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Electrically tunable infrared reflector with adjustable bandwidth broadening up to 1100 nm[†]

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A tunable infrared reflector has been fabricated using polymer stabilized cholesteric liquid crystals containing a negative dielectric, anisotropic liquid crystal and a long and flexible ethylene glycol twin crosslinker. The reflection bandwidth of this prototype smart window can be tuned from 120 nm to an unprecedented 1100 nm in the infrared region upon application of only a small DC electric field, without interfering with the incident visible solar light. Bandwidth broadening was induced using very low operational power with acceptable switching speeds but only takes place in cells with particular gap thicknesses. Calculations reveal that between 8% and 45% of incident solar infrared light can be reflected with a single cell. The infrared reflector can potentially be used as a smart window to maintain the indoor temperature throughout the year, thereby reducing reliance on artificial lighting, heating and cooling, resulting in more than 12% reduction of building operation costs.

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Introduction

Eco-friendly buildings that do not emit greenhouse gases such as carbon dioxide and are capable of self-regulating heating, ventilation and cooling (HVAC) to maintain comfortable indoor temperatures and lighting conditions are highly desirable.¹ Considerable research is in progress to achieve this goal in the built environment by utilizing photovoltaic panels,² luminescent solar concentrators (LSCs),³ and smart windows,⁴ among other options. In particular, windows are an important part of architectural structures as they control access of solar energy to regulate indoor temperature, maintain interior illumination level, and allow viewing of the outdoors.^{5,6}

Infrared (IR) light from the sun spans from 700 nm to ~1 mm and is responsible for the heating up of buildings and automobiles. Static IR reflectors and stimuli responsive absorbers have been reported^{7–12} but they often absorb visible solar light which necessitates extra energy expenditure on artificial lighting to balance interior illumination. In addition, the static reflectors cannot adjust their properties in response to changing environmental conditions, resulting in additional

energy demands for heating and/or cooling. User addressable, responsive broadband infrared reflecting/transmitting windows that are transparent over the entire visible light region (400–700 nm) so that extra energy is not required to maintain the illuminance level of the room would be very appealing. Hence, smart windows^{13–25} have been a focus of development for the past few years. An autonomous organic-based temperature responsive IR reflector which reflects light at elevated temperatures and transmits it at lower temperatures^{26–28} and a manually controlled electrically switchable IR/visible reflector based on an inorganic material (tin doped indium oxide nanocrystals in niobium oxide glass) have been reported.²⁹ Narrowband IR reflectors based on cholesteric liquid crystals have also been fabricated to help reduce the thermal transmission through a window.^{30–32} These latter reflectors reflect only a limited fraction of incident solar light. Furthermore, some of them interfere with visible light, requiring the use of artificial lighting to compensate.

Recently, we have fabricated an electrically switchable broadband IR reflector³³ based on a polymer stabilized positive dielectric anisotropic (+ $\Delta\epsilon$) cholesteric liquid crystal^{34–38} that could be switched between two states, reflecting (planar) or transmitting IR light (homeotropic). Such windows were shown to have more limited impact in seasons with more moderate temperatures like spring and autumn. Moreover, they required significant electrical fields (8.6 V μm^{-1}) to switch from the reflective (planar) state to the transmissive (homeotropic) state, reducing the energy saving benefits of using the smart window.

We now report on an electrically tunable IR reflector which provides more control to the user to selectively reflect different fractions of infrared radiation without affecting the transparency

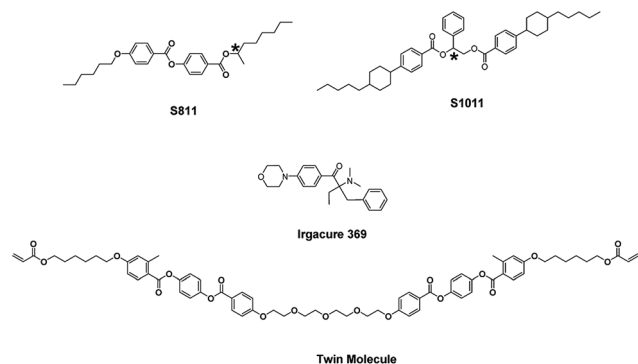
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Scheme 1 Molecular structures of the chemicals used for the fabrication of the tunable infrared reflector. The Ch-LC mixture consists of 87 wt% of a $-\Delta\epsilon$ nematic liquid crystal (MLC-2079), 3.7 wt% and 3.6 wt% of chiral dopants S811 and S1011, 5 wt% of an ethylene glycol twin crosslinker and 0.7 wt% of photoinitiator Irgacure 369.

