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## Atomistic simulations of thiol-terminated modifiers for hybrid photovoltaic interfaces

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### ABSTRACT

Small aromatic molecules such as benzene or pyridine derivatives are often used as interface modifiers (IMs) at polymer/metal oxide hybrid interfaces. We performed a theoretical investigation on prototypical thiol-terminated IMs aimed at improving the photovoltaic performances of poly(3-hexylthiophene)/TiO<sub>2</sub> devices. By means of first-principles calculations in the framework of the density functional theory we investigate 3-furanthiol (3FT), 4-mercaptobenzoic acid (4MB), and 6-isoquinolinethiol (6QT) molecules. We discuss the role of these molecules as modifiers alternative to 4-mercaptopyridine (4MP) which has recently shown to induce a large improvement in the overall power conversion efficiency of mesoporous films of TiO<sub>2</sub> infiltrated by poly(3-hexylthiophene). The IMs investigated are expected to keep the beneficial features of 4MP giving at the same time the possibility to further tune the interlayer properties (e.g., its thickness, stability, and density). Dense interlayers of 6QT turn out to be slightly unstable since the titania substrate induces a compressive strain in the molecular film. On the contrary, we predict very stable films for both 3FT and 4MB molecules, which makes them interesting candidates for future experimental investigations.

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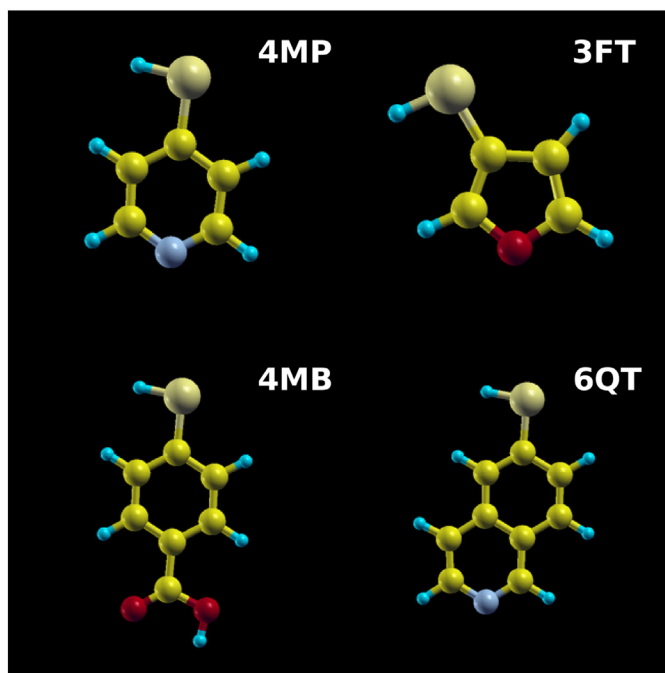
### 1. Introduction

Despite very promising in principle, hybrid polymer/metal oxide solar cells have relatively low photoconversion efficiencies, typically below 1% [1]. The reason why they are so inefficient is still not clearly understood [2]. Different strategies have been adopted over the past few years to overcome such limits. Among them, the use of molecular interface modifiers (IMs) has proven to be an effective way to improve the performances of functional interfaces for photovoltaics (PV) [3]. The main motivations addressed in the literature for using IMs in the development of hybrid PV devices are [3–11]: increasing the polymer/metal oxide interaction; enhancing charge transport; adjusting the work function of the substrate by introducing molecular dipoles; contributing to light harvesting; and reducing charge carriers recombination.

The pyridine molecule and its derivatives have been largely employed to optimize the performances of hybrid solar cells [4,5,7,11]. A recent work on mesoporous films of TiO<sub>2</sub> infiltrated by poly(3-hexylthiophene) (P3HT) [12] shows that the use as IM of the simple optically inactive and inexpensive 4-mercaptopyridine molecule (4MP, C<sub>5</sub>H<sub>5</sub>NS) is able to enhance the photocurrent of the cell, inducing a large improvement in the overall power conversion efficiency for this class of devices. The 4MP molecule, consisting of a pyridine aromatic ring with a thiol group in the position opposite to the nitrogen atom (see Fig. 1), is known to form well-ordered self-assembled monolayers on silver [13] and gold [14] surfaces.

