Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Synthesis and Electroactive Properties of Poly(amidoamine) Dendrimers with an Aniline Pentamer Shell

Wei-I Hung[a], Chih-Bing Hung[a], Ya-Han Chang[a], Jiun-Kuang Dai[a], Yan Li[b] , Hai He[b],

Shao-Wen Chen[a], Tsao-Cheng Huang[a], Yen Wei[c,*], Xin-Ru Jia[b,*], Jui-Ming Yeh[a,*]

[a]Department of Chemistry, Center for Nanotechnology at CYCU, Chung-Yuan Christian University, Chung Li 32023, Taiwan, R. O. C.

[b]Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[c]Chemistry Department, Drexel University, Philadelphia, PA 19104, USA

PAMAM G-0.5:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO_2{}^{e}CH_3)_2]_2$

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ_H: 3.66 (12H, s, e), 2.78-2.73 (8H, t, b), 2.48 (4H, s, a), 2.45-2.40 (8H, t, c). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ_C: 173.03 (C), 52.33 (CH_2), 51.60 (CH_3), 49.84 (CH_2) 32.70 (CH_2). ESI-TOF MS: Calcd for $C_{18}H_{32}N_2O_8$ [M]: 404.22. Found: 405.2239 $[M+H]^+$, 427.2055 $[M+Na]^+$. FT-IR (KBr pellet, cm^{-1}): 2956, 2830, 1735, 1438, 1251, 1189, 1034.

PAMAM G0:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2{}^{h}NH_2)_2]_2$

^{1}H NMR (300 MHz, D_2O, ppm) δ_H: 3.16-3.12 (8H, t, f), 2.73-2.69 (8H, t, b), 2.64-2.60 (8H, t, g), 2.51 (4H, s, a), 2.36-2.32 (8H, t, c). ^{13}C NMR (75 MHz, D_2O, ppm) δ_C: 174.94 (C), 49.99 (CH_2), 49.12 (CH_2), 41.62 (CH_2), 39.74 (CH_2), 32.66 (CH_2). ESI-TOF MS: Calcd for $C_{22}H_{48}N_{10}O_4$ [M]: 516.39. Found: 517.3984 $[M+H]^+$, 539.3792 $[M+Na]^+$. FT-IR (KBr pellet, cm^{-1}): 3402, 2956, 2852, 1633, 1560, 1485, 1326, 709.

PAMAM G0.5:

$(^{a}CH_2{}^{a}H_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2N(^{h}CH_2{}^{i}CH_2{}^{j}CO_2{}^{k}CH_3)_2)_2]_2$

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H: 7.19-7.17 (4H, t, e), 3.63 (24H, s, k), 3.25-3.20 (8H, q, f), 2.73-2.70 (24H, m, b, h), 2.50-2.48 (12H, m, a, g), 2.41-2.38 (16H, t, i), 2.33-2.30 (8H, t, c). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ_C: 173.14 (C), 172.52 (C), 52.96 (CH_2), 51.73 (CH_3), 51.30 (CH_2), 50.18 (CH_2), 49.31 (CH_2), 37.25 (CH_2), 33.83 (CH_2), 32.69 (CH_2). ESI-TOF MS: Calcd for $C_{54}H_{96}N_{10}O_{20}$ [M]: 1204.68. Found: 1205.6950 $[M+H]^+$, 1227.6737 $[M+Na]^+$. FT-IR (KBr pellet, cm^{-1}): 3392, 2953, 2836, 1727, 1642, 1546, 1443, 1353, 1260, 1199, 1044.

PAMAM G1.0:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2N$

$(^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2{}^{n}NH_2)_2)_2]_2$

^{1}H NMR (300 MHz, D_2O, ppm) δ_H: 3.23-3.14 (24H, bm, f, l), 2.74-2.62 (40H, m, b, h, m), 2.56-2.52 (12H, m, a, g), 2.37-2.32 (24H, m, c, i). ^{13}C NMR (75 MHz, D_2O, ppm) δ_C: 175.02 (C), 174.51 (C), 51.18 (CH_2), 49.92 (CH_2), 49.10 (CH_2), 49.01 (CH_2), 41.42 (CH_2), 39.71 (CH_2), 36.70 (CH_2), 32.72 (CH_2), 32.52 (CH_2). ESI-TOF MS: Calcd for $C_{62}H_{128}N_{26}O_{12}$ [M]: 1429.02. Found: 715.5139 $[(M+2H)/2]^+$, 1430.0224 $[M+H]^+$. FT-IR (KBr pellet, cm^{-1}): 3358, 3294, 2931, 2855, 1639, 1553, 1458, 1336, 688.

PAMAM G1.5:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2N$

$(^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2N(^{n}CH_2{}^{o}CH_2{}^{p}CO_2{}^{q}CH_3)_2)_2)_2]_2$

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ_H: 7.72 (4H, t, e), 7.08 (8H, t, k), 3.63 (48H, s, q), 3.24-3.23 (24H, q, f, l), 2.77-2.70 (56H, m, b, h, n), 2.52-2.50 (28H, m, a, g, m), 2.42-2.33 (56H, m, o, i, c). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ_C: 173.07 (C), 172.45 (C), 172.31 (C), 52.98 (CH_2), 52.53 (CH_2), 51.68 (CH_3), 51.20 (CH_2), 50.20 (CH_2), 49.95 (CH_2), 49.30 (CH_2), 37.56 (CH_2), 37.23 (CH_2), 33.85 (CH_2), 33.75 (CH_2), 32.73 (CH_2). ESI-TOF MS: Calcd for $C_{126}H_{224}N_{26}O_{44}$ [M]: 2805.61. Found: 951.0679 $[(M+H+2Na)/3]^+$, 1415.1110 $[(M+H+Na)/2]^+$, 2807.2500 $[M+H]^+$. FT-IR (KBr pellet, cm^{-1}): 3299, 2952, 2830, 1735, 1649, 1539, 1436, 1360, 1257, 1199, 1044.

PAMAM G2.0:

($^{a}CH_2{}^{a}CH_2$)[N($^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2$N

($^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2$N($^{n}CH_2{}^{o}CH_2{}^{p}CO^{q}NH^{r}CH_2{}^{s}CH_2{}^{t}NH_2)_2)_2)_2]_2$

^{1}H NMR (300 MHz, D_2O, ppm) δ_H: 3.20-3.13 (56H, m, f, l, r), 2.75-2.51 (116H, m, a, b, g, h, m, n, s), 2.36-2.31 (56H, m, c, i, o). ^{13}C NMR (100 MHz, D_2O, ppm) δ_C: 174.98 (C), 174.52 (C), 174.40 (C), 51.20 (CH_2), 49.96 (CH_2), 49.01 (CH_2), 48.78 (CH_2), 41.46 (CH_2), 40.28 (CH_2), 39.91 (CH_2), 39.72 (CH_2), 36.90 (CH_2), 36.69 (CH_2), 32.74 (CH_2), 32.64 (CH_2), 32.52 (CH_2). ESI-TOF MS: Calcd for $C_{142}H_{288}N_{58}O_{28}$ [M]: 3254.29. Found: 814.8141 $[(M+4H)/4]^+$, 1086.0813 $[(M+3H)/3]^+$, 1628.6172 $[(M+2H)/2]^+$. FT-IR (KBr pellet, cm^{-1}): 3418, 2962, 2867, 1641, 1562, 1488, 1326, 770.

