Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Synthesis of Multiple Shaped Gold Nanoparticles using Wet Chemical Method by Different Dendritic Peptides at Room Temperature

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Experimental

Reagents

HOBt (1-hydroxy benzotriazole), DCC (dicyclohexyl carbodiimide) and aminoacids (L-Glutamic acid and L-Tyrosine) were purchased from Sigma chemicals. Hydrogen tetrachloroaurate trihydrate (HAuCl4. 3H2O, 99.9%) were purchased from Aldrich and used without further purification. Sodium Hydroxide (Merck, India) and other AR grade chemicals were used as received. HPLC grade water and methanol was used throughout the experiment.

General method of Synthesis

The dendritic L-glutamic acid derivatives with ethyl protecting groups on the surface were synthesized by conventional solution phase method by using racemization-free fragment condensation strategy. The Boc group was used for N-terminal protection and the C-terminus was protected as ethyl ester. Couplings were mediated by dicyclohexylcarbodiimide-1-hydroxybenzotriazole (DCC/HOBt). All intermediates were characterized by ^{1}H-NMR (300MHz) and thin layer chromatography (TLC) on silica gel and used without further purification. The final products (dendrons) were purified by column chromatography using silica (100-200-mesh size) gel as stationary phase and chloroform-methanol (95:5) mixture as eluent. The purified dendrons have been fully characterized by 300 MHz ^{1}H -NMR spectroscopy.

Synthesis of dendrons

(i) Compound **A**: A sample of Boc-Glu-OH (2.47g, 10 mmol) dissolved in dimethylformamide (DMF) (30 mL) was cooled in an ice-water bath and H-Glu-$(OEt)_2$ was isolated from 6.1 g (25.0 mmol) of the corresponding ethyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 mL. It was then added to the reaction mixture, followed immediately by 4.12 g (20.0 mmol) DCC and 2.70 g (20.0 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken up in ethyl acetate (40 mL) and the DCU was filtered off. The organic layer was washed with 2N HCl (3 × 40 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 40 mL), brine (2 × 40 mL), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield **A** of white solid. Purification was done by silica gel column (100-200mesh) using chloroform-methanol (95:5) as eluent.

Yield = 5.13 g (8.3 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.24-1.31 (m, 12H), 1.42 (s, 9H), 1.92-2.47 (m, 12H), 4.08 (m, 1H), 4.11-4.24 (m, 8H), 4.65-4.75 (m, 2H), 5.04-5.06 (broad, 1H), 7.63-7.66 (broad, 1H), 7.87-7.91 (broad, 1H); MS (HRMS) m/z 640.3921 $(M+Na)^+$, m/z 641.4114 $(M+H+Na)^+$. Anal. Calcd. for $C_{28}H_{47}N_3O_{12}$ (617.68): C, 54.45; N, 6.80; H, 7.67. Found: C, 54.50; N, 6.90; H, 7.58.

(ii) Compound **B**: To 3.08 g (5.00 mmol) of **A**, 5 ml of trifluoroacetic acid was added and the removal of Boc group monitored by TLC. After 2 hr, trifluoroacetic acid was removed under *vacuum* .The residue was taken in water (20-30ml) and washed with diethyl ether (2 × 30ml). The pH of the aqueous solution was then adjusted to 8 with sodiumbicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 30ml), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield the white solid **B**.

Yield = 2.07 g (4.0 mmol, 80%). ^{1}H NMR (300 MHz, $CDCL_3$, δ ppm): 1.23-1.33 (m, 12H), 1.92-2.46 (m, 12H), 3.31-3.34 (m, 1H), 4.10-4.25 (m, 8H), 4.61-4.72 (m, 2H), 7.68 (d, *J*=7.5, 1H), 8.09 (d, *J*=7.1, 1H); MS (HRMS) m/z 518.0981$(M+H)^+$, m/z 540.0797 $(M+Na)^+$. Anal. Calcd. for $C_{23}H_{39}N_3O_{10}$ (517.570): C, 53.33; N, 8.11; H, 7.54. Found: C, 5340; N, 8.12; H, 7.50.

(iii) Compound **C**: A sample of Boc-Glu-OH (2.33g, 3 mmol) dissolved in dimethylformamide (DMF) (30 mL) was cooled in an ice-water bath and 2.90 g (2.0 mmol) of B was then added to the reaction mixture, followed immediately by 0.82 g (2.0 mmol) DCC and 0.54 g (2.0 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken up in ethyl acetate (40 mL) and the DCU was filtered off. The organic layer was washed with 2N HCl (3 × 40 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 40 mL), brine (2 × 40 mL), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield **C** of white solid. Purification was done by silica gel column (100-200mesh) using chloroform-methanol (95:5) as eluent.

Yield = 3.24 g (2.6 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.21-1.32 (m, 24H), 1.39 (s, 9H), 1.91-2.47 (m, 28H), 4.07-4.24 (m, 16H), 4.65-4.68 (m, 3H), 4.89 (broad, 3H), 7.70-7.80 (broad, 3H), 8.22-8.25 (broad, 2H), 8.50 (d, *J*=6.45, 1H); MS (HRMS) m/z 576.0724 $(M+H)^+$, m/z 599.0183 $(M+Na)^+$. Anal. Calcd. for $C_{56}H_{91}N_7O_{24}$ (1246.354): C, 53.92; N, 7.86; H, 7.30. Found: C, 553.80; N, 7.91; H, 7.20.

(iv) Compound **D**: To 2.88 g (4 mmol) of **C**, 5 ml of trifluoroacetic acid was added and the removal of Boc group monitored by TLC. After 2 hr, trifluoroacetic acid was removed under *vacuum* .The residue was taken in water (20-30ml) and washed with diethyl ether (2 × 30ml). The pH of the aqueous solution was then adjusted to 8 with sodiumbicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 30ml), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield the white solid **D**.

Yield = 2.30 g (2 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.21-1.33 (m, 24H), 1.91-2.48 (m, 28H), 2.90-3.11 (m, 1H), 4.07-4.26 (m, 16H), 4.65-4.68 (m, 4H), 4.68-4.84 (m, 2H), 7.74-7.85 (m, 3H), 8.21-8.25 (m, 3H), 8.47 (d, *J*=6.51, 1H); MS (HRMS) m/z 1147.1315$(M+H)^+$, m/z 1169.1119 $(M+Na)^+$, 1170.1217 $(M+Na+H)^+$. Anal. Calcd. for $C_{51}H_{83}N_7O_{22}$ (1146.239): C, 53.39; N, 8.55; H, 7.24. Found: C, 53.42; N, 9.01; H, 7.20.

(v) Synthesis of Compound **E:** A sample of Boc-Tyr-OH (0.236 g, 5 mmol) dissolved in dimethylformamide (DMF) (15 mL) was cooled in an ice-water bath and H-Glu-OEt was isolated from 1.84 g (10.0 mmol) of the corresponding ethyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 8 mL followed immediately by 0.82 g (5 mmol) DCC and 0.54 g (5.0 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken up in ethyl acetate (40 mL) and the DCU was filtered off. The organic layer was washed with 2N HCl (3 × 40 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 40 mL), brine (2 × 40 mL), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield **E** of white solid. Purification was done by silica gel column (100-200mesh) using chloroform-methanol (95:5) as eluent.

Yield = 2.07 g (4 mmol, 50.0%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.22-1.29 (m, 6H), 1.42 (s, 9H), 1.19-2.34 (m, 4H), 2.90-3.00 (m, 2H), 4.09-4.22 (m, 4H), 4.29-4.31 (m, 1H), 4.50-4.57 (m, 1H), 5.07 (broad, 1H), 6.66 (d, *J*=6.50, 1H), 6.74 (d, *J*= 8.31, 2H), 7.02 (d, *J*= 8.25, 2H). MS (HRMS) m/z 489.3525 $(M+Na)^+$, m/z 490.3625 $(M+Na+H)^+$. Anal. Calcd. for $C_{23}H_{34}N_2O_8$ (466.525): C, 59.16; N, 7.29; H, 6.00. Found: C, 59.10; N, 7.30; H, 6.20.

