Porphyrinoids

Deutsche Ausgabe: DOI: 10.1002/ange.201511702
Internationale Ausgabe: DOI: 10.1002/anie.201511702

Synthesis of Octafluoroporphyrin

Chiranjeevulu Kashi, Chu-Chun Wu, Chi-Lun Mai, Chen-Yu Yeh, and Chi K. Chang**

Abstract: *Despite the long list of known fluoroporphyrinoids, the most fundamental 2,3,7,8,12,13,17,18-octafluoroporphyrin (OFP) has not been synthesized until now. It is achieved by condensation of two molecules of tetrafluoro-dipyrrylmethane-2-carboxaldehyde in the presence of magnesium(II) salts. The fluorinated dipyrrylmethane also gives 5,15-bis(pentafluorophenyl)-OFP (F18P) with a reasonable yield. Both Mg/OFP and Zn/F18P in the solid-state reveal an essentially flat structure. The fluoro groups impart as much as a 0.5 V anodic shift for porphyrin ring oxidation/reduction, as well as hypsochromic shifts in the Uv-vis spectra.*

With the current state of the art in porphyrin syntheses, most porphyrins, biological or otherwise, have either already been made or may be assembled without great difficulty. Yet, 2,3,7,8,12,13,17,18-octafluoroporphyrin (OFP) is one seemingly simple and fundamental compound that, so far, has eluded all synthetic attempts. Fluorinated porphyrinoids are interesting for many reasons. Apart from the fact that fluoroorganic molecules are of increasing importance as bioactives in life science,[1] the electron-deficient nature of fluorinated porphyrinoids renders them ideal systems for modeling biomimetic mono-oxygenations.[2] In fact, Chang and Ebina employed Fe/F_{20}TPP and Mn/F_{20}TPP (Figure 1) to demonstrate, for the first time in 1981,[3] a robust and high-yielding catalytic model of cytochrome P450 (and hence termed second-generation catalysts)[4] which has spurred widespread interest in polyhalogenated porphyrins as oxidation catalysts, such as those later termed third-generation catalysts.[5,6] The pursuit to realize the perfluorinated F_{28}TPP, despite a false start,[7] had to wait for the arrival of 3,4-difluoropyrrole (**1**)[8] which was first synthesized by Leroy, et. al.,[9] and later by the group of DiMagno from a more-accessible starting material.[10] The totally fluorinated F_{28}TPP and its metal complexes proved to be electronegative as well as catalytically capable as expected.[11,12] Starting with **1**, Chang and co-workers were able to synthesize a totally fluorinated corrole, F_{23}TPC, and again proved its utility for studying the P450-type chemistry.[13a] These compounds are of considerable theoretical interest,[13b,c] and **1** has also been employed in the preparation

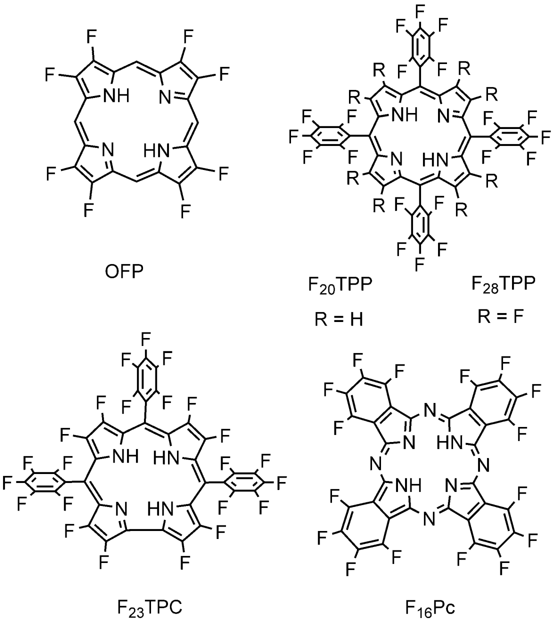


Figure 1. Polyfluorinated porphyrinoids. Pc = phthalocyanine, TPC = meso-triphenylcorrole, TPP = meso-tetraphenylporphyrin.