PAMAM G2.5:

($^{a}CH_2{}^{a}CH_2$)[N($^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2$N($^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2$N

($^{n}CH_2{}^{o}CH_2{}^{p}CO^{q}NH^{r}CH_2{}^{s}CH_2$N($^{t}CH_2{}^{u}CH_2{}^{v}CO_2{}^{w}CH_3)_2)_2)_2)_2]_2$

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ_H: 7.83-7.68 (11H, b, e, k), 7.13 (15H, b, q), 3.65 (90H, s, w), 3.26-3.25 (56H, q, f, l, r), 2.76-2.72 (126H, m, b, h, n, t), 2.54-2.34 (180H, m, a, g, m, s, u, o, i, c). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ_C: 173.12 (C), 172.51 (C), 172.43 (C), 53.00 (CH_2), 52.57 (CH_2), 51.72 (CH_3), 50.11 (CH_2), 49.92 (CH_2), 49.33 (CH_2), 37.58 (CH_2), 37.28 (CH_2), 33.89 (CH_2), 32.77 (CH_2). ESI-TOF MS: Calcd for $C_{270}H_{480}N_{58}O_{92}$ [M]: 6007.47. Found: 1017.2469 $[(M+6Na)/6]^+$, 1220.6929 $[(M+5Na)/5]^+$, 1514.3748 $[(M+4Na)/4]^+$, 2019.1670 $[(M+3Na)/3]^+$. FT-IR (KBr pellet, cm^{-1}): 3403, 2956, 2849, 1725, 1641, 1552, 1449, 1354, 1266, 1211, 1041.

PAMAM G3.0:

($^{a}CH_2{}^{a}CH_2$)[N($^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2$N($^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2$N

$(^{n}CH_2{}^{o}CH_2{}^{p}CO^{q}NH^{r}CH_2{}^{s}CH_2N(^{t}CH_2{}^{u}CH_2{}^{v}CO^{w}NH^{x}CH_2{}^{y}CH_2{}^{z}NH_2)_2)_2)_2)_2]_2$

^{1}H NMR (400 MHz, D_2O, ppm) δ_H: 3.23-3.16 (120H, m, f, l, r, x), 2.76-2.67 (184H, m, b, h, n, t, y), 2.56-2.53 (58H, m, a, g, m, s), 2.37-2.33 (120H, m, c, i, o, u). ^{13}C NMR (100 MHz, D_2O, ppm) δ_C: 175.09 (C), 174.56 (C), 164.45 (C), 51.27 (CH_2), 50.05 (CH_2), 49.04 (CH_2), 47.12 (CH_2), 44.41 (CH_2), 40.92 (CH_2), 40.35 (CH_2), 39.96 (CH_2), 39.70 (CH_2), 38.55 (CH_2), 36.74 (CH_2), 35.37 (CH_2), 32.76 (CH_2). ESI-TOF MS: Calcd for $C_{302}H_{608}N_{122}O$= [M]: 6904.83. Found: 955.2213 $[(M+7NH)/7]^+$, 1142.4306 $[(M+6H)/6]^+$, 1337.1132 $[(M+5H)/5]^+$. FT-IR (KBr pellet, cm^{-1}): 3408, 2962, 2858, 1638, 1562, 1488, 1326, 773.

PAMAM G3.5:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2N(^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2N$
$(^{n}CH_2{}^{o}CH_2{}^{p}CO^{q}NH^{r}CH_2{}^{s}CH_2N(^{t}CH_2{}^{u}CH_2{}^{v}CO^{w}NH^{x}CH_2{}^{y}CH_2N$

$(^{z}CH_2{}^{a'}CH_2{}^{b'}CO_2{}^{c'}CH_3)_2)_2)_2)_2]_2$

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ_H: 3.65 (172H, s, c'), 3.27-3.25 (120H, m, f, l, r, x), 2.77-2.72 (258H, m, b, h, n, t, z), 2.55-2.35 (442H, m, a, g, m, s, y, c, i, o, u, a'). ^{13}C NMR (75MHz, $CDCl_3$, ppm) δ_C: 173.21 (C), 172.96 (C), 172.70 (C), 172.53 (C), 52.89 (CH_2), 52.45 (CH_2), 51.72 (CH_3), 50.00 (CH_2), 49.88 (CH_2), 49.30 (CH_2), 37.52 (CH_2), 37.30 (CH_2), 33.80 (CH_2), 32.67 (CH_2). FT-IR (KBr pellet, cm^{-1}): 3418, 3296, 2946, 2852, 1641, 1558, 1457, 1342, 1038.

PAMAM G4.0:

$(^{a}CH_2{}^{a}CH_2)[N(^{b}CH_2{}^{c}CH_2{}^{d}CO^{e}NH^{f}CH_2{}^{g}CH_2N(^{h}CH_2{}^{i}CH_2{}^{j}CO^{k}NH^{l}CH_2{}^{m}CH_2N$
$(^{n}CH_2{}^{o}CH_2{}^{p}CO^{q}NH^{r}CH_2{}^{s}CH_2N(^{t}CH_2{}^{u}CH_2{}^{v}CO^{w}NH^{x}CH_2{}^{y}CH_2N$

$(^{z}CH_2{}^{a'}CH_2{}^{b'}CO^{c'}NH^{d'}CH_2{}^{e'}CH_2{}^{f'}NH_2)_2)_2)_2)_2]_2$

^{1}H NMR (300 MHz, D_2O, ppm) δ_H: 3.22-3.16 (244H, m, f, l, r, x, d'), 2.75-2.68 (358H, m, b, h, n, t, z, e'), 2.56-2.51 (128H, m, a, g, m, y), 2.36-2.32 (248H, m, c, i, o, u, a'). ^{13}C NMR (75MHz, D_2O, ppm) δ_C: 175.01 (C), 174.50 (C), 174.42 (C), 174.30 (C), 51.22 (CH_2), 49.00 (CH_2), 41.08 (CH_2), 40.97 (CH_2), 40.87 (CH_2), 40.31 (CH_2), 39.93 (CH_2), 39.68 (CH_2), 38.59 (CH_2), 36.69 (CH_2), 32.71 (CH_2). FT-IR (KBr pellet, cm^{-1}): 3396, 3303, 2950, 2834, 1731, 1643, 1544, 1445, 1202, 1042.

AP:

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ_H: 7.19-7.15 (m, due to Ar-H), 7.04 (s, due to Ar-H), 7.00-6.96 (m, due to Ar-H), 6.73-6.70 (m, due to Ar-H, -NH-). ^{13}C NMR (100MHz, DMSO-d_6, ppm) δ_C: 144.92 (C), 136.47 (C), 129.12 (CH), 119.76 (CH), 118.36 (CH), 115.09 (CH). ESI-TOF MS: Calcd for $C_{30}H_{25}N_5$ [M]: 455.21. Found: 456.2054 $[M+H]^+$. FT-IR (KBr pellet, cm^{-1}): 3378, 3258, 3028, 1594, 1504, 1299, 825.

AP-COOH:

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ_H: 7.19-7.15 (m, due to Ar-H), 7.03 (s, due to Ar-H), 6.96-6.92 (m, due to Ar-H), 6.73-6.69 (m, due to Ar-H, -NH-), 2.54 (-CH_2-). ^{13}C NMR (100MHz, DMSO-d_6, ppm) δ_C: 174.05 (C), 174.03 (C), 144.92 (C), 136.47 (C), 129.25 (CH), 129.25 (CH), 119.76 (CH), 118.37 (CH), 115.09 (CH), 31.11 (CH_2), 29.15 (CH_2). ESI-TOF MS: Calcd for $C_{34}H_{29}N_5O_3$ [M]: 555.23. Found: 556.2151 $[M+H]^+$. FT-IR (KBr pellet, cm^{-1}): 3622, 3385, 3281, 3038, 1662, 1591, 1507, 1299, 821.

PAMAM-AP G2:

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ_H: 7.25-6.92 (bm, due to Ar-H), 6.72-6.70 (m, due to Ar-H), 1.72-1.58 (m, due to PAMAM -CH_2-), 1.26-1.01 (m, due to PAMAM -CH_2-). ESI-TOF MS: Found: 752.4315 $[(M+8H)/8]^+$, 859.6425 $[(M+7H)/7]^+$, 1002.7478 $[(M+6H)/6]^+$, 1203.0924 $[(M+5H)/5]^+$, 1475.8351 $[(M+4H)/4]^+$, 2026.4760 $[(M+3H)/3]^+$. FT-IR (KBr pellet, cm^{-1}): 3327, 2928, 2849, 1628, 1576, 1509, 1312, 1086, 884, 651.

PAMAM-AP G3:

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ_H: 7.15-6.91 (bm, due to Ar-H), 6.72-6.70 (m, due to Ar-H), 1.69-1.47 (m, due to PAMAM -CH_2-), 1.25-1.01 (m, due to PAMAM -CH_2-). FT-IR (KBr pellet, cm^{-1}): 3323, 2921, 2846, 1625, 1570, 1503, 1308, 1154, 884.

