Formation of Rotaxane Dendrimers by Supramolecular Click Chemistry

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The concept of supramolecular click chemistry was recently introduced to describe self-assembling supramolecular systems.[1] The advantage of supramolecular click chemistry over traditional click chemistry is the reversible character of the supramolecular interactions used.[2] Cucurbit[8]uril (CB[8])[3] is an excellent host for supramolecular click chemistry which forms the stable 1:1:1 complex by the encapsulation of methyl viologen (MV^{2+}) and 2,6-dihydroxynaphthalene ($Np(OH)_2$) inside the cavity. Formation of the ternary complex is driven by the markedly enhanced charge-transfer (CT) interaction between the electron-deficient and electron-rich guest molecules inside the hydrophobic cavity of CB[8].[4] Kim *et al.* have applied the host-stabilized CT interactions to build several novel supramolecular assemblies such as vesicles,[5] molecular loops,[6] supramolecular polymers on surfaces,[7] and molecular necklaces.[8] The redox properties of methyl viologen (MV^{2+}) in the host-stabilized CT complexes, in particular, provide the reversible character, which have been utilized to demonstrate the exchange of the guest within the host in which methyl viologen (MV^{2+}) was efficiently dimerized by one-electron reduction in the presence of a CB[8] host.[9] These properties may provide a novel principle of stimuli-responsive materials.[10] Herein we report on the construction of rotaxane dendrimers, which is based on a new supramolecular click chemistry, *i.e.*, CB[8] mediated charge transfer interaction between an electron-deficient (MV^{2+}) and an electron-rich (Np) units existing at the focal point of dendrons (Figure 1).

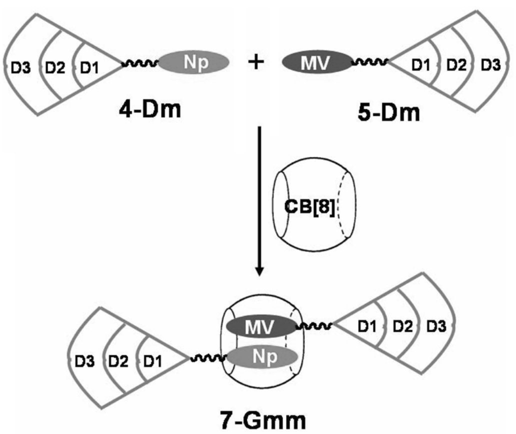


Figure 1. Strategy for rotaxane dendrimers.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on a 300 or 500 MHz NMR spectrometer. FAB and ESI mass spectra were obtained from Korea Basic Science Institute in Daegu or Daejeon.

Synthesis and characterization of HCl salt of the electron-rich PAMAM dendrons 4-Dm. A solution of propargyl-PAMAM dendrons **1-Dm** (0.10 mmol) and 2-(3-azido-propoxy)-6-methoxy-naphthalene **2** (0.11 mmol) in THF-H_2O (4:1, 1 mL) in the presence of 5 mol % $CuSO_4{\cdot}5H_2O$ with 10 mol % sodium ascorbate was stirred at room temperature for ~2.5 h. The reaction mixture was poured into brine (20 mL) and the resulting solution was extracted with EtOAc (20 mL × 3). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography (EtOAc or EtOAc/methanol system) to afford the desired product **4-Dm**. Then, the conc. HCl was added slowly to a solution of dendrons **4-Dm** in MeOH in an ice-bath. After 1 h, THF and diethyl ether were added to precipitate the product. The precipitates were collected by the filter or centrifugation and washed with diethyl ether. The solids were dried in vacuum to afford the desired product as a hydrochloride salt.

4-D1·HCl. 99% yield; ^1H NMR (300 MHz, D_2O): δ = 2.31 (quin, J = 5.3 Hz, 2H), 2.63 (t, J = 6.2 Hz, 2H), 2.98 (t, J = 6.1 Hz, 2H), 3.60 (s, 6H), 3.74 (s, 3H), 3.77 (t, 2H), 4.31 (s, 2H), 4.58 (t, J = 6.0 Hz, 2H), 6.86 (s, 1H), 6.91 (d, J = 9.0 Hz, 1H), 6.98 (d, J = 8.9 Hz, 1H), 7.04 (s, 1H), 7.43 (d, J = 8.9 Hz, 1H), 7.49 (d, J = 8.9 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR (125 MHz, D_2O): δ = 172.5, 156.0, 154.9, 135.4, 130.0, 129.8, 128.7, 128.6, 128.4, 119.1, 118.9, 107.6, 106.7, 65.0, 55.5, 53.1, 49.0, 48.0, 47.5, 29.1, 28.7. ESI-MS Calcd for $C_{25}H_{33}ClN_4O_6$: 520.2089. Found: m/z = 485.59 $[M-Cl^-]^+$.

