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Topical Review

Recent advances in 3D-printable aggregation-induced emission materials

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Abstract

Aggregation-induced emission (AIE) materials exhibit remarkable emission properties in the aggregated or solid states, offering numerous advantages such as high quantum yield, excellent photostability, and low background signals. These characteristics have led to their widespread application in optoelectronic devices, bio-detection markers, chemical sensing, and stimuli-responsive applications among others. In contrast to traditional manufacturing processes, 3D printing (3DP) enables rapid prototyping and large-scale customization with excellent flexibility in manufacturing techniques and material selection. The combination of AIE materials with 3DP can provide new strategies for fabricating materials and devices with complex structures. Therefore, 3DP is an ideal choice for processing AIE organic luminescent materials. However, 3DP of AIE materials is still in the early stages of development and is facing many challenges including limited printable AIE materials, poor printing functionalities and limited application range. This review aims to summarize the significant achievements in the field of 3DP of AIE materials. Firstly, different types of AIE materials for 3DP are studied, and the factors that affect the printing effect and the luminescence mechanism are discussed. Then, the latest advancements made in various application domains using 3D printed AIE materials are summarized. Finally, the existing challenges of this emerging field are discussed while the future prospects are prospected.

Keywords: 3D printing, aggregation-induced emission, luminescent materials, process monitoring

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1. Introduction

3D Printing (3DP), also referred to as additive manufacturing (AM), has emerged as a versatile and convenient technology [1]. This technique enables the rapid fabrication of parts with intricate geometries, providing an effective solution for model design, optimization, and customization [2]. Furthermore, 3DP technology offers the potential to reduce material waste in the production process. Consequently, an increasing number of industries are adopting this innovative technology [3]. In recent years, researchers have shown great interest in exploring the potential applications of 3D printed luminescent materials in bio-detection, sensors, and optoelectronic devices [4-6]. However, it is worth noting that most luminous materials currently employed in 3DP exhibit an aggregation-induced quenching (ACQ) effect, which arises from the stacking of large planar π -systems in the luminophores, leading to the quenching of their luminescence [7]. After 3DP, the ACQ effect causes molecules that were originally highly luminous in dilute solutions to weaken or completely disappear in aggregated or solid states, greatly limiting 3DP of luminous materials applications [8, 9]. Such as rhodamine, coumarin, pyrene and other traditional luminous materials, in the solution state show obvious fluorescence, while the solid structure formed by 3DP technology, but show a weakening or even complete disappearance of fluorescence. This is due to the luminescence quenching caused by the accumulation of large planar π systems in the luminescent group. Ji *et al* [7] prepared a thermosetting photocurable resin. When the resin was converted from liquid to solid state by 3DP technology, the concentration of 7-amino-4-methyl coumarin increased, and strong π -packing interaction occurred, which weakened the fluorescence intensity. In addition, Zhang et al [10] found that inkjet printing process causes aggregation reaction of cholesterol liquid crystal materials, and the interaction between fluorescent molecules is enhanced, which will cause fluorescence resonance energy transfer, showing ACQ effect, resulting in a decrease in fluorescence intensity. Overcoming the ACQ effect remains a formidable challenge for advancing lightemitting materials fabricated through 3DP.

In 2001, Tang and colleagues first introduced the concept of aggregation-induced emission (AIE) [11]. Through experiments, AIE materials have been found to restriction of intramolecular motion (RIM) mechanism, including intramolecular vibration and intramolecular rotation. The RIM mechanism works by limiting molecular motion, which blocks the non-radiative relaxation pathway and enables excitons to radiate down [12-14]. Chromophores with AIE effects are non-luminescent in their monomeric state but emit intense light when aggregated or under intramolecular restriction [15]. This unique solid-state luminescence characteristic offers a promising solution to overcome the ACQ problem [16], ensuring the continued luminescence performance of AIE materials during the 3DP curing phase. Furthermore, the intricate spatial structures enabled by 3DP technology expand the luminous capabilities of AIE materials from a two-dimensional plane to three-dimensional space [17–19]. The integration of AIE materials and 3DP technology holds great potential for applications such as flexible electronics, smart materials, printable inks, 4D printing, and sensors [20–24]. However, research on integrating 3DP and AIE material is still in its nascent stages and faces challenges such as limited availability of compatible printing materials and poor printability.

In recent years, although many studies on AIE materials have been reported, there remains a scarcity in systematic analysis and summarization of 3D printed AIE materials. To better facilitate the advancement of 3DP AIE materials and anticipate future research directions, we have conducted a comprehensive summary of relevant reports from recent years. This article commences with a concise discussion on the merits and demerits of 3DP technologies for luminescent materials. The current state of AIE small molecules, AIE cocrystals, AIE polymers and Metal-complex AIEgens in conjunction with 3DP technology was individually presented. Furthermore, we provide an overview of the applications of 3D printed AIE materials in process monitoring, bio/chemical sensing, and 4D print. Finally, the current challenges and future prospects of 3DP AIE materials were thoroughly discussed.

