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SUPPLEMENTARY INFORMATION

A plastically bendable and polar organic crystal

Sotaro Kusumoto[a], Akira Sugimoto[b], Daisuke Kosumi[c], Yang Kim[b], Yoshihiro Sekine[b,d], Masaaki Nakamura[b], Shinya Hayami[b,e*]

[a]*Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan.*

[b]*Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan.*

[c] *Department of Physics, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan.*

[d]*Priority Organization for Innovation and Excellence, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan.*

[e]*Institute of Industrial Nanomaterials (IINa), Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan.*

Corresponding author: S. Hayami
E-mail: hayami@kumamoto-u.ac.jp

Chemicals

All reagents and solvents were purchased from Tokyo Kasei Co. and Wako Pure Chemical Industries and used without further purification. 2,3,4-Trichloroacetophenone was purchased Tokyo Kasei Co.

Preparetion of single crystal

2,3,4-Trichloroacetophenone was dissolved in the mixed solvent of methanol/chloroform and evaporated slowly at ambient temperature to yield colorless crystals with macroscopic size (length ~2 cm). In other organic solvents such as THF, dichloromethane, acetone and methanol, the macroscopic size of crystal which are suitable for bending were not obtained.

Physical measurements

Single-crystal X-ray diffraction data for **1** was collected with a Rigaku XtaLAB mini II diffractometer. The structures were solved by direct methods (SHELXT[SI1]) and refined by full-matrix least-squares refinement using the SHELXL[SI2] program. Hydrogen atoms were refined geometrically using a riding model. Crystallographic data is summarised in Table S1. Powder X-ray diffraction data (PXRD) were collected on a RIGAKU MiniFlex II ultra (30 kV/15 mA) X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 2°−30° with a step width of 1.0°. Dielectric constants in the frequency range 1–100000 Hz were measured using an inductance capacitance and resistance (LCR) meter on a Wayne Kerr 6440B LCR meter. The determination of polarization was performed on an aixACT TF analyzer 1000. Differential scanning calorimetry (DSC) thermal analysis was performed on a SHIMADZU DSC50 instrument. SHG spectra were recorded employing a time-correlated single photon counting system (SPC130 EM, Becker&Hickle). Samples were excited by femtosecond near-IR pulses from the output of OPA (TOPAS-C, Spectra-Physics) seeded by Ti:Sapphire regenerative amplifier (Spitfire-pro, Spectra-Physics). The signals were detected by a single photo avalanche diode (PD-050-CTD) through a spectrometer (SP275, Acton Research).

Supplementary data

Table S1. Crystallographic data of **1**.

Compound	**1**
formula	$C_8H_5Cl_3O$
formula weight	223.49
crystal system	Monoclinic
space group	*P*c
a / Å	3.6879(8)
b / Å	11.923(2)
c / Å	9.1300(18)
α / º	90
β / º	97.392(19)
γ / º	90
V / Å^3	398.117
Z	2
T / K	150
R_1 [I > 2σ(I)]	0.0414
wR_2 [I > 2σ(I)]	0.1016
R_1 (all data)	0.0427
wR_2 (all data)	0.1022
G.O.F.	0.9422
CCDC	2084160

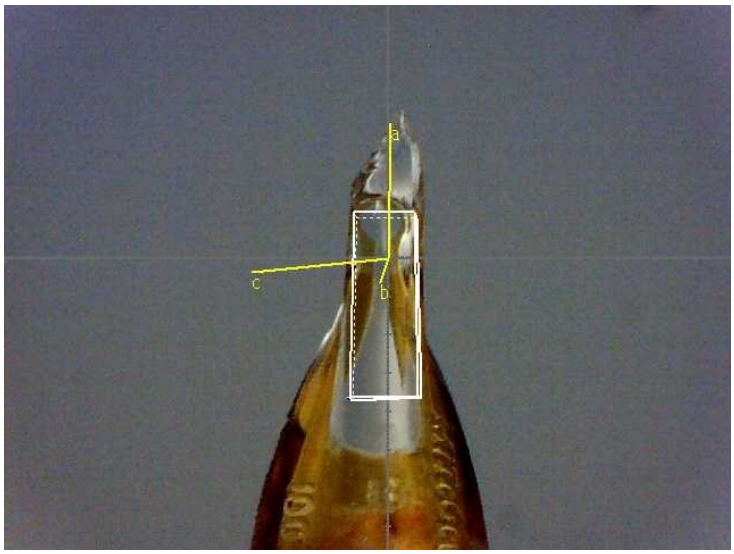

Fig. S1 Face indexing of **1**.

