Electronic Supplementary Information

Simultaneous one pot synthesis of two fractal structures by swapping of two fractal reaction kinetic states

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Movie 1. CEES for P PC PCM PCMS Triangular pathway.

Movie 2. Molecular dynamics simulation of the dendritic-bots.

Movie 3. PCMS vibration STM images.

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Though majority of molecular dynamics data of this paper are constructed using Hyperchem, to make this video, we use freely available XenoView for Windows (Visualization for Computer Simulation), The File Version: 3.7.3.0, we acknowledge Sergei Shenogin. This software uses universal PCFF-type force fields with anharmovic corrections, tailored to study the properties related to the vibrational spectra of the material (thermal properties first of all). Note that for non-bonded interactions the actual distance parameters are r^3 or r^6 (cube or the 6th power of zero-force distance), depending on the force field. Since electrostatic screening and hydrophobic effects are masked by viscous drags of the solvents, and vacuum conditions are strictly inapplicable, therefore, Langevin Dynamics is suited, however, XenoView provides similar output.

A. Simulation data table: Before starting the Molecular Dynamics simulation, global energy minimization was carried out on the molecular structure (pdb file) for 100 steps. Thus, we obtained the molecular car file after energy minimization, which was considered for the Molecular Dynamics simulation study. The values of the parameters set for the simulation are: Temperature 298K, Time step: 0.5 fs, number of steps: 50000, data output steps: 10, structure output steps: 500, at constant volume & shape, no thermostat & tolerance (kCal/mol) is 1.0000E-004.

Number of steps	Temp (K)	Time (ps)
10	185.3148346	0.005
20	182.2689819	0.01

30	187.6544189	0.015
40	117.0112762	0.02
50	179.6787262	0.025
60	168.2993164	0.029999999
70	157.2270203	0.035
80	199.3046875	0.039999999
90	168.1782074	0.045000002
100	158.7873077	0.050000001
110	155.147049	0.055
120	128.434906	0.059999999

130	160.7835541	0.064999998
140	135.7352448	0.07
150	156.5966339	0.075000003
160	176.0281525	0.079999998
170	140.1629333	0.085000001
180	197.8008728	0.090000004
190	170.1939697	0.094999999
200	154.4791565	0.100000001
210	174.7250977	0.104999997
220	126.1526566	0.109999999

230	150.2674408	0.115000002
240	187.6255493	0.119999997
250	139.8759003	0.125
260	161.077713	0.129999995
270	186.8777008	0.135000005
280	166.1507111	0.140000001
290	208.8686218	0.144999996
300	148.2095642	0.150000006
310	118.9892807	0.155000001
320	139.7511902	0.159999996

330	139.7906342	0.165000007
340	169.089798	0.170000002
350	152.4411316	0.174999997
360	144.3389893	0.180000007
370	154.3082275	0.185000002
380	129.9534149	0.189999998
390	155.0008087	0.194999993
400	149.8147583	0.200000003

Theoretical simulation of molecular machine, M: Summary of molecular dynamics simulation, spectroscopic confirmation of rotor ability is in the supporting online text A (see Figures S1 to S5).

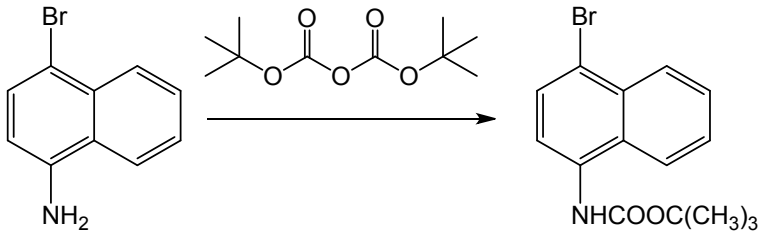
Theoretical simulation of PCM dendritic bots (Movie 2): Two kinds of theoretical simulations were carried out to generate the plots in Figure 1c. First, the dynamics of the PCM for different generations, second, we took only one branch of the dendrimer and placed within a potential box only keeping the nearest neighbor-hood of the PCM substrate and run the molecular dynamics. Theoretical simulation to track the energy transmission path was carried out by semi-empirical Austin Model AM1, on MOPAC, we repeated the same in Hyperchem 10.0 and VNL (Virtual nanolab) was used to get relative "difference potential" among different functional groups on PCM substrate surface. We increased the background temperature as to create noise 320K-350K artificially to emulate the environment in a reaction beaker (no ions were added in the potential box), higher the temperature, more pronounced is the dynamics (normal femto-second outputs are averaged over a million samples to generate real-time shape change of PCM). Thereafter, the surface potential is calculated and plotted; we could get kinetic and potential energies during periodic oscillations. During the second simulation, the figure 1c (main text) bottom panel shows variations in the location of the functional groups. Herein, we have superimposed 50 frames and plotted it, so that it is clear to us that during dynamics, there is an organized molecular rotor based dynamics that governs the lattice symmetry.

Calculation of reaction constants (Movie 4): Reaction constants were calculated by fixing the detection instrument permanently at a single fluorescence point (fixed excitation wavelength where the geometry say triangle shows a maxima), relative reaction constants were determined k/k_o

~intensity ratio between initial and the final product as a function of time t). An absolute measurement was not possible since the reaction switched too fast and inhomogeneity in the reaction beaker prohibits pristine, absolute fluorescence data collection. The Lock-in emission detection is only useful route, and such a study was possible because of 2D CEES (combined excitation emission spectroscopy) study, which exactly pin points the excitation energies for a particular product. We have detailed CEES tool in our previous communications.[10,11,13]

B. Synthesis protocol for the machine molecule (M): (This is brief synthetic details of the molecular machine used here; the entire synthetic route will be described later in a detailed manuscript wherein several versions of this machine and associated challenges will be described in details).

Step I



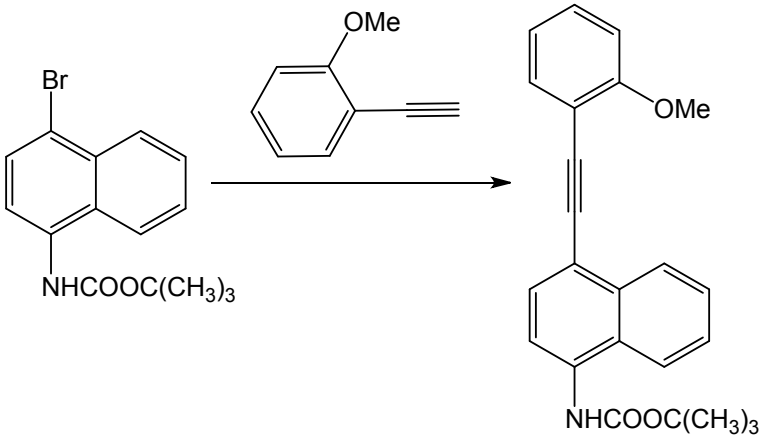
tert-butyl (4-bromonaphthalen-1-yl)carbamate

2-Aminobromo naphthalene (5 g, 0.023 mol) (**I, left, starting material**) is treated with di *t*-butyl dicarbonate (4.9 g, 5.18 mL, 0.023 mol, see above arrow for the structure) in dry toluene (100 mL) and heated at 70^{o}C for 15h. When TLC confirms the completion of the reaction, the reaction mixture is repeatedly washed with water, the remaining material is dried using anhydrous sodium sulfate so that the toluene is completely evaporated under vacuum.

The solid residue is re-crystallized from boiling hexane. Boc-derivative of 2-aminobromo naphthalene, (4-Bromo-naphthalen-1-yl)-carbamic acid tert-butyl ester (**II, right, the product**) was obtained as a violate color crystal, the yield of this product is 95%.

Technique: Boc-derivative product (**II**) is dissolved in hot hexane and filtered through the Whatman filter paper.

