Magnetic Nanocomposites and Their Incorporation into Higher Order Biosynthetic Functional Architectures

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Supporting Information

ABSTRACT: A magnetically active Fe₃O₄/poly(ethylene oxide)-b-block-poly(butadiene) (PEO-b-PBD) nanocomposite is formed by the encapsulation of magnetite nanoparticles with a short-chain amphiphilic block copolymer. This material is then incorporated into the self-assembly of higher order polymer architectures, along with an organic pigment, to yield biosynthetic, bifunctional optical and magnetically active Fe₃O₄/bacteriochlorophyll c/PEO-b-PBD polymeric chlorosomes.

INTRODUCTION

In nature, a wide range of structural architectures and functional responses are formed through lipid assemblies, leading to essential roles in a number of physiological processes.¹ Two biolike membrane structures have been mimicked via self-assembly of amphiphilic block copolymers, albeit typically with much larger molecular weight polymers relative to lipids.³,⁴ Amphiphilic block copolymers are composed of a hydrophobic domain and a hydrophilic domain and are known to self-assemble thermodynamically into spherical micelles, worm-like micelles, bilayers, and other structures, depending on the ratio of hydrophobicity to hydrophilicity.⁵⁻⁷ Furthermore, they have shown increased morphological flexibility when compared with lipids, as well as the ability to possess additional functionality.⁶,⁸⁻¹⁰ Such functionality can be introduced through the incorporation of nanoparticles (NPs), organic molecules, and functional groups. For example, magnetite (Fe₃O₄) nanoparticles were encapsulated by modified poly(ethylene oxide)—poly(propylene oxide)—poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer and used effectively as a temperature-responsive material for targeted drug delivery.¹¹,¹² Mai and Eisenberg incorporated magnetic nanoparticles into the central compartment of a number of different copolymer architectures, including vesicles, rods, and micelles.¹³,¹⁴ Likewise, Hickey et al. showed that small 5.6 nm iron oxide nanoparticles could be incorporated directly into the walls of copolymer vesicles.¹⁵,¹⁶

Recently, the block copolymer poly(ethylene oxide)-b-block-poly(butadiene) (PEO-b-PBD) was self-assembled along with the r-stacked organic pigment, molecule bacteriochlorophyll c (BChl c), to form an artificial supramolecular light-harvesting system.¹⁷ BChl c aggregates exhibit high exciton diffusion lengths and are strong candidates for developing bioinspired light-harvesting systems.¹⁸,¹⁹ The resulting polymer architectures therefore mimicked green bacterial light-harvesting systems called chlorosomes, yet with the simplicity of a single polymer species. Furthermore, these polymer—chlorosome nanocomposites (PCNs) allowed for incorporation of nonnative combinations of various BChl species, tuning the optical response of the system, as well as demonstrating the increased flexibility of polymer-based systems.²⁰ Importantly, such functional chlorosome mimics exhibited a long-range order which had never been achieved in a nanocomposite, even when using isolated components, including native lipids.²¹ The structure of the PCNs was a result of the flexibility of the amphiphilic block copolymers, which created an environment in which a long-range order of BChl c was possible, thereby demonstrating a tremendous advantage over lipids in creating bioinspired architectures.

Here, we exploit the morphological flexibility of PEO-b-PBD to form a Fe₃O₄/PEO-b-PBD magnetically active nanocomposite via nanoparticle encapsulation. This isotropic nanocomposite maintains the strong magnetic properties and tight size distribution of magnetite nanoparticles formed by solvothermal synthesis,²² while also showing long-term stability in aqueous solution. We show that this material can be included...
in the self-assembly of higher order architectures, leading to Fe₃O₄/BChl c/PEO-b-PBD magnetic polymer−chlorosome nanocomposites (m-PCNs), without any disruption in the organization of the BChl c long-range aggregates. These m-PCNs show not only an optical response but also a strong magnetic response, which will allow for spatial manipulation of an artificial light-harvesting system by the application of an external magnetic field.

## RESULTS AND DISCUSSION

To begin, we encapsulated magnetite (Fe₃O₄) nanoparticles with 2.5 kDa PEO-b-PBD by a modified film rehydration technique (for full experimental details, please see the Supporting Information). This particular molecular weight copolymer contains approximately 30 PEO and 22 PBD segments and has previously shown good morphological flexibility, including the ability to form higher order architectures. Transmission electron microscopy (TEM) revealed well-dispersed nanoparticles with a uniform spherical shape and an average size of 21.5 ± 1.0 nm (Figure 1a). The interparticle spacing was measured from multiple TEM images to be 4.7 nm, which is significantly larger than what has been observed with oleic acid-capped nanoparticles, suggesting successful encapsulation.

