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Perfluorinated Porphyrazines. 5. Perfluoro−α,β−dicyanostylbene: Molecular Structure and Derived (Sub)Porphyrazine Complexes with IIIa Group Elements

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Dedicated to Prof. Dieter Wöhrle on the occasion of his Birthday

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Template cyclomerization of perfluoro-α,β-dicyanostylbene in the presence of trichlorides of IIIa group elements results in formation of pentafluorophenyl substituted boron(III) subpophyrazinate ([(Cl)BsPAF$_{30}$]) and aluminum(III) and gallium(III) porphyrazinates ([(Cl)MPAF$_{40}$], M=Al, Ga). Their spectral-luminescence properties are discussed, revealing blue shift of the Q-band and brighter fluorescence comparatively to non-fluorinated analogues. In addition, the molecular structure of trans-perfluoro-α,β-dicyanostylbene was determined by single crystal X-ray diffraction.

Keywords: Perfluoro-α,β-dicyanostylbene, subporphyrazine, porphyrazine, complexes, IIIa group elements, X-ray, synthesis.

Перфторированные порфиразины. 5. Перфтор−α,β−дициано−стильбен: Молекулярная структура и комплексы (суб)порфиразинов с элементами IIIa группы на его основе

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При темплатной цикломеризации пентафтор-α,β-дицианостильбена в присутствии хлоридов элементов IIIa группы образуются пентафторфенилзамещенные субпорфиразинат бора ([(Cl)BsPAF$_{30}$]) и порфиразинаты алюминия и галлия ([(Cl)MPAF$_{40}$], M=Al, Ga). Приводится сравнительная характеристика спектрально-люминесцентных свойств полученных комплексов и их нефторированных аналогов. Структура транс-изомера пентафтор-α,β-дицианостильбена определена методом рентгеноструктурного анализа.

Ключевые слова: Перфтор-α,β-дицианостильбен, субпорфиразины, порфиразины, комплексы, элементы группы IIIa, рентгено-структурный анализ, синтез.

Introduction

Fluorinated porphyrinoids reveal a wide range of outstanding features that differ from nonfluorinated analogues due to electronegative character of fluorine atoms. Their peculiarities and potential of application in various fields highlighted by H. Hanack[1] (non-linear optics), D. Wöhrle[2] (organic electronics), T. Goslinski[3] (biochemical applications) and other authors (see review chapter[4]) inspired us for studying the perfluorinated porphyrazines. In a series of our works we have prepared octa(pentafluorophenyl)porphyrazine [H_2PAF_{40}] and its complexes with Mg^{II}, Zn^{II} and In^{III} and demonstrated the crucial role of perfluorination in regulation of acid-base properties of *meso*- and inner nitrogen atoms and in photophysical properties such as quantum yield of fluorescence and singlet oxygen generation.[5,6] In addition, the presence of fluorinated phenyl residues widens the opportunities for modification of periphery of the macrocycle by nucleophilic substitution of fluorine atom(s). Thus, S_NAr reaction was employed for preparation of butoxy and water soluble galactosyl derivatives from [$ZnPAF_{40}$], in which up to eight F-atoms in *p*-positions of phenyl rings can be substituted.[7]It was also demonstrated by Nemykin and coauthors[8] that μ-oxodiiron(III) complex, [μ-O($FePAF_{40}$)$_2$], is an effective catalyst of oxidation reactions.

Introduction of electronegative fluorine atoms in macrocycle allows controlling the properties of tripyrrolic macrocycles as well. Thus, it was observed that fluorinated subphthalocyanines [(Cl)B*sPc*F_n] are taken much stronger by breast tumor cells as compared with non-fluorinated species [(Cl)B*sPc*] and exhibit significant intracellular fluorescence.[9] Perfluorinated subphthalocyanine [(Cl)B*sPc*F_{12}] was shown to be efficient as an acceptor in organic photovoltaic devices for solar energy conversion.[10] A number of low-symmetry subporphyrazines containing fused tetrafluorobenzene moieties were reported (see [4] and refs. therein, [11]). It was also found that fluorination of polyphenylated quinoxalinosubporphyrazines gives rise to superior singlet oxygen quantum yields.[12] But still, there are only few examples of subporphyrazines bearing fluorinated residues.[9,13,14] Here we report on the pentafluorophenyl substituted macrocyclic complexes of IIIa group elements which are formed in the course of template cyclomerization of perfluoro-α,β-dicyanostylbene in the presence of corresponding trichlorides. In addition, the molecular structure of *trans*- perfluoro-α,β-dicyanostylbene was determined by single crystal X-ray diffraction.

