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Diporphyrins

Synthesis of Doubly β-to-β 1,3-Butadiyne-Bridged Diporphyrins: Enforced Planar Structures and Large Two-Photon Absorption Cross Sections**

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Covalently linked π-conjugated porphyrin oligomers are materials of great importance that display efficient energy and electron transfer, single-molecule conductivity, and nonlinear optical (NLO) properties.[1] Among them, peripherally ethyne- and 1,3-butadiyne-fabricated porphyrins hold a central position owing to their attractive electronic properties.[2–5] As representative examples, Therien and co-workers reported large hyperpolarizabilities for push–pull *meso*,-*meso*′-bis-arylethynylated porphyrins[3] and Anderson et al. reported large two-photon-absorption (TPA) properties of *meso*-ethyne- and *meso*-butadiyne-bridged porphyrin oligomers.[4] Most of the electronic properties of these conjugated porphyrins are considered to depend on the extent of overall π conjugation, which is a function of molecular coplanarity. However, there is a continuous distribution of rotational isomers because of small rotational barriers of triple-bond linkages[6] which duplicates their photophysics.[7] As an interesting approach, conformational control has been achieved with the aid of noncovalent interactions between a zinc porphyrin and a pyridine coordination site.[4b,8]

Herein, we report the synthesis of doubly β-to-β butadiyne-bridged diporphyrins as the first example of multiply 1,3-butadiyne-bridged diporphyrins. An apparent advantage of this double bridging strategy is a robust, enforced overall planar conformation, which causes significant enhancements of TPA properties. Large TPA compounds attract considerable interest for several innovative applications such as three-dimensional (3D) optical memory, deeper-penetrating photodynamic therapy (PDT) of cancer, 3D microfabrication, and others.[9]

Diporphyrins **1** and **2** were prepared from β-borylated porphyrins **3a** and **3b**[10] (Scheme 1). Treatment of mono- and diborylporphyrins **3a** and **3b** with Oxone in a THF/acetone/water suspension[11] successfully gave the corresponding mono- and dihydroxyporphyrins **4a** and **4b** in 80% and 88% yields, respectively. The trifluoromethanesulfonyl derivatives were prepared in DMF by reaction with $PhNTf_2$ and Cs_2CO_3,[12] and following metallation with $Zn(OAc)_2$ **6aZn** and **6bZn** were obtained in excellent yields. Installation of ethynyl groups was conducted through the standard Sonogashira coupling with trimethylsilylacetylene followed by desilylation to provide **8aZn** and **8bZn** in good yields. Then, **8aZn** and **8bZn** were subjected to a Cu^{II}-mediated oxidative coupling reaction to furnish the corresponding butadiyne-bridged porphyrin dimers **1Zn** and **2Zn** in 82% and 89% yields, respectively. Demetallation with trifluoroacetic acid provided **1H** and **2H** in good yields. Synthesis of **1Ni** and **2Ni** was achieved in a similar fashion to **1Zn** and **2Zn** from Ni^{II} triarylporphyrin as the starting material.

β-to-β-Linked diporphyrins have been explored to examine the influences of connectivity difference on the electronic interactions between the porphyrins,[1e,2a,6a,13,14] but **2H** and its metal complexes (**2Zn** and **2Ni**) are the first examples of doubly linked diporphyrins. These newly synthesized diporphyrins were fully characterized by high-resolution mass spectrometry, and ^1H NMR, UV/Vis, and fluorescence spectroscopy (Supporting Information). The *meso* protons (H^m) are observed at $\delta = 10.42$ ppm for **7aZn**, $\delta = 10.66$ ppm for **7bZn**, $\delta = 10.67$ for **1Zn**, and $\delta = 11.67$ ppm for **2Zn**. The observed large downfield shift of H^m in **2Zn** probably reflects the enhanced anisotropic effect of the nearby butadiyne segments that become distorted upon ring formation (Figure S8 in the Supporting Information).[15] Similar trends are also seen for the corresponding Ni^{II} complex and free-base porphyrins, **2Ni** and **2H**.

