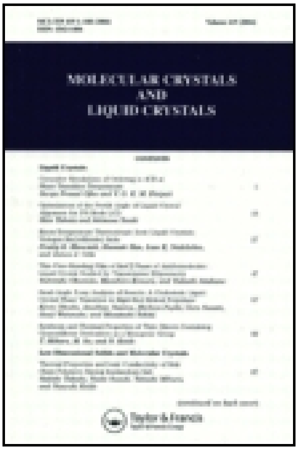

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Molecular Nano-Lenses: Directed Energy Migration and Back-Transfer in Dendrimeric Antenna Supermolecules

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ABSTRACT

Experimental and theoretical evidence is presented for the process of directed, multistep energy transport in a unique class of fractal-like dendrimeric supermolecules. Due to the meta-position branching arrangement of these Cayley trees, tight excitation localization is observed at the branching nodes. Particular forms of these dendrimers have been synthesized with localized states of decreasing energy toward the molecular locus, creating a rapid and efficient exciton funnel. Spectroscopic data is presented illustrating nearly unit transfer efficiency from the dendrimer periphery to a specialized trap at the molecular center. In addition, the energetics and spatial arrangement of these molecules allow for the destruction of multiphoton excitations at the trap, providing protection from permanent photochemical bleaching.

Keywords dendrimer; phenylacetylene; energy transfer; perylene; Cayley tree

INTRODUCTION

A unique class of dendrimer supermolecules have been developed(1, 2) and studied(3, 4, 5, 6), exhibiting novel characteristics which may allow future development of chemical and material devices. Akin to other dendrimer systems, these self-similar molecules are composed of repeating units, with successive generations expanding out from a central core. Due to this well defined molecular design and repetitive synthetic procedure, these supermolecules are the largest structurally controlled molecules thus far synthesized. In fact, the total number of basic elements increases exponentially with generation number, and the absolute sizes of the molecules are typically limited by steric hindrance from neighboring dendrimer branches. The tree-like structure of these species lead to many interesting chemical and physical properties.

Of primary influence in determining the chemical characteristics of a specific dendrimer are the identity of the fundamental chemical elements, the branching (coordination) number at each node, and the number of generations. Particular dendrimers which have a coordination number (Z) of three are a chemical realization of Cayley trees, or finite Bethe lattices. Current research is especially focused on the potential of developing chemical systems which exhibit efficient mechanisms of intramolecular energy transport. Due to the vital nature of photoinduced energy transfer in many large biological systems, such as in the reaction steps of photosynthesis(7, 8, 9), the control of a multi-step energy flow from a highly absorbing chromaphore to a reaction center is highly desirable. In general, these processes are energetically disordered, with energy transfer being dependent upon mechanisms such as thermal activation, exciton percolation, random walk, or a combination of these effects(10, 11, 12). In contrast, a large, well ordered molecule with organized local electronic excitation states, such as is observed with certain types of dendrimers, may provide a means of rapidly and efficiently directing this energy flow. We have developed and examined two classes of dendrimers which exhibit these properties, and present results which help to illustrate the conditions necessary for further improvements in the collection and trapping of photonic energy.

EXPERIMENTAL RESULTS AND DISCUSSION

Two series of these dendrimer molecules have been synthesized, both composed of linear phenylacetylene (PA) chains and designed with three-fold symmetry (see Figure 1). One form, referred to as "compact", have all branches of identical length and composition. This results in a perfectly self-similar structure, and thus creates an ideal molecular representation of Cayley trees(13). The second series, dubbed "extended", are also composed purely of PA subunits, but have branches or chains of varying lengths. This structure is only approximately self-similar, and gives rise to additional physical attributes. Due to the electronic structure of both series of dendrimers, these molecules provide an ideal means of photonic energy collection, and exhibit unique electronic characteristics. Photoinduced π-electron excitations are observed to be tightly localized on individual branches, rather than becoming delocalized over the large molecular backbone. The three-fold branching pattern at each node, arranged at the meta-positions, acts to electronically isolate each phenylacetylene chain from adjoining ring systems. This resonative decoupling of π-electronic excitations allows each chain to act as an individual photoabsorbing unit, which can then transfer this energy to nearby PA chains via rapid and discrete exciton hopping events. It has previously been observed(5) that this molecular structure does in fact give each phenylacetylene chain a well defined vibrationless electronic transition energy which is independent of the overall size of the molecule.

