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Synthesis, Crystal Structure, and Nonlinear Optical Behavior of β-Unsubstituted *meso*–*meso* *E*-Vinylene-Linked Porphyrin Dimers

Michael J. Frampton,[†] Huriye Akdas,[†] Andrew R. Cowley,[†] Joy E. Rogers,[‡] Jonathan E. Slagle,[‡] Paul A. Fleitz,[‡] Mikhail Drobizhev,[§] Aleksander Rebane,[§] and Harry L. Anderson*,[†]

Department of Chemistry, Oxford University, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, U.K., Air Force Research Laboratory, AFRL/MLPJ, 3005 Hobson Way, Wright-Patterson Air Force Base, Dayton, Ohio 45433-7702, and Department of Physics, Montana State University, Bozeman, Montana 59717

harry.anderson@chem.ox.ac.uk

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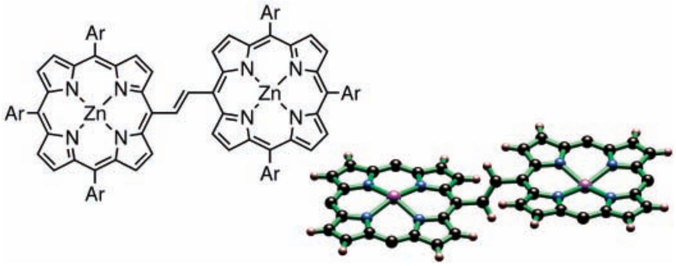
ABSTRACT



A vinylene-linked porphyrin dimer, with no substituents at the β-positions, has been synthesized by CuI/CsF promoted Stille coupling. In the crystal structure of this dimer, the C_2H_2 bridge is twisted by 45° relative to the plane of the porphyrins. The absorption, emission spectra, and electrochemistry reveal substantial porphyrin–porphyrin π-conjugation. The triplet excited-state absorption spectrum of this dimer makes it suitable for reverse saturable absorption at 710–900 nm.

Conjugated porphyrin oligomers[1] display outstanding characteristics for a variety of applications, including two-photon absorption,[2] reverse-saturable absorption in the near-infrared,[3] and single-molecule conductivity.[4] All these applications require efficient π-orbital overlap between the porphyrins, and this electronic coupling is generally maximized by locating the conjugated connections at the meso-positions of the porphyrin units. *Meso*−*meso* alkyne-linked porphyrin oligomers have been extensively investigated,[5−7] whereas *meso*−*meso* vinylene-linked structures have received little attention, except for β-alkyl systems such as Ni_2**1**,[8] in which conjugation is severely limited by steric interactions. For example, in Ni_2**1**, the ethyl substituents force the vinylene

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[†] Oxford University.
[‡] Air Force Research Laboratory.
[§] Montana State University.

[1] (a) Tsuda, A.; Osaka, A. *Science* **2001**, *293*, 79. (b) Arnold, D. P. *Synlett* **2000**, 296. (c) Anderson, H. L. *Chem. Commun.* **1999**, 1771.

[2] (a) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **2004**, *126*, 15352. (b) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Phys. Chem. B* **2005**, *109*, 7223.

[3] McEwan, K. J.; Fleitz, P. A.; Rogers, J. E.; Slagle, J. E.; McLean, D. G.; Akdas, H.; Katterle, M.; Blake, I. M.; Anderson, H. L. *Adv. Mater.* **2004**, *16*, 1933.

[4] Yoon, D. H.; Lee, S. B.; Yoo, K.-H.; Kim, J.; Lim, J. K. Aratani, N.; Tsuda, A.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2003**, *125*, 11062.

[5] (a) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972. (b) Screen, T. E. O.; Blake, I. M.; Rees, L. H.; Clegg, W.; Borwick, S. J.; Anderson, H. L. *J. Chem. Soc., Perkin Trans. 1* **2002**, 320.

[6] Arnold D. P.; James, D. A. *J. Org. Chem.* **1997**, *62*, 3460.

[7] (a) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105. (b) Susumu, K.; Duncan, T. V.; Therien, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 5186.

