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Control of Intrachromophore Excitonic Coherence in Electroluminescent Conjugated Dendrimers

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We present coupled electronic oscillator calculations on conjugated dendrimers that can be used in organic light-emitting diodes. The results indicate that the nature of the excited state in these materials can be strongly influenced by electronic coherences. We use the collective electronic oscillator model approach to compare and contrast primary excitations of two families of dendrimers consisting of tris(distyrylbenzenyl) chromophores attached to either nitrogen or benzene in the 1, 3, and 5 positions. The choice of the central moiety of the dendrimer provides a direct control of the coherence between the conjugated segments, which form the emissive region of the hyperbranched molecular structure. For the case of the amine-centered dendrimer, we find that excitations are delocalized across the amine unit, whereas delocalization between distyrylbenzene units is effectively blocked by the use of a benzene core unit. The calculations provide an accurate description of the measured absorption data and an understanding of the fluorescence dynamics observed. In particular, they suggest a microscopic route to controlling the polarization anisotropy of dendrimers through choice of the central moiety. Additionally, we are able to develop a qualitative reasoning for the dependence of the solid-state emission on dendrimer generation using the results from the calculation. The level of intermolecular interactions is found to depend sensitively on the location of emissive dipoles in the dendrimer cores.

I. Introduction

Conjugated dendrimers have recently been used as emitting layers in organic light-emitting diodes (LEDs).[1−6] Dendrimers are macromolecules and may be synthesized to consist of a core region and successively branched outer units, which are commonly referred to as dendrons. A broad range of work has revolved around the investigation of the chemical properties of these materials and the potential use in applications ranging from drug delivery systems to synthetic light-harvesting complexes.[6−11] A particularly exciting aspect of these macromolecular compounds is the ability to control the bulk material properties directly through the synthesis of the constituent molecules, which has led to a nanoscale approach to tuning the emission and transport properties of organic LEDs.[5]

There is considerable interest in predicting the photophysical and electronic properties of organic semiconductors from first principles. This coupled with the power of synthetic organic chemistry could lead to the rapid design and preparation of optimized materials. Previous quantum chemical investigations have been concerned predominantly with isolated chains or chromophores,[12−14] but it has recently been demonstrated that conventional techniques may be extended to include the effects of intermolecular interactions in calculations.[15−16] Interactions between chromophore units are of great significance for the operation of organic LEDs. Strong interactions may be beneficial for charge transport but have the disadvantage that they can lead to the formation of intermolecular excited states such as excimers with associated broad, red-shifted emission features and reduced luminescence efficiency.[17−18] A detailed knowledge of the nature of excitations on the emissive chromophores of organic semiconductors is hence imperative for the understanding of LED device operation and for the design of novel improved materials.

We have previously shown that the emission color of a conjugated dendrimer for use in LEDs may be tuned by the choice of the emissive component at the core.[4] Our present investigation focuses on the nature of the excited state at the core of a dendrimer. Using coupled electronic oscillator (CEO) calculations,[12] we are able to predict accurately the electron−hole oscillator energy and obtain insight into the coherences within the core chromophore of the dendrimer, which control the emission properties of these materials. In particular, this investigation has an important application in that the calculations provide a theoretical grounding of the electronic properties of dendrimers and hence allow an estimate of the emission wavelength, which is of importance when designing dendrimer core chromophores for a desired emission color.[4,6] Furthermore, we are able to suggest an explanation of the intriguing control of interchromophore interactions in the solid state provided by dendrimer generation.[5]

In this paper, we aim to study the nature of the excited state in our conjugated electroluminescent dendrimers by investigating the correlation between subtle changes in the chemical structure and the bulk material properties. The dendrimer systems studied are shown in Figure 1a in a reduced representation. For both

