Supporting Information for

Efficient quasi-2D tin perovskite solar cells based on mixed monoammonium and diammonium terminal molecules

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Experimental section

Materials

The following materials were used: Indium tin oxides (ITO, Liaoning Yike Precision New Energy Technology Co.,Ltd.); PEDOT:PSS (Heraeus-Clevios P VP AI 4083); Sn powder (Sigma, 99.8%); I_2 (Sigma, 99.8%); DMSO (Sigma-Aldrich, anhydrous, 99.9%); DMF (Sigma-Aldrich, anhydrous, 99.8%); SnF_2 (Sigma-Aldrich, 99%); formamidine acetate (FAAc, Admas, 99%); NH_4I (Sigma, ≥99%); 2-phenylethylamine thiocyanate (PS, 99.9%, Greatcell); p-Xylylenediamine (XDA, Macklin, 99%) NH_4SCN (Sigma, 99%); BCP (TCI, 99.0%); toluene (Sinopharm Chemical Reagent Co. Ltd., AR, ≥99.5%, redistilled); chlorobenzene (Sigma-Aldrich, anhydrous, 99.8%); ICBA (1-Materia, >99%).

Synthesis of p-Xylylenediammonium thiocyanate (XS_2)

1.3619 g p-Xylylenediamine and 1.5224 g NH_4SCN were added into 20 mL ethanol and 5 mL deionized water. After starring for 24 h, the solution was evaporated by a rotary evaporator to produce a faint yellow solid precipitate. The faint yellow solid precipitate was washed with diethyl ether at least three times until the diethyl ether was no longer discolored. Then the raw product was recrystallized three times with ethanol. Finally, the faint yellow crystal was placed in 60°C for drying overnight before use.

Preparation of the SnI_2 solution

To prepare 0.8 M SnI_2 solution, 10 mmol I_2 was dissolved in 2.5 ml DMSO and 10 ml DMF successively, and then sufficient Sn powder was added to the I_2-solution following stirring at room temperature overnight.

Preparation of the perovskite precursor solution

For control precursor, a 0.8 M perovskite precursor comprised PS, FAAc, NH_4I, SnI_2 solution, SnF_2, and NH_4SCN in the molar ratio of 0.2:0.8:0.8:1:0.075:0.05 were mixed and stirred at room temperature overnight. For XS2 precursor, a 0.8 M perovskite precursor comprised PS, XS_2, FAAc, NH_4I, SnI_2 solution, SnF_2, and NH_4SCN in the molar ratio of 0.18:0.01:0.8:0.8:1:0.075:0.05 were mixed and stirred at room temperature overnight.

Preparation of perovskite films

Both control and XS2 films were prepared by the same process. The ITO glass was cleaned with detergent, deionized water, and isopropanol, then further treated with ultraviolet-ozone for 20 min before fabricating the next layer. The PEDOT:PSS solution was spin-coated on the ITO at 5,000 rpm for 40 s and annealed at 140 °C for 20 min. And then, the filtered perovskite precursor was spin-coated on PEDOT:PSS at 1000 and 5000 rpm for 10 s and 35 s, respectively. (spin-coater, Jiangyin J.wanjia Technology Co., LTD) During the second stage, 600 μL toluene was dropped onto the surface at 22th second, and the substrate was annealed at 80 °C for 20 min.

Device fabrication

Both control and XS2 solar cells were fabricated by the same process. 20 mg mL^{-1} ICBA solution (dissolved in chlorobenzene) was spin-coating on the perovskite film at 1000 rpm for 30 s and then annealing at 70 °C for 10 min. Finally, 8 nm BCP and 100 nm Ag were deposited to form the solar cells. The vacuum during the evaporation process is less than $3×10^{-6}$ Torr. For tin perovskite TFTs, the Si substrate with 100 nm SiO_2 was treated with ozone for 30 min before use. The perovskite films for TFTs were fabricated by the same process as those for solar cells. 50 nm gold was thermally evaporated as source and drain electrodes. The channel length and width are 150 μm and 1200 μm, respectively.

Materials characterizations.

