Organic Hybrid Perovskite (MAPbI$_{3-x}$Cl$_x$) for Thermochromic Smart Window with Strong Optical Regulation Ability, Low Transition Temperature, and Narrow Hysteresis Width

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Recently, organic hybrid halide perovskites have been found to show thermochromism with good optical performance, which can be applied in smart windows to reduce building energy consumption. However, these perovskites have shortcomings regarding their thermochromatic performance, namely long transition time, high transition temperature, and large transition hysteresis width. In this study, a hydrated MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite smart window (H-MAPbI$_{3-x}$Cl$_x$, TPSW) is proposed, which undergoes a reversible transition between a transparent state and a dark reddish-brown tinted state with a high solar modulation ability of 23.7%. Most importantly, the H-MAPbI$_{3-x}$Cl$_x$, TPSW possesses a tunable low transition temperature of 29.4 to 51.4 °C, a controllable and narrow transition hysteresis width (7.7–13.2 °C) and a short transition time (1–4 min). Additionally, a mathematical model is developed to predict the transition temperature of the H-MAPbI$_{3-x}$Cl$_x$, TPSW. A field test is also conducted, demonstrating that the H-MAPbI$_{3-x}$Cl$_x$, TPSW fitted to a model house can reduce the indoor air temperature by 3.5 °C compared to using a quartz glass window. Overall, the H-MAPbI$_{3-x}$Cl$_x$, TPSW can yield excellent optical properties, while simultaneously providing remarkable transition properties, making it potentially useful for a wide range of applications in energy-efficient buildings.

1. Introduction

With the rapid development of technology and the economy, energy shortage has become a critical issue in urban cities, and the huge energy consumption by buildings is a main cause.[1] According to the statistics, nearly 60% of building energy is consumed by heating, ventilation, and air conditioning (HVAC) systems to achieve a thermally comfortable environment.[2] The major source of the huge consumption by HVAC systems is recognized as the heat transfer to building envelopes, especially the heat loss/gain through windows that accounts for 50% in a typical office building.[3] To reduce the energy consumption without sacrificing thermal comfort, energy-efficient smart windows are urgently needed, hence the extensive investigation in recent years.[4–8] Smart windows are glazed units coated with special materials having spectral response properties, that enable them to adjust the light transmittance in a dynamic and smart way according to the ambient environment. Normally, smart windows can be categorized as electrochromic, photochromic and thermochromic according to the kind of external stimuli inducing the response of the material.[9] Thermochromic smart windows are competitive because of their automatic passive controllability of solar irradiance, which does not require extra energy input.[10] Notably, for thermochromic smart windows, the high luminous transmittance $\tau_{\text{Lum}}$ (i.e., total transmitted light of materials from wavelength of 380–780 nm) and solar modulation ability $\Delta \tau_{\text{Sol}}$ (i.e., the difference of solar transmittance $\tau_{\text{Sol}}$ between the cold state and hot state of materials) are the keys to ensuring indoor light intensity as well as the energy saving performance. Meanwhile, transition properties including a reasonable transition temperature ($T_c$), relatively narrow hysteresis width ($\Delta T_h$) as well as short transition time ($t_t$) are vital for their practical application. $T_c$ is an important parameter in smart window applications. A $T_c$ ranging from 30 to 40 °C is required in building applications.[10] $\Delta T_h$ is another important indicator to examine the thermochromic smart window performance, defined as the difference of $T_c$ between the heating ($T_{c_h}$) and cooling processes ($T_{c_c}$) (i.e., $\Delta T_h = T_{c_h} - T_{c_c}$).[11–14]

In recent years, perovskites, in particular hybrid halide perovskites have become popular materials because of their unique material properties suitable for high efficiency solar...
Furthermore, it has been found that semi-transparent photovoltaics of some halide perovskites with a structure $\text{ABX}_3$ ($\text{A} = \text{CH}_3\text{NH}_3^+$ (MA), $\text{HCl(NH}_2)_2^+$ (FA), and $\text{Cs}^+$; $\text{B} = \text{Pb}^{2+}$, $\text{Sn}^{2+}$; $\text{X} = \text{I}^-$, $\text{Br}^-$, and $\text{Cl}^-$) can be developed and applied in power generation windows.\[23\] Notably, researchers discovered that some halide perovskite materials can also perform reversible color and phase change between low and high temperature, demonstrating their potential for thermochromic smart window applications.\[9\] J. Lin et al. reported that cesium lead iodide/bromide ($\text{CsPbI}_3$-$\text{Br}_x$, $0 \leq x \leq 3$) perovskite undergoes thermally-driven reversible transitions ($T_c$ of 150 °C) between non-perovskite phase and colored perovskite phase with 81.7% and 35.4% visible transparency, respectively.\[24\] L. M. Wheeler et al. leveraged low formation and dissociation energy of the methylammonium lead iodide ($\text{MAPbI}_3$)-methylamine complex to demonstrate a switchable solar cell between the transparent state (68% visible transmittance) and the opaque state ($<3\%$ visible transmittance) with a transition temperature of 35 °C.\[25\] However, the toxicity and flammability of methylamine may hinder its wide application.\[26\] M. D. Bastiani et al. synthesized methyl-ammonium iodide/bromide perovskite inks which can reversibly change from yellow at 25 °C to orange at 60 °C by increasing the iodide content in the crystals through an unusual crystallization process.\[27\] Recently, humidity related chromic perovskite has also been explored. B.A. Rosales et al. discovered a reversible multicolor chromism in layered formamidinium (FA) metal halide perovskites, which is stimulated by solvent vapor and temperature.\[28\] The dynamic color change can be performed by the transition from 2D $\text{FA}_3\text{PbX}_4$ to 3D $\alpha$-$\text{FAPbX}_3$ and 1D $\delta$-$\text{FAPbI}_3$. S.K. Sharma et al. studied the reversible dimensionality tuning and chromic behaviors of methylammonium lead halides ($\text{MAPbX}_3$) upon exposure to humidity.\[29\] The dimensionality reduction from 3D to 0D of $\text{MAPbX}_3$ leads to the reversible transformation from a colored state to colorless state. With the similar water-related mechanism, Halder et al. found that the color of $\text{MAPbI}_3$ can be reversibly tuned during the heating-cooling loop by synthesizing the precursor solution that consisted of 4:1 molar ratio of MAI to $\text{PbI}_2$. They suggested that the thermochromism was attributed to the hydration and dehydration process (Equation (1)):\[30\]