in the visible region (400 nm to 700 nm), while only requiring low powers to operate and not requiring switching between planar and homeotropic states. The design of this reflector is inspired by the recent work in which the reflection bandwidth of visible light of a so-called polymer stabilized negative dielectric anisotropic ($-\Delta\epsilon$) cholesteric liquid crystal (Ch-LC) mixture was enhanced seven fold on application of 0–6 V μm^{-1} DC fields.³⁹ It was proposed that positive charge impurities trapped by the polymer network delocalized on application of a DC field causing enhancement in the reflection bandwidth.⁴⁰ In order to design a “smart tunable window” to control IR passage and lower heating, cooling and lighting demands in the built environment, we have used a new long and flexible ethylene glycol crosslinker twin molecule^{41,42} (Scheme 1) to improve the ability of the polymer stabilizing network to trap the positively charged ionic impurities while simultaneously reducing the cross link density of the polymer network. The result is a tunable IR reflector that can produce more than a nine fold enhancement in reflection bandwidth ranging from 120 nm to ~ 1100 nm while maintaining high transparency in the visible region. The bandwidth broadening can be induced using very low operational power (1.2 V μm^{-1}) and at fast switching speeds; calculations reveal that between 8% and 45% of incident solar IR light can be reflected using a single cell. This distinctive optical phenomena could be employed as a smart window to maintain indoor temperature throughout the year while reducing reliance on artificial lighting, heating and cooling, resulting in more than 12% reduction of building operation costs.

Materials and methods

Scheme 1 shows the molecular structures of the chemicals used for the fabrication of the electrically tunable smart windows. The Ch-LC mixture was prepared by using 87 wt% of the $-\Delta\epsilon$ nematic liquid crystal MLC-2079 (Merck), 3.7 wt% and 3.6 wt% of chiral dopants S811 and S1011 (Merck), respectively, 5 wt% of ethylene glycol twin diacrylate crosslinker (Philips Research Lab) and 0.7 wt% of the photoinitiator Irgacure 369 (Ciba

Chemicals). This mixture was used to fill 10 μm and 50 μm thick Indium Tin Oxide (ITO) glass cells with rubbed polyimide antiparallel layers by capillary action. Mixtures were polymerized by exposure to high intensity UV light (75 mW cm^{-2}) at room temperature.

Results and discussion

In order to fabricate the tunable IR reflector, a cholesteric liquid crystal mixture similar to one reported earlier was used.³⁹ However, here we include a long ethylene glycol twin molecule to further enhance the ability of the polymer stabilizing network to trap positively charged ionic species as well as allow for greater distortion of the network when subjected to electromechanical force. A nematic liquid crystal mixture MLC-2079 with negative dielectric constant ($\Delta\epsilon = -6.1$) was chosen so that the LC director remains in a planar orientation upon application of relatively low electric fields. To explore the relevance of this phenomena to the applications described in this work, the chiral dopant concentration was chosen such that the reflection notch of the Ch-LC was centered near 1000 nm. The LC mixture consisted of both reactive (polymerizable) and non-reactive (non-polymerizable) mesogens mixed with a photoinitiator (Irgacure 369).

