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Aqueous Nanospheres Self-Assembled from Hyperbranched Polymers and Silver Ions: Molecular Inclusion and Photoreduction Characteristics

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ABSTRACT: Hyperbranched polymers with (*N*,*N*-diethylamino)dithiocarbamoyl (DC) units as peripheral groups (HBP-DC) spontaneously form nanospheres in aqueous silver nitrate. Although HBP-DC itself is insoluble in water, coordination of Ag(I) ions to surface DC units imparts cationic charges which make Ag(I)/HBP-DC complexes dispersible in water and drive their self-assembly into nanospheres. These Ag(I)/HBP-DC complexes show binding of hydrophobic guest molecules in the course of self-assembly. When mixtures of tetraphenylporphyrin (TPP) and HBP-DC in THF are added to aqueous silver nitrate, intense fluorescence of TPP was observed. As TPP molecules form nonluminescent aggregates when injected in water, the luminescence observed in aqueous Ag(I)/HBP-DC nanospheres indicates that TPP molecules are confined in the hydrophobic interior of aqueous nanospheres. The surface of Ag(I)/HBP-DC nanospheres, meanwhile, serve as scaffolds to produce silver nanocrystals. The Ag(I)−DC complexes formed on the surface of Ag(I)/HBP-DC nanospheres undergo photoreduction, which give small silver nanocrystals evenly distributed on nanospheres. The size and density of silver nanocrystals are tunable depending on the reaction condition. The coordination-assisted self-assembly of HBPs provides a simple and useful means to develop aqueous nanospheres whose interior and exterior surfaces are readily modifiable. It offers up considerable possibilities for their application as polymer−inorganic integrated vessels.

Introduction

Self-assembly of well-defined organic molecules, metal complexes, and biomolecules has been attracting considerable interest because they display integrated properties not accessible from individual components.[1] The use of macromolecules as building blocks is of particular importance, since they are expected to show functions unique to the ternary structures of components and interfaces formed in between them. In this regard, however, understanding of causal relationships between chemical structure of unit polymers and their assembled structures has been largely limited to amphiphilically modified polymers which possess block, rod−coil, graft, or dendritic structures.[2−4]

Hyperbranched polymers (HBPs) are growing family of nanosized macromolecules that exhibit highly branched architectures whose surface is terminated by varied functional groups.[5−8] They are basically one-pot synthesized in high yields and are highly soluble in organic solvents due to their globular structures which conduce to low solution viscosity. In spite of these excellent properties, studies on HBPs are lagging behind dendrimers because of their polydisperse molecular weight, size, and shape.[9] These drawbacks as a single macromolecule, however, may become irrelevant when HBPs are employed as building blocks for self-assembly.[10] Amphiphilic hyperbranched polymers with core−shell structures have been synthesized, which formed macroscopic tubes,[11] multicompartment micelles,[12] giant vesicles,[13] or nanofibers.[14] However, the synthesis of amphiphilic HBPs inevitably requires multistep reactions, which markedly impairs the favorable advantages of HBPs.

In this study, we present spontaneous formation of aqueous nanospheres from ligand-exhibiting HBPs and metal ions. As HBP, hyperbranched polystyrene terminated with *N*,*N*-diethyldithiocarbamate groups (HBP-DC) was employed.[15] We expected that the dithiocarbamate (DC) groups exhibited on the surface of HBP-DC show affinity to soft metal ions such as Ag(I).[16] Although HBP-DC itself is insoluble in water, coordination of surface DC groups to Ag(I) ions creates cationic charges on the surface. It imparts solubility and amphiphilic structural feature to globular HBP molecules, which guides their self-assembly into nanospheres. These Ag(I)/HBP-DC nanospheres show confinement of hydrophobic guest molecules in their interior and controlled formation of silver nanocrystals. The multiple ability to functionalize aqueous nanospheres renders the ligand-exhibiting HBPs useful components for self-assembly.

Experimental Section

General Methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed by Hitachi S-5000 (acceleration voltage, 25 kV) and JEOL JEM-2010 (acceleration voltage, 120 kV), respectively. For SEM and XPS measurements, Ag(I)/HBP-DC nanospheres were collected on a membrane filter (Isopore, pore size: 0.1 μm, Millipore Co.) by filtration, and the obtained membrane filter was dried in a vacuum. The sample was then sputter-coated with platinum to enable imaging with SEM. For TEM measurement, aqueous dispersion of Ag(I)/HBP-DC nanospheres was placed on carbon-coated copper grid. After 30 s, the excess dispersion was removed by using a filtration paper, and the resultant grid was dried in a vacuum. The sample was measured without staining.

