Journal of Functional Materials and Applied Engineering

Resview Paper

Research Progress on Aggregation Science-Enabled Luminescent Materials from Forest Biomass

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Abstract. Most traditional natural products exhibit weak or no luminescence owing to the lack of large conjugated systems. Moreover, the strategy of introducing luminescent chromophores to modify these natural products is often hampered by aggregation-induced quenching (AIQ) effects. In recent years, aggregate science-based research on forestry biomass-derived luminescent materials has successfully addressed this technical bottleneck, thus establishing forestry biomass as a vital reservoir for luminescent material development. From the perspective of aggregate science, this paper outlines two luminescence mechanisms centered on restricted molecular motion. It systematically summarizes the latest research progress in luminescent materials derived from forestry biomass and practical application attempts in intelligent anti-counterfeiting, bioimaging, food detection, and other fields, classified into three categories: natural small molecules, derivatives of natural small molecules, and natural polymers and their derivatives. Finally, future research directions are proposed, offering novel research insights and development directions for the innovative utilization of forestry biomass.

Keywords: *Forest biomass; aggregation science; restriction of molecular motion; luminescent materials*

Received on 15 Feb 2023, Accepted on 15 Apr 2023, Published on 28 Apr 2023

1 Introduction

Currently, luminescent materials derived from forest biomass are developing rapidly and have attracted widespread attention from researchers. The common preparation method for such materials is the chemical modification of forest biomass to introduce classic chromophores. However, these chromophores often exhibit aggregation-caused quenching (ACQ) effects, leading to poor performance of the materials under solid-state conditions, which are typical for practical applications. This is not only a challenge for forest biomass luminescent materials but also a significant problem in the design and application of organic luminescent materials. In 2001, Academician Tang Benzhong proposed the concept of aggregation-induced emission (AIE), which changed the perspective on forest biomass. AIE refers to a phenomenon where luminescence in the aggregated state is significantly stronger than in the dispersed state. Molecules exhibiting AIE typically possess highly twisted conformations, resulting in weak or no emission in the single-molecule state, but enhanced emission upon aggregation. On the 20th anniversary of the AIE concept, Academician Tang Benzhong and his international collaborators reviewed the history, current status, and future of AIE research, proposing the concept of Aggregate Science. The proposal of the Aggregate Science concept allows for a multi-dimensional examination of new structures and properties generated during aggregation. For most natural products, aggregation is the norm. Biological macromolecules such as DNA, proteins, cellulose, hemicellulose, and lignin are formed by the aggregation of individual molecular chains through intermolecular interactions, creating functional organizational structures that play crucial roles in biological physiological activities. Therefore, using the concept of Aggregate Science, researchers can re-examine the structures of these natural products, particularly exploring them in depth from the perspective of luminescent materials. In the traditional view, natural products are considered to have weak or no luminescence due to the lack of large aromatic rings or π-conjugated systems. However, recent research based on Aggregate Science has broken this inherent thinking, establishing natural products as a treasure trove for developing high-performance fluorescent materials. Forest biomass is an important source of natural products. Guided by Aggregate Science, developing luminescent materials from forest biomass can leverage its unique structure to impart renewable and sustainable characteristics to the materials while promoting the high-value utilization of forest biomass, thereby empowering its high-value application. Therefore, this article will introduce the luminescence mechanisms of aggregated luminescent materials from forest biomass and summarize recent research in this field from the perspective of Aggregate Science, aiming to provide references for the development and application of such materials.

2 Forest Biomass and Aggregate Science

2.1 Aggregate Science

Aggregate Science is an emerging paradigm and philosophical research approach, belonging to holistic thinking that starts from the system as a whole, distinct from reductionism which deconstructs systems. Before introducing Aggregate Science, it is necessary to first introduce the AIE concept. Some luminescent materials exhibit intense luminescence in the solid state or in concentrated solutions but do not emit in dilute solutions. This special luminescence mechanism is called AIE. Although this luminescence phenomenon was not uncommon, it did not receive much attention from researchers until Academician Tang Benzhong's team proposed AIE in 2001. The team discovered it by chance, investigated it in depth, and clearly defined 50% (volume fraction) as the threshold, beyond which luminescence intensity increases sharply with aggregation degree, thus naming it AIE and exploring the relationship between molecular structure and luminescent properties from the perspective of aggregates. Subsequently, AIE gained widespread recognition and developed rapidly over the past 20 years. Aggregate Science is a research paradigm distinct from traditional molecular science. Traditional molecular science focuses on the isolated relationship between molecular structure and properties, while Aggregate Science integrates molecular structure and intermolecular interactions to study the structure and properties of aggregates, breaking through the limitations of individual molecules on material performance and expanding application scenarios.

The properties or performance of aggregates are generally determined by intermolecular interactions, packing, blending, or different morphological forms. Currently, these aggregates can be classified into three categories: single-component aggregates, two-component aggregates, and multi-component aggregates. Single-component aggregates are the most common, and research on them generally involves only the intrinsic structure of the molecules and their stimulus responsiveness. Two-component and multi-component aggregates are relatively hot research areas in recent years, especially in the field of room-temperature phosphorescence materials, where blending small molecules with other small molecules or doping small molecules into polymer matrices is used to develop luminescent materials with long lifetimes and long afterglow. Compared to single-component systems, these two types of systems more frequently consider intermolecular interactions. The competitive or synergistic interactions involved in the aggregation process can be further subdivided into four effects: antagonism, synergism, emergence, and divergence. In summary, current research in Aggregate Science is no longer confined to simple luminescence phenomena; it reshapes the understanding of photophysical processes and material properties, motivating researchers to develop more novel functional materials.

2.2 Forest Biomass

Compared to Aggregate Science, an emerging disciplinary research paradigm, biomass is a concrete resource closely associated with human production and life. From crops in daily diet to flora, fauna, and microorganisms in nature, and even various organic wastes, biomass permeates all aspects of ecological cycles and socio-economic development in various forms. Among them, forestry biomass chemicals such as cellulose, lignin, hemicellulose, and natural small molecules generated during forestry production and processing are important raw materials for the high-value utilization of biomass. Their deep processing industry is a significant component of China's national economy. Technologies for processing forestry biomass include physical, chemical, or biochemical methods, collectively referred to as forest chemical processing technologies. The manufacturing industry formed based on this technology is called the "Forest Chemical Industry," an important part of the biomass deep processing industry. With technological advancements, biomass chemicals are extending from basic chemical raw materials to high-value-added fine chemicals. Improving the high-value utilization level of biomass chemicals is a core development direction for agroforestry processing industries (such as forest chemical engineering). Academician Jiang Jianchun, summarizing the current development status of the modern forest chemical industry, pointed out that bio-based functional materials and chemicals have become an important part of forest chemical product innovation, helping to promote the development of strategic emerging industries for forest biomass. Moreover, deep interdisciplinary integration has become a trend in forest chemical engineering technology, promoting the construction of a new cross-border integrated technological innovation system. Therefore, introducing Aggregate Science into the forest biomass field is beneficial for promoting the rapid development of the forest chemical engineering discipline.

