Effect of protonation on the spectral properties of subphthalocyanine and tripyrazinosubporphyrazine

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Abstract. Using well-known methodology perfluorinated subphthalocyanine (F\textsubscript{12}sPcBCl) and hexaphenyltripyrazinosubporphyrazine (Ph\textsubscript{6}Pyz\textsubscript{3}sPzBCl) were obtained and further its spectral and base properties have been studied by spectrophotometric titration and fluorescence spectroscopy. By means of spectrophotometric titration sequential protonation of two azomethine bridges was observed with the shifts of the absorption Q bands to 625-665 nm (for F\textsubscript{12}sPcBCl), to 584-683 nm and CT (charge transfer) band to 426-453 nm (for Ph\textsubscript{6}Pyz\textsubscript{3}sPzBCl). The spectral changes in the electronic absorption spectra of F\textsubscript{12}sPcBCl observed in an acid medium differ significantly compared to Ph\textsubscript{6}Pyz\textsubscript{3}sPzBCl. Protonation of Ph\textsubscript{6}Pyz\textsubscript{3}sPzBCl was observed in 0.08-0.35 M solution of trifluoroacetic acid in dichloromethane, in contrast to F\textsubscript{12}sPcBCl for which protonation in dichloromethane was observed at TFA concentration equal to 1.34 M. Bathochromic shift of the Q bands in the emission spectra was indicated for each of the protonated forms of the compounds, accompanied by a decrease in the fluorescence intensity with increasing acidity.

1. Introduction

Subphtalocyanines (sPc) are 14\pi electron aromatic macroheterocyclic compounds, contracted analogues of phthalocyanines [1,2]. But unlike phthalocyanines they are non-planar. These macrocycles consist of three isoindol fragments coordinated around the central boron atom, which bears halogen atom or group (usually aryloxy) in the axial position (Chart 1). Subphthalocyanines are used in various photonic processes, such as photovoltaics [3-8], and optical imaging [10-12]. Unsubstituted sPc are easily available and basically used as electron donors in OPVC, though there are examples of their accepting (n-type) behavior. Partial or full halogenation of benzene rings stabilizes the frontier \pi-molecular orbitals (both HOMO and LUMO) and enhances the electron affinity of the subphthalocyanine molecule, thus making halogenated sPc an attractive alternative to fullerenes as electron-acceptors for photovoltaic applications[13]. Direct azasubstitution in subphthalocyanines leads to the preparation of tripyrazinosubporphyrazines [14] (Chart 1).
This procedure is also a thin tool for adjusting physico-chemical properties (spectral and redox properties). The processes of acid ionization of subphthalocyanines strongly affect the spectral properties of the macrocycle. Protonation of sPc in acidic media, such as trifluoroacetic, methanesulfonic, sulfuric, and trifluoromethanesulfonic acids, is a stepwise process and leads to sequential ionization of three azamethine bridges [15,16]. Protonation of the mesomethine bridges of tripyrazinosubporphyrazines has a completely different nature due to the presence of additional donor pyrazine centers. In this work, we focused on the photophysical study of protonated and neutral forms of perfluorinated subphthalocyanine and hexaphenyl derivative of pyrazinosubporphyrazine.

2. Experimental section

2.1. Synthesis

By cyclotrimerization of tetrafluorophthalonitrile [17] and 5,6-diphenyl-pyrazine 2,3-dicarbonitrile [14] in the presence of 1 M solution of BCl₃ in a p-xylene in the inert gas atmosphere after 0.5-2 hours of stirring upon reflux perfluorinated sybphthalocyanine and hexaphenyltripyrazinosubporphyrazine were obtained. The end of the reaction has been determined by the presence of characteristic color spot in the thin layer chromatography (TLC). All compounds were purified and characterized with according literature procedures.

2.2. Fluorescence measurements

Fluorescence emission spectra were measured on spectrofluorophotometer Shimadzu RF-6000. Fluorescence quantum yields (Φₚ) were calculated by a comparative method using the equation:

$$\Phi_S^R = \Phi_S^S (F_S^R/F_S^S) (A_S^R/A_S^S) (n_S^R/n_S^S)^2,$$

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 $S$ are corresponded to the reference and the sample, respectively. As a reference was used rhodamine 6G, which has Φₚ = 0.94 in ethanol [18]. 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 ±10%.

The time-resolved fluorescence measurements were performed on a FluoTime 300 spectrometer (PicoQuant) with Sub-nanosecond Pulsed LEDs excitation at 480±25nm (PLS 500, pulse width ~800 ps). The decay curves were fitted to exponential functions with EasyTau software.

Electronic absorption spectral changes were recorded using a Cary 60 spectrophotometer.

3. Results and discussion

3.1. Photophysical properties

In the case of F₁₂₅PcBCl (see Figure 1) formation of two acid forms were observed stepwise protonation of meso-nitrogen atoms. Upon addition of trifluoroacetic acid (TFA) to solution of 4·10⁻⁶ M F₁₂₅PcBCl in dichloromethane (DCM) the intensity of the Q-band of the initial neutral form at 573 nm is decreased...
and new maximum appears at 625 nm (Figure 1 a) at 298.15 K. Such bathochromic shift is typical for protonation of one meso-nitrogen atom in phthalocyanines [20-21]. Spectral data indicate that F12sPcBCl is converted to the monoprotonated species F12sPcH+ at 1,3 M TFA and in 100% TFA the complete conversion is observed.

