Electronic Supplementary Information (ESI)

Bismuth Chalcogenide Iodides of $Bi_{13}S_{18}I_2$ and BiSI: Solvothermal Synthesis, Photoelectric Behavior, and Photovoltaic Performance

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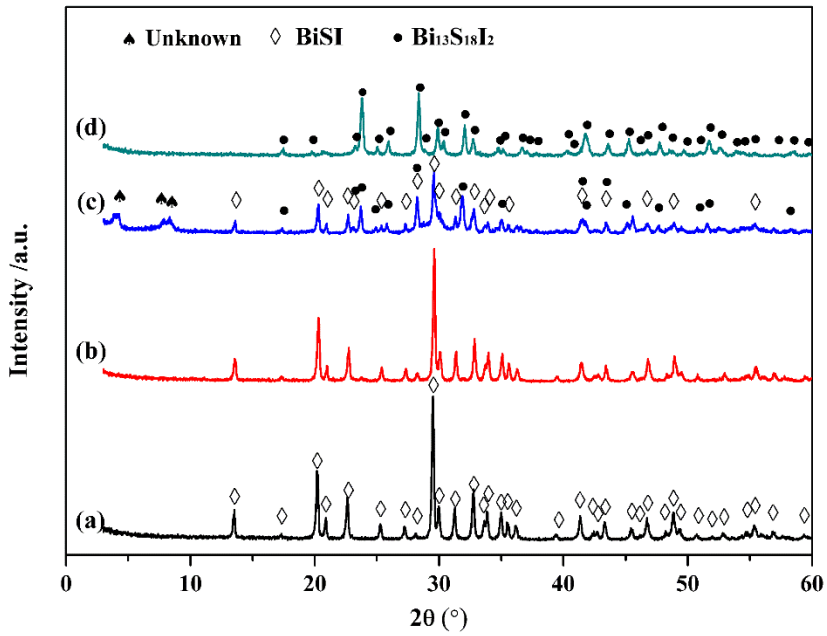

Fig. S1-A. XRD patterns of products synthesized by solvothermal treatments of MAI-BiI_3-CH_4N_2S mixtures with CH_4N_2S/BiI_3/MAI mole ratios of (a) 1:2:3, (b) 2:2:3, (c) 4:2:3, (d) 8:2:3 at 140 ^oC for 12 h, respectively.

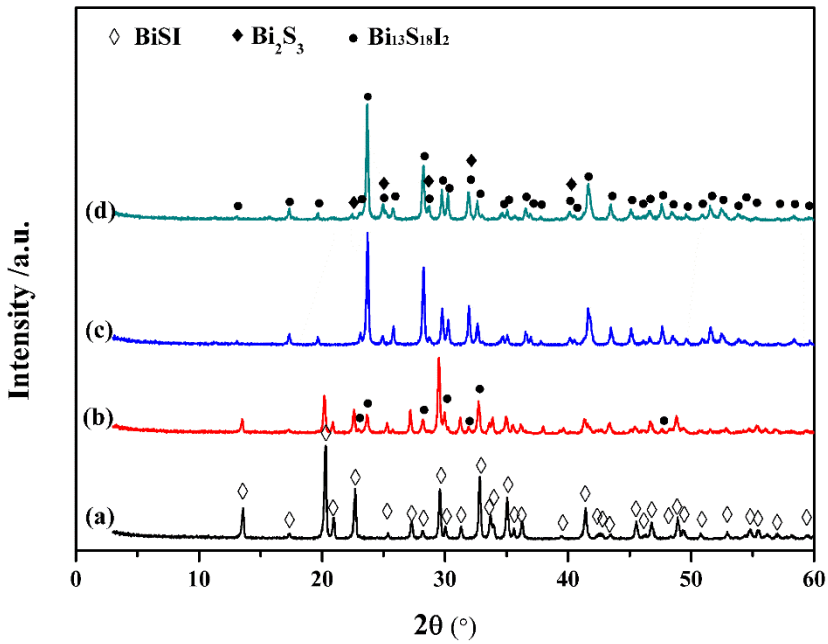

Fig. S1-B. XRD patterns of products synthesized by solvothermal treatments of MAI-BiI_3-CH_4N_2S mixtures with CH_4N_2S/BiI_3/MAI mole ratios of (a) 1:2:3, (b) 2:2:3, (c) 4:2:3, (d) 8:2:3 at 170 ^oC for 12 h, respectively.

