Bismuth A_3-Corroles: Useful Precursors for the Development of *meso*-Substituted Free-Base Corroles

Felix Faschinger,[a] Stefan Aichhorn,[a] Markus Himmelsbach,[c] Wolfgang Schoefberger*[a,b]

[a] Institute of Organic Chemistry, Johannes Kepler University Linz (JKU), Altenberger Straße 69, 4040 Linz, Austria
E-mail: wolfgang.schoefberger@jku.at

[b] Faculty of Science, University of South Bohemia, Branišovská 31, 37005 České Budějovice, Czech Republic

[c] Institute of Analytical Chemistry, Johannes Kepler University Linz (JKU), Altenberger Straße 69, 4040 Linz, Austria

Received: 01.07.2014; Accepted after revision: 01.08.2014

Dedicated to Prof. Dr. Heinz Falk on the occasion of his 75th birthday

Abstract: Systematic studies on regioselective functionalization reactions employing oxygen-, nitrogen-, and sulfur-containing nucleophiles with bismuth A_3-corroles under the influence of a strong non-nucleophilic base are reported. In the case of the thiols and dithiols a high-yielding reaction procedure was established to obtain mono-, di-, and tri-functionalized corroles at room temperature within short reaction times. The described method offers a possibility to attach bifunctional linker molecules to the *para*-position of the *meso*-pentafluorophenyl groups at positions 5, 10, and 15 of the corrole macrocycle. The described reaction strategy may serve as a versatile protocol for the covalent binding of corroles to proteins or antibodies and may be utilized to attach corroles on, for example, gold or titanium surfaces to study surface-supported reactions.

Key words: corrole, bismuth, nucleophiles, regioselective, S_NAr reaction

Corroles are ring-contracted tetrapyrrolic macrocycles, which are one carbon shorter and lack one *meso*-substituent compared to their parent porphyrins. Since the first corrole synthesis by Johnson and Kay in 1964,[1] a large variety of metal ions could be inserted into the macrocycle[2] and corrole based applications in the fields of catalysis,[3] biomedicine,[4,5] sensors,[6] and dye-sensitized solar cells[7] have been presented. While synthesis of A_3- and A_2B-corroles with small aromatic side chains at the *meso*-positions has become standard today,[8,9] the methods show only limited applicability for larger and more sophisticated *meso*-substituents, especially for side groups bearing basic subunits. Consequently, different derivatization strategies have been proposed for free-base and metallocorroles.[10] Substitution of the β-pyrrole protons has been performed via chlorination,[11] bromination,[12] nitration,[13] or chlorosulfonation,[14] while reactions performed at the *meso*-substituents among others include Suzuki,[15] Stille,[16,17] and Sonogashira couplings.[18]

The nucleophilic aromatic substitution reaction (S_NAr) of *para*-fluoro substituents was thoroughly investigated to functionalize 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin[19–21] and has been employed to modify the 5,10,15-tris(pentafluorophenyl)corrole (H_3TpFPC) to introduce several functionalities on the H_3TpFPC derivative.[22,23] Selective *para*-F substitution was initially observed during the reaction of in situ generated dimethylamine within refluxing *N*,*N*-dimethylformamide.[19] Gross et al. reported that the reaction of H_3TpFPC with 2-pyridyllithium gives, after methylation with iodomethane, the cationic trisubstituted product.[24,25] This tricationic corrole revealed to be very efficient in terms of inhibiting endothelial cell proliferation and tumor progression.[24] Recently, Osuka et al. examined the nucleophilic substitution reactions of 5,10,15-tris(pentafluorophenyl)corrole as a post-modification route to obtain new functionalized corroles.[22] This group showed that H_3TpFPC reacts with an excess of primary or secondary amines, affording the corresponding 5,10,15-tris(4-amino-2,3,5,6-tetrafluorophenyl)-substituted corroles in good yields.

However, diisopropylamine and dibenzylamine did not afford the expected tris(amino)derivative, probably due to their steric hindrance. Throughout this work it was proved that the 10- and 15-pentafluorophenyl-groups are less reactive than the one at the 5-position. This selectivity was explained by DFT calculations. Cavaleiro et al. explored the approach to introduce galactose residues in the *para*-positions of the pentafluorophenyl rings of H_3TpFPC. The synthesis strategy involved the reaction of H_3TpFPC with the commercially available 1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose in anhydrous toluene and in the presence of a base. The new corrole–galactose conjugates were isolated in moderate yields. The photodynamic potentialities of these compounds were tested in Jurkat cells, and it was found that the presence of the sugar moieties increases the uptake by the cells.[26]

Quite recently, our research group has developed a novel metalation procedure with bismuth hexamethyldisilazane (BiHMDS) to stabilize the inner core of the corrole macrocycle[27] and succeeded to functionalize these bismuth A_2B- and A_3-corroles on the *meso*-positions employing strong alkaline reaction conditions.[28,29] Compared to the rather elaborate demetalation procedures for Cu- or Ag-substituted A_2B- and A_3-corroles,[15,30] the ease of the demetalation step (with a few drops of aq 0.01 M HCl) makes this reaction strategy an interesting routine for a variety of functionalizations directly on the tetrapyrrolic macrocycle and at the *meso*-positions of the molecule.

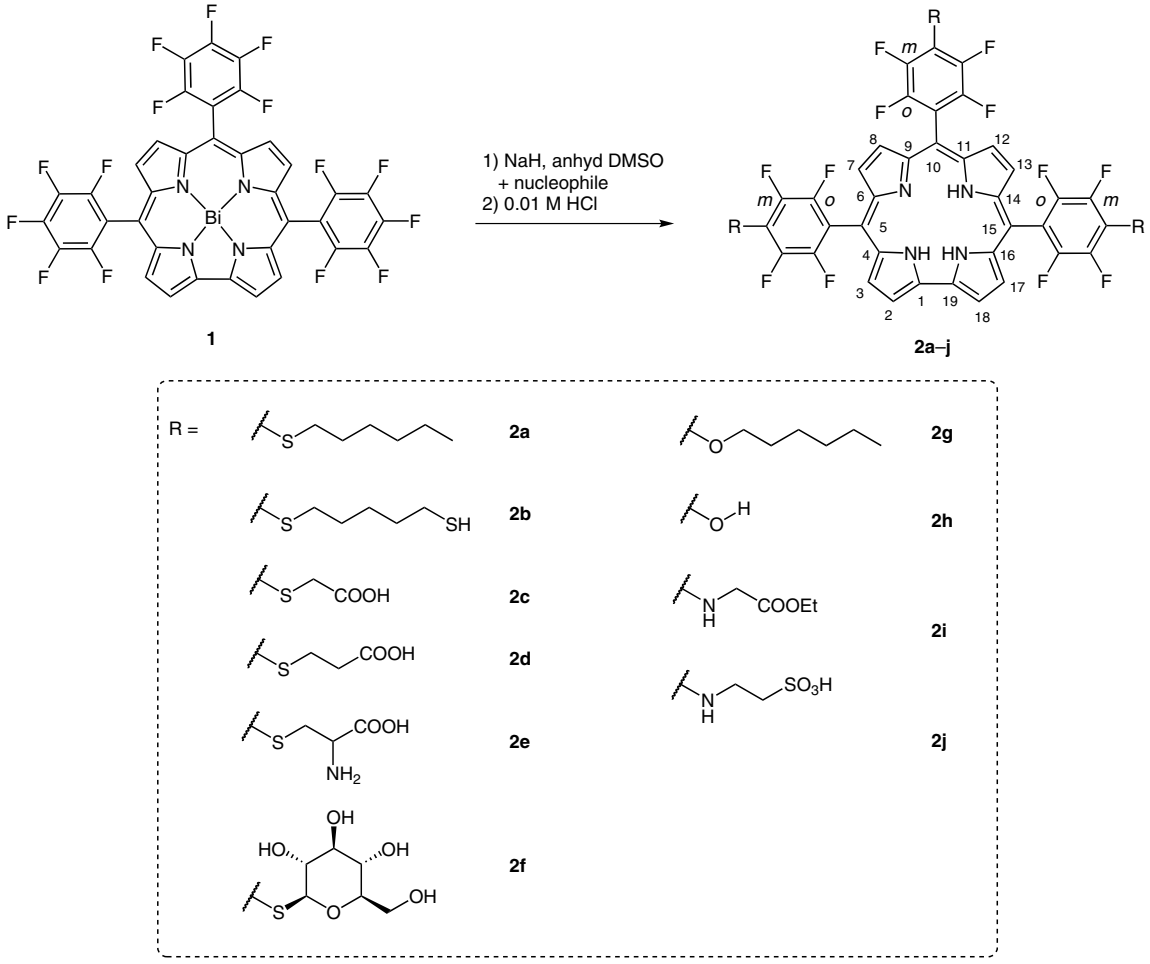
SYNTHESIS 2014, 46, 3085–3096
Advanced online publication: 28.08.2014
DOI: 10.1055/s-0034-1379012; Art ID: ss-2014-t0410-op

In our present study, the two reaction strategies were combined by inserting the bismuth ion into the H_3TpFPC in the first step and subsequently performing the regioselective aromatic substitution under strong basic conditions with nucleophiles like thiols, dithiols, alcohols, amines, and amino acids. Then, we compared the reaction conditions and illustrated a way to obtain the corresponding mono-, di-, and tri- functionalized corroles in the case of the thiol nucleophiles.

On the basis of our developed reaction method, the synthesis of a novel maleimido-functionalized corrole was illustrated with ready to use for covalent linkage to, for example, antibodies or proteins.[4,31] This strategy opens up a possible reaction pathway to study protein binding and the electronic properties of various metal corrole complexes attached to proteins in a covalent manner.

Preparation of the free-base corrole H_3TpFPC was performed as described in the literature[27] via condensation of pyrrole and pentafluorobenzaldehyde in dichloromethane under acidic catalysis employing TFA followed by subsequent oxidation with DDQ. The insertion of bismuth ions into the corrole macrocycles was achieved by treatment with 1.2 equivalents of $Bi[N(SiMe_3)_2]_3$ (BiHMDS)[32] in anhydrous THF under inert atmosphere.[28] Reliable indications for completion of the metalation reaction are both the characteristic bathochromic shifts of the Soret- and Q-bands (Figure 1) and the complete disappearance of the intense fluorescence of the nonmetalated ligand. BiTpFPC (**1**) was then treated with sodium hydride and reacted with one of the different S-, O-, N-containing nucleophiles (Scheme 1). After acidic workup, the demetalated trifunctionalized products **2a**–**j** were obtained in good to excellent yields (Table 1 and Figure 1). The ^{19}F NMR resonances of the *ortho*- and *meta*-fluorine atoms of compounds **2a**–**j** proved to be sensitive and gave four resonance signals between –134 and –157.5 ppm. An integral ratio of 2:1:1:2 of the four peaks was observed indicating the regioselective reaction at the *para*-position of the *meso*-phenyl groups (Figures S4–S11, Supporting Information).

