Supporting Information

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

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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 distillated 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 (EBr^{i}B, 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 (Φ_f = 1.0).[2] A dilute solution of QDs is prepared in dichloromethane, such that its absorbance at the excitation wavelength (λ_{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 λ_{exc}, and the quantum yield is obtained by where R stands for reference, ϕ are the quantum yields, A_{fluo} is he area under the fluorescence peak, α is the fraction of light absorbed, and η is the refractive index of the solvents.

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

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^{0}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.

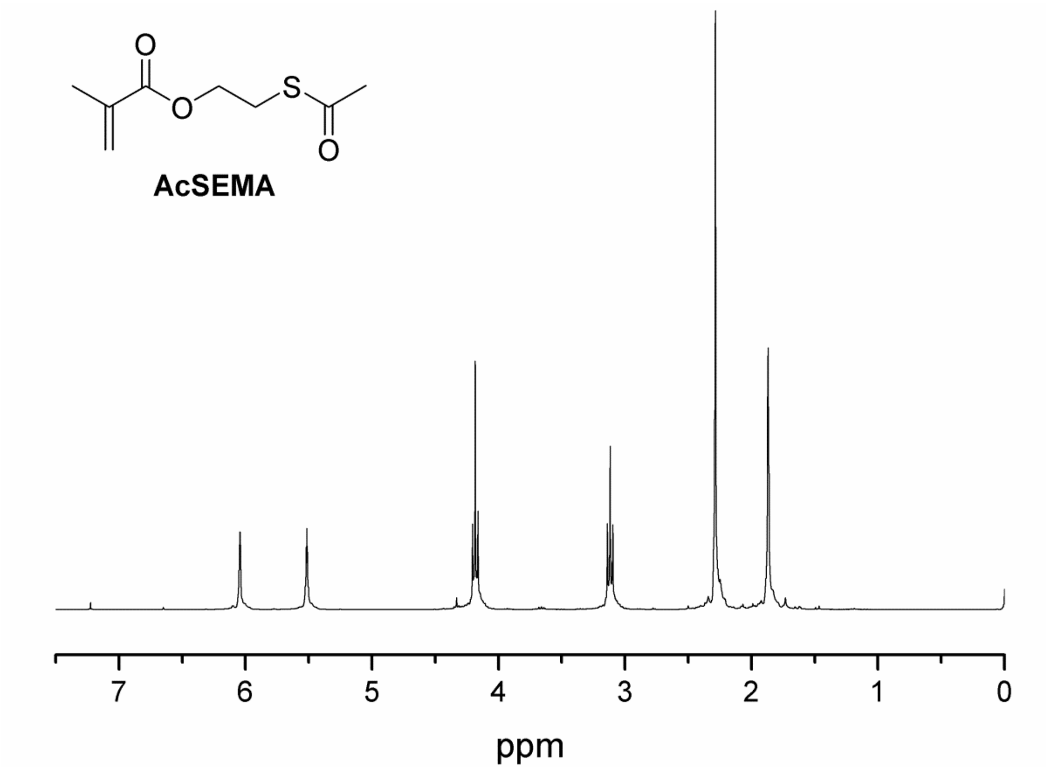

Figure S1. ^{1}H- NMR spectrum of AcSEMA in $CDCl_3$ 25°C.

