Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Lead-Free Zero-Dimensional Hybrid Antimony Halide Perovskite X-ray Scintillator with Exceptional Emission Efficiency and Excellent Stability as a Highly Sensitive Fluorescent Probe

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Experimental section

1. Materials

Antimony trichloride ($SbCl_3$, 99%, Aladdin), 1-(2-fluorophenyl)piperazine (FPPP, 98%, Aladdin), hydrochloric acid (HCl, 38%, Aladdin), hypophosphorous acid (H_3PO_2, AR, 50 wt. % in H_2O, Aladdin), and butyl alcohol ($CH_3(CH_2)_3OH$, , Aladdin). All chemicals were purchased and used without any further purification.

2. Synthesis of $[FPPP]_2SbCl_7$

Single crystal of $[FPPP]_2SbCl_7$ was facilely prepared through solution evaporation method. In the synthesis of $[FPPP]_2SbCl_7$ single crystals, powder antimony trichloride (6.757mmol, 1.54 g) was first dissolved in a concentrated mixture of hydrochloric acid (15 ml) and hypophosphorous acid (15 ml). Next, 45 ml organic solvent butyl alcohol and add 1-(2-fluorophenyl)piperazine (13.52 mmol, 2.435 g) were added to the solution. The solution rapidly produces a large amount of precipitation due to the formation of a large number of halides. The solution and halide precipitation were ultrasound until no precipitation, then placed on a hot plate and heated at 100 °C for 5 minutes. After cooling down to room temperature, the precipitated crystals were taken out, washed by butyl alcohol and dried with a vacuum oven at 60 ℃.

3. Characterization methods

Single-crystal X-ray diffraction data of $[FPPP]_2SbCl_7$ was collected using a Bruker D8 Quest diffractometer with Mo *K*a radiation (λ = 0.71073 Å). The structures were solved and refined by the SHELXL-2018/3 program within OLEX2, with all atoms being refined with anisotropic atomic displacement parameters. The powder X-ray diffraction (PXRD) pattern was collected using a Rigaku MiniFlex II diffractometer, operating at 40 kV and 40 mA with Cu *K*a radiation (λ = 1.5406 Å). The diffraction pattern was scanned over the angular range of 10–50° (2θ) with a step size of 1° min^{-1} at room temperature. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449C thermal system, with samples heated from room temperature to 800 °C at a rate of 10 °C min^{-1} under an N_2 atmosphere. Solid-state UV-vis optical absorption spectra were performed on a PE Lambda 900 UV-vis spectrophotometer. X-ray photoelectron

spectroscopy (XPS) spectra were tested using the Escalab XI+ instrument, USA. SEM and EDS images were obtained using the Hitachi SU-8010 field emission scanning electron microscopy. The PL spectrum was measured using an Edinburgh FLS1000 fluorescence spectrometer. The PLQY was acquired using an Edinburgh FLS980 fluorescence spectrometer equipped with a xenon lamp and a calibrated integrating sphere. Time-resolved attenuation data were collected using the Edinburgh FLS980 fluorescence spectrometer and a picosecond pulsed diode laser.