Step-II



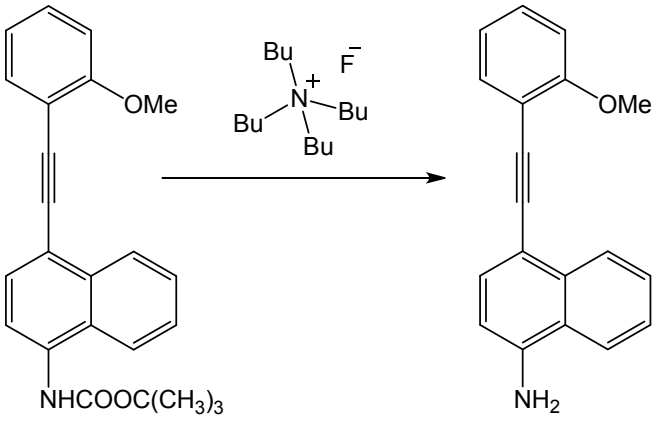
tert-butyl (4-((2-methoxyphenyl)ethynyl)naphthalen
-1-yl)carbamate

The Boc-derivative (**II, left, starting material, above**) (3.26 g, 0.01 mol) is mixed with dry 2-ethynyl anisole (1.52 g, 0.011 mol) in dry triethyl amine (40 mL) solvent (which also acts as a base). Then the palladium acetate (catalytic amount) and triphenylphosphine (a little excess than the catalyst) are added to the mixture and heated to 100^{o}C for 16h.

After completion of the reaction, triethylamine solvent is removed by keeping the mixture in vacuum and the residue is worked up with ethyl acetate. After the removal of the solvent, the

resultant mixture is subjected to a column chromatography over silica gel and eluted with 10% ethyl acetate in a hexane solvent. A white colored solid ([4-(2-Methoxy-phenylethynyl)-naphthalen-1-yl]-carbamic acid tert-butyl ester (**III, product, above, right**) is obtained, here the yield is 85%.

Step III



4-((2-methoxyphenyl)ethynyl)naphthalen
-1-amine

The ester (**III**) (380 mg, 1.02 mmol) is taken in dry THF (10 mL), 5 equivalent tetrabutyl ammonium fluoride (TBAF) (1.2 g, 5.1 mmol) is added and refluxed for 8h. The reaction mixture is worked with ethyl acetate after complete removal of THF. Washed with water for three times and the residue, obtained after removal of the solvent, is subjected to column chromatography. The product 4-((2-methoxyphenyl)ethynyl)naphthalen-1-amine (**IV**) is eluted with 30% ethyl acetate in a hexane solvent. The yield is 65%.

C. Synthesis of P, C, M and S compositions: Two vital points for the synthesis are that, (i) the NR or C molecules cannot be doped inside after MMs are bonded with PAMAM, doping should be done before. Moreover, (ii) the sensors are difficult to bind on PAMAM after MMs are attached. Hence, the first step is doping C; then, we attach the sensors, and finally connect the machines (MM).

The MM, C and sensor molecules are selected by optimizing synthetic possibility, non-overlapping of CEES-active regions and following several combinations, this particular set is chosen; they exhibit fluorescence in three distinct energy domains. Otherwise, identifying the role of one component is not possible. A 5^{th} generation PAMAM dendrimer is a tree like branched shaped, colourless, solid polymer purchased in methanol solution from Aldrich. From MALDI-TOF measurement, the average mass of the dendrimer was observed to be 26000 Da which is much less than the calculated mass for 128 terminal amine groups is 28000 Da. The loss in mass is due to some structural defects resulted during the synthesis procedure and it is expected that the number of terminal amine groups are much less than estimated in the ideal structure (exactly 128 primary amine terminals). To avoid inconsistency, the dendrimer was thoroughly characterized prior use in its pristine form and since mass quality varies sample to sample, extra care was taken to have consistency during the entire synthesis process. It is highly soluble in water, ethanol, methanol, but solubility is low in DMF and DMSO and almost insoluble in other organic solvents including acetone.

D. Synthesis of fractal supramolecular architectures:

(a) PC, PM, PCM, PCS, PMS & PCMS synthesis (4th and 5th generation PAMAM, Movie 1, Movie 4): To synthesize PC, PCM and PCMS, —first, PAMAM G5 dendrimer (1:2) aqueous sodium carbonate, methanol solution is taken at >9.5 pH, in presence of Nile-red dye molecules, to encapsulate two of them into the deep core of the four dendritic cavities, we get [PAMAM5-NR] dendritic box (PC, step I). Then, the PC is taken in a 10% and 40% mixture of dimethyl sulfoxide(DMSO) and acetonitrile, the sensor (NIR797isothiocyanate, S) solution in the borate buffer (50%of total volume) is added in one portion and the reaction is continued at room temperature. The primary amine groups at the PAMAM surface are then connected with the NIR797isothiocyanatedye molecule, the reaction product [PAMAM-NR] NIR797isothiocyanate (PCS, step II) is taken to the next step. A multi-component mixture of product PCS, M, diisopropylamine and triethylamineis dissolved in dry dimethyl sulfoxide, and glutaryl chloride is added slowly to the mixture at below20^{o}C. The reaction is carried out at room temperature for 48h and the final product is collected,[PAMAM-NLR]-NIR797isothiocyanate-M (PCMS, step III). For PCM, the step II is avoided, the rest remains the same; for PCM, instead of S, M attachment part is carried out on a PC (step I). In all steps the products are purified through extensive dialysis. MALDI-TOF, Raman, FTIR, NMR and step-by-step CEES spectroscopy were carried out to confirm the product nature (see Figures S6 to S12).

(b) Synthesis of different self-assembly from PCMs and various different generations of PAMAM: (basic synthetic process of PCMs remain common as above, specific synthetic route adopted distinctly for particular PAMAM generation is noted here):1. Aqueous PCM solution Dilute aqueous solution of the dendrimer is prepared in 18 milli ohm water. Using a micro-cuvett & Sn-electrode 5 volt ‘dc’ is passed for 1-5 min.; when white turbidity appeared the ‘dc’ is stopped and

the solution is used for SEM imaging. 2. PAMAM-succinamic acid, dendrimer, 1,6-diaminohexane

core, generation 6 solution, 10 wt% in H_2O: Dilute aqueous solution of the dendrimer is prepared in

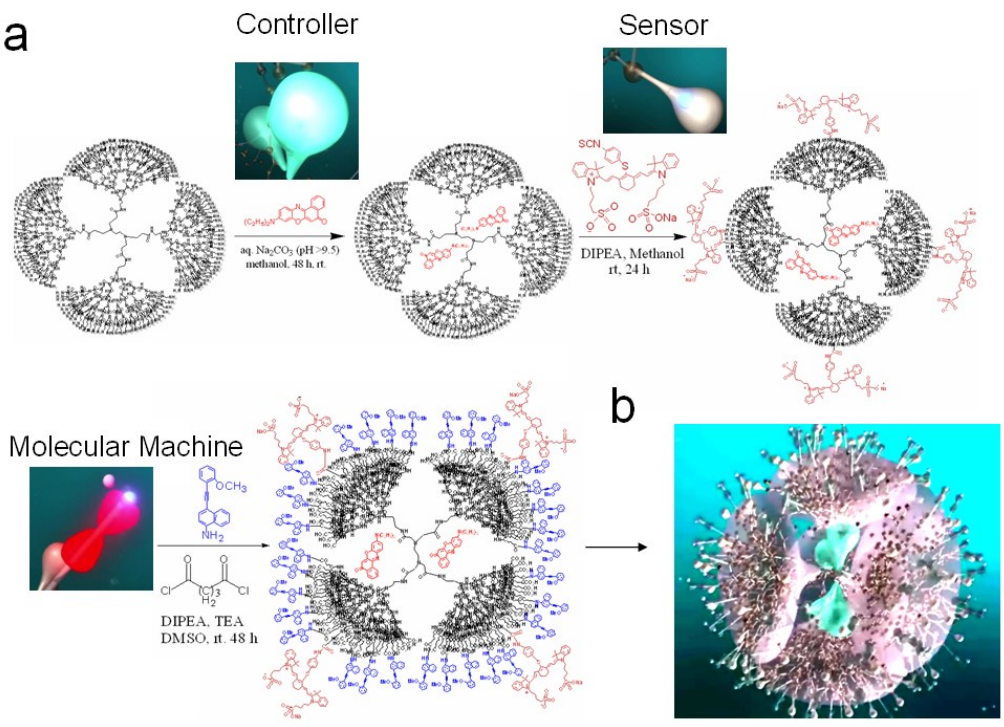
18 milli ohm water. Using a micro-cuvett & Sn-electrode 5 volt ‘dc’ is passed for 1-5 min.; when

