

Phase Patterning of Poly(oxime-ester) for Information Encryption by Photo-induced Isomerization

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 Electronic Supplementary Information

Abstract Crystal polymers or liquid crystal elastomers undergo a phase transition that results in a change in the corresponding optical properties, which has the potential to be applied in areas such as information encryption and anti-counterfeiting. The utilization of these materials for patterning purposes requires different phase transition temperatures. However, once prepared, altering the phase transition temperature of them presents significant challenges. Herein, a poly(oxime-ester) (POE) network is developed to achieve high-resolution and multilevel patterning by photo-induced isomerization. The as-prepared POE exhibits the ability to transition from an opaque state to a transparent state under temperature stimuli, with the transition temperature and kinetics dependent on UV light exposure time. Thus, complex patterns and information can be encrypted through different selective regional exposure time and decrypted under specific temperature or cooling time. Furthermore, we illustrate an example of temporal communication, where cooling time or temperature serves as the encoded information. This research expands the application scope of advanced encryption materials, showcasing the potential of POE in dynamic information encryption and decryption processes.

Keywords Poly(oxime-ester); Isomerization; Phase patterning; Information encryption

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INTRODUCTION

Stimulus-responsive materials as a branch of smart materials are able to change their properties adapt changes in the surrounding environment, a phenomenon observed in many living creatures.^[1,2] When subjected to stimuli such as light, heat, pH, and humidity changes, certain optical properties undergo changes including color, transparency, or grayscale. By leveraging this property, stimuli-responsive materials can be utilized for encrypted transmission of information and anti-counterfeiting. In recent years, various types of advanced anti-counterfeiting materials and information encryption technologies have been developed including structure-color materials,^[3–9] fluorescent ink,^[10–13] 3D codes,^[14–17] holographic anti-counterfeiting graphic,^[18–22] and self-erasing materials,^[23–25] which are designed to protect against the risk of leakage of information that may occur during transmission. However, the preparation of such materials typically requires the design of different smart-responsive molecular structures, which are then assembled into polymer matrix or gel in order to realize multiple encrypted forms of

information. This increases the complexity of the preparation and decryption process. Therefore, the development of a straightforward and simple procedure for local phase patterning on a single material still remains challenge.

Polymers featuring ordered phase structures, such as crystalline or liquid mesogens, offer a means to control material opacity *via* phase transitions since ordered phases scatter light, while disordered phases allow transmission.^[26–28] Phase transition temperature T_{trans} is the critical temperature at which the molecular chain segments or liquid crystal mesogens of such materials move from a disordered state to an ordered state. At a given temperature, if T_{trans} is higher than this temperature, some parts of the material are in a disordered state, allowing light to be transmitted through and appear transparent. Conversely, some parts are lower than this temperature, and these parts are in an ordered state, resulting in light being scattered and appearing opaque. This enables the same material to exhibit a pattern due to the difference in transparency. Consequently, the ability to tune T_{trans} of a polymer matrix represents a crucial technique for the development of advanced information encryption materials. Xie *et al.* prepared a phase transition material by modulating the light exposure time in different regions of the photo-curing process and successfully employed it as a time-dependent information encryption.^[29] Ko *et al.* employed a laser-induced dy-

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namic cross-linking technique, introducing allyl sulfide groups to liquid crystal elastomers to enable reconfiguration into desired phases or complex patterns for temporary information encryption at body temperature.^[30] Nevertheless, the strategy based on tunable T_{trans} on a single material for information encryption remains a challenging task. This is due to the fact that the T_{trans} is already determined during the material forming process, and dynamic groups with stimulus-response must be introduced into them to achieve tunable T_{trans} . In our previous study, we explored the dynamic exchange reaction of poly(oxime-ester) under thermal stimulation.^[31] However, we also noted isomerization of oxime ester bonds under UV light.^[32,33] To the best of our knowledge, this property has not been investigated for the development of polymeric materials with tunable T_{trans} .