of expanded porphyrins containing only fluoro substituents.[14] The subject of fluorinated porphyrins and related compounds has been reviewed recently.[2,15] Turning to the phthalocyanine category, completely fluorinated F_{16}Pc and metal complexes are well known commercial chemicals, and have been incorporated in various semiconductor and optoelectronic devices including the n-channel organic transistors.[16] Given this list of extensive fluorinated porphyrinoids, the absence of the iconic OFP is noticeable.

The absence of OFP from the known compounds is not due to a lack of effort. On the contrary, it has been the target of intense pursuit for over two decades. For example, Leroy[17] published an account of numerous attempts en route to OFP, including well-known strategies such as the cyclization of pyrryl-2-carbinol,[18] yet all failed to produce OFP. A decade ago, the group of Chang also tried various reaction conditions to effect the condensation of **1** and HCHO, or its equivalents, but they were unsuccessful, despite the synthesis of octachloroporphyrin, which was synthesized by a similar approach.[19] While the dismal yield of porphine (recalling the ca. 0.1 % yields first reported by the groups of Rothemund and Fischer[20]) is inherent to tetrapyrane cyclization without sizable substituents at the β-pyrrole or bridging carbon atoms, the presence of the fluorine groups appears to attenuate the reactivity to exacerbate an already difficult ring closure. Our strategy was then focused on indirect routes, for example, by a meso-tetra(*tert*-butyl)porphyrin and subsequent dealkyla-

---

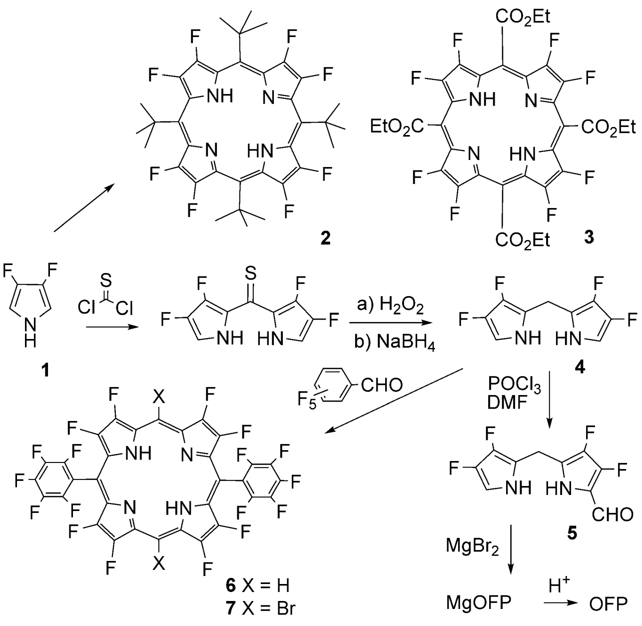
[*] Prof. C. K. Chang
Institute of Chemistry, Academia Sinica
Nankang, Taipei 115 (Taiwan)
E-mail: changc@msu.edu

C. Kashi, C.-C. Wu, Dr. C.-L. Mai, Prof. C.-Y. Yeh
Department of Chemistry, National Chung Hsing University
Taichung 402 (Taiwan)
E-mail: cyyeh@dragon.nchu.edu.tw

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201511702.

tion. Indeed, the nonfluorinated porphine could be obtained in good yields as reported by Neya et al.[21a,b] When **1** was used, meso-tetra(*tert*-butyl)-OFP (**2**; for structure see Scheme 1) was isolated in about 2%, but all attempts to improve the yield, as well as to bring about the dealkylation, failed. Alternatively, meso-tetra(ethoxycarbonyl)-OFP (**3**) was synthesized from **1** and ethyl glyoxalate. The synthesis and structural determination of this porphyrin, completed long ago, was published recently.[22] Again, unlike Neya's nonfluorinated counterpart, which smoothly underwent hydrolysis and decarboxylation,[21c] **3** proved to be remarkably resistant under similar reaction conditions. Scores of acids, bases, and heating conditions were tested for removing the meso-ester groups, but the results were either irreproducible or inconclusive.

