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Synthetic Routes to 5,10,15-Triaryl-tetrabenzocorroles

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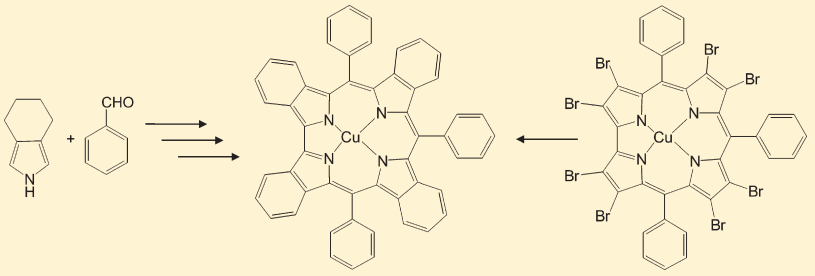
Supporting Information

ABSTRACT:



Two different synthetic routes for the preparation of 5,10,15-triaryl-tetrabenzocorroles have been developed. The first approach is based on the condensation of a tetrahydroisoindole with aryl-aldehydes, and the second pathway involves a cross-coupling reaction between a bromo-substituted corrole and a suitable substrate to form the four β-fused aryl rings. These routes are successful to lead to the target tetrabenzocorroles, obtained in both cases as the corresponding Cu complex and with the highest yield obtained via the one-step cross-coupling methodology. Demetalation of the Cu-tetrabenzocorrole produces the corresponding free base; this macrocycle was further exploited to obtain the Sn and Co complexes in good yields.

INTRODUCTION

Corroles are among the first members of the wide family of porphyrin analogues, as Johnson and Kay reported their first preparation[1] in the early 1960s, during the rush for the definition of the vitamin B12 synthetic route.[2] These macrocycles are in fact characterized by a corrin-like molecular skeleton, with a direct pyrrole−pyrrole link, while retaining an 18-electron aromatic π system like porphyrins. After a long period of silence, corroles regained popularity at the beginning of the new century, after the discovery of simple synthetic procedures for the preparation of 5,10,15-triarylcorroles.[3−7] The possibility to prepare corroles from commercially available precursors has allowed the great explosion of corrole related research and a better exploration of the intriguing chemistry of such a macrocycle, including investigations on its coordination chemistry,[8,9] photophysics,[10−13] and chemical reactivity,[14] which have opened the way for the application of corrole derivatives in the above-mentioned fields.

These synthetic advances have also allowed the investigation of more complex molecular architectures based on corroles, with the aim to investigate structure−properties relationships and to tune them for a particular application.

Among the different molecule constructs, a particularly interesting structure is represented by tetrabenzocorroles, the species represented in Figure 1.

These derivatives could be of particular interest, because the benzene rings fused at the β-pyrrolic positions lead to the extension of the π-aromatic system, with consequent modifications of their physicochemical properties. Considering the peculiar photophysical properties already reported for corrole derivatives,[10−13] tetrabenzocorroles could be of relevant interest for both theoretical and practical reasons.

To prepare such a functionalized species, two different routes could be followed: in the first one, the corrole ring is functionalized with proper substituents, which can later lead to the β-fused aromatic rings; in the second approach, which follows the most common way for the benzoporphyrin syntheses,[15−18] substituted pyrroles are used to prepared the functionalized corrole ring.

Both routes are challenging in the case of corrole, because the peripheral functionalization of such a macrocycle is a field still in its infancy, while the synthetic routes to triarylcorrole from functionalized pyrroles are not yet well-defined.

In this paper we investigate two different routes for the preparation of tetrabenzocorroles, following both the direct synthesis from pyrrole or the functionalization of a preformed corrole via a coupling methodology.

RESULTS AND DISCUSSION

Our first approach to tetrabenzocorrole synthesis involved their preparation from functionalized pyrrole rings. Following a

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route developed for the preparation of tetrabenzoporphyrins,[18] we decided to use 4,5,6,7-tetrahydroisoindole as starting material, reacting it with a corresponding arylaldehyde, adapting the protocol normally used for the preparation of triarylcorroles[6] (Scheme 1).

The product of this reaction is triaryl-tetrabutanocorrole (**1a,b**), which can be converted to the final tetrabenzocorrole upon oxidation of the peripheral rings.

We decided to use tetrahydroisoindole as starting pyrrole, because it is readily synthesized[19] and has been successful employed for the synthesis of tetrabenzoporphyrins.[18]

The reagents (pyrrole/aldehyde ratio 5/1) were dissolved in CH_2Cl_2 and stirred for 10 min under inert atmosphere before the addition of TFA as catalyst, and the resulting mixture was stirred for 90 min. The course of the reaction was monitored by UV−vis spectroscopy, and the presence of a strong absorption band between 400 and 450 nm in the optical spectrum upon oxidation of an aliquot of the reaction mixture with DDQ confirmed the formation of an aromatic macrocycle. TLC analysis of the reaction mixture showed a complex mixture of several spots other than that corresponding to the desired corrole. The attempts to purify this complex mixture failed, because of the low stability of the corrole free base, which mostly decomposed during the chromatographic separation. For this reason only a small quantity of pure corrole was isolated. The UV−vis spectrum of this compound was consistent with the formation of an aromatic macrocycle, as indicated by a Soret band at 431 nm and three Q bands at 531, 570, and 648 nm. When the reaction was carried out using the more reactive methyl-4-formylbenzoate, no improvement on the yield of tetrabutanocorrole formation was detected (Table 1).

The exploitation of $BF_3 \cdot OEt_2$ as the acidic catalyst, according to the Lindsey procedure,[20,21] gave only a slightly improvement of the reaction yield (Table 1). To avoid the decomposition of free base corrole during the purification process, we prepared its copper complex, with the aim to stabilize the corrole ring toward oxidative decomposition.

The coordination of copper ion to the corrole ring was readily achieved, and the course of the reaction could be followed by the appearance of a red spot on TLC and by UV−vis analysis, which showed the appearance of a Soret band blue-shifted to 409 nm, and a main Q-band at 552 nm.

The reaction mixture was purified by silica gel plug, eluted with chloroform, followed by preparative TLC on alumina, eluted with 55:45 $CHCl_3$/hexane. The first eluted band was identified as the corresponding Cu-tetrabutanoporphyrin, and the second red brownish band corresponded to the desired corrole **2a**, which was obtained in 8% yield. On the ^{1}H NMR spectrum of **2a** two main groups of signals were seen, one related to the phenyl protons in the range 7.23−7.38 ppm and a multiplet between 1.12 and 1.64 ppm for the protons on the cyclohexane rings. A broad peak at 2.96 ppm belongs to the four protons closer to the two directly bonded pyrrole units.