The reactions of **1** with S-nucleophiles afforded **2a**–**f** without the use of excess of nucleophile. Full conversion was obtained at room temperature after 35 minutes. In the case of the O-nucleophiles to form corroles **2g** and **2h**, the reaction was performed at 66 °C and 80 °C, respectively, and the reaction giving the trifunctionalized product **2g** was completed during 75 minutes. The complete conversion of the reaction in aqueous DMSO solution, with OH^-



Scheme 1 Synthesis of trifunctionalized corroles. 1. S_NAr reactions of the *para*-F atoms of the BiTpFPC (**1**) with various nucleophiles; 2. Demetalation reaction in dilute HCl.

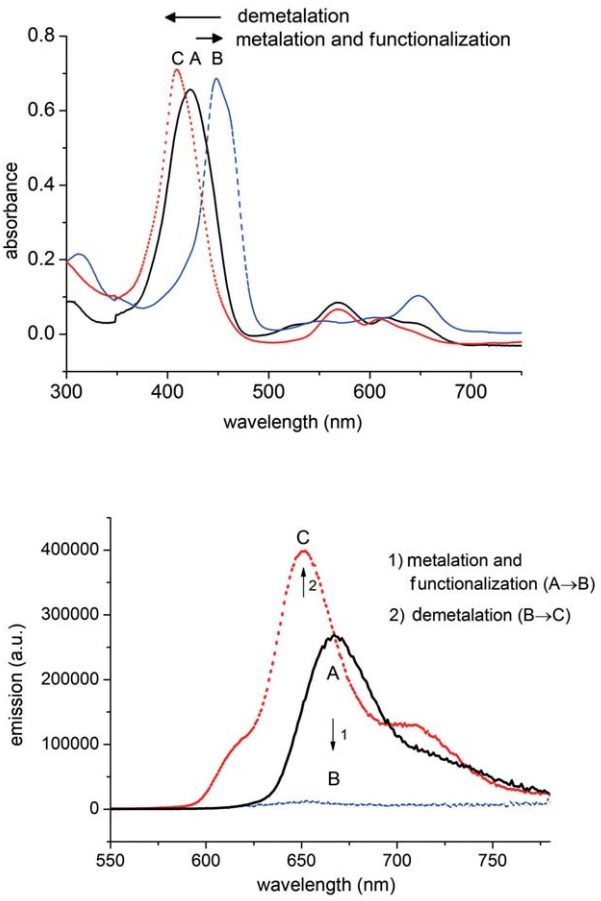


Figure 1 UV/Vis absorption spectra and emission spectra in $CHCl_3$ of A) H_3TpFPFC (black, solid line) and B) functionalized bismuth corroles (blue, dashed line). A few drops of aq 0.01 M HCl leads to the trifunctionalized free-base corroles (red, dotted line: spectrum C).

acting as nucleophile, is even faster. Hence, it is clearly a prerequisite to work in anhydrous solvents to succeed with all the other illustrated S_NAr reactions since hydroxide anions would always be competing agents.

The reactions of **1** with N-nucleophiles gave the final trisubstituted products **2i**,**j** under rather harsh conditions at 100 °C and finished after two hours. Compared to our previously reported results,[29] the reaction yields were increased from 68% to ca. 90% and reaction times were shortened by employing the BiTpFPC (**1**) precursor instead of using the free-base corrole H_3TpFPC.

The easiest way to obtain the mono- and disubstituted corroles is to charge BiTpFPC (**1**) with one or two equivalents of the S-nucleophile (e.g., 1-*S*-D-glucopyranose or mercaptopropionic acid, Scheme 2), respectively. These conversions proceed during thirty minutes at room temperature. The reaction mixtures have to be purified with column chromatography since both mono- and disubstituted corroles emerge simultaneously. Interestingly, the highest reaction yield of 93% was obtained when synthesizing monofunctionalized corrole **7** (see Scheme 3 and Table 2), where the conversion to the disubstituted corrole species is much less pronounced. The regioselective attachment of the nucleophile at the *para*-position of the *meso*-pentafluorophenyls is proved by ^{19}F NMR spectroscopy. Figure 2 (A and B) juxtaposes the ^{19}F NMR spectra of the mono- and disubstituted products **3** and **4**, respectively. Compared to the free-base corrole (H_3TpFPC), where an integral ratio of 2:1:2 is observed,[27] the NMR spectra of **3** and **4** consist of five distinct resonances with integral ratios of 1:1:2:1:2 and 4:2:4:1:2. The ^{19}F nuclei at the functionalized *meso*-tetrafluorophenyl group(s) differ in chemical shift to the ^{19}F nuclei on the nonsubstituted *meso*-pentafluorophenyl(s). The *ortho*-F (o^*) and *meta*-F (m^*) nuclei of the functionalized *meso*-tetrafluorophenyl moiety exhibit a significant downfield shift by about $\Delta\delta$ = 4.2 ppm and $\Delta\delta$ = 24.2, respectively, compared to the isochronous *ortho*- or *meta*-F nuclei (*o*, *m*) of the two remaining nonfunctionalized *meso*-pentafluorophenyl substituents.

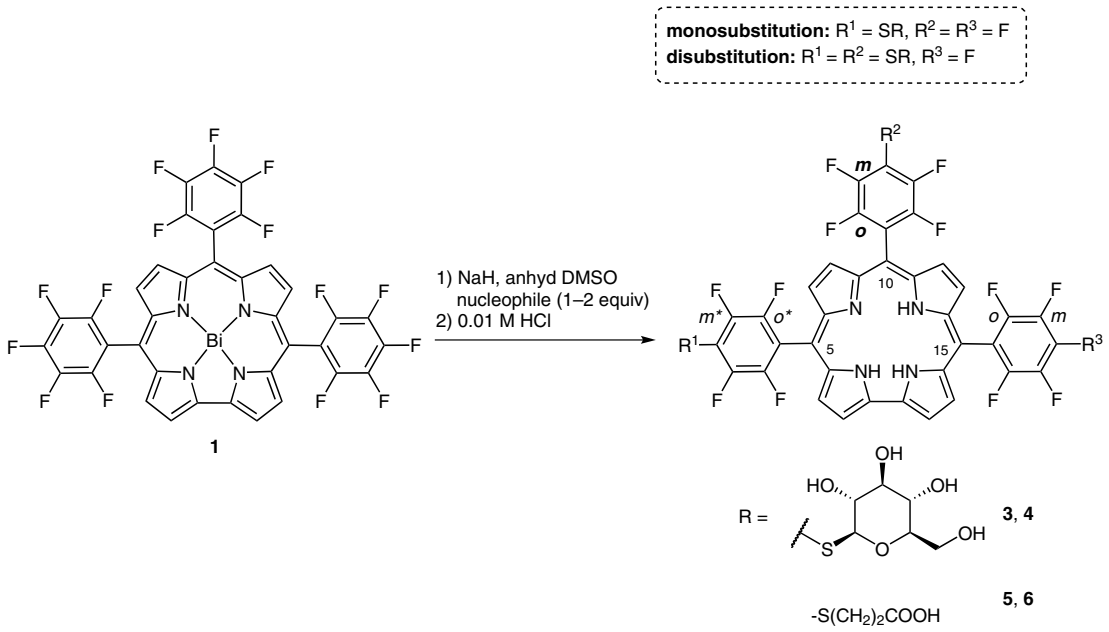
The reactivity of the *meso*-pentafluorophenyl groups towards S-nucleophiles is related to the isomeric ratio of their positions 5, 10, and 15. The procedure of determining the isomeric ratio is exemplified for the monosubstituted corrole **5** and is illustrated in Figure 3. The isomeric ratio is calculated by integrating the o^*-F resonances of the functionalized *meso*-tetrafluorenated phenyl moiety (see Scheme 2) and a value of 3.9 is deduced for **5**. The more intense o^*- resonances originate from the *meso*-phenyl groups 5 and 15 and confirm the higher reactivity of these groups (Table 2).[22]

In the case of corrole **5**, as the corresponding m^*-F signals are overlapping with the *o*-F signals of the nonsubstituted *meso*-pentafluorenated phenyls, an isomeric ratio cannot be determined accurately in the respective chemical shift region.

Table 1 General Reaction Conditions During the S_NAr Reaction with Strong Non-Nucleophilic Bases[a]

Corrole	Solvent[b]	Temp (°C)	Time (min)	No. of groups attached	Yield (%)
2a	DMSO	25	35	3	54
2b	DMSO	25	25	3	81
2c	DMSO	25	35	3	86
2d	DMSO	25	35	3	88
2e	DMSO	25	35	3	83
2f	DMSO	25	35	3	75
2g	THF	66	75	3	94
2h	DMSO	80	45	3	88
2i[c]	DMSO	100	120	3	92 (68)[c]
2j[c]	DMSO	100	120	3	89 (67)[c]

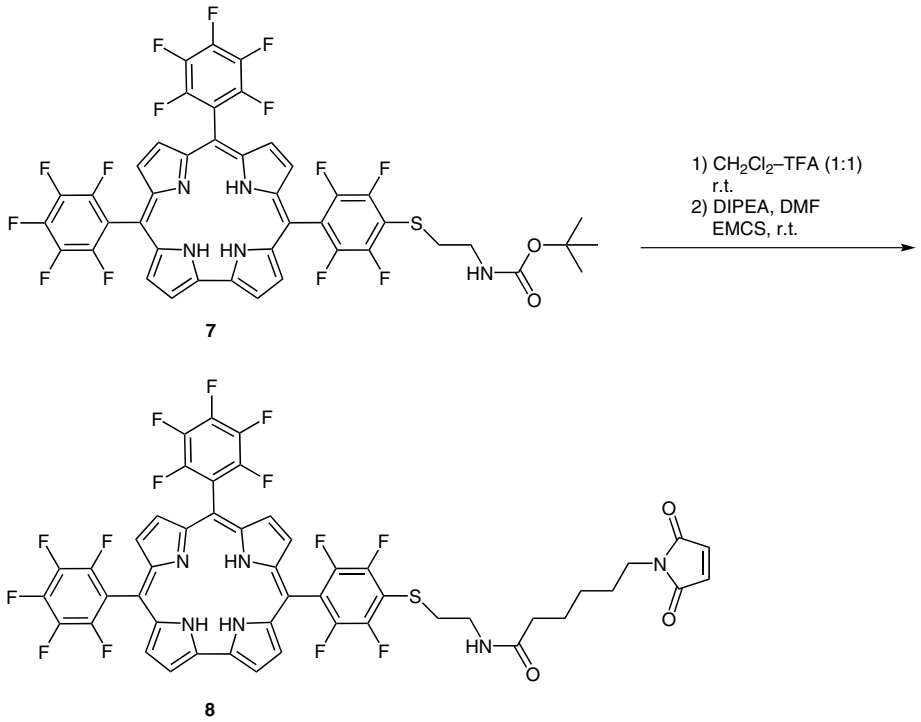
[a] NaH.
[b] Anhydrous solvents were used and all reactions were carried out under argon.
[c] Yield starting from free-base corrole H_3TpFPC. Reaction conditions: NaH, DMSO, 100 °C, 6 h.[29]



Scheme 2 Synthesis of monofunctionalized corroles **3** and **5** and difunctionalized corroles **4** and **6**. 1. S_NAr reaction of **1** with 1 or 2 equiv of S-nucleophiles; 2. Demetalation reaction in dilute HCl. The labeling scheme of the *o*- and *m*-F atoms on the *meso*-phenyl groups (with or without asterisks) is exemplified here for monofunctionalized reaction products.

