Metal nanoclusters, consisting of several to some tens of atoms, typically possess sizes below 2 nm. The spatial confinement of free electrons in metal nanoclusters results in size-dependent discrete energy levels, thus leading to “molecular” properties such as strong fluorescence.[1,2] The extremely small sizes and fluorescence properties have made metal nanoclusters excellent candidates for bioimaging labels.[3] The catalytic activity of metal nanoclusters has also been extensively investigated.[4] Recently, Dickson and co-workers demonstrated that Ag nanoclusters can significantly enhance the Raman scattering of scaffold molecules, which opened new application possibilities for metal nanoclusters.[5] Motivated by their broad application perspectives, research efforts dedicated to metal nanoclusters[5–10] have gone beyond the early focus on gas-phase-based preparation methods and mere characterization.[11,12] Recent advances in the template-based synthesis of metal nanoclusters have led to highly fluorescent, water-soluble metal nanoclusters.[5–8] Using poly(amideamine) (PAMAM) dendrimers and DNA as templates, Dickson and co-workers prepared photostable and water-soluble Ag or Au nanoclusters.[5–7] By taking advantage of the same concept, Kumacheva and co-workers recently reported the successful generation of fluorescent Ag nanoclusters in hydrogel-microspheres through photoreduction.[8] These developments are crucial for both fundamental studies and eventual technical applications of metal nanoclusters in biological environments. However, the demand to further define structure–property relationships and applications in complex environments necessitate new synthetic methods to create such materials.

In this Communication, we present a novel approach towards water-soluble fluorescent Ag nanoclusters that relies on multiarm star polyglycerol-block-poly(acrylic acid) (PG-b-PAA) copolymers as templates. Such unusual macromolecules represent, in fact, the single-macromolecule analogs of nanometer-sized hydrogel particles. The narrowly distributed multiarm star branched PG-b-PAA polymers (polydispersity index (PDI) 1.18–1.30) are synthesized via atom transfer radical polymerization (ATRP) of t-buty1 acrylate (tBA), initiated by functionalized hyperbranched polyglycerol followed by hydrolysis of the t-butyl group using CF<sub>3</sub>COOH as cleaving agent. Detailed synthetic procedures and characterization of the PG-b-PAAAs employed have been reported recently.[13,14] The relevant structural parameters of the PG-b-PAAAs used in this study are summarized in Table 1. It is well-known that charged carboxyl groups exhibit a strong affinity to Ag<sup>+</sup> ions. This concept has been widely used for the immobilization of Ag<sup>+</sup> ions on carboxyl-group-rich materials, to serve as Ag source for further reduction reactions.[8,15,16] For example, Kumacheva and co-workers[8] reported that the uptake of Ag<sup>+</sup> ions by a poly(acrylic acid) (PAA) moiety in microgels is critical for the successful preparation of Ag nanoclusters. On the other hand, the core/shell structure of the PAMAM dendrimers has been suggested to result in a “cage effect”, which provides enhanced stability for metal nanoclusters and prevents continued growth of nanoclusters to larger nanoparticles.[5] The multiarm PG-b-PAA polymers (Scheme 1) exhibit a core/shell structure with dense PAA grafts, and the local density of carboxyl groups may be viewed to gradually decrease from core to shell, which is likely to lead to a cage effect. Based on the analysis above, it is obvious that the structure of PG-b-PAA may be useful as a template for Ag nanocluster synthesis in the way of a “molecular hydrogel”.

To prepare Ag nanoclusters, a freshly prepared aqueous solution of AgNO<sub>3</sub> (0.1 M) was added dropwise to a solution of

Table 1. Structural parameters of star branched PG-b-PAA and linear PAA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; [x10&lt;sup&gt;4&lt;/sup&gt; g mol&lt;sup&gt;–1&lt;/sup&gt;]</th>
<th>Average number of arms</th>
<th>Average length of arms [b]</th>
<th>PDI [a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>6.60</td>
<td>36</td>
<td>35</td>
<td>1.20</td>
</tr>
<tr>
<td>S2</td>
<td>4.61</td>
<td>36</td>
<td>21</td>
<td>1.30</td>
</tr>
<tr>
<td>S3</td>
<td>2.78</td>
<td>6</td>
<td>38</td>
<td>1.18</td>
</tr>
<tr>
<td>L4</td>
<td>0.20</td>
<td>1</td>
<td>28</td>
<td>–</td>
</tr>
</tbody>
</table>

