Synthesis and Physicochemical Characterization of *meso*-Functionalized Corroles: Precursors of Organic–Inorganic Hybrid Materials

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Cobalt(III) corroles exhibit an infinite selectivity for the coordination of carbon monoxide towards dioxygen and dinitrogen. This peculiar property thus allows their use as sensing devices for CO detection. Here are described the syntheses and physico-chemical characterization of *meso* mono-, bis- and tris(triethoxysilyl)-functionalized corroles, precursors of organic–inorganic materials. The corrole ring formation was achieved in every case using the "2+1" method involving the reaction of two equivalents of an encumbered dipyrromethane with one equivalent of an aromatic aldehyde in the presence of a catalytic amount of trifluoroacetic acid. The functionalization of the corrole by triethoxysilyl chains was carried out by a condensation reaction of an isocyanate, bearing a triethoxysilyl termination, either on an amino or hydroxy group. Each final compound and intermediate were characterized by various physico-chemical techniques such as ^{1}H NMR, UV/Vis, MALDI/TOF or EI mass spectrometry and elemental analysis.

Introduction

The chemistry of corroles is now well-developed, and the increasing number of new metallocorrole derivatives opens the way to potential applications as it is the case for porphyrin analogs.[1–3] Some applications of metallocorroles in catalysis,[4] as functional models of hemoproteins[5] and by us as selective carbon monoxide sensors in the solid state have already been developed.[6] Moreover, we recently demonstrated, as a preliminary report, that the incorporation of cobalt(III) corroles into a solid inorganic matrix not only maintains the high selectivity towards CO, but also greatly enhances the long-term stability of the incorporated metallocorrole.[7]

In order to obtain such organic–inorganic hybrid materials, we focused on the synthesis of corroles bearing a hydrolysable trialkoxysilyl termination enabling the further anchoring on a silica support or the direct formation of the hybrid solid by the sol-gel process. From a synthetic point of view, we decided to introduce such functionalized chains on the corrole macrocycle by phenyl groups located at the periphery of the ring. Therefore, recently reported syntheses of *meso*-substituted corroles, rather than the multi-step syntheses of β-substituted corroles, were adapted to obtain these derivatives.[8,9] Moreover, these former methods allowed varying the number and the nature of the functionalized chains bound to the macrocycle. Mono-, di- and trifunctionalized free-base corroles were thus synthesized in respectable yields. We used a step-by-step approach starting firstly by the synthesis of corroles substituted by phenyl groups at the *meso*-positions bearing nitro, azidomethyl or hydroxy terminations. Secondly, trialkoxysilyl-functionalized arms were introduced using procedures affording these derivatives in quantitative yields. These latter compounds are indeed easily hydrolyzed and therefore difficult to be purified.

There are two main routes for the preparation of *meso*-substituted corroles. The "one-pot" method is theoretically the simplest one to have access to A_3-corroles.[10–12] However, this procedure is efficient only if the reacting aldehyde is activated by electron withdrawing groups. The "2+1" method leads to the formation of A_3- and *trans*-A_2B-corroles.[8,9,12–15] Even if this synthetic pathway requires the use of encumbered dipyrromethanes, in order to avoid the acidolysis reaction, it is convenient for the preparation of *meso* mono-, di- and tri-substituted corrole macrocycles. Therefore, we investigated the synthesis of the targeted corrole derivatives using the "2+1" method.

Here we described the synthesis and physico-chemical characterization of mono-, di- and trisubstituted corroles bearing triethoxysilyl terminations, which are the precursors of organic–inorganic hybrid materials. The description and the characterization of these latter materials will be developed in a forthcoming paper.[16]

Results and Discussion

Free-base corroles are generally more acidic than their porphyrin counterparts and are easily deprotonated (one

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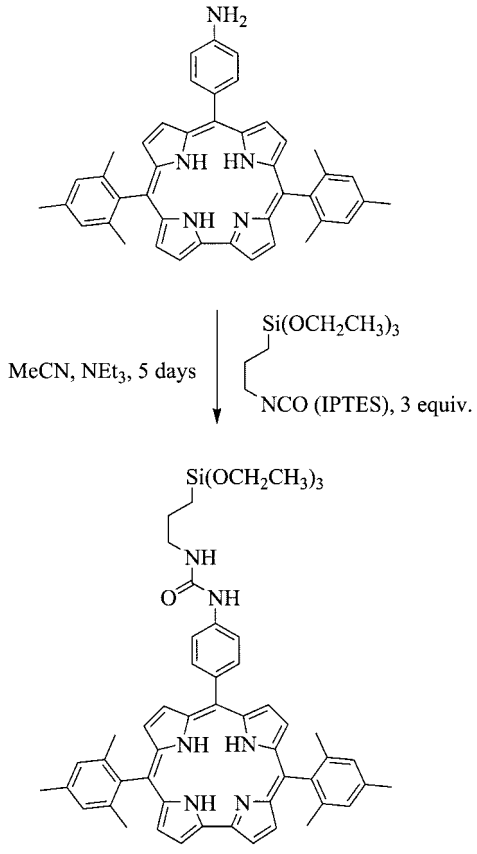
proton removed) in basic solutions.[17–19] Moreover, it has also been shown that their 4N cavity can be alkylated by electrophiles such as aryl halides and acyl chlorides.[19–22] Therefore, in order to complete the functionalization of the corrole by a chain bearing a trialkoxysilyl termination, it is necessary to use reactions involving weakly basic or weakly electrophilic reagents. As a consequence, IPTES [(3-isocyanatopropyl)triethoxysilane], which exhibits these properties, was used as vector of trialkoxysilyl groups in all the reactions described in this manuscript.

Mono-Functionalized Corroles

In our preliminary report on the synthesis of organic–inorganic hybrid materials obtained through the sol-gel process, we focused on the study of a mono-functionalized corrole. This latter precursor was prepared by the condensation of IPTES on the amino group of the corrole in acetonitrile in the presence of triethylamine (Scheme 1).[7]



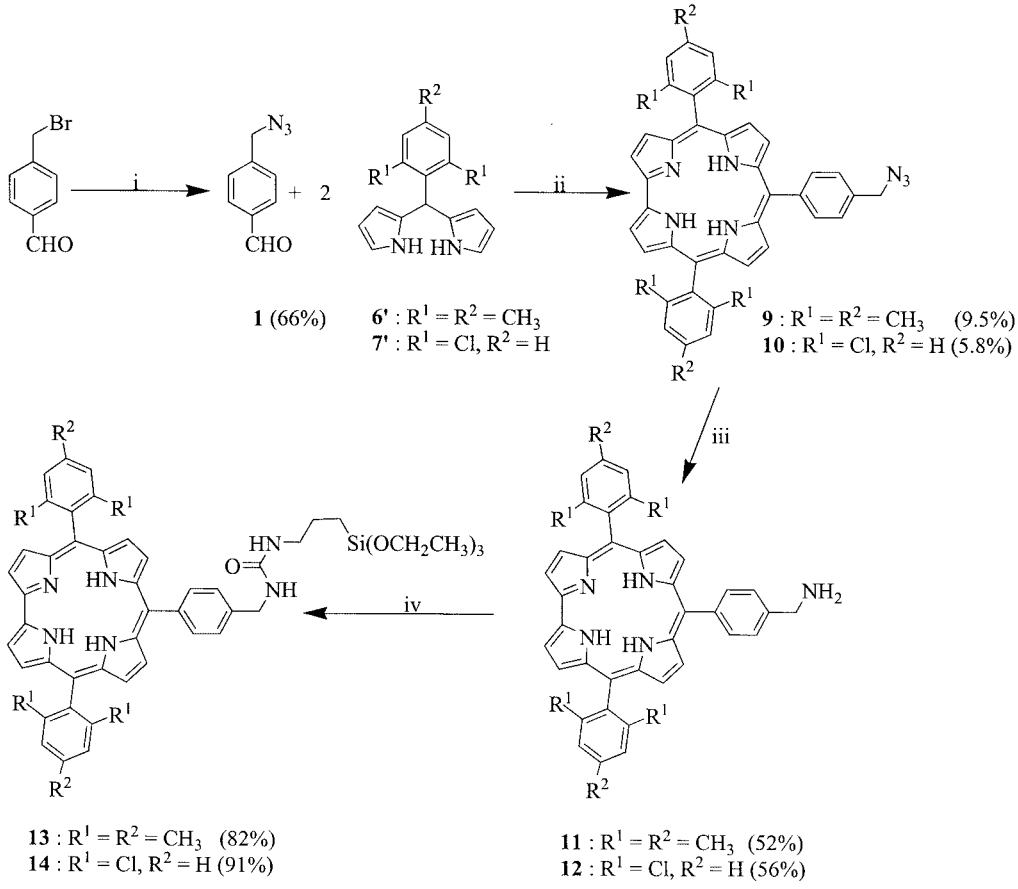
Scheme 1.

This reaction which requires an excess of IPTES (3 equiv.) led to the functionalized corrole in a yield close to 70%. The excess of IPTES was removed by crystallization of the free-base corrole. The weak reactivity of the amino corrole was explained by the low nucleophilicity of the aniline group. The mono-functionalized free corrole base, described in Scheme 1, was further metalated by cobalt, leading to the first inorganic–organic hybrid material incorporating a metallocorrole and exhibiting selective adsorption properties towards CO.[7]

In order to facilitate the anchoring of the triethoxysilyl-functionalized arm, we then moved to the synthesis of a corrole bearing a more reactive amine function. We chose a benzylamino group at the *meso*-position of the ring, which is known to be more nucleophilic than the aniline one. The overall synthetic procedure leading to the expected corrole is depicted in Scheme 2.

