Carbaporphyrinoids

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A Parallel-Displaced Directly Linked 21-Carba-23-Thiaporphyrin Dimer Incorporating a Dihydrofulvalene Motif

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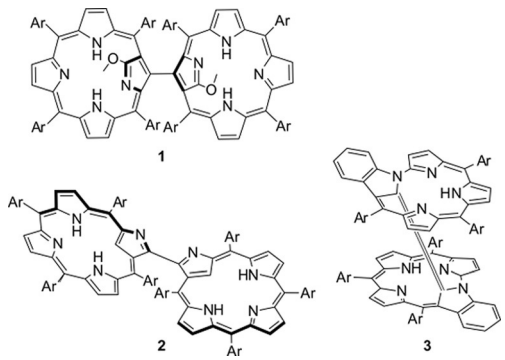
Abstract: *In the search of porphyrin arrays with a unique geometry, the efficient synthesis of a directly linked 21-carba-23-thiaporphyrin dimer with the distinctive dihydrofulvalene bridging motif has been developed. This compound acquires an uncommon parallel-displaced arrangement of two carbaporphyrin planes. The dimer undergoes an acid-triggered cleavage to create of the asymmetric carbathiaporphyrin–carbathiachlorin dyad or 2,3-dihalo-21-carba-23-thiachlorin depending on choice of acid. A formation of a reactive carbocation intermediate is postulated to account for mechanism of cleavage.*

Oligomeric porphyrin arrays with covalently linked porphyrin units[1] were extensively studied in light of their attractive electronic, optical, electrochemical and magnetic properties.[2] An important class among porphyrin oligomers are the assemblies in which porphyrin subunits are directly linked via direct meso–meso, β–β and β–meso bonds allowing interaction between closely adjacent porphyrins.[3]

The field of multimolecular porphyrin systems has been significantly enhanced by construction of a covalently linked dimers of N-confused porphyrin involving a reactive carbon atom of coordination core (**1**, **2**) (Scheme 1).[4,5] The face-to-face dimer of benzonorrole with a direct double bond between the internal carbon atoms (**3**) demonstrating strong π–π interaction between two π planes was reported.[6]



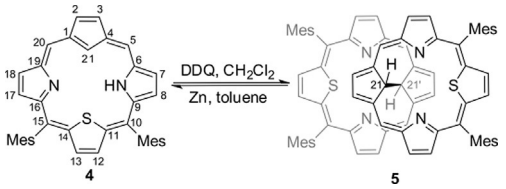
Scheme 1. Directly linked dimers of N-confused porphyrin (**1**, **2**) and benzonorrole (**3**).

Originally the inclusion of β-substituted cyclopentadiene moiety into a porphyrin frame yielding an aromatic carbaporphyrin with β-substitution at pyrrole rings was achieved by Berlin.[7] Lately Lash and co-workers described the synthesis of β-substituted carbaporphyrin via oxidation of carbachlorin with stoichiometric amount of DDQ.[8] Furthermore the β-substituted *adj*-dicarbachlorin with an internal methylene fragment was obtained as well.[9]

Recently we have reported on the formation of 5,10,15,20-tetraaryl-21-carbaporphyrin complexes, firmly stabilized via palladium(II), gold(III) or rhodium(III) coordination.[10] They were generated by metal ion mediated contraction of *p*-phenylene or *m*-phenylene to cyclopentadiene, embedded in metal *m*-benziporphyrin (rhodium(III)) or *p*-benziporphyrin (palladium(II), gold(III) or rhodium(III)). Inspired by the emerging chemistry of tetraaryl-21-carbaporphyrins we have originally devoted our synthetic effort to construct 21-carbaheteroporphyrins.[11]

Introduction of the cyclopentadiene or cyclopentene fragments may be beneficial for the efforts aimed at well-defined modification of the macrocycle and construction of the new directly linked arrays demonstrating uncommon electronic properties and reactivity. As a part of our research, aspired to explore the reactivity of carbaporphyrinoids,[12] here we report on the synthesis of bis(21-carbathiaporphyrin) with a direct sp^3–sp^3 covalent linkage between internal carbon atoms and the unusual parallel-displaced geometry.

