Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Halogen-free guanidinium-based perovskite solar cell with enhanced stability

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1. **Preparation of perovskite by Lewis acid-base adduct approach.** The Lewis acid–base adduct approach was also applied to prepare the perovskite film on FTO. DMSO, 4-*tert*-butylpyridine (TBP), and thiourea (TU) were used as Lewis bases. The 323 mg of $Pb(SCN)_2$, 118 mg of GASCN, and 78 mg of DMSO (or 135 mg of TBP or 76 mg of TU) (molar ratio 1:1:1) were mixed in 600 mg of DMF at room temperature with stirring, until a clear solution of adduct solution was achieved. Then, the solution was spin-coated on FTO at 3,000 rpm for 25 s, followed by the dripping of 0.5 ml of toluene on the rotating substrate within 10 s. During dripping, the surface was turbid by rapid evaporation of DMF, and become transparent. The adduct film was heated at 65 °C for 5 min, followed by the further heating at different temperatures ((150 to 200) °C) for 30 min.
2. **Preparation of TiO_2 electrodes.** FTO (25 mm × 25 mm) were cleaned by sonication with detergent, distilled water, and a mixture of acetone, IPA, and ethanol with 1:1:1 ratio, separately, in an ultrasonic bath for 20 min. Ultraviolet-Ozone (UVO) was treated for 15 min prior to use. The 0.339 M titanium diisopropoxide dis(acetylacetonate) (75 wt% in isopropanol) in 1-butanol was spin-coated on FTO substrates at 500 rpm for 5 s, 1,000 rpm for 5 s, and 2,000 rpm for 40 s, to prepare the TiO_2 blocking layer (bl-TiO_2), followed by heating at 500 °C for 10 min in heat gun. The bl-TiO_2 was treated with 40 mM aqueous $TiCl_4$ solution at 90 °C for 50 min, and cleaned with distilled water. The films were further heated at 500 °C for 10 min in heat gun. Then, the mesoporous TiO_2 (mp-TiO_2) layer was deposited on the bl-TiO_2 by spin-coating the TiO_2 colloidal solution consisting of 2.7 g TiO_2 nanopac paste (Dyesol, Australia) in 10 ml of anhydrous ethanol at 3,100 rpm for 30 s, which was annealed at 500 °C for 30 min in the box furnace. UVO was treated again for 15 min, prior to use.

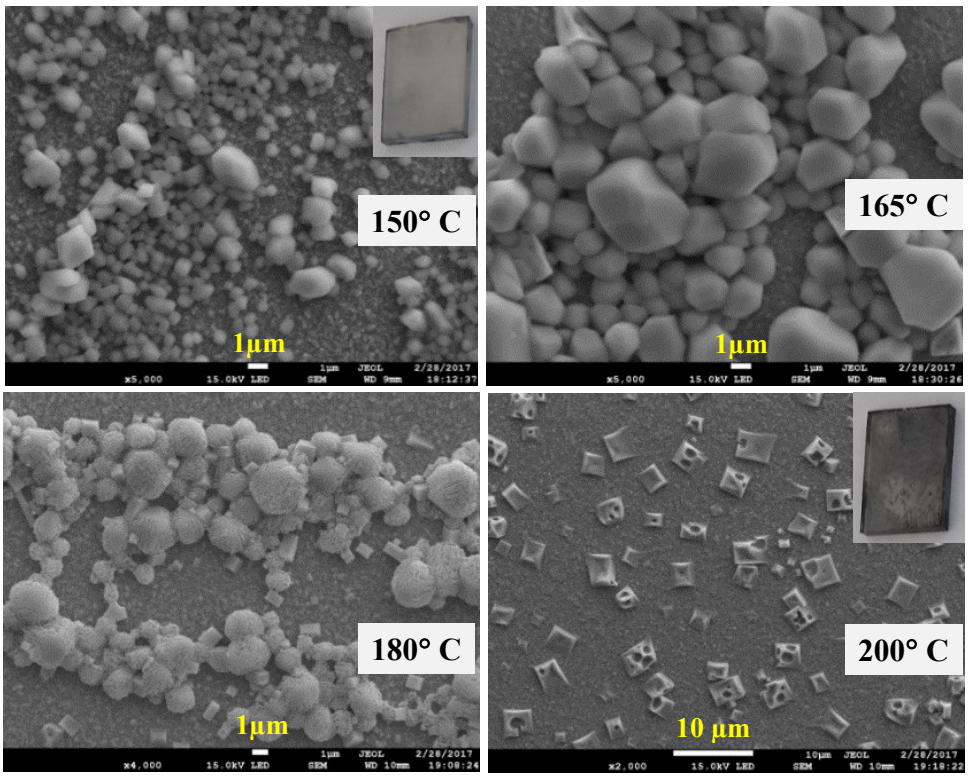

Fig. S1. SEM images of $GAPb(SCN)_3$ perovskites, which were prepared by two-step method, and activated at different temperatures for 30 min (insets show the photographs of compounds on FTOs). At 180 °C, the orthorhombic crystals became porous for the two-step method, indicating the degradation of the perovskite at higher temperature.

