

Block Copolymer-based Photonic Pigments: Towards Structural Non-iridescent Brilliant Coloration

Ullrich Steiner and Andrea Dodero*

Abstract: Creating color through the self-assembly of specific building blocks to fabricate photonic morphologies is a promising and intriguing approach to reproducing the flamboyant visual effects and dynamic properties observed in the natural world. However, the complexity and lack of robustness in the manufacture of these nanostructured materials hinder their technical exploitation on a large scale. To overcome such limitations, here we present a novel methodology to create bioinspired photonic pigments as dispersed and micrometer-scale particles based on highly ordered concentric lamellar microspheres made of block copolymers. First, we introduce the fabrication protocol and the advantages of this approach compared to the traditional colloidal self-assembly. Then, we discuss some possible future research directions focused on developing hybrid organic-inorganic photonic pigments with enhanced dielectric contrast, reduced scattering, and specific functionalities. Finally, we speculate on possible applications for these structures that go beyond their use as simple photonic pigments.

Keywords: Block copolymers · Photonic pigments · Self-assembly · Structural coloration



Ullrich Steiner studied physics at the University of Konstanz, Germany. He gained his PhD in 1993, working with Prof. J Klein and Prof. G. Schatz at the Weizmann Institute, Israel. After post-doc positions at the Weizmann Institute and the Institute Charles Sadron, France, he returned to Konstanz where he finished his Habilitation in 1998. He joined the faculty of the University of Groningen as a full professor in 1999 and be-

came the John Humphrey Plummer Professor of Physics of Materials at the University of Cambridge in 2004. Since 2014, he holds the chair of Soft Matter Physics at the Adolphe Merkle Institute in Switzerland.



Andrea Dodero studied materials science and engineering at the University of Genoa, Italy, where he received his PhD in May 2021 under the supervision of Prof. M. Castellano. Since June 2021, he holds a post-doc position at the Adolphe Merkle Institute in Switzerland within the NCCR Bio-Inspired Materials framework under the supervision of Prof. U. Steiner (chair of Soft Matter Physics) and Prof. C. Weder (chair of Polymer Chemistry

& Materials). He has been awarded a Marie-Curie Individual Global Fellowship (2022–2025) focused on developing bio-inspired photonic pigments.

1. Introduction

An interest in color is intrinsically rooted in human civilizations and the quest for increasingly stunning coloration effects has led to exciting discoveries, which have stimulated fundamental research to develop an understanding of the underlying physics of the observed phenomena.^[1,2] Modern times have seen a paradigm shift in the design of color effects from an empirical

approach toward a computer-aided, predictive design of optical materials.^[3,4] Commonly employed pigments (*i.e.* insoluble substances that show a certain color because they reflect specific wavelengths of visible light) can be divided into organic and inorganic ones. While the first provide high color quality and tuneability, they are expensive to synthesize and display limited stability over time. In contrast, inorganic pigments are typically low-priced and are characterized by a high lightfastness, but are often toxic and display poor tonality.^[5,6] Therefore, novel optical materials capable to control and manipulate light–matter interaction at the nanoscale are becoming crucial for several technological applications, from cosmetics to protective coatings.^[7–12] A particularly intriguing inspiration for coloration has been the natural world, where evolution has produced remarkable displays of optical effects, from the most brilliant iridescence and luster on display in bird feathers or butterfly wings to adaptive coloration in camouflaging chameleons or octopuses (Fig. 1).^[13–17] These optical effects typically arise from an intricate internal structure of the material at the nano- and microscale at which visible light is reflected, dispersively diffracted, or scattered.^[18]

Of particular interest is the structural coloration arising from photonic crystals (PhCs), which consist of an ordered lattice of alternating refractive index, where the lattice parameters are of the order of the optical wavelength. Comparably to electrons in a periodic potential, these structures are characterized by a photonic band structure that identifies spectral regions forbidden and allowed for the propagation of photons, giving rise to a photonic bandgap (PBG) that is responsible for their chromatic response.^[19] So far, this unique property has been mostly investigated to generate planar photonic coatings and films that reflect vibrant, iridescent colors.^[20–22] However, the large-scale applicability of such structures is strongly hindered by processing limitations, and more user-friendly and ready-to-use substitutes are needed.^[23]

In this perspective article, we focus attention on the recent advances in block copolymers-based dispersible photonic pigments. First, we briefly introduce the current approaches and limitations in creating structural color pigments based on colloidal assemblies. Then, we discuss the use of three-dimensional confined self-assembly of block copolymers in emulsion droplets to generate highly ordered concentric multilayer particles with

*Correspondence: Dr. A. Dodero

E-mail: andrea.dodero@unifr.ch

Adolphe Merkle Institute, University of Fribourg,
Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

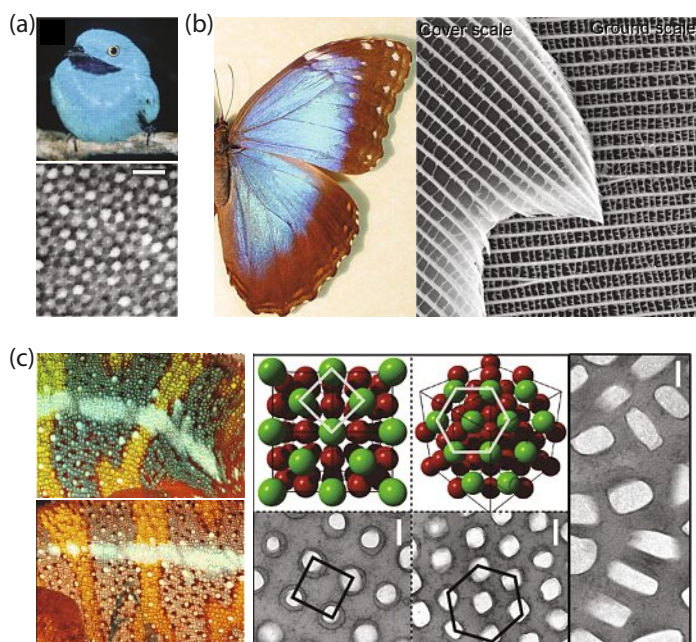


Fig. 1. (a) Photograph of *C. maynana* and TEM image of an assembly of β -keratin spheres and air nanostructure from the dark turquoise feather barbs of *C. maynana*. Adapted with permission from ref. [13]. Copyright 2012 The Royal Society. (b) Macroscopic view and SEM images of a *Morphidae* butterfly blue scales. Adapted with permission from ref. [14]. Copyright 2009 American Institute of Physics. (c) Reversible color change of a male panther chameleon (*Furcifer pardalis*) during excitation; TEM images of guanine nanocrystals in S-iridophores in the excited state and three-dimensional model of an FCC lattice. Adapted with permission from ref. [15]. Copyright 2015 The Authors.

brilliant coloration and angular independence. We speculate about the possibility to fabricate hybrid organic–inorganic photonic pigments with enhanced dielectric contrast, reduced scattering, and specific functionalities. Finally, we conclude by discussing several possible applications that go beyond the use of such structures as photonic pigments.

2. Photonic Pigments Fabricated in Confinement

The minimal requirement to mimic the structural color occurring in nature is the ability to precisely fabricate nanostructures within a material. To do so, connecting different scientific areas such as optics, soft-matter physics, colloidal chemistry, materials science, and biology is fundamental and provides an innovative, interdisciplinary research environment.