PAMAM-AP G4:

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ_H: 7.88-6.91 (bm, due to Ar-H), 6.72-6.70 (m, due to Ar-H), 1.73-1.48 (m, due to PAMAM –CH_2-), 1.25-1.01 (m, due to PAMAM –CH_2-). FT-IR (KBr pellet, cm^{-1}): 3325, 2926, 2849, 1625, 1537, 1521, 1306, 892.

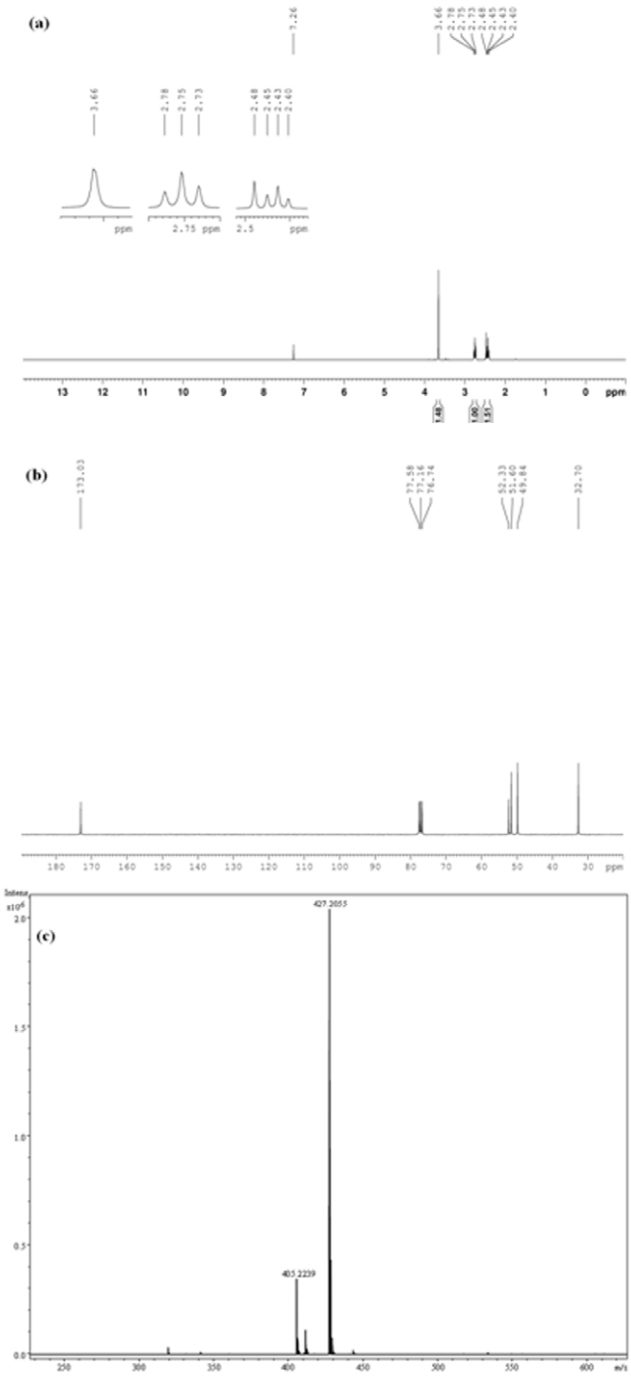

Figure S-1. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G-0.5

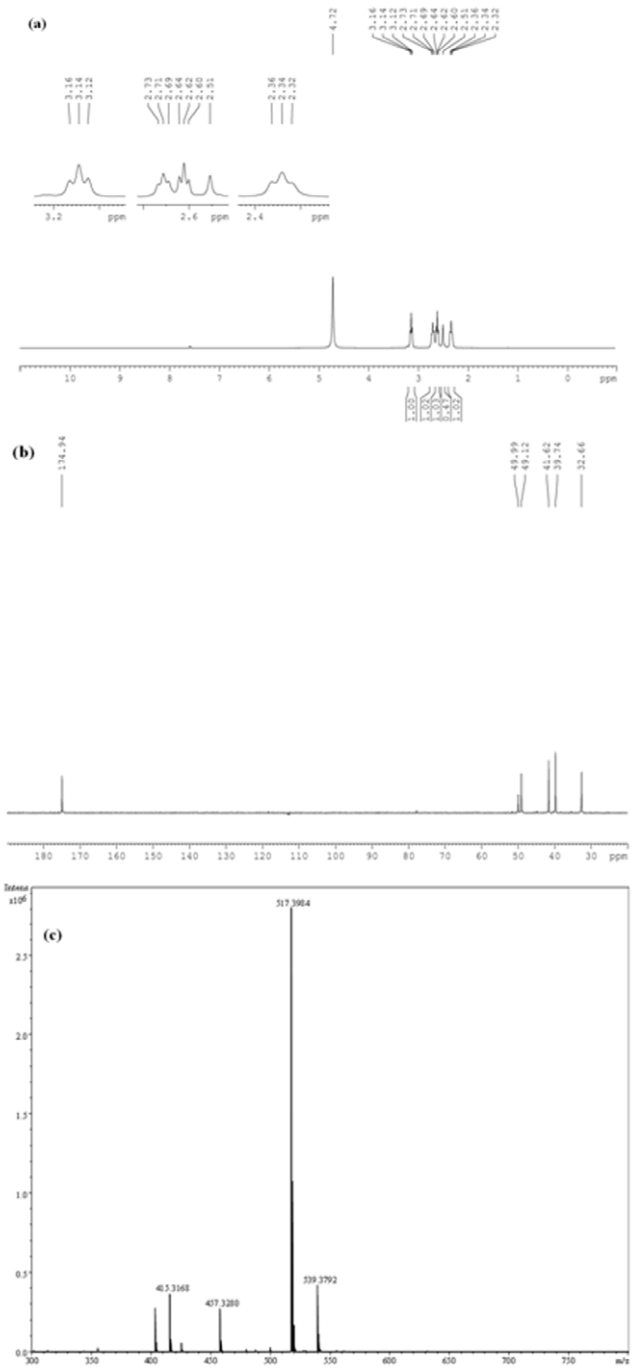

Figure S-2. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G0

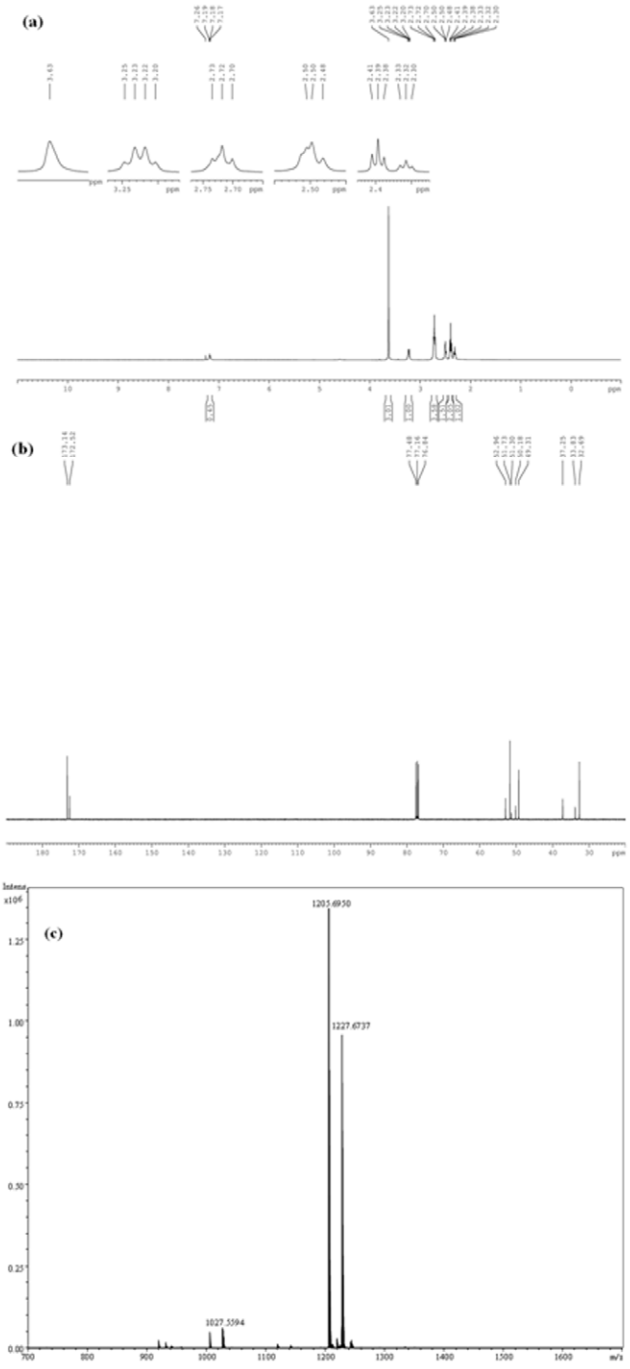