(vi) Synthesis of Compound **F**: A sample of Boc-Tyr-OH (0.236 g, 2 mmol) dissolved in dimethylformamide (DMF) (15 mL) was cooled in an ice-water bath and 2.90 g (2.0 mmol) of **B** was then added to the reaction mixture, followed immediately by 0.82 g (2.0 mmol) DCC and 0.54 g (2.0 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken up in ethyl acetate (40 mL) and the DCU was filtered off. The organic layer was washed with 2N HCl (3 × 40 mL), brine (2 × 50 mL), 1 M sodium carbonate (3 × 40 mL), brine (2 × 40 mL), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield **F** of white solid. Purification was done by silica gel column (100-200mesh) using chloroform-methanol (95:5) as eluent.

Yield = 1.17 g (1.5 mmol, 50.0%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.07-1.33 (m, 12H), 1.42 (s, 9H), 1.70-2.48 (m, 12H), 3.71-3.74 (m, 2H), 4.12-4.27 (m, 10H), 4.61-4.64 (m, 2H), 5.12 (d, *J*=7.68, 1H), 6.75 (d, *J*=8.31, 2H), 7.01 (d, *J*= 8.04, 2H), 7.51 (broad, 1H), 7.81 (broad, 1H). MS (HRMS) m/z 803.6011 $(M+Na)^+$, m/z 804.6061 $(M+Na+H)^+$. Anal. Calcd. for $C_{37}H_{56}N_4O_{14}$ (780.859): C, 56.86; N, 7.17; H, 7.17. Found: C, 56.40; N, 8.01; H, 7.20.

(vii) Synthesis of Compound **G**: A sample of Boc-Tyr-OH (0.33 g, 2 mmol) dissolved in dimethylformamide (DMF) (15 mL) was cooled in an ice-water bath and 1.90 g (2.0 mmol) of **D** was then added to the reaction mixture, followed immediately by 0.82 g (2.0 mmol) DCC and 0.54 g (2.0 mmol) of HOBt. The reaction mixture was stirred for three days. The residue was taken up in ethyl acetate (40 mL) and the DCU was filtered off. The organic layer was washed with 2N HCl (3x40 mL), brine (2 x 50 mL), 1 M sodium carbonate (3 × 40 mL), brine (2 × 40 mL), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield **G** of white solid. Purification was done by silica gel column (100-200mesh) using chloroform-methanol (95:5) as eluent.

Yield = 2.11 g (1.5 mmol, 50.0%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.18-1.37 (m, 24H), 1.45 (s, 9H), 1.52-2.49 (m, 28H), 2.79 (m, 2H), 4.10-4.17 (m, 16H), 4.18-4.25 (m, 4H), 4.66-4.69 (m, 2H), 4.88 (m, 2H), 5.43 (d, *J*=7.74, 1H), 5.53 (d, *J*=8.73, 2H), 6.67 (d, *J*= 8.25, 2H), 6.92 (d, *J*= 8.01, 2H), 7.86 (d, *J*= 8.88, 1H), 8.06 (d, *J*= 6.69, 1H), 8.20-8.27 (m, 2H), 8.45 (d, *J*= 9.40, 1H), 8.59 (broad, 1H). MS (HRMS) m/z 1432.4199 $(M+Na)^+$, m/z 1433.4127 $(M+H+Na)^+$. Anal. Calcd. for $C_{65}H_{100}N_8O_{26}$ (1409.528): C, 55.39; N, 7.95; H, 7.15. Found: C, 55.40; N, 8.10; H, 6.96.

(viii) Compound **G1**: To 2.88 g (1.00 mmol) of **E**, 2.5 ml of trifluoroacetic acid was added and the removal of Boc group monitored by TLC. After 2 hr, trifluoroacetic acid was removed under *vacuum* .The residue was taken in water (20-30ml) and washed with diethyl ether (2 × 30ml). The pH of the aqueous solution was then adjusted to 8 with sodiumbicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 30ml), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield the white solid **G1**.

Yield = 1.90 g (0.8 mmol, 80%). $[\alpha]_D^{20}$ –14.0 (c = 0.5 M, MeOH).

^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): 1.05-1.22 (m, 6H), 1.73-1.75 (m, 2H), 2.67-2.72 (m, 2H), 2.98-3.03 (m, 2H), 3.66 (m, 1H), 3.94-4.01 (m, 4H), 4.08 (m, 1H), 6.61 (d, *J* = 7.93, 2H), 6.91 (d, *J*=7.99, 2H), 8.08 (d, *J*= 7.93, 1H), 9.14 (broad, 1H); MS (HRMS) m/z 367.0438$(M+H)^+$, m/z 404.9992 $(M+K)^+$. ^{13}C NMR (75 MHz, RT, $CDCl_3$, δ ppm): 14.88, 29.44, 29.53, 38.12, 53.81, 56.32, 60.61, 115.65, 126.65, 132.05, 157.27, 167.30, 167.40, and 173.06. Anal. Calcd. for $C_{18}H_{26}N_2O_6$ (366.409): C, 59.00; N, 7.65; H, 7.15. Found: C, 59.40; N, 7.70; H, 7.10.

(ix) Compound **G2**: To 2.88 g (1.00 mmol) of **F**, 2.5 ml of trifluoroacetic acid was added and the removal of Boc group monitored by TLC. After 2 hr, trifluoroacetic acid was removed under *vacuum* .The residue was taken in water (20-30ml) and washed with diethyl ether (2 × 30ml). The pH of the aqueous solution was then adjusted to 8 with sodiumbicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 30ml), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield the white solid **G2**.

Yield = 0.672 g (0.8 mmol, 80%). $[\alpha]_D^{20}$ –15.0 (c = 0.5 M, MeOH).

^{1}H NMR (600 MHz, DMSO-d_6, δ ppm): 1.13-1.18 (m, 12H), 1.79-1.86 (m, 4H), 1.93-2.01 (m, 2H), 2.16-2.19 (m, 2H), 2.31-2.39 (m, 4H), 2.89-2.92 (m, 2H), 4.02-4.10 (m, 8H), 4.20-4.28 (m, 3H), 4.33-4.34 (m, 1H), 6.67 (d, *J*=8.4, 2H), 7.0 (d, *J*=8.4, 2H), 7.78 (d, *J*=8.4, 2H), 8.24 (d, *J*=7.8, 2H), 8.45 (d, *J*=7.2, 2H), 9.25 (broad, 1H); MS (HRMS) m/z 681.5450$(M+H)^+$, m/z 703.5477 $(M+Na)^+$.

^{13}C NMR (75 MHz, RT, $CDCl_3$, δ ppm): 13.44, 13.51, 13.55, 25.44, 25.53, 28.06, 29.31, 29.40, 30.75, 50.74, 50.98, 55.27, 59.45, 60.03, 60.18, 114.56, 127.47, 129.68, 155.37, 170.83, 170.88, 171.31, 171.40, 171.60, 172.77. Anal. Calcd. for $C_{32}H_{48}N_4O_{12}$ (680.743): C, 56.46; N, 8.23; H, 7.11. Found: C, 56.44; N, 8.30; H, 6.95.

(x) Compound **G3**: To 2.88 g (1.00 mmol) of **G**, 2.5 ml of trifluoroacetic acid was added and the removal of Boc group monitored by TLC. After 2 h, trifluoroacetic acid was removed under *vacuum* .The residue was taken in water (20-30ml) and washed with diethyl ether (2 × 30ml). The pH of the aqueous solution was then adjusted to 8 with sodiumbicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 30ml), dried over anhydrous sodium sulfate and evaporated in *vacuum* to yield the white solid **G3**.

Yield = 1.10 g (0.5 mmol, 80%). $[\alpha]_D^{20}$ –12.5 (c = 0.5 M, MeOH).

