Synthetic, Structural, and Photophysical Exploration of *meso*-Pyrimidinyl-Substituted AB₂-Corroles

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Abstract: meso-Pyrimidinyl-substituted AB₂-corroles were efficiently synthesized starting from 5-mesityldipyrromethane and various 2-substituted 4,6-dichloropyrimidine-5-carbaldehydes. The corrole yield was significantly enhanced by optimization of the amount of Lewis acid catalyst (BF₃·OEt₂). The main advantage of pyrimidinylcorroles over other meso-triarylcorroles is their wide range of functionalization possibilities, which has been explored by nucleophilic and electrophilic aromatic substitution, and Pd-catalyzed crosscoupling reactions. Stepwise substitution of the chlorine functions afforded asymmetrically substituted pyrimidinylcorroles. Due to the lability of the freebase corrole macrocycles, functionalization of the corrole periphery was preferentially performed on the Cu-metalated counterparts. Functionalized freebase AB_2 -pyrimidinylcorroles were, however, readily accessible by the reversible sequence Cu insertion and subsequent reductive demetalation. AB_2 -pyrimidinylcorroles can hence be regarded as highly versatile platforms towards more sophisticated corrole systems. X-ray analysis of a bis(4-*tert*-butylphenoxy)-substituted Cu-pyrimidinylcorrole showed the typical features of a Cu-corrole: short N-Cu distances

Keywords: charge transfer • corroles • luminescence • pyrimidines • UV/Vis spectroscopy

and a saddled corrole plane. The absorption spectra and photophysical properties of some representative freebase AB₂-pyrimidinylcorroles were examined in depth. The absorption spectra displayed typical corrole features: intense spin-allowed π - π * bands, which can be classified as Soret- and Q-type bands. The photophysical properties, investigated both in fluid solution at room temperature and in rigid matrix at 77 K, were governed by the lowestlying $\pi - \pi^*$ singlet state; however, in most cases, a state with partial chargetransfer character (from the corrole ring to the pyrimidinyl group) was proposed to contribute to the dynamic properties of the emissive level.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000008. It includes additional experimental and characterization data, ¹H and ¹³C NMR spectra for all novel (pyrimidinyl)corroles, luminescence spectra of **4a,b** in MeCN and CH₂Cl₂ at RT, and extra details and figures for the X-ray crystallographic structure of **7c**.

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Introduction

Since the first efficient one-pot syntheses of meso-triarylcorroles by Gross and Paolesse in 1999,^[1] corrole chemistry has grown almost exponentially, thus enabling its evolution over the past ten years from a narrow, mainly synthetically oriented research topic to a mature and flourishing interdisciplinary field. Driven by related studies on their well-known porphyrin congeners, corroles have recently been applied in various domains (e.g., catalysis, sensor design, molecular electronics, and medical imaging and therapy), in which corroles regularly display superiority compared to related oligopyrrolic macrocycles.^[2] In spite of the tremendous synthetic progress that has been made in the corrole field over the last decade,^[3,4] some synthetic challenges remain and further efforts are certainly still required to elucidate and exploit the full potential and promises that corroles hold for up-todate applications.

Among the strategies that can be used to obtain more sophisticated corrole structures, corrole functionalization has mostly been achieved by insertion of the required functional moieties on the corrole precursors (aromatic aldehydes and derived dipyrromethanes).^[3] However, not all aldehyde building blocks afford corroles in equally good yields and precious starting material may hence be lost. Furthermore, depending on the precursors, optimization of the macrocyclization conditions may be required. Alternatively, post-macrocyclization functionalization of the corrole perimeter is often achieved by the introduction of functional groups on the β -pyrrolic positions (e.g., by bromination, nitration, chlorosulfonation, or hydroformylation).^[3] A particular type of corrole modification through the pyrrolic units involves cycloaddition reactions.^[5] Only a few groups have reported post-macrocyclization elaborations by means of the meso positions of the contracted porphyrin framework.^[6] Advanced corrole research would certainly benefit from a general triarylcorrole scaffold that can be prepared in a high yield and on a large scale, is stable enough for further manipulations, and enables smooth access to a wide variety of functionalized corroles specifically designed for modern applications.

A noteworthy complication of performing functionalization reactions on free-base (Fb) corroles is the lability that is often observed for these metal-free derivatives under the combined influence of light and O_2 , thereby resulting in lower yields and troublesome purifications. This bottleneck could be solved by conversion to a more stable metallocorrole derivative if efficient demetalation protocols were to be available (as known for metalloporphyrins). Until recently, studies on corrole demetalation procedures were scarce.^[7] However, recent breakthroughs on the (reductive) demetalation of Cu– and Mn–corroles allow the use of a metalation/demetalation sequence as a protection/deprotection strategy towards elaborated Fb–corroles.^[8,9]

Within one of our research groups, we have been studying the synthesis and reactivity of 4,6-dichloropyrimidines as versatile structural building blocks for *meso*-pyrimidinylsubstituted porphyrins,^[10] heteracalix[m]arene[m]pyrimidines,^[11] and pyrimidine-based (porphyrin) dendrimers.^[12,13] During the course of our studies on pyrimidinylporphyrins, it was discovered that a slight modification of the reaction conditions, as optimized for porphyrins, results in the formation of either expanded (penta- and hexaphyrins)^[14] or contracted^[15] porphyrin analogues. The major advantage concerning the introduction of dichloropyrimidinyl moieties on the meso positions of a porphyrinoid macrocycle is the wide scope of functionalization reactions that can be performed on the dichloropyrimidine units. "Double-picket-fence"functionalized porphyrins and hexaphyrins have been obtained by efficient and operationally simple nucleophilic aromatic substitution (S_NAr) and Suzuki cross-coupling reactions.^[10,14] In previous communications, specific synthetic aspects of pyrimidinylcorroles have been described.^[9,15-17] In this paper, we report a detailed multidisciplinary study on the synthesis and functionalization, structural elucidation and photophysical properties of meso-pyrimidinyl-substituted AB₂-corroles (A=4,6-dichloropyrimidin-5-yl).^[18]

Results and Discussion

Synthesis of the AB₂-pyrimidinylcorrole scaffold: In 2001, one of our groups contributed to the early stages of synthetic corrole chemistry by exploring the synthesis of sterically encumbered triarylcorroles starting from aromatic aldehydes and 5-aryldipyrromethanes.^[16] Upon condensation of 4,6-dichloropyrimidine-5-carbaldehyde (1a) and 5-(2,6-dichlorophenyl)dipyrromethane (2a) in dichloromethane at room temperature (RT), catalyzed by borontrifluoride dietherate (BF₃·OEt₂), and subsequent oxidative cyclization with *p*chloranil, the first AB₂-pyrimidinylcorrole **3** was obtained in 20% yield (Scheme 1).

At that time, no corrole material could be isolated starting from **1a** and 5-mesityldipyrromethane (**2b**). The A_2B_2 porphyrin analogue was solely obtained in a remarkably high yield (53%). Later on, in a detailed study towards a more general procedure for AB₂-pyrimidinylcorroles, it was observed that the desired pyrimidinylcorrole **4a** could be



Scheme 1. Synthesis of AB₂-pyrimidinylcorrole 3.

Chem. Eur. J. 2010, 16, 5691-5705

synthesized in 18% yield upon using a tenfold decreased concentration of Lewis acid catalyst (0.085 equiv $BF_3 \cdot OEt_2$), simultaneously affording 25% of the A_2B_2 -porphyrin counterpart (Scheme 2).^[15]



Scheme 2. Synthesis of AB_2 -pyrimidinylcorroles **4a**-**d** and the corresponding Cu analogues **5a**-**d**.

As a first step towards variation of the pyrimidinylcorrole periphery, the possibility to synthesize AB₂-corroles starting from 2b and various 2-substituted 4,6-dichloropyrimidine-5carbaldehydes **1b-d** was explored. Mesityldipyrromethane was chosen for reasons of availability and solubility of the final corrole, and it can easily be prepared through a recently optimized procedure that allows one to obtain aryldipyrromethanes in high yields by simple precipitation from an acidic aqueous solution.^[19] An additional advantage of this method is the small excess of pyrrole (3 equiv) that is required. Pyrimidinecarbaldehyde building blocks 1a-d can readily be synthesized by chloroformylation of the 4,6-dihydroxypyrimidine precursors, in turn usually accessible starting from the respective amidines.^[20a-c] 4,6-Dichloro-2-methylsulfanylpyrimidine-5-carbaldehyde (1b) was obtained through methylation and subsequent chloroformylation of thiobarbituric acid.^[20d] Flash chromatographic purification of the pyrimidinecarbaldehydes is crucial to obtain satisfactory yields for the tetrapyrrolic chromophores. Pyrimidinylcorroles 4b-d were synthesized in a straightforward way in fairto-good yields (20% for 4b, 13% for 4c and 4d) from the substituted precursors upon condensation with mesityldipyrromethane catalyzed by 0.085 equiv BF₃·OEt₂ (Scheme 2). The AB₂-corroles had to be chromatographically separated from the concurrently formed A₂B₂-porphyrins.^[15]

The amount of Lewis acid catalyst appeared to be a crucial parameter to obtain either the *meso*-pyrimidinyl-substituted AB₂-corrole or the A₂B₂-porphyrin as the major product. Hence, an optimization study of the BF₃·OEt₂ content was performed to maximize the corrole yield. The optimization was done for corrole **4a** and a 1:1 ratio of mesityldipyrromethane and pyrimidinecarbaldehyde **1a** was used, rather than the stoichiometric 2:1 ratio. The excess of pyrimidinecarbaldehyde could, however, easily be recovered on chromatographic purification of the corrole. It was observed that the A₂B₂-porphyrin content gradually decreased when less BF₃·OEt₂ was used. The maximum corrole yield was obtained upon adding 0.043 equiv of Lewis acid. Under these conditions, corrole 4a was isolated in as much as 35% yield, an appreciable increase and a nice result compared to generally observed yields in corrole synthesis.^[3,4] By simple variation of the amount of BF3. OEt2, the reaction outcome could be varied from 50% A2B2-porphyrin and no AB2-corrole to 35% corrole and 6% porphyrin. On applying the optimized protocol to the synthesis of corroles 4b and 4c, the yield for 4c was increased to 22%, whereas the yield for 4b dropped to 14%. The highest yield (27%) for thiomethyl-substituted AB₂-corrole 4b was obtained on using 0.068 equiv of catalyst. The optimum catalyst concentration hence seems to be dependent on the substituent on the pyrimidinecarbaldehvde precursor.^[21]

It is worth mentioning that the same conditions, as optimized for condensation of mesityldipyrromethane (2b) and pyrimidinecarbaldehydes **1**a–d, could also be applied for the preparation of analogous AB₂-corroles **6**a–d, derived from **2**b and other aromatic aldehydes (Scheme 3).^[22]



Scheme 3. (Nonpyrimidinyl) AB_2 -corroles **6a–d** synthesized by means of the optimized procedure.