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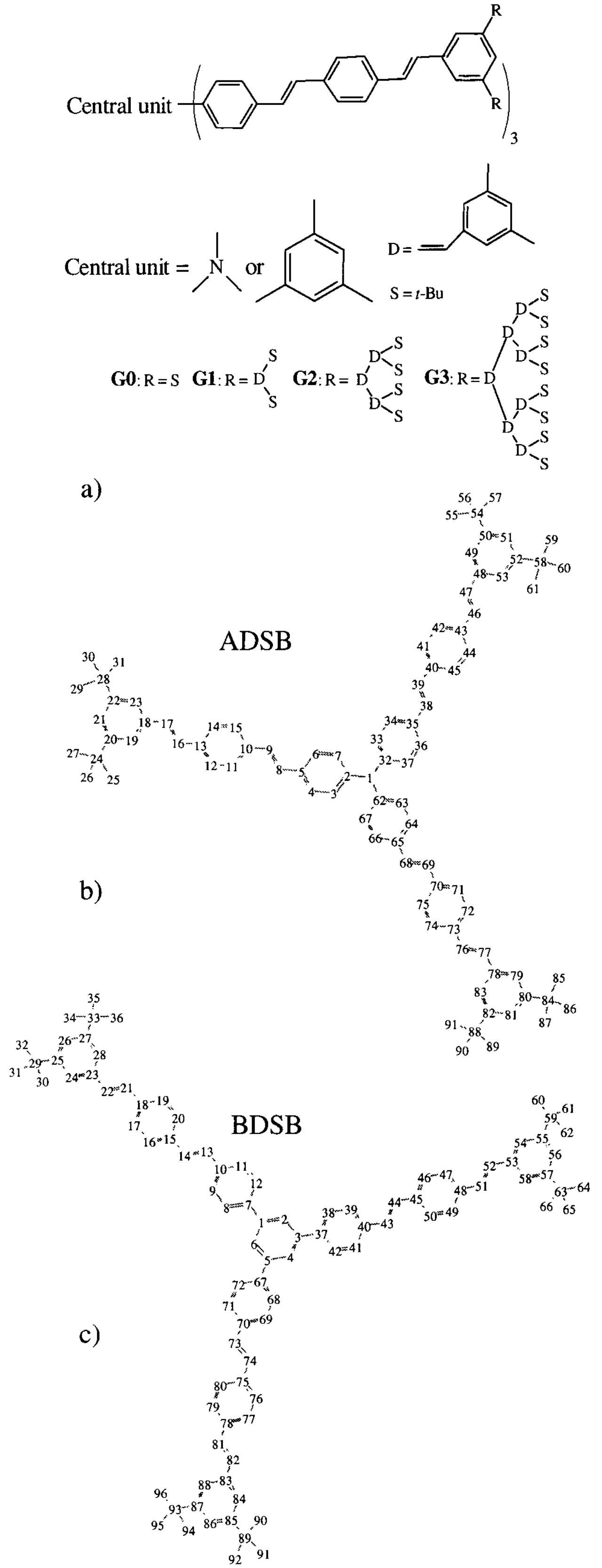

Figure 1. Distyrylbenzene (DSB)-based dendrimers (a) with stilbene dendrons in reduced representation. Three DSB units are grouped around a central unit, a nitrogen atom (ADSB) or a benzene ring (BDSB). Stilbene units branch from the distal end of the DSB units in a meta arrangement at branching points, forming the dendrons. The degree of dendron branching is described by the dendrimer generation (G). The structures of the dendrimer core chromophores (G0) are shown in panels b and c. The numbers indicate the atom labeling used in the CEO calculation.

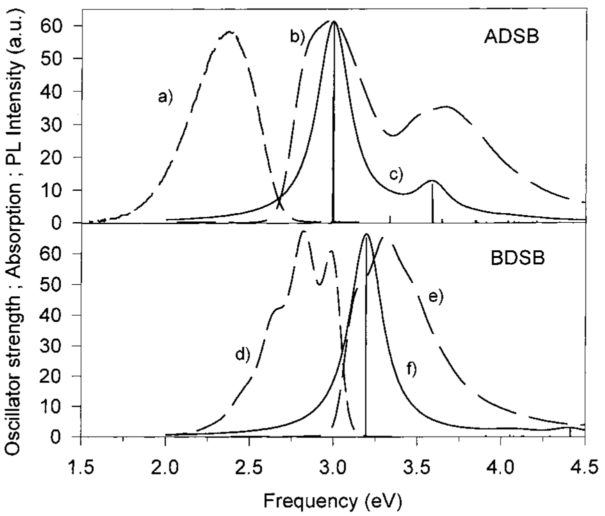

Figure 2. Measured absorption (b, e) and photoluminescence (a, d) spectra of zeroeth generation ADSB and BDSB dendrimers. Curves c and f show the calculated absorption spectrum. The vertical lines indicate the mode frequencies and the relative oscillator strengths.

dendrimer families, three distyrylbenzene (DSB) units are arranged around a central unit, either a nitrogen atom or a benzene ring. In each case, the central unit and the three DSB units make up the core of the dendrimers. The dendrons are marked **R** and consist of stilbene units, **D**, and *tert*-butyl surface groups, **S**. The number of different types of branch points defines the dendrimer generation. The nitrogen- and benzene-centered dendrimers are labeled ADSB and BDSB, respectively. In the following, we refer to the benzene ring or nitrogen atom at the center of the molecule as the "central unit" of the dendrimer, and the core is defined as the emissive chromophore. Calculations were performed on the core structures of the dendrimers. The counting of atoms used for the dendrimers is shown in Figure 1b,c. Carbon atoms were counted clockwise around the benzene rings and clockwise around the entire structure.

