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Dimeric Assemblies from 1,2,3-Triazole-Appended Zn(II) Porphyrins with Control of NH-Tautomerism in 1,2,3-Triazole

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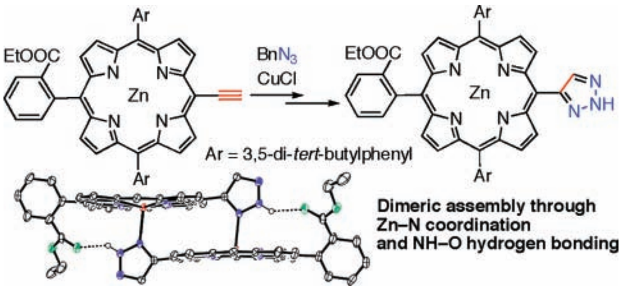
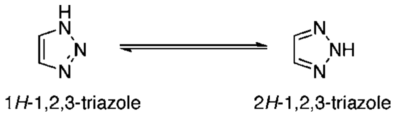
ABSTRACT



Cu(I)-catalyzed 1,3-dipolar cycloaddition of *meso*-ethynyl Zn(II) porphyrin with benzyl azide efficiently provides *meso*-1-benzyl-1*H*-1,2,3-triazolyl Zn(II) porphyrin, which assembles to form a slipped cofacial dimer by the complementary coordination of the triazole nitrogen atom at the 3-position to the zinc center of a second porphyrin moiety both in the solid and solution states. Removal of the benzyl protection and introduction of a 2-ethoxycarbonylphenyl moiety greatly stabilize the dimeric assembly through an additional hydrogen bonding interaction between the NH proton of 2*H*-1,2,3-triazole and the carbonyl oxygen.

Molecular fractionality given by tautomerism has been an intriguing topic in basic chemistry.[1] In particular, NH-tautomerism in 1,2,3-triazole between 1*H*- and 2*H*-forms has been argued on the basis of theoretical calculations, crystal structures, and basicity analysis (Scheme 1).[2]

Scheme 1. Tautomerism of 1,2,3-Triazole



Both forms are close in energy and easily interconvertible to each other in solution. Since 1,2,3-triazole plays a dual role as a donor and acceptor in hydrogen-bonding interactions, the fractional nature of 1,2,3-triazole would lead

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(1) (a) Mó, O.; De Paz, J. L. D.; Yáñez, M. *J. Phys. Chem.* **1986**, *90*, 5597. (b) Catalán, J.; Claramunt, R. M.; Elguero, J.; Laynez, J.; Menéndez, M.; Anvia, F.; Quian, J. H.; Taagepera, M.; Taft, R. W. *J. Am. Chem. Soc.* **1988**, *110*, 4105. (c) Nagy, P. I.; Tejada, F. R.; Messer, W. S., Jr. *J. Phys. Chem. B* **2005**, *109*, 22588.

(2) (a) Albert, R. A.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, *11*, 1903. (b) Tomás, F.; Abboud, J.-L. M.; Laynez, J.; Notario, R.; Santos, L.; Nilsson, S. O.; Catalán, J.; Claramunt, R. M.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 7348. (c) Tomás, F.; Catalan, J.; Perez, P.; Elguero, J. *J. Org. Chem.* **1994**, *59*, 2799. (d) Abboud, J.-L. M.; Foces-Foces, C.; Notario, R.; Trifonov, R. E.; Volovodenko, A. P.; Ostrovskii, V. A.; Alkorta, I.; Elguero, J. *Eur. J. Org. Chem.* **2001**, 3013.

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to flexible molecular recognition.[3] Furthermore, 1,2,3-triazole is also an important motif in coordination chemistry to construct metal complexes.[4]

Porphyrinic supramolecular assemblies constructed by noncovalent bonds have received much attention in wide areas of chemistry.[5] Such noncovalent assemblies often employ coordination of pyridine and imidazole moieties to the zinc center of porphyrins.[6] However, there are no precedent reports on the aggregation behavior of triazolyl-appended porphyrins. Recently, we have focused on 1,2,3-triazolylporphyrins due to the synthetic ease of Huisgen's 1,3-dipolar cycloaddition reaction between alkynylporphyrins and alkyl azides.[7] Syntheses of triazolyl-appended porphyrins have been independently reported by the Chen and Odobel groups very recently.[8] However, formation of molecular assemblies of 1,2,3-triazolylporphyrins both in solid and solution states remains unreported.