The subtle structural differences between the compact and extended series of dendrimers, however, lead to useful photophysical attributes. The

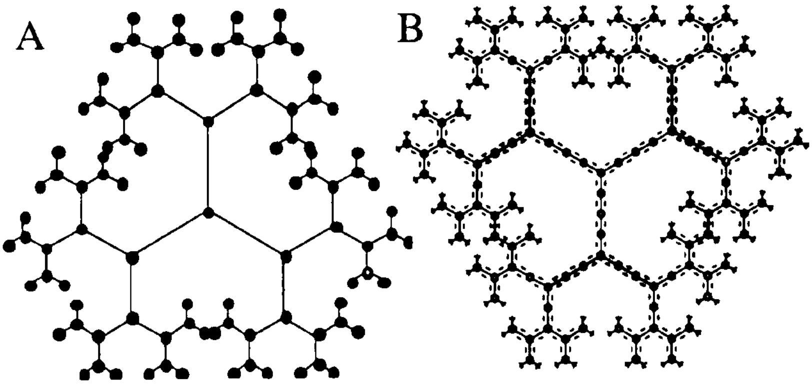

Figure 1. The largest members of the compact and extended series of phenylacetylene dendrimers, each composed of 5 generations, and terminated at the periphery by t-butyl groups. (A) is the perfectly self-similar compact form, with 94 phenyl groups (represented by filled circles), and termed D94. The connecting lines represent acetylene groups. (B) is the extended form, termed D127.

compacts, with all branches composed of a single diphenylacetylene unit, show very rigorous electronic absorption energy pinning: as the molecular size increases, the absorption coefficient also becomes larger (due to more absorbing units), but remains energetically fixed(5). This uniform nature allows energy transfer between localized excited states that is expected to occur via purely random hopping events. Due to the geometric bias of the molecular structure, it would thus be expected that the probability of motion would weight the hopping events toward the molecular periphery(6). In contrast, the extended forms have phenylacetylene chains of increasing length toward the center of the molecule. While these units still exhibit tight exciton localization, the electronic absorption energy decreases significantly as the chains become longer(5). Thus, an energy bias has been imposed, counteracting the inherent geometric bias. In this manner, it is possible to efficiently funnel the exciton toward the center of the molecule, where it can be trapped or used for further photochemical processes (vide infra).

Recent theoretical work(6) has examined the statistical probabilities of these exciton hopping events for dendrimer molecules of varying structure. With a given geometric bias (which depends on the branching pattern) and a competing energetic bias (dependent upon the ground state absorption energy of each dendrimer generation), it is possible to calculate the mean first passage time (MFPT): the average time which an exciton initially localized on the periphery takes to pass through a trap at the molecular center. For the standard case of a dendrimer with no energetic bias (such as the compact dendrimers), the results indicate that the MFPT increases exponentially with the generation number (g). Conversely, when an energetic bias is present that is large enough to override the geometric advantage, the MFPT is observed to increase only linearly. The intermediate case, in which the two effects are of exactly equal and opposite magnitude, results in a MFPT which increases proportional to g^2. The analysis assumes that each hopping step is a purely random event, with each probability weighted by the given biases. This allows a good qualitative understanding of the exciton transfer dynamics in these unique energy funneling supermolecules. Using a similar analysis, it is possible to study these photophysical dynamics using Monte Carlo simulation techniques, which can provide more quantitative results and allow for the inclusion of realistic complications such as fluorescence. In particular, this allows the calculation of excited state survival probabilities for each localized dendrimer state, which correspond to the time dependent fluorescence physical observables. These calculations are currently underway and will soon be presented with fits to experimental data. The results illustrate that, with proper molecular design, it is possible to direct molecular excitations along the molecular backbone of the dendrimer toward the center, with a rapid and efficient funneling process.

In fact, a set of molecular derivatives of the compact and extended dendrimer series have been developed to examine this photophysical reaction. To create useful derivatives of both the compact and extended species, one of the three main branches of each molecule has been replaced by 1-ethynylperylene (see Figure 2). Perylene was chosen because it has a strong absorption at somewhat lower energy than the dendrimer states, has a unit quantum yield of fluorescence, and exhibits a well localized electronic excitation when attached to the locus of these supermolecules: the absorption and fluorescence spectra consist of well defined peaks which are effectively unchanged from that of free ethynylperylene(5, 14). In addition, it has been observed that the perylene-substituted dendrimers display identical absorption and fluorescence curves as the unsubstituted dendrimers, with an additional peak about 5000 cm^{-1} to the red, due to localized excitations on the perylenic trap.