^{1}H NMR (600 MHz, DMSO-d_6, δ ppm): 1.14-1.18 (m, 24H), 1.77-1.97 (m, 14H), 2.18-2.39 (m, 14H), 3.01 (m, 2H), 4.01-4.09 (m, 16H), 4.20-4.31 (m, 8H), 6.69 (d, *J*=8.4, 2H), 7.04 (d, *J*=8.4, 2H), 8.03 (d, *J*=7.8, 1H), 8.21 (d, *J*=5.3, 1H), 8.22 (d, *J*=5.1, 1H), 8.32 (d, *J*=7.2, 1H), 8.42 (d, *J*=7.2, 1H), 8.43 (d, *J*=6.6, 1H), 8.62 (broad, 1H), 9.33 (broad, 1H); MS (HRMS) m/z 1310.1316$(M+H)^+$, m/z 1332.1250 $(M+Na)^+$. ^{13}C NMR (75 MHz, RT, $CDCl_3$, δ ppm): 13.43, 13.50, 13.56, 23.96, 24.83, 25.44, 25.54, 29.27, 29.33, 29.39, 31.05, 50.73, 50.77, 50.82, 50.87, 59.47, 60.07, 60.19, 114.91, 124.32, 129.98, 156.07, 167.52, 170.09, 170.91, 171.08, 171.19,171.28, 171.30, 171.42, 171.44, 171.59, 171.62, 173.13. Anal. Calcd. for $C_{60}H_{92}N_8O_{24}$ (1309.412): C, 55.04; N, 8.56; H, 7.08. Found: C, 54.81; N, 8.62; H, 7.00.

Preparation of Dendron-gold nanoparticle

An aqueous solution (100 μL) of $HAuCl_4$ (10 mg in 1 mL) prepared from HPLC grade distilled water was mixed with a metanol-water solution of either **G1** (dendron 1) / **G2** (dendron 2) or **G3** (dendron 3) (8 mg in 2 mL) with vigorous starring. Then freshly prepared 1N NaOH solution was added to the solution to maintain the proper pH (~11) of the medium. In this case, after 4 hours a color change is observed from colorless solution to yellowish then light pink, bluish pink to violet blue for **G1**, **G2** and **G3** respectively. The solutions were then taken in eppendrop and the particles were separated out from the solution by rotating the solutions at 10 rpm and the that particles were again solubilized in water-methanol system.

NMR Study

All NMR studies were carried out on a Brüker DPX 300 MHz and Brüker DPX 600 MHz spectrometer at 300K. Compounds concentrations were in the range 1-10 mmol in $CDCl_3$ and $(CD_3)_2SO$.

Mass Spectroscopy

Mass spectra were recorded on a HEWLETT PACKARD Series 1100MSD and Micromass Qtof Micro YA263 mass spectrometer by positive mode electrospray ionization.

UV-VIS Spectra

UV-visible absorption spectra of the diluted as-prepared dendron-GNP were recorded by using a Hewlett-Packard 8453 UV-visible spectrophotometer.

TEM Study

One drop of dendron-GNP colloidal suspensions was placed on a carbon coated copper grid and allowed to air dry. The grid was then observed under a JEOL high-resolution transmission electron microscope (TEM) and imaged at an accelerating voltage of 200KV.

FT-IR Study

FT-IR studies were carried out in order to check the presence, and the nature of the interaction of **G1**, **G2** and **G3** molecules with the gold nanoparticles. FT-IR spectral characteristics of the samples, collected in transmittance mode were recorded from KBr pellets, prepared from by mixing the corresponding solid and dried sample with KBr in a 1:100 (wt/wt ratio) by using a shimadzu FT-IR-8400S spectrometer.

Dark Field Light Scattering Spectra

Dark Field Light Scattering images were taken from OLYMPUS (BX-UCB) reflected-light microscope with a computer attachment having Q-Capture software such that colors observed in the images are true and not artifacts of the detector. All the images are taken with a 10x magnification having maximum resolution.

Fluorescent Spectroscopic measurements

Fluorescence Spectroscopic measurement for the nanoconjugate obtained from the peptidic dendrons **G1, G2** and **G3** were obtained using a Perkin-Elmer spectroflurimeter. The GNP solutions of peptidic-dendron **G1, G2** and **G3** (dendron concentration: 5.88×10^{-6} M) were excited at 317 nm and the corresponding emissions spectra were recorded.

