Supporting Information for:

Polymer-metal nanocomposites with bi- or tri-metallic compositions exhibiting catalytic properties

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1. Experimental Section

Materials. Poly(ethylene glycol) methyl ether ($mPEG_{113}$) (Average M_n = 5000 g/mol) and diisopropyl carbodiimide (DIC; > 99%) was purchased from Oakwood Chemical (USA). 4-Dimethylaminopyridine (DMAP; 99%) was purchased from Alfa Aesar. 4-Cyano-4 (((dodecylthio) carbonothioyl) thio) pentanoic acid (CDTPA; 97%) was purchased from Boron Molecular (Australia). 2-(Dimethylamino)ethyl methacrylate (DMAEMA), hydroxypropyl methacrylate (HPMA, mixture of 2-hydroxypropyl and 2-hydroxyisopropyl methacrylate; 97%), poly(*N*-vinylpyrrolidone) (PNVP, average M_n = 40,000 g/mol), sodium hydrogen carbonate ($NaHCO_3$, ≥ 99.7%), magnesium sulfate anhydrous ($MgSO_4$, ≥ 99.5%), sodium borohydride ($NaBH_4$, ≥ 98.0%), sodium tetrachloroaurate (III) dihydrate ($NaAuCl_4 \cdot 2H_2O$, 99%), sodium tetrachloropalladate (II) (Na_2PdCl_4, 98%), silver nitrate ($AgNO_3$, > 99%), 1-phenylethanol (98%), 4-iodophenol (99%), phenylboronic acid (95%) and tert-butyl hydroperoxide (TBHP, *t*BuOOH 70% wt in water) were purchased from Sigma Aldrich (Australia). 2,2'-Azobis(isobutyronitrile) (AIBN) and 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) were purchased from Wako Pure Chemical Industries, Ltd. All the other solvents were obtained from commercial source and were used as received unless noted otherwise.

Characterisation. Particle sizes and particle size distributions were measured using Dynamic Light Scattering (DLS), performed using Litesizer 500 equipped with Kalliope software (Anton Paar, USA) which uses a 40 mW, 658 nm laser for three measurement angles. The aqueous dispersions containing the block copolymer nanoparticles were diluted to 0.10 % w/v by ultrapure water. Light scattering was detected automatically by the instrument and hydrodynamic diameters were determined by assuming spherical, noninteracting, perfectly monodisperse particles. ^1H and ^{13}C Magnetic Nuclear Resonance Spectroscopy (^1H NMR and ^{13}C NMR) spectra were recorded on a Bruker Avance 400 and Bruker Avance 600 NMR spectrometer. NMR chemical shifts (δ) are reported in parts per million (ppm) and were calibrated against residual solvent signals of $CDCl_3$ (δ 7.26), DMSO-d_6 (δ 2.50). Samples were dissolved in $CDCl_3$, or DMSO-d_6 at 5-10 mg/mL. Gel Permeation Chromatography (GPC) was performed on a system comprising a Shimadzu LC-20AT pump, Shimadzu RID-20A refractive index detector, and SPD-20A UV−visible detector. The GPC is equipped with a guard column (WAT054415) and 3×Waters GPC columns (WAT044238, WAT044226, WAT044235, 300 mm×7.8 mm). The eluent is *N,N*-dimethylformamide (DMF) with 10 mM lithium bromide

(LiBr) and eluted at 1 mL/min for 45 min in total. The samples were dissolved in DMF with 10 mM LiBr, filtered through 0.20 μm polytetrafluoroethylene (PTFE) hydrophobic syringe filters. A calibration curve was obtained from poly(methyl methacrylate) (PMMA) standards (Agilent) ranging from 960 to 1,568,000 g/mol. Transmission Electron Microscopy (TEM): Copper grids (formvar/carbon-coated, 400 mesh) were plasma glow-discharged for 20 seconds to create a hydrophilic surface. After glow discharge, 0.10 % w/v aqueous dispersion was dropped on the grid and then negatively stained by uranyl acetate solution (3 μL, 2.0 % w/v). The grid was blotted again to remove excess stain and dried using a gentle nitrogen blow. Imaging was performed using a single-tilting holder inserted into FEI Tecnai G2 T20 TEM instrument equipped with a LaB_6 emitter operating at 200 kV, twin lens, 5-axis compustage, Orius SCD200D wide-angle CCD camera (diffraction capable). High-Resolution TEM (HR-TEM) was performed with Rio16 high-resolution CMOS camera. Scanning Transmission Electron Microscopy (STEM): same sample preparation method as TEM. Imaging was performed using a beryllium (low background) double-tilting holder inserted into FEI Tecnai F20 Field Emission Gun (FEG) TEM equipped with Super-Twin lens, 5-axis compustage, Fischione Instruments 3000 annular dark field detector, on-axis bright-field/dark-field (BF/DF) detector for High-Angle Annular Dark Field (HAADF) imaging, Orius SCD200D wide-angle CCD camera (diffraction capable), Gatan OneView IS 16MPixel CMOS camera, Gatan BF/ADF STEM detectors. STEM-Energy Dispersive X-ray (STEM-EDX) mapping was performed using Gatan Diffraction Imaging, Gatan EDX DigitalMicrograph plug-in.

Synthesis of the poly(ethylene glycol) methyl ether trithiocarbonate (PEG_{113}-CDTPA) macro-CTA. $mPEG_{113}$ (10.0 g, 1.2 mmol) was dissolved in 50 mL toluene in a round bottom flask to remove water azeotropically by rotary evaporation (repeated 3 times). Dichloromethane (DCM) (50 mL) was then added to the flask containing $mPEG_{113}$ (10.0 g, 1.2 mmol), followed by CDTPA (1.615 g, 2.4 mmol), DIC (0.505 g, 2.4 mmol) and DMAP (48.9 mg, 0.24 mmol) were added to the flask in order and sealed with a rubber septum. The esterification reaction was allowed to proceed with stirring at room temperature for 24 hours. The reaction mixture was washed with 5 × 100 mL 1.0 M HCl (aq), then with 2 × 150 mL saturated $NaHCO_3$, dried with excess anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The final product was then collected by precipitation of the reaction concentrate in cold *n*-hexane 3 times. PEG_{113}-CDTPA was obtained as a pale-yellow solid after drying under reduced pressure (65% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.26 (t, 3H), 3.46-3.83 (m, 452H), 3.38 (s, 3H), 3.33 (t, 3H), 2.33-2.70 (m, 4H), 1.88 (s, 3H), 1.70 (m, 2H), 1.22-1.41 (b, 18H), 0.89 (t,

3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 216.9, 171.4, 119.0, 71.9, 70.5, 68.9, 64.1, 59.0, 46.3, 37.0, 33.8, 31.8, 29.5, 27.6, 24.8, 22.6, 14.1.