This observation is supported by the emergence of good water solubility, provided by the expression of PEO at the surface (Figure 1a, inset). The stability of the Fe₃O₄/PEO-b-PBD nanocomposites in water was observed over time, with no evidence of flocculation occurring after one year. Small-angle X-ray scattering (SAXS) was performed on the oleic acid-capped Fe₃O₄ nanoparticles to confirm the size analysis provided by TEM. Figure 1B shows the raw scattering data overlaid with the Gaussian model fit and associated residuals. Vibrating sample magnetometry (VSM) performed on the nanoparticles before and after encapsulation. Saturation magnetizations measured 62 Am²/kg Fe₃O₄ and 56 Am²/kg Fe₃O₄. Zero-field-cooled−field-cooled (ZFC−FC) measurements performed before and after encapsulation. The blocking temperature (T_wire) was observed to increase slightly from 310 to 349 K, along with a broadening of the ZFC peak indicative of dipolar interactions.

Figure 1. Characterization of the Fe₃O₄/PEO-b-PBD block copolymer-encapsulated nanoparticles. (a) Transmission electron microscopy (TEM) image of 21.5 ± 1.0 nm Fe₃O₄ nanoparticles coated in 2.5 kDa PEO-b-PBD block copolymer, which provides good aqueous stability (inset). (b) Small-angle X-ray scattering (SAXS) size analysis showing raw scattering data overlaid with the Gaussian model fit and associated residuals. (c) Vibrating sample magnetometry (VSM) performed on the nanoparticles before and after encapsulation. Saturation magnetizations measured 62 Am²/kg Fe₃O₄ and 56 Am²/kg Fe₃O₄. (d) Zero-field-cooled−field-cooled (ZFC−FC) measurements performed before and after encapsulation. The blocking temperature (T_wire) was observed to increase slightly from 310 to 349 K, along with a broadening of the ZFC peak indicative of dipolar interactions.
To confirm that the nanoparticles were coated by encapsulation and not by a ligand exchange process, we first added a fluorescent agent to the Fe$_3$O$_4$ nanoparticle surface.\(^{27}\) This was carried out by refluxing an aliquot of oleic acid-capped Fe$_3$O$_4$ nanoparticles in the presence of BODIPY FL C16. The carboxylate moiety of BODIPY exchanged at the surface with the carboxylate moiety of BODIPY FL C16. The carboxylate moiety of BODIPY exchanged at the surface with the carboxylate moiety of BODIPY FL C16. The carboxylate moiety of BODIPY exchanged at the surface with the carboxylate moiety of BODIPY FL C16.

"Self-assembly occurs when a solution mixture containing the various component fractions is slowly infused with a buffer solution."
oleic acid, with the long C16 carbon chain providing good particle stability. Fluorescence emission measurements of the BODIPY-capped nanoparticles were performed with peak excitation and emission wavelengths of 509 and 514 nm measured, respectively (Figure S2). Following the PEO-b-PBD encapsulation step, the nanocomposite remained fluorescent with peak excitation and emission wavelengths measured at 509 and 514 nm, respectively (Figure S3). These measurements confirm that PEO-b-PBD is being added to the system by encapsulation.

The magnetic properties of the oleic acid-capped nanoparticles and the Fe3O4/PEO-b-PBD nanocomposite were then compared using vibrating sample magnetometry (VSM). Saturation magnetization, $M_{sat}$, was measured to be 62 Am$^2$/kg Fe3O4 before encapsulation and 56 Am$^2$/kg Fe3O4 following encapsulation, indicating the presence of PEO-b-PBD does not significantly affect the magnetization of the iron oxide nanoparticles (Figure 1c). The strong $M_{sat}$ meant that the Fe3O4/PEO-b-PBD nanocomposite particles could be readily isolated from solution with the application of an external magnetic field.

Zero-field-cooled–field-cooled (ZFC–FC) curves are given in Figure 1d. The oleic acid-capped Fe3O4 nanoparticles display a well-defined blocking temperature, $T_B$, 310 K, matching closely with previous observations of similar-sized magnetite nanoparticles. Following encapsulation, the ZFC curve broadened, accompanied by an increase in $T_B$ to 349 K. This is indicative of dipolar interactions, which would suggest there is a population of nanoparticles that have been encapsulated as dimers, trimers, or larger aggregates. This was confirmed with TEM (Figure S4).

