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Efficient Two-Step Synthesis of Face-to-Face *meso*-Substituted Bis(corrole) Dyads

Maya El Ojaimi,[a] Claude P. Gros,[a] and Jean-Michel Barbe*[a]

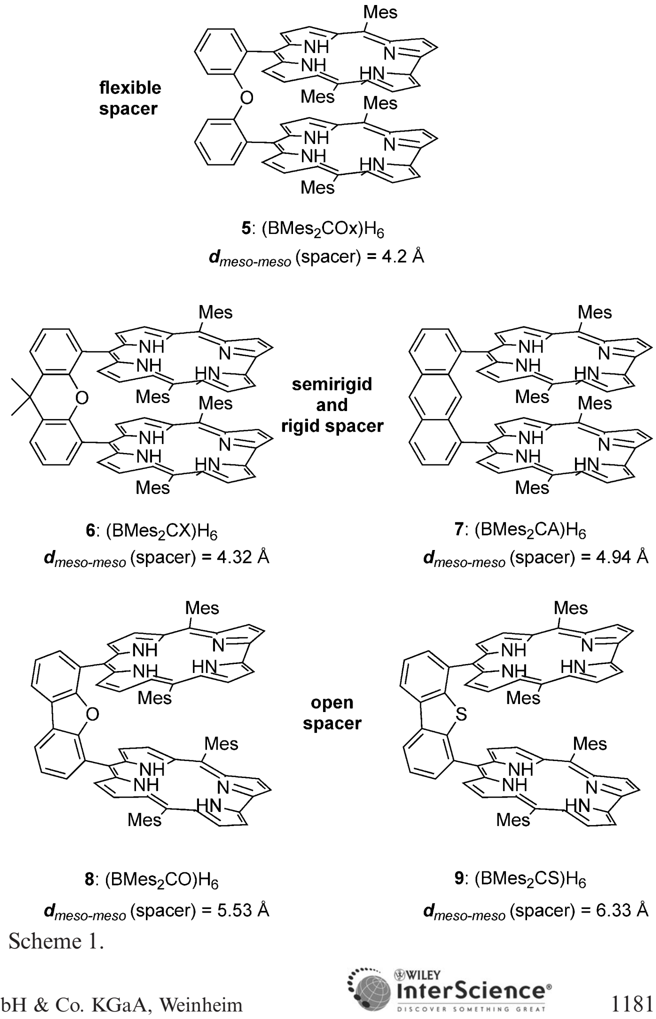
Keywords: Macrocycles / Corroles / Synthetic methods

The synthesis of face-to-face *meso*-substituted bis(corrole) systems was revisited. By using a new synthetic pathway, the reaction was generalized to any type of linker and the yield was considerably increased. The dyads were obtained in yields up to 20 % from a dialdehyde linker and dipyrromethane in a one-step reaction. The best reaction conditions required a decreased amount of TFA catalyst (1.4 equiv.) and a large excess of dipyrromethane (up to 8 equiv). Under these conditions, four bis(corrole)s linked by 2,2′-diphenyl ether, 9,9-dimethylxanthene, anthracene, and dibenzofuran spacers were synthesized.

Introduction

Corrole macrocycles have been used in many applications, such as, catalysis, CO and pH sensors, sensitizers for solar cells, and medicine;[1] their use was prompted by the publication of straightforward syntheses of stable *meso*-substituted corrole macrocycles.[2–24] For many years, we have been interested in the synthesis and characterization of cofacial bis(porphyrin), bis(corrole), and porphyrin–corrole dyads, where the two tetrapyrrolic macrocycles are covalently linked by a rigid or a more flexible spacer.[9,14,16,25–33] As a result of the close proximity of the two macrocycles, these dyads can be used in the reduction of oxygen to water,[34,35] in the oxidation of water to oxygen,[36] and probably in molecular recognition. In addition to this work, linear bis(corrole)s and porphyrin–corrole dyads have also been reported by other groups.[37–41]