II. Experimental Results

For the present investigation, we focus on the nature of excitations in the emissive chromophore of the dendrimers, which is illustrated by the zeroeth generation. Absorption and emission measurements were performed on dilute solutions (5 mg/L) of the dendrimer in tetrahydrofuran, as well as on films spin-coated from tetrahydrofuran solutions at a concentration of 10 mg/mL. Luminescence measurements were performed under excitation with the argon ion laser doublet at 351.1 and 363.8 nm detecting with a fiber-coupled CCD spectrometer. The solution photoluminescence (PL) and absorption spectra of the two dendrimers are shown in Figure 2 together with the calculated absorption spectra (solid lines) and the main transition energies and oscillator strengths (vertical lines). The measured ADSB absorption spectrum of the zeroeth generation shows peaks at 2.98 and 3.66 eV. These match well with the calculated spectra, although the calculation underestimates the strength of the higher energy feature. It should be noted that this feature coincides with the absorption of the stilbene dendrons at higher generations.[2] However, for the zeroeth generation dendrimer studied here, no dendrons are present. The solution luminescence spectrum of ADSB is featureless with the peak significantly shifted to the red by 0.6 eV with respect to the absorption spectrum.

The measured absorption spectrum of the zeroeth generation BDSB peaks at 3.30 eV and, in contrast to ADSB, consists of

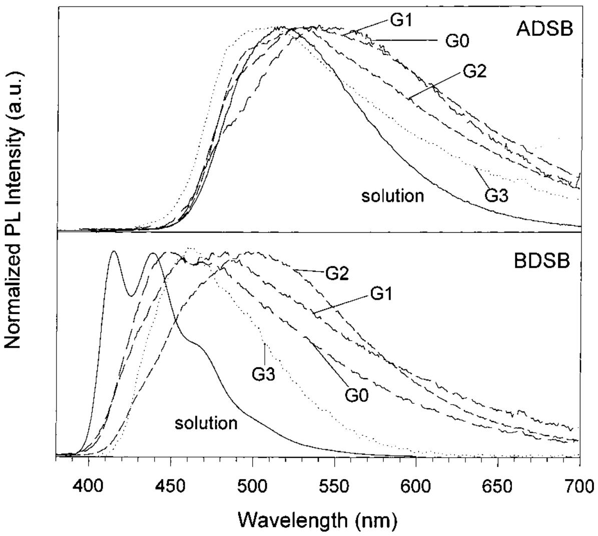

Figure 3. Film and solution (solid lines) photoluminescence spectra of the two dendrimer families showing the dependence of the solid-state emission on generation. The solution emission is identical for all generations.

a single absorption band. The emission spectrum of the BDSB dendrimer exhibits vibronic structure and a significantly greater overlap with the absorption spectrum than was observed for ADSB. The emission of ADSB is in the green, whereas BDSB emits in the blue.

The chemical structures of the two families of dendrimers are very similar, differing only in the choice of the central unit of the core. However, even this small difference has a strong effect on both emission and absorption. The most remarkable difference between these two systems is seen in the film PL spectra for the different dendrimer generations. We have previously reported that the dendrimer generation in ADSB allows a control of the level of interaction between the core chromophores in films.[5] This is seen in the upper panel of Figure 3. As the dendrimer generation increases, the spectra narrow and become more like the solution emission spectra, which are the same for all generations. This is due to a reduction in intermolecular interaction and excimer formation at high generations, because the dendrons act sterically to increase the distance between the chromophores.[5] Note that the PL was measured from the front face of the film to reduce self-absorption effects. A more detailed comparison of luminescence and absorption spectra is given in ref 5. Fluorescence measurements have clearly identified a long-lived low-energy emissive species present at low generations, which has been assigned to an excimer.[5]

A very different pattern is observed for the BDSB-based dendrimers. All film emission spectra are significantly broader than the solution PL. As the dendrimer generation increases from G0 to G2, the emission broadens substantially and shifts to the red. The trend is suddenly reversed for the G3 emission, which is the narrowest of the four film PL spectra and is closest to the solution PL in terms of line width.