The LC mixture was drawn into an alignment cell with a 50 μm gap, and after photopolymerization, the resulting stabilized Ch-LC exhibited a reflection band centered around 998 nm with a bandwidth of 120 nm. The transmission spectra of Ch-LC mixture in a 50 μm cell upon application of DC electric fields is shown in Fig. 1a. At up to 25 V (threshold voltage), no change in the reflection band was observed. On applying DC electric fields from 25 V (0.5 V μm^{-1}) to 60 V (1.2 V μm^{-1}), a continuous and nearly linear increase of the bandwidth was observed, increasing from 120 nm to 1090 nm. For example, reflection bandwidth of 219 nm and 584 nm were observed on application of 30 V and 45 V, respectively. At higher voltage, the decreased fraction of incident light reflected could be due to the number of pitches being insufficient to reflect fully 50% of unpolarised light in the 1100 nm broadband infrared reflector. In this manuscript our interest is restricted to maintaining transparency in the visible region, therefore we do not consider applications beyond 60 V, as scattering of visible light increases due to formation of the focal conic state. A more than nine fold increase of the bandwidth in the IR region was achieved upon application of an electric field of just 1.2 V μm^{-1} while maintaining relatively high transparency in the visible region (inset Fig. 1b and S1†). Polarized optical microscopy (POM) images of the sample show no significant changes on application of DC voltage (Fig. S2†). The applied voltage (1.2 V μm^{-1}) to achieve nine fold enhancement in the reflection band (Fig. 1b) is much lower than reported in previous efforts.³⁹ The inclusion of the long ethylene glycol twin crosslinker is the likely source of the improved performance.³⁹ Most likely, application of the DC field causes the attraction of positively charged ions on and within the polymer stabilizing network, resulting in the distortion towards the negative electrode, compressing the cholesteric pitch ($P - \Delta P$) and repulsion from the positive electrode,

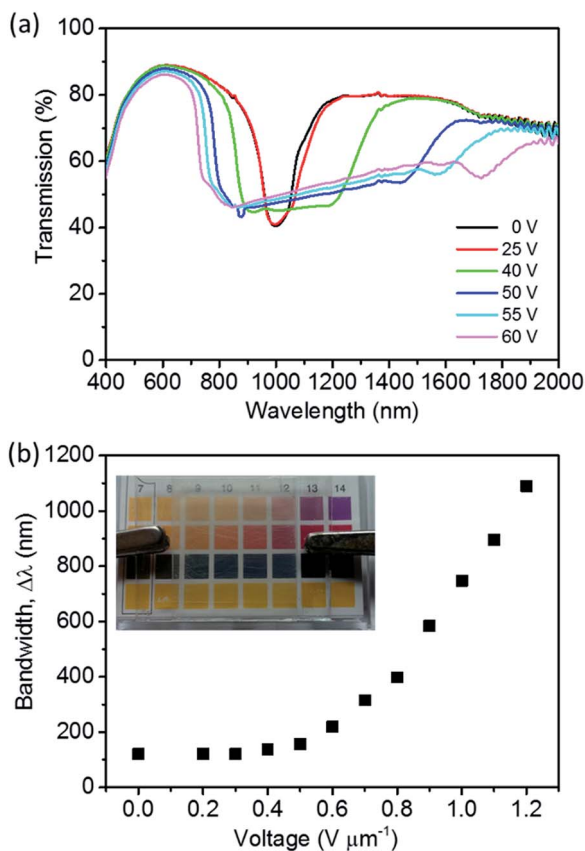


Fig. 1 (a) Transmission spectra of Ch-LC mixture in 50 μm cell on application of 0–60 V; (b) graph of the bandwidth of the Ch-LC with respect to the applied voltage per micron thickness of the cell (inset: photograph of the IR reflector showing the transparency for the visible light at 0 V).

expanding the cholesteric pitch ($P + \Delta P$).⁴⁰ Since the number of pitches in the larger gap cell (50 μm) is relatively high (approximately 77), there are a number of pitches (near the center of the cell) which would be undisturbed on application of relatively small electric field. The combination of compressed ($P - \Delta P$), expanded ($P + \Delta P$) and unchanged (P) pitches results in formation of broadband (Fig. 2a).⁴³ It is interesting to note that asymmetric broadening in the reflection band was observed on application of DC field (Fig. 1a). We speculate this is due to the increased difficulty in the extreme twisting and compression of the polymer network ($P - \Delta P$) at one side of the cell as compared to the unwinding and expansion ($P + \Delta P$) at the other.