GIWAXS measurement was performed by employing a beam energy of 10 keV and a PILATUS detector at the BL02U1 beamline of Shanghai Synchrotron Radiation Facility (SDRS), Shanghai, China. The SEM images were taken by JSM-7800, JEOL. AFM measurements were taken using Dimension Fastscan with a Pt-Ir coated conductive probe SCM-PIT-75 (NANOWORLD), which has a spring constant of k=2.8 N/m. Abs of the perovskite films were measured using an UV-vis spectrophotometer (Agilent cary5000). PL is recorded using HORIBA Fluorolog-3 with CCD detector. XRD was obtained using Bruker D8 Advance under Cu Kα radiation (λ = 1.54 Å). TRPL decay was detected using Fluorolog HORIBA FL-3 with a time-correlated single-photons counting (TCSPC) technique. Perovskite films were encapsulated by UV glue and the excitation at 504 nm pulse impinged on the glass substrate side, monitored at the peak emission of 840 nm.

Device characterizations

A Keithley 2400 source unit was employed to obtain J-V curves under simulated AM1.5G solar illumination at 100 mW cm^{-2}. For the measurement of the J-V curve, the active area of all the devices was masked using a metal mask with an area of 0.04 cm^2. The calibration of light was enabled by a KG-5 Si diode with a solar simulator (Enli Tech, Taiwan). The devices are measured in reverse scan (0.95 V to 0 V, step 0.01 V) and forward scan (0 V to 0.95 V, step 0.01 V) with a delay time of 30 ms at room temperature in a glovebox. The same equipment is used for investigating the J_{SC} and V_{OC} of TPSCs under variable light intensity as well. A commercial system (Solar cell scan 100, Beijing Zolix Instruments Co., Ltd) was used to measure the EQE spectra. And the calibration of light intensity was carried out by a standard photodetector (QE-B3/S1337-1010BQ, Zolix). The light beam was chopped at 180 Hz and the response of the cell was acquired by a Stanford Research SR830 lock-in amplifier. Transistor transfer characteristics were measured using a semiconductor parameter analyzer (Keithley 4200-SCS) in the continuous mode. For the TPC and TPV measurements, the solar cells were connected to a digital oscilloscope (DPO3034) and the internal impedance was set to 50 Ω and 1 MΩ for TPC and TPV, respectively. A 640 nm laser pulse (Coherent, OBIS 640, frequency of 10 Hz and pulse width of 1 μs.) was applied as a small perturbation to the device.

Calculation method of carrier diffusion length and mobility

For the TRPL method, Sn perovskite films were excited by a weak laser, thus the bimolecular recombination can be ignored and it can be treated as monomolecular process. The excitation light is incident from the substrate side. Carrier diffusion length is calculated by the one-dimensional diffusion model:

$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial x^2} - kn(z,t)$$

where D, k, n, z and t are diffusion coefficient, recombination rate, carrier concentration in perovskite, distance from the substrate, and delay time respectively. When considering the boundary conditions: 1. $n(z,0) = n_0 e^{-\alpha z}$, α is absorbance; 2. $n(L_0,t) = 0$, L_0 is the thickness of perovskite film, the total carrier concentration $N(t)$ is deduced as:

$$N_{(t)} = \frac{2n_0 L}{\pi} e^{-kT} \sum_{m=0}^{\infty} (e^{-\frac{\pi^2 D}{L^2}(m+\frac{1}{2})^2 t} \frac{e^{-\alpha L}\pi\left(m+\frac{1}{2}\right) + (-1)^m \alpha L}{((\alpha L)^2 + \pi^2\left(m+\frac{1}{2}\right)^2)(m+\frac{1}{2})})$$

Therefore, the relationship between L_D/L_0 and τ_q/τ_0 can be calculated in numerical, where L_D, L_0, τ_q, τ_0 are diffusion length, film thickness, lifetime with quenching layer, lifetime without quenching layer respectively (Fig S4).

