

Electronic supplementary information (ESI)

Molecular salt crystals with bis(head-to-tail) interionic complementary assembly for efficient organic THz generators

Deokjoong Kim,^{‡a} Won Tae Kim,^{‡b} Jin-Hong Seok,^a In Cheol Yu,^b Mojca Jazbinsek,^c
Woojin Yoon,^d Hoseop Yun,^d Dongwook Kim,^e Fabian Rotermund,^{*b} O-Pil Kwon^{*a}

^aDepartment of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea. E-mail: opilkwon@ajou.ac.kr

^bDepartment of Physics, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea. E-mail: rotermund@kaist.ac.kr

^cInstitute of Computational Physics, Zurich University of Applied Sciences (ZHAW), 8401 Winterthur, Switzerland.

^dDepartment of Chemistry & Department of Energy Systems Research, Ajou University, Suwon 443-749, Korea.

^eDepartment of Chemistry, Kyonggi University, San 94-6, Iui-dong, Yeongtong-gu, Suwonsi, Gyeonggi 443-760 (Korea)

[‡]These authors equally contributed to this work.

A. Supramolecular Directional Head-to-Tail Assembly

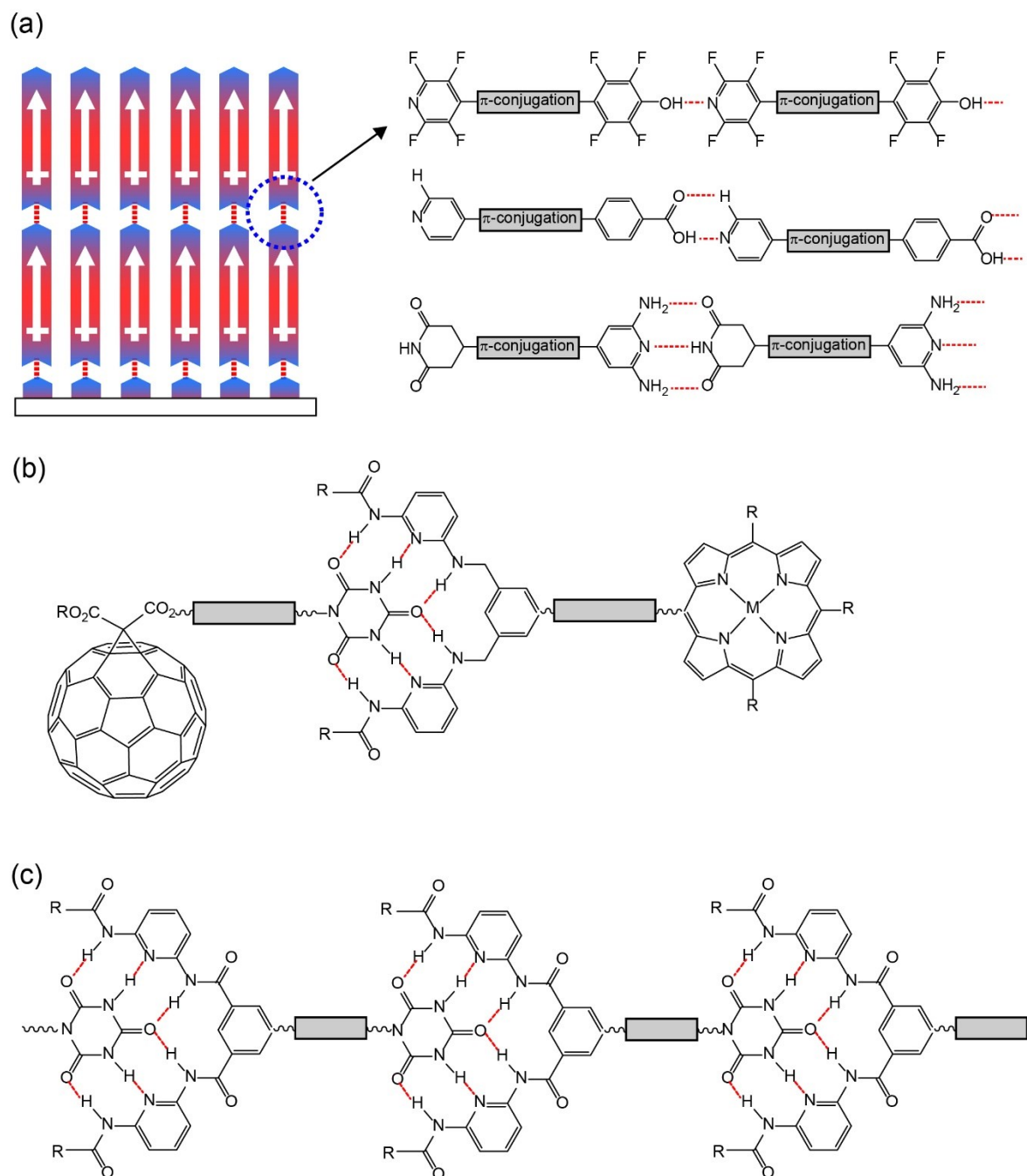


Figure S1. Schematic of head-to-tail (multiple) hydrogen-bond assembly in non-ionic materials for (a) nonlinear optics, (b) optoelectronics, and (c) synthesis of supramolecular polymers.

B. Synthesis

PMB-4TFS and PMB-3TFS were both synthesized by the condensation reaction between 4-(4-(hydroxymethyl)piperidin-1-yl)benzaldehyde and 2,3-dimethylbenzothiazol-3-ium with the corresponding trifluoromethyl)benzenesulfonate (TFS), i.e., 4-(trifluoromethyl)benzenesulfonate (4TFS) and 3-(trifluoromethyl)benzenesulfonate (3TFS), respectively.

