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Light Harvesting and Efficient Energy Transfer in a Boron-dipyrrin (BODIPY) Functionalized Perylenediimide Derivative

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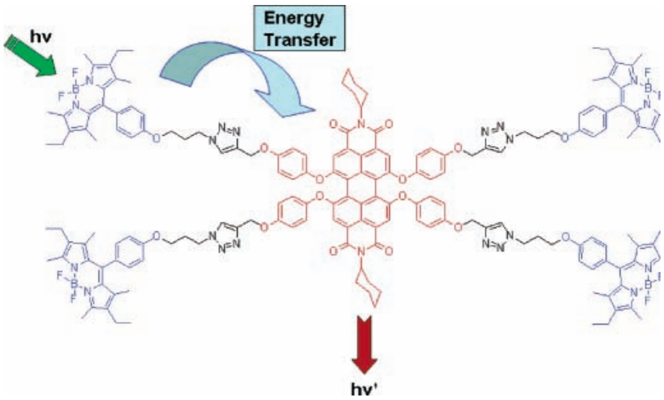
ABSTRACT



Click chemistry has been successfully applied in the synthesis of a bay region tetraboron-dipyrrin (BODIPY) appended perylenediimide (PDI). This light-harvesting molecule presents a large cross section for the absorption of light in the visible region. Excitation energy is efficiently channeled to the perylenediimide core. This novel antenna system is the first demonstration of the efficiency of energy transfer in a BODIPY–PDI bichromophoric system and appears to be highly promising for the design and synthesis of similar dendritic structures.

Effective biomimetic light harvesting requires the presence of a multitude of peripheral chromophores which could transfer the excitation energy to an energy acceptor “core” molecular species, thus concentrating energy in just one molecular unit. This has been achieved in a number of molecular systems,[1] some of which are dendritic.[2] The excitation energy transfer (EET) process can take place in principle, in either of two ways, through-space or through-bond. The predictable nature of the through-space EET allows accurate engineering of the energy transfer efficiency which is dependent on many factors, including but not limited to spectral overlap between the energy donor (D) and the energy acceptor (A), the average distance between the donor and the acceptor, orientation factors, and the effectiveness of alternative deexcitation modes. Perylenediimides (PDIs) and boron-dipyrrin (BODIPY)[3] dyes are well-known fluorophores, and many designs for light-harvesting molecules include perylenediimides either as the core[4] entity or as part of the antenna.[5] This is due to both photochemical and

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(3) BODIPY is a registered trademark of Molecular Probes, Inc.

10.1021/ol061110z CCC: $33.50

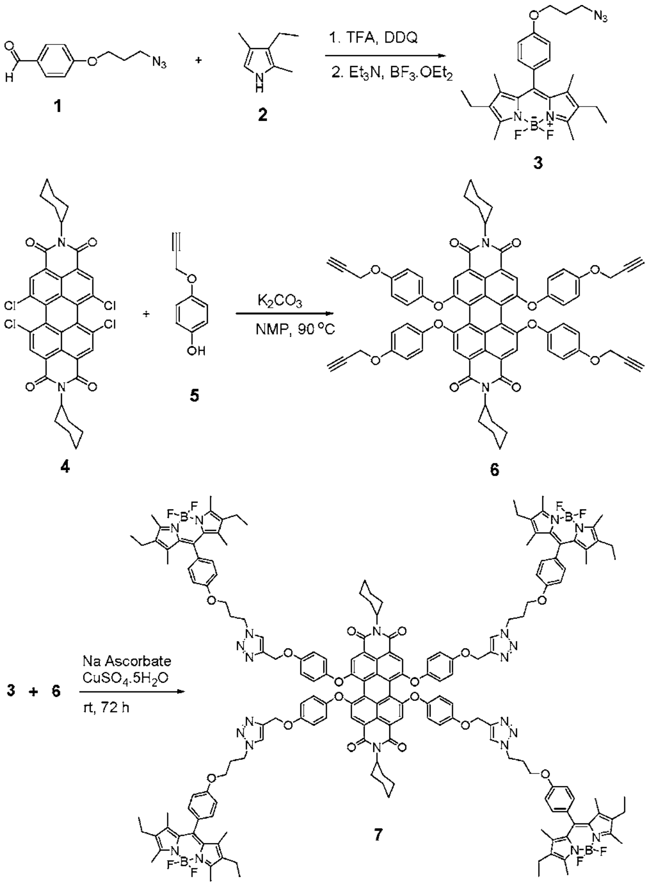

Figure 1. Synthesis of the light-harvesting molecule **7**.

chemical stability of PDIs and straightforward functionalization of the parent structure at the imide positions and more recently at the bay region. BODIPY dyes also have remarkable properties, including high extinction coefficients, high quantum yields, and good solubilities in many solvent systems. Since the first report of the synthesis of these dyes in 1968,[6] and especially after a significant improvement in the synthesis procedure,[7] many practical applications have been reported, including BODIPY moieties as accessory pigments[8] in optoelectronic gates[7a] and light-harvesting arrays.[7b]

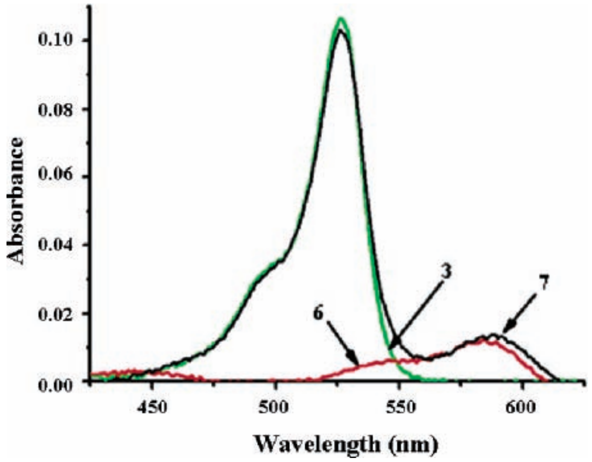

Figure 2. Absorbance spectra of compounds **3**, **6**, and **7** at equal absorbances in $CHCl_3$, at 526 nm for **3** and **6** and at 588 nm for **6** and **7**.

