



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Mousavi, Seyede Maryam; Alidaei, Maryam; Arabpour Roghabadi, Farzaneh; Ahmadi, Vahid; Sadrameli, Seyed Mojtaba; Vapaavuori, Jaana

Stability improvement of MAPbl₃-based perovskite solar cells using a photoactive solid-solid phase change material

Published in: Journal of Alloys and Compounds

DOI: 10.1016/j.jallcom.2021.163142

Published: 15/03/2022

Document Version Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Published under the following license: CC BY-NC-ND

Please cite the original version:

Mousavi, S. M., Alidaei, M., Arabpour Roghabadi, F., Ahmadi, V., Sadrameli, S. M., & Vapaavuori, J. (2022). Stability improvement of MAPb1 -based perovskite solar cells using a photoactive solid-solid phase change material. *Journal of Alloys and Compounds*, *897*, Article 163142. https://doi.org/10.1016/j.jallcom.2021.163142

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Stability improvement of MAPbI₃-based perovskite solar cells using a photoactive solid-solid phase change material

Seyede Maryam Mousavi^{1,2}, Maryam Alidaei³, Farzaneh Arabpour Roghabadi^{1,3*}, Vahid Ahmadi³, Seyed Mojtaba Sadrameli^{1,4*}and Jaana Vapaavuori²

¹ Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box: 14115-114, Tehran, Iran

² Department of Chemistry and Materials Science, Aalto University, Espoo, Finland
 ³Optoelectronics and Nanophotonics Research Group, Faculty of Electrical and Computer
 Engineering, Tarbiat Modares University, Tehran, Iran

⁴ Department of Engineering, German University of Technology in Oman, Muscat, Oman *Corresponding author: Arabpour@modares.ac.ir, Seyed.sadrameli@gutech.edu.om

Abstract

In this work, to increase the optical and thermal stability of perovskite solar cells, the composition of the perovskite layer is engineered by adding azobenzene (AZO) as a photoswitchable organic molecule. In this regard, solar cells with the FTO/b-TiO₂/m-TiO₂/CH₃NH₃PbI₃/HTM/Au structure are fabricated using spiro-OMETAD hole transporting layer. Remarkably, an improvement of the optical, thermal, and structural stability of the devices comprising 5, 10, and 20% AZO is observed. Through the solid-solid phase-change mechanism of AZO, harmful UV radiation is absorbed and leads to photoisomerization between the *trans* and *cis* isomers, thus aiding in the management of thermal stresses on the device. Devices with pure perovskite absorber layer and perovskite absorber layer containing 10wt% AZO retained 43% and 70% of their initial performances,

respectively, after 70 min of exposure to sunlight. Furthermore, after 1440 h of storage in ambient conditions (25°C and 42% relative humidity), the reference device maintains 35% of its initial performance while the device containing 10 wt% AZO retains 89% of its initial performance. In the case of thermal stability, the device containing 10% AZO shows superior thermal stability by keeping about 55% of its initial efficiency after exposure to a temperature of 85°C and one sun illumination, simultaneously, for 60 minutes, compared to the reference device which retains only 35% of its performance under the same condition.

Keywords: Perovskite solar cells, Photoswitchable molecule, Stability, Solid-solid phase change material



TOC

Introduction

Among three different generations of solar cells, the last generation, the low-cost perovskite sloar cells (PSCs) are of great interest, since their power conversion efficiencies show promise towards commercialization. These devices have been widely researched after the perovskite (PSK) absorber layer was firstly utilized by Kojima, et al. in 2009[1]. PSK materials can provide solar cells with an excellent optical to electrical energy conversion, demonstrated by the recently reported power conversion efficiencies (PCEs) of 25.6%. In addition, they possess other beneficial characteristics, such as suitable and tunable bandgap, strong optical absorption, long carrier diffusion length, and high extinction coefficients [2]. Furthermore, they offer easy and costeffective implementation methods which are vital for industrialization. The common drawback of these devices, which still impedes commercialization, is the natural instability of PSK material caused by internal and external factors[3]. Considering external stimuli, the main factors that initiate and accelerate the decomposition process are temperature (direct heating or heating during the operation [4], oxygen [5-7], humidity [4, 8], ultraviolet (UV) irradiation, and illumination [9]. Many efforts have been made to mitigate and overcome the degradation process, including compositional engineering via using multi halides or/and cations such as Cs₂FAPb₂I₇, using low dimensional or 2D/3D multidimensional PSK structures [10-15]. Engineering of the deposition methods or growth strategies is another proposed alternative, for instance, applying seed-assisted sequential deposition strategy for obtaining micron-scale perovskite grains [16] or using vacuumassisted methods [17]. Additive engineering has been employed for reducing the defect states and lifetime insufficiency by incorporation of different additives e.g. a mixture of PVP/PEG[18], poly(ethylene glycol) tridecyl ether polymer[19], ammonium benzenesulfonate[20] into PSK precursor. Furthermore, interfacial and surface modifications[14, 21, 22], employing different

charge transports and contacts materials [23], and encapsulation using different polymers, such as epoxy resin[24] and polydimethylsiloxane (PDMS) have proved to be effective for stability improvement[25].

While almost all researchers agree on the destructive effects of rising temperature and humidity, there have been contrasting ideas about UV exposure. The primary question under debate is to identify which layer is most affected by UV. For instance, considering mesoporous TiO₂ (m-TiO₂) material as the hot spot of UV-related degradation, numerous research groups have proposed additive engineering, bilayer engineering, interlayer engineering, and/or replacing m-TiO₂ with another electron transporting layer (ETL). It was reported that UV illumination has a catalytic effect on the oxidation of I⁻ ions in CH₃NH₃PbI₃ to be converted to I₂ and thus accelerates the charge recombination [26, 27]. Therefore, introducing an interlayer or an isolating interface is a noteworthy idea to tackle the effect of UV on both the ETL and PSK layer. In this regard, Sonmezoglu et al. introduced a 2-methylbenzimidazole (MBIm) molecule and formed an interlayer to modify the PSK and ETL interface [28]. Similarly, Guo et al. improved the lifetime of PSCs by applying mesoporous Sc³⁺ doped brookite TiO₂ scaffold onto a SnO₂ block layer and achieved better UV stability [29]. Furthermore, Hu et al. inhibited photocatalytic activity of TiO₂ using fluorination of low-temperature solution-processed TiO₂ nanocrystals [30]. Reports indicated that although replacing m-TiO₂ with other materials such as SnO₂, Sn₂O₃, Sn₃O₄, and ZnTiO₃ desirably improved the stability of the PSCs under low and moderate UV irradiation, the lack of long-term photostability, still, remains a critical issue [31-34]. Thereby, Wang et al. introduced carbon nanodots (CND) to the SnO₂ ETL layer for enhancing the performance and stability of the SnO₂ based devices. Devices with over 20% PCE were achieved due to the lower electron resistivity of the CND doped SnO₂ ETL [33-36]. Regarding the PSK materials, Lee et al

