classical model, on the other hand, predicts a high-order polynomial dependence of $\chi^{(2)}$ on $D/2R$.

For $D/2R < 1.2$, there is a discontinuity in both the $\chi^{(2)}$ versus $D/2R$ trend and in the reflectance (absorbance) behavior versus $D/2R$. Several spectra collected from an uncollapsed Langmuir film of 40 Å/C_3 particles are shown in Fig. 4. Upon initial compression, the film becomes more reflective, as described qualitatively above. In this region, $\chi^{(2)}$ is increasing exponentially. At the point where the SHG data exhibit a discontinuity, the reflectance drops precipitously; in the near-infrared, it is below measurable levels. This decrease in reflectivity is accompanied by an equally large increase in absorptivity. The final reflectance spectrum is similar to that reported for thin, metallic silver films (*32*) and indicates that the Langmuir film has become metallic.

Our experimental data provide strong evidence for the onset of quantum mechanical coupling between adjacent silver nanocrystals when interparticle separation distances are reduced below 12 Å, and for a reversible insulator-to-metal transition when the particle separation distance is reduced below 5 Å. Our observations thus provide evidence of quantum mechanical coupling in quantum dot superlattices. In addition, this work constitutes an example of a reversible metal-insulator transition in a solid-state system (*33*) under ambient conditions. These results imply the possibility of fabricating a new class of solids, composed of metal quantum dots, in which the electronic band structure of the solid is "tailored" through the adjustment of electronic wave function overlap between adjacent particles.

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25. Because of electron beam–induced particle instability, particle monolayers with $\delta < 8$ Å were difficult to image. For images of the 27 Å/C_6 particles, a previously unexposed portion of the TEM grid was quickly brought into view, and an image (exposure time, 0.033 s) was immediately captured.
26. Samples for TEM were prepared at UCLA and transported to the University of Southern California Center for Electron Microscopy. For this reason, films had to be stable for at least 2 hours or they could not be imaged. Compressed monolayers of 40 Å/C_3 particles did not exhibit sufficient stability.
27. SHG signals from static Langmuir monolayers were measured over time to ascertain whether the laser was damaging the monolayers. The signal was very stable for all time periods investigated (up to 20 min), and optical microscopic inspection of the illuminated spot revealed no evidence of film damage. Indeed, the monolayers could be redissolved in hexane after the experiments were carried out.
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Regioselective Stepwise Growth of Dendrimer Units in the Internal Voids of a Main Dendrimer

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Dendrimers constitute a class of polymers with unique properties and applications resulting from the presence of internal voids and of a large number of functionalities on the surface. The development of a macromolecular chemistry within the cavities of dendrimers is illustrated here. Two examples of construction of six dendrimer units within the cascade structure of a main dendrimer are reported. The preparation of these multidendritic systems involves the regioselective modification of the framework of the central dendrimer to create internal reactive centers, followed by the stepwise synthesis of the six dendritic macromolecules.

During the past decade, there has been an explosive growth in studies of dendrimers, a new class of macromolecules that can be considered as monodisperse, precisely ordered polyfunctional polymers. Several applications of these relatively soluble compounds have been proposed (*1*). Their remarkable properties result from the presence of a large number of chain-end functionalities that provide highly controlled surfaces and interfaces, and from the presence of internal voids allowing, for example, encapsulation of guest molecules (*2*) or molecular recognition at specific locations on the cascade superstructure (*3*).

A number of creative approaches to the synthesis of organic or inorganic "monodendrimers" have been reported (*1*). The reactivity of the core has been used to couple two or more dendrons leading, for example, to structures with two dissimilar halves (*4*). Coupling of cascade macromolecules through metal centers has also been achieved (*5*). Dendrons containing isophthalic acid units covalently attached to a rigid aromatic spacer have been shown to self-assemble through hydrogen bonding to form a hexameric dendritic aggregate whose stability varies in a generation-dependent manner (*6*). All these different routes to bis- or multidendrimers (*7*) involve the association of dendrons by their core.

