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Organic Materials for Time−Temperature Integrator Devices

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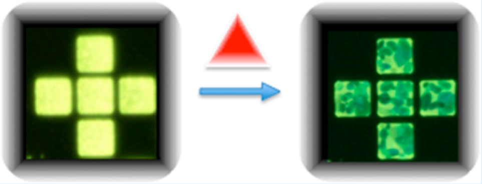

ABSTRACT: Time−temperature integrators (TTIs) are devices capable of recording the thermal history of a system. They have an enormous impact in the food and pharmaceutical industries. TTIs exploit several irreversible thermally activated transitions such as recrystallization, dewetting, smoothening, chemical decomposition, and polymorphic transitions, usually considered drawbacks for many technological applications. The aim of this article is to sensitize research groups working in organic synthesis and surface science toward TTI devices, enlarging the prospects of many new materials. We reviewed the principal applications highlighting the need and criticisms of TTIs, which offer a new opportunity for the development of many materials.

KEYWORDS: *time−temperature integrator, polymorphism, dewetting, fluorescence, smoothing, glass transition*

1. INTRODUCTION

Over the past 3 decades, organic functional materials have emerged as a low-cost alternative to inorganic materials for a variety of technological applications and devices. Limiting the application to solid-state, organic functional materials has been exploited in electronics, as both active[1] and passive[2,3] components, optoelectronics,[4,5] nonlinear optics,[6] photonics,[7] photovoltaics,[8] spintronics,[9] magnetism,[10,11] permanent/erasable memories,[12,13] sensing,[14] smart coating,[15] and other less conventional applications. New functional compounds with outstanding properties and promising technological potential are daily proposed in very important publications; however, despite their high number and the large spectrum of functionalities covered, only a few materials are deeply studied and even fewer find a real application in the proposed field. This strong selection, which sometime does not follow rational criteria, is based on the combination of several elements, which include difficult synthesis in a reasonable amount at high purity level, stability, processability, particular self-organization, and intrinsic defects that spontaneously form upon moving from the solution to solid state. Because many applications require homogeneous and often continuous thin films, materials forming defect-rich structures or inhomogeneous aggregates are often hindered in their use and development. Despite some cases in which these properties were transformed into advantages,[16,17] a big effort has been made to improve the quality of thin films by altering the chemical design and processing. In particular, one of the simplest and most used procedures consists of thermal annealing, which has been proven to be very efficient in many cases, especially in organic semiconductors.[18−20] Nevertheless, it can be detrimental because it produces irreversible damage to the film, which can originate from (re)crystallization, dewetting, phase transition, chemical decomposition, and so on. These phenomena are irreversible and are considered disadvantageous for many technological applications because they are the main cause of scientific failure for several new materials.

Here, we highlight an unusual application in which irreversible thermally activated transitions are advantageously exploited in time−temperature integrator (TTI) devices, i.e., devices capable of recording the thermal history of a system.

The aim of this spotlight article is to sensitize research groups working in organic synthesis and surface science toward TTI application, enlarging the prospects of many new functional materials.

TTI devices are very important for the traceability of perishable products, typically food, pharmceuticals and drugs but also for some electronic devices, whose temperature must be maintained at a controlled range throughout a shipping or life cycle.

Conventional TTIs use substances that can change their color by the influence of time and temperature. Existing systems are based on the diffusion on a structured label of a chemical compound because upon exposure at temperature higher than its melting point it starts to diffuse with a rate that depends on the temperature.[21] The degree of diffusion provides a direct measurement of the accumulated time−temperature history. Other reliable TTIs are based on enzymatic hydrolysis of lipid substrates[22] and on electronic devices such as Radio Frequency IDentificators (RFIDs),[23] but their cost and complexity limit their large-scale diffusion. The complexity of TTI devices dramatically increases when they have to monitor a spectrum of temperatures instead of a threshold temperature because it is often necessary to introduce different materials or components, each one sensitive to a specific critical temperature, in an independent device.

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Here, we reviewed several recent examples of TTI applications showing how different irreversible transitions acting on the morphological, structural, or functional properties can be advantageously exploited. We reviewed the most common compounds useful for TTIs and some synthetic strategies to tailor the properties and transition temperatures of a selected class of organic compounds. We focused our attention on the materials, deliberately neglecting complex devices in which the material transition does not play an active role, as well as devices behaving as simple real-time thermometers such as in the case of many thermochromic materials.[24] Figure 1 summarizes the main types of thermal transitions and the effect used for TTI devices.

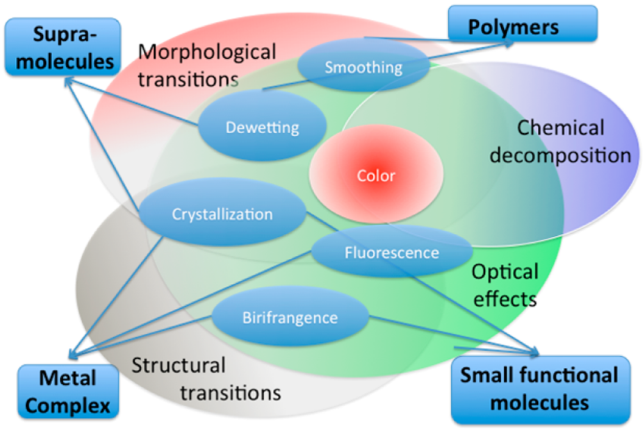

Figure 1. Scheme of the main thermal transition and readable effects exploitable in TTI devices.

Although, in principle, also bulk materials can be used in TTIs, all examples presented exploit transformation in thin films; this is due to the low cost of materials and the possibility of being processed by the present printing technology, such as gravure printing and inkjet printing. Furthermore, in some cases the presence of the surface is crucial to controlling the molecular self-assembly[25,26] and to inducing the exploitable transitions in TTIs, such as dewetting[15,27] and in latent pigment decomposition.[28]

1.1. Analysis of the Colors. TTI devices are based on irreversible thermal transitions that result in a color change; therefore, an accurate quantitative analysis of the colors is necessary for real devices. The color is defined by the wavelength; however, images are recorded by a charge-coupled device (CCD) image sensor as digital images. Therefore, the quantitative analysis of the color is performed by analyzing the output signal of the CCD used for recording the image or, alternatively, the color composition of the digital images[29] by a software. In a CCD, the colors are defined by a combination of red, green, and blue (RGB) or cyan, magenta, yellow, and green (CMYG), depending on the system. The CCDs registering the signal by CMYG systems usually record a greater signal because their broader spectral bands pass. However, because the signals must be converted to RGB (the largest format used in image processing), the conversion implies additional processing that adds noise and reduces the original gain in the signal-to-noise ratio.[30] On the other hand, the RGB system combines the primary colors, producing all colors visible by the human eye; therefore, it is the most used system for TTIs.

In all systems, the color components may depend on the particular CCD, on the filter used for detection, and, in the case of image analysis, on the software used. For instance, a quantitative detection of the color needs an accurate calibration of each system.

2. TTIS BASED ON MORPHOLOGICAL TRANSITIONS

It is well-known that upon thermal treatment many films reorganize, changing their morphology. Morphological transitions themselves can be directly exploited in TTI devices because the morphology influences some optical properties, such as the reflectivity and diffraction property. The possible causes of morphological transformations are (re)crystallization, smoothing, dewetting, and in some cases solid−solid structural transitions. All of these transformations are observed in a variety of materials ranging from the simplest molecule to more complex supramolecular aggregates; they are thermally activated and irreversible and evolve with time and temperature; therefore, once rationalized, they can be advantageously exploited in TTIs. The only real requirement is the possibility of providing an easy measurable property such as a change in color (originating both by a pigment and by an optical effect), diffraction, fluorescence, etc., correlated with time and temperature.

