

Multiamino polymeric capping of fluorescent silver nanodots as effective protective, amphiphilic and pH/thermo-responsive coating

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Electronic Supplementary Information (ESI)

Materials

For the synthesis of Boc-AEMA, methacryloyl chloride (99%, Aldrich), triethylamine ($\geq 99\%$, Aldrich) and Boc-ethanolamine (98%, Aldrich) were employed as received. The monomer 2-(2-methoxyethoxy) ethyl methacrylate (MEO₂MA, Aldrich 95%) was purified by passing through an alumina column to remove the inhibitor. The photoinitiator, Irgacure®2959 (I-2959) (1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-1-propan-1-one) from CIBA and the silver precursor, silver trifluoroacetate (CF₃COOAg, $\geq 99.9\%$), thiophenol (TPSH, 97%) and cyclohexylamine (CHA, $\geq 99\%$), all from Aldrich, were used as received. Solvents were dried by standard methods or by elution through a Pure Solv Innovative Technology column drying system. Unless otherwise noted, other reagents were commercially available and used without further purification.

Characterization methods

The copolymers and the hybrids obtained have been characterized by different analytical techniques, under the conditions listed below:

Thin Layer Chromatography (TLC) was performed on silica gel precoated aluminium foils, Merck 60F 254, 0.25 mm. Flash column chromatography was carried out on silica gel from Merck, 230-400 mesh. Yields are referred to isolated pure compounds. ¹H-NMR spectra were recorded in INNOVA-400 MHz spectrometer in CDCl₃ at room temperature. Chemical shifts are reported in parts per million (ppm) using the peak of the solvent as internal reference. Molecular weights (Mw) and molecular weight distributions were determined by size-exclusion chromatography (SEC) with a GPC Perkin-Elmer 200 series which mobile phase was dimethylformamide with LiBr (0.1 wt%) at 0.3 mL min⁻¹ and 70 °C with a differential refractometer Waters 410 detector. Poly(methyl methacrylate) (PMMA) standards were used for the calibration. Infrared spectra were obtained using a Spectrum One FTIR spectrometer (Perkin-Elmer) fitted with an ATR accessory under unforced conditions. The samples were placed in direct contact with the diamond crystal without previous preparation. Measurements were collected at 6 cm⁻¹ resolution and four scans per spectrum. Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano Z spectrometer with a 10 mW power HeNe laser at 633 nm. All measurements were performed from dilute solutions of the copolymer or the hybrid material (~ 1 -2 mg mL⁻¹) in toluene and water at different temperatures (from 10 °C to 70 °C) at a scattering angle of 173°. The lower critical solution temperature (LCST) was estimated from the cloud point temperature (T_{cp}) by determining the optical transmittance at 600 nm of the copolymers and hybrids as a function of temperature and pH. The analysis was made using a Cary 3 BIO-Varian UV/Visible spectrophotometer. The temperature was raised from 10 °C to 90 °C at a rate of 1 °C min⁻¹. The cloud point (T_{cp}) was defined as the temperature at the inflection point of the absorbance versus temperature curve. The pH measurements were done with a pH-Meter GLP 21 (Crison). UV/Vis absorption and fluorescence emission spectra were recorded on a Perkin-Elmer Lambda-35 and Perkin-Elmer LS50B spectrophotometer, respectively. The fluorescence quantum yield (QY; excitation at 450 nm) of the dilute toluene solutions of AgNDs were evaluated relative to Fluoresceine in basic water ($\Phi = 0.92$)¹ following standard fluorescence procedure in quartz cuvettes of 1 cm of optical path. Experiments of fluorescence emission as a function of pH and temperature, choosing one temperature below, 4 °C, and one

temperature above, 60 °C, the LCST (48 °C at pH 7), were carried out starting from basic aqueous solutions of at least three hybrid NPs samples and adding aliquots (20–40 mL) of HCl (aqueous, 0.1 M). After addition of each aliquot, samples were left to equilibrate at 4 °C, pH measured before recording their fluorescence emission spectra, and then the samples were equilibrated at 60 °C, pH measured and fluorescence emission spectra recorded. In fact, a variation of the pH with temperature was detected in agreement with Yang et al.² The samples were thermostated using a Huber-polycat cc1 cryostat system or a Julabo-paratherm U5-electronic thermostated bath. Fluorescence signals (excitation at 450 nm) were recorded in the front-face mode when the measures were done at different temperatures. The recorded fluorescence spectra were the average of at least three independent measurements made until reproducible fluorescence intensity was reached. Scanning Transmission electron microscopy (sTEM) images were taken using a FE-SEM HITACHI-SU8000 microscope operating at 100 kV equipped with a charge-coupled device (CCD) camera. Usually, for the preparation of AgNDs samples, 10 mL of a dilute solution of AgNDs (~0.5 mg mL⁻¹) in toluene were left to dry under air at room temperature on a formvar/carbon film supported on a 400 mesh copper grid (Electron Microscopy Sciences). For the preparation of the AgNDs samples for measure thermosensitive properties, 10 µL of a 1 mg mL⁻¹ of aqueous solution of the hybrid AgNDs were left to dry under vacuum at 4 °C or under hot air stream (~60 °C) on a formvar/carbon film supported on a 400 mesh copper grid.