The bromobenzyl aldehyde was synthesized according to the reaction reported by Wen et al.[23] The substitution of the bromine atom by the azido group leading to **1**, was carried out in 65% yield by using sodium azide in the mixture acetone/H_2O, 3:1. The condensation of **1** (1 equiv.) on the dipyrromethanes **6′** and **7′** (2 equiv.), respectively,[24,25] in the presence of a catalytic amount of trifluoroacetic acid (TFA, 0.08 equiv.), in dichloromethane as solvent, led to the corroles **9** and **10** in 9.5 and 5.8% yields, respectively, after cyclization and reoxidation by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) according to reported general conditions.[15] The subsequent reduction of the azido group to the amino one with triphenylphosphane in THF afforded after hydrolysis the free-base corroles **11** and **12** in 52 and 56% yields, respectively (Scheme 2). This latter reaction[26] leads firstly to an iminophosphorane by elimination of a dinitrogen molecule, the iminophosphorane being then hydrolyzed to an amine along with formation of triphenylphosphane oxide.

Contrary to the reaction described in Scheme 1, the condensation of IPTES with the corroles **11** and **12** was fast (12 hours) and only required a slight excess of IPTES (1.05 equiv.). The reaction was performed in MeCN (acetonitrile) finally giving the monotriethoxysilyl-functionalized corroles **13** and **14** in very good yields (82 and 91%, respectively) (Scheme 2). All corrole macrocycles (**9**–**14**) were characterized by several physico-chemical methods and elemental analyses (see Exp. Sect.). No peculiar variations were observed on the UV/Vis spectra along the same series of compounds, i.e. **9**, **11**, **13** and **10**, **12**, **14**, since the substitution reactions of the macrocycles only slightly affected the electron density on the corrole rings. Conversely, all the derivatives were well characterized by MALDI/TOF MS, the molecular ion being in each case the most intense ionic pattern in the spectrum (see Exp. Sect. for details). Similarly, the ^{1}H NMR spectra of derivatives **9** to **14** do not exhibit significant differences with the exception of the specific functional group resonances. For example, the main difference between spectra, on one hand of **9** and **11** and on the other hand of **10** and **12** is the resonance of the NH_2 group, which appears at ca. 1 ppm for **11** and **12**. Furthermore, the anchoring of the triethoxysilyl-functionalized chain is also clearly evidenced by the presence of new signals between 0.7 and 7 ppm relative to the $-NHCONHCH_2CH_2CH_2Si(OEt)_3$ group for the spectra of **13** and **14**.

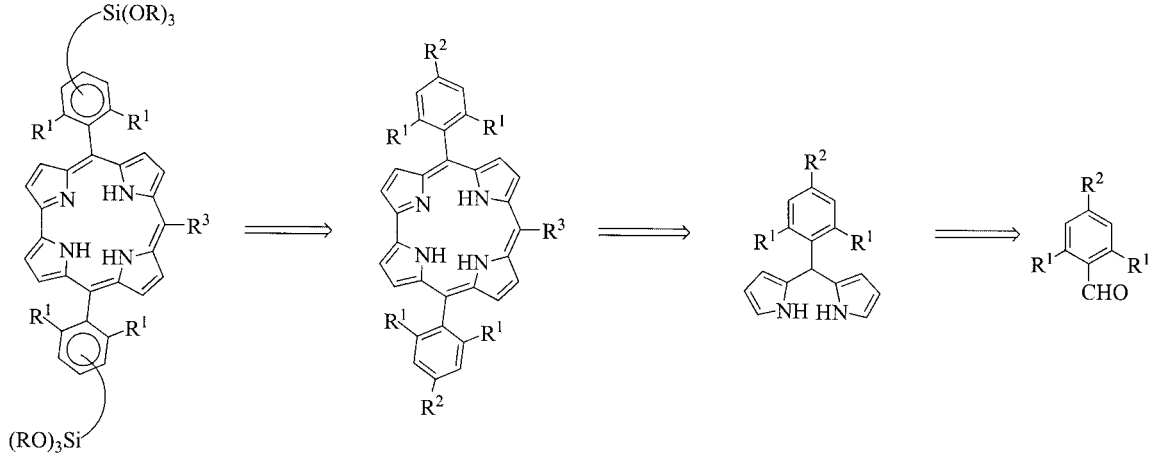


Scheme 2. i) NaN_3, acetone, H_2O. ii) 1: TFA, CH_2Cl_2; 2: DDQ. iii) PPh_3, H_2O, THF. iv) IPTES (1.05 equiv.), MeCN, 12 h.

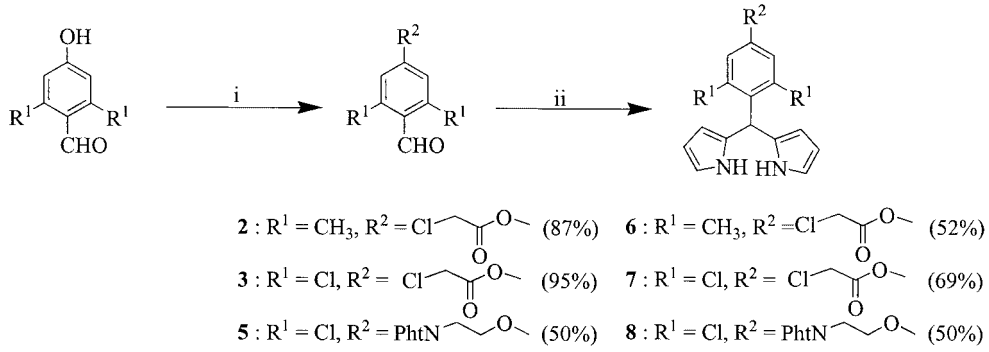
Di-Functionalized Corroles

The strategy we employed to synthesize di-functionalized free-base corroles was again the "2+1" method involving the reaction of an encumbered dipyrromethane with an aromatic aldehyde. In order to obtain such di-functionalized corrole derivatives, it was necessary to synthesize firstly an aldehyde (precursor of a dipyrromethane) substituted in 2- and 6-positions with hindered groups, and at the 4-position by another group allowing the further functionalization with trialkoxysilyl chains. The retrosynthetic pathway is given in Scheme 3.

Consequently, as starting reagents we proposed to use 4-hydroxy-2,6-dimethylbenzaldehyde and 2,6-dichloro-4-hy-



Scheme 3.

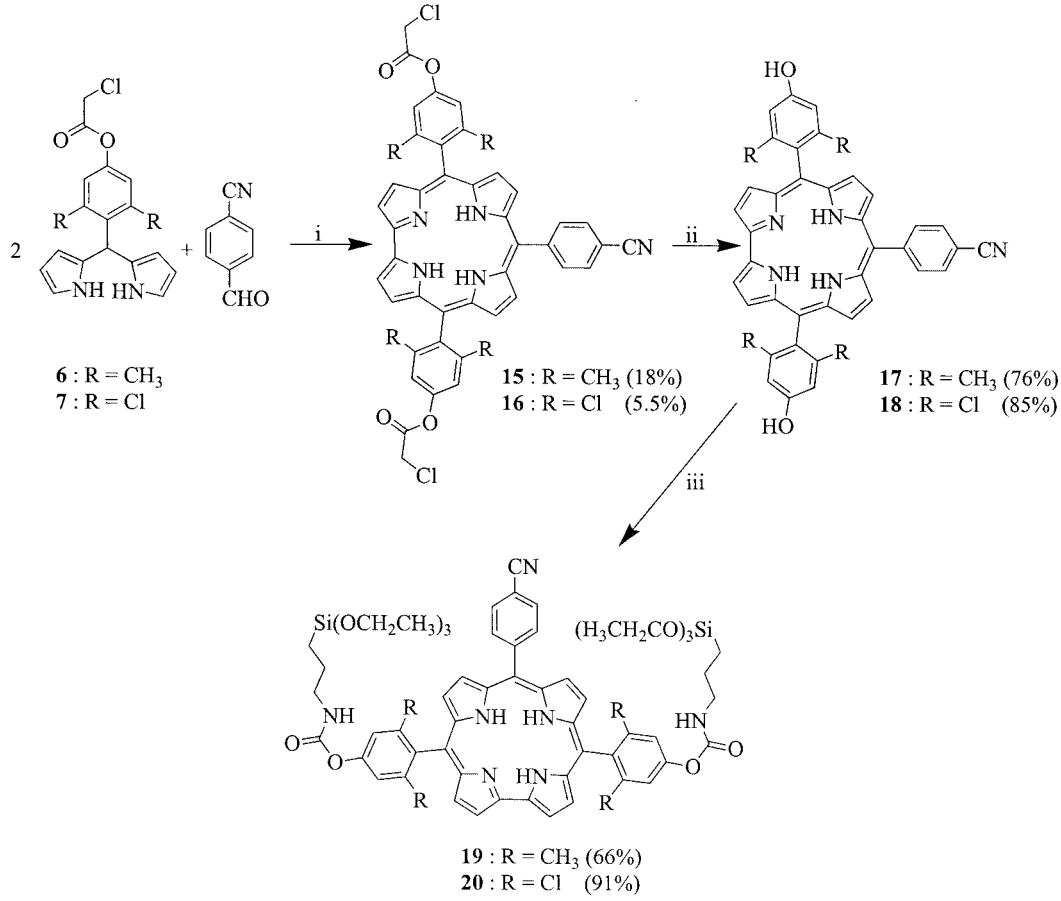


Scheme 4. i) (**2**) 1: NEt_3, THF; 2: $ClCOCH_2Cl$. (**3**) 1: iPr_2NEt, THF; 2: $ClCOCH_2Cl$. (**5**) *N*-(2-bromoethyl)phthalimide, K_2CO_3, MeCN. ii) pyrrole, TFA.

droxybenzaldehyde easily available by straightforward syntheses from commercial products.[27,28] In order to avoid any side reaction due to the presence of the hydroxy function, this latter one was protected by reaction either with chloracetyl chloride[29] or *N*-(2-bromoethyl)phthalimide[30] in a basic medium according to conditions given in Scheme 4.

The protected aldehydes **2**, **3** and **5** were obtained in rather good yields (50–95%). These derivatives are highly reactive and soluble in pyrrole thus leading, in the presence of a catalytic amount of trifluoroacetic acid (TFA), to the dipyrromethanes **6**, **7** and **8** in 52, 69 and 50% yield, respectively. Two equivalents of dipyrromethanes **6** and **7** were then condensed on an aromatic aldehyde bearing an electron withdrawing group such as CN using TFA as catalyst affording **15** and **16** in 18 and 5.5% yield, respectively (Scheme 5).

