

Synthesis and Two-Photon Spectrum of a Bis(Porphyrin)-Substituted Squaraine

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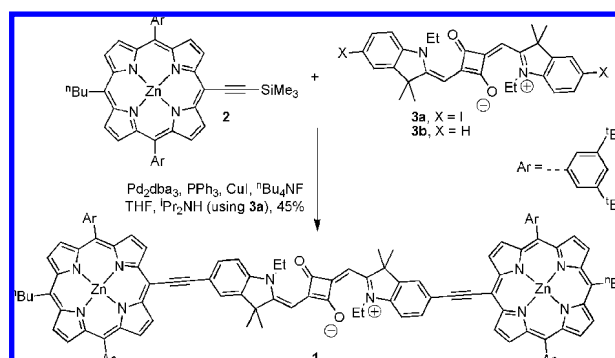
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Organic materials with large two-photon absorption (2PA) cross sections, δ , are of interest for applications including fluorescence microscopy,¹ microfabrication,² and optical pulse suppression.³ One of the design strategies that has been used to achieve large δ values is the use of π -conjugated molecules with donor–acceptor–donor (D–A–D) structural motifs.⁴ Squaraines can be considered as examples of D–A–D chromophores and have been found to exhibit large values of δ at wavelengths close to their one-photon absorption (1PA) edges,⁵ especially when bearing substituents with extended conjugation.⁶ Dimers and oligomers of conjugated zinc porphyrins have also been shown to exhibit very strong 2PA, with δ_{\max} values up to 500 times those of monomeric analogues.⁷ Moreover, linear absorption spectra of both squaraines and porphyrins exhibit bands characterized by large transition dipole moments, a key prerequisite for obtaining strong 2PA. In addition, the S_0 – S_1 transition energies of bis(indolinylidene)methyl squaraines closely match those of porphyrins, suggesting the possibility of substantial excitonic electronic coupling in a π -conjugated hybrid of these two components. On the basis of these observations, we were interested in investigating whether the electronic coupling between the constituent subunits of D–A–D bis(porphyrin)-substituted squaraines could be sufficiently strong to result in enhanced 2PA. Here we report on the synthesis and characterization of the new triad **1** (Scheme 1), in which a squaraine core is linked to zinc porphyrin donors using alkyne bridges.

Compound **1** was synthesized using in situ deprotection of the trimethylsilyl-protected meso-ethynyl-substituted porphyrin **2** followed by Sonogashira coupling with the diiodosquaraine derivative **3a** (Scheme 1). The in situ deprotection conditions were adopted because of the tendency of terminal alkyne derivatives of zinc porphyrins to undergo Glaser couplings [which would, in this case, give a bis(porphyrin)diacetylene], even without the addition of traditional alkyne-coupling reagents.⁸ Compound **1** is soluble in solvents including dichloromethane, tetrahydrofuran, benzene, and glycerols.

Compound **2** was synthesized in a fashion similar to that for previously reported porphyrin derivatives with alkynyl substituents in the meso position,⁹ with the specific substituents being chosen to facilitate solubility and recrystallization of the intermediates. The diiodosquaraine building block **3a** was synthesized by the conden-

Scheme 1. Synthesis of Compound 1



sation of squaric acid with 5-iodo-1-ethyl-3,3-dimethyl-2-methyl-eneindoline, which was obtained from its bromo analogue^{5a,6b} by bromine–lithium exchange with *n*-butyllithium followed by treatment with iodine. The noniodinated squaraine **3b**^{5a,6b} was also synthesized as a model squaraine for comparison with **1**. The structure of compound **1** was confirmed by ¹H, COSY, and ¹³C NMR spectroscopy and mass spectrometry; the characterization data are shown in the Supporting Information (SI) along with full synthetic details for **1** and its precursors.

The 1PA spectra for **1**, **2**, and **3b** are shown in Figure 1a. The spectrum of **2** is typical for a porphyrin, showing a relatively weak low-energy Q band and a more intense B (Soret) band at shorter wavelength, the splitting of which can be attributed to the lowering of symmetry by the ethynyl substituent. The absorption spectrum of **3b** shows a strong low-energy transition at 636 nm, which is typical for a squaraine of this type. The lowest-energy absorption band of **1** is intense and red-shifted by ~100 nm relative to that of **3b**, while the higher-energy features resemble the Q and B bands of **2**. All three compounds are fluorescent with small Stokes shifts; fluorescence spectra are shown in the SI.

