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Infrared Regulating Smart Window Based on Organic Materials

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Windows are vital elements in the built environment that have a large impact on the energy consumption in indoor spaces, affecting heating and cooling and artificial lighting requirements. Moreover, they play an important role in sustaining human health and well-being. In this review, we discuss the next generation of smart windows based on organic materials which can change their properties by reflecting or transmitting excess solar energy (infrared radiation) in such a way that comfortable indoor temperatures can be maintained throughout the year. Moreover, we place emphasis on windows that maintain transparency in the visible region so that additional energy is not required to retain natural illumination. We discuss a number of ways to fabricate windows which remain as permanent infrared control elements throughout the year as well as windows which can alter transmission properties in presence of external stimuli like electric fields, temperature and incident light intensity. We also show the potential impact of these windows on energy saving in different climate conditions.

(IR), here defined as light with wavelengths between 700 nm and 2500 nm, accounts for around 50% of the total energy emitted by the sun reaching Earth (Figure 1b),^[3,4] and this light produces interior heating but is invisible to the unaided eye.

The absorption of sunlight by building materials and passage of IR through transparent surfaces such as windows is responsible for much of the interior overheating of office rooms, automobile interiors, greenhouses, and other similar spaces. The use of artificial cooling and heating systems will only increase with the continued influence of global climate change, with energy used for cooling systems surpassing energy used for heating around the year 2070, and a 40 fold increase in air cooling energy use is expected by 2100.^[5] By controlling the influx of radiant heat transfer, calculations show that more than 50% of the energy

used in lighting, heating and cooling could be saved by deploying better control systems over only 18% of available window stock.^[6]

In areas with human inhabitants employing windows, more aspects must be considered than simply reducing the use of energy in the room: any switchable window used in, for example, a commercial office space has several other requirements that must be met before it may be installed. Among these requirements are reasonably fast switching speeds^[7] (although for IR control, relatively longer times compared to visible light switching should be acceptable), good optical transparency with minimum haze, an acceptable device lifetime,^[8] and functionality over a range of exterior temperatures. Controlling the excess of solar energy without compromising the visible transparency of the window is an important consideration for human health: maintaining inside/outside contact and daylighting are vital in retaining well-being and productivity, as well as providing economic and aesthetic gain by reducing the need for artificial lighting systems.^[9,10] These are challenging goals for a window to realize.

A number of materials have been developed over the past few decades to maintain indoor temperatures. Many of these focus on the opaque structural building elements like walls and roofing.^[10–13] Other solutions target the transparent window, employing external mechanical shutters and blinds,^[14] phase change materials (PCMs),^[15] thermochromic materials,^[16] aerogels,^[17] trapped gas in fluid membranes,^[18] and even phononic materials,^[19] among other options. Indeed, controlling heat passage through the window in response to changing climate conditions is a great challenge; ideally, one would accomplish

1. Introduction

More than 50% of the total energy used in the building envelope in the Western world is spent on cooling, heating and lighting the interior places (Figure 1a).^[1,2] A significant fraction of this energy use is related to our inability to control the ingress and egress of infrared light from the sun through windows. Near infrared light

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this without compromising the influx of visible light and the integrity of the view beyond the window.^[20]

The focus of this review is on infrared regulating windows based on organic materials which can adjust the transmittance of IR radiations depending on environmental conditions (Figure 2). There are advantages to employing organic rather than inorganic materials in IR window control systems: for instance, since they are non-metallic, they do not corrode or interfere with electromagnetic waves (signals from/to radios, cell phones, GPS, or garage door openers, for example)^[21–23] and often are much easier to process at lower temperatures than inorganic materials.

Cholesteric (or 'Chiral nematic') liquid crystalline (Ch-LC) materials have attracted much attention for development of infrared regulating windows. They are formed when nematic liquid crystals are doped with chiral molecules. The chiral dopants generate a LC organization wherein successive layers of nematic LC are displaced by a small rotation in molecular director with respect to their neighboring layers. The 'twist' generated may be either right- or left-handed, depending on the nature of the chiral dopant molecule. The central reflection band of Ch-LC is determined by the pitch (P), average refractive index (n_{avg}) of the material and incident angle of light (Equation (1)). Pitch (P) of the Ch-LC depends on the concentration (C) and helical twisting power (HTP) of the chiral dopants (Equation (2)). Ch-LC selective mirrors demonstrate a distinct advantage over, say, an inorganic Bragg reflector in that the LC self-organizes into a helical structure and can be easily processed from solution. Moreover, Ch-LCs can be made responsive to external stimuli, including temperature, electric/magnetic fields, light, pH, humidity and gasses that makes them interesting for a variety of applications.^[24,25] It is important to note that since a cholesteric-based reflector has a degree of angular dependence with respect to the incident light (Equation (1)), a blue shift in reflection band will be observed on deviating from the normal incident angle.^[26,27] The bandwidth of the light reflected by the Ch-LC is determined by the difference between the extraordinary (n_e) and ordinary (n_o) refractive indices and the pitch of the host LC (Equation (3)).

$$\lambda_0 = P \times n_{\text{avg}} \times \cos \theta \quad (1)$$

$$P = \frac{1}{C \times \text{HTP}} \quad (2)$$

$$\Delta\lambda = (n_e - n_o) \times P \quad (3)$$

The maximum reflection by the cholesteric reflector layer is limited to 50% of the incident sunlight, matching the polarization of the helix: that is, a right-handed cholesteric will reflect only right circularly-polarized light. Both left-circularly polarized light and light outside of the cholesteric reflection bandwidth are unaffected by the liquid crystal matrix and are transmitted normally (Figure 3).^[25]

LC molecules can be oriented in number of ways between two glass plates (Figure 4). The arrangements of the LC molecules determine their collective optical properties. For example, when the molecules are arranged in a helical fashion and parallel to the substrate, known as planar alignment, the layer reflects light of specific wavelengths depending on the pitch and



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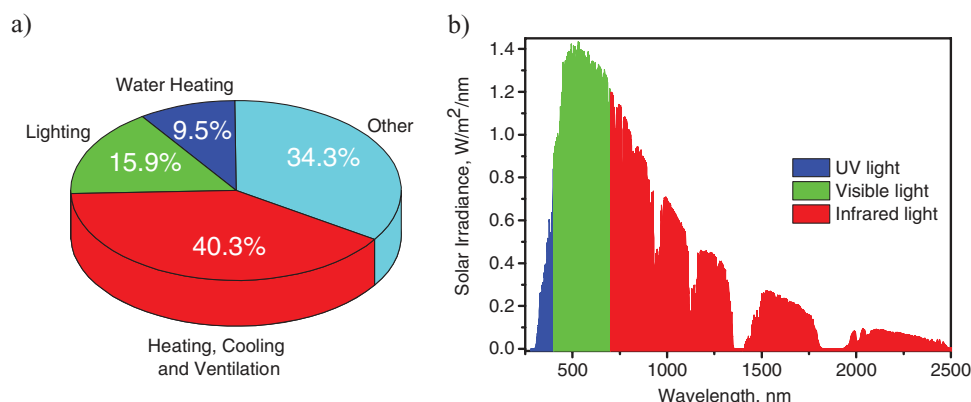


Figure 1. a) U.S. Buildings Energy End-Use in 2008.^[2] b) Solar spectrum on Earth (Data taken from National Renewable Energy Laboratory).

transparent for the rest of the wavelengths as described above. In a focal conic alignment, which consists of aligned molecules where the helical structure is preserved but tilted with respect to the substrate, results in more scattering of the incident light as the refractive index changes continuously from the top to the bottom of cell. In the homeotropic alignment, where molecules extend perpendicular to the substrate, the layer is transparent to all the wavelengths of light.

Apart from LCs, we also briefly discuss other organic materials originally intended for control of visible light that could be adapted to IR control elements. Furthermore, we also discuss the influence of these IR managing windows on temperature control and energy savings in the built environment. Inorganic-based window solutions, including metallic based reflective layers,^[28–31] photochromic,^[3,32,33] electrochromic,^[3,8,34–39] and thermochromic^[3,40–43] systems, plasmonic nanoparticles,^[36,44–46] aerogel glazing,^[47] privacy windows,^[48] thin film photovoltaics,^[49] and even microfluidic^[50] based windows have not been discussed in this review, as they have already received considerable attention and discussion. Additionally, organic based window devices and materials primarily intended to absorb and control visible light passage, including electro-,^[51–53] photo-, and thermochromic^[3] windows, are also beyond the scope of this review of infrared control materials: they have already been detailed in a number of excellent review articles.

This review is separated into three parts. The first two will describe efforts in the areas of static systems and dynamic

(adjustable) IR regulating elements. The final section will speculate as to some possible future research areas that are ripe for exploitation.

2. Static IR Regulating Window

We define a static IR regulating window as a window whose properties do not change with external stimuli. In other words, the infrared control is a permanent feature of the window, regardless of exterior conditions.

2.1. Absorption Based Technologies

The simplest IR control solution is to use a dye which is transparent in the visible region and absorbs only infrared radiation.^[54] The shortcoming of absorbing based systems is the majority of absorbed energy is eventually re-released as heat, with approximately half the heat being radiated into the room space. A more advanced absorption-based concept is the luminescent solar concentrator (or LSC),^[55] illustrated in **Figure 5**. The LSC uses dyes embedded in the polymer or glass plate which functions as the window. The dyes absorb the near IR sunlight and subsequently fluoresce at a longer wavelength. A fraction of this re-emitted light is trapped in the higher refractive index polymer or glass panel which acts as a lightguide.



Figure 2. Schematic diagram of an ideal smart window reflecting infrared radiations in warm days (left) and allowing it to enter in cold days (right), while remaining transparent in visible region in both climate conditions.

