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"Hetero multifunctionalization" in Gallium Corroles: Facile Synthesis, Phosphorescence, Redox Tuning, and Photooxidative Catalytic Improvement

Xuan Zhan^[a], Yael Zini^[a], Natalia Fridman^[a], Qiu–Cheng Chen^[a], David G. Churchill^{[a],[b],[c],[d]*}, Zeev Gross^{[a],*}

Abstract: Bromination of tris- and tetrakis-trifluoromethylated gallium corroles (3CF₃-Ga and 4CF₃-Ga) afforded tetra-brominated species 3CF₃-4Br-Ga and 4CF₃-4Br-Ga (Yields: 20% and 25%) characterized by NMR, UV-vis spectroscopy, and MS. Red shifted abs and emission bands were found; 3CF₃-4Br-Ga and 4CF₃-4Br-Ga displayed 5-12 nm shifts in their Soret bands and 8-17 nm shifts for their Q bands, compared to the respective non-Br species (3CF₃-**Ga** and **4CF₃–Ga**). Respective Φ_F values were found to be 0.013 and 0.016; phosphorescence (lifetime = 0.23 μ s) was observed for 3CF₃-4Br-Ga (anaerobic, RT). The tetra-Br effect on redox potentials (0.89 and 0.99 V), gave a 85 mV per Br shift in the reduction potential. 4CF₃-4Br-Ga allows for efficient catalytic photooxidative Br to Br₂ conversion compared to the β-octa-Br system (Br₈-Ga) structurally characterized here. "Hetero multifunctionalization" is substitution with different sets of β-substituents to help optimize porphyrinoid properties.

Introduction

Robust research on corroles, well-known contracted and aromatic tetrapyrrole–based macrocycles, continues to be produced and is considered in many technological applications. Facile and efficient synthetic methods to help obtain these systems cleanly and in good yields have been discovered, developed and optimized starting from about 1999.^[1] In recent years, researchers have aimed at new ways of tuning chemical and photophysical properties to help achieve desired molecular properties for particular applications. Such accomplishments are on the verge of strongly impacting energy–related fields such as photo–sensitizers, dye–sensitized solar cells, photocatalysis in driving photo–synthesis of small organic molecules and medicinal applications like photo–sensitizers in photodynamic therapy (PDT) due to ROS (reactive oxygen species) generation under irradiation with specific frequencies of incident light. ^[2]

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When investigating the properties of porphyrinoids, it has been found that corrole synthesis, for example, has been slow regarding rational substituent placement/incorporation because as stepwise formal substitution is imparted, the breakdown in molecular symmetry affords *eight* different β positions. The systems can also be difficult to access or predict if substitution proceeds by a radical mechanism. In comparing the effects imposed by different substituents, there is often a tendency to compare between separate corrole systems that have different central atoms but that bear the same β substituents, or a system possessing the same central metal, and with a different number of the same β-substituent or those with different attachments of the same substituent. Therefore, while these analogues, or constitutional isomers, help us establish important groundwork principles, it is also important to seek more complexity regarding β-position substitution. A particular challenge would be to have different non-H substituents present around the macrocyclic ring. Herein, we describe the results of studies aimed at generating closely related compounds containing different non-H sets of substituents at the β positions. Therefore, they can be both exhaustively compared with each other, and also compared back to the reference molecules that contain only one type of substituent. The differences in spectroscopic signals and electrochemical properties, for example, will help gauge what is possible when the system becomes saturated with different sets of non-H substituents at the β positions.

The structure–function relationship in corrole complexes has been increasingly studied in recent years; one important approach for corrole functionalization is the different ways substitution of β –protons of corroles have been made possible. By replacing β –protons with certain groups such as halogens^[3] and trifluoromethyl groups^[4], these substituent effects are at the "core" of physical organic investigations and *interrogations* of porphyrinoids. Therefore, while the bromine group is often considered to be a precursor to easily allow further substitution through, e.g., cross coupling, there is a need to synthetically access systems that are especially closely related but that have differences through the presence of two different sets of β substituents.

