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A Simple and Versatile One-Pot Synthesis of *meso*-Substituted *trans*-A_2B-Corroles

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We have developed a new methodology that affords regioisomerically pure *trans*-A_2B-corroles. The corrole formation reaction involves the acid-catalyzed condensation of a dipyrromethane and an aldehyde followed by oxidation with DDQ. Optimal conditions for the condensation were identified after examining various reaction parameters (solvent, acid, concentration, time). The conditions identified (CH_2Cl_2, [DPM] = 33 mM, [aldehyde] = 17 mM, [TFA] = 1.3 mM (for sterically hindered DPMs) or [TFA] = 0.26 mM (for sterically unhindered DPMs), 5 h, room temperature) resulted in the formation of corroles in 3−25% yield without detectable scrambling. The synthesis is compatible with diverse functionalities: ester, nitrile, ether, fluoro, hydroxy, iodo, nitro, thioacetate, methylsulfoxy. In total 21 corroles of type *trans*-A_2B were prepared. Three exemplary corrole syntheses were successfully carried out at 8 mmol scale. Corroles **23**, **30**, and **41** (160−600 mg) were obtained in essentially the same yield as in small scale experiments.

Introduction

Corroles[1] are aromatic tetrapyrrole macrocycles bearing a direct pyrrole−pyrrole link, thereby constituting a bridge between porphyrins (e.g., heme) and corrins (e.g., vitamin B_{12}). Most of the corrole syntheses known till 1999 (biladiene cyclization,[2] *meso*-carbon or sulfur extrusion of *meso*-thia-porphyrin,[3] or synthesis from monopyrrole precursors[4]) are lengthy. In 1999 two groups independently reported a direct synthesis of *meso*-aryl free-base corroles.[5] Gross et al.[6] and Paolesse and co-workers[7] isolated 5,10,15-triarylcorroles from the reaction of pyrrole with aromatic aldehydes under different but virtually neutral conditions in both cases. Simple modifications of the Rothemund approach by changing the ratio of pyrrole and aldehyde or employing solid support allowed them to establish a general route to previously inaccessible compounds. Also in 1999 Chandrashekar and co-workers[8] and Lee et al.[9] reported syntheses of core-modified corroles from acyclic precursors. The behavior of *meso*-A_3-substituted corroles as catalysts,[10] as molecular magnets,[11] and as ligands that stabilize higher oxidation states of metals[12] have been already studied. A potential use of corroles as surrogates for vitamin B_{12} and related compounds would benefit significantly from the ability to incorporate different groups at distinct sites at the perimeter of the macrocycle. Therefore, we set for ourselves a goal to develop a new protocol for the corrole-forming reaction, which would be experimentally simple and would allow broad access to the target *meso*-substituted *trans*-A_2B-corroles. Very recently we have reported the noncatalyzed reaction of dipyrromethanes with aromatic aldehydes possessing fluorine atoms leading to *meso*-substituted *trans*-A_2B-corroles in moderate to good yields.[13] For the rational synthesis described herein we had undertaken a detailed study aimed at refining the reaction conditions. This study had two principal aims: (1) to find reaction conditions that afford corroles starting from a broad variety of aldehydes and dipyrromethanes, and (2) to maximize the yield with no scrambling. The appropriate sphere of application of our new room-temperature procedure is not in the preparation of a model compound in higher yield but rather in the synthesis of those substituted corroles that are

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(6) (a) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed*. **1999**, *38*, 1427−1429. (b) Gross, Z.;. Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Blaser, D.; Boese R.; Goldberg, I. *Org. Lett*. **1999**, *1*, 599−602.

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(8) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Englich, U.; Ruhlandt-Senge, K. *Org. Lett*. **1999**, *1*, 587−590.

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inaccessible via the previous route. The detailed synthetic conditions, however, have been delineated by using the synthesis of 10-(2,6-difluorophenyl)-5,15-dimesitylcorrole as a model. Here we wish to report results of this study.

Results and Discussion

Refinement of Synthetic Conditions. The careful analysis of our results[13] obtained for the reaction of a dipyrromethane (DPM) and an aldehyde performed in the absence of any catalyst reveals some inconsistency. The most intriguing point is that all liquid aldehydes used (for example 2,6-difluorobenzaldehyde **2** or pentafluorobenzaldehyde **10**) furnished some amount of corroles, whereas reactive solid aldehydes (e.g., 2,4-dinitrobenzaldehyde, 2,6-dichlorobenzaldehyde, or 4-(*S*-acetylthio)-2,3,5,6-tetrafluorobenzaldehyde **11**) did not give any corrole. Moreover the addition of weakly basic TBAF stopped the reaction completely (while in the porphyrin formation reaction, it increases yield[14]). These two observations led to the hypothesis that a small amount of fluorobenzoic acids from autoxidation of aldehydes are real catalysts in previously[13] decribed corrole-forming reactions.[15,16]

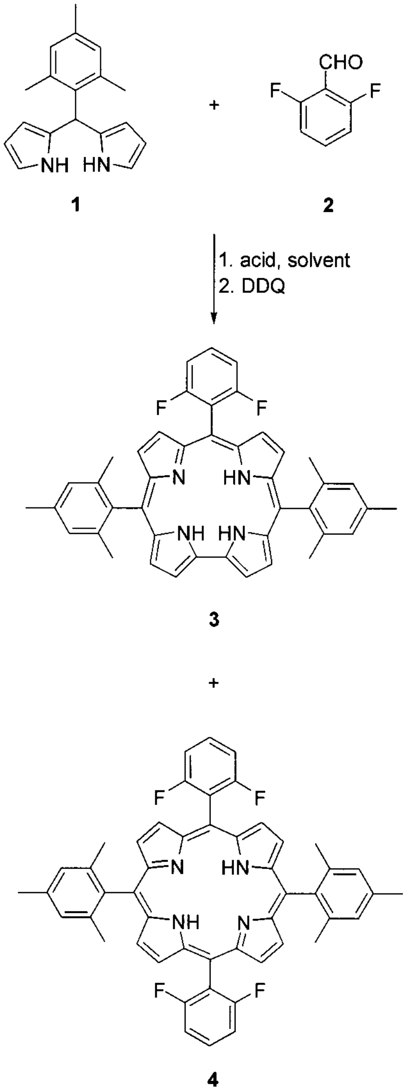
Although an acid-catalyzed reaction of dipyrromethanes (DPMs) with aldehydes leading to the corresponding *trans*-A_2B_2-porphyrins has been described,[17] we decided to revisit this issue, aiming to find conditions when corroles are the main products. The reaction of mesityldipyrromethane **1** (MesDPM)[18] and 2,6-difluorobenzaldehyde **2** was chosen again as a model system for the optimization study (Scheme 1, Tables 1−3, Figure 1). The reaction conditions chosen were based on our earlier study[13] (e.g., aldehyde/dipyrromethane ratio, 1:1; reaction time 2 h; room temperature; [DPM] = 270 mM; and 1 equiv of DDQ as an oxidant). We employed trifluoroacetic acid (TFA) because of its popularity in porphyrynoid-forming reactions. Treatment of the mixture of MesDPM **1** and 2,6-difluorobenzaldehyde **2** with TFA at concentration levels of 43 or 87 mM followed by the addition of DDQ gave neither corrole **3** nor porphyrin **4** (Table 1, entries 7 and 8). A contrasting picture emerged when a very small concentration of TFA (1.3 mM) was used. To our delight it led to corrole **3** in 19% yield and porphyrin **4** in 4% yield (Table 1, entry 1). During this study, it was found that porphyrin **4** also had been formed in a small amount during the previously[13] described experiments. In the presence of corrole **3**, porphyrin **4** is not detectable using silica-TLC, MALDI and ESI-MS. Finally porphyrin **4** was detected using alumina-TLC.

