

Camphor-Annulated Tripyrazinosubporphyrinatoboron(III) Chloride

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Dedicated to the memory of Academician Oskar Iosifovich Koifman

Series of porphyrazinoids containing fused chiral camphor units (tetrapyrizinoporphyrazines, hemiporphyrazines and [30]trithiadodecaazahexaphyrine) was expanded by novel subphthalocyanane azaanalogue – boron(III) tripyrazinosubporphyrazine which was prepared by trimerization of the corresponding pyrazine-2,3-dicarbonitrile derived by condensation of 1S(+)-camphorquinone and diaminomaleodinitrile in the presence of boron trichloride in o-dichlorobenzene. 1H NMR spectroscopy evidence that subporphyrazine is formed as a mixture of randomers with different orientation of 1S-camphor units, which was characterized by MALDI mass-spectrometry electronic absorption and emission spectroscopy.

Keywords: Boron(III) subporphyrazines, camphorquinone, pyrazine-dicarbonitrile, spectroscopy, fluorescence.

Камфорно-аннелированный трипиразиносубпорфиразинат бора(III)

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Посвящается памяти академика Оскара Иосифовича Койфмана

Серия порфиразиноидов, содержащих конденсированные хиральные камфорные фрагменты (тетрапиразинопорфиразины, гемипорфиразины и [30]тритиадодэкаазагексафурин), была дополнена новым субфталоцианиновым азааналогом – трипиразиносубпорфиразином бора(III), который был синтезирован тримеризацией в присутствии трихлорида бора в о-дихлорбензоле соответствующего пиразин-2,3-дикарбонитрила, полученного конденсацией 1S(+)-камфорхинона и диаминоmaleодинитрила. Спектроскопия ЯМР ¹H свидетельствует о том, что субпорфиразин образуется в виде смеси рандомеров с различной ориентацией 1S-камфорных фрагментов, которая была охарактеризована с помощью масс-спектрометрии MALDI, электронной абсорбционной и эмиссионной спектроскопии.

Ключевые слова: Субпорфиразины бора(III), камфорхинон, пиразиндикарбонитрил, спектроскопия, флуоресценция.

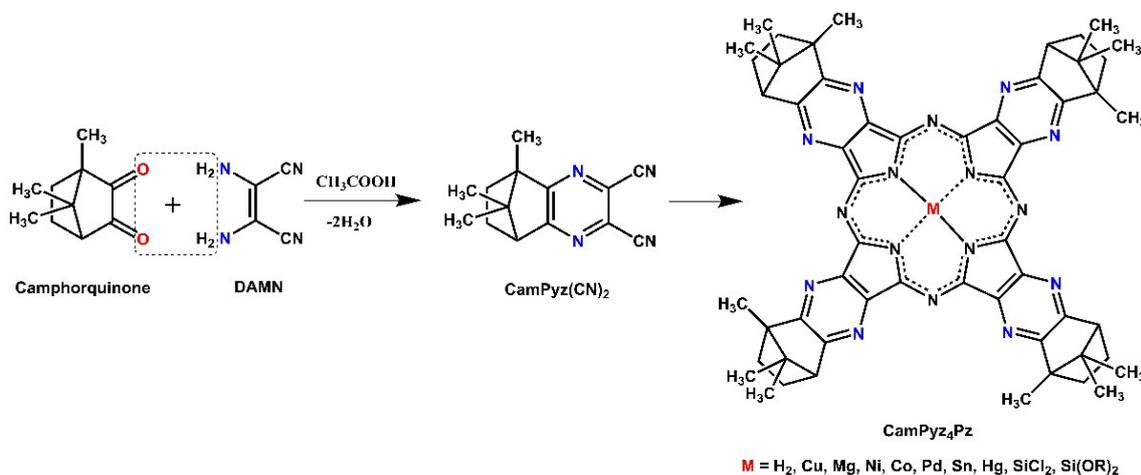
Subphthalocyanine (sPc, Chart 1), first obtained by Meller and Ossco in 1972,^[1] is a cone-shape macroheterocycle in which three isoindole fragments are connected by meso-nitrogen bridges located around a tetrahedral boron atom bearing an axial substituent. A key feature of such contracted phthalocyanine-type macrocycles is that they are known only as boron(III) derivatives.^[2] Subphthalocyanines

and their analogues are actively studied as promising materials for organic photovoltaics,^[3] fluorescence diagnostics^[4] and photodynamic therapy.^[5] Application of sPcs in these areas is determined by their unique optical properties and the absence of aggregation in solutions.