III. Calculations

To understand the origin of the differences in absorption and emission spectra of these two families of materials, we performed quantum chemical calculations on the emissive core chromophore units of the dendrimers corresponding to the zeroeth generation dendrimer. It should be noted that previous experimental and theoretical work[5] has established that the electronic properties of the higher generation dendrimers, such as the color of emission, are defined by the core chromophore, which is essentially the zeroeth generation dendrimer. The CEO approach has previously been used to investigate a number of molecules including phenylene−vinylene oligomers[12] and phenylacetylene[11] dendrimers. It provides a real space picture of the distribution of excitations present on the molecule, known as the electronic normal modes, as well as the excitation energies, which are the eigenenergies of the modes. The geometries of the dendrimer structures were calculated at the Austin Model 1 level using the Spartan package with no constraints on the molecular symmetry. By employing the numerical CEO-intermediate neglect of differential overlap/spectroscopy (INDO/S) procedure described in detail elsewhere,[12,19−20] the Hartree−Fock ground-state density matrices were calculated, from which the linear absorption spectra and the transition density matrices forming the electronic normal modes, ξ_ν, are 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, Ω_ν, corresponds to the eigenmode ξ_ν of the system, which allows the calculation of the linear absorption following $\alpha(\omega) = \sum_\nu(f_\nu/(\Omega_\nu^2 - (\omega + i\Gamma)^2)$, where f_ν is the oscillator strength and Γ is the dephasing. A value of 0.12 eV was chosen empirically for Γ to provide the best agreement with the measured spectra in terms of spectral width.

The comparison of calculated and measured spectra in Figure 2 shows good agreement. The vertical lines indicate the energetic positions and relative oscillator strengths of the normal modes. The ADSB absorption peak is calculated to be at 2.99 eV, resulting from two degenerate modes as a consequence of the molecular symmetry. The higher energy band at 3.59 eV is also reproduced in the calculation, albeit with an underestimate of the oscillator strength. The calculated absorption peak of BDSB coincides with the lowest energy shoulder of the measured absorption spectrum at 3.19 eV, again formed by two degenerate modes. For BDSB, in the energy range studied, the calculation only gives one absorption peak, in agreement with the measured spectrum.

We begin by discussing the electronic modes present on the core chromophore of the BDSB dendrimer. Figure 4 shows the four strongest electronic modes present in the molecule plotted as the transition probabilities between two carbon atoms. These transitions correspond to the creation of electrons and holes on the individual carbon atoms. Comparison with the chemical structure in Figure 1c shows that there are two main excitations present on the molecule. These are located on two of the three DSB units and are seen as on-diagonal blocks from C7 to C28 and from C37 to C58. A third much weaker feature is seen corresponding to a weak excitation on the DSB unit from C67 to C88. These on-diagonal features describe the excitonic coherences along the DSB units of the molecule. Electron−hole pairs can exist between any of the carbon atoms making up the benzene rings of a particular DSB unit, so the transitions on a DSB unit appear as three blocks on the diagonal of the matrix (marked red), corresponding to the three benzene rings comprising DSB. As the excitation is delocalized along the DSB units, the three smaller blocks corresponding to three benzene rings appear to interact, so the plot reveals two larger blocks on the diagonal of the matrix (marked purple). These two large on-diagonal blocks correspond to an excitation on a single DSB unit, of which modes $\nu = 1$ and $\nu = 2$ show two strong ones