confirmed the degradation of the PSK lattice after placing the MAPbI₃(MAPI)-based PSK thin film under UV exposure in controlled conditions (inert gas at <0.5 ppm humidity without encapsulation) for 1000 h. It was shown that the degradation mechanism was related to the structural change of the perovskite layer, UV irradiation causing the creation of trap states in the CH₃NH₃PbI₃ and decomposing the perovskite to its PbI₂ precursor[37]. Furthermore, Ouafi et al. showcased the destructive effect of UV exposure on PSK structure when observed the superior UV stability after incorporation of Br ions into the PSK matrix. They concluded that, on the molecular level, the degradation of the MAPI layer could be attributed to the structural degradation under UV irradiation, whereas the MAPbBr₃, which had a denser cubic morphology, turned out to be more UV-stable[38]. Following the same approach, Deng et al. improved the UV stability of the PSCs via introducing 6-chloro-1-hydroxybenzotriazole into the perovskite layer [39]. Contradictory to these reports, a facile optical method based on the high power UV-irradiation was presented for the recovery of the degraded PSCs[40, 41].

Solid-liquid phase change materials (S-L PCMs) have shown promising results for neutralizing the destructive effect of temperature fluctuation, thanks to their ability to store and release energy. In this regard, efforts have been made to introduce them to the structure of the PSCs. For instance, Fumani et al. reported that using an S-L PCM inside a resin shell not only blocked the moisture diffusion as an encapsulation system but also cooled the PSC device under operation. As a result, a two-year stable device was achieved while the controlled device lost 50% of its performance after only 10 days [24]. Thus far, the use of S-L PCMs has not been reported inside the structure of solar cells. The reason is, upon its phase change from solid to liquid, the PCM might leak to the structure of the PSC device and consequently damage the device performance. Therefore, using a Solid-Solid PCM (S-S PCM) could be a useful way to reduce the effect of both temperature and

UV on PSC. In this regard, azobenzene (AZO) molecule as a photoswitchable S-S PCM [42] can positively contribute to the stability improvement of the PSCs. Trans-cis isomerization of AZO molecule occurs upon UV irradiation. The absorption band of the trans-form is observed around λ =300-400nm [43]. Fortunately, the photoisomerization is reversible and the visible light with λ =425-500nm or heat can trigger the return of the cis to its trans isomer [43-47]. Thermodynamically, the cis isomer is 42-55 kJ/mol less stable than the trans-form [44]. Thus, it can moderate the damaging effects of light, UV radiation, and heat in its phase change cycle. Owing to its photoactivity, this substance has been used in medical, thermal, optical, and electrical applications. For instance, azobenzene-modified reduced graphene oxide@multiwall carbon nanotubes (Az-rGO@CNTs) have been applied onto a glassy carbon and used as a sensor for sensing curcumin for biomedical applications [48]. Sasai et al. confirmed that adding AZO derivatives can be optical photoluminescence (PL) controller in perovskite materials [46]. Moreover, a microstructure silicone surface was modified by azobenzene-calixarene [4]. Illumination of UV light could affect the macroscopic directional motion of a water droplet on the modified surface by changing the contact angle [49]. Additionally, a photoresponsive switchable pressure-sensitive adhesive was fabricated using an azopolymer which can switch the surface energy and modulus through trans-cis photoisomerization. It was used as a carrier for arraying mini-LEDs [50].

Herein we report the introduction of an S-S PCM based on a photoswitchable molecule into the PSK absorber layer of the PSC to retard the decomposition process following the heat, UV, and visible light exposure. The effect of using AZO on thermal stability, photostability (under visible light), UV durability, long-term functionality, and PCE are investigated by optical, electrical, morphological, and topological analysis. It is shown that the addition of the photoswitchable

molecule to the PSK layer improves the stability of the devices significantly as compared to conventional reference devices.

Experimental section

For solar cell fabrication, firstly, fluorine-doped tin oxide (FTO) substrates are etched using an HCl solution (2 M in deionized water) and Zn powder. The etched substrates are washed and ultrasonicated in a detergent, deionized water, acetone, ethanol, and isopropanol, for 10 min, dried at 100 °C, and then treated by UV-ozone for 15 min. A compact layer of TiO₂ is deposited by spin coating of an acidic solution of tetraisopropyl orthotitanate in ethanol (2000 RPM for 30s) onto the cleaned FTO substrates, annealing at 500°C for 30min and then treating with a 0.02 M TiCl₄ solution in deionized water at 70 °C for 30 min. After that, the substrates are washed with deionized water and then again annealed at 500°C for 30min. To deposit the mesoporous TiO₂ layer, the TiO₂ paste containing 20-nm-sized TiO₂ nanoparticles is diluted with ethanol (2:7 weight ratio). The resulted solution is spin-coated (5000 RPM, 30s) on top of the compact TiO₂ layer and subsequently heated at 70°C for 30 min. The procedure after deposition of the mesoporous layer is the same as the one carried out for the compact layer. For the deposition of the MAPI layer, first PbI_2 (1M) is dissolved in anhydrous DMF, and then *trans* AZO powder is added to the PbI_2 precursor in 5%wt, 10%wt, and 20% wt amounts. The precursors with and without AZO are spincoated on the TiO₂ mesoporous layers using a two-step spin-coating procedure:1) 3000 RPM, 5s; 2) 6500 RPM, 5s. Subsequently, the samples are heated in a two-step process including heating at 40°C for 3min and 100°C for 5min. CH₃NH₃I precursor is made by dissolving CH₃NH₃I powder in anhydrous isopropanol alcohol (40mg/ml). Further, to form the PSK matrix, CH₃NH₃I precursor is spin-coated on top of the PbI2 with or without AZO layers using a two-step spincoating procedure (1: 0RPM, 20s, 2: 4000RPM, 20s). The PSK layer is completely formed after heating at 100°C for 5min. To prepare the HTL solution, spiro-OMeTAD (72.3 mg) is dissolved in 1 mL chlorobenzene, followed by adding 28.8 μ L of 4-tert-butyl pyridine and 17.5 μ L of lithium bis-(trifluoromethanesulfonyl)imide (Li-TFSI) stock solution (520 mg Li-TSFI in 1 mL acetonitrile). The solution is spin-coated on the PSK layer (4000 RPM, 30s). Finally, the Au cathode is deposited through physical vapor deposition (PVD) using a shadow mask with a 0.09 cm² area (Nanostructured Coatings Co, Iran). It should be noted that all fabrication steps except Au deposition are carried out in the ambient condition with 42% relative humidity (out of glovebox).