Here, we introduce a straightforward method for fabricating information encryption materials based on a POE network with a programmable crystallization temperature T_c induced by UV light. By adjusting the ratio of cis- and trans-structures within the POE via UV light exposure, we achieve programmable T_c . The POE possessing a trans-structure exhibits a symmetric molecular configuration, promoting tight stacking of molecular chains into the crystal lattice, resulting in faster crystallization kinetics and a higher crystallization temperature. Conversely, the cis-structure enhances intermolecular forces and disrupts regular arrangement, leading to slower crystallization and a lower crystallization temperature. Under UV light exposure, the lower-energy trans structure can undergo partial conversion to the higher-energy cis structure. By modulating UV light intensity and exposure time, we can adjust the cis-trans isomerization ratio within the poly(oxime-ester), thereby regulating crystallization temperature and kinetics. This approach enables the creation of high-resolution, multiple pattern displays on poly(oxime-ester) films and facilitates the successful encryption of time- or temperature-dependent information on the single material using photomasks with a photo-patterning technique.

EXPERIMENTAL

Materials

The dithiol chain extenders 1,10-decanedithiol (97%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., the crosslinker pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, 95%) and the photo initiator 2,2-bimethoxy-2-phenylacetophenone (DMPA, 98%) were purchased from Energy Chemical. Dichloromethane (DCM, AR) was obtained from Guangdong Guanghua Sci-Tech Co., Ltd. All reagents were used as received without further purification.

Synthesis of POE Films

To synthesize POE films, oxime ester (1.00 g, 1.82 mmol), 1,10-decanedithiol (0.2257 g, 1.09 mmol), and tetra-functional thiol crosslinker PETMP (0.1781 g, 0.36 mmol) were dissolved into 2 mL of dichloromethane (DCM), and then, DMPA (1 wt%) was added as a photo initiator. Oxime ester and thiol groups were equimolar to create well-defined POE networks. The solution was stirred under UV light (365 nm, 20 W) for 30 s. Then the mixtures were placed between two glass plates separated by a silicone rubber spacer (thickness: 0.5 mm). The mixture was then

irradiated under UV light (365 nm, 20 W) for 1 min each side. After photo-polymerization, the obtained POE films were dried at 80 °C for 1 h.

Preparation of POE Films with Different Patterns

LCE film was covered with a photomask printed with different patterns on PET by a printer, and then exposed under UV light at 40 °C for different time according to the requirement.

Material Characterization

¹H-NMR spectra were recorded on a Bruker Avance 400MHz spectrometer at room temperature with CDCl₃ as a solvent. The Fourier transform infrared spectroscopy of reactants and was tested by a Nicolet-iS50 FT-IR Spectrometer. Wavelengths were scanned from 4000 cm⁻¹ to 550 cm⁻¹. Optical transmittance in the visible range (400–800 nm) was measured by SHIMADZU UV-2700 Spectrometer. Differential scanning calorimetry (DSC) tests were performed on SHIMADZU DSC-60Plus, samples were heated from room temperature to 50 °C, then cooled to -20 °C at a rate of 5 °C/min and isothermal at -20 °C for 5 min, followed by a heating scan at the same rate up to 50 °C. X-ray diffraction experiments were carried out with a Bruker D8 Advance instrument with the scanning rate was set as 3 (°)/min.