Figure 1 shows the X-ray crystal structure of **2Zn**.[16] The deviation from the mean plane composed of carbon and

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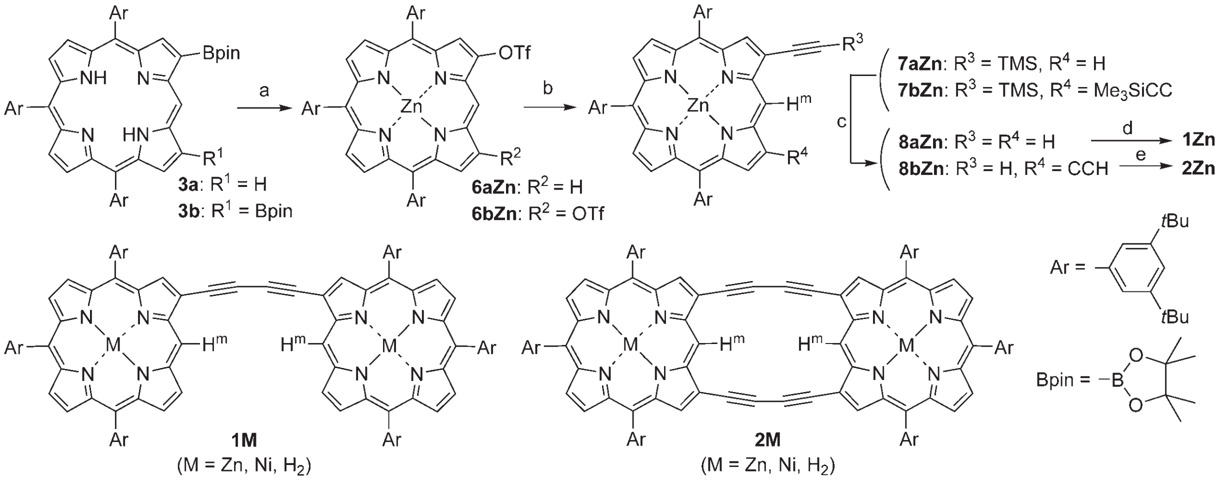

Scheme 1. Synthesis of diporphyrins **1** and **2**. Reaction conditions: a) 1) Oxone, THF/acetone/H_2O, RT, 1.5 h; 2) $PhNTf_2$, Cs_2CO_3, DMF, RT, 12 h; 3) $Zn(OAc)_2$, $CHCl_3$, MeOH, RT, 2 h; b) Me_3SiCCH, $[Pd(PPh_3)_4]$, CuI, Et_3N, DMF, toluene, 70 °C, 3 h; c) K_2CO_3, THF, MeOH, RT, 2 h; d) $Cu(OAc)_2$, toluene, pyridine, RT, 24 h; e) $Cu(OAc)_2$, THF, pyridine, RT, 24 h. Tf: trifluoromethanesulfonyl; DMF: *N*,*N*-dimethylformamide; TMS: trimethylsilyl.

