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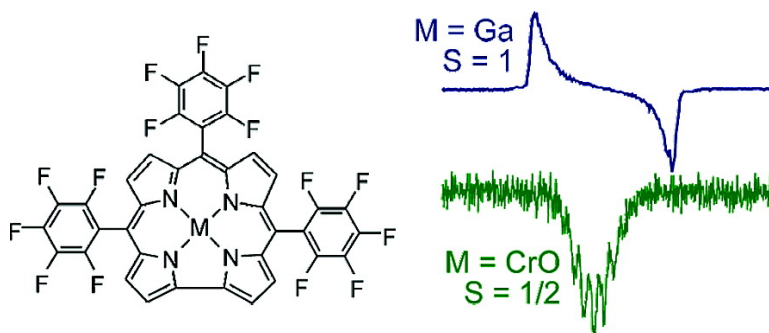
Electron Spin Dynamics in Photoexcited Diamagnetic and Paramagnetic Corroles

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Electron Spin Dynamics in Photoexcited Diamagnetic and Paramagnetic Corroles

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Abstract: Three corroles, which differ by their cavity's core, namely, diamagnetic free-base tris-(pentafluorophenyl)corrole and its gallium(III) complex and the paramagnetic oxo-chromium(V) complex, were studied by steady-state and time-resolved electron paramagnetic resonance (EPR) spectroscopy. The magnetic and orientational parameters of the corroles, oriented in a nematic liquid crystal, were determined and interpreted in terms of their structure, geometry, and excited states spin dynamics. It was shown that both diamagnetic corroles, photoexcited to their triplet states, exhibit similar EPR line shapes, which is characterized by a negative zero-field splitting parameter, D, whose origin is due to molecular "stretching". Photoexcited Cr(V)O-corrole exhibits polarized ground-state EPR spectrum in emission mode. This polarization stems from the sequence of photophysical and photochemical reactions, involving the formation of the trip-quartet/trip-doublet composite states and their selective quenching via a charge transfer state.

Introduction

Corroles, first synthesized by Johnson and co-workers (1965), are aromatic macrocycles with the basic structure of the ring framework of vitamin B_{12},[1,2] which plays a vital role in the metabolism and functioning of living cells. These compounds are typified by their smaller cavity size and different symmetry as compared to porphyrins. Evidently, their differences should be reflected by their photophysical and photochemical properties. One should also expect their macrocycle structure to modify the electronic properties of the metal ion inserted into the cavity, thus affecting its chemical reactivity.[3] This was demonstrated in extensive investigations of their unique coordination chemistry [4] and the recent advances in utilization of metallocorroles as catalysts.[5]

In the present study, we report on the excited states of 5,-10,15-tris(pentafluorophenyl)corrole and the corresponding gallium(III) and oxo-chromium(V) complexes, i.e., H_3(tpfc), Ga(tpfc), and CrO(tpfc), respectively (Figure 1). This specific corrole was chosen because it is by far the most stable one and is nowadays considered as the prototype corrole.[6,7]
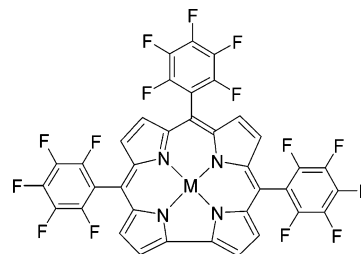
M = H₃, Ga, CrO

Figure 1. Corroles structure.

While H_3(tpfc) and Ga(tpfc) in their ground state are diamagnetic, CrO(tpfc) is paramagnetic. Thus, light excitation of H_3(tpfc) and Ga(tpfc) generates an excited triplet state, which is a two-spin system. Photoexcited CrO(tpfc) is a three-spin system, consisting of a doublet, Cr(V), d^1 configuration, and a ring triplet. Evidently, the different spin systems of the three corroles makes time-resolved electron paramagnetic resonance (TREPR) spectroscopy suitable for monitoring the spin dynamics in these compounds in the time regime of 150−200 ns, i.e., far below their triplet lifetime. All TREPR experiments were carried out using a nematic liquid crystal (LC) as a solvent. LCs are advantageous over traditional isotropic solvents, as they allow monitoring spin systems over a wide range of temperatures.[8−11]

