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Supplementary information

Green solvent blade-coated $MA_3Bi_2I_9$ for direct-conversion X-ray detectors

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EXPERIMENTAL SECTION

Materials

Ethanol (99.5 %) and γ-Butyrolactone (GBL, 99.9 %) were purchased from Aladdin Reagent Ltd. Methylammonium iodide (99.5 %) and methylammonium Chloride (MACl, 99.5 %) was purchased from Xi'an p-OLED Corp. Methylamine solution (MA, 40 % in H_2O) was purchased from Chron Chemicals. Acetic acid (HAc, 99 %) was acquired from Sinopharm Chemical reagent. BiI_3 (99 %) was acquired from Sigma Aldrich. All chemicals used in this work were used as received.

Synthesis of methylamine acetate (MAAc)

Acetic acid and methylamine were stirred in a 500 ml round-bottom flask in an ice bath for 2 h. Afterward, rotary evaporate at 80 °C for 1 hour to obtain the liquid product, and put it into a refrigerator for 2 hours to crystallize. The liquid product is cryopreserved for 2 hours to crystallize. The crystalline product was purified by washing with ether for 5 times. Finally, it was dissolved in ethanol and distilled at 80 °C for 1 hour with a rotary evaporator to remove excess impurities and obtain MAAc, which was then cooled to room temperature for use.

Characterization of materials

X-ray diffraction (XRD) measurements of $MA_3Bi_2I_9$ films were performed under Empyrean X-ray diffractometer (Cu tube with wavelengths of 1.54184 Å) with a scan rate of 2°/min. UV−vis absorption spectra were obtained on an UV-3600 spectrophotometer (Shimadzu Corporation) in reflection mode using $MA_3Bi_2I_9$ films on the glass substrate. Scanning electron microscope (SEM) images were obtained under an accelerating voltage of 5 kV (SIGMA HD ZEISS Company).

Carrier mobilities analysis by time of flight (TOF) method

TOF were performed by irradiating the devices with 6 ns width, 532 nm laser pulses on the transparent ITO electrode. The Keithley 2400 source meter and SR570 low-noise current preamplifier (Stanford Research Systems) were used to apply bias and detect current of the device, respectively. For mobility measurements, when the laser was irradiated on the transparent ITO electrode, the transit times of electrons and holes were obtained by changing the polarity of the voltage applied to the transparent ITO electrode, and then the corresponding mobility was obtained.

Detector performance measurement

For X-ray detection, a tungsten anode X-ray tube (Oxford Insturments' Series 5000) was used as the source, and the Be window thickness was 127 μm. The X-ray tube was fixed with a constant of 40 kV acceleration voltage, and the operational current was tuned from 0.01-0.60 mA to adjust the emitted X-ray dose rate from 0.36 to 22.12 $\mu Gy_{air}\ s^{-1}$. Dose rate calibrations of the X-ray were carried out by the 10X6-180 measurement chamber and Accu-Gold+ system (Radcal). $MA_3Bi_2I_9$ films detectors were measured at different voltages and the X-ray response was recorded by the low-noise current preamplifier (SR570, Stanford Research Systems).

Ion conduction measurement

The activation energy of ion conduction (E_a) was measured by temperature dependent conductivity under dark environment. Ion conduction is a thermal activation process, which is dominated by ion migration in the high temperature region and electron conduction in the low temperature region. E_a was obtained by fitting the slope of the straight line in the high temperature region using the Nernst-Einstein relationship:

$$\sigma(T) = \frac{\sigma_0}{T} exp(-\frac{E_a}{k_B T})$$

where T is the temperature, σ is the conductivity, σ_0 is a constant and, k_B is the Boltzmann constant.

Signal-to-noise ratio

The noise current density (J_n) is obtained from the variance of the photocurrent density ($\bar{J}_p$):

$$J_n = [\frac{1}{N}\sum_{i=1}^{N}(J_i - \bar{J}_p)^2]^{1/2}$$

where N is the number of current sampling points.

The J_s is obtained by:

$$J_s = J_p - J_d$$

where J_d is the dark current density of the detector.

Then, signal-to-noise ratio (SNR) is obtained by calculating the ratio of J_s to J_n.