For both the compact- and extended-substituted dendrimers, the perylene moiety acts as a supertrap state. As mentioned above, the self-similar compacts are expected to exhibit poor efficiency of exciton funneling from the molecular periphery to the central trap, while the extendeds should exhibit rapid and efficient funneling dynamics. The efficiency of this process can be directly observed by comparing the steady state absorption and excitation curves for each molecule. Using the vibrationless perylene electronic excitation peak at 475 nm (in dichloromethane) as a normalization value between the two curves, the intensity ratio at each wavelength gives the percentage of absorbed photons which are ultimately funneled to the molecular trap. (The perylene normalization values are valid due to the unit quantum yield of fluorescence of this moiety. If this were not true, then the value of the quantum yield would have to be included in the relative scaling factor between the two curves.) Figure 3 gives an illustration of these comparisons for the largest compact-perylene dendrimer,

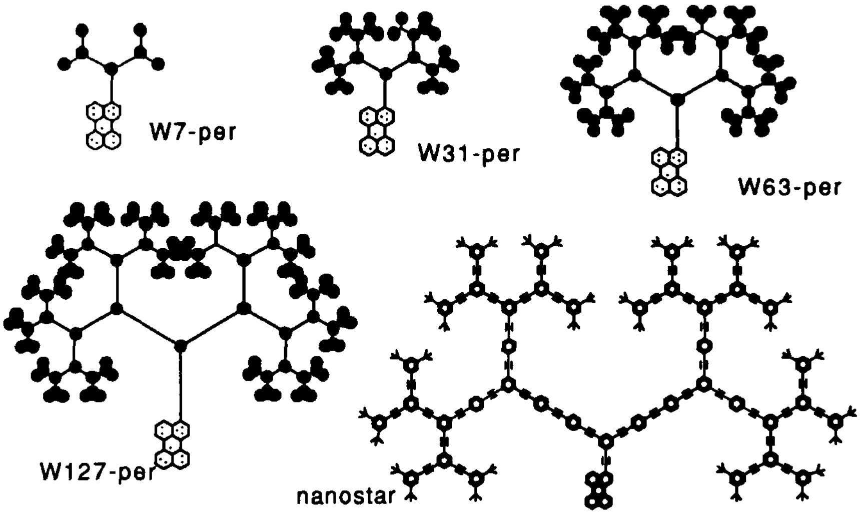

Figure 2. Perylene-substituted compact series (W7-per through W127-per) and the perylene-substituted extended molecule referred to as the nanostar.

and similarly for the largest extended-perylene, which has previously been dubbed "nanostar". Table 1 gives the calculated energy transfer efficiency results for the series of compacts, as well as for the nanostar. It is clear that the geometric bias of the compacts inhibits the funneling mechanism, particularly as the generation number increases. For the large extended nanostar, however, energy transfer occurs with essentially unit efficiency despite the large molecular size. The built-in energy bias acts to rapidly and effectively direct the exciton hopping toward the molecular locus.

In addition to the rapid and productive energy transferring capabilities of these perylene-substituted dendrimers, a particularly advantageous characteristic of these molecules is their excellent photostability. Long term exposure to light, including intense laser excitations, results in only a very slow decrease in the overall absorbance, presumably due to a small degree of chemical photobleaching(14). Given the extremely high extinction coefficient and rapid energy transfer funneling kinetics of these molecules, this is an issue of considerable import if these systems ultimately are to be used as molecular energy collection and funneling devices. The primary concern is the possible fusion of multiple excitons which may migrate from separate portions of the dendrimer backbone to the locus, within the fluorescence lifetime of the

