Supporting information for:

Photoluminiscence of CdSe/ZnS core-shell quantum dots stabilized in water with a pseudopeptidic gemini surfactant

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General: Reagents and solvents were purchased from commercial suppliers (Adrich, Fluka or Merck) and were used without further purification. A toluene solution of CdSe/ZnS core-shell quantum dots with a maximum emission at 530 nm (QDs) was purchased from Aldrich. The surfactant capping was hexadecylamine.

Electron microscopy: Transmission Electron Microscopy (TEM) was carried out in a in a JEOL 2100 microscope at 120 KV and 62 μA. Solutions were prepared as described below (preparation of water soluble QDs), using the optimal concentration of peptidomimetic compound **1a** (3×10^{-5} M). One drop of the resulting solution was added onto the holey carbon coated 200 mesh TEM copper grid and allowed to dry under air. The TEM micrographs were collected directly without staining.

NMR spectroscopy: The NMR experiments were carried out on a Varian INOVA 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts are reported in ppm using TMS as a reference.

Infrared spectroscopy: FT-IR spectra were acquired in a JASCO 6200 equipment having a MIRacle Single Reflection ATR Diamond / ZnSe accessory. We prepared a 20 mM sample of the corresponding pseudopeptide and we seeded it onto the ATR sample holder. We sequentially collected FT-IR spectra until the complete solvent evaporation. The raw IR data were processed with the JASCO spectral manager software and the deconvolution of the bands was performed with the Origin software, using Gaussian-shaped ideal peaks.

UV-visible spectroscopy. UV-visible absorption measurements were made using a Hewlett-Packard 8453 spectrophotometer. All the samples were measured in aerated conditions otherwise stated.

Steady-state fluorescence spectroscopy. Steady-state fluorescence spectra were recorded in a Spex Fluorog 3-11 equipped with a 450 W xenon lamp. Fluorescence spectra were recorded in the front face mode. All the samples were measured in aerated conditions otherwise stated.

Time-resolved fluorescence spectroscopy. Time-resolved fluorescence measurements were done with the technique of time correlated single photon counting (TCSPC) in an IBH-5000U. Samples were excited with an IBH 372 nm NanoLED with a FWHM of 1.3 ns and a repetition rate of 100 kHz. Data were fitted to the appropriate exponential model after deconvolution of the instrument response function by an iterative deconvolution technique, using the IBH DAS6 fluorescence decay analysis software, where reduced χ^2 and weighted residuals serve as parameters for goodness of fit. As commonly done for other reported QDs, the emission decays of our samples were fitted multiexponentially model using equation 1, where τ_i represents the individual fluorescence lifetime of each ith component and α_i represents its contribution to the total signal. All the samples were measured in aerated conditions otherwise stated.

$$f(t) = \Sigma\alpha_i \, exp(-t/\tau_i) \qquad (1)$$

Preparation of water soluble QDs. A toluene solution of core-shell CdSe/ZnS QDs stabilized with hexadecylamine was prepared by diluting commercial QDs in toluene (6.9×10^{-6} M). Such toluene solution (2 mL) was added to aqueous solutions (10 mL) containing the corresponding concentration of pseudopeptidic compounds **1a-c** (0 to 5×10^{-4} M), pure water or toluene. The toluene in the binary mixtures was allowed to evaporate overnight. A current of nitrogen was bubbled through the aqueous solutions to ensure total evaporation of the solvent. Samples prepared in this way allowed adquisition of the pertinent spectroscopic data.

Quantum Yield Measurements. Fluorescence quantum yields of **1a**-QDs composite in water and QDs in toluene upon excitation at 365 nm is reported relative to quinine sulphate (Φ_f = 0.55 in 0.1 N H_2SO_4). The experiments were done using optically matching solutions and the quantum yield is calculated using equation 2.

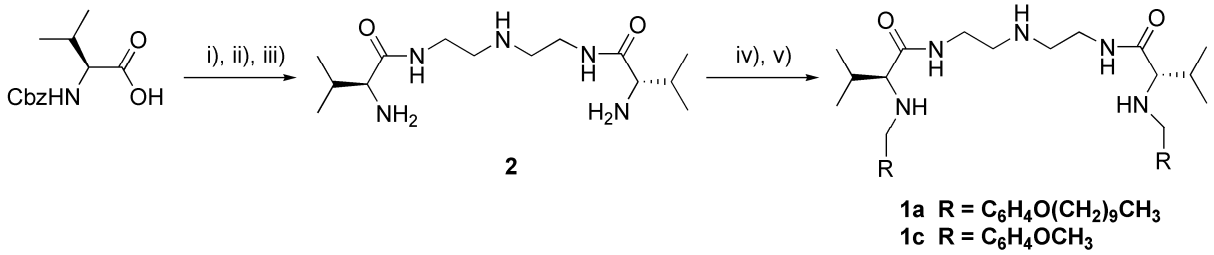
$$\Phi_f = \Phi_r \, (A_r F_s / A_s F_r) \, (\eta_s^2 / \eta_r^2) \qquad (2)$$

where, A_s and A_r are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities and η is the refractive index.

Preparation of samples to investigate the effect of different concentrations of chloride anion. Samples were prepared following the protocol described above for solubilisation of QDs in water. In this case, the toluene solution (2 mL) was added to different aqueous solutions (10 mL) containing peptidomimetic compound **1a** (3×10^{-5} M) and pure water. Different amounts of NaCl were added to the samples to achieve the corresponding final concentration of chloride (0 - 100 mM) in water.

Calculation of the critical micellar concentration (cmc) of peptidomimetic compound 1a. A series of aqueous solutions containing different concentrations of peptidomimetic compound **1a** (10^{-3} M – $10^{-6.3}$ M) were prepared. Each solution (2 mL) was mixed with a saturated pyrene solution (2 mL) and allowed to equilibrate (2 h). Steady state fluorescence spectra were recorded (λ_{exc} = 352 nm) and the ratio of the obtained I_1/I_3 was represented vs the concentration of **1a**.

General procedure for the preparation of 1a and 1c compounds.



Scheme 1. i) *N*-hydroxysuccinimide, DCC, THF; ii) $NH_2(CH_2)_2NH(CH_2)_2NH_2$, DME, room temperature; iii) HBr/AcOH (33 %), NaOH (aq); iv) aldehyde, $CHCl_3$; and v) Py·BH_3 complex, 95%.