Consequently, our work herein relates to a concept we will term as porphyrinoid "hetero multi–functionalization" (substitution with *different* functional groups involving *multiple* groups of each type). The incorporation of these sets of substituents may be made possible through treating a precursor involving one set with a second substituent that will be able to occupy remaining C–H positions through facile processes which (*i*) do not synthetically disrupt the first substituent set, and (*ii*) also which, when compared to H- substitution, help macrocycles/porphyrinoids access important physical or chemical properties. In this study,

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to lay a foundation for "hetero multi-functionalization," we used gallium corroles. Therefore, the combination of the two sets (two groups, Scheme 1) (or more than two sets) will further help shape the evaluation of novel and more sophisticated porphyrinoid designs in the future.

Results and Discussion

In order to prepare gallium corroles that contain two sets of substituents, in which both sets bear multiple substituents, we considered bromination of a well defined multi-substituted trifluoromethylated corrole system. In this study, we initiated our work from the β -unsubstituted *tpfc* gallium framework and then substituted the $-CF_3$ groups onto β positions and isolated these species.^{4c} Then, we were able to impart bromination using Br₂ without interfering with the already-attached -CF₃ groups. Specifically, we advanced our study with the gallium complexes tris-/tetra-trifluoromethylated tpfc (5, 10, 15 of tris(pentafluorophenyl) corrole) gallium corrole complexes: 3CF₃-Ga and 4CF₃-Ga (Scheme 1). Treating these corroles with excess bromine in methanol at room temperature allowed for the production of species in which the β C–H rich region (at the 7,8,12, and 13 β positions) was exhaustively converted to C-Br groups; this resulted in the formation of our target compounds bearing proximal tetra-bromine substitution, namely gallium (III) 5,10,15tris(pentafluorophenyl)-2,3,17-tris-trifluoromethyl-7,8,12,13tetrabromocorrolate (3CF₃-4Br-Ga) and gallium (III) 5,10,15tris(pentafluorophenyl)-2,3,17,18-tetra-trifluoromethyl-

7,8,12,13-tetrabromocorrolate (4CF₃-4Br-Ga). The reason we choose bromine rather than other bromination reagents such as NBS (*N*-bromosuccinimide) for this reaction is that relative higher selectivity could be obtained for the β -bromination of corrole when Br₂ was used based on previous reports.^[5]Purification was conducted via silica gel column chromatography using a 5:1 (volume ratio) mixture of n-hexane:ethyl acetate; several drops of pyridine were also added to the reaction mixture. The first eluents for both reactions were confirmed by multinuclear NMR spectroscopic and mass spectrometric characterization techniques. The respective isolated yields were found to be 20 % and 25 %. Bromination at the available 18 position in 3CF₃-4Br-Ga to give 3CF₃-5Br-Ga was not observed, as predicted due to steric and electronic considerations. The tetra-brominated species were the only dominant products after silica gel chromatography purification; no tribrominated corroles were detected.

It was important to interrogate the signals in the ¹H and ¹⁹F NMR spectra to confirm both the molecular symmetry and level of substitution/saturation of the products (Figure 1). The support for the occupation of the 7,8,12,13 positions was made possible by the observation of the diminution/absence of the signals assigned to the β -pyrrole protons resulting from addition of bromine atoms (via electrophilic substitution). Namely, only one signal was exhibited for **3CF₃-4Br-Ga**, whereas no β -pyrrole CH group signal appeared in the spectrum as acquired for compound **4CF₃-4Br-Ga**. In Figure 1, these spectra are overlayed to allow for a convenient and clear comparision; the chemical shift of C18–H

experiences a respective downfield shift (from 9.43 to 9.74 ppm) when going formally from species 3CF₃-Ga to 3CF₃-4Br-Ga; a small downfield shift was also observed in the signals appearing in the ¹⁹F–NMR spectrum once bromination was achieved. This is exemplified by the fluorine chemical shift in the -CF₃ signal region: the three -CF₃ peaks moved from -48.9 ppm, -50.5 ppm and -53.3 ppm; to -48.3 ppm, -50.1 ppm and -53.0 ppm. The downfield shifts observed in the ¹⁹F NMR spectrum are rationalized by the electron withdrawing effect imparted by multibromination. The $C_{2\nu}$ molecular symmetry was found to remain after bromination transformed 4CF₃-Ga to 4CF₃-4Br-Ga. One effective piece of evidence is to track the collection of the three -C₆F₅ group para-F resonances present in the ¹⁹F-NMR spectrum; when inspecting for these three nuclei, the three para-F resonance signals are grouped cleanly in a pattern with an integration ratio of 1:2 (Figure S2). The HR-MS spectra also supports our expected structures for compounds 3CF₃-4Br-Ga and 4CF₃-4Br-Ga.



