Porphyrinoids

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# Synthesis of 7,8-Dehydropurpurin Dimers and Their Conversion into Conformationally Constrained β-to-β Vinylene-Bridged Porphyrin Dimers**

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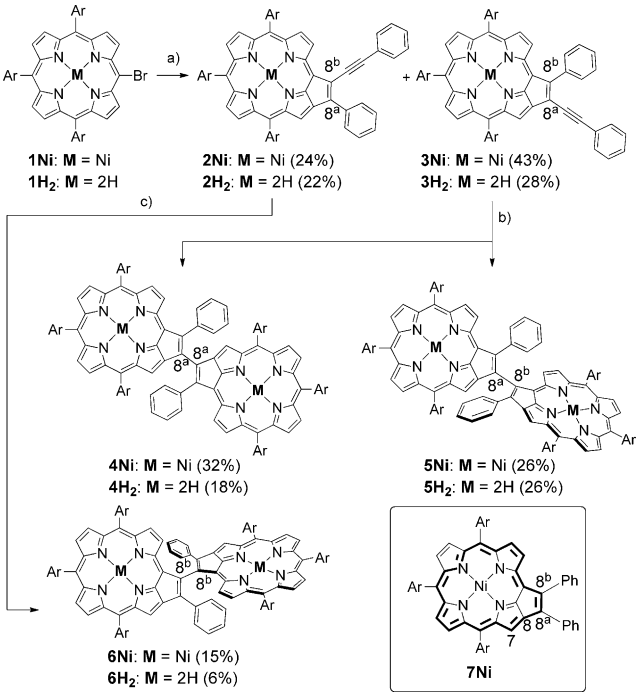
***Abstract:*** *7,8-Dehydropurpurin has attracted much attention owing to the dual 18π- and 20π-electron circuits in its macrocyclic conjugation. The two-fold Pd-catalyzed [3+2] annulation of meso-bromoporphyrin with 1,4-diphenylbutadiyne furnished 7,8-dehydropurpurin dimers. The 8ª,8ª-linked dimer displays a red-shifted and enhanced absorption band in the NIR region and a small electrochemical HOMO–LUMO band gap as a consequence of efficient conjugation between the two coplanar 7,8-dehydropurpurin units. Treatment of this dimer with N-bromosuccinimide in chloroform and ethanol gave β-to-β vinylene-bridged porphyrin dimers. Owing to the highly constrained conformations, these dimers exhibit perturbed absorption spectra, small Stokes shifts, and high fluorescence quantum yields.*

The 7,8-dehydropurpurins are intriguing porphyrinoids that exhibit altered absorption spectra, small HOMO–LUMO band gaps, and weakened aromaticity, as compared with standard porphyrins.[1–4] These properties arise from the presence of dual 18π- and 20π-electron circuits that resonate in the conjugated macrocyclic network.[1] Although a handful of 7,8-dehydropurpurin monomers have been synthesized in recent years, the chemistry of 7,8-dehydropurpurins remains relatively unexplored due to limited synthetic access to these macrocycles. In addition, there are no reports of multi-dehydropurpurinic compounds. Recently, we reported the efficient synthesis of 7,8-dehydropurpurin **7Ni** by Pd-catalyzed [3+2] annulation of *meso*-bromoporphyrin with diphenylacetylene.[2] Herein, we report the extension of this annulation reaction to the synthesis of directly linked 7,8-dehydropurpurin dimers **4M**–**6M** as the first examples of multi-dehydropurpurinic compounds (Scheme 1). Furthermore, dimers **4M** were efficiently converted into rigidly β-to-β vinylene-bridged porphyrins **8M** upon treatment with *N*-bromosuccinimide (NBS) in chloroform and ethanol. Zinc complexes **8Zn** exhibit fluorescence quantum yields of more than 0.17.