4-D2·3HCl. 99% yield; ^1H NMR (300 MHz, D_2O) δ = 2.42 (quin, J = 5.3 Hz, 2H), 2.73 (t, J = 6.2 Hz, 4H), 2.82 (t, J = 6.3 Hz, 8H), 3.19 (t, J = 6.3 Hz, 4H), 3.25 (t, J = 5.2 Hz, 4H), 3.40 (t, J = 6.2 Hz, 8H), 3.50 (t, J = 5.1 Hz, 4H), 3.66 (s, 12H), 3.86 (s, 3H), 4.00 (t, J = 5.1 Hz, 2H), 4.47 (s, 2H), 4.69 (t, J = 5.6 Hz, 2H), 7.03 (d, J = 8.9 Hz, 1H), 7.10-7.13 (m, 2H), 7.24 (s, 1H), 7.63 (d, J = 9.3 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 8.23 (s, 1H); ^{13}C NMR (125 MHz, D_2O): δ = 173.0, 172.9, 156.0, 154.9, 135.7, 130.1, 129.9, 128.9, 128.8, 128.4, 119.3, 119.1, 108.0, 107.0, 65.3, 55.9, 53.6, 53.2, 50.2, 49.8, 49.6, 48.3, 47.0, 35.0, 29.1, 28.6. ESI-MS Calcd for $C_{43}H_{67}Cl_3N_8O_{12}$: 992.3944. Found: *m/z* = 886.25 $[M\text{-}2H^+\text{-}3Cl^-]^+$, 443.61 $[M\text{-}H^+\text{-}3Cl^-]^{2+}$.

4-D3·7HCl. 98% yield; ^1H NMR (500 MHz, D_2O): δ = 2.52 (quin, *J* = 5.5 Hz, 2H), 2.87 (t, *J* = 6.2 Hz, 12H), 2.96 (t, *J* = 6.5 Hz, 6H), 3.02 (t, *J* = 6.5 Hz, 2H), 3.35 (t, *J* = 6.7 Hz, 4H), 3.41 (t, *J* = 6.1 Hz, 4H), 3.55 (t, *J* = 6.3 Hz, 4H), 3.64 (t, *J* = 6.7 Hz, 4H), 3.67 (t, *J* = 5.9 Hz, 8H), 3.77 (s, 24H), 3.96 (s, 3H), 4.15 (t, *J* = 5.3 Hz, 2H), 4.60 (s, 2H), 7.13 (dd, *J* = 2.3 Hz, 2.3 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.26 (s, 1H), 7.37 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (125 MHz, D_2O): δ = 173.0, 173.0, 172.6, 156.2, 155.1, 135.8, 130.2, 130.0, 129.0, 128.9, 128.5, 119.4, 119.3, 108.0, 107.1, 65.6, 56.0, 53.4, 53.3, 52.5, 50.0, 49.8, 49.7, 48.5, 47.2, 34.9, 34.6, 29.5, 29.1, 29.0, 28.6. ESI-MS Calcd for $C_{79}H_{135}Cl_7N_{16}O_{24}$: 1936.7655. Found: *m/z* = 844.66 $[M\text{-}5H^+\text{-}7Cl^-]^{2+}$, 563.11 $[M\text{-}4H^+\text{-}7Cl^-]^{3+}$, 563.11 $[M\text{-}3H^+\text{-}7Cl^-]^{4+}$.