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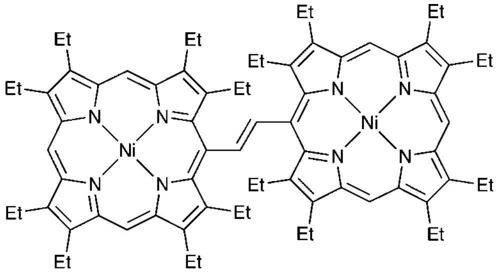
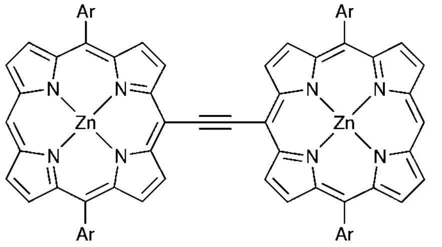
bridge to twist out of conjugation with the porphyrin π-system.[9–11] Here we report the synthesis of *meso*−*meso* vinylene-linked porphyrin dimers Zn_2**2a**,**b** without β-substituents, together with an analysis of the crystal structure of one of these dimers, Zn_2**2b**.[12] We compare the linear and nonlinear absorption behavior of Zn_2**2a** with those of its alkyne-linked analogue Zn_2**3**. Although the vinylene bridge is twisted by 45° relative to the plane of the porphyrin π-systems in the solid state, the degree of conjugation (as estimated from absorption spectra, emission spectra, and redox potentials) in these *E*-vinylene-linked dimers is similar to that of their alkyne-linked analogues. The vinylene-linked dimers exhibit superior reverse-saturable absorption in the near-infrared (710−900 nm).



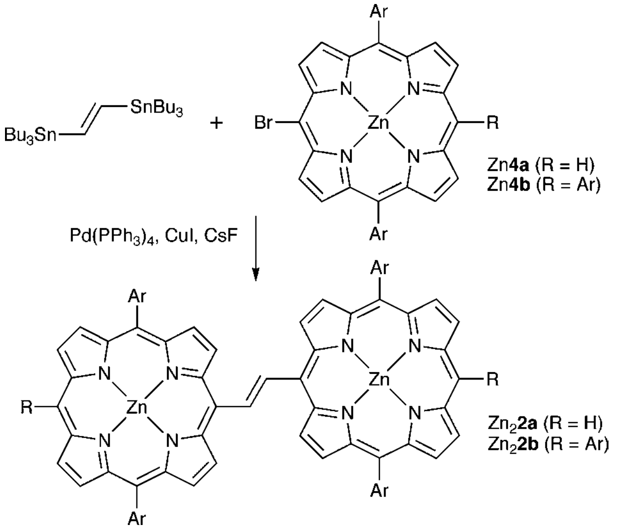
Ni_2**1**



Zn_2**3**

Initial attempts at synthesis of the C_2H_2-linked porphyrin dimer Zn_2**2a** by McMurry and Wittig couplings failed.[13] Palladium-catalyzed Stille coupling of bromoporphyrins with bis(tributylstannyl)ethene also failed to give the desired dimers until we tested Baldwin's protocol ($Pd(PPh_3)_4$, CuI, CsF).[14,15] When copper(I) iodide and cesium fluoride were added to the reaction mixture, Zn**4a** and Zn**4b** were converted to Zn_2**2a** and Zn_2**2b** in yields of 44 and 58%, respectively (Scheme 1).[16] The yield drops to around 10% in the absence of cesium fluoride, and no product is formed in the absence of copper iodide. We also used this method to synthesize the C_2-linked dimer Zn_2**3** from Zn**4a** using bis(tributylstannyl)ethyne, although the yield of Zn_2**3** is only 12%, so this approach may be inferior to the Heck−Sonogashira route pioneered by Therien and co-workers.[7]

Scheme 1. Synthesis of Dimers Zn_2**2a** and Zn_2**2b**[a]



[a] Ar = 3,5-Di-*tert*-butylphenyl.

