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Tunable and Responsive Photonic Bio-inspired Materials and their Applications

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Bio-enabled and bio-mimetic nanomaterials represent functional materials, which use bio-derived materials and synthetic components to bring the best of two, natural and synthetic, worlds. Prospective broad applications are flexibility and mechanical strength of lightweight structures, adaptive photonic functions and chiroptical activity, ambient processing and sustainability, and potential scalability along with broad sensing/communication abilities. Here, we summarize recent results on relevant functional photonic materials with responsive behavior under mechanical stresses, magnetic field, and changing chemical environment. We focus on recent achievements and trends in tuning optical materials properties such as light scattering, absorption and reflection, light emission, structural colors, optical birefringence, linear and circular polarization for prospective applications in biosensing, optical communication, optical encoding, fast actuation, biomedical fields, and tunable optical appearance.

Keywords

Active optical materials, bio-derived and bio-mimetic structures, stimuli-responsive bio-enabled materials, bio-photonic materials, multi-functional optical materials

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1. Introduction

Colors in nature are observed widely and frequently caused by organized natural structures in insects, plants, and other natural species.[1] The pitch dimensions of these helical structures determine the colors because of the specific wavelength scattered, diffracted, and interfered from their periodic and ordered nanostructures. Many natural organisms exhibit structural circularly polarized colors and iridescent appearance instigated by periodic and ordered nanostructures of helical type. Natural colored materials often reconcile multiple functional properties, such as high strength and toughness and bright iridescence such as those observed in butterflies,[2,3,4,5] beetles,[6,7,8] plants[9,10,11,12] and opal.[13,14,15,16,17]

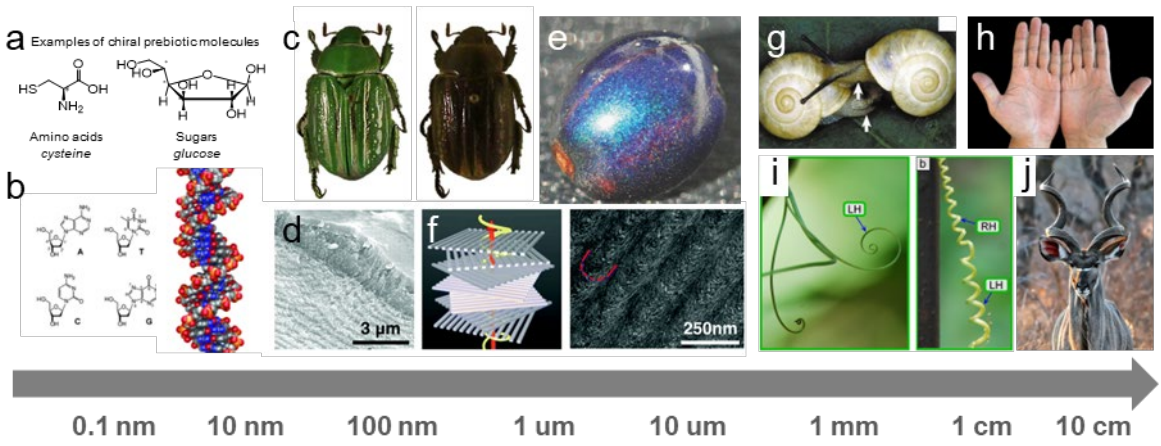

Figure 1. Chirality in nature across different length scales. Chemical structures of (a) chiral probiotic amino acids, *cysteine* (left), and sugars, *glucose* (right) and (b) biological molecules, *cytosine* (left) that make up a strand of DNA (right). Adapted with permission.[18] Copyright 2011, Royal Society of Chemistry. (c) Photographs of *C. gloriosa* under (left) left-circular polarizer and (right) right-circular polarizer. Adapted with permission.[19] Copyright 2014, Elsevier. (d) SEM micrograph of (c). Adapted with permission.[20] Copyright 2009, The American Association for the Advancement of Science. (e) Photograph of Polia Condensata fruit. Adapted with permission.[21] Copyright 2014, Wiley-VCH. (f) 3D illustration and SEM micrograph of (e). Adapted with permission.[22] Copyright 2012, National Academy of Sciences. (g) Dextral unbanded and sinistral banded morphs of the racemic strain established in *Bradybaena similaris*. Adapted with permission.[23] Copyright 2003, Springer Nature. (h) A pair of hands. (i) Towel Gourd tendrils. (left) Growing tendril helices without hooking and (right) tendril helices with hooking attached to a supporting object. "LH" and "RH" denote left and right handedness, respectively. Adapted with permission.[24] Copyright 2012, Springer Nature. (j) Spiral horns of Giant eland. Adapted with permission.[25] Copyright 2023, Springer Nature.

Optical chirality was discovered in 1848 by the French scientist Louis Pasteur.[26] Chirality or 'handedness', word derived from Greek χειρ (kheir), "hand", is a geometrical property of an

object or molecule when they cannot be superimposed on its mirror image by any translations or rotations. Nature often demonstrates a preference for specific symmetries, making chirality commonly observed across all length scales: from the molecular level (the single L- or D-amino acids) to the supramolecular level (the right-handed double helix of DNA), and to large-scale biomineralized materials (e.g., marine shells) or colored plants (Figure 1).

Bio-inspired chiral optical materials and photonic crystal structures are promising candidates for light-harvesting applications, which require light detection and manipulation. Hybridization of stimuli-responsive materials, functional materials and/or bio-derived materials provides tunability as well as dynamic control of optical properties. Under the various stimuli, including heat, humidity, light, magnetic field, and pressure the stimuli-responsive composite materials can reversibly control its mechanical properties, biological activities, as well as its macroscopic shape. By understanding and replicate their photonic nanostructures using the stimuli-responsive materials, the bio-inspired stimuli-responsive photonic structures can dynamically response to different environments that opens new potential applications for dynamic optical materials.

2. Chiral photonics

Chirality is frequently associated with the handedness of the helical organization that controls circular polarization of light.[27] The field of chiral photonics suggests that traditional photonics can be enhanced by making use of the spin degree of freedom of light. Unlike standard photonic platforms, chiral photonics aims to make use of the handedness of circularly polarized light to retain and propagate additional information in a photonic circuit and control the propagation and polarization of light. One example of chiral photonics is the use of chiral optical metamaterials.[28,29,30] Metamaterials are artificially engineered materials with properties not found in nature, and chiral metamaterials are designed to exhibit chiroptical effects on light. These materials can be used to design devices that manipulate the spin and polarization of light in unique ways, leading to advancements in areas like optical communication and processing.

