Porphyrins

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[1,2,3]Triazolo[4,5-*b*]porphyrins: New Building Blocks for Porphyrinic Materials**

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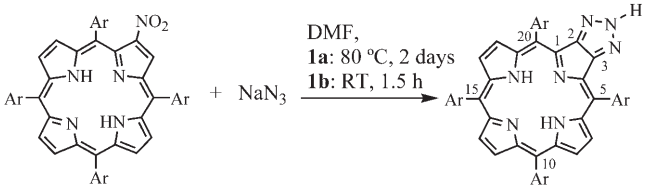
Dedicated to Professor Miha Tišler on the occasion of his 80th birthday

There has been a strong interest in recent years in developing multiporphyrin arrays through covalent or noncovalent synthetic methodologies.[1–8] The synthesis of porphyrin-based framework solids is also an active field.[9–12] These multiporphyrinic systems are of interest because of their potential application in a range of areas, such as electronics, materials, catalysis, and medicine.[13–16] In fact, porphyrins are one of the most attractive building blocks for supramolecular systems. They offer a variety of desirable features, such as rigid planar geometry, high stability, intense electronic absorption and emission, a small HOMO–LUMO energy gap, and the ability to tune their optical and redox properties by changing the metal center.[6] During the past decade, various synthetic strategies have been developed to make multiporphyrin oligomers with linear, cyclic, and cross-linked geometries. An elegant and versatile method developed by Osuka and Shimidzu consists of a Ag^{I}-promoted coupling reaction of *meso*-unsubstituted porphyrins.[17] This method allows the preparation of porphyrin arrays in which the constituent porphyrins are connected directly at their *meso* positions without any extra linking atoms. By using this method, Osuka's group prepared a wide range of covalently linked porphyrin arrays,[5] including *meso-meso*-linked linear porphyrin arrays,[18] two-dimensional windmill arrays,[19] three-dimensional gridlike arrays,[20] strapped *meso-meso*-linked diporphyrins,[21] and cyclic arrays.[8,22] Further oxidation of the *meso-meso*-linked porphyrin arrays under strong conditions (DDQ and $Sc(OTf)_3$) provides porphyrin tapes[23,24] and sheets (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, OTf = trifluoromethanesulfonate).[25] These fully conjugated porphyrin systems have planar structures and display drastically red-shifted absorption spectra that reach into the far-IR region, which reflects the extensive π conjugation over the molecules. Other very interesting linear,[26–29] dendritic,[30] and cyclic[31,32] multiporphyrin systems, as well as organometallic porphyrin arrays[33] have been published in recent years. All of these well-defined multiporphyrin arrangements are interesting for application such as molecular photonic and electronic wires. In particular, the cyclic porphyrin arrays are excellent light-harvesting antenna systems that mimic those found in the photosynthetic system.[8,31]

Herein we report the synthesis of the novel heterocyclic system [1,2,3]triazolo[4,5-*b*]porphyrin and its use in the preparation of porphyrinic dimers and pentamers. The 1,2,3-triazoles are an important type of heterocyclic compounds and are being studied by many research groups because of their theoretical interest and synthetic usefulness. They also find numerous applications in industry, in medicine, and as agrochemicals.[34,35] 1,2,3-Triazoles can be synthesized by many approaches;[36] one method involves the reaction of sodium azide with alkenes bearing strongly electron-withdrawing substituents to afford N-unsubstituted 1*H*-1,2,3-triazoles in good yields. We have considered a synthetic route involving the reaction of β-nitro-*meso*-tetraarylporphyrins with sodium azide; in these reactions the porphyrins should behave as nitroalkenes and the formation of triazoloporphyrins was anticipated. Indeed, the [1,2,3]triazolo[4,5-*b*]porphyrins **2** were obtained in moderate to good yields from the reaction of nitroporphyrins **1** with NaN_3. The alkylation and arylation of the triazole moiety allowed easy access to new porphyrinic materials with potentially interesting applications.

[1,2,3]Triazolo[4,5-*b*]porphyrins **2a,b**[37] were prepared by treating β-nitro-*meso*-tetraarylporphyrins **1a,b** with sodium azide in *N*,*N*-dimethylformamide (DMF, Scheme 1). The reaction with porphyrin **1b** occurs at room temperature, and after 1.5 h product **2b** was isolated in 80% yield; the reaction with the less reactive porphyrin **1a** requires stirring at 80 °C for two days to afford **2a** in 30% yield.