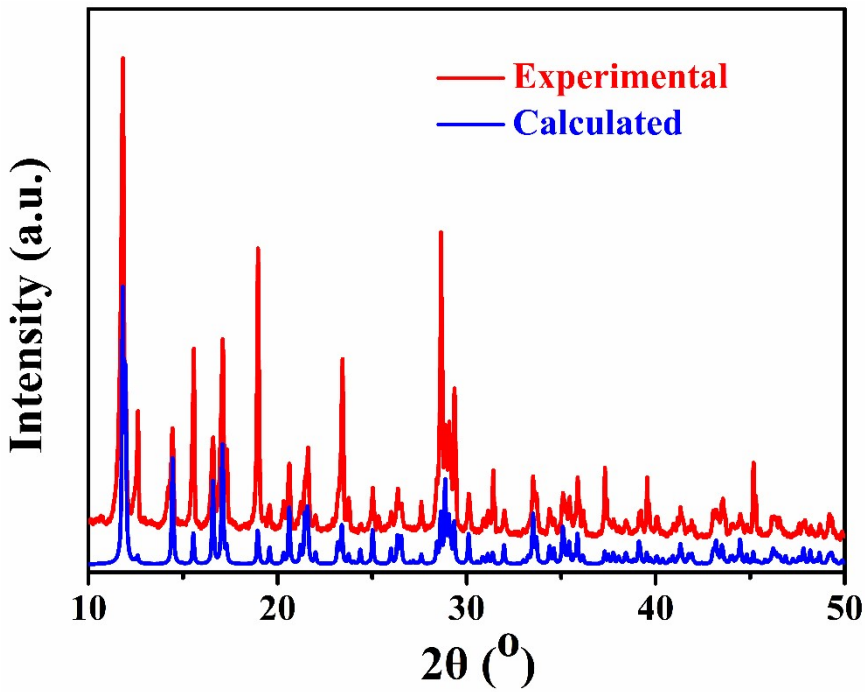

Figure S1. Experimental and simulated PXRD patterns of $[FPPP]_2SbCl_7$ powder at room temperature.

Figure S2. EDS result of $[FPPP]_2SbCl_7$ bulk crystal.

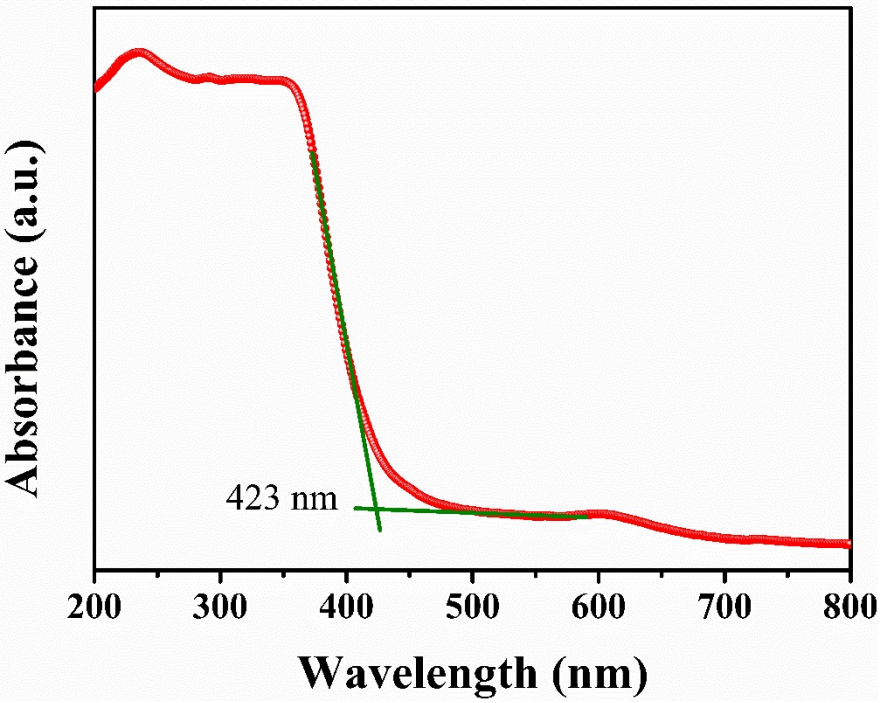

Figure S3. UV/Vis absorption spectra of $[FPPP]_2SbCl_7$.

