Efficient synthesis of aryldipyrromethanes in water and their application in the synthesis of corroles and dipyrromethenes

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Dedicated to Professor Alain Krief on the occasion of his 65th anniversary

Abstract

In this paper, we describe the efficient and selective synthesis of aryldipyrromethanes in aqueous medium by acid-catalyzed (HCl) condensations of aromatic aldehydes with 3 equivalents of pyrrole at room temperature. The precipitated aryldipyrromethanes can be isolated directly from the reaction mixture in an essentially pure state by simple filtration. Time control seems to be essential to avoid significant formation of the tripyrromethane analogue and the reaction time is strongly dependent on the nature of the aromatic aldehyde. A one-pot synthesis of several aryldipyrromethenes and various novel *meso*-aryl-substituted *trans*-A_2B-corroles was also achieved starting from the obtained aryldipyrromethanes. Trichloroacetic acid was the preferred acid catalyst for the preparation of *meso*-triarylcorroles from the condensation of 5-(2,6-dichlorophenyl)dipyrromethane with more reactive aldehydes, while trifluoroacetic acid was preferred for less reactive substrates.

Keywords: Condensation in water, dipyrromethanes, dipyrromethenes, *trans*-A_2B-corroles, *N*-alkylation

Introduction

Dipyrromethanes are widely being used as essential building blocks for the synthesis of a variety of functional porphyrins and (contracted and expanded) porphyrin analogues.[1] Moreover, dipyrromethanes are the precursors of BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene or boron dipyrromethene), which are currently receiving increasing attention due to their valuable properties, such as the relatively high absorption coefficients and fluorescence quantum yields, high (photo)chemical stability, and improved synthetic availability.[2] Nowadays, *meso*-substituted dipyrromethanes are usually prepared via a one-flask method based on the acid-catalyzed (e.g. trifluoroacetic acid) condensation of an appropriate aldehyde with an excess of pyrrole (used as

solvent) and flash chromatography is required in most cases to obtain the dipyrromethanes in high purity.[3] Although in recent years significant progress has been made regarding the efficient preparation of these dipyrrolic building blocks (e.g. to eliminate the use of chromatography),[4] most synthetic approaches still require an excess of pyrrole to ensure an optimal yield of the dipyrromethane (over the higher oligocondensates, e.g. tripyrromethane).

Recently, the use of water as a cheap and non-toxic solvent for organic reactions is of particular interest due to the increasing environmental concerns. In the search for 'green chemistry' methods, two research groups have reported the synthesis of dipyrromethanes via acid-catalyzed condensations in aqueous medium.[5] The first condensation reaction of unsubstituted pyrrole with carbonyl compounds (ketones and aldehydes) in water (at reflux temperature and catalyzed by HCl) has been described by Sobral *et al*.[5a] Their one-step procedure afforded β-free dipyrromethanes in moderate to high yields by using only a 2/1 ratio of pyrrole over the carbonyl compound. Moreover, the required dipyrromethane could be isolated in essentially pure form by a simple filtration from the (cooled) reaction mixture. Precipitation of the dipyrromethane from the aqueous layer as it is formed, forces the reaction to completion and protects the product from further reactions. Kral *et al.* reinvestigated the condensation of various aromatic aldehydes with pyrrole (at room temperature) and they found that a mixture of dipyrromethanes (DPMs) and tripyrromethanes (TPMs) is usually obtained and the selectivity for both oligocondensates depends on the nature of the carbonyl compound and can be controlled by the molar ratio and concentrations of the starting products and the acid catalyst (HCl).[5b] A high initial concentration and a 6/1 ratio (pyrrole/aldehyde) lead to preferential formation of the DPM. Based on the work of Kral, Gryko *et al.* have developed an efficient method for the synthesis of *meso*-substituted A_3- and *trans*-A_2B-triarylcorroles in a H_2O-MeOH mixture.[6] The increased solubility of the aryldipyrromethanes on adding methanol to the reaction mixture, allowed the efficient preparation of the bilane precursor, which was then oxidized to the corrole macrocycle (with DDQ).

For the last decade our group has dedicated a considerable part of its research to the development of synthetic methods for a variety of (macrocyclic) oligopyrrolic compounds, e.g. porphyrins,[7] corroles,[8] and BODIPY derivatives,[9] for which aryldipyrromethanes are crucial building blocks. Due to the attraction of the novel approach toward aryldipyrromethanes in aqueous medium,[5] we decided to (re)investigate the condensation of several aromatic aldehydes with pyrrole in water and expand the range of possible aldehyde substrates. Especially those (pyrrole unsubstituted) aryldipyrromethanes that are useful for our own research purposes were pursued.

Results and Discussion

We have observed that several aryldipyrromethanes **2a-i** could easily be obtained in high yields (69-97%) from the acid-catalyzed (HCl) condensation of the corresponding aldehyde precursors **1a-i** and 3 equivalents of pyrrole in water (Table 1, Scheme 1a). In the same way, bisdipyrromethane **2j** was obtained from terephthaldehyde (**1j**) and 6 equivalents of pyrrole (in 80% yield).

Table 1. Synthesis of aryldipyrromethanes

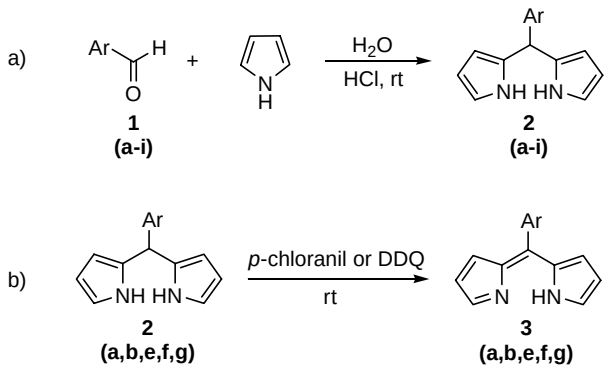
Aldehyde	Dipyrromethane	Time (h)	Ratio (pyrrole/aldehyde)	Yield (%)
benzaldehyde[a,b]	**2a**	4	3/1	86
p-tolualdehyde	**2b**	3	3/1	82
mesitaldehyde	**2c**	overnight	3/1	70
4-nitrobenzaldehyde[a,b]	**2d**	2	3/1	97
p-anisaldehyde[b]	**2e**	overnight	3/1	69
4-carboxybenzaldehyde	**2f**	8	3/1	72
methyl 4-formylbenzoate	**2g**	4	3/1	89
pentafluorobenzaldehyde[b]	**2h**	5	3/1	87
2,6-dichlorobenzaldehyde	**2i**	8	3/1	85
terephthaldehyde	**2j**	6	6/1	80
4-hydroxybenzaldehyde	**2k**	/	3/1	/

General conditions: room temperature, [HCl] = 0.18 M, [ald] = ~0.15 M. [a] ref. 5a. [b] ref. 5b.