A simple yet powerful strategy is based on the self-assembly of nanosized building blocks (*i.e.* bottom-up approach) under geometrical confinement. While it is well known that geometry might contribute to the overall optical response,^[24] soft confinement within micron-scale droplets is particularly interesting since it allows for hierarchical architectures to be produced.^[25–29] Most efforts have been so far based on confining the self-assembly of colloidal particles or liquid crystals in precise superstructures, either ordered (*i.e.* colloidal crystal) or disordered (*i.e.* colloidal glasses).^[30–37] However, significant limitations of synthesizing large quantities of photonic pigments based on these arrays include the lack of control over incoherent and multiple scattering as well as the difficulty in producing pigments with distinct colors across the entire visible spectrum. In this context, it has been recently demonstrated that such limitations can be overcome by exploiting the 3D confinement self-assembly of suitable block copolymers (BCPs) in emulsion droplets leading to photonic particles with brilliant coloration.^[38–44]

2.1 Highly Ordered Block Copolymer-based Photonic Particles

BCPs consist of at least two covalently linked polymer chains that are immiscible.^[45] The covalent link prevents macrophase separation while favorable interactions between the same blocks lead to the spontaneous formation of nanostructures with characteristic sizes of 10–100 nm.^[46–48] Therefore, it is not surprising that the 3D-confined self-assembly of block copolymers in emulsion droplets has received increasing attention for the synthesis of polymer particles with well-defined size, shape, and internal morphology.^[25,49–52] Generally speaking, BCPs exhibit rapid self-assembly kinetics when processed by solution, macroscopic ordering into self-assembled morphologies, tolerance to high loading of functional additives, and the possibility to manipulate the resulting domain spacing simply by tuning the polymer chain length and structure. Constraining the self-assembly process of BCPs within a confined environment offers several advantages, including exploiting the effects of unstable interfaces, entropy loss, kinetic effects, and symmetry breaking to allow the fabrication of novel architectures that are often challenging to obtain when processing BCPs into films from a polymer melt or solution.

Symmetric BCPs (*i.e.* block volume fractions $f_A = f_B = 0.5$) typically form planar lamellar structures which, when the lamellae are sufficiently thick (*i.e.* high enough block molecular weights M_w), result in structurally colored films, whose optical response is governed by the Bragg–Snell law.^[20] It has recently been reported that within spherical confinement, the same self-assembly process induces the formation of radially-aligned lamellar structures (*i.e.* onion-like particles) resulting in concentric photonic multilayer spheres as schematically shown in Fig. 2a,b.^[38–44] Here, a nearly symmetric block volume fraction, a preferential interaction (*i.e.* wetting) of one of the blocks with the confining medium, and a sufficiently slow evaporation rate trigger the formation of the concentric lamellar structure. For example, Yang *et al.*^[38] have shown that poly(styrene)-*b*-poly(2-vinyl pyridine) (PS-P2VP, $M_w = 265$ kDa) dissolved in chloroform produces concentric lamellar particles when emulsified in a poly(vinyl alcohol) (PVA) aqueous solution. The obtained particles displayed no evident coloration due to the small thicknesses of the lamellar domains, but the band-gap position was adjusted by the selective swelling of the pyridine domains with ethanol. Inspired by this pioneering study, researchers have been focused on tuning the particle optical appearance either *via* synthesis or supramolecular chemistry strategies. For instance, Song *et al.*^[41] reported on full-spectrum photonic onion-like microspheres (Fig. 2c) obtained by the confined self-assembly of bottlebrush block copolymers (BBCPs). Here, the domain spacing was controlled by synthesizing poly(norbornene)-graft-poly(styrene)-*b*-poly(norbornene)-graft-poly(dimethylsiloxane) chains with different lengths (M_w of 3300, 4100, 7100 kDa). A more practical, user-friendly, and scalable approach was presented by Yang *et al.*,^[39] who exploited the hydrogen bonding of pentadecylphenol (PDP) to the P2VP block of PS-P2VP ($M_w = 428$ kDa) to form comb-like supramolecular assemblies, using a low M_w polystyrene homopolymer to counterbalance the increased volume fraction of the P2VP(PDP) phase. Here, by adjusting the system composition, the lamellar periodicity was controlled, thus tuning the particle optical properties. Similarly, Moriceau *et al.*^[42] reported on poly(styrene)-*b*-poly(4-vinyl pyridine) (PS-P4VP, $M_w = 427$ kDa) photonic particles using ionic bonding between an alkyl sulfonate derivative and P4VP, where the particles were generated in a vortex-assisted emulsification approach.

While the optical response of planar multilayers can be easily explained in terms of the Bragg–Snell law, the visual appearance of concentric multilayer structures is more complex and several factors must be taken into account.^[53] When these spheres are subjected to diffuse illumination (*i.e.* illuminated uniformly from all directions), the maximum wavelength ($\lambda_{\max} = 2n_{\text{eff}}d$, with d being

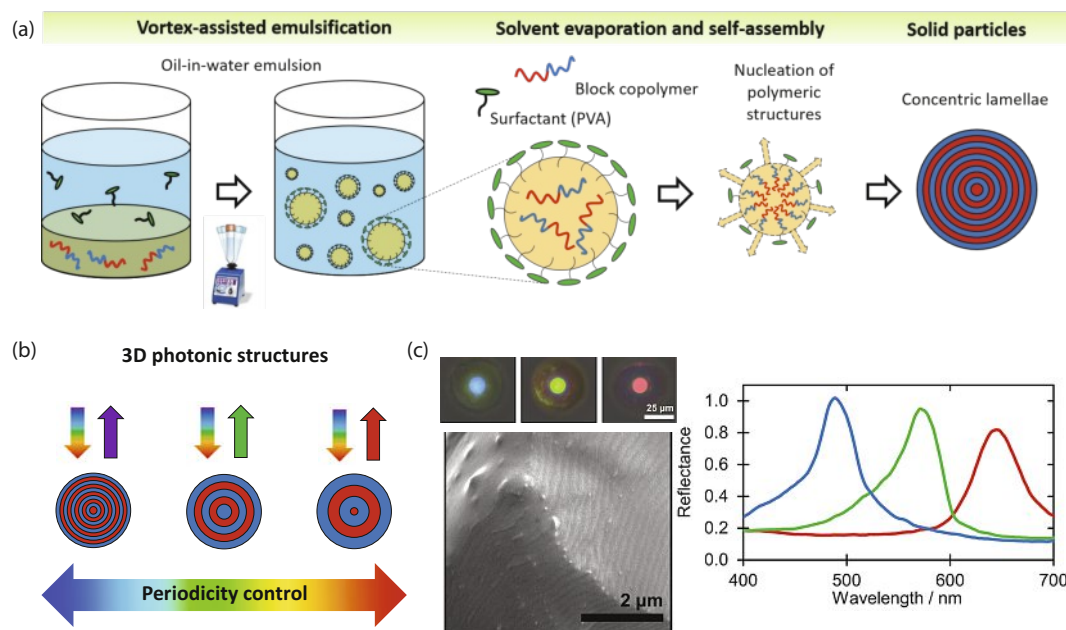


Fig. 2. (a) Schematic of the preparation method for block copolymer-based concentric lamellar particles via solvent evaporation and (b) color tunability by domain spacing control. (c) Reflection microscopy image, cross-sectional TEM micrograph and reflectance spectra of photonic particles prepared by the self-assembly of the bottlebrush block copolymer poly(norbornene)-graft-poly(styrene)-block-poly(norbornene)-graft-poly(dimethylsiloxane) in emulsion droplets. Adapted with permission from ref. [41]. Copyright 2019 American Chemical Society.

the domain periodicity) is reflected back isotropically. The result is a consistent and non-iridescent appearance. In contrast, under direct illumination, the light is dispersed and reflected into a wide angular range, resulting in an angular-dependent optical response. Nevertheless, when observed under bright-field illumination, where the numerical aperture of the objective determines both the illumination and the collection cone,^[54] concentric multilayers always reflect in the specular direction since the light incident on non-normal particle surfaces is reflected outside the numerical aperture of the objective lens and is thus not detected.