Functionalization scope: Variation of the AB₂-pyrimidinylcorrole framework can be achieved through substitution of the chlorine functions on the electron-deficient *meso*-pyrimidinyl unit. A unique feature of *meso*-pyrimidinylcorroles is the fact that the substituents are introduced at the *ortho,ortho'*-positions, and hence are located above and below the corrole plane. Such double-picket-fence corroles^[6] can have additional advantages for peculiar applications (e.g., energytransfer relays or regio- and stereoselective corrole-based catalysis).

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For further post-macrocyclization modifications of the corrole periphery, AB₂-corroles 4a and 4b were chosen as substrates of preference (highest optimized yield and additional synthetic versatility of 4b, vide infra). Functionalization was initially performed starting from the Fb derivatives. It was, however, quickly observed that the target substituted Fb-corroles were generally obtained in rather low yields, which can probably be ascribed to the inherent (oxidative) lability of the Fb AB₂-pyrimidinylcorroles. This oxidative degradation is also evident from the olive-green band that precedes the pyrimidinylcorrole on chromatographic purification (silica), earlier identified as a corrole oxidation product.^[4] Compared to the currently most widely studied and used relatively stable Fb 5,10,15-tris(pentafluorophenyl)corrole (tpfc),^[1a,b] only one stabilizing electron-withdrawing meso-group is available. Hence, it was decided to perform the functionalization studies on the Cu-pyrimidinylcorrole analogues 5a,b. Among the wide range of presently described metallocorroles, Cu-corroles occupy a special place. Cu-corroles are readily accessible, do not require additional ligands to complete their coordination sphere, and have a diamagnetic ground state, which has originally been oversimplified to a Cu^{III} state.^[23] More recent studies provide new insights on the electronic structure of Cu-corroles.^[24] Cu-corroles 5a-d were easily synthesized from AB₂-pyrimidinylcorroles 4a-d by employing copper(II) acetate in pyridine at RT (78-95% vield; Scheme 2).^[15] Cu insertion can also smoothly be achieved in THF.^[9]

Inspired by the success of similar modifications on pyrimidinylporphyrins, peripheral substitution of the pyrimidinylcorrole skeleton was first pursued by means of S_NAr reactions. Cu-metalated AB₂-pyrimidinylcorroles 5a,b were noticeably less reactive towards substitution than the analogous Fb A_2B_2 -porphyrins. Under S_NAr conditions that enable smooth substitution on a pyrimidinylporphyrin scaffold (excess 4-tert-butylphenol, DMF, 90°C, K₂CO₃ base, [18]crown-6, 48 h),^[10a, 12d] Cu-corrole 5a was converted into monosubstituted AB₂-corrole 7a in 87% yield, without significant disubstitution (Scheme 4). Under similar conditions, thiomethyl-substituted Cu-corrole 5b afforded 71% of monofunctionalized AB₂-corrole **7b**, whereas 9% of starting compound 5b could be recovered (Scheme 4). Selective monosubstitution by S_NAr is hence feasible on a pyrimidinylcorrole scaffold. On the other hand, twofold substitution could be achieved using rather harsh conditions (DMSO, 175°C by microwave irradiation, K₂CO₃, 1 h) to afford disubstituted Cu-corrole 7c in 85% yield (Scheme 4).^[15]

The introduction of functional groups on the β -pyrrolic positions of the corrole framework through electrophilic aromatic substitution (S_EAr) procedures is a generally applied strategy towards more elaborate corrole macrocycles.^[3] Chlorination of corroles has, however, not been reported yet, at least not for aromatic corroles.^[25] Treatment of Cucorrole **5a** with *N*-chlorosuccinimide (NCS) in *o*-dichlorobenzene at high temperature (140/90 °C) resulted in the formation of octachlorinated Cu-pyrimidinylcorrole **8**, which could be isolated in 46 % yield (Scheme 5).^[9]



Scheme 4. Functionalization of Cu–AB₂-pyrimidinylcorroles 5a,b by S_NAr .



Scheme 5. Functionalization of $Cu-AB_2$ -pyrimidinylcorrole **5a** by S_EAr (chlorination) and subsequent demetalation.

In 2003, we explored the functionalization of A_2B_2 -pyrimidinylporphyrins by Suzuki cross-coupling reactions to obtain sterically encumbered porphyrins with potential in regioselective catalysis.^[10b] Application of the same reaction conditions to Cu–pyrimidinylcorrole **5a** furnished AB₂-corrole **9** with a sterically shielded metal center in a satisfactory 75 % yield (Scheme 6). In like fashion, Cu–corrole **5a** was also subjected to a Stille cross-coupling reaction with 2-(tributylstannyl)thiophene to afford dithienyl-substituted Cu–corrole **10** in 73 % yield (Scheme 6).^[15]

The corrole substitution pattern could additionally be altered by Liebeskind–Srogl cross-coupling reactions. The 2thiomethyl moiety of Cu–corrole **5b** can be exchanged for other groups by Liebeskind–Srogl reactions, thus providing an alternative for the earlier described protocol in which the introduction of different groups at this site was established using specific pyrimidinecarbaldehyde precursors. This is particularly useful if the requisite 4,6-dichloropyrimidine-5carbaldehyde building block cannot trivially be obtained. Cu–corrole **11** was synthesized in 61% yield through substi-



Scheme 6. Functionalization of Cu–AB₂-pyrimidinylcorrole 5a by Pd-catalyzed cross-coupling reactions (Suzuki/Stille).

tution of the methylsulfanyl moiety with 4-cyanophenylboronic acid (Scheme 7).^[15]

The rather selective access to monosubstituted Cu–corrole **7a** by S_NAr is attractive, since it enables stepwise introduction of different moieties by sequential substitution of both



Scheme 7. Variation of the 2-pyrimidinyl position by Liebeskind–Srogl cross-coupling on thiomethyl-substituted Cu–corrole **5b**.

chlorine groups, which could give access to even more sophisticated asymmetrically substituted *meso*-pyrimidinylcorroles. It also provides a useful entry towards inherently chiral corrole macrocycles. For this purpose, additional S_NAr reactions were examined. Substitution on Cu–AB₂-corrole **5a** with *m*-cyanophenol (1.7 equiv) in DMF at 70 °C (K₂CO₃, [18]crown-6, 24 h) afforded majorly monosubstituted Cu–corrole **12a** (79 % yield). When the same procedure was carried out at 90 °C (1.6 equiv *m*-cyanophenol), a mixture of mono- and disubstituted Cu–corroles was obtained (57 % **12a**, 45 % **12b**). The optimum temperature for monoand disubstitution seems to be nucleophile dependent. Monosubstitution with 4-chlorothiophenol was achieved at 90 °C (**13**: 3.4 equiv thiophenol, DMF, K₂CO₃, 20 h, 81 %

FULL PAPER

yield). Disubstituted AB2-corroles 14 and 15 were both obtained in the same yield (81%) upon employing Cs₂CO₃ base at 120°C in DMF. p-Dodecylphenoxy-substituted corrole 14 was designed as an active electrode material for supramolecular sensor applications.^[26] The possibility to introduce two phenol nucleophiles in a stepwise manner was examined starting from monosubstituted Cu-corrole 12a. Upon treatment of this pyrimidinylcorrole with 4-bromophenol (\approx 4 equiv, DMF, K₂CO₃, 90/120 °C, 28+20 h), extensive scrambling was observed. Not only the desired asymmetrically substituted corrole 16a was obtained (28%), but also mono- and bis(4-bromophenoxy)-substituted corroles 16c (20%) and 16b (21%), indicative of the dynamic (reversible) character of the S_NAr reaction. A proper choice and order of substituting nucleophiles is required if one wants to enhance the efficiency of this strategy towards asymmetrically disubstituted derivatives. This complication can of course be avoided by performing Pd-catalyzed crosscoupling reactions on the monosubstituted derivatives or vice versa. AB₂-pyrimidinylcorrole 17 was obtained by a tandem Suzuki-S_NAr reaction in a modest 34% yield. When a similar protocol was applied to Cu-corrole 5b, selective monosubstitution by Suzuki cross-coupling (phenylboronic acid, [Pd(PPh₃)₄], toluene, aqueous Na₂CO₃) afforded pyrimidinylcorrole 18a in 79% yield. Subsequent treatment with an excess of 4-tert-butylphenol (4 equiv) yielded 76% of the asymmetrical AB₂-corrole **18b** (DMF, K₂CO₃, [18]crown-6, 1 h microwave at 175°C).

Both S_NAr and Suzuki reactions were also successful on Fb-corroles, but the obtained yields were significantly lower. Bis(4-tert-butylphenoxy)-substituted Fb-corrole 19 was, for instance, isolated in 29% yield (6 equiv 4-tert-butylphenol, 120°C, DMF, Cs₂CO₃, 14 h), compared with 81% for the analogous Cu-corrole 15.^[9] A Suzuki cross-coupling reaction with phenylboronic acid starting from Fb-AB2-corrole 3 afforded less than 40% of the (impure) disubstituted derivative, whereas a mixture of (almost pure) mono- and disubstituted AB₂-pyrimidinylcorroles **20a** (62%) and **20b** (29%) was obtained by means of a similar procedure starting from 4a (toluene, $[Pd(PPh_3)_4]$, 3 equiv phenylboronic acid, aqueous Na₂CO₃, 24 h). The functionalized Fb-corroles were often not completely pure upon the first chromatographic purification (silica) and significant decomposition occurred upon repeating this procedure, thus reflecting the modest (oxidative) stability of these macrocycles.