RESULTS AND DISCUSSION

Poly(oxime-ester) (POE) films were prepared by initiating polymerization of a solution containing an oxime ester (synthesis detail can be found in the electronic supplementary information, ESI), a chain extender, and a cross-linking agent (Fig. 1a), followed by solvent evaporation at 80 °C for 1 h. The FTIR and gel fraction results indicate that the double bonds and thiols have undergone a complete reaction to form a full cross-linked network. (Fig. S4 and Table S1 in ESI) We used decanedithiol here as the chain extender, which promotes crystallization more effectively. The resulting POE films were opaque at room temperature (25 °C) due to crystallization and became highly transparent when heated above the melting point (Fig. 1b). The simplicity of controlling the polymer's chemical structure with light and precise spatial-temporal control allows POE films to be patterned in a pixelated manner. Specifically, POE is selectively exposed to UV light above the melting temperature in specific regions. In the unexposed regions, the configuration of molecular chain remains unchanged, and the crystallization temperature and kinetics are unaffected. In contrast, in the exposed regions, the configuration of molecular chain partially changes from *trans* to *cis*, leading to a decrease in crystallization temperature and slower crystallization kinetics (Fig. 1c). Upon cooling (to 20 °C unless otherwise noted), different regions exhibit distinct crystallization behaviors. In the melt state, molecular chains are disordered and do not present patterned information. As the temperature decreases, regions unexposed to UV light crystallize first due to their higher crystallization temperature, reaching a point where patterned information is fully revealed. Subsequently, as the temperature further decreases, regions exposed to UV light begin to crystallize, hiding the previously patterned information due to reduced contrast. Therefore, this material exhibits temperature- or time-dependent characteristics in information encryption, wherein correct information is displayed only at specific temperatures or time.

