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DOI: 10.6060/mhc160424s

Heterocyclic Subphthalocyanine Analogue – Boron(III) Subporphyrazine with Fused 1,2,5–Thiadiazole Rings

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Dedicated to Professor Tomas Torres on the occasion of his 65th Birthday

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Novel subphthalocyanine analogue – tris(1,2,5-thiadiazolo)subporphyrazinatoboron(III) chloride was prepared by interaction of 1,2,5-thiadiazolo-3,4-dicarbonitrile with BCl_3 in chlorobenzene. Strong π-electron deficient nature of the fused 1,2,5-thiadiazole rings leads to hypsochromic shift of the Q-band to 538 nm.

Keywords: Subphthalocyanine analogues, 1,2,5-thiadiazole fused subporphyrazines, boron(III) complexes, UV-Vis spectra.

Гетероциклический аналог субфталоцианина – субпорфиразин бора(III) с аннелированными 1,2,5–тиадиазольными кольцами

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Посвящается профессору Томасу Торресу по случаю его 65-летнего юбилея

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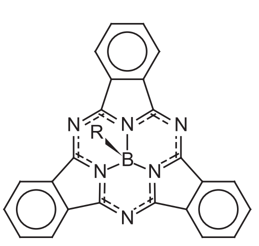
Новый аналог субфталоцианина – трис(1,2,5-тиадиазоло)субпорфиразинатобор(III) хлорид синтезирован при взаимодействии 1,2,5-тиадиазоло-3,4-дикарбонитрила с BCl_3 в хлорбензоле. Сильные π-акцепторные свойства аннелированных 1,2,5-тиадиазольных колец приводят к гипсохромному сдвигу Q-полосы до 538 нм.

Ключевые слова: Гетероциклические аналоги субфталоцианина, бор(III) субпорпорфиразины, 1,2,5-тиадиазол, ЭСП.

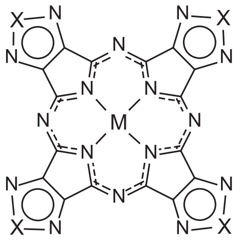
Subphthalocyanines (SubPc) – phthalocyanine analogues containing a contracted macrocycle consisting of three isoindole units assembled around the boron atom were first reported by Meller and Ossko more that 40 year ago.[1] Due to their unique spectral and other physico-chemical properties, subphthalocyanines were especially actively studied in the last two decades and the results were presented in more than 400 publications. Among them several reviews[2] and more than 60 full papers and communications published by the research group headed by *Professor Tomas Torres* who has made a really distinguished contribution to the field of subphthalocyanine chemistry and received *Linstead Career Award in Phthalocyanine Chemistry* during recent 9th International Conference on Porphyrins and Phthalocyanines.[3] The interest to subphthalocyanines is strongly connected with perspectives of their applications in organic photovoltaics and electronics.[4] They exhibit good performance as donor[5] or acceptor[6] layers in hybride organic solar cells, as hole transporter in perovskite solar cells.[7] Recently it was shown that subphthalocyanines can be used in fullerene-free organic photovoltaics.[8] In addition perspectives have been demonstrated for their application as light-harvesting,[9] light-emitting,[10] non-linear optical[11], liquid-crystalline materials,[12] as well as in medicine for antibacterial treatment.[13] A large variety of subphthalocyanines bearing various substituents in the benzene rings, as well as π-expanded subphthalocyanines with additionally fused aromatic systems (benzene or hetarene rings) have being reported.[2] Subporphyrazines with alkyl(sulfanyl) groups directly attached to β-pyrrole positions are also known[14] and the heterocyclic subnaphthalocyanine analogue containing 2,3-fused thianaphthene fragments was recently obtained.[15]

Subphthalocyanines



[SubPcBR]

Tetrakis(1,2,5-thiadiazolo)porphyrazins

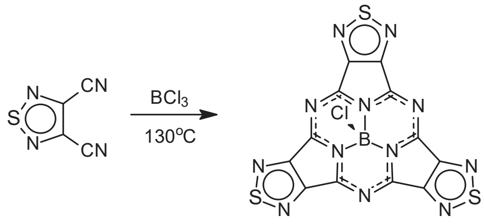


X = S, Se, Te

$[(XN_2)_4PAM]$

Subphthalocyanines are usually used as electron-donors in organic solar cells,[5] although their perfluorinated derivatives can act as electron acceptors.[6] We have also used subphthalocyanines as donors in the prototypes of multilayer tandem photovoltaic structures along with unsubstituted phthalocyanine ($In^{III}Cl$[16] and $V^{IV}O$[17] complexes) or 1,2,5-thiadiazole fused porphyrazines.[18]

