

Spectral properties and kinetics of interaction with the fluoride ion of aryl-substituted boron subphthalocyanines

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The objects of the study were boron subphthalocyanines. Boron subphthalocyanines are macroheterocyclic compounds with a 14π -electron aromatic system. Due to the cone-shaped structure that suppresses their aggregation in solution, subphthalocyanins are highly soluble in common organic solvents. Subphthalocyanines have intense absorption and fluorescence in a visible region, which allows them to be considered as promising for use in organic electronics. The aim of this work was to study the effect of

peripheral groups on the optical properties of the corresponding subphthalocyanines. A study was made of the kinetics of the

reaction between subphthalocyanine and fluoride ion. It is noteworthy that the reaction is selective to this ion.

Synthesis of Boron subphthalocyanines

R₂ CN
$$\frac{BCI_3 (1M \text{ in } CH_2CI_2)}{p\text{-xylene, } \Delta}$$

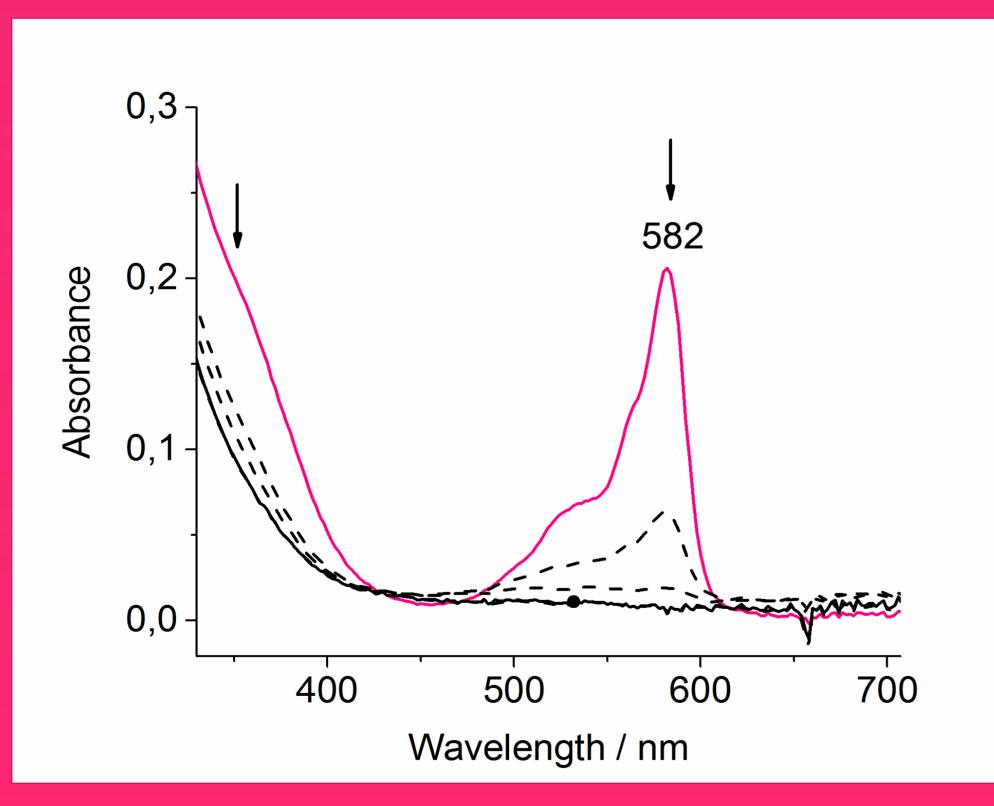
1a: R₁ = R₂ = * $\frac{R_2}{P}$

1b: R₁ = R₂ = * $\frac{R_2}{P}$

2a: R₁ = R₂ = * $\frac{R_2}{P}$

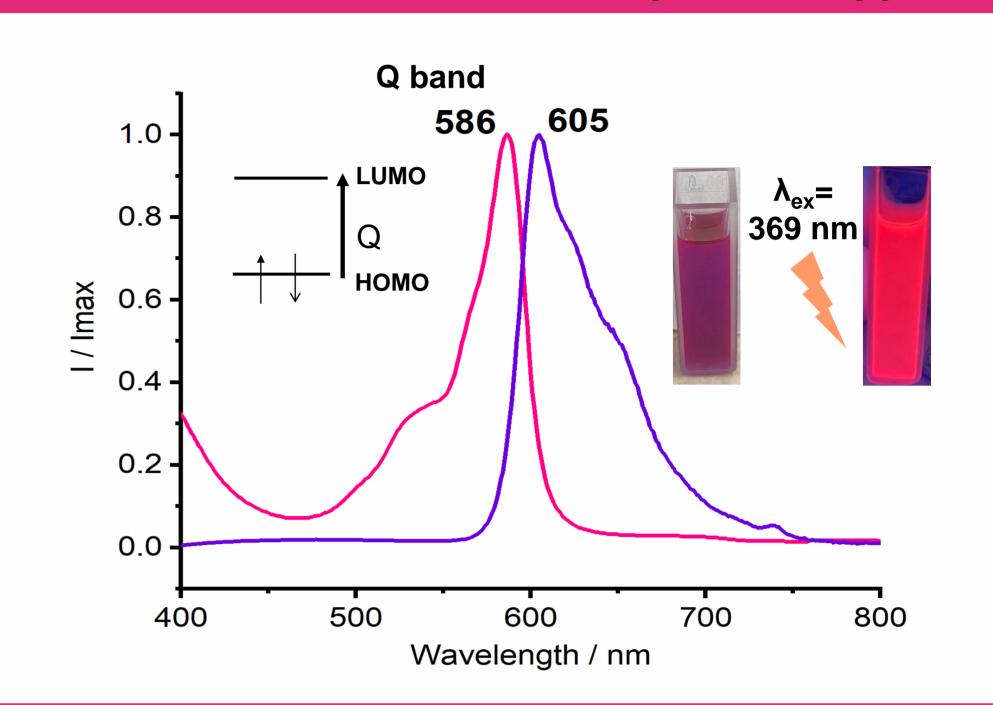
2b: R₁ = R₂ = * $\frac{R_2}{P}$

✓ Cone-shaped structure suppresses aggregation of subphthalocyanines in solution

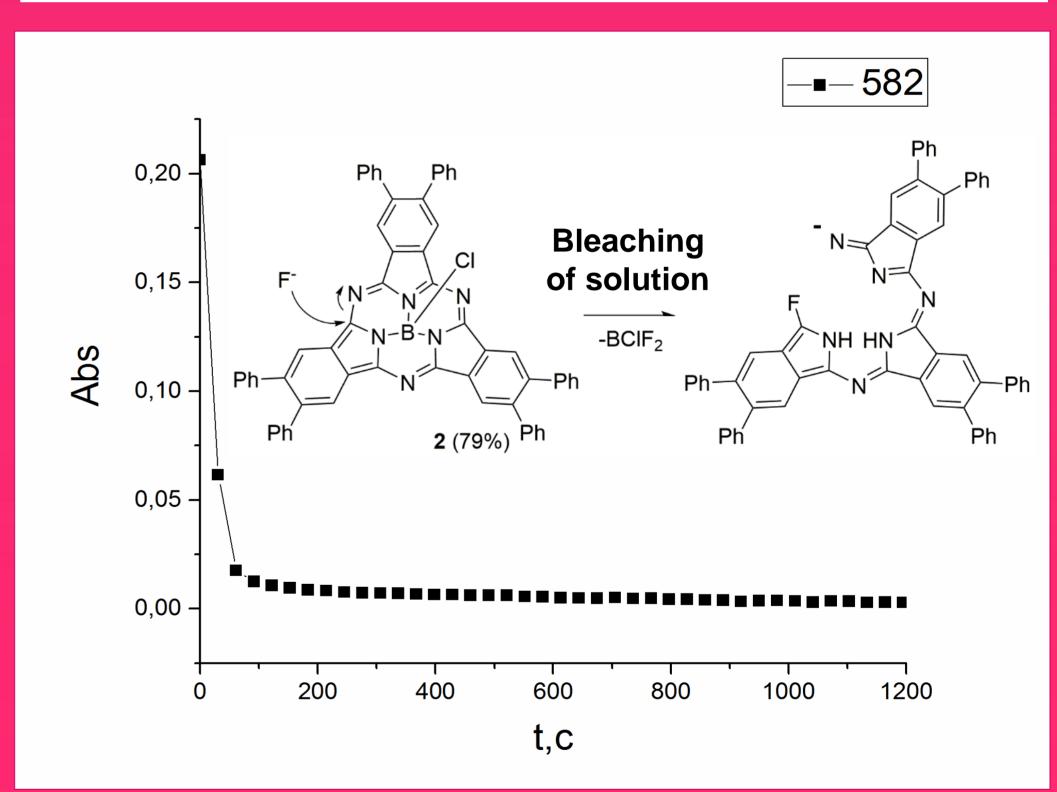


