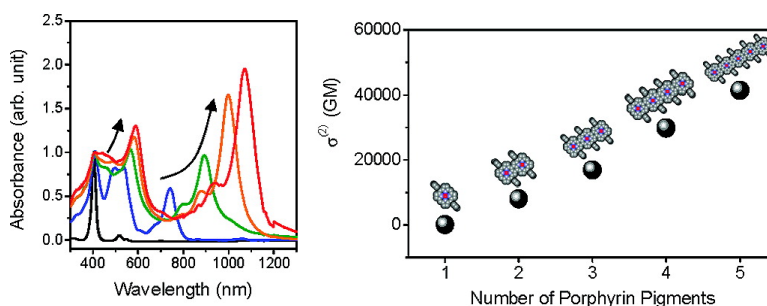Communication

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Photophysics of *meso-β* Doubly Linked Ni(II) Porphyrin Arrays: Large Two-Photon Absorption Cross-Section and Fast Energy Relaxation Dynamics

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During the past decade, porphyrin assemblies linked in a conjugative manner have emerged as a new class of molecules to exhibit extremely large two-photon absorption (TPA) cross-section values.[1] In the highly conjugated porphyrin arrays, molecular planarity and types of linkages to control π-delocalization length have been recognized as important factors to determine TPA values.[2] More specifically, butadiyne-bridged porphyrin arrays ensure the coplanarity and π-conjugation between neighboring porphyrin rings exhibiting an increase in TPA cross-section values.[3] Another extreme case is to prepare completely fused porphyrin structures to enhance the π-conjugation length and molecular planarity throughout the molecular framework of porphyrin arrays.[4] In our previous work, we observed that the lowest HOMO−LUMO transitions are continuously red-shifted up to the mid-IR region as the number of porphyrin pigments increases in the *meso−meso, β−β, β−β* triply linked Zn(II) porphyrin arrays.[5] The TPA cross-section values become very large ($\sim 10^5$ GM for triply linked Zn-(II) porphyrin pentamer), which is also consistent with the elongation of the π-conjugation pathway throughout the entire porphyrin arrays.[4a] However, the resonance one-photon contribution to TPA values cannot be totally eliminated because one-photon absorption occurs in the whole spectral region. In this regard, the determination of the authentic TPA cross-section values is still in question and practical applications are somewhat hampered.

As continuous efforts to explore new molecules for large TPA properties, we have synthesized another type of fused porphyrin arrays, *meso-β* doubly linked Ni(II) porphyrin arrays (**DLNi*n***, *n* = 2−5), which can be good candidates for useful nonlinear optical materials (Figure 1a).[6]

Similar to triply linked arrays, bands II and III were red-shifted in the steady-state absorption spectra of **DLNi*n*** as the overall molecular length increases (Figure 1b and Table 1). Bands II possess excitonic-like characteristics similar to low-energy Soret bands in *meso−meso* directly linked porphyrin arrays (Supporting Information). On the contrary, the positions of bands III were red-shifted due to the elongation of π-conjugation pathways through entire porphyrin macrocycles which was well described by a particle-in-a-box model (Figure 2a) and intensified by symmetry lowering effect on the basis of Gouterman's four-orbital model.[5a,7] The absorption spectra of doubly linked porphyrins are similar to each other regardless of central metal ions (Ni, Zn, Cu, and Pd), which indicates the overall features of absorption bands arise not from substituted Ni(II) ion but from doubly linked porphyrin macrocycle.[6b]

