Published in final edited form as:

J Porphyr Phthalocyanines. 2010 August 1; 14(8): 752–757. doi:10.1142/S1088424610002513.

One-pot synthesis of *meso*-alkyl substituted isocorroles: the reaction of a triarylcorrole with Grignard reagent

Sara Nardis^{a,*}, Giuseppe Pomarico^{a,◇◇}, Federica Mandoj^{a,◇}, Frank R. Fronczek^b, Kevin M. Smith^{b,◇}, and Roberto Paolesse^{a,◇}

^a Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, 00133 Roma, Italy

^b Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Abstract

The reaction of 5,10,15-tritolylicorrole with EtMgBr opens the way for novel functionalizations of the corrole ring. DDQ oxidation of the macrocycle, followed by addition of the Grignard reagent, led to the formation of 5- and 10-alkyl substituted isocorroles in satisfying yields. Together with the one-pot formation of these isocorrole isomers, the use of such a nucleophile evidenced the competitive reactivity of the macrocycle β -positions, leading to the formation of 2-bromo- and 3-bromo-5,10,15-tritolylicorrole. While the formation of these monobromocorrole derivatives is not unprecedented, this is the first time the isomers have been separated and fully characterized. Furthermore, the higher yields of the 2-substituted species highlight a useful regioselectivity for the substitution reaction.

Keywords

corrole; isocorrole; oxidation; synthesis

INTRODUCTION

Modification of the porphyrin molecular framework has been intensively investigated in the past [1] with two principal aims: to probe structure-property relationships, and to modulate the properties of the macrocycle for potential applications. One of the many possible variations consists of the introducing sp^3 hybridized carbon atoms in the porphyrin molecular core. Depending on the skeletal position where this modification is introduced, different hydroporphyrins can be obtained, both aromatic (chlorin) and non-aromatic (phlorin, isoporphyrin and porphodimethene) [2]. The importance of these hybrid materials has to be related not only to their role as intermediates in natural processes or in their occurrence in oxidative reactions involving porphyrins [3], but also to their distinctive electronic absorption and redox behavior, which make them promising as photosensitizers in PDT [4] or as receptors for anions and small molecules [5].

*Correspondence to: Sara Nardis, nardis@scienze.uniroma2.it, fax: +39 06-72594328.

◇SPP full member in good standing

◇◇SPP student member

Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers CCDC 780147 and 780148. Copies can be obtained on request, free-of-charge, via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or deposit@ccdc.cam.ac.uk).

Inspired by the well-established chemistry of the porphyrinoids, researchers have made several attempts to prepare their corrole analogs. In particular, isocorroles have been reported wherein the sp^3 -carbon atom is located in a *meso*-position and their occurrence in many corrole-related reactions has already been documented [6]. For the isocorrole non-aromatic macrocycle, two isomers have been isolated, depending on the *meso*-position involved; these are the 10-isocorrole and the 5-isomer (Fig. 1). After the first publication of a nickel 10-isocorrole complex [7], other groups have devoted their attention to the synthesis of these macrocycles. Deahen and co-workers reported the preparation of a Ni-5-isocorrole complex by using the MacDonald [2+2] condensation of a 1,9-diformyl-5,5-dipropylpyrromethane with a 5-aryldipyrromethane in the presence of Ni-acetate [8]. The isocorrole, called *pseudocorrole* to distinguish it from the (2.0.1.0)-type corrole analog, and reported in some articles also as isocorrole [9], was isolated in only trace amounts, along with calix[4]pyrins. Higher yields of isocorroles (10%) were obtained using 1-formyl-5,5-dipropylpyrromethane in the condensation, instead of the diformyl derivative. More recently, the synthesis of the free-base isocorroles has been reported. In 2006, Setsune *et al.* [10] described the isolation of 10,10-dimethylisocorrole in 28% yield, and more recently Geier and co-workers investigated two complementary routes leading to the formation of 5,5-dimethylisocorroles (31%) [11].

A common feature of these approaches is the lengthy and difficult preparation of the pyrrolic precursors, and the formation of one of the two possible isomers. We have taken a different route for the preparation of isocorroles, using a 5,10,15-triarylcorrole as starting material [12]. Oxidation of the corrole ring by DDQ in the presence of methanol afforded the simultaneous preparation of both 5- and 10-methoxy isocorroles (74% overall yield). The scope of the reaction was quite general, being successful with a wide range of 5,10,15-triarylcorroles. It is worth mentioning that this is the only reported method for the preparation of triaryl isocorrole derivatives and that these macrocycles can be further functionalized at the β -pyrrolic carbon atoms.