The ratios of integrals of the NMR resonances for the *o*-, *m*-, and *p*-positions of the two *meso*-pentafluorophenyls do not directly reflect the isomeric ratio. To clarify this fact, if *meso*-aryls 5 and/or 15 are the functionalized moieties, three possible ^{19}F NMR resonances for positions 5, 15, and 10 should appear in the NMR spectrum. But, if the *meso*-aryl position 10 is the substituted one, only two sets of ^{19}F NMR resonances should originate from the *meso*-pentafluorophenyl moieties 5 and 15.

The inserts in Figure 3 illustrate the ^{19}F–^{19}F scalar coupling patterns of the *o*-, *m*-, *p*-F nuclei and the respective o^*-, m^*-F nuclei (see also Scheme 2). The ^{19}F NMR signals of the nonsubstituted *p*-fluorine atoms exhibit a trip-



Scheme 3 Synthesis route to obtain the monofunctionalized corrole **8**. Step 1: Deprotection of **7** in trifluoroacetic acid solution. Step 2: Reaction with *N*-(ε-maleimidocaproyloxy) succinimide ester (EMCS) with Hünig's base at r.t. (yield: 15%).

Table 2 General Reaction Conditions to Obtain Mono- and Difunctionalized Corroles[a]

Corrole	Temp (°C)	Time (min)	No. of groups attached	Isomeric ratio[b]	Yield (%)
3	25	25	1	2.6	55
4	25	25	2	4.7	22
5	25	25	1	3.9	38
6	25	25	2	n. d.	24
7	25	25	1	3.0	93

[a] NaH is used as base and DMSO as solvent.
[b] Isomeric ratio of positions 5/15 compared to position 10 of the *meso*-pentafluorophenyl-substituted corroles. The ratio was determined from integrated ^{19}F NMR spectra.

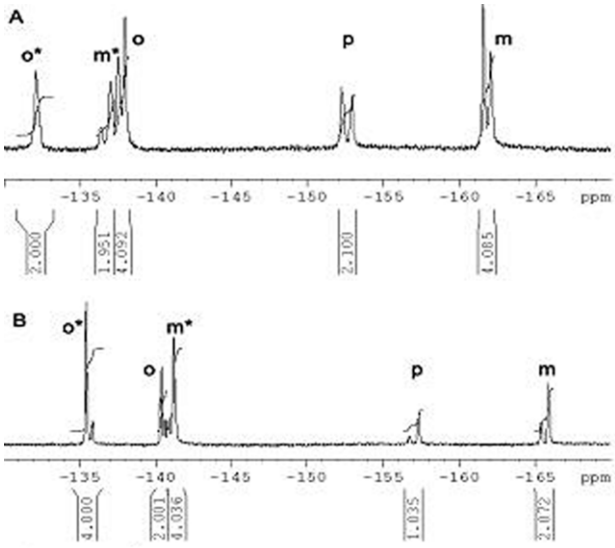


Figure 2 ^{19}F NMR spectra of A) mono- and B) difunctionalized corroles **3** and **4**

let with coupling constants with their neighboring *m*-F nuclei of typically $^3J_{F,F}$ = 20.9 Hz. The *m*-F resonances display a coupling pattern of triplets of doublets and emphasizes that the *m*-F nuclei do not only couple with their neighboring *o*- and *p*-F nuclei, but also with the second *m*-F position on the same aryl moiety via ^4J-couplings. The $^3J_{F,F}$- and $^4J_{F,F}$-scalar couplings of the *m*-F nuclei typically show values of ^3J = 22.5 Hz and ^4J = 7.5 Hz.

The *o**-F signals appear as doublet of doublets with $^3J_{F,F}$ = 25.4 Hz and $^4J_{F,F}$ = 12.2 Hz for the S-nucleophiles, compared to coupling constants of $^3J_{F,F}$ = 23.5 Hz and $^4J_{F,F}$ = 7.9 Hz for O-nucleophiles and $^3J_{F,F}$ = 21.8 Hz and $^4J_{F,F}$ = 7.1 Hz for the N-nucleophiles and $^3J_{F,F}$ = 24.8 Hz and $^4J_{F,F}$ = 8.1 Hz. Compared to the N-, O-, or F-nuclei, the lower electronegative sulfur nucleus at the *p*-position of the aromatic ring system leads to higher *J*-coupling constants.

Similar magnitudes of the $^3J_{F,F}$ and $^4J_{F,F}$ coupling constants were observed for the trifunctionalized corroles **2a**–**f**.

To illustrate the utility of the synthesis described above for a relevant application in bioconjugate chemistry, the monofunctionalized derivative **7** was synthesized and purified, and converted, after deprotection with *N*-(ε-maleimidocaproyloxy) succinimide ester (EMCS), to create the maleimido-functionalized corrole **8**.[33]

Here, EMCS serves as an amine-to-sulfhydryl crosslinker (for connection to proteins) with a medium-length spacer arm (9.4 Å) (Scheme 3). To obtain **8**, corrole **7** was deprotected in the first step using TFA in dichoromethane at room temperature and subsequently modified with the hetero-bifunctional crosslinker EMCS. In Figure S19 (Supporting Information), the ^{1}H NMR and ^{19}F NMR spectra of **8** are depicted and all necessary analytical data are presented in the experimental section.

To conclude, we have presented herein a versatile protocol for the S_NAr reaction on a Bi-corrole complex, whereby a variety of functional groups could be introduced under strong non-nucleophilic basic conditions with good yields. First examples of the syntheses of mono-, di-, and trisubstituted corrole complexes have been demonstrated employing sulfur, nitrogen, and oxygen containing nucleophiles. The reaction rate was highest for the S-nucleophiles compared to N- and O-nucleophiles, which demand higher temperatures and longer reaction times. With the aid of ^{19}F NMR spectroscopy, the level of substitution and the isomeric ratios could be determined.

As a consequence of this study, we have opened a synthetic pathway to attach bifunctional crosslinking reagents like dithiols, mercaptocarboxylic acids, amino acids, and an aminoalkanethiol to corroles. Our future work will focus to study the coupling reaction of the corroles to proteins like human serum albumin or human transferrin. Additionally, we will attach mono-, di-, trifunctionalized metal corroles obtained from derivatives on highly purified Au(111), Ag(111), ITO, or TiO_2 surfaces to study the electronic structure and charge state of the center metal ions by scanning tunneling microscopy (STM) and spectroscopy (STS). These studies should form the basis of employing metal corroles for surface-supported catalysis reactions.[34]

All chemicals were purchased from Sigma-Aldrich, Acros Chemicals, or Alfa Aesar, and used without further purification. Reagent grade solvents were purchased from Fischer chemicals and distilled prior to use. THF was distilled over Na and benzophenone under an argon atmosphere and stored over molecular sieves (4 Å) upon use. TLC was performed by using Fluka silica gel (0.2 mm) on aluminum plates. Silica gel columns for chromatography were prepared with silica gel 60 (0.060–0.20 mesh ASTM) from Acros. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 700 MHz Avance III NMR spectrometer equipped with a cryoprobe, DRX 500 MHz NMR spectrometer equipped with a cryoprobe (TXI), or on a Bruker Avance 300 MHz spectrometer. ^{19}F NMR spectra were recorded on a Bruker Avance 300 MHz at 282.4 MHz. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to the residual nondeuterated solvent for ^{1}H and TFA

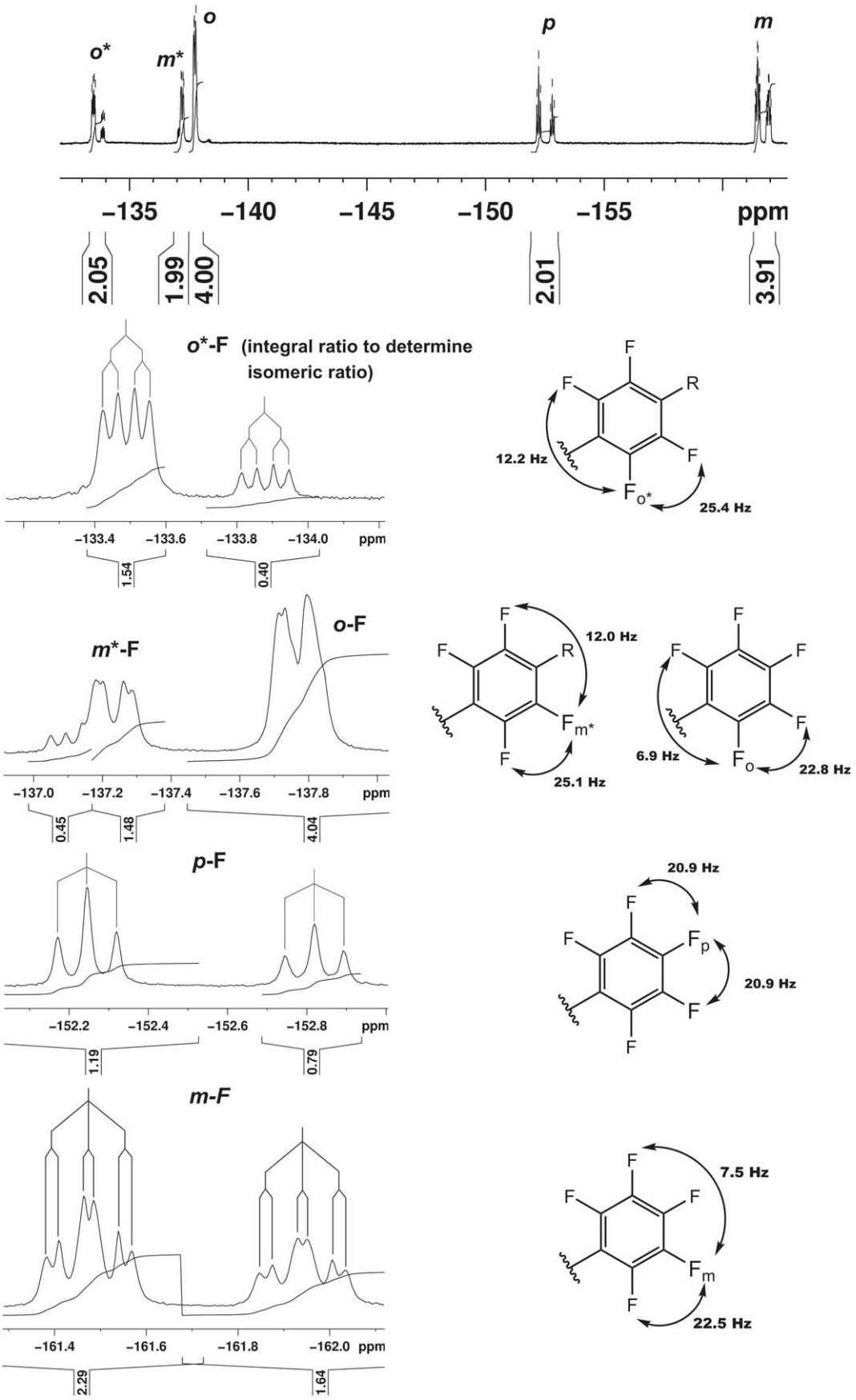


Figure 3 ^{19}F NMR spectrum of **5** and the ^{19}F-^{19}F scalar coupling patterns and the determination of the isomeric ratio illustrated for corrole **5**. The asterisks denote the positions on the functionalized moiety.

for ^{19}F. Mass spectra were collected on a Finnigan LCQ DecaXP-plus ion trap mass spectrometer with ESI ion source and MALDI-TOF measurements were collected with a Bruker Autoflex III Smartbeam spectrometer. UV/Vis absorption spectra were measured on a Varian CARY 300 Bio spectrophotometer.