2. The 3DP of AIE materials

2.1. Overview of 3DP technologies

According to ISO/ASTM 52900:2021 [25], the AM technology is divided into seven major techniques: vat photopolymerization (VPP), material extrusion (MEX), powder bed fusion (PBF), binder jetting, material jetting (MJT), directed energy deposition (DED), and sheet lamination (SHL). In these techniques, MJT uses liquid adhesives to selectively melt powder materials, and is mainly used for printing metals and ceramics [26]. PBF is mainly suitable for printing metal alloys [27]. SHL combines materials to form objects and is developed for aesthetic and visual structures made of paper or metal [28]. DED energy deposition uses focused thermal energy to fuse materials by melting as they are being deposited and is currently only used for metals [29]. Since most of the luminescent materials are polymer materials, the above 3DP technology will destroy the chemical stability of the luminescent materials, and then affect the luminescent characteristics. MEX, VPP, and MJT can avoid the impact on the chemical stability of luminescent materials, so these methods are considered more suitable for the printing of luminescent materials [30–32].

MJT printing technology enables the precise construction of complex structures, allowing for layer-by-layer precise stacking of materials to create complex geometric shapes that are difficult to achieve with traditional manufacturing techniques [33]. This provides high design freedom and customization possibilities for luminescent materials. However, the printing speed is relatively slow for large structures or high-resolution details, which limits its application in largescale production [34]. Additionally, material selection is limited, with a current scarcity of available luminescent material types and high requirements for printing parameters and post-processing. MEX 3DP technology, through a computercontrolled system maintaining constant pressure, enables the print head to move horizontally according to the slicing pattern of the 3D model, achieving layer-by-layer printing of thin sheet contours and stacking structures [35]. These extrusion technologies are compatible with luminescent materials and offer cost-effective preparation solutions. However, they have certain limitations: the fused deposition modeling (FDM) method is characterized by slow printing speed, and due to poor interlayer adhesion of the filaments, it has limited compatibility with low-melting-point luminescent materials; the DIW method is limited to shear-thinning gels or polymers [36, 37]. Currently, extrusion-based 3DP of luminescent materials still faces issues such as low luminescence efficiency, inaccurate color control, and poor luminescence stability. Compared to MEX, VPP 3DP technology, such as stereolithography (SLA) and digital light processing (DLP), offer better surface quality, consistent mechanical strength, higher printing resolution, and luminescence stability. However, the availability of optical printing materials is limited because it relies on the polymerization of free radicals in the pre-polymer [38]. The resin used to reduce photo-polymerization must be translucent to the light source used for curing to allow UV penetration and solidification. At the same time, viscosity must be controlled to ensure fluidity [39]. Table 1 presents an overview of these techniques applicable to luminous materials and summarizes their respective advantages.

2.2. Overview of 3DP AIE materials

As presented in table 2, we provide a comprehensive analysis of the merits and demerits of prevalent 3DP luminescent materials, as well as the constraints associated with their integration into 3DP technology and existing enhancement approaches. AIE materials overcome the ACQ effect of other luminous materials. Furthermore, 3DP of AIE materials has the following advantages: at the level of structural design, the unique printing processes and methods of 3DP can provide ondemand structural features for AIE materials, thereby enhancing the luminescent stability of AIE materials; At the level of functional design, the photoelectric physical properties of AIE materials can overcome the ACQ effect of traditional luminous materials, and expand the application potential of 3D printable materials in biomedicine, intelligent sensing, photoelectric devices and other fields [40]. However, research on 3DP of AIE materials is still in its infancy, facing issues such as limited printable materials and the need for further refinement of printing processes, and its application fields are currently at the laboratory stage [7]. In this chapter, we will focus on the research results of the combination of AIE materials and 3DP technology in the past 5 years. According to the classification of AIE initiator Tang [41], AIE materials are divided into four types: AIE small molecules, AIE cocrystals, AIE polymers and Metal-complex AIEgens. Then, the current situation of combining different types of AIE materials with 3DP technology is discussed respectively.

2.2.1. 3DP of AIE small molecules. AIE small molecules are a class of organic compounds capable of emitting strong

fluorescence in the aggregate state [41]. The emission of AIE small molecules is induced by π -conjugated aggregation, which overcomes the ACQ effect caused by the formation of π - π -packed aggregation or excimer. AIE small molecules are characterized by their straightforward chemical, electrical, and photophysical characteristics [60]. In addition, AIE small molecules also possess advantages such as ease of processing, responsiveness to stimuli [61]. These attributes significantly facilitate the analysis of structure-property relationships and the exploration of underlying mechanisms, thereby offering substantial potential in the field of 3DP technology. Li et al [62] synthesized a series of tetraphenyl AIE fluorescent dyes, including Cz-bi-Ph, cz-hexx-ph, DHBF-Ph and BP-Ph, and used anthracyl dyes to initiate free radical photocuring to realize DLP 3DP. During the photocuring process, the viscosity of the system increases with irradiation time. As a result of the increased viscosity, the free rotation of the dyes is restricted, leading to an enhancement of fluorescence intensity (figure 1(a)). In addition to playing the role of dyes in 3DP material systems, AIE small molecules also demonstrate potential as photoinitiators. As shown in figures 1(b) and (c), You et al [63] synthesized a novel flavonoid-based AIE photoinitiator, 3HF-S (3-hydroxyflavone sulfonate). In hydrogel photopolymerization with 3HF-S as photoinitiator, effective photopolymerization can be achieved even at low content (0.042 wt%). The aggregation of photoinitiators such as 3HF-S can significantly improve the photopolymerization efficiency and improve the quality of DLP 3D printed hydrogels. When the model is illuminated with ultraviolet light, its color changes to blue.

From the above research, it can be found that AIE small molecules usually need to be 3D printed by light curing, so the printing process must be able to provide the appropriate light intensity and wavelength to trigger the solidification. In addition, AIE small molecules are often doped in printable resins as monomers [64], so it is important to ensure that their uniform dispersion does not affect the rheology of the resin.