The availability of free-base isocorroles led us to investigate the coordination chemistry of this macro-cycle. The Ni and Cu complexes of isocorrole were obtained, but in the case of metal ions having formal oxidation states higher than +2 when coordinated to corroles, the metalation reaction induced the rearomatization of the macrocycle, affording the corresponding corrole metal complexes. Electrochemical studies showed that isocorroles were converted into the corresponding corroles upon reduction [13]. On the other hand, Setsune *et al.* reported the metalation of gem-dimethylisocorrole [14] to give stable four-, five- and six-coordinate complexes, with the exception of Zn(II) isocorrole that easily undergoes demetalation. Such a difference could confidently be attributed to the stabilization of the gem-dialkyl substitution in the starting isocorrole free bases, whereas the $-OCH_3$ group is a better leaving group, which can allow rearomatization during the metalation process.

These results showed that the coordination chemistry of 5- and 10-alkoxy substituted isocorroles is limited and led us to explore the possible preparation of more stable species following the same one-pot procedure. We report here the preparation of 5- and 10-ethyl-triaryl isocorroles together with the first characterization of monobromo-substituted corroles obtained using the same reaction pathway.

EXPERIMENTAL

General

Silica gel 60 (70–230 mesh, Carlo Erba) was used for column chromatography. PLC silica gel 60 (2 mm, Merck) was used for preparative TLC. Reagents and solvents (Aldrich, Merck

or Fluka) were of the highest grade available and were used without further purification. CH₂Cl₂ used for the spectrophotometric measurements was stored over activated molecular sieves. ¹H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to residual CHCl₃ (7.25 ppm). UV-vis spectra were measured on a Cary 50 spectrophotometer. Mass spectra (FAB mode) were recorded on a VG Quattro spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (Aldrich) as a matrix. Elemental analysis (C, H, N) were obtained at the Microanalytical Laboratory of the University of Padova, Italy.

Synthesis of isocorroles

Preparation—A solution of TTCorH₃ [15] (100 mg, 0.176 mmol) and DDQ (42 mg, 0.176 mmol) in anhydrous toluene (100 mL) was placed in a 250 mL round-bottomed flask and stirred at room temperature under nitrogen. After 5 min, a solution of EtMgBr 1 M in THF (352 μ L, 0.352 mmol) was added. The reaction progress was monitored both by TLC (CH₂Cl₂/hexane, 1:1) and UV-vis spectrophotometry. After 30 min, although there still remained some starting corrole, hydrazine was added to quench the unreacted DDQ and the crude mixture was filtered through a Celite bed. The solvent was then evaporated and the products were purified by chromatography on silica gel using a mixture of CH₂Cl₂/hexane (1:1) as the eluent. The first green band (R_f = 0.83, 40% overall yield) was further purified by preparative TLC on silica gel plates (CH₂Cl₂/hexane 1:3, eluent) to afford a first fraction corresponding to the 10-isomer, and a second one corresponding to the 5-isomer. Both of the isomers were recrystallized from CH₂Cl₂/MeOH (1:2), affording 10-ethyl-5,10,15-trityl-isocorrole (R_f = 0.22) and 5-ethyl-5,10,15-trityl-isocorrole (R_f = 0.10) in 25% (26 mg; 0.044 mmol) and 13% (14 mg; 0.023 mmol) yields, respectively.

10-ethyl-5,10,15-tritoly-isocorrole (1)—mp > 300 °C. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻³, M⁻¹.cm⁻¹) 358 (29.3), 432 (48.2), 648 (6.6), 692 (7.2). ¹H NMR (300 MHz, CDCl₃): δ, ppm 14.30 (s, 2 H, NH), 7.53 (d, 4 H, *J* = 7.38 Hz, 5- and 15-phenyl), 7.30 (m, 6 H, phenyl), 7.08 (d, 2 H, *J* = 7.92 Hz, 10-phenyl), 6.85 (s, 4 H, β-pyrrole), 6.75 (d, 2 H, *J* = 3.93 Hz, β-pyrrole), 6.15 (d, 2 H, *J* = 3.78 Hz, β-pyrrole), 2.88 (q, 2 H, -CH₂CH₃), 2.47 (s, 6 H, 5- and 15-phenyl-CH₃), 2.31 (s, 3 H, 10-phenyl-CH₃), 0.89 (t, 3 H, -CH₂CH₃). MS (FAB): *m/z* (%) 597 [M]⁺ (100). Anal. calcd. for C₄₂H₃₆N₄: C, 84.53; H, 6.08; N, 9.39%. Found: C, 84.47; H, 6.10; N, 9.43.