In 2007, the group of Lindsey reported a variation of the MacDonald [2+2] porphyrin synthesis by dimerizing dipyrrylmethane-2-carboxaldehyde in the presence of a magnesium(II) salt to furnish Mg/porphine in the 60% yield range.[23a] We deemed this route to be attractive and applicable, even though the formation of the fluoro counterparts were in uncharted territory. Fortunately, 3,4,3′,4′-tetrafluoro-2,2′-dipyrrylmethane (**4**) was obtained in three steps following the procedure reported by Clezy and Smythe[24] (Scheme 1), and **4** behaved normally in reactions involving nucleophiles. For example, **4** condensed, in 1:1 ratio, with pentafluorobenzaldehyde to afford 5,15-bis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octafluoroporphyrin (**6** or F18P) in 27% yield. Thus, under the standard Vilsmeier–Haack reaction conditions, the carboxaldehyde **5** was obtained (48%) and the final step of porphyrin-ring formation gave a yield of 8–10%. Unlike other Mg/porphyrins, Mg/OFP could not be demetallated by either CF_3COOH or washing in CH_2Cl_2 with 6N aqueous H_2SO_4 or HCl. The free base OFP was obtained by treating Mg/OFP with concentrated H_2SO_4 and then back-extracted into CH_2Cl_2 after diluting with water.



Scheme 1. Reactions of 3,4-difluoropyrrole. DMF = *N*,*N*-dimethylformamide.

The absorption spectra of Mg/OFP and OFP are shown in Figure 2 and Table 1. In comparison with the nonfluorinated porphine (P) and TPP, clearly there are hypsochromic shifts in both the B and Q bands, which seem to be a common feature of all β-octafluoro-porphyrins,[11,22] arising from the fluorine π-electron overlap which destabilizes the e_g LUMO orbitals. Other notable characteristics include very low intensities of the Q(0,0) absorption transitions, which according to the Gouterman four-orbital model, is an indication of the highly degenerate a_{1u} and a_{2u} filled orbitals.[25] The overall shape of the bands is actually not very dissimilar to that of porphine. However, the spectrum displays a larger splitting between the B(0,0)–Q(0,0) band, 8300 cm^{-1}, calculated from B(0,0)–[(Q_x(0,0) + Q_y(0,0))/2], as compared to porphine's 7580 cm^{-1}, thus giving further evidence of the π interactions.[11] The λ = 360 nm shoulder of the Soret band of OFP is likely caused by aggregate formation (of the face-to-face H-type producing blue shift[26]), and while relatively unaffected by solvent or dilution, it is temperature-dependent, for example, at 60 °C (in $ClCH_2CH_2Cl$), the λ = 377 nm peak is sharper at the expense of the shoulder.

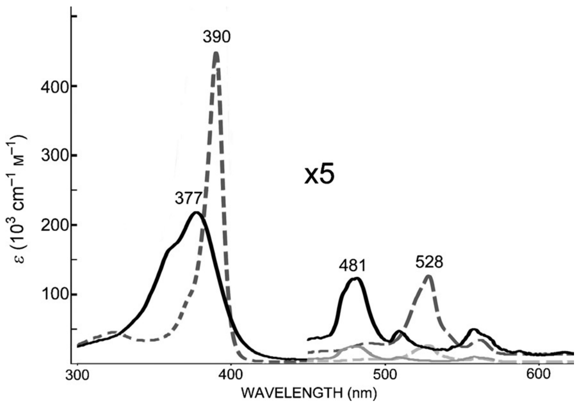


Figure 2. Absorption spectra (in CH_2Cl_2) of Mg/OFP (dash) and OFP (solid).

