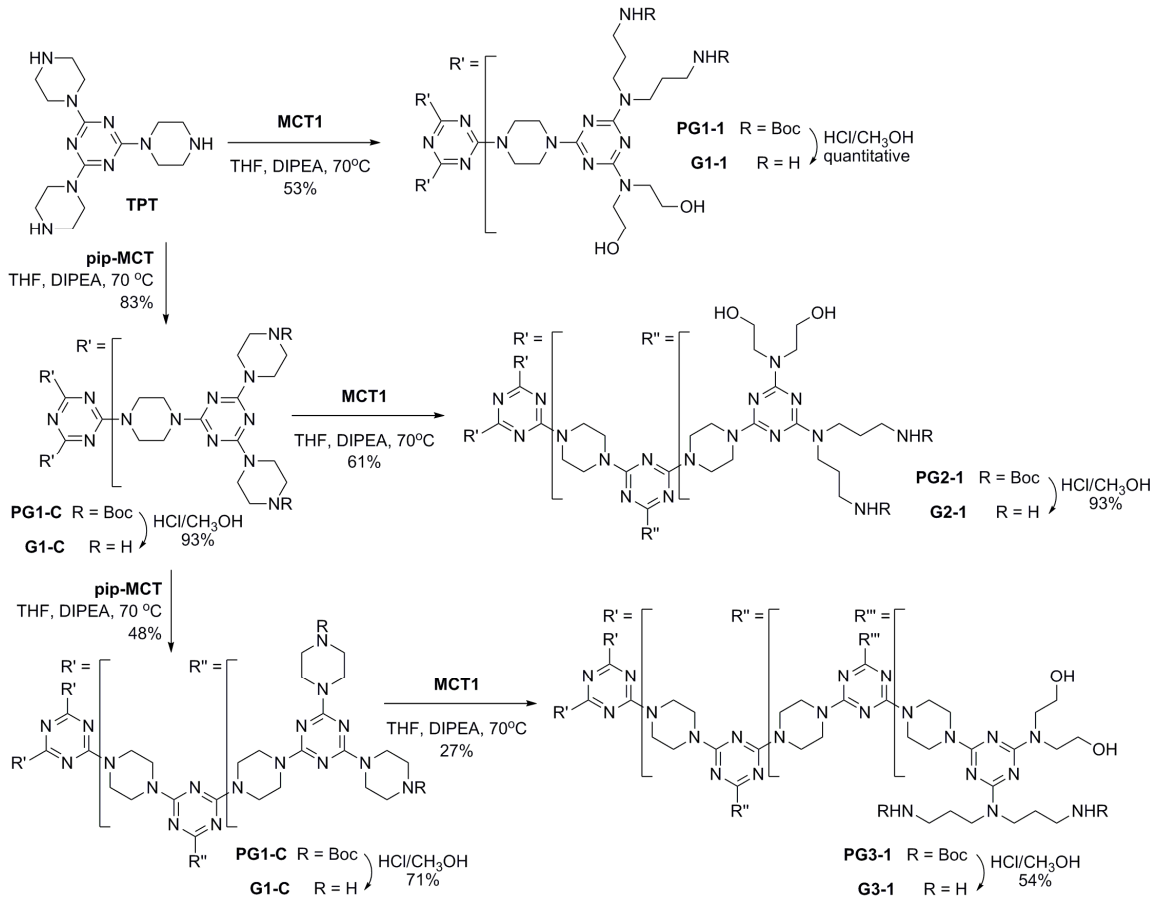
Supplementary Material:

Synthesis of Triazine Dendrimers:

Monochlorotriazine 1 (MCT1). Cyanuric chloride (0.9220g, 5.000 mmol) and Boc-protected 3,3'-bisaminopropylamine (1.6575g, 5.00 mmol) were each dissolved in 60 mL tetrahydrofuran and cooled to 0 °C. The Boc-protected triamine was added dropwise to cyanuric chloride followed by the addition of DIPEA (1.75 mL, 10.046 mmol). After 3 hours, diethanolamine (0.5276g, 5.018 mmol) and DIPEA (1.75 mL, 10.046 mmol) were dissolved in 60 mL tetrahydrofuran, cooled to 0 °C, and added dropwise to the reaction mixture. The mixture was allowed to warm to room temperature. After 20 hours the solvent was evaporated under reduced pressure. The crude product was dissolved in dichloromethane and the salt byproducts were extracted with distilled water. The organic layer was condensed and the product purified by column chromatography (10:1 CH_2Cl_2:ethyl acetate) to yield MCT1 (2.4937g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.76 (b, 1H, O**H**) 5.36 (t, 2H, N**H**Boc), 3.77 (d, 4H, C**H**$_2$OH), 3.67 (d, 4H, NC**H**$_2$CH$_2$OH), 3.51-3.43 (br, 4H, NC**H**$_2$CH$_2$CH$_2$), 3.01 (m, 4H, C**H**$_2$NHBoc), 1.79-1.67 (m, 4H, CH$_2$C**H**$_2$CH$_2$), 1.37 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 168.4 (C_3N_3), 165.0 (C_3N_3), 164.1 (C_3N_3), 156.3 (CO), 79.3 (O**C**(CH$_3$)$_3$), 61.7 (**C**H$_2$OH), 51.7 (NC**H**$_2$CH$_2$OH), 44.6 (NC**H**$_2$CH$_2$CH$_2$), 38.0 (**C**H$_2$NHBoc), 28.2 (C(**C**H$_3$)$_3$), 27.7 (CH$_2$**C**H$_2$CH$_2$). MS (ESI): calcd 547.29 (M^+); found 548.30 ($M + H^+$).



Scheme S1: Synthesis of rigid generation 1-3 dendrimers (G1-1, G2-1, G3-1)

Protected G1-1 Dendrimer (P-G1-1). Tris(piperazyl)triazine (TPT) (0.1837g, 0.551 mmol) and MCT1 (0.9071g, 1.655 mmol) were dissolved separately in 10 mL dichloromethane. The monochlorotriazines solution was added to the solution containing TPT followed by the addition of DIPEA (0.6mL, 3 mmol), and the mixture was heated to reflux. After two days reaction mixture was washed three times with H_2O, condensed under reduced pressure, and purified by column chromatography (1:1 CH_2Cl_2:ethyl acetate with 4% CH_3OH → 1:1 CH_2Cl_2:ethyl acetate with 20% CH_3OH) to afford G1-1

in 53% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.68 (s, 3H, O**H**) 5.10 (s, 6H, N**H**Boc), 3.85 (br, 12H, C**H**$_2$OH), 3.80 (br, 24H, piperazine), 3.75 (br, 12H, NC**H**$_2$CH$_2$OH), 3.59-3.48 (br, 12H, NC**H**$_2$CH$_2$CH$_2$), 3.08-3.15 (br, 12H, C**H**$_2$NHBoc), 1.73 (br, 12H, CH$_2$C**H**$_2$CH$_2$), 1.42 (s, 54H, C(C**H**$_3$)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 167.2 (C_3N_3), 164.6 (C_3N_3), 164.6 (C_3N_3), 156.1 (CO), 79.3 (O**C**(CH$_3$)$_3$), 63.0 (**C**H$_2$OH), 51.3 (NC**H**$_2$CH$_2$OH), 44.1 (NC**H**$_2$CH$_2$CH$_2$), 43.5 (piperazine), 38.1 (**C**H$_2$NHBoc), 28.6 (C(**C**H$_3$)$_3$), 27.8 (CH$_2$**C**H$_2$CH$_2$). MS (MALDI): calcd 1867.17 (M^+); found 1869.07 (M + H^+).

G1-1. P-G1-1 (0.3326g, 0.178 mmol) was dissolved in 3 M HCl:CH_3OH. After 2 days, the reaction was condensed and neutralized with $NaCO_3$ to pH=7. NaCl byproduct was removed from the mixture using an Amicon apparatus and a millipore membrane with NMWL = 1,000 under 35 psi N_2. The water that was pushed through the membrane was tested for Cl^- using $AgNO_3$. When no AgCl precipitate formed from the filtrate, the solution remaining inside the Amicon vessel was condensed *in vacuo* to afford G1-1 (0.5276 g, 129%). MS (MALDI): calcd 1267.59 (M^+); found 1267.91 (M + H^+).

Protected G2-1 (P-G2-1). MCT1 (0.5686g, 1.037 mmol) and G1-C (0.1826g, 0.1698 mmol) were each dissolved in 10mL of 9:1 CH_2Cl_2:CH_3OH. The solutions were mixed at room temperature followed by the addition of DIPEA (0.5mL, 2.8704 mmol). The reaction mixture was heated to 70 °C. After 10 days the reaction mixture was condensed, re-dissolved in dichloromethane, and washed with distilled water. The organic layer was condensed and purified by column chromatography (4:1 CH_2Cl_2:ethyl acetate with 1 → 3% CH_3OH) to yield P-G2-1 (0.4267g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.64 (s,