Mass analysis (MALDI) showed a molecular peak at 803.94 *m*/*z*, confirming the formation of **2a**, which was further characterized by X-ray crystallographic analysis of a chloroform solvate (Figure 2).

In both of the two molecules in the asymmetric unit, the coordination of the Cu is square planar with a slight pyramidal distortion. The Cu−N distances are in the range 1.894(3)−1.922(3) Å, with a mean value of 1.905 Å. The pyramidal twist is such that the two N atoms opposite the five-membered chelate ring lie on average ±0.31 Å out of the CuN_2 plane of the five-membered ring. The 24-atom Cu-corrole system is reasonably planar, with mean deviation 0.21 Å and maximum deviation 0.503(5) Å from coplanarity. The distortion observed in **2a** is similar to the conformations observed for other copper corroles, and this saddling effect has been recently reported by Ghosh as a common feature of such metal derivatives.[22,23] This conformation has been in fact observed regardless the presence of steric congestion at the peripheral position of the macrocycle and has been attributed to the noninnocent nature of copper corroles.[23]

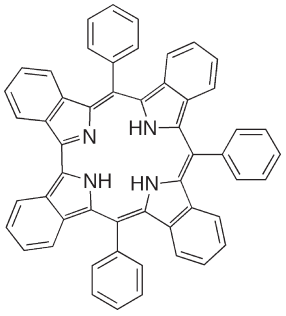

Figure 1. Molecular structure of a triaryl-tetrabenzocorrole.

Scheme 1. Condensation Route to Benzocorrole Formation

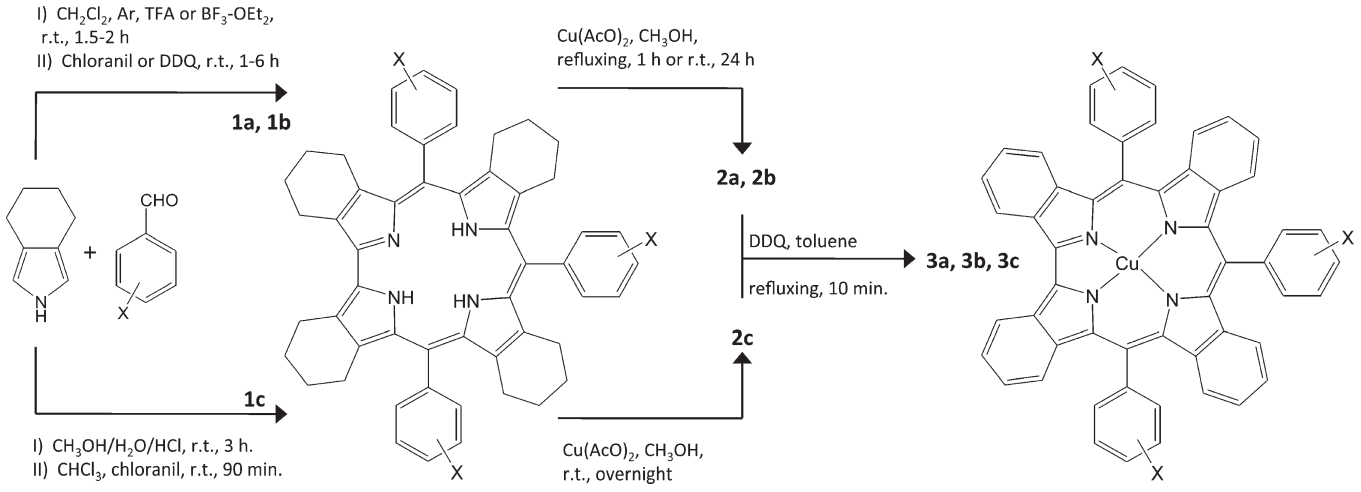

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Table 1. Yield of Benzocorrole Formation via Condensation Route

aldehyde	ratio pyrrole/aldehyde	solvent	catalyst	yield of **1** (%)
benzaldehyde	5/1	CH_2Cl_2	TFA	<1
methyl-4-formylbenzoate	5/1	CH_2Cl_2	TFA	<1
benzaldehyde	5/1	CH_2Cl_2	$BF_3 \cdot OEt_2$	8[a]
3-cyanobenzaldehyde	2/1	CH_3OH/H_2O	HCl	11

[a] Calculated for copper complex.

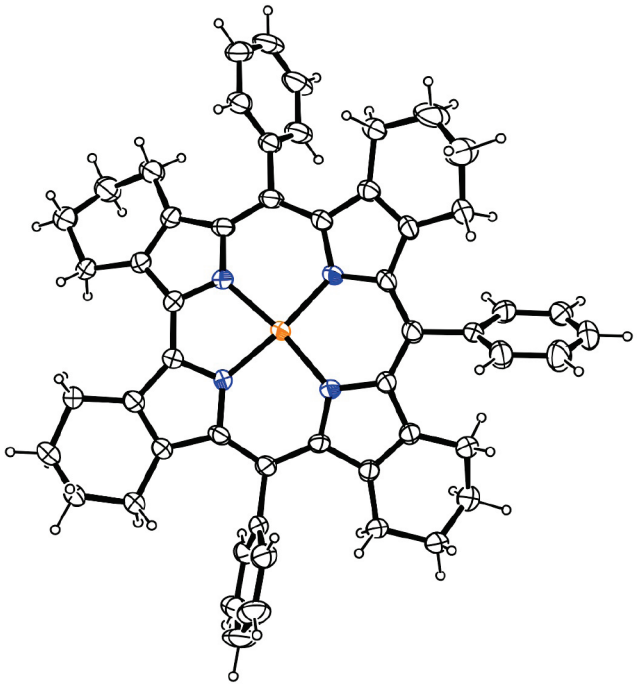

Figure 2. Molecular structure of **2a**.

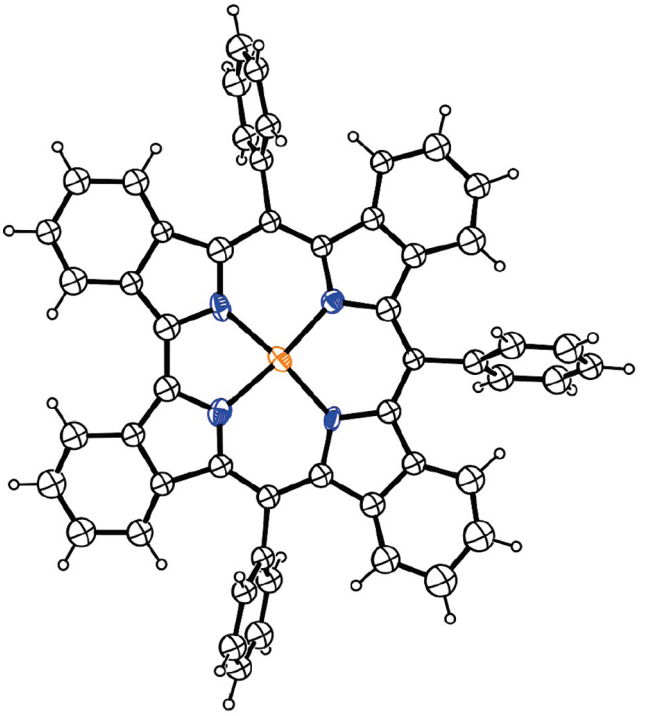

Figure 3. Molecular structure of **3a**.