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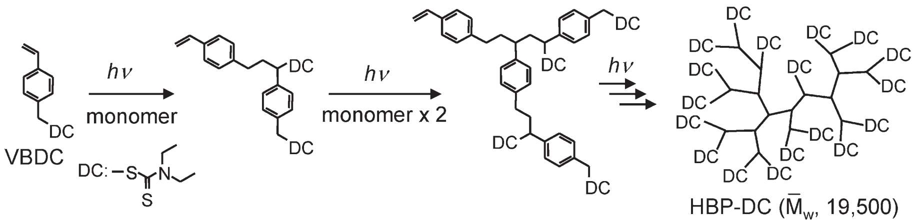
Scheme 1. Synthesis of HBP-DC by Self-Condensing Vinyl Polymerization (SCVP)[6] of VBDC



Dynamic light scattering (DLS) and ζ-potential were measured using the Malvern Zeta sizer Nano-ZS. UV−vis absorption and fluorescence spectra were recorded on a JASCO V-560 and PerkinElmer LS55 spectrophotometer at 25 °C, respectively. Quartz cells with 1 cm or 1 mm path lengths were used. Absolute photoluminescence quantum yields were determined by absolute PL quantum yield measurement system (Hamamatsu Photonics K.K., C9920-02). X-ray photoelectron spectroscopy (XPS) was performed for nanospheres collected on a membrane filter with a ULVAC-PHI ESCA 5800. The photoirradiation of aqueous Ag(I)/HBP-DC nanospheres was performed with an ultrahigh-pressure mercury lamp (Ushio UI-501C) equipped with an all-reflective mirror. The light intensity (310−390 nm) was recorded by using a Custom UVA-365.

Materials. Technical grade solvents were used, unless otherwise indicated. THF was distilled before use. The water used in all experiments was purified with a Direct-Q system (Millipore Co.) and had a resistivity higher than 18.2 MΩ·cm. Tetraphenylporphyrin (TPP) was prepared by the procedure described in the literature.[17] All other chemicals were purchased and used as received.

Synthesis of Hyperbranched Polystyrene Having DC Groups (HBP-DC). 4-Vinylbenzyl *N*,*N*-diethyldithiocarbamate (VBDC) was synthesized as follows. A solution of 4-(chloromethyl)styrene (120 g, 0.78 mol) and sodium *N*,*N*-diethyldithiocarbamate trihydrate (181 g, 0.80 mol) in 1.8 L of acetone was stirred at 40 °C for 1 h. The sodium chloride formed was filtered, and the solvent was removed under reduced pressure. The resulting solid was dissolved in toluene and was washed with water several times. The product was recrystallized from toluene to give colorless powder: yield 206 g (97%). Photopolymerization of VBDC (108 g, 0.41 mol) in 83 mL of toluene was carried out in a sealed glass ampule under photoirradiation with high-pressure mercury lamp (Sen Lights Co., Ltd., HL-100) at 30 °C for 12 h. The reaction mixture was then poured into methanol, and the precipitate formed was dissolved in THF. The hyperbranched polystyrene obtained was purified by repeating a simple precipitation into methanol. A colorless solid obtained was dried in vacuum: yield 48 g. The chemical structure and molecular weight distribution of HBP-DC were determined by ^{1}H NMR and gel permeation chromatography (GPC) using polystyrene standard samples.

Synthesis of Hydrogen-Terminated Hyperbranched Polystyrene (HBP-H). A toluene solution (160 mL) containing HBP-DC (14 g, 53 unit mmol) and tri-*n*-butyltin hydride (28 g, 96 mmol) was deaerated by bubbling nitrogen rigorously. It was then photoilluminated by high-pressure mercury lamp for 15 min at room temperature. After photoillumination, toluene (580 mL) was added to the reaction mixture, and it was poured into excess methanol to give colorless solid. The precipitate was collected on a filter paper by filtration and dried in vacuo: yield 5.3 g. The elimination of DC groups from HBP-DC was confirmed by ^{1}H NMR spectroscopy.

Results and Discussion

Formation of Aqueous Nanospheres from HBP-DC and Ag(I) Ions. HBP-DC was synthesized by photopolymerization of 4-vinylbenzyl *N*,*N*-diethyldithiocarbamate (Scheme 1).[15] The weight-average molecular weight of HBP-DC was determined as 19 500 (polydispersity, 4.0) by gel permeation chromatography (GPC, Supporting Information, Figure S1). The ^{1}H NMR spectrum of HBP-DC shows that the integration ratio of aromatic protons (6.1−7.4 ppm) to *N*-alkyl protons of DC groups (3.7 and 4.0 ppm) to be 1:0.89, indicating that at least 89% of DC groups are retained on HBPs (Supporting Information, Figure S2).