The bis(carbathiaporphyrin) **5** was initially produced during oxidation of 21-carba-23-thiachlorin with DDQ, however the best yield was obtained by oxidation of **4** in the same conditions (46%, Scheme 2). The identity of the dimer **5** was



Scheme 2. Synthesis of carbathiaporphyrin dimer **5**.

confirmed by high-resolution mass spectrometry (*m*/*z* calcd for $[M+H^+]$: 1123.4807; found: 1123.4776) reflecting the presence of two porphyrinic subunits.

The UV/Vis electronic absorption spectrum (Figure 1) is consistent with aromaticity of **5**. The spectral features are related to those of **4**,[11] considered here as a reference. A Soret band is observed at the same position (417 nm), while the Q bands at 687 and 758 nm are bathochromically shifted

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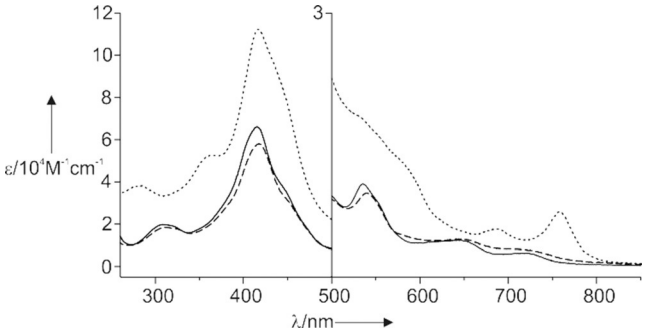


Figure 1. The UV/Vis electronic spectra of **4** (solid line), **5** (dotted line) and **7**-Cl (dashed line) in CH_2Cl_2.

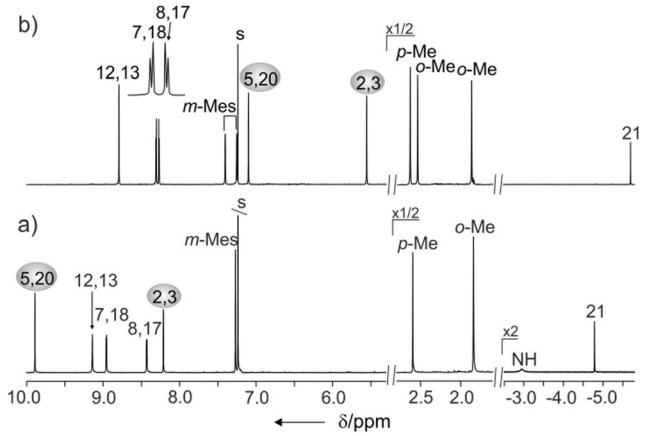


Figure 2. ^{1}H NMR spectra of: a) **4** and b) **5** (300 K, $CDCl_3$). Atom assignments correspond to the systematic position numbering of 21-carbaporphyrin (Scheme 2).

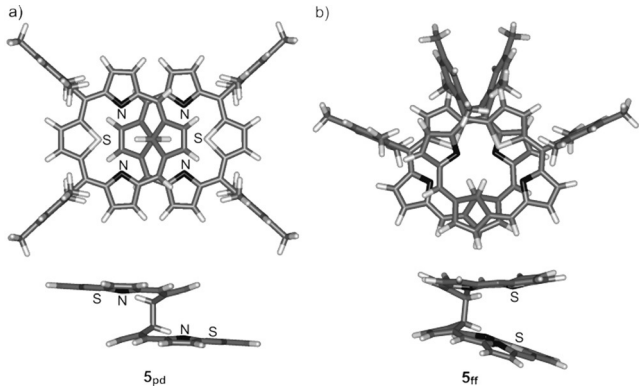


Figure 3. DFT-optimized structures of **5**: a) the parallel-displaced conformer (**5**$_{pd}$) and b) the face-to-face skewed conformer (**5**$_{ff}$). C(21)–C(21′) bond lengths: a) 1.52 Å, b) 1.65 Å.

relative to **4** (651 and 718 nm), thus signifying the weak interaction between two carbaporphyrin subunits.

