

## Molecular Structure of 1,2,5–Selenadiazolodibenzosubporphyrazinato–boron(III) Chloride and Influence of Perfluorination and Perchlorination on Its Spectral Properties

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*Novel Se-containing heterocyclic subphthalocyanine analogue – (1,2,5-selenadiazolo)dibenzosubporphyrazinato–boron(III) chloride **3a** was prepared by template cross-cyclomerization of 1,2,5-selenadiazolo-3,4-dicarbonitrile **1** and phthalonitrile **2a** with BCl<sub>3</sub> in *p*-xylene. Similar reactions of **1** and tetrafluoro- or tetrachlorophthalonitriles (**2b** or **2c**) afford octafluorinated and octachlorinated subporphyrazines **3b** and **3c**. The formation of **3a–c** was established by MALDI-TOF mass-spectrometry and the structure of **3a** was determined by single crystal X-ray diffraction. Influence of halogenation on the spectral properties is discussed.*

**Keywords:** Subphthalocyanine analogues, subporphyrazines, 1,2,5-selenadiazole, perfluorinated and perchlorinated derivatives, boron(III) complexes, crystal structure, UV-Vis spectra.

## Молекулярная структура 1,2,5–селенадиазолдобензо–субпорфиразинатобор(III) хлорида и влияние перфторирования и перхлорирования на его спектральные свойства

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*Новый Se-содержащий гетероциклический аналог субфталоцианина – (1,2,5-селенадиазоло)добензо-субпорфиразинатобор(III) хлорид **3a** синтезирован темплатной социкломеризацией 1,2,5-селенадиазоло-3,4-диказонитрила **1** и фталонитрила **2a** в присутствии BCl<sub>3</sub> в *p*-ксиоле. Аналогично из динитрила **1** и тетрафтор- или тетрахлорфталонитрилов (**2b** или **2c**) были получены октафтор- и октахлорзамещённые субпорфиразины **3b** и **3c**. Образование **3a–c** установлено на основании данных MALDI-TOF масс-спектрометрии, а структура **3a** определена при помощи рентгено-структурного анализа. Обсуждается влияние галогенирования на спектральные свойства.*

**Ключевые слова:** Аналоги субфталоцианина, субпорфиразины, 1,2,5-селенадиазол, перфторированные и перхлорированные производные, комплексы бора(III), кристаллическая структура, электронные спектры поглощения.

Subphthalocyanines – phthalocyanine analogues containing a contracted macrocycle consisting of three isoindole units<sup>[1]</sup> are actively studied in the last decades<sup>[2,3]</sup> especially due to their potential application in organic electronics.<sup>[4]</sup> While subphthalocyanines with non-substituted benzene rings are usually used as donor *p*-type layers in photovoltaic cells,<sup>[5]</sup> their halogenated derivatives can serve as effective *n*-type acceptor materials.<sup>[6]</sup> Another way to endow phthalocyanine dyes with high electron affinity is heteroatom substitution in benzene rings. Recently heterocyclic subphthalocyanine analogues containing fused pyrazine or 1,2,5-thiadiazole ring(s) instead of benzene rings have been reported in our works.<sup>[7-9]</sup> The properties of their vacuum-sublimed thin films and prototypes of photovoltaic cells have been also presented in a preliminary communication.<sup>[10]</sup> The energy level of the frontier molecular orbitals in phthalocyanine-type dyes and gap between them is important parameters determining the performance of these materials in organic electronic devices.<sup>[11]</sup> It was also shown that substitution of S by Se in the 1,2,5-chalcogenadiazole ring fused to porphyrazine macrocycle can tune the MO energy levels what leads to the bathochromic shift the maximum of the lowest  $\pi$ - $\pi^*$  absorption band<sup>[12,13]</sup> due to stronger destabilization of HOMO than LUMO.<sup>[14]</sup> The presence of fused 1,2,5-selenadiazole rings which can be cleaved also opens various facilities of the peripheral modification of the macrocycle.<sup>[15]</sup> Recently subporphyrazine containing three annulated 1,2,5-selenadiazole rings have been prepared,<sup>[9]</sup> but very low yield and instability prevent the further investigation. Here we report the synthesis, spectral properties of subporphyrazine containing one 1,2,5-selenadiazole ring and two benzene rings and its perfluorinated and perchlorinated derivatives, and single crystal X-ray structure of non-halogenated compound.