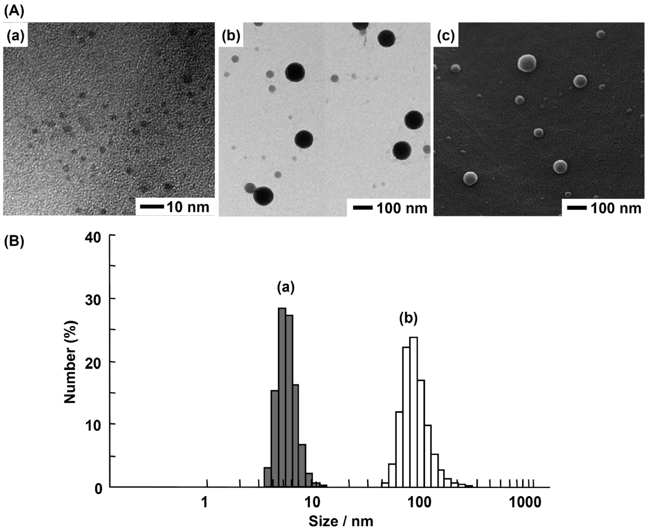


Figure 1. (A) Electron microscopic images of HBP-DC in THF (a, TEM), Ag(I)/HBP-DC nanospheres formed in aqueous silver nitrate (b, TEM; c, SEM). (B) Size distribution histograms obtained by DLS measurement. HBP-DC in THF (a); Ag(I)/HBP-DC nanospheres in aqueous silver nitrate (b). HBP-DC was dissolved in THF at the concentration of 20 mM per DC unit. Aqueous nanospheres of Ag(I)/HBP-DC were prepared by mixing THF solution of HBP-DC and aqueous silver nitrate at equimolecular ligand: Ag(I) ratio; $[\text{HBP-DC}]_{\text{unit}} = [\text{AgNO}_3] = 1$ mM, 1 vol % THF.

HBP-DC is monomerically dissolved in THF, as shown by transmission electron microscopy (TEM) (Figure 1A(a), diameter, ca. 3 nm). The TEM diameter observed is consistent with an average diameter of 5.4 ± 1.2 nm determined by dynamic light scattering (DLS, Figure 1B(a)). Although HBP-DC is not soluble in water, when THF solution of HBP-DC was injected into pure water (stirring rate, 500 rpm), aqueous suspension was transiently obtained ([HBP-DC] = 1 mM per DC unit, THF, 1 vol %). This suspension, however, is not stable, and HBP-DC was gradually separated from water. In contrast, when THF solution of HBP-DC was injected into aqueous silver nitrate (concentration, 1 mM), stable dispersions were obtained. The presence of DC groups is indispensable to obtain such stable dispersions, since hydrogen-terminated hyperbranched polystyrene (HBP-H) showed no solubility in aqueous silver nitrate. These results indicate that DC units on HBP-DC serve as ligands which coordinate to Ag(I) ions. It imparts cationic charges to the formed Ag(I)/HBP-DC complexes, as indicated by a positive ζ-potential (+45 mV) observed for HBP-DC dispersed in aqueous silver nitrate. Coordination of Ag(I) ions to the DC