Compared to the traditional photonic pigments prepared by colloidal self-assembly, these hierarchical and highly ordered onion-like microspheres present several advantages. First, ordered spherical colloidal crystals are typically comprised of a few ordered outer layers with close-packed particles and a more disordered core, which results in multiple scattering of light, decreasing in color purity, which causes a whitish appearance. Similarly, disordered spherical colloidal crystals display poor reflectivity with their color resulting from the coherent scattering of individual colloidal particles with a defined short-range interparticle distance. In contrast, the long-range order of concentric lamellar particles based on BCP self-assembly provides brilliant and monochromatic coloration. Second, these structures allow for greater color tunability and optical response control. Indeed, whereas preparing colloidal photonic crystals with a red hue is a major challenge due to the difficulty in obtaining big enough periodicities, block copolymer-based assemblies can be easily prepared with a domain spacing that gives rise to a photonic bandgap in the red spectral region. Additionally, BCP-based photonic pigments can be crosslinked to increase their long-term stability in most organic solvents. Also, when exposed to specific solvents (*i.e.* good solvents for only one of the blocks), such structures display a certain degree of mechanical stability due to the concentric lamellar morphology and can display reversible color changes attributed to the selective swelling of the lamellar domains. Finally, the rapid increase of commercially available BCPs and the possibility to prepare large quantities of concentric lamellar particles on relatively short timescales make this approach extremely versatile and interesting also from an industrial point of view.

3. Future Perspectives

Despite the recent advances discussed above, the efficient fabrication of highly ordered photonic particles based on block co-

polymers is still hampered by the empirical nature of the process, the low dielectric contrast among the blocks, the difficult synthesis of high molecular weight BCP chains, and the low color purity due to the presence of structural defects leading to incoherent scattering. Furthermore, the formulation of a dry coating consisting of closely packed photonic particles is problematic, because of the light scattering from the particle surfaces and the voids between them. These aspects prevent the exploitation of their full potential as photonic pigments. Therefore, in the following sections, we discuss promising strategies to reduce or overcome some of the mentioned limitations, and we speculate on possible future research directions and applications.

3.1 Incorporated Broadband Absorbing Materials

Self-assembled structures inherently contain defects. This causes the backscattering of the light transmitted through the lamellae and, as a result, a whitish, opaque appearance is typically observed.^[55] In nature, evolution has mitigated this problem by the use of broadband absorbing materials, which are typically present in the form of melanin or other dark pigments.^[56] Typical examples are the Steller's jay (*Cyanocitta Stelleri*) bird that displays bright blue and black feathers stemming from a combination of disordered nanostructures and a basal melanin layer,^[57] whereas the *Pollia condensata* fruit presents a metallic blue coloration arising from the combination of layers in thick-walled cells and cell-cores containing dense brown tannin pigments.^[58] Several researchers have applied this concept to artificial photonic materials, where synthetic melanin colloidal particles have been used as absorbing building blocks^[59–61] or carbon black has been added to nanostructured films^[61–63] to enhance the intensity contrast between band-gap peaks and the background.

While highly ordered concentric lamellar particles made from block copolymers have relatively low defect densities compared to photonic colloidal assemblies, the scattering of light becomes a problem, once many particles are deposited from a solution to form a coating. In this case, high scattering from the particle boundaries reduces the color contrast between the band gap of individual particles and the background. The incorporation of broadband absorbing materials into these coatings is required to maximize the contrast and improve the color appearance. Here, the easiest strategy is to directly add black solid nanoparticles (*e.g.* carbon black, magnetite, *etc.*) or black hydrophobic dyes (*e.g.* Sudan black) to the BCP solution before emulsification. However,

two main challenges are expected with this approach. First, the overall intensity of reflected light is significantly lower because all wavelengths of light are absorbed. Second, the thermodynamics and kinetics of the self-assembly process are altered, which might lead to unexpected and uncontrolled structures. Therefore, we discuss two possible strategies to fabricate core-shell photonic particles, where the core contains the absorbing element and the shell the reflective assemblies (Fig. 3a).

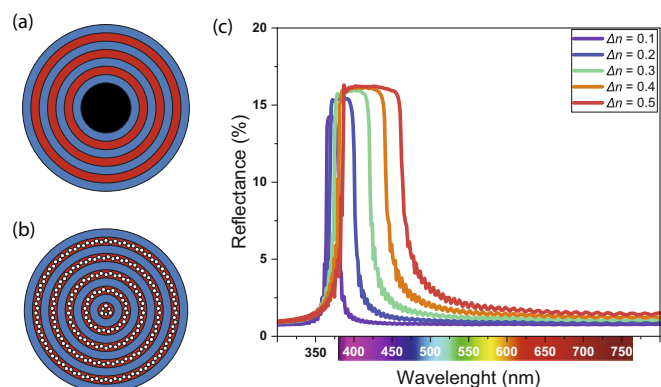


Fig. 3. Concentric lamellar particles where (a) the incoherent scattering is reduced using a broadband absorbing core and (b) the dielectric contrast between the domains is enhanced by the addition of high refractive index inorganic nanoparticles. (c) Simulated reflectance spectra obtained from FDTD simulations of concentric lamellar particles with a diameter of 20 μm and layer thicknesses of 60 nm, varying Δn between 0.1 and 0.5 (*i.e.* $n_L = 1.5$, $1.6 \leq n_H \leq 2.0$).

3.1.1 Core-shell Photonic Particles via Two-step Double Emulsification

Among the variety of double emulsions, so-called Water-in-Oil-in-Water emulsions (W/O/W) are water droplets dispersed in oil droplets which themselves are dispersed in an aqueous phase.^[64,65] These can be efficiently produced by two-step emulsification processes, where water (*i.e.* the inner phase) is first emulsified in oil (*i.e.* the middle phase) by high-energy homogenization generating a primary emulsion that is then re-emulsified in a second aqueous solution (*i.e.* the outer phase).^[66] Despite the resulting droplets often lacking structural uniformity due to interfacial instabilities, this method holds great promise to fabricate core-shell photonic particles.^[67,68] Indeed, by using two suitable surfactants (*i.e.* a hydrophobic one for the preparation of the primary W/O emulsion and a hydrophilic one for the preparation of the secondary W/O/W emulsion) and dispersing the selected broadband absorber into the first aqueous phase, a black core surrounded by self-assembled concentric lamellae can be envisaged. In such an assembly, the band-gap spectral range is reflected from the photonic concentric multilayer, and subsequently, the transmitted spectral range is efficiently absorbed in the core giving rise to a brilliant coloration even when many colloidal spheres are present in a coating. Adjusting the emulsification conditions, or using precise microfluidic devices^[69] enables precise control over the dimension of the core and the thickness of the shell, providing an additional way to tune the particle optical response.