1a, Ar = C_6H_5
1b, Ar = C_6F_5

2a, Ar = C_6H_5, 30%
2b, Ar = C_6F_5, 80%

Scheme 1. Synthesis of triazoloporphyrins.

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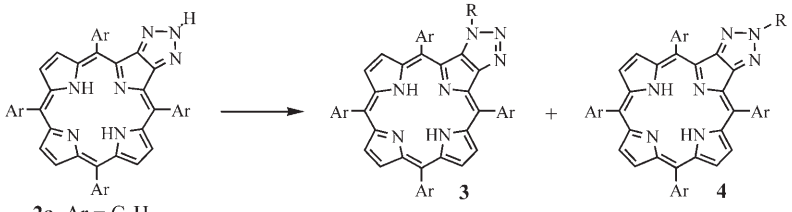
Supporting information (full characterization data of synthesized products) for this article is available on the WWW under http://www.angewandte.org or from the author.

The structure of compounds **2a,b** was unambiguously established by spectroscopic data from mass spectrometry, as well as UV/Vis and NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, and 2D HSQC and HMBC). The NMR spectra showed the compounds to be C_2-symmetric and the UV/Vis spectra were typical for etio-type porphyrins.[38] The main feature of their ^{1}H NMR spectra is a singlet at low field attributable to the resonance of the triazole NH proton ($\delta = 11.32$ ppm for **2a** and $\delta = 12.38$ ppm for **2b**).

The synthesis of the closely related [1,2,3]triazolo[4,5-*b*]phthalocyanine system was reported recently. However, a completely different synthetic approach was used: 5,6-dicyano-1*H*-benzotriazole was prepared first, and then it was used to synthesize tetra-[39] and monotriazolophthalocyanines.[40] 1*N*-Amination of the latter compound and oxidation of the resulting amino derivative resulted in the generation of a dehydrophthalocyanine, which could be trapped in situ with several dienes to afford the corresponding Diels–Alder adducts.[41]

The N-alkylation and N-arylation of triazoloporphyrins **2** are convenient routes to other porphyrinic derivatives. For example, their methylation and benzylation afford mixtures of the isomeric products **3** and **4** (Scheme 2). The ratio of the two isomers in each reaction can be controlled by the choice of solvent used (Table 1). As an example, N-methylation of **2a** with dimethyl sulfate in boiling acetone favors the formation of the 2-methyl isomer, whereas the main product in toluene is the 1-methyl isomer. A similar effect is observed with porphyrin **2b**.



Scheme 2. N-Methylation and N-benzylation of triazoloporphyrins.

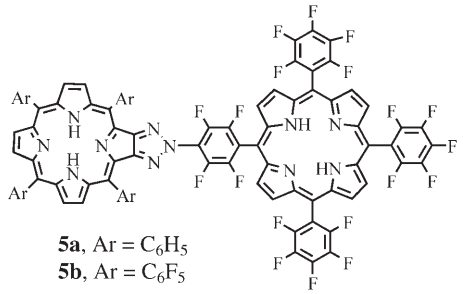
The ^{1}H NMR spectra of compounds **4a1** and **4b1** are similar to those of the corresponding N-unsubstituted precursors, except for the presence of a singlet ascribed to the *N*-methyl group and the absence of the singlet at low field assigned to the NH proton. The ^{1}H NMR spectra of the 1-methyl derivatives **3a1** and **3b1** show clearly that these compounds are not symmetrical. A NOESY spectrum of **3a1** shows space proximity between the methyl group and a phenyl group, thus confirming substitution at triazole N-1. In the ^{1}H NMR spectrum of **3b1** the two protons of the porphyrin nucleus appear as two singlets at $\delta = -3.11$ and -3.06 ppm,which indicates that the macrocycle tautomers are not degenerated.