The structure of subphthalocyanines can be modified by annulation of pyrazine fragments instead of benzene

rings which leads to tripyrazinosubporphyrazines (Pyz₃sPz, Chart 1). The unsubstituted boron(III) complex was obtained from pyrazine-2,3-dicarbonitrile and BCl₃ with very low yield (0.3%).^[6] Methyl and ethyl substituted Pyz₃sPz were formed from the corresponding 5,6-dialkylpyrazine-2,3-dicarbonitriles only in trace amounts and cannot be isolated from the reaction mixture. Higher yields of Pyz₃sPz were obtained from dinitriles bearing either aryl groups or saturated quaternary carbon atom adjacent to pyrazine ring. Thus, hexaphenyl substituted derivative Ph₆Pyz₃sPz was obtained in 6.2% yield.^[6] For *tert*-butyl substituted compound ^tBu₃Pyz₃sPz two positional isomers having C₁ and C₃ symmetry were obtained and effectively separated by column chromatography with a total yield of 7%.^[7] A symmetric Pyz₃sPz with 2,3-fused 1,1,4,4-tetramethylcyclohexane fragments was obtained in 35% yield.^[8]

It is of great interest to introduce chiral substituents into macrocycles in order to obtain optically active molecules, which could be potentially suitable for use as sensors for chiral biological molecules, or for selective interaction with biopolymers. Phthalocyanines and their analogues with chiral fragments attract considerable attention.^[9,10] Subporphyrazines with intrinsic chirality could be obtained from non-symmetrical dicarbonitriles, e.g. from thionaphthene-2,3-dicarbonitrile^[11] or benzo-thiazole-5,6-dicarbonitrile.^[12] Chirality can be introduced in the dinitrile precursor itself. Camphor and its derivatives which are available as pure enantiomers are frequently used for introduction of chirality in different molecular systems.^[13,14] Thus, pyrazine-2,3-dicarbonitriles with fused chiral camphor moiety (1*R*-(+)- and 1*S*-(-)-CamPyz(CN)₂) were prepared by condensation of 1*R*-(-) and 1*S*-(+)-enantiomers of camphorquinone (or their racemic mixture) with diaminomaleonitrile (DAMN) in ethanol^[15] or better in acetic acid.^[16] These chiral dinitriles were first used in 1998 by Professor Kobayashi for preparation of optically active camphor-fused tetrapyrazinoporphyrazine (CamPyz₄PzH₂) and its Cu^{II} complex.^[20] Later complexes with Mg^{II}, Ni^{II}^[17] and Si^{IV}^[18,19] were also prepared (Scheme 1).



Scheme 1. General scheme for the synthesis of tetrapyrazinoporphyrazines with camphor units (enantiomer with (1*S*)-configuration is shown).

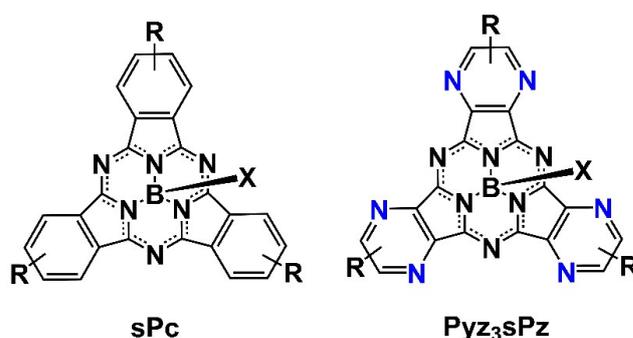


Chart 1. Structure of subphthalocyanine (sPc) and tripyrazinosubporphyrazine (Pyz₃sPz).

