

Synthesis and Functionalization of Germanium Triphenylcorrole: The First Example of a Partially Brominated Corrole

Sara Nardis,^[a] Federica Mandoj,^[a] Roberto Paolesse,^{*,[a]} Frank R. Fronczek,^[b] Kevin M. Smith,^[b] Luca Prodi,^[c] Marco Montalti,^[c] and Gionata Battistini^[c]

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Ge complexes of 5,10,15-triphenylcorrole were prepared in refluxing dry DMF using GeCl_4 as the source of Ge. Chromatographic separation of the crude reaction mixture afforded the μ -oxo dimer **1** and the methoxy derivative **2a**. The corresponding chloride **2b** can be obtained by treatment of **1** or **2a** with HCl. The reaction of **2a** with Br_2 in CHCl_3/py afforded the hexabromo derivative **3** as the main product, giving the first indication of the regioselective substitution of pyrroles B and C on the corrole ring. The fully brominated open-chain tetrapyrrole **4** was also characterized as a reac-

tion by-product. Different partially brominated Ge complexes **5** and **6** have been obtained by variation of reaction conditions, while the heptabromo derivative was obtained in a mixture with the corresponding fully brominated Ge corrole. Photophysical characterization of Ge corrolates confirmed the high fluorescence quantum yield of such complexes, and also led to the first observation of phosphorescence emissions from corrole complexes.

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Introduction

In the last few years corrole has been the object of an increasing number of studies, which have resulted in the exploitation of this macrocycle in different fields, such as catalysis,^[1] PDT^[2] and chemical sensors.^[3] The impetus for this renewed interest is the intriguing behaviour shown by corrole, which makes its chemistry unique in the porphyrinoid scenario. This intriguing character can be related to the molecular structure; since it lacks the C20 *meso* bridge (which confers a corrin-like skeleton) corrole retains an 18 π electron aromatic system, closely resembling porphyrins. It is a trianionic ligand, a feature which, together with a contracted porphyrinoid skeleton, leads to the stabilization of formal high oxidation states^[4,5] for coordinated metals, and also to the pronounced non-innocent character of corrole as a ligand.^[6] The coordination chemistry of this macrocycle is therefore a challenging arena.

Besides its coordination characteristics, another intriguing aspect of corrole chemistry is the reactivity of the peripheral positions of corrole. The recent definition of dif-

ferent synthetic routes^[7] for the preparation of *meso*-arylcorroles from commercially available precursors has allowed the functionalization of β -pyrrolic positions to be studied. This constitutes the first step towards the preparation of more elaborate molecular architectures based on corroles.

The β -functionalization of triphenylcorroles, however, introduces the possible formation of different regioisomers due to the lower symmetry of corrole compared with porphyrin, a further challenging feature that should be taken into account. Many research groups have studied different electrophilic reactions such as nitration, formylation, chlorosulfonation or bromination;^[8–13] it is worth mentioning that the first three of these were shown to be regioselective, leading to the isolation of partially substituted corroles. For example, chlorosulfonation and nitration reactions^[8] were successfully carried out both on the free base and on the gallium complex of tris-pentafluorophenylcorrole, using chlorosulfonic acid and $\text{NaNO}_2/\text{CH}_3\text{CN}$ respectively. The interesting result of these synthetic approaches is that it has been possible to isolate only a few isomers among the several possible regioisomers. In the case of the chlorosulfonation reaction, purification of the 2,17- and the 3,17-sulfonic acid derivatives has been reported, while the $\text{NaNO}_2/\text{CH}_3\text{CN}$ reaction afforded the mono-nitro, the 3,17-dinitro and the 2,3,7-trinitro derivative, depending on the amount of the nitrating agent used.

Also, in the case of the formylation^[8,9] and carboxylation^[13] reactions, mono and bis β -regio-substituted corroles have been obtained as the major products, even though the novelty of these kinds of reactions is probably better deter-

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma, "Tor Vergata" 00133 Rome, Italy
Fax: +39-0672594328
E-mail: roberto.paolesse@uniroma2.it

[b] Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

[c] Dipartimento di Chimica "G. Ciamician", Latemar Unit, Università di Bologna, Bologna, Italy

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mined by the isolation of inner nitrogen substituted compounds. A general feature of these functionalizations is the regioselectivity; 3 and 17 β -pyrrolic positions of the directly linked A and D pyrroles are the sites of the substitution, in agreement with calculations of electron density at those positions already reported in the literature.^[8]

It is interesting to note that in the case of bromination,^[10–12] attempts to isolate partially brominated corroles have failed to date. Previous studies have demonstrated that bromination reactions carried out on corroles mainly afford the octabromo products both using the corrole free-base and metal complexes, even in the presence of very small amounts of the brominating agent (either NBS and Br₂).

Since brominated corroles have been shown to be useful substrates for palladium(0) mediated cross-coupling reactions,^[14] we have been keen to explore the possibility of preparing partially brominated corroles. We have previously reported the bromination of the corrole free base,^[10] while other groups studied the same reaction with metal complexes, mainly copper^[11] and manganese^[12] derivatives. In these studies the major reaction product was always the β -octabromocorrole, in which all pyrrolic positions were substituted. No partially substituted derivatives have been isolated, although mixtures of different isomers were reported when the stoichiometry of the brominating agent was reduced. Yields of reaction carried out with the corrole free base, and either NBS or Br₂ as brominating agent, are in general quite low; this is probably due to the instability of the macrocycle, which undergoes decomposition before the substitution takes place if oxidizing reagents are present. For this reason, we decided to investigate the reactivity of germanium derivatives of corroles. We chose this metal complex because it is diamagnetic, thereby allowing an easier characterization of the reaction products, and because corrole stabilizes the coordinated metal in the +4 oxidation state. We suspected that this would allow us to better control the substitution reaction and obtain partially brominated derivatives.

