Supporting Information

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Strong two-photon absorption of singlet diradical hydrocarbons

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Characterization of the compounds
Synthetic route and characterization of 1a and 1b were reported previously. Synthetic route of 2 is reported elsewhere.

Scheme S1. Resonance structures of 1a, 1b, and 2.

One-Photon Absorption Measurement
One-photon (linear) absorption spectrum was measured for the compounds dissolved in spectroscopic-grade chloroform with a commercial spectrophotometer (Shimadzu UV-3150). All compounds have the lowest-energy absorption bands in near infrared region, which is assigned to the HOMO-LUMO transition. The absorption bands of 1a and 1b are very narrow and intense. 1a shows little bathochromic shift in the absorption bands compared to 1b. The absorption band of 2 is weaker but very broader compared to those of 1. This peak shows large bathochromic shift compared to others, suggesting the extension of π-conjugation with the naphthalene bridge.

Two-Photon Absorption Measurement and Analysis

Z-scan Measurement
Two-photon absorption (TPA) was measured by the open-aperture Z-scan method. Details of our Z-scan setup were reported previously. Degenerate TPA spectrum was obtained by changing the incident wavelength, so an optical parametric amplifier (SpectraPhysics OPA-800) operating at 1 kHz pumped by a Ti:sapphire regenerative amplifier system (SpectraPhysics Spitfire, Merlin, Tsunami, and Millennia) was used as light source of the experiment. The pulse width was 120 fs typically. The pulse width was measured for each set of measurements and used for the calculation of the TPA coefficients. We put a small aperture away from the focusing lens to form an Airy-like spatial profile, which is close to a Gaussian distribution. The incident pulses can be regarded as temporally and spatially Gaussian. We
measured the open-aperture traces at several different powers of the incident beam for each wavelength as described below.

**Procedure of analysis of the open-aperture traces**

For temporally- and spatially-Gaussian pulses, the energy transmittance through a TPA media is obtained as a function of the sample position: \(^{S5}\)

\[
T(\zeta) = T_l \frac{1}{\sqrt{\pi q(\zeta)}} \int_{-\infty}^{\infty} \ln[1 + q(\zeta)e^{-x^2}]dx
\]

with

\[
q(\zeta) = \frac{q_0}{1 + \zeta^2},
\]

where \(\zeta\) is the normalized sample position defined as \(\zeta = (z-z_0)/z_R\) (\(z_0\) and \(z_R\) are the focal position and the Rayleigh range, respectively). \(T(\zeta)\) is unity at a sample position far from the focal position, i.e. \(T(\zeta \to \pm \infty) = 1\), when one-photon absorption is absent. \(T_l = (1-R)^2 e^{-\alpha^{(1)}L}\) means the transmittance by the one-photon absorption, where \(\alpha^{(1)}\) is the one-photon (or linear) absorption coefficient, \(L\) is the physical length of the sample, and \(R\) is the Fresnel reflectance at the cell surface. \(q_0\) is the two-photon absorbance\(^{S6}\) at the focal position (\(\zeta = 0\)) defined as

\[
q_0 = \alpha^{(2)} I_0 (1-R) L_{eff},
\]

where \(\alpha^{(2)}\) is TPA coefficient, \(I_0\) is the on-axis peak intensity of the incident pulse, and \(L_{eff}\) is the effective path length defined as \(L_{eff} = [1-\exp(-\alpha^{(1)}L)]/\alpha^{(1)}\). \(L_{eff}\) is reduced to \(L\) when one-photon absorption is absent.

\(q_0\) is obtained by curve fitting with Eqs. 1 and 2 to the experimental data of open-aperture trace. It is expected from Eq. 3 that \(q_0\) is in proportion to \(I_0\) (or the incident power) in the case of TPA. We determined \(\alpha^{(2)}\) from slope of the plot between \(q_0\) and the incident power. It is important to confirm the proportionality because the plot sometimes deviates from the proportionality relation due to the effect of other process such as the three-photon absorption or excited state absorption. Finally, TPA cross section \(\sigma^{(2)}\) was given by

\[
\sigma^{(2)} = \frac{\hbar \omega \alpha^{(2)} / N}{\text{the photon energy of the incident light}}.
\]

We determined TPA cross section by the absolute method described above, so we did not use the reference materials to determine the cross section. However, it is important to measure the TPA materials, the cross section of which was reported previously, in order to check if our setup and the analysis procedure works well. We always measured some previously reported compounds (including our in-house standard compounds MPPBT) as reference and have confirmed the reproducibility.\(^{S7}\)

**Correction for one-photon absorption**

Contributions of one- and two-photon absorption to the total transmittance are analytically separable as shown in Eq.1. This is due to the different nature in intensity dependence of one- and two-photon absorption: absorbance is independent of the light intensity for the former, but it is not for the latter (Eq. 3). Thus, the correction for one-photon absorption was made by putting the experimentally-obtained \(\alpha^{(1)}\) in Eqs. 1 and 3.

