

# Photoexcited Triplet State Properties of Brominated and Nonbrominated Ga(III)-Corroles as Studied by Time-Resolved Electron Paramagnetic Resonance<sup>†</sup>

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The effect of the corrole macrocycle bromination on its photoexcited triplet state parameters was examined in a comparison study of brominated and nonbrominated Ga(III) 5,10,15-tris(pentafluorophenyl)corroles, employing X-band (9.5 GHz) time-resolved electron paramagnetic resonance (TREPR) spectroscopy. It is demonstrated that the spectrum of the brominated Ga-corrole is characterized by an opposite polarization pattern and a larger zero-field splitting (ZFS) parameter  $|D|$ , compared to nonbrominated Ga-corrole. With the assignment of a negative sign for the ZFS parameter  $D$ , the dominant intersystem crossing (ISC) pathways are evaluated. Spectral line shape analysis reveals that in the brominated Ga-corrole, the out-of-plane triplet sublevel is overpopulated ( $A_z > A_x, A_y$ ), while in nonbrominated Ga-corrole, the in-plane triplet sublevels are preferentially populated ( $A_x, A_y \gg A_z$ ). The differences in the photophysical properties of the corroles are attributed to the heavy atom effect upon corrole skeleton bromination, which enhances the spin–orbit coupling strength in the brominated complex, thus affecting its ISC and ZFS parameters.

## Introduction

The development of a simple and efficient procedure of corroles synthesis<sup>1,2</sup> has revived substantial interest in employing these porphyrinoids in various fields of science and technology.<sup>3,4</sup> Corroles retain the aromatic character of the porphyrin ring, but due to the lack of one *meso* bridge, they possess a lower symmetry and a smaller cavity size as compared to porphyrins.<sup>1,5–11</sup> The ability of the triprotonic corrole macrocycles, in their deprotonated form, to stabilize metal ions in higher oxidation states than other tetrapyrroles continues to be one research emphasis,<sup>7,10–13</sup> while quite exceptional photophysical and photochemical properties have been recently revealed for the corrole complexes.<sup>14–18</sup> Moreover, tuning of physical and chemical parameters of the corroles can be achieved over a wide range by varying the peripheral substituents, axial ligands, and central metal.<sup>19–22</sup> These peculiarities have motivated rapidly growing applications of the corroles such as catalysts,<sup>23–26</sup> photosensitizers,<sup>27–29</sup> multifunctional therapeutic agents,<sup>16–18,29–31</sup> as well as light harvesting<sup>30,32,33</sup> and molecular recognition compounds.<sup>34</sup>

During the past few years, the special features of the corroles were studied by different experimental methods, aiming to reveal correlation between the structure and functions in various corrole complexes bearing different core ions and axial ligands.<sup>3,4</sup> Since many light-induced processes involving corroles proceed via transient paramagnetic states, the time-resolved electron paramagnetic resonance (TREPR) spectroscopy combined with selective laser light excitation is a suitable tool to provide unique information on the nature and fate of these states. This experimental approach was employed in our previous studies, which was aimed at characterizing the spin dynamics and

kinetics of free-base and various metallo-tris(pentafluorophenyl) corroles (tpfc) differing by their core and symmetry.<sup>35–38</sup>

Ordering the corroles in magnetically oriented nematic liquid crystal (LC) allows for a thorough determination of their magnetic, structural, and orientational parameters over a wide range of temperatures.<sup>35–38</sup> The results were interpreted in terms of the structure–function relationship in these promising compounds.

Among the important features of the corroles, one could mention the value and sign of the zero-field splitting (ZFS) parameters  $D$  and  $E$ .<sup>39</sup> Generally, determination of the sign of  $D$  and  $E$  requires a special experimental setup, not available in our experiments. Such corrole measurements are very scarce, and as far as we know, they were performed only for two Mn(III)-corroles with different peripheral substituents.<sup>39,40</sup> In both corroles, the parameter  $D$  was determined to be negative and similar by absolute value, i.e., of  $-2.72\text{ cm}^{-1}$  (averaged by different media) for one of them and of  $-2.69\text{ cm}^{-1}$  for another one.

