Review

Emerging Luminescent Materials for Information Encryption and Anti-Counterfeiting: Stimulus-Response AIEgens and Room-Temperature Phosphorescent Materials

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Emerging Luminescent Materials for Information Encryption and Anti-Counterfeiting: Stimulus-Response AIEgens and Room-Temperature Phosphorescent Materials

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Abstract: Information encryption and anti-counterfeiting play an important role in many aspects of daily life, such as in minimizing economic losses, protecting secure communication and public security, and so on. Owing to the high information capacity and ease of operation, luminescent materials for advanced information encryption and anti-counterfeiting are essential to meet the increasing demand on encryption security. Herein, we summarize two emerging luminescent materials for information encryption and anti-counterfeiting, the AIE materials and room-temperature phosphorescent materials. At last, we discuss the opportunities and anticipations of these two information encryption and anti-counterfeiting materials.

Keywords: AIEgens; RTP materials; information encryption; anti-counterfeiting; multilevel encryption

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1. Introduction

With the rapid development of economy, the amount of fake products and information is rapidly increasing [1,2]. In such case, the information encryption and anti-counterfeiting technologies are essential to minimize the economic losses and protect public security [3], and have always been considered a major challenge. Up to now, there has been various designs for information encryption and anti-counterfeiting， which are based on different stimuli-responsive materials, such as the thermochromic photonic crystal [4], photoresponsive liquid crystal lasing materials [5], time-dependent luminescent materials [6,7], anisotropically shaped complex materials [8], circularly polarized luminescence (CPL) materials [9–11], and so on. In addition, numerous functional materials with multimodal emission have also been investigated and used for advanced information encryption and anti-counterfeiting [12]. Attributed to the single particle analysis accuracy of dark-field microscopy (DFM) imaging [13–17], the single particle level data encryption could also be achieved recently [18].

Among these intelligent response materials, the luminescent materials are most widely used, which could always be easily regulated by various external stimuli, such as the chemical reagent, heat, mechanical force, excitation light, and acid or alkaline. The output signals are abundant and can be ranged from the elementary parameters, such as the emission intensity and emission color, to the dynamic parameters, such as the time of emission duration and discoloration process. Furthermore, the incident light has rich dimensions (wavelength, excitation duration, polarization, and power), and thus the multilevel stimulus can effectively improving the security level [19,20].

Actually, most of the luminescent materials for information encryption and anti-counterfeiting are used in the form of aggregated and solid state. So the aggregated materials should display excellent luminescent properties. As known， the aggregates always show completely different properties and behaviors to the dispersed molecules [21,22]. The aggregation-induced emission (AIE) phenomenon meets this requirement that the luminescence in the aggregated state is much better.

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And the AIE materials not only contains the commonly used aggregation-induced emission luminogen (AIEgens)， but also the materials that exhibit the CPL property, aggregation-induced delayed fluorescence (AIDF) property, room-temperature phosphorescence (RTP) property, the clusterization-triggered emission (CTE) property, and so on [23]. In this review, part of AIEgens and RTP materials based designs and applications for information encryption and anti-counterfeiting are introduced.

We hope this review will offer insight into the AIEgens and RTP materials based technologies and their recent applications for information encryption and anti-counterfeiting to help further develop and update this technique.

2. Application of the AIE Materials in the Information Encryption and Anti-Counterfeiting

The concept of AIE was firstly proposed in 2001 [24], which is a phenomenon different from the traditional aggregation-caused quenching (ACQ). After two decades, AIE has developed into a thriving field, and the AIEgens have been widely investigated and applied in various fields, such as the theranostics [25–27], biosensing [28–30], organic luminescent materials [31,32], metal batteries [33]. For the information encryption and anti-counterfeiting applications, the AIE materials should be responsive to external stimulus, resulting in the change of the luminescent properties. Recently, various stimuli-responsive AIEgens have been developed [34]. For example, the AIEgens with mechanochromic property is an ideal candidate materials for the encryption application [35,36]. To obtain higher signal change ratio, AIEgen with force-trigger photoluminescence property was also investigated [37]. Obviously, the AIEgens with multi-stimuli responsive and reversible fluorescence switching facilitate the designs for the advanced encryption applications [38–40]. Herein, several kinds of AIE materials for information encryption and anti-counterfeiting are summarized.

2.1. AIEgens

Tetraphenylethene (TPE) is one of the mostly used AIE molecules, which exhibits blue luminescence under UV irradiation. By linking two sulfonate spiropyrans with one TPE covalently, Liu and coworkers prepared an AIE-active orange–red/blue switch with photochromism property, sulfonate spiropyran–TPE–sulfonate spiropyran (STS) [41]. The STS can response not only to the acid/base stimulation, but also to the visible light irradiation and heating. Visible light irradiation could transfer orange–red STS into its ring-closed form, RSTRS, and the emission convert to blue. Both these two forms exhibit obvious AIE characteristic. Through incorporating STS into polyvinylpyrrolidone matrix, advanced information encryption was investigated. 0.5% volume fraction of nonvolatile sulfuric acid (0.5%) could stabilize the AIEgen in the STS form. while the AIEgen treated with 0.02% volume fraction of acid would be in the STS form, but light irradiation could covert it into the blue emissive RSTRS. Combined with the nonfluorescent red dye, three level of date encryption (“337”,”377”, and “71”) could be achieved simply (Figure 1A).

In addition to the light, heat, acid/base responsive material, the mechanoresponsive AIEgen is also suitable for anti-counterfeiting and information encryption. By combing the spiro[fluorene-9,90-xanthene] and 9,9-dimethyl-9,10-dihydroacridine, Guo at al. prepared an AIE-active molecule (SFX-Ad) [42]. The SFX-Ad displays mechanoresponsive property, and an obvious enhanced of the luminescence is companied with the crystal-to-amorphous transition. Based on this characteristic, the SFX-Ad could be the same as the non-emissive Na_2CO_3, no matter under UV or visible light. However, after the grinding treatment, the emission enhancement of SFX-Ad would supply the true information. And thus, the anti-counterfeiting and information encryption could be realized easily.

By tailoring the -bridge, Guo and coworkers regulated the luminescent behaviors of two carbazole derivatives, CPDI and CTDI [43]. The phenyl -bridge of CPDI could led to an AIE characteristic accompanied with thermally stimulated emission turn-off. While the thienyl -bridge of CTDI led to an ACQ characteristic accompanied with thermally stimulated emission turn-on. By using UV-light irradiation and thermal treatment as two sequential keys, fourth-level information encryption was realized by combining these two AIE and ACQ molecules (Figure 1B).

To achieve more color adjustments, a group of full-color-tunable AIEgens with mechanofluorochromic property were prepared by Tang and coworkers [44]. By adjusting the electron-withdrawing ability of the acceptors in the D- -A structure, a broad emission color was achieved. The emission wavelength could be from 460 nm to 640 nm by simply increasing grind time or variating the degree of the grind. And the emission was mainly dependent on the packing morphologies of the molecules in the crystals. Besides, the ethyl acetate (EA) steam treatment could lead to the recrystallization of the ground compounds and a blue shift of the luminescence was also accompanied. Based on this property, these AIEgens were used for the design of 4D code, which has the advantages such as strong fault tolerance and high reliability. Furthermore, the random grinding degrees was used to prevent counterfeiting and avoid duplication. To investigate the anti-counterfeiting applications of these AIEgens, a figure of ''Starry Night'' was prepared with these colorful AIEgens with random forces. Obviously, the color and luminescence information in this figure is difficult to forge. And the blue shifted color and emission of this figure after the treatment with EA further enhanced the level of the anti-counterfeiting. This design could also be used for the anti-counterfeiting of the identification (ID) card (Figure 1C).