Basic conditions were tentatively employed for the deprotection of the hydroxy functions but they were found to be ineffective in the present case. Indeed these conditions required a subsequent protonation of the phenolate groups, which was made difficult by the concomitant protonation

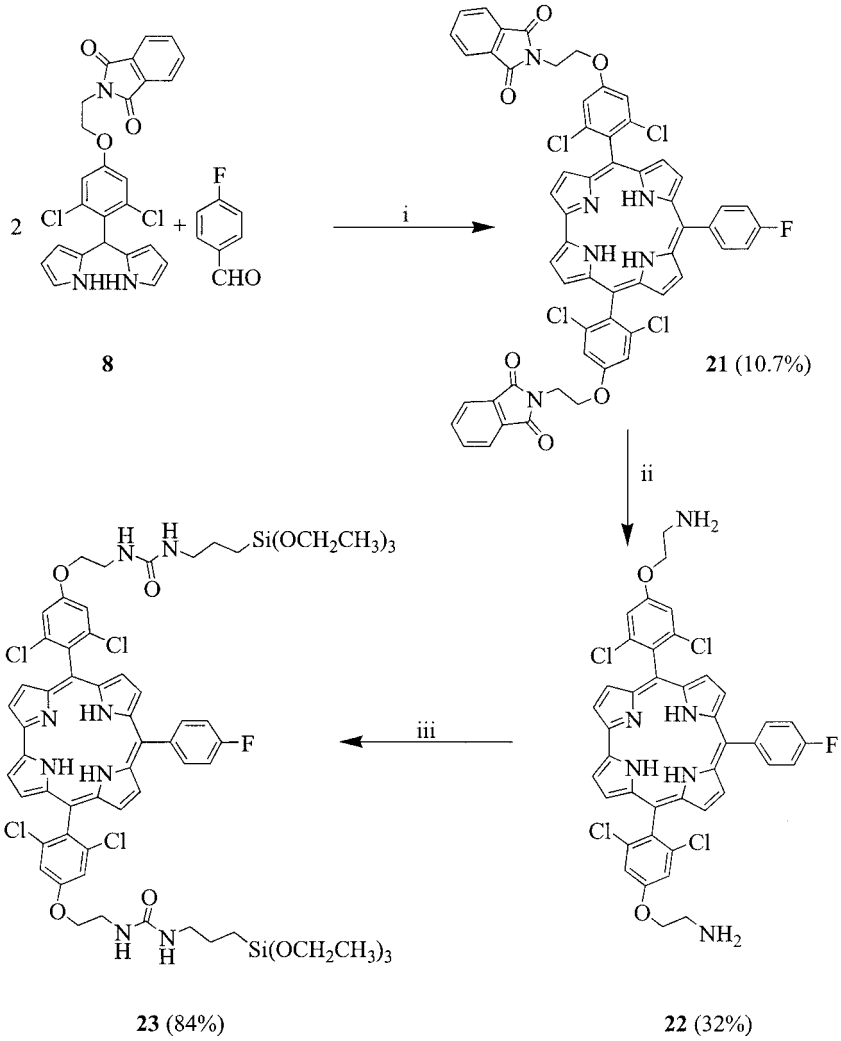


Scheme 5. i) 1: TFA, CH_2Cl_2; 2: DDQ. ii) $PhCH_2NH_2$, THF, EtOH. iii) IPTES (8 equiv.), iPr_2NEt (8 equiv.), MeCN, 7 days.

of the 4N cavity of the corrole in the acidic medium. In this regard, we turned towards the deprotection using amines. The chloro ester group on corroles **15** and **16** is sufficiently activated to react with amines to lead to amides. Benzylamine was found to be, on one hand nucleophilic enough to react with the ester function and on the other hand not sufficiently basic to deprotonate the –OH and –NH functions. The excess of benzylamine and corresponding amide was easily removed by crystallization affording the compounds **17** and **18** in 76 and 85% yield, respectively (see Scheme 5). Generally, the condensation of a nucleophile on an isocyanate function is catalyzed by triethylamine that activates the isocyanate towards the subsequent attack of the nucleophile. Here the phenol groups of the corroles **17** and **18** were not nucleophilic enough to condense with the isocyanate in the presence of triethylamine. Diisopropylethylamine (iPr$_2$NEt) is, in turn, less nucleophilic than triethylamine due to the steric hindrance of the substituents. Furthermore, its basicity allows the deprotonation of the phenol groups and enhances their nucleophilic character, which favors the reaction with the isocyanate function. Then the treatment of the corroles **17** and **18** with an excess of IPTES in the presence of iPr$_2$NEt led to di-functionalized corroles **19** and **20** in 66 and 92% yield, respectively (Scheme 5).

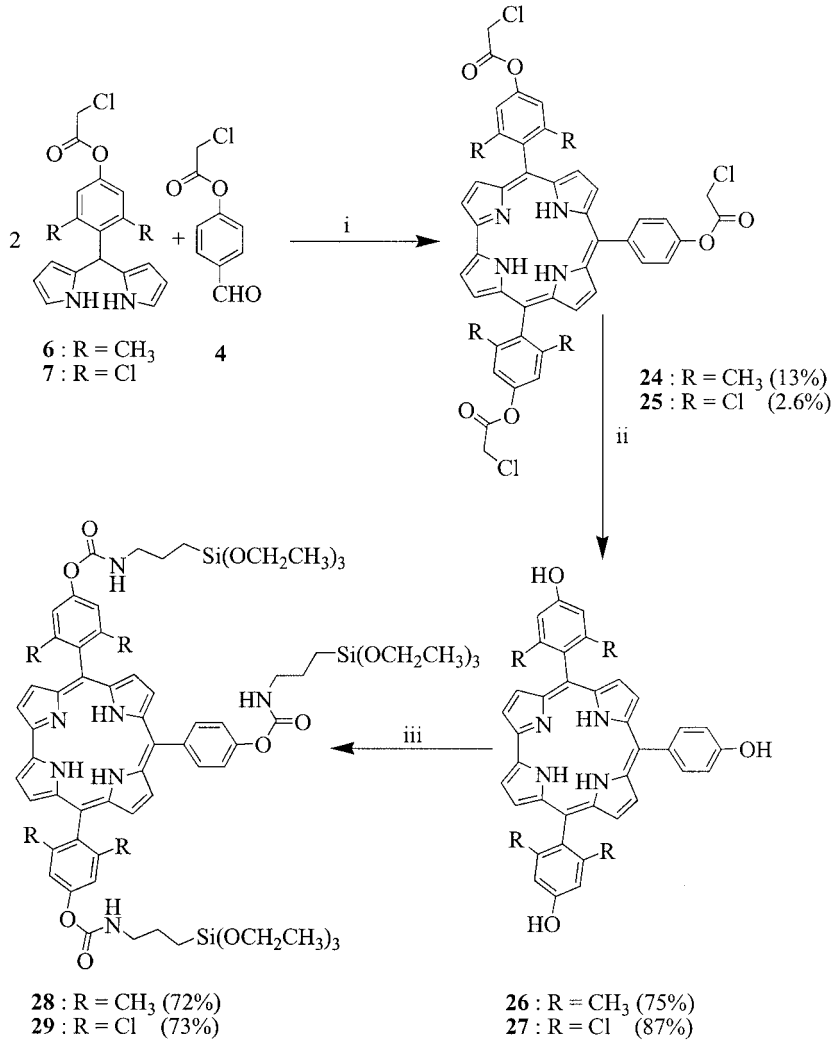
We investigated another possibility to introduce a reactive amino group allowing the grafting of trialkoxysilyl chain. Phthalimide is a well-known precursor of –NH$_2$ function when linked to an aliphatic chain such as in the dipyrromethane **8**.[30] Two equivalents of **8** were treated with one equivalent of 4-fluorobenzaldehyde leading to the free-base corrole **21** in 10.7% yield under the same conditions as for the synthesis of **15** and **16** (Scheme 6). The deprotection of the amine group (**22**, 32% yield) was performed using hydrazine hydrate in ethanol as solvent.[31] The grafting of the triethoxysilyl-functionalized chains was carried out using a slight excess of IPTES in MeCN as solvent, yielding the di-functionalized free base **23** (84% yield) (Scheme 6).

As for mono-functionalized corroles, di-functionalized ones were characterized by elemental analysis, UV/Vis, ^{1}H NMR and MALDI/TOF mass spectrometry (see Exp. Sect. for details).



8 **21** (10.7%) **22** (32%) **23** (84%)

Scheme 6. i) 1: TFA, CH_2Cl_2; 2: DDQ. ii) NH_2NH_2, H_2O, EtOH. iii) IPTES (2.5 equiv.), iPr$_2$NEt (6 equiv.), MeCN, 12 h.



Scheme 7. i) 1: TFA, CH_2Cl_2; 2: DDQ. ii) $PhCH_2NH_2$, THF, EtOH. iii) IPTES (12 equiv.), iPr$_2$NEt (6 equiv.), THF, MeCN, 7 days.

Tri-Functionalized Corroles

Tri-functionalized derivatives of corroles are powerful precursors of organic–inorganic hybrid materials elaborated through the sol-gel process since they provide more polycondensation directions. All our attempts towards the preparation of such derivatives using the one-pot synthesis of corroles were unsuccessful, mainly due to the low yield of the reactions.[11] Therefore, we employed again the "2+1" procedure starting from functionalized dipyrromethanes and aromatic aldehyde. The overall procedure is depicted on Scheme 7.

The condensation of 2 equivalents of dipyrromethanes **6** or **7** on one equiv. of the protected aldehyde **4** led, according to classical conditions, to the corroles **24** and **25** in 13 and 2.6% yield. Despite the moderate yields of the reactions, appreciable amounts (0.5 to 1 g) of these two corroles were obtained due to the availability of dipyrromethanes **6** and **7**, and aldehyde **4**.

