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A FRET-Based Ultraviolet to Near-Infrared Frequency Converter

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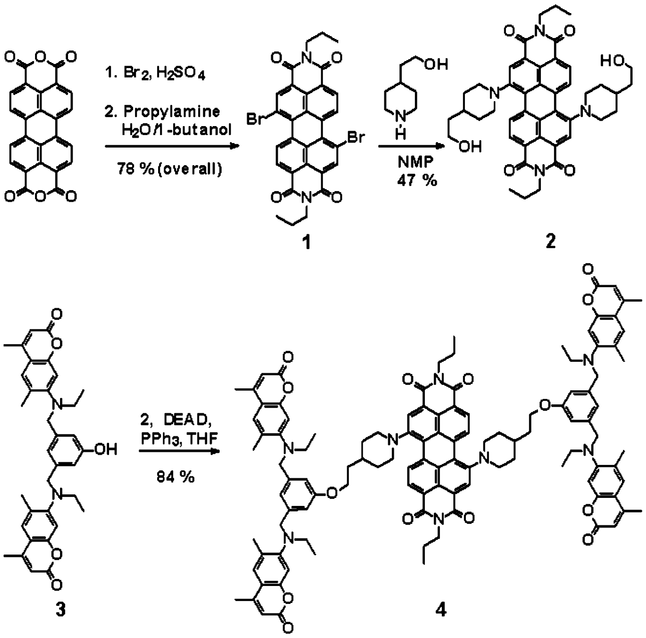
Presented here is a soluble, nonionic dendritic material that transforms ultraviolet (UV) directly into near-infrared (NIR) radiation. Furthermore, this first generation dendrimer (**4**) absorbs strongly in most regions of the visible spectrum due to the absorption properties of the core perylenebis(dicarboximide) chromophore. As a result, the energy of any photon absorbed by either the donor (coumarin 2) or the acceptor chromophores is converted into a single NIR emission of the perylene dye. Amplified emission is observed when the system is excited at the donor λ_{max} due to fluorescence resonance energy transfer (FRET) of the absorbed UV radiation to the perylene core. Unlike ionic dyes that have similar absorption and fluorescence properties, this material is highly soluble in common organic solvents. This system could potentially be applied as the gain medium of solid-state organic-based lasers or as a component of high value photovoltaic (PV) materials where destructive high energy UV radiation would be converted to useful low energy NIR radiation.

Perylenebis(dicarboximide) derivatives have been extensively studied as components of organic-based PV devices,[1] artificial light-harvesting complexes,[2] lasers,[3] and other photonic devices.[4] This is due to their excellent thermal, chemical, and photochemical stability, as well as their high molar absorptivity and fluorescence quantum yields.[5] They belong to a small family of dyes that absorb above 500 nm and remain processable due to their solubility in common organic solvents.[5,6] These derivatives are relatively easy to functionalize at several symmetrical positions, making them ideally suited for use in functional supramolecular materials.[2a,c,7] It is for these reasons that the perylene bis(dicarboximide) derivative (**1**, Scheme 1) was chosen to serve as the core structure of our dendritic system.

In the search for soluble chromophores that emit in the red or NIR regions, several approaches using perylene dyes have been pursued.[6] The most successful route includes incorporating an electron-rich amine in conjugation with the π-system of a perylene chromophore. Such dyes have been shown to have a 170 nm bathochromic shift relative to the precursor compound (**1**) due to the electron-donating ability of the amines.[8] Therefore, **2** was synthesized and used as the difunctional red absorbing core chromophore.

The synthesis of **4** began by first performing a double aromatic substitution of bromine onto the bay positions of commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (Scheme 1).[9] This resulted in an insoluble material, which was coupled (using a modified literature procedure)[7] with propylamine in a water/1-butanol mixture to form a bright red, soluble compound (**1**) in 78% overall yield. The core (**2**) of the dendrimer was then synthesized in 47% yield by substitution of **1** with 4-piperidine-ethanol in 1-methyl-2-pyrrolidinone (NMP). In contrast to the red color of the starting material, compound **2** had a dark-green appearance, a property that facilitated its purification. In addition, compound **2** had no observable fluorescence when excited with either short wave (254 nm) or long wave UV radiation. Coumarin 2 labeled dendron **3**[10] was attached to **2** under Mitsunobu coupling conditions in 84% yield, providing dendrimer **4** in 31% overall yield starting from the commercially available 3,4,9,10-perylenetetracarboxylic dianhydride.