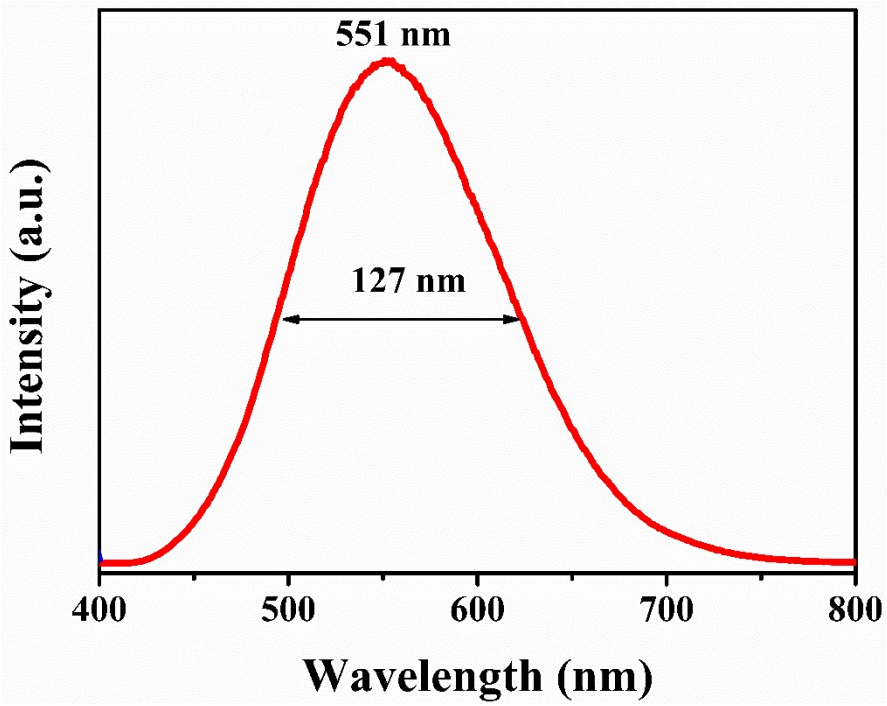

Figure S4. Full-width at half-maximum (FWHM) of the PL intensity of $[FPPP]_2SbCl_7$ crystals.

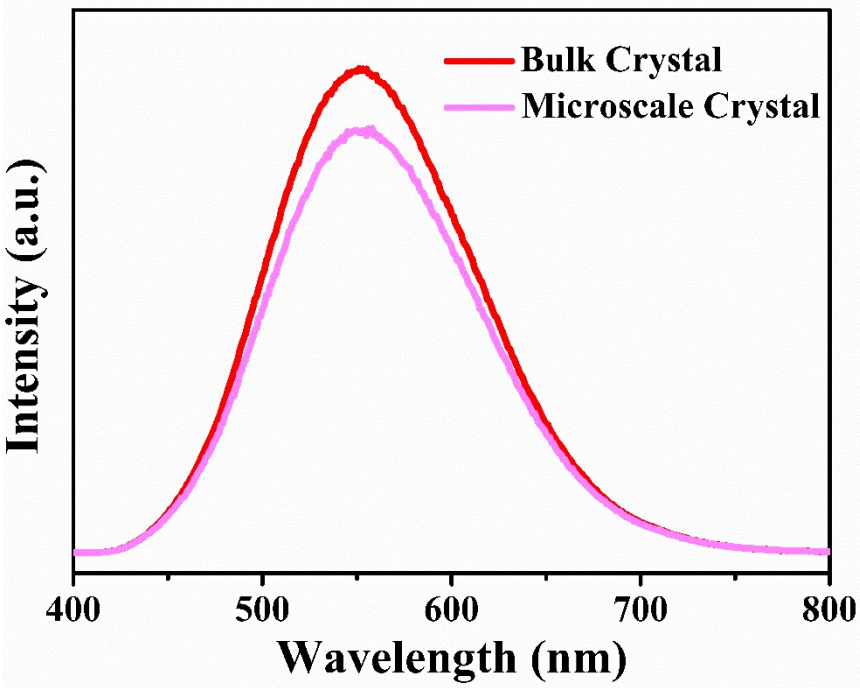

Figure S5. Comparison of PL emission spectra of bulk and microscale crystals for $[FPPP]_2SbCl_7$.