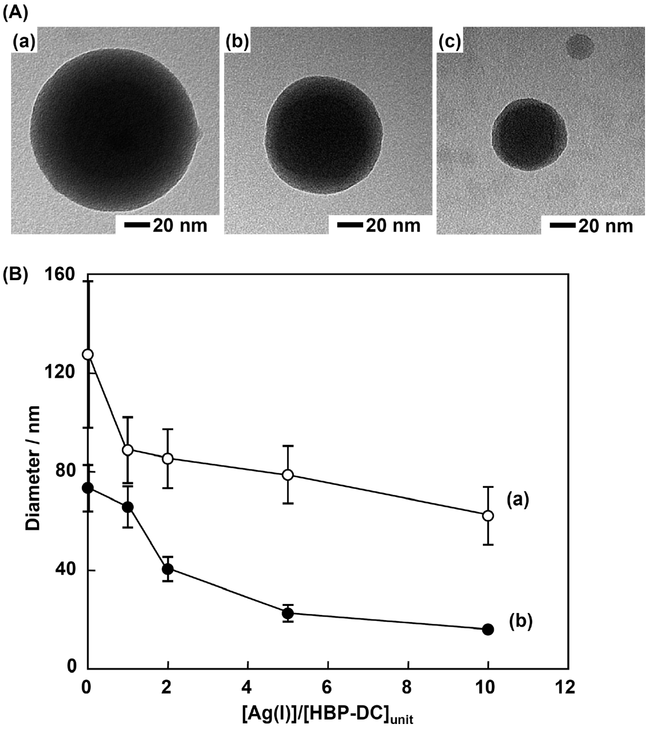


Figure 2. (A) TEM images of Ag(I)/HBP-DC nanospheres prepared at different silver nitrate concentrations. (a) $[AgNO_3]$ = 0 mM, (b) 1 mM, (c) 10 mM. $[HBP\text{-}DC]_{unit}$ = 1 mM. The sample (a) was poststained by aqueous $AgNO_3$ (2 mM). (B) Dependences of particle size on the molar ratio Ag(I)/HBP-DC. (a) $[HBP\text{-}DC]_{unit}$ = 1 mM, (b) $[HBP\text{-}DC]_{unit}$ = 0.2 mM, 1 vol % THF.

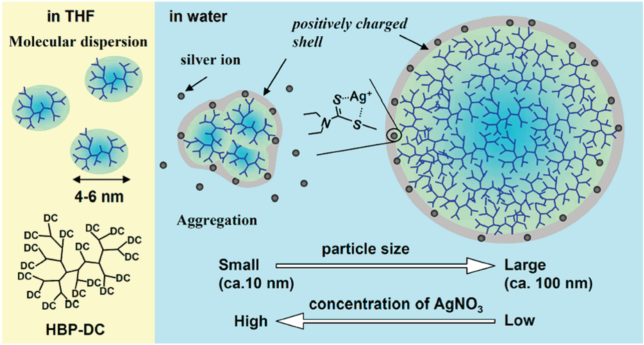


Figure 3. Schematic representation for the spontaneous formation of Ag(I)/HBP-DC nanospheres. The size of Ag(I)/HBP-DC nanospheres is affected both by the concentration of silver nitrate and HBP-DC molecules.

groups was further confirmed by FT-IR spectroscopy. The C=S stretching vibration of HBP-DC was observed at 1486 cm^{-1} (Supporting Information, Figure S3), whereas in Ag(I)/HBP-DC nanospheres the peak shifted to 1488 cm^{-1} with appreciable broadening. All these observations manifest coordination of Ag(I) ions to the surface DC groups.

In TEM and scanning electron microscopy (SEM), nanospheres with diameter of several tens of nanometers were observed (Figures 1A(b,c)). The size of nanospheres are comparable to those determined by DLS (Figure 1B(b), average diameter, 89 ± 27 nm), which is much larger than that observed for a monomeric HBP-DC (DLS-diameter; 5.4 ± 1.2 nm in THF). Apparently, these nanospheres are formed by aggregation of Ag(I)/HBP-DC complexes in water. To determine the elemental composition, X-ray photoelectron spectroscopy (XPS) was conducted for Ag(I)/HBP-DC nanospheres (Supporting Information, Figure S4). XPS spectra showed peaks at 374.5 eV ($Ag(3d_{3/2})$) and 368.4 eV ($Ag(3d_{5/2})$) in addition to the peaks of C 1s, N 1s, and S 2p (Supporting Information, Figure S4). The elemental composition of Ag(I)/HBP-DC nanospheres prepared under the mixing ratio ($[HBP\text{-}DC]_{unit}$ = $[AgNO_3]$ = 1 mM) was determined as N:S:Ag = 1.0:2.0:0.23, which indicates the stoichiometry of DC group:Ag(I) = 4.3:1. It was found that the DC group:Ag(I) ratio in Ag(I)/HBP-DC nanospheres vary depending on the mixing ratio of two components, as described below.

