

# MORPHOLOGICAL PROPERTIES AND PHOTOCONDUCTIVITY OF SELF-ASSEMBLED Sn/Co PORPHYRIN NANOSTRUCTURES

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Received: October 21, 2015

**Abstract.** In this study the synthesis and characterization of *meso*-substituted Sn and Co porphyrin nanostructures were carried out. The effect of pH of medium on the formation of Sn/Co-porphyrin nanostructures was studied. The formation process is caused by the net charge on the porphyrin, which is controlled by protonation/deprotonation of the oppositely charged periphery. This charge determines also stoichiometric ratios of porphyrins in the nanostructures. It was found that the contact of the donor (Co-porphyrin) with acceptor (Sn-porphyrin) provides photoconductivity of nanostructures under illumination with visible light. It was shown that the increase of temperature decreases their conductance both in the dark and under illumination.

## 1. INTRODUCTION

Porphyrins being photosensitizers can build up nanostructures by self-assembly, which gives new opportunities to create new functional nanomaterials applicable in the field of visible light energy conversion. The potential range for usage is wide: solar cells, photocatalysis, photo- and molecular electronics [1–10]. Uniqueness of porphyrin nanostructures is given by the binding different porphyrin molecules which leads to the appearance of systems where each structural element contributes to the spatial arrangement and ordering of nanostructures. By now, there are a number of publications on the research of self-assembled structures consisting of various porphyrins: free-base porphyrins and metalloporphyrins [11–15]. Based on the existence of such systems we synthesized porphyrin nanostructures consisting of photoactive

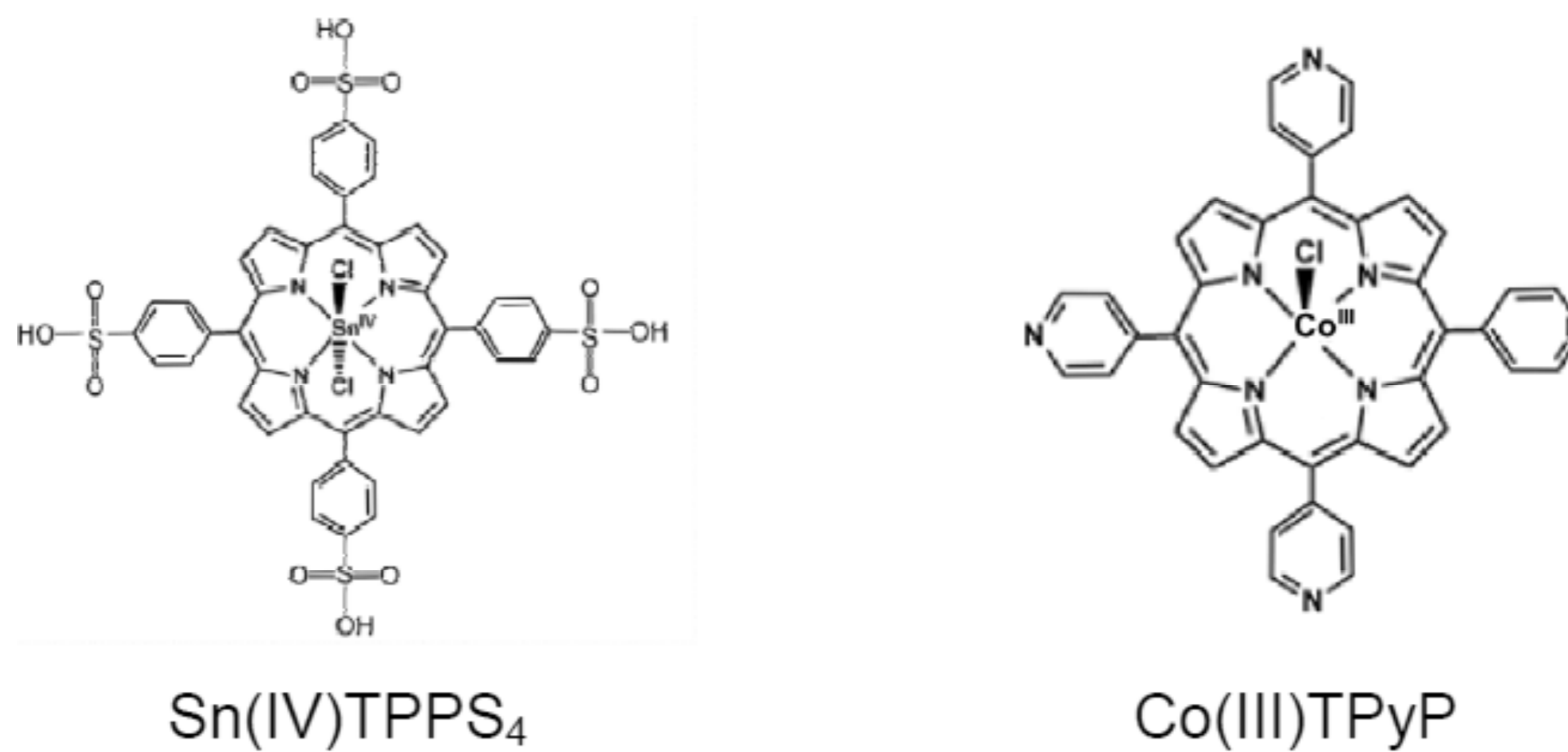
Sn [11, 16] and electroactive Co [17–19] porphyrins with oppositely charged periphery, investigated their morphological and electrochemical properties and studied photoconductivity of these systems.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Hydrochloric acid, sodium hydroxide, potassium chloride, disodium phosphate and monosodium phosphate, acetone, isopropanol, ethanol were purchased from Sigma-Aldrich. SnTPPS<sub>4</sub> (Sn (IV) *meso*-tetra (4-sulfonatophenyl) porphine dichloride) and CoTPyP (Co (III) *meso*-tetra (4-pyridyl) porphinechloride) were purchased from Frontier Scientific and used as received. All solutions for syntheses were prepared using distilled water and adjusted to the desired pH with HCl and NaOH.