As a film is exposed to a temperature higher than a threshold temperature, the morphological transformation irreversibly changes the morphology and possibly the corresponding "readable" properties, which often results in a color change. It must be considered that TTI devices require homogeneous (but not necessarily continuous) films and a highly reproducible morphological transformation; both characteristics depend on a precise initial morphology of the films, related to the method employed for their fabrication.

2.1. Smoothing. Figure 2a shows as an example the effect of smoothing on diffraction in a patterned film. When the patterned film is observed at fixed illumination and with defined direction (i.e., the standard conditions used by a commercial optical microscope), it appears colored; the different colors were selected using a grating with different periodicities and controlled considering Bragg's conditions. As the film is heated to the glass transition temperature, the polymer becomes smooth under the action of surface tension and, consequently, the pattern loses the diffraction properties, as indicated by the observed color in the microscope/CCD. Noticeably, if some molecules are dispersed into the polymer, during the thermal treatment the solute may accumulate in correspondence with film protrusion due to the higher surface contraction with correspondence of the film protrusion, as observed by both thermal and solvent annealing in polymers embedding small molecules.[27,31] This effect can further enhance the response of the device in terms of optical contrast.

Figure 2 shows an example of the diffraction color evolution under thermal treatment of a patterned film of polycarbonate.

Here, the device was obtained by replica molding[32] of a diffraction grating by a thermoplastic polymer (polycarbonate). The quantitative analysis of the color evolution shows that the color intensity decreases linearly with the time of exposure to a temperature higher than the polymer glass transition temperature; this behavior allows one to estimate the time of treatment by simply measuring the loss of specific color components. In this particular case, the color change recorded by the CCD is essentially due to a variation of the green

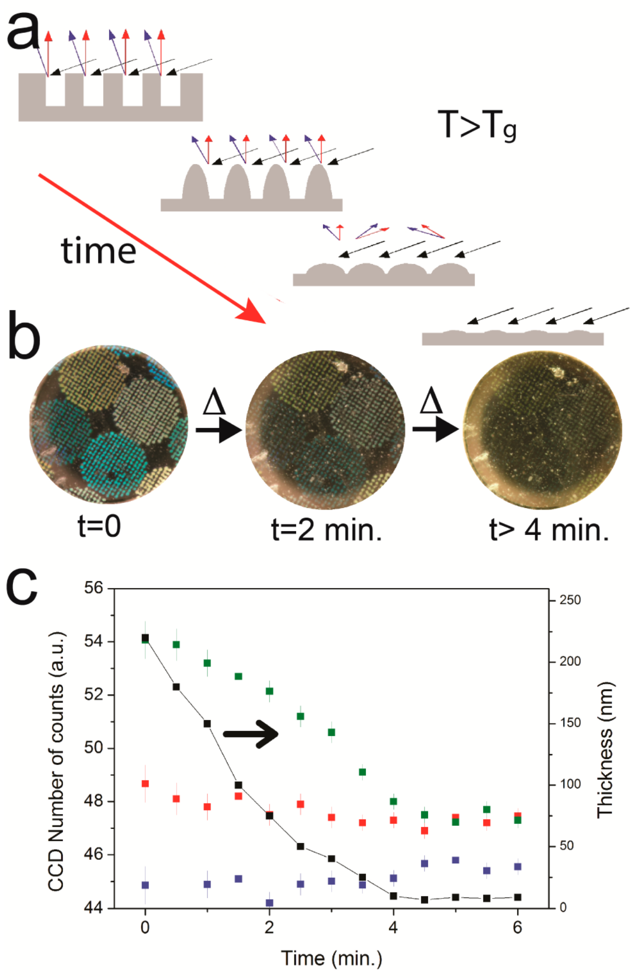

Figure 2. (a) Scheme of diffraction evolution upon smoothing of a patterned film. Adapted from ref 41 with permission. Copyright RCS 2015. (b) Diffraction color evolution under thermal treatment of the patterned film of polycarbonate. (c) Corresponding analysis of the color composition (respectively red, green, and blue) recorded by a CCD during the smoothing. The black curve shows the reduction of the thickness of printed features measured by atomic force microscopy.

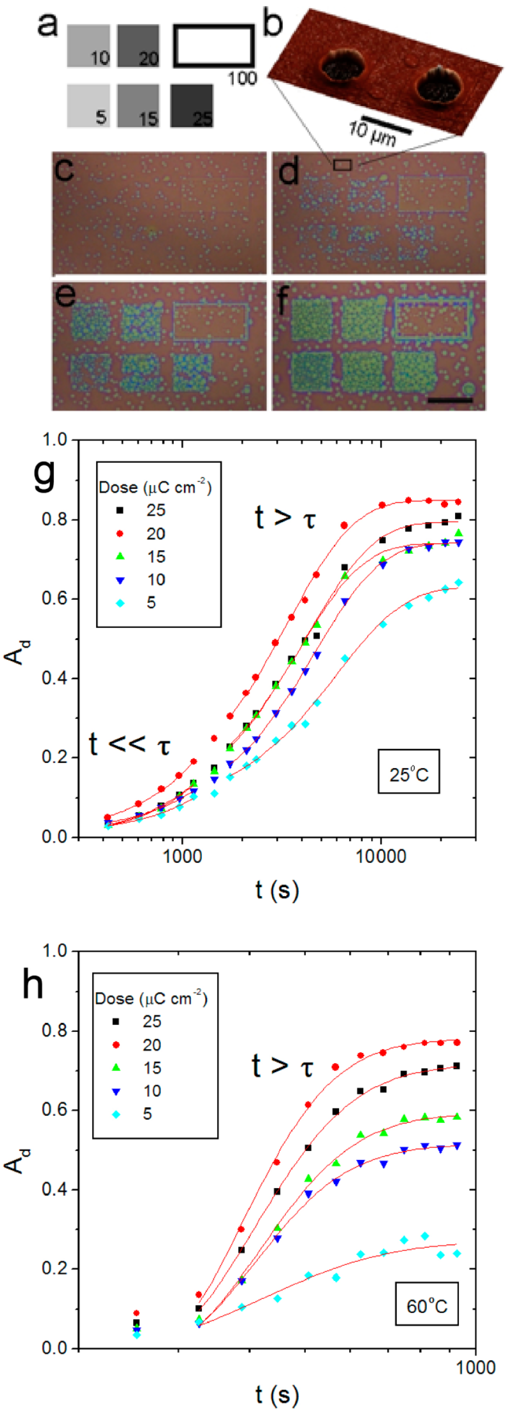

Figure 3. Time–temperature integration functionality by dewetting. (a) Scheme of the irradiated zones of the polymeric thin film. The gray level is proportional to the electron dose; the numbers indicate the exact doses expressed in μC·cm^{-2}. (b) Atomic force microscopy topography of holes formed at the beginning of dewetting. Optical images of the evolution of an irradiated PIB film at T = 60 °C after (c) 253, (d) 387, (e) 507, and (f) 927 s. The bar is 50 μm. Time evolution of the percentage of the area free of PIB in each irradiated square at (g) 25 and (h) 60 °C. The continuous curves are data fits obtained using the model of dewetting described in the text. Figure adapted with permission from ref 35. Copyright 2010 American Chemical Society.

component, which decreases linearly with the reduction of the thickness of the printed features (Figure 2c).