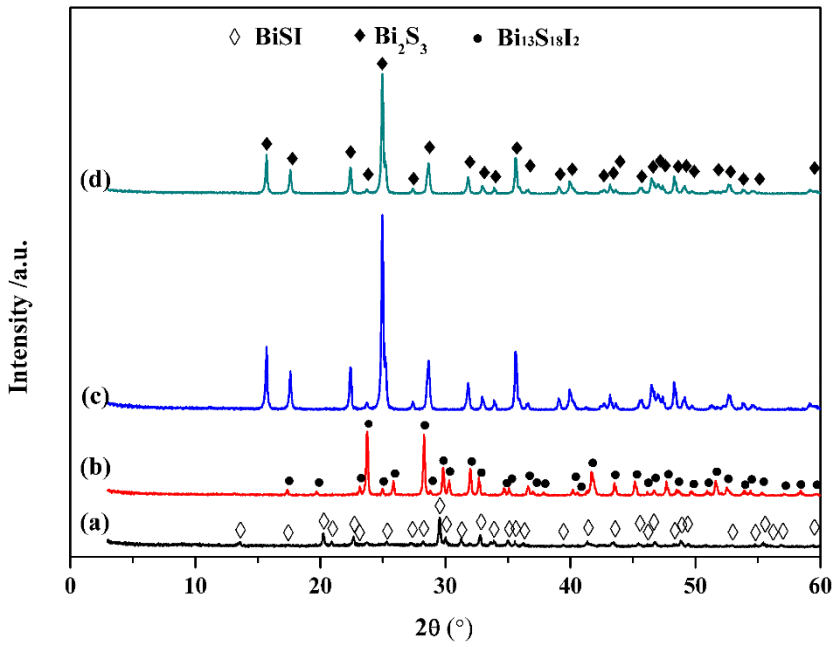

Fig. S1-C. XRD patterns of products synthesized by solvothermal treatments of MAI-BiI_3-CH_4N_2S mixtures with CH_4N_2S/BiI_3/MAI mole ratios of (a) 1:2:3, (b) 2:2:3, (c) 4:2:3, (d) 8:2:3 at 210 ^oC for 12 h, respectively.

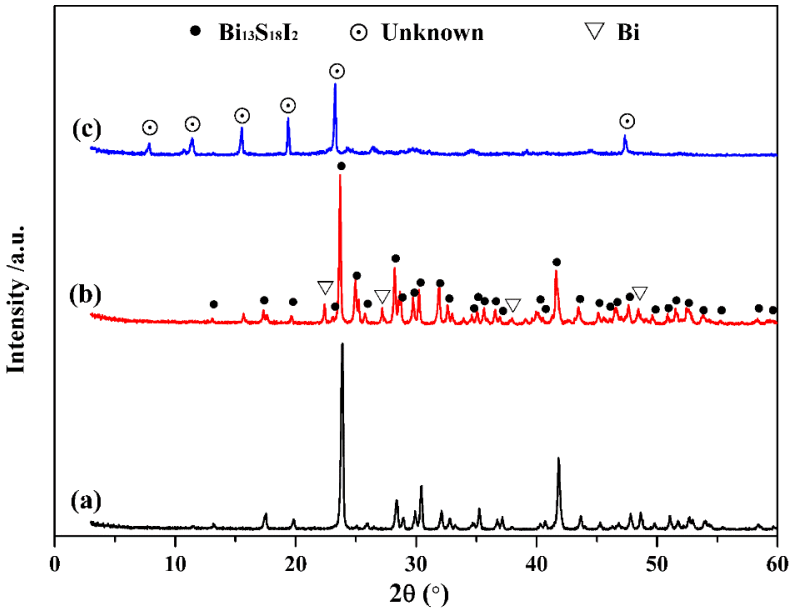

Fig. S2. XRD patterns of products synthesized by solvothermal treatments CH_4N_2S-BiI_3-MAI mixture with CH_4N_2S/BiI_3/MAI mole ratio of 4:2:3 in (a) acetone, (b) DMF and (c) DMSO solvents at 195 ^oC for 12 h, respectively.