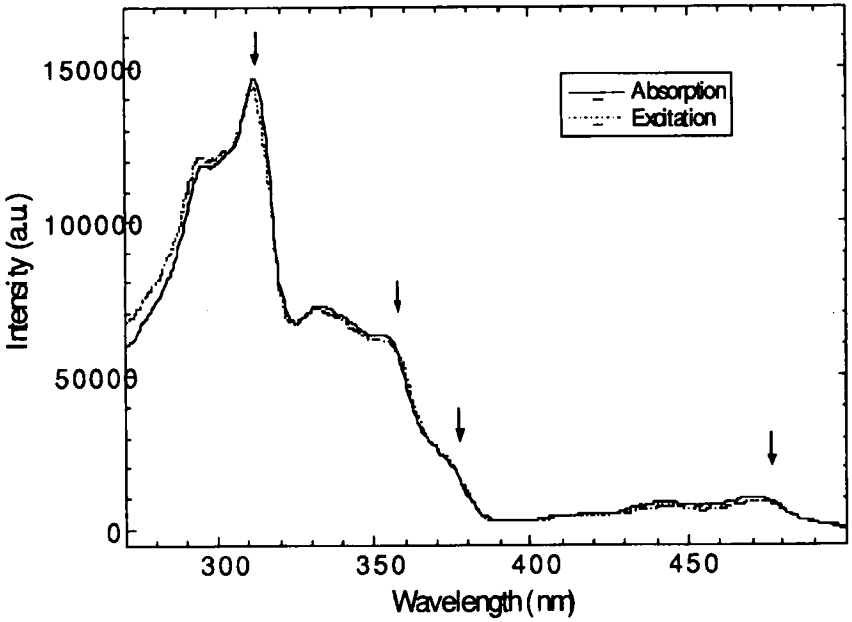

Figure 3a. Absorption and excitation spectra of the nanostar molecule in dichloromethane, with a sample concentration of 3×10^{-7}. The arrows indicate the localized vibrationless electronic absorptions of chains in the dendrimer backbone of 1, 2, and 3 phenylacetylene units, and the perylene (left to right).

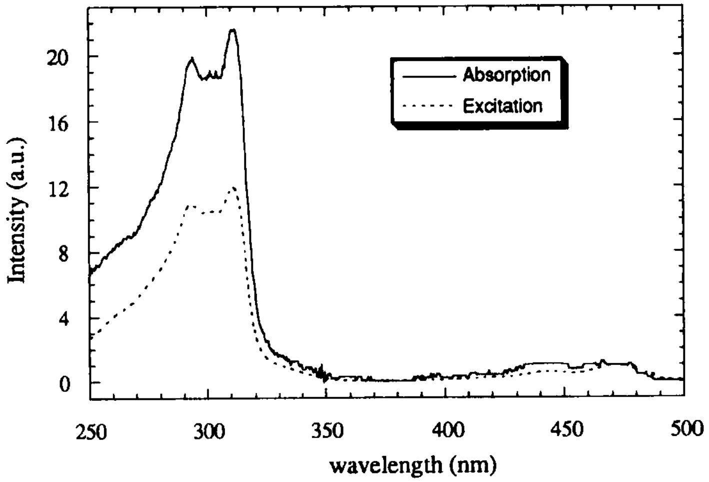

Figure 3b. Absorption and excitation spectra of W127-per in dichloromethane. All phenylacetylene chains in this dendrimer are of unit length, giving rise to the single electronic absorption peak at 312 nm (with associated higher energy vibronic peaks to the blue).

molecule	(g)	peak wavelength	transfer efficiency
W127-perylene	5	312 nm	56%
W63-perylene	4	312 nm	85%
W31-perylene	3	312 nm	90%
W7-perylene	1	312 nm	91%
nanostar	4	312 nm	98%
nanostar	4	353 nm	99%
nanostar	4	372 nm	100%

Table 1. Efficiency of energy transfer from localized dendrimer excited states to the perylenic trap for perylene-substituted dendrimers.

supertrap. Should this fusion occur, rapid photo-initiated degradation may cause photobleaching via molecular decomposition. However, the particular energetic structure of these extended dendrimers provides additional excitation relaxation pathways. As shown in Figure 4, this can significantly reduce the probability of molecular destruction. Following the trapping of an exciton at the perylenic locus, a second exciton may be funneled to this moiety within its roughly 2 ns lifetime. This would induce an excitation into a high-lying, short-lived electronic state which very rapidly relaxes nonradiatively to a lower, more stable state, S_n. If no back transfer pathways exist, then perhaps on the order of one in 10^7 molecules will suffer photobleaching during each excitation cycle. The remainder will decay back nonradiatively to the trap's first electronic excited state, S_1, followed by fluorescence relaxation (assuming unit quantum yield of fluorescence, such as is observed for perylene.) In contrast, the geometric and energy level structures of the extended dendrimer exciton funnel allow back-transfer into the two nearest-neighbor localized states of the dendrimer backbone. Based upon the rapid and efficient intramolecular energy transfer events previously observed in these molecules(5), this back-transfer is expected to be a strongly competing relaxation process out of the trap state S_n. These three-unit phenylacetylene chains, which behave effectively as individual tris-tolan moieties(15), have ground state excitations roughly 5000 cm^{-1} above the S_1 state of the perylene trap. Thus, both energetically and spatially, these dendrimer moieties are readily able to absorb the nonradiative decay out of the higher lying trap state S_n. From these localized phenylacetylene states, the single exciton can then be rapidly returned to the perylene trap, regenerating the first