In 2017 the Russian group from the *Research Institute of Macroheterocycles* founded by Professor Koifman has prepared Cu^{II}, Ni^{II}, Co^{II}, Pd^{II}, Sn^{II} and Hg^{II} complexes of tetrapyrazinoporphyrazine by template tetramerization of the racemic CamPyz(CN)₂ in the presence of the corresponding metal salts.^[20] In development of this work other camphor-fused macrocycles were also synthesized. Thus, hemiporphyrazine (CamPyz₂HemPz, Chart 2) with two camphor fragments was obtained using microwave activated synthetic procedure from the CamPyz(CN)₂ (*R*-(+) form or racemic mixture) and *m*-phenylenediamine and used for induction of the chiral nematic phase in solutions of 4-*n*-alkyloxy-4'-cyanobiphenyles.^[21] In the reaction of CamPyz(CN)₂ (*R*-(+) or *S*-(-)-enantiomers) with 2,5-diamino-1,3,4-thiadiazole the first chiral [30]trithia-dodecaazahexaphyrins (CamPyz₃HexPhyr, Chart 2) were obtained as a mixture of enantio-pure regioisomers with C₁ and C₃ symmetry, which were separated by chromatography.^[22]

In this communication, we report the synthesis and spectral characterization of a novel subphthalocyanine aza-analogue, tripyrazinosubporphyrazinoboron(III) chloride with fused (1*S*)-camphor moieties, [CamPyz₃sPz].

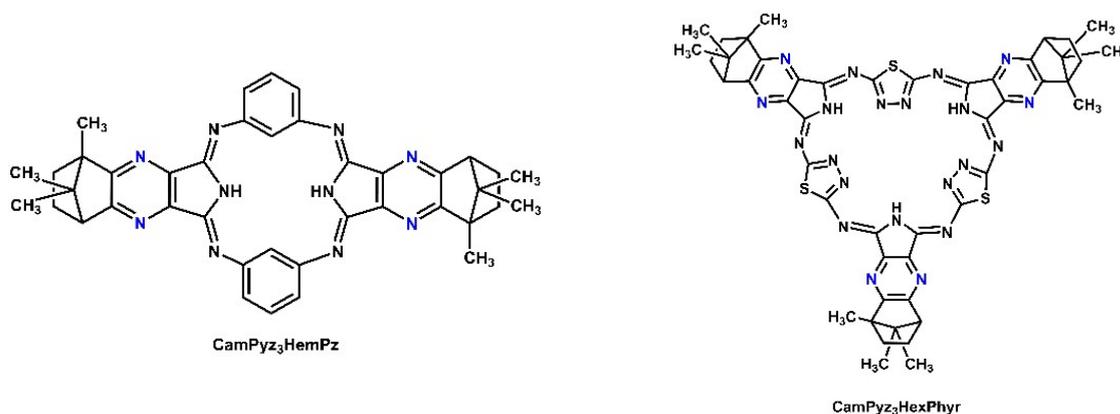
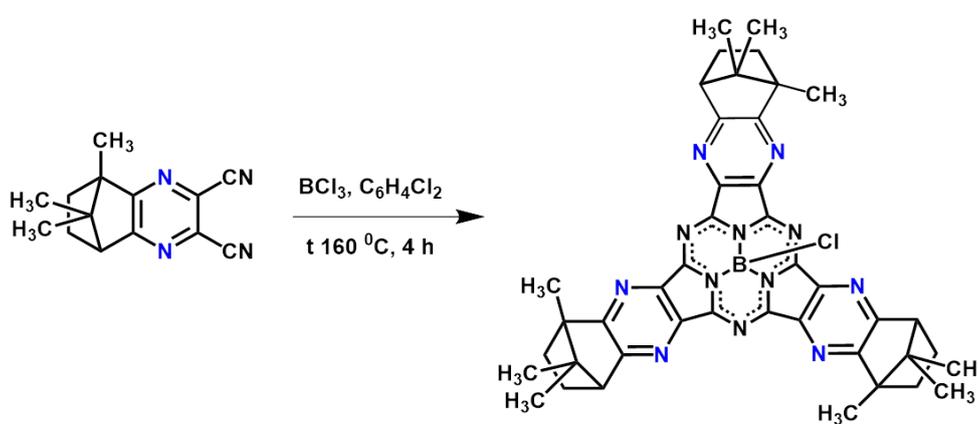


Chart 2. Structures of hemiporphyrazine (left) and [30]trithiadodecaazahexaphyrine (right) containing camphor-annulated pyrazine fragments.



