Theoretical study of anchoring group effect on electron transfer in dye-sensitized TiO_2 using large scale nanoparticle.

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Dye-sensitized photocatalysts, where dyes are adsorbed onto a photocatalyst surface, represent a promising approach for hydrogen production, particularly due to their ability to absorb visible light.[1] However, the choice of anchoring groups, which mediate the adsorption of dyes onto photocatalysts, plays a crucial role in determining electron injection efficiency. Despite their importance, many dyes desorb in aqueous solutions, leading to reduced hydrogen production rates.[2] In this study, we investigate the effect of anchoring groups on the performance of dye-sensitized photocatalysts using quantum chemical calculations, aiming to optimize anchoring groups design for improved electron injection efficiency. The anchoring groups analyzed include pyridyl, carboxyl, phosphonic acid, and silil acid groups, which were incorporated into a porphyrin-titanium oxide anatase model.

Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) calculations were performed to evaluate structural, electronic, and optical properties. The anatase model used, $Ti_{78}O_{160}H_8$, contains approximately 1.6 times more atoms than those in previous studies,[3] making it closer to experimental values. Geometry optimization results indicate that the highest occupied molecular orbital (HOMO) is localized on the dye, while the lowest unoccupied molecular orbital (LUMO) is localized on the titanium oxide anatase. UV-Vis spectral calculations, shown in Fig, reveal that the maximum oscillator strength is significantly higher for anatase with pyridyl group adsorption compared to other anchor groups. This difference is likely attributed to the stronger bonding interactions of the pyridyl group with the anatase surface. In this presentation, I will provide a detailed discussion on how anchor groups influence electronic excitation and electron transport, drawing insights from electronic transport calculations to guide the design of efficient and stable dye-sensitized photocatalysts.

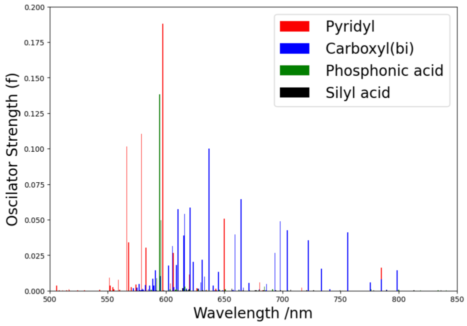

Fig. *The calculated UV-Vis spectra for each anchoring groups with porphyrin on the anatase*

1) M. Grätzel, *J. Photochem. Photobiol., C*, **2003**, *4*, 145-153. 2) K. Takijiri, K. Morita et. al, *Chem. Commun.*, **2017**, *53*, 3043. 3) J. Zhang, H-C. Zhu, et. al, *Organic Electronics*, **2018**, *54*, 104–113.