According to procedure described for di-functionalized corroles, the deprotection of the phenol functions was achieved by reaction with benzylamine (**26**, **27** in 75, 87% yield, respectively). Finally, the trifunctionalization of the corrole ring with triethoxysilyl arms was performed using, as for di-functionalized macrocycles, an excess of IPTES in the presence of iPr$_2$NEt. Again the yield of the reaction was correct and close to 75% for both **28** and **29** derivatives.

Physico-chemical data and elemental analyses for all the synthesized compounds are given in the Exp. Sect.

Conclusions

Mono-, bis- and tris(triethoxysilyl)-functionalized free-base corroles were synthesized in good yields using the so-called "2+1" method. In our hands, this method proved to be more efficient for the synthesis of tri-functionalized derivatives than the "one-pot" procedure.

In a forthcoming paper, we will describe the metalation reaction of these ligands by cobalt, their hydrolysis, and polycondensation leading to inorganic-organic hybrid materials and their carbon monoxide selective adsorption properties.[16]

Experimental Section

General Remarks: All reagents of analytical grade were obtained from commercial suppliers and used without further purification. 4-Bromomethylbenzaldehyde,[32] 4-hydroxy-2,6-dimethylbenzaldehyde,[27] 2,6-Dichloro-4-hydroxybenzaldehyde,[28] 5-(2,6-dichlorophenyl)dipyrromethane (**7′**) and 5-mesityldipyrromethane (**6′**) [24,25] were synthesized according to previously reported procedures. All the triethoxysilyl-functionalized derivatives were synthesized under argon. ^{1}H NMR spectra were recorded either at 300 MHz with a Bruker Avance 300 or at 500 MHz with a Bruker DRX-500 Avance spectrometer of the "Centre de Spectrométrie Moléculaire de l'Université de Bourgogne" of the FR 2604. Chemical shifts are expressed in ppm relative to residual peaks of chloroform (δ = 7.26 ppm), acetone (δ = 2.05 ppm) or dimethyl sulfoxide (δ = 2.50 ppm). UV/Visible spectra were recorded in solution with a Varian Cary 50 spectrophotometer. Mass spectra were obtained either with a Kratos Concept 32S at 70 eV (EI) and or with a Bruker ProFLEX III spectrometer (MALDI/TOF) using dithranol as matrix. Microanalyses were performed with a Fisons EA 1108 CHNS instrument.

4-(Azidomethyl)benzaldehyde (1): 4-(Bromomethyl)benzaldehyde (9.52 g, 47.9 mmol) and sodium azide (6.25 g, 95.7 mmol, 2 equiv.) were dissolved in a mixture of acetone (120 mL) and distilled water (40 mL). The solution was refluxed during 24 h. After cooling to room temperature, the reaction mixture was extracted twice with ether. The combined organic phases were washed with distilled water, brine and dried with magnesium sulfate. The solvent was evaporated under vacuum and the resulting oil was chromatographed on a silica gel column using CH_2Cl_2/heptane (85:15) as eluent to afford the pure aldehyde **1** (4.99 g, 65%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.42 (s, 2 H, CH_2), 7.45 (d, ^3J = 8.03 Hz, 2 H, Ar-H), 7.86 (d, ^3J = 8,03 Hz, 2 H, Ar-H), 9.98 (s, 1 H, CHO). MS (EI): *m*/*z* = 161 $[M]^{+\cdot}$. $C_8H_7N_3O$ (161.2): calcd. C 59.62, H 4.38, N 26.07; found C 59.55, H 4.30, N 24.58.

4-(Chloroacetoxy)-2,6-dimethylbenzaldehyde (2): 4-Hydroxy-2,6-dimethylbenzaldehyde (27.21 g, 0.18 mol) and triethylamine (30.5 mL, 0.22 mol, 1.2 equiv.) were dissolved in tetrahydrofuran (400 mL). The mixture was stirred at room temperature for 20 min. before chloroacetyl chloride (17.3 mL, 0.22 mol, 1.2 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 1 h and the solvents evaporated. The resulting solid was dissolved in dichloromethane and washed with water. The organic phase was dried with $MgSO_4$ and the solvents evaporated under vacuum. The resulting solid was chromatographed on silica gel with CH_2Cl_2 as eluent giving **2** (35.60 g, 87%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.61 (s, 6 H, CH_3), 4.29 (s, 2 H, CH_2), 6.88 (s, 2 H, Ar-H), 10.55 (s, 1 H, CHO). MS (EI): *m*/*z* = 226 $[M]^{+\cdot}$. $C_{11}H_{11}ClO_3$ (226.7): calcd. C 58.29, H 4.89; found C 58.62, H 4.91.

2,6-Dichloro-4-(chloroacetoxy)benzaldehyde (3): 2,6-Dichloro-4-hydroxybenzaldehyde (4.87 g, 25.5 mmol) and diisopropylethylamine (4.7 mL, 26.8 mmol, 1.05 equiv.) were dissolved in tetrahydrofuran (50 mL). The mixture was stirred at room temperature for 30 min and chloroacetyl chloride (2.13 mL, 26.8 mmol, 1.05 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 1 h and the solvents evaporated. The resulting solid was dissolved in dichloromethane and washed with water. The organic phase was dried with $MgSO_4$ and evaporated to afford **(3)** (6.50 g, 95%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.31 (s, 2 H, CH_2), 7.28 (s, 2 H, Ar-H), 10.44 (s, 1 H, CHO). MS (EI): *m*/*z* = 266 $[M]^{+\cdot}$. $C_9H_5Cl_3O_3$ (267.5): calcd. C 40.41, H 1.88; found C 40.61, H 2.35.

4-(Chloroacetoxy)benzaldehyde (4): The same procedure as described for **3** was used from 4-hydroxybenzaldehyde (24.42 g, 0.2 mol), triethylamine (30.9 mL, 0.22 mol, 1.1 equiv.), chloroacetyl chloride (17.5 mL, 0.22 mol, 1.1 equiv.) and tetrahydrofuran (400 mL). After column chromatography on silica gel with CH_2Cl_2/heptane (85:15) as eluent, **4** (29.80 g, 75%) was obtained as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.35 (s, 2 H, CH_2), 7.32 (d, ^3J = 8.49 Hz, 2 H, Ar-H), 7.93 (d, ^3J = 8.49 Hz, 2 H, Ar-H), 9.99 (s, 1 H, CHO). MS (EI): *m*/*z* = 198 $[M]^{+\cdot}$. $C_9H_7ClO_3$ (198.6): calcd. C 54.43, H 3.55; found C 54.36, H 3.67.

2,6-Dichloro-4-(2-phthalimidoethoxy)benzaldehyde (5): *N*-(2-Bromoethyl)phthalimide (11.87 g, 46.7 mmol, 1.05 equiv.) and 2,6-dichloro-4-hydroxybenzaldehyde (8.5 g, 44.5 mmol) were dissolved in a suspension of KI (0.83 g, 5 mmol) and K_2CO_3 (9.22 g, 69 mmol, 1.4 equiv.) in acetonitrile (250 mL). The mixture was refluxed for 48 h. After cooling down to room temperature, the solvent was removed under vacuum. The resulting solid was dissolved in CH_2Cl_2, washed with water, and dried with $MgSO_4$. After evaporation of the solvent, the solid was chromatographed on silica gel with CH_2Cl_2 giving **5** (8.05 g, 50%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.13 (t, ^3J = 5.66 Hz, 2 H, CH_2), 4.29 (t, ^3J = 5.66 Hz, 2 H, CH_2), 6.90 (s, 2 H, Ar-H), 7.73–7.76 (m, 2 H, Ar-H), 7.87–7.89 (m, 2 H, Ar-H), 10.37 (s, 1 H, CHO). MS (EI): *m*/*z* = 363 $[M]^{+\cdot}$. $C_{17}H_{11}Cl_2NO_4$ (364.2): calcd. C 56.07, H 3.04, N 3.85; found C 55.96, H 3.27, N 4.02.

5-(4-Chloroacetoxy-2,6-dimethylphenyl)dipyrromethane (6): Trifluoroacetic acid (590 μL, 7.9 mmol, 0.15 equiv.) was added to a solution of **2** (12 g, 53 mmol) dissolved in freshly distilled pyrrole (93 mL, 1.33 mol, 25 equiv.). The mixture was stirred under argon at room temperature during 1 h and then dissolved in dichloromethane. The organic phase was washed with an aqueous solution of NaOH (1.0 M), dried with $MgSO_4$ and the solvents evaporated under vacuum. The resulting oil was chromatographed on silica gel with CH_2Cl_2 as eluent, thus affording the pure dipyrromethane **6** (9.49 g, 52%) as a white solid by precipitation in cold pentane. ^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ = 2.10 (s, 6 H, CH_3), 4.29 (s, 2 H, CH_2), 5.93 (s, 1 H, H-*meso*), 5.97 (m, 2 H, H-β), 6.17 (m, 2 H, H-β), 6.69 (m, 2 H, H-α), 6.82 (s, 2 H, Ar-H), 7.97 (br. s, 2 H, NH). MS (MALDI/TOF): *m*/*z* = 342.1 $[M]^{+\cdot}$. $C_{19}H_{19}ClN_2O_2$ (342.8): calcd. C 66.57, H 5.59, N 8.17; found C 66.35, H 5.66, N 8.09.

5-[2,6-Dichloro-4-(chloroacetoxy)phenyl]dipyrromethane (7): The same procedure as described for **6** was used starting from **3** (24.84 g, 92.8 mmol), pyrrole (260 mL, 3.7 mol, 40 equiv.) and TFA (1.03 mL, 7.9 mmol, 0.15 equiv.). After the same purification process, **7** (24.77 g, 69%) was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.28 (s, 2 H, CH_2), 6.06 (m, 2 H, H-β), 6.19 (m, 2 H, H-β), 6.44 (s, 1 H, H-*meso*), 6.73 (m, 2 H, H-α), 7.20 (s, 2 H, Ar-H), 8.25 (br. s, 2 H, NH). MS (MALDI/TOF): *m*/*z* = 382.3 $[M]^{+\cdot}$. $C_{17}H_{13}Cl_3N_2O_2$ (383.7): calcd. C 53.22, H 3.42, N 7.30; found C 53.60, H 3.94, N 6.78.