Table 1. Optimization of Conditions for Reaction of MesDPM 1 with Aldehyde 2 by Changing Concentrations of Substrates and TFA[a]

entry	DPM **1** (mM)	TFA (mM)	yield (%) corrole **3**[b]	yield (%) porphyrin **4**[b]
1	270	1.3	19	4
2	133	1.3	19	4
3	100	1.3	21	4
4	66	1.3	21	4
5	33	1.3	22	4
6	10	1.3	20	5
7	270	43	0	0
8	270	87	0	0
9	133	0.87	19	4
10	10	17.8	<1	12
11	2.5	0.25	0	0
12	33	1.3[c]	22	4
13	33	16	16	5

[a] All reactions were performed under the following constant conditions: CH_2Cl_2, MesDPM/aldehyde **2** = 1:1, 5 h, room temperature). [b] Isolated yields. [c] After 2 h an additional 0.1 equiv of TFA was added followed by an addition 0.1 equiv of TFA 2 h later. The reaction was stopped after 6 h.

Scheme 1



The comparison of modified Lindsey's conditions[17b] for the reactions of MesDPM with aldehydes in CH_2Cl_2 in the presence of TFA leading to *trans*-A_2B_2-porphyrins with our experiments reveals an interesting difference.

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(15) Various amounts of respective fluorobenzoic acids in commercial samples of 2,4-difluorobenzaldehyde **7**, 2,3,6-trifluorobenzaldehyde **9**, and 2,6-difluorobenzaldehyde **2** can explain why their reactions with mesityldipyrromethane **1** (MesDPM) afforded respective corroles **20**, **22**, and **3** in significantly various yields (4%, 10%, and 19%). The presence of di- or trifluorobenzoic acids in commercially available aldehydes was confirmed using GC−MS. An addition of extra amounts of 2,4-difluorobenzoic acid to the mixture of 2,4-difluorobenzaldehyde with mesitydipyrromethane in CH_2Cl_2 increased reaction rate and yields of corrole significantly.

(16) To obtain further evidence we decided to try basic conditions for the corrole formation reaction. When the reaction of MesDPM **1** with 2,6-difluorobenzaldehyde **2** was carried out in the presence of triethylamine or 4-dimethylaminepirydine, no corrole was obtained.

(17) (a) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440. (b) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

(18) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.

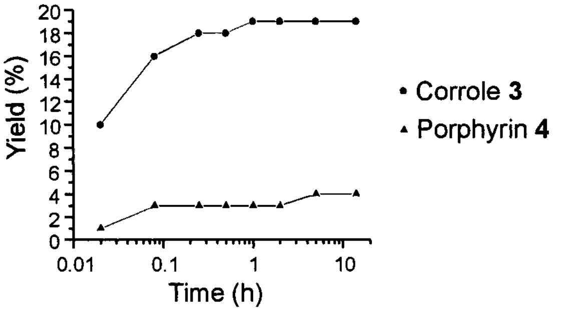

Figure 1. Optimization of the time of the reaction of **1** with **2**. All reactions were performed under the following constant conditions: CH_2Cl_2, [MesDPM] = 133 mM, [aldehyde] = 133 mM, [TFA] = 1.3 mM, room temperature). Time given is of condensation prior to DDQ addition. Isolated yields given. Note the log plot of time axis.

Table 2. Results of an Acid Survey in the Reaction of MesDPM 1 with Aldehyde 2[a]

entry	acid	yield (%) corrole **3**[b]	yield (%) porphyrin **4**[b]
1		18	3
2	TFA	19	4
3	HOAc[c]	8	2
4	$BF_3.OEt_2$	12	12
5	CH_3SO_3H	13	5
6	$Yb(OTf)_3$[d]	18	3
7	K-10[e]	18	3

[a] All reactions were performed under the following constant conditions: CH_2Cl_2, [MesDPM] = 133 mM, [aldehyde] = 133 mM, [acid] = 1.3 mM, 5 h, room temperature). [b] Isolated yields. [c] [AcOH] = 6.5 mM. [d] 0.005 mmol of $Yb(OTf)_3$ and 0.4 mmol of MesDPM were used. [e] 10 mg of K-10 and 0.4 mmol of MesDPM were used.

While a high concentration of acid and a low concentration of substrates were used for porphyrin-forming reaction, we used low concentrations of acid and high concentrations of substrates. The reaction of **1** with 2,6-difluorobenzaldehyde under the above-mentioned Lindsey's conditions led to porphyrin **4** in 12% yield (Table 1, entry 10); the only traces of corrole **3** were observed under these conditions. 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 reasonable yield of product. Thus, the corrole-forming reaction was carried out under more diluted conditions. When the reactants' concentration was changed from 270 to 33 mM, the yield of corrole slightly increased (Table 1, entries 2−5). Further dilution to a concentration of 10 mM (reported by Lindsey)[17b] caused a gentle drop in the yield of corrole **3**, increased the amount of porphyrin **4**, and caused the formation of unidentified fluorescent species (Table 1, entry 6). On the other hand a slight decrease in the amount of TFA did not lead to a decrease in the yield of corrole **3** (Table 1, entry 9).

Very recently Lindsey and Geier[19] have found that changing an acid can lead to a different course of the porphyrin-forming reaction. This inclined us to perform an acid survey of our reaction. Different types of acids were used in this study ($BF_3 \cdot OEt_2$, Yb $(OTf)_3$, K-10, CH_3SO_3H, AcOH). Results are collected in Table 2. In the reactions catalyzed by $Yb(OTf)_3$ or K-10, yields of products were as in an "uncatalyzed" reaction. Acetic acid as a catalyst led to a significant decrease in yields of both corrole and porphyrin. When $BF_3 \cdot OEt_2$ or CH_3SO_3H were used as catalysts the ratio of corrole to porphyrin changed significantly, reaching 1:1 in the case of the $BF_3 \cdot OEt_2$ catalyzed reaction. Hence, for further reactions TFA was exclusively used as the catalyst.

Table 3. Optimization of the Solvent in the Reaction of MesDPM 1 with Aldehyde 2[a]

entry	solvent	yield (%) corrole **3**[b]	yield (%) porphyrin **4**[b]
1	CH_2Cl_2	22	4
2	$CHCl_3$	21	4
3	$(CH_2Cl)_2$	22	4
4	THF	2	<1
5	MeCN	18	4
6	EtCN	21	4

[a] All reactions were performed under the following constant conditions: [MesDPM] = 33 mM, [aldehyde] = 33 mM, [TFA] = 1.3 mM, 5 h, room temperature). [b] Isolated yields.

We also resolved to survey the solvent used in the corrole-forming reaction (Table 3). Five different solvents, chlorinated ($CHCl_3$, $ClCH_2CH_2Cl$) and non-chlorinated (MeCN, EtCN and THF), were chosen. No appreciable difference was observed between the yield of corrole **3** in all chlorinated solvents. The reaction carried out in MeCN did not give any improvement of the yield of corrole **3** either. In a very recent report by Lee et al.[20] the advantage of the use of EtCN in the oxidative cyclization of bilanes leading to corroles was strongly emphasized. We did use it, but only a slight difference was observed (Table 3, entry 5). Changing the solvent from CH_2Cl_2 to THF caused a sudden drop in the yield of corrole **3**.