Up to now, several homo- and heterobimetallic derivatives exhibiting interesting ligand binding properties have been synthesized and characterized by X-ray diffraction, spectroscopic techniques, and electrochemistry.[27–29,33,42–44] The ability of bis(cobalt) complexes of porphyrin–corrole and bis(corrole) dyads to catalyze efficiently the reduction of oxygen to water was more interesting.[34,35] Despite their enhanced catalytic activities, these β-substituted porphyrin–corrole or bis(corrole) dyads suffered from multistep syntheses that afforded final complexes in less than 1% overall yield. *meso*-Substituted porphyrins are readily available, in comparison to their β-substituted counterparts, from reactions of pyrrole or dipyrromethane derivatives. This is the same for the syntheses of *meso*-substituted corrole macrocycles which can now be produced at the gram scale. Here we described a revisited two-step synthesis and spectroscopic characterization of *meso*-substituted bis(corrole) derivatives (Scheme 1).



Scheme 1.

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[a] ICMUB UMR 5260, Université de Bourgogne,
9 avenue Alain Savary, B. P. 47870, 21078 Dijon Cedex, France
Fax: +33-03-80-39-61-17
E-mail: Jean-Michel.Barbe@u-bourgogne.fr

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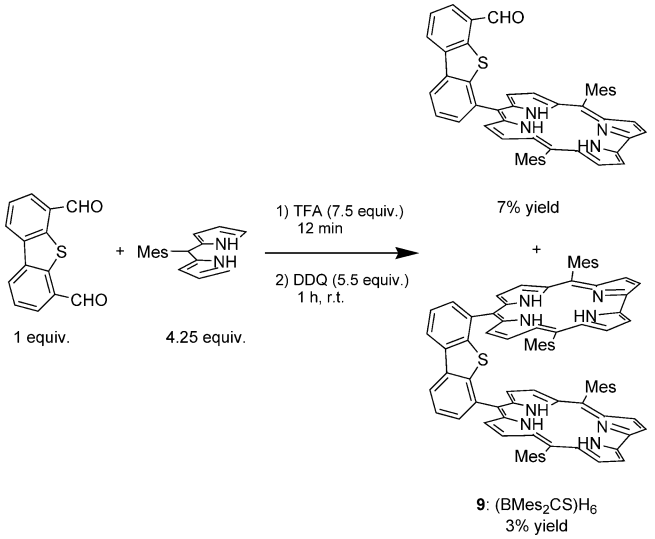
Results and Discussion

Our first synthesis of β-substituted bis(corrole)s is described in Scheme 2.[29,32,33] Starting from the dialdehyde linker (Scheme 2, Step 4; e.g. **1**–**4**), the bis(corrole)s were prepared in 11 steps due to the step-by-step nature of this synthetic procedure. The main drawback of this multistep synthesis is the low overall yield (<1%). Moreover, any variation in the structure of the desired bis(corrole) macrocycle requires a multistep preparation of a new pyrrolic precursor by using Barton–Zard[45,46] or Friedman[47] procedures.