2.2.2. 3DP of AIE polymers. AIE polymers are a class of polymer materials with enhanced luminescence properties in the aggregate state [41]. Compared with other AIE materials, AIE polymer has excellent functional composability and processing properties and film forming properties [65]. The formation of aggregates causes the polymer chain structural rigidity, which limits intramolecular vibration and rotation and reduces non-radiative energy loss. At the same time, inhibition of intermolecular $\pi - \pi$ accumulation and enhancement of hydrogen bonding promoted the improvement of luminescence properties [66]. In comparison to extensively studied low molecular weight AIE luminogens, AIE polymers offer notable advantages including high efficiency of solid-state emission, signal amplification effects, excellent functional compatibility, processability, and film-forming properties [67–71].

Currently, Ji *et al* [7] have demonstrated, for the first time, the fluorescent thermosetting AIE resin formed by covalent crosslinking, and non-covalent cross-linked thermoplastic

Tabl	e 1. The comparison c	of light-emitting materials 3D printi	ing technology, the advantages and]	limitations of light-emitting material	ls combined with 3D printing techno	ology.
ing iique	Printing methods	Advantages of the printing method	Disadvantages of the printing method	Advantages of printing methods combined with luminescent materials	Limitations of printing methods combined with luminescent materials	Reference
	Inkjet Printing	Higher print resolution than MEX; Good surface finish; Print faster than MEX	For large structures or high resolution details, printing speed is slower than VPP; materials must exhibit strong surface tension	Capable of achieving high-definition pattern printing; Compatible with a wide range of luminous materials	Requiring light-emitting material inks to have appropriate viscosity and surface tension to ensure spray uniformity and substrate spread	[26, 42]
	FDM	Wide selection of materials; low cost; mass manufacturing	Lowest print resolution; printing speed is slower thanVPP and MJT; out-of-plane anisotropy	Wide selection of materials; low cost; mass manufacturing	The luminescent material is required to be heat sensitive	[30, 43, 44]
~	MIQ	Wide selection of materials; easy to print with multiple materials	Printing speed is slower than VPP and MJT; The print resolution is lower than VPP and MJT; Shear thinning of the material is required	Luminous materials and other functional materials can be integrated in the printing process; DIW can print continuous fibers, which can guarantee the mechanical strength of the luminous material	Shear thinning of the luminescent material is required	[31, 44]
	SLA	The printing resolution is higher than MJT and MEX; Good surface finish	Only photosensitive materials; Printing speed is slower than DLP	It can prepare complex three-dimensional structures and improve the luminous effect	Material selection is limited, requiring light-emitting materials to be photosensitive and rheological	[45, 46]
	DLP	The printing resolution is higher than MJT and MEX; Print faster than MJT and MEX	Only photosensitive polymers	The microstructures are prepared to expand the application of luminescent materials in the biomedical field	Material selection is limited, requiring light-emitting materials to be photosensitive and rheological	[7, 47, 48]

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Table	2. The advantages and disadvantages o	of 3D printing luminescent materials, thei	r limitations of combining with 3D print	tting technology, and the existing efforts.	
Materials	Material advantage	Material defect	Limitations in combination with 3D printing	Existing efforts	Reference
AlEgens	High quantum yield, improved photostability, and low background signal; excellent biocompatibility; absence of ACO effect: stimulus restonse	Low mechanical properties; high preparation cost	Limited variety of materials; limited print resolution	Developing new materials; developing 3D printing technology	[7-9]
Quantum dots	High quantum yield; high photoluminescence stability	Self-absorption; oxidation problem; low mechanical properties; ACQ effects	Complex preparation and post-processing, Limited high-precision printing technology	Developing post-processing technology; developing 3D printing technology	[48–51]
Metal–organic frameworks	High quantum yield processability; environmentally friendly	Poor material compatibili;low printing resolution; low mechanical strength; ACQ effects	Limited variety of materials; complex preparation and post-processing process; difficult formation	Develop new materials; developing 3D printing technology; developing post-processing	[52–54]
Fluorescent nanoparticles	High quantum yield; tunable optical properties	ACQ effects; low bio-safety	Limited variety of materials; limited accuracy and stability	Developing new material systems; developing 3D printing technology:	[55–57]
Fluorescent dyes	Good mechanical properties; good biocompatibility;	Poor optical stability; photodegradation; ACQ effects	Material compatibility issues; poor post-printing dye stability	Development of new material systems; developing 3D printing technology	[58, 59]

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Figure 1. 3D printing studies of AIE small molecules. (a) High resolution and strong blue fluorescence printing of four AIE characteristic fluorescent dyes (Cz-bi-Ph, Cz-hex-Ph, DHBF-Ph and BP-Ph). (i) The synthetic route of tetraphene derivatives. (ii) The photochemical mechanism of tetraryl fluorescent dye on the photoinitiator diaromatic iodide (ONI). (iii) High-resolution and strong blue fluorescent 3D printing models using Cz-bi-Ph, Cz-hex-Ph, DHBF-Ph and BP-Ph as fluorescent dyes. Reproduced from [62]. CC BY 3.0. (b) Schematic illustration of the moving-up DLP. Reprinted from [64], © 2021 Elsevier Ltd. All rights reserved. (c) The synthetic route of flavonol sulfonate (3HF-S) and the printed model with photoinitiator 3HF-S are yellow, and when the model is illuminated with ultraviolet light, its color changes to blue. Reprinted from [63], © 2020 Published by Elsevier Ltd.

resin doped with fluorescent AIE material. As depicted in figure 2, high-resolution printing of two resins was achieved using DLP 3DP technology. Furthermore, by incorporating different types of AIE fluorescent molecules into the thermoplastic resin, multi-color 3DP can be accomplished. The covalent cross-linking of AIE molecules within the polymer network will exert an influence on the mechanical properties, while the incorporation of AIE molecules into the photocurable resin will impact its rheology and diminish printing efficacy.