In our preliminary results[13] we found that in the absence of an "external" acid prolongation of the reaction time from 2 to 5 h did not change the yield of corrole **3**, while a further extension to 16 h probably caused the decomposition of the precursor of corrole (0% yield). During the present study (Figure 1) we found that despite a low concentration of TFA, the corrole-forming reaction is surprisingly fast, at least for aldehydes possessing electron-withdrawing groups. There is no real difference in the yield of corrole **3** when the reaction time is 15 min, 2 h, or 14 h.

In our earlier communication we reported[13] that there was a significant increase in the yield of corrole **3** when the ratio of MesDPM/2,6-difluorobenzaldehyde was changed from 2:1 to 1:1. Because we could clearly associate it with the increase in the amount of 2,6-difluorobenzoic acid as the catalysts, there was reason to return to a more stoichiometric (e.g., 2:1) ratio. Indeed, under these conditions (CH_2Cl_2, [DPM] = 33 mM, [aldehyde] = 17 mM, [TFA] = 1.3 mM, 5 h, room temperature) the yield of corrole **3** increased from 22% (Table 1, entry 5) to 25%. Hence, for further experiments the ratio of reactants was kept constant at 2:1.

The mechanism of the studied reaction has not been unequivocally established, but one of the possibilities involves the acid-catalyzed reaction of an aldehyde with a DPM leading to tetrapyrromethane **5** as the first step (Scheme 2). Next, pyrrole−pyrrole coupling occurs (analogous to that which occurs in dimerization of pyrrole)

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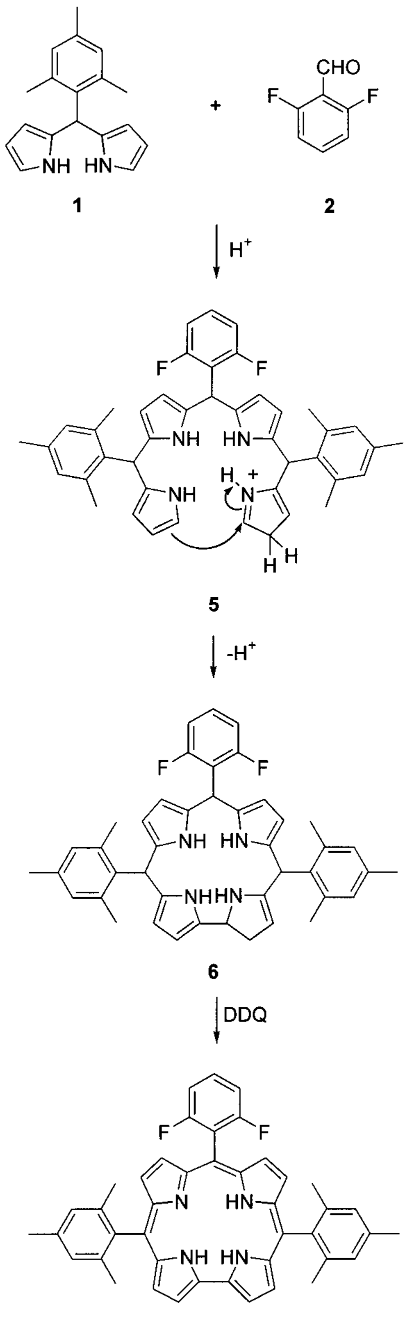
(19) (a) Geier, G. R., III; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455−1458. (b) Geier, G. R., III; Ciringh, Y.; Li, F.; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **2000**, *2*, 1745−1748.

(20) Ka, J.-W.; Cho, W.-S.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 8121−8125.

Scheme 2



leading to direct corrole precursor **6**. This type of an acid-catalyzed coupling of the two pyrrole moieties were employed by Chandrashekar et al.[21] in the reaction of dipyrromethanes with tripyrrodimethanes leading to smaragdyrins. The last step involves aromatization of **6** to **3** after addition of DDQ. An oxidative DDQ-mediated coupling of tetrapyrromethanes in neutral conditions in CH_3CN leading to *meso*-substituted A_3-corroles has been proposed by Lee et al.[20] recently. In the same paper no corrole formation was reported when the reaction was performed in CH_2Cl_2. This observation indicates that in our reactions, carried out in CH_2Cl_2, the oxidative coupling is rather less probable than the formation of compound **6** (Scheme 2). Given that the enamine moiety formed in the cyclization step could be protonated by TFA to form the iminium salt and that the amount of acid in the reaction mixture is smaller than the theoretical amount of **6** (assuming 100% reaction yield), one can conclude that the addition of a greater amount of acid could increase the yield of corrole. It might also explain why MesDPM and an aldehyde are still present in the reaction mixture even after 14 h.

These mechanistic considerations inclined us to perform a few more experiments. First, the concentrations of both reactants and acid were adjusted to those employed by Chandrashekar[21] (Table 1, entry 11). Neither corrole nor porphyrin was formed in this reaction. In the second experiment extra amounts of TFA (altogether 0.2 equiv in relation to aldehyde) were added after 2 h to the reaction mixture (details: Table 1, entry 12) prepared as in entry 5. The reaction was stopped by the addition of DDQ when no MesDPM was present in the reaction mixture (6 h). It did not produce any improvement. Furthermore in the next experiment TFA concentration was kept at the same level as concentration of 2,6-difluorobenzaldehyde. It led to the decrease in the yield of corrole **3** while the yield of porphyrin **4** increased (Table 1, entry 13). If the proposed mechanism is correct the above experiments suggest that the enamine moiety present in **6** is not significantly protonated by TFA.

One striking feature of the corrole-forming reaction is the weak dependence of the corrole yield on dilution (Table 1). While the yield of *trans*-A_2B_2-porphyrin increases up to three times upon dilution[17b] (100 to 31.6 mM), the yield of corrole increases only 1.2 times upon dilution (270 to 33 mM). Moreover, the DPM concentration of 270 mM gives reasonable yield, but that is not the case for *trans*-porphyrins if the concentration is 100 mM. Among two competitive processes of closing the macrocyclic ring (via the reaction of linear tetrapyrrole with another aldehyde molecule or via the intramolecular pyrrole−pyrrole condensation), only the second one should be favored in high dilution; these experimental results contradict that. However, high dilution does not necessarily afford higher yields of the desired cyclic compound when the cyclization step is preceded by a reversible association step.[22] To sum up, the concentration of TFA used here represents some compromise between a value favoring the pyrrol−-pyrrole condensation and a value favoring the reaction of an aldehyde with a dipyrromethane.

Exploration of Scope. The optimized procedure (CH_2Cl_2, [DPM] = 33 mM, [aldehyde] = 17 mM, [TFA] = 1.3 mM, 5 h,[23] room temperature, 1 equiv of DDQ) was subsequently used in the preparation of various corroles. Thirteen aldehydes **5**−**17** with various substituents (OMe, OH, NO_2, CN, SOMe, F, SAc) were reacted with mesityldipyrromethane **1** (Scheme 3). All reactions gave rise to *trans*-A_2B-corroles **20**−**32** in moderate to good yields (10−22%) regardless of the electronic nature of substituents in the starting aldehyde. The only exception is 3-hydroxybenzaldehyde **19**, which furnished corrole **32** in 3% yield. Less reactive aldehydes possessing

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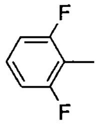
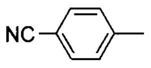
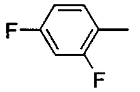
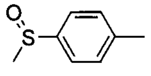
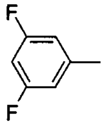
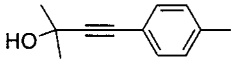
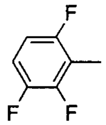
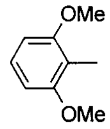
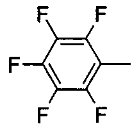
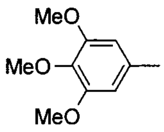
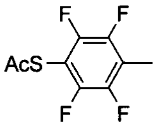
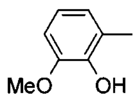
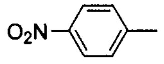
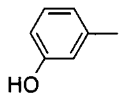
[21] Sridevi, B.; Narayanan, S. J.; Rao, R.; Chandrashekar, T. K.; Englich, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **2000**, *39*, 3669−3677.

