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## COMMUNICATIONS

# Exciton confinement in organic dendrimer quantum wells for opto-electronic applications

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Organic dendrimers are a fascinating new class of materials for opto-electronic applications. We present coupled electronic oscillator calculations on novel nanoscale conjugated dendrimers for use in organic light-emitting diodes. Strong confinement of excitations at the center of the dendrimers is observed, which accounts for the dependence of intermolecular interactions and charge transport on the degree of branching of the dendrimer. The calculated absorption spectra are in excellent agreement with the measured data and show that benzene rings are shared between excitations on the linear segments of the hyperbranched molecules. The coupled electronic oscillator approach is ideally suited to treat large dendritic molecules. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1431542]

Dendrimers form an exciting new group of macromolecular materials in between the monomolecular and polymeric regimes.[1–11] Rather than employing a linear geometry like in polymers, dendrimers are based on a self-similar fractal branching geometry, where the amount of branching increases with the size of the molecule. Through elegant synthetic routes it has been possible to create large, almost nanoscale molecules with a wide range of functional properties ranging from molecular recognition, such as in drug delivery systems[1] to artificial light-harvesting antennae.[3,4,9] A particularly interesting area of applications is in opto-electronic devices such as light-emitting diodes (LEDs), where dendrimers have been used both as emitting layers[6,7,10] and as charge transport layers.[11,12] The well defined chemical structure of dendrimers allows a systematic correlation to be drawn between the device properties and the dendrimer structure. Conjugated polymers and small organic molecules have attracted considerable attention from quantum chemists, who have successfully described a wide range of material properties.[13–15] Advances in the field of dendrimers make it very important to also develop a way of relating structure to properties. In particular this requires a theoretical framework capable of dealing with such complicated molecules. Here we present coupled electronic oscillator calculations on molecules with up to 600 carbon atoms and show how they account for the optoelectronic properties of a family of conjugated dendrimers.

In a recent study we demonstrated that the properties of dendrimer based LEDs are controlled by the dendrimer generation, which describes the degree of branching of the outer moieties, the dendrons.[10,11] We found that the level of interaction between core chromophores in the solid state is reduced with increasing generation, resulting in a narrowing of the emission spectrum. At high generations the film and solution luminescence spectra become similar. In addition, we found that the dendrimer generation allows a control of the charge carrier mobility, which is reduced by two orders of magnitude as the dendrimer generation ($G$) increases from $G=0$ to $G=3$.[11]

In order to understand the physical origin of the microscopic effect of dendrimer generation on the macroscopic observable device properties and spectra, we performed coupled electronic oscillator (CEO) calculations on the dendrimer structures. This provides a real space picture of the electronic transitions present in the dendrimers and also allows a calculation of the core and dendron absorption bands. CEO calculations have previously been carried out on organic molecules and oligomers.[13,16,17] It was recently shown that the calculation of the electronic properties of dendrimers can be simplified by constructing a Frenkel exciton Hamiltonian from the monomer, dimer, and trimer units constituting the dendrimer.[16,18] In this paper we present for the first time calculations on entire dendrimer structures, which allow a real space visualisation of the distribution of excitations in

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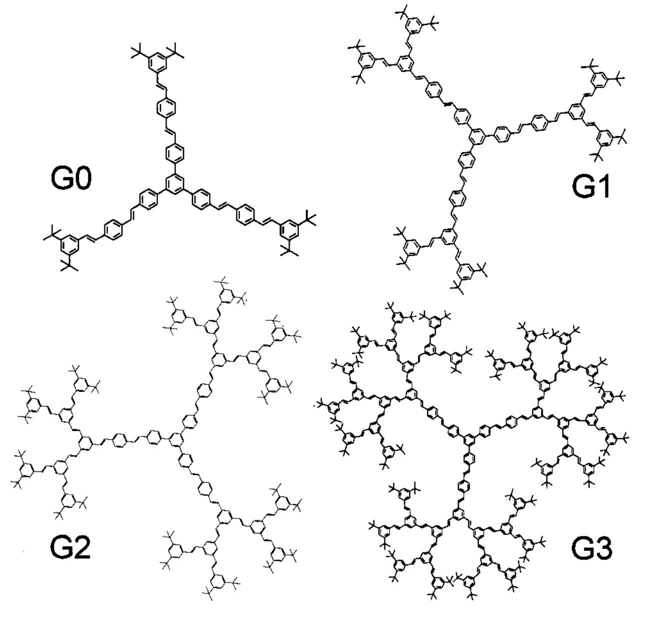

FIG. 1. Distyrylbenzene based dendrimers with stilbene dendrons. Three distyrylbenzene units are grouped around a central core unit, in this case a benzene ring. Stilbene units branch off in the *meta*-position, forming the dendrons. The dendrimer generation is defined by the number of successive branching points and described as $G0$ to $G3$. An analogous structure previously studied in LEDs has a central nitrogen atom rather than a benzene ring (Ref. 10).

