ORGANIC
LETTERS

2009
Vol. 11, No. 14
3080−3083

Meso-β Doubly Linked Zn(II) Porphyrin Trimers: Distinct *anti*-versus-*syn* Effects on Their Photophysical Properties

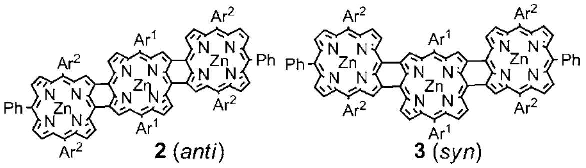
Toshiaki Ikeda,[†] Naoki Aratani,[†] Shanmugam Easwaramoorthi,[‡] Dongho Kim,*,[‡] and Atsuhiro Osuka*,[†]

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, and Spectroscopy Laboratory for Functional π-electronic Systems and Department of Chemistry, Yonsei University, Seoul 120-749, Korea

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

Received May 25, 2009

ABSTRACT



Meso-β **doubly linked Zn(II) porphyrin dimer 1 and *anti*- and *syn*-trimers 2 and 3 were synthesized by DDQ−Sc(OTf)$_3$ oxidation of the corresponding *meso-β* singly linked porphyrin precursors. The absorption and fluorescence spectra and TPA cross-section values of 2 and 3 are distinctly different, reflecting their molecular shapes.**

Extensively π-conjugated porphyrin arrays have attracted considerable attension in light of their possible applications to organic conducting materials, nonlinear optical (NLO) materials, and near-infrared dyes.[1−6] One of the promising candidates are porphyrin tapes that have planar structures and highly π-conjugated networks as a consequence of two or three covalent linkages.[7−10] Recently, our group has explored two types of porphyrin tapes: *meso-meso*, $\beta-\beta$, $\beta-\beta$ triply linked porphyrin tapes[9] and *meso-β*, *meso-β* doubly linked porphyrin tapes.[10] The former tapes are exceptional molecules which exhibit enhanced Q-band-like transitions that are extremely red-shifted deeply into the IR region and large two-photon absorption (TPA) cross-section values.[9] While the latter arrays are also interesting in view of the progressively enhanced and red-shifted absorption bands as well as certainly large TPA cross-section values,[10] only scattered studies have been reported so far, due mainly to synthetic difficulty. *Meso-β* doubly linked porphyrin arrays have been limited to the Ni(II) porphyrin case, since they were synthesized from oxidative oligomerization of a 5,15-diaryl Ni(II) porphyrin, in which a_{1u} HOMO of Ni(II) plays a central role for coupling regiochemistry. This synthetic strategy allowed the isolation of only *anti* isomers in low yields (Scheme 1). Although the corresponding *meso-β* doubly linked Zn(II) porphyrin analogues are interesting molecules for their ground-state and excited-state electronic properties, such molecules have not been synthesized. Our attempts to convert the *meso-β* doubly linked Ni(II) por-

---

[†] Kyoto University.

[‡] Yonsei University.

(1) (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377. (b) Chou, J.-H.; Nalwa, H. S.; Kosal, M. E.; Rakow, N. A.; Suslick, K. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, Chapter 41.

(2) (a) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366–370. (b) Arnold, D. P.; Heath, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 12197–12198.

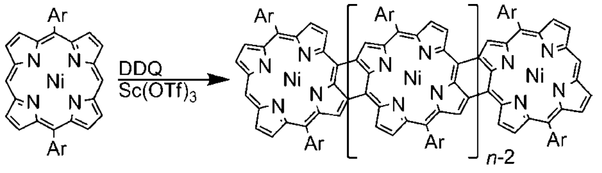
(3) (a) Lin, V. S. Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105–1111. (b) LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497–1503.

(4) Wytko, J.; Berl, V.; McLaughlim, M.; Tykwinski, R. R.; Schreiber, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J. P.; Jones, W. E. *Helv. Chim. Acta* **1998**, *81*, 1964–1977.

(5) (a) Anderson, H. L. *Chem. Commun.* **1999**, 2323–2330. (b) Taylor, P. N.; Wylie, A. P.; Huuskonen, J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 986–989. (c) Blake, I. M.; Anderson, H. L.; Beljonne, D.; Brédas, J.-L.; Clegg, W. *J. Am. Chem. Soc.* **1998**, *120*, 10764–10765.