Scheme 1



Prior to performing photophysical measurements, several preparative TLC purifications were performed on **2**, **3**, and **4** to ensure their high purity. Figure 1 shows the steady-state absorption spectra of **2**, **3**, and **4** in chloroform at room temperature. The absorption spectrum of **4**, which is a composite of the absorption spectra of both **2** and **3**, has a strong band at 345 nm from its coumarin 2

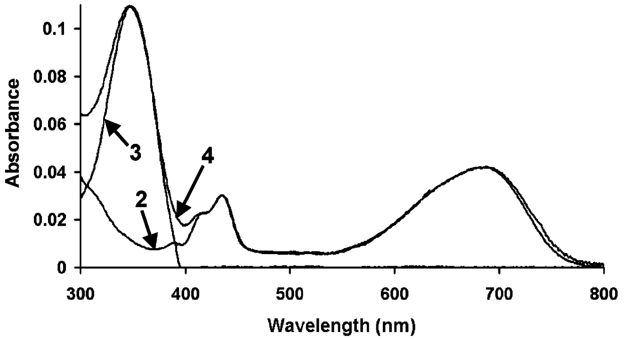


Figure 1. Steady-state absorption spectra of **2**, **3**, and **4** in $CHCl_3$ at room temperature. Both **2** and **3** have been normalized to **4**.

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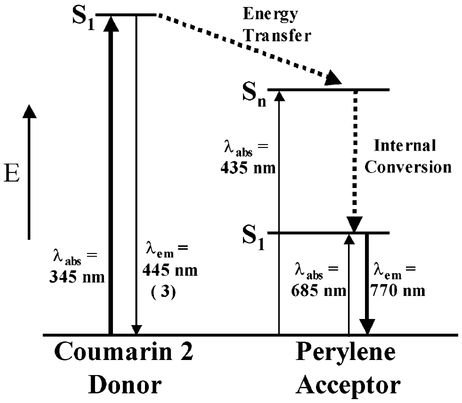

Figure 2. Energy level diagram illustrating the photophysical processes of **2**, **3**, and **4**. Excitation of **4** at the coumarin 2 λ_{max} ($\lambda_{ex} = 345$ nm) results in FRET to the higher excited state of the perylene core. This state is rapidly converted to S_1, from which emission is observed. This entire process is highlighted with bold arrows. Emission of the coumarin 2 donor at 445 nm occurs only when the perylene acceptor chromophore is not present.

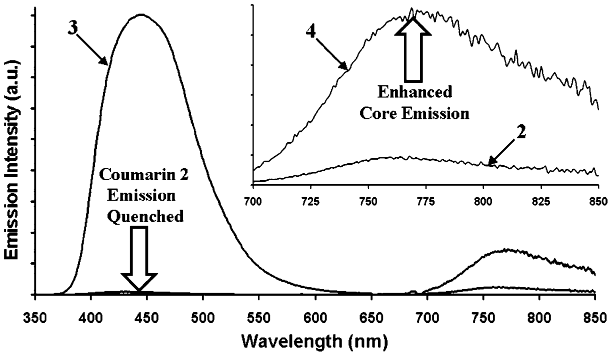

Figure 3. Normalized steady-state emission of **2**, **3**, and **4** ($\lambda_{ex} = 345$ nm) in $CHCl_3$ at room temperature. Complete quenching of coumarin 2 fluorescence emission is observed when **4** is excited at the coumarin 2 (donor) λ_{max}, resulting in a 6.2-fold increase in the core emission. The inset shows an expansion of the region from 700 to 850 nm.

component, along with two smaller absorption bands at 414 and 435 nm, which are indicative of higher level excited states (i.e., S_2 and/or S_3). As with most analogous compounds, the excitation of **2** at these higher excited states results in rapid internal conversion to the first singlet excited state (S_1, Kasha's rule).[11] Therefore, no fluorescence was observed in the visible region when either **2** or **4** is excited anywhere in the visible. The broad absorption band centered at 685 nm is due to excitation of the core from S_0 to S_1. Figure 2 shows an energy level diagram that gives a generalized illustration of these photophysical processes.

The emission spectra of **2**, **3**, and **4**, all excited at 345 nm, are shown in Figure 3. A comparison of Figures 1 and 3 shows that the emission of coumarin 2 overlaps well with the higher level excited-state absorption of the core, thus creating a pathway for FRET to occur from coumarin 2 to the perylene core derivative.[12] Indeed, when dendrimer **4** is excited at the donor λ_{max} ($\lambda_{ex} = 345$ nm), the donor emission is completely quenched due to energy transfer to the core. This results in a 99% energy transfer efficiency, which was calculated by comparing the integration of donor emission in the absence of the core (**3**) and in the target dendrimer **4** at the same excitation wavelength.[12] Furthermore, a 6.2-fold increase in the core emission relative to the emission of the core lacking the peripheral donors (**2**, $\lambda_{ex} = 345$ nm) is observed. This amplification effect is calculated by obtaining the ratio of the integrated emissions of both **2** and **4** when each is excited at 354 nm. The significant increase in core emission is due to the light-harvesting properties of the donor coumarin 2 chromophores located at the periphery of the dendrimer and to their ability to very efficiently transfer their absorbed energy to the core.[12,13]

To the best of our knowledge, dendrimer **4** represents the first reported organic-based nonionic material that transforms UV and visible light directly to NIR radiation based on FRET. In addition to possibly being applicable to optoelectronic devices, this light-harvesting antenna[14] might find use in increasing the performance of dye-sensitized solar cells,[15] a current focus of our investigations.

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

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