Table 1: UV/Visible absorption maxima, in CH_2Cl_2 [nm].

Compd[a]	Soret band	Q bands[b]				Ref.
F_8PH_2 (OFP)	377	481	509	557	610	this work
PH_2	395	490	520	564	615	[23]
F_8TEPH_2 (**3**)	385	486	523	572	625	[22]
$F_{28}TPPH_2$	392	493	530	579	632	[11]
$TPPH_2$	418	514	549	590	646	[23]
MgF_8P (Mg/OFP)	390		528	561		this work
Mg/P	402		536	575		[23]
ZnF_8TEP (Zn/**3**)	402		535	567		[22]
$ZnF_{28}TPP$	407		537	568		[11]
ZnTPP	427		556	595		[23]

[a] For names, refer to Figure 1 and Scheme 1. P = porphine, TPP = meso-tetraphenylporphyrin. [b] Using PH_2 as an example, Q(1,0) bands: 490 and 564 nm, Q(0,0) bands: 520 and 615 nm.

Crystals of Mg/OFP suitable for X-ray diffraction were grown by the slow evaporation of a dichloromethane/THF/hexanes solution, thus giving a five-coordinate THF adduct. Figure 3 shows a perspective drawing from the crystal structure determination. The porphine core is essentially flat (planarity deviations are provided in the Supporting Information). The planar structure is consonant with the large hypsochromic shifts observed in the absorption spectra. The Mg atom is displaced by 0.376 Å from the mean plane (defined by the 24 atoms) in the direction of the THF molecule, thus rendering the five-coordinate complex into a shallow cymbal shape with the peripheral atoms all moving approximately 0.1 Å to the opposite direction from the mean plane. The Mg–O bond (2.052 Å) is short because of the electron-deficient ring while the Mg–N bond lengths (2.073–2.080 Å) are consistent with those of a planar complex. All C–C and C–N bond lengths are remarkably similar to the parent porphine.[27]

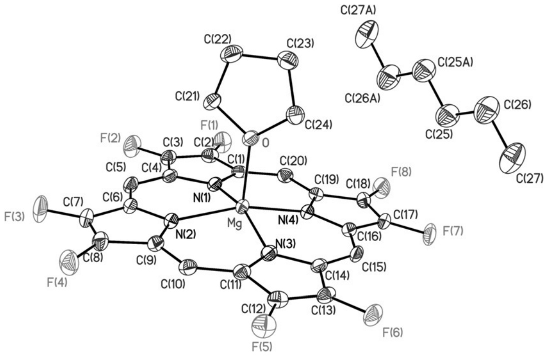


Figure 3. ORTEP drawing (50% thermal ellipsoid) of MgOFP with hydrogen atoms eliminated for clarity.

Fluorescence data are given in the Supporting Information. The emission spectra of Mg/OFP ($\lambda_{max} = 568$ and 617 nm) and OFP (612, 675 nm) exhibit only small Stokes shifts (220 and 80 cm^{-1}, respectively), and are comparable to the reference porphine, thus suggesting that the planar β-fluoro porphyrins do not undergo significant reorganization of nuclear coordinates in the excited state as expected. In contrast, nonplanar Zn(F_8TPP) was reported to have a larger Stokes shift.[11b] The slight decrease in fluorescence yield is consistent with the notion that aromatic fluorine groups which are in conjugation with the π-system could enhance the intersystem crossing, such as observed in Zn(F_{16}Pc).[28] However, porphyrin examples are very limited.[11b]

