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Intramolecular energy transfer in a synthetic dendron-based light harvesting system



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ABSTRACT

Single-molecule experiments based on Förster resonant energy transfer (FRET) or on single molecule absorption spectroscopy (SMA) are now capable of studying energy funneling, exciton blockade, singlet fission, and a variety of other processes that involve multiple photoactive groups interacting on a single molecular backbone. Here, we present synthesis and optical characterization of a new dendron functionalized with two green donor dyes (Cy3) and one red acceptor dye (Cy5) through flexible linkers. We describe in detail the synthesis of the conjugated network and the flexible dye coupling. Characterization of the dendron and of control molecules with fewer donors or no acceptor by ensemble absorption and emission spectroscopy shows that the system is capable of light harvesting, producing an intramolecular FRET signal from the acceptor greater than expected from a single donor. We also investigate intramolecular energy transfer upon UV excitation of the conjugated backbone. The photophysical behavior of this light harvesting dendron can be rationalized by a simple Förster/superexchange model. Simulations and scanning tunneling microscopy of single dendron molecules show that the dyes can fold over onto the dendron, creating a heterogeneous distribution of conformations suitable for single molecule studies of light harvesting.

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1. Introduction

Many naturally evolved systems act as antennae to concentrate light energy. The most ubiquitous is the light harvesting system found in plants and some unicellular organisms. In these molecular assemblies, energy from many ring-shaped oligomers of donors is eventually funneled with high efficiency to a single acceptor, the reaction center.

Correspondingly, there has been much interest in artificial antenna molecules. They are of fundamental interest because they can be used to study competition among multiple excited chromophores coupled to one another and to an acceptor [1], but they also have practical applications in efficient light-energy conversion by increasing the available absorption cross section and transferring energy to an active center [2,3]. Many different synthetic strategies for light harvesting molecules have been

employed, ranging from coupling of organic building blocks (e.g., porphyrins) [4], to transition metal-based networks [5], and non-covalent self-assembled structures [6]. Among dendrimers, the donor acceptor systems range from relatively inefficient perylene (single chromophore) derivatives on the same type of phenylacetylene network we discuss here [7], to systems with different coumarin derivatives as donors and acceptors on other backbones (e.g., poly(benzyl)ether) [3,8].

Dendrimers, with their alternative energy flow paths, have also attracted theoretical interest. For example, Bar-Haim and Klafter discuss the possibility of controlling the pathway of excitation in such molecules [9]. Localization of pathways can occur in asymmetrically branched systems [10], and the complexities of such systems have attracted modeling from superexchange matrix models [11] to full quantum dynamics [12].

New experimental techniques have become available recently to allow a more stringent test of these models. Single molecule Förster resonance energy transfer (FRET) of individual multi-chromophore dendrimers has revealed excitation annihilation processes [13], and similar single molecule FRET studies have revealed 'exciton blockade' due to the presence of multiple chromophores [14]. Very recently,

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single molecule absorption spectroscopy with sub-nm spatial resolution has become feasible at room temperature, opening up the possibility of resolving spatially and spectrally the off-resonant backbone during the chromophore-to-chromophore energy transport [15,16].

Our goal was to design and characterize a simple dendron system that would allow single molecule techniques such as scanning tunneling microscopy (STM) and Förster energy transfer (FRET) to test computational models and theories of energy transfer, localization and competition between donor and acceptor. Our design goals were: two donors plus one acceptor to allow energy funneling; robust donor/acceptor dyes suitable for single molecule studies and with known FRET overlap; asymmetry of donor/acceptor branches so they can be distinguished by STM; high FRET efficiency; and a rigid aromatic backbone suitable for STM imaging on metal or semiconductor surfaces.

Here, we report the synthesis of a light harvesting dendron that satisfies all these requirements. It has a highly conjugated phenylacetylene backbone flexibly linked to dyes suitable for ensemble and single molecule studies: **Cy3₂-dendron-Cy5** (**Cy3₂-D-Cy5**). This model system has two Cy3 donors that can be excited with green 532 nm light, and one Cy5 acceptor that emits red 680 nm light. We use these commercially available dyes because they are one of the most commonly used FRET pairs. We describe in detail the synthesis of the branched phenylacetylene backbone, as well as the click and hydrazide couplings that allow for variable numbers of donors and acceptors to be installed. By comparing the dendron's absorption and emission spectra with one another and with a control compound, we conclude that the system can funnel light energy from two donors to the acceptor with high quantum yield. We also study direct energy transfer from the aromatic backbone, which absorbs near 330 nm, to both the donor and acceptor dyes. Finally, STM imaging of the dendron on an ultrathin gold film shows that the system is conformationally heterogeneous (i.e., can fold on itself or not), making it a useful model system for single molecule energy transfer studies by SMA-STM [17,18].

