Supporting Information

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

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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 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 Rf 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 tetra-substituted product with several other faint spots. (Figure S1, lane 3).

**Figure S1.** TLC profiles of the reactions of [Core:1,4-butylenediamine]4-(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).
Figure S2. TLC profiles of reaction products obtained by reaction of PAMAM\(_{(G=0)}\); dodecylene core; star-branched 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.
Table S1. $R_f$ values by TLC of products from reactions in Scheme 1.

<table>
<thead>
<tr>
<th>Core</th>
<th>B$_4$</th>
<th>A$_1$B$_3$</th>
<th>A$_2$B$_2$ (v)</th>
<th>A$_2$B$_2$ (g)</th>
<th>A$_3$B$_1$</th>
<th>A$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0.90</td>
<td>0.79</td>
<td>0.54</td>
<td>0.46</td>
<td>0.26</td>
<td>0.07</td>
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<tr>
<td>Butylene</td>
<td>0.91</td>
<td>0.78</td>
<td>0.55</td>
<td>0.45</td>
<td>0.28</td>
<td>0.08</td>
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<tr>
<td>Hexylene</td>
<td>0.91</td>
<td>0.80</td>
<td>0.62</td>
<td>0.49</td>
<td>0.32</td>
<td>0.13</td>
</tr>
<tr>
<td>Dodecyline</td>
<td>0.93</td>
<td>0.83</td>
<td>0.73</td>
<td>0.56</td>
<td>0.41</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure S4. TLC profiles of differentiated PAMAM; (G=1) dendrimers using a three solvent system (i.e., CHCl$_3$/MeOH/NH$_4$OH=2:1.5:0.6)