Scheme 1. Synthesis of tetra–brominated tris–/tetra–CF₃–substituted species: $3CF_3-4Br-Ga$ and $4CF_3-4Br-Ga$.



Figure 1. Comparisons of the pertinent regime in the ¹H (400 MHz) and ¹⁹F (377 MHz) NMR spectra (CDCl₃) of **3CF₃-Ga**, **3CF₃-4Br-Ga**, **4CF₃-Ga** and **4CF₃-4Br-Ga**, with a focus on the β -pyrrole CH's and the CF₃ groups.

Another important characterization method for corrole complexes is UV–vis spectroscopy. As shown in Figure 2, a typical Soret band is around 430 nm and several Q bands were observed; all data are provided in Table 1. Our previous work ^[4c] showed that β -trifluoromethylation induced red shifts in terms of absorption and emission spectra. Compared to the non-substituted complex

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(tpfc)Ga, the tris/tetra-CF3 substituted complex 3CF3-Ga and 4CF₃-Ga exhibited small red shifts of 3 and 6 nm in the Soret band and more evident red shifts of 18 and 30 nm in the Q bands. Red shifts of 20 and 32 nm were also observed for complexes 3CF₃-Ga and 4CF₃-Ga, relative to (tpfc)Ga, in terms of the emission peaks (Table 1). Further bromination produced more red shifts in terms of UV and emission spectra; the different tetrabrominated gallium corrole species 3CF3-4Br-Ga and 4CF3-4Br-Ga display a small 5-12 nm shift in the Soret band and larger shifts of 8-17 nm for the Q bands in these species, compared to the respective non-brominated species 3CF₃-Ga and 4CF₃-Ga. The fluorescent properties of the two new brominated compounds were also probed; a miniscule amount of fluorescence was observed as expected, for these two heavily brominated gallium corroles (Figure 2b); the fluorescence quantum yields (Φ_F) decreased from 0.57 and 0.55 for the non-brominated species 3CF₃-Ga and 4CF₃-Ga to 0.013 and 0.016 for 3CF₃-4Br-Ga and 4CF₃-4Br-Ga. respectively. Tetra-bromination also induced a red shift of 20–35 nm for the emission peak ($\lambda_{em.max}$) when going from the 3/4 CF₃-Ga to the 3/4 CF₃-4Br-Ga species (Table 1). Shortened fluorescence lifetimes were observed (Table 1) compared to the non-brominated species. One important and interesting finding was the discovery and quantification of room temperature phosphorescence ($\lambda_{max} = 900 \text{ nm}$) (Figure 2c) for compound 3CF₃-4Br-Ga, under N₂. The phosphorescence lifetime was determined to be 0.23 µs (Figure 2d); corrole complexes which were reported to emit room temperature phosphorescence in anaerobic toluene above 800 nm were confined to several cases; [4a],[6] for example, the iridium coordinated species (tpfc)Ir with two pyridine as the axial ligands exhibited room temperature phosphorescence with a wavelength at around 800 nm; the corresponding lifetime was 4.91 µs under argon atmosphere. Another tetra-β-trifluoromethylated gold (III) tpfc complex was reported to emit room temperature phosphorescence at a wavelength of 835 nm. This finding therefore enlightened us about how bromination in these systems imparts the heavy atom effects to help establish room temperature phosphorescence.





was recorded in toluene at room temperature and under aerobic conditions; the excitation wavelength was 420 nm. (c) The emission spectra comparison of compound **3CF₃-4Br-Ga** under aerobic and N₂ atmosphere in toluene was acquired at room temperature. (d) A time-resolved phosphorescence decay curve with χ^2 -fitting was recorded under N₂ atmosphere in toluene; the excitation wavelength was 643 nm and the emission wavelength was 900 nm when operating the decay assay.

