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Superazaporphyrins: Meso-Pentaazapentaphyrins and One of Their Low-Symmetry Derivatives**

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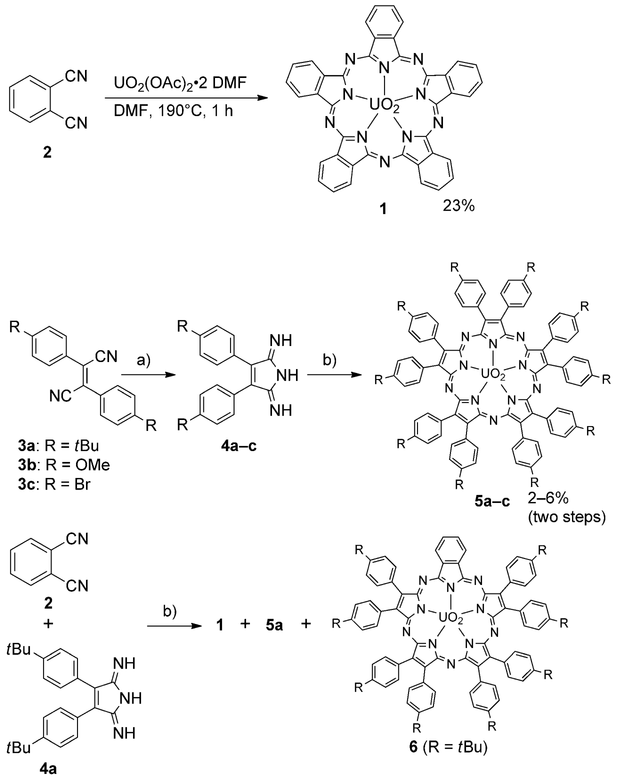
The chemistry of tetrapyrrolic tetraazaporphyrin (TAP), phthalocyanine (Pc), naphthalocyanine (Nc), and anthracocyanine (Ac) has been intensively explored by many researchers in the last decade.[1] Their properties, such as color, depend, for example, on the size of the π system, the size, position, number, and type of substituent, the type, oxidation state, and spin state of the central metal, and the mode of stacking in the solid state.[2] These compounds are also important in materials science because of their potential application in various leading-edge fields such as organic electronic devices, deodorants, and photodynamic therapy.[3] As ring-contracted tri-pyrrolic TAP, Pc, and Nc derivatives, the compounds called subporphyrazines, have attracted increasing attention since 1990.[4] A common feature of these compounds is that they contain boron in the center, and despite many attempts, its removal has not yet been achieved. Since the π system of these tri-pyrrolic subcompounds is smaller than the corresponding tetrapyrrolic congeners, the main absorption band, called the Q band, of the former appears at shorter wavelengths than that of the latter in the visible region. In contrast, as a ring-expanded pentapyrrolic congener, only the compound called superphthalocyanine (SPc), consisting of five isoindole units, is known.[5] The first SPc was reported more than 40 years ago,[5a] with only four papers appearing since then.[5b–e] SPcs are attractive in modern technology in that they show a Q band in the near-IR region beyond $\lambda = 900$ nm. To date, researchers in the fields of, for example, solar cells and photodynamic therapy, have tried to obtain stable compounds having strong absorption in the near-IR region. This absorption may be attained by going from smaller to larger compounds, since the absorption bands generally shift to longer wavelengths (reduction of the HOMO–LUMO gap).[6]

However, when easily prepared Ncs and Acs are used, the problem has been the instability of the larger compounds as they generally decompose within a few days.[7] Herein, we report the synthesis and properties of the so-called superazaporphyrins (SAzP) which consist of five pyrrole units. In particular, we show why they are stable even though their Q band appears beyond $\lambda = 800$ nm. After SPc, SAzP is the second example of a compound consisting of five pyrrolic rings and meso-nitrogen atoms.