Cyclic voltammetry was employed to determine the redox potentials. All complexes were measured under the same reaction conditions, and data are summarized in Table 2 (owing to the poor solubility, OFP behavior requires further investigation and is not included). The first oxidation and first reduction of Mg/OFP are nearly reversible, along with an irreversible second oxidation. The electrochemical HOMO–LUMO energy gap of Mg/OFP is 2.28 eV from these data, and slightly larger than that of Mg/P as well as consistent with the blue-shift observed in absorption maxima. As expected, the electron-withdrawing fluorine atoms induce large anodic shifts for both oxidation and reduction reactions as compared to Mg/P: the differences in $E_{1/2}$ and E_{pa} values for the first and second oxidations between Mg/OFP and Mg/P are 500 mV and 280 mV, respectively, and for the reduction, it is 430 mV. In the absence of planar distortions these shifts can be attributed entirely to the peripheral electronic effects.[29,8a]

Table 2: Oxidation and reduction potentials (vs. Ag/AgCl, CH_3CN, 0.1 M TBAP).

Compd	E_{pa} (ox2)	$E_{1/2}$ (ox1)	$E_{1/2}$ (red1)	$E_{1/2}$ (red2)	Gap (ox1/red1)
Mg/OFP	+1.43 V	+1.19 V	−1.09 V	–	2.28 eV
MgP	+1.15 V	+0.69 V	−1.52 V	–	2.21 eV
Zn/**6**	+1.77 V[a]	+1.60 V	−0.78 V	−1.17 V	2.38 eV

[a] Overlapped with oxidation wave of solvent.

While it is gratifying that a long-standing synthetic target has been achieved, more importantly this synthesis may pave the way to exploring the unique capability of the new molecule. In this regard, porphine, the parent compound of all porphyrins, has not been utilized to its full potential because of obstacles such as poor solubility in most solvents.[30] OFP unfortunately suffers from the same solubility problem. One solution is to make derivatives that preserve the β-octafluoroporphine core. The diphenyl OFP **6**, that is, F18P, offers a pertinent example. First, it can be prepared in reasonable yields from the new F_4-dipyrrylmethane **4**. Secondly, it retains all the crucial elements of the core OFP: the anodically shifted (i.e. to more positive) redox potentials, which are larger because of the two electronegative pentafluorophenyl substituents (Table 2), and essentially a flat structure (Figure 4, for bond lengths and other details, see the Supporting Information). Thirdly, it has the two *para*-phenyl positions ready to undergo S_N2 reactions with amines, alkoxides, and other nucleophiles to give derivatives, having better solubility and functionality, similar to those established for F_{20}TPP and F_{28}TPP.[31, 15b] Finally, it also has the two unsubstituted meso positions available for electrophilic substitutions. Indeed, when Zn/**6** was treated with NBS, the 5,15-dibromo derivative (Zn/**7**) was obtained (in 62% yield). This step demonstrates the potential of incorporating the OFP core as a building block for a diverse range of applica-

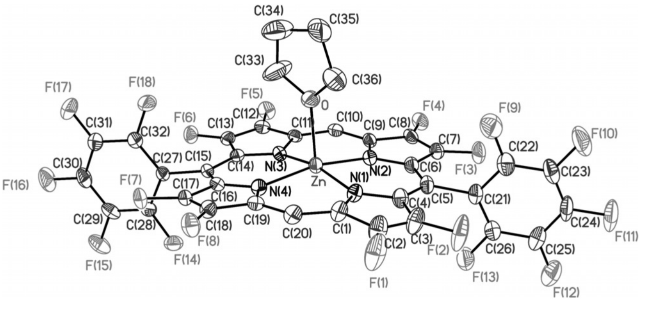


Figure 4. ORTEP drawing (50% thermal ellipsoid) of Zn/**6**. Zn is 0.263 Å out-of-plane, other data of interest: Zn–O 2.139 Å, Zn–N 2.062–2.071 Å, the dihedral angles of the two meso-phenyl rings: 89.0° and 84.0°.

tions.[15b,32] Our synthesis will surely encourage new and more extensive investigations into the still under-exploited subarea of β-perfluorinated porphyrinoids.

