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Switchable Full-Color Reflective Photonic Ellipsoidal Particles

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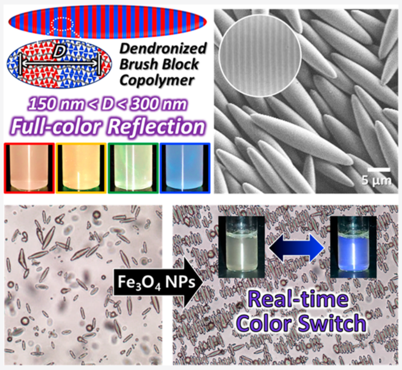
ABSTRACT: Full-color reflective photonic ellipsoidal polymer particles, capable of a dynamic color change, are created from dendronized brush block copolymers (*den*-BBCPs) self-assembled by solvent-evaporation from an emulsion. Surfactants composed of dendritic monomer units allow for the precise modulation of the interfacial properties of *den*-BBCP particles to transition in shape from spheres to striped ellipsoids. Strong steric repulsions between wedge-type monomers promote rapid self-assembly of polymers into large domains (i.e., 153 nm ≤ D ≤ 298 nm). Of note, highly ordered axially stacked lamellae (i.e., number of layers >100) within an ellipsoid give rise to a near-perfect photonic multilayer. The reflecting color is readily tunable across the entire visible spectrum by alteration of the molecular weight from 477 to 1144 kDa. Finally, the photonic ellipsoids are functionalized with magnetic nanoparticles organized into bands on the particle surface to produce real-time on/off coloration by magnetic field-assisted activation. In total, the reported photonic ellipsoidal particles represent a new class of switchable photonic materials.



INTRODUCTION

Photonic crystals having periodic nanostructures display selective diffraction/reflection of light and can produce what is known as structural color.[1−7] Recent reports have revealed the potential of encapsulated colloidal photonic structures, which can serve as structural colorants for paints with easy processing and dynamic reconfigurability.[8−12] Brush block copolymers (BBCPs), which promote a highly extended backbone at high graft density, have emerged as a powerful material for the creation of photonic crystals. In particular, they assemble into lamellar structures with domain spacings capable of strong reflection in the visible region of the electromagnetic spectrum.[13−17] Compared to other photonic materials (e.g., colloidal particles or liquid crystals),[18,19] the BBCP is more tunable by numerous parameters including backbone structure, side-chain length, composition, and grafting density.[20−22] Further dynamic control of these periodic structures (i.e., domain size and orientation) and the fabrication of composites with high refractive index contrast offer an attractive approach to switchable coloration and display.[23,24] Therefore, the BBCP is a promising design element for the creation of colloidal units with tunable photonic behavior. To date, the majority of studies about BBCP photonic crystals have focused on bulk and thin films rather than their assembly within the three-dimensionally confined geometries.[25−27]

We have been interested to expand the formation of nonspherical polymer particles beyond the confined self-assembly of linear coil−coil diblock copolymers. In such systems, the polymer particles usually lack sufficient domain spacing and number of layers to function as photonic reflectors.[28−33] Therefore, alternative macromolecular architectures are a promising direction. In particular, striped ellipsoids with transverse isotropy exhibit orientation-dependent optical responses, wherein controlled alignment affords anisotropic optical behavior that is not possible in spherical particles. Despite the significant progress toward the shape control of polymer particles, major challenges in the achievement of shape-controlled BBCP particles include the (i) obtaining of near-perfect order over tens of micrometer-scales in confined geometries and (ii) tailored engineering of particle interfaces with the supporting medium (solvent). To address these issues, we have targeted dendritic polymers that exhibit low chain entanglement as a result of steric repulsion between pendant substituents, which promotes rapid self-assembly.[34,35] These materials can generate photonic bandgaps at lower total molecular weights than typical BBCP systems with long polymeric side chains, and this feature results in lower viscosity to facilitate self-assembly.[35,36] In addition, the dendritic units provide a simple route to design and synthesize surfactant molecules capable of tailoring the interactions between polymers and the surrounding media.

