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Citation	He, Qilin et al. "Switchable Full-Color Reflective Photonic Ellipsoidal Particles." <i>Journal of the American Chemical Society</i> 142, 23 (May 2020): 10424–10430 © 2020 American Chemical Society
As Published	http://dx.doi.org/10.1021/jacs.0c02398
Publisher	American Chemical Society (ACS)
Version	Author's final manuscript
Citable link	https://hdl.handle.net/1721.1/128149
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Switchable Full-Color Reflective Photonic Ellipsoidal Particles

Qilin He,^{1,‡} Kang Hee Ku,^{1,‡} Harikrishnan Vijayamohanam,¹ Bumjoon J. Kim,^{2,*} and Timothy M. Swager^{1,*}

¹ Department of Chemistry, Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts 02139, United States

² Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

KEYWORDS. *dendronized brush block copolymers, photonic particles, full-color reflection, ellipsoidal polymer particles, real-time color response*

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.*, $153 \text{ nm} \leq D \leq 298 \text{ nm}$). 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 altering 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 high refractive index contrast composites 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 (3D) confined geometries.²⁵⁻²⁷

We have been interested to expand the formation of non-spherical 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 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 for the first time 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 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 adjusting the interfacial interactions between the *den*-BBCPs and the surrounding environment, the particle shapes transform 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 reflected color is tunable across the entire visible spectrum. Finally, we demonstrate how the reflecting colors of striped ellipsoidal photonic 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 (\mathcal{D}) were maintained (Table 1). (See the experimental 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).

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 cetyltrimethylammonium bromide (CTAB)-derived complementary surfactants having AW (S_{AW}) or BnW (S_{BnW}) groups. (Figure 1b, See the Supporting Information for synthetic details.)

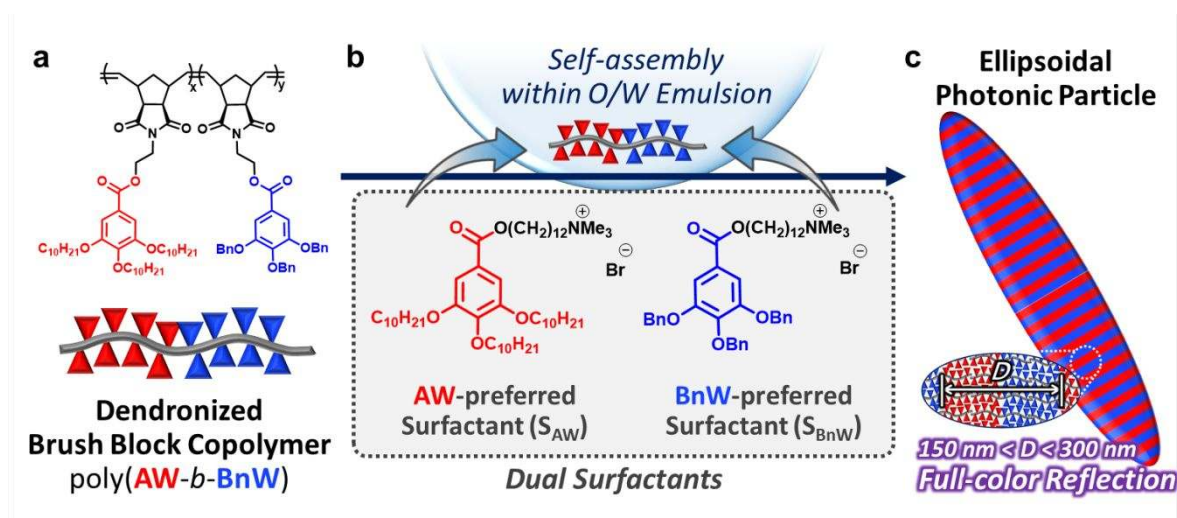


Figure 1. Schematic illustration for the preparation of photonic ellipsoidal particles by self-assembly of dendronized brush block copolymers (*den*-BBCPs), composed of monomers functionalized with alkyl ether wedge (AW) and benzyl ether wedge (BnW) groups, within an interface-engineered oil-in-water 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.