white turbidity appeared the ‘dc’ is stopped and the solution is used for SEM imaging. 3. PAMAM-

succinamic acid dendrimer, 1,4-diaminobutane core, generation 4 solution, 10 wt% in H_2O: Dilute

aqueous solution of the dendrimer is prepared in 18 milli ohm water. Using a micro-cuvett & Sn-

electrode 5 volt ‘dc’ is passed for 1-5 min.; when white turbidity appeared the ‘dc’ is stopped and the solution is used for SEM imaging. 4. PAMAM dendrimer, ethylenediamine core, generation 3.5 solution, 10 wt% in methanol:(1:1) aqueous methanol solution of the dendrimer is added 50 micro liter of formic acid, stirred for 3 h and dialyzed through a parchment membrane for two times. Then the dilute aqueous solution obtained is prepared in 18 milli ohm water. Using a micro-cuvett & Sn-electrode 5 volt ‘dc’ is passed for 1-5 min.; when white turbidity appeared the ‘dc’ is stopped and the solution is used for SEM imaging. 5. PAMAM dendrimer, ethylenediamine core, generation 5.5 solution, 5 wt% in methanol: (1:1) aqueous methanol solution of the dendrimer is added 50 micro liter of formic acid, stirred for 3 h and dialyzed through a parchment membrane for two times. Then the dilute aqueous solution obtained is prepared in 18 milli ohm water. Using a micro-cuvett & Sn-electrode 5 volt ‘dc’ is passed for 1-5 min.; when white turbidity appeared the ‘dc’ is stopped and the solution is used for SEM imaging.



Step-I:

Encapsulation of Nile-red dye molecule (C) inside PAMAM 5.0 dend. cavity (P):

Encapsulation of Nile-red dye molecule inside PAMAM 5.0 dendrimer cavity is highly pH dependent.

After Changing a number of experimental conditions like different mixed solvent systems, elevated temperature, pH etc., it is found that after a particular pH 9.0 and above the Nile-red molecules to be encapsulated inside the dendritic cavities.

40 mg (0.0015 mmol, 1 mL methanol solution is pipette out) of [PAMAM G5(-NH_2)x] dendrimer (m/z 26000 Da) is taken into a glass vial containing a magnetic bar and 1 mL methanol and 1 mL aqueous sodium carbonate (pH > 9.5) are added. The solution is stirred well and 10 mg solid crystal of Nile-red (Molecular Weight ~318.3 Da) is added in excess, the solution is allowed to stir for 2 days at room temperature (~22-25^{o}C).

After 2 days of continuous stirring, the solution is concentrated by removing methanol under vacuum and the aqueous solution is filtered through Whatman filter paper, the filtrate is then dialyzed through cellulose parchment. The aqueous solution is washed with ethyl acetate and dichloromethane with mechanical shaking for several times until the organic layer becomes completely colorless that ensures the complete removal of all weakly bind Nile-red on the dendrimer surface. After removal of the solvent, the product obtained (yield 99%) is Nile-red encapsulated PAMAM dendritic box which we call as PC.

Step-II:

Synthesis protocol for connecting NIR797 Isothiocyanate (S) on [NR or C encapsulated PAMAM G5 dendrimer]:

20 mg ($7.4x10^{-4}$ mmol) of [PAMAM G5$(-NH_2)_x$-NR] is dissolved into 3mL solution of 10%+40%+50% mixture of dimethyl sulfoxide, acetonitrile, and borate buffer containing 4 equivalent amount of dye. The reaction is stirred at room temperature for consiqutive 2 days. The acetonitrile is removed under vacuum and the reaction mixture was diluted with DI water and dialyzed for 2 days and dried to get the product PCS to use it for the next step.

Step-III:

Synthesis protocol for MM attachment on {NIR797 Isothiocyanate connected [NLR encapsulated PAMAM G5 dend.]}:

20 mg {[PAMAM G5$(-NH_2)_x$-NLR_{encap}] NIR797 isothiocyanate} is added to 2 mL of dry DMSO and then we add a mixture of 1 mL of TEA (Et_3N) and 1 mL of DIPEA ($EtiPr_2N$). The mixture is stirred for 5 h then 42 mg (excess) of Molecular Machine (III) solution in DMSO (1 mL) alongwith glutaryl chloride are added and allowed to stir for 2 days at 300K, finally, the mixture is dialyzed in neutral water for 24 h to get the final product PCMS.

To confirm living cell compatibility of PCMS, first, we measured the CEES spectroscopy by applying an electric field (1V to 10V) across the supramolecular solution; we did not find any change in any of the peaks for the components. Second, we checked by changing the concentration

of Na, K and other salts, yet there was no change in the response, which suggests that in the living cell routine functions will not be disrupted by PCMS.

E. What is CEES?

Combined excitation emission spectroscopy (CEES):

Combined excitation emission spectroscopy (CEES): ~200 emission spectra are recorded at excitation wavelengths with 5nm intervals. The output intensities are plotted as a function of excitation and emission wavelengths, converted into energies (eV). From iso-contour plot, we detect peaks; at each peak, we get three values, excitation energy (E_x), emission energy (E_m) and depending on the negative or positive sign of ΔE ($=E_x - E_m$), absorbed or emitted energy by the molecular structure during the emission process, using solution Raman & molecular dynamics we find which atomic groups use ΔE. Using this concept we evaluate band transitions for every single event, neglecting regions above Raman ridge at 45^0 (since $E_x < E_m$), around 45^0, $\Delta E \sim 0$, there is no absorption, entire applied energy emits out.

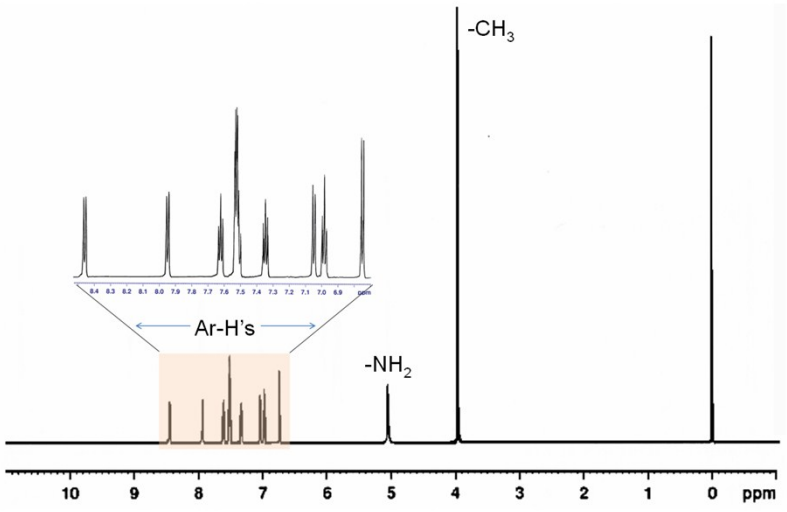


Figure S1: ^{1}H NMR (600 MHz, in CD_3CN, RT) of 4-((2-methoxyphenyl)ethynyl)naphthalen-1-amine; ppm: δ 8.46 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.94 (d, 1H, *J* = 9.0 Hz, Ar-H), 7.62 (t, 1H, *J* = 9.0 Hz, Ar-H), 7.54-7.49 (m, 3H, Ar-H), 7.34 (t, 1H, *J* = 9.0 Hz, Ar-H), 7.05 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.98 (t, 1H, *J* = 8.4 Hz, Ar-H), 6.75 (d, 1H, *J* = 9.0 Hz, Ar-H), 5.05 (s, 2H, Ar-NH_2), 3.95 (s, 3H, Ar-OCH_3).