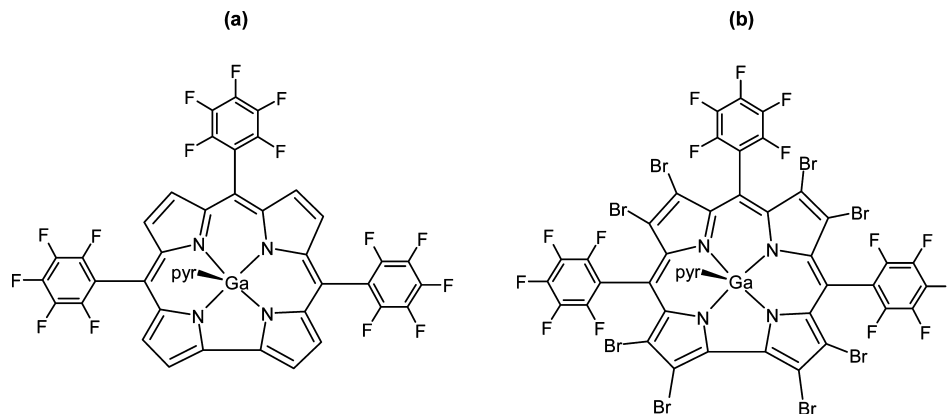
Nevertheless, analysis of the TREPR spectra of free-base and various metallocorroles points toward a negative sign of  $D$ , which is unusual for planar and nearly planar tetrapyrrolic compounds.<sup>35–37</sup> This phenomenon was attributed to the lower corrole symmetry (relative to porphyrins), which is further amplified by the asymmetric  $\pi$ -electron withdrawal effect generated by the perfluorinated aryl rings. The electron withdrawal toward the periphery of the molecule was confirmed by density functional theory calculations, which demonstrated that the electron spin density on the inner nitrogen atoms in corroles is much smaller compared to porphyrins.<sup>41</sup> Such “stretching” of the triplet molecular orbitals along one of the molecular axes enforces the corresponding electron spins to align in a head-to-tail configuration, resulting in a negative sign of  $D$ .<sup>35,42–44</sup> The proposed negative value of  $D$  allowed us to explain the unusual TREPR spectral polarization patterns observed in corroles differing by core metal ion and symmetry. Clearly, it

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**Figure 1.** Structures of (a) nonbrominated Ga-corrole Ga(pyr)(tpfc) and (b) brominated Ga-corrole Ga(pyr)(tpfc-Br<sub>8</sub>).

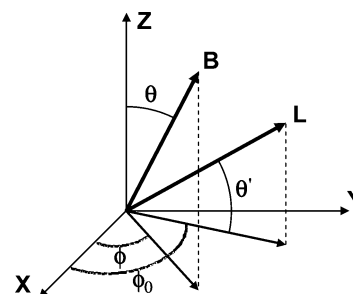
would be important to obtain more compelling evidence, which could evaluate the hypothesis regarding the negative sign of  $D$ . We believe that this can be accomplished by modifying the intersystem crossing (ISC) process to overpopulate selectively a specific dipolar axis, which would cause certain changes in the spectral polarization pattern.<sup>45–47</sup> If so, the analysis of these changes could examine our conclusion on the sign of the  $D$  parameter.

Here we report the TREPR study of newly synthesized  $\beta$ -pyrrole brominated Ga-corrole (Ga(pyr)(tpfc-Br<sub>8</sub>)) in comparison with the nonbrominated Ga-corrole (Ga(pyr)(tpfc)) (Figure 1), performed at the same experimental conditions. We believe that in the present case (contrary to the case of nonbrominated and brominated Al-corroles),<sup>36</sup> when both the corroles exhibit TREPR spectra, the analysis of their lineshapes could allow us not only to characterize excited state properties of the new corrole and to reveal bromination effects but also to further validate our conclusion concerning the sign of the  $D$  parameter in these complexes.