3.1.2 Core-shell Photonic Particles via the Co-assembly of Functionalized Nanoparticles

The self-assembly of block copolymers with inorganic nanoparticles in three-dimensionally confined geometries has been demonstrated to be a facile and robust method to generate

hierarchical hybrid nanostructures.^[70,71] The inorganic NPs endow the resulting hybrid particle structures with various optical, electrical, and catalytic properties, with the BCP matrix serving as a stable support platform.^[72] Here, spatial control of NPs within the organic matrix is fundamental as their local distribution, orientation, and interparticle distance greatly influence the properties of the final nanocomposite materials. In general, entropic effects have a great influence on the self-assembly of BCP/NP hybrid materials with the ratio of the NP size to the associated domain size being one of the most critical factors.^[73] Additionally, recent studies reported that the location of polymer-grafted NPs within a block copolymer matrix can be precisely controlled by the chemical structure, areal density, and length of the ligand, by inducing favorable enthalpic interactions between the NPs and one BCP block. Among others, Xu *et al.*^[74,75] prepared concentric lamellar PS-P4VP particles loaded with gold nanoparticles functionalized with a polystyrene homopolymer. Increasing the ligand length led to crusted onion-like, seeded onion-like, and finally alternate-layered onion-like hybrid particles. Similarly, changing the grafting density of NPs allowed controlling their location within the lamellar structure, whereas their loading concentration can be varied to tune the core size.

These results suggest that broadband absorbing NPs could be segregated to the center (*i.e.* forming a black core) inside highly ordered photonic particles if properly functionalized. In this regard, the synthesis of linear polystyrene-functionalized magnetite, cobalt ferrite, palladium, and platinum nanoparticles with sizes ranging from a few nm to one hundred nm is well established and several protocols are available in the literature.^[76–79] Therefore, we foresee this method as a fast and user-friendly approach to improve the optical appearance of block copolymer-based photonic particles.

3.2 Enhanced Dielectric Contrast

Photonic crystals comprised of materials with a large refractive index (*e.g.* GaAs, GaN, Si, *etc.*) containing air voids have become a paradigm for light control in photonic devices.^[80,81] Polymer PhCs, in contrast, intrinsically suffer from low dielectric contrast (Δn) in the visible spectrum and are thus ill-suited for applications requiring accurate light control.^[82] Specifically, for BCP-based photonic pigments, Δn is often lower than 0.1, which, combined with incoherent light scattering, limits their applicability. This is illustrated in Fig. 3, showing Finite-Difference Time-Domain (FDTD) simulated reflectance spectra of concentric multilayer particles with a diameter of 20 μm , a periodicity of 120 nm (*i.e.* a layer thickness of 60 nm), and Δn ranging from 0.1 to 0.5. In agreement with Bragg-Snell's law, the spectral position of the bandgap is given by $\lambda_{\text{max}} = 2(d_H n_H + d_L n_L)$. All spectra have similar maximal reflectances and similar short wavelength onsets of the optical band gap. Increasing Δn however substantially widens the optical bandgap towards lower wavelengths.

One common approach to increasing Δn in BCP-based structures is the synthesis of specialty polymers.^[76,83–85] However, the high molecular weights required for the self-assembly into photonic structures are difficult to synthesize and their equilibration into self-assembled morphologies is very slow. Alternatively, high or low refractive index organic additives/swelling agents can be added to the block copolymer morphologies to selectively modify the dielectric properties of one of the two domains.^[86,87] However, the limited volume of additives that can be accommodated in the microphase separated BCP assemblies limits the achievable Δn values. New strategies are therefore required to increase the dielectric contrast in block copolymer photonic pigments. In the following sections, we propose two promising possibilities based on the use of high refractive index inorganic fillers and hybrid structures (Fig. 3b).

3.2.1 Addition of Inorganic Nanoparticles

One successful method to obtain high refractive index materials is the blending of inorganic nanoparticles, such as TiO_2 and ZrO_2 with n values of 2.1–2.7, into one of the polymer phases.^[88–90] Nanoparticles in polymeric matrices have, however, the tendency to agglomerate due to the strong attractive van der Waals forces between them, causing the formation of undesired scattering centers.^[91] In highly ordered BCP photonic particles, their localization within the lamellar stack has to be precisely controlled. As discussed in Section 3.1.2, the co-assembly of block copolymers with functionalized NPs represents a promising method to achieve such structures. For example, Song *et al.*^[92] showed that commercially available zirconium oxide nanoparticles functionalized with gallic acid could be loaded into a polynorbornene-graft-poly(tert-butyl acrylate)-block-polynorbornene-graft-poly(ethylene oxide) (PtBA-PEO) planar multilayer structure, up to volume fractions of 40%. The strong hydrogen-bonding interactions between the ligand and PEO brushes enabled the selective incorporation of the nanoparticles into the PEO phase avoiding their aggregation, resulting in a large difference in the refractive index with respect to PtBA ($\Delta n > 0.27$). Based on this result, we speculate that functionalized high refractive index NPs can be loaded into concentric lamellar photonic particles, controlling their selective enrichment in one of the two polymer phases. Thus, an enhanced dielectric contrast between the two blocks can be obtained, while preserving the particle optical quality.

3.2.2 Sol-gel Chemistry

An alternative route to achieve high dielectric contrast hybrid PhCs exploits sol-gel reactions of precursors into metal or metalloid oxides.^[93,94] In these processes the oxide precursors are typically hydrolyzed to form a sol which is then cast by spin- or dip-coating to form dry xerogel thin films, which are subsequently densified by high-temperature annealing. The large reactivity of the precursors induces however the formation of scattering centers and the high annealing temperatures – up to and exceeding 500 °C – hinder their incorporation into temperature-sensitive materials. Alternatively, polymers can be used as stabilizers, allowing temperature decrease in the post-deposition processes. For instance, Bachevillier *et al.*^[95] reported high optical quality thin films and Distributed Bragg Reflectors (DBRs) with outstanding dielectric contrast based on high refractive hybrid titania achieved by the hydrolyzation of precursors in cold water and subsequent mixing of the hydrated oxide product with a water solution of poly(vinyl alcohol). More recently, Bertucci *et al.*^[96] developed a mild condition sol-gel reaction to obtain high index photoactive polymer-titania hybrids that can be combined with a low refractive index polymer-silica phase.

On this basis, concentric lamellar photonic particles based on block copolymers presenting high dielectric contrast could be envisaged using a combination of self-assembly and sol-gel chemistry. Using selective solvents, a phase of pre-formed concentric lamellar particles can, for example, be infiltrated with a sol precursor. The formation of the inorganic phase can subsequently be induced by changing the temperature or chemical and UV treatments. Alternatively, specific interactions between precursors and one of the blocks might be exploited to form supramolecular assemblies that are subsequently used to produce hybrid concentric lamellar structures. Despite this approach presenting several challenges, including the accurate control of the sol-gel reactions to maintain a good optical quality, this approach is expected to lead to highly performing photonic structures.

3.3 Iridescence, Dynamic Optical Properties, and Hybrid Photonic-plasmonic Structures

The previous sections discussed recent progress in block copolymer-based photonic pigments with a focus on possible strate-

gies to enhance their optical appearance. This section briefly presents several related research directions that might open pathways toward other exciting applications.