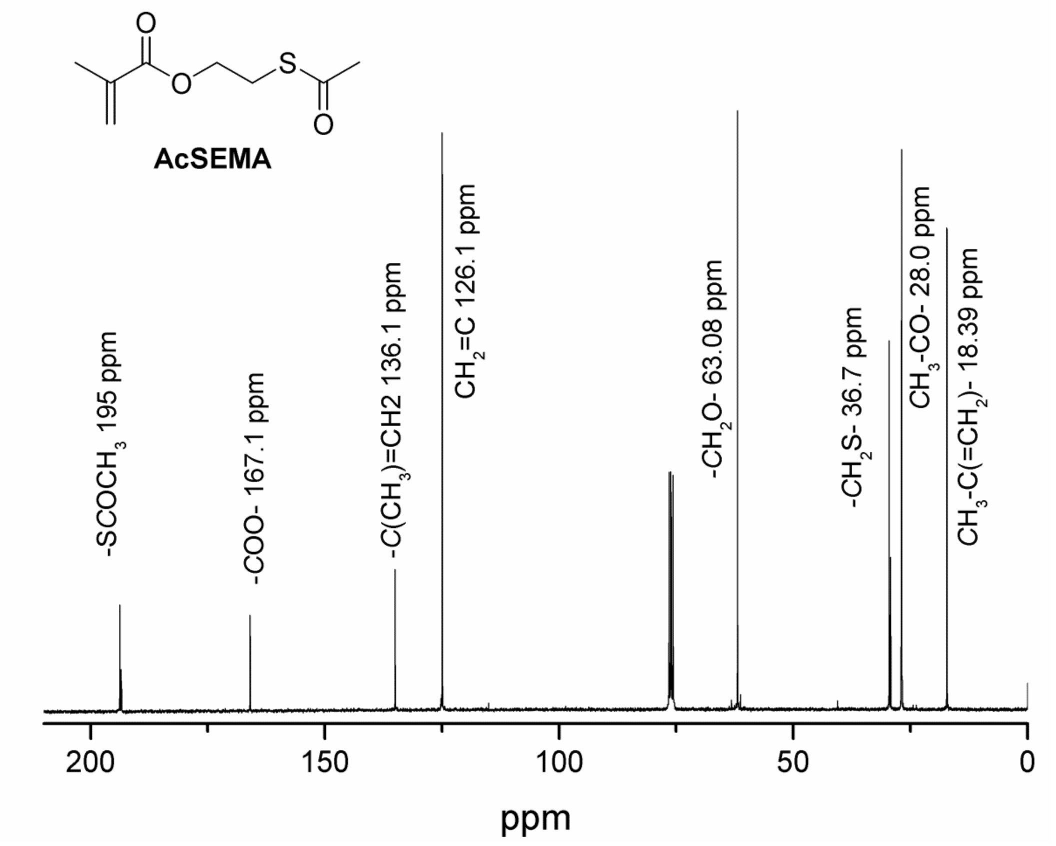

Figure S2. ^{13}C- NMR spectra of AcSEMA in $CDCl_3$ 25°C.

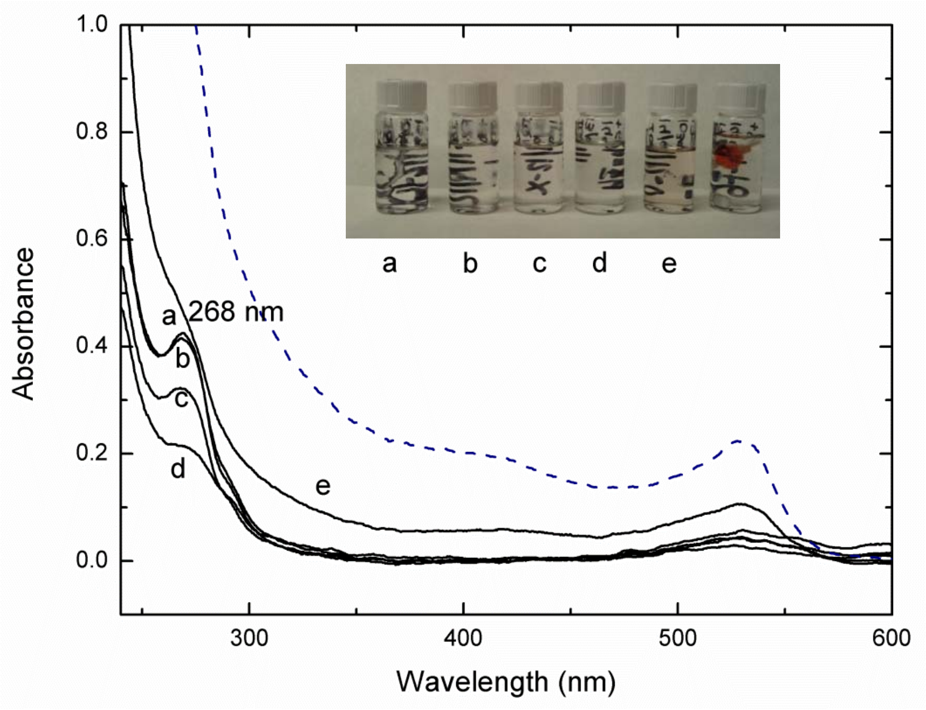

Figure S3. UV-vis-spectra for dialyzed dichloromethane solution of CdSe@P(MMA-co-SEMA) 9%, 15 mL taken each 24 h (from **a** to **e** curves) and UV-vis-spectrum of the content from the dialysis bag after diluted with 10 mL of dichloromethane (dash line).

