Thermochromism to tune the optical bandgap of a lead-free perovskite-type hybrid semiconductor for efficiently enhancing photocurrent generation†‡

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Thermochromic materials have recently attracted great attention due to their controllable and rich physicochemical properties. However, until now, no studies have been reported on thermochromic materials for photovoltaic and optoelectronic applications. Here we report a new lead-free hybrid semiconductor material, (C6H20N2)SbBr5 (1), which adopts the zero-dimensional (0-D) perovskite-type inorganic framework. Strikingly, the thermochromism in 1 leads to a wide tunable bandgap and superior photovoltaic properties. Three distinct color-varying stages were first observed, i.e. colorless to yellow (I), yellow to red (II), and red to black brown (III). In particular, the figure-of-merits for thin-film photodetectors based on II-thermochromism were greatly improved, with the dark current lowered to one quarter and light photocurrent enhanced at least 12-fold. The photocurrent on/off switching ratio was thus improved by ~ 50 times through thermochromism. As a new conceptual strategy to engineer the optical bandgap and meet specific photoelectric functions, our study paves the way for building high-performance optoelectronic devices based on thermochromic materials.

The development of stimuli-responsive smart materials has caught much attention because of their potential physicochemical properties,1 such as photochromic,2,3 piezochromic,4,5 halo-chromic,6 and thermochromic7–10 behaviors. Thermochromic materials, which enable the optical bandgap to be altered in response to a temperature change, have been studied by researchers for centuries and have made tremendous progress.11,12 However, controllable thermochromic materials are still rarely applied in the fields of photovoltaics and optoelectronics, although diverse thermochromic systems have been explored, such as photonic systems,13 surface plasmon absorption14 and quantum dots,15 etc. Recently, hybrid organic–inorganic perovskite-type semiconductor materials have taken a dominant position within the fastest growing areas of materials chemistry because their chemical diversity exhibits vast opportunities for creating technologically optical and electronic properties.16 The most notable compounds are organometal trihalide perovskites (CH3NH3PbX3, X = Cl, Br and I), which have boosted the photovoltaic conversion efficiency higher than 22.1%,17–21 catching up with commercial silicon-based solar cells. For these hybrids, tunable optical absorption plays an increasingly important role for their photoelectric application.22 For instance, the chemical substitution of halogens in CH3NH3PbX3 enables tunable bandgaps in the range of 2.97–1.53 eV, which is favorable for diverse functions.23,24 Meanwhile, the modification of cationic components in two-dimensional (2-D) perovskite hybrids, such as (RNH3)2(CH3NH3)X2PbX6 (where R = an alkyl or aromatic moiety and X = Cl, Br or I), has also fueled enormous interest for optoelectronic researchers.25,26 The previously-reported method for changing the optical absorption bandgap consists of controlling organic cations and/or halogens.27,28 These studies, however, only extend the absorption range to a specific wavelength.29 In this context, it still remains challenging to continuously tune the bandgaps of hybrid perovskites to the wide visible-light range. Alternatively, pioneering studies reveal that the colors of metal-halide hybrids could be changed by the expansion or contraction of the metal and halide interatomic distances.30 This mechanism suggests that thermochromism might act as an effective strategy to engineer optical bandgaps and to improve the potential optoelectronic performance.
In this work, we attempted to explore new thermochromic candidates in the organic–inorganic lead-free\(^1\) perovskite hybrids for potential photovoltaic applications. As some of the most outstanding charge-transfer units, configuration-locked stilbazolium chromophores have been found to show structural changes in which the C=C bonds generally behave as photoactive moieties. Herein, we report the first lead-free organic–inorganic thermochromic hybrid, (\(\text{C}_{16}\text{H}_{20}\text{N}_{2}\))\(\text{SbBr}_5\) (compound 1, \(\text{C}_{16}\text{H}_{20}\text{N}_{2}\text{SbBr}_5\) is 1,3-dimethylamino-styryl)-2,4-(4-methyl-pyridinium)-cyclobutane), which features a 0-D perovskite-type inorganic binuclear framework. It is noteworthy that 1 undergoes three distinct color-changing stages, i.e., colorless to yellow (I), yellow to red (II), and red to black brown (III). This unprecedented thermochromism extends to widely tunable optical bandgaps, ranging from 2.5 to 1.5 eV, which is almost comparable with those of \(\text{CH}_3\text{NH}_3\text{PbI}_3\).

