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The Siamese-Twin Porphyrin and Its Copper and Nickel Complexes: A Non-Innocent Twist

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Lina K. Blusch

The Siamese-Twin Porphyrin and Its Copper and Nickel Complexes: A Non-Innocent Twist

Doctoral Thesis accepted by
the Georg-August-University Göttingen, Germany

 Springer

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ISSN 2190-5053

ISBN 978-3-319-01673-3

DOI 10.1007/978-3-319-01674-0

Springer Cham Heidelberg New York Dordrecht London

ISSN 2190-5061 (electronic)

ISBN 978-3-319-01674-0 (eBook)

Library of Congress Control Number: 2013946220

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Printed on acid-free paper

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Parts of this thesis have been published in the following journal articles:

“The Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin Providing a Bimetallic Cavity” L. K. Frensch, K. Pröpper, M. John, S. Demeshko, C. Brückner, F. Meyer, *Angew. Chem.* **2011**, *123*, 1456–1460; *Angew. Chem. Int. Ed.* **2011**, *50*, 1420–1424.

“Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin of Persistent Helical Conformation” L. K. Blusch, Y. Hemberger, K. Pröpper, B. Dittrich, F. Witterauf, M. John, G. Bringmann, C. Brückner, and F. Meyer, *Chem. Eur. J.* **2013**, *19*, 5868–5880.

“Hidden Non-Innocence in an Expanded Porphyrin: Electronic Structure of the Siamese-Twin Porphyrin’s Dicopper Complex in Different Oxidation States” L. K. Blusch, K. E. Craigo, V. Martin-Diaconescu, E. Bill, A. B. McQuarters, S. Dechert, S. DeBeer, N. Lehnert, F. Meyer, DOI: [10.1021/ja406176e](https://doi.org/10.1021/ja406176e).

*Believe those who are seeking the truth.
Doubt those who find it.*

André Guide

Supervisor's Foreword

The highly impressive dissertation by Mrs. Blusch describes, for the first time, the formal fusion of two porphyrin-like chromophores into an expanded porphyrin dubbed Siamese-twin porphyrin, whereby the fusion points are pyrazole moieties. The design of expanded porphyrins has become a key topic in contemporary porphyrin chemistry. This is because these systems contribute to the general understanding of the factors controlling the conformation of larger π -conjugated oligopyrrolic macrocycles, and particularly how structural and conformational effects modulate and interconvert aromatic/anti-aromatic/non-aromatic conjugated π -systems.

The Siamese-twin porphyrin structure was long sought-after, but all previous attempts had been unsuccessful and it was only once Mrs. Blusch became involved that this novel expanded porphyrin could firstly be made. The availability of this unprecedented type of macrocycle now opens up an entirely new field of study. As described in this thesis, physicochemical investigations (using multi-nuclear, 1D and 2D NMR spectroscopy, UV-vis spectroscopy, and mass spectrometry) characterize the connectivity of the macrocycle and support the conclusions derived with respect to macrocycle conformation, the electronic coupling of the two near-isolated π -conjugated systems present in the macrocycle, its acid/base properties, and its conformational flexibility. The intrinsically helimeric (chiral) conformation of the twin porphyrin was shown spectroscopically as well as by single crystal diffractometry and rationalized using computational studies.

One more and major aspect of the twin-porphyrins is evaluated: the Siamese-twin porphyrin contains two pseudoplanar $\{N_4\}$ porphyrin-like coordination sites that each can accommodate a transition metal ion. Once metalated, the twin-porphyrin features a bimetallic complex in which the metals are bridged by two pyrazoles. Mrs. Blusch prepared the homobimetallic nickel(II) and copper(II) complexes as well as the heterometallic nickel(II)/copper(II) analog and characterized them by X-ray diffractometry, spectro-electrochemistry, cyclic voltammetry, SQUID magnetometry, X-ray absorption, and MCD spectroscopy, some of this in collaboration with specialty groups. Much of the investigations were focused on defining the degree of electronic coupling of the two metal centers and the involvement of the non-innocent ligand framework in redox events. An unusual ferromagnetic coupling of the two adjacent pyrazolate-bridged copper(II) ions and a sequence of multiple redox processes were found, whereby initial oxidations

appear to be largely ligand-based. This now offers exciting prospects for exploiting novel metal–metal as well as metal–ligand cooperativity effects when activating and transforming substrates at the metalated Siamese-twin porphyrin.