5-[2,6-Dichloro-4-(2-phthalimidoethoxy)phenyl]dipyrromethane (8): The same procedure as described for **6** was used starting from **5** (8.00 g, 22 mmol), pyrrole (60 mL, 0.88 mol, 40 equiv.) and TFA (244 μL, 3.3 mmol, 0.15 equiv.). After the same purification process, **8** (5.29 g, 50%) was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 4.09 (t, ^3J = 5.55 Hz, 2 H, CH_2), 4.20 (t, ^3J = 5.55 Hz, 2 H, CH_2), 6.00 (m, 2 H, H-β), 6.14–6.17 (m, 2 H, H-β), 6.34 (s, 1 H, H-*meso*), 6.68–6.70 (m, 2 H, H-α), 6.88 (s, 2 H, Ar-H), 7.71–7.75 (m, 2 H, Ar-H), 7.85–7.88 (m, 2 H, Ar-

H), 8.21 (br. s, 2 H, NH). MS (MALDI/TOF): *m/z* = 478.9 $[M]^{+\cdot}$. $C_{25}H_{19}Cl_2N_3O_3$ (480.3): calcd. C 62.51, H 3.99, N 8.75; found C 62.30, H 4.14, N 8.84.

10-(4-Azidomethylphenyl)-5,15-dimesitylcorrole (9): Compound **1** (1.62 g, 10 mmol) and 5-mesityldipyrromethane (**6′**) (5.28 g, 20 mmol, 2 equiv.) were dissolved in dichloromethane (600 mL). The mixture was stirred at room temperature for 5 min. and TFA (60 μL, 0.8 mmol, 0.08 equiv.) was added. After stirring at room temperature for 5 h, the mixture was diluted with dichloromethane (1.5 L) and a solution of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (4.5 g, 20 mmol, 2 equiv.) was added. The mixture was stirred at room temperature for 30 min, concentrated under vacuum and filtered through a silica pad. After evaporation, the resulting solid was chromatographed twice on silica gel using CH_2Cl_2 as eluent. After recrystallization in a CH_2Cl_2/heptane mixture, **9** (0.63 g, 9.5%) was obtained as dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.95 (br. s, 3 H, NH), 1.94 (s, 12 H, CH_3), 2.61 (s, 6 H, CH_3), 4.67 (s, 2 H, CH_2), 7.28 (s, 4 H, Ar-H), 7.67 (d, ^3J = 7.89 Hz, 2 H, Ar-H), 8.19 (d, ^3J = 7.89 Hz, 2 H, Ar-H), 8.34 (d, ^3J = 4.04 Hz, 2 H, H-β), 8.48 (d, ^3J = 4.72 Hz, 2 H, H-β), 8.50 (d, ^3J = 4.72 Hz, 2 H, H-β), 8.90 (d, ^3J = 4.04 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 665.7 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max}, = 408 (112.8), 426 (91.3), 567 (18.7), 604 (14.2), 636 nm (9.5). $C_{44}H_{39}N_7\cdot 0.5H_2O$ (674.8): calcd. C 78.31, H 5.97, N 14.53; found C 78.75, H 6.17, N 13.51.

10-(4-Azidomethylphenyl)-5,15-bis(2,6-dichlorophenyl)corrole (10): The same procedure as described for the corrole **9** was used starting from **1** (2.45 g, 15.2 mmol), 5-(2,6-dichlorophenyl)dipyrromethane (**7′**) (8.84 g, 30.4 mmol, 2 equiv.), dichloromethane (0.91 L) and TFA (91 μL, 3.3 mmol, 0.08 equiv.). The reaction mixture was diluted by the addition of CH_2Cl_2 (3.5 L) before the addition of DDQ (6.8 g, 30.4 mmol, 2 equiv.) in tetrahydrofuran (200 mL). The solution was stirred at room temperature for 30 min, concentrated under vacuum and filtered through a silica pad. After evaporation, the resulting solid was chromatographed on silica gel with CH_2Cl_2/heptane (2:1) as eluent. After recrystallization from CH_2Cl_2/heptane, **10** (0.63 g, 5.8%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.05 (br. s, 3 H, NH), 4.68 (s, 2 H, CH_2), 7.64–7.69 (m, 4 H, Ar-H), 7.75–7.78 (m, 4 H, Ar-H), 8.20 (d, ^3J = 7.77 Hz, 2 H, Ar-H), 8.42 (br. s, 2 H, H-β), 8.54 (d, ^3J = 4.65 Hz, 2 H, H-β), 8.58 (d, ^3J = 4.65 Hz, 2 H, H-β), 9.01 (d, ^3J = 4.00 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 717.1 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (136.5), 425 (107.9), 567 (19.6), 608 (12.6), 636 nm (6.2). $C_{38}H_{23}Cl_4N_7$ (719.4): calcd. C 63.44, H 3.22, N 13.63; found C 63.39, H 3.46, N 13.33.

10-(4-Aminomethylphenyl)-5,15-dimesitylcorrole (11): A solution of the corrole **9** (0.60 g, 0.90 mmol) in tetrahydrofuran (30 mL) was added dropwise to a solution of triphenylphosphane (0.48 g, 1.85 mmol, 2 equiv.) in tetrahydrofuran (20 mL). The mixture was stirred at room temperature for 24 h before the addition of distilled water (0.5 mL). The mixture was then refluxed during 2 h and the solvents evaporated under vacuum. The resulting solid was chromatographed on basic alumina with mixtures of CH_2Cl_2/MeOH (99:1, 98:2, 95:5, 90:10) as eluents. After recrystallization from CH_2Cl_2/MeOH/heptane, **11** (0.30 g, 52%) was obtained as a dark blue solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 1.00–1.05 (br. s, 2 H, NH_2), 1.89 (s, 12 H, CH_3), 2.56 (s, 6 H, CH_3), 4.25 (s, 2 H, CH_2), 7.22 (s, 4 H, Ar-H), 7.71 (d, ^3J = 7.65 Hz, 2 H, Ar-H), 8.13 (d, ^3J = 7.65 Hz, 2 H, Ar-H), 8.30 (d, ^3J = 4.04 Hz, 2 H, H-β), 8.44–8.49 (m, 4 H, H-β), 8.86 (d, ^3J = 4.04 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 639.1 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 407 (103.3), 426 (84.8), 567 (15.5), 604 (12.2), 638 nm (8.7). $C_{44}H_{41}N_5\cdot CH_3OH$ (671.9): calcd. C 80.44, H 6.75, N 10.42; found C 80.97, H 6.37, N 10.43.

10-(4-Aminomethylphenyl)-5,15-bis(2,6-dichlorophenyl)corrole (12): The same procedure as before was used for the synthesis of **12** from triphenylphosphane (0.29 g, 1.11 mmol, 1.3 equiv.), distilled water (60 μL, 3.42 mmol, 4 equiv.), THF (20 mL) and corrole **10** (0.62 g, 0.86 mmol) in THF (30 mL). **12** (330 mg, 56%) was obtained as a dark blue solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 1.05 (br. s, 2 H, NH_2), 4.04 (s, 2 H, CH_2), 7.57 (d, ^3J = 7.80 Hz, 2 H, Ar-H), 7.65 (d, ^3J = 8.13 Hz, 2 H, Ar-H), 7.77 (d, ^3J = 8.13 Hz, 4 H, Ar-H), 8.12 (d, ^3J = 7.80 Hz, 2 H, Ar-H), 8.40 (d, ^3J = 4.10 Hz, 2 H, H-β), 8.51 (d, ^3J = 4.64 Hz, 2 H, H-β), 8.58 (d, ^3J = 4.64 Hz, 2 H, H-β), 8.99 (d, ^3J = 4.10 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 691.2 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (88.9), 425 (72.3), 562 (12.8), 608 (8.8), 636 nm (4.9). $C_{38}H_{25}Cl_4N_5$ (693.4): calcd. C 65.82, H 3.63, N 10.10; found C 65.38, H 3.39, N 10.20.

5,15-Dimesityl-10-{4-[3-(3-triethoxysilylpropyl)ureidomethyl]-phenyl}corrole (13): A solution of (3-isocyanatopropyl)triethoxysilane, (IPTES, 0.12 g, 0.50 mmol, 1.2 equiv.) in acetonitrile (5 mL) was added to a solution of the corrole **11** (0.27 g, 0.42 mmol) in the same solvent (15 mL). The mixture was refluxed for 12 h. After cooling down to room temperature, the mixture was taken with dichloromethane (20 mL) and then evaporated under vacuum. After recrystallization from CH_2Cl_2/heptane, compound **13** (0.30 g, 82%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.50 (br. s, 3 H, NH), 0.71 (m, 2 H, C*H*$_2$Si), 1.23 (m, 9 H, OCH$_2$C*H*$_3$), 1.72 (m, 2 H, C*H*$_2$CH$_2$Si), 1.92 (s, 12 H, Ar-CH$_3$), 2.60 (s, 6 H, Ar-CH$_3$), 3.29 (m, 2 H, C*H*$_2$CH$_2$CH$_2$Si), 3.84 (m, 6 H, OC*H*$_2$CH$_3$), 4.70 (s, 2 H, Ar-CH$_2$), 4.93 (br. s, 1 H, N*H*CO), 6.91 (br. s, 1 H, N*H*CO), 7.26 (s, 4 H, Ar-H), 7.64 (d, ^3J = 6.88 Hz, 2 H, Ar-H), 8.11 (d, ^3J = 6.88 Hz, 2 H, Ar-H), 8.32 (d, ^3J = 3.90 Hz, 2 H, H-β), 8.45–8.48 (m, 4 H, H-β), 8.88 (d, ^3J = 3.90 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 887.2 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 408 (112.8), 426 (89.4), 568 (14.9), 605 (10.3), 637 nm (5.4). $C_{54}H_{62}N_6O_4Si$ (887.2): calcd. C 73.10, H 7.04, N 9.47; found C 73.20, H 6.76, N 9.54.

