Supplementary Information

A photoluminescent second-order nonlinear optical molecular crystal with cold crystallization

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Experimental

Synthesis of (*S,S*), (*R,R*) and *Rac*-BCYD. (1*S*,2*S*)-(+)-1,2-Cyclohexanediamine (1.14 g, 10.0 mmol), 5-bromosalicylaldehyde (4.02 g, 20.0 mmol), and 60 mL of ethanol were added to a 100 mL round-bottom flask. The mixture was stirred at 80 °C for 1 hour and then cooled to room temperature to form yellow crystalline precipitates. The product was collected by filtration, washed three times with 10 mL of ethanol each time. Subsequently, the product was dried at 80 °C in an oven until a constant weight was reached before weighing. As a result, 4.52 g of yellow solid was obtained. Subsequently, the compound was dissolved in ethyl acetate to form a clear solution. The solution was slowly evaporated at room temperature to obtain yellow transparent blocky crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.33 (dd, J = 8.8, 2.5 Hz, 2H), 7.26 (d, J = 1.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.39 – 3.23 (m, 2H), 1.99 – 1.83 (m, 4H), 1.60 – 1.46 (m, 4H). By replacing (1*S*,2*S*)-(+)-1,2-cyclohexanediamine with the corresponding amine, the crystals of (*R*,*R*) and *Rac*-BCYD were grown in the same way.

Single-crystal X-ray crystallography (XRD). Single-crystal X-ray diffraction at room temperature was carried out on a Rigaku Oxford diffractometer with Cu-Kα radiation (λ = 1.54184 Å). The SHELX program package on the Olex2 program solves the structural data and structural refinement problems. Table S1 summarizes the data collection and structural improvement of the crystal. (Central Development Council number: 2389142 and 2411527-2411528).

CD Measurements: Circular dichroism (CD) spectra are obtained by JASCO J-1700. The CD measurements are performed on the (*S*,*S*), (*R*,*R*) and *Rac*-BCYD polycrystalline powders dispersed in the KBr pellets. The samples used for testing were obtained by mixing and grinding KBr and the sample to be tested at a ratio of 98 mg: 2 mg. After that, the ground powder was pressed into tablets.

Powder X-ray diffraction (PXRD) and Infrared spectrometer (IR) measurements. PXRD data were measured using a Rigaku D/MAX 2000 PC X-ray diffraction system with Cu Kα radiation in the 2θ range of 5°–50° with a step size of 0.02°. The PXRD pattern of Cr1 powder of (*S*,*S*)-BCYD was measured at 25 °C. Then, the powder sample was heated to 220 °C to melt and then cooled to room temperature. The sample was transformed into a glassy state. The PXRD pattern of the glassy state of (*S*,*S*)-BCYD

was measured at 25 °C. Next, the glassy state sample was heated to 100 °C. The sample was transformed into Cr2. It was ground into powder and the PXRD pattern of Cr2 powder of (*S*,*S*)-BCYD was measured. A Bruker INVENIO-R infrared spectrometer has been used to record the IR absorption by using the KBr tablet method.

Second Harmonic Generation (SHG). SHG measurements were performed on an Ins1210058 optical testing stage (INSTEC Instruments) with a Vibrant 355 II laser generator (OPOTEK). The laser beam was excited by pulsed Nd: YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, and 10 Hz repetition rate. The intensities of the SHG signals for samples have been compared with the KDP reference. Powder second-harmonic generation measurements were carried out by the Kurtz-Perry method with a Q-switched Nd: YAG laser (Quantel, Ultra) with a wavelength of 1064 nm as the excitation source. SHG measurement was conducted on a commercial confocal scanning microscope (Metatest, ScanPro Advance). A 1064 nm picosecond laser (Rainbow 1064 OEM, NPI lasers) was used as excitation source. A 50X objective (N.A = 0.6, Nikon TU Plan ELWD) was selected to focus the laser onto the sample and collect the reflected SHG signal. The SHG signal was detected by a spectro-graph (SpectraPro HRS-300, Teledyne Princeton Instruments). Polarization-dependent SHG measurement was realized by rotating a 1064 nm half-wave plate in the excitation path.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyses (TGA) Measurements. DSC measurements of (*S*,*S*), (*R*,*R*) and *Rac*-BCYD were performed on a PerkinElmer DSC 6000 under nitrogen atmosphere in aluminum crucibles with a heating or cooling rate of 20 K/min. Furthermore, more heating/cooling cycles were performed at a rate of 20 K/min, and heating/cooling cycles were also conducted at different heating rates ranging from 10 to 30 K/min under a constant cooling rate (20 K/min). TGA curves were carried out on a PerkinElmer TGA 8000 instrument by heating crystalline samples at a rate of 40 K/min under a nitrogen atmosphere.

Ultraviolet-visible (UV-vis) absorbance spectra and Photoluminescence (PL) emission spectra. UV-vis absorbance spectra of (*S*,*S*), (*R*,*R*) and *Rac*-BCYD were measured on polycrystalline powder samples by using Shimadzu (Tokyo, Japan) UV-3600 Plus spectrophotometer equipped with ISR-603 integrating sphere at room temperature, respectively. $BaSO_4$ was used as a 100% reflectance reference. The steady-state and transient time-resolved PL spectra of (*S*,*S*) -BCYD were measured on Horiba Fluorolog-QM modular research-grade spectrofluorometer. The excitation light source for steady-state is Xeon lamp. The excitation wavelength is 380 nm. The delta diode with a peak wavelength of 518 nm was used for the time-resolved PL measurement. The integrating sphere was used for photoluminescence quantum yield measurement. The ColorCalculator software (version 7.75) was used for calculating the CIE chromaticity coordinates, CRI, CCT values based on the emission spectra. PL spectra of (*R*,*R*) and *Rac*-BCYD were obtained at room temperature on an FLS1000 Photoluminescence Spectrometer (Edinburgh Instruments).