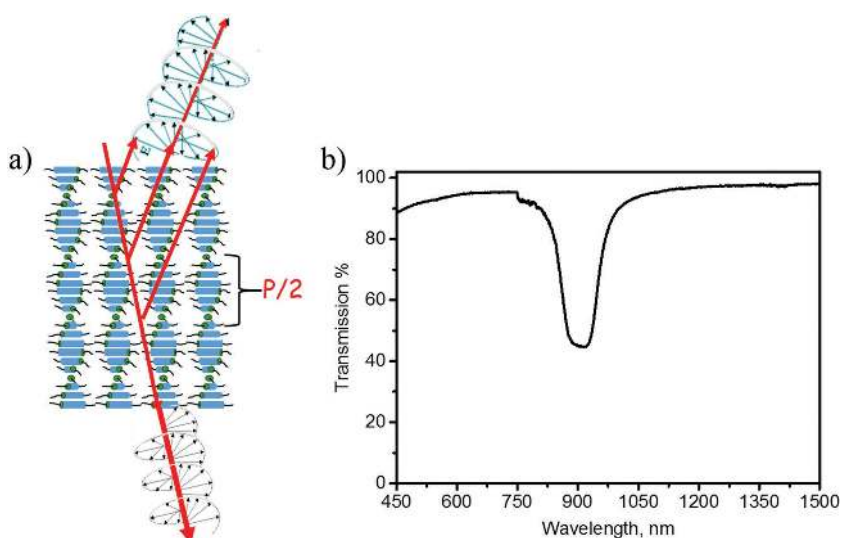


Figure 3. a) Schematic diagram showing the reflection of light by Ch-LCs: reflecting circular polarized light of same handedness. b) Typical transmission spectrum of Ch-LC.

The trapped emission light is transported by total internal reflection and only exits at the edges of the window, where it may be converted to electricity via the use of attached photovoltaic cells.^[56] A significant fraction of absorbed light energy in LSCs is still lost through the top and bottom surfaces,^[57] and thus still would contribute towards interior heating. In addition, the absorption ranges of the dyes in such devices are still quite limited, often with significant absorption in the visible wavelength region and thus only process a small fraction of the total incident light.^[58]

2.2. Reflection Based Technologies

There is an enormous literature of Ch-LCs being employed to reflect visible light for a wide variety of (display) applications.^[59] What has not been as widely exploited are cholesterics as IR control elements in transparent windows in buildings and automobiles. One of the key challenges to employ Ch-LCs as IR reflectors are their limited bandwidths when directly processed from solution. For regular cholesterics, bandwidth is restricted to around 100 nm in the IR due to the limited Δn

of the LC itself (Equation (3)), which would have limited impact on controlling interior temperatures.

The range of IR wavelengths reflected may be increased by creating a broadband cholesteric reflector. There are a variety of ways in which this may be achieved. The simplest is to simply layer narrow band cholesterics of different pitches on top of one another.^[60] The drawback of this is that the layers need to be laminated together in an extra processing step, and the number of layers necessary for effective IR control grow rapidly: to cover the spectrum from 750–1100 nm requires a minimum of three cholesterics layers. However, as mentioned earlier, even this will allow a maximum of 50% reflection (one handedness of the incident light), so a full six layers will be minimally required for effective IR control. The lamination of additional layers has an added potential disadvantage of introducing additional haze into the system,

something that an IR reflector to be employed in a window should seek to avoid as much as possible.

A second option to obtain a broadband reflector is to create a pitch gradient in a single layer; in other words, for the Ch-LC to display a number of different pitches within the same film. A number of methods have been developed to fabricate pitch gradient broadband reflectors in the visible region,^[59] some of these methods have produced reflection bands in the infrared region appropriate for window applications. The most common method for creating broadband Ch-LC reflectors was developed by Broer et al.,^[61] and employed a liquid crystal mixture consisting of a nematic monoacrylate and chiral diacrylate which acts as the dopant. Exposing the acrylate mixture to a low-intensity UV light induces polymerization in a non-uniform manner.^[62] The differing reaction rates of the monoacrylate and diacrylate to the UV light results in diffusion of more reactive (diacrylate) materials towards the illuminated side, generating a variation of the chiral dopant concentration between the top and bottom of the film (Figure 6a), resulting in a pitch gradient. In this way, a broadband Ch-LC reflecting from 750 to 1050 nm was fabricated.^[62] By combining two broadband reflectors, either stacking a right- and left-handed film on top of one

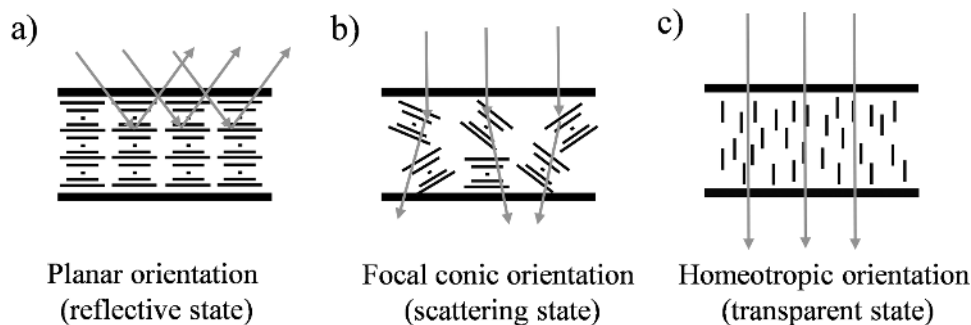


Figure 4. Different orientation of Ch-LC molecules in the cell and their optical behaviors. a) Planar orientation: reflecting a certain wavelength of light depending on the pitch, b) focal conic orientation: scattering the incident light, c) homeotropic orientation: transparent for all the wavelengths of light.

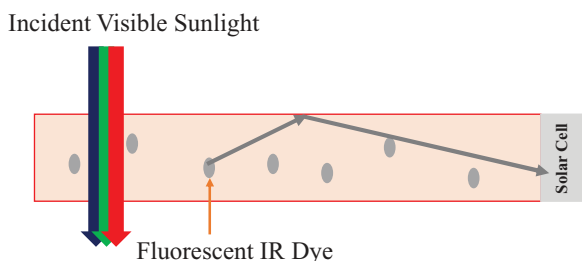


Figure 5. Schematic of the visible transparent luminescent solar concentrator. Infrared radiations from the sun is absorbed by the fluorescent IR dye and re-emitted at the longer wavelength which undergoes total internal reflection and reaches to the edge where an attached solar cell converts it to electricity.

another or by stacking two identical like-handed films separated by half-wave plate which converts right-circular to left-circular polarized light (and vice versa), a full IR reflector for sunlight (reflecting both the polarization of light) with a bandwidth of 300 nm has been produced (Figure 6b).^[62] The amount of the

infrared light that is reflected by this broadband Ch-LC is close to 60% of the total infrared energy while remaining transparent in the visible region (inset Figure 6b).

Using the transmission spectra of the fully-reflecting broadband cholesterics, the effects of using such films on windows in various locations across the globe were simulated, and it was determined that such reflectors could result in differences between exterior and interior temperatures of up to 6 °C compared to standard double glazing window (Figure 6c) in a Chicago environment, as an example. However, since the reflectors are permanent (static), in temperate climates the net effect of using a permanent reflector was actually negative in wintertime, when entry of IR light might be considered a benefit.^[62] At steeper incident angles of light, there is a pronounced blue shift in the reflection band, approaching some 140 nm or more at incident angles around 60 degrees. Thus, care must be taken that the short band edge of the broad reflector does not shift into visible wavelength reflection range, else a pink reflection color will be evident at greater incidence angles.

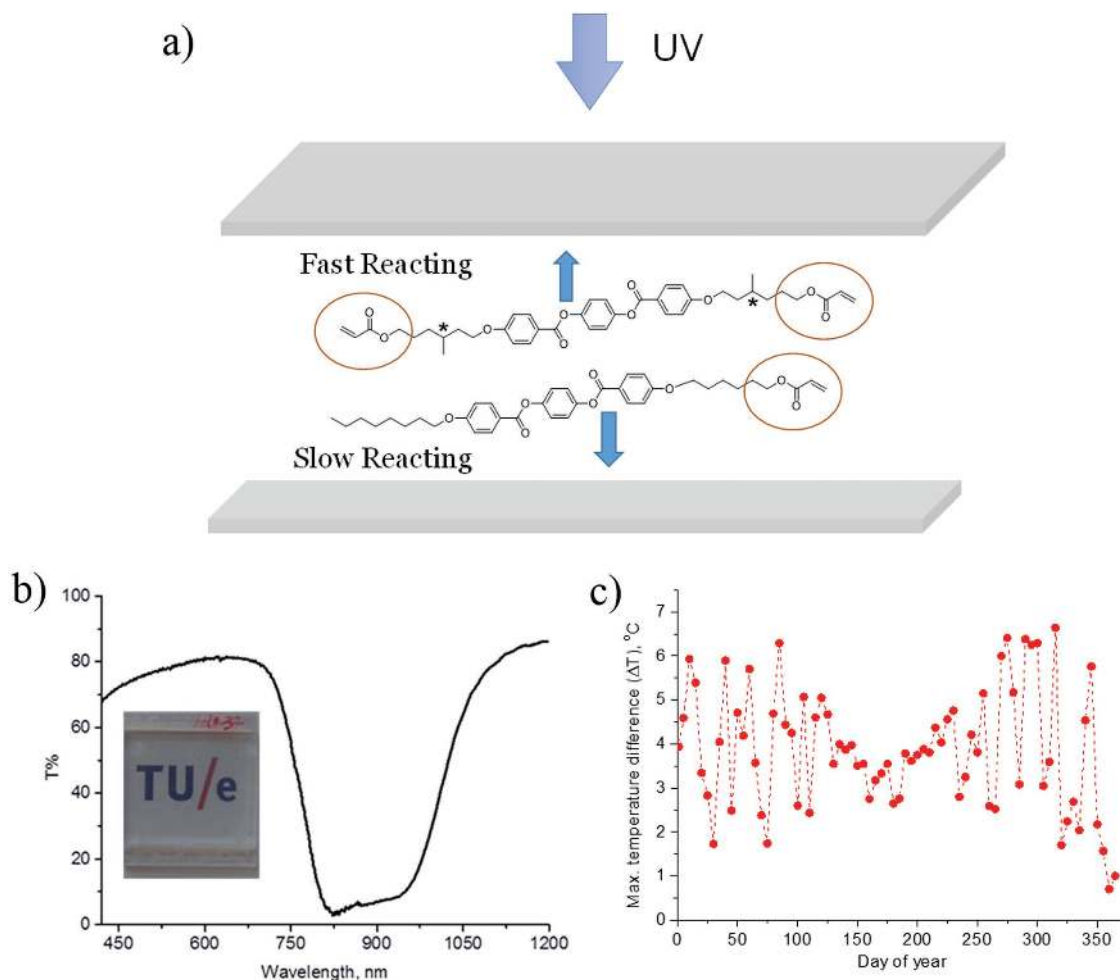


Figure 6. a) Schematic diagram showing the diffusion direction of different monomers in the film during polymerization in the cell. b) Cell transmission spectrum of right- and left- handed films superimposed on each other (inset: photograph of the sample demonstrating the transparency in the visible region). c) Predicted decrease in interior maximum temperature as a function of the day of the year for superimposed right-and left-handed cholesterics compared to standard double glazing window for an office room in Chicago, USA. Reproduced with permission.^[62] Copyright 2014, The Royal Society of Chemistry.