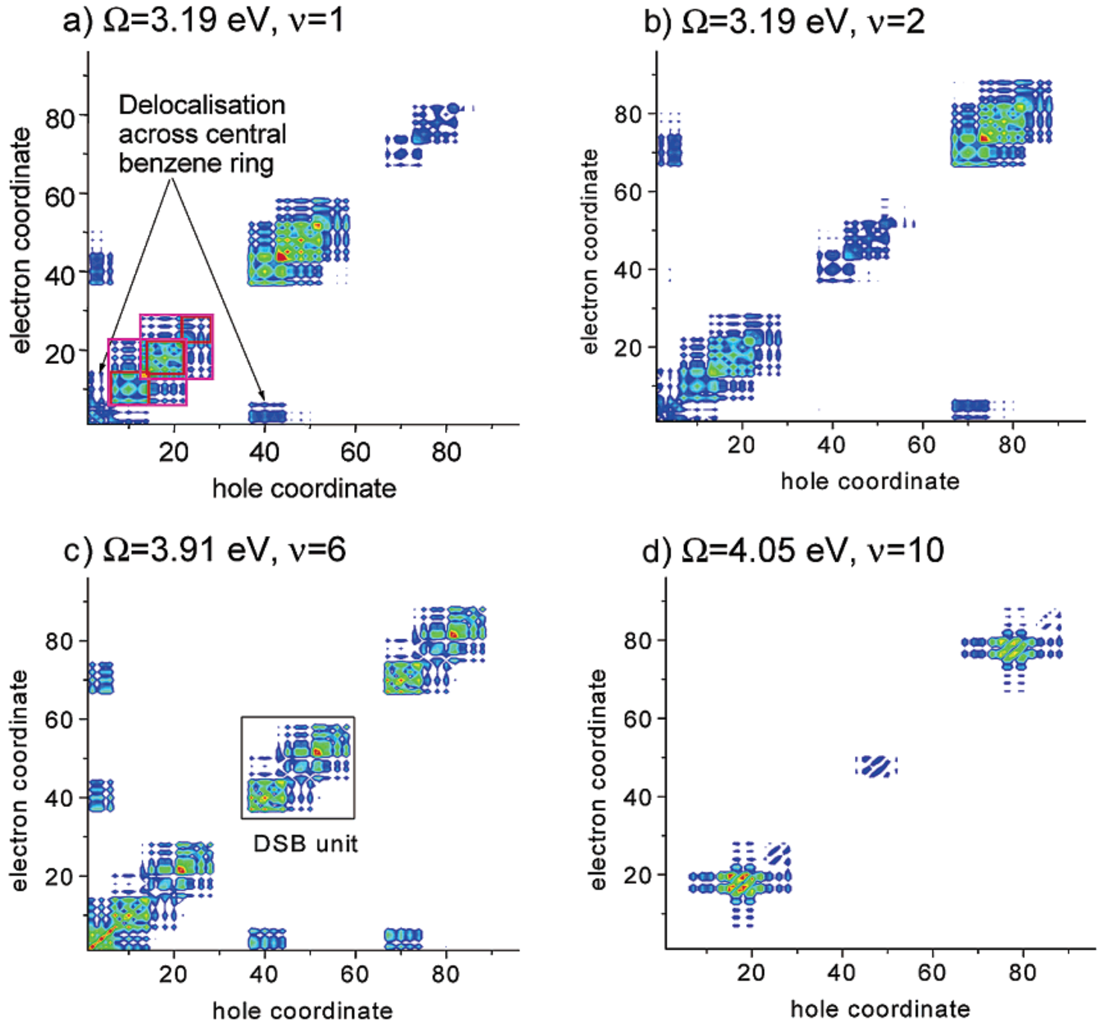

Figure 4. Transition matrices for the BDSB dendrimer modes 1, 2, 6, and 10. The transition probability is plotted as a function of the two atoms involved in the transition. The three individual benzene rings making up DSB are drawn as red squares. Two of the three squares appear larger due to the inclusion of the vinylene unit. The interaction of two adjacent phenylene rings results in a larger on-diagonal coherence, marked by a purple box. Modes not shown are similar to the modes shown because of the 3-fold molecular symmetry.

and one weaker one. Two further features are seen, which are located off the diagonal and at the origin of the matrix. These result from a slight electron delocalization from the DSB units onto the central benzene ring. However, it is important to note that there are no further off-diagonal elements. The meta arrangement of the three DSB chromophores around the central benzene ring blocks electron delocalization between the three DSB units in the core chromophore. The structure of the higher order modes is similar to the $\nu = 1$ mode. For $\nu = 10$, the excitations are strongly localized to the central benzene ring of the DSB units, so the off-diagonal transitions vanish.