***Scheme 1.*** Synthesis of **2M**–**6M** and the structure of 8ª,8ᵇ-diphenyl-7,8-dehydropurpurin **7Ni.** Ar = 3,5-di-*tert*-butylphenyl. Reaction conditions: a) 1,4-diphenylbutadiyne (1.6 equiv for **M** = Ni, 1.5 equiv for **M** = 2H), (*o*-tol)$_3$P (28 mol%), [Pd$_2$(dba)$_3$] (7 mol%), NEt$_3$ (5 equiv), toluene, 110°C; b) *meso*-bromoporphyrin (3.5 equiv for **M** = Ni, 3.4 equiv for **M** = 2H), (*o*-tol)$_3$P (2 equiv), [Pd$_2$(dba)$_3$] (50 mol%), NEt$_3$ (5 equiv), DMF, 110°C; c) *meso*-bromoporphyrin (5 equiv), (*o*-tol)$_3$P (2 equiv), [Pd$_2$(dba)$_3$] (50 mol%), NEt$_3$ (5 equiv), DMF, 110°C. dba = dibenzylideneacetone, DMF = *N*,*N*-dimethylformamide.

First, Pd-catalyzed [3+2] annulation[2] of Ni$^{II}$ *meso*-bromoporphyrin **1Ni** with 1,4-diphenylbutadiyne under slightly modified conditions[5] gave alkynyl-7,8-dehydropurpurins **2Ni** and **3Ni** (Scheme 1 a,b). Atmospheric pressure chemical ionization (APCI) mass spectra of **2Ni** and **3Ni** display parent ion peaks at 1130.5693 and 1130.5711, respec-

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tively (calc'd for $C_{78}H_{80}N_4Ni$, *m/z* 1130.5731 $[M]^+$). The structures of **2Ni** and **3Ni** have been unequivocally determined by X-ray diffraction analysis (Figure 1). The $C8^a$–$C8^b$ bond lengths are 1.406 Å in **2Ni** and 1.405 Å in **3Ni**, which is strong evidence for $sp^2$ hybridization. The $^1H$ NMR spectra of **2Ni** and **3Ni** in $CDCl_3$ (see the Supporting Information) exhibit considerably decreased diatropic ring currents, as reported in the other 7,8-dehydropurpurins.[1–4]

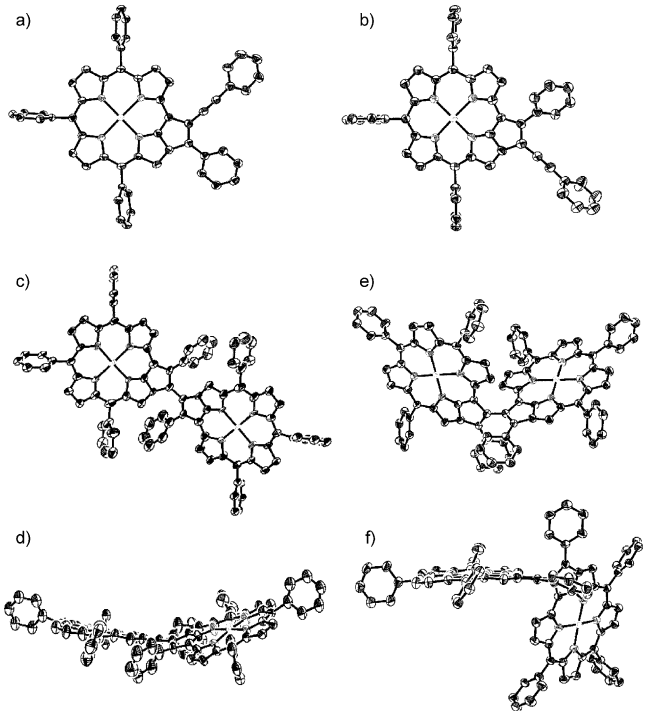



***Figure 1.*** X-Ray crystal structures. a) Top view of **2Ni**, b) top view of **3Ni**, c) top view and d) side view of **4Ni**, e) front view and f) side view of **6Ni**. Thermal ellipsoids are drawn at the 50% probability level for **2Ni**, and at the 30% probability level for **3Ni**, **4Ni**, and **6Ni**. Solvent molecules, *tert*-butyl groups and all hydrogen atoms are omitted for clarity.