5-ethyl-5,10,15-tritolylyl-isocorrole (2)—mp > 300 °C. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻³, M⁻¹.cm⁻¹) 408 (37.2), 655 (5.8), 722 (4.7). ¹H NMR (300 MHz, CDCl₃): δ, ppm 14.76 (s, 1 H, NH), 14.39 (s, 1 H, NH), 7.50 (d, 2 H, *J* = 8.07 Hz, phenyl), 7.32 (m, 8 H, phenyl), 7.15 (d, 1 H, *J* = 5.13 β-pyrrole), 7.05 (m, 3 H, phenyl and β-pyrrole), 6.77 (m, 1 H, β-pyrrole), 6.73 (d, 1 H, *J* = 4.41 Hz, β-pyrrole), 6.54 (m, 1 H, β-pyrrole), 6.44 (d, 1 H, *J* = 4.41 Hz, β-pyrrole), 6.37 (m, 1 H, β-pyrrole), 5.99 (m, 1 H, β-pyrrole), 2.88 (q, 2 H, -CH₂CH₃), 2.48 (s, 3 H, phenyl-CH₃), 2.46 (s, 3 H, phenyl-CH₃), 2.30 (s, 3 H, phenyl-CH₃), 0.70 (t, 3 H, -CH₂CH₃). MS (FAB): *m/z* (%) 597 [M]⁺ (100). Anal. calcd. for C₄₂H₃₆N₄: C, 84.53; H, 6.08; N, 9.39%. Found: C, 84.55; H, 6.07; N, 9.36.

From the first chromatographic purification, two other fractions were isolated. Recrystallization from CH₂Cl₂/MeOH (1:2) afforded 2-bromoTTCorH₃ (R_f = 0.72, 30% yield) (34 mg; 0.053 mmol) and the 3-bromoTTCorH₃ (R_f = 0.63, 10% yield) (11 mg; 0.018 mmol).

2-bromo-5,10,15-tritolylcorrole (3)—mp > 300 °C. UV-vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻³, M⁻¹.cm⁻¹) 421 (122.5), 525 (sh), 564 (15.4), 612 (10.0), 657 (21.4). ¹H NMR (300 MHz, CDCl₃): δ, ppm 9.17 (d, 1 H, J = 3.87 Hz, β-pyrrole), 8.89 (d, 1 H, J = 4.62 Hz, β-

pyrrole), 8.82 (d, 1 H, $J = 4.50$ Hz, β -pyrrole), 8.65 (s, 1 H, β -pyrrole), 8.54 (m, 3 H, β -pyrrole), 8.34 (d, 2 H, $J = 7.53$ Hz, phenyl), 8.15 (d, 2 H, $J = 7.47$ Hz, phenyl), 8.06 (d, 2 H, $J = 7.50$ Hz, phenyl), 7.62 (m, 6 H, phenyl), 2.71 (s, 9 H, phenyl- CH_3). MS (FAB): m/z (%) 648 $[\text{M}]^+$ (100). Anal. calcd. for $\text{C}_{40}\text{H}_{31}\text{BrN}_4$: C, 74.19; H, 4.82; N, 8.65%. Found: C, 74.21; H, 4.83; N, 8.61.

3-bromo-5,10,15-tritolylcorrole (4)—mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max} , nm ($\epsilon \times 10^{-3}$, $\text{M}^{-1}\cdot\text{cm}^{-1}$) 417 (100.5), 524 (sh), 563 (13.9), 617 (9.7), 651 (15.2). ^1H NMR (300 MHz, CDCl_3): δ , ppm 8.92 (s, 1 H, β -pyrrole), 8.87 (d, 2 H, $J = 4.25$ Hz, β -pyrrole), 8.66 (d, 1 H, $J = 4.93$ Hz, β -pyrrole), 8.57 (d, 1 H, $J = 4.22$ Hz, β -pyrrole), 8.50 (d, 2 H, $J = 4.64$ Hz, β -pyrrole), 8.29 (d, 2 H, $J = 7.83$ Hz, phenyl), 8.04 (m, 4 H, phenyl), 7.65 (d, 2 H, $J = 7.81$ Hz, phenyl), 7.56 (m, 4 H, phenyl), 2.70 (s, 9 H, phenyl- CH_3). MS (FAB): m/z (%) 648 $[\text{M}]^+$ (100). Anal. calcd. for $\text{C}_{40}\text{H}_{31}\text{BrN}_4$: C, 74.19; H, 4.82; N, 8.65%. Found: C, 74.17; H, 4.84; N, 8.64.