Demetalation: For a number of corrole applications, it could be desirable to take advantage of particular intrinsic Fb–corrole features (e.g., their luminescent properties). On the other hand, functionalization of Fb–corroles is often troubled by the modest stability of many metal-free derivatives, which is considerably less of a problem for metallocorroles. One of the obvious solutions to this dilemma would be to apply a metalation/demetalation cycle as a protective strategy, thereby enabling smooth corrole derivatization.

Within one of our groups, a highly efficient, generally applicable, reductive demetalation protocol for Cu-corroles



has been established.^[9] In the presence of tin(II) chloride, Cu–corroles, which are nonemissive, are smoothly converted to their fluorescent Fb analogues in acidic medium at RT. The demetalation procedure is also applicable to Cu–AB₂pyrimidinylcorroles and, as an illustration of the potential of the method, functionalized Fb–pyrimidinylcorroles **19**, **22**, and **23** were prepared in high yields. Two specific cases merit closer attention. Since the direct S_NAr functionalization of pyrimidinylcorrole **4b** with 4-*tert*-butylphenol afforded only 29% of the desired disubstituted AB₂-corrole **19**, the three-step detour by means of Cu metalation (94%), functionalization on the Cu–corrole stage (81%), and reductive demetalation (90%) was proven to be more efficient (68% general yield).^[9] Moreover, both the metalation and demetalation procedures are operationally simple and proceed very fast. Another particular case is octachlorinated Cu–corrole **8** (Scheme 5). When this corrole was subjected to the demetalation conditions, partial dehalogenation was

5696

observed. To limit dechlorination, only one equivalent of tin(II) chloride had to be used and 20% of the unique Fb–corrole **21** was isolated, whereas 70% of unreacted starting material could be recovered as well.^[9]

Metallocorroles: Besides Cu–pyrimidinylcorroles, some other metallocorrole derivatives were also prepared (Scheme 8). Rather modest yields were obtained for these



Scheme 8. meso-Pyrimidinyl-substituted AB2-metallocorroles 25-27.

metal-insertion reactions under standard literature conditions (not optimized for AB₂-pyrimidinylcorroles). Co^{III}-pyrimidinylcorrole **25** was synthesized in 41 % yield upon treatment of Fb-corrole **4a** with an excess of cobalt(II) acetylacetonate (CH₂Cl₂/ethanol, 24 h) and subsequent addition of triphenylphosphine.^[27] Ag^{III} insertion in AB₂-corrole **4a** was achieved in 32 % yield by means of reaction with silver(I) acetate in pyridine (5 min at 80 °C),^[7b] whereas Ga^{III}-corrole **27** was obtained in 16 % yield through addition of gallium-(III) chloride to Fb precursor **4a** in pyridine at reflux conditions.^[28] The low yield for the Ga-corrole might be due to partial hydrolysis of the dichloropyrimidinyl moiety initiated by (very hygroscopic) GaCl₃.

A meso-pyrimidinylcorrole could also be prepared starting from 5-(pentafluorophenyl)dipyrromethane.^[19] Under the conditions optimized for the combination of pyrimidinecarbaldehyde 1a and mesityldipyrromethane (0.043 equiv BF₃·OEt₂), AB₂-corrole 24 was isolated in only 3% yield. The macrocyclization reaction therefore needs to be optimized for each dipyrromethane building block independently. Functionalization by S_NAr on this corrole may be complicated due to competitive fluorine substitution, especially in view of the elevated temperature required for meso-chloropyrimidinyl substitution, but smooth and selective Pd-catalyzed cross-coupling reactions can be foreseen. Unfortunately, upon Cu metalation of 24, most of the corrole material was lost. It seems that particular care has to be taken to obtain the Cu derivatives of the most electron-deficient corrole macrocycles, as earlier observed for Cu-(tpfc).^[9] Metalation might, however, not be essential in this case due to the higher stability of the electron-deficient Fb-corrole framework.

Structural characterization: All AB₂-pyrimidinylcorroles were fully characterized by NMR spectroscopy (¹H and ¹³C),

electrospray mass spectrometry (ESIMS), and UV/Vis spectroscopy. The developing paramagnetism with increasing temperature is clearly identifiable in the ¹H NMR spectra of the Cu–pyrimidinylcorroles, which show broadened signals for the β -pyrrolic protons at RT (see the Supporting Information).

In view of recent hypotheses on the true electronic nature of Cu–corrole complexes and the related noninnocence of the corrolato ligand,^[24] additional structural elucidations of novel Cu–corroles are of particular appeal. Diffraction-quality single crystals of Cu–corrole **7c** were obtained by slow evaporation from a CHCl₃/hexane solution. Two crystallographically independent corrole entities, with similar structural features, are observed in the asymmetric unit (Figure 1). The Cu atom resides in the center of the corrola-



Figure 1. ORTEP representation (with standard corrole numbering) of Cu–AB₂-pyrimidinylcorrole **7c**, determined by X-ray crystallography (top). Thermal ellipsoids are set at 50% probability. Only one out of two crystallographically independent molecules is shown. Hydrogen atoms, disorder, and incorporated solvent (CHCl₃) have been omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°] (one entity): Cu–N1 1.873, Cu–N2 1.899, Cu–N3 1.888, Cu–N4 1.884, C1–C19 1.421, C4–C5 1.395, C5–C6 1.421, C9–C10 1.392, C10–C11 1.415, C14–C15 1.419, C15–C16 1.390; N1-Cu-N2 91.7, N1-Cu-N4 81.6, N2-Cu-N3 96.7, N3-Cu-N4 91.8, N1-Cu-N3 166.9, N2-Cu-N4 167.8, C4–C5-C6 122.0, C9-C10-C11 125.1, C14-C15-C16 122.5, N1-C1-C19-N4 11.6. Side view along the C18–C12 axis (bottom): Hydrogen atoms and all atoms of the *meso*phenyl groups, except for the *ipso*-carbon atom of the pyrimidinyl moiety, have been removed for clarity.

to N_4 cavity with a distorted square-planar coordination. The Cu–N_{pyrrole} bond lengths are not near-identical, as observed for a few earlier obtained structures, and range from 1.880 to 1.892 Å in one unit and 1.873 to 1.899 Å in the other entity.^[23a,c,e,f,24] These relatively short distances have been used to confirm the postulated low-spin Cu^{III} center in the past, but recent results have shown that the ground state

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might be better described as an open-shell singlet Cu^{II}-corrolato²⁻ state.^[23a,c,e,f,24] As previously observed for other Cucorroles, the corrole macrocycle shows a saddled conformation, that is, the pyrrole rings lie (1,3)-alternately above and below the corrole plane. Ghosh and co-workers have recently reported that Cu-corroles are inherently saddled, even without sterically hindered substituents that engender nonplanarity, as a result of Cu(d)-corrole(π) orbital interactions.^[24b] The saddling for pyrimidinylcorrole **7c**, defined as the average angle between the mean planes of opposite pyrrole rings, has been determined to be 13.4° in one species and 12.2° for the second independent corrole (Figure 1).^[23a,c,e,f,24] The meso substituents are approaching perpendicular positions with respect to the mean plane through the four pyrrolic subunits (75.6° for the pyrimidinyl moiety in one entity, 69.2° in the other, and an angle ranging from 77.5 to 82.1° for the mesityl units). The introduced 4-tert-butylphenoxy substituents of 7c are oriented to the opposite side with respect to the corrolato macrocyclic plane.

Absorption spectra and photophysical properties: The broad scope of smooth modifications of the AB₂-pyrimidinylcorrole periphery allows fine-tuning and optimization of certain corrole properties towards application needs. Fine-tuning of the electrochemical and photophysical features is, for instance, important if one desires to use corrole-based materials (as alternatives for traditional porphyrins) as active (biomimetic) photosensitizers in molecular devices exploiting sunlight.^[2c] Photophysical properties of corroles are particularly interesting; it has been stated that the fluorescence intensities (Φ) of Fb-corroles are generally larger than those of porphyrins and other related macrocycles, whereas the (Q-band) absorption coefficients in the visible range are also overall higher than for porphyrins.^[2c,d,29] In this work, we have examined the photophysical features of a number of Fb pyrimidinylcorroles upon changing the substitution pattern. The representative compounds for which the absorption spectra and luminescence properties have been investigated are gathered in Scheme 9. Experiments in fluid solution at RT have been performed in acetonitrile and dichloromethane, whereas experiments at 77 K were done using a toluene rigid matrix. The metalated Cu-, Co-, and Ag-corroles reported in this paper did not exhibit any luminescence under the applied experimental conditions.

The absorption spectra of all pyrimidinylcorroles studied are dominated by bands that can be attributed to spin-allowed π - π^* transitions analogous to those of porphyrins,^[2c,d,29,30] with intense Soret band(s) around 420 nm and moderately intense Q bands in the range 500–700 nm. Moderate splitting of the Soret band was observed (14–18 nm in CH₂Cl₂, Table 1), previously described as an intrinsic property of corroles with sterically demanding *meso* substituents.^[29b,c] Figures 2 and 3 show the absorption spectra of prototypical Fb-pyrimidinylcorroles **4b** and **19**, and Table 1 collects the relevant features of all species. It should be noted that the absorption spectra of all pyrimidinylcorroles studied in a specific solvent are quite similar, with only



Scheme 9. Overview of pyrimidinylcorroles, the photophysical properties of which have been investigated in detail.



Figure 2. Absorption spectra of **4b** in dichloromethane (——) and acetonitrile (–––).



Figure 3. Absorption spectra of **19** in dichloromethane (——) and acetonitrile (---).

5698

Table 1. Absorption and luminescence data of selected pyrimidinylcorroles.