Fig. S2 Crystal **1** was brittle when the stress was applied to the (001) face.

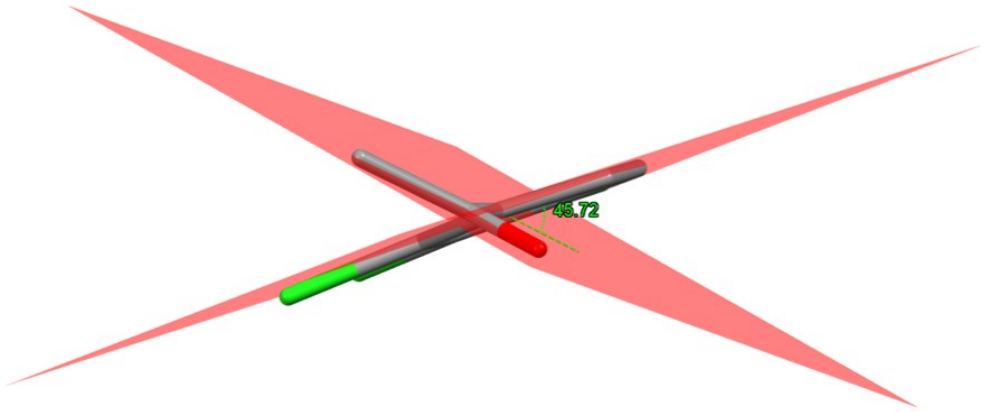

Fig. S3 The acetyl group is tilted to the benzene ring by 45.72°.

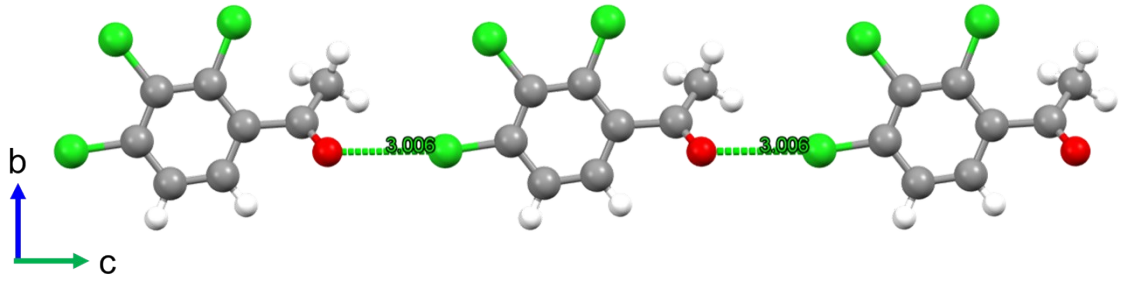

Fig. S4 The molecules are arranged in a head-to-tail fashion along with *c*-axis directed by Cl···O (*d*= 3.006 Å) and C-H···Cl (*d*= 2.911 Å) interactions.