[22] Spanagel, E. W.; Carothers, W. H. *J. Am. Chem. Soc.* **1935**, *57*, 929.

[23] Although the methodological study showed that there is no difference in the yield of corrole **3** when the reaction time was 0.25 or 5 h, taking into consideration that most of aldehydes are less reactive than 2,6-difluorobenzaldehyde we decided to apply 5 h as the “safe” reaction time.

Scheme 3

1

Aldehyde	R	Corrole	Yield	Aldehyde	R	Corrole	Yield
2		**3**	25%	**13**		**26**	18%
7		**20**	20%	**14**		**27**	21%
8		**21**	19%	**15**		**28**	10%
9		**22**	19%	**16**		**29**	19%
10		**23**	22%	**17**		**30**	16%
11		**24**	19%	**18**		**31**	16%
12		**25**	19%	**19**		**32**	3%

electron-donating substituents (even sterically hindered 2,6-dimethoxybenzaldehyde **16**) reacted equally well. It is noteworthy that judging from TLC and ESI-MS respective *trans*-A_2B_2-porphyrin is always present as a side-product in this reaction. In a few cases it was possible to isolate them from the reaction mixture in 1−4% yield. It seems that the yield of porphyrin is smaller if an aldehyde possesses electron-donating groups.

Usually, on column chromatography and TLC corroles are proceeded by an olive-green band. All attempts to purify this compound have failed. When the apparently homogenic band was collected, TLC was performed, which showed the presence of at least four molecules including parent corrole (although the latter one created a separate band on the column). As a result of the impossibility of obtaining a pure substance it is hard to unequivocally establish the structure of the main component. It has been reported that solutions of *meso*-aryl substituted corroles are light-sensitive, creating linear diamides.[24] Taking into consideration the low polarity of this substance, the acceleration of its formation during chromatography on alumina, the very weak IR absorption in the 1600−1800 cm^{-1} region, and probable partial reversibility of its formation, we think that the olive-green compounds are a radical cation of corroles. This radical cation could next form more polar unsaturated amides via pyrrole−pyrrole bond cleavage. The formation of a π dication radical during the oxidation of corroles in the presence of acid has been reported.[25] Because of the relatively low oxidation potential of corroles these green species are always present in samples after the chromatographical separation in ~1%.

When the same conditions were subsequently employed in the reaction using phenyldipyrromethane **33**

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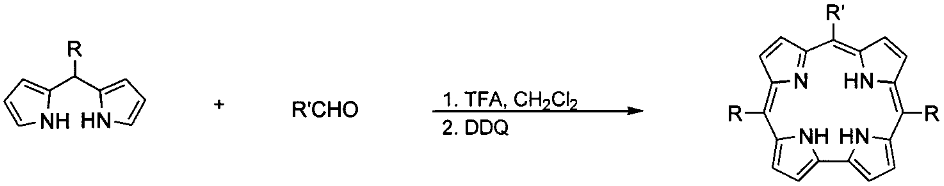
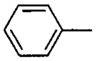
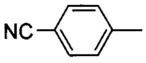
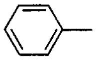
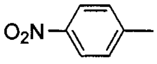
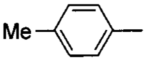
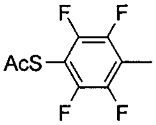
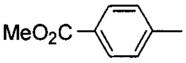
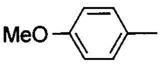
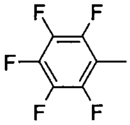
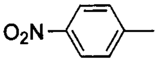
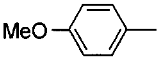
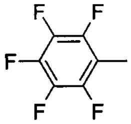
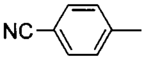
(24) Tardieux, C.; Gros, C. P.; Guilard, R. *J. Heterocycl. Chem.* **1998**, *35*, 965−970.

(25) Endeward, B.; Plato, M.; Will, S.; Vogel, E.; Szycewski, A.; Mobius, K. *Appl. Magn. Reson.* **1998**, *14*, 69.

Scheme 4



DPM	R	Aldehyde	R'	Corrole	Yield
33		**13**		**41**	7%
33		**12**		**42**	6%
34		**11**		**43**	10%
35		**39**		**44**	6%
36		**10**		**45**	7%
37		**40**		**46**	7%
38		**13**		**47**	6%

and pentafluorophenyldipyrromethane **38** some scrambling was detected using TLC and ESI-MS of the crude reaction mixture. On the basis of ESI-MS spectra scrambling was estimated as Level 1 (for phenyldipyrromethane **33**) or Level 2 (for pentafluorophenyldipyrromethane **38**) according to Lindsey's classification.[17b] Therefore a smaller amount of TFA was used to solve this problem. When a five times smaller amount of acid was used, no detectable scrambling (Level 0) was observed according to ESI-MS. These modified conditions were successfully applied to the reaction of various dipyrromethanes **33**−**38** (possessing both electron-donating and electron-withdrawing substituents) with aldehydes **10**−**13** and **39** and **40** (Scheme 4). All reactions furnished *trans*-A_2B-corroles **41**−**47** regardless of the combination of the electronic nature of the substituents in both substrates. Yields were in the range of 6−10%, substantially lower than those obtained starting from mesityldipyrromethane.

The spectral characteristics of these corroles are in good agreement with those obtained for the 5,10,15-triphenylcorrole.[7] Their electronic spectra show a Soret-like band around 415−420 nm and broad Q-bands in the 515−650 region. Although the color of solutions of corroles varies from pink-violet (**3**, **20**−**24**, **26**−**32**, **47**) through red (**25**, **42**) to blue-green (**41**, **43**−**45**) there are no significant differences in their UV−vis spectra. The only exception is corrole **46**, whose solution exhibits a grass-green color and whose Soret band is very broad and relatively weak. On the other hand there are only two Q-bands, relatively strong. ^1H NMR spectra of corroles **41**−**47** exhibit broad AB patterns in the aromatic region, while spectra of corroles **20**−**32** derived from mesityldipyrromethane have rather sharp signals. In the case of corroles **41**, **42**, and **44** the NH signal is probably so broad that it is not really visible.

To prove the scalability of this process, a large scale preparation of corroles **23**, **30**, and **41** was attempted. The reactions of MesDPM **1** with pentafluorbenzaldehyde **10** and 3,4,5-trimethoxybenzaldehyde **17** performed at 8 mmol scale (10 times greater than standard experiments described in this paper) furnished 500−600 mg of corrole **23** and **30** in essentially the same yield as in the small scale (respectively, 22% and 18%). Similarly, scale-up of the reaction of phenyldipyrromethane **33** with 4-cyanobenzaldehyde **13** led to 160 mg (7%) of corrole **41**.