The case is very different for ADSB as seen in Figure 5. In all modes, strong coherences within the DSB units are visible as diagonal blocks in the matrix. However, there is also a significant contribution to the transition matrix from off-diagonal elements, which can be assigned to electronic delocalization across the central triphenylamine unit. Modes $\nu = 1$ and $\nu = 2$ are degenerate because of the 3-fold symmetry of the molecule (i.e., they have virtually the same energy, cf. Figure 2), and it is seen that the modes consist predominantly of transitions on two of the three DSB units. Modes $\nu = 4$ and $\nu = 5$ also exhibit off-diagonal elements corresponding to coherences extending across the central triphenylamine unit; however, the excitation is now no longer delocalized across the entire length of the DSB units. Comparison of the chemical structure in Figure 1b reveals that excitations are localized on the outer two benzene rings of the DSB unit, which form a stilbene unit, rather than being spread over the entire DSB unit. The slight asymmetry between off-diagonal elements seen in all of the ADSB modes indicates a charge-transfer excitation, with electrons moving across the amine core between different DSB units.

IV. Discussion

The results show that the electronic properties of the two families of dendrimers are very different, although their chemical structures differ only by the choice of a few atoms. Whereas the calculations show only one absorption peak for the zeroeth generation benzene-cored dendrimer BDSB in the energy range under consideration, two peaks are seen for the amine-cored dendrimer ADSB. In addition, the calculations show that strong interactions are present between the DSB units in the case of ADSB but not in the case of BDSB. The CEO calculations provide an accurate prediction of the absorption spectra of the two molecules. Despite the similarity in the chemical structure of these two dendritic compounds, we have found that their emission and absorption properties are very different. Furthermore, there is also a significant difference in the way that the dendron architecture influences the emission spectra in the solid state. The CEO calculations can enable us to gain a qualitative