Synthesis of 2. The N-hydroxysuccinimide ester of N-Cbz-L-valine (5.069 g, 12.800 mmol) was dissolved in anhydrous DME (150 mL) cooled in an ice bath. N-(2-aminoethyl)ethane-1,2-diamine (680.1 mg, 6.394 mmol, 715.9 µL) dissolved in dry DME (170 mL) was added in several times. The reaction mixture was stirred at room temperature for 24 h. The white solid was filtered off and washed with cold water and cold methanol. Then the solid (3.060 g, 5.371 mmol) was added to HBr/AcOH (33 %) (30 mL) and the mixture was stirred at room temperature until CO_2 evolution ceased. At this point, diethyl ether was added to clear solution, which led to the deposition of a white precipitate. This precipitate was dissolved in distilled water, the resulting solution was extracted with chloroform (30 ml, 3x). Solid NaOH was then added up to a pH value of 12 and the resulting solution was saturated with NaCl and

extracted with chloroform (80 mL, 3x). The organic phase was dried over $MgSO_4$ and evaporated under vacuum to obtain a white solid. Yield (924 mg, 57%); mp 58-61 ºC; $[\alpha]_D^{25}$ = -45.9 (c = 0.01, $CHCl_3$); IR (ATR) 3275, 3099, 2960, 2872, 1644, 1632, 1559 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.81 (d, 6H, J = 6.8 Hz), 0.95 (d, 6H, J = 6.9 Hz), 1.78 (s, 5H), 2.20 (qd, 2H, J = 6.8, 11.1 Hz), 2.75 (t, 4H, J = 5.8 Hz), 3.18 (d, 2H, J = 3.8 Hz), 3.33 (dd, 4H, J = 5.6, 11.3 Hz), 7.52 (s, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 16.3, 19.6, 31.0, 38.7, 48.6, 60.4, 174.8; ESI-MS m/z = 302.3 $(M + H^+)$; Anal. Calcd. for $C_{14}H_{31}N_5O_2$: C, 55.78; H, 10.37; N, 23.23. Found: C, 56.03; H, 10.49; N, 23.53.

General procedure for the reductive amination reaction. Synthesis of 1a. Peptidomimetic bis(amidoamine) **2** (298.4 mg, 0.990 mmol) was dissolved in 10 mL of $CHCl_3$ and the solution was placed inside a flask under nitrogen atmosphere. 4-Decyloxybenzaldehyde (563.7 µL, 519.5 mg, 1.980 mmol) was dissolved in 5 mL of $CHCl_3$, this solution was added over the solution of **2** and then, 5 mL of $CHCl_3$ were added until a final volume of 20 mL (0.05 M final concentration each). The mixture was stirred overnight, then a large excess of Py·BH_3 complex, 95% (1052.7 µL, 968.5 mg, 9.900 mmol) was carefully added at 35 ºC, and the mixture was allowed to react for 24 h before being hydrolyzed (conc. HCl, to acidity) and evaporated to dryness. The residue obtained was dissolved in water, basified with 1N NaOH, and extracted with $CHCl_3$. The combined organic layers were dried ($MgSO_4$) and evaporated in vacuum. The product was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent, increasing slowly the polarity with MeOH and several drops of aqueous ammonia. Yield (472 mg, 60%); mp 79-81 ºC; $[\alpha]_D^{25}$ = -32.4 (c = 0.01, $CHCl_3$); IR (ATR) 3314, 2955, 2920, 2869, 2851, 1640, 1622, 1613, 1546, 1510 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.88 (m, 12H), 0.93 (d, 6H, J = 6.9 Hz), 1.32 (m, 24 H), 1.44 (m, 4H), 1.76 (m, 4H), 2.07 (dtd, 2H, J = 4.8, 6.9, 13.8 Hz), 2.79 (t, 4H, J = 6.0 Hz), 2.94 (d, 2H, J = 4.6 Hz), 3.38 (dd, 4H, J = 5.9, 11.9 Hz), 3.55 (d, 2H, J = 12.9 Hz), 3.68 (d, 2H, J = 12.9 Hz), 3.93 (t, 4H, J = 6.6 Hz), 6.85 (d, 4H, J = 8.6 Hz), 7.19 (d, 4H, J = 8.6 Hz), 7.51 (t, 2H, J = 5.6 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.1, 17.7, 19.6, 22.6, 26.0, 29.3, 29.3, 29.4, 29.5, 29.5, 31.3, 31.9, 38.7, 48.9, 52.8, 67.8, 68.0, 114.5, 129.3, 131.6, 158.4, 174.0; HRMS $(ESI\text{-}TOF)^+$ calc for $C_{48}H_{83}N_5O_4$ $(M + H)^+$: 794.6523; found 794.6532; Anal. Calcd. for $C_{48}H_{83}N_5O_4$: C, 72.59; H, 10.53; N, 8.82. Found: C, 72.45; H, 10.65; N, 8.94.

Synthesis of 1b. Compound **1b** was prepared and characterized as described previously (ref. Rubio, J.; Alfonso, I.; Bru, M.; Burguete, M. I.; Luis, S. V., *Tetrahedron Lett.* **2010,** 51, (45), 5861-5867).

Synthesis of 1c. This compound was obtained as described above starting from the Peptidomimetic bis(amidoamine) **2** and 4-methoxybenzaldehyde. Yield 71%; mp 58-65 ºC; $[\alpha]_D^{25}$ = -29.21 (c = 0.01, $CHCl_3$); IR (ATR) 3313, 2953, 2829, 1626, 1550, 1511, 1460 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (d, 6H, J = 6.9 Hz), 0.91 (d, 6H, J = 7.0 Hz), 2.03 (m, 2H), 2.08 (s, 3H), 2.76 (t, 4H, J = 6.0 Hz), 2.91 (d, 2H, J = 4.7 Hz), 3.35 (dd, 4H, J = 5.9, 11.9 Hz), 3.54 (d, 2H, J = 12.9 Hz), 3.66 (d, 2H, J = 12.9 Hz), 3.75 (s, 6H), 6.82 (d, 4H, J = 8.6 Hz), 7.18 (d, 4H, J = 8.6 Hz), 7.52 (t, 2H, J = 5.6 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 17.9, 19.6, 31.3, 38.5, 48.8, 52.6, 55.2, 67.8, 113.9, 129.3, 131.8, 158.8, 174.1; HRMS $(ESI\text{-}TOF)^+$ calc for $C_{30}H_{47}N_5O_4$ $(M + H)^+$: 542.3702; found 542.3704; Anal. Calcd. for $C_{30}H_{47}N_5O_4$: C, 66.51; H, 8.74; N, 12.93. Found: C, 66.88; H, 8.82; N, 12.60.

