

Supplementary Material

Dendronised Polymers as Templates for In Situ Quantum Dot Synthesis

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Materials and Methods

Copper (I) bromide (CuBr), 2-hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GMA), 2,2'-bipyridine (bpy), dimethylformamide (DMF), sodium azide, ammonium chloride, pentamethyldiethylene triamine, *N*-hydroxysuccinimide, dichloromethane, 3-mercaptopropionic acid, 1,3-dicyclohexylcarbodiimide, methanol (MeOH), diethyl ether, and sodium borohydride (NaBH₄) were purchased from Sigma Aldrich, Australia. Cadmium nitrate tetrahydrate was obtained from Analar, Australia. Sodium hydroxide (NaOH) was obtained from Fluka, Australia. Hydrochloric acid (HCl, 32%) was purchased from Merck, Australia. 2-(4-Morpholino)ethyl 2-bromoisobutyrate was prepared as reported by Weaver *et al.*¹ Milli-Q water was used to prepare all aqueous solutions. All chemicals were used as received without any purification.

Instrumental characterisation of polymer

¹H NMR spectra were measured using a Bruker 500 MHz spectrometer, with CD₃OD as the solvent for copolymers, azido-functionalised copolymers and dendronised polymers. CDCl₃ was used for 3-mercaptopropanyl-*N*-hydroxysuccinimide ester. The chemical shifts were referred to the solvent peak, $\delta = 3.31$ ppm for CD₃OD and 7.26 ppm for CDCl₃. IR spectra were obtained using PerkinElmer Spectrum One FT-IR spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weight and polydispersity index of polymers (Waters Styragel HR 4 DMF 4.6 × 300 mm column, 5 μ m). Agilent Technologies 1100 Series GPC and Agilent GPC software were utilised for measurements and data analysis respectively. Measurements were taken using DMF as the eluent at a flow rate of 0.3 mL/min at 50 °C, and calibrated against poly(methyl methacrylate) (PMMA) standard. Elemental analysis was conducted at the Campbell Microanalytical Laboratory, University of Otago. The carbon, hydrogen and nitrogen content of each sample was determined via the 'flash combustion' method using a Carlo Erba Elemental Analyser EA 1108.

Characterisation of CdTe QD–polymer nanocomposites

Morphologies of CdTe QDs-polymer nanocomposites were studied using transmission electron microscopy (TEM). A drop of colloidal QDs-polymer nanocomposites was placed and dried on carbon-coated copper grids and imaged using JEOL 2100F TEM with an accelerating voltage of 120 kV. Energy-dispersive X-ray spectroscopy (EDX), elemental maps, and high-resolution transmission

electron image, were acquired using an FEI Titan G2 80–200 TEM/STEM at an accelerating voltage of 200 kV.

Photophysics of CdTe QDs-polymer nanocomposites

Absorption spectra were recorded at room temperature using a Perkin-Elmer Lambda 35 UV-Vis spectrometer. Uncorrected steady-state emission and excitation spectra were recorded on an Edinburgh FLSP980 spectrometer equipped with a 450 W Xenon arc lamp, double excitation and single emission monochromators, and a Peltier-cooled Hamamatsu R928P photomultiplier tube (185–850 nm). Emission and excitation spectra were corrected for the source intensity (lamp and grating) and emission spectral response (detector and grating) by using a calibration curve supplied with the instrument. Quantum yields (Φ) were determined using the optically dilute method of Demas *et al.*² at excitation wavelengths obtained from absorption spectra on a wavelength scale (nm) and compared to the reference emitter by using the following equation:

$$\Phi = \Phi_r \left[\frac{A_r(\lambda_r) I_r(\lambda_r) n_s^2 D_s}{A_s(\lambda_s) I_s(\lambda_s) n_r^2 D_r} \right]$$

Where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the excitation wavelength (λ), n is the refractive index of the solvent, D is the integrated intensity of the luminescence, and Φ is the quantum yield. The subscripts r and s refer to the reference and the sample, respectively. An air-equilibrated water solution of quinine sulphate in 0.1 M H₂SO₄ ($\Phi_r = 0.546$) was used as the reference.³ The quantum yield determinations were performed at identical excitation wavelengths for the sample and the reference, therefore deleting the $I(\lambda_r)/I(\lambda_s)$ term in the equation. Emission lifetimes (τ) were determined by the single photon counting technique (TCSPC) with the same Edinburgh FLSP980 spectrometer using a pulsed picosecond LED (ELED 295 or ELED 360, fwhm <800 ps) as the excitation source, at repetition rates between 1 kHz and 1 MHz, and the above-mentioned R928P PMT as the detector.