$$\text{MAPbI}_3 + 3\text{MAI} \rightarrow \text{MA}_4\text{PbI}_4 \cdot 2\text{H}_2\text{O}$$

At the cold state, the dihydrated perovskite $\text{MA}_4\text{PbI}_4 \cdot 2\text{H}_2\text{O}$ is transparent, and at the hot state it becomes opaque because of the existence of organic-inorganic lead halide perovskite $\text{MAPbI}_3$. Following that work, Y. Zhang et al. successfully developed a hydrated $\text{MAPbI}_3$ ($\text{H-MAPbI}_3$) thermochromic perovskite smart window, recording a $\tau_{\text{sum}}$ of 90% at the cold state, 34.3% at the hot state, and $\Delta \tau_{\text{sol}}$ of 25.5%.\[31\] The high transparency at the cold state and the high $\Delta \tau_{\text{sol}}$ of $\text{H-MAPbI}_3$ thermochromic perovskite demonstrate it to be a good candidate for thermochromic smart window applications. But, the transition temperature of $\text{H-MAPbI}_3$ perovskite thermochromic smart windows is relatively high (>50 °C in the heating process), and this limits its real-life application in buildings since in most places window temperatures normally do not reach 50 °C, even in the summer. In addition, the difference of transition temperature between heating and cooling cycles is large (i.e., larger than 18 °C), implying that the thermochromism of $\text{H-MAPbI}_3$ smart windows may suffer from severe transition hysteresis, such as insensitive optical response to temperature. Therefore, these problems must be addressed before the widespread deployment of perovskite thermochromic smart windows in buildings.

Although significant advancements have been reported on the thermochromism of halide perovskites, both the optical properties and transition properties of thermochromic perovskites remain unsatisfactory. Therefore, this work aims to develop a perovskite thermochromic smart window that has good optical properties (high $\tau_{\text{sum}}$ and $\Delta \tau_{\text{sol}}$), lower $T_c$, narrower $\Delta T_c$ and shorter $\tau_c$. To achieve these goals, a novel hydrated $\text{MAPbI}_{3-x}\text{Cl}_x$ ($\text{H-MAPbI}_{3-x}\text{Cl}_x$) thermochromic perovskite smart window ($\text{TPSW}$) is proposed, which utilizes thermal heating to dissociate $\text{H}_2\text{O}$ from the $\text{MAPbI}_{3-x}\text{Cl}_x$ layer, thus transforming from the transparent state to the colored state. And this phenomenon is reversible upon cooling to rebind $\text{H}_2\text{O}$. $\text{H-MAPbI}_{3-x}\text{Cl}_x$ TPSW demonstrates high $\tau_{\text{sum}}$ and $\Delta \tau_{\text{sol}}$ and excellent transition properties. In addition, a thermodynamic mathematic model was developed to predict the $T_c$ and $\Delta T_c$ of the $\text{H-MAPbI}_{3-x}\text{Cl}_x$ thermochromic perovskite, providing a convenient way for users to control the $T_c$ of perovskite smart windows according to their needs. Most importantly, a model house field test was conducted in Hong Kong (sub-tropical climate) to examine the feasibility and energy saving performance of the $\text{H-MAPbI}_{3-x}\text{Cl}_x$ TPSW in practical applications. Overall, the novel $\text{H-MAPbI}_{3-x}\text{Cl}_x$ thermochromic perovskite proposed in this study is competitive among all the thermochromic perovskites reported for smart window applications, and it shows great potential to reduce the high energy consumption in buildings.