To study the time required to tune the reflection bandwidth, we monitored the change in transmission at 1150 nm on application of 50 V. In the rest state (0 V) the tunable IR reflector shows 77% transmission at 1150 nm which decreases very rapidly on application of 50 V, before stabilizing at $\sim 55\%$ (in steady state) in about 80–100 seconds (Fig. 3a). Subsequent removal of electric field demonstrated rapid recovery with gradual stabilization to 77% transmission in about 100–130 seconds. More detailed analysis of Fig. 3a revealed that the transmission at 1150 nm initially decreases rapidly before

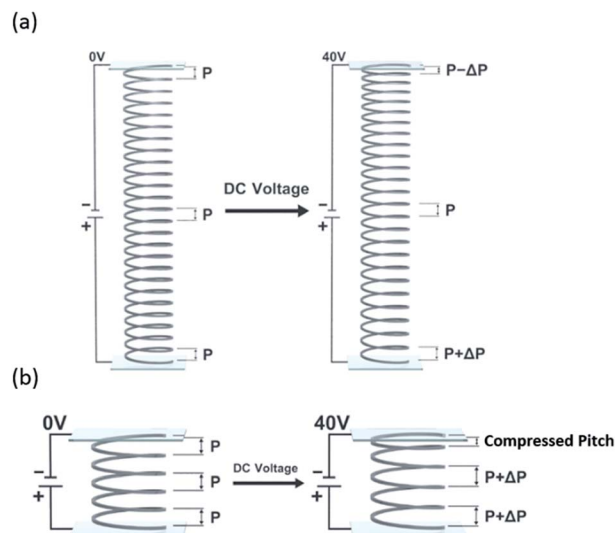


Fig. 2 Normalized schematic diagram to explain the different transmission behaviors between cells with smaller and larger cell gaps. The polymer network is depicted as a coil with a helical pitch that determines the wavelength of light this is reflected. Broadening or shifting of the reflection band depending on the cell gap (50 versus 10 μm , (a and b), respectively) occurs on application of a potential across the cell.

slowly increasing again on removing the electric field. This can be explained from Fig. 1a; where the reflection of the Ch-LC at 1150 nm is actually greater at 40 V than at 50 V. Removal of the electric field allows the polymer network at 50 V to relax, pass through the intermediate, high reflection state before the effective ‘memory state’ of the crosslinked matrix manifests itself, whereupon the transmission spectrum returns to the initial state. Fig. 3b shows that the tunable IR reflector can be switched reversibly from rest state to broad reflection (at 50 V) state without significantly affecting its transmission properties. The relatively short time required by the Ch-LC to change from the rest state to a broad reflection state (at 50 V) is adequate for using the tunable IR reflector for smart window applications.

We have also studied the effect of changing the polarity of the electric field on the cell transmittance (Fig. 3c). As shown earlier, application of +50 V resulted in a decrease of transmittance of the Ch-LC at 1150 nm to 55%. On inverting the polarity of electric field from +50 V to -50 V, it was observed that transmittance first increased (74%) and then decreased before reaching the steady state. A similar observation was seen upon further reversal of the polarity from -50 V to +50 V. This behavior suggests that upon changing the polarity, the electromechanically deformed polymer network first passes through the conformation found in the rest state (0 V), enhancing the transmittance at 1150 nm before further deforming towards the opposite electrode, leading to the decrease in transmittance.

To determine if the cells can also be used with a narrower gap so that less material is needed for scaling up, we have investigated the same liquid crystal mixture in a 10 μm cell. Fig. 4a shows the transmission spectra of the 10 μm Ch-LC cell upon application of DC electric fields. Remarkably, in contrast