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**Fig. 1.** Structures of SnTPPS<sub>4</sub> and CoTPyP.

## 2.2. Synthesis

Sn/Co-porphyrin nanostructures were prepared by mixing 10 mM stock solutions of individual metalloporphyrins in equal volumes. The reaction mixture was left undisturbed in the dark for 2 days. Samples for scanning electron microscopy were prepared by pipetting 50  $\mu$ L of the precipitate on to Si-substrate. The samples were allowed to dry for 12 hours, washed with distilled water, and allowed to dry. Scanning electron microscopy was performed on Gemini 1550VP, Carl Zeiss, Jena, Germany.

Nanostructure precipitates for the analysis by inductively coupled mass-spectrometry (ICP-MS) were obtained by centrifugation of the reaction mixture. The ratio of Sn:Co atoms was determined by Agilent 7500ICP-MS (Agilent Technologies, Japan). The relative standard error was 2.5%.

## 2.3. Conductivity measurements

For conductance measurements thin film Au-electrodes were used (50 nm thick on a 10 nm Ti adhesion layer) with 400 nm distance between the electrodes. The electrodes were fabricated by an electron beam lithography on a Si-substrate with 1  $\mu$ m oxide layer (Si 525  $\mu$ m/SiO<sub>2</sub> 1  $\mu$ m/Ti adhesion layer 10 nm/Au 50nm). Before pipetting, the nanostructured solution prepared by the procedure mentioned above at pH=4.8, the electrodes were cleaned in acetone, isopropanol, followed by the treatment with oxygen plasma in «Plasma system FEMTO», at 100 W, 0.8 mBar. Ethanol and distilled water were used at the final washing stage. Solution of porphyrin nanostructures (2  $\mu$ L) was dropped on to the electrodes, then samples were left in the dark for 2 hours, rinsed with distilled water and dried for 12 h at room temperature.