In addition to photo-curable resins, AIE-active gels have also received considerable attention from researchers. AIE-active gels not only possess multimodal luminescent properties, such as combinations with circularly polarized luminescence, phosphorescence, electrochemiluminescence, and white light emission, but also exhibit responsiveness to various stimuli including heat, pH, light, chemicals, and solvents [24, 72]. Li et al [73] fabricated a double-layer hydrogel brake with AIE characteristics through DIW 3DP, employing tetra- (4-pyridyl phenyl) ethylene (TPE-4Py) as the core functional component and poly (acrylamide-R-sodium styrene sulfonate) (PAS) as the substrate material (figure 3(a)). Upon immersion in an aqueous solution of pH 3. 12, this AIE-active gel exhibits simultaneous alterations in fluorescence color, brightness, and shape. However, mechanical properties of these hydrogels were not investigated in this study. Yang et al [74] successfully developed a novel type of poly lactic acid (PLA) composite with AIE characteristics by incorporating TPE into the PLA matrix. The incorporation of TPE not only conferred high luminescent performance and remarkable thermal stability to the resulting TPE/PLA composite but also significantly enhanced its mechanical



Figure 2. DLP printing studies of AIE polymers. (a) Illustration of the top–down printing process in the DLP 3D apparatus. (b) Two different fluorescence mechanism maps of covalent and non-covalent interactions of AIE molecules (i) AIE molecular covalently cross-linked thermosetting photocuring resin, (ii) AIE molecules are doped into thermoplastic photocurable resins, and multi-color 3D printing. Reprinted from [7], © 2020 Published by Elsevier Ltd.

properties and the interlayer adhesion during the printing process, thus improving the printing effect [75]. Moreover, the 3D-printed Chinese knot model made from PLA-TPE exhibited consistent dimensions and intricate structure, validating the excellent compatibility between the composite material and FDM technology (figure 3(b)). As shown in figure 3(c), Liu et al [76] uniformly mixed and melted PLA and (E) -2-{5, 5-dimethyl-3-[2- (4-oxo-4H-chromen-3-yl) vinyl]cyclohex-2en-1-ylidene} malononitrile (CMVM) powders to develop an AIE-characteristic material printable via melt electrowriting (MEW) 3DP. Under a nozzle temperature of 190 °C and a printing speed of 200 mm s⁻¹, they produced PLA-CMVM microfibers with an average diameter of about 27 micrometers. MEW technology enables high-precision manufacturing of microfibers and grid structures from AIE materials, opening new avenues for the structural and performance optimization of AIE materials.

Based on the excellent tunability of AIE polymer materials, AIE polymer materials have been shown to be suitable for VPP and MEX 3DP technologies. When employing VPP technology, careful consideration should be given to the impact of viscosity and rheology of AIE polymer materials on the printing outcome. Furthermore, the luminescent properties of AIE materials can influence the print quality by affecting the resin's light absorption curing limit. When using MEX technology, introducing AIE material into the extrudable printing substrate will alter its shear thinning behavior, consequently affecting the overall printing performance [74]. 2.2.3. 3DP of AIE metal-organic complexes. Metal complexes AIEgens are compounds containing metal centers that exhibit excellent luminescence properties when aggregated [41]. Metal-organic Complexes possess exceptionally high surface areas, adjustable pore sizes, and modifiable inner surface properties. These characteristics facilitate the synthesis of tunable and ordered AIE materials, allowing for precise control over their optical and physical properties. Many research groups have successfully developed a series of new supramolecular metal-organic complexes with AIE properties [77-80]. For instance, TPE, known for its simple synthesis and ease of modification, has been widely utilized in constructing metal-organic complex systems with AIE characteristics [81-86]. Metal-complex AIEgens are regarded as an effective approach for fabricating novel luminescent functional materials that possess long luminescence lifetimes (on the millisecond scale), substantial Stokes shifts (in the hundreds of nanometers), and high quantum yields [87-89]. Compared to traditional chromophores, this advantage allows for thinner AIE chromophore conversion layers, offering benefits in terms of light coupling efficiency, thermal management, and response time. However, it is challenging to fabricate large-area optical quality films with high AIE luminescent efficiency. As shown in figures 4(a) and (b), Baroni et al [90] demonstrated that by incorporating AIE dyes (based on tetraphenylethene, H4ETTC) into surfaceanchored metal-organic framework (SURMOF) films, efficient luminescence can be achieved. Even at low dye concentrations, AIE dyes within SURMOF exhibit high internal



Figure 3. MEX 3D printing studies of AIE polymers. (a) Schematic illustration of simultaneous changes in fluorescent color and brightness and shape of a TPE-4Py/PAS-based bilayer hydrogel actuator and the mechanism involved. [73] John Wiley & Sons.© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) TPE/PLA composite filament is prepared by melt extrusion and subsequent parts are printed under FDM printer. Reprinted from [74], © 2021 Elsevier Ltd. All rights reserved. (c) Fabrication and characterisation of PLA microfibre-based assemblies. (i) Photograph of the MEW unit for PLA microfibre-based assemblies in the bioprinting equipment. (ii) Photographs of PLA microfibres prepared at different writing speeds (scale bar: 1 mm). (iii) SEM images of PLA meshes with straight microfibres at writing angles of 45°, 60°, and 90° (unit cell width: 800 μ m). Reproduced from [76]. CC BY 4.0.