The best fit was assessed by minimising the reduced χ^2 function and by visual inspection of the weighted residuals. Experimental uncertainties were estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for quantum yields, and ± 2 nm and ± 5 nm for absorption and emission peaks, respectively.

Synthesis of CdTe QDs-polymer nanocomposite

The CdTe QDs-polymer nanocomposite was synthesised following a multistep method as reported below:

Synthesis of P(HEMA_{0.72}-*ran*-GMA_{0.28}) copolymer

Synthesis of poly(hydroxyethyl methacrylate-*ran*-glycidyl methacrylate) was adapted from Weaver *et al.*¹ A random statistical copolymer consisting of 72 mol% hydroxyethyl methacrylate and 28 mol%

glycidyl methacrylate was synthesised using an atom transfer radical polymerisation method. Briefly, inhibitors for hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) were removed using a basic alumina column. Each monomer was dissolved in methanol (MeOH) at a volume ratio of 1:3 (monomer: MeOH). Prior to use, each monomer solution was degassed using standard 'freeze-pump-thaw' method and backfilled with argon gas. Copper (I) bromide (CuBr, 100 mg, 0.70 mmol) was added to the flask, followed by 2,2'-bipyridine (bpy, 392 mg, 2.5 mmol) before monomer solutions were added. Feed ratios of each of the monomer solutions were as follows: HEMA (9.6 mL, 19.7 mmol) and GMA (6.4 mL, 12.0 mmol). 2-(4-Morpholino)ethyl 2-bromoisobutyrate initiator (ME-Br, 210 μ L, 1 mmol) was added, and the reaction was completed at 80 °C in standard Schlenk conditions for 2 h. The reaction was opened to air and MeOH (15 mL) added. The product was collected under reduced pressure and redissolved in minimal MeOH, then collected and purified by repeated precipitation in excess diethyl ether and centrifugation (3000 rpm, 10 min). The solid product was dried overnight under vacuum and collected at ~70% yield with M_w of 17.5 kDa and PDI of 1.30. Resulting copolymer was identified via ^1H NMR (500 MHz, CD_3OD), where the appearance of peaks δH 2.70 (1H, br) and 2.87 (1H, br) correspond to the epoxide moiety, confirming the presence of GMA.

Azido functionalisation

The copolymer (1.0 g, 2.1 mmol epoxide) was dissolved in dimethylformamide (DMF, 20 mL). Sodium azide (1.2 g, 18.4 mmol) followed by ammonium chloride (1.0 g, 18.6 mmol) were added to the stirring solution. The reaction proceeded at 60 °C for 72 h before the solution was cooled and centrifuged to remove solid. The azide-functionalised polymer was collected at ~80% yield by repetitive precipitation in ether, and dried under vacuum.

Synthesis of dendron

3.5 generation propargyl-functionalised poly(amidoamine) (PAMAM) dendrons were synthesised via a method adapted from J.W. Lee *et al.* and Y.-J. Lin *et al.*^{4,5}

Click reaction

3.5 generation propargyl-PAMAM dendron (1.6 g, 0.53 mmol) was dissolved in DMF (15 mL) before the addition of azido-functionalised copolymer (100 mg, 211.4 μ mol epoxide). Pentamethyldiethylene triamine (PMDETA, 112 μ L, 0.55 mmol) was added to the reaction solution and then the solution was degassed via 'freeze-pump-thaw' methods and backfilled with argon. Reaction commenced under argon with the addition of CuBr (I) (78.9 mg, 0.55 mmol) for 72 h at r.t. The product was purified via dialysis (4 L \times 4) against deionised water and the product collected via lyophilisation. Dendron generation was completed for fourth generation PAMAM dendrons by reaction with ethylene diamine. The product was dissolved in minimal MeOH and added dropwise to a solution of excess

ethylene diamine at 0 °C. The reaction was left to warm to room temperature for a week before the final product was purified by dialysis (4 L × 4) against deionised water and collected using lyophilisation at ~90% yield. Method was adapted from P. Zhao *et al.*⁶

Synthesis of 3-mercaptopropanyl-*N*-hydroxysuccinimide ester

The 3-mercaptopropanyl-*N*-hydroxysuccinimide ester was synthesised as per published procedures.⁷ *N*-hydroxysuccinimide (1 g) was dissolved in dichloromethane (500 mL) and stirred for 30 min to yield a colourless solution followed by the addition of 3-mercaptopropionic acid (0.76 mL) in dichloromethane (5 mL). Next, 1,3-dicyclohexylcarbodiimide (1.97 g) in dichloromethane (50 mL) was added dropwise to the reaction mixture and stirred vigorously for 30 min. The mixture was left for 24 h under constant stirring before being filtered to remove solid. The product was collected by removing the solvent under reduced pressure.