An unsubstituted SPc containing a linear and rigid O=U=O[8] central core (**1**) was obtained by condensation of **2** in the presence of $UO_2(OAc)_2 \cdot 2\,DMF$[9] in DMF in 23 % yield. The SAzPs **5** were obtained by uranium-templated cyclization of five molecules of **4** which were synthesized from the fumaronitrile **3** (Scheme 1). The reaction is generally applicable for aryl-substituted precursors equipped either with donor (**5b**) or acceptor (**5c**) groups, although SPc **1** is known



Scheme 1. Synthesis of the superphthalocyanine (SPc) **1**, superazaporphyrins (SAzPs) **5a–c**, and the low-symmetry SAzP **6**. Reagents and conditions: a) Na, NH_3 (gas), $nC_5H_{11}OH$, 105 °C, 3 h; b) $UO_2(OAc)_2 \cdot 2\,DMF$, 190 °C, 1 h. DMF = *N*,*N'*-dimethylformamide.

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to be obtained practically only when substituent-free **2** is used. The incorporation of a bromo substituent in the macrocycle (**5c**) also allowed further synthetic modification utilizing Pd^0- or Ni^0-catalyzed reactions. In the case of the low-symmetry **6**, which contains one isoindole and four pyrroline rings, a mixed condensation was carried out using **2** and **4a** at a mole ratio of 1:1 at 190 °C for 1 hour. From the reaction mixture, analytically pure **6** was obtained as a brown powder after chromatography. All of the substituted SAzPs can be stored as solids in air under ambient light.

Formation of the compounds was first confirmed by HR/MALDI-FT-ICR/MS and ^{1}H NMR spectroscopy. Compound **1** showed only two ^{1}H NMR signals assignable to the α and β protons of the isoindoles ($\delta = 9.15$ and 8.09 ppm), whereas **5a–c** showed only two sets of signals arising from the *ortho* and *meta* protons of the phenyl groups, thus suggesting a highly symmetrical structure in solution. The compound **6** showed both α and β protons of the isoindoles and *ortho* and *meta* protons of the phenyl groups in the expected ratio (1:1:8:8), all at different positions, thus reflecting the low symmetry of the molecule.

Single crystals of **5b** suitable for X-ray crystallography were grown by slow diffusion of *n*-hexane into a toluene solution of **5b** (Figure 1). The crystal structure of **5b**[10] reveals that the macrocycle comprises five pyrroline rings linked by five nitrogen atoms, with the U^{VI} ion sitting in the center of the SAzP 5N mean plane ($\Delta 5N < 0.005$ Å). **5b** is not planar, but has a severely saddled structure, as reported for the crystal structure of SPc.[5c,d] The peripheral aryl moieties are oriented essentially perpendicularly to the macrocycle, thus suggesting only a weak electronic interaction between the substituents and the macrocycle. No significant bond-length alternation was observed for the C−N and C−C bonds of the core structure of **5b** (see Figure S1 in the Supporting Information), as would be anticipated for a nonplanar heteroaromatic π system.

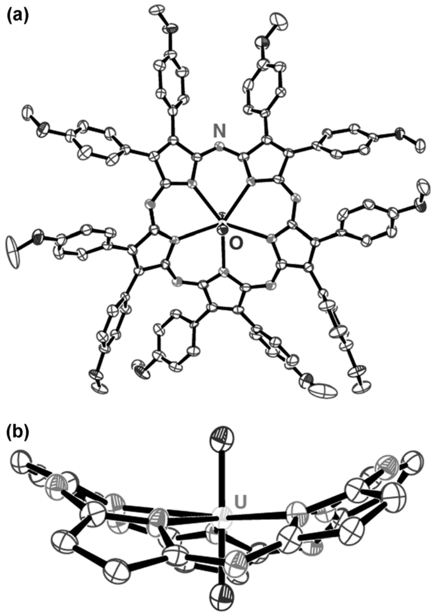

Figure 1. The molecular structure of **5b**. The thermal ellipsoids are shown at 50% probability. a) Top view and b) side view (peripheral substituents omitted). Hydrogen atoms and solvent molecules are omitted for clarity.