Conclusions

This paper establishes the foundation for the first comprehensive method for the synthesis of *trans*-A_2B-corroles.[26] Our detailed study of the 2 + 1 condensation of a dipyrromethane and an aldehyde has led to the following conclusions. (1) The reaction at high concentration of substrates and in the presence of a very small amount of TFA favors the formation of corroles and suppresses the formation of porphyrins. The optimal conditions for the corrole-forming reaction are as follows: CH$_2$Cl$_2$, [DPM] = 33 mM, [aldehyde] = 17 mM, [TFA] = 1.3 mM (for sterically hindered DPMs) or [TFA] = 0.26 mM (for sterically unhindered DPMs), 5 h, room temperature, 1 equiv of DDQ). (2) A variety of substituents (OMe, OH, NO$_2$, CN, I, SOMe, F, SAc, CO$_2$Me) are tolerated in this reaction. (3) Yields of corroles obtained from mesityldipyrromethane are usually significantly higher than yields of corroles obtained from other dipyrromethanes. These results are not only of theoretical significance in that they provide new insight into factors influencing the course of the reaction of pyrrole derivatives with aldehydes leading to macrocyclic structures, but they may also open the door to practical applications. The use of the 2 + 1 approach can open the way to the synthesis of a wide range of *meso*-substituted corroles, which can serve as an ideal platform to obtaining more complex systems based on these macrocycles.

Experimental Section

General. All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH$_2$Cl$_2$, hexanes) were distilled prior use. All reported ^{1}H NMR spectra were collected in CDCl$_3$ unless otherwise noted. UV−vis absorption spectra were recorded in toluene (Cary). Chromatography was performed on silica (Kieselgel 60, 200−400 mesh) or alumina (Fluka). Mass spectra were obtained via electrospray (ESI-MS). The following compounds were prepared as described in the literature: aldehydes **11**,[27] **14**,[28] **15**;[29] dipyrromethanes **1** and **33**−**38**.[18] Purity of all new corroles and porphyrins was established on the basis of ^{1}H NMR spectra and ESI-MS spectra.

General Procedure for the Preparation of Corroles starting from Mesityldipyrromethane 1. Samples of mesityldipyrromethane **1** (210 mg, 0.80 mmol) and an aldehyde (0.04 mmol) were added to 24 mL of the pre-prepared solution of TFA (10 μL, 0.13 mmol) in CH$_2$Cl$_2$ (100 mL). The reaction was left at room temperature. After 5 h, the solution of DDQ (180 mg, 0.80 mmol) in toluene (2 mL) was added, and the reaction was stirred at room temperature for a further 5 min. The purification details are described for each case as follows.

10-(2,6-Difluorophenyl)-5,15-dimesitylcorrole (3). The reaction mixture was filtered through the silica pad (CH$_2$Cl$_2$/hexanes, 1:1) followed by column chromatography (silica, CH$_2$Cl$_2$/hexanes, 4:6). A broad pink-violet band (containing corrole **3** and porphyrin **4**) proceeded by a dark-green band was collected. The dark-violet residue was triturated with acetone and filtered through glass wool in a Pasteur pipet. Purple crystals collected are pure porphyrin **4** (12 mg, 4%), and evaporation of filtrate gave pure corrole **3** (64 mg, 25%) as a violet solid. Data for **3**: ^{1}H NMR (500 MHz) δ −1.60 (bs, 3H), 1.95 (s, 12H), 2.61 (s, 6H), 7.28 (s, 4H), 7.30−7.38 (m, 2H), 7.66−7.74 (m, 1H), 8.31 (d, J = 3.9 Hz, 2H), 8.37−8.42 (m, 2H), 8.49−8.54 (m, 2H), 8.85 (d, J = 4.1 Hz, 2H); ESI-MS obsd 647.3 [M + H$^+$]; ESI-HR obsd 647.3000 [M + H$^+$], calcd exact mass 647.2981 (C$_{43}$H$_{37}$F$_2$N$_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (138), 424 (112), 566 (22), 598 (12), 632 (4.0) nm.

10,20-Bis(2,6-difluorophenyl)-5,15-dimesitylporphyrin (4): ^{1}H NMR (200 MHz) δ −2.72 (s, 2H), 1.83 (s, 12H), 2.64 (s, 6H), 7.20−7.40 (m, 8H), 7.70−7.90 (m, 4H), 8.72 (d, J = 4.8 Hz, 4H), 8.79 (d, J = 4.8 Hz, 4H); ESI-MS obsd 771.5 [M + H$^+$]; ESI-HR obsd 771.3124 [M + H$^+$], calcd exact mass 771.3111 (C$_{50}$H$_{39}$F$_4$N$_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 416 (239), 511 (13), 544 (3.3), 588 (3.8), 644 (1.6) nm.

10-(2,4-Difluorophenyl)-5,15-dimesitylcorrole (20). The reaction mixture was passed over a column (silica, CH$_2$Cl$_2$/hexanes, 1:1) affording corrole **20** contaminated with the small amount of porphyrin. Subsequent chromatography (alumina, CH$_2$Cl$_2$/hexanes, 1:4) afforded pure corrole (51 mg, 20%) as a violet solid: ^{1}H NMR (500 MHz) δ −1.77 (brs, 3H), 1.91 (s, 6H), 1.92 (s, 6H), 2.59 (s, 6H), 7.18−7.28 (m, 6H), 7.97−8.06 (m, 1H), 8.30 (d, J = 3.9 Hz, 2H), 8.34−8.38 (m, 2H), 8.47−8.50 (m, 2H), 8.85 (d, J = 4.1 Hz, 2H); ESI-MS obsd 647.3 [M + H$^+$]; ESI-HR obsd 647.2995 [M + H$^+$], calcd exact mass 647.2981 (C$_{43}$H$_{37}$F$_2$N$_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (92), 425 (73), 567 (15), 601 (8.9), 634 (3.6) nm.

10-(3,5-Difluorophenyl)-5,15-dimesitylcorrole (21). The reaction mixture was passed over a silica column (silica, CH$_2$Cl$_2$/hexanes, 1:1) affording corrole **21** contaminated with unidentified compounds. The subsequent chromatography (silica, hexanes then CH$_2$Cl$_2$/hexanes, 1:4) afforded pure corrole (48 mg, 19%) as a violet solid: ^{1}H NMR (500 MHz) δ −1.86 (brs, 3H), 1.91 (s, 12H), 2.59 (s, 6H), 7.10−7.20 (m, 1H), 7.26 (s, 4H), 7.65−7.75 (m, 2H), 8.32 (d, J = 4.0 Hz, 2H), 8.47 (d, J = 4.7 Hz, 2H), 8.51 (d, J = 4.7 Hz, 2H), 8.87 (d, J = 4.1 Hz, 2H); ESI-MS obsd 647.3 [M + H$^+$]; ESI-HR obsd 647.2995 [M + H$^+$], calcd exact mass 647.2981 (C$_{43}$H$_{37}$F$_2$N$_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 409 (159), 426 (133), 568 (25), 602 (15), 636 (7.0) nm.

5,15-Dimesityl-10-(2,3,6-trifluorophenyl)-corrole (22). The reaction mixture was passed over a silica column (silica, CH$_2$Cl$_2$/hexanes, 1:1) affording corrole **22** contaminated with the small amount of porphyrin and less polar dark-green compound. Subsequent chromatography (alumina, CH$_2$Cl$_2$/hexanes, 1:4) afforded pure corrole **22** (50 mg, 19%) as a violet solid:^{1}H NMR (500 MHz) δ −1.62 (brs, 3H), 1.91 (s, 12H), 2.58 (s, 6H), 7.20−7.28 (m, 5H), 7.48−7.57 (m, 1H), 8.27 (d, J = 3.9 Hz, 2H), 8.33−8.37 (m, 2H), 8.47−8.51 (m, 2H), 8.81 (d, J = 4.1 Hz, 2H); ESI-MS obsd 665.3 [M + H$^+$]; ESI-HR obsd 665.2923 [M + H$^+$], calcd exact mass 665.2887 (C$_{43}$H$_{36}$F$_3$N$_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (112), 425 (88), 565 (18), 597 (9.1), 631 (2.9) nm.