**Analysis in the case of saturable absorption**

Some open-aperture traces exhibit increase of transmittance (pump) around the focal position (\(z = z_0\)), which is a sign of saturable absorption (SA). We analyzed such traces with a phenomenological treatment as follows. One-photon absorption coefficient can be modified by taking account of SA of a two-level system,\(^{S8}\)

\[
\alpha^{(1)} \Rightarrow \alpha^{(1)}(I) = \frac{\alpha^{(1)}_0}{1 + I/I_S},
\]

where \(\alpha^{(1)}_0\) is SA-sensitized absorption coefficient and \(I_S\) is saturation intensity.
where $\alpha_0^{(1)}$ is intensity-independent absorption coefficient (which is identical to $\alpha^{(1)}$ in the case without SA) and $I_s$ is the saturation intensity. As $I$ is a function of the sample position for a Z-scan experiment, Eq. 5 can be written as a function of the normalized sample position,

$$\alpha^{(1)}(\zeta) = \frac{\alpha_0^{(1)}}{1 + \frac{I}{I_s(1 + \zeta^2)}}. \quad (6)$$

Thus, the transmittance by one-photon absorption including SA is obtained as

$$T_{SA}(\zeta) = (1-R)^2 \exp\left[-\alpha^{(1)}(\zeta)L\right] = (1-R)^2 \exp\left[\frac{-\alpha_0^{(1)}L}{1 + \frac{I}{I_s(1 + \zeta^2)}}\right]. \quad (7)$$

The total transmittance in presence of SA is obtained by substituting $T_i$ in Eq. 1 with $T_{SA}(\zeta)$ as

$$T(\zeta) = T_{SA}(\zeta) \frac{1}{\sqrt{\pi q(\zeta)}} \int_{-\infty}^{\infty} \ln[1 + q(\zeta)e^{-x^2}]dx. \quad (8)$$

We use Eq. 8 for curve fitting to the open-aperture traces showing SA, where $I_s$ is treated as a fitting parameter. In this case, we use $L$ instead of $L_{eff}$ in the calculation of $\alpha^{(2)}$ with Eq. 3. This treatment seems inconsistent because $L_{eff}$ is also affected by SA according to the definition. However, the rigorous treatment under coexistence of SA and TPA gives no simple analytical equation that can be used for curve fitting, so we adopted this phenomenological approach. Using $L$ instead of $L_{eff}$ for Eq. 3 causes underestimation of $\sigma^{(2)}$ because $0(\alpha^{(0)} = \infty) < L_{eff} < L(\alpha^{(0)} = 0)$, so the values determined by using this procedure can be the minimum limit of the $\sigma^{(2)}$.

**Analysis of the data of 1a**

The solution of 1a (2.81 mM) in chloroform was measured at wavelengths between 1200-1450 nm, where one-photon absorption is negligible. At all wavelengths we measured, depression of transmittance (dip) was observed around the focal position for each open aperture traces. Curve using Eq. 1 fits the experimental data very well. A typical example is shown in Figure S1A. The $z_R$ is obtained to be 6-8 mm from the curve fitting. TPA absorbance $q_0$ obtained by the curve fitting shows a good proportionality (Figure S1B) against the incident power varying from 0.1 to 1.4 mW (corresponding to $I_0$ of 20-170 GW/cm² approximately). $\alpha^{(2)}$ was obtained from the slope of each plot and $\sigma^{(2)}$ was calculated by using Eq. 4.

![Figure S1](image_url)

**Figure S1.** (A) Open-aperture Z-scan traces at different incident powers of 1a in chloroform at the incident wavelength of 1500 nm. The dots are experimental data and the gray lines are fitting curves. The power increases as shown with the arrow. (B) Power-dependence of the two-photon absorbance $q_0$ at several different wavelengths.

**Analysis of the data of 1b**
The solution of 1b (1.98 mM) in chloroform was measured at wavelengths between 880-1450 nm. This wavelength range is divided into three regions based on the pattern of the recorded open-aperture traces: Region 1 (880-930 nm) where a dip at the focal point was observed with existence of one-photon absorption (Figure S2A), Region 2 (960-1022 nm) where overlap of dip and bump was observed with existence of one-photon absorption (Figure S2B), and Region 3 (1050-1450 nm) a dip was only observed again but without one-photon absorption (Figure S2C).

**Figure S2.** Open-aperture Z-scan traces at different incident powers of 1b at 880 (A), 960 (B), and 1425 nm (C). The power is increased as shown with the arrows. The dots are the experimental data and the gray lines are the fitting curves.

