Thermochromic Circularly Polarized Luminescence via Chiral AIEgen-loaded Microcapsules for Adaptive Camouflage and Security

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Stimuli-responsive circularly polarized luminescence (CPL) materials show great promise for dynamic camouflage, information encryption, and smart sensing. However, synthesis complexity and limited practical versatility hinder current research. This study demonstrates novel thermochromic CPL microcapsules (MCs) that contain chiral aggregation-induced emission luminogens (AIEgens) doped alkane phase change materials (PCMs). The synthesized AIEgens, characterized by a high photoluminescence quantum yield of 73.3% and obvious chiroptical properties, were successfully incorporated into PCMs to form thermochromic CPL

materials. Microencapsulation of the AIEgen-doped PCMs effectively addressed practical concerns of leakage and corrosion, yielding stable and thermally reliable MCs. These MCs exhibited versatility across diverse polymeric matrices and substrate surfaces, highlighting their adaptability. Leveraging the thermochromic CPL properties, 2D and 3D information encryption systems based on MC-embedded coatings were developed, ensuring high-level data security. Furthermore, their application in high-end camouflage effectively adapted military vehicle coatings to diverse environmental terrains, improving stealth and survivability. The easy scalable fabrication and multifunctionality of these thermochromic CPL MC-embedded coatings hold transformative potential for security and defense applications, offering innovative solutions for protecting sensitive information and concealing military assets.

1. Introduction

Circularly polarized luminescence (CPL), characterized by the differential emission of leftand right-handed circularly polarized light, emerges as a macroscopic expression of chiral molecular properties.^[1] It enriches the optical information content and opens up avenues for sophisticated applications in 3D displays, optoelectronic devices, chiroptical sensing, secure communications, and high-end camouflage systems.^[2–4] Therefore, scientists and engineers have devoted tremendous efforts to creating a wide variety of CPL materials by mimicking the distinctive chirality of natural matters, encompassing metal complexes^[5], organic compounds^[6], synthetic polymers^[4], supramolecular assemblies^[7], and chiral liquid crystalline materials^[8]. Among them, stimuli-responsive CPL materials, have attracted considerable interest due to their potential in intelligent displays, smart sensors, and adaptive camouflage systems.^[9]

The development of a CPL system that exhibits a controlled and predictable response to external stimuli remains a formidable challenge for synthetic chemists. A primary hurdle in the creation of intelligent CPL materials is the precise and accurate functional control over molecular integration. Despite several stimuli-responsive luminescent materials have demonstrated substantial structural and photoemission property alterations in response to external stimuli such as light^[10], temperature^[11], pH^[12], solvent^[13], and electricity^[14], significant challenges persist. One such challenge is the propensity for luminescent materials to aggregate in the solid state, which can lead to luminescence quenching.^[15] Nevertheless, the fabrication of highly sensitive stimuli-responsive CPL aggregates in solid-state forms is deemed highly advantageous for the development of practical smart devices and luminescent sensors. In this regard, luminogens with aggregation-induced emission (AIE) characteristics have emerged as a promising solution. These AIE luminogens (AIEgens) are distinguished by their robust

luminescence in the aggregated state, contrasting with their negligible emission in a monodispersed solution.^[16–18] As a result, AIEgens are considered to be one of the optimal candidates for the development of intelligent luminescent materials suitable for real-life applications, thereby stimulating considerable interest in the advancement of smart CPL materials design.

Compared to other stimuli-responsive CPL systems, temperature is a universally applicable and easily controlled parameter, allowing for the direct modulation of CPL properties without the need for complex external setups. Furthermore, temperature can passively influence CPL properties, offering a distinct advantage in scenarios where dynamic changes are desired without continuous energy input or active control. The current strategies for constructing thermo-responsive CPL systems have primarily focused on the chiral self-assemblies, including chiral molecules^[19,20], liquid crystals^[11,21–23], and metal complexes^[24]. These self-assemblies can undergo structural changes in response to temperature variations, thereby altering their chiroptical properties. Additional strategies have involved the design and synthesis of temperature-sensitive chiral molecules^[25], helical polymers^[26], hydrogel^[27], and chiral macrocycles^[28] that are covalently linked with emitters. However, the successful implementation of thermo-responsive CPL characteristics in materials is limited, and existing examples often necessitate precise design and complex synthesis, which can be lacking in versatility. There is, therefore, a significant need for the development of a robust and versatile method for preparing temperature-adaptable CPL materials.