The reactions were carried out in a 0.18 M aqueous HCl medium and 3 equivalents of pyrrole (compared to the 6-fold molar excess used by Kral *et al.*[5b]) were added, followed by the addition of 1 equivalent of the appropriate aromatic aldehyde **1a-i** (~0.15 M). The reaction mixture was stirred at room temperature and the reaction progress was followed by both TLC and mass spectrometry (until complete disappearance of the aldehyde was observed). After the indicated time (Table 1), the precipitated (semi-) solid product, which often sticks to the walls of the flask and the stirring bar and might hamper the stirring, was filtered off and washed with water and petroleum ether to afford DPMs **2a-i** in high yields. The reaction appears to be quite general. Only in the case of 4-hydroxybenzaldehyde (**1k**), no aryldipyrromethane was obtained, probably due to interference of the electron rich phenol moiety. The amount of TPM (and other side products) was usually negligible (as observed by ^{1}H NMR, MS and TLC) and DPMs **2a-i** were obtained in good purity (i.e. above 95%, as analyzed by ^{1}H NMR), although the DPMs (which are essentially white) often showed a grey or brown color. This result is similar to the observations made by Sobral *et al.* (at reflux temperature),[5a] but is in contrast to the results obtained by Kral *et al.*,[5b] where significant amounts of TPM were detected. It has to be noted however that the latter authors did not isolate the aryldipyrromethanes by filtration, but through extraction (thereby losing the benefit of selective DPM precipitation), while the reaction was generally run for 17 h. Time control seems to be crucial to obtain the required DPMs in high purity. Longer reaction times lead to a higher content of TPM impurity. Analysis (^{1}H NMR, TLC) of the initially formed precipitate showed a very high purity of the DPM, while the precipitate that is formed after longer reaction times showed a gradual increase in TPM content. Hence, it might be beneficial to filter the reaction mixture at an early stage of the reaction if a batch of DPM with superior purity is required, but the subsequent batches (which can be obtained from the filtrate after a longer reaction time) still show only a minimal content of TPM and can generally be applied as bipyrrolic building blocks. From Table 1 it can be observed that for the less reactive aldehydes, e.g. the electron rich *p*-anisaldehyde (**2e**), and the sterically hindered

aldehydes **2c** and **2i**, longer reaction times (8-12 h) are required to obtain the DPMs in an optimum yield, while for very reactive aldehydes, e.g. *p*-nitrobenzaldehyde (**2d**), a much shorter reaction time (only 2 h) was required.

Although these aryldipyrromethanes **2a-j** have been prepared before by other authors using 'classical' conditions,[3,4] the presented mild and efficient green method has the advantage that a large excess of pyrrole is no longer required. Moreover, the dipyrromethanes can be isolated easily from the reaction medium by simple filtration in an essentially pure state.



Scheme 1

From the obtained dipyrromethanes **2a,b,e,f,g**, the corresponding dipyrromethenes **3a,b,e,f,g** were synthesized according to a general procedure (Table 2, Scheme 1b).[10] Considering the limited stability of the (α'-unsubstituted) dipyrromethane skeleton, the observed yields (50-78%) are quite high. The oxidation of aryldipyrromethanes **2a,b,g** was conducted with *p*-chloranil (in dichloromethane), while for dipyrromethanes **2e,f** the use of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) was necessary to obtain the corresponding dipyrrins in good yields. Dipyrromethenes **3a** and **3g** have been prepared by other groups,[10] but the other dipyrrin derivatives **3b,e,f** have, to the best of our knowledge, never been isolated (and characterized) before.

Table 2. Synthesis of aryldipyrromethenes

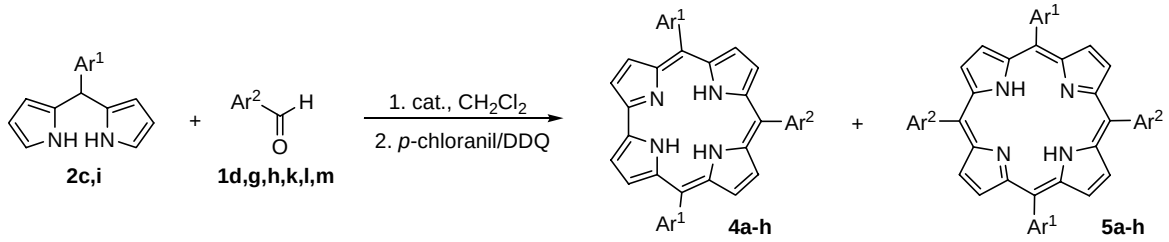
Dipyrromethane	Dipyrromethene	Oxidant	Time (h)	Yield (%)
2a	**3a**	*p*-chloranil	0.5	75
2b	**3b**	*p*-chloranil	1	78
2e	**3e**	DDQ	0.5	53
2f	**3f**	DDQ	0.5	50
2g	**3g**	*p*-chloranil	1	71

Corroles are ring-contracted porphyrin analogues lacking one *meso*-carbon atom.[1c] Until 1999, corroles were considered rather rare chemicals, quite unstable and difficult to prepare, but pioneering studies by Gross and Paolesse have afforded novel pathways toward (more) stable *meso*-triaryl-A_3-corroles.[11] This increased synthetic accessibility has triggered several other groups to

search for efficient synthetic procedures for a variety of triarylcorroles, in order to be able to explore their intriguing properties and potential applications (e.g. in catalysis) to a further extent.[12] The synthesis of *trans*-A_2B-corroles via the 2+1 (MacDonald type) condensation of aryldipyrromethanes with aromatic aldehydes has been investigated by several research groups (mainly by D. Gryko *et al.*) and has evolved to one of the most important pathways toward functional corroles.[6,13]

Interest in the synthesis of corroles in our laboratory was initially triggered by a rather unexpected result. As part of a project to prepare porphyrin derivatives out of 4,6-dichloropyrimidine-5-carbaldehyde,[7c] a 1+1 condensation of this aldehyde and 5-(2,6-dichlorophenyl)dipyrromethane (**2i**), catalyzed by boron trifluoride etherate ($BF_3{\cdot}OEt_2$), was performed (under Lindsey conditions). Surprisingly, the only identifiable product formed (in 25% yield) after *p*-chloranil oxidation, was the *trans*-A_2B-corrole, without formation of the corresponding A_2B_2-porphyrin.[8a] Under similar conditions, 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) could also be condensed with 2,6-dichlorobenzaldehyde (**1i**) and pentafluorobenzaldehyde (**1h**) to obtain the corresponding triarylcorroles (in 22 and 18% yield, respectively). However, oxidation was carried out using the Lee method[13a] (DDQ and NH_4Cl in propionitrile). Reaction of the same DPM **2i** with benzaldehyde (**1a**) or 4-nitrobenzaldehyde (**1d**) did not afford any corrole under these conditions. Some of these corroles have already been used as analytically active compounds in liquid membrane electrodes (ISEs) that are sensitive toward neutral nitrophenol isomers or salicylic acid and salicylate.[8b,8d,14]

In the present work, some of the obtained sterically hindered aryldipyrromethanes were used for the synthesis of both known (optimized procedures) and novel *trans*-A_2B-corroles **4a-h** (Scheme 2, Structure Block 1, Table 3).



Scheme 2

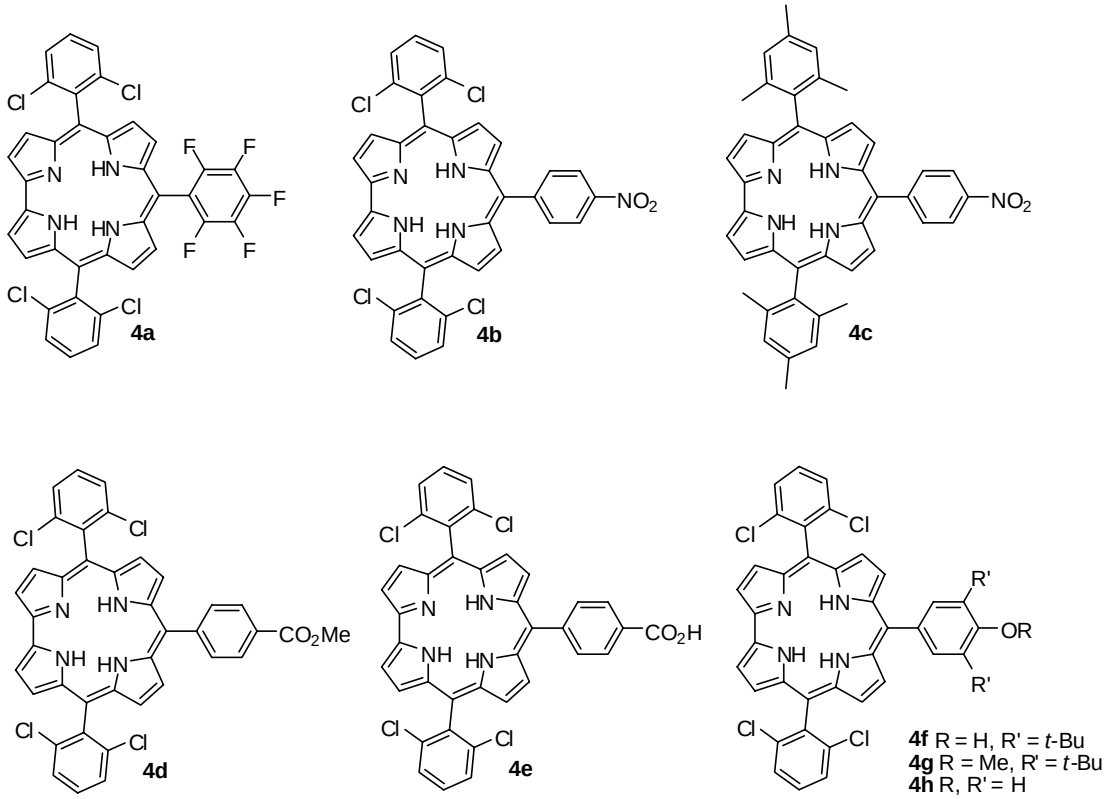
As a starting point, the previously prepared 5,15-bis(2,6-dichlorophenyl)-10-(pentafluorophenyl)corrole **4a** was chosen and we have tried to improve its yield (18%) by varying some reaction parameters.[8a] When the DPM/aldehyde content was raised to 1.5/1 and the $BF_3{\cdot}OEt_2$ concentration was raised to 0.85 equivalents, the only identifiable product was the corresponding A_2B_2-porphyrin **5a** (Table 3, entry 1). While it is well known that the porphyrin-forming reaction, as well as many other macrocyclization reactions, requires a rather low concentration of reactants to achieve a reasonable yield of product and a rather high concentration of acid is also needed, it appears from Gryko's work[13] that exactly the opposite, *i.e.* a high concentration of reactants and a