If multicolor fluorescence changes could be achieved through a single luminogen, it would be easier to be used as intelligent material. Tang and coworkers designed an AIEgen, (Z)-2-(5,5-dimethyl-3-(2-(4-oxo-4H-chromen-3-yl)-1-phenylvinyl)cyclohex-2-en-1-ylidene)malononitrile (CPVCM) [45]. Firstly, the CPVCM could react with primary amines through amination reaction, resulting in fast and reversible color change. Secondly, it can also be response to the UV irradiation through photoarrangement accompanied with the blue-shifted emission. By using thin-layer chromatography plate as carrier, the multifunctional CPVCM was used for blue emissive information writing with UV lamp and mask. Then the propylamine vapor treatment could change the surrounding into red and orange emission. At last, the UV irradiation could change the whole plate into blue emissive, and thus the information was erased easily. According to the different response model of the amination process and the photoarrangment, the authors further combined polymethyl methacrylate (PMMA) to regulate the degree of the amination process. In such case, the higher PMMA doping led to weaker amination process and the corresponding red shift. A multicolor and advanced information encryption was realized (Figure 1D).

Another group of multiresponsive AIEgens, a series of 2-phenylazulene-1,1(8aH)-dicarbonitrile derivatives (DHAP-R, R=H, Br, Me, OMe, and NO_2), were also designed and prepared by Tang and coworkers [46]. The DHAP-R could response to both UV irradiation and heating, resulting in ring-opening (VHFP-R, non-emissive) and ring-closed (DHAP-R, emissive) form reversibly. Based on this characteristic, DHAP-Br and PMMA (1:2) were used for information storage. The UV irradiation induced date information could be erased by the heating, which was dependent on the temperature and time. The extraction and deletion of information is important for an excellent information encryption system. In this system, the decrypted information could be erased in a period at a specific temperature.

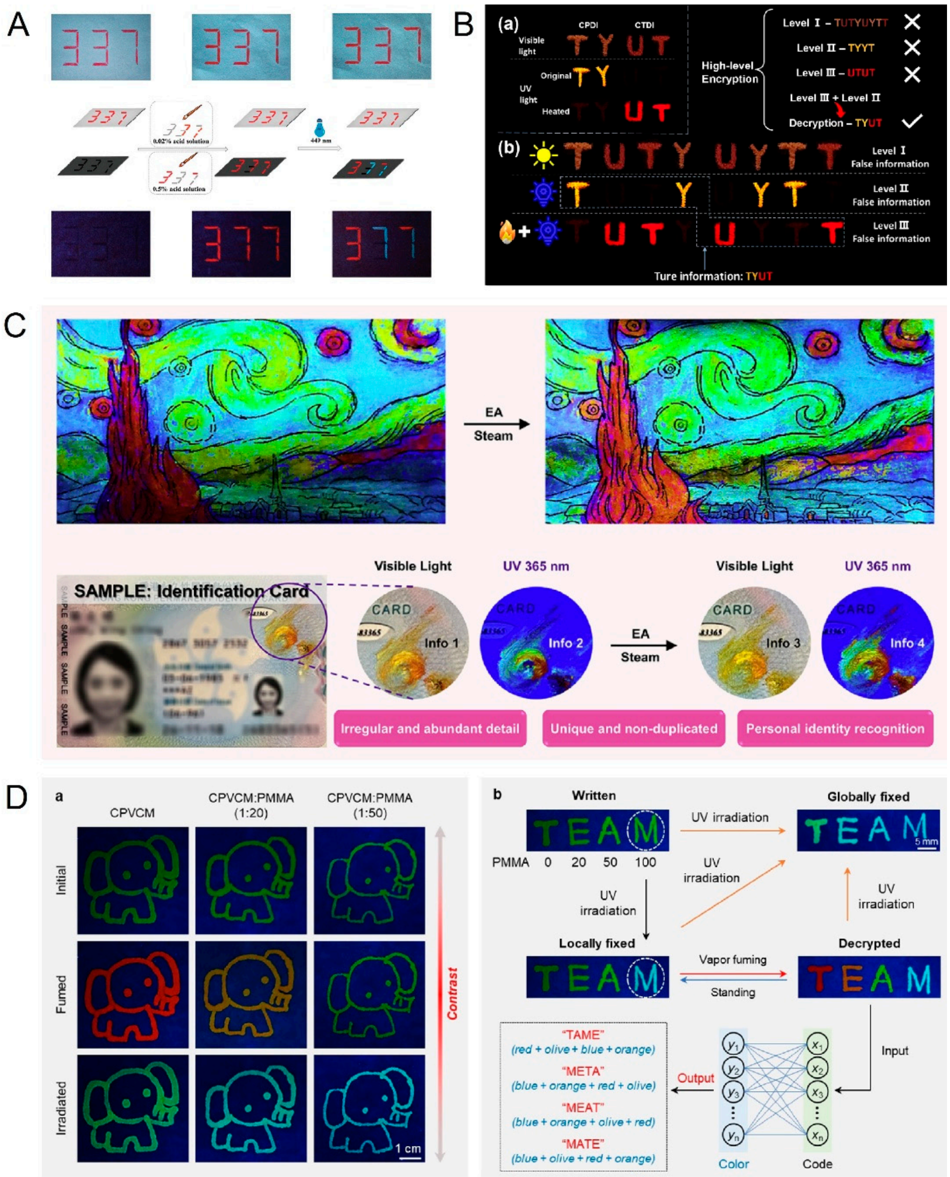

Figure 1. AIEgens based information encryption and anti-counterfeiting. (A) Light irradiation and acid triggered three level of date encryption by the STS-RSTRS system [41]. Copyright 2021, with permission of The Royal Society of Chemistry. (B) The AIEgen CPDI and ACQ molecule CTDI based fourth-level information encryption [43]. Copyright 2023, with permission from Elsevier. (C) Photographs of the ''Starry Night'' and identification card that was painted or hallmarked by the crystals of TPE-B, TPE-G, TPE-Y, and TPE-R with random force and deal with EA [44]. Copyright 2023, with permission from Elsevier. (D) Multicolor encryption based on CPVCM security ink [45]. Copyright 2023 Wiley.

When time is introduced into the information encryption systems, there will be some new opportunities and designs for high-level security. By combing the cationic TPE derivative (TPE4N^{4+}) with the anionic spiropyran (ASP), which could be transformed from the fromsulfonato-merocyanine photoacid (SMEH) under the 420 nm light irradiation, Tang et al. reported a time-dependent information encryption system [47]. Once the ASP was formed, the electrostatic interactions between TPE4N^{4+} and ASP would lead to the restriction of the molecular rotation of the TPE, resulting in the enhanced fluorescence emission. In such case, at the right time of UV irradiation, the true information could be decrypted. And after a period of dark condition, the emerged information would be erased, confirming an excellent self-erased property.