Phase change materials (PCMs), such as paraffin and fatty acids, are a class of substances that exhibit physical phase transitions in response to temperature fluctuations. Their commercial availability, cost-effectiveness, and diversity have made them invaluable in a wide range of applications.^[29] Thereby, in this study, we propose the development of a novel thermoresponsive CPL material by integrating chiral AIEgens into PCMs. Furthermore, the chiral AIEgen-doped PCMs will be encapsulated into microcapsules to address issues of leakage and corrosion. The integration of such thermo-responsive CPL microcapsules into polymer matrices could enable coatings with various high-end applications, including temperature monitoring, information decryption, and advanced camouflage technologies. In particular, the application demo in advanced camouflage technologies showcased their ability to adapt to different environmental terrains for dynamic camouflage of military vehicles.

2. Results and Discussion

2.1. Synthesis, Photophysical, and Chiroptical Properties of Chiral AIEgens

The chiral AIEgens, (*S*, *R*)-BBT2TPA were successfully prepared according to the routes outlined in Figure 1a and S1. Comprehensive structural confirmation of the molecules was achieved through ¹H NMR, ¹³C NMR, and mass spectra (Figure S2-13). The photophysical properties of (*S*, *R*)-BBT2TPA in the solid state were initially investigated, revealing fluorescence emission at 600 nm with nanosecond-scale lifetimes (5.2 ns for (*S*)-BBT2TPA and 3.96 ns for (*R*)-BBT2TPA) and high photoluminescence quantum yields (PLQY) approaching 73.3% for (*S*)-BBT2TPA and 72.0% for (*R*)-BBT2TPA (Figure S14-15). It is well-documented that molecules with donor-acceptor-donor (D-A-D) structures exhibit solvent polarity-dependent photophysical changes, known as the twisted intramolecular charge transfer (TICT) effect. Despite minimal changes in the absorption spectra of (*S*, *R*)-BBT2TPA across various solvents (Figure S16), a pronounced red-shift in the photoluminescence wavelength was observed with increasing solvent polarity (Figure 1b and S17).

The photoluminescence (PL) spectra of (*S*, *R*)-BBT2TPA were measured in tetrahydrofuran (THF)-water mixtures with varying water fractions (f_w). The PL intensity of (*S*, *R*)-BBT2TPA in THF solution initially decreased but subsequently increased with the addition of water as the poor solvent, indicative of the typical AIE characteristics of these enantiomers (Figure 1c,1d, and S18). Furthermore, the PL maximum wavelength of (*S*, *R*)-BBT2TPA in hexane exhibited a significant red shift from 540 nm in the solution state to 569 nm in the aggregated state due to precipitation (Figure 1e and S19). This observation prompted us to explore the photophysical properties of (*S*, *R*)-BBT2TPA in non-polar matrices, such as alkane PCMs.

The chiroptical properties of the enantiomeric compounds were examined using circular dichroism (CD) and CPL spectra. As shown in Figure S20, (*S*, *R*)-BBT2TPA displayed strong CD signals at room temperature, with their CD spectra exhibiting a characteristic mirror-image relationship and alternating positive and negative Cotton effects from 200 to 500 nm, correlating well with the absorption bands in dilute acetonitrile solution. This behavior can be ascribed to intrinsic π - π * and n- π * electronic transitions and the intramolecular charge transfer (ICT) from triphenylamine (TPA) to benzothiadiazole. The CPL spectra of (*S*, *R*)-BBT2TPA in solutions showed barely visible signals (Figure 1f and S21), but a typical mirror-image CPL profile was observed for their film state with luminescence dissymmetry factors ($|g_{lum}|$) of approximately 3.8×10^{-3} and -2.4×10^{-3} (Figure 1g). These findings confirm that the enantiomers exhibit chirality in both the ground and singlet excited states, attributable to the intrinsic axial chiral structure of the binaphthol unit. Moreover, it shows significant aggregation-induced CPL (AICPL) properties because of excellent aggregate-state luminescence.

The X-ray crystallographic analysis shows that (*R*)-BBT2TPA adopts homochiral helical orientations (Table S1). As illustrated in Figure 1h, the dihedral angle between the two naphthalene rings is 52.2°. In the crystal packing structure, π - π interaction and other intermolecular interactions can largely prevent the nonradiative decay process caused by intramolecular rotation. This can also explain why chiral enantiomers exhibit AIE and AICPL properties.