Bulk yellow crystals of 1 were obtained from a concentrated hydrobromic acid (HBr) solution of antimonous oxide (\(\text{Sb}_2\text{O}_3\)) and trans-4-(4-dimethylanilino-styryl)-N-methyl-pyridinium iodide (DAM\(\text{S}^+\)) by slow evaporation at room temperature. The purities and structures were confirmed by infrared spectroscopy (IR) and \(^1\)H NMR (Fig. S1, ESI\(\uparrow\)). Details on the sample preparation and basic characterization are given in the methods section in the ESI\(\uparrow\). As shown in Fig. 1a, crystal 1 crystallizes in the monoclinic system with a space group of \(\text{P}2_1/\text{a}\) (Table S1, ESI\(\uparrow\)). The asymmetric unit contains one \([2+2]\) photodimerization of DAM\(\text{S}^+\) and half of a \(\text{Sb}_2\text{Br}_{10}\) anionic cluster. The binuclear unit \([\text{Sb}_2\text{Br}_{10}]^{14-}\) clusters make a dominant contribution to charge transport in 1, resembling that of tin- and lead-based perovskites.

Ammonium counter-cations ([\(\text{C}_{16}\text{H}_{20}\text{N}_{2}\text{S}^{2+}\)]) are situated inside the cavities and are bonded to the binuclear unit \([\text{Sb}_2\text{Br}_{10}]^{14-}\) through N–H···Br hydrogen bonds (Fig. S5, ESI\(\uparrow\)). Each organic cation was clamped with alternate binuclear units Sb–Br along the a-direction, forming a 0-D perovskite-like anionic framework. It is noteworthy that 1 displays rich thermochromic behaviors, changing from colorless to black brown in the range of 100–500 K, which was observed by single crystal X-ray diffraction at different temperatures. As shown in part c of Fig. 1, the room-temperature yellow crystals of 1 gradually turned colorless upon cooling down to 100 K. Contrarily, the crystal color changed to red (~450 K) and black-brown (~500 K) in the heating mode. For convenience, the thermochromic course was approximately sorted into three stages: colorless to yellow (I, 100–350 K), yellow to red (II, 350–450 K) and red to black brown (III, 450–500 K). However, the black-brown crystals could not return to yellow upon cooling, but remained stable in the red-color state to 300 K (the cooling stage in Fig. 2a (C–RT) and Fig. S8, ESI\(\uparrow\)). Here, the thermochromism-induced color variations of 1 between the yellow and red states provide an excellent platform for assembling potential photodetectors.

For a deeper understanding of this thermochromic phenomenon, a crystal wafer of 1 with a thickness of ~0.8 mm was heated and kept at the corresponding temperatures for five minutes. Then ultraviolet-visible absorption spectra were collected at room temperature on a LAMBDA 950 UV/Vis Spectrophotometer. As shown in Fig. 2a and Fig. S6a (ESI\(\uparrow\)), the curves of 300, 325 and 350 K almost overlap, which illustrates that 1 is reversible in this temperature range (stage I). Within the temperature range of 350 to 450 K, the absorption edges were obviously red-shifted to ~680 nm, corresponding to a bandgap of 1.85 eV. However, the red color of the sample heated at 450 K remained stable even as the temperature cooled down to room temperature, behaving as the metastable state, which reveals that thermochromism-II...
is irreversible. A low bandgap of ~1.5 eV was further achieved through thermochromism-II, as revealed by the edge of the curve obtained at 500 K. Unexpectedly, the black color at 500 K was unstable, and returned to a red color as the temperature decreased to 300 K (as shown in the C-RT trace).

Structural transformation or phase transition is closely associated with color changes in thermochromic compounds. Hence, variable-temperature PXRD patterns and dielectric constants were performed on single crystals, which showed that the thermochromic behavior was not caused by structural phase transition (Fig. S3, S4 and S9, ESI†). Moreover, some studies disclose that thermochromism is likely induced by the variation of Sb–Br interatomic distances. To certify the structural evolution with temperature, crystallographic data of 1 were collected from different batch samples at 100, 295, 300, 400 and 295 K (preheated at 450 K) (Table S2, ESI†). Fig. 1c and 2b show that the Sb–Br bond lengths contract with an increase in temperature and recover after cooling down to 295 K. However, the Sb–Br1 and Sb–Br2 bonds could not return back to their original states. This is proposed to be one possible reason why crystals still display a red color at 300 K after heating. The bond changes were also confirmed by Raman spectroscopy (Fig. 2c) using a 532 nm laser under ambient conditions. The bond changes were also confirmed by Raman spectroscopy (Fig. 2c) using a 532 nm laser under ambient conditions.

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To further study the optical absorption and electronic mechanisms of the semiconducting properties, density functional theory was used to calculate the bandgaps of 1 at 400 and 450 K. The calculated values are 1.93 and 1.76 eV, which are in good accordance with the experimental results (1.92 and 1.8 eV, Fig. S6, ESI†).