Using density functional theory (DFT)-optimized (B3LYP/6-31G**) geometries, we calculated the 1PA and 2PA properties of **1**, following the INDO/MRD-CI methodology we successfully used previously in the case of large conjugated molecules^{6b} (see the SI). The frontier orbitals (Figure S3 in the SI) show significant delocalization across the whole molecular backbone. The 1PA calculations indicate the presence of three main peaks in the visible region, with the lowest-energy feature primarily due to a mixing of HOMO-to-LUMO and (to a lesser extent) HOMO–1-to-LUMO+1 transitions.

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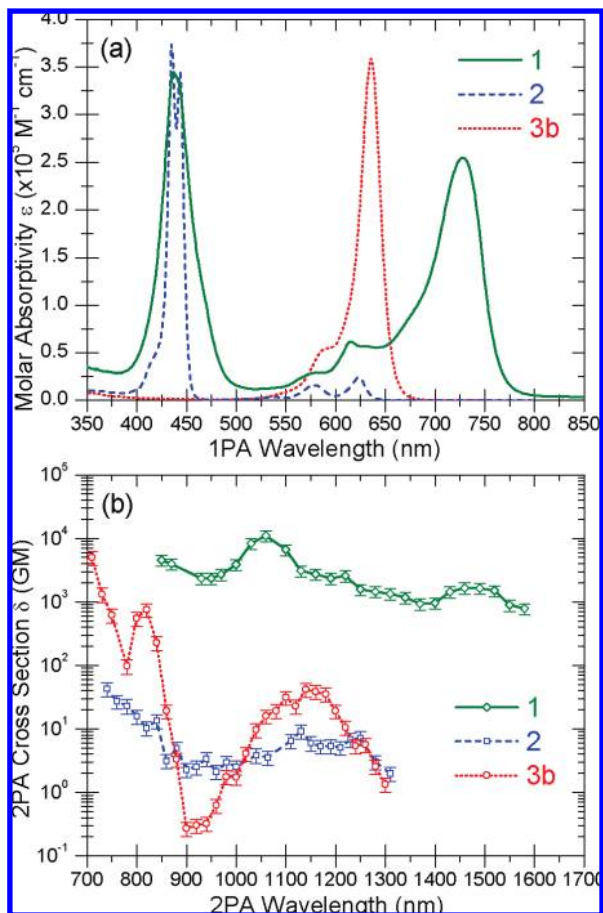


Figure 1. (a) 1PA and (b) semilogarithmic 2PA spectra of **1**, **2**, and **3b** in dichloromethane with 1% pyridine. The spectra are plotted so the transition wavelengths can be directly compared (i.e., with the 2PA excitation wavelengths twice those of the 1PA wavelengths).

2PA spectra for compounds **1**, **2**, and **3b** measured by 2PA-induced fluorescence are shown in Figure 1b. The 2PA spectrum of **3b** is very similar to that previously reported for a similar compound,^{5b} with the largest values of δ observed at wavelengths approaching the onset of 1PA, while **2** shows $\delta < 50$ GM (1 GM = 10^{-50} cm⁴ s/photon) over the investigated range, consistent with other studies showing only weak 2PA in monomeric zinc porphyrins.⁷ The δ_{\max} value of 11 000 GM measured for **1** is much larger than that for either **2** or **3b** but is similar in magnitude to those measured for several other porphyrin dimers with conjugated bridges, for which, however, the maxima are observed at somewhat shorter wavelengths.⁷ More unusually, and in contrast to the 2PA spectra of **2**, **3a**, and other porphyrin dimers,⁷ the 2PA absorption of **1** is very broad, with $\delta > 780$ GM over the entire measurable region, which includes the telecommunications range (1300–1550 nm), while **2** and **3b** exhibit $\delta < 100$ GM at all wavelengths >900 nm.

The enhancement of δ_{\max} for **1** relative to those for **2** and **3b** suggests substantial electronic coupling between the porphyrin and squaraine moieties; this idea is confirmed by the DFT frontier orbitals (Figure S3). The complexity of **1** and the porphyrin–squaraine coupling are anticipated to lead to a large number of low-lying excited states; indeed, Figure 1a indicates the presence of several 1PA states. Therefore, the broad 2PA spectrum of **1** is likely to arise from overlap of several transitions. The calculations support this idea, as they reproduce the main features of the experimental spectrum of **1**, indicating peaks with $\delta = \sim 6.9 \times 10^3$ and 9.7×10^3 GM at transition energies between those of the two strong 1PA states. The observation of large δ over a 750 nm-wide wavelength range suggests that **1** could have applications in broadband NIR pulse suppression.

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Supporting Information Available: Experimental details; ¹H NMR and COSY spectra of the aromatic region of **1**; fluorescence spectra for **1**, **2**, and **3b**; details of quantum-chemical calculations for **1**; and complete refs 2, 4a, and 6a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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