Photonic particles consisting of onion-like morphologies represent the most studied PhC geometry. Stacked lamellar structures are an interesting alternative because they afford an anisotropic optical behavior that is not possible in concentric lamellar particles.^[97] Despite the significant advancements toward the shape control of polymer particles obtained through the confined self-assembly in emulsion droplets, a major challenge remains the achievement of a near-perfect order over tens of micrometers. Recently, a simple method was described for the preparation of ellipsoid-shaped particles comprised of stacked lamellae using a mixture of two surfactants that have selective interactions with each BCP domain in order to tune the interfacial interactions.^[98,99] By exploiting this approach, He *et al.*^[43] developed photonic ellipsoidal particles with a highly ordered axially stacked lamellar morphology whose color was tuned by controlling the molecular weight of the used bottle brush block copolymers. These particles displayed a strong orientation-dependent photonic behavior (*i.e.* iridescence), which was controlled by adding magnetic nanoparticles. These interesting structures might, for example, find use as iridescent coatings and films in design applications.

Notably, BCP-based photonic particles hold promise not only as pigments but also as sensing platforms. Indeed, several external stimuli can be used to modify the domain periodicity, inducing appreciable changes in the particle optical appearance. For instance, pyridine moieties are pH sensitive due to the protonation of the nitrogen atom occurring in acidic conditions, which makes them partially water-soluble. As a consequence, when pyridine-containing photonic particles are exposed to low pH media they display a significant red-shift of the bandgap caused by the selective swelling of pyridine domains.^[100] Similarly, the domain periodicity could be altered by introducing magnetic nanoparticles within the photonic structure and controlling their orientation and/or location by applying a magnetic field.

Concentric lamellar photonic particles can also be used as mechanochromic sensors when glassy-rubbery microdomains are created. Dong *et al.*^[101] reported on onion-like microparticles consisting of polystyrene and cross-linked bottlebrush polydimethylsiloxane, which show not only visible color changes under compression but also a rapid recovery upon unloading, with no obvious damage after 250 cycles. These studies suggest that block copolymer-based photonic pigments might find applications in several sensing systems.

Another unexplored research direction is the combination of concentric lamellar photonic particles with plasmonic nanoparticles (*e.g.* gold or silver NPs) to create hybrid structures with unique functionalities.^[102] Since the resonance of plasmonic NPs can be tuned by varying their size and shape, they could be used as selective absorbers, to increase the observed macroscopic hue without affecting the intensity of the photonic bandgap.^[103] The spatial arrangement of the NPs within the concentric lamellar matrix can be controlled by using specific ligands or the interactions as discussed in the previous sections. Similarly, single-crystal emitters could be also encapsulated within block copolymer-based photonic microspheres to develop advanced optoelectronic devices.^[104–107] Generally speaking, these hybrid structures can be used as platforms for realizing strong light–matter interactions.

4. Conclusions

Nature is a continuous source of inspiration with its incredible level of functionalities that are achieved through the sophisticated self-organization of relatively simple building blocks. For example, the brilliant colors occurring in the natural world exhibit some of the most flamboyant visual effects and remarkable dynamic properties. Driven by the continuous advancements in nano-struc-

turing techniques and analysis tools, research has started to investigate and reproduce these stunning effects. In this perspective article, we introduce the preparation of highly ordered concentric lamellar photonic particles made of block copolymers, exploiting the 3D confined self-assembly in emulsion droplets to design photonic pigments as dispersed and micrometer-scale particles. The importance of the incorporation of broadband absorbing elements and the increase in the dielectric contrast are necessary strategies to fully develop observable hues by controlling the incoherent scattering and bandgap properties. These discussions underline the interplay of multiple physical phenomena that, along with the structural assembly process, require to be precisely modulated to obtain the desired optical effects. Finally, strategies for the fabrication of advanced optical materials are introduced through the combination of polymer sciences, chemistry, engineering, and fundamental physics for future developments in the thriving field of block copolymer-based photonic assemblies.

Acknowledgments

This study was financially supported by the Swiss National Science Foundation (SNSF) through the National Center of Competence NCCR) in Research Bio-Inspired Materials (Grant No. 51NF40-182881), the European Research Council (ERC) through grant PrISMoid (833895), and the Adolphe Merkle Foundation.