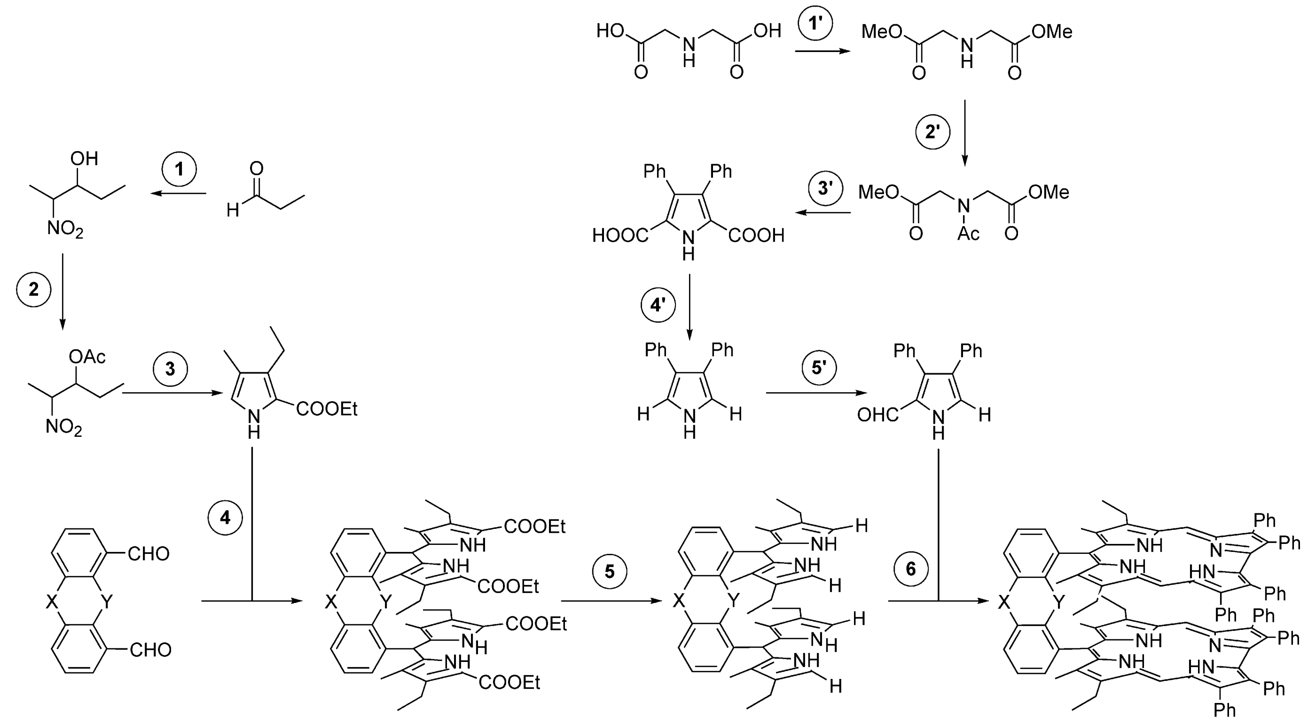
Recently, we reported refined conditions for the synthesis of β-substituted bis(corrole) and porphyrin–corrole dyads.[9] In particular, the simple replacement of sodium hydrogen carbonate by sodium acetate in the final cyclization step increased the yield by at least a factor of three. However, despite this appreciable increase in yield of β-substituted bis(corrole) derivatives, the great interest in *meso*-substituted derivatives stems from their theoretical one-step synthesis from dipyrromethane and a dialdehyde spacer.

We already described the synthesis of a dibenzothiophene *meso*-substituted bis(corrole) dyad,[48] and it was prepared on the basis of methods previously reported for monocorroles (Scheme 3).[8,49] The first step of the reaction sequence involved TFA-catalyzed condensation of the dialdehyde linker with 5-mesityldipyrromethane (4.25 equiv.), followed, in a second step, by neutralization with using NEt_3 and subsequent oxidation with DDQ (Table 1, Entry 1; Scheme 3). However, the bis(corrole) derivative was obtained in less than 3% yield along with the monosubstituted corrole–dibenzothiophene–monoaldehyde isolated in 7% yield as the major side product.[48] Moreover, the synthesis was specific to the open dibenzothiophene spacer.



Scheme 3.

Therefore, we refined and developed a new procedure that allowed the preparation of four new cofacial bis(corrole)s in 12–19% yield (Scheme 1). Four different rigid and



1: X = 2H, Y = O: diphenyl ether
2: X = C(CH$_3$)$_2$, Y = O: 9,9-dimethylxanthene
3: X= CH, Y = CH: anthracene
4: X= –, Y = O: dibenzofuran

10: (BCOx)H$_6$
11: (BCX)H$_6$
12: (BCA)H$_6$
13: (BCO)H$_6$

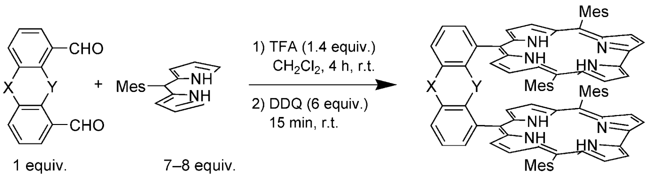
Scheme 2.