low concentration of acid catalyst is beneficiary if corroles are to be obtained. Increasing the DPM/aldehyde ratio to 3.9/1, while also lowering the concentrations of the substrates and the acid catalyst (0.24 equiv.) at the same time, provided corrole **4a** in 8% yield, with 11% of the A_2B_2-porphyrin analogue **5a** (entry 2). Also in this case Lee's method of oxidation was used.[13a] Finally, keeping relatively low concentrations of the substrates, but increasing the DPM/aldehyde ratio to 5/1 (approaching the preferred DPM/aldehyde ratio of Brückner[13c]), with a relatively low concentration of $BF_3{\cdot}OEt_2$ (0.37 equiv.) and using Lee-type oxidation (3 equiv. *p*-chloranil), corrole **4a** was obtained in 22% yield without detectable porphyrin formation (entry 3). Using similar conditions but a shorter reaction time (30 min) resulted in a sharp decrease of the corrole yield (11%, entry 4).

Table 3. Synthesis of *trans*-A_2B-corroles

Entry	Corr.	Ratio DPM/ald.	[ald] (mM)	Catalyst	Cond. time (h)	T	Yield (%)	Side products (%)
1	**4a**	1.5	11.7	$BF_3{\cdot}OEt_2$ 0.85 eq.	1	rt	0	A_2B_2-porphyrin **5a** (23)
2	**4a**	3.9	5.9	$BF_3{\cdot}OEt_2$ 0.24 eq.	1	rt	8	A_2B_2-porphyrin **5a** (11)
3	**4a**	5.2	4.3	$BF_3{\cdot}OEt_2$ 0.37 eq.	1	rt	22	/
4	**4a**	6.4	3.5	$BF_3{\cdot}OEt_2$ 0.37 eq.	0.5	rt	11	/
5	**4b**	3.5	17.9	TFA 0.32 eq.	5	rt	6	A_3-corrole (2)[a]
6	**4b**	3	11.9	TFA 0.076 eq.	7	0 °C	9	A_3-corrole (2)[a]
7	**4b**	4	12.4	$BF_3{\cdot}OEt_2$ 0.11 eq.	72	0 °C	4	/
8	**4b**	3.2	11.1	TCA 0.014 eq.	24	0 °C	17	A_3-corrole (2)[a], traces A_2B_2 + open chain prod.
9	**4c**	3.2	11.6	TCA 0.014 eq.	20	0 °C	18	traces, no A_2B_2
10	**4d**	3.2	11.5	TCA 0.016 eq.	22	0 °C	23	A_3-corrole (1)[a], DPM **2i**
11	**4f**	3.2	11.6	TCA 0.016 eq.	22	0 °C	0.2	A_3-corrole (2)[a], DPM **2i**
12	**4f**	5	4.4	$BF_3{\cdot}OEt_2$ 0.29 eq.	1	rt	/	A_2B_2-porphyrin **5f** (12.0) A_3B-porphyrin (2.8)
13	**4g**	3.2	15.3	TFA 0.18 eq.	18	rt	27	A_2B_2-porphyrin **5g** (1.8)
14	**4f**	3	15.3	TFA 0.18 eq.	48	rt	30	A_2B_2-porphyrin **5f** (0.7)
15	**4h**	3	15.3	TFA 0.18 eq.	17	rt	34/10	A_4-porphyrin (traces)

[a] with respect to DPM **2i**.



Structure Block 1

Contrary to the synthesis of corrole **4a**, preparation of 5,15-bis(2,6-dichlorophenyl)-10-(4-nitrophenyl)corrole **4b** had not been accomplished before.[8a] Therefore, we decided to try out synthetic conditions similar to those described by Gryko and Jadach.[13d] Reacting DPM **2i** and 4-nitrobenzaldehyde (**1d**) in a 3.5/1 ratio in dichloromethane with trifluoroacetic acid (TFA, 0.32 equiv.) as the catalyst, with subsequent oxidation by direct addition of a 2-fold molar excess (with respect to the aldehyde) of *p*-chloranil, afforded corrole **4b** in 6% yield (entry 5). However, several side-products were formed and the most prominent of them was identified as the corresponding A_3-corrole (5,10,15-tris(2,6-dichlorophenyl)corrole). Its formation can be explained by the well-known phenomenon of acid-induced 'scrambling' or 'redistribution' of the pyrrole rings of oligopyrrolic intermediates, which is caused by the acidic reagents that are often used to induce macrocyclization.[15] To avoid or at least lessen the amount of scrambling, we tried to carry out further experiments at 0 °C. However, this did not suppress the unwanted side reaction and the A_3-corrole could always be observed and isolated in 1–2% yield (with respect to the starting DPM **2i**). Applying a lower concentration of TFA (entry 6) caused an increase in the yield of the desired corrole **4b**, in agreement with Gryko's findings.[13d] Monitoring the reaction by TLC suggested that the condensation did not require 7 h and indeed, shortening the reaction time to 2 h gave a similar yield of corrole **4b** (10%). $BF_3{\cdot}OEt_2$ has also been tested as the acid catalyst for this reaction (entry 7). The A_3-corrole was not detected among the reaction products, but the formation of the desired corrole **4b** was also severely impeded (only 4%, even after 3 days of reaction). Using trichloroacetic

acid (TCA) as the acid catalyst provided higher yields of corrole **4b** (entry 8). Reaction with TCA in a concentration as low as ~1/75 (0.014 equiv.) compared to the concentration of the starting aldehyde **1d** afforded corrole **4b** in 17% yield. The reaction is rather sluggish and optimal yields are achieved only overnight. In this case, traces of the corresponding A_2B_2-porphyrin were also observed as well as a substantial amount of a red oligopyrrolic material.