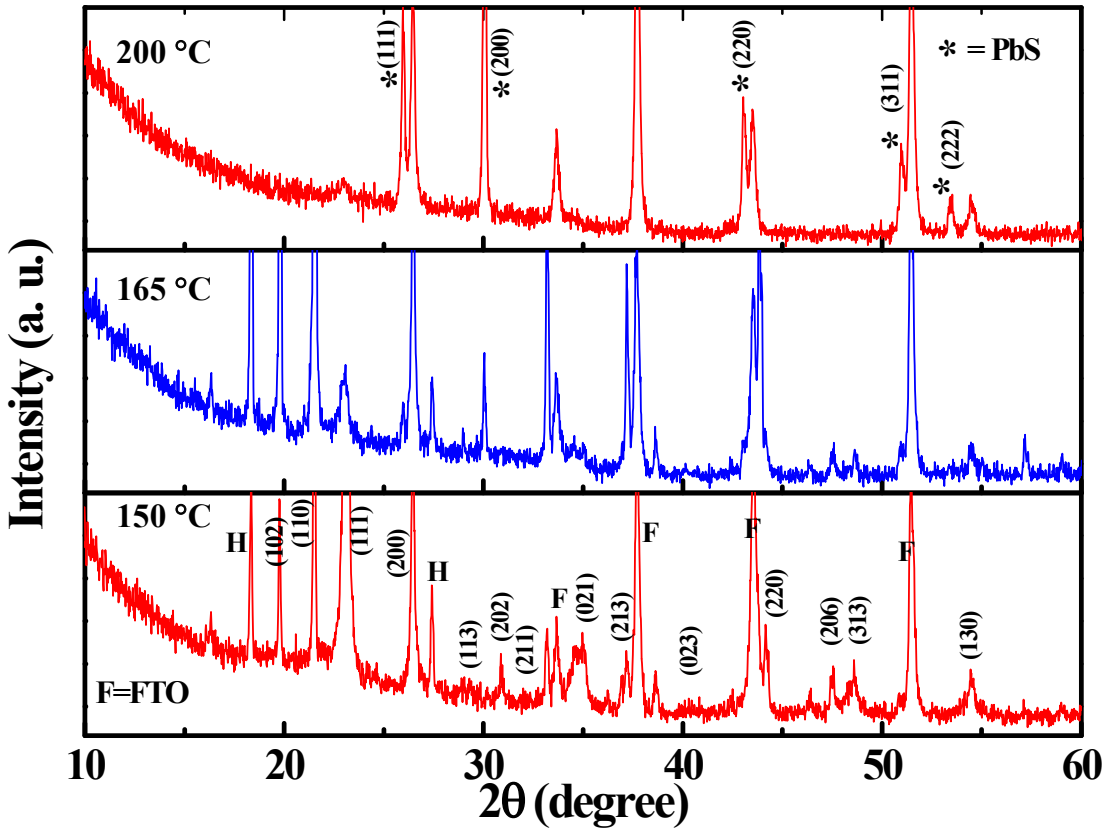

Fig. S2. XRD spectra of $GAPb(SCN)_3$ perovskites prepared by the two-step method, and activated from (150 to 200) °C for 30 min. The XRD responses were more intense for the two-step method, as it showed better crystal growth compared with the one-step. This phenomenon was also consistent with the conventional perovskite, $MAPbI_3$, prepared by the two-step method.[1]