General procedure for the preparation of the electron-deficient PAMAM dendrons 5-Dm. A solution of propargyl-PAMAM dendrons **1-Dm (**0.22 mmol) and *N*-methyl-*N'*-(3-azidopropoyl)-4,4'-bipyridinium diiodide **3** (0.20 mmol) in DMF (1 mL) in the presence of 10 mol % CuI was stirred at room temperature for ~3.5 h. Methanol were added and the generated solid was filtered off. The filtrate was treated with THF and diethyl ether to precipitate. The precipitate was redissolved with MeOH and the resulting solution was treated with conc HCl. Then THF was added to precipitate the product. The precipitates were collected by the filter or centrifugation and washed with THF and diethyl ether. The solids were dried in vacuum to afford the desired product as a hydrochloride salt.

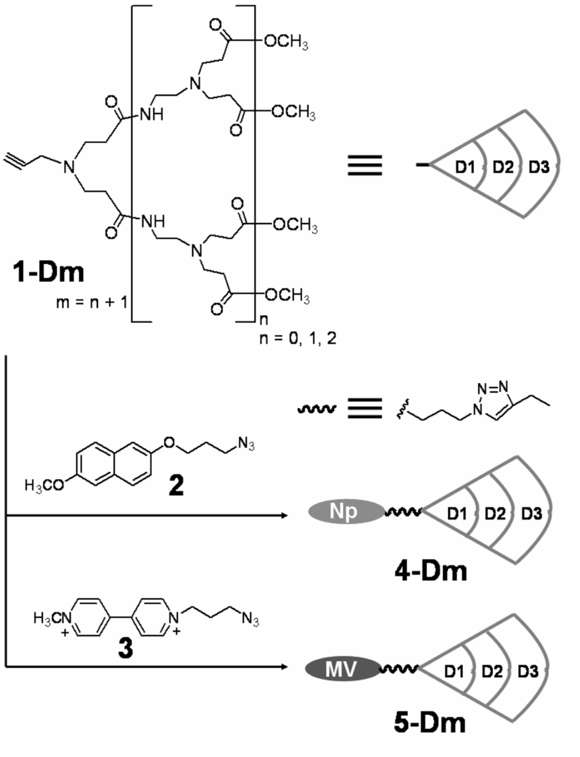
5-D1·3HCl. 92% yield; ^1H NMR (300 MHz, D_2O): δ = 2.76 (quin, *J* = 6.9 Hz, 2H), 2.99 (t, *J* = 6.4 Hz, 2H), 3.51 (t, *J* = 6.0 Hz, 2H), 3.70 (s, 6H), 4.47 (s, 3H), 4.61 (s, 2H), 4.66 (t, *J* = 6.6 Hz, 2H), 4.80 (t, 2H), 8.37 (s, 2H), 8.50 (d, *J* = 6.2 Hz, 1H), 8.55 (d, *J* = 6.3 Hz, 1H), 9.03 (d, *J* = 6.3 Hz, 1H), 9.13 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ = 173.0, 151.0, 150.1, 146.8, 146.2, 136.3, 128.6, 127.7, 127.2, 59.4, 53.3, 49.5, 48.9, 47.9, 47.6, 31.0, 28.9. ESI-MS Calcd for $C_{25}H_{35}Cl_3N_6O_4$: 588.1785. Found: *m/z* = 241.37 $[M\text{-}H^+\text{-}3Cl^-]^{2+}$.

5-D2·5HCl. 90% yield; ^1H NMR (500 MHz, D_2O): δ = 2.85 (quin, *J* = 6.2 Hz, 2H), 3.03 (t, *J* = 5.5 Hz, 12H), 3.49 (t, 4H), 3.70 (s, 6H), 4.47 (s, 3H), 4.61 (s, 2H), 4.66 (t, *J* = 6.6 Hz, 2H), 4.80 (t, 2H), 8.37 (s, 2H), 8.50 (d, *J* = 6.2 Hz, 1H), 8.55 (d, *J* = 6.3 Hz, 1H), 9.03 (d, *J* = 6.3 Hz, 1H), 9.13 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ= 173.0, 151.0, 150.1, 146.8, 146.2, 136.3, 128.6, 127.7, 127.2, 59.4, 53.3, 49.5, 48.9, 47.9, 47.6, 31.0, 28.9. ESI-MS Calcd for $C_{43}H_{69}Cl_5N_{10}O_{10}$: 1060.3641. Found: *m/z* = 177.13 $[M\text{-}5Cl^-]^{5+}$.

