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PERSPECTIVE

Stimuli-Responsive Molecules: Emerging Materials for Advanced Data-Encryption and Anti-Counterfeiting

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Data security is a long-term challenge that spans the whole history of human society, particularly in the field of commercial activities and military actions. To date, a variety of data protection techniques have been developed. Early examples include watermarks and holograms.[1] Later, color-shifting inks and luminescent patterns had been developed as well. These techniques are widely used in daily life, such as banknotes, passports, certifications, identification cards, packaging, product labels, authorized documents, and many others.[2] Among these, luminescent materials are particularly attractive due to their characteristic emission features, naked eye readout upon UV light irradiation, and good handleability. The progresses in the development of fluorescent/phosphorescent molecules have greatly nourished the research on security ink and notably advanced the date-encryption and anticounterfeiting technologies. However, unicolor luminophores or blends of luminescent materials are not secure anymore, as it is not difficult to find other fluorophores with similar emission colors or wavelengths.[1]

To further enhance the data security level, a wealth of stimuli-responsive fluorophores that are capable of providing diverse and dynamic emission features has been developed recently (Figure 1). Photo-controlled supramolecular switches represent the first type of dynamic security ink showing reversible color change upon light irradiation with a specific wavelength. For example, co-assembling diarylethene (DAE) with ionic ligands,[3] metal-organic framework (MOF), or dibenzo-24-crown-8 results in supramolecular inks that could be reversibly and repeatedly erased and recovered by altering the wavelength of irradiation light.[4] Azobenzene and anthracene units have also been used in photo controlled supramolecular inks via a photo-isomerization and photo-oxidization mechanism,[5] respectively. Additionally, thermochromic dyes such as fluoran derivatives and polydiacetylenes (PDA) are also highly promising materials for secret codes. Specifically, fluoran derivatives are able to undergo a rapid ring opening and closing upon heating up and cooling down, and thus change the emission intensity and color of the assembly.[6] As for PDA, it exhibits a blue-to-red transition when being heated up due to the structural distortion of the alternating eneyne polymeric backbone.[7] Similar structural transition of PDA was obtained by exposure/removal of water as well, giving rise to a new type of smart molecule, denoted as “hydrochromic” dye,[8] and enabling water-jet-based rewritable printing. Later, the electrical field is exploited to switch the emission of luminophores via reversible redox reactions, which is termed “electroluminochromism”. For example, Sun et al. developed a security ink with a multicolor “on-off” luminescence based on viologen-substituted iridium(III) complexes through regulating the ligand orbital energy levels and electric communication between the viologen pendants and the iridium(III) complex core. Moreover, the emission wavelength of electroluminescent materials can be extended to near-infrared regions, and therefore offers an attractive platform for information encryption.[9] Besides the above luminophores, mechanoluminescent material is another interesting dye for data protection. Sun et al. reported a hybrid $Sr_3Al_2O_6:Eu^{3+}$/polydimethylsiloxane elastomer composite that shows highly efficient mechanoluminescence under mechanical stimulation. The data are invisible initially but can be clearly seen upon stretching the elastomer.[10] Photochromic molecules such as multi-responsive donor-acceptor Stenhouse adducts (DASAs) have also been intensively studied as novel data-encryption data. For example, Huang et al. realized a sequential data encryption via harnessing the isomerization of DASAs in the polymer gels.[11]

Notably, with the fast development and deeper understanding of aggregation-induced emission (AIE) behavior, AIEgens have been intensively applied to data encryption.[12] Tang et al. incorporated a pH-responsive AIE luminogen into a hydrogel containing clays and achieved input of fluorescent information with a high contrast ratio in the gel by acid stimulation.[13] The same group developed a novel tetraphenylethylene (TPE) derivative that is susceptible to external forces, heating and vapor fuming, and provides double enhancement of a multimode guarantee in advanced anti-counterfeiting.[12]

Remarkably, luminophores producing ultralong room temperature phosphorescent (RTP) via efficient intersystem crossing (ISC) after switching off the excitation light are of high interest as well and have been widely used in data protection through a time-gated readout fashion.[14] Similar concept has also been applied in a fluorescent system, though the readout is implemented by a time-gated imaging device rather than the naked eyes.[1]

Our group has recently developed a type of novel fluorophores based on phenanthridine derivatives that show bathochromic emissions in rigidifying mediums.[15] Due to their opposite photophysical behaviors with regard to the conventional probes, they were termed as “anti-rigidochromic” fluorophores. In these fluorophores, the phenanthridine unit strongly interacts with the polymer via polar-π interactions and sequentially forms a charge-transfer