In the syntheses targeting light-harvesting molecular systems with covalently appended antenna molecules, Williamson ether synthesis has demonstrated its utility in many examples[1] in the recent literature. Nevertheless, for very efficient functionalization of the terminal groups, click chemistry[9] which is an improved version of the Huisgen cycloaddition should be a better alternative. The Cu(I)-catalyzed 1,3-dipolar cycloaddition between azides and alkynes to yield regiospecifically 1,2,3-triazoles is highly reliable. In addition, the click reactions are essentially quantitative and experimentally straightforward, with a high level of tolerance to solvent changes.[10] There are already examples of click-chemistry-based synthesis of dendritic structures.[11] Thus, with these considerations, we targeted the tetra-BODIPY functionalized PDI derivative compound **7** (Figure 1).

The synthesis starts with the reaction of 4-(2-bromoethoxy)benzaldehyde with NaN_3 in polar aprotic solvents such as DMF. This aldehyde (**1**) was then used in the usual manner[6] in the synthesis of a BODIPY dye, reacting it with 3-ethyl-2,4-dimethylpyrrole (kryptopyrrole) in the presence of TFA and DDQ, followed by the addition of BF_3-Et_2O. The perylenediimide core was synthesized starting from 1,6,7,12-tetrachloroperylenediimide (**4**). Reaction of the imide **4** with a slight excess of 4-propargyloxyphenol in NMP at 90 °C in the presence of K_2CO_3 yields the tetraaryl-substituted perylenediimide **6** with four alkyne groups poised for dipolar cycloaddition. In the final step, the azido-functionalized BODIPY and the alkyne carrying PDI were reacted together in the presence of sodium ascorbate and

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$CuSO_4$ at room temperature. The reaction reached essentially completion in 72 h with very good isolated yields (80% after chromatographic purification).

To assess the efficiency of energy transfer, the spectroscopic properties of compound **7** were studied in comparison with the fragments and the model compounds. The absorption spectra of compounds **3**, **6**, and **7** at equal absorbance values at 526 nm (for **3** and **7**) and 588 nm (for **6** and **7**) are shown in Figure 2. The spectrum of compound **7**, as expected, is essentially equal to the sum of the other two spectra.

The extinction coefficient of the dye **7** at 526 nm (collective absorption of four BODIPY units) is 240 000 and 45 000 M^{-1} cm^{-1} at 582 nm (PDI core). This indicates that there are no ground-state interactions between the chromophores as the design dictates. The fluorescence spectrum is even more revealing: the bright greenish-yellow fluorescence compound **3** is not observed in $CHCl_3$ solution of compound **7**, and there is very little residual emission corresponding to peripheral BODIPY emission (Figure 3).

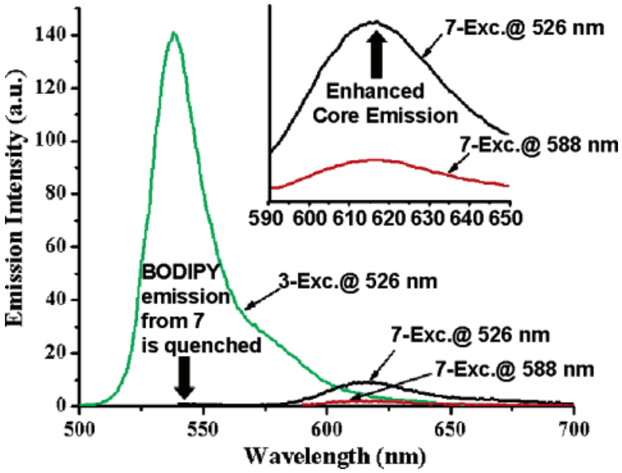

Figure 3. The emission spectra of **3** and **7** at equal absorbances at 526 nm in $CHCl_3$. Inset: enhanced core emission on excitation of the peripheral BODIPY units in the light-harvesting molecule **7**.

The quantum yield of emission for compound **3** was determined using a reference dye (Rhodamine 6G, with a quantum yield of 0.95 in ethanol),[12] but in the antenna system **7**, the quantum yield of emission from the BODIPY units decreased to less than 0.01 (for additional spectroscopic data, see Supporting Information). We estimate the efficiency of energy transfer as 99%, which yields a Förster critical radius of 47 Å.[13] Not surprisingly, the PDI dye **6**, when excited at 526 nm, emits poorly as the extinction coefficient is small at this wavelength for the PDI core. However, in compound **7**, excitation at 526 nm produces an emission peak centered at 618 nm. To assess the magnitude of the antenna effect in the light-harvesting molecule **7**, we compared the emission intensities at 618 nm when excited at the BODIPY antenna at 526 nm and directly at the core PDI at 588 nm. The antenna effect demonstrated and quantified in this way is 3.5-fold.

The observed antenna effect is remarkable and comparable to the best cases.[4c,14] The fact that this light-harvesting system is assembled via very efficient click chemistry suggests that more elaborate dendritic systems can be designed using these two remarkable fluorescent dyes, BODIPY and PDI. Our work to that end is in progress.

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Supporting Information Available: Syntheses, experimental details, ^{1}H and ^{13}C NMR spectra, and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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