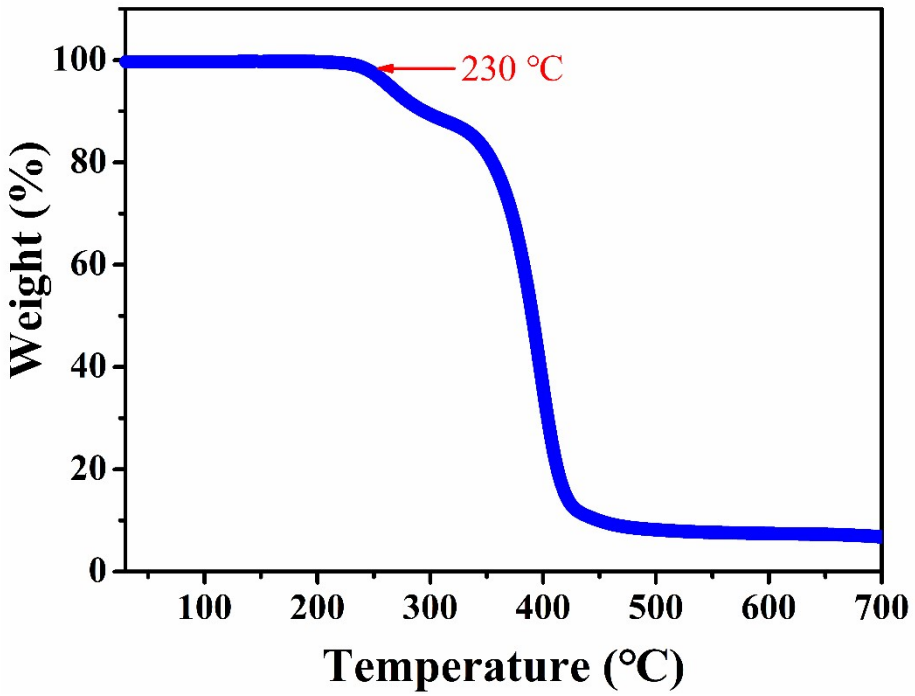

Figure S6. TG spectrum of $[FPPP]_2SbCl_7$.

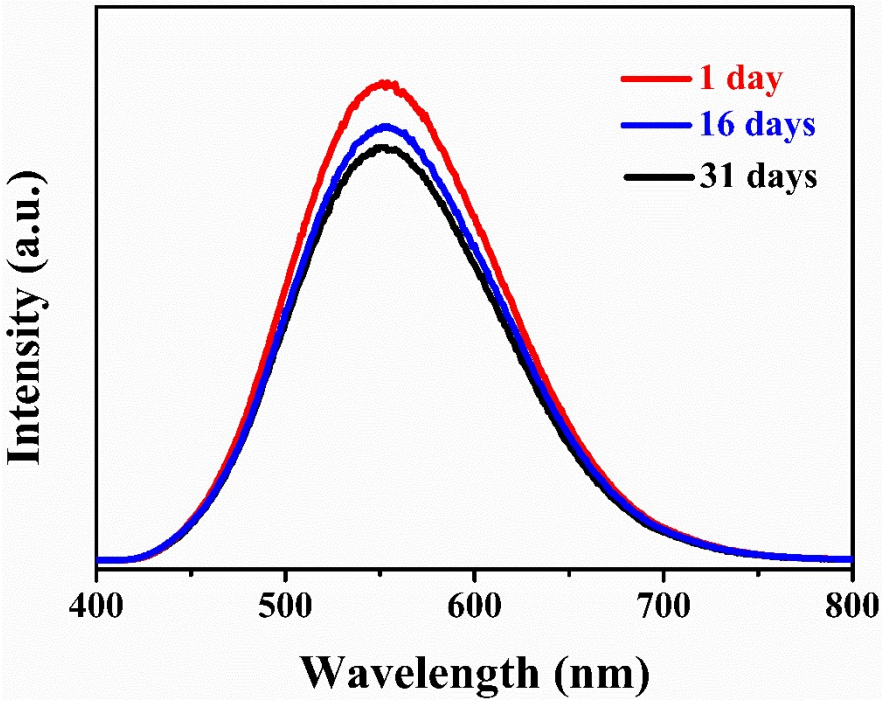

Figure S7. PL emission spectra of $[FPPP]_2SbCl_7$ after storage in humid air for various days.

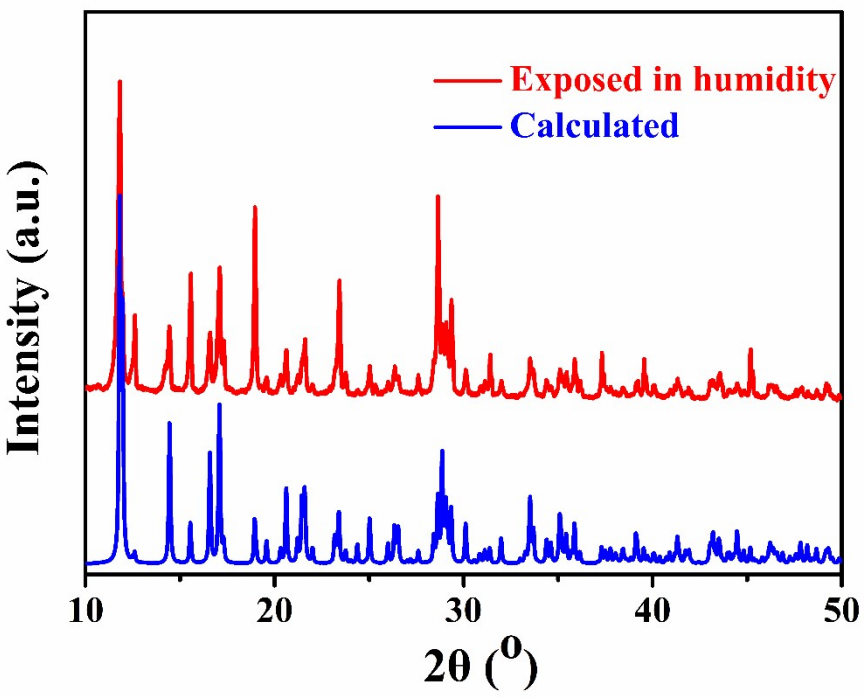

Figure S8. PXRD pattern of $[FPPP]_2SbCl_7$ after storing in humid air.