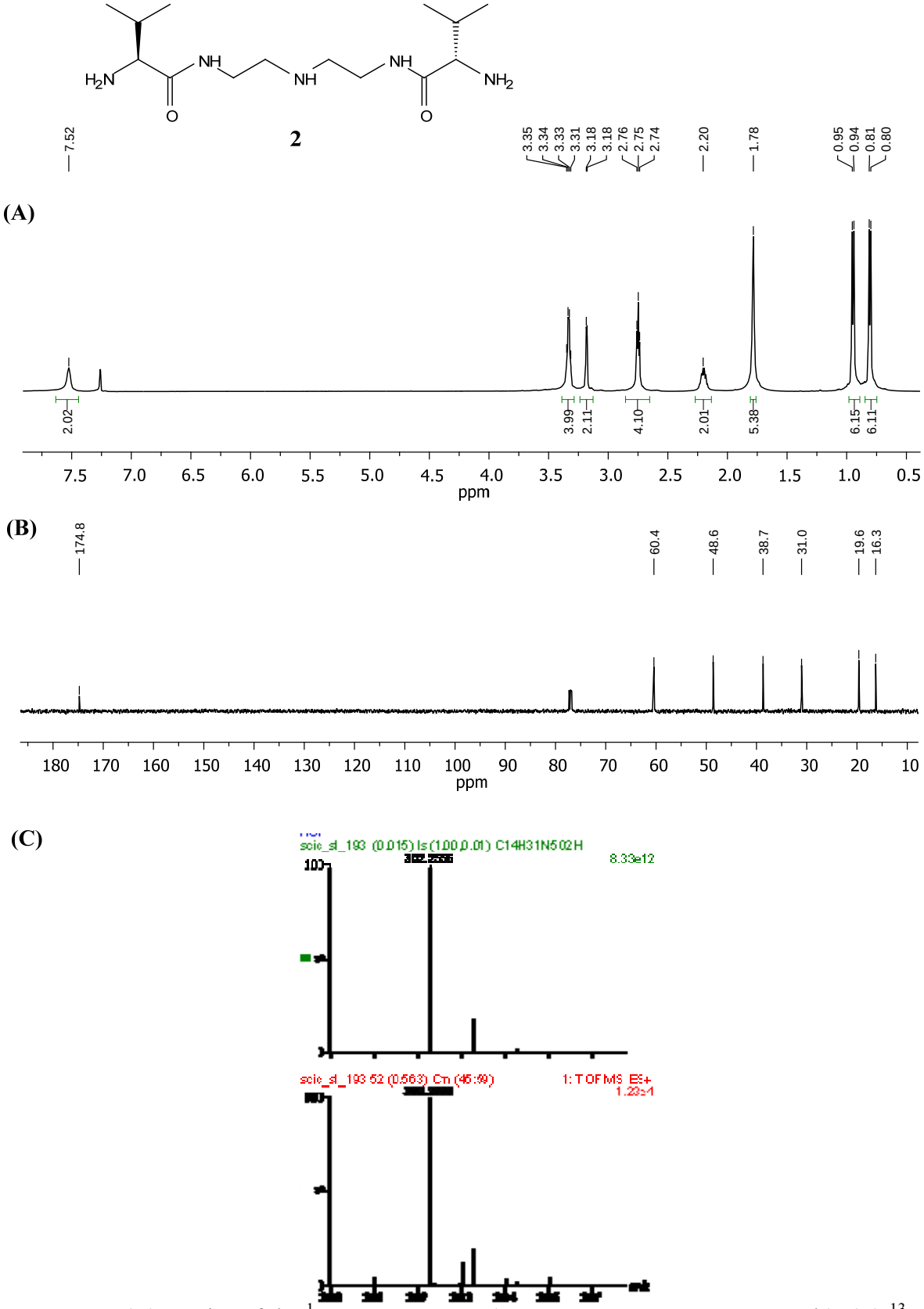


Figure S - 1. (A) Copies of the ^{1}H- NMR spectra (500 MHz, 303K, 20 mM, $CDCl_3$), (B) ^{13}C-NMR spectra (135 MHz, 303K, 20 mM, $CDCl_3$), (C) HRMS spectra of compound **2**.

