

## Two-Photon Absorption at Telecommunications Wavelengths in a Dipolar Chromophore with a Pyrrole Auxiliary Donor and Thiazole Auxiliary Acceptor

Luca Beverina,<sup>†</sup> Jie Fu,<sup>‡</sup> Amalia Leclercq,<sup>†</sup> Egbert Zojer,<sup>†,§</sup> Peter Pacher,<sup>§</sup> Stephen Barlow,<sup>†</sup> Eric W. Van Stryland,<sup>‡</sup> David J. Hagan,<sup>‡</sup> Jean-Luc Brédas,<sup>†</sup> and Seth R. Marder<sup>\*,†</sup>

*School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, College of Optics and Photonics: CREOL and FPCE, and Department of Physics, University of Central Florida, Orlando, Florida 32816-2700, and Institute of Solid-State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria*

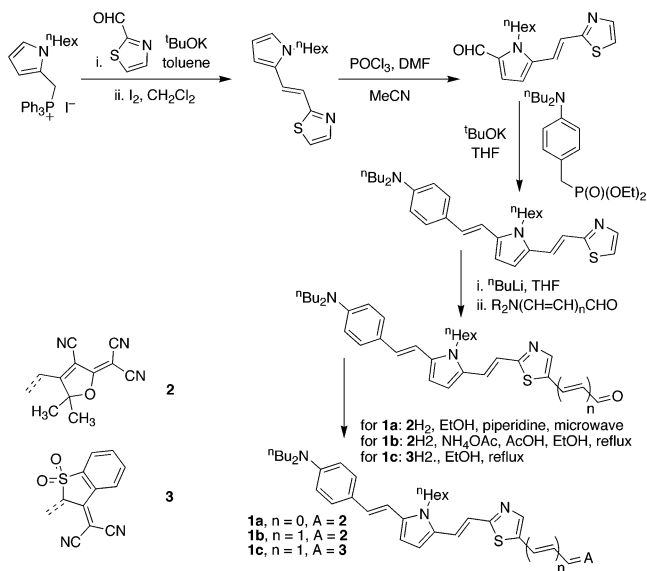
Received February 2, 2005; E-mail: seth.marder@chemistry.gatech.edu.

Two-photon absorption (2PA) in organic molecules has gained growing attention due to potential applications including optical limiting,<sup>1</sup> upconverted lasing,<sup>2</sup> fluorescence microscopy,<sup>3</sup> and microfabrication.<sup>4</sup> Recently, considerable progress has been made in developing structure–property relationships for dipolar<sup>5</sup> and quadrupolar<sup>6</sup> chromophores; large two-photon cross sections,  $\delta$ , (several hundred to several thousand GM; 1 GM =  $10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>) have been achieved throughout the visible part of the spectrum. A few studies have also included species with 2PA maxima extending into the NIR as far as 1.0  $\mu$ m, have focused on determination of  $\delta$  at 1064 nm, or have measured absorption features tailing to ca. 1.1  $\mu$ m or beyond.<sup>7</sup> However, to the best of our knowledge, there have been no measurements of molecular 2PA peaks in the NIR telecommunication wavelength range (1.3–1.55  $\mu$ m). While, in principle, species with strong 2PA in this range could be achieved using quadrupolar chromophores, dipolar species possess some attractive features. First, appropriate donor and acceptor substitution can lead to relatively low-lying charge-transfer-type one-photon absorption (1PA). Second, whereas in centrosymmetric quadrupolar species the mutually exclusive selection rules for 1PA and 2PA mean that the 2PA peak is typically seen at a photon energy greater than that corresponding to half the energy of the 1PA peak, in dipolar systems a 2PA maximum can be anticipated at half the energy of the 1PA maximum.