Starting from 4-nitrobenzaldehyde (**1d**) and 5-mesityldipyrromethane (**2c**), the analogous *trans*-A_2B-corrole **4c** was also pursued using the same TCA-catalyzed condensation conditions (entry 9). The observed yield is similar to the one obtained using Gryko's conditions ([DPM] = 33 mM, [ald] = 17 mM, [TFA] = 1.3 mM, 5 h, rt; 19%).[13d]

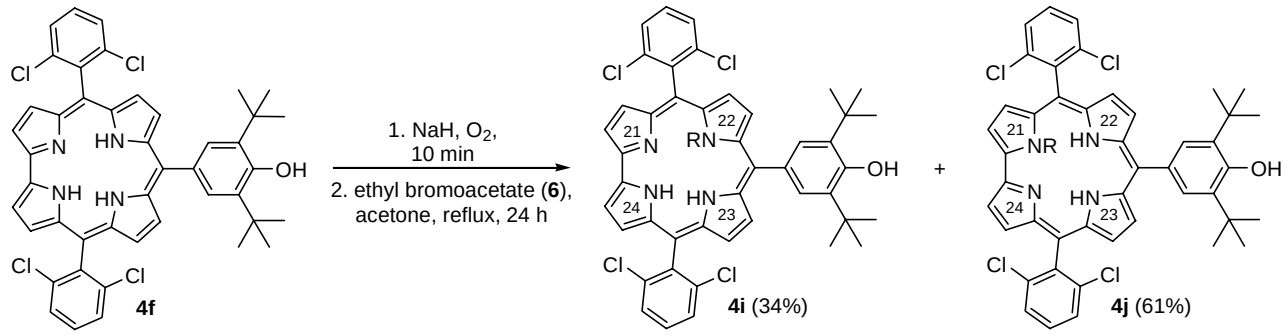
Using the same TCA-catalyzed reaction, a novel ester-functionalized A_2B-corrole **4d** was synthesized starting from 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and methyl 4-formylbenzoate (**1g**) (entry 10). The usual small amount (~1%) of A_3-corrole was again isolated from the reaction mixture, but the largest impurity was unreacted DPM **2i**, which could be chromatographically separated with some difficulty. The yield of the main corrole **4d** is rather high (23%) for corrole synthesis and several hundred milligrams (in one batch) of corrole could be collected and smoothly saponified to afford acid-functionalized corrole **4e** in a high yield (88%).

Finally, prompted by the interesting results that were previously obtained on the oxidative *N*-alkylation of porphyrins,[16] it was reasoned that the same type of reaction could also be carried out with corroles. For that purpose, the synthesis of a *meso*-hydroxyphenyl substituted corrole **4f** was required (Structure Block 1). However, procedures toward such corroles are hardly documented in the literature.[13,17] An attempt to synthesize corrole **4f** from commercial 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**1l**) and DPM **2i**, using the optimized TCA-conditions, afforded only traces of the desired corrole (entry 11). As indicated by TLC, most of the DPM remained unreacted under these conditions. Usage of $BF_3{\cdot}OEt_2$ in a higher concentration and Lee's oxidation method lead to significant formation of the A_2B_2- (**5f**) and A_3B-porphyrin. No corrole was detected in these experiments. In one case, with lowered concentrations of the starting compounds, the porphyrins were obtained in rather high yields, even though the DPM/aldehyde ratio should have strongly favoured corrole formation (entry 12). This turned actually out to be a good method for preparation of *trans*-A_2B_2-porphyrin **5f**. The failure to obtain large amounts of the desired corrole **4f** was first attributed to an oxidation of the di-*tert*-butyl-4-hydroxyphenyl substituent. Therefore aldehyde **1l** was methylated to obtain 3,5-di-*tert*-butyl-4-methoxybenzaldehyde (**1m**).[18] With this aldehyde, synthesis of the corresponding corrole **4g** was attempted under the usual TCA-conditions. Unfortunately, corrole **4g** was again obtained in a negligible quantity. Most of the starting materials remained unreacted under these conditions. Applying TFA as the acid catalyst (in a higher concentration) changed the picture (entry 13). Good yields of corrole **4g** (up to 27%) could be isolated upon column chromatographic separation from a small amount of A_2B_2-porphyrin **5g**. Demethylation of **4g** (with boron tribromide or diisobutylaluminium hydride) to afford hydroxyphenyl-substituted corrole **4f** was not successful. However, application of the obtained TFA-catalyzed conditions to the synthesis of corrole **4f** afforded the desired A_2B-corrole in 30% yield (entry 14).

Synthesis of the related *meso*-hydroxyphenylcorrole **4h** has also been attempted under exactly the same conditions (entry 15). After a tedious chromatographic procedure, A_2B-corrole **4h**, as apparent from ^{1}H NMR, could be isolated in a yield as high as 34%. However, the product seems to be rather unstable and could not be kept in pure form. The apparent yield after the next column chromatographic purification (carried out 2 days after the previous yield estimation) was only 10%.

From the performed condensation reactions toward *trans*-A_2B-corroles it can be concluded that TCA (and $BF_3{\cdot}OEt_2$ for **4a**) was the acid catalyst of choice, giving best yields, for the synthesis of corroles **4a,b,c,d**, starting from quite reactive aldehydes possessing electron-withdrawing substituents (and sterically hindered 5-(2,6-dichlorophenyl)dipyrromethane (**2i**)). On the other hand, TFA was preferred for the preparation of corroles **4f,g,h** from less reactive substrates possessing electron-donating substituents (-OR). Direct oxidation of the tetrapyrromethane formed (without its isolation), with adding an excess of *p*-chloranil into the crude reaction mixture, was the preferred method for the final oxidative ring closure.

Once a good and reliable method for the synthesis of corrole **4f** was established, it was possible to obtain enough of this product to serve as a substrate for the oxidative *N*-alkylation of the type described in one of our previous papers.[16] The reaction was performed under the general *N*-alkylation conditions (Scheme 3). Within 15 min of the addition of the alkylating agent (ethyl bromoacetate (**6**)), the major spot on TLC was still that of the starting corrole **4f**, without any spot similar to that of the oxidized intermediate in the analogous reaction with porphyrins. Running the reaction overnight changed the TLC picture into two (main) spots: one weaker, less polar green-brownish spot with a weak red fluorescence (under 366 nm excitation) and another stronger, somewhat more polar, blue-greenish spot with a strong red fluorescence. Upon isolation of the two products by column chromatography, it became rapidly clear that two isomeric *N*-alkylated non-oxidized corroles **4i** and **4j**, in about 1/2 ratio, had been obtained (Scheme 3).



Scheme 3

Lack of porphyrin-type conjugation probably inhibits formation of the necessary intermediates on the oxidation pathway.[16] The ability to introduce only one substituent per macrocycle molecule reflects the smaller size of the corrole cavity. The distribution of the substituent groups over the core nitrogen atoms (*i.e.* the ratio of the isomers) is in accordance with earlier published research on *N*-alkylation of corroles.[19] It has been shown that substitution on N(22) of triarylcorroles results in a

more crowded environment (as compared to the N(21)-substituted isomer), reflected in higher deformation of the corrole ring from planarity and of the *meso*-aryl groups from perpendicular orientation, rendering this isomer (**4i** in this case) less stable.

Conclusions

We have optimized a convenient and mild methodology for the synthesis of 5-aryldipyrromethanes in aqueous medium, needing little or no work-up (simple filtration from the reaction mixture). The synthetic route is based on the condensation of an aromatic aldehyde with a small excess of pyrrole (3 equiv.) in water as a solvent and catalyzed by HCl (0.18 M). This method appears to be quite general and by careful control of the reaction time, which is strongly dependent on the nature of the aldehyde, the dipyrromethanes can be obtained in a very selective way (essentially no tripyrromethane or other oligomeric side products are observed). This 'green' synthetic route toward dipyrromethanes in water, which we feel is undervalued at present, has been (and will be) an impulse for research toward oligopyrrolic macromolecules. The aryldipyrromethanes obtained by this efficient method were engaged in the synthesis of dipyrromethenes (toward BODIPY-derivatives) and *trans*-A_2B-corroles and the results obtained show essentially the same yields as for dipyrromethanes synthesized by standard literature methods. Several novel aryldipyrromethenes were synthesized in high yields. A number of *trans*-A_2B-corroles have also been prepared by several methods. Some novel corroles were obtained and the yields of others, known from literature, have been improved. Trichloroacetic acid (in very low concentration) was the acid catalyst of choice, giving best yields, for the preparation of corroles from sterically hindered 5-(2,6-dichlorophenyl)dipyrromethane and more reactive aldehydes possessing electron-withdrawing substituents (-C_6F_5, -$C_6H_4NO_2$, -$C_6H_4CO_2Me$), while the use of stronger trifluoroacetic acid (in higher concentration) was preferred for less reactive substrates with electron-donating substituents (-$C_6H_2R_2(OH)$, -$C_6H_2R_2(OCH_3)$, -C_6H_4OH). An attempt to perform oxidative *N*-alkylation of an appropriately substituted *trans*-A_2B-corrole resulted in the formation of two isomeric *N*-alkylated non-oxidized corroles.