The proposed approach is not specific because it takes advantage of the glass transition temperature and the viscous properties of a polymer, and it can be easily extended to a variety of polymers or small molecules, giving softening under thermal treatment.

2.2. Dewetting. Another common thermal effect in morphology, noted as dewetting, consists of a spontaneous phenomenon occurring when a thin film on a surface ruptures into separated objects, like droplets and pillars. Dewetting is an irreversible process that requires activation energy and displays a temperature- and time- dependent characteristic length scale; the ideal prerequisites for TTI applications. An example was reported by Calò et al., in which it is demonstrated how a patterned thin film of polyisobutylene acts as a TTI device.[33] The polymeric film was patterned by electron irradiation of spatially defined zones by an electron beam (Figure 3a–f). Upon controlled irradiation, polymer chains fragment, generating zones with controlled (reduced) molecular weight. The zones containing polymer with lower molecular weight dewetted at lower temperature and faster than the zones with higher molecular weight (Figure 3g,h). The time–temperature integration was demonstrated by measuring the morphological evolution of the irradiated area and by modeling dewetting according to the Brochard-Wyart theory.[34] The evolution with time of exposure was followed by measuring the percentage of dewetted area that depends on the percentage of electron dose received by the polymer.

As in the case of smoothing, the proposed approach is not specific and can be easily extended to a variety of polymers whose molecular weight can be modified upon irradiation with electrons or light by fragmentation or induction of cross-linking (i.e., the inverse process of fragmentation; in this last case, the irradiation induces local polymerization, in which the molecular weight is proportional to the electron dose). The chance of tuning the molecular weight by irradiation allows the fabrication of devices working in wide temperature ranges. Moreover, because dewetting is not a peculiarity of polymers,[36] similar configurations of TTI devices can also be adopted using both small molecules or supramolecular systems.[15]

2.3. TTIs Based on Structural Transitions. Liquid crystals are examples of how controlling the self-assembly via chemical design and processing leads to novel applications. A remarkable example on how the temperature may influence the optical properties and can be exploited in TTIs was reported by Davies et al.[37]

In particular, the authors fabricated an optical TTI based on the shape memory of a mechanically embossed cholesteric liquid crystalline (CLC) polymer network. TTI devices were obtained by the imprinting of thin films of CLC. In the imprinted zones, a moderated mechanical deformation was accompanied by a higher average distance between hydrogen bonding and a relevant shift to lower wavelengths of the reflection band, which results in a significant change of color in correspondence with the printed areas when observed by optical microscopy. The imprinted zones were capable of returning to the original state as a function of the temperature and time, which causes an observable color variation.

Remarkably, the transition temperature was related to the glass transition temperature of the polymer and could be tuned by acting on the film composition. Figure 4 shows the microscopy images recorded in reflection mode at room temperature upon thermal treatment of printed CLC-TTI devices.

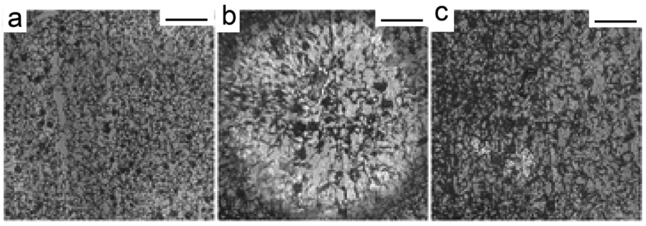

Figure 4. CLC films embossed at 60 °C. Microscopy images recorded in reflection mode at room temperature showing (a) the nonembossed film, (b) the embossed film, and (c) the embossed film after heating to 60 °C. The bars are 100 μm. Figure adapted with permission from ref 37. Copyright 2013 Wiley.

3. TTIS BASED ON THE CHANGE OF THE OPTICAL PROPERTIES

3.1. Birefringence. Another efficient approach for TTI devices consists of measurement of the change in birefringence, as reported by our group, a TTI based on discotic liquid crystals (DLCs).[33]

Birefringence allows one to see colored crystals when observed by a polarized optical microscope with crossed polars, and it is associated with an ordered structure of the sample. Under crossed polars, birefringent materials appear colored while amorphous or nonbirefringent materials appear dark. For TTI devices, the birefringence images were treated as normal digital optical images.

DLCs consist of columnar superstructures formed by the stacking of disklike molecules and are formed by a rigid core surrounded by flexible external chains that provide solubility and self-organizing properties. Columns organize in hexagonal and rectangular phases depending on the temperature and exhibit strong anisotropy properties. DLCs were originally proposed for electronic and photovoltaic applications; unfortunately, the high number of defects that spontaneously form in thin film limits their impact in their industrial development.[38]

The alignment can be directly visualized using polarized optical microscopy; i.e., planar alignment results in a highly birefringent texture, whereas homeotropic alignment exhibits almost an absence of birefringence.

When deposited onto a surface, the DLC columns spontaneously orient flat on the surfaces (edge-on phase) and exhibit a high birefringence. On the other hand, if the film is confined between two surfaces and treated by a melting and quenching process, the columns orient perpendicular to the surfaces, forming the so-named homeotropic phase, which is almost not birefringent.[39]

Recently, our group demonstrated that, using a stamp instead of a surface, is also possible to locally modify the alignment of DLC columns in the film,[33] obtaining a homeotropic phase in correspondence with the stamp protrusions and an edge-on phase in correspondence with the stamp recesses. Figure 5 shows the scheme of the process and the resulting patterning. The process allows specific column orientation at preselected regions of the film.

When the temperature overcomes the hexagonal–rectangular transition temperature, the individual edge-on domains progressively reorient into the dominant phase. The reorientation is proportional to the number of times that the patterned film is exposed to a temperature higher than the transition temperature, and the time spent above the transition temperature is monitored from the irreversible change of the local birefringence (Figure 5 c).

Here the authors exploited the birefringence of DLCs. Nevertheless, like color and fluorescence, birefringence is a common property of ordered materials; therefore, it can be efficiently exploited in many other systems both alone or associated with other observables in the so-named multimodal sensing.[40,41] Noticeably, the possibility of tuning the transition temperature by acting on the chemical shape of the molecules increases the range of applications of this class of materials. Moreover, in the presented applications, the authors exploited a common behavior of DLCs;[39] therefore, the proposed approach can easily be extended to other similar compounds.

3.2. Fluorescence and Polymorphism. Another property exploitable for TTI is the change of fluorescence, which depends on the molecular structure and packing and therefore is very sensitive to crystal transitions including polymorphic ones (i.e., different crystal structures with the same composition). Very recently, Gentili et al. exploited the

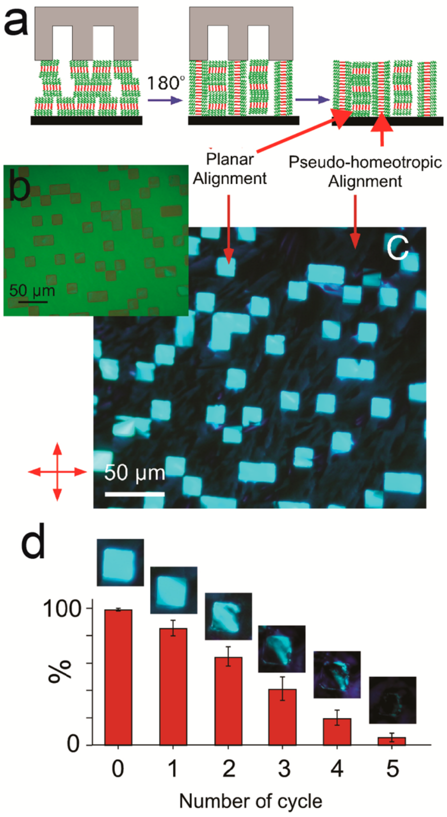

Figure 5. Stamp-assisted melting/quenching process inducing a spatially controlled column orientation in continuous thin films. (a) Scheme of the process applied on an isotropic (fluid) phase. (b) Optical micrographs in the bright field of the stamp and (c) with cross polars of the patterned polycarbonate film. (d) Evolution of the area of the birefringent zone inside a bit containing the planar-aligned columns upon five thermal cycles around $T_{\text{r-h}}$. The graph shows the percentage of area that lost birefringence. Figure adapted with permission from ref 33. Copyright 2010 Wiley.