Dipolar species containing auxiliary donors (D') and acceptors (A') along the conjugated backbone between the primary donors and acceptors (D and A, respectively) have previously been studied as second-order nonlinear optical materials.<sup>8</sup> Here we have synthesized three new examples, incorporating for the first time the electron-rich pyrrole ring as D'. For A', we used the mildly electron-poor thiazole ring, which has previously been reported to be effective in this role.<sup>9</sup> As the primary acceptor, A, we have used the efficient and stable groups, **2**<sup>10</sup> and **3**.<sup>11</sup> As shown in Scheme 1, the final step is a Knoevenagel condensation between the acceptor group and the  $n = 0$  or 1 aldehydes. In the case of **1a**, this reaction can be conveniently and rapidly (8 min) effected under microwave conditions. However, the same conditions are unsuitable for use with the  $n = 1$  aldehyde, with **1a**, rather than the expected **1b**, being the dominant product. Hence, **1b** and **1c** were synthesized using conventional heating.

Figure 1 shows the linear spectra of **1a–1c**. Interestingly, the conjugation-length increase between **1a** and **1b** results in a slight blue-shift of the main charge-transfer transition, together with a decrease in the transition dipole moment,  $\mu_{ge}$ , whereas a red-shift

### Scheme 1



is seen with chain-length increase in many other D–A systems. The origin of this effect is unclear, but the blue-shift (although not the change in  $\mu_{ge}$ ) is reproduced qualitatively by calculations (Table 1).

The 2PA spectrum of **1a**, acquired using a pump–probe technique with a 100 fs white-light continuum source as a probe and a pump wavelength of 1800 nm (see Supporting Information for details),<sup>12</sup> is shown in Figure 2, plotted vs state energy (sum of pump and probe photon energies). The high-energy limit of the data shown was dictated by linear absorption, which precluded the use of probe wavelengths shorter than ca. 950 nm.

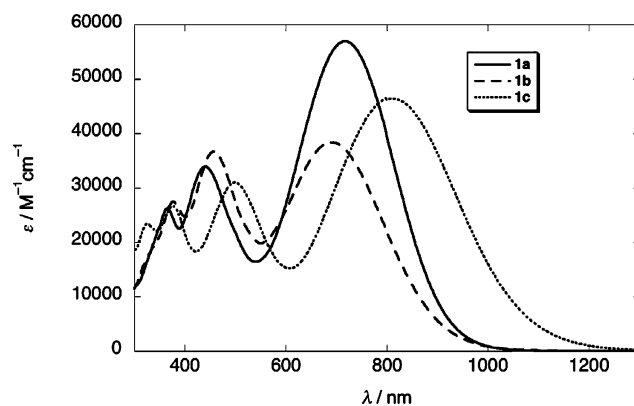


Figure 1. UV–vis–NIR absorption spectra in THF for **1a–1c**.

<sup>†</sup> Georgia Institute of Technology.

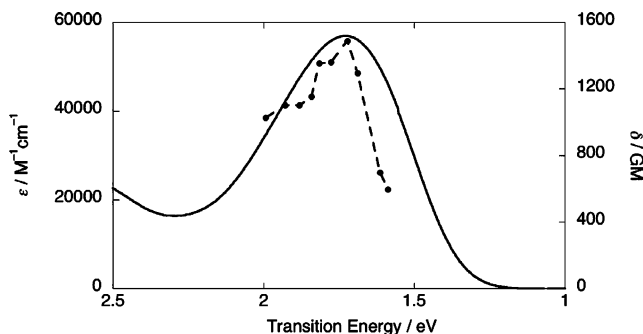
<sup>‡</sup> University of Central Florida.

<sup>§</sup> Graz University of Technology.