Figure 2 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of compounds **1**, **5a**, and **6**. The SPc **1** exhibited Q- and Soret-like bands at $\lambda = 915$ and 424 nm, respectively, which are at longer wavelengths than those of normal Pcs (ca. $\lambda = 650$–700 nm and $\lambda = 330$–350 nm, respectively), and the corresponding dispersion-type, Faraday *A* MCD curves, thus experimentally supporting the fact that the excited state is orbitally degenerate. The SAzP **5a** exhibited these bands at $\lambda = 878$ and 437 nm. Therefore, in going from **1** to **5a**, the Q band shifted to a shorter wavelength, while the Soret band shifted to a longer wavelength, both of which are phenomena similar to those observed in going from Pc to octaaryltetraazaporphyrin.[3b] A weak absorption on the longer-wavelength side of the Soret band, at about $\lambda = 500$–600 nm, is characteristic of AzPs having many phenyl groups.[11] The substitution effect at the aryl position is relatively weak so that the positions of the Q bands of **5a–c** are close together (see Figure S2 in the Supporting

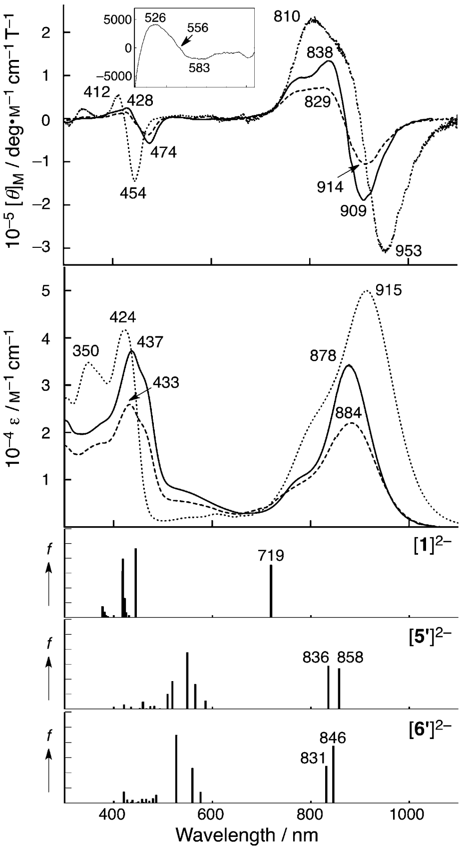

Figure 2. Magnetic circular dichroism (top) and electronic absorption (middle) spectra of **1** (dotted lines), **5a** (solid lines), and **6** (dotted broken lines). Inset: Magnified MCD spectrum of **5a**. Theoretical absorption spectra (bottom); the solid lines are those calculated by the TD-DFT method. Calculations were carried out for the free-base dianion species without *tert*-butyl groups at the B3LYP/6-31G* level of theory.

Information). These results imply that the peripheral aryl groups can be used as anchoring groups for further functionalization. The low-symmetry **6** showed a Q band at $\lambda =$ 884 nm, which is between that of **5a** ($\lambda = 878$ nm) and **1** ($\lambda =$ 915 nm), thus suggesting indeed that **6** is an intermediate compound between **1** and **5a**. The dispersion-type MCD curves corresponding to the Q bands of **5a** and **6** are theoretically Faraday *A* and pseudo Faraday *A* terms, respectively.[12] In the case of **6**, it is thought that the splitting of the Q band is so small that the superimposition of two oppositely-signed Faraday *B* terms give seemingly *A*-term-like MCD signals. A larger MCD intensity in the Q band than in the Soret band also indicates that the angular momentum change in the Q transitions is larger than that in the Soret transitions. As shown later in the section on molecular orbital (MO) calculations, the transition of the Q band corresponds to an angular orbital momentum change of ±11. Furthermore, a minus-to-plus MCD sign change in ascending energy suggests that the energy difference between the HOMO and HOMO−1 (ΔHOMO) is larger than that between the LUMO and LUMO + 1 (ΔLUMO).[13]