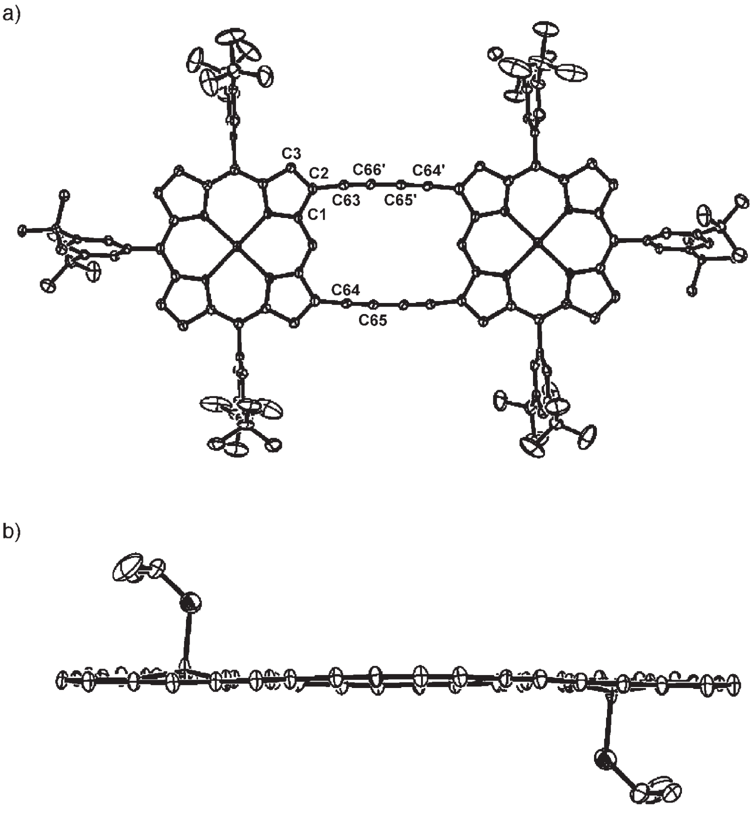

Figure 1. X-ray crystal structure of **2Zn**. Thermal ellipsoids are shown at the 50% probability level. a) Top view (*i*PrOH ligands not shown) and b) side view (aryl substituents not shown).

nitrogen atoms of the porphyrin cores and butadiyne bridges is only 0.053 Å, which indicates its overall remarkably planar structure. The angles around C63 and C66′ are 174.62° for C2-C63-C66′ and 177.90° for C63-C66′-C65′, indicating that two triple bonds are slightly distorted. The bond lengths of C2–C63, C63–C66′, C66′–C65′, and C65′–C64′ are 1.414, 1.205, 1.368, 1.202, and 1.417 Å, respectively, which reveal distinct bond-length alternation.

Figure 2 displays the UV/Vis absorption and fluorescence spectra of Zn^{II} porphyrins measured in chloroform. Soret and Q-bands are observed, respectively, at 429 and 555 nm for **7aZn**, and at 440 and 564 nm for **7bZn**, indicating an increasing red shift upon the increment of β-ethynyl substituents. In line with this trend, **7aZn** and **7bZn** have fluorescence maxima at 605 and 654 nm and 613 and 663 nm, respectively. On the other hand, the absorption spectrum of the diporphyrin **1Zn** is significantly perturbed with broader Soret bands with three distinct peaks at 431, 452, and 479 nm and Q-bands at 563 and 606 nm. Also, its fluorescence spectrum shows a typical porphyrin-like vibronic structure with a relatively high quantum yield ($\Phi_F = 0.12$), which is quite similar to those of the previously reported β-to-β butadiyne-bridged Zn^{II} diporphyrin.[3a,6a] The diporphyrin **2Zn** displays a more perturbed absorption spectrum, in which the Soret band is split into peaks at 441 and 501 nm and Q-bands are observed at 580, 605, and 645 nm. The fluorescence spectrum of **2Zn** is observed in a lower energy region with maxima at 615, 657, 732, and 779 nm and a considerably attenuated quantum yield ($\Phi_F = 9\times10^{-3}$). The significant red shift may be ascribed to the expansion of effective π conjugation, and the reduced fluorescence quantum yield may arise from the structural distortion upon the double bridging.

The TPA cross-section values were measured at 800 nm by an open-aperture Z-scan method[17] with wavelength-tunable 120-fs pulses and are listed as follows: **1H** (5150 GM), **1Zn** (5220 GM), **1Ni** (4890 GM), **2H** (8830 GM), **2Zn** (9620 GM), and **2Ni** (8540 GM) (Figure S1 in the Supporting Information) These values are certainly larger than those for their corresponding porphyrin monomers (< 100 GM). Interestingly, the double bridge leads to almost doubling of the TPA

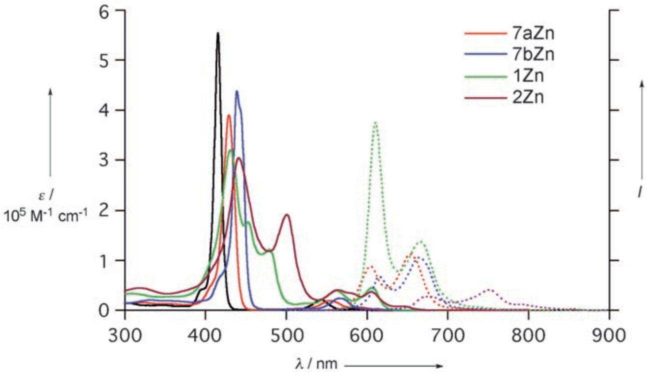

Figure 2. UV/Vis absorption (solid lines) and fluorescence (dotted lines) spectra of **7aZn**, **7bZn**, **1Zn**, and **2Zn** in $CHCl_3$. The absorption spectrum of Zn^{II} 5,10,15-tris(3,5-di-*tert*-butylphenyl) porphyrin is indicated as a solid black line for comparison.