Results and Discussion

The first phase of our study focused on the preparation of the Ge corrole complex. We have reported the preparation of germanium derivatives in the case of β -alkylcorroles,^[15] and, to the best of our knowledge, in the triphenylcorrole series there is only one example of a Ge complex, the Ge(TPF₅PC)OH reported by Gross.^[16] We used the same metalation procedure, reacting triphenylcorrole with GeCl₄ in refluxing anhydrous DMF, and observed a prompt colour change of the solution from green to red-violet. The UV/Vis spectrum of the reaction mixture also indicated the formation of the complex, with the disappearance of the free base absorbance bands.

TLC of the crude mixture obtained after vacuum evaporation of the DMF showed the presence of two reaction products. We decided to perform a chromatographic separation of the reaction mixture, despite the possible hydrolysis

of the Ge–Cl bond, as observed in the case of previous Ge corrole derivatives. Column chromatography on alumina, using CH₂Cl₂ as the eluent, afforded a dichroic green-purple fraction followed by a second purple compound which required a mixture of CHCl₃/MeOH (95:5) for elution. The UV/Vis spectra of both fractions were in agreement with the coordination of germanium to the corrole macrocycle, but with a significant blue shift of the absorbance bands of the first fraction with respect to the second. This result, together with a high-field shift of the β -pyrrolic proton resonances in the ¹H NMR spectrum suggested the formation of a μ -oxo dimer derivative (**1**), which was unambiguously characterized by X-ray crystallography. To the best of our knowledge, this is the first example of such a derivative in the corrole series, other than the iron corrole complexes.^[16]

Figure 1 shows one of the two Ge μ -oxo dimers in the asymmetric unit. The Ge atoms have square-pyramidal coordination, lying 0.439 Å (average of four) from the N₄ plane. The Ge–N distances are in the range 1.881(9)–1.930(9) Å, with axial Ge–O distances in the range 1.718(11)–1.773(13) Å and Ge–O–Ge angles 147.3(5) and 149.0(4)°. Thus the N₄ planes within each dimer are not parallel, forming dihedral angles of 19.4(6) and 19.9(5)°.

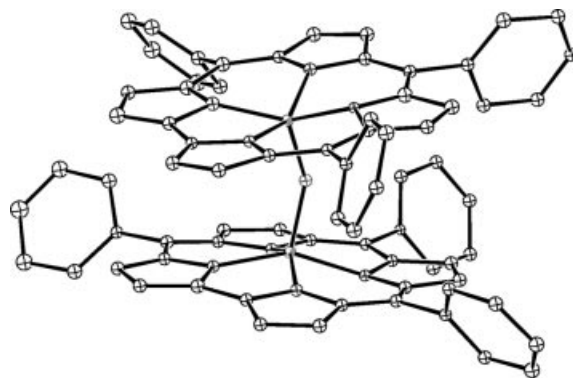


Figure 1. The X-ray structure of **1**.

The characterization of the second fraction indicated the formation of **2a**, in which a methoxy group is present at the axial position. The presence of the methoxy group is due to the well known lability of the Ge–Cl bond toward oxygen ligands and in this case to the solvent mixture used for the elution of the second chromatographic fraction. We also explored the possibility of modifying the nature of the axial ligand, as already observed in the case of β -alkylcorrole complexes,^[15] but found not to be possible in the case of TPF₅PC.^[16] Treating a CHCl₃ solution of **1** or **2a** with a dilute HCl solution afforded the complex GeTPCCl (**2b**): in the case of **2a** the formation of the chloride complex was monitored by observing the disappearance of the ¹H NMR signal characteristic of the axial methoxy group which appears at around –1 ppm (Figure 2).

However it should be noted that, in some cases, the isolated complex was contaminated with variable amounts of the corresponding hydroxy derivative, as demonstrated by

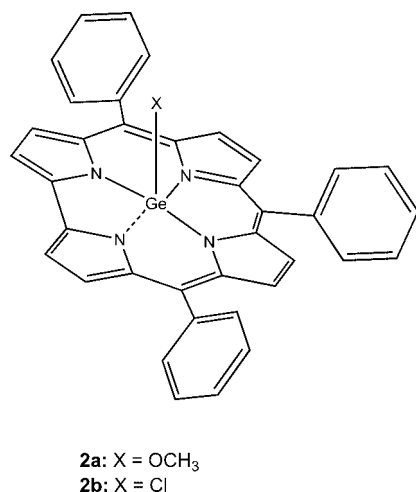


Figure 2. Molecular structures of the germanium complexes **2a** and **2b**.