### 2. Results and Discussion

#### 2.1. Synthesis and Composition Analysis of $\text{H-MAPbI}_{3-x}\text{Cl}_x$

**Thermochromic Perovskite**

The $\text{H-MAPbI}_{3-x}\text{Cl}_x$ thermochromic perovskite was synthesized by the spin coating method using a solution precursor of MAI and $\text{PbCl}_2$ in dimethylformamide (DMF) solvent. The precursor was spin-coated on quartz glass substrates, followed by thermal annealing in the glovebox at 100 °C for 60 min (Figure 1a). It should be noted that the thermochromism of $\text{H-MAPbI}_{3-x}\text{Cl}_x$ is attributed to hydration and dehydration, so the reversible color change cannot be observed in the inert environment (glovebox). After the $\text{H-MAPbI}_{3-x}\text{Cl}_x$ thermochromic perovskite samples were removed from the glovebox to ambient environment, the thermochromism could be observed upon heating and cooling. To identify the proper concentration ratio of MAI and $\text{PbCl}_2$ that can achieve remarkable thermochromism, a series of precursor solutions were made with the molar ratio of MAI and $\text{PbCl}_2$ varied from 4:1 to 7:1. At the hot state (60 °C), all these samples are dark reddish-brown. As the temperature is reduced, discoloration of the film occurs until it becomes transparent at the cold state (25 °C). However, it is found that only the samples with the relative molar concentration of MAI to $\text{PbCl}_2$ higher than 6:1 (i.e., MAI/$\text{PbCl}_2 = 6.5:1$ and $7:1$) can achieve complete...
transparency at the cold state, while other samples appear a dark grey (Figure S1, Supporting Information). X-ray diffraction (XRD) measurements on the sample with 4:1 MAI:PbCl\textsubscript{2} ratio at the cold state clearly shows the tetragonal structure of MAPbI\textsubscript{3}, and yet the intensity of the MAPbI\textsubscript{3} characteristic peak decreases with an increase of MAI concentration (Figure S2, Supporting Information). The MAPbI\textsubscript{3} characteristic peak completely disappears when the MAI:PbCl\textsubscript{2} ratio of the precursor is higher than 6:1. The existence of MAPbI\textsubscript{3} perovskite at the cold state leads to the dark grey appearance. At the same time, with the increase of MAI in the precursor, the strong MAI characterization peak can be detected when the MAI:PbI\textsubscript{2} ratio reaches 7:1. Notably, for the mixing ratio of 6.5:1, no characterization peak relating to diffractions from the residual MAPbI\textsubscript{3} and MAI can be observed, therefore, the mixing ratio of 6.5:1 of MAI and PbCl\textsubscript{2} is chosen for further experiment. It should be noted that the reversible thermochromism can also be controlled by the ambient relative humidity (RH) without heating/cooling process. Figure S3, Supporting Information exhibits an H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} thermochromic perovskite under different annealing times. f) XRF analysis of precipitate on the blank glass attached on the petri dish of Figure S4, Supporting Information.

Figure 1. a) Schematics of the fabrication process and photos of H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} thermochromic perovskite at the cold and hot states. b) FTIR spectrum comparison of H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} thermochromic perovskite at the cold and hot states. c) XRD patterns of H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} and H-MAPbI\textsubscript{3} thermochromic perovskite at the hot state as well as the zoom-in pattern from 14° to 14.7°. d) Photos of H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} thermochromic perovskite during the annealing process. e) XRF analysis of H-MAPbI\textsubscript{3−x}Cl\textsubscript{x} thermochromic perovskite under different annealing times. f) XRF analysis of precipitate on the blank glass attached on the petri dish of Figure S4, Supporting Information.
that the sample changed from a transparent state to a reddish-brown state when the RH reduced to ~10%. The modulation of humidity was then reversed (i.e., from 10% to 30%) to perform the humidification process. The reddish-brown started to fade and the sample recovered its transparent state during the increase of RH to 30%. This phenomenon indicates that water vapor plays an essential role in the thermochromic process of H-MAPbI$_3$-Cl$_x$.

To investigate the effect of water vapor on the reversible thermochromism, Fourier transform infrared spectroscopy (FTIR) measurements were conducted for the H-MAPbI$_3$-Cl$_x$ thermochromic perovskite. Figure 1b shows the FTIR spectra of the novel H-MAPbI$_3$-Cl$_x$ thermochromic perovskite (synthesized by the precursor of MAI: PbCl$_2$ (6.5:1) at both the hot state and cold state. It can be seen from the spectrum that a clear signature peak of H–O bond appears at around 3500 cm$^{-1}$ when the perovskite sample is at 25 °C. When the sample is heated to 60 °C, the H–O bond completely disappears, while the other chemical bonds remain the same. The H–O bond appears again when the sample is cooled back to 25 °C. In addition, no color change can be observed in the glove box where the humidity level is low (<1 ppm). These results not only indicate the existence of condensed water at the clear state of H-MAPbI$_3$-Cl$_x$, but also prove that water functions as the essential driving force in the reversible thermochromism of H-MAPbI$_3$-Cl$_x$ thermochromic perovskite.

Moreover, the measurement of energy dispersive X-ray spectroscopy (EDS) was also conducted for the H-MAPbI$_3$-Cl$_x$ at the cold state, showing the atomic ratio of I:Cl:Pb = 5.98:0.40:1, proving that only a small amount of Cl exists in the perovskite samples during the annealing procedure as shown in Figure S4, Supporting Information. After the H-MAPbI$_3$-Cl$_x$ thermochromic perovskite samples were fully annealed, a deposition of white residue could be observed on the blank glass. The composition of the white residue was analyzed by XRF, and the strong Cl peak is shown in Figure 1f. Note that no Pb and I X-rays can be detected from the glass. This is direct evidence showing the sublimation of Cl-containing vapor during the annealing process. Since the sublimation temperature of MACl is lower than that of MAI, PbCl$_2$, and PbI$_2$, it is possible that the Cl escapes in the form of MACl vapor. The above XRD and XRF analysis clearly suggest that the release of Cl-containing vapor plays an essential role in the formation of H-MAPbI$_3$-Cl$_x$ thermochromic perovskite film.