Another method to fabricate the broadband reflector is developed by Zhang et al. They fabricated an ultra-broadband reflector using the properties of so-called layered smectic A (SmA)-like short-range ordering (SSO) structures. SSO structures are formed just above the SmA to cholesteric transition temperature where the layers start to twist and consist of very large pitches. The LC mixture was photo-polymerized just above the SmA-Ch transition temperature to induce diffusion of the nematic (diacrylate) molecules toward the illuminated side (Figure 7a), resulting in a gradient from cholesteric to SmA-like short-range ordering structures (Figure 7b), forming the ultra-broad reflector which reflects light from 780 to 14000 nm (Figure 7c).^[63] Using two layers of opposite handedness (reflecting 100% of total infrared energy), such an ultra-broadband reflector could have a significant impact on energy savings in the built environment.

Chen et al. made a broadband infrared reflector reflecting light from 1000 nm to 2400 nm by polymerizing LC crosslinker in the presence of a chiral photoisomer, which was an azobenzene derivative displaying different HTPs in the cis and

trans forms (Figure 8a).^[64] Upon illuminating the monomer mixture with UV light, the trans- azobenzene isomerizes into cis. Due to absorption of UV by the azobenzene, a UV light gradient was formed through the thickness of the film. This causes the crosslinker to polymerize faster at the illuminated side compared to the bottom of the cell, resulting in diffusion of the crosslinker from the bottom to the top of the cell.^[65] Upon subsequent exposure of the film to visible light, the cis-azobenzene isomerizes back to the trans- form, but only in the lightly crosslinked region at the bottom of the cell, whereas the higher crosslinked areas at the top of the cell remain in the cis-form as there is less network flexibility to allow the embedded azobenzene to isomerize (Figure 8b). Due to the presence of both cis (low HTP) and trans (high HTP) state azobenzenes throughout the thickness of the film, there is a gradient of the pitch from top to bottom, and hence there is formation of a broadband ($\Delta\lambda = 1400$ nm) reflector (Figure 8c). However, due to absorption of the azobenzene at shorter wavelengths, such reflectors are colored and thus, are not completely transparent in the visible region.

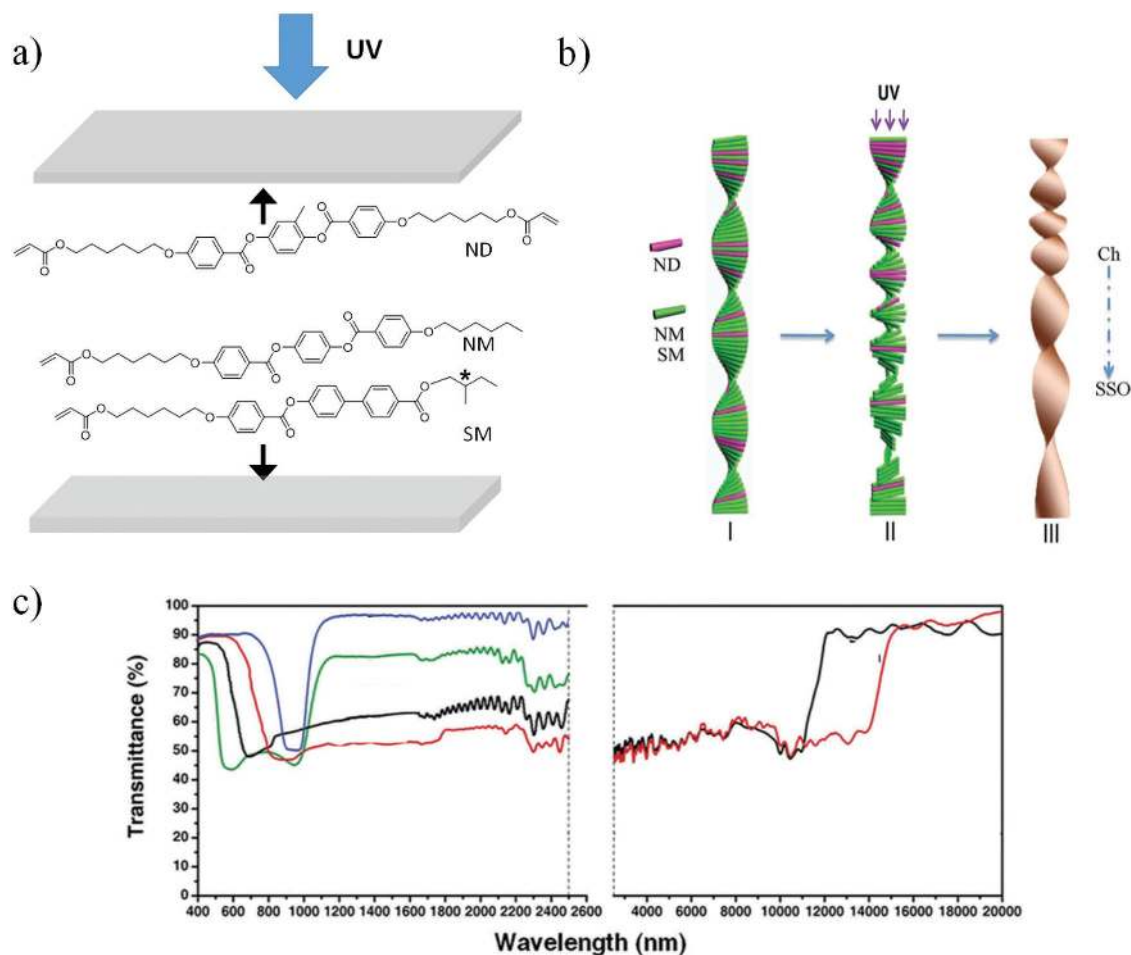


Figure 7. a) Schematic diagram of diffusion of the monomers. b) Schematic presentation of the procedure of film preparation: (I) formation of a homogenous Ch-LC thin film from a mixture of nematic monoacrylate (NM), nematic diacrylate (ND), smectic monoacrylate (SM), dye and photoinitiator; (II) UV radiation creates a ND concentration gradient inducing the intensity gradient of the SSO, and (III) a film with a pitch gradient is prepared after polymerization. c) Transmission spectra of different Ch-LC polymer films showing that the bandwidth of the reflection band can be tuned by varying the composition and polymerization conditions. Adapted with permission.^[63] Copyright 2016, Taylor & Francis Ltd.

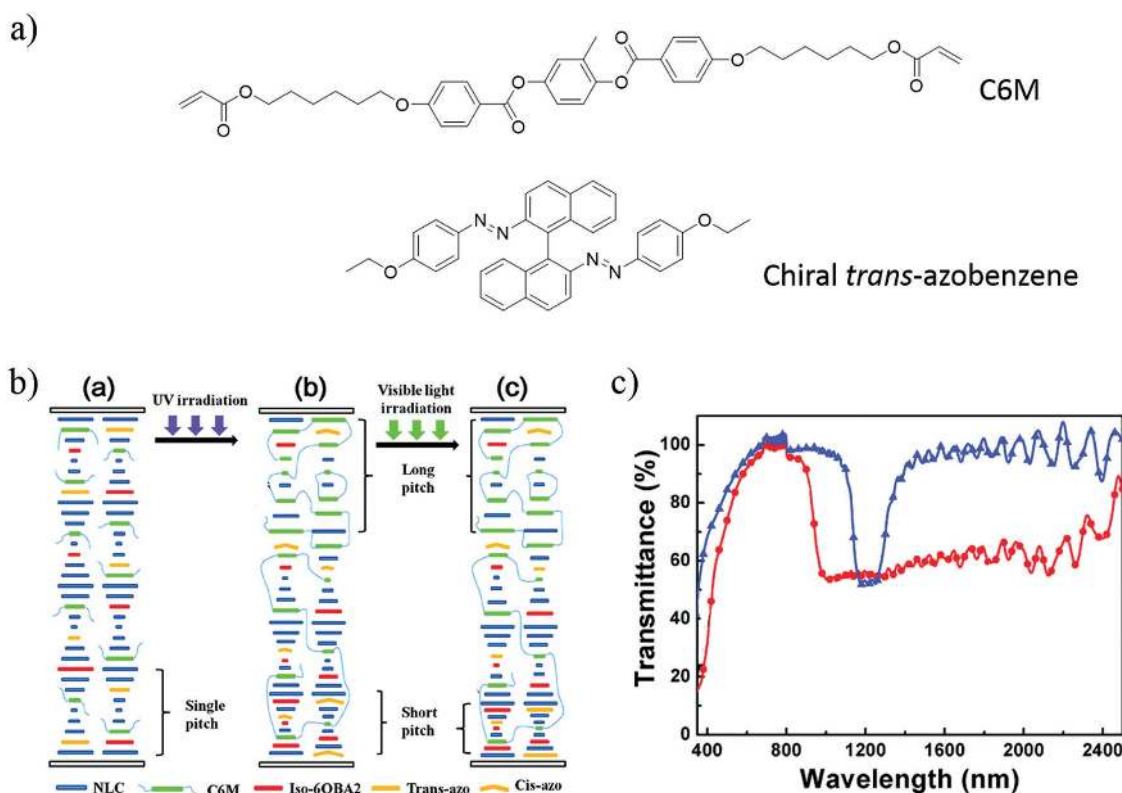


Figure 8. a) Molecular structure of the crosslinker C6M and chiral *trans*-azobenzene. b) Schematic diagram showing the principle of fabrication of broadband reflector using chiral azobenzene in polymer-stabilized Ch-LC. c) Transmission spectrum Ch-LC film before (blue) and after illuminating the UV-light (red). Adapted with permission.^[64] Copyright 2013, The Royal Society of Chemistry.

