THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2005, *109,* 2996−2999
Published on Web 03/15/2005

Large Two-Photon Absorption (TPA) Cross-Section of Directly Linked Fused Diporphyrins

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Received: February 11, 2005; In Final Form: March 4, 2005

The excited state dynamics and two-photon absorption properties of four novel triply linked porphyrin dimers in toluene have been investigated. The fused porphyrin dimers exhibit extremely increased two-photon absorption cross-section values (12 000−15 000 GM) compared with porphyrin monomers owing to much enhanced π-electron delocalization throughout the porphyrin dimer ring.

I. Introduction

Recently, organic molecules with large nonlinear optical susceptibilities have attracted much attention due to the flexibilities in molecular design and the ease of fabrication.[1] It has been known that the π-electron delocalization throughout the molecular framework gives rise to large optical nonlinearities such as intensity-dependent refractive index and nonlinear absorption. In this regard, the rigid flat structure of porphyrins and phthalocyanines and their derivatives makes them ideally suited as components for optical nonlinear materials.[2,3] The other well-known organic nonlinear optical material is one-dimensional π-conjugated polymer chain, of which π-electron conjugation along the chain gives rise to large optical nonlinearity.[4] From this, it can be inferred that by linking porphyrin and phthalocyanine molecules into oligomers the extended delocalization of π electrons into the neighboring molecules can further enhance their optical nonlinearities.[5,6] Previously, it was reported that the real and imaginary parts of $\chi^{(3)}$ are strongly amplified for ladder-type conjugated Zn(II)porphyrin trimer linked by alkyne groups, which results in 5×10^4 GM per macrocyle at 1064 nm.[7]

In this context, the connection of as many molecules as possible with a completely flat structure (as long as its synthetic strategy is not so outrageous) is highly desirable, which would lead to the maximization of π-electron conjugation. In line with this strategy, the triply linked fused porphyrin arrays, which have been synthesized by connecting two additional β positions from the adjacent porphyrin moieties in the directly linked porphyrin arrays, can be a good candidate for possible future application as molecular nonlinear optical and electronic materials.[8] In this study, we have explored the excited-state dynamics of fused porphyrin dimers with various central metals by femtosecond transient absorption measurement (**T2Zn**, **T2Cu**, **T2FB**, and **T2Ni**; inset of Figure 1). The central metals of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** are Zn, Cu, metal-free, and Ni, respectively. Furthermore, we have examined their two-photon absorption (TPA) properties to find the relationship between the central metals and their π-electron delocalization extended throughout the porphyrin dimer ring.

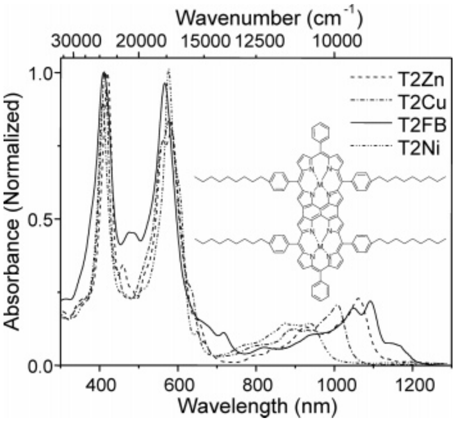

Figure 1. Absorption spectra of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** in toluene at room temperature. The inset shows the molecular structures of various fused porphyrin dimers.

II. Experimental Section

Synthesis. The details of synthetic and purification procedures of fused porphyrin dimers were given elsewhere.[8,9] Basically,

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10.1021/jp050747h CCC: $30.25

the oxidative double-ring closure (ODRC) reaction of meso–meso linked porphyrin dimers yields the corresponding fused porphyrin dimers. The ODRC reaction was conducted by refluxing a solution of *meso*, *meso*-diphenyl-capped meso–meso linked porphyrin array in toluene in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and scandium trifluoromethanesulfonate. This type of ODRC reaction was nicely applied to longer fused porphyrin arrays.

Measurement of TPA Cross-Section Values. The TPA cross-section values were measured by an open-aperture Z-scan method with wavelength tunable 130 fs pulses at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane) (Supporting Information). Sufficiently high power pulses easily afford the power density enough for TPA process without tight focusing, which eliminates unwanted nonlinear effects such as self-focusing and white-light continuum generation. All of the samples were measured with 10^{-4} M in toluene except an AF-50 (3.3 mM in benzene).

