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
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, \(I_o\), ranged from 40 to 60 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient \(\beta\) can be obtained by curve fitting to the observed open aperture traces with the following equation:

\[
T(z) = 1 - \frac{\beta I_o (1 - e^{-\alpha_o})}{2\alpha_o (1 + (z/z_o)^2)},
\]

where \(\alpha_o\) is the linear absorption coefficient, \(l\) the sample length, and \(z_o\) the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient \(\beta\), the TPA cross-section \(\sigma^{(2)}\) (in units of 1 GM = 10\(^{-50}\) cm\(^4\)-s/photon-molecule) of a single solute molecule sample can be determined by using the following relationship:
\[ \beta = \frac{8N_A d \times 10^{-3}}{h \nu}, \]

where \( N_A \) is the Avogadro constant, \( d \) the concentration of the TPA compound in solution, \( h \) is Planck’s constant, and \( \nu \) is the frequency of the incident laser beam. So as to satisfy the condition of \( a_0 l \ll 1 \), 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