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From the TREPR spectra obtained in isotropic and LC environments, important structural and dynamic parameters can be obtained. We mention briefly some of them: (1) the dipolar interaction in terms of the zero-field splitting (ZFS) parameters, including the absolute values of *D* and *E*; (2) orientational parameters relating the dipolar frame of reference with respect to the director **L**, of the LC. This allows to obtain structural features not available by other methods; (3) kinetic and spin dynamics parameters of paramagnetic transients in terms of electron spin polarization.[11,12] The rationale in choosing these compounds lies in their different structures and magnetic properties, which represent different classes of corroles, namely, free-base, diamagnetic, and paramagnetic metallocorroles.

Experimental Section

H$_3$(tpfc), Ga(tpfc) (containing one molecule of coordinated pyridine), and CrO(tpfc) were synthesized as described elsewhere.[13−15] The LC (E-7, Merck Ltd., dielectric constants $\epsilon_{||}$ = 19.6, $\epsilon_{\perp}$ = 5.1), an eutectic mixture of R$_i$C$_6$H$_5$C$_6$H$_5$CN: R$_1$ = C$_5$H$_{11}$ (51%); R$_2$ = C$_7$H$_{15}$ (25%); R$_3$ = C$_8$H$_{17}$O (16%); R$_4$ = C$_5$H$_{11}$C$_6$H$_5$ (8%), was used without further purification. Toluene (Merck Ltd.) was dried over molecular sieves and kept under vacuum during sample preparation. The corroles were first dissolved in toluene (concentrations used ∼5 × 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 on a vacuum line and sealed under vacuum. For the triplet−triplet absorption experiments, the samples in toluene were diluted to ∼2 × 10^{-7} M to avoid concentration effects.
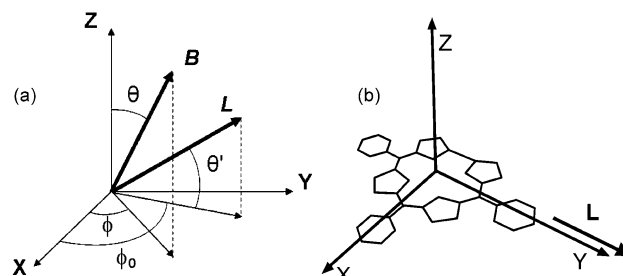
For both triplet−triplet absorption and EPR measurements, photoexcitation wavelengths correspond to the bands in the low-energy portion of the absorption spectra (Q-band) of H$_3$(tpfc), Ga(tpfc), and CrO(tpfc) (574, 590, and 556 nm, respectively). The samples were photoexcited by a OPO (Panther III, Continuum Corp.) pumped by the third harmonic (355 nm) of a Nd:Yag laser (Surelite II, Continuum Corp.: 5 mJ/pulse, 10 Hz repetition rate and 10 ns pulse duration).

Triplet−triplet absorption measurements were performed using a homemade laser flash photolysis setup. Light-induced absorbance changes in the samples were recorded using a continuous 75 W xenon lamp, a monochromator (Jarrell Ash 82-410), and photomultiplier (Hamamatsu R928). The data were collected using a LeCroy 9400 digital oscilloscope. The triplet decay times were extracted by computer fittings of the relevant kinetic traces. Steady-state EPR experiments were performed with a Bruker ESP 380 EPR spectrometer (100 kHz field modulation). TREPR measurements (response time of 150−200 ns) were carried out using the same setup but with field modulation disconnected, as described elsewhere.[11,16]

The orientation of the LC director, **L**, with respect to the magnetic field, **B**, was determined from the sign of the diamagnetic susceptibility, $\Delta\chi$ ($\Delta\chi = \chi_{||} - \chi_{\perp}$).[9] E-7 is characterized by $\Delta\chi > 0$ and its phase transitions are described by the following scheme:

$$crystalline \xleftrightarrow{210\ K} soft\ crystalline \xleftrightarrow{263\ K} nematic \xleftrightarrow{333\ K} isotropic$$

where, the default orientation in the nematic (fluid) phase is **L**||**B**. Line