2,3-Dimethylbenzothiazol-3-ium 4-(trifluoromethyl)benzenesulfonate: 2-Methylbenzothiazole (3.95 g, 0.03 mol) and methyl 4-(trifluoromethyl)benzenesulfonate (6.29 g, 0.03 mol) were dissolved in 1,2-dimethoxyethane (40 ml). The solution was stirred at 60 °C for 68 h and cooled to room temperature. The beige powder was obtained by filtration and dried in a vacuum oven at 65 °C overnight. Yield = 76%. ¹H NMR (600 MHz, DMSO-*d*₆, δ): 8.42 (d, 1H, *J* = 8.4 Hz, C₆H₄), 8.28 (d, 1H, *J* = 7.8 Hz, C₆H₄) 7.89 (t, 1H, *J* = 7.5 Hz, C₆H₄) 7.80 (m, 1H, C₆H₄), 7.79 (m, 2H, C₆H₄SO₃⁻), 7.69 (d, 2H, *J* = 7.8 Hz, C₆H₄SO₃⁻) 4.19 (s, 3H, NCH₃), 3.16 (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆, δ): 177.81, 152.43, 142.03, 129.65, 129.17, 128.45, 126.77, 125.40, 125.38, 124.84, 117.21, 36.66, 17.51. Elemental analysis for C₁₆H₁₄F₃NO₃S₂: Calcd. C 49.35, H 3.62, N 3.60, S 16.47; found: C 49.27, H 3.59, N 3.65, S 17.02.

2,3-Dimethylbenzothiazol-3-ium 3-(trifluoromethyl)benzenesulfonate: 2-Methylbenzothiazole (2.35 g, 0.016 mol) and methyl 3-(trifluoromethyl)benzenesulfonate (3.75 g, 0.016 mol) were dissolved in 1,2-dimethoxyethane (30 ml). The solution was stirred at 60 °C for 46 h and cooled to room temperature. The mint powder was obtained by filtration and dried in a vacuum oven at 65 °C overnight. Yield = 68%. ¹H NMR (600 MHz, DMSO-*d*₆, δ): 8.42 (d, 1H, *J* = 7.8 Hz, C₆H₄), 8.28 (d, 1H, *J* = 9 Hz, C₆H₄), 7.90 (m, 1H, C₆H₄) 7.88 (m, 1H, C₆H₄), 7.84 (s, 1H, C₆H₄SO₃⁻), 7.80 (t, 1H, *J* = 7.8 Hz, C₆H₄SO₃⁻) 7.69 (d, 1H, *J* = 7.8 Hz, C₆H₄SO₃⁻), 7.59 (t, 1H, *J* = 8.4 Hz, C₆H₄SO₃⁻) 4.19 (s, 3H, NCH₃), 3.16 (s, 3H, CH₃). ¹³C NMR (DMSO-*d*₆, δ): 177.81, 149.76, 142.07, 129.96, 129.74, 129.69, 129.19, 128.50, 125.73, 125.71, 124.89, 122.43, 122.41, 117.24, 36.66, 17.50. Elemental analysis for C₂₉H₂₉F₃N₂O₄S₂: Calcd. C 58.97, H 4.95, N 4.74, S 10.86; found: C 58.89, H 4.83, N 4.71, S 10.94.