For the AIEgens, a simple change in a substituent or functional group might lead to a significant change in the properties of the molecule. Pu and coworkers obtained a group of benzothiadiazole derivatives, which exhibited AIE characteristic and different force-responsive fluorescence

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characteristics [48]. One exhibits red-shifted mechanofluorochromism behavior, and three exhibit blue-shifted mechanofluorochromism behavior. While another two don't response to the external mechanical stimulation. Based on this characteristic, multilevel information encryption was achieved easily.

Tetraphenylpyrazine (TPP) is also an important AIE structural unit and has various applications. To investigate its application in information storage, Chen and coworkers synthesized three AIEgens (TPP-o-py, TPP-m-py, TPP-p-py) with TPP as electronic donor to the acrylonitrile and pyridine as electronic acceptor [49]. These AIEgens exhibited solvatochromic effect due to the twisted intramolecular transfer (TICT) effect, and they can response to the light and acid/base stimulus. With the silica gel plate as carrier, the reversible memory storage of the "JNU" could be achieved. In this process, the hydrochloric acid induced protonation effect transfers the AIEgens into a weak and red emission state. While the triphenylamine could erase this information. Once the AIEgens on the silica gel plate was irradiated with the UV light, an irreversible memory storage of the "AIE" could be realized which was attributed to the photodimerization reaction.

2.2. AIEgens-Matrix Composite Materials

For the above AIEgens based information encryption and anti-counterfeiting designs, the excellent stimuli-responsive property is essential. If some functional matrix is introduced, the common AIEgens could also be used for intelligent. By combing the TPE and the widely used energy acceptor in the spectroanalysis, graphene oxide (GO), Chen and coworkers designed a composite material, TPE@GO, which showed switchable microstructure and the corresponding fluorescence [50]. The main working principle was as follows: Firstly, the TPE@GO was non-emissive duo to the fluorescence quenching capability of the GO through fluorescence resonance energy transfer. Once the THF/H_2O mixture (V_{THF} = 60%, with the higher fluorescence enhancement) was added, the TPE was dissolved in the THF and then aggregated into nanoparticles after the volatilization of H_2O. In such state, the blue emission of the TPE was recovered, and the information could be decrypted. While the formed TPE nanoparticles was further sprayed with pure THF, the TPE nanoparticles were dissolved and accompany with the information encryption again. Based on this mechanism, the authors designed the information encryption with this TPE@GO functional material (Figure 2A).

Different from the regulation of luminescence with different water fraction, Zhang et al. designed a series of AIE-active freeze-tolerant hydrogels [51]. The freezing temperatures (Tf) could be regulated by the betaine concentration, and once the temperature was lower than the Tf of the AIE-active hydrogels, the luminescence of the AIEgen, 2,2′,2″,2‴-((ethane-1,1,2,2-tetrakis(benzene-4,1-diyl)) tetrakis-(oxy)) tetraacetate (TPE-4CO_2Na) would turn on. Based on this temperature dependent luminescent property, this hydrogel was used for information encryption. Furthermore, the authors achieved the *in situ* sulfidation of Cu_2O nanparticles into Cu_9S_8 nanoparticles, which exhibited excellent photothermal property. Combined with the near infrared light response, advanced could be achieved easily, and partial of the luminescence around the Cu_9S_8 nanoparticles could be selectively erased. Thanks to that the decrypted information was irreversibly sensitive to temperature fluctuation, this hydrogels could be used for the real-time monitoring of the cryopreserved biosamples during the cold-chain transportation.

In a similar way, Min and coworkers designed and prepared a functional composite phase change fiber containing the pyrene-based AIEgens (Py-CH) through by electrospinning technology [52]. Accompanied with the increased temperature from 30 to 160^oC, the fluorescence of the Py-CH showed a blue shift from the green-yellow to purple. Combined with the excellent latent heat and stability to thermal cycling, this fiber displayed the potential application in various fields in addition to the anti-counterfeiting applications, such as the solar energy conversation and storage, and the high-temperature warning.

For the thermoresponsive materials, high contrast ratio (CR), fast and reversible thermoresponse were all attractive parameters. Li et al. synthesized a deep-red emissive squaraine-based AIEgen (TPE-SQ12) [53]. By dispersed this AIEgen into the elastomer, a thermal-responsive luminescent materials was obtained. With the increased temperature, the free volume of elastomer was significantly expanded, resulting in the enhanced intramolecular movements of the AIEgens and the corresponding decreased luminescent intensity. Attributed to this responsive property, the authors achieved double encryption (Figure 2B).

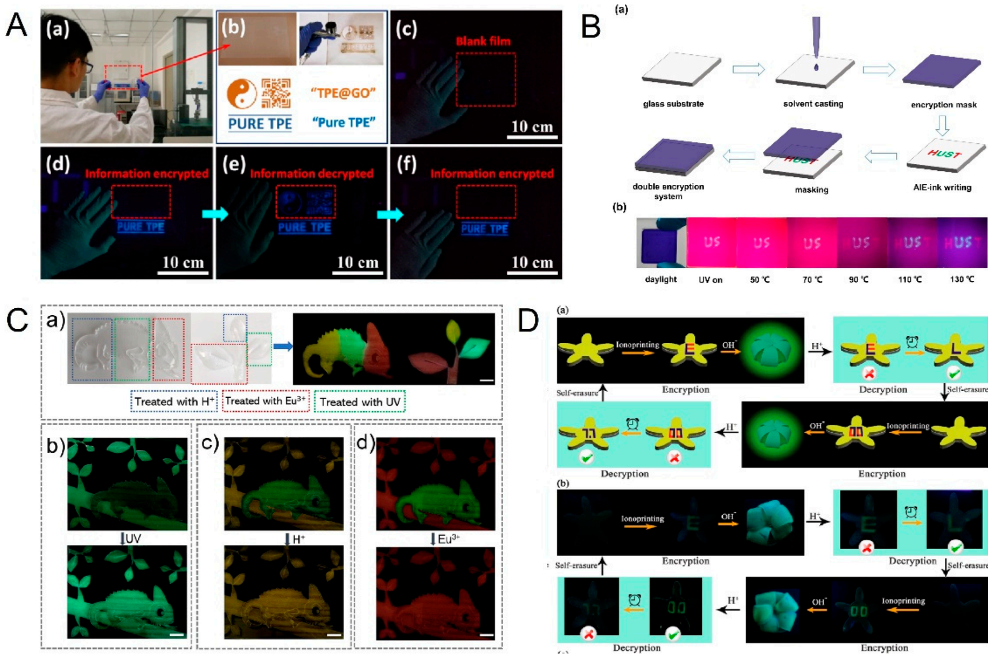

Figure 2. AIEgens-matrix composite materials based information encryption and anti-counterfeiting. (A) TPE@GO for reversible information encryption [50]. Copyright 2019 American Chemical Society. (B) Double encryption system based on SBR/TPE-SQ12 film [53]. Copyright 2022 Wiley-VCH GmbH. (C) The color changes of the self-healing hydrogel responsive to UV light, H^+ and Eu^{3+} [54]. Copyright 2022, with permission of The Royal Society of Chemistry. (D) 3D multistage information encryption, decryption and self-erasure processes based on the functional bilayer hydrogel [55]. Copyright 2023, with permission of The Royal Society of Chemistry.