Scheme 2. Synthesis of camphor-annulated tryprazinoboraphyrine boron(III), [CamPyz₃sPz].

Camphor-annulated pyrazine-2,3-dicarbonitrile ((1*S*)-(–)-enantiomer, 0.3 g, 0.0013 mol), prepared by condensation of (1*S*)-(+)-camphorquinone and diaminomaleodinitrile (DAMN) in glacial acetic acid under reflux,^[16] was dissolved in *o*-dichlorobenzene (DCB, 1.5 mL) and after purging with argon solution of boron(III) trichloride (1.5 mL of 1 M in *p*-xylene) was added. The reaction mixture immediately changed color to dark red and then turned brown upon heating under reflux for 4 h. The progress of the reaction was monitored by TLC till appearance of characteristic pink spot typical for subporphyrazine. After cooling, the reaction mixture was poured into hexane and formed precipitate was purified using column chromatography on silica gel. Intermediates and by-products were extracted with CH₂Cl₂, and the target subporphyrazine [CamPyz₃sPz] was eluted with a mixture CH₂Cl₂:EtOAc (10:1).[#]

The constitution of the product is confirmed by LDI-mass spectrum which contains the intense peak at 726.3 Da and minor peak at 762.3 Da corresponding to the positive molecular ions [M–Cl]⁺ and [M+H]⁺, respectively (Figure 1). Such fragmentation with loss of the axial halogen atom is typical for subporphyrazines and subphthalocyanines.

Comparison of the ¹H NMR spectrum recorded for [CamPyz₃sPz] with the spectral parameters of other compounds containing camphor fragment fused to pyrazine ring (Table 1) reveals some structural peculiarities. Since the dinitrile precursor is not symmetrical, its template

cyclotrimerization can lead to formation of four positional isomers (randomers) of [CamPyz₃sPz], differing in the location of the ⁷C bridge in respect to the conical subporphyrazine macrocycle and the central boron atom.

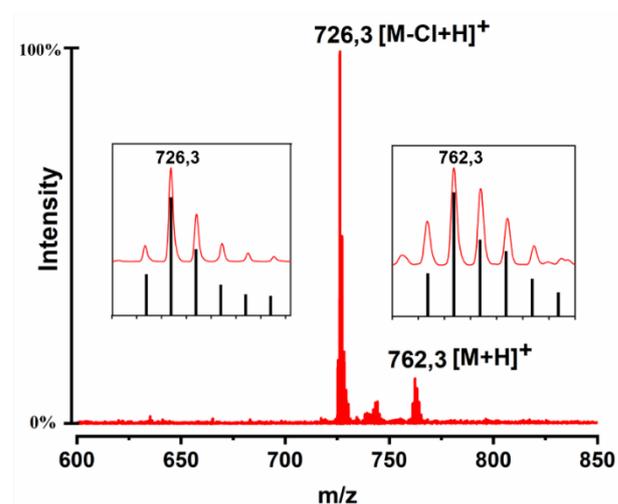


Figure 1. Mass spectrum of [CamPyz₃sPz] in the positive region. The inserts show the calculated isotope distribution for the molecular ions.

One can consider two symmetrical C_3 isomers and two C_1 isomers. In $C_3(\Delta_3)$ isomer one all three ${}^7\text{C}$ atoms are located similarly with the boron atom on the convex side and in another $C_3(\nabla_3)$ isomer on the opposite concave side of the macrocycle. Less symmetrical isomers can have $C_1(\Delta_2\nabla)$ or $C_1(\Delta\nabla_2)$ structure.

