Indolic Squaraines as Two-Photon Absorbing Dyes in the Visible Region: X-ray Structure, Electrochemical, and Nonlinear Optical Characterization

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Squaraines are the condensation product of electron rich molecules, usually activated arenes, π-excessive heterocycles, and heteroaromatic anhydrobases, with squaric acid.[1] They possess a sharp and intense absorption mainly localized in the red-NIR region, frequently associated with strong fluorescence.[2] These peculiar spectral features along with remarkable stability and wide molecular structure diversity promoted their exploitation in a number of technologically relevant applications including photoconductivity,[2,3] data storage,[4] light emitting field-effect transistors,[5] solar cells,[6] nonlinear optics,[7] fluorescent histological probes,[8] highly stable fluorescent near-IR dyes,[9] fluorescence patterning,[10] and photodynamic therapy.[11] Furthermore, it has been shown that squaraines behave as very efficient active materials in two-photon absorption (TPA) applications.[12] Some of us recently reported the design and synthesis of π-extended squaraines exhibiting very large TPA cross section efficiencies[13] localized in the NIR region, with peak performances above 1 μm. However, for two prominent TPA technological applications, optical limiting and two photon induced photopolymerization, shorter wavelength operational windows are required. While an ideal TPA photoinitiator should absorb at the shortest possible wavelengths to enable the best possible 3D resolution,[14] optical limiting aimed at the eye protection usually requires peak performances only in the 700−1000 nm window.[15]

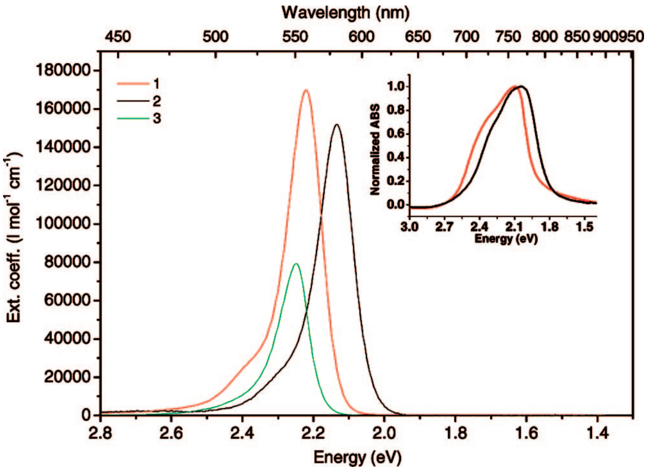

Figure 1. UV−vis absorption spectra of compounds **1**−**3** in CH_2Cl_2. Inset: compound **1** and **2** cast film normalized absorption.

Some of us proposed to combine the TPA properties of a quadrupolar dye with the reverse saturable absorption (RSA) characteristics of a fullerene derivative to achieve efficient optical limiting devices.[16] Although this approach could be successful, the limited stability and insufficient efficiency of so far employed TPA dyes represent a major issue yet to be fulfilled. Further advances along this approach require the use of new TPA materials combining (i) high transparency in the 690 nm region, where fullerene exhibits maximum RSA efficiency; (ii) enhanced dye TPA cross section; and (iii) photostability and laser damage resistance of the host matrix in which the TPA dye is embedded. In this paper, we report on the synthesis, structural characterization, and TPA properties of new indolic TPA squaraine dyes

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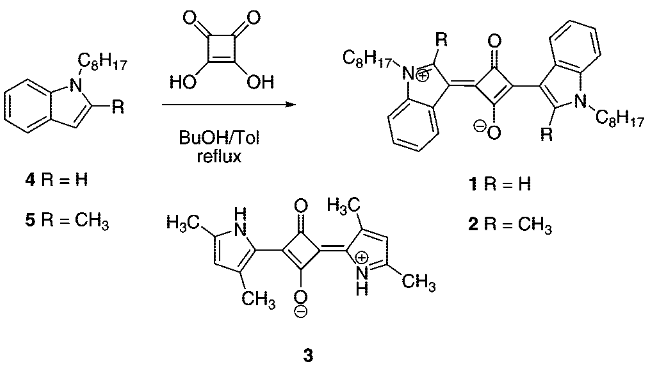
Scheme 1



1 and **2** (Scheme 1) addressing the above-mentioned problems.