**Table 1.** Parameters<sup>a</sup> Characterizing the S<sub>0</sub>–S<sub>1</sub> Transitions of **1a–c** from INDO/MRDCI Calculations<sup>b</sup>

compd <sup>a</sup>	E <sub>ge</sub> /eV	μ <sub>ge</sub> /D	Δμ <sub>ge</sub> /D	δ <sub>deg</sub> /GM	δ <sub>non-deg</sub> <sup>c</sup> /GM
<b>1a</b>	2.43	15.2	15.1	752	1224
<b>1b</b>	2.47	16.2	17.7	1070	1888
<b>1c</b>	2.36	14.0	18.5	904	1113

<sup>a</sup> See text for definitions. <sup>b</sup> Alkyl groups were replaced with Me groups in the calculations. <sup>c</sup> Calculated for a pump energy chosen so that E<sub>pump</sub>/E<sub>ge</sub> is the same as the ratio between that of 1800 nm photons and the experimental value of E<sub>ge</sub>; see Supporting Information for details.

**Figure 2.** 1PA (solid line) and non-degenerate ( $\lambda_{\text{pump}} = 1800 \text{ nm}$ ) 2PA spectra (broken line) for a THF solution of **1a**.

As expected for a dipolar molecule, 1PA and 2PA access the same state, both processes being symmetry allowed. The peak transition energy corresponds to two 1.44  $\mu\text{m}$  photons, and the 2PA is also high for 1.3 and 1.55  $\mu\text{m}$  photons. The peak  $\delta$  of ca. 1500 GM is unprecedented for dipolar dyes, which often display values ranging from tens to a few hundreds of GM,<sup>5</sup> and is of similar magnitude to that of some of the most effective 2PA dyes known.<sup>6</sup> Preliminary data (see Supporting Information) also indicate that **1b** and **1c** have cross sections of comparable magnitude at transition energies similar to those of their 1PA transitions.

It is important to note that the pump–probe value of  $\delta$  refers to non-degenerate 2PA (i.e. using photons of different energies), which, due to pre-resonance enhancement effects, is anticipated to be slightly larger than the value for degenerate excitation,  $\delta_{\text{deg}}$ . We performed highly correlated quantum-chemical calculations<sup>13</sup> to gain insight into the relative magnitudes of  $\delta_{\text{deg}}$  and  $\delta_{\text{non-deg}}$  for **1a** (see Supporting Information for details). Table 1 shows the calculations overestimate the transition energies, E<sub>ge</sub> (typical for the method), but reproduce the value of  $\delta_{\text{non-deg}}$  for **1a** reasonably well.<sup>14</sup> To a first approximation within the two-state model, the large transition dipoles, μ<sub>ge</sub>, and changes in state dipole moment, Δμ<sub>ge</sub>, associated with the S<sub>0</sub>–S<sub>1</sub> transition can be held responsible for the large cross sections. The results also show significant differences between  $\delta_{\text{deg}}$  and  $\delta_{\text{non-deg}}$ ; nevertheless, the computational results clearly indicate that the cross sections for degenerate 2PA,  $\delta_{\text{deg}}$ , into S<sub>1</sub> in these species are still anticipated to be large. The differences between  $\delta_{\text{deg}}$  and  $\delta_{\text{non-deg}}$  are smallest in **1c** because it has the smallest excitation energy, resulting in reduced pre-resonance enhancement.

In summary, we have found that D–D′–A′–A dipolar chromophores can act as efficient 2PA dyes in the NIR communications frequency range. We anticipate these dyes will find applications for limiting optical power in this wavelength range and as 2PA sensitizers for NIR photorefractive composites. The exact absorption

maxima of these species can be readily tuned through structural modification of the D and A groups. Moreover, the solvatochromism of dipolar systems (e.g. **1a** shows 1PA maxima at 751 and 718 nm in in CH<sub>2</sub>Cl<sub>2</sub> and THF, respectively) means that it will be possible to tune the 2PA maxima of these species through choice of medium.

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**Supporting Information Available:** Complete refs 4b and 6a; synthetic procedures, and NMR, UV–vis–NIR, and electrochemical data for **1a–c**; computational details; details of the 2PA measurement with preliminary 2PA spectra for **1b** and **1c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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