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Phosphorescence of free base corroles

Valeriy N. Knyukshto,[a] Thien Huynh Ngo,[bc] Wim Dehaen,[b] Wouter Maes*[d] and Mikalai M. Kruk*[e]

**The phosphorescence spectra of a series of free base halogenated *meso*-triarylcorroles are obtained and systematically analysed for the first time. Phosphorescence quantum yields and lifetimes are reported and rationalised in terms of the internal heavy atom effects, and the reasons for the unusually large S_1-T_1 energy gap in the studied compounds are discussed.**

Singlet to triplet (S_1-T_1) intersystem crossing (ISC) is well known to be the main excitation energy deactivation route in porphyrins and related macrocycles.[1] For most compounds with planar macrocycle conformation, the sum of the fluorescence and ISC quantum yields is close to 1, whereas up to 60% of excitation energy dissipates through radiationless internal S_1-S_0 conversion for the nonplanar derivatives.[2] Corroles represent a peculiar family of contracted tetrapyrrolic macrocycles with a direct pyrrole-pyrrole linkage and the non-metallated or free base (Fb) derivatives show pronounced nonplanar distortions.[3] To date, studies on the excitation energy deactivation pathways in corroles have mainly focused on the radiative deactivation of the lowest S_1 state, and the fluorescence spectra, quantum yields and lifetimes have been measured and discussed for a number of Fb corrole derivatives.[4] Recently, individual ground state absorption and fluorescence features have been distinguished for the two NH tautomers (see Scheme 1) of Fb *meso*-pyrimidinylcorroles.[5] The solvent dependence of both the ground state absorption and lowest singlet state emission spectra was rationalized in terms of two equilibria, (i) between the NH tautomers and (ii)

between the Fb and monodeprotonated species. NH tautomerization was also observed in the excited singlet state. Due to the pronounced temperature dependence of the tautomerization rate, the long wavelength T1 tautomer mainly contributes to the corrole fluorescence at room temperature, while the short wavelength T2 tautomer dominates the fluorescence at low temperature.[5]
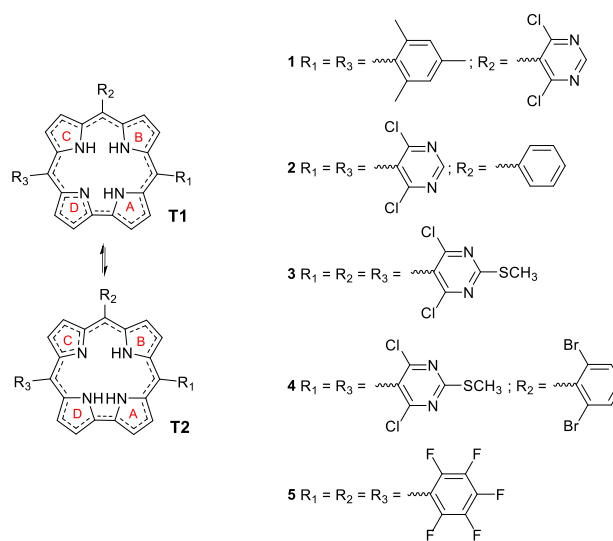
Scheme 1 Molecular structures of the studied Fb corroles (with annotation of the two NH tautomers).

Compared to these deepened insights in the fluorescence behaviour of Fb corroles, much less is known on the triplet state features of these macrocycles. For a series of six *meso*-triphenylcorroles with differing substitution pattern, it was found that the triplet states are populated and S_1-T_1 ISC quantum yields were reported.[4a,6] On the other hand, the fluorescence properties of AB_2-, A_2B- and A_3-type *meso*-pyrimidinylcorroles have been interpreted in relation to the internal heavy atom effects (of the ortho,ortho'-halogen substituents), leading to fluorescence quenching and enhancement of the radiationless ISC rate.[7] Corrole phosphorescence has been reported for a number of

