SUPPORTING INFORMATION

Materials

Poly(styrene-*b*-methacrylic acid) (PS_{52}-$PMAA_{48}$) (M_n=74 kDa) amphiphilic block copolymer was prepared by living anionic polymerization. Silver salts used as precursors are $AgNO_3$ (Riedel-de Haën, >99.8%), $AgPF_6$ (Aldrich, 99.99%) and $AgClO_4$ (anhydrous, Alpha Aesar). The solvents used are 1,2-dichloroethane (Riedel-de Haën, 99.8%), toluene (Sigma-Aldrich, 99.8%), tetrahydrofuran (Sigma-Aldrich, 99.9%), *N,N*-dimethylformamide (Sigma-Aldrich, 99.8%). All chemicals were used as received. Water was purified by a Milli-Q system (Millipore).

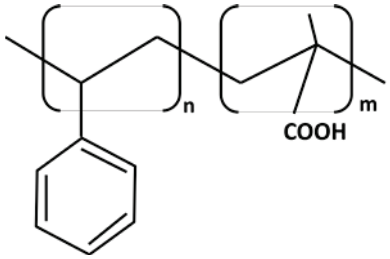

Figure S1. Chemical structure of poly(styrene-*b*-methacrylic acid).

Synthesis

The block copolymer PS_{52}-$PMAA_{48}$ (0.087 mmol in PMAA) was mixed with 6 ml of the desired solvent. Separately, 0.261 mmol of silver salt was dissolved in 3 ml of the same solvent. Different silver salts were used depending on the selected solvent, $AgNO_3$ for water solution, $AgPF_6$ for dichloroethane solution and $AgClO_4$ for all the other solvents.
The mixture was irradiated with a fluorescent lamp (11 W) under magnetic stirring, see spectrum of the lamp below.

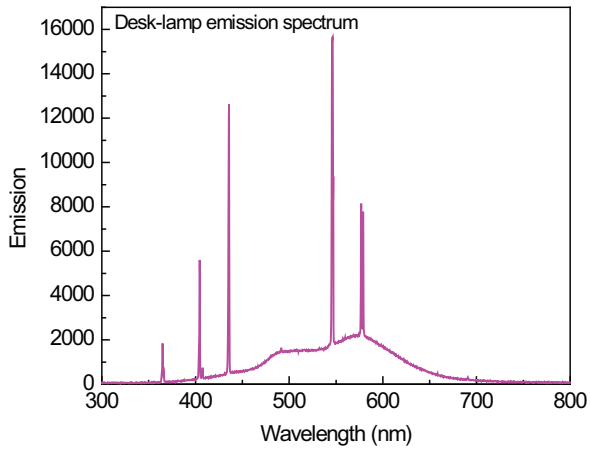

Figure S2. Emission spectrum of the lamp used to irradiate and synthesize the clusters.

Characterization:

Optical absorption spectra of the Ag clusters solutions were obtained using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Fluorescence spectra were obtained with a Varian Cary Eclipse fluorescence spectrometer. All spectra were recorded with quartz cells of 10 mm path length.

Analysis of excitation-emission functions was obtained based on the dependence of excitation spectra on emission wavelength and of emission spectra on excitation wavelength obtained with the intervals of 10 nm on Cary Eclipse spectrofluorimeter at room temperature. Experimental conditions: excitation and emission monochromator slits 5 nm, medium scan speed.

Quantum yield of samples in DMF and dichloroethane were determined using as reference Rhodamine 101 in ethanol and 9,10-Diphenylanthracene in cyclohexane respectively.

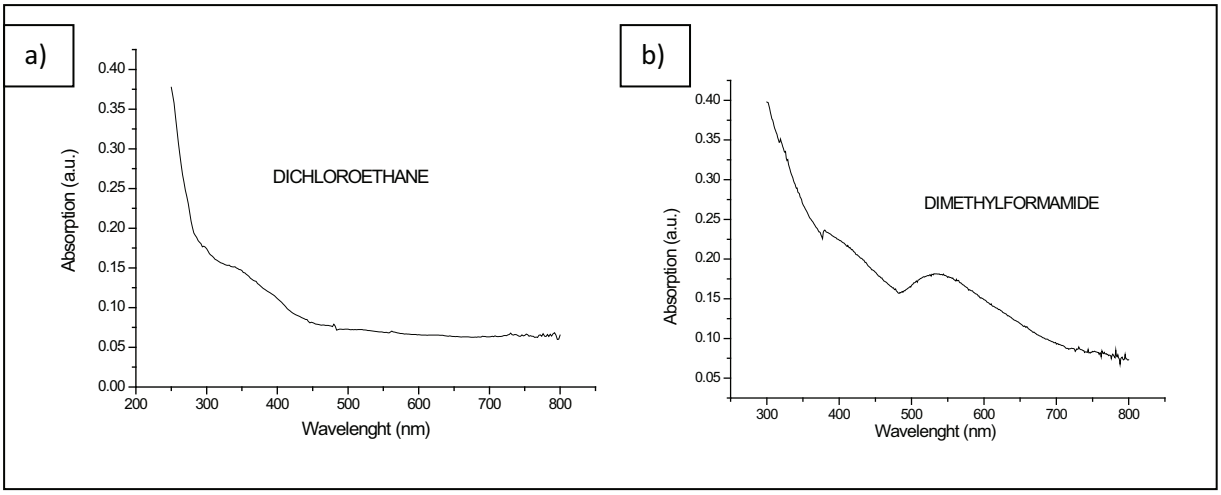

Figure S3. Absorption spectra of clusters prepared in a) dichloromethane and b) dimethylformamide.