In the media with known Hammett acidity function the basicity of meso-nitrogen atoms in phthalocyanines is estimated as the stability constant of acidic form using the Hammett equation [22-23]:

\[
pK_a = H_0 + \lg I_i
\]

where \(I_i\) is the indicator ratio for the corresponding protonated form. Well known that in 100% TFA the Hammett acidity function \(H_0 = -3.03\) [24] and in 1,3 M (see Figure 1 b) solutions of TFA in DCM \(H_0 \sim -2.03\) [25], the stability constant of the monoprotonated form F12sPcH+ should be \(pK_a \sim -2.03\).

In the system TFA-H2SO4 the maximum of the Q-band undergoes bathochromic shift to 665 nm indicating protonation of the 2nd meso-nitrogen atom (Figure 1 c). Since the Hammett acidity function \(H_0\) is known for the TFA-H2SO4 mixtures [22-23] the \(pK_a = -9.16\) can be determined for the diprotonated form F12sPc(H+)2. Recently the spectra behavior of non-substituted subphthalocyanines sPc and its perfluorinated derivative F12sPc in acid medium have been studied by Decréau at al [15]. Only monoprotonated species were observed in TFA, while in methanesulfonic and trifluormethanesulfonic acid (\(H_0 = -1.9\) and -14.1, respectively [26]) all three meso-nitrogens are protonated [15].

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**Fig. 1.** a) variations in absorption spectra of F12sPcBCl in DCM solutions (pink is initial spectrum), after addition of 1.3 M TFA (purple) and normalized spectrum in 100% TFA (lilac); b) dependence of logarithm of concentration of TFA (\(\lg CTFA\)) on logarithm of indicator ratio (\(\lg I\)); c) variations in TFA solutions (lilac is initial), after addition of 10.3 M H2SO4 (green); d) dependence of optical densities on \(\lg CTFA\); e) dependence of logarithm of Hammett acidity function (\(H_0\)) on \(\lg I\); f) emission spectra at different concentration of acids.

Transformations of hexaazaanalogue Ph6Pyz3sPzBCl in acidic medium (Figure 2) is quite different due to the presence of the pyrazine nitrogen atoms as additional basic centers.

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**Fig. 2.** a) variations in absorption spectra of Ph6Pyz3sPzBCl in DCM solutions (red is initial spectrum), after addition of 0.08-0.35 M TFA (purple); b)-c) dependence of optical densities on \(\lg CTFA\) for two
steps of protonation; d) dependence of logarithm of lgCTFA on lgI for two steps of protonation; e) variations in TFA solutions (purple is initial), after addition of 2.1 M H2SO4 (green); f) dependence of optical densities on lgCTFA; g) dependence of logarithm of H0 on lgI; h) emission spectra at different concentration of acids.

The 1st protonation form was observed in 0.08 M TFA solution in DCM (pK1s = 0.43) that can be indicated on formation of Ph6Pyz3(H+)sPz. This process was recorded by the shift in the absorption maximum of the charge transfer band from 390 nm to 426 nm and bathochromic shift of Q-band to 15 nm. Although this derivative to hexachlorinated tripyrazinosubporphyrazine in DCM-TFA system similar changes were not observed [16]. The 2nd protonation form was fixed in a more acidic medium in 0.35 TFA in DCM (pK1s = -1.44) and can be indicated the combined acid-base interaction of pyrazine rings and one of the three meso-nitrogen atoms of subporphyrazine (Ph6Pyz3(H+)sPz(H+)).

Addition of 2.1 M H2SO4 to solution of Ph6Pyz3sPz in TFA leads to growth of the acidity and considerable spectral changes. The intensity of the Q-band at 584 nm is decreased and new broad band with maximum at 683 nm. This spectral evolution occurs without definite isosbestic points, indicating the presence of several absorbing species in the equilibrium. Such spectral changes can be indicative of also concomitant acid-base interaction with nitrogen atoms in meso-positions and in pyrazine rings affording presumably Ph6Pyz3(H+)sPz(H+)n. The overall stability constant for this acid form is pK2s = -8.50. In general, the processes of protonation of perfluorinated subphthalocyanine and its hexaphenylazaanalogue can be represented as Scheme 1.

### Scheme 1. Stepwise protonation of F12sPc and Ph6Pyz3sPz

| Form                | pK value |
|---------------------|----------|
| F12sPc              | pK1s = -2.03 |
| F12sPc(H+)          | pK2s = -9.16 |
| Ph6Pyz3sPz          | pK1s = 0.43 |
| Ph6Pyz3sPz(H+)sPz   | pK2s = -1.44 |
| Ph6Pyz3sPz(H+)2sPz(H+) | pK3s = -8.50 |

A decrease in the fluorescence intensity for protonated forms (Figure 1 f and Figure 2 h) can be indicated on enhance the non-radiative de-excitation of the excited singlet state as was observed for protonation forms of phthalocyanines [27]. The lifetime and quantum yields values of the fluorescence of neutral forms F12sPcBCl and Ph6Pyz3sPzBCl were τ=2.85±0.0035 ns, Φf=0.28 and τ=2.57±0.0031 ns, Φf=0.31 [14], respectively.

### 4. Conclusions

In this work, a comparative spectral study of the protonation processes of two dyes of the subphthalocyanine type was carried out. Two protonation processes were identified for perfluorinated subphthalocyanine and the corresponding constants of protonated forms were determined. However, a completely different behavior of hexaphenyltripyrazinosubporphyrazine was found in DCM-TFA system, in contrast to F12sPcBCl. The first stage of protonation is inherent in the ionization of pyrazine nitrogen atoms, as evidenced by the value of the corresponding stability constant of the protonated form. Subsequent addition of acid led to combined protonation of both meso-methine bridges and nitrogen atoms in pyrazines. The introduction of a proton into the azomethine bridges enhances the nonradiative deexcitation of the excited singlet state.

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