To enhance the interpretation of the electronic absorption spectra, MO calculations have been performed for unsubstituted and pyrrole proton-deprotonated Pc, uranium ion-free and pyrrole proton-deprotonated **1**, **5a**, and **6** without *tert*-butyl groups, that is, $[\mathrm{Pc}]^{2-}$, $[\mathbf{1}]^{2-}$, $[\mathbf{5'}]^{2-}$, and $[\mathbf{6'}]^{2-}$, at the DFT level. This analysis omitting the metal is due to the fact that it is difficult to evaluate accurately the electron density of f-block metals such as uranium. The uranyl dication in this study acts only as a template for stabilizing the macrocycle. Accordingly, it appears possible to use these structures as model structures for the calculations. Calculated stick absorption spectra are attached at the bottom of Figure 2, with obtained data summarized in Table S1 of the Supporting Information, and the MO energy levels and isosurface plots of some frontier MOs shown in Figure 3. The optimized structures of $[\mathbf{1}]^{2-}$, $[\mathbf{5'}]^{2-}$, and $[\mathbf{6'}]^{2-}$ are also distorted, thus agreeing well with the crystal structures of the reported SPc[6c,d] and **5b**, which, therefore, suggests that the influence of the uranyl cation on the structure is indeed marginal. The calculated Q bands, which are transitions mainly from the HOMO to LUMO and LUMO + 1, were estimated at wavelengths close to the experimental values for the compounds. In addition, as can be judged from the configuration in Table S1, the contribution of the four frontier orbitals is large in both the Q- and Soret-band regions, thus indicating that these bands can be explained using Gouterman's four-orbital model.[14] The calculated Q-band intensity increases on going from $[\mathbf{5'}]^{2-}$ to $[\mathbf{1}]^{2-}$, that is, with increasing size of the π system, as generally observed among tetraazaporphyrins of varying sizes.[15]

As shown in Figure 3, the LUMO and LUMO + 1 of $[\mathbf{1}]^{2-}$ and $[\mathbf{5'}]^{2-}$ are degenerate, similar to $[\mathrm{Pc}]^{2-}$, whereas the degeneracy is lifted slightly in the case of $[\mathbf{6'}]^{2-}$. In going from $[\mathrm{Pc}]^{2-}$ to $[\mathbf{1}]^{2-}$, that is, from cyclic tetramer (Pc) to pentamer (**1**), the energy of the four frontier orbitals is stabilized, but since the stabilization of the LUMO is larger than that of the HOMO, the Q band shifts to a longer wavelength. Comparison between the cyclic pentamer $[\mathbf{5'}]^{2-}$ and $[\mathbf{1}]^{2-}$ reveals a similar change as observed when the cyclic tetramers Pc and Nc are compared. In going from Pc to Nc, with increasing π-molecular size by fusion of the benzo rings, both the HOMO and LUMO destabilize and the Q band shifts to a longer wavelength. However, even the LUMOs and HOMO of $[\mathbf{1}]^{2-}$ (SPc **1**) lie lower in energy than those of Pcs. This lower energy of the HOMO appears to be the reason for high stability of the SAzPs **5** and SPc **1**. It is well known that Pcs are susceptible to oxidation because the meso positions are prone to oxidation depending on the extent of the destabilization of the HOMO. Although the SAzPs **5** and SPc **1** in this study have their Q bands at around $\lambda = 840$–880 nm and $\lambda = 915$ nm, respectively, they appear to be much more stable than Ncs.[7a]

