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Double Exponential Dendrimer Growth

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Abstract: An exponentially accelerated convergent growth scheme for the synthesis of dendritic macromolecules is described and demonstrated. By this process, the number of repeat units per dendrimer accumulates according to a double exponential function in terms of generation, *n*. The process employs a single trifunctional monomer of the type $A_p(B_p)_2$ having orthogonally protected functional groups. The repetitive process involves selective removal of the protecting groups on A_p in one portion, selective removal of the protecting groups on B_p in a second portion, and subsequent coupling of the two monoprotected intermediates in a proper stoichiometric ratio. The new monodendron maintains a single A_p group at its focal point but contains x^2 B_p peripheral groups where x is the number of peripheral groups in the preceding generation. The double exponential growth scheme is demonstrated by the synthesis of a third-generation (255-mer) phenylacetylene monodendron that is characterized by ultraviolet matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (calculated molecular weight 39.972 kDa, observed *m/z* 39.969 kDa).

Introduction

Few synthetic methods are known that yield macromolecules with a narrow molecular weight distribution. These include addition polymerizations that follow "living" criteria,[1] genetically directed macromolecular syntheses,[2] and nonlinear repetitive syntheses including dendrimer growth.[3] Several variations of dendrimer synthesis have been reported during the past decade including the divergent,[3a,b] convergent,[3c,d] the double stage convergent,[3e] and the comb−burst[3f] strategies. Each of these is an example of nonlinear repetitive synthesis in which the degree of polymerization, dp, increases nonlinearly against the generation number, *n*, of the stepwise process. In general, dendrimer syntheses follow some form of geometric progressive growth. For the convergent method with trifunctional monomers, the exact relationship[4] is given in eq 1 where dp grows as a power of *n*. We report here a new dendrimer growth

$$\mathrm{dp} = 2^{(n+1)} - 1 \tag{1}$$

scheme in which the degree of polymerization depends on the generation number raised to a power, raised to a power, i.e. double exponential dendrimer growth (DEDG).[5] The result is a significantly accelerated growth rate, even when measured against other dendrimer strategies.[6]

The concept of double exponential growth developed from a generalization of the nonlinear repetitive method which we previously described for synthesizing straight-chain oligomeric sequences of "AB" monomers.[7] This process begins with a diprotected monomer of the type A_pB_p and involves the repetitive use of a set of three reactions (selective deprotection of $A_p \rightarrow A$, selective deprotection of $B_p \rightarrow B$, and coupling of $A + B \rightarrow A{-}B$). The result of this method is discrete, straight-chain sequences of the type $A_p{-}(BA)_{(2^n-1)}{-}B_p$. This process can be generalized to include monomers of higher functionality, and doing so leads to double exponential dendrimer growth. Scheme 1 shows the first two generations of DEDG starting from the trisubstituted monomer **1**. Each repeat unit is represented by the symbol "●", and the functional group descriptors are the same as mentioned above. The first generation (**2**) is a trimer obtained by combining the monoprotected derivatives of **1** in a 2:1 ratio. Monodendron **2** has types

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(1) (a) Szwarc, M. *Carbanion, Living Polymers and Electron Transfer Processes*; Interscience: New York, 1968. (b) Webster, O. W. *Science* **1991**, *251*, 887.

(2) McGrath, K. P.; Fournier, M. J.; Mason, T. L.; Tirrell, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 727.

(3) (a) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 192−313 and references therein. (b) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichimica Acta* **1992**, *25*, 31−38. (c) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (d) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018. (e) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252. (f) Tomalia, D. A.; Hedstrand, D. A.; Ferritto, M. S. *Macromolecules* **1991**, *24*, 1435.

(4) An alternative formalism for describing repetitive processes involves recursion relations (see: Brousseau, A. *Linear Recursion and Fibonacci Sequences*; The Fibonacci Association: San Jose, CA, 1971). A more meaningful connection exists between the recursion formalism and the repetitive constructions used in dendrimer syntheses. The recursion relationship that describes the growth of monodendrons by the convergent method is given by eqs i and ii where T_n is the number of monomers per dendrimer at generation *n*. Note that all previously reported dendrimer growth schemes follow a linear recursion relationship (i.e. T_{n+1} are linearly related to T_n).

$$T_0 = 1 \tag{i}$$

$$T_{n+1} = 2T_n + 1 \tag{ii}$$

(5) (a) A preliminary account of this work has been published: Kawaguchi, T.; Moore, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 669. (b) An accelerated growth scheme which resembles DEDG in its first generation has recently been reported: Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 82−85.

(6) In the synthetically accessible molecular weight regime, the comb−burst strategy is competitive with DEDG in terms of monomers added per synthetic step. From a purely mathematical point of view, DEDG is ultimately a more powerful combinatory engine. Note also that all generations of comb−burst polymers will have a distribution in molecular weight, whereas nearly monodisperse third-generation products of DEDG can be obtained.

(7) (a) Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (b) See also: Igner, E.; Paynter, O. I.; Simmonds, D. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2447−2454.

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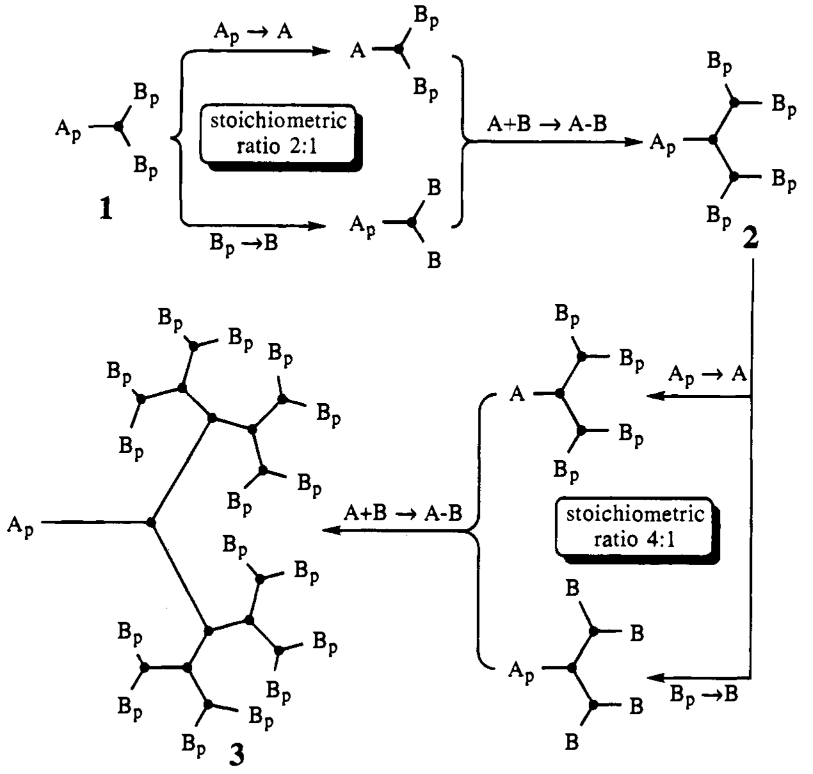
Scheme 1. The First Two Generations of Double Exponential Dendrimer Growth