Experimental

General

UV-vis spectra were recorded using Cary-60 spectrophotometer. Mass-spectrometric measurements were carried out on a MALDI-TOF Bruker Ultraflex (the Center of the Collective Usage of ISUCT). NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AV-400 or AV-500 spectrometers operating at 376.31 MHz for ^{19}F (CF_3COOH). IR spectra were recorded on Cary 630 FTIR (KBr). Fluorescence was measured on Shimadzu RF-6000 spectrofluorophotometer. Fluorescence quantum yields were determined by comparative method using ZnPc as a reference (Φ_F = 0.32 in THF) as described in [22]. Commercially available solvents were dried and distilled prior use.

Synthesis

Perfluoro-α,β-dicyanostylbene (**1**) was obtained following the previously described procedure[5] as a mixture of *cis*- and *trans*-isomers which was used for template cyclomerization reactions without separation. The single crystals of the *trans*-isomer, *trans*-**1**, were obtained occasionally by slow evaporation of the first fraction collected in the course of purification of **2** by column chromatography (see below).

Hexakis(pentafluorophenyl)subporphyrazinatoboron(III) chloride, [(Cl)B*sPA*F_{30}] (**2**). Perfluoro-α,β-dicyanostylbene **1** (mixture of *cis*- and *trans*-isomers, 300 mg, 0.73 mmol) was placed into two-necked flask and purged with argon for 10 minutes. Then BCl_3 (0.75 mL of 1 M solution in p-xylene, Aldrich) was added by syringe. The mixture was refluxed at 150 °C under argon for two hours. At the beginning of heating the color of mixture changed from orange to green and then to dark-blue. The color got a "burgundy" tone after the cooled reaction mixture was allowed to contact with air. The obtained solution was passed through a column with silica (eluent: CH_2Cl_2) to remove unreacted dinitrile. Slow evaporation of the 1st fraction which was slightly colored due to admixture of the cyclotrimerization product afforded crystals of the *trans*-isomer of the dinitrile precursor, *trans*-**1**, which were suitable for X-ray diffraction analysis. The second intensively colored pink-purple fraction contained the target subporphyrazine **2** which was isolated as burgundy solid (70 mg, yield 30 %). R_f = 0.61 (CH_2Cl_2-hexane 1:1). MS (LDI-TOF) negative mode: *m/z* = 1277.3 (100 %) $[M+H]^-$; positive mode: 1241.3 (100 %) $[M-Cl]^+$, 1276.2 (48 %) $[M]^+$ (calculated for $C_{48}F_{30}N_6BCl$ – 1276.0). ^{13}C NMR ($CDCl_3$) δ ppm: 152.5, 146.3(m), 142.8(m), 140.1(m), 136.7(m), 129.1. ^{19}F NMR ($CDCl_3$) δ ppm: –135.6 (d, ^3J = 21.2 Hz), –144.7 (t, ^3J = 21.2 Hz), –158.0 (t, ^3J = 21.2 Hz). IR (KBr), ν cm^{-1}: 820m, **993s**, 1126m, 1260w, 1310w, 1390w, 1400m, **1498vs**, 1523m, 1560w. UV-Vis (CH_2Cl_2) λ_{max} nm: 528.

Octakis(pentafluorophenyl)porphyrazinatoaluminum(III) chloride, [(Cl)Al*PA*F_{40}] (**3**). Mixture of *cis*- and *trans*-perfluoro-α,β-dicyanostylbenes **1** (1.87 g, 4.56 mmol) was melted with anhydrous $AlCl_3$ (670 mg, 5 mmol) at 260 °C until solidification (*ca*. 30 min.). The residue was dissolved in CH_2Cl_2, filtrated and chromatographed on neutral alumina (II grade Brockmann, eluent CH_2Cl_2 with 1–5 % methanol). After evaporation of the solvent the product was obtained as green solid (760 mg, 40 %). MS (LDI-TOF), *m/z* : 1667.7 (100 %) $[M-Cl]^-$ (calc. for $C_{64}F_{40}N_8AlCl$ 1701.91), 1686.7 (48 %) $[M-Cl+F]^-$, 1702.7 (6 %) $[M-Cl]^-$ (calc. for $C_{64}F_{40}N_8AlCl$ 1701.91). IR (KBr), ν cm^{-1}: 819m, 874m, 994s, 1156w, 1258m, 1313m, 1401w, 1500s. UV-Vis (CH_2Cl_2) λ nm (log ε): 361 (4.41), 571 (3.54), 620 (4.12).