Corrole Absorption Luminescence $\Phi^{[a,c]}$ 298 K $\lambda_{max} \ [nm]^{[a,b]} \ (\epsilon \ [M^{-1} cm^{-1}])$ $\tau [ns]^{[a,c]}$ $\lambda_{\max} [nm]^{[a]}$ $\lambda_{max} [nm]$ τ [ns] 77 K^[d] 77 K^[d] 298 K 298 K 4a 412 (107 300), 428 (89 000), 570 (2090), 600 (11 200), 635 609 (sh), 647 2.4 (2.5) 0.066 600 2.5 (0.021)(3370)4b 412 (106100), 428 (93800), 570 (21500), 600 (11300), 635 0.050 597 2.4 609 (sh), 647 2.3 (2.3) (2940)(0.022)4c 411 (100500), 425 (82700), 568 (21400), 600 (10500), 635 0.053 598 2.0 614 (sh), 649 2.3 (2.3) (2400)(0.014)415 (126800), 570 (25000), 608 (13100) 3 620 (sh), 650 0.8(1.0)0.020 601 1.4 (0.015)19 410 (102100), 428 (91700), 571 (19300), 605 (10700), 637 615 (sh), 650 5.6 (5.7) 0.152 602 12.0 (4200)(0.164)410 (103 000), 428 (90 000), 570 (21 300), 603 (10 500), 634 7.0 22 606 (sh), 644 4.9 (4.6) 0.098 600 (3100)(0.100)

[a] Air-equilibrated dichloromethane. [b] 298 K. [c] Data in parentheses are in air-equilibrated acetonitrile. [d] Toluene rigid matrix.

minor changes in the molar absorption values. However, a clear solvent dependence has been observed. Besides some redshift in the Soret bands upon passing from nonpolar to more polar solvents, the main effects of such a solvent dependence of the absorption spectra are changes in the relative intensities of the various contributions to the Q-band region, with the lowest-energy absorption feature increasing in molar absorbtivity upon increasing the polarity of the solvent (compare spectra in Figures 2 and 3). Solvent dependence of absorption spectra of Fb–corroles has been attributed to perturbations due to hydrogen bonding between an internal N–H group and solvent molecules,^[29a] which clearly is enhanced in polar solvents such as acetonitrile. Our results are in line with such an attribution.

All the corroles examined exhibit a relatively intense, structured emission in any solvent and at every temperature condition, which in all cases decays within the nanosecond timescale. Figures 4 and 5 show representative luminescence spectra and the relevant data are again gathered in Table 1. The luminescence properties are independent of the excitation wavelength, both exciting in the Soret band (in the range 380–410 nm) and in the Q bands (520–560 nm range). On the basis of emission energy, lifetimes, and spectral shapes, as well as by comparison with literature data,^[2,29–31] the emission is assigned to the lowest-lying singlet excited state in all circumstances.



Figure 4. Emission spectra of **4b** in dichloromethane fluid solution at RT (---) and toluene rigid matrix at 77 K (----).



FULL PAPER

Figure 5. Emission spectra of **19** in dichloromethane fluid solution at RT (---) and toluene rigid matrix at 77 K (----).

By analysis of the luminescence spectra and data, the following considerations can be made:

1) The luminescence spectra of all compounds are very similar in shape (see Figure S1 in the Supporting Information; compare also with the spectra in Figures 4 and 5). They are also structured, with the highest energy feature not changing significantly on passing from RT fluid solution to a 77 K rigid matrix (Table 1 and Figures 4 and 5), although the relative intensity of such a feature with respect to the lower-energy features is greatly enhanced on passing to low temperature. Corrected excitation spectra overlap with absorption spectra.

These results indicate that the nature of the emitting level does not change upon passing from RT to 77 K and is also constant within the series of solvents. Moreover, the geometry of the emitting excited state, populated with identical efficiency from any upper-lying excited state (as shown by the excitation spectra), is weakly distorted in comparison to the ground state and its energy is not significantly affected by changing the substituents on the pyrimidinyl ring (compare data of 4a-c) or the other *meso*-aryl moieties (compare data of 3 and 4a).

2) The luminescence quantum yields (Table 1) are slightly larger in less polar solvents (e.g., dichloromethane) than in the more polar solvent acetonitrile (with the exception of **19**

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and 22). Regardless of the solvent, luminescence quantum yields of 19 and 22 are significantly larger than those of the other species. The difference is about one order of magnitude in acetonitrile and slightly smaller in less polar solvents. Compounds **4a–c** exhibit approximately the same emission quantum yield in all solvents. Differences in luminescence lifetimes (Table 1) qualitatively agree with quantum yield data, with a longer luminescence lifetime for corroles 19 and 22 relative to the other pyrimidinylcorroles. Luminescence lifetimes do not change significantly with solvent polarity (Table 1). It can also be noted that the quantum yields of most of the compounds are lower than 0.1, atypically low in comparison with literature data,^[2,29–31] which usually report emission quantum yields in the range 0.1–0.5 for Fb–corroles.

These data suggest that in the pyrimidinylcorrole species investigated here another excited level, besides the emitting level, is involved in determining the excited-state properties. We propose that such a level is a state with partial chargetransfer (CT) character and involves the pyrimidine ring as the acceptor. This state could lead to photoinduced electron-transfer quenching of the π - π * emissive state or could mix with the emitting state: in both cases, the result would be an acceleration of the nonradiative rate constant, that is, reduced emission quantum yields.

Actually, pyrimidine has low-lying π^* empty orbitals, so pyrimidine-containing moieties are often involved as acceptor units in CT processes.^[32] In the compounds studied here it can therefore be reasonable that a CT state that involves the corrole ring as the donor subunit-it is known that corroles are able to play the role of electron donor in chargeseparated processes^[33] and, in general, to be oxidized at relatively mild potentials^[34]—and the pyrimidinyl group as the acceptor can lie at a similar energy as the emitting $\pi - \pi^*$ corrole-based excited state and contribute to deactivation of the excited state by means of nonradiative processes, even without perturbing the luminescence spectra. In fact, upperlying states can have an effect on the dynamic properties of lower-lying excited states, even in the absence of sizeable perturbation of excited-state level energies.^[35-37] This line of reasoning also justifies the larger quantum yields (and longer emission lifetime) of 19 and 22 in comparison with the other corroles studied. The two phenoxy substituents on the pyrimidinyl moiety in 19 are electron-donor substituents and therefore make reduction of the pyrimidinyl group more difficult, thus destabilizing the CT state, which hence does not contribute (to such a large extent) to the dynamic properties of the emitting π - π * corrole level in such a species. The pyrimidinyl moiety in monosubstituted corrole 22 bears one phenoxy and one chlorine group. Apparently, the presence of the phenoxy substituent is dominant, so that the behavior of 22 is similar to that of 19 as far as the photophysical properties are concerned. The decrease of the quantum yield of all corroles except 19 and 22 upon passing from less polar solvents to acetonitrile is also in line with the presence of a CT state: acetonitrile can stabilize the CT state, which becomes lower in energy so that its contribution

to the nonradiative processes of the emitting state can increase accordingly. The fact that this does not take place for the species containing phenoxy-substituted pyrimidinyl groups, the luminescence quantum yields of which are substantially unaffected by the solvent (Table 1), further confirms that the CT state is not significantly involved in the decay process for such compounds. It should also be recalled that the presence of CT states has already been assumed before to explain the reduced emission quantum yield of corroles that contain acceptor substituents (e.g., nitro groups).^[29a,31]

The roughly identical emission lifetimes and quantum yields of **4a-c** indicate that the presence of a thiomethyl or phenyl substituent on the 2-position of the pyrimidinyl moiety does not have any influence on the photophysical properties of the pyrimidinylcorroles. In fact, such substituents are expected to be almost neutral from an electronic viewpoint, so their effect on the CT-state energy is negligible. On the contrary, compound 3 exhibits shorter emission lifetimes and lower emission quantum yields compared to AB₂-corrole 4a. As it has been reported that the decrease of planarity of the corrole ring because of steric hindrance usually translates into reduced luminescence performance,^[31] the diminished luminescence of 3 compared with 4a might be attributed to distortion of the corrole ring, as a consequence of steric hindrance imposed by the chlorine substituents.

3) The 77 K emission lifetimes of all compounds except 19 (and, to a minor extent, 22) are quite close to the corresponding values recorded at RT. This is indeed quite common for corroles, the emission lifetimes of which are usually only weakly dependent on temperature,^[2c,31] but it is not expected to be the case for the Fb-pyrimidinylcorroles 4a-c and 3 studied here, for which a CT state is assumed to partially quench the RT luminescence. In fact, in the event that the emissive state was a "pure" π - π * corrole-based fluorescent level and the CT state behaves as a quencher of the emissive state by photoinduced electron transfer, this quenching effect should be inefficient at 77 K, at which electron-transfer processes are usually slowed down by nuclear barriers,^[38] and longer emission lifetimes should be found at 77 K. This is indeed what has been reported for the luminescence properties of nitrophenyl-substituted corroles.^[31] The small temperature dependence of the emission lifetimes of 4a-c and 3 in this case seems to indicate that the emitting state of such compounds is better described as a mixed state between the common $\pi - \pi^*$ corrole-based fluorescent level and a state with partial CT character. Finally, it can also be noted that the emission lifetimes of 19 and 22 are significantly longer at 77 K than at RT. We suggest that the (bulky) phenoxy substituents of the pyrimidinyl group in 19 and 22 can deactivate vibrational modes at 77 K that play some role in the nonradiative decay process operating at RT.

Conclusion

In conclusion, we have demonstrated that AB₂-pyrimidinylcorroles represent attractive corrole scaffolds towards innovative corrole materials for applications. The broad scope of (post-macrocyclization) substitution possibilities of the pyrimidinylcorrole macrocycle, as demonstrated by S_NAr, S_EAr, and Pd-catalyzed cross-coupling reactions, allows facile and efficient access to a diversity of (elusive) functional Cu-corroles hitherto unprecedented in synthetic corrole chemistry. A further advantage is the fact that sophisticated functionalized free-base pyrimidinylcorroles are also readily accessible by a smooth reductive demetalation pathway. For a series of representative free-base AB2-pyrimidinylcorroles, the absorption spectra and luminescence features have been studied. The results showed that the photophysical properties of the studied compounds are governed by the lowest-lying π - π^* singlet state; for a few corroles, a state with partial charge-transfer character (from the corrole to the meso-pyrimidinyl moiety), which contributes to the dynamic properties of the emissive levels, is plausible. Further studies will be directed towards the construction of photoactive multichromophoric arrays based on meso-pyrimidinyl-substituted (metallo)corroles and their possible incorporation in real devices that exploit sunlight, an area of particular economical and environmental appeal to date.