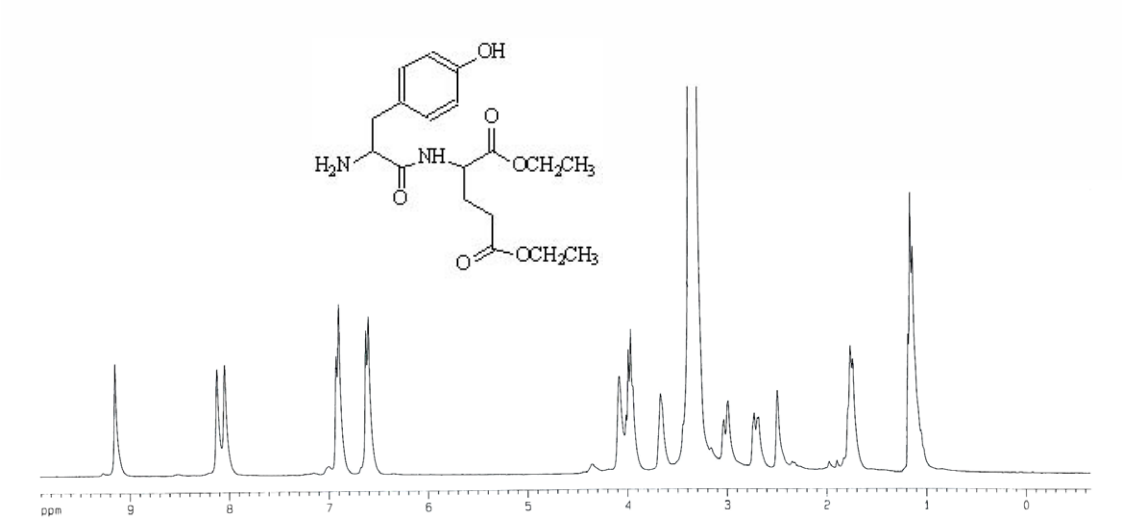

Fig. S1: 300MHz-^{1}H NMR Spectra of Dendron **G1**

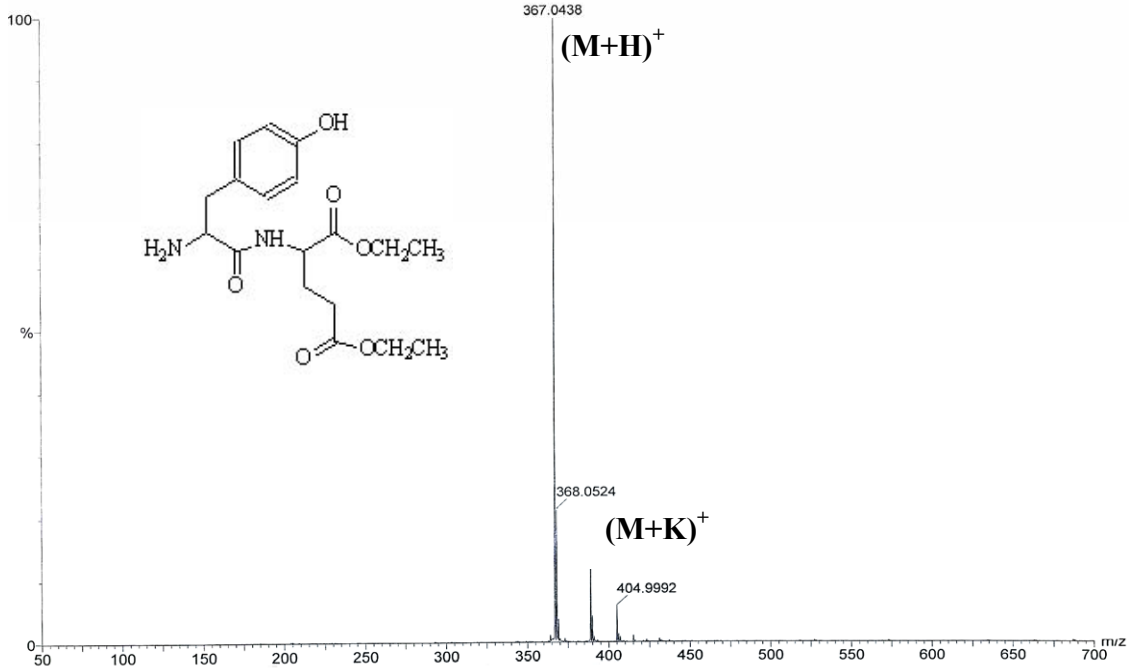

Fig. S2: HRMS Spectra of Dendron **G1**

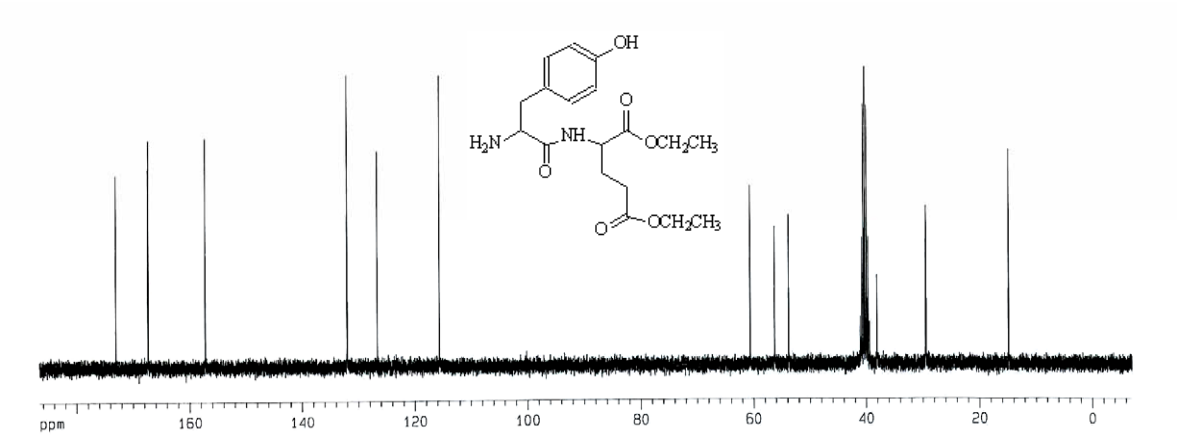

Fig. S3: ^{13}C NMR Spectra of Dendron **G1**

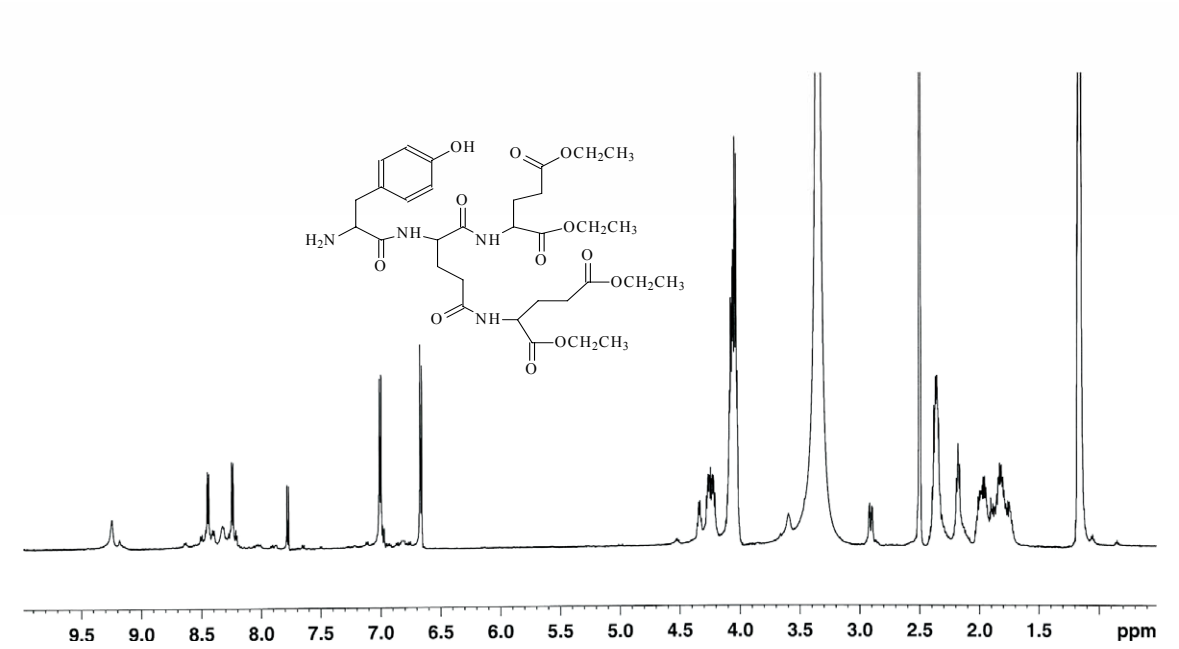

Fig. S4: 600MHz-^{1}H NMR Spectra of Dendron **G2**

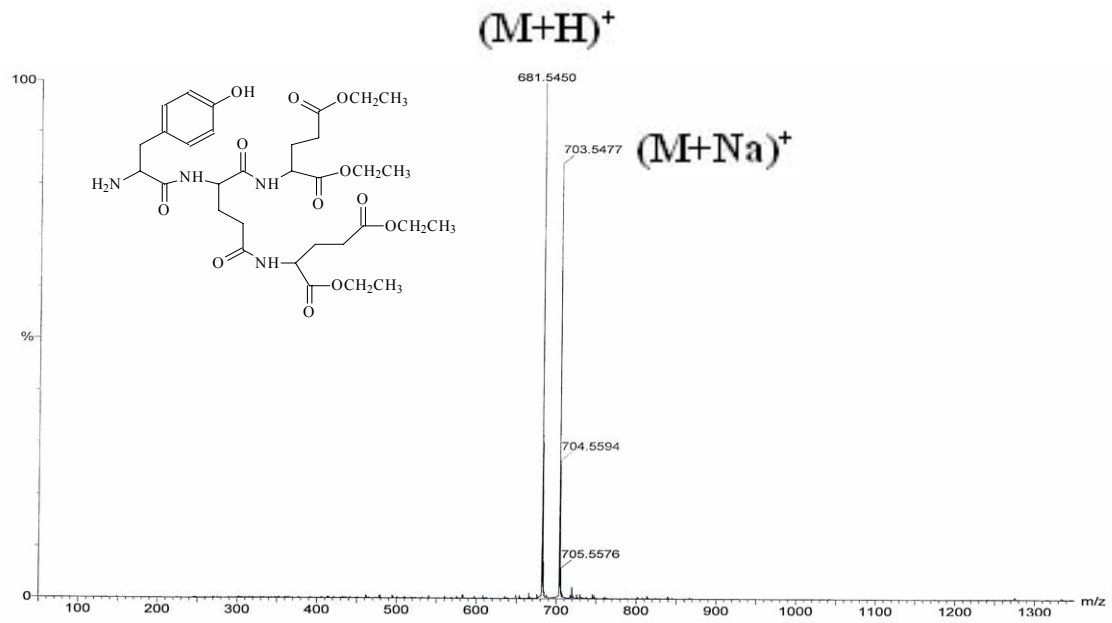

Fig. S5: HRMS Spectra of Dendron **G2**

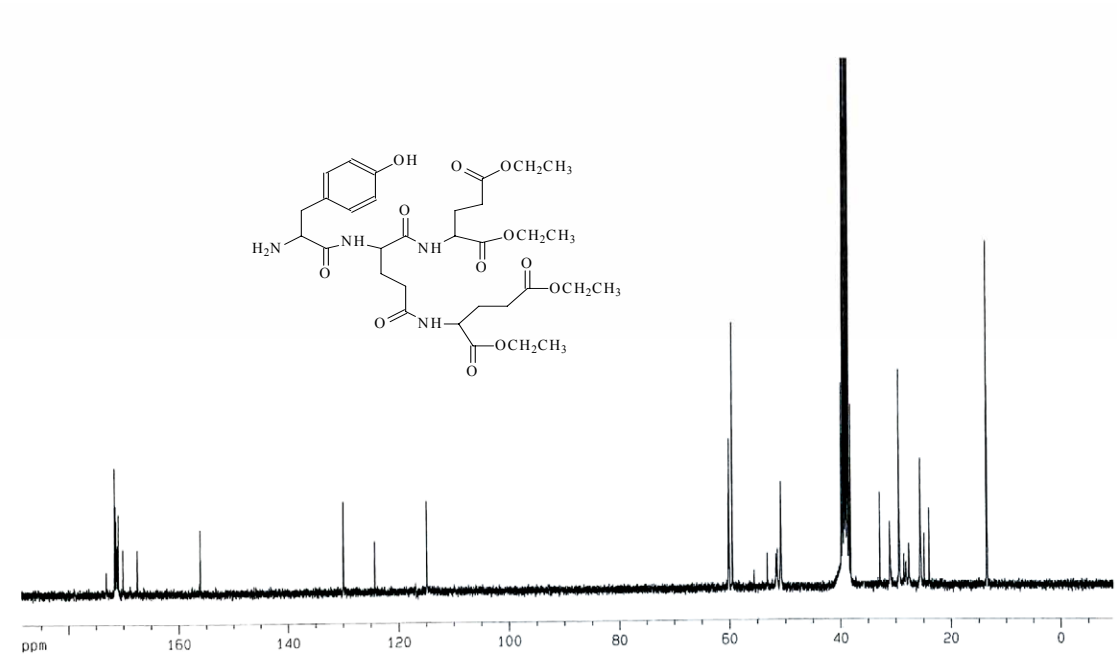

Fig. S6: ^{13}C NMR Spectra of Dendron **G2**