Octakis(pentafluorophenyl)porphyrazinatogallium(III) chloride, [(Cl)Ga*PA*F_{40}] (**4**), was obtained analogously to **3** from dinitrile **1** (0.6 g, 1.46 mmol) and $GaCl_3$ (1.47 mmol). The product was obtained as emerald green solid (270 mg, 42 %). MS (LDI-TOF), *m/z*: 1710.3 (100 %) $[M-Cl]^-$, 1729.0 (11 %) $[M-Cl+F]^-$, 1746.0 (17 %) $[M]^-$ (calculated for $C_{64}F_{40}N_8GaCl$ 1745.9). IR (KBr), ν cm^{-1}: 818m, 862m, 996 s, 1124w, 1157m, 1413m, 1501s. UV-Vis (CH_2Cl_2) λ nm (log ε): 372 (4.49), 571 (3.89), 624 (4.59).

Crystal Structure Determination

The diffraction data for **1** were collected on a XTaLab Pro P200K MM003 diffractometer with MoKα radiation (λ = 0.71073, MicroMax 003) by doing ω scan at 100 K temperature. Absorption correction was done empirically using spherical harmonics in CrysAlisPro software.[15] Crystallographic data and refinement details for **1** are given in Table 1 (see Supplementary information).

The primary structure was solved by direct methods using SHELXL-2018/1 [16] and WinGX.[17] The positions of other atoms were determined by the difference syntheses of electron density and were refined against $|F|^2$ by the least squares method.

The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition codes CCDC 1967396.

Results and Discussion

Synthesis

The dinitrile precursor **1** for perfluorinated complexes **2–4** was prepared as a mixture of *cis*- and *trans*-isomers following the previously described procedure.[5] Earlier it was shown that tedious chromatographic separation of *cis*- and *trans*-isomers of **1** is a dispensable procedure and their mixture can be successfully used in template cyclotetramerization leading to formation of porphyrazine complexes [M*PA*F_{40}] (M = Mg^{II}, Zn^{II} and (X)In^{III}).[5,6] Non-fluorinated compounds – complexes of octaphenylporphyrazine, *e.g.* [(X)M*PA*H_{40}] (M = Al^{III}, Ga^{III} and In^{III}),[18] can be easily obtained directly from *trans*-dicyanostylbene (*i.e.* fumaric acid derivative) by melting with corresponding metal halides. So in the present work a mixture of *cis*-**1** and *trans*-**1** was also used in the template cyclotetramerization in a melt with anhydrous Al^{III} and Ga^{III} salts affording the corresponding porphyrazine complexes **3** and **4** [(Cl)M*PA*F_{40}] (M = Al and Ga, respectively) with moderate yields *ca*. 40 % (after chromatographic purification).