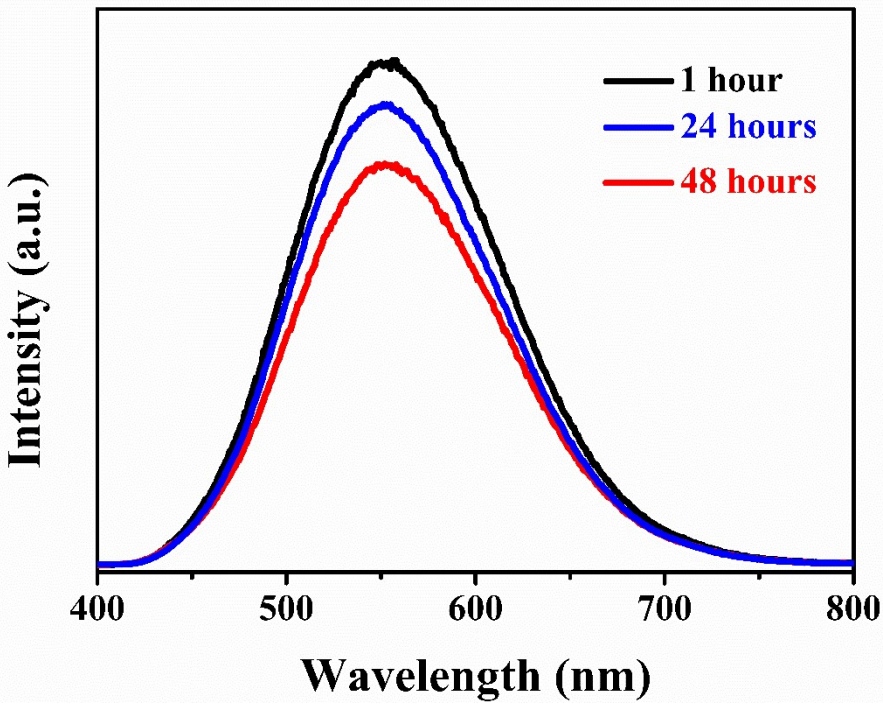

Figure S9. PL emission spectra of $[FPPP]_2SbCl_7$ after exposing in the light condition.

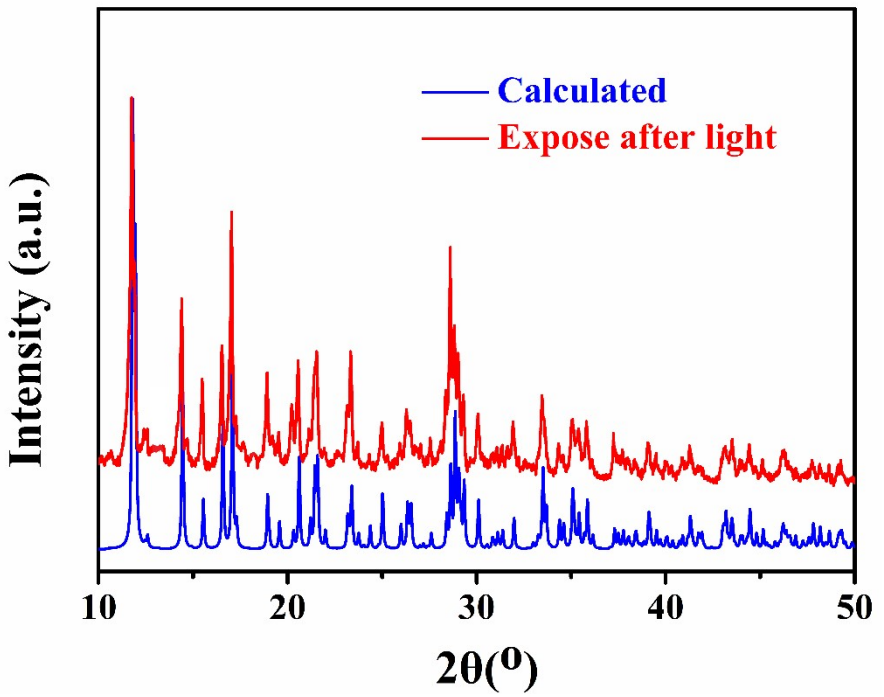

Figure S10. PXRD of $[FPPP]_2SbCl_7$ after exposing in the light condition for 48 hours.