x-ray crystallography data

For **1**. $\text{C}_{42}\text{H}_{36}\text{N}_4\cdot\text{CHCl}_3$, monoclinic space group $\text{P}2_1/\text{n}$, $a = 13.904(3)$, $b = 10.158(2)$, $c = 25.288(5)$ Å, $\beta = 93.148(15)^\circ$, $V = 3566.2(13)$ Å³, $Z = 4$, calcd = 1.334 $\text{g}\cdot\text{cm}^{-3}$, ($\text{CuK}\alpha$) = 2.614 mm^{-1} , $R = 0.123$ for 1353 data with $\text{Fo}^2 > 2(\text{Fo}^2)$ of 5169 unique data and 455 refined parameters. A total of 23,449 data was collected at $T = 90.0(5)$ K to $= 59.7^\circ$ with $\text{CuK}\alpha$ radiation ($= 1.54178$ Å) on a Bruker Kappa Apex-II diffractometer, using a green lath crystal of dimensions $0.40 \times 0.12 \times 0.01$ mm.

For **3**. $\text{C}_{40}\text{H}_{31}\text{BrN}_4\cdot 2\text{CHCl}_3$, monoclinic space group $\text{P}2_1/\text{c}$, $a = 16.0322(15)$, $b = 14.6126(14)$, $c = 16.8920(15)$ Å, $\beta = 103.071(5)^\circ$, $V = 3854.8(6)$ Å³, $Z = 4$, calcd = 1.527 $\text{g}\cdot\text{cm}^{-3}$, ($\text{CuK}\alpha$) = 5.575 mm^{-1} , $R = 0.048$ for 5415 data with $\text{Fo}^2 > 2(\text{Fo}^2)$ of 6895 unique data and 519 refined parameters. A total of 24,302 data was collected at $T = 90.0(5)$ K to $= 68.5^\circ$ with $\text{CuK}\alpha$ radiation on a Bruker Kappa Apex-II diffractometer, using a dark green plate crystal of dimensions $0.31 \times 0.22 \times 0.06$ mm. Absorption correction were by face-indexed numerical methods. For both compounds, refinement was by full-matrix least-squares using SHELXL, with H atoms in idealized positions. NH hydrogen atoms were placed in idealized positions, guided by difference maps, and their positions were refined for **3**. There is a slight disorder in **3**, in which the bromo substituent is located at the C18 position with approximately 15% occupancy, as well as disorder in one of the solvent molecules.

RESULTS AND DISCUSSION

With the aim to obtain stable isocorroles using the same one-pot approach developed for methoxy-substituted derivatives, TTCorH₃ was used as the starting material. Since the plausible reaction mechanism for the isocorrole formation was the initial oxidation of corrole by DDQ, followed by the addition of methanol [12] (or water [6c]), it was decided to attempt the oxidation in toluene, followed by the addition of an opportune nucleophile. To obtain an alkyl-substituted isocorrole, the suitable reagents used were organolithium or Grignard reagents, both of which have been used in the case of porphyrins [16]. An organolithium compound, BuLi, was first investigated but no reaction occurred; oxidation of the corrole was observed, but after the quenching step, only the starting material was recovered. Attention was then focused on Grignard reagents and, in particular, on EtMgBr. The reaction was attempted without the addition of DDQ but no reactivity was observed other than the corrole anion formation. The reaction was performed in anhydrous toluene under inert atmosphere with the initial oxidation of corrole by addition of an equimolar amount of DDQ and then adding EtMgBr in a 1:2 molar ratio. The reaction monitoring by

UV-vis and TLC showed, along with some unreacted material, the presence of three new green bands characterized by higher R_f than the starting TTCorH₃. The excess of DDQ was quenched using hydrazine and, after filtering the solution through a bed of Celite, the solvent was evaporated under reduced pressure.