a. B.I. Stepanov Institute of Physics of National Academy of Sci., 220072, Independence Ave., 70, Minsk, Belarus
b. Molecular Design and Synthesis, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
c. International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan
d. Design & Synthesis of Organic Semiconductors (DSOS), Institute for Materials Research (IMO-IMOMEC), Hasselt University, B-3590 Diepenbeek, Belgium. E-mail: wouter.maes@uhasselt.be
e. Belarusian State Technological University, Physics Department, 220006, Sverdlov Str., 13a, Minsk, Belarus. E-mail: m.kruk@belstu.by, krukmikalai@yahoo.com; Fax: +375 17 226 14 32; Tel: +375 17 399 49 60
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metallocorroles (Ir, Al, Au, Rh, Ge, Ga and Sn),[8] but there has been only one single mention of Fb corrole emission in the near-infrared (NIR) range, tentatively assigned to phosphorescence.[9] A thorough study of the Fb corrole phosphorescence features remains notably absent at this stage. Phosphorescence in the NIR region is currently attracting considerable attention because of its widespread applications, for example in bioimaging[10] and the design of organic light-emitting diodes (OLEDs) or dye-sensitized solar cells (DSSCs).[11] Considering this, the main goal of the present investigation is to extend our previous studies on the excited singlet state properties of Fb corroles[4c,5,7] to the radiative properties of the triplet states and to analyse the individual properties of the corrole NH tautomers in the triplet states.

First of all, fluorescence spectra were measured at room temperature to elucidate the equilibrium between the two corrole NH tautomers in the toluene:EtOD (10:1) mixture applied for all further spectroscopic studies (Fig. 1). Most of the fluorescence originates from the long wavelength T1 tautomer, with a minor contribution from the T2 tautomer. The proportion of the latter is found to depend on the substitution pattern. For brominated Fb corrole **4**, this contribution seems to be most pronounced, resulting in a clearly visible shoulder at the short wavelength side of the main fluorescence peak. According to our previous findings,[5a,b] a decrease in temperature down to 77 K leads to the inversion of these contributions due to the reduced NH tautomerization rate in the excited S_1 state. One can see that the emission at 77 K indeed mainly bears the features of the short wavelength T2 tautomers (Fig. 2). The temperature decrease also leads to a sharpening of the fluorescence bands. In case of AB$_2$-pyrimidinylcorrole **1**, very weak peaks at 635 and 725 nm belonging to the T1 tautomer are visible, whereas for A$_2$B-pyrimidinylcorrole **2**, the two maxima at 620 and 660 nm correspond to the 0-0 band for the T2 and T1 tautomers, respectively. This means that a substantial contribution to the total fluorescence spectrum at 77 K is coming from the T1 tautomer for this corrole. Both sets of fluorescence spectra were measured at the same excitation wavelengths to provide the same proportion of excitation for the two NH tautomers at the two temperatures. As a result, the fluorescence quantum yields at 77 K (Φ_{fl}^{77K}) can be calculated as a simple proportion of the absorbance-normalised integral fluorescence intensities at the two temperatures, *i.e.* $\Phi_{fl}^{77K} = \Phi_{fl}^{293K}(I_{fl}^{77K}/I_{fl}^{293K})$ (Table 1). Taking into account the temperature-driven switching of the S_1 state deactivation channels,[5] it should be mentioned that the Φ_{fl}^{293K} value refers (mainly) to the long wavelength T1 tautomer and the Φ_{fl}^{77K} value can (mainly) be assigned to the short wavelength T2 tautomer. Moreover, one needs to bear in mind that due to the shift of the ground state equilibrium between the NH tautomers (towards the T2 tautomer) at low temperatures, the whole set of photophysical parameters for the studied Fb corroles at 77 K should (mainly) be related to the properties of the short wavelength T2 tautomer.
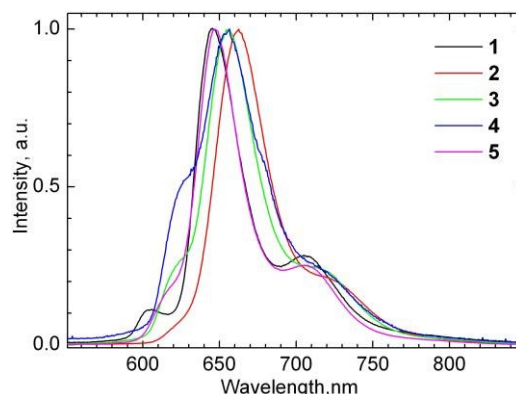