2.2. Optical Properties of H-MAPbI$_3$-Cl$_x$ Thermochromic Perovskite Smart Windows

Generally, H-MAPbI$_3$-Cl$_x$ TPSW allows the solar irradiance to pass through at the cold state. However, at the hot state, it blocks most of the visible light for saving energy (Figure 2a). A scanning electron microscope (SEM) image of an H-MAPbI$_3$-Cl$_x$ film is shown in Figure 2b and the cross-sectional image shows that the thickness of the film is around 1.05 μm. The optical transmittance of the H-MAPbI$_3$-Cl$_x$ TPSW was measured at room temperature (cold state) and 60 °C (hot state) and the results are shown in Figure 2c together with the solar irradiance intensity and photopic luminous efficiency. Figure 2c shows that the thermochromism in H-MAPbI$_3$-Cl$_x$ perovskite primarily tunes the visible light transmittance (380–780 nm), without affecting the infrared transmittance (780–2500 nm).
The luminescence τ_lum of H-MAPbI_{3-x}Cl_{x} at the cold and hot states is 85.2% and 30.3%, respectively. Accordingly, Δτ_{sol} can reach 23.7%. It should be noted that the high Δτ_{sol} can be attributed to the significant difference in the solar transmittance between the cold state and hot state in the ultraviolet and visible light regions, accounting for around 57% of total solar energy in the solar spectrum. The high τ_lum at the cold state and high Δτ_{sol} result in its promising optical properties compared with other thermochromic smart windows (e.g., τ_lum and Δτ_{sol} of vanadium dioxide (VO₂) thermochromic smart windows are normally ≈50% and ≈10% respectively[35]). Table 1 compares the optical performance of the H-MAPbI_{3-x}Cl_{x} and the H-MAPbI_{3} TPSWs. Since the Cl content in the H-MAPbI_{3-x}Cl_{x} is low, it is not surprising that its optical performance is very similar to H-MAPbI_{3}. However, we found that the dilute Cl doping in the H-MAPbI_{3-x}Cl_{x} results in

![Figure 2. a) Working principle of H-MAPbI_{3-x}Cl_{x} TPSW. b) SEM image of H-MAPbI_{3-x}Cl_{x} thermochromic perovskite thin film. c) Transmittance spectrum of H-MAPbI_{3-x}Cl_{x} TPSW at the cold and hot states.](image)

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<th>τ_lum,hot [%]</th>
<th>τ_lum,cold [%]</th>
<th>Δτ_{sol} [%]</th>
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<td>H-MAPbI_{3} TPSW</td>
<td>37.4</td>
<td>85.4</td>
<td>23.1</td>
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<tr>
<td>H-MAPbI_{3-x}Cl_{x} TPSW (MAI:PbCl_{2} = 6.5:1)</td>
<td>30.3</td>
<td>85.2</td>
<td>23.7</td>
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a dramatic improvement in transition properties (discussed in the next section).

### 2.3. Transition Properties of H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW

Apart from the comparable optical properties, H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW also showed a remarkable improvement in transition properties when compared to H-MAPb\textsubscript{1} TPSW. In order to characterize $T_c$ and $\Delta T_c$, the transmittance at 550 nm as a function of temperature for the heating and cooling cycles of the two TPSWs was measured under the ambient condition of 25 °C and RH 50% as shown in Figure 3a, and $T_{c,h}$, $T_{c,c}$ as well as $\Delta T_c$ were calculated accordingly. As the largest transmittance difference of thermochromic perovskites is observed at the wavelength of 550 nm (Figure 2c), which is also the peak in CIE photopic luminous efficiency of the human eye, the transmittance at the wavelength of 550 nm was selected to monitor the thermochromism. It should be noted that to show the relative difference between the two TPSWs, the transmittance intensities shown in Figure 3a are just the relative values rather than absolute figures. The results reveal the $T_{c,h}$ and $T_{c,c}$ of the H-MAPb\textsubscript{1} TPSW to be 53.2 and 30.3 °C, respectively. However, the $T_{c,h}$ of the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW shows a significant reduction of 8.3 to 44.9 °C compared to the H-MAPb\textsubscript{1} TPSW, and an increase of 5 to 35.3 °C in the cooling process. Most importantly, a much narrower $\Delta T_c$ of 9.6 °C is achieved by the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW, which is significantly lower than that of 22.9 °C obtained by the H-MAPb\textsubscript{1} TPSW. Such a narrow width can be comparable with tungsten doped VO\textsubscript{2} thermochromatic smart windows (i.e., 9.4 °C).