Synthesis of thiolated polymer

3-Mercaptopropanyl-*N*-hydroxysuccinimide ester (1 g, 4.9 mmol) was dissolved in MeOH (30 mL). P(HEMA-*ran*-GMA) 4G polymer (50 mg) was dissolved in minimal DMF (5 mL) and transferred to the stirred reaction solution. The reaction proceeded for 24 h at 40 °C under argon, before being centrifuged (3000 rpm, 10 min) to remove the solids, and purified via dialysis for 48 h (4 L × 4) against deionised water. The product was collected by lyophilisation at ~30% yield.

Synthesis of CdTe QD–polymer nanocomposite

CdTe QD–polymer nanocomposite was prepared by mixing cadmium nitrate tetrahydrate (0.43 mM, 0.8 mL) and polymer solution (1.4 mg, 0.4 mL) in Milli-Q (6 mL) water while stirring. The resulting solution was degassed using the freeze-pump-thaw technique. Meanwhile, tellurium powder (Te, 5 mg) was mixed with an excess of sodium borohydride (NaBH₄) in Milli-Q water (4 mL) and reduced with heating to form a colourless NaHTe solution. Next, NaHTe (48 μl) was injected quickly into the cadmium/polymer reaction mixture to yield an orange solution. The pH of the mixture was adjusted to 9 with the addition of 1 M sodium hydroxide (NaOH) or hydrochloric acid (HCl) solution. The preparation was at a molar ratio 1:0.3:1 of Cd²⁺:HTE⁻:SH. Under argon, the reaction was refluxed (80 °C) and CdTe QD–polymer nanocomposites were collected at different times for varying sizes and colours. Two different fluorescence emission wavelengths CdTe QD–polymer nanocomposites were achieved: green (537 nm) and yellow (561 nm), by changing the refluxing time to 10 h and 19 h respectively.

Determination of the size of CdTe QDs–polymer nanocomposite

Using the empirical relationship given by Peng *et al.*,⁸ the size of the green and yellow CdTe QD–polymer nanocomposite were calculated using the following:

$$D (\text{CdTe}) = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84)$$

Where D is the diameter of CdTe QDs (nm) and λ is the wavelength of the first absorption peak (nm).