values. To explore the relationship between the photoexcited-state dynamics and molecular structures, the fluorescence lifetimes were determined by a time-correlated single-photon-counting technique for **1H** (8.34 ns), **2H** (8.12 ns), **1Zn** (1.97 ns), and **2Zn** (1.78 ns). The lifetimes suggested no particular difference in the fluorescence-decay process for singly and doubly butadiyne-bridged diporphyrins. The transient absorption decays of Ni^{II} diporphyrins at 610 nm exhibit a biexponential decay with time constants of 17 ps (71%) and 230 ps (29%) for **1Ni** and 13 ps (57%) and 470 ps (43%) for **2Ni**. The initial fast decay processes can be attributed to the vibrational-relaxation processes including vibrational cooling and solvent-relaxation processes.[18] It has been well established that the (d,d) state acts as a quenching state in the energy-relaxation dynamics of photoexcited Ni^{II} porphyrins, accelerating decay to the ground state with a time constant of a few hundred ps.[19] Thus, it has been shown that the TPA behaviors of singly and doubly butadiyne-bridged diporphyrins do not show any dependence on the excited-state dynamics. This feature can be explained by the fact that TPA involves instantaneous and simultaneous two-photon-absorption processes through a virtual ladder state to reach the two-photon allowed excited states. Instead, it may be concluded that the double-butadiyne bridges force the overall planar conformation, hence enhancing the TPA properties through the effective π conjugation.

In summary, β-to-β doubly 1,3-butadiyne-bridged diporphyrins **2** were synthesized on the basis of the newly developed direct borylation of porphyrins. The diporphyrins **2** show large TPA values as a result mainly of the fully π-conjugated electronic structure that arises from the two 1,3-butadiyne bridges.

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[1] a) M. G. H. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771; b) H. L. Anderson, *Chem. Commun.* **1999**, 2323; c) D. P. Arnold, *Synlett* **2000**, 296; d) A. K. Burrell, D. L. Officer, *Synlett* **1998**, 1297; e) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57; f) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735; g) A. Tsuda, A. Osaka, *Science* **2001**, *293*, 79.

[2] a) D. P. Arnold, L. J. Nitschink, *Tetrahedron* **1992**, *48*, 8781; b) D. P. Arnold, G. A. Heath, *J. Am. Chem. Soc.* **1993**, *115*, 12197; c) D. P. Arnold, G. A. Heath, D. A. James, *J. Porphyrins Phthalocyanines* **1999**, *3*, 5; d) D. P. Arnold, R. D. Hartnell, G. A. Heath, L. Newby, R. D. Webster, *Chem. Commun.* **2002**, 754.

[3] a) V. S.-Y. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105; b) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 1497; c) L. Karki, F. W. Vance, J. T. Hupp, S. M. LeCours, M. J. Therien, *J. Am. Chem. Soc.* **1998**, *120*, 2606.

[4] a) H. L. Anderson, S. J. Martin, D. D. C. Bradley, *Angew. Chem.* **1994**, *106*, 711; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 655; ; b) P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538; c) T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall, H. L. Anderson, *J. Am. Chem. Soc.* **2002**, *124*, 9712; d) M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **2004**, *126*, 15352.

[5] a) J. J. Gosper, M. Ali, *J. Chem. Soc. Chem. Commun.* **1994**, 1707; b) K. Sugiura, Y. Fujimoto, Y. Sakata, *Chem. Commun.* **2000**, 1105; c) H. Aihara, L. Jaquinod, D. J. Nurco, K. M. Smith, *Angew. Chem.* **2001**, *113*, 3547; *Angew. Chem. Int. Ed.* **2001**, *40*, 3439; .