5-D3·9HCl. 88% yield; ^1H NMR (500 MHz, D_2O): δ = 2.84 (quin, *J* = 6.7 Hz, 2H), 2.93 (t, *J* = 6.3 Hz, 8H), 2.99 (t, *J* = 6.3 Hz, 4H), 3.03 (t, *J* = 6.4 Hz, 16H), 3.48 (t, *J* = 5.0 Hz, 12H), 3.55 (t, 4H), 3.61 (t, *J* = 6.3 Hz, 8H), 3.63 (t, *J* = 6.5 Hz, 16H), 3.73 (t, 12H), 3.80 (s, 24H), 4.55 (s, 3H), 4.70 (s, 2H), 4.66 (t, *J* = 6.6 Hz, 2H), 4.80 (t, 2H), 8.37 (s, 2H), 8.50 (d, *J* = 6.2 Hz, 1H), 8.55 (d, *J* = 6.3 Hz, 1H), 9.03 (d, *J* = 6.3 Hz, 1H), 9.13 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, D_2O): δ = 173.0, 151.0, 150.1, 146.8, 146.2, 136.3, 128.6, 127.7, 127.2, 59.4, 53.3, 49.5, 48.9, 47.9, 47.6, 31.0, 28.9. ESI-MS Calcd for $C_{79}H_{137}Cl_9N_{18}O_{22}$: 2004.7352. Found: *m/z* = 188.23 $[M\text{-}9Cl^-]^{9+}$.

Results and Discussion

The PAMAM dendrons having electron-deficient and electron-rich groups, linked by the triazole units, were synthesized by the click chemistry between the electron-deficient and electron-rich guest azides and the alkyne-functionalized PAMAM dendrons **1-Dm** (Scheme 1). The propargyl-functionalized PAMAM dendrons **1-Dm** (m = 1-3: generation of dendron) are synthesized by the divergent approach using propargylamine as an alkyne-focal point.[11] 2,6-Dialkoxynaphthalene **2** and *N,N'*-dialkyl viologen **3** were designed to serve as the electron-rich and electron-deficient guests, respectively. To efficiently connect the propargyl focal point PAMAM dendrons with the electron-deficient and electron-rich guests, the synthetic approach selected is based on the click condition using Cu(I) species.[12,13] Click reactions were carried out in a 4:1 solvent ratio of THF to H_2O using 5 mol % $CuSO_4{\cdot}5H_2O$ with 10 mol % sodium ascorbate as in situ reducing agent to generate the active Cu(I) species. The reaction between alkyne-dendron **1-D1** and compound **2** conducted for 1 h at room temperature afforded the desired product **4-D1** in yield of 99% (Scheme 1). Given the success in the synthesis of first-



Scheme 1

generation dendron, therefore we expanded this reaction condition to get higher-generation dendrons. Reactions of the compound **2** with **1-D2** and **1-D3** afforded the electron-rich PAMAM dendrons **4-D2** and **4-D3** in yields of 99% and 98%, respectively, after 1.5 h and 2.5 h. The dendrons **4-Dm** were purified by column chromatography and followed by the treatment of HCl to obtain as a hydrochloric salt. The electron-deficient PAMAM dendrons **5-Dm** were obtained from the reactions between *N*-azidopropyl *N'*-methyl viologen **3** and alkyne PAMAM dendrons **1-Dm**. Reactions of the compound **3** with **1-D1**, **1-D2**, and **1-D3** in the presence of 10 mol% of CuI in DMF afforded the electron-deficient PAMAM dendrons **5-D1**, **5-D2**, and **5-D3** in yields of 92%, 90%, and 88%, respectively, after 2.5 h, 3 h, and 3.5 h. The dendrons **5-Dm** were obtained as a hydrochloric salt. The structures of these compounds **4-Dm** and **5-Dm** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Before the construction of rotaxane dendrimers *via* CB[8] mediated supramolecular click chemistry as shown in Figure 1, we tested if the electron-deficient group of **5-Dm** takes $Np(OH)_2$. Treatment of 1 equiv. of CB[8] into a solution of the electron-deficient dendrons **5-Dm** and $Np(OH)_2$ results in a drastic change in the UV/Vis spectrum. The appearance of new absorption bands at λ = 560 nm supports the formation of the charge transfer complex[4] (CT rotaxane dendrons **6-Dm**) between 2,6-dihydroxynaphthalene and an electron-deficient units existing at the focal point of dendrons inside the hydrophobic cavity of CB[8]. NMR spectroscopic data also confirm the formation of the charge-transfer complexes (Figure 2). In particular, the upfield-shifted signals for the protons of the Np and viologen units in dendrons are consistent with the formation of 1:1:1 inclusion complex.