Table 1. Comparison of photophysical properties of all							
investigated gallium corrole complexes (recorded at room							
temperature in toluene).							

Complex	Soret band (nm) (ε, ×10 ⁴)	Q–band (nm) (ε,×10 ⁴)	λ _{em} ª(nm)	$\Phi_{\text{F}}{}^{\text{b}}$	т(ns) ^с
tpfc-Ga	402, 424 (28.30)	571, 597 (2.40)	602, 657	0.28	2.61
3CF₃– Ga	405 (2.96), 427 (7.16)	590 (1.48), 615 (2.02)	623, 677	0.57	2.49
3CF₃– 4Br–Ga	413 (1.40), 437 (5.96)	598 (0.69), 626 (0.88)	643, 698	0.013	0.24
4CF₃– Ga	416 (4.67), 430 (6.36)	574 (1.56), 596 (2.03), 627 (3.39)	634, 689	0.55	4.54
4CF ₃ – 4Br–Ga	421 (4.42), 442 (6.10)	586 (1.36), 609 (1.69), 644 (2.42)	669	0.016	0.26

[a] λ_{em} represents the wavelength of the emission peak (λ_{ex} = 420 nm). [b] Calculated fluorescence quantum yields in aerated toluene with TPP (tetraphenylporphyrin) as a standard ($\Phi_{\rm F}$ = 0.11). [c] Experimental fluorescence lifetimes (prompt) measured in aerated toluene (λ_{ex} = 420 nm).

The observation of how bromination changes the photophysical properties encouraged us to seek quantitative data as acquired from electrochemistry. We found that certain substituents may exert a profound influence on the basic electronic redox potentials such as $-CF_3$ substitution in gallium corroles that was recently found to be dramatic; compared to non-substituted species **3CF_3-Ga** and **4CF_3-Ga** displayed positive shifts of 400 and 440 mV of the 1st oxidation potential, respectively (the 1st oxidation potential of 0.37 V for *(tpfc)Ga* was recorded).^[4c] It is of great interest to probe the effect from further bromination on redox properties; Herein, additional CV (cyclic voltammetry) experiments (Figure 3, Table 2) were conducted to help elucidate the electronic effects of tetra–

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bromination as well as assessing HOMO-LUMO energy levels. Large positive redox shifts were evident, observed after tetrabromination was achieved. Specifically, whereas the 1st oxidation potentials appeared at 0.77 and 0.83 V for non-brominated species 3CF₃-Ga and 4CF₃-Ga, these features formally moved significantly to 0.89 and 0.99 V for the tetra-brominated species 3CF₃-4Br-Ga and 4CF₃-4Br-Ga, affording respective positive shifts that break down to 30 and 40 mV per Br. These values are less than those previously reported: a positive oxidation shift of 51 mV from the effect of bromination.^[7] Surprisingly, more significant positive shifts were seen, compared to complexes 3CF₃-Ga and 4CF₃-Ga and 3CF₃-4Br-Ga and 4CF₃-4Br-Ga, which produced reduction shifts of 340 mV and 290 mV, once tetra-bromination was achieved. The much larger effect on reduction rather than oxidation (Table 2), a previously noted phenomenon,^[8] reduces the HOMO–LUMO energy gap from 2.03 V in 3CF₃-Ga to 1.77 V in 4CF₃-4Br-Ga.



Figure 3. CV traces of $3CF_3$ -Ga, $4CF_3$ -Ga, $3CF_3$ -4Br-Ga, $4CF_3$ -4Br-Ga. Glassy carbon working electrode, and an Ag/AgNO₃ ref. electrode. Solvent: CH₃CN with TBAP. Scan rate of 100 mV s⁻¹ were applied.

Table 2. Halfwave potentials for the first redox features of studied corroles. Glassy carbon working electrode, and an Ag/AgNO₃ ref. electrode were used. Solvent: CH₃CN with TBAP. Scan rate of 100 mV s⁻¹ was applied.