the ^1H NMR signal for the $-\text{OH}$ at -4.4 ppm, thus confirming the easy hydrolysis of the $\text{Ge}-\text{Cl}$ bond under acidic conditions (Figure 2). The bromination of complex **2a** was carried out according to the previously reported procedure,^[11,18] by using liquid bromine in CHCl_3/py at room temperature. The reaction was initially carried out with an excess of Br_2 in order to drive the reaction to the formation of the fully substituted derivative. This protocol is usually adopted with other metal complexes^[11,12] to avoid the potential formation of a mixture of regioisomers. The progress of the reaction was followed by spectrophotometry. A clear red shift of the Soret band was observed, consistent with the presence of halogen atoms in the metal complex structure. However, also with a large excess of Br_2 , in the case of **2a** TLC of the crude reaction mixture showed a number of products. Work up and purification with a silica plug afforded two main fractions, eluted with CHCl_3 and $\text{CHCl}_3/\text{CH}_3\text{OH}$ (95:5) respectively. The first fraction contained some residual impurities and was further purified with a silica gel column and CHCl_3 as eluent to give an analytically pure product.

The UV/Vis spectrum of this fraction showed the presence of a Soret band, indicating the retention of the corrole macrocycle, but it was interesting to note the presence of a singlet in the β -pyrrolic proton region of the ^1H NMR, also indicating incomplete peripheral substitution of the complex. The integration ratio corresponded to the presence of two pyrrolic protons, but the presence of a single resonance indicated that substitution had occurred with good regioselectivity. This hypothesis was fully confirmed by the X-ray structure of crystals obtained from $\text{CHCl}_3/\text{CH}_3\text{OH}$.

The complex obtained was identified as **3**, possessing six bromine atoms on the peripheral positions. To the best of our knowledge this is the first example of an isolated and characterized partially brominated corrole. The formation of **3**, not only confirms the higher reactivity of the pyrrolic positions on the two directly linked pyrroles A and D, but also gives an indication of the substitution regioselectivity

on pyrrole subunits B and C. In this case the reaction leads to the substitution of the protons H8 and H12, closer to the *meso* bridge, with the formation of only one of the three possible regioisomers. This result confirms the behaviour previously observed by Gross and Mahammed in the deuteration of the tris-(pentafluorophenyl)corrole, for which a similar reactivity order, $\text{C3} > \text{C2} \gg \text{C8} > \text{C7}$, was reported^[19] (Figure 3).

Characterization of the material isolated from the second fraction was more difficult. A Soret-like band was absent from the UV/Vis spectrum, and we observed more resonances than expected in the ^1H NMR spectrum. In this case, X-ray crystallography was necessary to characterize compound **4**: this derivative is a fully brominated open chain tetrapyrrole (Figure 4).

There are several peculiar features of this compound to be noted. An ethoxy group is added at the former 10-methine bridge of the corrole ring, with the formation of a methane bridge and the consequent interruption of the π conjugation. The ring is opened at the 5-methine bridge and the pyrrole-pyrrole direct link is retained in the tetrapyrrole. The ring opening in this case is different from that observed previously with 10-phenyl-substituted corrole, which afforded the corresponding biliverdin derivatives on reaction with molecular oxygen.^[20] As a consequence of the ring opening, a benzoyl group and a pyridinium substituent are present at the terminal α -pyrrolic positions. While the origin of the benzoyl group can be confidently attributed to the oxidation of the methine bridge, the presence of the pyridinium group is more surprising. Furthermore, the positive charge of this group is balanced by the presence of a central divalent ion, which consequently infers a zwitterionic character to the complex. While the identity of the central metal atom is not completely unambiguous, Zn appears most consistent with all available information. Its coordination geometry is square planar, somewhat twisted from planarity by the spiral nature of the ligand. Thus N2 lies $0.62(1)$ Å and N5 lies $-0.43(1)$ Å out of the plane defined by the metal and the two central N atoms. Zn–N distances vary $1.901(9)$ – $2.016(1)$ Å.

Further confirmation of the presence of Zn as coordinated metal was given by MALDI mass spectrum, in which a molecular peak at 1360 m/z was observed. In the FAB spectrum a peak was found at 1299 m/z , corresponding to the free base derivative after loss of the Zn ion, probably induced by the acidic matrix used in this technique. The source of the coordinated Zn is probably the silica gel used for the chromatographic separation. A similar Zn complex of a fully brominated open chain tetrapyrrole has recently been reported in the literature and was obtained by bromination induced ring-opening of tetraphenylporphyrin.^[21]

To explore the possibility of achieving complete bromination of **2a**, the reaction was carried out at reflux for a prolonged time (2 h); in this case we observed significant decomposition of the starting material, with the formation of a mixture of three brominated products. A complete chromatographic separation was difficult to achieve from this mixture, although ^1H NMR and MALDI-MS charac-