To gain a theoretical understanding of the solvent effects and chiroptical properties of (*S*, *R*)-BBT2TPA, the density functional theory (DFT) and TD-DFT calculations were performed using the Gaussian 16 package. In Figure S22, the highest occupied molecular orbital (HOMO) is spreading over the triphenylamine (TPA) and benzothiadiazole moiety, and the lowest unoccupied molecular orbital (LUMO) is mostly localized on the benzothiadiazole moiety. HOMO and LUMO distributions demonstrated that the S₀–S₁ transition was attributed to a hybridized local and charge-transfer (HLCT)-type transition between the donor and the acceptor segments, which was further confirmed by natural transition orbital (NTO) analysis (Figure S23). To deduce the theoretical g_{lum} values, electronic transition moment (μ), magnetic transition moment (m), and angles (θ) between m and μ for their ground states and excited state are shown in Figure S24. Due to almost perpendicular angles, the predicted values of g_{lum} are small at the molecular level. This corresponds to CPL spectra that are almost invisible in solution.



Figure 1. (a) Synthetic route of BBT2TPA. (b) Normalized PL spectra of (*S*)-BBT2TPA in different polar solvents: hexane, toluene, ethyl acetate (EA), tetrahydrofuran (THF), acetonitrile (ACN), and dimethylsulfoxide (DMSO). Insets are fluorescence images of (*S*)-BBT2TPA in different organic solvents taken under 365 nm UV light illumination. (c) PL spectra of (*S*)-BBT2TPA in THF/water mixtures with different water fractions (f_w). Insets are fluorescence images of (*S*)-BBT2TPA dissolved in THF/water mixtures with different water fractions (f_w) taken under 365 nm UV light illumination. (d) Plots of the relative maximum emission intensity (α_{AIE} , I/I₀) and maximum emission wavelength of (*S*)-BBT2TPA in THF/water mixtures as a function of water fraction. (e) Normalized PL spectra of (*S*)-BBT2TPA with different mass fractions in hexane solution. Insets are fluorescence images of (*S*)-BBT2TPA with different mass

mass fractions in hexane solutions taken under 365 nm UV light illumination. CPL spectra and DC spectra of (*S*, *R*)-BBT2TPA in (f) THF solution (10^{-5} M) and (g) film state upon excitation at 360 nm. (h) Single-crystal X-ray diffraction crystallographic packing units and structures of (*R*)-BBT2TPA.

2.2. Photophysical Properties of (S, R)-BBT2TPA-dopped Alkane PCM

Octadecane (OD) is a representative alkane PCM with a melting point of approximately 28 °C. In order to investigate the photophysical properties of (*S*, *R*)-BBT2TPA-doped PCM, OD was chosen as the matrix. In Figure 2, the samples with (*S*)-BBT2TPA concentration below 0.002 wt% did not exhibit any thermochromic effect. However, as the concentration of (*S*)-BBT2TPA increased, the emission color of the solid-state samples changed progressively from green to orange, with a maximum emission peak at 580 nm (Figure 2a, 2b, and S25-26). This shift suggests that (*S*)-BBT2TPA molecules tend to form self-aggregates in solid-state samples with higher concentrations due to the high crystallinity of OD (Figure S27).^[30,31]

A sample with a (*S*)-BBT2TPA fraction of 0.1 wt% was selected for further study. As shown in Figure 2c, the solid-state sample emitted orange fluorescence with a maximum emission wavelength (λ_{max}) of 580 nm at 20 °C, which shifted to green ($\lambda_{max} = 541$ nm) upon melting to a liquid state at 40 °C. During ten cycles of heating and cooling, a steady change in color between green and orange confirmed the excellent reversibility of its thermochromic properties (Figure 2d). Additionally, both the solid (*S*)-BBT2TPA-dopped OD (SOD) and (*R*)-BBT2TPAdopped OD (ROD) films that are prepared by grinding and pressing method exhibited distinct CPL signals (Figure 2e, 2f). Upon heating to a liquid state, no CPL signals were detected, indicating the AICPL and thermo-induced switching behavior of SOD and ROD.