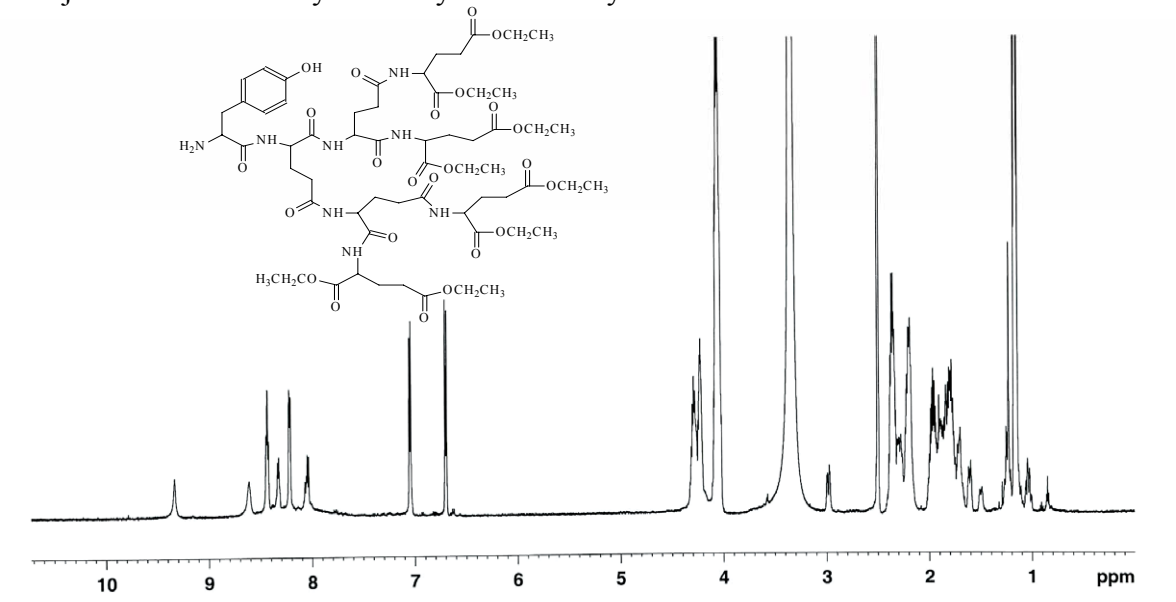

Fig. S7: 600MHz-^{1}H NMR Spectra of Dendron **G3**

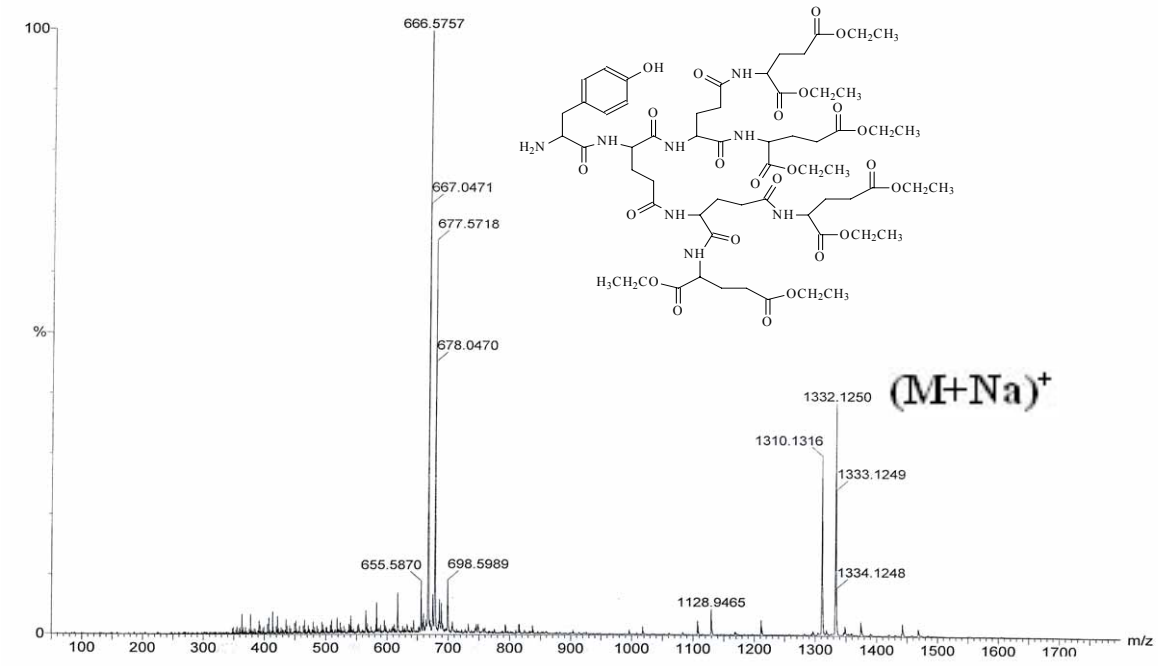

Fig. S8: HRMS Spectra of Dendron **G3**

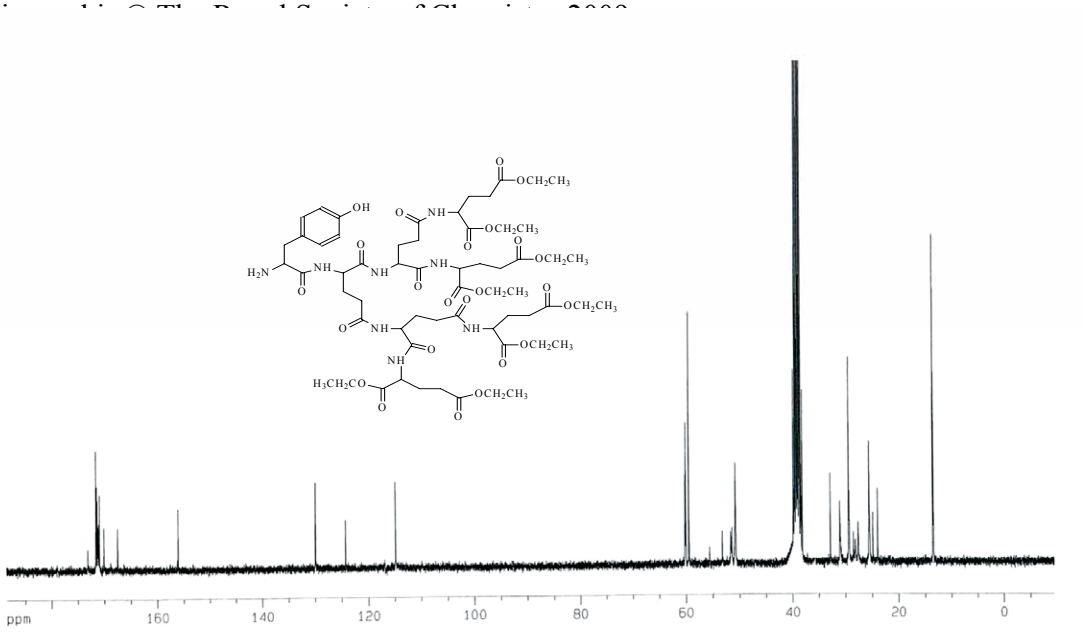

Fig. S9: ^{13}C NMR Spectra of Dendron **G3**

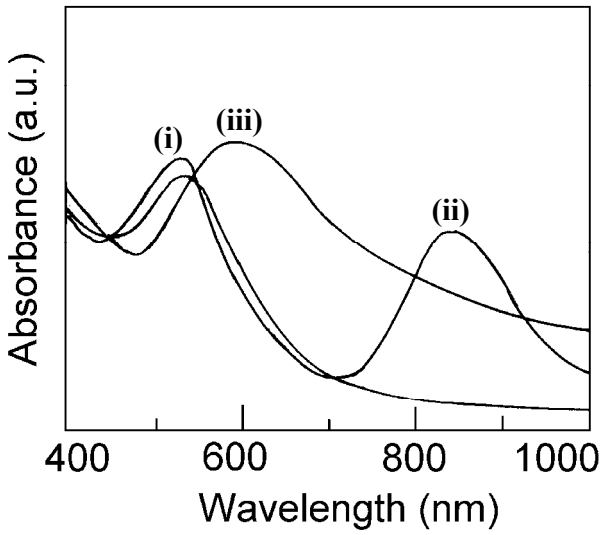

Fig. S10 UV-vis absorption spectra of peptide dendron-GNP suspension: (i) for G1-GNP solutions: concentration: 8.82×10^{-6} M; (ii) for G2-GNP solution: concentration: 8.82×10^{-6} M & (iii) for G3-GNP solution: concentration: 8.82×10^{-6} M