of functional groups identical to those of **1** except that the number of peripheral B_p groups has doubled. Repeating this process in a 4:1 ratio from **2** gives the second-generation product **3**, a 15-mer with 16 peripheral B_p groups. If **3** is subjected to this reaction sequence once more in a 16:1 ratio, a monodendron having a degree of polymerization of 255 is expected. This macromolecule can be prepared in only nine synthetic steps from monomer **1**.

Several aspects of the DEDG scheme are noteworthy. First, dendrimer growth occurs bidirectionally. At the end of each generation, the new monodendron maintains a single A_p group at its focal point, but it contains x^2 B_p peripheral groups where x *is* the number of peripheral groups in the preceding generation. Second, the general form for degree of polymerization vs generation n follows double exponential growth as shown in eq 2.[8] The significance of this expression becomes obvious on

$$dp = 2^{2^n} - 1 \qquad (2)$$

examination of Figure 1, which plots degree of polymerization vs generation number for convergent and double exponential growth. Double exponential growth is capable, in theory, of generating a macromolecule with dp > 250 in just three generations (nine synthetic steps), while the conventional convergent growth scheme would require seven generations to reach this same size (14 synthetic steps). The scheme offers advantages similar to those of the double stage convergent method[3e] and has the additional advantage that the hypercore grows concomitantly with the required peripheral monodendrons. Because of the potential synthetic economy of the DEDG method, we set out to establish its feasibility.

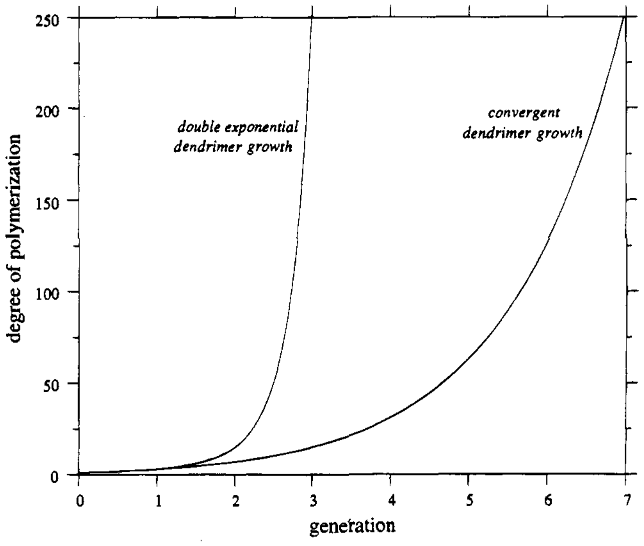


Figure 1. Plot showing the ideal degree of polymerization vs generation number for triconnected monodendrons prepared by the convergent and double exponential dendrimer schemes.

Results and Discussion

To test the feasibility of double exponential growth, we began with phenylacetylene monomer **4** (Scheme 2). The trio of reactions that make up the double exponential repetitive cycle with **4** are identical to those which we used to prepare straight-chain phenylacetylene oligomers.[7a] The first two cycles of synthesis proceed smoothly, yielding monodendrons **Et_2N_3-M_3-TMS_4** and **Et_2N_3-M_{15}-TMS_{16}** (Scheme 2).[9] Complete ^1H NMR

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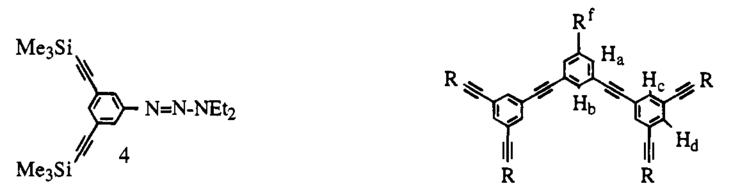
[8] Double exponential dendrimer growth is described by a *nonlinear recursion* relation (eqs iii and iv, compare to ref 4).

$$T_0 = 1 \qquad (iii)$$

$$T_{n+1} = 2T_n + T_n^2 \qquad (iv)$$

[9] The symbol **Et_2N_3-M_y-TMS_x** is used to represent a monodendron with a focal point triazene (Et_2N_3) group and y monomers (M) capped with x peripheral TMS groups. Similarly, the symbol **I-M_y-TMS_x** is used to represent an identical monodendron except that an iodo group now occupies the focal point position. Finally, the symbol **Et_2N_3-M_y-H_x** is used to represent a monodendron with x terminal ethynyl groups on its periphery. These descriptors follow the progression used in the nomenclature scheme developed by Newkome et al.[15]

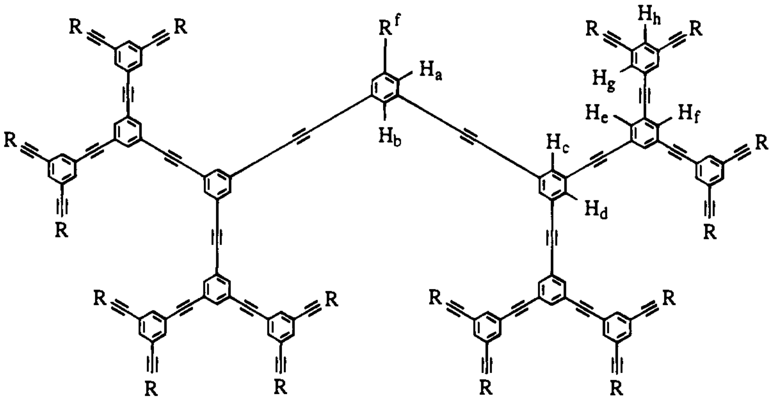
Scheme 2. Chemical Structures of Monomer **4** and the Products of the First Two Generations of DEDG[a]