Gao et al. fabricated IR reflecting films by blending cholesteric side chain liquid crystal polymers (ChSCLCPs) with the glass laminating transparent material ethylene-vinyl acetate (EVA) copolymer.^[66] ChSCLCPs were used for window application due to their thermal stability and easy processability. ChSCLCPs of different pitches with reflection bands centered at 1000 nm (PI), 1400 nm (PII) and 1800 nm (PIII) were blended with EVA and stacked together (Figure 9). The film was then heated and compressed to thermally diffuse the different pitches into each other so that a continual infrared-broadband reflector could be achieved. An energy conservation efficiency of 40.4% was determined by calculating the change in the absorbed energy of the model house with and without the IR reflector. A temperature difference of 3 to 4 °C was observed using these materials compared to window consisting of only two layers of a polyethylene terephthalate film laminated with EVA. Peeling strength of the EVA/ChSCLCPs film was measured to be the same as pure EVA laminated film, which makes the mix suitable for practical application. Unfortunately, the scattering of visible light was relatively high, impairing vision of objects through the window.

Apart from LC materials, distributed Bragg reflectors using purely organic materials can also be made,^[67] but in general the difference in refractive indexes of the organic materials are too low to make effective reflectors without a great number of layers. Hybrid organic/inorganic distributed Bragg reflectors are also an option, for example using three alternating pairs of sputtered CF_x/TiO_x ,^[68] or $\text{CF}_x/\text{CF}_x(\text{Au})$ resulting in reflection bands 400–500 nm broad.^[69]

Organometallics display reflective properties in the IR, including copper phthalocyanines^[70] and chlorophyll,^[71] although the cause of reflection of IR by the latter has not been confirmed; it may well be a supramolecular or other structure in the leaf that is actually responsible for the reflection.^[72] More exotic structures are found in nature, such as fractal superlattices that can reflect a broadband of IR light, although they often reflect components of visible light as well.^[73]

3. Dynamic IR Regulating Window

In areas of the world under constant heat stress, such as the Middle East, continual rejection of IR light could be quite desirable. However, in more temperate zones, such as the Midwestern United States, it may be more appropriate to employ materials capable of reflecting unwanted IR light in periods of high environmental temperatures in summer months, but allowing passage of IR light in periods when warming from external sunlight would be desirable, such as spring, autumn, and winter (Figure 2). This section describes several responsive systems that regulate their properties to reflect/transmit the IR light to balance the indoor temperature conditions throughout the year. The trigger for this switch could be a variety of stimuli: electrical field, temperature, or perhaps even the intensity of incident light. However, electric fields, used to regulate window properties manually, and temperature, used to regulate window properties autonomously

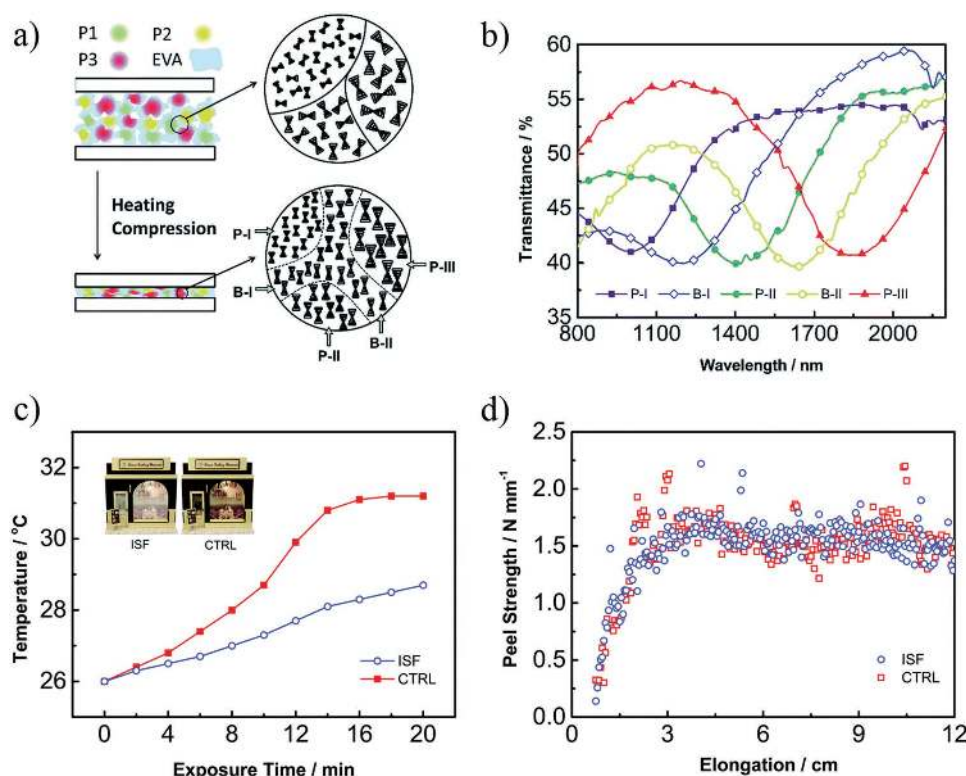


Figure 9. a) Schematic showing the fabrication of IR shielding film with different pitch length shown as PI, PII and PIII. b) Transmission spectra of the film in different regions. c) Change in temperature of the model house under exposure of sunlight. Here, ISF: the house with the IR shielding film attached to its window, CTRL: the house with two layers of Polyethylene terephthalate film laminated with EVA attached to its window as a control experiment (inset picture is the photo of the model houses). d) Peeling strength results of the samples (ISF) and control film (CTRL). Reproduced with permission.^[66] Copyright 2016, The Royal Society of Chemistry.

with environment changes, are the most common triggers for the window application. We will discuss these different aspects under separate headings, with the last approach (intensity of light as trigger) delayed until part 3, future options.

3.1. Electrically Responsive Window

Before we discuss infrared regulators based on LC materials, it is important to understand the anisotropy of the LC molecules. In simple terms, a positive dielectric ($+\Delta\epsilon$) anisotropic rod-like LC molecule exhibits dipole moment along the molecular axis, whereas negative dielectric ($-\Delta\epsilon$) anisotropic molecules display dipole moments perpendicular to the main molecular axis. Therefore, on application of an electric field between two glass plates of a planar aligned LC cell, LC molecules with $+\Delta\epsilon$ undergo homeotropic orientation, in contrast to $-\Delta\epsilon$ LCs, which remain undisturbed in their initial planar state under the same electric field. In this review, the anisotropy of the molecule should be considered as positive, if not mentioned specifically.

3.1.1. Scattering and Absorption Based Technologies

A number of switchable privacy windows based on polymer dispersed liquid crystals (PDLC) and polymer stabilized liquid

crystals (PSLC) have been designed to control visible light. In PDLC based windows, micrometer sized LC droplets are dispersed in a polymer matrix, whereas PSLC windows employ composites of non-polymerizable LC mesogens and a polymer network. (Figure 10). Two modes are generally available in these privacy based windows: a normal mode, where the window is in a scattering/privacy mode in the 'off' state, and a reverse mode, where the window is transparent in the 'off' state.^[74] Generally, the reverse mode is preferred, since in case of 'power failure', the window remains in a transparent state rather than in a scattering state. These privacy windows which are focused on visible light control have been reviewed, and beyond the scope of this work.^[75–80] PDLC based windows are already commercially available^[78] but mostly used for indoor purpose. Privacy based windows have also been developed using smectic/cholesteric liquid crystal phases where the window can be switched reversibly between transparent (planar and homeotropic) and scattering (focal conic) states.^[81–83]

A recent nanoparticle/polymer construct using indium tin oxide (ITO) nanoparticles and polythiophenes showed electrochromic behavior and demonstrated promising characteristics in being able to reversibly control IR ingress above 800 nm by applying just 1.25 V (Figure 11).^[84] However, there is evidence of considerable absorption in the visible light range. A similar situation is seen in Co(II)-based metallo-supramolecular polymer systems.^[85] Other options, such as organic

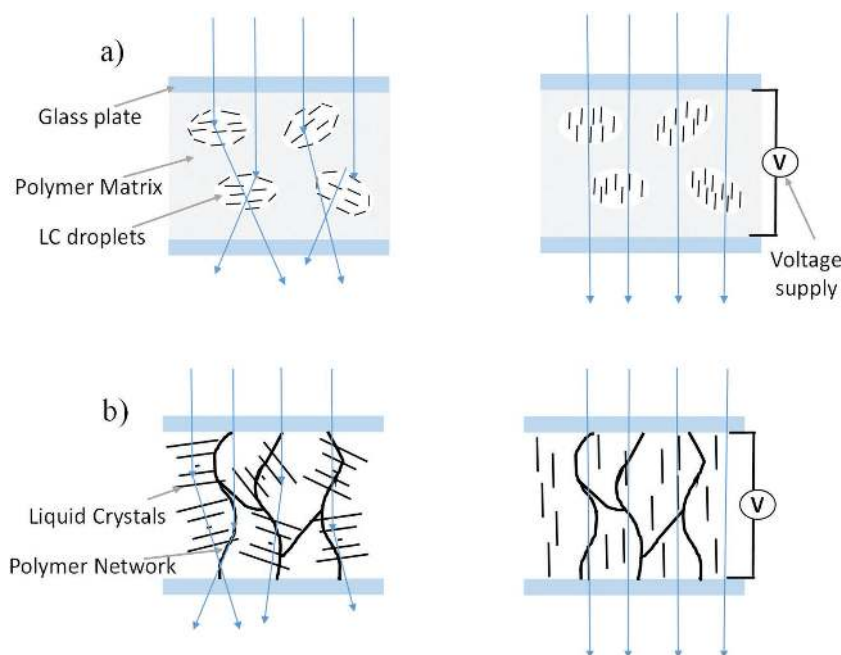


Figure 10. Schematic diagram of normal mode a) PDLC and b) PSLC based window showing scattering of light in 'off' state (left) and transparent in presence of electric field (right).

electrochromics, appear confined to visible wavelengths.^[86–88] An electrically responsive system which functions by redox reaction of the organic based ionic liquid crystals to control visible light passage has also been studied,^[89] but to our knowledge no subsequent efforts in the IR region have been reported.