Herein, we report full-color reflective photonic ellipsoids based on the self-assembly of dendronized brush block copolymers (*den*-BBCP), wherein the color can be rapidly switched on/off. Our strategy to achieve photonic particles relies

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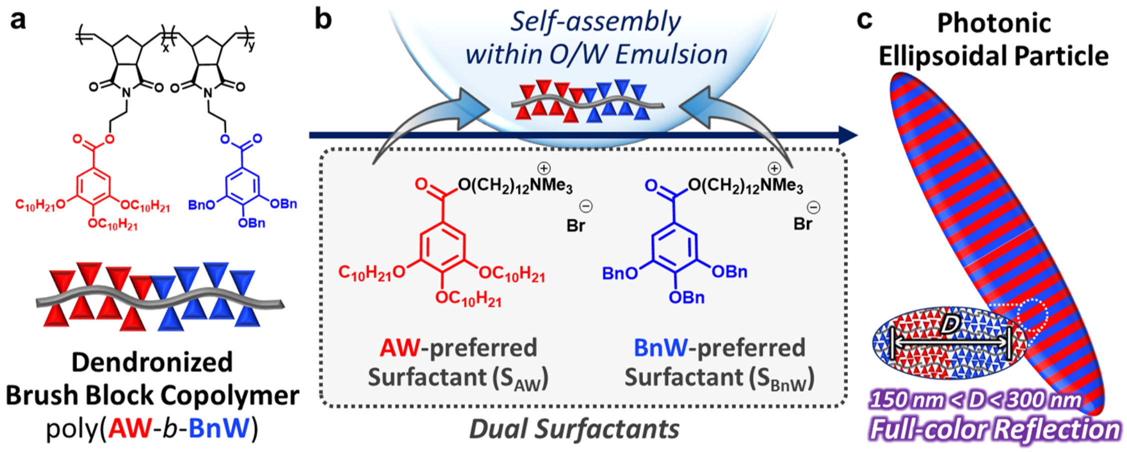

Figure 1. Schematic illustration for the preparation of photonic ellipsoidal particles by self-assembly of dendronized brush block copolymers (*den*-BBCPs), composed of monomers functionalized with alkyl ether wedge (AW) and benzyl ether wedge (BnW) groups, within an interface-engineered oil-*in*-water emulsion. Two different surfactants having a selective affinity to AW (S_{AW}) or BnW (S_{BnW}) are used to control the interfacial interactions between the *den*-BBCPs and surrounding aqueous media.

on high molecular weight *den*-BBCP, which is paired to two different dendronized surfactants with selective affinity to each block. We then utilize the dynamic emulsion interface to induce a spontaneous deformation of the particle shape. Specifically, by adjustment of the interfacial interactions between the *den*-BBCPs and the surrounding environment, the particle shapes are transformed from spheres to ellipsoids. We observe a remarkable elongation of ellipsoids along the major axis (i.e., aspect ratio over 7.0) to minimize the bending strain of *den*-BBCP driven by steric repulsion between pendant wedge side groups. Variation of the molecular weight in a range from 477 to 1144 kDa demonstrates that the reflecting color is tunable across the entire visible spectrum. Finally, we demonstrate how the reflecting colors of striped photonic ellipsoidal particles create an optically switchable system when functionalized with magnetic nanoparticles. The magnetic field-assisted alignment in bulk solutions of photonic ellipsoids exhibits an efficient rapid on/off color reflection.

■ RESULTS AND DISCUSSION

To prepare *den*-BBCPs, we synthesized two norbornene wedge-type monomers functionalized with alkyl ether wedge (AW) and benzyl ether wedge (BnW) groups and subjected them to ring-opening metathesis polymerization (ROMP) (Figure 1a) in accord with published procedures.[34,35] The poly(AW-*b*-BnW) *den*-BBCPs were synthesized with the weight-average molecular weight (M_w) ranging from 477 to 1144 kDa while low dispersity (Đ) was maintained (Table 1). (See the Methods section and Supporting Information for the synthetic details.) To produce solid *den*-BBCP particles, a dichloromethane (DCM) solution of *den*-BBCPs (2 wt %) was emulsified into an aqueous solution containing surfactants (i.e., cetyltrimethylammonium bromide (CTAB)) using a vortex for 5 s (Figure 1b). The evaporation of DCM initiates nucleation of ordered *den*-BBCP domains near the interface between the emulsion and the surrounding aqueous solution, which is followed by the propagation of polymer ordering into the particle center.[37,38] This rapid self-assembly of *den*-BBCPs from a volatile solvent affords long-range-ordered periodic nanostructures capable of reflecting light (Figure 1c).

