

Modification of Multi-Wall Carbon Nanotube Surface with Poly(amidoamine)

Dendrimers: Synthesis and Metal Templating

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1.0 General

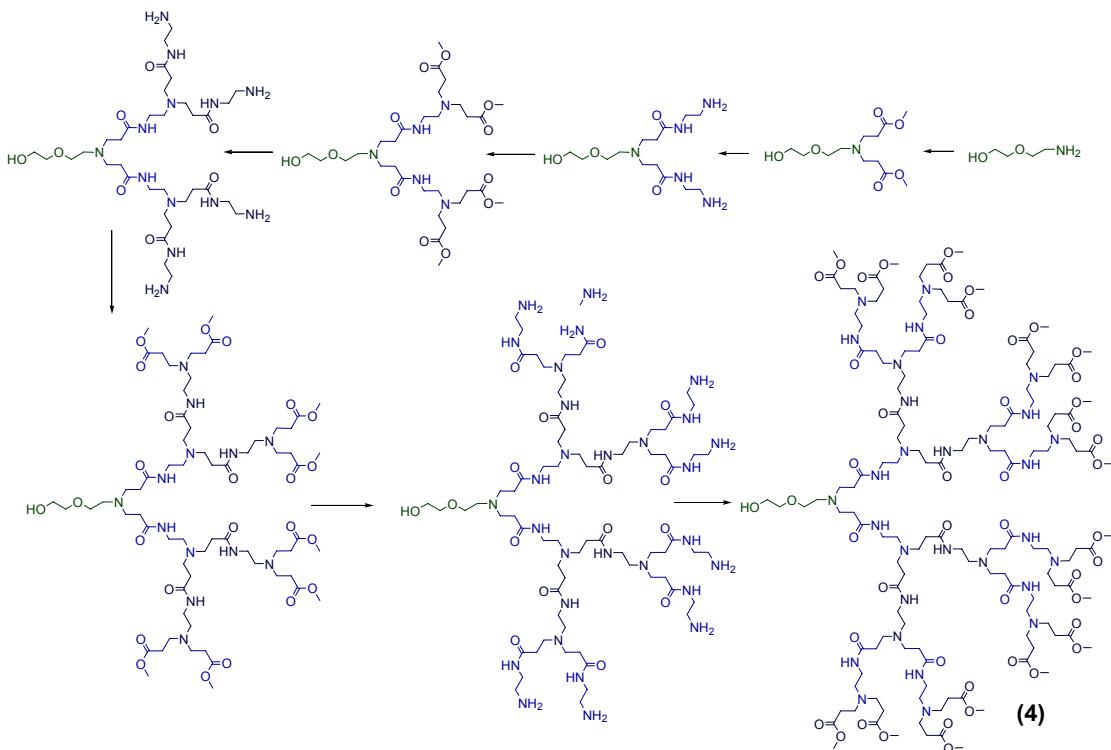
1.1 Reagents

2-(2-Amino-ethoxy)-ethanol (Aldrich, 98.0%), ethylene diamine (Aldrich, 99.0%) were used as received, methyl acrylate (MA, Aldrich, 99.0%) was stored at 4°C and used as received. Triethylamine (Fischer, 99.0%) was stored over sodium hydroxide pellets. All other reagents and solvents were obtained at the highest purity available from Aldrich Chemical Company and used without further purification unless stated.

1.2 Analysis

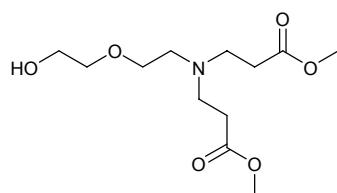
Analytical TLC were performed using pre-coated silica gel 60 F254 and developed in the solvent system indicated. Compounds were visualized by use of UV light (254 nm) or a basic solution (10.0% w/w K₂CO₃ in water) of KMnO₄. Merck 60 (230-400 mesh) silica gel was used for column chromatography. NMR spectra were obtained on a Bruker DPX400 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (¹H and ¹³C). The following abbreviations were used to explain the multiplicities: s = singlet, t = triplet, bs = broad singlet, m = multiplet. Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell. The thermal gravimetric analysis (TGA) data were collected on a Perkin Elmer TGA 7, heating from 50°C ~ 700°C at 20°C/min. Transmission electron microscopy (TEM) was recorded by JEOL 2000 FX TEM with accelerating voltage of 200 KV, the energy dispersive spectrum (EDS) was obtained by EDAX analytical system.