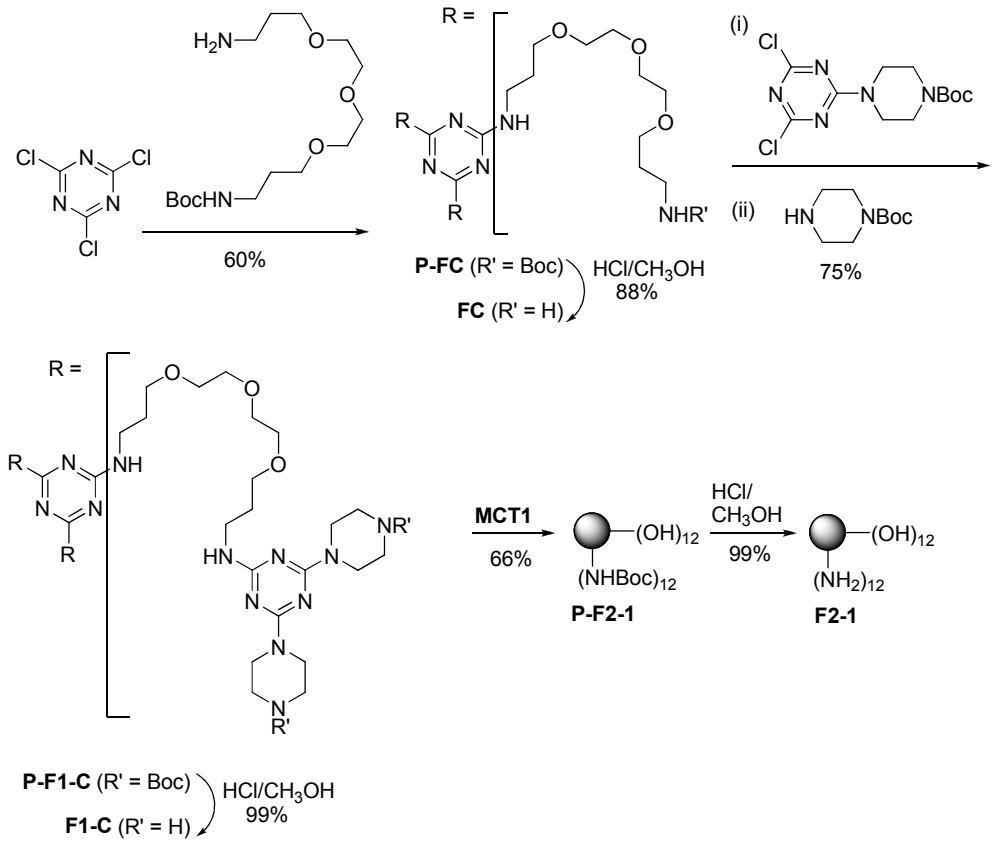
12H, O**H**) 5.09 (s, 12H, N**H**Boc), 3.87 (br, 24H, C**H**$_2$OH), 3.81 (br, 72H, piperazine), 3.77 (br, 24H, NC**H**$_2$CH$_2$OH), 3.61 (br, 24H, NC**H**$_2$CH$_2$CH$_2$), 3.11 (br, 24H, C**H**$_2$NHBoc), 1.67 (br, 24H, CH$_2$C**H**$_2$CH$_2$), 1.44 (s, 108H, C(C**H**$_3$)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 165.6 (C_3N_3), 165.5 (C_3N_3), 156.2 (CO), 79.2 (O**C**(CH$_3$)$_3$), 62.0 (**C**H$_2$OH), 51.3 (NC**H**$_2$CH$_2$OH), 44.2 (NC**H**$_2$CH$_2$CH$_2$), 43.6 (piperazine), 38.2 (**C**H$_2$NHBoc), 28.7 (C(**C**H$_3$)$_3$), 27.9 (CH$_2$**C**H$_2$CH$_2$). MS (MALDI): calcd 4142.57 (M^+); found 4142.71 ($M + H^+$).

G2-1. P-G2-1 was dissolved in 3 M HCl:CH_3OH. After 2 days the reaction was condensed and neutralized with $NaCO_3$ to pH=7. NaCl byproduct was removed from the mixture using an Amicon apparatus and a millipore membrane with NMWL = 1,000 under 35 psi N_2. The water that was pushed through the membrane was tested for Cl^- using $AgNO_3$. When no AgCl precipitate formed from the filtrate, the solution remaining inside the Amicon vessel was condensed *in vacuo* to afford G2-1 (0.2463g, 93%). MS (MALDI): calcd 2941.94 (M^+); found 4142.90 ($M + H^+$). HPLC (2:1 H_2O with 0.14% TFA:acetonitrile): 3.196 min.