TPA cross-section values for band III of **DLNi*n*** in CHCl₃ were measured by an open-aperture Z-scan method using NIR femto-second optical pulses. Two-photon excitation wavelengths were carefully chosen to be free from any contribution of one-photon
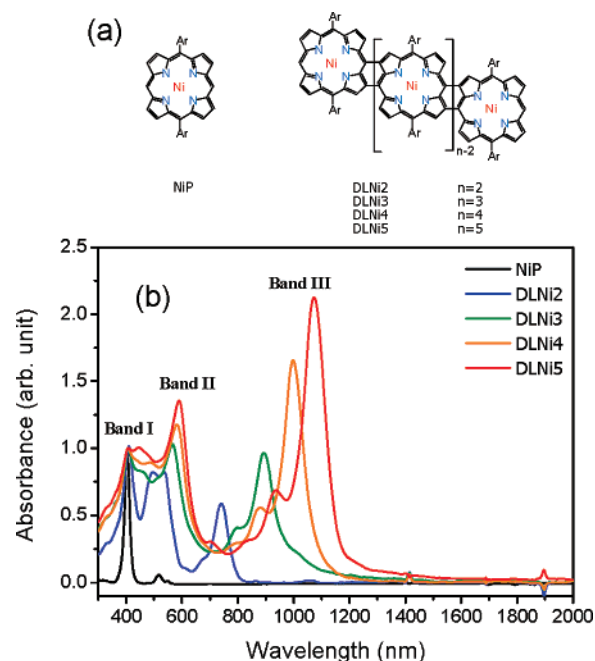

Figure 1. (a) Molecular structure of 5,15-bisaryl-substituted Ni(II) porphyrin monomer and *meso-β* doubly linked Ni(II) porphyrin arrays (Ar = 3,5-di-*tert*-butylphenyl) and (b) steady-state absorption spectra in CHCl₃. Small peaks at 1400 and 1900 nm are artifacts from the stabilizer in the solvents.

Table 1. Absorption Maxima, TPA Cross-Section Values, and Transient Absorption Decay Parameters

	absorption (nm)					
sample	Soret (high)	Soret (low)	Q(1,0)	Q(0,0)	$\sigma^{(2)}$ (GM)[a]	τ (ps)[b]
NiP	404		517	547	<100	
DLNi2	411	538	676	741	8000 ± 200	3.2 ± 0.1
DLNi3	408	567	797	892	16900 ± 500	5.1 ± 0.1
DLNi4	408	583	879	996	29900 ± 600	5.8 ± 0.2
DLNi5	408	590	936	1075	41400 ± 800	8.8 ± 0.3

[a] TPA cross-section values were measured at 800, 1400, 1700, 1900, and 2100 nm for **NiP**, **DLNi2**, **DLNi3**, **DLNi4**, and **DLNi5**, respectively. [b] Pump and probe wavelengths used in TA experiments were 550 and 530 nm, respectively, for **DLNi2**. TA decay signals were probed at 540 nm with photoexcitation at 580 nm for other arrays.

excitation (Table 1). In the case of **NiP**, we measured a very small TPA cross-section value of less than 100 GM, which agrees with the fact that various porphyrin monomers have TPA cross-section values of less than 200 GM for Q-bands.[1a] However, the TPA cross-section values for doubly linked porphyrin arrays increased from ~ 8000 to $\sim 41\,400$ GM as the molecular length of arrays increases from **DLNi2** to **DLNi5** (Figure 2b). This feature reflects that the TPA values are strongly associated with the effective π-conjugation

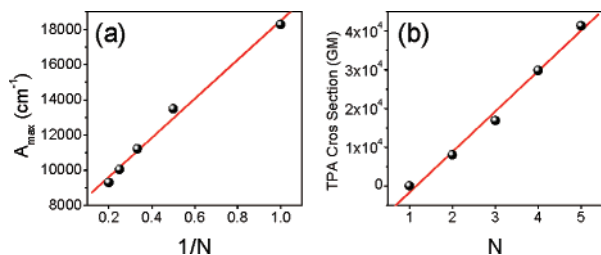[†] Yonsei University.
[‡] Kyoto University.