R = -SiMe$_3$, R^f = -N$_3$Et$_2$; **Et$_2$N$_3$-M$_3$-TMS$_4$**

R = -H, R^f = -N$_3$Et$_2$; **Et$_2$N$_3$-M$_3$-H$_4$**

R = -SiMe$_3$, R^f = -I; **I-M$_3$-TMS$_4$**



R = -SiMe$_3$, R^f = -N$_3$Et$_2$; **Et$_2$N$_3$-M$_{15}$-TMS$_{16}$**

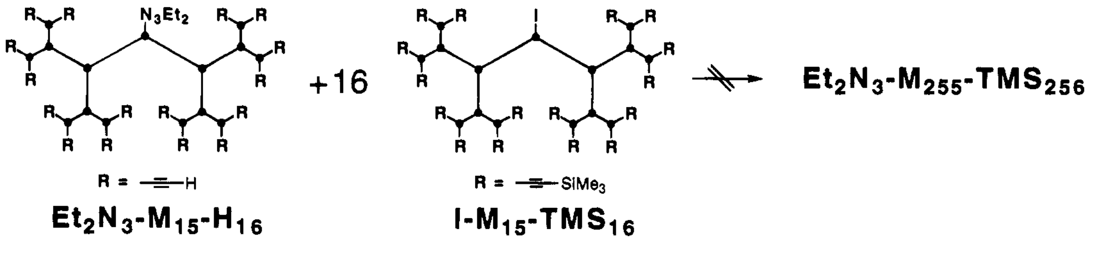
R = -H, R^f = -N$_3$Et$_2$; **Et$_2$N$_3$-M$_{15}$-H$_{16}$**

R = -SiMe$_3$, R^f = -I; **I-M$_{15}$-TMS$_{16}$**

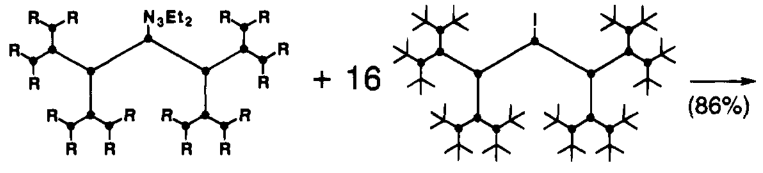
[a] The indicated hydrogen atom labels are used in ^{1}H NMR assignments.

assignments for these monodendrons have been made on the basis of integral ratios and COSY spectra (see Experimental Section; proton descriptors are as indicated in Scheme 2). Deprotection of the focal point triazene of **Et$_2$N$_3$-M$_{15}$-TMS$_{16}$** gave **I-M$_{15}$-TMS$_{16}$** in high yield. In contrast, complete removal of the 16 peripheral trimethylsilyl groups from **Et$_2$N$_3$-M$_{15}$-TMS$_{16}$** was difficult due to poor solubility of the resulting product. However, when KOH was used in a solvent mixture of THF and methanol, complete deprotection could be achieved. The resulting monodendron **Et$_2$N$_3$-M$_{15}$-H$_{16}$** was obtained as an unstable, white amorphous solid. If this material is stored in ambient conditions, decomposition as indicated by the appearance of higher molecular weight impurities in size-exclusion chromatography (SEC) traces takes place in a few days. We found, however, that the solid can be stored at −50 °C for several weeks without a loss of purity. Fortunately, this material exhibited reasonable solubility in THF and DMF, and a ^{1}H NMR spectrum in THF-d_8 revealed the total absence of trimethylsilyl groups. Because of its instability, the product was not characterized further but used immediately in the next coupling reaction.

Attempts were next made to prepare the third-generation product of DEDG by coupling an excess of **I-M$_{15}$-TMS$_{16}$** with the hypercore **Et$_2$N$_3$-M$_{15}$-H$_{16}$** under a variety of conditions (eq 3). Because of the poor solubility of the latter compound in triethylamine, we initially performed the coupling using a solvent mixture of THF and triethylamine. All attempts under these conditions, however, led to complex mixtures in which there was no discrete high molecular weight product. We suspect that intermolecular self-coupling (oxidative dimerization) between terminal acetylenes on hypercore **Et$_2$N$_3$-M$_{15}$-H$_{16}$** is the source of the problem. Attempts were then made to perform the cross-coupling under conditions where **Et$_2$N$_3$-M$_{15}$-H$_{16}$** was suspended in the reaction medium. We reasoned that the low solubility of the hypercore would slow the rate of bimolecular self-coupling. It follows that once any of the suspended hypercore dissolved, it would quickly react with the large excess of **I-M$_{15}$-TMS$_{16}$**. Reaction progress was monitored by SEC, whereby injections of the reaction mixture showed the gradual appearance of a new high molecular weight product and the disappearance of **I-M$_{15}$-TMS$_{16}$**. The reaction was allowed to proceed until the ratio of high molecular weight product to excess **I-M$_{15}$-TMS$_{16}$** remained constant (12 d at 60 °C). Using 40 equiv of **I-M$_{15}$-TMS$_{16}$** per hypercore, we were able to obtain a product with an apparently well-defined higher molecular weight, albeit in rather poor yield (16% after purification). As



(3)



Et_2N_3-M_{15}-H_{16} I-M_{15}-t-Bu_{16} $\longrightarrow$ Et_2N_3-M_{255}-t-Bu_{256} (4)

shown in Figure 2, the purified high molecular weight product gave a single peak by SEC with M_n = 21 500 relative to polystyrene (M_w/M_n = 1.05). The ^1H NMR spectrum of this product shows one singlet corresponding to the peripheral TMS groups, but the aromatic region is too complicated to be assigned. The integral ratio of trimethylsilyl protons to aromatic protons is observed to be 2.96:1 in good agreement with the calculated ratio of 3.01:1.