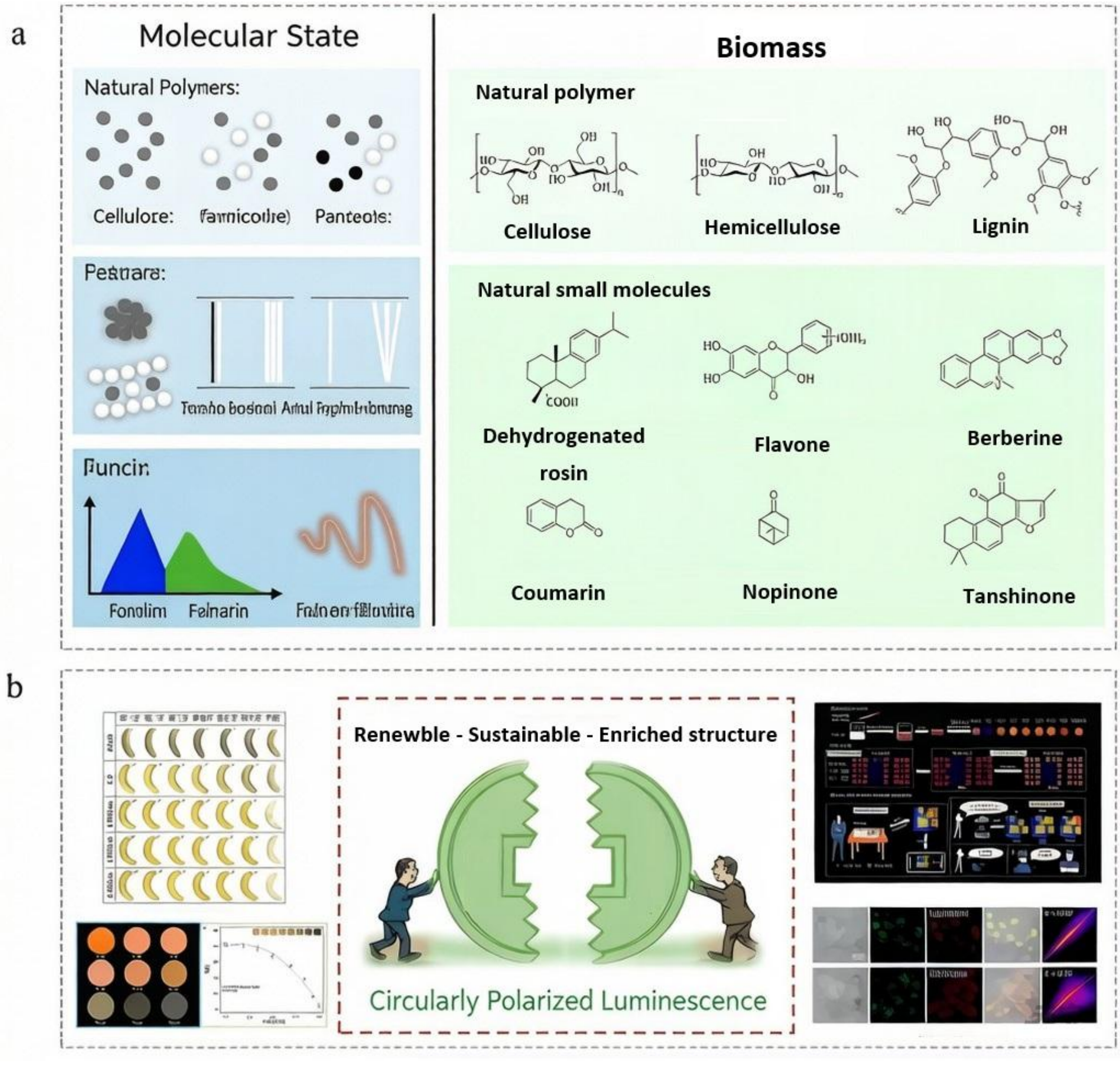

Figure 1 Aggregate Science (AS) and Forest Biomass (FB)

a. Basic concepts of AS and structural classification of FB; b. A win-win strategy between AS and FB

2.3 The Relationship between Forest Biomass and Aggregate Science

Is there a connection between Aggregate Science and forest biomass? A deeper understanding reveals that they are indeed intricately linked. Taking proteins as an example: the basic building blocks of proteins are 22 amino acids, which form polypeptides via peptide bonds; proteins are constituted and function through the intermolecular interactions of one or more polypeptides, a process analogous to the "emergence" property in Aggregate Science. Another example closer to the field of forest biomass is cellulose: cellulose is a natural polymer formed by D-glucopyranose units connected via β-1,4-glycosidic bonds. Through hydrogen bonding interactions, it further forms microfibrils, which, together with other polysaccharides like hemicellulose and pectin, and components like lignin and proteins, construct the plant cell wall through intermolecular interactions. This process is analogous to the "synergism" property in Aggregate Science. Furthermore, the concept of clusteroluminescence in Aggregate Science originated from the study of luminescent behaviors of natural polymers. Academician Tang Benzhong's team first reported that natural compounds and polymers such as starch, cellulose, bovine serum albumin, and some carbohydrates, which emit almost no light in solution, emit bright phosphorescence in the crystalline state with lifetimes reaching the microsecond level. Common natural small molecules in the forest biomass field, such as quercetin, myricetin, morin, berberine, palmatine, tannic acid, digitonin, vitamin B2, and tanshinone IIA, have also been reported to exhibit AIE phenomena. Additionally, developing AIE materials using natural molecular structures as the core is an important research direction in the current AIE field.

In short, Aggregate Science provides theoretical and technical support for the in-depth development of forest biomass, while forest biomass provides typical application scenarios and research carriers for Aggregate Science. Therefore, forest biomass and Aggregate Science do not exist in isolation but can learn from and co-develop each other, achieving a win-win situation.

