Macrocyclic Porphyrins

DOI: 10.1002/anie.200802026

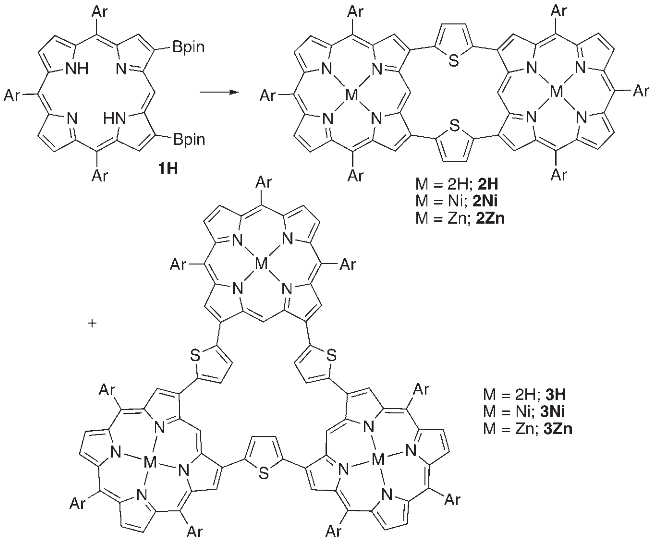
2,5-Thienylene-Bridged Triangular and Linear Porphyrin Trimers**

Jianxin Song, So Young Jang, Shigeru Yamaguchi, Jeyaraman Sankar, Satoru Hiroto, Naoki Aratani, Jae-Yoon Shin, Shanmugam Easwaramoorthi, Kil Suk Kim, Dongho Kim, Hiroshi Shinokubo,* and Atsuhiro Osuka**

Highly conjugated porphyrin arrays have received much attention in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, nonlinear optical (NLO) materials, and pigments for photodynamic therapy.[1] The manipulation of interporphyrinic π conjugation is often essential to achieve desirable electronic and photophysical properties. With this in mind, we have reported doubly β-to-β butadiyne-bridged diporphyrins as the first examples of multiply β-to-β-bridged diporphyrins.[2] This double-bridging strategy secures a rigid and coplanar porphyrin conformation, which induces significant enhancements of two photon absorption (TPA) properties. In general, large TPA cross-section values are considered to arise from effective electronic delocalization, but the general understanding of the structural factors that influence TPA properties still remains incomplete.

π Conjugation through thienylene linkages is often quite effective because of their relatively weak aromaticity as well as their small rotational barriers.[3] Although several thienylene-bridged porphyrin systems have been reported,[4] no examples of porphyrins that are directly bridged by thienylene groups at the β positions or contain multiple thienylene bridges have been reported to date. Encouraged by the large TPA cross-section values of doubly β-to-β 1,3-butadiyne-bridged diporphyrins, we embarked on the synthesis of doubly β-to-β 2,5-thienylene-bridged diporphyrins with the expectation that they would display enhanced TPA properties. Recently, expanded porphyrins with a thiophene-modified core have been reported to have exceptionally large TPA cross-section values.[5]

β,β′-Diborylporphyrin **1H**[6] was cross-coupled with 2,5-dibromothiophene under Suzuki–Miyuara coupling conditions. The desired product, doubly 2,5-thienylene-bridged diporphyrin **2H**, was obtained in 29 % yield (Scheme 1). The ^{1}H NMR and high-resolution ESI-TOF spectra of **2H** confirm its expected structure. To our surprise, the thienylene-bridged porphyrin trimer **3H** was also isolated in 10 % yield. The ^{1}H NMR spectrum of **3H** is quite simple, exhibiting a singlet peak for the meso proton, one singlet and two doublets for the β protons, and a singlet for the thiophene protons, thus confirming the high symmetry of the trimer. The parent ion peak of **3H** was observed at *m/z* 2866.6962 (calculated for $[C_{198}H_{223}N_{12}S_3]^+$ 2866.7034 ($[M+H]^+$)) in the high-resolution ESI-TOF mass spectrum. Complexation of nickel(II) and zinc(II) ions was carried out by treatment of **2H** and **3H** with either $Zn(OAc)_2$ or $[Ni(acac)_2]$ (acac = acetylacetonato) to provide dimers **2Ni** and **2Zn** and trimers **3Ni** and **3Ni,** respectively, in quantitative yields.