2.0 Synthesis of hydroxy-PAMAM dendrimer (4)



Scheme S1: Synthesis of 4th-generation hydroxyl terminated PAMAM dendrimer (**4**)

3-[[2-(2-Hydroxy-ethoxy)-ethyl]-(2-methoxycarbonyl-ethyl)-amino]-propionic acid methyl ester (HO-PAMAM-(COOCH₃)₂).

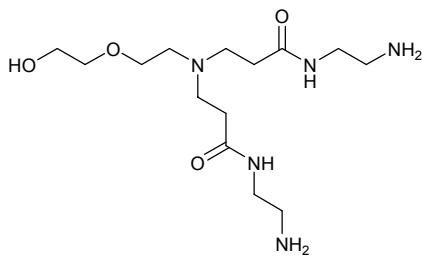


2-(2-Amino-ethoxy)-ethanol (2.10 g, 20.0 mol), methyl acrylate (17.8 mL, 0.200 mol) were dissolved in methanol (30 mL) and the solution was stirred at ambient temperature for 48h. The volatile materials were removed under reduced pressure and the expected product was obtained in quantitative yield as colourless oil.

IR (neat): $\tilde{\nu}$ =3431, 2951, 2851, 1733, 1438, 1197, 1122 cm⁻¹. ¹H NMR (400.03 MHz, CDCl₃, 298 K) δ = 2.47 (t, *J* = 7.0 Hz, 4H, CH₂C=O); 2.65 (t, *J* = 5.3 Hz, 2H, CH₂N);

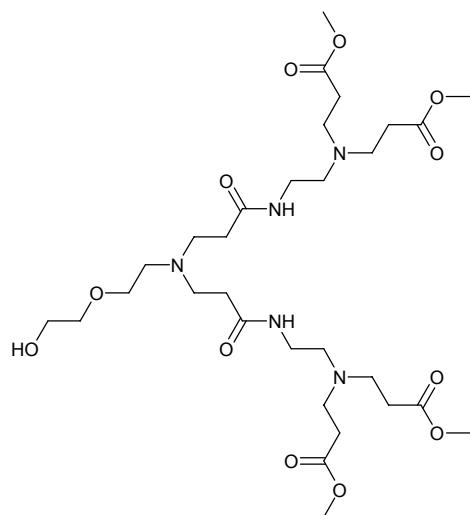
2.83 (t, $J = 7.0$ Hz, 4H, N(CH₂)₂), 3.53-3.56 (m, 4H, CH₂OCH₂), 3.66 (s, 6H, CH₃), 3.68-3.69 (m, 2H, CH₂OH). ¹³C{¹H} NMR (100.59 MHz, CDCl₃, 298 K) δ = 32.44 (2C, CH₂C=O), 50.05 (2C, N(CH₂)₂), 51.76 (2C, CH₃), 53.82 (1C, CH₂N), 61.95 (1C, HOCH₂), 69.64 (1C, CH₂CH₂N), 72.61 (1C, HOCH₂CH₂), 173.13 (2C, C=O). Anal. Calcd. for C₁₂H₂₃NO₆: C, 51.97; H, 8.36; N, 5.05. Found C, 51.90; H, 8.41; N, 5.00. MS: 278 (M+1)

N-(2-Amino-ethyl)-3-{|[2-(2-amino-ethylcarbamoyl)-ethyl]-[2-(2-hydroxy-ethoxy)-ethyl]-amino}-propionamide.