III. Results and Discussion

Figure 1 shows the UV/vis/IR absorption spectra of fused diporphyrins in toluene normalized at the 23 800–24 600 cm^{-1} region. The absorption bands of fused porphyrin dimers are roughly categorized into three distinct well-separated subgroups in near UV, visible, and NIR regions. The near UV absorption bands remain nearly at the same position as that of porphyrin monomer with significant broadening. The fused porphyrin dimers exhibit much stronger exciton coupling in the Soret bands along with a red-shift of the Q-bands to the IR region of 900–1200 nm due to much enhanced π-electron delocalization (Figure 1).[10] As a consequence, the Q-bands can be utilized as a ladder state for TPA transition to reach the density of states at near UV to the blue region, providing effective two-photon allowed excited states.

An interesting observation is nonlinear transmittance at NIR excitation around 1100 nm, which corresponds to absorption saturation instead of two-photon absorption (Supporting Information, Figure S1). Furthermore, the saturable absorption was found at wavelengths longer than 1200 nm. Typically saturable absorption is observed when ground state depletion and/or final state filling occur. In our case, saturable absorption is observed when the number of two-photon allowed higher-lying excited states is not sufficient in comparison with the number of intermediate one-photon allowed states though we cannot observe two-photon allowed state directly by conventional absorption measurements.

The TPA cross-section $\sigma^{(2)}$ values of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** exhibit approximately 12 000–15 000 GM at 800 nm where linear absorption is not so significant (Figure 2). We also measured the TPA cross-section value of AF-50 as a reference compound which exhibits 50 GM at 800 nm. This value is roughly consistent with 30 GM measured by Prasad's group.[11] Thus, fused diporphyrins show at least 2 orders of magnitude larger TPA cross-section values than AF-50.[12] Overall, fused diporphyrins have much larger TPA cross-section values in comparison with the previously reported ones for directly linked orthogonal porphyrin oligomers,[5] self-assembled porphyrin tetramer,[13] porphyrin dimers,[14] and porphyrin diacid aggregates[15] (Table 1).

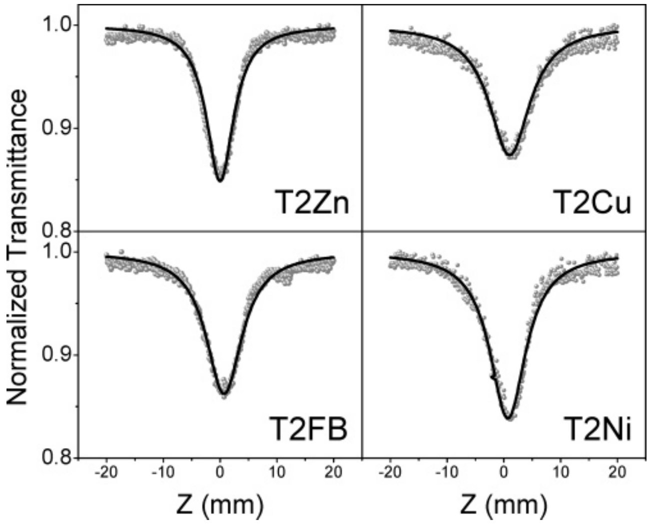


Figure 2. Open-aperture Z-scan traces (circles) of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** in toluene measured under the same experimental conditions. The sample concentration is 0.10 mM. The peak irradiance at the focal point is 80 GW/cm^2 at 800 nm. The solid lines are the best fitted curves of experimental data.

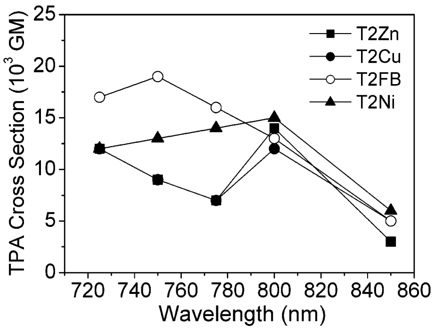


Figure 3. Two-photon absorption spectra in 720–850 nm region of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** in toluene. The solid lines are just a guide for the eye. In the case of **T2FB** (open circles), there might be large errors in the TPA cross-section values in the 720–750 nm region due to a contribution of relatively strong linear absorption near the low-energy Soret band edge.

TABLE 1: TPA Cross-Section $\sigma^{(2)}$ (GM) of T2Zn, T2Cu, T2FB, T2Ni, and Some Other Porphyrin Systems Measured by Femtosecond and Picosecond Laser Pulses

sample	$\sigma^{(2)}$ (GM)	wavelength (nm)	pulse width	solvent	ref
T2Zn	14000	800	130 fs	toluene	this work
T2Cu	12000	800	130 fs	toluene	this work
T2FB	13000	800	130 fs	toluene	this work
T2Ni	15000	800	130 fs	toluene	this work
AF-50	50	800	130 fs	benzene	this work
self-assembled porphyrin tetramer	7600	887	120 fs	$\mathrm{CHCl_3}$	13b
ZnOEP	4.4	780	150 fs	toluene	16
$\mathrm{H_2TPP}$	15	780	150 fs	toluene	16
$\mathrm{Bu_4TAP}$	70	780	150 fs	toluene	17
$\mathrm{(NO_2Ph)_8TAP}$	1600	770	150 fs	benzene	17
ethyne-bridged porphyrin dimer	3000–10000	820–890	100 fs	$\mathrm{CH_2Cl_2}$	14
$\mathrm{H_4TPPS^{2-}}$ aggregates	900	812	160 fs	water	15
$\mathrm{(Zn_n\mathbf{3})_2{\cdot}Bipy_n}$	50000	1064	50 ps	$\mathrm{CHCl_3}$	7