An alternative way to build multidendritic systems is based on the use of internal functional groups of a dendrimer. To apply such a concept, it is first necessary to

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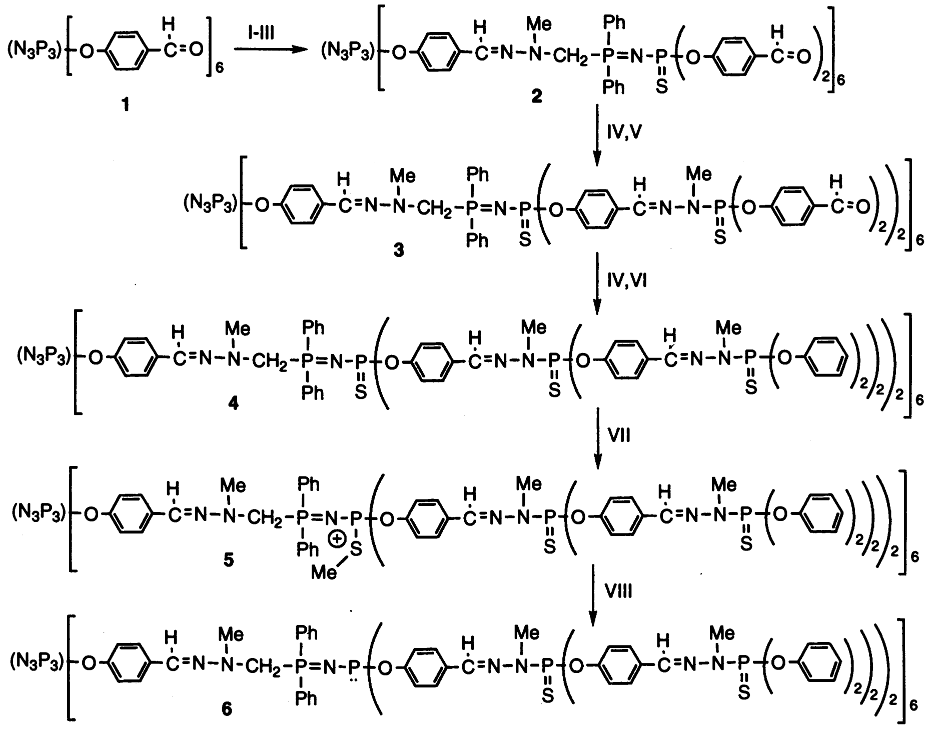
be able to generate very reactive functional groups within the cascade structure, either during the construction of the dendrimers or through regioselective postmodification of the macromolecular framework. It is crucial that the size of the cavities of the central dendrimer be large enough and the internal branches be flexible enough to permit the construction of several dendritic units within the cascade skeleton. The metalation of dendrimers by a superbase, followed by reaction with electrophiles, has been used to introduce functional groups into internal sites of preformed dendritic poly(benzyl ethers) (*8*). The activation of internal functional groups within the cascade superstructure of dendrimers has been exploited to incorporate boron clusters at precise depths on the macromolecular framework (*9*). Therefore, chemical reactions inside the cavities can be performed.

We report two examples of the regioselective stepwise growth of six dendrimer units in the internal voids of a main dendrimer, illustrating that these cavities are accessible and that internal functional groups can be used for the synthesis of covalently linked multidendritic systems.

The synthesis of the central dendrimer is based on the strategy outlined in Fig. 1, using a divergent method (*10*). The formation of generation 1 involves three steps: (i) a condensation reaction between the flexible core, hexaaldehyde **1**, and six equivalents of monomethylhydrazine; (ii) a "Mannich reaction" between the resulting product and six equivalents of the phosphane Ph_2PCH_2OH, giving an hexaaminophosphane; and (iii) a "Staudinger reaction" between this latter compound and the azide $N_3P(S)(OC_6H_4CHO)_2$ to form the dendrimer **2** (generation 1) with six P=N–P(S) fragments in the framework.

From **2**, the construction of dendrimers of generation 2 (**3**) and 3 (**4**) involves the reiteration of a sequence of two reactions: a condensation reaction between the polyaldehyde with the dichlorophosphane sulfide $Cl_2P(S)N(CH_3)NH_2$, followed by addition of the sodium salt of hydroxybenzaldehyde. The sodium salt of phenol was used as the end of the sequence of reactions leading to **4** in order to avoid the presence of terminal aldehyde groups, which might interfere with the reagents used for the stepwise growth of internal dendrimers.



I) H_2NNHMe II) Ph_2PCH_2OH III) $N_3P(S)(OC_6H_4CHO)_2$ IV) $Cl_2P(S)NMeNH_2$ V) $NaOC_6H_4CHO$ VI) $NaOC_6H_5$ VII) CF_3SO_3Me VIII) $P(NMe_2)_3$

Fig. 1. Construction and internal functionalization of a dendrimer of generation 3.