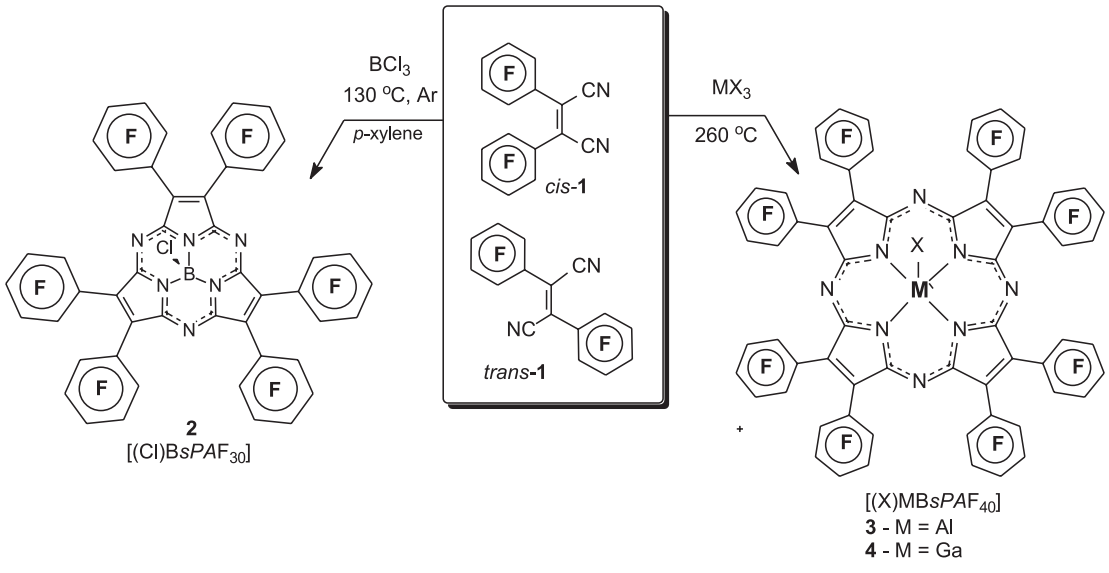
It is known that the boron atom is too small to assist the cyclo**tetra**merization of phthalodinitriles with formation of phthalocyanines and B^{III} halides can serve as templates only for cyclo**tri**merization process affording boron(III) subphthalocyanines.[19,20,21] Similar cyclotrimerization with formation of subporphyrazine macrocycle was also observed for heterocyclic vicinal dinitriles (*e.g.* with pyrazine[22] or 1,2,5-chalcogenadiazole rings[11b,23]) and for alkyl and alkylsulfanyl substituted maleodinitriles.[24,25] It was reported that alkyl or aryl substituted fumarodinitriles having *trans*-configuration are inactive in cyclotrimerization with formation of subporphyrazines.[25] Since diaryl substituted maleodinitriles were not availalable, hexaarylated subporphyrazines were obtained[14] only by peripheral arylation of ethylsulfanyl substituted subporphyrazines using Pd-catalyzed Cu-mediated cross-coupling reaction with arylboronic acids with overall yield from di(ethylsulfanyl)maleonitrile not exceeding 6 %. We have observed that reaction of *cis/trans*-**1** mixture with BCl_3 in *p*-xylene under reflux leads to cyclotrimerization product – perfluorophenyl substituted subporphyrazine **2**, which was isolated with *ca*. 30 % yield as chloroboron(III) complex, [(Cl)B*sPA*F_{30}]. During column chromatography (silica, CH_2Cl_2) it was eluted as a second fraction, while the first fraction contained the unreacted fumaric isomer *trans*-**1**, which was obtained as single crystals suitable for X-ray diffraction study. Evidently *cis*-configuration of two cyano groups is not strictly necessary requirement for cyclotetramerazation, but is essential for successful cyclotrimerization.

*X-Ray Crystal Structure of trans-**1***

Unreated bis(pentafluorophenyl)fumarodinitrile, *trans*-**1**, isolated at purification of subporphyrazine complex **2** could be crystallized and its molecular structure was determined using single crystal X-ray diffraction (Figure 1). In a centrosymmetric molecule the carbon atom of the ethylene fragment is disordered between two positions (C7A – 76.7 % and C7B – 23.3 %). The pentafluorophenyl fragments form the dihedral angle 61.1° with the central dicyanoethylene moiety, thus excluding the conjugation. The ethylene fragment contains C=C double bond (1.346 Å) and the C7A-C1 distance to aryl group is typical for C-C single bond (1.509 Å). In the case of non-fluorinated precursor (diphenylfumarodinitrile) the dihedral angle 42.5° allows some conjugation leading to elongated C–C bond (1.455 Å).[26]

Characterization of Macrocyclic Complexes

Mass-spectra. Formation of the macrocyclic complexes in the course of template cyclomerization



Scheme 1. Template cyclomerization of **1** in the presence of IIIa group chlorides.

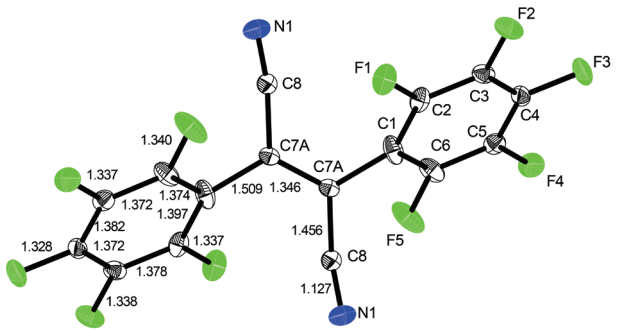


Figure 1. Molecular structure of bis(pentafluorophenyl) fumarodinitrile *trans*-**1** with atom numbering and bond length. Thermal ellipsoids are shown with 30% probability.

of the dinitrile **1** was confirmed using MALDI-TOF mass-spectrometry. Perfluorophenyl groups strongly enhance the electron affinity of the macrocycles and facilitate formation of the negative ions, while ionization with appearance of cations becomes difficult. For subporphyrazine complex **2** the positive molecular ion peak $[M]^+$ observed at 1276 Da is accompanied by more intense peak $[M\text{-}Cl]^+$ at 1241 Da. For porphyrazine complexes **3** and **4** no positive molecular ion peaks could be seen. The negative molecular ion peaks with characteristic isotope distribution are present in the LDI-TOF mass-spectra of all compounds (Figure 2). For subporphyrazine **2** only negative molecular ion $[M]^-$ is present. For porphyrazines **3** and **4** the molecular ion $[M]^-$ is much less intense than fragmentation anion $[M\text{-}Cl]^-$ which formally corresponds to the complex between M^{III} and doubly reduced porphyrazine macrocycle. Formation of the secondary anion $[M\text{-}Cl+F]^-$ due to exchange of axial chlorine by fluorine is also observed.

