Influence of carboxyl groups on the porphyrin morphology

L. Zajac\textsuperscript{a}, P. Olszowski\textsuperscript{a}, R. Jöhr\textsuperscript{b}, T. Glatzel\textsuperscript{b}, E. Meyer\textsuperscript{b}, B. Such\textsuperscript{a}, M. Szymoński\textsuperscript{a}

\textsuperscript{a}Faculty of Physics, Jagiellonian University, Ul. Lojasiewicza 11, 30-348 Krakow, Poland
\textsuperscript{b}Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland
*e-mail: lukasz.1.zajac@uj.edu.pl

Understanding and engineering the molecule-substrate interaction is essential for technologies relevant for dye-sensitized solar cells (DSSC). In the presentation we present the results of studies into the influence of carboxyl groups on the molecular structure of the thin porphyrin layer. Porphyrins were one of the first sensitizers used in dye-sensitized light harvesting applications\cite{1}. The presence of anchoring carboxylic group plays important role in the adsorption as well as the electron transfer processes\cite{2}. We have used carboxyphenyl-substituted porphyrin, tetrakis(4-carboxyl-phenyl)porphyrin cooper(II) (CuTCPP), 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin-Zn(II), meso-Tetraphenylporphine-Zn(II) as shown in Fig.1(a). Depending on the number of anchoring groups, we have noticed different behaviour of molecules. The CuTCPP molecules are immobilized and adsorbed flat on surface in the positions which allows the binding of the carboxylic groups into surface oxide rows (a square geometry). The COOH-ZnTPP are absorbed in two forms: stable and mobile. The stable molecules adsorbed flat in cross geometry. The mobile molecules are observed as dashed lines. In the case of the ZnTPP molecules there are no stable molecules.

Fig.1(a) Molecular structure of CuTCPP;(b) 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin-Zn(II), (c) meso-Tetraphenylporphine-Zn(II)

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\cite{1} A. Hagfeldt, G.Boschloo, L. Sun et al., Chem. Rev. 110,6595-6663, (2010).