The crystal structure of Zn_2**2b**·$2(C_6H_5N)$ was determined using single crystals grown from a solution in chlorobenzene/pyridine.[17] One pyridine molecule is coordinated to each zinc atom (not shown in Figure 1). There is a crystallographic inversion center at the center of the dimer molecule, so the mean planes of the two porphyrins are exactly parallel, but they are off-set by a distance of 1.47 Å, rather than being coplanar. The mean plane of the C−CH=CH−C bridge makes an angle of 45° to the mean plane of each porphyrin macrocycle. The main cause for this twist is a 1,5-C···C interaction between carbon atoms of the bridge and the

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[8] (a) Ponomarev, G. V.; Shul'ga, A. M. *Chem. Heterocyl. Compd. (Engl. Transl.)* **1986**, *22*, 228. (b) Vicente, M. G. H.; Smith, K. M. *J. Org. Chem.* **1991**, *56*, 4407. (c) Yashunsky, D. V.; Ponomarev, G. V.; Arnold, D. P. *Tetrahedron Lett.* **1995**, *36*, 8485.

[9] (a) Kitagawa, R.; Kai, Y.; Ponomarev, G. V.; Sugiura, K.; Borovkov, V. V.; Kaneda, T.; Sakata, Y. *Chem. Lett.* **1993**, 1071. (b) Senge, M. O.; Vicente, M. G. H.; Gerzevske, K. R.; Forsyth, T. P.; Smith, K. M. *Inorg. Chem.* **1994**, *33*, 5625.

[10] Several related structures of β-alkyl *meso*-vinylene-linked porphyrin-chlorin dimers and bischlorins have been reported, as well as a bispyropheophorabide-a: (a) Jaquinod, L.; Nurco, D. J.; Medforth, C. J.; Pandey, R. K.; Forsyth, T. P.; Olmstead, M. M.; Smith, K. M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1013. (b) Kalisch, W. W.; Senge, M. O.; Ruhlandt-Senge, K. *Photochem. Photobiol.* **1998**, *67*, 312. The angles between the mean planes of the C−CH=CH−C bridge and the macrocycle are 44° and 42° in the Ni_2 porphyrin-chlorin, 53° and 80° in the Ni_2 bischlorin, 27° in the Cu_2 bischlorin, and 79° in the free-base bispyropheophorabide-a. The presence of a saturated tetrahedral center at the β-position adjacent to the *E*-vinylene bridge reduces the steric interaction of a β-ethyl substituent at this position with the *E*-vinylene bridge and favors a more conjugated conformation.

[11] (a) Chachisvilis, M.; Chirvony, V. S.; Shulga, A. M.; Källebring, B.; Larsson, S.; Sundström, V. *J. Phys. Chem.* **1996**, *100*, 13857. (b) Chachisvilis, M.; Chirvony, V. S.; Shulga, A. M.; Källebring, B.; Larsson, S.; Sundström, V. *J. Phys. Chem.* **1996**, *100*, 13867.

[12] To the best of our knowledge, *meso*−*meso* *E*-vinylene-linked porphyrin dimers without β-substituents, such as Zn_2**2a/b**, have not been previously reported in the literature, although D. P. Arnold's group has prepared several analogues of **2a** by Suzuki coupling (unpublished, personal communication). The synthesis of a *Z*-vinylene-linked analogue of Zn_2**2b** (with Ph rather than Ar substituents), by a route similar to Scheme 1, has been reported in a patent: (a) Therien, M. J.; DiMagno, S. G. U.S. Patent 5,371,199, 1994. β−β *E*-vinylene-linked porphyrin dimers have also been investigated: (b) Johnson, S. G.; Small, G. J.; Johnson, D. G.; Svec, W. A.; Wasielewski, M. R. *J. Phys. Chem.* **1989**, *93*, 5437. (c) Zhilina, Z. I.; Ishkov, Y. V.; Voloshanovskii, I. S.; Andronati, S. A.; Fel'dman, S. V. *J. Org. Chem. USSR (Engl. Transl.)* **1989**, *25*, 2444.

[13] Screen, T. E. O., D.Phil. Thesis, Oxford University, Oxford, 2002.

[14] (a) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 1132. (b) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Chem.*−*Eur. J.* **2005**, *11*, 3294.

[15] For previous examples of Stille coupling with *meso*-bromo porphyrins, see: (a) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983. (c) Shi, X.; Amin, S. R.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 1650.