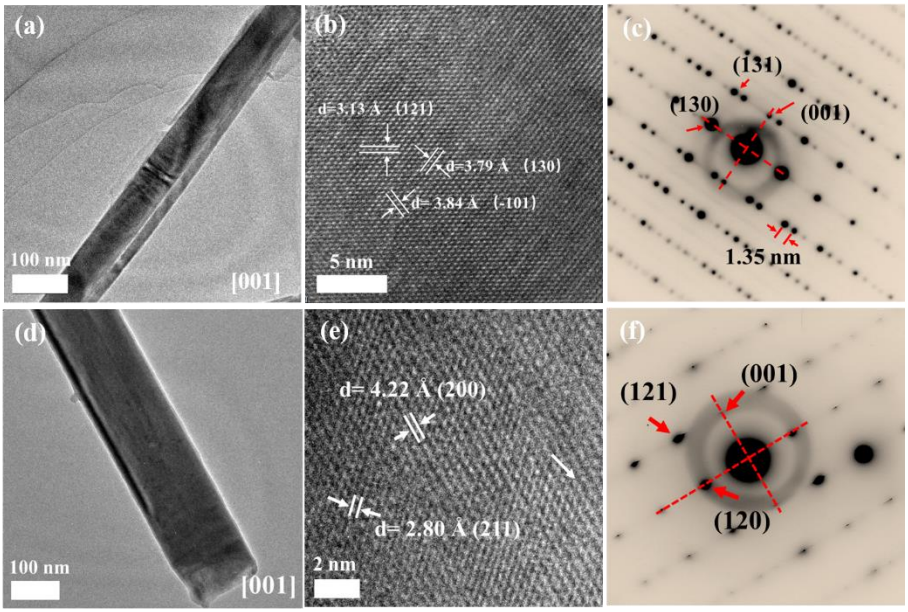

Fig. S3. (a, d) TEM images, (b, e) HRTEM images, and (c, f) SAED patterns of (a, b, c) $Bi_{13}S_{18}I_2$ and (d, e, f) BiSI nanorods, respectively.

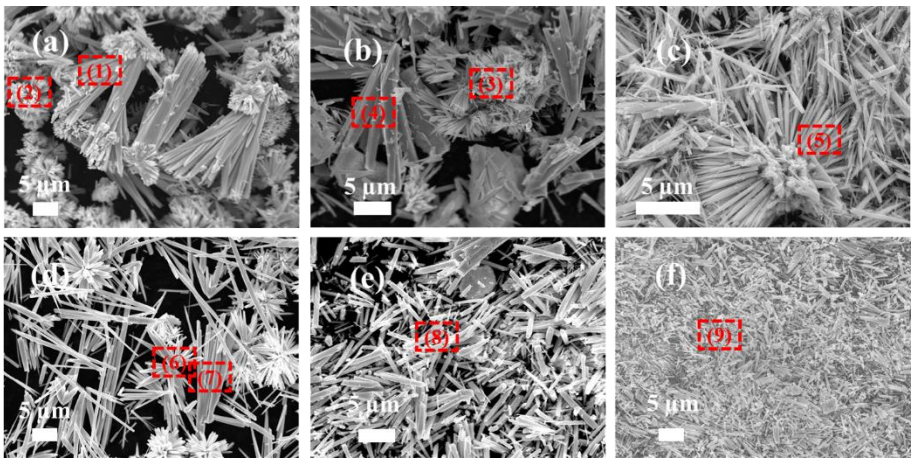

Fig. S4-A. FE-SEM images of products synthesized by solvothermal treatments of solution with CH_4N_2S/ BiI_3/MAI mole ratio of 4:2:3 at 195 ^oC for (a) 0.5, (b) 1, (c) 2, (d) 4, (e) 6, (f) 12 h, respectively. Selected Energy Dispersive X-ray spectroscopy (EDS) analysis positions marked with red boxes.