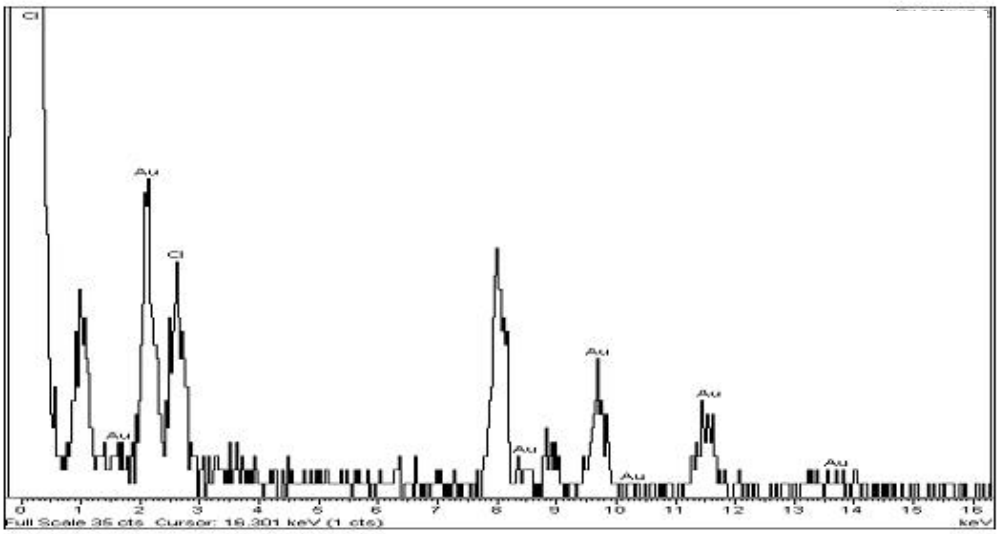

Fig. S11: Energy dispersive X-ray analysis of GNP-Dendron **G1** conjugate (concentration: 5.88×10^{-6} M).

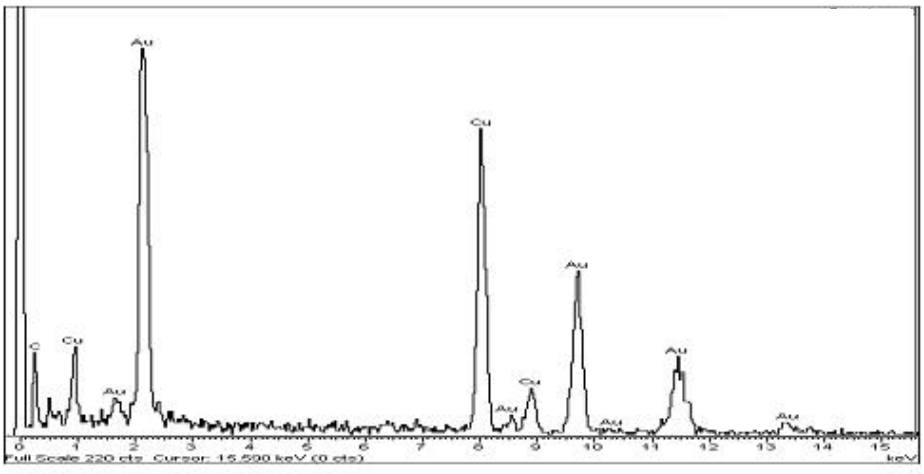

Fig. S12: Energy dispersive X-ray analysis of GNP-Dendron **G2** conjugate (concentration: 5.88×10^{-6} M)

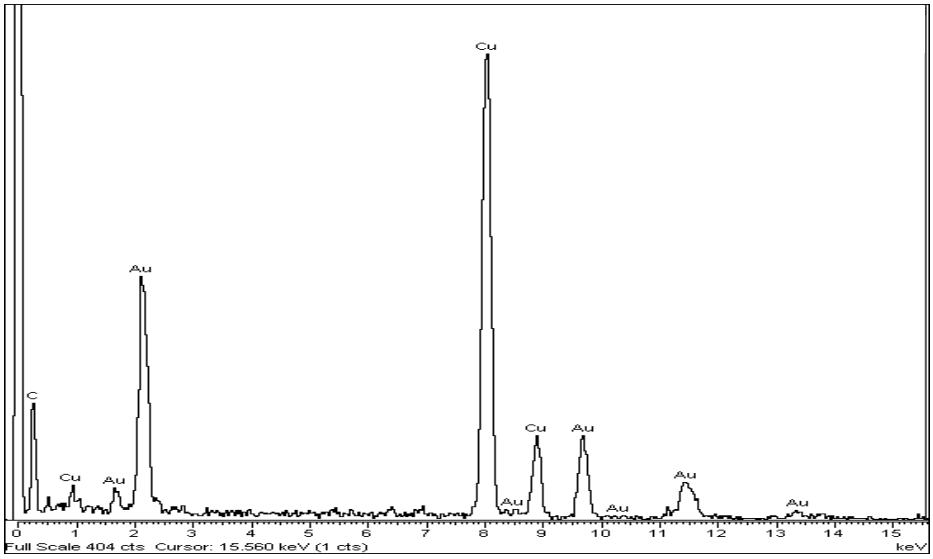

Fig. S13: Energy dispersive X-ray analysis of GNP-Dendron **G3** conjugate (concentration: 5.88×10^{-6} M)