The oxidation of the peripheral rings to obtain the desired tetrabenzocorrole was carried out with DDQ in refluxing toluene; the progress of the reaction was monitored by UV−vis spectroscopy. After 10 min, the solution color turned from red to green; both TLC and the UV−vis spectrum confirmed the disappearance of starting material and the formation of a new compound.

The reaction was stopped, and the resulting mixture was purified by a short alumina plug eluted with $CHCl_3$. The UV−vis spectrum of **3a** showed a red-shifted and split Soret band with λ_{max} at 447 and 459 nm and a very intense Q-band at 647 nm, with a shoulder at 598 nm. These features were consistent with the formation of the fused benzene rings at the β-pyrrolic positions of the corrole ring, since the extension of the β-aromatic system is expected to cause a red shift of the absorption bands and an increase of intensity of the Q bands, as observed in the case of benzoporphyrins.

However, the resulting complex **3a** showed low solubility in different solvents, which hampered its ^{1}H NMR characterization due to the broadness of the signals. This result could be ascribed to a paramagnetic character of the complex or to the aggregation of **3a**, supported also by the observed splitting of the Soret band. The formation of **3a**, with an overall yield of 6% from tetrahydroisoindole, was unambiguously confirmed both by MALDI-MS, by which a molecular peak was observed at 787.73 m/z, and by X-ray crystal structure determination, performed on a single crystal of a chloroform solvate, obtained by the slow diffusion of methanol in chloroform (Figure 3).

The asymmetric unit contains two corrole complex molecules, one of which lies on a 2-fold axis, and they differ in conformation. The 24-atom Cu-corrole system is quite planar for the C_2-symmetric molecule, with mean deviation 0.014 Å and maximum deviation 0.02(1) Å from coplanarity. The molecule not lying on a C_2 axis has a much less planar corrole, with mean deviation 0.18 Å and maximum 0.46(1) Å, similar to values seen in **2a**. The distortion is a twisted saddle. Coordination of the Cu atoms is square planar, with Cu−N distances in the range 1.906(11)−1.940(13) Å, and a mean value of 1.922 Å over the two independent molecules. It is interesting to note that in this case the characteristic saddling distortion of copper corroles is far less evident for both conformations of **3a**, suggesting that the extension of the aromatic system drives the macrocycle toward a more planar conformation.

While these results showed the successful preparation of the target benzocorrole, important drawbacks were represented by the low solubility of the target product and the relative low yields obtained for this synthetic route. To solve these problems, we turned our attention to the method reported by Gryko[7] (Scheme 1, **1c**−**3c**), using the more reactive 3-CN-benzaldehyde. This aldehyde and tetrahydroisoindole were dissolved in methanol and an aqueous solution of HCl was added. The

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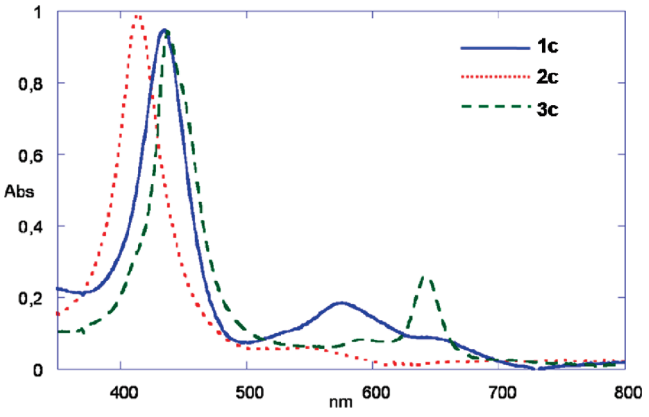

Figure 4. UV−vis spectra of **1c**, **2c**, and **3c** in CH_2Cl_2 (5−10 μM concentration).

mixture was stirred at room temperature for 3 h and extracted with chloroform, and after workup, the organic phase containing bilane was oxidized with chloranil.

The yields obtained for **1c** were increased to 11%, and the resulting corrole also showed good solubility in several solvents, thus allowing us to better characterize the product.

Due to the instability of the free base corrole during chromatographic separation, only a small amount of free base was purified for characterization purposes, while the remaining of the reaction mixture was converted to the complex **2c**.

The free base corrole **1c** was purified by silica gel column chromatography eluted with CH_2Cl_2/CH_3OH/TEA (98:1:1). The addition of TEA in the eluting mixture was necessary to avoid the protonation of the corrole ring on silica. UV−vis characterization of purified **1c** (Figure 4) was consistent with corrole formation, showing a red-shifted Soret band at 434 nm and three Q bands at 525, 576, and 650 nm.

The ^{1}H NMR spectrum of **1c** showed several signals in the region 7.89−8.38 ppm corresponding to the phenyl protons, and a multiplet, between 1.76 and 2.74 ppm, which belongs to the alkyl protons, while protons adjacent to C2 and C18 appeared as a broad signal centered at 4.09 ppm. MALDI mass spectrum of **1c** showed a molecular peak at 818.77 m/z.

The copper complex was prepared using the same methodology described above, and product **2c** was purified by silica gel column chromatography eluted with CH_2Cl_2. The main red band corresponding to Cu-corrole **2c** was collected and crystallized from CH_2Cl_2/CH_3OH. The UV−vis spectrum of **2c** shows a Soret band at 414 nm, blue-shifted by 20 nm, and only two Q bands, at 549 and 600 nm, instead of three, due the higher symmetry of **2c** compared with **1c**, induced by metal coordination.

On the other hand, the ^{1}H NMR spectrum of **2c** was not deeply affected by metal insertion, and only a slight shift of the peaks was observed. Mass spectrum analysis gave further proof of the structure of Cu-corrole **2c**, with the molecular peak at 878.79 m/z.