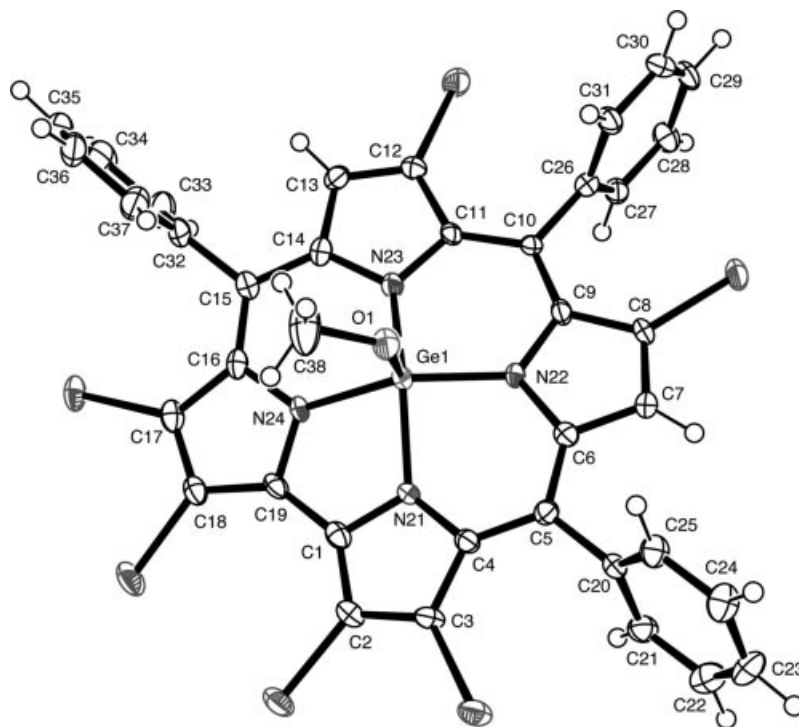


Figure 3. Characterization of **3** by X-ray crystallography.

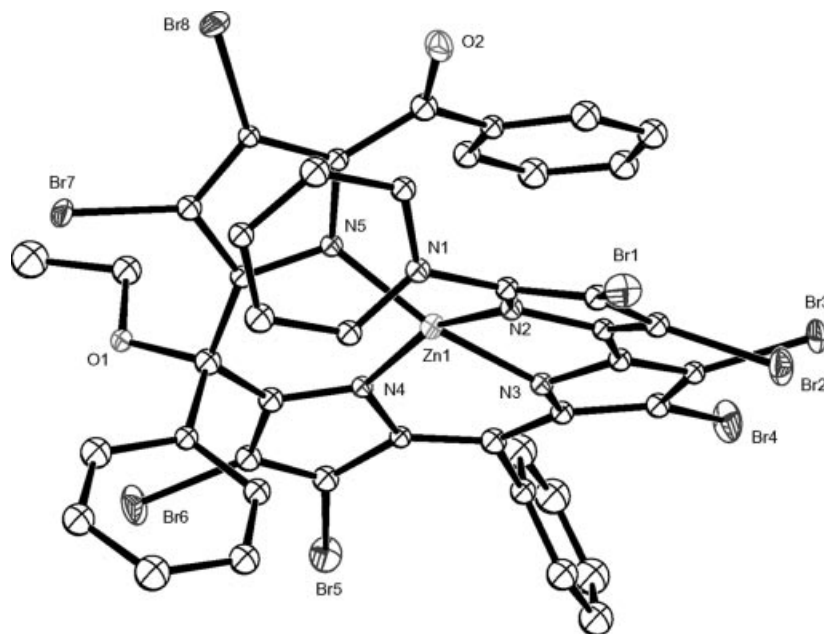


Figure 4. The X-ray structure of **4** (hydrogen atoms omitted).

terization indicated that the main component of the mixture was the heptabromo derivative, with the presence of the fully brominated complex as a minor component. The third component of the mixture, although in a significantly lower amount, was easily identified as **3**, by comparison of the spectroscopic data.

Consequently, these results led us to explore the possibility of obtaining other partially brominated Ge derivatives

by reducing the Br₂:**2a** ratio. Initially we carried out the reactions reducing the reagent ratio in the range 70:1 to 10:1, obtaining the corresponding pentasubstituted complex as the reaction product. This complex can be reasonably assumed to be **5**, considering that it is the necessary precursor of **3** (Figure 5).

The formation of **5** even with a slight excess of bromine seems to indicate a pronounced reactivity of pyrrole sub-

units A and D, which are completely substituted, while the substitution of pyrroles B and C can be modulated by the amount of reagent used.

When we further reduced the amount of Br_2 to 1.1 equiv., adding methanol as co-solvent, we observed the formation of a tri-substituted derivative, which can be confidently assumed to be (**6**). Significant decomposition of the starting material was observed in this case, however.

The unprecedented formation of **1** led us to perform a photo-physical characterization of the Ge corrole deriva-

tives, considering that corroles present quantum yield values higher^[17] than those of the corresponding porphyrins and that the efficiency of the photophysical process can even be increased by the coordination of small metal ions such as Gallium.^[13]

The absorption spectra of compounds **1**, **2a** and **3** in dichloromethane are reported in Figure 6, with the most relevant photophysical data reported in Table 1. As expected, because of the already observed validity of the porphyrin four-orbital model for corroles, all three compounds show a Soret band in the 380–440 nm region, and a set of Q bands in the 540–620 nm region. The absorption spectrum of **2a** [that of **2b** is almost identical] is very similar to the one described for $\text{Ge}(\text{TPF}_5\text{PC})\text{Cl}$. This is as expected because the positions of the absorption maxima of corroles are typically unaffected by the nature of the *meso* substituents.^[22] For **1**, relevant differences are observed instead: its Soret band, while undergoing an expected almost doubling in intensity, is shifted to a shorter wavelength by 13 nm. On the other hand, the Q bands are much broader and shifted to longer wavelengths. These findings clearly indicate a strong interaction between the two macrocycles in the dimer. It is interesting to note that, at concentrations lower than 10^{-6} M, **1** is not stable, since its spectrum slowly changes to become very similar to that of **2a**. As already mentioned, all the bands in **3** are red-shifted compared to **2a**, indicating that the substituents on the β positions are able to affect the photophysical properties of corroles, as already observed for Ga complexes.^[23] As far as the fluorescence spectra are concerned, the maximum of the fluorescence band of **2a** (Figure 7) is close to that observed for $\text{Ga}(\text{TPF}_5\text{PC})\text{Py}$ (no fluorescence has been previously reported for Ge corroles). In this case, the fluorescence quantum yield, although higher than that of a metallated porphyrin, is lower than that reported for $\text{Ga}(\text{TPF}_5\text{PC})\text{Py}$, probably because of a lower planarity of the macrocycle (Table 2).