5,15-Dimesityl-10-(pentafluorophenyl)corrole (23). Large Scale Preparation. Mesityldipyrromethane **1** (2.10 g, 7.95 mmol) and pentafluorobenzaldehyde **10** (480 μL, 3.98 mmol) was dissolved in CH$_2$Cl$_2$ (240 mL). Then TFA (24 μL, 0.31 mmol) was added, and the reaction mixture was left at room temperature. After 5 h, DDQ (1.80 g, 7.95 mmol) in toluene (30 mL) was added, and the reaction was stirred at room temperature for a further 15 min. The reaction mixture was concentrated and filtered twice through pads of silica (silica, CH$_2$Cl$_2$/hexanes, 2:3). The violet solid was subsequently chromatographed (silica, CH$_2$Cl$_2$/hexanes, 1:4) to afford pure corrole **23** (598 mg, 21.5%) and pure porphyrin **23a** as a purple solid (110 mg, 3%). Data for **23**: ^{1}H NMR (500 MHz) δ −1.71 (brs, 3H), 1.92 (s, 12H), 2.59 (s, 6H), 7.26 (s, 4H), 8.25−8.35 (m, 4H), 8.52 (d, J = 4.7 Hz, 2H), 8.83 (d, J = 4.1 Hz, 2H); ESI-MS obsd 701.3 [M + H$^+$]; ESI-HR obsd 701.2679 [M + H$^+$], calcd exact mass 701.2698 (C$_{43}$H$_{34}$F$_5$N$_4$); Anal. Calcd for C$_{43}$H$_{33}$F$_5$N$_4$: C, 73.70; H, 4.75; N, 8.00. Found: C, 73.81; H, 4.46; N, 8.02; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (166), 425 (131), 566 (28), 596 (12), 631 (3.5) nm. For **5,15-dimesityl-10,20-bis(pentafluorphenyl)porphyrin (23a)** spectral and physical properties concur with published data.[17b]

10-[4-(*S*-Acetylthio)-2,3,5,6-tetrafluorophenyl]-5,15-dimesitylcorrole (24). The reaction mixture was passed over a silica column (silica, CH$_2$Cl$_2$/hexanes, 1:1) affording corrole **24** contaminated with unidentified compounds. The subsequent chromatography (silica, CH$_2$Cl$_2$/hexanes, 1:1) afforded pure corrole **24** (58 mg, 19%) as a violet solid: ^{1}H NMR (200 MHz) δ −1.55 (s, 3H), 1.93 (s, 12H), 2.59 (s, 6H), 2.63 (s, 3H), 7.26 (s, 4H), 8.28 (d, J = 4.1 Hz, 2H), 8.35−8.45 (m, 2H), 8.54

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(26) After the acceptance of our paper a short communication by Brückner et al. describing the acid-mediated condensation of the excess of dipyrromethanes with aldehydes quenched by the addition of DDQ was published (Briñas, R. P.; Brückner, C. *Synlett* **2001**, 442−444). It is noteworthy to comment that apparently high yields (20−40%) obtained for corroles derived from sterically unhindered dipyrromethanes were calculated on the basis of the amount of aldehydes, while more valuable DPMs have been used in three times excess in relation to the stoichiometric ratio. Porphyrin formation is observed under these conditions also (contrary to author's statement).

(27) Gryko, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7345−7355

(28) Creary, M.; Mehrsheikh-Mohammadi, M. *J. Org. Chem.* **1986**, *51*, 1110−1114.

(29) Gryko, D.; Li, J.; Dabke, R. B.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Mater. Chem.* **2001**, *11*, 1162−1180.

(d, J = 4.8 Hz, 2H), 8.82 (d, J = 4.2 Hz, 2H); ESI-MS obsd 757.3 [M + H$^+$]; ESI-HR obsd 757.2640 [M + H$^+$], calcd exact mass 757.2619 ($C_{45}H_{37}F_4ON_4S$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 409 (145), 427 (127), 566 (27), 596 (13), 631 (3.2), 673 (1.5) nm.

10-(4-Nitrophenyl)-5,15-dimesitylcorrole (25). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **25** contaminated with unidentified compounds comprised the first red band. Subsequent chromatography (silica, CH_2Cl_2/hexanes, 1:1) afforded pure corrole **25** (48 mg, 19%) as a deep red solid: ^{1}H NMR (500 MHz) δ −1.78 (s, 3H), 1.92 (s, 12H), 2.58 (s, 6H), 7.26 (s, 4H), 8.30−8.36 (m, 4H), 8.41 (d, J = 4.6 Hz, 2H), 8.51−8.56 (m, 4H), 8.88 (d, J = 4.2 Hz, 2H); ESI-MS obsd 656.3 [M + H$^+$]; ESI-HR obsd 656.3035 [M + H$^+$], calcd exact mass 656.3020 ($C_{43}H_{38}O_2N_5$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 410 (83), 426 (71), 570 (19), 603 (11), 639 (4.0) nm.

10-(4-Cyanophenyl)-5,15-dimesitylcorrole (26). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **26** contaminated with unidentified compounds comprised violet-pink band. The subsequent chromatography (silica, CH_2Cl_2/hexanes, 1:1) afforded pure corrole **26** (46 mg, 18%) as a violet solid: ^{1}H NMR (200 MHz) δ −1.81 (brs, 3H), 1.92 (s, 12H), 2.58 (s, 6H), 7.26 (s, 4H), 7.95−8.05 (m, 2H), 8.25−8.37 (m, 4H), 8.39 (d, J = 4.7 Hz, 2H), 8.52 (d, J = 4.8 Hz, 2H), 8.88 (d, J = 4.2 Hz, 2H); ESI-MS obsd 636.3 [M + H$^+$]; ESI-HR obsd 636.3128 [M + H$^+$], calcd exact mass 636.3122 ($C_{44}H_{38}N_5$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 410 (113), 430 (100), 569 (19), 603 (11), 639 (4.2) nm.

10-(4-Methylsulfoxyphenyl)-5,15-dimesitylcorrole (27). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/EtOAc, 9:1) affording corrole **27** contaminated with an unidentified compounds. Two subsequent chromatographies [(1) silica, CH_2Cl_2 then CH_2Cl_2/EtOAc, 9:1; (2) silica, THF/hexanes, 1:3 then 2:3, 1:1] afforded pure corrole **27** (28 mg, 21%) as a violet solid: ^{1}H NMR (200 MHz) δ −1.78 (brs, 3H), 1.92 (s, 12H), 2.59 (s, 6H), 2.95 (s, 3H), 7.26 (s, 4H), 7.90−8.00 (m, 2H), 8.25−8.37 (m, 4H), 8.41 (d, J = 4.7 Hz, 2H), 8.51 (d, J = 4.7 Hz, 2H), 8.88 (d, J = 4.2 Hz, 2H); ESI-MS obsd 673.3 [M + H$^+$]; ESI-HR obsd 673.2980 [M + H$^+$], calcd exact mass 673.2996 ($C_{44}H_{41}N_4OS$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 410 (93), 428 (81), 568 (14), 604 (8.9), 639 (4.1) nm.

10-[4-(Methyl-3-hydroxy-1-butyn-1-yl)phenyl]-5,15-dimesitylcorrole (28). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/EtOAc, 19:1) affording corrole **28** contaminated with unidentified compounds. The subsequent chromatography (silica, CH_2Cl_2) afforded pure corrole **28** (28 mg, 10%) as a violet solid: ^{1}H NMR (500 MHz) δ −1.67 (brs, 4H), 1.72 (s, 6H), 1.91 (s, 12H), 2.59 (s, 6H), 7.25 (s, 4H), 7.77, 8.11 (AA′BB′, 4H), 8.32 (d, J = 4.0 Hz, 2H), 8.42−8.51 (m, 4H), 8.87 (d, J = 4.1 Hz, 2H); ESI-MS obsd 693.4 [M + H$^+$]; ESI-HR obsd 693.3597 [M + H$^+$], calcd exact mass 693.3588 ($C_{48}H_{45}N_4O$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 410 (130), 430 (112), 569 (18.7), 605 (11.8), 632 (6.3) nm.