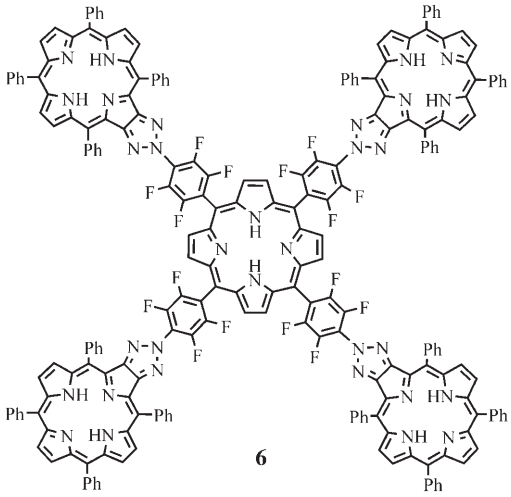
Table 1: Yields of products obtained by N-methylation of **2a** and **2b** in various solvents.

	N-Methylation of **2a**		N-Methylation of **2b**	
Solvent	**3a1**	**4a1**	**3b1**	**4b1**
acetone	34%	59%	10%	80%
toluene	62%	15%	40%	55%

Benzylation of porphyrin **2a** with benzyl bromide in DMF afforded compounds **3a2** (13% yield) and **4a2** (72% yield), along with some precursor **2a** (13%). Under similar conditions, benzylation of **2b** was highly selective; the 2-benzyl isomer was obtained in 90% yield and only a trace amount of the 1-benzyl isomer was present.

The N-arylation of triazoloporphyrins **2** was carried out using 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPFPP) as arylating agent. The reaction of triazoloporphyrin **2a** with an excess of TPFPP (2 equivalents) for 4 h at 80°C afforded dyad **5a** in 57% yield and other minor compounds whose mass and ^{19}F NMR spectra are consistent with further fluorine substitution (triads and tetrads). The formation of dyad **5b** required careful control of the reaction temperature: it was obtained in 30% yield after stirring for 3 days at 60°C, with 35% of the triazoloporphyrin **2b** being recovered. When longer reaction times or higher temperatures were used, the amount of side products increased significantly. When TPFPP was treated with a large excess of triazoloporphyrin **2a** (5 equivalents), the pentamer **6** was obtained in 40% yield as the main product. The reaction occurred smoothly for a period of 22 h and led to the substitution of the four *para*-fluorine atoms of TPFPP by the triazoloporphyrin. Such aromatic nucleophilic substitu-





tion of the *para*-fluorine on one or more phenyl rings of TPFPP by amines and other nucleophiles is a well-known reaction;[42,43] it has recently been used to prepare galactose–[44] and PEG–porphyrin[45] conjugates (PEG = poly(ethylene glycol)).

The mass, ^{1}H, ^{13}C, and ^{19}F NMR spectra of pentamer **6** are consistent with the proposed structure. The UV/Vis spectrum of **6** shows an etio-type pattern similar to that of the triazoloporphyrin **2a**, but with a bathochromic shift (10 nm) of the Soret band. The electrospray ionization mass spectrum does not show the expected $[M+H]^+$ ion, but rather the peaks corresponding to the multiply charged ions $[M+2H]^{2+}$, $[M+3H]^{3+}$, and $[M+4H]^{4+}$, which result from multiple protonation of the molecule. Deconvolution of the ESIMS spectrum reveals an ion with m/z 3516.190, which corresponds to the monoisotopic mass (3516.035) of the $[M+H]^+$ ion. The simplicity of the NMR spectra of **6** is consistent with the high symmetry of the molecule. The main features of the ^{1}H NMR spectrum are a singlet at $\delta = -2.69$ ppm, assigned to all the NH protons of the five porphyrin nuclei, a singlet at $\delta =$ 8.79 ppm, assigned to the eight β-pyrrolic protons of the antipodal pyrrole rings of the four TPP moieties, a broad singlet at $\delta = 9.02$ ppm, assigned to the sixteen β-pyrrolic protons in the adjacent pyrroles of the four TPP moieties, and a singlet at $\delta = 9.29$ ppm, assigned to the eight β-pyrrolic protons of the TPFPP moiety. The ^{19}F NMR spectrum shows only two double doublets assigned to the *ortho*- and *meta*-fluorine atoms.