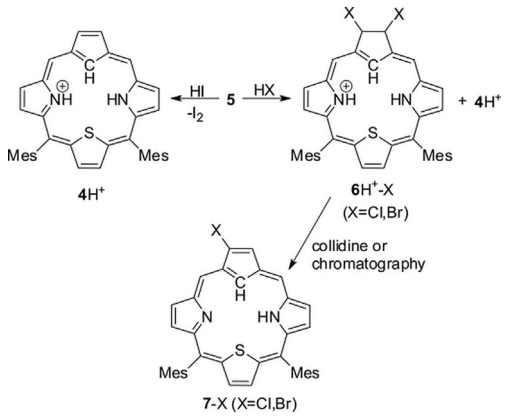
The ^{1}H NMR spectrum of **5** (Figure 2 b) reflects the effective C_{2h} symmetry. The internally located H(21) protons gave the remarkable shielded signal at −5.61 ppm. Singlets of meso H(5,20) and cyclopentadienyl protons H(2,3) are markedly upfield relocated to 7.10 and 5.55 ppm in comparison to monomeric **4** (9.89 and 8.21 ppm, correspondingly).[11] Thus the dimer acquires a conformation with respect to C(21)–C(21′) bond in which meso and cyclopentadienyl hydrogen atoms of one subunit are located in the shielding zone of the second one (Figure 3).

The unsubstituted 5,20 meso positions diminish the steric hindrance which seems to be the crucial factor to allow the straightforward dimerization. Presumably the process proceeds with a prearrangement of **4** to acquire a geometry of less stable tautomer resulting in the sp^2 to sp^3 rehybridization of the internal carbon atom.[11] Such a profound structural change was firmly confirmed by the position of C(21) resonances of **4** and **5** determined by ^{1}H-^{13}C HSQC experiment (113.6 ppm and 39.9 ppm, respectively).[11]

The two DFT optimized rotamers of **5** are presented in Figure 3. The limited libration about single bond C(21)–C(21′) is possible but nevertheless restricted. In fact the bulky meso mesityl substituents freeze conformationally two rotamers **5**$_{pd}$ and **5**$_{ff}$. At this stage, it is difficult to imagine sterically prohibited **5**$_{pd}$ and **5**$_{ff}$ interconversion. The carbathiaporphyrin subunits of **5**$_{pd}$ are almost planar and parallel to each other. The H(21)-C(21)-C(21′)-H(21′) dihedral angle equals 180°. The interporphyrin distance between two macrocyclic planes (defined by four meso carbons) equals 3.22 Å and is slightly larger to that observed for the reduced benzonorrole dimer with single bond (3.14 Å),[6] however shorter than for **3** and other arrays with the face-to-face arrangement (over 3.4 Å).[6,13] The NICS value of each subunit, determined for the central 16-membered ring, equals −14.2 ppm evidently consistent with their diatropicity. The alternative rotamer **5**$_{ff}$ with the face-to-face arrangement (the H(21)-C(21)-C(21)′-H(21′) dihedral angle: 47°) is evidently less stable as the energy difference between **5**$_{pd}$ and **5**$_{ff}$ equals 9.4 kcal mol^{-1}. In fact the structural model of **5**$_{pd}$, reflects the structural constraints determined by NOE measurements (contact between H(2,3) and *o*-Me protons). Importantly the satisfactory agreement between the experimental and calculated ^{1}H chemical shifts have been found solely for **5**$_{pd}$ geometry in contrast to essential deviations seen for **5**$_{ff}$ (Table S1, Figures S14 and S15 in the Supporting Information).