Studies of porphyrinoid systems have recently entailed (i) fuels research related to renewable energy sources, as well as (ii) molecular catalysis/photocatalysis; these various applications have been increasingly "hot" research topics in recent years with regard to corrole systems in particular. Besides catalytic water splitting reactions,^[9] the aerobic oxidation of bromide-to-bromine was also considered important in the design of H₂/Br₂ fuel cells.^[10] Compared to the previous reported fully β-brominated gallium tpfc corrole (8Br-Ga) which exhibited excellent photocatalytic performance in bromide to bromine conversion,^[11] the complex 4CF₃-4Br-Ga, owing to a more positive oxidation potential seemed to be more efficient in driving photooxidation reactions. While the 8Br-Ga compound has been reported before,[11] its Xray study is now included for the first time having been successfully obtained through this study (Figure 4). In the structure, the tetra N-pyrrolyl pocket containing the central metal reveals [Ga-N] bond lengths ranging from 1.920 to 1.956 Å; these are considered normal Ga-N bond-length values in comparison to previous reports.^{[4c],[12]} One pyridine was observed as the axial ligand coordinating to the Ga with Ga-N bond length of 2.033 Å, close to that observed in other gallum corrole complexes reported before.^{[4c],[12]} Unlike trifluoromethylation which most likely induces evident planar distortion as reported before by us,[4] the macrocyclic distortion based on measurements of dihedral angles suggested no evident planar distortion exists upon octabromination of the macrocycle. The hetero multifunctionalized corrole with bromines and substituted -CF₃ groups (4CF₃-4Br-Ga) may exhibit a relatively more distorted planarity compared to that found for the purely brominated species (8Br-Ga). Comparative photo-catalytic experiments using these two fully β-substituted complexes 8Br-Ga and 4CF₃-4Br-Ga were performed. Detailed experimental procedures are described; additional data is provided in the Supporting Information. Two types of photobromination reactions were attempted. The experimental approaches are as follows: (1) irradiation (LED, $\lambda_{max} = 450$ nm, power = 150 mW·cm⁻²) a Pyrex vial of 5 mL-acetonitrile reaction mixture charged with 0.10 M 47 % HBr (58 µL) and 25 µM catalyst; (2) the same as above, but with 0.10 M phenol (49 mg) presented in the reaction mixture. The simplified reaction schemes for these procedures are shown in Figure 5. The formed bromine in assay 1 was detected and quantified by UV-vis methods monitoring the absorbance of Br_3^- (λ_{max} = 269 nm, ϵ = 55000 L mol⁻¹ cm⁻¹, in acetonitrile). [4c] The photocatalytic results revealed compound 4CF₃-4Br-Ga possessed better catalytic efficiency (TOF = 980 h⁻¹) than complex 8Br-Ga (816 h⁻¹). The photo-bromination of phenol which produced ortho- and para- substituted phenol with a ratio of ca. 1:1, i.e., assay #2 was further checked to compare the photo-catalytic performance of these two gallium corrole complexes. Since the scope of this photo-catalytic reaction was limited in that it used only two catalysts, the reaction mechanism for giving a ratio of 1:1 is at present unclear which demands more research is required to make an understanding of the mechanistic process clear in these present cases.. Similarly, species 4CF₃-4Br-Ga possessed better catalytic efficiency with TOF determined at 384 h⁻¹ compared to that of 296 h⁻¹ for catalyst 8Br-Ga. The improved performance for species 4CF₃-4Br-Ga lies in one important factor, that this complex owns a larger 1st oxidation