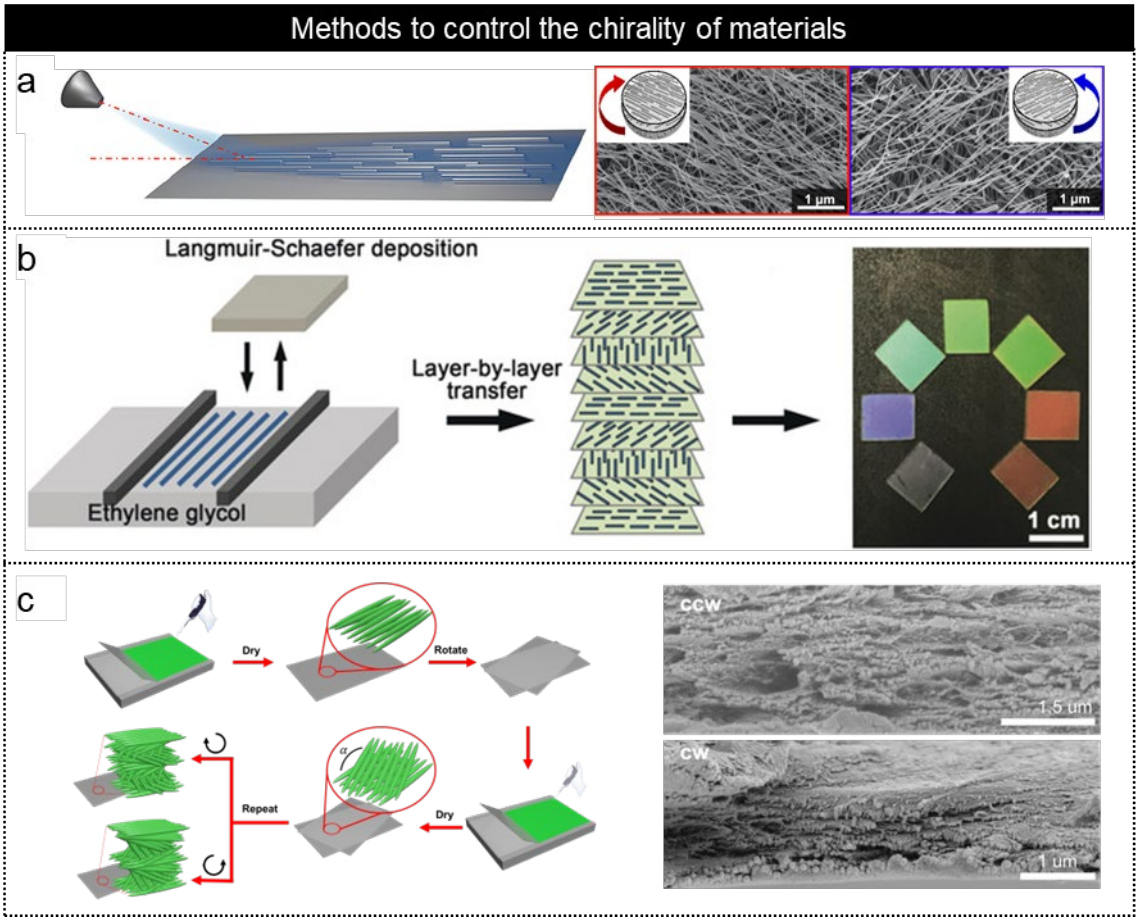

Figure 2. Methods to prepare chiral materials. (a) Schematic of the spray-induced orientation of nanowires, and SEM of the resulting monolayer of oriented AgNWs color-coded according to their orientation. Adapted with permission.[31] Copyright 2021, American Chemical Society. (b) (left) schematic illustration of compressing barriers to obtain aligned nanowire films, followed by transferring the aligned layer onto a substrate by horizontal lifting (Langmuir–Schaefer deposition). (Middle) Helical arrangement of aligned layers in the chiral photonic crystals. (Right) Chiral photonic crystals. Adapted with permission.[34] Copyright 2019, Wiley-VCH. (c) Schematic of the sequential printing of twisted photonic structures with orientational direction changing from layer to layer. On the right are the cross-sectional SEM of the printed photonic structures. CW and CCW denote clockwise and counterclockwise deposition direction.[39]

Design and engineering of chiral optical metamaterials is essential for the advancement of chiral photonics field. These materials can be fabricated via twisted stacking of the highly oriented nano objects even without formal chirality (Figure 2 and 3).[32,33] This stacking can be achieved by Langmuir–Schaeffer assembly,[34] grazing incidence spraying or template-assisted assembly,[35] 3D printing,[36,37,38] and shearing-controlled deposition.[39] Recent studies have developed into chiral plasmonic metasurfaces such as those constructed via alignment of gold or silver nanorods or nanowires.[35] It is important to note that most of the twisted stacking of oriented layers of 1D objects replicates nature found as classical Bouligand structure. For example, Hu et al., showed how grazing incidence spraying of plasmonic 1D nano-objects,

plasmonic nanowires, can be assembled into chiral Bouligand structures.[31] Specifically, grazing incidence spraying resulted in well-organized layers of, first, chiral nanohelices on polymer[40] and then, employed to prepare monolayers of oriented rods that can be stacked at different angles (Figure 2a).[31,41] Langmuir-Schaefer deposition allows ultrathin $W_{18}O_{49}$ and $NiMoO_4 \cdot xH_2O$ nanowires to be deposited by sequential dipping in diverse chiroptical photonic crystals (Figure 2b).[34] By varying the number of layers deposited, and thus the pitch length, those photonic crystals demonstrated vivid colors ranging from violet to red, as well as mirror symmetrical circular dichroism (CD) spectra that can be tuned (Figure 2c).

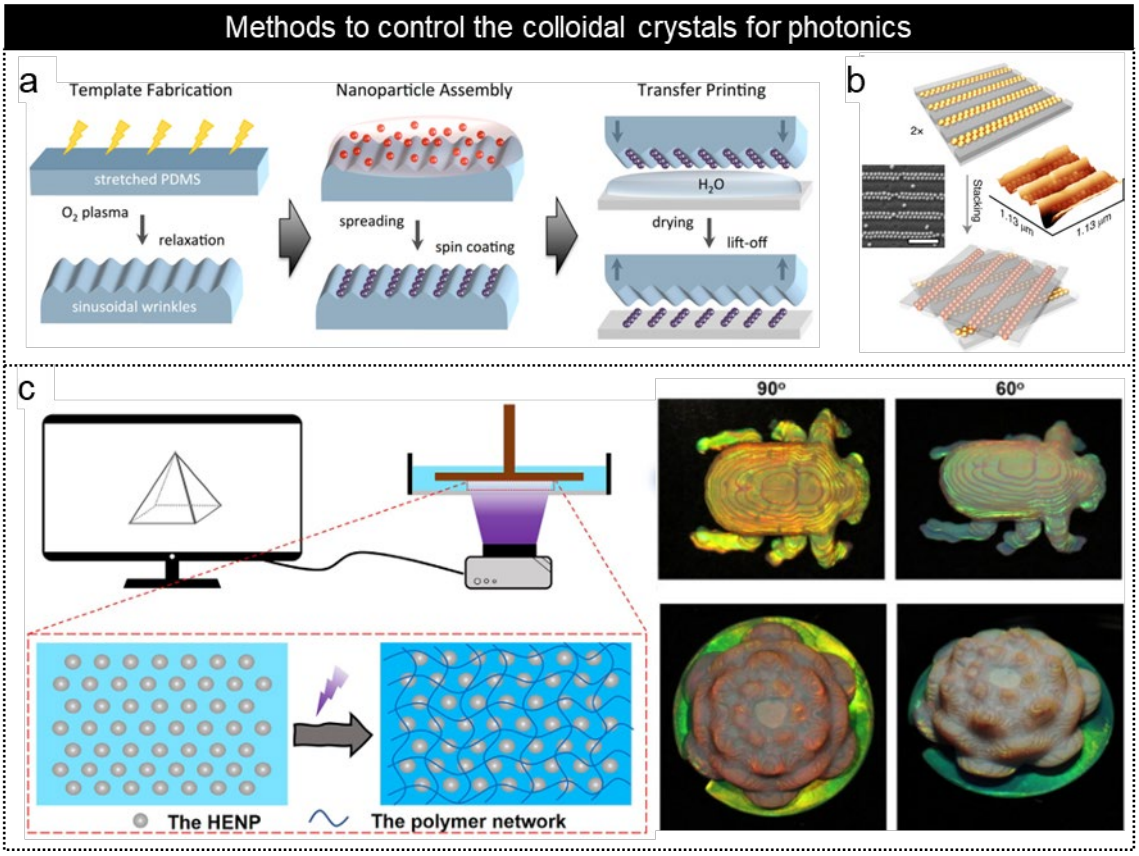

Figure 3. Stacking of colloidal photonic crystals. (a) Schematic of template-assisted chiral assembled gold nanoparticles by macroscopic stacking. Adapted with permission.[42] Copyright 2019, Wiley-VCH. (b) structure observed by SEM and AFM of (a). Adapted with permission.[35] Copyright 2023, Sringer Nature. (c) Schematic illustration of 3D printing of colloidal photonic crystals.[36] Copyright 2023, Elsevier

Template-assisted colloidal assembly of gold nanoparticles (AuNPs) can be assembled into one-dimensional (1D) chain arrays (Figure 3a and 3b). To achieve nanoparticle chains, structured templates were fabricated by plasma oxidation of stretched PDMS stripes and after spin coating the nanoparticle assemblies were transferred onto flat substrates by wet contact

printing resulted in single particle chains, dimer chains, or tetramer chains.[35] The template could be twisted during the transfer process resulting in chiroptical helical stacking. Low defect macro-scaled photonic structures are also important for applications. To this end, 3D printing of colloidal crystals inspired by opal structures can be considered as the emerging candidates to construct large scaled photonic crystal structures. Indeed, by integrating colloidal crystals and photo-crosslinkable resin, the large-scale colloidal photonic crystals superstructures with structural colors can be fabricated.[36]

Finally, for naturally homochiral CNCs, shear deposition was implemented to obtain Bouligand structures of opposite handednesses.[39] By using doctor blade printing and sequentially rotating the substrate by a fixed angle, CNCs chiral thin films were layer-by-layer constructed (Figure 2b, c). The rotation in the opposite direction during the deposition (clockwise vs counterclockwise) results in construction of chiral photonic crystals with mirror symmetrical CD signals, not achieved in nature.

3. Tunable photonic materials

Tunable biophotonic materials have been demonstrated through complex manufacturing of tunable periodic refractive index distribution.[43,44,45,46]

3.1. Stimuli Responsive Biopolymeric Photonic Structures

Many natural biomaterials have been used to create responsive photonic structures that can display dynamic optical changes due to tunable periodicity of its photonic structure.[33] For example, liquid crystalline colloidal biopolymers including cellulose nanocrystals (CNC), chitin, hydroxypropyl cellulose (HPC), and polysaccharides, offers various structural design platform for stimuli-responsive photonic architectures in response to various external stimuli, such as temperature, light, chemical environments, electric field, magnetic field and mechanical stress.[33,47]

Temperature response presents another way for tuning of photonic structure.[33] By carefully selecting and these temperature-responsive components, reversible color changes in the bio-photonic structure can be realized. For example, incorporating thermally responsive polymers, such as poly(N-isopropylacrylamide) (PNIPAAm), into the biophotonic matrix enables the tuning of structural properties in response to changes in temperature, leading to the modulation of its photonic bandgap.[48] Responsive hydrogels that are designed to undergo reversible phase

transitions or swollen state, can be explored as tunable photonic bandgap materials. For instance, Wu et al. developed a thermochromic photonic film with large color shift by infiltrating thermoresponsive poly(oligo ethylene glycol acrylate) copolymers in SiO_2-coated ZnS photonic crystals (Figure 4a). [49] Shang et al. fabricated photonic ink that features cholesteric cellulose liquid crystals, gelatin, and a thermally responsive hydrogels (Figure 4b). [50] This bio-photonic ink maintains a helicity-caused structural color with thermal responsive behavior during 3D printing.