3-|[2-(2-Hydroxy-ethoxy)-ethyl]-(2-methoxycarbonyl-ethyl)-amino]-propionic acid methyl ester (2.77g, 0.0100 mol) and ethylene diamine (6.70 mL, 0.100 mol) were dissolved in methanol (20 mL) and the resulting solution was stirred at ambient temperature for 48 h. The ethylene diamine was removed by azeotropic distillation using a toluene/methanol solvent mixture and the product was obtained as pale yellow oil which was used directly for next step without further purification.

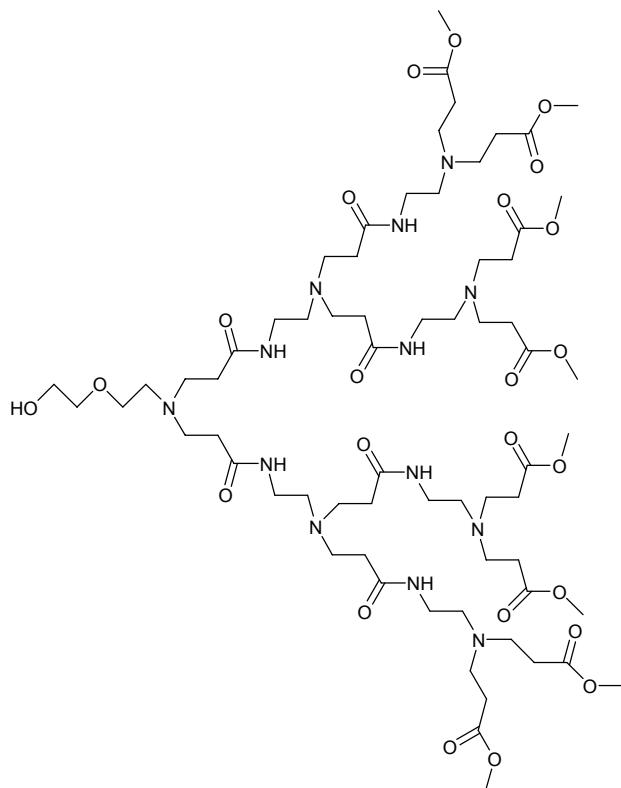
3-|[2-(3-{|2-{|2-[Bis-(2-methoxycarbonyl-ethyl)-amino]-ethylcarbamoyl}-ethyl}-2|[2-(2-hydroxy-ethoxy)-ethyl]-amino)-propionylamino]-ethyl]-|(2-methoxycarbonyl-ethyl)-amino]-propionic acid methyl ester (HO-PAMAM-(COOCH₃)₄).



N-(2-Amino-ethyl)-3-{[2-(2-amino-ethylcarbamoyl)-ethyl]-[2-(2-hydroxy-ethoxy)-ethyl]-amino}-propionamide (1.67 g, 0.0100 mol), methyl acrylate (17.80 mL, 0.200 mol) were dissolved in methanol (30 mL) and the solution was stirred at ambient temperature for 48h. Methanol and excess of methyl acrylate were removed under vacuum and the residue was purified by flash chromatography (CC, SiO_2 , ethyl acetate/methanol 7:1) to give the expected product as pale yellow oil. (5.33 g, 7.86 mmol, 78.6%)

IR (neat): $\tilde{\nu} = 3325, 2951, 2831, 1735, 1649, 1542, 2437, 1358 \text{ cm}^{-1}$. ^1H NMR (400.03 MHz, CDCl_3 , 298 K) $\delta = 2.37\text{-}2.43$ (m, 12H); 2.52 (t, $J = 6.0 \text{ Hz}$, 4H); 2.70-2.75 (m, 10H), 2.87 (t, $J = 6.8 \text{ Hz}$, 4H), 3.25-3.29 (m, 4H), 3.52-3.58 (m, 4H), 3.66 (s, 12H), 3.68-3.70 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.59 MHz, CDCl_3 , 298 K) $\delta = 32.79, 33.54, 37.28, 49.34, 50.89, 51.79, 53.08, 53.20, 61.73, 69.31, 72.88, 172.45, 173.23$. Anal. Calcd. for $\text{C}_{30}\text{H}_{55}\text{N}_5\text{O}_{12}$: C, 53.16; H, 8.18; N, 10.33. Found C, 52.97; H, 8.21; N, 10.17. MS: 678 (M+1)