Mean energy calculation of the continuum bremsstrahlung X-ray spectrum

The mean energy of the continuum bremsstrahlung X-ray spectrum was derived by following equation:

$$\bar{E} = \int_0^{E_{max}} p(E)dE$$

$p(E)$ is the distribution probability of X-rays with the energy of E.

$$\bar{E} = \sum_i p(E_i)\Delta E_i$$

where $p(E_i)$ and ΔE_i are the distribution probability and the energy bin width of the X-rays at the energy bin. For the tube at 40 kV tube voltage, the mean energy is calculated to be 30.6 keV.

RESULTS AND DISCUSSION

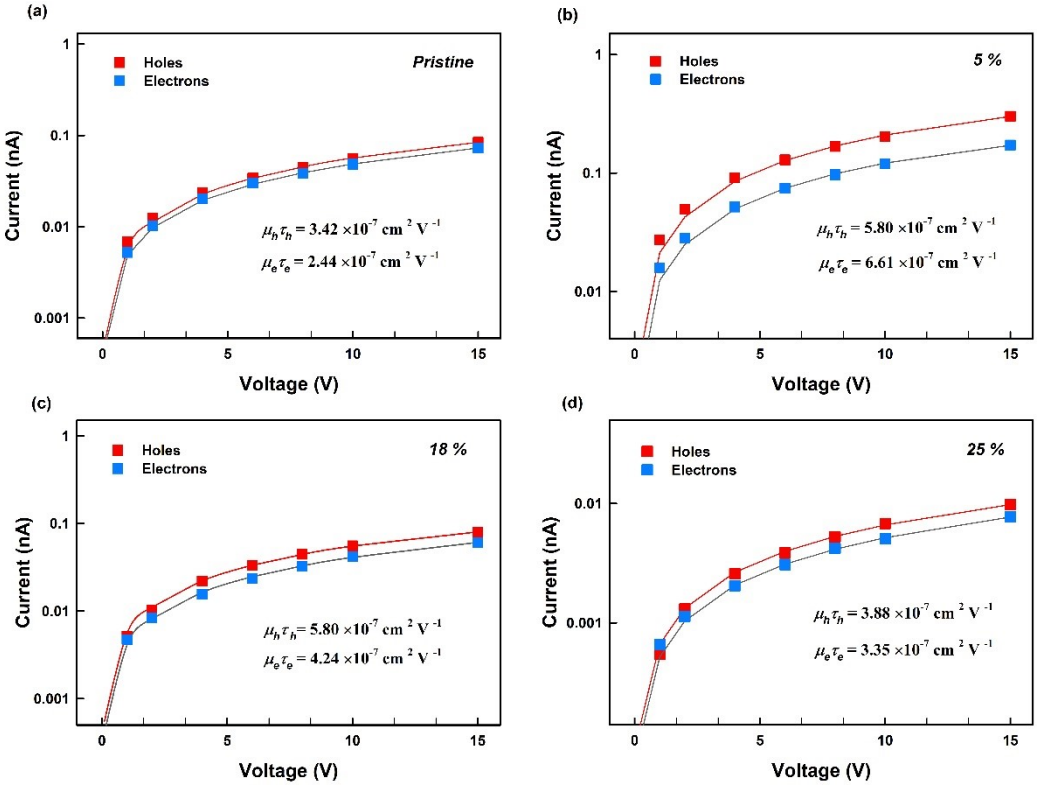

Figure S1. Bias-dependent light-induced signal current of $MA_3Bi_2I_9$ films with (a) 0%, (b) 5%, (c) 18%, and (d) 25% MACl additive.