temperature-dependent fluorescence of a model compound that at the solid state exhibits polymorphism.[29]

In particular, they demonstrated that a logic pattern (i.e., a pattern able to store information as a miniaturized data matrix code) of a model compound works as a TTI in a wide temperature range. They used thieno(bis)imide end-functionalized terthiophene, which was highly processable in solution and exhibits a continuous variation of fluorescence upon thermal treatment that allowed one to advantageously exploit polymorphism for TTI purposes.[29]

When thermally treated, polycrystalline films exhibited an irreversible structural change accompanied by changes in the photoluminescent properties whose spectra shift from yellow to green. Figure 6 shows the fluorescence evolution of printed TAG upon thermal treatment observed in a fluorescence microscope.

Quantitative analysis of the fluorescence evolution (Figure 6b) shows that for each temperature the color is defined by a unique combination of RGB components and that the red component undergoes a linear decrease with temperature; therefore, the temperature at which the device was exposed can be analytically derived from the color composition. It must be noted that this kind of devices is able to record the highest temperature of which it was exposed for more than a defined time, which depends on the response time of the material used.

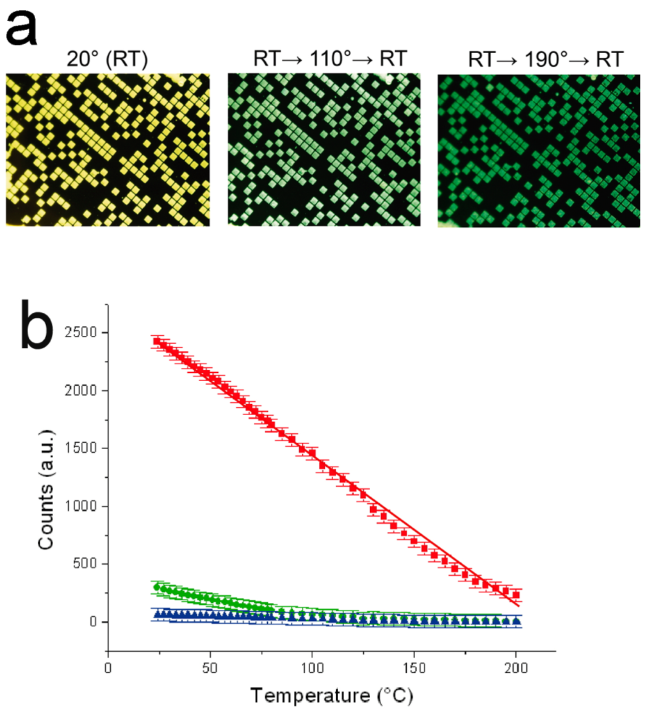

Figure 6. (a) Evolution of the fluorescence in a patterned film recorded by a CCD versus the temperature. The images were taken at room temperature after heating the pattern at the indicated temperature for 30 s (no further changes were observed after this time). (b) Quantitative analysis of the fluorescence images. Number of counts versus temperature obtained using a band-pass filter >475 nm. Figure adapted from ref 29 with permission. Copyright NPG 2013.

Similar devices were proven using inhomogeneous thin deposits of different fluorescent compounds by changing both the functional core and the surrounding chains.[42,43]

3.3. Latent Pigments. Very recently, Beverina et al. demonstrated the TTI capability of thermochromic molecular materials; in particular, they used the so-named "latent pigment" approach.[28] This process enables one to induce the transformation of organic compounds from a colorless precursor to a pigment by the temperature. In particular, they used thin-film squaraines[44] treated with di-*tert*-butyl dicarbonate and 4-(*N*,*N*-dimethylamino)pyridine as the active material. In these condition, the deeply colored squarine is converted into a betaine, which is colorless. Upon thermal treatment, the process can be reverted, thus restoring the blue color.

Remarkably, because the reaction is sensitive to the pH, the transition temperature can be tailored in a wide range of temperatures (in the reported example from room temperature to 140 °C), acting on the pH of the surface, which can be performed by an appropriate chemical functionalization. Figure 7 shows a scheme of the chemical reaction and color change in thin-layer chromatography plates.

4. MATERIALS WITH THERMAL HYSTERESIS

In principle, the ideal candidates for TTI devices are materials with thermal hysteresis, in which a readable physical property depends on the temperature and on the thermal history.

Important materials that exhibit thermal hysteresis are the so-named spin-transition compounds, which include spin-crossover[45,46] and valence tautomer compounds.[47−49]

Spin-transition compounds are switching metal complex compounds able to change their spin state upon external

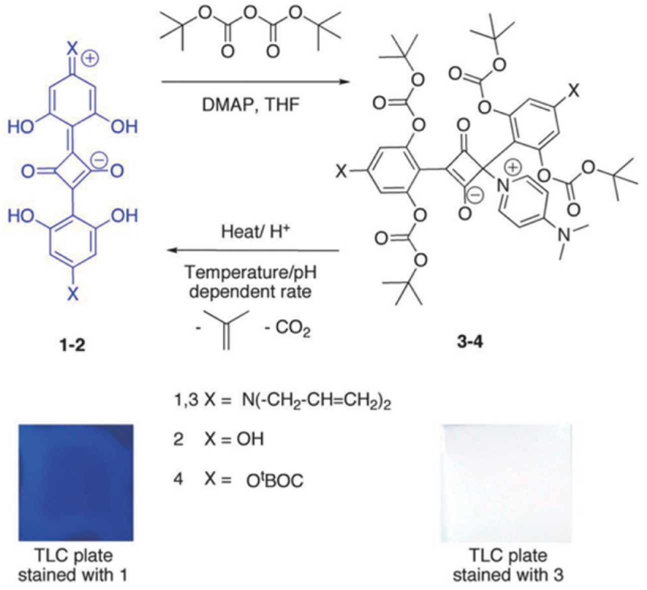

Figure 7. Chemical reaction for the preparation of latent pigments **3** and **4** starting form squaraines **1** and **2** along with the corresponding cleavage conditions. The two pictures show thin-layer chromatography plates stained with squaraine **1** and the corresponding latent pigment **3**. Figure adapted with permission from ref28, Copyright 2015 Wiley.