## Experimental Section

Nonbrominated Ga-corrole, Ga(pyr)(tpfc), was synthesized as described elsewhere.<sup>41</sup> Brominated Ga-corrole, Ga(pyr)(tpfc-Br<sub>8</sub>), was synthesized as follows: initially adding bromine (200  $\mu$ L, 1.6 mmol) to a benzene solution (3 mL) of Ga(pyr)(tpfc) (30 mg, 32  $\mu$ mol), and after an overnight stirring, the solvent was evaporated by a stream of N<sub>2</sub>. The residue was passed through a column of silica with CH<sub>2</sub>Cl<sub>2</sub>/pyridine 100:1. After recrystallization from *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, Ga(pyr)(tpfc-Br<sub>8</sub>) was obtained in 90.1% yield (45 mg, 29  $\mu$ mol). <sup>19</sup>F NMR (188 MHz, CD<sub>3</sub>OD,  $\delta$ ): −139.9 (dd, 3J(F,F) = 23.9, 4J = 8.3 Hz, 2F; ortho-F), −140.2 (dd, 3J(F,F) = 23.9, 4J = 7.7 Hz, 4F; ortho-F), −156.1 (t, 3J(F,F) = 20.3 Hz, 2F; para-F), −156.2 (t, 3J(F,F) = 19.4 Hz, 1F; para-F), −166.6 (m, 4F; meta-F), −167.00 (m, 2F; meta-F). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>, nm,  $\epsilon \times 10^{-3}$  M<sup>−1</sup> cm<sup>−1</sup>): 436 (103.5), 586 (11.0), 612 (8.8). MS (TOF LD-)  $m/z$  (%) 1574 (100%) [M], 1494 [M − pyridine] (15%).

The LC (E-7, Merck Ltd.), a eutectic mixture of R<sub>1</sub>–C<sub>6</sub>H<sub>5</sub>–C<sub>6</sub>H<sub>5</sub>–CN [R<sub>1</sub> = C<sub>5</sub>H<sub>11</sub> (51%); R<sub>2</sub> = C<sub>7</sub>H<sub>15</sub> (25%); R<sub>3</sub> = C<sub>8</sub>H<sub>17</sub>O (16%); R<sub>4</sub> = C<sub>5</sub>H<sub>11</sub>C<sub>6</sub>H<sub>5</sub> (8%)], was used without further purification. Toluene (Merck Ltd.) was dried over molecular sieves and kept under vacuum during sample preparation. For the TREPR experiments, corroles were first dissolved in toluene (concentrations used  $\sim 5 \times 10^{-4}$  M), which was then evaporated, and the LC was introduced into the 4 mm o.d. Pyrex tube. The samples were degassed by several freeze–pump–thaw cycles and sealed under vacuum.



**Figure 2.** Relation between the molecular frame of reference ( $X$ ,  $Y$ ,  $Z$ ), the magnetic field **B**, and the LC director **L**, defined in the laboratory frame of reference. The orientational parameters are described in the Experimental Section.

The photoexcitation wavelengths for TREPR measurements were 590 nm for nonbrominated Ga-corrole and 593 nm for brominated Ga-corrole, which correspond to the bands in the low-energy portion of their absorption spectra. The samples were illuminated by an optical parametric oscillator (Panther III, Continuum Corp.) pumped by the third harmonic (355 nm) of an Nd:Yag laser (Surelite II, Continuum Corp.: 5–8 mJ/pulse, 10 Hz repetition rate, and 10 ns pulse duration).

The orientation of the LC director, **L**, with respect to the magnetic field, **B**, was determined from the sign of the diamagnetic susceptibility,  $\Delta\chi = (\chi_{\parallel} - \chi_{\perp})$ .<sup>48</sup> LC E-7 is characterized by  $\Delta\chi > 0$ , and its phase transitions are:



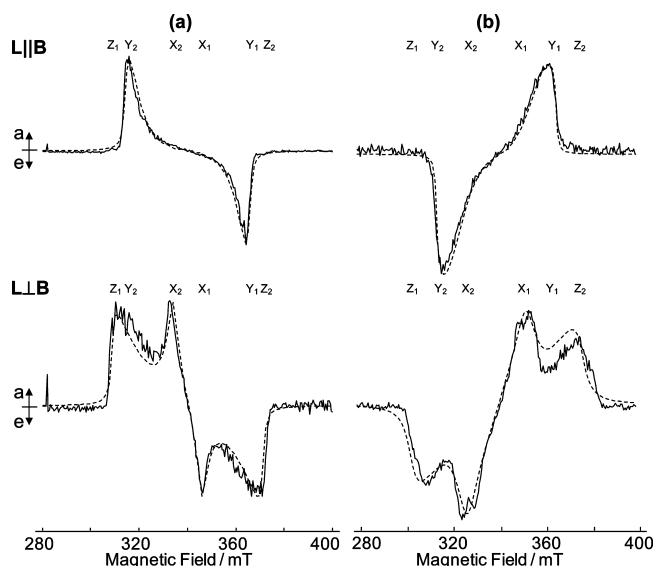
The default orientation in the nematic phase is **L**||**B**. Rotating the frozen sample by 90° about an axis perpendicular to the magnetic field yields the director orientation **L**⊥**B**.

