Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for:

Speedy one-pot electrochemical synthesis of giant octahedrons from *in situ* generated pyrrolidinyl PAMAM dendrimer

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General information

In all experiments, the required chemicals were purchased from Sigma-Aldrich and Merck. For the purpose of electrochemical reactions commercially available soldering wire was purchased from market. A dc power source is used to supply the required voltage between the electrodes. ^{1}H NMR spectra were measured in BRUKER AVANCE III 500 MHz FT-NMR Spectrometer. Data is reported in ppm using D_2O as solvent. Data reported as: chemical shifts (δ), multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants (Hz).

The morphology of the prepared samples was determined using High-Resolution Transmission Electron Microscopy, (HRTEM) [model: JEOL JEM-2100] operated at an accelerating voltage of 200 kV. The surface structure was determined by Field Emission Scanning Electron Microscopy (FESEM) Make: Carl ZEISS Microscopy, Germany model: ZEISS, SIGMA. The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV, the apparatus requires an extreme vacuum (~10^{-6} Pa) in the column of the microscope.

X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Thermo-Scientific ESCALAB Xi$^+$ spectrometer having a monochromatic Al kα X-ray source (1486.6 eV) and a spherical energy analyzer that operates in the CAE (constant analyzer energy) mode using the electromagnetic lens mode. The CAE for the survey spectra is 100 eV and that for High-resolution spectra is 50 eV. Ultraviolet photoelectron spectroscopy (UPS) measurement was carried out in UPS lens mode. The CA for UPS Spectrum was 50 eV. He I (21.22 eV) excitation line was used for UPS measurement.

IR Affinity, Shimadzu, Japan FTIR spectrophotometer equipped with a Shimadzu DRS-8000 DRIFT accessory and IR solution software were used to record the Fourier transform infrared (FTIR) spectra with 4 cm^{-1}. To obtain the FT-IR spectra, samples (1–2 mg) were prepared by mixing them with dried KBr (100–200 mg) and then pressing the mixture into a pellet. The measurement acquired in the range of 4000–400 cm^{-1}.

Experimental procedures

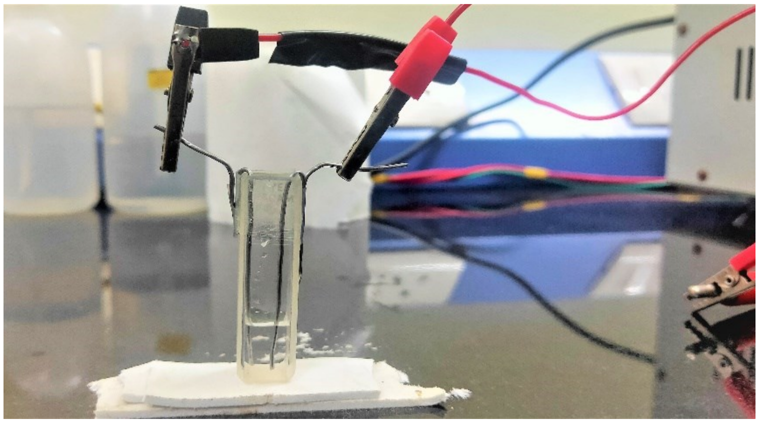
Synthesis of G3.5 PAMAM$(NHCH_2CH_2COOH)_{64}$ from G3.5 PAMAM$(NHCH_2CH_2COONa)_{64}$

The methanolic solution of PAMAM dendrimer, ethylenediamine core generation 3.5 was dried. Freshly prepared Formic acid in water in 1:1 was added to dried PAMAM dendrimer and the solution was stirred in room temperature for 5 hours. The solution was dialyzed through cellulose membrane to remove the salt for next overnight. The aqueous solution was filtered off and filtrate was dried thoroughly.^{1}H NMR(500 MHz, D_2O) δ 8.25 (s, N*H*), 3.56 (dd, CONH-CH_2), 3.45 (d, CONH-CH_2-CH_2), 3.37 – 3.25 (m, N-CH_2), 2.76 (s,CH_2-COOH), 2.59 (s, N-CH_2-CH_2).

Synthesis of G5.5 PAMAM$(NHCH_2CH_2COOH)_{256}$ from G5.5 PAMAM$(NHCH_2CH_2COONa)_{256}$

The methanolic solution of PAMAM dendrimer, ethylenediamine core generation 5.5 was dried, and 1:1 formic acid in water was added to the dried compound. The solution was stirred for 5 hours at room temperature. After completion of the reaction, the solution was dialyzed through cellulose membrane for next overnight. The aqueous solution was filtered off and the filtrate was dried. ^{1}H NMR (500 MHz, D_2O) δ 8.25 (s, N*H*), 3.63 – 3.50 (m, CONH-CH_2), 3.45 (d, CONH-CH_2-CH_2), 3.37 – 3.23 (m, N-CH_2), 2.76 (s, CH_2-COOH), 2.59 (s, N-CH_2-CH_2).