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Figure 2. (a) Molecular frame of reference (*X*, *Y*, *Z*) and its relation to magnetic field **B** and the LC director, **L**, defined in the laboratory frame of reference. The orientational parameters are defined in the text. (b) Molecular structure and the most probable orientation of the corroles in E-7, as deduced from line shape analysis.

shape analysis of the TREPR spectra was described in details in previous papers.[17,18] Here we provide the reader with a brief description of the analysis using the density matrix formalism.[17,19]

The EPR spectra χ''(**B**,*t*), taken at different sample orientations, with respect to the external magnetic field, **B**, is given by:

$$\chi''(\mathrm{B},t) \propto \sum_{\substack{i=1,2\\j=i+1}} \int_0^{\pi/2} f(\theta') \int_{\theta_{\min}}^{\pi/2} \int_0^{\pi/2} \mathrm{Im}[\rho_{ij}(\theta,\phi,t)]\, f(\phi) \mathrm{d}\theta\ \mathrm{d}\phi\ \mathrm{d}\theta'$$

(1)

where $\rho_{ij}(\theta,\phi,t)$ is the density matrix element connecting the *i*, *j* levels and θ and ϕ are the angles between the external magnetic field **B** and the molecular axes. The distribution functions $f(\theta')$ and $f(\phi)$ express the fluctuation of the solute prior to freezing. The Gaussian $f(\phi) = \exp(-[\phi_0 - \phi]^2/\sigma_\phi^2)$ with the variance σ_ϕ^2 gives the probability of the chromophore rotation by an angle ϕ, about an axis perpendicular to the molecular plane, and having a peak probability at an angle ϕ_0. The function $f(\theta') = \cos^2 \theta' \exp(- \theta'^2/\sigma_{\theta'}^2)$ expresses the fluctuations of the molecular plane about the director, **L**, with the variance $\sigma_{\theta'}^2$, where θ' is the angle between the molecular plane and **L**. The angle relations between the molecular and laboratory place of reference are shown in Figure 2a. The summation is on each of the two allowed $\Delta M_S = \pm 1$ EPR transitions. In all EPR experiments, the kinetic curves did not depend on microwave power (22−93 mW) and did not exhibit any oscillations, satisfying underdamping conditions.[20,21]

Results and Discussion

Free-Base and Gallium Corroles. The photoexcited triplet lifetimes of H$_3$(tpfc) and Ga(tpfc) at room temperature were determined by nanosecond laser flash photolysis to be ∼800 μs and ∼80 μs, respectively, ensuring nonsilent EPR behavior. The former value is in agreement with literature data.[14] With CrO(tpfc), no photoexcited triplet state could be optically observed. Nevertheless, as we shall show below, the analysis of the TREPR data suggests that the triplet state does exist but decays very fast, escaping direct EPR detection.

Spin-polarized triplet spectra of H$_3$(tpfc) and of Ga(tpfc) oriented in a LC are shown in Figure 3. Both spectra exhibit an absorption/emission (a/e) pattern and in the parallel orientation do not display any contribution from the out-of-plane canonical

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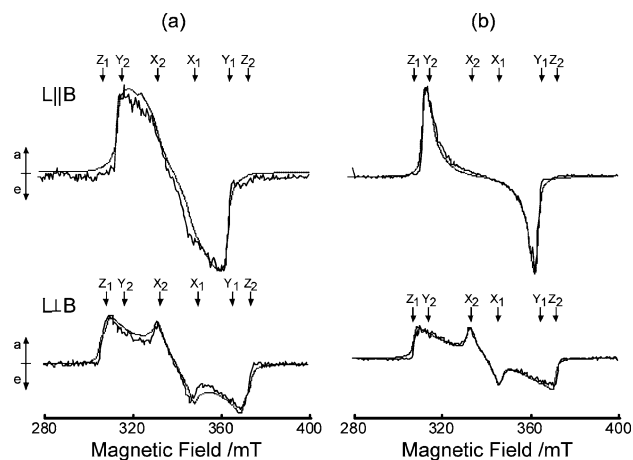
Figure 3. TREPR spectra (χ''(B) presentation) of the corroles embedded in E-7 at 175 K: (a) H$_3$(tpfc); (b) Ga(tpfc). Spectra were taken 1 μs after the laser pulse photoexcitation at 574 nm (a) and 590 nm (b) (7 mJ/pulse). Positive and negative signals indicate absorption (a) and emission (e), respectively. Dotted curves, superimposed on the experimental spectra, are computer simulations with the best-fit parameters given in Table 1. The canonical orientations are indicated by arrows on the top of each spectrum.