Analysis of the TREPR spectra and the time profiles of the magnetization,  $M_y(t)$ , obtained from the corroles oriented in a uniaxial LC, was performed as described elsewhere.<sup>49–51</sup> The orientational distribution functions  $f(\phi)$  and  $f(\theta')$  describe the alignment of the molecules embedded in LC relative to the LC director **L**. The Gaussian  $f(\phi) = N_{\phi} \exp[-(\phi_0 - \phi)^2/\sigma_{\phi}^2]$ , with the variance  $\sigma_{\phi}$ , determines the probability of the guest molecule to rotate by an angle  $\phi$ , about an axis perpendicular to the molecular plane, and having a peak probability at an angle  $\phi_0$  (Figure 2). The function,  $f(\theta') = N_{\theta'} \cos^2 \theta' \exp[-\theta'^2/\sigma_{\theta'}^2]$ , characterizes the fluctuations of the molecular plane about the director **L** with the variance  $\sigma_{\theta'}$ , where  $\theta'$  is the angle between the molecular plane and **L** (Figure 2). Generally, the orientational parameters  $\phi_0$ ,  $\sigma_{\phi}$ , and  $\sigma_{\theta'}$  are related to the order

**TABLE 1: Magnetic and Orientational Parameters Evaluated by TREPR for the Photoexcited Triplet States of the Nonbrominated and Brominated Ga-corroles and Brominated Al-corrole, in E-7 at 170–175 K**

sample	magnetic parameters			orientational parameters		
	$D^a$	$ E ^a$	$A_X:A_Y:A_Z^c$	$\sigma_{\theta'}$	$\phi_0$	$\sigma_{\phi}$
Ga(pyr)(tpfc)	−294	60	0.6:0.4:0.0	29	85	17
Ga(pyr)(tpfc-Br <sub>8</sub> )	−341	42	0.3:0.3:0.4	25	70	20
Al(pyr) <sub>2</sub> (tpfc-Br <sub>8</sub> ) <sup>b</sup>	−318	61	0.3:0.3:0.4	15	90	30

<sup>a</sup>  $\times 10^{-4} \text{ cm}^{-1}$  (uncertainty is  $\pm 5\%$ ). <sup>b</sup> The parameters are taken from ref 36. <sup>c</sup> The triplet sublevel population ratios are normalized to unity.



**Figure 3.** TREPR spectra ( $\chi''(B)$  presentation) of (a) nonbrominated Ga-corrole and (b) brominated Ga-corrole, embedded in LC E-7 at 175 K, at  $L||B$  and  $L\perp B$  orientations. Experimental spectra (solid lines) were taken 1320 (a) and 1200 ns (b) after the laser pulse photoexcitation at 590 (a) and 593 nm (b). Positive and negative signals with respect to the baseline indicate absorption a and emission e, respectively. Dashed curves, superimposed on the experimental spectra, are computer simulations with the best-fit parameters given in Table 1. The canonical orientations are indicated on the top of each spectrum.

parameters  $S_{||}$  and  $S_{\perp}$  by mean value integrals,  $S_{||\perp} = (1/2)f(\alpha)(3\cos^2\alpha - 1)d\Omega$ , where  $S_{||}$  and  $S_{\perp}$  are obtained by substituting  $f(\alpha)$  in the corresponding equations with  $\alpha = 0^\circ$  and  $90^\circ$  for  $S_{||}$  and  $S_{\perp}$ , respectively.