3 Luminescence Mechanisms—Restricted Molecular Motion

3.1 Overview

Before introducing the luminescence mechanisms involved in current forest biomass luminescent materials, the basic principles of molecular luminescence are briefly explained: Luminescence is the process where a substance absorbs energy, causing electrons to transition from the ground state to an excited state, followed by the release of energy via radiative transition. After a molecule absorbs a photon, an electron transitions from the ground state (S0) to an excited singlet state (S1, S2, etc.). Through vibrational relaxation and internal conversion, it descends to the lowest vibrational level of S1 and returns to S0 via radiative transition, emitting fluorescence. Alternatively, it can undergo intersystem crossing from S1 to an excited triplet state (T1), relax vibrationally, and then return to S0 via radiative transition, emitting phosphorescence. If the electron returns to the ground state via non-radiative transitions, the energy is dissipated as heat or other non-luminescent forms. Therefore, the core idea for achieving molecular luminescence is to suppress non-radiative transitions from the excited state and promote radiative transitions. So, how can non-radiative dissipation of excited-state energy be suppressed? Aggregate Science achieves this by restricting molecular motion. Currently, the luminescence mechanisms of forest biomass luminescent materials designed based on Aggregate Science are mainly divided into two categories: 1) Restricted intramolecular motion (RIM) for small molecules; 2) Spatial confinement involving polymers.

3.2 Restricted Intramolecular Motion

The restricted intramolecular motion (RIM) mechanism is the core of AIE luminescence mechanisms. When molecules are in an aggregated or crystalline state, due to steric hindrance or intermolecular interactions (such as hydrogen bonding, π-π stacking), their intramolecular motions are inhibited. This leads to the blocking of non-radiative transition pathways for excited-state energy, ultimately releasing energy in the form of radiative transitions, thereby enhancing luminescence efficiency.

When a molecule is in the single-molecule state, upon excitation, it can dissipate energy through rotational and vibrational processes of the molecular skeleton, resulting in extremely low luminescence efficiency in the single-molecule state. After molecular aggregation, due to intermolecular interactions, the motion of rotatable or vibrational groups within the molecule is hindered or restricted. Simultaneously, highly twisted molecular structures can effectively avoid strong π-π interactions caused by planar rigid structures (such interactions easily lead to fluorescence quenching). The combined effect of these factors allows the molecules to maintain high fluorescence emission efficiency in the aggregated state. For example, our research group modified dehydroabietic acid to obtain the precursor compound 1,2-brominated methyl dehydroabietate (DAMB), and then reacted it with different substituted salicylaldehydes, successfully developing a novel bio-based aggregation-induced emission material (BioAIEgen). Its core mechanism is that the alicyclic part of dehydroabietic acid suppresses excited-state molecular motion, reducing non-radiative transitions. At the same time, molecular interactions are regulated through substituents, ultimately achieving AIE characteristics.

3.3 Spatial Confinement

The restricted intramolecular motion mechanism mentioned in Section 2.2 is primarily based on small molecules. Expanding the research perspective to the polymer field, a similar phenomenon of restricted molecular motion exists, referred to as spatial confinement. Its core mechanism lies in: the rigid structure formed by polymer chains spatially restricts or inhibits the rotation or vibration of chromophores through intermolecular interactions. Simultaneously, the steric hindrance of polymer chains can also prevent excessive π-π stacking of chromophores leading to quenching, thereby maintaining efficient luminescence. This confinement can be achieved through three approaches: polymerizing the chromophore into the polymer backbone, grafting it onto the polymer side chains, or directly physically doping it into the polymer network. When non-conjugated system polymers like cellulose and hemicellulose contain heteroatoms such as oxygen and nitrogen, they can not only provide a rigid environment through hydrogen-bond networks to restrict molecular motion but also stabilize the excited triplet state of molecules and isolate oxygen, which is conducive to achieving phosphorescence emission and preparing room-temperature phosphorescence (RTP) materials. The phenomenon where substances lacking traditional aromatic conjugated structures do not emit light in the single-molecule state but emit bright visible light in the aggregated state upon photoexcitation is called clusteroluminescence (CTE). Professor Chen Zhijun's group prepared a photoactivated RTP material, PLA-Lig, by in-situ polymerization covalently grafting lignin (chromophore) with polylactic acid (PLA, matrix). Compared to blending, the covalent grafting of PLA and lignin reduces the distance between aromatic units to 0.42 nm, enhancing the spatial confinement effect, promoting π-π interactions, and stabilizing triplet excitons, providing a structural basis for RTP. Simultaneously, PLA restricts lignin molecular motion via covalent bonds, inhibiting non-radiative transitions.

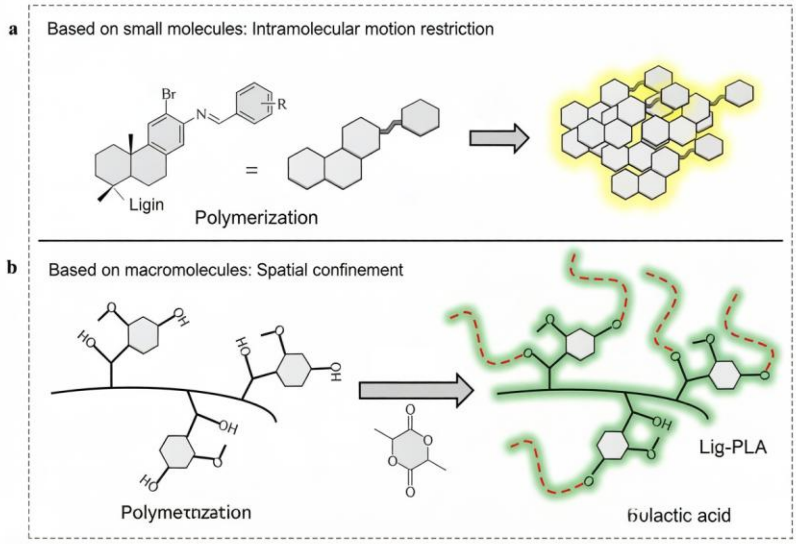

Figure 2 Types of restricted molecular motion

Based on the above analysis, it can be seen that whether it is the RIM luminescence mechanism based on small molecules or the spatial confinement luminescence mechanism based on polymers, the core of both is based on restricting the molecular motion of chromophores, minimizing non-radiative losses in the excited state and favoring the release of energy via radiative transitions.

4 Aggregate Science-Based Luminescent Materials from Forest Biomass

4.1 Natural Small Molecules

Some common natural product categories (such as alkaloids, polyphenols, saponins, diterpenes, and sugars) contain natural small molecules reported to exhibit AIE phenomena.

Academician Tang Benzhong's team reported the AIE phenomenon of berberine (hydrochloride) in 2018. The study found: the nitrogen-containing heterocyclic ring in the molecular structure is prone to torsional vibration, and berberine exhibits emission redshift in solvents of different polarities. Its AIE phenomenon originates from restricted intramolecular torsional vibration and the twisted intramolecular charge transfer (TICT) effect. Li et al. reported the application of berberine as an aggregation-induced emission photosensitizer in photodynamic antibacterial therapy. Through minimum inhibitory concentration determination and anti-biofilm experiments, it was found that berberine could completely kill Listeria monocytogenesat a concentration of 10^5 CFU/mL under white light irradiation. Furthermore, palmatine from Fibraurea recisa, sanguinarine, and chelerythrine from Chelidonium majushave also been reported as natural products with AIE properties.