Bismuth 5,10,15-tris(pentafluorophenyl)corrole (**1**)[8,27] and $Bi[N(SiMe_3)_2]_3$[32,35] were prepared according to established protocols.

S_NAr Reactions; General Procedure

Bismuth 5,10,15-tris(pentafluorophenyl)corrole (**1**; 50 μmol, 1 equiv) NaH (60% suspension in mineral oil, 30 equiv) and of the corresponding nucleophile (3 equiv) were placed in a Schlenk tube and dissolved in degassed DMSO (8 mL). The solution was purged with N_2 for further 30 min. The Schlenk tube was sealed and the reaction mixture was stirred for 24 h (unless otherwise denoted). After completion, the mixture was extracted with CH_2Cl_2 (2 × 15 mL) and the combined organic extracts were washed with H_2O (2 × 15 mL) and dried (Na_2SO_4), followed by evaporation of the solvent. The crude product was purified via column chromatography (eluents, as well as exact initial weight of the educts are listed for each product).

Demetalation Reactions; General Procedure

The functionalized Bi-metalated corrole derivatives (50 μmol), were immediately demetalated after functionalization with dropwise addition of aq 0.15 M HCl (1 mL). After 15 min, CH_2Cl_2 (20 mL) was added to the solution, which was then washed with H_2O (2 × 15 mL). The extract was dried (Na_2SO_4) and the solvent evaporated. Final purification of the product was achieved via column chromatography (eluents, as well as exact initial weight of the educts are listed for each product).

5,10,15-Tris(pentafluorophenyl)corrole

In a 100 mL flask pentafluorobenzaldehyde (295.1 mg, 1.5 mmol) was placed and a previously prepared solution containing TFA (1.5 mL, 18 μmol, 0.012 equiv) in CH_2Cl_2 (13.5 μL) (1:10) was added. Freshly distilled pyrrole (157.5 mL, 2.25 mmol, 1.5 equiv) was quickly added and the mixture was stirred for 10 min at r.t. Subsequently, CH_2Cl_2 (15 mL) and a previously prepared solution of DDQ in toluene–THF (1:1, 3 mL, 409.5 mg, 1.8 mmol, 1.2 equiv) was added to dissolve the reaction mass. After stirring for 5 min, the solvent was quickly evaporated. A first silica gel chromatography was performed (CH_2Cl_2–cyclohexane, 2:3), all fluorescent bands were collected, and evaporated to dryness. A second silica gel chromatography was performed (CH_2Cl_2–cyclohexane, 1:2) and the fluorescent bands were collected. Removal of the solvent under reduced pressure gave the product; yield: 64 mg (0.080 mmol, 16%); dark green solid; mp > 400 °C (dec.).

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.10 (d, *J* = 4.1 Hz, 2 H, H2 + H18), 8.76 (d, *J* = 4.5 Hz, 2 H, H7 + H13), 8.55–8.60 (4 H, 2 d overlapping, H8 + H12 and H3 + H17).

^{19}F NMR (564.7 MHz, $CDCl_3$, 30 °C): δ = –137.2 (2 F), –137.7 (4 F), –152.2 (2 F), –152.7 (1 F), –161.4 (4 F), –161.9 (2 F).

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{37}H_{10}F_{15}N_4$: 795.0744; found: 795.0741 .

UV/Vis (THF): λ_{max} = 408, 418 (sh), 563, 604 nm.

Bismuth Trispentafluorophenylcorrole [Bi(TpFPC), 1]

Under N_2 atmosphere, H_3(TpFPC) (50 mg, 0.063 mmol) was dissolved in anhydrous THF (15 mL) and a solution of $Bi[N(SiMe_3)_2]_3$ (55 mg, 0.078 mmol) dissolved in anhydrous THF (2 mL) was added dropwise under permanent stirring. After 12 h at r.t., during which the color of the reaction mixture changed from dark violet to dark green and the intense red fluorescence of the free-base corrole completely vanished (the reaction progress was followed by UV/Vis spectroscopy), the solvent was evaporated and the crude product was purified with column chromatography (silica gel, hexane–CH_2Cl_2, 2:1) to afford **1**; yield: 45 mg (0.045 mmol, 71%); dark green solid; mp > 400 °C (dec.).

^1H NMR (500 MHz, THF-d_8, 25 °C): δ = 9.12 (d, *J* = 4.1 Hz, 2 H), 8.91 (d, *J* = 4.0 Hz, 2 H), 8.63 (d, *J* = 4.1 Hz, 2 H), 8.49 (d, *J* = 4.0 Hz, 2 H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ = 116.8 (CH, 2 C, C2 + C18), 126.3 (CH, 2 C, C7 + C13), 122.5 (CH, 2 C, C8 + C12), 121.5 (CH, 2 C, C3 + C17).

^{19}F NMR (282.4 MHz, THF-d_8, 30 °C): δ = –138.9 (dd, ^3J = 24.3 Hz, ^4J = 8 Hz, 1 F, F_o), –139.3 (dd, ^3J = 24.4 Hz, ^4J = 8.2 Hz, 2 F, F_o), –139.6 (dd, ^3J = 24.9 Hz, ^4J = 8.2 Hz, 2 F, F_o), –140.0 (dd, ^3J = 24.9 Hz, ^4J = 8 Hz, 1 F, F_o), –157.3 (t, ^3J = 20.6 Hz, 2 F, F_p), –157.6 (t, ^3J = 20.8 Hz, 1 F, F_p), –164.9 (dd, ^3J = 21.0 Hz, ^4J = 7.9 Hz, 2 F, F_m), –165.2 (dd, ^3J = 21.0 Hz, ^4J = 8.1 Hz, 1 F, F_m), –165.6 (m, 3 F, F_m).

HRMS (MALDI): *m*/*z* [M$^+$] calcd for $C_{37}H_8BiF_{15}N_4$: 1002.031; found: 1002.198.

UV/Vis (THF): λ_{max} (ε) = 322 (21300), 446 (112300), 552 (5100), 591 (9200), 631 nm (14200).

Three-Fold-Substituted Corroles from the Reaction of 1 with S-Nucleophiles; General Procedure

Bismuth corrole **1** (40 mg, 40 μmol) and NaH (60% suspension in mineral oil, 30 equiv) were placed in a 50 mL 3-necked round-bottomed flask under argon. DMSO (30 mL) and S-nucleophile (3 equiv) were added and the reaction mixture was stirred for 25–35 min at r.t. The progress of the reaction was monitored by TLC (eluent: as denoted for column chromatography of each compound) and after complete conversion H_2O (8 mL) was added to the mixture. To the H_2O–DMSO phase was added sat. aq NH_4Cl (15 mL) and the solution was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic phases were washed with H_2O (3 × 15 mL) and the solvent was evaporated under reduced pressure.

5,10,15-Tris[2,3,5,6-tetrafluoro-4-(hexylthio)phenyl]corrole (2a)

Purification by silica gel chromatography was performed (CH_2Cl_2–cyclohexane, 1:3) and the first fluorescent band was collected. Removal of the solvent under reduced pressure gave product **2a**; yield: 8.0 mg (6.7 μmol, 54%); dark green solid; mp > 400 °C (dec.).

^1H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.09 (d, *J* = 3.84 Hz, 2 H, H_β), 8.79 (d, *J* = 3.72 Hz, 2 H, H_β), 8.60 (br s, 4 H, H_β), 3.24 (t, *J* = 7.23 Hz, 6 H), 1.84 (quint, *J* = 7.23 Hz, 6 H), 1.59 (quint, *J* = 6.12 Hz, 6 H), 1.45–1.38 (m, 12 H), 1.00–0.95 (m, 9 H).

^{13}C NMR (176.1 MHz, $CDCl_3$, 30 °C): δ = 148.0, 147.7, 147.1, 146.5, 146.3, 145.7, 145.1, 142.1, 140.8, 134.6, 130.6, 127.6, 126.3, 121.6, 120.5, 118.1, 117.1, 116.2, 101.2, 99.4, 95.4, 35.0, 31.5, 30.2, 28.4, 21.2, 14.3.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –134.25 (dd, ^3J = 24.8 Hz, ^4J = 11.4 Hz, 4 F, F_o), –134.66 (dd, ^3J = 25.0 Hz, ^4J = 11.3 Hz, 2 F, F_o), –137.76 (dd, ^3J = 24.5 Hz, ^4J = 10.7 Hz, 2 F, F_m), –138.38 (dd, ^3J = 23.9 Hz, ^4J = 10.6 Hz, 4 F, F_m).

HRMS (ESI+): *m*/*z* calcd for $C_{55}H_{50}F_{12}N_4S_3$: 1091.3079 [M + H]$^+$, 1113.2898 [M + Na]$^+$; found: 1089.2967 [M – H]$^-$, 1091.3056 [M + H]$^+$, 1113.2892 [M + Na]$^+$.

5,10,15-Tris{2,3,5,6-tetrafluoro-4-[(5-mercaptopentyl)thio]phenyl}corrole (2b)

Purification by silica gel chromatography was performed (CH_2Cl_2–MeOH, 1:1) and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **2b**; yield: 234.2 mg (204.5 μmol, 81%); dark green solid; mp > 400 °C (dec.).

^1H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.00–8.90 (m, 2 H, H_β), 8.76 (br s, 2 H, H_β), 8.57–8.53 (m, 4 H, H_β), 3.41–2.84 (m, 10 H), 2.66–2.48 (m, 2 H), 2.34–2.21 (m, 8 H), 2.08–1.76 (m, 10 H).