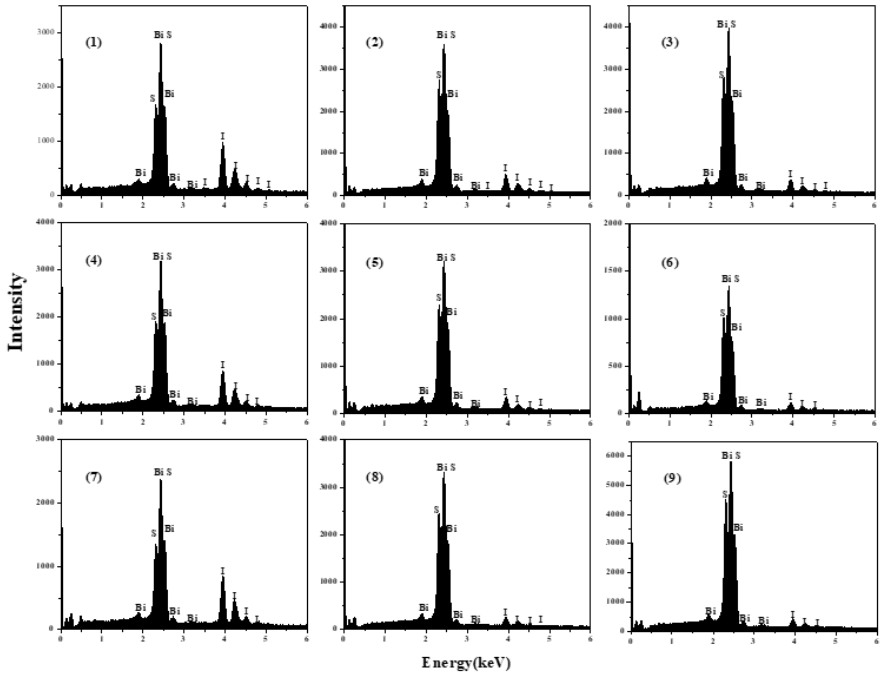

Fig. S4-B. EDS spectra of synthesized products at positions marked in Fig. S4-A. Numbers correspond to positions marked in FE-SEM images of Fig. S4-A.

Table S1. EDS analysis results of atonic percentages of samples at positions of red boxes marked in Fig. S4-A.

Position	**Bi%**	**S %**	**I%**
(1)	33.38	33.81	32.81
(2)	36.60	49.47	13.93
(3)	39.37	50.89	9.73
(4)	35.50	36.68	27.82
(5)	39.78	50.21	10.00
(6)	38.42	53.17	8.41
(7)	33.29	32.07	34.64
(8)	39.39	53.20	7.41
(9)	39.09	54.35	6.56
Expected BiSI	33.3%	33.3%	33.3%
Expected $Bi_{13}S_{18}I_2$	39.4%	54.5%	6.06%

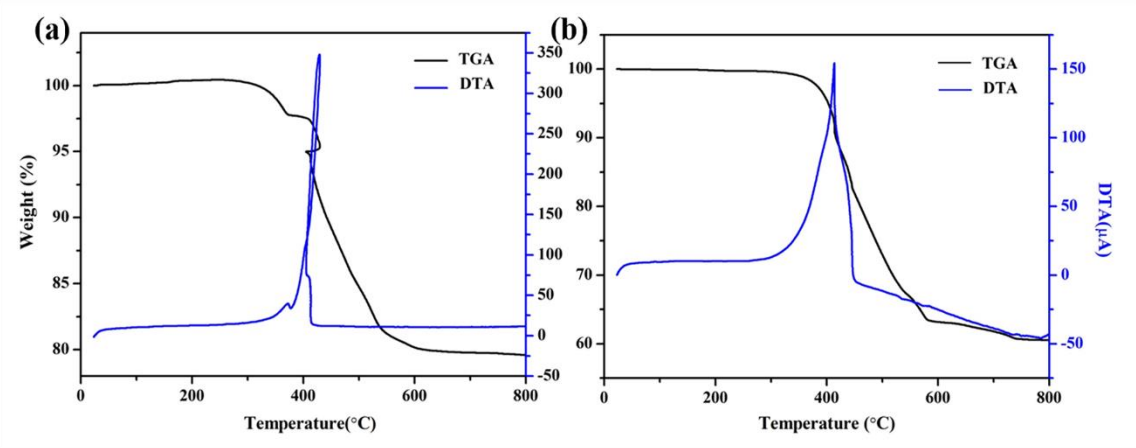

Fig. S5. TGA-DTA curves for (a) $Bi_{13}S_{18}I_2$ and (b) BiSI samples.