Table 1. Magnetic and Orientational Parameters Extracted for the Triplet State of the H$_3$(tpfc) and Ga(tpfc) Oriented in the LC at 175 K

sample	D^a	$|E|^a$	A_X:A_Y:A_Z	$\sigma_\theta{}^b$	$\phi_0{}^b$	$\sigma_\phi{}^b$
H$_3$(tpfc)	−302	51	0.5:0.6:0.0	30	80	15
Ga(tpfc)	−299	60	0.7:0.5:0.0	30	90	15
H$_2$TPP^c	371	90	1.0:0.6:0.3	12	40	25
ZnTPP^c	298	98	0.0:0.0:1.0	12	45	25
H$_2$OEPC^d	280	50	1.0:0.9:0.5			
ZnOEPC^d	266	80	1.0:0.8:0.2			
H$_5$Sap^{2+e}	−285	75	1.0:0.43:0.3			
"stretched" porphycene^f	−318	43	0.7:0.8:1.0			

$^a \times 10^{-4}$ cm^{-1} (in present calculation $\pm$ 5%). ^{b} In degrees (in present calculation $\pm$ 5%). ^{c} Taken from ref 17. ^{d} Octaethylporphycene, taken from ref 24. ^{e} Sapphyrin dication in LC ZLI-1083, taken from ref 30. ^{f} Octaethyl-5,6,17,18-tetrahydro[22]porphyrin, taken from ref 29.

orientation, as typical of planar molecules[22] and verified by the line shape analysis. These findings point toward a positive sign of the zero-field splitting (ZFS) parameter D,[23] as found in a number of related terapyrrolic compounds, such as porphyrins,[16] porphycenes,[24] and phthalocyanines.[25] With $D > 0$, line shape simulation of both triplet spectra results in selective singlet−triplet population rates A_i ($i = x, y, z$), obeying $A_z \gg A_x, A_y$, namely, overpopulation of the out-of-plane Z axis in both corroles, as reflected by the a/e polarization pattern (Table 1). Selective population of the out-of-plane Z-axis is due to enhanced spin−orbit coupling (heavy atom effect),[26] found in the triplets of ZnTPP,[23] Zn-substituted chlorophyll,[27] GaTPP,[25] and Ga(tpfc) studied here. With the above considerations, one would expect an e/a polarization pattern in the case of H$_3$(tpfc), as found in many other free-base porphyrins. However, as inferred from Figure 3a, the triplet H$_3$(tpfc) behaves differently

with respect to the phase pattern i.e., displaying the a/e pattern, which implies out-of-plane active axis.

This discrepancy can be resolved by assuming $D < 0$ for both corroles. A negative D value was previously found in stretched porphycenes and sapphyrin[28,29] and was interpreted in terms of elongated molecular structures, which enforce the triplet electron spins to align in a head-to-tail configuration. In corroles, such "stretching" may result from the intrinsically lower symmetry (relative to porphyrins), which is further amplified by the asymmetric π-electron withdrawal effect caused by perfluorinated aryl rings, located asymmetrically with respect to the Y molecular axis (see below) (Figure 2b). This electron withdrawal toward the periphery of the molecule is confirmed by density functional theory calculation, which demonstrated that the spin density on the inner nitrogen atoms in corroles is much smaller compared to porphyrins.[14] Such electronic reconfiguration results in "stretching" of the triplet molecular orbitals along one of the molecular axis, in our case the Y-axis. Although their cavity size, defined by the four nitrogen atoms, is smaller (7.21 Å^2) than that of porphyrin (8.29 Å^2),[24] the stretching effect in H$_3$(tpfc) and Ga(tpfc) increases the effective size of their cavities (i.e., the distance between triplet electrons) as reflected by the smaller D values compared to porphyrins (Table 1).[28,29]