Preparation of PEG_{113}-*b*-PDMAEMA-CDTPA block copolymer *via* RAFT polymerisation. The following representative protocol was used for the preparation of PEG_{113}-*b*-PDMAEMA-CDTPA diblock copolymer: PEG_{113}-CDTPA (0.5 g, 92.6 μmol, 1.0 equiv.), DMAEMA (0.44 g, 2.8 mmol, 30.0 equiv.) and AIBN (3.0 mg, 18.5 μmol, 0.2 equiv.) were dissolved in 3 mL 1,4-dioxane and transferred to a Schlenk flask. The flask was deoxygenated by 3 cycles of freeze-pump-thaw. It was then immersed in an oil bath at 70 °C for 24 h. The block copolymer was purified by precipitation in *n*-hexane once and dried in the vacuum oven at 40 °C until constant weight to yield a yellow solid (0.70 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) (**Figure S2**): δ 4.05 (b, 32H), 3.45-3.80 (m, 434H), 3.36 (s, 3H), 2.55 (b, 66H), 2.27 (b, 189H), 1.80 (b, 54H), 1.24 (b, 25H), 0.88-1.04 (m, 89H). GPC (DMF, PMMA standards): M_n =13,800 g/mol, $Đ$ = 1.17.

Synthesis of polymeric colloids by thermal-RAFT-PISA. The following representative protocol was used for the thermally-initiated RAFT dispersion PISA (thermal-RAFT-PISA) process for the synthesis of PEG_{113}-*b*-$PDMAEMA_{32}$-*b*-$PHPMA_{398}$-CDTPA. HPMA monomer was disinhibited by passing through a column of basic alumina, it was further purified by passing through a silica gel column (*n*-hexane: diethyl ether= 1:1 as eluent) to remove any dimethacrylate impurity. PEG_{113}-*b*-$PDMAEMA_{32}$-CDTPA macro-CTA (30.62 mg, 2.94 μmol, 1.0 equiv.) was dissolved in ultrapure water (1.80 mL, 10% w/w). HPMA monomer (169.4 mg, 1.175 mmol, 400 equiv.) and VA-044 initiator (0.297 mg, 0.918 μmol, 0.3125 equiv.) were then added in a 10 mL round-bottom flask. The flask was sealed with a rubber septum and purged gently with argon gas for 15 minutes. Reaction was carried out at 50 °C for 4 hours with stirring at a constant speed of 700 rounds per minute (rpm), and quenched upon exposure to air.

Ultrasound-assisted *in situ* synthesis of PMNCs. A representative procedure for the preparation of gold-based PMNCs (Au@PEG_{113}-*b*-$PDMAEMA_{32}$-*b*-$PHPMA_{398}$-CDTPA) is as follows: 4.7 μL $NaAuCl_4$ solution (0.1 mmol/mL) and 20 μL PNVP (0.2 mg/mL) were mixed with 20 μL of the diluted polymer nanoparticles (0.2 mg polymer/mL, containing 0.00047 mmol/mL tertiary amine group), and topped up to 1 mL with ultrapure water in a 3 mL screw-cap glass vial. The contents were purged with argon for 5 min and properly sealed. The vial

was then immersed into an ultrasonic water bath comprising the ultrasonic generator (Shinka, SF-400) operating at 400 kHz, 100W, maintained at room temperature (~23 °C) for 2 hours throughout the reaction process. A colour change can be observed for the successful reduction of pale-yellow Au (III) ions to magenta AuNPs.

For the stepwise growth of AuNPs, an identical method was performed as described above, except those subsequent additions comprises 4.7 μL $NaAuCl_4$ solution (0.1 mmol/mL) and freshly prepared 14.1 μL $NaBH_4$ solution (0.1 mmol/mL) with at least 5 minutes interval between each addition.

For the formation of PNVP-stabilized AuNPs, a similar method was performed as describe above, except that polymer nanoparticles were not added.

For the preparation of PMNCs containing bi/tri-metallic compositions, a similar step was performed as described above, except that the same amount of Na_2PdCl_4 and $AgNO_3$ were added as required to form the different combinations of PMNCs.

Typical procedure for aerobic alcohol oxidation using Au-based PMNCs. A representative procedure is a follows: The aqueous dispersion of Au@PEG_{113}-*b*-$PDMAEMA_{32}$-*b*-$PHPMA_{398}$-CDTPA (425.5 μL, 1.0 mM Au-containing solution, 0.02 mol%), 1-phenylethanol (122.2 mg, 1.0 mmol, 1.0 equiv.), *tert*-butyl hydroperoxide (70% wt in water) (372.1 mg, 2.5 mmol, 2.5 equiv.), KOH (168.3 mg, 3.0 mmol, 3.0 equiv.) and ultrapure water (4.5 mL) were added into a round bottom flask equipped with a magnetic stirring bar (washed with aqua regia). The flask was then sealed properly with a rubber septum and the mixture was stirred at 80 °C for 2 hours. 0.5 mL of the reaction mixture was withdrawn from the flask and extracted once with $CDCl_3$ to determine the conversion of 1-phenylethanol to acetophenone by ^1H NMR analysis (**Figure S12**).

Typical procedure for Suzuki-Miyaura cross coupling reaction using Pd-based PMNCs. A representative procedure is as follows: 4-Iodophenol (55 mg, 0.25 mmol, 1.0 equiv.), phenylboronic acid (30.5 mg, 0.25 mmol, 1.0 equiv.), K_2CO_3 (103.7 mg, 0.75 mmol, 3.0 equiv.), ultrapure water (5 mL) and Pd@PEG_{113}-*b*-$PDMAEMA_{32}$-*b*-$PHPMA_{398}$-CDTPA (100 μL, 1.0 mM Pd-containing solution, 0.02 mol%) were added to a 50 mL screw cap vial equipped with a magnetic stirring bar (washed with aqua regia). The vial was then sealed properly with a cap and the mixture was stirred at 70 °C for 1 hour. 5.0 mL methanol was then added to the reaction mixture to dissolve the product and any unreacted starting materials. 1.0 mL solution was collected and dried, the solid was dissolved in $CDCl_3$ and ^1H NMR spectrum

(**Figure S13**) was taken for determining conversion. For kinetic studies, 0.3 mL of the reaction mixture was withdrawn and dissolved in $CDCl_3$ every 10 minutes for a total reaction period of 1 hour. For reusability studies, new batches of starting materials were weighed and added directly into the reaction mixture at every 1-hour interval, up till a total reaction time of 5 hours.