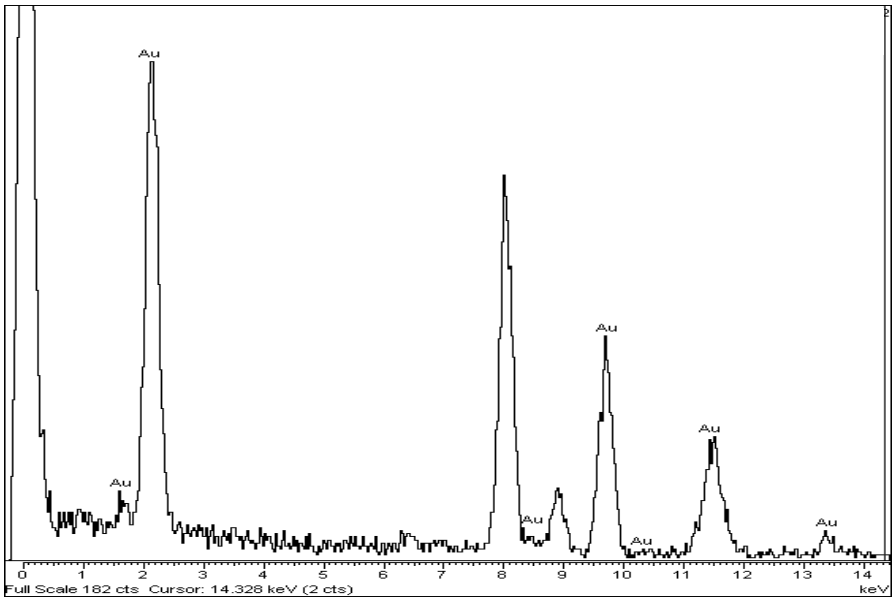

Fig. S14: Energy dispersive X-ray analysis of GNP-Dendron **G1** conjugate (concentration: 2.94×10^{-6} M)

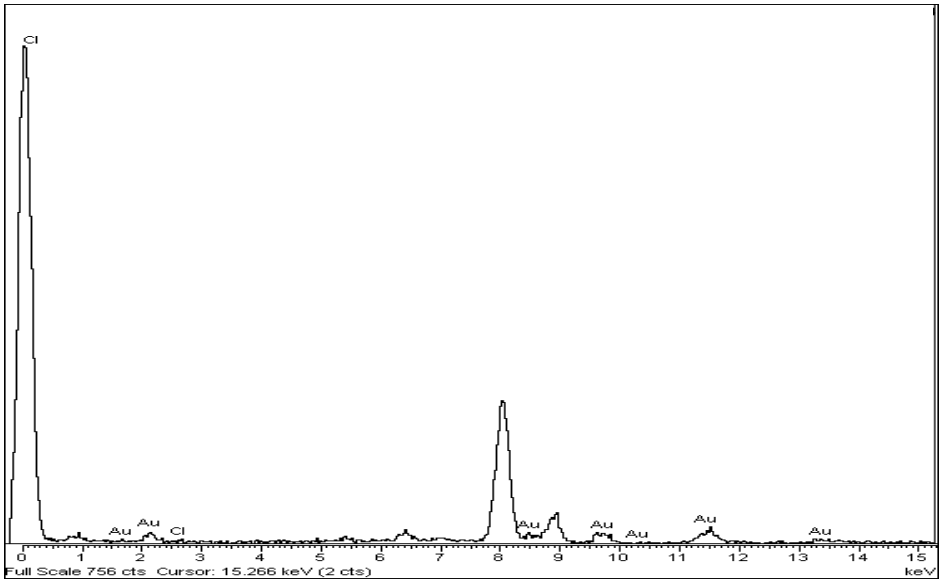

Fig. S15: Energy dispersive X-ray analysis of GNPs obtained from peptide dendron **G2** conjugate (concentration: 2.94×10^{-6} M)

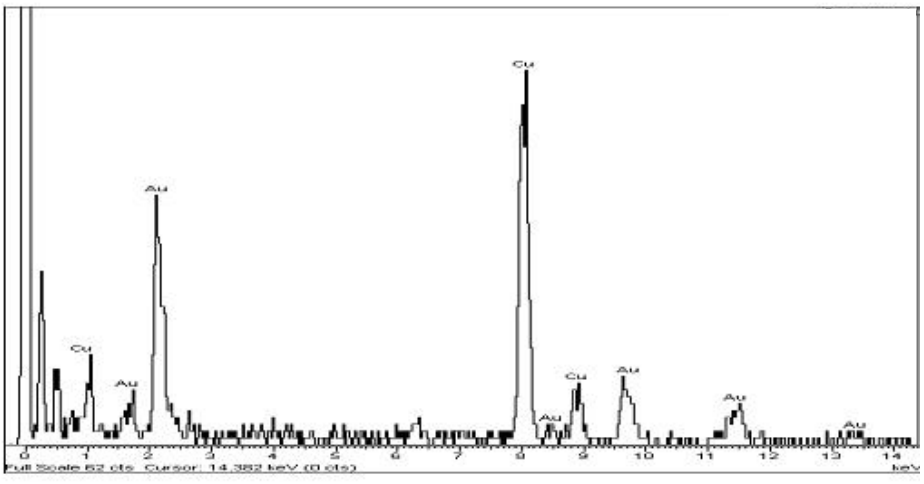

Fig. S16: Energy dispersive X-ray analysis of GNPs obtained from peptide dendron **G3** conjugate (concentration: 2.94×10^{-6} M)

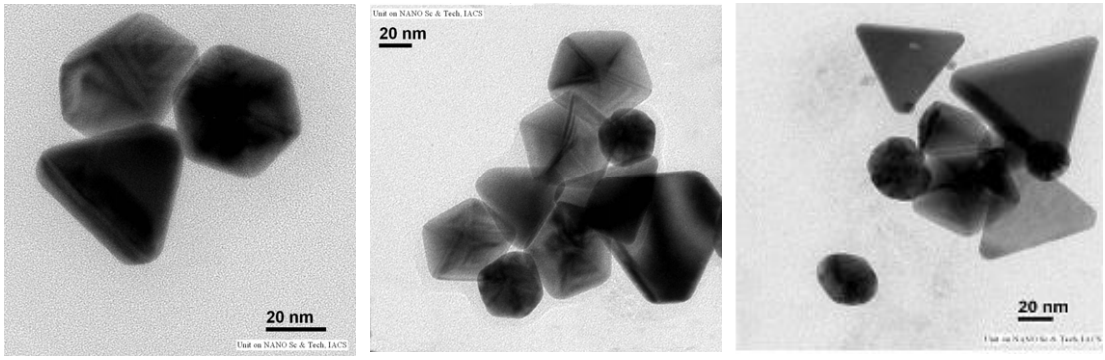

Fig. S17: TEM pictures of GNPs obtained from peptide dendron **G1** (concentration: 5.88×10^{-6} M) showing the different shapes of nanoparticles including hexagonal, pentagonal, triangular and spherical.