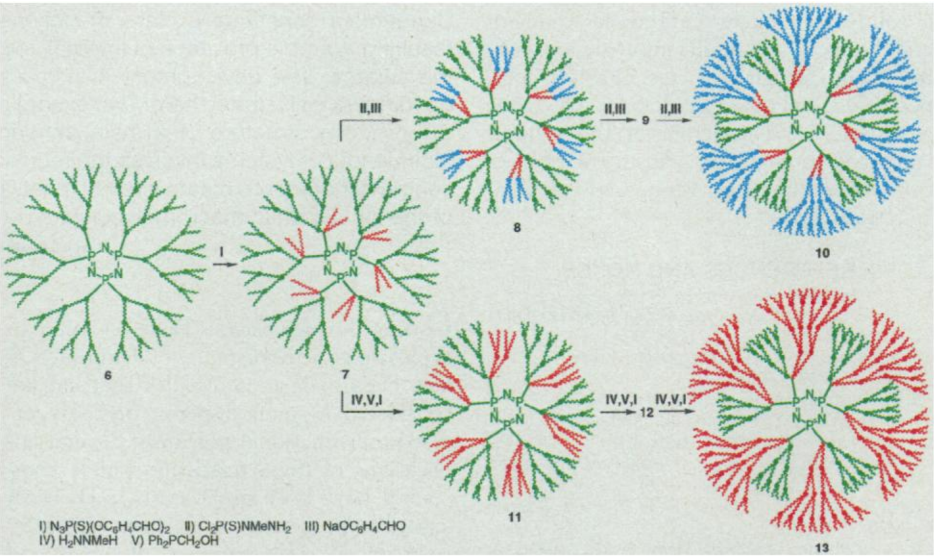
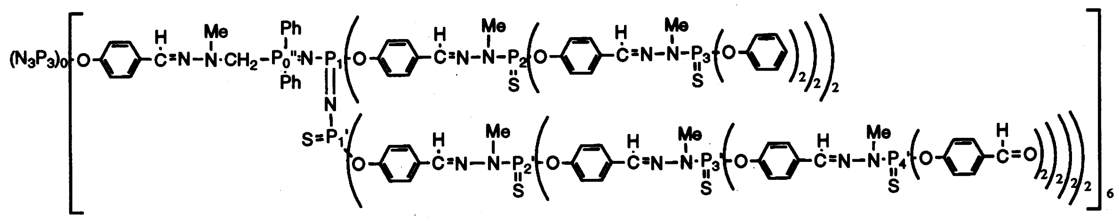


Fig. 2. Stepwise buildup of six internal dendrimers into dendrimer **6**.

To create the reactive centers within the dendrimer **4**, it was treated with an alkylating agent such as methyltrifluoromethane sulfonate, resulting in selective alkylation on the sulfur atom of the six internal P=N–P(S) fragments to form a hexacationic dendrimer **5** (Fig. 1). When **5** was reacted with tris(dimethylamino)phosphane, a clean transfer of the SMe fragments from the P=N–P(SMe) units to $P(NMe_2)_3$ took place, resulting in the formation of six internal and very reactive P=N–P moieties incorporated in the skeleton of the new dendrimer **6**.

At this stage two different strategies can be used to start the construction of dendrimers within the cascade structure of **6** (Fig. 2).

In the first, six equivalents of the azide $N_3P(S)(OC_6H_4CHO)_2$ are added to **6**, leading to the formation of internal P=N–P(S)$(OC_6H_4CHO)_2$ fragments in the resulting dendrimer **7**; subsequent treatment with $H_2NN(CH_3)P(S)Cl_2$ (12 equivalents) and then with the sodium salt $NaOC_6H_4CHO$ (24 equivalents) allows the grafting of six dendrimers of generation 2 into the cavities



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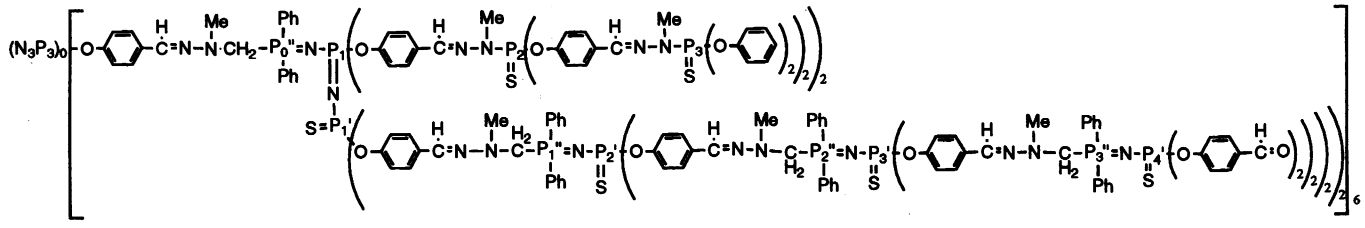

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Fig. 3. Developed structure for polydendritic compounds **10** and **13**.