28 February 2013, Göttingen

Prof. Dr. Franc Meyer

Acknowledgments

At the beginning I would like to thank my mentor Prof. Franc Meyer for his support, the scientific freedom combined with his precious guidance and advice, for this challenging and versatile project and the supply of several analytical devices and funding. Further, I would like to thank him for the possibility to participate at national and international conferences, the introduction to the scientific community, and the opportunity to do research at the University of Connecticut in Prof. Brückner's laboratory. With respect to this, I also would like to thank Prof. Christian Brückner for his support, the good collaboration, his expertise in porphyrin chemistry, and the possibility to accommodate me in his laboratory. Special thanks are accredited to Prof. Ulf Diederichsen for being my correferent and writing several endorsements for scholarship application processes.

I further would like to thank all my collaborators, who are Yasmin Hemberger, Franziska Witterauf, Prof. Gerhard Bringmann, Dr. Eckhard Bill, Prof. Nicolai Lehnert, Kevin Pröpper, Birger Dittrich, Prof. Serena DeBeer, and Dr. Vlad Martin-Diaconescu for the good communication and teamwork.

I gratefully acknowledge the funding of the "Fonds der Chemischen Industrie" and the DAAD without whom the fruitful international experiences would not have been realized.

I thank the people from the analytic laboratories, the mass spectrometry division, Dr. Michael John, and Wolfgang Zolke from the NMR spectroscopy division Dr. Claudia Stückl for measuring several EPR spectra and the scientific discussions and my bachelor students and all other students who supported me in the laboratory. Thank to Adam, Kai, Andreas, and Jörg for the wonderful atmosphere in our common laboratory. I thank Anne, Adam, Kai, Antonia, Sven, Anett, Michael, Les, Jill, Michelle, Victoria, Esther, and Kristian for correcting parts of the present Ph.D. work and the whole Meyer group for the pleasant atmosphere throughout my Ph.D. time.

Finally, I thank my husband for being my husband and his strong support in any way and also my family for their continuous support.

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Abbreviations

| | |
|-----------|---|
| AM1 | Austin model 1 |
| antiferro | Antiferromagnetic |
| Bn | Benzyl |
| BP86 | Becke–Perdew-1986 |
| Bz | Benzoyl |
| CA | Chloranil |
| CD | Circular dichroism |
| COSY | Correlation spectroscopy |
| CT | Charge transfer |
| CV | Cyclic voltammetry |
| D | Donor atom |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| DDQ | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone |
| DFc | Decamethylferrocene |
| DFT | Density functional theory |
| DMF | Dimethylformamide |
| DMSO | Dimethylsulfoxide |
| EDG | Electron donating group |
| EPR | Electron paramagnetic resonance |
| ESI | Electrospray ionization |
| Et | Ethyl |
| EWG | Electron withdrawing group |
| ex | Exchange |
| EXAFS | Extended X-ray absorption fine structure |
| Fc | Ferrocene |
| ferro | Ferromagnetic |
| h | Hour |
| HMBC | Heteronuclear multiple-bond correlation |
| HOMO | Highest occupied molecular orbital |
| HPLC | High pressure liquid chromatography |
| HR | High resolution |
| IAM | Independent atom model |
| IBX | 2-Iodoxybenzoic acid |
| IR | Infrared |

| | |
|--------|---|
| IV | Intervalence |
| LC | Liquid chromatography |
| lcp | Left circular polarized |
| LL | Ligand-to-ligand |
| LUMO | Lowest unoccupied molecular orbital |
| m. p. | Melting point |
| Me | Methyl |
| min | Minute |
| MM | Metal-to-metal |
| MRI | Magnetic resonance imaging |
| MS | Mass spectrometry |
| NIR | Near infrared |
| NLO | Non-linear optics |
| NMR | Nuclear magnetic resonance |
| NOE | Nuclear overhauser effect |
| OAc | Acetate |
| OEP | Octaethylporphyrin |
| PDT | Photodynamic therapy |
| Ph | Phenyl |
| ppm | Parts per million |
| PS | Polystyrene |
| py | Pyridine |
| pyr | Pyrrole |
| pz | Pyrazole |
| r. t. | Room temperature |
| rcp | Right circular polarized |
| sMMO | Soluble methane monooxygenase |
| SQUID | Superconducting quantum interference device |
| SVP | Split valence polarization |
| SWV | Square wave voltammetry |
| t | Total |
| TEMPO | 2,2,6,6-Tetramethyl-1-piperidinyloxy |
| TFA | Trifluoroacetic acid |
| TLC | Thin layer chromatography |
| TPP | Tetraphenylporphyrin |
| UV-vis | Ultraviolet-visible |
| VTVH | Variable temperature variable field |
| XAS | X-ray absorption spectroscopy |
| ZFS | Zero field splitting |