2. Supplementary Figures and Tables

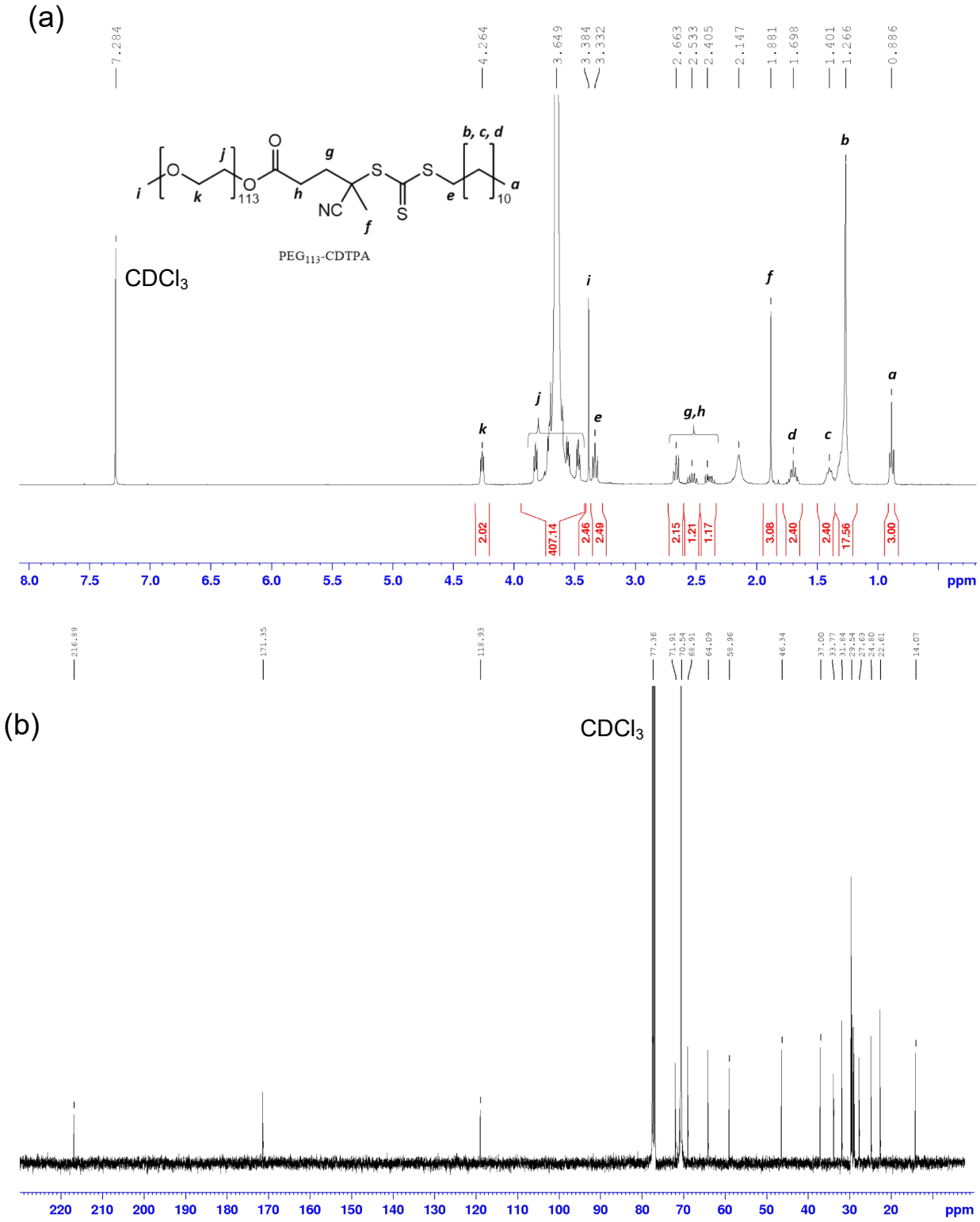

Figure S1. (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum of PEG_{113}-CDTPA. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26 (t, 3H), 3.46-3.83 (m, 452H), 3.38 (s, 3H), 3.33 (t, 3H), 2.33-2.70 (m, 4H), 1.88 (s, 3H), 1.70 (m, 2H), 1.22-1.41 (b, 18H), 0.89 (t, 3H). ^{13}C NMR (150 MHz,

$CDCl_3$): δ 216.9, 171.4, 119.0, 71.9, 70.5, 68.9, 64.1, 59.0, 46.3, 37.0, 33.8, 31.8, 29.5, 27.6, 24.8, 22.6, 14.1.

Table S1. Characterisation data values for PEG_{113}-CDTPA and the corresponding PEG_{113}-*b*-PDMAEMA-CDTPA block copolymers with varying DP of DMAEMA units.

Entry	Sample[a]	M_n (g/mol)			$Đ^e$
		$M_{n,NMR}{}^b$	$M_{n,theoretical}{}^c$	$M_{n,GPC}{}^d$	
1	PEG_{113}-CDTPA	5400	-	11000	1.14
2	PEG_{113}-$PDMAEMA_{16}$-CDTPA	7900	8500	12800	1.19
3	PEG_{113}-$PDMAEMA_{32}$-CDTPA	10400	10900	13800	1.17
4	PEG_{113}-$PDMAEMA_{50}$-CDTPA	13300	14000	16000	1.18

[a]DP and conversion of listed polymer samples are determined from ^{1}H NMR (Figure S2 - S4), by analysing the integral ratio of the *N,N'*-dimethyl protons against the methyl protons of the CH_3 group towards the end of the PEG_{113} moiety at approximately 3.3 ppm. [b]$M_{n,NMR}$ = (integral value of the *N,N'*-dimethyl protons/6) × $M_{n,DMAEMA}$ + $M_{n,PEG113\text{-}CDTPA}$. [c]$M_{n,theoretical}$ = $M_{n,DMAEMA}$ × ([DMAEMA]/[PEG_{113}-CDTPA]) + $M_{n,PEG113\text{-}CDTPA}$. [d]As determined from GPC (DMF, PMMA standards). [e]Dispersity values determined from GPC.

