Supporting Information

**Acetyl protected thiol methacrylic polymers as effective ligands to keep Quantum Dots in luminescent standby mode**

Marta Liras*, Isabel Quijada-Garrido, Marta Palacios-Cuesta, Sonia Muñoz-Durieux, Olga García*

Instituto de Ciencia y Tecnología de Polímeros. Consejo Superior de Investigaciones Científicas ICTP-CSIC
Juan de la Cierva, 3. E-28006, Madrid, Spain Phone: +34 91 562 2900Fax: +34 91 564 4853
E mail: martaliras@ictp.csic.es; ogarcia@ictp.csic.es

Materials.................................................................................................................................................. S2
Methods................................................................................................................................................... S2
Figure S1. ................................................................................................................................................. S4
Figure S2.................................................................................................................................................S4
Figure S3.................................................................................................................................................S5
Figure S4.................................................................................................................................................S5
Figure S5.................................................................................................................................................S6
Figure S6.................................................................................................................................................S6
Figure S7.................................................................................................................................................S7
Figure S8.................................................................................................................................................S7
**Materials.** For the synthesis of the AcSEMA monomer, potassium thioacetate (98%, Aldrich), 2-bromo-ethanol (99%, Aldrich) and methacryloyl chloride (99%, Aldrich) were employed as received. For the preparation of the polymers, the monomer methyl methacrylate (MMA, 95%, Aldrich) was washed several times with a sodium hydroxide 10 wt % aqueous solution and pure water, dried over sodium sulfate and distilled to remove the radical inhibitor. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 99%, Aldrich), N,N,N',N″,N‴-Pentamethyldiethylenetriamine (PMDETA, 99% Aldrich), ethyl 2-bromoisobutyrate (EBriB, 99%, Aldrich), CuBr (99.999%, Aldrich), CuCl (99.999%, Aldrich), and the solvent benzonitrile (99.6%, Panreac) were used as received. For the CdSe nanocrystals trioctylphosphine oxide (TOPO, 99%, Aldrich), selenium powder (Aldrich), trioctylphosphine (TOP, 97%, Aldrich), cadmium oxide brown (CdO, 99%, Fluka) and 1-tetradecylphosphonic acid (TDPA, 98%, Alfa Aesar) sodium methoxide (95%, Aldrich) were used as received. Solvents were dried by standard methods or by elution through a Pure Solv Innovative Technology column drying system. Dialysis was carried out using a regenerate cellulose membrane tubing of MWCO 50kDa from RC Spectra/Por®7-Spectrum Labs.

**Methods.** 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. $^1$H and $^{13}$C NMR spectra were registered at room temperature in CDCl$_3$ solution in Varian INOVA-300 and INOVA-400 spectrometers. Chemical shifts are reported in parts per million (ppm) using as internal reference the peak of the solvent. The following abbreviations are used to describe signals: s (singlet), d (doublet), t (triplet), q (quartet), m (complex multiplet). Assignments were based on HSQC and HMBC experiments. $^1$Infrared spectra were obtained using a Spectrum One FTIR spectrometer (Perkin-Elmer) fitted with an attenuated total reflectance (ATR) accessory under unforced conditions. The samples were placed in direct contact with the diamond crystal without previous preparation. Measurements were collected at 8 cm$^{-1}$ resolution and 6 scans per spectrum. UV–Vis absorption and fluorescence spectra were recorded on a Perkin-Elmer LS5OB spectrophotometer, respectively. The fluorescence quantum yield (QY) (excitation at 450 nm) was evaluated relative to that of the reference dye Rhodamine 6G (Rh6G) in ethanol solution ($\Phi = 1.0$). A dilute solution of QDs is prepared in
dichloromethane, such that its absorbance at the excitation wavelength ($\lambda_{\text{exc}}$) would be <0.10, as well as a diluted solution of the reference of comparable absorbance. Then an emission spectrum is recorded using this $\lambda_{\text{exc}}$, and the quantum yield is obtained by where R stands for reference, $\phi$ are the quantum yields, $A_{\text{flu}}$ is the area under the fluorescence peak, $\alpha$ is the fraction of light absorbed, and $\eta$ is the refractive index of the solvents.

$$
\phi_{\text{QD}} = \phi_R \frac{A_{\text{fluQD}} \alpha_R \eta_R^2}{A_{\text{fluR}} \alpha_{\text{QD}} \eta_R^2}
$$

Low resolution mass spectra were registered AutoSpecEQ EI apparatus by electron impact (EI, 70 eV). Differential scanning calorimetry (DSC) analyses were run in a Perkin Elmer DSC6 model in hermetic aluminum pans under nitrogen flow (50 mL min$^{-1}$). Tests were performed with ca. 5 mg samples, heating from 30°C to 190°C at a heating rate of 10°C min$^{-1}$. Thermogravimetry analysis (TGA) was performed on a TA Q500 instrument on 3-5 mg samples on platinum pans under nitrogen, heating from 50°C to 600°C at 10°C min$^{-1}$. Molecular weights ($M_n$) and molecular weight distributions (MWD) were determined by SEC with a GPC Perkin Elmer with tetrahydrofuran (THF) as mobile phase at 1 mL min$^{-1}$ and 70°C (using PMMA standards for the calibration) provided with a Waters 410 Differential Refractometer detector. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 microscopy operating at 200kV equipped with a charged-coupled device (CCD)-camera (Gatan Orius SC1000). One drop of a ~ 3μM solution of modified QDs was evaporated on ultrathin carbon type-A film supported on a 400 mesh copper grid (3 mm in diameter) (from Ted Pella, Inc.). Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano Z spectrometer with a 10 mW HeNe laser at 633 nm. All measurements were performed at a scattering angle of 173°. All the samples are measured immediately after the dialysis and are around 3μM in dichloromethane.
**Figure S1.** $^1$H-NMR spectrum of AcSEMA in CDCl$_3$ 25°C.

**Figure S2.** $^{13}$C-NMR spectra of AcSEMA in CDCl$_3$ 25°C.
Figure S3. UV-vis-spectra for dialyzed dichloromethane solution of CdSe@P(MMA-co-SEMA) 9%, 15 mL taken each 24 h (from a to e curves) and UV-vis-spectrum of the content from the dialysis bag after diluted with 10 mL of dichloromethane (dash line).

Figure S4. $^{13}$C-NMR of multidentate thiolacetylated polymers CdSe@P(MMA-co-AcSEMA) in CDCl$_3$ at 25°C.
**Figure S5.** FTIR-ATR of multidentate thiolacetyl polymers P(MMA-co-AcSEMA).

**Figure S6.** $^1$H-NMR of (a) TOPO and (b) CdSe@PMMA-SH
Figure S7. $^{31}$P-NMR of (a) TOPO, (b) CdSe@P(MMA-AcSEMA) 6% and (c) CdSe@P(MMA-SEMA) 6%.

Figure S8. FTIR-ATR spectra of P(MMA-co-AcSEMA) 9% (black line) and CdSe@P(MMA-co-SEMA) 9% (blue line).