3.1.2. Reflection Based Technologies

Using uniform pitch Ch-LCs, a number of narrowband reflectors with bandwidths of 100–200 nm have been fabricated. Upon exposure to an electric field, they could be switched between

planar (reflective state) to homeotropic (transparent state) orientations (Figure 4). A number of Ch-LC based narrowband reflectors, both in visible and infrared regions, have also been developed which can tune the position of reflection notch within a limited wavelength region in presence of an electric field.^[90,91] Such narrow bandwidth reflectors can influence only a minor fraction of infrared light, and would have only limited impact on interior temperatures.

Binet et al. have fabricated broadband infrared reflectors by inter-diffusing two layers of different pitch lengths, consisting of polymer stabilized siloxane and non-reactive LC mesogens.^[92] Interestingly, the reflection band obtained is not simply the sum of the reflection band of the individual layers and can be controlled by UV curing conditions (Figure 12a). These siloxane-based layers can be further switched between planar and homeotropic states by application of an electric field, and therefore can be used to make switchable IR reflectors (Figure 12b). The bandwidth of the broadband, centered around 1810 nm, is 310 nm. However, this

can further be tuned to an onset wavelength 700 nm to have greater impact on the energy savings.

Recently, we have fabricated an electrically switchable IR reflector using a low molar mass non-reactive LC mesogens in a polymer stabilized network.^[93,94] By using a mixture of reactive chiral mesogens and non-reactive materials in the presence of a UV-absorbing dye, the reactive fraction in the LC mix begins to polymerize at the side being illuminated. This causes a diffusion of chiral reactive mesogens to the polymerized region, which in turn leads to formation of the pitch gradient throughout the thickness of the film. This results in a cell containing a skeletal network of polymerized materials to act as a 'memory' state for the unpolymerized materials, which at rest will assume the order instilled by the polymerized network. Upon exposure to an electric field, the non-polymerized molecules can reorient to the homeotropic state (Figure 13a). Since there is not enough polymerized network to form a reflection state by itself, the reflective state is lost and the system becomes purely transmissive. Upon removal of the field, the LCs relax and are directed by the polymerized skeleton to resume their original orientation and reflective state.^[93,95] Using this technique, we have fabricated a broadband infrared reflector which reflects light from 700 to 1400 nm that remains transparent in the visible region.^[93] On application of $8.6 \text{ V } \mu\text{m}^{-1}$, the LC molecule arranges themselves homeotropically, which results in transparency in the visible as well as infrared region (Figure 13b).

To better understand the relation between global climate conditions and potential energy savings using these particular switchable IR control windows, simulations were carried out assuming three different climates: (1) Abu Dhabi, United Arab Emirates (a warm climate) (2) Amsterdam, the Netherlands (a cold climate) and (3) Madrid, Spain (a moderate climate). For

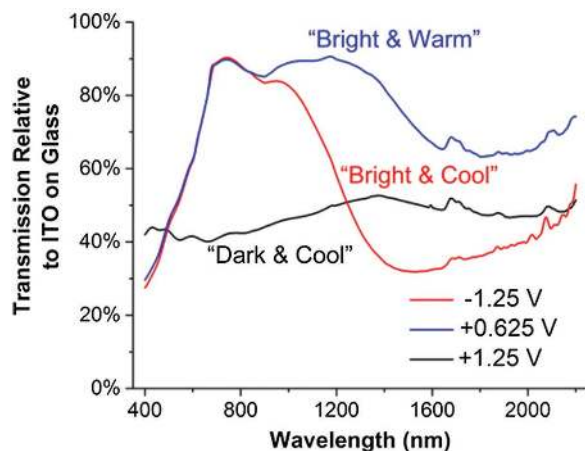


Figure 11. Transmission spectrum of the poly (3,3-dimethyl-2,2-bithiophenyl)-ITO film showing that different fraction of IR and visible light can be control by applying different voltage. Reproduced with permission.^[84] Copyright 2016, American Chemical Society.

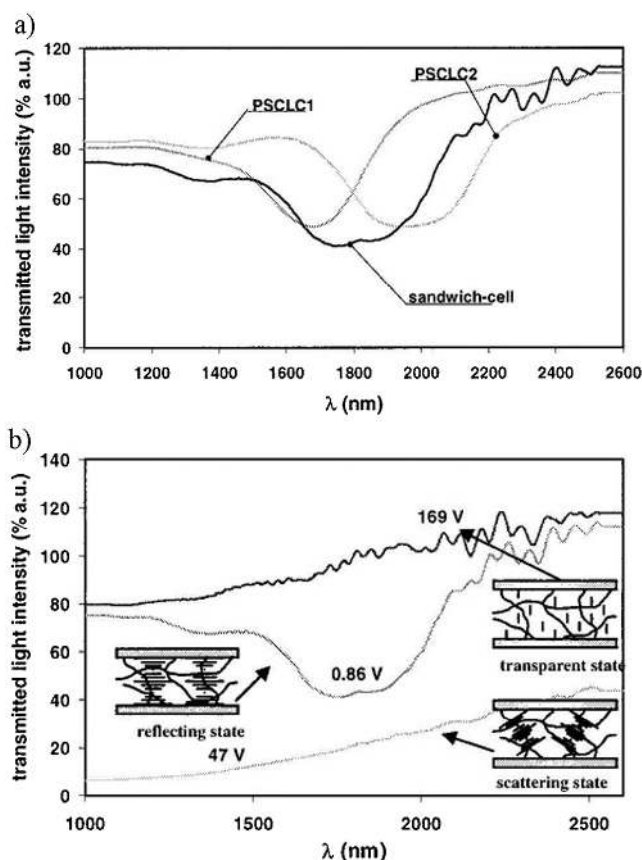


Figure 12. a) Transmission spectra of films PSCLC1, PSCLC2 and UV-cured sandwich cell of PSCLC1 and PSCLC2. b) Transmission spectra of sandwich cell upon application of different voltage showed that polymer stabilized Ch-LC can be switched from reflection (0.86 V) to scattering (47 V) to transparent state (169 V). Adapted with permission.^[92] Copyright 2001, AIP Publishing.

each climate condition, we calculated the energy consumption of a standard office building equipped with double glazing windows, and compared its performance to a building using either a broadband static or dynamic IR reflector; the latter window was to switch to the transparent state whenever the external temperature dropped below 22 °C. As shown in Figure 13c, it was found that static IR reflectors performed best in warm climates like Abu Dhabi, as IR needs to be reflected almost constantly throughout the year. Double glazing was found to be optimum in cold regions like Amsterdam where IR radiations were desirable throughout the year. The performance of the switchable IR reflector was most favorable in the moderate climate of Madrid. It was predicted that the switchable IR reflectors could save more than 12% on the building's energy consumption, whereas static IR reflectors could save only 3% on energy compared to standard double glazing window. It is important to note that the energy required to switch the window from reflective to transparent states was not included in this initial simulation study; the power/voltages needed to switch the window were relatively high. In addition, switchable IR reflectors were revealed not to be user friendly in moderate climate condition, as it is difficult to decide whether to keep window in the reflection or transmission state.

To reduce the switching voltage/power and fabricate a more user-friendly window, we employed a negative dielectric anisotropic ($-\Delta\epsilon$) LC and the technique of designing an ion-accepting linker molecule suggested by the work of White et al.^[96] The (poly)ethylene glycol (PEG) based linker molecule (Figure 14a) enhanced the collection of positive charges and increased the distortion of the partially polymerized LC network under an electric field, resulting in compression of pitches at negative electrode whereas at positive electrode, it expanded (Figure 14b).^[97] In a cell of sufficient thickness so that the number of pitches is relatively high, there are pitches in the middle of the cell which remain undisturbed by an applied field. So, the combination of expanded, compressed and unchanged pitches results in formation of a 1100 nm broad reflection band spanning from 700 to 1800 nm with minimum impact on visible light transmission, while simultaneously reducing the voltage required to switch the system to around 1.2 V μm^{-1} (Figure 14c,d).^[97] By applying 0 to 1.2 V μm^{-1} , a bandwidth from 120 nm to 1100 nm can be tuned, corresponding to rejection of 8 to 45% of the total incident infrared energy. Using this system, one could select the fraction of infrared to be reflected depending on the external climate conditions so that a comfortable indoor temperature can be maintained throughout the year. Calculation shows that more than 12% (including the energy to switch the window) of the total energy used in the built environment can be saved in the Madrid climate using the fabricated bandwidth tunable reflector compared to a standard double glazing window.^[93,97]

Hu et al. demonstrated a broadband reflector in the infrared region by using a charged chiral ionic liquid in a Ch-LC mixture (Figure 15a).^[98,99] Due to diffusion of the charged chiral dopant in a negative dielectric anisotropic ($-\Delta\epsilon$) Ch-LC mixture in the presence of DC electric field, a pitch gradient is created throughout the thickness of the cell, leading to formation of the broadband (Figure 15b). At the same time, DC electric fields also introduce disorder in alignment of the LC molecules, resulting in light scattering. To reduce scattering, an AC electric field was applied and turned off quickly just after application of a DC field to obtain the planar orientation of the Ch-LC mixture. On further applying the reverse DC bias with a suitable field, broadband was switched to narrowband as a result of uniform distribution of the chiral dopant throughout the thickness of the film (Figure 15c). Similar mechanisms using chiral ionic polymer networks in $-\Delta\epsilon$ Ch-LC has also been used to generate tunable broad-to-narrow bandwidth reflectors upon application of electric fields.^[100] These systems can be further optimized for real applications by tuning the broadband to the near infrared region and improving the transparency in the visible region.