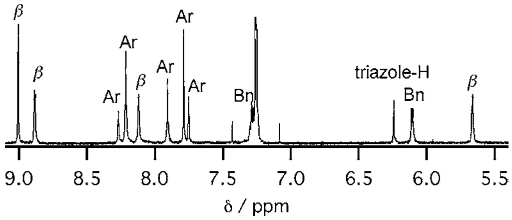
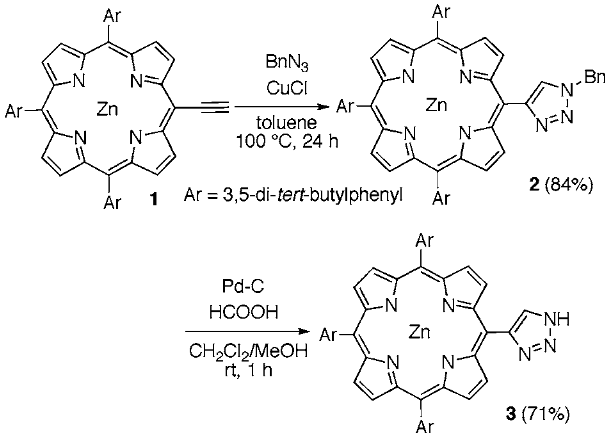


Figure 1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

A toluene solution of *meso*-ethynyl Zn(II) porphyrin **1** and benzyl azide was heated in the presence of a catalytic amount of CuCl. After chromatographic separation, *meso*-triazolyl Zn(II) porphyrin **2** was obtained in over 80% yield. Despite high temperatures, none of the other regioisomer was detected in the reaction mixture, probably because of the large steric effect of the porphyrin substituent. Importantly, the ^{1}H NMR spectrum of **2** in $CDCl_3$ exhibits a simple set of peaks with a large upfield shift for one β-proton at δ 5.7 ppm and for the triazole proton at δ 6.3 ppm (Figure 1). This characteristic is typical for dimeric porphyrin assemblies due to the aromatic ring current effect.[9] The benzyl group was then removed with Pd/C and formic acid as the hydrogen source to provide **3** (Scheme 2). The ^{1}H NMR spectrum of **3** in $CDCl_3$ also displays typical features for dimeric porphyrin assemblies in a similar manner to **2** (Supporting Information, SI).

Scheme 2. Synthesis of 1,2,3-Triazolylporphyrins **2** and **3**



Slow diffusion of acetonitrile into a chloroform solution of **2** afforded single crystals, suitable for X-ray crystallography. X-ray analysis of **2** unambiguously elucidated that **2** formed a dimeric assembly **(2)$_2$** constructed by the coordination between nitrogen and zinc atom (Figure 2a).[10]