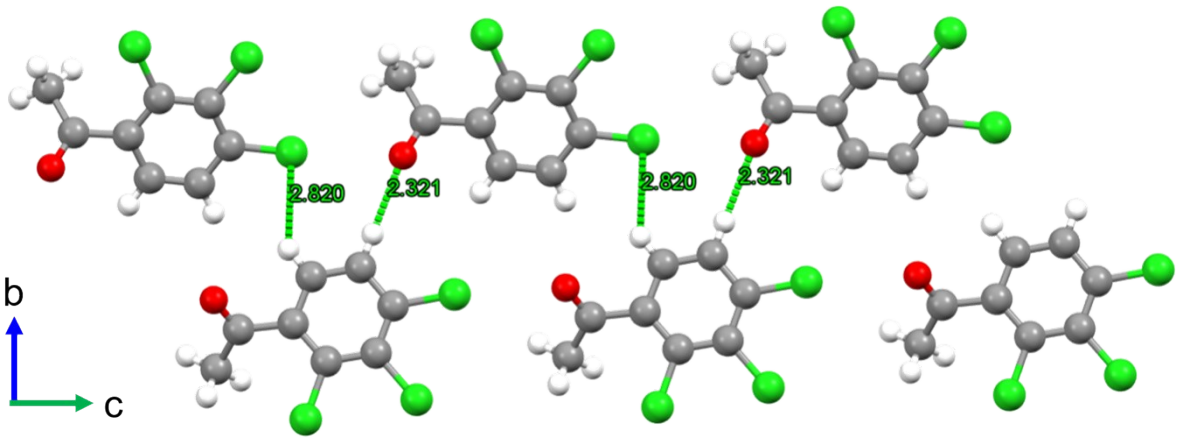

Fig. S5 One-dimensional (1D) molecules are interacted with neighbouring 1D chains by C–H···O (*d* = 2.321 Å) and C–H···Cl (*d* = 2.820 Å) interactions, forming dimeric 1D chain.

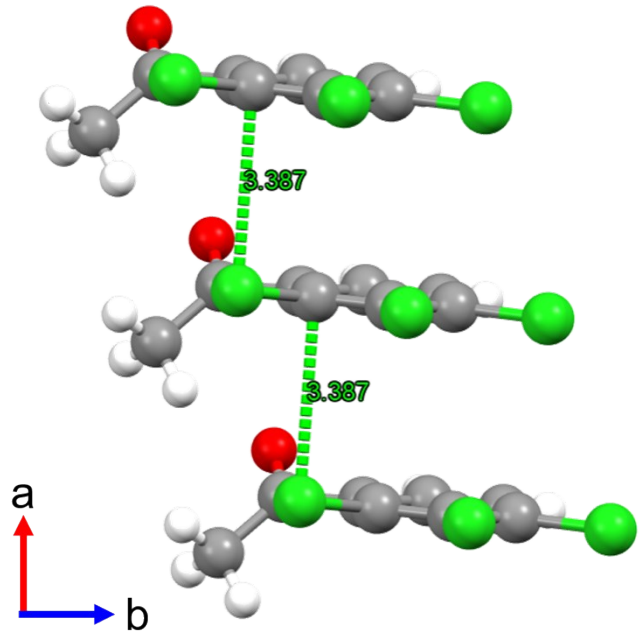

Fig. S6 (a) The dimeric 1D chain is arranged along *a*-axis with C···Cl contacts (*d*= 3.387 Å).