[a] Number-average molecular weight (M<sub>n</sub>) and PDI of PtBA precursors, measured by using gel permeation chromatography (GPC). Detailed GPC conditions can be found elsewhere [14]. [b] Average degree of polymerization (DP<sub>n</sub>) of arms calculated from<sup>1</sup>H NMR. [c] Commercial sample.
polymer S1 (0.1 M) under stirring. The molar ratio of acrylic acid (AA) groups to Ag⁺ ions was 2:1. The system was mixed for half an hour, and then dialyzed against Millipore water to remove traces of free ions. Subsequently, photoreduction was carried out under UV irradiation at \( \lambda = 365 \) nm for various time intervals. During a total irradiation time of 9 h, the color of the solution gradually changed from colorless to light pink (as shown in the inset of Fig. 1a), then to purple, and finally to dark violet. Figure 1a shows absorption spectra of the solution of polymer S1 with Ag⁺ ions after UV irradiation for different periods of time. Before irradiation, the initial S1–Ag⁺ solution showed no absorption in the 300–700 nm range. After 10 min of UV irradiation a peak centered at 500–520 nm appeared, and further irradiation led to an increased intensity of this peak. However, no obvious peak shift was observed for UV irradiation times below 200 min. The absorption peak at 500–520 nm is associated with Ag\(_n\) nanoclusters, with \( n \) from 2 to 8 atoms, and has also been observed in Ag nanoclusters prepared by templating with DNA\(^{[7]}\) and hydrogel microspheres.\(^{[8]}\) After 200 min, the absorption peak shifted to longer wavelength (560–580 nm), which should be a result of the complexation of AA residues with Ag nanoclusters.\(^{[8,15]}\) The increase in absorption intensity and red-shift of the absorption peak confirm the generation of Ag nanoclusters under prolonged illumination.

We noticed that after an irradiation time of 10 min the reaction mixture of the polymer S1 and Ag⁺ ions became photoluminescent (Fig. 1b). Irradiation between 10–200 min led to an emission peak centered at about 590 nm and spanning the wavelength range 450–750 nm. The emission spectra of the Ag nanoclusters formed are similar to those of Ag\(_{2n}\)-Ag\(_{n}\) nanoclusters obtained in hydrogel microspheres,\(^{[8]}\) which agrees...
well with our analysis. All spectra exhibit a shoulder peak at about 690 nm, which indicates the presence of a distribution of Ag nanoclusters with different association numbers. It is worth noting that extending the irradiation time up to 200 min gave rise to a gradual increase of the fluorescence intensity, which is consistent with Figure 1a on the sustaining generation of Ag nanoclusters in that time range. In our study, an irradiation time of 200 min led to the maximum photoluminescence intensity, as shown in Figure 1c; however, additional illumination for 100 min only slightly diminished the emission of the Ag nanoclusters, which suggests excellent photostability. Exhaustive UV irradiation (up to 9 h) did not lead to complete disappearance of the fluorescence of the hybrid system in our experiments. In contrast, the fluorescence of Ag nanoclusters in hydrogel microspheres has been reported to disappear completely after 100 min illumination, which resulted in large Ag nanoparticles (>2 nm) exhibiting a strong plasmon-band adsorption at around 400 nm.[8] The improved photostability of the Ag nanoclusters is tentatively explained by the higher AA-segment density of the multiarm star PG-b-PAA in comparison to the less dense hydrogel networks, which leads to a more pronounced cage effect and thereby provides better protection of the nanoclusters against quenching in solution, but also appears to prevent further growth of nanoclusters by confining the nanoclusters generated in the “cages”. Analysis by transmission electron microscopy (TEM) (Fig. 1d) shows that Ag nanoparticles with a diameter of 2–3 nm are also present in the as-prepared nanocluster solution after 60 min irradiation. However, as addressed above (Figs 1b,c), the fluorescence of the reaction solution keeps increasing in the irradiation time range of 60–200 min, indicating that these larger nanoparticles do not have an obvious quenching effect on the fluorescence of the nanoclusters. This further supports our assumption concerning the stronger cage effect of multiarm star PG-b-PAA templates. It is important to mention that the Ag nanoclusters prepared in our studies remained luminescent after a storage time of three months. The photostability of such nanoclusters is a key issue for their future application as bioimaging labels, especially when long-term tracking becomes necessary.

