Spectroscopic Evidence for Excitonic Localization in Fractal Antenna Supermolecules

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Direct experimental evidence is presented for the existence of localized excitations on fractal supermolecular structures that may serve as photonic antenna systems. For one dendrimer family the electronic spectra show no redshift with system size, indicating that the excitations are localized at the nodes of the Cayley trees describing these ordered structures. In contrast, similar dendrimers with varying lengths of the molecular branches exhibit a decrease in the band edge energy with a growing size of the system, consistent with a hierarchy of localization lengths. The latter corresponds to an energy funnel property of these ordered nanostructures. [S0031-9007(97)02375-2]

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A new class of macromolecules known as dendrimers, which are synthesized by repeating units in a hierarchical self-similar fashion [1], has opened possibilities for designing and controlling chemical processes based on the Cayley tree topology of these objects. Dendrimers are characterized by the number of generations they are made of, by the basic building element, and by the branching of the end groups. The total number of the basic elements grows exponentially with the number of generations and the number of periphery elements is of the order of the bulk elements. Dendrimers are the only synthetic realizations of the, up to now, theoretical Cayley trees [2,3]. Their unique structure is expected to provide a broad range of possible applications, one of which is as large single molecule photonic antenna systems [4]. What makes these Cayley tree molecules work as antennas is the large number of absorbing elements at the periphery and an efficient transfer of the absorbed energy to the center where a fluorescent trap, or a reaction center, or a chemical sensor group, can be located [4].

Here we concentrate on the first step in such possible antenna systems, namely, the nature of electronic absorption. We find that the lowest lying excitations are spatially localized and are characteristic of the basic repeating element. For the study here we selected a set of dendrimer supermolecules that we call compact [Fig. 1(a)]. We note that the structures consist of three Cayley trees with common origin and threefold symmetry. To our knowledge these are the largest atomic level systems with a perfect finite Cayley tree structure [5]. Furthermore, they are on a sufficiently large scale to display the topological characteristics of infinitely large Cayley trees [6–8]. Generally, the size of dendrimers in terms of the number of generations is determined by steric effects of the periphery elements [9], which also lead to compactness. Below we present a choice of experimental data that we believe to be sufficient for the demonstration of the localized nature of electronic excitations on these fractal structures. We also present data on a different family of supermolecule dendrimers that we call extended, which have a completely ordered structure but only an approximate self-similarity [Fig. 1(b)]. The apparently small difference between the compact and extended structures of these dendrimers has quite drastic consequences. In contrast to the compact dendrimer family, in the extended dendrimers the lowest excitonic energy state does shift down with size, indicating that the excitations become less localized, with a hierarchy of localization lengths.

The spatial arrangement of the dendrimers in Fig. 1 is based on branching at the meta positions of the benzene nodes [5]. Branching at different positions would grow linear chains (para position) or will terminate the tree structure quickly due to steric hindrance (ortho positions). The fractal nature, using metapositions, is therefore the optimum possibility for a symmetric large

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FIG. 1. Two families of phenylacetylene dendrimers. (a) D4–D94, which are referred to as compact Cayley dendrimers, whereas D25–D127 are referred to as extended Cayley dendrimers. (b) The structural elements are represented in an abbreviated format as follows: ( ), 1,3,5-tri-connected arene, (—), 1,4-di-connected arene, ( — ), 1,3-di-tert-butylphenylene, ( ) carbon-carbon triple bond. The indicated molecular diameters were determined by size-exclusion chromatography.
Recent calculations suggest that, at least for electron transfer, spatial localization is expected for branching at the meta positions. In addition, the meta positions allow for orientational flexibility which allows distortions from a planar configuration. This nonplanarity enables the synthesis of much larger systems, i.e., more generations, by overcoming steric hindrance. Electronically, it decouples the resonative conjugation among benzene rings, introducing a kind of local disorder which localizes the $\pi$-electron excitations of the benzene rings.