Experimental Section

The synthetic details, as well as additional UV-vis and structural analyses are included in the Supporting Information. X-ray data for Mg/OFP: $C_{24}H_{12}F_8MgN_4O \cdot 1/2[C_6H_{14}]$, formula weight M_r 591.77, crystal size $0.47 \times 0.42 \times 0.38$ mm, triclinic, P-1, $a = 9.9453(8)$ Å, $b = 11.0103(9)$ Å, $c = 13.1591(9)$ Å, $\alpha = 65.871(7)°$, $\beta = 80.045(6)°$, $\gamma = 68.594(7)°$, volume = 1223.84(16) Å^3, $Z = 2$, $\rho_{calcd} = 1.606$ mg mm^{-3}, absorption coefficient $\mu = 0.165$ mm^{-1}, Mo$_{K\alpha}$ radiation 0.71073 Å, temperature 150 °K, θ range for data collection: 2.82 to 29.41°, measured reflections: 9923, independent reflections: 5618 [$R_{int} = 0.0261$], R 0.0600, $wR2$ 0.1547, GOF 1.081, residual electron density peak and hole = 0.522 and −0.322 e$^-$ Å^{-3}, X-ray data collected on an Oxford Diffraction Gemini S, and the solution and refinement method: full-matrix least squares on F^2. The detailed results are deposited at CCDC 1430796.

X-ray data for Zn/**6**: $C_{36}H_{10}F_{18}N_4OZn$, formula weight M_r 921.85, crystal size $0.56 \times 0.23 \times 0.12$ mm, triclinic, P-1, $a = 9.1468(6)$ Å, $b = 11.7091(7)$ Å, $c = 16.3682(11)$ Å, $\alpha = 105.217(6)°$, $\beta = 103.493(6)°$, $\gamma = 93.942(5)°$, volume = 1629.0(2) Å^3, $Z = 2$, $\rho_{calcd} = 1.879$ mg mm^{-3}, absorption coefficient $\mu = 0.898$ mm^{-1}, Mo$_{K\alpha}$ radiation 0.71073 Å, temperature 150 °K, θ range for data collection: 2.933 to 29.175°, measured reflections: 13020, independent reflections: 7506 [$R_{int} = 0.0410$], R 0.0613, $wR2$ 0.1243, GOF 1.045, residual electron density peak and hole = 0.968 and −0.594 e$^-$ Å^{-3}, X-ray data collected on an Oxford Diffraction Gemini S, and the solution and refinement method: full-matrix least squares on F^2. The detailed results are deposited at CCDC 1430797.

Acknowledgments

We acknowledge current research funding from the Ministry of Science & Technology (MOST) and Academia Sinica, as well as support received in the past from RGC (Hong Kong) and P2 Research, for this decade-long pursuit. C.K.C. also thanks his hosts, Professor Chen-Hsiung Hung and Professor Shie-Ming Peng, for encouragement.

Keywords: electron-deficient compounds · fluorine · macrocycles · porphyrinoids · redox chemistry

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 5035–5039
Angew. Chem. **2016**, *128*, 5119–5123

---

[1] a) P. Maienfisch, R. G. Hall, *Chimia* **2004**, *58*, 93–99; b) T. Liang, C. N. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214–8264; *Angew. Chem.* **2013**, *125*, 8372–8423.

[2] J. Leroy, A. Bondon, *Eur. J. Org. Chem.* **2008**, 417–433.

[3] C. K. Chang, F. Ebina, *J. Chem. Soc. Chem. Commun.* **1981**, 778–779.

[4] B. Meunier, *Chem. Rev.* **1992**, *92*, 1411–1456.

[5] a) P. S. Traylor, D. Dolphin, T. G. Traylor, *J. Chem. Soc. Chem. Commun.* **1984**, 279–280; b) D. Dolphin, T. G. Traylor, L. Y. Xie, *Acc. Chem. Res.* **1997**, *30*, 251–259.