The crystalline structure of the layers is investigated using X-ray diffraction (XRD, Cu ka radiation, $\lambda = 1.5406$ Å, Bruker, AXS). The morphology and surface roughness of the deposited films are examined by a field emission scanning electron microscope (FESEM, FEI Nova NanoSEM 4500) and an atomic force microscope (AFM, Veeco). Furthermore, the absorption spectra of the PSK layers are recorded by an Avantes UV–Visible spectrophotometer (AvaSpec 2048 model). To measure the photoluminescence intensity of the samples, they are excited using a light source with the wavelength of 400nm and the emission spectra are recorded by Avantes spectrophotometer. For UV treatment of samples, each sample is placed under high-power UV irradiance with a wavelength of 300 nm(more details in the supporting information).

The current density-voltage (J-V) characteristic of the fabricated devices based on the CH₃NH₃PbI₃ absorber layer with or without AZO is measured using an Ivium Stat potentiostat (model: XRE, Netherlands) under a calibrated AM 1.5 solar simulator with a light intensity of 100 mW/cm² (Sharif Solar 10-2, Iran). Furthermore, the thermal behavior of the PSK with and without AZO is analyzed by differential scanning calorimetry (DSC) (NETZSCH 200F).

Results and discussion

Figure 1a shows the FESEM images of the PSK layer containing various amounts of AZO S-S PCM. As observed, there is no significant difference between the morphology of the pristine PSK layer and the layer containing 5% AZO. The top-view FESEM images of the PSK layers containing 10 and 20% of AZO show a distinguishable change in their surface structure in the presence of AZO. While continuous surface morphology is observed for the PSK with 10% AZO, adding 20wt% AZO causes the formation of obvious pinholes through the entire MAPI PSK, which can influence the performance of the PSCs. According to the results of AFM analysis (Figure 1b), the root mean square (RMS) of the PSK layers decreases from 72.88 nm for pristine MAPI to 57.30nm, 52.84nm, and 63.28nm for 5wt%, 10wt%, and 20wt% AZO containing PSKs, respectively. AFM results are consistent with the FESEM ones, corroborating a smoother surface in the case of the 5% and 10wt% AZO added PSK films compared to the layer containing 20wt% AZO and the reference layer without added AZO. Considering the vast majority of the AZO in the trans-state, it can be concluded that the high share of planar trans-AZO can reduce the roughness of the PSK layer. Additionally, AZO as a small photoswitchable organic molecule can also help the layer uniformity and filling pores. However, once the concentration of AZO is increased over a certain threshold, there is also a possibility of partial crystallization of the AZO as macrophase-separated domains. This could be one of the reasons for observing a higher roughness in the case of the sample containing 20% AZO.



Figure 1 a) FESEM and b) AFM images of MAPI films with different percentages of AZO deposited on a glass substrate

To verify the effect of photoswitchable AZO molecules on the photophysical properties of the PSK layer, the UV-visible absorption measurements (Figure 2a) are carried out. The Tauc's equation (Equation 1) is used for determining the optical bandgap of the samples:

 $\alpha h v = A(h v - Eg)^{1/2}$ Equation 1

where h is Planck's constant, hv is the incident photon energy, and A is an energy-independent constant. Then, the bandgap of the layers is determined based on the extrapolated linear regression of $(\alpha hv)^2 - hv$ curves (Figure 2b). The values obtained for the bandgap are listed in Table 1.

In the UV-visible absorption spectrum of pure AZO, two absorption peaks are observed, one in the UV region and the other in the visible region [51]. The intensity of absorption in these two areas depends on the photostationary state of AZO molecules in the structure [44]. As depicted in Figure 2a, the addition of AZO to the PSK layer enhances absorption in the UV region. Furthermore, according to Table 1, after the introduction of AZO to the PSK structure, a descending trend in the bandgap value is observed. On the molecular level, the bandgap reduction can be attributed to two interconnected factors, namely pressure and phase transition. Pressure can change (distorting, titling, or rotation) lattice structure and induce complex phase transitions [52]. So, increasing the pressure on the perovskite lattice by the addition of AZO is one of the probable reasons for the observed bandgap redshift. This pressure-driven bandgap reduction is mainly a result of lattice shrinkage[53]. Additionally, this bandgap decrement is analogous to the results of Baikie et al., who observed that the bandgap of the cubic phase of MAPI is lower than that of the tetragonal phase [54].