Figure 2. (a) Plot of absorption maxima (A_{max}) of bands III as a function of reciprocal numbers of porphyrin subunits ($1/N$) based on particle-in-a-box model and (b) TPA cross-section values of doubly linked Ni(II) porphyrin arrays as a function of the number of porphyrin moieties (N) in $CHCl_3$.

lengths. Strong enhancement of TPA properties as a function of the number of porphyrin pigments seems to originate from large polarizability due to effective π-delocalization through the two meso-β direct linkages. Triply linked Zn(II) porphyrin arrays show extremely large TPA cross-section values (e.g., 12 000 and 93 000 GM for dimer and tetramer, respectively) which have, however, a possibility of overestimation since one-photon absorption contribution could not be eliminated in the whole vis−NIR absorption region.[4a] We believe that the TPA value of ∼41 400 GM ($\sigma^{(2)}/n$ = ∼8000 GM, TPA cross-section values per subunit) in **DLNi5** is the largest one among the covalently linked and supramolecular assembled conjugated porphyrin array systems ever investigated without any one-photon absorption contribution.[1a] In addition, the effect by central metal ions on the TPA properties seems to be negligible in **DLNi***n* because it was found that butadiyne-bridged porphyrin dimers[3b] and triply linked porphyrin dimers[4b] metalated by Zn, Cu, and Ni have similar TPA cross-section values.

To seek for a relationship between the TPA values and the energy relaxation dynamics, we have carried out femtosecond TA experiments for **DLNi***n*. Temporal profiles of femtosecond transient absorption changes show ultrafast energy relaxation dynamics within a few picosecond time scale (Supporting Information). Interestingly, the decay times become slower from 3.2 (**DLNi2**) to 8.8 ps (**DLNi5**) as the number of porphyrin units increases (Table 1). In other types of porphyrin arrays, the lifetimes of lowest excited states become shorter as the number of porphyrin moieties increases, mainly due to the acceleration of nonradiative processes caused by reduced HOMO−LUMO energy gap for singly and triply linked Zn(II) porphyrin arrays.[5a,8] In **DLNi***n*, on the other hand, the energy relaxation processes are somewhat complicated since various CT (MLCT and LMCT) and (d,d) states caused by the central d^8 Ni-(II) ion exist below the $^1(\pi,\pi^*)$ states of the porphyrin macrocycle.[9] In Ni(II) porphyrin monomers, after photoexcitation at the Q-state, highly vibrationally excited (d,d) states are formed by rapid internal conversion processes within <200 fs and relaxed by vibrational cooling processes within a few tens of picoseconds (Supporting Information). Numerous CT, ^{1}(d,d), and ^{3}(d,d) states of the Ni(II) ion act as ladder states for fast energy relaxation. Observed decay times in TA measurements should not correspond to the lifetimes of the (d,d) state but to vibrational cooling times in (d,d) states because the lifetimes of (d,d) states in Ni(II) porphyrins are longer than a few hundreds of picosecond.[10,11] In **DLNi***n*, the energy of the lowest $^1(\pi,\pi^*)$ states becomes lower in going from **DLNi2** to **DLNi5** without a change in the energy of (d,d) states. Higher vibrational modes possess greater density of acceptor modes for energy transfer than the lower energy modes, leading to faster deactivation rates by vibrational cooling processes.[10] Thus vibrational cooling processes become faster for shorter arrays since the

large energy gap between the lowest $^1(\pi,\pi^*)$ and (d,d) states results in an excess of vibrational energy in (d,d) states. On the basis of theoretical predictions and experiments for Ni(II) porphyrins, we can conclude that CT and (d,d) states do not affect the TPA efficiency, reinforcing that the TPA is the instantaneous and simultaneous two-photon absorption process through a virtual ladder state to reach the higher excited two-photon allowed states. Nevertheless, under our TPA measurement conditions, the CT and (d,d) states of **DLNi***n* are energetically lower than the virtual ladder states for TPA measurements.[9−11] Accordingly, the enhancement of TPA cross-section values as the number of porphyrin pigments increases in **DLNi***n* is mainly determined by the degree of elongation of π-conjugation lengths and the relaxed selection rule for TPA transition due to symmetry lowering as seen in the intensified bands III in the absorption spectra.

