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Excited state absorption and decay kinetics of near IR polymethine dyes

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ABSTRACT

We performed a detailed experimental investigation and quantum-chemical analysis of linear, excited state absorption (ESA) spectra, and lifetime dynamics of a new series of near IR symmetrical cationic polymethine dyes, with 5-butyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indolium terminal groups. Additionally, two neutral dyes, squaraine and tetraone, were synthesized with the same terminal groups. We compare the nonlinear absorption properties of these three dyes with an analogous set of three "visible" dyes with simpler benzo[*e*]indolium terminal groups. Measurements are performed using laser systems with femtosecond and picosecond pulsewidths. We find that the dyes with dihydrobenzo[*cd*]furo[2,3-*f*]indolium terminal groups are characterized by a remarkably large red shift (200–300 nm) of their linear and excited state absorption bands. The absorption bands for these dyes can now be shifted systematically to the near IR region by a contribution from their terminal group that strongly increases the total length of conjugation. ESA spectra in the "near IR" set of molecules have strong absorption bands with excited state absorption cross sections increasing from 2×10^{-16} cm^2 for the shortest polymethine chain (trimethine cyanine) to 9×10^{-16} cm^2 for the longer chain (heptamethine cyanine). The peak ESA magnitude for heptamethine cyanine is approximately twice as large compared to its peak ground state absorption, but the oscillator strengths of the two bands are almost equal. This observation indicates that the ESA oscillator strengths can be as large as those of ground state transitions. The results of these experiments combined with agreement of the quantum-chemical calculations move us closer to a predictive capability for molecular structure–nonlinear properties relations of cyanine-like molecules.

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1. Introduction

Strong and selective absorption across a broad spectral region of cyanine and cyanine-like dyes have made them attractive for applications as fluorescent probes in chemistry and biology, active and passive laser media, photosensitizers, optical data storage and electroluminescence materials [1–5]. The structural modification of dyes, allowing a shift of their absorption bands to the near infrared (NIR) region, can expand the existing areas of applications and reveal new ones such as highly efficient nonlinear optical materials for all-optical signal processing [6]. In spite of the increasing information available about near IR absorbing dyes, their thermal stabilities, photochemical stabilities, and solubilities are the main issues limiting their practical applications. Most of the known synthetic methods to decrease the energy gap between the ground and excited states consist of lengthening the polymethine chain usually leading to a decrease in photochemical stability. By novel chemical modifications to the terminal groups, we have bypassed this difficulty with the purpose of improving their functionality for the previously mentioned applications. The main absorption band for these dyes can now be shifted systematically to the near IR region by increasing the contribution from the terminal groups to the total length of conjugation. In this work we analyze the excited state absorption spectra (ESA) and lifetime dynamics of cyanine structures, introduced in our previous manuscript Ref. [16], with specific terminal groups of dihydrobenzo[*cd*]furo[2,3-*f*]indolium, which have their own extended π conjugation system, which in turn can interact strongly with the main chromophore. This leads to an increase of the total conjugation without increasing the length of the chromophore and without decreasing its photochemical stability.

In order to understand the origin of charge localization on some specific molecular orbitals, local orbitals that are connected with the structure of the terminal groups, and how those orbitals influence the linear and nonlinear absorption, we synthesized

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and studied a new series of near IR symmetrical cationic polymethines with 5-butyl-7,8-dihydro-benzo[*cd*]furo[2,3-*f*]indolium terminal groups with different chain lengths (number of vinylene groups increases from $n = 1–4$). Compared to dyes with the same chain length but simpler terminal groups, such as indolium or benzo[*e*]indolium studied in previous articles [7,8], we notice a remarkably large shift of ~300 nm in their linear absorption bands to the near IR region.

We synthesized and studied two additional neutral dyes, squaraine and tetraone, with identical terminal groups and acceptor bridges in the main conjugation backbone in order to gain a better understanding of the relations between structure and nonlinear absorption properties. The nonlinear characterization has been based on detailed spectroscopic studies and focused on measuring ESA spectra over a broad spectral range and investigating their excited-state decay kinetics. We show that these dyes can satisfy two requirements important for nonlinear optical applications. First, the new dyes are characterized by sufficiently large ground state absorption cross sections to nearly completely populate the excited state (i.e., $\geqslant 10^{-18}$ cm^2) over a large portion of the visible spectrum. Secondly, their excited state absorption cross sections are of the order of 10^{-16}–10^{-15} cm^2 at the peak, which is comparable with the peak ground state absorption cross section values. This produces a large difference between excited and ground state cross sections with cross section ratios up to 100.