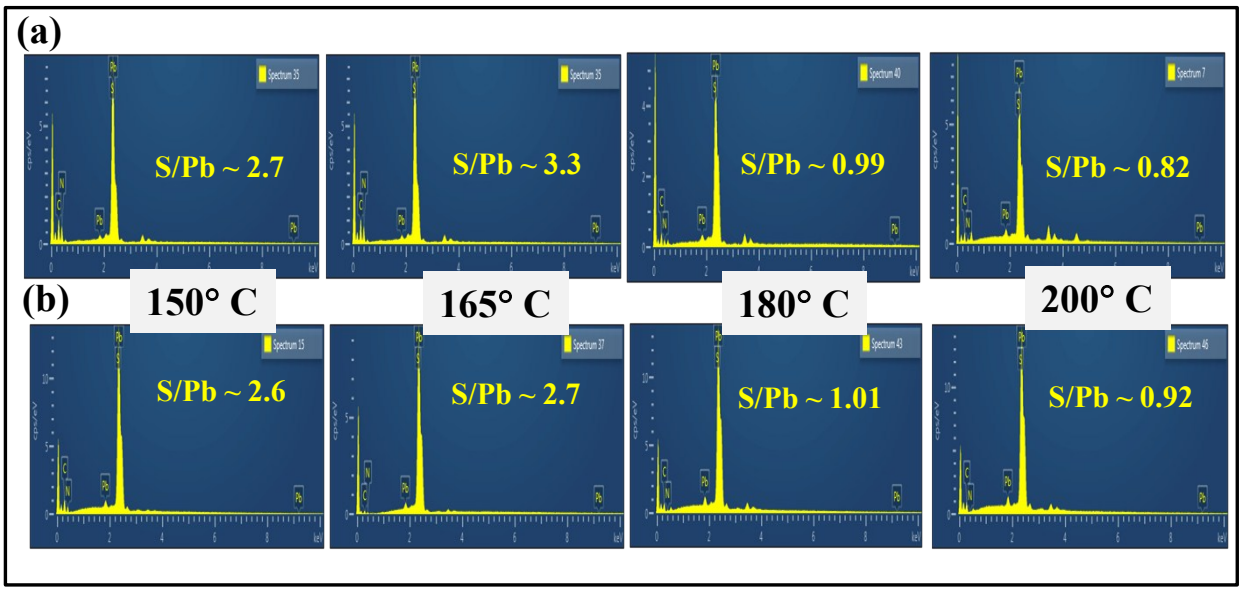

Fig. S3. EDX spectra of $GAPb(SCN)_3$ perovskites, which were prepared by (a) one-step, and (b) two-step methods, and activated at different temperatures for 30 min.