A schematic representation of the thermochromic CPL mechanism for BBT2TPA-doped PCMs is depicted in Figure 2g based on the results mentioned above. Before heating (or during the cooling process), the alkane PCM molecules self-assemble into well-ordered crystals through van der Waals forces between their alkyl chains. This assembly causes the (*S*, *R*)-BBT2TPA molecules into a non-dispersed and aggregated state, leading to the CPL emission characteristic of these aggregates. Upon heating, the PCM changes to a liquid state, acting as a solvent for (*S*, *R*)-BBT2TPA and allowing for a dispersed chiral AIEgens state. Consequently, the emission color experiences a blue shift due to the monomer emission in the non-polar solvent environment. Furthermore, the dissolved (*S*, *R*)-BBT2TPA molecules show nearly invisible CPL signals. This mechanism provides a straightforward yet powerful way to impart



thermo-responsive characteristics to chiral AIEgens and to develop thermochromic CPL materials with variable transition temperatures by selecting appropriate PCMs.

Figure 2. (a) Fluorescence images and (b) maximum PL wavelength of (*S*)-BBT2TPA/OD (SOD) with different (*S*)-BBT2TPA fraction (f_s) at solid and liquid state taken under 365 nm UV light illumination. The scale bar indicates 10 mm. (c) Normalized PL spectra of SOD at 20 °C and 40 °C. (d) Maximum PL wavelength of SOD at 20 °C and 40 °C measured for ten cycles. CPL spectra and DC spectra of SOD and ROD at (e) solid state and (f) liquid state. (g) Schematic illustration describing the thermochromic fluorescence and CPL induced by reversible phase change.

2.3. Preparation and Characterization of Microcapsules containing BBT2TPA-doped PCM

To address the practical application challenges of PCMs, such as leakage and corrosion,^[32] microencapsulation was employed to fabricate stable double-layered poly(urea-formaldehyde) (PUF) microcapsules (MCs) with a BBT2TPA-doped PCM core. The process involved a two-

step method of urea-formaldehyde in situ polymerization^[33,34], as depicted in Figure 3a and detailed in the Experimental Section. The optical microscopy (OM) and scanning electron microscopy (SEM) images in Figure 3b-3d reveal that the synthesized SOD MCs are spherical with smooth outer surfaces and exhibit good morphology uniformity. The average diameter of the MCs was determined to be $82 \pm 12 \mu m$ (Figure S28), and their core-shell structure is distinctly observable in Figure 3e. Thermogravimetric analysis (TGA) demonstrated that the microencapsulated SOD displayed enhanced thermal stability compared to non-encapsulated samples, ascribed to the protective double-layer PUF/PUF shells (Figure S29). Differential scanning calorimetry (DSC) was utilized to analyze the melting and crystallization behavior of SOD and SOD MCs, indicating similar phase change characteristics with a melting temperature of approximately 28 °C (Figure 3f). The latent heats (ΔH_m) for SOD and SOD MCs were measured as 226.6 J/g and 203.7 J/g, respectively. Employing Equation (1)^[35], the core fraction of SOD MCs was calculated to be approximately 89.9 wt%, reflecting the high efficiency of the microencapsulation process.

$$\Delta H_{\rm m, \ SOD \ MCs} = \Delta H_{\rm m, \ SOD} \times \omega \tag{1}$$

Here, $\Delta H_{m, SOD MCs}$ and $\Delta H_{m, SOD}$ represent the phase transition enthalpies of the unencapsulated SOD and SOD MCs, respectively, and ω denotes the mass fraction of SOD within the SOD MCs.

The photophysical properties of SOD MCs were further examined using a PL spectrophotometer. As shown in Figure 3g, SOD MCs displayed orange emission with a λ_{max} of 581 nm at 20 °C, which shifted to a λ_{max} of 544 nm upon heating to 40 °C. Moreover, no significant variation in λ_{max} was observed after 10 consecutive thermal cycles (Figure 3h). The DSC curve of SOD MCs after 50 cycles of heating and cooling closely resembled the initial curve (Figure S30). These results were consistent with the results for unencapsulated SOD, indicating the excellent reversibility, pronounced switching contrast, and superior thermal reliability of SOD MCs.