The conductance was measured using a Keithley 4200 semiconductor characterization system at an

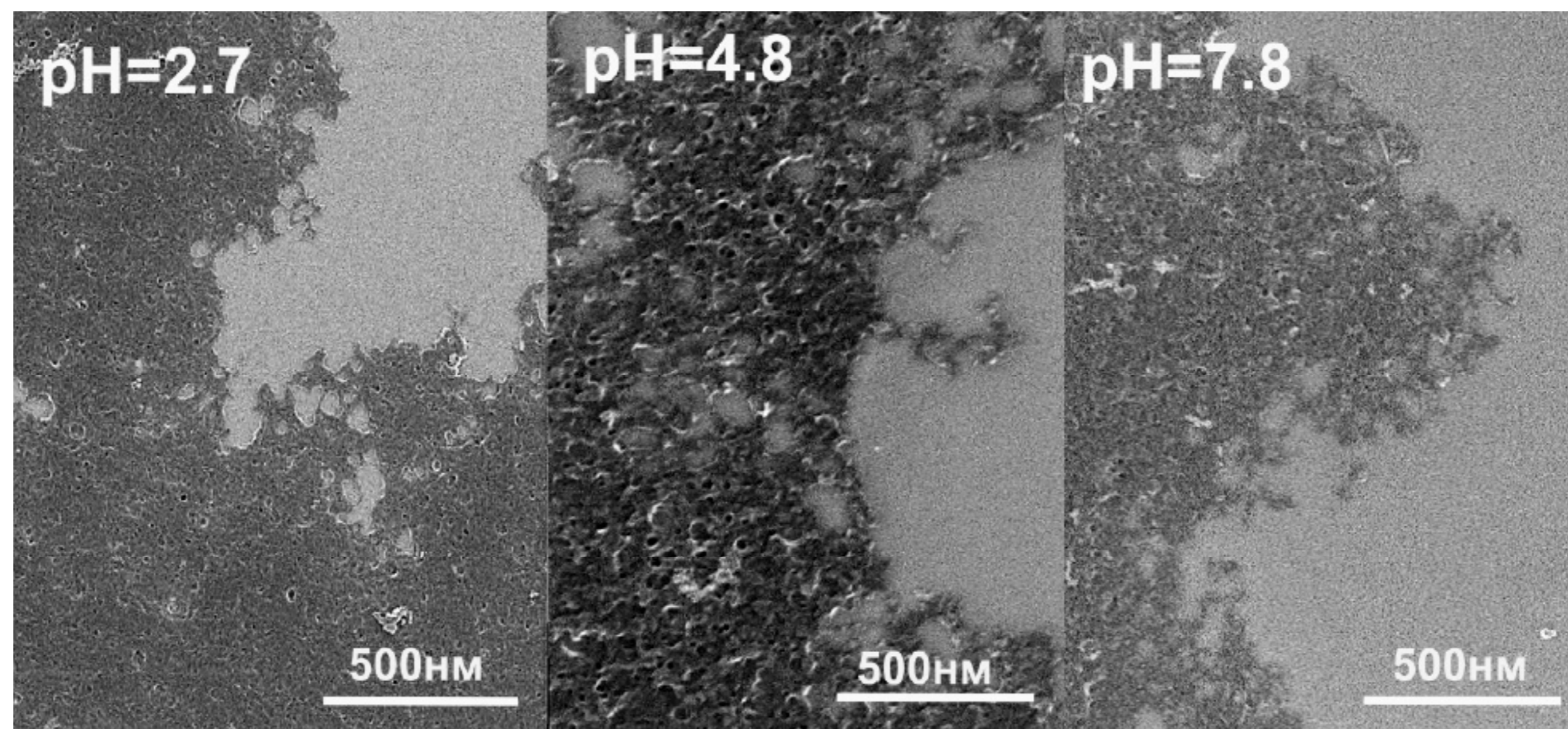
applied potential of 0.5 V. The light source was a 150 W Xenon ArcLamp with a 420-630 nm visible light filter (Oriel Instruments, Model No.6255). The intensity of the beam focused on the sample was 25 mW/cm<sup>2</sup>.