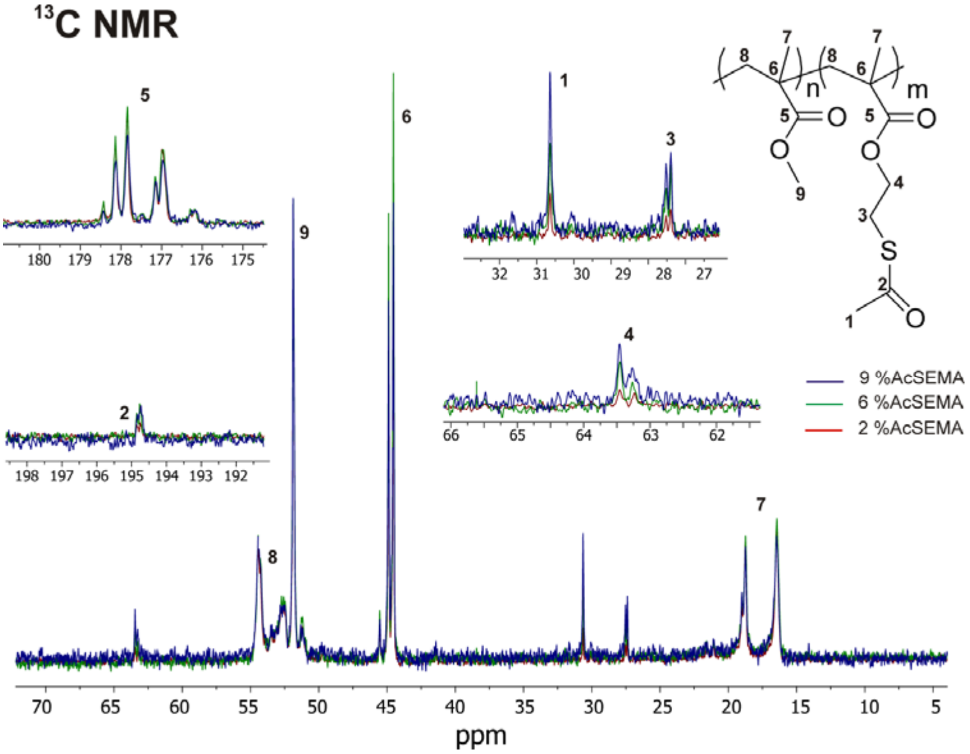

Figure S4. ^{13}C-NMR of multidentate thiolacetylated polymers CdSe@P(MMA-*co*-AcSEMA) in $CDCl_3$ at 25°C.