2-(4-(4-(Hydroxymethyl)piperidin-1-yl)styryl)-3-methylbenzothiazol-3-ium

4-

(trifluoromethyl)benzenesulfonate (PMB-4TFS): 4-(4-(Hydroxymethyl)piperidin-1-yl)benzaldehyde (4.51 g, 0.02 mol) and 2,3-dimethylbenzothiazol-3-ium 4-trifluoromethylbenzenesulfonate (8.01 g, 0.02 mol) were dissolved in methanol (100 ml). Piperidine (0.41 ml, 0.004 mol) was added to the solution as a catalyst. The solution was stirred at 40 °C for 13 h and cooled to room temperature. The deep-red powder was obtained by filtration. The final crystalline powder was obtained by recrystallization in methanol and dried in a vacuum oven at 105 °C overnight. Yield = 55%. ¹H NMR (600 MHz, DMSO-*d*₆, δ): 8.30 (d, 1H, *J* = 7.2 Hz, C₆H₄), 8.10 (d, 1H, *J* = 8.4 Hz, C₆H₄), 8.06 (d, 1H, *J* = 15.6 Hz, C₂H₂), 7.89 (d, 2H, *J* = 9 Hz, C₆H₄), 7.79 (m, 1H, C₆H₄), 7.79 (m, 2H, C₇H₄F₃SO₃⁻), 7.70 (m, 1H, C₆H₄), 7.70 (m, 2H, C₇H₄F₃SO₃⁻), 7.65 (d, 1H, *J* = 16.2 Hz, C₂H₂), 7.06 (d, 2H, *J* = 9 Hz, C₆H₄), 4.50 (t, 1H, *J* = 4.8 Hz, OH), 4.24 (s, 3H, C₄H₃SN⁺), 4.10 (d, 2H, -CH₂OH), 3.28 (t, 2H, *J* = 4.8 Hz, C₅H₉N), 2.96 (t, 2H, *J* = 11.4 Hz, C₅H₉N), 1.76 (m, 2H, C₅H₉N), 1.69 (m, 1H, C₅H₉N), 1.18 (m, 2H, C₅H₉N). ¹³C NMR (DMSO-*d*₆, δ): 171.96, 154.05, 152.81, 150.21, 142.48, 133.39, 129.43, 128.04, 127.42, 126.88, 125.40, 125.37, 124.33, 122.84, 116.54, 114.04, 107.46, 66.05, 47.16, 38.73, 36.14, 28.66. Elemental analysis for C₂₉H₂₉F₃N₂O₄S₂: Calcd. C 58.97, H 4.95, F, 9.65, N 4.74, O 10.83, S 10.86; found: C 59.06, H 4.93, N 4.82, S 10.89.

2-(4-(4-(Hydroxymethyl)piperidin-1-yl)styryl)-3-methylbenzothiazol-3-ium

3-

(trifluoromethyl)benzenesulfonate (PMB-3TFS): 4-(4-(Hydroxymethyl)piperidin-1-yl)benzaldehyde (2.34 g, 0.01 mol) and 2,3-dimethylbenzothiazol-3-ium 3-trifluoromethylbenzenesulfonate (4.16 g, 0.01 mol) were dissolved in methanol (90 ml). Piperidine (0.21 ml, 0.002 mol) was added to the solution as a catalyst. The solution was stirred at 40 °C for 4 h and cooled to room temperature. The deep-red powder was obtained by filtration. The final crystalline powder was obtained by recrystallization in methanol and dried in a vacuum oven at 105 °C overnight. Yield = 28%. ¹H NMR (600 MHz, DMSO-*d*₆, δ): 8.31 (d, 1H, *J* = 8.4 Hz, C₆H₄), 8.11 (d, 1H, *J* = 8.4 Hz, C₆H₄), 8.06 (d, 1H, *J* = 15 Hz, C₂H₂), 7.90 (d, 2H, *J* = 9 Hz, C₆H₄), 7.87 (d, 1H, *J* = 7.8 Hz, C₇H₄F₃SO₃⁻), 7.84 (s, 1H, C₇H₄F₃SO₃⁻), 7.79 (t, 1H, *J* = 8.4 Hz, C₆H₄), 7.67 (m, 1H, C₂H₂) 7.67 (m, 1H, C₇H₄F₃SO₃⁻), 7.67 (m,