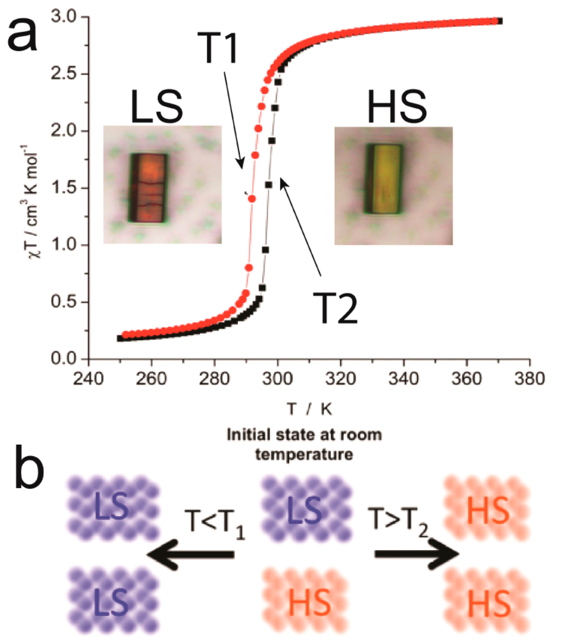

Figure 8. (a) Room temperature hysteresis and bistability in an Fe^{II}-based spin-crossover compound. (b) Schematic representation of a possible TBC.

stimuli. The switching process involves a structural transition that produces an electron redistribution, as well as the change of other physical properties such as color, magnetic susceptibility, thermal and electric conductivity, birefringence, dielectric constant, and mechanical properties.[46,50−54] The transition is triggered by external stimuli, such as temperature, pressure, light, magnetic field, or a combination of them, and if strong cooperative effects are present, it exhibits hysteresis.[55] Spin-transition compounds are processable by unconventional wet lithography[56] and have been proposed in TTIs.[57] Figure 8 shows an example of room temperature hysteresis in a Fe^{II}-based spin-crossover compound where the evidence of bistability is clearly shown by the change of color.

It should be noted that in spin-transition materials the transition is reversible; therefore, the devices must be slightly more complex than the patterned system used in the previous demonstration. In particular, materials with thermal hysteresis are more suitable for fabricating the so-named “temperature-band controllers (TBCs)”, which are devices capable of monitoring temperature changes also at reduced scales (space and time) and, in particular, to detect whether a product has been exposed to a temperature higher or lower than a defined range. In this case, the device needs to be patterned by zone with materials in different states. The simplest scheme of the TBC is shown in Figure 8b. It consists of patterning two zones with different spin states, where T1 and T2 are associated with the temperature hysteresis (see Figure 8a) defining the threshold temperatures of the TBC. If the system is exposed to a temperature lower than the transition temperature [e.g., where the compound exists only in the low-spin (LS) state], the pattern structures will be transformed in a LS−LS state; on the other hand, if the system is exposed to a temperature higher than the transition temperature [where the compound exists only in the high-spin (HS) state], the pattern structures will be transformed in a HS−HS state. This system will be able to record only the last temperature over the threshold (i.e., it will not be able to record if a product was first exposed to $T > T2$ than to $T < T1$), but it will provide crucial information regarding the preservation of perishable products. Considering the number of proposed compounds and the impressive range of temperature covered, these materials are particularly promising for TTI/TBC applications. Spin-crossover compounds can be applied in TTIs and TBCs directly exploiting some physical properties both as nanoelectromechanical actuators[58] or in association with gas sensing.[59,60]

5. MATERIAL DESIGN STRATEGY TO TAILOR THE TTI PROPERTIES

The fabrication of TTI devices has so far been realized by exploiting material systems of different nature that were already known in the literature for applications in different organic electronics subfields. Figure 9 shows the chemical structures of such molecular and polymeric materials.

Depending on the functionality of the active layer, different working mechanisms have been exploited for the temperature control function. However, further device sensitivity and performance optimization and expression of the TTI full potential could be achieved only if ad hoc material engineering will be performed in parallel with device implementation. Indeed, thermal transitions, wetting properties, morphology fluorescence, and spin transition exploited in TTI can all be tuned by proper tailoring of the molecular/polymeric structure of the responsive TTI organic component.

For example, a common strategy to the tailor solubility, thermal transitions, and wetting properties of organic π-conjugated materials relies on the insertion of a long aliphatic chain with precise regiochemistry. Longer aliphatic chains as well as branched alkyl ones are also known to decrease the melting point and to promote liquid-crystalline behavior.[61,62] In thienoimide-based molecular materials, recently exploited by our group for TTI fabrication,[29,43,61] deep structure−property relationship investigations have proven the efficiency of the

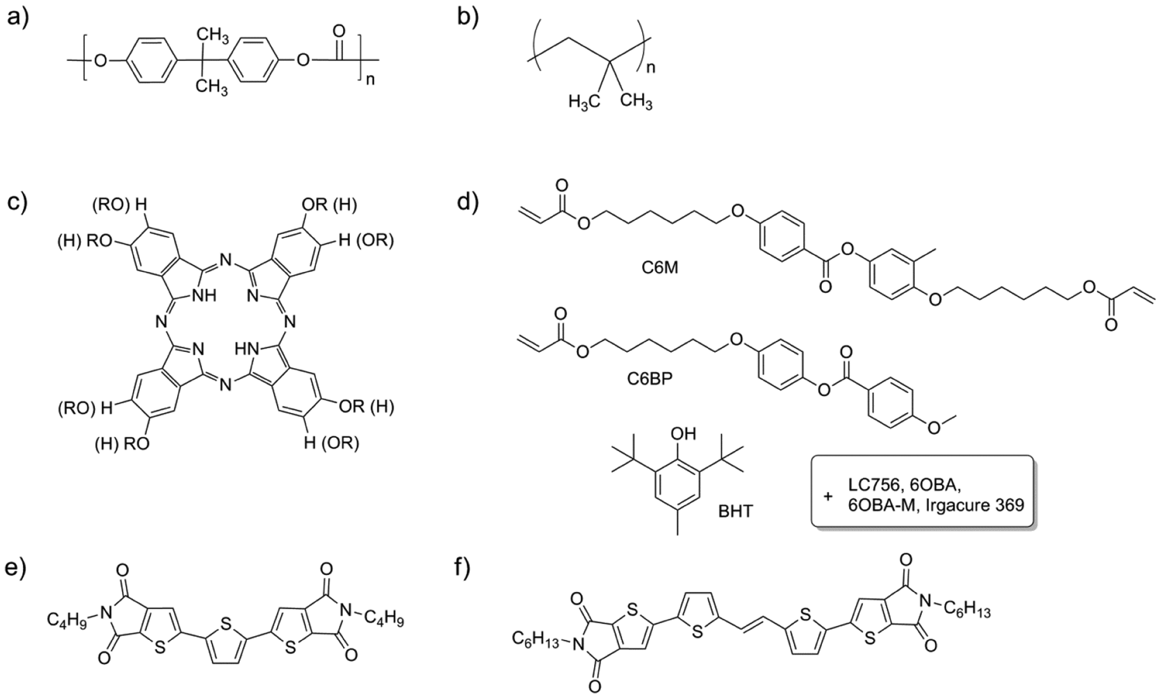

Figure 9. Chemical structures of the organic materials so far used as active layers or substrates in TTI devices: (A) polycarbonate used as devices based on smoothing;[27,31] (b) polyisobuthylene used in TTIs based on dewetting;[33] (c) mesogenic phthalocyanine used in devices based on the change in birefringence;[40] (d) representative components of the mesogenic mixture used in ref 37; (e and f) polymorphic thienoimide based molecules used in devices based on fluorescence and polymorphic transitions.[29,43]

insertion of unsaturated inner spacers in promoting polymorphism.

The thienoimide moiety itself induces conformational polymorphism, i.e., the possibility of different molecular conformation by rotation of the thiophene ring adjacent to the thienoimide moiety with respect to the thienoimide.[42] Indeed, an even−odd effect of the *N*-alkyl end on the molecular conformation type and crystal packing has recently been reported for these molecules and was reflected in the emission color of microcrystals deposited on the substrates. Figure 10 shows the fluorescence microscopy images of microfiber and crystallite evolution of the fluorescence color for a thienoimide-based trimer (Figure 9e) by heating the thin deposits up to 200 °C.