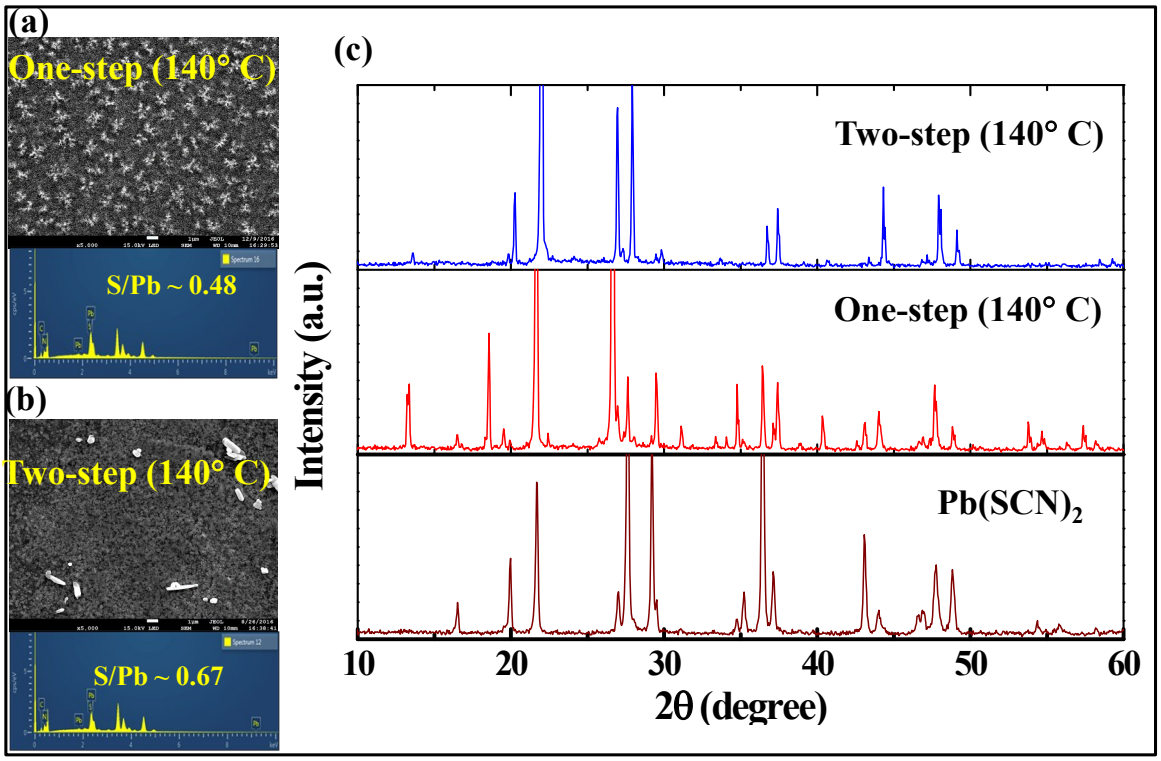

Fig. S4. SEM images with EDX spectra (a and b) and XRD spectra (c) of $GAPb(SCN)_3$ perovskites, which were prepared by (a) one-step, and (b) two-step methods and activated at 140 °C for 30 min.

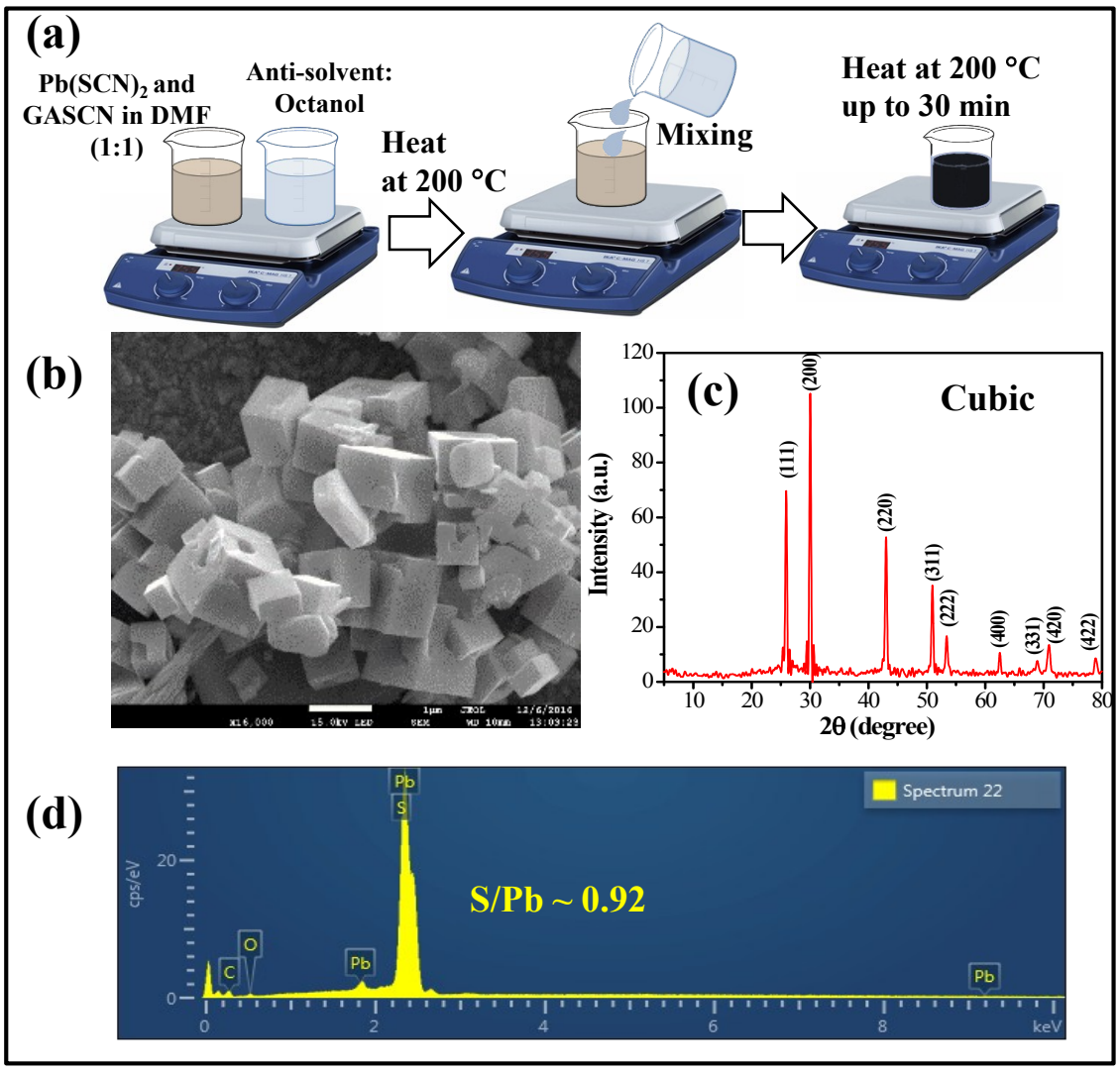

Fig. S5. (a) Synthetic scheme, (b) SEM image, (c) XRD, and (d) EDX spectra of PbS prepared by the anti-solvent method, with octanol heated at 200 °C for 30 min.