Absorption peak	QD size
498 nm	2.3 nm
515 nm	2.7 nm

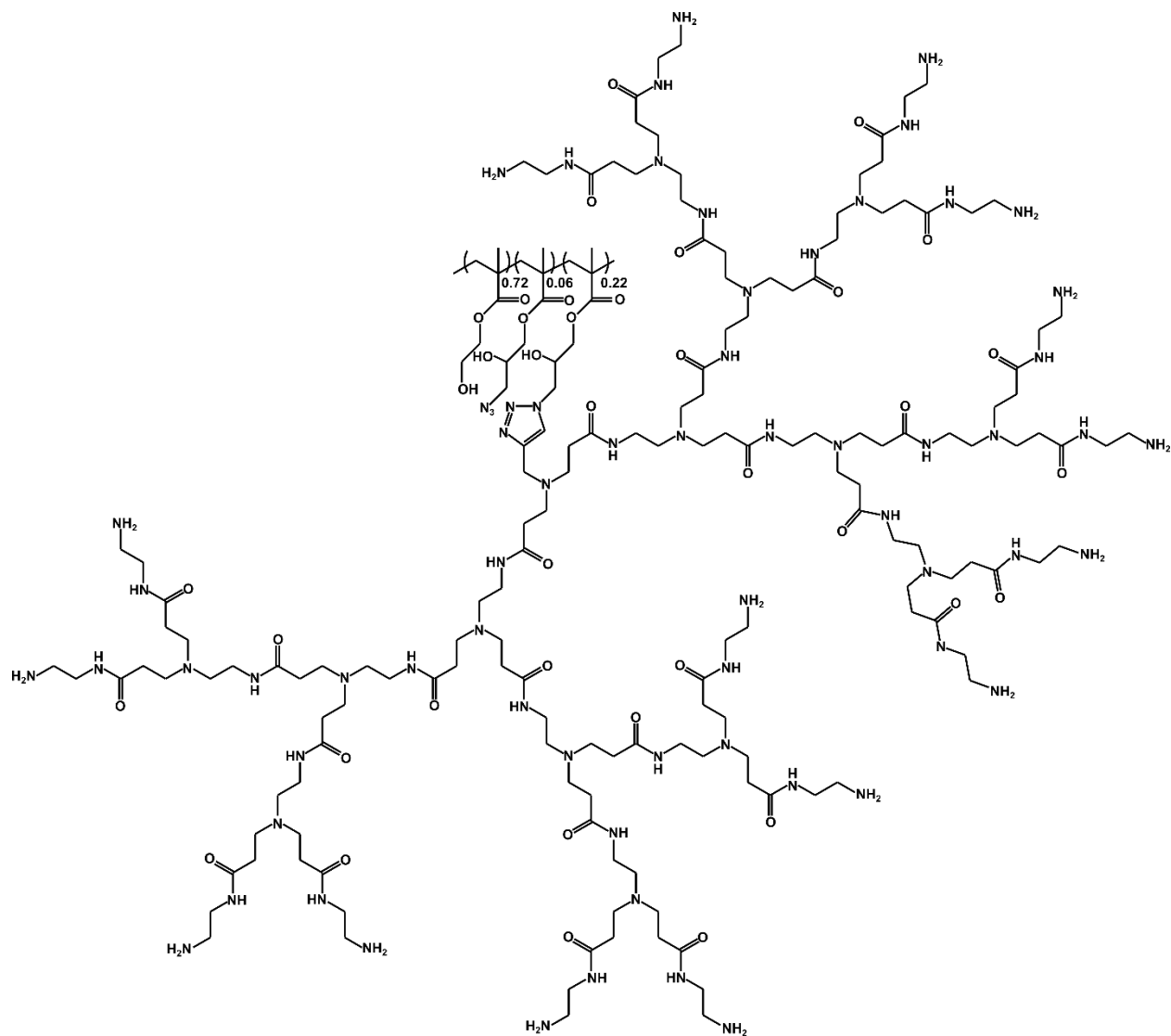


Fig S1. The chemical structure of P(HEMA-*ran*-GMA) polymer with 4th generation PAMAM dendrons (4G).