The oxidation of the peripheral cyclohexane rings to obtain **3c** was carried out with DDQ in refluxing toluene. After 10 min the solvent was removed, and the mixture was purified using neutral alumina column chromatography, eluted with $CHCl_3$. The UV−vis spectrum of the main green fraction has a 30 nm red-shifted Soret band at 437 nm with respect to its precursor, and a strong Q-band at 641 nm. The red shift of the main absorption band observed going from **2c** to **3c** is ascribed to the extended

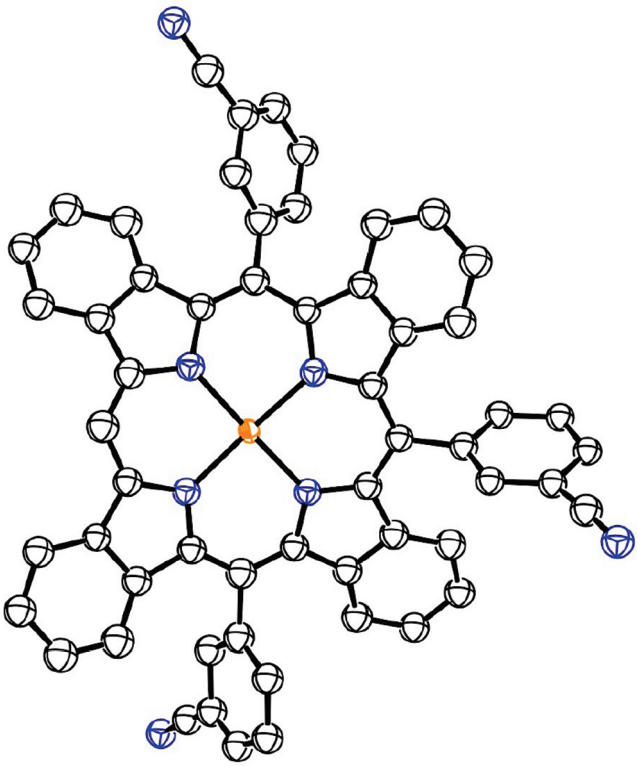

Figure 5. X-ray crystal structure of **4**.

π-conjugation with β-fused aromatic rings and is in the same range of the Soret band changes noticed in the case of analogous tetrabenzoporphyrins, as reported in the literature.[24]

The ^{1}H NMR spectrum of **3c** showed no signals below 7 ppm, supporting the formation of a molecule with only aromatic protons. Mass spectrometry confirmed that aromatization took place, as suggested by the molecular peak at 861.87 m/z.

Crystals of **3c** were grown by slow diffusion of methanol into the $CDCl_3$ solution exploited for the ^{1}H NMR analysis; however, X-ray crystal structure determination gave an unexpected result, because the molecular structure revealed that the compound was the triaryl-tetrabenzoporphyrin **4** (Figure 5).

This porphyrin was likely formed during the slow crystallization step, in a process catalyzed by air and light, as previously described.[25] The reaction probably involved two molecules of corrole, followed by a rearrangement of the intermediate to form one porphyrin molecule (i.e., **4**) and an open chain benzobiliverdine-like derivative, which was not isolated.

The overall yield of **3c**, based on the amount of aldehyde used, was only 8%. Therefore we decided to explore alternative synthetic routes. Considering previous works in the porphyrin field,[26,27] we decided to explore a route where the first step is the functionalization of the preformed corrole ring with appropriate substituents, which can later allow the buildup of the β-fused benzene rings.

A recently reported route for the preparation of tetrabenzoporphyrins involves a "cross-coupling" methodology, based on the Heck procedure.[27] This route allows direct formation of the final product in a one-pot reaction, with no isolation of intermediate compound needed (Scheme 2).

$CuBr_8TPC$ (**5a**), prepared following literature methods,[6,28,29] was reacted with methyl acrylate under the Heck conditions for 3 days at 125 °C. After removal of the solvent, the residue was

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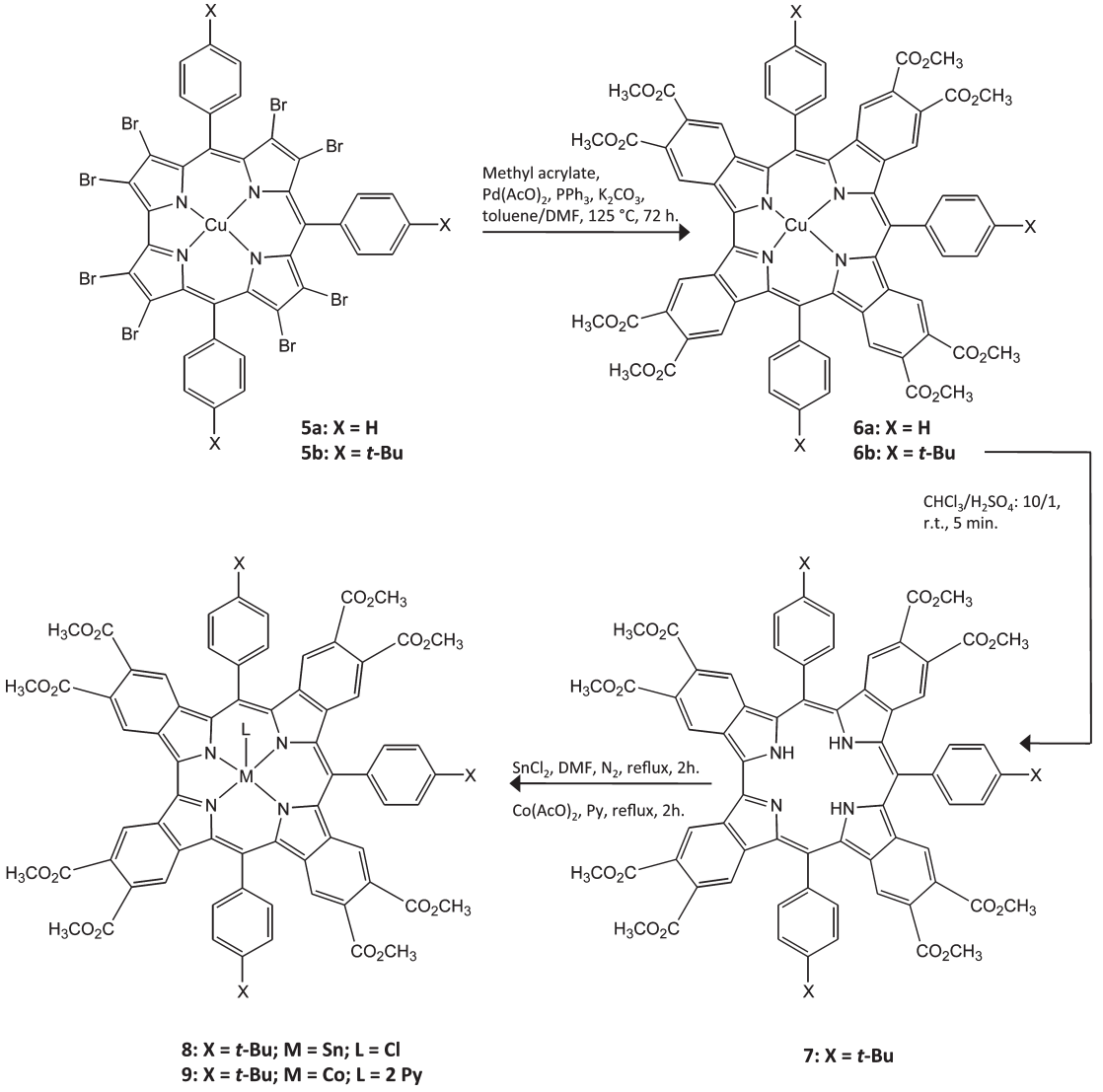
Scheme 2. Benzocorroles via a Heck Cross-Coupling Reaction