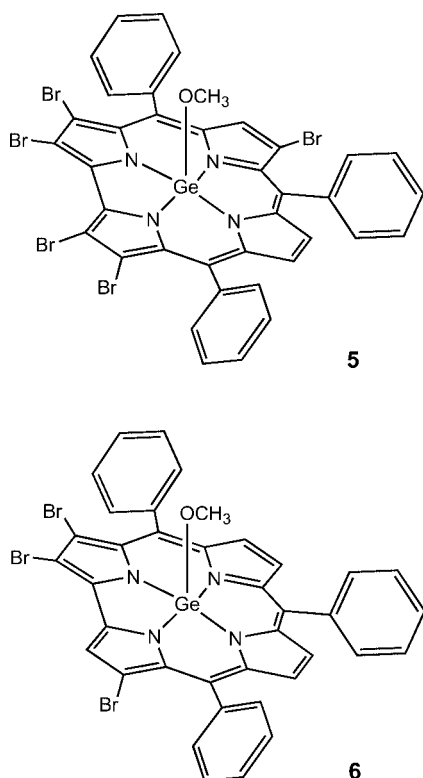


Figure 5. Molecular structures of **5** and **6**.

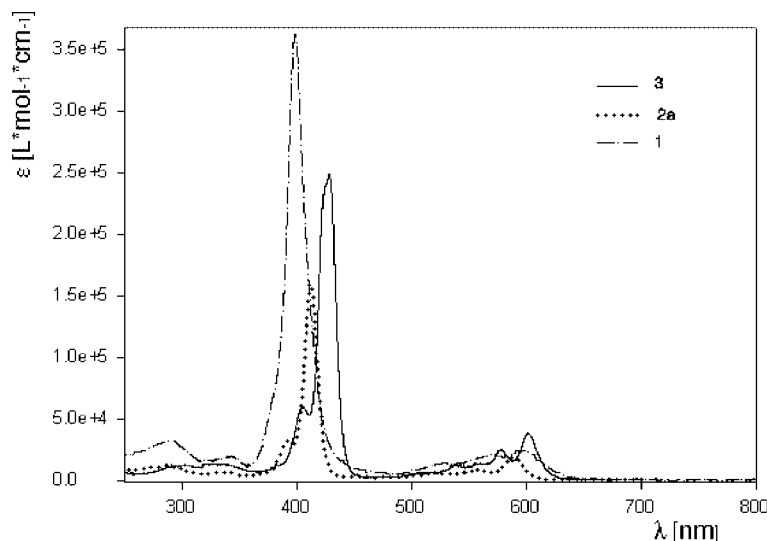


Figure 6. UV/Vis spectra of germanium corroles.

Table 1. Most relevant absorption parameters of **1**, **2a** and **3** in CH₂Cl₂ solutions at room temperature and at 77 K.

Compound	λ_{max} [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]
1	399	363000
	528	13400
	567	21300
	598	24050
2a	412	160000
	5220	7600
	560	9650
	590	20600
3	428	248000
	538	12050
	578	25100
	603	38000

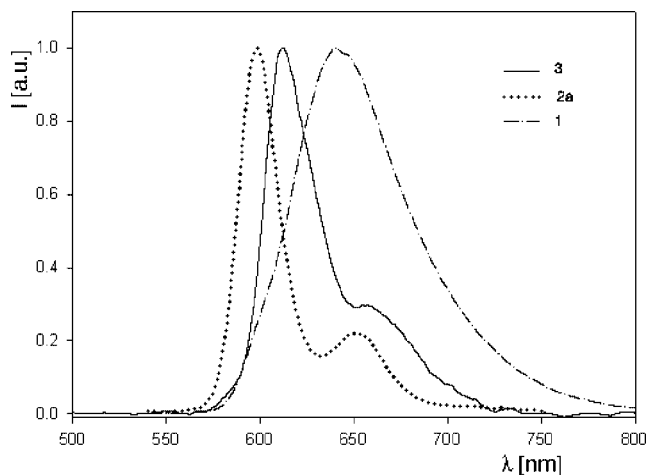


Figure 7. Fluorescence spectra of germanium corrolates.

Table 2. Most relevant luminescence parameters of **1**, **2a** and **3** in CH₂Cl₂ solutions at room temperature and at 77 K.