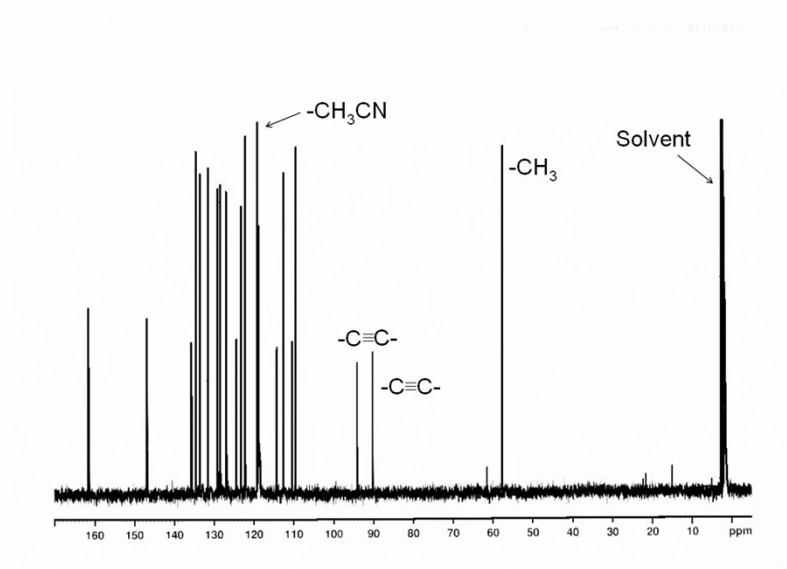


Figure S2: ^{13}C NMR (150 MHz, in CD_3CN, RT) of 4-((2-methoxyphenyl)ethynyl)naphthalen-1-amine; ppm: δ 161.13, 146.44, 135.58, 133.85, 132.80, 130.75, 128.37, 127.86, 126.38, 124.00, 123.19, 121.91, 114.35, 112.39, 110.36, 109.36, 94.11, 89.92, 56.86.

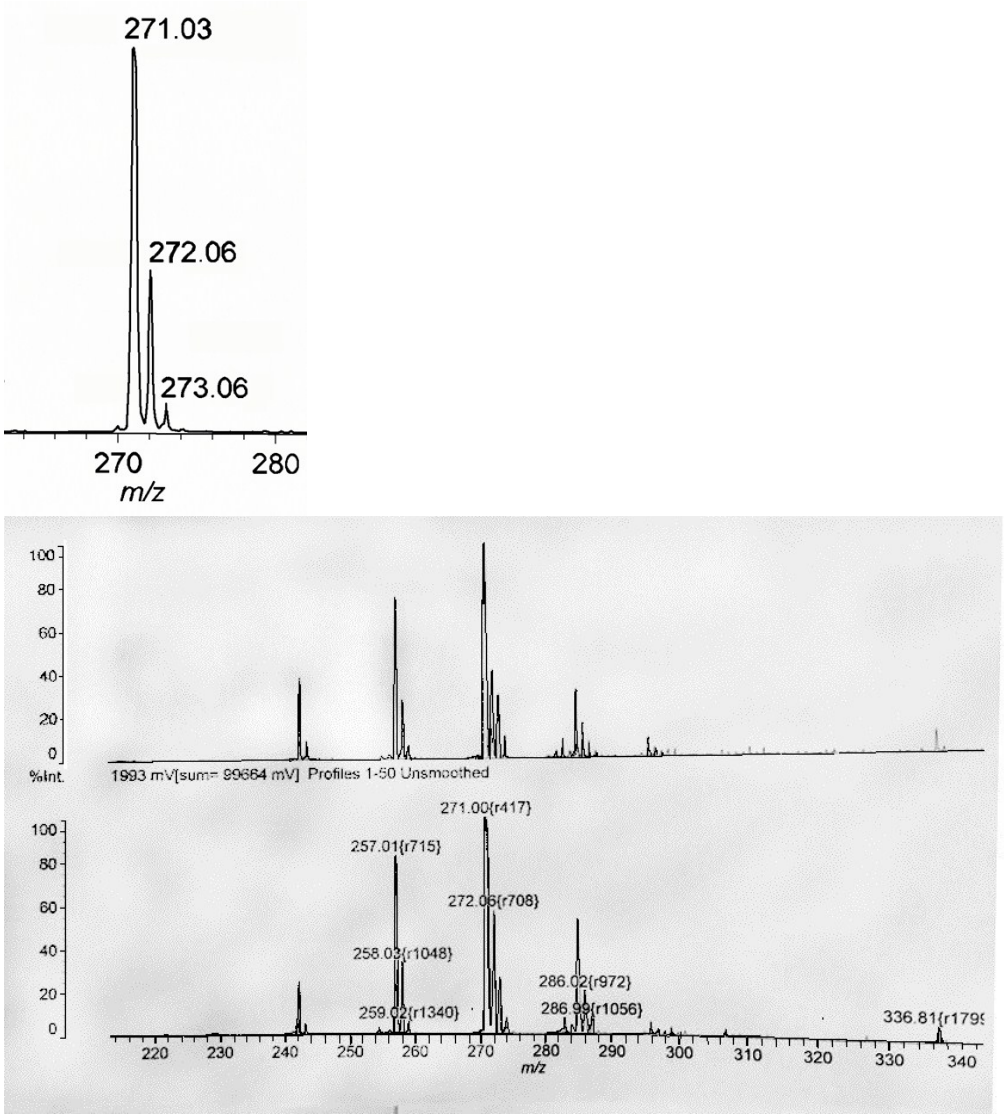


Figure S3: MALDI-TOF (THAP matrix in acetonitrile): m/z calcd for $C_{19}H_{15}NO$: 273.11, found [M-2H$^+$]: 271.03 (calcd 271.10), [M-H$^+$]: 272.06 (calcd 272.12), [M$^+$]: 273.06 (calcd 273.11). Matrix background peaks are observed at 241.93, 257.01.