Table 1. Summary of the *den*-BBCPs used in this study.

Polymer	M_w (kDa) ^a	Dispersity (\mathcal{D}) ^a	BnW (mol %) ^b	λ_{max} (nm) ^c	Domain size (D , nm) ^d
<i>den</i> -BBCP ₄₇₇	477	1.15	47.3	369	153
<i>den</i> -BBCP ₅₉₄	594	1.19	48.7	426	189
<i>den</i> -BBCP ₈₀₉	809	1.11	51.0	515	235
<i>den</i> -BBCP ₈₉₅	895	1.20	52.2	585	259
<i>den</i> -BBCP ₁₁₄₄	1144	1.18	48.7	659	298

^a determined by GPC, ^b determined by ¹H NMR, ^c determined by UV/Vis spectrometer, and ^d measured by SEM

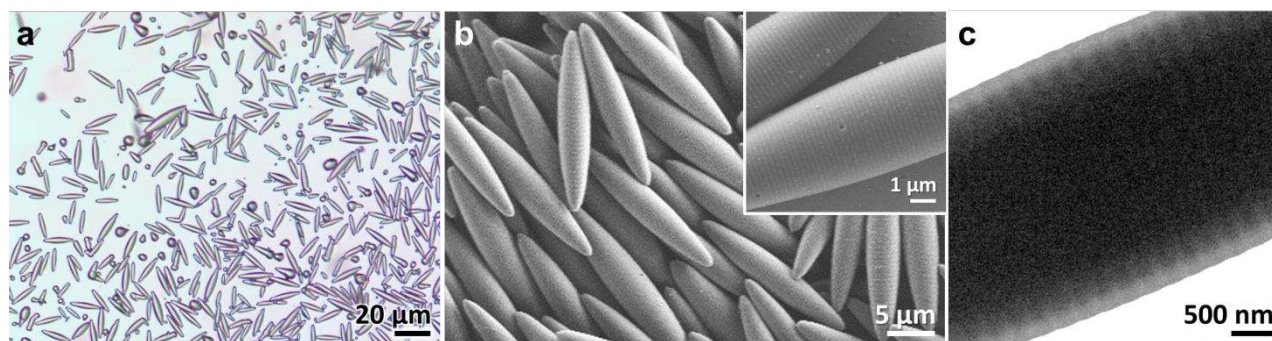


Figure 2. a) Optical microscopy, b) scanning electron microscopy (SEM), and c) transmission electron microscopy (TEM) images of ellipsoidal *den*-BBCP₅₉₄ particles prepared with 1 wt% S_{AW}, and 9 wt% S_{BnW} (weight percent relative to polymer), and aqueous CTAB solution as the continuous phase.

These surfactants were dissolved in DCM with *den*-BBCP before the emulsification and **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**).

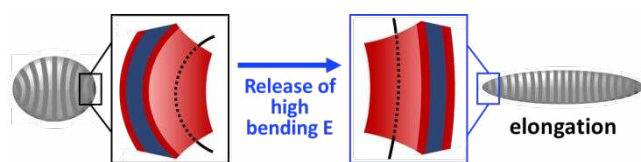


Figure 3. Schematic illustration for the release of the high bending energy of curved lamellar *den*-BBCP chains to have a highly elongated striped ellipsoid.

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 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. These features with the release of the high entropic penalty of *den*-BBCP chains 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 domain spacing (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 beam, the relationship between λ_{max} and D is described by the following equation¹³

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

where n_i is the refractive index of component i and d_i is the thickness of the i th layer. Compared with the *den*-BBCP films, the trend in the reflecting color is almost preserved in the particles, while slightly broaden 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.