Experimental Section

General experimental methods: NMR spectra were acquired using commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz, or Bruker Avance II⁺ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane or residual NMR spectroscopic solvent signals.^[39] Mass spectra were run using a Thermo Finnigan LCQ Advantage apparatus (ESI). All microwave irradiation experiments were carried out using a dedicated CEM-Discover mono-mode microwave apparatus operating at a frequency of 2.45 GHz and using sealed (aluminum-Teflon crimp-top), large (10 mL) microwave process vials. For column chromatography, 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. DMF and DMSO were dried on 4 Å molecular sieves. UV/Vis absorption spectra were taken using a Perkin–Elmer Lambda 20 (KU Leuven) or a Jasco V-560 (Università di Messina) spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier; the spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. As excitation sources, a Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or the nitrogen discharge (pulse width 2 ns at 337 nm) were employed. Emission quantum yields for deaerated solutions were determined using the optically diluted method, with $[Ru(bpy)_3]^{2+}$ in air-equilibrated aqueous solution ($\Phi_{\rm em}\!=\!0.028$) as quantum yield standard. Experimental uncertainties on the absorption and luminescence data are as follows: absorption maxima, 2 nm; molar absorption, 10%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; luminescence quantum yields, 15%.

Experimental procedures and data, and $({}^{1}H/{}^{13}C)$ NMR spectra for AB₂-pyrimidinylcorroles **3**, **4a–d**, **5a–d**, **7a**, **7c**, **9–11**,^[15] and **8**, **15**, **19**, **21**^[9] can be retrieved from previous communications.

FULL PAPER

meso-Pyrimidinyl-substituted AB₂-corroles 4a–d (general procedure 1): 5-Mesityldipyrromethane (2b) (0.750 g, 2.84 mmol) and the appropriate 2-substituted 4,6-dichloropyrimidine-5-carbaldehyde 1a–d (2.84 mmol) were added to stirred CH₂Cl₂ (1 L), purged with Ar for 15 min, immediately followed by the addition of the suitable amount of BF₃-OEt₂ (mostly 0.043 equiv),^[15] and the resulting solution was stirred at RT for 1 h (under Ar and protected from light). *p*-Chloranil (0.698 g, 2.84 mmol) was subsequently added and the mixture was heated at reflux for 1 h. The solvent was evaporated and the products were separated and purified by column chromatography (silica) to afford AB₂-corroles 4a–d and the corresponding A₂B₂-porphyrin analogues as purple solids.

Corrole **24**: Synthesis according to general procedure 1. Eluent CH₂Cl₂/ petroleum ether 1:1. Yield: 3%. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 9.13 (s, 1H; H_{pyrim}), 9.10 (d, *J*(H,H) = 4.6 Hz, 2H; H_β), 8.76 (d, *J*(H,H) = 4.6 Hz, 2H; H_β), 8.57 (d, *J*(H,H) = 4.6 Hz, 2H; H_β), 8.43 (d, *J*-(H,H) = 5.2 Hz, 2H; H_β), -0.6-2.4 ppm (brs, 3H; NH); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 164.6, 164.2, 158.1 (CH), 141.2, 141.0, 134.7, 134.2, 130.5, 127.9, 125.6, 121.7, 117.5, 113.7 (br), 102.2, 98.5 ppm; MS (ESI⁺): *m*/*z*: calcd for C₃₅H₁₂Cl₂F₁₀N₆: 776.0; found: 779.6 [*M*+H]⁺.

General procedure for the Cu insertion in Fb–meso-triarylcorroles (general procedure 2): Anhydrous $Cu(OAc)_2$ (54 mg, 0.3 mmol, 3 equiv) was added to a solution of the respective Fb–corrole (0.1 mmol) in THF (15 mL), and the mixture was stirred at RT under Ar for 10 min. THF was removed under reduced pressure and the Cu–corroles were obtained in pure form as brown-red solids after flash column chromatography (silica, eluent CH₂Cl₂/heptane mixtures).

Nucleophilic aromatic substitution

Monosubstituted Cu-corrole 7b: A mixture of Cu-corrole 5b (26 mg, 33 µmol, 1 equiv), 4-tert-butylphenol (19.8 mg, 132 µmol, 4 equiv), finely ground K₂CO₃ (27.3 mg, 198 µmol, 6 equiv), and [18]crown-6 (3 mg, 29 µmol) in dry DMF (5 mL) was heated overnight at 90 °C under an Ar atmosphere. Diethyl ether (20 mL) was added to the resulting cooled mixture, and the mixture was washed with distilled water (3×20 mL). The organic layer was subsequently dried over MgSO4, filtered, and evaporated to dryness. After column chromatographic purification (eluent CH₂Cl₂/heptane 1:1), monosubstituted corrole **7b** (21 mg, 71 %) was obtained as a red-brown solid (2.3 mg (9%) of starting corrole 5b was recovered). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.99$ (brs, 2H; H_{β}), 7.30–7.25 (m, 6H; $H_{\beta}+H_{Ph}$), 7.12 (br s, 2H; H_{β}), 7.04 (s, 4H; H_{mesit}), 6.89 (d, J(H,H) = 8.6 Hz, 2H; H_{Ph}), 2.40 (s, 6H), 2.38 (s, 3H), 2.09/2.07 (2 s, 12 H), 1.27 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 172.3$ (C-SMe), 150.1, 148.8, 148.7, 144.0, 139.0, 137.8 132.5 (CH), 128.4/128.3 (CH), 126.1 (CH), 121.1/121.0 (CH), 34.6, 31.5 (CH₃), 29.3 (CH₃), 20.0 (CH₃), 14.4 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 263 (4.65), 402 (4.95), 537 nm (3.93); MS (ESI+): m/z: calcd for C₅₂H₄₆ClCuN₆OS: 900.2; found: 902.4 [M+H]+.

Monosubstituted Cu-corrole 12 a: A mixture of Cu-corrole 5a (30.8 mg, 41.5 µmol, 1 equiv), *m*-cyanophenol (5.2 mg, 43.7 µmol, 1.7 equiv), [18]crown-6 (4.8 mg, 18 µmol), and (finely ground) K₂CO₃ (9.5 mg, 69 µmol, 6 equiv) in dry DMF (3 mL) was heated over 24 h at 70 °C under an Ar atmosphere. DMF was evaporated under vacuum and the resulting residue was dissolved in Et₂O (20 mL), washed with aqueous NH₄Cl (20 mL) and distilled water (3×20 mL), and the organic fraction was dried over MgSO₄, filtered and evaporated to dryness. After column chromatographic purification (silica, eluent CH₂Cl₂/petroleum ether 5:1), monosubstituted corrole 12a (27.0 mg, 79%) was obtained as a redbrown solid (4 mg (13%) of starting corrole **5a** was recovered). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.65$ (s, 1H; H_{pyrim}), 8.02 (br s, 2H; H_{β}), 7.51 (dt, J(H,H) = 7.6/1.4 Hz, 1H), 7.46 (t, J(H,H) = 7.9 Hz, 1H), 7.34-7.31 (m, 3H), 7.29-7.24 (m, 3H), 7.05/7.04 (2s, 4H; H_{mesit}), 6.99 (d, $J(H,H) = 4.0 \text{ Hz}, 2 \text{ H}; H_{\beta}$, 2.40 (s, 6H), 2.10 (s, 6H), 2.07 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 157.3$ (CH), 152.3, 148.7, 144.0, 139.5-138.0 (br), 137.8, 132.8 (CH), 130.5 (CH), 129.7 (CH), 128.27 (CH), 128.24 (CH), 126.7 (CH), 125.6 (CH), 121.2 (CH), 117.6, 113.6, 21.2 (CH₃), 19.8 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 260 (4.485), 402 (4.858), 506 (3.859), 535 nm (3.860); MS (ESI⁺): m/z: calcd for C₄₈H₃₅ClCuN₇O: 823.2; found: 825.3 [*M*+H]⁺.

When the reaction was performed (on a similar scale) at 90 °C with 1.6 equiv of *m*-cyanophenol, monosubstituted corrole 12a was isolated in 57% yield, and the disubstituted corrole derivative 12b was also obtained under these conditions in 45% yield.

Disubstituted Cu–corrole **12***b*: Eluent gradient CH₂Cl₂/petroleum ether 5:1 to CH₂Cl₂/ethyl acetate 30:1. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ =8.46 (s, 1 H; H_{pyrim}), 8.02 (brs, 2 H; H_β), 7.50 (dt, *J*(H,H)=7.8/ 1.2 Hz, 2H), 7.46 (t, *J*(H,H)=7.8 Hz, 2H), 7.38–7.26 (m, 8H), 7.18 (d, *J*(H,H)=4.0 Hz, 2H; H_β), 7.05 (s, 4H; H_{mesit}), 2.41 (s, 6H), 2.08 ppm (s, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ =157.2 (CH), 152.8, 148.7, 144.1, 139.5–138.5 (br), 138.0, 132.8 (CH), 130.6 (CH), 129.6 (CH), 128.4 (CH), 126.9 (CH), 125.7 (CH), 121.3 (CH), 117.9, 113.7, 21.3 (CH₃), 20.0 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε)=402 (4.885), 505 (3.841), 536 nm (3.850); MS (ESI⁺): *m/z*: calcd for C₅₅H₃₉CuN₈O₂: 906.2; found: 907.4 [*M*+H]⁺.