Scheme 1 shows the formation of higher order bifunctional Fe3O4/BChl c/PEO-b-PBD magnetically and optically active polymeric chlorosome nanocomposites (m-PCNs). We first performed a simple size selection step to remove any larger aggregates in the Fe3O4/PEO-b-PBD nanocomposite, via centrifugation. The resulting particles are then dissolved in tetrahydrofuran (THF), along with certain amounts of PEO-b-PBD and BChl c. Each component is initially well solvated by THF; however, as a buffer is slowly introduced, the polarity of the solution increases and there is a driving force for self-assembly. This is the well-known cosolvent processing method of block copolymers, which is often used to introduce “cargo” to lipid and polymer vesicles. Here, the BChl c and Fe3O4 nanoparticles can be considered analogous to hydrophobic drug cargo.

Incorporating oleic acid-capped Fe3O4 nanoparticles into the chlorosomes was unsuccessful, primarily due to low solubility in THF.

Figure 2 shows the results from the self-assembly of PEO-b-PBD to form polymeric chlorosomes, as well as the incorporation of Fe3O4/PEO-b-PBD nanocomposite particles. Figure 2a,b shows linear sucrose density gradient (10−30%) experiments for the various self-assembled PEO-b-PBD architectures, which give a facile means of separation and product selection from nonideal synthesis. Figure 2a shows the results when no Fe3O4/PEO-b-PBD nanocomposites were included in the self-assembly step. Here, we observed the emergence of a strong band at ~25% sucrose, which has previously been attributed to PEO-b-PBD polymeric chlorosomes containing self-aggregated BChl c in the hydrophobic region. Figure 2b shows the results of the sucrose gradient formed after adding 0.225 mg of Fe3O4/PEO-b-PBD nanocomposite in the THF solution prior to self-assembly. We observe a second fraction as a pellet, forming at the lower limit of the sucrose gradient, which indicates the incorporation of much more dense Fe3O4 nanoparticles and the formation of m-PCNs. The respective bands of interest were then measured using UV−vis absorbance spectroscopy (Figure 2c). The m-PCNs also showed an absorbance peak located at 740 nm, characteristic of aggregated Bchl c, indicating incorporation and aggregation of the chromophore similar to native chlorosomes and PCNs. The closely matched absorbance profiles confirm that the optical characteristics of aggregated Bchl c are not affected by the incorporation of Fe3O4. TEM experiments were then performed on both the unloaded and loaded PCNs. Figure 2d shows a TEM image of PCNs collected from the band at 25% sucrose in Figure 2a. The unloaded PCNs range in size from 131 to 359 nm, with aspect ratios measuring between 1.9 and 7.3 (Figure S5). Figure 2e–i show TEM images of m-PCNs collected from the dense pellet in Figure 2b, formed from the incorporation of Fe3O4/PEO-b-PBD nanocomposite particles. The m-PCN shown in Figure 2e possesses seven nanoparticles, segregated toward one end of the structure. This localization may be due to either magnetic effects or gravitational effects arising during the sucrose gradient separation step. Figure 2e–i shows a number of different TEM images of m-PCNs, with nanoparticle loading ranging from 2 to 6. In all m-PCNs, the interparticle spacing has reduced significantly and is consistent with interdigitated oleic acid.

This would indicate that the PEO-b-PBD is being removed from the corona of the Fe3O4/PEO-b-PBD nanocomposite upon self-assembly and that its role is primarily to render the nanoparticles soluble in THF prior to buffer infusion. This is also consistent with the incorporation of hydrophobic cargo into the polymer architecture; i.e., the oleic acid-capped nanoparticles are incorporated alongside Bchl c. The m-PCNs could be easily separated from solution by the application of an external magnetic field. It is important to note that the m-PCNs exhibit spectral and morphological properties of PCNs while still allowing for the incorporation of the Fe3O4 particles, which could easily be imagined to disrupt the long-range order. The morphological flexibility of PEO-b-PBD therefore allows the incorporation of multiple components, and bifunctionality is induced. This result is another indication of the usefulness of amphiphilic block copolymers in generating biosynthetic nanocomposites and indicates the potential of extending design principles to develop new functional, complex materials.

**CONCLUSIONS**

In conclusion, we have utilized the morphological flexibility of the block copolymer PEO-b-PBD to form a magnetically active Fe3O4/PEO-b-PBD nanocomposite. The nanocomposite shows excellent aqueous stability, while maintaining the strong magnetic properties of the magnetite nanoparticles. We then incorporate the nanocomposite into the self-assembly step of higher order polymeric chlorosome architectures. By including magnetic nanoparticles alongside a self-aggregating chromophore (BChl c) in the self-assembly step, we form bifunctional magnetic and optically active Fe3O4/BChl c/PEO-b-PBD polymeric chlorosome nanocomposites (m-PCNs). The polymeric backbone structure is capable of including the large, Fe3O4 nanoparticles, while still resulting in the expected PCN morphology and spectral properties. Introducing a magnetic response to the m-PCNs will allow for easier integration into functional, hierarchical assemblies, as well as ordered films. Furthermore, because the optical profile of the π-stacked BChl c is directional, the application of a magnetic field will allow for control over the absorption characteristics of the chlorosomes and a switching response will be possible.
EXPERIMENTAL SECTION