## 3. RESULTS AND DISCUSSION

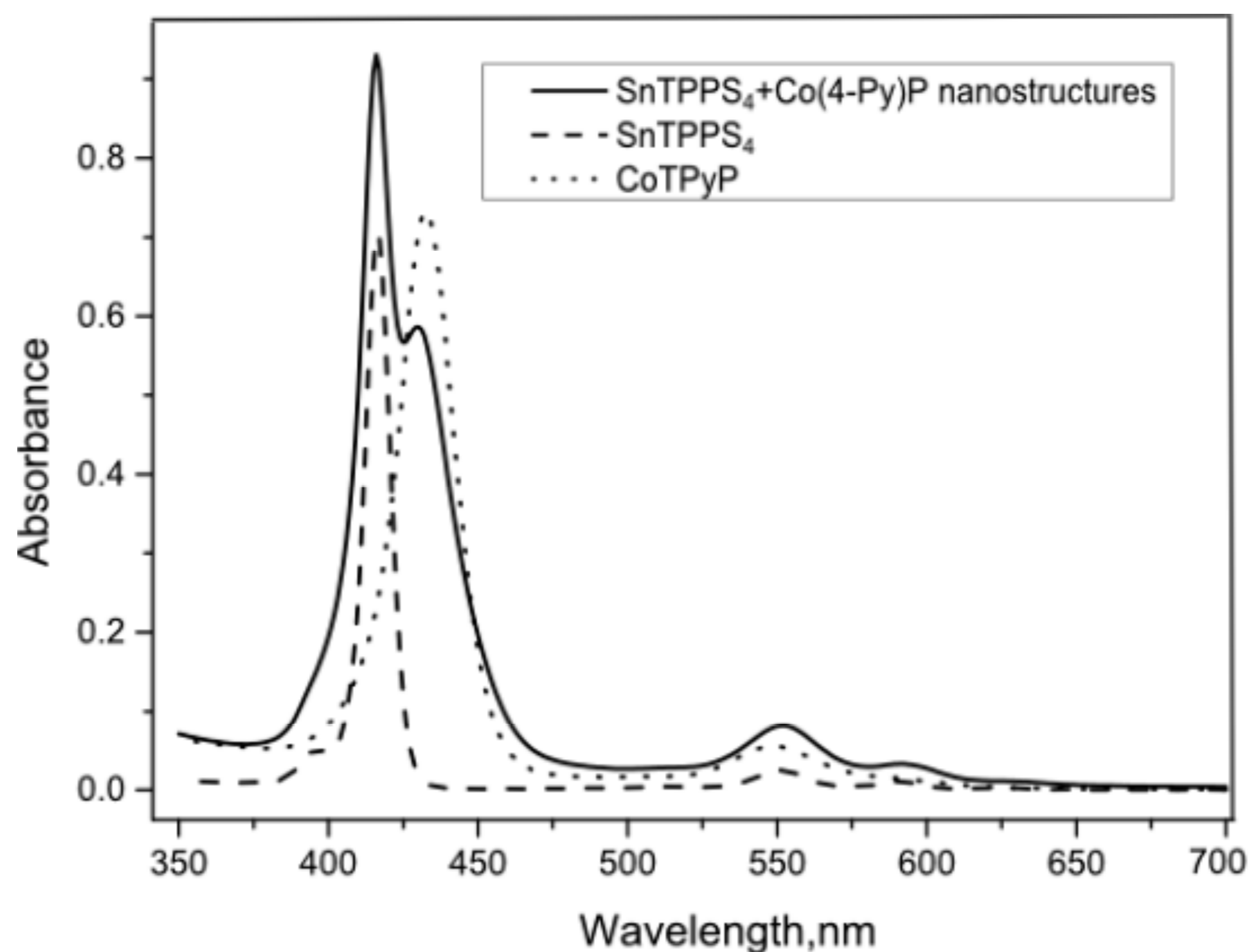
After mixing SnTPPS<sub>4</sub> and Co(4-Py)P (Fig. 1) at different pH values the solution became turbid after 1 hour. After 2 days red precipitates were observed. The experiments were carried out at pH = 2.7, 4.8, and 7.8. The lowest yield of the nanostructures was observed at pH = 7.8. At pH = 2.7 and 4.8 the amount of the precipitates were higher.