10.1021/ol9011585 CCC: $40.75

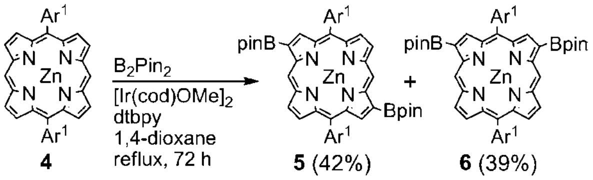
Scheme 1. Oxidative Oligomerization of Ni(II) Porphyrin



phyrin arrays to the corresponding Zn(II) porphyrin arrays failed due to the stability of the former under acidic conditions. In this paper, we wish to report the rational synthesis of *meso*-β doubly linked Zn(II) porphyrin dimer and *syn*- and *anti*-trimers.

We prepared 5,15-bis(2,4,6-tris(3,5-di-*tert*-butylphenoxy)phenyl)-substituted Zn(II) porphyrin **4** as a building block for the synthesis of extremely long porphyrin tapes that can escape from serious $\pi-\pi$ stacking.[11] In the course of this study, we examined its borylation under Ir-catalyzed conditions,[12] since this reaction has been shown to be quite sensitive to steric effect. In contrast to the effective tetraborylation of similar substrates with much less steric hindrance, the borylation of **4** under our standard conditions in 1,4-dioxane gave only diborylated products **5** and **6** in a 1:1 ratio (Scheme 2). Curiously, only the diborylation products were obtained under more forcing borylation conditions such as longer reaction time and/or more catalyst amount. These two products were separated by repeated recrystallizations from chloroform/acetonitrile. This diborylation selectivity is ascribed to severe steric hindrance of the bulky *meso*-aryl group.[12] However, we also found that the same borylations proceeded more extensively from the corresponding free base and Ni(II) porphyrin substrates and that the reaction in THF gave a tetraborylated product exclusively under the forcing conditions. These results indicate that the selective diborylation is arising from the combined steric effects of the bulky aryl groups of **4** and 1,4-dioxane molecule coordinated to the central Zn.

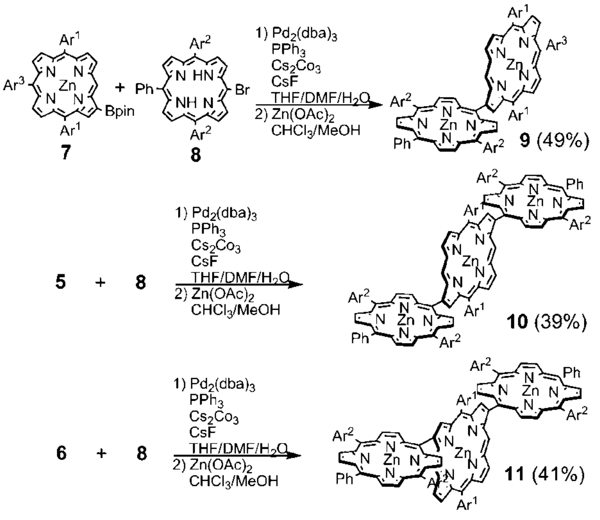
Scheme 2. Ir(I)-Catalyzed β-Borylation of **4**[a]



[a] Ar^1 = 2,4,6-tris(3,5-di-*tert*-butylphenoxy)phenyl. B$_2$Pin$_2$ = bis(pinacolato)diboron. dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl.

With **5** and **6** in hand, we envisoned synthetic routes to **2** and **3** via Suzuki−Miyaura coupling with brominated porphyrin **8** and subsequent oxidative ring closure with DDQ−Sc(OTf)$_3$. For this purpose, β-borylated porphyrin **7** was prepared from 5,15-bis(3,5-dioctyloxyphenyl)-10-(3,5-dimethylphenyl)-substituted zinc(II) porphyrin, and mono-*meso*-brominated porphyrin **8** was prepared from 5,15-bis(3,5-dioctyloxyphenyl)-10-phenyl-substituted porphyrin (for synthetic details, see the Supporting Information). *Meso*-β singly linked porphyrin dimer **9** and *anti*- and *syn*-trimers **10** and **11** were synthesized by Suzuki−Miyaura coupling as shown in Scheme 3. The diporphyrin **9** was oxidized with 4 equiv of DDQ and Sc(OTf)$_3$ in toluene at 80 °C for 2 h to afford *meso*-β doubly linked diporphyrin **1** as a reddish-purple solid (Scheme 4). The ^{1}H NMR spectrum of **1** shows two singlets for the β-protons at 9.26 and 9.58 ppm, 12 doublets for the β-protons in a range of 8.5−10.0 ppm, and two sets of signals for Ar^1 and Ar^2 protons, reflecting its low symmetric structure differing in the edge *meso*-aryl substituents, phenyl, and Ar^3 (Figure 1a). Oxida-

Scheme 3. Synthesis of *Meso*-β-Linked Porphyrin Arrays[a]



[a] Ar^2 = 3,5-dioctyloxyphenyl. Ar^3 = 3,5-dimethylphenyl.