[6] a) J. E. Lyons, P. E. Ellis, *Catal. Lett.* **1991**, *8*, 45–51; b) J. F. Bartoli, O. Brigaud, P. Battioni, D. Mansuy, *J. Chem. Soc. Chem. Commun.* **1991**, 440–442; c) J. E. Lyons, P. E. Ellis, H. K. Myers, *J. Catal.* **1995**, *155*, 59–73.

[7] S. Tsuchiya, M. Seno, *Chem. Lett.* **1989**, 263–264.

[8] a) E. K. Woller, S. G. DiMagno, *J. Org. Chem.* **1997**, *62*, 1588–1593; b) J. Leroy, A. Bondon, L. Toupet, C. Rolando, *Chem. Eur. J.* **1997**, *3*, 1890–1893.

[9] J. Leroy, C. Wakselman, *Tetrahedron Lett.* **1994**, *35*, 8605–8608.

[10] E. K. Woller, V. V. Smirnov, S. G. DiMagno, *J. Org. Chem.* **1998**, *63*, 5706–5707.

[11] a) E. Porhiel, A. Bondon, J. Leroy, *Eur. J. Inorg. Chem.* **2000**, 1097–1105; b) V. V. Smirnov, E. K. Woller, D. Tatman, S. G. DiMagno, *Inorg. Chem.* **2001**, *40*, 2614–2619.

[12] C.-M. Che, J.-L. Zhang, R. Zhang, J.-S. Huang, T.-S. Lai, W.-M. Tsui, X.-G. Zhou, Z.-Y. Zhou, N. Zhu, C. K. Chang, *Chem. Eur. J.* **2005**, *11*, 7040–7053.

[13] a) H.-Y. Liu, T.-S. Lai, L.-L. Yeung, C. K. Chang, *Org. Lett.* **2003**, *5*, 617–620; b) For other F8-triaryl-corroles, but not F23-corrole, see E. Steene, A. Dey, A. Ghosh, *J. Am. Chem. Soc.* **2003**, *125*, 16300–16309; c) A. Ghosh, *J. Am. Chem. Soc.* **1995**, *117*, 4691–4699; d) For more on corrole P-450 models, see H.-Y. Liu, F. Yam, Y.-T. Xie, X.-Y. Li, C. K. Chang, *J. Am. Chem. Soc.* **2009**, *131*, 12890–12891.

[14] S. Shimizu, J.-Y. Shin, H. Furuta, R. Ismael, A. Osuka, *Angew. Chem. Int. Ed.* **2003**, *42*, 78–82; *Angew. Chem.* **2003**, *115*, 82–86.

[15] a) S. G. DiMagno, J. C. Biffinger, H. Sun in *Fluorine in Heterocyclic Chemistry, Vol. 1: 5-Membered Heterocycles and Macrocycles* (Ed.: V. Nenajdenko), Springer, Berlin, **2014**, pp. 589–620; b) N. V. S. D. K. Bhupathiraju, W. Rizvi, J. D. Batteas, C. M. Drain, *Org. Biomol. Chem.* **2016**, *14*, 389–408.

[16] Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.* **1998**, *120*, 207–208.

[17] a) J. Leroy, *Electronic Conference on Trends in Organic Chemistry* (ECTOC-1) ISBN 0854048995 (Eds.: H. S. Rzepa, J. M. Goodman, C. Leach), Royal Society of Chemistry Publications, **1995**. See also Ref. [2]; b) http://www.ch.ic.ac.uk/ectoc/papers/40.

[18] a) S. J. Krol, *J. Org. Chem.* **1959**, *24*, 2065–2067; b) N. Bag, S. S. Chern, S. M. Peng, C. K. Chang, *Tetrahedron Lett.* **1995**, *36*, 6409–6412; c) C. K. Chang, C.-Y. Yeh, T. S. Lai, *Macromol. Symp.* **2000**, *156*, 117–124.

[19] M. O. Senge, O. Flögel, K. Ruhlandt-Senge, *J. Porphyrins Phthalocyanines* **2001**, *5*, 503–506.