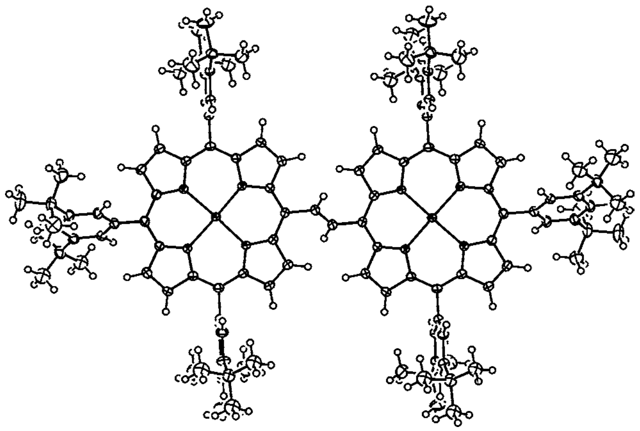

Figure 1. Molecular structure of Zn_2**2b**·2(C_6H_5N) viewed perpendicular to the mean plane of the porphyrin macrocycles (omitting coordinated pyridine ligands, 50% probability ellipsoids).

neighboring β-pyrrole carbons; this C···C distance is 3.09 Å (compared to 3.54 Å for twice the van der Waals radius of carbon). The 45° twist in Zn_2**2b** does not completely block conjugation between the two porphyrin π-systems, because the orbital overlap depends on the cosine of the angle. The two reported crystal structures of Ni_2**1** have porphyrin to C−CH═CH−C bridge mean plane twist angles of 89° and 74° (for the toluene and chloroform solvates, respectively),[9,10] and therefore the absence of β-ethyl substituents clearly leads to a more planar conformation in Zn_2**2b**.

The degree of porphyrin−porphyrin π-conjugation in Zn_2**2a** and Zn_2**3** can be evaluated from their absorption and emission spectra and redox potentials. The ground-state S_0-S_n absorption spectra of Zn_2**2a** and Zn_2**3** are compared in Figure 2 (solid lines). The maxima of Zn_2**2a** (422, 480, and 665 nm) are similar to those of Zn_2**3** (408, 483, and 710 nm), although the spectrum of Zn_2**2a** is broader. Under the same conditions, Zn_2**2a** and Zn_2**3** give fluorescence maxima at 765 nm (Φ_F 0.041, τ_S 0.76 ns) and 731 nm (Φ_F 0.10, τ_S 1.1 ns).[18,19] The first oxidation and reduction potentials for these dimers are: Zn_2**2a**: E_1^{ox} +0.39 V; E_1^{red} −1.53 V; Zn_2**3**: E_1^{ox} +0.29 V; E_1^{red} −1.69 V (all potentials versus Fc/Fc$^+$ in THF containing 0.1 M Bu_4NBF_4), corresponding to electrochemical gaps ($E_1^{ox} - E_1^{red}$) of 1.92 and 1.98 V, respectively.[19] The greater Stokes shift in Zn_2**2a** together with its lower fluorescence quantum yield and broader absorption spectrum all indicate greater flexibility in the *E*-vinylene bridge. Conformations are populated with a range of torsional twist angles at the vinylene bridge, leading to a distribution in the efficiency of porphyrin−porphyrin π-conjugation.[11] The more widely split B band and more red-shifted Q-band of Zn_2**3** demonstrate that its average ground state conformation is more conjugated than that of Zn_2**2a**, whereas the more red-shifted emission and smaller electrochemical gap of Zn_2**2a** indicate that its S_1 excited state, radical cation, and radical anion are more conjugated than those of Zn_2**3**.