purified by alumina (grade III) column chromatography, eluted with chloroform.

The desired product was collected and further purified by column chromatography on alumina (grade IV) eluted with CH_2Cl_2. The UV−vis spectrum of **6a** showed a Soret band strongly red-shifted at 454 nm, with no intense Q-bands, while the ^{1}H NMR spectrum showed several signals between 3 and 4 ppm belonging to the -CO_2CH_3 groups, and a second cluster of multiplets in the aromatic region from 7 to 8 ppm.

It is worth noting the absence of signals around 6 ppm characteristic of unreacted olefin, supporting the ring closure of the peripheral substituents to give the β-fused aromatic rings. The benzocorrole formation was confirmed by MALDI mass spectrum, which showed the molecular peak at 1252.82 m/z.

The reaction was repeated starting with **5b** in place of **5a**, to increase the solubility of the corresponding corrole **6b** and to facilitate its characterization. The reaction was carried out as described above, and the reaction mixture was purified by neutral alumina (grade III) column chromatography eluted with $CHCl_3$. As expected, the increased solubility of **6b** allowed the complete spectroscopic characterization of the complex. In the ^{1}H NMR spectrum of **6b** three sets of signals were observed, with the singlet at 1.42 ppm assigned to the *tert*-butyl groups (27 protons), and the other two groups of signals, down shielded with respect to the *tert*-butyl singlet, appeared in the range 3−4 ppm (-CO_2CH_3, 24 H) and 7−8 ppm (aromatic protons, 20 H). The MALDI mass spectrum showed the molecular peak of **6b** at 1422.41 m/z. It is interesting to note that also in this case the UV−vis spectrum showed a broadened and red-shifted Soret band, around 471 nm. This red shift could be reasonably attributed to the electronic effect of the methoxycarbonyl substituents, as already observed in the case of the corresponding tetrabenzoporphyrins,[24] considering also that the analogous complex **3a** shows the Soret band at 447 nm.

The yield for this reaction was 16%, thus allowing the preparation of a larger amount of the free base, which was used as starting material for the preparation of different metal complexes. These complexes were prepared via demetalation[30] of **6b** to give the corresponding free base **7**, followed by insertion of Sn (**8**) or Co (**9**).

The copper corrole was demetalated upon addition of a few drops of concentrated H_2SO_4 to a chloroform solution of the complex.

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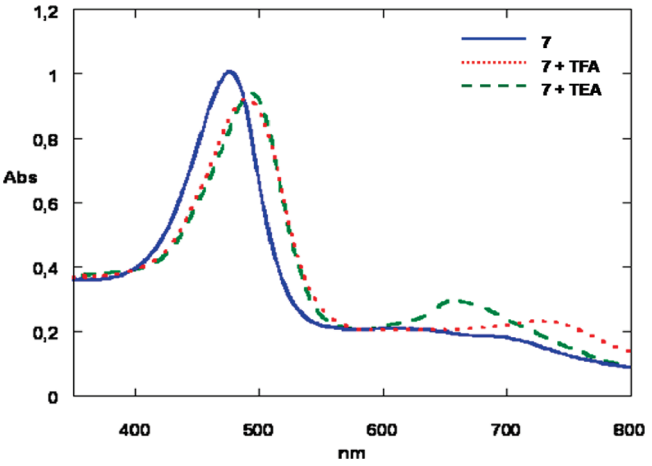

Figure 6. UV−vis spectra of **7** (blue line) at 10 μM in CH_2Cl_2 and upon addition of one drop of TFA (red line) or TEA (green line).

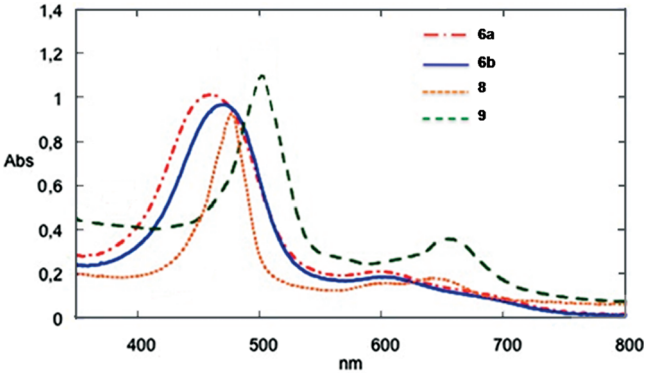

Figure 7. UV−vis spectra of benzocorrole metal complexes (5−20 μM in CH_2Cl_2).

The formation of the tetrabenzocorrole cation was indicated by the appearance of a peak around 730 nm in the UV−vis spectrum. Variations in the UV−vis spectrum of the free base upon addition of acid (TFA) or base (TEA) are shown in Figure 6, indicating the formation of the characteristic cationic and anionic species. These changes are similar to those observed in the case of unsubstituted triarylcorroles[31] and confirm the peculiar N−H acidicity also observed for tetrabenzocorrole. This feature has been attributed to the nonplanar structure of corrole free bases, caused by the presence of three inner core protons, and the related steric release experienced upon deprotonation, which can be induced even by weak bases like TEA. This steric effect explains the limited range of stability of free base corrole and is similar to the instability of monoprotonated porphyrin species.

The Sn complex was synthesized by reaction of the free base **7** with $SnCl_2$ in refluxing DMF. The isolated green complex **8** showed a UV−vis spectrum characterized by a red shifted and narrow Soret band, as seen in Figure 7. The MALDI MS confirmed the formation of this complex, showing a parent peak at 1667.05 m/z due to the coordination of the α-cyano-4-hydroxycinnamic acid, used as matrix for the MALDI measurement.