Interestingly, the size of nanospheres is tunable depending on the concentrations of aqueous silver nitrate and HBP-DC (Figure 2, Supporting Information, Figure S5). Figure 2B shows DLS diameter as a function of the mixing molar ratio Ag(I)/HBP-DC. In the absence of silver nitrate, an average DLS-diameter of 128 ± 59 nm was observed with a relatively large size distribution (Figure 2B(a), $[Ag(I)]/[HBP\text{-}DC]_{unit}$ = 0, Supporting Information, Figure S5(g)). As described previously, these HBP-DC nanospheres are unstable without Ag(I) ions, and they gradually precipitate from the suspension. In contrast, stable dispersions were obtained in aqueous silver nitrate. The particle size showed decrease upon increasing the concentration of silver nitrate and gave an average diameter of 62 ± 23 nm at $[Ag(I)]/[HBP\text{-}DC]_{unit}$ = 10 (Figure 2B(a), Figure S5(g→k)). Figure 2A shows TEM images of Ag(I)/HBP-DC nanospheres prepared under varied silver nitrate concentrations. Consistent with the results of DLS measurement (Figure S5), the size of Ag(I)/HBP-DC nanospheres decreased at higher silver nitrate concentrations. Figure 3 schematically shows self-assembly of HBP-DC in aqueous silver nitrate. Coordination of surface DC groups to Ag(I) ions imparts cationic charges on the surface of HBP-DC, which induces their amphiphilic self-assembly via hydrophobic association. It is reasonable to assume that surface fraction of cationic Ag(I) dithiocarbamate complexes increases at higher concentration of silver nitrate. It will promote hydration of Ag(I)/HBP-DC and consequently suppresses their hydrophobic aggregation, resulting in the reduction in nanosphere diameters. This is further supported by the effect of HBP-DC concentration on the particles size. When the concentration of HBP-DC was decreased to 0.2 mM, nanosphere size was reduced to 16 ± 3.5 nm (Figure 2B(b), $[Ag(I)]/[HBP\text{-}DC]_{unit}$ = 10, Figure S5(a→e)). This DLS diameter indicates that the nanospheres consist of only ca. 10 HBP-DC molecules.

Inclusion of Guest Molecules in Ag(I)/HBP-DC Nanospheres. As described in the former section, formation of aqueous nanospheres occurs due to hydrophobic interactions operating between Ag(I)/HBP-DC molecules. As the molecular shape of HBP is not in perfect spherical symmetry, it is natural to assume that hydrophobic patches (domains) exist on the surface of Ag(I)/HBP-DC, depending on the surface fraction of Ag(I)−DC complexes. The presence of such hydrophobic domains reasonably explains their hydrophobic association in water, which would also occur with the other coexisting molecules. To investigate binding of hydrophobic guest molecules in the course of Ag(I)-induced aggregation of HBPs, tetraphenylporphyrin (TPP) was employed. HBP-DC and TPP molecules were mixed in THF at a molar ratio of 10:1, and the mixture was injected into aqueous silver nitrate ($[HBP\text{-}DC]_{unit}$ = 0.2 mM, $[AgNO_3]$ = 0.2 mM, [TPP] = 0.02 mM, THF, 1 vol %). TPP alone is hardly soluble in aqueous silver nitrate and in pure water. Consequently, its fluorescence is nearly nondetectable in these aqueous mixtures (Figure 4B(b), Supporting Information, Figure S6). In contrast, when the mixture of TPP and HBP-DC

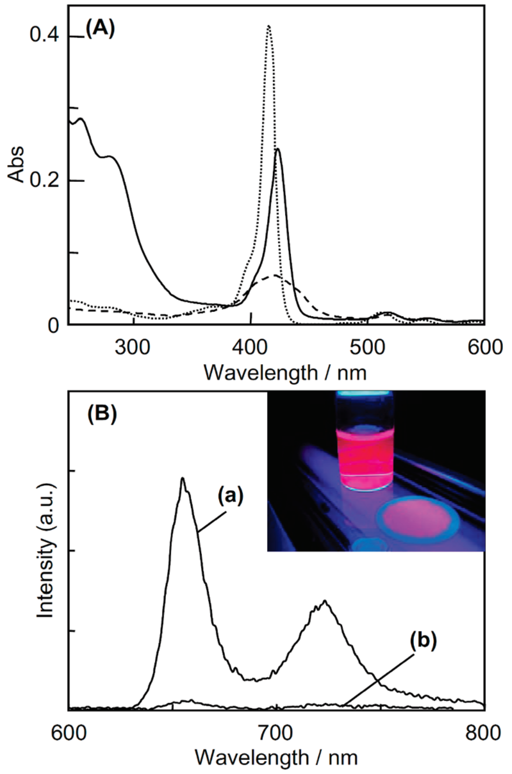


Figure 4. Inclusion of TPP into aqueous Ag(I)/HBP-DC nanospheres. (A) UV−vis absorption spectra of TPP in different media: dotted line, in THF; solid line, in aqueous dispersion of Ag(I)/HBP-DC nanospheres; dashed line, in aqueous $AgNO_3$ solution. (B) Fluorescence emission spectra of TPP excited at 415 nm: (a) in aqueous dispersion of Ag(I)/HBP-DC nanospheres; (b) in aqueous $AgNO_3$ solution. [TPP] = 0.02 mM, $[\text{HBP-DC}]_{\text{unit}}$ = $[AgNO_3]$ = 0.2 mM, 1 vol % THF. The inset in (B) shows a photograph of TPP-doped Ag(I)/HBP-DC nanospheres dispersed in water and in the solid state (collected on a membrane filter).

was injected into aqueous silver nitrate, intense red luminescence was observed (Figure 4B(a), bottom left in Figure S6). It indicates that TPP molecules are effectively introduced into the hydrophobic interior of aqueous Ag(I)/HBP-DC nanospheres and stably dispersed in water.