1H, C₆H₄), 7.58 (t, 1H, $J = 7.8$ Hz, C₇H₄F₃SO₃⁻), 7.06 (d, 2H, $J = 9$ Hz, C₆H₄), 4.52 (t, 1H, $J = 5.4$ Hz, OH), 4.23 (s, 3H, C₄H₃SN⁺), 4.10 (d, 2H, $J = 12.6$ Hz, CH₂OH), 3.28 (t, 2H, $J = 6$ Hz, C₅H₉N), 2.95 (t, 2H, $J = 11.4$ Hz, C₅H₉N), 1.76 (d, 2H, $J = 12.6$ Hz, C₅H₉N), 1.68 (m, 1H, C₅H₉N), 1.18 (m, 2H, C₅H₉N). ¹³C NMR (DMSO-*d*₆, δ): 171.96, 154.02, 150.19, 149.92, 142.49, 133.39, 130.07, 129.73, 129.42, 128.05, 127.42, 125.70, 124.36, 122.83, 122.49, 122.47, 116.55, 114.04, 107.48, 66.05, 47.16, 38.77, 36.13, 28.68. Elemental analysis for C₂₉H₂₉F₃N₂O₄S₂: Calcd. C 58.97, H 4.95, F, 9.65, N 4.74, O 10.83, S 10.86; found: C 58.89, H 4.83, N 4.71, S 10.94.