There is almost no mass loss up to 300 ^{o}C for $Bi_{13}S_{18}I_2$. The observed mass loss in a temperature range of 350 to 600 ^{o}C of Fig. S5(a) corresponds to the decomposition reaction (1) of $Bi_{13}S_{18}I_2$.

$$4Bi_{13}S_{18}I_2 + 111O_2 \rightarrow 26Bi_2O_3(s) + 72SO_2(g) + 4I_2(g) \quad (1)$$

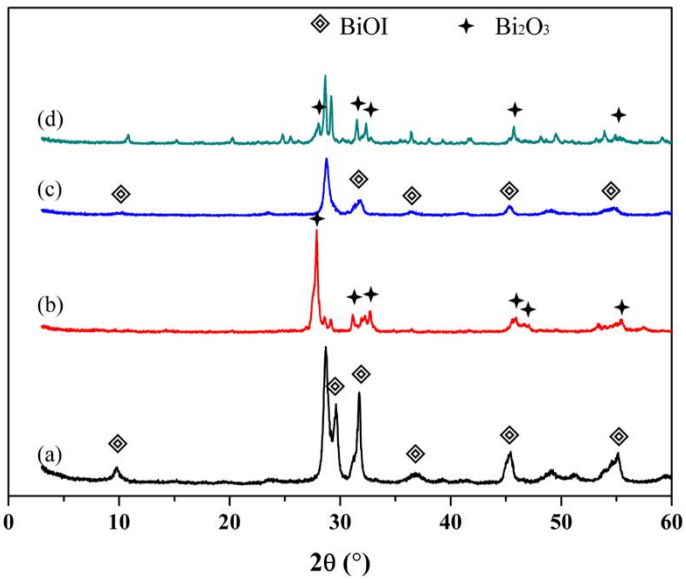

Fig. S6. XRD patterns of $Bi_{13}S_{18}I_2$ sample after heated at (a) 380 ^{o}C and (b) 500 ^{o}C, and BiSI sample after heated at (c) 400 ^{o}C and (d)500 ^{o}C for 2 h, respectively.

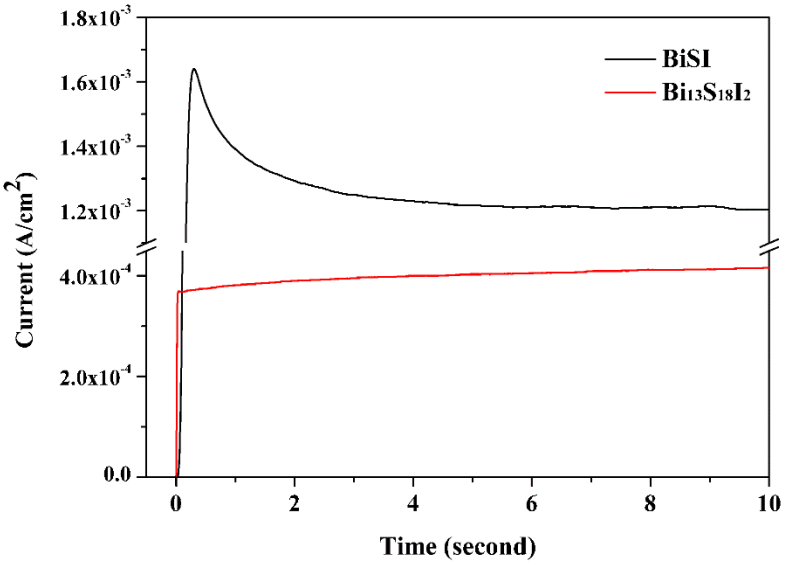

Fig. S7. Dependences of current density of $Bi_{13}S_{18}I_2$ and BiSI pellet samples on time under applied voltage of 100 V, respectively.

