Review Article

The BCL approach for the molecular design of new ruthenium complexes for dye sensitized solar cells

Abstract

The Global Efficiency Index (E) obtained from the Barrera-Crivelli-Loeb (BCL) approach is compared with the calculated photo conversion efficiency of four dyes reported in literature. The calculated values reproduce the experimental trends. The model also predicts an enhancement of the efficiency of the N3 dye if the dicarboxy bipyridine is replaced with monocarboxy bipyridine.

Keywords: dicarboxy bipyridine, monocarboxy bipyridine, literature, greenhouse effect, dye sensitized, titanium dioxide

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Abbreviations: BCL, barrera-crivelli-loeb; DSSC, dye sensitized solar cell; Ea, harvested energy; F_1, first index; F_2, second index; PPF2, difluorophenylpyridine; SCN, thiocianate; BPY, bipyridine; TCTPD, tricarboyy terpyridine; GS, ground state; T1, first lowest triplet

Introduction

During the past years, solar energy has received great attention because of its potential as clean a renewable source of energy with no contribution to the greenhouse effect.[1] This interest has also grown by the appearance of new photoelectric cells capable of competing with the known silicon cells at lower production costs and easy to build.

At the beginning of 1980 O´Reagan et al.,[2] publish a paper showing how a Dye Sensitized Solar Cell (DSSC), composed with mesoporous Titanium Dioxide film covered with a thin layer of a Ruthenium pigment shows an impressive 7% of yield in solar-to electric power conversion efficiency under standard illuminating condition (AM 1.5G, 100 =mWcm2 intensity). Figure 1 shows a typical architecture of a DSSC with the most relevant process.

Since then, many ruthenium compounds are each day synthesized in laboratories worldwide[3] in a sort of race to find a champion dye: the best dye with outstanding performance. For example, replacing thiocianate with difluorophenylpiridine (PPF2) gives compound YE05 with a 10.1% of yield.[4] Employing tricarboxy terpyridine instead of dicarboxi bipyridine gives complexes N749 known as the "black dye" with an efficiency of 11.1%[5] and more recently, a 12.5% was reached with a Zinc Porphyrin complex.[6] However, and despite of all of this effort, after 25 years of continuous research the theoretical limits of 25% is still faraway.[7]

Interestingly, most of this research is achieved by employing the trial and error method. However in recent times and because of the growing computational capacity, theoretical tools[8] have become available for chemist and predictive models with increasing accuracy have been developed.[9]

The BCL conceptual model[10]

With the aim to facilitate the design and synthesis of new dyes we develop a computational model based on TDDFT calculations that would enable the theoretical study of series of complexes with the purpose to search the best one and focus the greater effort in its synthesis. Through a first step It is necessary to adapt the physical model consisting of a series of complexes anchored to the surface of a solid semiconductor to a simpler one that maintains the characteristics of been an interacting system (Dye+Semiconductor). With this purpose in mind, the band structure of titanium dioxide usually simulated through by cluster will be reduced to two $Ti(OH)_3+$ units as showed in Figure 2.
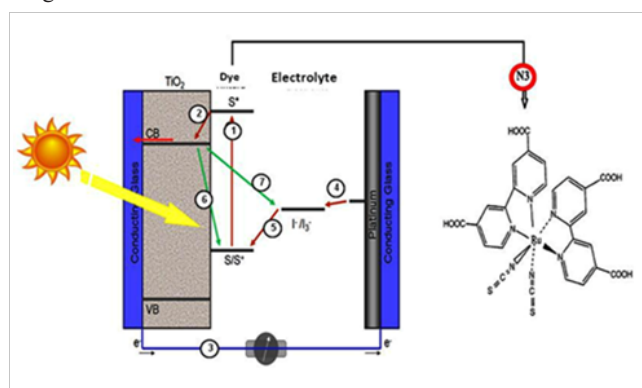

Figure 1 Scheme for Dye Sensitized Solar Cell.
1: The sensitizer (S) absorb sunlight energy and it is promoted to an excited state, 2: From the thexi state the dye inject one electron into the conduction band of the semiconductor (TiO2), 3: The electron moves outside of the cell and perform electric work, 4: The electron is collected on the platinum cathode and used to reduce the iodine from the electrolyte, 5: Iodine is able to reduce the oxidized dye and initiate e new photocatalytic cycle, 6 & 7: Are deactivation process.