Figure S-3. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G0.5

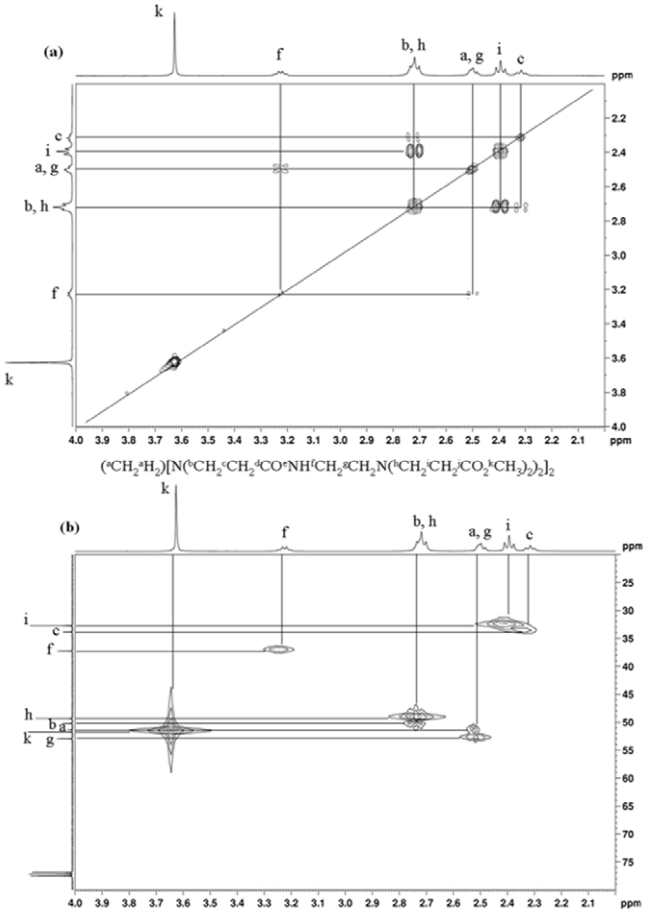

Figure S-4. ^{1}H-^{1}H COSY (a), HMQC (b) NMR spectra of PAMAM G0.5

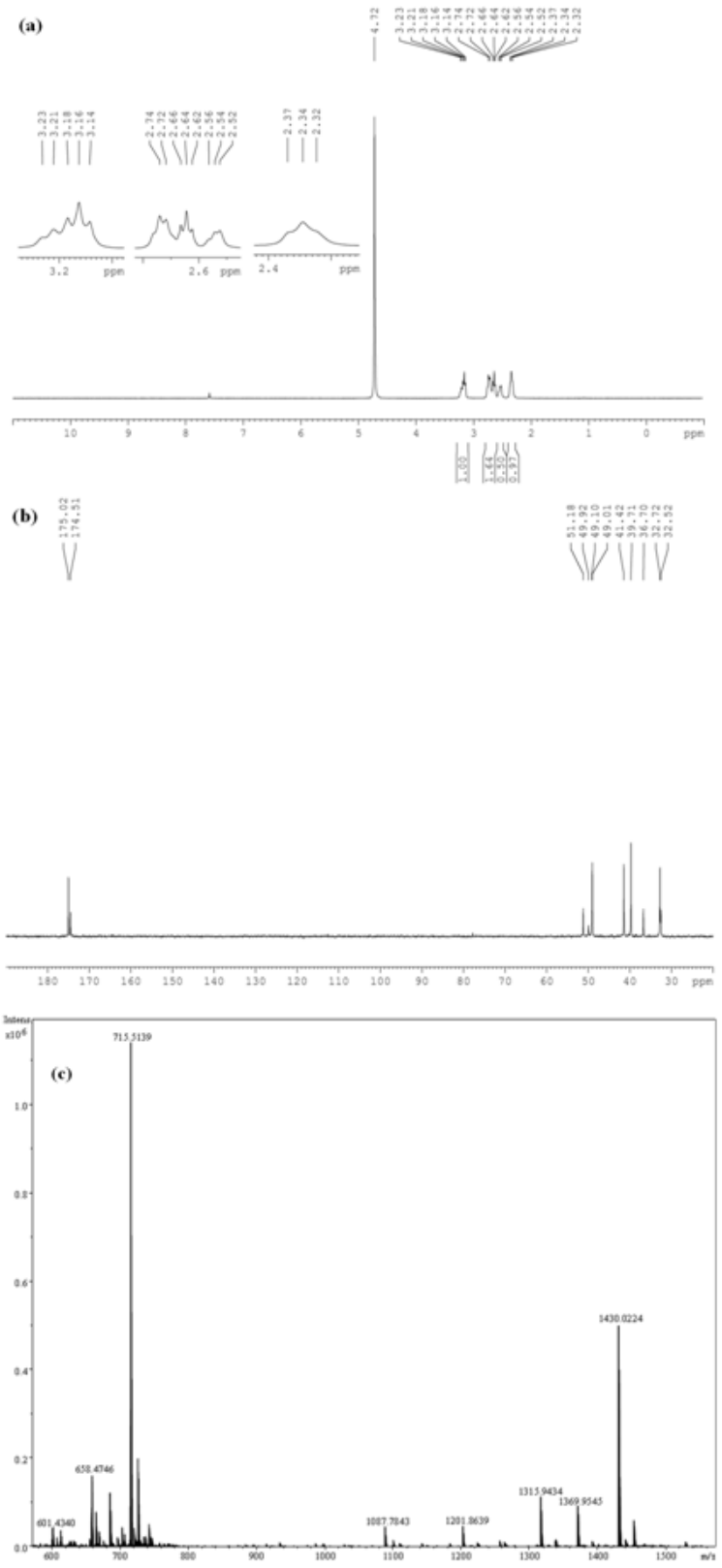

Figure S-5. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G1.0

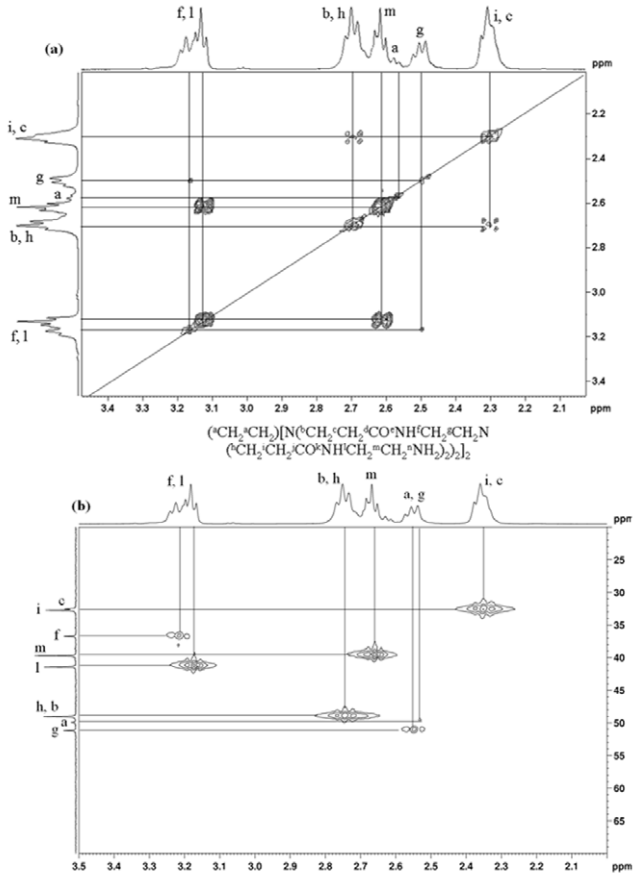

Figure S-6. ^{1}H-^{1}H COSY (a), HMQC (b) NMR spectra of PAMAM G1.0

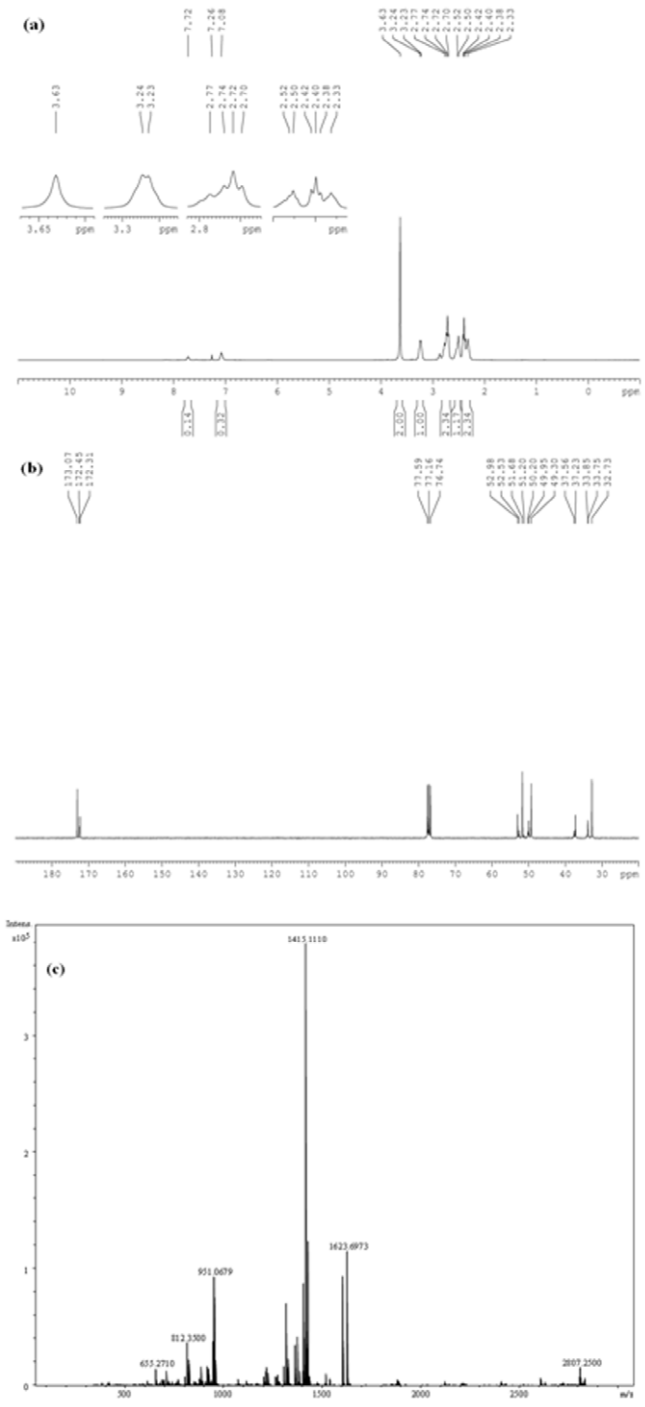

Figure S-7. ^{1}H (a), ^{13}C (b) NMR spectra (c) and ESI-TOF MS spectrum of PAMAM G1.5