In order to endow the multi-responsive luminescent materials with self-healing capability, Jia and coworkers developed a self-healing hydrogel which exhibited multicolor luminescence and could be responsive to three external stimulus, including the UV light, acid, and Eu^{3+} [54]. The treatment with UV light would lead to the green emission, and the treatment with acid would lead to the yellow emission. While the Eu^{3+} could lead to the red luminescence, which was attributed to the coordination between the Eu^{3+} and the carboxyl. The UV light triggered emission enhancement could be recovered, so this hydrogel could be used for reversible information encryption and decryption. Based on the multi-responsive property, a multicolor chameleon-shaped hydrogel could be obtained. And a sequential color change from green to yellow could be achieved through adding acid to the UV irradiation triggered green emissive chameleon-shaped hydrogel. Furthermore, the sequential color change from green to red could be achieved by the addition of Eu^{3+} to the green emissive chameleon-shaped hydrogel simply (Figure 2C).

Endowing the multi-responsive luminescent materials with shape recovery capability is another interesting design for the intelligent materials. Tang et al. developed a functional bilayer hydrogel with synergistic deformation and fluorescence color (SDFC) change property. The fluorescence enhancement was attributed to the pH-driven aggregation of the AIEgens, and the electrostatic interaction and dynamic covalent bonds were also contributed to the aggregation. Based on this fluorescence change property, 2D information encryption could be realized easily. Together with the pH-triggered deformation capability, a sequential 3D multistage information encryption, decryption and self-erasure processes could be achieved (Figure 2D), which was a typical advanced information encryption design and exhibited larger information storage capacities.

2.3. AIE Carbon Dots

Usually, the AIEgens refer to the organic molecules that exhibit AIE property. Actually, various nanomaterials, such as the metal clusters, carbon dots (CDs), have already exhibited typical AIE property and could be regarded as functional AIEgens. Recently, many AIE CDs has been prepared and used for anti-counterfeiting and information encryption applications.

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Hydrothermal method is one of the most widely used methods for preparation of the CDs. By this simple method, Wang and coworkers synthesized a blue-emissive CDs with a quantum yield of 7.6% in aqueous state and 29.2% in solid state [56]. So the CDs exhibited classical AIE property due to the functionalization by Na^+, and its emission color turned to cyan in solid state which was attributed to the surface state change caused by aggregation. Based on these characteristics, the authors used it for anti-counterfeiting designs. An image of waxberry on a filter paper was printed with the security inks composed by the CDs. Under 365 nm UV lamp, the waxberry showed cyan emission and blue emission once been wetted by water. In addition, this security inks could also be used for the printing of various text and patterns (Figure 3A).

To develop the multi-color anti-counterfeiting and information encryption technologies, the multi-color AIE CDs were prepared by Gao and coworkers [57]. By using crystal violet as the precursor, four AIE CDs with different emission color (B-AIE-CDs, G-AIE-CDs, Y-AIE-CDs, and O-AIE-CDs) were synthesized. The sulfuric acid concentrations, the temperatures and reaction times, played important roles, but the concentration of the sulfuric acid was the most important one due to its function in regulation of the carbonization degree, and the type and content of nitrogen. Combined with the acid-sensitive property of partial of these AIE CDs, the applications for anti-counterfeiting and information encryption were investigated. Firstly, the acid triggered orange fluorescence of the real password could be clearly distinguished from the false password showed other fluorescence. Besides, the acid triggered decryption of the hidden information “123456789” displayed the excellent information encryption capability of these multi-color CDs (Figure 3B).

Through the simple one-pot solvothermal method, Hu et al. synthesized a kind of functional hydrophobic CDs, which exhibited blue emission in the dispersed state and red emission in the aggregated state [58]. The water could induced the aggregation of the hydrophobic CDs, leading to - stacking interactions of the carbonized cores and the accompanied red emission. And the AIE property might be from the restriction of the surfaces’ intramolecular rotation around disulfide bonds. Interestingly, the blue-red emission change is reversible by the regulation between the dissolved and aggregated state. The authors used this AIE CDs as luminescence ink for advanced anti-counterfeiting and dual-encryption applications. The blue emission of the pattern from the commercially available highlighter pen was almost stable after the water treatment no matter under 365 nm or 254 nm irradiation. However, the blue emission of the pattern from the luminescent ink of this hydrophobic CDs turned to pink under 365 nm irradiation, and it turned to red emission under the 254 nm irradiation. Obviously, this could be used for high level security and anti-counterfeiting. Combined with the wax sealing, this luminescent ink could be used for multilevel encryption information encryption. Because the “C”, “S” and “U” were covered with wax, their emission was no longer sensitive to the water treatment. And only the bare “S”, “U” and “N” showed the red emission under 254 nm irradiation, showing the true information (Figure 3C).

Similarly, by using dithiosalicylic acid and precursors containing amino groups, Wang and coworkers also prepared CDs exhibited AIE property and dual-emission in different states [59]. And the emission regulation was also reversible. When this CDs was used for information encryption, the water treatment could lead to the orange emission under 254 nm irradiation. While the emission of the words written by the commercially available highlighter pen showed no obvious changes (Figure 3D).

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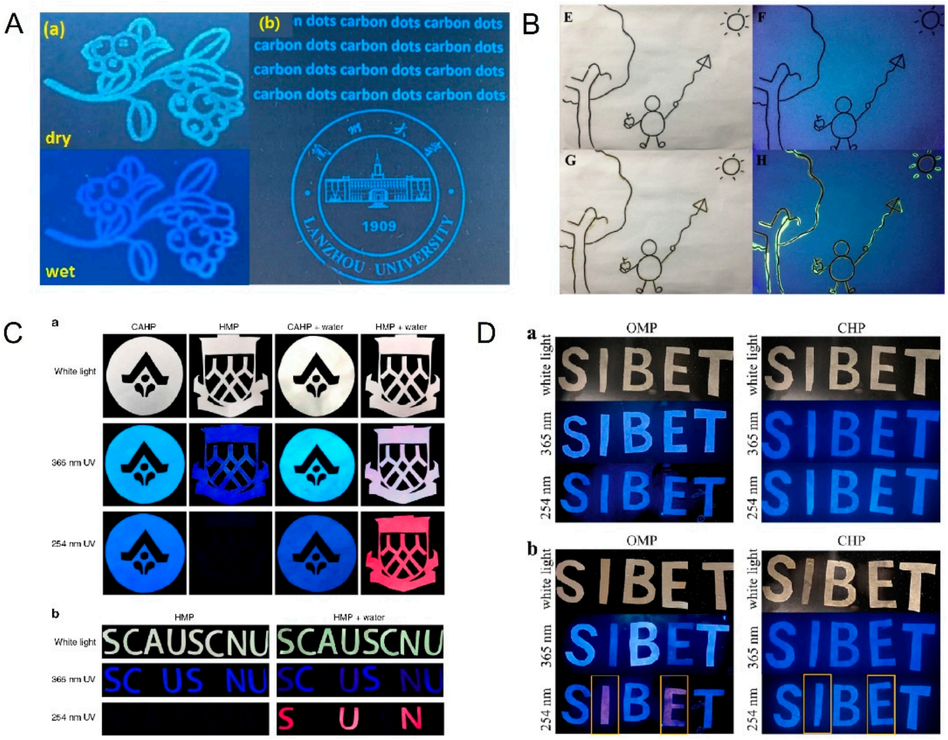

Figure 3. AIE carbon dots based information encryption and anti-counterfeiting. (A) Na^+ functionalized CDs for anti-counterfeiting and printing [56]. Copyright 2021, with permission from Elsevier. (B) Acid-sensitive multi-color AIE CDs for advanced information encryption [57]. Copyright 2022, with permission from Elsevier. (C) Hydrophobic AIE CDs for advanced anti-counterfeiting and dual-encryption applications [58]. Copyright 2019 Nature Publishing Group. (D) Water-sensitive CDs for information encryption [59]. Copyright 2022, with permission from Elsevier.