The two-electron reduction of dimeric **5** with zinc dust results in C(21)–C(21′) bridge splitting to recover monomeric **4** (Scheme 2). Furthermore the dimer **5** is very sensitive for the presence of even trace amount of acid in solution and easily undergoes splitting to monomeric species. Such a transformation does not have any precedence in chemistry of covalently linked dimers of porphyrinoids.[3–6]

Thus the reaction of **5** with HX (X = Cl or Br, 7–10 equiv) was followed by ^{1}H NMR spectroscopy (Scheme 3). Two major products were identified: the carbathiaporphyrin monocation **4**H$^+$ and 2,3-dihalo-21-carba-23-thiachlorin monocation **6**H$^+$-X, which is highly reactive and readily converted to 2-halo-21-carba-23-thiaporphyrin **7**-X by HX elimination in course of column chromatography or by collidine addition. In contrast an addition of HI (5 equiv) to **5** afforded exclusively **4**H$^+$ suggesting that HI acts both the splitting and reducing reagent.



Scheme 3. Reactivity of **5** in the presence of HX.

The electronic absorption spectrum of **7-**Cl (Figure 1, dashed line) displays the profile in the 250–850 nm region resembling one of **4**.

The ^{1}H NMR spectra of **6**H$^+$-X and **7**-X show resonances in the range found for other aromatic carbaporphyrins with internal H(21) signal at characteristic upfield locations (**6**H$^+$-Cl −5.89 ppm, **6**H$^+$-Br −5.78, **7**-Cl −4.75 ppm, and **7**-Br −4.72) (Figures 4 a,b; Figures S6 and S7). The H(2,3) protons of transient 2,3-dihalocarbachlorins **6**H$^+$-X afforded significantly shifted downfield singlets at 7.29 ppm (X = Cl) or 7.56 ppm (X = Br) (Figures 4 a and S6). Further ^{13}C characterization has shown the presence of tetrahedral C(2,3) carbon atoms at 70.7 and 59.1 ppm for **6**H$^+$-Cl and **6**H$^+$-Br, respectively.

The variable-temperature ^{1}H NMR studies on **6**H$^+$-X (X = Cl, Br) in CD_2Cl_2 revealed the conformational equilibrium. The exchange involves two energetically equivalent unsymmetrical conformers differentiated by direction of folding (Figures 5 and S20, Table S8). Thus the ^{1}H NMR spectra of **6**H$^+$-X at 300 K reflect the effective C_s symmetry (Figure 4 a). Eventually, at low temperature (190–210 K), the exchange process is sufficiently slow on the ^{1}H NMR time scale and the double the number of resonances is observed (Figures S8 and S9). The energy barrier ($\Delta G^{\neq}$) for this process has been estimated to be 10.7 kcal mol^{-1} and 9.7 kcal mol^{-1} for **6**H$^+$-Cl and **6**H$^+$-Br, respectively (Supporting Information).

The addition of the large excess of concentrated TFA (trifluoroacetic acid, ca. 150 equiv) to **5** resulted in a cleavage affording carbathiaporphyrin dication **4**H$_2^{2+}$ as a sole ^{1}H NMR identified species (Scheme 4). Two additional protons are located on C(21) and N(24) atoms (Figure S4).

In fact the acid-triggered chemistry is quite complex as the addition of 8–10 equiv of TFA or dichloroacetic acid to **5** produced a unique set of resonances attributed to the peculiar asymmetric carbathiaporphyrin–carbathiachlorin dyad **8**, presumably as the monocation **8**H$^+$ in given acidic conditions, accompanied by **4**H$^+$ (Scheme 4). **8**H$^+$ reveals high reactivity. Accordingly, all attempts of isolation (column chromatography, crystallization) failed. Presumably the trace amount of water contained in an acid and solvent was a source of oxygen in identified hydroxy and carbonyl group of **8**H$^+$.

