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Charge transfer induced enhancement of near IR two-photon absorption of 5,15-bis(azulenylethynyl) zinc(II) porphyrins

Kil Suk Kim,[a] Su Bum Noh,[a] Takayuki Katsuda,[b] Shuji Ito,[c]

Atsuhiro Osuka*,[b] and Dongho Kim*,[a]

[a]*Department of Chemistry, Yonsei University, Seoul 120-749, Korea*

[b]*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.*

[c]*Department of Material Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan.*

*To whom it may correspondence should be addressed.

E-mail: osuka@kuchem.kyoto-u.ac.jp; dongho@yonsei.ac.kr

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Two-photon Absorption Cross-Section ($\sigma^{(2)}$). The TPA experiments were performed using the open-aperture Z-scan method (Figure S1) with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a 5 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Ge/PN photodiode (New Focus) as intensity reference, and the other was used for the transmittance studies. After passing through an f = 10 cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell was 1 mm. The transmitted laser beam from the sample cell was then probed using the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 60 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)},$$

where α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient β, the TPA cross-section $\sigma^{(2)}$ (in units of 1 GM = 10^{-50} $cm^4 \cdot s/photon \cdot molecule$) of a single solute molecule sample can be determined by using the following relationship:

$$\beta = \frac{\delta N_A d \times 10^{-3}}{h\nu},$$

where N_A is the Avogadro constant, d the concentration of the TPA compound in solution, h is Planck's constant, and υ is the frequency of the incident laser beam. So as to satisfy the condition of $\alpha_0 l \ll 1$, which allows the pure TPA $\sigma^{(2)}$ values to be determined using a simulation procedure, the TPA cross-section value of AF-50 was measured as a reference compound; this control was found to exhibit a TPA value of 50 GM at 800 nm.

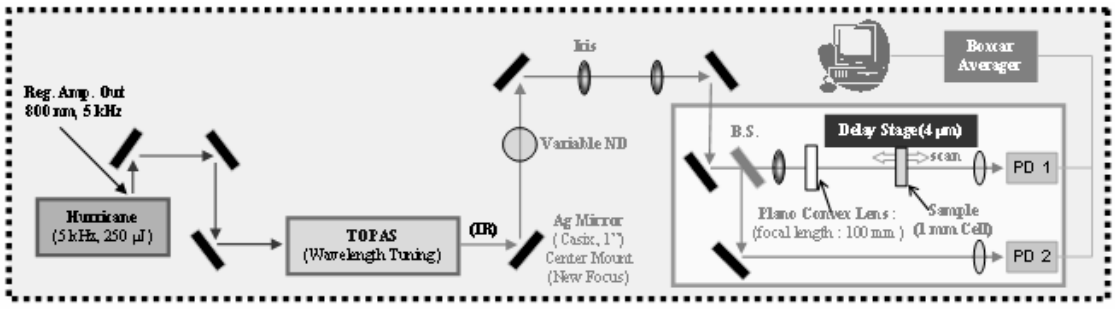

Figure S1. Schematic diagram of femtosecond open-aperture Z-scan set-up