Boron trichloride (3 mL of 1 M solution in *p*-xylene, Aldrich) was added to freshly sublimed 1,2,5-selenadiazole-3,4-dicarbonitrile<sup>[16]</sup> **1** (2 mmol) and phthalonitrile **2** (1 mmol) (Scheme 1). The reaction mixture was refluxed for 1.5 h, then it was placed on column filled with silica and chromatographed with  $\text{CH}_2\text{Cl}_2$  to remove yellow by-products and unreacted dinitrile. After addition of 10 % THF the dark violet fraction containing mixture of subphthalocyanine

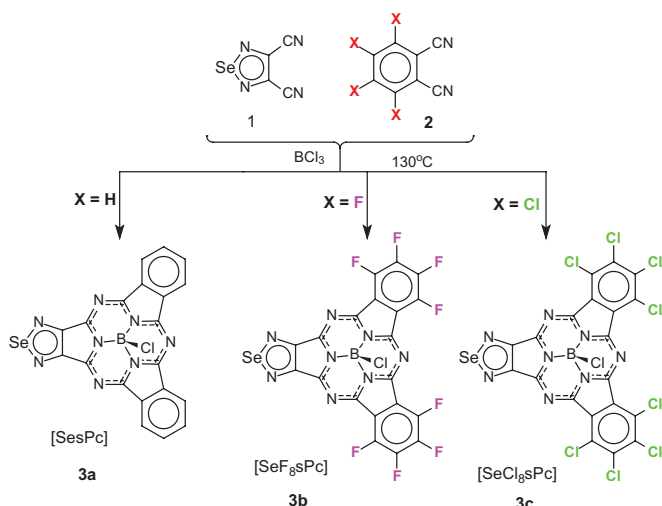
cyanine dyes was eluted. Following gradual chromatography on silica with  $\text{CH}_2\text{Cl}_2$ -hexane mixture afforded subphthalocyanine as the 1<sup>st</sup> rose fraction and its Se-containing analogue [Se<sub>8</sub>S<sub>4</sub>Pc] **3a** as the 2<sup>nd</sup> violet fraction. When tetrafluoro- or tetrachlorophthalonitriles (**2b** or **2c**) were used in a similar synthetic and isolation procedure the 1<sup>st</sup> rose-pink fraction obtained in the course of column chromatography contained perfluorinated or perchlorinated subphthalocyanines, [F<sub>12</sub>S<sub>4</sub>Pc] or [Cl<sub>12</sub>S<sub>4</sub>Pc], and the 2<sup>nd</sup> violet fraction – octafluoro- or octachlorodibenzo(1,2,5-selenadiazolo)subporphyrazines, [SeF<sub>8</sub>S<sub>4</sub>Pc] **3b** or [SeCl<sub>8</sub>S<sub>4</sub>Pc] **3c** (Scheme 1).

The results of the LDI-TOF mass-spectrometry confirm formation and isolation of subphthalocyanine analogues containing fused 1,2,5-selenadiazole fragment instead of one benzene ring (Figure 1). LDI-TOF mass-spectrum of the product obtained from phthalonitrile contains the positive molecular ion peak  $[\text{M}]^+$  at 486 Da and fragmentation ion  $[\text{M}-\text{Cl}]^+$  at 451 Da confirming formation of 1,2,5-selenadiazolosubporphyrazine with two fused non-substituted benzene rings [Se<sub>8</sub>S<sub>4</sub>Pc]. For subporphyrazines obtained from halogenated phthalonitriles the intense molecular ion peaks can be observed only in the negative modes reflecting their strong electron affinity.