Monosubstituted Cu-corrole 13: A mixture of Cu-corrole 5a (23.7 mg, 31.9 µmol, 1 equiv), 4-chlorothiophenol (15.6 mg, 108 µmol, 3.4 equiv), [18]crown-6 (4.8 mg, 18 μ mol), and (finely ground) K₂CO₃ (17.5 mg, 127 µmol, 4 equiv) in dry DMF (3 mL) was heated over 20 h at 90°C under an Ar atmosphere. DMF was evaporated under vacuum and the resulting residue was dissolved in Et₂O (20 mL), washed with aqueous NH₄Cl (20 mL) and distilled water (3×20 mL), and the organic fraction was dried over MgSO4, filtered, and evaporated to dryness. After column chromatographic purification (silica, eluent CH2Cl2/heptane 1:1), monosubstituted corrole 13 (21.9 mg, 81%) was obtained as a red-brown solid (1 mg (4%) of starting corrole **5a** was recovered). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.69$ (s, 1 H; H_{pyrim}), 8.00 (br s, 2 H; H_β), 7.37–7.30 (m, 6H), 7.23 (brs, 2H; H_{β}), 7.04 (s, 4H; H_{mesit}), 6.94 (d, J(H,H) = 3.8 Hz, 2H; $H_{\beta}),\ 2.40$ (s, 6H), 2.11 (s, 6H), 2.09 ppm (s, 6H); $^{13}C\,NMR$ (100 MHz, CDCl₃, 25 °C, TMS): δ=157.3 (CH), 149.1, 144.3, 138.8 (br), 137.9, 136.9 (CH), 136.4, 133.0 (CH), 129.6 (CH), 128.42/128.37 (CH), 126.6, 121.3 (CH), 21.3 (CH₃), 20.03/19.96 ppm (CH₃); UV/Vis (CH₂Cl₂): $\lambda_{\max} \ (\log \varepsilon) = 266 \ (4.564), \ 406 \ (4.913), \ 538 \ nm \ (3.896); \ MS \ (ESI^+): \ m/z:$ calcd for C47H35Cl2CuN6S: 848.1; found: 850.4 [M+H]+

Disubstituted Cu-corrole 14: A mixture of Cu-corrole 5a (25.0 mg, 33.7 µmol, 1 equiv), p-dodecylphenol (50 mg, 191 µmol, 5.6 equiv), and Cs₂CO₃ (88 mg, 269 µmol, 8 equiv) in dry DMF (3 mL) was heated over 48 h at 120 °C under an Ar atmosphere. DMF was evaporated under vacuum and the resulting residue was dissolved in Et₂O (20 mL), washed with aqueous NH₄Cl (20 mL) and distilled water (3×20 mL), and the organic fraction was dried over MgSO4, filtered, and evaporated to dryness. After column chromatographic purification (silica, eluent CH2Cl2/petroleum ether 1:1), disubstituted corrole $14\ (32.6\ \text{mg},\ 81\ \%)$ was obtained as a red-brown film. ¹H NMR (400 MHz, CDCl₃, 55 °C, TMS): $\delta = 8.47$ (brs, 1H), 8.25 (brs, 2H), 7.54 (brs, 2H), 7.34-7.15 (m, 12H), 7.00-6.95 (m, 4H), 2.46 (s, 6H), 2.17 (s, 12H), 1.75–0.60 ppm (m, 50H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 157.6$ (CH), 150.5, 148.6, 147.1, 143.7, 139.3 (br), 137.7, 132.5 (CH), 128.3 (CH), 127.6 (CH), 128.0-127.0 (br, CH), 127.0 (CH), 121.04/120.97/120.81 (CH), 40.9 (CH₂), 37.6 (CH₂), 29.4 (CH₂), 29.1 (CH₂), 21.3 (CH₃), 20.0 (CH₃), 8.9 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 402 (4.886), 510 (3.853), 538 nm (3.886); MS (ESI⁺): m/z: calcd for C₇₇H₈₉CuN₆O₂: 1192.6; found: 1193.4 [M+H]⁺. Due to their modest intensity and the presence of solvent impurities (petroleum ether), the C signals for the dodecyl chains could not be identified unambiguously.

Asymmetric disubstitution by double S_NAr reaction: A mixture of monosubstituted Cu–corrole 12a (17.5 mg, 21.2 µmol, 1 equiv), *p*-bromophenol (14.3 mg, 82.7 µmol, 3.9 equiv), [18]crown-6 (4.8 mg, 18 µmol), and (finely ground) K₂CO₃ (18.6 mg, 135 µmol) in dry DMF (3 mL) was heated over 20 h at 90°C under an Ar atmosphere, and subsequently the temperature was elevated to 120°C (since some starting material remained) and the reaction was continued for another 28 h. DMF was evaporated under vacuum and the resulting residue was dissolved in Et₂O (20 mL), washed with aqueous NH₄Cl (20 mL) and distilled water (3×20 mL), and the organic fraction was dried over MgSO₄, filtered, and evaporated to dryness. After column chromatographic purification (silica, eluent CH₂Cl₂/heptane 1:1), three main corroles 16a (5.7 mg, 28%), 16b (4.6 mg, 21%), and 16c (3.7 mg, 20%) were obtained. *Disubstituted Cu–corrole* **16***a*: ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ =8.47 (s, 1H; H_{pyrim}), 8.00 (brs, 2H; H_β), 7.52–7.41 (m, 4H), 7.37–7.25 (m, 6H), 7.20 (d, *J*(H,H)=3.8 Hz, 2H; H_β), 7.05 (s, 4H; H_{mesit}), 6.92 (d, *J*(H,H)=7.7 Hz, 2H), 2.41 (s, 6H), 2.08 ppm (s, 12H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ =157.3 (CH), 152.9, 151.8, 148.7, 144.0 (br), 139.0 (br), 137.9, 132.7 (CH), 132.6, 130.5 (CH), 129.5 (CH), 128.41/ 128.38 (CH), 126.9 (CH), 125.8 (CH), 123.7 (CH), 121.2 (CH), 119.1, 118.0, 113.6, 21.3 (CH₃), 20.0 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 401 (4.987), 535 nm (3.973); MS (ESI⁺): *m/z*: calcd for C₅₄H₃₉BrCuN₇O₂: 959.2; found: 961.7 [*M*+H]⁺.

Disubstituted Cu–corrole **16b**: ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ =8.46 (s, 1H; H_{pyrim}), 8.00 (brs, 2H; H_β), 7.44 (d, J(H,H) =9.1 Hz, 4H), 7.32 (brd, J(H,H) = 3.0 Hz, 2H; H_β), 7.29 (brs, 2H; H_β), 7.05 (s, 4H; H_{mesit}), 6.91 (d, J(H,H) = 9.1 Hz, 4H), 2.41 (s, 6H), 2.07 ppm (s, 12H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ =157.4 (CH), 151.8, 148.7, 137.9, 132.7 (CH), 128.4 (CH), 123.7 (CH), 121.1 (CH), 119.0, 21.3 (CH₃), 20.0 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε)=402 (5.167), 536 nm (4.137); MS (ESI⁺): *m*/*z*: calcd for C₅₃H₃₉Br₂CuN₆O₂: 1012.1; found: 1014.7 [*M*+H]⁺.

Monosubstituted Cu–corrole **16***c*: ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.64$ (s, 1 H; H_{pyrim}), 8.02 (brs, 2H; H_β), 7.45 (d, *J*(H,H) = 8.8 Hz, 2H), 7.32 (d, *J*(H,H) = 3.5 Hz, 2H; H_β), 7.26 (brs, 2H; H_β), 7.04 (2s, 4H; H_{mosil}), 7.00 (d, *J*(H,H) = 4.0 Hz, 2H; H_β), 6.88 (d, *J*(H,H) = 8.8 Hz, 2H), 2.40 (s, 6H), 2.10 (s, 6H), 2.06 ppm (s, 6H); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta = 157.6$ (CH), 151.4, 148.8, 137.9, 132.8 (CH), 128.41/128.35 (CH), 123.7 (CH), 121.3 (CH), 119.4, 21.3 (CH₃), 19.98/19.96 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 402 (5.404), 506 (4.363), 535 nm (4.371); MS (ESI⁺): *m*/*z*: calcd for C₄₇H₃₅BrClCuN₆O: 876.1; found: 878.2 [*M*+H]⁺.

Asymmetric disubstitution by tandem Suzuki-S_NAr reaction: Aqueous Na₂CO₃ (2M, 0.1 mL) was added to a mixture of Cu-corrole 5a (16.0 mg, 21.6 µmol, 1 equiv), phenylboronic acid (8 mg, 65.6 µmol, 3 equiv), and [Pd(PPh₃)₄] (1 mg, 4 mol%) in toluene (3 mL), and the resulting mixture was heated by microwave irradiation at 100 °C (100 W) for 1 h. After cooling to RT, the solvent was evaporated under vacuum and the residue was redissolved in CH_2Cl_2 (20 mL), washed with distilled water (3× 20 mL), and the organic layer was dried over MgSO4 and filtered. The solvent was evaporated under vacuum and the monosubstituted corrole was separated from the remaining starting material (36%) and traces of the disubstituted derivative by flash column chromatography (silica, eluent CH2Cl2). Dry DMF (5 mL) was added to a round-bottom flask that contained the monosubstituted Cu-corrole, 4-tert-butylphenol (13 mg, 86 $\mu mol),$ [18]crown-6 (2 mg, 8 $\mu mol),$ and (finely ground) $K_2 CO_3$ (15 mg, 109 µmol), and the resulting mixture was heated by microwave irradiation at 175°C (100 W) over 1 h. DMF was evaporated under vacuum and the resulting residue was dissolved in Et₂O (20 mL), washed with aqueous NH₄Cl (20 mL) and distilled water (3×20 mL), and the organic fraction was dried over MgSO₄, filtered, and evaporated to dryness. After column chromatographic purification (silica, eluent CH2Cl2/heptane 7:3), asymmetrically disubstituted Cu-corrole 17 (6.6 mg, 34%) was obtained as a red-brown solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.94$ (s, 1H; H_{pyrim}), 7.97 (br s, 2H; H_{β}), 7.57–7.51 (m, 2H; H_{β}), 7.37– 7.31 (m, 4H), 7.20–7.10 (m, 7H), 7.01 (s, 4H; H_{mesit}), 6.94 (d, J(H,H) =8.6 Hz, 2H), 2.39 (s, 6H), 2.04 (s, 6H), 1.98 (s, 6H), 1.29 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 158.0$ (CH), 150.4, 148.5, 145.0-143.0 (br), 137.8, 132.0 (CH), 129.5 (CH), 128.5 (CH), 128.34/ 128.28 (CH), 126.5 (CH), 121.1/121.0 (CH), 34.6, 31.5 (CH₃), 21.3 (CH₃), 20.0 (CH₃), 19.8 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 263 (4.664), 407 (4.870), 540 nm (3.973); MS (ESI⁺): m/z: calcd for C₅₇H₄₉CuN₆O: 896.3; found: 897.9 [M+H]+.