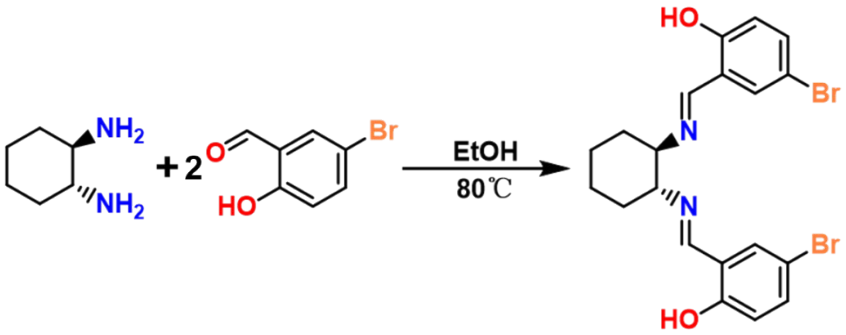


Figure S1. Synthesis routes of (*S*,*S*)-BCYD.

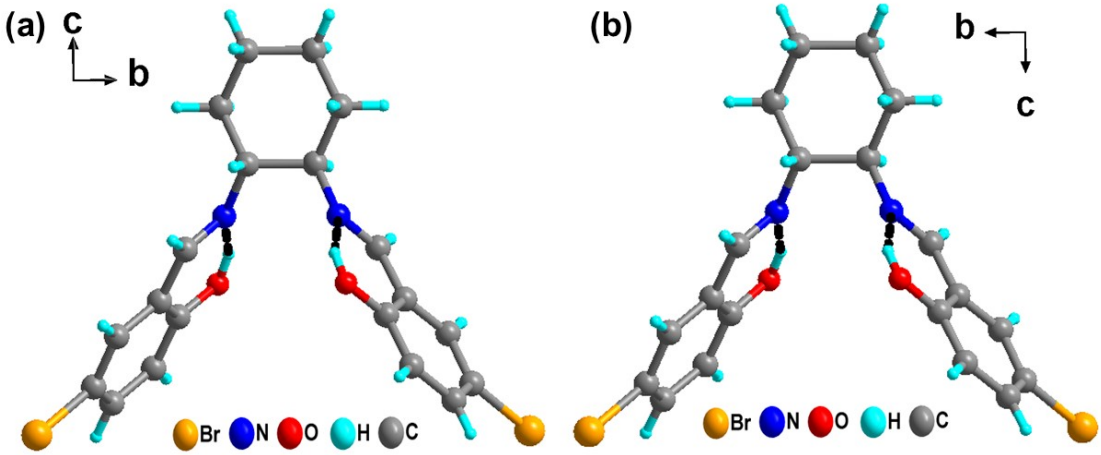


Figure S2. The asymmetric unit of the crystal structure of (*R*,*R*)-BCYD (a) and *Rac*-BCYD (b) at 298 K.

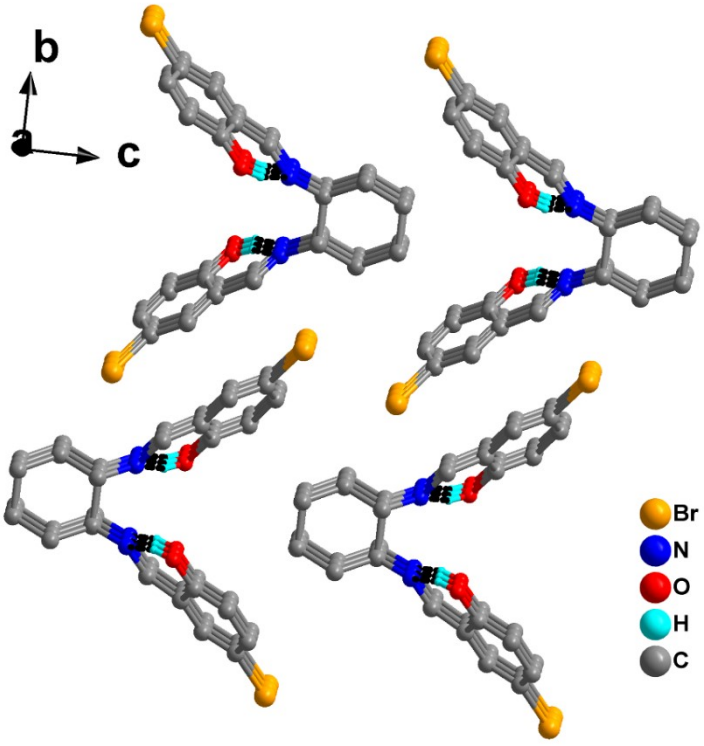


Figure S3. Packing diagram of (*S*,*S*)-BCYD along the *a*-axis at 298 K.

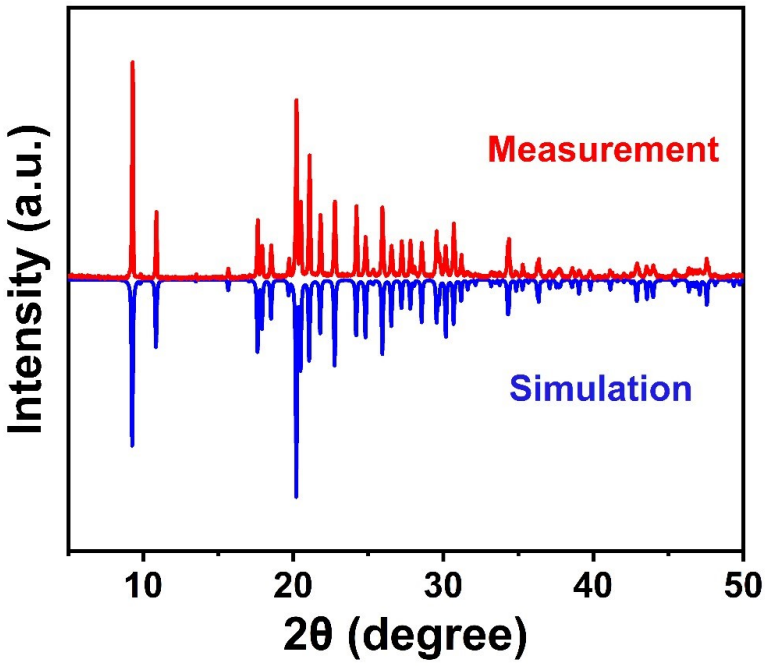


Figure S4. The measured and simulated PXRD patterns of (*S*,*S*)-BCYD.

