

Cite this: *Nanoscale*, 2012, **4**, 4434

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**Blue, green and red emissive silver nanoclusters formed in organic solvents†‡**Isabel Díez,<sup>§\*</sup> Mykola I. Kanyuk,<sup>b</sup> Alexander P. Demchenko,<sup>b</sup> Andreas Walther,<sup>¶\*</sup> Hua Jiang,<sup>a</sup> Olli Ikkala<sup>a</sup> and Robin H. A. Ras<sup>\*a</sup>

Received 16th March 2012, Accepted 28th April 2012

DOI: 10.1039/c2nr30642e

**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.<sup>1–6</sup> Being of much smaller size than semiconductor quantum dots and exhibiting nontoxicity and lack of blinking<sup>1</sup> they are attractive for biosensor applications, biological imaging,<sup>7,8</sup> optoelectronic devices,<sup>9,10</sup> chemical sensing<sup>11–13</sup> and optical recording media.<sup>14,15</sup> Since the first report on stable fluorescent silver clusters in solution<sup>16</sup> much attention has been paid to optimize and tune their emission properties and stability by varying the type of scaffold and synthesis procedure. Silver nanoclusters are usually encapsulated in water-soluble, polar, organic scaffolds that provide multiple binding sites for silver including polymers,<sup>17–21</sup> dendrimers,<sup>16,22</sup> peptides<sup>23,24</sup> and DNA oligonucleotides.<sup>1,3,25–28</sup> A common feature of silver nanoclusters in organic scaffolds is that their synthesis is carried out in water as a 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,<sup>29</sup> by precipitation from water followed by redissolution<sup>19</sup> or by phase transfer.<sup>30,31</sup> On the other hand, inorganic glasses<sup>15,32</sup> and silver nanoparticles<sup>33</sup> have been shown as a suitable support for silver nanoclusters in the 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) (PS<sub>52</sub>-PMAA<sub>48</sub>,  $M_n = 74$  kDa). The PMAA homopolymer was already reported to be an excellent template for silver clusters in aqueous medium.<sup>17,19,31,34</sup> In the current work the PS block was selected to extend the solubility to polar and apolar organic solvents. The silver precursors are organo-soluble silver salts such as AgClO<sub>4</sub> or AgPF<sub>6</sub>. The clusters were synthesized under identical overall concentrations and molar ratios of silver to methacrylic acid segments. After mixing the block copolymer with the silver salt in selected solvents, the mixtures were irradiated with visible light while controlling the appearance of fluorescence. The strong luminescence of the silver nanocluster solutions is shown in Fig. 1, top. Different solvents allow tuning the fluorescence across the visible spectrum (Fig. 1, bottom).

During photoactivation, the emission intensity increases gradually with irradiation time. In the initial steps this change is linear 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 significantly affecting the type 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 (Fig. S4†). Fig. 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 the 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 they are very close to each other, the silver atoms do

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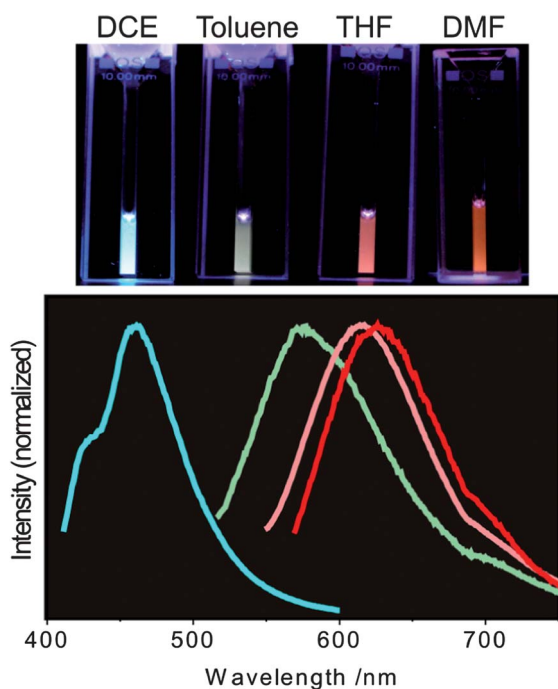
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† We thank Markus Linder, Myhailo Losytskyy and Valentyna Tokar for providing access to the fluorescence spectroscopic instrumentation.