In the next step, the [3+2] annulation reaction of **1Ni** with **3Ni** was attempted under similar conditions. The reaction was sluggish in toluene but proceeded smoothly in DMF[6] to provide 7,8-dehydropurpurin dimers **4Ni** and **5Ni** in 32% and 26% yields, respectively. The structure of **4Ni** has been determined by X-ray analysis (Figure 1 c,d ), in which the two 7,8-dehydropurpurin units were linked at the $C8^a$ and $C8^{a\prime}$, positions with a $C8^a$–$C8^{a\prime}$ bond distance of 1.451 Å, and are arranged in a coplanar manner with a small dihedral angle of 35.55°. The minor dimer, which has a $C8^a$–$C8^{b\prime}$ connection, has thus been assigned as **5Ni**. Dimers **4Ni** and **5Ni** were isolated as purple and brown solids, respectively. These results have demonstrated that a peripherally alkynylated 7,8-dehydropurpurin such as **3Ni** can serve as an alkyne substrate in the Pd-catalyzed [3+2] annulation reaction. Encouraged by the successful formation of **5Ni**, which should be formed by a more-congested carbopalladation step, the [3+2] annulation reaction of **1Ni** with **2Ni** has been also attempted under similar conditions, and furnished **6Ni** in 15% yield as brown solids with a 42% recovery of **2Ni** (Scheme 1). The dimer **6Ni** was expected to be much more sterically congested. This has been confirmed by its crystal structure, as shown in Figure 1 e,f. In **6Ni**, the two 7,8-dehydropurpurin units are linked together with a larger dihedral angle of 74.55° and a longer $C8^b$–$C8^{b\prime}$ bond distance of 1.462 Å. Free base 7,8-dehydropurpurins $\mathbf{2H_2}$ and $\mathbf{3H_2}$ and dimers $\mathbf{4H_2}$, $\mathbf{5H_2}$, and $\mathbf{6H_2}$ were similarly synthesized.

The UV/Vis/NIR absorption spectra of **3Ni**–**6Ni** in $CH_2Cl_2$ are shown in Figure 2. The absorption spectra of **2Ni** and **3Ni** are similar, showing split Soret bands located at

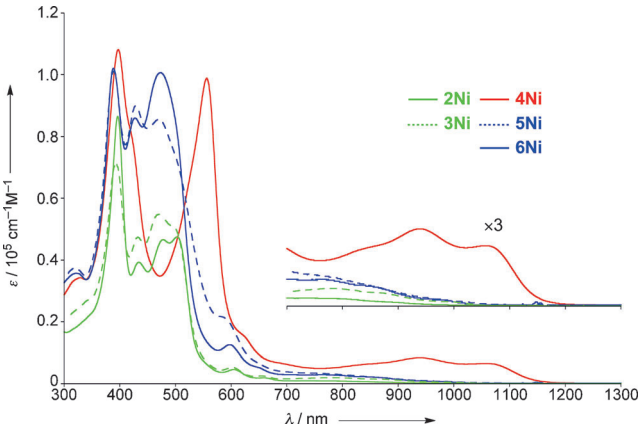



***Figure 2.*** UV/Vis/NIR absorption spectra of **2Ni**–**6Ni** in $CH_2Cl_2$.

350–550 nm, almost featureless Q-like bands around 600 nm, and weak and extremely broad bands reaching out to around 1050 nm. The broad and weak bands reflect forbidden HOMO–LUMO transitions related to a 20π-antiaromatic 7,8-dehydropurpurin system, as previously observed.[1–4] The absorption spectra of **5Ni** and **6Ni** are both roughly similar to those of **2Ni** and **3Ni**, except for some intensification of the longer split Soret bands. In contrast, the absorption spectrum of **4Ni** is more distinguished from those of **5Ni** and **6Ni**, showing split Soret bands at 397 and 556 nm, and well-defined near-infrared (NIR) bands at 939 and 1056 nm. These characteristic spectral features have been interpreted in terms of effective conjugation of the two 7,8-dehydropurpurin units in **4Ni**, which is aided by its coplanar structure. On the other hand, the electronic conjugation is interrupted in **5Ni** and **6Ni**, owing to the tilted relationship between their subunits.