Fig. 1(d) illustrates the encryption-decryption process of

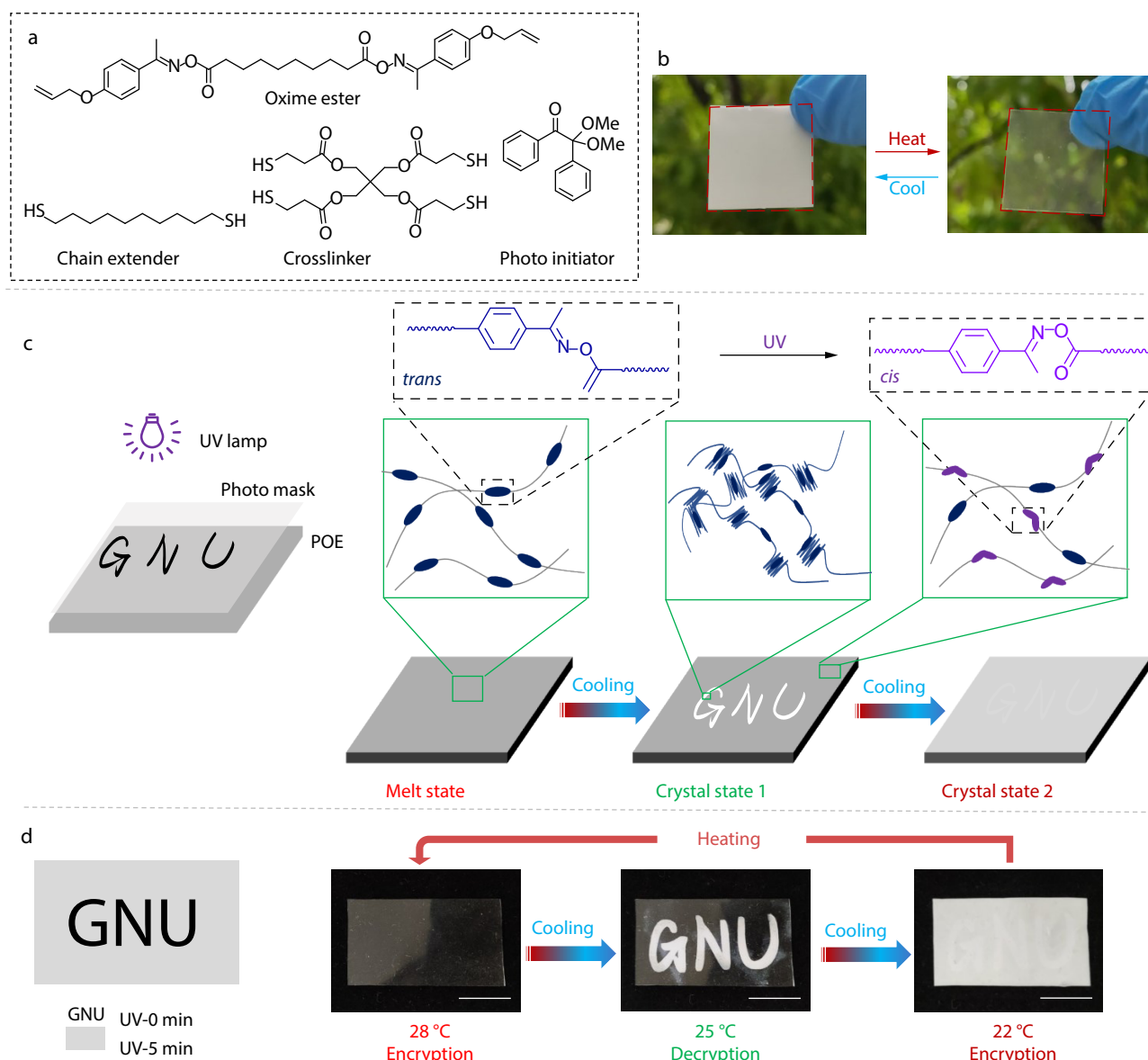


Fig. 1 (a) Composition of the chemical structure of POE; (b) Reversible optical properties of POE; (c) UV-induced patterning and its encryption process; (d) Photos of patterned POE film at different cooling temperatures. Scale bar: 1 cm.

POE as an information encryption material as described above. A POE film with a pattern of the letters "GNU" was prepared by exposing the corresponding patterned photomask to UV light (1 mW/cm^2) for 5 min at 40°C . Above the crystallization temperature (28°C), the film remains transparent and unreadable (encrypted state). However, upon cooling, the region not exposed to UV (region of the "GNU" letters) begin to crystallize and turn opaque. By 25°C , the pattern with the "GNU" letters becomes fully visible and readable (decrypted state). As the temperature continues to decrease, the UV exposed areas start to crystallize, leading to reduced contrast between the two regions. At 22°C , the "GNU" letters become unreadable (encrypted state) due to the diminished contrast. This evolution of information display is fully reversible by heating the POE film to a melt state at 40°C , resetting the process for re-encryption.

Fig. 2(a) demonstrates the controllable nature of the crystallization temperature of POE by varying the intensity of UV light and exposure time, thereby influencing transparency. For example, after irradiation with UV light at an intensity of 5 mW/cm^2 for 5 min, the material is transparent at 25°C . However, as the temperature drops to 22°C , some parts begin to crystallize, resulting in increased opacity. Based on experimental results, it can be qualitatively inferred that the crystallization temperature decreases with longer UV illumination time and higher intensities. To further investigate this phenomenon, a series of POE films with different crystallization temperatures was prepared by maintaining a fixed light intensity of 5 mW/cm^2 and exposing the films to UV light for varying durations (0, 2, 5 and 10 min). Fig. 2(b) illustrates the variation in light transmittance of these samples with temperature following different exposure time (more detail in Fig. S5