Monosubstituted Cu-corrole **18a**: Aqueous Na₂CO₃ (2M, 0.1 mL) was added to a mixture of Cu-corrole **5b** (25.0 mg, 31.7 µmol, 1 equiv), phenylboronic acid (7.7 mg, 63.2 µmol, 2 equiv), and $[Pd(PPh_3)_4]$ (1.8 mg, 5 mol%) in toluene (3 mL), and the resulting mixture was heated by microwave irradiation at 120°C (100 W) for 2 h. After cooling to RT, the solvent was evaporated under vacuum and the residue was redissolved in Et₂O (20 mL), washed with distilled water (3×20 mL), and the organic layer was dried over MgSO₄ and filtered. The solvent was evaporated

5702 -

under vacuum and, after purification by column chromatography (silica, eluent CH₂Cl₂/heptane 2:3), monosubstituted corrole **18a** (20.1 mg, 79%) was obtained as a red-brown solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.96 (brs, 2H; H_β), 7.49 (d, *J*(H,H) = 7.0 Hz, 2H; H_{Ph}), 7.35 (d, *J*(H,H) = 3.8 Hz, 2H; H_β), 7.19–7.10 (m, 5H; H_{Ph}+H_β), 7.00–6.99 (m, 6H; H_{mesit}+H_β), 2.69 (s, 3H), 2.38 (s, 6H), 2.05/1.96 ppm (2s, 12H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 172.6 (C-SMe), 149.4, 144.3/144.1, 138.5/138.4, 137.9/137.3 (CH), 132.1 (CH), 130.0 (CH), 128.4/ 128.2 (CH), 121.2, 21.3 (CH₃), 20.0/19.8 (CH₃), 14.7 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 265 (4.185), 407 (4.345), 540 nm (3.373); MS (ESI⁺): *m*/z: calcd for C₄₈H₃₈ClCuN₆S: 828.2; found: 829.3 [*M*+H]⁺.

Disubstituted Cu-corrole 18b: A mixture of Cu-corrole 18a (12.8 mg, 15 µmol, 1 equiv), 4-tert-butylphenol (9.2 mg, 60 µmol, 4 equiv), finely ground K2CO3 (12.7 mg, 90 µmol, 6 equiv), and [18]crown-6 (3 mg, 60 umol) in dry DMF (5 mL) was heated by microwave irradiation at 175°C (150 W) for 1 h. Et₂O (20 mL) was added to the resulting mixture, and the mixture was washed with distilled water (3×20 mL), dried over MgSO₄, filtered, and evaporated to dryness. After column chromatographic purification (silica, eluent CH2Cl2/heptane 2:3), disubstituted corrole 18b (10.6 mg, 76%) was obtained as a red-brown solid. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.94$ (brs, 2H; H₆), 7.52 (d, J(H,H) =7.5 Hz, 2H; H_{Ph}), 7.28 (d, J(H,H) = 8.8 Hz, 2H; H_{Ph}), 7.19 (d, J(H,H) =4.0 Hz, 2H; H_{β}), 7.14–7.11 (m, 5H; H_{Ph}), 7.00 (2s, 4H; H_{mesit}), 6.93 (d, J(H,H)=8.7 Hz, 4H; H_{Ph}), 2.44 (s, 3H), 2.39 (s, 6H), 2.04/1.97 (2s, 12H), 1.28 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 171.7$ (C-SMe), 150.4, 149.3, 148.2, 143.9, 138.5, 137.9/137.8, 131.6 (CH), 129.4 (CH), 128.6 (CH), 128.3/128.1 (CH), 125.9 (CH), 121.3 (CH), 120.9 (CH), 34.6, 31.6 (CH₃), 21.3 (CH₃), 20.0/19.8 (CH₃), 14.3 ppm (CH₃); UV/Vis $(CH_2Cl_2): \lambda_{max} (\log \varepsilon) = 260 (5.672), 405 (5.803), 510 (4.845), 540 \text{ nm}$ (4.858); MS (ESI⁺): m/z: calcd for C₅₈H₅₁CuN₆OS: 942.3; found: 943.5 $[M+H]^+$.

Suzuki cross-coupling on Fb–AB₂-pyrimidinylcorrole 4a: Phenylboronic acid (41 mg, 0.34 mmol, 3 equiv) was added to a mixture of Fb–AB₂-corrole 4a (76 mg, 0.11 mmol, 1 equiv) and [Pd(PPh₃)₄] (4 mg, 3.5 µmol) in toluene (6 mL) under Ar, immediately followed by the addition of aqueous Na₂CO₃ (2 M, 0.75 mL), and the mixture was heated at reflux for 24 h under an Ar atmosphere. After cooling to RT, the solvent was evaporated under vacuum and the residue was redissolved in CH₂Cl₂ (20 mL), washed with distilled water (3×20 mL), and the organic layer was dried over MgSO₄ and filtered. The solvent was evaporated under vacuum and the crude corrole mixture was separated by column chromatography (silica, eluent CH₂Cl₂), thereby affording monosubstituted pyrimidinylcorrole 20a (50 mg, 62%) and the disubstituted congener 20b (25 mg, 29%) as purple-greenish solids.

Monosubstituted pyrimidinylcorrole **20***a*: ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 9.38 (s, 1 H; H_{pyrim}), 8.80 (d, *J*(H,H) = 4.1 Hz, 2 H; H_β), 8.38 (d, *J*(H,H) = 4.7 Hz, 2 H; H_β), 8.25 (d, *J*(H,H) = 4.1 Hz, 2 H; H_β), 8.19 (d, *J*(H,H) = 4.7 Hz, 2 H; H_β), 7.24 (s, 2 H; H_{mesit}), 7.21 (s, 2 H; H_{mesit}), 7.17 (d, *J*(H,H) = 7.4 Hz, 2 H; H_α), 6.67 (t, *J*(H,H) = 7.4 Hz, 1 H; H_β), 6.53 (t, *J*(H,H) = 7.4 Hz, 2 H; H_m), 2.58 (s, 6H), 1.97 (s, 6H), 1.78 (s, 6H), -0.6-2.5 ppm (brs, 3 H; NH); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 168.8, 165.1, 157.9 (CH_{pyrim}), 142 (br; C_α), 140 (br; C_α), 139.3, 139.1, 138.1, 137.9, 135.2, 135.0, 132.9, 130.1, 128.9 (CH), 128.7 (CH_β), 128.19 (CH), 128.12 (CH), 127.5 (CH), 124.2 (CH_β), 121.0 (br; CH_β), 115.2 (CH_β), 100.3, 21.5 (CH₃), 21.3 (CH₃), 21.0 ppm (CH₃); MS (ESI⁺): *m*/*z*: calcd for C₄₇H₃₉ClN₆: 722.3; found: 723.4 [*M*+H]⁺.

Disubstituted pyrimidinylcorrole **20b**: ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 9.70 (s, 1H; H_{pyrim}), 8.79 (d, *J*(H,H) = 4.1 Hz, 2H; H_β), 8.26–8.19 (m, 6H; H_β), 7.21 (s, 4H; H_{mesit}), 7.05 (d, *J*(H,H) = 7.4 Hz, 4H; H_α), 6.59 (t, *J*(H,H) = 7.4 Hz, 2H; H_β), 6.48 (t, *J*(H,H) = 7.4 Hz, 4H; H_α), 2.57 (s, 6H), 1.81 (s, 12H), -0.6–2.6 ppm (brs, 3H; NH); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 168.7, 158.3 (CH_{pyrim}), 150.0 (br), 139.2, 139.0 (br), 137.9, 135.7 (br), 135.3, 131.7 (br), 129.2 (CH_β), 128.8 (CH), 128.2 (CH), 127.9 (CH), 127.40/127.33 (CH), 127.0 (CH), 124.2 (CH_β), 121.8 (br, CH_β), 115.8 (CH_β), 101.4, 21.5 (CH₃), 21.1 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 417 (5.017), 431 (5.001), 572 (4.176), 607 (4.006), 642 nm (3.785); MS (ESI⁺): *m*/*z*: calcd for C₅₃H₄₄N₆: 764.4; found: 765.4 [*M*+H]⁺.

General procedure for the demetalation of Cu-meso-triarylcorroles (general procedure 3): $SnCl_2 H_2O$ (113 mg, 0.5 mmol, 10 equiv) was added to a solution of the respective Cu-corrole (0.05 mmol) in acetonitrile/dichloromethane (2:1; 15 mL), and the resulting mixture was stirred for 10 min at RT under Ar. Subsequently, concentrated aqueous HCl (1 mL) was added and stirring was continued for 10 min at RT under Ar. The completion of the demetalation process was monitored by ESIMS and TLC. The mixture was diluted with diethyl ether, washed with water till neutral, dried over Na₂SO₄, and the drying agent was filtered off. The solvent was evaporated under reduced pressure and the pure free-base corroles were obtained as purple solids after flash column chromatography (silica).