Figure 2 a) Absorbance spectra of MAPI PSK layers with different percentages of AZO S-S PCM, b) Tauc plot of MAPI PSK layers with different percentages of AZO S-S PCM, c) PL spectra of MAPI PSK layers with different percentages of AZO S-S PCM

Table 1 Bandgap value of MAPI PSK active layers with different percentages of AZO S-S PCM

Sample	Bandgap
MAPI	1.582eV
MAPI+5% AZO	1.575 eV

MAPI+10% AZO	1.572eV
MAPI+20% AZO	1.56eV

According to the PL spectra of the pure PSK film and films containing different amounts of AZO (Figure 2c), the peak located around 790 nm is attributed to the radiative recombination [55] that occurs in the MAPI PSK material. Interestingly, the addition of AZO has no significant undesirable effect on the overall PL intensity of the PSK. This result demonstrates that the selected approach does not induce further non-radiative defect states to the perovskite lattice. Furthermore, as illustrated in Figure 2c, a slight red shift is observable in the PL spectra of the samples upon addition of AZO, which further confirms the bandgap reduction. Crystalline phase change, which will be discussed further, and the pressure inside the lattice domain are held responsible for the bandgap reduction and the consequent slight redshift in the PL spectra. This result demonstrates that the selected approach does not induce further non-radiative further non-radiative defect states to the perovskite lattice impacts the bandgap reduction of AZO, which further confirms the bandgap reduction. Crystalline phase change, which will be discussed further, and the pressure inside the lattice domain are held responsible for the bandgap reduction and the consequent slight redshift in the PL spectra. This result demonstrates that the selected approach does not induce further non-radiative defect states impacting the luminescent properties of the perovskite lattice[56].

Furthermore, to study the effect of incorporation of AZO into stability improvement of PSK materials against UV light and heat, a comparison of the PL spectra of samples before and after exposure to UV light at a temperature of 85°C for 20 min is presented in Figure S1. Astonishingly, while the PL intensity of the MAPI sample decreases after UV irradiation and thermal stress due to a combination of higher non-radiative loss and creation of Pb metallic clusters in perovskite lattice [57], the PL of the AZO-containing samples remains nearly the same after the treatment. This can further confirm the positive effect of AZO addition on improving the UV and heat stability of the perovskite layers.

In order to determine the crystalline structures of the perovskite layers, the X-ray diffraction (XRD) patterns of MAPI PSK with different amounts of AZO molecule are shown in Figure 3. The observed diffraction peaks at 14.21°, 20.09°, 23.56°, 24.59°, 28.54°, 31.94°, 35.04°, 38.68°, 40.66°, and 43.22° are assigned to the (110), (200), (211), (202), (004), (220), (310), (312), (224), and (314) planes of the tetragonal PSK structure [2, 58, 59]. The unconverted PbI₂ peak can also be observed at 12.6° in the patterns which can desirably improve the performance of the devices via passivating the grain boundary defects [60]. According to data extracted from Figure 3 and summarized in Table 2, the results of XRD analysis of PSK thin films with various AZO PCM contents indicate the structural changes in the presence of the AZO. The peak located at 23.5° corresponding to (211) plane is representitive of a tetragonal structure [58, 59]. The comparison of peak intensity related to (211) and (202) planes is conducted to understand the process of phase transferring from tetragonal towards semi-cubic phase (Table 2).

To showcase the phase transition, a comparison is made between the intensity of the peaks assigned to (211) and (202) planes (see Table 2). It is observed that by adding 5%, 10%, and 20% of the PCM, the intensity of the peak assigned to the (211) plane decreases in comparison with others. As a result, the system experiences a closer phase structure to the cubic phase [54]. As reported in the literature, during the deposition and formation of perovskite crystals, the cubic crystalline phase appears when the layer is exposed to high temperatures. After cooling down the perovskite layer to room temperature, the phase transition from cubic to tetragonal takes place [54]. It is speculated that the presence of AZO hinders the cubic to the tetragonal phase transition. Consequently, the initially formed cubic crystalline phase remains the same upon cooling to room temperature because of both pressure and adhesion of the AZO to the crystal domain. Thus, the created steric hindrance in the crystals domain acts as a great barrier toward the crystalline phase-

change phenomenon [61]. Subsequently, since the Goldschmidt tolerance factor of the cubic structure lies in the range of 0.8-1 (almost near unity), the cubic structure is more stable than its distorted tetragonal phase [62]. Therefore, it is expected that the PSK composition containing AZO leads to the formation of a more stable structure. The lattice strain and crystallite size associated with each sample (Table 3) are calculated using the Williamson-Hall method:

$$\beta \cos\theta = \frac{\kappa_{\lambda}}{D} + 4 \varepsilon \sin\theta$$
 Equation 2

where β is the peak broadening or (full width at half-maximum (FWHM) of the diffraction peak in radians), k, D, λ , and ε are shape factor, crystallite size, wavelength of Cuk_a radiation, and the lattice strain, respectively. By plotting $\beta \cos\theta$ as a function of $4 \varepsilon \sin\theta$, the Williamson-Hall plot of each sample is achieved (Figure 4). Values of the lattice strain obtained from the Williamson-Hall equation (Table 3) demonstrate that by increasing the concentration of AZO the lattice strain is reduced which can, also, lead to stability improvement of the structure[52, 53].



Figure 3 X-ray diffraction pattern of PSK layer containing different amounts of AZO. (*)

represents the unconverted PbI₂ peak

Table 2 The intensity ratio of two peaks assigned to (202) and (211) planes

Height sample	H ₍₂₁₁₎	H ₍₂₀₂₎	$x = \frac{H_{(211)}}{H_{(202)}}$
МАРІ	124.11	170.4	0.73
MAPI+5%AZO	49.46	79.37	0.62
MAPI+10%AZO	120.96	230.75	0.52
MAPI+20%AZO	28.63	81.77	0.35



Figure 4 Williamson-Hall plots of MAPI active layers, a) pure, b) containing 5 wt% AZO, c) containing 10 wt% AZO, d) containing 20 wt% AZO.

Table 3 Calculated average crystallite size and lattice strain for MAPI PSK absorber layer containing different percentages of AZO S-S PCM

Sample	Crystallite size (nm)	Lattice strain (*10 ⁻³)
MAPI	91.4	2.5
MAPI+5%AZO	65.2	2.2

MAPI+10%AZO	63	2.0
MAPI+20%AZO	57.6	1.6

In order to investigate the structural changes upon thermal and UV irradiation stresses, the XRD patterns are also recorded after the films are exposed to UV light at temperatures of 85°C for 20 min. As depicted in Figure S2, the intensity of the peak assigned to PbI₂ shows a significant increase only in the pure sample, revealing PSK degradation caused by UV light coupled with increased temperature. In contrast, in the samples containing AZO, no significant changes occur after the UV irradiation at elevated temperatures. Notably, these results correlate well with the earlier PL observations (Figure S 1).