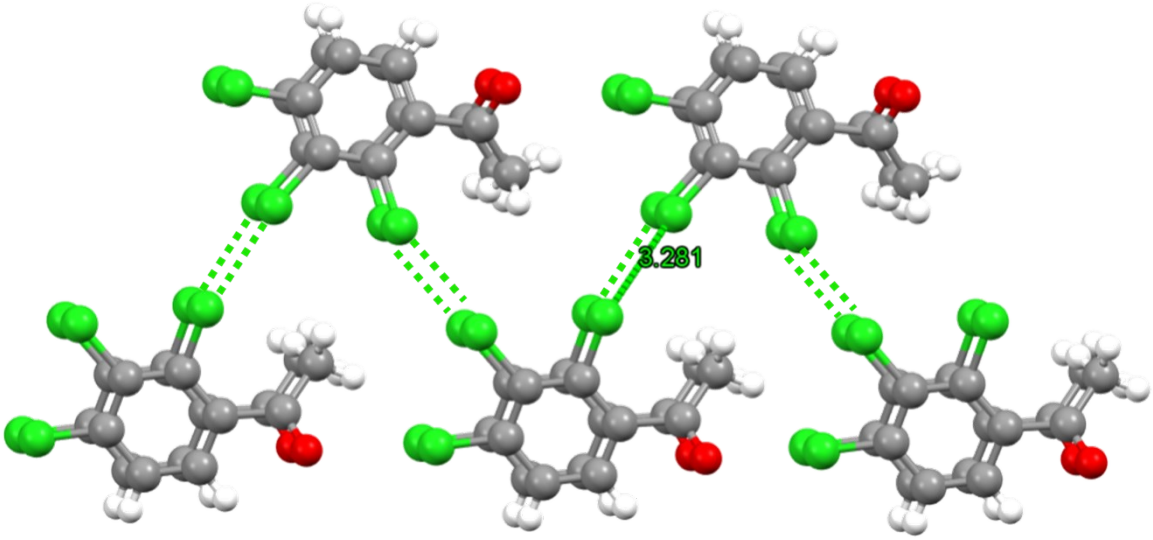

Fig. S7 Cl···Cl (*d* =3.281 Å) interactions between 2D layers.

Energy framework calculation

Energy frameworks were constructed from pairwise interamolecular interaction energy calculations (at crystal geometry) using the CE-B3LYP/ 6-31g (d, p) molecular wave functions in CrystalExplorer17.5 (Reference 6b in the main manuscript). Total interaction energy contains electrostatic, polarization, dispersion and exchange-repulsion terms. [Reference number 6a in the main manuscript].

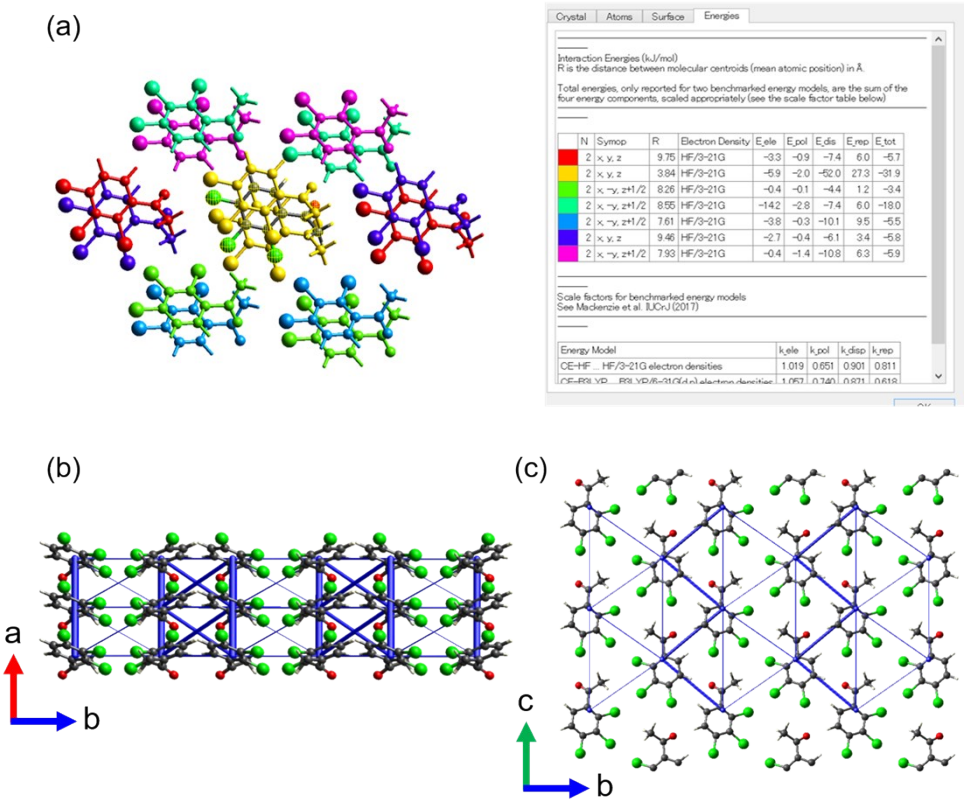

Fig. S8 (a) Output of total interaction energy decomposition. (b) Energy frameworks of **1** in total interaction strengths viewed down the *a*-axis and (c) viewed down the *b*-axis.