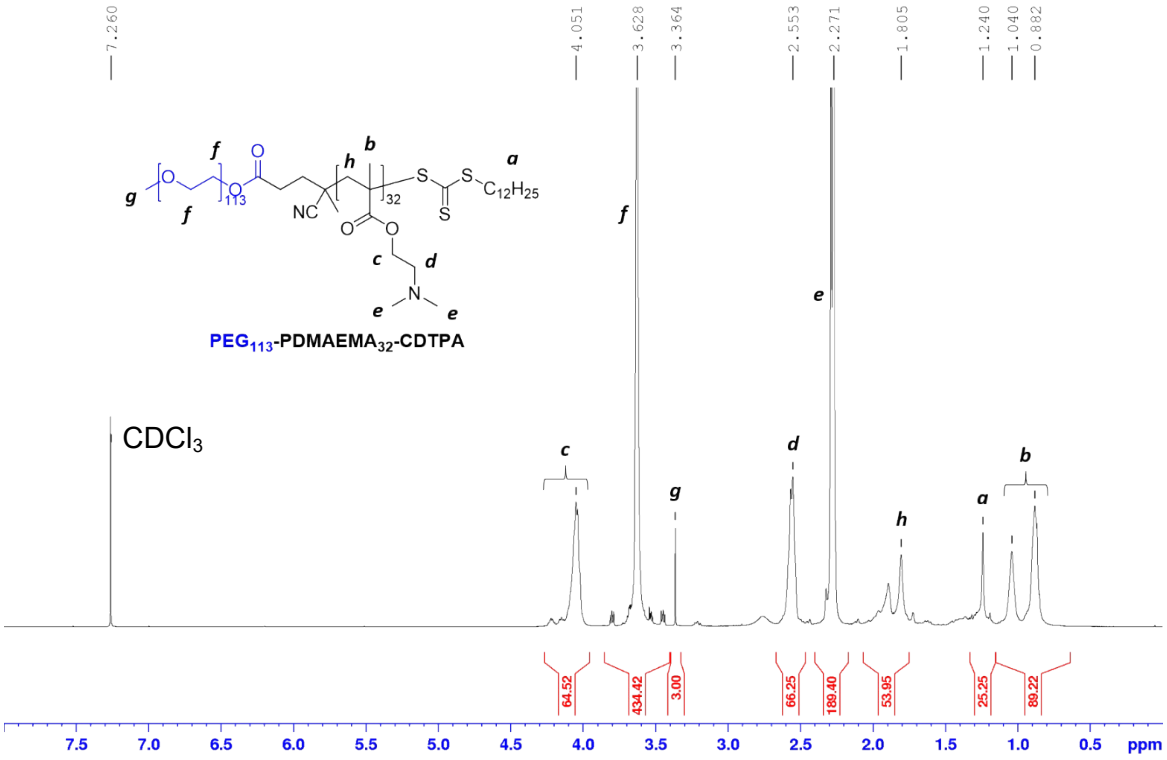

Figure S2: ^{1}H NMR spectrum of PEG_{113}-$PDMAEMA_{32}$-CDTPA. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (b, 32H), 3.45-3.80 (m, 434H), 3.36 (s, 3H), 2.55 (b, 66H), 2.27 (b, 189H), 1.80 (b, 54H), 1.24 (b, 25H), 0.88-1.04 (m, 89H).

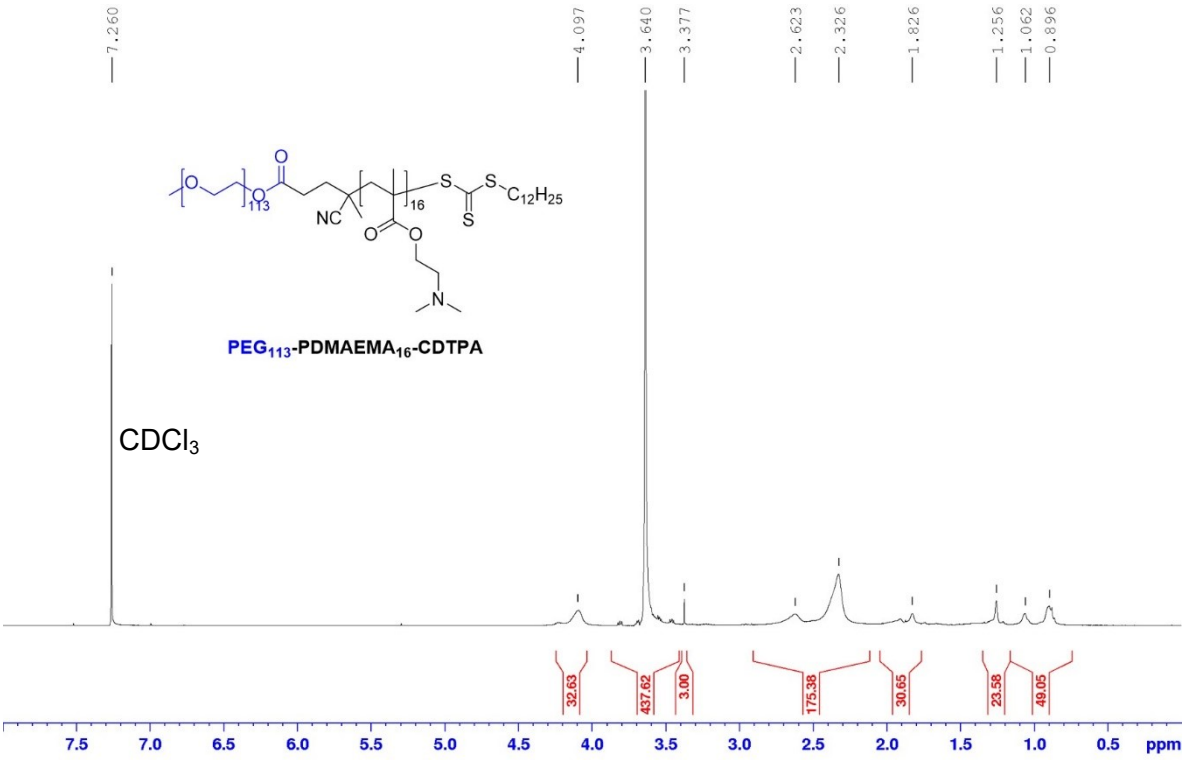

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PEG_{113}-$PDMAEMA_{16}$-CDTPA.

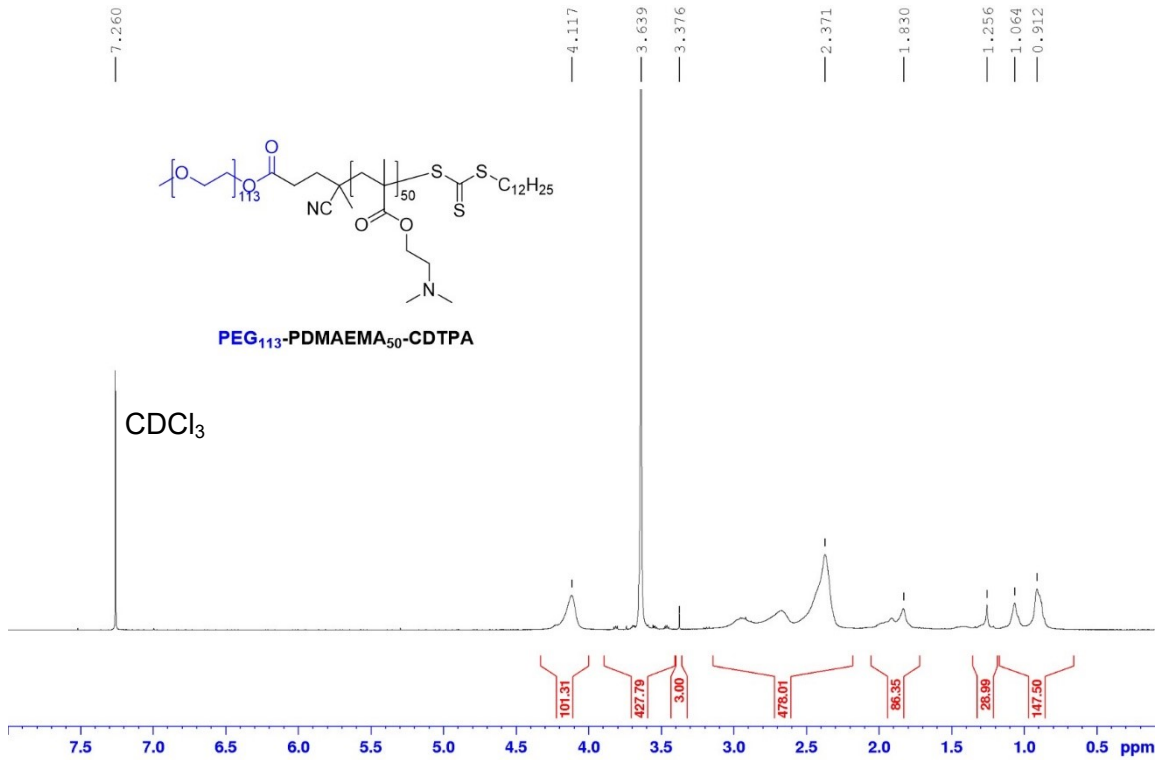

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PEG_{113}-$PDMAEMA_{50}$-CDTPA.