^{13}C NMR (176.1 MHz, $CDCl_3$, 30 °C): δ = 158.6 (C), 157.2 (C), 147.7 (C), 147.1 (C), 146.5 (C), 145.7 (C), 134.5 (C), 130.4 (C), 127.7 (CH), 126.3 (CH), 121.4 (C), 120.8 (C), 119.1 (C), 118.4 (C),

116.8 (CH), 115.6 (C), 96.4 (C), 95.2 (C), 34.8 (CH_2), 33.5 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 24.5 (CH_2).

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –134.04 (dd, ^3J = 25.1 Hz, ^4J = 11.1 Hz, 4 F, F_o), –134.44 (dd, ^3J = 25.4 Hz, ^4J = 12.1 Hz, 2 F, F_o), –137.52 (dd, ^3J = 25.2 Hz, ^4J = 11.8 Hz, 2 F, F_m), –138.17 (dd, ^3J = 24.8 Hz, ^4J = 11.8 Hz, 4 F, F_m).

HRMS (MALDI+): *m*/*z* [M – H]$^-$ calcd for $C_{52}H_{44}F_{12}N_4S_6$: 1143.1626; found: 1143.1606.

5,10,15-Tris{2,3,5,6-tetrafluoro-4-[(carboxymethyl)thio]phenyl}corrole (2c)

Purification by silica gel chromatography was performed [gradient solvent, starting from a mixture ratio of CH_2Cl_2–MeOH (4:1) to a final ratio of CH_2Cl_2–MeOH (1:4)] and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **2c**; yield: 10.9 mg (10.8 μmol, 86%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.09–9.07 (m, 2 H, H_β), 8.80–8.79 (m, 2 H, H_β), 8.60 (br s, 4 H, H_β), 3.94 (s, 6 H, CH_2).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –137.02 to –137.08 (m, 4 F, F_o), –137.49 (br s, 2 F, F_o), –140.69 (dd, ^3J = 23.5 Hz, ^4J = 10.1 Hz, 2 F, F_m), –141.23 (br s, 4 F, F_m).

5,10,15-Tris{2,3,5,6-tetrafluoro-4-[(carboxyethyl)thio]phenyl}corrole (2d)

Bismuth corrole **1** (40 mg, 40 μmol) and NaH (60% suspension in mineral oil, 30 equiv) were placed in a 50 mL 3-necked round-bottomed flask under argon. DMSO (3 mL) and mercaptopropionic acid (3 equiv) were added and the reaction mixture was stirred for 25–35 min at r.t. The progress of the reaction was monitored by TLC (eluent: MeOH–CH_2Cl_2, 3:1) and after complete conversion, H_2O (8 mL) was added to the mixture. To the H_2O–DMSO mixture was added sat. aq NH_4Cl (15 mL) and the solution was extracted with EtOAc (2 × 15 mL). The combined organic phases were extracted with H_2O (3 × 15 mL) and the solvent was evaporated under reduced pressure. Purification by silica gel chromatography was performed [first solvent: cyclohexane–CH_2Cl_2 (1:1); second solvent: MeOH–CH_2Cl_2 (3:1)] and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **2d**; yield: 111.0 mg (105 μmol, 88%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.16–9.10 (m, 2 H, H_β), 8.98–8.94 (m, 2 H, H_β), 8.77–8.70 (m, 4 H, H_β), 3.46 (t, *J* = 5.7 Hz, 6 H, CH_2), 2.89 (t, *J* = 6.4 Hz, 6 H, CH_2).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ = 175.0 (C), 149.6 (C), 148.2 (C), 148.0 (C), 147.0 (C), 146.5 (C), 135.3 (C), 129.8 (CH), 127.0 (CH), 95.9 (C), 36.2 (CH_2), 31.0 (CH_2), 30.8 (CH_2).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –135.62 (s, 4 F, F_o), –135.95 (s, 2 F, F_o), –140.48 (s, 2 F, F_m), –140.96 (s, 4 F, F_m).

HRMS (MALDI+): *m*/*z* calcd for $C_{46}H_{26}F_{12}N_4O_6S_3$: 1054.0823 [M]$^+$, 1055.0901 [M + H]$^+$; found: 1053.0759 [M – H]$^-$, 1054.0820 [M]$^+$, 1055.0803 [M + H]$^+$.

5,10,15-Tris{2,3,5,6-tetrafluoro-4-[(2-amino-2-carboxyethyl)thio]phenyl}corrole (2e)

Purification was performed by flash silica gel chromatography. With a solvent mixture of CH_2Cl_2–MeOH (10:1), the starting material and some by-products eluted first and the product eluted later with MeOH. Removal of the solvent under reduced pressure afforded as **2e**; yield: 57.0 mg (51.8 μmol, 83%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.14 (s, 2 H, H_β), 8.93 (s, 2 H, H_β), 8.74–8.67 (m, 4 H, H_β), 3.94–3.80 (m, 5 H), 3.64–3.55 (m, 4 H).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ = 171.61 (C), 149.7 (C), 148.3 (C), 148.0 (C), 146.6 (C), 135.9 (C), 132.1 (C), 129.1 (C), 121.3 (CH), 117.4 (CH), 114.7 (CH), 95.8 (C), 55.8 (CH), 55.7 (CH), 30.7 (CH_2).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –135.42 (dd, ^3J = 22.9 Hz, ^4J = 10.1 Hz, 4 F, F_o), –135.83 (dd, ^3J = 24.5 Hz, ^4J = 11.0 Hz, 2 F, F_o), –139.72 (dd, ^3J = 24.9 Hz, ^4J = 10.8 Hz, 2 F, F_m), –140.26 to –140.48 (m, 4 F, F_m).

HRMS (MALDI+): *m*/*z* calcd for $C_{46}H_{30}F_{12}N_7O_6S_3$: 1100.1223 [M + H]$^+$; found: 1100.1221.

Anal. Calcd for $C_{46}H_{29}F_{12}N_7O_6S_3$: C, 50.23; H, 2.66; N, 8.91; O, 8.73; S, 8.75; F, 20.73. Found: C, 50.09; H, 2.81; N, 8.84; S, 8.68.

5,10,15-Tris[2,3,5,6-tetrafluoro-4-(2,3,4,6-tetra-*O*-acetyl-1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole

Purification was performed by silica gel chromatography with a solvent mixture of CH_2Cl_2–MeOH (10:1). Removal of the solvent under reduced pressure afforded the intermediate tetraacetylcorrole; yield: 17.1 mg (9.3 μmol, 75%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.14 (d, *J* = 4.35 Hz, 2 H, H_β), 8.86 (d, *J* = 4.80 Hz, 2 H, H_β), 8.68–8.66 (m, 3 H, H_β), 8.59 (d, *J* = 4.47 Hz, 1 H, H_β), 5.39–5.30 (m, 4 H), 5.35–5.18 (m, 7 H), 5.14–5.09 (m, 4 H), 4.31–4.29 (m, 6 H), 2.08–2.06 (m, 24 H, CH_3), 2.04–2.00 (m, 12 H, CH_3).

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –131.61 (dd, ^3J = 22.2 Hz, ^4J = 10.9 Hz, 4 F, F_o), –132.13 (dd, ^3J = 24.8 Hz, ^4J = 11.4 Hz, 2 F, F_o), –136.53 (dd, ^3J = 24.9 Hz, ^4J = 11.4 Hz, 2 F, F_m), –140.96 (dd, ^3J = 23.2 Hz, ^4J = 9.2 Hz, 4 F, F_m).

5,10,15-Tris[2,3,5,6-tetrafluoro-4-(1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole (2f)

Deacylation was achieved by dissolving the above crude solid (21.5 mg, 11.7 μmol) in MeOH (1.5 mL), adding aq 1.0 M NaOH (0.3 mL, 24 equiv based on the corrole), and stirring for 1 h at 40 °C. After neutralization with sat. aq NH_4Cl (0.5 mL) and extraction with EtOAc (2 × 10 mL), the organic solvent from the combined extracts was removed under reduced pressure. Purification by flash chromatography with silica gel was performed (CH_2Cl_2–MeOH, 1:2) and the fluorescent band was collected. Removal of the solvent under reduced pressure and recrystallization from CH_2Cl_2 and MeOH afforded **2f**; yield: 11.4 mg (8.7 μmol, 93%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.16 (s, 2 H, H_β), 8.85 (s, 2 H, H_β), 8.65 (s, 2 H, H_β), 8.61 (s, 2 H, H_β), 7.40 (v br s, OH), 5.14 (d, *J* = 8.9 Hz, 4 H), 4.45 (d, *J* = 9.1 Hz, 2 H), 3.99–3.87 (m, 4 H), 3.79–3.66 (m, 6 H), 3.57–3.51 (m, 5 H).

^{13}C NMR (125.8 MHz, CD_3OD, 30 °C): δ = 149.85, 148.05, 147.90, 146.65, 146.21, 135.92, 132.06, 128.83, 127.29, 120.57, 117.45, 113.96, 91.35, 87.14, 82.51, 82.31, 79.58, 79.37, 77.91, 75.78, 73.11, 71.55, 71.12, 62.85, 62.75.

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –135.14 (dd, ^3J = 24.4 Hz, ^4J = 11.5 Hz, 4 F, F_o), –135.55 (dd, ^3J = 24.9 Hz, ^4J = 11.7 Hz, 2 F, F_o), –140.46 (dd, ^3J = 25.7 Hz, ^4J = 12.0 Hz, 2 F, F_m), –141.03 to –141.09 (m, 4 F, F_m).

MS (ESI–): *m*/*z* calcd for $C_{55}H_{44}F_{12}N_4O_{15}S_3$: 1323.1701 [M – H]$^-$, 1359.1468 [M + Cl]$^-$; found: 1323.1736 [M – H]$^-$, 1359.1508 [M + Cl]$^-$.

Three-Fold-Substituted Corroles from the Reaction of 1 with O-Nucleophiles; General Procedure

Bismuth corrole **1** (20 mg, 20 μmol) and NaH (60% suspension in mineral oil, 30 equiv) were placed in a 50 mL 3-necked round-bottomed flask under argon. THF (1 mL) and the requisite hydroxy-nucleophile (4 equiv) were added and the reaction mixture was refluxed and stirred for 75 min. The progress of the reaction was monitored by TLC (eluent: as denoted for column chromatography of each compound) and after complete conversion H_2O (8 mL) was added to the mixture. The organic solvent was evaporated under re-

duced pressure. Sat. aq NH_4Cl (10 mL) was added to the aqueous phase and the solution was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were washed with H_2O (3 × 10 mL) and the solvent was evaporated under reduced pressure.