Table 1. Summary of the *den*-BBCPs Used in This Study

Polymer	M_w (kDa)[a]	Dispersity (Đ)[a]	BnW (mol %)[b]	λ_{max} (nm)[c]	Domain size (*D*, nm)[d]
den-BBCP$_{477}$	477	1.15	47.3	369	153
den-BBCP$_{594}$	594	1.19	48.7	426	189
den-BBCP$_{809}$	809	1.11	51.0	515	235
den-BBCP$_{895}$	895	1.20	52.2	585	259
den-BBCP$_{1144}$	1144	1.18	48.7	659	298

[a]Determined by GPC. [b]Determined by ^1H NMR. [c]Determined by UV/vis spectrometer. [d]Measured by SEM.

Surfactants play a critical role in the emulsification of BCPs as the nature of the surfactant determines which block is exposed at the outer surface of the particle.[39−44] To promote favorable interactions to each block of *den*-BBCP, we synthesized CTAB-derived complementary surfactants having AW (S_{AW}) or BnW (S_{BnW}) groups. (Figure 1b; see the Supporting Information for synthetic details.) These surfactants were dissolved in DCM with *den*-BBCP before the emulsification. Figure 2 shows the particles prepared with 1 wt % S_{AW} and 9 wt % S_{BnW} (weight percent relative to polymer), which are dispersed in an aqueous CTAB continuous phase. As shown in the optical microscopy image in Figure 2a, more than 90% of the particles have an ellipsoidal shape (i.e., 92% ellipsoid, 2% cone, and 6% sphere). Moreover, an extremely ordered axially stacked lamellar structure extends over the entire area of particles with sizes up to 50 μm (Figure 2b,c). The formation of a striped ellipsoid is attributed to a surfactant-balanced interface that leads to the exposure of both AW and BnW blocks at the particle surface, generating axial stacking of lamellae.[43,45] Further adjustment of the surfactant ratio of S_{AW} to S_{BnW} allowed the transition of particle shapes to include sphere or cone shapes (Supporting Information Figure S1).

It is worth noting that these ellipsoids have a significant elongation behavior along the major axis. The formation mechanism of the ellipsoidal BCP particles has been described by theoretical calculations that quantify the degree of particle elongation.[45] In brief, when the ellipsoidal particle elongates, the entropic penalty of bending polymer chains can be released by reducing the curvature of the lamellar layers, but at the expense

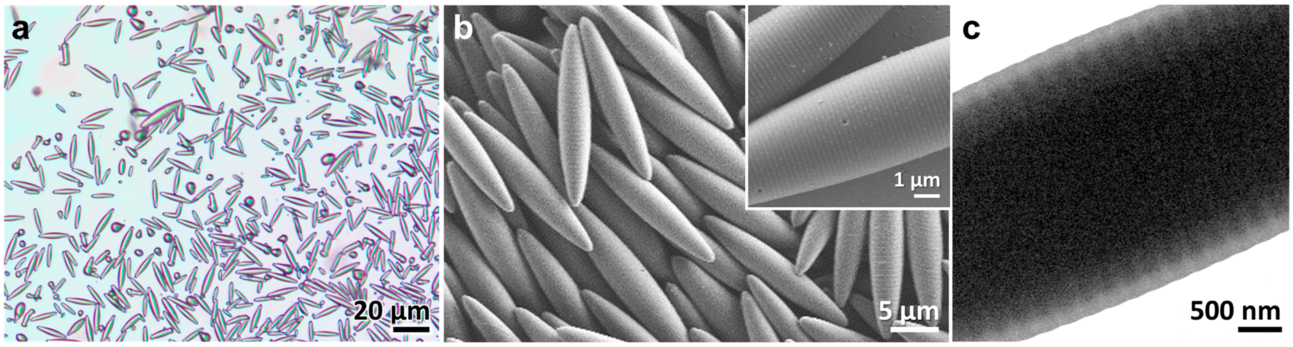

Figure 2. (a) Optical microscopy, (b) scanning electron microscopy (SEM), and (c) transmission electron microscopy (TEM) images of ellipsoidal *den*-BBCP$_{594}$ particles prepared with 1 wt % S_{AW}, 9 wt % S_{BnW} (weight percent relative to polymer), and aqueous CTAB solution as the continuous phase.