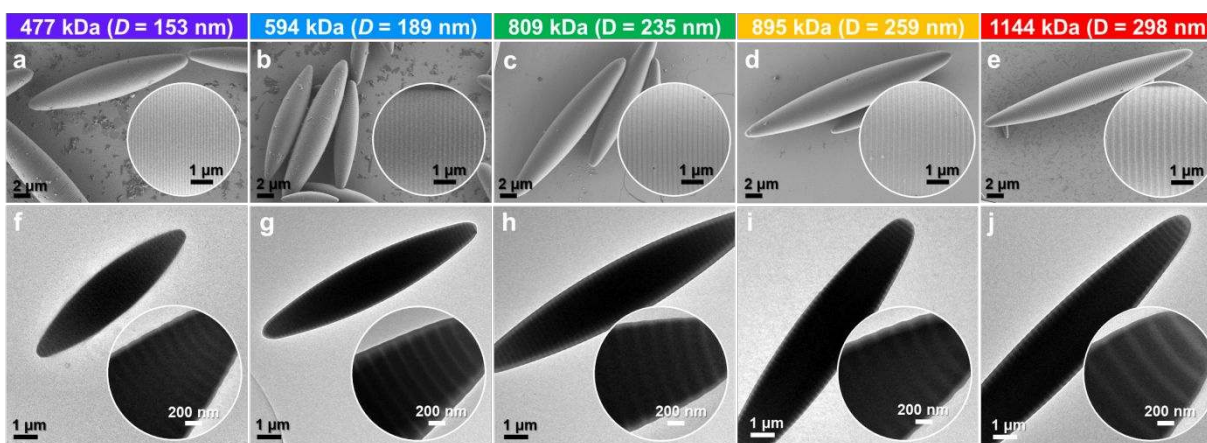


Figure 4. Influence of the M_w of the *den*-BBCP particles on overall shape and inner nanostructure: a-e) SEM and f-j) TEM images of ellipsoidal *den*-BBCP particles having different M_w of a, f) 477 kDa (domain spacing (D) = 153 nm), b, g) 594 kDa (D = 189 nm), c, h) 809 kDa (D = 235 nm), d, i) 895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

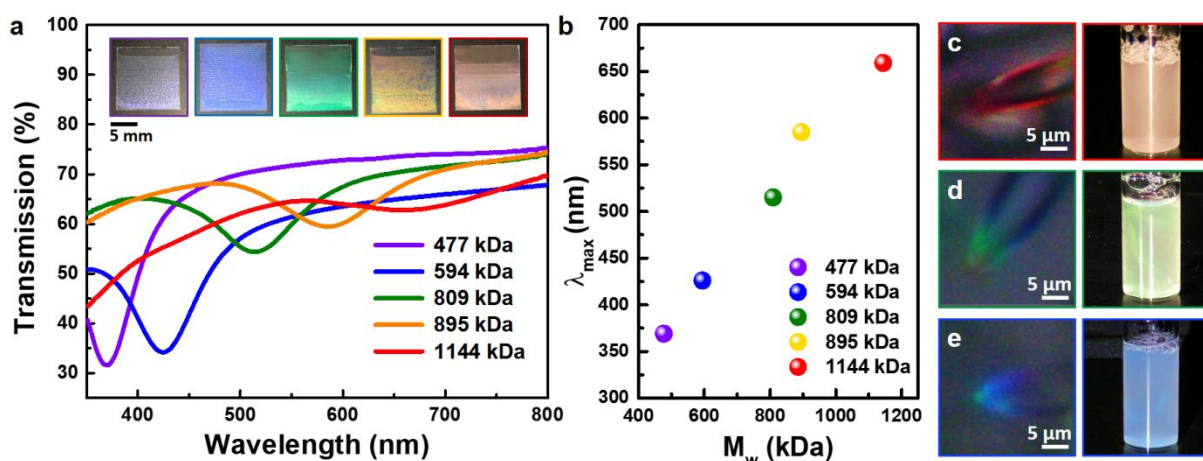


Figure 5. a) Transmission spectra and photographs of *den*-BBCPs films. b) Plots of λ_{\max} as a function of M_w of *den*-BBCPs. c-e) Reflection micrographs of individual ellipsoidal *den*-BBCP particles and the photographs of particle suspension in water with different M_w of 1144 kDa (c, red color), 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° .

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 θ as in the following equation:

$$N_{\text{eff}} = \frac{N \cos \theta}{\sqrt{(\cos \theta)^2 + (AR * \sin \theta)^2}}$$

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 The theoretical simulation of the reflectance spectrum of the particle suspension is provided in the Supporting Information. Regardless of the direction of the incident light, the bulk suspension of the particle exhibits the predominant reflecting color.