Carrier mobility is calculated by Einstein relation based on diffusion length and lifetime without quenching layer:

$$D = \mu k_B T / q$$

For the TFT method, the mobility was calculated as

$$\mu = \frac{2L}{WC_i}\left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}}\right)^2$$

where L, W, C_i, I_{DS} and V_{GS} are the channel length, channel width, dielectric areal capacitance, source–drain current and gate–source voltage, respectively. In our TFT devices the thickness of SiO_2 on Si substrates is 100 nm, and the capacitance is ~30 nF cm^{-2}.
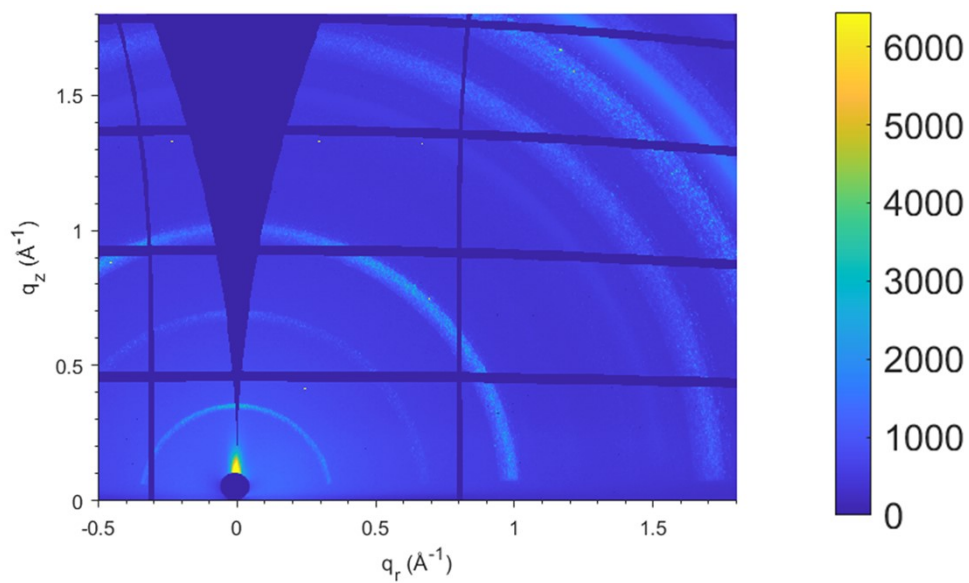
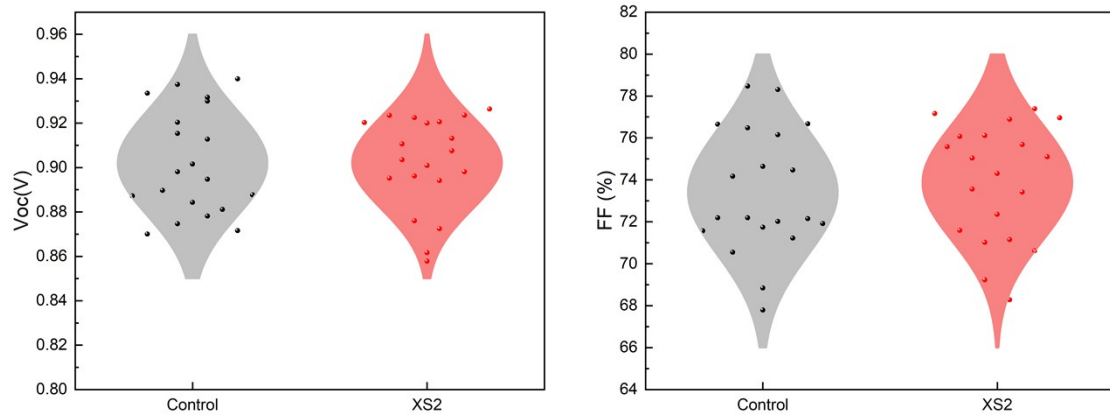Figure S1. GIWAXS patterns of $XDA_{0.1}FA_{0.8}SnI_{2.8}SCN_{0.2}$ with incident angle of 0.5°.