To confirm the isomerization behavior of AZO, four samples including as prepared trans AZO, AZO powder placed under the 1.5 AM light intensity for 20 min (AZO under light), MAPbI₃ powder, and MAPbI₃ containing 10% AZO are analyzed using DSC (Figure 5). The PSK samples are prepared by scratching off the PSK thin films deposited on the glass substrate from the substrate. Melting and crystallization temperatures and the respective enthalpies are summarized in Table 4.



Figure 5 a) Heating cycles of pure AZO, AZO after being exposed to one sun illumination for 20 min, b) cooling cycles of AZO, AZO after being exposed to one sun illumination for 20 min, c) exothermic peak assigned to the cis isomer, d) the DSC diagram of MAPI PSK containing 10%wt AZO, e) comparison of heating cycles of MAPI and MAPI PSK containing 10wt% AZO, f) proposed conformation change of

AZO in the PSK layer

Table 4 Thermal behavior of pure AZO, the AZO sample after being exposed to 100 mW/cm^2

	1			
Sample	Melting point	Enthalpy of	Crystallization point	Enthalpy of
1	01	17	2 1	1.5
	(°C)	maltima (:/.)	(90)	amustallization (1)
	(°C)	menting (J/g)	(16)	crystallization (j/g)
AZO	72.5	132.2	52.2	-122.3
		-	_	_
AZO after 20min	72.6	119	53	-116.7
	,			
. 1. 1.				
exposure to light				
MAPI+10wt% AZO	50.4	0.4	-	-
	••••	011		

illumination for 20min, and MAPI PSK containing 10wt% AZO.

Figure 5a shows the heating of the AZO and illuminated AZO samples from zero to 100°C where the peaks seen in the diagrams show the melting point of the samples. Additionally, peaks in Figure 5b depict the crystallization of samples cooling from 100°C to zero. As can be seen in Figure 5b, within both cooling curves, the peaks related to the crystallization of samples are seen at temperatures of about 52°C. In the cooling cycle of AZO, an exothermic peak is observed at a temperature of about 20°C which is absent in the diagram assigned to AZO under light sample (Figure 5c). Observation of this kind of exothermic peak can be proof of the existence of *cis*-isomer inside the AZO powder [63]. It is speculated that after being under sunlight, the cis isomer in the AZO sample is isomerized to its trans state. There is, therefore, no sign of it in the illuminated AZO sample diagram. Remarkably, adapting Figure 5c and the cooling cycle of MAPI containing AZO in Figure 5d confirms that both exothermic peaks, 20°C in the cooling curve of AZO and 29°C in MAPI containing AZO, most probably are the signs of energy released from *cis* isomer [51][64]. It is plausible that reversible trans-cis-trans cycling is occurring inside the perovskite film driven by UV and the visible part of the sunlight spectrum.

Although the origin of the 9°C peak displacement in the MAPI containing AZO sample is unclear, it appears that it may have arisen from the special hindrance inside the perovskite lattice. Since trans-cis isomerization needs more space, one possibility is that upon additional pressure and limited space this relaxation will take place in higher temperatures. Furthermore, during the formation of PSK crystals, the amount of the bent shape cis isomer increases because of surrounding pressure and tension. Thus, the intensity of the peak assigned to the cis isomer in the PSK with AZO is higher than that of AZO. This increment in the share of the cis isomer inside the perovskite lattice suggests the possibility of isomerization within the perovskite structure. Furthermore, according to the DSC diagram of the MAPI sample containing AZO (Figure 5d), peaks located at 58°C and 56.7°C in the heating and cooling charts, respectively, can represent the transformation of tetragonal to cubic which is not present in the graph of pure MAPI sample as illustrated in Figure 5e [58]. This finding confirms the XRD results that proposed the crystalline phase transition within the perovskite layer. Ultimately, as it is proposed, the introduction of AZO can neutralize the effect of the generated heat and suggests a phase change from tetragonal to quasi-cubic crystalline phase in the PSK lattice.

For investigating the performance of the devices with added AZO, solar cells including MAPI absorber layer without PCM and containing 5%, 10%, 20% PCM with the FTO/block-TiO₂/mesoporous TiO₂/PSK/HTL/Au architecture are fabricated (Figure 6a). The diagram of the energy levels of the device components is presented in Figure 6b.



The current density-voltage (J-V) characteristic curves of the devices are shown in Figure 7. The parameters extracted from the J-V curves such as PCE, fill factor (FF), short circuit current density (J_{sc}), and open-circuit voltage (V_{oc}) are summarized in Table 5.



Figure 7 J-V characteristics of devices with FTO/b-TiO₂/m-TiO₂/PSK/spiro-OMETAD/Au configuration.

Table 5 Photovoltaic parameters of fabricated solar cells based on MAPIPSK absorber layer with different concentrations of AZO using spiro-OMETAD as HTL (champion devices).

Sample	PCE (%)	V _{oc} (V)	Jsc (mA/cm ²)	FF
MAPI	14.02	1.07	20.81	0.63
MAPI+5% AZO	13.5	1.03	19.95	0.66
MAPI+10% AZO	8.95	0.90	15.57	0.64
MAPI+20% AZO	6.5	0.90	11.33	0.64

As evidenced in Table 5, the PCE of the device containing 5% PCM is very close to the PCE obtained for the control device. As explained (Figure 1), the reduction of PCE in the presence of AZO can be attributed to the morphological changes that occur. Besides, AZO does not participate in the photovoltaic process. Therefore, it leads to a decrease in efficiency though in the sample with 5% wt AZO this change is not significant. As the scope of this study is to investigate the stability of the PSK layer of the device with the presence of AZO PCM, it is discussed in detail in the following sections.

