Computational screening of functionalized porphyrins for dye sensitized solar cells

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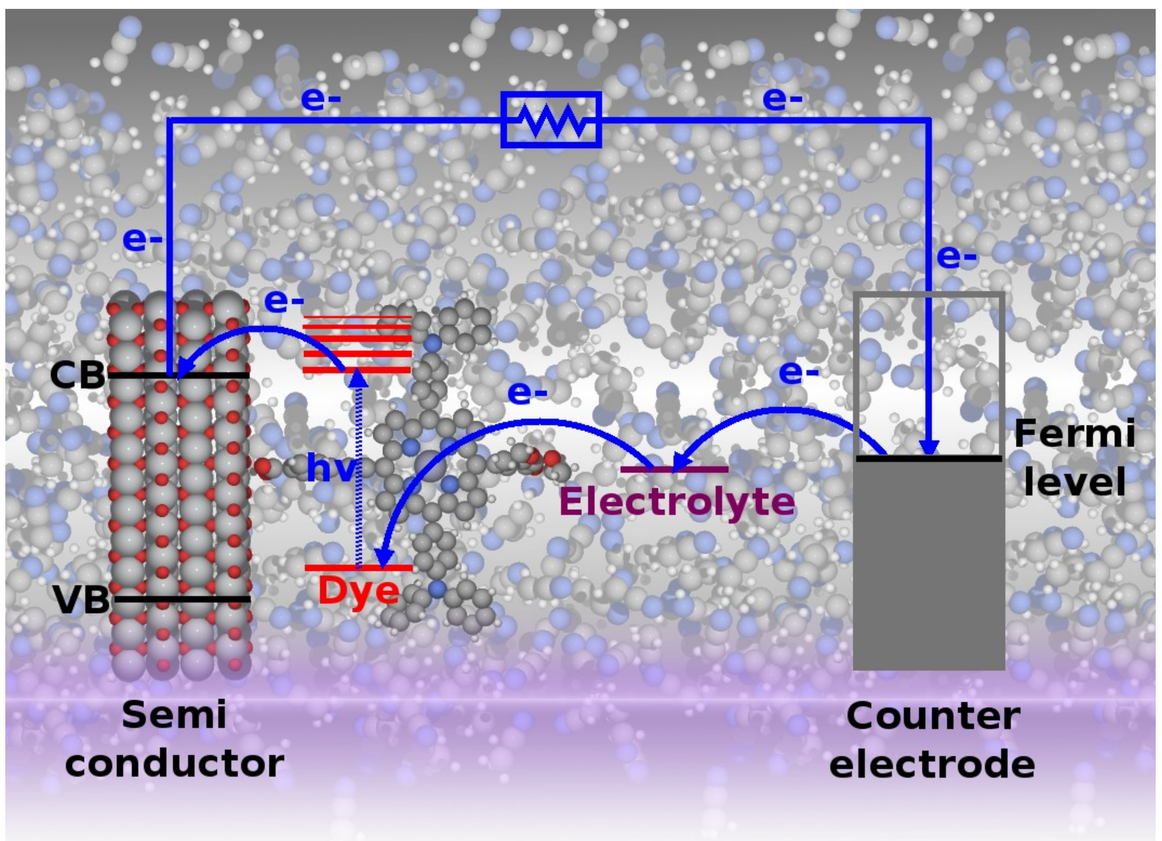
Introduction

An efficient dye sensitized solar cell (DSSC)[1,2] is one possible solution to meet the world's rapidly increasing energy demands and associated climate challenges. This requires inexpensive and stable dyes with well-positioned frontier energy levels for maximal solar absorption, efficient charge separation, and high output voltage. Here we demonstrate an extensive computational screening of 5000+ porphyrins systematically functionalized with electron donating side groups and electron accepting anchoring groups. The trends in frontier energy levels versus side groups are analyzed and a no-loss DSSC level alignment quality is estimated. All frontier energy levels, gaps and level alignment quality values are stored in a database publicly available.[3,4]

