

OPTICAL FEATURES OF INDIVIDUAL CORROLE NH TAUTOMERS

¹Kruk M., ¹Starukhin A., ^{2,3}Maes W., ³Ngo T., ³Dehaen W.

¹*B. I. Stepanov Institute of Physics of National Academy of Sciences,
Minsk, Belarus, kruk@imaph.bas-net.by*

²*Hasselt University, Institute for Materials Research (IMO-IMOMEC),
Design & Synthesis of Organic Semiconductors (DSOS), Diepenbeek, Belgium*

³*Katholieke Universiteit Leuven, Department of Chemistry,
Molecular Design and Synthesis, Leuven, Belgium*

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. One of the groups involved in this work has developed specific synthetic aspects of *meso*-pyrimidinylporphyrinoids, and *meso*-pyrimidinylcorroles in particular,[1-2] with varying substitution patterns. Three families of *meso*-pyrimidinyl-substituted AB₂-, A₂B- and A₃-corroles have been prepared (A = 4,6-dichloropyrimidin-5-yl). Extensive results on the synthesis and functionalization, structural elucidation, spectral features and photophysical properties have recently been reported for these compounds [2-5].

Two major structural peculiarities of corroles relative to porphyrins are the presence of three rather than two NH protons in the coordination core and their lower symmetry. The presence of three NH protons in the corrole macrocyclic core and the inherent asymmetry impose many questions concerning the specific details of the corrole tautomerization mechanism. The lower symmetry of the free-base corrole macrocycle (*C_s*) compared to that of a free-base porphyrin (*D_{2h}*) implies that the two tautomeric forms are distinct and structurally quite different (Figure 1), which opens the possibility to detect the two NH tautomers for any corrole derivative, independently of the peripheral substitution pattern and even in fluid solutions at room temperature, in contrast to porphyrins where NH tautomers of symmetrically substituted derivatives have been indistinguishable. Thus, any change in the equilibrium between the two corrole NH tautomers may contribute to the pattern of the ground state absorp-

tion spectra as well as to the solvent dependent spectral features of corroles in general.

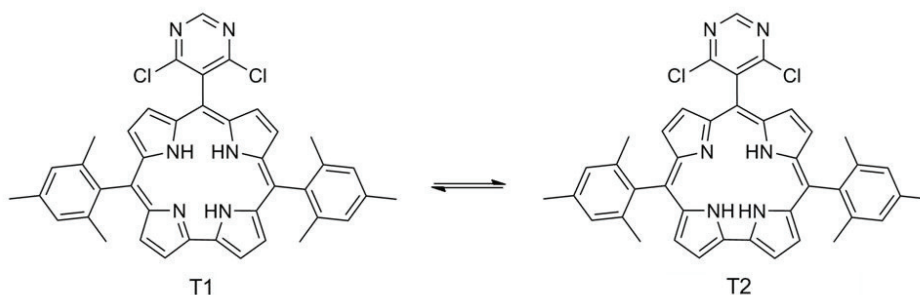


Figure 1 – Equilibrium showing two NH tautomers of the AB₂-corrole.

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 (hereafter AB₂-corrole). The bands in the absorption and fluorescence spectra in a wide temperature range have been assigned to the individual NH tautomers (Figure 2). 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.

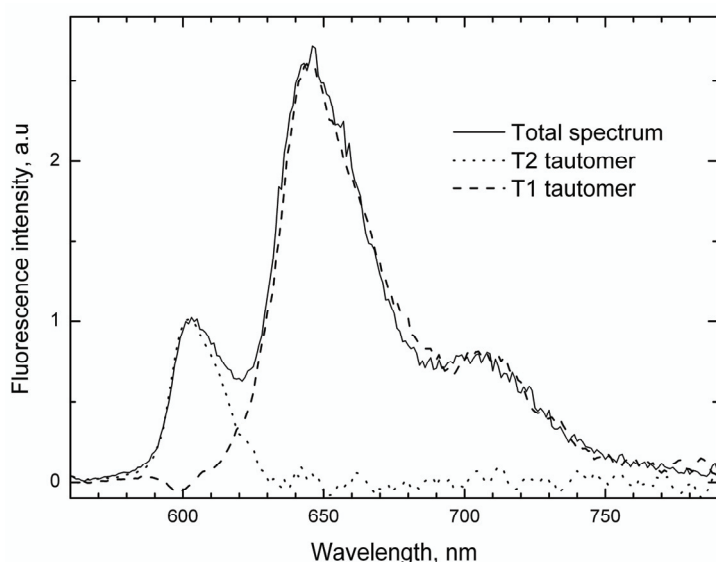


Figure 2 – Fluorescence spectrum of the AB₂-corrole measured in EtOD at 295 K and individual fluorescence spectra of its two NH tautomers.

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 data presented here bring unambiguous proofs for the coexistence of two corrole NH tautomers in fluid and solid solutions in a wide temperature range. The results allow clarifying previously observed problems in the interpretation of the 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.

This work has been carried out with partial financial support from FP-7 project DphotoD-PEOPLE-IRSES-GA-2009-247260.

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