[6] a) V. S.-Y. Lin, M. J. Therien, *Chem. Eur. J.* **1995**, *1*, 645; b) R. Stranger, J. E. McGrady, D. P. Arnold, I. Lane, G. A. Heath, *Inorg. Chem.* **1996**, *35*, 7791.

[7] a) R. Kumble, S. Palese, V. S.-Y. Lin, M. J. Therien, R. M. Hochstrasser, *J. Am. Chem. Soc.* **1998**, *120*, 11489; b) A. Nakano, A. Osuka, T. Yamazaki, Y. Nishimura, S. Akimoto, I. Yamazaki, A. Itaya, M. Murakami, H. Miyasaka, *Chem. Eur. J.* **2001**, *7*, 3134.

[8] A. Tsuda, H.-F. Hu, R. Tanaka, T. Aida, *Angew. Chem.* **2005**, *117*, 4962; *Angew. Chem. Int. Ed.* **2005**, *44*, 4884; .

[9] a) B. Kippelen, P.-A. Blanche, A. Schülzgen, C. Fuentes-Hernandez, G. Ramos-Ortiz, J.-F. Wang, N. Peyghambarian, S. R. Marder, A. Leclercq, D. Beljonne, J.-L. Brédas, *Adv. Funct. Mater.* **2002**, *12*, 615; b) T.-Z. Lin, S.-J. Chung, K.-S. Kim, X. Wang, G. S. He, J. Switantkiewicz, H. E. Puddavar, P. N. Prasad, *Adv. Polym. Sci.* **2003**, *161*, 157, and references therein.

[10] 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*, DOI: 10.1002/asia.200700086.

[11] R. E. Maleczka Jr. , F. Shi, D. Holmes, M. R. Smith, *J. Am. Chem. Soc.* **2003**, *125*, 7792.

[12] M. Oestreich, F. Sempere-Culler, A. B. Machotta, *Angew. Chem.* **2005**, *117*, 152; *Angew. Chem. Int. Ed.* **2005**, *44*, 149.

[13] S. I. Yang, J. Seth, T. Balasubramanian, D. Kim, J. S. Lindsey, D. Holten, D. F. Bocian, *J. Am. Chem. Soc.* **1999**, *121*, 4008.

[14] For examples of β-β singly bridged or directly linked diporphyrins, see: a) A. K. Burrell, D. L. Officer, D. C. W. Reid, *Angew. Chem.* **1995**, *107*, 986; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 900; b) B. Krattinger, D. J. Nurco, K. M. Smith, *Chem. Commun.* **1998**, 757; c) Y. Deng, C. K. Chang, D. G. Nocera, *Angew. Chem.* **2000**, *112*, 1108; *Angew. Chem. Int. Ed.* **2000**, *39*, 1066.

[15] I. Hisaki, T. Eda, M. Sonoda, H. Niino, T. Sato, T. Wakabayashi, Y. Tobe, *J. Org. Chem.* **2005**, *70*, 1853.

[16] Crystallographic data for **2Zn**: $C_{152}H_{179}N_8O_6Cl_{17}Zn_2$, $M_w = 2947.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.287(5)$, $b = 20.381(5)$ $c = 21.529(5)$ Å, $\alpha = 77.218(5)$, $\beta = 80.967(5)$, $\gamma =$

80.500(5)°, $V = 3889(2)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.259$ g cm^{-3}, $T = -183$ °C, 37697 measured reflections, 13643 unique reflections ($R_{\text{int}} = 0.0420$), $R_1 = 0.0990$ ($I > 2\sigma(I)$), $wR_2 = 0.2942$ (all data), GOF = 1.058. CCDC 635463 contains 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.

[17] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. G. Hagan, E. W. van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760.
[18] H. S. Eom, S. C. Jeoung, D. Kim, J-. H. Ha, Y. R. Kim, *J. Phys. Chem. A* **1997**, *101*, 3661.
[19] a) D. Kim, C. Kirmaier, D. Holten, *Chem. Phys.* **1983**, *75*, 305; b) J. Rodriguez, C. Kirmaier, D. Holten, *J. Am. Chem. Soc.* **1989**, *111*, 6500.