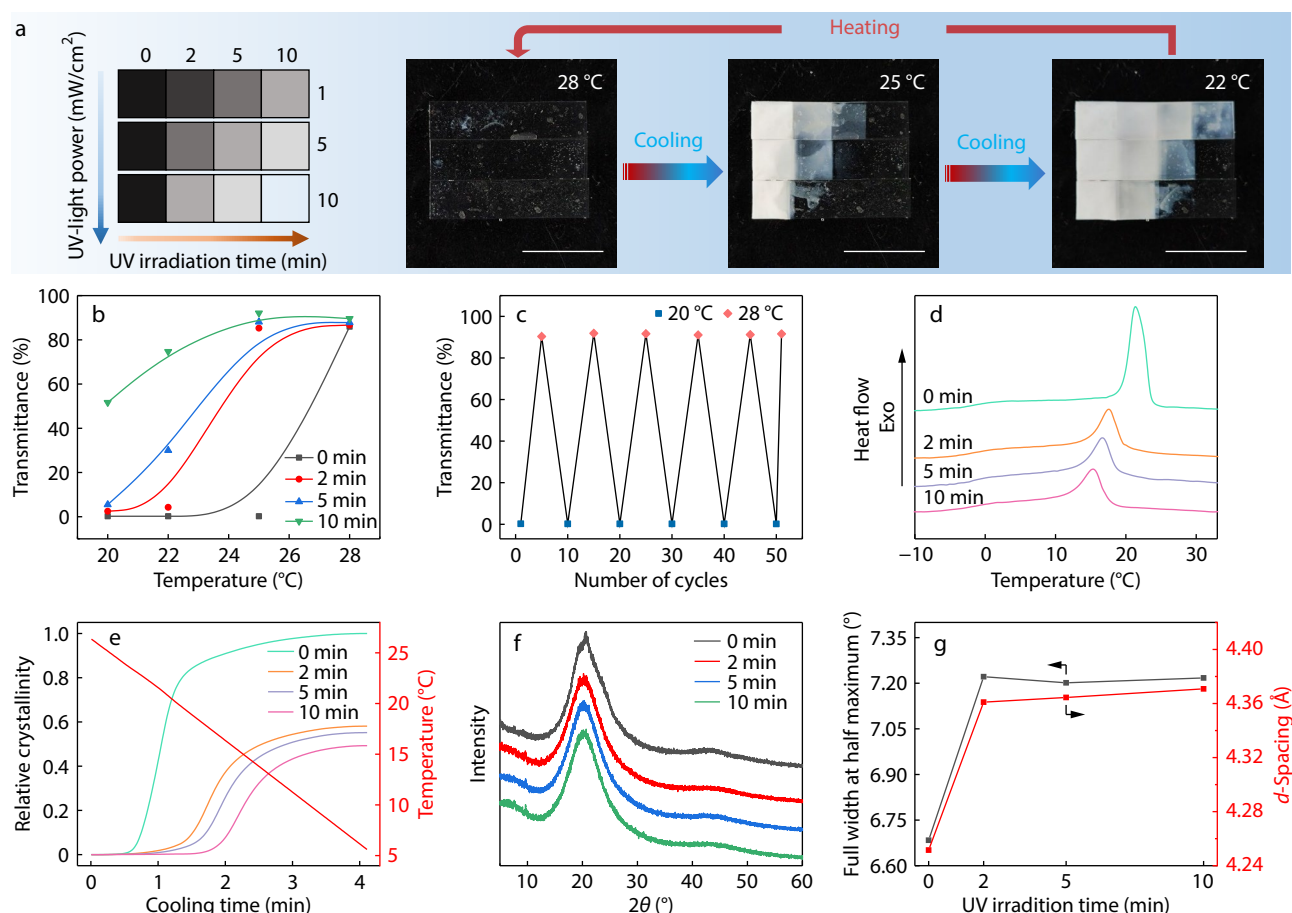


Fig. 2 (a) Images of POEs subjected to the different UV light parameters at different temperatures. Scale bars, 10 mm. (b) Visible light transmittance varies with cooling temperature; (c) Cyclic stability of the reversible optical property changes between 20–28 °C; (d) Differential scanning calorimetry (DSC) crystallization curves; (e) Evolution of the relative crystallinity for POEs under different UV exposure time. (Cooling rate of 5 °C/min). (f) XRD patterns for POEs; (g) FWHM and *d*-spacing varies with UV irradiation time.

in ESI). Initially, all samples exhibited approximately 85% transmittance at 28 °C. However, the decreasing trend in transmittance with temperature was non-uniform, with the rate of decline gradually slowing down with increasing light exposure time compared to the unexposed samples. Additionally, the temperature at which transmittance reached approximately 0% decreased with longer exposure time. For instance, the unexposed sample reached 25 °C, while the 2-min and 5-min exposed samples reached 22 and 20 °C, respectively. These results are consistent with the phenomenon depicted in Fig. 1(c). Moreover, the cyclic stability of the reversible optical property changes of this material was investigated. As shown in Fig. 2(c), when the temperature was varied between 20 and 28 °C, the transmittance exhibited a range of 0% to 85% and remained stable after 50 cycles.