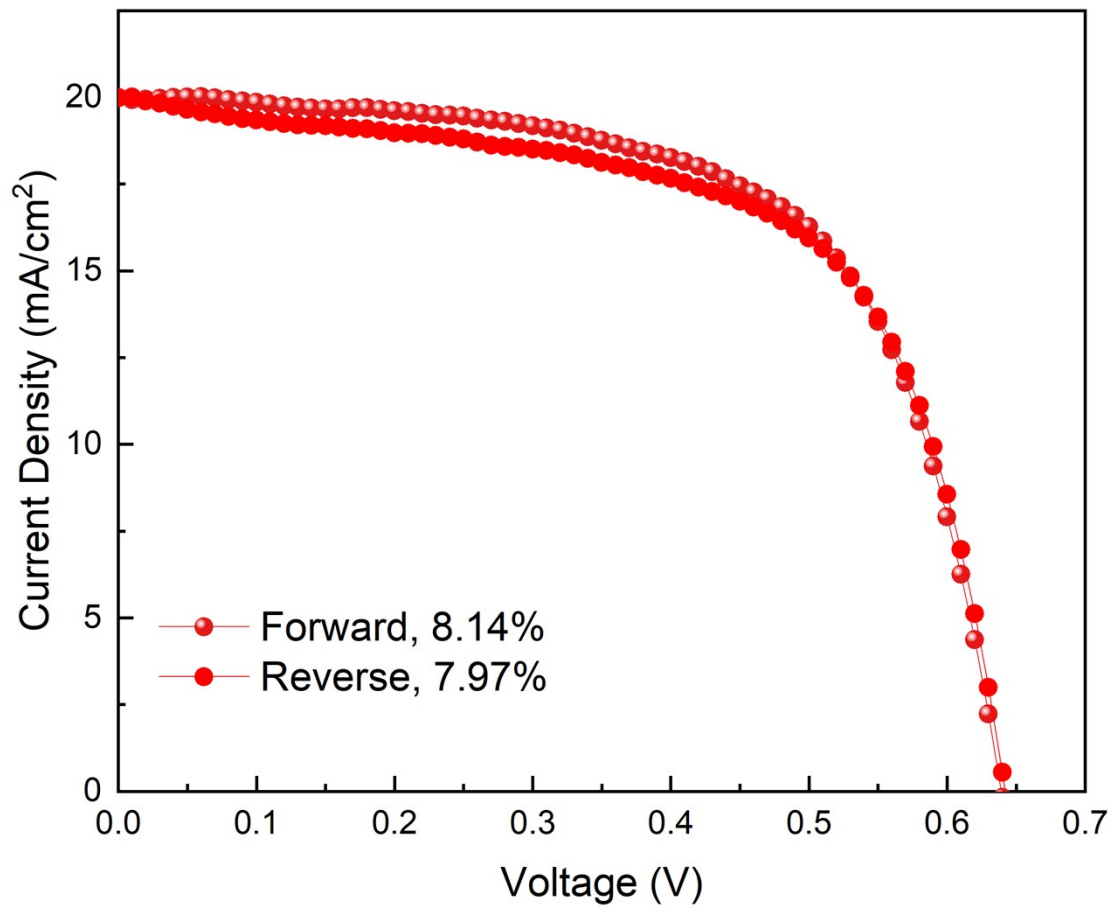Figure S2. Statistical V_{OC} and FF from 20 control and XS2 solar cells.

Figure S3. The *J-V* curve of solar cells based on $XDA_{0.1}FA_{0.8}SnI_{2.8}SCN_{0.2}$.