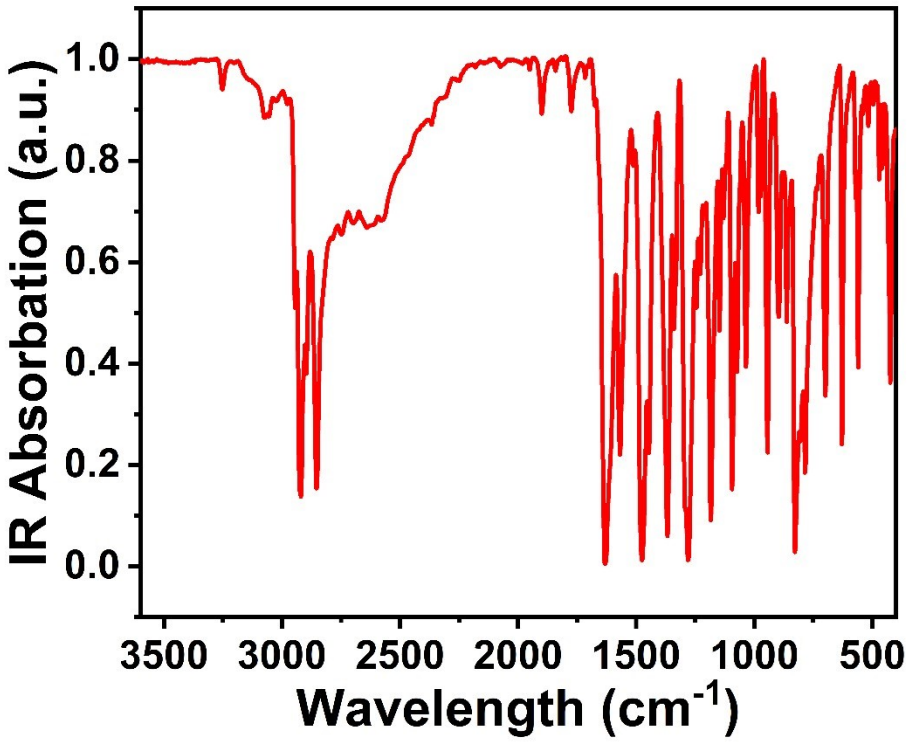


Figure S5. IR spectrum of (*S*,*S*)-BCYD.

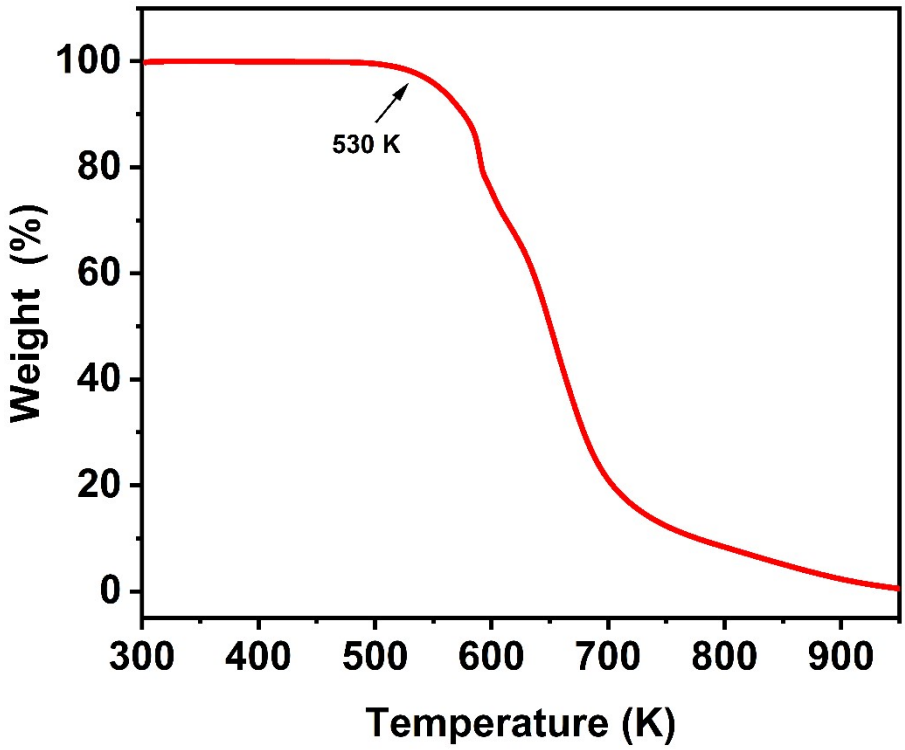


Figure S6. Thermogravimetric analysis (TGA) curve of (*S*,*S*)-BCYD.