Porphyrazines with annulated 1,2,5-chalcogenadiazole rings are known as strongly electron-deficient phthalocyanine analogues[19-21] which can be considered as perspective functional materials for design of organic electronic devices. Thus, tetra(1,2,5-thiadiazolo)porphyrazine, $[(SN_2)_4PAH_2]$, and its metal complexes $[(SN_2)_4PAM]$ (M=Zn^{II}, $V^{IV}O$, and Fe^{II}) were used as *n*-type organic semiconductors in the prototypes of field-effect transistors and photovoltaic cells by Awaga and co-workers[22] and in our works.[18,23] The 1,2,5-thiadiazole-fused porphyrazine macrocycle exhibits even stronger π-electron-acceptor properties in complexes with the IIIA group metals $[(SN_2)_4PAM]$ (M=$Al^{III}Cl$, $Ga^{III}Cl$, $In^{III}OAc$).[24] In the present communication we report the synthesis of 1,2,5-thiadiazole fused subporphyrazine with the central $B^{III}Cl$ unit, $[(SN_2)_3SubPABCl]$.



$[(SN_2)_3SubPABCl]$

Boron trichloride (2 ml of 1 M solution in *p*-xylene, Aldrich) was added to freshly sublimed 1,2,5-thiadiazole-3,4-dicarbonitrile[25] (2 mmol). The reaction mixture immediately became orange and upon heating thickened and then turned dark green, the colour finally changing to dark violet upon refluxing under Ar for 1 h. Significant UV-visible spectral changes were observed during the reaction process. The spectrum of the greenish mixture, showing initially two main absorption bands with maxima at 518 and 579 nm and a shoulder at 675 nm (Figure 1, spectra *a* and *b*), turns gradually to a final spectrum characterized by an absorption with maximum at 538 nm accompanied by shoulders on the higher energy side (dark violet reaction mixture; Figure 1, spectrum *c*). After evaporation of the solvent the residue was chromatographed on silica and the product was eluted with a CH_2Cl_2:ethyl acetate mixture 3:1. The UV-VIS spectrum of the pink fraction (Figure 1, spectrum *d*) has an intense absorption band at 538 nm and is typical for subphthalocyanine complexes (see below).

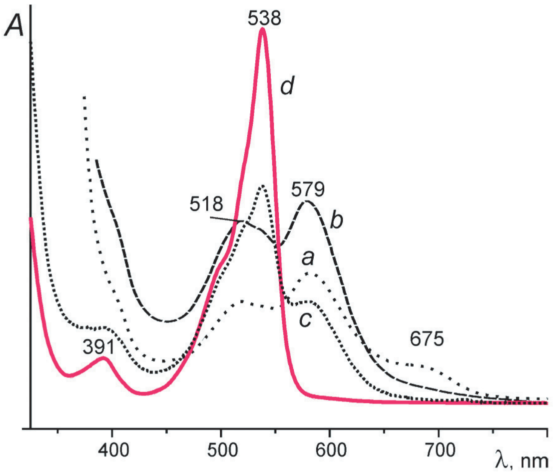


Figure 1. UV-Vis spectral changes observed during reaction of 1,2,5-thiadiazole-3,4-dicarbonitrile with BCl_3 in *p*-xylene upon reflux (curves *a*,*b*,*c*). The spectrum of the reaction product after chromatographic isolation (*d*).

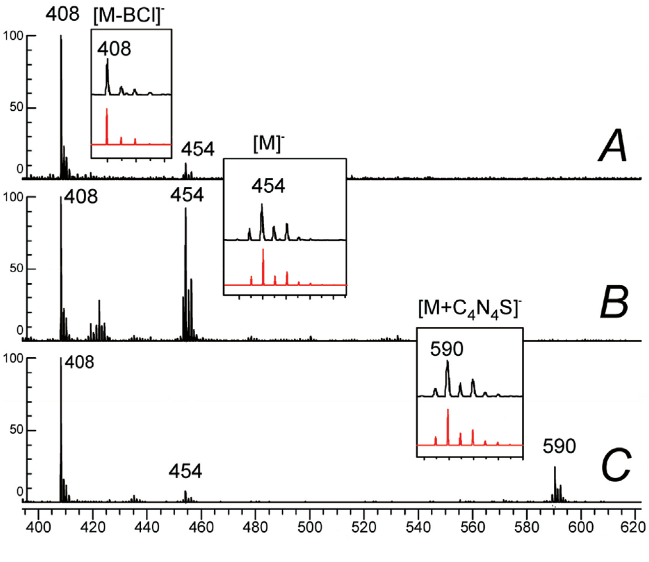


Figure 2. Mass spectra of $[(SN_2)_3SubPABCl]$ in the negative region. *A* – LDI mass-spectrum; *B* – MALDI mass-spectrum with DHB matrix. *C* – LDI mass-spectrum of the reaction mixture containing the violet intermediate product. The inserts show the calculated isotope distribution for the molecular ions.