Our conclusion on the sign of D is based on the following arguments: (a) Sapphyrins[30] and stretched porphycenes[29] are characterized by a frame of reference where Z-axis lines up with the molecular plane. This axes configuration results in spectral width larger for **L∥B** than that for **L⊥B**. On the other hand, inspection of Figure 3 shows that the width of the triplet spectra of H$_3$(tpfc) and of Ga(tpfc) is smaller in the **L∥B** configuration than that taken for **L⊥B**. This is typical for planar and near planar tetrapyrrolic molecules, where the Z-axis is out of the molecular plane. (b) For both corroles the spectral intensity at **L∥B** orientation is larger than that of **L⊥B**, implying that in-plane X and Y axes are overpopulated. This situation is common to free-base porphyrins. Furthermore, the computer simulation of the triplet line shapes allows to fully assign the corroles frame of reference with respect to the laboratory frame (Figure 2a). Assuming that the corrole molecule is oriented with its long molecular axis parallel to the LC director, and having $\phi_0 \sim 85°$ as obtained by the line shape analysis, we conclude that the Y-axis lines up with the long molecular axis (Figure 2b).

With these arguments, the polarization pattern a/e observed for both H$_3$(tpfc) and Ga(tpfc) could be explained only by having $D < 0$. Supporting evidence for $D < 0$ stems from the fact that X-ray data shows some deviation from planarity for the corrole molecule.[13] Moreover, spin density calculations result in significant withdrawal effect of the perfluorinated aryl rings, which intensifies such a deviation. Obviously, these arguments hold for corroles in their ground state. It is reasonable to assume that this effect will be stronger in the excited state. The slight molecular distortion combined with the asymmetric withdrawal effect (the latter does not appear in porphyrins) allows us to apply the point dipole approximation, i.e., $D \propto \{(1 - 3 \cos^2$

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$\theta)\}/\{r^3\}$, which for $\theta < 54.7°$ results in $D < 0$ (head-to-tail configuration). To summarize this part, the observed line shape, with $D < 0$, implies that the population rates obey the inequality, $A_x, A_y \gg A_z$, for both corroles.

It should be noticed that the free-base corrole $H_3(tpfc)$ and the metallocorrole $Ga(tpfc)$ exhibit practically the same magnetic and orientational parameters. It is attributed to the small cavity size which forces the metal ion out of the molecular plane.[14] Moreover, the withdrawal effect of the perfluorinated aryl rings decreases the interaction between the metal d-electrons and the π-electons of the corrole ring. Both effects lead to poor interaction of the metal with the corrole π-system. This behavior is close to that found for free-base and zinc porphycenes[24] but different from that found with free-base and Zn porphyrins,[16] where the metal strongly interacts with the π-system. The relationship between molecular structure and the sign of the ZFS parameters as well as the corresponding population rates A_i ($i = x, y, z$) are summarized in Table 1.

At this stage we exclude an alternative explanation of the a/e phase pattern in both $H_3(tpfc)$ and $Ga(tpfc)$. It assumes $D > 0$ and overpopulating of the out-of-plane Z-axis. Such overpopulation arises from enhanced spin−orbit coupling (SOC),[26] which, in our case, may be due to fluorine substitution in the corrole periphery. This enhanced SOC was reported to occur in fluorinated porphyrins.[31] Nevertheless, the fluorine effect on the SOC strength is somewhat ambiguous, since it depends on several parameters, namely, site of fluorination, number of fluorine atoms, and their mutual location in the molecule.[31,32] Moreover, Z-axis overpopulation was not observed with free-base tetra(perfluorophenyl)porphyrin, which, unlike the corroles, exhibits the same polarization pattern as H_2TPP.[33]

Chromium Corrole. The paramagnetic chromium ion in oxochromium(V) (Cr(V)O) complexes is characterized by a d^1 electronic configuration, displaying a steady-state EPR spectrum over a wide range of temperatures, i.e., 77−300 K.[34,35] Among these compounds we should mention Cr(V)O tetrapyrrolic complexes, featuring an isotropic signal of nine lines, due to the hyperfine (hf) coupling between the unpaired electron and the four ^{14}N nuclei, with satellites due to hf coupling with ^{53}Cr.[15,35,36] Thus, one should expect a similar behavior in the case of $CrO(tpfc)$ (Figure 4). Photoexcitation of $CrO(tpfc)$ in the crystalline and the nematic phases of E-7 generates a polarized spectrum in emission (Figure 4), which does not depend on the **L** orientation. These spectra are identical to the integrated and inverted steady-state EPR spectra taken at the corresponding temperature. A similar behavior was observed with paramagnetic Cu(II) porphyrins.[37]