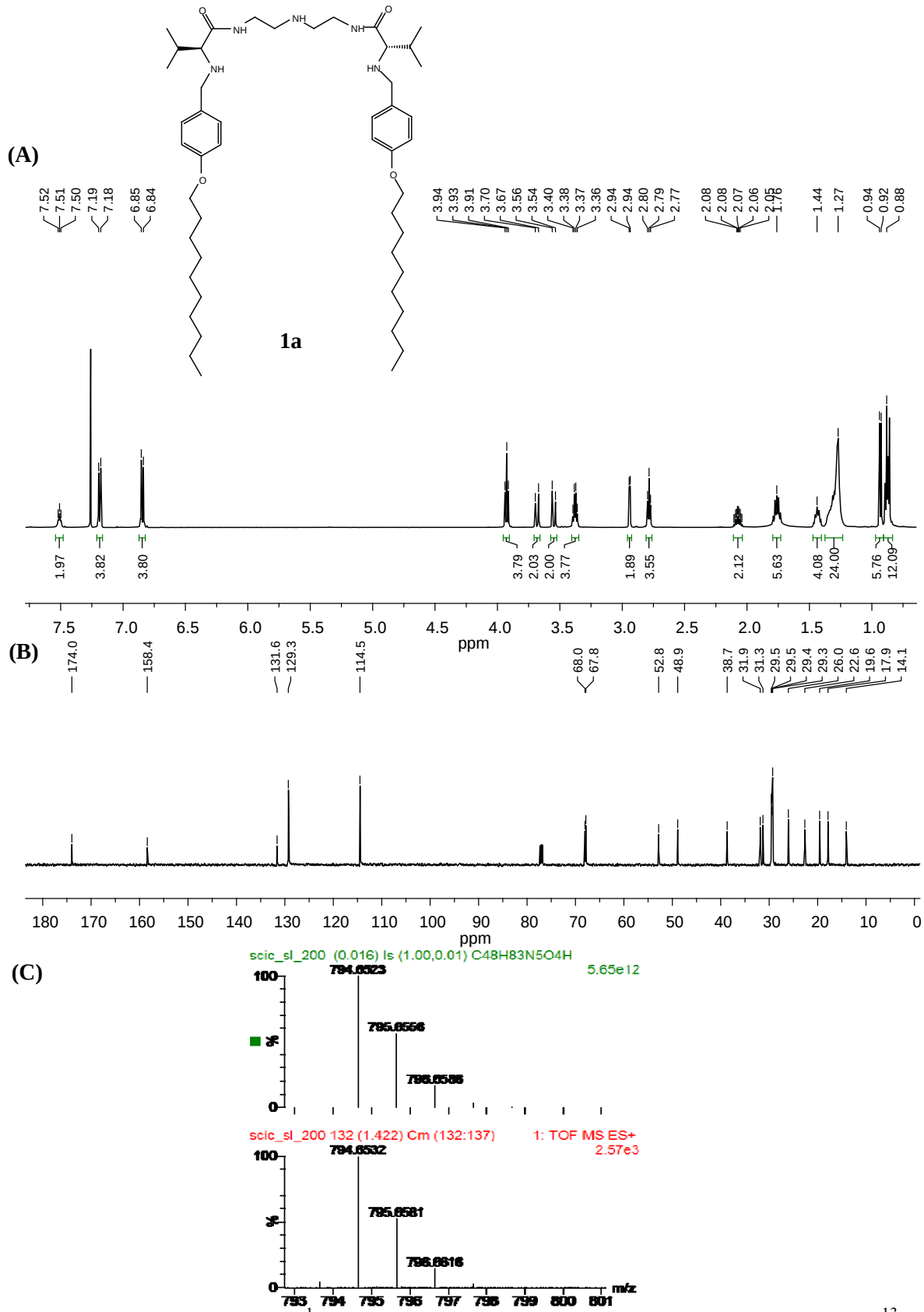


Figure S - 2. (A) Copies of the ^{1}H- NMR spectra (500 MHz, 303K, 20 mM, $CDCl_3$), (B) ^{13}C-NMR spectra (135 MHz, 303K, 20 mM, $CDCl_3$), (C) HRMS spectra of compound **1a**.

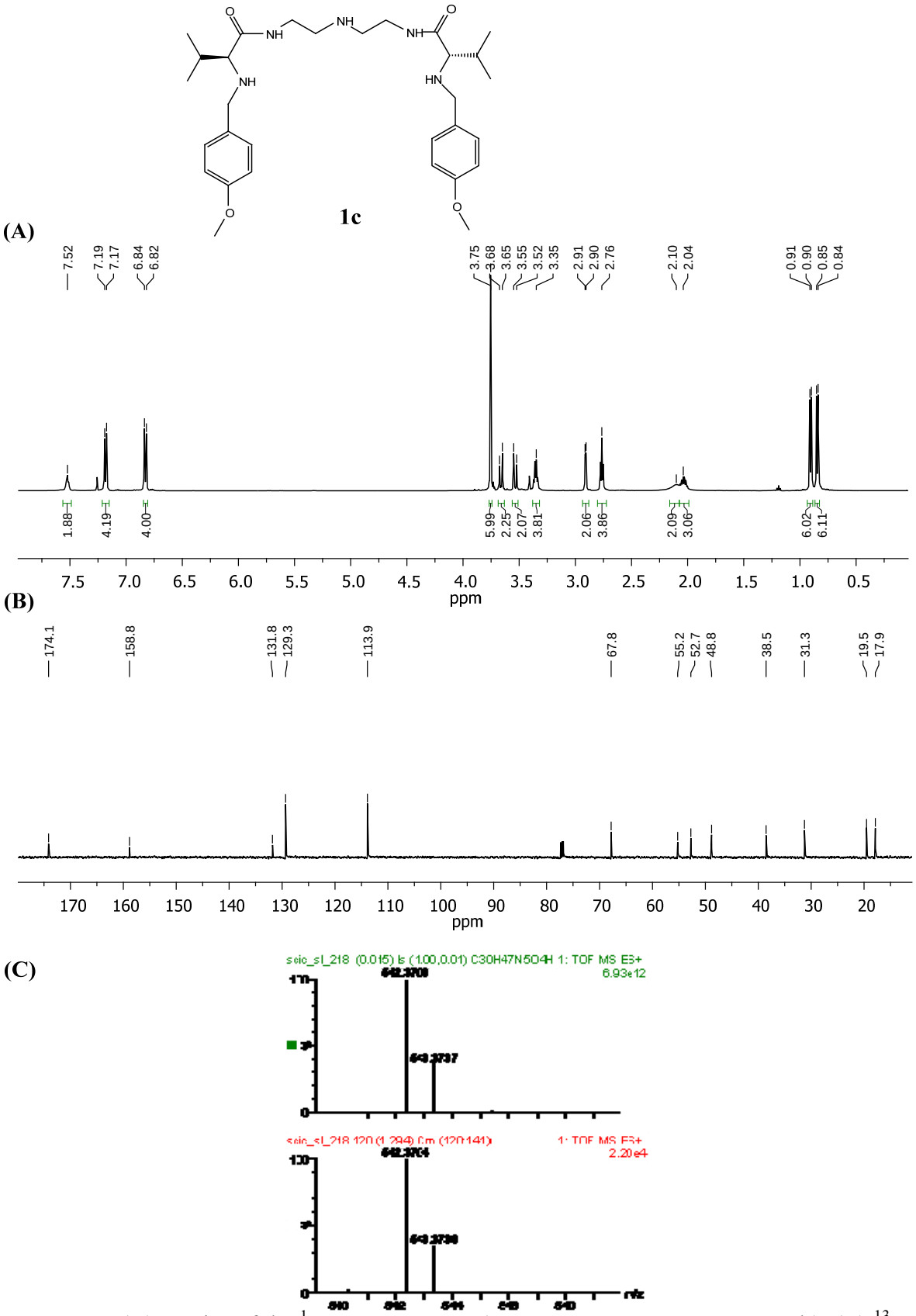


Figure S - 3. (A) Copies of the ^{1}H- NMR spectra (500 MHz, 303K, 20 mM, $CDCl_3$), (B) ^{13}C-NMR spectra (135 MHz, 303K, 20 mM, $CDCl_3$), (C) HRMS spectra of compound **1c**.