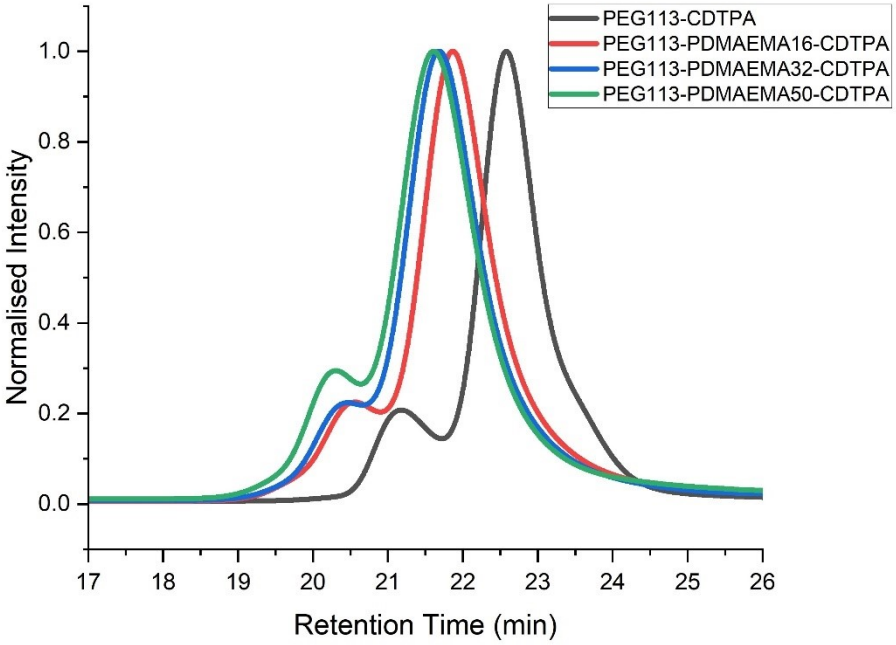

Figure S5. Normalised GPC trace (using PMMA standards) obtained for PEG_{113}-CDTPA and PEG_{113}-*b*-PDMAEMA-CDTPA.

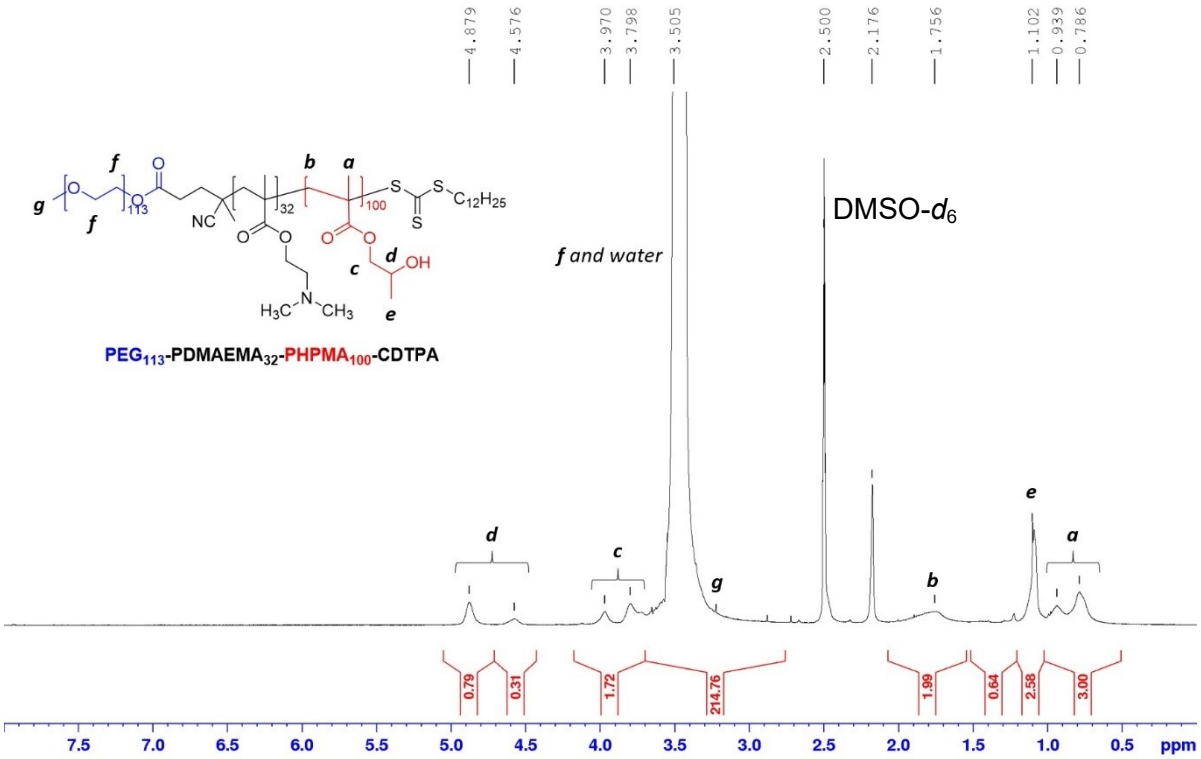

Figure S6. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG_{113}-$PDMAEMA_{32}$-$PHPMA_{100}$-CDTPA synthesised by thermal-RAFT-PISA.