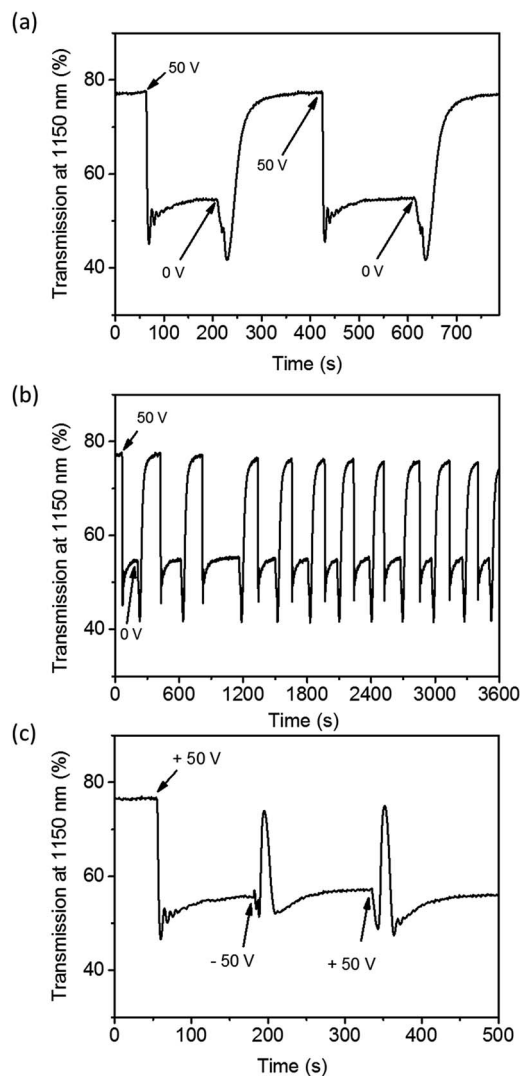


Fig. 3 (a) Effect of 0 and 50 V on the transmission spectra of the Ch-LC cell and (b) measurement demonstrating reproducibility of the Ch-LC on repeated switching between 0 and 50 V. (c) Effect of changing the bias applied to the cell on the transmission at 1150 nm in a 50 μm cell.

to the transmission behavior of the 50 μm cell, we observed predominantly a red shift in the position of the reflection band from 995 nm to 1545 nm (Fig. 4b), with only a modest increase of the bandwidth of the reflection band on application of the DC field from 0 V to 60 V (6 $\text{V } \mu\text{m}^{-1}$). Apparently, application of threshold electric field ($V > 25 \text{ V}$) affects all the pitches (including those in the middle of the cell), as there are only a few pitches (approximately 15). Most likely, the polymer network near the electrode deforms the most by the electro-mechanical forces. As the total number of pitches remains constant on application of electric field,⁴⁴ there must be a few pitches which are compressing ($P - \Delta P$) and therefore the rest of the pitches could expand ($P + \Delta P$) which leads to red shift in the position of the reflection band (Fig. 2b). The number of pitches which compresses should be less as we did not observe any compressed pitches (blue shifted reflection band) in the

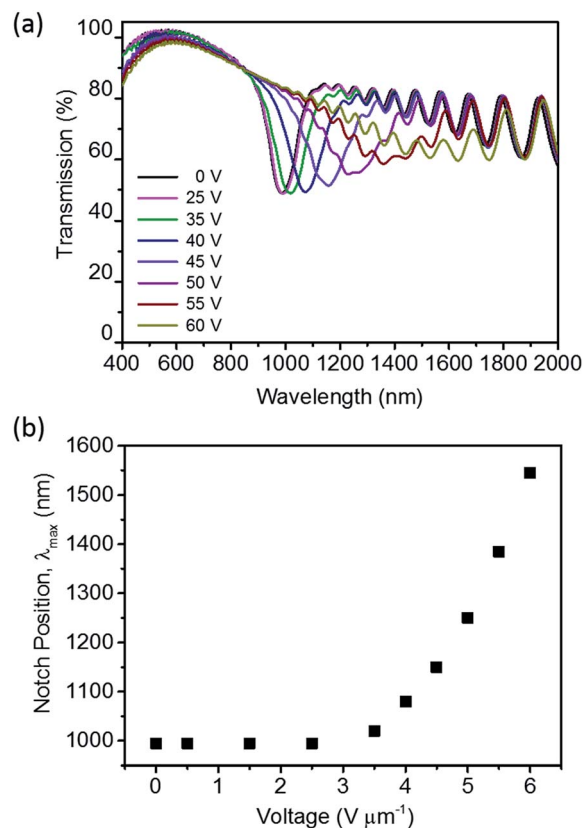


Fig. 4 (a) Transmission spectrum of the Ch-LC mixture upon application of 0–60 V (note: the oscillations seen at long wavelengths are due to interference effects of the cell) and (b) change in notch position as a function of the applied voltage per micron in a 10 μm cell.