REFERENCES

1. D. Magde, R. Wong and P. G. Seybold, *Photochemistry and Photobiology*, 2002, **75**, 327-334.
2. Y. Yang, A. J. Mijalis, H. Fu, C. Agosto, K. J. Tan, J. D. Batteas and D. E. Bergbreiter, *Journal of the American Chemical Society*, 2012, **134**, 7378-7383.

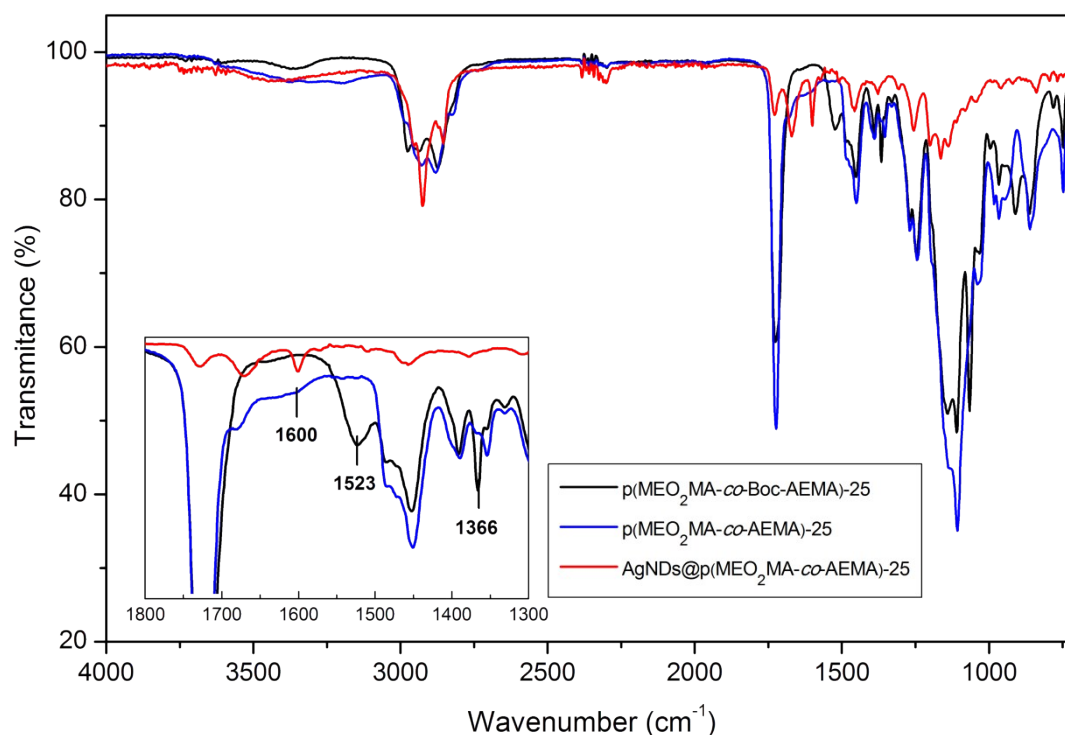


Fig. S1. FTIR-ATR spectra of multiamino deprotected (blue line) and protected (black line) p(MEO₂MA-co-Boc-AEMA)-25 copolymers and AgNDs@p(MEO₂MA-co-AEMA)-25 hybrids (red line).