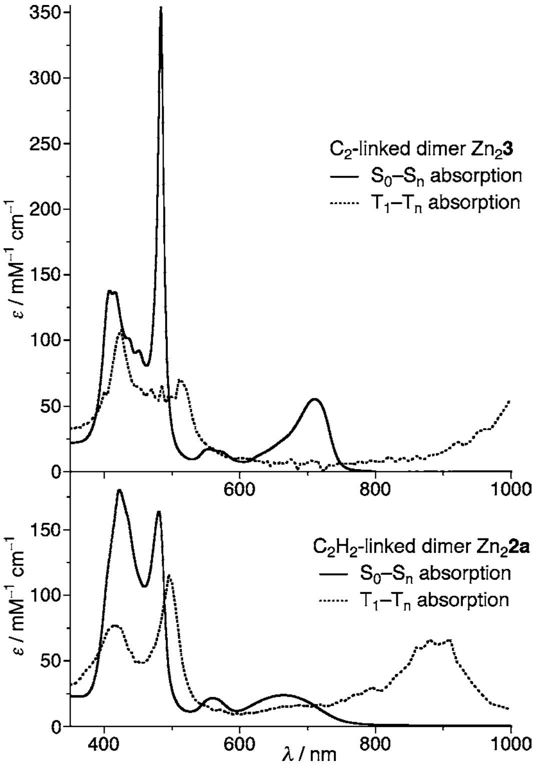

Figure 2. Ground-state and excited-state absorption spectra of Zn_2**2a** and Zn_2**3** in benzene containing 1% pyridine.

The nonlinear optical behavior of conjugated porphyrin oligomers leads to important applications, such as reverse

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(16) *Experimental procedure* for synthesis of Zn_2**2b**: (*E*)-1,2-Bis(tri-*n*-butylstannyl)ethene (25 μL, 47 μmol) was added to Zn**4b** (80 mg, 79 μmol), cesium fluoride (29 mg, 0.19 mmol), copper(I) iodide (5.5 mg, 29 μmol), tetrakis(triphenylphosphine)palladium(0) (17 mg, 15 μmol), and DMF (1.5 cm^3). The mixture was stirred at 115 °C under nitrogen for 42 h. Purification by chromatography over silica with light petroleum (bp 40−60 °C)/ethyl acetate/pyridine (10:1:1) as eluent and recrystallization from dichloromethane by layered addition of methanol gave dimer Zn_2**2b** (35 mg, 58%) as a purple powder. λ_{max} (C_6H_6/pyridine 99:1)/nm 432 (log(ϵ/M^{-1} cm^{-1}) 5.31), 487 (5.34), 570 (4.35), and 674 (4.55); δ_H (500 MHz, $CDCl_3/C_5D_5N$) 1.52 (72H, s), 1.53 (36H, s), 7.76 (4H, t, *J* = 1.6), 7.77 (2H, t, *J* = 1.6), 8.08 (4H, d, *J* = 1.6), 8.11 (8H, d, *J* = 1.6), 8.91 (8H, ABq), 9.06 (4H, d, *J* = 4.7), 10.02 (4H, d, *J* = 4.7), 10.03 (2H, s); δ_C (125.7 MHz, $CDCl_3/C_5D_5N$) 31.8, 35.0, 118.1, 120.5, 122.2, 122.4, 129.6, 129.8, 130.1, 131.8, 132.4, 142.57, 142.64, 144.1, 148.2, 149.8, 150.0, 150.2, 150.3; *m/z* (MALDI-TOF, dithranol) 1900.5; (M$^+$, $C_{126}H_{144}N_8Zn_2$ requires 1901.0).

(17) *Crystal data* for Zn_2**2b**·2(C_5H_5N): Crystals were grown from chlorobenzene/pyridine by vapor diffusion of ethanol. The structure was solved on an Enraf-Nonius Kappa CCD diffractometer using Mo Kα radiation. $C_{136}H_{154}N_{10}Zn_2\cdot 3(C_6H_5Cl)\cdot 3(H_2O)$, ($M_r$ = 2451.27): triclinic, space group $P\bar{1}$, D_c = 1.131 g cm^{-3}, a = 10.3948(2), b = 13.8919(2), c = 25.1936(3) Å, α = 90.6016(4), β = 91.8742(4), γ = 97.9594(5)°, V = 3600.65(10) Å^3, Z = 1, λ = 0.71073 Å, μ = 0.442 mm^{-1}, T = 150 K, R = 0.0805 for 10 198 observed reflections [$I > 3\sigma I$] and R_w = 0.0878 for all 16 237 unique reflections. The data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 276947.

(18) Fluorescence quantum yields were standardized to tetraphenyl porphyrin in benzene, Φ_F = 0.11; Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.