The reasons of the beneficial effects of 4MP on the photovoltaic performances of TiO<sub>2</sub>/P3HT hybrid solar cells have been extensively investigated both experimentally and theoretically [12,15]. A comparative analysis on different pyridine-based modifiers has shown that the good performances of 4MP are most likely due to the spontaneous self-assembling of IM molecules on titania and to the formation of a stable and ordered interlayer; this molecular interlayer is bound to the substrate through Ti–N bonds and exposes thiol groups to the polymer phase [12,15]. X-ray photoemission spectroscopy results on the interaction between 4MP and the anatase TiO<sub>2</sub> surface reveal, indeed, that the covalent interaction between the N atom and the under-coordinated Ti surface is the dominant bonding type, though a substantial amount of 4MP molecules binds via hydrogen mediation [16]. The simulations, performed in the ideal conditions of defect-free surface and completely saturated IMs, reveal a crystalline 4MP monolayer with a zig-zag motif in which, in principle, all of the available TiO<sub>2</sub> adsorption sites are passivated. Notably, it has been found that small details in the structure of the single molecule imply very large differences in the morphology of the corresponding self-assembled monolayer [15]. For example, by modifying the position of the thiol group from 4 to 2 in the pyridine ring (by considering 2-mercaptopyridine instead of 4-mercaptopyridine), the corresponding interlayer is not anymore crystalline but disordered. This morphological difference is associated to the loss of the PV response of the corresponding interface [12]. On the other hand, the thiol group of 4MP in a position opposite to the nitrogen atom has two beneficial effects: it contributes to stabilize the monolayer and it favors the formation of a dense and ordered assembling. In addition, the thiol-terminated interlayer gives

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**Fig. 1.** Stick and ball representations of the thiol terminated interface modifiers considered: 4-mercaptopyridine (4MP, reported for comparison), 3-furanthiol (3FT), 4-mercaptobenzoic acid (4MB), and 6-isoquinolinethiol (6QT).

good compatibility with the polymer by increasing its diffusivity and eventually yielding a larger polymer/substrate interface area, as measured by positron annihilation spectroscopy [12,15].

In the present work, by a comparative theoretical analysis, we discuss alternative IMs that, in principle, are expected to keep the beneficial properties of 4MP while extending the possibility of tuning the interlayer properties (e.g., its thickness, stability, and density) to further optimize the PV performances of polymer/metal oxide devices. We identify the requirements that must be fulfilled by a good IM candidate: (i) It must be a small molecule with aromatic and donor characters. The aromatic character is expected to favor assembling and layer stabilization by  $\pi \rightarrow \pi$  interactions. The donor character should favor the electron transfer to the substrate which is expected to adjust the work function of the metal oxide thus increasing the open circuit voltage of the cell. (ii) It must efficiently bind to the surface (binding energy of the order of 1 eV per molecule) in a configuration perpendicular to the substrate and (iii) it must show a spontaneous assembling into a dense and crystalline monolayer. The formation of a dense interlayer driven by an attractive molecule–molecule interaction makes it possible to modify the polymer–substrate interaction over a sizable portion of the hybrid interface. In particular, the crystalline structure of the interlayer should preserve the efficient electron injection by the polymer and avoid the larger resistance of a disordered molecular interlayer (as observed in the case of the 2-mercaptopyridine interlayer [12,15]). (iv) It must provide a smooth electrostatic surface in order to induce a good polymer diffusivity on the substrate. In particular, thiol-terminated IMs have the potential to keep the same features observed in the case of 4MP, namely a larger polymer mobility on the surface and a tendency to spontaneously form ordered interlayers. In addition to the requirements (i)–(iv) described above it would be highly desirable to identify IMs giving rise to interlayers of different thickness, thus allowing for a tuning of the polymer–metal oxide separation in order to optimize charge injection and suppress back recombination.