The synthesis and characterization of the dendrimer supermolecules has been described before. The absorption spectra [Figs. 2(a) and Fig. 2(b)] were taken in the standard method. At about 320 nm the vibronic optical absorption spectra of the compact dendrimer series [Fig. 2(a)] all show a common vibrationless (0-0) transition (within the error of measurement of less than 2 nm). The higher energy absorption peaks are assigned to the vibronic 0-1 and 0-2 transitions, and are ignored below. The lowest energy peaks (see arrows in Fig. 2) are plotted versus the number of benzene rings (a measure of dendrimer size) in Fig. 3. The interesting point here is the clearly visible energy pinning in the compact series [see arrows and vertical line in Fig. 2(a) and upper curve in Fig. 3]. Another interesting feature is the monotonic increase with size of the optical absorbance. On the other hand, the extended dendrimer systems [Fig. 1(b)] show a very different optical absorption spectrum [Fig. 2(b)]. Here the lowest excitation energy shifts to the red with increasing size. A comparison of these spectral shifts, where shifts are

![Figure 2](image-url)

**FIG. 2.** Dendrimer absorption spectra in hexane at ambient temperature and pressure. (a) Cayley dendrimers from bottom to top: D4, D10, D22, D46, D94; (b) Cayley and extended Cayley dendrimers (SYNDROME) from bottom to top: D4, D10, D25, D58, D127. The vertical line (319.1 nm), common to both (a) and (b), highlights the localization of energy in the periphery states of both the compact and extended series of dendrimers. Arrows designate approximate locations of lowest energy peaks.

![Figure 3](image-url)

**FIG. 3.** Lowest energy absorption peaks with increasing dendrimer size (see arrows in Fig. 2). We emphasize the nearly horizontal line connecting the compact dendrimer series: D4, D10, D22, D46, and D94. The constancy of the energy from D10 to D94 proves the localization. For the extended dendrimer series D10, D25, D58, and D127, the descending energies indicate the increasing delocalization with size. “1” designates single line chain (periphery) states, “2” designates two-membered linear chains, etc. The circles are theoretical points for the extended dendrimer series, derived from a linear cluster exciton model. It is based on the presence of only linear “monomers” in D10, linear “dimers” (2), as well as monomers, in D25, linear trimers (3), as well as dimers, in D58, and linear tetramers (4), as well as dimers and trimers, in D127. The dimer-monomer energy interval $E_1 - E_2$ (equal to the excitation exchange matrix element $M$) is given by the experimental interval of about 4600 cm$^{-1}$. The trimer-monomer $E_1 - E_3$ and tetramer-monomer $E_1 - E_4$ intervals are calculated by the Hornig-Hiebert [13] and Hoshen-Kopelman [12] theories (the two agree for the band edge, though the first theory does not give energy splittings). The most important point to be gleaned from this figure, in combination with Fig. 2, is that the D25 and D58 energy points also characterize the linear dimer and trimer chains of D127 while the D127 point characterizes its locus tetramer chains (and D10 characterizes the D127 periphery portion). We can thus see the complete funnel of the D127 molecule given by the descending energy ladder $E_1 > E_2 > E_3 > E_4$. Similarly, for the D58 we find the three descending steps of the energy funnels at roughly $E_1 = 31300$ cm$^{-1}$, $E_2 = 27750$ cm$^{-1}$, and $E_3 = 25000$ cm$^{-1}$. 

based on 0-0 peaks [see arrows in Fig. 2(b)], is given in Fig. 3 (lower curve), together with theoretical results from a simple literature model [12,13], based on linear clusters. We note that such a redshift with size is common to conjugated organic molecules, e.g., the series of benzene, naphthalene, anthracene, tetracene, or that of conjugated polymers [10,11].

The most significant result, Fig. 2(a) and Fig. 3 (upper curve), is thus the energetic coincidence of all the excitations of the compact dendrimers [from D4 to D94; see Fig. 1(a)]. The simplest interpretation is that even in the larger dendrimers (D10 to D94) the excitation is localized at the nodes of the Cayley tree, where the local electronic structure is essentially the same as that of the smallest dendrimer of the family (D4) (and actually of the even smaller D2 unit) [4]. The majority of D4 groups are at the periphery and therefore their excitations are expected to behave in analogy with surface states of finite crystals, which we know to be localized [7]. In addition, because of the above mentioned decoupling of the resonant conjugation due to meta positions, the bulk D4 excitations are also localized.

It is well known that any delocalization of the electronic excitation over a larger molecular domain should reduce its energy [10,11]. The nonreduction in energy can mean only the absence of delocalization, i.e., the presence of localization. Furthermore, based on our localized picture, it is obvious that such localized excitations should be created independently via photon absorption, resulting in a molar absorbance that increases monotonically with size, as is indeed observed [Fig. 2(a)].