Scheme 1. Suzuki–Miyaura coupling of borylated porphyrins with 2,5-dibromothiophene. Reaction conditions: 2,5-dibromothiophene, $[Pd_2(dba)_3]$, PPh_3, Cs_2CO_3, CsF, toluene/DMF/H_2O, reflux, 48 h. Ar = 3,5-di-*tert*-butylphenyl, Bpin = 3,3,4,4,-tetramethyl-2,5-dioxaborolanyl, dba = *trans*, *trans*-dibenzylideneacetone.

---

[*] S. Y. Jang, J. Y. Shin, Dr. S. Easwaramoorthi, K. S. Kim, Prof. Dr. D. Kim
Centre for Ultrafast Optical Characteristics Control and Department of Chemistry
Yonsei University
Seoul 120-749 (Korea)
Fax: (+82) 2-2123-2434
E-mail: dongho@yonsei.ac.kr

Dr. J. Song, S. Yamaguchi, Dr. J. Sankar, S. Hiroto, Dr. N. Aratani, Prof. Dr. H. Shinokubo, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science
Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: hshino@kuchem.kyoto-u.ac.jp
osuka@kuchem.kyoto-u.ac.jp

[**] The work at Kyoto University was supported by a Grant-in-Aid for Scientific Research (Nos 18685013 and 20037034) from MEXT (Japan). S.Y., J.S., and S.H. thank the JSPS for Research Fellowships. The work at Yonsei University was supported by the Star Faculty program from the Ministry of Education and Human Resources Development, Korea. S.Y.J., J.Y.S., S.E., and K.S.K. were supported by BK21 fellowships.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802026.

Definitive structural assignments of the dimer and trimer were accomplished by X-ray diffraction analyses of **2Ni** and **3Ni**, which revealed highly symmetrical structures of the porphyrin dimer and triangular trimer bridged by 2,5-thienylene linkages (Figure 1).[7] The porphyrin macrocycles, in both **2Ni** and **3Ni**, are nearly coplanar to each other, although the porphyrin cores are slightly ruffled, as is often seen in the case of nickel porphyrins. The maximum displacements of the β-carbon atoms from the mean plane composed of carbon and nitrogen atoms (except the thiophene bridges) are 0.546 Å for **2Ni** and 0.915 Å for **3Zn**. The thiophene moieties in **2Ni** are tilted by 40.5° and 49.3° relative to the adjacent pyrrole rings, while the tilt angles of the thiophene moieties range from 26.6° to 36.1° in **3Ni**. The meso protons H_{meso} appear at $\delta = 12.16$ ppm in the ^1H NMR spectrum of **2Ni**. This signal is shifted substantially downfield from that of **3Ni** ($\delta = 10.99$ ppm), probably because of the ring current effect of the adjacent porphyrin moiety. On the other hand, the thiophene protons H_{th} of **3Ni** ($\delta = 8.51$ ppm), which point inwards, show a downfield shift relative to those of **2Ni** ($\delta = 7.90$ ppm). Similar trends are also observed for the corresponding zinc complexes and free-base porphyrins, thereby suggesting that they adopt similar structures to **2Ni** and **3Ni**. Interestingly, the thienylene bridge is able to adapt to the size of the macrocycle by adopting conformations with the sulfur atom pointing either into or out of the core, thus maintaining the overall conjugation of the system.