Single crystals of **6** were obtained by recrystallization from a mixture of chloroform and methanol. The crystal and molecular structures of **6** were determined by X-ray crystallographic analysis. The crystal is triclinic with space group $P\bar{1}$ and $Z = 2$ (see Experimental Section). The molecules are located around crystallographic inversion centers, and therefore there are two half molecules in the asymmetric unit of the crystal cell. Figure 1 shows an overlay representation of the two molecules with the central porphyrin rings used as a reference. All the peripheral porphyrin moieties in both molecules display the same tautomeric form; however, the positions of the NH protons in the central porphyrin rings are switched. The inner hydrogen atoms could not be found in the difference Fourier synthesis map; nevertheless, their positions were determined unambiguously by considering the significant differences among the bond angles of the nitrogen atoms (110.0(4), 105.6(4), 109.3(4), and 107.0(4)° for N1, N101, N201, and N301, respectively). The situation is the same for the hydrogen atoms defining the tautomeric form of the triazoloporphyrin rings (see Supporting Information for values of the bond angles at the nitrogen atoms). All triazoloporphyrin moieties display the same tautomeric form (Figure 1), which is expected because of the fused triazole ring.

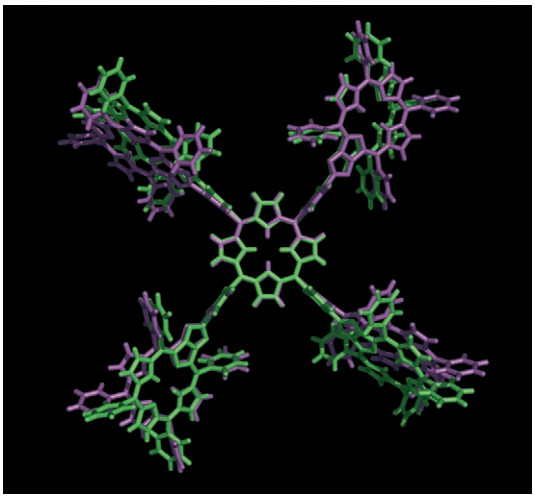


Figure 1. Overlay of the two crystallographically independent molecules of **6** showing the conformational similarities and the different locations of the inner hydrogen atoms in the central porphyrin ring. The same tautomeric form is shown for all triazoloporphyrin substituents. The symmetry-related atoms are included to show the complete molecules.

In conclusion, we have shown that triazoloporphyrins, which can be easily prepared from β-nitroporphyrins, are valuable building blocks for the preparation of novel porphyrinic materials. Currently, we are extending these studies to the synthesis of di(triazolo)porphyrins and their use in the construction of molecular rods.

Experimental Section

5,10,15,20-Tetraphenyl[1,2,3]triazolo[4,5-*b*]porphyrin (**2a**)**:** A solution of **1a** (100.0 mg, 151 μmol) and sodium azide (29.6 mg, 455 μmol, 3 equiv) in DMF (20 mL), under a nitrogen atmosphere, was stirred for 2 days at 80 °C. After cooling to room temperature, the product was precipitated with an aqueous solution of citric acid, filtered, and washed with water. The solid was dissolved in dichloromethane and then washed with water. The organic phase was dried (Na_2SO_4) and then concentrated. The residue was purified by column chromatography (silica gel) using dichloromethane as eluent. Compound **2a** (a pink fraction) was then crystallized from dichloromethane/methanol (30.0 mg, 30 % yield).

5,10,15,20-Tetrakis(pentafluorophenyl)[1,2,3]triazolo[4,5-*b*]porphyrin (**2b**): A solution of **1b** (50 mg, 49 μmol) and sodium azide (3.2 mg, 49 μmol, 1 equiv) in DMF (10 mL), under a nitrogen atmosphere, was stirred at room temperature for 1.5 h. Workup was as described above. The residue was purified by column chromatography (silica gel) using a mixture of dichloromethane/light petroleum (7:3). Compound **2b** was crystallized from dichloromethane/methanol (80 mg, 80 % yield).

Methylation of **2a**: *Reaction in toluene:* To a solution of **2a** (15.9 mg, 24 μmol) and potassium carbonate (10.0 mg, 72 μmol, 3 equiv) in dry toluene (3 mL) was added an excess of dimethyl sulfate (1 drop). This mixture was stirred under a nitrogen atmosphere at 80 °C overnight. After cooling to room temperature, the reaction mixture was evaporated to dryness, and the residue was recovered in dichloromethane, washed with water, and dried (Na_2SO_4), and then the solvent was evaporated. The obtained residue was purified by silica gel column chromatography using a mixture of dichloromethane/light petroleum (1:1) to give two pink fractions. The first fraction was **4a1** (2.5 mg, 15 % yield) and the second was **3a1** (10.0 mg, 62 % yield).