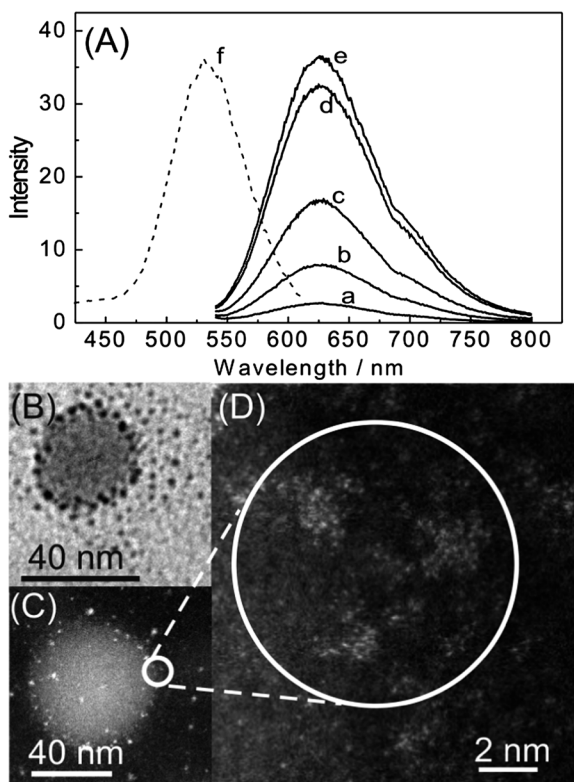
‡ Electronic supplementary information (ESI) available: Materials, synthesis and characterization. See DOI: 10.1039/c2nr30642e

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**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).



**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).

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 a PMAA homopolymer.<sup>31</sup>

Previously we had shown that silver clusters in a PMAA homopolymer dispersed in polar solvents exhibit moderate solvatochromism, *i.e.* solvent-dependent shifts of the spectrum.<sup>19</sup> Solvatochromism was also studied for silver clusters prepared in ssDNA.<sup>29</sup> Here we demonstrate significant larger shifts when the nanoclusters are made in low-polarity solvents (Fig. 1). For instance, in polar solvents such as DMF and THF, red emissive silver clusters are formed, of which the emission spectra are comparable to our previous work on nanoclusters in PMAA homopolymer in water solution.<sup>19</sup> For an apolar solvent such as toluene, the clusters emit in the green region, and in DCE the emission is centred in the blue. The estimated quantum yields in DCE and DMF (Table 1) are remarkably larger, 6-fold, than reported for silver clusters formed in aqueous solutions of the homopolymer (PMAA).<sup>19</sup> Samples in THF and toluene are also highly luminescent but turbidity does not allow determination of their quantum yield.

The use of different solvents leads to significant differences in fluorescence properties of the silver clusters. Short-wavelength excitation/emission maxima at 365/420 nm for DCE contrasts with the longer wavelength positions of these bands at 490/574 nm for toluene and further long-wavelength shifted positions at 515/599 nm, 535/613 nm and 534/626 nm in THF, water and DMF correspondingly (Table 1).

We checked if fluorescence spectra can be excited in the UV region and discovered bands that closely resemble the characteristic high-energy absorption bands typical of organic dyes. The UV excitation band for silver clusters in DMF is located at 320 nm (see ESI†). When excited by UV light the fluorescence bands are located at exactly the same positions as obtained by common excitation in the visible region. 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 the large shift of emission band position as a function of excitation wavelength and it was explained by structural heterogeneity of formed clusters.<sup>17,20,22,27</sup> 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