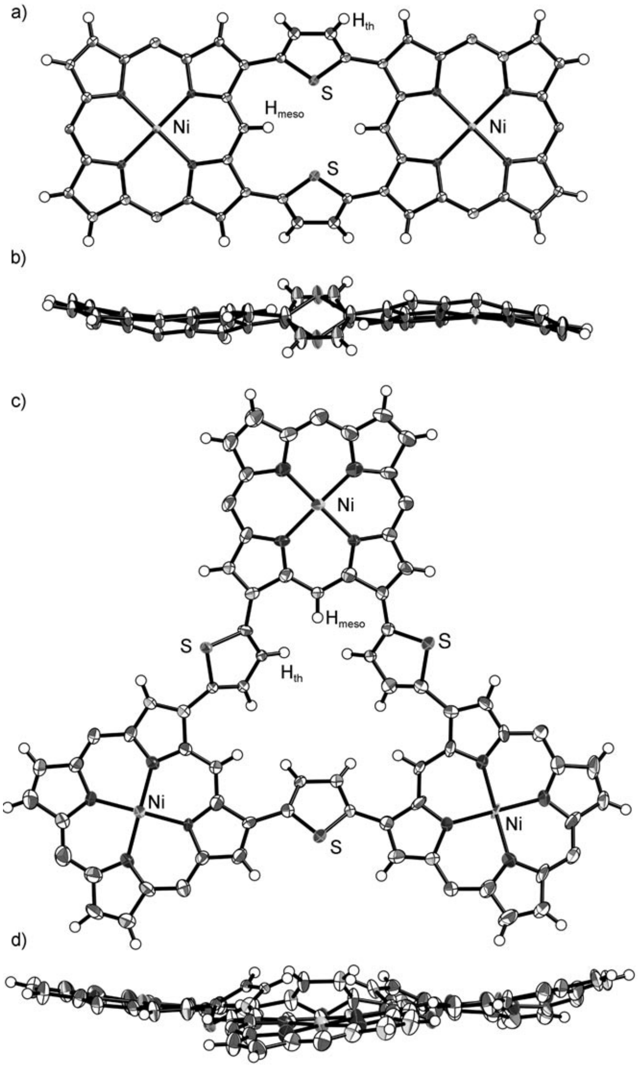


Figure 1. X-ray structures. a) Top view and b) side view of **2Ni** and c) top view and b) side view of **3Ni**. The thermal ellipsoids are 50% probability level. Meso aryl groups are omitted for clarity.

The UV/Vis absorption and fluorescence spectra of the Zn^{II} porphyrins measured in CH_2Cl_2 is shown in Figure 2. The broadened Soret band of **2Zn** is observed (with a shoulder) at 429 nm, along with an ill-defined Q band at 557 nm. The absorption spectrum of the triporphyrin **3Zn** is significantly perturbed, and exhibits broader Soret bands with three peaks at 427, 462, and 494 nm and Q bands at 570 and 601 nm. The fluorescence spectrum of **3Zn** exhibits a typical vibronic structure with a relatively high fluorescence quantum yield ($\Phi_F = 0.056$), while the quantum yield of **2Zn** is much lower ($\Phi_F = 0.008$). The reduced fluorescence quantum yield of **2Zn** may arise from the structural distortion of the molecule caused by the double bridging.

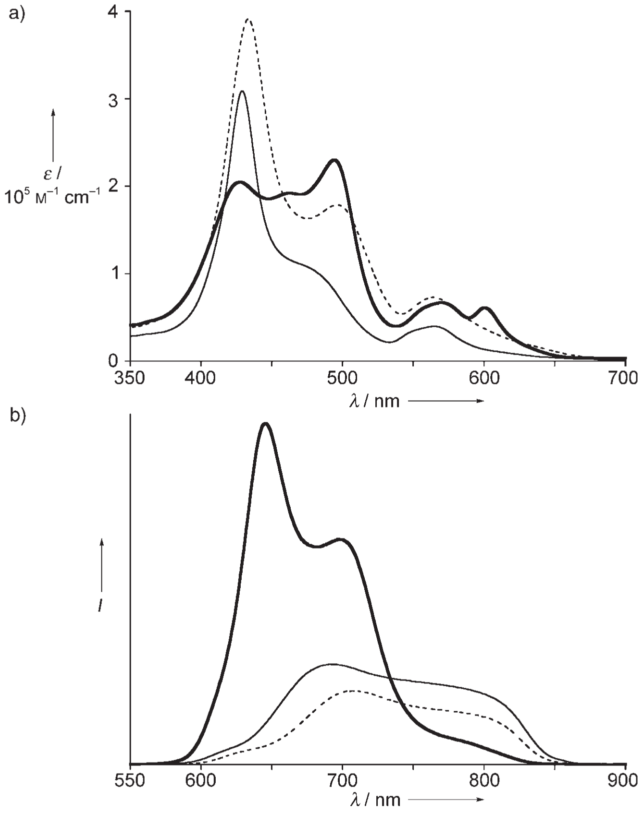


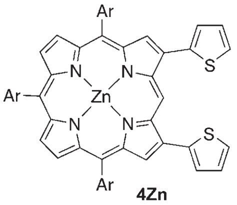
Figure 2. a) UV/Vis absorption and b) emission spectra of **2Zn** (——), **3Zn** (——), and **8Zn** (-----) in CH_2Cl_2. Samples were excited at the absorption maxima.