Reaction in acetone: The experimental procedure was similar to that described above, but using acetone as solvent at reflux temperature. The reaction of **2a** (15.0 mg, 23 μmol) gave compound **4a1** in 59 % yield (8.6 mg) and **3a1** in 34 % yield (4.9 mg).

Methylation of **2b**: *Reaction in toluene:* To a solution of **2b** (17.3 mg, 17 μmol) and sodium carbonate (5.4 mg, 51 μmol, 3 equiv) in dry toluene (3 mL) was added an excess of dimethyl sulfate (1 drop). This mixture was stirred for 2 h under a nitrogen atmosphere

at room temperature. The reaction mixture was then evaporated to dryness, and the residue was recovered in dichloromethane, washed with water, and dried (Na_2SO_4), and finally the solvent was evaporated. The obtained residue was purified by silica gel column chromatography using a mixture of dichloromethane/light petroleum (3:7) to give two brown fractions. The first fraction was **4b1** (9.4 mg, 54% yield) and the second was **3b1** (6.9 mg, 40% yield).

Reaction in acetone: To a solution of **2b** (18.3 mg, 18 μmol) and sodium carbonate (5.7 mg, 54 μmol, 3 equiv) in acetone (5 mL) was added an excess of dimethyl sulfate (1 drop). This mixture was stirred for 2.5 h under a nitrogen atmosphere at room temperature. Workup was the same as described above. Compound **4b1** was obtained in 79% yield (8.6 mg) and **3b1** in 10% yield (2.0 mg).

Benzylation of **2a**: To a solution of **2a** (11.5 mg, 18 μmol) and sodium carbonate (3.7 mg, 35 μmol, 2 equiv) in DMF (2 mL) was added an excess of benzyl bromide (1 drop). This mixture was stirred under a nitrogen atmosphere at room temperature for 2 h. Workup was the same as described above for procedures with DMF. The residue was purified by silica gel column chromatography. Elution with a mixture of dichloromethane/light petroleum (6:4) afforded **4a2** (10.7 mg, 82% yield) followed by **3a2** (1.9 mg, 15% yield).

Benzylation of **2b**: To a solution of **2b** (24.2 mg, 24 μmol) and sodium carbonate (5.0 mg, 48 μmol, 2 equiv) in DMF (2 mL) was added an excess of benzyl bromide (1 drop). This mixture was stirred under a nitrogen atmosphere at room temperature for 2 h. Workup was the same as described above for procedures with DMF. The residue was purified by silica gel column chromatography. Elution with a mixture of dichloromethane/light petroleum (2:8) afforded **4b2** (23.6 mg, 90% yield) followed by a trace amount of **3b2**.

Dyad **5a**: A solution of **2a** (14.9 mg, 23 μmol), TPFPP (44.3 mg, 45 μmol, 2 equiv), and potassium carbonate (6.3 mg, 45 μmol, 2 equiv) in DMF (3 mL) was stirred under a nitrogen atmosphere at 80°C for 4 h. Workup was the same as described above for procedures with DMF. The residue was purified by column chromatography (silica gel) using a gradient of dichloromethane/light petroleum. The first fraction was the precursor TPFPP (2.7 mg, 6%), followed by **5a** (20.7 mg, 57% yield). Other minor fractions were discharged.

Dyad **5b**: A solution of **2b** (20.0 mg, 20 μmol), TPFPP (38.6 mg, 40 μmol, 2 equiv), and sodium carbonate (4.2 mg, 40 μmol, 2 equiv) in DMF (4 mL) was stirred under a nitrogen atmosphere at 60°C for 3 days. Workup was the same as described above for procedures with DMF. The residue was purified by column chromatography (silica gel) using a gradient of dichloromethane/light petroleum. The first fraction was the precursor TPFPP, then **5b** (11.2 mg, 29% yield), and finally the precursor **2b** (7.0 mg, 35%).