The synthesis of squaraines **1** and **2** is reported in Scheme 1. They were synthesized by refluxing the appropriate indole precursor and squaric acid in a BuOH/toluene mixture under a Dean−Stark trap for the required period of time.[17] These two derivatives are the simplest improvement of the 700 nm transparent, but almost TPA inactive,[11d] parent pyrrolic derivative **3**. We will show that these dyes exhibit sizable TPA efficiencies in the 700−800 nm region.

The linear absorption spectra of derivatives **1** and **2** along with that of parent squaraine **3** are shown in Figure 1. The inset also shows the cast film solid state absorption spectra of **1** and **2**. All of these dyes possess the required transparency above 690 nm. Importantly, by analyzing the extinction coefficient values, it is evident that pyrrole benzofusion strongly enhances the oscillator strength but marginally narrows the optical gap. We previously explored different structural modifications of derivative **3**, such as the use of indolizine instead of pyrrole, to achieve dyes with enhanced TPA efficiencies. However, in all of the cases we observed a substantial contraction of the optical gap.[18]

While structures similar to **1** and **2** are mentioned in the patent literature,[19] synthetic details are vague and convincing structural characterizations are missing. Note that while the structure of derivative **2** can be straightforwardly assigned by ^{1}H NMR spectroscopy and elemental analysis, structural characterization of **1** is challenging. In fact, even if indole electrophilic substitution usually occurs at the 3 position, the regioselectivity of the reaction leading to **1** is not obvious and in any case may not be easily probed by multinuclear NMR spectroscopy. Therefore, to further confirm the molecular structure and provide additional structural characterization, single crystals of both derivatives were grown from solution. Figure 2 shows the crystal structure of **1** and **2** whereas Table S1 (Supporting Information) collects selected bond distances and dihedral angles. Clearly, the X-ray data confirms the reaction regiochemistry leading to derivative **1**. Structural analysis of **2** reveals a slight core torsion (12.43°) likely due to the steric hindrance between the indole methyl substituent and the squarate moiety. Note that only one of the two indole rings is twisted leading to a break of the *D2h* molecular symmetry.

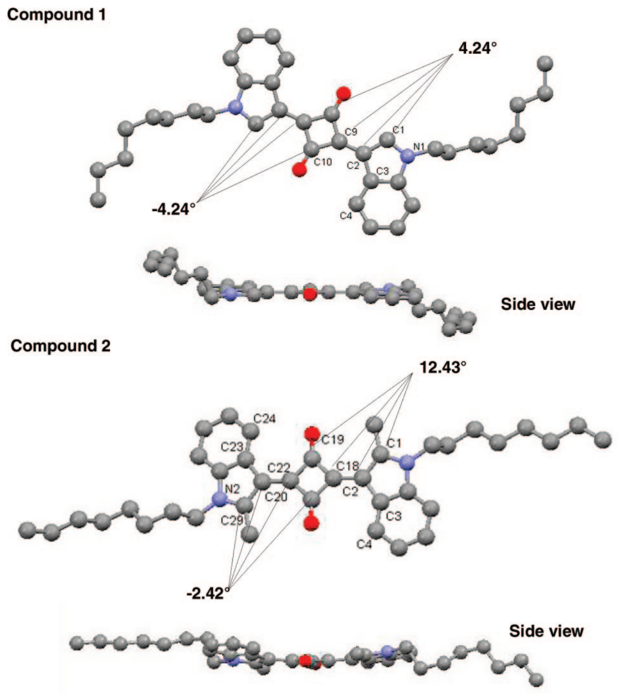


Figure 2. Crystal structure of compounds **1** (a) and **2** (b). Hydrogen atoms are omitted for clarity.