Figure 4A shows UV−vis absorption spectra of TPP in aqueous Ag(I)/HBP-DC (solid line) and in THF (dotted line). A UV−vis spectrum of TPP injected in aqueous silver nitrate (broken line) is also shown for comparison. In THF, TPP is molecularly dispersed and gives a Soret band at 416 nm and Q-bands at 512, 547, 591, and 648 nm ([TPP] = 0.02 mM, dotted line in Figure 4A). In contrast, TPP in aqueous silver nitrate gave a significantly broadened Soret band at 420 nm with considerably decreased absorption intensity (Figure 4A, broken line). This is consistent with the very low solubility of TPP in aqueous silver nitrate (Figure S6, upper center). On the other hand, TPP in aqueous Ag(I)/HBP-DC gave a red-shifted Soret band at 424 nm, together with Q-band peaks at 518, 551, 591, and 649 nm (Figure 4A, solid line). The absorption bands observed below 300 nm are ascribed to those of DC and polystyrene groups in HBP-DC. It is noticeable that the intensity of Soret band is decreased to ca. 60% of that observed in THF but is much larger than that shown in aqueous silver nitrate (broken line).

The red-shifted Soret band with hypochromism observed in aqueous Ag(I)/HBP-DC nanospheres ([TPP] = 0.02 mM) reflect aggregation of TPP molecules and/or difference in microporality.[18] In Figure 4B, TPP in aqueous Ag(I)/HBP-DC nanospheres showed intense red fluorescence with emission peaks at 655 and 724 nm (a). This is in remarkable contrast to the very weak fluorescence of TPP observed in aqueous silver nitrate (b). In Figure S7a (Supporting Information), UV−vis spectra of aqueous TPP@Ag(I)/HBP-DC nanospheres were measured at varied TPP concentrations. The dependence of Soret band intensity on the concentration of TPP molecules is plotted in Figure S7b. A linear increase is observed up to the TPP concentration of ca. 6 μM; beyond this concentration the slope decreased (Figure S7). The observed change in slope implies that TPP molecules are encapsulated as aggregates in aqueous Ag(I)/HBP-DC at concentrations above the inflection point (6 μM). Consistent with the absorption data, fluorescence intensity of TPP showed linear increase below the TPP concentration of ca. 6 μM; beyond that concentration it turned to decrease (Supporting Information, Figure S8). Interestingly, absolute photoluminescence quantum yield Φ_{PL} determined for aqueous TPP-doped Ag(I)/HBP-DC nanospheres ([TPP] = 5 μM) is comparable to that observed in homogeneous THF solution (Φ_{PL}: TPP in Ag(I)/HBP-DC nanospheres, 6.5%; TPP in THF, 6.6%, Figure S9). These observations confirm that TPP is monomerically confined in Ag(I)/HBP-DC nanospheres at concentrations below 6 μM. It is also to note that the TPP-doped Ag(I)/HBP-DC nanospheres showed intense fluorescence even in the solid state (Figure 4B, inset). This is surprising because fluorescent molecules in the solid state generally do not show luminescence due to overwhelming nonradiative deactivation of excited states which is governed by nonfluorescent aggregates acting as energy traps.[1f]

The ability of Ag(I)/HBP-DC nanospheres to enfold hydrophobic guest molecules in their interior is in contrast to the encapsulation behavior of aqueous coordination networks which uptake water-soluble anionic molecules.[1f] Encapsulation of hydrophobic molecules have been also reported for dendrimers in the aim of their biomedical applications.[19,20] Although fluorescent guest molecules were entrapped in water-soluble poly(propylenimine) or poly(amidoamine) dendrimers, their fluorescence intensity was quenched by these amino groups.[20] In contrast, the interior of Ag(I)/HBP-DC nanospheres consists of polystyrenes which are photochemically uninfluential for guest molecules; thereby, fluorescence properties of encapsulated TPP molecules are well preserved. Thus, Ag(I)/HBP-DC nanospheres not only offer hydrophobic microenvironments in water but also provide innocent matrices to explore the photochemistry of guest molecules.

