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Tuning the Photophysical and Redox Properties of Metallocorroles by Iodination

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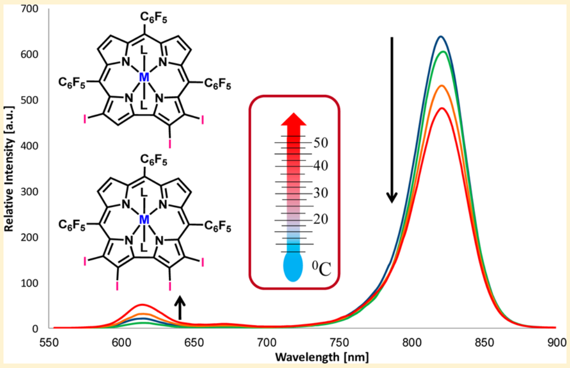
Supporting Information

ABSTRACT: Facile procedures were developed for selective iodination of aluminum and gallium corroles; crystallographic characterization shows that the main structural aspects are not changed (the macrocycle remains planar). Absorption maxima are red-shifted by 3−5 nm/iodine, singlet lifetimes are reduced to <80 ps, and emissions from long-lived excited states come into effect. The iodinated corroles display prompt fluorescence, phosphorescence, and delayed thermal fluorescence, all at room temperature. The effect on redox potentials appears to be additive for each additional iodine and, surprisingly, is practically identical to that of the other three halides. The conclusions of this work are of large importance for the design of metallocorroles that are best suited for the various applications where metallocorroles are used as catalysts and photosensitizers.



INTRODUCTION

The porphyrin related corroles display quite remarkable chemical and photophysical properties.[1−3] Development of simple and efficient procedures for corrole synthesis,[4,5] combined with facile tuning of physical and chemical characteristics by varying the peripheral substituents, axial ligands, and central metal, has raised substantial interest in employing them in various fields.[6] With the same basic structure and only few minor synthetic adjustments, they are utilized in dye-sensitized solar cells,[7] photodynamic detection,[8] optical imaging,[9] formation of singlet oxygen for catalysis[10] and photodynamic therapy[11a,b]/inactivation,[11c] and electron and energy transfer systems,[12] as well as used as drug candidates for diseases characterized by oxidative stress.[13] Increased elucidation of the variables that dictate the fundamental photophysical properties of corroles is crucial for designing optimal molecules for specific applications.

Halogenation of porphyrins has been used for gaining access to both *meso*- and *β*-substituted derivatives. Bromination is most facile, most commonly achieved by using either *N*-bromosuccinimide (NBS) or molecular bromine.[14] Chlorination requires catalysts and high temperatures,[14a,15] while iodination is limited to the *meso*-C atoms and does not occur on *β*-pyrrole CH's.[16] The *π*-system of corroles is much more electron-rich than of porphyrins, and one consequence is that full bromination[17] and chlorination[18] of the *β*-pyrrole positions of the corresponding metal complexes are much easier. A quite unexpected outcome, observed in all octahalogenated metallocorroles reported so far,[3b,17b,f,18c] is that it hardly affects their structures (the macrocycle remains planar). One consequence is that their absorption spectra are less red-shifted than expected, while the effect of halogenation on redox potential is very large: up to 600 mV more positive than of the nonhalogenated analogues. Much less is known about the heavy atom effect of the covalently attached halogen atoms, i.e., how it comes into play regarding emission from photoexcited states. Another shortcoming is that it is almost impossible to achieve selectivity in polyhalogenation of corroles (or porphyrins).[19]

In previous work we have introduced the selective iodination of the aluminum(III) corrole (**1-Al**), where substitution took place on only one pole of the molecule.[3c] The 2,3,17,18-tetraiodinated complex (**4-Al**) displayed both short-lived (ns) and long-lived (*μ*s) excited states at room temperature, an intriguing feature that could be useful for particular applications. While the photophysical properties of some corroles have been reported,[3,12,20−22] the corresponding research on metallocorroles is still incomplete, and there is no fundamental knowledge about the effect of selective halogenation on these properties. In order to reconcile this gap, we decided to synthesize a series of partially iodinated metallocorroles that differ in the identity of the chelated metal and to elucidate the factors that affect the photophysical properties.