Spectral changes for solutions of subphthalocyanine 2a in THF: the initial form (pink line), after adding Bu₄N⁺F⁻(black line). Dotted lines show intermediate spectra. Arrows indicate the direction of change of UV-Vis spectra.

UV-Vis and fluorescence spectroscopy



UV-Vis (pink line) and emission (blue line) spectra for thienyl-substituted complex 2b (λ_{ex} =369 nm) (left).



The kinetic curve of the Q band intensity drop under the action of Bu₄N+F- in acetonitrile (right). The bleaching of the 2b solution, probably accompanied by the opening of the macrocycle, occurs in less than 5 min.

Conclusions:

- > Novel boron subphthalocyanines were obtained and identified.
- A bathochromic shift of the absorption maxima (586 and 592 nm) and fluorescence (598 and 605 nm) was observed going from phenyl to thienyl-substituted subphthalocyanine.
- >An increase in the fluorescence quantum yield from 14% (phenyl-substituted) to 17% (thienyl-substituted) was found.
- ➤When F⁻ was added to a solution of subphthalocyanine, a rapid establishment of equilibrium was observed, accompanied by a bleaching of the solution. Probably this phenomenon results from the opening of the macrocycle.
- ➤In this case, using the isomolar series method, it is shown that a complex of subphthalocyanine with fluorine is formed in a ratio of 1:1.