The crude mixture was purified by column chromatography using silica gel as stationary phase and a CH₂Cl₂/hexane solution (1:1) as the eluent. The unreacted corrole was separated and three fast-moving green fractions were collected. The most polar fraction (40% overall yield) showed a UV-vis spectrum having features characteristic of an isocorrole derivative. TLC analysis indicated the presence of two compounds, which were then separated by preparative TLC on silica gel (CH₂Cl₂/hexane, 1:3), leading to the isolation of **1** and **2**, in an approximately 2:1 ratio, respectively (Chart 1).

The ¹H NMR spectrum of the first eluted band was consistent with the symmetrical structure of **1**, with the presence of a single peak at 14.30 ppm, assigned to the inner NHs, and two signals (2:1 intensity ratio) for the -CH₃ of the tolyl groups in the 5,15- and 10-positions respectively. The second eluted fraction was in accord with the less symmetrical structure of **2**, presenting two different signals, at 14.79 and 14.39 ppm, for the inner core NHs, and three separate resonances for the above-mentioned -CH₃ of the tolyl groups.

Slow diffusion of MeOH into a CHCl₃ solution of **1** afforded a single crystal that allowed the characterization by X-ray crystallography (Fig. 2). Although the quality of the structure determination was not high, the identity of the compound was however confirmed.

The 23-atom core shows only minor deviations from coplanarity, with mean deviation 0.07 Å and maximum deviation 0.16(1) Å. The four N atoms are coplanar with 0.04(1) Å, and the two pyrrole rings in the background in Fig. 2 tilt slightly in the same direction, out of the N₄ plane by 7° and 9°. The ethyl substituent at C10 is turned inward over the central core of the molecule and is coplanar with the tolyl group also at C10. The plane of the ethyl and tolyl substituents on C10 is approximately perpendicular to the main ring system, forming a dihedral angle of 88.3(2)° with the N₄ plane. The other two tolyl planes form dihedral angles of 55.1(4) and 57.1(2)° with the N₄ plane and a dihedral angle of 67.8(4)° with each other.

While these products indicated the successful formation of the desired isocorrole species, the other two chromatographic fractions showed UV-vis spectra, indicating the retention of the aromatic corrole structure. This result indicated the formation of β-substituted corroles, as confirmed by their ¹H NMR spectra; the presence of a singlet at 8.65 ppm for the first isolated compound and at 8.92 ppm for the second fraction provided evidence of the monosubstitution (Fig. 3). However, no ethyl group resonances were present in either spectrum, thereby excluding the substitution by the ethyl group of the Grignard reaction at the β-pyrrolic position of the corrole ring. FAB mass spectra for both fractions, on the other hand, were compatible with the presence of a Br substituent. This result suggested that the nucleophile reacting at the pyrrolic position of the oxidized corrole was the bromide group of the Grignard reagent, leading to the monobromo-substituted corrole. In agreement with the data reported in the literature for the ¹H NMR assignment of pyrrolic resonances of corrole [17], the two fractions were respectively characterized as the 2- and 3-Br substituted corrole (Fig. 3).

We were able to obtain single crystals of **3** that were characterized by X-ray crystallography (Fig. 4). While the four N atoms are reasonably coplanar, with mean deviation 0.013 Å; the 23-atom core is quite distorted from planarity, with mean deviation 0.19 Å and maximum deviation 0.496(3) Å. The distortion can be described as tipping of the pyrrole rings out of the N₄ plane. The two directly-linked pyrroles tip toward the same side of the molecule, forming dihedral angles of 21.6(1) and 32.0(1)° with the N₄ plane. One of the other pyrroles

tips toward the opposite side of the molecule, forming a dihedral angle of $32.6(1)^\circ$ with the N_4 plane. The fourth pyrrole is more nearly coplanar with N_4 , tipping by only $6.1(1)^\circ$. The pyrrole tipping allows avoidance of extremely short intramolecular N-H...H-N contacts, the nearest being 2.18 Å. The C-Br distance is 1.874(3) Å, and the tipping of the brominated pyrrole causes the Br atom to be 1.586(1) Å out of the N_4 plane.