Scanning electron microscopy showed the identity of the nanostructure morphologies prepared at different pH, since all three samples gave nanoscale networks regardless of pH of the medium (Fig. 2). The network appeared to be resistant to light and temperature. The amount of nanostructures formation critically depends on the pH of media. It is explained by the dependence of the charge balance of tecton (porphyrin ion) on its protonation state [11]. Such dependence on the pH gives reason to believe that the ionic organization contributes to the formation of these nanostructures. By varying the pH of the medium, it is possible to choose the ideal conditions for the synthesis when periphery of the porphyrins has proper charges. More acidic medium gives the protonated pyridyl groups and more alkaline medium - dissociated sulfonate groups ( $pK_a = 2.6$  for benzenesulfonic acid and  $pK_a = 5.2$  for pyridine).

Thermodynamically reversible non-covalent interactions such as hydrogen bonding, metal ion coordination and the van der Waals forces may also participate in these kinds of self-organization [11,20,21]. The presence of axial ligands in porphy-



**Fig. 2.** Scanning electron microscopy images of porphyrin nanostructures composed of SnTPPS<sub>4</sub> and Co(4-Py)P at different pH.



**Fig. 3.** Absorption spectra of the Sn- and Co-porphyrins and their nanostructures at pH = 2.7.

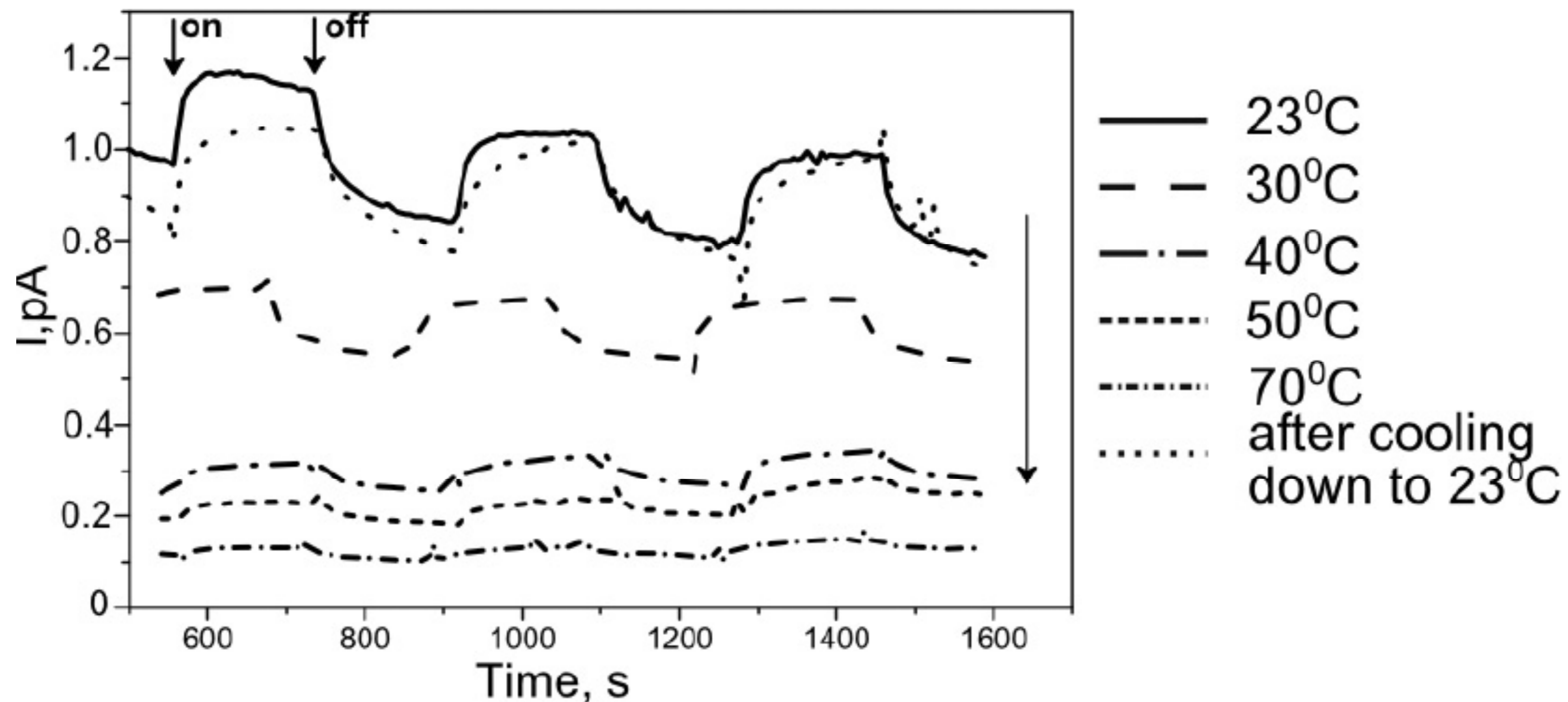
rins is also very important for the formation of the nanostructures, since it has been shown that the substitution of the central metal for the metal ions having no axial ligands, does not produce the necessary structures [11].