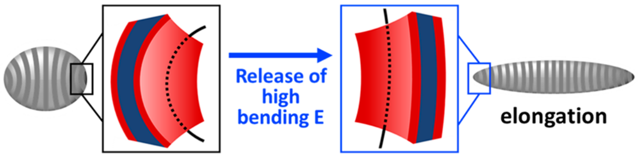

Figure 3. Schematic illustration for the release of the high bending energy of curved lamellar *den*-BBCP to have a highly elongated striped ellipsoid.

of increased surface area of the particle (Figure 3). Therefore, the competition between these energy contributions dictates the most thermodynamically stable structure. In the case of lamella-forming linear diblock copolymers, the low bending energy of curved lamellae within ellipsoidal particles prevents the particles from having a high anisotropy.[41,42,45] In contrast, BBCPs allow ellipsoidal particles with an exceptionally high shape-anisotropy and regular structure. Importantly, we find that particle sizes can increase up to a few tens of micrometers without any defects as a result of their rapid self-assembly kinetics and large domain size. Additionally, the wedge-type monomers lead to a considerable elongation of the polynorbornene backbone, resulting in high entropic penalty of bending *den*-BBCP chains. These features yield ellipsoidal particles with remarkable size, domain spacing, and aspect ratio (AR) compared to previous reports.[28,37,45] For example, the AR of these ellipsoidal particles can be enhanced up to 7 with a particle size of 50 μm (Figures S2 and S3), which is a stark contrast to the previously reported AR values that are limited to the range from 1.0 to 3.0.

We prepared a series of *den*-BBCP particles having different molecular weights (M_w) of 477, 594, 809, 895, and 1144 kDa. All particles exhibit long-range ordering of axially stacked lamellae with domain sizes of 153, 189, 235, 259, and 298 nm (Figure 4). To analyze the relationship between the measured domain spacing (D) and M_w value, D is plotted as a function of M_w in the log−log plot (Figure S4). The exponents α in the scaling form $D \sim (M_w)^\alpha$ resulted in the slope of $\alpha = 0.82$. This value is greater than the power index of typical linear BCPs which have the scaling relation of $D \sim (M_w)^{2/3}$.[46] This behavior of *den*-BBCPs originates from the rigid architectures that display a reduced degree of chain entanglement.[47,48]

The excellent self-assembly of *den*-BBCPs into defect-free, long-range-ordered periodic nanostructures with D ranging from 153 to 298 nm enables light reflection across the visible spectrum. Figure 5a shows the transmission spectra and the photographs of *den*-BBCP films having different M_w. Increasing M_w from 477 to 1144 kDa causes a commensurate shift in the peak of reflection (λ_{max}) from 369 to 659 nm (Figure 5b). This is attributed to the linear increase of λ_{max} as a function of D, which is in agreement with the previous report.[35] For normal incident