In the described process, the formation of a subporphyrazine with three fused 1,2,5-thiadiazole rings represented as $[(SN_2)_3SubPABCl]$ is confirmed by analytical data and mass-spectrometry.§ In the LDI and MALDI mass-spectra only the negative molecular ion cluster peak $[M]^-$ with maximum at 454 was observed (Figure 2 *A*,*B*), while no positive ions with isotopic distribution typical for boron-containing compounds could be seen. Interestingly, the negative fragmentation peak $[M\text{-}BCl]^-$ at 408 Da has practically equal intensity with the molecular ion $[M]^-$ in the LDI mass-spectrum and is predominant in the spectrum recorded with DHB matrix. Such fragmentation is not common for subphthalocyanines [SubPcB(Hal)] which usually exhibit a strong positive peak $[M\text{-}Hal]^+$ due to easy loss of axial halogen or other axial ligands. In the case of $[(SN_2)_3SubPABCl]$ the absence of the positive peak $[(SN_2)_3SubPAB]^+$ at 418 Da is consistent with the very strong π-acceptor properties of 1,2,5-thiadiazole annulated subporphyrazine macrocycle, which instead stabilize the negative deborylated ion $[(SN_2)_3SubPA]^-$ found at 408 Da.

The violet intermediate product with absorption bands 518 and 579 nm was not so far isolated because of its low stability during column chromatography affording brown destruction products along with some amount of pure $[(SN_2)_3SubPABCl]$. It is interesting, that the LDI mass-spectrum of the reaction mixture containing this violet product contains in addition to peaks at 408 Da (100 %) and 454 Da (8 %) the cluster peak with maxima at 490 Da (21 %) corresponding to the ion with added dinitrile molecule $[M+C_4N_4S]^-$. The same *m/z* value and isotopic distribution pattern is expected for boron(III) complex of porphyrazine $[(SN_2)_4PABCl]$. Therefore the origin of this peak and the structure of the violet intermediate needs further investigation.

The electronic absorption spectrum of $[(SN_2)_3SubPABCl]$ (Figure 3) contains two intense absorption bands due to π → π* transitions of the subporphyrazine π-chromophore positioned at 538 nm (*Q*-band) and 308 nm (*B*-band). These bands are typical for subphthalocyanines[26,27] and their origin can be similarly assigned to HOMO → LUMO and HOMO-1 → LUMO transitions, respectively. The additional band of lower intensity which is observed at 390 nm very likely originates from the *n* → π* transition between the heteroatoms of the annulated 1,2,5-thiadiazole and the central subporphyrazine π-chromophore. Indeed, this type of absorption band is not present in the spectra of subphthalocyanines and subporphyrazines and their substituted derivatives with alkyl or electron-withdrawing groups, but a similar or even stronger band at *ca.* 380–400 nm appears in the spectra of subphthalocyanines containing substituents attached through O or S atoms[10a] and for 2,3-thianaphthene fused subporphyrazines.[15]

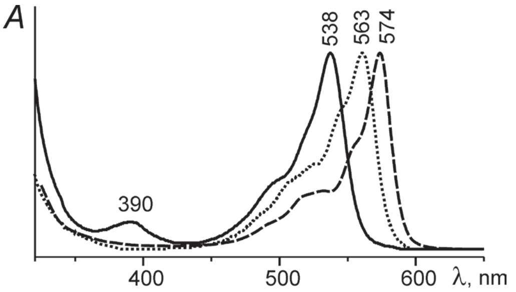


Figure 3. Normalized electronic absorption spectra of 1,2,5-thiadiazole annulated subporphyrazine $[(SN_2)_3SubPABCl]$ (solid line), subphthalocyanine [SubPcBCl] (dotted line) and its perfluorinated derivative $[F_{12}SubPcBCl]$ (dashed line) in CH_2Cl_2.