Electronic absorption spectra of perfluorinated complexes with IIIa group elements and their non-fluorinated analogues are shown in Figure 3. The spectra of the Al^{III} and Ga^{III} complexes **3** and **4** are typical for porphyrazines and contain intense *Q*-band in the visible region (620 and 624 nm) and Soret band in the UV-region (361 and 372 nm). For the subporphyrazine complex **2** the Q-band is much broader and its maximum is shifted by *ca*. 100 nm to the shorter wavelength (to 528 nm) due to contraction of the π chromophoric system as compared to porphyrazines. The maxima of the *Q*- and Soret bands for macrocyclic complexes **2**, **3** and **4** containing perfluorinated phenyl rings are shifted hypsochromically as compared to non-fluorinated species. A similar effect of perfluorination was observed in the case of In^{III} and Zn^{II} complexes[5,6] and was explained by stronger stabilization of HOMO than LUMO. The effect of perfluorination on the Q-band position correlates with electronegativity of the central coordinating atom and for the IIIa group elements is decreased in the order: B^{III} (387 cm^{-1}) > Al^{III} (381 cm^{-1}) > Ga^{III} (302 cm^{-1}) > In^{III} (222 cm^{-1}). In the spectra of non-fluorinated phenyl substituted macrocyclic complexes the intense charge transfer (CT) band from peripheral aryl groups to the central macrocycle is observed: Ar→subporphyrazine at *ca*. 400 nm[14,22] or Ph→porphyrazine at 450–480 nm[5,6]). This CT band disappears when peripheral phenyl groups are perfluorinated and become strong electron-acceptors. In addition perfluorination increases the dihedral angles of aryl groups with pyrrole rings of macrocycle,[6] thus diminishing the π–interaction.

Fluorescence spectra. Fluorescence emission and excitation spectra of perfluorinated macrocyclic complexes with IIIa group elements and their non-fluorinated analogues are shown in Figure 4. For porphyrazine complexes $[(X)MPAF_{40}]$ the values of the Stock's shifts increase in the order Al^{III} (4 nm, 140 cm^{-1}) < Ga^{III} (8 nm,

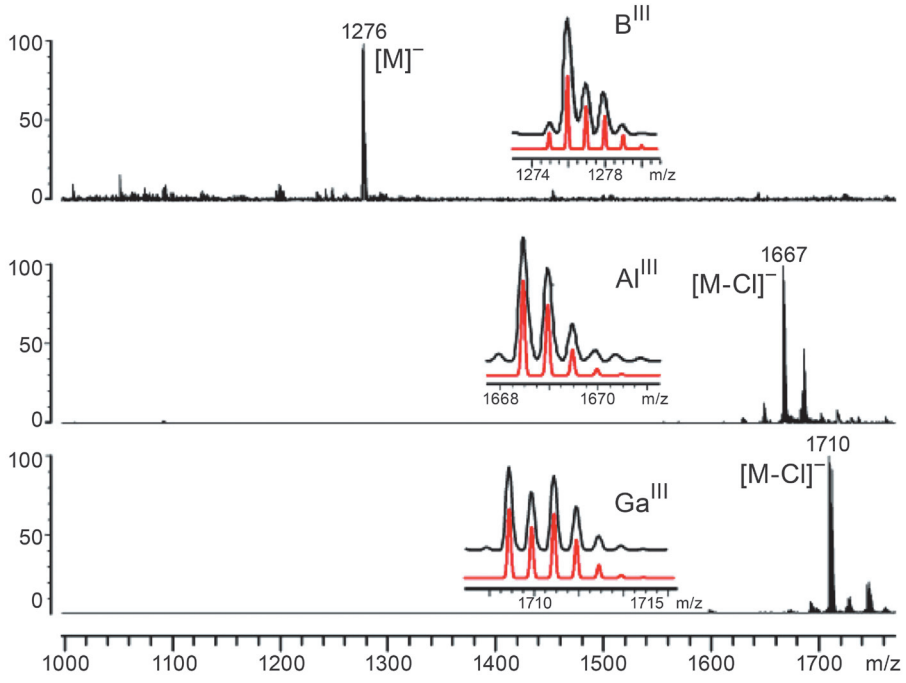


Figure 2. LDI-TOF mass-spectra of macrocyclic complexes **2**, **3** and **4** obtained by template cyclomerization of perfluoro-α,β-dicyanostylbene **1** in the presence of MCl_3 (M = B, Al, Ga).