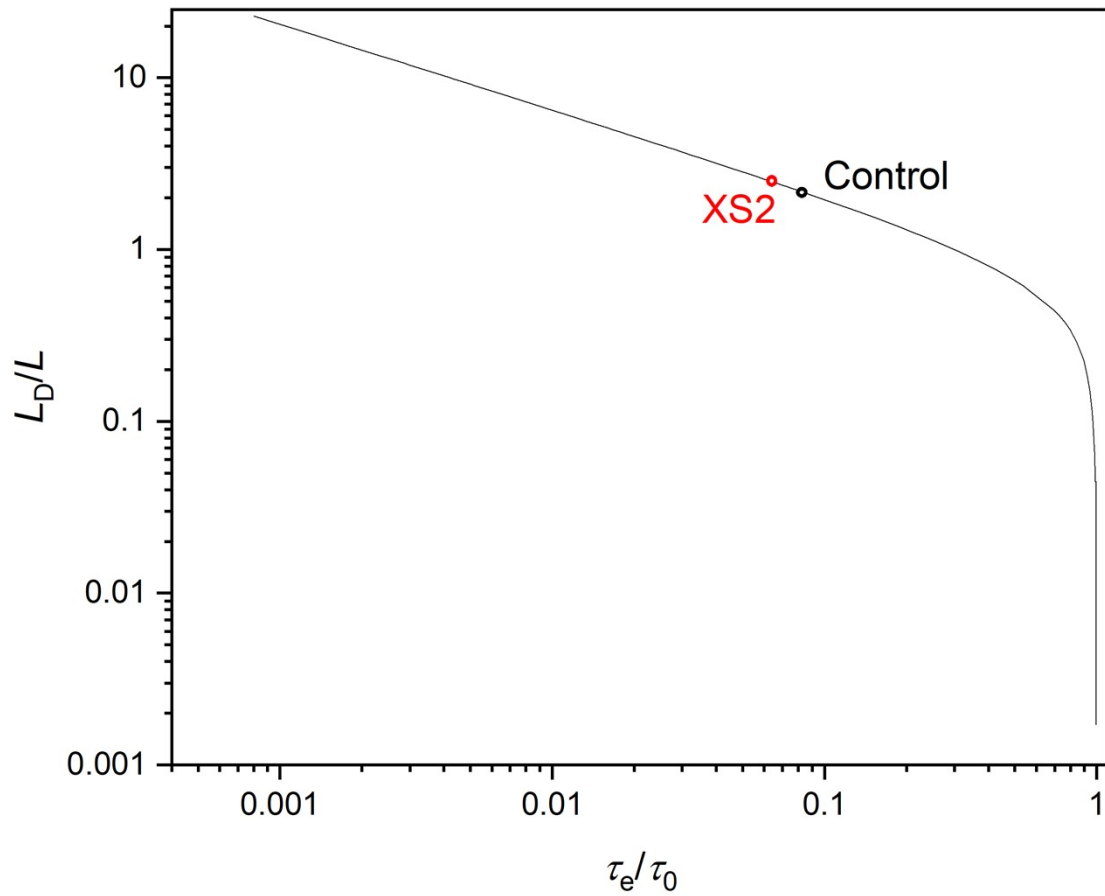Figure S4. Relationship between L_D/L_0 and τ_q/τ_0. L_D is diffusion length. L is film thickness. τ_e is lifetime with a quenching layer. τ_0 is lifetime without quenching layer.
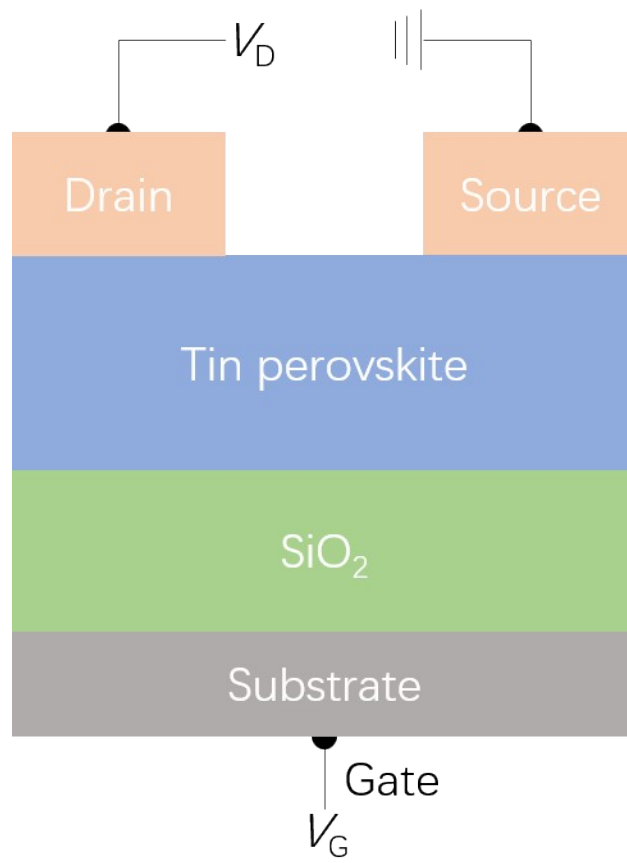
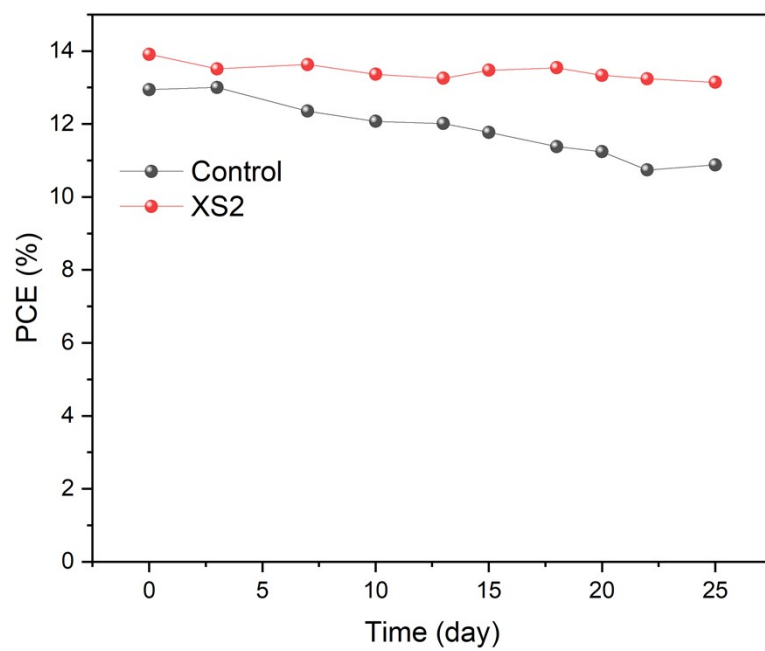Figure S5. Structural scheme of the Sn perovskite TFT.
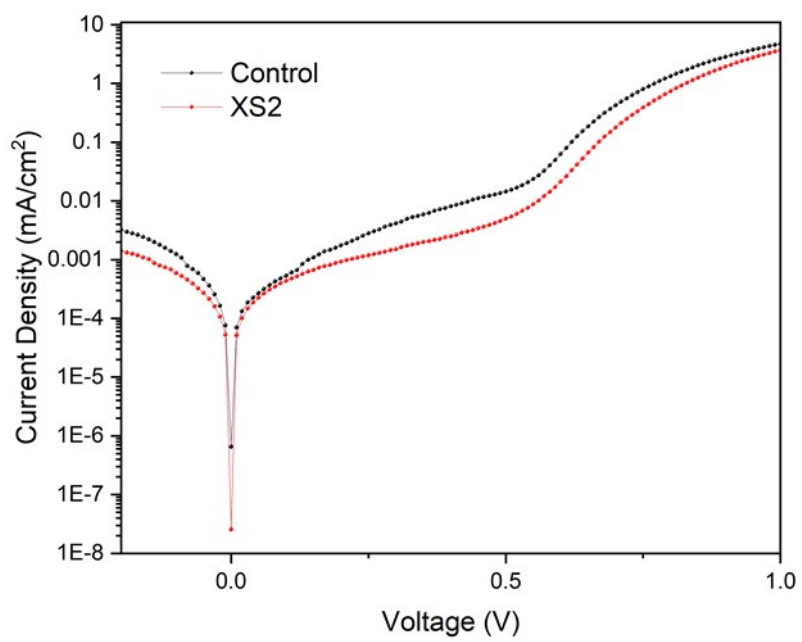
Figure S6. Storage stability of Sn PSCs.

Figure S7. Dark *J–V* curves of Sn PSCs.

Table 1. The performance of the devices measured under AM1.5 illumination.

Device		PCE (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)
Control	forward	12.84	0.91	18.89	74.47
	reverse	13.26	0.92	18.91	76.65
	average	12.86 ± 0.28	0.90 ± 0.02	19.44 ± 0.64	73.41 ± 2.93
XS2	forward	14.20	0.90	20.60	77.15
	reverse	14.31	0.90	20.70	76.95
	average	13.6 ± 0.35	0.90 ± 0.02	20.42 ± 0.41	73.87 ± 2.72

Table S2. Table summarizing the bi-exponential fitting parameters obtained from fits to the photoluminescence data of perovskite thin films.

Samples	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{aver} (ns)
Control	40.52	76.97	10.12	89.88	70.59
Control-ICBA	1.10	9.59	45.11	54.89	5.77
XS2	48.47	94.09	11.53	88.47	84.88

In order to obtain accurate fitting results, the PL lifetime decay of XS$_2$-ICBA was fitted by three-exponential method.

Samples	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1 (%)	A_2 (%)	A_3 (%)	τ_{aver} (ns)
XS2-ICBA	0.86	3.19	17.44	22.40	58.59	19.01	5.39