General procedure for the electrocatalytic synthesis of giant octahedron architectures



A quartz cuvette/vial, soldering wire (Sn:Pb) as electrodes, Milli-Q water, and a dc power source with copper cables were used for the electrolysis reaction. At first two electrodes were firmly fixed inside the quartz cuvette/vial (as shown in the photo). Then the electrodes were connected to the power source to complete the circuit so that one electrode act as anode and another electrode as cathode. Now freshly prepared dendrimer samples of 153, 307, 384 µmol (by dissolving different dendrimers, PAMAM$(NHCH_2CH_2COOH)_{64}$ or PAMAM$(NHCH_2CH_2COOH)_{256}$, separately in Milli-Q water) was used as electrolytic solution. The two electrodes were immersed into the electrolytic solution. Then, 3.5 V electricity was passed through the solution for 10 min, formation of white cloudy solution was observed along with the generation of bubbles. The current was passed until the bubbles completely ceased. Afterward, the solution was transferred in 2 ml Eppendorf and centrifuged it at 2,000 rpm for 5 min. The supernatant was removed and 1 ml ethanol was added and centrifuged in the same condition. The process was repeated two times to remove all the unwanted particles. The characterizations were done by FTIR, FESEM, XPS, XRPD and HRTEM.

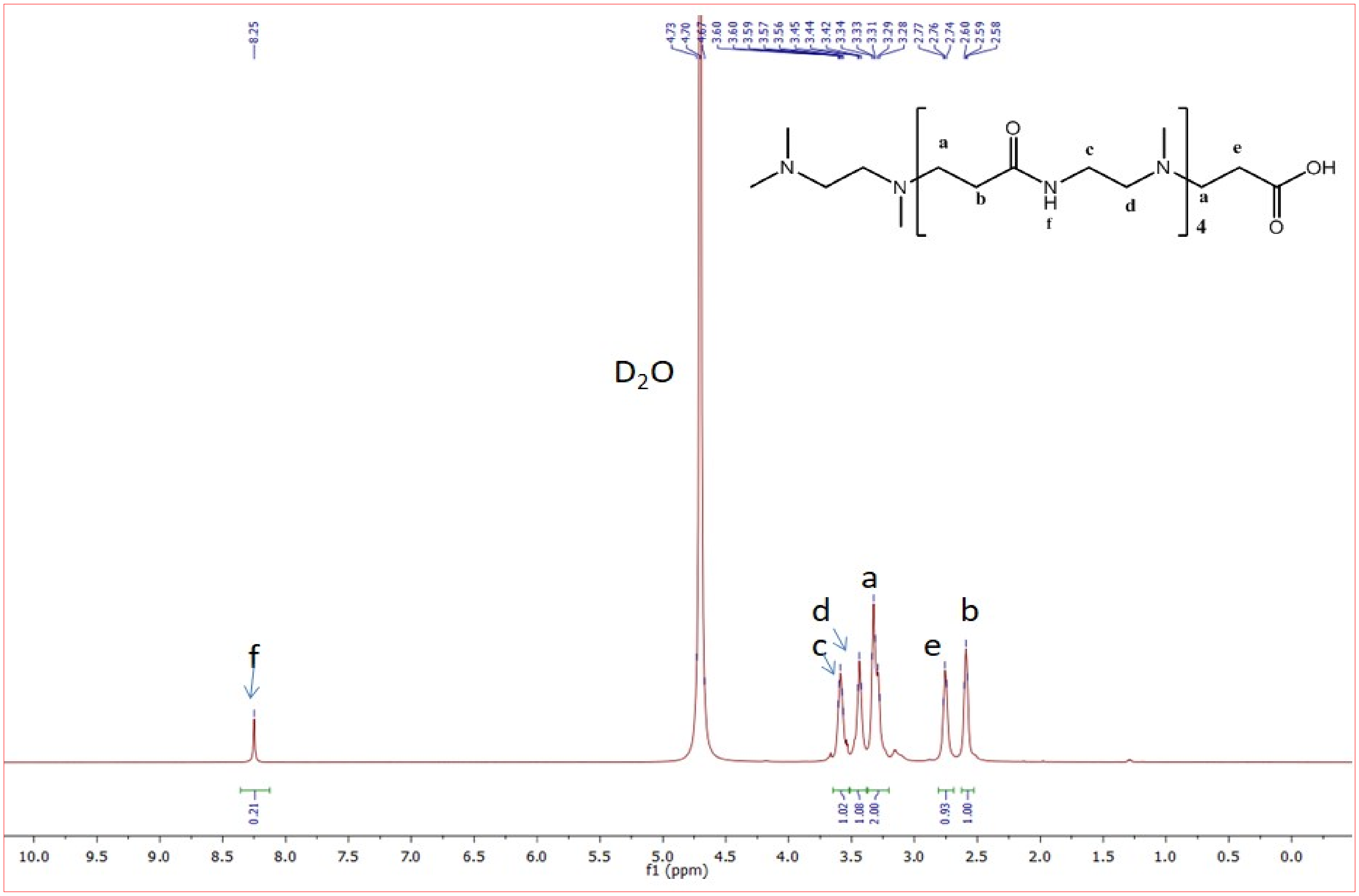


Figure S1a. ^{1}H NMR (500 MHz) of COOH-terminal/EDA core PAMAM dendrimer generation 3.5 in D_2O.