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*-BBCP₅₄₀ and Fe_3O_4 NPs (volume fraction $\sim 3\%$) 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*-BBCP₅₄₀ 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 predominantly 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.

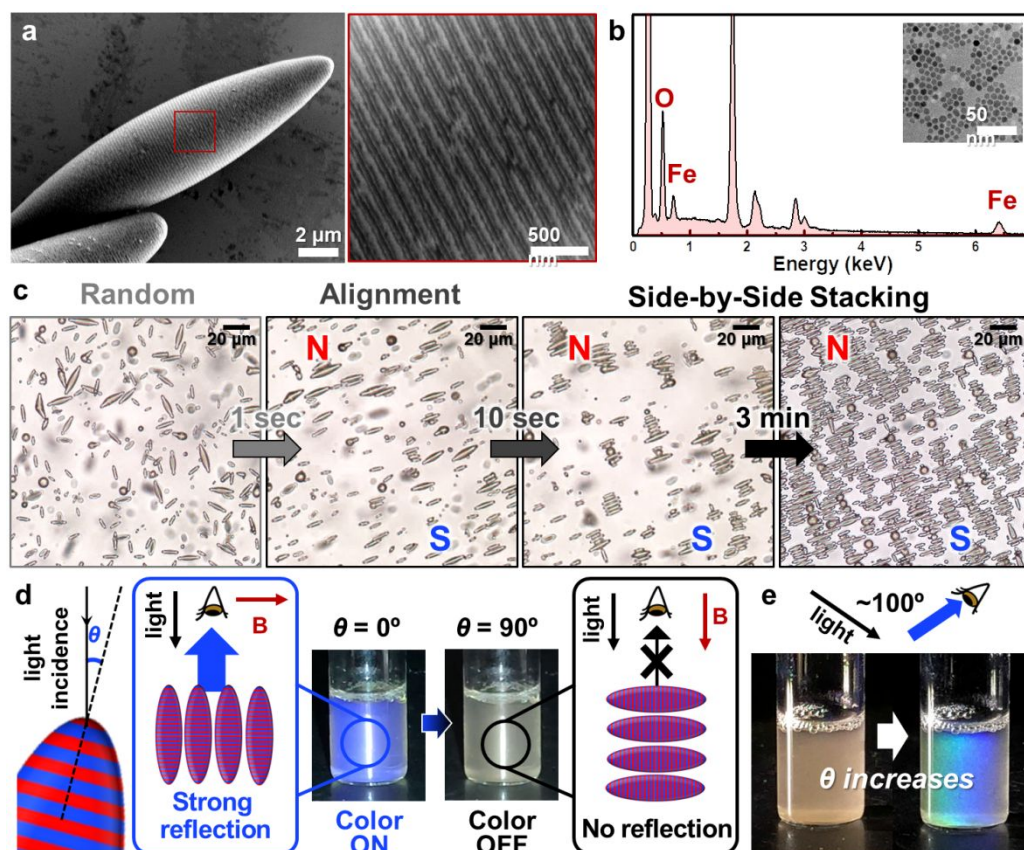


Figure 6. a) SEM image and b) corresponding EDX spectrum of Fe_3O_4 NP-attached *den*-BBCP₅₉₄ ellipsoids (Inset figure is the TEM image of the Fe_3O_4 NPs). c) Magnetic field-assisted alignment of Fe_3O_4 /*den*-BBCP₅₄₀ particles depending on the time: (i) random assembly, (ii) linear alignment, and (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 d) *den*-BBCP₅₄₀ ellipsoids and e) *den*-BBCP₁₁₄₄ ellipsoids under the magnetic field illustrating the light incident angle-dependent color reflection. The light source and the camera are kept at a fixed angle of d) 0° and e) 100° .