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Experimental Section

General Procedures. The chemicals used for synthetic procedures were of reagent grade quality. They were obtained from commercial sources and used as received. NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz or Bruker AMX 400 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (TMS) (^{1}H) or the carbon signal of deuterated solvents (^{13}C). Coupling constants (*J*) are given in Hz. Detailed ^{13}C NMR peak assignments were obtained by careful analysis of DEPT, HMQC and HMBC NMR spectra. Mass spectra were run using a HP5989A apparatus (CI and EI, 70 eV ionisation energy) with Apollo 300 data system, a Kratos MS50TC instrument for exact mass measurements (performed in the EI mode at a resolution of 10000) or a Micromass Quattro II apparatus (electrospray ionization (ESI), usual solvent mixture: CH_2Cl_2-MeOH + NH_4OAc) with MASSLYNX data system. UV-Vis spectra were taken on a Perkin-Elmer Lambda 20 Spectrometer. Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase.

General procedure for the synthesis of aryldipyrromethanes 2a-j in aqueous medium

To 100 mL of 0.18 M aqueous HCl (1.5:98.5), pyrrole (3 equiv.) was added, followed by the addition of the appropriate aromatic aldehyde **1a-j** (1 equiv., 2 g, 0.010–0.019 mol). The reaction mixture was stirred at room temperature and the reaction progress was monitored by both TLC and mass spectrometry (CI). After the indicated time (Table 1), the precipitated (semi-) solid product, which often sticks to the walls of the flask and the stirring bar and might hamper the stirring, was filtered off and washed with water (and petroleum ether) to afford aryldipyrromethanes **2a-j** in high yields (Table 1). 5-Phenyldipyrromethane (**2a**),[3,4a] 5-(4-methylphenyl)dipyrromethane (**2b**),[3,4a] 5-mesityldipyrromethane (**2c**),[3,4a] 5-(4-nitrophenyl)dipyrromethane (**2d**),[4a,10a] 5-(4-methoxyphenyl)dipyrromethane (**2e**),[4a] 5-(4-carboxyphenyl)dipyrromethane (**2f**),[4b] 5-(4-methoxycarbonylphenyl)dipyrromethane (**2g**),[10b] 5-(pentafluorophenyl)dipyrromethane (**2h**),[4a] 5-(2,6-dichlorophenyl)dipyrromethane (**2i**),[4a] and 1,4-bis(2,2'-dipyrromethyl)benzene (**2j**)[3] were characterized by their melting point, mass (EI) and NMR (^{1}H and ^{13}C) spectra and showed essentially the same values as those reported in literature.

General procedure for the synthesis of aryldipyrromethenes 3a,b,e,f,g

To 1 g of aryldipyrromethane **2a,b,g** or **2e,f**, respectively, dissolved in 50 mL of CH_2Cl_2, was added *p*-chloranil or DDQ (1 equiv.), respectively (Table 2), dissolved in 10 mL of CH_2Cl_2, and the reaction mixture was stirred at room temperature for the indicated time (30 min to 1 h, Table 2). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica) to afford aryldipyrromethenes **3a,b,g** and **3e,f**, respectively (yields in Table 2). 5-Phenyl-4,6-dipyrrin (**3a**)[10a,c] was characterized by its melting point, mass (EI) and NMR (^{1}H and ^{13}C) spectra and showed essentially the same values as those reported in literature.

5-(4-Methylphenyl)-4,6-dipyrrin (3b). Eluent: CH_2Cl_2-petroleum ether, 1-1; Yellow crystals; Mp 123-124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.1 (br s, 1H, NH), 7.76 (d, J = 8.1, 2H), 7.5 (m, 2H),

6.8 (d, J = 8.1, 2H), 6.5 (m, 2H), 6.1 (m, 2H), 2.4 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.3, 143.5, 134.6, 134.0, 132.5, 129.2, 126.3, 115.3, 111.6, 23.2; HRMS (EI) calcd for $C_{16}H_{14}N_2$: 234.1157; found: *m/z* 234.1150.

5-(4-Methoxyphenyl)-4,6-dipyrrin (3e). Eluent: CH_2Cl_2-ethyl acetate, 4-1; Pale yellow crystals; Mp 117-118 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (m, 2H), 7.46 (d, J = 8.2, 2H), 6.98 (d, J = 8.2, 2H), 6.65 (m, 2H), 6.4 (m, 2H), 3.89 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.2, 145.6, 135.2, 131.9, 125.4, 118.3, 114.5, 112.2, 109.4, 54.8; HRMS (EI) calcd for $C_{16}H_{14}N_2O$: 250.1106; found: *m/z* 250.1092.

5-(4-Carboxyphenyl)-4,6-dipyrrin (3f). Eluent: CH_2Cl_2-methanol, 95-5; Yellow-brown solid; Mp 225-226 °C; ^1H NMR (DMSO, 300 MHz) δ 8.05 (d, J = 8.2, 2H), 7.78 (m, 2H), 7.58 (d, J = 8.2, 2H), 6.45 (m, 4H); ^{13}C NMR (DMSO, 75 MHz) δ 167.9, 145.8, 142.0, 140.4, 132.1, 131.5, 129.6, 129.2, 119.1, 110.0; HRMS (EI) calcd for $C_{16}H_{12}N_2O_2$: 264.0899; found: *m/z* 264.0905.

5-(4-Methoxycarbonylphenyl)-4,6-dipyrrin (3g).[10b] Eluent: CH_2Cl_2-methanol, 98-2; Dark yellow solid; Mp 130-131 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.15 (d, J = 8.2, 2H), 7.69 (m, 2H), 7.6 (d, J = 8.2, 2H), 6.55 (m, 2H), 6.42 (m, 2H), 3.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.0, 144.5, 142.2, 140.2, 137.1, 131.1, 129.5, 129.2, 118.3, 110.6, 52.7; HRMS (EI) calcd for $C_{17}H_{14}N_2O_2$: 278.1055; found: *m/z* 278.1050.

5,15-Bis(2,6-dichlorophenyl)-10-(pentafluorophenyl)corrole (4a).[8a] To 197 mg (0.67 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 25 mg (0.13 mmol) of pentafluorobenzaldehyde (**1h**), stirred in 30 mL of CH_2Cl_2 under an Ar atmosphere at room temperature for 15 min (the flask was wrapped in aluminium foil for light protection), was added 60 μL of a 10% solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (0.048 mmol). After 1 h, the reaction was quenched with dilute aqueous NaOH and the reaction mixture was washed with water and dried over $MgSO_4$. After filtration and evaporation to dryness, 70 mg (1.3 mmol) of NH_4Cl was added to the crude residue and the mixture was dissolved in 100 mL of propionitrile. To this mixture, 100 mg (0.4 mmol) of *p*-chloranil was added and the reaction mixture was stirred overnight. The solvent was evaporated and 22 mg (22%) of corrole **4** was isolated from the mixture by column chromatography (silica, eluent CH_2Cl_2-petroleum ether, 1-1 to 1-4, with addition of 1% Et_3N). Purple solid; Mp >300 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.96 (d, *J* = 4.4, 2H), 8.58 (d, *J* = 4.7, 2H), 8.45 (d, *J* = 4.7, 2H), 8.39 (d, *J* = 4.4, 2H), 7.78–7.71 (m, 4H), 7.66–7.61 (m, 2H), -2.00 (br s, 3H, NH); MS (ESI) m/z 754.6 (MH^+); UV-Vis λ (log ε) 410 (5.122), 564 (4.256), 600 (3.962).