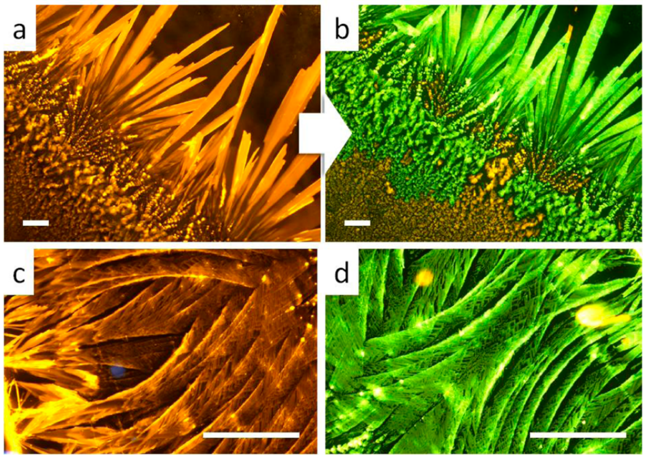

Figure 10. Fluorescence microscopy images of thin deposits of thienoimide-based molecules[36] showing crystalline fibers of different size and shape changing fluorescence from orange (a) to green (b) upon thermal treatment. (c and d) Images showing morphological details of parts a and b, respectively. Scale bars are 100 *μ*m.

Figure 11 shows a general structure of 2,3-thienoimide-ended molecular materials with some possible chemical modification targets that have been exploited to tailor the thin-film fluorescence, morphology, thermal behavior, and electrical properties of these materials.[43,63]

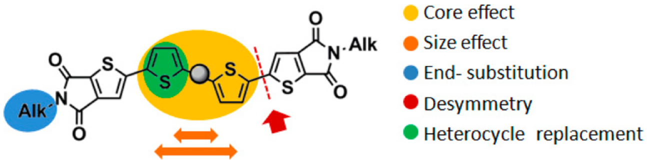

Figure 11. Sketch of the molecular structure of a thienoimide-based material and the possible targets of structure modification (indicated by the arrows).

Interestingly, a variety of crystalline morphologies associated with a wide range of absorption and emission frequencies have been observed in cast films of thienoimide-based materials of different molecular structures. These features combined with the intrinsic multifunctionality (charge-transport and optoelectronic properties) make thienoimide-based compounds a valuable class of materials for TTI applications.

Nevertheless, the huge number of material families so far developed within the organic electronics scenario offers the possibility of performing a rational investigation on the TTI response and performance versus material structure, useful for defining new working mechanisms for TTI and to enlarge their application range.[64]

6. CONCLUSIONS

In summary, we presented an unusual application of thin films subject to irreversible thermal transitions. In particular, we advantageously exploited several phenomena that are usually considered drawbacks for technological applications. These properties allow the fabrication of devices with time−temperature integration functionalities by using several active materials.

We demonstrated several feasible approaches by simple fabrication methods, using model compounds; however, the proposed approaches are general and based on common properties and, therefore, can be extended to all functional materials and to other kinds of thermal transitions whose fluorescence, color, or other photophysical properties change irreversibly with temperature.

The simplicity of the devices and the large number of exploitable properties make the proposed application extremely appealing for the development of a new generation of low-cost TTI devices working in a wide range of temperatures.

The presented examples are general for functional materials designed for self-organization, and therefore they open novel prospects for fabricating nanostructured organic devices, which can be further enhanced by the synthesis of specific new compounds.

To date, most of the proposed materials for TTIs are demonstrated for temperatures higher than room temperature; however, considering the potential impact and the industrial need, we expect that the same approach can be extended to low temperature with special attention to frozen product preservation.

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■ REFERENCES

(1) Dimitrakopoulos, C. D.; Malenfant, P. R. L. Organic Thin Film Transistors for Large Area Electronics. *Adv. Mater.* **2002**, *14*, 99−117.

(2) Greco, P.; Cavallini, M.; Stoliar, P.; Quiroga, S. D.; Dutta, S.; Zacchini, S.; Iapalucci, M. C.; Morandi, V.; Milita, S.; Merli, P. G.; Biscarini, F. Conductive Sub-Micrometric Wires of Platinum-Carbonyl Clusters Fabricated by Soft-Lithography. *J. Am. Chem. Soc.* **2008**, *130*, 1177−1182.

(3) Serban, D. A.; Greco, P.; Melinte, S.; Vlad, A.; Dutu, C. A.; Zacchini, S.; Iapalucci, M. C.; Biscarini, F.; Cavallini, M. Towards All-Organic Field-Effect Transistors by Additive Soft Lithography. *Small* **2009**, *5*, 1117−1122.

(4) Melucci, M.; Zambianchi, M.; Favaretto, L.; Gazzano, M.; Zanelli, A.; Monari, M.; Capelli, R.; Troisi, S.; Toffanin, S.; Muccini, M. Thienopyrrolyl Dione End-Capped Oligothiophene Ambipolar Semiconductors for Thin Film- And Light Emitting Transistors. *Chem. Commun.* **2011**, *47*, 11840−11842.

(5) Muccini, M. A Bright Future for Organic Field-Effect Transistors. *Nat. Mater.* **2006**, *5*, 605−613.

(6) Lambert, A. G.; Davies, P. B.; Neivandt, D. J. Implementing the Theory of Sum Frequency Generation Vibrational Spectroscopy: A Tutorial Review. *Appl. Spectrosc. Rev.* **2005**, *40*, 103−145.

(7) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, *280*, 1741−1744.

(8) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S.; Ree, M. A Strong Regioregularity Effect in Self-Organizing Conjugated Polymer Films and High-Efficiency Polythiophene: Fullerene Solar Cells. *Nat. Mater.* **2006**, *5*, 197−203.

(9) Taliani, C.; Dediu, V.; Biscarini, F.; Cavallini, M.; Murgia, M.; Ruani, G.; Nozar, P. Organic-Inorganic Hybrid Spin-Valve: A Novel Approach to Spintronics. *Phase Transitions* **2002**, *75*, 1049−1058.

(10) Cavallini, M.; Facchini, M.; Albonetti, C.; Biscarini, F. Single Molecule Magnets: From Thin Films to Nano-Patterns. *Phys. Chem. Chem. Phys.* **2008**, *10*, 784−793.

(11) Coronado, E.; Marti-Gastaldo, C.; Galan-Mascaros, J. R.; Cavallini, M. Polymetallic Oxalate-Based 2D Magnets: Soluble Molecular Precursors for the Nanostructuration of Magnetic Oxides. *J. Am. Chem. Soc.* **2010**, *132*, 5456−5468.

(12) Cavallini, M.; Biscarini, F.; Gomez-Segura, J.; Ruiz, D.; Veciana, J. Multiple length Scale Patterning of Single-Molecule Magnets. *Nano Lett.* **2003**, *3*, 1527−1530.

(13) Murray, K. S.; Kepert, C. J. Cooperativity in spin crossover systems: Memory, magnetism and microporosity. Spin Crossover in Transition Metal Compounds. I. *Top. Curr. Chem.* **2004**, *233*, 195−228.

(14) Melucci, M.; Zambianchi, M.; Favaretto, L.; Palermo, V.; Treossi, E.; Montalti, M.; Bonacchi, S.; Cavallini, M. Multicolor, Large-Area Fluorescence Sensing Through Oligothiophene-Self-Assembled Monolayers. *Chem. Commun.* **2011**, *47*, 1689−1691.