Compd.	Room temperature			77 K		77 K	
	λ_{max} [nm]	Φ	τ [ns]	λ_{max} [nm]	τ [ns]	λ_{max} [nm]	τ [ms]
1	660	0.033	< 0.4	660	2.3	818	35.2
2a	598	0.14	< 0.4	599	2.1	784	28.4
3	614	0.005	< 0.4	603	3.0	806	3.2

The very short excited state lifetime observed in this case supports this hypothesis, indicating the presence of a very fast ($k_{\text{nr}} \geq 2 \times 10^9 \text{ s}^{-1}$) non radiative deactivation process. It is interesting to note, however, that the radiative rate constant is also very high ($k_{\text{r}} \geq 2 \times 10^8 \text{ s}^{-1}$), especially if compared with other porphyrins and corroles.^[22b] This finding is clearly in line with the indication that corroles can be of great interest for their photophysical properties, especially if it is possible to design new systems showing slower non radiative processes. Additionally, for **2a** this latter process is thermally activated as shown by the remarkable increase in the excited state lifetime at 77 K. The brominated compound **3** shows a red shifted fluorescence spectrum in line with its absorption spectrum, with a relatively low quantum yield, most probably due to the heavy atom effect introduced by the presence of bromine atoms. The fluorescence

maximum of this compound at 77 K is the only one that shows a blue shift with respect to the maximum observed at room temperature, most probably because its excited state shows a reduced dipole moment compared to the ground state.^[22b] The fluorescence spectrum of the dimer **1** is much broader and shifted even more towards longer wavelengths in comparison to the monomer **2a**, again indicating a strong interaction between the two macrocycles. The quantum yield (0.033), although reduced, is still in the same range as those of two very well known metal complexes, ZnTPP and Ru(bpy)₃²⁺. Again, the lifetime is very short, indicating the occurrence of a relatively fast radiative deactivation process also in this case.

Finally, we were able, for the first time, to observe the phosphorescence coming from a corrole complex at 77 K (Figure 8).

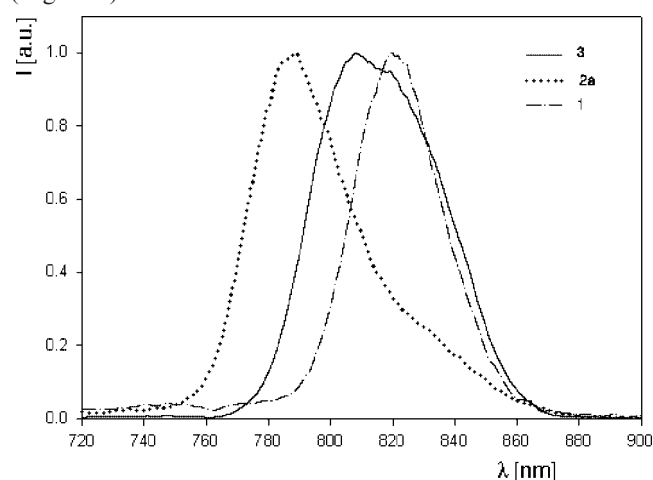


Figure 8. Phosphorescence spectra of germanium corrolates.

All the phosphorescence bands observed were in the 760–840 nm region, following the energetic order observed for the fluorescence bands. It is worth noting that **1** and **2a** showed an excited state lifetime of around 30 ms, while **3** decayed ten times more quickly, indicating a much faster inter-system crossing process, which confirms the presence of the already invoked heavy atom effect in **3**.

Conclusions

In conclusion, we have detailed here a useful, never previously reported route for the preparation of partially substituted corroles by bromination of the Ge triphenylcorrole complex, together with a further example of the peculiar reactivity of this macrocycle. Photophysical characterization of Ge complexes also led to the first example of phosphorescence emission from corrole derivatives.

Experimental Section

Physical Methods: ¹H NMR spectra were recorded with a Bruker AM400 (400 MHz) or Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). Routine UV/Vis spectra were measured with a Varian Cary

50 Spectrophotometer, whereas more precise measurements were performed with a Perkin–Elmer 18 Spectrophotometer equipped with a temperature-controlled cell holder.

Materials: Silica gel 60 (70 ± 230 mesh) was used for column chromatography. Reagents and solvents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. CH_2Cl_2 used for the spectrophotometric measurements was stored over activated molecular sieves.

Synthetic Methods: Triphenylcorrole was prepared as previously reported in the literature.^[7b]

Germanium 5,10,15-Triphenylcorrolates: In a 100 mL round-bottomed flask equipped with a stirring bar, corrole (0.1 g; 0.2 mmol), was dissolved in anhydrous DMF (20 mL). GeCl_4 (96 μL ; 0.8 mmol) was added under nitrogen and the mixture was refluxed for about two hours, monitoring the progress of the reaction by UV/Vis spectroscopy. After the absorption peaks of the starting material had disappeared (the color of the solution changed from green to deep purple), the solvent was evaporated and the product purified by chromatography on silica gel, using CHCl_3 as the eluent. The first fraction eluted corresponded to the μ -oxo dimer (**1**), while the second fraction, eluted with a mixture of $\text{CHCl}_3/\text{MeOH}$ (95:5), was characterized as the monomeric germanium methoxide (**2a**). GeTPC-Cl was obtained by treatment of fractions (**1**) and (**2a**) with HCl (4 M). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:2), afforded GeTPC-Cl (**2b**) in 60% yield (76 mg, 0.12 mmol).

