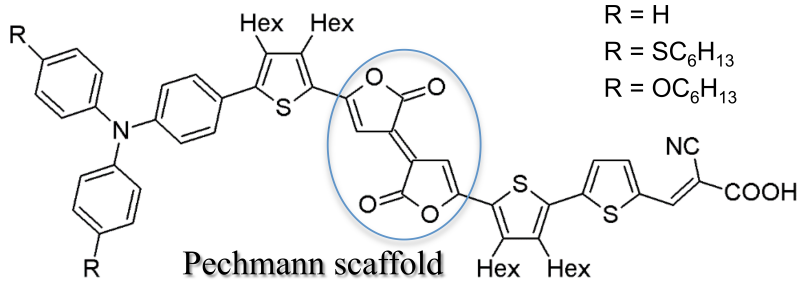
In silico design of near-IR D-A-π-A Sensitizers for Dye-Sensitized Solar Cells

Sanaz Mohammadpourasl[a,b], Alessio Dessì[c], Lorenzo Zani[c], Gianna Reginato[c], Riccardo Basosi[a,b], Adalgisa Sinicropi[a,b]

[a]Department of Biotechnology, Chemistry and Pharmacy, University of Siena, via A. Moro, 2, 53100 Siena, Italy; [b]CSGI, Center for colloid and surface science, via della Lastruccia 3, 50019, Sesto Fiorentino, Italy; [c]Italian National Council for Research - Institute for the Chemistry of OrganoMetallic Compounds (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy E-mail: adalgisa.sinicropi@unisi.it

In this work we focused on the computational design of novel organic sensitizers for dye-sensitized solar cells. The proposed dyes contain the *Pechmann* scaffold (see Figure below), which is a strong electron-withdrawing system with a brilliant red-purple colour [1]. The use of the *Pechmann* scaffold allows extending the light absorption spectrum of the dyes in the red/near-infrared (NIR) region and obtaining unusual blue-green coloured dyes that are currently of high interest [2,3]. The light absorption feature would enhance the light harvesting efficiency and, consequently, increase the overall efficiency of the solar device [4]. In order to raise the light-harvesting properties beyond the usual D-π-A dyes, an additional acceptor unit inside the π-bridge (D-A-π-A structure) is also used. Several types of modifications on the structure shown below were considered (including replacement of the molecular anchor and modification of the spacer groups) and 13 derivatives were investigated by means of Density Functional Theory (DFT) and time dependent DFT calculations performed with the Gaussian09 program package. The same strategy was successfully applied in previous studies [5,6]. We found that the new dyes show: i) vertical absorption maxima ranging from 600 to 800 nm that confirms their red to infrared light absorption; ii) high oscillator strength values which in turns should give high extinction coefficients; iii) wave function plots of frontier molecular orbitals involved in the excitation process in favour of an intramolecular charge-transfer nature of the excitation. All these features, along with an appropriate alignment of the dye energy levels, suggest that the novel designed *Pechmann*-based organic sensitizers are compatible with a proper and potentially successful use in DSSCs.



1. Von Pechmann H. Ber., **1882**, 15, 885
2. De Angelis F., Kamat, P. "A Conversation with Michael Grätzel" ACS Energy Lett., **2017**, 2, 1674
3. Wu Y., Zhu W. H. Chem. Soc. Rev., **2013**, 42, 2039
4. Jradi F. M., Kang X., O'Neil D., Pajares G., Getmanenko Y. A., Szymanski P., Parker T. C., El-Sayed M. A., Marder S. R. Chem. Mater., **2015**, 27, 2480
5. Dessì A., Calamante M., Mordini A., Peruzzini M., Sinicropi A., Basosi R., Fabrizi de Biani F., Taddei M., Colonna D., Di Carlo A., Reginato G. and Zani L., RSC Advances, 2015, 5, 32657
6. Dessì A., Calamante M., Mordini A., Peruzzini M., Sinicropi A., Basosi R., Fabrizi de Biani F., Taddei M., Colonna D., Di Carlo A., Reginato G., Zani L., Chemical Communications, 2014, 50, 13952