In all EPR experiments, the kinetic curves did not depend upon microwave power (in the range of 22–93 mW) and did not exhibit any oscillations, indicating the absence of the saturation effects.<sup>52</sup> The extracted ZFS parameters,  $D$  and  $E$ , the relative population ratios  $A_X:A_Y:A_Z$ , and orientational parameters are summarized in Table 1.

## Results and Discussion

Photoexcitation of the brominated and nonbrominated Ga-corroles in a liquid crystalline matrix gives rise to the spin polarized TREPR spectra, which are presented in Figure 3. Inspection of Figure 3 shows that the triplet spectra of the complexes exhibit similar lineshapes but opposite polarization patterns, namely, an absorption/emission (a/e) for nonbrominated Ga-corrole and an emission/absorption (e/a) for brominated Ga-corrole (Figure 3). At an  $L||B$  orientation, both spectra do not display any contribution from the out-of-plane canonical orientation, as typical of planar and near planar molecules.<sup>53</sup> In

addition to being verified by line shape analysis, this result is also in accord to the finding that the corroles, even fully substituted at the peripheral positions, are able to maintain a planar conformation.<sup>54</sup>

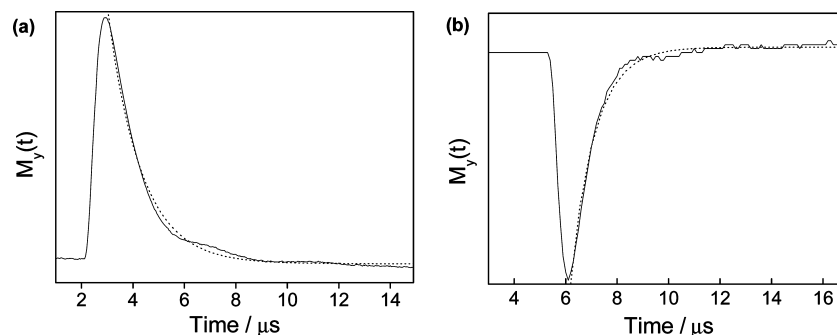
The computer simulations of the spectra show additional differences in their parameters. More specifically, the brominated Ga-corrole is characterized by a larger value of ZFS parameter  $|D|$  as compared to the nonbrominated Ga-corrole (Table 1). In addition, contrary to the case of the nonbrominated complex, the spectral line shape of brominated Ga-corrole displays a slight but noticeable asymmetry. This effect is manifested by a minor discrepancy between the experimental and simulated spectral lineshapes, calculated by employing a program which does not take into account spectral asymmetry.

These findings can be attributed to the spin–orbit coupling (SOC) effects resulting from the insertion of the heavy bromine atoms into the Ga-corrole macrocycle. In this case, the  $|D|$  value should be corrected to include both the dependency of the dipole–dipole interaction and the SOC. Indeed, the larger SOC in the brominated complex could contribute both to its ZFS parameter  $|D|$  value and to the spectral g-anisotropy.<sup>38,55,56</sup>

It should be noticed here that estimation of SOC effects is not a trivial task.<sup>57</sup> Generally, the SOC is the main spin-dependent magnetic interaction, which causes the mixing of the singlet and triplet states. At first glance, it would seem that insertion of eight heavy bromine atoms (the atomic SOC constant of bromine is  $2460 \text{ cm}^{-1}$ ) into the corrole skeleton should result in drastic changes of the photophysical parameters of the brominated complex as compared to the nonbrominated one. However, even in simple organic molecules, SOC effects depend on several factors and hence become difficult to predict.<sup>57–59</sup> Indeed, the Ga-corrole is not simple but represents a multicenter system with its molecular orbitals spread out over the entire molecule. It consists of various atoms, which are linked together by different chemical bonds and possess quite different individual SOC constant values. In this case, the SOC constant cannot be presented as a simple function of the effective SOC constants  $\xi_A$  of isolated atoms ( $2460 \text{ (Br)}$ ,  $800 \text{ (Ga)}$ ,  $350 \text{ (F)}$ ,  $76 \text{ (N)}$ ,  $28 \text{ (C)}$ ,  $151 \text{ (O)}$ , and  $0.24 \text{ (H)}$ , all in  $\text{cm}^{-1}$ ).<sup>57–59</sup> Thus, for a polyatomic system such as brominated Ga-corrole, the SOC constant is essentially a phenomenological parameter whose effective value may significantly differ from those of the atoms comprising the complex.<sup>38,58,60,61</sup> This is probably what causes the SOC influence on the spectral g-anisotropy and absolute value of the ZFS parameter  $D$  in brominated Ga-corrole to be noticeable but not drastic (Figure 3 and Table 1). Nevertheless, the enhanced SOC becomes large enough to change the triplet sublevel population ratio in the brominated complex, which results in the inversion of the spin polarization pattern of its spectra, as compared to that of nonbrominated Ga-corrole.