Spectroscopic Data for 1: ^1H NMR (300 MHz, CDCl_3): δ = 8.92 (d, 1J = 4.2 Hz, 4 H, β -pyrrolic), 8.62 (d, 1J = 4.2 Hz, 4 H, β -pyrrolic), 8.55 (d, 1J = 4.8 Hz, 4 H, β -pyrrolic), 8.18 (d, 1J = 4.8 Hz, 4 H, β -pyrrolic), 7.67 (m, 30 H, phenyl) ppm. MS (FAB): m/z (%): 1208 (60) [M^+]. $\text{C}_{74}\text{H}_{46}\text{Ge}_2\text{N}_8\text{O}$ (1208.45): calcd. C 73.55, H 3.83, N 9.27; found C 73.42, H 3.61, N 9.55.

Crystal Data for 1: Color: dark purple, $\text{C}_{74}\text{H}_{46}\text{Ge}_2\text{N}_8\text{O} \cdot 0.5 \text{CH}_2\text{Cl}_2$, M_r = 1250.9, triclinic space group $P\bar{1}$, a = 14.6167(15), b = 19.802(3), c = 23.156(4) Å, α = 72.715(7), β = 85.464(8), γ = 68.930(6)°, V = 5968.8(15) Å³, Z = 4, $\rho_{\text{calcd.}}$ = 1.440 g cm⁻³, Mo- K_α radiation (λ = 0.71073 Å; μ = 1.11 mm⁻¹), T = 110 K, 31760 data by Nonius KappaCCD, R = 0.098 ($F^2 > 2\sigma$), R_w = 0.269 (all F^2) for 16529 unique data having $\theta < 23.2^\circ$ and 759 refined parameters. Two Ge oxo dimers were found in the asymmetric unit. Because of the limited crystal quality, it was possible to refine only Ge, Cl and O anisotropically. Further disordered solvent was modeled with partially-populated C positions.

Spectroscopic Data for 2a: ^1H NMR (300 MHz, CDCl_3): δ = 9.40 (d, 1J = 4.2 Hz, 2 H, β -pyrrolic), 9.21 (d, 1J = 4.8 Hz, 2 H, β -pyrrolic), 9.08 (d, 1J = 4.2 Hz, 2 H, β -pyrrolic), 8.91 (d, 1J = 4.8 Hz, 2 H, β -pyrrolic), 8.44 (m, 2 H, phenyl), 8.35 (m, 1 H, phenyl), 8.21 (m, 2 H, phenyl), 8.09 (m, 1 H, phenyl), 7.81 (m, 9 H, phenyl), -0.96 (s, 3 H, OCH_3) ppm. MS (FAB): m/z (%): 627 (100) [M^+]. $\text{C}_{38}\text{H}_{26}\text{GeN}_4\text{O}$ (627.26): calcd. C 72.76, H 4.18, N 8.93; found C 72.83, H 4.42, N 8.96.

Spectroscopic Data for 2b: ^1H NMR (300 MHz, CDCl_3): δ = 9.45 (d, 1J = 4.3 Hz, 2 H, β -pyrrolic), 9.24 (d, 1J = 4.9 Hz, 2 H, β -pyrrolic), 9.12 (d, 1J = 4.3 Hz, 2 H, β -pyrrolic), 8.94 (d, 1J = 4.9 Hz, 2 H, β -pyrrolic), 8.42 (m, 2 H, phenyl), 8.34 (m, 1 H, phenyl), 8.24 (m, 2 H, phenyl), 8.11 (m, 1 H, phenyl), 7.81 (m, 9 H, phenyl) ppm. MS (FAB): m/z (%): 631 (100) [M^+]. $\text{C}_{37}\text{H}_{23}\text{ClGeN}_4$ (631.68): calcd. C 70.35, H 3.67, N 8.87; found C 70.44, H 3.69, N 8.96.

Bromination of 2 ($\text{Br}_2:2 = 300:1$): In a 250 mL round-bottomed flask equipped with a dropping funnel, complex **2a** (50 mg, 0.08 mmol) was dissolved in CHCl_3 (80 mL) and a solution of Br_2

(1.2 mL, 24 mmol; $d = 3.119$) in 30 mL of CHCl_3 was added dropwise during 15 min. The resulting mixture was stirred at room temperature for one hour; after this period, pyridine (0.24 mL, 3.02 mmol; $d = 0.978$) dissolved in CHCl_3 (30 mL) was added and the mixture stirred for a further hour. The crude mixture was then washed with an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$ (20% w/v). The organic phase was dried with anhydrous Na_2SO_4 , the solvent was evaporated and the crude mixture purified with silica gel (plug), using CHCl_3 as the eluent. A second fraction was eluted with a mixture of $\text{CHCl}_3/\text{MeOH}$ (95:5). The first fraction was further purified by column chromatography on silica gel, using CHCl_3 as the eluent. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:2) of both fractions afforded respectively **3** (34%, 30 mg, 0.027 mmol) and **4** (5%, 5.3 mg, 0.004 mmol).

Spectroscopic Data for 3: ^1H NMR (300 MHz, CDCl_3): δ = 9.11 (s, 1 H, β -pyrrolic), 7.99 (m, 5 H, phenyl), 7.78 (m, 10 H, phenyl), -0.78 (s, 3 H, $-\text{OCH}_3$) ppm. MS (MALDI): m/z (%): 1101.6 (50) [M^+]. $\text{C}_{38}\text{H}_{20}\text{Br}_6\text{GeN}_4\text{O}$ (1100.64): calcd. C 41.47, H 1.83, N 5.09; found C 41.58, H 1.79, N 5.22.

