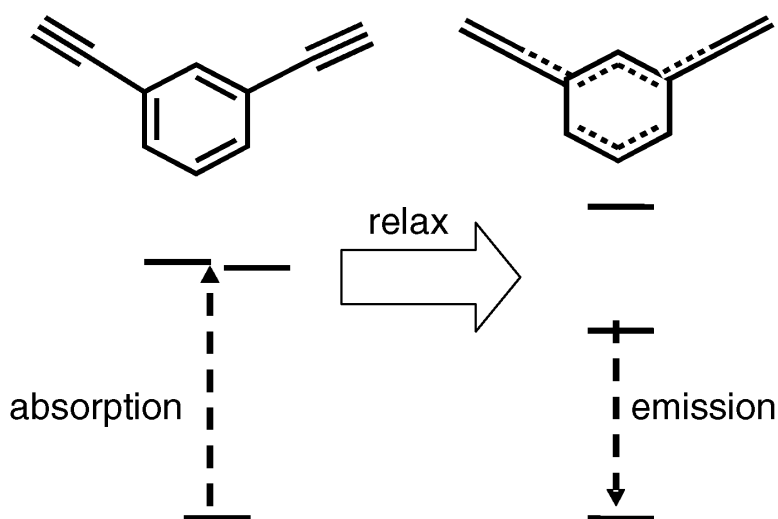Communication

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Meta-Conjugation and Excited-State Coupling in Phenylacetylene Dendrimers

Kevin M. Gaab, Alexis L. Thompson, Jianjun Xu, Todd J. Martínez,* and Christopher J. Bardeen*

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received November 26, 2002; E-mail: tjm@spawn.scs.uiuc.edu; bardeen@scs.uiuc.edu

Multichromophore dendrimers are able to transfer energy rapidly and efficiently to a central core.[1,2] To understand energy flow in these molecules, one must identify the relevant light-absorbing units and determine their electronic coupling. This is straightforward for well-separated chromophores interacting through a Forster mechanism[1] but more difficult for conjugated supermolecules such as the highly efficient phenylacetylene (PA) dendrimers.[2] Previous workers have postulated that the electronic states in the PA dendrimers are localized on the dendrimer branches,[3,4] under the assumption that meta-conjugation blocks electronic delocalization. This reasoning is based on ground-state considerations, however, and the situation may be quite different for excited states.[5] In this Communication, we use theory and experiment to show that, while the subunits of the PA dendrimers are weakly coupled in their equilibrium ground-state geometry, they can become strongly coupled in the excited state. This geometry-dependent electronic coupling will affect the modeling of energy transfer in these molecules.

Chart 1 shows the simplest building blocks for larger PA dendrimers. Normalized steady-state absorption spectra for compounds **1-Ph** through **3-Ph** are shown in Figure 1a. Progressing through the series, there are only modest changes in the absorption spectra: the low energy peak shifts by $\sim$600 cm^{-1} and is slightly enhanced. The lack of significant shifting or reshaping with increasing dendrimer size led others to conclude that the excitations were localized to the individual dendrimer branches.[4] Yet while the absorption spectra suggest a common chromophore, the emission spectra change dramatically with dendrimer size (Figure 1b) and are inconsistent with this picture. The high energy peak of the fluorescence shifts by $\sim$2000 cm^{-1} with each additional PA group, while the spectral shape evolves from a relatively broad emission spectrum with an anomalous peak progression in **1-Ph** to a well-defined Franck−Condon progression in **3-Ph**. Measurements of fluorescence lifetimes and quantum yields give values of 0.74 ns, 0.55 (**1-Ph** at 77 K), 28 ns, 0.15 (**2-Ph**), and 14.9 ns, 0.35 (**3-Ph**). Fluorescence decays are all single exponential and independent of concentration, ruling out the presence of aggregates. These values lead to radiative lifetimes increasing from 1.35 ns in **1-Ph** to 28 ns in **2-Ph** to 43 ns in **3-Ph**. A Strickler−Berg analysis predicts radiative lifetimes of 1−2 ns in all three molecules. As expected, the trimethylsilane (TMS)- and H-terminated analogues of **(1−3)-Ph** absorb at higher energy. However, apart from some differences in the relative absorption peak ratios, the spectroscopy of **(1−3)-TMS** and **(1−3)-H** parallels that of **(1−3)-Ph**, suggesting photophysics which is relatively unperturbed by substituents on the ends of the acetylene groups. The decay times and spectral shapes are essentially independent of solvent, from cyclohexane to tetrahydrofuran to CH$_2$Cl$_2$.