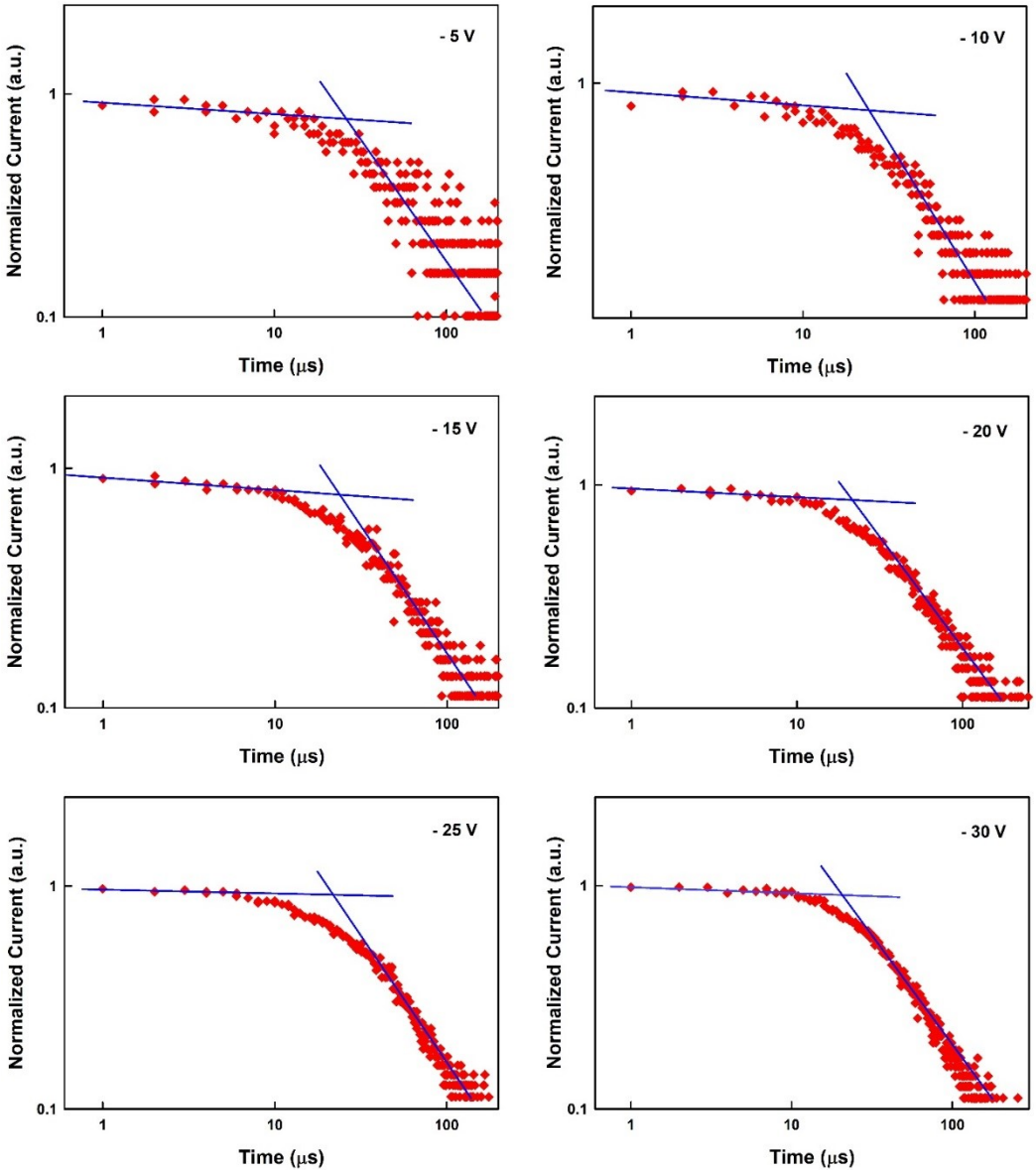

Figure S2. TOF method measurement of $MA_3Bi_2I_9$ with 10% MACl additive under a bias from 5 to 30 V. Electron mobility of 0.04-0.19 $cm^2\ V^{-1}\ s^{-1}$ were derived from the TOF results.