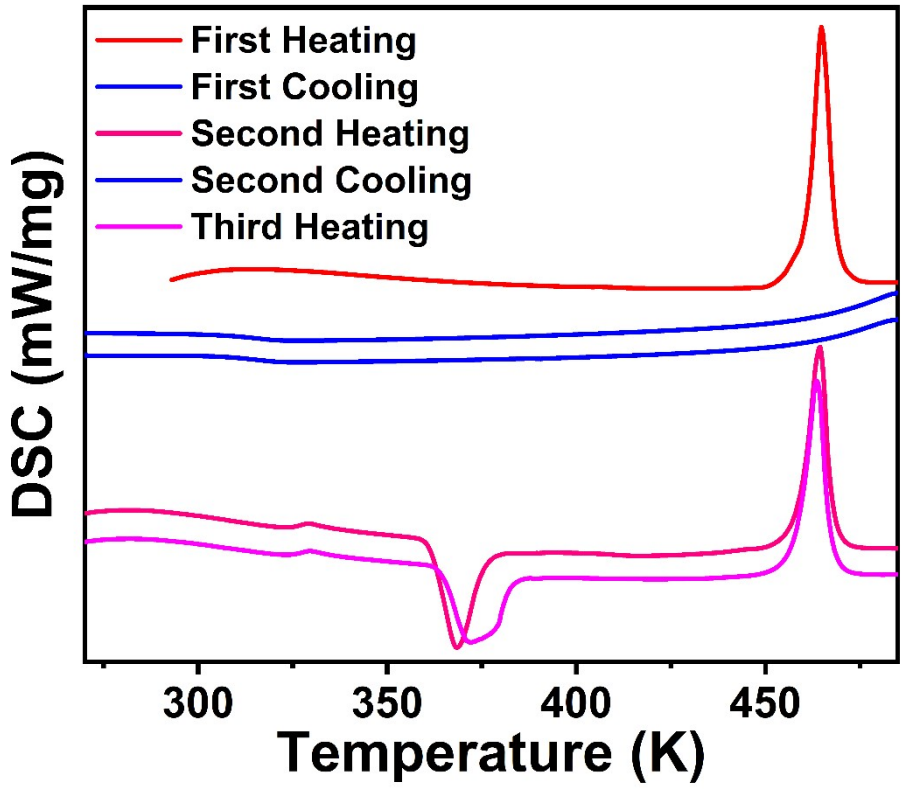


Figure S7. The DSC curves of conducting multiple heating/cooling cycles of (*S*,*S*)-BCYD at a rate of 20 K/min.

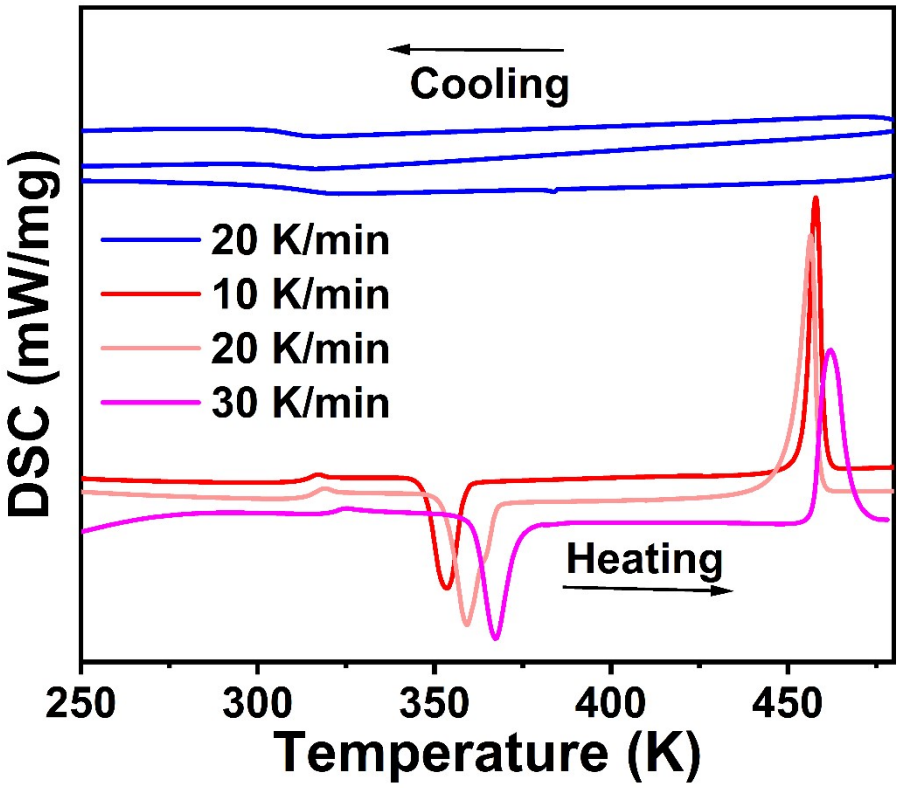


Figure S8. The DSC curves of (*S*,*S*)-BCYD at different heating rates (10 K/min ~ 30 K/min) under a constant cooling rate (20 K/min).

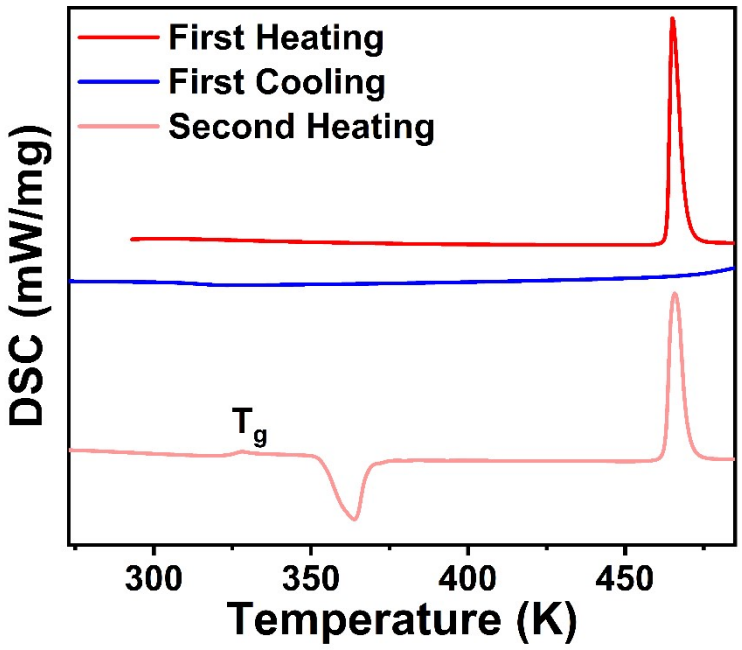


Figure S9. The DSC curves of (*R*,*R*)-BCYD.