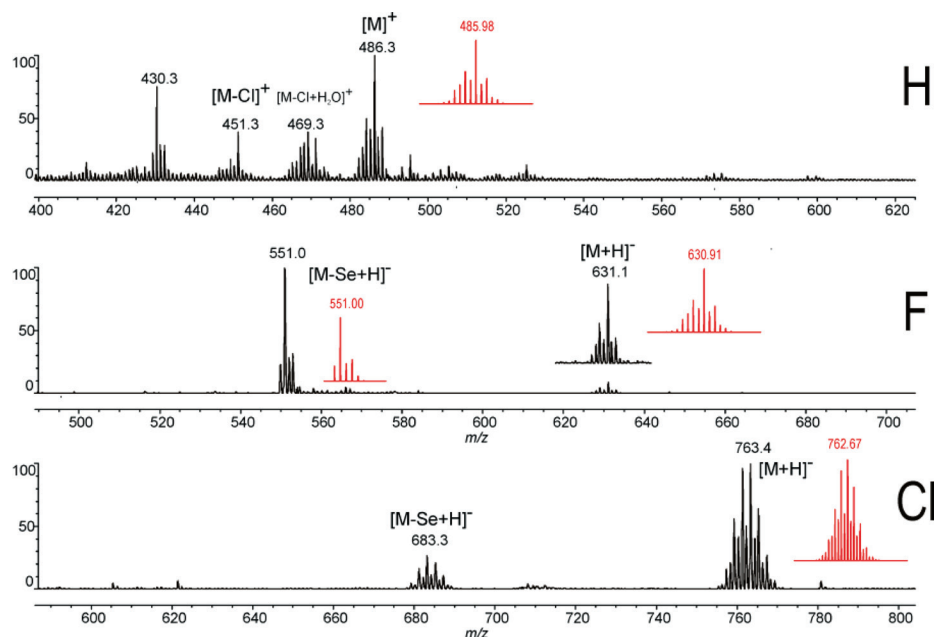
In the LDI-TOF mass-spectrum of octafluorinated subporphyrazine [SeF<sub>8</sub>S<sub>4</sub>Pc] **3b** a weak molecular ion peak  $[\text{M}+\text{H}]^+$  at 631 Da is accompanied by much stronger deselenated anion  $[\text{M}-\text{Se}+\text{H}]^-$  at 551 Da. Mass-spectrum of octachlorinated subporphyrazine [SeCl<sub>8</sub>S<sub>4</sub>Pc] **3c** recorded using cyanohydroxycinnamic acid as a matrix contains intense molecular ion peak  $[\text{M}+\text{H}]^+$  at 763 Da and less intense deselenated anion  $[\text{M}-\text{Se}+\text{H}]^-$  at 683 Da. The observed and theoretical isotopic distribution of all peaks are in perfect correspondence (Figure 1, inserts).

UV-Vis spectra of the obtained 1,2,5-selenadiazolo-dibenzoporphyrazines contain three absorption maxima arising from  $\pi$ - $\pi^*$  electronic transition (Figure 2). The long-wave band at 595–610 nm can be assigned to the HOMO→LUMO transition and the band at 507–517 nm to the HOMO→LUMO+1 transition. They can be denoted as Q<sub>1</sub> and Q<sub>2</sub> components of the split Q-band typical for subphthalocyanines-type dyes. The maxima of the long-wave Q<sub>1</sub>-band is observed at 595 nm for [Se<sub>8</sub>S<sub>4</sub>Pc] and fluorinated derivative [SeF<sub>8</sub>S<sub>4</sub>Pc] and shifted bathochromically to 610 nm for chlorinated species [SeCl<sub>8</sub>S<sub>4</sub>Pc]. In the case of symmetrically substituted subphthalocyanines and subporphyrazines two LUMO are degenerated and the spectra contain a single Q-band (563 nm for unsubstituted subphthalocyanines [S<sub>8</sub>Pc]). The position of the Q-band is slightly shifted bathochromically for perfluorinated and perchlorinated derivatives ([F<sub>12</sub>S<sub>4</sub>Pc] – 574 nm, [Cl<sub>12</sub>S<sub>4</sub>Pc] – 569 nm<sup>[2]</sup>), and for subporphyrazine [Se<sub>3</sub>S<sub>4</sub>Pc] with three 1,2,5-selenadiazole rings (574 nm<sup>[9]</sup>). Fusion of one 1,2,5-selenadiazole and two benzene rings leads to strong polarization of the  $\pi$ -chromophore and causes appearance of the split Q-band. It is interesting that the halogenation of benzene rings increases the splitting of the Q-band in Se-containing subporphyrazines (2570 cm<sup>-1</sup> for [Se<sub>8</sub>S<sub>4</sub>Pc], 2900 cm<sup>-1</sup> for [SeF<sub>8</sub>S<sub>4</sub>Pc], 2950 cm<sup>-1</sup> for [SeCl<sub>8</sub>S<sub>4</sub>Pc]) and its value is much larger than that observed for S-containing species (554 and 578 nm, 780 cm<sup>-1</sup> for [SF<sub>8</sub>S<sub>4</sub>Pc]<sup>[7b]</sup>).