Fig. 1 Normalised fluorescence spectra of the studied Fb corroles at 293 K in toluene:EtOD (10:1). The samples were excited in the T2 tautomer Soret band in the wavelength range λ_{exc} = 400–410 nm.
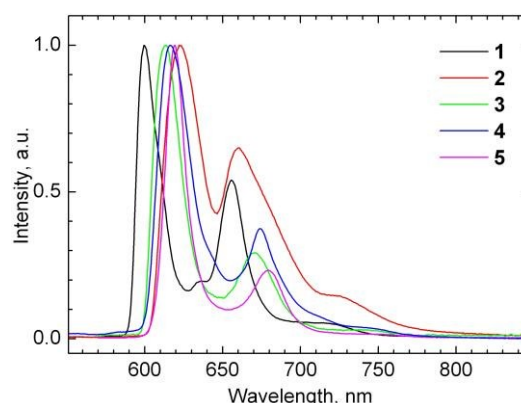

Fig. 2 Normalised fluorescence spectra of the studied Fb corroles at 77 K in toluene:EtOD (10:1) (λ_{exc} = 400–410 nm).
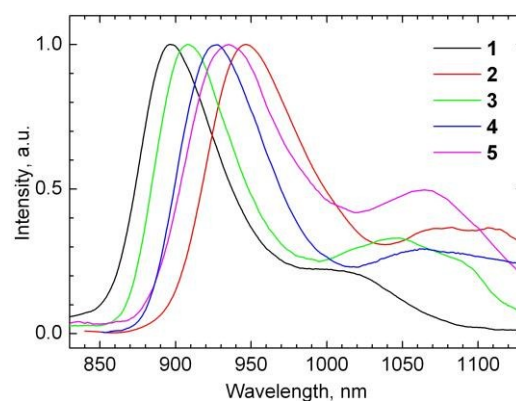
Fig. 3 Normalised phosphorescence spectra of the studied Fb corroles at 77 K in toluene:EtOD (10:1) (λ_{exc} = 400–410 nm).

Measurements of the Fb corrole emission in the far red and NIR range revealed weak emission signals (Fig. 3). The spectral shape of these emission spectra is similar to those reported for the phosphorescence spectra of porphyrins,[12] so it can reasonably be expected that corrole T$_1$-S$_0$ phosphorescence is observed. To achieve unambiguous proof for this assignment, the set of obtained spectral-luminescent and photophysical data was analysed in more detail (Table 1).

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Table 1 Spectral-luminescent and photophysical properties of the series of *meso*-triarylcorroles at 293 and 77 K (in toluene:EtOD, 10:1).

Corrole (No. of halides[a])	$\lambda_{fl}^{max\ 77K}$ (nm)	$\lambda_{ph}^{max\ 77K}$ (nm)	$\Delta E(S_1-T_1)^{77K}$ (cm^{-1})	τ_{fl}^{293K} (ns)	Φ_{fl}^{293K} ×10^2	k_{fl}^{293K} ×10^7 (s^{-1})	$k_{ISC}(S_1-T_1)^{293K}$ ×10^8 (s^{-1})	$\Phi_{ISC}(S_1-T_1)^{293K}$	Φ_{fl}^{77K} ×10^2	Φ_{ph}^{77K} ×10^4	τ_{ph}^{77K} (ms)
1 (2 Cl)	600	897	5518	2.30	6.0	2.61	3.69	0.85	11.0	9.7	6.6
2 (4 Cl)	623	947	5491	1.40	4.6	3.29	6.41	0.90	6.0	3.8	5.1
3 (6 Cl)	613	908	5300	0.85	2.5	2.94	11.1	0.94	2.5	12.5	2.2
4 (4 Cl + 2 Br)	617	927	5440	>0.1[b]	0.45	<4.5	99.1	0.99	0.46	17.0	0.4
5 (15 F)	619	935	5460	4.50	11.5	2.56	1.58	0.72	22.0	9.4	6.6

[a] Spin-orbit coupling constants ζ: 269, 587 and 2460 cm^{-1} for F, Cl and Br, respectively.[13] [b] Estimated in between of 0.1 and 0.8 ns.

