**Supplementary Information for**

# Strong two-photon absorption and its saturtion of self-organized dimer of an ethynylene-linked porphyrin tandem

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## 1. Theoretical models for the saturation of two-photon transition

The transmittance data with various incident optical intensity taken from the open aperture Z-scan traces at the focal point ($z$ = 0 mm) shows significant deviation from the theoretical model in which saturation of two-photon transition is not taken into account (Model 0, Figure S1). Therefore, the saturation term is phenomenologically introduced to understand the observed data. For Model 1, the saturation term is introduced as the same way as for the saturable absorption for one-photon transition. In Model 2, the saturation term has square dependence against the optical intensity.

**Model 0**

$$\beta(I) = \beta \quad \text{(i.e., treated as constant.)}$$

**Model 1**

$$\beta(I) = \frac{\beta}{1 + I/I_s}$$

**Model 2**

$$\beta(I) = \frac{\beta}{1 + \left(I/I_s\right)^2}$$

Here, $\beta$ is two-photon absorption coefficient and $I_s$ is the saturation intensity. The other formulas for calculating the transmittance through a two-photon active media with temporally and spatially Gaussian laser pulse are the same as reported elsewhere.[S1] Model 1 does not give a satisfactory fit, but Model 2 gives a good fit to the measured data with $I_s$ = 40.5 GW cm$^{-2}$ (Figure S1). This is reasonable because the population of the sample molecules in the ground state is expected to decrease with square dependence against the optical intensity because of the two-photon transition. Therefore, it is justified that the intense two-photon transition caused the observed saturation.

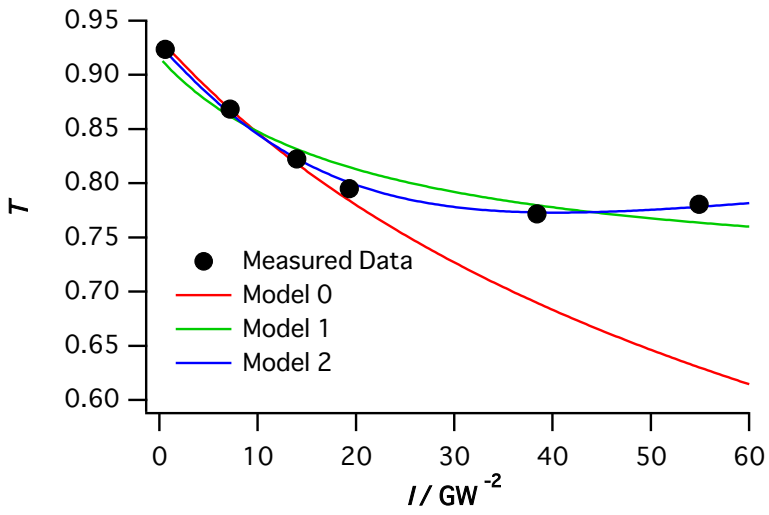


Figure S1. Optical intensity $I$ dependence of the transmittance $T$ of **1** in 1,1,2,2-tetrachloroethane (0.12 mM) at 918 nm at the focal point (z = 0 mm) (solid circle, same data in Figure 4A) with theoretical best fits based on **Models 0** ($\beta$ = 0.31 cm/GW), **Model 1** ($\beta$ = 0.31 cm/GW, $I_s$ = 30.8 GW cm$^{-2}$), and **Model 2** ($\beta$ = 0.31 cm/GW, $I_s$ = 40.5 GW cm$^{-2}$).

**2. Analysis of the Z-scan traces**

In Figure S2, the open-aperture Z-scan traces at various wavelengths except 822 and

918 nm, which are shown in the manuscript (Figure 3 and 4). The theoretical equations used [S1] assume that the sample has one- and two-photon absorptions and the saturation of the one-photon absorption for the temporally and spatially Gaussian laser pulses. The analysis was performed for the data with negligible saturation of the two-photon absorption, in order to make the curve fitting analysis as simple as possible for more reliability. The results of the analysis are summarized in Figure 5 as spectrum.