5,15-Bis(2,6-dichlorophenyl)-10,20-bis(pentafluorophenyl)porphyrin (5a). To 380 mg (1.31 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 138 mg (0.70 mmol) of pentafluorobenzaldehyde (**1h**), dissolved in 60 mL of CH_2Cl_2 and stirred at room temperature under an Ar atmosphere for 15 min (light protection), was added 750 μL of a 10% solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (0.60 mmol). After 1 h, the reaction was quenched with dilute aqueous NaOH. The reaction mixture was washed twice with water and dried over $MgSO_4$. After filtration and evaporation to dryness, the yellow half-solid was dissolved in 350 mL of propionitrile. Subsequently, 377 mg (7.1 mmol) of NH_4Cl and 475 mg (2.1 mmol) of DDQ were added and the mixture was stirred for 1 h. After evaporation of the solvent, 75 mg (23%) of porphyrin **5a** was isolated by column chromatography (silica, eluent CH_2Cl_2-petroleum ether, 1-1, with addition of 1% Et_3N). Purple

solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.78 (m, 8H, β-pyrrole H), 7.83 (m, 4H, dichlorophenyl *m*-H), 7.75 (m, 2H, dichlorophenyl *p*-H), -2.71 (br s, 2H, NH); MS (ESI) *m/z* 931 (MH^+); UV-Vis λ (log ε) 415.5 (5.410), 509.3 (3.415).

5,15-Bis(2,6-dichlorophenyl)-10-(4-nitrophenyl)corrole (4b). To 2.077 g (7.13 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 335 mg (2.22 mmol) of 4-nitrobenzaldehyde (**1d**), dissolved in 200 mL of CH_2Cl_2, was added 5 mg of CCl_3CO_2H (0.03 mmol) in 1–2 mL of CH_2Cl_2 and the mixture was stirred at 0 °C for ~24 h under Ar (light protection). The water bath was warmed to ~40 °C, 1.110 g (4.43 mmol) of *p*-chloranil was added and the mixture was stirred for an additional 3 h. The mixture was evaporated to dryness with silica and chromatographed (silica, eluent CH_2Cl_2-heptane, 1-1 to 2-1) to afford 267 mg (17%) of corrole **4b**. Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.01 (d, J = 4.2, 2H, 2-H and 18-H of corrole), 8.59 (d, J = 8.6, 2H, *p*-nitrophenyl *m*-H), 8.57 (d, J = 4.8, 2H, 8-H and 12-H of corrole), 8.51 (d, J = 4.8, 2H, 7-H and 13-H of corrole), 8.43 (d, J = 4.2, 2H, 3-H and 17-H of corrole), 8.36 (d, J = 8.6, 2H, *p*-nitrophenyl *o*-H), 7.77 (d, J = 8.0, 4H, dichlorophenyl *m*-H), 7.65 (dd, J_1 = 8.0, J_2 = 8.6, 2H, dichlorophenyl p-H), -2.20 (br s, 3H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 147.5, 138.5, 137.1, 135.3 (*p*-nitrophenyl *o*-C), 134.3, 130.5 (dichlorophenyl *p*-C), 130.1, 128.1 (dichlorophenyl *m*-C), 126.9 (7-C and 13-C of corrole), 126.5 (8-C and 12-C of corrole), 122.3 (*p*-nitrophenyl *m*-C), 121.0 (C-3 and C-17 of corrole), 116.3 (C-2 and C-18 of corrole), 109.3; MS (ESI) *m/z* 708 (MH^+); UV-Vis λ (log ε) 410.4 (5.009), 568.3 (3.380).

5,15-Dimesityl-10-(4-nitrophenyl)corrole (4c).[13d] To 1.597 g (6.04 mmol) of 5-mesityldipyrromethane (**2c**) and 289 mg (1.91 mmol) of 4-nitrobenzaldehyde (**1d**), dissolved in 165 mL of CH_2Cl_2 and placed in an ice bath (light protection), was added 4.3 mg (0.026 mmol) of CCl_3CO_2H and the mixture was stirred at 0 °C for 20 h under Ar. The water bath was warmed gently to 40 °C and 990 mg (3.99 mmol) of *p*-chloranil was added. After 1 h, the mixture was evaporated to dryness with silica. Repeated chromatography (silica, eluent CH_2Cl_2-heptane, 2-1 to 1-1) and recrystallization from CH_2Cl_2-heptane afforded 230 mg (18%) of corrole **4c**.

5,15-Bis(2,6-dichlorophenyl)-10-(4-methoxycarbonylphenyl)corrole (4d). To 2.138 g (7.34 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 395 mg (2.29 mmol) of methyl 4-formylbenzoate (**1g**), dissolved in 200 mL of CH_2Cl_2 and placed in an ice bath (light protection), was added 6.0 mg (0.037 mmol) of CCl_3CO_2H and the mixture was stirred at 0 °C for 22 h under Ar. The water bath was warmed gently to 40 °C and 1.180 g (4.76 mmol) of *p*-chloranil was added. After 1 h, the mixture was evaporated to dryness with silica. The residue was chromatographed twice (silica, eluent CH_2Cl_2-heptane, 2-1) and the crude product was recrystallized from CH_2Cl_2-heptane to afford 374 mg (23%) of corrole **4d**. Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.00 (d, J = 4.4, 2H, 2-H and 18-H of corrole), 8.55–8.54 (m, 4H), 8.42–8.38 (m, 4H), 8.27 (d, J = 8.0, 2H, methoxycarbonylaryl H), 7.76 (m, 4H, dichlorophenyl *m*-H), 7.64 (dd, J_1 = 7.1, J_2 = 9.0, 2H, dichlorophenyl *p*-H), 4.08 (s, 3H, CH_3), -2.06 (br s, 3H, NH); MS (ESI) *m/z* 721 (MH^+); UV-Vis λ (log ε) 421.8 (5.064), 567.8 (3.301), 608.4 (3.230).

5,15-Bis(2,6-dichlorophenyl)-10-(4-carboxyphenyl)corrole (4e). To 257 mg (0.356 mmol) of corrole **4d**, dissolved in 20 mL of EtOH, was added 350 μL of a 5 M aqueous solution of NaOH (1.75 mmol). The reaction mixture was stirred at room temperature and then heated at reflux

temperature. As a spot of the starting material could still be observed on TLC after 1.5 h of reflux, another aliquot (350 μL, 1.75 mmol) of NaOH solution was added. After an additional h of reflux, the reaction mixture was cooled to room temperature, 25 mL of water was added and the whole mixture was poured directly into 15 mL of water containing 0.3 mL of conc. HCl (3.6 mmol). The precipitate formed was filtered through a Büchner funnel and rinsed with an abundant volume of water. Upon drying, 223 mg (88%) of corrole **4e** was obtained. Purple solid; Mp >300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.17 (br s, 1 H, COOH), 9.07 (d, J = 4.0, 2H, 2-H and 18-H of corrole), 8.46 (s, 4H), 8.34 (d, J = 8.0, 2H, carboxyaryl H), 8.25–8.22 (m, 4H), 7.96 (d, J = 7.7, 4H, dichlorophenyl *m*-H), 7.85 (m, 2H, dichlorophenyl *p*-H), -2.70 (br s, 3H, NH); MS (ESI) *m/z* 707 (MH^+).