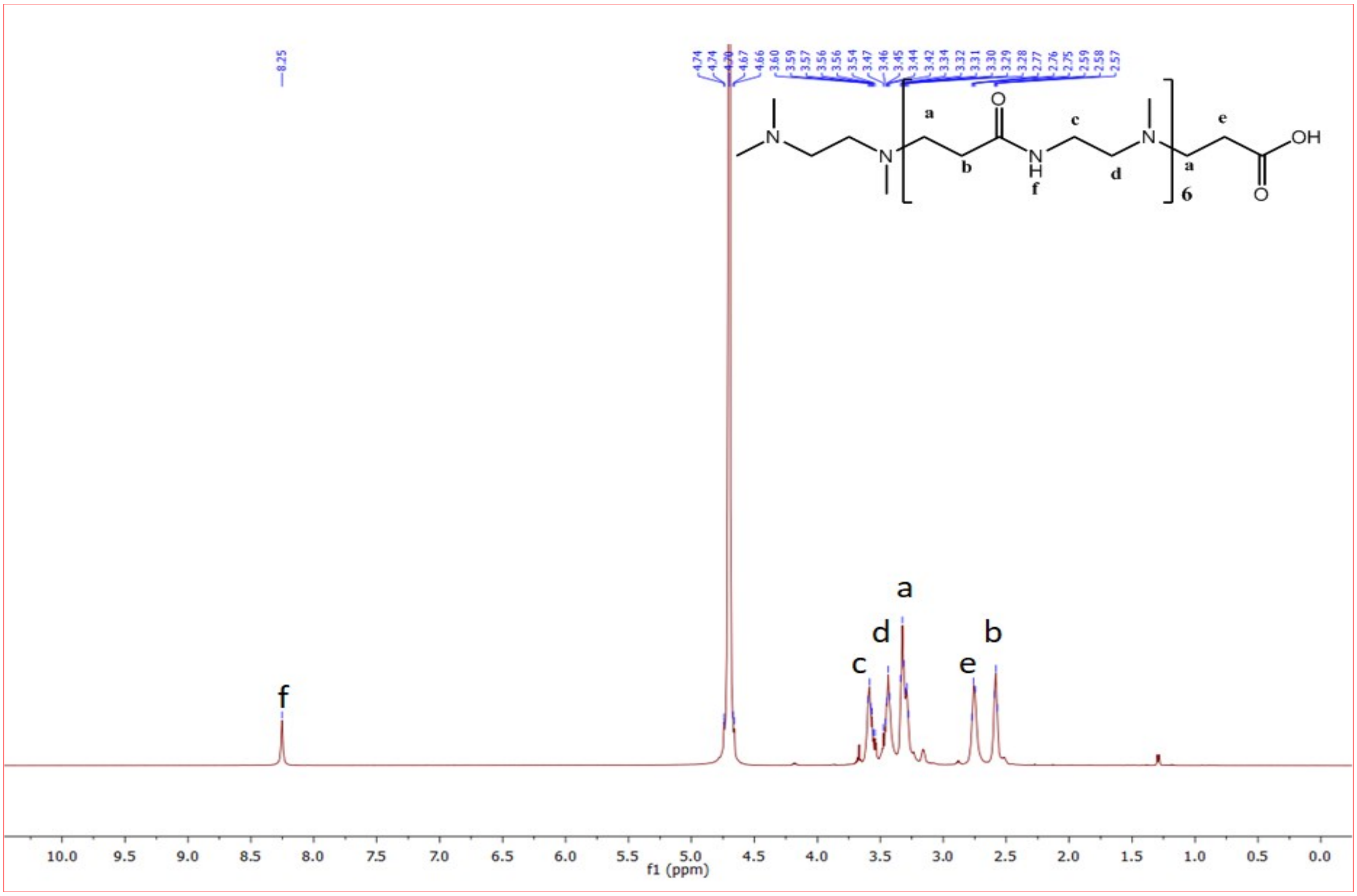


Figure S1b. ^{1}H NMR (500 MHz) of COOH-terminal/EDA core PAMAM dendrimer generation 5.5 in D_2O.