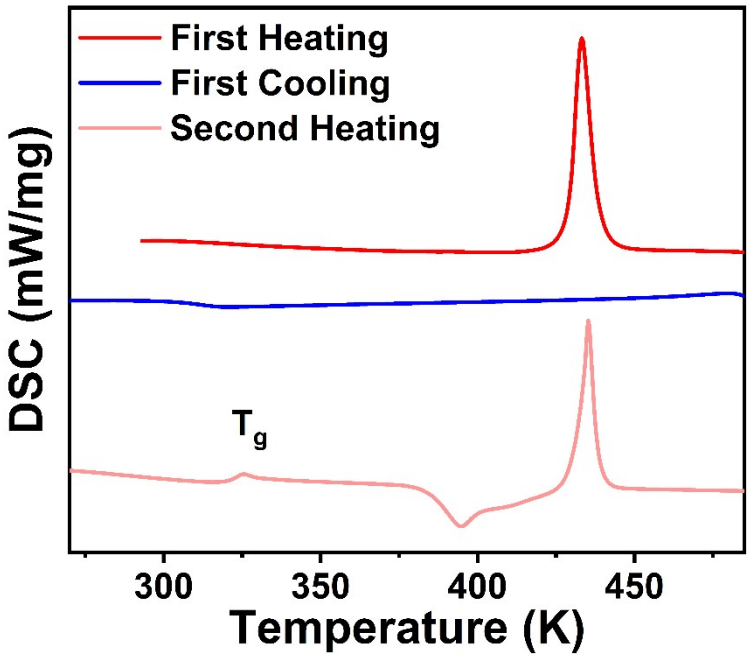


Figure S10. The DSC curves of *Rac*-BCYD.

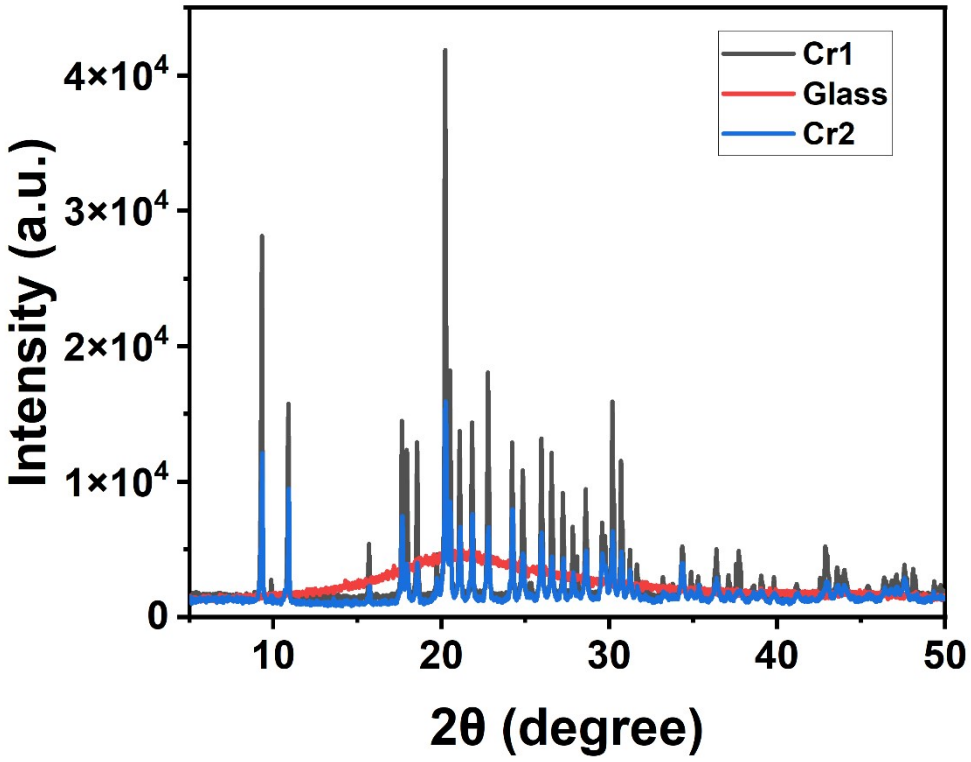


Figure S11. PXRD patterns of (*S*,*S*)-BCYD in different states. Black line: Cr1 powder measured at 298 K. Red line: Glassy state measured at 298 K. Blue line: Cr2 powder measured at 298 K.

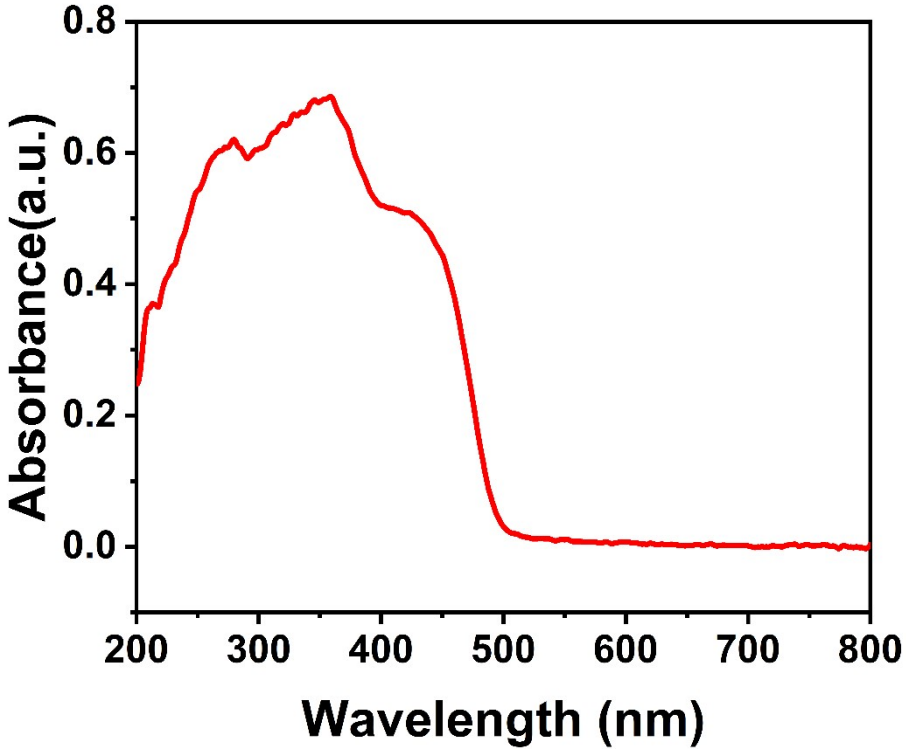


Figure S12. UV-vis absorption spectra of (*S*,*S*)-BCYD.