Generally, in planar or nearly planar molecules such as porphyrins and their analogues, enhanced SOC leads to an overpopulation of the out-of-plane Z-axis.<sup>45,46,49,62,63</sup> In this case, for the compounds with a positive  $D$ , the population ratios of the triplet sublevels obey  $A_Z \gg A_X, A_Y$ , and the spectra exhibit an a/e polarization pattern. On the other hand, in porphyrinoids with reduced SOC, a preferential population of the in-plane axes is found ( $A_X$  or  $A_Y$ ), which is reflected by an inverted e/a polarization pattern in the spectra.<sup>45,46,64–66</sup> This effect was demonstrated for a large number of tetrapyrroles. For example, in both Zn porphyrin and Pd porphycene, the metal–ring d– $\pi$  interaction is strong enough to change the triplet sublevel population as compared to those in their free-base complexes.





**Figure 4.** Kinetic profiles of triplet states of Ga-corroles in LC at **L||B** orientation. (a) Nonbrominated Ga-corrole taken at 175 K, at the low-field absorption outermost line. (b) Brominated Ga-corrole taken at 170 K, at the low-field emission outermost line. Superimposed dotted lines are the best fit of the corresponding experimental curves. Parameters extracted:  $T_1 = 1.3 \mu\text{s}$  for nonbrominated Ga-corrole and  $T_1 = 0.9 \mu\text{s}$  for brominated Ga-corrole.

As a result, the metallocomplexes display inverted spectral polarization patterns as compared to their free-base analogues. Similarly, free-base, Mg, and Na porphyrins possess *e/a* polarization patterns, while Ga, Zn, Y, Pd, and La complexes exhibit *a/e* patterns.<sup>49,63,66–68</sup> Furthermore, free-base and Zn porphycenes exhibit an *e/a* pattern contrary to Pd complexes with an *a/e* pattern.<sup>62,69</sup> In phthalocyanines (Pc), the free base displays an *e/a* pattern, whereas Zn and Ge complexes show an *a/e* pattern.<sup>46</sup>

As far as we know, there are only a few exceptions to these findings, i.e., the inclusion of Zn into the porphycene core<sup>62</sup> and of Ge into the center of tetraphenylporphyrin (TPP) (containing two OH groups or two Cl ions),<sup>66</sup> which do not lead to an overpopulation of their Z-axis. This is reflected by the close similarity of their TREPR spectral polarization patterns with those of free-base porphycene and free-base TPP, respectively. In the case of Zn porphycene, the small effect of the Zn incorporation on the population rates was attributed to the weak interaction of the metal with the  $\pi$ -electron system of the porphycene ring due to the out-of-plane Zn location, which was confirmed by X-ray data.<sup>62</sup> For the Ge porphyrins, the effect was interpreted by a weak interaction between the  $d_{\pi}$ -orbital of Ge and LUMO ( $e_g$ ) of the porphyrin ligand, resulting in a small SOC. This conclusion was confirmed by molecular orbital calculations.<sup>66</sup> It was demonstrated that the incorporation of two bromine ions into GeTPP leads to the dominant population of the Z-axis, due to the heavy atom effect of the bromines. The authors underlined the unusual ISC process in Ge(TPP)(OH)<sub>2</sub> and Ge(TPP)Cl<sub>2</sub> and showed that in several other metalloporphyrins and phthalocyanines (including GePc(OH) and GePc(OH)<sub>2</sub>) the heavy atom effect operates conventionally, resulting in preferential population of the out-of-plane axis.<sup>66</sup>