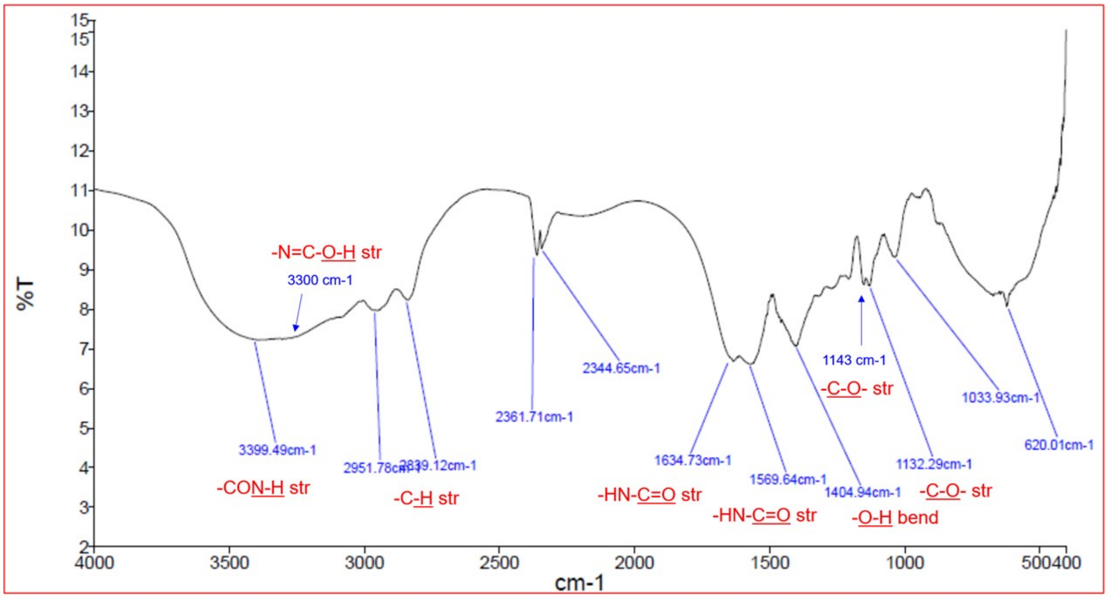


Figure S2a. FTIR spectrum of PAMAM G3.5 EDA core/COOH dendrimers. FTIR ν_{max}/cm^{-1} 3399 (strong, CON-H stretch), 3300 (strong, COOH stretch), 1634 (strong, HN-C=O stretch), 1569 (strong, HN-C=O stretch), 1404 (medium, O-H bend).

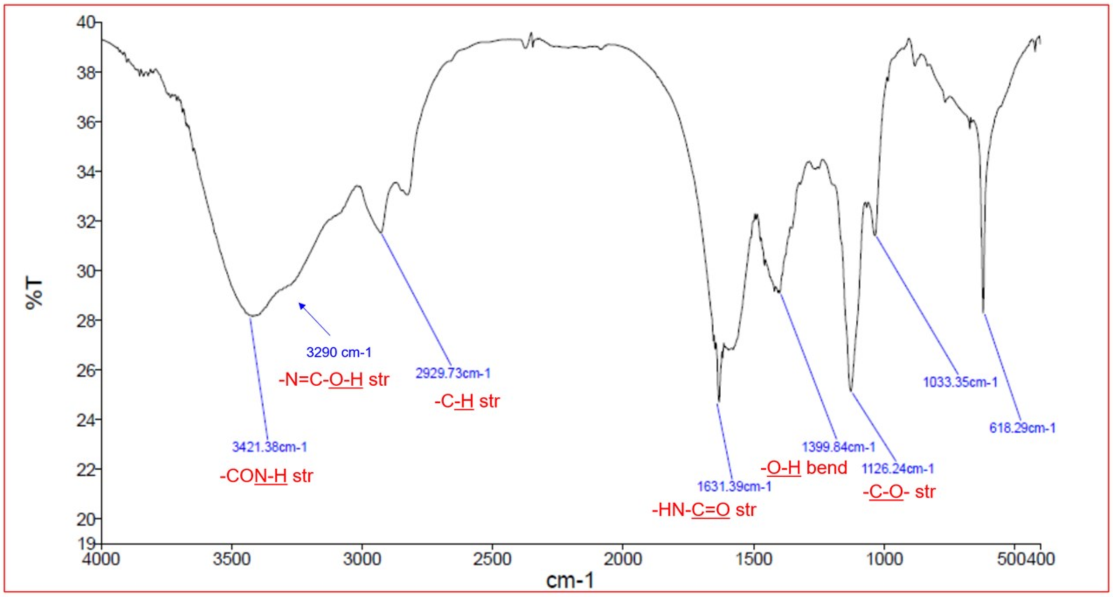


Figure S2b. FTIR spectrum of PAMAM G5.5 EDA core/COOH dendrimers. FTIR ν_{max}/cm^{-1} 3421 (strong, CON-H stretch), 3290 (medium, N=C-O-H stretch), 1631 (strong, HN-C=O stretch), 1572 (strong, HN-C=O stretch), 1399 (medium, O-H bend).