In the case of dinitrile [CamPyz(CN)₂] and derived planar macrocyclic compounds (Si^{IV} porphyrazine complex, hemiporphyrazine and [30]trithiadodecaazahexaphyrin) the methyl groups attached to the quaternary ${}^7\text{C}$ atoms of the fused camphor moiety give singlets in the strong field at ~0.6 ppm for *endo*- ${}^7\text{CH}_3$ located above the pyrazine ring and at ~1.1 ppm for *exo*- ${}^7\text{CH}_3$. Protons of the methylene groups in the 5 and 6 positions are diastereotopic and appear as broad multiplets at ~2.3–2.4 and ~2.0–2.2 ppm for *exo*- ${}^5\text{CH}_2$ and *exo*- ${}^6\text{CH}_2$, while resonances of *endo*- ${}^{5,6}\text{CH}_2$ overlap with ${}^3\text{CH}_3$ singlet in the 1.1–1.4 ppm region. Protons of the ${}^1\text{CH}$ group which are nearest to the pyrazine ring give doublet at 3.1–3.4 ppm with typical *gauche* constant ${}^3J \sim 4.5$ Hz.

The ${}^1\text{H}$ NMR spectrum of the obtained subporphyrazine [CamPyz₃sPz] provides clear evidence about presence of randomers with different orientation of camphor moieties. The protons of *endo*- ${}^7\text{CH}_3$ group appear as four closely lying singlets at 0.320, 0.330, 0.344 and 0.346 ppm and corresponding *exo*- ${}^7\text{CH}_3$ give two close signals at 0.973 and 0.978 ppm and overlapping ${}^3\text{CH}_3$ and *endo*- ${}^{5,6}\text{CH}_2$ signals at 1.10–1.16 ppm. Protons of *exo*- ${}^5\text{CH}_2$ and *exo*- ${}^6\text{CH}_2$ appear as broad multiplets at ~2.3 and ~2.1 ppm and ${}^1\text{CH}$ group, which is nearest to the macrocycle, gives closely lying doublets at 3.3–3.4 ppm with *gauche* constant ${}^3J \sim 4.3$ Hz.

The high-field shift observed for the *endo*- ${}^7\text{CH}_3$ resonances (*ca* 0.3 ppm) is indicative about their stronger shielding by aromatic current of the pyrazine ring than in the dinitrile and in planar macrocycles. This can be explained by the location of the ${}^7\text{C}$ -bridge on the concave side of the macrocycle and the presence of four signals correlates with four possible arrangements in one symmetrical $C_3(\nabla_3)$ and two low-symmetry $C_1(\Delta_2\nabla)$ or $C_1(\Delta\nabla_2)$ randomers. Series of signals in the weaker field at 1.21–1.24,

1.01–1.03 and 0.62–0.72 ppm can be very likely assigned to the protons attached to the convex (Δ) oriented camphor units (${}^3\text{CH}_3$ /*endo*- ${}^{5,6}\text{CH}_2$, *exo*- ${}^7\text{CH}_3$ and *endo*- ${}^7\text{CH}_3$, respectively). Since their integral intensity is about half the intensity of concavely (∇) oriented camphor units, formation of subporphyrazine randomers with predominant convex orientation $C_1(\Delta_2\nabla)$ and $C_3(\Delta_3)$ during template cyclotrimerization is evidently less favorable.

It should be noted that ${}^1\text{H}$ NMR data presented for the planar porphyrazine [CamPyz₄PzSi(OH)₂] evidence about formation of only one most symmetrical randomer,^[19] and in the case of planar [30]hexaphyrin two randomers (C_1 and C_3) were observed.^[22]

The electronic absorption spectrum of [CamPyz₃sPz] (Figure 2) contains intense absorption bands at 525 and 300 nm which are typical for subphthalocyanines^[2] and subporphyrazines with fused heterocycles,^[6,8,23,24] and appear due to $\pi \rightarrow \pi^*$ transitions of the subporphyrazine π -chromophore – HOMO \rightarrow LUMO (Q band) and HOMO-1 \rightarrow LUMO (B band) (Figure 2). In addition, the medium intensity band is seen at 333 nm. The maximum of the Q band is located at a slightly shorter wavelength (by 5–10 nm) than in the case of unsubstituted [Pyz₃sPz], its tri-*tert*-butyl substituted and 1,1,4,4-tetramethylcyclohexane fused derivatives, [*t*Bu₃Pyz₃sPz] and [Me₄cHxPyz₃sPz]; and by 25 nm more hypsochromically than in hexaphenyl substituted compound [Ph₆Pyz₃sPz] (Table 2). Interestingly that the additional band observed at 333 nm is not seen in the spectrum of unsubstituted [Pyz₃sPz], but is present as a shoulder for [*t*Bu₃Pyz₃sPz] and as a similar maximum for [Me₄cHxPyz₃sPz]. The origin of this band is different from the band at 386 nm observed for [Ph₆Pyz₃sPz] due to charge transfer transition from phenyl rings to subporphyrazine macrocycle. Most likely two bands in the UV region are similar to the B₁ and B₂ bands observed for hexachlorinated subporphyrazine [Cl₆Pyz₃sPz] and appear due to excited states involving electronic transitions from two a_1 -type orbitals ($2a_1 \rightarrow e_g^*$ and $3a_1 \rightarrow e_g^*$) which lie closely in unsubstituted subporphyrazine, but are differentiated and gain intensity upon peripheral alkylation or chlorination.