Fig. 2(d) presents the differential scanning calorimetry (DSC) curves of POE exposed under UV light for various durations during the cooling process. The as-prepared POE exhibits a maximum exothermic peak at 21.4 °C. As the UV exposed time increases from 2 min to 10 min, the crystallization temperature decreases from 17.5 °C to 15.5 °C, accompanied by a corresponding decrease in the enthalpy of crystallization (area of the crystallization peak). Fig. 2(e) illustrates the relative crystallinity of the samples during cooling, with the total

cumulative enthalpy of the un-exposed samples used as a normalized baseline. The exposed samples exhibit a notable decrease in relative crystallinity, with longer exposure times resulting in lower crystallinity. This is attributed to the partial transformation of crystalline POE into the amorphous state, confirmed by X-ray diffraction (XRD) results shown in Fig. 2(f). In comparison to the un-exposed sample, the full width at half maximum (FWHM) of the diffraction peaks and the crystal spacing (*d*-spacing), depicted in Fig. 2(g), increase for the exposed sample, indicating reduced crystallinity. In order to ascertain the nature of the reaction occurring in this system for the oxime ester, the gel fraction of the un-exposed sample and the sample exposed for different times was measured, respectively. The results demonstrated that the gel fraction did not have significantly drop (Table S4 in ESI), indicating that the oxime ester undergoes an isomerization reaction instead of a cleavage reaction in this system.

Based on the results discussed above, we achieved patterning from microscopic to macroscopic scales on POE film. The patterns obtained at 25 °C under UV exposure using copper mesh with different mesh sizes as photomasks (at an intensity of 5 mW/cm² for 5 min) are shown in Fig. 3(a). Even with a 400-mesh copper mesh, the boundaries and pores are clearly defined, demonstrating pattern resolution on the order of

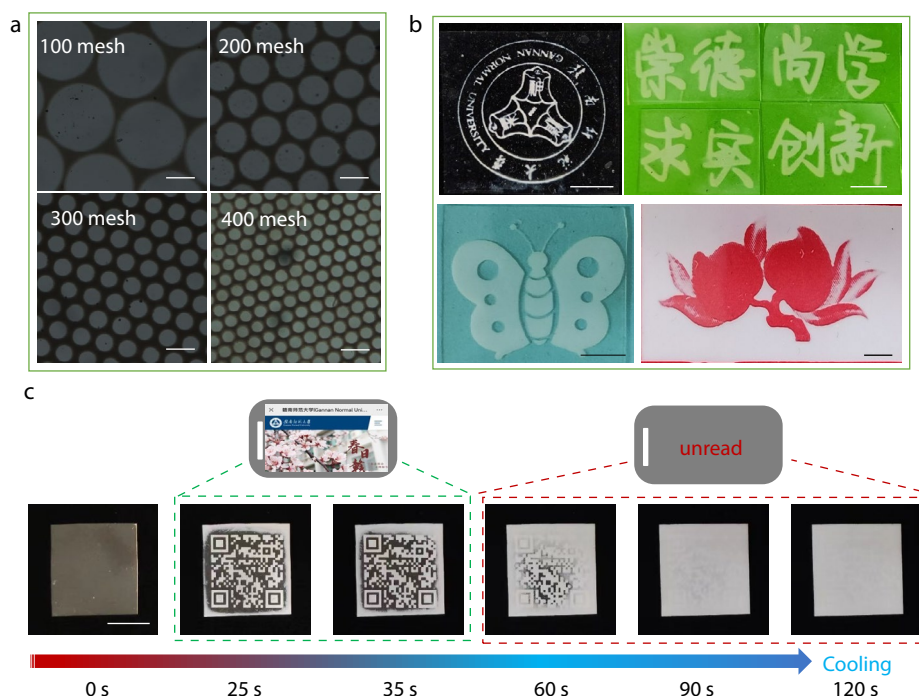


Fig. 3 (a) Microscopic patterns formed by copper mesh. Scale bar: 100 μm . (b) Diverse optical patterns with colored backgrounds. All scale bars are 0.5 cm. (c) Temporally programmed optical QR codes, with the green rectangular background indicating the readable ranges. Scale bar: 1 cm.