In our previous studies, it was found that the free-base and metallocorroles containing metal ions such as Ga(III), Sn(IV), Sb(III), and Sb(V) display the same spectral polarization patterns. In other words, there is no indication of a heavy atom effect, i.e., changes in the ISC parameters due to the insertion of a heavy atom into the molecule. This points to a similar population ratio of the triplet sublevels in the free-base corrole and in the different metallocomplexes.<sup>35–37</sup> These unusual results were explained by the experimentally determined domed structure of the penta-coordinated corroles, which decreases the  $d-\pi$  electronic interaction between the central metal and the corrole ring.<sup>35,36</sup> As mentioned above, a similar effect was found in Zn porphycenes, with weak interaction of the metal ion with the porphycene ring due to out-of-plane metal location.<sup>62,69</sup>

In this context, we would like to emphasize the experimentally determined, and noticeable, effect of the axial ligands on the

excited state properties of the corroles, namely, the ISC rates of the triplet sublevel population and ZFS parameter values. This effect, found for corroles containing either diamagnetic or transition metal central ions, was attributed to the modification of the electronic metal–ring ( $d-\pi$ ) interaction caused by axial ligation.<sup>36–38</sup>

It should be noted that in the corroles studied analysis of the triplet lineshapes allowed full assignment of the molecular frame of reference with respect to the laboratory frame. The possibility of the molecular Z-axis lying in the molecular plane of the corroles was ruled out. This is because in the corroles the spectral width in the **L||B** configuration is smaller than that taken in **L⊥B** (Figure 3) (as opposed to sapphyrins<sup>43</sup> and stretched porphycenes<sup>44</sup>).

As mentioned above, a negative  $D$  was assigned for all corroles studied previously. With a negative  $D$  value, an inverted polarization pattern should be obtained as compared to the case of a positive  $D$  value. Namely, in compounds with an enhanced SOC, the overpopulation of the out-of-plane Z-axis ( $A_Z \gg A_X, A_Y$ ) will result in *e/a* spectral polarization pattern, while in compounds with a reduced SOC the preferential population of the in-plane axes ( $A_X$  or  $A_Y$ ) will be reflected by inverted *a/e* polarization pattern of the spectra.

In light of these findings, the computer simulations of the Ga-corrole spectra were performed with a negative  $D$  as suggested. The analysis reveals that in nonbrominated Ga-corrole, with *a/e* spectral polarization, the triplet sublevels corresponding to the in-plane molecular axes are overpopulated, i.e.,  $A_X, A_Y \gg A_Z$ , while in brominated Ga-corrole, with *e/a* spectral polarization, the out-of-plane triplet sublevel that corresponds to the out-of-plane molecular axis is preferentially populated, namely,  $A_X, A_Y < A_Z$  (Table 1).

In addition, the analysis reveals that the orientational parameters of the brominated and nonbrominated corroles in LC, as well as their kinetics, are similar to each other and to other corroles studied previously (Figure 4, Table 1). As in other corroles, it permits us to rule out the possibility of the molecular Z-axis lying in the molecular plane. Assuming that the molecule is oriented with its long molecular axis parallel to the LC director, with an obtained angle of  $\phi_0 \sim 70^\circ$ , we conclude that the Y-axis lines up with the long molecular axis (Figure 2), which implies that the Z-axis is perpendicular to the corrole macrocycle plane.

Indeed the above data support our suggestion that the studied corroles are characterized by a negative  $D$  value and that the insertion of eight bromine atoms to the  $\beta$ -pyrrole positions of the Ga-corrole macrocycle enhances the ISC process in the

photoexcited molecule, which results in a selective overpopulation of the molecular out-of-plane *Z*-axis.

Moreover, in one of our recent studies, the identical bromination of an Al-corrole macrocycle led to a much more efficient corrole triplet state formation, as compared to what was observed in the nonbrominated complex.<sup>36</sup> Unfortunately, a low triplet quantum yield in the nonbrominated Al-corrole did not allow detection of its TREPR spectrum, and the bromination effect which caused significant increase of the triplet state formation was evaluated using the optical emission data. On the basis of the findings that the bromination of the tetrapyrrolic macrocycle enlarges SOC strength in the complex,<sup>68,70–74</sup> we utilized this approach for changing the dominant ISC path in the Ga-corrole to overpopulate selectively the molecular out-of-plane *Z*-axis.