2. Materials and methods

2.1. Reagents

All reagents were commercially obtained and used without further purification unless otherwise noted. Anhydrous solvents were obtained from an anhydrous solvent delivery system (SDS), using activated alumina columns. Dry trimethylacetylene was transferred under nitrogen environment. Reactions were performed in an inert gas environment, either utilizing nitrogen from a standard Schlenk line or the argon environment of a glove box. The precursor of the dendron centerpiece, (*E*)-1-((3,5-dibromophenyl)diazenyl)pyrrolidine was prepared as described by Kawaguchi et al. [19] and was taken from Moore group (UIUC) stock. Likewise, tetrakis(triphenylphosphine)palladium(0) Pd(PPh₃)₄ was previously prepared by a group member following an established procedure [20], and used as-is from Moore group stock. All dyes were obtained from Lumiprobe and used without further purification.

2.2. Purification

Purification of the intermediate products was done by flash column chromatography using silica gel 60 (230–400 mesh) from Silicycle. For purification of the final **Cy3₂-D-Cy5**, a size exclusion column (Bio Beads S-X1, Gel Permeation Gel 200–400 mesh, Catalog: 152-2150, BIO-RAD) was chosen, as the high polarity of the dyes made standard flash chromatography impossible.

2.3. Instrumentation

¹H and ¹³C NMR spectra were obtained on a Varian VXR500 or Varian U500/U400 in the SCS NMR laboratory at the University of Illinois and referenced to the residual solvent peak of CDCl₃ or perdeuterated dimethyl sulfoxide (DMSO-d₆). Purity of the intermediates and products was confirmed by proton assignments/intensities, and by monitoring the unreacted ketone peak in the final coupling reaction.

In addition to NMR spectroscopy, reaction success was checked *via* mass spectrometry. High resolution (HR) mass spectra were recorded by the School of Chemical Science (SCS) mass spectrometry facility at the University of Illinois. Generally HR-ESI (electrospray ionization) mass spectrometry was performed, EI (electron impact) mass spectrometry was recorded only for the highly hydrophobic unlabeled full dendron, as ESI did not yield results. Comparison of the experimental isotope pattern to the calculated pattern provided conclusive identification of the desired products.

Absorption spectra were acquired as solutions in chloroform on a Shimadzu UV-1650 PC spectrometer at room temperature using standard 1 cm quartz cuvettes. Transmission spectra of the dendron on a transparent gold film (10 nm Au on a substrate of 5 nm Pt on c-plane sapphire) were taken at an incident angle of 58° using the same instrument. The dendron was deposited by aerosol deposition using an airbrush (Iwata CM-SB). Spectra were obtained repeatedly after deposition of 100 μL 0.6 μM **Cy3₂-D-Cy5** in chloroform solution up to 10 depositions of a total deposition of 1000 μL. The sample was not moved between deposition/solvent evaporation cycles.

Emission spectra were obtained using an Agilent Cary Eclipse Fluorescence Spectrophotometer, at excitation wavelengths of 330 nm, 532 nm, 632 nm and 642 nm in chloroform in 1 cm quartz cells. Solvent-induced wavelength shifts caused the measured absorption spectra and emission spectra of Cy3/Cy5 to differ from the literature values obtained in aqueous solution by about 10 nm [9,21].

2.4. Calculations

Simulations to minimize dendron energy were performed using the MM2 vacuum force field in Chem3D Pro. The simulation started from a fully extended dendron. Singular value decomposition (SVD) analysis of the transmission spectra was performed using commercial Matlab software.

2.5. Scanning tunneling microscopy

STM studies were performed on a home-built ultrahigh-vacuum (UHV) STM similar to ones previously reported [22], using electrochemically etched tungsten tips on a H₂-flame annealed commercial Au [111] on mica surface (SPI Supplies). The dendron was drop cast from a highly dilute chloroform solution. Prior to imaging the sample underwent a 12 h degas at 100 °C in UHV.

3. Results and discussion

Previous light harvesting dendrimers have been synthesized by Aronov et al. [2,3] based on poly(aryl ether) backbones. These allowed for very high yield energy transfer (>90%), consistent with the FRET mechanism from the donors (coumarin 2) located on the peripheral chain ends of the dendrimer to the single acceptor (coumarin 343) situated at the core. Other light harvesting dendrons synthesized by Devadoss et al. [7] were based on perylene terminated poly(phenylacetylene) backbones. These also

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