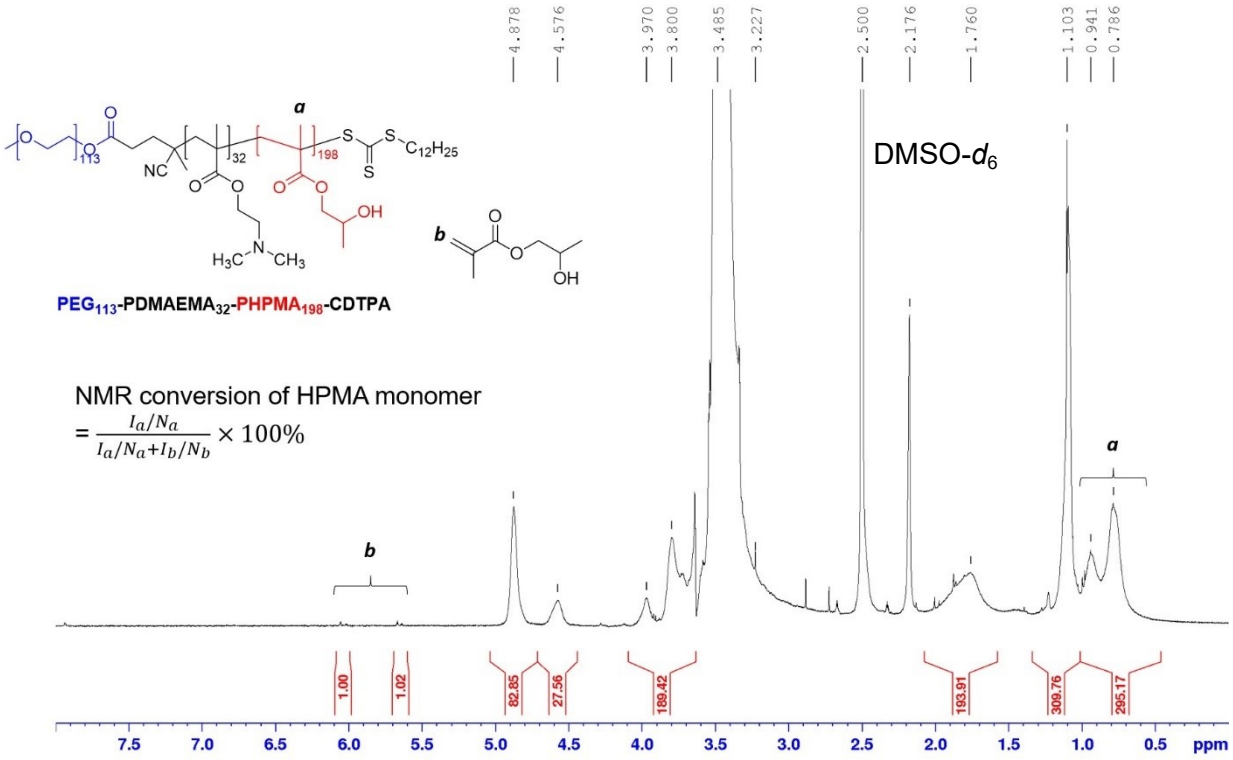

Figure S7. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG$_{113}$-PDMAEMA$_{32}$-PHPMA$_{198}$-CDTPA synthesised by thermal-RAFT-PISA displaying HPMA monomer NMR conversion. NMR conversion = [295.17/3]/[(295.17/3)+((1.00+1.02)/2)] × 100% = 99.0%

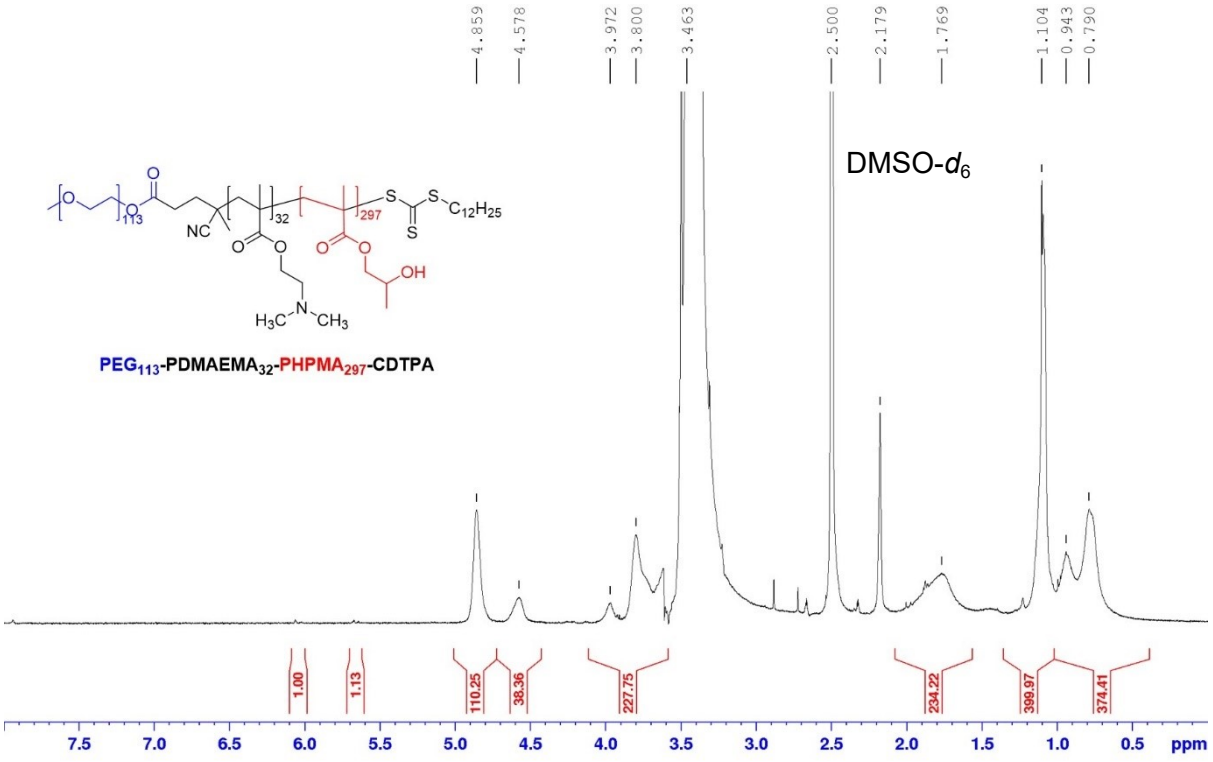

Figure S8. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG$_{113}$-PDMAEMA$_{32}$-PHPMA$_{297}$-CDTPA.

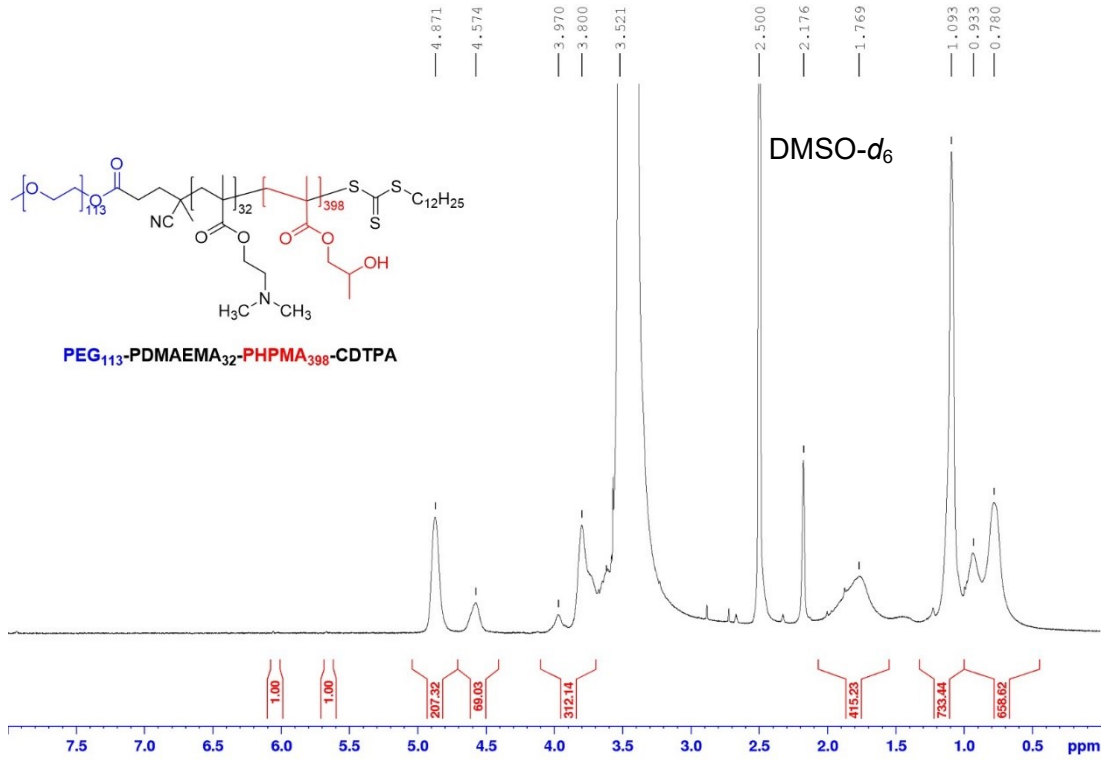

Figure S9. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG_{113}-$PDMAEMA_{32}$-$PHPMA_{398}$-CDTPA.