A representative AIE molecule among polyphenolic compounds is quercetin, which was found to exhibit excited-state intramolecular proton transfer (ESIPT) behavior. Due to its low cytotoxicity and sensitive fluorescence response, Professor Chen Zhijun's group further applied quercetin as a fluorescent probe for fluorescence imaging and tracking in mice. Some flavonoid polyphenols such as myricetin, morin, kaempferol, mangiferin, and epigallocatechin gallate have been reported to exhibit AIE phenomena. Li et al. prepared flavonol nanocrystals derived from quercetin, myricetin, and kaempferol, which combine AIE characteristics with antibacterial, antioxidant, and alkali-sensitive (colorimetric and fluorescence dual-mode) functions. Among them, myricetin nanocrystals, due to a higher number of phenolic hydroxyl groups, are most sensitive to alkalinity. Verified by hemolysis tests (hemolysis rate <5%) and acute oral toxicity tests, these nanocrystals exhibit good biocompatibility in vitro and in vivo, providing a green solution for multifunctional food packaging materials.

Tanshinone IIA (Tan IIA) is a diterpenoid quinone compound. In 2022, Academician Tang Benzhong's team reported the AIE properties of tanshinone IIA. Tan IIA dissolved in DMSO exhibits almost no fluorescence emission, but as the water content increases, red fluorescence emission significantly enhances. Tan IIA has good Diels-Alder (D-A) interaction and electron delocalization, allowing free vibration in the solution state. Upon aggregation, the molecules adopt a twisted conformation, leading to restricted molecular motion, thereby achieving AIE luminescence enhancement.

Furthermore, the latest report found that sucrose exhibits AIE and crystallization-induced emission (CIE) properties. Its CIE mechanism originates from the polyhydroxy structure of sucrose forming oxygen clusters upon aggregation, generating spatial conjugation effects. Intermolecular and intramolecular interactions form a rigid conformation, inhibiting non-radiative transitions. The solid-state quantum yield (6.05%) is much higher than in the solution state. Meanwhile, due to its good water solubility and low cytotoxicity, sucrose can serve as a biosensor for real-time monitoring of fruit freshness. On the other hand, under 660 nm illumination, it can form a complex with Fe^{3+}, generating singlet oxygen ($^1O_2$) and reactive oxygen species (ROS) via a Fenton-like reaction, exerting photodynamic antibacterial effects against E. coliand S. aureus.

Fluorescence is a characteristic physical property of coumarins, often showing blue fluorescence under UV light. Therefore, AIE materials with coumarin as the core are numerous, but reports on the AIE properties of natural coumarin structures are relatively few. The latest research first reported two rotor-free AIE coumarin isomers isolated from the fluorescent roots of the medicinal plant Toddalia asiatica, namely 5-methoxyoxypeucedanin (5-MOS) and 6-methoxyoxypeucedanin (6-MOS). Among them, 6-MOS achieves aggregation-enhanced emission (AIEE) through the traditional RIM mechanism; while 5-MOS requires the assistance of protic solvents (like water) to form aggregates of varying degrees. Photoexcitation leads to electron/energy transfer, resulting in weak emission in the aqueous aggregated state (almost no emission at 99% water content, fw), but its crystals exhibit strong emission (quantum yield 18.5%) due to ordered assembly avoiding energy transfer.

Currently, although natural small molecules have advantages such as renewability, non-toxicity/low toxicity, biodegradability, biocompatibility, and pharmacological activity, they still account for a relatively small proportion in Aggregate Science research due to disadvantages like low content, difficult extraction, and limited variety. Nevertheless, natural small molecules remain a vast treasure trove to be deeply explored. Currently, research related to the clusteroluminescence mechanism is emerging and continuously improving. It is believed that with the aid of the clusteroluminescence mechanism, the development of natural small molecules in the forest chemical engineering field will accelerate, thereby promoting the rapid development of the forest chemical industry.