Synthesis and Immobilization of Silver Nanocrystals on HBP-DC Nanospheres. In the present Ag(I)/HBP-DC nanospheres, Ag(I) ions are accumulated on the surface as *N*,*N*-diethyldithiocarbamate complexes. They provide another opportunity to functionalize nanosphere surfaces. Photoillumination of DC groups in aqueous Ag(I)/HBP-DC nanospheres was tested to investigate their performance to promote reduction of bound Ag(I) ions and to stabilize the derived Ag^0 nanocrystals. Ag^0 nanocrystals are one of the current key nanomaterials due to their performance as active substrates for surface-enhanced Raman scattering (SERS),[21] fluorescence,[22] and catalysis.[23] The size, shape, and aggregation behavior of AgNPs are essential features to direct their optical and electronic properties. Aqueous dispersion of Ag(I)/HBP-DC nanospheres was prepared in 0.2 mM silver nitrate, which showed diameters of ca. 20−70 nm in TEM ($[\text{HBP-DC}]_{\text{unit}}$ = 0.2 mM). This colorless dispersion was photoilluminated vertically with an ultrahigh-pressure mercury lamp for 30 min (light intensity: $I_{310-390}$ = 45 mW/cm^2, temperature at 20 °C). The color of dispersion turned pale yellow with time, and an absorption component emerged

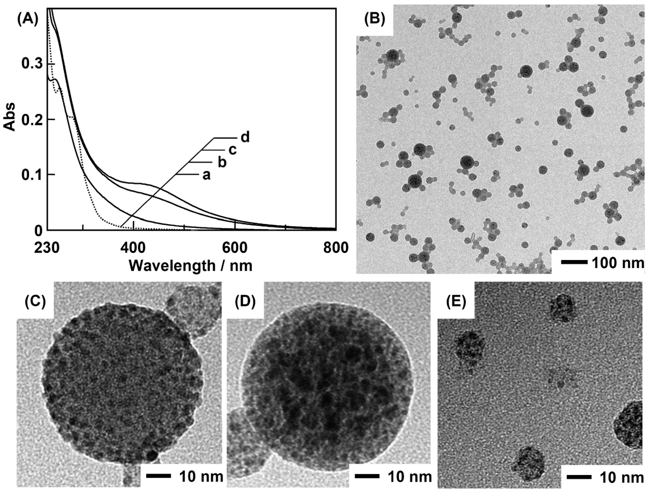


Figure 5. (A) UV−vis absorption spectra of Ag(I)/HBP-DC nanospheres before and after photoirradiation. Ag(I)/HBP-DC nanospheres were prepared as described previously ($[\text{HBP-DC}]_{\text{unit}}$ = $[AgNO_3]$ = 0.2 mM). Subsequently, predetermined quantity of aqueous silver nitrate was added to these dispersions. Total concentration of $AgNO_3$: (a, b) 0.2, (c) 1.2, and (d) 2.2 mM; photoirradiation time: (a) 0, (b) 30, and (c, d) 60 min. (B) A TEM image of Ag(I)/HBP-DC nanospheres after photoirradiation (a higher magnification image is shown in (D)). The experimental conditions to prepare samples (C) and (D) are the same as those shown in part A, curve b, and part A, curve d, respectively. (E) Ag(I)/HBP-DC nanospheres were prepared from an aqueous mixture ($[\text{HBP-DC}]_{\text{unit}}$ = 0.2 mM, $[AgNO_3]$ = 2 mM). Photoirradiation time: 30 min.

around at 350−450 nm (Figure 5A, curve b), which is attributable to the surface plasmon resonance of Ag^0 nanocrystals. TEM image of this photoilluminated dispersion showed the presence of small silver nanocrystals (diameter, ca. 3 nm) homogeneously distributed on HBP-DC nanospheres, giving an undulating surface structure as shown in Figure 5C. On the other hand, prolonged photoillumination of Ag(I)/HBP-DC nanospheres for 60 min in aqueous silver nitrate (0.2 mM) caused precipitation as a consequence of decreased surface charges associated with photoreduction of surface-bound Ag(I) ions.

To enhance surface concentration of Ag(I)/DC complexes on nanospheres, aqueous silver nitrate was sequentially added to the preformed Ag(I)/HBP-DC nanospheres (final Ag(I) concentration: 1.2 and 2.2 mM). Upon photoillumination of these Ag(I)-enriched dispersions, a surface plasmon resonance band of Ag^0 nanocrystals appeared around at 430 nm (Figure 5A, curves c and d; photoirradiation time, 60 min). In the TEM image, Ag^0 nanocrystals with diameter smaller than 10 nm were observed (Figure 5D, $[AgNO_3]$ = 2.2 mM). The size of Ag nanocrystals in Figure 5D is somewhat larger than those obtained by photoilluminating aqueous Ag(I)/HBP-DC under the lower silver nitrate concentration of 0.2 mM (Figure 5C). Apparently, at higher Ag(I) ion concentration in the aqueous phase, photoreduction of Ag(I)/DC complexes gives Ag^0 clusters with increased surface density, and they coalescence into larger Ag^0 nanocrystals. It is however noticeable that the size of Ag^0 nanocrystals observed in Figure 5D is still below 10 nm, and they are well dispersed in nanospheres. It suggests that the surface of Ag^0 nanocrystals is stabilized by HBP-DC molecules in nanospheres, as discussed later. The nanospheres prepared at Ag(I) concentrations of 1.2 and 2.2 mM were stably dispersed in water during the photoillumination period of 60 min but are eventually precipitated after prolonged illumination for 120 min.

