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# *meso*-Pyrimidinyl-Substituted $A_2B$- and $A_3$-Corroles

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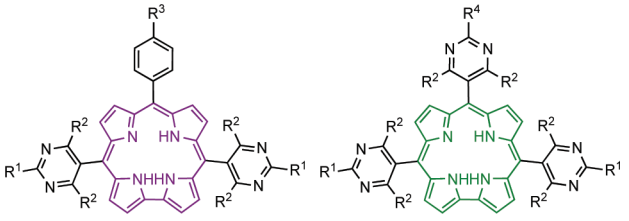

A variety of *meso*-pyrimidinyl-substituted $A_2B$- and $A_3$-corroles (A = 4,6-dichloropyrimidin-5-yl) have been synthesized by careful optimization of the macrocyclization conditions. *meso*-Pyrimidinylcorroles offer the distinct advantage of an unprecedented broad scope of functionalization options. Highly sterically encumbered triarylcorroles were readily prepared via efficient nucleophilic aromatic substitution and Suzuki cross-coupling procedures.

Due to their distinctive properties and envisaged advantages for particular applications, corroles are widely studied nowadays, in the sense that they are currently even challenging porphyrins as the "crown jewels" within the porphyrinoid family. Studies on these contracted porphyrin macrocycles have focused on their coordination chemistry, electrochemistry, and applicability in sensors, catalysis, medicine, and molecular electronics.[1] The recent success of corrole chemistry is in great part due to the impressive synthetic progress that has been made in the field over the past decade.[2] *meso*-Triarylcorroles show an improved stability over the previously studied $\beta$-alkylated (partially) *meso*-free analogues, and they have been prepared from a variety of aromatic aldehyde and aryldipyrromethane building blocks in acceptable to good yields by different cyclocondensation pathways.[2] As the knowledge, interest, and activity in the corrole field are steadily growing, the pressure on synthetic (porphyrinoid) chemists to create increasingly complex corrole derivatives with peculiar properties rises accordingly. So far, modification of the corrole framework, apart from the introduction of specific moieties on the corrole building blocks, has mostly been achieved by (regioselective) functionalization of the $\beta$-pyrrolic positions.[2,3] Postmacrocyclization elaboration via the *meso*-positions has only been reported in a few cases.[4] Double picket fence corroles are particularly attractive considering the success of the analogous porphyrins, e.g., as second-generation oxidation catalysts.[4]

To date, functionalization of corroles has mostly been performed on the metalated rather than the free-base (Fb) macrocycles, since they are considerably more robust. Metallocorroles have, however, demonstrated peculiar reactivities, and liberation of the Fb congener from a metallocorrole is often not trivial.[2] Recent achievements in the demetalation of certain metallocorroles (Ag, Mn, and especially Cu) now enable application of a metalation−demetalation protocol as a protective strategy toward functionalized Fb corroles.[5]

In continuation of our studies on pyrimidinylporphyrinoids,[6] we have previously explored the synthetic chemistry of *meso*-pyrimidinyl-substituted $AB_2$-corroles (A = 4,6-dichloropyrimidin-5-yl).[7,8] These pyrimidinylcorroles were proven to be versatile scaffolds for the construction of sophisticated functional corroles, since smooth functionalization on the 4,6-dichloropyrimidinyl *meso*-moieties via nucleophilic aromatic substitution ($S_NAr$) and Pd-catalyzed cross-coupling reactions (Suzuki, Stille, Liebeskind−Srogl)

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(8) These corroles have previously been denominated as $A_2B$-pyrimidinylcorroles (B = 4,6-dichloropyrimidin-5-yl) (ref 7).

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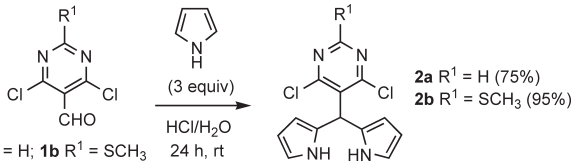
**SCHEME 1. Synthesis of 5-Pyrimidinyldipyrromethanes 2a,b**