In principle the species **8**H$^+$ was created by formation of C–C bond between the internal C(21) carbon atom of one carbathiaporphyrin unit and the external C(3′) carbon atom of the second carbathiachlorin unit. Two subunits are

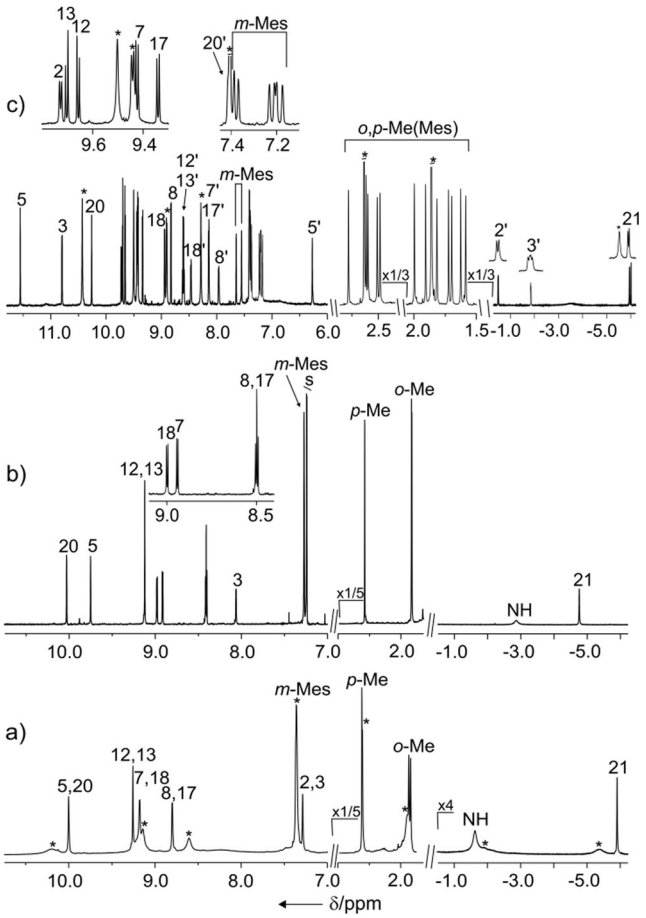


Figure 4. ^{1}H NMR spectra of: a) **6**H$^+$-Cl (300 K, CD_2Cl_2); b) **7**-Cl (300 K, $CDCl_3$) and c) **8**H$^+$ (300 K, CD_2Cl_2). Stars (*) denote signals of **4**H$^+$. Atom assignments correspond to the systematic position numbering (Schemes 2 and 4).

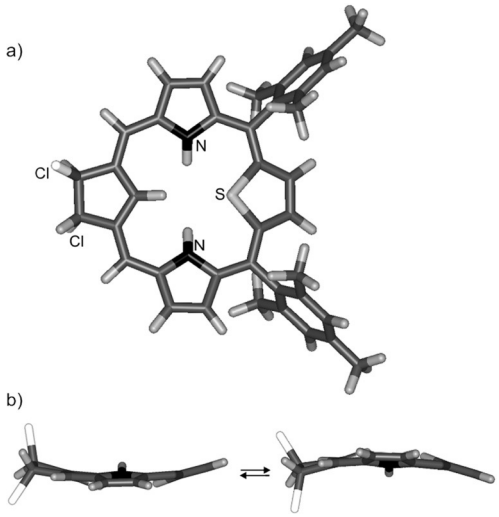
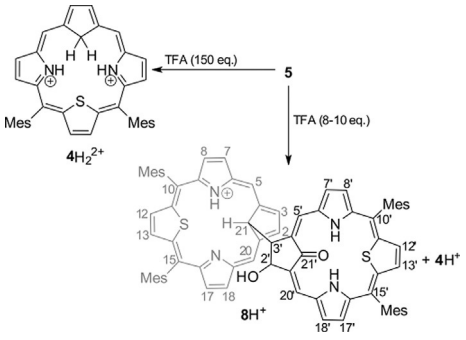


Figure 5. DFT-optimized structure of **6**H$^+$-Cl: a) perspective view and b) side view, the conformational equilibrium.



Scheme 4. Splitting of **5** and formation of **8**H$^+$ in CD_2Cl_2.

structurally different, one preserves the identity of the maternal macrocycle, nevertheless the second is noticeably modified via oxygen functionalization at C(2′) and C(21′) atoms embedded in the frame of carbathiachlorin.