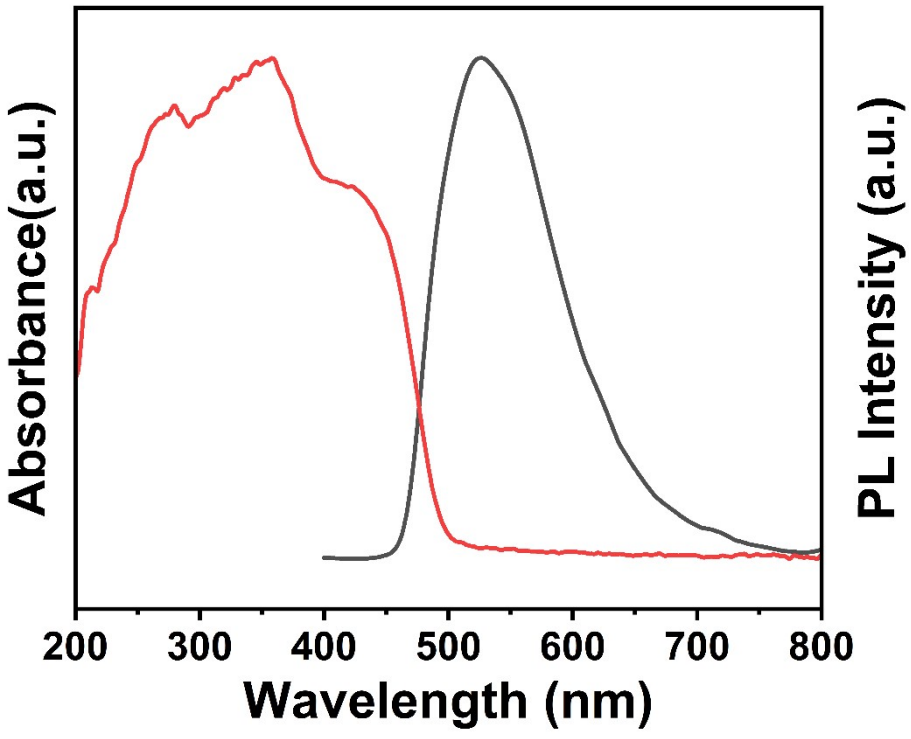


Figure S13. Normalized absorption and emission spectra of (*S*,*S*)-BCYD.

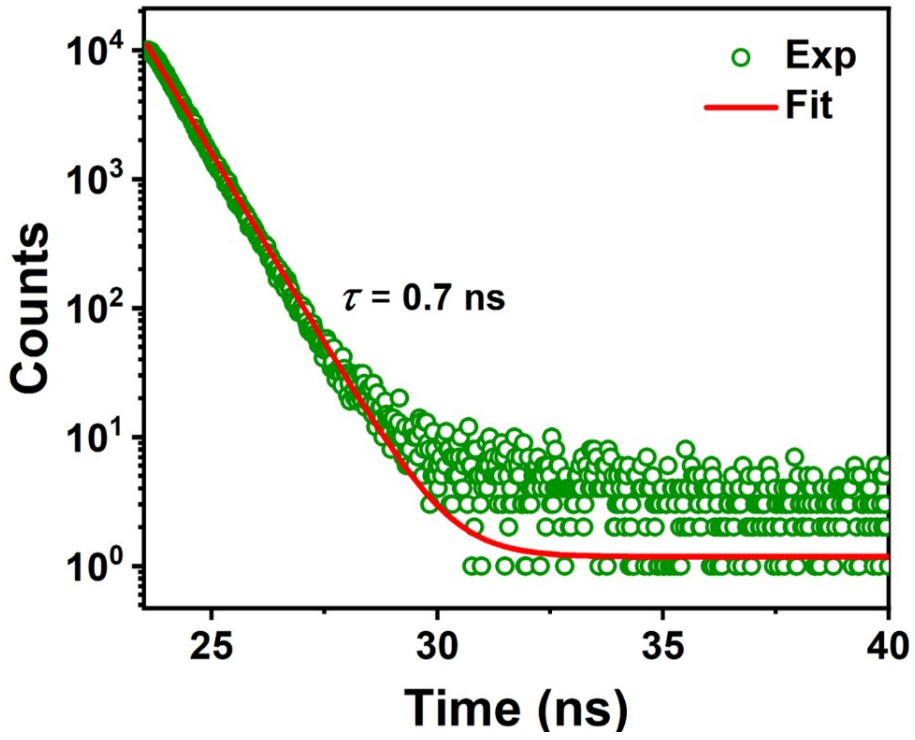


Figure S14. Time-resolved PL spectra of (*S*,*S*)-BCYD.

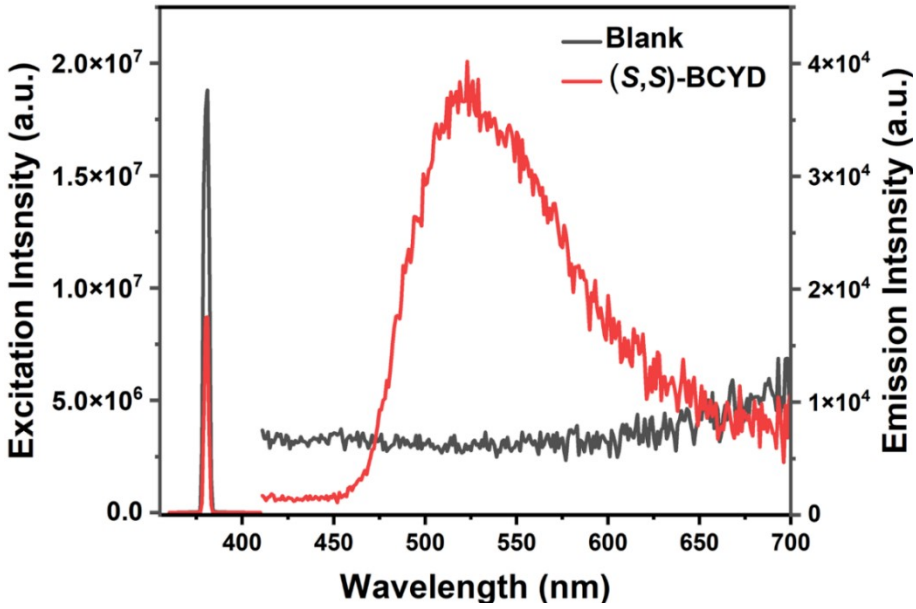


Figure S15. Photoluminescence quantum yield measurements of (*S*,*S*)-BCYD.