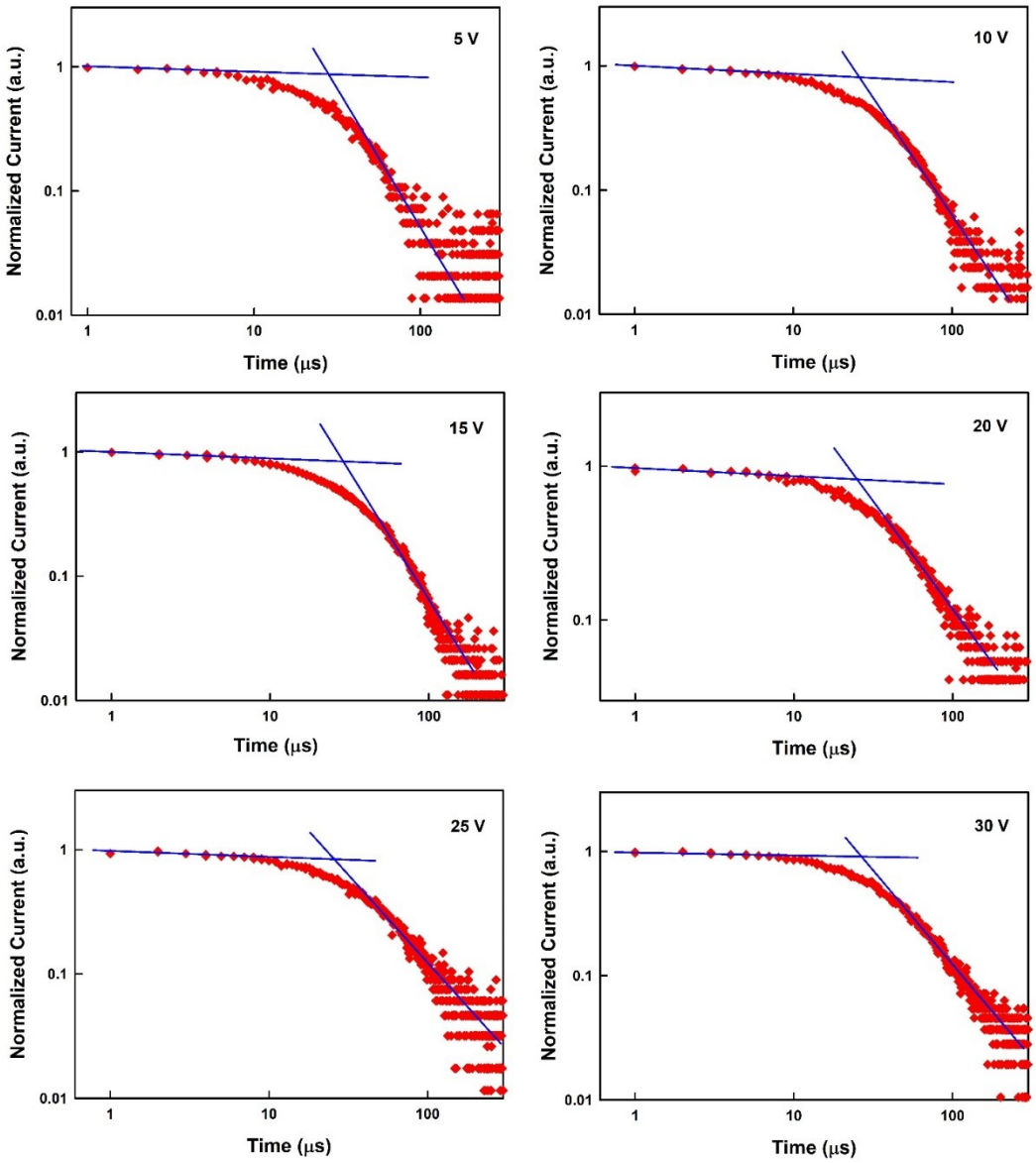

Figure S3. TOF method measurement of $MA_3Bi_2I_9$ with 10% MACl additive under a bias from 5 to 30 V. Hole mobility of 0.03-0.18 $cm^2\ V^{-1}\ s^{-1}$ were derived from the TOF results.