transmission spectrum (from 400–2000 nm). It is interesting to note the potential across the cell required to shift the spectrum in the cells with the 10 μm gap was greater than that required to broaden the reflection band in the cells with the 50 μm cell gap (compare Fig. 4b to 1b). Our results reveal that for making our IR reflector with adjustable bandwidth broadening a certain minimum cell gap thickness is required, if the same experimental conditions are used.^{45,46}

To evaluate if the electrically tunable IR reflector can be potentially used as a smart window to save energy, we have calculated the power needed to switch the Ch-LC cell from 0 V to 50 V. Fig. 5 shows an exponential decay in the current flow on application of 50 V. The current reaches the steady state after 300 seconds. The power (P) consumption on application of 50 V could be calculated as:

$$P = V \times I$$

where the voltage (V) is 50 V and current (I) is 1.57 μA in steady state (2.5 cm \times 2.6 cm cell). The total power consumption to switch and maintain the window in a broad reflection state from rest state is only around 0.12 W m^{-2} . The potential impact on energy savings of using the tunable IR reflector in the built environment was calculated based on our earlier reported switchable IR reflector,³³ yielding a control over 8–45% of total

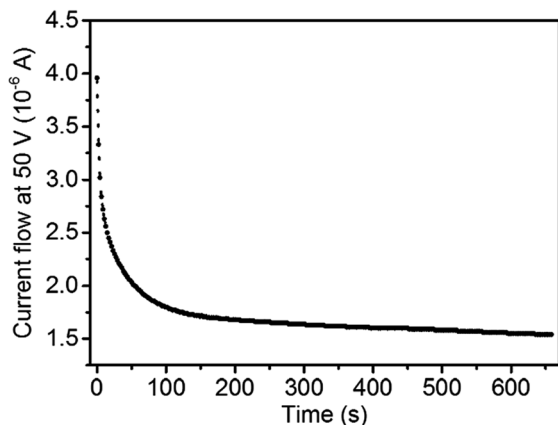


Fig. 5 Current flow in the 50 μm cell in the presence of 50 V.

incident solar IR light (Table S1 in ESI†). The power needed to operate the IR reflector as a smart tunable window throughout the year is very low (ESI†). A simple calculation (ESI†) where we assume that the performance at least as good as our switchable IR reflector³³ predicts that the minimum amount of energy normally used on heating and cooling that can be saved in office spaces on using the smart tunable window, including the energy cost to switch and maintain the window compared to a standard window employing double glazing, is 12.2% ($15.34 \text{ kW h}^{-1} \text{ m}^{-2} \text{ y}^{-1}$).

Conclusions

The fabrication of electrically tunable IR reflectors using a long, flexible ethylene glycol crosslinker twin molecule has been demonstrated. Through molecular design, we have shown an unprecedented 1100 nm broad reflection band can be achieved within 1–2 minutes on application of only a small electric field ($1.2 \text{ V } \mu\text{m}^{-1}$), making this reflector effective for the use in energy saving smart windows. The new design provides direct control to the user, allowing bandwidth adjustable selective reflection ranging from 120 to 1100 nm of infrared light to avoid both overheating and cooling, reducing extra energy expenditures. The IR reflector produces a broad reflection band in cells with a large cell gap and a red shift in the reflection position in cells with smaller gaps on application of an electric field. A simple calculation has shown that at least 12% of a standard building's energy usage can be saved by using this smart tunable window. Further improvements are possible by forming a 'double cell' arrangement to allow reflection of both right- and left-circularly polarized light: the current design is restricted to reflecting one-handedness. The application of smart windows is not limited to the built environment: there is also an enormous potential of such smart window in automobiles, as a significant amount of fuel energy that is spent on cooling and heating the car interior can be saved.

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