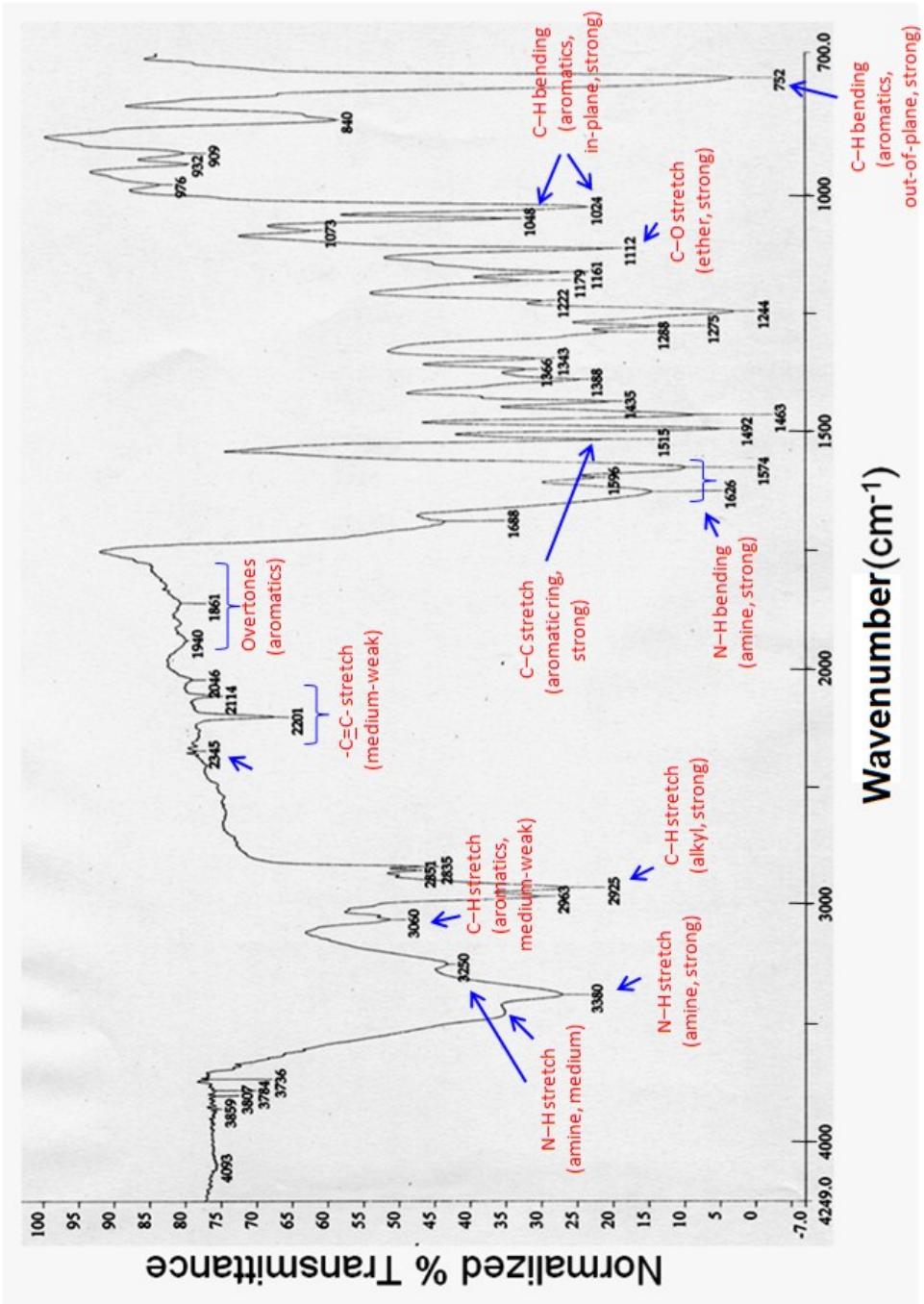

Normalized % Transmittance
Wavenumber(cm-1)
N–H stretch (amine, medium)
C–H stretch (aromatics, medium-weak)
N–H stretch (amine, strong)
C–H stretch (alkyl, strong)
-C≡C- stretch (medium-weak)
Overtones (aromatics)
C–C stretch (aromatic ring, strong)
N–H bending (amine, strong)
C–H bending (aromatics, in-plane, strong)
C–O stretch (ether, strong)
C–H bending (aromatics, out-of-plane, strong)

Figure S4: IR (Neat): Characteristic peaks are pointed with blue arrows and brackets; some of the notable peaks are: 3380 cm^{-1} (N-H), 2201 cm^{-1} (C≡C).

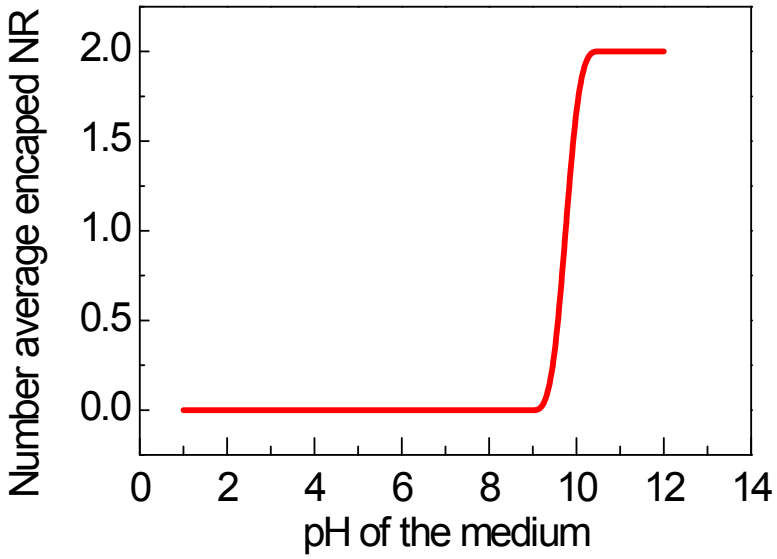
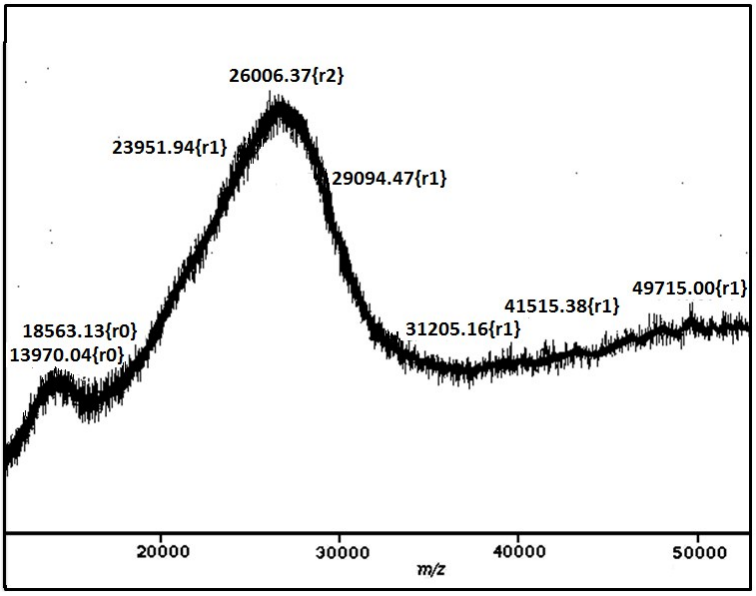


Figure S5: Number of encapsulated NR molecule inside PAMAM as a function of pH.