5,15-Bis(2,6-dichlorophenyl)-10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)corrole (4f). To 1.630 g (5.60 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 454 mg (1.88 mmol) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**1l**), dissolved in 123 mL of CH_2Cl_2, purged with Ar for 30 min and protected from light, was added 27 μL (0.35 mmol) of TFA, and the mixture was stirred under an Ar atmosphere for ~48 h. Subsequently, 945 mg (3.81 mmol) of *p*-chloranil was added and the reaction mixture was stirred for an additional 45 min at room temperature. The mixture was evaporated to dryness with silica and chromatographed twice (silica, eluent CH_2Cl_2-hexane, 4-3 and 1-1, respectively) to afford 444 mg (30%) of corrole **4f**. Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.98 (d, J = 4.1, 2H, 2-H and 18-H of corrole), 8.65 (d, J = 4.7, 2H, 8-H and 12-H of corrole), 8.52 (d, J = 4.7, 2H, 7-H and 13-H of corrole), 8.40 (d, J = 4.1, 2H, 3-H and 17-H of corrole), 7.98 (s, 2H, 2-H and 6-H of hydroxydialkylphenyl), 7.75 (d, J = 8.1, 4H, dichlorophenyl *m*-H), 7.62 (dd, J_1 = 8.1, J_2 = 8.1, 2H, dichlorophenyl *p*-H), 5.47 (s, 1H, OH), 1.61 (s, 18H, *t*-butyl), ~ -2 (br s, 3H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4 (COH), 138.5 (2-C and 6-C of dichlorophenyl), 137.5 (1-C of dichlorophenyl), 134.5 (3-C and 5-C of hydroxydialkylphenyl), 132.7, 131.6 (2-C and 6-C of hydroxydialkylphenyl), 130.2 (4-C of dichlorophenyl), 128.0 (3-C and 5-C of dichlorophenyl), 127.5 (B and C ring β-pyrrole C), 125.6 (B and C ring β-pyrrole C), 121.0 (A and D ring β-pyrrole C), 116.1 (A and D ring β-pyrrole C), 113.3 (10-C of corrole), 34.6 (*t*-butyl quaternary C), 30.7 (*t*-butyl CH_3); MS (ESI) *m/z* 791 (MH^+); UV-Vis λ (log ε) 411.5 (5.021), 421.9 (4.000), 561.6 (3.230).

5,15-Bis(2,6-dichlorophenyl)-10,20-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (5f). Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.92 (d, J = 4.7, 4H, β-pyrrole H), 8.65 (d, J = 4.7, 4H, β-pyrrole H), 8.04 (s, 4H, 2-H and 6-H of hydroxydialkylphenyl), 7.78 (d, J = 7.9, 4H, 3-H and 5-H of dichlorophenyl), 7.67 (m, 2H, 4-H of dichlorophenyl), 5.52 (s, 2H, OH), 1.62 (s, 36H, *t*-butyl), ~ -2.5 (s, 2H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7 (COH), 140.3 (1-C of dichlorophenyl), 138.8 (2-C and 6-C of dichlorophenyl), 134.2 (3-C and 5-C of hydroxydialkylphenyl), 132.8 (1-C of hydroxydialkylphenyl), 132.0 (β-pyrrole C correlated with the H at 8.91 ppm), 130.3 (4-C of dichlorophenyl), 129.2 (β-pyrrole C correlated with the H at 8.65 ppm), 127.7 (3-C and 5-C of dichlorophenyl), 121.6 (porphyrin *meso*-C bearing hydroxydialkylphenyl), 113.7 (porphyrin *meso*-C bearing dichlorophenyl), 34.6 (*t*-butyl quaternary C), 30.7 (*t*-butyl CH_3); MS (ESI) *m/z* 1007 (MH^+); UV-Vis λ (log ε) 423.8 (5.301), 465.6 (3.898), 517.6 (3.176), 666.5 (3.204).

5,15-Bis(2,6-dichlorophenyl)-10-(3,5-di-*tert*-butyl-4-methoxyphenyl)corrole (4g). To 2.283 g (7.84 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 609 mg (2.45 mmol) of 3,5-di-*tert*-butyl-4-methoxybenzaldehyde (**1m**), dissolved in 160 mL of CH_2Cl_2, purged with Ar for 10 min and protected from light, was added 35 μL (0.45 mmol) of TFA, and the mixture was stirred under an Ar atmosphere for 18 h at room temperature. Subsequently, 1.200 g (4.83 mmol) of *p*-chloranil was added and the reaction mixture was stirred for an additional 30 min at room temperature. The mixture was evaporated to dryness with silica and chromatographed twice (silica, eluent CH_2Cl_2-hexane, 1-1 to 2-1) to afford 536 mg (27%) of corrole **4g**. Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.02 (d, J = 4.2, 2H, 2-H and 18-H of corrole), 8.69 (d, J = 4.7, 2H, 8-H and 12-H of corrole), 8.57 (d, *J* = 4.7, 2H, 7-H and 13-H of corrole), 8.43 (d, *J* = 4.2, 2H, 3-H and 17-H of corrole), 8.11 (s, 2H, 2-H and 6-H of hydroxydialkylphenyl), 7.78 (d, *J* = 8.0, 4H, 3-C and 5-C of dichlorophenyl), 7.65 (dd, 2H, 4-C dichlorophenyl), 3.99 (s, 3H, CH_3), 1.63 (s, 18H, *t*-butyl), -2.37 (br s, 3H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9 ($COCH_3$), 142.3, 142.0, 139.8, 138.5 (2-C and 6-C of dichlorophenyl), 137.4 (1-C of dichlorophenyl), 135.8, 134.4 133.4 (2-C and 6-C of hydroxydialkylphenyl), 130.3 (4-C of dichlorophenyl), 128.0 (3-C and 5-C of dichlorophenyl), 127.5 (B and C ring β-pyrrole C), 125.8 (B and C ring β-pyrrole C), 120.6 (A and D ring β-pyrrole C), 116.1 (A and D ring β-pyrrole C), 112.9 (5-C and 15-C of corrole), 108.8 (10-C of corrole), 64.5 (CH_3), 36.0 (*t*-butyl quaternary C), 32.4 (*t*-butyl CH_3); MS (ESI) *m/z* 805 (MH^+); UV-Vis λ (log ε) 420.2 (5.262), 616.8 (3.398).

5,15-Bis(2,6-dichlorophenyl)-10,20-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)porphyrin (5g). Purple solid; Mp >300 °C; MS (ESI) *m/z* 1035 (MH^+); UV-Vis λ (log ε) 421.2 (5.579), 456.8 (4.806), 516.5 (4.398), 652.9 (4.176).

5,15-Bis(2,6-dichlorophenyl)-10-(4-hydroxyphenyl)corrole (4h). To 1.823 g (6.26 mmol) of 5-(2,6-dichlorophenyl)dipyrromethane (**2i**) and 259 mg (2.10 mmol) of *p*-hydroxybenzaldehyde (**1k**), dissolved in 137 mL of CH_2Cl_2, purged with Ar for 10 min and protected from light, was added 30 μL (0.39 mmol) of TFA, and the mixture was stirred under an argon atmosphere for 17 h at room temperature. Subsequently, 1.077 g (4.34 mmol) of *p*-chloranil was added and the reaction mixture was stirred for an additional 40 min at room temperature. The mixture was evaporated to dryness with silica. After repeated chromatography with CH_2Cl_2, 139 mg (10%) of corrole **4h**, which decomposed throughout the purification process, was obtained. Purple solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.98 (d, *J* = 4.0, 2H, 2-H and 18-H of corrole), 8.58 (d, *J* = 4.6, 2H, B and C ring β-pyrrole H), 8.51 (d, *J* = 4.6, 2H, B and C ring β-pyrrole H), 8.39 (d, *J* = 4.0, 2H, 3-H and 17-H of corrole), 7.96 (d, *J* = 8.0, 2H, 2-H and 6-H of hydroxyphenyl), 7.73 (d, *J* = 8.1, 4H, 3-H and 5-H of dichlorophenyl), 7.60 (dd, 2H, 4-H of dichlorophenyl), 7.00 (d, *J* = 8.0, 2H, 3-H and 5-H of hydroxyphenyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1 (COH), 142.2 (B and C ring α-pyrrole C), 139.7 (B and C ring α-pyrrole C), 138.5 (2-C and 6-C of dichlorophenyl), 137.3 (1-C of dichlorophenyl), 132.7, 135.5 (2-C and 6-C of hydroxyphenyl), 134.6 (A and D ring α-pyrrole C), 134.1 (1-C of hydroxyphenyl), 130.6 (A and D ring α-pyrrole C), 130.3 (4-C of dichlorophenyl), 128.0 (3-C and 5-C of dichlorophenyl), 127.1 (B and C ring β-pyrrole C), 125.7 (B and C ring β-pyrrole C), 120.8 (A and D ring β-pyrrole C), 116.2 (A and D ring β-pyrrole C), 114.0 (3-C and 5-C

of hydroxyphenyl), 111.4 (10-C of corrole), 109.0 (5-C and 15-C of corrole); MS (ESI) *m/z* 679 (MH^+).