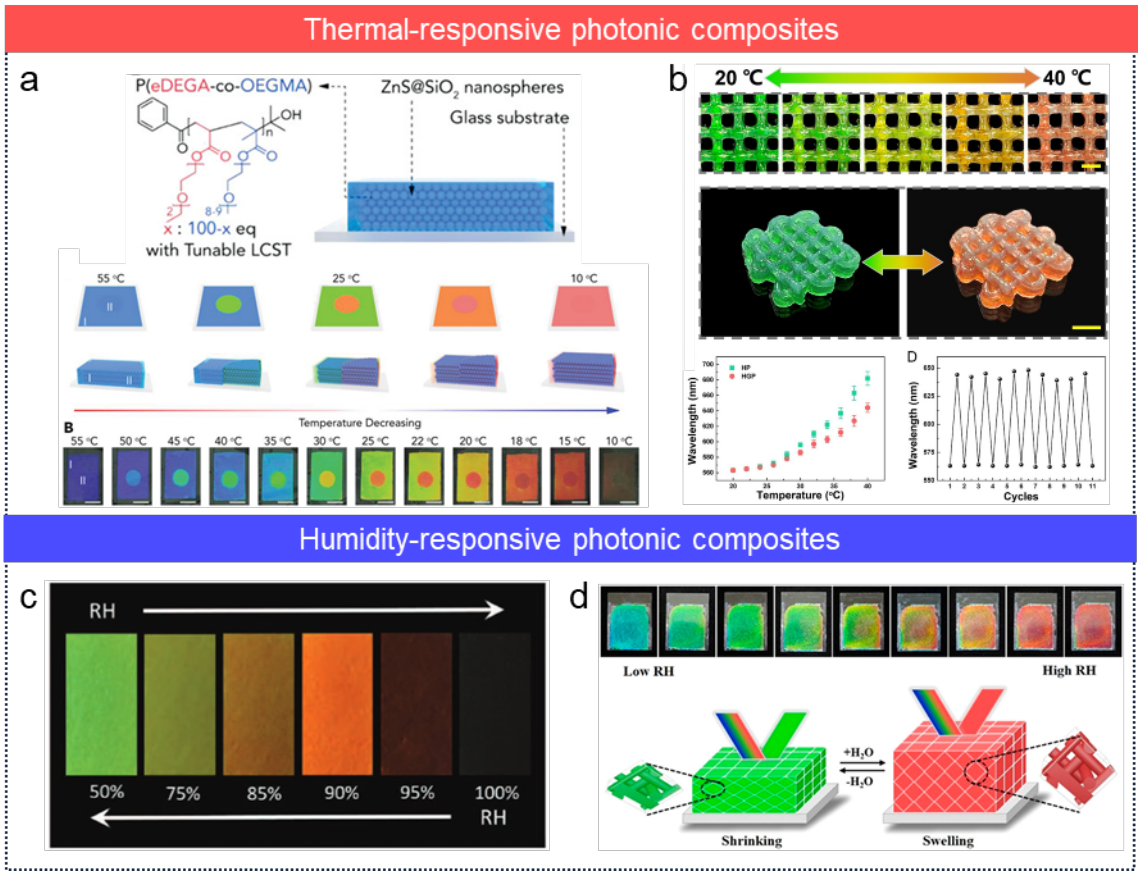

Figure 4. Stimuli-responsive biophotonic materials. (a) Tunable structural color by POEGA copolymers and ZnS@SiO2 photonic crystals. Adapted with permission.[49] Copyright 2022, Wiley-VCH. (b) Thermally-responsive hydrogel ink incorporating with gelatin and poly(acrylamide-coacrylic acid, PACA) combined with cholesteric liquid crystalline hydroxypropyl cellulose (HPC). Adapted with permission.[50] Copyright 2022, National Academy of Sciences. The photonic ink provides vivid and angle-independent structure color with dynamic thermal responsive color variation. (c) Chiral nematic CNC photonic films that show reversible structure color change at variable relative humidity. Adapted with permission.[51] Copyright 2017, Wiley-VCH. (d) Colorimetric photonic polymer coatings based on humidity-responsive blue phase liquid crystals. Adapted with permission.[52] Copyright 2021, American Chemical Society.

On the other hand, humidity-triggered response is simple and most widely explored. For instance, chiral nematic CNC films can provide a fast switching in their color from blue to red in response to relative humidity due to the intercalation of water molecules in each nematic layers, resulting in an increased helical pitch length.[51] Remarkable example is that Yao et al. fabricated chiral nematic CNC composite films co-assembled with poly(ethylene glycol) (PEG) that show dynamic shifting in Bragg's reflection from 495 nm (Green) to 930 nm (NIR) in response to relative humidity changes from 30% to 100% (Figure 4c).[51]

In addition to PEG, different types of small hygroscopic components such as glucose, polyurethanes, and glycerol, can be intercalated for controlling helical pitch distance, resulting in tunable photonic color in response to humidity.[52,53,54,55] For instance, to enhance a humidity-driven color-changing, a hygroscopic polymer coating that is highly sensitive to humidity was developed via alkaline treatment (Figure 4d).[52]

Pressure-sensitive colorimetric structures in bio-inspired composite systems play a critical role in various applications by offering a visually enabled response to mechanical stresses.[56,57,58,59,60] The pressure responsive photonic systems provide dynamic changes in color under external pressure, serving as effective indicator of mechanical stress monitoring for a quick distinguishable response to pressure variations.

For example, MacLachlan et al. demonstrated pressure-responsive chiral photonic aerogels, fabricated through a combination of self-assembly of CNCs and ice-templating.[61] These photonic aerogels exhibit 2D chiral nematic walls formed by CNCs, organizing into ribbons that support a secondary 3D cellular network. The aerogels allow easy transformation from a 3D to a 2D structure through pressure-induced rearrangement. The color of the aerogels varies from white, due to light scattering, to a reflective photonic crystal that displays vibrant iridescent colors depending on the immersed solvent. In other study, Jeong et al. constructed multi-layered photonic film with HPC that performed photonic skin with adaptable to various surfaces.[62] The multi-layered photonic film is composed of HPC layer, electronic sensor layer and bio-inspired reversible shape-memory adhesive layer that adheres to various substrate including human skin.

3.2. Dynamic chiro-optical bio-inspired composites

A known, cholesteric (chiral nematic) liquid crystals with their helical molecular arrangements exhibit chiro-optical behavior that enables to control the polarization of incident light.[63] The helical pitch determines which circular polarization is preferentially reflected or transmitted with the tunable helical pitch enabling shifting colors.

Electrically responsive bio-photonic structures have been reported with featuring iridescent chiral nematic phases to precisely manipulate CNC suspension in a nonpolar solvent (Figure 5a).[64] This study includes the precise control over the orientation of the cholesteric phase, enabling the tuning of iridescence and the formation of nematic phase, indicating that twisting energy density for unwinding the cholesteric phase. Moreover, it was also demonstrated that time-modulated electric field at different frequencies results in dynamic color changes.

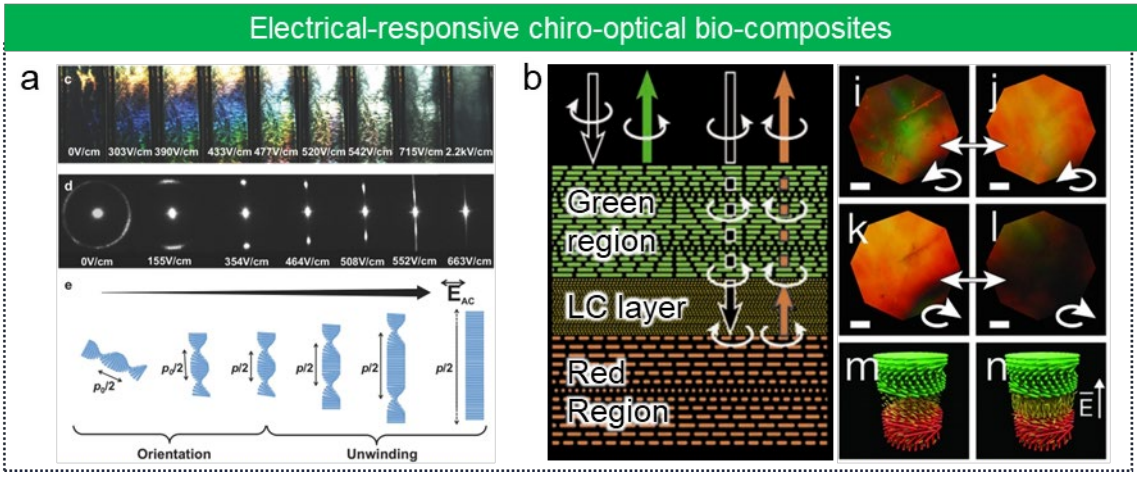

Figure 5. Dynamic chiro-optical bio-inspired composites. (a) Iridescence cholesteric liquid crystalline CNC suspension, displaying increase of light intensity with red shift of the color under an increase of applying different electric field (Top), and corresponding light diffraction patterns (Bottom). Adapted with permission. [64] Copyright 2017, Wiley-VCH. (b) Scheme of simple principle showing selective light propagation and reflection of circularly polarized light (CPL) in multi-stacked organization composed of the gap filled with the anisotropic LC layer inserted between the two left cholesteric CNC films (left). Electrically triggered tunable CPL reflection (right). Adapted with permission.[65] Copyright 2016, Wiley-VCH.