Less intense absorption band at 435–450 nm is absent in the spectra of subphthalocyanine and its halogenated



Scheme 1.



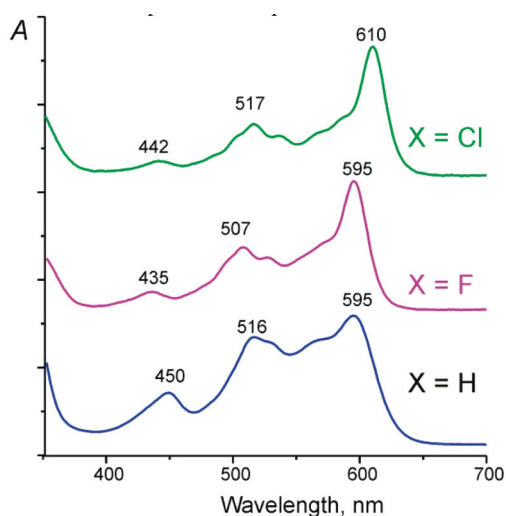
**Figure 1.** LDI-TOF mass-spectra of 1,2,5-selenadiazolodibenzosubporphyrazine (H), and its perfluorinated (F) and perchlorinated (Cl) derivatives. Spectra recorded in the positive (H) and in the negative (F, Cl) modes without matrix (H, F) and with CHCA matrix (Cl). Theoretical isotope distribution patterns of the molecular ions are shown as red inserts.

derivatives, but appearance of this additional band is a typical feature for subporphyrazines containing fused electron-deficient 1,2,5-thiadiazole or 1,2,5-selenadiazole rings (415 nm for  $[SF_8S]Pc$ , 390 nm for  $[S_3S]Pc$ <sup>[7]</sup> and 408 nm for  $[Se_3S]Pc$ <sup>[9]</sup>). It was shown<sup>[9]</sup> that this band is associated with electronic transition from HOMO to unoccupied  $\pi$ -MO localized predominantly on the fused heterocyclic rings and can be considered as a charge transfer transition.

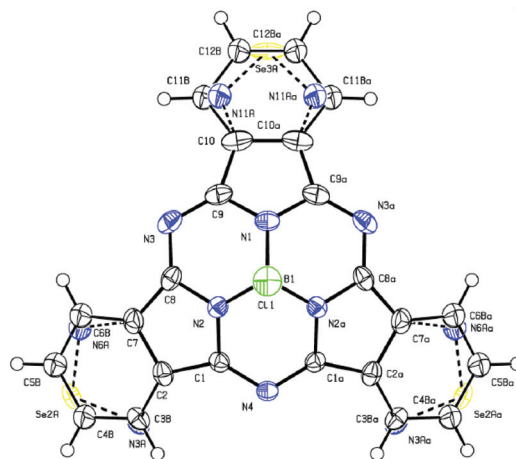
The structure of non-halogenated Se-containing subporphyrazine  $[Ses]Pc$  was determined by X-ray diffraction study of single crystal obtained by slow evaporation of its solution in  $CH_2Cl_2$ .<sup>8</sup> The molecule has a bowl-shaped structure typical for subphthalocyanines. In a crystal it has a symmetry plane passing through chlorine, boron and one