(15) Cavallini, M.; Lazzaroni, R.; Zamboni, R.; Biscarini, F.; Timpel, D.; Zerbetto, F.; Clarkson, G. J.; Leigh, D. A. Conformational Self-Recognition as the Origin of Dewetting in Bistable Molecular Surfaces. *J. Phys. Chem. B* **2001**, *105*, 10826−10830.

(16) Cavallini, M. Inhomogeneous Thin Deposits: A Strategy to Exploit Their Functionality. *J. Mater. Chem.* **2009**, *19*, 6085−6092.

(17) Cavallini, M.; Facchini, M.; Massi, M.; Biscarini, F. Bottom-Up Nanofabrication of Materials for Organic Electronics. *Synth. Met.* **2004**, *146*, 283−286.

(18) Menozzi, C.; Corradini, V.; Cavallini, M.; Biscarini, F.; Betti, M. G.; Mariani, C. Pentacene Self-Aggregation at the Au(110)-(1 × 2) Surface: Growth Morphology and Interface Electronic States. *Thin Solid Films* **2003**, *428*, 227−231.

(19) Cavallini, M.; Simeone, F. C.; Borgatti, F.; Albonetti, C.; Morandi, V.; Sangregorio, C.; Innocenti, C.; Pineider, F.; Annese, E.; Panaccione, G.; Pasquali, L. Additive Nanoscale Embedding of Functional Nanoparticles on Silicon Surface. *Nanoscale* **2010**, *2*, 2069−2072.

(20) Corradini, V.; Menozzi, C.; Cavallini, M.; Biscarini, F.; Grazia Betti, M.; Mariani, C. Growth Morphology and Electronic Structure of 2D Ordered Pentacene on the Au(110)-(1 × 2) Surface. *Surf. Sci.* **2003**, *532*, 249−254.

(21) Manske, W. J. Selected Time Interval Indicating Device. U.S. Patent 3,954,011, 1976.

(22) Taoukis, P. S.; Labuza, T. P. Applicability of Time-Temperature Indicators as Shelf Life Monitors of Food Products. *J. Food Sci.* **1989**, *54*, 783−788.

(23) Bo, Y.; Danyu, L. Application of RFID in Cold Chain Temperature Monitoring System. *CCCM 2009: ISECS International Colloquium on Computing, Communication, Control, and Management,*

Sanya, China, Aug 8 and 9, 2009; IEEE: Piscataway, NJ, 2009; pp 258−261.

(24) Hadjoudis, E.; Vittorakis, M.; Moustakalimavridis, I. Photochromism and Thermochromism of Schiff-Bases in the Solid-State and in Rigid Glasses. *Tetrahedron* **1987**, *43*, 1345−1360.

(25) Leclere, P.; Surin, M.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Jonkheijm, P.; Biscarini, F.; Cavallini, M.; Feast, W. J.; Meijer, E. W.; Schenning, A. Surface-Controlled Self-Assembly of Chiral Sexithiophenes. *J. Mater. Chem.* **2004**, *14*, 1959−1963.

(26) Cavallini, M.; Aloisi, G.; Bracali, M.; Guidelli, R. An in Situ STM Investigation of Uracil on Ag(111). *J. Electroanal. Chem.* **1998**, *444*, 75−81.

(27) Cavallini, M.; Gomez-Segura, J.; Albonetti, C.; Ruiz-Molina, D.; Veciana, J.; Biscarini, F. Ordered Patterning of Nanometric Rings of Single Molecule Magnets on Polymers by Lithographic Control of Demixing. *J. Phys. Chem. B* **2006**, *110*, 11607−11610.

(28) Galliani, D.; Mascheroni, L.; Sassi, M.; Turrisi, R.; Lorenzi, R.; Scaccabarozzi, A.; Stingelin, N.; Beverina, L. Thermochromic Latent-Pigment-Based Time−Temperature Indicators for Perishable Goods. *Adv. Opt. Mater.* **2015**, n/a.

(29) Gentili, D.; Durso, M.; Bettini, C.; Manet, I.; Gazzano, M.; Capelli, R.; Muccini, M.; Melucci, M.; Cavallini, M. A Time-Temperature Integrator Based on Fluorescent and Polymorphic Compounds. *Sci. Rep.* **2013**, *3*, 2581.

(30) http://classic.www.axis.com/files/whitepaper/wp_ccd_cmos_40722_en_1010_lo.pdf.

(31) Cavallini, M.; Gomez-Segura, J.; Ruiz-Molina, D.; Massi, M.; Albonetti, C.; Rovira, C.; Veciana, J.; Biscarini, F. Magnetic Information Storage on Polymers by Using Patterned Single-Molecule Magnets. *Angew. Chem., Int. Ed.* **2005**, *44*, 888−892.

(32) Cavallini, M.; Murgia, M.; Biscarini, F. Patterning a Conjugated Molecular Thin Film at Submicron Scale by Modified Microtransfer Molding. *Nano Lett.* **2001**, *1*, 193−195.

(33) Cavallini, M.; Calo, A.; Stoliar, P.; Kengne, J. C.; Martins, S.; Matacotta, F. C.; Quist, F.; Gbabode, G.; Dumont, N.; Geerts, Y. H.; Biscarini, F. Lithographic Alignment of Discotic Liquid Crystals: A New Time-Temperature Integrating Framework. *Adv. Mater.* **2009**, *21*, 4688−4691.

(34) Redon, C.; Brochard-Wyart, F.; Rondelez, F. Dynamics of Dewetting. *Phys. Rev. Lett.* **1991**, *66*, 715−718.

(35) Calo, A.; Stoliar, P.; Matacotta, F. C.; Cavallini, M.; Biscarini, F. Time-Temperature Integrator Based on the Dewetting of Polyisobutylene Thin Films. *Langmuir* **2010**, *26*, 5312−5315.

(36) Gentili, D.; Foschi, G.; Valle, F.; Cavallini, M.; Biscarini, F. Applications of Dewetting in Micro and Nanotechnology. *Chem. Soc. Rev.* **2012**, *41*, 4430−4443.

(37) Davies, D. J. D.; Vaccaro, A. R.; Morris, S. M.; Herzer, N.; Schenning, A.; Bastiaansen, C. W. M. A Printable Optical Time-Temperature Integrator Based on Shape Memory in a Chiral Nematic Polymer Network. *Adv. Funct. Mater.* **2013**, *23*, 2723−2727.

(38) Calo, A.; Stoliar, P.; Cavallini, M.; Geerts, Y. H.; Biscarini, F. Doping and Photo-Induced Current in Discotic Liquid Crystals Thin Films: Long-Time and Temperature Effects. *Org. Electron.* **2011**, *12*, 851−856.

(39) Sergeyev, S.; Pisula, W.; Geerts, Y. H. Discotic liquid crystals: A New Generation of Organic Semiconductors. *Chem. Soc. Rev.* **2007**, *36*, 1902−1929.

(40) Di Maria, F.; Calo, A.; Stoliar, P.; Kengne, J. C.; Martins, S.; Matacotta, F. C.; Quist, F.; Gbabode, G.; Dumont, N.; Geerts, Y. H.; Biscarini, F. A Successful Chemical Strategy To Induce Oligothiophene Self-Assembly into Fibers with Tunable Shape and Function. *J. Am. Chem. Soc.* **2011**, *133*, 8654−8661.