The stability of solar cells is assessed under different aging conditions. First, the solar cells are irradiated for about 70 min under one-sun illumination and RH of 42%. The trend of changes in the device characteristics is recorded with 3 min intervals. As observed, the presence of the PCM improves the stability of solar cells under illumination. According to Figure 8a, devices with MAPI absorber layer retain 43% of their initial PCEs after 70 min of exposure to light and RH of 42%, while devices containing 5%, 10%, and 20% of the AZO PCM retained about 56%, 70%, and 70% of their initial PCEs, respectively. These results are observed in several consecutive series of devices. Although a considerable change in Voc of devices is not observable (Figure 8b), the fill factor (FF) (Figure 8d) is improved with the addition of 10% AZO and has only a few changes after exposure to light for 70 min. As mentioned in the introduction, AZO can dissipate energy through isomerizing from its trans isomer to the cis isomer by absorbing the UV part of the spectrum (Figure 8e)[38, 65]. During the selective absorption of UV irradiation by AZO, the destructive effect of UV on the PSK structure is reduced. Structural change and isomerization of AZO require appropriate volume and space [66]. In some crystalline structures due a the suitable free space between the constituent elements, especially in the PSK structure, isomerization can be predicted [67]. Returning from the cis structure to the trans isomer requires more time and, due to

the spatial shape of the trans isomer, also requires more space volume. Therefore, cis to trans isomerization requires more absorption intensity or heat and more time [47, 68].



Figure 8 Photovoltaic parameters, a) Power conversion efficiency (PCE), b) Open circuit voltage (Voc), C) Short circuit current density (Jsc), and d) Fill factor (FF) of fabricated devices with or

without S-S PCM as the function of illumination time under the light with the intensity of 100 mW/cm², e) Schematic presentation of AZO isomerization.

To determine the long-term stability of the fabricated devices and the effect of the incorporation of PCM, the characteristics of the solar cells are measured during 1440 h after their fabrication (Figure 9). Through this storage time, the devices are kept at room temperature of about 25 and at RH of 42% without encapsulation. The results show that the devices fabricated with MAPI absorber layer maintain only 35% of their original performance at the end of 1440 h storage while devices containing 5%, 10%, and 20% AZO maintain 86%, 89%, and 65% of their initial performances, respectively. As discussed earlier, by adding AZO to the PSK absorber layer, a change from the tetragonal to the quasi-cubic structure is observed. The improved stability in the presence of the PCM can be attributed to this tetragonal- quasi cubic structural change and greater stability of the cubic structure compared to the tetragonal structure (Figure 9b).



Figure 9 a) Stability behavior of the devices containing different percentages of AZO for 1440 hr, b) crystalline phase transition of MAPI from tetragonal to quasi-cubic

Finally, to study the effect of AZO incorporation on the thermal stability of the devices, they are kept at the temperature of 85°C under continuous illumination. As seen in Figure 10, the device containing 10% AZO holds 55% of its initial performance whereas the pristine device maintained just 35% of its efficiency after 60 mins of being simultaneously under 1 sun illumination and temperature of 85°C. It can be concluded that the addition of AZO in MAPI+10% AZO helps to neutralize the thermal stress generated in the perovskite lattice. It seems that MAPI+10% AZO provides an optimized free space for the photoisomerization of AZO molecules. Thus, as explained, heat drives the reverse *cis-trans* reaction and the continuous isomerization cycle is responsible for the stability enhancement in the AZO-containing devices.



Conclusion

In conclusion, a novel approach for improving the stability of PSCs was introduced by adding S-S PCMs to the PSK absorber layer of PSCs. As deduced based on XRD, PSK underwent the crystalline phase transition from tetragonal to a quasi-cubic crystalline phase with the addition of AZO to the PSK precursors. Devices containing AZO had better photo-stability and thermal stability i.e. devices containing 10%wt AZO held 70% of their initial performances due to the photoswitching behavior of the AZO molecules, while the reference cells retained only 43% of

their initial performances after being under continuous light exposure for 70 min. Similarly, after 60 min of being under unceasing one sun illumination and temperature of 85°C, the efficiency of the MAPI+10%AZO based device dropped to 55% of its initial PCE compared to the pristine device which kept only 35% of its efficiency. Moreover, the long-term stability examination also demonstrated the striking effect of AZO on device stability which is attributed to the crystalline phase transition of the PSK layer. After 1440h of storage in the dark and RH of 42%, the devices with 10% AZO kept 89% of their initial efficiencies compared to the reference ones which retained 35% of their primary PCE.

Acknowledgment

The authors would like to acknowledge the financial support from the research department of Tarbiat Modares University (Research group of phase change materials, Grant No. IG-39710 and research group of nano plasma photonic, IG-39704). Maryam Mousavi would acknowledge the financial support from Fortum and Nestse Foundation (Grant No. 20210045), Espoo, Finland.

References

- 1. Kojima, A., et al., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. Journal of the American Chemical Society, 2009. **131**(17): p. 6050-6051.
- Alidaei, M., et al., Efficiency enhancement of perovskite solar cells using structural and morphological improvement of CH3NH3PbI3 absorber layers. Materials Research Express, 2018.
 5(1): p. 016412.
- 3. Arabpour Roghabadi, F., et al., *Stability progress of perovskite solar cells dependent on the crystalline structure: From 3D ABX3 to 2D Ruddlesden–Popper perovskite absorbers.* Journal of Materials Chemistry A, 2019. **7**(11): p. 5898-5933.
- 4. Han, Y., et al., *Degradation observations of encapsulated planar CH 3 NH 3 Pbl 3 perovskite solar cells at high temperatures and humidity.* Journal of Materials Chemistry A, 2015. **3**(15): p. 8139-8147.
- 5. Conings, B., et al., *Intrinsic thermal instability of methylammonium lead trihalide perovskite*. Advanced Energy Materials, 2015. **5**(15): p. 1500477.
- 6. Aristidou, N., et al., *The role of oxygen in the degradation of methylammonium lead trihalide perovskite photoactive layers*. Angewandte Chemie, 2015. **127**(28): p. 8326-8330.