The electrochemical properties of **2Ni**–**7Ni** were studied by cyclic voltammetry (CV) in $CH_2Cl_2$ (Table 1). Reference monomer **7Ni** exhibited two reversible oxidation and reduction waves. Monomers **2Ni** and **3Ni** exhibited similar waves, but their second oxidation waves became irreversible and their reduction waves were shifted to lower potentials versus those of **7Ni**. These CV data allowed for the estimation of electrochemical HOMO–LUMO band gap: 1.53 and 1.56 eV for **2Ni** and **3Ni**, respectively. Dimer **4Ni** showed oxidation waves at −0.05, 0.17, and 0.88 V, and reduction waves at −1.31 and −1.48 V. The two lower oxidation waves have been interpreted as split first potentials with $\Delta E = 0.22$ V, owing to

***Table 1:*** Redox potentials of **2Ni–7Ni**.[a]

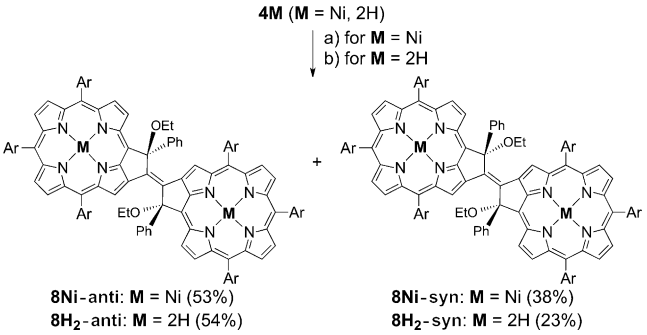
| | Oxidation [V] | | | | Reduction [V] | | $E^{1/2}_{ox1}-E^{1/2}_{red1}$ |
|---|---|---|---|---|---|---|---|
| | $E^{1/2}_{ox1}$ | $E^{1/2}_{ox2}$ | $E^{1/2}_{ox3}$ | $E^{1/2}_{ox4}$ | $E^{1/2}_{red1}$ | $E^{1/2}_{red2}$ | [eV] |
| **2Ni** | 0.22 | – | – | – | −1.31 | −1.77 | 1.53 |
| **3Ni** | 0.17 | – | – | – | −1.39 | −1.76 | 1.56 |
| **4Ni** | −0.05 | 0.17 | 0.88 | – | −1.31 | −1.48 | 1.26 |
| **5Ni** | 0.08 | 0.29 | 0.73 | – | −1.44 | −1.57 | 1.52 |
| **6Ni** | 0.17 | 0.35 | 0.58 | 0.73 | −1.45 | −1.56 | 1.62 |
| **7Ni** | 0.19 | 0.64 | – | – | −1.47 | −1.90 | 1.63 |

[a] The redox potentials were measured by cyclic voltammetry in anhydrous $CH_2Cl_2$, with $Bu_4NPF_6$ (0.1 M) as a supporting electrolyte and $Ag/AgClO_4$ as a reference electrode; ferrocene/ferrocenium ion couple was used as an external reference.

the electronic interaction of the two 7,8-dehydropurpurins. The electrochemical HOMO–LUMO gap has been calculated to be 1.26 eV, which is distinctly smaller than those of dimers **5Ni** (1.52 eV) and **6Ni** (1.62 eV).