Pentamer **6**: A solution of TPFPP (5.9 mg, 6 μmol), **2a** (20.0 mg, 30 μmol, 5 equiv), and potassium carbonate (4.2 mg, 30 μmol, 5 equiv) in DMF (2 mL) was stirred under a nitrogen atmosphere at 80°C for 20 h. Workup was the same as described above for procedures with DMF. The residue was purified by silica gel column chromatography. Using a gradient of dichloromethane/light petroleum, a pink major fraction was eluted, followed by several other fractions, and precursor triazoloporphyrin **2a** (15%). The major product was identified as **6** (40% yield).

Crystal data for **6**: $C_{220}H_{122}F_{16}N_{32}$; triclinic; space group $P\bar{1}$; $a = 23.003(2)$, $b = 23.446(2)$, $c = 25.998(2)$ Å, $\alpha = 63.8390(10)$, $\beta = 83.8860(10)$, $\gamma = 88.325(2)°$, $V = 12511.0(18)$ Å^3, $Z = 2$; $T = 120.0(1)$ K; $M = 3517.51$; $\mu(Mo_{K\alpha}) = 0.065$ mm^{-1}, crystal dimensions $0.38 \times 0.37 \times 0.07$ mm^3, $1.76 \le 2\theta \le 36.20°$. In total 49763 reflections were measured, of which 17325 were independent ($R_{int} = 0.0653$, Friedel pairs merged) and employed for refinement: 2413 parameters, 5208 restraints, $R1 = \Sigma | F_o - F_c | / \Sigma F_o = 0.0536$ $[I > 2\sigma(I)]$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2} = 0.1468$ (all data); min./max. difference electron density $-0.22/0.23$ e Å^{-3}. Intensity data were collected with a Bruker SMART CCD X-ray diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator by performing four ω-scans (0.2° oscillation) at different φ angle settings (0, 90, 180 and 270°). Raw images were integrated using SAINT+,[46] and the resulting intensities were corrected from absorption effects and scaled using SADABS.[47] Crystal cell constants were calculated by global refinement. The structure was solved by direct methods with SHELXD[48] employing real/reciprocal space recycling and peaklist optimization and refined with no intensity cutoff using the block-matrix least-squares refinement implemented in SHELXL97.[49] For block-matrix refinement, the model was split into three blocks containing approximately the same number of parameters. The crystal packing of **6** left a big cavity located around the crystallographic inversion center at the unit-cell origin that is filled with disordered solvent, probably a mixture of chloroform, methanol, and water. The cavity is connected to symmetry equivalent ones through narrower channels in a three-dimensional fashion. The void volume per unit cell is 5194.2 Å^3 (41.3%). Attempts to model solvent molecules into the solvent electron density did not result in an acceptable model. The contribution of the disordered solvent to the scattering factors was taken into account with PLATON/SQUEEZE.[50] A total of 1560 e$^-$ per unit cell was found, corresponding to approximately 26 chloroform molecules per cavity, that is, 13 molecules per each molecule of compound **6**, or even more molecules if the disordered solvent is a mixture of chloroform, methanol, and water. The crystal data reported earlier in this paper are given without the contribution of the disordered solvent. Throughout the refinement, bond length, bond angle, and planarity restraints were imposed because the best diffracting crystal found diffracts only to 1.15 Å resolution. All non-hydrogen atoms were refined anisotropically with suitable rigid bond and similarity restraints. Hydrogen atoms were included as isotropic using a "riding model" in later stages of the refinement. Molecular diagrams have been generated using Pymol.[51]

CCDC-276180 (**6**) 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.