The TPA cross-section values were measured at 800 nm by using an open-aperture Z-scan method with wavelength-tunable 120 fs pulses.[8,9] The TPA cross-section values of **2Zn** (7020 GM) and **3Zn** (8600 GM) are certainly larger than those of β,β′-dithienylporphyrin **4Zn** (970 GM) and singly bridged diporphyrin **5Zn** (3300 GM, Table 1). The TPA cross-section value of **2Zn**, which is double that of **5Zn**, seemingly originates from the effective π delocalization through the rigidified planar conformation enforced by the two thiophene bridges. However, the observed enhancement in the TPA cross-section values from **2Zn** to **3Zn** is unexpectedly small considering that the highly planar structure of **3Zn**, which also contains one additional porphyrin segment, should be advantageous for global electronic delocalization. This result may be interpreted as follows: the two porphyrin chromophores in **2Zn** can communicate with each other through the double thiophene bridges, while only a single thiophene bridge is available for delocalization in **3Zn**, thus lowering the efficacy of the TPA cross-section value per porphyrin unit. Furthermore, it is known that the dimensionality of the conjugated backbones has a decisive role in predicting the TPA properties.[10]

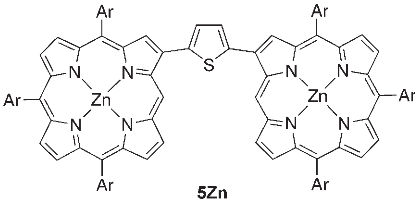
Table 1: Optical properties of Zn^{II} porphyrins.

Compound	$\sigma^{(2)}$ [GM][a]	τ_F [ns][b]	Φ_F[c]
2Zn	7020	1.75	0.008
3Zn	8600	1.38	0.056
4Zn	970	2.44	0.032
5Zn	3300	1.83	0.099
8Zn	17300	1.25	0.005

[a] TPA cross-section value determined for excitation at 800 nm. [b] Singlet excited-state lifetime. [c] Fluorescence quantum yield.