Crystal Data for 3: Color: maroon, $\text{C}_{38}\text{H}_{20}\text{GeBr}_6\text{N}_4\text{O}$, M_r = 1105.2, monoclinic space group $P2_1/n$, a = 13.330(2), b = 17.952(3), c = 15.974(3) Å, β = 114.325(6)°, V = 3483.2(10) Å³, Z = 4, $\rho_{\text{calcd.}}$ = 2.107 g cm⁻³, Mo- K_α radiation (λ = 0.71073 Å; μ = 7.87 mm⁻¹), T = 110 K, 48918 data points by Nonius KappaCCD, R = 0.051 ($F^2 > 2\sigma$), R_w = 0.115 (all F^2) for 10534 unique data points having $\theta < 30.5^\circ$ and 460 refined parameters. Residual electron density peaks near C7 and C13 indicated the presence of small amounts of heptabromo and/or octabromo compounds. Refinement of partially populated Br atoms at these positions led to populations of 2.6%.

Spectroscopic Data for 4: ^1H NMR (300 MHz, CDCl_3): δ = 7.78–7.41 (m, 20 H), 3.77 (q, 2 H, $-\text{OCH}_2\text{CH}_3$), 1.25 (t, 3 H, $-\text{OCH}_2\text{CH}_3$) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3}$) = 440 (9.3), 601 (3.7), 642 nm (2.4). MS (MALDI): m/z (%): 1360.2 (20) [M^+]. $\text{C}_{44}\text{H}_{25}\text{Br}_8\text{N}_5\text{O}_2\text{Zn}$ (1360.33): calcd. C 38.85, H 1.85, N 5.15; found C 38.90, H 1.83, N 5.24.

Crystal Data for 4: Color: dark blue, $\text{C}_{44}\text{H}_{25}\text{Br}_8\text{N}_5\text{O}_2\text{Zn} \cdot \text{CHCl}_3 \cdot \text{C}_4\text{H}_{10}\text{O}$, M_r = 1457.1, monoclinic space group $P2_1/a$, a = 15.599(10), b = 13.913(7), c = 24.280(17) Å, β = 90.87(2)°, V = 5269(6) Å³, Z = 4, $\rho_{\text{calcd.}}$ = 1.837 g cm⁻³, Mo- K_α radiation (λ = 0.71073 Å; μ = 6.65 mm⁻¹), T = 110 K, 22209 data points by Nonius KappaCCD, R = 0.072 ($F^2 > 2\sigma$), R_w = 0.154 (all F^2) for 7321 unique data having $\theta < 23.5^\circ$ and 352 refined parameters. Because of limited crystal quality and disordered solvent, it was possible to refine only Zn, Br, Cl and O anisotropically. Refinement of the central metal as Ge led to unrealistically high displacement parameters for this atom as well as significantly higher R values.

Bromination of 2 ($\text{Br}_2:2 = 70:1$): When the bromination is carried out under the reaction conditions described above, with a reduced amount of Br_2 (0.3 mL, 5.8 mmol; $d = 3.119$), the subsequent chromatographic purification afforded **5** in 43% yield (35 mg, 0.034 mmol).

Spectroscopic Data for 5: ^1H NMR (300 MHz, CDCl_3): δ = 9.07 (s, 1 H, β -pyrrolic), 8.91 (d, 1J = 4.98 Hz, 1 H, β -pyrrolic), 8.66 (d, 1J = 4.98 Hz, 1 H, β -pyrrolic), 7.85 (m, 15 H, phenyl), -0.78 (s, 3 H, OCH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3}$) = 423 (215), 533 (10.3), 575 (22), 596 nm (33) ppm. MS (FAB): m/z (%): 1022 (60) [M^+]. $\text{C}_{38}\text{H}_{21}\text{Br}_5\text{GeN}_4\text{O}$ (1021.74): calcd. C 44.67, H 2.07, N 5.48; found C 44.56, H 1.98, N 5.52.

Bromination of 2 ($\text{Br}_2:2 = 1.1:1$): When the bromination is carried out under the reaction conditions described above, with **2** (70 mg,

0.11 mmol) and 1.1 equiv. of Br₂ (6.3 µL, 0.12 mmol; d 3.119), the subsequent chromatographic purification afforded **6** in 49% yield (47 mg, 0.054 mmol).

Spectroscopic Data for 6: ¹H NMR (300 MHz, CDCl₃): δ = 9.38 (s, 1 H, β-pyrrolic), 8.96 (d, ¹J = 4.80 Hz, 2 H, β-pyrrolic), 8.81 (d, ¹J = 4.80 Hz, 2 H, β-pyrrolic), 8.12 (m, 5 H, phenyl), 7.77 (m, 10 H, phenyl), −0.84 (s, 3 H, OCH₃) ppm. UV/Vis (CH₂Cl₂): λ_{max} (ε × 10^{−3}) = 414 (198), 525 (8.2), 565 (21.5), 589 nm (30.8) ppm. MS (FAB): m/z (%): 864 (70) [M⁺]. C₃₈H₂₃Br₃GeN₄O (863.95): calcd. C 52.83, H 2.68, N 6.49; found C 52.71, H 2.73, N 6.34.

CCDC631925 (for **1**), −631926 (for **3**) and −631927 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ¹H NMR spectra of new compounds are reported.

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