Recognizing the inability of both SEC and ^1H NMR to resolve possible defect structures such as incomplete couplings, we turned to ultraviolet matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry. The matrix and sample preparation methods that we previously described for smaller hydrocarbon dendrimers[10,11] were adequate to obtain spectra from these much larger macromolecules. A typical spectrum is shown in Figure 3. Surprisingly, four main high-mass peaks corresponding approximately to *m/z* of 47.270, 44.208, 41.203, and 38.181 kDa are observed. Moreover, the expected mass of the 255-mer (50.237 kDa) is clearly absent from the spectrum shown in Figure 3. The peak of highest-observed mass is consistent with that of the 240-mer, the product obtained by coupling 15 equiv of **I-M₁₅-TMS₁₆** with **Et₂N₃-M₁₅-H₁₆** (calculated mass of the weighted average $(M + H)^+$ ion is 47.220 kDa). The observed mass difference between contiguous peaks (3.062, 3.005, and 3.022 kDa) corresponds to that expected for the mass of a 15-mer monodendron residue (calculated mass of a 15-mer residue is 3.017 kDa). Thus, the other three peaks are assigned as the 225-mer, the 210-mer, and the 195-mer (i.e. 255 − 30, 255 − 45, and 255 − 60) which have expected masses of 44.202, 41.185, and 38.168 kDa, respectively.[12] Although there is good agreement between the observed masses (peak centroids) and those expected based on partially coupled products, we note that the peaks are broad ($m/\Delta m$ ca. 100). On the basis of the purity of **I-M₁₅-TMS₁₆** and **Et₂N₃-M₁₅-H₁₆** and the possible defects that could arise from incomplete coupling based on DEDG, we do not believe that the widths of these peaks reflect sample heterogeneity, but rather, the resolution limit for these particular samples. In addition to the four products of discrete mass, there also appears to be a rising base line toward the high-mass side that spans the range from 37 to 65 kDa. The origin of this base line rise is not known at present, although it is thought to be due to either high-mass impurities of unknown origin or adduct formation with the matrix, matrix fragments, or alkali metal contaminants. Returning to the SEC trace in Figure 2, we note the extremely low resolving power of SEC relative to MALDI mass spectrometry.

We have made numerous attempts to drive the reaction shown in eq 3 to completion. In all cases, we have yet to observe the 255-mer. One possibility is that steric crowding has become too severe for the reaction to reach completion. This suggests that the monodendrons should contain unreacted terminal acetylenes buried within their interior. However, no indication of such groups could be found upon examination of the infrared C−H-stretching region (3310 cm^{-1}). This implies that either the abundance of such groups is too low or possibly that intramolecular self-coupling (oxidative dimerization) of these groups has occurred, creating cyclic diacetylene structures. This latter possibility cannot be the case for the 240-mer since all but one terminal acetylene has reacted. On the basis of the presence of the 240-mer, we suspected that the observed product distribution is a consequence of severe steric crowding. Indeed, reasonable computer-generated molecular models of the third-generation product are difficult to construct, owing to the crowdedness and complexity of this structure. Therefore, we decided to prepare a closely related 255-mer using peripheral monodendrons of slightly smaller size.

To test this idea, we reacted the hypercore **Et₂N₃-M₁₅-H₁₆** with monodendrons of the type **I-M₁₅-*t*-Bu₁₆**, available from our previous studies[13] (eq 4). Although these monodendrons also contain 15 monomer units, the *tert*-butyl periphery groups are slightly smaller in size than the ethynyltrimethylsilyl groups of **I-M₁₅-TMS₁₆**. The SEC trace (Figure 4) of the product from our initial attempt at this coupling gave a single peak with a slightly smaller number average molecular weight (M_n = 16 600, M_w/M_n = 1.04) than that with **I-M₁₅-TMS₁₆**. This observed decrease in mass by SEC is consistent with our expectation that **Et₂N₃-M₂₅₅-*t*-Bu₂₅₆** is of smaller size than **Et₂N₃-M₂₅₅-TMS₂₅₆**. The MALDI mass spectrum of the product obtained from this reaction is shown in Figure 5 and reveals a four-component mixture with observed masses of 39.957, 37.592, 35.278, and 32.975 kDa, consistent with those expected for the 255-mer, 240-mer, 225-mer, and 210-mer of this system (calculated

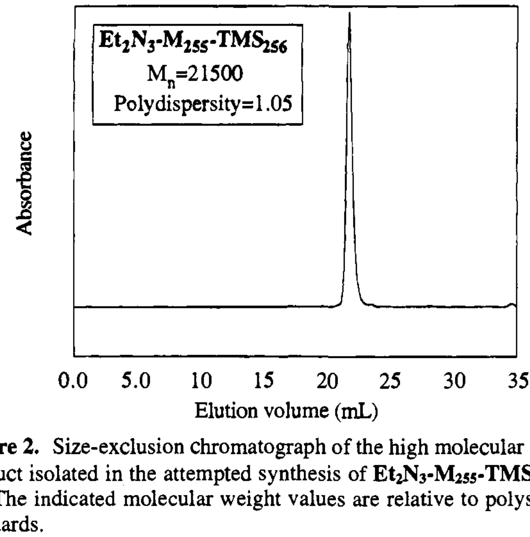


Figure 2. Size-exclusion chromatograph of the high molecular weight product isolated in the attempted synthesis of **Et₂N₃-M₂₅₅-TMS₂₅₆** (eq 3). The indicated molecular weight values are relative to polystyrene standards.

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(10) (a) Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537−4550. (b) Walker, K. L.; Kahr, M. S.; Wilkins, C. L.; Xu, Z.; Moore, J. S. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 731−739.

(11) The matrix was retinoic acid with matrix−analyte ratios in the range 5300:1 to 16 800:1. All dendrimer mass spectra were externally calibrated using the singly and doubly proton-attached ions of horse heart cytochrome *c*.

(12) Using the terminology outlined by Tomalia, all four of these peaks correspond to products with "unfilled monomer shells". See: Tomalia, D. A. *Aldrichimica Acta* **1993**, *26*, 91−101.