As discussed above, the thermochromic effect of H-MAPb\textsubscript{1-x}Cl\textsubscript{x} is caused by the hydration and dehydration processes, implying that the humidity level of the ambient environment is crucial to the transition properties. To further investigate the humidity effect on transition properties of H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW, its $T_{c,h}$, $T_{c,c}$, and $\Delta T_c$ were measured under various RH conditions and the results are shown in Figure 3b. It can be seen that the $T_{c,h}$ and $T_{c,c}$ both increase with the increase in humidity of the environment, and the average $T_c$ between the heating and cooling processes increases from 29.4 to 51.4 °C. To explain that, during the heating cycle, the high humidity hinders the water molecules escaping from the thermochromic perovskite film, and hence a higher temperature is required to boost the dehydration process. However, in the cooling cycle under high humidity conditions, the water molecules can be more easily absorbed by the thermochromic perovskite even at the high temperature, so that at a RH of 80%, we observe a $T_{c,h}$ and $T_{c,c}$ of 54 and 46 °C, respectively. When the RH decreases to 25%, the $T_{c,h}$ and $T_{c,c}$ of the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW are 35.5 and 22.3 °C, respectively.

### Figure 3.  a) The temperature-dependent thermochromic hysteresis loops of the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} and H-MAPb\textsubscript{1} TPSWs upon heating and cooling processes (optical transmittance at 550 nm as a function of temperature). b) Effect of RH on the $T_c$ and $\Delta T_c$ of the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW. c) Effect of RH on the $t_c$ of the H-MAPb\textsubscript{1-x}Cl\textsubscript{x} TPSW upon heating and cooling processes.
thermochromic perovskite materials before, and this low $T_c$ makes perovskite materials useful as practical smart window coatings. Regarding the effect of the hysteresis width, opposite to that on the transition temperatures, a negative correlation between the $\Delta T_c$ of H-MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite and humidity was found as shown by the dash line in Figure 3b. With the increase of humidity level, the hysteresis width decreases from 13.1 to 7.7° as the increase of humidity hinders the dehydration while promoting moisture absorption.

As temperature fluctuates during the day, rapid response, namely a short transition time ($t_c$), is crucial for thermochromic materials in practical applications. Even though there is no strict requirement, an acceptable transition time should be in several minutes for energy efficient smart windows.$^{[10]}$ The $t_c$ in the heating and cooling cycles of the H-MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite was investigated under RH ranging from 25% to 80%, corresponding to the measurement of $T_c$. The results in Figure 3c reflect the humidity dependence of the $t_c$ in both heating and cooling processes. With the increase of RH, the $t_c$ in the heating process drastically increases from 60 (RH = 25%) to 240 s (RH = 80%). However, the opposite trend can be observed in the cooling process, where the $t_c$ can be reduced to even lower than 30 s when the RH increases to 80%. When the RH is 50%, H-MAPbI$_{3-x}$Cl$_x$ shows shorter $t_c$ than H-MAPbI$_3$ TPSW in both heating (120 s vs 240 s) and cooling processes (60 s vs 90 s), proving the enhancement in transition properties.

From the above analysis, a close relationship can be found between humidity (partial water pressure in the air) and transition properties on H-MAPbI$_{3-x}$Cl$_x$ TPSWs. To further quantitatively analyze the reversible dilyhydrated perovskite formation and dissociation process of H-MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite in relation to humidity, a thermodynamic model is developed. The thermodynamics of hydration and dehydration can be explained by the Clausius–Clapeyron (C–C) relation that reveals the relationship between pressure and temperature in the phase transition boundary (Equation (3)).$^{[38,39]}$ The solution of the C–C relation is shown in Equation (4).

$\Delta G(T) = \Delta G^o(T) + xRT \ln \frac{p(T)}{p_o} = 0$  

(4)

where $\Delta G$ is the molar Gibbs energy change of the reaction, $p_o$ is a reference pressure, $\Delta G^o$ is the Gibbs energy change at $p_o$, and $R$ the gas constant ($R = 8.314$ J mol$^{-1}$ K$^{-1}$). Considering that $\Delta G^o = \Delta H^o - T \Delta S^o$, where $H$ represents enthalpy and $S$ is entropy, the relationship between pressure and temperature is clearly demonstrated in Equation (5).

$\ln \frac{p(T)}{p_o} = \left(\frac{\Delta H^o}{xR} \right) \left(\frac{1}{T} \right) + \Delta S^o(T) \frac{1}{xR}$

(5)

According to the C–C relationship, the partial water pressure-transition temperature dependence of the dehydration and hydration process between MA$_4$Pb$_{6}$xCl$_{1-x}$-2H$_2$O and MAPbI$_{3-x}$Cl$_x$ can be drawn in the C–C diagram as shown in Figure 4a, where the red line represents the dehydration process (heating process) and the blue line represents the hydration process (cooling process). The hysteresis width is shown as the area of pseudo-equilibrium between the hydration and dehydration. The thermochromism takes place at a certain temperature $T$ when another parameter (e.g., water vapor pressure $P$) is fixed. The dotted line from point A to point B demonstrates an isobaric transition from the transparent state (MA$_4$Pb$_{6}$-xCl$_x$-2H$_2$O) to the colored state (MAPbI$_{3-x}$Cl$_x$), that requires a minimum temperature $T_{min}$, namely the transition temperature of the heating process. Similarly, the line from point C to point A illustrates the isothermal transition from the semitransparent state to the transparent state at room temperature ($T_o$) by controlling the water vapor pressure. To verify the model, the transition temperatures of H-MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite in the heating and cooling processes were measured at various partial water vapor pressure conditions as shown in Figure 4b. The measured data points in the heating and cooling processes can be well fitted by the linear regression model $\ln P = -6030.2 \left(\frac{1}{T}\right) + 26.3$ (red solid line) and $\ln P = -4408.3 \left(\frac{1}{T}\right) - 21.6$ (blue solid line), respectively. Through the model, the transition temperature of H-MAPbI$_{3-x}$Cl$_x$ thermochromic perovskite can be easily estimated. This model provides the feasibility to customize the transition temperature of TPSW. In practical
applications, the thermochromic perovskite could be coated at the inner face of a conventional double-glazed window, and by modifying the humidity (the required humidity can be conveniently calculated based on the model) of the air gap in the double-glazed system, the customized transition temperature for the TPSW can be easily achieved. It should be noted that the model is also suitable for H-MAPbI$_3$ thermochromic perovskite as shown in Figure 4b.