tens of micrometers. We anticipate that the resolution of patterns obtained using this method could be further improved depending on the smaller size photomask. Similarly, we printed a series of differently patterned photomasks, resulting in high-contrast images on the POE film (Fig. 3b). These results lay the foundation for developing programmable temporal encryption devices, exemplified in Fig. 3(c). We prepared a POE film containing a QR code pattern ($1 \text{ mW}/\text{cm}^2$ for 5 min). The film was transparent at high temperatures (40°C), making the QR code pattern unreadable. As the film cooling down, at around 25 s, the un-exposed regions began to crystallize, becoming opaque, while the exposed background remained amorphous and transparent, allowing complete reading of the QR code information. By 35 s of cooling, the exposed regions also started to crystallize, reducing the contrast between the two regions and causing the QR code pattern to blur, making it impossible to read any information from the QR code. It should be noted that the duration time to reveal information depends on the rate of cooling, as well as the difference in exposure time between the pattern and the background. Since the crystallization temperature of our material is lower than human body temperature, the information can be concealed by applying the POE film to human skin, and the information can be read again in a cooler environment. (Fig. S6 in ESI) Thus, this approach enables transient information encryption using human body temperature.

Among most 3D coded materials, color change is commonly used for anti-counterfeiting or information encryption. In this system, although there is no color change, we achieve a change in transparency. We encode the opaque state as 1 and the transparent state as 0. The encoded information is then determined by analyzing the difference between the

transparent and opaque states at different temperatures, as illustrated in Fig. 4(a). At high temperatures, all cubes are transparent, which indicates an incorrect display of the coded information. As the temperature decreases to 25°C , the un-exposed cubes begin to crystallize and become opaque, revealing the correct coded information. Further cooling causes the cubes that were exposed for 5 and 10 min to also crystallize, thus overwriting the correct coded information with incorrect data. Therefore, obtaining the correct coded information requires knowing the correct temperature. As described previously, this process is reversible. By rearranging the positions of the cubes, a different set of coded messages can be obtained, providing versatility and adaptability in the encryption process.

Exposing a specific pattern at multiple levels under UV light provides a more complex depiction of information evolution over time. By exposing different segments of the digit "8" to UV light for varying durations, as illustrated in Fig. S7 (in ESI), the displayed pattern transitions from "1" to "4," then "9," and ultimately returns to "8" as the cooling time changes. This approach enables the design of a sequence of digits, each undergoing a unique evolution process with respect to cooling time. In Fig. 4(b), after multi-layer UV light exposure, the number information is inscribed into the POE material. As the cooling time extends, the numerical sequence transitions from "7415" to "3906," eventually stabilizing at "8888." This demonstrates that different digital information emerges at distinct cooling time intervals. By encoding both the number and time, a series of distinct four-digit combinations can be generated based on the time and location of the number. Fig. 4(c) illustrates the specific evolution of digital information over time. Thus, many complex messages can be conveyed through this type of temporal communication.