Time-dependent density functional theory (TD-DFT) calculations (Gaussian) at the B3LYP/6-31G*(C,H,N)+LANL2DZ(Ni) level have been performed on dimers **4Ni** and **6Ni** along with **7Ni** (Supporting Information, Figures S60–65).[7] Unlike $Ni^{II}$–porphyrin, **7Ni** has non-degenerate HOMO-1, HOMO, LUMO, and LUMO+1 that lie at distinctly different energy levels. The HOMO–LUMO excitation of **7Ni** is symmetry forbidden, for which the oscillator strength was calculated to be ca. 0.0244. In dimer **6Ni**, the interaction of two HOMOs (LUMOs) of 7,8-dehydropurpurin units led to a slightly perturbed HOMO and HOMO-1 (LUMO and LUMO+1). The energy differences are quite small: 0.145 eV for the HOMO–HOMO-1 energy gap and 0.085 eV for the LUMO–LUMO+1 energy gap. In contrast, larger energy differences are calculated for **4Ni**: 0.522 eV for the HOMO–HOMO-1 energy gap and 0.367 eV for the LUMO–LUMO+1 energy gap. More importantly, the HOMO–LUMO transition in **4Ni** becomes symmetry-allowed and its oscillator strength was calculated to be 0.2399, which is consistent with the observed moderate absorbance of the NIR bands. The HOMO–LUMO transition in **6Ni** remains symmetry prohibited and the oscillator strength was calculated to be 0.0163. The HOMO–LUMO gaps of **4Ni** and **6Ni** were calculated to be 1.684 and 2.002 eV, respectively, showing the same trend with the experimental results.

The two fused five-membered rings in **4Ni** are well conjugated and were expected to show high reactivity. This was indeed the case, and **4Ni** cleanly reacted with *N*-bromosuccinimide in $CHCl_3$ and ethanol. To our surprise, no brominated products were obtained. Instead, we were delighted to isolate β-to-β vinylene-bridged porphyrin dimer **8Ni**-anti and **8Ni**-syn (Scheme 2). They would be formed through bromoetherification of the butadiene linkage followed by nucleophilic substitution of the resulting highly reactive bromide with ethanol. X-ray crystallographic analysis unambiguously revealed the interesting structure of **8Ni**-anti (Figure 3), in which the two $Ni^{II}$ porphyrin units are bridged in a coplanar manner by a vinylene unit that is fixed by two $sp^3$ carbons (Figure 4). Although a similar conformationally fixed vinylene-bridged dimer was reported for pheophorbides,[8] this is, to the best of our knowledge, the first example of porphyrin congeners.[9] Through similar treatment, $Zn^{II}$-complexes **8Zn**-anti and **8Zn**-syn were prepared from $\mathbf{4H_2}$ followed by zinc metalation (Scheme 2). The UV/Vis absorption and fluorescence spectra of **8Zn**-anti and **8Zn**-syn are shown in Figure 4. These two isomers show largely perturbed absorption spectra that are panchromatic up to ca. 650 nm. Characteristically, the Q bands at 637 nm are sharp and intensified, reflecting the enhanced transition




***Scheme 2.*** Structures and synthesis of **8**. Ar = 3,5-di-*tert*-butylphenyl. Reaction conditions: a) NBS (1.0 equiv), pyridine (2 drops), $CHCl_3$/EtOH, 0 °C; b) NBS (1.0 equiv), pyridine (2 drops), $CHCl_3$/EtOH, 0 °C; then $Zn(OAc)_2{\cdot}2H_2O$, $CH_2Cl_2$/MeOH.

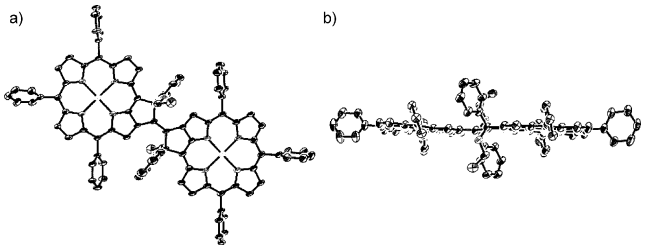



***Figure 3.*** X-Ray crystal structures. a) Top view and b) side view of **8Ni**-anti. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules, *tert*-butyl groups, and all hydrogen atoms are omitted for clarity.