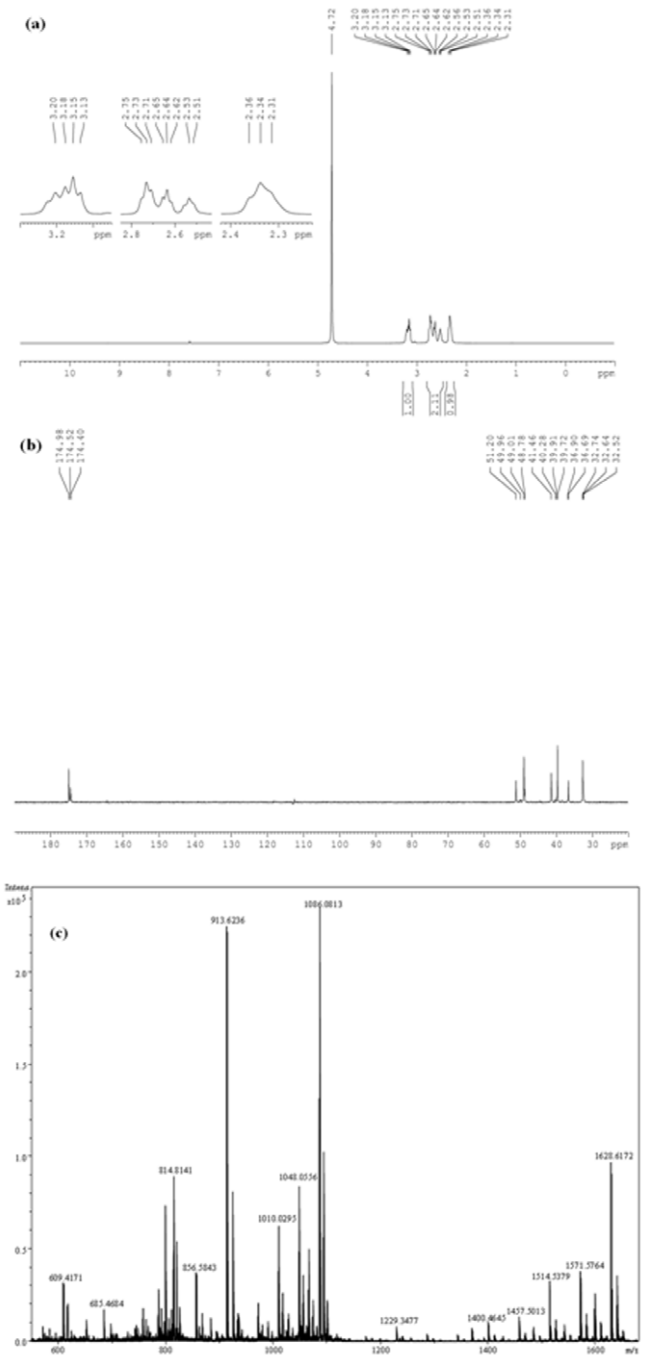

Figure S-8. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G2.0

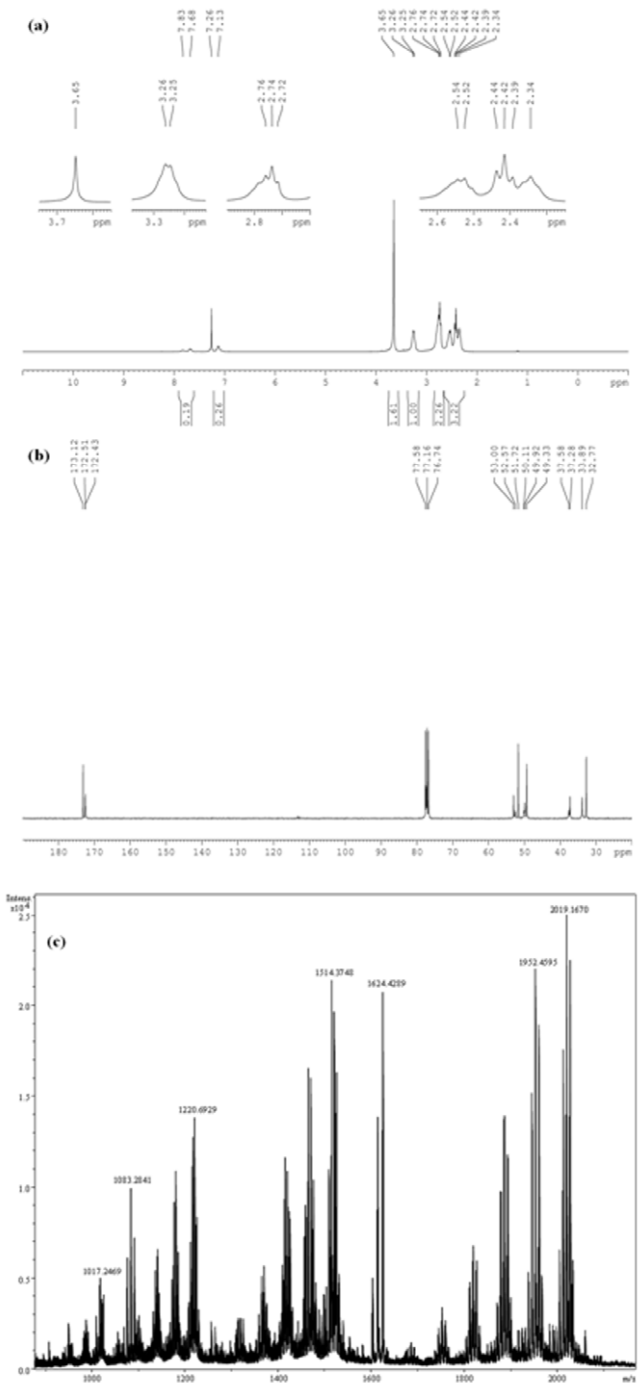

Figure S-9. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G2.5

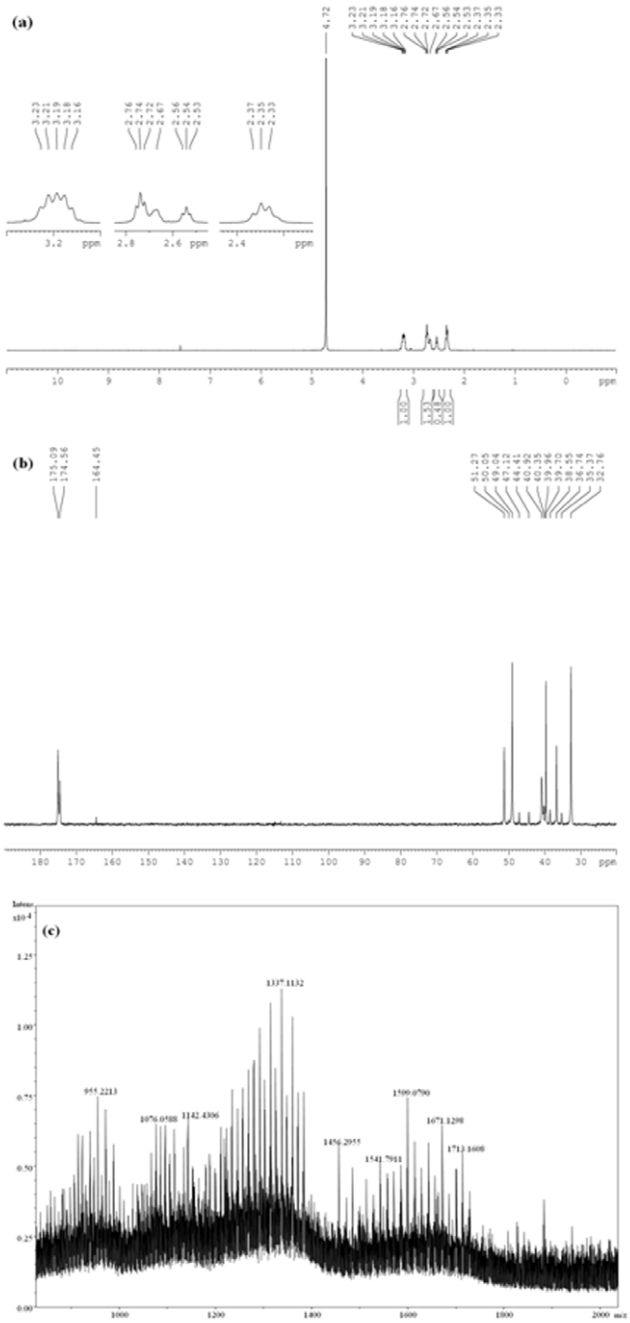