Xiang et al. have designed narrowband tunable reflectors which can modify their reflection positions over a wide range by utilizing the properties of the heliconical Ch-LC state.^[101] By systematically increasing the electric field, a blue shift in the reflection band with changes in the position of reflection notch from 1100 to 300 nm was observed. The limitation of these systems is that they reflect only a fraction of infrared energy because of their inherent narrowband nature, which results in limited impact on indoor temperature. However, this system can be improved by stacking multiple switchable cholesteric windows for full spectral coverage, but this would be a considerable design and manufacturing challenge.

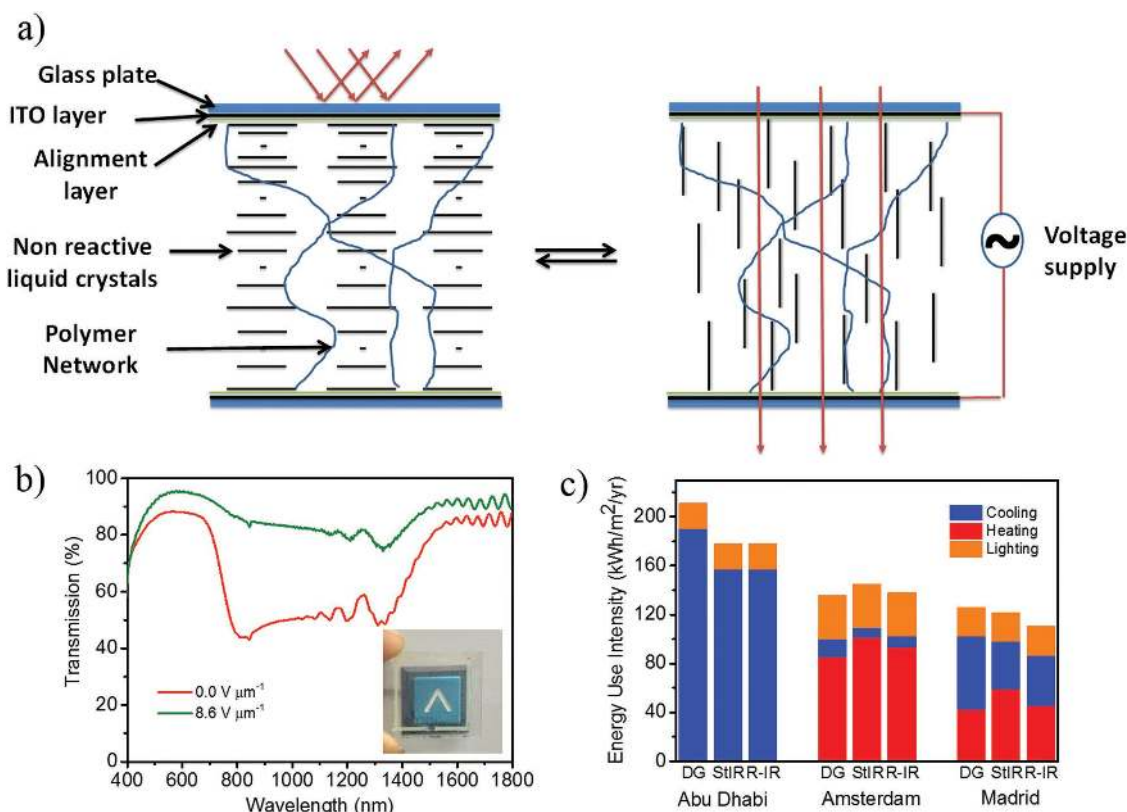


Figure 13. a) Schematic diagram showing the planar (left) and homeotropic (right) states on applying an electric field. b) Transmission spectrum of cholesteric gel in reflective and transmissive states at $0 \text{ V } \mu\text{m}^{-1}$ and $8.6 \text{ V } \mu\text{m}^{-1}$ (inset: photograph of the sample demonstrating transparency in visible region). c) Comparison of energy use intensity for a normal double glazed window (DG), static IR reflector (StIR) and switchable (responsive) infrared reflector (R-IR) for three different climates. Adapted with permission.^[93] Copyright 2015, Nature Publishing Group.

3.2. Temperature Responsive Windows

3.2.1. Scattering and Absorption Based Technologies

Hydrogels based on poly(*N*-isopropylacrylamide) have been used to control visible light at elevated temperatures.^[102] The hydrogel film of a specific thickness is transparent at room temperature but as the temperature rises above the lower critical solution temperature (LCST), the film starts scattering, resulting in less light entering the interior spaces (Figure 16). Similar behavior has also been demonstrated using hydroxypropylcellulose based hydrogel.^[103] Photo-thermotropic hydrogels can alter their transparency and reflective properties when illuminated by sunlight.^[104] In these systems, a material such as graphene is dispersed in a hydrogel network. The graphene enhances uptake of energy which is stored in the water while maintaining transparency. Upon an increase in the water temperature to a specified level, the network breaks apart, resulting in a semi-reflective scattering state and loss of transparency.

Phase change materials (PCMs) have most often been applied to opaque elements but there are examples of application in window systems.^[105] The PCM takes advantage of the latent heat storage potential in the phase transition between the liquid and solid states. This transition can be used for heat storage and by increasing the thermal inertia of the window, which both aid in maintaining interior temperatures. The

transmission of light through the window for both the solid and liquid states have, however, often proven to be only modest using commercially available materials^[106] and often resulted in scattering, and thus completely disrupt the exterior view.^[107] While the commercial materials tend to be inorganic based, there are organic PCMs that could conceivably fill this role,^[108] but it remains to be seen if they could be considered for use in window applications.

The phase transition from SmA to cholesteric at elevated temperature has been used to fabricate a scattering-based visible light controlling window. Homeotropic orientation of SmA LC at lower temperatures results in the transparent state of the window whereas at elevated temperature, LC changes to cholesteric phase, leading to change in the orientation of the molecules to a focal conic state, resulting in scattering of light.^[109] A particularly interesting system employed a printed organic-based photovoltaic with embedded inorganic VO_2 nanoparticles that would change transmission upon exposure to increased temperature.^[110] While the device interfered with visible light, the authors were clear in their desire to target the NIR spectrum for purposes of interior temperature control while simultaneously generating electricity from visible light. If this could be accomplished by using embedded organic materials absorbing outside the visible range, this could be a very attractive device.

An exotic example of a dynamic heat control element using organics are holographic polymer dispersed liquid crystals.^[111]

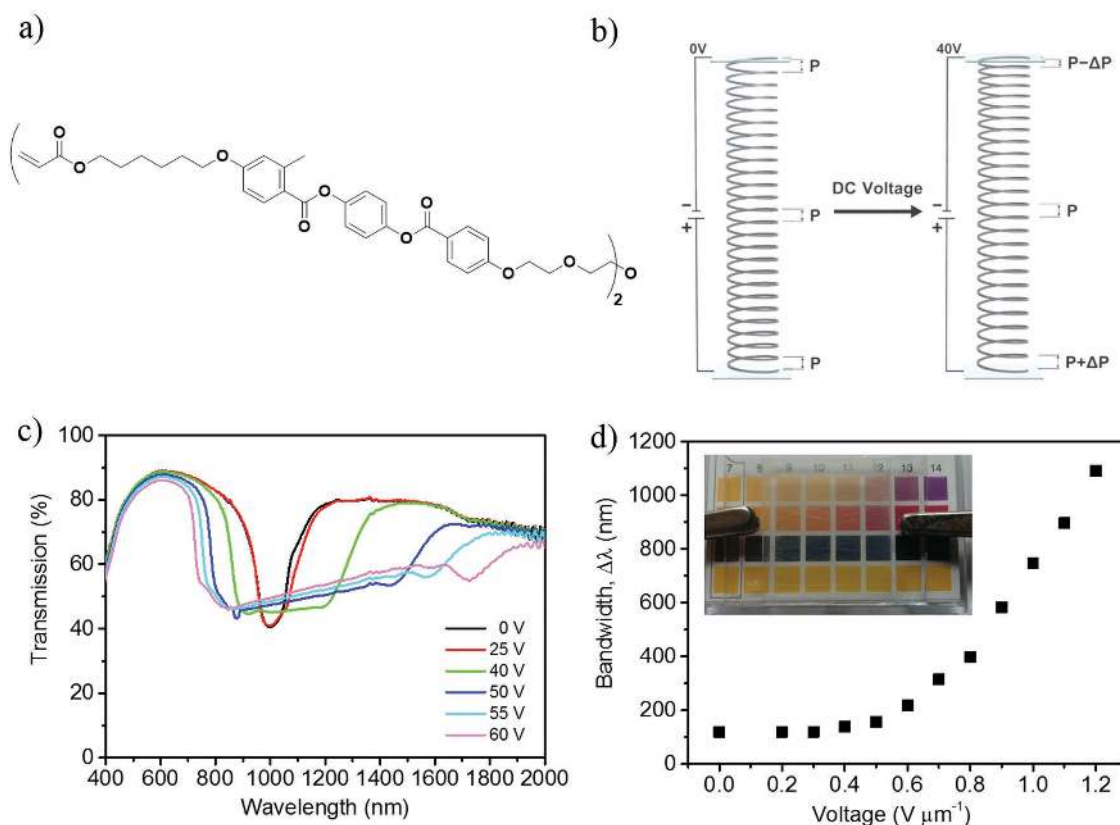


Figure 14. a) Molecular structure of the twin molecule used to fabricate the smart tunable window. b) Schematic diagram showing the working principle. c) Transmission spectra of Ch-LC mixture in 50 μm cell on application of 0–60 V. d) Bandwidth of the Ch-LC with respect to the applied voltage per micron thickness of the cell (inset: photograph of the IR reflector showing the transparency for the visible light at 0 V). Reproduced with permission.^[97] Copyright 2016, The Royal Society of Chemistry.

These films are quite angularly dependent, and while can be efficient on excluding IR light at specific incident angles, they are generally transparent at other incident angles, which makes control of diffuse light difficult. The report demonstrated a change of 15% in transmission through a sample cell as the temperature approached 30 °C.