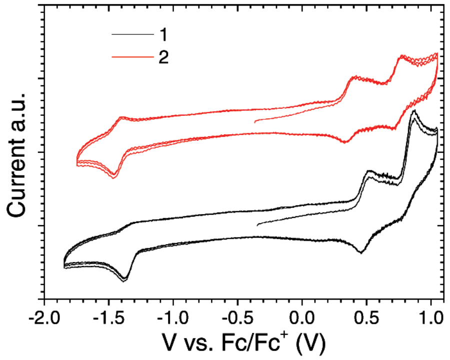


Figure 3. CV plots of compounds **1** and **2** in CH_3CN using 0.1 M tetrabutylammonium *p*-toluenesulphonate as the supporting electrolyte at a scan rate of 100 mV/s.

Cyclic voltammetry (CV) experiments were performed to probe molecular energy levels and the extent of intramolecular donor−acceptor interactions. Figure 3 shows the CV plots for **1** and **2** in acetonitrile. Both derivatives exhibit two partially reversible oxidations (compound **1**, $E_{1/2}^1 = 0.50$ V, $E_{1/2}^2 = 0.82$ V; compound **2**, $E_{1/2}^1 = 0.37$ V, $E_{1/2}^2 = 0.74$ V) and one irreversible reduction (compound **1**, $E_{pc}^{red} = -1.38$ V; compound **2**, $E_{pc}^{red} = -1.46$ V) associated with the oxidation of the electron rich indole rings and the reduction of the electron deficient squaraine core, respectively. The occurrence of two different oxidation processes in both compounds is the consequence of the strong coupling between the two indole rings, resulting from the delocalized electronic structure of these squaraines. Interestingly, dye **2** is significantly easier to oxidize than **1** due to the presence of the electron donating methyl substituents and possibly to

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(17) The complete experimental procedure, along with full NMR characterization, is reported in the Supporting Information.

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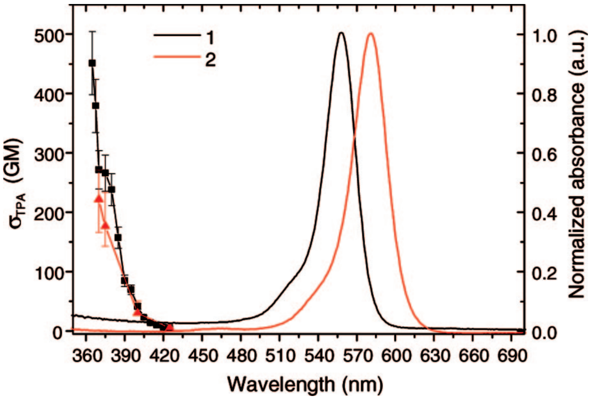

Figure 4. Linear (lines) and TPA (data points and lines) spectra in CH_2Cl_2 for compounds **1** (black) and **2** (red). TPA spectra plotted vs the halved photon wavelength corresponding to the TPA transition energy.

a reduced core planarity. Squaraines **1** and **2** can be described as a donor−acceptor−donor compounds with the two indolyl moieties acting as the electron donors and the central squarylium ring as the electron acceptor. Reduced core planarity in **2** would result in a partial decoupling of one donor from the acceptor, thus reducing the amount of charge transfer. Consequently the electron rich nature of the indole ring would be less affected by the presence of an electron withdrawing substituent, leading to the observed lower oxidation potentials. Derivative **2** is, however, harder to reduce with respect to **1**, suggesting that the presence of the methyl group in **2** also plays a significant role in the indole donor strength increase. Shortly, the observed oxidation potential decrease is likely due to both a net donor strength increase and a molecular structure torsion.