Encouraged by this successful proof of concept for supramolecular click chemistry, we applied this methodology to the construction of rotaxane dendrimers *via* CB[8] mediated charge transfer interaction between an electron-deficient and an electron-rich units existing at the focal point of dendrons. Treatment of 1 equiv. of CB[8] into a solution of the electron-rich PAMAM dendrons **4-Dm** and the electron-deficient dendrons **5-Dm** in water resulted in the formation of the rotaxane dendrimers **7-Gmm** through the formation of the CT complex between the Np and viologen units inside CB[8]. This is clearly evidenced by the development of a charge-transfer band when the rotaxane dendrimers **7-Gmm** from the dendrons **4-Dm** and dendrons **5-Dm** are formed in the presence of CB[8]. Figure 3 shows the charge-transfer band at 550 nm in **7-G33** that develops upon mixing **4-D3**, **5-D3**, and CB[8]. The charge transfer band is essentially undetectable unless CB[8] is added to the solution. Similar bands are observed when two rotaxane dendrimers **7-G11** and **7-G22** are obtained from **4-D1** and **5-D1** and **4-D2** and **5-D2** in the presence of CB[8], respectively. NMR spectroscopic data also confirm the formation of the rotaxane dendrimers **7-Gmm**. As shown in Figure 4, in the absence of CB[8], the aromatic protons on the Np residue and the aromatic protons on the viologen unit resonate at the same chemical shifts as observed in the NMR spectra of each dendron, indicating that the charge-transfer complex may not be formed. Meanwhile, upon addition of CB[8], the ^{1}H signals for the Np protons of **4-Dm** and the viologen protons of **5-Dm** shift upfield relative to those in the free dendrons (Figure 4). These observations are consistent with the formation of a charge-transfer complex in which the Np and viologen units of the dendrons reside inside the hydrophobic cavity of CB[8] as illustrated in Figure 1. The rotaxane dendrimers, **7-Gmm**, were characterized by pulsed-field gradient (or diffusion) NMR technique. For example, the diffusion coefficients of dendrons (**4-D2** and **5-D2**) and **7-G22** were measured to be 2.45×10^{-10} m/s^2 and 1.55×10^{-10} m/s^2, respectively. From the diffusion NMR data, the estimated hydrodynamic volume of **7-G22** is 8780 Å^3, which is also almost 4 and 6 times, respectively, those of the dendrons, **4-D2** and **5-D2**, (~2200 Å^3) and CB[8] (1500 Å^3). Taken together, the NMR data support the formation of a rotaxane dendrimer via CB[8] mediated CT interaction.

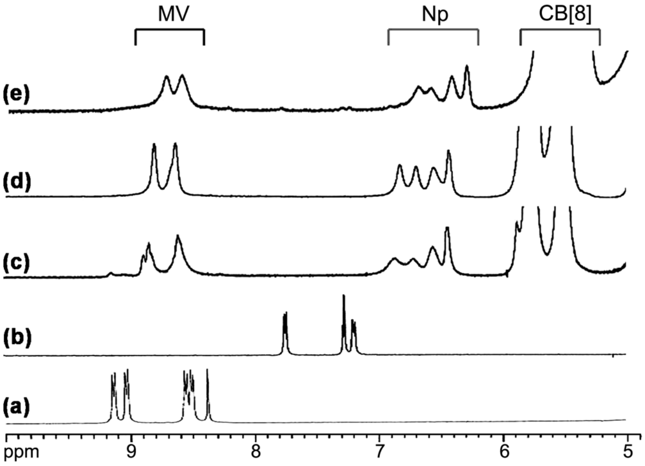


Figure 2. Partial ^{1}H-NMR spectra (D_2O) for (a) **5-D3**, (b) **$Np(OH)_2$**, (c) **6-D1**, (d) **6-D2**, and (e) **6-D3**.