In Region 1, the transmittance at the off-focus position ($z = 40$ or 90 mm) is much smaller than unity because of strong one-photon absorption; however, a bump, which is a sign of SA, was not observed at the focal position. The dip at the focal position ($z = 65$ mm) became deeper as increasing incident power. We used Eq.1 with the one-photon absorption correction for curve fitting of the open-aperture traces of this region. In Region 2, one-photon absorption is still significant at the concentration of the sample solution. A bump was observed at a low incident power but it gradually turns to a dip as the incident power increases. This change of the trace is interpreted as follows; SA is significant at a low power, but then TPA becomes dominant at a high power. We used Eq. 8 for the curve fitting of the traces of this region. In Region 3, the one-photon absorption is negligible and only a dip was observed. We adopted Eq. 1 with keeping $\alpha^{(1)} = 0$ for the curve fitting. The $z_R$ obtained from the curve fitting of the data of each region is 7-10 mm.

TPA absorbance $q_0$ obtained from the curve fitting shows a good proportionality for all regions as shown in Figure S3A and S3B. The incident power was varied from 0.1 to 0.7 mW (corresponding to $I_0$ of 15-100 GW/cm$^2$ approximately). $\alpha^{(2)}$, then $\alpha^{(2)}$, were obtained by the procedure described in the above sections.
**Figure S3.** Power-dependence of two-photon absorbance $q_0$ of 1b in chloroform at some different wavelengths.

**Analysis of the data of 2**

The solution of 2 (2.24 mM) in chloroform was measured at wavelengths between 840-150 nm. This wavelength range is divided into two regions as in the case of 1b. In the shorter wavelength region (1055-1150 nm), a bump was observed at a low incident power and then it turns to a dip as the power increases. The transmittance of the off-focus part also increased simultaneously. This suggests that SA occurs around the focal position at the low power and then the saturation increases for all the z-positions as the power increases. At the same time, TPA occurs around the focal position where the light intensity is higher than other z-positions. The curve fitting with Eq. 8 gave good results to reproduce the recorded traces at each wavelength in this region (Figure S4A). In the longer wavelength region (1200-1500 nm), one-photon absorption is negligible and only a dip was observed around the focal position, so we used Eq. 1 for the curve fitting of the traces (Figure S4B). The $z_R$ obtained from the curve fitting of the data of each region is 9-12 mm.

**Figure S4.** Open-aperture Z-scan traces of 2 at different incident powers at 1150 nm (A) and at 1500 nm (B). The dots are the experimental data and the gray lines are the fitting curve. The power increased as shown with the arrows.

TPA absorbance $q_0$ obtained from the curve fit shows a good proportionality at all wavelengths we measured as shown in Figure S5A and S5B. The incident power was varied from 0.1 to 1.0 mW (corresponding to $I_0$ of 15-140 GW/cm$^2$ approximately). $\alpha^{(2)}$, and then $\sigma^{(2)}$, were obtained as the procedure described in the above sections.
Figure S5. Power-dependence of two-photon absorbance $q_0$ of 2 in chloroform (2.24 mM) at different wavelengths.

Measurement of TIPS-pentacene
TIPS-pentacene (6,13-bis(triisopropylsilylethynyl)-pentacene) was also measured under the same experimental condition for comparison. TIPS-pentacene from Prof. J. Anthony was used as received. As the sample, TIPS-pentacene solution in tetrahydrofuran (18.4 mM) was used.

Scheme S2. Structure of TIPS-pentacene.
The dip was observed around the focal position for each open aperture trace measured at wavelengths from 700 to 1200 nm. The theoretical curve using Eq. 1 fits the recorded traces well at all wavelengths. Very good proportionality was obtained between the TPA absorbance obtained from the curve fit and the incident power at all wavelengths. The obtained TPA spectrum is shown in Figure S6.

Figure S6. TPA spectrum of TIPS-pentacene in tetrahydrofuran.
The cross section increases with decreasing the wavelength shorter than 800 nm and the maximum value is obtained at 700 nm ($\sigma^{(2)} = 35$ GM). Since the one-photon absorption lasts up to around 700 nm, this
values are under influence of by the resonance enhancement. On the other hand, two sharp peaks were observed for 800-900 nm, where the one-photon absorption is absent. The larger peak located at 874 nm have $\sigma^{(2)} = 27 \pm 3$ GM, which is the maximum peak value observed in the non-resonant region of the one-photon absorption.

References

S6 From the analogy with the absorbance of one-photon absorption ($A = \alpha^{(1)} L$), we call $q_0$ “TPA absorbance”.
S8 R. L. Sutherland, Handbook of Nonlinear Optics, 2nd Ed.; Marcel Dekker; New York, 2003; Chapter 7, 463.