By means of a predictive theoretical investigation using first-principles calculations at the density functional theory level, we show that it is possible to identify suitable candidates. For the selected molecules we calculate the structure and the electronic properties of the

isolated and self-assembled bound molecules. We discuss the candidates that best satisfy the above technological requirements and, as such, are possible candidates for further experimental investigations. More specifically, we propose three prototypical small aromatic molecules alternative to 4MP: 3-furanthiol (3FT,  $C_4H_4OS$ ), in which the six-membered ring of pyridine is replaced by the five-membered ring of furan, 4-mercaptobenzoic acid (4MB,  $C_7H_6O_2S$ ), differing from 4MP for the presence of a carboxyl group in place of the nitrogen atom, and 6-isoquinolinethiol (6QT,  $C_9H_7NS$ ) with an additional benzene ring fused to the pyridine ring. This latter molecule, in particular, is similar to 2-naphthalenethiol, a small conductive molecule composed of two consecutive benzene rings with a thiol side group, which has been recently used to enhance charge transport in hybrid polymer/ZnO nanorod solar cells [17]. 6QT belongs to the family of thiol-functionalized benzopyridines and enables to investigate the effect of interlayer thickness by varying the number of benzene rings. The interface modifiers considered in the present work are reported in Fig. 1.

## 2. Computational details

Density functional theory (DFT, [18]) calculations have been performed using a plane-wave pseudopotential approach as implemented in the QUANTUM-ESPRESSO package [19]. We used the Perdew–Burke–Ernzerhof exchange–correlation functional [20] and ultrasoft pseudopotentials [21]. Dispersion corrections have been included according to Grimme’s parametrization [22,23]. Satisfactorily converged results have been obtained by using kinetic energy cutoffs of 25 Ry for wavefunctions and of 200 Ry for charge density. The k-point sampling of the Brillouin zone was limited to the  $\Gamma$  point. For geometry optimizations we used the Broyden–Fletcher–Goldfarb–Shanno algorithm, with threshold values of 0.0026 eV/Å and  $1.4 \times 10^{-4}$  eV for residual forces and energy variation, respectively. The anatase (101) surface was modeled with a periodically repeated slab cut from the bulk. The optimized bulk lattice parameters ( $a, b, d = 3.79, 9.74, 2.01$  Å) are consistent with previous calculations ( $a, b, d = 3.786, 9.737, 2.002$  Å [24,25]) and agree with available experimental data ( $a, b, d = 3.782, 9.502, 1.979$  Å [26]). To simulate IMs interacting with the anatase (101) surface we used supercells containing four atomic layers (72 atoms, 5.9 Å thick) separated by a vacuum of  $\sim 15$  Å. The surface has dimensions  $2 \times 3$  in the  $[10\bar{1}]$  and  $[010]$  directions, respectively, corresponding to a surface area of  $11.37 \times 10.45$  Å. During geometry optimizations the atoms in the bottom layer were fixed to their bulk positions. Test calculations with a  $TiO_2$  surface of six atomic layers (108 atoms, 9.4 Å thick) did not show any significant difference. To estimate the optical gap of the molecules we performed time-dependent DFT calculations [27] using the TURBOMOLE code [28]; we used a Gaussian atomic orbital basis set of split valence triple- $\zeta$  quality (TZVP) and the hybrid exchange–correlation functional B3LYP, which has proven to give a good description of the optical gap of small polyaromatic hydrocarbons [29]. The same code has been used to compute the dipole moment of each molecule. Molecular graphics have been generated by using the XCRYSDEN [30] and VMD [31] packages.

## 3. Results and discussion

We first calculated the electronic properties of the isolated molecules by means of B3LYP time-dependent DFT calculations. As expected, all of the molecules considered are optically transparent, the first optically active transition falling at about 4.9, 5.0, 4.5, 4.1 eV for 4MP, 3FT, 4MB, and 6QT, respectively. Note that the same computational scheme gives  $\sim 4.8$  eV for the optical gap of pyridine, which is in reasonable agreement with the experimental value of about 4.6 eV (see compilation in Ref. [32]).

To compare the different IMs we first calculated the minimum-energy configuration of the isolated molecule adsorbed on the ideal  $TiO_2$  anatase (101) surface (see Fig. 2). All of the molecules bind to a

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