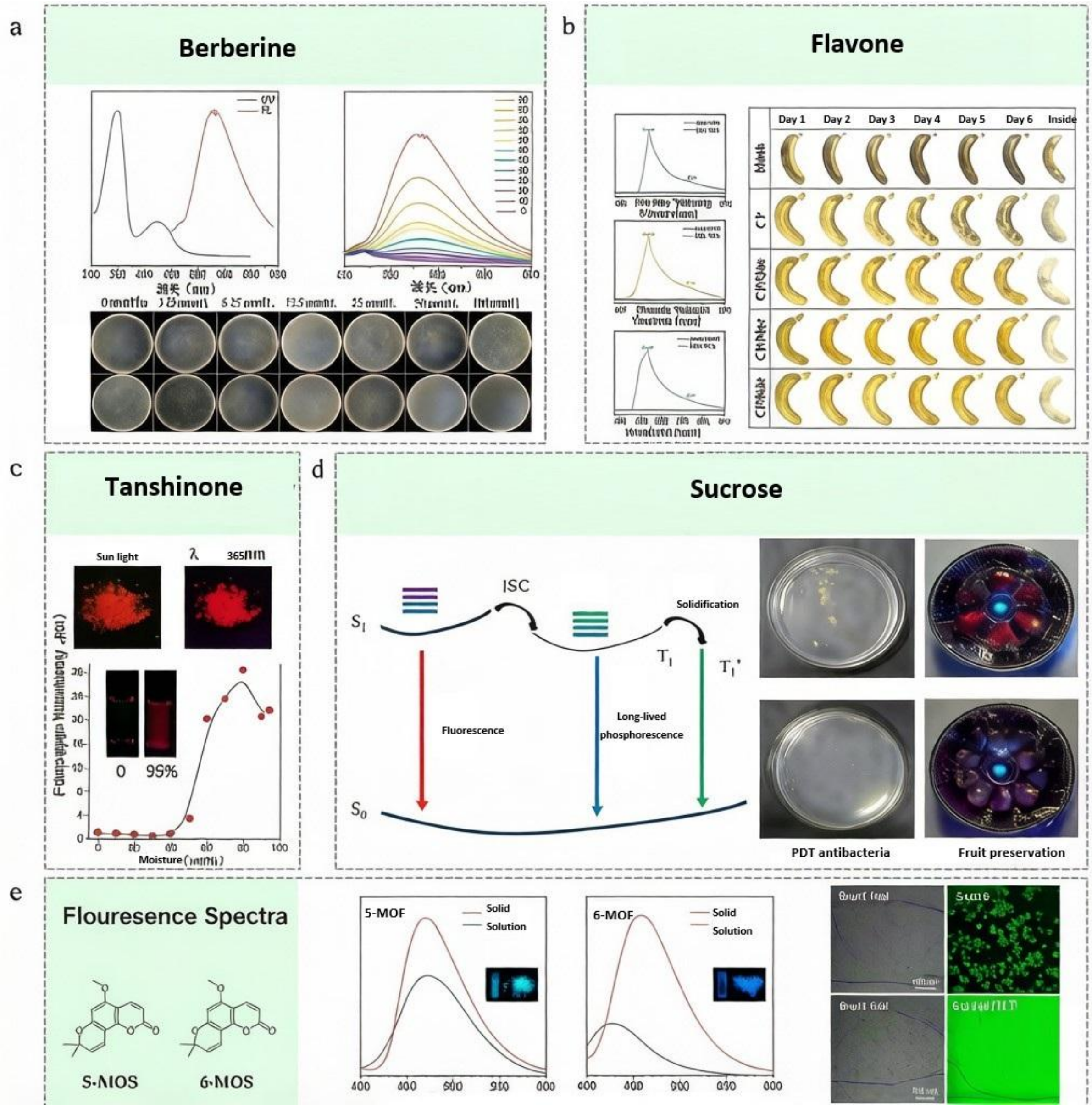

Figure 3 Aggregation luminescence behavior of natural active molecules

4.2 Natural Small Molecule Derivatives

Compared to natural small molecules, guided by the concept of Aggregate Science, research on naturally derived AIE materials, involving structural design and development using natural small molecules as the core, is developing rapidly. This design strategy leverages the structural uniqueness, renewability, and sustainability of natural small molecules while utilizing the classic structural design of AIE molecules to improve luminescence efficiency and expand application scenarios.

Rosin is an important industrial product in the forest chemical engineering field. The main component of rosin is resin acids, which are monocarboxylic acids with a tricyclic phenanthrene skeleton and two double bonds. Dehydroabietic acid is a highly promising structural platform. After chemical modification, dehydroabietic acid can serve as a natural electron acceptor to construct D-A type AIE materials. Our research group modified dehydroabietic acid with a quinoxaline structure to construct the electron acceptor dehydroabietic acid-quinoxaline (DAQx). Introducing the donor triphenylamine (TPA), three novel BioAIEgens with dual TICT and AIE characteristics were synthesized. By regulating the conjugation degree and electron-withdrawing ability of the DAQx acceptor, their photophysical properties were optimized. Building on this, our group further coupled DAQx with TPA to construct a series of D-A type BioAIE materials with tunable conjugation and charge transfer characteristics. These materials exhibit polarity-dependent (in solution) and polymorph-dependent (in solid) dual-state responsive fluorescence. Among them, DAQx-BP presents two different fluorescence colors, green and yellow, under molecular packing differences of less than 0.001 nm. Based on these unique photophysical properties, the material was successfully applied in dual-modal (solution and aggregated state) intelligent anti-counterfeiting. Furthermore, rosin-derived dehydroabietylamine (DAA) can also be combined with pyrene (Py) to obtain AIE materials like Py-DAA. In the molecular state of Py-DAA, significant molecular motion due to the bulky DAA skeleton favors non-radiative transitions, resulting in very weak fluorescence. In the aggregated state, molecular aggregation restricts intramolecular motion, and steric hindrance regulates pyrene packing to inhibit non-radiative transitions, enhancing fluorescence and exhibiting typical AIE characteristics.

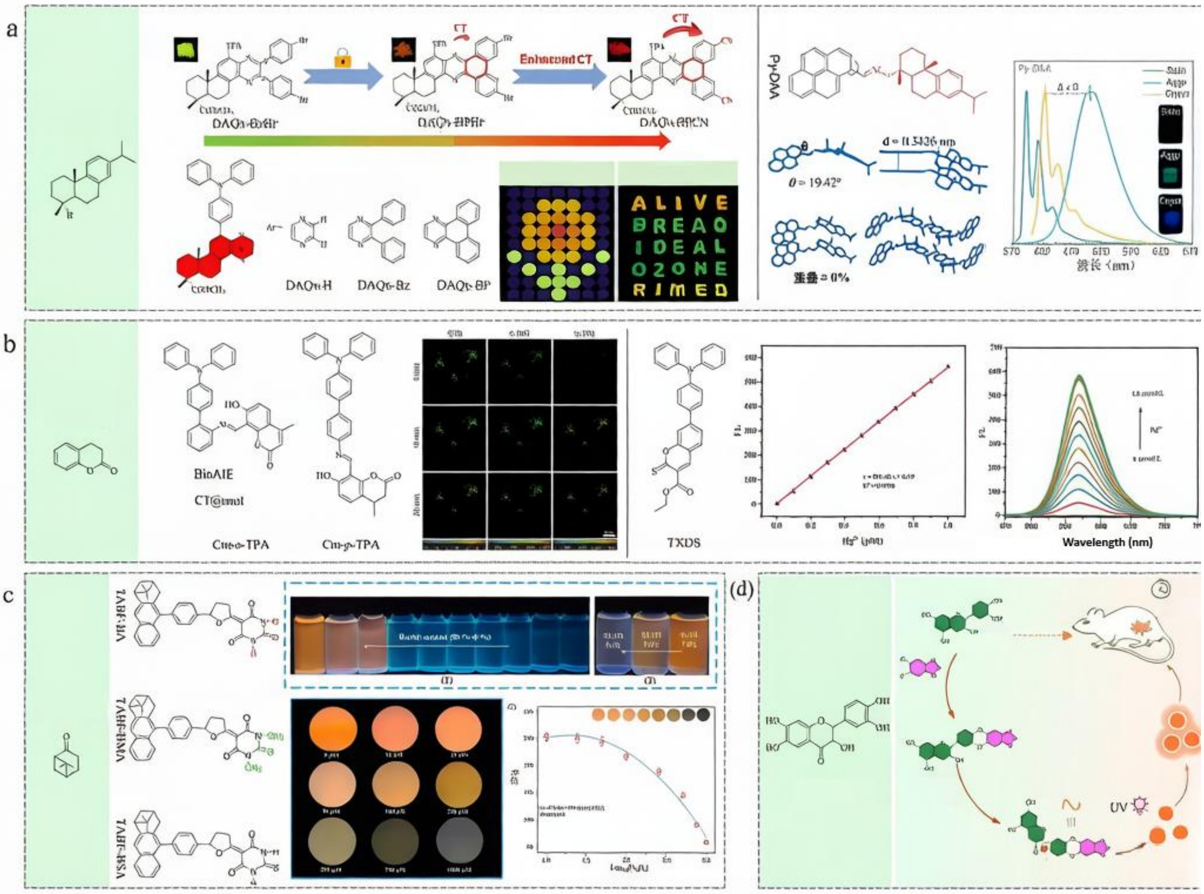

Figure 4 Aggregation luminescence behavior of naturally derived small molecules

a. Rosin derivatives; b. Coumarin derivatives; c. Nopinone derivatives; d. Catechin derivatives

Guided by the concept of Aggregate Science, both purely natural AIE molecules and AIE molecules derived from natural structures are developing rapidly, broadening the application scope of forest biomass chemicals in the field of luminescence. With the refinement of the clusteroluminescence mechanism, the luminescent behaviors of molecules containing multiple heteroatoms in forest biomass remain to be deeply explored by researchers, as such chemicals hold great potential for development into RTP materials.