5,15-Bis(2,6-dichlorophenyl)-10-{4-[3-(3-triethoxysilylpropyl)-ureidomethyl]phenyl}corrole (14): The same procedure as described for **13** was used for the synthesis of **14**, starting from **12** (0.31 g, 0.45 mmol) in acetonitrile (15 mL) and (3-isocyanatopropyl)triethoxysilane (0.14 g, 0.56 mmol, 1.25 equiv.) in acetonitrile (15 mL). Corrole **14** (0.38 g, 91%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.10 (br. s, 3 H, NH), 0.72 (t, ^3J = 7.98 Hz, 2 H, C*H*$_2$Si), 1.23 (t, ^3J = 7.00 Hz, 9 H, OCH$_2$C*H*$_3$), 1.70–1.75 (m, 2 H, C*H*$_2$CH$_2$Si), 3.30 (m, 2 H, C*H*$_2$CH$_2$CH$_2$Si), 3.84 (q, ^3J = 7.00 Hz, 6 H, OC*H*$_2$CH$_3$), 4.67 (m, 1 H, N*H*CO), 4.70 (d, ^3J = 5.75 Hz, 2 H, Ar-CH$_2$), 4.89 (m, 1 H, N*H*CO), 7.62–7.66 (m, 4 H, Ar-H), 7.76 (d, ^3J = 8.21 Hz, 4 H, Ar-H), 8.13 (d, ^3J = 7.92 Hz, 2 H, Ar-H), 8.41 (d, ^3J = 4.04 Hz, 2 H, H-β), 8.51 (d, ^3J = 4.64 Hz, 2 H, H-β), 8.56 (d, ^3J = 4.64 Hz, 2 H, H-β), 8.99 (d, ^3J = 4.04 Hz, 2 H, H-β). MS (MALDI/TOF): *m/z* = 938.2 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (121.0), 425 (98.6), 563 (17.5), 608 (11.7), 636 nm (6.5). $C_{48}H_{46}Cl_4N_6O_4Si\cdot H_2O$ (958.8): calcd. C 60.13, H 5.05, N 8.76; found C 60.42, H 5.04, N 8.45.

5,15-Bis(4-chloroacetoxy-2,6-dimethylphenyl)-10-(4-cyanophenyl)-corrole (15): The same procedure as described for the corrole **9** was used from 4-cyanobenzaldehyde (1.57 g, 12 mmol), dipyrromethane **6** (8.23 g, 24 mmol, 2 equiv.), dichloromethane (0.72 L) and TFA (72 μL, 0.96 mmol, 0.08 equiv.). The reaction mixture was diluted

by the addition of CH_2Cl_2 (1.5 L) and then a solution of DDQ (5.4 g, 24 mmol, 2 equiv.) in tetrahydrofuran (500 mL). This mixture was stirred at room temperature for 30 min, concentrated under vacuum and filtered through a silica pad. After evaporation, the resulting solid was chromatographed on silica gel with CH_2Cl_2 as eluent. After recrystallization from CH_2Cl_2/heptane, the corrole **15** (1.68 g, 18%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.01 (br. s, 3 H, NH), 1.95 (s, 12 H, CH_3), 4.46 (s, 4 H, CH_2), 7.26 (s, 4 H, Ar-H), 8.03 (d, ^3J = 8.11 Hz, 2 H, Ar-H), 8.28 (d, ^3J = 8.11 Hz, 2 H, Ar-H), 8.37 (d, ^3J = 4.18 Hz, 2 H, H-β), 8.43 (d, ^3J = 4.75 Hz, 2 H, H-β), 8.53 (d, ^3J = 4.75 Hz, 2 H, H-β), 8.95 (d, ^3J = 4.18 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 790.8 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (141.5), 428 (115.3), 566 (23.3), 602 (13.4), 634 (5.3). $C_{46}H_{35}Cl_2N_5O_4$ (792.7): calcd. C 69.70, H 4.45, N 8.83; found C 69.54, H 4.43, N 8.73.

5,15-Bis(4-chloroacetoxy-2,6-dichlorophenyl)-10-(4-cyanophenyl)-corrole (16): The same procedure as described for the corrole **9** was carried out using 4-cyanobenzaldehyde (2.10 g, 16 mmol), the dipyrromethane **7** (12.28 g, 32 mmol, 2 equiv.), dichloromethane (0.96 L) and TFA (96 μL, 1.30 mmol, 0.08 equiv.). The reaction mixture was diluted with CH_2Cl_2 (2.5 L) and a solution of DDQ (7.2 g, 32 mmol, 2 equiv.) in tetrahydrofuran (500 mL) added. This mixture was stirred at room temperature for 30 min, concentrated under vacuum and filtered through a silica pad. After evaporation, the resulting solid was chromatographed on silica gel using CH_2Cl_2 as eluent. After recrystallization from CH_2Cl_2/heptane, the corrole **16** (0.77 g, 5.5%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.05 (br. s, 3 H, NH), 4.47 (s, 4 H, CH_2), 7.66 (s, 4 H, Ar-H), 8.04 (d, ^3J = 8.02 Hz, 2 H, Ar-H), 8.31 (d, ^3J = 8.02 Hz, 2 H, Ar-H), 8.46 (d, ^3J = 4.14 Hz, 2 H, H-β), 8.51 (d, ^3J = 4.58 Hz, 2 H, H-β), 8.58 (d, ^3J = 4.58 Hz, 2 H, H-β), 9.04 (d, ^3J = 4.14 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 871.0 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 410 (139.5), 425 (116.6), 568 (21.9), 607 (12.8), 636 nm (4.5). $C_{42}H_{23}Cl_6N_5O_4\cdot CH_2Cl_2$ (959.3): calcd. C 53.84, H 2.63, N 7.30; found C 53.82, H 2.84, N 7.34.

10-(4-Cyanophenyl)-5,15-bis(4-hydroxy-2,6-dimethylphenyl)corrole (17): The corrole **15** (1.35 g, 1.71 mmol) and benzylamine (2 mL, 18.3 mmol, 10 equiv.) were dissolved in tetrahydrofuran (200 mL) and ethanol (200 mL). The reaction mixture was refluxed for 1 h and the solvents evaporated under vacuum. The resulting solid was crystallized from CH_2Cl_2/heptane, filtered off and then chromatographed on silica gel with two different elution mixtures of CH_2Cl_2 and EtOAc (95:5 and 85:15). After recrystallization from CH_2Cl_2/heptane, the corrole **17** (0.83 g, 76%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.13 (br. s, 3 H, NH), 1.26 (br. s, 2 H, OH), 1.89 (s, 6 H, CH_3), 6.89 (s, 4 H, Ar-H), 8.02 (d, ^3J = 8.24 Hz, 2 H, Ar-H), 8.29 (d, ^3J = 8.24 Hz, 2 H, Ar-H), 8.34 (d, ^3J = 3.96 Hz, 2 H, H-β), 8.40 (d, ^3J = 4.88 Hz, 2 H, H-β), 8.52 (d, ^3J = 4.88 Hz, 2 H, H-β), 8.90 (d, ^3J = 3.96 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 639.8 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (162.3), 428 (125.2), 567 (36.1), 602 (27.9), 636 (19.7). $C_{42}H_{33}N_5O_2\cdot 0.5H_2O$ (648.8): calcd. C 77.76, H 5.28, N 10.79; found C 77.37, H 5.35, N 10.60.

5,15-Bis(2,6-dichloro-4-hydroxyphenyl)-10-(4-cyanophenyl)corrole (18): The corrole **16** (0.75 g, 0.86 mmol) and benzylamine (207 μL, 1.89 mmol, 2.2 equiv.) were dissolved in tetrahydrofuran (50 mL) and ethanol (50 mL). The mixture was refluxed for 5 h and then evaporated under vacuum. The resulting solid was chromatographed on silica gel with CH_2Cl_2 and CH_2Cl_2/EtOAc (95:10) as eluents. After recrystallization from CH_2Cl_2/EtOAc/heptane, the corrole **18** (0.53 g, 85%) was obtained as a dark violet solid. ^{1}H NMR [500 MHz, $(CD_3)_3CO$, 303 K]: δ = 7.38 (s, 4 H, Ar-H), 8.18 (d, ^3J = 6.40 Hz, 2 H, Ar-H), 8.37 (d, ^3J = 6.40 Hz, 2 H, Ar-H), 8.42 (br. s, 2 H, H-β), 8.50 (br. s, 2 H, H-β), 8.61 (br. s, 2 H, H-β), 9.07 (br. s, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 719.6 $[M]^{+\cdot}$. UV/Vis (EtOAc, $\varepsilon \times 10^{-3}$ $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 410 (134.0), 428 (99.4), 570 (23.8), 607 (13.8), 642 nm (3.0). $C_{38}H_{21}Cl_4N_5O_2\cdot 0.5EtOAc$ (765.5): calcd. C 62.76, H 3.29, N 9.15; found C 62.81, H 3.52, N 9.14.