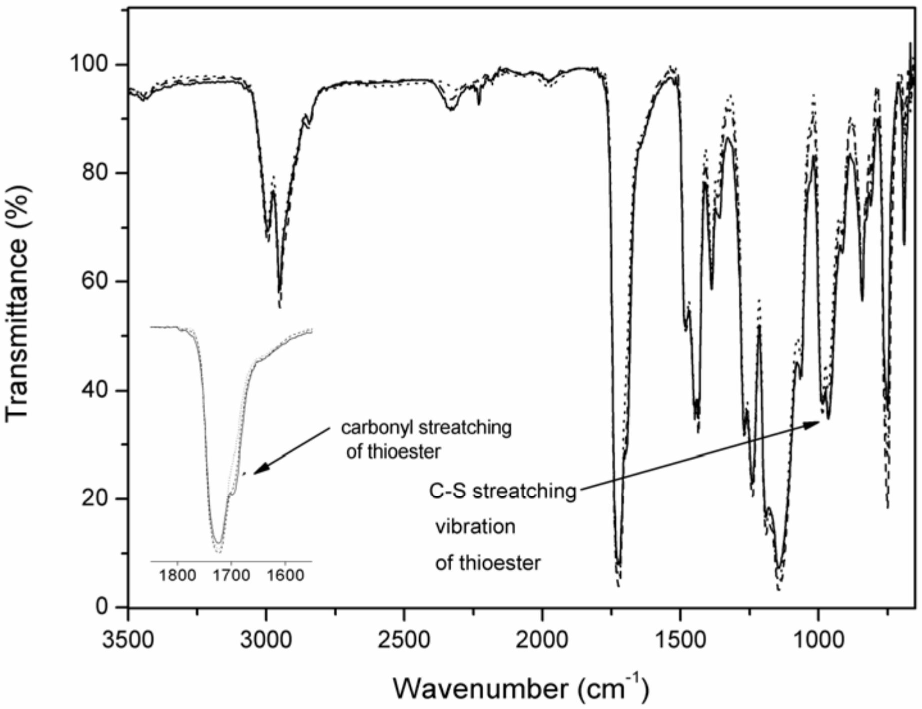

Figure S5. FTIR-ATR of multidentate thiolacetyl polymers P(MMA-co-AcSEMA).