The large shifts and shape changes in the emission spectra, along with changes in lifetime and oscillator strength, indicate that the emitting states are different from the absorbing states in **(1−3)-Ph**. To clarify the origin of the asymmetry between absorption and

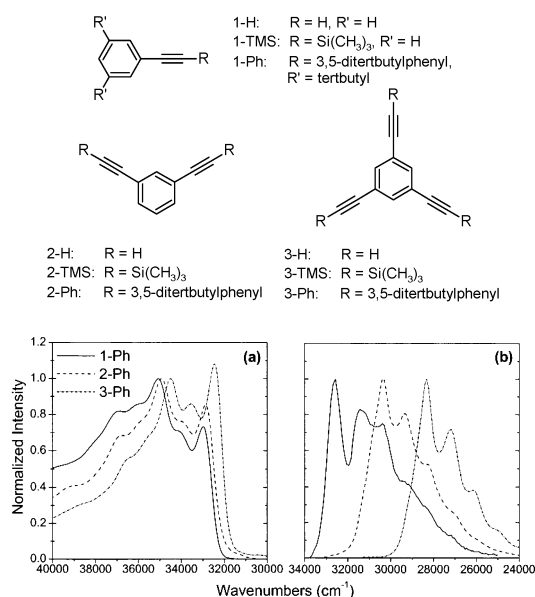**Chart 1.** Building Blocks of PA Dendrimers Studied in This Work

Figure 1. Absorption (a) and emission (b) spectra in cyclohexane.

emission in these molecules, we apply ab initio quantum chemistry for the low-lying electronic states. Because the spectroscopy of the **(1−3)-H** series resembles that of the **(1−3)-Ph** series, we investigate the simplest dendrimers at the highest level of theory possible. Calculations were carried out for the **(1−3)-H** series, where we perform ground- and excited-state geometry optimizations using state-averaged CASSCF[6] with the 6-31G basis set. Dynamic electron correlation is included with CASPT2 corrections.[7] For the larger **(1−3)-Ph** series, B3LYP-DFT with the 6-31G** basis set is used to optimize ground-state geometries, and the excited-state electronic structure in the Franck−Condon region is modeled as above. States are equally weighted in the averaging, and the number of states included was as small as possible while capturing the optically bright states.

In Figure 2a, we show the results of calculations for the electronic excited states of the **2-H** and **3-H** dendrimers at their relaxed ground- and excited-state geometries (which determine the absorption and emission spectra, respectively). The level ordering is clearly different for the two nuclear configurations. In **3-H**, for example, absorption from the ground state goes to three quasi-degenerate excited states. Optimizing the excited-state geometry leads to a cumulenic structure, lifting the electronic state degeneracy and leading to a weakly emissive state below two higher states that carry most of the oscillator strength. Similar effects are observed for **2-H**, where two quasi-degenerate states split into two nonequivalent states in the relaxed excited-state geometry. These results are qualitatively similar to what would be expected from an exciton model[8] where the excited-state coupling is negligible during the absorption event, but grows as the molecule relaxes to a different
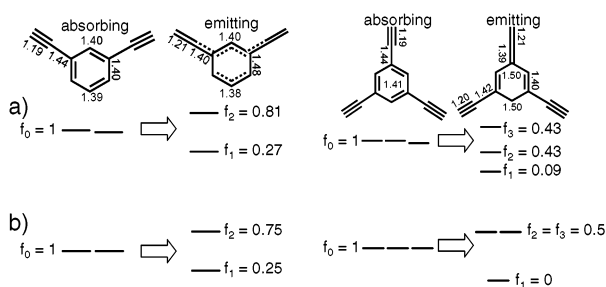
Figure 2. (a) Calculated electronic level structure for the **2-H** and **3-H** dendrimers for both absorbing and emitting geometries. Also shown are the transition energies and transition dipole moments. (b) The results of a simple exciton model with intermolecular coupling V growing more negative after absorption and relaxation on the excited state.