In a second stage, the compounds under study need to be rate with a theoretical index measuring their efficiency as dye sensitizer. The global index efficiency (E) is obtained as the product of three indexes and each one is related with the efficiency of one of the three basic process occurring during the operation of the cell ($E=F_1 F_2 F_3$).

The first index (F_1) is a measure of how much of the harvested energy is delivered to the anchor group in the thermally equilibrated excited state: $F_1=EdfT$, here Ed is the amount of the harvested energy (Ea) reaching the anchor ligand and fT is the participation of the anchor group in the thexi state.

The second index (F_2) takes account for the amount of charge injected into the LUMO of the $Ti(OH)_3$ group: $F_2=(\Delta\mu DA-\Delta VDA)/2(hD+hA)$, with $\Delta\mu DA$ is the difference of energy between the SOMO of the dye and the LUMO of $Ti(OH)_3$, ΔVDA is a reorganization parameter

while hD and hA are the global hardness of the dye and the $Ti(OH)_3^+$ group. The third index measures the efficiency of the regeneration process and it is calculated by $F_3=exp(-\Delta\mu)$ and $\Delta\mu$ is obtained as the difference between the reduction potential of the oxidized dye and the oxidation potential of iodide (I^-).
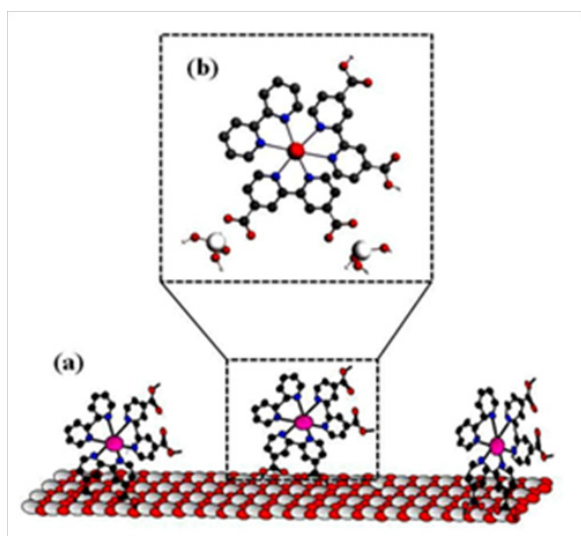

Figure 2 a: Scheme of the first monolayer of TiO_2 with three Ruthenium dyes (grey circles represent titanium, red circles, oxygen, black circles, carbon, pink circles, ruthenium, hydrogen atoms are not shown). b: General structure of the interacting model $[[Ru(bpy)(L1)(bpy(COOTi(OH)_3)_2]^{+2}$ (L1=dcbpy).[10]
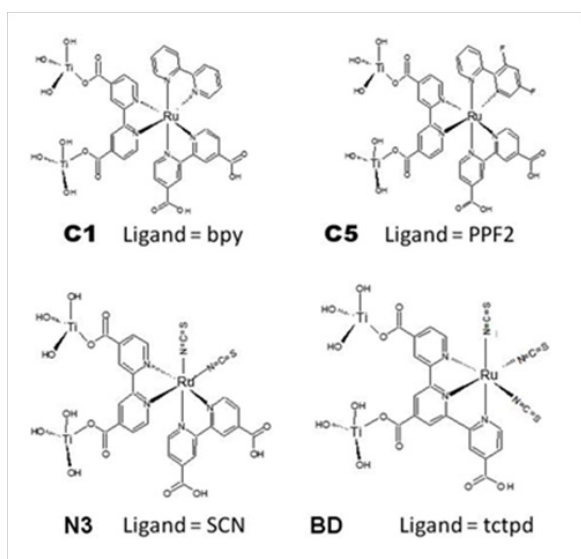

Figure 3 Molecular structures of C1,C5,N3,BD dyes.

Results and Discussion

Validation of the model

Calculations of the global index efficiency of a series of four dyes with well-known photo conversion efficiencies (PCE) and whose structures are display in Figure 3 & 4. The four dyes contains different types of ligand like bipyridine (bpy), difluorophenylpyridine (PPF2), thiocianate (SCN) and tricarboyy terpyridine (tctpd), their calculated values are showed in Table 1.