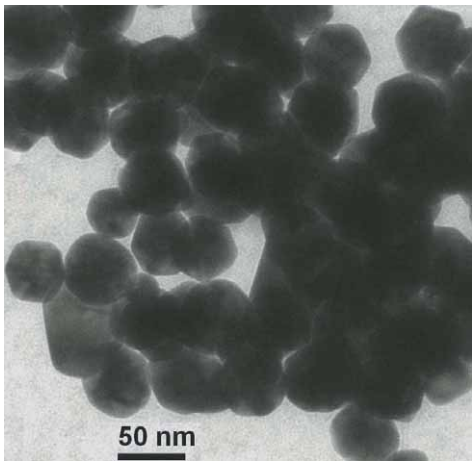

Fig. S18: TEM pictures of GNPs obtained from peptide dendron **G2** (concentration: 5.88×10^{-6} M) showing exclusively the formation of hexagonal shaped nanoparticles

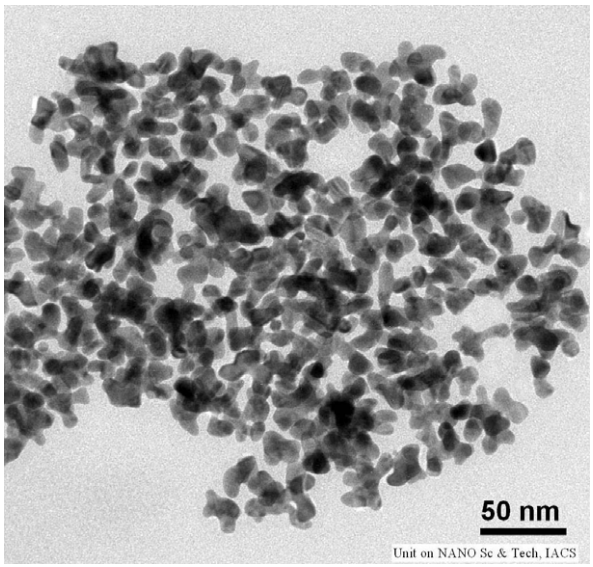

Fig. S19: TEM pictures of GNPs obtained from peptide dendron **G3** (concentration: 5.88×10^{-6} M) showing the formation of branched shaped nanoparticles.

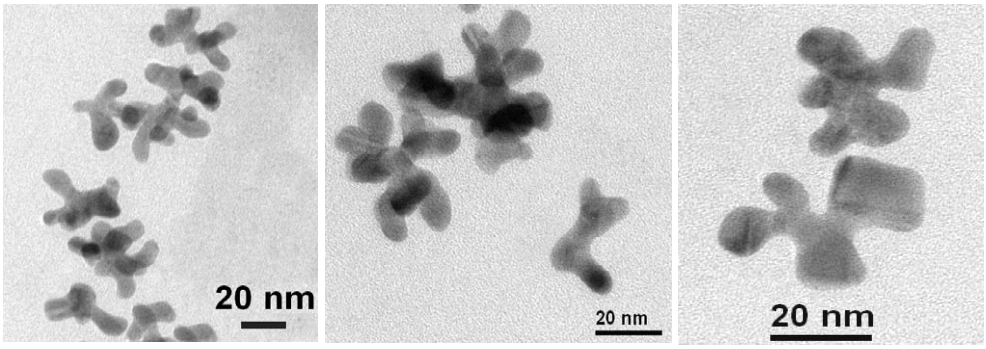

Fig. S20: ETM pictures of GNPs obtained from peptide dendron **G3** (concentration: 5.88×10^{-6} M) showing the different shapes of branched nanoparticles with multiple arms.

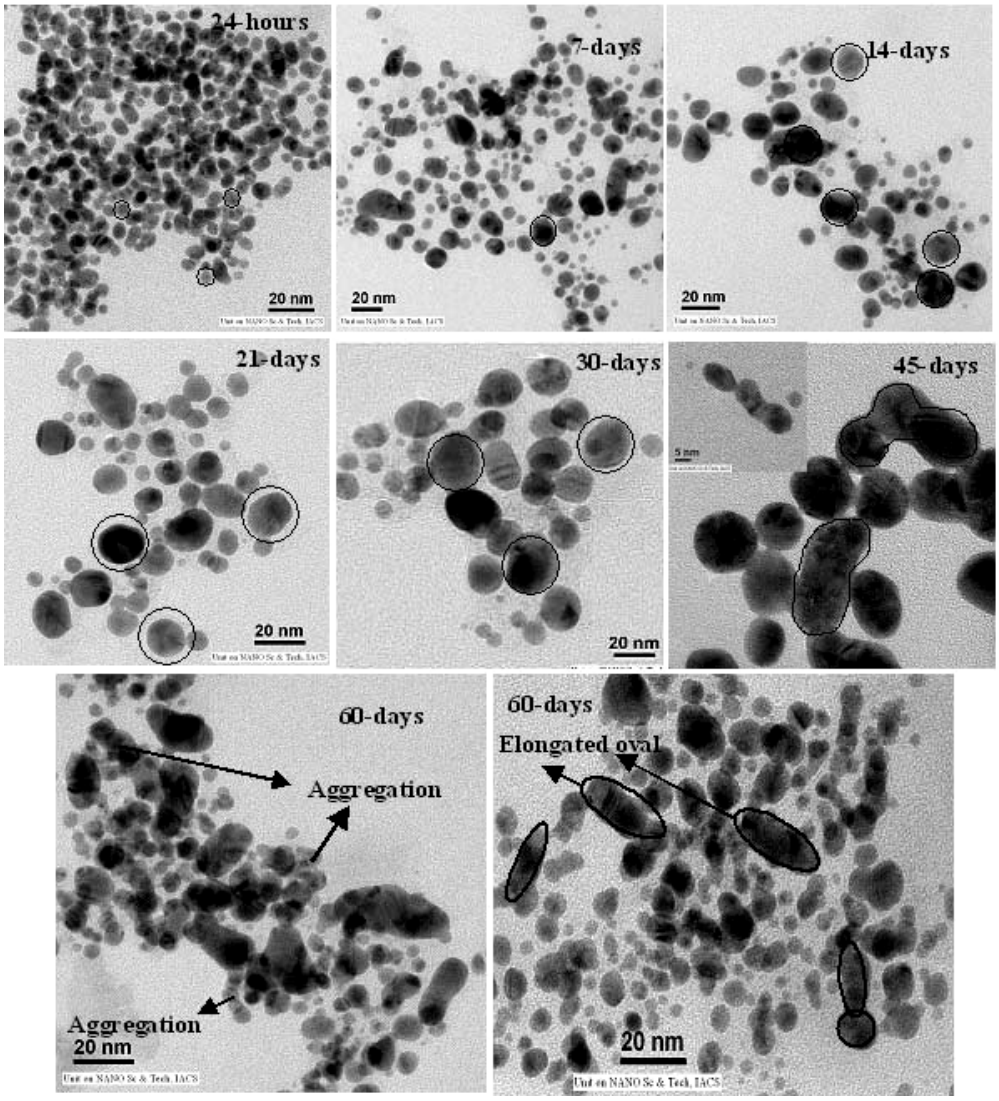

Fig. S21: Kinetic study for GNPs obtained from peptide dendron **G3** (concentration: 2.94×10^{-6} M).

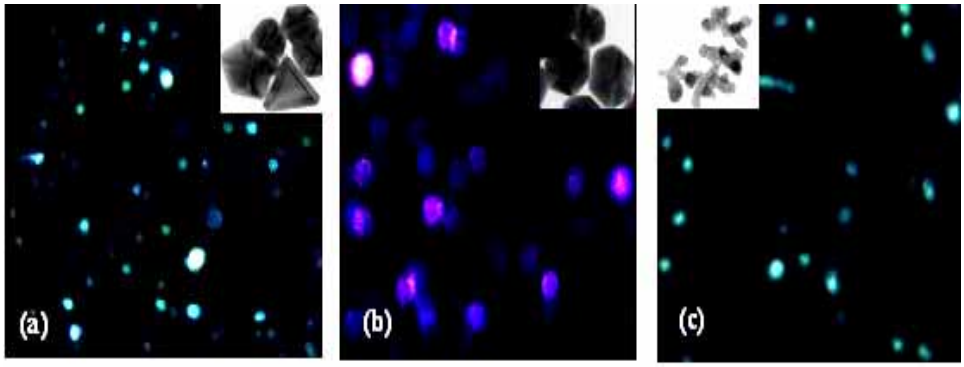

Fig. 22: Dark-field light-scattering images from gold nanoparticles and corresponding TEM images (insets). (a) For multiple shapes obtained from **G1** (concentration: 5.88×10^{-6} M) (b) For mainly hexagonal shape obtained from **G2** (concentration: 5.88×10^{-6} M) and (c) For branched shape obtained from **G3** (concentration: 5.88×10^{-6} M).