RESULTS AND DISCUSSION

Synthesis. Treatment of Ga(tpfc) (**1-Ga**) with *N*-iodosuccinimide (NIS) for 1 h at room temperature in

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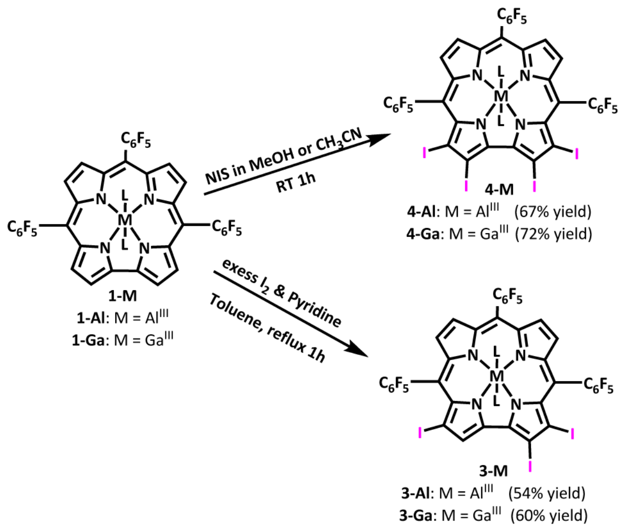
methanol yielded the 2,3,17,18-tetraiodinated derivative (**4-Ga**), in analogy to what has been reported for **1-Al** (Scheme 1).[3c] The characterization of the product was based on NMR, UV–vis, and high resolution mass spectroscopy. The ^{1}H NMR spectrum of **4-Ga** displays only two *β*-pyrrole C–H doublets (2H each) with a relatively large *J* coupling constant (4.6 Hz),[23c] which indicates that the substitution proceeded only on the directly connected pyrrole subunits. This phenomenon is consistent with the known reactivity of 5,10,15-trispentafluorophenylcorrole (tpfc) complexes.[23] The ^{19}F NMR spectrum (Figure 1) also clearly shows that the C_{2v} symmetry is preserved in the transformation of **1-Ga** to **4-Ga**.

Scheme 1. Selective Iodination of the Metallocorroles 1-Al and 1-Ga (L = Pyridine)



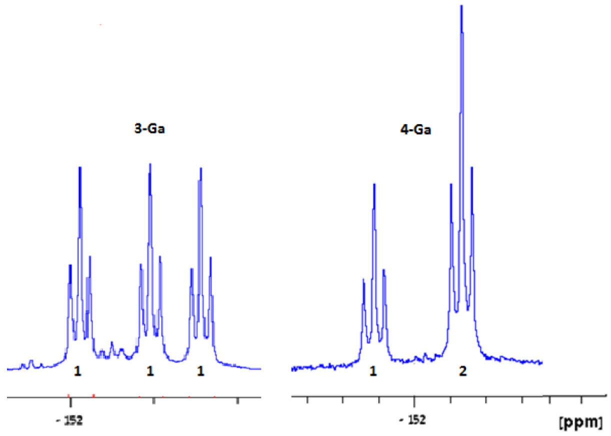


Figure 1. ^{19}F NMR spectra of the *para*-F region reflecting three different C_6F_5 groups in **3-Ga** (left) and the 2:1 ratio of two kinds of C_6F_5 groups in **4-Ga** (right).

After the successful utilization of NIS, iodination by molecular iodine was re-examined. Previously reported attempts on **1-Al** disclosed a very slow reaction that yielded a mixture of products.[3c] Much better results were obtained now by using the combination of iodine and pyridine (both in excess), which may be considered a milder iodination system.[24] A 1 h period of reflux in toluene provided only one main product for both **1-Al** and **1-Ga** (Scheme 1), and they were not the tetraiodinated derivatives **4-Al** and **4-Ga**. The initial identification of the new compounds as tris-iodinated Ga (**3-Ga**) and Al (**3-Al**) corroles was based on high resolution mass spectroscopy. They were further characterized by the lack of any symmetry axis, which is reflected by three *para*-F resonances (1F for each C_6F_5 moiety) rather than the 1:2 ratio in the tetraiodinated complexes where two of the C_6F_5 groups are magnetically equivalent (Figure 1). The ^{1}H NMR spectra disclosed one singlet (9.90 and 10.02 ppm for **3-Al** and **3-Ga**, respectively), supportive of bis-iodination of one pyrrole moiety and monoiodination of another one. These conclusions, a well as the positioning of all iodine atoms on the directly connected pyrrole rings, were confirmed for **3-Ga** by X-ray crystallography.