The two photon absorption properties of both derivatives were measured in the femtosecond (fs) regime using the two photon induced fluorescence (TPIF) method in the 700−850 nm range. Figure 4 shows the TPA spectra of **1** and **2** plotted versus the halved photon wavelength (corresponding to the TPA transition energy) along with their linear spectra. Table 1 summarizes the TPA cross section values of derivatives **1**−**3** along with those of 4,4′-[(9,9-dinonyl-9*H*-fluorene-2,7-diyl)bis[(1*E*)-2,1-ethenediyl-5,2-thiophenediyl-(1*E*)-2,1-ethenediyl]]bis(*N*,*N*-dioctylbenzenamine) (**4**) and 4,4′-[(9,9-dinonyl-9*H*-fluorene-2,7-diyl)bis[(1*E*)-2,1-ethenediyl-7,2-(9,9-dinonyl-9*H*-fluorenediyl)-(1*E*)-2,1-ethenediyl]]bis(*N*,*N*-dibutylbenzenamine) (**5**) measured under the same experimental conditions. The latter are among the most efficient quadrupolar TPA dyes operating in the 700−900 nm region.[20] Compounds **1** and **2** exhibit large TPA performances in the 700−800 nm target region. Within this spectral region, derivative **1** reaches a TPA cross section value as high as 450 GM, which is remarkable considering the simple molecular structure, limited π-conjugation length, and high thermal and photochemical stability.[21]

Even if compounds **4** and **5** possess larger absolute TPA cross sections, their net activity (σ_2/N_e), defined as the TPA cross section normalized with respect to the number of π electrons effectively involved in the conjugation,[22] is only ∼3−6 times larger than that of **1**. Therefore, indole-based squaraines represent a valuable and easily accessible alternative to other far more elaborate TPA dyes. Furthermore, synthetic routes to **4** and **5** are not straightforward. Dealing with the comparison of the performances of **1** and **2**, although in both cases we could not access the TPA absorption maxima, in the spectral region accessible to our experimental conditions the TPA efficiency for **1** is always larger than that of **2**. This data, along with the CV characterization and the reduction in the molar extinction coefficient, suggest a partial deviation from planarity for derivative **2** in solution too. In fact, it is well-known that any deviation from planarity in the conjugation path of a TPA dye leads to a drop in the overall performances.[20]

Table 1. TPA Performance of Derivatives 1−5

dye	λ_{max}(abs) (nm)	σ(GM)	λ_{max}(TPA) (nm)	N_e	σ_2/N_e[a]
1	558	450 ± 50	730	22	20.4
2	581	220 ± 50	750	22	10
3	552	not measurable		14	
4[20]	470	1530	880	44	124.5
5[20]	429	2960	730	56	62.0

[a] Effective number of π electrons in the conjugated system.

The most promising squaraine (**1**) was also characterized by z-scan measurements with nanosecond pulses, the experimental setup of interest for the optical limiting applications, in the 690−730 nm region. From the fitting of the open-aperture z-scan curves, the effective TPA cross section (σ_2^{eff}) is ∼10000 GM, at 700 nm, to be compared with the 6500 GM at 700 nm obtained for the quadrupolar dye *N*-methyl-2,5-bis[1-(*N*-methylpyrid-4-yl)eten-2-yl]-pyrrolo triflate (PEPEP, **6**) so far employed for this application.[23]

In summary, we have shown that it is possible to design large optical gap squaraines displaying a sizable fs regime TPA activity in the technologically relevant 700−800 nm region. Also, we unequivocally assigned, through single crystal X-ray analysis, the regiochemistry of the squaric acid condensation reaction at the 3-position of unsubstituted indole derivatives. Finally, we demonstrated that derivative **1** TPA activity in the optical limiting relevant ns regime exceeds that of one of the most promising quadrupolar derivative so far employed.

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Supporting Information Available: Crystallographic data and experimental details for the preparation of **1** and **2**; details on the TPA and cyclic voltammetry experiments. Complete ref . Thermal stability of compound **1** and **2** cast films. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available from the Cambridge Crystallographic Data Centre.

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