- 7. Sun, Q., et al., *Role of microstructure in oxygen induced photodegradation of methylammonium lead triiodide perovskite films*. Advanced Energy Materials, 2017. **7**(20): p. 1700977.
- 8. Frost, J.M., et al., *Atomistic origins of high-performance in hybrid halide perovskite solar cells.* Nano letters, 2014. **14**(5): p. 2584-2590.
- 9. Domanski, K., et al., *Systematic investigation of the impact of operation conditions on the degradation behaviour of perovskite solar cells.* Nature Energy, 2018. **3**(1): p. 61-67.
- 10. Bush, K.A., et al., *Compositional engineering for efficient wide band gap perovskites with improved stability to photoinduced phase segregation.* ACS Energy Letters, 2018. **3**(2): p. 428-435.
- 11. Lau, C.F.J., et al., *Enhanced performance via partial lead replacement with calcium for a CsPbI 3 perovskite solar cell exceeding 13% power conversion efficiency.* Journal of Materials Chemistry A, 2018. **6**(14): p. 5580-5586.
- 12. Niu, G., et al., *Enhancement of thermal stability for perovskite solar cells through cesium doping.* RSC advances, 2017. **7**(28): p. 17473-17479.
- 13. Grancini, G., et al., *One-Year stable perovskite solar cells by 2D/3D interface engineering.* Nature communications, 2017. **8**(1): p. 1-8.
- 14. Mahon, N.S., et al., *Photoluminescence kinetics for monitoring photoinduced processes in perovskite solar cells.* Solar Energy, 2020. **195**: p. 114-120.
- 15. Zhang, X., et al., *Stable high efficiency two-dimensional perovskite solar cells via cesium doping.* Energy & Environmental Science, 2017. **10**(10): p. 2095-2102.
- 16. Li, X., et al., *Structural regulation for efficient and stable perovskite solar cell via mixed-vapor deposition.* ACS Applied Energy Materials, 2020.
- 17. Pinsuwan, K., et al., *Solar perovskite thin films with enhanced mechanical, thermal, UV, and moisture stability via vacuum-assisted deposition.* Journal of Materials Science, 2020. **55**(8): p. 3484-3494.
- 18. Zhong, M., et al., *Enhanced efficiency and stability of perovskite solar cell by adding polymer mixture in perovskite photoactive layer.* Journal of Alloys and Compounds, 2021. **864**: p. 158793.
- 19. Hong, J., H. Kim, and I. Hwang, *Defect site engineering for charge recombination and stability via polymer surfactant incorporation with an ultra-small amount in perovskite solar cells.* Organic Electronics, 2019. **73**: p. 87-93.
- 20. Yang, Y., et al., *Bi-functional additive engineering for high-performance perovskite solar cells with reduced trap density*. Journal of Materials Chemistry A, 2019. **7**(11): p. 6450-6458.
- 21. Arora, N., et al., *Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%.* Science, 2017. **358**(6364): p. 768-771.
- 22. Sun, Y., et al., Enhanced UV-light stability of organometal halide perovskite solar cells with interface modification and a UV absorption layer. Journal of Materials Chemistry C, 2017. **5**(34): p. 8682-8687.
- 23. Wu, Z., et al., *Highly efficient and stable perovskite solar cells via modification of energy levels at the perovskite/carbon electrode interface.* Advanced Materials, 2019. **31**(11): p. 1804284.
- 24. Mansour Rezaei Fumani, N., et al., *Prolonged Lifetime of Perovskite Solar Cells Using a Moisture-Blocked and Temperature-Controlled Encapsulation System Comprising a Phase Change Material as a Cooling Agent.* ACS omega, 2020. **5**(13): p. 7106-7114.
- 25. Amjadi, A., et al., Durable Perovskite UV Sensor Based on Engineered Size-Tunable Polydimethylsiloxane Microparticles Using a Facile Capillary Microfluidic Device from a High-Viscosity Precursor. ACS omega, 2020. **5**(2): p. 1052-1061.
- 26. Guo, X., et al., *Multifunctional MgO layer in perovskite solar cells*. ChemPhysChem, 2015. **16**(8): p. 1727-1732.

- 27. Leijtens, T., et al., Overcoming ultraviolet light instability of sensitized TiO 2 with meso-superstructured organometal tri-halide perovskite solar cells. Nature communications, 2013.
 4(1): p. 1-8.
- 28. Sonmezoglu, S. and S. Akin, *Suppression of the interface-dependent nonradiative recombination by using 2-methylbenzimidazole as interlayer for highly efficient and stable perovskite solar cells.* Nano Energy, 2020. **76**: p. 105127.
- 29. Guo, Q., et al., *Low-temperature processed rare-earth doped brookite TiO2 scaffold for UV stable, hysteresis-free and high-performance perovskite solar cells.* Nano Energy, 2020. **77**: p. 105183.
- 30. Hu, W., et al., In Situ Surface Fluorination of TiO2 Nanocrystals Reinforces Interface Binding of Perovskite Layer for Highly Efficient Solar Cells with Dramatically Enhanced Ultraviolet-Light Stability. Advanced Science, 2021. **8**(10): p. 2004662.
- 31. Wei, J., et al., *UV-Inert ZnTiO3 Electron Selective Layer for Photostable Perovskite Solar Cells.* Advanced Energy Materials, 2019. **9**(40): p. 1901620.
- 32. Li, S., et al., van der Waals Mixed Valence Tin Oxides for Perovskite Solar Cells as UV-Stable Electron Transport Materials. Nano Letters, 2020. **20**(11): p. 8178-8184.
- 33. Liu, R., et al., *UV degradation of the interface between perovskites and the electron transport layer.* RSC Advances, 2020. **10**(20): p. 11551-11556.
- 34. Jia, J., et al., *Combustion procedure deposited SnO2 electron transport layers for high efficient perovskite solar cells.* Journal of Alloys and Compounds, 2020. **844**: p. 156032.
- 35. Wang, S., et al., Introduction of carbon nanodots into SnO 2 electron transport layer for efficient and UV stable planar perovskite solar cells. Journal of Materials Chemistry A, 2019. **7**(10): p. 5353-5362.
- 36. Wang, S., et al., *Introduction of carbon nanodots into SnO2 electron transport layer for efficient and UV stable planar perovskite solar cells.* Journal of Materials Chemistry A, 2019. **7**(10): p. 5353-5362.
- 37. Lee, S.-W., et al., UV degradation and recovery of perovskite solar cells. Scientific reports, 2016.
 6(1): p. 1-10.
- 38. Ouafi, M., et al., *Improving UV stability of MAPbI3 perovskite thin films by bromide incorporation.* Journal of Alloys and Compounds, 2018. **746**: p. 391-398.
- 39. Deng, X., et al., *Benzotriazole derivative inhibits nonradiative recombination and improves the UV-stability of inverted MAPbI3 perovskite solar cells.* Journal of Energy Chemistry, 2022. **65**: p. 592-599.
- 40. Roghabadi, F.A., et al., *High power UV-Light Irradiation as a New Method for Defect passivation in Degraded perovskite solar Cells to Recover and enhance the performance.* Scientific reports, 2019. **9**(1): p. 1-11.
- 41. Roghabadi, F.A., et al., *Recovering a degraded solar cell*. 2019, Google Patents.
- 42. Wu, S., et al., *Photoswitchable phase change materials for unconventional thermal energy storage and upgrade.* Matter, 2021. **4**(11): p. 3385-3399.
- 43. Yu, Q. and H. Chen, Interaction of switchable biomaterials surfaces with proteins, in Switchable and Responsive Surfaces and Materials for Biomedical Applications. 2015, Elsevier. p. 167-188.
- 44. Vetráková, Ľ., et al., *The absorption spectrum of cis-azobenzene*. Photochemical & Photobiological Sciences, 2017. **16**(12): p. 1749-1756.
- 45. Oliveira, O., M. Raposo, and A. Dhanabalan, *Langmuir-blodgett and self-assembled polymeric films.* Handbook of surfaces and interfaces of materials, 2001. **4**: p. 1-58.
- Sasai, R. and H. Shinomura, *Preparation and optical characteristics of layered perovskite-type lead-bromide-incorporated azobenzene chromophores*. Journal of Solid State Chemistry, 2013.
 198: p. 452-458.