Chapter 1

General Introduction

Porphyrins are planar aromatic macrocycles and ubiquitous in nature [1]. Their monometallic complexes are involved in many key processes of life, such as: respiration and photosynthesis [2–4]. Since their discovery, these exceptional systems stimulated enormous interest. Their isolation and subsequent total synthesis shed light on their constitution and function and in turn this research was rewarded with several nobel prizes [5]. With the synthetic procedures in hand, a range of synthetic modifications [6] were made viable utilizing the attachment of various backbone residues, replacement of subheterocyclic units and the expansion of the core structure. The latter opens a completely new subfield of porphyrinoids: the class of expanded porphyrins [7–11]. These higher analogs of porphyrins are excellent candidates to study fundamental questions of aromaticity [12, 13] and with their larger cavities they provide ligand scaffolds capable of supporting late transition metal or even bimetallic complexes [14–16]. Sessler, Osuka, Kim, Latos-Grazynski, Chandrashekar and Vogel pioneered the field, which has developed rapidly within the last 40 years.

In the present work, a novel expanded porphyrin system with biomimetic elements is introduced: the Siamese-twin porphyrin [17]. Inspired by the mechanisms of cytochrome P450 and the bimetallic active center of methane monooxygenase [3, 4], it was designed to combine their motifs and to yield fascinating redox properties.

1.1 Porphyrins

After the short introduction, the porphyrinic macrocycle is now described in more detail (Fig. 1.1). Pyrrole, as the basic unit of porphyrins, is an aromatic five-membered nitrogen heterocycle and belongs to the group of azoles [18, 19]. Due to its six π -electrons distributed over five atoms, pyrroles are π -excessive and therefore good π -donors. Its new nomenclature of arabic numbers is not consistently used. Particularly, in porphyrin chemistry, the old greek letters are common, because they retain its validation when pyrrole is part of the porphyrinic scaffold.

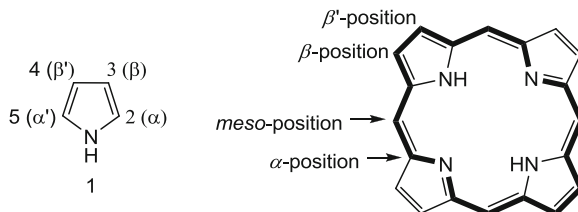
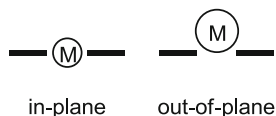


Fig. 1.1 *Left:* Pyrrole labeled according to the old (*Greek letters*) and new (*Arabic numbers*) nomenclature; *Right:* Chemical structure of the porphyrin system with labeling and the highlighted 18 π -electrons counting conjugation pathway (Sect. 1.2.1)

Fig. 1.2 Different possibilities of metal complexation by porphyrin ring systems depending on the metal ion size



Porphyrin consists of all together four pyrrole units that are linked between their α -positions via methine bridges, also denoted as *meso* carbon atoms. Porphyrins are planar and have an extended π -system, in which only 18 out of 24 π -electrons contribute to the delocalized “conjugation pathway” which is highlighted in Fig. 1.1. Due to their delocalized system, the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap shrinks and light absorption is seen in the visible region, which explains their intense colors. Porphyrins show characteristic absorption at around 400 nm with an extinction coefficient of around $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, the so called Soret-band [20, 21].

In its twice deprotonated form, porphyrins are tetradentate chelating ligands offering a rigid, square planar cavity (radius of 0.6 – 0.7 Å) [2]. Only with metal ions of distinct size in-plane coordination modes can be formed (Fig. 1.2) [22, 23]. With larger metal ions complexes can only be formed adopting an out-of-plane coordination mode. A change of the metal oxidation or spin state can introduce a geometry flip due to the change of the metal ion’s size.

1.1.1 Natural Porphyrins

The most famous natural porphyrins are heme and chlorophyll (Fig. 1.3). The first is an iron porphyrin complex, which is part of many active sites of different proteins, such as hemoglobin and cytochrome P450. Chlorophyll is a magnesium porphyrin complex which is indispensable for photosynthesis [3]. In photosynthesis light energy is converted to chemical energy stored as glucose (Scheme 1.1).