The chiral CNC films possess left-handedness that results in selective reflection of left circularly polarized light. The tailored CNC photonic films, assembling the chiral nematic phase with dynamically controlled light reflection remain a great challenge. Godinho et al. demonstrated free-standing CNC-based photonic films that reflect both right and left circularly

polarized light simultaneously, achieved by inserting a nematic layer, acting as a λ/2 retardation plate, between two left-handed cholesteric domains (Figure 5b).[65] The reflective of right circularly polarized light is intricately linked to the LC birefringence, resulting in dynamic chiro-optical performance with fast, millisecond response times.

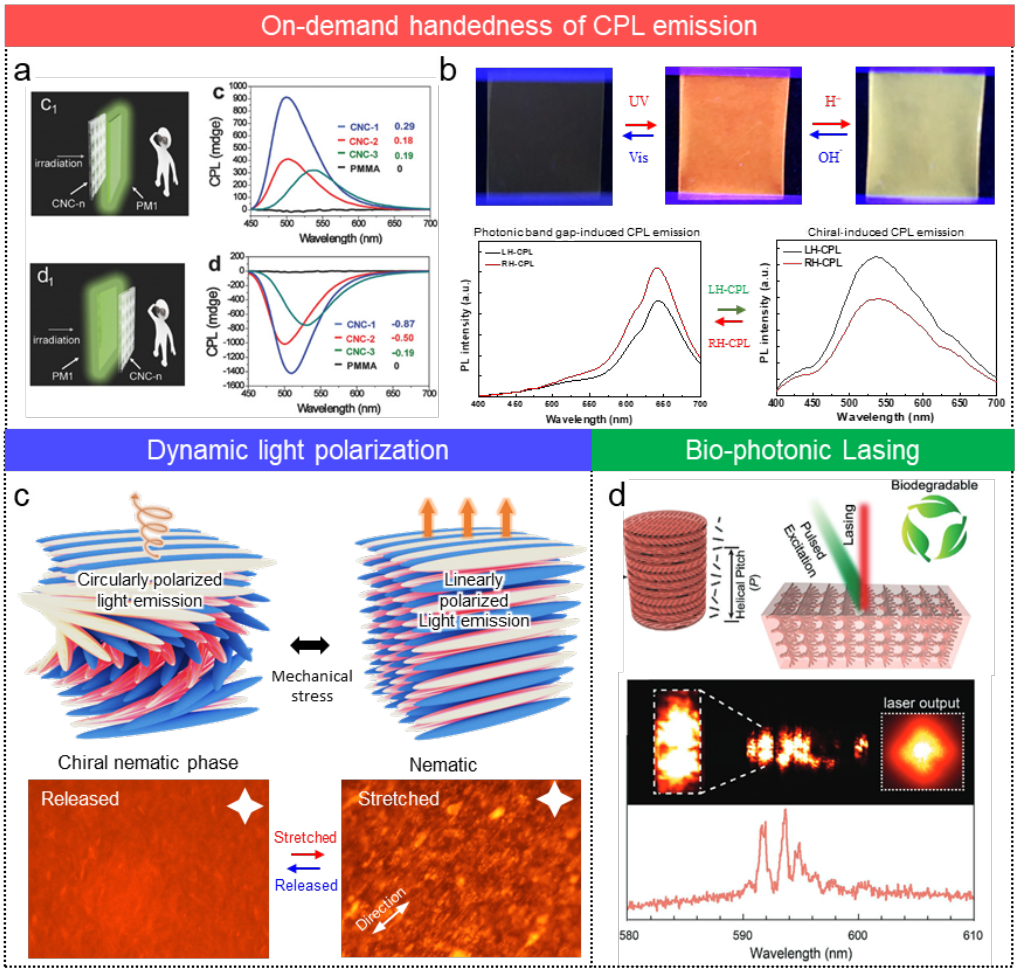

Figure 6. On-demand light emission/lasing/polarization. (a) Circularly polarized light (CPL) emission of chiral photonic CNC films composed of achiral fluorescent dyes, presenting passive LH-CPL and RH-CPL emission. Adapted with permission.[66] Copyright 2018, Wiley-VCH. (b) On-demand CPL emission of chiral nematic CNC composites incorporating with fluorescent spiropyran molecules that enable to switch emission wavelength and the handedness of CPL emission in response to chemical stimuli. Adapted with permission.[67] Copyright 2021, Wiley-VCH. (c) Chiral nematic CNC elastomeric composites combined with emissive quantum nanorods that can control the light polarization of their photoluminescence from circular to linear polarization in response to mechanical stretching. Adapted with permission.[68] Copyright 2021, Wiley-VCH. (d) Self-assembled liquid crystal laser with CNCs capable of acting as switchable bandgap laser. Adapted with permission.[69] Copyright 2020, Wiley-VCH.

3.3. Responsive bio-enabled circularly polarized light (CPL) emission/lasing materials

Integrating optically active synthetic components into periodic helical structures can provide intriguing optical functionalities depending on the types of optical dopants by realizing host-guest co-assembly. Optically active nanostructures, such as quantum dots (QDs) (emission), metal nanoparticles (NPs) (plasmonic absorbance), and organic dyes (multicolored emission) have been employed to control light polarization and induce emission resulting in chiral photoluminescence and lasing.[66, 70 , 71 , 72] For instance, chiral emissive CNC composites incorporating achiral optically active molecules have demonstrated strong right-handed (RH)-CPL emission with high asymmetry factor, |g|, of -0.68 (Figure 6a).[66] The key features for obtaining a high asymmetry value are the formation of a twisted stacking of host optical materials, uniform pitch orientation, and a high twisting power.[73]

Recent studies have been focused on enabling both RH-CPL and left-handed (LH)-CPL on-demand. Real-time active control of handedness of CPL emission was realized by integration of dyes and CNCs (Figure 6b).[67] The addition of hydroxyl-functionalized spiropyran molecules into CNCs results in active left-handed CPL emission with large asymmetry due to twisted stacking of spiropyran molecules. Controlled helical pitch of chiral nematic CNC films led to tunable selective reflection of CPL emission with variable asymmetric factor. Moreover, reversible isomerization of spiropyran molecules by changing the pH environment triggers dynamic CPL emission with different handedness and wavelength.

In another study, it was demonstrated that chiral luminescent can be established by co-assembling semiconducting quantum nanowires and CNCs into elastomeric polyurethane matrix (Figure 6c).[68] The resulting chiral CNC-QNR composites showed dynamically reversible chiroptical properties, resulting in LH-CPL emission with high asymmetry converted to linearly polarized light emission due to mechanically induced phase transformation to unidirectional orientation.

The bio-enabled lasers are composed of optical cavity of photonic matrix integrated with emitting materials in order to provide optical resonant amplification or the creation of mirrorless laser cavities that generate optical feedback through the integration of photonic stopbands (Figure 6d).[69] Recently, Guo et al. demonstrated a photonic crystal laser by introducing ethylene glycol-hydroxyethyl methacrylate into cholesteric CNCs with controlled helical pitch that results in the maximum emission.[69] The amphiphilic nature of CNCs allows

for humidity-based switching between lasing and emitting.

4. Programmable stimuli-responsive actuators

Among the responsive materials, photo- and magneto-responsive materials can be designed to perform rapid actuation. Photo-responsive materials not only can transduce photochemical energy to mechanical energy but also change their optical properties. Programmable magneto-responsive composite materials can be utilized for tuned photonics, [74,75,76] soft robotics,[77,78,79,80] switchable surface,[81,82,83] and object guiding.[84,85]

4.1. Photo-responsive composites materials

Photo-responsive behavior can be photo-chemical and photo-thermal in nature (Figure 7a). For instance, the azobenzene molecules undergoes through isomerization from trans to cis under ultraviolet (UV) light irradiation and recovers from cis to trans by applying visible light and/or heat.[86] The geometric change of azobenzene under UV light can generate macroscopic shape changes due to photo-thermal effect is the phenomenon. Light-absorption induced temperature rise transfers the thermal energy to elevated stresses that induces geometric changes and/or dehumidification of materials.

A hybridization of LC mixtures including photochromic azobenzene was elaborated for switchable optical properties in porous silicon matrix (Figure 7b).[87] Repetitive alternation of irradiated surface (front or back) can generate perpetual motion of photo-responsive composite materials. Embedding the acrylate functionalized azobenzene into liquid crystal polymer networks (LCNs) can result in rapid actuations such as oscillations [88,89,90,91] and jumping.[92]

In this approach, oscillation of photo-responsive LCN was achieved by focused laser irradiation to monodomain azobenzene embedded LCN strip. When the laser irradiated to one side of the strip, the irradiated point undergoes contractile force to parallel to alignment that deforms the strip toward light direction. Then, the back side of the strip starts to be exposed and the deformed strip recovers to upright position of strip. Even higher light intensity accelerates bending and unbending behavior that induces high frequency actuation.[88]

Furthermore, introduction of non-isometric structures into azobenzene embedded LCN film enables the film to jump via snap-through upon actinic light exposure (Figure 7c).[92] The LC mixture with super twisted nematic geometry to form macroscopic bi-stability state that can be

exploited for fast actuation. The perpendicular molecular alignment at the top and bottom of the photo-responsive LCNs provides for effective accumulation of photogenerated stress, realizing photomechanical jumping by instantaneously releasing energy via snap-through behavior.