Dielectric property

Dielectric constants of the straight and bent crystal of **1** were measured by an inductance capacitance and resistance (LCR) meter on a Wayne Kerr 6440B LCR meter in the frequency range of 10^2-10^6 Hz.
The dielectric constants were premeditated using the relation;

$$\varepsilon_r = Cd/\varepsilon_0 A$$

where C is the capacitance (F), d is the thickness of the crystal used (m), ε_0 is the vacuum dielectric constant (8.854 $\times 10^{-12}$ Fm^{-1}) and A is the area of the crystal used (m^2).

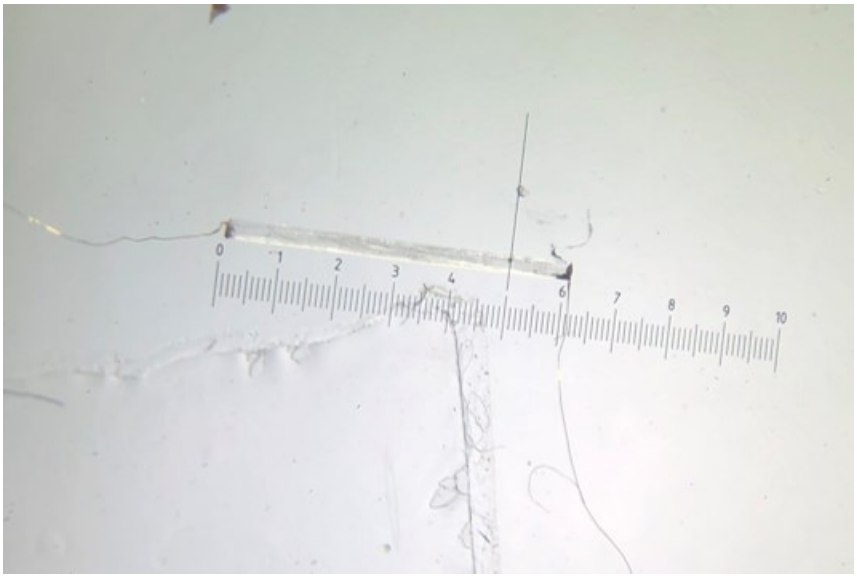

Fig. S9 Straight crystal (6 mm length x 0.1 mm thickness x 0.3 mm width) for measurement of dielectric constants by Wayne Kerr 6440B LCR meter. Both ends of a single crystal were attached to gold wires.

Fig. S10 Plastically bent crystal (6 mm length x 0.1 mm thickness x 0.3 mm width) for measurement of

dielectric constants by Wayne Kerr 6440B LCR meter. Both ends of a single crystal were attached to gold wires.

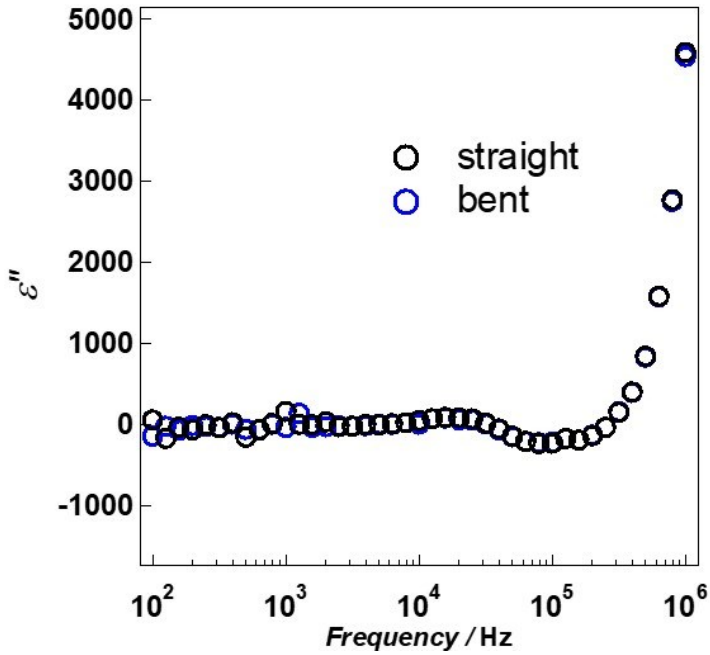

Fig. S11 Frequency dependent dielectric constant (ε") measured by using straight (black circle) and plastically bent (blue circle) crystals.