X-ray Crystallography. The crystallographic determination of **3-Ga** confirmed both the MS-based tris-iodo substitution and the NMR-based positioning of the iodine atoms on the corrole skeleton. Two of the I atoms are bound to the C3 and C18 *β*-pyrroles of the macrocycle, while the third iodine is disordered with regard to the occupation of the symmetry-equivalent C2 and C19 positions. The two molecules that compose the asymmetric unit of the crystal structure are characterized by somewhat different partitioning of this third iodine between the two equivalent sites. A ball-and-stick representation of the asymmetric unit of the structure is shown in Figure 2. It consists of two molecules of the planar 6-coordinate Ga-corrole moiety with two pyridyl rings as axial ligands. The two molecules form a supramolecular dimer through interactions between the iodine substituents of one moiety and the *π*-cloud of the pyridyl axial ligand of the neighboring species. These interactions affect a slight bending of the axial pyridyls (from a strict perpendicular orientation with respect to the Ga-corrole macrocycle) of one molecule toward the I-sites of the adjacent species (Figure 2). The electronic effects associated with the presence of the I-substituents and their apparent involvement in the halogen-*π* interactions affect the coordination geometry around the Ga-ions. The electron-withdrawing nature of the iodo substituents on one side of the corrole ring is manifested by a significant difference in the observed Ga–N(pyrrole) bond lengths. They are within the 1.948–1.953 Å range for the I-substituted pyrroles, as opposed to the 1.913–1.937 Å range for the nonsubstituted pyrrole rings in the second half of the corrole (Table 1). In addition, some reduction in the electron density of those pyridyl ligands (one axial ligand in each of the two corroles) that interact with the proxime I-sites (with an electron

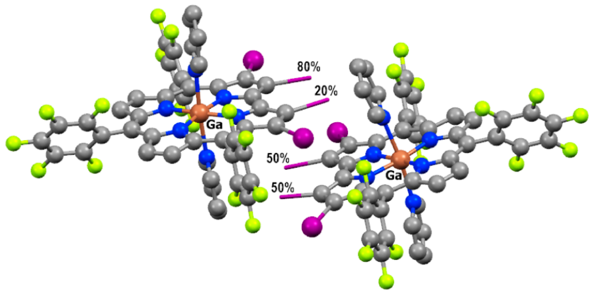


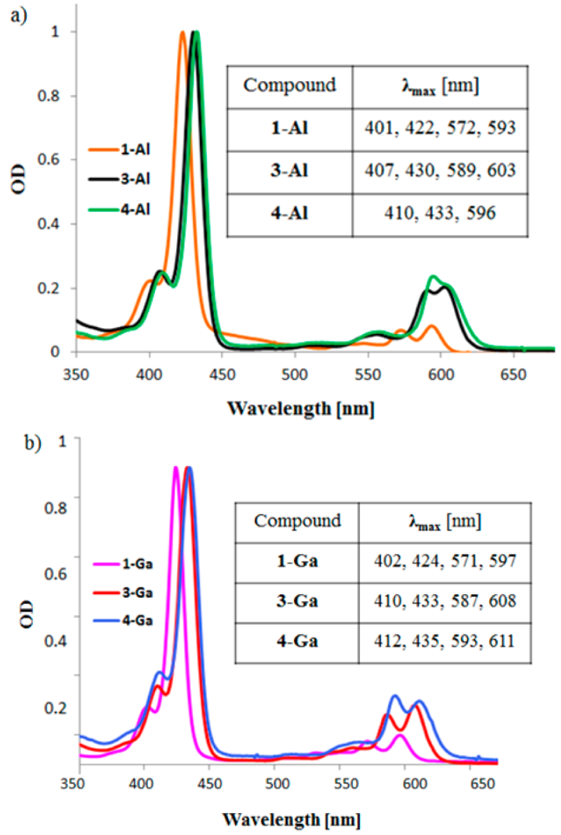
Figure 2. Content of the asymmetric unit in the crystal structure of the **3-Ga** complex (two molecules). The iodine substituents with full occupancy are denoted by violet spheres, those with partial occupancy by capped sticks. The molecular pair exhibits I···*π* interactions.

Table 1. Selected Crystallographic Data for 3-Ga

bond	length range (Å)
M−N pyridine	2.208(5)−2.292(6)
M−N unsubstituted pyrrole	1.913(6)−1.937(6)
M−N substituted pyrrole	1.948(6)−1.953(6)

deficient π-hole at their cap) results in marked elongation of the respective Ga−N(pyridyl) bond lengths: 2.256 and 2.292 Å in contrast with 2.209 and 2.230 Å for the other pyridyl ligands away from the halogen-bonded sites.