Figure 4. 3D printing studies of AIE metal–organic complexes. (a) The chemical structure of zinc paddlewheel metal nodes (red squares) and terephthalic acid connectors (blue lines) for forming the ZnBDC structure, as well as tetraphenylvinyl-based AIE chromore (H4ETTC, green bow tie) are loaded into SURMOF. (b) The process of loading SURFOF with AIE chromophores by drip casting. (c) Uniform SURMOF films containing AIE chromophores exhibit bright emission under UV light and magnified image from optical microscope of test pattern prepared by inkjet printing with circular features of 70 μ m. Reprinted with permission from [90]. Copyright (2018) American Chemical Society.

photoluminescence quantum yields, indicating that SURMOF can effectively confine AIE molecules, thereby activating their luminescent properties. Subsequently, they have successfully prepared AIE dye patterns featuring on SURMOF films utilizing inkjet printing technology (figure 4(c)). The study further elucidates the unique optical properties of AIE dyes in confined spaces, offering novel strategies for synthesizing 3D-printable AIE metal complexes. However, the uniform distribution of AIE material in the metal complex can affect the consistency and overall performance of the printed device.

Due to their favorable surface tension and rapid drying rate, AIE metal–organic Complexes is suitable for MJT. However, the uniform distribution of AIE material in the metal complex can affect the consistency and overall performance of the printed device [22]. In addition, nozzle diameter, printing rate and printing path will affect the printing quality of AIE metal– organic Complexes [10].

2.2.4. 3DP of AIE cocrystals. AIE cocrystals is a crystal formed by the interaction of two or more molecules through non-covalent (hydrogen bond, halogen bond, $\pi-\pi$, charge transfer force) [41]. AIE cocrystals can be divided into hydrogen/halogen cocrystals and charge transfer cocrystals [91]. Due to the synergistic effect and aggregation effect between different molecules in cocrystals, the luminescence function is realized and the ACQ effect is effectively avoided AIE [92]. The application spectrum of AIE eutectics is broad, exerting significant impact in fields such as fluorescence, optical waveguiding, nonlinear optics, and electronic devices [93–95]. As multi-component eutectic systems continue to be explored, it is anticipated that the AIE phenotype will be further amplified within these complex frameworks, yielding materials with a spectrum of luminous colors and a new generation of high-efficiency luminescent materials. Within the domain of 3DP eutectics, certain advancements have been realized. Notably, our research group [96] have developed a novel photosensitive ionic liquid, the polymerizable deep eutectic solvent, which serves as a precursor solution for UVcurable 3DP (figure 5). The conductive ionoelastomers synthesized via UV curing exhibit exceptional mechanical properties, with a tensile elongation of 565%, and a pronounced self-healing efficiency of up to 99% at room temperature. These materials also showcase degradability and the capacity to sustain electrical conductivity and self-healing across an expansive temperature range ($-23 \degree C-50 \degree C$). Despite the proliferation of studies on the 3DP of eutectic materials [97-100], the exploration of 3D printed AIE eutectics remains in its infancy. The 3DP of AIE eutectics may confront technical hurdles, including the luminous stability of materials during the printing process, the precise manipulation of microstructures, and the complexity of post-processing techniques. Current 3DP technology may struggle to fulfill the specialized printing demands of AIE eutectic materials, particularly concerning the regulation of the printing milieu and the selection of energy sources. Moreover, the synthesis and 3DP of AIE eutectics could entail substantial financial investment, potentially constraining research progress in this arena.



Figure 5. 3D printing of self-healing, degradable, conductive ionic elastomers based on polymerizable deep eutectic solvents. Reprinted from [96], © 2024 Elsevier B.V. All rights reserved.

3. Applications of 3D printed AIE materials

The combination of AIE and 3DP opens up new possibilities for manufacturing complex structures with specific optical properties. Significant research progress has been made to date, and broad application prospects are emerging across various fields. This chapter provides a comprehensive review of their recent applications in process monitoring, bio/chemical sensors and 4D print.

3.1. Process monitoring

Real-time visualization of 3DP processes is crucial for artificial intelligence manufacturing, bioprinting, aerospace component manufacturing [101–104]. However, achieving effective monitoring of 3DP processes remains a significant challenge [105]. A distinctive characteristic of AIE materials is their enhanced fluorescence emission in solid or aggregated states compared to solution or dispersed states. This unique advantage makes AIE materials particularly suitable for process monitoring [106, 107].