As compared to subphthalocyanine [SubPcBCl] (λ_Q=563 nm, λ_B=305 nm[26]) the *Q*-band in $[(SN_2)_3SubPABCl]$ is shifted hypsochromically by 25 nm (830 cm^{-1}) and the position of the *B*-band maximum undergoes a slight bathochromic shift (340 cm^{-1}). Therefore annulation of the π-electron-deficient 1,2,5-thiadiazole rings instead of benzene rings increases the HOMO-LUMO gap due to stronger stabilization of HOMO as compared to LUMO, just like it is observed in going from the phthalocyanine complexes [PcM] to corresponding 1,2,5-thiadiazole fused analogues $[(SN_2)_4PAM]$.[28] It is interesting, that perfluorination of subphthalocyanine macrocycle, which endows it with *n*-type behavior[6] leads to stronger stabilization of LUMO than HOMO and associated bathochromic shift of both π → π* transitions (for $[F_{12}SubPcBCl]$ λ_Q=574 nm, λ_B=311 nm[27]). In perfluorinated (sub) phthalocyanines, the strong negative inductive effect (*–I*) of electronegative fluorine atoms is partly compensated by their positive conjugation effect (*+C*). For 1,2,5-thiadiazole fused subporphyrazines the combined *–C* and *–I* effects of heterocyclic moieties allow expecting increased π-electron-acceptor properties.

The fluorescence spectrum of $[(SN_2)_3SubPABCl]$ has emission maximum at 556 nm. As can be seen from Figure 4 it has mirror symmetry with the *Q*-band in the fluorescence excitation spectrum which in turn is similar with the electronic absorption spectrum. The value of the Stock's shift $\Delta\lambda$=18 nm is typical for subphthalocyanines and subporphyrazines and indicates that geometry of the bowl-shaped subporphyrazine macrocycle in $[(SN_2)_3SubPABCl]$ is changed upon excitation more strongly than in the case of essentially planar and rigid 1,2,5-thiadiazole annulated porphyrazines $[(SN_2)_4PAM]$ ($\Delta\lambda$ = 1–4 nm for M = Mg^{II}, $Al^{III}Cl$, $Ga^{III}Cl$, Zn^{II}, Cu^{II}[29]).

In conclusion, we have synthesized the new heterocyclic subphthalocyanine analogue containing fused 1,2,5-thiadiazole fragments instead of benzene rings. Its

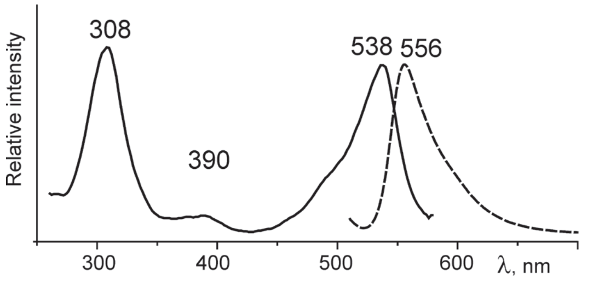


Figure 4. Fluorescence spectra of 1,2,5-thiadiazole annulated subporphyrazine $[(SN_2)_3SubPABCl]$ in CH_2Cl_2: emission at λ_{ex}=500 nm (dashed line), excitation at λ_{ex}=590 nm (solid line).

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§ Tris(1,2,5-thiadiazolo)subporphyrazinatoboron(III) chloride, $[(SN_2)_3SubPABCl]$. Yield 9 %. LDI-TOF MS (negative) *m/z*=454 (92 %) $[M]^+$ (calcd for $C_{12}BClN_{12}S_3$ – 453.93), 408 (100 %) $[M\text{-}BCl]^+$. MALDI-TOF MS (DHB, negative) *m/z*=454 (11 %) $[M]^+$, 408 (100 %) $[M\text{-}BCl]^+$. Anal. Found: C, 31.84; H, 0.12; N, 36.45; S, 20.62 %. Calcd. for calcd for $C_{12}BClN_{12}S_3$ (454.66) C, 31.70; N, 36.97; S, 21.15 %. IR (KBr), ν (cm^{-1}): 1534s, 1469m, 1281m, 1125m, 1071w, 813m, 552w..

further investigation and characterization of the violet intermediate product are now in progress in our group.

Acknowledgements. This work was supported by Russian Foundation of Basic Research (grant 16-03-01048a). PAS thanks Professor Claudio Ercolani (Universita di Roma “La Sapienza”) for useful comments and discussion.

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Received 10.09.2016
Accepted 16.10.2016