Figure 2 shows the emission spectra of S1–Ag nanocluster solutions at various excitation wavelengths. For excitation wavelengths between 410 and 510 nm, the maximum emission is observed at an excitation wavelength of 480 nm. An increase of the excitation wavelength gives rise to a red-shift of the emission maximum, which further confirms the presence of a distribution of nanoclusters with different numbers of Ag atoms in the star-branched PG-b-PAA polymer structure. Dickson and co-workers observed the same trends when using DNAs as templates for Ag-nanocluster synthesis.[7]

The initial Ag⁺:AA stoichiometry has a strong influence on the generation rate of Ag nanoclusters. When the stoichiometry was reduced from 1:2 to 1:4, the fluorescence intensity of an Ag nanocluster solution decreased to 50% after the same irradiation times (60 and 90 min), as shown in Figure 3a. However, the emission spectra of the resulting nanoclusters remained unchanged, which suggests that the S1 structure favors Ag nanoclusters with a defined stoichiometry. This is actually strong evidence for the presence of cage structures of a certain size in this template. This point is further confirmed when one uses PAA S2, which possesses an equal number of shorter arms, to produce Ag nanoclusters. Under the same conditions, the shorter-armed PAA S2 template results in nanoclusters with a maximum emission at ca. 500 nm (Fig. 3b), which obviously are of smaller size compared to the nanocluster prepared with the S1 template. Our current efforts are devoted to the elucidation of a correlation between the central structure parameters (e.g., arm number and arm length) of the multiarm star PG-b-PAA and the size and properties of the formed nanoclusters. It is important to mention that preliminary results show that the model star polymers PAA S3 (with 6 arms) and linear PAA L4 do not lead to fluorescent nanoclusters, thus confirming the importance of high AA-segment density for the successful generation of fluorescent Ag nanoclusters.

In conclusion, we have described a facile approach to synthesize robust, highly fluorescent Ag nanoclusters by using star-branched PG-b-PAA as templates, in a manner similar to molecular hydrogels, with dimensions that can conveniently be controlled by the synthetic conditions. The cage effect associated with densely grafted PAA and strong binding of protonated AA groups with Ag⁺ are two essential factors for the formation of such fluorescent nanoclusters. Recent progress in using quantum dots as fluorescent imaging markers has generated enormous impact on the development of bioimaging techniques.[17–19] Stable fluorescent nanoclusters of the kind described here could represent an interesting alternative to quantum dots as a new class of fluorescent labels, considering the extremely small size and biocompatibility of these materials.
Experimental

Multiarm star PG-b-PAA was synthesized as described elsewhere [14]. The obtained star PAAs were neutralized with NaOH (by adjusting the pH to around 8) and dialyzed against deionized water to remove traces of low-molecular-weight impurities.

A typical procedure to prepare the photoluminescent Ag nanoclusters included the following steps: PG-b-PAA-Ag⁺ solutions (2 mL) with different [AA⁺]:[Ag⁺] ratios (2:1, 4:1) were prepared by mixing AgNO₃ (0.1 M) and PG-b-PAA (AA unit 0.1 M) solutions under stirring. The solution was kept for 30 min, and then dialyzed against deionized water for 2 days. The solution was then diluted to 4 mL and transferred into a fluorescence cuvette with a poly(tetrafluoroethylene) lid. Subsequently, the solutions were subjected to UV exposure (Vilber Lourmat, France, Model VL-6.1C, 6 W, average UV intensity 0.5 mW cm⁻²) to produce Ag nanoclusters.

Photoluminescence of the PAA–Ag nanocluster solutions was measured using a Spex Fluorolog 2 1681 spectrometer. UV-vis spectra were obtained with a Perkin–Elmer Lambda 2 UV/Vis Spectrophotometer. A Philips EM-420 transmission electron microscope, operating at an acceleration voltage of 120 kV, was used to analyze the silver nanoparticles obtained. The nanoparticles were deposited from diluted solutions onto copper grids with a carbon support, and studied after drying in air overnight.

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