---

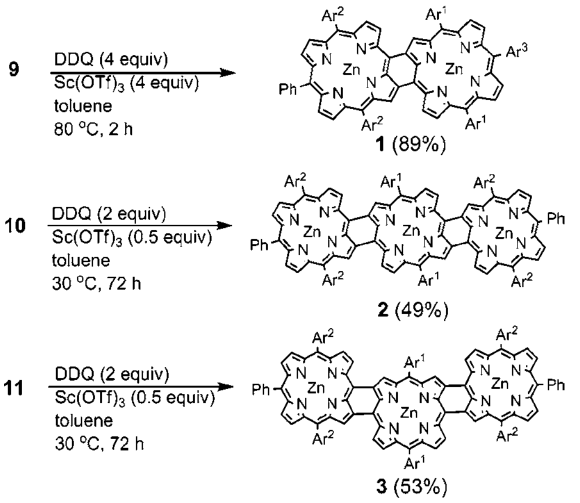
(6) (a) Aratani, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1361–1379. (b) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135–137. (c) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458–1462. (d) Aratani, N.; Takagi, A.; Yanagawa, Y.; Matsumoto, T.; Kawai, T.; Yoon, Z. S.; Kim, D.; Osuka, A. *Chem.—Eur. J.* **2005**, *11*, 3389–3404.

(7) (a) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569–1571. (b) Sendt, K.; Johnston, L. A.; Hough, W. A.; Crossley, M. J.; Hush, N. S.; Reimers, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 9299–9309.

(8) (a) Vicente, M. G. H.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1999**, 1771–1782. (b) Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261–1262. (c) Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355–2356. (d) Paolesse, R.; Jaquinod, L.; Sala, F. D.; Nurco, D. J.; Prodi, L.; Montalti, M.; Natale, C. D.; D'Amico, A.; Carlo, A. D.; Lugli, P.; Smith, K. M. *J. Am. Chem. Soc.* **2000**, *122*, 11295–11302. (e) Aihara, H.; Jaquinod, L.; Nurco, D. J.; Smith, K. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3439–3441. (f) Nath, M.; Huffman, J. C.; Zaleski, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 11484–11485.

(9) (a) Tsuda, A.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 558–561. (b) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549–2552. (c) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304–10321. (d) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79–82. (e) Ikeue, T.; Aratani, N.; Osuka, A. *Isr. J. Chem.* **2005**, *45*, 293–302. (f) Ikeda, T.; Lintuluoto, J. M.; Aratani, N.; Yoon, Z. S.; Kim, D.; Osuka, A. *Eur. J. Org. Chem.* **2006**, 3193–3204.

Scheme 4. Oxidation of *Meso*-β Linked Porphyrin Arrays



tion of **10** and **11** with 2 equiv of DDQ and 0.5 equiv of Sc(OTf)$_3$ in toluene at 30 °C for 72 h afforded doubly linked porphyrin tapes **2** (49%) and **3** (53%), respectively. The ^{1}H NMR spectra of **2** and **3** show two singlets and eight doublets for the β-protons and two sets of Ar^2 protons similarly except for the signal due to the protons of Ar^1, a single set for **2** and two sets for **3**, reflecting C_{2h} and C_{2v} symmetries, respectively (Figure 1b,c). It is interesting to note that the ^{1}H NMR spectra of **2** and **3** are clearly sharper than that of the previously reported *meso*-β doubly linked Ni(II) porphyrin trimer bearing 3,5-di-*tert*-butylphenyl groups.[10a] This difference may be ascribed to the large *meso*-aryl substituents in the former.[11]

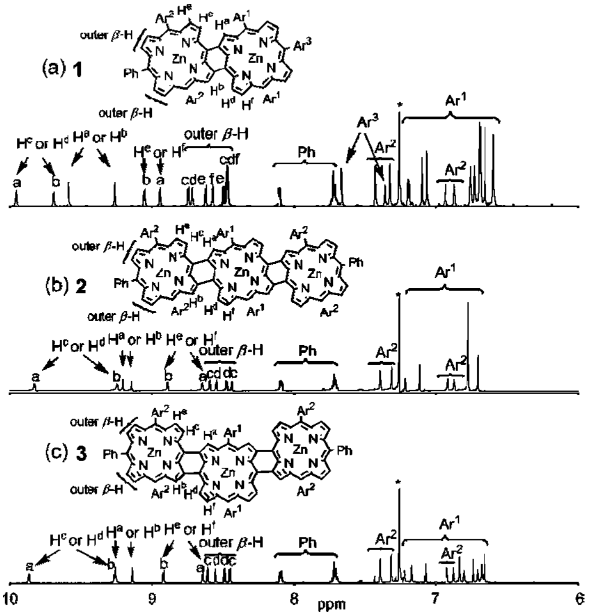


Figure 1. ^{1}H NMR spectra of **1**, **2**, and **3** in CDCl$_3$. Letters show mutual coupling of protons. Asterisks indicate solvent and solvent impurity.