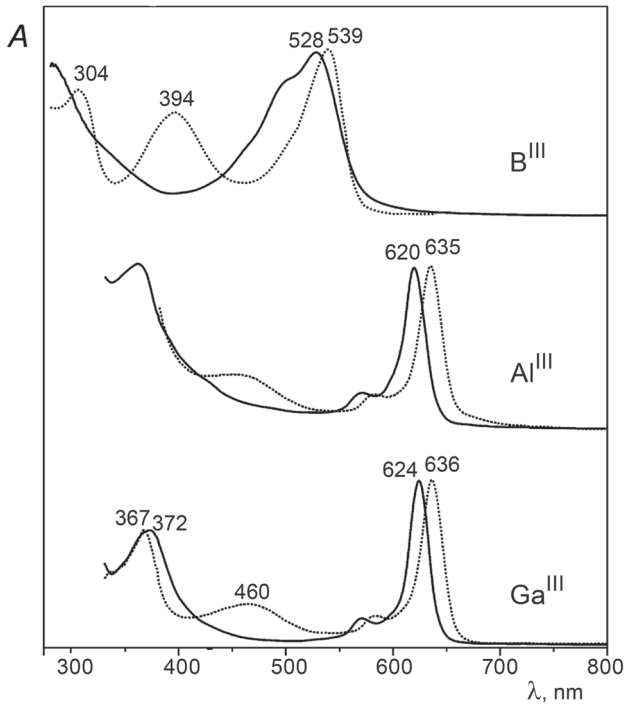


Figure 3. Electronic absorption spectra of macrocyclic complexes **2**, **3** and **4** obtained by template cyclomerization of perfluoro-α,β-dicyanostylbene **1** in the presence of MCl_3 (M = B, Al, Ga). Spectra of corresponding non-fluorinated complexes adopted from ref. [18,27] are shown by dotted lines.

200 cm^{-1}) < In^{III} (28 nm, 680 cm^{-1}). The emission bands become broader and less structured in the same sequence. Coordination of metal ions with larger ionic radius, especially In^{III} causes dome deformation of the porphyrin-type macrocycle (see *e.g.* [27]). This increases the conformational flexibility of the skeleton in the excited state leading to larger Stock's shifts.

The fluorescence quantum yields (Φ_F) of perfluorinated porphyrazines [(Cl)M*PA*F_{40}] determined in THF decrease due to heavy atom effect in the order Al^{III} (0.13) > Ga^{III} (0.085) > In^{III} (0.019). Complexes of non-fluorinated octapheylporphyrazines [(Cl)M*PA*] which we have studied for comparison are less fluorescent (Φ_F = 0.031 and 0.012 for M = Ga^{III} and In^{III} , respectively). The effect of brighter fluorescence of perfluorinated complexes, also observed for the Zn^{II} complexes (Φ_F = 0.19 for [Zn*PA*F_{40}] and 0.12 for [Zn*PA*][6]), was explained by lesser involvement of more orthogonal pentafluorophenyl groups than phenyl groups in non-radiative deactivation of the excited state. Interestingly that complexes of porphyrazines with more rigid macrocycle are more fluorescent and have higher Φ_F values (*e.g.* for the Al^{III}, Ga^{III} and Zn^{II} complexes of tetrakis(1,2,5-thiadiazolo)porphyrazine Φ_F = 0.53, 0.21 and 0.24, respectively[24]). Evidently non-radiative pathways of deactivation become more significant in more flexible aryl substituted porphyrazines allowing stronger deformation of the macrocyclic skeleton in the excited state than in more rigid 1,2,5-thiadiazole fused species resulting in a considerable decrease of fluorescence.