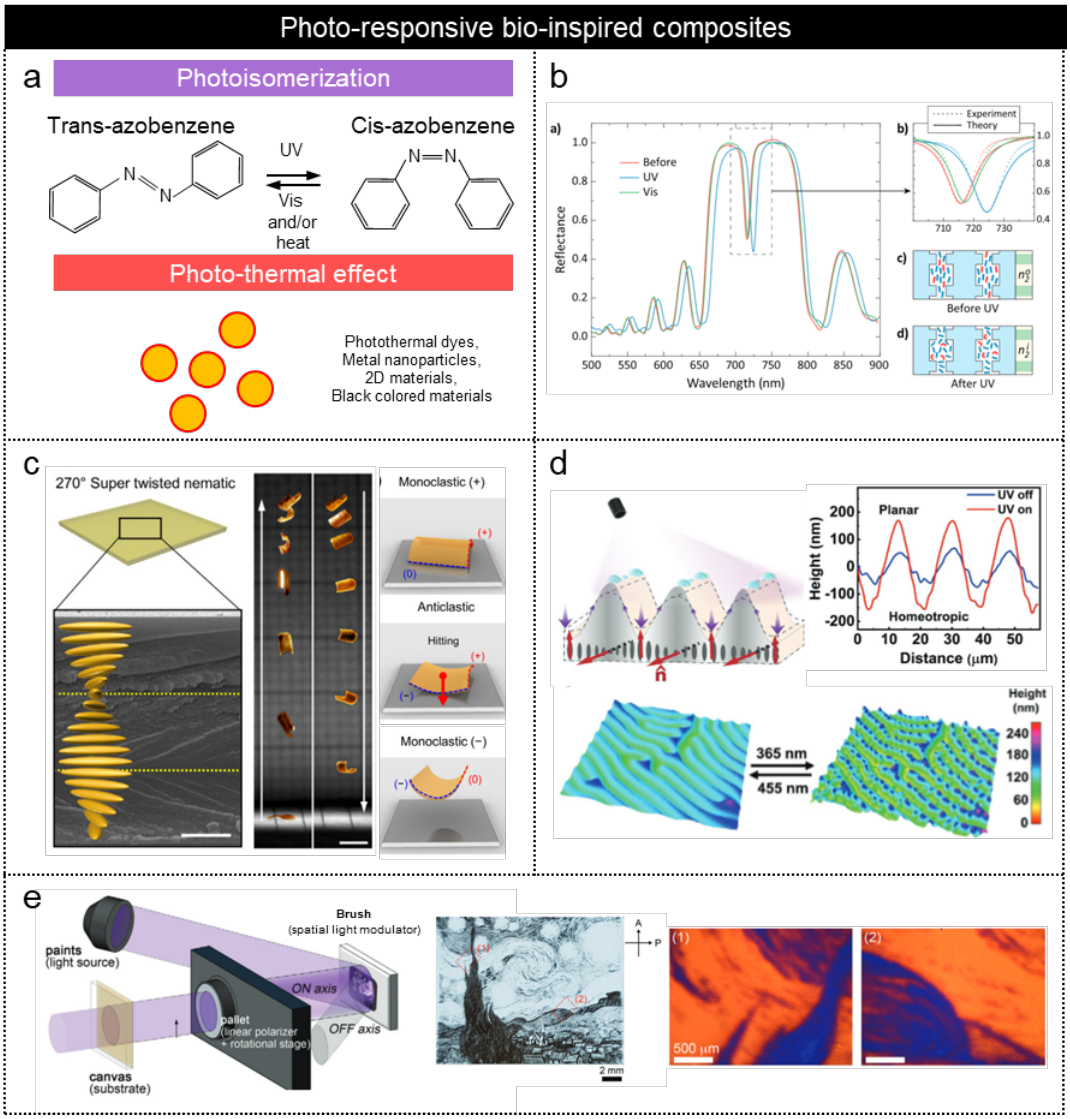

Figure 7. Photo-responsive bio-inspired composite materials. (a) Mechanisms of photo-responsive components. (b) Reflectance spectra of the photonic LC composite before/after UV light irradiation and after subsequent visible light action. Adapted with permission.[87] Copyright 2020, Wiley-VCH. (c) Jumping behavior of azobenzene embedded liquid crystal-based polymer through snap-through behaviors. Adapted with permission.[88] Copyright 2021, Elsevier. (d) Photo-switchable fingerprint composed with azobenzene embedded liquid crystal-based polymer. Adapted with permission.[93] Copyright 2023, Wiley-VCH. (e) photo-patternable azobenzene assisted liquid crystal surface through the SLM technique. Adapted with permission.[94] Copyright 2020, Wiley-VCH.

Inspired by the dermis and epidermis of human skin, cholesteric liquid crystal organization is recreated to mimic extensive human perspiration and friction.[93] To generate perspiration, UV illumination has been applied to acrylate-functional azobenzenes and liquid crystals in order to induce the homeotropically-aligned regions (Figure 7d).

In addition, the surface of azobenzene containing materials can be patterned by irradiation of polarized light. The azobenzene molecules can be patterned perpendicular to polarized direction through trans-cis-trans isomerizaton, which called Weigert's effect.[86, 95] These azobenzene contained materials can perform shape fixation,[96] light patterning,[94, 97, 98] and directional actuation.[99,100,101,102] Photoalignment layers can be patterned through spatial light modulator (SLM) that the light subsequently passes through a linear polarizer mounted on a motorized rotation stage (Figure 7e).[94] The pixelated mosaics wrinkles with multiple orientations are formed by the sequential illumination with different polarization angles to produce a 2D wrinkle array (Figure 7e). The blue and red interference colors correspond to the orientation of molecules along $\theta = 45°$ and $\theta = 0°$, respectively, and coincide to the orientation of wrinkles.

4.2. Magneto-responsive composite materials

In the case of superparamagnetic magnetic nanoparticles with diameter under 10 nm such as iron oxides (Fe_2O_3 and Fe_3O_4) show random Brownian motion in suspensions without external magnetic field.[103] Under the magnetic field, magnetic nanoparticles undergo preferential alignment along magnetic field (Figures 8a, b, c).[104,105,106,107] It was demonstrated that Janus magnetic nanoparticles can be designed with a permanent magnetic moment for switching structural colors (Figure 9a).[75,76] They are produced by photopolymerization of paired droplets through microfluidic channel under external magnetic field. The paired droplets have two emulsified phases with immiscible photocurable resins into the continuous water phase using a capillary microfluidic device.

The assembly of CNCs with arranged magnetic nanoparticles is different from normal evaporation induced self-assembly (EISA) of CNCs. The CNC decorated with Fe_3O_4 nanoparticles are arranged parallel to the magnetic field direction that leads to the formation of homeotropic concentric helix orientation (Figure 9b).[108] Their chiroptical properties can be

tuned by modifying the suspension characteristics. The film surface appears blue under normal incidence, and the cross-polarized optical micrograph (POM) of the film plane surface displays a blue birefringence with azimuthal pattern around localized homeotropic Fe_3O_4-rich spots.

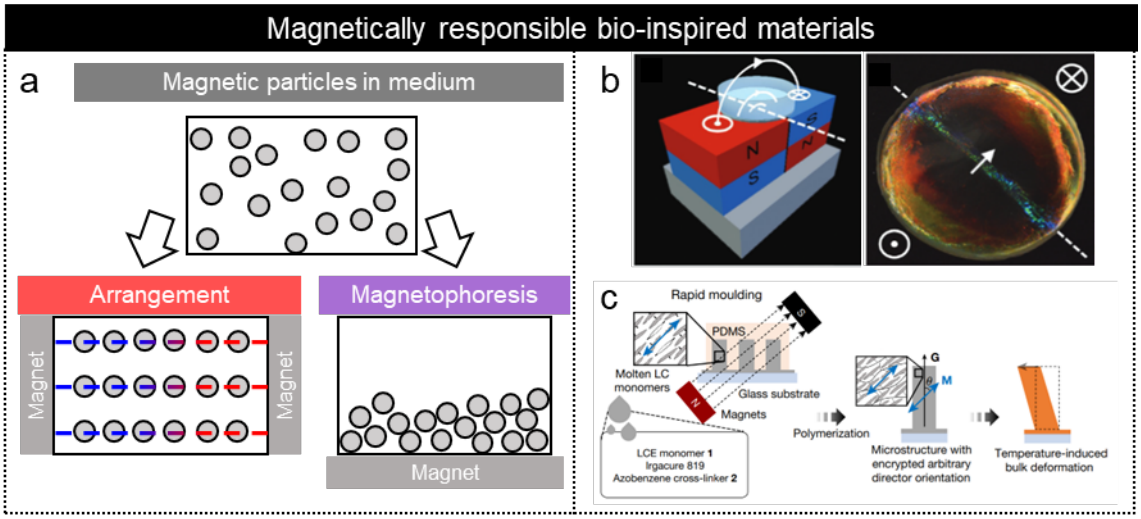

Figure 8. Magneto-responsive bio-inspired materials. (a) Mechanisms of magnetically induced behavior of magnetic particles in the medium. (b) Patterned evaporation induced self-assembly (EISA) on the various magnets. Adapted with permission.[107] Copyright 2017, Wiley-VCH. (c) Liquid crystal molecules are pre-oriented along an arbitrary direction by a magnetic field before polymerization. Adapted with permission.[106] Copyright 2022, Springer Nature.