Photophysical Characterization. All examined corroles exhibit typical near-UV (Soret) and far-visible (Q) absorption bands, whose λ_{max} values are tabulated in the inset of Figure 3.



Compound	λ_{max} [nm]
1-Al	401, 422, 572, 593
3-Al	407, 430, 589, 603
4-Al	410, 433, 596

Compound	λ_{max} [nm]
1-Ga	402, 424, 571, 597
3-Ga	410, 433, 587, 608
4-Ga	412, 435, 593, 611

Figure 3. Normalized (for the strongest absorption band) UV−vis spectra (in toluene) of the (a) aluminum and (b) gallium complexes and a table with all relevant absorption data.

Addition of electron-withdrawing groups on the macrocycle periphery is expected to induce red shifts,[3c,17,18] which is the case indeed. The iodinated aluminum and gallium corroles display 8−13 nm shifted Soret and 15−24 nm shifted Q-bands relative to **1-Al** and **1-Ga**, i.e., about 3−5 nm for each iodine (Figure 3). This is less than the 4.5−7 nm red shifts reported for the only di-iodinated porphyrin.[25]

Iodination may safely be predicted to have a large influence on the excited states characteristic of corroles, due to the heavy atom effect. Shi et al. have indeed shown that even addition of only one iodine atom to one remote aryl ring of triarylcorroles already induces a 4-fold decrease in fluorescence quantum yield and a 60-fold increase in intersystem crossing rate constant.[21a] The effect of multiple iodination, and directly on the corrole skeleton, is much larger. The RT emission spectra of the β-pyrrole-iodinated derivatives display two components, derived from the radiative decays of both short- and long-lived excited states. The 620−660 nm emission is clearly due to fluorescence as may be appreciated by its insensitivity to air, as well as from its absence when emission is recorded 100 μs after excitation. The lifetimes of the short-lived emission were addressed by time-correlated single photon counting (TCSPC). All iodinated derivatives displayed very fast kinetics, beyond the resolution of the applied instrument that is limited to 50 ps. Only a lower limit could hence be assigned: <80 ps. Fluorescence emission maxima are red-shifted relative to the noniodinated complexes: 11−13 nm for the tris-iodo and even more, 17−24 nm, for the tetra-iodo derivatives. The fluorescence quantum yields were measured in toluene using tetraphenylporphyrin (H_2TPP) as a reference (Φ_f = 0.13),[26] revealing that those of the iodinated corroles are almost 2 orders of magnitude lower than of the noniodinated derivatives (Table 2). Nevertheless, they are still quite respectable, as may be appreciated by comparison with the commonly used fluorophore ZnTPP. The large decrease in the quantum yields can be rationalized by the heavy atom effect, which in this series of compounds could be evaluated for two different elements, gallium and iodine. The **3-Al** versus **3-Ga** and **4-Al** versus **4-Ga** comparisons disclose 13−29% lower quantum yields of Ga versus Al complexes. The **3-Al** versus **4-Al** and **3-Ga** versus **4-Ga** comparisons reveal that the fourth iodine contributes an additional 34−46% decrease in quantum yields. The latter effect is demonstrated in Figure 4, wherein the 1.5−2-fold decrease in emission intensity may be easily appreciated.

Table 2. Short- and Long-Lived Emission Maxima and the Fluorescence Quantum Yields (Φ_f) of Iodinated Corroles[a]

compd	short-lived emission[b] λ_{max}/nm	Φ_f (presented in percentages)	long-lived emission[c] λ_{max}/nm
H_2TPP	654, 720	13[d]	n.r.[e]
ZnTPP	600, 648, 715	3.3[d]	n.r.[e]
1-Al[f]	627, 689	76	n.r.[e]
1-Ga	602, 657	28	n.r.[e]
3-Al	610, 667	0.51	814 (604)[g]
3-Ga	614, 671	0.44	818 (608)[g]
4-Al	616, 672	0.34	824 (614)[g]
4-Ga	624, 682	0.24	830 (636)[g]

[a]Toluene, under Ar, with Φ_f = 0.13 for H_2TPP as reference, at RT. [b]Lifetimes are <80 ps. [c]Lifetimes are ≥192 μs. [d]Ref 26. [e]n.r. = not reported. [f]Data from ref 31a, in 5% pyridine/toluene. [g]Minor maximum.

Examination of the emission spectra of the iodinated derivatives 100 μs after excitation revealed two widely (≥194 nm) separated features, both of which are quenched by oxygen (Figure 5). The more intense bands displayed maxima of about 820 nm, corresponding to regular phosphorescence, while the lower-intensity bands maximized at the same wavelength as the earlier discussed main fluorescence peak (about 620 nm).