5,10,15-Tris[2,3,5,6-tetrafluoro-4-(hexyloxy)phenyl]corrole (2g)

Purification was performed by silica gel chromatography with a solvent mixture of CH_2Cl_2–heptane (2:3). Removal of the solvent under reduced pressure afforded **2g**; yield: 12.3 mg (11.8 μmol, 94%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.06 (d, *J* = 4.26 Hz, 2 H, H_β), 8.79 (d, *J* = 4.71 Hz, 2 H, H_β), 8.60 (d, *J* = 4.77 Hz, 2 H, H_β), 8.58 (d, *J* = 4.23 Hz, 2 H, H_β), 4.55 (t, *J* = 6.50 Hz, 6 H), 2.00 (quint, *J* = 7.04 Hz, 6 H), 1.65 (quint, J = 7.24 Hz, 9 H), 1.47 (m, 18 H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 30 °C): δ = 147.87, 147.35, 145.93, 145.39, 142.39, 141.06, 140.48, 138.75, 134.98, 130.43, 127.65, 126.29, 121.59, 116.89, 114.05, 111.88, 99.42, 95.20, 75.84, 31.71, 30.27, 25.54, 22.82, 19.89, 14.24.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –139.46 (dd, ^3J = 22.9 Hz, ^4J = 7.9 Hz, 2 F, F_o), –140.00 (dd, ^3J = 22.0 Hz, ^4J = 7.3 Hz, 4 F, F_o), –157.11 (dd, ^3J = 22.2 Hz, ^4J = 7.4 Hz, 4 F, F_m), –157.54 (dd, ^3J = 23.1 Hz, ^4J = 8.0 Hz, 2 F, F_m).

MS (ESI+): *m*/*z* calcd for $C_{55}H_{50}F_{12}N_4O_3$: 1043.3764 $[M + H]^+$, 1065.3584 $[M + Na]^+$; found: 1043.3763 $[M + H]^+$, 1065.3577 $[M + Na]^+$.

5,10,15-Tris[2,3,5,6-tetrafluoro-4-(hydroxy)phenyl]corrole (2h)

Bismuth corrole **1** (10 mg, 13 μmol) and NaH (60% suspension in mineral oil, 15 mg, 377 μmol, 30 equiv) were placed in a 25 mL 3-necked round-bottomed flask under argon. DMSO (1.5 mL) and H_2O (1 μL, 50 μmol, 4 equiv) were added and the reaction mixture was refluxed and stirred for 75 min. The progress of the reaction was monitored by TLC (eluent: MeOH–CH_2Cl_2, 1:1) and after complete conversion, H_2O (5 mL) was added to the mixture. To the H_2O–DMSO phase was added sat. aq NH_4Cl (10 mL) and the mixture was extracted with EtOAc (2 × 10 mL). The combined organic phases were washed with distilled H_2O (3 × 10 mL) and the solvent was evaporated under reduced pressure. Purification was performed by silica gel chromatography with a solvent mixture of CH_2Cl_2–heptane (1:3) followed by a mixture of CH_2Cl_2–MeOH (1:1). Removal of the solvent under reduced pressure afforded **2h**; yield: 10.5 mg (11.1 μmol, 88%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.03 (s, 2 H, H_β), 8.77 (s, 2 H, H_β), 8.57 (s, 2 H, H_β), 8.50 (s, 2 H, H_β).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ = 148.9 (C), 148.4 (C), 147.5 (C), 147.1 (C), 145.7 (C), 140.7 (C), 140.5 (C), 139.8 (C), 139.5 (C), 139.1 (C), 136.8 (C), 131.7 (C), 128.8 (CH), 127.1 (CH), 121.4 (CH), 116.9 (CH), 111.1 (C), 108.7 (C), 101.0 (C), 95.7 (C).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –143.76 (d, *J* = 16.2 Hz, 2 F, F_o), –144.32 (d, *J* = 16.2 Hz, 4 F, F_o), –165.42 (d, *J* = 15.6 Hz, 4 F, F_m), –165.81 (d, *J* = 15.7 Hz, 2 F, F_m).

MS (MALDI+): *m*/*z* calcd for $C_{37}H_{14}F_{12}N_4O_3$: 790.0874 $[M]^+$, 791.0953 $[M + H]^+$; found: 790.0960 $[M]^+$, 791.0974 $[M + H]^+$.

Three-Fold-Substituted Corroles from the Reaction of 1 with N-Nucleophiles

5,10,15-Tris-{4-[(*N*-ethoxycarbonylmethyl)amino]2,3,5,6-tetrafluorophenyl}corrole (2i)

Bismuth corrole **1** (0.035 g, 43.9 μmol), glycine ethyl ester hydrochloride (0.116 g, 0.83 mmol), and NaH (60% suspension in mineral oil, 0.071 g, 1.7 mmol) were dissolved in DMSO (1.5 mL) and stirred for 2 h at 100 °C. The mixture was extracted with $CHCl_3$ (25 mL) and H_2O (25 mL) and the organic phase was collected and evaporated to dryness. Purification by silica gel chromatography (MeOH–$CHCl_3$, 1:3) afforded **2i**; yield: 0.029 g (30 μmol, 92%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (500 MHz, CD_3OD, 30 °C): δ = 9.29 (d, *J* = 4 Hz, 2 H, H_β), 8.99 (d, *J* = 4 Hz, 2 H, H_β), 8.73 (m, 4 H, H_β), 4.44 (br s, 4 H, CH_2) 4.40 (br s, 2 H, CH_2).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ = 129.00 (CH), 125.91 (CH), 122.29 (CH), 119.20 (CH), 46.81 (CH).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –145.06 (d, *J* = 15 Hz, 2 F, F_o), –145.29 (d, *J* = 15 Hz, 4 F, F_o), –163.14 (d, *J* = 15 Hz, 4 F, F_m), –163.43 (d, *J* = 15 Hz, 2 F, F_m).

MS (ESI): *m*/*z* calcd for $C_{43}H_{23}F_{12}N_7O_6$: 962.16 $[M + H]^+$, 960.14 $[M]^-$; found: 962.47 $[M + H]^+$, 960.53 $[M]^-$.

UV/Vis (MeOH): λ_{max} = 412, 569, 605 nm.

5,10,15-Tris-{4-[(2-sulfoethyl)amino]-2,3,5,6-tetrafluorophenyl}corrole (2j)

Bismuth corrole **1** (0.035 g, 43.9 μmol) was dissolved in DMSO (1.5 mL), taurine (0.087 g, 690 μmol), and NaH (60% suspension in mineral oil, 0.035 g, 0.86 mmol) were added and the mixture was stirred for 2 h at 100 °C. After addition and removal of H_2O (2 mL), silica gel chromatography was performed (MeOH–$CHCl_3$, 2:3). The fluorescent bands were collected, evaporated to dryness, dispersed in H_2O (20 mL) and extracted with $CHCl_3$ (2 × 20 mL). Removal of the solvent under reduced pressure afforded **2j**; yield: 0.017 g (15.3 μmol, 89%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (500 MHz, CD_3OD, 30 °C): δ = 9.06–9.05 (m, 2 H, H_β), 8.83–8.80 (m, 2 H, H_β), 8.63–8.58 (m, 2 H, H_β), 8.54–8.51 (m, 2 H, H_β), 4.13–4.11 (m, 6 H, CH_2), 3.34–3.31 (m, 6 H, CH_2).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ =125.4 (CH), 123.6 (CH), 117.9 (CH), 113.3 (CH), 39.5 (CH), 46.7 (CH), 46.0 (CH).

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –143.78 (m, 2 F, F_o), –144.39 (m, 4 F, F_o) -162.41 (m, 2 F, F_m), –162.69 (m, 1 F, F_m), –165.62 (m, 2 F, F_m), –165.95 (m, 1 F, F_m).

MS (ESI+): *m*/*z* calcd for $C_{43}H_{29}F_{12}N_7O_9S_3$: 554.54 $[M - 2 H]^{2-}$, 369.36 $[M - 3 H]^{3-}$; found: 554.76 $[M - 2 H]^{2-}$, 369.67 $[M - 3 H]^{3-}$.

UV/Vis (buffer solution pH 7): λ_{max} = 415, 586, 614 nm.

Mono- and Disubstituted Corroles from the Reaction of 1 with S-Nucleophiles; General Procedure

Bismuth corrole **1** (20 mg, 20 μmol) and NaH (60% suspension in mineral oil, 30 equiv) were placed in a 3-necked round-bottomed flask under argon. DMSO (1.5 mL) and the requisite S-nucleophile (1 or 2 equiv, respectively) were added and the reaction mixture was stirred for 25 min at r.t. The progress of the reaction was monitored by TLC (eluent: as denoted for column chromatography of each compound) and after complete conversion, H_2O (10 mL) was added to the mixture. To the H_2O–DMSO phase was added sat. aq NH_4Cl (10 mL) and the mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were washed with H_2O (3 × 10 mL). The solvent was evaporated under reduced pressure.

5,10-Bis(pentafluorophenyl)-15-[2,3,5,6-tetrafluoro-4-(1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole and 5,15-Bis(pentafluorophenyl)-10-[2,3,5,6-tetrafluoro-4-(1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole (3)

Deacylation was achieved by dissolving the crude solid (20 mg, 17.5 μmol) in MeOH (1.5 mL), adding aq 1.0 M NaOH (0.1 mL, 8 equiv based on the corrole), and stirring for 1 h at 40 °C. After neutralization with sat. aq NH_4Cl (0.5 mL) and extraction with EtOAc (2 × 10 mL), the organic solvent was removed under reduced pressure. Purification by silica gel chromatography was performed [first solvent: CH_2Cl_2–MeOH (10:1); second solvent: CH_2Cl_2–MeOH (5:1)] and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **3**; yield: 6.6 mg (6.9 μmol, 55%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 8.74–8.58 (4 H, H_β), 8.47–8.32 (4 H, H_β), 5.19 (1 H), 4.14–3.95 (5 H), 3.77 (1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 30 °C): δ = 148.9, 147.4, 146.9, 145.5, 144.9, 142.8, 140.8, 138.9, 136.9, 136.5, 134.3, 129.9, 127.4, 126.0, 121.2, 116.9, 116.6, 94.3, 87.5, 80.2, 78.1, 73.9, 69.9, 62.2.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –132.11 (br s, 2 F, F_o*), –136.37 to –137.02 (m, 2 F, F_m*), –137.53 (s, 1.8 F, F_o), –137.95 (s, 2.2 F, F_o), –152.25 (s, 1.1 F, F_p), –152.90 (s, 0.9 F, F_p), –161.59 (s, 2.2 F, F_m), –162.08 (s, 1.8 F, F_m).

MS (ESI–): *m*/*z* calcd for $C_{43}H_{22}F_{14}N_4O_5S$: 971.1015 $[M - H]^-$; found: 971.1019.