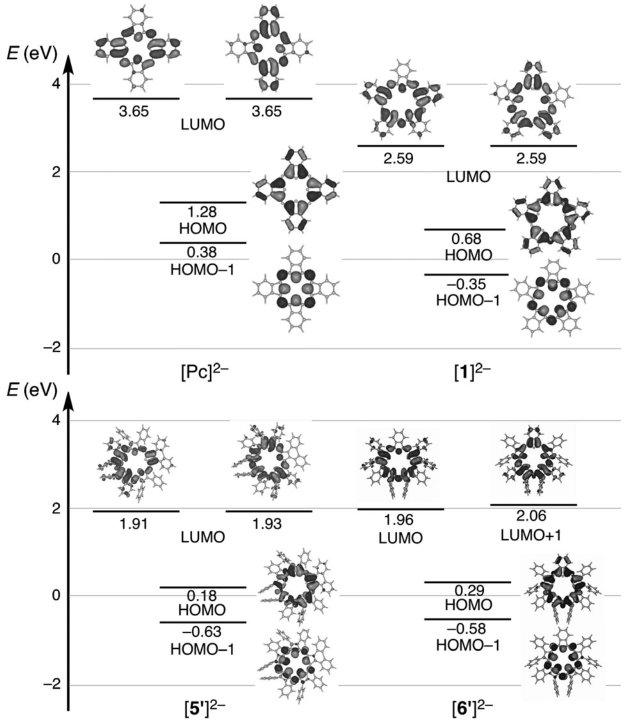

Figure 3. Energies and some frontier orbitals of $[\mathrm{Pc}]^{2-}$, $[\mathbf{1}]^{2-}$, $[\mathbf{5a'}]^{2-}$, and $[\mathbf{6'}]^{2-}$. Calculations were performed at the B3LYP/6-31G* level of theory.

The cyclic π-electron systems can also be interpreted using the $(4n+2)$ electron perimeter model.[13] A 22-electron [20]-annulene ($[\mathrm{C}_{20}\mathrm{H}_{20}]^{2-}$) was calculated as a model of the inner ring of **1**, and it was found that the number of nodal planes of the frontier MOs of $[\mathbf{1}]^{2-}$ is the same as that of $[\mathrm{C}_{20}\mathrm{H}_{20}]^{2-}$ (see Figure S3 in the Supporting Information). Thus, from the number of nodes, it is clear that the compounds **1** and **5** are aromatic compounds satisfying $n = 5$ in $(4n+2)$, that is, Hückel's aromaticity rule. The angular momentum change in the Q and Soret bands are therefore ±11 and ±1, respectively.

Cyclic voltammograms of the tetra-*tert*-butyl-substituted $\mathrm{H_2Pc}$ ($t\mathrm{Bu_4H_2Pc}$), SPc **1**, and **5a** were measured in *o*-dichlorobenzene (*o*-DCB; Figure 4). The $t\mathrm{Bu_4H_2Pc}$ showed redox couples at 0.26, −1.44, and −1.79 V ($E_{1\mathrm{ox}}-E_{1\mathrm{red}} =$ 1.70 V), whereas the SPc **1** exhibited couples at 0.24, −0.94, −1.29, −1.69 V ($E_{1\mathrm{ox}}-E_{1\mathrm{red}} = 1.18$ V). Although the oxidation

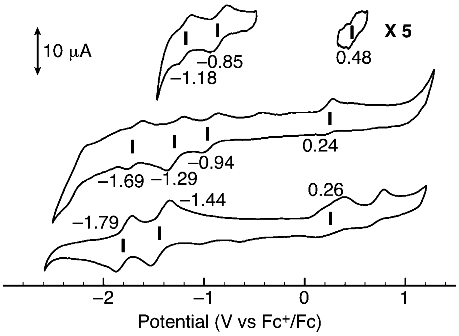

Figure 4. Cyclic voltammograms for 1.0 mm *t*BuH$_2$Pc (bottom), **1** (middle), and **5a** (top) in *o*-DCB containing 0.1 m *n*Bu$_4$NClO$_4$. Ferrocene was used as an internal standard and set to 0 V.

potentials are similar, the reduction of the SPc **1** is much easier (by $\Delta E = 0.50$ V) than that of *t*Bu$_4$H$_2$Pc, thus indicating marked stabilization of the LUMOs of the SPc **1**. This result implies that the origin of the narrow HOMO–LUMO gap of **1** is attributable to the low-lying LUMOs. The SAzP **5a** showed redox couples at 0.48, −0.85, and −1.18 V ($E_{1\text{ox}}-E_{1\text{red}} = 1.33$ V), thus revealing that the frontier orbitals of **5a** are further stabilized compared with those of the SPc **1**, and provides support for the predicted MO energy level. Thus, the longer-wavelength shift of the Q bands of the SAzP **5** and SPc **1** is attributable to the stabilization of the frontier orbitals, particularly the LUMOs. The position of the Q band of general Pcs (ca. $\lambda = 650$–700 nm), **5**, and **1** is also in accord with the order of the ($E_{1\text{ox}}-E_{1\text{red}}$) values.