The UV/vis absorption spectra of **9**−**11** display split Soret bands and red-shifted Q-bands (Figure 2 and Supporting Information). Such a split Soret-band is a typical feature of directly linked porphyrin oligomers and can be explained in terms of exciton coupling as a result of Coulomic interactions of transition dipole moments between neighboring two porphyrins.[13] Importantly, the width between two split Soret bands is larger in *meso*-*meso* linked porphyrin trimer **12** (2945 cm^{-1}) than in *meso*-β linked porphyrin trimers **10** (1573 cm^{-1}) and **11** (1021 cm^{-1}). Furthermore, it is larger in *anti*-trimer **10** than in *syn*-trimer **11**. These observations suggest that the exciton interactions between porphyrins are stronger in this order: *meso*-*meso* linked porphyrin > *anti* *meso*-β linked porphyrin > *syn* *meso*-β linked porphyrin.

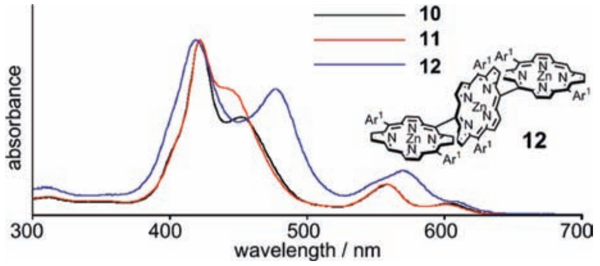


Figure 2. UV/vis absorption spectra of **10**, **11**, and *meso*-*meso* linked porphyrin trimer **12** in CHCl$_3$.

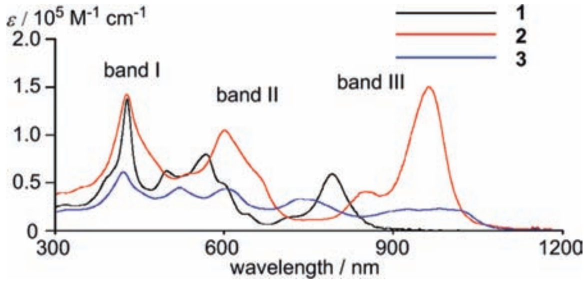


Figure 3. UV/vis absorption spectra of **1**, **2**, and **3** in CHCl$_3$.

Figure 3 shows the UV/vis absorption spectra of *meso*-β doubly linked porphyrin tapes. The absorption spectrum of **1** shows three major bands at 429, 568, and 792 nm, which may correspond to bands I, II, and III of the triply linked

---

(10) (a) Tsuda, A.; Nakamura, Y.; Osuka, A. *Chem. Commun.* **2003**, 1096–1097. (b) Yoon, M.-C.; Noh, S. B.; Tsuda, A.; Nakamura, Y.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2007**, *129*, 10080–10081.

(11) (a) Ikeda, T.; Tsuda, A.; Aratani, N.; Osuka, A. *Chem. Lett.* **2006**, *35*, 946–947. (b) Ikeda, T.; Aratani, N.; Osuka, A. *Chem. Asian J.* **2009**, *4*, in press.

(12) (a) Hata, H.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8264–8265. (b) Hata, H.; Yamaguchi, S.; Mori, G.; Nakazono, S.; Katoh, T.; Takatsu, K.; Hiroto, S.; Shinokubo, H.; Osuka, A. *Chem. Asian J.* **2007**, *2*, 849–859. (c) Hiroto, S.; Hisaki, I.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6763–6766.

(13) Kasha, M. *Radiat. Res.* **1963**, *20*, 55–70.

porphyrin tapes,[9c,d] respectively. Similar features are observed for **2**, which, however, exhibits band peaks at 427, 852, and 963 nm, indicating large red-shifts only for the latter two bands. In contrast, the absorption spectrum of **3** is considerably different, showing band peaks at 422, 522, 604, 734, 927, and 982 nm with molar extinction coefficients that are apparently smaller than those of **1** and **2**. While the fluorescence is hardly detected from **1** and **2**, the *syn*-isomer **3** emits the fluorescence to a clearly detectable level at 1048 nm with a vibronic structure that is commonly observed for porphyrins (Figure 4). The fluorescence of porphyrinoids in an infrared region is quite rare[14] and interesting in view of sensing or optical communications.