3. Application of the RTP Materials in the Information Encryption and Anti-Counterfeiting

Time resolved spectral and imaging information is ideal candidate for high-level encryption and anti-counterfeiting. Among the luminescent materials with time resolution ability, the RTP materials, especially the purely organic ones [60–63], have been a topic of keen interest in various applications. Recently, several organic RTP materials that emit bright red emission have been developed and exhibited potential applications in the bioimaging [64–66]. Obviously, these RTP materials could also expand and enrich the design choices of the anti-counterfeiting and information encryption. Although all kinds of RTP materials, including the inorganic ones, organic ones, and even the organic-doped inorganic ones, could be used for information encryption and anti-counterfeiting, the stimuli-responsive organic RTP materials were better choices due to the significant signal changes [67,68]. Besides, some new constructing strategies, for example through manipulating intermolecular interactions, could no matter enrich the variety of RTP materials, but also supply much design choices for the stimuli-responsive RTP materials [69,70]. Herein, the RTP molecules, RTP molecules-matrix composite materials, and the phosphorescent CDs based information encryption and anti-counterfeiting are summarized.

3.1. RTP Molecular Systems

Recently, the host-guest doping has proven to be an efficient route to construct RTP materials with long lifetimes, high quantum, and various wavelengths [71–74]. By using the triphenylphosphine and triphenylarsenic as the guest and a series of triphenylamine derivatives as host, Dong et al. synthesized a range of RTP materials with multi-color emission [75]. The RTP emission could be effective in a wide range of host-guest ratio from 50:1 to 20000:1, which might be much wider. In these systems, the host molecules could provide a rigid environment, which avoided the quenching of the triplet excitons by oxygen. These RTP systems were sensitive to temperature because of the temperature regulated vibrational freedoms of the host–guest systems. The authors

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successfully used these temperature sensitive RTP materials for multilevel thermochromic anti-counterfeiting.

Similarly, Dong and coworkers also prepared a series of RTP materials through the host-guest doping method [76]. Herein, the host molecules played the roles as the bridge to enhance the intersystem crossing and rigid environment to limit the nonradiative decay of the triplet excitons. And one of the optical systems, TPA-FL-CN/CBN exhibited a lifetime of 847 ms and phosphorescence quantum yield of 4.7%. Based on these RTP systems, the authors developed the phosphorescence encryption and decryption applications. By using the FL-2CN/ABN ethyl acetate as the phosphorescence ink, the dragonflies and the dandelions patterns could be hidden under the 365 nm UV irradiation or under the ambient light. However, after removing the UV irradiation, these patterns with yellow phosphorescence could be decrypted easily. Furthermore, the RGB color value at different time could be used as secret keys in the phosphorescence encryption system (Figure 4A).

The energy transfer process can enrich the fluorescence emission wavelengths and application designs of the RTP materials [77–80]. Yang and coworkers designed and synthesized a range of host-guest RTP systems based on several asymmetric diarylamine guests [81]. Firstly, they investigated the multi-stimulus responsive properties of these materials. Further applications of these RTP systems for anti-counterfeiting were explored based on the time resolved characteristic of the MDPA-Ph@DMAP system and energy transfer. For the RTP system only, the green RTP emission of the badge pattern and words could be observed after the removing of the UV irradiation. However, if the rhodamine B was added into the RTP system, a pink emission was observed under the UV irradiation. And after removing the UV irradiation, the emission turned to green and pink color, and the latter one should be attributed to the emission of the rhodamine B, resulting from the energy transfer from the green RTP emission (Figure 4B).

With the development of the host-guest RTP materials, there is still a challenge that the effective matching between the host and guest molecules for the efficient intersystem crossing. Up to now, the trial-and-error method is still widely used. To better predict the host molecules for matching the guest RTP emitters, Liu et al. provided a simple descriptor ΔE, based on the intersystem crossing via higher excited states mechanism [82]. According to this descriptor, they predicted five commercially available host components to pair with naphthalimide and naphtho[2,3-c]furan-1,3-dione emitters. Interestingly, the accuracy of this prediction was as high as 83 %. This was an important exploration for the further development of the host-guest RTP materials. Based on the developed RTP systems with different lifetimes and wavelengths, the authors investigated their anti-counterfeiting applications, which exhibited classical time resolution characteristic.

Another important host-guest interaction is the complexation between the supramolecular macrocyclic hosts and the guest, for example the crown ethers and the K^+. Tang and coworkers firstly reported the ultralong RTP emission form the traditional crown ethers [83]. And the RTP lifetime from the crown ethers could be effectively prolonged through the interaction with the K^+. In such case, the invisible RTP could be changed into a visible RTP, which is suitable for the information encryption and decryption. Based on this newly discovered smart luminescence system, advanced encryption application was designed. Firstly, an encryption pattern of "8" was printed with functional ink containing different components of the dyes, the B15C15 crown esters, and K^+. Upon the 254 nm irradiation, all parts of the "8" were emissive attributed to the dyes. After removing the UV irradiation, only the pre-activated part in the "7" with K^+ was visible. Once sprayed with a solution of K^+, the parts containing B15C15 in the pattern of "3" could be seen clearly (Figure 4C). As a result, a multilevel encryption was achieved.

In addition to the host-guest RTP systems, the single component RTP emitters were also widely studied and applied, including in the anti-counterfeiting and information encryption. Through a molecular design strategy, Zhao et al. explored the photoactivated persistent RTP behaviors of a series of triphenylphosphine oxide derivatives [84]. The photoactivation speeds and emission decay times of these materials could be regulated by the change of the substituent groups. And the different RTP emission behaviors were attributed to the molecular stacking modes. By choosing three RTP systems, FPPO, MeOPPO, and TMeOPPO, an application of multilevel information encryption was investigated. At first, after removing the UV irradiation, only the green RTP of the small house was visible. Upon irradiation at 300 nm for 1 min, the MeOPPO was activated and exhibited a prolonged lifetime. When the photoirradiation time was changed to 20 min, all the pattern could be activated.

This three level encryption could effectively enhance the security level (Figure 4D). Besides, the authors also designed the anti-counterfeiting application based on the thermochromic RTP behaviors of these materials, which also exhibited the great potential for visual temperature detection.