Figure S11. The photo image of crystals under X-ray light for $[FPPP]_2SbCl_7$.

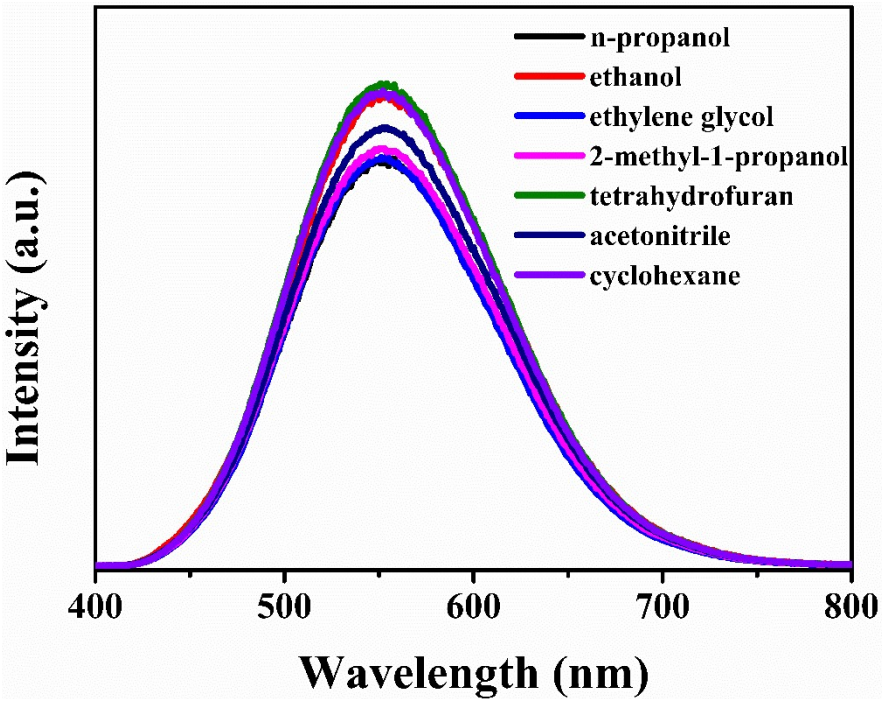

Figure S12. PL emission spectra of $[FPPP]_2SbCl_7$ after soaking in various organic solvents for one day.

Table S1. Crystal Data and Structural Refinements for $[FPPP]_2SbCl_7$ single crystal.

Compound	$[FPPP]_2SbCl_7$
Empirical formula	$(C_{10}H_{16}N_2F)_2SbCl_7$
CCDC number	2328997
Formula weight	736.39
Crystal system	monoclinic
Space group	*C2/c*
a (Å)	12.7608(12)
b (Å)	28.083(3)
c (Å)	8.4298(7)
α (°)	90
β (º)	102.424(3)
γ (°)	90
V (Å^3)	2950.2(5)
Z	4
ρ_{calcd} (g·cm^{-3})	1.658
Temperature (K)	273.15
μ (mm^{-1})	1.600
F (000)	1472.0
Reflections collected	23164
Theta range for data collection (°)	5.442 to 56.748
Index ranges	$-16 \le h \le 16$, $-37 \le k \le 37$, $-11 \le l \le 11$
Independent reflections	3690 [R_{int} = 0.0443, R_{sigma} = 0.0328]
Data/restraints/parameters	3690/171/147
Goodness-of-fit on F^2	1.036
Final R indexes ($I > 2\sigma(I)$)[a]	R_1 = 0.0930, wR_2 = 0.2705
Final R indexes [all data]	R_1 = 0.1079, wR_2 = 0.2860

[a] $R_1 = \Sigma\left||F_0|-|F_c|\right| / \Sigma|F_0|$, $wR_2 = [\Sigma(F_0^2 - F_c^2) / \Sigma w(F_0)^2]^{1/2}$