Protected G3-1 (P-G3-1). G2-C (0.0408g, 0.016 mmol) and MCT1 (0.1053g, 0.192 mmol) were each dissolved in 1 mL of 9:1 $CHCl_3$:CH_3OH. The monochlorotriazine solution was added to the G2-C solution at room temperature. The reaction was heated to 70 ºC. After 6 days the reaction mixture was condensed, dissolved in chloroform and washed with distilled water. The organic layer was condensed and purified by column chromatography (10:1 CH_2Cl_2:EtOAc → 1:1 CH_2Cl_2:EtOAc) to yield P-G3-1 (0.0374g, 27%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.01-5.69 (s, 24H, N**H**), 3.82 (br, 192H, C**H**$_2$OH,

piperazine), 3.75 (br, 48H, NC**H**$_2$CH$_2$OH), 3.47-3.57 (br, 48H, NC**H**$_2$CH$_2$CH$_2$), 3.09 (br, 48H, C**H**$_2$NHBoc), 1.71 (br, 48H, CH$_2$C**H**$_2$CH$_2$), 1.43 (s, 216H, C(C**H**$_3$)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 167.0 (**C**$_3$N$_3$), 165.7 (**C**$_3$N$_3$), 164.6 (**C**$_3$N$_3$), 164.4 (**C**$_3$N$_3$), 156.2 (**C**O), 79.3 (**C**(CH$_3$)$_3$), 63.0 (**C**H$_2$OH), 51.4 (N**C**H$_2$CH$_2$OH), 46.0 (N**C**H$_2$CH$_2$CH$_2$NHBoc), 43.0 - 43.3 (N**C**H$_2$**C**H$_2$N), 38.2 (**C**H$_2$NHBoc), 28.7 (C(CH$_3$)$_3$), 27.9 (NCH$_2$**C**H$_2$CH$_2$NHBoc). MS (MALDI): calcd 8693.4 (M^+); found 8700.1 (M + H^+).

G3-1. P-G3-1 (0.0330g, 0.004 mmol) was dissolved in 3 mL CH_3OH. Concentrated HCl (2 mL) was added to the solution. After 24 hours the reaction was condensed and neutralized using NaOH. NaCl byproduct was removed from the solution using an Amicon apparatus and a millipore membrane with NMWL = 3,000 under 25 psi N_2. The filtrate was tested for Cl^- using $AgNO_3$. When no AgCl precipitate formed the solution remaining inside the Amicon vessel was condensed *in vacuo* to afford G3-1 (0.0129g, 54%).



Scheme S2: Synthesis of second generation flexible dendrimer (F2-1)

Protected Flexible Core (P-FC). Cyanuric chloride (0.1596g, 0.866 mmol) and N-Boc-4,7,10-trioxa-1,13-tridecanediamine (0.9512g, 2.769 mmol) were each dissolved in 15 mL THF. The N-Boc-diamine solution was added to the cyanuric chloride solution and the mixture was heated to 70 ºC. After 4 days the reaction mixture was condensed, dissolved in dichloromethane, and washed three times with distilled water. The organic layer was collected, condensed, and purified by column chromatography (30:1 CH_2Cl_2:CH_3OH → 10:1 CH_2Cl_2:CH_3OH) to yield P-FC (0.5338g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.09 (s, 4H, NH), 3.45-3.62 (m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.41 (q, 6H, NHC**H$_2$**), 3.20 (q, 6H, C**H$_2$**NHBoc),1.81 (m, 6H, NHCH$_2$C**H$_2$**), 1.73 (m, 6H, C**H$_2$**CH$_2$NHBoc), 1.41 (s, 27H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 165.9

(**C**$_3$N$_3$), 156.2 (**C**O), 79.0 (**C**(CH$_3$)$_3$), 70.7-70.8 (**C**H$_2$O**C**H$_2$), 70.4-70.5 (**C**H$_2$CH$_2$OCH$_2$**C**H$_2$), 69.6-69.7 (NHCH$_2$CH$_2$**C**H$_2$O), 39.1 (NH**C**H$_2$), 38.7 (**C**H$_2$NHBoc), 29.8 (**C**H$_2$CH$_2$NHBoc), 29.0 (NH**C**H$_2$**C**H$_2$). (N**C**H$_2$**C**H$_2$NBoc), 28.6 (C(**C**H$_3$)$_3$). MS (MALDI): calcd 1035.7 (M^+); found 1036.7 ($M + H^+$).