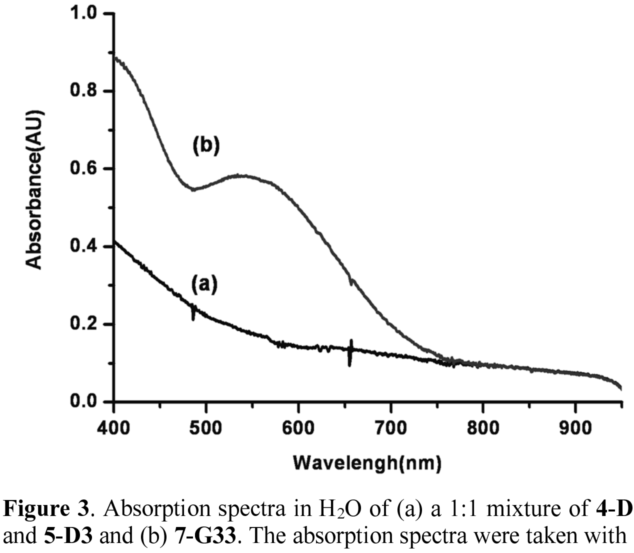


Figure 3. Absorption spectra in H_2O of (a) a 1:1 mixture of **4-D3** and **5-D3** and (b) **7-G33**. The absorption spectra were taken with 3 mM solutions.

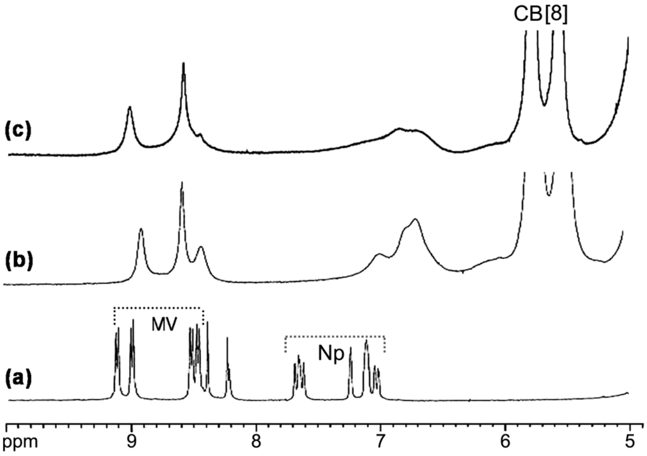


Figure 4. Partial ^{1}H-NMR spectra (D_2O) for (a) **4-D3** and **5-D3** (1:1 mixture), (b) **7-G22**, **(c) 7-G33**.

The preliminary investigation for the formation of unsymmetric rotaxane dendrimers was conducted from the combination of different generations with the electron-rich PAMAM dendrons **4-Dm** and the electron-deficient PAMAM dendrons **5-Dm** in the presence of CB[8]. For example, the formation of rotaxane dendrimers **7-G23** from **4-D2** and **5-D3** in the presence of CB[8] was confirmed by UV/Vis spectroscopy to show the charge-transfer band at 550 nm and by NMR spectroscopy to result in the upfield-shifted signals for the protons of the Np and viologen units. The application of the redox properties of methyl viologen (MV^{2+}) in the host-stabilized CT rotaxane dendrimers can provide the reversible conversion of hetero- and homo-guest-pair inclusion inside CB[8] and a novel principle of stimuli-responsive materials.[10,14]

In summary, we have demonstrated the formation of [2]rotaxane dendrimers having rotaxane unit at core *via* supramolecular click chemistry which is based on the cucurbit[8]uril mediated charge transfer interaction between the electron donor (Np) functionalized PAMAM dendrons and the electron acceptor (MV) functionalized PAMAM dendrons. Therefore, the formation of 1:1:1 inclusion complex between an electron-deficient (MV) and an electron-rich (Np) units existing at the focal point of dendrons in the presence of CB[8] can be regarded as a new and efficient method to construct various dendrimers. This novel and pivotal strategy can be applied for the fast and efficient synthesis of the dendrimers and dendritic materials with specific structures and properties in conjunction with their applications in nanotechnology.

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