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[1] J. Wojaczynski, L. Latos-Grazynski, *Coord. Chem. Rev.* **2000**, *204*, 113 – 171.
[2] A. K. Burrell, D. L. Officer, P. G. Plieger, D. C. W. Reid, *Chem. Rev.* **2001**, *101*, 2751 – 2796.
[3] N. Aratani, A. Tsuda, A. Osuka, *Synlett* **2001**, 1663 – 1674.
[4] M.-S. Choi, T. Aida, T. Yamazaki, I. Yamazaki, *Chem. Eur. J.* **2002**, *8*, 2667 – 2678.
[5] D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735 – 745.
[6] N. Aratani, A. Takagi, Y. Yanagawa, T. Matsumoto, T. Kawai, Z. S. Yoon, D. Kim, A. Osuka, *Chem. Eur. J.* **2005**, *11*, 3389 – 3404.
[7] C. M. Drain, I. Goldberg, I. Sylvain, A. Falber, *Top. Curr. Chem.* **2005**, *245*, 55 – 88.
[8] T. Hori, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, M.-C. Yoon, Z. S. Yoon, S. Cho, D. Kim, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1319 – 1327.
[9] Y. Diskin-Posner, S. Dahal, I. Goldberg, *Angew. Chem.* **2000**, *112*, 1344 – 1348; *Angew. Chem. Int. Ed.* **2000**, *39*, 1288 – 1292.
[10] I. Goldberg, *Chem. Eur. J.* **2000**, *6*, 3863 – 3870.
[11] I. Goldberg, *Chem. Commun.* **2005**, 1243 – 1254.
[12] M. Vinodu, I. Goldberg, *CrystEngComm* **2005**, *7*, 133 – 138.
[13] M. Morisue, S. Yamatsu, N. Haruta, Y. Kobuke, *Chem. Eur. J.* **2005**, *11*, 5563 – 5574.