In summary, the large TPA cross-section values of **DLNi***n* were obtained without one-photon absorption contribution. CT and (d,d) states play an important role in energy deactivation processes as intermediate ladder states. These results will provide us with useful information on future applications based on porphyrins as molecular building blocks.

Supporting Information Available: Experimental details on femtosecond Z-scan and TA measurements, electronic natures of absorption bands, Z-scan curves, temporal profiles of femtosecond TA and schematic energy relaxation diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kadish, K. M.; Smith, K. M.; Guilard, R. *The Porphyrin Handbook*; Academic Press: Oxford, UK, 2003; Vols. 1−20. (b) Drobizhev, M.; Stepanenko, Y.; Rebane, A.; Wilson, C. J.; Screen, T. E. O.; Anderson, H. L. *J. Am. Chem. Soc.* **2006**, *128*, 12432.
(2) (a) Zhang, T.-G.; Zhao, Y.; Asselberghs, I.; Persoons, A.; Clays, K.; Therien, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 9710. (b) Ogawa, K.; Ohashi, A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Am. Chem. Soc.* **2003**, *125*, 13356.
(3) (a) Screen, T. E. O.; Thorne, J. R. G.; Denning, R. G.; Bucknall, D. G.; Anderson, H. L. *J. Am. Chem. Soc.* **2002**, *124*, 9712. (b) Hisaki, I.; Hiroto, S.; Kim, K. S.; Noh, S. B.; Kim, D.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5125.
(4) (a) Ahn, T. K.; Kim, K. S.; Kim, D. Y.; Noh, S. B.; Aratani, N.; Ikeda, C.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2006**, *128*, 1700. (b) Kim, D. Y.; Ahn, T. K.; Kwon, J. H.; Kim, D.; Ikeue, T.; Aratani, N.; Osuka, A.; Shigeiwa, M.; Maeda, S. *J. Phys. Chem. A* **2005**, *109*, 2996.
(5) (a) Cho, H. S.; Jeong, D. H.; Cho, S.; Kim, D.; Matsuzaki, Y.; Tanaka, K.; Tsuda, A.; Osuka, A. *J. Am. Chem. Soc.* **2002**, *124*, 14642. (b) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79.
(6) (a) Tsuda, A.; Nakamura, Y.; Osuka, A. *Chem. Commun.* **2003**, 1096. (b) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304.
(7) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.
(8) Kim, Y. H.; Jeong, D. H.; Kim, D.; Jeoung, S. C.; Cho, H. S.; Kim, S. K.; Aratani, N.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 76.
(9) (a) Drain, C. M.; Gentemann, S.; Roberts, J. A.; Nelson, N. Y.; Medforth, C. J.; Jia, S.; Simpson, M. C.; Smith, K. M.; Fajer, J. F.; Shelnutt, J. A.; Holten, D. *J. Am. Chem. Soc.* **1998**, *120*, 3781. (b) Kim, D.; Kirmaier, C.; Holten, D. *Chem. Phys.* **1983**, *75*, 305.
(10) (a) Eom, H. S.; Jeoung, S. C.; Kim, D.; Ha, J.-H.; Kim, Y. R. *J. Phys. Chem. A* **1997**, *101*, 3661. (b) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Zimin, M.; Rodgers, M. A. J.; Matsumoto, S.; Ono, N. *Inorg. Chem.* **2005**, *44*, 6609.
(11) (a) Liao, M.-S.; Cheiner, S. *J. Comput. Chem.* **2002**, *23*, 1391. (b) Barends, E. J.; Ricciardi, G.; Rosa, A.; van Gisbergen, S. J. A. *Coord. Chem. Rev.* **2002**, *230*, 5.

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