10-(2,6-Dimethoxyphenyl)-5,15-dimesitylcorrole (29). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **29** contaminated with porphyrin **29a** and a few unidentified compounds comprised a red-violet band. The subsequent chromatography (silica, CH_2Cl_2/hexanes, 2:3) afforded pure corrole **29** (50 mg, 19%) as a violet solid and respective porphyrin **29a** (2 mg, 0.6%) as a purple solid. Data for **29**: ^{1}H NMR (200 MHz) δ −1.51 (brs, 3H), 1.91 (s, 12H), 2.57 (s, 6H), 3.54 (s, 6H), 6.93 (d, J = 8.4 Hz, 2H), 7.23 (s, 4H), 7.60 (t, J = 8.5 Hz, 1H), 8.21 (d, J = 4.1 Hz, 2H), 8.30 (d, J = 4.7 Hz, 2H), 8.38 (d, J = 4.7 Hz, 2H), 8.75 (d, J = 4.1 Hz, 2H); ESI-MS obsd 671.3 [M + H$^+$]; ESI-HR obsd 671.3405 [M + H$^+$], calcd exact mass 671.3381 ($C_{45}H_{43}N_4O_2$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (134), 426 (106), 567 (22), 605 (14), 634 (6.9) nm. Data for **10,20-bis(2,6-dimethoxyphenyl)-5,15-dimesitylporphyrin (29a)**: ^{1}H NMR (500 MHz) δ −2.48 (s, 2H), 1.85 (s, 12H), 2.61 (s, 6H), 3.50 (s, 12H), 6.99 (d, J = 8.5 Hz, 4H), 7.24 (s, 4H), 7.70 (t, J = 8.5 Hz, 2H), 8.55−8.70 (m 8H); ESI-MS obsd 819.4 [M + H$^+$]; ESI-HR obsd 819.3914 [M + H$^+$], calcd exact mass 819.3937 ($C_{54}H_{51}N_4O_4$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 419 (833), 513 (39), 545 (11), 591 (11), 647 (4.5) nm.

10-(3,4,5-Trimethoxyphenyl)-5,15-dimesitylcorrole (30). Large Scale Preparation. Mesityldipyrromethane **1** (2.10 g, 7.95 mmol) and 3,4,5-trimethoxybenzaldehyde **17** (780 mg, 3.98 mmol) was dissolved in CH_2Cl_2 (240 mL). Then TFA (24 μL, 0.31 mmol) was added, and the reaction mixture was left at room temperature. After 5 h, DDQ (1.80 g, 7.95 mmol) in toluene (30 mL) was added, and the reaction was stirred at room temperature for a further 15 min. The reaction mixture was concentrated and filtered through a pad of silica (silica, CH_2Cl_2/hexanes, 1:1, then 2:1, 3:1). All fractions containing titled corrole (contaminated with yellow impurities) were collected and evaporated under reduced pressure. The crude product was crystallized from hexanes to afford pure corrole **30** (514 mg, 18.5%) (45 mg, 16% in small scale experiment) as a violet solid: ^{1}H NMR (200 MHz) δ −1.79 (brs, 3H), 1.92 (s, 12H), 2.59 (s, 6H), 3.95 (s, 6H), 4.14 (s, 3H), 7.26 (s, 4H), 7.41 (s, 2H), 8.32 (d, J = 4.2 Hz, 2H), 8.49 (d, J = 4.8 Hz, 2H), 8.57 (d, J = 4.7 Hz, 2H), 8.87 (d, J = 4.1 Hz, 2H); ESI-MS obsd 701.4 [M + H$^+$]; ESI-HR obsd 701.3506 [M + H$^+$], calcd exact mass 701.3486 ($C_{46}H_{45}N_4O_3$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 409 (97), 427.6 (78), 567.7 (15), 605.7 (9.7), 638 (5.2), 673 (1.5) nm

10-(2-Hydroxy-3-methoxyphenyl)-5,15-dimesitylcorrole (31). The reaction mixture was passed over a silica column (silica, CH_2Cl_2) affording corrole **31** contaminated with unidentified compounds. Two subsequent chromatographies [(1) silica, CH_2Cl_2; (2) silica, CH_2Cl_2/hexanes, 3:1] afforded pure corrole **31** (43 mg, 16%) as a violet solid: ^{1}H NMR (500 MHz) δ 1.27 (brs, 4H), 1.90 (s, 6H), 1.93 (s, 6H), 2.58 (s, 6H), 4.08 (s, 3H), 7.14−7.26 (m, 6H), 7.58 (dd, J = 1.4 Hz, J = 7.6 Hz, 2H), 8.27 (d, J = 4.0 Hz, 2H), 8.42−8.47 (m, 4H), 8.82 (d, J = 4.0 Hz, 2H); ESI-MS obsd 657.3 [M + H$^+$]; ESI-HR obsd 657.3218 [M + H$^+$], calcd exact mass 657.3224 ($C_{44}H_{41}N_4O_2$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 408 (98), 426 (82), 568 (15), 603 (9.7), 635 (5.2) nm.

10-(3-Hydroxyphenyl)-5,15-dimesitylcorrole (32). The reaction mixture was passed over a silica column (silica, CH_2Cl_2) affording corrole **32** contaminated with unidentified compounds. The subsequent chromatography (silica, CH_2Cl_2) afforded pure corrole (8 mg, 3%) as a violet solid: ^{1}H NMR δ (500 MHz) 0.10 (brs, 4H), 1.90 (s, 6H), 1.93 (s, 6H), 2.60 (s, 6H), 6.95−7.05 (m, 1H), 7.25 (s, 4H), 7.43−7.53 (m, 2H), 7.68 (d, J = 7.4 Hz, 1H), 8.31 (d, J = 4.1 Hz, 2H), 8.46 (s, 4H), 8.87 (d, J = 4.0 Hz, 2H); ESI-MS obsd 627.3 [M + H$^+$]; ESI-HR obsd 627.3136 [M + H$^+$], calcd exact mass 627.3118 ($C_{43}H_{39}N_4O$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 409 (80), 427 (65), 568 (12), 604 (8.0), 637 (4.3), 672 (1.0) nm.

General Procedure for the Preparation of Corroles Starting from Other Dipyrromethanes. Samples of a dipyrromethane (0.80 mmol) and an aldehyde (0.04 mmol) were dissolved in 24 mL of the pre-prepared solution of TFA (4 μL, 0.13 mmol) in CH_2Cl_2 (200 mL). The reaction was left at room temperature. After 5 h, the solution of DDQ (180 mg, 0.80 mmol) in toluene (2 mL) was added, and the reaction was stirred at room temperature for further 15 min. Then the reaction mixture was purified as described below.