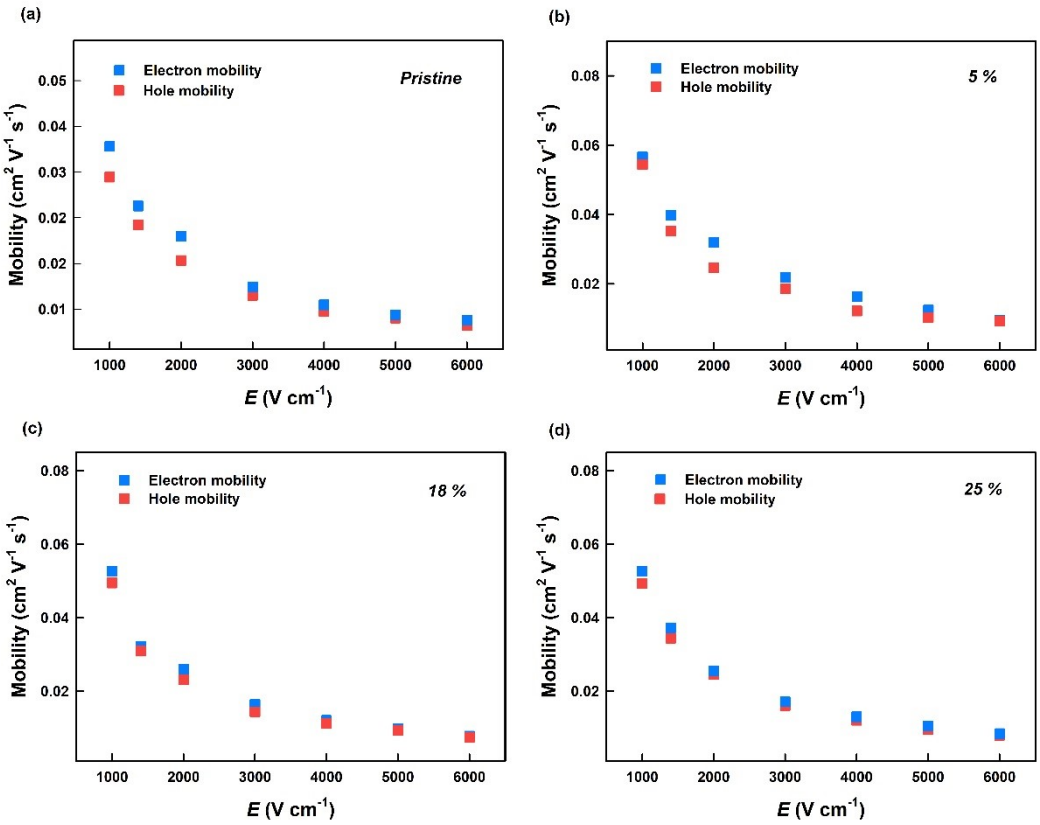

Figure S4. Electric field dependent mobility of (a) Pristine and (b) 5%, (c) 18%, (d) 25% MACl modified $MA_3Bi_2I_9$ films.