The suspension of *den*-BBCP₅₄₀ ellipsoids shows a strong reflected violet color when the light incident angle is small (*i.e.*, $\theta \sim 0^\circ$, the direction of the magnetic field is perpendicular to the incident light), while almost no reflection at $\theta \sim 90^\circ$, 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 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 range from 153 to 298 nm, and the reflected color was readily tunable across the entire visible spectrum. Fe_3O_4 -attached hybrid photonic particles provided for 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 crystal, providing a 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-

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

12 **Fabrication of photonic ellipsoidal particles.** DCM
13 solutions of *den*-BBCPs (20 mg/mL), S_{BnW} (1 mg/mL), and S_{AW}
14 (1 mg/mL) were mixed to prepare stock solution where the
15 weight ratio of S_{AW} and S_{BnW} to *den*-BBCP were adjusted as
16 follow: the weight percentages of S_{BnW} and S_{AW} to *den*-BBCP
17 were 9 wt% and 1 wt% for *den*-BBCP₄₇₇, *den*-BBCP₅₉₄, *den*-
18 BBCP₈₀₉ and *den*-BBCP₈₉₅, and 10 wt% of S_{BnW} for *den*-
19 BBCP₁₁₄₄. Then, the mixture (50 μ L) was emulsified in an
20 aqueous solution of CTAB (0.1 wt%, 1.0 mL) by vortexing for
21 5 s. Following evaporation of the organic solvent at room
22 temperature for 24 h generated a dispersion of solid particles.
23 The excess surfactants were removed by repeated washing
24 before SEM and TEM characterization.

25 **Fabrication of Fe₃O₄ NPs-attached photonic ellipsoids and
26 their color-switching under the magnetic field.** Detailed
27 synthetic procedures for magnetic NPs are provided in the
28 Supporting Information. First, the 6.4 nm-sized, surface-
29 modified Fe₃O₄ NPs were synthesized according to the previous
30 report.⁵⁰ A DCM solution of Fe₃O₄ NPs was prepared and added
31 to the stock solution of *den*-BBCPs, S_{BnW}, and S_{AW}, where the
32 volume fraction of Fe₃O₄ NPs was adjusted to be ~ 3 % for *den*-
33 BBCP₅₄₀, and ~1.5 % for *den*-BBCP₁₁₄₄. The mixture was
34 emulsified and evaporated in the same condition as preparing
35 the photonic ellipsoids. For the illumination of particle
36 dispersions, a white LED as the light source was provided in a
37 fixed direction. A magnetic field was applied by placing a
38 neodymium magnet near the vials (*i.e.*, ~ 2 cm distance).

39 **Characterization.** NMR spectra were recorded on a Bruker
40 Advance Neo 400. The chemical shift data are reported in units
41 of δ (ppm) relative to the residual solvent. SEM (Merlin and
42 Crossbeam 540 Zeiss) and TEM (FEI-Tecna) were used to
43 characterize the overall shape and internal structures of the
44 photonic ellipsoidal particles. The samples were prepared by
45 drop-casting polymer particle suspensions onto the silicon
46 wafers or TEM grids. For the TEM analysis, the prepared
47 samples were exposed to RuO₄ vapor to stain the benzyl ether
48 group of *den*-BBCPs selectively. The molecular weight of the
49 polymer was measured in an Agilent 1260 Infinity gel
50 permeation chromatography calibrated with polystyrene
51 standard with THF as the eluent. A Leica DMRXP polarized-
52 light microscopy was used to take optical images. Transmission
53 spectra were measured by an Agilent Cary 4000 UV/Vis
54 spectrophotometer.

55 ASSOCIATED CONTENT

56 **Supporting Information.** Supporting movies for real-time switch
57 on/off and blue-shift coloration of photonic ellipsoids,
58 experimental details, theoretical simulation of reflectance spectra
59 of photonic ellipsoids, and additional characterization data (NMR,
60

optical microscopy, SEM and TEM). This material is available free
of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* tswager@mit.edu

* bumjoonkim@kaist.ac.kr

Author Contributions

‡Q.H. and K.H.K. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was supported by a Vannevar Bush Faculty
Fellowship to T.M.S. (Grant # N000141812878). B.J.K.
acknowledges the support from National Research Foundation
Grant (2019R1A2B5B03101123) from the Korean Government.

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ToC Figure