Figure 3. (a) Schematic illustration of the preparation procedures of double-layered poly (ureaformaldehyde) (PUF) microcapsules (MCs) containing (*S*, *R*)-BBT2TPA-doped PCM core. (b) Optical image and (c)-(e) SEM images of (*S*)-BBT2TPA-doped OD (SOD) MCs. (f) DSC curves and phase change enthalpies of naked SOD and SOD MCs. (g) Normalized PL spectra of SOD MCs at 20 °C and 40 °C. (h) Maximum PL wavelength of SOD MCs at 20 °C and 40 °C measured for ten cycles.

2.4 Applications of Thermochromic CPL Microcapsules

Expanding on the potential applications of thermochromic CPL microcapsules, we integrated SOD MCs into a spectrum of polymeric matrices, including epoxy, polyurethane, and polydimethylsiloxane (PDMS) (Figure 4a). The uniform dispersion of microcapsules within these diverse matrices underscored their robust and versatile nature, thereby facilitating the environmental temperature sensing capabilities of the coatings. These coatings exhibited an orange fluorescence in a cooled state, with a reversible shift to green fluorescence upon

warming. Furthermore, the SOD MC-embedded epoxy coatings demonstrated adaptability across a range of substrate surfaces, including glass, plastic, metal, paper, and plastic foam. This allows for a non-invasive approach to monitor the temperature of substances within various containers (Figure 4b and 4c). The exceptional compatibility and versatility of SOD MCs are reflective of their innovative microcapsule design, which allows for widespread applicability and robust performance across different platforms. The successful integration and performance of SOD MCs in various matrices and on different substrates highlight their potential for high-end applications.



Figure 4. (a) Images of different coating matrices containing SOD MCs taken under white light and 365 nm UV light illumination in cooled and heated states. The scale bar indicates 10 mm. (b) Images of SOD MC-embedded epoxy coating on glass bottles containing cool water and hot water taken under white light and 365 nm UV light illumination. The scale bar indicates 30 mm. (c) Images of SOD MC-embedded epoxy coatings on different surfaces: plastic, metal, paper, and plastic foam. The scale bar indicates 20 mm.

Based on the working mechanism of BBT2TPA-doped PCM, modulating the transition temperature of the thermochromic CPL coating is easily achievable by incorporating PCMs

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with different melting points into the system. To test this hypothesis, (*S*)-BBT2TPA was combined with alkane PCMs such as octadecane (OD, $T_m \sim 28$ °C), eicosane (EC, $T_m \sim 36$ °C), and docosane (DC, $T_m \sim 43$ °C). The resultant coatings exhibited orange-to-green switchable fluorescence at particular temperatures. Specifically, the emission color was orange for all the samples at 20 °C, and then gradually changed to green for SOD, SEC, and SDC at 30 °C, 40 °C, and 45 °C, respectively (Figure 5a). Furthermore, when the hexyl acetate (HA) solution of (*S*)-BBT2TPA was used as the core of MCs, the system maintained a liquid-state orange fluorescence throughout the entire temperature range of interest (Figure S31). Encouraged by these results, we demonstrated a two-dimensional (2D) information encryption system based on fluorescence and a specific decoded temperature (Figure 5b). A pattern of "888" was encoded using epoxy coatings embedded with SOD MCs, SEC MCs, SDC MCs, and SHA MCs. Direct UV illumination under decryption yielded a false code of "888". However, by incorporating temperature as a second key, the true information of "735" was revealed within a precise temperature range of 35 °C to 40 °C.

To explore the thermochromic CPL properties of these coatings, SOD MCs and ROD MCs were embedded into an epoxy matrix, creating an eagle pattern coating. The coatings showcased reversible color emission, transitioning from orange in a cooled state to green upon heating, attesting to their thermochromic fluorescence properties (Figure 5c). While the thermoresponsive fluorescence features of SOD and ROD MC-embedded coatings were indistinguishable, they displayed distinct mirror-image CPL signals in the cooled state with g_{lum} values of 5.8×10^{-3} and -9.8×10^{-3} (Figure 5d). Furthermore, the CPL signals ceased upon heating, consistent with the thermochromic CPL attributes of SOD and ROD (Figure 5e). These findings suggest the utility of CPL as an additional decryption key.