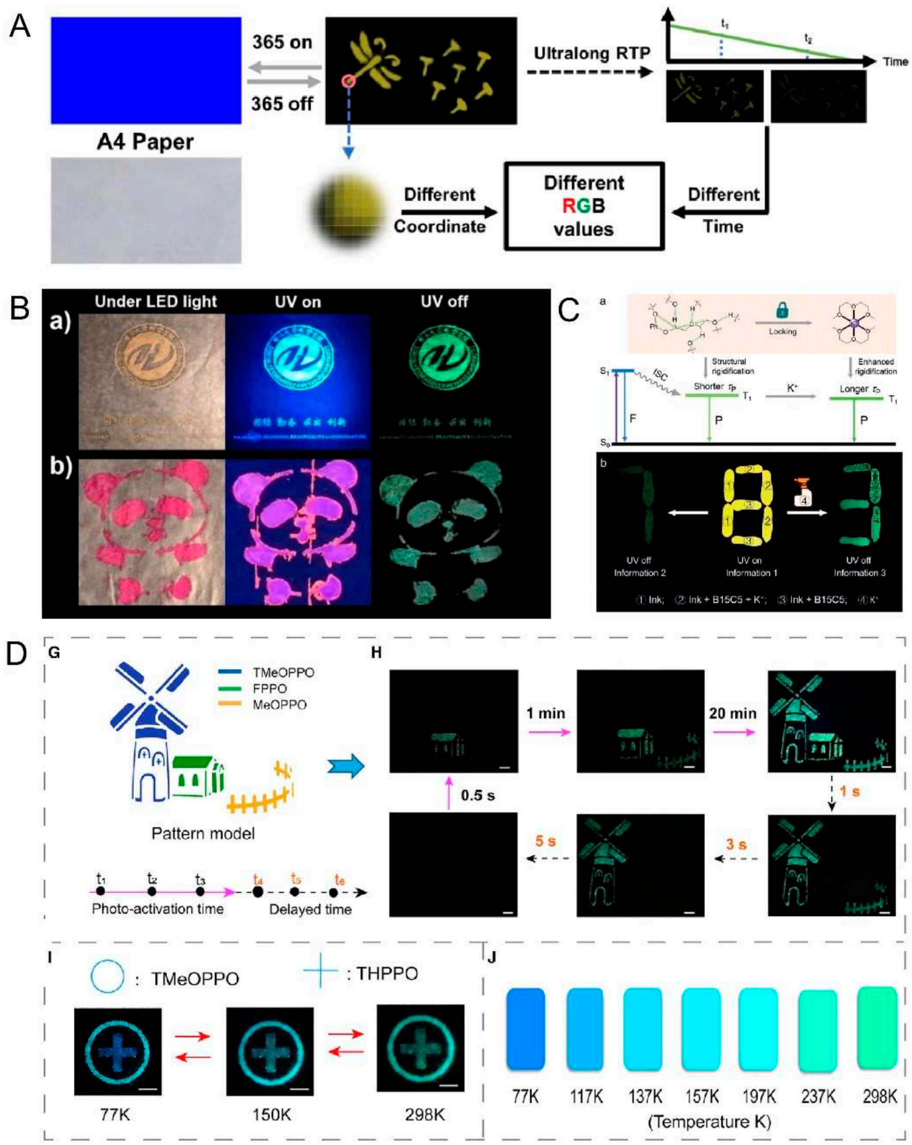

Figure 4. RTP molecular systems based information encryption and anti-counterfeiting. (A) FL-2CN/ABN ethyl acetate ink for information encryption and the RGB value based high level encryption [76]. Copyright 2021, with permission from Elsevier. (B) The MDPA-Ph@DMAP system and energy transfer based anti-counterfeiting application [81]. Copyright 2023, with permission of The Royal Society of Chemistry. (C) RTP from the crown ethers and K^+ for deep information encryption [83]. Copyright 2020 Wiley-VCH GmbH. (D) Triphenylphosphine oxide derivatives with photoactivated persistent RTP behaviors for multilevel information encryption, anti-counterfeiting and temperature sensing applications [84]. Copyright 2021, with permission from Elsevier.

Recently, Ge at al. reported a triphenylmethylamine based single-component phosphors that emitted color-tunable ultralong RTP [85]. Under UV irradiation of different wavelengths, the emission of this RTP material could be ranged from cyan to orange. This characteristic was used for the high level of anti-counterfeiting. In addition, due to the high sensitivity of this RTP material, the UV light ranging from 350 to 370 nm could be detected in a minimal interval of 2 nm.

3.2. RTP Molecules-Matrix Composite Materials

To enhance the spin–orbital coupling, and reduce the nonradiative relaxation induced quenching of the triplet state, crystallization was a usually adopted method to construct RTP materials. Many efforts have been made to pursue RTP materials without the crystallization process. Among these explorations, a simple method that radical binary copolymerization of acrylamide and different phosphors was developed by Tian and coworkers [86]. Through this method, the phosphors could be effectively immobilized with the formed rigid polymer matrix. Besides, the hydrogen bond cross-linking between the polymeric chains could also enhance the rigidity of the luminescence polymers. The authors used this easily prepared amorphous RTP materials for encryption ink. In dry state, the pattern written by this ink showed obvious RTP emission, while the wetting treatment could lead to the hidden of these information.

Similarly, Zhao et al. also designed a strategy to construct amorphous RTP materials [87]. To achieve the embedding of molecular phosphors into the rigid polymer matrices, they used poly (vinyl alcohol) (PVA) as matrix and the hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene as guest molecule. In this system, the nonradiative relaxation of the triplet excitations could be effectively suppressed. Firstly, the diffusional motions of the composite material could be reduced by the strong interaction formed by the hydrogen bonds between the guest and matrix. Secondly, the hydrogen bonds between guest molecules were useful for the promotion of the intersystem crossing processes and the restriction of the vibration. In such case, an RTP film with long lifetimes (up to 0.75 s) and high phosphorescent quantum yields (and 11.23%) was obtained. And this strategy was proven to be suitable for some other molecules. This RTP materials with PVA matrix showed excellent application potentials in the anti-counterfeiting and security. In addition to the normal security based on the afterglow emission, the water in air induced the quenching of RTP through breaking the hydrogen bonds enriched the revisable design for advanced anti-counterfeiting.

Attributed to strong hydrogen bonding with PVA matrix, a series of vanilla derivatives based RTP polymers were also reported by Zhao and coworkers [88]. These polymers exhibited ultralong RTP emission under ambient condition, and the longest lifetime could be up to 7 s from the methyl vanillate-PVA composite materials. Besides, the vanilla-doped PVA films showed temperature-dependent phosphorescence behavior, which should be attributed to the water-related hydrogen bonds breakage and reformation. The authors explored the security ink application of these luminescent materials. The invisible information on a postcard could be visible after the UV irradiation triggered phosphorescence emission. The temperature-dependent RTP emission and quenching showed high reversibility in 50 circles of repeated temperature changes between 0^{o}C and 65^{o}C (Figure 5A). The functional ink could be refilled in the pen and this process was highly feasible and reproducible.