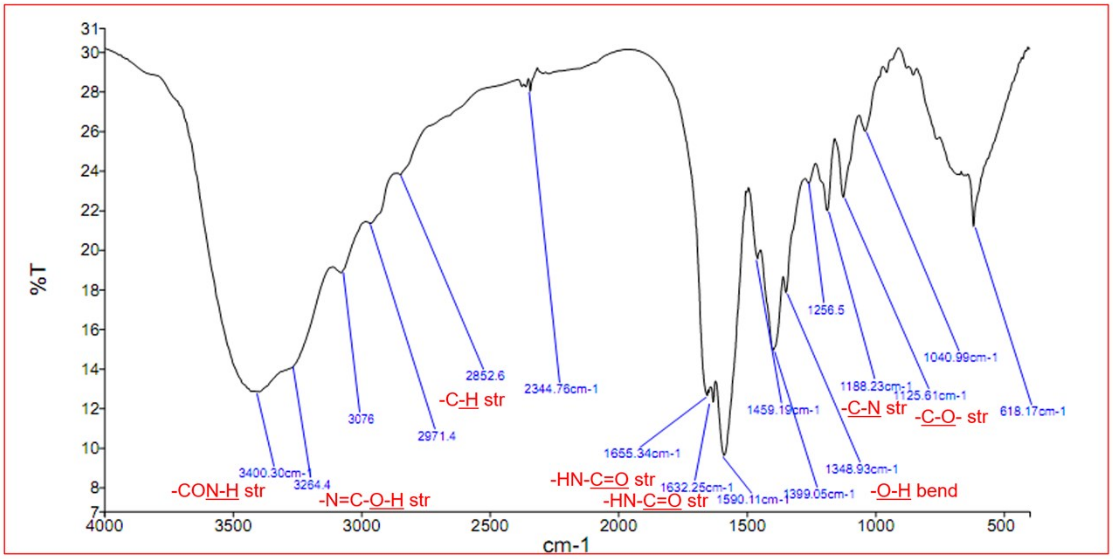


Figure S2c. FTIR spectrum of octahedron megamers resulted from electro catalyzed self-assembly of G3.5 PAMAM EDA core/COOH dendrimer. FTIR ν_{max}/cm^{-1} 3400 (strong, CO<u>N-H</u> stretch), 3264 (medium, N=C-<u>O-H</u> stretch), 1655 (strong, HN-<u>C=O</u> stretch), 1590 (strong, HN-<u>C=O</u> stretch), 1399 (medium, <u>O-H</u> bend).