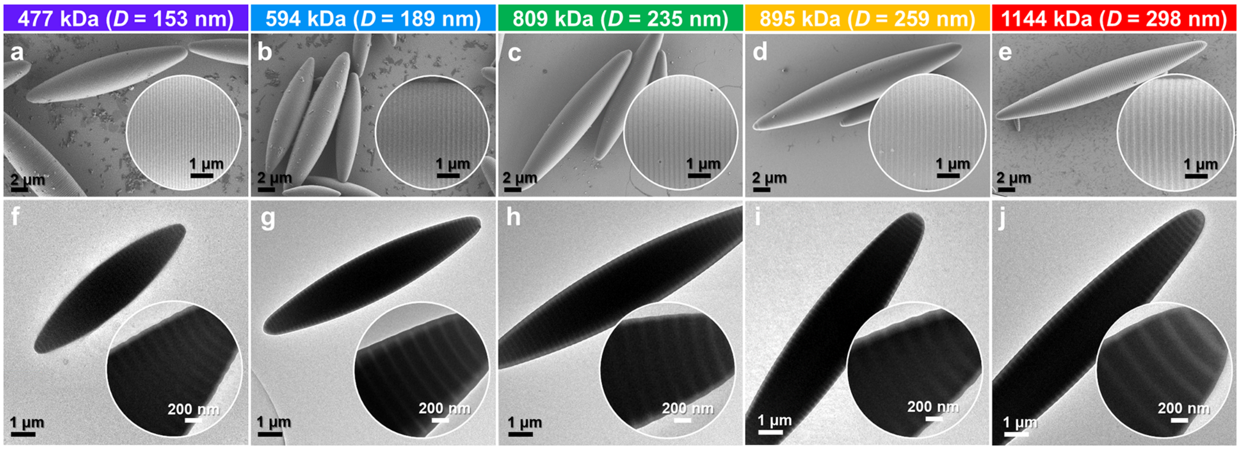

Figure 4. Influence of the M_w of the *den*-BBCP particles on overall shape and inner nanostructure: (a−e) SEM and (f−j) TEM images of ellipsoidal *den*-BBCP particles having different M_w of (parts a and f) 477 kDa (domain spacing (D) = 153 nm), (parts b and g) 594 kDa (D = 189 nm), (parts c and h) 809 kDa (D = 235 nm), (parts d and i) 895 kDa (D = 259 nm), and (parts e and j) 1144 kDa (D = 298 nm).

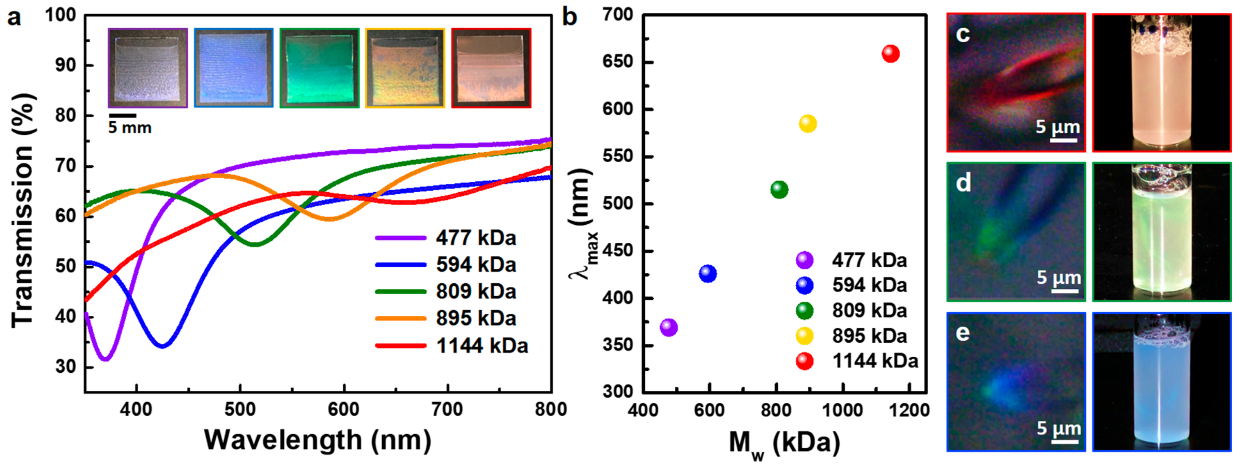

Figure 5. (a) Transmission spectra and photographs of *den*-BBCPs films. (b) Plots of λ_{max} as a function of M_w of *den*-BBCPs. (c−e) Reflection micrographs of individual ellipsoidal *den*-BBCP particles and the photographs of particle suspension in water with different M_w of 1144 kDa (c, red color), 809 kDa (d, green color), and 594 kDa (e, blue color). The light source and the camera were kept at a fixed angle of 0°.