Figure 5. (a) Fluorescence images of SOD, SEC, and SDC taken under 365 nm UV light illumination at different temperatures (20 °C, 30 °C, 40 °C, 45 °C). (b) Demonstration of 2D information encryption using fluorescence and certain temperatures as the decryption elements. The correct output information is 735. The scale bar indicates 20 mm. (c) Images of epoxy eagle pattern containing SOD MCs (left wing) and ROD MCs (right wing) taken under white light and 365 nm UV light illumination in cooled and heated states. The scale bar indicates 10 mm. CPL spectra and DC spectra of left-wing (SOD MC-embedded coating) and right-wing (ROD MC-embedded coating) in (d) a solid state and (e) a liquid state.

To enhance information security, a three-dimensional (3D) information encryption concept was devised by integrating CPL into the 2D encryption technology (Figure 6). An array of epoxy coatings embedded with SOD MCs, SEC MCs, and ROD MCs was arranged according to a predefined program. When the array was exposed to room temperature UV irradiation, it displayed incorrect information of "888". Even with heating, the correct message could not be accessed (Figure S32). The true information could only be decrypted with a CPL analysis tool, which first eliminated the interference from ROD MCs and then deciphered the correct output of "CPL" when the temperature was raised from 30 °C to 35 °C. This multifaceted decryption process, requiring both fluorescence, CPL, and specific temperature as keys, renders the MC-embedded coatings highly suitable for high-security information protection applications.



Figure 6. Demonstration of 3D information encryption using fluorescence (FL), CPL, and specific temperature as the decryption elements. The correct output information is CPL. The scale bar indicates 5 mm.

Considering the thermochromic features, high-level anti-counterfeiting characteristics, ease of large-scale fabrication, and compatibility with various substrates, these MC-embedded coatings are promising for high-end camouflage applications in warfare. For instance, tanks often operate across diverse terrains such as deserts, jungles, and grasslands. Therefore, they require real-time adaptative camouflage to evade detection by enemy forces. As a proof-ofconcept, a tank model was coated with SOD MC-embedded epoxy to serve as a dynamic camouflage coating (Figure 7a). Without dynamic disguise, the tank was easily detectable when transitioning from a desert to a grassland environment (Figure 7b). However, with UV irradiation, the tank could switch into a camouflage mode, blending seamlessly with the desert surroundings (Figure 7c). Upon entering grassland terrain, the appearance of the tank rapidly adapted to a green hue with the aid of UV irradiation and heating. This adaptive coating significantly enhances the survivability and stealth of military vehicles across diverse terrains and conditions. Moreover, leveraging the anti-counterfeiting feature of SOD MC-embedded coatings, friendly forces can be distinguished from foes using CPL analysis tools (Figure 7d). This is a crucial capability for preventing enemy infiltration and friendly fire incidents. Collectively, the MC-embedded coatings offer not only effective camouflage but also a discreet and reliable means of authentication, bolstering the security and operational effectiveness of military forces in the field.



Figure 7. (a) Image of a tank model with the SOD MC-embedded epoxy coating. (b) Scheme illustration and images of the tank in its original state moving from desert to grassland. (c) Scheme illustration and images of the tank in a camouflage state triggered by either UV excitation or the combination of UV and heating excitation. (d) The CPL criteria to distinguish the friendly forces by CPL analysis tools.

3. Conclusion

In summary, this work presents a straightforward yet potent approach to developing thermochromic CPL MC-embedded coatings with tunable and versatile properties. The synthesized chiral AIEgens exhibited significant chiroptical properties and high PLQY. Incorporating these AIEgens into alkane PCMs led to the development of thermochromic CPL materials with reversible emission color transitions and CPL switch upon temperature changes. The integration of temperature-sensitive PCMs with different melting points facilitated precise control over fluorescence color and CPL transitions. Moreover, microencapsulation of these AIEgen-doped PCMs addressed practical challenges such as leakage and corrosion, resulting in stable and thermally reliable thermochromic CPL MCs. The versatility of such MCs was demonstrated across diverse polymeric matrices and substrate surfaces, highlighting their adaptability. The thermochromic CPL properties of the MCs have been utilized to create 2D

and 3D information encryption systems, providing a high level of security for data protection. Moreover, the potential of these MCs in high-end camouflage applications was explored, showcasing their capacity to adapt to diverse environmental terrains for dynamic camouflage of military vehicles, thus augmenting their survivability and stealth capabilities. The application of these MCs in high-end camouflage has further been explored, showcasing their ability to adapt to different environmental terrains for dynamic camouflage of military vehicles, thereby enhancing their survivability and stealth. The combination of ease of large-scale fabrication and multifunctionality of these thermochromic CPL microcapsule-embedded coatings has the potential to revolutionize the fields of security and defense. They offer novel possibilities for protecting sensitive information and concealing military assets, thereby contributing to advancements in security technology.