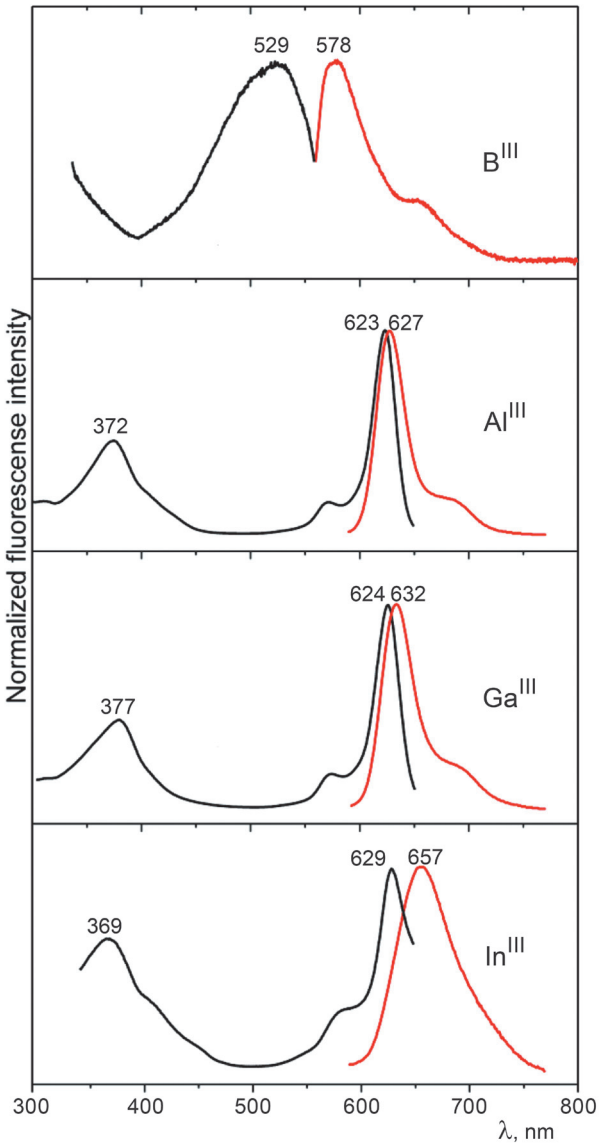


Figure 4. Normalized fluorescence emission (red lines) and excitation (black lines) of perfluorinated B^{III} complex of subporphyrazine 2 (λ_{ex} = 550 nm, λ_{em} = 650 nm) and porphyrazine complexes with Al^{III} (3), Ga^{III} (4) and In^{III} (λ_{ex} = 580 nm, λ_{em} = 660 nm).

The perfluorinated B^{III} subporphyrazine complex **2** has very low fluorescence (Φ_F < 0.01) and its fluorescence emission spectrum is characterized by very large Stock's shift value (51 nm, 1600 cm^{-1}). For B^{III} complex of non-fluorinated hexaphenylsubporphyrazine and other aryl substituted subporphyrazines the very low fluorescence was also observed (Φ_F < 0.001–0.03[14]). At the same time boron(III) complexes of more rigid 1,2,5-thiadiazole and pyrazine fused subporphyrazines exhibit stronger fluorescence (Φ_F = 0.11–0.15[23]), and phenyl substitution on pyrazine rings even increases it (Φ_F = 0.31[22]). Therefore we can make a general conclusion that aryl substituted porphyrazines and subporphyrazines are more sensitive to the factors causing deformation of the macrocycle and promoting radiationless deactivation of the excited states than more rigid (sub)porphyrazines with fused heteroarenes.

Conclusions

The interaction of perfluoro-α,β-dicyanostylbene **1** with salts of IIIa group elements allows the corresponding products of its tri- (**2**) and tetramerization (**3**, **4**). In the case of subporphyrazine **2**, [(Cl)Bs*PA*F_{30}], the role of *cis*-*trans*-isomerization of **1** is more crucial than for formation of porphyrazines **3**, **4**, [(Cl)M*PA*F_{40}] (M = Al, Ga), for synthesis of which *cis*-configuration of two cyano groups is not strictly necessary requirement. According to the data of single crystal X-ray diffraction of *trans*-isomer of **1**, the conjugation of dicyanoethylene moiety with pentafluorophenyl fragments is excluded in contrast to non-fluorinated precursor (diphenylfumarodinitrile). Perfluorination of phenyl rings in **2**-**4** leads to the hypsochromic shift of the *Q*-band and the disappearance of the CT-band in their UV-Vis spectra. The subporphyrazine **2** is practically non-fluorescent, while porphyrazine complexes **3**, **4** acquire slightly more pronounced fluorescent properties at perfluorination.