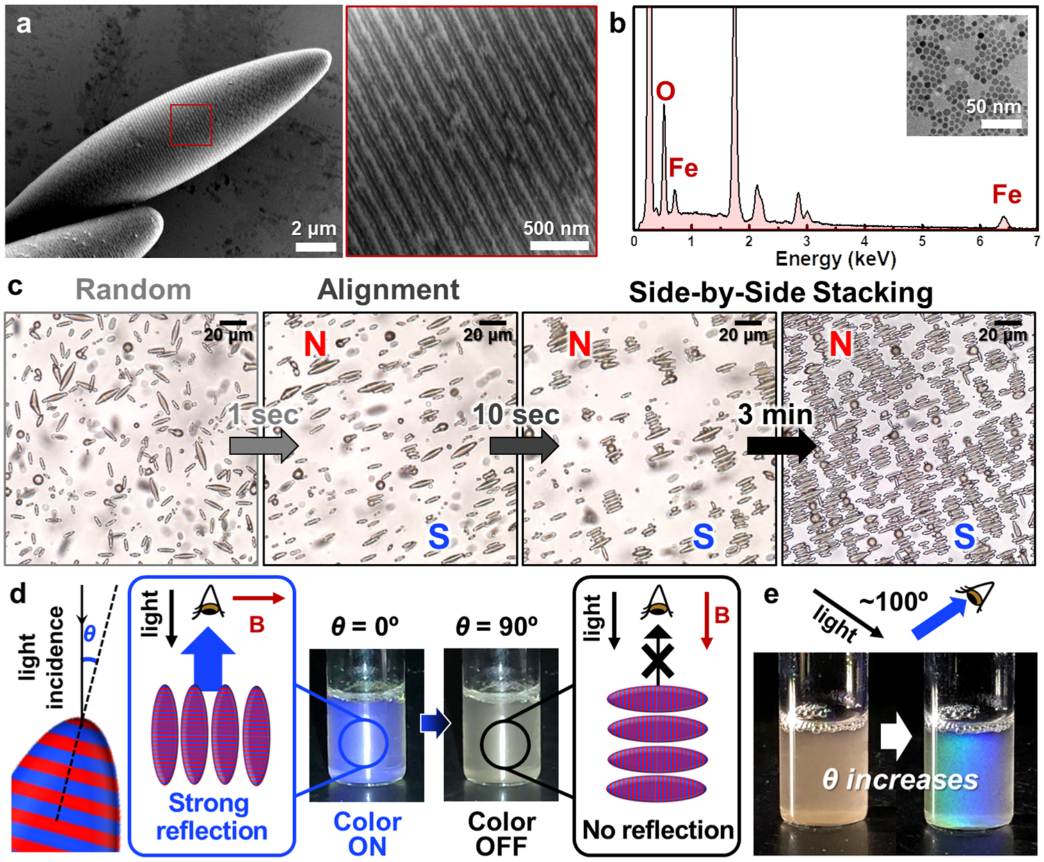

Figure 6. (a) SEM image and (b) corresponding EDX spectrum of Fe_3O_4NP-attached *den*-BBCP$_{540}$ ellipsoids (inset figure is the TEM image of the Fe_3O_4 NPs). (c) Magnetic field-assisted alignment of Fe_3O_4/*den*-BBCP$_{540}$ particles depending on the time: (i) random assembly, (ii) linear alignment, and (iii) side-by-side stacking. (d, e) Real-time on/off or blue-shift coloration of the particle suspension by precise control of the particle orientation: photographs of the suspension of (part d) *den*-BBCP$_{540}$ ellipsoids and (part e) *den*-BBCP$_{1144}$ ellipsoids under the magnetic field illustrating the light incident angle-dependent color reflection. The light source and the camera were kept at a fixed angle of (part d) 0° and (part e) 100°.

beam, the relationship between λ_{max} and D is described by the following equation[13]

$$\lambda_{max} = 2(n_1d_1 + n_2d_2)$$

where n_i is the refractive index of component i and d_i is the thickness of the ith layer. In comparison with the *den*-BBCP films, the trend in the reflecting color is almost preserved in the particles, while slightly broader and blue-shifted reflection is expected due to the random orientation of the particles. As shown in Figure 5c−e, individual *den*-BBCP particles display red, green, and blue colors in reflective optical microscopy as a result of the highly ordered multilayer (more than 100) lamellar structures within an individual particle. For 1D photonic crystals, the wavelength of reflected light changes with the angle of light incidence with respect to the plane of the photonic layer, causing the bandgap to be angle-dependent.