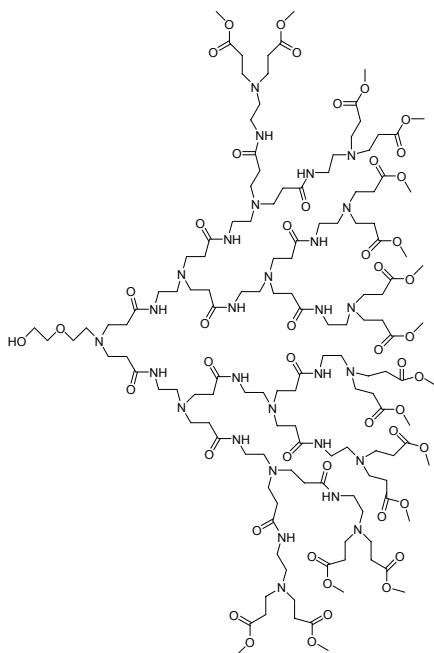
HO-PAMAM-(COOCH₃)₈



The product was purified by flash chromatography (CC, SiO₂, ethyl acetate/methanol 2:1). Yield: 71.4%.

IR (neat): $\tilde{\nu}$ = 3291, 2951, 2828, 1731, 1643, 1538, 1436, 1358 cm⁻¹. ¹H NMR (400.03 MHz, CDCl₃, 298 K, selected peaks) δ = 2.34-2.44 (m, 28H), 2.51-2.59 (m, 12H), 2.72-2.82 (m, 30H), 3.24-3.29 (m, 12H), 3.51-3.57 (m, 4H), 3.66 (s, 24H), 3.69-3.71 (m, 2H). ¹³C{¹H} NMR (100.59 MHz, CDCl₃, 298 K) δ = 32.73, 33.51, 33.89, 37.32, 37.60, 49.32, 49.95, 50.47, 51.75, 52.55, 52.96, 53.18, 61.53, 69.27, 72.80, 172.74, 172.93, 173.21. MS: 1480 (M+2)

HO-PAMAM-(COOCH₃)₁₆



The product was purified by flash chromatography (CC, SiO₂, ethyl acetate/methanol 1:2). Yield: 68.3%.

IR (neat): $\tilde{\nu}$ = 3282, 2952, 2828, 1733, 1644, 1542, 1437, 1198 cm⁻¹. ¹H NMR (400.03 MHz, CDCl₃, 298 K, selected peaks) δ = 2.32-2.42 (m, 60H), 2.50-2.57 (m, 28H), 2.71-2.80 (m, 62H), 3.23-3.26 (m, 28H), 3.50-3.55 (m, 4H), 3.64 (s, 48H), 3.66-3.68 (m, 2H). ¹³C{¹H}NMR (100.59 MHz, CDCl₃, 298 K, selected peaks) δ = 32.73, 33.82, 37.24, 37.52, 49.29, 49.88, 50.13, 50.45, 51.68, 52.53, 52.96, 61.42, 72.78, 172.38, 172.55, 173.09 MS: 3083 (M+3)

3.0 IR spectra

A carboxylic acid typical band at ~1720 cm⁻¹ appeared after treatment of MWCNT's with nitric acid. After conjugation with (4) a band at ~1640 cm⁻¹ relative to the dendrimer amide moieties was observed (Figure S1).