Flexible Core (FC). P-FC (0.5332g, 0.5166 mmol) was dissolved in 7.5 mL CH$_3$OH. Concentrated HCl (2.5 mL was added to the solution. After 24 hours, the reaction mixture was condensed, and 5 M NaOH was added to obtain a basic solution (pH=14). The product was extracted from the aqueous solution with dichloromethane. The organic fractions were condensed to yield FC (0.3331g, 88%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.15 (s, 3H, NH), 3.52-3.62 (m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.41 (q, 6H, NHC**H$_2$**), 2.76 (q, 6H, C**H$_2$**NHBoc),1.79 (m, 6H, NHCH$_2$C**H$_2$**), 1.69 (m, 6H, C**H$_2$**CH$_2$NHBoc), 1.58 (s, 6H, NH$_2$). ^{13}C NMR (300 MHz, CDCl$_3$) δ: 166.3 (**C**$_3$N$_3$), 70.7-70.8 (**C**H$_2$O**C**H$_2$), 70.3-70.4 (**C**H$_2$CH$_2$OCH$_2$**C**H$_2$), 69.5-69.6 (NHCH$_2$CH$_2$**C**H$_2$O), 39.8 (**C**H$_2$NH$_2$), 38.3 (**C**H$_2$NH), 33.5 (CH$_2$CH$_2$NH$_2$), 29.8 (**C**H$_2$CH$_2$NH). MS (MALDI): calcd 735.5 (M^+); found 736.8 ($M + H^+$).

Protected, Flexible G1 Core (P-F1-C). FC (0.3069g, 0.417mmol) and Boc-piperazyldichlorotriazine were each dissolved in 10 mL THF and cooled to 0 ºC. The dichlorotriazine solution was added dropwise to the FC solution followed by the addition of DIPEA (0.7 mL, 4.019 mmol). The mixture was allowed to warm to room temperature, and 1M K$_2$CO$_3$ was added to the solution. After 16 hours, Boc-piperazine was added to reaction, and the solution was heated to 70 ºC. After 24 hours the reaction

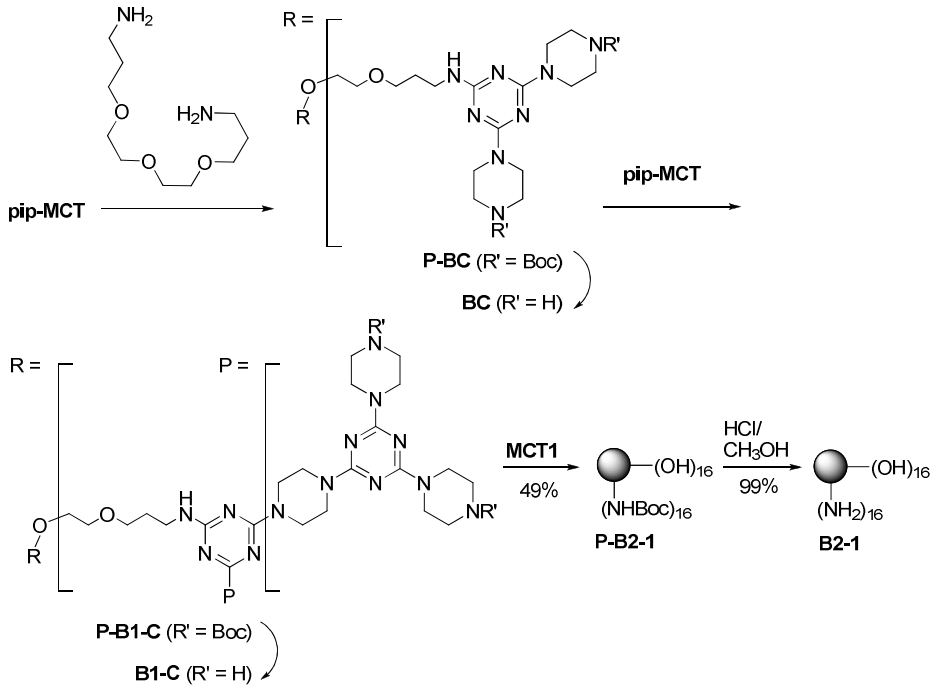
was condensed, dissolved in dichloromethane, and washed three times with distilled water. The organic layer was purified by column chromatography (30:1 CH_2Cl_2:CH_3OH → 15:1 CH_2Cl_2:CH_3OH) to yield P-F1-C (0.6529g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.23 (s, 6H, NH), 3.71 (s, 24H, NC**H$_2$**CH_2NBoc), 3.53-3.63 (m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.42 (br, 36H, NHC**H$_2$**, CH_2C**H$_2$**NBoc), 1.82 (m, 12H, C**H$_2$**NH), 1.46 (s, 54H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.5 (**C**$_3$N$_3$), 165.4 (**C**$_3$N$_3$), 155.0 (**C**O), 80.1(**C**$(CH_3)_3$), 70.78 (**C**H_2O**C**H_2), 70.4 (**C**$H_2CH_2OCH_2$**C**H_2), 69.5 ($NHCH_2CH_2$**C**H_2O), 43.1 (piperazine), 38.3 (**C**H_2NH), 29.8 (**C**H_2CH_2NH), 28.6 (C(**C**$H_3)_3$). MS (MALDI): calcd 2077.3 (M^+); found 2078.6 ($M + H^+$).