The Co complex **9** was prepared by reaction of **7** with $Co(AcO)_2$ in pyridine; this compound shows a further red shift of the Soret band (499 nm) and an intense Q band at 651 nm (Figure 7), typical signatures of pyridine coordination to form the hexacoordinated complex. Also in this case MALDI MS confirmed the complex formation with a molecular ion peak at 1418.39 m/z, with the loss of the axial pyridine ligands.

It should be noted that for both complexes **8** and **9** the ^{1}H NMR characterization showed severe line broadening, with broad multiplets for the aromatic signals and unresolved groups of singlets for the carboxymethyl and *tert*-butyl substituents. This behavior could be reasonably attributed to complex dynamic processes, involving conformers generated by macrocycle distortions upon metal coordination. Crystallographic characterization of these complexes would be necessary to clarify such a point, but unfortunately all our attempts to obtain single crystals suitable for X-ray structural analysis were unsuccessful.

CONCLUSIONS

Two different approaches for the preparation of 5,10,15-triaryl-tetrabenzocorroles have been investigated, and the first examples of such corrole derivatives were synthesized. The first synthetic route involves the condensation of a benzaldehyde with tetrahydroisoindole, leading to the formation of the tetrabenzocorrole in moderate yields, upon oxidation of the intermediate tetrabutanocorrole. The alternative approach exploits an intermediate octabromocorrole, which gives the target tetrabenzocorrole in one step after reaction with methyl acrylate under the Heck conditions; this second route could result in an easier approach, avoiding the preparation of the tetrahydroisoindole reagent and giving moderate yields of the final tetrabenzocorrole.

Tetrabenzocorroles show chemical stability similar to that of the corrole precursors, and we observed a corrole-porphyrin ring expansion transformation upon standing for several weeks in solution.

Tetrabenzocorroles show interesting UV−vis spectra, with features similar to those of the related tetrabenzoporphyrins; a detailed study of their photophysical properties is currently under way in our laboratories and these results will be reported in due time.

EXPERIMENTAL SECTION

2-Carboxyethyl-3,4,5,6-tetrahydroisoindole[19]**.** Mp: 80−82 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.77 (s br, 1H), 6.64 (d, J = 2.7 Hz, 1H), 4.29 (q, J = 8.4 Hz, 2H), 2.82 (t, J = 6.0 Hz, 2H), 2.54 (t, J = 5.5 Hz, 2H), 1.74 (m, 4H) 1.34 (t, J = 8.4 Hz 3H). MS (MALDI, m/z): 193.12 (M^+).

3,4,5,6-Tetrahydroisoindole[19]**.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.27 (s br, 1H), 6.11 (d, J = 2.7 Hz, 2H), 2.39 (t, J = 2.7 Hz, 4H), 1.52 (m, 4H).

5,10,15-Triphenylcorrole[6]**.** UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 415 (5.04), 567 (4.20), 615 (4.10), 648 (4.02). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.93, 8.86, 8.58, 8.53 (each d, 2H, J = 4 Hz), 8.39 (d, 4H, J = 7 Hz), 8.16 (d, 2H, J = 5 Hz), 7.82−7.72 (m, 9H), −2.91 (s, 3H). MS (FAB, m/z): 527 (M^+). Anal. Calcd for $C_{37}H_{26}N_4$: C, 84.39; H, 4.98; N, 10.64. Found: C, 84.24; H, 4.92; N, 10.49.

(5,10,15-Triphenylcorrolato)Cu[28]**.** UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 410 (5.09), 538 (3.89). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.89 (br s, 2H), 7.76 (d, J = 7.3 Hz, 4H), 7.65 (d, J = 7.3 Hz, 4 H), 7.59−7.54 (m, 3H), 7.51−7.44 (m, 6H), 7.35 (d, J = 3.1 Hz, 2H), 7.24 (d, J = 3.1 Hz, 2H). MS (MALDI-TOF, m/z): 586.96 (M^+). Anal. Calcd for $C_{37}H_{23}N_4Cu$: C, 75.69; H, 3.95; N, 9.54. Found: C, 75.57; H, 3.92; N, 9.45.

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(2,3,7,8,12,13,17,18-Octabromo-5,10,15-triphenylcorrolato)-Cu (5a)[29]**.** UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 454 (4.93), 653 (3.80). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.67−7.63 (m, 2H), 7.53−7.39 (m, 13H). MS (MALDI-TOF, m/z): 1217.65 (M^+). Anal. Calcd for $C_{37}H_{15}N_4Br_8Cu$: C, 36.48; H, 1.24; N, 4.60. Found: C, 36.39; H, 1.28; N, 4.52.

5,10,15-Tris(4-*tert*-butylphenyl)corrole[6]**.** UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 418 (5.11), 573 (4.25), 619 (4.22), 651 (4.14) nm. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.94 (br s, 4H), 8.63 (br s, 4H), 8.33 (br d, 4H), 8.13 (br d, 2H), 7.84 (br d, 4H), 7.79 (br d, 4H), 1.61 (s, 27 H). MS (FAB, m/z): 695 (M^+). Anal. Calcd for $C_{49}H_{50}N_4$: 84.69; H, 7.25; N, 8.06 Found: C, 84.56; H, 7.18; N, 7.99.

(5,10,15-Tris(4-*tert*-butylphenyl)corrolato)Cu (5b)[28]**.** UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 421 (5.17), 539 (3.92), 627 (3.68). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.92 (br s, 2H), 7.75 (m, 6H), 7.67 (br s, 2H) 7.50 (m, 6H), 7.43 (m, 2H), 7.35 (m, 2H), 1.56 (s, 18H), 1.44 (s, 9H). MS (FAB): m/z 755 (M+). Anal. Calcd for $C_{49}H_{47}N_4Cu$: C, 77.90; H, 6.27; N, 7.41 Found: C, 77.82; H, 6.19; N, 7.34.

[2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(4-*tert*-butylphenyl)corrolato]Cu. This compound was prepared following literature method.[29] UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 456 (4.91), 655 (3.79). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.78 (br s, 8H), 7.44 (br s, 4H), 1.44 (s, 18H), 1.42 (s, 9H). Anal. Calcd for $C_{49}H_{39}N_4Br_8Cu$: C, 42.44; H, 2.83; N, 4.04. Found: C, 42.35; H, 2.86; N, 3.99.