2.4. Cycle Performance Test of the H-MAPbI$_{3-x}$Cl$_x$ TPSW

After characterizing the optical and transition properties of H-MAPbI$_{3-x}$Cl$_x$ TPSW, the cycle performance was investigated to ensure its applicability in smart window applications, where the capability of performing stable thermochromism over substantial cycles of heating and cooling processes is expected. A cycle test was conducted on H-MAPbI$_{3-x}$Cl$_x$ TPSW with a total of 50 cooling and heating cycles. The heating and cooling operations were conducted in an air enthalpy testing laboratory (±0.1 °C and ±3% RH of error) where the ambient temperature was set at a constant 25 °C with a RH of about 50%. It should be noted that in smart window applications, extreme environmental conditions barely occur so that the window temperature is mostly within the normal range (i.e., from room temperature to around 50 °C), thus the heating and cooling temperatures in the cycle test were set as 60 and 25 °C, respectively. During the heating and cooling cycles, the fast and reversible transition between the transparent state (i.e., cold state) and reddish-brown state (i.e., hot state) was consistently displayed throughout the cycle test. Regarding the cycling optical performance, the $\tau_{\text{lum}}$ at both the hot and cold states of the H-MAPbI$_{3-x}$Cl$_x$ TPSW was detected at five-cycle intervals, using the method as described in Characterization (Experimental Section). Figure 5a illustrates the optical property test results, in which the $\tau_{\text{lum}}$ of the H-MAPbI$_{3-x}$Cl$_x$ TPSW at both the hot and cold states remained almost unchanged over the 50 cycles, resulting in a stable $\Delta\tau_{\text{sol}}$. As for the transition properties, the $T_c$ at both the hot and cold states of the H-MAPbI$_{3-x}$Cl$_x$ TPSW was recorded at 10-cycle intervals. Figure 5b shows the transition property test results, in which the sample demonstrated nearly the same transition temperature at both the hot and cold states over the 50 cycles, contributing to the constant hysteresis width. The cycle test results strongly indicate that the H-MAPbI$_{3-x}$Cl$_x$ TPSW has the ability to undergo substantial heating and cooling cycles while maintaining the stable and promising thermochromic performance.

2.5. Model House Field Test

To test the energy saving performance of this H-MAPbI$_{3-x}$Cl$_x$ TPSW, a field test using a model house was conducted in the early autumn of Hong Kong (weather information is shown in Table S1, Supporting Information). Two glass pieces (each 9 cm × 9 cm) were sealed together to build a double-glazed window (Figure 6a) and the perovskite film was coated on the inner faces of the windows. The H-MAPbI$_{3-x}$Cl$_x$ TPSW was installed on a heat-insulated acrylic model house (Model House 1) with the volume of 20 × 20 × 20 cm$^3$. Another model house (Model House 2) with a quartz glass double-glazed window (Figure S5, Supporting Information) was also constructed as a reference for comparison. The experimental setup is shown in Figure 6b and the field test was conducted on the rooftop of a building. The windows of the model houses faced the sky to mimic the roof window. Two thermocouples (T-type) were utilized to monitor the indoor air temperature and window temperature, respectively. The ambient temperature and global solar irradiation were measured by a weather station. The test results are shown in Figure 6c. After sunrise (7:00 AM), the indoor air temperature increased rapidly with the increase of solar intensity. The indoor air temperature of Model House 1 equipped with the H-MAPbI$_{3-x}$Cl$_x$ TPSW was lower than that of Model House 2 during the daytime, which confirms the sunlight shielding effect induced by the H-MAPbI$_{3-x}$Cl$_x$ TPSW. The largest indoor air temperature reduction of 3.5 °C was achieved in Model House 1 at 1:00 PM. It should be noted that the temperature of the H-MAPbI$_{3-x}$Cl$_x$ TPSW in Model House 1 was always higher than the quartz glass window in Model House 2, but the indoor air temperature of Model House 1 was lower than that of Model House 2, implying that the direct solar

![Figure 5. a) Optical performance ($\tau_{\text{lum,hot}}$, $\tau_{\text{lum,cold}}$, and $\Delta\tau_{\text{sol}}$) of the H-MAPbI$_{3-x}$Cl$_x$ TPSW after 50 cycles. b) Transition properties ($T_{\text{ch}}$, $T_{\text{cc}}$, and $\Delta T_c$) of the H-MAPbI$_{3-x}$Cl$_x$ TPSW after 50 cycles.](image-url)
radiation is the dominant factor to heat the indoor environment rather than heat conduction between the window and indoor air. Furthermore, when the solar intensity decreased in the late afternoon, the indoor air temperature difference between the two model houses gradually reduced, because H-MAPbI$_3$-$\chi$TPSW mainly mitigates energy loss/gain through modulating the solar radiation. It should be noted that the field test was conducted in the autumn in Hong Kong where the highest solar irradiance is only \(\approx 860 \text{ W m}^{-2}\). It is expected that the indoor air temperature reduction can be larger in summer when the solar irradiance exceeds 1000 W m$^{-2}$. Overall, the field test results prove that the H-MAPbI$_3$-$\chi$TPSW can effectively block the solar radiation, demonstrating great potential as smart windows in building applications.