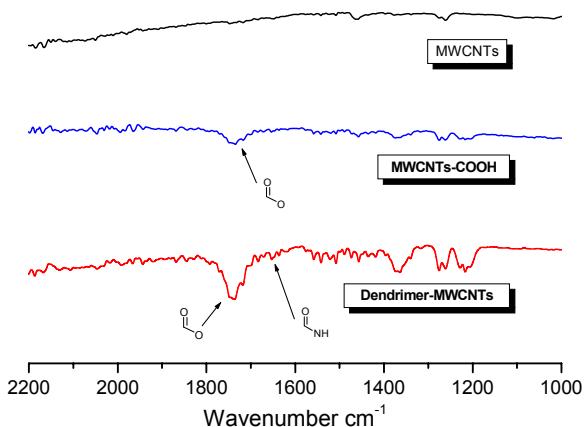


Figure S1. IR spectra of native and functionalized MWCNT's

4.0 Synthesis of PAMAM-MWCNT's conjugate (3)

4.1 MWCNT-COOH (1)

MWCNT's were converted into MWCNT's-COOH (**1**) by treatment with HNO₃ as previously described¹⁻⁴. Briefly, 0.5 g of MWCNT's was ultrasonicated in 50 mL of 70% HNO₃ aqueous solution for 30 minutes, then the suspension was warmed to reflux for 48 h. The MWCNT's-COOH (**1**) was collected by filtration, washed with water, acetone, diethyl ether, and dried in a vacuum oven overnight.

4.2 Dendrimer-MWCNTs (3)

0.2 g of the MWCNT's-COOH, 50 mL of toluene, 10 mL of SOCl₂ were poured into a 100 mL round bottom flask, the system was ultrasonicated for 30 mins, warmed to 70°C under N₂ and stirred at this temperature for 24 h. The excess of SOCl₂ was then removed by distillation together with excess toluene, until the volume was reduced to about half of the initial volume. The suspension was then cooled down to

ambient temperature under nitrogen and a solution of (**4**) (2.00 g) in toluene (20 mL) was added via syringe and the resulting suspension was stirred at ambient temperature for 24 h then at 100°C for further 24h. The PMAM-MWCNT's (**3**) was collected by filtration, washed with methanol/triethylamine (9:1), methanol, diethyl ether, and dried in vacuum oven overnight.

5.0 Silver particles deposition experiments

5.1 Hydroxy-PAMAM dendrimer (**4**) - Ag(0)

7.0 mg of dendrimer was dissolved in 1.0 mL of 0.5M AgNO_3 aqueous solution. To 0.5 mL of the resulting solution 0.1 mL of 37.0% aqueous formaldehyde solution was added to give almost instantaneous precipitation of black Ag(0) (Figure S2)

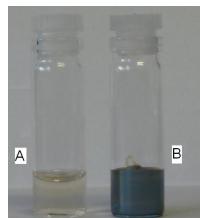


Figure S2. A) AgNO_3 + formaldehyde; B) AgNO_3 + formaldehyde + hydroxy-PAMAM dendrimer (**4**).

5.2 PAMAM-MWCNT's-Ag(0)

PAMAM-MWCNT's (**3**) (10 mg) and 1.0 mL of 0.5 M AgNO_3 aqueous solution were mixed in a brown vial and the mixture was ultrasonicated for 20 mins in the dark. The solid present in suspension was isolated by centrifugation, and the isolated solid was suspended in pure water and ultrasonicated as second time. This procedure was repeated several times, until no visible AgCl precipitate was observed upon addition

of NaCl aqueous solution. The Ag⁺/**(3)** complex was suspended again in 1.0 mL of pure water, subjected to ultrasonication, then 0.10 mL of 37% formaldehyde aqueous solution was added. The mixture was ultrasonicated for 20 mins, then centrifuged and the solid was washed with pure water, methanol, diethyl ether, and finally dried in vacuum overnight. The control reaction was performed following the same procedure, using MWCNT-COOH (**1**) in place of PAMAM-MWCNT (**3**).

7.0 References

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