Looking to the above Table it can be seen how the type of ligand influence the different calculated parameters. For example C1 has the higher value for F_3 while F_2 is maximum for C5. The increase

in one parameter is compensated, in some cases, by the decrease in another. It is interesting to note the high rate between the absorbed and the delivered energy for BD. Focusing on the global index value, the calculated values reproduce the experimental trend showed on the PCE and also predict, within this small sample of dyes, that N3 and BD are the best.
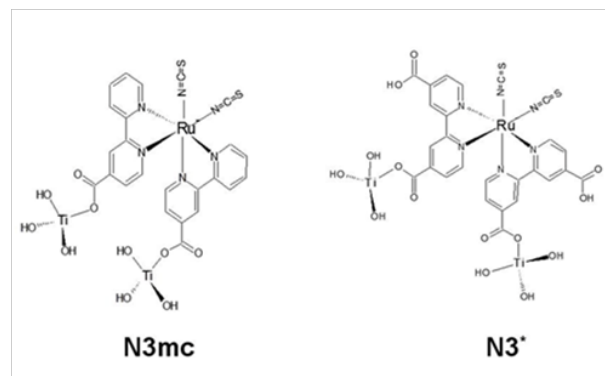

Figure 4 Molecular Structure for N3mc and N3*.

Table 1 Calculated values for: Absorbed Energy (Ea), Delivered Energy(Ed), Participation of the anchor group (ϕT), Amount of energy delivered to the anchor (F_1), Amount of charge injected (F_2), Efficiency of regeneration (F_3) and Global index efficiency (E)

	Ea	Ed	ϕT	F1	F2	F3	E	PCE
C1	0.92	0.38	0.053	0.02	0.09	5.87	0.27	1
C5	1.58	0.45	0.104	0.047	0.13	2.77	0.4	4.0 [11]
N3	0.91	0.59	0.118	0.069	0.12	3.06	0.64	6.9 [11]
BD	1.06	0.96	0.153	0.147	0.11	3.13	1.27	11.1 [5]

F1-EdϕT E-100F1F2F3/Esun   Esun=4.13

Table 2 Calculated parameters for N3mc and N3*

	Ea	Ed	ϕT	F1	F2	F3	E
N3mc	0.62	0.56	0.17	0.094	0.17	2.91	1.15
N3*	0.81	0.73	0.1	0.075	0.13	3.03	0.69

Improvements

The characteristics of a good model not only refer to its ability to report experimental tendencies but also to predict the behavior of new complexes. In this sense it is possible to propose the development of new types of ligand that increase the overall yield. For examples an issue that has not been clarify it is, if the anchoring ligand, dicarboxybipyridine request two carboxi or only one? This problem can be addressed by employing the non-symmetric monocarboxy bipyridine ligand [11] and synthesize the following complex labeled N3 mc.

Calculated values for N3mc and the corresponding N_3* are displayed on Table 2. To perform a more accurate comparative analysis, the N_3 complex was calculate with a molecular structure were the two $Ti(OH)_3$ groups are anchored in different dcbp ligands.

From the above results it can be clearly see that the replacement of the dcbp ligand by mcbp results in an enhancement of the global efficiency respect to the parent N_3. Note that while the absorbed energy diminish in N_3mc, the Ed/Ea rate remains constant but fT increase and therefore the product F_1=EdfT is greater for N3mc. Because the two carboxi groups are absent in N3mc, the anchoring is less stabilized,

the SOMO of the modified complex moves to higher energies cause also an increase in F_2. Finally the third index is little influenced. In summary, by replacing dcbp ligand with mcbp, the response of the two indexes F1 and F_2 is increase causing an enhancement of the global efficiency index from 0.69 to 1.15, a value closer to the BD (1.21). The synthesis of N_3mc is in progress in our laboratory.

Computational details

All calculations were performed on the ADF 2010 package.[12] Geometry optimization of ligands and complexes (ground state and first triplet), was performed with the PBE exchange correlation functional in conjunction with DZP quality basis set for first row elements and ZORA-TZP basis set for transition metals (Ru,Ti). The resulting optimized geometries were checked for the presence of a local minimum. TDDFT calculations were performed in ACN as solvent. The SAOP exchange correlation was employed in conjunction with SZ basis set for C, H, N, O and a DZ basis set for F, S, I, and ZORA-TZP for transition metals. Hirschfeld fragment molecular decomposition was performed for the first 30 allowed excitations. To calculate the amount of absorbed energy, only excitations with oscillator strengths greater than, or equal to, 0.05 were considered. Solvent effects were incorporated by means of the COSMO [model with a cavity defined by the solvent excluding surface (Esurf) and Klam`s atomic radii. Population analysis for the ground state (GS) and the first lowest triplet (T1) was achieved using Mulliken's method.

Acknowledgments

Conflicts of interest

Author declares there are no conflicts of interest.

Funding

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