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OPTICAL PROPERTIES OF THE FREE BASE CORROLES

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Corroles, contracted tetrapyrrolic macrocycles lacking one *meso*-carbon atom, have emerged as attractive porphyrinoid materials, notably during the last decade, in which novel synthetic pathways toward *meso*-triaryl-substituted corroles and numerous post-macrocyclization functionalization protocols have considerably enlarged the set of available corrole structures and their potential applications. Corrole-based materials are nowadays extensively studied as novel catalysts, antitumor treatment and imaging agents as well as active materials in the design of new sensors and optoelectronic devices.

Asymmetry of the tetrapyrrolic corrole macrocycle (one direct C_a-C_a dipyrrole linkage instead of the methine C_a-C_m-C_a bridge) leads to lower molecular symmetry of free base corrole (C_s) as compared to that of free base porphyrin (D_{2h}). This can result in two different positions of the three protons in the core of a free-base corrole, i.e. two NH tautomers are not more equivalent and can contribute to the optical properties of free base corroles.

An experimental study has been undertaken to disclose the individual absorption and fluorescence profiles of the two NH tautomers of 10-(4,6-dichloropyrimidin-5-yl)-5,15-dimesitylcorrole [1,2]. The bands in the fluorescence spectra at room temperature and below have been assigned to the individual NH tautomers. The Stokes shift between the peaks of the 0-0 transition in absorbance and fluorescence at room temperature was found to be larger for the long wavelength T1 tautomer compared to the short wavelength T2 tautomer (270 cm⁻¹ vs. 165 cm⁻¹), indicating that the T1 tautomer structure seems to be more flexible and undergoes slightly larger rearrangements in the excited singlet S₁ state as compared to the T2 tautomer. At low temperatures (4.2–77 K), the solid solution prevents conformational relaxation and no Stokes shift was observed. It was found that the fluorescence from the long wavelength T1 tautomer dominates in the total emission spectrum at room temperature, in contrast to the situation at low temperatures, where the short wavelength T2 tautomer dominates. This phenomenon of temperature-controlled "switching" between the fluorescence emissions from the two corrole NH tautomers is observed for the first time and was explained by a reduced T2→T1 tautomerization rate with a decrease in temperature. Energy level diagrams explaining the excitation energy deactivation channels at different temperatures are proposed.

H/D substitution of the core pyrroles also led to a substantial decrease in the NH tautomerization rate, resulting in an increase in the contribution of the T2 tautomer to the total fluorescence spectrum at the expense of the T1 tautomer. A temperature dependence of the fluorescence spectra in the temperature range 277–332 K was observed and used to evaluate the spectral profiles for the individual NH tautomers. The pronounced increase in the overall fluorescence quantum yield upon going from 332 to 277 K was explained in terms of the difference in fluorescence quantum yields of the individual tautomers. The fluorescence quantum yield of the T1 tautomer was found to be as low as 0.045 and 0.065 in EtOH and EtOD solutions, respectively. On the other hand, values of 0.155 and 0.175 were calculated for the T2 tautomer.

The solvent dependence of the absorption and emission spectra of 10-(4,6-dichloropyrimidin-5-yl)-5,15-dimesitylcorrole has been studied in a series of solvents [3]. It was shown that dramatic changes in the absorption spectrum in MeCN, acetone, DMF and DMSO are due to the formation of deprotonated $H_2AB_2^-$ corrole species. The relationship of the formation of deprotonated species with physico-chemical solvent properties is discussed in detail, concluding that there is no observable correlation with a single solvent parameter and either multiparameter correlations or specific interactions between the corrole and the solvent molecules should be considered. The possible contribution of the two corrole NH tautomers to this issue has also been considered. The fluorescence properties of the deprotonated *meso*-pyrimidinylcorrole have been characterized. In contrast with previous observations made for other corrole derivatives, it was found that the fluorescence quantum yield of the deprotonated form decreases as compared to the free-base species.

The obtained results demonstrate that pronounced solvent dependent spectral changes in corroles probably originate from several factors. In addition to the contribution due to NH tautomerization, in several cases the free base – deprotonated corrole equilibrium can contribute or even be dominating factor. For future detailed analysis of the photophysical properties of free-base corroles, the contribution of the separate corrole NH tautomers and possible deprotonation should always be taken into account. The results allow clarifying previously observed problems in the interpretation of absorption and fluorescence spectra of both *meso*-pyrimidinylcorroles and, in a more general sense, probably the whole family of *meso*-triarylcorroles, as well as on the understanding of their luminescence properties as a function of temperature.

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