In addition to the above temperature-dependent RTP intensity, the smart PVA functionalized RTP materials with temperature sensitive tunable emission color was also attractive. Xu et al. prepared two RTP materials with two indolocarbazole derivatives IaCzA and IbCzA by using PVA as the matrix [89]. And the IbCzA-doped PVA film exhibited intense blue RTP with excellent phosphorescence quantum yield of 19.8% and long lifetime as 1.8 s. Combined with the fluorescence dye and the temperature sensitivity of the RTP color, a high level anti-counterfeiting and information encryption application was designed. The parts composed of IaCzE-0.1 %-PVA in the patterns exhibited blue fluorescence was shown in the dark gray and gray parts, which was no longer visible after the removing of the UV irradiation. In such case, the pattern of "blooming deep-blue rose" was seen when the UV irradiation was on. However, that parts composed of IbCzA-0.1 %-PVA could still be visible as "rosebud" when the irradiation was off. Besides, the emission color of the rose could be tuned by changing the temperature. And it gradually changed to green when the temperature was changed from 28^{o}C to 0^{o}C, and this process was reversible. This ink was also used for temperature controlled information encryption.

Cucurbit[7]uril (CB[7]) has also been proved to be effective matrix for amorphous RTP materials. Liu et al. prepared a series of RTP materials with CB[7] and acrylamidephenylpyridium copolymers with various substituent groups (P-R: R=-CN, -CO_2Et, -Me, -CF_3) [90]. These RTP materials exhibited second-level RTP emission with lifetimes from 0.9 s to 2.2 s. By introducing the energy acceptors, such as the organic dyes Eosin Y and SR101, room temperature afterglow (RTA) materials was successfully synthesized with the yellow (568 nm) and red (620 nm) emission. With the increased ratio of the energy acceptors, the lifetimes of the RTA emission turned shorter. Based on these characteristics, the authors designed anti-counterfeiting and encryption applications. The time resolution information reading could be achieved with the combination of the RTP and RTA materials. The long lifetime of RTP materials could lead to selectively information reading after the removing of the UV irradiation, such as the green lotus, the "Me" and the tree. And the RTA materials with longer wavelengths could enrich the color of the patterns under the UV irradiation and at the short time after the removing of the UV irradiation. Besides, with the different choices of the RTP materials, time resolved information could also be achieved easily (Figure 5B).

In the above researches, the matrix, such as the PVA and cucurbit uril, are mainly used as the rigid environment to enhance the RTP emission. Actually, the introduced matrix could also be used for the regulation of the RTP emission, or introducing stimulus response attributes. Gao and coworkers for constructed temperature sensitive RTP materials based on a new strategy of the molecular thermal motion modulated RTP emission [91]. Most of the stimulus responsive host-guest RTP systems were based on the reduction of the distances between the two components, resulting in the turn on of the RTP emission. Up to now, there's rare effective methods to enlarge the distances between the two components and led to the reducing of the emission. Combined the usual chromatographic separation method with ubiquitous molecular thermal motion, the authors achieved the separation of the hosts and guests, accompanied by the quenching of the RTP emission. All the normal silica gel, reverse silica gel, and neutral silica oxide could be used for the separation matrix, and the regulation efficiency was determined by the chromatographic separation efficiency of the matrix. Experimental characterization, such as the nuclear magnetic resonance spectroscopy, mass spectrometry, X-ray diffraction spectroscopy, together with the calculation of Gibbs free energy by Gaussian simulation, all confirmed that the quenching mechanism was attributed to the separation of the hosts and guests. This newly constructed stimulus responsive RTP materials was used for multilevel encryption applications. Firstly, with the abundant host-guest RTP systems, a six level temperature responsive encryption was achieved easily. Secondly, decryption of valid messages triggered by specific temperatures further expand the design choices of this material. Thirdly, combined with the RTP systems with different colors and responsive temperatures, thermochromic RTP materials for advanced information encryption could be realized, resulting in the scene of "the resurrection of withered flowers". At last, the detection of the cold chain break could also be achieved due to the wide responsive range of temperature, from the high temperature to room temperature and then to refrigerated temperature (Figure 5C).

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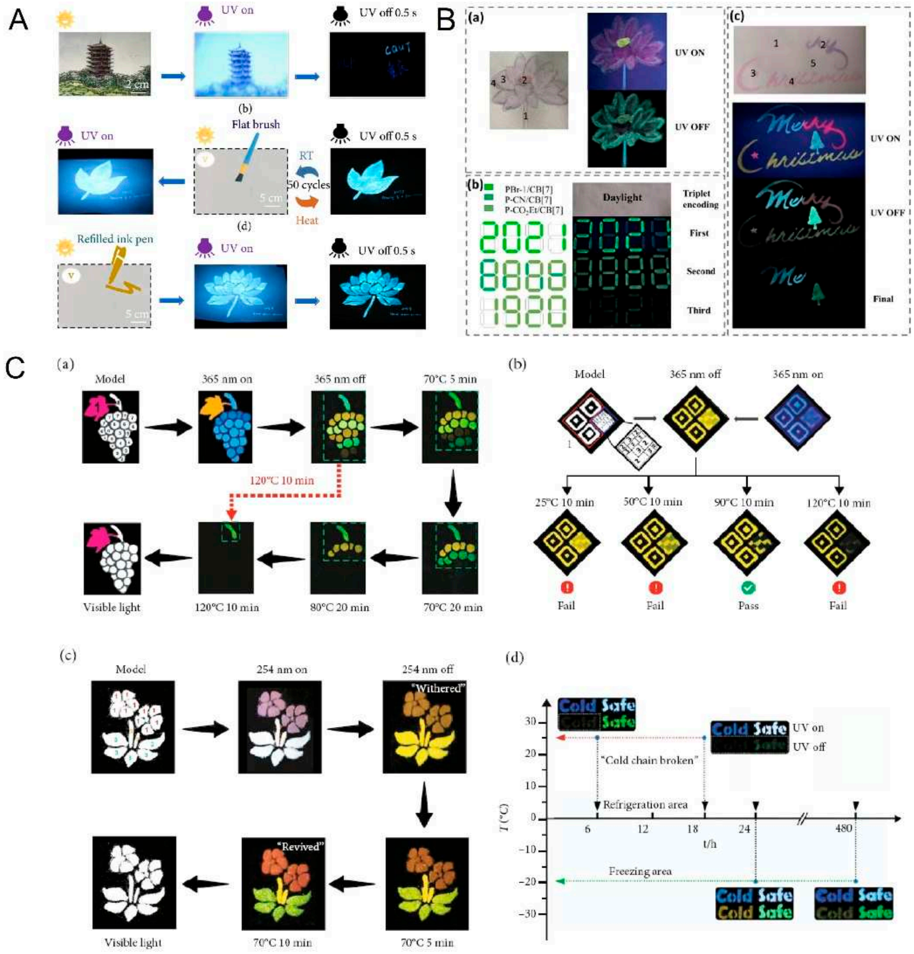

Figure 5. RTP molecules-matrix composite materials based information encryption and anti-counterfeiting. (A) Vanilla derivatives-PVA composite RTP ink for encryption and decryption [88]. Copyright 2021 Exclusive Licensee American Association for the Advancement of Science, distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC). (B) RTP materials from cucurbit[7]uril and acrylamidephenylpyridium copolymersm, together with some energy transfer composites, for anti-counterfeiting and information encryption [89]. Copyright 2022 Wiley-VCH GmbH. (C) Molecular thermal motion modulated RTP for multilevel information encryption and detection of cold chain break [91]. Copyright 2022 Exclusive Licensee American Association for the Advancement of Science, distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

3.3. Phosphorescent Carbon Dots

PVA, which had been proven a universal matrix for constructing temperature responsive RTP materials, was also successfully used for preparation of thermal-treatment controlled RTP CDs/PVA composite materials [92]. Qu et al. embedded originally synthesized CDs (CD 1) or 200 °C thermal-treated CDs (CD 2) into the PVA matrix through post-synthetic thermal annealing at 200 or 150 °C. After annealing, both of these two films showed phosphorescence. The control experiment with bare PVA film revealed that the luminescence was attributed to the embedded CDs. The CD 2 embedded PVA films showed visible phosphorescence after the annealing at 150°C or 200°C, while the CD 1 embedded films only showed phosphorescence after the annealing at 200°C. According to these characteristics, multilevel encryption was realized. Under UV irradiation, all the information could be visible in the form of blue luminescence. However, only the first level of encryption “CD”, which was written with the CD 2, could be seen after the annealing of 150°C. All the CD 1 and CD 2 based information “CDots” showed green phosphorescence, which was the second level information decryption (Figure 6A).