(5,10,15-Triphenyl-2:3,7:8,12:13,17:18-tetrabutanocorrolato)Cu (2a). Tetrahydroisoindole (250 mg, 2.1 mmol) was dissolved in 5 mL of dichloromethane and allowed to stir for 10 min. Benzaldehyde (0.04 mL, 0.41 mmol) and 5 μL of $BF_3\cdot OEt_2$ (0.03 mmol) were then added to the reaction and allowed to stir for another 2 h. DDQ was then added, and mixture was allowed to stir for 6 h at room temperature. To the mixture containing 5,10,15-triphenyl-2:3,7:8,12:13,17:18-tetrabutanocorrole (**1a**) was added a saturated solution of $Cu(AcO)_2$ in methanol was added, and the mixture was stirred at room temperature for 24 h. The metalation was considered complete when a Soret band at 409 nm was evident. The reaction mixture was then purified through a silica gel plug, eluting with chloroform, and the first red band eluted was collected. The red fraction was dissolved in dichloromethane and purified on an alumina gel preparative TLC eluting with 55:45 chloroform/hexane. The first band was the Cu(II)-tetrabutanoporphyrin, and the second reddish brownish band was the desired **2a** (9 mg, 8% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 409 (4.39), 552 (3.56). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.38−7.23 (m, 15 H), 2.96 (s br, 4H), 1.64−1.12 (m, 28 H). MS (MALDI, m/z): 803.94 (M^+). Anal. Calcd for $C_{53}H_{47}N_4Cu$: C, 79.22; H, 5.90; N, 6.96. Found: C, 79.03; H, 5.68; N, 6.79.

(5,10,15-Triphenyl-2:3,7:8,12:13,17:18-tetrabenzocorrolato)-Cu (3a). Compound **2a** (20 mg, 0.02 mmol) was dissolved in toluene, and DDQ (45 mg, 0.19 mmol) was added to the mixture before heating at reflux for 10 min. The reaction progress was followed by TLC (alumina, chloroform) for the appearance of a green streak at the baseline. Once the reaction was complete, the mixture was allowed to cool, filtered through a very short alumina plug, and eluted with around 100 mL of chloroform. (12 mg, 77% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 447 (4.57), 459 (4.5), 598 (3.78), 647 (4.1). MS (MALDI, m/z): 787.73 (M^+). Anal. Calcd for $C_{53}H_{31}N_4Cu$: C, 80.85; H, 3.97; N, 7.11. Found: C, 80.63; H, 3.58; N, 7.02.

5,10,15-Tris(3-cyanophenyl)-2:3,7:8,12:13,17:18-tetrabutanocorrole (1c). Tetrahydroisoindsole (500 mg, 4.1 mmol) and 3-cyano-benzaldehyde (269 mg, 2.05 mmol) were dissolved in CH_3OH (150 mL). Subsequently, a solution of HCl (36%, 7.5 mL) in H_2O (150 mL) was added, and the reaction was stirred at room temperature for 3 h. The mixture was extracted with $CHCl_3$, and the organic layer washed twice with H_2O, dried over Na_2SO_4, filtered, and diluted to 700 mL with $CHCl_3$. Chloranil (1.47 g, 6.0 mmol) was added, and the mixture was stirred at room temperature for 90 min, monitoring the course via UV−vis spectrometry.

After the appearance of the typical corrole free base absorption bands, an aliquot (20%) of the reaction mixture was removed and solvent was evaporated to dryness. Residue was dissolved with CH_2Cl_2, passed on a silica gel column eluted with CH_2Cl_2/CH_3OH/TEA (98:1:1). A green fraction was collected and crystallized from CH_2Cl_2/CH_3OH, to give the titled corrole (13 mg, 11% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 434 (5.12), 525 (4.25), 576 (4.46), 650 (4.18). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.38 (s, 3 H), 8.36−8.34 (m, 3 H), 8.06−8.03 (d, J = 7.17 Hz, 3H), 7.89−7.83 (m, 3 H), 4.09 (br m, 4 H), 2.74−2.70 (m, 8 H), 2.44 (br m, 4 H), 2.28−2.25 (m, 4 H), 1.94−1.92 (m, 4 H), 1.79−1.76 (m, 8 H). MS (MALDI, m/z): 818.77 (M^+). Anal. Calcd for $C_{56}H_{47}N_7$: C, 82.22; H, 5.79; N, 11.99. Found: C, 82.13; H, 5.69; N, 11.87.

[5,10,15-Tris(3-cyanophenyl)-2:3,7:8,12:13,17:18-tetrabutanocorrolato]Cu (2c). To the mixture containing corrole **1b** was added a solution of $Cu(AcO)_2$ in CH_3OH, and the mixture was stirred overnight at room temperature, monitoring the course of the reaction by UV−vis spectrometry. When analysis showed complex formation, solvent was removed under vacuum; purification by column chromatography (silica gel, CH_2Cl_2) afforded a red fraction that was crystallized from CH_2Cl_2/CH_3OH. (50 mg, 90% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 414 (5.12), 549 (4.04), 600 (3.71). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.79−7.64 (m, 8 H), 7.55−7.48 (m, 4 H), 3.01 (br m, 4 H), 1.74 (br s, 6 H), 1.65 (br m, 6 H), 1.52 (br m, 8 H), 1.38 (br m, 8 H). MS (MALDI, m/z): 878.79 (M^+). Anal. Calcd for $C_{56}H_{44}N_7Cu$: C, 76.56; H, 5.05; N, 11.16. Found: C, 76.47; H, 4.99; N, 11.02.

[5,10,15-Tris(3-cyanophenyl)-2:3,7:8,12:13,17:18-tetrabenzocorrolato]Cu (3c). Corrole **2c** (24 mg, 0.027 mmol) was dissolved in toluene, and DDQ (59 mg, 0.26 mmol) was added to the mixture before heating at reflux for 10 min. The progress of the reaction was followed by TLC (alumina) for the appearance of a green streak at the baseline and by UV−vis spectrometry for the red shifting of the absorption bands. Once the reaction was complete, the mixture was allowed to cool, filtered through a short alumina plug eluted with chloroform, and then was purified again on column chromatography (alumina, CH_2Cl_2 then $CHCl_3$). A green fraction was collected, crystallized from CH_2Cl_2/CH_3OH (18 mg, 77% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 437 (4.94), 641 (4.39). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80 (br m, 7 H), 7.71 (br m, 4 H), 7.69 (br m, 4 H), 7.66 (br m, 3 H), 7.62 (br m, 4 H), 7.52 (br m, 2 H), 7.49 (br m, 3 H), 7.47 (br m, 1 H). (MALDI, m/z): 861.87 (M^+). Anal. Calcd for $C_{56}H_{28}N_7Cu$: C, 77.99; H, 3.27; N, 11.37. Found: C, 77.88; H, 3.18; N, 11.29.