C. Electrostatic Potential Surfaces

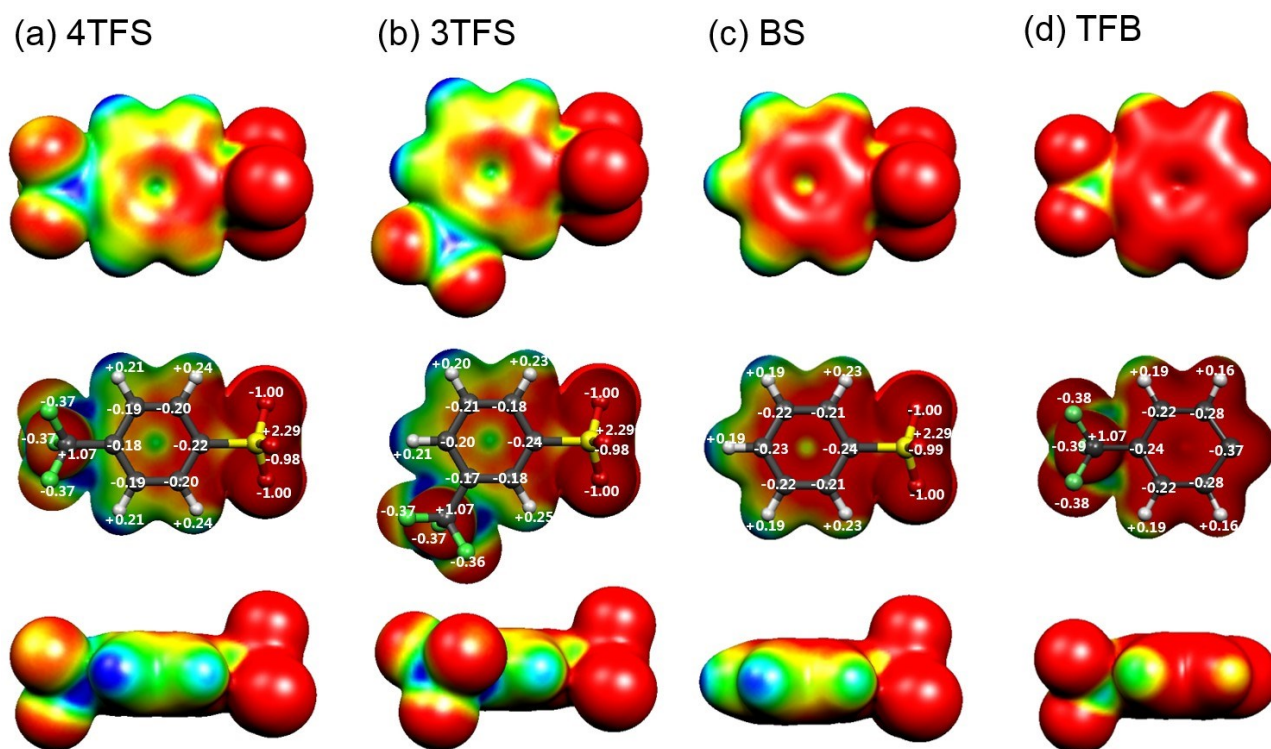


Figure S2. Electrostatic potential surfaces of optimized structure (OPT) of (a) 4TFS, (b) 3TFS, (c) benzenesulfonate (BS), and (trifluoromethyl)benzene (TFB) at the B3LYP/6-311+G(d,p) level. The numbers are the calculated atomic charges.

D. Crystal Structure and Interionic Interactions of PMB-4TFS Crystals

For X-ray crystal structure analysis, PMB-4TFS single crystals were grown in methanolic solution by the slow evaporation method. $C_{22}H_{25}N_2OS \cdot C_7H_4F_3O_3S$, $M_r = 590.66$, monoclinic, space group Cc , $a = 20.576(2) \text{ \AA}$, $b = 10.261(1) \text{ \AA}$, $c = 13.0032(13) \text{ \AA}$, $\beta = 100.020(3)^\circ$, $V = 2703.4(4) \text{ \AA}^3$, $Z = 4$, $T = 150(1) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 0.257 \text{ mm}^{-1}$. Of the 11418 reflections collected in the θ range of $3.2\text{--}26.0^\circ$ using ω scans on a Rigaku R-axis Rapid S diffractometer, 4700 were unique reflections ($R_{\text{int}} = 0.0521$). The structure was solved and refined against F^2 using SHELXL-2017/1, [G. M. Sheldrick, Acta Cryst. 2015, 3, C71] 361 variables, $wR_2 = 0.1700$, $R_1 = 0.0537$ ($F_o^2 > 2\sigma(F_o^2)$), GOF = 1.112, and a max/min residual electron density of $0.751/-0.604 \text{ e\AA}^{-3}$ (CCDC-1939793).

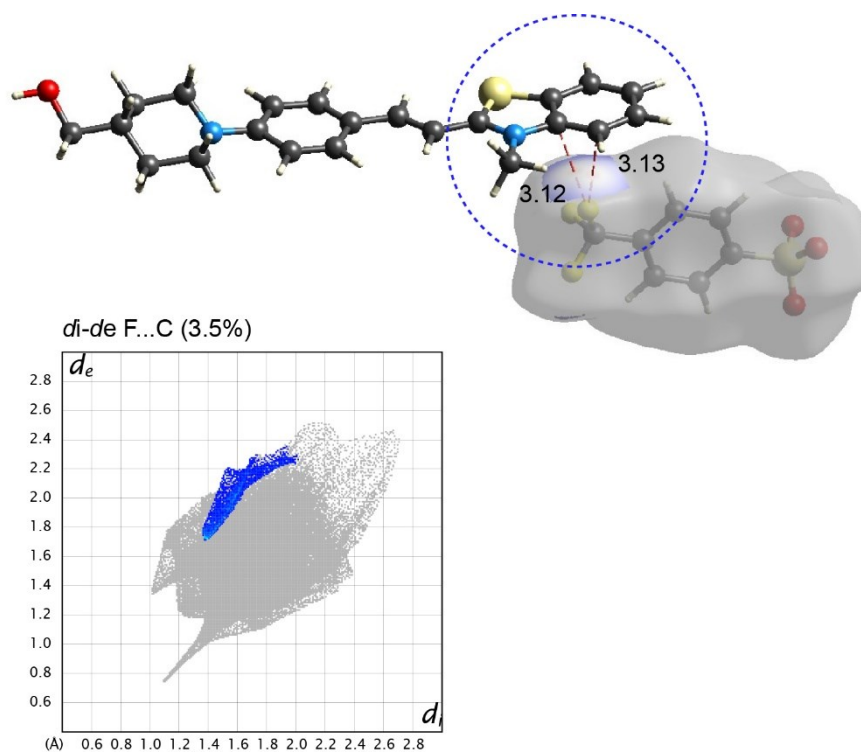


Figure S3. Halogen-bond-like feature of $-\text{CF}_3$ group on 4TFS anions: Hirshfeld surface of anion with $\text{F}\cdots\text{C}$ atom contacts between anions and cations. The red dotted lines represent $\text{F}\cdots\text{C}$ halogen-bonds with a distance of less than 3.17 \AA .

