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Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons**

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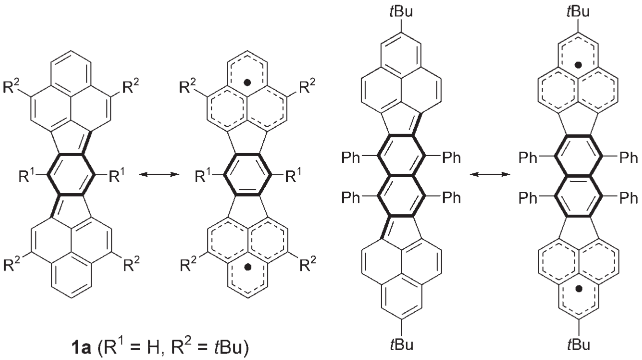
Two-photon absorption (TPA) of organic materials has attracted considerable attention owing to its growing application in various fields, such as photonics and nanotechnology.[1] Nowadays, TPA can be induced readily by using high-intensity laser pulses. Nevertheless, it is still important to explore molecules that exhibit intense TPA as this may open new pathways into its use and broaden existing TPA applications. It is also a scientific challenge to explore the limits[2] of the TPA cross section ($\sigma^{(2)}$) and to establish structure–property relationships. With these aims in mind, many research groups have done extensive research over the past decade.[3–5]

One of the most widely accepted guiding principles of molecular design for large TPA cross sections is the introduction of electron donors (D) and/or acceptors (A) to the ends of a π-conjugate system. Symmetric (or quadrupolar, D–π–A–π–D and A–π–D–π–A) and asymmetric (or dipolar, D–π–A) substitution arrangements have been tested for linear molecules with various D and A groups[3,4] and also for different π-conjugated bridges.[5] There is still no general agreement about the best arrangement for large TPA cross sections because it depends on the molecular system. However, the D–π–A–π–D arrangement has had widespread success.[3]

Another widely accepted guiding principle is the extension of electronic communication through π-conjugation[3b,6–8] and excitonic coupling.[9] Recently, huge values of TPA cross sections have been reported for various porphyrin derivatives: for example, conjugate-linked porphyrin dimers,[6] dual-strand ladder polymers,[7] fused porphyrin arrays.[8] These results show that extension of the electronic system through self-assembly and π conjugation is also a key factor in enhancing the cross sections of these systems. Moreover, enhancement is expected for branched structures because of the excitonic coupling between the arms.[9]

Through recent theoretical studies, we found that molecules with a singlet diradical nature have an enhanced third-order nonlinear optical response, and consequently TPA activity, in the intermediate region of the diradical character *y*, which takes on a value between 0 (closed shell) and 1 (pure diradical).[10] The intermediate region refers to the partial breaking of the π bond which allows the electronic distribution along the π-conjugated system to distort more easily. However, in spite of the theoretical prediction, enhanced TPA activity of singlet diradical species has not been proved experimentally, because singlet diradical species are generally unstable and decompose easily.

Very recently, we isolated some singlet diradical compounds on the basis of the thermodynamic stabilization strategy by using spin delocalization of the phenalenyl ring.[11] The compounds consist of two phenalenyl rings linked to each other by an aromatic π bridge (Scheme 1). The central benzo- and naphthoquinoid moieties contribute to large diradical character of **1** and **2**, as a result of the gain in aromatization energy of the six-membered rings of the central moieties in the diradical forms. The resonance between the closed-shell Kekulé and the diradical forms leads to a singlet ground state in the diradicaloid molecules. These compounds are stable at room temperature and can be stored even in air. We explored the TPA activity of these compound (**1a**, **1b**, and **2**) and found that these diradical hydrocarbons have much stronger TPA activity than the closed-shell π-conjugated hydrocarbons.



1a (R^1 = H, R^2 = *t*Bu)
1b (R^1 = Ph, R^2 = H)

2

Scheme 1. Resonance structures of **1** and **2**.

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The syntheses and characterization of **1a**, **1b**, and **2** have been published elsewhere.[11] These compounds exhibit intense linear absorption peaks assigned to HOMO–LUMO transitions (764 nm for **1a**, 746 nm for **1b**, and 875 nm for **2** in chloroform, Figure 1). These low-energy HOMO–LUMO transitions are characteristic for these singlet diradicals. The TPA cross sections were measured by the open-aperture Z-scan method with a femtosecond optical parametric amplifier operating at 1 kHz.[12] The compounds were dissolved in chloroform (ca. 2 mM) and placed in 1-mm quartz cuvettes.

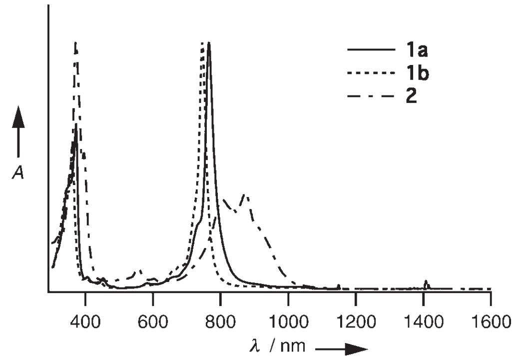

Figure 1. One-photon absorption spectra of **1a**, **1b**, and **2** in chloroform (scaled to the maximal peaks).