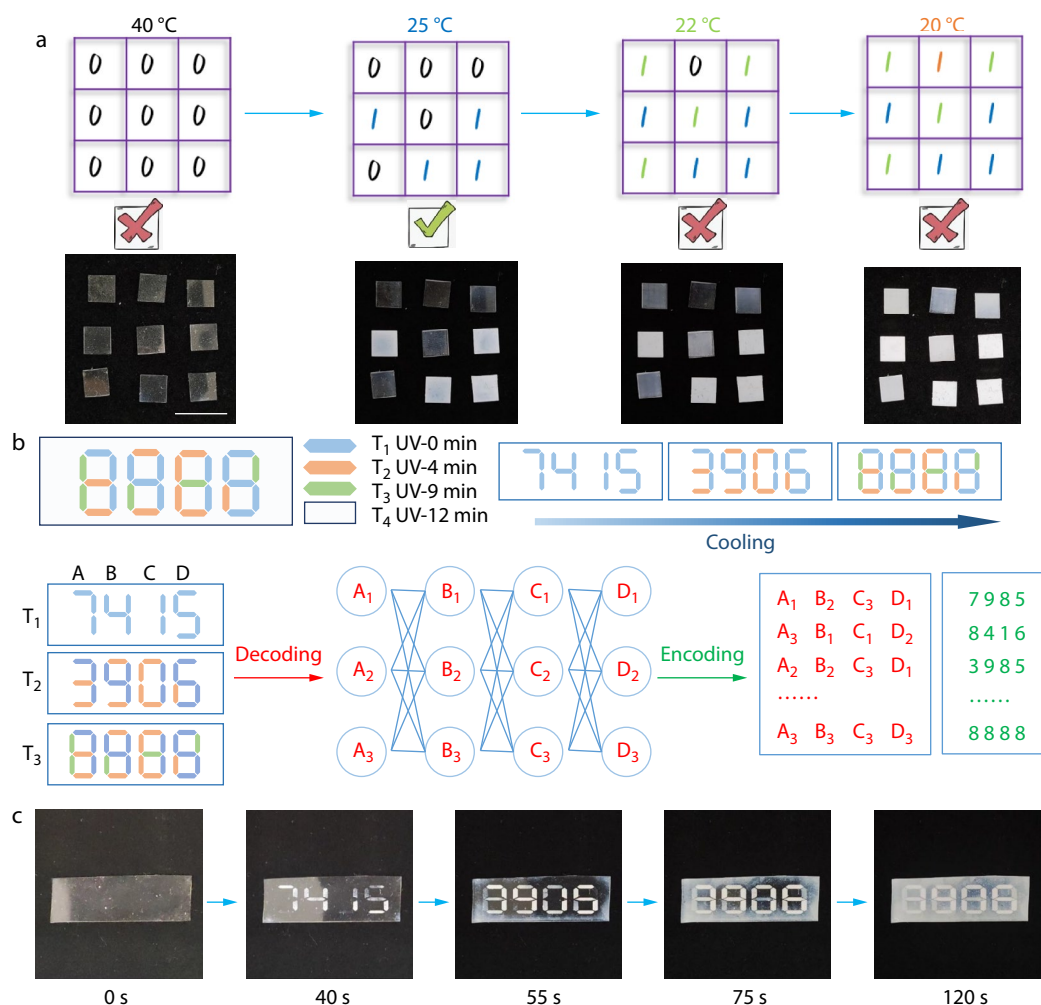


Fig. 4 (a) 3D codes for information decryption at specific temperature; (b) Illustration of the process of encoding complex messages. (c) Images of POE to show specific evolution of digital information over time. All scale bar is 1 cm.

CONCLUSIONS

This study introduces a straightforward approach to patterning using POE, leveraging UV-induced molecular isomerization. The optical properties of crystallized POE can be reversibly altered from transparent to opaque, depending on the melting and crystallization of the material. UV-induced isomerization changes the molecular structure, thereby tune the crystallization temperature and relative crystallinity, which in turn modifies the material's optical properties through selective exposure to UV light. By employing this strategy, the study demonstrates the creation of multi-information encrypted materials and spatio-temporal communication of complex information based on temperature or cooling time responses. This research opens new pathways for the development of responsive and smart materials, expanding the scope of materials used for information storage, encryption, and communication.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-024-3183-8>.

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