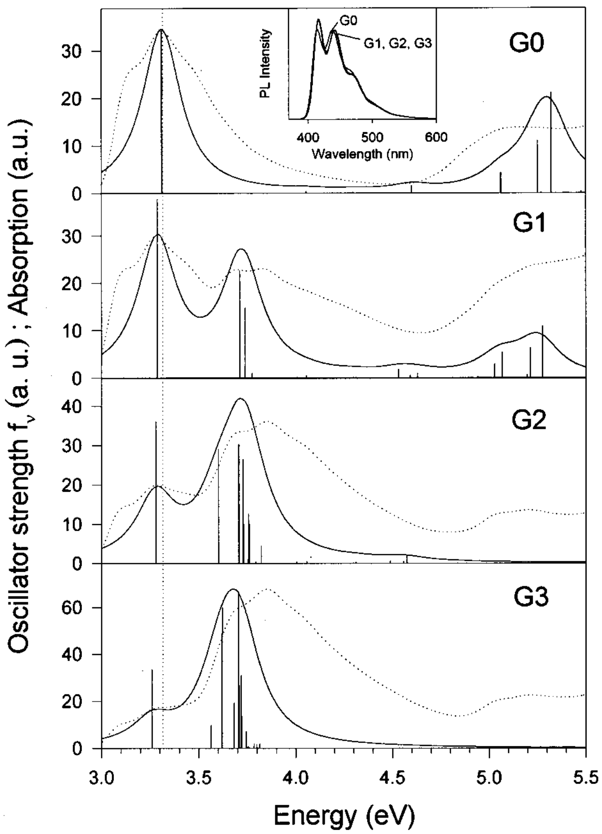

FIG. 2. Calculated (solid line) and measured (dashed line) absorption spectra of the benzene core dendrimers generation 0 to 3. The solid lines indicate the energies of the eigenmodes and the relative oscillator strengths. Inset is the solution PL for the four dendrimer generations, excited at 370 nm.

these large and complicated molecules as well as a quantitative investigation of the relative absorption strengths of dendrimer core and dendrons.

The dendrimers studied are shown in Fig. 1. Three distyrylbenzene units are linked around a central benzene ring. Stilbene units form the dendrons, which are *meta*-linked to the distyrylbenzene units. An analogous structure, having the central benzene ring exchanged for a nitrogen atom, has previously been used for LEDs and exhibits very similar properties to the dendrimers discussed in the following. The solution absorption spectra of the benzene core dendrimers in tetrahydrofuran are shown in Fig. 2. For $G1$ to $G3$, two main features are observed, centered at 3.3 eV and 3.7 eV. These correspond to the absorption of the distyrylbenzene core chromophore and the stilbene dendrons, respectively,[5] and agree with previously reported absorption wavelengths of distyrylbenzene and stilbene. For $G0$, only the distyrylbenzene peak is observed and not the stilbene absorption. Remarkably, the position of the peaks is virtually independent of molecular size, suggesting that the *meta*-linkages between generations result in strong confinement of excitations on the distyrylbenzene core chromophore and the stilbene dendrons, respectively, in agreement with observations on phenylacetylene dendrimers.[19] The experimental data show a small red shift of the lower lying band with increasing generation, which we attribute to a result of excitonic coupling between the core and the dendron chromophore units. Inset in the figure is the solution photoluminescence (PL) of the dendrimers, excited at 370 nm, which is found to be independent of generation, demonstrating a common emissive species for all four dendrimer generations.

The increase of the dendron absorption feature at 3.7 eV with generation is associated with the increasing size of the dendrons. The number of stilbene units in the dendrons scales as 1:3:7 for $G1$, $G2$, and $G3$. However, the phenylene units in the dendrons are shared between up to 3 stilbene units, so the 1:3:7 ratio includes multiple counting of some phenylene units. Assuming phenylene rings are not shared between simultaneous stilbene excitations, the dendron absorption would be expected to scale with generation as 1:2:5. By normalizing the absorption spectra to the core absorption at 3.3 eV and correcting for the residual core absorption of $G0$ at 3.7 eV, the ratios of dendron absorption may be calculated. Experimentally, a scaling of 1:3:7 is observed accurately both for the dendrimers shown in Fig. 1 and their nitrogen cored analogues[10] (data not shown), which have an even larger separation between dendron and core bands of 0.7 eV. It will be seen below that the excitonic map of the molecule provided by the CEO calculations accounts for this and other observations.