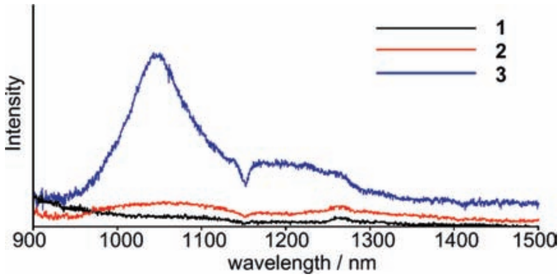


Figure 4. Fluorescence spectra of **1**, **2**, and **3** in $CHCl_3$ taken for excitation at 420 nm (OD = 1.0).

TPA cross-section values ($\sigma^{(2)}$) of **1**, **2**, and **3** in $CHCl_3$ were measured by an open-aperture Z-scan method using NIR femtosecond optical pulse.[15] Because the absorption spectra of these porphyrinoids spread across a wide spectral range down to the IR region, excitation wavelengths were chosen, 1600−1450 nm for **1** and 2000−1800 nm for **2** and **3**, to be free from any contribution of one-photon excitation. The $\sigma^{(2)}$ values for **1**, **2**, and **3** were measured to be 7000 (1500 nm), 16800 (1850 nm), and 7900 GM (1850 nm), respectively. Strong enhancement in $\sigma^{(2)}$ value as a function of number of porphyrin units originates from the increased polarizability due to the effective π-electron delocalization along the planar and rigid molecular framework. Furthermore, $\sigma^{(2)}$ values of **1** and **2** are similar to those of the corresponding Ni(II) porphyrin tapes (8000 and 16900 GM for the dimer and trimer).[10b] This suggests that central metal has no serious effect on TPA property and the observed $\sigma^{(2)}$ values are solely due to π-conjugation pathway of porphyrinoids. In contrast, the $\sigma^{(2)}$ value of **3** is distinctly smaller than that of **2**, indicating that not only π-conjugation length or size but also its shape is important. The substantial symmetric charge redistribution after photoexcitation exhibited by the linear π-conjugation pathway of **2** as compared to the bent one of **3** increases $\sigma^{(2)}$ values.[16] Similar conjugation-shape effect on TPA was also reported for triply linked porphyrin tapes; namely, $\sigma^{(2)}$ values of L-shaped trimer (8700 vs 18500 GM) and T-shaped tetramer (35700 vs 41200 GM) are smaller than the respective linear systems.[16]

In summary, *meso*-β doubly linked Zn(II) porphyrin dimers and trimers were synthesized. Although doubly linked Zn(II) porphyrin tapes dimer **1** and trimer **2** showed similar absorption to doubly linked Ni(II) porphyrin tape, **3** showed different absorption from them, indicating it has a different electronic structure. Our studies have shown that the TPA cross-section value depends on length and shape of the π-conjugated system and that the value is larger for linear than bended π-conjugation.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 19205006, and 20108001 “pi-Space”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. N.A. acknowleges a Grant-in-Aid for Young Scientists (B) and GCOE program “Integrated Materials Science” for financial support. T.I. thanks the JSPS Research fellowships for Young Scientists for support. The work at Yonsei University was supported by Star Faculty, and World Class University (no.2008-8-1955), of the Ministry of Education, Science, and Technology of Korea and the AFSOR/AOARD grant (FA4869-08-1-4097) (D.K.).

Supporting Information Available: Experimental details and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9011585

---

[14] (a) Bonifazi, D.; Scholl, M.; Song, F.; Echegoyen, L.; Accorsi, G.; Armaroli, N.; Diederich, F. *Angew. Chem. Int. Ed* **2003**, *42*, 4966–4970. (b) Ahn, T. K.; Kwon, J. H.; Kim, D. Y.; Cho, D. W.; Jeong, D. H.; Kim, S. K.; Suzuki, M.; Shimizu, S.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2005**, *127*, 12856–12861.

[15] (a) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769. (b) 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*, 1700–1704.

[16] Nakamura, Y.; Jang, S. Y.; Tanaka, T.; Aratani, N.; Lim, J. M.; Kim, K. S.; Kim, D.; Osuka, A. *Chem.—Eur. J.* **2008**, *14*, 8279–8289.