Owing to the temperature stability of the samples in thermochromism-II, thin-film photodetectors were fabricated via spin-coating of a dimethylsulfoxide solvent followed by temperature annealing (400 K, 10 min) under a nitrogen atmosphere, and identified by X-ray diffraction (Fig. 2d). Most of the Bragg main peaks were indexed through the simulated and PXRD patterns, indicating that 1 is stable and easy to crystallize in thin films. The surface topography and electrical properties of the thin films were characterized by atomic force microscopy (AFM) and conducting atomic force microscopy (C-AFM) at the nanoscale. Fig. 3a and b show the surface topography changes obviously after heating from 400 to 450 K, with a decrease in the surface roughness from 9.3 to 7.1 nm, revealing that the film quality was improved by heating treatment. Furthermore, the C-AFM method uses a conductive tip to measure the surface conductivity of thin-films by the contact mode. The conductivity images shown in Fig. 3c and d display that both temperature states had weak electric currents over most of the sample area. The roughnesses of these conductive areas were between ~9.1 and 9.3, and ~5.3 and 7.1 nm, respectively. The sizes and distribution patterns are almost the same for the thin films. Most strikingly, the current density of the conductivity peaks at 400 K (~4.08 pA) is obviously higher than that at 450 K (~3.37 pA), which indicates that the dark current was reduced through thermal-induced thermochromism (see Fig. S7, ESI†). Some conductive areas appear to be clustered together at the same location, whereas others appear to be completely isolated. This phenomenon might be associated with the grain boundaries on the thin-films and the intrinsic reasons such as a lower dark current might be relative to the variation of the Sb–Br interatomic distances.

To further evaluate the effects of stable thermochromism-II on photoelectric behaviors, thin-film photodetecting devices were fabricated using the thermochromic crystals preheated at 400 and 450 K. The lateral device architecture was employed and photo-excitation was performed under a light source with a 300 mW cm−2 xenon lamp at room temperature (Fig. 4a). As illustrated in Fig. 4b, the device based on the 400 K sample exhibited a low dark current (~10−10 A), and under illumination the corresponding photocurrent rapidly increased to about 15-fold the dark current. In comparison, the light current of the device based on the 450 K sample was obviously enhanced about 10-fold, and the dark current became one quarter of that of the 400 K sample. In detail, at a voltage of 10 V, the light-induced photocurrent was enhanced from 1.645×10−10 (400 K) to 3.124×10−8 (450 K). The corresponding dark current was lowered from 1.645×10−10 (400 K) to 2.376×10−11 (450 K). As a result, the “on/off” switching ratio was improved by at least ~50 times through thermochromism. The time-dependent photocurrent response of the device with a 520 nm laser operated at a bias voltage of 5 V and an incident power of 100 μW mm−2 is shown in Fig. 4c. The multi-switching measurements show that the switching was steady and reversible, which could allow the device to act as a photosensitive switch. In addition, it distinctly shows that the dark current was decreased and light photocurrent was enhanced by the 520 nm laser. The rise and decay times of the film device based on the 450 K
sample were estimated to be 0.079 s and 0.0168 s, which are almost equivalent to those measured on the device based on the 400 K sample (0.105 s and 0.0171 s, Fig. 4d). This remarkable enhancement in the device photo-detection performance is greatly attributed to the thermochromism-induced narrower bandgaps, which are closely associated with the electronic structure of the Sb–Br binuclear frameworks. A previous report on the iodo-bismuthate hybrid [metal(1,10-phen)$_3$][Bi$_3$I$_{11}$],$	extsuperscript{17}$ showed that thermochromism enables photodetecting materials to broaden their absorption capability. In the case of 1, thermochromism plays a dominant role in tuning its optical bandgap, which greatly enhances the photocurrent generation. To the best of our knowledge, this is the first report on thermochromism to enhance the photodetecting performance in hybrid materials.

In summary, we have reported a new lead-free perovskite hybrid semiconductor, of which the optical bandgap is widely tuned by thermochromism ranging from 2.5 to 1.5 eV. It is notable that crystal 1 exhibits three distinct thermochromic stages: colorless to yellow (I), yellow to red (II) and red to black brown (III). Based on the stable II-thermochromism stage, we developed a new conceptual strategy to improve the intrinsic photo-responses of thin-film photodetectors for the first time. Through thermochromism, the photocurrent was enhanced at least 12-fold, the dark current was lowered to about one quarter, and the photocurrent on/off switching ratio was greatly improved by ~50 times. Our study may open up a new avenue to exploit the stimuli-responsive smart candidates of perovskite hybrids for device application in the field of optoelectronics.

Conflicts of interest

There are no conflicts to declare.

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Notes and references