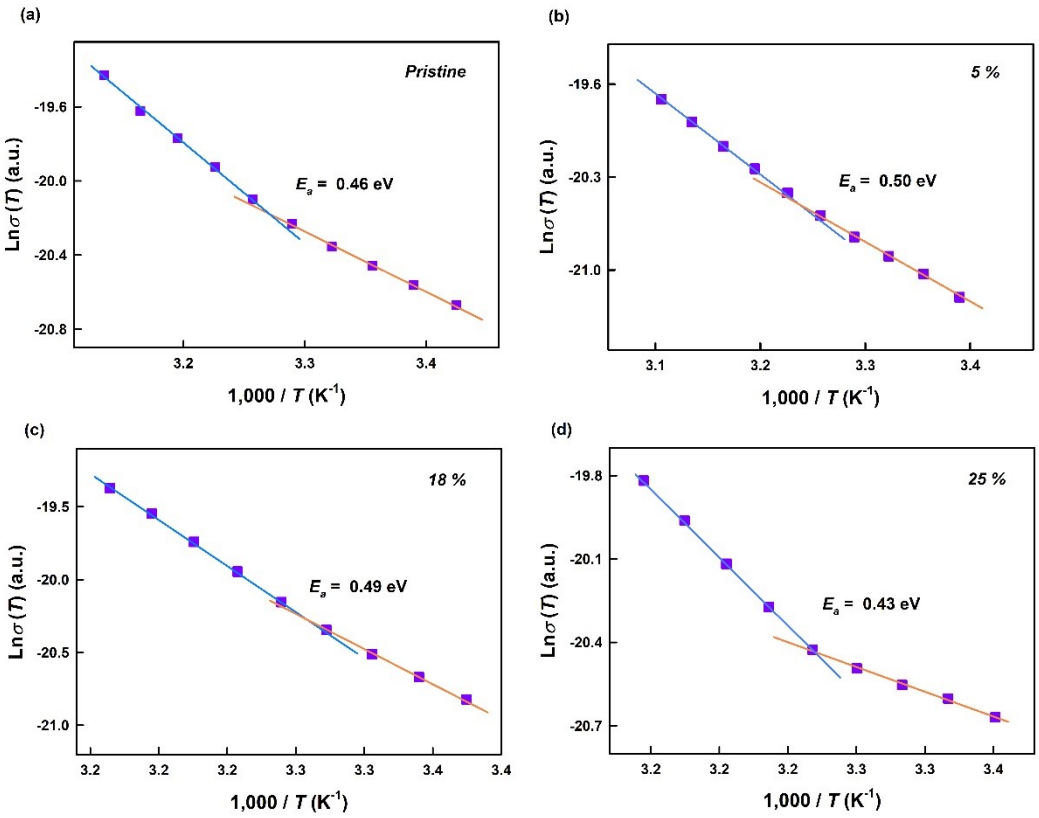

Figure S5. Temperature-dependent conductivity of (a) Pristine, and (b) 5%, (c) 18%, (d) 25% MACl modified $MA_3Bi_2I_9$ films.

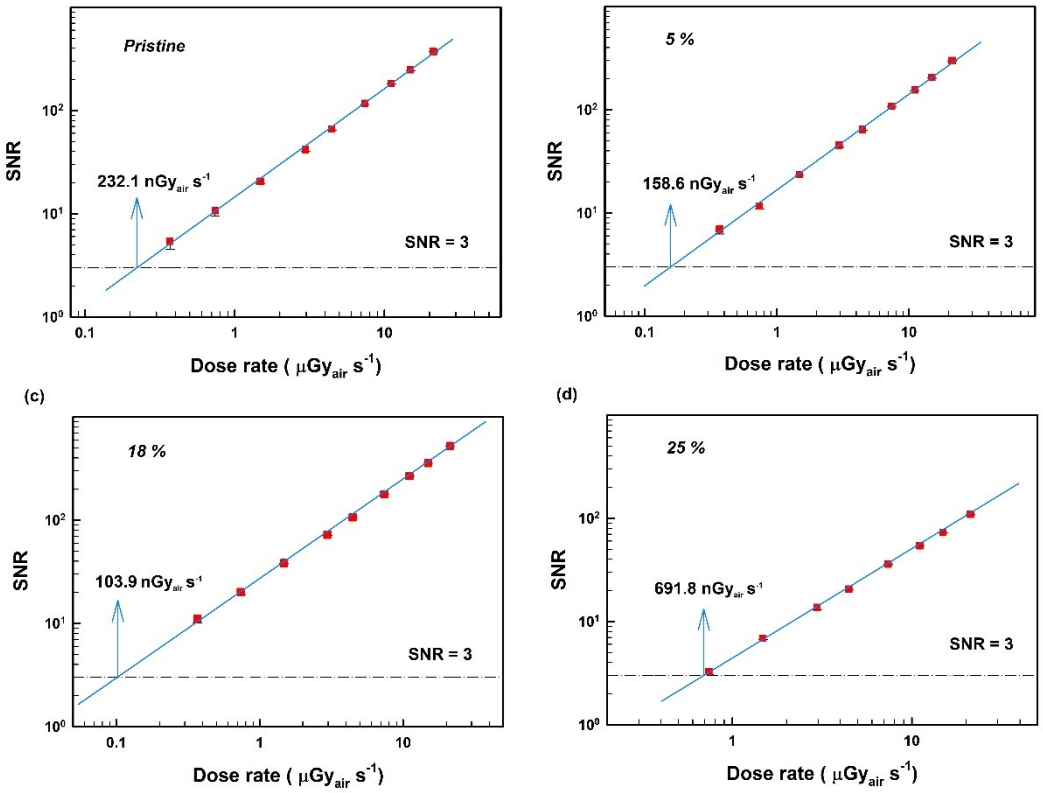

Figure S6. X-ray dose rate dependent signal-to-noise ratio (SNR) of (a) Pristine, and (b) 5%, (c) 18%, (d) 25% MACl modified $MA_3Bi_2I_9$ films under a bias 15 V, and the error bars represent the standard deviation. The LoD is derived from the fitting line with an SNR of 3.