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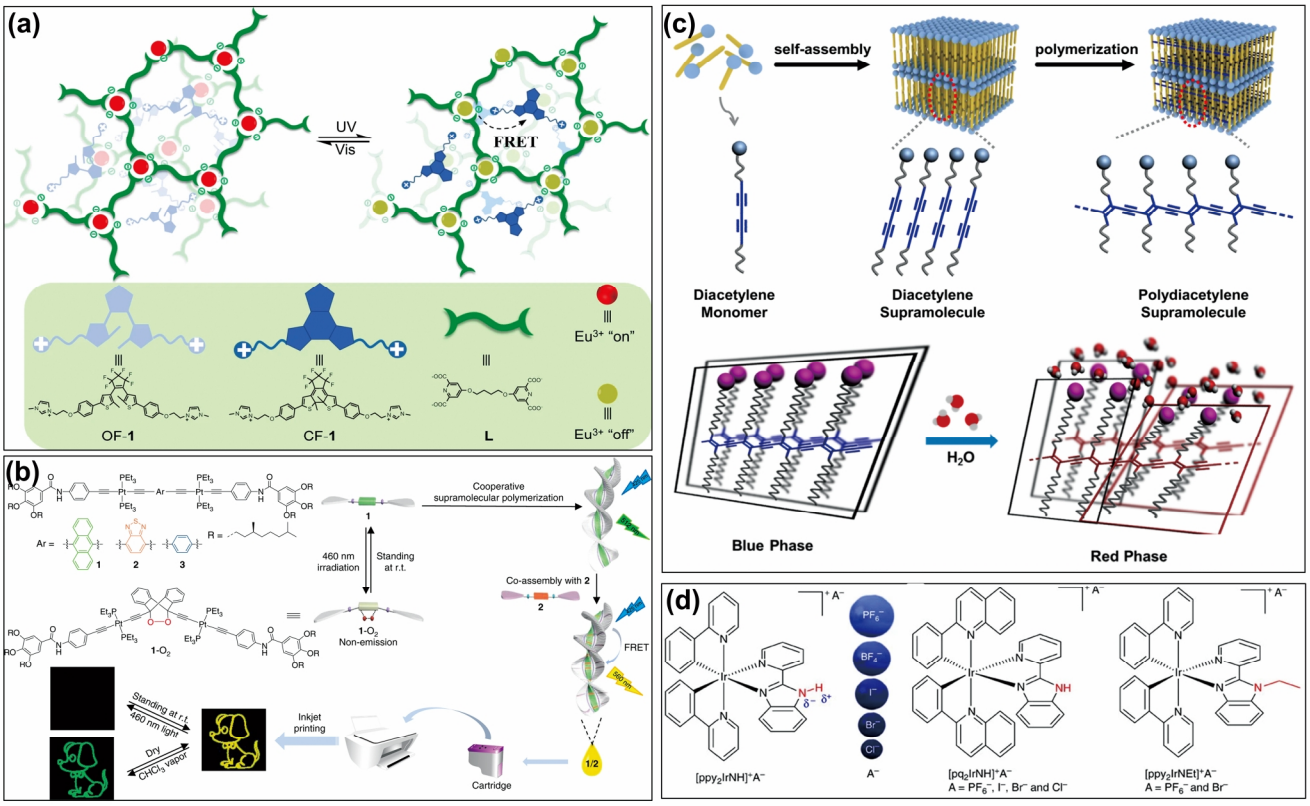

Figure 1. Photo controlled supramolecular switch based on (a) co-assembly of DAE with ionic ligand, and (b) anthracene-endoperoxide. (c) Schematic illustration of self-assembly of diacetylenes and the sequential polymerization, and water-promoted phase transition of the PDA. Reprinted with permission from Ref 7. Copyright 2022 American Chemical Society. (d) Chemical structures of the iridium (III) complexes.

complex between the fluorophore and polymer matrixes, leading to the "anti-rigidochromism". Moreover, the efficient coupling between anti-rigidochromism and polymer hierarchical structures/topologies renders a multi-dimensional (wavelength and chirality) tunability to the fluorophore emissions (Figure 2).

Relying on above unique features, we developed a free-volume-based data encryption and anticounterfeiting method with a high-security level.[15] Note that this free-volume-based data encryption is fundamentally different from those invisible ink-based methods. Those inks are chemically different from the substrates where they have been written on, therefore rising the risk of data deciphering by advanced instrumental analysis, e.g., elemental analysis, XPS, and many others. However, in this free-volume encrypted film, the data and the background share identical chemi cal structures, elemental compositions and ratios, making it virtually impossible to chemically decipher the data and remarkably improve the security level.[15]

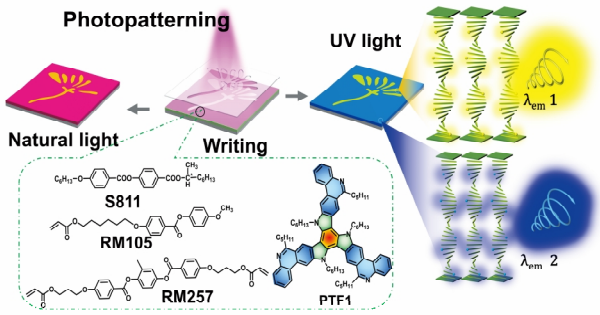

Figure 2. Schematic illustration of the anti-counterfeiting technique based on the coupling between anti-rigidochromism and polymer topology.

Overall, significant progress has been made in the field of smart molecule-based security ink, which is driven by the advancements of synthetic/supramolecular chemistry, a deeper understanding of photophysical behaviors and underlying mechanisms, and inspiring interdisciplinary achievements. The diverse and dynamic emission features of the smart multi-stimuli responsive molecules render a very low risk of counterfeiting and thus significantly enhance the data security level. However, there are several unmet challenges of stimuli-responsive molecule-based security inks before their practical applications, such as poor long-term stability, inferior antifatigue ability, low handleability, and high cost. It is envisioned that exploiting new fluorophores with fused molecular structures would improve the stability and antifatigue ability. Moreover, the progress in synthetic chemistry as well as achievements in the chemical engineering would notably bring down their costs. Tackling the above challenges will be the definite goal of future endeavors, and helps to commercialize these smart materials for much broader applications.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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