4.3 Natural Polymers and Their Derivatives

4.3.1 Overview

Natural polymers represented by cellulose, lignin, and hemicellulose are the absolute mainstream forest chemicals in the field of forest biomass. Compared to other small molecules, natural polymers have characteristics such as abundant yield, mature and ecxcellent processing technology, diverse modification methods, and are rich in heteroatoms. From the perspective of Aggregate Science, natural polymers possess both spatial confinement and clusteroluminescence characteristics, making them excellent aggregate materials. Therefore, natural polymers can either serve as matrices blended with luminescent molecules or undergo chemical modification for structural tailoring to prepare various luminescent materials, such as AIE materials, RTP materials, and circularly polarized luminescence (CPL) materials.

4.3.2 Cellulose and Its Derivatives

Cellulose is the most abundant natural polymer in nature, widely found in wood, bamboo, straw, and other agricultural and forestry wastes. Simultaneously, cellulose materials possess unique physical and chemical properties, such as good breathability, moisture absorption, and biocompatibility. Therefore, developing novel cellulose luminescent materials can fully leverage the characteristics of cellulose while offering significant economic and environmental benefits. Academician Huang Wei's team found that sodium carboxymethyl cellulose exhibits ultralong organic phosphorescence (UOP) characteristics. Its UOP shows multi-stimulus responsiveness to excitation wavelength, pressure, and humidity. This characteristic originates from the CTE mechanism of the carboxylate groups in sodium carboxymethyl cellulose (carboxylate groups accelerate intersystem crossing (ISC) and inhibit non-radiative transitions). Furthermore, cellulose nanocrystals (CNCs) are excellent cholesteric lyotropic liquid crystals. Through helical aggregation, they can be used to develop CPL materials. Professor Zhang Jinming's group combined CPL with RTP. Using anionic cellulose derivatives (sodium cellulose tricarboxylate (CBtCOONa), sodium carboxymethyl cellulose (CMCNa)) as chiral matrices and non-chiral luminophores (such as lithium naphthalene tetracarboxylate (NtCOOLi)) through an aqueous solution processing strategy, they constructed full-color circularly polarized room-temperature phosphorescence (CPRTP) materials for the first time. The highest luminescence asymmetry factor (|g|lum|) reached 1.93×10^{-2}, providing a new scheme for the large-scale preparation and multifunctional application of CPRTP materials.

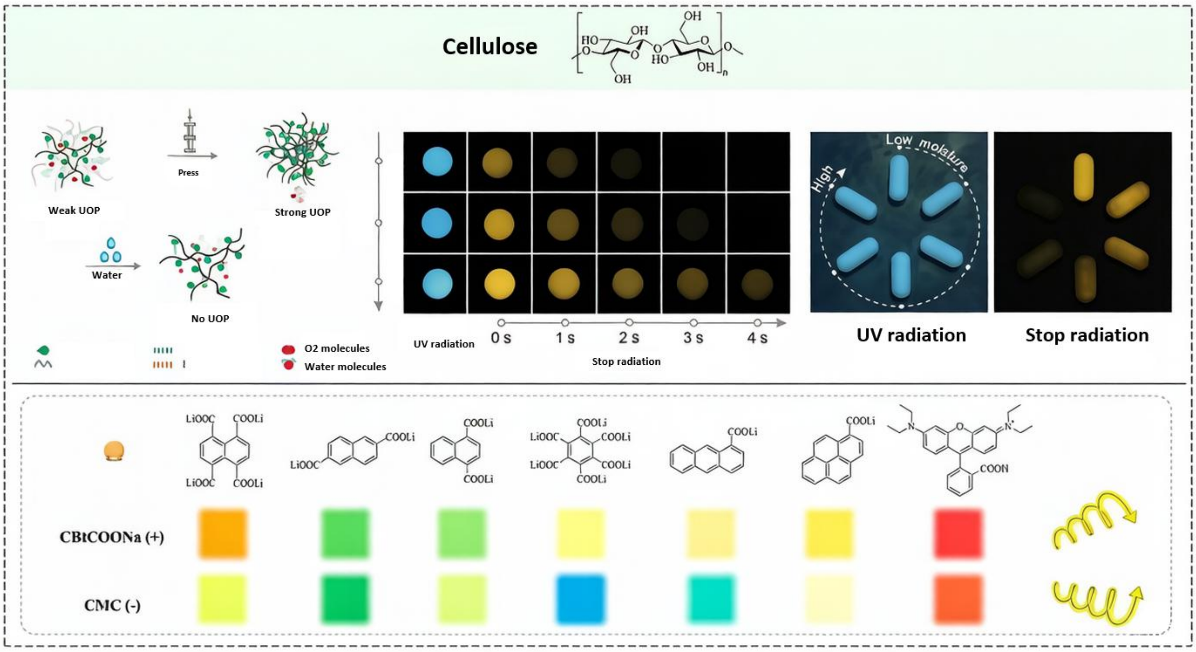

Figure 5 Aggregation luminescence phenomenon of cellulose and its derivatives

4.3.3 Lignin and Its Derivatives

Lignin is a three-dimensional network polymer in plant cell walls formed by phenylpropane units cross-linked via ether bonds (C—O—C) and carbon-carbon bonds (C—C), characterized by high complexity, heterogeneity, and rich aromatic groups and oxygen-containing functional groups. As a renewable natural aromatic polymer, its direct utilization or catalytic conversion is of great significance. From a structural perspective, lignin is an ideal raw material for preparing luminescent materials. Our research group, in collaboration with Academician Zhang Tao's group and Professor Zhang Bo's group at Dalian Institute of Chemical Physics, and Professor Huang Genping's group at Tianjin University, developed a method for the catalytic conversion of lignin β-O-4 segments into carbazole derivatives. This is a sustainable route catalyzed by vanadium-based complexes, using lignin β-O-4 segments containing γ-OH and 3-alkenylindoles as raw materials. Through a cascade reaction involving dual C—O bond cleavage / Diels-Alder cycloaddition / dehydrogenative aromatization, A-D-A type carbazole derivatives were synthesized in one pot (highest yield 92%). These carbazole products exhibit AIE performance with TICT characteristics. Building on this, our group continued to optimize the process with Professor Zhang Bo's group, achieving the one-pot two-step synthesis of such BioAIE molecules using inexpensive copper catalysts. From the perspective of Aggregate Science, directly utilizing natural lignin to prepare luminescent materials is another important approach besides lignin catalytic conversion. Professor Chen Zhijun's group at Northeast Forestry University used lignin as the raw material and introduced the 1-(6-isocyanatohexyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (Upy) unit through covalent modification to prepare Lig-Upy. The multiple hydrogen bond network of Upy can enhance interactions between aromatic units, reduce the molecular energy gap, and achieve red room-temperature phosphorescence (RTP) at 625 nm (lifetime 24.2 ms). Its RTP performance can be regulated by the matrix, constructing time-dependent phosphorescent color materials, filling the gap for biomass-based red RTP. The same group also found that lignin can achieve good dissolution in the liquid monomer 2-hydroxyethyl acrylate (HEA) through hydrogen bonding and non-bonding interactions. Based on this, they developed a solvent-free system consisting of HEA monomer and the crosslinker urethane dimethacrylate (UDMA). Under UV irradiation, lignin generates radicals initiating polymerization. The rigid network fixes lignin and provides spatial confinement, activating moisture/water-resistant RTP, realizing the high-value sustainable transformation of lignin.