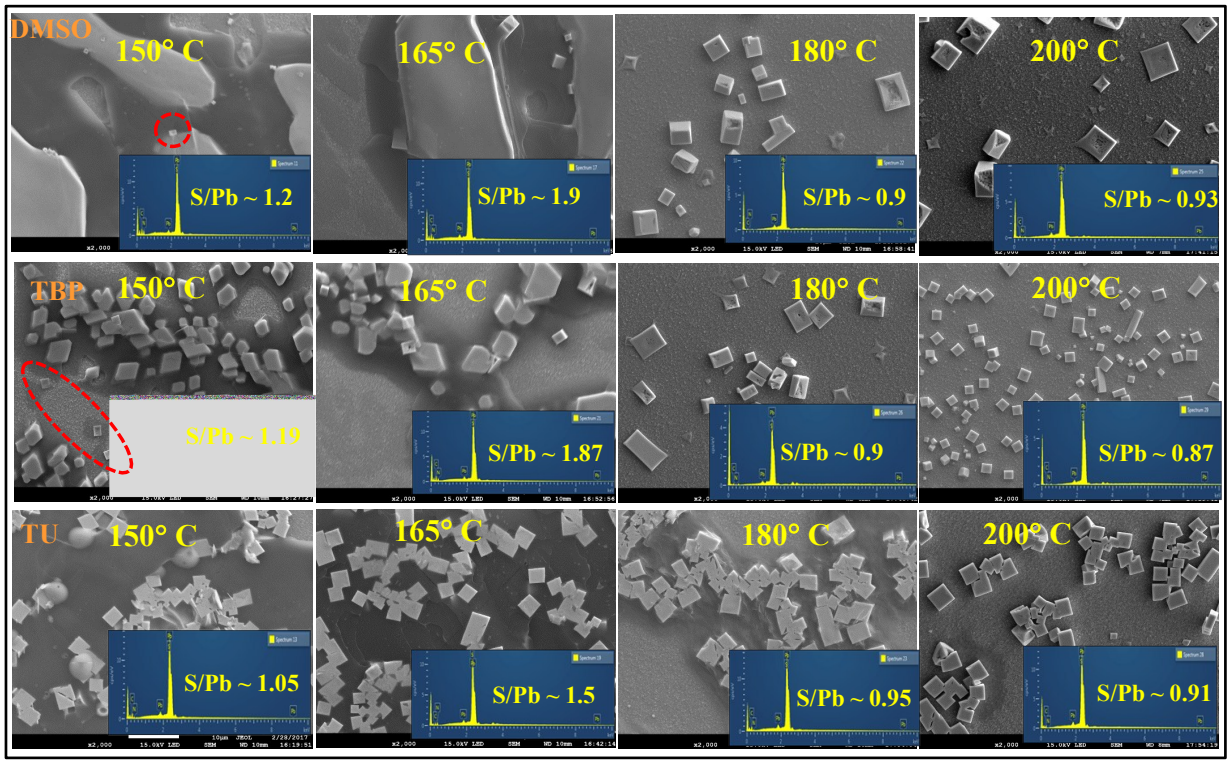

Fig. S6. SEM images and EDX spectra of $GAPb(SCN)_3$ perovskites prepared by the Lewis acid–base adduct approach with DMSO, TBP, and TU as adductants, and activated at (150 to 200) °C for 30 min.