10-(4-Cyanophenyl)-5,15-bis{2,6-dimethyl-4-[(3-triethoxysilylpropyl)aminocarbonyloxy]phenyl}corrole (19): The corrole **17** (1.12 g, 1.75 mmol), (3-isocyanatopropyl)triethoxysilane (3.47 g, 14.0 mmol, 8 equiv.) and diisopropylethylamine (1.81 g, 14.0 mmol, 8 equiv.) were dissolved in acetonitrile (125 mL). The mixture was refluxed for 7 days. After cooling down to room temperature, the mixture was diluted with dichloromethane (50 mL) and the solvents evaporated under vacuum. The solid was twice recrystallized from CH_2Cl_2/heptane, filtered off and washed with pentane leading to corrole **19** (1.314 g, 66%) as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.90 (br. s, 3 H, NH), 0.79 (t, ^3J = 7.98 Hz, 4 H, CH_2Si), 1.29 (t, ^3J = 7.06 Hz, 18 H, OCH_2CH_3), 1.79–1.87 (m, 4 H, CH_2CH_2Si), 1.93 (s, 12 H, Ar-CH_3), 3.39–3.43 (m, 4 H, $CH_2CH_2CH_2Si$), 3.91 (q, ^3J = 7.06 Hz, 12 H, OCH_2CH_3), 5.52–5.55 (m, 2 H, NHCO), 7.24 (s, 4 H, Ar-H), 8.02 (d, ^3J = 7.86 Hz, 2 H, Ar-H), 8.28 (d, ^3J = 7.86 Hz, 2 H, Ar-H), 8.36 (d, ^3J = 3.84 Hz, 2 H, H-β), 8.40 (d, ^3J = 4.56 Hz, 2 H, H-β), 8.54 (d, ^3J = 4.56 Hz, 2 H, H-β), 8.91 (d, ^3J = 3.84 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 1133.8 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (107.0), 427 (82.1), 567 (16.2), 602 (11.0), 635 nm (5.5). $C_{62}H_{75}N_7O_{10}Si_2\cdot H_2O$ (1152.5): calcd. C 64.61, H 6.73, N 8.51; found C 64.77, H 7.07, N 8.73.

5,15-Bis{2,6-dichloro-4-[(3-triethoxysilylpropyl)aminocarbonyloxy]-phenyl}-10-(4-cyanophenyl)corrole (20): The same procedure as described for corrole **19** was used starting from **18** (0.46 g, 0.64 mmol), (3-isocyanatopropyl)triethoxysilane (1.26 g, 5.10 mmol, 8 equiv.), diisopropylethylamine (0.66 g, 5.10 mmol, 8 equiv.) in acetonitrile (40 mL). After purification, **20** (0.707 g, 91%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.03 (br. s, 3 H, NH), 0.78 (t, ^3J = 7.85 Hz, 4 H, CH_2Si), 1.31 (t, ^3J = 6.98 Hz, 18 H, OCH_2CH_3), 1.82–1.86 (m, 4 H, CH_2CH_2Si), 3.42 (m, 4 H, $CH_2CH_2CH_2Si$), 3.92 (q, ^3J = 6.98 Hz, 12 H, OCH_2CH_3), 5.73 (m, 2 H, NHCO), 7.63 (s, 4 H, Ar-H), 8.03 (d, ^3J = 7.92 Hz, 2 H, Ar-H), 8.31 (d, ^3J = 7.92 Hz, 2 H, Ar-H), 8.46 (d, ^3J = 4.06 Hz, 2 H, H-β), 8.50 (d, ^3J = 4.61 Hz, 2 H, H-β), 8.61 (d, ^3J = 4.61 Hz, 2 H, H-β), 9.01 (d, ^3J = 4.06 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* 1212.9 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 411 (120.2), 426 (99.0), 568 (19.4), 607 (11.7), 635 nm (4.9). $C_{58}H_{63}Cl_4N_7O_{10}Si_2\cdot 2\,H_2O$ (1252.2): calcd. C 55.63, H 5.39, N 7.83; found C 55.43, H 5.64, N 8.08.

5,15-Bis[2,6-dichloro-4-(2-phthalimidoethoxy)phenyl]-10-(4-fluorophenyl)corrole (21): The same procedure as described for corrole **9** was used starting from 4-fluorobenzaldehyde (0.68 g, 5.5 mmol), dipyrromethane **8** (5.29 g, 11 mmol, 2 equiv.), dichloromethane (0.33 L) and TFA (33 μL, 0.44 mmol, 0.08 equiv.). The reaction mixture was diluted by the addition of CH_2Cl_2 (3.3 L) and of a solution of DDQ (2.48 g, 11 mmol, 2 equiv.) in tetrahydrofuran (200 mL). The mixture was stirred at room temperature during 30 min, concentrated under vacuum and filtered through a silica pad. After evaporation, the solid was chromatographed on silica gel with CH_2Cl_2 as eluent. Recrystallization from CH_2Cl_2/heptane, led to **21** (0.63 g, 10.7%) as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.05 (br. s, 3 H, NH), 4.28 (t, ^3J

= 5.57 Hz, 2 H, CH_2), 4.49 (t, ^3J = 5.57 Hz, 2 H, CH_2), 7.31 (s, 4 H, Ar-H), 7.40 (m, 2 H, Ar-H), 7.79 (m, 4 H, Ar-H), 7.95 (m, 4 H, Ar-H), 8.10 (m, 2 H, Ar-H), 8.36 (d, ^3J = 3.95 Hz, 2 H, H-β), 8.50 (m, 4 H, H-β), 8.95 (d, ^3J = 4.19 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 1057.7 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 410 (89.1), 424 (73.4), 568 (13.0), 609 (9.8), 635 nm (5.3). $C_{57}H_{35}Cl_4FN_6O_6$ (1060.7): calcd. C 64.54, H 3.33, N 7.92; found C 64.37, H 3.88, N 7.69.

5,15-Bis[4-(2-aminoethoxy)-2,6-dichlorophenyl]-10-(4-fluorophenyl)-corrole (22): Corrole **21** (0.62 g, 0.58 mmol) and hydrazine monohydrate (2.84 mL, 58.4 mmol, 100 equiv.) were dissolved in ethanol (80 mL). The reaction mixture was then refluxed during one night and the solvents evaporated. The resulting solid was dissolved in dichloromethane, washed two times with an aqueous solution of NaOH (5%), water, dried with $MgSO_4$ and the solvents evaporated to dryness. The solid was chromatographed on basic alumina with CH_2Cl_2/MeOH (90:10) as eluent. Recrystallization from CH_2Cl_2/heptane gave the corrole **22** (0.15 g, 32%) as a dark violet solid. ^{1}H NMR [500 MHz, $(CD_3)_2SO$, 303 K]: δ = 3.22 (t, ^3J = 5.07 Hz, 2 H, CH_2), 3.23–3.40 (br. s, 7 H, NH and NH_2), 4.38 (t, ^3J = 5.07 Hz, 2 H, CH_2), 7.50–7.53 (m, 4 H+2 H, Ar-H), 8.09–8.12 (m, 2 H, Ar-H), 8.18–8.23 (m, 6 H, H-β), 8.84 (d, ^3J = 4.05 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 798.2 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 410 (85.4), 425 (65.4), 570 (13.4), 609 (9.3), 639 nm (4.1). $C_{41}H_{31}Cl_4FN_6O_2\cdot 0.5H_2O$ (809.6): calcd. C 60.83, H 3.98, N 10.38; found C 61.02, H 4.29, N 10.21.

5,15-Bis{2,6-dichloro-4-[2-(3-triethoxysilylpropylureido)ethoxy]-phenyl}-10-(4-fluorophenyl)corrole (23): Corrole **22** (0.13 g, 0.16 mmol) was dissolved in acetonitrile (15 mL) followed by the addition of a solution of (3-isocyanatopropyl)triethoxysilane (0.10 g, 0.41 mmol, 2.5 equiv.) in acetonitrile (5 mL). The mixture was refluxed for 12 h, diluted with dichloromethane (25 mL) and the solvents evaporated. The resulting solid was recrystallized from CH_2Cl_2/heptane, yielding the corrole **23** (0.18 g, 84%) as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 323 K): δ = –1.90 (br. s, 3 H, NH), 0.70 (t, ^3J = 7.91 Hz, 4 H, CH_2Si), 1.26 (t, ^3J = 6.95 Hz, 18 H, OCH_2CH_3), 1.68–1.73 (m, 4 H, CH_2CH_2Si), 3.24–3.28 (m, 4 H, $CH_2CH_2CH_2$Si), 3.75 (m, 4 H, OCH_2CH_2NH), 3.87 (q, ^3J = 6.95 Hz, 12 H, OCH_2CH_3), 4.30 (m, 4 H, OCH_2CH_2NH), 4.70 (m, 2 H, NHCO), 4.89 (m, 2 H, NHCO), 7.33 (s, 4 H, Ar-H), 7.38–7.42 (m, 2 H, Ar-H), 8.10–8.13 (m, 2 H, Ar-H), 8.39 (d, ^3J = 3.96 Hz, 2 H, H-β), 8.52–8.55 (m, 4 H, H-β), 8.96 (d, ^3J = 3.96 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 1292.7 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (112.4), 424 (86.4), 569 (19.2), 609 (13.7), 639 nm (7.3). $C_{61}H_{73}Cl_4FN_8O_{10}Si_2$ (1295.3): calcd. C 56.56, H 5.68, N 8.65; found C 56.45, H 5.76, N 8.54.

10-[4-(Chloroacetoxy)phenyl]-5,15-bis(4-chloroacetoxy-2,6-dimethylphenyl)corrole (24): The same procedure as described for the corrole **9** was carried out using 4-(chloroacetoxy)benzaldehyde (**4**) (3.18 g, 16 mmol), the dipyrromethane **6** (10.96 g, 32 mmol, 2 equiv.), dichloromethane (0.96 L) and TFA (96 μL, 1.28 mmol, 0.08 equiv.). The reaction mixture was diluted by CH_2Cl_2 (1.92 L) and a solution of DDQ (7.2 g, 32 mmol, 2 equiv.) in tetrahydrofuran (200 mL). This mixture was then stirred at room temperature for 30 min, concentrated and filtered through a silica pad. After evaporation, the resulting solid was chromatographed on silica gel with CH_2Cl_2/heptane (7:1 and 9:1) as eluents. Recrystallization from CH_2Cl_2/heptane led to the corrole **24** (1.72 g, 13%) as dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.72 (br. s, 3 H, NH), 1.95 (s, 12 H, CH_3), 4.46 (s, 4 H, CH_2), 4.48 (s, 2 H, CH_2), 7.25 (s, 4 H, Ar-H), 7.52 (d, ^3J = 8.54 Hz, 2 H, Ar-H), 8.18 (d, ^3J = 8.54 Hz, 2 H, Ar-H), 8.35 (d, ^3J = 3.97 Hz, 2 H, H-β), 8.51 (m, 4 H, H-β), 8.93 (d, ^3J = 3.97 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 857.9 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 407 (124.0), 426 (95.4), 566 (18.6), 603 (12.0), 635 (5.9). $C_{47}H_{37}Cl_3N_4O_6$ (860.2): calcd. C 65.63, H 4.34, N 6.51; found C 65.56, H 4.15, N 6.47.