5-(Pentafluorophenyl)-10,15-bis[2,3,5,6-tetrafluoro-4-(1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole and 10-(Pentafluorophenyl)-5,15-bis[2,3,5,6-tetrafluoro-4-(1-*S*-D-glucopyranos-1-*S*-yl)phenyl]corrole (4)

Deacylation was achieved by dissolving the crude solid (19 mg, 12.8 μmol) in MeOH (1.5 mL), adding aq 1.0 M NaOH (0.1 mL, 8 equiv based on the corrole) and stirring for 1 h at 40 °C. After neutralization with sat. aq NH_4Cl (0.5 mL) and extraction with EtOAc (2 × 10 mL), the organic solvent was removed under reduced pressure. Purification by silica gel chromatography was performed [first solvent: CH_2Cl_2–MeOH (5:1); second solvent: CH_2Cl_2–MeOH (3:1)] and the third fluorescent band was collected. Removal of the solvent under reduced pressure afforded **4**; yield: 3.1 mg (2.7 μmol, 22%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.12 (s, 2 H, H_β), 8.85 (s, 2 H, H_β), 8.64–8.61 (m, 4 H, H_β), 5.13 (d, *J* = 8.1 Hz, 2 H), 4.60 (s, 1 H), 3.97 (d, *J* = 11.9 Hz, 2 H), 3.76 (d, *J* = 10.0 Hz, 2 H), 3.51–3.48 (m, 4 H), 3.46 (br s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 30 °C): δ = 149.9, 149.0, 148.2, 147.9, 146.3, 144.3, 136.0, 132.1, 128.7, 127.0, 125.8, 117.4, 94.7, 87.1, 82.6, 79.7, 75.8, 71.6, 63.0.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –135.39 (dd, ^3J = 22.9 Hz, ^4J = 10.0 Hz, 3.3 F, F_o*), –135.80 (dd, ^3J = 23.4 Hz, ^4J = 9.1 Hz, 0.7 F, F_o*), –140.35 (d, *J* = 24.6 Hz, 1.4 F, F_o), –140.58 (dd, ^3J = 24.6 Hz, ^4J = 11.5 Hz, 0.6 F, F_o), –140.84 (d, *J* = 20.5 Hz, 0.7 F, F_m*), –141.15 to –141.20 (m, 3.3 F, F_m*), –156.67 (br s, 0.3 F, F_p) –157.25 to –157.37 (m, 0.7 F, F_p), –165.32 to –165.47 (m, 0.6 F, F_m), –165.81 to –165.94 (m, 1.4 F, F_m).

MS (ESI–): *m*/*z* calcd for $C_{49}H_{33}F_{13}N_4O_{10}S_2$: 1147.1358 $[M - H]^-$; found: 1147.1372.

5,10-Bis(pentafluorophenyl)-15-{2,3,5,6-tetrafluoro-4-[(carboxyethyl)thio]phenyl}corrole and 5,15-Bis(pentafluorophenyl)-10-{2,3,5,6-tetrafluoro-4-[(carboxyethyl)thio]phenyl}corrole (5)

Purification by silica gel chromatography was performed (CH_2Cl_2–MeOH, 10:1) and the first fluorescent band was collected. Removal of the solvent under reduced pressure afforded **5**; yield: 4.3 mg (4.9 μmol, 38%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.03 (s, 0.4 H, H_β), 8.91 (s, 1.6 H, H_β), 8.79 (d, *J* = 4.5 Hz, 1 H, H_β), 8.73 (d, *J* = 4.2 Hz, 1 H, H_β), 8.62 (d, *J* = 4.5 Hz, 0.4 H, H_β), 8.55 (d, *J* = 4.4 Hz, 1.6 H, H_β), 8.50 (m, 2 H, H_β), 3.51 (m, 2 H, CH_2), 2.98 (m, 2 H, CH_2).

^{13}C NMR (176.1 MHz, $CDCl_3$, 30 °C): δ = 174.6, 148.1, 147.4, 146.9, 146.7, 146.0, 145.6, 145.2, 142.7, 142.5, 142.0, 141.3, 140.6, 138.7, 138.5, 137.3, 137.0, 134.7, 134.3, 130.5, 130.3, 127.8, 126.4, 126.2, 121.8, 121.6, 117.4, 117.3, 99.2, 98.5, 95.5, 94.6, 42.8, 34.9.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –133.49 (dd, ^3J = 25.0 Hz, ^4J = 11.8 Hz, 1.6 F, F_o*), –133.88 (dd, ^3J = 25.3 Hz, ^4J = 12.2 Hz, 0.4 F, F_o*), –137.05 to –137.28 (m, 2 F, F_m*), –137.71 to –137.80 (m, 4 F, F_o), –152.25 (t, *J* = 20.9 Hz, 1.2 F, F_p), –152.82 (t, *J* = 20.9 Hz, 0.8 F, F_p), –161.48 (dt, ^3J = 22.2 Hz, ^4J = 7.5 Hz, 2.4 F, F_m), –161.94 (dt, ^3J = 22.5 Hz, ^4J = 7.6 Hz, 1.6 F, F_m).

MS (MALDI+): *m*/*z* calcd for $C_{40}H_{16}F_{14}N_4O_2S$: 882.0770 $[M]^+$, 883.0849 $[M + H]^+$; found: 882.0825 $[M]^+$, 883.0846 $[M + H]^+$.

5-(Pentafluorophenyl)-10,15-bis{2,3,5,6-tetrafluoro-4-[(carboxyethyl)thio]phenyl}corrole and 10-(Pentafluorophenyl)-5,15-bis{2,3,5,6-tetrafluoro-4-[(carboxyethyl)thio]phenyl}corrole (6)

Purification by silica gel chromatography was performed [first solvent: CH_2Cl_2–MeOH (10:1); second solvent: CH_2Cl_2–MeOH (4:1)] and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **6**; yield: 3.0 mg (3.1 μmol, 24%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, CD_3OD, 30 °C): δ = 9.06 (br s, 2 H, H_β), 8.69 (br s, 2 H, H_β), 8.58 (br s, 1 H, H_β), 8.55 (s, 1 H, H_β), 8.50 (br s, 2 H, H_β), 3.44 (t, *J* = 7.3 Hz, 4 H, CH_2), 2.70 (t, *J* = 7.6 Hz, 4 H, CH_2).

^{13}C NMR (176.1 MHz, CD_3OD, 30 °C): δ = 179.7, 179.5, 170.3, 149.3, 148.0, 146.6, 142.1, 139.9, 138.4, 122.5, 117.4, 91.1, 39.6, 32.8.

^{19}F NMR (282.4 MHz, CD_3OD, 30 °C): δ = –137.26 (m, 4 F, F_o*), –139.98 (s, 2 F, F_o), –140.30 (s, 4 F, F_m*), –159.04 (s, 1 F, F_p), –166.49 (s, 2 F, F_m).

MS (MALDI+): *m*/*z* calcd for $C_{43}H_{21}F_{13}N_4O_4S_2$: 969.0875 $[M + H]^+$; found: 969.0816.

5,10-Bis(pentafluorophenyl)-15-[4-({2-[(*tert*-butoxycarbonyl)amino]ethyl}thio)-2,3,5,6-tetrafluorophenyl]corrole and 5,15-Bis(pentafluorophenyl)-10-[4-({2-[(*tert*-butoxycarbonyl]amino}ethyl)thio]-2,3,5,6-tetrafluorophenyl)corrole (7)

Purification by silica gel chromatography was performed [first solvent: CH_2Cl_2–heptanes (2:3); second solvent: CH_2Cl_2–heptanes (4:1)] and the second fluorescent band was collected. Removal of the solvent under reduced pressure afforded **7**; yield: 44.5 mg (46.7 μmol, 93%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): δ = 9.07–9.04 (m, 2 H, H_β), 8.79–8.76 (m, 2 H, H_β), 8.60–8.50 (m, 4 H, H_β), 3.66–3.62 (m, 2 H), 3.47–3.42 (m, 2 H), 1.42 (m, 9 H).

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –134.67 (dd, ^3J = 22.9 Hz, ^4J = 11.2 Hz, 0.5 F, F_o*), –135.36 (dd, ^3J = 24.4 Hz, ^4J = 13.2 Hz, 1.6 F, F_o*), –137.19 to –137.36 (m, 2 F), –137.76 (dd, ^3J = 22.5 Hz, ^4J = 6.3 Hz, 2 F), –139.19 to –139.40 (m, 2 F), –152.30 (t, *J* = 20.9 Hz, 1.1 F, F_p), –152.88 (t, *J* = 21.0 Hz, 0.8 F, F_p), –161.41 to –161.60 (m, 2.3 F, F_m), –161.87 to –162.06 (m, 1.7 F, F_m).

5,10-Bis(pentafluorophenyl)-5-{4-[(2-aminoethyl)thio]-2,3,5,6-tetrafluorophenyl}corrole and 5,15-Bis(pentafluorophenyl)-10-{4-[(2-aminoethyl)thio]-2,3,5,6-tetrafluorophenyl}corrole

The product **7** (44.5 mg, 46.7 μmol) was dissolved in CH_2Cl_2 (2 mL) and TFA (2 mL) was added. The mixture was stirred at r.t. for 1 h. After extraction with CH_2Cl_2 (3 × 15 mL), the solvent was removed under reduced pressure to give the intermediate deprotected product; yield: 39.0 mg (46 μmol, 98%); dark green solid; mp > 400 °C (dec.).

***N*-(ε-Maleimidocaproyloxy) Succinimide Ester (EMCS)**

A solution of 6-aminohexanoic acid (202 mg, 1.52 mmol, 1 equiv) in DMF (2 mL) was reacted with maleic anhydride (166 mg, 1.75 mmol, 1.15 equiv) at r.t. under N_2 atmosphere for 2.5 h. The mixture was cooled to 0 °C and *N*,*N*′-dicyclohexylcarbodiimide (723 mg, 3.50 mmol, 2.3 equiv) and *N*-hydroxysuccinimide (232 mg, 1.98 mmol, 1.3 equiv) were added. After 10 min at 0 °C, the mixture was stirred at r.t. under N_2 for 18 h. The mixture was concentrated under reduced pressure at 30 °C, the residue was diluted with $CHCl_3$ (15 mL) and sat. aq $NaHCO_3$ (5 mL), the phases were separated, and the aqueous phase was extracted with $CHCl_3$ (10 mL). The organic phases were combined, dried (Na_2SO_4), and the solvent was removed under reduced pressure at 30 °C. The crude product was purified by careful column chromatography (CH_2Cl_2–MeOH, 20:1) to give a pale orange solid; yield: 129 mg (0.42 mmol, 27%); mp 69–71 °C.

^{1}H NMR (300 MHz, CD_3OD, 25 °C): δ = 1.44–1.54 (m, 2 H), 1.62 (quint, *J* = 7.1 Hz, 2 H), 1.76 (quint, *J* = 7.3 Hz, 2 H), 2.65 (t, *J* = 6.9 Hz, 2 H), 2.84 (s, 4 H), 3.32 (t, *J* = 6.9 Hz, 2 H), 6.24 (d, *J* = 12.7 Hz, 1 H), 6.47 (d, *J* = 12.7 Hz, 1 H).

^{13}C NMR (75 MHz, CD_3OD, 25 °C): δ = 25.3, 26.5 (2 C), 27.0, 29.3, 31.5, 34.8, 40.6, 133.7, 134.2, 167.7, 168.1, 170.2, 171.9.

