Photo-responsive Self-Assembled Porphyrin Nanostructures

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Introduction

Molecular self-assembly of porphyrins and subsequently formation of nanostructures are of great interest due to their promising applications in such fields as electronics, optoelectronics, sensors and photocatalysis. It has been shown that the ionic self-assemble, as well as thermodynamically reversible non-covalent interactions such as hydrogen bonding, metal-ion coordination and the van der Waals interaction can produce close molecular packing. In addition, their ability to absorb certain wavelengths in the visible spectrum promote intermolecular transfer or delocalization of the excitation energy.

Methods

1. Transmission electron microscopy (TEM)
2. Absorption spectroscopy
3. Elemental analysis (EA)
4. Photo conductance measurements

Setup:

Solar simulator:

1 μm and 2 μm chips

Used chips: 400 nm and 600 nm chips

Aim

Study the morphological, spectral and photoelectrochemical properties of free base, Sn- and Co-porphyrins and their nanostructures.

Results

Nanostructures

pH<3

H2TPPS4+ (meso-tetra(4-sulfonatophenyl)porphine dihydrochloride)

CoT(4-Py)P
(Co(III)meso-tetra(4-pyridyl)porphine chloride)

pH=2

H2TPPS4+ (meso-tetra(4-sulfonatophenyl)porphine dihydrochloride)

SnT(4-Py)P
(Sn(IV)meso-tetra(4-pyridyl)porphine dichloride)

Absorption spectra of H2TPPS4+CoT(4-Py)P monomers and J-aggregates

Absorption

wavelength, nm

EA of nanostructures:

H2TPPS4 : CoT(4-Py)P = 3.3 : 1

Photo-response behavior of the device designed with H2TPPS4+CoT(4-Py)P nanostructures depending on temperature

Absorption

wavelength, nm

EA of nanostructures:

H2TPPS4 : SnT(4-Py)P = 3 : 2

Photo-response behavior of the device designed with H2TPPS4+SnT(4-Py)P nanostructures depending on temperature

Discussion

We suppose that the formation of H2TPPS4 + CoT(4-Py)P and H2TPPS4 + SnT(4-Py)P nanostructures occurs by two mechanism: ion organization, i.e. the formation of J-aggregates and the interaction between the peripheral functional groups acting as axial ligands and the central metal.

Conductivity and photoconductivity of the above mentioned porphyrin nanostructures were investigated. For both types of the nanostructures under study a low dark current of ~10^{-11} A was observed at a bias of 0.5 V. Upon exposure to the simulating sunlight the nanostructures exhibited photoconductivity. In the case of H2TPPS4 + SnT(4-Py)P nanostructures the current was increased 10 times and in the case of H2TPPS4+CoT(4-Py)P nanostructures ~2 time.

Summary

Porphyrin nanostructures consisting of H2TPPS4 + CoT(4-Py)P and H2TPPS4 + SnT(4-Py)P were synthesized and investigated with respect to their morphology. Photoconductivity was observed and investigated at different temperatures. Further experiments will allow to make a conclusion about applicability of these structures for hydrogen production and chemical sensors.