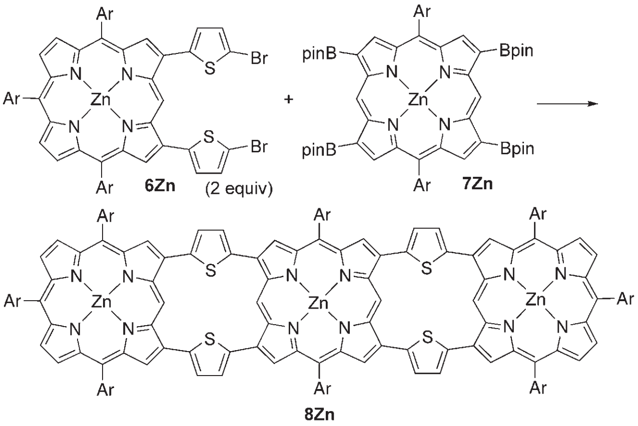


4Zn



5Zn

We then decided to synthesize linear porphyrin trimer **8Zn** and compare the TPA value with that of the triangular trimer **3Zn**. Suzuki–Miyaura coupling of **6Zn** with **7Zn**[6] successfully provided the ladderlike porphyrin trimer **8Zn** in 11% yield (Scheme 2). The parent ion peak was observed at m/z 2948.2549 (calculated for $[C_{188}H_{197}N_{12}S_4Zn_3]^+$ 2948.2544 ($[M+H]^+$)) in the high-resolution ESI-TOF mass spectrum. The ^{1}H NMR spectrum of **8Zn** displays two signals for the meso proton ($\delta = 12.73$ and 12.71 ppm), in agreement with its ladderlike structure. The absorption spectrum of **8Zn** is similar to that of **2Zn** except for the Soret band, which is red-shifted and intensified. The red-shift of the emission peak of **8Zn** from that of **2Zn** is not so large (16 nm). To explore the relationship between the photoexcited dynamics and molecular structure of the porphyrin systems, their fluorescence lifetimes were determined by a time-correlated single-photon-counting technique. The fluorescence lifetime decreased as the number of porphyrin units increased because of the accelerated nonradiative decay caused by the decreased energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The fluorescence lifetime of **3Zn** is shorter than that of **2Zn** and nearly identical to that of **8Zn**, which indicates that the slightly more flexible motions of **3Zn** through one thiophene bridge between the porphyrin units contributes to the acceleration of nonradiative decay channels. On the other hand, the TPA cross-section value of the linear trimer **8Zn** reached 17300 GM, more than double the value of its triangular counterpart **3Zn**. In this case, π delocalization between the porphyrin units arises from the three and four thiophene bridges in **3Zn** and **8Zn**, respectively. Hence, the increased TPA cross-section value could not be simply accounted for by the enhanced π delocalization through an additional thiophene bridge. Other contributing factors can be one- versus multidimensional π delocalization and its associated molecular hyperpolarizability, which is in fact proportional to the TPA cross-section value. In general, the hyperpolarizability of linear annulenes are much larger than their corresponding two-dimensional isomers.[11] Moreover, for linear systems, centrosymmetric charge redistribution has been shown to stimulate a significant enhancement in TPA cross-section values.[12] Thus, our investigation suggests that linear one-dimensional π delocalization yields better TPA properties than delocalization over a triangular shape.



Scheme 2. Synthesis of linear trimer **8Zn**. Reaction conditions: $[Pd_2(dba)_3]$, PPh_3, Cs_2CO_3, CsF, toluene/DMF, reflux, 24 h. Ar = 3,5-di-*tert*-butylphenyl.

In summary, we have achieved the synthesis of a β-to-β 2,5-thienylene-bridged porphyrin dimer, a triangular trimer, and a ladderlike trimer. The doubly linked diporphyrin exhibits a large TPA cross-section value, but the enhancement of that in the cyclic trimer is not significant. In sharp contrast, the ladderlike trimer shows a very large TPA cross-section value by virtue of enhanced charge redistribution and larger hyperpolarizability along the long molecular axis. Investigations on higher 1,4-thienylene-bridged porphyrin oligomers are currently underway.

Received: April 30, 2008

Keywords: cross-coupling · macrocycles · porphyrinoids · thiophenes · two-photon absorption

---

[1] a) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **1993**, *26*, 198; b) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469; c) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40; d) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435; e) M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771; f) H. L. Anderson, *Chem. Commun.* **1999**, 2323; g) D. P. Arnold, *Synlett* **2000**, 296; h) A. K. Burrell, D. L. Officer, *Synlett* **1998**, 1297; i) A. K. Burrell, D. L. Officer, P. G. Plieger, D. C. W. Reid, *Chem. Rev.* **2001**, *101*, 2751; j) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57; k) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735; l) M. J. Crossley, P. L. Burn, *J. Chem. Soc. Chem. Commun.* **1991**, 1569; m) V. S.-Y. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105; n) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79; o) J.-H. Chou, M. E. Kosal, N. H. Nalwa, S. A. Rakow, K. S. Suslick in *The Porphyrin Handbook*, *Vol. 6* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 43.

[2] I. Hisaki, S. Hiroto, K. S. Kim, S. B. Noh, D. Kim, H. Shinokubo, A. Osuka, *Angew. Chem.* **2007**, *119*, 5217; *Angew. Chem. Int. Ed.* **2007**, *46*, 5125.

[3] T. Otsubo, Y. Aso, K. Takimiya, *J. Mater. Chem.* **2002**, *12*, 2565.