Figure S-10. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of PAMAM G3.0

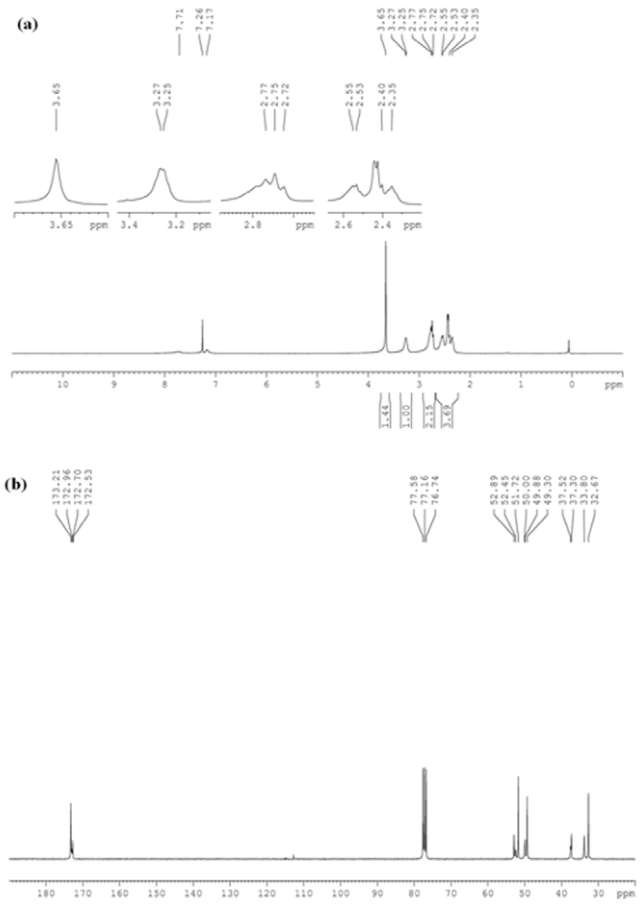

Figure S-11. ^{1}H (a), ^{13}C (b) NMR spectra and of PAMAM G3.5

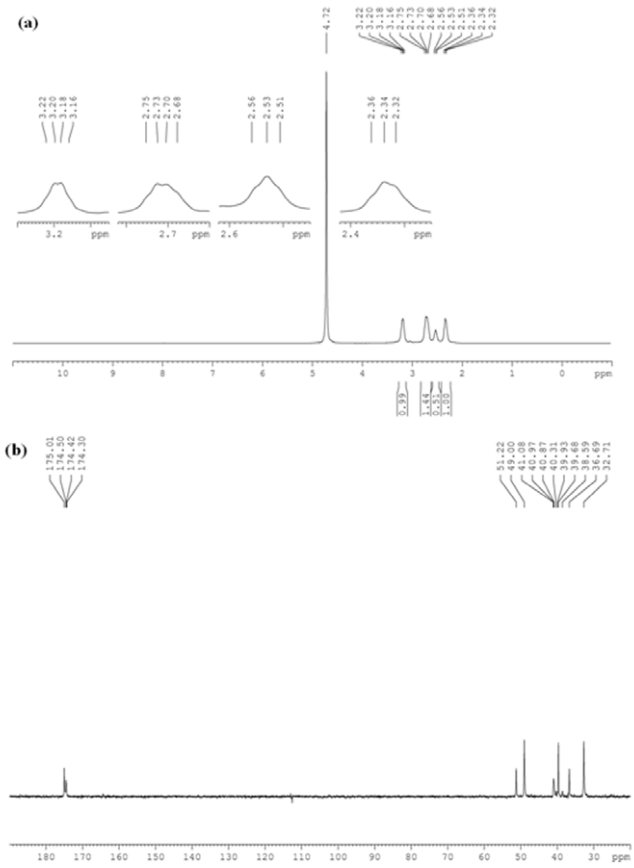

Figure S-12. ^{1}H (a), ^{13}C (b) NMR spectra and of PAMAM G4.0

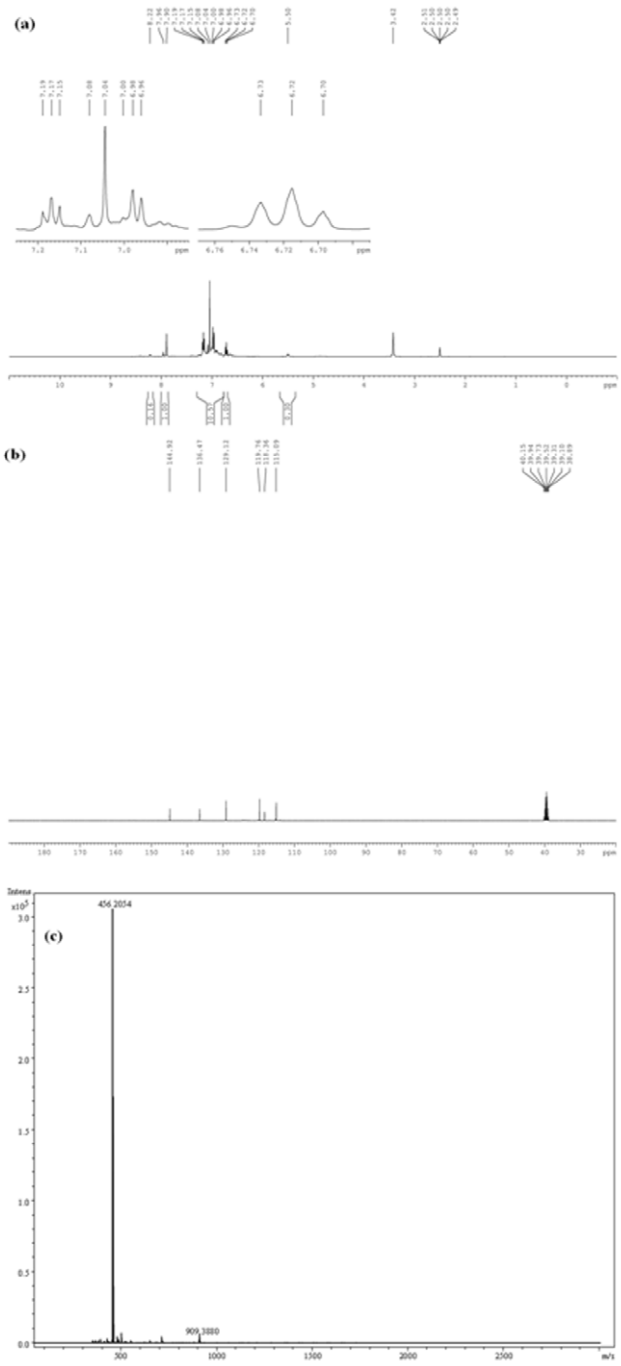