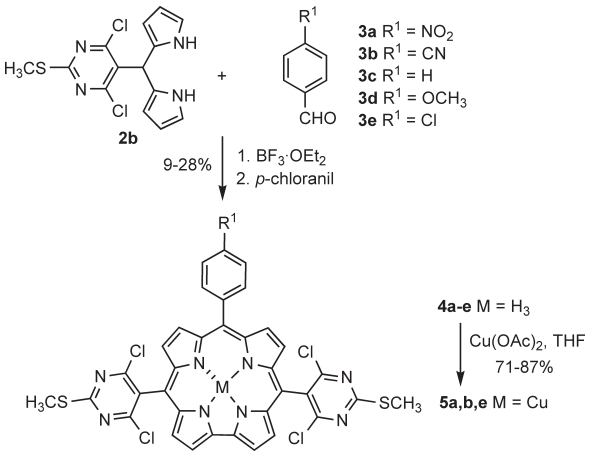



afforded a variety of $AB_2$-corrole derivatives. Our pyrimidinylcorrole research has now been extended to $A_2B$- and $A_3$-corroles. The extra *meso*-dichloropyrimidinyl units enable the introduction of additional functional groups, resulting in greater structural complexity and higher sterical encumbrance.

**$A_2B$-Pyrimidinylcorroles.** To prepare $A_2B$-corroles with two *meso*-dichloropyrimidinyl substituents, 5-pyrimidinyldipyrromethanes are required as precursors. We have recently reported the synthesis of aryldipyrromethanes in water as an attractive procedure avoiding large quantities of pyrrole.[9] Starting from 4,6-dichloropyrimidine-5-carbaldehydes **1a**,**b**, 5-pyrimidinyldipyrromethanes **2a**,**b** were obtained in high yields (75% and 95%, respectively) on applying optimized conditions (Scheme 1).[10] The methylthio group might enable insertion of other moieties on a later stage.[7] The main problem associated with the synthesis of dipyrromethanes (DPMs) in water is the aggregation tendency of the DPM precipitate, enclosing pyrrole and unreacted aldehyde. Depending on the aldehyde used, the precipitate may be too sticky for efficient stirring of the reaction mixture. A fine precipitate could be obtained through sonication or, alternatively, via slow addition of the pyrimidinecarbaldehyde to the acidic $H_2O$/pyrrole mixture.[10]

The synthesis of $A_2B$-pyrimidinylcorroles was initially performed starting from DPM **2b** and an electron-poor aromatic aldehyde, either 4-nitro- or 4-cyanobenzaldehyde. These aldehyde precursors were chosen to maximize the electron-deficient nature of the final $A_2B$-corrole, ensuring good structural stability. As a starting point, the conditions as carefully optimized for $AB_2$-pyrimidinylcorroles were chosen. The maximum $AB_2$-corrole yield (35%; precursors mesityl-DPM and **1a**) was obtained on condensation of the building blocks in a 1:1 ratio, catalyzed by a small amount of borontrifluoride dietherate catalyst (0.043 equiv).[7] Application of these conditions to the macrocyclization of DPM **2b** and 4-nitrobenzaldehyde (**3a**), in a stoichiometric 2:1 ratio, afforded only trace amounts of the desired $A_2B$-corrole **4a** (after oxidation with *p*-chloranil), even after 24 h (the reaction progress being monitored by ESI-MS) (Table S1 in the Supporting Information, Scheme 2).[10] Even upon variation of the catalyst content, the corrole yield did not rise above 3% (Table S1, Supporting Information). Starting from 4-cyanobenzaldehyde (**3b**), the yield could be enhanced to a still modest 10% $A_2B$-corrole **4b** through optimization of the reaction time, the amount of $BF_3 \cdot OEt_2$, and the building block ratio (Table S1, Supporting Information; Scheme 2).[10] Still not satisfied with the yield and the generality of the method, a more powerful synthetic protocol was pursued. It was observed during the optimization study that the corresponding $A_2B_2$-porphyrins were generally obtained as the

**SCHEME 2. Synthesis of $A_2B$-Pyrimidinylcorroles 4a−e**




main products. A larger excess of DPM might avoid insertion of the second aldehyde moiety and favor the formation of the [2 + 1] tetrapyrrane intermediate. Rather than adding DPM **2b** in significantly larger amounts, the excess was created in situ by slow addition of the aldehyde, activated with $BF_3 \cdot OEt_2$ (0.043 equiv), to a dilute solution of **2b** (3 equiv) in dichloromethane over several hours. When this procedure was applied to 4-cyanobenzaldehyde, $A_2B$-corrole **4b** was isolated in a substantially improved 28% yield. Likewise, $A_2B$-corroles **4a**,**c**−**e** were synthesized in fair yields (9−24%) from aldehyde precursors with either electron-donating or -withdrawing substituents (Scheme 2). The optimum reaction and oxidation time were slightly different depending on the aromatic aldehyde used. In a similar way, $A_2B$-corrole **4f** was synthesized starting from DPM **2a** and benzaldehyde (14% yield).