(41) Gentili, D.; Demitri, N.; Schäfer, B.; Bergenti, I.; Liscio, F.; Ruben, M.; Ruani, G.; Cavallini, M. Multi-Modal Sensing in Spin Crossover Compounds. *J. Mater. Chem. C* **2015**, DOI: 10.1039/C5TC00845J.

(42) Maini, L.; Gallino, F.; Zambianchi, M.; Durso, M.; Gazzano, M.; Rubini, K.; Gentili, D.; Manet, I.; Muccini, M.; Toffanin, S.; Cavallini, M.; Melucci, M. Chemical Design Enables the Control of Conformational Polymorphism in Functional 2,3-Thieno(Bis)Imide-Ended Materials. *Chem. Commun.* **2015**, *51*, 2033−2035.

(43) Melucci, M.; Durso, M.; Bettini, C.; Gazzano, M.; Maini, L.; Toffanin, S.; Cavallini, S.; Cavallini, M.; Gentili, D.; Biondo, V.; Generali, G.; Gallino, F.; Capelli, R.; Muccini, M. Structure-Property Relationships in Multifunctional Thieno(Bis) Imide-Based Semiconductors With Different Sized and Shaped N-Alkyl Ends. *J. Mater. Chem. C* **2014**, *2*, 3448−3456.

(44) Beverina, L.; Sassi, M. Twists and Turns Around a Square: The Many Faces of Squaraine Chemistry. *Synlett* **2014**, *25*, 477−490.

(45) Bousseksou, A.; Molnar, G.; Salmon, L.; Nicolazzi, W. Molecular Spin Crossover Phenomenon: Recent Achievements and Prospects. *Chem. Soc. Rev.* **2011**, *40*, 3313−3335.

(46) Gutlich, P.; Garcia, Y.; Goodwin, H. A. Spin Crossover Phenomena in Fe(II) Complexes. *Chem. Soc. Rev.* **2000**, *29*, 419−427.

(47) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. Quinonoid Metal Complexes: Toward Molecular Switches. *Acc. Chem. Res.* **2004**, *37*, 827−835.

(48) Costa, J. S.; Rodríguez-Jiménez, S.; Craig, G. A.; Barth, B.; Beavers, C. M.; Teat, S. J.; Aromí, G. Three-Way Crystal-to-Crystal Reversible Transformation and Controlled Spin Switching by a Nonporous Molecular Material. *J. Am. Chem. Soc.* **2014**, *136*, 3869−3874.

(49) Poneti, G.; Poggini, L.; Mannini, M.; Cortigiani, B.; Sorace, L.; Otero, E.; Sainctavit, P.; Magnani, A.; Sessoli, R.; Dei, A. Thermal and Optical Control of Electronic States in a Single Layer of Switchable Paramagnetic Molecules. *Chem. Sci.* **2015**, *6*, 2268−2274.

(50) Breuning, E.; Ruben, M.; Lehn, J. M.; Renz, F.; Garcia, Y.; Ksenofontov, V.; Gutlich, P.; Wegelius, E.; Rissanen, K. Spin Crossover in a Supramolecular Fe-4(II) [2 × 2] Grid Triggered by Temperature, Pressure, and Light. *Angew. Chem., Int. Ed.* **2000**, *39*, 2504−2507.

(51) Sato, O. Optically Switchable Molecular Solids: Photoinduced Spin-Crossover, Photochromism, and Photoinduced Magnetization. *Acc. Chem. Res.* **2003**, *36*, 692−700.

(52) Bonhommeau, S.; Guillon, T.; Lawson Daku, L. M.; Demont, P.; Sanchez Costa, J.; Letard, J. F.; Molnar, G.; Bousseksou, A. Photoswitching of the Dielectric Constant of the Spin-Crossover Complex [Fe(L)(CN)(2)] Center Dot H_2O. *Angew. Chem., Int. Ed.* **2006**, *45*, 1625−1629.

(53) Bousseksou, A.; Molnar, G.; Demont, P.; Menegotto, J. Observation of a Thermal Hysteresis Loop in the Dielectric Constant of Spin Crossover Complexes: Towards Molecular Memory Devices. *J. Mater. Chem.* **2003**, *13*, 2069−2071.

(54) Varret, F.; Boukheddaden, K.; Codjovi, E.; Goujon, A. Molecular Switchable Solids: Towards Photo-Controlled Magnetism. *Hyperfine Interact.* **2007**, *165*, 37−47.

(55) Kahn, O.; Martinez, C. J. Spin-Transition Polymers: From Molecular Materials Toward Memory Devices. *Science* **1998**, *279*, 44−48.

(56) Cavallini, M.; Bergenti, I.; Milita, S.; Kengne, J. C.; Gentili, D.; Ruani, G.; Salitros, I.; Meded, V.; Ruben, M. Thin Deposits and Patterning of Room-Temperature-Switchable One-Dimensional Spin-Crossover Compounds. *Langmuir* **2011**, *27*, 4076−4081.

(57) Cavallini, M. Status and Perspectives in Thin Films and Patterning of Spin Crossover Compounds. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11867−11876.

(58) Shepherd, H. J.; Gural'skiy, I. y. A.; Quintero, C. M.; Tricard, S.; Salmon, L.; Molnár, G.; Bousseksou, A. Molecular Actuators Driven by Cooperative Spin-State Switching. *Nat. Commun.* **2013**, *4*, 2607.

(59) Akou, A.; Gural'skiy, I. A.; Salmon, L.; Bartual-Murgui, C.; Thibault, C.; Vieu, C.; Molnar, G.; Bousseksou, A. Soft Lithographic Patterning of Spin Crossover Complexes. Part 2: Stimuli-Responsive Diffraction Grating Properties. *J. Mater. Chem.* **2012**, *22*, 3752−3757.

(60) Akou, A.; Bartual-Murgui, C.; Abdul-Kader, K.; Lopes, M.; Molnar, G.; Thibault, C.; Vieu, C.; Salmon, L.; Bousseksou, A. Photonic Gratings of the Metal-Organic Framework {Fe(Bpac)[Pt-$(CN)_4$]} with Synergetic Spin Transition and Host-Guest Properties. *Dalton Trans.* **2013**, *42*, 16021−16028.

(61) Lei, T.; Wang, J.-Y.; Pei, J. Roles of Flexible Chains in Organic Semiconducting Materials. *Chem. Mater.* **2014**, *26*, 594−603.

(62) Mei, J.; Bao, Z. Side Chain Engineering in Solution-Processable Conjugated Polymers. *Chem. Mater.* **2014**, *26*, 604−615.

(63) Durso, M.; Bettini, C.; Zanelli, A.; Gazzano, M.; Lobello, M. G.; De Angelis, F.; Biondo, V.; Gentili, D.; Capelli, R.; Cavallini, M.; Toffanin, S.; Muccini, M.; Melucci, M. Synthesis, Size-Dependent Optoelectronic and Charge Transport Properties of Thieno(Bis)Imide End-Substituted Molecular Semiconductors. *Org. Electron.* **2013**, *14*, 3089−3097.

(64) Surin, M.; Sonar, P.; Grimsdale, A. C.; Mullen, K.; De Feyter, S.; Habuchi, S.; Sarzi, S.; Braeken, E.; Van Heyen, A.; Van der Auweraer, M.; De Schryver, F. C.; Cavallini, M.; Moulin, J. F.; Biscarini, F.; Femoni, C.; Lazzaroni, R.; Leclere, P. Solid-State Assemblies and Optical Properties of Conjugated Oligomers Combining Fluorene and Thiophene Units. *J. Mater. Chem.* **2007**, *17*, 728−735.