Figure S-13. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of AP

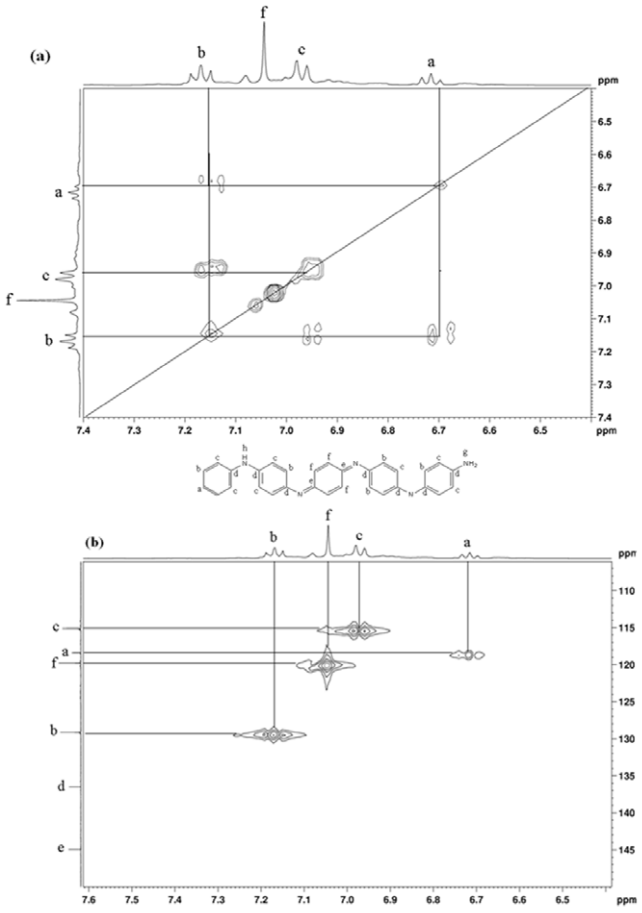

Figure S-14. ^{1}H-^{1}H COSY (a), HMQC (b) NMR spectra of AP

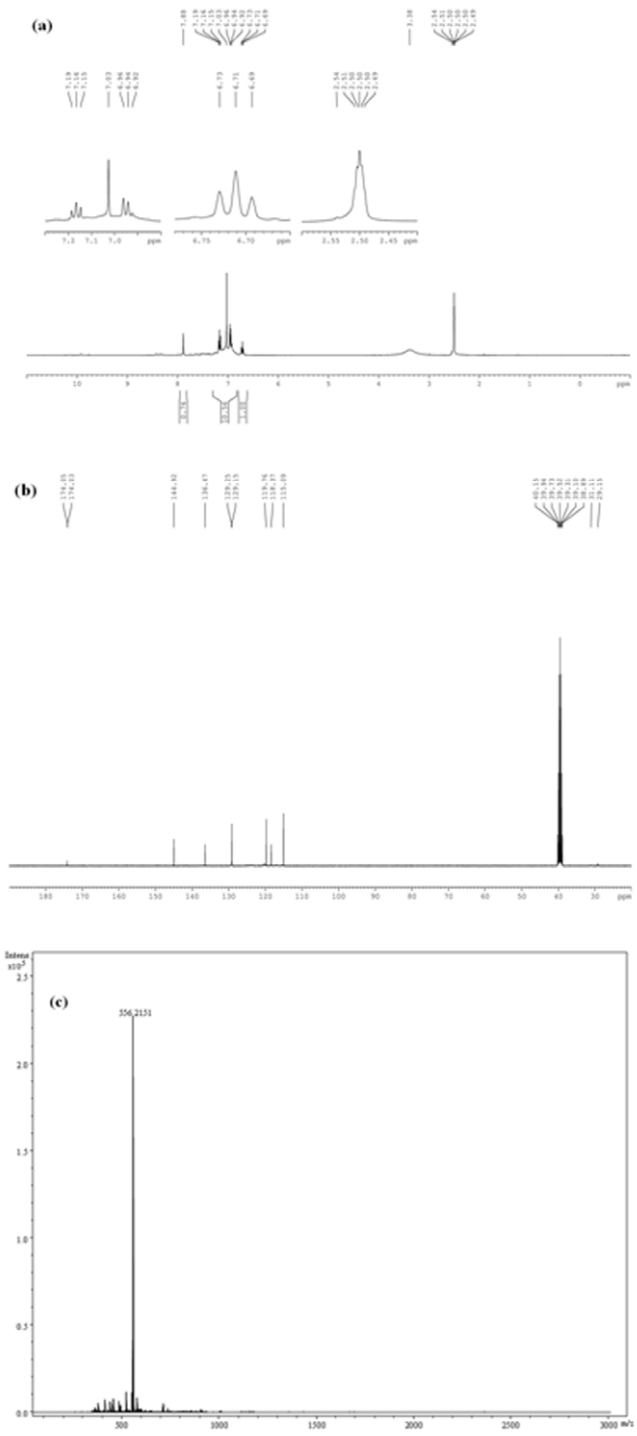

Figure S-15. ^{1}H (a), ^{13}C (b) NMR spectra and ESI-TOF MS (c) spectrum of AP-COOH