Table 1. Comparison of the bis(corrole) yields and the optimal reaction conditions.

Entry	Dialdehyde[a] [equiv.]	DPM[b] [equiv.]	Acid (equiv.) / time [h][c]	NEt_3 [equiv.]	Oxidant (equiv.) / time [h]	Monocorrole yield [%]	Bis(corrole) yield [%]	Ref.[d]
1	1	4.25	TFA (7.5) / 0.2	7.5	DDQ (5.5) / 1	7	3	[48]
2	1	8	TFA (1.4) / 4	–	DDQ (6) / 0.25	–	10–15	tw
3	1	8	TFA (1.4) / 4	–	*p*-Chloranil (6) / 0.25	–	[e]	tw
4	1	8	TFA (1.4) / 4	–	DDQ (8) / 0.25	–	–	tw
5	1	8	TFA (1.4) / 4	–	*p*-Chloranil (8) / 0.25	–	[e]	tw
6	1	7	TFA (1.4) / 4	–	DDQ (6) / 0.25	–	12–19	tw
7	1	4	HCl (100) / 16	–	DDQ (4.6) / 3	–	–	tw
8	1	4	HCl (100) / 16	–	*p*-Chloranil (4.6) / 3	–	–	tw

[a] Reactions were performed on a scale of 0.44 mmol (Entries 1–6) to 1.3 mmol (Entries 7 and 8). [b] DPM = 5-mesityldipyrromethane. [c] TFA in CH_2Cl_2 and HCl in $MeOH/H_2O$ were used. [d] tw = this work. [e] Mixture of bis(corrole) and tris(mesitylcorrole); because of similar elution properties, separation was not possible.

more flexible spacers were investigated with C_{meso}–C_{meso} distances varying from 4.2 to 6.3 Å (Scheme 1). The synthesis of these bis(corrole)s is outlined in Scheme 4. They were obtained in one step starting from the dialdehyde linker and 5-mesityldipyrromethane, where the latter reagent was prepared in one step from commercially available pyrrole and mesitylaldehyde.[50,51] Indeed, we were interested to learn whether a substantial increase in the stoichiometric ratio of 5-mesityldipyrromethane (DPM) to a twofold ratio (8 equiv. of DPM) would affect the yield of the bis(corrole)s (Table 1, Entries 2–6).



1: X = 2H, Y = O: diphenyl ether
2: X = $C(CH_3)_2$, Y = O: 9,9-dimethylxanthene
3: X= CH, Y = CH: anthracene
4: X= –, Y = O: dibenzofuran

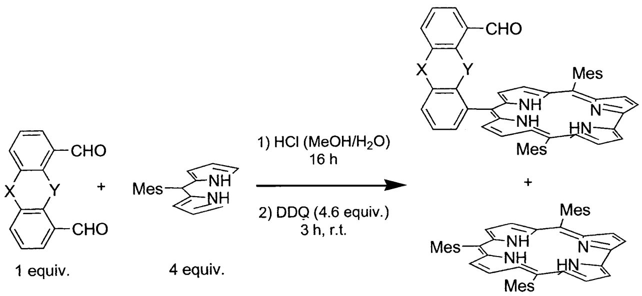
5: ($BMes_2COx$), 19%
6: ($BMes_2CX$), 17%
7: ($BMes_2CA$), 15%
8: ($BMes_2CO$), 12%

Scheme 4.