In order to investigate the electronic properties of the dendrimers we performed CEO calculations on the lowest (three fold) symmetry elements of the dendrimers shown in Fig. 1, i.e. on one third of the entire dendrimer structure consisting of one DSB unit and associated stilbene dendrons. The structures were geometry optimized at the Austin Model 1 level employing the Spartan package. The DSB units were found to be planar for all generations, with a small twist being introduced in the benzene ring closest to the dendrons in $G3$. Using the numerical CEO-intermediate neglect of differential overlap/spectroscopy (INDO/S) procedure described in detail elsewhere[13,20] the Hartree–Fock ground-state density matrices were then calculated, from which the linear absorption spectra and the transition density matrices forming the electronic normal modes $\xi_\nu$ were computed. The calculated mode corresponds to the transition matrix between the ground state, $|g\rangle$, and an excited state, $|\nu\rangle$, with the elements $(\xi_\nu)_{mn} = \langle \nu | c_m^+ c_n | g \rangle$, where $c_m^+$ and $c_m$ are the creation and annihilation operators of an electron on the outer orbital of the $m$th carbon atom. An eigenenergy $\Omega_\nu$ corresponds to the eigenmode $\xi_\nu$ of the system, which allows the calculation of the linear polarizability following $\alpha(\omega) = \Sigma_\nu (f_\nu / \Omega_\nu^2 - (\omega + i\Gamma)^2)$, where $f_\nu$ is the oscillator strength and $\Gamma$ is the dephasing. The measured linear absorption intensity is then in turn proportional to $\omega \, \mathrm{Im}\, \alpha(\omega)$, where Im denotes the imaginary part of the complex linear polarizability. A value of 0.12 eV for $\Gamma$ was found to provide the best fit to the measured data.

We first consider the mode structure and subsequently the nature of electronic modes on the molecules. The calculated absorption spectra of the dendrimers are compared to the measured data in Fig. 2. Good agreement is observed between experiment and calculation both in terms of the peak positions of the central absorption feature and the relative strengths of the absorption bands. Note that the spectra were not shifted in energy, and that the good fit is a direct consequence of the oscillator model. The central benzene core of the dendrimer inhibits any delocalization between the three distyrylbenzene units, as was also confirmed by calculations on the entire $G0$ structure, which yielded a symmetric structure upon geometry optimization. The calculation on the threefold symmetry element of the dendrimer hence yields an accurate description of the entire system. The small shift to the red with increasing generation, which we attribute to excitonic coupling, is also observed in the calculations. The vibronic structure present in the experimental absorption data is not reproduced in the calculation. Also, the increase in absorption beyond 4.8 eV is only observed for the calculation of the $G0$ dendrimer. This is a consequence of computational constraints, which limit the number of calculated modes to the first 20, located at decreasing energies for increasing generations. Finally, it should be noted that the calculations were performed *in vacuo* due to the setup of the code, whereas the measurements were performed in tetrahydrofuran. The good agreement between experiment and theory suggests that solvatochromism has little influence on the electronic properties of these particular molecules.

We next consider the real space distribution of excited state modes on the dendrimers. This is shown schematically in Fig. 3 for modes 2 and 3 of the $G2$ dendrimer symmetry element. The carbon atoms are counted clockwise around benzene rings and around the entire structure. Due to the fractal geometry of the dendrimer there is a discontinuity in numbering of the conjugated elements. The transition matrix gives the probability of an electron or hole being located on a carbon atom. Diagonal components of the matrix relate to the distance over which an exciton can move on the molecule, corresponding to electron-hole pairs present on one carbon atom, whereas off-diagonal components describe the motion of charge carriers between carbon atoms, i.e., the coherences. The transition matrix pictured next to the molecule shows the transition probability between different carbon atoms of the dendrimer. For simplicity, these carbon atoms can be broken down into blocks labeled $A$ through $G$. A comparison of the transition matrix with the dendrimer structure shows the benzene rings involved in excitations.