Flexible G1 Core (F1-C). P-F1-C (0.6295g, 0.303 mmol) was dissolved in 7.5 mL CH_3OH. Concentrated HCl (2.5 mL) was added to the solution. After 24 hours, the reaction mixture was condensed and the solution was made basic by adding 5 M NaOH. The product was extracted with dichloromethane to yield F1-C (0.4438g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.23-5.33 (s, 6H, NH), 3.69 (s, 24H, NC**H$_2$**CH_2NBoc), 3.53-3.63 (m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.41 (br, 12H, NHC**H$_2$**, CH_2C**H$_2$**NBoc), 2.83 (s, 24H, NCH_2C**H$_2$**NH), 1.80 (m, 12H, C**H$_2$**NH). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.5 (**C**$_3$N$_3$), 165.3 (**C**$_3$N$_3$), 70.73 (**C**H_2O**C**H_2), 70.4 (**C**$H_2CH_2OCH_2$**C**H_2), 69.4-69.5 ($NHCH_2CH_2$**C**H_2O), 46.1 ((CH_2**C**$H_2)_2NH$), 44.3 ((**C**$H_2CH_2)_2NH$), 38.3 (**C**H_2NH), 29.8 (CH_2**C**H_2CH_2NH). MS (MALDI): calcd 1477.0 (M^+); found 1478.2 ($M + H^+$).

Protected F2-1 (P-F2-1). MCT1 (0.2804g, 0.512 mmol) and P-F1-C (0.1006g, 0.068 mmol) were each dissolved in 5mL dichloromethane. The MCT1 solution was added to

the solution containing F1-C followed by the addition of DIPEA (0.2 mL, 1.148 mmol). The mixture was heated to 70 ºC. After two days the reaction mixture was washed three times with distilled water. The organic layer was condensed and purified by column chromatography (30:1 CH_2Cl_2:CH_3OH → 4:1 CH_2Cl_2:CH_3OH) to yield P-F2-1 (0.2058g, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.68 (s, 6H, NH), 5.23 (s, 12H, NH), 3.84 (br, 24H, C**H$_2$**OH), 3.75 (s, 72H, NC**H$_2$**CH_2OH, piperazine), 3.59 (br, 60H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**, NC**H$_2$**CH_2CH_2NHBoc), 3.45 (br, 48H, piperazine), 3.08-3.14 (br, 24H, NCH_2CH_2C**H$_2$**NHBoc), 1.80 (m, 12H, C**H$_2$**NH), 1.72 (br, 24H, NCH_2C**H$_2$**CH_2NHBoc), 1.42 (s, 108H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 167.1 (**C**$_3N_3$), 166.5 (**C**$_3N_3$), 165.3 (**C**$_3N_3$), , 164.6 (**C**$_3N_3$), 164.4 (**C**$_3N_3$), 156.5 (**C**O), 79.2 (**C**$(CH_3)_3$), 70.8 (**C**H_2O**C**H_2), 70.4 (**C**$H_2CH_2OCH_2$**C**H_2), 69.4 (NHCH_2CH_2**C**H_2O), 62.4 (**C**H_2OH), 51.3 (N**C**H_2CH_2OH), 43.5 (N**C**$H_2CH_2CH_2$NHBoc), 43.0 (piperazine), 38.3 (**C**H_2NH), 37.5 (**C**H_2NHBoc), 29.8 (**C**H_2CH_2NH), 28.7 (C(**C**$H_3)_3$), 27.9 (NCH_2**C**H_2CH_2NHBoc). MS (MALDI): calcd 4544.9 (M^+); found 4546.5 ($M + H^+$).

F2-1. P-F2-1 (0.2056g, 0.045 mmol) was dissolved in 7.5 mL methanol. Concentrated HCl (2.5 mL) was added to the solution. After 24 hours the reaction was condensed and neutralized with NaOH. NaCl byproduct was removed from the solution using an Amicon apparatus and a millipore membrane with NMWL = 1,000 under 35 psi N_2. The filtrate was tested for Cl^- using $AgNO_3$. When no AgCl precipitate formed the solution remaining inside the Amicon vessel was condensed *in vacuo* to afford F2-1 (0.1506g, 99%).