The effects of a lower concentration of TFA as well as an increase in reaction time were compared to the results obtained in the previously reported procedure. We concluded that the addition of a very small amount of TFA to the dichloromethane solution was advantageous, as already observed in the literature in the synthesis of *meso*-substituted *trans*-A_2B-corroles. Indeed, it was shown that in the reaction of aldehydes with sterically hindered dipyrromethanes, a low concentration of substrates and a high concentration of TFA favored the formation of the *trans*-A_2B_2-porphyrins instead of the aimed A_2B-corrole.[19,52] The best reaction conditions identified from the acid-screening experiments are summarized in Table 1. We first decreased the concentration of TFA progressively from 7.5 equiv. to 1.4 equiv. and at the same time increased the reaction time from 12 min to 4 h. The yield of the bis(corrole) derivatives was finally optimized upon an increase in the ratio of dipyrromethane (twofold) starting from 4.25 equiv. to 7–8 equiv. These results suggest that optimal formation of the bis(corrole) dyads requires a fairly large excess of dipyrromethane, as already observed in the synthesis of cofacial porphyrin-*meso*-substituted corrole dyads.[53,54]

The use of 6.0 equiv. of DDQ (vs. the dialdehyde spacer) led to a substantial increase in the yield, whereas a further increase to 8.0 equiv. caused a sudden drop in the yield of bis(corrole)s (Table 1, Entries 2 and 4). As shown in the literature, the choice of the oxidant appears to be critical to the success of the reaction and to the ease of corrole isolation.[17,52] We further decided to investigate the oxidation conditions by replacing DDQ by *p*-chloranil. Indeed, DDQ oxidation has been generally applied with best success in the preparation of corroles bearing withdrawing groups and/or facially bulky substituents, but, in some cases, oxidation with *p*-chloranil provided a higher yield.[17,52] It is now well known that *p*-chloranil appears to be best suited for corroles that tend to interact strongly with DDQ, whereas DDQ appears to be more efficient for reactions leading to corroles that require stronger oxidizing conditions.[17] Control experiments under optimized conditions with *p*-chloranil instead of DDQ (Table 1, Entries 3 and 5) led to the formation of the bis(corrole) dyad as well as some free-base tris(mesitylcorrole) as a side product. Unfortunately, at this stage, column chromatography separation of the unexpected tris(mesitylcorrole) and the aimed bis(corrole) derivatives on silica or alumina gels was impossible due to similar elution characteristics. It is noteworthy that the amount of corrole–spacer-aldehyde derivative (resulting from the formation of only one corrole macrocycle instead of two) was negligible when this new procedure was followed, whereas a 7% yield was observed in the initial procedure (Table 1, Entry 1). In all cases, the reaction mixture was diluted before the addition of DDQ by following the procedure described for the synthesis of monocorroles.[17,24]

Very recently, a new and efficient synthesis of *meso*-substituted corroles was reported by the reaction of sterically unhindered dipyrromethanes with aldehydes in a H_2O/MeOH mixture in the presence of HCl.[24] The same experimental procedure was employed to access the cofacial *meso*-substituted bis(corrole)s (Table 1, Entries 7 and 8). Unfortunately, the formation of the *meso*-substituted bis(corrole) system was not observed with this new procedure.[24] Only the tris(mesitylcorrole) and the monocorrole–spacer-aldehyde (not isolated) derivatives were detected (Scheme 5).



Scheme 5.

The UV/Vis data of the free-base bis(corrole)s are given in Table 2. As a result of the steric hindrance introduced by the bulky mesityl substituents (almost perpendicular to the mean corrole ring), we did not observed a blueshift in the Soret band, as was the case for the β-substituted bis(corrole) analogs (Table 2). Moreover, because of the presence of bulky mesityl substituents at the *meso* positions, the distance between the two corrole rings is probably large enough to avoid significant interaction between the two macrocycles. As a consequence, the optical spectra of the free-base bis(corrole) are characterized by absorption bands that are nearly identical in wavelength to those of the monocorrole [$(Mes_2Ph_1Cor)H_3$: λ_{max} = 407, 567, 604, 637 nm], witnessing the absence of any significant electronic interactions between the two corrole macrocycles (Table 2).