For modes 2 and 3, excitations are present on the dendrons and not on the distyrylbenzene core. The two matrices are very different, showing that different modes involve different dendron units. For mode 2, two main stilbene excitations may be identified, namely $A-B$ and $E-F$. The stilbene units $A-E$ and $B-D$ are only excited very weakly. Due to the discontinuity in the carbon atom counting resulting from the fractal geometry of the dendrimer, dendron units $A-E$ and $B-D$ appear as off-diagonal elements in the transition matrix. In contrast, for mode 3 the two dendron units with the strongest transitions are $B-C$ and $E-G$. Due to the discontinuity in counting seen in the structure, $E-G$ appears as an off-diagonal transition, whereas $B-C$ is seen on the diagonal of the transition matrix. There are again weak coherences, which give rise to further transitions in the dendrons on units $B-D$ and $E-F$. It is important to note that the $E-F$ excitation for mode 3 is much weaker than for mode 2, whereas the presence of excitations on ring $G$ in mode 3 is a signature of the $E-G$ coherence. By comparing these two modes it is important to note that each mode consists of two dominant stilbene excitations, which do not share benzene rings in any given mode. However, as the total absorption is a sum of all the modes, the calculation and measurement show excitations present on all of the stilbene units.

The fact that the linear polarizability of the dendrons is larger than expected from a direct superposition of the linear segments, with all stilbene dendron units contributing to the absorption, has profound implications on the design of novel artificial light-harvesting complexes. Our results suggest that the absorbance of the dendrons increases more strongly than the absorbance of the sum of the linear constituents, due to the observed sharing of benzene rings between different stilbene units in different modes. This points to the possibility of designing highly efficient light-absorbing peripheries for artificial light-harvesting antennae.

We next compare the modes for the different generations of the dendrimers. The first mode is shown in Fig. 4. The result is remarkable: For all generations, the lowest mode involves the same number of carbon atoms, which correspond to the central distyrylbenzene unit. The lowest mode is hence confined to the core chromophore of the dendrimer. In contrast, the second mode of the system shows exactly the opposite behavior in Fig. 5, with no transitions present in the core chromophore region. All excitation energy is on the dendrons (except for $G0$, which has no dendrons). For higher energy modes this picture is maintained. The calculations hence show that the lowest energy excitations are confined to the core region of the molecule. A consequence of this is that excitations generated on the dendrons will rapidly relax to the lower energy core mode due to the built-in energy gradient.[17,18] Note that the third benzene ring of the DSB unit

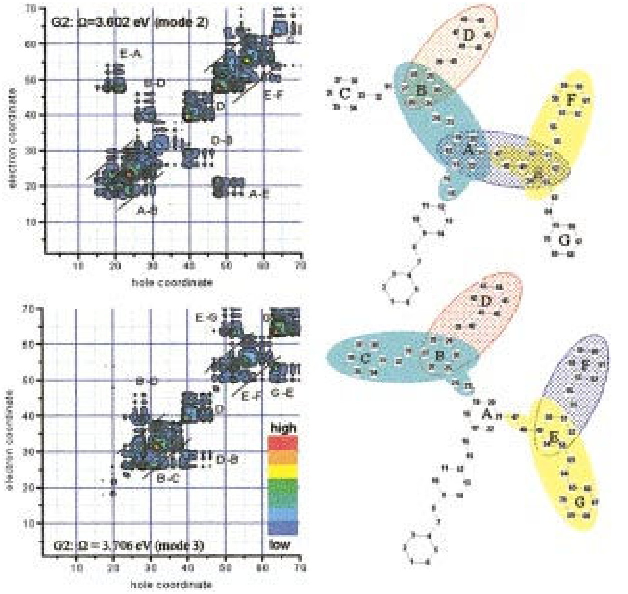

FIG. 3. (Color) Real space mapping of excitations on the chemical structure of the $G2$ dendrimer for modes 2 and 3. The inset shows the color coding.

$(C_{17}-C_{22})$ is conjugated with both the dendrons and the core so that it can contribute both to core excitations and also to dendron excitations.

These calculations demonstrate that it is possible to predict the electronic properties and obtain a microscopic picture of excitations even in very large molecules using the CEO approach. From the calculations and experiment it is seen that these dendrimers in effect act as organic quantum wells, where excitations are confined in the center of the molecule through a built-in energy gradient resulting from the dendrons. The direct observation of exciton confinement in conjugated dendrimers has important implications for the operation of LEDs based on these materials. Firstly, through the confinement the emission color of the LED may be tuned by the choice of the central chromophore.[8] As the calculation shows, an excitation on the core has lowest energy, so that excitations initially formed on the dendrons will be rapidly transferred to the core before emission occurs. Luminescence in solution is hence independent of the dendrimer generation.