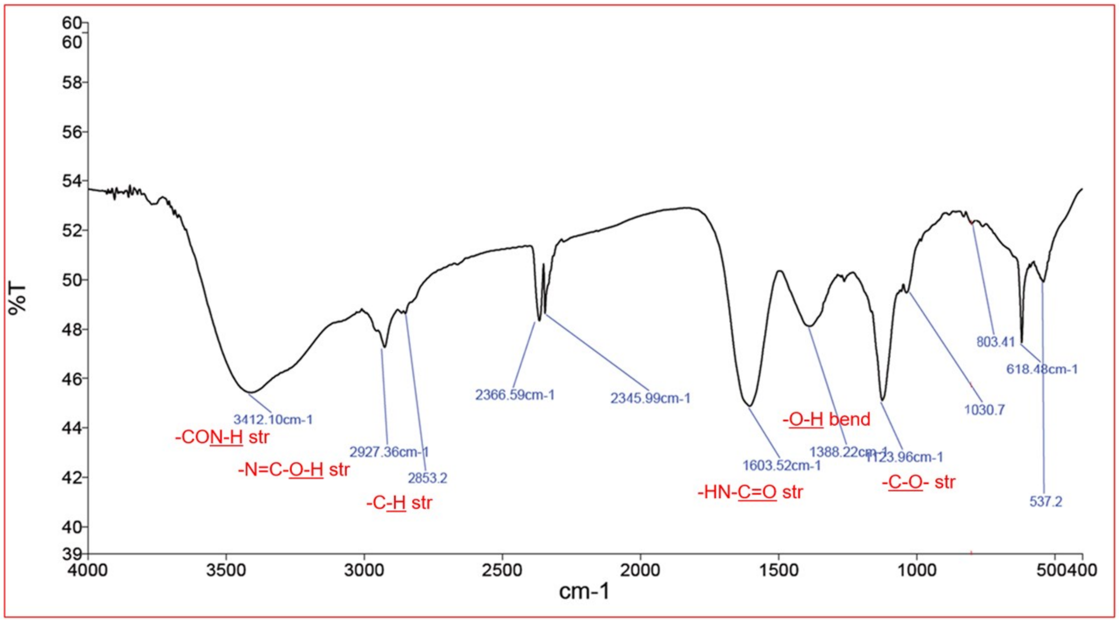


Figure S2d. FTIR spectrum of octahedron megamers resulted from electro catalyzed self-assembly of G5.5 PAMAM EDA core/COOH dendrimer. FTIR ν_{max}/cm^{-1} 3412 (strong, CO<u>N-H</u> stretch), 3250 (medium, N=C-<u>O-H</u> stretch), 1603 (strong, HN-<u>C=O</u> stretch), 1388 (medium, <u>O-H</u> bend).

We expected the ideal characteristic IR absorption (cm-1) peaks for three main functional groups, which correspond to the -COOH (carboxylic acid), -CONH- (amide), -N=C(OH)- (imidic acid, SI ref. 1) in the starting PAMAM dendrimer. We investigated similarities and differences of characteristic IR absorption (stretching and bending) frequencies in both starting materials and products. By this comparison, we can detect the reaction progress. Due to the structural complexity of the higher generation PAMAM dendrimers pristine IR absorption bands for PAMAM dendrimers, and their derivatives are not easy to obtain, also there are not many literatures reports available to us. We mainly identified IR absorption bands which are corresponded to the O-H (stretch, bend), N-H (stretch), and C=O (stretch) of -COOH, -CONH-, -N=C(OH)- functional groups in both the starting PAMAM dendrimers and the resulted megamers. The changes are a clear indication of the reaction sequences.

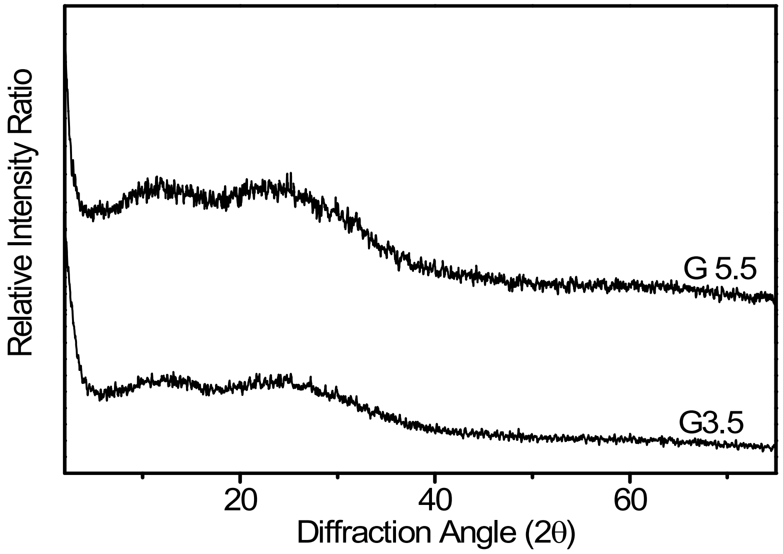


Figure S3. XRPD spectrum of the white particles (megamer architectures) resulted from electro catalyzed self-assembly of PAMAM EDA core/COOH dendrimers.

X– ray powder diffraction (XRPD) analysis was carried out to determine the crystal structure of the megamer resulted from PAMAM G3.5 dendrimer and PAMAM G5.5 dendrimer using a X – ray diffractometer. XRPD instrument was operated with a scanning rate of 3^{0} min^{-1} in the 2θ value ranging from 2–75^{0} with a CuKα X – ray radiation (λ = 1.54056 Å). In case of PAMAM G3.5 dendrimer, the diameter of dendrimer molecule is around 4 nm, which should correspond to the peak at 2.2^{0}. Whereas, diffraction at 1.45^{0} can be expected for PAMAM G5.5 dendrimer as it has the 6 nm molecular diameter. Due to measuring limitation in the diffractometer, both of these two peaks cannot be observed here prominently. However, both the compounds diffract extremely poorly and are exhibiting two broad peaks around 12^o and 24.5^o. As these are not the sharp peaks, we cannot determine the exact d-spacing between two planes. The average distance 0.74 nm (corresponds to 12^o) and 0.36 nm (corresponds to 24.5^o) came from intramolecular packing pattern, which is not possible to determine for the conformational variation in solid state. While electrolysis, the nanocrystals formed within few seconds. This rapid growing rate makes the molecular arrangement extremely poor for generating the sharp diffraction pattern in X-ray.