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potential value: 0.99 V (4CF₃-4Br-Ga) > 0.75 V (8Br-Ga); this suggests that the photo-catalyst with a more positive redox potential tended to have a better photo-oxidation efficiency. Besides, the absorbed optical density of these gallium complexes at the wavelength (450 nm) of emitting LED lamp were also measured: 0.31 (4CF₃-4Br-Ga) > 0.29 (8Br-Ga); this small improvement in terms of the absorbance may ultimately benefit our photo-catalytic reactions. In other words, the designed multifunctionalized photo-catalyst is better matched with the wavelength of the emitting light source and is expected to perform better. Plausible reaction mechanisms were suggested in our previous studies and are only briefly recapped here: [11] the excited state of the photo-sensitizer formed after irradiation can donate an electron to oxygen to allow for the formation of superoxide (O_2^{-}) which then generates hydrogen peroxide (H_2O_2) under acidic conditions. The formed H₂O₂ may oxidize bromide to bromine; then, Br₂ undergoes reaction with phenol to produce mono-brominated phenols by way of electrophilic substitution. Formation of disubstituted products is not promoted considering the relative concentrations of HBr and phenol.



Figure 4. (*left*) Top view of the X-ray structure of 8Br-Ga(pyridine) and (*right*) determined dihedral angles and Ga-N bond lengths based on the X-ray structural information.



Figure 5. (a) Reaction schemes described in this investigation; molecular structures of catalysts and photo-catalytic performance in TOF (turnover frequency, h^{-1}). (b) (*left*) The comparison of the UV-vis spectra for the two gallium complexes in acetonitrile at the same concentration of 1.4×10^{-5} mol·L⁻

¹; inset: absorbance value at a wavelength of 450 nm. (*right*) CV traces of **8Br–Ga** and **4CF₃–4Br–Ga**. Glassy carbon working electrode, and an Ag/AgNO₃ reference electrode were used. Solvent: CH₃CN with TBAP. A scan rate of 100 mV s⁻¹ was applied.

Conclusions

In summary, bromination is a simple and conveniently applied substitution method; the degree to which bromine groups in a given macrocyclic type helps impart phosphorescence to create novel emitting materials, from non-phosphorescent starting materials is an important issue for current and future research. Our results, involved, two novel mixed poly-brominated gallium corrole complexes 3CF3-4Br-Ga and 4CF3-4Br-Ga with two sets of functional groups at the β-positions prepared via a facile synthesized complexes were carefully method: newlv characterized by NMR spectroscopy, mass spectroscopic and UV-vis techniques. Further bromination results in red shifts in both the UV-vis absorption and emission spectra, compared to their non-brominated counterparts. Interestina roomtemperature phosphorescence was observed under the N₂ atmosphere for one brominated species 3CF₃-4Br-Ga in which the phosphorescence (λ_{max} , em = 900 nm) lifetime was measured to be 0.23 µs. The redox properties were probed with cyclic voltammetry and revealed that further bromination produces positively shifted redox potentials, especially on the reduction side. There was, at most, an 85 mV·Br atom⁻¹ positive shift (reduction) observed for these systems. Positive redox shifts for the polybromination was observed resulting in the enhanced performance of species 4CF₃-4Br-Ga in terms of photocatalytic efficiency when compared to e.g. the previously reported octabrominated species 8Br-Ga in photocatalytic of bromide-tobromine conversion. Our study offers well-defined examples and a new mindset on the extent to which β substitution can be varied and structure-function relationships can be revealed. We are aiming at improved photo-catalytic efficiency and stability within biomedical uses among other applications by introducing different functional groups at the β-positions within the confines of accessible synthetic routes, low cost systems, and alternatives to precious metal containing systems.

Experimental Section

Instrumental operations and further experimental information was described in the Supporting Information.

The corrole complexes **3CF₃-Ga** and **4CF₃-Ga** were synthesized based on previously reported literature and used as starting materials for further mixed substituted compounds here (below). ^[4c]

Synthesis of complex **3CF₃-4Br-Ga**. A flask charged with a pyridine solution (15 mL) of **3CF₃-Ga** (20 mg) and excess bromine (1 mL) was stirred at room temperature for 2 hours. Then, the dark brown reaction suspension mixture was taken up into dichloromethane (25 mL) and washed with distilled water three times. Then, after the organic phase was filtered and evaporated, the dry reaction mixture was then separated and