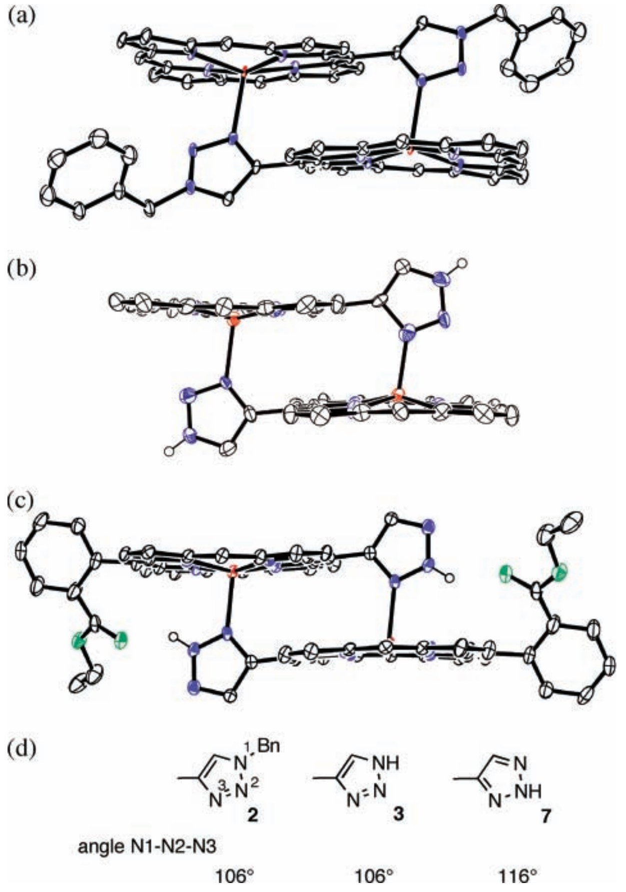


Figure 2. X-ray crystal structures of dimeric assembly of (a) **(2)$_2$**, (b) **(3)$_2$**, and (c) **(7)$_2$**. Hydrogen atoms except NH protons and *meso*-3,5-di(*tert*-butyl)phenyl groups were omitted for clarity. The thermal ellipsoids were at the 50% probability level. (d) N1−N2−N3 angle of triazole rings in **2**, **3**, and **7**.

Furthermore, the slipped cofacial dimer structure of **(3)$_2$** was also revealed by X-ray analysis of **3** (Figure 2b).[11] The coordination bond length in **(3)$_2$** is 2.13 Å and the distance between two porphyrin planes is 3.2 Å, which suggests $\pi-\pi$ interaction. The Zn atom is displaced by 0.36 Å from the porphyrin plane. The structure of the triazole was determined

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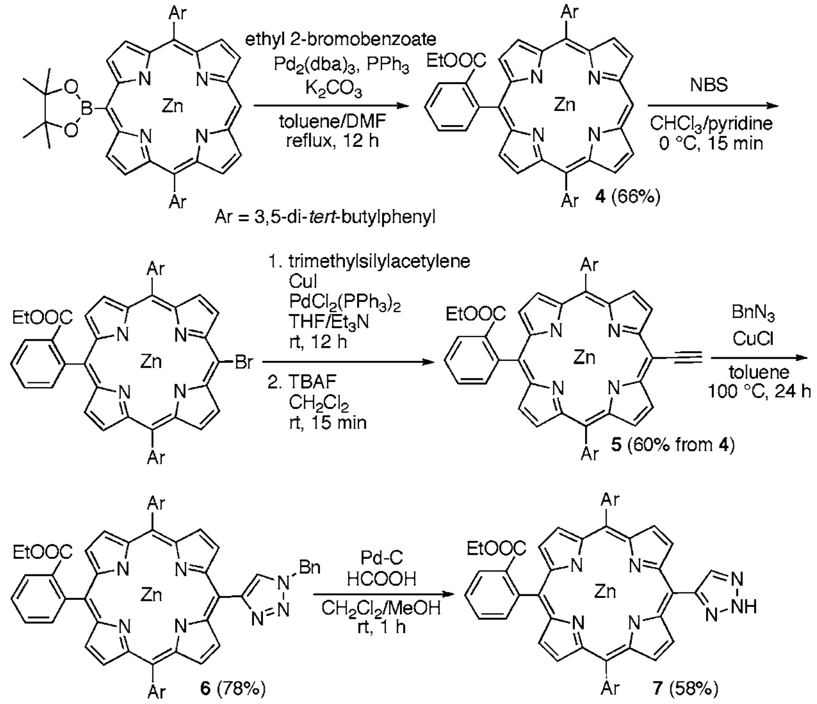
(5) (a) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133. (b) Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113. (c) Ingeno, E.; Zangrando, E.; Alessio, E. *Eur. J. Inorg. Chem.* **2003**, 2371. (d) Satake, A.; Kobuke, Y. *Tetrahedron* **2005**, *61*, 13. (e) Maeda, C.; Kamada, T.; Aratani, N.; Osuka, A. *Coord. Chem. Rev.* **2007**, *251*, 2743.

Scheme 3. Synthesis of 1,2,3-Triazolylporphyrins **6** and **7**[a]



to be the 1*H*-form on the basis of angles around the nitrogen atoms,[2d] indicating a preference for the 1*H*-tautomer in the solid state (Figure 2d).

Although the ^{1}H NMR spectrum in $CDCl_3$ reveals complete formation of the dimeric assembly $(\mathbf{3})_2$ at relatively high concentration (>1 mM), UV/vis absorption spectra in $CHCl_3$ are concentration dependent in a range from 10^{-5} to 10^{-3} M, showing the weak nature of this molecular assembly constructed by the coordination of 1,2,3-triazole to zinc atom. Upon an increase in concentration, the shape of the Soret band becomes dramatically broadened and Q-band becomes red-shifted (SI). A good fit for the observed sigmoidal curve was obtained by assuming porphyrin dimer formation, giving an association constant of $K_2 = 1.0 \times 10^4$ M^{-1}. This association constant, compared with that ($K_2 = 1.0 \times 10^{11}$ M^{-1}) of a *meso*-imidazolyl Zn(II) porphyrin, indicates that the stability of $(\mathbf{3})_2$ is only modest.