$CrO(tpfc)$ may be considered as a coordination complex, where the nitrogen atoms of the corrole ring and the unique oxygen atom define the equatorial plane and the Z-axis, respectively. Additional bonding is achieved via π-overlapping, between the empty d_{xz} and d_{yz} metal orbitals, the filled p_x and p_y oxygen orbitals, and the π-orbitals of the corrole.[15] Such a
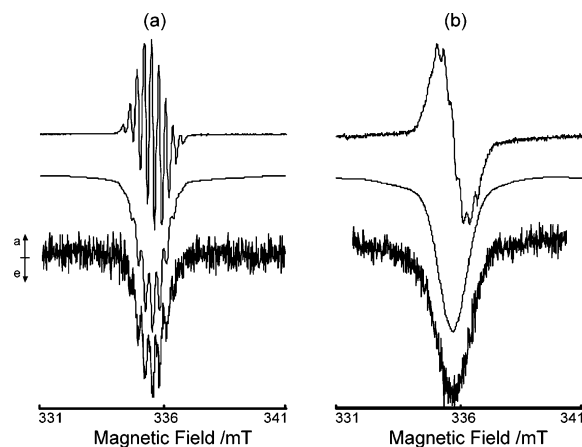
Figure 4. Comparison of the light-induced and steady-state EPR spectra of $CrO(tpfc)$ in E-7 at room temperature (a) and at 175 K (b). Upper trace: steady-state spectra ($d\chi''(B)/dB$) measured using 100 kHz field modulation (microwave power 56 mW, modulation amplitude 0.3 G). Middle trace: numerically integrated and inverted steady-state spectra ($\chi''(B)$), which are presented in the upper trace. Lower trace: spin-polarized TREPR spectra ($\chi''(B)$) taken 1 μs after laser pulse at 556 nm photoexcitation (8 mJ/pulse).
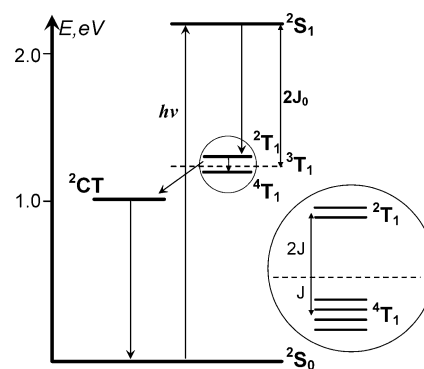
Figure 5. Energy scheme describing the excited states dynamics for $CrO(tpfc)$. All parameters and processes are described in the main text.

molecular structure will also result in a noticeable interaction between the chromium d-electrons and the π-electrons of the pyrrole photoexcited triplet state. The two interacting species with spin S = 1/2 (chromium) and S = 1 (corrole ring) generate two composite states, i.e., doublet and quartet. Thus, the lowest excited states of such a three-spin system are referred to as a "sing-doublet" ($^2S_1$), "trip-doublet" (^2T), and "trip-quartet" (^4T). The terms "sing" and "trip" indicate either a singlet or triplet configuration of the π-electrons.[38] The unpaired electrons of the doublet and triplet are coupled by an exchange interaction, J, whose value in transition metal complexes spans from a few to several hundreds wavenumbers,[39] i.e., values, much larger than the corresponding Zeeman, ZFS, and hf interaction. In such a case, the exchange interaction removes the spin degeneracy and forms a doublet and a quartet state, with a fixed energy separation $\Delta E = 3J$ (Figure 5). It should be noted that the two π-electrons of the triplet are usually coupled by a much higher exchange interaction,[40] with the energy gap $\Delta E = 2J_0$, between the first excited sing-doublet state $^2S_1 \equiv (^2Cr, ^1tfpc)$, and the degenerate doublet/quartet state $^3T_1 \equiv (^2Cr, ^3tfpc)$. The parameters of these photoexcited states, such as populations, exchange

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interaction strength, and relaxation rates, govern the electron spin polarization (ESP) patterns observed in the TREPR spectra.