5,10-Bis(pentafluorophenyl)-5-{4-[*N*-(ε-maleimidocaproyl)(2-amidoethyl)thio]-2,3,5,6-tetrafluorophenyl}corrole and 5,15-Bis(pentafluorophenyl)-10-{4-[*N*-(ε-maleimidocaproyl)(2-amidoethyl)thio]-2,3,5,6-tetrafluorophenyl}corrole (8)

The deprotected corrole from **7** (39 mg, 45.7 μmol), EMCS (17 mg, 55 μmol, 1.2 equiv), and DIPEA (39.2 μL, 225 μmol, 4.9 equiv) were dissolved in DMF (5 mL) and the mixture stirred at r.t. for 2 h. After extraction with CH_2Cl_2 (2 × 15 mL), the solvent was removed under reduced pressure. Purification by silica gel chromatography was performed [first solvent: CH_2Cl_2–MeOH (20:1); second solvent: CH_2Cl_2–MeOH (5:1)] and the fluorescent band was collected. Removal of the solvent under reduced pressure afforded **8**; yield: 7.3 mg (7.0 μmol, 15%); dark green solid; mp > 400 °C (dec.).

^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ = 9.11–9.09 (m, 2 H, H_β), 8.83–8.79 (m, 2 H, H_β), 8.60–8.58 (m, 4 H, H_β), 7.34 (d, *J* = 12.6 Hz, 1 H), 7.30 (d, *J* = 12.6 Hz, 1 H), 4.13 (t, *J* = 13.5 Hz, 2 H), 3.80–3.85 (m, 1 H), 3.58–3.71 (m, 2 H), 3.36 (m, 1 H), 2.88 (m, 1 H), 1.93 (m, 1 H), 1.38 (m, 2 H), 1.22 (m, 2 H), 1.16 (m, 2 H).

^{13}C NMR (75 MHz, CD_3OD, 25 °C): δ = 25.3, 26.5 (2 C), 27.0, 29.3, 31.5, 34.8, 40.6, 126.2, 127.9, 129.3, 130.3, 134.2, 134.5, 136.9, 137.2, 138.3, 138.6, 139, 140.3, 141.2, 142.7, 144.3, 145.4, 145.7, 145.9, 146.8, 147.3, 147.6, 156.8, 170.5, 175.4.

^{19}F NMR (282.4 MHz, $CDCl_3$, 30 °C): δ = –136.8 to –138.0 (m, 6 F), –144.8 (dd, ^3J = 24.0 Hz, ^4J = 13.6 Hz, 1 F), –150.6 (d, ^3J = 23.4 Hz, 1 F), –152.3 (t, ^3J = 20.3 Hz, 1 F), 152.9 (t, ^3J = 20.1 Hz, 1 F), –161.2 to –161.7 (m, 2 F), –161.7 to –162.2 (m, 2 F).

HR-MS (MALDI+): *m*/*z* calcd for $C_{49}H_{28}F_{14}N_6O_3S$: 1047.1793 [M + H]$^+$; found: 1047.1785.

Anal. Calcd for $C_{49}H_{28}F_{14}N_6O_3S$: C, 56.22; H, 2.70; N, 8.03; O, 4.59; S, 3.06; F, 25.41. Found: C, 56.09; H, 2.67; N, 8.12; S, 3.08.

Acknowledgment

We kindly acknowledge financial support of the project I958 ('High-Valent Metal Tetrapyrroles for Surface-Supported Catalysis') by the Austrian Science Fund (FWF). The NMR spectrometers were acquired in collaboration with the University of South Bohemia (CZ) with financial support from the European Union through the EFRE INTERREG IV ETC-AT-CZ program (project M00146, 'RERI-uasb'). We would like to thank Dr. Clemens Schwarzinger, Dr. Manuela List, and Dr. Klaus Bretterbauer for the measurement of ESI and MALDI MS spectra.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000084.

References

(1) (a) Johnson, A. W.; Kay, I. T. *Proc. Chem. Soc.* **1964**, 89. (b) Johnson, A. W.; Kay, I. T. *J. Chem. Soc.* **1965**, 1620.
(2) Aviv-Harel, I.; Gross, Z. *Coord. Chem. Rev.* **2011**, *255*, 717.
(3) (a) Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599. (b) Gross, Z.; Gray, H. B. *Adv. Synth. Catal.* **2004**, *346*, 165.
(4) Agadjanian, H.; Ma, J.; Rentsendorj, A.; Valluripalli, V.; Hwang, J. Y.; Mahammed, A.; Farkas, D. L.; Gray, H. B.; Gross, Z.; Medina-Kauwe, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 6105.
(5) Haber, A.; Aviram, M.; Gross, Z. *Chem. Sci.* **2011**, *2*, 295.
(6) Barbe, J.-M.; Canard, G.; Brandès, S.; Jérôme, F.; Dubois, G.; Guilard, R. *Dalton Trans.* **2004**, 1208.
(7) Walker, D.; Chappel, S.; Mahammed, A.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B.; Zaban, A.; Gross, Z. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1259.
(8) Gryko, D. T.; Koszarna, B. *Org. Biomol. Chem.* **2003**, *1*, 350.
(9) (a) Gryko, D. T.; Koszarna, B. *Synthesis* **2004**, 2205. (b) Koszarna, B.; Gryko, D. T. *J. Org. Chem.* **2006**, *71*, 3707.
(10) Lemon, C. M.; Brothers, P. J. *J. Porphyrins Phthalocyanines* **2011**, *15*, 809.
(11) Mahammed, A.; Botoshansky, M.; Gross, Z. *Dalton Trans.* **2012**, *41*, 10938.
(12) Golubkov, G.; Bendix, J.; Gray, H. B.; Mahammed, A.; Goldberg, I.; DiBilio, A. J.; Gross, Z. *Angew. Chem. Int. Ed.* **2001**, *40*, 2132.
(13) Tortora, L.; Nardis, S.; Fronczek, F. R.; Smith, K. M.; Paolesse, R. *Chem. Commun.* **2011**, *47*, 4243.
(14) Saltsman, I.; Mahammed, A.; Goldberg, I.; Tkachenko, E.; Botoshansky, M.; Gross, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7411.
(15) König, M.; Reith, L. M.; Monkowius, U.; Knör, G.; Bretterbauer, K.; Schoefberger, W. *Tetrahedron* **2011**, *67*, 4243.
(16) Ngo, T. H.; Puntoriero, F.; Nastasi, F.; Robeyns, K.; van Meervelt, L.; Campagna, S.; Dehaen, W.; Maes, W. *Chem. Eur. J.* **2010**, *16*, 5691.
(17) Ngo, T. H.; Nastasi, F.; Puntoriero, F.; Campagna, S.; Dehaen, W.; Maes, W. *J. Org. Chem.* **2010**, *75*, 2127.
(18) Tasior, M.; Voloshchuk, R.; Poronik, Y. M.; Rowicki, T.; Gryko, D. T. *J. Porphyrins Phthalocyanines* **2011**, *15*, 1011.
(19) Kadish, K. M.; Han, B. C.; Franzen, M. M.; Araullo-McAdams, C. *J. Am. Chem. Soc.* **1990**, *112*, 8364.
(20) Samaroo, D.; Vinodu, M.; Chen, X.; Drain, C. M. *J. Comb. Chem.* **2007**, *9*, 998.
(21) Costa, J. I.; Tomé, A. C.; Neves, M. G.; Cavaleiro, J. A. *J. Porphyrins Phthalocyanines* **2011**, *15*, 1116.
(22) Hori, T.; Osuka, A. *Eur. J. Org. Chem.* **2010**, 2379.
(23) Barata, J. F. B.; Santos, C. I. M.; Neves, M.; Graça, P. M. S.; Faustino, M. A. F.; Cavaleiro, J. A. S. *Functionalization of Corroles*, In *Topics in Heterocyclic Chemistry*; Vol. 33; Paolesse, R., Ed.; Springer: Berlin, **2014**, 79–141.
(24) Avieza, D.; Cotton, S.; David, M.; Segev, A.; Khaselev, N.; Galili, N.; Gross, Z.; Yayon, A. *Cancer Res.* **2000**, 2973.
(25) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem. Int. Ed.* **1999**, *38*, 1427.
(26) Cardote, T. A.; Barata, J. F.; Faustino, M. A. F.; Preuß, A.; Neves, M.; Graça, P. M. S.; Cavaleiro, J. A.; Ramos, C. I.; Santana-Marques, M.; Graça, O.; Röder, B. *Tetrahedron Lett.* **2012**, *53*, 6388.
(27) Reith, L. M.; Stiftinger, M.; Monkowius, U.; Knör, G.; Schoefberger, W. *Inorg. Chem.* **2011**, *50*, 6788.
(28) Reith, L. M.; Koenig, M.; Schwarzinger, C.; Schoefberger, W. *Eur. J. Inorg. Chem.* **2012**, 4342.
(29) Schmidlehner, M.; Faschinger, F.; Reith, L. M.; Ertl, M.; Schoefberger, W. *Appl. Organomet. Chem.* **2013**, *27*, 395.
(30) (a) Ngo, T. H.; van Rossom, W.; Dehaen, W.; Maes, W. *Org. Biomol. Chem.* **2009**, *7*, 439. (b) Stefanelli, M.; Shen, J.; Zhu, W.; Mastroianni, M.; Mandoj, F.; Nardis, S.; Ou, Z.; Kadish, K. M.; Fronczek, F. R.; Smith, K. M.; Paolesse, R. *Inorg. Chem.* **2009**, *48*, 6879.
(31) (a) Timerbaev, A. R.; Hartinger, C. G.; Aleksenko, S. S.; Keppler, B. K. *Chem. Rev.* **2006**, *106*, 2224. (b) Warnecke,

A.; Fichtner, I.; Garmann, D.; Jaehde, U.; Kratz, F. *Bioconjugate Chem.* **2004**, *15*, 1349.
(32) Vehkamäki, M.; Hatanää, T.; Ritala, M.; Leskelä, M. *J. Mater. Chem.* **2004**, *14*, 3191.
(33) Ikeda, M.; Ochi, R.; Kurita, Y.-s.; Pochan, D. J.; Hamachi, I. *Chem. Eur. J.* **2012**, *18*, 13091.
(34) (a) Li, G.; Sproviero, E. M.; McNamara, W. R.; Snoeberger, R. C. III; Crabtree, R. H.; Brudvig, G. W.; Batista, V. S. *J. Phys. Chem. B* **2010**, *114*, 14214. (b) Li, G.; Sproviero, E. M.; Snoeberger, R. C. III; Iguchi, N.; Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W.; Batista, V. S. *Energy Environ. Sci.* **2009**, *2*, 230. (c) Kärkäs, M. D.; Johnston, E. V.; Verho, O.; Åkermark, B. *Acc. Chem. Res.* **2014**, *47*, 100.
(35) Errington, R. J.; Fisher, G. A.; Moenadar, I.; Norman, N. C. *Inorg. Synth.* **1997**, *31*, 98.