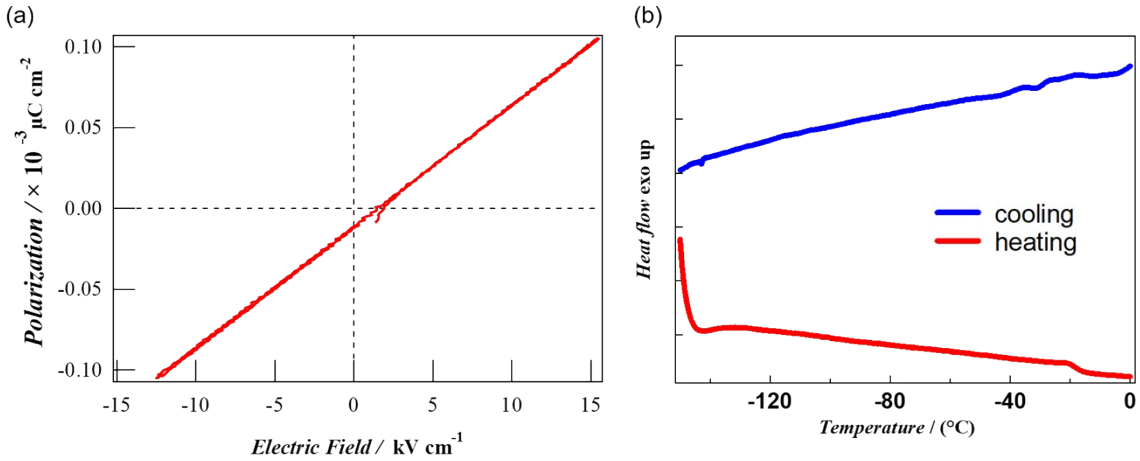

Fig. S12 (a) *P*–*E* curve of a single crystal **1** at 50 Hz at 223 K. (b) DSC curves of a single crystal **1** at 5 K/min in the temperature range from 140 K to 273 K.

SHG measurements

SHG spectra were recorded by employing a time-correlated single photon counting system (SPC130 EM, Becker&Hickle). Samples were excited by femtosecond near-IR pulses from the output of OPA (TOPAS-C, Spectra-Physics) which was seeded by Ti:Sapphire regenerative amplifier (Spitfire-pro, Spectra-Physics). The signals were detected by a single photo avalanche diode (PD-050-CTD) through a spectrometer (SP275, Acton Research).

Sampling was performed by fixing both sides of bent crystal on a glass plate with grease to prevent them from dropping, then irradiated laser (λ_{ex}= 1064 nm) at straight and bent position. The radius of the laser is 50 μm.