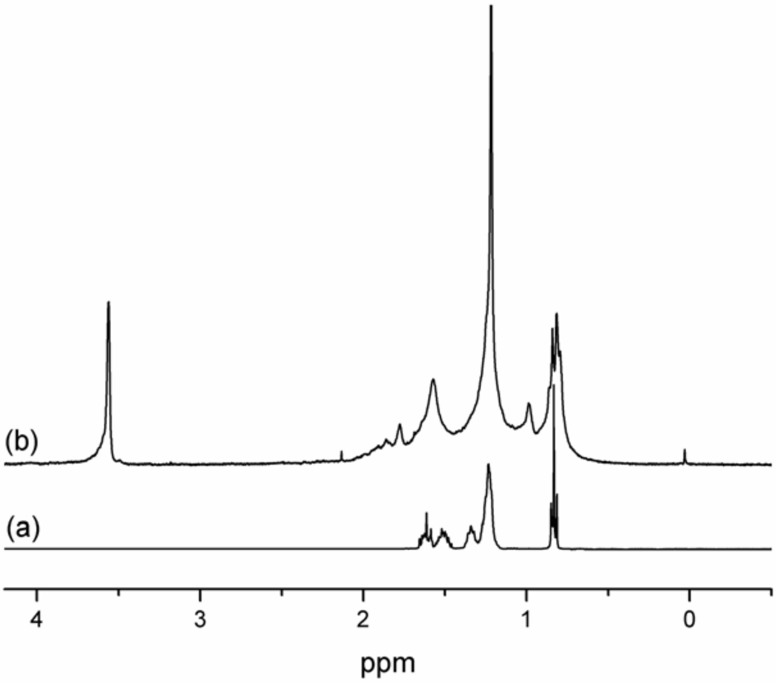

Figure S6. ^{1}H-NMR of (a) TOPO and (b) CdSe@PMMA-SH

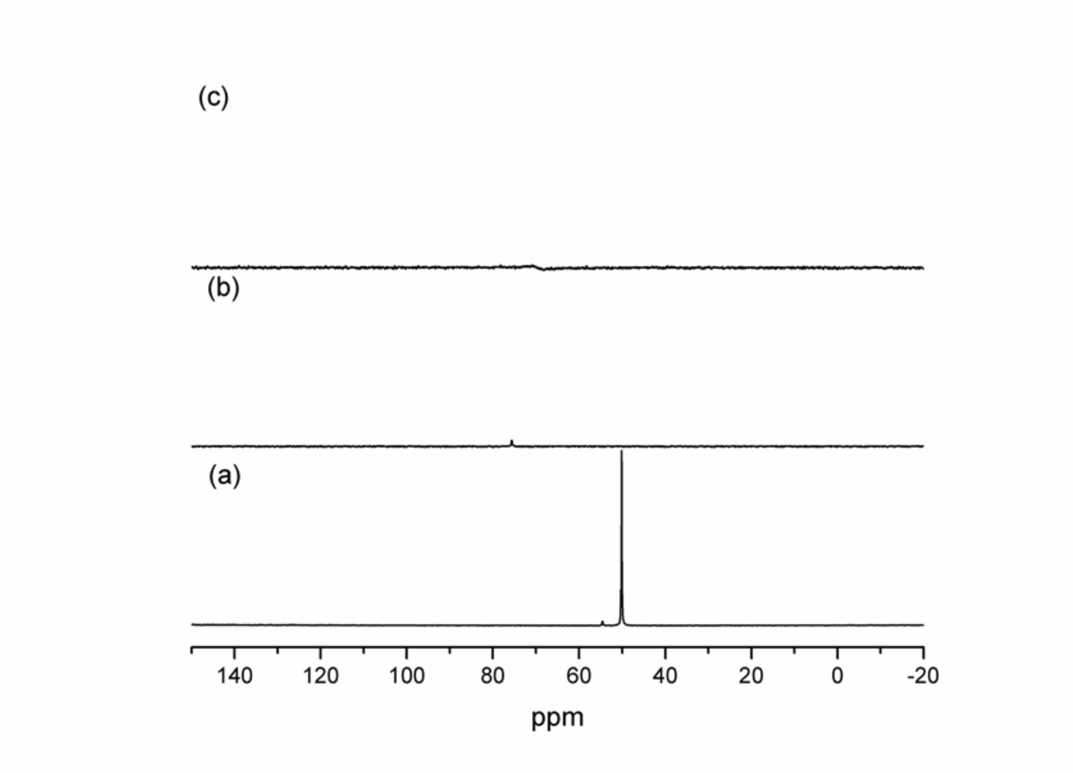

Figure S7. ^{31}P-NMR of (a) TOPO, (b) CdSe@P(MMA-AcSEMA) 6% and (c) CdSe@P(MMA-SEMA) 6%

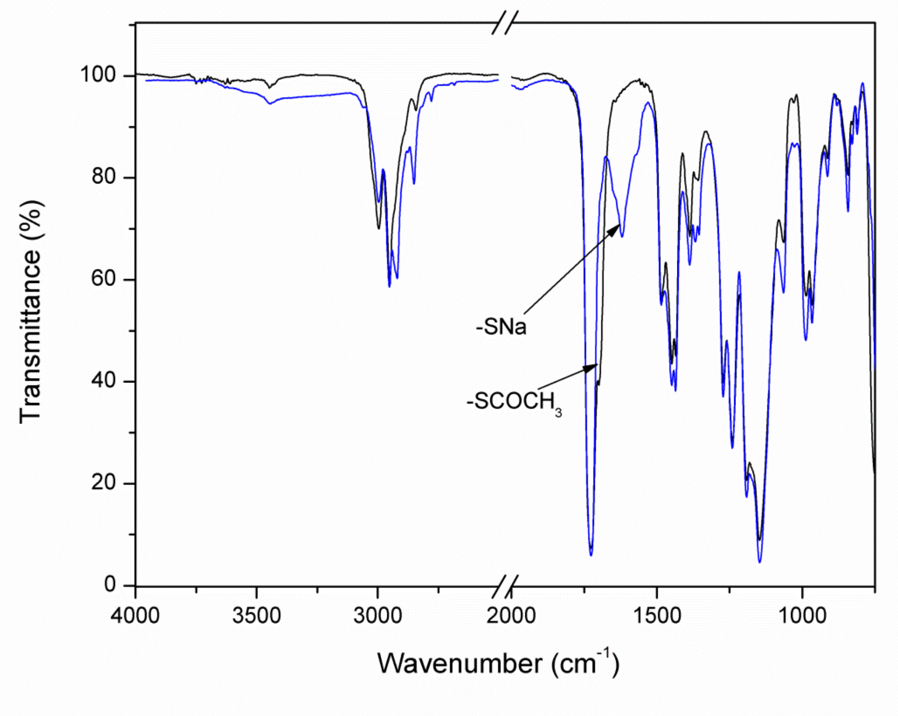

Figure S8. FTIR-ATR spectra of P(MMA-co-AcSEMA) 9% (black line) and CdSe@P(MMA-co-SEMA) 9% (blue line).