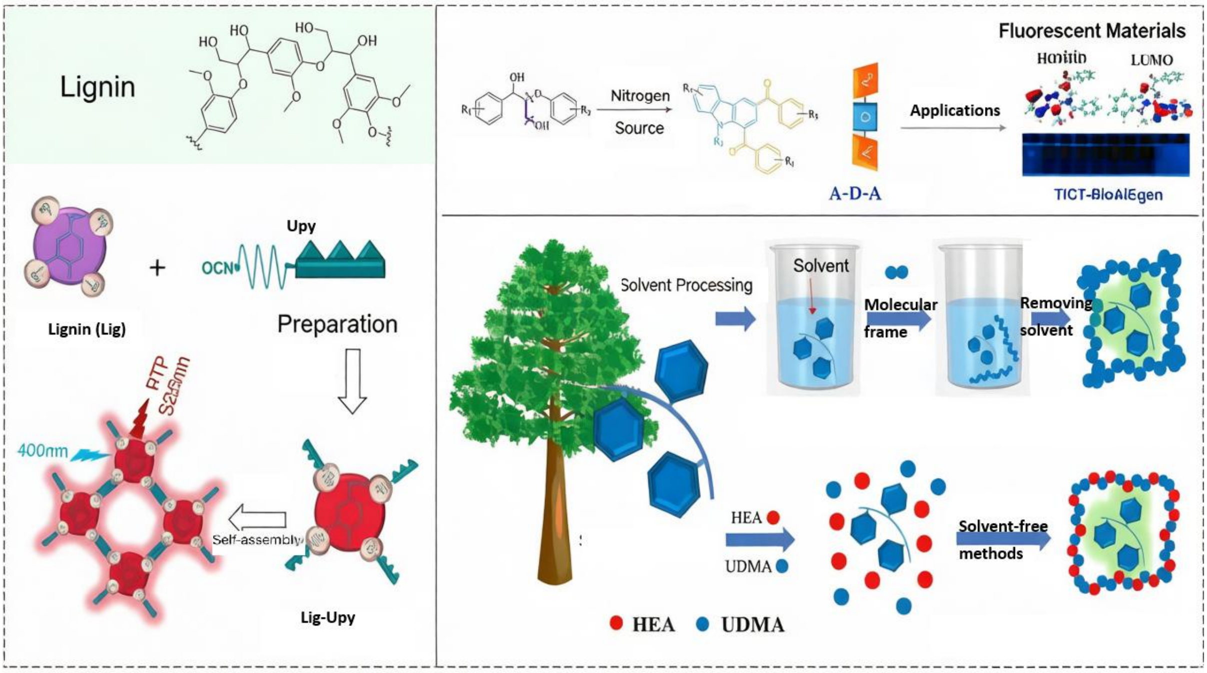

Figure 6 Aggregation luminescence phenomenon of lignin and its derivatives

4.3.4 Hemicellulose and Its Derivatives

The composition units of hemicellulose are complex, including xylose, arabinose, glucose, mannose, galactose, etc. Therefore, hemicellulose has many types, such as xylan, glucomannan, galactoglucomannan, mannan, and β-glucan. Professor Peng Feng's team used xylan from paper mill waste as raw material and obtained reconstructed xylan (RDAX) bioplastic through a directed oxidation-reduction strategy. This material, without any doping, exhibits excellent RTP performance relying on the CTE effect of oxygen-based groups in the rigid polysaccharide environment. The same group used edible konjac glucomannan (KGM) as the matrix and anchored arylboronic acids with different π-conjugation degrees onto the KGM chains through B-O covalent bonds, preparing a 3D printing ink. The synergistic effect of hydrogen bonds between KGM molecular chains and B-O covalent bonds restricts the molecular vibration/rotation of arylboronic acids, reducing the non-radiative transition rate. This material combines excitation-dependent and water/thermal stimulus-responsive characteristics and can achieve non-destructive recovery and repeated printing through water dissolution.

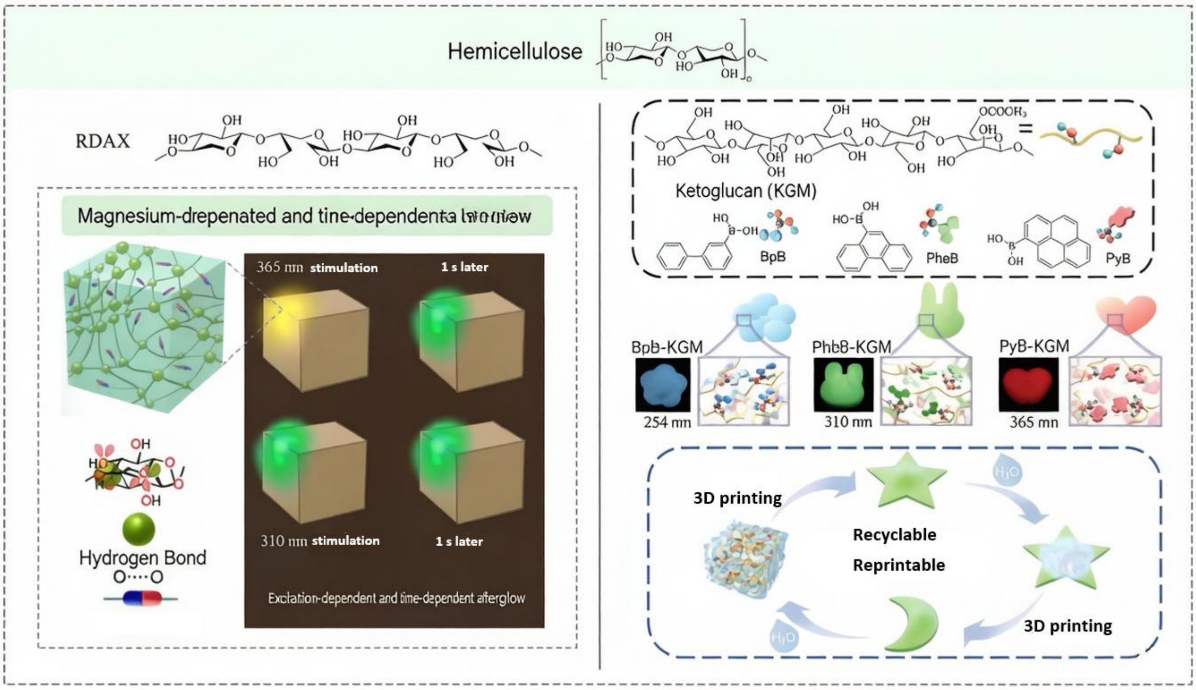

Figure 7 Aggregation luminescence phenomenon of hemicellulose and its derivatives