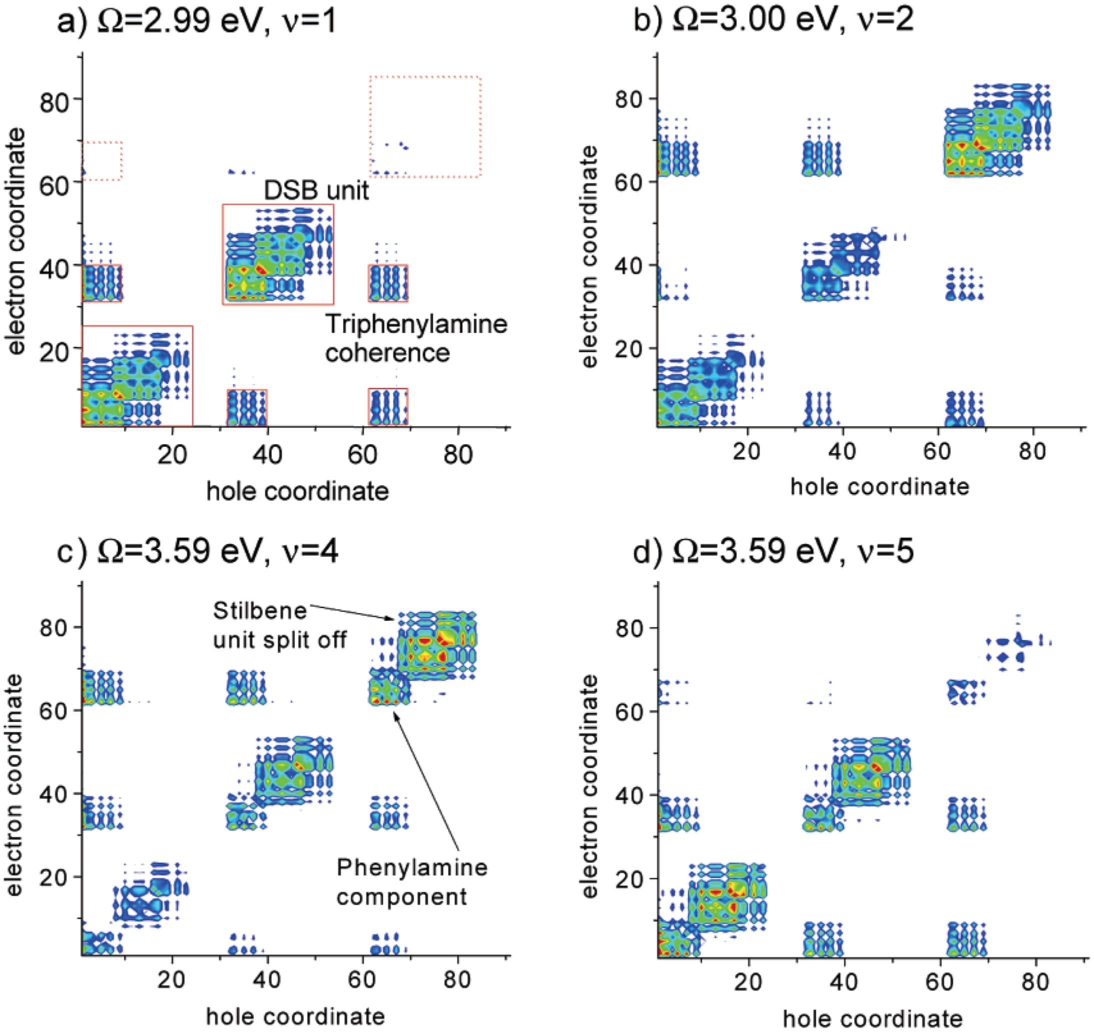

Figure 5. Transition matrices for the ADSB dendrimer modes 1, 2, 4 and 5. The transition probability is plotted as a function of the two atoms involved in the transition. The DSB units and the off-diagonal triphenylamine coherences are marked by boxes. Modes not shown are similar to the modes shown because of the 3-fold molecular symmetry.

understanding of this difference. The calculations show that the simple choice of the central unit of the dendrimer influences the degree of excitonic coherence within the dendrimer core, which has profound implications for the emission and absorption properties of the material in solution and in the solid state.

We begin by discussing the results for ADSB. The core of the ADSB dendrimers exhibits a number of remarkable features. First, there is a large shift between the absorption and luminescence, as seen in Figure 2. In contrast to DSB,[2] the solution emission of ADSB appears broad and featureless with no distinct vibronic structure. Furthermore, fluorescence up-conversion measurements on solutions of this family of dendrimers have shown a substantial rise time of over 10 ps in emission for both G0 and G2 dendrimer generations when detected at wavelengths longer than 515 nm.[21] Ultrafast polarized fluorescence measurements also revealed a rapid depolarization occurring in less than 200 fs.[21] The relatively slow rise in emission and the increase in rise time at longer wavelengths suggest that a molecular rearrangement occurs upon excitation.

To investigate the origin of the ultrafast fluorescence dynamics, we performed configuration interaction singles (CIS) calculations on the Austin Model 1 level optimized ground-state geometry using the package Gaussian 98 and a STO-3G basis set. This provides the excited-state geometry of the molecule, which in turn was used to calculate the CEO transition matrices of the molecule in the excited state. This calculation gives insight into the dependence of the normal modes and energy eigenvalues on nuclear arrangement. We found that the geometric symmetry of the dendrimer was broken in the excited state and that one of the DSB units of the dendrimer in the excited state was slightly less twisted than the segments of the ground-state structure. Whereas the three DSB units are at dihedral angles of 35° to each other in the ground state, for the excited-state geometry, one DSB unit was found to have a dihedral angle of 32° whereas the other two units are at angles of 42° to each other. We found that even such a relatively small change in molecular geometry has profound effects on the calculation of the oscillator energies. The two lowest and strongest modes of the CEO calculation on the excited-state geometry are ($\nu = 1$, $\Omega = 2.58$ eV) and ($\nu = 2$, $\Omega = 3.20$ eV). The lowest mode of the system is hence lowered in energy by 0.4 eV with respect to the ground-state structure. Only one of the three DSB units, corresponding to the least twisted unit, was found to constitute the mode $\nu = 1$. There are also coherences extending across the triphenylamine core, so a total of five benzene rings are involved in the excitation. Emission occurs invariably from the lowest-energy mode of the oscillator picture.[16] The lowest mode for emission is hence shifted by at least 0.4 eV to the red, which compares well to the experimental difference in absorption and emission peaks of 0.6 eV.

The calculations show that the excited-state mode responsible for emission is spread out across the central triphenylamine unit, which can provide an explanation for the experimental observations. Excitation energy is freely interchangeable between the three DSB units of the core chromophore, explaining the rapid loss of polarization memory observed experimentally.[21] As the dendrimer generation increases, the dendrons act as spacers between these core chromophore units. As the excited state is spread out across the core chromophore region, the dendrimer may be thought of as consisting of a single core chromophore surrounded by dendrons. In other words, the 3-fold symmetry of the core chromophore structure does not apply to the dendrimer in the excited state, because the core chromophore forms one single excited-state unit. The molecular symmetry is hence not conserved upon excitation of the molecule. Because the entire unit of the zeroeth generation dendrimer constitutes the emissive chromophore, the dendrons in this case encapsulate the emitter and act as a protective shield. The generation-dependent solid-state PL spectra hence exhibit a reduction in red-tail emission with increasing generation, corresponding to a reduction in intermolecular interactions with increasing chromophore spacing.[5,16−18,22]