[4] a) D. P. Arnold, D. A. James, *J. Org. Chem.* **1997**, *62*, 3460; b) F. Odobel, S. Suresh, E. Blart, Y. Nicolas, J.-P. Quintard, P. Janvier, J.-Y. L. Questel, B. Illien, D. Rondeau, P. Richomme, T. Häupl, S. Wallin, L. Hammarström, *Chem. Eur. J.* **2002**, *8*, 3027; c) H. Higuchi, T. Ishikura, K. Miyabayashi, M. Miyake, K. Yamamoto, *Tetrahedron Lett.* **1999**, *40*, 9091; d) J. Ikemoto, K. Takimiya, Y. Aso, T. Otsubo, M. Fujitsuka, O. Ito, *Org. Lett.* **2002**, *4*, 309; e) T. Oike, T. Kurata, K. Takimiya, T. Otsubo, Y. Aso, H. Zhang, Y. Araki, O. Ito, *J. Am. Chem. Soc.* **2005**, *127*, 15372.

[5] a) H. Rath, J. Sankar, V. PrabhuRaja, T. K. Chandrashekar, A. Nag, D. Goswami, *J. Am. Chem. Soc.* **2005**, *127*, 11608; b) H. Rath, V. Prabhuraja, T. K. Chandrashekar, A. Nag, D. Goswami, B. S. Joshi, *Org. Lett.* **2006**, *8*, 2325.

[6] a) H. Hata, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 8264; b) H. Hata, S. Yamaguchi, G. Mori, S. Nakazono, T. Katoh, K. Takatsu, S. Hiroto, H. Shinokubo, A. Osuka, *Chem. Asian J.* **2007**, *2*, 849.

[7] Crystal data for **2Ni**: $C_{67}H_{73}Cl_3N_4NiS$, $M_r = 1131.41$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.857(5)$, $b = 16.135(5)$, $c = 18.457(5)$ Å, $\alpha = 87.305(5)$, $\beta = 73.755(5)$, $\gamma = 80.146(5)$, $V = 3340(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.125$ g cm^{-3}, $T = 90(2)$ K, 38372 measured reflections, 15266 unique reflections, $R = 0.0643$ ($I > 2.0\sigma(I)$), $R_w = 0.1780$ (all data), GOF = 1.012 ($I > 2.0\sigma(I)$). Crystal data for **3Ni**: $C_{200}H_{216}Cl_7N_{12}Ni_3S_3$, $M_r = 3308.31$, triclinic, space group $P\bar{1}$ (No. 2), $a = 18.846(5)$, $b = 27.958(5)$, $c = 27.989(5)$ Å, $\alpha = 112.376(5)$, $\beta = 103.171(5)$, $\gamma = 103.126(5)°$, $V = 12445(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.883$ g cm^{-3}, $T = 90(2)$ K, 75926 measured reflections, 53119 unique reflections, $R = 0.1161$ ($I > 2.0\sigma(I)$), $R_w = 0.3156$ (all data), GOF = 1.012 ($I > 2.0\sigma(I)$). The contribution to the scattering arising from the presence of disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package.[13] CCDC 685452 (**2Ni**) and CCDC 685451 (**3Ni**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. G. Hagan, E. W. van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760.

[9] As a fast repetition rate of theexcitation pulse (5 kHz, 200 µs delay between the pulses) was used, there is a possibility that the observed TPA values would have been artificially augmented by the contribution from the triplet–triplet excited-state absorption (ESA). However, it is expected that, considering the lifetime of the lowest triplet state lifetime of the similar molecules (< 200 µs), the triplet state may be depopulated before ESA by a subsequent pulse. Hence, the TPA augmentation by ESA will be very minimal or negligible and does not affect the general trend observed for these molecules.

[10] D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder, J.-L. Bredas, *Adv. Funct. Mater.* **2002**, *12*, 631.

[11] E. F. Mcintyre, H. F. Hameka, *J. Chem. Phys.* **1978**, *69*, 4814.

[12] a) M. Albota, D. Beljonne, J.-L. Bredas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Gogej, M. D. Levin, S. R. Mardar, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Web, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653; b) M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Y. Hu, D. McCord-Maughon, H. Rockel, S. Thayumanavan, S. R. Mardar, D. Beljonne, J.-L. Bredas, *J. Am. Chem. Soc.* **2000**, *122*, 9500.

[13] Squeese-Platon: a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, **2005**; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.