Experimental Section

Synthesis of chiral AIEgens: The (S, R)-BBT2TPA molecules were synthesized via a two-step process. In the first step, the enantiomers (S)-[1,1'-binaphthalene]-2,2'-diol ((S)-BINOL) and (R)-[1,1'-binaphthalene]-2,2'-diol ((R)-BINOL) were each reacted with diffuorobenzothiadiazoles with different substituents. These nucleophilic substitution reactions proceeded with high yields, respectively. Subsequently, the resulting (S, R)-intermediates were engaged in a Suzuki coupling reaction with an electron-donating group. This coupling process culminated in the production of the target (S, R)-BBT2TPA molecules.

Preparation of Microcapsules: Double-layered microcapsules were prepared through a twostep in situ polymerization process within an oil-in-water emulsion. Initially, 0.8 g of urea, 0.08 g of resorcinol, and 0.08 g of NH₄Cl were introduced into a 50 mL aqueous solution of poly(ethylene-alt-maleic anhydride) (EMA, 0.25wt%). After adjusting the pH to 3.5, preheated BBT2TPA-doped PCM was added dropwise into the aqueous solution followed by homogenized at 5000 rpm for 5 min. Subsequently, 1 g of formaldehyde was added to the mixture, and the temperature was elevated and maintained at 55 °C for 3 h. The mixture was then heated to 55 °C In the subsequent step, a urea-formaldehyde (UF) prepolymer was synthesized by reacting 2.5 g of formaldehyde solution, 1 g of urea, and 5 g of water at a pH of 8 and a temperature of 70 °C for 1 h. The UF prepolymer and 0.6 g of resorcinol were then introduced into the mixture from the first step. After the pH was readjusted to 3, the reaction was allowed to proceed at 55 °C for an additional 1 h. The resulting microcapsules containing the BBT2TPA-doped PCM were subsequently washed with deionized water several times and air-dried overnight to obtain the final product. *Preparation of microcapsule-embedded coatings*: The epoxy coating was prepared by first mixing the epoxy resin (Epolam 5015) with its hardener, followed by the addition of 10 wt% microcapsules (MCs). The mixture was then degassed in a vacuum oven for 20 minutes before being applied onto various substrates, including glass, plastic, metal, paper, and plastic foam. The coated samples were left to cure completely at room temperature to achieve the final coating. Similarly, polyurethane prepolymer (Suprasec 2644) and PDMS prepolymer (Sylgard 184) were used to prepare polyurethane and PDMS coatings, respectively, following the same procedure.

Supporting Information

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

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References

- [1] S. Jiang, N. A. Kotov, Adv. Mater. 2023, 35, 2108431.
- [2] Y. Sang, J. Han, T. Zhao, P. Duan, M. Liu, Adv. Mater. 2020, 32, 1900110.
- [3] C. Zhang, S. Li, X.-Y. Dong, S.-Q. Zang, Aggregate 2021, 2, e48.
- [4] H. Yan, Y. He, D. Wang, T. Han, B. Z. Tang, Aggregate 2023, 4, e331.
- [5] Z.-L. Gong, Z.-Q. Li, Y.-W. Zhong, Aggregate 2022, 3, e177.
- [6] J. Jiménez, L. Cerdán, F. Moreno, B. L. Maroto, I. García-Moreno, J. L. Lunkley, G. Muller, S. de la Moya, J. Phys. Chem. C 2017, 121, 5287.
- [7] J. Kumar, T. Nakashima, T. Kawai, J. Phys. Chem. Lett. 2015, 6, 3445.
- [8] X. Wang, B. Zhao, J. Deng, Adv. Mater. 2023, 35, 2304405.
- [9] Y. He, S. Lin, J. Guo, Q. Li, Aggregate 2021, 2, e141.
- [10] Y. Kim, N. N. Mafy, S. Maisonneuve, C. Lin, N. Tamaoki, J. Xie, ACS Appl. Mater. Interfaces 2020, 12, 52146.
- [11] J. Yan, F. Ota, B. A. San Jose, K. Akagi, Adv. Funct. Mater. 2017, 27, 1604529.
- [12] H. Yu, B. Zhao, J. Guo, K. Pan, J. Deng, J. Mater. Chem. C 2020, 8, 1459.
- [13] K. Takaishi, K. Iwachido, T. Ema, J. Am. Chem. Soc. 2020, 142, 1774.