The ^{1}H NMR spectra of 2′-hydroxy-21′-oxo dicarbaporphyrinic form **8**H$^+$ (Figure 4c) shows it has a lower symmetry compared to **5**. The resonances of carbathiaporphyrin moiety are in the typical range of carbaporphyrins with the characteristic doublet of inner H(21) located at −6.00 ppm.[7–9,11] The perimeter resonances of carbathiachlorin unit are relocated upfield (8.61–6.27 ppm,) that reflects mutual special arrangement of both subunits. The structural model of *cis*-**8**H$^+$-1, generated by DFT optimization reflects the structural constraints determined by NOE measurements (Figure 6). The

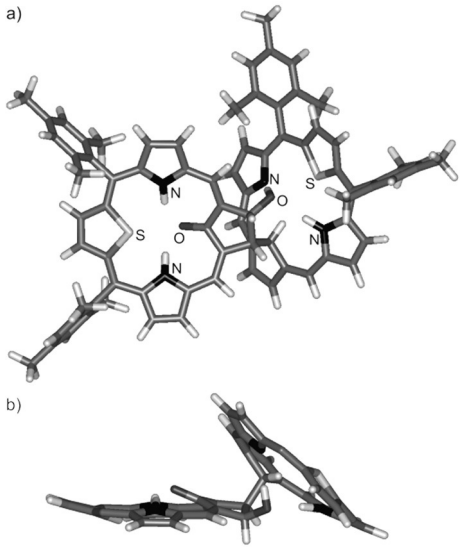
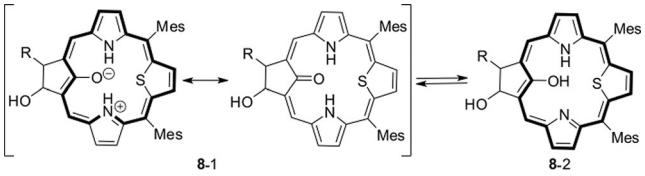


Figure 6. DFT-optimized structure of *cis*-**8**H$^+$-1: a) perspective view and b) side view. Selected bond lengths [Å]: C(21)−C(3′) 1.61, C(21′)−O 1.27; C(2′)−O 1.42.

H(2′) and H(3′) protons afford multiplets significantly shifted upfield at −0.5 and −1.85 ppm, correspondingly. Further ^{13}C characterization has shown the presence of three tetrahedral C(21), C(2′) and C(3′) carbon atoms ($\delta = 45.5$, 61.6 and 46.6 ppm, respectively), what is in agreement with the structure of **8**H$^+$. The indirect evidence of the presence of substituents involving oxygen at the C(2′) and C(21′) atoms was proved by ^{1}H-^{13}C HMBC experiment showing appropriate ^{13}C chemical shifts at 61.6 and 167.5 ppm as a result of substitution by more electronegative hydroxyl and the presence of carbonyl group, respectively.[14] The formation of **8** was confirmed by high resolution mass spectrometry (m/z calcd for $[M-OH]^+$: 1139.4756, found: 1139.4711).