[14] S. A. Chavan, W. Maes, L. E. M. Gevers, J. Wahlen, I. F. J. Vankelecom, P. A. Jacobs, W. Dehaen, D. E. De Vos, *Chem. Eur. J.* **2005**, *11*, 6754 – 6762.
[15] D. Bonifazi, G. Accorsi, N. Armaroli, F. Song, A. Palkar, L. Echegoyen, M. Scholl, P. Seiler, B. Jaun, F. Diederich, *Helv. Chim. Acta* **2005**, *88*, 1839 – 1884.
[16] C. M. Drain, G. Bazzan, T. Milic, M. Vinodu, J. C. Goeltz, *Isr. J. Chem.* **2005**, *45*, 255 – 269.
[17] A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93 – 95; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135 – 137.
[18] N. Aratani, A. Osuka, D. Kim, Y. H. Kim, D. H. Jeong, *Angew. Chem.* **2000**, *112*, 1517 – 1521; *Angew. Chem. Int. Ed.* **2000**, *39*, 1458 – 1462.
[19] A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, Y. Nishimura, *Angew. Chem.* **1998**, *110*, 3172 – 3176; *Angew. Chem. Int. Ed.* **1998**, *37*, 3023 – 3027.
[20] A. Nakano, T. Yamazaki, Y. Nishimura, I. Yamazaki, A. Osuka, *Chem. Eur. J.* **2000**, *6*, 3254 – 3271.
[21] N. Yoshida, D. H. Jeong, H. S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Osuka, *Chem. Eur. J.* **2003**, *9*, 58 – 75.
[22] X. Peng, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, I.-W. Hwang, T. K. Ahn, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 4468 – 4469.
[23] a) A. Tsuda, H. Furuta, A. Osuka, *Angew. Chem.* **2000**, *112*, 2649 – 2652; *Angew. Chem. Int. Ed.* **2000**, *39*, 2549 – 2552; b) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304 – 10321; c) A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79 – 82; d) H. S. Cho, D. H. Jeong, S. Cho, D. Kim, Y. Matsuzaki, K. Tanaka, A. Tsuda, A. Osuka, *J. Am. Chem. Soc.* **2002**, *124*, 14642 – 14654; e) A. Tsuda, Y. Nakamura, A. Osuka, *Chem. Commun.* **2003**, 1096 – 1097.
[24] a) I. M. Blake, A. Krivokapic, M. Katterle, H. L. Anderson, *Chem. Commun.* **2002**, 1662 – 1263; b) D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli, F. Diederich, *Angew. Chem.* **2003**, *115*, 5116 – 5120; *Angew. Chem. Int. Ed.* **2003**, *42*, 4966 – 4970.
[25] Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 4119 – 4127.
[26] P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121,* 11538 – 11545.
[27] T. E. O. Screen, K. B. Lawton, G. S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson III, S. J. Martin, D. D. C. Bradley, H. L. Anderson, *J. Mater. Chem.* **2001**, *11*, 312 – 320.
[28] A. Ambroise, C. Kirmaier, R. W. Wagner, R. S. Loewe, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Org. Chem.* **2002**, *67*, 3811 – 3826.
[29] P. Thamyongkit, J. S. Lindsey *J. Org. Chem.* **2004**, *69*, 5796 – 5799.
[30] W. Maes, J. Vanderhaeghen, S. Smeets, C. V. Asokan, L. M. Van Renterghem, F. E. Du Prez, M. Smet, W. Dehaen, *J. Org. Chem.* **2006**, *71*, 2987 – 2994.
[31] K. Tomizaki, L. Yu, L. Wei, D. F. Bocian, J. S. Lindsey, *J. Org. Chem.* **2003**, *68*, 8199 – 8207.
[32] F. Hajjaj, Z. S. Yoon, M.-C. Yoon, J. Park, A. Satake, D. Kim, Y. Kobuke, *J. Am. Chem. Soc.* **2006**, *128*, 4612 – 4623.
[33] R. D. Hartnell, D. P. Arnold, *Organometallics* **2004**, *23*, 391 – 399.
[34] M. R. Grimmett in *Comprehensive Organic Chemistry*, *Vol. 4* (Eds.: D. H. R. Barton, W. D. Ollis), Pergamon, Oxford, **1979**, p. 357.
[35] H. Wamhoff in *Comprehensive Heterocyclic Chemistry*, *Vol. 5* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford, **1984**, Part 4A, p. 669.
[36] "1,2,3-Triazoles": A. C. Tomé in *Science of Synthesis—Houben-Weyl Methods of Molecular Transformations*, *Vol. 13* (Eds.: R. C. Storr, T. L. Gilchrist), Thieme, Stuttgart, **2004**, Chap. 13.
[37] N-Unsubstituted 1,2,3-triazoles exist in two tautomeric forms (1*H*- and 2*H*-) that are in equilibrium both in solution and in the gas phase. For simplification, compounds **2** are represented as 2*H*-triazoles, independently of the predominant tautomer.
[38] "General features of the structure and chemistry of porphyrin compounds" K. M. Smith in *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, Amsterdam, **1975**, p. 21.
[39] A. E. Balakirev, V. E. Maizlish, G. P. Shaposhnikov, *Russ. J. Gen. Chem.* **2002**, *72*, 311 – 314.
[40] S. Vagin, A. Frickenschmidt, B. Kammerer, M. Hanack, *Eur. J. Org. Chem.* **2005**, 3271 – 3278.
[41] S. I. Vagin, A. Frickenschmidt, B. Kammerer, M. Hanack, *Chem. Eur. J.* **2005**, *11*, 6568 – 6573.
[42] K. M. Kadish, C. Araullo-McAdams, B. C. Han, M. M. Franzen, *J. Am. Chem. Soc.* **1990**, *112*, 8364 – 8368.
[43] P. Battioni, O. Brigaud, H. Desvaux, D. Mansuy, T. G. Taylor, *Tetrahedron Lett.* **1991**, *32*, 2893 – 2896.
[44] J. P. C. Tomé, M. G. P. M. S. Neves, A. C. Tomé, J. A. S. Cavaleiro, A. F. Mendonça, I. N. Pegado, R. Duarte, M. L. Valdeira, *Bioorg. Med. Chem.* **2005**, *13*, 3878 – 3888.
[45] J.-L. Zhang, J.-S. Huang, C.-M. Che, *Chem. Eur. J.* **2006**, *12*, 3020 – 3031.
[46] SAINT+. Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA, **2003**.
[47] G. M. Sheldrick, SADABS, Bruker Nonius area detector scaling and absorption correction, Version **2004**/1.
[48] G. M. Sheldrick, H. A. Hauptman, C. M. Weeks, R. Miller, I. Usón, *International Tables for Crystallography*, *Vol. F* (Eds.: E. Arnold, M. Rossmann), Kluwer Academic Publishers, Dordrecht, **2001**, pp. 333 – 351.
[49] a) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universitat Gottingen, Gottingen, **1997**; b) G. M. Sheldrick, T. R. Schneider, *Methods Enzymol.* **1997**, *277*, 319 – 343.
[50] a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194 – 201.
[51] "The PyMOL Molecular Graphics System": W. L. DeLano, DeLano Scientific, San Carlos, CA, USA, **2002**. http://www.pymol.org