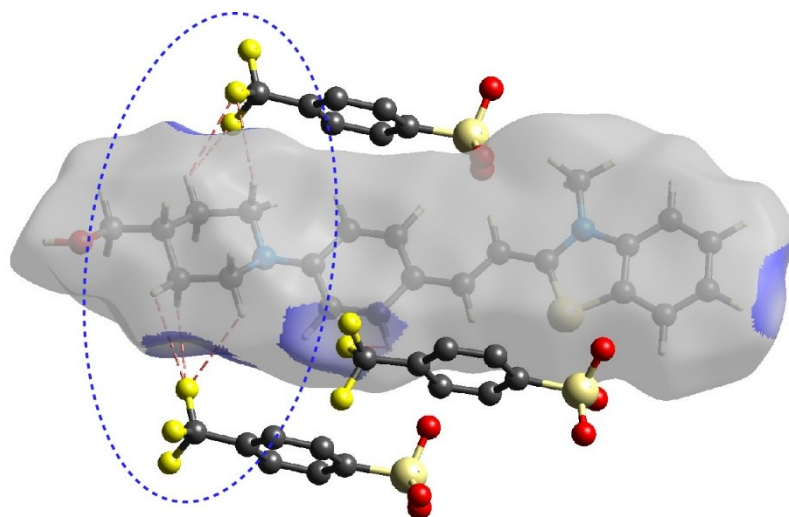


Figure S4. Hirshfeld surface of the PMB cation with H...F atom contacts between cation and anions. The red dotted lines represent H...F hydrogen bonds between H atoms on piperidinylium electron donor part of PMB cation and F atoms on 4TFS anions with a distance of less than 3.0 Å. Hydrogen atoms on anions are omitted for clarity.

E. THz Spectroscopy

The absorbance of the PMB-4TFS crystals was measured using THz time-domain spectroscopy in the frequency range of 0.5–7.5 THz. The broadband THz pulses were generated and detected in nonlinear crystals (generator: 0.3-mm-thick HMQ-TMS, detector: 0.3-mm-thick GaP). Femtosecond pulses with a pulse duration of 150 fs at 1300 nm at repetition rate of 1 kHz, generated from an optical parametric amplifier system (TOPAS Prime-F, Spectra Physics), were used for THz wave generation. Near-infrared pulses from a 1 kHz Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra Physics) operating at 800 nm with a pulse duration of 100 fs were employed for THz detection through electro-optic sampling (EOS). The test crystals were attached to a sample mount with an aperture size of 2 mm. The data in the gray-shadowed region near 5.0–5.5 THz in Figure S5 are not reliable because the field strength of the THz waves was very low due to the strong reabsorption of the THz generator in our THz spectroscopy system. All measurements were performed under low humidity conditions (<4%) to suppress the absorption of water vapor.

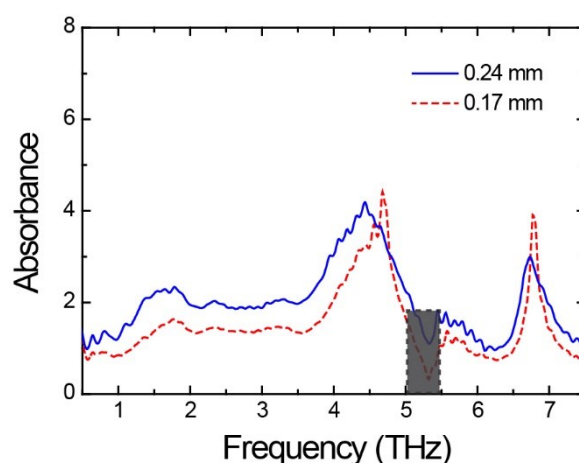


Figure S5. Absorbance of 0.17- and 0.24-mm-thick PMB-4TFS crystals in THz frequency range. THz waves incident to the (100) plane of as-grown PMB-4TFS crystals are normal. The polarization direction of the THz waves is parallel to the projection of the polar axis of PMB-4TFS to the (100) plane.