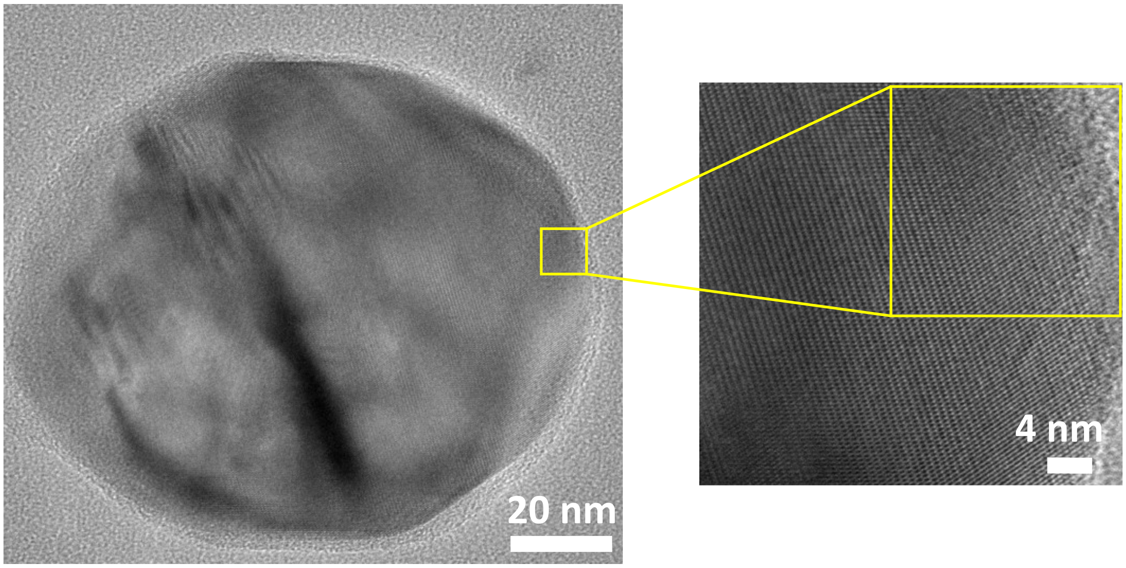


Figure S4. HRTEM images of the white particles (octahedron architectures) resulted from electro catalyzed self-assembly of PAMAM EDA core/COOH dendrimers.

XPS analysis

Sample of the octahedron architectures resulted from 3.5 generation were mixed with milli-Q water and were drop cast on coverslip for XPS analysis. Blank sample (the Sn:Pb electrodes under >3.5 V in Milli-Q water in absence of any dendrimer electrolyte), as well as Milli-Q water, was also analyzed in XPS instrument. From the atomic percentage of the samples it was confirmed that the metals have no important role in the said self-assembly process of the dendrimer. The respective XPS spectra and survey data are shown below.

Element name	Octahedron architecture resulted under >3.5 V from G3.5 PAMAM($NHCH_2CH_2COOH$)$_{64}$	Blank sample	Milli-Q water
	Atomic %	Atomic %	Atomic %
C1s	66.74	94.72	97.86
O1s	20.38	----	----
N1s	11.67	1.6	1.14
Sn3d	0.32	0.41	0.19
Sn3d3	----	0.43	0.41
Sn3d5	----	0.37	0.01
Pb4f	0.6	1.29	0
Pb4f7	----	----	0
Pb4f5	----	----	0
Zn2p1	0.1	0.18	0.01
Zn2p	0.16	0.58	0.2
Zn2p3	0.04	0.41	0.16

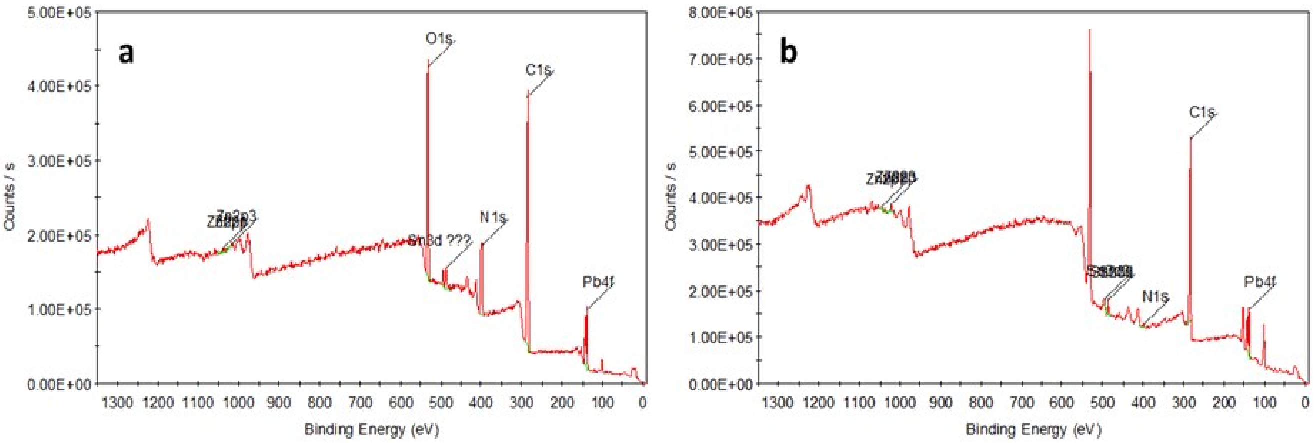


Figure S5. XPS survey spectra of (a) octahedron architecture resulted from electro catalyzed self-assembly of G3.5 PAMAM($NHCH_2CH_2COOH$)$_{64}$ dendrimer under >3.5 V, (b) blank sample.