It is worth mentioning that even though the formation of a mixture of monobrominated corrole isomers has been previously reported in the literature [18], the separation of the regioisomers was not at that time possible. This is the first example where the regioisomers have been separated and fully characterized. Moreover, it is interesting to note that the regioselectivity of this reaction does not follow the usual pattern observed for corrole, where the reactivity order is $C3 > C2 \geq C8 > C7$ [19,20]. In the past, in fact, tribromo-derivatives [18,21] have been isolated and unambiguously characterized by crystallography: the substitution pattern, as in the case of deuteration of other corrolic rings [22], suggested a higher reactivity for the C3 (or C17) position. On the other hand, in our case the first eluted isomer **3** represents the most abundant species (30%), in contrast with the hypothetical identification reported by Du *et al.* [18]. In this case the most reactive site for the A-pyrrole (D-pyrrole) is the one closer to the direct bond, namely the C2 position. One can hypothesize that the different reactivity suggests a different reaction mechanism in this case and further studies are now in progress in our laboratories to thoroughly investigate this topic; these results will be reported in due course.

CONCLUSION

The results obtained have demonstrated that stable isocorroles can be successfully synthesized using our new approach. This methodology can be of great importance since it is based on the use of different and readily available macrocycles as starting material that are still susceptible, after the isocorrole formation, to further functionalization; this can subsequently be used to tune the properties of the products for use in real applications.

The use of Grignard reagents illustrates the competitive reactivity of the β -pyrrole positions compared with the *meso*-positions. This allows, along with the formation of isocorroles, the isolation of previously unreported mono-bromocorrole isomers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by MIUR, Italy (PRIN project 2007C8RW53) and the US National Institutes of Health (K.M.S., Grant CA-132861).

References

1. a) Kadish, KM.; Smith, KM.; Guillard, R., editors. The Porphyrin Handbook. Vol. 2. Academic Press; San Diego, CA: 2000. b) Sessler, JL.; Weghorn, SJ. Expanded, Contracted & Isomeric Porphyrins. Pergamon Press; 2000.
2. a) Vicente, MGH. The Porphyrin Handbook. Kadish, KM.; Smith, KM.; Guillard, R., editors. Vol. 1. Academic Press; San Diego, CA: 2000. p. 149-199. b) Li X, Chmielewski PJ, Xiang J, Xu J, Jiang L, Li Y, Liu H, Zhu D. J Org Chem 2006;71:9739–9742. [PubMed: 17168592] c) Senge MO. Accounts of Chemical Research 2005;38:733–743. [PubMed: 16171316] d) O'Brien AY, McGann JP, Geier GR III. J Org Chem 2007;72:4084–4092. [PubMed: 17461598] e) Abhilash GJ, Bhuyan J,