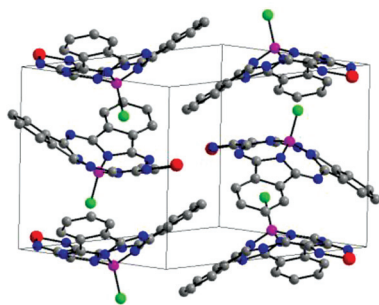
of the coordinating nitrogen atoms (Cl1-B1-N1 plane). The boron atom has a tetrahedral coordination forming bonds with chlorine and three internal nitrogen atoms (bond length in Å: B1-Cl1 – 1.872; B1-N1 1.466 and B1-N2 1.479). It is located at 0.565 Å above the plane formed by three coordinating nitrogen atoms.

In the crystal the molecules form stacks typical for subphthalocyanines bearing strong electron acceptor substituents (Figure 4). The important feature of the crystal structure is the disorder of the fused benzene and 1,2,5-selenadiazole rings. The molecule in the stacks are rotated around B1-Cl1 bond. Very likely this disorder is determined by  $\pi\pi$  interactions between the benzene rings in the molecule in one stack and 1,2,5-selenadiazole ring in the molecule in a neighboring stack. The shortest intermolecular interatomic contacts are observed between the carbon atoms in  $\beta$ -pyrrole posi-



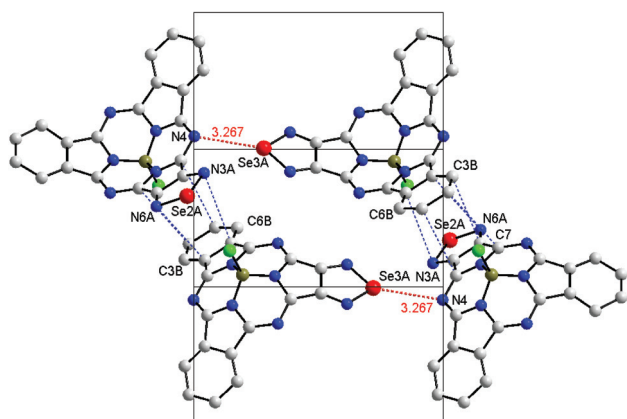
**Figure 2.** UV-Vis spectra of 1,2,5-selenadiazolodibenzosubporphyrazine and its perfluorinated and perchlorinated derivatives in  $CH_2Cl_2$ .





**Figure 4.** Molecular packing of 1,2,5-selenadiazole annulated subporphyrazine [SesPc].

tions with non-peripheral carbons of benzene rings (e.g. C7...C3B – 3.496 Å; C2...C6B – 3.676 Å) and with nitrogen atoms of 1,2,5-selenadiazole rings (C2...N6A – 3.638 Å; C7...N3A – 3.696 Å). In addition short interatomic contacts due to VdW interaction are observed between Se3A atom in one molecule and *meso*-nitrogen atom N4 in the molecule in another stack. Such type of molecular arrangement might facilitate electron transfer processes between neighboring stacks and can be favorable for semiconducting properties.



**Figure 5.** View along [1.2.0] axis showing intermolecular interactions in crystalline 1,2,5-selenadiazolodibenzosubporphyrazine [SesPc]. Van der Waals interactions Se3A...N4 are shown by red dashed lines. Short interatomic contacts (< 3.6 Å) due to  $\pi\pi$ -interaction between 1,2,5-selenadiazole fragment containing Se2A and benzene ring attached to C2C7 are shown by blue dashed lines.

In conclusion, we have prepared and characterized a series of novel subphthalocyanine analogues which contain 1,2,5-selenadiazole fragment fused instead of one benzene ring. These molecules can be considered as perspective acceptor materials for application in organic electronics and the presence of 1,2,5-selenadiazole ring allows further structural modification of the macrocycle.

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## Notes and References

- § Structural data have been deposited in Cambridge Crystallographic data Center CCDC#1971769.
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