(19) 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinato zinc(II) has absorption spectrum: λ_{max} 420, 588 nm; fluorescence spectrum: λ_{max} 596, 649 nm (both in 1% pyridine/benzene); its redox potentials are: E_1^{ox} +0.39 V; E_1^{red} −1.87 V (versus Fc/Fc$^+$ in CH_2Cl_2 containing 0.1 M Bu_4NBF_4). Thus, the longest wavelength absorption band of Zn_2**2a** is red-shifted by 77 nm, relative to the corresponding porphyrin monomer, and its electrochemical gap is reduced by 0.34 V.

saturable absorption (RSA)[3] and two-photon absorption (TPA),[2] and therefore we have compared the RSA and TPA characteristics of the C_2H_2- and C_2-linked dimers Zn_2**2a** and Zn_2**3**. A compound exhibits RSA if the excited-state T_1-T_n absorption is stronger than the ground-state S_0-S_n absorption, provided that it has a significant triplet yield (Φ_T) and provided that the S_0-S_n absorption is high enough to achieve significant population of excited states.[20] The T_1-T_n absorption spectra of Zn_2**2a** and Zn_2**3** were measured by laser flash photolysis, in deoxygenated benzene with 1% pyridine (Figure 2, dashed curves, excitation at 355 nm with a 5-ns pulse). Zn_2**2a** has a triplet yield of $\Phi_T = 0.21$ and a triplet lifetime of $\tau_T = 10\ \mu s$, whereas Zn_2**3** has $\Phi_T = 0.44$ and biexponential decay, $\tau_T = 143\ \mu s$ and 1.65 ms. The T_1-T_n absorption of the C_2-linked dimer Zn_2**3** peaks beyond 1000 nm, where there is essentially no S_0-S_n absorption, making it unsuitable for RSA. In contrast, the C_2H_2-linked dimer Zn_2**2a** exhibits a T_1-T_n band at 880 nm. There is good overlap between this excited-state absorption and the broad tail of the ground-state Q-band, making it suitable for RSA in the near-infrared at 710−900 nm.

We also tested the two-photon absorption behavior of Zn_2**2a** using two-photon excited fluorescence. Previously we used this technique to show that Zn_2**3** has a remarkably strong TPA band at 821 nm ($\sigma_2^{max} = 8200$ GM), as well as a weaker red-shifted band at 940 nm (255 GM).[2] Zn_2**2a** shows a similar broad red-shifted TPA transition peaking at ca. 975 nm (60 GM) in the excitation wavelength range 940−1100 nm. The 4-fold lower cross section of this peak, as compared to that of Zn_2**3**, is consistent with the weaker conjugation in the C_2H_2-linked dimer. Unfortunately, it was impossible to measure the TPA spectrum of Zn_2**2a** at excitation wavelengths shorter than 940 nm because the long tail on the S_0-S_1 absorption makes the power dependence of the fluorescence nonquadratic in this region. This weak one-photon absorption at 710−900 nm, which prevents us from measuring the TPA spectrum of Zn_2**2a**, is the same feature that makes this chromophore promising for RSA.

In conclusion, we have developed an efficient synthetic route to *meso*−*meso* *E*-vinylene-linked porphyrin dimers. While the most populated conformation of the C_2H_2-linked dimer Zn_2**2a** has the vinylene bridge partly twisted out of conjugation with the porphyrins (45° twist in the solid state), making it less conjugated than the C_2-linked dimer Zn_2**3**, more planar conformations are also populated, which are more conjugated than the C_2-linked dimer, resulting in a long red tail in the absorption at 710−900 nm. In combination with a strong excited-state T_1-T_n absorption band at 700−1000 nm, these photophysical characteristics make C_2H_2-linked dimers promising materials for reverse saturable absorption.

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Supporting Information Available: Experimental procedures, full spectroscopic data for all new compounds, and crystal data (CIF) for porphyrin dimer **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] (a) Miles, P. A. *Appl. Opt.* **1994**, *33*, 6965. (b) Miles, P. A. *Appl. Opt.* **1999**, *38*, 566. (c) Kobyakov, A.; Hagan, D. J.; Van Stryland, E. W. *J. Opt. Soc. Am. B* **2000**, *17*, 1884.