As shown in figure 6(a), Ji *et al* [7] synthesized a thermoset photo-curable resin with AIE properties. Initially nonfluorescent in its solution form before 3DP, the resin exhibits changes in fluorescence intensity during the printing process due to the movement of AIE luminogen in the polymer network is limited, enabling continuous monitoring. After completion of printing, the cured object exhibits a pronounced level of fluorescence. In addition, Yang *et al* [74] fabricated TPE/PLA composite filaments, and utilized FDM 3DP technology to fabricate a series of samples. When exposed to ultraviolet light, the bending damage of the samples manifests as a vivid blue fluorescent arc, enabling clear assessment of the degree of material deformation. Simultaneously, minuscule defects in the sample exhibit distinct bright blue fluorescence against a dark background (figure 6(b)). Recently, Kang *et al* [108] demonstrated a new method that uses AIE molecules as fluorescent probes to monitor internal structural changes in 3D printed stimulus-responding materials by monitoring changes in their fluorescence intensity and wavelength (figure 6(c)). Russell *et al* [109] employed TPE-OA, a water-soluble derivative of TPE with AIE properties. This material was printed layer by layer into an oil phase (e.g. silicone oil) containing POSS-NHNH2, resulting in the formation of a liquid-inliquid structure depicted (figure 6(d)). The interface between TPE-OA-based AIEgen surfactant and the oil phase exhibited remarkable blue fluorescence upon irradiation with 365 nm ultraviolet light. Due to the inherent AIE property of TPE-OA, fluorescence intensity significantly increased when it accumulated at the interface, enabling process monitoring for allliquid 3DP (figure 6(e)).

AIE luminogens have been frequently used as fluorescent markers to study the properties of the polymer materials [7]. Leveraging the unique characteristics of AIE for real-time monitoring of print quality and progress presents a novel approach, yet it encounters challenges including quantification of fluorescence intensity, susceptibility to environmental interference, molecular dispersion issues associated with AIE materials, limitations in print resolution and size, as well as material compatibility concerns. Overcoming these limitations necessitates interdisciplinary collaboration and technological innovation to facilitate broader application of AIE materials in the realm of 3DP monitoring.

In the study of process monitoring, existing AIE materials for 3DP predominantly employ AIE polymer materials. The tunability of polymer materials enables the fulfillment of both AIE luminescence and compatibility with 3DP. However, the uncontrollable curing effect of AIE polymers during the printing process adversely affects luminous stability. By designing material systems and optimizing 3DP technology, the application effectiveness of 3D printed AIE materials in process monitoring can be enhanced.



Figure 6. 3D printing of AIE materials for process monitoring. (a) AIE molecules are combined with DLP 3D printing photosensitive polymers to observe the printing process in real time by monitoring changes in fluorescence intensity. Reprinted from [7], © 2020 Published by Elsevier Ltd. (b) (i-ii) FDM printing of TPE/PLA composite filaments and Chinese knots. (iii) Fluorescence visualization of a neat PLA strip specimen containing a thin layer of 0. 4 mm PLA-1. 0TPE in a bend test under a handheld 365 nm UV lamp (scale: 2 cm). (iv) Under a 365 nm UV lamp, the defect displays bright blue fluorescence against a dark background. Reprinted from [74], © 2021 Elsevier Ltd. All rights reserved. (c) The use of AIE molecules as fluorescent probes to monitor the internal structural changes of materials. (d) 3D printed all-liquid system with images under UV irradiation at 365 nm. (e) Real-time monitoring of print structure formation and interface dynamics by fluorescence microscopy. (d), (e) [109] John Wiley & Sons.© 2021 Wiley-VCH GmbH.

3.2. Bio/chemical sensors

Currently, bio/chemical Sensors play a crucial role in various fields, including biomedical research, forensic science, environmental monitoring, food safety, and national security [110]. Therefore, these applications has led to new requirements for the design of sensing materials and devices [111]. AIE materials, with their high luminescence, large Stokes shifts, excellent photophysical stability, and superior biocompatibility, offer several advantages over traditional fluorescent sensors and have seen rapid development [112, 113]. Concurrently, 3DP technology can prepare devices with complex structures, achieve customized and miniaturized production of sensors, and enhance the potential of sensor manufacturing [114].

Liu *et al* [76] have employed MEW technique to 3D print a polylactic acid-aggregation-induced emission chemosensor. This chemosensor is capable of visually detecting chemical vapors through colorimetric changes (figure 7(a)). The device takes advantage of the designability of AIE polymer materials, have realized 3DP compatible with the optical properties of AIE fluorophore, and demonstrates the potential for applications in smart wearable devices. In another study, Jiao *et al* [115] have designed a smartphone-based, 3D printed portable fluorescence sensing platform (figure 7(b)). This platform employs AIE small molecules, specifically maleimide functionalized tetraphenylethylene (TPE-MI), for the detection of organophosphorus (OP) residues. Upon interaction with thiols, the hydrolysis products of OP compounds, TPE-MI exhibits a strong fluorescence signal. This signal can be utilized to quantitatively analyze the concentration of OP residues in vegetables, offering a novel approach to food safety monitoring.

Additionally, AIE materials have demonstrated significant potential in the realm of bioimaging [116, 117]. For instance, Wang *et al* [118] have developed a red-light-emitting AIE polymer known as 4BC, which can be readily adsorbed onto the surface of 3D-printed biological scaffolds through a simple surface adsorption process. As illustrated in figure 7(c), fluorescence in situ imaging of the subcutaneously implanted



Figure 7. 3D printing of AIE materials for bio/chemical sensors. (a) Optical photographs of the maple leaf sensor under white and ultraviolet light ($\lambda = 365$ nm), and the chameleon sensor placed on the mask. Reproduced from [76]. CC BY 4.0. (b) 3D printed portable fluorescence sensing platform to detect OP residues via smartphones. Reprinted with permission from [115]. Copyright (2021) American Chemical Society. (c) *In situ* imaging, amplified fluorescence and x-ray images of 3D printed scaffolds implemented by AIEgen. Reprinted with permission from [118]. Copyright (2023) American Chemical Society.

scaffolds can be conducted under excitation light irradiation. Furthermore, 4BC has a high reactive oxygen species (ROS) release efficiency when activated by light, and ROS production efficiency is an important factor in photodynamic therapy. ROS can play a bactericidal and antiinflammatory role by attacking cell membranes, destroying proteins, damaging nucleic acids, and activating the immune system. Therefore, the introduction of 4BC can enhance the bactericidal ability of the biological scaffold [119, 120].