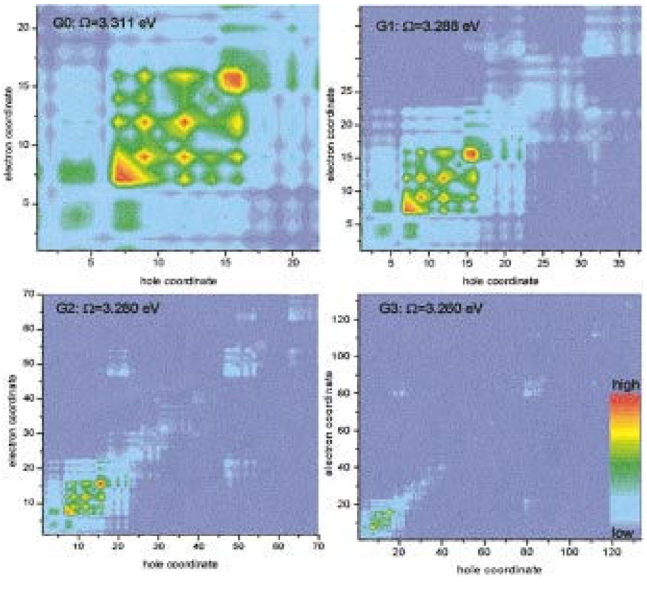

FIG. 4. (Color) Lowest energy modes of the four dendrimer generations showing the region of the dendrimer excited corresponding to the distyrylbenzene unit. The axes mark the carbon atoms of the structures as labeled in Fig. 3. The inset in $G3$ shows the color coding of transition probabilities.

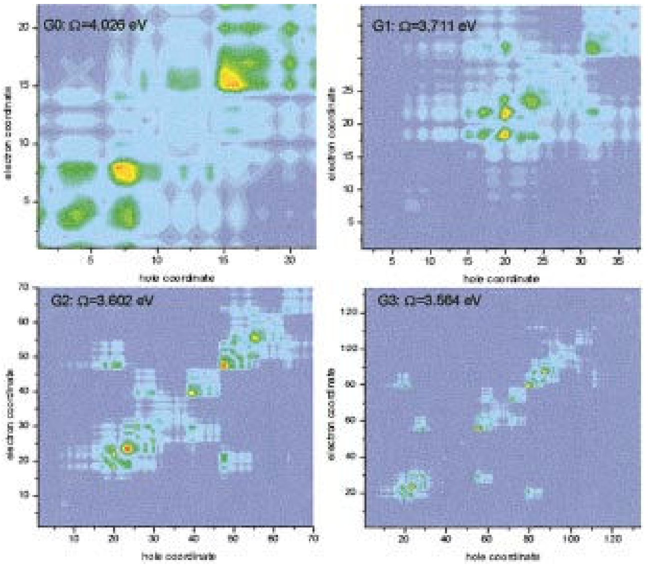

FIG. 5. (Color) Second lowest energy modes of the four dendrimer generations showing excitations located on the dendrons. The color coding is as in Fig. 4.

In dendrimer films, the spacing between core chromophores increases with increasing generation. Localisation of excitations on the core means that inter-chromophore interactions (which can lead to undesirable formation of aggregates or excimers) are reduced, explaining why higher generations have purer solid state emission closely resembling the solution luminescence spectra.[10] One further remarkable consequence of this energy gradient built into the dendrimer is that the charge transport through dendrimer films occurs through the core chromophore units rather than through the dendrons, which act as insulators in this case. Increasing generation hence results in a slowing of charge transport and the generation can be used as a microscopic control of the charge carrier mobility.[11] In contrast to conjugated polymers or small organic molecules, our dendrimer based molecular semiconductors exploit the physical process of exciton localisation on a molecular unit. The nature of excitations in organic semiconductors has recently been a topic of great debate. It appears that whereas some materials exhibit more band-like properties, other systems are better described by exciton models.[21] In our dendrimers, the case is clear-cut with the molecular design yielding molecular semiconductors with no intermolecular delocalization. The CEO calculation hence provides a highly accurate picture of the electronic properties of the material, which in turn relate directly to macroscopic device properties due to the nature of the insulating dendrons.

In summary we have for the first time presented electronic oscillator calculations on a complete set of conjugated dendrimers with up to 600 carbon atoms, which have previously been used in organic LEDs.[22] Strong exciton confinement at the core of the dendrimers is observed, which explains the dependence of macroscopic device properties, such as emission spectrum and charge transport, on generation. In these dendrimers, all dendron units are found to contribute to the dendron absorption explaining the observed scaling of the dendron absorption with generation. The excellent agreement between our calculations and the experimental results shows that the electronic properties of novel compounds for organic LEDs may be accurately predicted prior to synthesis. Quantum chemical techniques are hence powerful tools for developing novel materials for optoelectronic applications.

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