(13) Patel, U.; Kawaguchi, T.; Moore, J. S. Unpublished results. See also ref 10.

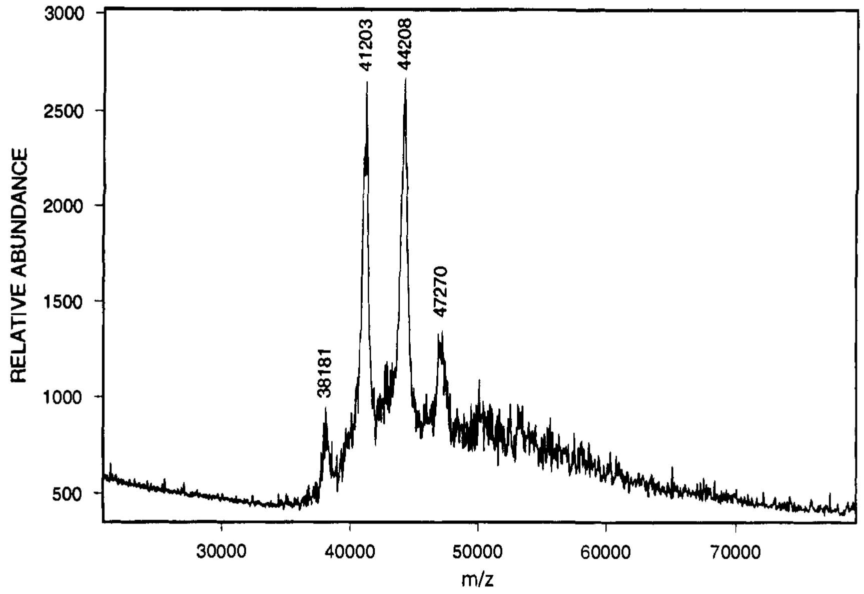

Figure 3. MALDI-TOF spectrum of the product mixture obtained by coupling 40 equiv of **I-M$_{15}$-TMS$_{16}$** with hypercore **Et$_2$N$_3$-M$_{15}$-H$_{16}$** at an initial **I-M$_{15}$-TMS$_{16}$** concentration of 100 mM and initial catalyst concentration of 4 mM in [Pd(dba)$_2$] (60 °C/12 d). The four peaks correspond to incompletely coupled products as explained in the text. The spectrum was measured using a retinoic acid matrix with a matrix—analyte ratio of 5300:1 and horse heart cytochrome *c* as an external calibrant. An aliquot corresponding to 9 pmol of the analyte was deposited on the laser target.

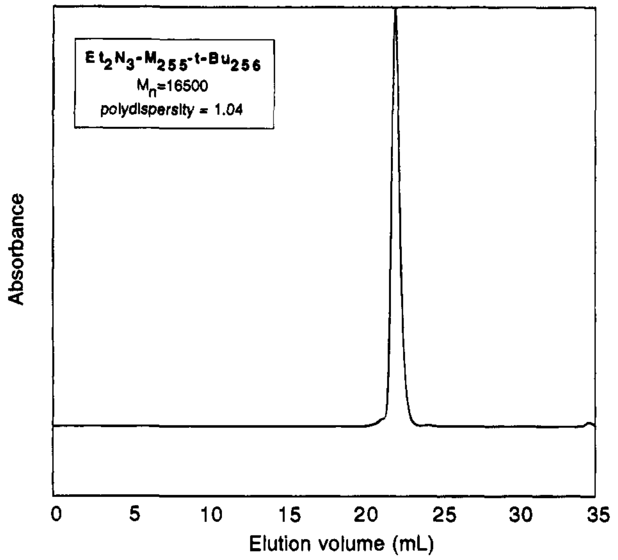

Figure 4. Size-exclusion chromatograph of the high molecular weight product isolated in the initial attempted synthesis of **Et$_2$N$_3$-M$_{255}$-*t*-Bu$_{256}$**. The indicated molecular weight values are relative to polystyrene standards.

masses of the weighted average (M + H)$^+$ ions are 39.972, 37.596, 35.221, and 32.846 kDa, respectively). Noteworthy is the fact that the isolated yield of this product was significantly improved (64%) compared to that obtained from **I-M$_{15}$-TMS$_{16}$**. The observation of the existence of the 255-mer prompted us to try to optimize reaction conditions in an attempt to obtain this species in a pure state.

Extensive experimentation at optimizing the coupling reaction eventually led to conditions that produced predominantly the 255-mer as indicated in Figure 6. It can be seen that a small amount of the 240-mer product remains, but none of the other defect structures are observed. As was the case for the other MALDI mass spectra, a rising base line to the high-mass side is present in Figure 6, although it is much less pronounced. The key to the optimization was identifying a concentration that allowed the reaction to proceed at a reasonable rate while maintaining a low solution viscosity at all times. Under these conditions, the purified product was obtained in a yield of 86%.

It should be emphasized here that very subtle changes in reaction conditions can apparently have dramatic consequences on the level of defects in these high molar mass dendritic structures. Without concomitant analysis by mass spectrometry, this point could easily have gone unnoticed. Finally, it should be mentioned that these optimized conditions failed to improve the situation with **Et$_2$N$_3$-M$_{255}$-TMS$_{256}$**. In this case, a mixture of products with a distribution similar to that seen in Figure 3 was again obtained (no 255-mer observed). Thus, at least from a kinetic point of view, it is possible that we have located a crossover point in size to the dense packed state.[14] Further investigations to explore this possibility are in progress.

Conclusions

In summary, double exponential dendrimer growth is an accelerated convergent scheme for the preparation of monodendrons via a bi-directional synthesis. This scheme offers advantages similar to those of the double stage convergent method[3e] but has the additional advantage that the hypercore grows concomitantly with the peripheral monodendrons. The growth rate is significantly accelerated relative to other known dendrimer syntheses.[6] The disadvantages of DEDG are that a pair of orthogonal protecting groups (rather than one) is required and the number of generations that can be realized before steric crowding occurs is apparently very limited. The DEDG scheme was demonstrated by the preparation of a third-generation monodendron, **Et$_2$N$_3$-M$_{255}$-*t*-Bu$_{256}$** as shown in eq 4. Noteworthy in this preparation was that subtle changes in reaction conditions had dramatic consequences on the distribution of defect structures. Of further significance is the fact that without mass spectral analysis, one might have assumed defect-free dendrimers to have been obtained, which in fact contained none of the desired product (e.g. eq 3). The successful preparation of **Et$_2$N$_3$-M$_{255}$-*t*-Bu$_{256}$** represents, by more than a factor of 2, the largest phenylacetylene monodendron synthesized to date.