Drying bacterial CNC-Fe_3O_4 suspensions under static magnetic field using Nd-magnet placed beneath Petri dish induced radial Marangoni flow (Figure 9c).[109] In drying suspension, magnetic nanoparticles move to the area with higher magnetic flux density, thus, generating shear-induced Marangoni flow that induces radial alignment of decorated nanocrystals.

In the end, completely dried flexible and semi-transparent magnetic films possess uniformly aligned morphology and optical appearance with high unidirectional optical anisotropy instead of random birefringent tactoids with fingerprint-like texture and sharp boundaries of tactoids observed for traditional CNC film (Figure 9d).

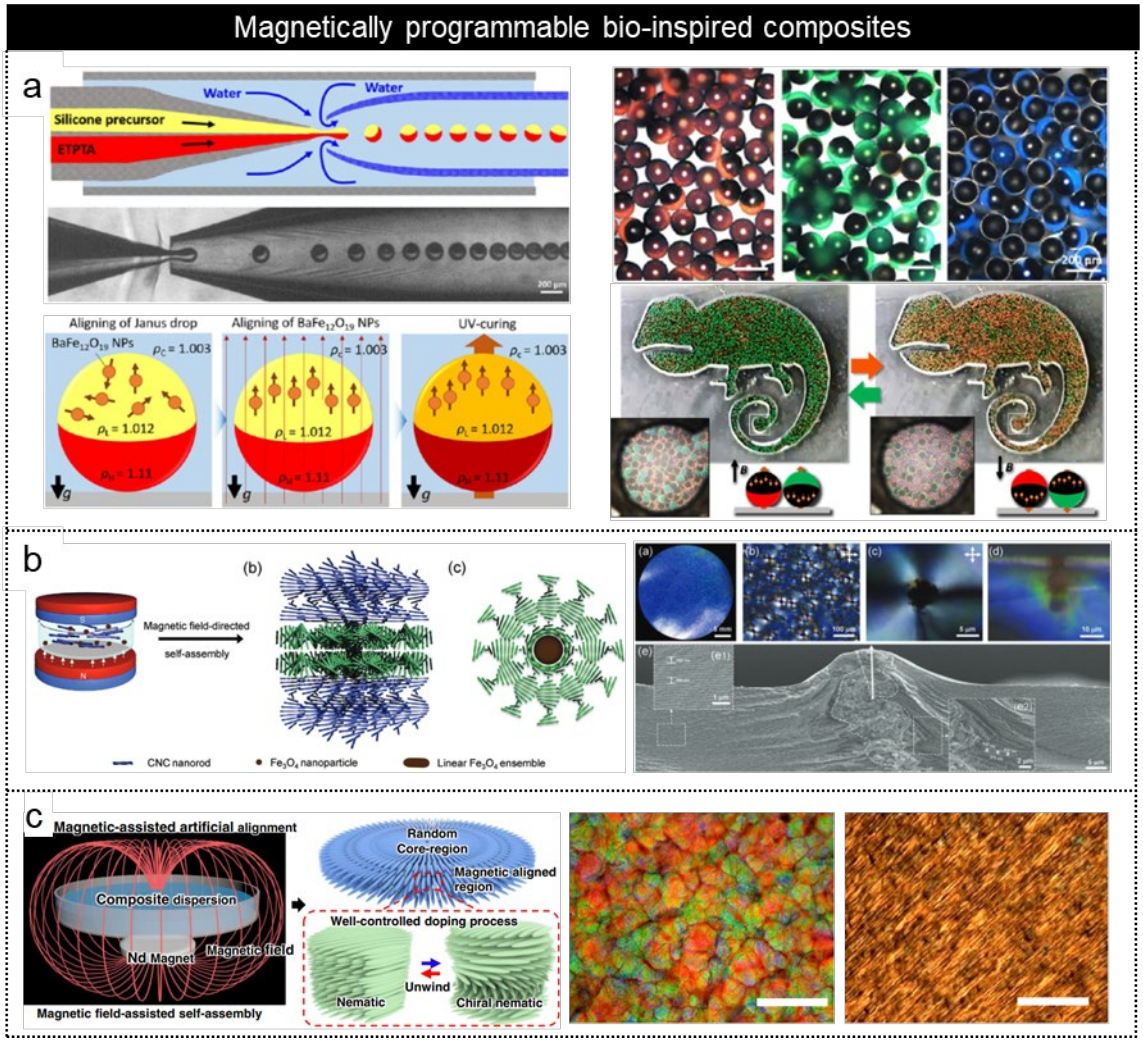

Figure 9. (a) Janus particles with controlled magnetic moment and colors and nanoparticle sizes. Optical images showing a chameleon pattern containing the mixture of the red and green particles for the four different field conditions. Adapted with permission.[76] Copyright 2020, American Chemical Society. (e) Magnetic field induced arrangement of magnetic nanoparticles and CNCs. Adapted with permission.[108] Copyright 2022, Wiley-VCH. (f) Schematic of formation of unidirectional nematic ordered CNC magnetic film in the presence of a magnetic field and POM images with/without magnetic field in CNC suspensions. Adapted with permission.[109] Copyright 2022, Springer Nature.

5. Multi-functional bio-optical applications

By integrating with bio-photonic materials and functional components, the multifunctional performances can be monitored through the colorimetric response as demonstrated in several examples below. These visual changes can be used to monitor adhesion strength, applied pressures, humidity, added chemicals, and cell behavior. Especially, the photonic crystals can

visualize the processing of cell capture, cell culture, and organ-on-a-chip platform.[110] The color of opal structures is very sensitive to interparticle distance that enables the nanostructures to visualize responses of micro/nanoscale cell motion thus enabling real-time monitoring the cells or microenvironmental transitions[111] as well as a bio-optical substrate[112,113]. This way, the imaging vertical cellular forces can be enabled at high speed and quantification with high throughput.[112]

5.1. Responsive bio-optical adhesives

Recent study demonstrated that responsive optical adhesives change their color appearance and adhesive strength in synchronized manner under the physical and/or chemical stimuli. [114] Color- and adhesion strength- switchable photonic bio-adhesives were fabricated by combining CNCs with polyacrylamide and glucose (Figure 10a). These films possess humidity response correlated with switchable adhesion strength and structural color shift. Adhesive strength and elastic modulus of these bio-adhesives were rapidly reduced as the relative humidity increase as induced by the continuous bonding of water molecules into hygroscopic hydroxyl group-rich network. Concurrently, the structural color moves from blue to red and then to clear state reversibly over multiple cycles.

In other research, free radical polymerization was conducted to prepare the adhesive that includes the stimuli responsive hetero Diels-Alder moiety (Figure 10b).[115] The degradation of adhesive occurs at ~80 °C by debonding of the hetero Diels–Alder crosslinker, leading to decrease in adhesion forces as well as mechanical strength. These changes are accompanied by color change from pale pink to dark pink. Additionally, it was demonstrated that exposing the adhesives to UV light can lead to continuous adhesion strength reduction due to the cleavage of o-nitrobenzyl ester moiety, resulting in reversed color change of adhesives from pale brown to dark brown (Figure 10c).[116]

5.2. Responsive bio-optical strain/stress sensor

In the realm of various stimuli, touch, which is a fundamental perception, plays a crucial role in many forms of sensory experiences.[117,118,119] Bio-inspired photonic tactile sensors emerge

as key contributors, offering instantaneous visualization and spatiotemporal distribution of tactile stimuli.[62] In particular, the hybridization of optical and electrical signals in dual-mode tactile detection has attracted attention, due to the complementary of each signal, enhanced sensitivity, and multimodal feedback.[120,121,122,123] Dual-mode bio-inspired tactile sensors have implemented a variety of tactile functionalities for object recognition, texture perception, and sensory feedback for health monitoring, intelligent robotics, and human–machine interface for augmented reality.[124,125]

In very recent study, Li et al. developed responsive mechanochromic materials with tailored ionic conductivity by infiltrating fluorine-rich ionic liquids into a swollen CNC film (Figure 10d).[126] The resulting CNC composites exhibited high flexibility, stretchability, and excellent ionic conductivity. Moreover, optical and electrical dual-mode tactile response facilitates real-time monitoring of human motions using both dynamic structural color and electrical resistance variation.