5,15-Bis[2,6-dichloro-4-(chloroacetoxy)phenyl]-10-[4-(chloroacetoxy)phenyl]corrole (25): The same procedure as described for the corrole **9** was carried out using 4-(chloroacetoxy)benzaldehyde **4** (3.24 g, 16 mmol), dipyrromethane **7** (12.50 g, 32 mmol, 2 equiv.), dichloromethane (0.96 L) and TFA (96 μL, 1.28 mmol, 0.08 equiv.). The reaction mixture was diluted by the addition of CH_2Cl_2 (2.5 L) and a solution of DDQ (7.2 g, 32 mmol, 2 equiv.) in tetrahydrofuran (200 mL). This mixture was stirred at room temperature for 30 min, concentrated and filtered through a silica pad. After evaporation, the resulting solid was chromatographed on silica gel with CH_2Cl_2/heptane (85:15 and 9:1) as eluents. After recrystallization from CH_2Cl_2/heptane, the corrole **25** (394 mg, 2.6%) is obtained as dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –2.07 (br. s, 3 H, NH), 4.47 (s, 4 H, CH_2), 4.48 (s, 4 H, CH_2), 7.52 (d, ^3J = 8.41 Hz, 2 H, Ar-H), 7.66 (s, 4 H, Ar-H), 8.21 (d, ^3J = 8.41 Hz, 2 H, Ar-H), 8.45 (d, ^3J = 4.18 Hz, 2 H, H-β), 8.56 (d, ^3J = 4.63 Hz, 2 H, H-β), 8.62 (d, ^3J = 4.63 Hz, 2 H, H-β), 9.03 (d, ^3J = 4.18 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 938.3 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 409 (130.1), 424 (104.3), 567 (19.0), 608 (12.2), 636 nm (5.8). $C_{43}H_{25}Cl_7N_4O_6$ (941.9): calcd. C 54.83, H 2.68, N 5.95; found C 54.54, H 2.57, N 5.95.

5,15-Bis(4-hydroxy-2,6-dimethylphenyl)-10-(4-hydroxyphenyl)-corrole (26): Corrole **24** (2.23 g, 2.6 mmol) and benzylamine (3 mL, 18.3 mmol, 10 equiv.) were dissolved in tetrahydrofuran (200 mL) and ethanol (200 mL). The mixture was refluxed for 1 h and the solvents evaporated under vacuum. The solid was crystallized CH_2Cl_2/heptane, filtered off and then chromatographed on silica gel with different elution mixtures of CH_2Cl_2 and EtOAc (9:1 and 8:2). After recrystallization from CH_2Cl_2/heptane, the corrole **26** (1.23 g, 75%) was obtained as a dark violet solid. ^{1}H NMR [500 MHz, $(CD_3)_2CO$, 303 K]: δ = 1.90 (s, 6 H, CH_3), 2.84 (br. s, 3 H, OH), 6.97 (s, 4 H, Ar-H), 7.23 (d, ^3J = 8.54 Hz, 2 H, Ar-H), 7.94 (d, ^3J = 8.54 Hz, 2 H, Ar-H), 8.25 (d, ^3J = 3.66 Hz, 2 H, H-β), 8.44–8.48 (m, 4 H, H-β), 8.94 (d, ^3J = 4.27 Hz, 2 H, H-β). MS (MALDI/TOF): m/z = 630.2 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 404 (88.9), 425 (62.8), 567 (12.9), 605 (10.7), 636 (8.2). $C_{41}H_{34}N_4O_3\cdot 0.5H_2O$ (639.8): calcd. C 76.98, H 5.51, N 8.76; found C 76.80, H 5.87, N 8.43.

5,15-Bis(2,6-dichloro-4-hydroxyphenyl)-10-(4-hydroxyphenyl)corrole (27): The corrole **25** (0.35 g, 0.38 mmol) and benzylamine (135 μL, 1.23 mmol, 3.3 equiv.) were dissolved in tetrahydrofuran (30 mL) and ethanol (30 mL). The mixture was refluxed for 6 h and the solvents evaporated. The solid was chromatographed on silica gel with EtOAc/heptane (1:3) as eluent. Recrystallization from EtOAc/heptane led to the corrole **27** (0.23 g, 87%) as a dark violet solid. ^{1}H NMR [500 MHz, $(CD_3)_2CO$, 303 K]: δ = 7.25 (br. s, 4 H, Ar-H), 7.37 (br. s, 4 H, Ar-H), 7.97 (br. s, 2 H, H-β), 8.39 (br. s, 2 H, H-β), 8.56 (br. s, 2 H, H-β), 9.04 (br. s, 2 H, H-β). MS (MALDI/TOF): m/z = 709.6 $[M]^{+\cdot}$. UV/Vis [$(CH_3)_2CO$, $\varepsilon \times 10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$]: λ_{max} = 405 (60.5), 424 (47.5), 569 (13.2), 608 (9.3), 633 nm (9.5). $C_{37}H_{22}Cl_4N_4O_3\cdot 0.5$ EtOAc (756.5): calcd. C 61.92, H 3.46, N 7.41; found C 61.74, H 3.62, N 7.39.

5,15-Bis{2,6-dimethyl-4-[(3-triethoxysilylpropyl)aminocarbonyloxy]-phenyl}-10-{4-[(3-triethoxysilylpropyl)aminocarbonyloxy]-phenyl}corrole (28): The corrole **26** (0.51 g, 0.80 mmol), (3-isocyanatopropyl)triethoxysilane (2.4 g, 9.7 mmol, 12 equiv.) and diiso-

propylethylamine (0.63 g, 4.85 mmol, 6 equiv.) were dissolved in acetonitrile (30 mL) and tetrahydrofuran (30 mL). The mixture was refluxed for 7 days. After cooling to room temperature, the solution was diluted with dichloromethane (30 mL) and the solvents evaporated. The resulting solid was twice recrystallized from CH_2Cl_2/heptane, filtered off and washed with pentane. The corrole **28** (0.80 g, 72%) was obtained as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.95 (br. s, 3 H, NH), 0.79 (m, 6 H, CH_2Si), 1.30 (m, 27 H, OCH$_2$CH_3), 1.82 (m, 6 H, CH_2CH$_2$Si), 1.93 (s, 12 H, Ar-CH$_3$), 3.41 (m, 6 H, CH_2CH$_2$CH$_2$Si), 3.90 (m, 18 H, OCH_2CH$_3$), 5.55 (m, 3 H, N*H*CO), 7.23 (s, 4 H, Ar-H), 7.49 (d, ^3J = 8.21 Hz, 2 H, Ar-H), 8.12 (d, ^3J = 8.21 Hz, 2 H, Ar-H), 8.34 (d, ^3J = 3.95 Hz, 2 H, H-β), 8.49 (d, ^3J = 4.69 Hz, 2 H, H-β), 8.52 (d, ^3J = 4.69 Hz, 2 H, H-β), 8.89 (d, ^3J = 3.95 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* 1372.0 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon\times10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 408 (113.2), 426 (89.3), 566 (15.1), 604 (10.1), 635 nm (5.1). $C_{71}H_{97}N_7O_{15}Si_3\cdot H_2O$ (1390.9): calcd. C 61.31, H 7.17, N 7.05; found C 61.52, H 7.41, N 7.31.

5,15-Bis{2,6-dichloro-4-[(3-triethoxysilylpropyl)aminocarbonyloxy]-phenyl}-10-{4-[(3-triethoxysilylpropyl)aminocarbonyloxy]-phenyl}corrole (29): A solution of (3-isocyanatopropyl)triethoxysilane (0.90 g, 3.64 mmol, 12 equiv.) and diisopropylethylamine (0.24 g, 1.82 mmol, 6 equiv.) in acetonitrile (5 mL) was added to a solution of the corrole **27** (0.22 g, 0.30 mmol) in acetonitrile (8 mL) and tetrahydrofuran (8 mL). The reaction mixture was refluxed for 7 days. After cooling to room temperature, this mixture was diluted with dichloromethane (30 mL) and the solvents evaporated. The solid was twice recrystallized from CH_2Cl_2/heptane, filtered off and washed with pentane leading to the corrole **29** (324 mg, 73%) as a dark violet solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = –1.90 (br. s, 3 H, NH), 0.78 (m, 6 H, CH_2Si), 1.30 (m, 27 H, OCH$_2$CH_3), 1.83 (m, 6 H, CH_2CH$_2$Si), 3.41 (m, 6 H, CH_2CH$_2$CH$_2$Si), 3.90 (m, 18 H, OCH_2CH$_3$), 5.57 (m, 1 H, N*H*CO), 5.74 (m, 2 H, N*H*CO), 7.50 (d, ^3J = 7.82 Hz, 2 H, Ar-H), 7.63 (s, 4 H, Ar-H), 8.15 (d, ^3J = 7.82 Hz, 2 H, Ar-H), 8.44 (d, ^3J = 3.80 Hz, 2 H, H-β), 8.56 (d, ^3J = 4.47 Hz, 2 H, H-β), 8.62 (d, ^3J = 4.47 Hz, 2 H, H-β), 8.99 (d, ^3J = 3.80 Hz, 2 H, H-β). MS (MALDI/TOF): *m*/*z* = 1451.6 $[M]^{+\cdot}$. UV/Vis (CH_2Cl_2, $\varepsilon\times10^{-3}$, $mol^{-1}\cdot L\cdot cm^{-1}$): λ_{max} = 410 (78.1), 423 (64.9), 568 (14.4), 609 (9.8), 636 nm (6.3). $C_{67}H_{85}Cl_4N_7O_{15}Si_3\cdot 3.5H_2O$ (1517.6): calcd. C 53.03, H 6.11, N 6.46; found C 52.78, H 6.47, N 6.83.

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