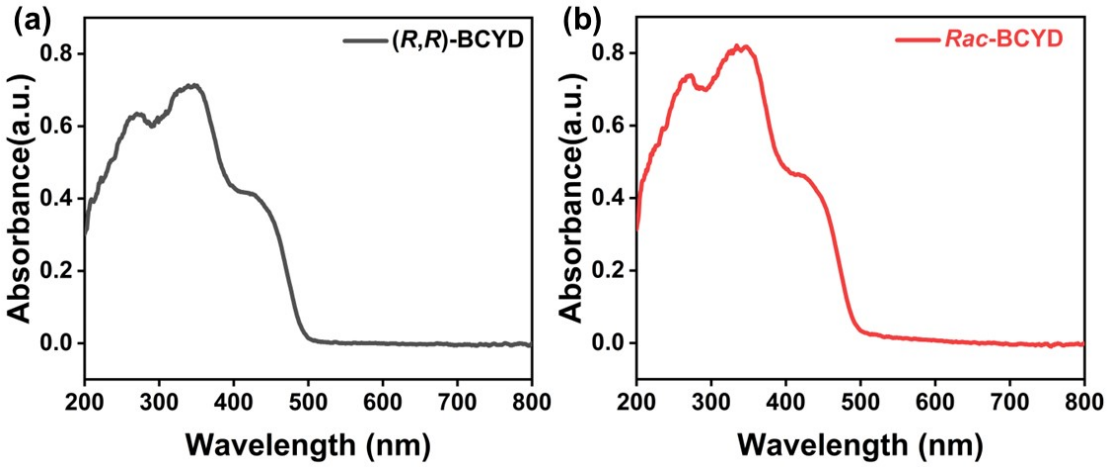


Figure S16. UV-vis absorption spectra of (*R*,*R*)-BCYD and *R*ac-BCYD.

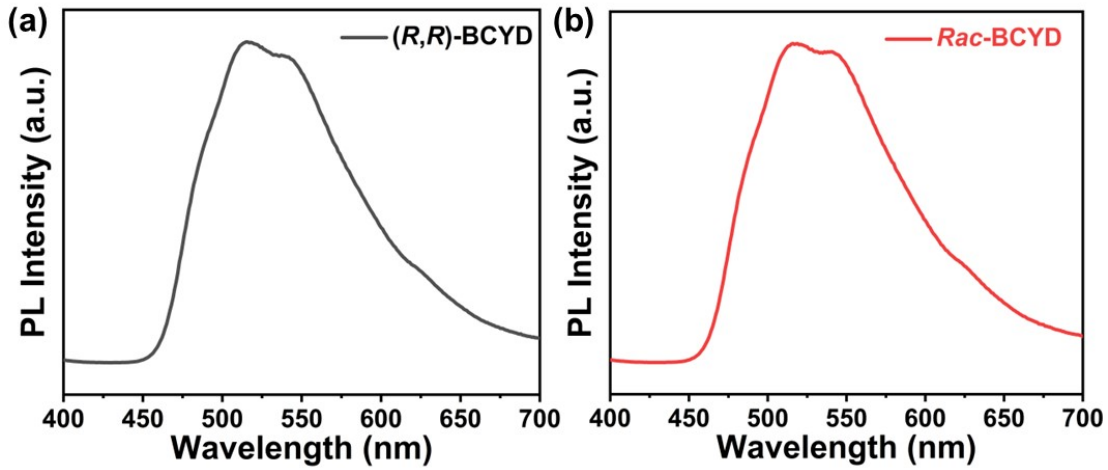
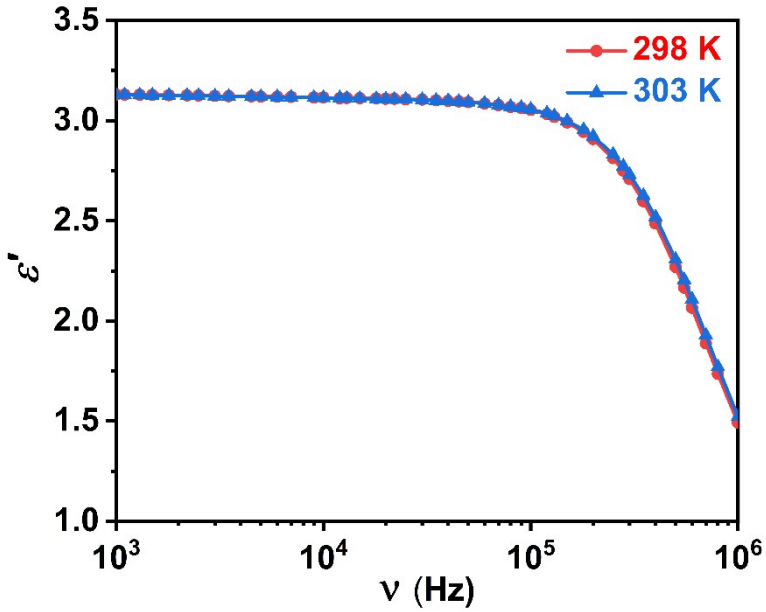


Figure S17. PL spectra of (*R*,*R*)-BCYD and *R*ac-BCYD.



Figures S18. Real part ε' of the dielectric constant versus frequency at different temperatures below the glass-transition temperature T_g (322 K) in the second heating.