3.2.2. Reflection Based Technologies

Yang et al. developed a method which would be quite effective if used as a temperature responsive window.^[112] The device used a chiral dopant which increases its helical twisting power in a polymer stabilized Ch-LC upon increasing the temperature (Figure 17a). At higher temperatures, the LC molecules will not be able to twist as much in areas of high polymer network density due to the anchoring effect from the polymer network, whereas in the low polymer network density region, the LC molecule will be able to twist to accommodate the increased HTP of the chiral dopant.^[113–115] Therefore, via the combination of lower (larger wavelength reflection band) and higher (smaller wavelength reflection band) twisting in a single sample, a broadband infrared reflector was formed at higher temperature (Figure 17b). At lower temperatures (around 5 °C), the device reflected light from 2050–2400 nm. As the temperature increased to 40 °C and 50 °C, this polymer stabilized system

reflected light from 950–2400 nm and 800–2400 nm, respectively (Figure 17c). This configuration allows the maximum amount of infrared energy to enter in winter while reflecting a large amount of solar infrared energy in summer, so that it would save on both heating and cooling energy demands in the built environment.

Natarajan et al. have demonstrated a remarkable blue shift of a narrow band reflector from 2300 to 500 nm on increasing the ambient temperature, as shown in Figure 18.^[91] This thermal tuning was attributed to the pre-transitional effect of smectic-to-cholesteric phase transition. As the infrared energy from the sun increases continuously from far to near infrared region, with this method a lesser-to-greater amount of infrared energy can be reflected on continual increase in temperature. However, the tuning temperature is not ideal for window applications (from 30–60 °C), but could be further optimized. The total amount of energy reflected is limited as only a small bandwidth of IR light is reflected, but by optimizing the LC mixture it could be useful where the change in the temperature is not extreme.

4. Outlook and Future Challenges

So far, we have discussed different kinds of infrared regulating devices using primarily organic materials. Many of these

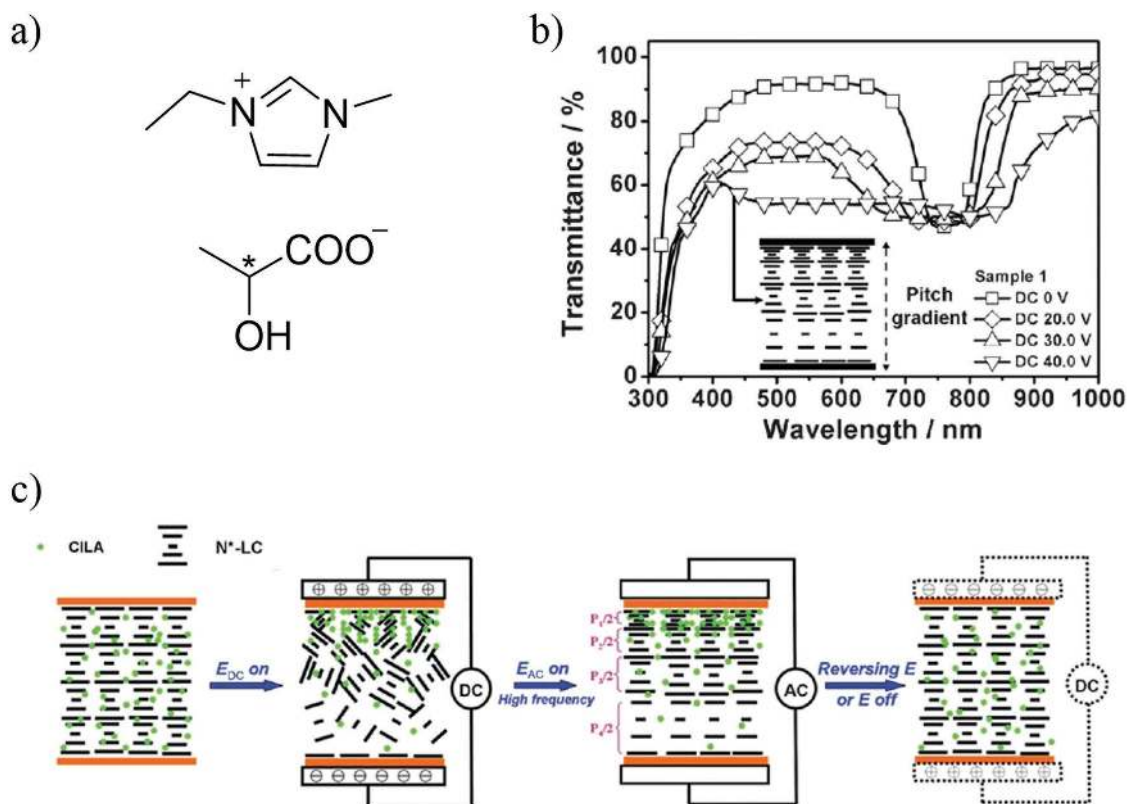


Figure 15. a) Molecular structure of the ionic chiral dopant used. b) Transmission spectra of the cell upon application of different DC voltages. c) Schematic drawing showing the mechanism of fabrication of broadband from narrowband reflector and vice versa. Adapted with permission.^[99] Copyright 2010, John Wiley & Sons.

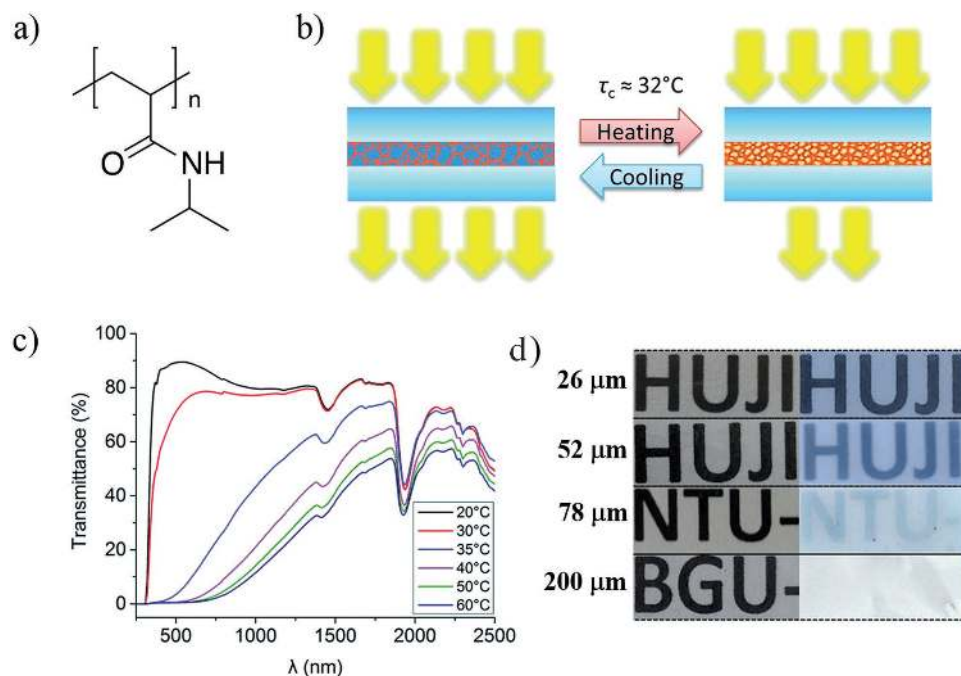


Figure 16. a) Molecular structure of the poly(N-isopropylacrylamide) hydrogel. b) Schematic diagram showing the change in solar transmittance below and above LCST (τ_c). c) Temperature dependence transmission spectra of the sample of 200 μm thickness. d) Hydrogel of different thickness at room temperature (left) and 35 °C (right). Reproduced with permission.^[102] Copyright 2014, The Royal Society of Chemistry.

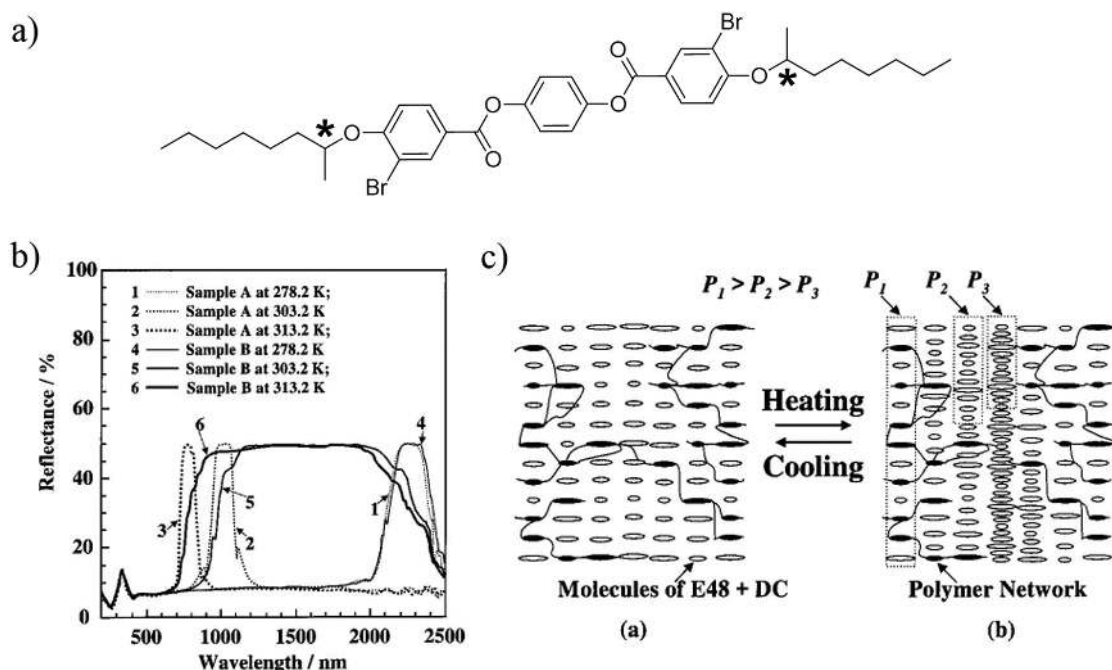


Figure 17. a) Molecular structure of the chiral dopant used. b) Temperature dependent change in transmission of cell containing polymer stabilized and non-polymer stabilized Ch-LC (Sample A and B are non-polymerized and polymerized LC mixture, respectively). c) Mechanism of formation of broadband at elevated temperature. Reproduced with permission.^[112] Copyright 2003, AIP Publishing.

systems were designed for visible region and targeted for some other applications. However, the potential use of the materials as infrared control elements for buildings or automobiles were not considered in the original work. As more attention is directed towards solving the increasing energy problem, more materials can be adapted for this application. In this section we discuss some potential future options.