Corrole **22**: According to general procedure 3: monosubstituted Cu–corrole **7b** (20 mg, 22 μmol), SnCl₂·2H₂O (20 mg, 89 μmol), MeCN/CH₂Cl₂ (2:1; 15 mL), concentrated HCl (1 mL), eluent CH₂Cl₂/heptane 2:1. Yield: 98% (18.3 mg). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): *δ* = 8.79 (d, *J*(H,H) = 4.0 Hz, 2H; H_β), 8.51 (d, *J*(H,H) = 4.8 Hz, 2H; H_β), 8.46 (d, *J*(H,H) = 4.8 Hz, 2H; H_β), 8.26 (d, *J*(H,H) = 3.8 Hz, 2H; H_β), 8.46 (d, *J*(H,H) = 4.8 Hz, 2H; H_β), 7.17 (d, *J*(H,H) = 8.8 Hz, 2H; H_β), 6.84 (d, *J*(H,H) = 8.6 Hz, 2H; H_{Ph}), 2.59 (s, 6H), 2.52 (s, 3H), 1.94/1.91 (2s, 12H), 1.18 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): *δ* = 171.9, 163.5, 150.3, 148.4, 139.4/139.3, 137.9, 135.5, 134.6, 129.5, 128.2 (br; CH), 125.9 (CH), 124.7 (CH), 121.0 (CH), 116.4, 114.8 (CH), 97.5, 34.5, 31.4 (CH₃), 21.6/21.3 (CH₃), 14.5 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ε) =410 (5.013), 428 (4.954), 570 (4.328), 603 (4.021), 634 nm (3.491); MS (ESI⁺): *m/z*: calcd for C₅₂H₄₉ClN₆OS: 840.3; found: 842.0 [*M*+H]⁺.

Corrole **23**: According to general procedure 3: asymmetrically disubstituted Cu–corrole **17** (10 mg, 11 µmol), SnCl₂·2H₂O (10 mg, 44 µmol), MeCN/CH₂Cl₂ (2:1; 15 mL), concentrated HCl (1 mL), eluent CH₂Cl₂. Yield: 84 % (7.8 mg). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ =9.21 (s, 1H; H_{pyrim}), 8.79 (d, *J*(H,H) = 4.0 Hz, 2H; H_β), 8.45–8.37 (m, 4H; H_β), 8.24 (d, *J*(H,H) = 4.0 Hz, 2H; H_β), 7.27–7.20 (m, 8H), 6.88 (d, *J*(H,H) = 6.8 Hz, 2H), 6.68 (t, *J*(H,H) = 7.3 Hz, 1H), 6.59 (t, *J*(H,H) = 7.7 Hz, 2H), 2.58 (s, 6H), 1.96 (s, 6H), 1.79 (s, 6H), 1.19 (s, 9H), -0.75–2.5 ppm (brs, 3H; NH); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ =170.2, 158.0 (CH), 150.5, 148.2, 139.2, 138.6, 137.9, 135.5, 129.1 (CH), 128.3/ 128.2 (CH), 127.7/127.6 (CH), 126.4 (CH), 124.7 (CH), 121.0/120.9/120.7 (CH), 115.1 (CH), 34.5, 31.5 (CH₃), 21.5 (CH₃), 21.4 (CH₃), 21.1 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 281 (3.806), 412 (5.037), 427 (4.952), 569 (4.238), 604 (4.033), 636 nm (3.690); MS (ESI⁺): *m/z*: calcd for C₅₇H₃₂N₆O: 836.4; found: 838.6 [*M*+H]⁺.

Pyrimidinylcorrole metalation reactions

Co^{III}(PPh₃)-corrole 25: Co-insertion procedure according to a combination of the procedures described by Gross and Guilard.^[27] AB2-pyrimidinylcorrole 4a (27.0 mg, 39.6 μ mol) and anhydrous [Co(acac)₂] (acac= acetylacetonate; 51 mg, 198 µmol, 5 equiv) were dissolved in CH2Cl2/ EtOH (3.5:1.5 mL) and heated at reflux for 24 h; the reaction was monitored by ESIMS. Subsequently, PPh3 (34 mg, 130 µmol, 3.3 equiv) was added, and the mixture was stirred for 15 min at RT and evaporated to dryness. The residue was passed through a silica column (eluent CH2Cl2/ heptane 2:1), thereby affording bright red Co^{III}(PPh₃)-corrole 25 (16.2 mg, 41%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): $\delta = 9.18$ (s, 1 H; H_{pyrim}), 8.17 (d, J(H,H) = 4.3 Hz, 2H; H_{β}), 8.12 (d, J(H,H) = 4.6 Hz, 2H; H_{β}), 8.03 (d, J(H,H) = 5.5 Hz, 2H; H_{β}), 7.74 (d, J(H,H) = 4.6 Hz, 2H; H_{\beta}), 7.06 (s, 2H; H_{mesit}), 7.03 (s, 2H; H_{mesit}), 6.98 (t, \textit{J}(H,H)\!=\!7.3 Hz, 3H; PPh₃), 6.68–6.58 (m, 6H; PPh₃), 5.09–4.98 (m, 6H; PPh₃), 2.49 (s, 6H), 1.67 (s, 6H), 1.32 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS): $\delta = 157.6$ (CH), 146.4, 144.7, 143.7, 138.0, 137.1, 136.9, 136.6, 136.3, 136.1, 131.6 (CH), 131.4 (CH), 129.8 (CH), 129.4 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 123.9 (CH), 123.6, 121.9 (CH), 120.2 (CH), 21.3 (CH₃), 20.3 (CH₃), 19.9 ppm (CH₃); UV/Vis (CH₂Cl₂): λ_{max} $(\log \varepsilon) = 381$ (4.661), 410 (4.582), 532 (sh; 3.859), 572 nm (sh; 3.833); MS (ESI⁺): m/z: calcd for C₅₉H₄₆Cl₂CoN₆P: 998.2; found: 998.0 [M+H]⁺, 736.4 [M+H-PPh3]+.

 Ag^{III} -corrole **26**: Ag-insertion procedure according to Brückner et al.^[7b] AB₂-pyrimidinylcorrole **4a** (25.2 mg, 37.0 µmol) was dissolved in pyridine (3 mL), and silver(I) acetate (20 mg, 120 µmol, 3.3 equiv) was added. The solution was heated to 80 °C and kept at this temperature for 5 min. The

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- 5703

reaction mixture was filtered through a plug of Celite and the solvent was removed under vacuum. After column chromatographic purification (silica, eluent ethyl acetate/heptane 1:4), Ag^{III}–corrole **26** was isolated as a dark red solid (9.3 mg, 32 %). ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ =9.20 (s, 1H; H_{pyrim}), 9.10 (d, *J*(H,H)=4.3 Hz, 2H; H_β), 8.71 (d, *J*(H,H)=4.6 Hz, 2H; H_β), 8.53 (d, *J*(H,H)=3.7 Hz, 2H; H_β), 8.89 (d, *J*(H,H)=3.7 Hz, 2H; H_β), 7.28 (s, 4H; H_{mesit}), 2.62 (s, 6H), 1.88 ppm (s, 12H); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ =164.8, 157.9 (CH), 139.4, 138.1, 135.7, 134.2, 132.8, 129.9 (CH), 129.5, 128.2 (CH), 122.5 (CH), 119.2 (CH), 118.3 (CH), 116.9, 21.6 (CH₃), 21.4 ppm (CH₃); UV/ Vis (CH₂Cl₂): λ_{max} (log ε)=284 (4.319), 324 (4.136), 426 (5.354), 495 (3.843), 520 (4.102), 532 (4.183), 557 (4.569), 572 nm (4.648); MS (ESI⁺): *m/z*: calcd for C₄₁H₃₁AgCl₂N₆: 784.1; found: 786.3 [*M*+H]⁺.

Ga^{III}-corrole 27: Ga-insertion procedure according to Gross et al.^[28] Dry pyridine (7.5 mL) was added to AB2-pyrimidinylcorrole 4a (25 mg, 37 µmol) and gallium(III) chloride (65 mg, 369 µmol, 10 equiv), and the mixture was heated at reflux under an Ar atmosphere for 1 h. The solvent was evaporated under vacuum and the residue was passed through a silica gel column (eluent CH2Cl2/ethyl acetate gradient with 1% pyridine), thereby affording Ga^{III}-corrole 27 (5 mg, 16%) as a purple-greenish solid. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): $\delta = 9.13$ (s, 1H; H_{pyrim}), 8.99 (d, J(H,H) = 3.6 Hz, 2H; H_{β}), 8.62 (d, J(H,H) = 4.6 Hz, 2H; H_{β}), 8.54 (d, J(H,H) = 4.6 Hz, 2H; H_{β}), 8.23 (d, J(H,H) = 4.6 Hz, 2H; H_{β}), 7.26 (s, 4H; H_{mesit}), 6.76 (t, J(H,H) = 7.3 Hz, 1H; pyridine), 5.96–5.89 (m, 2H; pyridine), 3.39-3.36 (m, 2H; pyridine), 2.61 (s, 6H), 1.87 ppm (s, 12H); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 258 (3.908), 286 (3.876), 336 (3.582), 406 (sh; 4.488), 425 (4.843), 529 (3.603), 569 (3.759), 603 nm (4.034); MS (ESI⁺): m/z: calcd for $C_{46}H_{36}Cl_2GaN_7$: 825.2; found: 788.5 $[M+K-pyridine]^+$.

Crystallographic data for 7c: Crystallization from CHCl₃/hexane; $C_{61}H_{57}CuN_6O_2$; $M_r = 969.69$; crystal dimensions $0.45 \times 0.3 \times 0.1$ mm; triclinic; space group $P\bar{1}$ (no. 2); a=13.2624(4), b=17.7902(5), c=25.9222(6) Å; V = 5814.4(3) Å³; Z = 2; $\rho_{calcd} = 1.176 \text{ g cm}^{-3}$; $\mu = 1.516 \text{ cm}^{-1}$; $2\theta_{\max} = 143.06^{\circ}; R_1 = 5.95\% (I > 2\sigma(I)); 7.78\%$ (all data) and $wR_2 =$ 15.47 % $(I > 2\sigma(I))$; 16.58 % (all data); goodness of fit: 1.023. 100119 reflections were measured, of which 22030 were unique. Full-matrix leastsquares refinement based on $|F^2|$, 1439 parameters, hydrogen atoms were placed at calculated positions with temperature factors 20% higher than parent atoms (50% higher for methyl groups), min./max. residual electron density -0.331/0.756 e Å-3. The data were measured (omega and phi scans) using a Bruker SMART 6000 detector $Cu_{K\alpha}$ ($\lambda = 1.54178$ Å) with crossed Göbel mirrors. The crystals were cryo-cooled to 100 K. The data were corrected for Lorentz, absorption (Bruker SADABS), and polarization effects. The structure was solved by direct methods. CCDC-757471 (7c) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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