- 47. Han, G.G., H. Li, and J.C. Grossman, *Optically-controlled long-term storage and release of thermal energy in phase-change materials.* Nature communications, 2017. **8**(1): p. 1-10.
- 48. Mousaabadi, K.Z., et al., *Reduced graphene oxide and carbon nanotubes composite functionalized by azobenzene, characterization and its potential as a curcumin electrochemical sensor.* Journal of Electroanalytical Chemistry, 2020. **873**: p. 114418.
- 49. Zhu, F., et al., *The light-driven macroscopic directional motion of a water droplet on an azobenzene–calix[4]arene modified surface.* Chemical Communications, 2020. **56**(74): p. 10922-10925.
- 50. Lee, T.-H., et al., *Rapid Photoresponsive Switchable Pressure-Sensitive Adhesive Containing Azobenzene for the Mini-Light Emitting Diode Transfer Process.* ACS Applied Materials & Interfaces, 2021. **13**(36): p. 43364-43373.
- 51. Han, G.D., et al., *Photon energy storage materials with high energy densities based on diacetylene–azobenzene derivatives.* Journal of Materials Chemistry A, 2016. **4**(41): p. 16157-16165.
- 52. Hu, Z., et al., A Review on Energy Band-Gap Engineering for Perovskite Photovoltaics. Solar RRL, 2019. **3**(12): p. 1900304.
- 53. Wang, F., et al., Unusual pressure-induced electronic structure evolution in organometal halide perovskite predicted from first-principles. Organic Electronics, 2019. **67**: p. 89-94.
- 54. Baikie, T., et al., Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solidstate sensitised solar cell applications. Journal of Materials Chemistry A, 2013. **1**(18): p. 5628-5641.
- 55. Wu, W.-Q., et al., *Reducing Surface Halide Deficiency for Efficient and Stable Iodide-Based Perovskite Solar Cells.* Journal of the American Chemical Society, 2020. **142**(8): p. 3989-3996.
- 56. Wang, B., et al., *Crystallinity and defect state engineering in organo-lead halide perovskite for high-efficiency solar cells.* Journal of Materials Chemistry A, 2016. **4**(10): p. 3806-3812.
- 57. Dou-Dou Qian, L.L., Zhi-Xue Xing, Rui Dong, Li Wu, Hong-Kun Cai, Yong-Fa Kong, Yi Zhang, and J.-J. Xu, *Improvement of Photoluminescence of Perovskite CH\$_{3}\$NH\$_{3}\$PbI\$_{3}\$ by Adding Additional <cblk>CH\$_{3}\$NH\$_{3}\$I</cblk> during Grinding.* Chin. Phys. Lett., 2021(8): p. 087801%V 38.
- 58. Baikie, T., et al., Synthesis and crystal chemistry of the hybrid perovskite (CH 3 NH 3) PbI 3 for solid-state sensitised solar cell applications. Journal of Materials Chemistry A, 2013. **1**(18): p. 5628-5641.
- 59. Luo, S. and W.A. Daoud, *Crystal structure formation of CH3NH3PbI3-xClx perovskite.* Materials, 2016. **9**(3): p. 123.
- 60. Shi, B., et al., *Unraveling the Passivation Process of PbI2 to Enhance the Efficiency of Planar Perovskite Solar Cells.* The Journal of Physical Chemistry C, 2018. **122**(37): p. 21269-21276.
- 61. Xu, G., et al., *Photoswitchable Adhesives Using Azobenzene-Containing Materials*. Chemistry An Asian Journal, 2020. **15**(5): p. 547-554.
- 62. Ye, F., et al., *Applications of cesium in the perovskite solar cells*. Journal of Semiconductors, 2017. **38**(1): p. 011003.
- 63. Zhou, H., et al., *Photoswitching of glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions.* Nature Chemistry, 2017. **9**(2): p. 145-151.
- 64. Bandara, H.M.D. and S.C. Burdette, *Photoisomerization in different classes of azobenzene*. Chemical Society Reviews, 2012. **41**(5): p. 1809-1825.
- 65. Niu, G., X. Guo, and L. Wang, *Review of recent progress in chemical stability of perovskite solar cells.* Journal of Materials Chemistry A, 2015. **3**(17): p. 8970-8980.

- 66. Bushuyev, O.S., et al., *Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photomechanical Effect in Fluorinated Azobenzenes.* Journal of the American Chemical Society, 2013. **135**(34): p. 12556-12559.
- 67. Harada, J., K. Ogawa, and S. Tomoda, *Molecular motion and conformational interconversion of azobenzenes in crystals as studied by X-ray diffraction*. Acta Crystallographica Section B: Structural Science, 1997. **53**(4): p. 662-672.
- 68. Maciejewski, J., et al., *Photochromic Torsional Switch (PTS): a light-driven actuator for the dynamic tuning of* π *-conjugation extension.* Chemical science, 2017. **8**(1): p. 361-365.