In this paper we will describe: (1) the electronic structure of near IR dyes along with their linear absorption and fluorescence properties (more details can be found in Ref. [16]), (2) the experimental methods used for nonlinear absorption measurements including femtosecond pump-white light continuum probe and *Z*-scans in the pico- and femtosecond time regimes, (3) a detailed analysis of the ESA spectra and their decay kinetics, (4) comparison of nonlinear properties of near IR dyes with their counterparts dyes in the visible region, and (5) quantum-chemical analyses allowing us to understand the nature of the linear absorption and ESA bands. The combination of these methods gives us information about the dye's energy level structure, which accurately predicts the nonlinear absorption properties in cyanine-like molecules.

2. Experimental methods and results

2.1. Materials and linear characterization

The molecular structures of the dyes studied in this paper are shown in Figs. 1 and 2. Their chemical names are: 5-butyl-4-[3-(5-butyl-8-methyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ylidene)prop-1-enyl]-8-methyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-5-ium tetrafluoro-borate (labeled as PD 2371); 5-butyl-4-[5-(5-butyl-8-methyl-7,8-dihydro-benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ylidene)penta-1,3-dienyl]-8-methyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-5-ium tetrafluoroborate (labeled as PD 2658), 5-butyl-4-[7-(5-butyl-8-methyl-7,8-dihydro-benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ylidene)hepta-1,3,5-trienyl]-8-methyl-7,8-dihydrobenzo[*cd*]-furo-[2,3-*f*]indol-5-ium tetrafluoroborate (labeled as PD 2716), 5-butyl-4-(3-{3-[3-(5-butyl-8-methyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ylidene)prop-1-enyl]-5,5-dimethylcyclo-hex-2-en-1-ylid- ene}prop-1-enyl)-8-methyl-7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-5-ium tetra-fluoroborate (labeled as PD 2892). These dyes differ by the length of polymethine chromophore (number of vinylene groups $n = 1–4$). Corresponding tetracarbocyanine PD 2892 includes a trimethylene bridge in the chromophore to increase

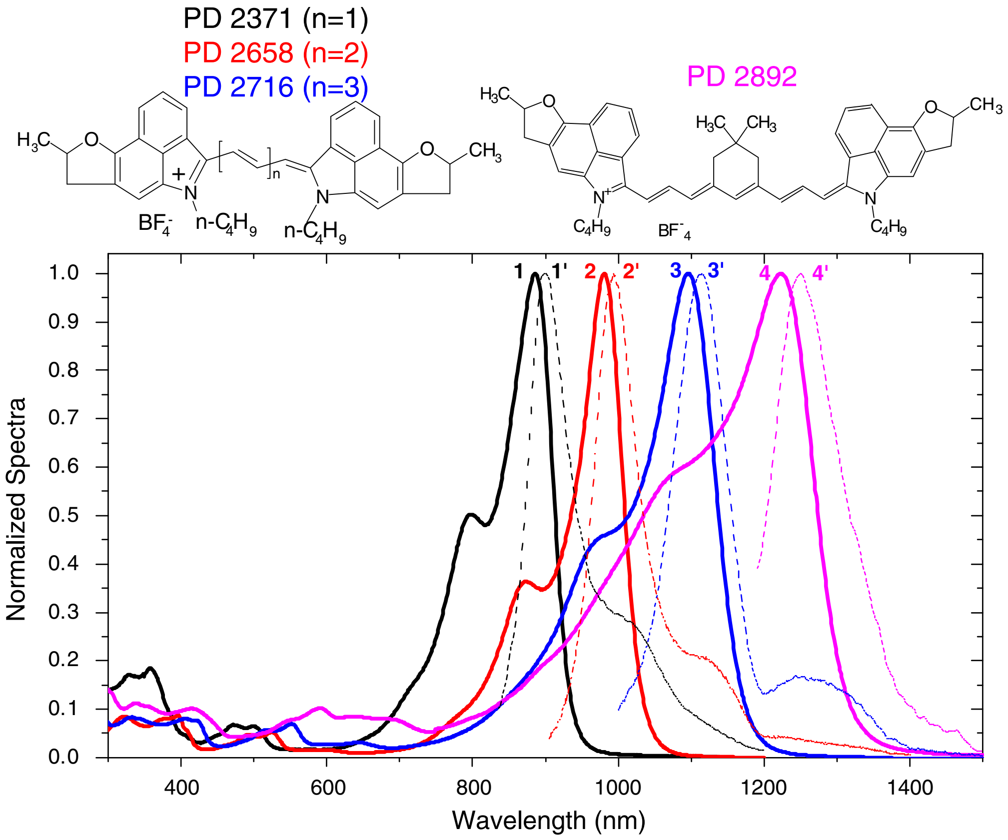

Fig. 1. Molecular structures, linear absorption, and fluorescence spectra for PD 2371 (1, 1′), PD 2658 (2, 2′), PD 2716 (3, 3′), and PD 2892 (4, 4′), respectively, in butanol. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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