3.3. 4D print

Most conventional stimulus-responsive smart fluorescent materials exhibit the ACQ effect, while materials with AIE characteristics can overcome this limitation [121].

Stimulation-responsive smart materials with AIE characteristics have garnered significant attention in fields such as soft robotics, optical sensors, and biological imaging due to their ability to display distinct color changes in response to external stimuli [122]. The development of Stimulus-responsive AIE materials has greatly propelled advancements in the field of smart materials for 4D printing [40, 123].

Luminescent hydrogel actuators hold promising application prospects in biomedical soft robots owing to their excellent biocompatibility and shape-changing abilities triggered by stimuli [124]. For instance, Li *et al* [73] utilized a stimulus-responsive AIEgen as a core functional component to fabricate a bio-inspired actuator with intricate morphology (figure 8(a)). Upon submersion of the floral-shaped actuator in an acidic aqueous solution, the actuator underwent a



Figure 8. 3D printing of AIE materials for 4D print. (a) The 3D printing process of the three-arm actuator. (b) The fluorescentcolour-fluorescent-luminance-shape response of the three-arm actuator. (a), (b) [73] John Wiley & Sons.© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) The continuous discoloration process of the PLA-CMVMN chameleon sensor at different time intervals (0–180 s: diethylamine vapor, 190–330 s: n-butylamine vapor). Reproduced from [76]. CC BY 4.0.

blooming phenomenon, with its emission color and luminescence intensity exhibiting temporal changes (figure 8(b)). The protonation of TPE-4Py leads to a decrease in fluorescence emission redshift and fluorescence intensity. First, TPE-4Py is protonated in an acidic environment, resulting in a redshift of fluorescence emission, which is manifested as a color change; Secondly, protonation increases the solubility of TPE-4Py, and the increase of solubility enhances the intramolecular rotation effect and decreases the fluorescence quantum yield, resulting in a decrease in brightness. Furthermore, the authors employed 3DP technology to create an actuator based on the PAS system that simultaneously alters its complex shape, emission color, and brightness-a remarkable achievement enabling pH-responsive 4D printing of AIE-active hydrogel actuators. Liu et al [76] successfully integrated AIEgens into biodegradable PLA, resulting in the development of a microfiber suitable for wearable device printing. These materials exhibit tunable fluorescence properties and shape-changing capabilities in response to environmental stimuli such as pH variations, making them highly promising for applications in chemical sensing and biological fluid management. As shown in figure 8(c), by combining MEW printing strategies with AIE active compounds, they achieved remarkable outcomes including the creation of intricate 'embroidery-like' patterns, chameleonlike sensors capable of color changes, and Janus PLA-cotton fabrics featuring hydrophobic/hydrophilic structures. These studies focused on the utilization of AIE polymer materials, which possessed designability for developing material systems with stimulus response, AIE luminescence, and printability. This advancement in smart material 4D printing holds great potential for promoting its development and application.

4. Conclusion

The aggregation-induced luminescence properties of AIE materials, combined with the highly customizable and intricately engineered structure manufacturing capabilities offered by 3DP technology, present novel prospects for the advancement of high-performance luminescent products. Firstly, this paper have summarized the advantages and disadvantages of common 3DP luminous materials, finding that they were all affected by the ACQ effect, and the RIM mechanism of AIE overcame the defects of the ACQ effect. Besides that, significant advances in the interdisciplinary field of 3DP AIE materials have been summarized including: 3DP of AIE small molecules, 3DP of AIE polymers, 3DP of AIE metal-organic complexes, and 3DP of AIE cocrystals. Furthermore, 3D printable AIE materials and their applications in process monitoring, biological/chemical sensors and 4D print have been introduced. The final section discusses the current challenges faced

by 3D printed AIE materials and provides prospects for their future development.

5. Future perspectives

The combination of AIE materials and AM exhibits promising application prospects, significantly advancing both academic research and industrial production. However, as a nascent field, several challenges remain to be addressed: (1) printable AIE materials are limited; (2) further optimization is required for the 3DP process of AIE materials; (3) the existing range of applications remains constrained.

First, the development of novel printable AIE materials plays a fundamental and pivotal role in the research of 3DP AIE materials. Currently, most 3D printable AIE materials are organic compounds, with limited investigations on the integration of AIEgens and inorganic substances. Due to the complex conditions required for combining inorganic materials and AIEgens molecules, such as photothermal and photoacoustic, a universal construction strategy is currently lacking. Incorporating AIEgens into various easily synthesized inorganic materials possessing distinctive rigid pore structures represents a viable strategy to advance the diversification of AIEgen applications [125]. The combination between an AIE active substance and an inorganic printable matrix can be achieved through post-loading or co-doping strategies [126]. In the post-loading approach, desired forms of inorganic matrices are initially prepared followed by non-covalent or covalent interactions for binding with the AIE active substance. For example, Zhang et al [127] used hydrophobic dendritic mesoporous silica (HMSN) as a carrier to payload the AIE material. Due to the pore domain restriction effect and hydrophobic interaction of HMSN, the obtained silica based AIE material has bright fluorescence and the maximum mass yield reaches 68.38%. By using HMSN as a carrier, different types of AIE molecules can be loaded to achieve multi-color fluorescence emission, which is beneficial for the development of 3DP materials with multiple functions. Alternatively, within the co-doping strategy, composite nanoparticles are fabricated via a 'one-pot method' by mixing either an unmodified or silane-modified form of the AIE active substance with a silicon source. By combining AIE active polymer TPE-P (a polymer containing tetraphenylethylene side chain) with silicone rubber matrix, Chen et al [128] successfully prepared fluorescent silicone rubber with good dispersion and dissolution resistance, and the fluorescence characteristics of silicone rubber could be adjusted by changing the molecular weight or aggregation state of fluorescent macromolecules. The rigid structure of inorganic AIE materials restricts intramolecular motion, resulting in high brightness and stable luminescent properties. Moreover, the anisotropy exhibited by these materials is advantageous for 3DP applications. Research on inorganicbased AIE materials contributes to the advancement of smart materials for 3DP.