While performing functionalization reactions on the $AB_2$-pyrimidinylcorroles, it was observed that the Fb derivatives are not really suitable for elaboration of the substitution pattern. Modest yields were obtained in both $S_NAr$ and Suzuki cross-coupling reactions.[7] The same reactions did, however, provide high yields when performed on the corresponding Cu-corroles. Functionalized Fb corroles were more efficiently prepared by reductive demetalation of the Cu-corrole derivatives, rather than through direct modification on the metal-free $AB_2$-corroles.[5f,7] Prior to studying the functionalization scope of the $A_2B$-pyrimidinylcorroles, they were hence first metalated to afford their Cu analogues. Copper insertion can readily be achieved by simple stirring of the Fb corrole with copper(II) acetate in THF,[5f] and Cu-pyrimidinylcorroles **5a**,**b**,**e** were obtained in 71−87% yield (Scheme 2). Cu-corroles, formally being Cu(III) species, are diamagnetic at rt and can hence be characterized via NMR spectroscopy. Recent studies have provided new insights on the true electronic nature of corrolato copper complexes.[11]

Substitution of the four *meso*-chlorine functions was first pursued by $S_NAr$ reactions. Gradual substitution depending on the reaction temperature was observed. Treatment of Cu-corrole **5b** with 2.3 equiv of 4-*tert*-butylphenol in DMF at 90 °C afforded mainly the disubstituted $A_2B$-corrole as a

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(10) See the Supporting Information for more details.
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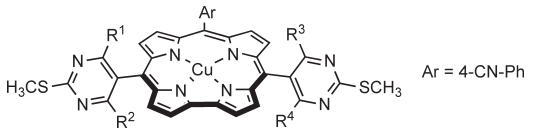
mixture of atropoisomers **6b**,**c**. After chromatographic separation, the α,*β*- (**6b**) and α,α-atropoisomers (**6c**) were isolated in 69 and 21% yield, respectively. Identification of the atropoisomers is based on their respective $^1$H NMR spectra.[10] Sterical reasons might be responsible for the higher yield of the *anti*-isomer **6b**. α,*β*-Atropoisomer **6b** is inherently chiral, even without considering the fact that Cu-corroles have recently been described as being chiral due to their saddled conformation.[11b] Under less forcing (70 °C) or less effective $S_NAr$ conditions,[10] monosubstituted $A_2B$-corrole **6a** remained in appreciable amounts (32% **6a** was isolated from a reaction at 70 °C). When the reaction was performed at an elevated temperature (120−140 °C) with a large excess of 4-*tert*-butylphenol (12 equiv), tetrasubstituted Cu-corrole **6d** was obtained as the main product (57−71%),[10] with only trace amounts of the trifunctionalized derivative. Performing the $S_NAr$ reaction under the (harsh) conditions required for full substitution of the corresponding Cu-$AB_2$-pyrimidinylcorrole (DMF, $K_2CO_3$, 175 °C, microwave, 1 h) resulted in 62% **6d**, with trace amounts of another Cu-corrole with higher molecular mass (*m*/*z* 1403), apparently due to additional substitution of a methylsulfanyl moiety.

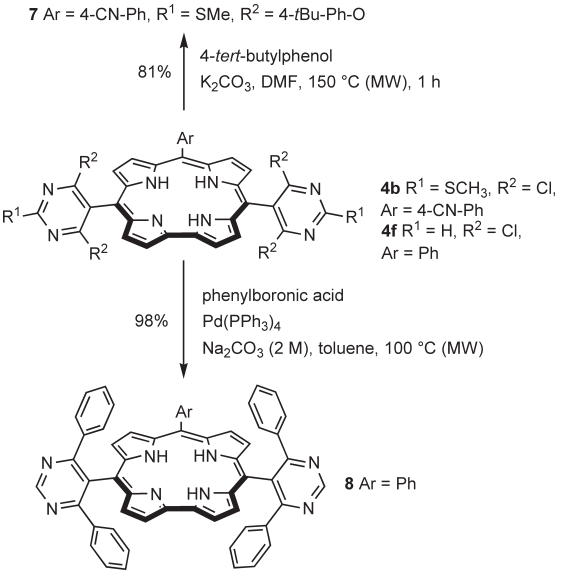



**6a** $R^1$ = 4-*t*Bu-Ph-O; $R^2$-$R^4$ = Cl
**6b** $R^1$,$R^4$ = 4-*t*Bu-Ph-O; $R^2$,$R^3$ = Cl
**6c** $R^1$,$R^3$ = 4-*t*Bu-Ph-O; $R^2$,$R^4$ = Cl
**6d** $R^1$-$R^4$ = 4-*t*Bu-Ph-O