- [14] X. Li, Y. Shen, K. Liu, Y. Quan, Y. Cheng, *Mater. Chem. Front.* 2020, *4*, 2954.
- [15] H. Zhang, Z. Zhao, A. T. Turley, L. Wang, P. R. McGonigal, Y. Tu, Y. Li, Z. Wang, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Adv. Mater.* **2020**, *32*, 2001457.
- [16] S. Chen, T. Han, B. Z. Tang, Adv. Funct. Mater. 2023, 33, 2307267.
- [17] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, Chem. Rev. 2015, 115, 11718.
- [18] J. Zhang, B. He, Y. Hu, P. Alam, H. Zhang, J. W. Y. Lam, B. Z. Tang, Adv. Mater. 2021, 33, 2008071.
- [19] K. Hirano, T. Ikeda, N. Fujii, T. Hirao, M. Nakamura, Y. Adachi, J. Ohshita, T. Haino, *Chem. Commun.* **2019**, *55*, 10607.
- [20] W. Qi, C. Ma, P. Liao, H. Li, T. Gu, T. Wu, J. Huang, Y. Yan, *Adv. Opt. Mater.* **2023**, *11*, 2201229.
- [21] Y. Chen, P. Lu, Q. Gui, Z. Li, Y. Yuan, H. Zhang, J. Mater. Chem. C 2021, 9, 1279.
- [22] W. Kang, Y. Tang, X. Meng, S. Lin, X. Zhang, J. Guo, Q. Li, Angew. Chem. Int. Ed. 2023, 62, e202311486.
- [23] Y. Chen, P. Lu, Z. Li, Y. Yuan, Q. Ye, H. Zhang, ACS Appl. Mater. Interfaces 2020, 12, 56604.
- [24] J.-Y. Wang, J.-W. Yuan, X.-M. Liu, Y.-J. Liu, F. Bai, X.-Y. Dong, S.-Q. Zang, *Aggregate* **n.d.**, *n/a*, e508.
- [25] K. Takaishi, F. Yoshinami, Y. Sato, T. Ema, *Chem. Eur. J.* n.d., *n/a*, e202400866.
- [26] H. Duan, H. Pan, J. Li, D. Qi, J. Mater. Chem. C 2023, 11, 172.
- [27] C. Gao, Z. Zhang, X. Zhang, J. Chen, Y. Chen, C. Zhao, L. Zhao, L. Feng, Soft Matter 2022, 18, 3125.
- [28] X. Song, X. Zhu, S. Qiu, W. Tian, M. Liu, Angew. Chem. Int. Ed. 2022, 61, e202208574.
- [29] G. Wang, Z. Tang, Y. Gao, P. Liu, Y. Li, A. Li, X. Chen, *Chem. Rev.* 2023, DOI 10.1021/acs.chemrev.2c00572.
- [30] J. Du, L. Sheng, Q. Chen, Y. Xu, W. Li, X. Wang, M. Li, S. X.-A. Zhang, *Mater. Horiz.* 2019, 6, 1654.
- [31] K. Xue, C. Wang, J. Wang, S. Lv, B. Hao, C. Zhu, B. Z. Tang, J. Am. Chem. Soc. 2021, 143, 14147.
- [32] Y. Guo, T. Hou, J. Wang, Y. Yan, W. Li, Y. Ren, S. Yan, *Adv. Sci.* **2023**, *n/a*, 2304580.
- [33] T. Han, S. Chen, X. Wang, X. Fu, H. Wen, Z. Wang, D. Wang, A. Qin, J. Yang, B. Z. Tang, Adv. Sci. 2022, 9, 2105395.
- [34] H. Zhang, X. Zhang, C. Bao, X. Li, F. Duan, K. Friedrich, J. Yang, Chem. Mater. 2019, 31, 2611.
- [35] J. Huang, Y. Liu, J. Lin, J. Su, C. Redshaw, X. Feng, Y. Min, Adv. Compos. Hybrid Mater. 2023, 6, 126.