It is also interesting to note that the molecular symmetry of the core chromophore is broken at higher energy excitation by forming an excitation localized to the outer stilbene units of the DSB branches rather than on the entire triphenylamine−DSB unit. Experimental and quantum chemical investigations have shown that higher energy modes of phenylene−vinylene oligomers are more localized than the lower energy modes.[12,14] In a star-shaped system such as our nitrogen-centered dendrimer (rather than a linear system), this results in the strong, more localized excitation at higher energy corresponding to an excitation on a stilbene unit. An important achievement of the investigation of the electronic properties by the CEO technique is hence the ability to explain the higher energy absorption feature at 3.66 eV of the zeroeth generation dendrimer.

The case is very different for the benzene-cored dendrimer, in which the excited-state wave functions are clearly confined to the individual DSB units with no discernible excitonic coherences between them. The only off-diagonal coherences visible correspond to a slight delocalization of DSB excitations onto the central benzene ring. The solution emission spectra of this material family are slightly narrower, display vibronic structure, and exhibit a much smaller red shift with respect to the absorption than for the case of ADSB. The emission and absorption of the dendrimer are very similar to those of neat DSB.[2] Because there are no excitations in these molecules that extend between the individual DSB units, BDSB is not expected to exhibit a significant luminescence rise time or a rapid loss of polarization memory as observed in ADSB. Future experiments will address these issues. The ground-state geometry of BDSB is comparable to that of ADSB, with the DSB units forming slightly larger dihedral angles in the case of BDSB.

A striking difference between the two dendrimer families is the generation dependence of the solid-state luminescence. In contrast to ADSB, the CEO calculations show that the dendrimer with the central benzene unit consists of three independent core chromophores. In this case, the 3-fold molecular symmetry may hence be used to describe not only the ground-state geometry but also the excited state of all generations of the molecule. The position of the dipoles on the molecule—whether across the center as in the case of ADSB or along the DSB units as for BDSB—evidently influences the formation of intermolecular excitations. It is likely that the molecular packing of the dendrimers in the solid state is very similar for the two classes of material, yet because the emissive dipoles have different positions and orientations within the two molecules, the way in which the dendrimer generation influences interactions differs. Electrical measurements suggest that films of the BDSB dendrimer become more insulating with increasing generation,[23] as in the case of ADSB.[5] However, the red-shifted emission spectra of G1 and G2 in Figure 2 show that the interaction between DSB units is actually increased with respect to G0. Because the level and nature of intermolecular interactions depends critically on the relative orientation of neighboring dipoles, this will strongly influence the way in which intermolecular excitations are formed in the solid state, which are in turn manifested through broad, red tail emission features. Whereas the dipoles in the case of BDSB are aligned along the individual DSB chains, the dipole in ADSB actually extends across the center of the dendrimer. BDSB can therefore support three dipoles, which can in turn interact with emissive dipoles present on adjacent molecules in the solid state, whereas ADSB is described by one more extended dipole, for which the dendron shielding turns out to be more effective.

As the experimental results show, the choice of the dendrimer central moiety, whether amine or benzene, strongly influences the formation of intermolecular excitations. The calculations reveal that this choice also controls the location of excitations in the emissive core chromophore unit, the zeroeth generation dendrimer. Although it is conceivable that the bulk packing of the dendrimers in films is comparable for the two materials, the separation between excitations on adjacent molecules differs and hence the likelihood of the formation of intermolecular emissive species. It is an interesting observation that the level of intermolecular interactions decreases with generation for ADSB yet increases up to G = 2 for BDSB simply due to the location of the excitation on the dendrimer.

V. Conclusions

We have demonstrated that the choice of central unit of a conjugated dendrimer has profound implications on the emission and absorption properties of dendrimers, as well as the level of intermolecular interactions in the solid state. We were able to identify excitonic coherences within the molecules and hence demonstrate a molecular control of the coherences within the emissive chromophore of a conjugated dendrimer. The CEO technique provides an accurate description of the electronic structure of dendrimers for electroluminescence applications but also gives valuable insight into the nature of the excited state. These results show that the CEO approach is a valuable technique for guiding the development of improved materials for OLEDs.

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