It is known that the T_1-S_0 phosphorescence can be identified based on the pronounced dependence of the phosphorescence quantum yield (Φ_{ph}) and both ISC rates ($k_{ISC}(S_1{\rightarrow}T_1)$ and $k_{ISC}(T_1{\rightarrow}S_0)$) on the spin-orbit perturbation.[14] Thus, the series of Fb corroles studied in this work was analysed in this framework. All of the compounds bear halide moieties at the ortho-positions of the *meso*-aryl substituents (see Scheme 1), which are considered as heavy atoms and sources of spin-orbit perturbation.[7] Correlations between the photophysical properties and the sum of the squared spin-orbit coupling constants ($\Sigma\zeta^2$) were hence examined. The obtained double logarithmic plots are shown in Fig. 4. To build the plots, only Fb corroles **1**–**4** were used, all bearing ortho-halogenated *meso*-aryl substituents. Corrole **5** was excluded from the correlation plots to avoid interference from the meta- and para-fluorine atoms, whose contributions to the overall heavy atom effect are distinctly different.[12-14] The ISC rate $k_{ISC}(S_1{\rightarrow}T_1)$ is inversely proportional to the fluorescence lifetime (τ_{fl}), according to the relation $\tau_{fl} = (k_{fl} + k_{ISC}(S_1{\rightarrow}T_1) + k_d)^{-1}$, where k_{fl} and k_d are the fluorescence and internal conversion rates, respectively. We have previously demonstrated that the sum of the two radiationless rates in Fb corroles is substantially higher than k_{fl}.[7] Keeping in mind the independence of k_d on the heavy atom effect, the decrease in fluorescence lifetime with increase in $\Sigma\zeta^2$ (Fig. 4, left) indicates the enhancement of $k_{ISC}(S_1{\rightarrow}T_1)$. The ISC rate $k_{ISC}(T_1{\rightarrow}S_0)$ is reciprocal to the phosphorescence lifetime (τ_{ph}). The τ_{ph}^{-1} value increases with increase in $\Sigma\zeta^2$ (Fig. 4, right) due to the heavy atom effect. Thus, the left and right panels in Fig. 4 reflect the increase in $k_{ISC}(S_1{\rightarrow}T_1)$ and $k_{ISC}(T_1{\rightarrow}S_0)$, respectively. Based on the above considerations, k_{fl} and $k_{ISC}(S_1{\rightarrow}T_1)$ have been calculated (Table 1). From the $k_{ISC}(S_1{\rightarrow}T_1)$ values, the quantum yields of the $S_1{\rightarrow}T_1$ intersystem crossing were obtained as well (Table 1).

The phosphorescence quantum yield rises with increase in $\Sigma\zeta^2$, mainly due to the lifting of the forbiddenness of the radiative $T_1{\rightarrow}S_0$ transition. The obtained Φ_{ph} data (Table 1) indicate that this trend holds for all compounds except corrole

