Supporting Information

Regio-Specific Size, Shape and Surface Chemistry Designed Dendrimers Based on Differentiated Dendroid Templates

Shengzhuang Tang, a Donald A. Tomalia, b Bradford G. Orr a , James R. Baker, Jr., a and Baohua Huang, $^{a^*}$

^a Michigan Nanotechnology Institute for Medicine and Biological Sciences, 9220 MSRB III, Box 0648 University of Michigan, Ann Arbor, MI 48109

^b NanoSynthons, 1200 N. Fancher Road, Mt. Pleasant, MI 48858

^{*} Corresponding author: Tel (734)615-0623; Fax (734)615-0621; E-mail: Baohua@umich.edu

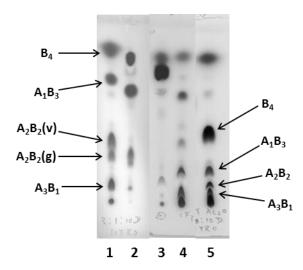


Figure S1. TLC profiles of the reactions of [Core:1,4-butylenediamine];(4->2);{*star-branched*-poly(amidoamine)-(NH₂)₄};(G=0) (PAMAM) structure with Boc anhydride (lane 1), dimethyl itaconate (lane 2), benzoyl chloride (lane 3), trifluoroacetic anhydride (lane 4), and acetic anhydride (lane 5).

All reaction mixtures were rapidly assayed by TLC protocols using iodine staining since these PAMAM structures possess no UV chromophores. In parallel, a second set of identical TLC plates were stained with ninhydrin solution in order to test for the presence of primary amine groups and allow identification of respective substituted products. For example, the tetra-Boc product would not exhibit a ninhydrin stain, whereas, the other lessor substituted DDT products would manifest a stain intensity inversely related to substitution level. Interestingly, TLC results showed that the product distributions obtained for sub-stoichiometric reactions of Boc anhydride or dimethyl itaconate reactions with star-branched; PAMAM; (G=0) substrates were very similar (Figure S1, lanes 1 and 2). The TLC based product profiles for reactions of star-branched; PAMAM;(G=0) substrates with acetic anhydride or trifluoroacetic anhydride were similar with different R_f values for a given species, however, the disubstituted products from these two reactions could not be adequately resolved under these conditions (Figure S1, lanes 4 and 5). The sub-stoichiometric, benzoyl chloride reaction gave mostly tetrasubstituted product with several other faint spots. (Figure S1, lane 3).

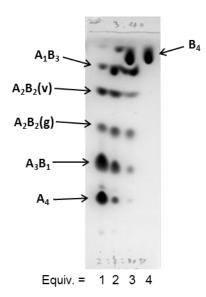


Figure S2. TLC profiles of reaction products obtained by reaction of PAMAM;(G=0); dodecylene core;starbranched structure with:

1, 2, 3, and 4 equivalents of Boc anhydride.

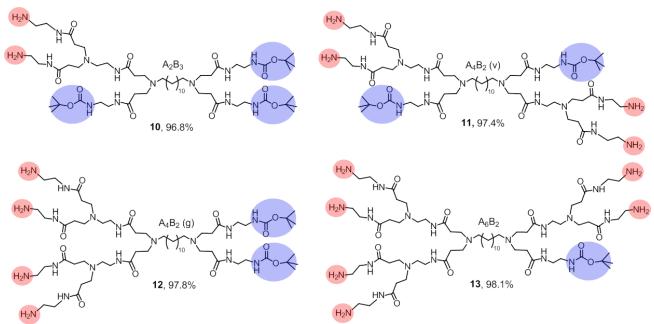


Figure S3. Structures of differentiated PAMAM;(G=1) dendrimers where isolated yields are calculated for two steps from PAMAM;(G=0) star-branched precursors.

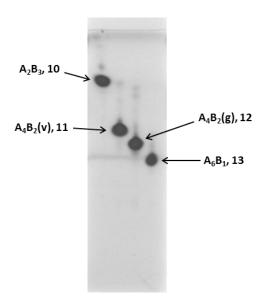


Figure S4. TLC profiles of differentiated PAMAM; (G=1) dendrimers using a three solvent system

(i.e.,CHCl₃/MeOH/NH₄OH=2:1.5:0.6)

Table S1. R_f values by TLC of products from reactions in Scheme 1.

Core	B_4	A_1B_3	$A_2B_2(v)$	$A_2B_2(g)$	A_3B_1	A_4
Ethylene	0.90	0.79	0.54	0.46	0.26	0.07
Butylene	0.91	0.78	0.55	0.45	0.28	0.08
Hexylene	0.91	0.80	0.62	0.49	0.32	0.13
Dodecylene	0.93	0.83	0.73	0.56	0.41	0.27