The TPA spectra of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** in the 720–850 nm region indicate that two-photon allowed states should exist in 370–410 nm which corresponds to the high-energy Soret band region in the two exciton-split Soret bands of diporphyrins (Figures 1 and 3). This feature is regarded as an analogous result observed in other porphyrin systems such as the self-assembled porphyrin tetramer,[13] porphyrin dimers,[14] and porphyrin diacid aggregates.[15] In general, the TPA state is often found in the Soret band or higher energy band regions

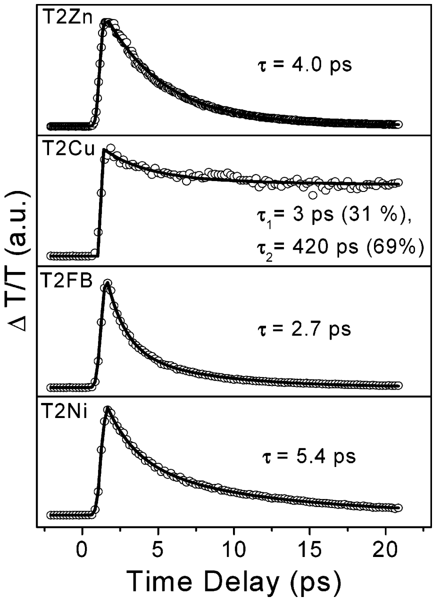


Figure 4. Ground-state bleaching recovery dynamics of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** after photoexcitation at 400 nm. The fast recovery dynamics within 10 ps were observed except for **T2Cu**, which indicates ultrafast internal conversion process to the ground state.

for porphyrin monomers and porphyrin oligomers including self-assembled porphyrin tetramer,[13] porphyrin dimers,[14] and porphyrin diacid aggregates.[15] In those cases, the excitation energy should be below the Q-band energy to reach the two-photon allowed state located near the Soret band, because the Q-bands exist in visible region which is higher than intermediate states. In our case, however, porphyrin monomers are triply linked to form fused dimers so that π-electron delocalization is very efficient throughout the porphyrin dimer ring as compared to other porphyrin molecules, resulting in the red-shift of Q-bands to the near-IR region. The excitation energy should be higher than the Q-band to reach the two-photon allowed states located near the high-energy Soret band, because the two-photon intermediate states lie between the low-energy Soret band and Q-band. Accordingly, upon absorption of a photon an electron is promoted to intermediate states, which then a second photon is absorbed either directly by S_1-S_n transition or following intersystem crossing the photon is absorbed by T_1-T_n transition. In the other case, the two-photon absorption occurs simultaneously to reach the higher S_n levels without stepwise excited-state absorption.

We have also investigated the excited-state dynamics by transient absorption measurement to explore the relationship between the two-photon absorption processes and excited-state dynamics. The time-resolved spectroscopic investigations reveal that the photoexcited states of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** are short-lived with average lifetimes of 4.0, 290, 2.7, and 5.4 ps, respectively, and thus the population of excited triplet state is very inefficient (Figure 4).[10] The relatively long lifetime for the fused Cu(II)porphyrin dimer compared with other fused dimers is presumably due to the decay of the tripmultiplet states formed efficiently from the photoexcited doublet states. The spin-multiplet states seem to be produced in fused the Cu(II)-porphyrin dimer through electronic mixing between the odd electron in d_{z^2} orbital of the Cu(II) d^9 system and the normal singlet and triplet porphyrin ring (π, π^*) states, which can be inferred from the photophysics of Cu(II)porphyrin monomer.[18] Although the porphyrin ring (π, π^*) states are likely to be the lowest excited states for Zn(II) and free-base fused porphyrin dimers, it is unclear for Ni(II) porphyrin dimer whether the porphyrin ring (π, π^*) state or metal (d, d) state is the lowest excited state.[19] Nevertheless, the relatively short excited state lifetimes for the fused dimers studied here lead us to consider only three levels in the interpretation of our TPA phenomena especially measured by the femtosecond Z-scan method. For resonant two-photon state, the following simple equation can explain the enhanced optical nonlinear properties of fused diporphyrins