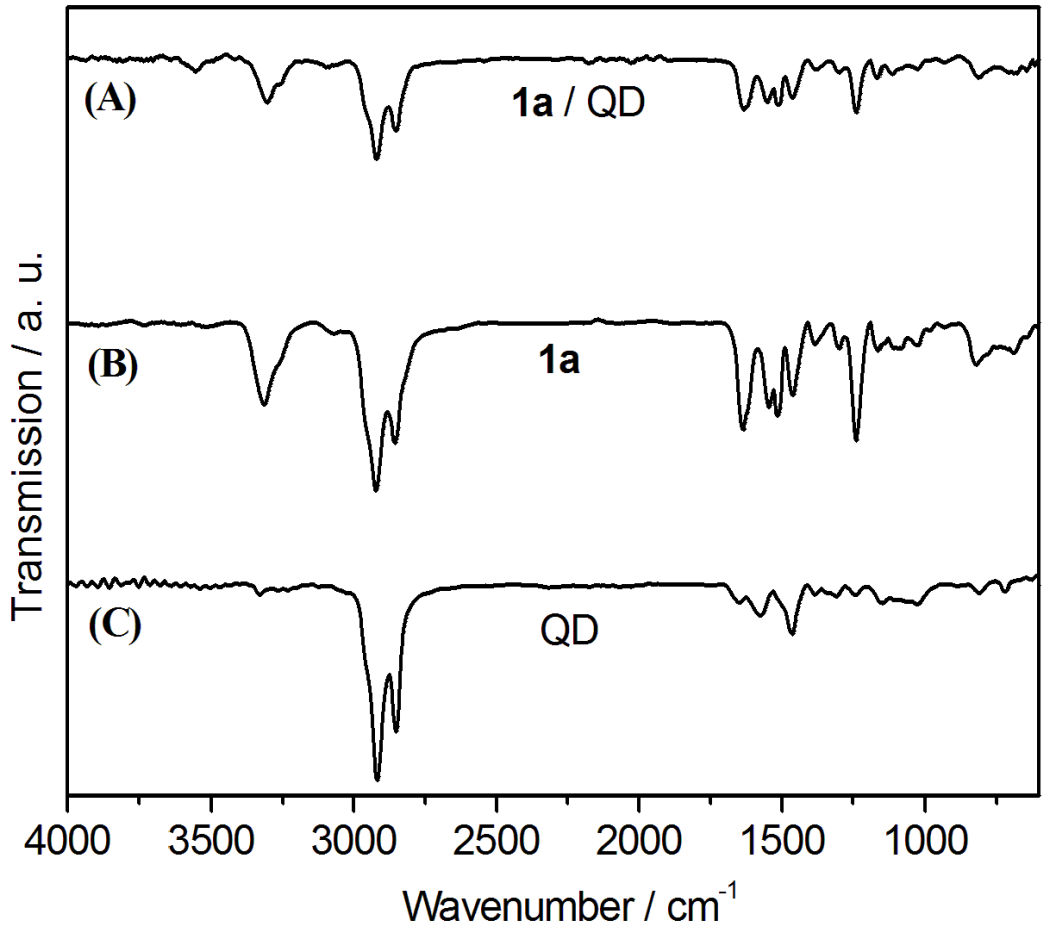


Figure S - 4. FTIR spectra of: (A) water soluble CdSe/ZnS QDs prepared in the presence of **1a**, (B) peptidomimetic compound **1a**, (C) toluene soluble CdSe/ZnS QDs stabilized by hexadecylamine ligands.

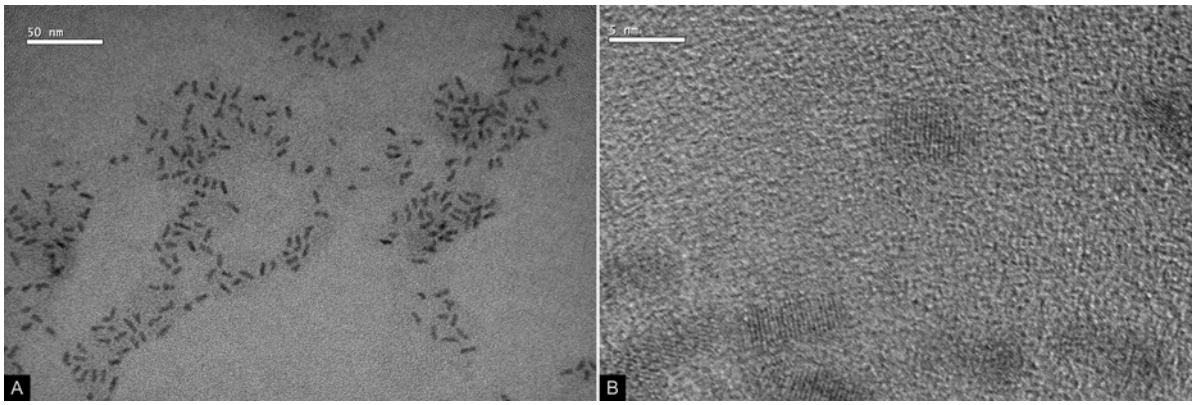


Figure S - 5. TEM micrographs of water soluble CdSe/ZnS QDs prepared in the presence of **1a**. Samples were prepared containing the optimal concentration of peptidomimetic compound **1a** (3×10^{-5} M). Scalebar is: A) 50 nm and B) 5 nm.