A 2-ethoxycarbonylphenyl group was introduced at the *meso*-position opposite to the triazole group to explore extra stabilization of the dimer by a possible hydrogen bonding interaction.[6h] As shown in Scheme 3, 5-(2-ethoxyphenyl) substituted Zn(II) porphyrin **4** was prepared by Suzuki–Miyaura coupling of 5-borylated Zn(II) porphyrin with ethyl 2-bromobenzoate. Subsequent bromination with NBS, Sonogashira coupling, and click reaction afforded 1,2,3-triazole-appended Zn(II) porphyrin **6**. Finally, debenzylation was effected by Pd/charcoal to provide **7**. Whereas the ^{1}H NMR spectrum of **6** is simple in pyridine-d_5, indicating its existence as a monomer, that of **6** in $CDCl_3$ is slightly complicated, involving several upfield shifted signals. The latter spectrum indicated the presence of several not well-defined assemblies, which are probably constructed from atropisomers with respect to the direction of the ethoxycarbonyl group toward the triazole group. On the other hand, the ^{1}H NMR spectrum

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(6) Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936. (b) Knapp, S.; Vasudevan, J.; Emeg, T. J.; Arion, B. H.; Potenza, J. A.; Schugar, H. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2368. (c) Wilson, G. S.; Anderson, H. L. *Chem. Commun.* **1999**, 1539. (d) Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **1999**, *121*, 11538. (e) Haycock, R. A.; Yartsev, A.; Michelsen, U.; Sundström, V.; Hunter, C. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3616. (f) Ogawa, K.; Kobuke, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 4070. (g) Ikeda. C.; Nagahara, N.; Yoshioka, N.; Inoue, H. *New J. Chem.* **2000**, *24*, 897. (h) Ikeda, C.; Tanaka, Y.; Fijihara, T.; Ishii, Y.; Ushiyama. T.; Yamamoto, K.; Yoshioka, N.; Inoue, H. *Inorg. Chem.* **2001**, *40*, 3395. (i) Ogawa, K.; Zhang, T.; Yoshihara, K.; Kobuke, Y. *J. Am. Chem. Soc.* **2002**, *124*, 22. (j) Tsuda, A.; Sakamoto, S.; Yamaguchi, K.; Osuka, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2817. (k) Takahashi, R.; Kobuke, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2372. (l) Tsuda, A.; Sakamoto, S.; Yamaguchi, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 15722. (m) Hwang, I.-W.; Kamada, T.; Ahn, T. K.; Ko, D. M.; Nakamura, T.; Tsuda, A.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2004**, *126*, 16187. (n) Kamada, T.; Aratani, N.; Ikeda, T.; Shibata, N.; Higuchi, Y.; Wakamiya, A.; Yamaguchi, S.; Kim, K. S.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2006**, *128*, 7670. (o) Maeda, C.; Shinokubo, H.; Osuka, A. *Org. Lett.* **2007**, *9*, 2493.

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(10) Crystallographic data for **2**: $C_{142}H_{164}N_{14}Cl_{18}Zn_2$, M_W 2907.82, triclinic, space group *P*-1 (No. 2), $a = 13.959(5)$ Å, $b = 14.301(5)$ Å, $c = 18.276(5)$ Å, $\alpha = 95.686(5)°$, $\beta = 99.037(5)°$, $\gamma = 91.849(5)°$, $V = 3581(2)$ Å^3, $T = 90$ K, $D_{calcd} = 1.348$ g cm^{-3}, $Z = 1$. For 18670 reflections measured; $R_1 = 0.0991$, w$R_2 = 0.2463$ for 12393 reflections with $[I > 2\sigma(I)]$, GOF = 1.117.