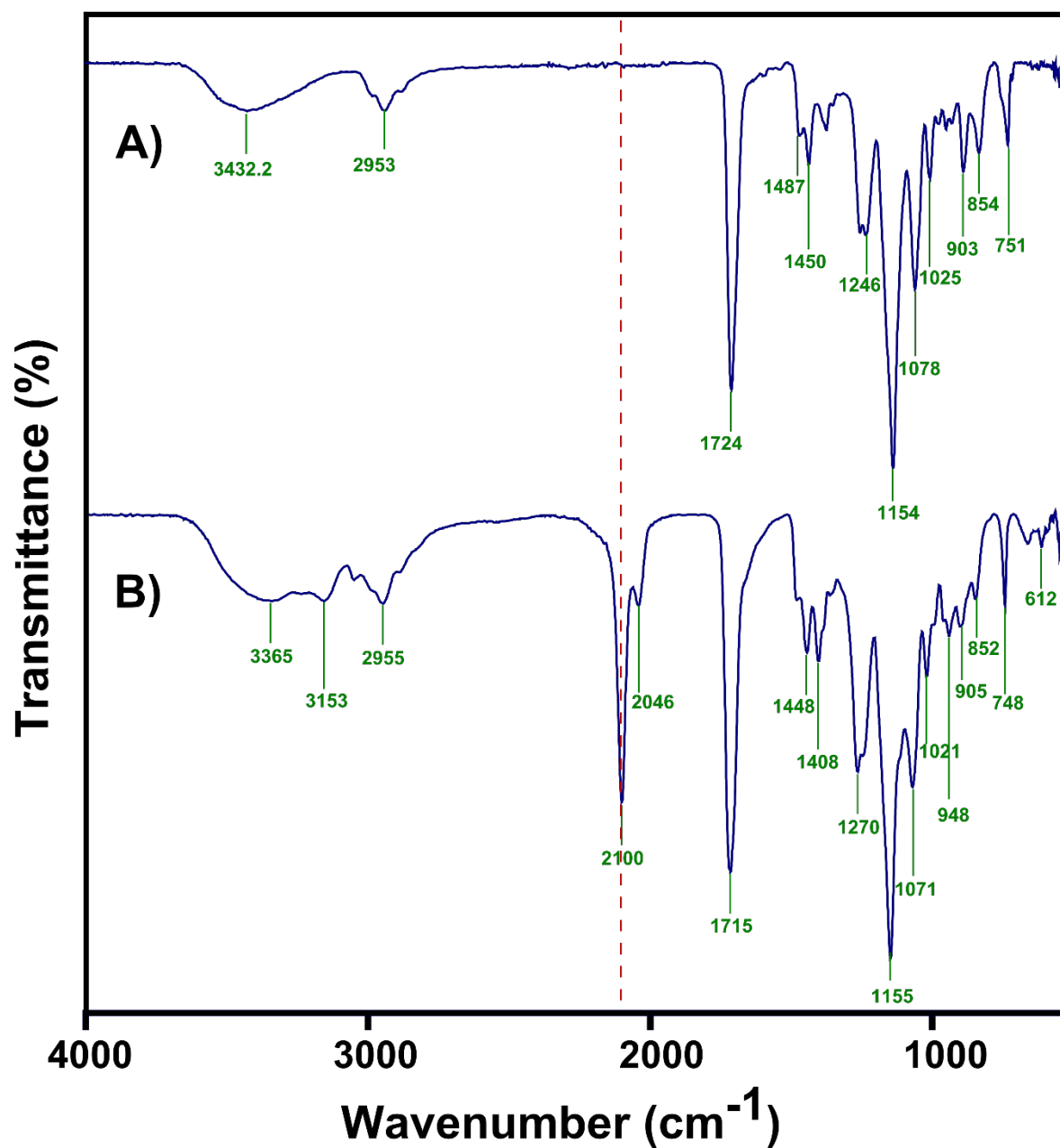


Fig S2. FT-IR spectrum of (A) the polymer backbone P(HEMA-*ran*-GMA) and (B) azide functionalised copolymer P(HEMA-*ran*-GMA). The peak at 2100 cm⁻¹ is associated with azide.

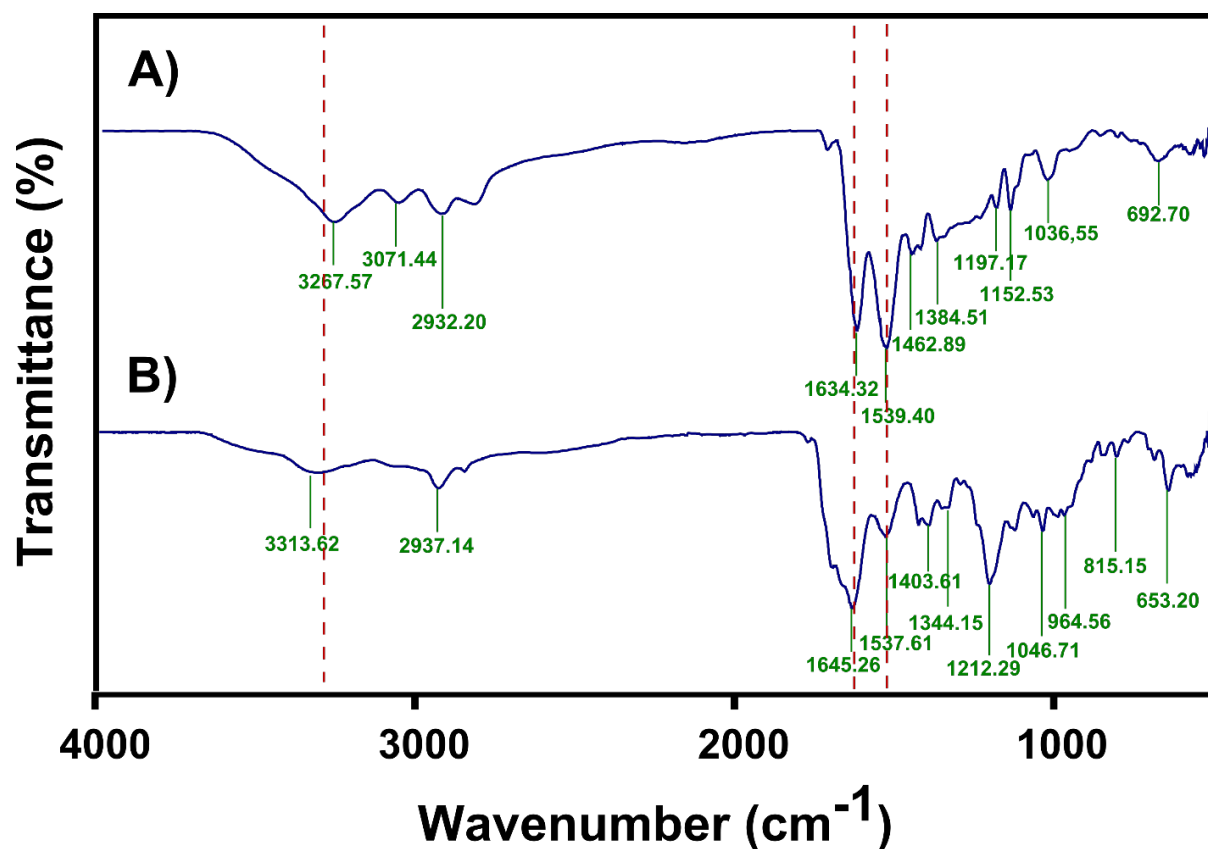


Fig S3. FT-IR spectrum of (A) the P(HEMA-*ran*-GMA) 4G polymer and (B) thiolated P(HEMA-*ran*-GMA) 4G polymer. Reduction of peaks at 3000–3300 cm⁻¹ are associated with amine and amide bending, and a significant decrease in peak intensity at ~1539 cm⁻¹ (associated with N–H stretching) in comparison to peak at ~1640 cm⁻¹ (associated with amide carbonyl), indicates that the primary amines have reacted.