We note that in the case of these particle suspensions, the distribution of the orientation of the lamellae is random and the grain size is small. In detail, by considering the shape of the particle as a perfect ellipsoid, the effective number of the photonic layers (N_{eff}) is expressed as a function of incident angle θ as in the following equation

$$N_{eff} = \left[\frac{N\cos\theta}{\sqrt{(\cos\theta)^2 + (AR \times \sin\theta)^2}} \right]$$

where N is the number of photonic layers in the particle. The photons incident at a significant angle from the particle axis interact with fewer layers, so the reflections are much weaker.[49] Therefore, regardless of the direction of the incident light, the bulk suspension of the particle exhibits the predominant reflecting color. The theoretical simulation of the reflectance spectrum of the particle suspension is provided in the Supporting Information.

In contrast to spherical particles with concentric lamellae, the photonic behaviors (i.e., reflecting color and intensity) of the ellipsoidal particles having axially stacked lamellae are strongly dependent on the incident light angle to the photonic layer. To illustrate this feature, we demonstrated magnetic field-assisted versatile alignment of photonic particles by attaching Fe_3O_4 magnetic nanoparticles (NPs). We first synthesized 6.4 nm-sized Fe_3O_4 NPs capped with 1,2-hexadecanediol (Figure S5).[50] Then, a solution of *den*-BBCP and Fe_3O_4 NPs (volume fraction ~3%) were emulsified to yield hybrid magnetic photonic ellipsoids. As a result of the large entropic barriers arising from polymer stretching to incorporate NPs and additional enthalpic gain from the preferential affinity with the surrounding medium, the NPs segregated on the surface of the *den*-BBCP particles and the overall ellipsoidal shape and inner lamellar structure were maintained.[39,51] Highly magnified SEM image (Figure 6a) and the energy-dispersive X-ray spectroscopy (EDX) analysis of the Fe (Figure 6b) confirm that the NPs localize at the AW block's aqueous interface, forming bands of Fe_3O_4 NPs. This partitioning is a result of the 1,2-hexadecanediol giving predominately alkyl character to the NPs.[50] When subjected to the magnetic field, the hybrid particles are rapidly magnetized and further interact with each other forming a side-by-side stacking pattern (Figure 6c). The ellipsoids are magnetized along the minor axis so that the magnetic NPs assembling on the surface could achieve maximum interactions between particles.[52]

Finally, we explored the particle orientation-dependent photonic behavior by varying the direction of the magnetic field. The suspension of *den*-$BBCP_{540}$ ellipsoids shows a strong reflected violet color when the light incident angle is small (i.e., $\theta \sim 0°$, the direction of the magnetic field is perpendicular to the incident light), while there is almost no reflection at $\theta \sim 90°$, leading to a rapid on/off response in coloration activated by the magnetic field (Figure 6d and Supporting Information Movie S1). The ellipsoids with higher M_w show the angle-dependent blue-shift coloration and finally switch off the color (Figure 6e and Supporting Information Movie S2). In this case, the light source and the camera were put at an angle of 100° to observe the blue-shifted color. The significance of the lamellar structure in ellipsoids can be emphasized by comparing the magnetic response of the Fe_3O_4 NPs-attached spherical particles having concentric lamellae as a control sample. As shown in Figure S6, the spherical particles react to the magnet; however, they do not display color switching.

CONCLUSIONS

We have developed a robust and effective strategy to prepare photonic ellipsoids with a rapid color-switching response to magnetic field. Rapid, confined self-assembly of dendronized BBCPs generated highly elongated ellipsoids having a near-perfect ordering of axially stacked lamellae. Simple tuning of M_w afforded the formation of domain sizes that ranged from 153 to 298 nm, and the reflecting color was readily tunable across the entire visible spectrum. Fe_3O_4-attached hybrid photonic particles provided controlled alignment of the photonic ellipsoids, and their bulk reflectance displayed dynamic on/off color-switching assisted by directional magnetic field. We envision that the magnetic NPs-functionalized photonic ellipsoids represent a new class of magnetically responsive photonic crystals, providing promising potential in smart photonic pigments and photonic devices.

METHODS

Synthesis of Dendronized Brush Block Copolymers (*den*-BBCPs). Detailed synthetic procedures are provided in the Supporting Information. Alkyl wedge monomers (AW) and benzyl wedge monomers (BnW) were synthesized according to the previous report.[35] Under the rapid stirring, the Grubbs Catalyst (3rd Generation) was added into the solution of BnW in tetrahydrofuran (THF), followed by the addition of AW. The polymerization was allowed to proceed for 5 min. The product was precipitated with methanol to afford *den*-BBCP.