Received: August 19, 2022

- [1] P. Vukusic, J. R. Sambles, *Nature* **2003**, *424*, 852, <https://doi.org/10.1038/nature01941>.
- [2] W. Ma, Z. Liu, Z. A. Kudyshev, A. Boltasseva, W. Cai, Y. Liu, *Nat. Photonics* **2020**, *15*, 77, <https://doi.org/10.1038/s41566-020-0685-y>.
- [3] Y. Fu, C. A. Tippets, E. U. Donev, R. Lopez, *WIREs Nanomed. Nanobiotechnol.* **2016**, *8*, 758, <https://doi.org/10.1002/wnan.1396>.
- [4] Z. Xuan, J. Li, Q. Liu, F. Yi, S. Wang, W. Lu, *Innov.* **2021**, *2*, 100081, <https://doi.org/10.1016/j.xinn.2021.100081>.
- [5] J. C. De Carvalho, C. R. Soccol, S. Babitha, A. Pandey, A. L. Wojciechowski, 'Production of Pigments', in 'Current Developments in Solid-State Fermentation', Eds. A. Pandey, C. R. Soccol, C. Larroche, Springer, New York, **2008**, pp. 337-355, https://doi.org/10.1007/978-0-387-75213-6_15.
- [6] A. Gürses, M. Açıkyıldız, K. Güneş, M. S. Gürses, 'Dyes and Pigments: Their Structure and Properties', in 'Dyes and Pigments', SpringerBriefs in Molecular Science, Springer, Cham, **2017**, pp 13-29, https://doi.org/10.1007/978-3-319-33892-7_2.
- [7] C. W. Qiu, D. Palima, A. Novitsky, D. Gao, W. Ding, S. V. Zhukovsky, J. Gluckstad, *Nanophotonics* **2014**, *3*, 181, <https://doi.org/10.1515/nanoph-2013-0055>.
- [8] R. Gutzler, M. Garg, C. R. Ast, K. Kuhnke, K. Kern, *Nat. Rev. Phys.* **2021**, *3*, 441, <https://doi.org/10.1038/s42254-021-00306-5>.
- [9] Y. Xu, D. Ji, H. Song, N. Zhang, Y. Hu, T. D. Anthopoulos, E. M. Di Fabrizio, S. Xiao, Q. Gan, *Adv. Opt. Mater.* **2018**, *6*, 1800444, <https://doi.org/10.1002/adom.201800444>.
- [10] M. Stefik, S. Guldin, S. Vignolini, U. Wiesner, U. Steiner, *Chem. Soc. Rev.* **2015**, *44*, 5076, <https://doi.org/10.1039/C4CS00517A>.
- [11] T. J. Yeong, K. P. Jern, L. K. Yao, M. A. Hannan, S. T. G. Hoon, *Molecules* **2019**, *24*, 2025, <https://doi.org/10.3390/molecules24102025>.
- [12] H. Megahd, P. Lova, D. Comoretto, *Adv. Funct. Mater.* **2021**, *31*, 2009626, <https://doi.org/10.1002/adfm.202009626>.
- [13] V. Saranathan, J. D. Forster, H. Noh, S. F. Liew, S. G. J. Mochrie, H. Cao, E. R. Dufresne, R. O. Prum, *J. R. Soc. Interface* **2012**, *9*, 2563, <https://doi.org/10.1098/rsif.2012.0191>.
- [14] Y. Ding, S. Xu, Z. L. Wang, *J. Appl. Phys.* **2009**, *106*, 074702, <https://doi.org/10.1063/1.3239513>.
- [15] J. Teyssier, S. V. Saenko, D. Van Der Marel, M. C. Milinkovitch, *Nat. Commun.* **2015**, *6*, 1, <https://doi.org/10.1038/ncomms7368>.
- [16] R. Yu, L. Zhu, Y. Xia, J. Liu, J. Liang, J. Xu, B. Wang, S. Wang, *Adv. Mater. Interfaces* **2022**, *9*, 2200401, <https://doi.org/10.1002/admi.202200401>.
- [17] J. Sun, B. Bhushan, J. Tong, *RSC Adv.* **2013**, *3*, 14862, <https://doi.org/10.1039/c3ra41096j>.
- [18] P. Lalanne, W. Yan, K. Vynck, C. Sauvan, J. P. Hugonin, *Laser Photon. Rev.* **2018**, *12*, 1700113, <https://doi.org/10.1002/lpor.201700113>.
- [19] V. Berger, *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 209, [https://doi.org/10.1016/S1359-0286\(99\)00004-2](https://doi.org/10.1016/S1359-0286(99)00004-2).
- [20] P. Lova, G. Manfredi, D. Comoretto, *Adv. Opt. Mater.* **2018**, *6*, 1800730, <https://doi.org/10.1002/adom.201800730>.
- [21] X. Wang, Y. Cui, T. Li, M. Lei, J. Li, Z. Wei, *Adv. Opt. Mater.* **2019**, *7*, 1801274, <https://doi.org/10.1002/adom.201801274>.
- [22] S. Yu, X. Wu, Y. Wang, X. Guo, L. Tong, *Adv. Mater.* **2017**, *29*, 1606128, <https://doi.org/10.1002/adma.201606128>.
- [23] C. M. Soukoulis, M. Wegener, *Nat. Photonics* **2011**, *5*, 523, <https://doi.org/10.1038/nphoton.2011.154>.
- [24] P. C. Ray, *Chem. Rev.* **2010**, *110*, 5332, <https://doi.org/10.1021/cr900335q>.
- [25] N. Yan, Y. Zhu, W. Jiang, *Chem. Commun.* **2018**, *54*, 13183, <https://doi.org/10.1039/C8CC05812A>.
- [26] Y. Zhang, Y. He, N. Yan, Y. Zhu, Y. Hu, *J. Phys. Chem. B* **2017**, *121*, 8417, <https://doi.org/10.1021/acs.jpcc.7b06701>.
- [27] K. H. Ku, J. M. Shin, H. Yun, B. J. Kim, G. G.-R. Yi, S. G. Jang, B. J. Kim, *Adv. Funct. Mater.* **2018**, *28*, 1802961, <https://doi.org/10.1002/adfm.201802961>.
- [28] N. Ioannou, H. Liu, Y. H. Zhang, *J. Comput. Sci.* **2016**, *17*, 463, <https://doi.org/10.1016/j.jocs.2016.03.009>.
- [29] Q. Zhang, B. Lin, J. Qin, *Microfluid. Nanofluidics* **2012**, *12*, 33, <https://doi.org/10.1007/s10404-011-0846-x>.