Transmission electron microscope (TEM) image was taken on Tecnai 12 Bio Twin TEM operated at 120 kV. A Gatan Ultrascan 1000 and a camera (2048*2048 px) for higher resolution were used for digital recording.

High-resolution scanning transmission electron microscopy (STEM) measurements were carried out with a JEOL 2200FS double aberration corrected FEG TEM/STEM, operated at 200 kV.

For imaging the solutions were dropped onto a TEM grid (Carbon films 400 mesh Au).

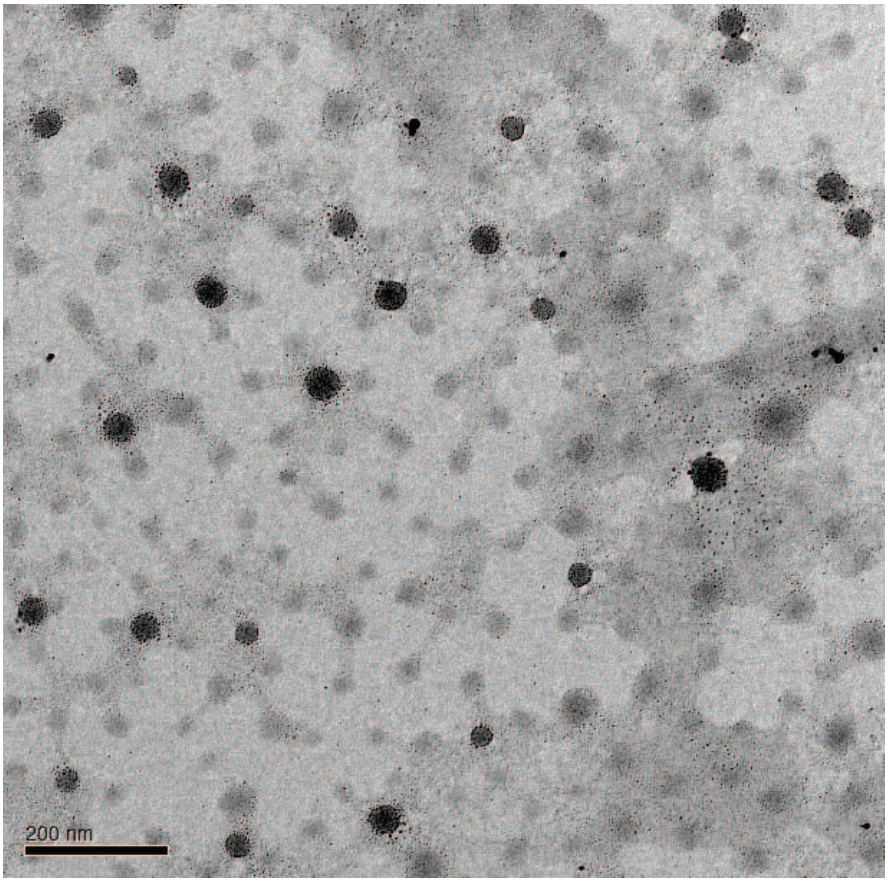

Figure S4. TEM image of silver clusters in DMF. Micelles of the block copolymer surrounded by dots can be recognized. A detailed TEM image is given in the manuscript (Figure 2B-D).

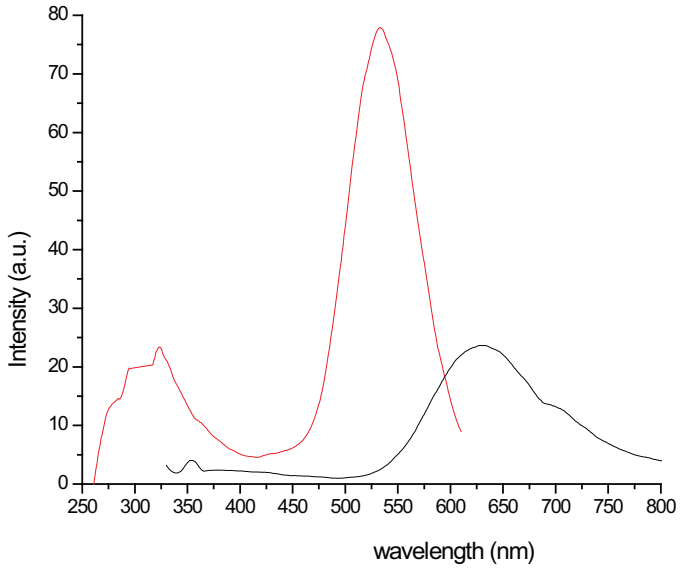

Figure S5. Excitation spectrum (red; emission at 620 nm) and emission spectrum (black; excitation at 320 nm) of a sample prepared in DMF.