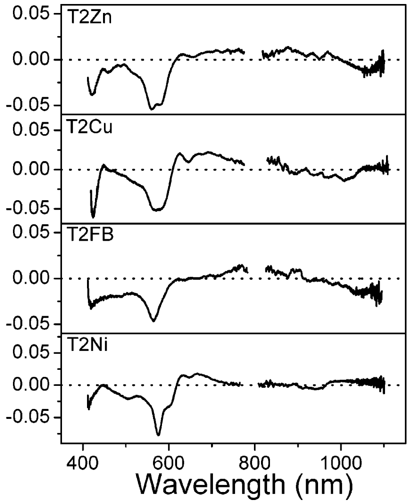


Figure 5. Transient absorption spectra of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** in toluene at zero time delay between pump and probe pulses.

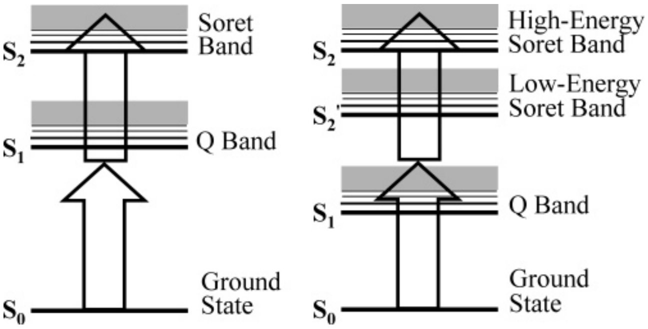
$$\delta(\omega) \propto [M_{01}^2/(\omega_{01} - \omega_L)^2][M_{12}^2/\Gamma_{02}] \qquad (1)$$

where M_{01} and M_{12} represent the ground- and excited-state transition moments, respectively, Γ_{02} is the line width of the resonant two-photon state, and ($\omega_{01} - \omega_L$) is the energy difference between the one-photon state and the measurement frequency. The spectral features in 720−850 nm in the TPA spectra of various fused dimers indicate the possibility of stepwise two-photon absorption as S_1 manifolds as a ladder, because there exists a broad and featureless S_1-S_n absorption band in the same region (Figure 5).[10] However, the contribution to the large TPA values at 800 nm by the S_1-S_n transition is not so significant as revealed by the femtosecond transient absorption spectra of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni** (Figure 5). Thus, the contribution by the excited state absorption can be avoided effectively as often superimposed in the case of nanosecond pulse excitation.[20] In this study, considering the relatively weak excited-state absorption and short S_1 state lifetimes for fused dimers, the observed TPA values can be assigned to the contribution by true TPA phenomena corresponding not to stepwise two-photon absorption but to simultaneous two-photon absorption in three-level energy diagram (Scheme 1). Consequently, the enhanced optical nonlinear properties of fused diporphyrins indicate the effective π-electron delocalization in both one- and two-photon near-resonant states. From the TPA cross-section values of **T2Zn**, **T2Cu**, **T2FB**, and **T2Ni**, it is noteworthy that the central metal dependence is negligible, suggesting that only π-electron delocalization through the diporphyrin skeleton and the completely flat structure are the determining factors in optical nonlinear properties.[21]

IV. Conclusions

This work demonstrates that the dimerization of transition metal porphyrins in a completely flat manner leads to a large enhancement ~10^3 of TPA cross-section values compared with

SCHEME 1: Three-Level Energy Diagram of Various Porphyrin Derivatives; (a) Other Porphyrins (Self-Assembled Porphyrin Tetramer,[13] Porphyrin Dimers,[14] and Porphyrin Diacid Aggregates[15]), (b) Fused Porphyrin Dimers (T2Zn, T2Cu, T2FB, and T2Ni)



their constituent monomers due to a very efficient π-electron delocalization throughout the porphyrin dimer ring. The transient absorption spectral features as well as the relatively short excited-state lifetimes of fused porphyrin dimers suggest the TPA processes contributed by simultaneous two-photon absorption via S_1 manifolds as intermediate states. Overall, the fused porphyrin dimers have proved to be a strong candidate for future applications in nonlinear optical materials. Currently the TPA measurements for fused porphyrin arrays are underway to explore much enhanced optical nonlinear properties by elongation of π-conjugation pathways through the framework of fused porphyrin arrays.

Acknowledgment. The work at Yonsei University was supported by the National Creative Research Initiative Program of the Korea Science and Engineering Foundation, Korea. The work at Kyoto University was supported by International Innovative Center, Kyoto University (KU-IIC) (Industry/University Alliance), Japan.

Supporting Information Available: The experimental details for transient absorption and TPA cross section measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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