Here, we would like to deepen the discussion on our conclusion regarding the negative sign of the ZFS parameter *D* in all studied corroles. First of all, the unusual behavior of the corroles in terms of the polarization patterns of their TREPR spectra should be underlined. As previously mentioned, unlike another tetrapyrroles, all tpfc's (either free-base or coordinated diamagnetic central metal ions) exhibit similar a/e polarization patterns in their TREPR spectra. It was demonstrated that the incorporation of such different ions (Ga, Sn, Sb) into the corrole core practically does not affect their spectral polarization patterns, as compared to the free-base complex, indicating a similarity of the triplet sublevel population ratios in all these corroles. The phenomenon was attributed to weak interaction of the central metal ion and the corrole ring due to the dome-structure of the penta-coordinated metallocorroles. (For example, the central Ga(III) ion is displaced by  $\sim 0.41 \text{ \AA}$ <sup>41</sup> and the Sn(IV) ion by  $\sim 0.6 \text{ \AA}$ <sup>36</sup> out of the corresponding corrole plane).

At first glance, it seems logical to suggest that the peripheral fluorine atoms (the SOC constant of fluorine is  $370 \text{ cm}^{-1}$ ) in all tpfc's increase SOC, enough to overpopulate the out-of-plane *Z*-axis, which in the case of a positive *D* will result in an a/e polarization pattern. This would be in agreement with the TREPR spectra of MgTPP, which was previously found to invert its polarization pattern (from e/a to a/e) upon perfluorination of the peripheral phenyl groups.<sup>75</sup> The authors demonstrated that the heavy atom effect achieved by sequential incorporation of 20 fluorine atoms in the porphyrin results in the preferential population of its out-of-plane *Z*-axis, which in turn causes inversion of the spectral polarization pattern. However, we believe that this is not true for our case. Certainly, insertion of eight bromine atoms (the SOC constant of bromine is  $2460 \text{ cm}^{-1}$ ) into the Ga-corrole macrocycle should increase SOC and thus amplify the influence of the fluorine atoms in the overpopulation of the *Z*-axis. In this case, we should observe the same polarization patterns in the spectra of nonbrominated Ga-corrole and brominated Ga-corrole. However, bromination of the Ga-corrole results in the inversion of the spectral polarization pattern, namely, inversion of the a/e polarization pattern observed in the nonbrominated Ga-corrole, to e/a pattern in the brominated Ga complex (Figure 3). This effect can be interpreted in terms of the negative *D* sign in the corroles. Evidently this is the case, and the overpopulation of the *Z*-axis is reflected by the e/a polarization pattern of the brominated corrole spectra.

As to the influence of the fluorine atoms on the ISC process in the corroles, we suppose it is not strong enough to lead to the dominant population of the dipolar *Z*-axis. This is because the net fluorination effect on the SOC strength is somewhat ambiguous since it depends on a variety of parameters such as the site of fluorination, the number of fluorine atoms, and their

mutual location in the molecule.<sup>76,77</sup> In this context, we should mention that the *Z*-axis overpopulation was not found in free-base pentafluorotetraphenyl porphyrin, which as well as perfluorinated MgTPP<sup>75</sup> contains 20 fluorine atoms but exhibits a similar population ratio of the triplet sublevels as a regular free-base tetraphenylporphyrin.<sup>78</sup>

To summarize, comparison of the TREPR spectra of the brominated and nonbrominated Ga-corroles with those of recently examined free-base, Al(III), Sb(III), Sb(V), and Sn(IV) complexes, verifies the regular trends in the corrole structure–function relationships. In other words, the peculiarities observed in the TREPR spectra of the corroles relative to other porphyrinoids can be interpreted in terms of the distinguishing features in the corrole structure and symmetry. We believe that the results are in line with our previous suggestions regarding the influence of the central metal, axial ligands, and substituents on the corrole excited state properties and, in particular, with an assumption that all studied tpfc complexes bearing diamagnetic central metal ions as well as free-base corrole are characterized by a negative ZFS parameter *D*.

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