Table 1. Chemical shifts (δ , ppm) of proton resonances in the camphor fragments.

Compound	4-CH	5-CH ₂ (<i>exo</i>)	6-CH ₂ (<i>exo</i>)	5,6-CH ₂ (<i>endo</i>)	1-CH ₃	7-CH ₃ (<i>exo</i>)	7-CH ₃ (<i>endo</i>)	Ref.
CamPyz(CN) ₂	3.14d (4.5Hz)	2.38–2.35m	2.15–2.10m	1.25, 1.28	1.36s	1.11s	0.60s	[16,22]
[CamPyz ₄ PzSi(OH) ₂]	3.15d (4.5Hz)	2.40–2.32m	2.12p (10Hz)	1.31q (10Hz)	1.36s	1.11s	0.60s	[19]
[CamPyz ₂ HemiPz]	3.25s	2.36m	2.10	1.30m	1.46–1.38m	1.13s	0.69s	[21]
C_3 [CamPyz ₃ HxPhyr]	3.15 (4.3Hz)	2.34–2.28	1.96–1.89	1.32–1.29; 1.36–1.34	1.40	1.06s	0.60s	[22]
C_1 [CamPyz ₃ HxPhyr]	3.24	2.43–2.37	2.04–1.99	1.43, 1.41	1.50	1.15	0.69	[22]
Mixture of isomers	3.16	2.31–2.38	2.12–2.07	1.41–1.42		1.08	0.66, 0.64, 0.63, 0.61	[22]
[CamPyz ₃ sPz] (∇) fragments	3.36d, 3.39d (4.2 Hz)	2.31	2.07	1.15	1.17	0.97, 0.98	0.33, 0.32, 0.340, 0.345	This work
[CamPyz ₃ sPz] (Δ) fragments	3.43m		2.4–2.0	1.1–1.2 (1.22–1.23)		1.02, 1.03	0.62–0.72	This work

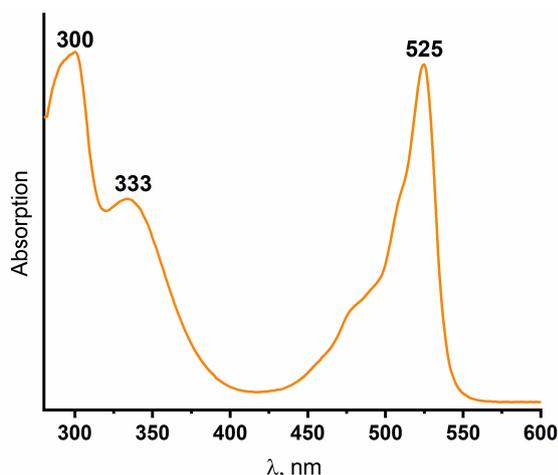


Figure 2. Electronic absorption spectrum of [CamPyz₃sPz] in CH₃CN.