(11) Crystallographic data for **3**: $C_{168}H_{191}N_{22}Zn_2$, M_W = 2649.22, triclinic, space group *P*1, $a = 13.1202(13)$ Å, $b = 16.6253(16)$ Å, $c = 17.5706(17)$ Å, $\alpha = 78.601(2)°$, $\beta = 81.694(2)°$, $\gamma = 89.735(2)°$, $V = 3716.5(6)$ Å^3, $T = 90$ K, $D_{calcd} = 1.184$ g cm^{-3}, $Z = 1$. For 22936 reflections measured; $R_1 = 0.0807$, w$R_2 = 0.1580$ for 18998 reflections with $[I > 2\sigma(I)]$, GOF = 1.052.

of **7** in $CDCl_3$ showed a simple set of peaks, indicating formation of a dimeric assembly of only one atropisomer. In the ^1H NMR spectrum of **7**, one of the pyrrolic β-protons was considerably shifted to high field at δ 5.7 ppm, and the triazole NH proton appeared at δ 8.7 ppm, suggesting hydrogen-bonding interaction. Finally, X-ray diffraction analysis clearly proved the dimeric structure of $(\mathbf{7})_2$ (Figure 2c).[12] The angle $N_1N_2N_3$ was found to be 116°, which is typical for 2*H*-triazole.[2d] The distance between NH proton and carbonyl oxygen is 2.02 Å, supporting hydrogen bonding. Clearly, the hydrogen bond fixes the NH proton at the 2-position of 1,2,3-triazole. This finding is significant because it is usually difficult to determine the position NH proton of 1,2,3-triazole. The UV-absorption spectrum of **7** in $CHCl_3$ shows splitting of the Soret band, which is characteristic for dimeric assemblies,[9] down to 10^{-7} M (Figure 3). Fluorescence spectra are also concentration independent in the range from 10^{-8} to 10^{-6} M, indicating very tight assembly. In fact, the association constant is calculated to be $K_2 > 1.0 \times 10^{11}$ M^{-1} (SI).[13] The additional two hydrogen bonding interactions, which fixes NH-tautomerism and atropisomerism at the same time, enhances the stability of the assembly by more than 6 orders of magnitude.

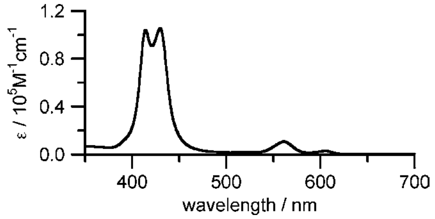

Figure 3. UV−vis absorption spectra of $(\mathbf{7})_2$ in $CHCl_3$.

In summary, *meso*-1,2,3-triazolyl Zn(II) porphyrins **2**, **3**, **6**, and **7** were synthesized via click reaction and self-assembling behaviors to form dimeric assemblies by Zn−N coordination were confirmed by ^1H NMR, X-ray analysis, and electronic spectra. Especially in the case of **7**, the additional hydrogen-bonding provided by the remote 2-ethoxycarbonylphenyl group contributes to fixation of both NH-tautomerism of 1,2,3-triazole and atropisomerization to afford a highly stable porphyrin assembly. Further investigations on the supramolecular chemistry and photochemistry of porphyrin arrays are currently being investigated in our laboratory.

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Note Added after ASAP Publication There was a spelling error in ref 8a in the version published ASAP January 24, 2008; the corrected version was published ASAP January 29, 2008.

Supporting Information Available: Experimental procedures, compound data, association constants for **2**, **3**, and **7**, and crystallographic data for **2**, **3**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystallographic data for **7**: $C_{122}H_{122}Cl_{12}N_{16}O_4Zn_2$, $M_W = 2432.50$, triclinic, space group *P*-1, $a = 17.527(5)$ Å, $b = 19.313(5)$ Å, $c = 19.410(5)$ Å, $\alpha = 80.678(5)°$, $\beta = 70.485(5)°$, $\gamma = 70.749(5)°$, $V = 5837(3)$ Å^3, $T = 90$ K, $D_{calcd} = 1.384$ g cm^{-3}, $Z = 2$. For 24729 reflections measured; $R_1 = 0.0929$, $wR_2 = 0.2828$ for 16916 reflections with $[I > 2\sigma(I)]$, GOF = 1.166.

(13) This strong binding is due to the cooperative effect of two Zn−N coordination bonds and two NH−O hydrogen bonds. This value is not too high according to the precedent reports.[5d] Unfortunately, the insolubility of **7** in methanol and DMSO did not allow us to investigate NMR spectra in these solvents. The ^1H NMR spectrum of **7** in pyridine-d_5 indicated complete dissociation.