For BiSI pellet sample, the current increases with increasing time, and then decreases, finally keeps constant. The current peak at the beginning may be due to a large permittivity of BiSI, which causes a large capacitor effect.[1] The peak area corresponds to charge capacity of capacitor. Such phenomenon is observed usually for ferroelectric materials with large permittivity.

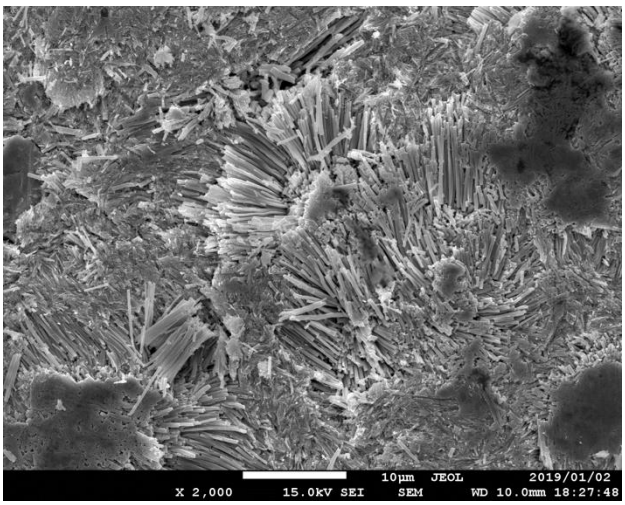

Fig. S8. FE-SEM image of $Bi_{13}S_{18}I_2$ pellet sample fabricated by pressing powder sample.