Since higher (oxidative) stability of $A_2B$-pyrimidinylcorroles compared to the one-pyrimidine $AB_2$-analogues can be envisaged, modification of the corrole skeleton was also studied on Fb $A_2B$-corrole **4b**. Tetrasubstituted corrole **7** was isolated in 81% yield after $S_NAr$ involving efficient substitution in DMF at 150 °C (microwave, 1 h) (Scheme 3). The same reaction at 175 °C again caused pentasubstitution (∼10%). Cu-metalation to enhance the stability of the contracted porphyrin skeleton is apparently not required. The electron-deficient and sterically shielding influence of the *meso*-pyrimidinyl units endow sufficient stability to the Fb derivatives. Alternatively, modification of the pyrimidinylcorrole periphery can also be achieved via Pd-catalyzed cross-coupling reactions. As an example, Fb $A_2B$-pyrimidinylcorrole **4f** was treated with phenylboronic acid under standard Suzuki conditions (Scheme 3), and sterically congested $A_2B$-corrole **8** was isolated in a nearly quantitative yield (98%).

While functionalization of the $A_2B$-pyrimidinylcorrole platform has only been performed by rather simple nucleophiles or arylboronic acids, one can easily see the potential of these methods toward preparation of more complex (asymmetrically substituted) functional corrole derivatives. While the inserted phenol groups above and below the macrocyclic plane are conformationally mobile and might be located away from the corrole ring, the aryl groups introduced by Pd-catalyzed methods are inherently located close to the corrole plane. Both types of double picket fence corroles might have beneficial properties for metallocorrole-based (stereo- or regioselective) catalysis.

**SCHEME 3. Functionalization of Fb $A_2B$-Pyrimidinylcorroles**



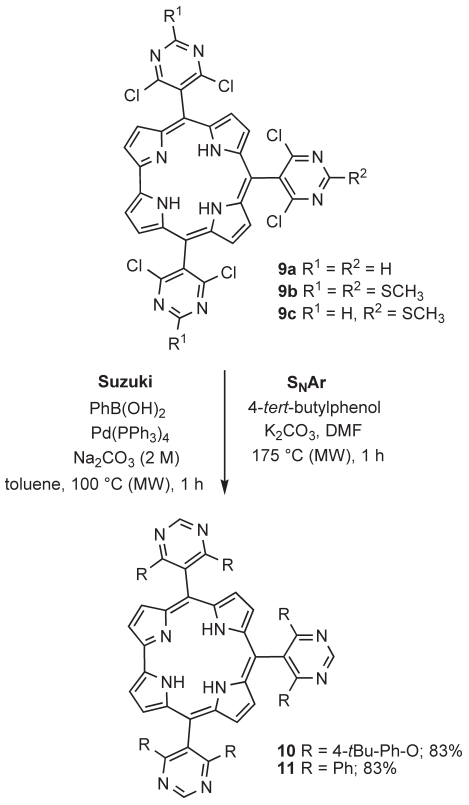

**$A_3$-Pyrimidinylcorroles.**[12] $A_3$-pyrimidinylcorroles can also be prepared by a [2 + 1] method employing a pyrimidinyl-DPM and a pyrimidinecarbaldehyde precursor. Both the procedures optimized for $AB_2$- and $A_2B$-pyrimidinylcorroles could be applied. On employing the condensation conditions optimized for $A_2B$-corroles, $A_3$-corrole **9a** was prepared in 7% yield. On the other hand, methylthio-substituted $A_3$-corrole **9b** was isolated in 19% yield by a protocol derived from $AB_2$-pyrimidinylcorroles (0.043 equiv $BF_3 \cdot OEt_2$). The former method was also applied for the synthesis of unsymmetrical pseudo-$A_3$-corrole **9c** (17% yield) starting from pyrimidinecarbaldehyde **1b** and DPM **2a** (Scheme 4).[10]

