Blue, green and red emissive silver nanoclusters formed in organic solvents†

Isabel Díez,a, Mykola I. Kanyuk,b Alexander P. Demchenko,b Andreas Waltherad, Hua Jiang,a Olli Ikkalaa and Robin H. A. Rasad

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Strongly luminescent silver nanoclusters with tunable emission are directly synthesized in organic polar and apolar solvents. We show that an amphiphilic polystyrene-block-poly(methacrylic acid) block copolymer can be universally used as their support medium. A remarkable similarity in spectroscopic properties is observed between these clusters and charge-transfer organic dyes.

Few-atom silver nanoclusters are fluorophores with an attractive set of properties including sub-nanometer size, high quantum yield and photostability.1–6 Being of much smaller size than semiconductor quantum dots and exhibiting nontoxicity and lack of blinking1 they are attractive for biosensor applications, biological imaging,7, 8 optoelectronic devices,9, 10 chemical sensing11–13 and optical recording media.14, 15 Since the first report on stable fluorescent silver clusters in solution16 much attention has been paid to optimize and tune their emission properties and stability by varying the type of scaffold and synthesis procedure.17, 18 Silver nanoclusters are usually encapsulated in water-soluble, polar, organic scaffolds that provide multiple binding sites for silver including polymers,17, 21 dendrimers,16, 22 peptides23, 24 and DNA oligonucleotides.1, 3, 25–28 A common feature of silver nanoclusters in organic scaffolds is that their synthesis is carried out in water as solvent. A few reports describe silver nanoclusters dispersed in polar organic solvents such as alcohols, however, these clusters were synthesized first in water, and subsequently transferred to the other solvent, either by mixing the aqueous solution with the organic solvent,29 by precipitation from water followed by redissolution30 or by phase transfer.30, 31 On the other hand, inorganic glasses35 and silver nanoparticles33 have been shown as suitable support for silver nanoclusters in absence of water. This raises the question whether organic scaffolds would allow formation of silver clusters also in non-aqueous solvents.

In this study we present the first recipe to synthesize fluorescent silver nanoclusters directly in polar and apolar organic solvents without the use of water. We show that local environments formed by the polymer in these solvents allow formation of brightly emissive silver clusters of which the fluorescence output is strongly solvent-dependent. The scaffold for the formation of silver clusters is an amphiphilic polystyrene-block-poly(methacrylic acid) block copolymer (PS-b-PMAA) (PS52-PMAA48, Mw=74kDa). The PMAA homopolymer was

![Fig. 1. Photographs and corresponding emission spectra of polymer-supported silver clusters in various solvents: 1,2-dichloroethane (DCE), toluene, tetrahydrofuran (THF) and dimethylformamide (DMF).](image-url)
to activation, the emission intensity increases exponentially with subsequent observation of tendency to saturation.

Fig. 2. (A) Emission (a-e) and excitation (f) spectra of silver clusters formed in DMF with increasing irradiation time: (a) 1, (b) 4, (c) 8, (d) 12 and (e) 16 hours. (B) TEM and (C) spherical aberration corrected HAADF STEM images of the same sample after 8 hours of irradiation time. (D) Higher magnification of a region in image (C).

During photoactivation, the emission intensity increases exponentially with subsequent observation of tendency to saturation. Essentially, the positions of the spectra remain unchanged with irradiation time, indicating that during the photoactivation the number of silver clusters increases without affecting the type of major part of emitters. For instance, in Fig. 2A we show the results of this observation for a sample prepared in DMF.

In studied solvents the polymer molecules combined with silver form micellar structures (Figure S4). Figure 2B shows the bright-field low-resolution TEM image of a single micelle having a PS-core (about 40 nm in diameter), and a PMAA-shell containing clearly observable dots smaller than 2 nm. Spherical aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF STEM) (Fig. 2C) shows comparable features at low magnification. On the other hand, higher magnification allows imaging the arrangement of silver in the micelle shell with resolution approaching atomic scale (Fig. 2D). The dots of about 2 nm visible at low magnification (Fig. 2C, circle) are identifiable at higher magnification as non-crystalline assemblies of silver atoms (Fig. 2D, circle). Although being very close to each other, the silver atoms do not form a crystalline nanoparticle, which demonstrates their effective stabilization by the PMAA chains. Comparable assemblies of silver atoms were as well reported for silver nanoclusters prepared in water with PMAA homopolymer.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{em}}^*$(nm)</th>
<th>$\lambda_{\text{ex}}^*$(nm)</th>
<th>$\Delta\nu$(cm$^{-1}$)</th>
<th>$\Delta\nu_{\text{1/2}}$(cm$^{-1}$)</th>
<th>$\Phi$(%)</th>
</tr>
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<tbody>
<tr>
<td>DCE</td>
<td>365</td>
<td>420</td>
<td>n.d.</td>
<td>n.d.</td>
<td>33</td>
</tr>
<tr>
<td>Toluene</td>
<td>490</td>
<td>574</td>
<td>2990</td>
<td>3120</td>
<td>-</td>
</tr>
<tr>
<td>THF</td>
<td>515</td>
<td>599</td>
<td>2720</td>
<td>3300</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>535</td>
<td>613</td>
<td>2380</td>
<td>2663</td>
<td>-</td>
</tr>
<tr>
<td>DMF</td>
<td>534</td>
<td>626</td>
<td>2750</td>
<td>2470</td>
<td>24</td>
</tr>
</tbody>
</table>