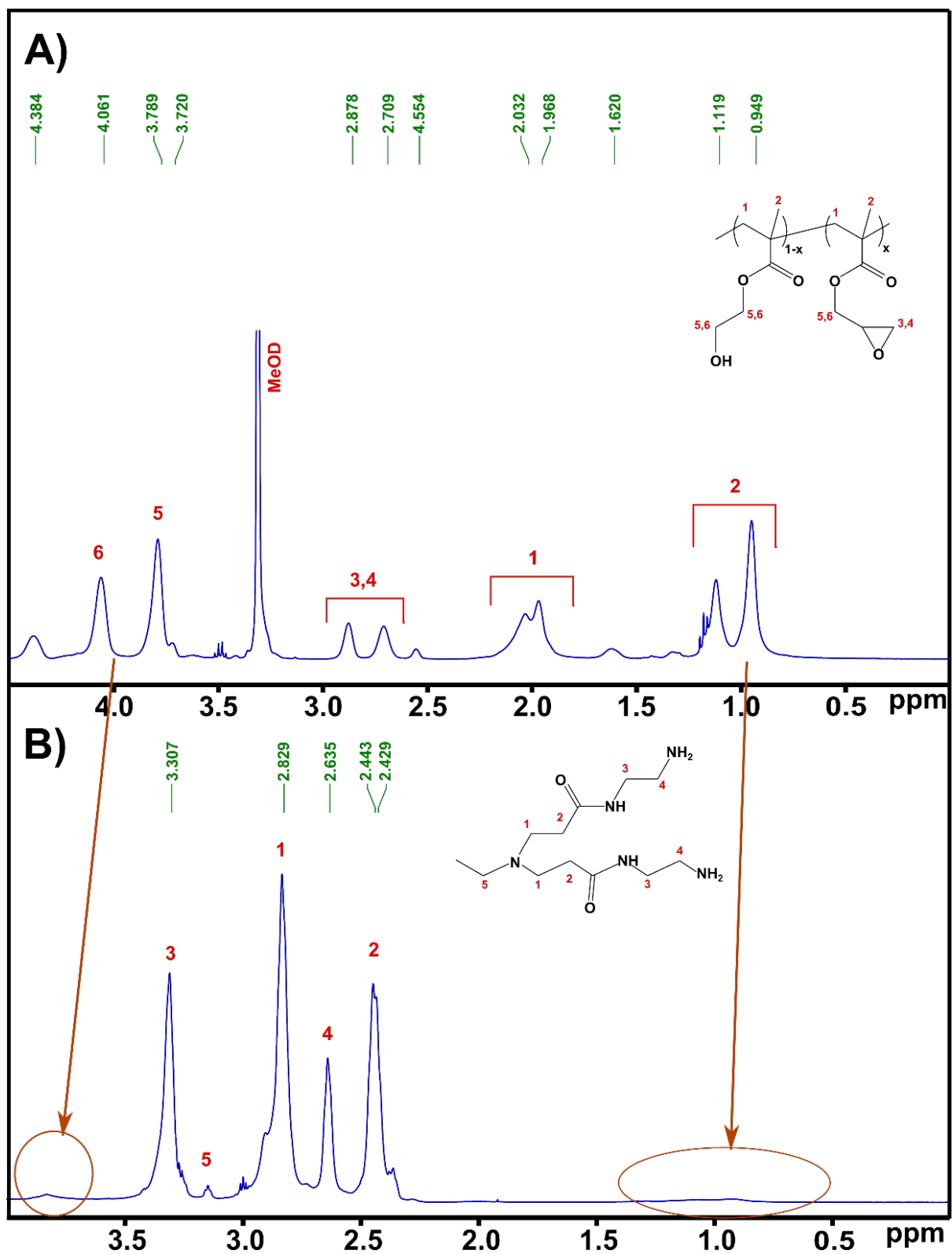


Fig S4. ^1H NMR spectra of (A) the polymer backbone P(HEMA-*ran*-GMA) (B) the P(HEMA-*ran*-GMA) 4G polymer. Polymer backbone signal in (A) is suppressed after attachment of dendrons in (B), indicated by the arrows.