By a two-step hydrothermal process, Li et al. prepared a kind of phosphorescent CDs, which showed blue fluorescence and green phosphorescence [93]. During the synthesis process, the Vitamin B1 was used as the raw material, and the ethylenediamine was used as a passivator. After the first

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hydrothermal process, the boric acid was used as a phosphorescent enhancer, which led to the enhanced intersystem crossing efficiency. The lifetime of the green phosphorescence was 293 ms, which could be used for the simple time resolved anti-counterfeiting together with the blue fluorescence emission. With the assistance of non-phosphorescent material, the CDs could be used for higher level encryption by selectively turning on the phosphorescence of the "U" and "T". Furthermore, The stimulus responsive property could enrich the design choices. For these CDs, the wetting treatment could also lead to the quenching of the phosphorescence of the "S" and "C" accompanied with the decreased blue fluorescence emission of these two letters (Figure 6B).

Through the fluorine-nitrogen co-doping strategy, Feng et al. also synthesized a kind of phosphorescent CDs exhibited ultralong lifetime of 1.14 s and an excellent quantum yield of 8.3% [94]. Similarly, the co-doping of fluorine and nitrogen was achieved by the second hydrothermal process. By using a commercial inkjet printer, the fluorine and nitrogen co-doping CDs (FNCDS) and the nitrogen doping CDs (NCDS) was used as security ink. Based on the time resolution, the true information, including the "1895", the "JOB", the QR code, and the school badge, could be visible attributed to the green phosphorescence emission (Figure 6C).

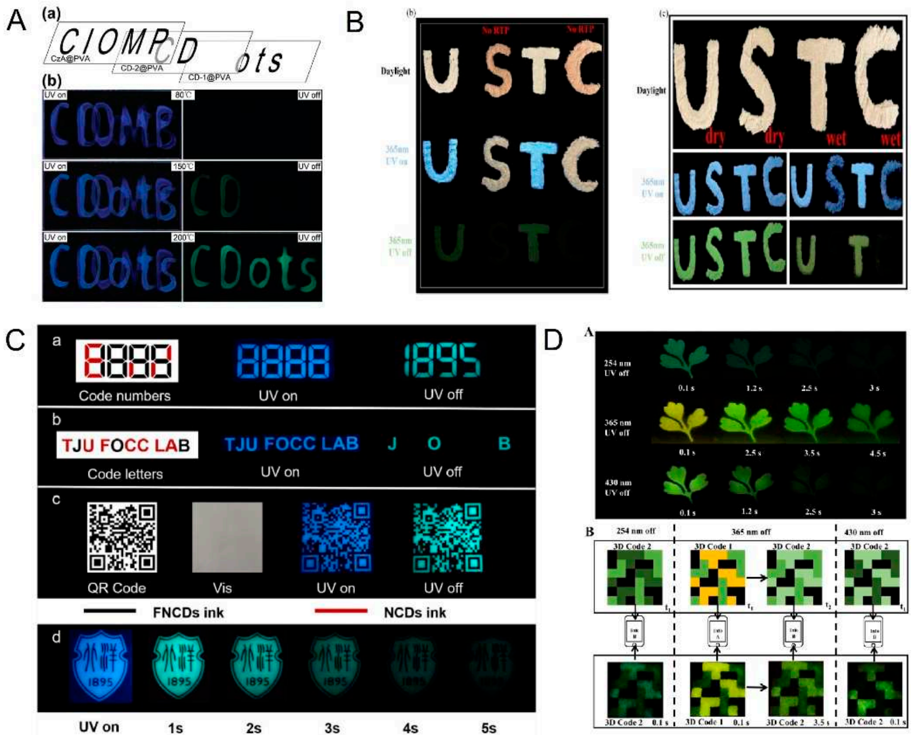

Figure 6. Phosphorescent carbon dots based information encryption and anti-counterfeiting. (A) Thermal-treatment controlled multilevel fluorescence/phosphorescence encryption with citrazinic acid (CzA@PVA), CD-1@PVA, and CD-2@PVA composites. [92]. Copyright 2018 Wiley-VCH GmbH. (B) Boron doping phosphorescent CDs for anti-counterfeiting and information encryption [93]. Copyright 2022, MDPI. (C) FNCDs and NCDs based information storage and anti-counterfeiting [94]. Copyright 2021, with permission from Elsevier. (D) Multilevel information encryption based on the CDs/$Na_{0.5}Mg_{0.25}Cl$ with UV irradiation of different wavelengths [95]. Copyright 2023 Wiley-VCH GmbH.

The time-dependent phosphorescence color (TDPC) materials play important roles in the high level information encryption and security. Recently, Lu and coworkers realized the TDPC property of CDs by binary salt matrices, namely the inorganic NaCl and metal (Mg^{2+} or Ca^{2+} or Ba^{2+}) doping. Besides, the TDPC of the CDs could be excited by the UV irradiation at extent wavelengths. Based on these characteristics, these TDPC CDs were used for high level information encryption. Firstly, only after the irradiation with 365 nm, the CDs/$Na_{0.5}Mg_{0.25}Cl$ exhibited the obvious TDPC property with the emission color from yellow to green. However, after removing the 254 nm and 430 nm irradiation, the phosphorescence color was green, without clearly visible changes. Furthermore, a 3D code with switchable phosphorescence colors was realized based on this material, which can realize a dynamic phosphorescence signal over time with the decryption wavelength of 365 nm (Figure 6D).

4. Conclusions and Perspective

The AIEgens and RTP materials are two classical AIE materials, and they exhibit attractive applications in the field of anti-counterfeiting and information encryption recently. Furthermore, the AIEgens and RTP materials with stimulus responsive property are essential to the intelligent and high level security designs, which can be applied to more application scenarios elementary encryption and anti-counterfeiting technologies, for example the time resolution based ones.

Undoubtedly, more and more stimuli-responsive AIEgens and RTP materials will be developed in the future, and it's worth looking forward to the their important contributions in the information protection market. For further development of stimulus responsive AIEgens and RTP materials, two types are highly expected: (a) the decryption of information depends on specific stimuli, such as a specific temperature or acidity. (b) Combing with the functional matrix, to obtain smart luminescent materials with multilevel responsive or multi-stimulus responsive properties. In such cases, high level of security and information protection could be realized.

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