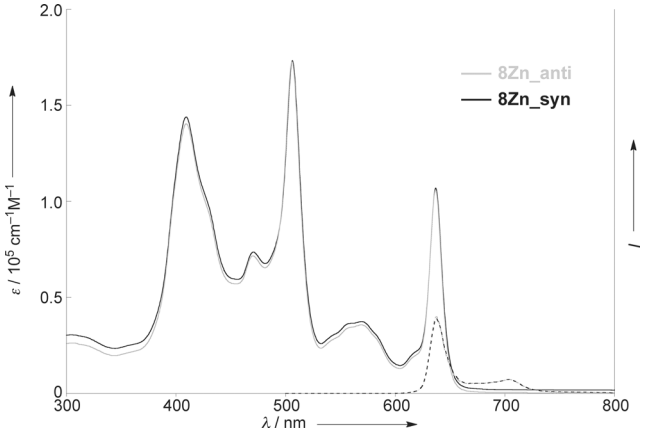



***Figure 4.*** UV/Vis absorption (solid lines) and fluorescence (dashed lines) spectra of **8Zn**-anti and **8Zn**-syn in $CH_2Cl_2$.

dipole moment along the long molecular axis. The rigidly held conjugated structures of **8Zn** result in very small Stokes shifts ($15\ cm^{-1}$). In addition, **8Zn**-anti and **8Zn**-syn exhibit high fluorescence quantum yields, 0.172 and 0.173, respectively, and fluorescence lifetimes of 1.73 ns. Based on these data, the radiative rate constants of **8Zn**-anti and **8Zn**-syn have been estimated to be $9.9\times10^7\ s^{-1}$, which are distinctly larger than that of $Zn^{II}$ tetraphenylporphyrin ($1.5\times10^7\ s^{-1}$).[10,11] The larger radiative rates of **8Zn** can be ascribed to the large transition dipole moments along the long molecular axis.

In summary, two-fold Pd-catalyzed [3+2] annulation of *meso*-bromoporphyrin **1M** with 1,4-diphenylbutadiyne furnished 7,8-dehydropurpurin dimers **4M**, **5M**, and **6M** through **2M** or **3M**. Whereas the electronic interactions between the 7,8-dehydropurpurins are weak in **5M** and **6M**, the two 7,8-dehydropurpurin units are effectively conjugated in **4M**, as indicated by the red-shifted and enhanced absorption bands in the long wavelength region, the small electrochemical HOMO–LUMO band gap, and TD-DFT calculations. The dimer **4M** was converted into β-to-β vinylene-bridged porphyrin dimers **8M**, which display largely perturbed absorption spectra with small Stokes shifts and high fluorescence quantum yields, reflecting the well-conjugated electronic networks and constrained conformations. These attractive attributes are promising for use in many elaborate applications. Further studies related to this work are actively in progress in our laboratories.