Table 2. Comparison of the UV/Vis absorption data of the mono- and bis(macrocycle) compounds (CH_2Cl_2).

Compound	λ_{max} [nm] ($\varepsilon \times 10^{-3}$, $M^{-1}\,cm^{-1}$)		Ref.[a]
	Soret band	Q-bands	
$(Mes_2PhCor)H_3$	407	567, 604 635	[54]
$(BMes_2COx)H_6$ (**5**)	406 (128)	568 (16), 603 (10), 635 (4)	tw
$(BMes_2CX)H_6$ (**6**)	405 (128)	567 (16), 604 (10), 634 (5)	tw
$(BMes_2CA)H_6$ (**7**)	407 (117)	567 (15), 604 (9), 634 (3.5)	tw
$(BMes_2CO)H_6$ (**8**)	406 (140)	565 (17), 601 (10), 634 (3.5)	tw
$(BMes_2CS)H_6$ (**9**)	406	566, 601, 632	[48]
$(Me_4Ph_5Cor)H_3$	419 (8.5)	567 (1.5), 607 (1.3)	[58]
$(BCOx)H_6$ (**10**)	409 (9.5)	510 (2.1), 574 (1.9), 607 (1.5)	[59]
$(BCX)H_6$ (**11**)	409 (11.0)	517 (2.5), 563 (2.4), 606 (2.1)	[33]
$(BCA)H_6$ (**12**)	416 (13.2)	572 (3.5), 608 (2.9)	[29]
$(BCO)H_6$ (**13**)	408 (13.0)	509 (2.2), 567 (2.2), 604 (1.9)	[33]
$(BCS)H_6$	410 (16.0)	512 (2.2), 567 (2.5), 604 (2.1)	[33]

[a] tw = this work.

High-resolution mass spectrometry (HRMS) was used to further characterize the free-base bis(corrole)s. Measurements were carried out by using the PEG-ion series as an internal calibrant. Molecular formulae were all confirmed with a maximum absolute deviation of 2.8 ppm with respect to the theoretical values.

The ^1H NMR spectra of the C_2 symmetric derivative exhibit the characteristic pattern of two *meso*-substituted corrole units cofacially linked by an aromatic bridge (See Experimental Section). Peak assignments were made on the basis of chemical shifts, multiplicity, integrations, and spectral intercomparisons by using monocorrole derivatives as reference compounds.

Conclusions

We showed that refined conditions can now lead to *meso*-substituted cofacial bis(corrole) dyads in only one step from the dialdehyde linker and dipyrromethane. Up to 20% yield of bis(corrole)s linked by four different spacers can be obtained under these conditions. It is noteworthy that these *meso*-substituted dyads are as stable in solution towards air and light as their monocorrole counterparts. Work is in progress to obtain dyads bearing less bulky substituents in the *meso*-position. The geometry of these derivatives would allow more electronic interactions between the two corrole macrocycles.

Experimental Section

Instrumentation: ^1H NMR spectra were recorded with a Bruker DRX-300 AVANCE transform spectrometer at the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne; chemical shifts are expressed in ppm relative to chloroform (δ = 7.26 ppm). UV/Vis spectra were recorded with a Varian Cary 1 spectrophotometer. Mass spectra and accurate mass measurements (HRMS) were obtained with a Bruker Daltonics Ultraflex II spectrometer in the MALDI/TOF reflectron mode by using dithranol as a matrix. Accurate mass measurements (HRMS) were carried out under the same conditions as before by using the PEG-ion series as an internal calibrant. Both measurements were made at the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne.