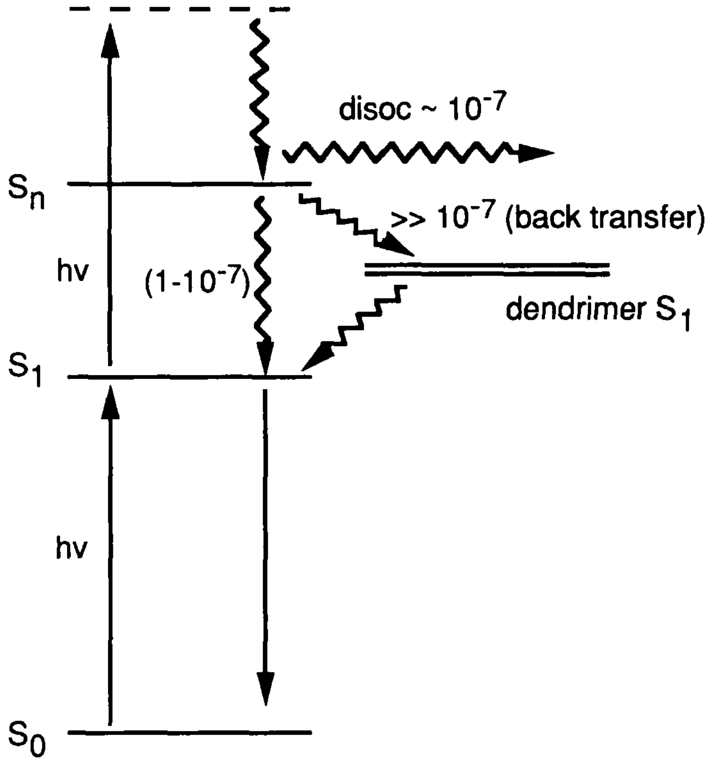

Figure 4. Energy level diagram of the perylene-substituted extended dendrimer "nanostar", illustrating the back-transfer kinetics which protect the molecule from chemical photobleaching due to multiphoton absorption. The high-lying excited state formed by the rapid absorption of two excitons in the supertrap moiety relaxes very rapidly to the more stable singlet S_n state. Back-transfer into nearby localized dendrimer excited states provides additional relaxation pathways which significantly decrease the probability of molecular dissociation.

excited electronic singlet S_1 state. This additional relaxation pathway can compete rapidly with the possible photodissociation, helping to quench this destructive process. Qualitative steady state and time dependent absorption and fluorescence experiments have suggested that a protective back transfer mechanism such as this does exist in these molecules(14). In addition, further time-correlated single photon counting fluorescence measurements are underway which can directly examine these reaction kinetics.

CONCLUSION

These unique classes of phenylacetylene dendrimers are the largest structurally controlled purely hydrocarbon molecules which have thus far been synthesized. The geometry and energy level structure of these molecules provide a means of rapidly and efficiently funneling excitons from the periphery to a supertrap state at the locus, giving a practical means of light harvesting. They combine the necessary requirements of a useful photochemical cell: very high extinction coefficient, excellent photostability, and efficient funneling and transduction of absorbed energy to a well-localized supertrap state. The data presented here illustrate the excellent funneling characteristics of the nanostar molecule. Further experiments on these and other derivatives of the extended dendrimers, including time-resolved absorption-bleaching and detailed time-dependent fluorescence lifetime studies, will permit a more accurate determination of the rates of individual hopping events. These dendrimers are ideal for the use as single molecule light and exciton sources, allowing the development of "supertips" for optical nanoprobes and nanosensors(16, 17, 18, 19), as exciton sources for near-field and scanning exciton microscopy(18, 20), and possibly as material for organic light emitting diodes(7) or sensitization of photovoltaics(21).

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