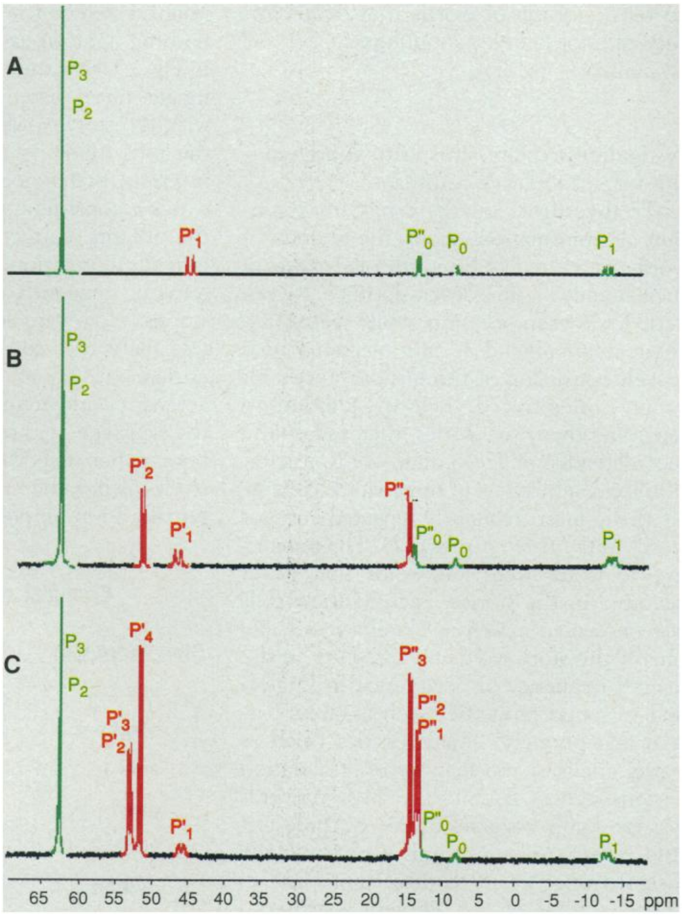

Fig. 4. ^{31}P NMR spectra of the polydendritic macromolecules **7**, **11**, and **13**. Scale at bottom indicates chemical shifts measured in parts per million (ppm). Green signals originate from the central dendrimer, red signals from internal dendrimers. (**A**) Compound **7**. Central dendrimer: P_0, P''_0, P_1, P_2, P_3. Internal dendron: P'_1. (**B**) Compound **11**. Central dendrimer: P_0, P''_0, P_1, P_2, P_3. Internal dendrimers: P'_1, P''_1, P'_2. (**C**) Compound **13**. Central dendrimer: P_0, P''_0, P_1, P_2, P_3. Internal dendrimer: P'_1, P''_1, P'_2, P''_2, P'_3, P''_3, P'_4.

(8). Reiteration of this process permits the growing of these internal dendrimers to generation 3 (**9**) and 4 (**10**) (Fig. 3).

The second strategy also involves addition of $N_3P(S)(OC_6H_4CHO)_2$ (6 equivalents) to **6** to form **7**, which is then reacted first with methylhydrazine (12 equivalents), next with the phosphane Ph_2PCH_2OH, and last with $N_3P(S)(OC_6H_4CHO)_2$. Such a branching pattern results in the grafting of six other dendrons of generation 2 within the internal cavities of **6** (**11**). Generations 3 (**12**) and 4 (**13**) (Fig. 3) of the six internal dendrimers can also easily be built up with this divergent method.

^{31}P nuclear magnetic resonance (NMR) was used to monitor the construction of these controlled polydendritic structures (Fig. 4). The chemical shifts of the phosphorus groups and the intensities of the signals are different from one generation to another. N–N–P–O fragments give a singlet; P=N–P(S) linkages give a doublet of doublet (phosphorus-phosphorus coupling constant, $^2J_{PP}$ = 31 Hz); and the P=N–P=N–P(S) unit gives a doublet of doublet for the central phosphorus atom ($^2J_{PP}$ = 22 to 23 and 58 to 59 Hz) and a doublet for each of the two other phosphorus atoms.