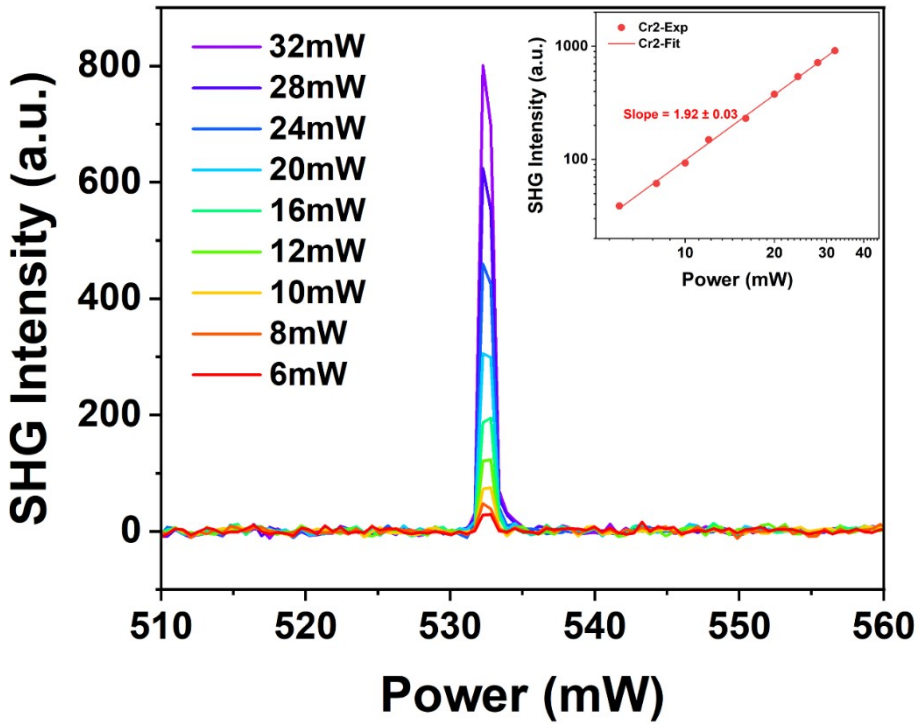


Figure S19. The SHG intensity of (*S*,*S*)-BCYD in the Cr2 state under different laser powers. The inset shows a logarithmic plot of the second harmonic intensity as a function of the incident power. The solid line is a linear fit with a slope of 1.92.

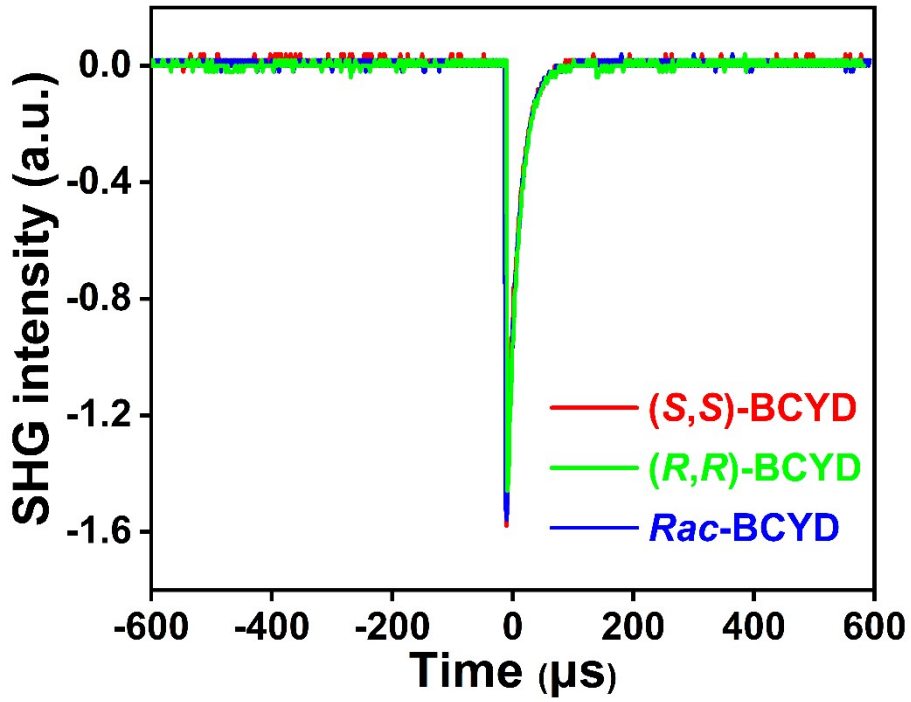


Figure S20. SHG intensity of (*S*,*S*), (*R*,*R*) and *Rac*-BCYD.

Table S1. Crystal data and structure refinements for (*S*,*S*), (*R*,*R*) and *Rac*-BCYD at 298 K.

Compound	(*S*,*S*)-BCYD	(*R*,*R*)-BCYD	*Rac*-BCYD
Formula	$C_{20}H_{20}Br_2N_2O_2$	$C_{20}H_{20}Br_2N_2O_2$	$C_{20}H_{20}Br_2N_2O_2$
Temperature	298 K	298 K	298 K
Formula weight	480.20	480.20	480.20
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$	$P2_12_12$
a/Å	5.9191(3)	5.9248(1)	5.9364(2)
b/Å	19.0670(7)	19.0854(3)	19.0616(8)
c/Å	9.0123(5)	9.0135(1)	9.0086(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	1017.12(9)	1019.22(3)	1019.39(7)
Z	2	2	2
$R_1[I >= 2\sigma(I)]$	0.0730	0.0435	0.0678
$wR_2[I >= 2\sigma(I)]$	0.1621	0.1243	0.1978
GOF	1.154	1.070	1.081

Table S2. Hydrogen bond lengths (Å) and angles (º) for (*S*,*S*)-BCYD at 298 K.

D—H···A	d(D—H)/Å	d(D···A)/Å	d(H···A)/Å	D—H···A/°
O1—H1···N1	0.82	2.602(15)	1.87	148
$O1^i$—$H1^i$···$N1^i$	0.82	2.602(15)	1.87	148

Symmetry codes: (i)1-x,1-y, +z