Scheme S3: Synthesis of second generation bow-tie dendrimer (B2-1)

Protected Bow-tie core (P-BC). Pip-MCT (0.9713g, 2.007 mmol) and 4,7,10-trioxa-1,13-tridecanediamine (0.2009g, 0.912 mmol) were each dissolved in 7.5 mL THF. The monochlorotriazine solution was added to the diamine solution, and the mixture was heated to 70 ºC. After 24 hours the reaction mixture was condensed and purified by column chromatography (10:1 CH_2Cl_2:EtOAc → 1:1 CH_2Cl_2:EtOAC) to yield P-BC (0.5802g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.09 (t, 2H, NH), 3.71 (s, 16H, NC**H$_2$**CH_2NBoc), 3.53-3.66 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.43 (br, 20H, NHC**H$_2$**, CH_2C**H$_2$**NBoc), 1.82 (m, 4H, C**H$_2$**CH_2NH), 1.46 (s, 36H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.5 (**C**$_3$N$_3$), 165.4 (**C**$_3$N$_3$), 155.0 (**C**O), 80.1(**C**$(CH_3)_3$), 70.8 (**C**H_2O**C**H_2), 70.4 (**C**$H_2CH_2OCH_2$**C**H_2), 69.6 (NHCH_2CH_2**C**H_2O), 43.1 (piperazine), 38.5

(**C**H_2NH), 29.8 (**C**H_2CH_2NH), 28.6 (C(**C**H_3)$_3$). MS (MALDI): calcd 1114.7 (M^+); found 1115.6 ($M + H^+$).

Bow-tie Core (BC). P-BC (0.2384g, 0.214 mmol) was dissolved in 7.5 mL methanol. Concentrated HCl (2.5 mL) was added to the solution. After 24 hours the reaction was condensed and NaOH was added until the solution was at pH 14. The product was extracted from solution using dichloromethane to yield BC (0.0896g, 59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.03 (t, 2H, N**H**CH_2), 3.70 (s, 16H, NC**H$_2$**CH_2NBoc), 3.53-3.63 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.41 (q, 4H, NHC**H$_2$**), 2.84 (s, 16H, NCH_2C**H$_2$**NH), 1.82 (m, 4H, C**H$_2$**CH_2NH), 1.57 (br, 4H, N**H**). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.6 (**C**$_3N_3$), 165.4 (**C**$_3N_3$), 70.8 (**C**H_2O**C**H_2), 70.5 (**C**$H_2CH_2OCH_2$**C**H_2), 69.6 ($NHCH_2CH_2$**C**H_2O), 46.2 ((CH_2**C**$H_2)_2$NH), 44.4 ((**C**$H_2CH_2)_2$NH), 38.4 (**C**H_2NH), 29.8 (CH_2**C**H_2CH_2NH).

Protected G1 Bow-tie Core (P-B1-C). BC (0.0778g, 0.109 mmol) and pip-MCT (0.2158g, 0.446 mmol) were each dissolved in 2 mL 9:1 $CHCl_3$:CH_3OH. Pip-MCT solution was added to the core solution followed by the addition of DIPEA (1.4 mL, 8.037 mmol). The solution was heated to 70 ºC. After 24 hours the reaction was condensed, dissolved in chloroform and washed three times with distilled water. The organic layer was condensed and purified by column chromatography (30:1 CH_2Cl_2:CH_3OH) to yield P-B1-C (0.2017g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.12 (t, 2H, N**H**CH_2), 3.77 (s, 32H, NC**H$_2$**C**H$_2$**N), 3.74 (s, 32H, C**H$_2$**CH_2NBoc), 3.53-3.63 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.43 (q, 36H, NHC**H$_2$**, NCH_2C**H$_2$**NBoc), 1.85 (m, 4H, C**H$_2$**CH_2NH), 1.47 (s, 72H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.6

(**C**$_3$N$_3$), 165.5 (**C**$_3$N$_3$), 155.0 (**C**O), 80.1 (**C**(CH$_3$)$_3$), 70.8 (**C**H$_2$O**C**H$_2$), 70.5 (**C**H$_2$CH$_2$OCH$_2$**C**H$_2$), 69.6 (NHCH$_2$CH$_2$**C**H$_2$O), 43.2-44.0 (piperazine), 38.4 (**C**H$_2$NH), 29.9 (CH$_2$**C**H$_2$CH$_2$NH), 28.6 (C(**C**H$_3$)$_3$). MS (MALDI): calcd 2503.5 (M^+); found 2504.8 ($M + H^+$).