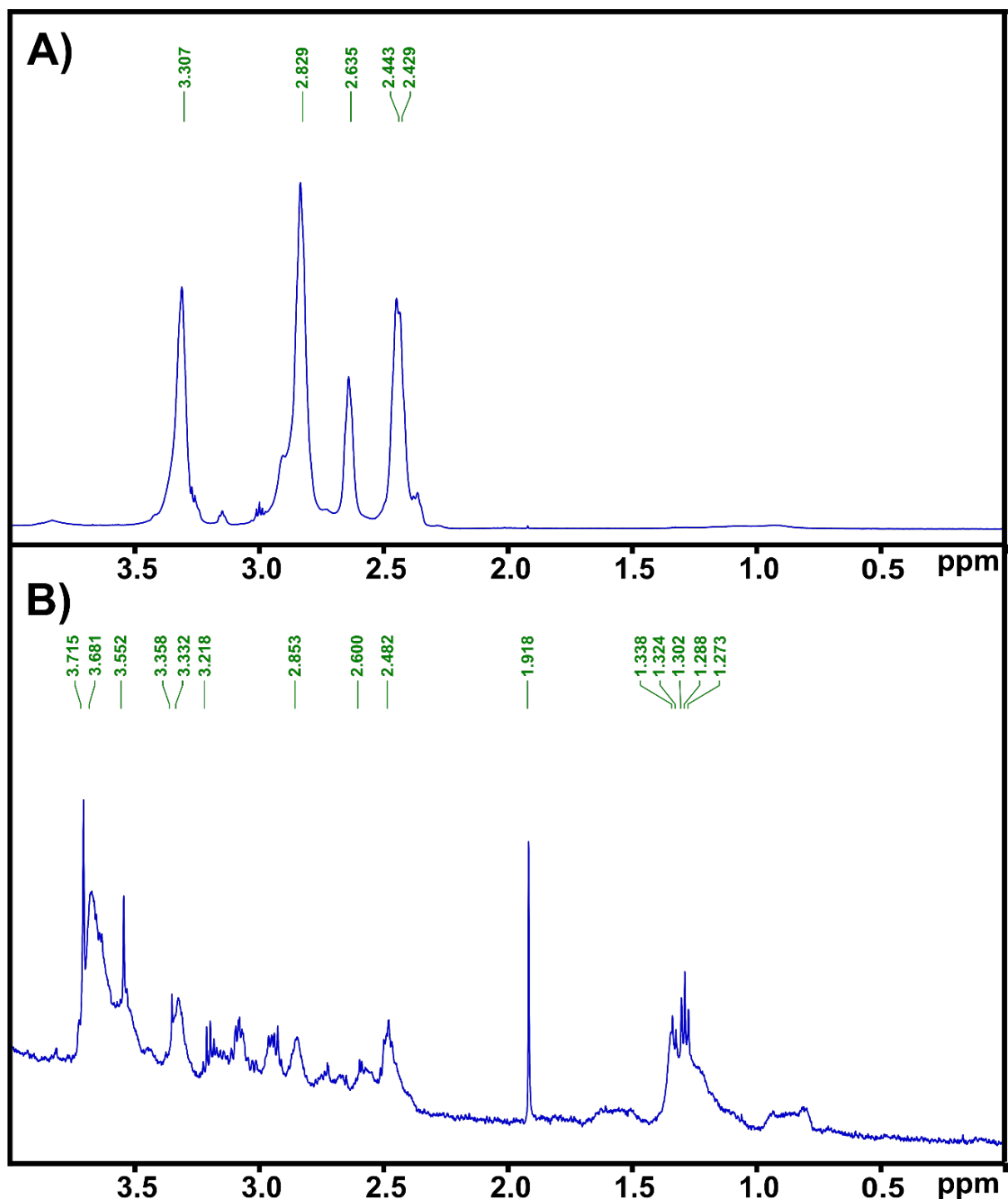


Fig S5. ^1H NMR spectra of (A) the P(HEMA-*ran*-GMA) 4G polymer and (B) thiolated P(HEMA-*ran*-GMA) 4G polymer. Signals due to dendron branches visible in (A) appear split in (B) due to incomplete substitution.

Table S1. Elemental analysis data of the non-thiolated and thiolated P(HEMA-*ran*-GMA) 4G polymer.

	Composition (%)			
	C	H	N	S
P(HEMA-<i>ran</i>-GMA) 4G polymer	50.47	8.77	21.62	-
	50.24	8.81	21.57	-
Thiolated P(HEMA-<i>ran</i>-GMA) 4G polymer	42.52 (47.45)*	6.08	5.35 (10.28)*	3.73 (8.66)*

* Corrected for water content.