Dye Sensitized Solar Cells

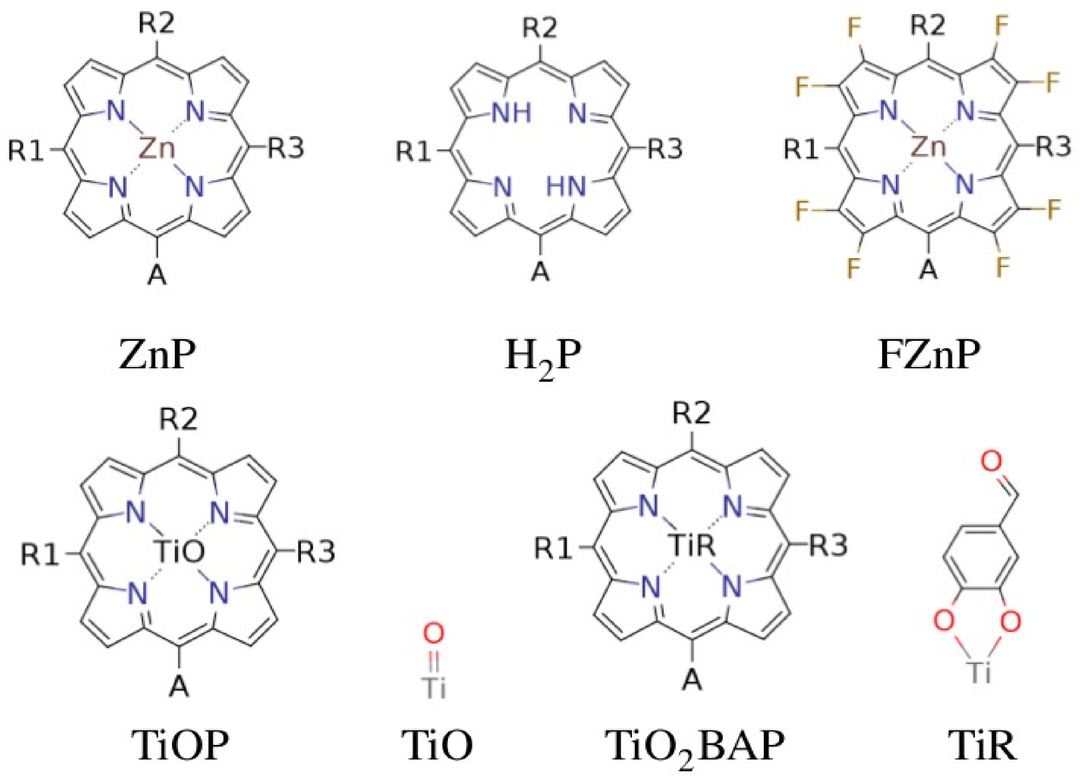


Computational methods

- *In vacuo* Density Functional Theory with PBE in the GPAW code.
- Geometry optimization of all candidates.
- Fundamental gaps using total energies.
- Triplet excitation energies used to compute the level alignment quality.

GPAW!

Building blocks



7 donating side groups and 3 accepting anchor groups

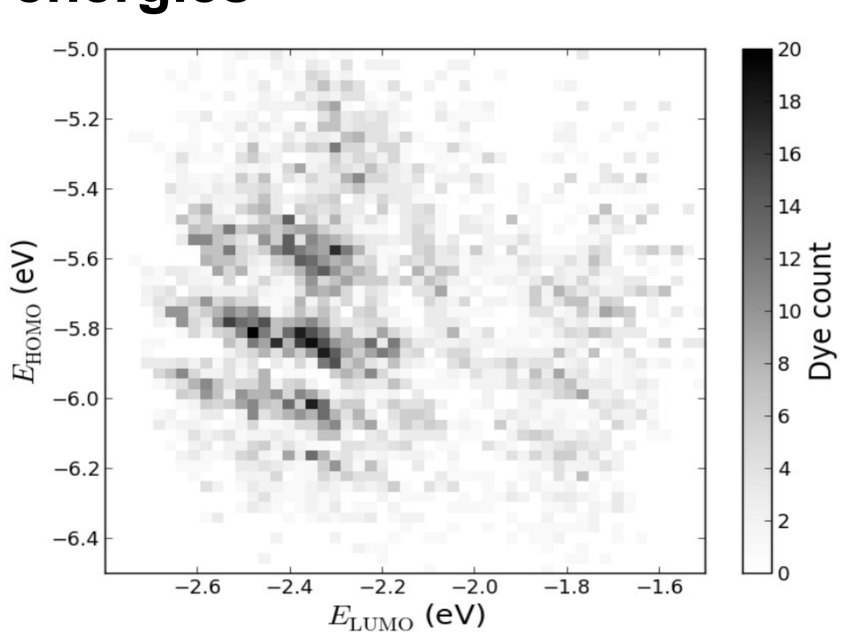
Further information online

Paper 1 DOI: 10.1039/C3CP54050B

Paper 2 DOI: 10.1039/C4CP01289E

Paper 1: Paper 2: Data:

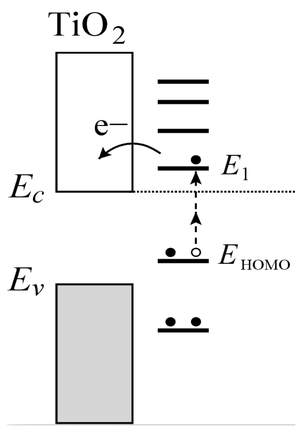
Orbital energies

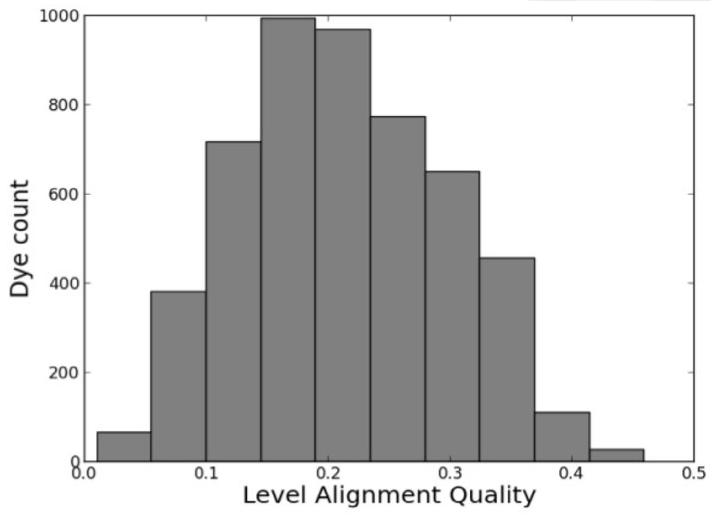


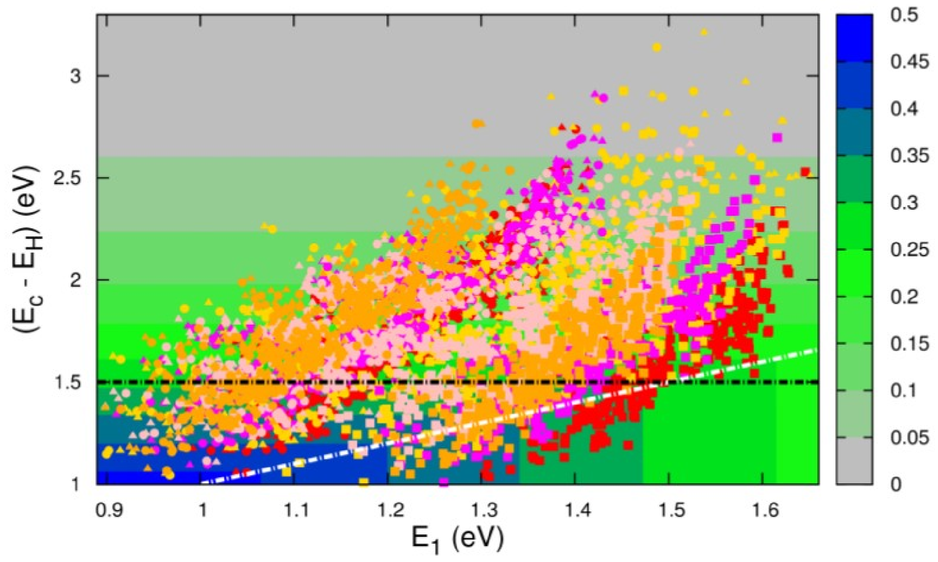
Level alignment quality

$$\eta = \frac{V_{oc}\int_{E_c-E_H}^{\infty}\Theta(E-E_1)\cdot I_{solar}(E)\mathrm{d}E}{\int_0^{\infty}E\cdot I_{solar}(E)\mathrm{d}E}$$

$$\Theta(E-E_1)=\begin{cases}1 & \text{for} \quad E-E_1\geq 0\\ 0 & \text{for} \quad E-E_1<0\end{cases}$$







Conclusions

By systematically changing the side groups and anchor groups of porphyrin dyes we obtain a handle to control the frontier orbitals and the level alignment to match the requirements for Dye Sensitized Solar Cells which may be used to improve the efficiency.

References:

[1] O'Regan, B. & Grätzel, M., *Nature*, **1991**, *353*, 737-740
[2] Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L. & Pettersson, H., *Chem. Rev.*, **2010**, *110*, 6595-6663
[3] Ørnsø, K. B.; Garcia-Lastra, J. M. & Thygesen, K. S., *PCCP*, **2013**, *15*, 19478-19486
[4] Ørnsø, K. B.; Pedersen, C. S; Garcia-Lastra, J. M. & Thygesen, K. S., *PCCP*, **2014**, accepted.

Acknowledgment:

The authors would like to thank A. Rubio and F. J. Himpsel for inspiring discussions. KBØ and KST would further like to thank the Danish Council for Independent Research DFF-Sapere Aude program (grant no. 11-1051390) for financial support. JMGL acknowledges support from the Spanish Ministry of Economy and Competitiveness under Projects FIS2009-07083,FIS2010-21282-C02-01 and FIS2012-30996 and through Ramon y Cajal grant RYC-2011-07782.