Figure 3. Stokes shifts for H (■)- and Ph (▲)-terminated compounds. Theoretical CASPT2 values (□) for **(1−3)-H**. Exciton model (○) Stokes shifts offset by 5500 cm^{-1}, where $V = -1434$ cm^{-1}.

nuclear geometry on the excited state. For example, in **2-H** a nonzero negative intermolecular coupling V leads to a splitting of the excited states to form an H-type dimer, where the lower state has a weaker transition dipole than the upper state. Figure 2b shows the results of a simple excitonic coupling model where $V = 0$ in the ground-state geometry and becomes negative in the relaxed excited-state geometry, leading to an observable Stokes shift. This model, where the exciton coupling varies depending on geometry, predicts the qualitative trends for the emission cross section **f** (inversely proportional to radiative lifetime) in the calculations and the experiments. It also predicts that the two higher-lying excited states in **3-H** are degenerate, which is not the case in the calculation, a discrepancy possibly due to additional vibrational distortion and symmetry-breaking which cannot be taken into account by the simple exciton model.

To check the calculations which lead to the state reorderings seen in Figure 2, we compare the theoretical and experimental absorption−fluorescence energy difference for **(1−3)-H**. The absorbing state is chosen to be the low-lying electronic state with the largest oscillator strength at the S_0 minimum. The emitting geometry is determined by finding the lowest energy excited-state minimum with significant oscillator strength. The calculated excitation energies of **(1−3)-H** are 50 000 ± 2000 cm^{-1}. Considering the expected error of the CASPT2 method,[7] this is in good agreement with the experimental results, which show small shifts in the absorption maximum of ∼1000 cm^{-1} or less within each series of compounds. Large active space CASSCF calculations predict a negligible shift in the absorption maximum between **1-Ph** and **2-Ph**, and the **2-Ph** calculation yields two nearly degenerate bright states. These results indicate that the coupling vanishes at the absorbing but not the emitting geometry. The calculated Stokes shifts for **(1−3)-H** are compared to the experimental shifts for the −**H** and −**Ph** series, and the exciton model with $V = -1434$ cm^{-1}, in Figure 3. Both the calculations and the exciton model follow the experimental trend.

In conclusion, both theory and experiment demonstrate that the absorbing and emitting states in PA dendrimers are not the same and that their differences are qualitatively consistent with a variable excitonic coupling V. The use of an exciton model to understand the photophysics of covalently bonded conjugated molecules is not new[8] and has been applied to gas-phase DPA.[9] The novel phenomenon here is that V is usually regarded as a constant that produces large shifts in both the emission and the absorption spectra, while we observe such shifts in the emission spectra only. Simple point dipole theory would predict a positive V, and thus an inverted level structure with shorter radiative lifetimes from **1-H** to **3-H**. But the approximations in that theory (no orbital overlap, well-separated chromophores) clearly break down in the case of the PA dendrimers. Electronic coupling can be strongly influenced by
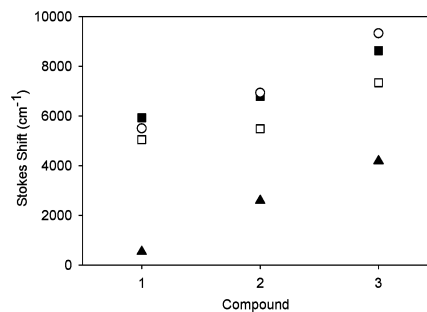
through-bond electronic interactions between chromophores,[10] and the relaxed excited state of DPA has considerable cumulenic character, and thus more charge-transfer character, which could lead to larger coupling. The origin of the negative sign of V is currently under investigation. The last question is what role these new states play in the energy transfer dynamics. Femtosecond studies of transient absorption and fluorescence, as have been carried out for other multichromophoric molecules,[3,11] would be very useful in this context. At a minimum, our results imply that Förster models of energy transfer in PA dendrimers should be modified to take different distances and dipole orientations into account. Asymmetric branching, for example, a funnel structure,[2] could affect the structure of the excitonic state and energy transfer.

Supporting Information Available: Theoretical and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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