Since Fb $A_3$-pyrimidinylcorroles can be expected to be even more robust than the $A_2B$ counterparts, they can be considered valuable alternatives for the most commonly used electron-deficient corrole to date, tris(pentafluorophenyl)corrole (tpfc). Moreover, pyrimidinylcorroles are more versatile scaffolds since numerous substitution patterns are readily available for these derivatives. $S_NAr$ and Suzuki cross-coupling reactions were conducted in high yields (83%) starting from **9a** affording even more sterically encumbered functionalized corroles (Scheme 4). Cu-metalation of the $A_3$-corroles was not required, since the Fb analogues were found very robust. Previous experiences with Cu-insertion reactions in highly electron-deficient corroles (e.g., tpfc) have even demonstrated some degree of instability for these derivatives.[5f,7] Partial, and subsequent asymmetrical, substitution of the $A_3$-corroles has not been pursued yet. The purification and identification of the partially substituted isomers might be cumbersome due to regio- and atropoisomerism.

In conclusion, *meso*-pyrimidinyl-substituted $A_2B$- and $A_3$-corroles are versatile building blocks for the construction of elusive functional corroles toward particular applications. Both corrole types have been synthesized in an efficient way by optimization of the macrocyclization conditions earlier

(12) Collman and Decréau synthesized $A_3$-corrole **9a** directly from **1a** using either conventional or microwave heating (in 4.5% or 6.2% yield, respectively). Collman, J. P.; Decréau, R. A. *Tetrahedron Lett.* **2003**, *44*, 1207.

**SCHEME 4. Derivatization of Fb $A_3$-Pyrimidinylcorroles**




applied for $AB_2$-pyrimidinylcorroles, and modification of the corrole perimeter was conducted by effective $S_NAr$ and Suzuki reactions affording highly sterically encumbered double picket fence functionalized corrole macrocycles.

## Experimental Section

**Synthesis of $A_2B$-Pyrimidinylcorroles 4a−f (General Procedure 1).** A solution of the respective aldehyde (0.381 mmol) in $CH_2Cl_2$ (50 mL), activated with $BF_3 \cdot OEt_2$ (2 $\mu$L, 0.043 equiv), was added dropwise over 6−10 h to a stirred solution of pyrimidinyldipyrromethane **2a**/**b** (1.143 mmol, 3 equiv) in $CH_2Cl_2$ (200 mL), under an Ar atmosphere and protected from light. After complete addition, the reaction was continued for 14−18 h (total reaction time ~24 h). A solution of *p*-chloranil (1.143 mmol, 3 equiv) in THF (20 mL) was then added, and the mixture was heated at reflux (the heating time dependent on the aldehyde). Subsequently, the solvent was evaporated under reduced pressure. Pure $A_2B$-corroles were obtained as purple solids after column chromatographic purification (silica, eluent $CH_2Cl_2$/heptane mixtures).

**5,15-Bis(4,6-dichloro-2-methylsulfanylpyrimidin-5-yl)-10-(4-nitrophenyl)corrole (4a):** addition time 24 h, continued stirring for 24 h, oxidation time 2 h; eluent $CH_2Cl_2$/heptane 4:1; yield 14%; MS (ESI+) *m*/*z* 806.4 $[M + H]^+$; FTMS (ESI+) calcd for $C_{35}H_{22}N_9O_2S_2Cl_4$ $[M + H]^+$ 804.0087, found *m*/*z* 804.0093; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.10 (d, $J$ = 4.3 Hz, 2H, $H_\beta$), 8.67 (d, $J$ = 4.8 Hz, 2H, $H_\beta$), 8.63 (d, $J$ = 8.6 Hz, 2H), 8.59 (d, $J$ = 4.8 Hz, 2H, $H_\beta$), 8.54 ($d_{br}$, $J$ = 4.0 Hz, 2H, $H_\beta$), 8.37 (d, $J$ = 8.6 Hz, 2H), 2.84 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 174.0 (C-$SCH_3$), 163.4 (C-Cl), 148.6, 147.8, 135.4 (CH), 127.5 (CH), 125.8, 124.1 (CH), 122.6 (CH), 117.5 (CH), 110.7, 15.0 ($CH_3$-S); UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 263 (4.63), 300 (4.45), 427 (5.062), 572 (4.236), 614 (4.156).