[20] a) P. Rothemund, *J. Am. Chem. Soc.* **1935**, *57*, 2010–2011; b) P. Rothemund, *J. Am. Chem. Soc.* **1936**, *58*, 625–627; c) H. Fischer, W. Gleim, *Justus Liebigs Ann. Chem.* **1936**, *521*, 157–160; d) C. K. Chang, *Israel J. Chem.* **2016**, *56*, 130–143.

[21] a) S. Neya, N. Funasaki, *Tetrahedron Lett.* **2002**, *43*, 1057–1058; b) S. Neya, J. Quan, T. Hoshino, M. Hata, N. Funasaki, *Tetrahedron Lett.* **2004**, *45*, 8629–8630; c) S. Neya, J. Quan, M. Hata, T. Hoshino, N. Funasaki, *Tetrahedron Lett.* **2006**, *47*, 8731–8732.

[22] H.-H. Wang, Y.-Y. Jiang, M. H. R. Mahmood, H. Y. Liu, H. H. Y. Sung, I. D. Williams, C. K. Chang, *Chin. Chem. Lett.* **2015**, *26*, 529–533.

[23] a) D. K. Dogutan, M. Ptaszek, J. S. Lindsey, *J. Org. Chem.* **2007**, *72*, 5008–5011; b) PhotochemCAD developed by J. S. Lindsey and co-workers http://www.photochemCAD.com.

[24] a) P. S. Clezy, G. A. Smythe, *Aust. J. Chem.* **1969**, *22*, 239–249; b) J. A. de Groot, J. H. Koek, J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 405–408.

[25] P. J. Spellane, M. Gouterman, A. Antipas, S. Kim, Y. C. Liu, *Inorg. Chem.* **1980**, *19*, 386–391.

[26] N. K. Giri, A. Banerjee, R. W. J. Scott, M. F. Paige, R. P. Steer, *Phys. Chem. Chem. Phys.* **2014**, *16*, 26252–26260.

[27] a) C. H. Devillers, A. K. D. Dimé, H. Cattey, D. Lucas, *C. R. Chim.* **2013**, *16*, 540–549; b) L. E. Webb, E. B. Fleischer, *J. Chem. Phys.* **1965**, *43*, 3100–3111; this structure was contaminated with CuP; c) B. M. L. Chen, A. Tulinsky, *J. Am. Chem. Soc.* **1972**, *94*, 4144–4151; d) A. Tulinsky, *Ann. N. Y. Acad. Sci.* **1973**, *206*, 47–69.

[28] M. Durmus in *Photosensitizers in Medicine*, *Environment*, *and Security* (Eds.: T. Nyokong, V. Ahsen), Springer, Netherland, **2012**, pp. 135 – 266.

[29] Y. Fang, P. Bhyrappa, Z. Ou, K. M. Kadish, *Chem. Eur. J.* **2014**, *20*, 524 – 532.

[30] M. O. Senge, M. Davis, *J. Porphyrins Phthalocyanines* **2010**, *14*, 557 – 567.

[31] a) P. Battioni, O. Brigaud, H. Desvaux, D. Mansuy, T. G. Traylor, *Tetrahedron Lett.* **1991**, *32*, 2893 – 2896; b) J. I. T. Costa, A. C. Tomé, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *J. Porphyrins Phthalocyanines* **2011**, *15*, 1116 – 1133.

[32] a) M. Fazekas, M. Pintea, M. O. Senge, M. Zawadzka, *Tetrahedron Lett.* **2008**, *49*, 2236 – 2239; b) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 1497 – 1503; c) J. T. Fletcher, M. J. Therien, *J. Am. Chem. Soc.* **2002**, *124*, 4298 – 4311; d) N. Aratani, A. Takagi, Y. Yanagawa, T. Matsumoto, T. Kawai, Z. S. Yoon, D. Kim, A. Osuka, *Chem. Eur. J.* **2005**, *11*, 3389 – 3404.

Received: December 17, 2015