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## Temperature Control of the NH-tautomerization Rate and Photophysical Properties of Free Base Corroles

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The NH-tautomers of the free base corroles are formed due to intrinsic asymmetry of the corrole macrocycle and presence of three protons in the macrocycle core. As a result, in addition to the radiative deactivation of the lowest singlet  $S_1$  state and intersystem  $S_1$ - $T_1$  crossing, the NH tautomerization needs to be considered as an additional channel of the excitation energy transport in the free base corroles [1]. In case of symmetrical  $AB_2$  meso-substitution architecture two NH-tautomers are formed. For the long wavelength T1 tautomer NH-tautomerization provides the additional nonradiative channel of the  $S_1$  state population, and the photophysical properties of this tautomer do not depend on temperature. On the contrary, in case of the short wavelength T2 tautomer, tautomerization forms an efficient depopulation funnel for the  $S_1$  state. For this tautomer the photophysical properties would depend on the temperature since the NH tautomerization rate constant distinctly increases with temperature. Since the NH tautomerization was found to be associated with overcoming the potential barrier in the lowest singlet  $S_1$  state [1,2], therefore according to the Arrhenius equation a decrease/increase in temperature ultimately leads to a decrease/increase in the NH-tautomerization rate. The direct spectroscopic determination of the NH tautomerization rate and understanding of its pathway(s) is quite complicated task. At the same time there are several indirect data obtained with spectroscopic methods which allow shedding light on the NH tautomerization.

The energy level balance equations system is developed to describe the NH tautomerization rate constant. The set of the experimental data, consisting of the fluorescence spectra and quantum yields measured in the temperature range from 265 to 338 K are satisfactory reproduced with the theoretical solution of the above mentioned system of equations. The obtained theoretical temperature dependences of the fluorescence intensities for two NH-tautomers fit the experimental ones.

## REFERENCES

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2. Beenken WJD, Presselt M, Ngo TH, Dehaen W, Maes W and Kruk MM. *J. Phys. Chem. A.* 2014; **118**: 862-871.