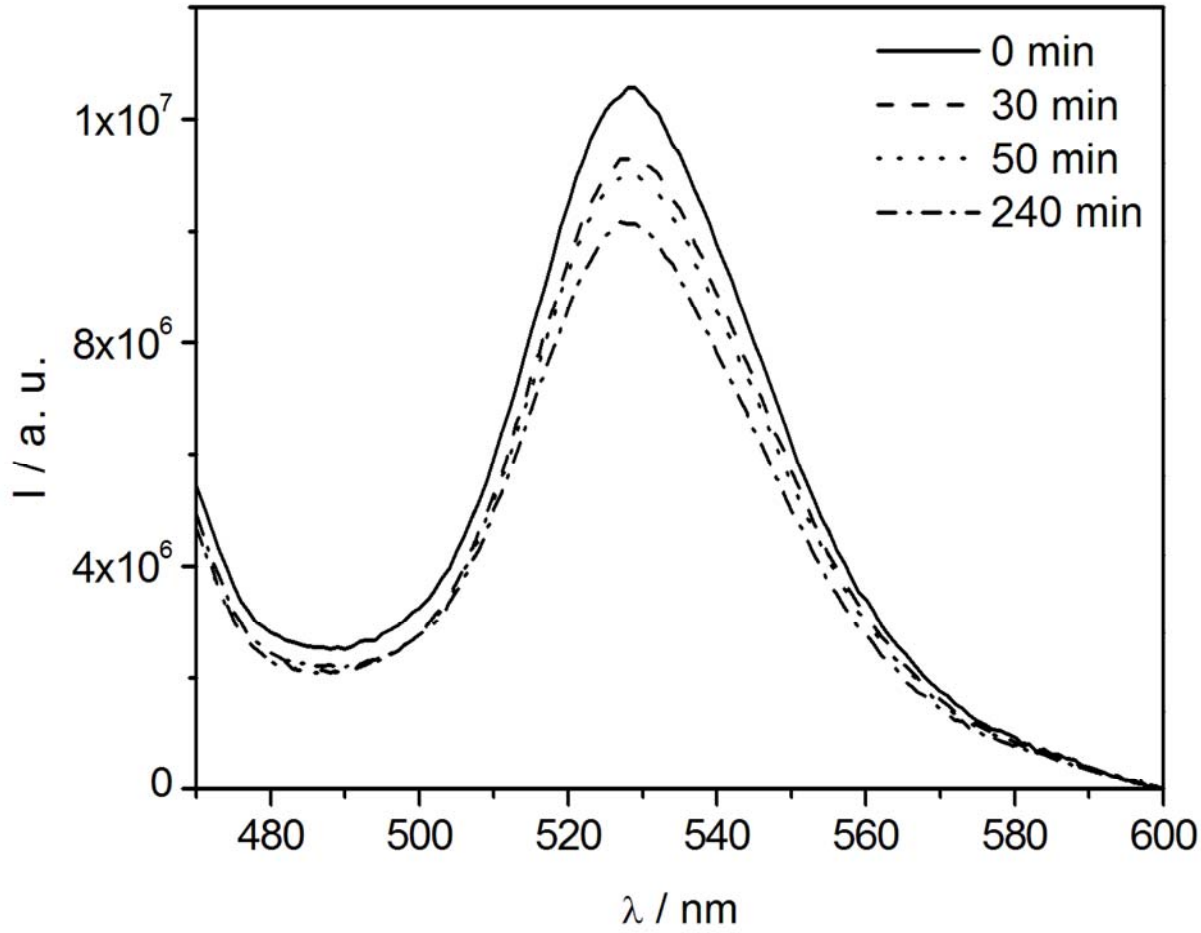


Figure S - 6. Evolution along the time of the emission spectra of a solution containing **1a** (5×10^{-4} M) and CdSe/ZnS in water (λ_{exc} = 400 nm).

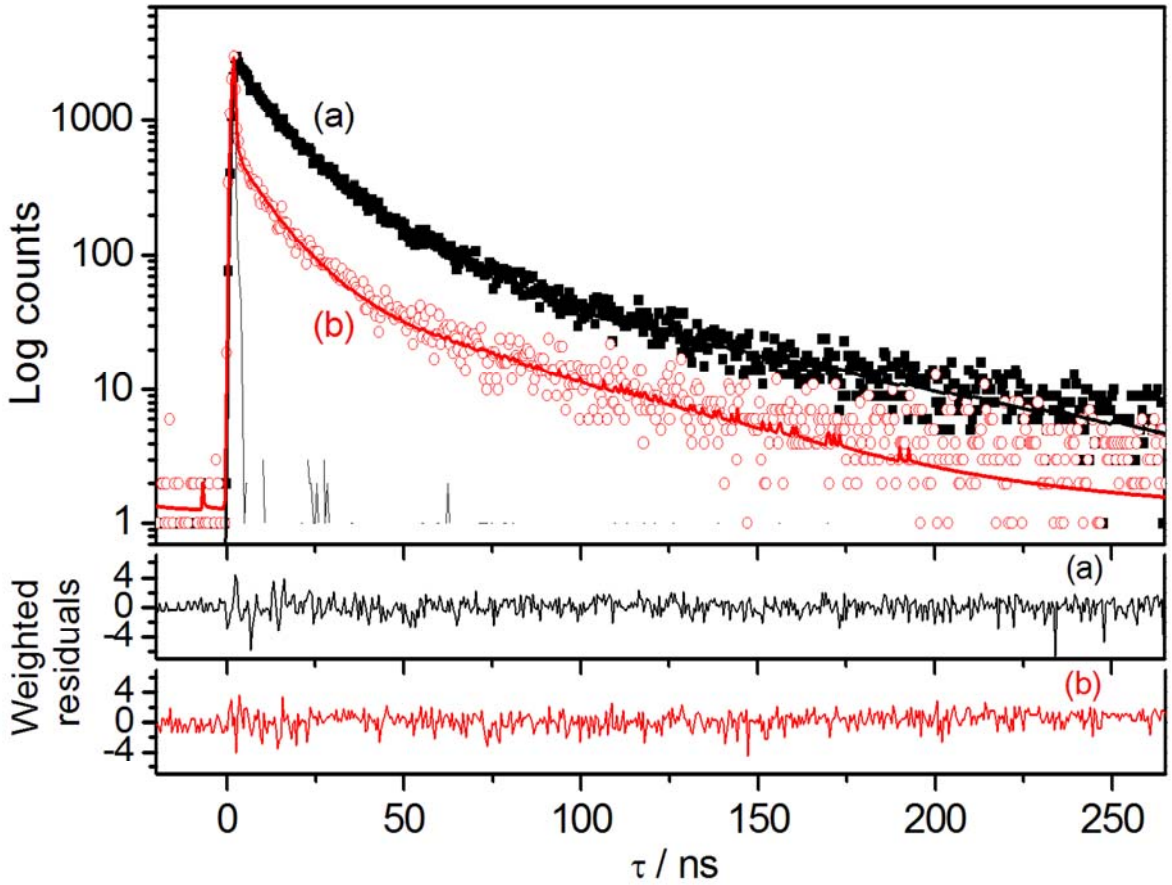


Figure S - 7. Fluorescence decay curves of CdSe/ZnS QDs in toluene (a, solid squares) and water containing **1a** (b, open cicles), (λ_{exc} = 365 nm, λ_{em} = 530 nm). The incident light pulse is also shown (solid line).