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References

1. Dini D., Yang G.Y., Hanack M. *J. Chem. Phys.* **2003**, *119*, 4857–4864.
2. Brinkmann H., Kelting C., Makarov S., Tsaryova O., Schnurpfeil G., Wöhrle D., Schlettwein D. *Physica Status Solidi A Appl. Res.* **2008**, *205*, 409–420.
3. Goslinski T., Piskorz J. *Photochem. Photobiol.* **2011**, 304–321.
4. Stuzhin P.A. Fluorinated phthalocyanines and their analogues. In: *Fluorine in Heterocyclic Chemistry*, Vol. 1, 5-Membered Heterocycles and Macrocycles (Nenajdenko V.G., Ed.), Springer, Heidelberg, 2014, pp. 621–681.
5. a) Stuzhin P.A., Goryachev M.Yu., Ivanova S.S., Nazarova A., Pimkov I., Koifman O. I. *J. Porphyrins Phthalocyanines* **2013**, *17*, 905–912; b) Stuzhin P.A., Ivanova S.S., Koifman O.I., Petrov O.A., Nazarova A. *Inorg. Chem. Commun.* **2014**, *49*, 72–75.
6. Lebedeva (Yablokova) I.A., Ivanova S.S., Novakova V., Zhabanov Yu.A., Stuzhin P.A. *J. Fluorine Chem.* **2018**, *214*, 86–93.
7. Ivanova S.S., Lebedeva I.A., Stuzhin P.A. *Russ. Chem. Bull.* **2018**, *67*, 2246–2249.
8. Yusubov M.S., Celik C., Geraskina M.R., Yoshimura A., Zhdankin V.V., Nemykin V.N. *Tetrahedron Lett.* **2014**, *55*, 5687–5690.
9. McAuliffe K.J., Kaster M.A., Szlag R.G., Trivedi E.R. *Int. J. Mol. Sci.* **2017**, *18*, 1177.
10. Cnops K., Zango G., Genoe J., Heremans P., Martinez-Diaz M.V., Torres T., Cheyns D. J. *Am. Chem. Soc.* **2015**, *137*, 8991–8997.
11. (a) Hamdoush M., Skvortsov I.A., Mikhailov M.S., Pakhomov G.L., Stuzhin P.A. *J. Fluorine Chem.* **2017**, *204*, 31–36; b) Pakhomov G.L., Travkin V.V., Hamdoush M., Zhabanov Yu.A., Stuzhin P.A. *Macroheterocycles* **2017**, *10*, 548–551.
12. Munnich R., Loser P., Winzenburg A., Faust R. *J. Porphyrins Phthalocyanines* **2016**, *20*, 1277–1283.
13. Kobayashi N., Ishizaki T., Ishii K., Konami H. *J. Am. Chem. Soc*. **1999**, *121*, 9096–9110.
14. Higashino T., Rodriges-Morgade M.S., Osuka A., Torres T. *Chem Eur. J.* **2013**, *19*, 10353–10359.
15. CrysAlisPro 1.171.39.8e (Rigaku Oxford Diffraction, 2015)
16. Sheldrick G.M. *Acta Cryst. Sect. A*. **2015**, *71*, 3–8.
17. Farrugia L.J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
18. Ivanova S.S., Stuzhin P.A. *Russ. J. Coord. Chem.* **2004**, *30*, 765–773.
19. Meller A., Ossko A. *Monatsh. Chem.* **1972**, *103*, 150–155.
20. Claessens C.G., González-Rodríguez D., Torres T. *Chem. Rev.* **2002**, *102*, 835–853.
21. Tolbin A.Yu., Tomilova L.G. *Russ. Chem. Rev.* **2011**, *80*, 531–551.
22. Stuzhin P.A., Skvortsov I.A., Zhabanov Yu.A., Somov N.V., Razgonyaev O.V., Nikitin I.A., Koifman O.I. *Dyes Pigm.* **2019**, 162, 888–897.
23. Hamdoush M., Nikitin K., Skvortsov I., Somov N., Zhabanov Yu., Stuzhin P.A. *Dyes Pigm.* **2019**, 107584.
24. Rodriges-Morgade M.S., Esperanza S., Torres T., Barbera J. *Chem. Eur. J.* **2005**, *11*, 354–360.
25. Stork J.R., Brewer J.J., Fukuda T., Fitzgerald J.P., Yee G.T., Nazarenko A.Y., Kobayashi N., Durfee W.S. *Inorg. Chem.* **2006**, *45*, 6148–6151.
26. Wallwork S.C. *Acta Cryst.* **1961**, *14*, 375–378.
27. Stuzhin P.A., Goeldner M., Homborg H., Semeikin A.S., Migalova I.S., Wolowiec S. *Mendeleev Commun.* **1999**, (4), 134–136.
28. Donzello M.P., Viola E., Giustini M., Ercolani C., Monacelli F. *Dalton Trans.* **2012**, *41*, 6112–6121.
29. Shannon R.D. Acta Cryst. **1976**, *A32*, 751.

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