**5,15-Bis[4,6-bis(4-*tert*-butylphenoxy)-2-methylsulfanylpyrimidin-5-yl]-10-(4-cyanophenyl)corrole (7).** A solution of $A_2B$-corrole **4b** (13.9 mg, 17.7 $\mu$mol), 4-*tert*-butylphenol (32 mg, 213 $\mu$mol, 12 equiv), and (finely grounded) $K_2CO_3$ (37.5 mg, 271 $\mu$mol) in dry DMF (5 mL) was heated by microwave irradiation at 150 °C (100 W) for 1 h. After the mixture was cooled to rt, ethyl acetate was added, and the resulting mixture was washed with distilled water, dried over $MgSO_4$, filtered, and evaporated to dryness. After purification by column chromatography (silica, eluent ethyl acetate/heptane 1:10) pure tetrasubstituted Fb $A_2B$-corrole **7** (17.8 mg, 81%) was obtained as a purple solid: MS (ESI+) *m*/*z* 1240.4 $[M + H]^+$; FTMS (ESI−) calcd for $C_{76}H_{72}N_9O_4S_2$ $[M - H]^-$ 1238.5143, found *m*/*z* 1238.5091; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.02 (d, $J$ = 4.0 Hz, 2H, $H_\beta$), 8.95 (d, $J$ = 4.8 Hz, 2H, $H_\beta$), 8.72 (d, $J$ = 3.8 Hz, 2H, $H_\beta$), 8.50 (d, $J$ = 4.8 Hz, 2H, $H_\beta$), 8.30 (d, $J$ = 7.8 Hz, 2H, CN-Ph), 8.04 (d, $J$ = 7.8 Hz, 2H, CN-Ph), 7.17 (d, $J$ = 8.8 Hz, 8H), 6.93 (d, $J$ = 8.8 Hz, 8H), 2.37 (s, 6H), 1.16 (s, 36H), −1.0--3.0 ($s_{br}$, 3H, NH); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 171.4 (C-$SCH_3$), 169.3, 150.7, 147.9, 135.4 (CH), 131.0 (CH), 125.9 (CH), 120.9 (CH), 116.2 (CH), 100.8, 34.4, 31.4 ($CH_3$), 31.1 ($CH_3$), 14.3 ($CH_3$-S); UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 261 (4.760), 419 (5.038), 574 (4.363), 612 (4.236).

**5,15-Bis(4,6-diphenylpyrimidin-5-yl)-10-phenylcorrole (8).** To a solution of $A_2B$-corrole **4f** (22 mg, 33 $\mu$mol), phenylboronic acid (32.1 mg, 263 $\mu$mol, 8 equiv), and $Pd(PPh_3)_4$ (2 mg, 5 mol %) in toluene (3 mL) was added aq $Na_2CO_3$ (2 M, 0.3 mL), and the mixture was heated by microwave irradiation at 100 °C (100 W) for 1 h. After the mixture was cooled to rt, diethyl ether was added, and the resulting mixture was washed with distilled water, dried over $MgSO_4$, filtered, and evaporated to dryness. After purification by column chromatography (silica, eluent ethyl acetate/$CH_2Cl_2$ 1:9), tetrasubstituted Fb $A_2B$-corrole **8** was nearly quantitatively (27.0 mg, 98%) obtained: MS (ESI+) *m*/*z* 836.5 $[M + H]^+$; FTMS (ESI+) calcd for $C_{57}H_{38}N_8$ $[M^+]$ 834.3214, found *m*/*z* 834.3178; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 9.72 (s, 2H, $H_{pyrim}$), 8.70 (d, $J$ = 4.1 Hz, 2H, $H_\beta$), 8.48 (d, $J$ = 4.0 Hz, 2H, $H_\beta$), 8.35−8.32 (m, 4H, $H_\beta$), 7.98−7.95 (m, 2H, *meso*-Ph), 7.69−7.64 (m, 3H, *meso*-Ph), 7.10 (d, $J$ = 7.9 Hz, 8H, *o*-Ph), 6.70 (t, $J$ = 7.6 Hz, 4H, *p*-Ph), 6.57 (t, $J$ = 7.9 Hz, 8H, *m*-Ph); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 168.5, 158.4 (CH; pyrim), 141.3, 139.1, 134.7 (CH), 132.4, 128.9 (CH), 128.3 (CH), 127.7 (CH), 127.4 (CH), 116.4 (CH), 111.9, 100.1 (CH); UV−vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 277 (4.618), 436 (4.858), 588 (3.917), 653 (3.965).

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**Supporting Information Available:** Additional experimental procedures and data and $^1$H and $^{13}$C NMR spectra for all novel corroles and precursors. This material is available free of charge via the Internet at http://pubs.acs.org.