We checked if fluorescence spectra can be excited in the UV region and discovered bands that closely resemble the characteristic high-energy absorption bands of organic dyes. The UV excitation band for silver clusters in DMF is located at 320 nm.
Fig. 3. Fluorescence excitation spectra at fixed emission wavelengths (left) and fluorescence emission spectra at fixed excitation wavelengths (right) for silver clusters formed on block copolymer in (A) DCE, (B) THF, (C) water and (D) DMF.

When excited by UV light the fluorescence bands are located at exactly the same positions as obtained by common excitation in the visible. To the best of our knowledge, this is the first report showing that the Kasha rule (i.e. ultra-rapid relaxation to the lowest excited-state level and the emission only from this level), which is common for organic dyes, is also valid for silver nanoclusters. Several publications on fluorescent silver clusters in water reported on the large shift of emission band position as a function of excitation wavelength and it was explained by structural heterogeneity of formed clusters. Although the cluster size remains unknown we show here that silver clusters with different optical properties can be synthesized without changing the scaffold, just by varying the nature of the solvent. And since we are able to record undistorted excitation spectra for clusters formed in different solvents, this important issue was studied in detail. For the case of DCE we observe the presence of discrete bands both in excitation and emission with clear possibility of their photoselection by variation of excitation wavelength or emission wavelength, indicating the presence of such heterogeneity (Fig. 3A). In all other cases smooth and symmetrical dominant components are observed that are mirror-imaged between excitation and emission bands (Fig. 3, B-D). By gradual variation of emission wavelength there occurs the gradual shift of excitation bands, and vice versa by the gradual variation of excitation wavelength a gradual shift of emission bands is seen. Previously such effects were observed in fluorescence of organic dyes under very specific conditions: the presence of equally strong transition dipole moments in the ground and excited states causing distribution of their interactions with dielectric environment and slow mobility of this environment making this distribution persistent on a time scale of emission. Typical for such heterogeneity causing “inhomogeneous broadening” of spectra are the strong Stokes shifts and solvatochromism that we also observed here. Therefore
the analogy in photophysical behaviour of presently studied clusters and organic dyes can be much stronger than it was previously thought. In view of the presence of electron-rich oxygen atoms in the stabilizing carboxylic acid group, we may suggest the formation of ligand-to-metal charge transfer (LMCT) complexes. Similar idea was already suggested to explain the behaviour of Au nanoclusters.

We believe that the polymer conformation depends on the solvent providing different environments for the cluster formation. Formed in different environments, the clusters might have different structure and exhibit different interaction with the environment. Several discrete maxima in spectra (as in DCE) might be due to variations in composition, whereas in spectra of the same symmetrical shape (as in DMF and water) the molecular environment may influence the energies of electronic transitions causing the spectral shifts or solvatochromism. Meantime we believe that mechanistically the excited states are the same, showing LMCT. This state is strongly dipolar and interacts with surrounding dipoles producing a distribution in energies due to variability of dipole-dipole interactions. This makes the excitation and emission contours symmetric and the excitation-dependent changes of emission spectra as well as the emission-dependent changes of excitation spectra gradual.

In conclusion, we present the first and universal recipe to synthesize highly fluorescent silver clusters directly not only in water, but also in polar and apolar organic solvents, in a very simple way, using photoactivation of a solution of block copolymer and silver salt. The amphiphilic block copolymer plays a very important role being the template for preparing the silver clusters and enabling their stabilization in various organic solvents. The choice of the organic solvent determines the emission wavelength of the clusters, covering a wide region of the spectrum from red via green to blue. The fluorescence is characterized by large, almost solvent-independent Stokes shifts, by spectral inhomogeneous broadening observed in excitation and emission and by a second excitation band in the UV region. This report on the water-free synthesis of strongly fluorescent silver clusters in even apolar solvents is anticipated to open pathways for a variety of novel applications of these attractive fluorophores.

References