Experimental Section

General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Dry triethylamine was obtained by vacuum transfer from calcium

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[14] deGennes, P. G.; Hervet, H. J. *Phys. Lett. (Paris)* **1983**, *44*, 351.

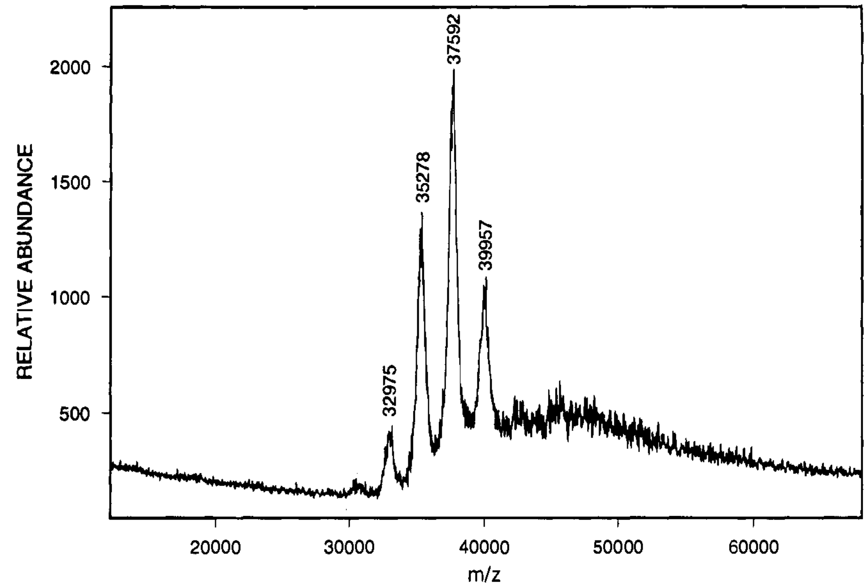

Figure 5. MALDI-TOF spectrum of the product obtained by coupling 40 equiv of **I-M$_{15}$-*t*-Bu$_{16}$** with **Et$_2$N$_3$-M$_{15}$-H$_{16}$**. Reaction conditions were as follows: monodendron **I-M$_{15}$-*t*-Bu$_{16}$** at an initial concentration of 100 mM and an initial catalyst concentration of 4 mM in [Pd(dba)$_2$] (55 °C/6 d). The spectrum was measured using a retinoic acid matrix with a matrix−analyte ratio of 5700:1 and horse heart cytochrome *c* as an external calibrant. An aliquot corresponding to 18 pmol of the analyte was deposited on the laser target.

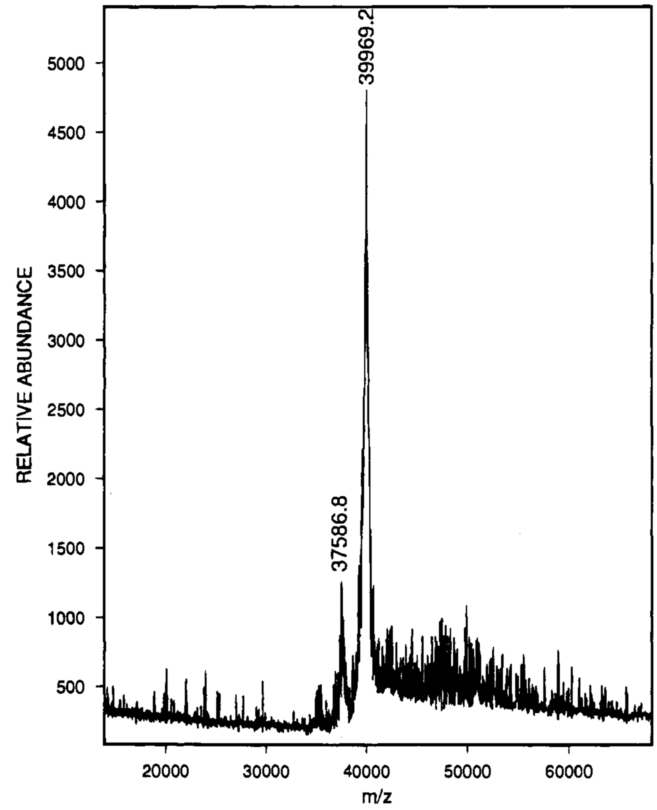

Figure 6. MALDI-TOF spectrum of the product obtained by coupling 40 equiv of **I-M$_{15}$-*t*-Bu$_{16}$** with **Et$_2$N$_3$-M$_{15}$-H$_{16}$** (eq 4). Reaction conditions were as follows: monodendron **I-M$_{15}$-*t*-Bu$_{16}$** at an initial concentration of 20 mM and an initial catalyst concentration of 2 mM in [Pd(dba)$_2$] (60 °C/7 d). The spectrum was measured using a retinoic acid matrix with a matrix−analyte ratio of 16 800:1 and horse heart cytochrome *c* as an external calibrant. An aliquot corresponding to 3 pmol of the analyte was deposited on the laser target.

hydride. Methyl iodide was vacuum transferred from molecular sieves. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer in the indicated solvents at the indicated fields; chemical shifts are expressed in parts per million (δ) using residual solvent protons as the internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Analytical thin liquid chromatography was performed on KIESELGEL F-254 precoated TLC plates. Silica for flash chromatography was silica gel 60 (230−400 mesh) from EM Science. Elemental analyses were performed by the School of Chemical Science Microanalytical Laboratory, University of Illinois. Size-exclusion chromatography (SEC) was performed using a Waters 510 HPLC pump. Waters 996 photodiode array detector, and a series of three Waters styragel HR 4E 7.8 × 300 mm columns which were calibrated with narrow molecular weight polystyrene standards. SEC data were obtained in THF at 35 °C. Cascade nomenclature follows the procedure reported by Newkome et al.[15]