### 2.6. Comparisons with Previous Studies

To further demonstrate the improved optical and thermochromic performance of the H-MAPbI$_3$-$\chi$TPSW in this
study, an inclusive comparison with other related works, such as perovskite, hydrogel, VO₂, and nickel (II) iodide thermochromic smart windows, is presented in Table 2. For various thermochromic smart windows, several different materials or synthesizing methods were included with the references of published works. The optical and transition properties were considered for evaluation in terms of the smart window performance.

Among perovskite materials, the H-MAPbI₃ₓClₓ TPSW shows comparatively high average 𝜃ᵣum and Δ𝜏sol. Most importantly, it exhibits the shortest transition time for both heating and cooling processes, and the hysteresis width is even half that of the similar H-MAPbI₃ TPSW. Compared with the hydrogel thermochromic smart window, the optical properties of the studied H-MAPbI₃₋ₓClₓ TPSW can be eliminated since the H-MAPbI₃₋ₓClₓ thermochromic perovskite is a thin film deposited on the glass. With regard to the VO₂ thermochromic smart window, because optical regulation only occurs in the near infrared region, the average Δ𝜏sol of VO₂ is only half that of the studied H-MAPbI₃₋ₓClₓ TPSW. At the cold state, unlike the transparent H-MAPbI₃₋ₓClₓ TPSW, the VO₂ thermochromic smart windows are brownish in color, and therefore provide less visual clarity for building occupants. In addition, a nickel (II) iodide based thermochromic smart window was recently proposed that possesses relatively high optical modulation ability, and yet the hysteresis width was still large. Overall, H-MAPbI₃₋ₓClₓ TPSW provides outstanding thermochromic properties compared with different thermochromic smart windows. Most importantly, a great reduction in hysteresis width is also achieved by the H-MAPbI₃₋ₓClₓ TPSW, making it more suitable in real applications.

### 3. Conclusion

In this study, a novel H-MAPbI₃₋ₓClₓ thermochromic perovskite is proposed as a material for smart windows with its thermochromism achieved by the manipulated phase transitions between dihydrated perovskite (low-temperature) and perovskite (high-temperature) phases. It demonstrates highly reversible color change during heating and cooling processes with a transmittance record of 𝜃ᵣum = 85.2% and 30.3% at the cold and hot states, respectively. The significant transmittance contrast in the visible light region leads to a high Δ𝜏sol of 23.7%. EDS, XRD, and XRF measurements show that only a small amount of Cl remains in the fully annealed perovskite films. By monitoring the annealing process and analyzing the released vapor product, it is found that the formation of the H-MAPbI₃₋ₓClₓ thermochromic perovskite is likely driven by the release of gaseous MACl (or other organic chloride compounds). Furthermore, due to the existence of a small amount of Cl, the H-MAPbI₃₋ₓClₓ thermochromic perovskite shows remarkable transition properties compared with H-MAPbI₃ thermochromic perovskite, namely, a much lower 𝜃ᵣum (29.4–51.4 °C) and narrower Δ𝜏sol (7.7–13.2 °C) as well as a shorter 𝜏ᵣ (1–4 min) could be achieved by controlling the humidity of the environment. Furthermore, using the obtained data, we developed a thermodynamic model which can easily predict the 𝜃ᵣ of H-MAPbI₃₋ₓClₓ thermochromic perovskite at different RH conditions. Most importantly, a 3.5 °C indoor air temperature reduction was achieved in a field test using a model house equipped with the H-MAPbI₃₋ₓClₓ TPSW, showing a promising energy saving potential compared with conventional windows. However, it should be pointed out that, similar to perovskite solar cells, the long-term stability of H-MAPbI₃₋ₓClₓ thermochromic perovskite should be further comprehensively studied. In summary, H-MAPbI₃₋ₓClₓ TPSW presents advanced optical performance and delivers an alternative method to further improve the transition properties of thermochromic perovskite materials, opening up a new research direction to develop high performance thermochromic smart windows.

### 4. Experimental Section

**Materials and Chemicals:** CH₃NH₂I (MAI, 99.5%) was supplied from Xi’an Polymer Light Technology. PbCl₂ (99%) and PbI₂ (99%) were.