Absorption spectra (Fig. 3) of the nanostructures did not show any change as compared with the spectra of the monomers. Therefore, the mechanism does not involve the formation of the H- or J-aggregates.

Good stability of these nanostructures in the solution was observed. Examination with the scanning electron microscopy and the absorption spectroscopy did not reveal any changes of their structural form after 6 months.

The composition of the nanostructures was determined by ICP-MS. Determination of the Sn:Co ratio in the SnTPPS<sub>4</sub>+Co(4-Py)P samples prepared at different pH gave an atomic ratio of 1:1.15 at pH = 2.7 and 1:3.03 at pH = 4.8. It was impossible

to collect enough quantity of the precipitate for the determination of the Sn:Co ratio in the SnTPPS<sub>4</sub>+Co(4-Py)P sample prepared at pH = 7.8. As these ratios are the result of the neutralization of porphyrin cations and anions, pH is the key factor influencing the electrostatic interaction of tectonic couples. In the first case, at the lower pH participation of two porphyrins in the formation of the structures was almost equivalent. The low pH provides a higher number of protonated sulfonate groups and reduces the negative charge of the tecton from -4 to a more positive one that means its partial neutralization. But, at the same time, the lower pH increases the positive charge on the porphyrin with pyridyl groups to +4, which is favorable for the formation of structures. At the less acidic pH (pH = 4.8), amount of SnTPPS<sub>4</sub> molecules in nanostructures 3 times less than that of Co(4-Py)P. Most likely, in this case, the sulfonate groups are almost completely deprotonated and provide a



**Fig. 4.** Photoresponse of the SnTPPS<sub>4</sub> + Co(4-Py)P system (pH = 4.8) at different temperatures.

higher negative charge on the porphyrin, while the pyridyl groups are less protonated than at pH 2.7. There is a need to neutralize the charge on SnTPPS<sub>4</sub> with a higher number of molecules of Co(4-Py)P, and thus the ratio of the porphyrins in the nanostructures changes.

It is known, that the systems consisting of porphyrin macrocycles with different electronic characteristics may possess the properties of charge-transfer complexes [7,8]. Shelnut et al. [7] considered similar couples of porphyrins with Sn(IV) and Zn(II) metals according to the donor-acceptor principle and reported a system with free charge carriers which provide photoconductivity.