1-(3,5-Bis(1-(trimethylsilyl)ethynyl)phenyl)-3,3-diethyltriazene (4). A heavy-walled flask was charged with 1-(3′,5′-dibromophenyl)-*N,N*-diethyltriazene (2.5 g, 7.5 mmol), (trimethylsilyl)acetylene (2.62 mL, 18.75 mmol), bis(dibenzylideneacetone)palladium(0) (172 mg, 0.3 mmol), triphenylphosphine (391 mg, 1.5 mmol), copper(I) iodide (57 mg, 0.3 mmol), and triethylamine (30 mL). The flask was evacuated under liquid nitrogen, back-filled with nitrogen three times, sealed, and stirred at 75 °C for 18 h. The disappearance of 1-(3′,5′-dibromophenyl)-*N,N*-diethyltriazene was monitored by TLC. After the reaction was complete, the mixture was filtered, and the solvent was evaporated. The product was purified by flash chromatography, eluting with 7:1 petroleum ether/CH$_2$Cl$_2$ to give 1-[3′,5′-bis(trimethylethynyl)phenyl)]-*N,N*-diethyltriazene as a pale yellowish viscous oil: yield 84%; R_f 0.37 (3:1 hexane/CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 1.6 Hz, 2H, H$_a$), 7.34 (t, J = 1.2 Hz, 1H, H$_b$), 3.74 (q, J = 7.2 Hz, 4H, CH$_2$), 1.25 (br, s, 6H, CH$_3$), 0.24 (s, 18H, SiMe$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.96, 131.72, 124.05, 123.52, 104.52, 94.03, −0.07. Anal. Calcd for C$_{20}$H$_{31}$N$_3$Si$_2$: C, 64.98; H, 8.45; N, 11.37. Found: C, 64.86; H, 8.50; N, 11.35.

General Procedure for Deprotection of Trimethylsilyl Groups of Monodendrons Et$_2$N$_3$-M$_y$-TMS$_x$. The monodendron **Et$_2$N$_3$-M$_y$-TMS$_x$** was dissolved in dichloromethane, and absolute methanol was added dropwise to the point of saturation. Excess solid potassium hydroxide was added and the suspension stirred under nitrogen at room temperature for about 30 min. After complete deprotection (verified by TLC and/or NMR), the product was purified by flash chromatography to give **Et$_2$N$_3$-M$_y$-H$_x$**.

General Procedure for Deprotection of the Triazene Group of Monodendrons Et$_2$N$_3$-M$_y$-TMS$_x$. A heavy-walled glass tube joined to a Teflon screw valve was charged with the monodendron **Et$_2$N$_3$-M$_y$-TMS$_x$** and was taken up in freshly distilled iodomethane (concen-

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(15) Newkome, G. R.; Baker, G. R.; Young, J. K.; Traynham, J. G. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 641−651.

tration ca. 0.1 M in monodendron). The solution was degassed and placed under a nitrogen head space, and the tube was sealed. After the mixture was heated at 110 °C for 12 h, the starting triazene had completely reacted. During this time, salt precipitates from the solution. After complete deprotection (verified by TLC and/or NMR), the product was purified by flash chromatography to give **I-M$_y$-TMS$_x$**.

2-Cascade: **1-phenyl-3,3-diethyltriazene [2-3,5]**: **5-ethynyl-1,3-bis(1-(trimethylsilyl)ethynyl)benzene (Et$_2$N$_3$-M$_3$-TMS$_4$).** A heavy-walled flask was charged with **Et$_2$N$_3$-M$_1$-H$_2$** (0.5 g, 2.22 mmol), **I-M$_1$-TMS$_2$** (1.88 g, 4.74 mmol), bis(dibenzylideneacetone)palladium(0) (52 mg, 0.09 mmol), triphenylphosphine (119 mg, 0.45 mmol), copper(I) iodide (17 mg, 0.09 mmol), and triethylamine (18 mL). The mixture was degassed and back-filled with nitrogen three times, and then the flask was sealed and stirred at 55 °C for 20 h. The disappearance of **Et$_2$N$_3$-M$_1$-H$_2$** was monitored by TLC. The mixture was filtered, and the solvent was evaporated. The product was purified by flash chromatography, eluting with 6:1 petroleum ether/CH$_2$Cl$_2$ to give **Et$_2$—N$_3$-M$_3$-TMS$_4$** as a colorless powder: yield 97%; R_f 0.42 (3:1 hexane/CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, J = 1.6 Hz, 2H, H$_a$), 7.56 (d, J = 2.0 Hz, 4H, H$_c$), 7.53 (t, J = 1.6 Hz, 2H, H$_d$), 7.39 (t, J = 1.6 Hz, 1H, H$_b$), 3.84 (q, J = 7.2 Hz, 4H, CH$_2$), 1.31 (br s, 6H, CH$_3$), 0.24 (s, 36H, SiMe$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.31, 134.81, 134.61, 130.91, 123.93, 123.72, 123.68, 123.37, 103.17, 95.66, 89.97, 87.69, −0.16. Anal. Calcd for $C_{46}H_{55}N_3Si_4$: C, 72.48; H, 7.27; N, 5.51. Found: C, 72.24; H, 7.23; N, 5.50.