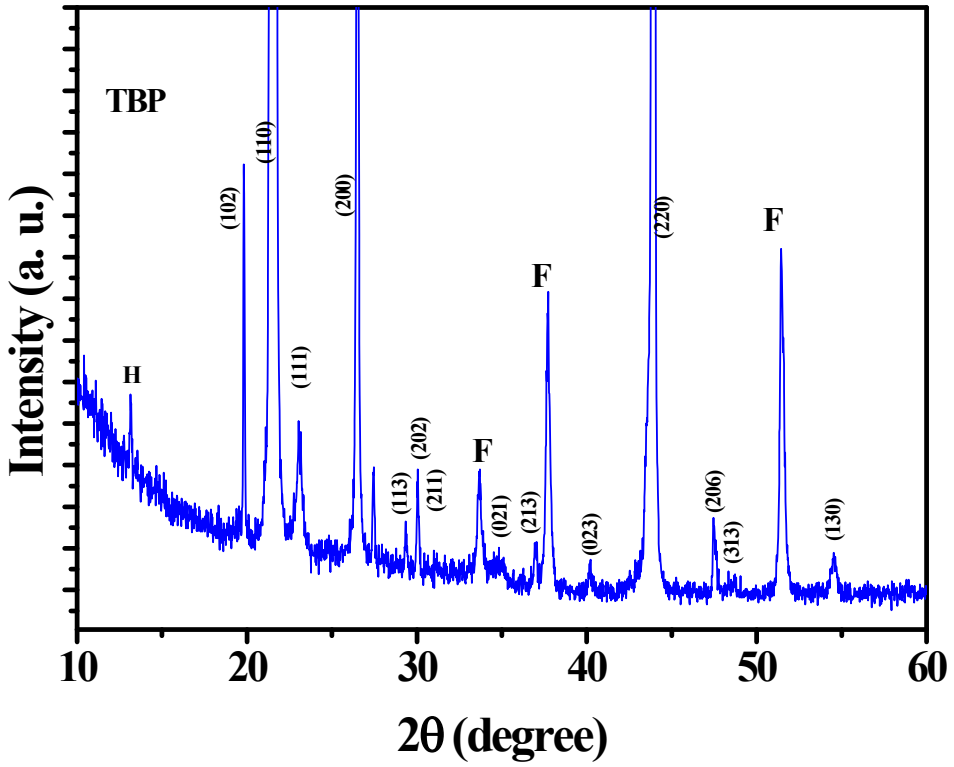

Fig. S7. XRD spectra of $GAPb(SCN)_3$ perovskites prepared by the Lewis acid–base adduct approach with TBP, and activated at 150 °C for 30 min.

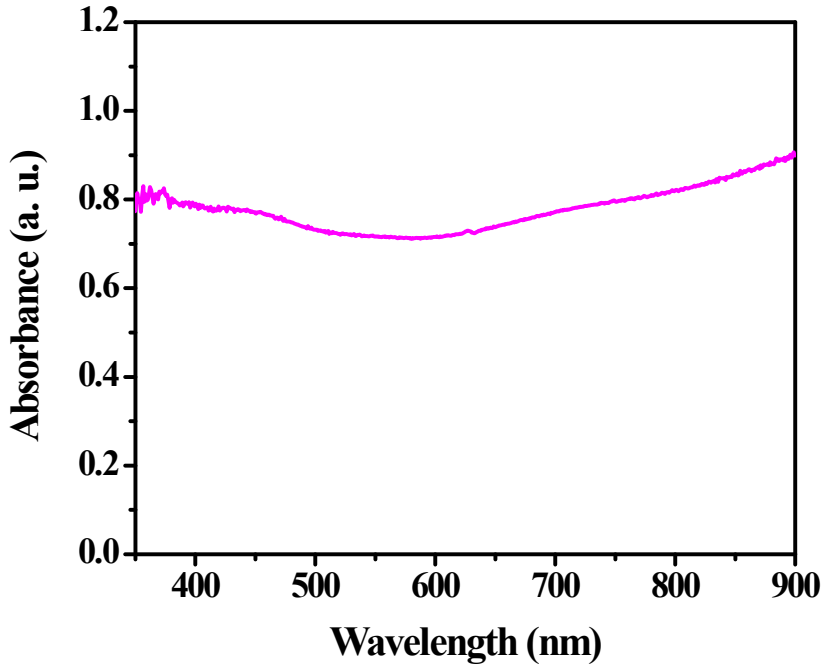

Fig. S8. UV-Vis spectra of $GAPb(SCN)_3$ perovskites prepared by two-step method, and activated at 150 °C for 30 min. It showed a broad absorption shoulder at long visible region, due to the formation of larger crystals.

[1] J.-H. Im, I.-H. Jang, N. Pellet, M. Grätzel, N.-G. Park, Growth of CH3NH3PbI3 cuboids with controlled size for high-efficiency perovskite solar cells, Nat. Nanotech. 9(11) (2014) 927-932.