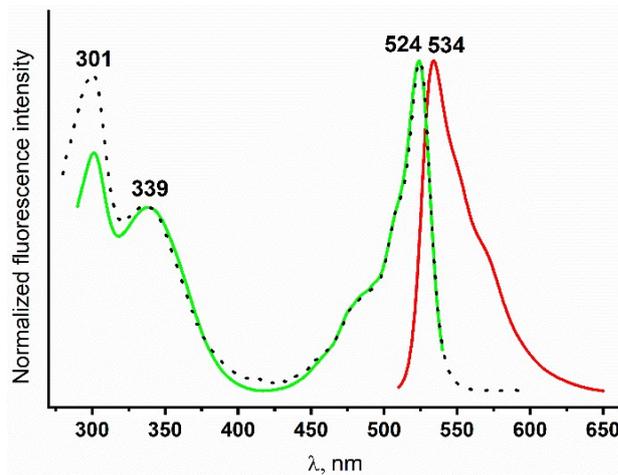


Figure 3. Fluorescence emission ($\lambda_{\text{ex}}=500$ nm, red line) and excitation ($\lambda_{\text{em}}=550$ nm, green line) spectra of [CamPyz₃sPz] in CH₂Cl₂. Absorption spectrum is shown by dotted line.

Table 2. Spectral luminescence properties of pyrazine fused boron(III) subporphyrines in dichloromethane.

Subporphyrine	Absorption, λ (nm)		Fluorescence		Ref.
	Soret region	Q band	λ_{em} (nm)	Φ_{F}	
[Pyz ₃ sPz]	306	532	542	0.15	[6]
[^t Bu ₃ Pyz ₃ sPz]	295	330sh	530	0.37 (<i>C</i> ₁), 0.28 (<i>C</i> ₃)	[7]
[Me ₄ cHxPyz ₃ sPz]	303	334	534	0.19	[8]
[CamPyz ₃ sPz]	303	333	525	0.31	This work
[Ph ₆ Pyz ₃ sPz]	310	386	551	0.31	[6]
[Cl ₆ Pyz ₃ sPz]	311	340	535	0.20	[23]

The fluorescence spectrum for [CamPyz₃sPz] in CH₂Cl₂ is shown in Figure 3. The emission band has mirror symmetry with the Q band in the excitation spectrum, which is almost identical to the absorption spectrum. The value of the Stokes shift is ~10 nm and indicates that only small geometric rearrangements occur in excited state, which is typical for subphthalocyanines and subporphyrines. The fluorescence quantum yield values Φ_{F} for [CamPyz₃sPz] in CH₂Cl₂ are $\Phi_{\text{F}} = 0.31$ and $\Phi_{\text{F}} = 0.39$ in toluene.[†] This value is close to data determined for other alkyl and aryl substituted tripyrazinoporphyrazines (Table 2). For unsubstituted species [Pyz₃sPz] Φ_{F} values are lower due to aggregation effects and for hexachloro derivative [Cl₆Pyz₃sPz] due to heavy atom effect of chlorine atoms.

Thus, we have synthesized a new azaanalogue of subphthalocyanine containing fused chiral *S*-camphor units and studied its spectral and fluorescent properties. The study of the analogues with *R*-camphor units is in progress.

Notes

[#][CamPyz₃sPz]. Yield 10%. $R_{\text{f}} = 0.68$ (15% EtOAc in CHCl₃). LDI-mass spectrum: $m/z = 726.3$ (100%) [M-Cl]⁺ (calcd. 726.38), 762.3 (10%) [M+H]⁺ (calcd. 761.35). UV-Vis (CHCl₃) λ_{max} nm (lg ϵ): 302 (4.23), 333 (3.99), 525 (4.17).

[†]Fluorescence quantum yields (Φ_{F}) were determined by a comparative method using Rhodamine 6G as a reference ($\Phi_{\text{F}}^{\text{R}}=0.94$ in ethanol^[25]) according to the equation: $\Phi_{\text{F}}^{\text{S}}=\Phi_{\text{F}}^{\text{R}}(F^{\text{S}}/F^{\text{R}})(A^{\text{R}}/A^{\text{S}})(n^{\text{S}}/n^{\text{R}})^2$, where F is the integrated area

under the emission spectrum, A is the absorbance at the excitation wavelength (500 nm), n is the refraction index of the solvent, superscripts R and S correspond to the reference and the sample, respectively. The emission spectra were corrected for the instrument response. Absorption in the Q-band region was kept below 0.1 in order to eliminate an inner filter effect. All measurements were performed three times and presented data represent the mean values of three experiments with the estimated error $\pm 10\%$.

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Received 18.06.2024

Accepted 14.07.2024