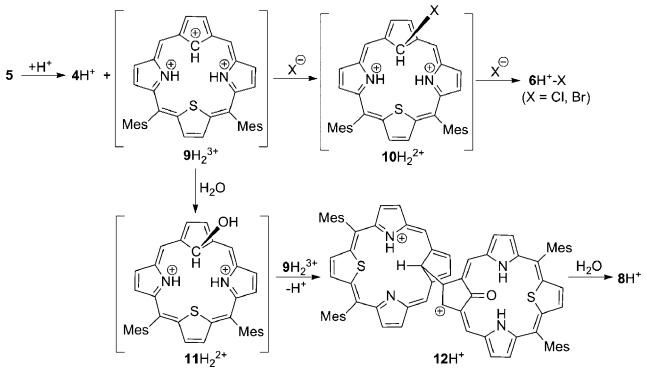
Initially the keto and enol tautomers of **8**H$^+$ with different configuration at C(2′) and C(3′) have been subjected to DFT studies (Figure S18). Evidently the estimated energies of the formally non aromatic keto tautomers are 30 kcal mol^{-1} lower than the energy of the corresponding aromatic enol forms with preserved macrocyclic π-delocalization pathway (Table S6). In fact the *cis*-stereoisomer of the keto tautomer of **8**H$^+$ (the C(21)-C(3′)-C(2′)-O dihedral angle is 24.5°) presented in Figure 6 has the lowest energy, consistent with its preference in solution. The NICS values calculated for the center of the individual macrocyclic ring equal −9.8 and −15.2 ppm for carbathiaporphyrin and carbathiachlorin-like units, respectively. In order to account for diatropicity of 2′-hydroxy-21′-oxo carbathiachlorin an attempt has been made to analyze the above ^{1}H NMR features in terms of the classical valence bond approach. The structure of monomeric 2′-hydroxy-21′-oxo carbathiachlorin can be thought of as a resonance hybrid of two canonical forms (Scheme 5). The diatropicity of 2'-hydroxy-21'-oxocarba-23-thiachlorin sug-



Scheme 5. The keto (two mesomeric structures) and enol tautomers of **8** (R = carbathiaporphyrin unit).

gests the significant participation of a dipolar contributor with a well-defined 18 π-electron delocalization pathway (Scheme 5). The corresponding monomeric enol and keto tautomers have been also optimized by the DFT method (Figure S19). For both tautomers the calculated chemical shifts and NICS values are in the range observed for diatropic porphyrinoids molecules (Table S5 and S7).

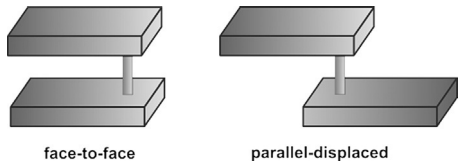
The feasible mechanism describing the acid triggered splitting of dimer is presented in Scheme 6. Initially, the dimer **5** is protonated and undergoes a heterolytic cleavage to form the **4**H$^+$ and the accompanying hypothetical carbathiaporphyrinic carbocation **9** formally two-electron oxidation product of **4**. Immediately **9** is attacked at C(21) position by any accessible nucleophile, i.e. halide anions or water molecules depending on the type of acid used. Both the carbocation **9** and substituted carbathiaporphyrin transient species (**10** or **11**) formed at initial stages of reaction were not directly detected. Subsequently, 21-hydroxycarbathiaporphyrin **11** acts as nucleophile reacting with carbocation **9** to form the diporphyrinic carbocation **12**, which reacts with water to generate the asymmetric species **8**H$^+$ (Scheme S5). In the case of reaction with hydrogen halide, the proposed mecha-



Scheme 6. Postulated mechanism of the dimer **5** splitting in acidic conditions. Only selected resonance contributors shown for carbocationic $\mathbf{9}H_2^{3+}$ and $\mathbf{12}H^{2+}$.

nism involves the migration of the halide,[15] and then attack of the second halide ion leading to the formation of $\mathbf{6}H^+$-X (Scheme S4).

In summary the oxidation of 21-carba-23-thiaporphyrin yielded bis(21-carba-23-thiaporphyrin) containing the unique dihydrofulvalene covalently bridging motif. In fact the very first example of a directly linked parallel-displaced dimer based on carbaporphyrinoid building blocks has been reported. Structurally it introduces an uncommon geometry for the layered face-to-face dimers, presenting the peculiar parallel-displaced conformation with limited π–π interaction (Scheme 7).



Scheme 7. Rotamers of a directly linked parallel dimer **5**.

The carbathiaporphyrin dimer has been cleaved by two-electron reduction or in a more triggered way by acids. The postulated mechanism involves the carbocation of carbathiaporphyrin as the fundamental intermediate inferred from the formation of 2,3-dihalo-21-carbathiachlorin and carbathiaporphyrin–carbathiachlorin dyad. The described examples open the way to explore reactivity of the cyclopentadiene ring built-in a macrocyclic platform towards a variety of nucleophilic reagents.

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