i)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29094.47{r1}
49715.00{r1}
41515.38{r1}
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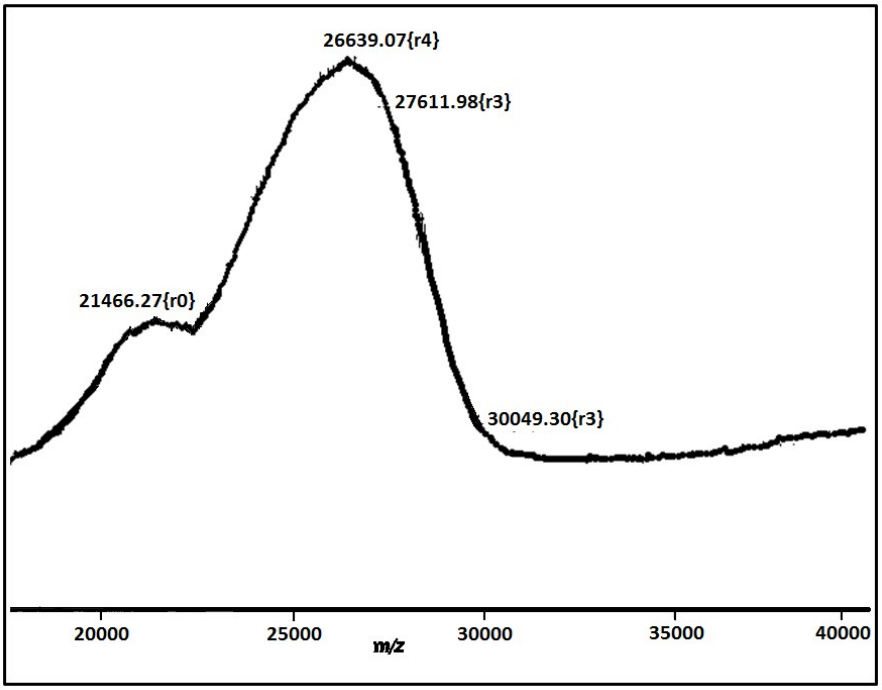
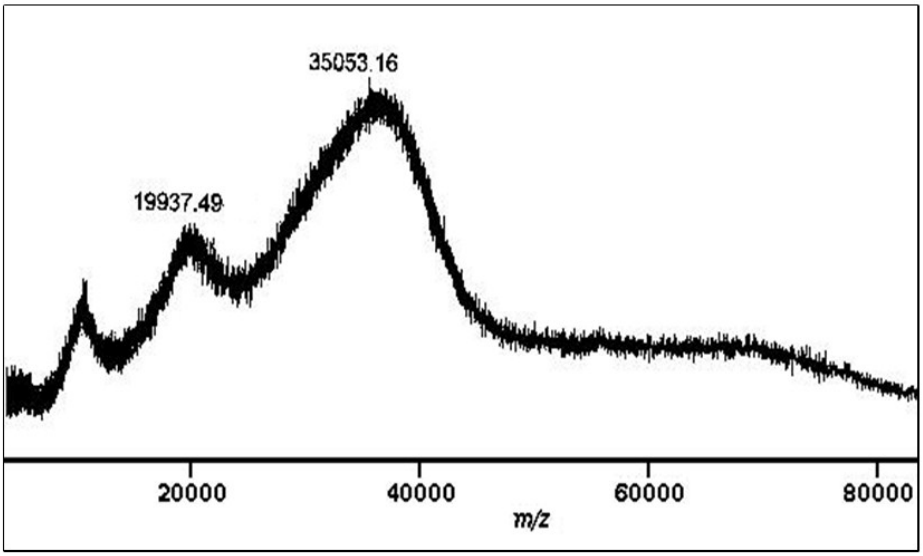
20000
30000
40000
50000
m/z

ii)


26639.07{r4}
27611.98{r3}
21466.27{r0}
30049.30{r3}
20000
25000
30000
35000
40000
m/z

iii)


35053.16
19937.49
20000
40000
60000
80000
m/z

iv)

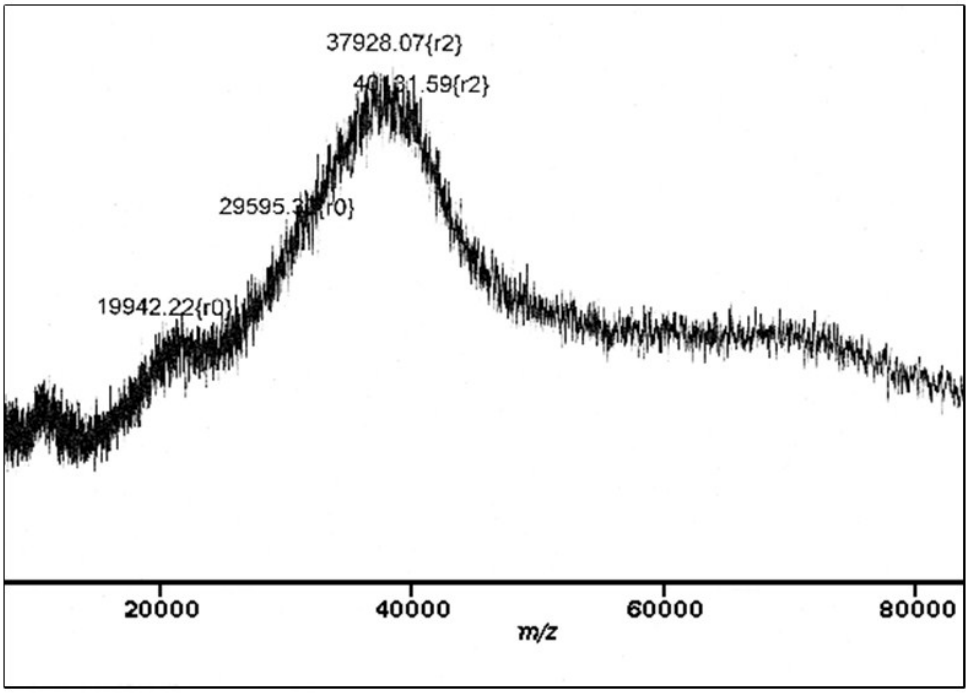

37928.07{r2}
40131.59{r2}
29595.3{r0}
19942.22{r0}
20000
40000
60000
80000
m/z

Figure S6a: (i) MALDI-TOF mass spectrum of pristine PAMAM G5.0 (or P) (ii) MALDI-TOF mass spectrum of PAMAM after NR doping (or PC). (iii) and (iv) MALDI-TOF mass spectrum of PAMAM-NR dendritic box attached with MM, (water soluble lower mass part and DMSO soluble higher mass part respectively). With an increasing molecular weight, discrete isolated proton peaks merge in NMR, so are the peaks of MALDI-TOF response. Ref. Lesniak et al. *Bioconjugate Chemistry* 2007, 18, 1148-1154; Peterson et al. *European Polymer Journal* 2003, 39, 33-42.

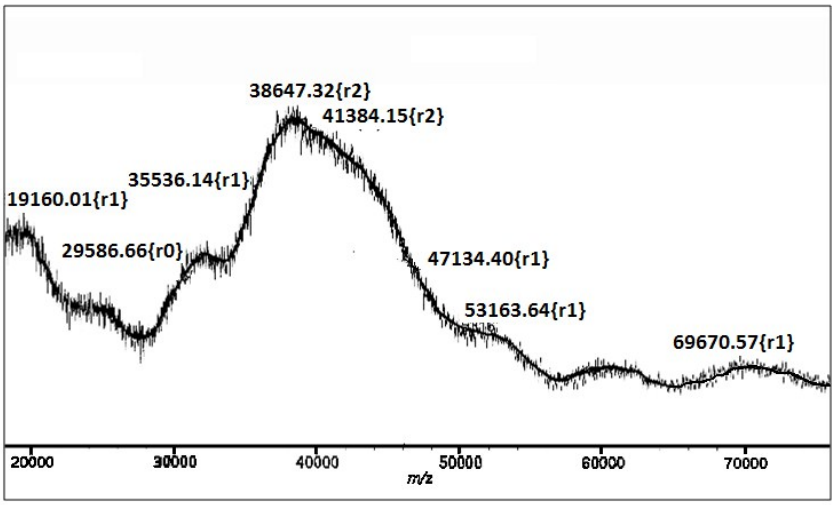


Figure S6b: MALDI-TOF for the final PAMAM-sensor-NR-MM system, which is named as PCMS. With an increasing molecular weight, discrete isolated proton peaks merge in NMR, so are the peaks of MALDI-TOF response. Ref. Lesniak et al, Bioconjugate Chemistry 2007, 18, 1148-1154; Peterson et al, European Polymer Journal 2003, 39, 33-42