This implies existence of a configuration comprising the hole and the electron on different molecules, which are free charge carriers at applied potential [7].

This hypothesis may explain the existence of photoconductivity in the SnTPPS<sub>4</sub>+Co(4-Py)P system. Conductivity measurements of porphyrin nanostructures in the dark showed current of about 1 pA, but under irradiation with visible light the current increased by approximately 20% (Fig. 5, solid line). That means the electrons being excited by light move from the excited levels of Co-porphyrins - donors to Sn-porphyrins - acceptors. When the light was switched off, the current started to decrease slowly. This effect is explained by the difficulty of electron movement on the filled highest occupied molecular orbitals, where the electron goes from the lowest unoccupied molecular orbitals when the light is off [9].

Dark conductivity of SnTPPS<sub>4</sub>+Co(4-Py)P nanostructures at 23 °C was found to be  $2 \cdot 10^{-9} \Omega^{-1} \text{cm}^{-1}$  which is consistent with the literature data

for similar systems [9] and corresponds to the low conductivity of the porphyrin molecules which occupy an intermediate position between semiconductors and insulators [22].

The S<sub>1</sub> excited state, which corresponds to the absorption of the Q-band, is involved in the subsequent photochemical process, because the S<sub>2</sub> state corresponding to the absorption of the Soret band, has a very short lifetime,  $\tau_{1/2} \sim 10^{-12} \text{ s}$ , and the molecule goes to a long-lived S<sub>1</sub> state,  $\tau_{1/2} \sim 10^{-9} \text{ s}$ , with a release of energy (heat).

Heating of the investigated nanostructures (Fig. 4) resulted in a decrease of their conductance, a decrease current both in the dark and under illumination was observed. We assume that this effect is associated with central metal ions of Co and Sn in porphyrins, which prevent the passage of current similar to the conductance in metals. After cooling, the conductance properties recovered back to the previous level, thus the destruction of structures and restructuring of bonds did not occur during heating.

## 4. CONCLUSIONS

The investigation of self-assembled porphyrin nanostructures formed mainly due to electrostatic interactions at different pH was carried out. Their formation was observed even with partially dissociated peripheral groups. Different ratios of porphyrins in the structures can be obtained by varying the pH of the medium and hence the charge on a tecton. It was shown by the ICP-MS measurement that increasing the pH from 2.7 to 4.8 resulted in decrease of a molar ratio of SnTPPS<sub>4</sub> to Co(4-Py)P from 1:1.15 to 1:3, respectively, due to the neutral-

ization of a larger charge on SnTPPS<sub>4</sub> because of the deprotonated peripheral sulfonate groups.

The phenomenon of photoconductivity of the investigated nanostructures can be explained by the separation of electron-hole pair occurring under illumination at applied potential.

With an additional source of excitation, namely, the heating, the opposite effect was found: the current decreases with increasing temperature. The presence of Sn and Co ions allows us to refer to the properties of metals and find the similarity with them: an increase in resistance with increasing temperature.

The functional properties of porphyrin nanostructures can be controlled by varying the pH of media and the temperature. In the first case, changes of the composition of the self-assembled porphyrin nanostructures take place. Their ratio may be varied depending on the required properties of porphyrin nanostructures, which are needed to be obtained: catalytic or absorptive. In the second case, it is possible to achieve higher conductivity of the structures decreasing the temperature. The properties described above may be promising in optoelectronic devices [23,24] and for the design of systems for photocatalytic generation of hydrogen [25].

## ACKNOWLEDGEMENTS

The authors thank I. Muratova for providing thin-film electrodes (St. Petersburg State University).

The results presented in the article were obtained with financial support from the St. Petersburg State University, Event 6, Project 12.42.1264.2014. Financial support from St. Petersburg State University grant 12.38.218.2015 for the studies on the photoconductivity is gratefully acknowledged.

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