On the other hand, Park et al. demonstrated a hierarchical nanoparticle-in-micropore architecture in porous mechanochromic composites comprising spiropyran, polydimethylsiloxane, and silica nanoparticles (Figure 10e).[123] The spiropyran mechanophore molecules are well known in their force-induced reversible ring-opening process from colorless spiropyran to colored merocyanine state. Especially, in multi-component materials the hierarchical nanoparticle-in-micropore architecture provides stress-concentration-induced activation of color appearance. The dual mode mechanochromic composite materials can colorimetrically detect real-time tactile location and intensity of external pressure using mechanochromic color shift. Furthermore, triboelectric-related patterning can be conducted by varying the writing speed.

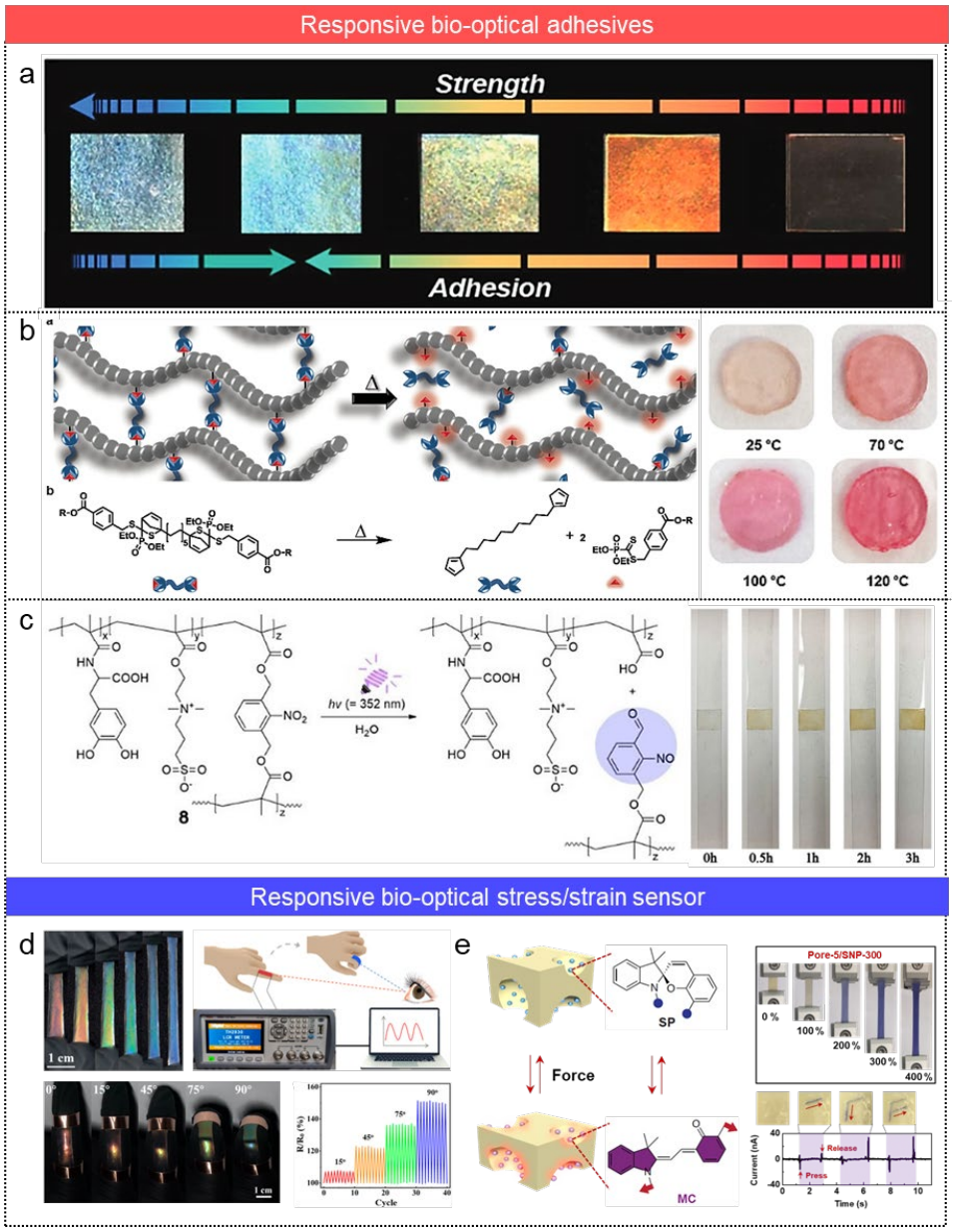

Figure 10. Examples of bio-optical devices. (a) Structural color-adhesion-mechanical strength-concurrent change of CNC/polyacryl amide/glucose adhesives depending on relative humidity from 0 % (left) to 97 % (right). Adapted with permission.[114] Copyright 2021, Wiley-VCH. (b) Degradation of polymeric adhesives by cleavage of hetero Diels-Alder crosslinker by heating and photos of the polymers depending on the heating time. Adapted with permission.[115] Copyright 2016, Wiley-VCH. (c) Photodegradation of terpolymer containing photo-cleavable o-nitrobenzyl group and photos of adhesive samples sandwiched between substrates with function of UV irradiation time. Adapted with permission.[116] Copyright 2017, Royal Society of Chemistry. (d) Dynamic structural color of FIL−CNC nanostructured films and their strain sensing capability. Adapted with permission.[126] Copyright 2023, American Chemical Society. (e) Hierarchical NP-MP architecture and properties in porous mechanochromic composites. Adapted with permission.[123] Copyright 2019, Wiley-VCH.

5.3. Bio-optical multi-valued logic system

Multi-valued logic system (MVLS) is a computing system possessing more than two distinct electrical states while traditional binary logic system uses only two levels (Figure 11a).[127,128] Materials with ternary, quaternary, and higher levels were used in fabricating MVLS devices. For those, two-dimensional transition metal dichalcogenides (TMDCs), such as MoS_2,[129] WSe_2,[130] and ReS_2[131] have been employed (Figure 11b).[131] For instance, ternary voltage output levels have been obtained by utilizing tunneling diodes and anti-ambipolar transistors, displaying the folded current-voltage characteristics (Figures 11c, d).[127,132] The ZnO layer sandwiched between organic barriers consisted of ZnO quantum dots wrapped by amorphous ZnO provided a narrow quantized extended state near the mobility edge. When the second ZnO layer was positioned on top of the quantum wells, the drain current restarted increasing after undergoing a saturation, resulting in three-level output voltages.

Photons can be employed to process data in the same manner as electrons.[133,134] For processing optical information, fiber-optic multiplexing allowed concurrent data flow over a single channel, thus, significantly speeding data processing.[135,136,137] Pereira and co-workers exploited multi-beam fiber multiplexing. They fabricated biofield-effect transistor (BOFET) with a CNC:Na dielectric layer, that can be tuned by using different circular polarization lights.[138]

Optical MVLS computing can be facilitated via a reconfigurable photonic bandgap of chiral biomaterials (Figure 11e).[139] The photonically active photonic CNC dielectric layer was combined with printed-in p- and n-type organic semiconductors as a bifunctional logical component. The photonic CNC layer controls the amount of transmitted light to organic semiconductor channels through pre-programmed bandgap, generating four different output voltage levels, creating a reconfigurable ternary logic system (Figure 11f).[139] In addition, CNC-based bio-inspired composites can be employed as bio-synaptic transistors through combination of responsive CNC material with humidity-controlled dielectric properties (Figures 11g, h).[140,141] It has been demonstrated that a photonic CNC layer facilitates electronic recognition of green and red colors as tuned by circular light polarization.