All sample solutions exhibited strong TPA in the range of wavelengths employed (Figure 2). Compounds **1a** and **1b** have TPA peaks at 1300 and 1425 nm with cross-sectional values of $\sigma^{(2)} = (330 \pm 40)$ and (424 ± 64) GM (1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}), respectively. The TPA peak was not clearly found for **2**; however, the cross section increases as the wavelength increases from 1300 to 1500 nm, which is the long-wavelength limit of our setup. The maximum value observed in this wavelength region is $\sigma^{(2)} = (890 \pm 130)$ GM at 1500 nm. The peak is located at a longer wavelength than 1500 nm with the $\sigma^{(2)}$ value of 890 GM or larger.

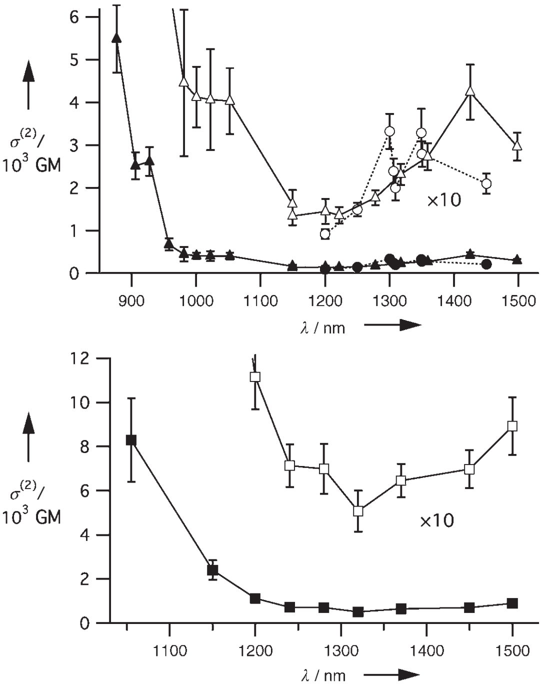

Figure 2. Two-photon absorption spectra of **1a** (circles, top), **1b** (triangles, top), and **2** (squares, bottom). The vertical scales for the open symbols are magnified by 10.

These peak or maximum cross-sectional values observed at one-photon off-resonant wavelengths are comparable to those of reported TPA chromophores with strong D or A peripheral groups. As mentioned above, the TPA cross section is greatly enhanced by introduction of strong D and A groups. For example, a cross section of 900 GM is reported for a bis(styryl)benzene substituted with dibutylamino groups,[3a] but only 66 GM for that with methyl groups.[13b] Compounds **1** and **2** exhibit such large TPA cross sections without strong D or A substituents. Theoretical calculations on model compounds with the same structure as **1** and **2** but with $R^1,R^2,R^3 = H$ give $y = 0.75$ for the model compound of **1**[10b] and 0.83 for **2**. Thus, **1** and **2** are considered to have intermediate diradical character whereby TPA activity is enhanced. Clearly, the best comparison to test the enhancement due to the intermediate diradical character would be with a condensed-ring aromatic hydrocarbon of similar size with a closed-shell structure; however, it is difficult to find such compounds. Unsubstituted hydrocarbons exhibit very weak TPA and the reports are limited.[13] As an alternative, we measured a pentacene derivative (6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), which is the condensed-ring, closed-shell aromatic hydrocarbon with the closest size to which we have access) under the same conditions. Table 1 shows a comparison of the TPA cross sections of **1**, **2**, and other hydrocarbons. The values obtained for **1** and **2** are much larger than those of the other hydrocarbons. The maximum $\sigma^{(2)}$ value of **2** is more than double the values for **1a** and **1b**, which suggests that extension of the π conjugation by replacing the benzene π bridge with naphthalene works well.

Table 1: Two-photon absorption properties of hydrocarbons.

Compound	$\sigma^{(2)}$[a] [GM]	$\lambda^{(2)}$[b] [nm]	Ref.
1a	330	1300	this work
1b	424	1425	this work
2	890[c]	1500	this work
TIPS-pentacene[d]	27	875	this work
diphenyloctatetraene	61	608	[13a]
bis(*o*-methylstyryl)benzene	66	590	[13b]

[a] Peak two-photon absorption cross section. [b] Wavelength of the two-photon peak. [c] Maximum value observed in the one-photon off-resonance region. [d] The full spectrum is available in the Supporting Information.

Moreover, the TPA cross sections of **1b** and **2** are found to increase drastically as the incident wavelength is decreased to less than 1200 nm, where one-photon absorption begins to appear (**1a** could not be measured within this region because of a shortage of sample). Also saturable absorption (SA) was observed at 960–1022 nm for **1b** and at 1050 and 1150 nm for

2. The cross section in this region was obtained after linear absorption and SA corrections.[12] The drastic increase near the tail of the one-photon absorption band is thought to arise from resonance enhancement[14] in addition to the sequential TPA process. The maximum TPA cross-sectional values observed are (5450 ± 790) GM for **1b** and (8300 ± 1900) GM for **2**. These cross-sectional values assisted by resonance enhancement are comparable to those of porphyrin derivatives with larger conjugation systems.[6a]

In conclusion, we have studied the TPA properties of three singlet diradical hydrocarbons and found that they have exceptionally large TPA cross sections for pure hydrocarbons with no strong D or A substituents. To the best of our knowledge, this result is the first evidence in support of the previous theoretical study predicting intense TPA for singlet diradical systems with intermediate diradial character and opens the way to the application of singlet diradical compounds as a new class of TPA chromophores. Compound **2** exhibits the largest cross section reported to date at short wavelengths for a pure hydrocarbon in the femtosecond timescale, although resonance enhancement and sequential TPA are probably involved. Further enhancement of the TPA cross section is expected by optimizing the diradical character with various substituents and by forming multiradical oligomer systems.[10d] Detailed study of the contribution of the diradical character to the TPA cross section is in progress.

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