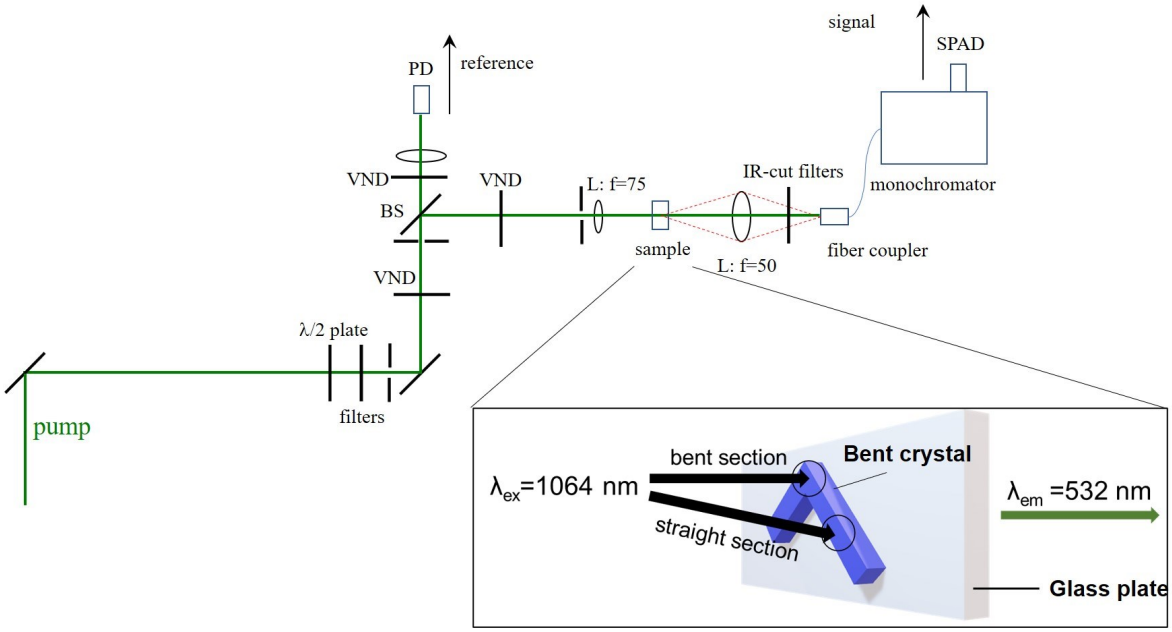

Fig. S13 Schematic diagram of equipment configuration and sampling in the SHG measurement.

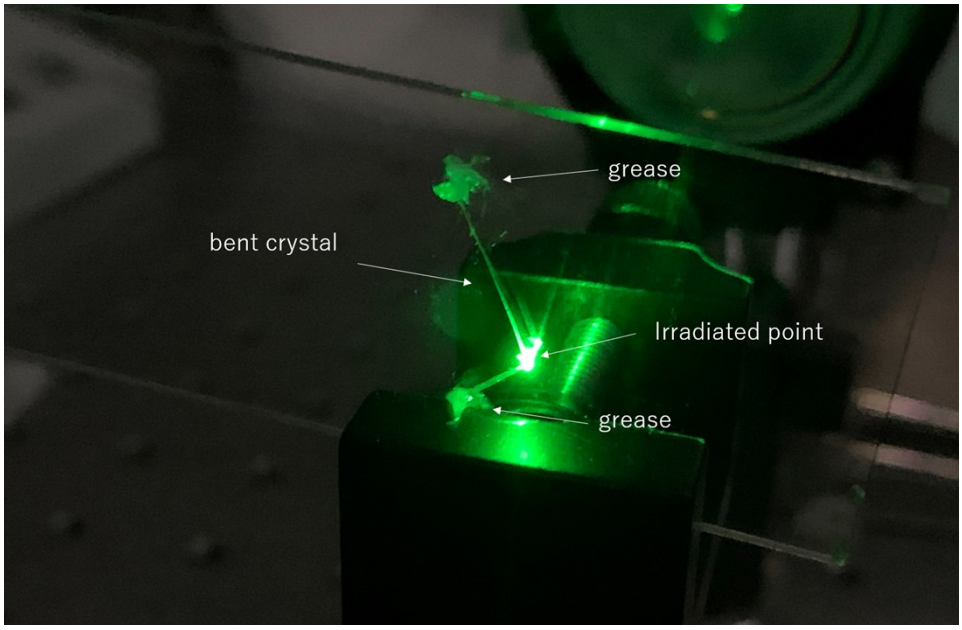

Fig. S14 The femtosecond near-IR pulses (λ_{em}= 1064 nm) were applied to the bent position of **1** in the SHG measurement. The focus point is shown with a green light.

References

[1] G. M. Sheldrick, SHELXT – Integrated Space-Group and Crystal-Structure Determination, Acta Crystallogr., Sect. A: Found. Adv., **2015**, *71*, 3–8.
[2] G. M. Sheldrick, Crystal Structure Refinement with SHELXL. Acta Crystallogr Sect. C **2015**, *71*, 3–8.