[5,10,15-Triphenyl-2:3,7:8,12:13,17:18-tetrabenzo-2″,3″,7″,8″,12″,13″,17″,18″-octacarboxymethylcorrolato]Cu (6a). Corrole **5a** (60 mg, 0.049 mmol), $Pd(AcO)_2$ (11 mg, 0.049 mmol), PPh_3 (34 mg, 0.128 mmol), K_2CO_3 (58 mg, 0.42 mmol), and methyl acrylate (437 μL, 4.9 mmol) were dissolved in anhydrous toluene/DMF (8 + 10 mL) in a Schlenk tube under nitrogen. The mixture was then degassed via five freeze−pump−thaw cycles before the vessel was purged with nitrogen again, then sealed, and heated at 125 °C for 72 h. Solvents were removed, and the residue purified with a neutral alumina column eluted with $CHCl_3$. Fractions containing corrole were combined and purified again with a neutral alumina (grade IV) column eluted with CH_2Cl_2. Brown fraction collected was crystallized from CH_2Cl_2/Hexane. (8 mg, 13% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 454 (4.90), 604 (4.16). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.73−7.46 (m, 23 H), 3.98−3.57 (m, 24 H). MS (MALDI, m/z): 1252.82 (M^+). Anal. Calcd for $C_{69}H_{47}N_4O_{16}Cu$: C, 66.21; H, 3.78; N, 4.48. Found: C, 66.08; H, 3.69; N, 4.38.

[5,10,15-Tris(4-*tert*-butylphenyl)-2:3,7:8,12:13,17:18-tetrabenzo-2″,3″,7″,8″,12″,13″,17″,18″-octacarboxymethylcorrolato]Cu (6b). Corrole **5b** (136 mg, 0.098 mmol), $Pd(AcO)_2$ (22 mg, 0.098 mmol), PPh_3 (70 mg, 0.256 mmol), K_2CO_3 (118 mg,

0.84 mmol), and methyl acrylate (874 μL, 9.8 mmol) were dissolved in anhydrous toluene/DMF (16 + 20 mL) in a Schlenk tube under nitrogen. The mixture was then degassed via five freeze−pump−thaw cycles before the vessel was purged with nitrogen again, then sealed and heated at 125 °C for 72 h. Solvents were removed and residue purified with a neutral alumina column eluted with $CHCl_3$. Brown fraction collected was crystallized from CH_2Cl_2/hexane. (22 mg, 16% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 471 (4.93), 602 (4.18). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.69−7.49 (m, 20 H), 3.95−3.47 (m, 24 H), 1.42 (br m, 27 H). MS (MALDI, m/z): 1422.41 (M^+). Anal. Calcd for $C_{81}H_{71}N_4O_{16}Cu$: C, 68.51; H, 5.04; N, 3.94. Found: C, 68.08; H, 4.84; N, 3.82.

5,10,15-Tris(4-*tert*-butylphenyl)-2:3,7:8,12:13,17:18-tetrabenzo-2″,3″,7″,8″,12″,13″,17″,18″-octacarboxymethylcorrole (7). Corrole **6b** (80 mg, 0.056 mmol) was dissolved in 8 mL of $CHCl_3$, and 1 mL of concentrated H_2SO_4 was added. An aliquot of the reaction mixture was diluted in methanol to monitor the progress of the demetelation process by UV−vis spectroscopy. After 5 min the formation of cation was observed, and distilled water (50 mL) was added to quench the reaction. The organic phase was extracted with chloroform, then washed twice with water, neutralized with aqueous $NaHCO_3$, and dried over Na_2SO_4 anhydrous. Solvent was removed, and the residue was purified with a neutral alumina (grade IV) plug eluted with $CHCl_3$. Brown fraction collected was crystallized from CH_2Cl_2/hexane. (59 mg, 77% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 476 (4.72), 606 (3.94) 699 (3.86). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.77−7.49 (m, 20 H), 4.01−3.51 (m, 24 H), 1.61 (br s, 27 H). Anal. Calcd for $C_{81}H_{74}N_4O_{16}$: C, 71.56; H, 5.49; N, 4.12. Found: C, 71.47; H, 5.54; N, 4.06.

[5,10,15-Tris(4-*tert*-butylphenyl)-2:3,7:8,12:13,17:18-tetrabenzo-2″,3″,7″,8″,12″,13″,17″,18″-octacarboxymethylcorrolato]SnCl (8). Complex **6b** (24 mg, 0.017 mmol) was demetalated to give the corresponding free base **7**, which was dissolved in DMF with $SnCl_2$ (15 mg, 0.079 mmol), and the mixture was stirred to reflux under nitrogen for 3 h. The reaction was monitored by UV−vis spectrometry and TLC (alumina, CH_2Cl_2−CH_3OH 5%). When the reaction was complete, the solvent was removed and the residue purified with short plug ran in the same condition of TLC. The fraction containing **8** was crystallized from CH_2Cl_2/hexane (13 mg, 51% yield). UV−vis (CH_2Cl_2), λ_{max} nm (log ε): 478 (5.35), 599 (4.35), 642 (4.45). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.37−7.63 (m, 20 H), 4.22−3.69 (m, 24 H), 1.37 (br m, 27 H). MS (MALDI, m/z): 1667.05 (M^+). Anal. Calcd for $C_{81}H_{71}N_4O_{16}ClSn$: C, 64.40; H, 4.74; N, 3.71. Found: C, 64.22; H, 4.26; N, 3.51.

[5,10,15-Tris(4-*tert*-butylphenyl)-2:3,7:8,12:13,17:18-tetrabenzo-2″,3″,7″,8″,12″,13″,17″,18″-octacarboxymethylcorrolato]CoPy$_2$ (9). Complex **6b** (24 mg, 0.017 mmol) was demetalated to give the corresponding free base **7**, which was dissolved in 15 mL of pyridine with $Co(AcO)_2$ (10 mg, 0.056 mmol). The mixture was stirred to reflux for 2 h, monitoring the course by UV−vis spectrometry and TLC (alumina, $CHCl_3$). After completion of the reaction, the solvent was removed and the residue purified by a short plug on alumina, eluting with $CHCl_3$. The fraction containing **9** was crystallized from CH_2Cl_2/CH_3OH (17 mg, 63% yield). UV−vis (pyridine), λ_{max} nm (log ε): 499 (4.70), 651 (4.21). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.69−7.47 (m, 20 H), 4.14−3.54 (m, 24 H), 1.63 (br m, 27 H). MS (MALDI, m/z): 1418.39 (M^+ − 2Py). Anal. Calcd for $C_{91}H_{81}N_6O_{16}Co$: C, 69.46; H, 5.19; N, 5.34. Found: C, 69.37; H, 5.06; N, 5.22.

■ ASSOCIATED CONTENT

Supporting Information. General experimental methods, ^{1}H NMR and mass spectra of compounds, CIF files for **2a**, **3a**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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