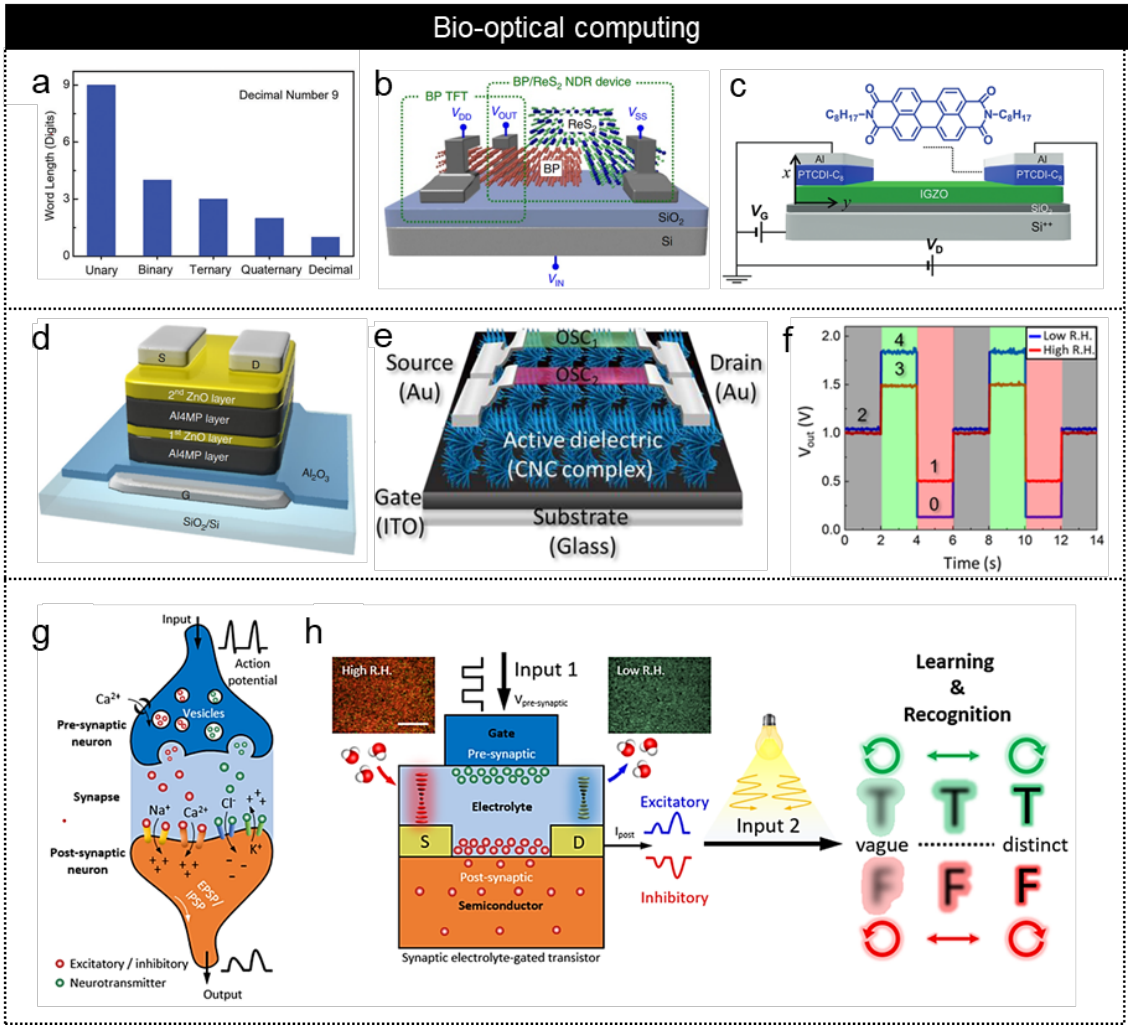

Figure 11. Multi-valued logic systems, their materials components, and diverse related phenomena. (a) Illustration a number of digits required to display the decimal 9 in each logic system. Adapted with permission.[128] Copyright 2021, Royal Society of Chemistry. (b) schematic for the black phosphorus/ReS_2 heterojunction that can show ternary logic values. Adapted with permission.[131] Copyright 2016, Springer Nature. (c) a scheme for inverter which can show ternary logic values by using metal–oxide–semiconductor–semiconductor field-effect transistor. Adapted with permission.[127] Copyright 2021, Wiley-VCH. (d) ZnO composite nanolayers which can act as a ternary transistor. Adapted with permission.[132] Copyright 2019, Springer Nature. (e) structure of CNC-based bio- field-effect transistor. Adapted with permission.[139] Copyright 2022, American Chemical Society. (f) photonic bandgap and photon energy-dependent voltage outputs of (e). Adapted with permission.[139] American Chemical Society. (g) Scheme of a synaptic system in bio-materials. Adapted with permission.[140] Copyright 2020, AIP publishing. (h) The electrolyte-gated transistor which responded by voltage (input 1) and direction of exposed chiral light (input 2), mimicking neuromorphic computing. By changing the polarization direction of the incident light, the developed system recognizes the letter differently. Adapted with permission.[141] Copyright 2022, American Chemical Society.

Conclusions and perspectives

In this review, we provide a comprehensive summary of various aspects of tunable and responsive bio-derived photonic materials and structures for versatile multi-functional applications. Bio-enabled stimuli-responsive materials exhibit dynamic properties under various stimuli, including heat, humidity, light, electrical and magnetic fields, and mechanical stress. Thermo- and humidity-responsive composite materials are particularly noteworthy for their ability to react to minimal pressure-triggered stimuli, enhancing sensitivity to touch, shearing, or blowing. Notably, many bio-derived materials are hygroscopic, which allows for control and integration with thermo- and/or humidity-responsive components.

Magneto-responsive composite materials are emerging as promising candidates for multi-functional bio-mimetic materials due to their intuitive and rapid response, programmability, and feasibility for operation in obstructed environments. However, their inherent colors, typically brown or black, pose challenges for photonic applications in visible wavelength range. Organized magnetic nanoparticles can function as photonic crystals, with colors controllable by adjusting the diameter and interparticle distance. Leveraging their magnetic properties, magnetic photonic composites can be programmed to exhibit switchable optical properties. Mechano-responsive materials also can demonstrate rapid response, but their application is constrained by the requirement for a tethered system and the limits of deformation. It worth to note that for the operation of photochromic materials, short-wavelength, high-intensity light is typically required. However, modification of functional groups on photo-responsive materials to develop responses to visible light requires multi-step synthesis processes and might obscure the overall color appearance.

The multi-functionality of bio-inspired responsive photonic materials/structures is crucial for a wide range of practical applications. Coupling these materials with other functional attributes like multi-surface adhesion, high conductivity, and shape reconfigurability broadens their application potential. Applications ranging from medical adhesives and bio-computing to wearable sensors, soft robotics, painting, and packaging can be considered for colorimetric visualized monitoring. In biomedical applications, they can be employed for precise and secure monitoring of surgical procedures and implants status. In a diverse range of fields, the bio-inspired stimuli responsive photonic composite materials/structures will expand greatly their potentials.

Abbreviations

SEM; Scanning electron microscopy.

LH; Left-handed

RH; Right-handed

RH; relative humidity

DNA; Deoxyribo nucleic acid

AuNPs; gold nanoparticles

AgNWs; gold nanowires

AFM; Atonic force microscopy

CW; clockwise

CCW; counter-clockwise

CD; circular dichroism

CNCs; cellulose nanocrystals

HPC; hydroxypropyl cellulose

PNIPAAm; poly(N-isopropylacrylamide)

PEG; poly(ethylene glycol)

NIR; near-infrared

PACA; poly(acrylamide-coacrylic acid)

CPL; circularly polarized light

LC; liquid crystal

RCP; right circularly polarized

QDs; quantum dots

NPs; nanoparticles

QNR; quantum nanorods

UV; ultraviolet

LCNs; liquid crystal polymer networks

SLM; spatial light modulator

EISA; evaporation induced self-assembly

Polarized optical micrograph (POM)

FIL; fluorine-rich ionic liquid

MP; microparticle

MVLS; multi-valued logic system

TMDCs; dichalcogenides

Biofield-effect transistor (BOFET)

Author contributions

Jisoo Jeon: Writing – original draft (lead); writing – review & editing (supporting). **Daria Bukharina**: Writing – original draft (supporting), Minkyu Kim: Writing – original draft (supporting). **Saewon Kang**: Writing – original draft (supporting). **Jinyoung Kim**: Writing – original draft (supporting). **Yiming Zhang**: Writing – original draft (supporting). **Vladimir Tsukruk**: Conceptualization (lead); project administration (lead); resources (lead); supervision (lead); writing – review & editing (lead).

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Conflict of interest statement

The authors declare no conflict of interest.

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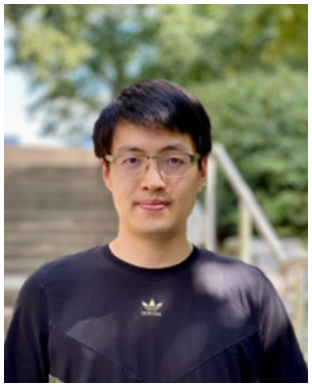
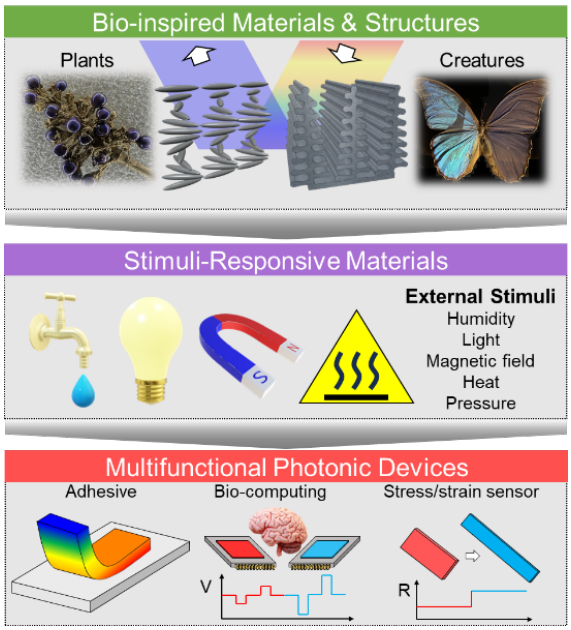


Yiming Zhang is pursuing his PhD degree in Materials Science and Engineering at Georgia Institute of Technology under the supervision of Prof. Tsukruk. Prior to that, he received his master's degree in Macromolecular Science and Engineering at Case Western Reserve University in Cleveland, Ohio. Currently, his research focuses on developing polymer ionic liquids, bio-derived responsive materials and investigating the corresponding composite nanostructures for energy-related applicatins.

Graphical abstract

Introduction of stimuli-responsive and/or functional materials into bio-inspired materials and structures enables multi-functional photonic devices such as switchable colorimetric adhesives, multi-logic value bio-computing, and colorimetric stress/strain sensor.



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