The phosphorescence maxima displayed red shifts of 10−12 nm upon addition of the fourth iodine atom, comparing the tris- and the tetra-iodo derivatives, with lifetimes of 192−373 μs. Additional attention was devoted to the smaller bands that appear in the spectra of all iodinated corroles, for the following reason. While intersystem crossing (ISC) most frequently occurs from the lowest excited singlet state (S_1) of a molecule to an even lower-lying triplet state (T_1), the reverse process

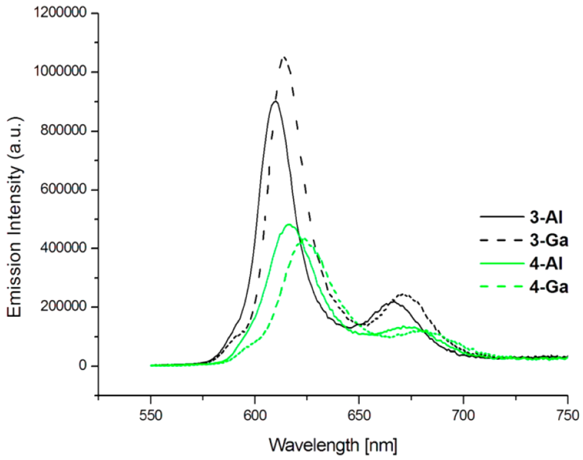


Figure 4. Emission from the short-lived excited states of the iodinated corrole derivatives, recorded with identical optical densities at the λ_{exc} wavelengths.

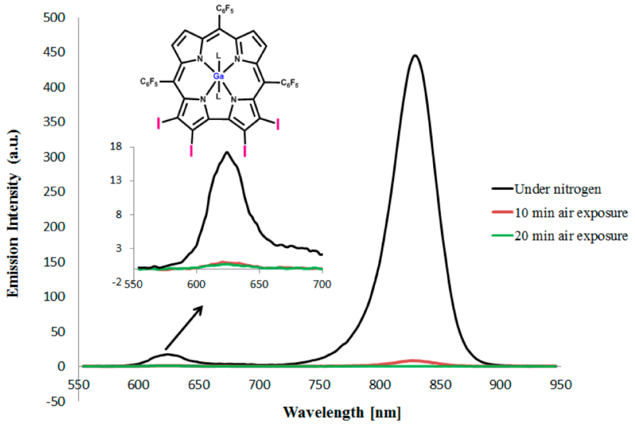


Figure 5. Long-lived emission spectra of **4-Ga** in toluene, under N_2 and under air exposure.

also may occur.[27a] This phenomenon is known as delayed fluorescence, and includes E- and P-type delayed fluorescence and recombination fluorescence.[27b] A relatively small energy gap between the S_1 and the T_1 states is one main condition for E-type delayed fluorescence, also known as delayed thermal fluorescence (DTF). In such a case, thermal activation induces population transfer from T_1 back to the more energetic S_1.[27c] The outcome is a fluorescence-characteristic emission wavelength, but with a lifetime that is only slightly shorter than phosphorescence, and temperature dependent intensity. In the current case, the wavelength of DTF was practically identical to that of the prompt fluorescence, but with >100 μs rather than sub-nanosecond lifetimes.

The energetic difference (ΔG) between the singlet and triplet excited states may easily be calculated from the difference in the emission maxima of the DTF and the phosphorescence, as 50 kJ/mol. To check if the shorter wavelength emission is due to DTF indeed, its T-dependent intensity was examined. The data from the spectra shown in Figure 6 for **3-Al** were analyzed in terms of the equilibrium constant at the edge temperatures via $K = \exp(-\Delta G/RT)$. Using $\Delta G = 50$ kJ/mol, a 7.5−10.5% increase in the intensities of the DTF at the applied temperature range is predicted, which corresponds perfectly with what has been obtained. We may hence conclude that the iodinated corrole complexes display three kinds of emission: (a) prompt fluorescence, (b) delayed thermal fluorescence, and (c) phosphorescence.

