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Extended Squaraine Dyes with Large Two-Photon Absorption Cross-Sections

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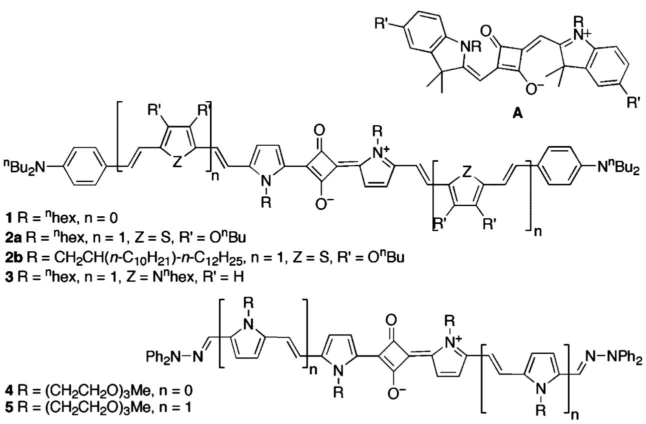
Organic materials exhibiting large two-photon absorption (2PA) cross-sections (δ) are of interest for applications including photodynamic therapy, optical pulse suppression, two-photon fluorescence microscopy, 3D microfabrication, and 3D optical data storage.[1] Structural motifs found to exhibit high δ include donor−acceptor−donor (D-A-D) conjugated species.[2] Recently, Scherer et al.[3] studied D-A-D squaraines (structure **A**, Chart 1), with indole donors bearing a variety of substituents; $\delta_{\max}$ of 200−500 GM was observed for excitation into a vibrational sublevel of the 1PA state, while a 2PA state with $\delta_{\max}$ of 300−5000 GM was observed at higher energy (photon wavelength, $\lambda^{(2)}_{\max}$ = 820−890 nm). 2PA was also studied in conjugated oligomers based on these chromophores.[4] Since extension of the conjugated π-system in symmetric chromophores has been found to increase $\delta_{\max}$ and red-shift $\lambda^{(2)}_{\max}$,[2a] we were interested in studying the 2PA properties of squaraines in which the terminal D groups were separated from the central squarylium, A, core by longer conjugated bridges. Here, we report the 2PA properties of squaraines **1**−**5** (Chart 1) in which D and A are separated by bridges composed of vinylene groups and electron-rich heterocycles.

Chart 1



1 R = ^{n}hex, n = 0
2a R = ^{n}hex, n = 1, Z = S, R' = O^{n}Bu
2b R = CH$_2$CH(n-C$_{10}$H$_{21}$)-n-C$_{12}$H$_{25}$, n = 1, Z = S, R' = O^{n}Bu
3 R = ^{n}hex, n = 1, Z = N^{n}hex, R' = H
4 R = (CH$_2$CH$_2$O)$_3$Me, n = 0
5 R = (CH$_2$CH$_2$O)$_3$Me, n = 1

1−**5** were synthesized by the condensation of the appropriate donor-substituted pyrrole species, which were obtained through Horner-based routes, with squaric acid in refluxing arene/alcohol mixtures and were obtained as pure compounds after column chromatography on silica gel.

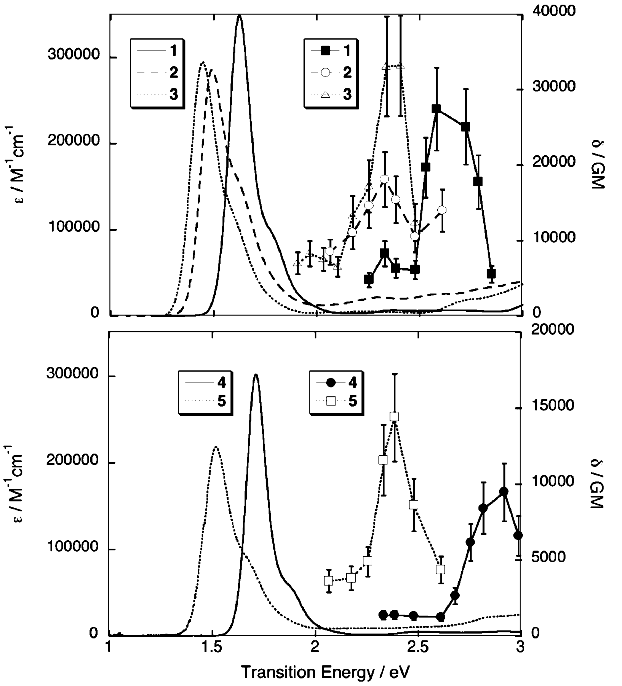


Figure 1. 1PA (lines) and degenerate (Z-scan) 2PA (data points and lines) spectra for **1** in CH$_2$Cl$_2$ and for **2a** and **3**−**5** in THF. Note that the two graphs have different δ scales and that 2PA spectra are plotted versus transition energy, i.e., twice the photon energy.