- [30] D. Patra, A. Sanyal, V. M. Rotello, *Chem. - An Asian J.* **2010**, *5*, 2442, <https://doi.org/10.1002/asia.201000301>.
- [31] R. McGorty, J. Fung, D. Kaz, V. N. Manoharan, *Mater. Today* **2010**, *13*, 34, [https://doi.org/10.1016/S1369-7021\(10\)70107-3](https://doi.org/10.1016/S1369-7021(10)70107-3).
- [32] Z. Cai, Z. Li, S. Ravaine, M. He, Y. Song, Y. Yin, H. Zheng, J. Teng, A. Zhang, *Chem. Soc. Rev.* **2021**, *50*, 5898, <https://doi.org/10.1039/D0CS00706D>.
- [33] E. S. A. Goerlitzer, R. N. Klupp Taylor, N. Vogel, *Adv. Mater.* **2018**, *30*, 1706654, <https://doi.org/10.1002/adma.201706654>.
- [34] S. H. Kim, S. Y. Lee, S. M. Yang, G. R. Yi, *NPG Asia Mater.* **2011**, *3*, 25, <https://doi.org/10.1038/asiamat.2010.192>.
- [35] A. F. Demirörs, E. Poloni, M. Chiesa, F. L. Bargardi, M. R. Binelli, W. Woigk, L. D. C. de Castro, N. Kleger, F. B. Coulter, A. Sicher, H. Galinski, F. Scheffold, A. R. Studart, *Nat. Commun.* **2022**, *13*, 1, <https://doi.org/10.1038/s41467-022-32060-2>.
- [36] P. D. García, R. Sapienza, C. López, *Adv. Mater.* **2010**, *22*, 12, <https://doi.org/10.1002/adma.200900827>.
- [37] L. Schertel, L. Siedentop, J. J.-M. Meijer, P. Keim, C. M. Aegerter, G. J. Aubry, G. Maret, *Adv. Opt. Mater.* **2019**, *7*, 1900442, <https://doi.org/10.1002/adom.201900442>.
- [38] Y. Yang, H. Kim, J. Xu, M.-S. Hwang, D. Tian, K. Wang, L. Zhang, Y. Liao, H.-G. Park, G.-R. Yi, X. Xie, J. Zhu, *Adv. Mater.* **2018**, *30*, 1707344, <https://doi.org/10.1002/adma.201707344>.
- [39] Y. Yang, T.-H. Kang, K. Wang, M. Ren, S. Chen, B. Xiong, J. Xu, L. Zhang, G.-R. Yi, J. Zhu, *Small* **2020**, *16*, 2001315, <https://doi.org/10.1002/sml.202001315>.
- [40] Y. Yang, Y. Chen, Z. Hou, F. Li, M. Xu, Y. Liu, D. Tian, L. Zhang, J. Xu, J. Zhu, *ACS Nano* **2020**, *14*, 16057, <https://doi.org/10.1021/acsnano.0c07898>.
- [41] D.-P. P. Song, T. H. Zhao, G. Guidetti, S. Vignolini, R. M. Parker, *ACS Nano* **2019**, *13*, 1764, <https://doi.org/10.1021/acsnano.8b07845>.
- [42] G. Moriceau, C. Kilchoer, K. Djeghdi, C. Weder, U. Steiner, B. D. Wilts, I. Gunkel, *Macromol. Rapid Commun.* **2021**, *42*, 2100522, <https://doi.org/10.1002/marc.202100522>.
- [43] Q. He, K. H. Ku, H. Vijayamohan, B. J. Kim, T. M. Swager, *J. Am. Chem. Soc.* **2020**, *142*, 10424, <https://doi.org/10.1021/jacs.0c02398>.
- [44] Q. Guo, Y. Li, Q. Liu, Y. Li, D. P. Song, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113759, <https://doi.org/10.1002/anie.202203409>.
- [45] H. Feng, X. Lu, W. Wang, N. G. Kang, J. W. Mays, *Polymers* **2017**, *9*, 494, <https://doi.org/10.3390/polym9100494>.
- [46] Y. Mai, A. Eisenberg, *Chem. Soc. Rev.* **2012**, *41*, 5969, <https://doi.org/10.1039/c2cs35115c>.
- [47] H. Hu, M. Gopinadhan, C. O. Osuji, *Soft Matter* **2014**, *10*, 3867, <https://doi.org/10.1039/c3sm52607k>.
- [48] K. Koo, H. Ahn, S. W. Kim, D. Y. Ryu, T. P. Russell, *Soft Matter* **2013**, *9*, 9059, <https://doi.org/10.1039/c3sm51083b>.
- [49] R. Deng, H. Li, J. Zhu, B. Li, F. Liang, F. Jia, X. Qu, Z. Yang, *Macromolecules* **2016**, *49*, 1362, <https://doi.org/10.1021/acs.macromol.5b02507>.
- [50] C. K. Wong, X. Qiang, A. H. E. Müller, A. H. Gröschel, *Prog. Polym. Sci.* **2020**, *102*, 101211, <https://doi.org/10.1016/j.progpolymsci.2020.101211>.
- [51] I. Wyman, G. Njikang, G. Liu, *Prog. Polym. Sci.* **2011**, *36*, 1152, <https://doi.org/10.1016/j.progpolymsci.2011.04.005>.
- [52] U. Tritschler, S. Pearce, J. Gwyther, G. R. Whittell, I. Manners, *Macromolecules* **2017**, *50*, 3439, <https://doi.org/10.1021/acs.macromol.6b02767>.
- [53] Z. Wang, C. L. C. Chan, T. H. Zhao, R. M. Parker, S. Vignolini, *Adv. Opt. Mater.* **2021**, *9*, 2100519, <https://doi.org/10.1002/adom.202100519>.
- [54] A. G. Valdecasas, D. Marshall, J. M. Becerra, J. J. Terrero, *Micron* **2001**, *32*, 559, [https://doi.org/10.1016/S0968-4328\(00\)00061-5](https://doi.org/10.1016/S0968-4328(00)00061-5).
- [55] P. D. García, R. Sapienza, C. Toninelli, C. López, D. S. Wiersma, *Phys. Rev. A - At. Mol. Opt. Phys.* **2011**, *84*, 023813, <https://doi.org/10.1103/PhysRevA.84.023813>.
- [56] M. Sakai, T. Seki, Y. Takeoka, *Small* **2018**, *14*, 1800817, <https://doi.org/10.1002/sml.201800817>.
- [57] M. D. Shawkey, G. E. Hill, *J. Exp. Biol.* **2006**, *209*, 1245, <https://doi.org/10.1242/jeb.02115>.