5 Conclusion and Outlook

As a major agricultural and forestry country, China is rich in biomass resources. Achieving the high-value transformation of agricultural and forestry resources holds significant practical importance. Luminescent materials from forest biomass are an important direction for high-value utilization. Traditionally, there are few luminescent molecules from forest biomass, primarily because most natural structures lack large aromatic or conjugated systems. The development of AIE materials and the proposal of the Aggregate Science concept have inspired the research and development of luminescent materials from forest biomass, breaking free from the inherent thinking that requires large aromatic or conjugated structures, thereby enriching material choices. Additionally, the rich luminescence mechanisms in Aggregate Science can improve design strategies, enhance luminescence performance, and broaden application ranges. Currently, significant progress has been made in this field. Future research directions should focus on the following aspects (Figure 8): 1) Continue to explore the luminescent potential of natural small molecules, optimize the extraction processes of natural molecules, and, guided by Aggregate Science, develop natural small molecules into multifunctional materials integrating tracing, imaging, and therapy. 2) Expand the derivative structures of inexpensive natural small molecules, optimize reaction steps, achieve green synthesis, and, leveraging their natural, renewable, non-toxic, and biocompatible characteristics, replace petroleum-based luminescent materials in areas of daily life and scientific research where people have direct contact. 3) Currently, natural polymers are one of the preferred raw materials for preparing RTP materials. Therefore, only by clarifying the structure-property relationship of natural polymers and their derivatives in RTP, especially in the directions of clusteroluminescence and spatial conjugation, can RTP materials with high luminescence efficiency, rich color, and long lifetime be prepared. In future research, if these scientific issues can be resolved, related scientific achievements in forest biomass luminescent materials will take a significant step towards practical applications in real life. Furthermore, in future research, constructing biological probes, dyes, inks, optical devices, and anti-counterfeiting labels using forest biomass luminescent materials are also promising research directions.

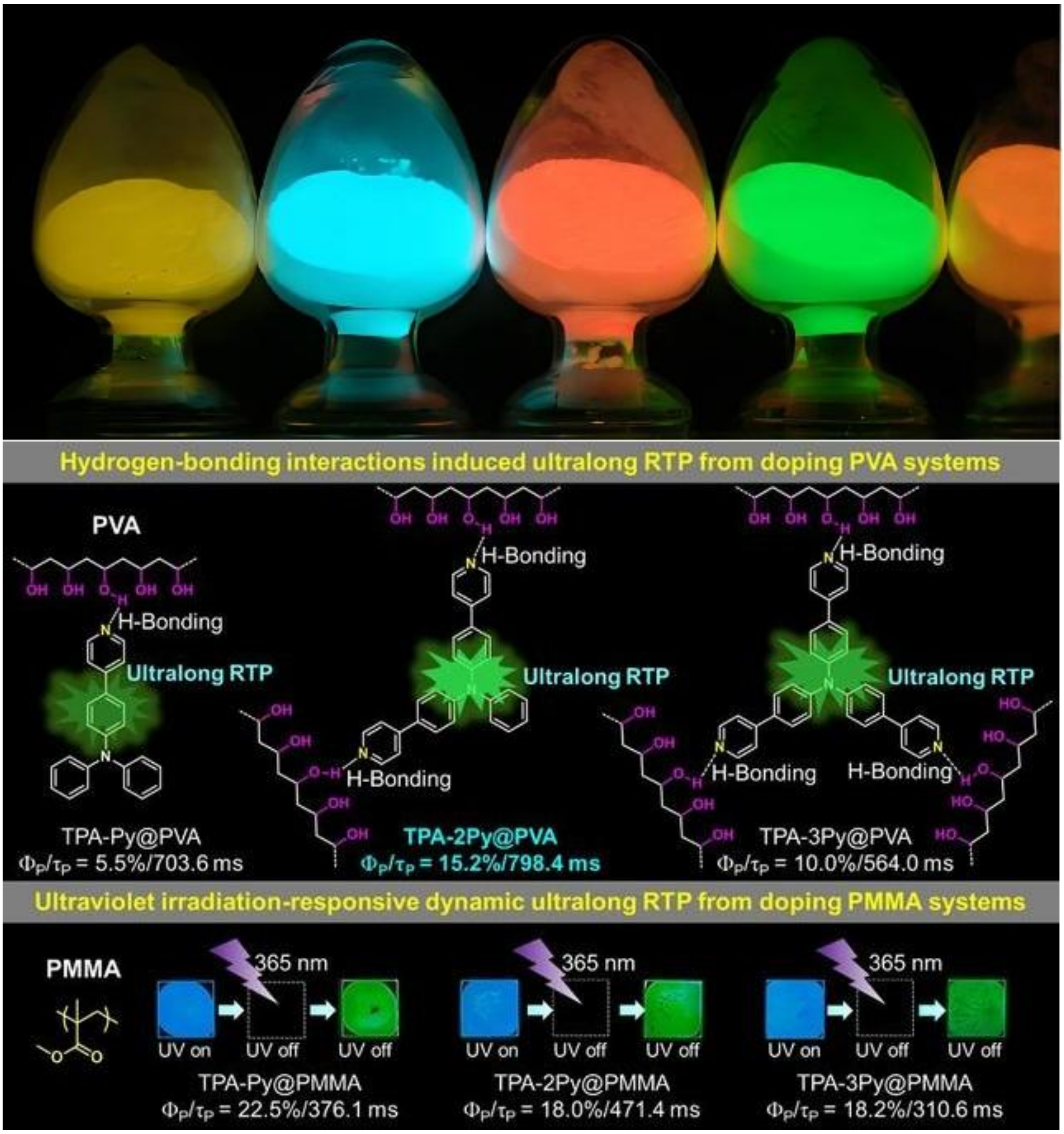

Figure 8 Future applications of forestry biomass luminescent materials

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