Materials. PrecisionMRX oleic acid-coated magnetite (Fe₃O₄) nanoparticles were supplied by Imagion Biosystems, Inc (Albuquerque, NM). 4,4-Difluoro-5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene-3-hexadecanoic acid (BODIPY FL C16) was purchased from Invitrogen (#D-3821). PEO-b-PBD (2.5 kDa) was purchased from polymer source (#FP2904-BDEO). BChl c was purified, as described previously. Tris-(hydroxymethyl)aminomethane (Tris) and all organic solvents were purchased from Sigma-Aldrich.

Encapsulation of Fe₃O₄ NPs. Oleic acid-coated Fe₃O₄ NPs (0.5 mg) and 2.5 kDa PEO-b-PBD (8.47 mg) were added to 3 mL of toluene along with 10.3 μL of a 1 mg/mL solution of BODIPY FL C16 in methanol. This was heated to reflux and left to react for 4 h, after which the solution was allowed to cool to room temperature and the toluene and methanol were removed by rotary evaporation. The fluorescent nanoparticles were then washed once with toluene and methanol by centrifuging at 4000 rcf for 10 min. The supernatant was collected and characterized by dynamic light scattering (DLS), then used for further experiments.

Fluorescent Labeling of PEO-b-PBD-Fe₃O₄ NPs. Oleic acid-coated Fe₃O₄ NPs (0.5 mg) were added to 3 mL of toluene along with 10.3 μL of a 1 mg/mL solution of BODIPY FL C16 in methanol. This was heated to reflux and left to react for 4 h, after which the solution was allowed to cool to room temperature and the toluene and methanol were removed by rotary evaporation. The fluorescent nanoparticles were then washed once with toluene and methanol by centrifuging, then dispersed in hexane. PEO-b-PBD encapsulation was then carried out as outlined above.

Formation of Fe₃O₄/BChl c/PEO-b-PBD Polymer−Chlorosome Nanocomposites (m-PCNs). PCNs with encapsulated Fe₃O₄ NPs were prepared by solvent exchange. First, 30 μmol BChl c, 1.5 μmol PEO-b-PBD, and 0.225 mg of Fe₃O₄/PEO-b-PBD nanocomposite particles were dissolved in 50 μL of THF. One milliliter of Tris buffer (pH = 8.0) was infused into the THF mixtures at 2 mL/h, while stirring. The final concentration of THF was approximately 5% of the total sample volume. Samples were purified on continuous sucrose (10%−30%) density gradients containing 20 mM Tris (pH = 8.0) at 250 000g for 15 h and 4 °C. Sucrose density gradients centrifugation is a separation and purification of the overall assembly and thus particles containing and lacking magnetite can be separated and purified.

Characterization. Fluorescence data were acquired on a Photon Technology International (Edison, NJ) fluorometer. Dynamic light scattering (DLS) was measured on a Zetasizer Photon Technology International (Edison, NJ) spectrometer. TEM samples were prepared by drop-casting the hexane dispersion on a carbon-coated copper grid. Images were collected using a Philips Tecnai high-resolution transmission electron microscopy operating at 300 keV. SAXS analysis was performed by injecting concentrated solutions of samples suspended in hexanes into glass capillary tubes with a 1.0 mm diameter (Charles Supper Company, Natick, MA). Samples were analyzed using a Rigaku SmartLab II diffractometer system with the SmartLab Guidance system control software. Data analysis was performed using Rigaku NANO-Solver version 3.5 software, assuming a spherical form factor and Gaussian size distribution. Magnetization measurements were collected using a Quantum Design Versalab Vibrating Sample Magnetometer. Magnetization curves were recorded from −3 to +3 T at 50 K. Zero-field-cooled (ZFC) magnetization curves were obtained by cooling the sample to 50 K with no applied field, then applying a field of 10 Oe and recording the magnetization from 50 to 400 K. With the field still applied, the sample was then cooled from 400 to 50 K to obtain the field-cooled (FC) magnetization. The precise iron mass of each sample was determined destructively by heating the sample in a 600 °C furnace for 1 h to incinerate the organic material and then dissolving the iron-containing residue in hydrochloric acid. A phenanthroline/Fe²⁺ complex was formed in solution and spectrophotometrically quantified.

ASSOCIATED CONTENT

Supporting Information
Additional dynamic light scattering (DLS), fluorescence spectroscopy, and transmission electron microscopy (TEM) data (PDF)

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Notes
The authors declare no competing financial interest.

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