Chemicals and Reagents: Absolute dichloromethane (CH_2Cl_2) was obtained from Carlo Erba and used as received. Silica gel (Merck; 70–120 mm) was used for column chromatography. Analytical thin-layer chromatography was performed with Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography and UV/Vis spectroscopy. Bis(2-formylphenyl) ether is commercially available and was used as received. 5-Mesityldipyrromethane,[50,51] 4,5-diformyl-9,9-dimethylxanthene (**2**),[55–57] 1,8-diformylanthracene (**3**),[29] and 4,6-diformyldibenzofuran (**4**)[55–57] were synthesized as already described.

2,2′-Bis(5,15-dimesitylcorrol-10-yl)diphenyl Ether ($BMes_2CO_x)H_6$ (5): Bis(2-formylphenyl) ether (**1**; 0.300 g, 1.33 mmol, 1 equiv.) and mesityldipyrromethane (2.45 g, 9.29 mmol, 7 equiv.) were dissolved under an atmosphere of argon and shielded from light in dichloromethane (300 mL). The mixture was stirred at room temperature for 5 min, and TFA (140 µL, 1.88 mmol, 1.4 equiv.) was added. After stirring at room temperature for 4 h, the mixture was diluted 6 times with dichloromethane (1.5 L) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone; 1.80 g, 7.98 mmol, 6 equiv.) was added. The mixture was stirred at room temperature for 15 min, concentrated, and filtered through a silica pad by using CH_2Cl_2 as the eluent. The first fraction was collected. After evaporation, the resulting solid was chromatographed on silica gel (CH_2Cl_2) to give the title compound in 19% yield (0.308 g, 0.250 mmol) as a dark-violet solid. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = –1.93 (br. s, 6 H, NH), 1.81 (s, 12 H, CH_3-mesityl), 2.22 (s, 6 H, CH_3-mesityl), 2.43 (s, 6 H, CH_3-mesityl), 2.75 (s, 12 H, CH_3-mesityl), 7.02 (s, 4 H, H_{meta}-mesityl), 7.15 (s, 4 H, H_{meta}-mesityl), 7.41 (d, $^3J_{H,H}$ =

8.1 Hz, 2 H, H-diphenyl ether), 7.68 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-diphenyl ether), 7.75 (d, $^3J_{H,H}$ = 4.3 Hz, 4 H, H_{β}-corrole), 7.85 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-diphenyl ether), 7.87 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, H-diphenyl ether), 8.06 (d, $^3J_{H,H}$ = 4.3 Hz, 4 H, H_{β}-corrole), 8.27 (d, $^3J_{H,H}$ = 3.9 Hz, 4 H, H_{β}-corrole), 8.92 (d, $^3J_{H,H}$ = 3.9 Hz, 4 H, H_{β}-corrole) ppm. UV/Vis (CH_2Cl_2): λ ($\varepsilon \times 10^{-3}$, $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) = 406 (128), 568 (16), 603 (10), 635 (4) nm. HRMS (MALDI-TOF): calcd. for $C_{86}H_{74}N_8O$ $[M]^{+\cdot}$ 1234.5986; found 1234.5959.

4,5-Bis(5,15-dimesitylcorrol-10-yl)-9,9-dimethylxanthene ($(BMes_2C_x)H_6$) (6): Title compound **6** was synthesized according to the procedure described above for **5**, starting from 4,5-diformyl-9,9-dimethylxanthene (**2**; 0.360 g, 1.35 mmol, 1 equiv.) and mesityldipyrromethane (2.50 g, 9.45 mmol, 7 equiv.) in 17% yield (0.285 g, 0.22 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = –3.35 (s, 3 H, NH), –2.09 (s, 3 H, NH), 1.04 (s, 12 H, CH_3-mesityl), 1.32 (s, 12 H, CH_3-mesityl), 2.54 (s, 12 H, CH_3-mesityl), 2.57 (s, 3 H, CH_3-dimethylxanthene), 2.59 (s, 3 H, CH_3-dimethylxanthene), 7.01 (s, 4 H, H_{meta}-mesityl), 7.05 (s, 4 H, H_{meta}-mesityl), 7.16 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, H-dimethylxanthene), 7.23 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, H-dimethylxanthene), 7.73 (d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_{β}-corrole), 7.77 (d, $^3J_{H,H}$ = 4.6 Hz, 4 H, H_{β}-corrole), 7.88 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, H-dimethylxanthene), 7.95 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 8.34 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole) ppm. UV/Vis (CH_2Cl_2): λ ($\varepsilon \times 10^{-3}$, $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) = 405 (128), 567 (16), 604 (10), 634 (5) nm. HRMS (MALDI-TOF): calcd. for $C_{89}H_{78}N_8O$ $[M]^{+\cdot}$ 1274.6299; found 1274.6298.