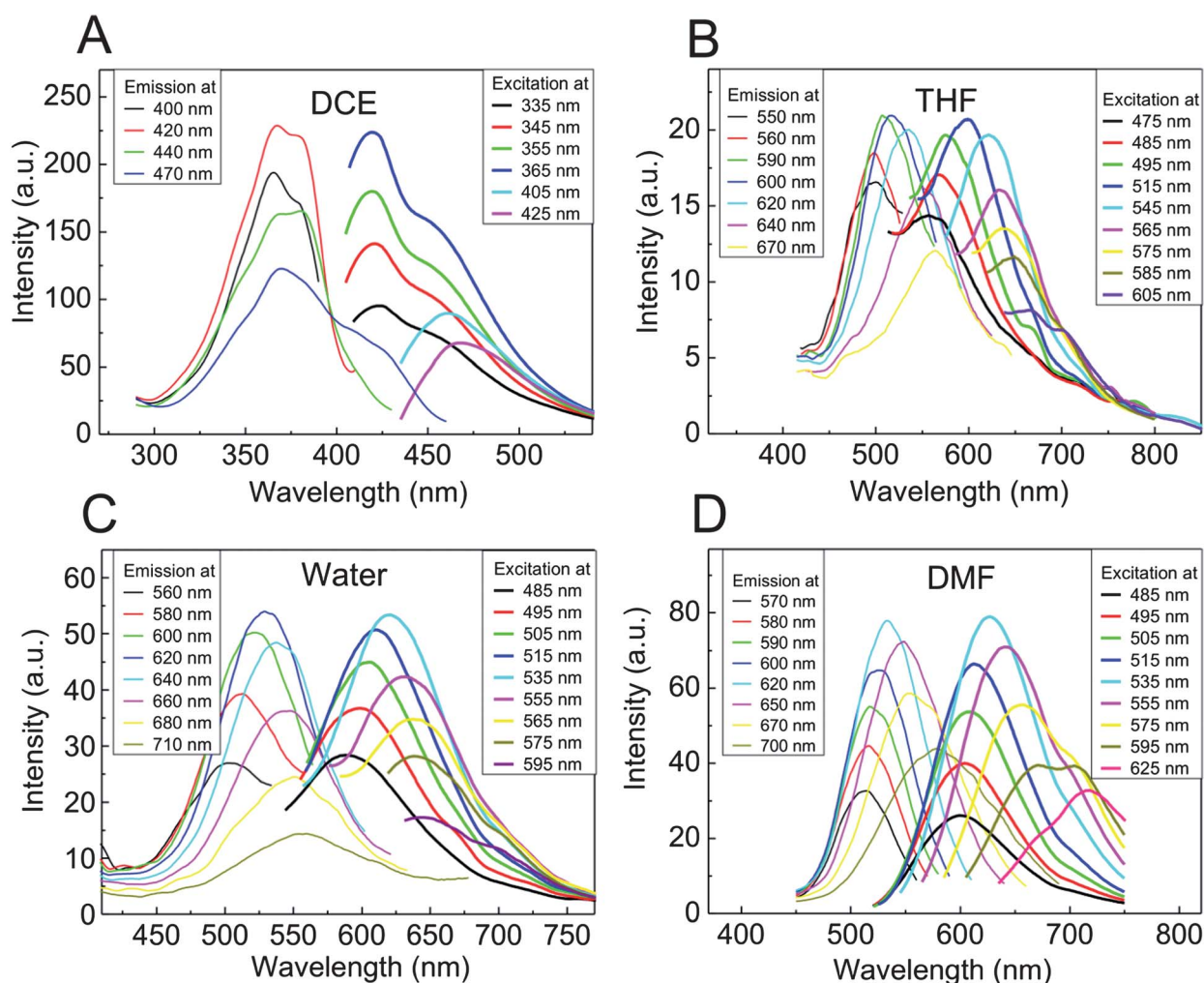
**Table 1** Photoluminescence data of silver clusters. Positions of excitation ( $\lambda_{\max}^{\text{ex}}$ ) and emission ( $\lambda_{\max}^{\text{em}}$ ) maxima, Stokes shifts ( $\Delta\nu$ ), widths of emission bands ( $\Delta\nu_{1/2}$ ) and quantum yields ( $\Phi$ )

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

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. 3B–D). By gradual variation of emission wavelength the gradual shift of excitation bands occurs, and *vice versa* by the gradual variation of excitation wavelength a gradual shift of emission bands is seen. Previously such effects were observed in the 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 the dielectric environment and slow mobility of this environment making this distribution persistent on a time scale of emission.<sup>35</sup> 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. A similar idea was already suggested to explain the

behaviour of Au nanoclusters.<sup>36</sup> We believe that the polymer conformation depends on the solvent providing different environments for the cluster formation. The clusters formed in different environments might have different structures and exhibit different interactions 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 a block copolymer and a silver salt. The amphiphilic block copolymer plays a very important role being



**Fig. 3** Fluorescence excitation spectra at fixed emission wavelengths (left) and fluorescence emission spectra at fixed excitation wavelengths (right) for silver clusters formed on a block copolymer in (A) DCE, (B) THF, (C) water and (D) DMF.

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.

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