### Table 2. Optical and transition properties comparison of various thermochromic smart windows.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Materials/methods</th>
<th>Optical properties</th>
<th>Transition properties</th>
<th>Refs.</th>
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<td>-------------</td>
<td>------------------</td>
<td>--------------------</td>
<td>----------------------</td>
<td>-------</td>
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<tr>
<td>Hydrogel smart windows</td>
<td>PNNIPAm</td>
<td>59.9</td>
<td>87.9</td>
<td>73.9</td>
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<tr>
<td>VO₂ smart windows</td>
<td>Chemical doping</td>
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<td>68.4</td>
<td>65.2</td>
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<tr>
<td></td>
<td>Polymer-assisted deposition</td>
<td>39.9</td>
<td>43.3</td>
<td>41.6</td>
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<tr>
<td></td>
<td>Bio-inspired moth eye</td>
<td>45.3</td>
<td>43.6</td>
<td>44.5</td>
</tr>
<tr>
<td>Nickel (II) iodide smart windows</td>
<td>Nickel (II) iodide</td>
<td>10.7</td>
<td>87.5</td>
<td>49.1</td>
</tr>
</tbody>
</table>

The optical and transition properties were calculated based on the figures presented in ref. [41].
Fabrication of Smart Windows: The sample fabrication was conducted in a glovebox (water content ≤ 1 ppm, oxygen content ≤ 1 ppm). Noted that two groups of samples were fabricated: H-MAPbI$_3$Cl, thermochromic perovskite synthesized by MAI and PbCl$_2$ in different molar ratio of 6.5:1, and H-MAPbI$_3$ thermochromic perovskite synthesized by MAI and PbI$_2$ in the molar ratio of 4:1. Perovskite precursor solution was prepared by the one-step deposition process. More specifically, 6.5 m MAI and 1 m PbCl$_2$ or 4 m MAI and 1 m PbI$_2$ were dissolved in DMF solvent, respectively, and then vigorously stirred at 50 °C until the solution was completely dissolved and the solution was absolutely clear. Quartz glass substrates were cleaned with detergent, then ethanol and then deionized water in an ultrasonic bath for 10 min, respectively. The cleaned substrates were then air-dried and treated in UV ozone cleaner for 15 min to improve surface wettability.[49] Perovskite thin film was spin-coated on the treated surface of the substrates, with a certain amount of the precursor, at 2000 rpm for 30 s. Then the 6.5MAI:1PbCl$_2$ and 4MAI:1PbI$_2$ coated thin films were immediately annealed on a hot plate at 100 °C for 1 h and 15 min, respectively, to evaporate the residual solvents and facilitate crystallization.[44] Characterization: All characterization processes were conducted under an ambient condition. Crystal structure was characterized by XRD (XRD PANalytical). Elemental composition was measured by XRF Spectrometer (S2 PUMA Series 2, Bruker) by monitoring the CI (K), I (L), and Pb (M) characteristic X-ray lines. The measurement of FTIR spectrum was conducted by SHIMADZU IRAffinity 1 spectrometer. The perovskite precursor was spin coated on the silicon wafer, and attenuated total reflectance mode was used to scan the spectrum. EDS was conducted by Hitachi S4800 Field Emission SEM. Luminous transmittance was characterized by a UV–vis–NIR spectrophotometer from 300 to 2500 nm (Lambda 950, Perkin Elmer equipped with an integrating sphere detector, USA). A temperature controller (including a heater, a T-type thermocouple, and a Digi-sense TC9600 temperature controller) was attached to modulate the temperature of the sample in order to measure the transmission at both cold state (including a heater, a T-type thermocouple, and a Digi-sense TC9600 temperature controller) was attached to modulate the temperature of the sample in order to measure the transmission at both cold state (300 °C) and hot state (2500 °C). The amount of transmitted visible light and solar radiation could be quantified by calculating luminous transmittance $\tau_{\text{Lum}}$ and solar transmittance $\tau_{\text{Sol}}$ with the following equation:

$$\tau_{\text{Lum}} = \int_{380}^{780} \tau(\lambda)(l/\tau(\lambda))d\lambda$$

$$\tau_{\text{Sol}} = \int_{300}^{2500} \tau(\lambda)d\lambda$$

where $\tau(\lambda)$ is the transmittance of the windows at wavelength $\lambda$, $l/\tau(\lambda)$ is the photopic luminous efficiency of the human eye defined by the CIE (International Commission on Illumination) standard, and $AM_{1.5}(\lambda)$ is the solar irradiance spectrum for an absolute air mass of 1.5 which is known as the reference or standard spectra. A wavelength range 300 nm ≤ $\lambda$ ≤ 2500 nm was chosen which accounted for 99.2% of terrestrial solar energy.[40] For the transition temperature measurement ($T_c$), the experiments were conducted at an air enthalpy testing laboratory where the temperature and RH could be controlled at constant set values and the experiment setup is shown in Figure S6. The experiments were conducted at an air enthalpy testing laboratory where the temperature and RH could be controlled at constant set values and the experiment setup is shown in Figure S6, Supporting Information. More specifically, four groups of experiments were carried out, under 25%, 50%, 65%, and 80% RH, while keeping the room temperature constant at 25 °C. For each level of humidity, the samples were heated on a hot plate from room temperature to 60 °C and then cooled back to 20 °C by a tailor-made electronic cooling plate, at intervals of 2 °C. The samples were kept on the hot/cold plate for 2 min to ensure the stability of the color. Simultaneously, under each temperature, the visible light transmittance of the samples was measured using Lens Transmission meter (SDR8508) at 550 nm wavelength. $T_c$ was determined by plotting the first derivative of the transmittance to the temperature as a function of temperature, and the $T_c$ is the temperature showing the minimum value at the first derivative.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

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