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[1] For thiophene-fused 7,8-dehydropurpurins, see: Y. Mitsushige, S. Yamaguchi, B. S. Lee, Y. M. Sung, S. Kuhri, C. A. Schierl, D. M. Guldi, D. Kim, Y. Matsuo, *J. Am. Chem. Soc.* **2012**, *134*, 16540.
[2] A. K. Sahoo, S. Mori, H. Shinokubo, A. Osuka, *Angew. Chem.* **2006**, *118*, 8140; *Angew. Chem. Int. Ed.* **2006**, *45*, 7972.
[3] A. Nakano, N. Aratani, H. Furuta, A. Osuka, *Chem. Commun.* **2001**, 1920.
[4] For benzo-fused 7,8-dehydropurpurins, see: a) S. Fox, R. W. Boyle, *Chem. Commun.* **2004**, 1322; b) D.-M. Shen, C. Liu, Q.-Y. Chen, *Chem. Commun.* **2005**, 4982; c) D.-M. Shen, C. Liu, Q.-Y. Chen, *J. Org. Chem.* **2006**, *71*, 6508; d) S. Hayashi, Y. Matsubara, S. Eu, H. Hayashi, T. Umeyama, Y. Matano, H. Imahori, *Chem. Lett.* **2008**, *37*, 846; e) G. Bringmann, D. C. G. Götz, T. A. M. Gulder, T. H. Gehrke, T. Bruhn, T. Kupfer, K. Radacki, H. Braunschweig, A. Heckmann, C. Lambert, *J. Am. Chem. Soc.* **2008**, *130*, 17812; f) T. D. Lash, B. E. Smith, M. J. Melquist, B. A. Godfrey, *J. Org. Chem.* **2011**, *76*, 5335; g) A. M. V. M. Pereira, M. G. P. M. S. Neves, J. A. S. Cavaleiro, C. Jeandon, J.-P. Gisselbrecht, S. Choua, R. Ruppert, *Org. Lett.* **2011**, *13*, 4742; h) T. Ishizuka, Y. Saegusa, Y. Shiota, K. Ohtake, K. Yoshizawa, T. Kojima, *Chem. Commun.* **2013**, *49*, 5939; i) N. Fukui, W.-Y. Cha, S. Lee, S. Tokuji, D. Kim, H. Yorimitsu, A. Osuka, *Angew. Chem.* **2013**, *125*, 9910; *Angew. Chem. Int. Ed.* **2013**, *52*, 9728.
[5] Although we used $NCy_2Me$ (Cy = cyclohexyl) as the base in the previously reported procedures, use of $NEt_3$ enhanced the yield of **2Ni** and **3Ni**.
[6] a) R. C. Larock, E. K. Yum, *J. Am. Chem. Soc.* **1991**, *113*, 6689; b) G. Zeni, R. C. Larock, *Chem. Rev.* **2006**, *106*, 4644.
[7] Gaussian 09, revision A.02, M. J. Frisch. et al. Gaussian, Inc.: Wallingford, CT, **2009**.
[8] L. Jaquinod, M. O. Senge, R. K. Pandey, T. P. Forsyth, K. M. Smith, *Angew. Chem.* **1996**, *108*, 1982; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1840.
[9] For β-to-β vinylene-bridged porphyrin dimers, see: a) Z. I. Zhilina, Y. V. Ishkov, I. S. Voloshanovskii, A. S. A. Andronati, *Dokl. Akad. Nauk SSSR* **1988**, *303*, 326; b) E. E. Bonfantini, D. L. Officer, *Tetrahedron Lett.* **1993**, *34*, 8531; c) E. G. Levinson, N. A. Reztsova, A. F. Mironov, *Mendeleev Commun.* **1995**, *5*, 44; d) A. K. Burrell, D. L. Officer, *Synlett* **1998**, 1297; e) S. Hiroto, K. Suzuki, H. Kamiya, H. Shinokubo, *Chem. Commun.* **2011**, *47*, 7149; f) X. Jiang, P. Li, Y. Wang, Q. Shen, J. Tao, W. Shi, *Chin. J. Chem.* **2012**, *30*, 405.
[10] The fluorescence quantum yield and lifetime of $Zn^{II}$ tetraphenylporphyrin were reported to be 0.033 and 2.2 ns; see: J.-P. Strachan, S. Gentemann, J. Seth, W. A. Kalsbeck, J. S. Lindsey, D. Holten, D. F. Bocian, *J. Am. Chem. Soc.* **1997**, *119*, 11191.
[11] The quantum yield of $Zn^{II}$ triphenylporphyrin was measured to be 0.023 by our apparatus.

  