8-Cascade: **1-phenyl-3,3-diethyltriazene [2-3,5]**: **(5-ethynyl-1,3-phenylene)^2**: **5-ethynyl-1,3-bis(1-(trimethylsilyl)ethynyl)benzene (Et$_2$N$_3$-M$_{15}$-TMS$_{16}$).** A heavy-walled flask was charged with **Et$_2$N$_3$-M$_3$-H$_4$** (48 mg, 0.1 mmol), **I-M$_3$-TMS$_4$** (373 mg, 0.47 mmol), bis(dibenzylideneacetone)palladium(0) (5.6 mg, 0.01 mmol), triphenylphosphine (12.7 mg, 0.05 mmol), copper(I) iodide (1.8 mg, 0.01 mmol), and triethylamine (5 mL). The mixture was degassed and back-filled with nitrogen three times, and then the flask was sealed and stirred at 50 °C for 21 h. The disappearance of **Et$_2$N$_3$-M$_3$-H$_4$** was monitored by TLC. The mixture was filtered, and the solvent was evaporated. The product was purified by flash chromatography, eluting with 6:1 petroleum ether/CH$_2$Cl$_2$ to give **Et$_2$N$_3$-M$_{15}$-TMS$_{16}$** as a colorless powder: yield 80%; R_f 0.52 (3:1 hexane/CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, benzene-d_6) δ 8.16 (d, J = 1.6 Hz, 2H, H$_a$), 7.86 (t, J = 1.6 Hz, 1H, H$_b$), 7.79 (t, J = 1.4 Hz, 2H, H$_d$), 7.77 (d, J = 2.0 Hz, 4H, H$_c$), 7.65 (m, 32H, H$_e$, H$_g$, H$_h$), 7.55 (t, J = 1.6 Hz, 4H, H$_f$), 3.21−3.47 (br, d, 4H, CH$_2$), 1.28 (br s, 6H, CH$_3$), 0.22 (s, 144H, SiMe$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.02, 135.16, 134.64, 134.49, 134.39, 130.72, 124.28, 124.21, 123.85, 123.73, 123.67, 123.59, 123.37, 123.17, 103.03, 95.89, 90.39, 89.06, 88.98, 88.81, 88.54, 87.57, −0.18. Anal. Calcd for $C_{202}H_{199}N_3Si_{16}$: C, 77.81; H, 6.43; N, 1.35. Found: C, 77.84; H, 6.48; N, 1.33.

8-Cascade: **1-phenyl-3,3-diethyltriazene [2-3,5]**: **(5-ethynyl-1,3-phenylene)^2**: **5-ethynyl-1,3-diethynylbenzene (Et$_2$N$_3$-M$_{15}$-H$_{16}$).** A heavy-walled flask was charged with **Et$_2$N$_3$-M$_{15}$-TMS$_{16}$** (50 mg, 16 μmol), THF (1 mL), and KOH (0.2 g, 1.36 M MeOH solution). The mixture was degassed and back-filled with nitrogen three times, and then the tube was sealed and stirred at room temperature for 0.5 h. The reaction mixture was passed through a short silica column to remove KOH, eluting with THF. The solvent was evaporated under nitrogen gas flow to give **Et$_2$N$_3$-M$_{15}$-H$_{16}$** as a white amorphous solid: yield 98%; ^{1}H NMR (400 MHz, THF-d_8) δ 7.79 (d, J = 1.6 Hz, 4H, H$_c$), 7.70 (d, J = 2.0 Hz, 8H, H$_e$), 7.76−7.73 (m, 6H, H$_d$, H$_f$), 7.65 (d, J = 1.2 Hz, 16H, H$_g$), 7.63 (d, J = 1.6 Hz, 2H, H$_a$), 7.57 (t, J = 1.4 Hz, 8H, H$_h$), 7.51 (t, J = 1.4 Hz, 1H, H$_b$), 3.89−3.79 (br, 4H, CH$_2$), 3.74 (s, 16H, terminal acetylene H), 1.40−1.20 (br, 6H, CH$_3$).

Attempted Synthesis of 128-Cascade: **1-phenyl-3,3-diethyltriazene [2-3,5]**: **(5-ethynyl-1,3-phenylene)^6**: **5-ethynyl-1,3-bis(1-(trimethylsilyl)ethynyl)benzene (Et$_2$N$_3$-M$_{255}$-TMS$_{256}$).** A heavy-walled glass tube was charged with **Et$_2$N$_3$-M$_{15}$-H$_{16}$** (4.95 mg, 2.52 μmol), **I-M$_{15}$-TMS$_{16}$** (320 mg, 104 μmol), bis(dibenzylideneacetone)palladium(0) (2.3 mg, 4.0 μmol), triphenylphosphine (6.2 mg, 24 μmol), copper(I) iodide (1.08 mg, 5.5 μmol), and triethylamine (1 mL). The mixture was degassed and back-filled with nitrogen three times, and then the tube was sealed and stirred at 55 °C for 7 d. The product was purified by flash chromatography, eluting with 6:1 hexane/CH$_2$Cl$_2$ increasing to 3:1 hexane/CH$_2$Cl$_2$ to give a colorless powder: yield 16%; ^{1}H NMR (400 MHz, benzene-d_6) δ 7.94−7.50 (br, m, aromatic H), 0.31−0.23 (br, s, SiMe$_3$); integral ratio of TMS H and aromatic H calcd 3.01, found 2.96.

128-Cascade: **1-phenyl-3,3-diethyltriazene [2-3,5]**: **(5-ethynyl-1,3-phenylene)^6**: **5-ethynyl-1,3-di-*tert*-butylbenzene (Et$_2$N$_3$-M$_{255}$-*t*-Bu$_{256}$).** A heavy-walled glass tube was charged with **Et$_2$N$_3$-M$_{15}$-H$_{16}$** (3.0 mg, 1.53 μmol), **I-M$_{15}$-*t*-Bu$_{16}$** (151 mg, 0.06 mmol), bis(dibenzylideneacetone)palladium(0) (3.5 mg, 6.1 μmol), triphenylphosphine (8.0 mg, 30.5 μmol), copper(I) iodide (1.2 mg, 6.3 μmol), and triethylamine (3 mL). The mixture was degassed and back-filled with nitrogen three times, and then the tube was sealed and stirred at 60 °C for 7 d. The product was purified by flash chromatography, eluting with 9:1 hexane/CH$_2$Cl$_2$ increasing to 4:1 hexane/CH$_2$Cl$_2$ to give **Et$_2$N$_3$-M$_{256}$-*t*-Bu$_{256}$** as a colorless powder: yield 86%; ^{1}H NMR (400 MHz, benzene-d_6) δ 7.94−7.40 (br, m, aromatic H), 1.30−1.18 (br, s, *tert*-butyl H); integral ratio of *tert*-butyl H and aromatic H calcd 3.01, found 3.00. Anal. Calcd for $C_{3066}H_{3079}N_3$: C, 92.13; H, 7.76; N, 0.11. Found: C, 90.78; H, 7.66; N, 0.14.

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