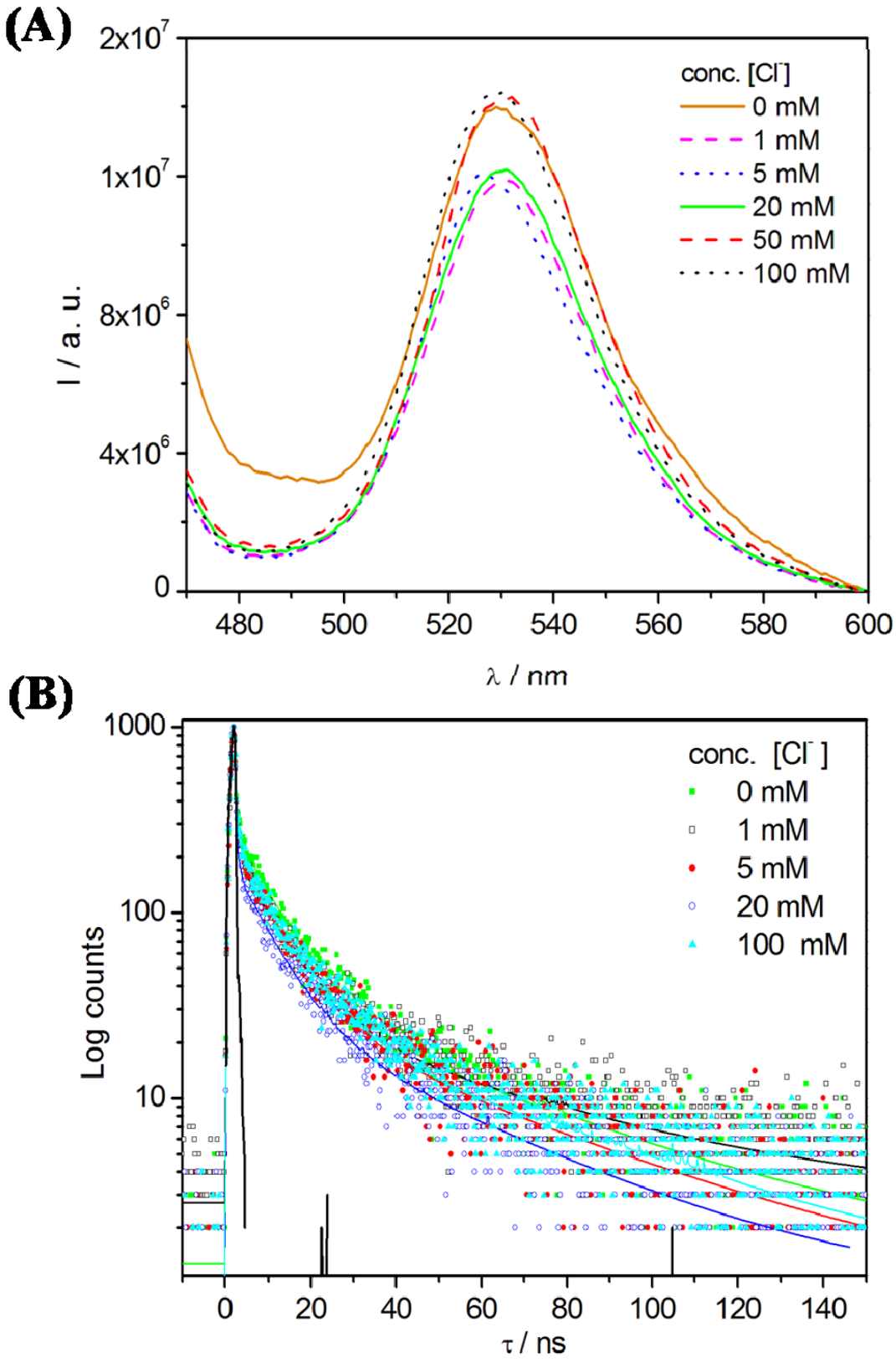


Figure S - 8. (A) Emission spectra of samples containing **1a** (3×10^{-5} M) and CdSe/ZnS QDs in water in the presence of different concentrations of chloride ion. (B) Fluorescence decay curves of samples containing **1a** (3×10^{-5} M) and CdSe/ZnS QDs in water in the presence of different concentrations of chloride ion.