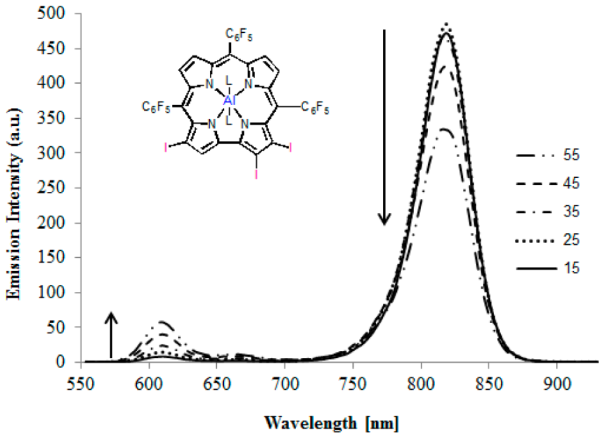
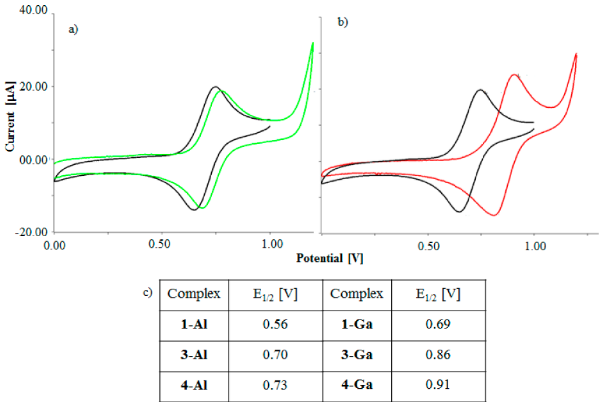


Figure 6. Temperature dependent intensity changes of the long-lived emissions for **3-Al**.

Effect of Iodination on Redox Potentials. Cyclic voltammetry (CV) was used for estimating if and how iodination affects the redox potential of the corroles. Scans at negative potentials revealed only irreversible processes, which prevented the determination of the electrochemical HOMO−LUMO gap.[17i,28] Nevertheless, the effect of iodination on oxidation potentials could be examined since the positive potentials scans were reversible. Representative CV scans and all half-wave potentials ($E_{1/2}$) are shown in Figure 7. The data reveals a 140−150 mV more positive redox potentials for the tris- vs noniodinated corroles, as well as a further 30−50 mV increase for the tetraiodinated derivatives. One conclusion from these studies is that each iodine atom shifts the redox potential by about 56 mV. The gallium corroles are harder to oxidize by about 150 mV than the aluminum analogues, consistent with the electronegativity of the chelated metal ions.[29]



Complex	$E_{1/2}$ [V]	Complex	$E_{1/2}$ [V]
1-Al	0.56	**1-Ga**	0.69
3-Al	0.70	**3-Ga**	0.86
4-Al	0.73	**4-Ga**	0.91

Figure 7. (a) CV traces of **3-Al** (black) and **4-Al** (green). (b) CV traces of **3-Al** (black) and **3-Ga** (red). (c) Table of halfwave potentials for the first oxidation of corroles. Spectra and data are in V vs Ag/AgCl, in CH_3CN with TBAP as supporting electrode.

To put these findings into perspective, it is interesting to compare the effect of I versus Br versus Cl versus F. The data compiled in Table 3, based on the findings for the halogenated Ga corroles, reveals that the average positive shift of oxidation potentials is about 55 mV/halogen substituent for all four halides. The naively expected trend of a positive shift of redox

Table 3. First Oxidation Potentials (V vs Ag/AgCl) of *β*-Halogeno-Substituted Gallium(III) Corroles[a]

Ga complex	1st oxidation	Δ/nX^c
Ga(tpfc)(py)	0.7[b]	
Ga(F_8-tpfc)(py)	1.13[b]	0.054
Ga(Cl_8-tpfc)(py)	1.16[b]	0.058
Ga(Br_8-tpfc)(py)	1.11[b]	0.051
Ga(I_4-tpfc)(py)	0.91	0.053
Ga(I_3-tpfc)(py)	0.86	0.053

[a] CH_3CN, TBAP. [b] Ref 30. [c] X = F, Cl, Br, or I, and *n* = number of halide substituents.

potentials with an increase in the electronegativity of the halides is clearly not fulfilled. Apparently, the *σ*-electron-withdrawing effect is almost perfectly canceled by *π*-donation ability, as both are in the order F > Cl > Br > I. This comprehension has recently been demonstrated to be of prime importance for the electrocatalytic hydrogen evolution reaction by fluorinated cobalt corrole.[30]