- [58] S. Vignolini, P. J. Rudall, A. V. Rowland, A. Reed, E. Moyroud, R. B. Faden, J. J. Baumberg, B. J. Glover, U. Steiner, *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15712, <https://doi.org/10.1073/pnas.1210105109>.
- [59] M. Kohri, K. Yanagimoto, A. Kawamura, K. Hamada, Y. Imai, T. Watanabe, T. Ono, T. Taniguchi, K. Kishikawa, *ACS Appl. Mater. Interfaces* **2018**, *10*, 7640, <https://doi.org/10.1021/acsmi.7b03453>.
- [60] J. G. Park, S. H. Kim, S. Magkiriadou, T. M. Choi, Y. S. Kim, V. N. Manoharan, *Angew. Chem. Int. Ed.* **2014**, *53*, 2899, <https://doi.org/10.1002/anie.201309306>.
- [61] Y. Takeoka, S. Yoshioka, A. Takano, S. Arai, K. Nueangnoraj, H. Nishihara, M. Teshima, Y. Ohtsuka, T. Seki, *Angew. Chem. Int. Ed.* **2013**, *52*, 7261, <https://doi.org/10.1002/anie.201301321>.
- [62] S. Yoshioka, Y. Takeoka, *ChemPhysChem* **2014**, *15*, 2209, <https://doi.org/10.1002/cphc.201402095>.
- [63] D. P. Josephson, M. Miller, A. Stein, *Zeitschr. Anorg. Allg. Chem.* **2014**, *640*, 655, <https://doi.org/10.1002/zaac.201300578>.
- [64] S. Ding, C. A. Serra, T. F. Vandamme, W. Yu, N. Anton, *J. Control. Release* **2019**, *295*, 31, <https://doi.org/10.1016/j.jconrel.2018.12.037>.
- [65] N. Leister, H. P. Karbstein, *Coll. Interf.* **2020**, *4*, 8, <https://doi.org/10.3390/colloids4010008>.
- [66] J. Wang, S. Hahn, E. Amstad, N. Vogel, *Adv. Mater.* **2022**, *34*, 2107338, <https://doi.org/10.1002/adma.202107338>.
- [67] F. M. Galogahi, Y. Zhu, H. An, N. T. Nguyen, *J. Sci. Adv. Mater. Devices* **2020**, *5*, 417, <https://doi.org/10.1016/j.jsamd.2020.09.001>.
- [68] E. E. Ekanem, Z. Zhang, G. T. Vladislavlevic, *J. Colloid Interface Sci.* **2017**, *498*, 387, <https://doi.org/10.1016/j.jcis.2017.03.067>.
- [69] M. Jeyhani, N. Abbasi, S. S. H. Tsai, R. Thevakumaran, D. K. Hwang, *Small* **2020**, *16*, 1906565, <https://doi.org/10.1002/smll.201906565>.
- [70] Q. Yu, N. Sun, D. Hu, Y. Wang, X. Chang, N. Yan, Y. Zhu, Y. Li, *Polym. Chem.* **2021**, *12*, 4184, <https://doi.org/10.1039/D1PY00744K>.
- [71] X. B. Nie, C. Y. Yu, H. Wei, *Mater. Today Chem.* **2021**, *22*, 100616, <https://doi.org/10.1016/j.mtchem.2021.100616>.
- [72] S. K. Kumar, B. C. Benicewicz, R. A. Vaia, K. I. Winey, *Macromolecules* **2017**, *50*, 714, <https://doi.org/10.1021/acs.macromol.6b02330>.
- [73] N. Yan, Y. Zhang, Y. He, Y. Zhu, W. Jiang, *Macromolecules* **2017**, *50*, 6771, <https://doi.org/10.1021/acs.macromol.7b01076>.
- [74] M. Xu, K. H. Ku, Y. J. Lee, J. J. Shin, E. J. Kim, S. G. Jang, H. Yun, B. J. Kim, *Chem. Mater.* **2020**, *32*, 7036, <https://doi.org/10.1021/acs.chemmater.0c02459>.
- [75] M. Xu, K. H. Ku, Y. J. Lee, T. Kim, J. J. Shin, E. J. Kim, S. H. Choi, H. Yun, B. J. Kim, *Macromolecules* **2021**, *54*, 3084, <https://doi.org/10.1021/acs.macromol.1c00370>.
- [76] F. Zhang, Z. Su, F. Wen, F. Li, *Colloid Polym. Sci.* **2008**, *286*, 837, <https://doi.org/10.1007/s00396-008-1854-6>.
- [77] A. Ohtaka, T. Teratani, R. Fujii, K. Ikeshita, T. Kawashima, K. Tatsumi, O. Shimomura, R. Nomura, *J. Org. Chem.* **2011**, *76*, 4052, <https://doi.org/10.1021/jo200485q>.
- [78] G. Carrot, F. Gal, C. Cremona, J. Vinas, H. Perez, *Langmuir* **2009**, *25*, 471, <https://doi.org/10.1021/la802862q>.
- [79] K. Jainae, K. Sanuwong, J. Nuangjamnong, N. Sukpirom, F. Unob, *Chem. Eng. J.* **2010**, *160*, 586, <https://doi.org/10.1016/j.cej.2010.03.080>.
- [80] P. Lova, V. Robbiano, F. Cacialli, D. Comoretto, C. Soci, *ACS Appl. Mater. Interfaces* **2018**, *10*, 33434, <https://doi.org/10.1021/acsmi.8b10370>.
- [81] M. R. Jorgensen, B. P. Yonkee, M. H. Bartl, *Scr. Mater.* **2011**, *65*, 954, <https://doi.org/10.1016/j.scriptamat.2011.08.018>.
- [82] P. Lova, H. Megahd, P. Stagnaro, M. Alloisio, M. Patrini, D. Comoretto, *Appl. Sci.* **2020**, *10*, 4122, <https://doi.org/10.3390/app10124122>.
- [83] N. H. O. You, N. Fukuzaki, Y. Suzuki, Y. Nakamura, T. Higashihara, S. Ando, M. Ueda, *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 4428, <https://doi.org/10.1002/pola.23497>.
- [84] N. H. You, Y. Suzuki, D. Yorifuji, S. Ando, M. Ueda, *Macromolecules* **2008**, *41*, 6361, <https://doi.org/10.1021/ma800982x>.
- [85] Q. Li, K. L. Ng, X. Pan, J. Zhu, *Polym. Chem.* **2019**, *10*, 4279, <https://doi.org/10.1039/C9PY00660E>.
- [86] E. P. Petrov, V. N. Bogomolov, I. I. Kalosha, S. V. Gaponenko, *Phys. Rev. Lett.* **1998**, *81*, 77, <https://doi.org/10.1103/PhysRevLett.81.77>.
- [87] M. Yasir, T. Sai, A. Sicher, F. Scheffold, U. Steiner, B. D. Wilts, E. R. Dufresne, *Small* **2021**, *17*, 2103061, <https://doi.org/10.1002/smll.202103061>.
- [88] C. Lü, B. Yang, *J. Mater. Chem.* **2009**, *19*, 2884, <https://doi.org/10.1039/b816254a>.
- [89] J. L. H. Chau, Y. M. Lin, A. K. Li, W. F. Su, K. S. Chang, S. L. C. Hsu, T. L. Li, *Mater. Lett.* **2007**, *61*, 2908, <https://doi.org/10.1016/j.matlet.2007.01.088>.
- [90] C. Liu, T. J. Hajagos, D. Chen, Y. Chen, D. Kishpaugh, Q. Pei, *ACS Appl. Mater. Interfaces* **2016**, *8*, 4795, <https://doi.org/10.1021/acsmi.6b00743>.
- [91] S. V. Sokolov, K. Tschulik, C. Batchelor-McAuley, K. Jurkschat, R. G. Compton, *Anal. Chem.* **2015**, *87*, 10033, <https://doi.org/10.1021/acs.analchem.5b02639>.
- [92] D. P. Song, C. Li, W. Li, J. J. Watkins, *ACS Nano* **2016**, *10*, 1216, <https://doi.org/10.1021/acsnano.5b06525>.
- [93] A. E. Danks, S. R. Hall, Z. Schnepf, *Mater. Horizons* **2016**, *3*, 91, <https://doi.org/10.1039/C5MH00260E>.
- [94] M. Parashar, V. K. Shukla, R. Singh, *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 3729, <https://doi.org/10.1007/s10854-020-02994-8>.
- [95] S. Bachevillier, H.-K. Yuan, A. Strang, A. Levitsky, G. L. Frey, A. Hafner, D. D. C Bradley, P. N. Stavrinou, N. Stingelin, *Adv. Funct. Mater.* **2019**, *29*, 1808152, <https://doi.org/10.1002/adfm.201808152>.
- [96] S. Bertucci, H. Megahd, A. Doderò, S. Fiorito, F. Di Stasio, M. Patrini, D. Comoretto, P. Lova, *ACS Appl. Mater. Interfaces* **2022**, *14*, 19806, <https://doi.org/10.1021/acsmi.1c23653>.
- [97] H. Wang, Y. Liu, Z. Chen, L. Sun, Y. Zhao, *Sci. Adv.* **2020**, *6*, 2, <https://doi.org/10.1126/sciadv.aay1438>.
- [98] K. H. Ku, Y. J. Lee, Y. Kim, B. J. Kim, *Macromolecules* **2019**, *52*, 1150, <https://doi.org/10.1021/acs.macromol.8b02465>.
- [99] J. Lee, K. H. Ku, M. Kim, J. M. Shin, J. Han, C. H. Park, B. J. Kim, G. Yi, S. G. Jang, *Adv. Mater.* **2017**, *29*, 1700608, <https://doi.org/10.1002/adma.201700608>.
- [100] J. G. Kennemur, *Macromolecules* **2019**, *52*, 1354, <https://doi.org/10.1021/acs.macromol.8b01661>.
- [101] Y. Dong, Z. Ma, D.-P. P. Song, G. Ma, Y. Li, *ACS Nano* **2021**, *15*, 8770, <https://doi.org/10.1021/acsnano.1c01147>.
- [102] I. Pastoriza-Santos, C. Kinnear, J. Pérez-Juste, P. Mulvaney, L. M. Liz-Marzán, *Nat. Rev. Mater.* **2018**, *3*, 375, <https://doi.org/10.1038/s41578-018-0050-7>.
- [103] N. Koay, I. B. Burgess, T. M. Kay, B. A. Nerger, M. Miles-Rossouw, T. Shirman, T. L. Vu, G. England, K. R. Phillips, S. Utech, N. Vogel, M. Kolle, J. Aizenberg, *Opt. Express* **2014**, *22*, 27750, <https://doi.org/10.1364/OE.22.027750>.
- [104] S. Wu, H. Xia, J. Xu, X. Sun, X. Liu, *Adv. Mater.* **2018**, *30*, 1803362, <https://doi.org/10.1002/adma.201803362>.
- [105] J. H. Kim, S. Aghaeimeibodi, C. J. K. Richardson, R. P. Leavitt, D. Englund, E. Waks, *Nano Lett.* **2017**, *17*, 7394, <https://doi.org/10.1021/acs.nanolett.7b03220>.
- [106] P. D. García, P. Lodahl, *Ann. Phys.* **2017**, *529*, 1600351, <https://doi.org/10.1002/andp.201600351>.
- [107] J. Lee, V. Leong, D. Kalashnikov, J. Dai, A. Gandhi, L. A. Krivitsky, *AVS Quantum Sci.* **2020**, *2*, 031701, <https://doi.org/10.1116/5.0011316>.

License and Terms



This is an Open Access article under the terms of the Creative Commons Attribution License CC BY 4.0. The material may not be used for commercial purposes.

The license is subject to the CHIMIA terms and conditions: (<https://chimia.ch/chimia/about>).

The definitive version of this article is the electronic one that can be found at <https://doi.org/10.2533/chimia.2022.826>