1,8-Bis(5,15-dimesitylcorrol-10-yl)anthracene ($(BMes_2CA)H_6$) (7): Title compound **7** was synthesized according to the procedure described above for **5**, starting from 1,8-diformylanthracene (**3**; 0.300 g, 1.28 mmol, 1 equiv.) and mesityldipyrromethane (2.37 g, 8.97 mmol, 7 equiv.) in 15% yield (0.225 g, 0.18 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = –3.28 (br. s, 3 H, NH), –1.98 (br. s, 3 H, NH), 1.03 (s, 12 H, CH_3-mesityl), 1.58 (s, 12 H, CH_3-mesityl), 2.52 (s, 12 H, CH_3-mesityl), 7.00 (s, 4 H, H_{meta}-mesityl), 7.08 (s, 4 H, H_{meta}-mesityl), 7.62 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-anthracene), 7.68 (t, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-anthracene), 7.84 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 7.86 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 7.90 (d, $^3J_{H,H}$ = 4.1 Hz, 4 H, H_{β}-corrole), 8.46 (d, $^3J_{H,H}$ = 4.1 Hz, 4 H, H_{β}-corrole), 8.48 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-anthracene), 8.58 (s, 1 H, H-anthracene), 9.05 (s, 1 H, H-anthracene) ppm. UV/Vis (CH_2Cl_2): λ ($\varepsilon \times 10^{-3}$, $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) = 407 (117), 567 (15), 604 (9), 634 (3.5) nm. HRMS (MALDI-TOF): calcd. for $C_{88}H_{74}N_8$ $[M]^{+\cdot}$ 1242.6036; found 1242.6024.

4,6-Bis(5,15-dimesitylcorrol-10-yl)dibenzofuran. ($(BMes_2CO)H_6$) (8): Title compound **8** was synthesized according to the procedure described above for **5**, starting from 4,6-diformyldibenzofuran (**4**; 0.300 g, 1.34 mmol, 1 equiv.) and mesityldipyrromethane (2.48 g, 9.38 mmol, 7 equiv.) in 12% yield (0.198 g, 0.16 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = –1.85 (br. s, 6 H, NH), 1.74 (s, 12 H, CH_3-mesityl), 1.95 (s, 6 H, CH_3-mesityl), 1.96 (s, 6 H, CH_3-mesityl), 2.54 (s, 12 H, CH_3-mesityl), 6.85 (s, 4 H, H_{meta}-mesityl), 7.13 (s, 4 H, H_{meta}-mesityl), 7.98 (d, $^3J_{H,H}$ = 4 Hz, 2 H, H-dibenzofuran), 8.01 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 8.16 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 8.32 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, H-dibenzofuran), 8.36 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, H-dibenzofuran), 8.45 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, H-dibenzofuran), 8.58 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole), 8.87 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{β}-corrole) ppm. UV/Vis (CH_2Cl_2): λ ($\varepsilon \times 10^{-3}$, $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) = 406 (140), 565 (17), 601 (10), 634 (3.5) nm. HRMS (MALDI-TOF): calcd. for $C_{86}H_{72}N_8O$ $[M]^{+\cdot}$ 1232.5829; found 1232.5864.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR, UV/Vis, and HRMS (MALDI-TOF) spectra of compounds **5**–**8**.

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