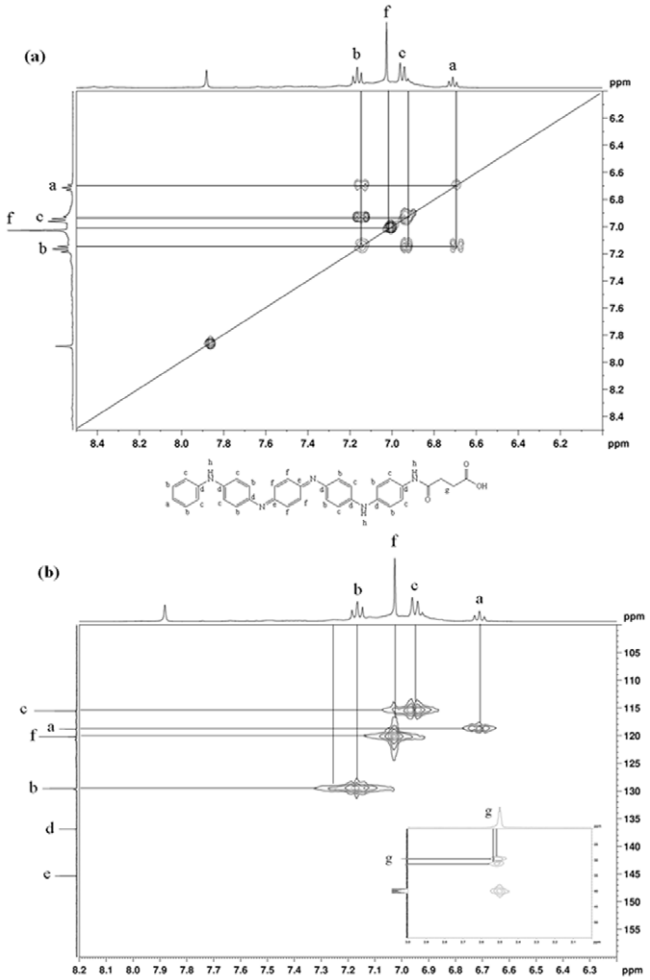

Figure S-16. ^{1}H-^{1}H COSY (a), HMQC (b) NMR spectra of AP-COOH

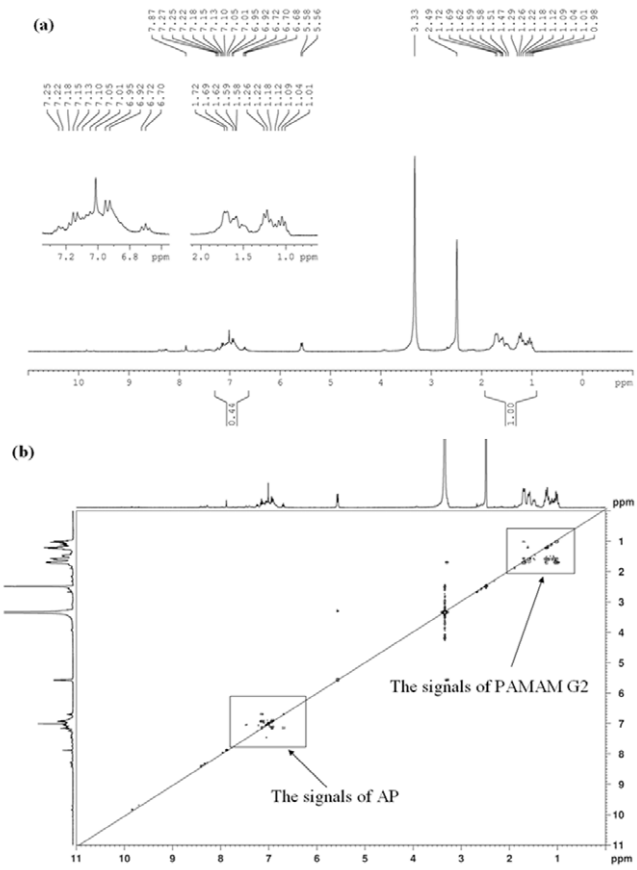

Figure S-17. ^{1}H (a), ^{1}H-^{1}H COSY (b) NMR spectra of PAMAM-AP G2

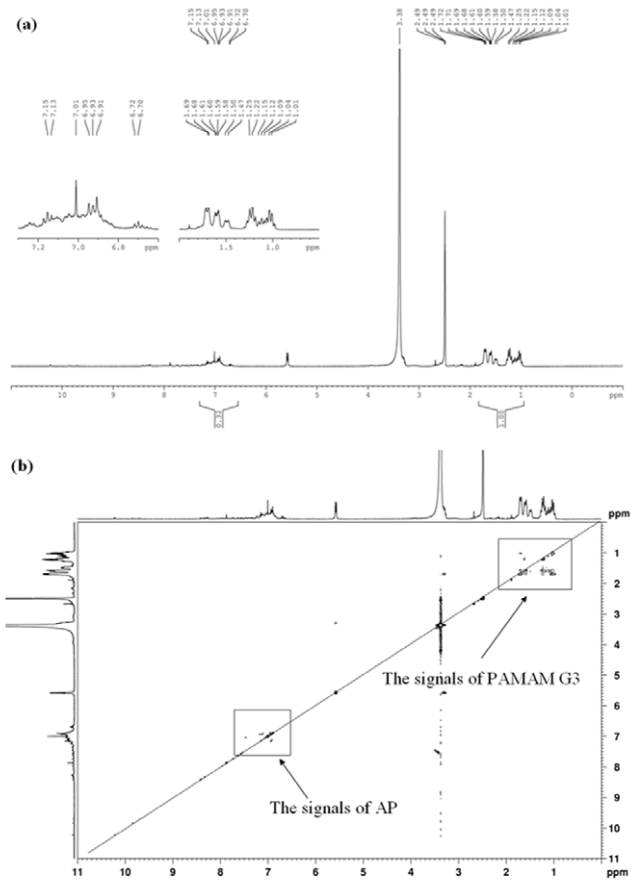

Figure S-18. ^{1}H (a), ^{1}H-^{1}H COSY (b) NMR spectra of PAMAM-AP G3

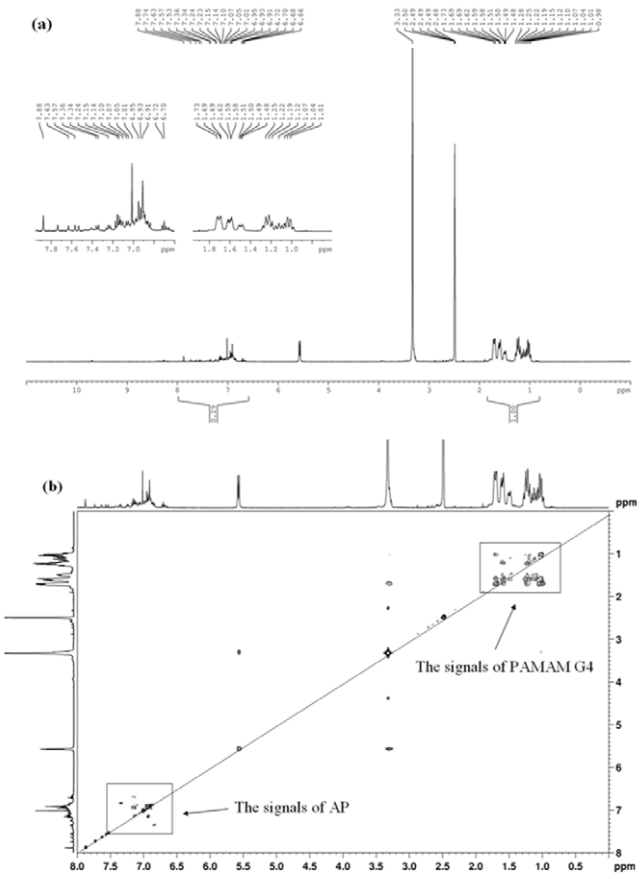

Figure S-19. ^{1}H (a), ^{1}H-^{1}H COSY (b) NMR spectra of PAMAM-AP G4