5,15-Bis(2,6-Dichlorophenyl)-10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-N_{22}-[(ethoxycarbonyl) methyl]corrole (4i) and 5,15-bis(2,6-dichlorophenyl)-10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-N_{21}-[(ethoxycarbonyl)methyl]corrole (4j). To 109 mg (0.14 mmol) of corrole **4f** and 35 mg of NaH (80% wt. in mineral oil; 1.17 mmol), stirred in 19 mL of acetone for 7 min, was added a solution of 400 μL of ethyl bromoacetate (**6**) (94%; 3.39 mmol) in 6 mL of acetone, and the mixture was refluxed for ~24 h. Upon cooling, the reaction mixture was taken into Et_2O, washed thrice with water and dried over $MgSO_4$. After filtration and removal of the solvent under reduced pressure, the mixture was fractionated by column chromatography (silica, eluent CH_2Cl_2-hexane, changing the ratio from 7-8 to 1.6-1) which afforded 41 mg (34%) of the green-brownish corrole **4i** and 73 mg (61%) of its blue-greenish isomer **4j**. **Corrole 4i.** Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.01 (d, *J* = 4.1, 1H, 2-H or 18-H of corrole), 8.96 (d, *J* = 4.2, 1H, 2-H or 18-H of corrole), 8.60 (d, *J* = 4.6, 1H, 12-H of corrole), 8.56 (d, *J* = 4.1, 1H, 3-H or 17-H of corrole, correlated with the H at 9.01 ppm), 8.47 (d, *J* = 4.6, 1H, 13-H of corrole), 8.36 (overlapped d, 1H, 3-H or 17-H of corrole, correlated with the H at 8.96 ppm), 8.33 (br s, 1H, hydroxydialkylphenyl H close to the B pyrrole ring), 8.24 (d, *J* = 4.7, 1H, 7-H of corrole), 8.10 (d, *J* = 4.7, 1H, 8-H of corrole), 7.88 (br s, 1H, hydroxydialkylphenyl H close to the C pyrrole ring), 7.74 (m, 4H, 3-H and 5-H of dichlorophenyl), 7.61 (m, 2H, 4-H of dichlorophenyl), 5.52 (s, 1H, OH), 3.11 (m, 1H, ethyl CH_2), 3.05 (m, 1H, ethyl CH_2), 1.65 (m, 9H, *t*-butyl closer to the B pyrrole ring), 1.59 (m, 9H, *t*-butyl closer to the C pyrrole ring), 0.45 (t, *J* = 7.1, 3H, ethyl CH_3), -2.78 (br s, 1H, NH), -3.73 (d, ^2J = 18.0, 1H, NCH_2), -3.76 (d, ^2J = 18.0, 1H, NCH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.0 (COO), 153.9 (COH), 151.8 (9-C of corrole), 147.3 (6-C of corrole), 145.1 (α-pyrrole C), 141.8 (α-pyrrole C), 138.7 (quaternary C of dichlorophenyl), 138.5 (quaternary C of dichlorophenyl), 137.9 (quaternary C of dichlorophenyl), 137.3 (quaternary C of dichlorophenyl), 135.8 (α-pyrrole C), 135.6 (α-pyrrole C), 134.9 (hydroxydialkylphenyl C bearing *t*-butyl), 134.2 (hydroxydialkylphenyl C bearing *t*-butyl), 133.4 (hydroxydialkylphenyl CH), 132.1 (hydroxydialkylphenyl CH), 130.4 (4-C of dichlorophenyl), 130.0 (4-C of dichlorophenyl), 129.8 (β-pyrrole C, correlated with the H at 8.56 ppm), 129.0 (α-pyrrole C), 128.3 (*m*-dichlorophenyl C), 128.1 (*m*-dichlorophenyl C), 127.9 (*m*-dichlorophenyl C), 127.8 (*m*-dichlorophenyl C), 127.6 (α-pyrrole C), 124.7 (12-C of corrole), 123.2 (13-C of corrole), 122.9 (B ring β-C), 122.7 (B ring β-C), 121.4 (β-pyrrole C, correlated with the H at 9.01 ppm), 119.0 (β-pyrrole C, correlated with the H at 8.36 ppm), 115.8 (β-pyrrole C, correlated with the H at 8.96 ppm), 113.9 (*meso*-C), 113.7 (*meso*-C), 106.1 (10-C of corrole), 59.8 (ethyl CH_2), 43.2 (NCH_2), 34.6 (*t*-butyl quaternary C), 30.7 (*t*-butyl CH_3), 13.3 (ethyl CH_3); MS (ESI) *m/z* 877 (MH^+); UV-Vis λ (log ε) 424.2 (5.173), 661.7 (3.322); **Corrole 4j.** Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (d, *J* = 4.2, 1H, 18-H of corrole), 8.59 (d, *J* = 4.7, 1H, 12-H of corrole), 8.46 (d, *J* = 4.5, 1H, 8-H of corrole), 8.43 (d, *J* = 4.2, 1H, 17-H of corrole), 8.36 (overlapped d, 3H, 2-H, 7-H and 13-H of corrole), 8.03 (d, *J* = 1.8, 1H, hydroxydialkylphenyl H), 7.78 (m, 3H, 2 dichlorophenyl H and 1 hydroxydialkylphenyl H), 7.62 (m, 5H, 4 dichlorophenyl H and 3-H of corrole), 5.43 (s, 1H, OH), 3.32 (m, 1H, ethyl CH_2), 3.24 (m, 1H, ethyl CH_2), 1.62 (s, 9H, *t*-butyl), 1.56 (s, 9H, *t*-butyl), 0.61 (t, *J* = 7.1, 3H, ethyl CH_3), -2.89 (br s, 1H, NH), -2.13 (d, ^2J = 18.0, 1H, NCH_2), -2.19

(d, ^2J = 18.0, 1H, NCH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.7 (COO), 154.2 (B ring α-C), 153.2 (COH), 149.9 (B ring α-C), 148.8 (A ring α-C), 141.7 (A ring α-C), 139.3, 138.3, 138.2 (quaternary C of dichlorophenyl), 137.9 (quaternary C of dichlorophenyl), 137.4 (quaternary C of dichlorophenyl), 134.7 (α-pyrrole C), 134.4 (hydroxydialkylphenyl C bearing *t*-butyl), 134.3 (hydroxydialkylphenyl C bearing *t*-butyl), 133.7 (α-pyrrole C), 132.7 (1-C of hydroxydialkylphenyl), 131.4 (2 hydroxydialkylphenyl CH), 131.2 (8-C of corrole), 131.1 (α-pyrrole C), 131.0 (β-pyrrole C, correlated with an H at 8.36 ppm), 130.0 (4-C of dichlorophenyl), 129.9 (4-C of dichlorophenyl), 128.3 (*m*-dichlorophenyl C), 128.1 (*m*-dichlorophenyl C), 127.9 (*m*-dichlorophenyl C), 127.8 (*m*-dichlorophenyl C), 127.3 (12-C of corrole), 124.0 (13-C of corrole), 122.6 (17-C of corrole), 115.2 (β-pyrrole C, correlated with an H at 8.36 ppm), 115.0 (18-C of corrole), 114.2 (10-C of corrole), 113.7 (*meso*-C), 112.1 (3-C of corrole), 106.9 (*meso*-C), 60.1 (ethyl CH_2), 44.8 (NCH_2), 34.6 (*t*-butyl quaternary C), 30.7 (*t*-butyl CH_3), 13.4 (ethyl CH_3); MS (ESI) *m/z* 877 (MH^+); UV-Vis λ (log ε) 414.3 (5.061), 432.8 (3.934), 577.2 (3.447), 621.4 (3.204).

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