■ CONCLUSIONS

We have demonstrated facile and selective iodination of aluminum and gallium corroles and shown that it induces significant changes onto the photophysical properties. The absorption and emission spectra are shifted to the red, but less than for porphyrins, because the macrocycle remains planar. Comparison between the tris- and the tetra-derivatives revealed that while the effect of an additional iodine atom on absorption spectra is small, the emission properties are much more sensitive. The iodinated corroles display prompt fluorescence, phosphorescence, and delayed thermal fluorescence, all at room temperature. Electrochemical investigations suggest that the effect on redox potentials is additive for each additional halogen and that halogenation of the *β*-pyrrole periphery shifts the oxidation potential by practically the same amount for the four halides. The conclusions of this work are of large importance for the design of metallocorroles that are best suited for the various applications[6,8,9] where they play a major role, such as catalysts for energy- and medicine-relevant small molecules (proton, oxygen, water, and reactive oxygen/nitrogen species),[10,12,13] photodynamic processes,[11] and dye sensitized solar cells.[7]

■ EXPERIMENTAL SECTION

Materials. Reagents (Aldrich) and solvents were used without further purification. Silica gel 60 (230−400 mesh) was used for column chromatography. **1-Al**, **1-Ga**, and **4-Al** were synthesized as previously reported.[31,3c]

Synthetic Methods. *Synthesis of 3-Al.* **1-Al** (30 mg, 30 *μ*mol) and I_2 (780 mg, 3 mmol) were dissolved in toluene (7 mL), pyridine (600 *μ*L, 7.6 mmol) was added, and the solution was stirred for 1 h under reflux. This was followed by washing with a 10% $Na_2S_2O_3$ solution, drying over Na_2SO_4, and evaporating solvent. The green-purple solid material was purified by chromatography (hexanes/DCM/EtOAc = 5:5:1 with a few drops of pyridine). Crystallization of the product from DCM/hexanes and a drop of pyridine afforded pure **3-Al** (19 mg, 54% yield). ^{1}H NMR (400 MHz, C_6D_6): *δ* 9.9 (s, 1H), 8.8 (overlapping doublets, 2H), 8.5 (overlapping doublets, 2H), 5.7 (broad t, 2H), 5.3 (broad, 4H), 4.5 (broad, 4H). ^{19}F NMR (376 MHz, C_6D_6): *δ* −138.51 (unresolved m, 6F, *ortho*-F), −152.59 (t, 1F, *para*-F), −152.93 (t, 1F, *para*-F), −153.23 (t, 1F, *para*-F), −162.32 (dt, 2F, 10-*meta*-F), −163.27 (unresolved, 4F, 5,15-*meta*-F). HRMS (TOF, ES^-): [M − OH^-] = $C_{37}H_5N_4OF_{15}AlI_3$, calculated for *m*/*z* = 1213.7155, observed =1213.7142. UV−vis (toluene) λ_{max} [*ε* (M^{-1} cm^{-1})]: 407 [43 182], 430 [170 654], 589 [30 393], 603 [35 280].

Synthesis of 3-Ga. The above procedure was used, but starting with **1-Ga** (20 mg, 21 *μ*mol). The green-purple product was purified by chromatography (hexanes/DCM = 3:1 with few drops of pyridine), which afforded pure **3-Ga** (15 mg, 60% yield). ^{1}H NMR (400 MHz, C_6D_6): *δ* 10.0 (s, 1H), 8.8 (overlapping doublets, 2H), 8.5 (unresolved, 2H), 5.0 (unresolved t, 1H), 4.4 (broad, 2H), 3.0 (broad, 2H). ^{19}F NMR (376 MHz, C_6D_6): *δ* −138.38 (unresolved t, 4F, 5,15-*ortho*-F), −138.68 (d, 2F, 10-*ortho*-F), −152.05 (t, 1F, *para*-F), −152.48 (t, 1F, *para*-F), −152.78 (t, 1F, *para*-F), −161.97 (dt, 2F, 10-*meta*-F), −163.00 (unresolved t, 4F, 5,15-*meta*-F). HRMS (TOF, ES^-): [M − OH^-] = $C_{37}H_5N_4OF_{15}GaI_3$, calculated for *m*/*z* = 1255.6614, observed =1255.6621. UV−vis (toluene) λ_{max} [*ε* (M^{-1} cm^{-1})]: 410 [36 633], 433 [147 267], 587 [23 651], 608 [27 879].