The extended dendrimers [Fig 1(b)] show a reduction of excitation energy with size, the expected textbook behavior [11], in contrast to the energetically pinned spectra of the compact ones. However, this does not prove the nonexistence of localized excitations. We rather believe that localized excitations of approximately D4 size (or smaller) are found on the dendrimer’s periphery (“rim” states), the same as for the compact dendrimers. This periphery excitation energy pinning is indicated by the vertical line in Fig. 2(b) (see below). However, in contrast to the compact dendrimers, there should exist different, less localized excitations, closer to the center (linear D3 to D5 “spokes” states). These more delocalized excitations can indeed be associated with the observed lower energies [see arrows in Fig. 2(b)]. This more complex behavior is obviously associated with the linear lengthening of the branches with decrease in generation number (see below). The absorption spectra and corresponding band edge energies of the extended dendrimers are therefore a manifestation of the energetic funnel nature of these structures. The lower curve in Fig. 3 can symbolize the descending steps in the energy ladder of excitations in D127. This descending energy ladder or funnel turns these extended dendrimers into potentially efficient photonic antenna systems [14].

On the quantitative side we note the following: (1) The lowest observed excitation is about 3.75 eV, based on the 320 nm purely electronic (0-0) transition. (2) The upper limit for the delocalization matrix element (“stabilization energy”), for the compact dendrimers, can be derived in two ways: (a) It is given by the linewidth of the 0-0 transition which is about 200 cm\(^{-1}\), i.e., 0.02 eV, or (b) it is given by the 0-0 energy shift from D4 to D94, which is also at most 0.02 eV (2 nm). (3) In contrast, the stabilization energy for the extended dendrimers is about 0.75 eV (based on the roughly 6000 cm\(^{-1}\) shift from D4 to D127). Thus, the extended dendrimers show a delocalization caused reduction of energy about 40 times larger than that of the compact ones.

As mentioned, these dendrimers and Cayley trees have no delocalized energy band states, in contrast to crystals or molecular chains with translational symmetry [6,7]. However, a quasiband approach has been used before [6], in analogy with atomic or molecular cluster quasibands. Assuming nearest neighbor only interactions, the matrix element (\(M\)) that is responsible for the formation of the excitation quasiband must be of the order (but smaller) of the above discussed energy shift, giving \(\sim z M\) where \(z\) is the coordination number. Based on the discussion above, with \(z = 3\) for the compact dendrimer, we thus find \(M \approx 0.02\) eV. However, for the extended dendrimers or their internal spokes, apparently, \(M \approx 0.75\) eV (but see discussion below). We believe that these much larger matrix elements originate from the “hub” portion of the dendrimer, which is rich in linear chains (spokes). We note that the strongest absorption features of the extended dendrimers [Fig. 2(b), vertical line] show the same energies as those of the compact dendrimers, as well as the same linewidths and negligible energy shifts (\(\leq 0.02\) eV). We attribute these spectral features to the periphery portion of these dendrimers. Here we note that the peripheries have a much larger number of rings (phenylacetylene groups) than the hub portions and, assuming that each of these groups is an independent photon absorber, these periphery groups are expected to give the major contribution to the optical absorbance. Returning to the spokes and hubs of the extended dendrimers, they exhibit longer and longer linear chains with increasing dendrimer size. However, the larger dendrimers (D25 to D127) also include all chain lengths of the smaller ones. We can therefore correlate the increasing energy shifts with the longer and longer conjugated chains, thus giving a hierarchy of longer and longer excitation localization lengths. To the experimental data in Fig. 3, we have added the results of model estimates [12,13], essentially equivalent to matrix diagonalization, based on the presence of one, two, or three rings in the linear chain portions of the extended dendrimer family. We see that the agreement between the experimental results and the simplified models is satisfactory.

In summary, in the large compact fractal supermolecules, the lowest energy band excitations have
exactly the same energy as that of a small fragment thereof (which is nearly 25 times smaller). This pinning of the energy with size argues strongly for localized excitons. The monotonically increasing absorbances are also consistent with this model. On the other hand, for the extended dendrimers, the situation is found to be more complex, with an apparent hierarchy of localization lengths and descending steps of an energy ladder or funnel. This funnel nature makes these extended dendrimers into candidates for potentially efficient photonic antenna.

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