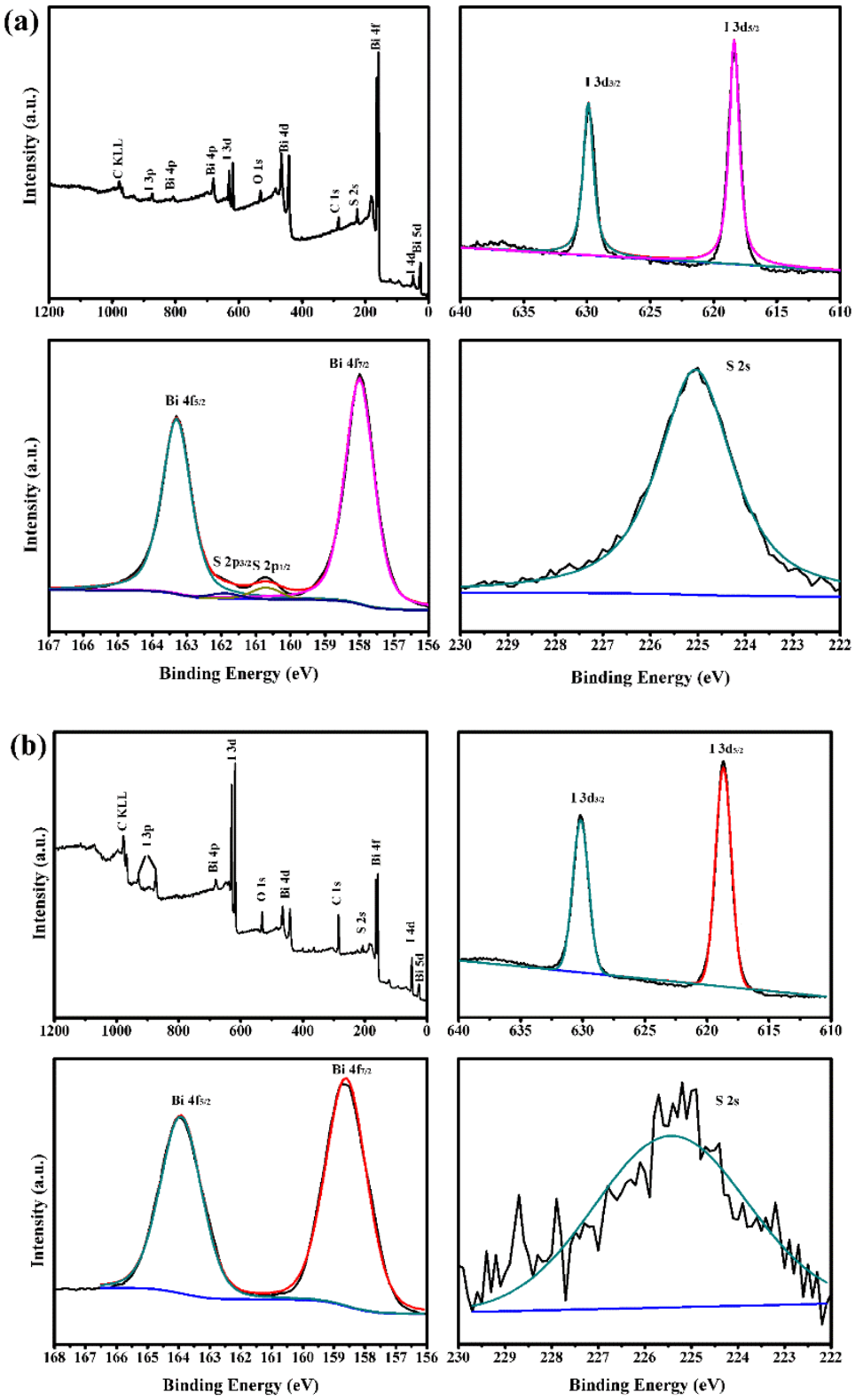

Fig. S9. XPS survey spectra and high-resolution XPS scan spectra of (a) $Bi_{13}S_{18}I_2$ and (b) BiSI samples.

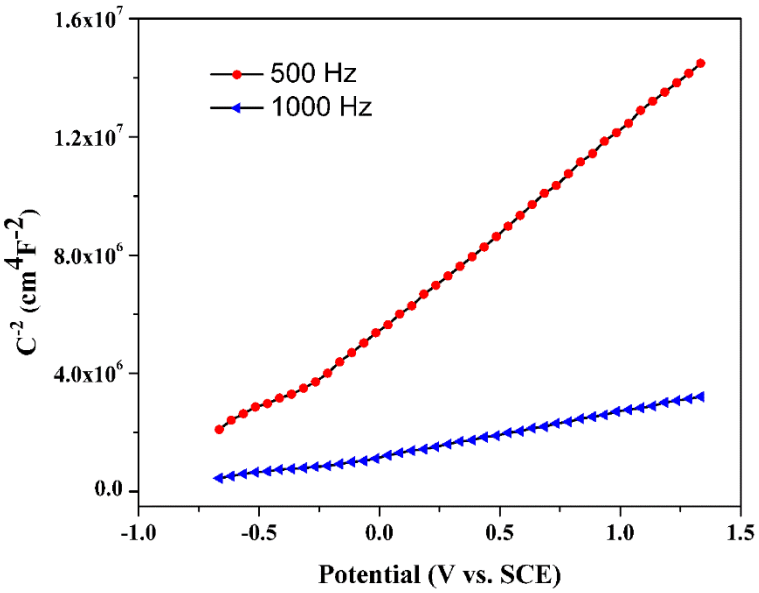

Fig. S10. Mott-Schottky plot for $Bi_{13}S_{18}I_2$ at frequencies of 500 and 1000 Hz.

Table S2. PV performance parameters of solar cells with architecture FTO/TiO_2/$Bi_{13}S_{18}I_2$/Electrolyte solution/Pt under irradiation of AM 1.5.

Cell number	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
1	0.58	3.82	38.3	0.85
2	0.58	3.52	36.5	0.75
3	0.56	3.48	33.4	0.65
4	0.56	3.22	31.1	0.56
5	0.54	3.71	33.4	0.67
6	0.53	3.70	33.6	0.66
7	0.52	3.80	33.9	0.67
8	0.51	3.52	29.3	0.53

References

1. W. Shockley and H. J. Queisser, *Journal of Applied Physics*, 1961, **32**, 510-519.