Synthesis of S_{AW} and S_{BnW} Surfactants. A mixture of AW (or BnW) precursor, 12-bromo-1-dodecanol, 4-dimethylaminopyridine, *N*,*N*′-dicyclohexylcarbodiimide in DCM was stirred at room temperature overnight. The product was purified by column chromatography with hexane/ethyl acetate to yield 12-bromododecyl 3,4,5-tris-(decyloxy)benzoate (66 mg, 46% yield) (or 12-bromododecyl 3,4,5-tris(benzyloxy)benzoate (123 mg, 52% yield)). The products were added in a sealed tube with trimethylamine and THF and stirred for 4 d at room temperature. The product was purified with a short column using DCM and methanol to yield a solid white powder of S_{AW} (40 mg, 60% yield) or S_{BnW} (100 mg, 77% yield).

Fabrication of Photonic Ellipsoidal Particles. DCM solutions of *den*-BBCPs (20 mg/mL), S_{BnW} (1 mg/mL), and S_{AW} (1 mg/mL) were mixed to prepare stock solution where the weight ratio of S_{AW} and S_{BnW} to *den*-BBCP were adjusted as follows: the weight percentages of S_{BnW} and S_{AW} to *den*-BBCP were 9 and 1 wt % for *den*-$BBCP_{477}$, *den*-$BBCP_{594}$, *den*-$BBCP_{809}$, and *den*-$BBCP_{895}$, and 10 wt % of S_{BnW} for *den*-$BBCP_{1144}$. Then, the mixture (50 μL) was emulsified in an aqueous solution of CTAB (0.1 wt %, 1.0 mL) by vortexing for 5 s. Following this the evaporation of the organic solvent at room temperature for 24 h generated a dispersion of solid particles. The excess surfactants were removed by repeated washing before SEM and TEM characterization.

Fabrication of Fe_3O_4 NPs-Attached Photonic Ellipsoids and Their Color-Switching under Magnetic Field. Detailed synthetic procedures for magnetic NPs are provided in the Supporting Information. First, the 6.4 nm-sized, surface-modified Fe_3O_4 NPs were synthesized according to the previous report.[50] A DCM solution of Fe_3O_4 NPs was prepared and added to the stock solution of *den*-BBCPs, S_{BnW} and S_{AW}, where the volume fraction of Fe_3O_4 NPs was adjusted to be ~3% for *den*-$BBCP_{540}$ and ~1.5% for *den*-$BBCP_{1144}$. The mixture was emulsified and evaporated in the same condition as that of the preparation of the photonic ellipsoids. For the illumination of particle dispersions, a white LED as the light source was provided in a fixed direction. A magnetic field was applied by placing a neodymium magnet near the vials (i.e., ~2 cm distance).

Characterization. NMR spectra were recorded on a Bruker Advance Neo 400. The chemical shift data are reported in units of δ (ppm) relative to the residual solvent. SEM (Merlin and Crossbeam

540 Zeiss) and TEM (FEI-Tecnai) were used to characterize the overall shape and internal structures of the photonic ellipsoidal particles. The samples were prepared by drop-casting polymer particle suspensions onto the silicon wafers or TEM grids. For the TEM analysis, the prepared samples were exposed to RuO_4 vapor to stain the benzyl ether group of the *den*-BBCPs selectively. The molecular weight of the polymer was measured in an Agilent 1260 Infinity gel permeation chromatography calibrated with a polystyrene standard and THF as the eluent. A Leica DMRXP polarized-light microscopy was used to take optical images. Transmission spectra were measured by an Agilent Cary 4000 UV/vis spectrophotometer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02398.

Experimental details, theoretical simulation of reflectance spectra of photonic ellipsoids, and additional characterization data (NMR, optical microscopy, SEM, and TEM) (PDF)

Supporting movie for real-time switch on/off coloration of photonic ellipsoids (MP4)

Supporting movie for blue-shift coloration of photonic ellipsoids (MP4)

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Notes

The authors declare no competing financial interest.

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