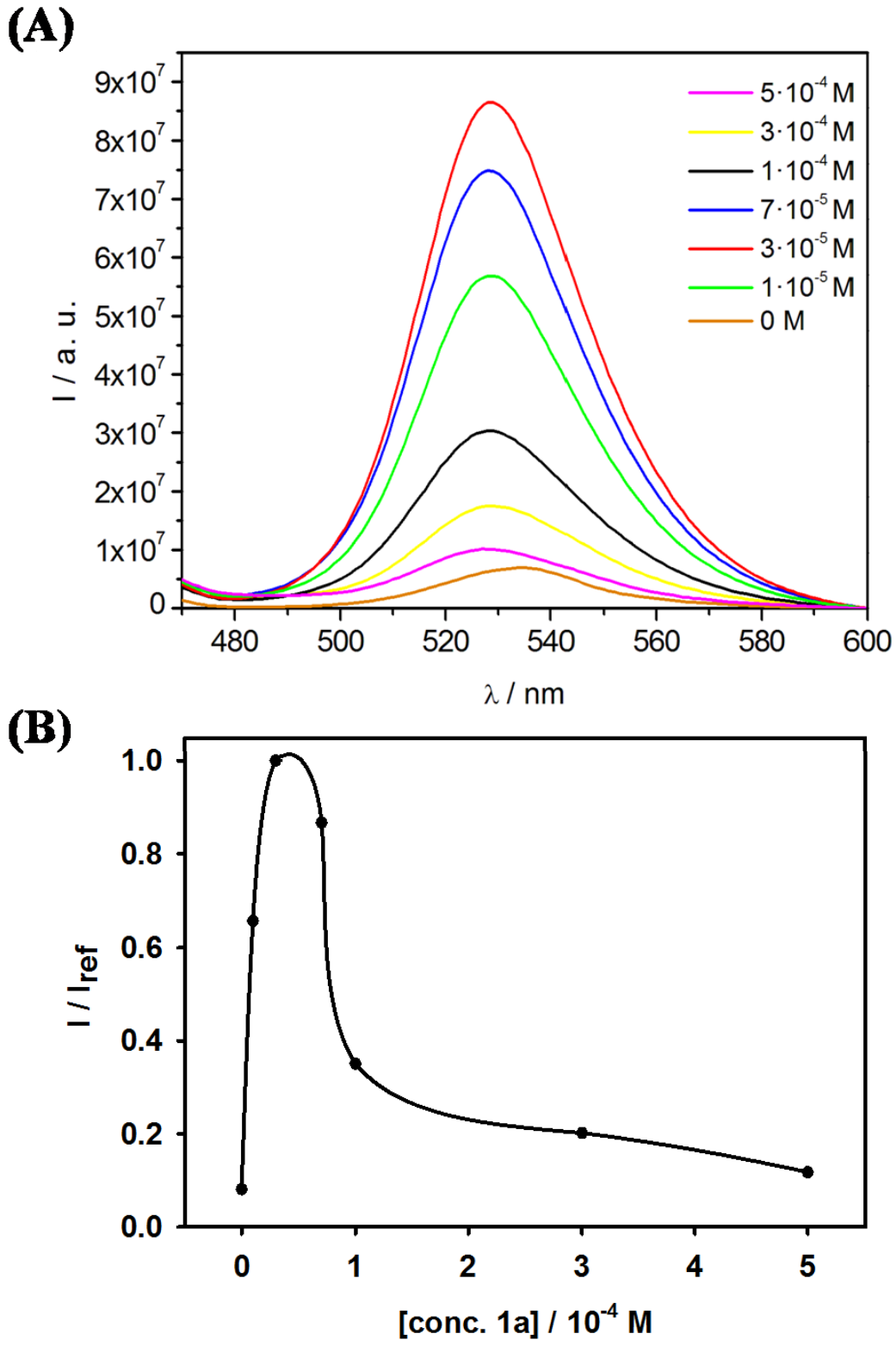


Figure S - 9. Effect of the concentration of peptidomimetic compound **1a** on the photoluminiscence of CdSe/ZnS QDs in water, (A) Emission spectra of the QDs in the presence of different amounts of **1a** (λ_{exc} = 400 nm). (B) Relative emission intensity of the QDs in the presence of different amounts of **1a**, where I_{ref} is the highest intensity recorded at 3 × 10^{-5} M.

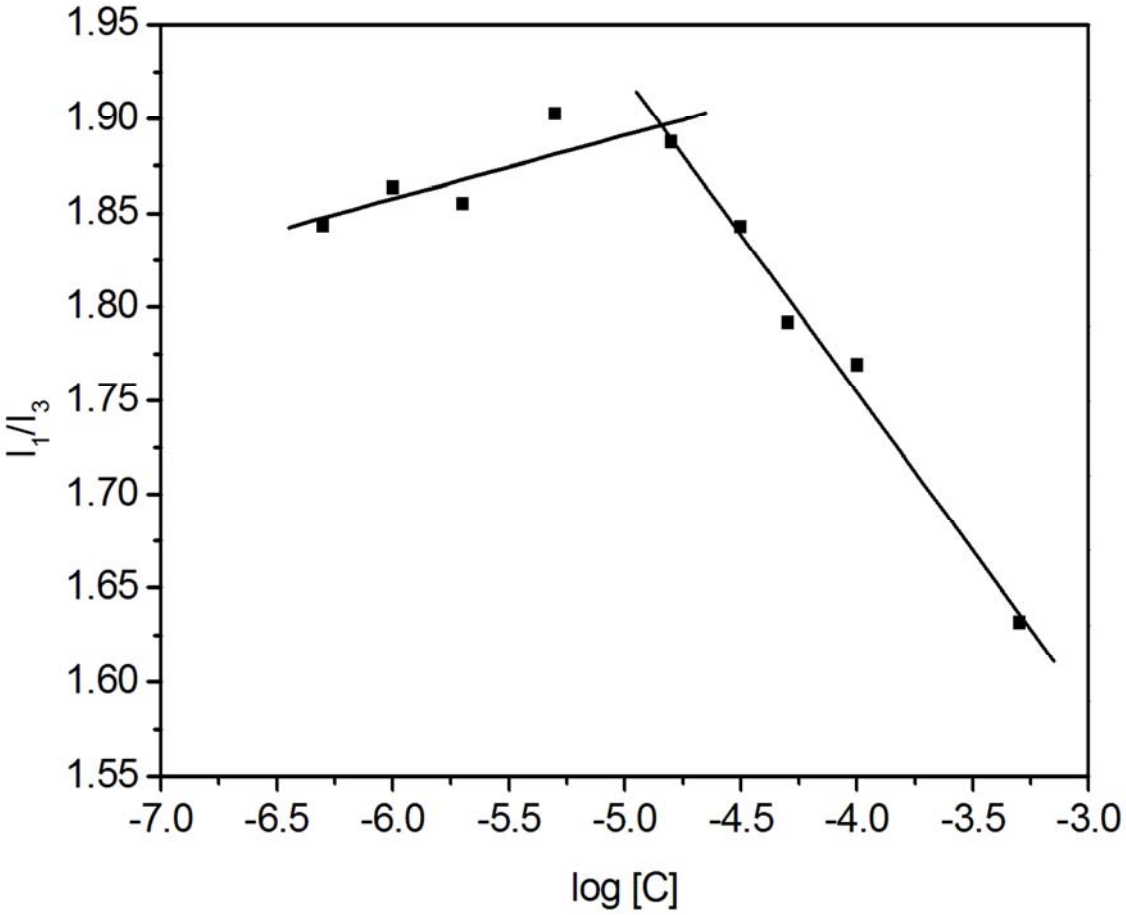


Figure S - 10. Change in the I_1/I_3 fluorescence ratio of pyrene as a function of peptidomimetic compound **1a** concentration.