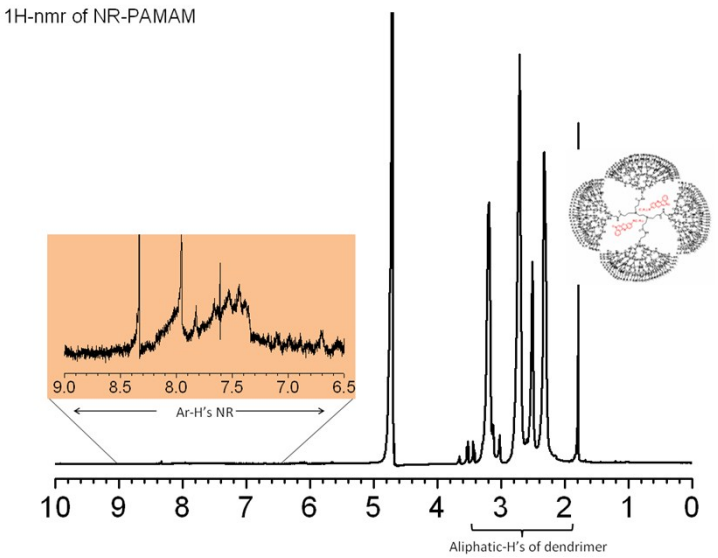


Figure S7: ^{1}H NMR (600 MHz, in D_2O, RT) for PC (NR-PAMAM). With an increasing molecular weight, discrete isolated proton peaks merge in NMR, so are the peaks of MALDI-TOF response. Ref. Lesniak et al, Bioconjugate Chemistry 2007, 18, 1148-1154; Peterson et al, European Polymer Journal 2003, 39, 33-42

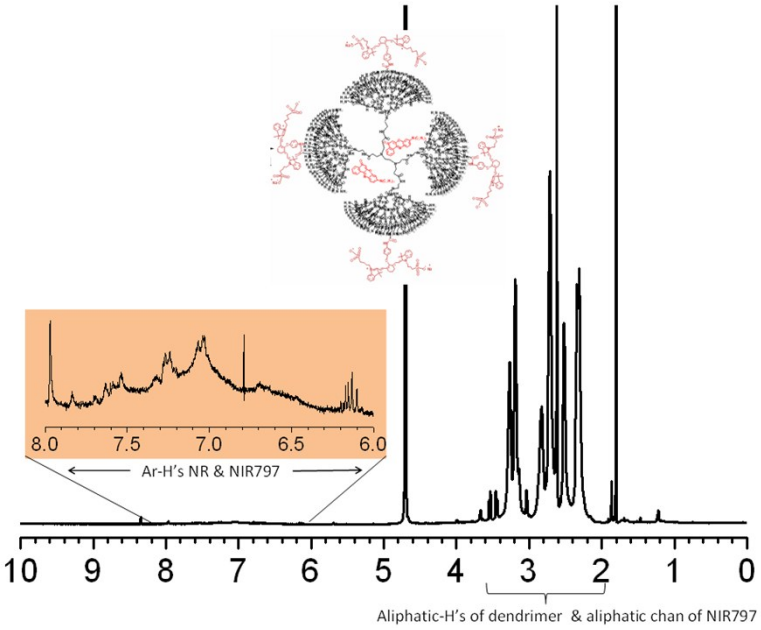


Figure S8: ^{1}H NMR (600 MHz, in D_2O, RT) for PCS (NR-PAMAM-NIR-797). With an increasing molecular weight, discrete isolated proton peaks merge in NMR, so are the peaks of MALDI-TOF response. Ref. Lesniak et al, Bioconjugate Chemistry 2007, 18, 1148-1154; Peterson et al, European Polymer Journal 2003, 39, 33-42

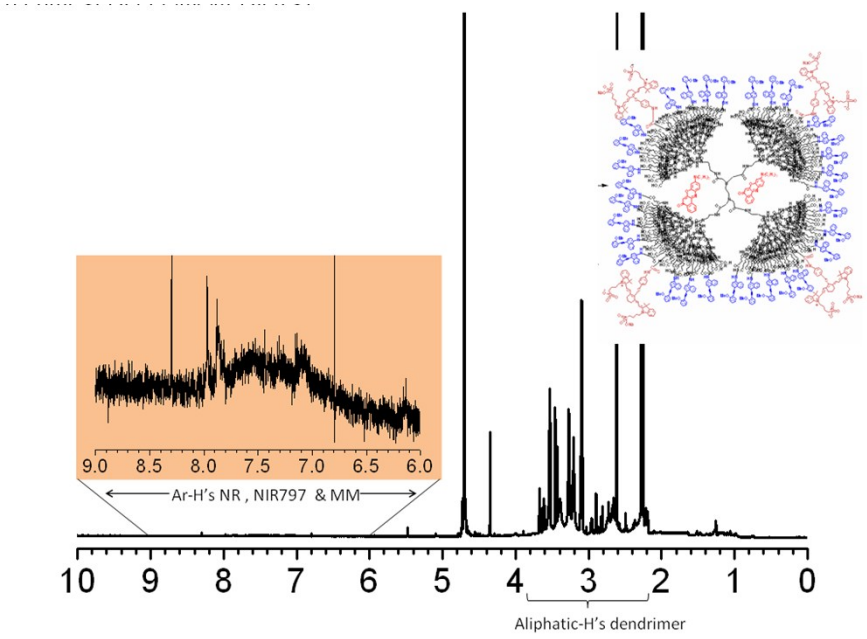


Figure S9: ^{1}H NMR (600 MHz, in D_2O, RT) for PCMS (NR-PAMAM-NIR797-MM). With an increasing molecular weight, discrete isolated proton peaks merge in NMR, so are the peaks of MALDI-TOF response. Ref. Lesniak et al, Bioconjugate Chemistry 2007, 18, 1148-1154; Peterson et al, European Polymer Journal 2003, 39, 33-42

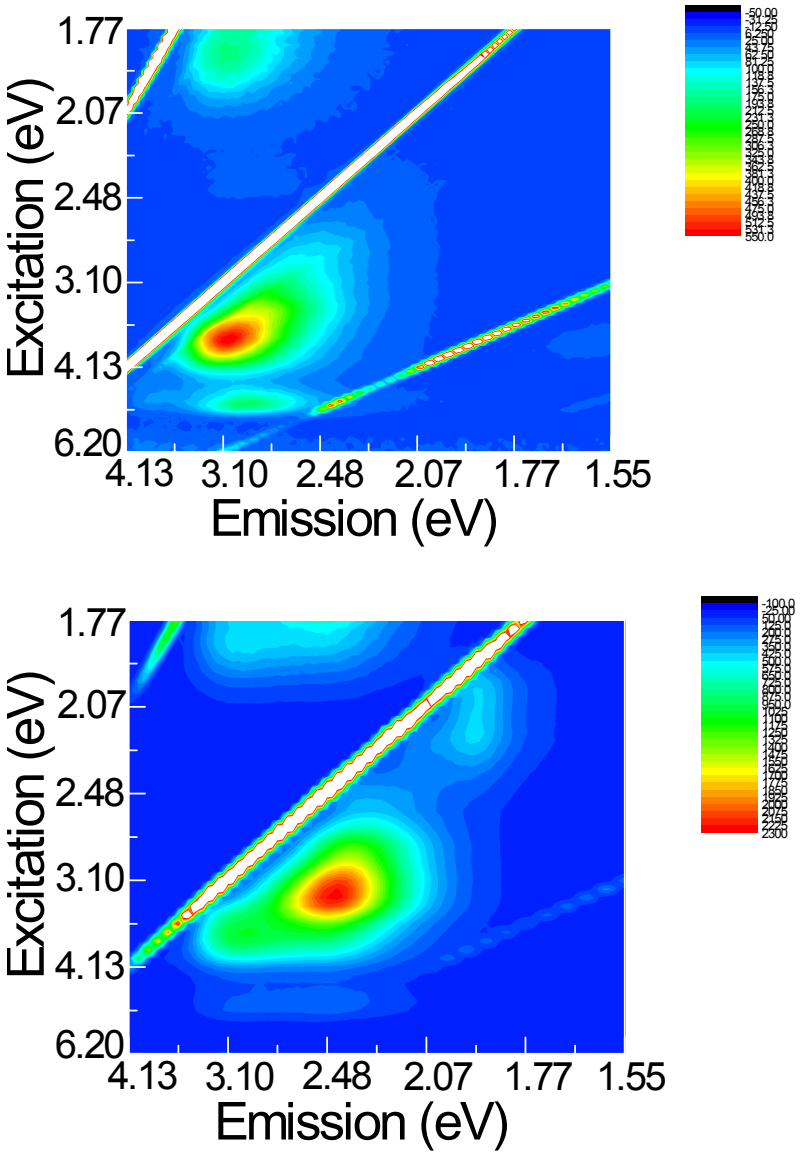
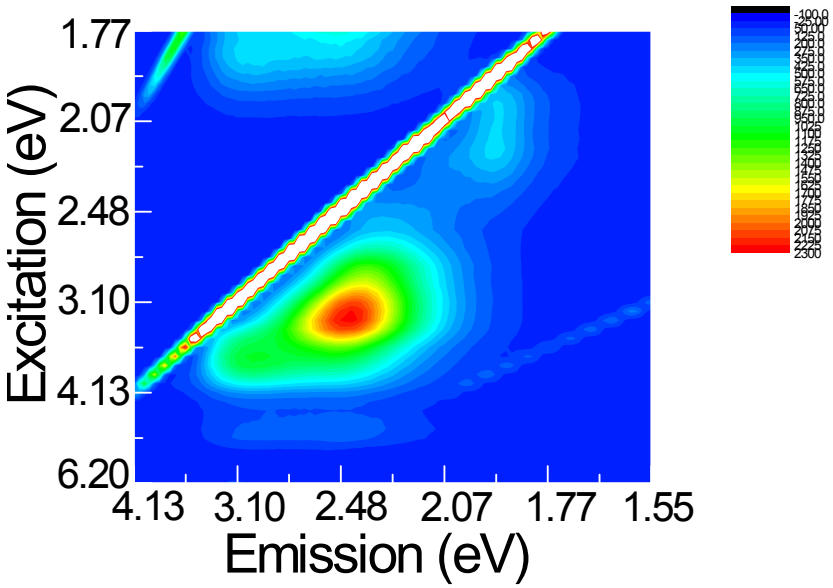