purified by silica gel chromatography using n-hexane: ethyl acetate (5: 1 by volume) and a few drops of pyridine as an eluent. The first eluent was darkly colored and clearly isolated after workup as a green solid; it was found to be our target product (isolated yield: 20 %). **3CF₃-4Br-Ga**: ¹H-NMR (400 MHz, CDCl₃): δ = 9.74 (s, 1H), 7.45 (s, 2H, pyridine-H), 6.64 (m, 4H, pyridine-H), 6.23 (m, 4H, pyridine-H). ¹⁹F-NMR (377 MHz, CDCl₃): δ = -48.28 (m, 3F), -50.09 (m, 3F), -52.97 (m, 3F), -137.53 (m, 6F, *ortho-F*), -150.86 (t, *J* = 22.22 Hz, 1F, *para-F*), -151.00 (t, *J* = 23.14 Hz, 1F, *para-F*), -151.57 (t, *J* = 25.25 Hz, 1F, *para-F*), -163.63 (m, 4F, *meta-F*), -163.89 (m, 2F, *meta-F*). MS⁺ (APCI, positive mode) for C₄₀HBr₄F₂₄GaN₄: m/z = 1381.5769 (calculated), 1381.5181 (observed). UV-vis (toluene) λ_{max} (ϵ) [nm (x 10⁴ cm⁻¹ M⁻¹)]: 413 (1.40), 437 (5.96), 598 (0.69), 626 (0.88).

Synthesis of complex 4CF3-4Br-Ga. A flask charged with a pyridine solution (15 mL) of $4CF_{3}\text{-}Ga$ (20 mg) and excess bromine (1 mL) was stirred at room temperature for 2 hours. Then, the dark brown reaction suspension mixture was taken up into dichloromethane (25 mL) and washed with distilled water three times. Then, after the organic phase was filtered and evaporated, the dry reaction mixture was then separated and purified by silica gel chromatography using n-hexane: ethyl acetate (5:1 by volume) and a few drops of pyridine as an eluent. The first eluent was darkly colored and clearly isolated after workup as a green solid: it was found to be our target product (isolated yield: 25 %). 4CF₃-4Br-Ga: ¹⁹F-NMR (377 MHz, CDCl₃): δ = -48.93 (s, 6F), -49.50 (s, 6F), -136.72 - -137.01 (m, 6F, ortho-F), -151.02 (t, J = 21.69 Hz, 2F, para-F), -151.46 (t, J = 21.73 Hz, 1F, para-F), -162.73 (m, 2F, meta-F), -163.26 (m, 4F, meta-F). MS⁻ (APCI, positive mode) for $C_{41}Br_4F_{27}N_4Ga$: m/z = 1450.5721 (calculated), 1450.5669 (observed). UV-vis (toluene) λ_{max} (ϵ) [nm (x 10⁴ cm⁻¹ M⁻¹)]: 421 (4.42), 442 (6.10), 586 (1.36), 609 (1.69), 644 (2.42).

Crystal Data for **8Br-Ga**: moiety formula: $C_{42}H_5Br_8F_{15}GaN_5$, 0.5(C6), C_2H_3N , $C_{2.50}$, 0.5(C3), sum formula: $C_{51}H_8Br_8F_{15}GaN_6$, M = 1698.55; monoclinic, space group *C*2/c (15), a = 39.074(6) Å, b = 12.1109(19) Å, c = 27.670(4) Å, V = 10610.1 Å³, Z = 8, T = 100 K, $D_x = 2.127$ g cm⁻³, μ (mm⁻¹) = 6.641, Data completeness = 0.746, θ (max) = 25.104, R (reflections) = 0.0701 (4302), wR₂ (reflections) = 0.1780 (9221), S = 0.908, Npar = 670, CCDC code: CCDC1957515. CCDC1957515 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: β -substitution• corroles • oxidation • phosphorescence • photocatalysis

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FULL PAPER

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A synthetic and electrochemical study of a new conceptual class of corroles enables assessment of how β substitution better enables facile lightassisted C–H activation processes such as the mono-bromination of phenol. The corroles feature 3 and 4 CF₃ groups and 4 Br groups. "Hetero multifunctionalization" signifies β substitution to help optimize porphyrinoid (photophysical) properties.



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"Hetero multifunctionalization" in gallium corroles: facile synthesis, phosphorescence, redox tuning, and photooxidative catalytic improvement