10-(4-Cyanophenyl)-5,15-diphenylcorrole (41). **Large Scale Preparation.** Phenyldipyrromethane **33** (1.77 g, 7.95 mmol) and 4-cyanobenzaldehyde **13** (520 mg, 3.98 mmol) was dissolved in CH_2Cl_2 (240 mL). Then TFA (4.8 μL, 0.06 mmol) was added, and the reaction mixture was left at room temperature. After 5 h, DDQ (1.80 g, 7.95 mmol) in toluene (30 mL) was added, and the reaction was stirred at room temperature for a further 15 min. The reaction mixture was directly filtered through pad of silica (silica, CH_2Cl_2/hexanes, 2:3). All fractions containing titled corrole contaminated with other species were collected and eveporated. The dark green residue was triturated with 4:1 hexanes/acetone, and crystals were filtered, dissolved in hot acetone, and cooled in the freezer. After filtration crystals were washed with hexanes and cold acetone giving corrole **41** (151 mg, 7%): ^{1}H NMR (200 MHz, THF-d_8) δ 7.60−7.90 (m, 6H), 8.06−8.18 (m, 2H), 8.24−8.60 (m, 10H), 8.74−8.98 (m, 4H); ESI-MS obsd 552.4 [M + H$^+$]; ESI-HR obsd 552.2204 [M + H$^+$], calcd exact mass 552.2188 ($C_{38}H_{26}N_5$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 421 (54), 578 (7.9), 614 (5.7), 649 (4.2) nm.

10-(4-Nitrophenyl)-5,15-diphenylcorrole (42). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **42** contaminated with porphyrin and unidentified compounds comprised a first, green band. After evaporation, hexanes was added to dark crystals and the resulting suspension was filtered through glass wool using a Pasteur pipet. Crystals were washed thoroughly with hexanes until the filtrate was colorless. Then the crystals (mixture of corrole and porphyrin) were redissolved and chromatographed (silica, CH_2Cl_2/hexanes, 1:1) to obtain pure corrole **42** (13 mg, 6%): ^{1}H NMR (200 MHz, THF-d_8) δ 7.6−7.9 (m, 6H), 8.2−8.7 (m, 12H), 8.82 (d, J = 4.7 Hz, 2H), 8.94 (d, J = 4.1 Hz, 2H), ESI-MS obsd 572.2 [M + H$^+$]; ESI-HR obsd 572.2099 [M + H$^+$], calcd exact mass 572.2081 ($C_{37}H_{26}N_5O_2$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 421 (96), 582 (18), 608 (13), 648 (7.2) nm.

10-[4-(*S*-Acetylthio)-2,3,5,6-tetrafluorophenyl]-5,15-bis-(4-methylophenyl)corrole (43). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **43** contaminated with unidentified compounds comprised a first green-blue band. The mixture was chromatographed (silica, THF/hexanes, 1:3), and the broad blue-green band was collected. After evaporation, hexanes was added to dark crystals, and the suspension was filtered through glass wool using a Pasteur pipet to obtain pure corrole (29 mg, 10%): ^{1}H NMR (500 MHz) δ −2.61 (brs, 3H), 2.63 (s, 6H), 2.66 (s, 3H), 7.61 (d, J = 7.7 Hz, 4H), 8.1−8.5 (m, 8H), 8.7−9.0 (m, 4H); ESI-MS obsd 701.2 [M + H$^+$]; ESI-HR obsd 701.1970 [M + H$^+$], calcd exact mass 701.1993 ($C_{41}H_{29}N_4OF_4S$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 418 (120), 517 (6.6), 560 (15), 581 (19), 605 (13), 643 (5.4) nm.

10-(4-Carboxymethylo)-5,15-bis(4-iodophenyl)corrole (44). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **44** contaminated with unidentified compounds comprised a first brown-red band. After evaporation, hexanes was added to dark crystals, and the suspension was filtered through glass wool using a Pasteur pipet. Crystals were washed thoroughly with hexanes and hexanes/acetone, 3:1 until the filtrate was colorless. Then the crystals (mixture of corrole and porphyrin) were redissolved and chromatographed (silica, CH_2Cl_2/hexanes, 2:3, then 1:1, 3:2, 3:1). The blue-green band was collected and evaporated to obtain pure corrole (21 mg, 6%): ^{1}H NMR (200 MHz, THF-d_8) δ 4.03 (s, 3H); 8.0−8.3 (m, 16H), 8.35−8.55 (m, 4H); ESI-MS obsd 837.0 [M + H$^+$]; ESI-HR obsd 837.0221 [M + H$^+$], calcd exact mass 837.0218 ($C_{39}H_{27}N_4O_2I_2$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 425 (103), 581 (14), 618 (10), 650 (8.9) nm.

10-(Pentafluorophenyl)-5,15-bis(4-methoxyphenyl)corrole (45). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **45** contaminated with porphyrin and unidentified compounds comprised a green band. After evaporation, hexanes was added to dark crystals, and the suspension was filtered through glass wool using a Pasteur pipet. The crystals were washed thoroughly with hexanes until the filtrate was colorless. Then the crystals (mixture of corrole and porphyrin) were redissolved and chromatographed (silica, CH_2Cl_2/hexanes, 2:3). The blue-green band was collected containing pure corrole **45** (18 mg, 7%): ^{1}H NMR (200 MHz, THF-d_8) δ −2.56 (brs, 3H), 4.02 (s, 6H), 7.36 (d, J = 8.3 Hz, 4H), 8.1−8.5 (m, 8H), 8.7−8.9 (m, 4H); ESI-MS obsd 677.2 [M + H$^+$]; ESI-HR obsd 677.1968 [M + H$^+$], calcd exact mass 677.1970 ($C_{39}H_{26}N_4O_2F_5$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 418 (127), 563 (17), 585 (19), 607 (16), 645 (6.3) nm.

10-(4-Methoxyphenyl)-5,15-bis(4-nitrophenyl)corrole (46). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 3:2). Corrole **46** contaminated with porphyrin and unidentified compounds comprised a first dark green band. After evaporation, 4:1 hexanes/acetone were added to dark crystals, and the suspension was filtered through glass wool using a Pasteur pipet to remove yellow impurities. The crystals were washed thoroughly with the same system until the filtrate was colorless. Then compound was recrystalyzed (grass green solution) from THF/CH_2Cl_2/hexanes to afford corrole **46** (18 mg, 7%) as dark fine crystals: ^{1}H NMR (200 MHz, THF-d_8) δ −3.6-(−1.0) (brs, 3H), 4.05 (s, 3H), 7.20−7.50 (brs, 2H), 7.95−8.10 (brs, 2H), 8.13−9.25 (m, 16H); ESI-MS obsd 647.2 [M + H$^+$]; ESI-HR obsd 647.2054 [M + H$^+$], calcd exact mass 647.2037 ($C_{38}H_{27}N_6O_5$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 448 (46), 592 (14), 660 (13) nm.

10-(4-Cyanophenyl)-5,15-bis(pentafluorophenyl)corrole (47). The reaction mixture was passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). Corrole **47** contaminated with unidentified compounds comprised the second dark band. After evaporation, mixture was subsequently chromatographed (silica, CH_2Cl_2/hexanes, 2:3, then 1:1 and 3:2). Because some impurities were still present crystals were dissolved in hot hexanes and cooled in a freezer. After the filtration the crystals were washed with hexanes to obtain corrole **47** (16 mg, 6%) as a violet solid: ^{1}H NMR (200 MHz) δ −2.45 (brs, 3H), 8.05, 8.29 (AA′BB′, 4H), 8.54−8.80 (m, 6H), 9.12 (d, J = 4.3 Hz, 2H); ESI-MS obsd 732.1 [M + H$^+$]; ESI-HR obsd 732.1243 [M + H$^+$], calcd exact mass 732.1241 ($C_{38}H_{16}N_5F_{10}$); λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 418 (108), 567 (18), 613 (10), 639 (5.5) nm.

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Supporting Information Available: ^{1}H NMR spectra (including expansions) of corroles **3**, **20**−**32**, and **4**1−**47** and porphyrins **4** and **29a**; ESI-MS spectra of corroles **3**, **20**−**32**, and **41**−**47** and porphyrins **4** and **29a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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