Crystal Data. $C_{47}H_{18}F_{15}GaI_3N_6$, *M* = 1398.06, orthorhombic, space group $P2_12_12_1$, *a* = 16.7265(8) Å, *b* = 22.7706(11) Å, *c* = 26.4205(14) Å, *V* = 10 062.8(9) $Å^3$, *Z* = 8, *T* = 110(2) K, D_c = 1.846 Mg/m^3, *μ* = 2.48 mm^{-1} (excluding the crystallization solvent). There were 50 508 reflections measured, of which 23 582 were unique (R_{int} = 0.056) and 19 345 with $I > 2\sigma(I)$ to $2\theta_{max}$ = 56.6°. Final R1 = 0.052 and wR2 = 0.123 for the 19 345 data above the intensity threshold, and R1 = 0.065 and wR2 = 0.128 for all data. CCDC 988072.

Synthesis of 4-Ga. A sample of **1-Ga** (50 mg, 53 *μ*mol) and 10 equiv of crystallized (acetone/hexane) NIS were dissolved in MeOH (5 mL) and stirred for 1 h at room temperature in the dark. The reaction mixture solution was washed with water, dried over Na_2SO_4, and evaporated. The green-purple solid material was purified by chromatography (hexanes/DCM = 3:1 with few drops of pyridine), which afforded pure **4-Ga** (52 mg, 72% yield). ^{1}H NMR (400 MHz, C_6D_6): *δ* 8.7 (d, *J* = 4.6 Hz, 2H), 8.4 (d, *J* = 4.6 Hz, 2H), 5.9 (unresolved t, 1H), 5.6 (broad, 2H), 5.4 (broad, 2H). ^{19}F NMR (376 MHz, C_6D_6): *δ* −138.37 (dd, 4F, 5,15-*ortho*), −138.67 (dd, 2F, 10-*ortho*), −151.78 (t, 1F, 10-*para*), −152.27 (t, 2F, 5,15-*para*), −161.82 (dt, 2F, 10-*meta*), −162.93 (dt, 4F, 5,15-*meta*). HRMS (TOF, ES^-): [M − OH^-] = $C_{37}H_4N_4OF_{15}GaI_4$, calculated for *m*/*z* = 1381.5580, observed =1381.5592. UV−vis (toluene) λ_{max} [*ε* (M^{-1} cm^{-1})]: 412 [45 958], 435 [148 410], 593 [34 721], 611 [31 847].

Physical Methods. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a 5 mm, automated tuning and matching broad band probe (BBFO) with *z*-gradients, operating at 400.4 MHz for ^{1}H and 376.7 MHz for ^{19}F, respectively. Chemical shifts are reported in ppm relative to the residual hydrogen atoms in the deuterated solvent benzene-d_6 (*δ* = 7.15). Absorption spectra of the samples were measured on an HP 8453 diode array spectrophotometer. High-resolution mass spectra were performed on a Waters LCT Premier mass spectrometer, using TOF electron spray negative mode in CH_3CN/water 70:30, flow 0.25.

Spectroscopy. Steady-state short-lived emission spectra were recorded on a Fluorolog-3 spectrofluorometer (model FL3−11; HORIBA JobinYvon Inc., Edison, NJ) equipped with a Xenon-arc lamp. The data were recorded at room temperature, under nitrogen. Steady-state long-lived emission spectra were recorded on a Cary Eclipse fluorimeter, at room temperature, under nitrogen. The short-lived emission lifetimes were determined by a IBH 5000 U SPC instrument (HORIBA JobinYvon Inc.) with a picosecond diode laser (PicoQuant LDH-P-C, 405 nm peak wavelength, 0.1 ns pulse width, 2.5 MHz repetition rate) and a cooled Hamamatsu R3809U-50 microchannel plate photomultiplier (Hamamatsu) with 7 ps time-resolution. In order to eliminate scattered light, a 380 nm cut-on filter was used behind the excitation monochromator, and a 550 nm cutoff filter was used in front of the emission monochromator. The signal was kept below 2% of the light source repetition rate. The data were recorded at room temperature, under nitrogen. The long-lived emission lifetimes were recorded by a Cary Eclipse fluorimeter, at room temperature, under nitrogen.

Electrochemistry. The cyclic voltamograms were obtained utilizing a WaveNow USB potentiostat galvanostat (Pine Research Instrumentation), using Pine AfterMath Data Organizer software. A three electrode system was used, consisting of a mini glassy carbon electrode (diameter of the active zone: 2.8 mm; Metrohm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The CV measurements were performed in acetonitrile solutions (HPLC grade), 0.1 M in tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized twice from methanol), and 1 mM substrate at ambient temperature. Scan rates of 100 mV/s were applied. The $E_{1/2}$ value for the ferrocene/ferrocenium couple under these conditions was 0.42 V.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Overlaid full and partial ^{19}F NMR spectra of **3-Ga** and **4-Ga**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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