The reported SPc contains only UO$_2$ in the center, but attempts at removing the UO$_2$ have always resulted in the formation of free-base Pcs.[5b,c] Finally, experiments to obtain free-base SAzP were attempted using acids such as H$_2$SO$_4$ or TFA, and resulted in the decomposition of **5**. The transmetallation reaction of **5** using Ni, Zn, Sn, Cu, or Lu salts did not yield other metal-containing SAzPs, but instead decomposed or produced metalloTAPs.

In conclusion, we have synthesized superazaporphyrins (SAzPs) consisting of five pyrroline-2,5-diimine units and a uranium atom, and one of their low-symmetry derivatives, by using pyrroline-2,5-diimine as a precursor. We have also reinvestigated superphthalocyanine (SPc) using methods which were not used 35–40 years ago. X-ray crystallography revealed a distorted macrocyclic structure for the superazaporphyrins. Decaaryl SAzPs showed Q bands at approximately $\lambda = 840$–880 nm, and the spectra could be interpreted by Gouterman's four-orbital model. Both SAzPs and SPcs are aromatic and can be explained by the $(4n+2)$ aromaticity rule, where $n = 5$. MCD spectroscopy and MO calculations strongly suggest that the Q-excited state is doubly degenerate. Although the Q bands of SAzPs and SPcs appear at longer wavelengths than those of Ncs, electrochemical measurements and MO calculations indicated that they are relatively air stable, since the energy of both the LUMOs and HOMO is lower than those of Pcs and Ncs. These molecules can be new candidates for functional near-IR dyes and produce new insights into the chemistry of expanded phthalocyanines. Further work is currently underway to prepare a series of low-symmetry superphthalocyanines and to develop novel functional expanded Pcs absorbing in the near-IR region.

Experimental Section

For full experimental details, spectroscopic data, and calculation procedures, see the Supporting Information. X-ray crystal data is available from the Cambridge Structural Database.

Synthesis of **5a**: A mixture of 3,4-bis (4-*tert*-butylphenyl)pyrroline-2,5-dimine (**4a**, 70 mg, 0.20 mmol), and UO$_2$(OAc)$_2$·2DMF (105 mg, 0.20 mmol) was dissolved in DMF (0.50 mL). The solution was stirred at 190 °C for 1 h and concentrated. The product was purified by silica gel column chromatography (CHCl$_3$/*n*-hexane = 1:1). The target compound was obtained (7 mg, 6% over two steps based on compound **3a**) as a brown solid. Mp: >280 °C. 500 MHz ^{1}H NMR (CDCl$_3$): $\delta = 7.87$ (d, 20H, $J = 9.0$ Hz), 7.42 (d, 20H, $J = 9.0$ Hz), 1.44 ppm (s, 90H). HRMS-MALDI: Calcd for C$_{120}$H$_{130}$N$_{10}$O$_2$U $[M]^+$: 1981.0881. Found: 1981.0855. UV/Vis (CHCl$_3$) ($\varepsilon \times 10^{-4}$): $\lambda_{\text{max}} = 878$ nm (3.4), 437 nm (3.7).

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[1] V. N. Nemykin, E. A. Lukyanets, *Handbook of Porphyrin Science*, *Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**, pp. 1–323.

[2] a) *Functional Dyes* (Ed.: S.-H. Kim), Elsevier, Oxford, **2006**; b) *Phthalocyanines—Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever), Wiley-VCH, Weinheim, **1989**, **1992**, **1993**, **1996**; c) *Phthalocyanine Materials*, N. B. McKeown, Cambridge Univ. Press, Cambridge, **1998**.

[3] a) *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**; b) *Handbook of Porphyrin Science* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**.