Second, although 3DP AIE materials can fulfill the demand for fabricating structures with high functionality and intricate

multi-scale geometry, certain requirements need to be met during the printing process. In terms of enhancing printing resolution and accuracy, it is currently unattainable to achieve the level of precision necessary for manufacturing fine optoelectronic devices using 3D printed AIE materials. Therefore, optimization of existing printing processes becomes imperative. For instance, Two-photon polymerization printing exhibits high precision in light-curing 3DP but suffers from slow speed and low efficiency. To address this issue, Saha et al [129] proposed a projection-based layer-by-layer parallelization strategy that utilizes ultrafast lasers focused in space and time. This approach significantly enhances print speed/throughput by three orders of magnitude while maintaining sub-100 nm resolution levels. Another innovative technique called Continuous Liquid Interface Production introduces continuous and rapid printing capabilities within DLP technology, reducing layered projections and enabling the fabrication of complex structures at a height of 5 cm in just 10 min [130]. Furthermore, during the printing process, AIE materials may encounter interference from factors such as high temperature, electric fields, or light sources which can impact their luminous performance and structural integrity. Incorporating advanced environmental control strategies, such as incorporating temperature regulation equipment and implementing environmental isolation devices within the 3DP system, can effectively mitigate the influence of external factors on print quality. By integrating multiple 3DP technologies, AIE materials can be fabricated with enhanced complexity and functionality by capitalizing on the unique advantages offered by different printing methods. This hybrid printing technology simplifies the manufacturing process for intricate structures made of diverse materials, which would otherwise be challenging to achieve using a single printing technique. Consequently, hybrid 3DP holds great potential in expanding the application scope of AIE materials in AM.

Third, 3D-printed AIE materials exhibit significant potential in process monitoring, sensing, flexible robotics, wearable devices, 4D printing and other fields. Furthermore, due to their unique luminous properties, AIE materials hold great promise for information storage and dynamic anti-counterfeiting applications across various domains. Lu et al [131] developed a series of fluorescent nanoparticles with AIE characteristics, known as the TPEL series. These nanoparticles enable colorchanging anti-counterfeiting through ultraviolet irradiation and have been innovatively applied to 2D information encryption. By employing carefully designed AIE fluorescent materials using 3DP technology that combines three-dimensional geometry with surface fluorescence images, the information storage capacity can be significantly enhanced beyond traditional two-dimensional forms [132, 133]. This advancement holds great significance for upgrading encryption technology and anti-counterfeiting measures. Furthermore, the unique luminescent characteristics of AIE materials offer broad prospects for application in optoelectronic devices. The deep red/near infrared AIE active electroluminescent emitters developed by Wan et al [134] have achieved high efficiency in OLED devices; Li et al [135] utilized blue AIEgen to realize efficient two-color mixed white OLEDs; by modifying the molecular structure of AIE, Zuo et al [136] successfully achieved a continuous tunable emission wavelength from blue to red, enabling the creation of full-color OLEDs. As demonstrated by the aforementioned cases, functional materials derived from AIEs hold an indispensable position in the field of organic optoelectronics. However, current fabrication methods for AIE light-emitting devices such as hot pressing, lithography, and ultrasonic spraying are associated with high production costs and complex processes that hinder the realization of complex structural designs, thereby limiting their application potential. Leveraging 3DP technology in manufacturing AIE material optoelectronic devices presents significant prospects for achieving precise construction and personalized design of intricate structures while advancing the development of AIE optoelectronic device technology towards enhanced efficiency, multifunctionality, and intelligence [137, 138].

In conclusion, future research should prioritize the advancement of 3D-printable AIE materials and the enhancement of 3DP technology to attain superior precision in printing effects, as well as ensure compatibility with efficient and stable luminescence. The utilization of 3DP technology holds promise for expanding the application scope of AIE materials in areas such as process monitoring, biological/chemical sensing, security and anti-counterfeiting measures, as well as 4D printing. As research on 3D printed AIE materials continues to advance, it will unlock further opportunities for spatially structured optical devices in industrial applications.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this work.

Authors' contributions

Mingtao Zhang: Writing—original draft, Visualization, Investigation. Yu Li: Writing—original draft, Investigation. Guangmeng Ma: Writing—original draft, Investigation. Fawei Guo: Writing—original draft, Investigation. Haixin Wu: Validation, Investigation. Han wu: Review & editing. Qingxin Jin: Review & editing. Xin Luo: Review & editing. Chunyi Luo: Review & editing. Jiaqi Li: Review & editing. Yu Long: Writing—review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition.

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