Table 1. 1PA and Degenerate 2PA Data for Squaraines in THF[a]

	1[a]	**2a**	**3**	**4**	**5**
$\lambda^{(1)}_{\max}$ (nm)	765	832	856	724	816
$\epsilon_{\max}$ (10^5 M^{-1} cm^{-1})	3.5	2.9	2.9	3.0	2.2
μ_{ge} (D)	18.9	20.4	19.7	15.8	17.2
$\lambda^{(2)}_{\max}$[b] (nm)	960	1100	1050	850	1040
$\delta_{\max}$ (10^3 GM)	27	18	33	9.5	14
$E_{ge} - (E_{ge'}/2)$[c] (eV)	0.33	0.36	0.27	0.25	0.33

[a] Data for **1** in CH$_2$Cl$_2$. [b] Photon wavelength for 2PA peak. [c] See text.

Degenerate 2PA spectra were acquired using the open-aperture Z-scan method.[5] Figure 1 and Table 1 indicate that all our chromophores, which include squaraines with amine and hydrazone donor groups, and with a variety of heterocycle-vinylene bridges, show extremely strong 2PA in the near-IR. Even if one considers the extensive π systems of these chromophores by calculating $\delta_{\max}$ *per π-electron*, one obtains values (ca. 300 GM for **2a**, **4**, **5**; ca. 600 GM for **1** and **3**) much larger than the corresponding quantities

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for D-π-D stilbenes (ca. 20 GM[2a]) and D-A-D bis(styryl)benzenes (ca. 60 GM[2b]).

For centrosymmetric chromophores, δ for degenerate 2PA between ground and 2PA excited states, denoted by the subscripts g and e′, respectively, is determined by terms of the form

$$\delta_{\mathrm{e}',3-\mathrm{state}} \propto E_{\mathrm{ge}'}^{2}\,\frac{\mu_{\mathrm{ge}}^{2}\,\mu_{\mathrm{ee}'}^{2}}{(E_{\mathrm{ge}}-(E_{\mathrm{ge}'}/2))^{2}}$$

where the e denotes an intermediate 1PA-allowed state, μ_{ge} and $\mu_{\mathrm{ee}'}$ are transition dipole moments, and the denominator is the square of the detuning energy between the 1PA state and the virtual state midway in energy between ground and 2PA states. Values of μ_{ge} and the detuning energy from the experimental 1PA and 2PA spectra are included in Table 1. Values of μ_{ge} are large, as is typical for squaraines. The detuning energies are rather small compared to those in other classes of chromophores we have studied; indeed, in many cases, measurement of 2PA at such low detuning energies is precluded by the onset of 1PA, whereas in squaraines this is possible because of the sharp 1PA absorption edges. Other chromophores with similarly small detuning energies and consequently large δ include perylene derivatives (up to 8.5×10^3 GM; 270 GM/π electron)[6] and porphyrin dimers (up to 10×10^3 GM; 200 GM/π electron).[7] The differences in $\delta_{\max}$ between **2a** and **3**, for which μ_{ge} values are similar, can be largely rationalized in terms of the differences in experimental detuning energies.

Quantum-chemical calculations were carried out for **1** and **3** (details in Supporting Information);[8] these suggest that an excited singlet state, $3A_g$, is strongly 2PA allowed, with $\delta_{\max}$ values of the same order of magnitude as observed experimentally, and lies at a similar energetic position relative to the 1PA-allowed S_1 state as the experimentally observed 2PA peaks in Table 1. The calculations also suggest that 2PA into $3A_g$ can be well-described by considering a single 3-level term (eq 1) with S_1 as the intermediate state. Consistent with the experimental result, the calculations give comparable μ_{ge} for **1** and **3** (18.4 and 20.4 D, respectively) and small detuning energies, with the smaller detuning energy for **1** (0.32 and 0.39 eV for **1** and **3**, respectively). The calculated $\mu_{\mathrm{ee}'}$ is somewhat larger for **3** (18.5 D) than for **1** (15.4 D). Although the two large (albeit not exceptional) transition dipole moments that are responsible for 2PA into $3A_g$ increase somewhat with molecular size, the resulting $\delta_{\max}$ for **1** and **3** (42 and 41×10^3 GM, respectively) are comparable, owing to the compensating change in detuning energy.