[4] a) C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835–853; b) N. Kobayashi in *The Porphyrin Handbook*, *Vol. 15* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2003**, pp. 161–262.

[5] a) J. E. Bloor, J. Schlabitz, C. C. Walden, *Can. J. Chem.* **1964**, *42*, 2201; b) T. J. Marks, D. R. Stojakovic, *J. Chem. Soc. Chem. Commun.* **1975**, 28; c) V. W. Day, T. J. Marks, W. A. Wachter, *J. Am. Chem. Soc.* **1975**, *97*, 4519; d) T. J. Marks, D. R. Stojakovic, *J. Am. Chem. Soc.* **1978**, *100*, 1695; e) E. A. Cuellar, T. J. Marks, *Inorg. Chem.* **1981**, *20*, 3766.

[6] a) N. Kobayashi, T. Furuyama, K. Satoh, *J. Am. Chem. Soc.* **2011**, *133*, 19642; b) R. K. Kanaparthi, J. Kandhadi, L. Giribabu, *Tetrahedron* **2012**, *68*, 8383; c) O. Matsushita, V. M. Derkacheva, A. Muranaka, S. Shimizu, M. Uchiyama, E. A. Luk'yanets, N. Kobayashi, *J. Am. Chem. Soc.* **2012**, *134*, 3411; d) A. Muranaka, S. Ohira, D. Hashizume, H. Koshino, F. Kyotani, M. Hirayama, M. Uchiyama, *J. Am. Chem. Soc.* **2012**, *134*, 190; e) Y. Koide, Y. Urano, K. Hananoka, W. Piao, M. Kusakabe, N. Saito, T. Terai, T. Okabe, T. Nagano, *J. Am. Chem. Soc.* **2012**, *134*, 5029.

[7] a) N. Kobayashi, S.-i. Nakajima, H. Ogata, T. Fukuda, *Chem. Eur. J.* **2004**, *10*, 6294; b) T. Fukuda, N. Kobayashi, *Handbook of Porphyrin Science*, *Vol. 9* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**, pp. 1–644.

[8] R. G. Denning, *J. Phys. Chem. A* **2007**, *111*, 4125.

[9] N. A. Frigerio, R. F. Coley, *J. Inorg. Nucl. Chem.* **1963**, *25*, 1111.

[10] Crystallographic data for **5b**·3PhMe: $C_{111}H_{94}N_{10}O_{12}U$, $M_w =$ 1998.00, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.2931(11)$ Å, $b = 19.270(2)$ Å, $c = 24.443(3)$ Å, $\alpha = 69.593(1)°$, $\beta = 84.516(1)°$, $\gamma = 89.051(1)°$, $V = 4522.4(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.424$ g cm^{-3}, $T =$ 93 K, $R_1 = 0.0560$ $(I > 2\sigma(I))$, $R_w = 0.1375$ (all data), GOF = 0.968. CCDC 876819 (**5b**) 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.

[11] a) N. Kobayashi, S. Nakajima, T. Osa, *Chem. Lett.* **1992**, *21*, 2415; b) K. Toyota, J. Hasegawa, H. Nakatsuji, *Chem. Phys. Lett.* **1996**, *250*, 437.

[12] a) J. Mack, M. J. Stillman, N. Kobayashi, *Coord. Chem. Rev.* **2007**, *251*, 429; b) J. Mack, N. Kobayashi, *Chem. Rev.* **2011**, *111*, 281.

[13] a) J. Michl, *J. Am. Chem. Soc.* **1978**, *100*, 6801; b) J. Michl, *J. Am. Chem. Soc.* **1978**, *100*, 6812; c) J. Michl, *J. Am. Chem. Soc.* **1978**, *100*, 6819.

[14] M. Gouterman in *The Porphyrins*, *Vol. 3* (Ed.: D. Dolphin), Academic Press, New York, **1978**, Part A, p. 1 – 165.

[15] R. Fukuda, M. Ehara, H. Nakatsuji, *J. Chem. Phys.* **2010**, *133*, 144316.