This work demonstrates that functionalization of the internal cavities of various dendrimers can be done through a modification of the skeleton. Various functional groups can be selectively introduced, such as aminophosphite, aldehyde, hydrazone, and dichlorophosphane sulfide. Therefore, all the chemistry reported on the surface of dendrimers can now be done in the cavities.

The results illustrate the flexibility of the chains and the ease of access to the cavities, which allows modification of the structure, compactability, and properties of polydendritic structures. Our strategy could be extended to the preparation of a large number of multipolydendritic systems incorporating organic or inorganic dendritic subunits or both.

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Infants' Memory for Spoken Words

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Infants' long-term retention of the sound patterns of words was explored by exposing them to recordings of three children's stories for 10 days during a 2-week period when they were 8 months old. After an interval of 2 weeks, the infants heard lists of words that either occurred frequently or did not occur in the stories. The infants listened significantly longer to the lists of story words. By comparison, a control group of infants who had not been exposed to the stories showed no such preference. The findings suggest that 8-month-olds are beginning to engage in long-term storage of words that occur frequently in speech, which is an important prerequisite for learning language.

The latter half of the infant's first year is a critical point in acquiring a language. During this period, language learners take their first steps toward acquiring a vocabulary. Young infants already possess many of the speech perception capacities required for learning words (*1*). Infants younger than 6 months distinguish a wide range of speech contrasts (*2*) and have some capacity to compensate for differences in voices (*3*) and speaking rates (*4*). Moreover, after 6 months, infants demonstrate some recognition of the particular phonetic and prosodic characteristics of their native language (*5*). Finally, 7.5-month-olds have another important prerequisite for lexical development: the ability to segment fluent speech into word-sized units (*6–8*).

As important as these speech perception capacities are, the acquisition of vocabulary requires many other capacities, such as the ability to learn meanings and to attach them to the appropriate verbal labels. Most critically, vocabulary acquisition requires some long-term retention of both meanings and verbal labels. Yet this latter aspect of vocabulary acquisition has not been well documented. In contrast to the considerable information that exists about early speech perception capacities (*9*), it is surprising that so little is known about infants' long-term memory for the sound patterns of words. The present investigation explores this critical prerequisite for vocabulary acquisition.

To investigate infants' long-term retention of information about the sounds of words, we visited 15 8-month-old infants in their homes 10 times each during a 2-week period. On each occasion, while seated in a chair, infants heard 30 min of prerecorded speech consisting of three short stories for young children (*10, 11*). In addition to recording the three stories, each talker also recorded a list of 72 content words, in citation form. Thirty-six of these words consisted of the most frequently repeated content words in the three stories (*12*). The remaining 36 words were foil words that never occurred in the stories. Each of these foils was chosen to match as closely as possible one of the story words with respect to the overall frequency of occurrence in English and to sound properties such as stress pattern and phonetic characteristics (such as vowel qualities and manner of articulation of consonants). Each of the 36 story words was randomly assigned to one of three test lists. Then the same words were randomly assigned once again to three more lists to create a total of six different story-word lists. The same procedures were followed with the foil words to create six different lists of these items. Examples of typical story-word and foil lists are shown in Fig. 1.

Two weeks after the last of the 10 home visits, each infant was brought to the laboratory so that her or his retention of the sound patterns of words in the stories could be examined. Our hypothesis was that if infants attended to and stored in memory the sound patterns of frequently occurring words in the stories, they might show subsequent recognition of these sound patterns by demonstrating listening preferences for these items over unfamiliar items. The head-turn preference procedure—a widely used computer-automated method in infant speech research (*6, 7, 13, 14*)—was selected for testing the infants (*15, 16*).

Mean times of listening to the story-word and foil lists were calculated for each infant, based on the infant's fixations of the flashing light on each trial (*17*). As shown in Fig. 2 (left), the infants had significantly longer mean listening times for the lists with the story words than for the lists with the foils [$t(14) = 3.44$, $P < 0.005$]. This listening preference for the lists of story words is consistent with the prediction that the infants extracted, encoded, and retained information about the sound patterns of frequently occurring words in the stories. However, despite the efforts made to equate the story-word and foil lists in critical aspects such as their phonetic characteristics and frequency of occurrence in the language, it is possible that the infants' prior experience with these words in the stories is not the crucial factor responsible for the listening preferences observed. Per-

Examples of Test Materials

Story-Word List	Foil Word List
sneeze	aches
elephant	apricot
ants	sloth
gray	jaunt
vine	ox
python	lanterns
peccaries	caribous
back	front
laugh	burp
out	change
best	beach
jungle	camel

Fig. 1. Examples of typical story-word and foil lists.

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