Photoreduction of Ag(I) ion was further investigated for smaller HBP-DC nanospheres. Ag(I)/HBP-DC nanospheres with TEM diameter of 10−20 nm were prepared in 2 mM aqueous silver nitrate. After photoillumination for 30 min, Ag^0 nanocrystals with diameters less than 3 nm were observed on HBP-DC nanospheres (Figure 5E).

Importantly, photoreduction of aqueous silver nitrate did not proceed in the absence of HBP-DC under the experimental condition employed. It clearly indicates that photoreduction of Ag(I) ions is promoted by HBP-DC. This is probably attributable to (*N*,*N*-diethylamino)dithiocarbamoyl radicals formed by UV irradiation, which serve as sacrificial reducing agents for Ag(I) ions and converted them to Ag^0 species.[24] Although metal nanoparticles have been also prepared in the presence of HBPs[25] or dendrimers,[26,27] they are single nanoparticles protected by inner[26] or outer[27] surface of the polymers. In contrast, small Ag^0 nanocrystals are stably accumulated in HBP-DC nanospheres with size and density controlled by tuning the reaction conditions. It indicates that DC groups in the Ag^0/HBP-DC nanospheres serve to passivate the surface of Ag^0 nanoclusters and prevent their uncontrolled agglomeration into larger particles (Figure 5C,D).

It is to note that terminal DC groups on HBPs exert multiple functions. First, they serve as specific ligands for Ag(I) ions and the formation of Ag(I)/DC complexes ensures solubility to the resultant Ag(I)/HBP-DC nanospheres in water. Second, they promote photoreduction of Ag(I) ions, which proceeds selectively on Ag(I)/HBP-DC nanospheres. This is a feature not available with chemical reduction techniques, where the reduction of Ag(I) ions present in the bulk aqueous phase also proceeds, resulting in lesser degree of structural control. Third, small Ag^0 clusters produced are stably supported by DC groups which prevent coalescence into large Ag^0 crystals. The multiple performances of aqueous nanosphere formation, encapsulation of functional guest molecules, and formation and stabilization of small Ag^0 nanoclusters render the present metal ion-induced assembly of HBPs a versatile means to develop multifunctional polymer nanomaterials.

Conclusions

Hydrophobic HBP-DC becomes dispersible in water upon complexation with Ag(I) ions, which spontaneously forms nanospheres. TPP molecules were facilely encapsulated in aqueous Ag(I)/HBP-DC nanospheres, demonstrating their adaptive potential to accommodate hydrophobic molecules in water. Although self-assembly of amphiphilically modified hyperbranched polymers have been reported to date,[11−14] to the best of our knowledge, this is the first report for converting hydrophobic HBPs to aqueous nanospheres via a supramolecular approach. The size-regulated Ag^0 nanocrystals densely assembled on HBP-DC nanospheres would find many applications including surface-enhanced Raman scattering (SERS).[21] We envisage that the use of hyperbranched polymers as units of self-assembly would encourage a new trend in polymer and nanomaterials chemistry.

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Supporting Information Available: Additional details for characterization of HBP-DC, aqueous Ag(I)/HBP-DC nanospheres and spectroscopic studies on TPP-doped Ag(I)/HBP-DC nanospheres; Figure S1, GPC profile of HBP-DC; Figure S2, ^1H NMR spectrum of HBP-DC; Figure S3, FTIR spectra of Ag(I)/HBP-DC nanospheres; Figure S4, XPS spectra of Ag(0)/HBP-DC nanospheres, Ag(I)/HBP-DC nanospheres, and HBP-DC;

Figure S5, size distribution histograms of aqueous Ag(I)/HBP-DC nanospheres; Figure S6, photographs of aqueous mixtures of TPP, HBP-DC and $AgNO_3$; Figure S7, UV−vis absorption spectra of aqueous TPP-doped Ag(I)/HBP-DC nanospheres; Figure S8, fluorescence emission spectra of aqueous TPP-doped Ag(I)/HBP-DC nanospheres; Figure S9, absolute photoluminescence quantum yield measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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