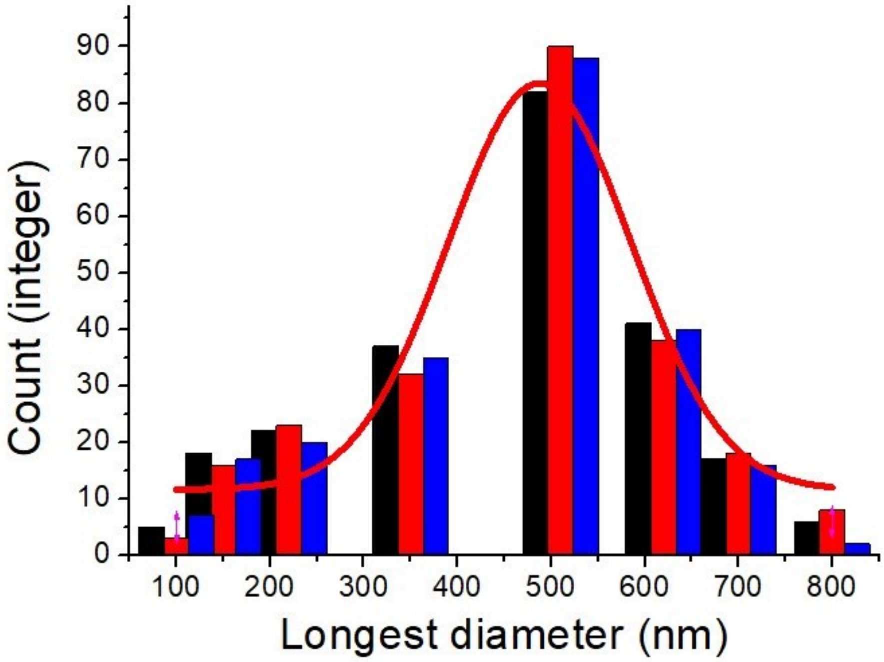


Figure S6. Three separately synthesized sample surfaces were scanned (blue, red and black), we have plotted longest diameter of the octahedron with the count of instances we observed, size variation is ±10 nm maximum for particular column. Octahedron size varies in a quantized manner, the random size distribution was not observed. Gaussian fit shows peak at 487 nm and error ±12 nm.

Computational details:

Theoretical calculations were performed using density functional theory (DFT) with the Gaussian 16 (G16) suite of programs [SI ref. 2]. The structure of the reactants, intermediates, and products was optimized at the B3LYP level of theory using the 6-31G(d) basis set. The Gibbs free energy change of the overall cell reaction, ΔG_{cell}, is calculated as the difference between the summation of free energy values for products and reactants.

$$\Delta G_{cell} = \sum \Delta G_{pdt} - \sum \Delta G_{reactant}$$

Where the overall cell reaction is:

$$X\text{-}N(CH_2CH_2COOH)_2 \longrightarrow X\text{-}N(CH_2CH_2)_2 + CO_2 + H_2$$

For a spontaneous cell reaction, the driving force is a negative value of ΔG_{cell}. Calculating the optimized electronic energies of reactants and products considering thermal free energy correction we found that the ΔG_{cell} =-28.357761 Kcal/mol.

Gibb's free energy of the above reaction is highly negative, indicates/support the stability of the final products. To find out the probability of formation of alkane radical (IV) from carboxylate anion (II) via formation of carboxylate radical (III), we have performed the optimization calculation for molecule II and III in their corresponding singlet and triplet states. We observed that for carboxylate radical it is stable in its triplet state than singlet state whereas corresponding alkane radical is stable in its singlet state, supports the formation of a five-membered ring from alkane radical after realizing CO_2 and overall Gibbs free energy for this reaction is -107.95 Kcal/mol. As the Gibbs free energy for this reaction is highly negative, formation of alkane radicals, realizing CO_2 from carboxylate ion is a favorable process. The Gibbs free energy for the formation of pyrrolidine ring from alkane radical is -8.42 Kcal/mol, which is also a favorable process.

References:

1. Y. Ji, X. L. Yang, Y. Qian, RSC Adv., 2014, 4, 49535-49540.
2. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.