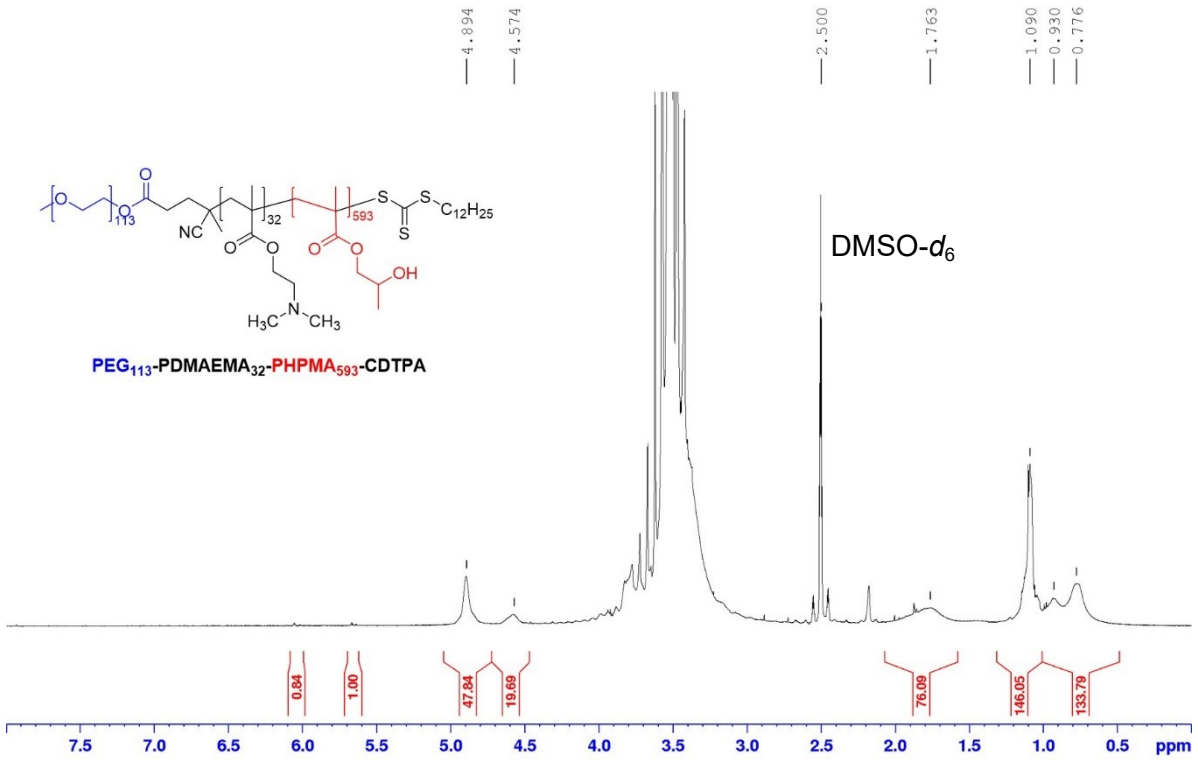

Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG_{113}-$PDMAEMA_{32}$-$PHPMA_{593}$-CDTPA.

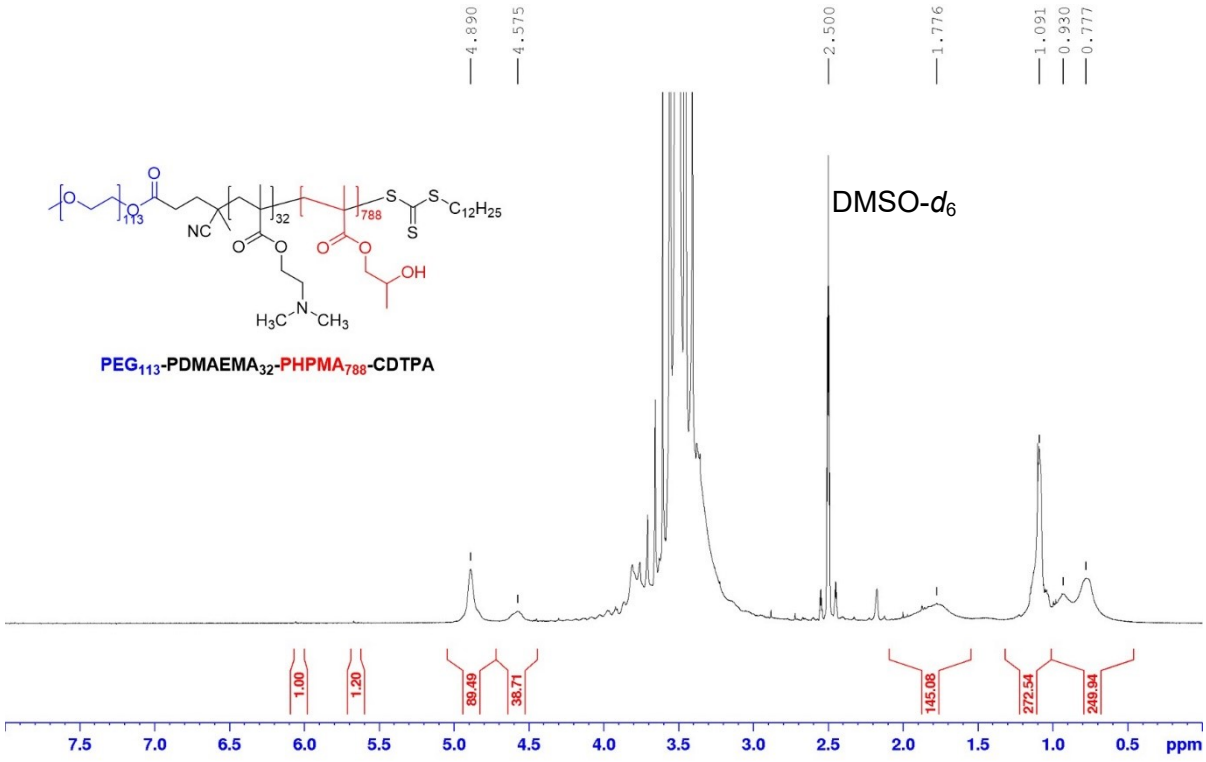

Figure S11. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEG$_{113}$-PDMAEMA$_{32}$-PHPMA$_{788}$-CDTPA.