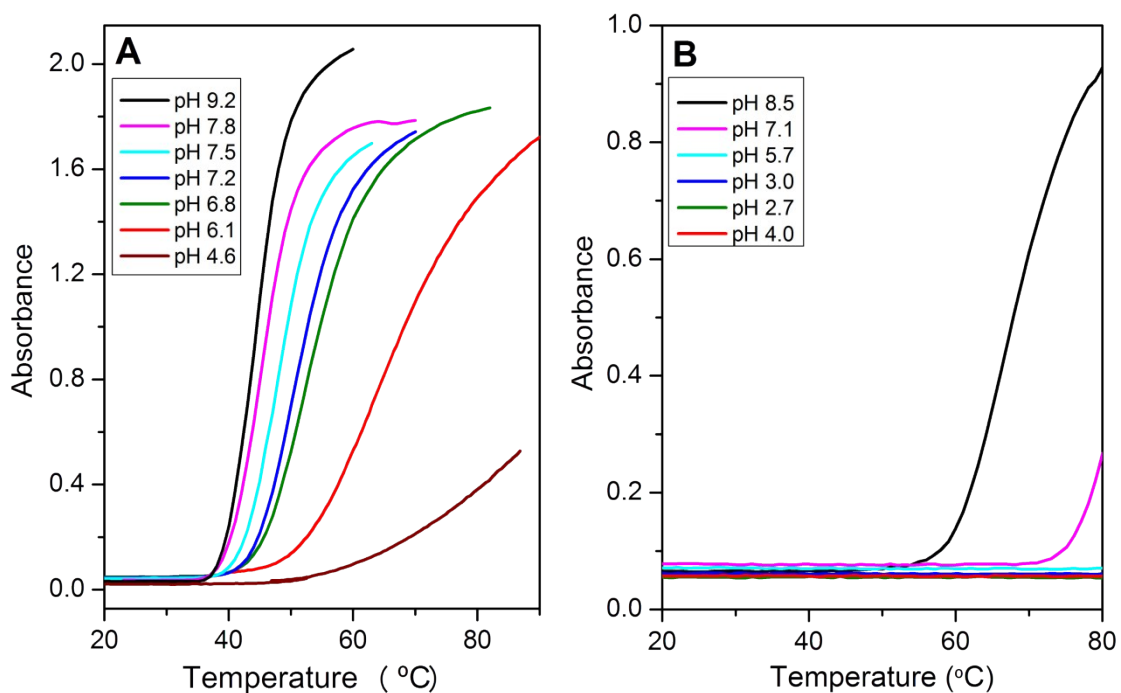


Fig. S2. Absorbance at 600nm *versus* temperature corresponding to aqueous solutions (1 mg mL⁻¹) of (A) p(MEO₂MA-co-Boc-AEMA)-10 and (B) p(MEO₂MA-co-Boc-AEMA)-25 at different pHs.

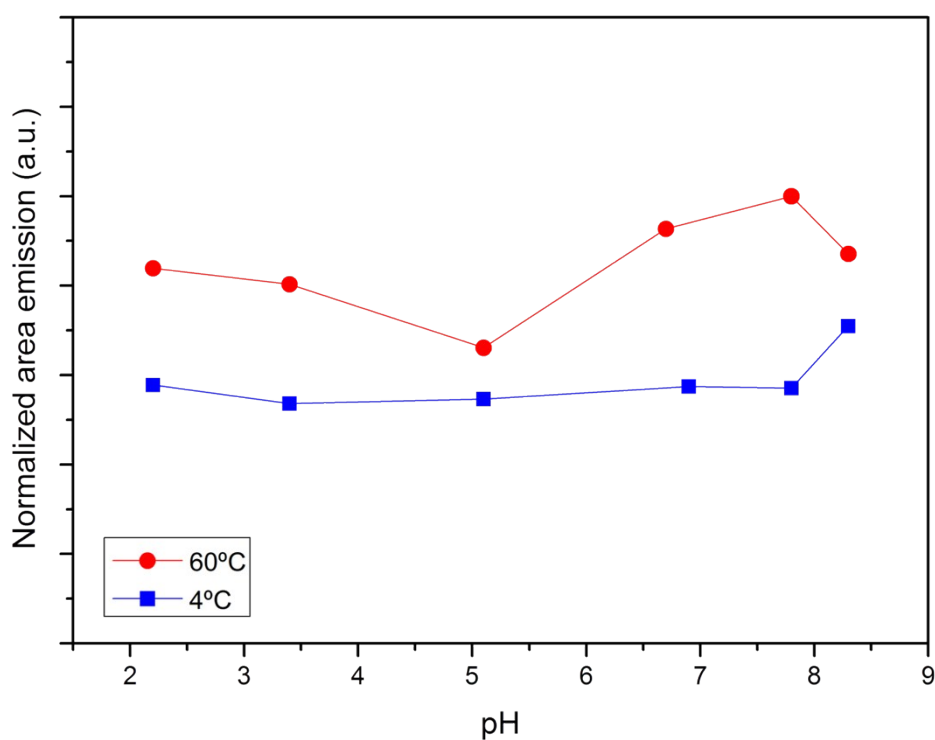


Fig. S3. Fluorescence emission evolution with pH and temperature for hybrids of AgNDs@p(MEO₂MA-co-AEMA)-25. Data recorded in *front-face* mode.