COMPLEXATION OF $TPPS_4$ WITH POLYVINYL ALCOHOL POLYMER IN AIR-DRIED FILMS

Simona Pusvaškytė[1], Skaistė Talanovaitė[1], Greta Tamoliunaitė[1], Vilius Poderys[1], Ričardas Rotomskis[1,2]

[1]Biomedical Physics Laboratory of National Cancer Institute, Baublio 3B, LT-08406, Vilnius, Lithuania
[2]Vilnius University, Biophotonics Group of Laser Research Centre, Saulėtekio 9, c.3, LT-10222, Vilnius, Lithuania
simona.pusvaskyte@gmc.stud.vu.lt

Porphyrin-based materials have attracted considerable attention due to their unique electro-optical properties and ability to form well-defined supramolecular structures [1]. Achieving controlled organization and stability of these structures is essential for their application in functional solid-state systems. Polymer films offer a versatile platform for immobilizing porphyrins, enabling regulation of molecular interactions and assembly while providing mechanical and environmental stability. In this work, the complexation of $TPPS_4$ with poly(vinyl alcohol) in air-dried films is explored as a model system for studying porphyrin–polymer interactions and supramolecular organization.

This work presents the results of the determination of interaction of 5,10,15,20-Tetrakis(4-sulfonatophenyl) porphyrin ($TPPS_4$) with polyvinyl alcohol polymer (PVA) in films, possible interactions are shown in Figure 1. $TPPS_4$ tetra sodium salt and poly (vinyl alcohol) stock solutions were made by dissolving $TPPS_4$ and PVA polymer powder separately in deionized water.

When $TPPS_4$ is deposited with PVA from acidic aqueous solutions (pH = 3) to form air-dried films, the Soret band of protonated $TPPS_4$ appears around 434 nm, while the two Q-bands are observed at approximately 595 nm and 645 nm. These features resemble those seen in the corresponding acidic aqueous solutions, indicating that the protonated monomer retains its basic spectral characteristics in the solid film. However, as additional layers of $TPPS_4$ - PVA are added, the overall absorption intensity increases, reflecting the accumulation of porphyrin in the multilayer structure.

In thicker films, new absorption bands emerge around 490 nm and 710 nm, which are indicative of partial formation of J-aggregates. The intensity of the 490 nm band associated with the J-aggregates is lower compared to pure aqueous J-aggregate solutions, suggesting that PVA influences the organization and stability of aggregates in the solid - state films.

The spectra remain essentially unchanged after two days, showing that the $TPPS_4$ - PVA complexes and any formed aggregates are stable in the air-dried films. In contrast, in aqueous solutions at pH 7, $TPPS_4$ remains mostly monomeric, and the spectral pattern does not show J-aggregate formation, highlighting that acidification and film deposition strongly affect porphyrin organization in the presence of PVA.

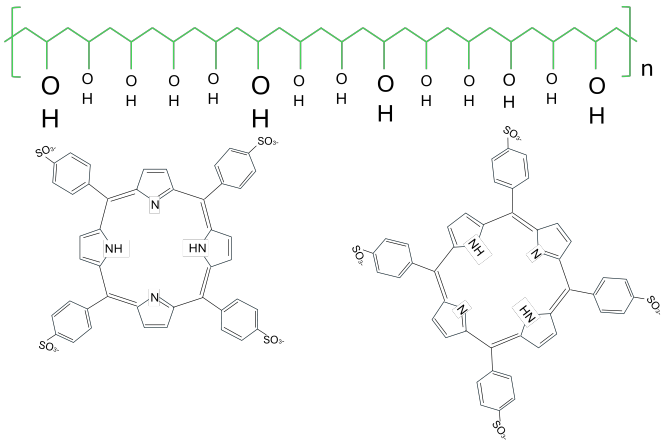

Fig. 1. Possible interaction between $TPPS_4$ and PVA polymer

[1] Y. Hu et al., "Porphyrin-Based Supramolecular Self-Assemblies: construction, charge separation and transfer, stability, and application in photocatalysis," Molecules, vol. 29, no. 24, p. 6063, Dec. 2024, doi: 10.3390/molecules29246063.