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**BORON(III) COMPLEXES OF HETEROCYCLIC (SUB)PHTHALOCYANINE  
ANALOGUES: 1,2,5-THIADIAZOLE FUSED (SUB)PORPHYRAZINES**

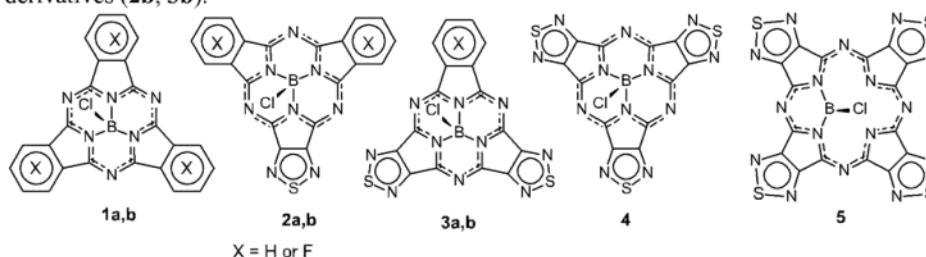
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Boron(III) subphthalocyanines (**1a**) are widely investigated as perspective materials for organic electronics [1]. Usually they behave as *p*-type materials; their perfluorinated derivatives (**1b**) exhibit the *n*-type conductivity. Another way to enhance the electron acceptor properties of subporphyrzine core is annulation of  $\pi$ -deficient heterocycles instead of benzene rings. Thus, fusion of 1,2,5-thiadiazole rings strongly increases  $\pi$ -electron-deficiency of porphyrzine core [2] and tetra(1,2,5-thiadiazolo)porphyrzines were used as *n*-type layers in the prototypes of photovoltaic cells and other electronic devices [3]. Recently, we have prepared the first heterocyclic subphthalocyanine analogue with strongly electron deficient 1,2,5-thiadiazole rings (**4**) [4]. In order to reveal the influence of these heterocycles on the electronic properties of boron(III) subporphyrzines we have synthesized the series of macrocycles combining 1,2,5-thiadiazole and benzene rings (**2a**, **3a**) and their perfluorinated derivatives (**2b**, **3b**).



The electronic absorption and emission spectra, electrochemical properties, conductivity of the sublimed thin films have been studied and the results are compared with the properties of boron(III) subphthalocyanine **1a** and perfluorosubphthalocyanine **1b**.

The evidence have been obtained that reaction of 1,2,5-thiadiazole-3,4-dicarbonitrile with  $\text{BCl}_3$  along with boron(III) subporphyrzine **4** affords also boron(III) porphyrzine complex **5** as a cyclotetramerization by-product.

The influence of the 1,2,5-thiadiazole annulation on the electronic properties and geometrical features of subporphyrzine complexes as well as possible structures of boron(III) porphyrzines is discussed on the basis of DFT calculations results.

[1] G.E. Morse, T.P. Bender, *ACS Applied Materials and Interfaces*, **2012**, 4, 5055–5068.

[2] M.P. Donzello, C. Ercolani, P.A. Stuzhin, *Coord. Chem. Rev.* **2006**, 250, 1530–1561.

[3] P. Stuzhin, M. Mikhailov, V. Travkin, E. Gudkov, G. Pakhomov, *Macroheterocycles* **2012**, 5, 162–165.

[4] M. Hamdoush, S. Ivanova, G. Pakhomov, P.A. Stuzhin, *Macroheterocycles*, **2016**, 9, 230-233

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