We have also investigated the third-order nonlinear optical properties of **2b**, an analogue of **2a**, which is an oil and can readily be processed into optical quality high-number-density films, to see if the proximity of the strong 2PA absorption at higher energies would lead to a strong dispersive enhancement of the third-order susceptibility, $\chi^{(3)}$.[9,10] Closed-aperture Z-scan measurements at 1.3 μm on thick (48−80 μm) films of **2b** sandwiched between two glass slides do indeed reveal a large Re($\chi^{(3)}$) value of $(6.0 \pm 0.9) \times 10^{-11}$ esu. However, open-aperture measurements indicate that there is also significant 2PA at this wavelength; the imaginary part of the susceptibility, Im($\chi^{(3)}$), was measured to be $(3.5 \pm 0.5) \times 10^{-11}$ esu,[11] which corresponds to a 2PA coefficient of $(4.6 \pm 0.7) \times 10^{-10}$ mW^{-1} and a δ at this wavelength of ca. 2100 GM. The Z-scan measurements in toluene show the magnitude of the corresponding molecular second hyperpolarizability, $|\gamma|$, to be 3.3 and 2.6×10^{-32} esu at 1.3 and 1.5 μm, respectively.[9] Again there is significant 2PA, with $\delta = 1600$ and 800 GM at 1.3 and 1.5 μm, respectively (these wavelengths corresponding to 2PA transition energies of 1.91 and 1.65 eV).[12] Although **2b** shows a reasonably large Re($\chi^{(3)}$) and $|\chi^{(3)}|$ at telcommunications wavelengths, the sizable 2PA is expected to be detrimental to performance in applications such as all-optical switching. However, these 2PA properties could be useful for optical limiting, all-optical beam stabilization, or dynamic range compression.[13]

The strong 2PA shown by **2b** in the telecommunications band is consistent with the observation of significant δ by nondegenerate solution measurements for **2a** at equivalent transition energies (see Supporting Information). At these transition energies, 2PA could arise from the low-energy tail of the $3A_g$ absorption and/or from lower energy 2PA transitions.[14]

In summary, we have synthesized stable extended bis(donor) squaraines that show extremely large δ at photon wavelengths of ca. 1 μm, close to the 1PA absorption edge. For one example, we have demonstrated a large third-order susceptibility and significant 2PA in a film at telcommunications wavelengths.

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Supporting Information Available: Complete citation for ref 2a; synthetic procedures and characterizing data; details of 2PA measurements and quantum-chemical calculations; 1PA and degenerate and nondegenerate 2PA spectra for **1−5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Other squaraine oligomers are known, including examples with pyrrole-squaraine links like to those in **1−5**; for example, see Ajayaghosh, A.; Eldo, J. *Org. Lett.* **2001**, *3*, 2595 and references therein.

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(8) The values quoted refer to MRD-CI calculations with an MO-active space of 7/7 for **1** and 11/9 for **3**, respectively The impact of the choice of the CI-active space, a comparison between CCSD and MRD-CI calculations as well as a brief discussion of conformers can be found in the Supporting Information.

(9) $\chi^{(3)}$ and γ are defined here as in Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, 1990.

(10) For examples of measurements of $\chi^{(3)}$ and γ for squaraines and for discussion of the role of 2PA resonances upon these quantities see (a) Dirk, C. W.; Kuzyk, M. G. *Chem. Mater.* **1980**, *2*, 4. (b) Dirk, C. W.; Herndon, W. C.; Cervantes-Lee, F.; Selnau, H.; Martinez, S.; Kalamegham, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am. Chem. Soc.* **1995**, *117*, 2214.

(11) $|\chi^{(3)}|$ derived from the Z-scan values of Re($\chi^{(3)}$) and Im($\chi^{(3)}$) is $(7.0 \pm 1.1) \times 10^{-11}$ esu, consistent with a value of $(6.6 \pm 0.3) \times 10^{-11}$ esu from degenerate four-wave mixing.

(12) Differences between solution and solid-state values are likely to be due to local-field effects.

(13) There are only a few reports of strong 2PA in this range: (a) Beverina, L.; Fu, J.; Leclercq, A.; Zojer, E.; Pacher, P.; Barlow, S.; Van Stryland, E. W.; Hagan, D. J.; Brédas, J.-L.; Marder, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 7282, (b) Kurotobi, K.; Kim, K. S.; Noh, S. B.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3944.

(14) Specifically, 2PA into vibrational sublevels of the 1PA state, analogous to that observed by Scherer and co-workers for squaraines with less extensive conjugation (ref 3), the possibility of which is not addressed by our calculations, or 2PA into the $2A_g$ state, for which small δ (<100 GM) are calculated for **1** and **3** (see Supporting Information).

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