2, which reveals a phosphorescence quantum yield somewhat lower than expected. This can be explained by the fact that its phosphorescence spectrum results from an overlap of the individual T2 and T1 phosphorescence spectra. Since a noticeable proportion of the fluorescence at 77 K originates from the T1 tautomer (*vide supra*), the corresponding $T_1{\rightarrow}S_0$ emission should also be observed. The overall phosphorescence quantum yield decreases as the Φ_{ph} value of the T1 tautomer is likely to be lower compared to the one of the T2 tautomer. Since the integral emission intensity is the sum of the relative tautomer concentrations times the individual quantum yields, the phosphorescence spectrum of corrole **2** reflects the features of the major T2 tautomer. The minor contribution of the T1 tautomer accounts for the slightly larger band halfwidths in the phosphorescence spectrum compared to those found for the other Fb corroles. This explanation is also supported by the multi-exponential phosphorescence decay observed for Fb corrole **2**, in contrast with the purely mono-exponential decay for all other compounds (the τ_{ph} value in Table 1 refers to the lifetime of the major component, assigned to the T2 tautomer). In case of corrole **1**, the very minor proportion of the T1 tautomer at 77 K, combined with the selective excitation, enabled us to measure the phosphorescence spectrum of the T2 tautomer, as for the Fb corrole derivatives **3**–**5**. Thus, based on the information presented above, one can conclude that the emission spectra in the NIR range (Fig. 3) indeed represent the $T_1{\rightarrow}S_0$ phosphorescence spectra of the T2 tautomer for the presented series of Fb corroles.
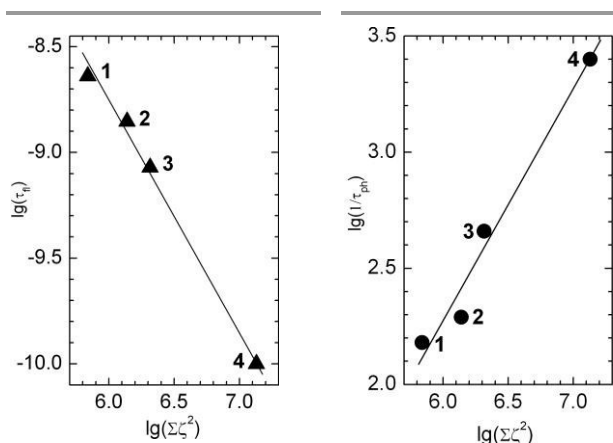
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Fig. 4 Double logarithmic plots for the fluorescence lifetime (left) and the reciprocal phosphorescence lifetime (right) as a function of the sum of the squared spin-orbit coupling constants ($\Sigma\zeta^2$) of the ortho-halides on the *meso*-aryl substituents for the studied series of Fb corroles.

The energy gaps $\Delta E(S_1\text{-}T_1)$ for all studied Fb corroles, measured as the energy differences between the fluorescence and phosphorescence maxima for the T2 tautomer (dominating at 77 K), are situated in the range of ~5300–5500 cm^{-1} (Table 1). These values are almost 1500 cm^{-1} higher than those reported for any of the studied metallated corroles, which revealed $\Delta E(S_1\text{-}T_1)$ values around 4000 cm^{-1}.[8,‡] The $\Delta E(S_1\text{-}T_1)$ values observed here are also substantially higher than those reported for Fb *meso*-aryl-substituted porphyrins, where they do not exceed 4000 cm^{-1}, with a slight variation depending on the aryl rings.[12] The S_1-T_1 energy gap tends to go up with increase in the degree of nonplanar macrocycle distortion. For highly nonplanar tetraaryloctaalkylporphyrins and diprotonated tetraarylporphyrins, $\Delta E(S_1\text{-}T_1)$ values of about 4400 and 4800 cm^{-1}, respectively, have been reported.[12,15] According to X-ray crystallography data and DFT calculations,[3,16b] the Fb corrole macrocycle shows smaller macrocycle atom deviations as compared to the above mentioned porphyrin counterparts. On the other hand, removal of one of the *meso*-carbon atoms in the corrole macrocycle causes a large perturbation of the electronic structure, with a lifting of the degeneracy of the two LUMO orbitals. As a result, the LUMO+1 – LUMO energy gap becomes larger than the HOMO – HOMO-1 gap,[8i,16] leading to a distinctly different pattern of the configuration interaction.

In conclusion, the phosphorescence spectra for a set of free base (halogenated) *meso*-triarylcorroles are reported for the first time and analysed on the basis of the heavy atom effect. The observed $\Delta E(S_1\text{-}T_1)$ values of 5300–5500 cm^{-1} seem to be an intrinsic feature of the studied free base *meso*-triaryl-corroles. This large $\Delta E(S_1\text{-}T_1)$ gap is of particular importance for photodynamic therapy. When this value is close to 7880 cm^{-1}, two singlet oxygen molecules can be produced for each absorbed photon upon sequential quenching of the S_1 and T_1 states of the photosensitizer.[17] Thus, the design of corroles with a large S_1-T_1 energy gap can be considered a promising directive for new corrole synthesis endeavours.

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Notes and references

‡ Direct comparison with the data reported by D'Souza et al.[9] is not possible, since the low-temperature fluorescence spectrum was not reported there.

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The phosphorescence features of free base corroles have been analysed, completing the picture on their excited state photophysical properties.