Since the exchange interaction in CrO(tpfc) is larger than the Zeeman energy and the molecular structure is rigid, level crossings in the weak coupling regime are not accessible. Therefore, the spin polarization cannot be explained by conventional chemically induced dynamic electron polarization, or polarization transfer mechanisms, which require diffusion-driven encounters of the interacting species.[41] In a recent study of three-spin copper porphyrins, it was shown that an intersystem crossing (ISC) process is responsible for generating net polarization in the trip-doublet/trip-quartet manifold.[37] This polarization can be further transferred to the ground state, possibly, via intermediate quenching state(s), such as charge transfer (CT) or d−d* states.

It was shown that a CT state in metalloporphyrins, generated by ligand-to-metal partial electron transfer (ET), quenches their excited states.[42−44] The combination of the noncoordinating solvent, such as E-7, the absence of any indication for dimer formation, and the high oxidation state of the metal makes the contribution of d−d* transitions to the excited states quenching in CrO(tpfc) unlikely. Consequently, we assume that the excited states are quenched predominantly via a ligand-to-metal CT intermediate state, whose energy position E_{CT} (Figure 5) can be estimated from the redox potentials of the corresponding reactions, the dielectric constant (ϵ) of E-7, and the distance between species, r: $E_{CT} = eE_{ox} - eE_{red} - e^2/\epsilon r$.[45] Since the spectra of the CrO(tpfc) are independent of **L** orientation, ϵ was taken as an average between $\epsilon_{\parallel}$ and $\epsilon_{\perp}$. The identical spectral width of the steady-state and TREPR spectra rules out the possibility that the latter spectrum is due to transitions within the trip-doublet or trip-quartet manifolds. For these transitions, the hf splitting, which dictates the spectral width, obeys the relationship $A^{Cr,N}$ (trip-doublet) $= -(1/3)A^{Cr,N}$ (ground state) and $A^{Cr,N}$(trip-quartet) $= (1/3)A^{Cr,N}$(ground state).[39] In other words, the corresponding spectra are expected to be three times narrower than the ground-state spectrum. Obviously, this is not the case here (Figure 4).

In view of the above arguments, we outline the following scheme to generate a net emissive doublet ground state (Figure 5). Light absorption at 556 nm populates the sing-doublet $^2S_1$ which is converted very fast ($\sim$10 ps)[46,47] and selectively[48] to the trip-doublet $^2T_1$. The genesis of the emission polarization

generated in the ground-state doublet of the CrO(tpfc) is the overpopulation of the upper level of the $^2T_1$ state (Figure 5). Justification of this process is based upon the kinetic considerations obtained by ultrafast optical spectroscopy.[46,49,50] The polarization generated in the $^2T_1$ can be transferred to the chromium sing-doublet ground state $^2S_0$, involving a CT state,[51,52] namely, $^2CT \leftarrow {}^2T_1$ route, which occurs by an order of magnitude faster than the depletion route $^4T_1 \leftarrow {}^2T_1$.[46,49,50] ^2CT state is quenched by back metal-to-ligand electron transfer. Since CT state formation and decay reactions occur within a few nanoseconds or less, i.e., faster than the spin lattice relaxation within $^2T_1$ and ^2CT, spin polarization should be conserved.[53] It should be emphasized that ET reaction to generate a CT state is essential, keeping the spin polarization unchanged and thus leading to the emissive ESP pattern. Direct quenching of $^2T_1$ to the ground state (via internal conversion) is ruled out since it is not spin-selective, thus resulting in complete scrambling of the selectivity effect.

Conclusions

In this study, we provide new results associated with the excited states spin dynamics of three typical corroles, namely, the diamagnetic (H$_3$(tpfc), Ga(tpfc)) and the paramagnetic (CrO-(tpfc)). It was demonstrated that the magnetic and kinetic parameters of the relevant excited states are governed mainly by the magnetic properties of the corrole core. Specifically, the diamagnetic corroles exhibit practically the same triplet spectra, with a negative ZFS parameter D, attributed to the strong electron withdrawing by the perfluorinated aryl groups. The TREPR spectrum of CrO(tpfc) is due to the sequence of reactions, i.e., photoexcitation and subsequent quenching involving a CT state to generate a doublet ground-state emissive signal.

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