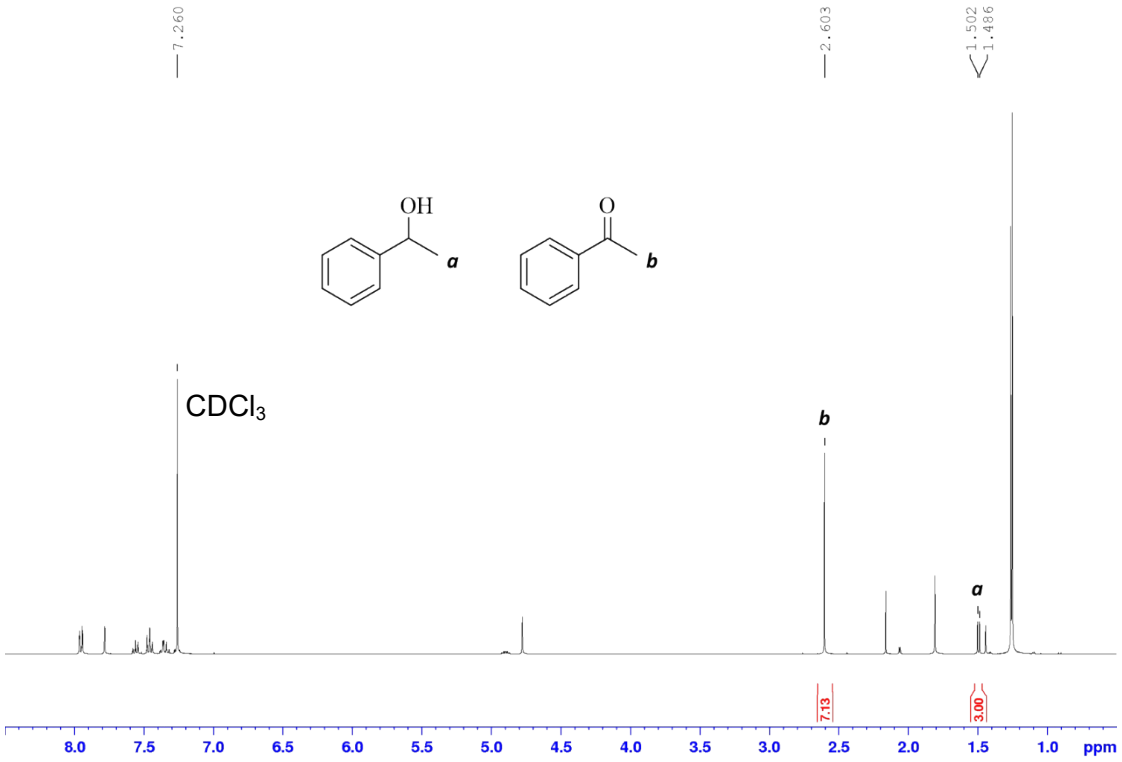

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-phenylethanol oxidation to acetophenone using Au@PEG$_{113}$-PDMAEMA$_{32}$-PHPMA$_{398}$-CDTPA (Stepwise growth: Step 5) as catalyst.

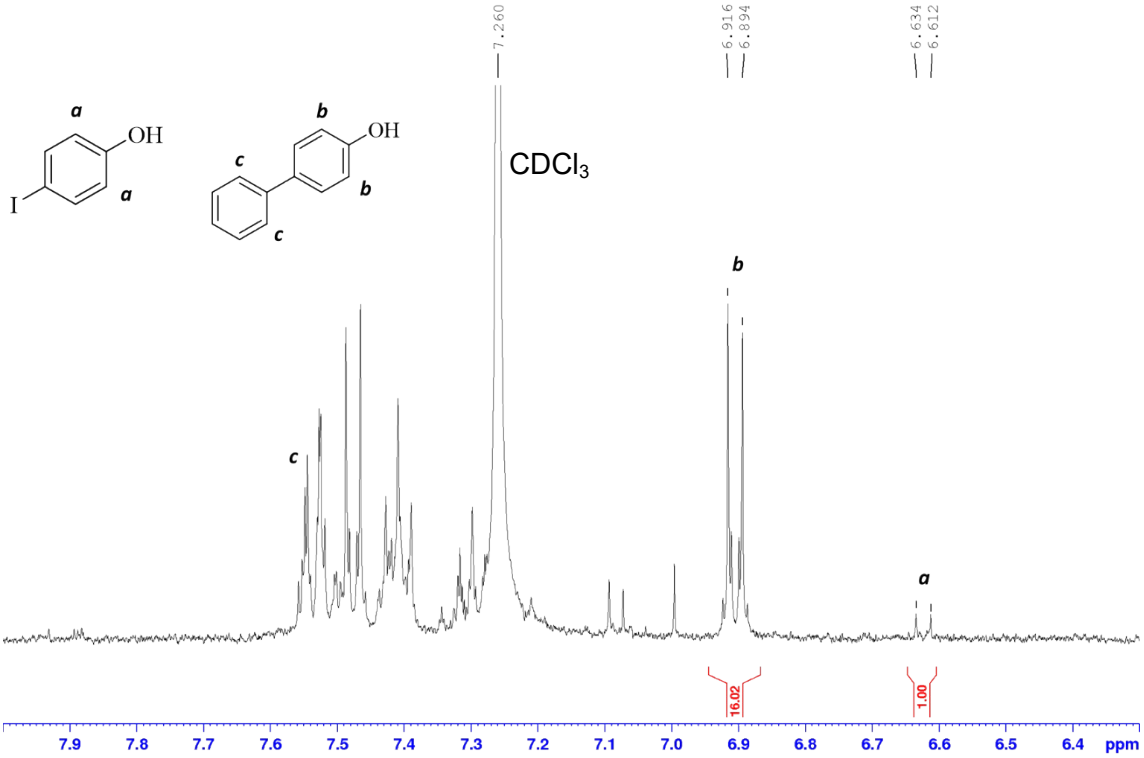

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Suzuki-Miyaura cross-coupling reaction between 4-iodophenol and phenylboronic acid to form 4-phenylphenol using Pd@PEG_{113}-$PDMAEMA_{32}$-$PHPMA_{398}$-CDTPA as catalyst.

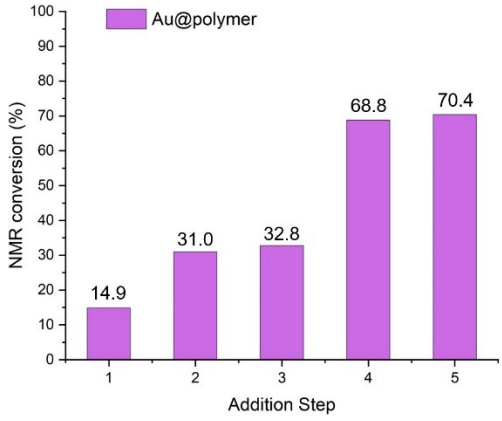

Figure S14. Stepwise growth of AuNPs for Au@PEG_{113}-*b*-$PDMAEMA_{32}$-*b*-$PHPMA_{398}$-CDTPA PMNCs catalyst, plotted against NMR conversion values for each addition step.