- Singh P, Maji S, Pal K, Sarkar S. *Inorg Chem* 2009;48:1790–1792. [PubMed: 19235937] f) Lash TD, El-Beck JA, Colby DA. *J Org Chem* 2009;74:8830–8833. [PubMed: 19908914]
3. a) Scheer, H. *Chlorophylls*. CRC Press; Boca Raton, FL: 1991. b) Balaban TS. *Acc Chem Res* 2005;38:612–623. [PubMed: 16104684] c) Senge, MO.; Wiehe, A.; Ryppa, C. In *Advances in Photosynthesis and Respiration*. Grimm, B.; Porra, R.; Rudiger, W.; Scheer, H., editors. Vol. 25. Springer; Dordrecht: 2006. p. 27-37.
4. Pandey, RK.; Zheng, G. *The Porphyrin Handbook*. Kadish, KM.; Smith, KM.; Guillard, R., editors. Vol. 6. Academic Press; San Diego, CA: 2000. p. 157-230.
5. a) Sessler, JL.; Gale, PA. *The Porphyrin Handbook*. Kadish, KM.; Smith, KM.; Guillard, R., editors. Vol. 6. Academic Press; San Diego, CA: 2000. p. 257-278. b) Sessler JL, Zimmerman RS, Bucher C, Kral V, Andrioletti B. *Pure Appl Chem* 2001;73:1041–1057. c) Sessler JL, Gross DE, Chow S, Lynch VM, Schmidtchen FP, Bates GW, Light ME, Gale PA. *J Am Chem Soc* 2006;128:12281–12288. [PubMed: 16967979] d) Finnigan EM, Giordani S, Senge OM, McCabe T. *J Phys Chem A* 2010;114:2464–2470. [PubMed: 20112903]
6. a) Mandoj F, Nardis S, Pomarico G, Stefanelli M, Schiaffino L, Ercolani G, Prodi L, Genovese D, Zaccheroni N, Fronczek FR, Smith KM, Xiao X, Shen J, Kadish KM, Paolesse R. *Inorg Chem* 2009;48:10346–10357. [PubMed: 19795835] b) Stefanelli M, Shen J, Zhu W, Mastroianni M, Mandoj F, Nardis S, Ou Z, Kadish KM, Fronczek FR, Smith KM, Paolesse R. *Inorg Chem* 2009;48:6879–6887. [PubMed: 19548683] c) Mandoj F, Nardis S, Pomarico G, Paolesse R. *J Porphyrins Phthalocyanines* 2008;12:19–26. d) Stefanelli M, Mastroianni M, Nardis S, Licocchia S, Fronczek FR, Smith KM, Zhu W, Ou Z, Kadish KM, Paolesse R. *Inorg Chem* 2007;46:10791–10799. [PubMed: 17985873]
7. Hohlneicher G, Bremm D, Wytko J, Bley-Esrich J, Gisselbrecht JP, Gross M, Michels M, Lex Johann, Vogel E. *Chem Eur J* 2003;9:5636–5642.
8. Orlewska C, Maes W, Toppet S, Dehaen W. *Tetrahedron Lett* 2005;46:6067–6070.
9. a) Will S, Rahbar A, Schmickler H, Lex J, Vogel E. *Angew Chem Int Ed Engl* 1990;29:1390–1393. b) Vogel E, Binsack B, Hellwig Y, Erben C, Heger A, Lex J, Wu YD. *Angew Chem Int Ed Engl* 1997;36:2612–2615.
10. Setsune J, Tsukajima A, Watanabe J. *Tetrahedron Lett* 2006;47:1817–1820.
11. Flint DL, Fowler RL, LeSaulnier TD, Long AC, O'Brien AY, Geier GR III. *J Org Chem* 2010;75:553–563. [PubMed: 20041697]
12. Nardis S, Pomarico G, Fronczek FR, Vicente MGH, Paolesse R. *Tetrahedron Lett* 2007;48:8643–8646.
13. Pomarico G, Xiao X, Nardis S, Paolesse R, Fronczek FR, Smith KM, Fang Y, Ou Z, Kadish KM. *Inorg Chem* 2010;49:5766–5774. [PubMed: 20499899]
14. Setsune J, Tsukajima A, Okazaki N. *J Porphyrins Phthalocyanines* 2009;13:256–265.
15. Paolesse R, Marini A, Nardis S, Froiio A, Mandoj F, Nurco DJ, Prodi L, Montalti M, Smith KM. *J Porphyrins Phthalocyanines* 2003;7:25–36.
16. a) Senge MO. *Acc Chem Res* 2005;38:733–743. [PubMed: 16171316] b) Sergeeva NN, Shaker YM, Finnigan EM, McCabe T, Senge MO. *Tetrahedron* 2007;63:12454–12464. c) Senge MO, Richter J, Bischoff I, Ryan A. *Tetrahedron* 2010;66:3508–3524.
17. Balazs YS, Saltsman I, Mahammed A, Tkachenko E, Golubkov G, Levine J, Gross Z. *Magn Reson Chem* 2004;42:624–635. [PubMed: 15181633]
18. Du RB, Liu C, Shen DM, Chen QY. *Synlett* 2009;16:2701–2705.
19. Paolesse R, Nardis S, Venanzi M, Mastroianni M, Russo M, Fronczek FR, Vicente MGH. *Chem Eur J* 2003;9:1192–1197.
20. Paolesse R. *Synlett* 2008:2215–2230.
21. Nardis S, Mandoj F, Paolesse R, Fronczek FR, Smith KM, Prodi L, Montalti M, Battistini G. *Eur J Inorg Chem* 2007;16:2345–2352.
22. Gross Z, Mahammed A. *J Porphyrins Phthalocyanines* 2002;6:553–555.

Fig. 1.
Molecular structure of (a) 10-isocorrole and (b) the corresponding 5-isomer

Fig. 2.
X-ray molecular structure of **1**

Fig. 3.
 ^1H NMR spectra (aromatic region) of (a) TTCorH_3 , (b) **3**, (c) **4**

Fig. 4.
X-ray molecular structure of 2-bromoTTCorH₃

Chart 1.