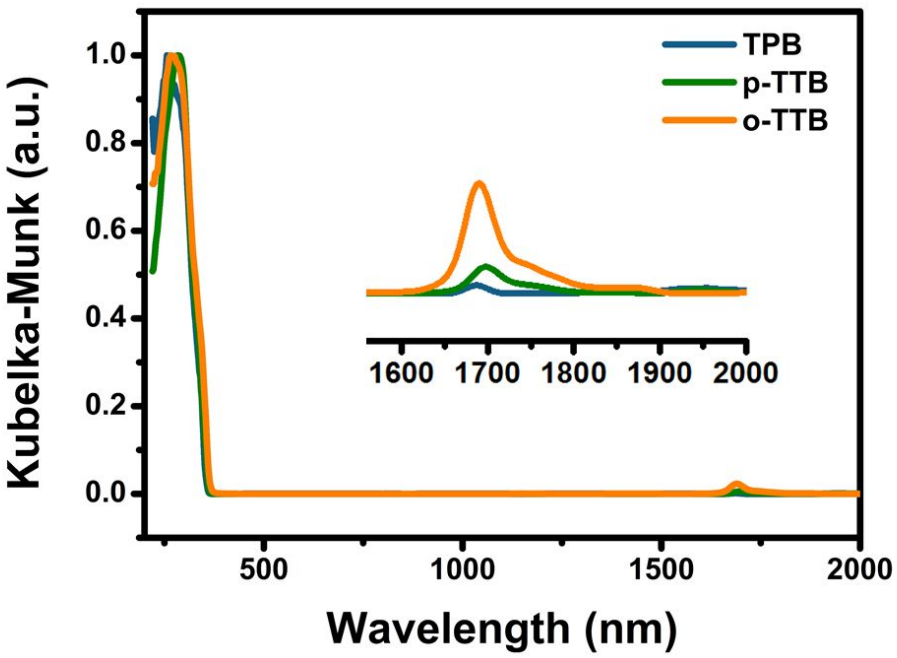


Figure S8. UV-VIS-NIR absorption spectra of **TPB**, **p-TTB** and **o-TTB** crystals.

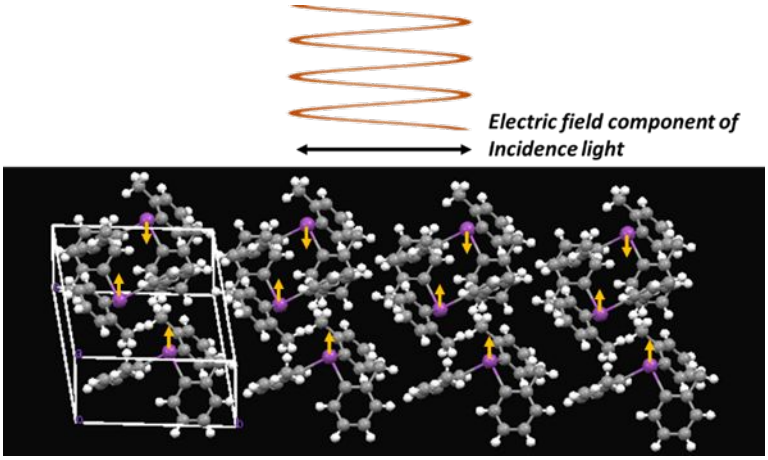


Figure S9. Interaction between the electric field of incident light and the dipole moment of (010) plane of the obtained **o-TTB** crystal

References

1) Otwinowski Z.; Minor, W. *Methods Enzymol.,* Processing of X-ray Diffraction Data Collected in Oscillation Mode **1997**, *276*, 307-326.

2) Spek, A. L. *Acta Crystallogr. D,* **2009**, *65*, 148-155.

3) Sheldrick, G. M. University of Göttingen, Germany, 1996.

4) Sheldrick, G. M. *Acta Crystallogr. A,* **2008**, *A64*, 112-122.