G1 Bow-tie Core (B1-C). P-B1-C (0.1794g, 0.072 mmol) was dissolved in 4 mL methanol. Concentrated HCl (2 mL) was added to the solution. After 24 hours the reaction mixture was condensed, and the product was precipitated using 5 M NaOH. The precipitate was dissolved in chloroform and washed with 1 M NaOH. The organic layer was condensed to yield P-B1-C (0.1201g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.12 (t, 2H, N**H**CH$_2$), 3.76 (s, 32H, NC**H$_2$**C**H$_2$**N), 3.73 (s, 32H, NC**H$_2$**CH$_2$NH), 3.55-3.65 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.46 (q, 4H, NHC**H$_2$**), 2.85 (s, 32H, NCH$_2$C**H$_2$**NH), 1.83 (m, 4H, C**H$_2$**CH$_2$NH). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 166.6 (**C**$_3$N$_3$), 165.6 (**C**$_3$N$_3$), 70.8 (**C**H$_2$O**C**H$_2$), 70.5 (**C**H$_2$CH$_2$OCH$_2$**C**H$_2$), 69.6 (NHCH$_2$CH$_2$**C**H$_2$O), 46.2 (NCH$_2$**C**H$_2$NH), 44.5 (N**C**H$_2$CH$_2$NH), 43.3 (N**C**H$_2$**C**H$_2$NH), 38.4 (**C**H$_2$NH), 29.9 (CH$_2$**C**H$_2$CH$_2$NH). MS (MALDI): calcd 1703.1 (M^+); found 1704.2 ($M + H^+$).

Protected B2-1. MCT1 (0.1138g, 0.208 mmol) and B1-C (0.0294g, 0.017 mmol) were each dissolved in 3 mL 10:1 $CHCl_3$:CH_3OH. The MCT1 solution was added to the core solution followed by the addition of DIPEA (0.1 mL, 0.574 mmol). The solution was heated to 70 ºC. After three days the reaction was condensed, dissolved in chloroform, and washed three times with distilled water. The chloroform solution was condensed and

purified by column chromatography (30:1 CH_2Cl_2:CH_3OH → 9:1 CH_2Cl_2:CH_3OH) to yield P-B2-1 (0.0492g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.12 (t, 16H, N**H**Boc), 3.83 (s, 32H, C**H$_2$**OH), 3.77 (s, 128H, NC**H$_2$**C**H$_2$**N, NC**H$_2$**CH_2OH), 3.67 (s, 32H, NC**H$_2$**CH_2CH_2NHBoc), 3.58 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.47 (q, 4H, NHC**H$_2$**), 3.07-3.15 (br, 32H, NCH_2CH_2C**H$_2$**NHBoc), 1.85 (m, 4H, C**H$_2$**CH_2NH), 1.72 (s, 32H, NCH_2C**H$_2$**CH_2NHBoc), 1.42 (s, 144H, C(C**H$_3$**)$_3$). ^{13}C NMR (300 MHz, $CDCl_3$/CD_3OD) δ: 167.0 (**C**$_3N_3$), 165.4 (**C**$_3N_3$), 164.4 (**C$_3$**N_3), 156.2-156.5 (**C**O), 79.2-79.3 (**C**$(CH_3)_3$), 70.8 (**C**H_2O**C**H_2), 70.4 (**C**$H_2CH_2OCH_2$**C**H_2), 69.5 ($NHCH_2CH_2$**C**H_2O), 62.4-63.1(**C**H_2OH), 51.3 (N**C**H_2CH_2OH), 44.2 (N**C**$H_2CH_2CH_2$NHBoc), 43.0-43.5 (N**C**H_2**C**H_2N), 38.2 (**C**H_2NH), 37.5 (**C**H_2NHBoc), 29.8 (OCH_2**C**H_2CH_2NH), 28.7 (C(**C**$H_3)_3$), 27.9 (NCH_2**C**H_2CH_2NHBoc). MS (MALDI): calcd 5793.6 (M^+); found 5794.9 ($M + H^+$).

B2-1. P-B2-1 (0.0453g, 0.008 mmol) was dissolved in 7 mL methanol. Concentrated HCl (2.5 mL) was added to the solution. After 24 hours the solution was condensed and neutralized with sodium hydroxide. NaCl byproduct was removed from the solution using an Amicon apparatus and a millipore membrane with NMWL = 1,000 under 35 psi N_2. The filtrate was tested for Cl^- using $AgNO_3$. When no AgCl precipitate formed the solution remaining inside the Amicon vessel was condensed *in vacuo* to afford B2-1 (0.0365g, 99%).