An interesting trigger to switch the properties of the window could be intensity of light. In the past decade, a number of light responsive chiral dopants which can change their HTP either upon isomerization or helical inversion have been used to tune the position of a cholesteric reflection notch over a wide

range.^[116–118] A light responsive system which can change its reflection bandwidth based on the intensities of light would be very attractive. First steps for such a responsive system in the visible and infrared regions have been taken by White et al. using a chiral azobenzene photoisomer doped in a Ch-LC cell.^[119] The reflection bandwidth was increased to 1700 nm with a specific sample thickness and intensity of light. This system would be even more interesting if the effective reflection bandwidth is stable for longer duration of time and could be accomplished using a light responsive dye which does not absorb visible light. Other potential approach is to design systems responsive to multiple triggers simultaneously. As an

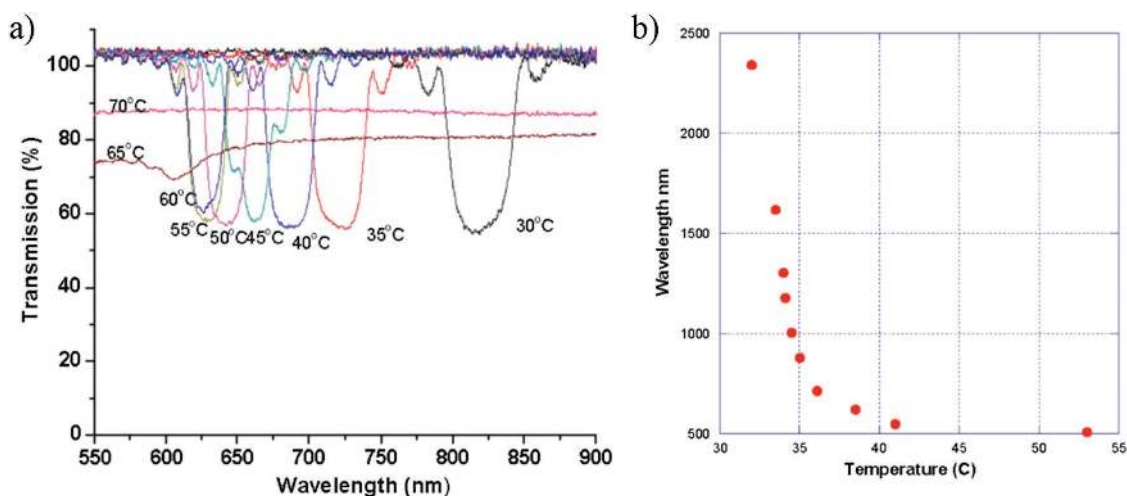


Figure 18. a) Temperature dependent transmission spectra of Ch-LC containing S811 (chiral dopant, 28 wt%) in nematic LC host. b) Change in the position of reflection notch of the cell containing 26 wt% S811 in nematic LC host. Reproduced with permission.^[91] Copyright 2008, AIP Publishing.

example of a multi-trigger system, an IR reflective matrix that may be manually tuned by exposure to an electric potential, or automatically in response to temperature increases has been produced which relies on a polymer stabilization network very finely tuned as to its crosslink density.^[120] Such a system architecture would be interesting if this can be produced without scattering light in the visible region.

Responsive liquid crystal blue phases reflecting in the infrared region could also be employed for window applications. Most research carried out to date using blue phases has concentrated on controlling visible light.^[121] A red shift in reflection band has been demonstrated in the presence of an electric field.^[122] Recently, broadening of the reflecting bandwidth upon application of electric fields has been shown in polymer stabilized blue phase LCs in the visible region.^[123] The broadening was attributed to the inhomogeneously distributed polymer network throughout the thickness of the cell, which causes non-uniform displacement of the polymer in presence of a DC electric field. Temperature-dependent blue shifts in the reflection band due to lattice distortion have also been reported.^[124–126] Red shifts in the reflection band upon illuminating azobenzene doped blue phases with light have also been demonstrated in the visible region.^[127,128] Furthermore, there are also number of other organic based 2D and 3D photonic materials which reflect narrow bandwidths of light, mostly in the visible region.^[129,130] These materials could be adjusted to interact in the infrared region. If multilayers of these photonic materials reflecting in different wavelengths could be produced, this would allow for broad reflection bands, and could find application as a smart window.

As discussed in the previous sections, there are several advantages of using Ch-LCs for the window application but one of the main limitations of existing Ch-LC based technologies is that they reflect only one polarization of light, which leads to maximum 50% reflection of unpolarized light. Reflection can be improved to 100% by using two films of opposite handedness or inserting a halfwave plate between same-handed films.^[131] Few methods have also been developed to enhance the reflection past 50% in a single film. One example is using thermal helicity inversion of the chiral dopant;^[132,133] in this system, a chiral dopant is used that changes its handedness upon heating. A second example is using a wash-out procedure where non-polymerizable LC is removed from a lightly-crosslinked LC cholesteric polymer network, and the resulting empty space is refilled with cholesteric forming LCs with opposite handedness.^[134–136] However, a scalable method which can reflect a broad wavelength region and both polarization of infrared light is yet to be realized.

Reflection properties of Ch-LCs, similar to all other standard Bragg reflectors, are incident angle dependent. To reduce the angular dependency of Bragg reflection based smart windows, polymer stabilized Ch-LC particles could be a good alternative.^[137] Other advantages of using the polymer stabilized Ch-LC particles are that they do not require an alignment layer on the substrate used to fabricate the device. Moreover, they can be scaled up in large quantities for effective commercial application, unlike the polymer stabilized cholesteric films.^[138] These particles could be dispersed in a polymer matrix and applied as a coating for existing windows. Other polymer based

systems, such as using dispersed cholesteric flakes reflecting IR light, and siloxane based responsive broadband reflectors which can directly be coated on the existing windows should also be researched.^[139] Other responsive polymer-based photonic materials could also be developed in the infrared region for coating purposes.^[140]

To reduce the power consumption of the various electrically switchable cholesteric-based LC windows, some form of bistable system could be envisioned.^[141] Bistable systems consume energy only to switch from one state to another and no energy is required to remain in any one state. Earlier reports have provided some examples, such as the switchable scattering-to-clear state system using the cholesteric/SmA phase.^[82,141–145] Of course, these mixtures often rely on polymer stabilization, with its concomitant challenges in reducing scattering in the visible spectrum.

Another future application could combine the function of the cholesteric-based switchable broadband reflective window with an energy generating window.^[146,147] Most of the reported organic and inorganic materials based energy generating window absorb in the visible region.^[148–151] These energy generating windows relied on luminescent dye absorbing incident light and re-emitting it at a longer wavelength, based on the principle of LCS. In this modified device, rather than deploying fluorescent dyes in the nematic LC host, the fluorophores are instead introduced into a polymer stabilized broadband IR reflecting Ch-LCs.^[93] It was demonstrated that the visible-light control aspects of the dye are preserved (and thus the potential to generate an electrical current), as is the ability to control IR light. To make this device commercially viable the level of visible light control need to be improved.^[152,153] It is also important to show significant potential for electricity generation (at least enough to switch the window) by using IR dyes which are completely transparent in the visible region.^[156]

As mentioned in the introduction, one of the key features required for deployment of organic IR control elements will be their stability. While to our knowledge no in-depth study has yet probed this question, other liquid crystal based devices have solved these problems to a large extent: for example, large area LCD screens designed for outdoor use are in the marketplace. This gives some confidence that stability challenges to be faced in the emerging smart IR window industry could be similarly addressed. Another important factor for commercial acceptance of the windows is their eventual cost. Since the windows will offer a type of 'pay back' via the reduction of building energy use (and financial outlay for) electricity for lighting, heating, and cooling, this could offset a somewhat higher price.

We also envisage these responsive windows to be employed as a single glazing layer in a standard double or triple glazing window unit. This would allow retrofitting of existing windows while maintaining similar insulation and sound control qualities.

Currently, a number of industries are working for the development of both privacy and infrared reflection based smart windows for energy savings. BASF has developed a static IR reflecting coating which is transparent to visible light and reflecting near infrared light. SABIC Specialty Film and Sheet, FUJIFIM and 3M have also developed a film/sheet which can block infrared radiations. Merck chemical company has

developed dye doped nematic LC based smart windows that can tune their absorption or transparency on application of an electric field. These examples demonstrate the intense commercial interest in these visibly transparent heat control systems.

5. Conclusions

Windows have a significant influence on energy consumption in the built environment and human health of the occupants of the buildings. Several methods, starting from blinds and shutters to advanced liquid crystals-based technologies have been developed to control indoor temperatures. Recent requirements for windows demand that they should simultaneously regulate indoor temperatures by controlling passage of excess of solar energy while also maintaining high transparency in the visible region to reduce dependence on artificial lighting. In this direction, a static infrared reflector which can completely block IR radiation from the sun without interfering with the visible transparency has been developed. Static systems are very useful in hot climates like Abu Dhabi, where continuous rejection of heat is required, but have limited usefulness in the moderate climate conditions. Manually controlled, electrically responsive and autonomous temperature responsive technologies which can change reflection properties depending on the external environmental conditions have also been developed. Various experimental and simulation studies have shown that significant amount of energy can be saved by responsive IR reflectors compared to the standard double glazing windows. Developing new technologies like bistable or energy generating windows could lead to significant improvement in energy savings and healthier, happier room occupants. It is also important to mention that most of the IR regulating based window technologies are still in the research and development phase and limited to the sample size. One of the biggest challenge while scaling-up is to achieve minimum haze in the visible region with good thermal and UV stability. The advantages of using smart windows is not only limited to the built environment: the interior temperature of automobiles could be better maintained by using such windows, leading to additional savings in fuel energy that is spent on running air-conditioners. Finally, such smart windows could also be very helpful in improving the growing conditions within greenhouses where control of temperature is seasonal and vital for the health of the plant.

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