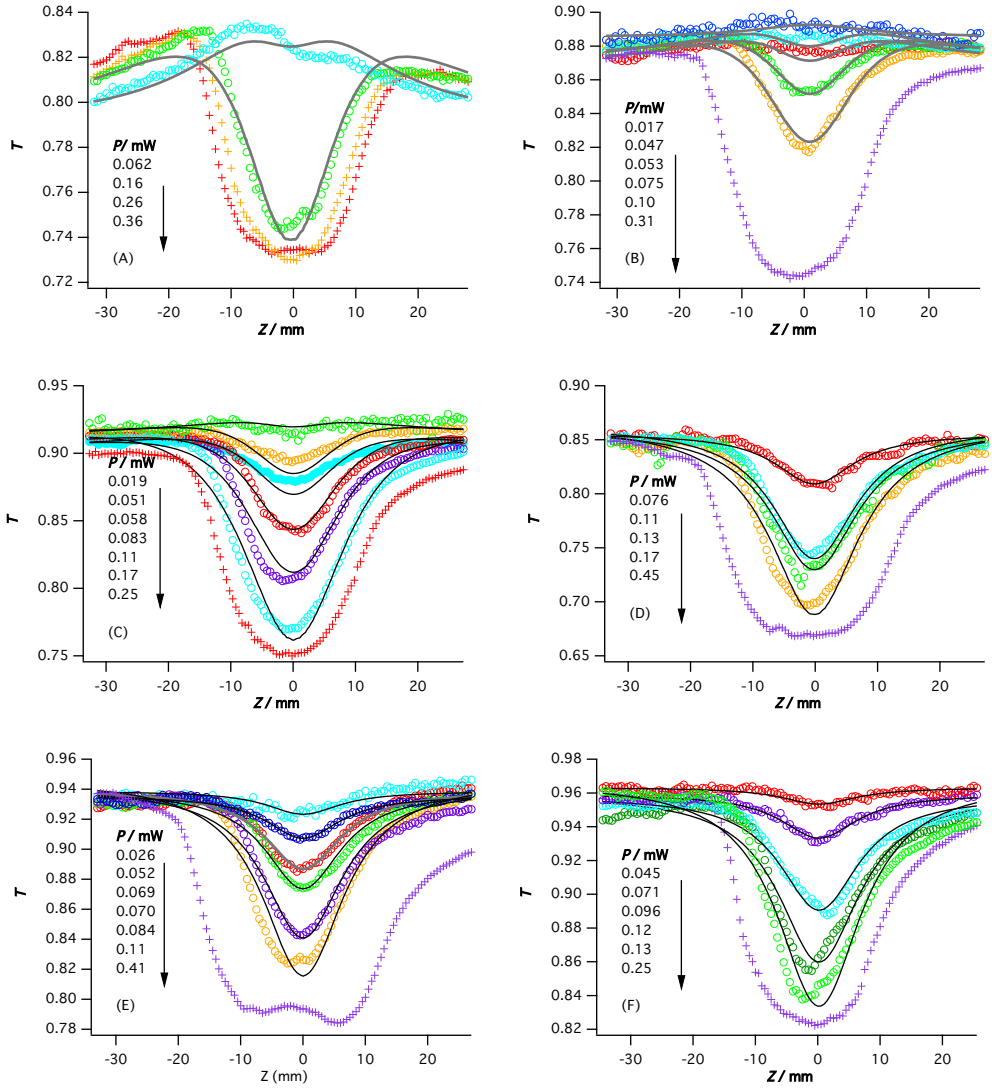


Figure S2. The Z-scan traces of **1** in 1,1,2,2-tetrachloroethane (0.12 mM) at (A) 835 nm, (B) 855 nm, (C) 875 nm, (D) 893 nm, (E) 905 nm, and (F) 940 nm. Solid curves are theoretical fits and the open circles are the corresponding data. The crosses are the data that show significant saturation of the two-photon transition and did not use for the analysis.

**Reference**

S1. Supplementary Information of M. Morisue, K. Ogawa, K. Kamada, K. Ohta, Y. Kobuke, *Chem. Comm.* 2010, **46,** 2121–2123.