Figure S10: CEES spectrum for the PAMAM (P, above) and NR-PAMAM (PC, below).



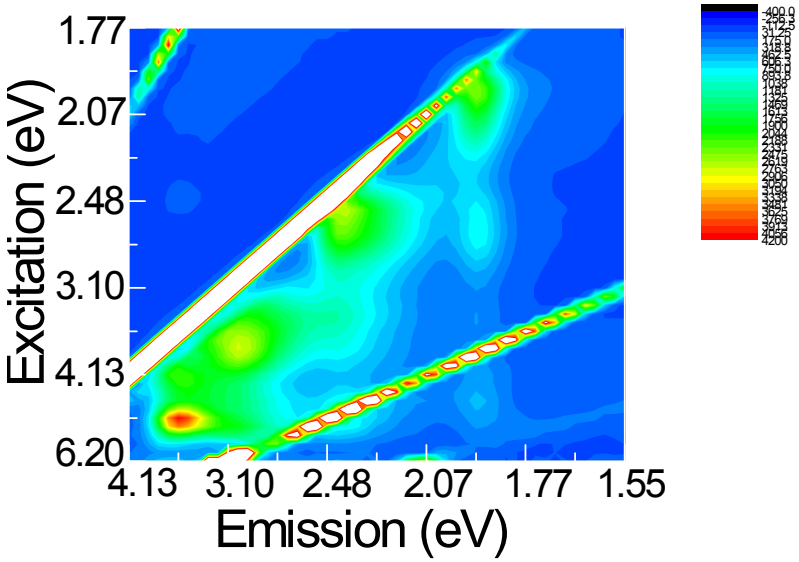


Figure S11: CEES spectrum for PAMAM-NR (PC, above) and PAMAM-NR-NIR797 (PCS below).

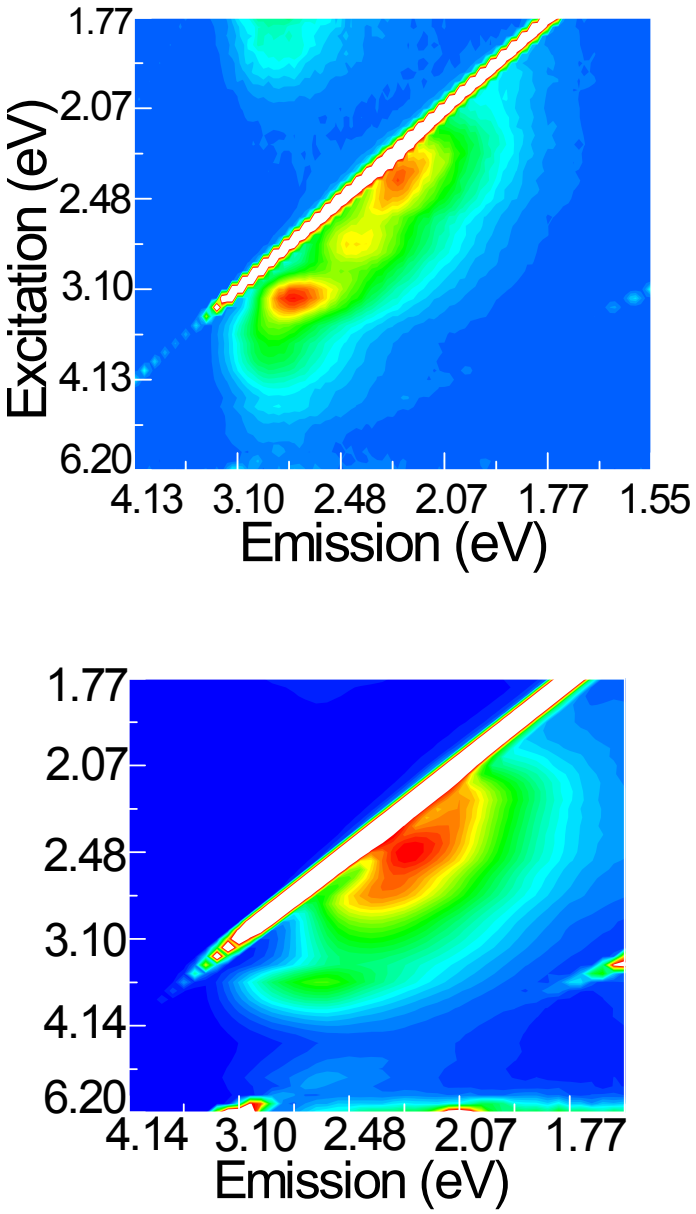


Figure S12: CEES for PAMAM-NR-MM (PCM, above), PAMAM-NR-NIR797-MM (PCMS, below) . Note that this data is extremely density and pH dependent.

F. Failed attempts:

In order to understand the pristine role of acidic groups COOH on the surface potential we have used 6th generation PAMAM-succinamic acid, dendrimer with 1,6-diaminohexane core. Therein, the repetitive self-assembly does not initiate, only a sphere like structure is observed as the output product. We have also varied the number of surface groups by choosing another dendrimer 4th generation PAMAM-succinamic acid dendrimer, 1,4-diaminobutane core, wherein in the SEM images we observe the complex chain formation.In both cases described above, dendritic substrates fail to generate two system points; 3.5th generation PAMAM dendrimer, ethylenediamine core, produces isolated octahedron crystal structures. Finally, we could see octahedrons of different sizes in case of 5.5th PAMAM dendrimer, ethylenediamine core, just that we expect in a fractal reaction dynamics, which suggested that with 256 COOH groups, ethylenediamine core based structure generates two out of phase oscillating system points. However, 1,6-diaminohexane core weakens the sync oscillations between the two cores of PAMAM probably due to the extended alkyl chain length in the core, thus restricting the system to generate a coherent homogeneous electronic potential on the substrate surface. Both fail to sustain distinct potential distribution required for the two lobes on the substrate surface to initiate a fractal reaction kinetics.The details of four synthetic products are summarized in the experimental section (SI).