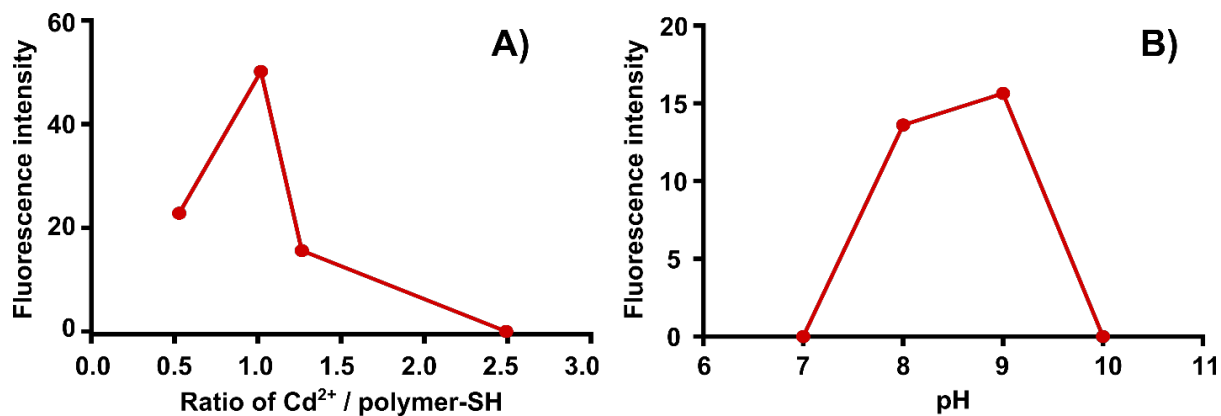


Fig S6. Fluorescence intensity of the emission peak of CdTe QD–polymer nanocomposite (A) at different Cd²⁺/polymer SH molar ratio with same pH and (B) at different pH with the same Cd²⁺/polymer SH molar ratio.

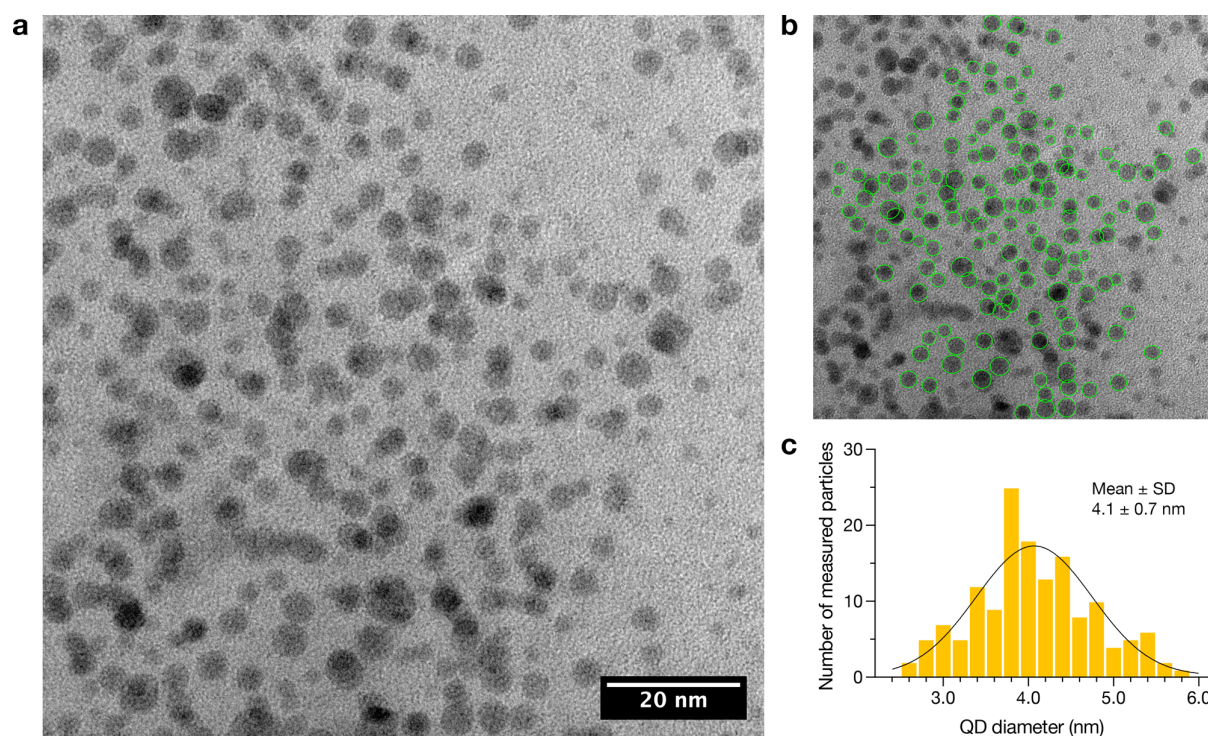


Fig S7. (a) TEM image of yellow-emitting CdTe QD–polymer nanocomposite, with (b) analysed particles outlined in green, and (c) histogram showing particle diameters (yellow bars) and the Gaussian curve of best fit (black line).

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