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Theory of Covalent Adsorbate Frontier Orbital Energies on Functionalized Light-Absorbing Semiconductor Surfaces

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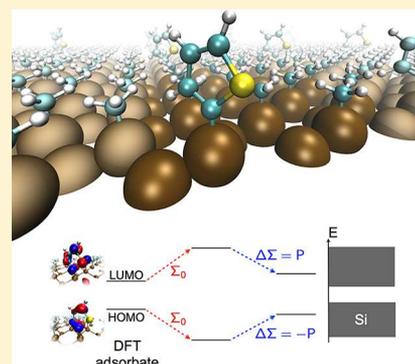
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S Supporting Information

ABSTRACT: Functional hybrid interfaces between organic molecules and semiconductors are central to many emerging information and solar energy conversion technologies. Here we demonstrate a general, empirical parameter-free approach for computing and understanding frontier orbital energies – or redox levels – of a broad class of covalently bonded organic–semiconductor surfaces. We develop this framework in the context of specific density functional theory (DFT) and many-body perturbation theory calculations, within the GW approximation, of an exemplar interface, thiophene-functionalized silicon (111). Through detailed calculations taking into account structural and binding energetics of mixed-monolayers consisting of both covalently attached thiophene and hydrogen, chlorine, methyl, and other passivating groups, we quantify the impact of coverage, nonlocal polarization, and interface dipole effects on the alignment of the thiophene frontier orbital energies with the silicon band edges. For thiophene adsorbate frontier orbital energies, we observe significant corrections to standard DFT (~ 1 eV), including large nonlocal electrostatic polarization effects (~ 1.6 eV). Importantly, both results can be rationalized from knowledge of the electronic structure of the isolated thiophene molecule and silicon substrate systems. Silicon band edge energies are predicted to vary by more than 2.5 eV, while molecular orbital energies stay similar, with the different functional groups studied, suggesting the prospect of tuning energy alignment over a wide range for photoelectrochemistry and other applications.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



Hybrid interfaces between organic molecules and semiconductors are central to many emerging information^{1–3} and solar energy conversion technologies.^{4,5} In particular, covalent functionalizations of silicon – resulting in chemically tunable, well-defined interfaces⁶ stable against oxidation^{3,7,8} or corrosion^{8–13} and imparting novel electronic properties^{5,14,15} – have been explored and are in use for wide-ranging applications from organic electronics^{16,17} to biochemical sensors.^{18,19} More recently, adsorbate molecules have been used to template more complex functionality, such as supporting molecular catalysts for photochemical water-splitting,^{4,5} and for pollutant remediation applications.^{20,21} For any such application, there is significant need for understanding the mutual changes of the structural, electronic, and optical properties of the semiconductor surface and molecule upon formation of their interface.¹

Optoelectronic or catalytic properties of hybrid interfaces are fundamentally related to adsorbate electronic structure, where the alignment of frontier orbital energies (that is, electron addition or removal “redox” energy levels) with the substrate Fermi level or band edges is central. Modifications of gas-phase molecular frontier orbital energies, upon adsorption to a surface, are well-known to be significant.^{22–26} When placed in

contact with a surface, the adsorbate ionization potential (or, equivalently, highest occupied molecular orbital, HOMO) and electron affinity (lowest unoccupied molecular orbital, LUMO) are altered in several ways. First, covalent bonding between the molecule and the semiconductor surface can result in significant hybridization and potentially modify orbital character, resulting in a shift in orbital energies and energetic broadening of discrete levels. Second, the Coulomb interaction associated with added holes or electrons in the molecule induces polarization of the semiconductor substrate, a nonlocal correlation effect further stabilizing the added hole or electron and reducing the gap between molecular ionization and affinity levels relative to the isolated molecule.²³ Third, the self-consistent interaction between molecule and surface will rearrange the electron density – inducing a so-called “interface dipole” – and modify the alignment of frontier orbital energies with, for example, the valence and conduction band edges. A common framework capable of treating each of these effects on

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equal footing is required to predict frontier orbital energy level alignment at hybrid interfaces and rationalize optoelectronic or catalytic behaviors.

First-principles density functional theory (DFT) is the standard approach for computing structural and electronic properties of relatively large-scale systems. Unfortunately, ionization potentials, electron affinities, and level alignments predicted from standard DFT Kohn–Sham energy spectra using standard functionals fail to reproduce experiment,^{23,26–28} where frontier orbitals are commonly too close to the Fermi level, sometimes by well over 1 eV. Conversely, many-body perturbation theory within the GW approximation can bring adsorbate orbital energies into good agreement with spectroscopy measurements,^{26,29} capturing quantitative trends in hybridization, surface polarization, and interface dipole effects. Prior studies within the GW approximation have focused predominately on physisorbed molecular adsorbates on metals^{23,26} and semiconductors,^{24,25} where level alignment was predicted to be in good agreement with spectroscopy,³⁰ notably at significant computational expense. Intuition from these results has been used to efficiently approximate self-energy corrections to DFT orbital energies for more complex, chemisorbed systems, explaining single-molecule junction conductance^{31,32} and electron transfers in dye-sensitized solar cells.³³ Despite this recent case-by-case progress, a general and yet computationally practical framework for level alignment at the interface between complex covalently chemisorbed adsorbates and semiconductors, in particular for photo- and electrochemical applications, is lacking.

In what follows, we develop and use an efficient, empirical parameter-free approach for predicting and understanding frontier orbital energies – redox levels – of covalently bonded organic–semiconductor surfaces. Using model and more rigorous GW self-energy approaches, we study thiophene covalently attached to Si(111) either as an exemplar linker for catalyst/surface assembly or as the first monomer of a polythiophene molecular wire attached to the surface. Through detailed calculations of structural and binding energetics of mixed-monolayers consisting of both covalently attached thiophene and hydrogen, chlorine, methyl, and other passivating groups, we quantify, in general terms, the impact of coverage, nonlocal polarization, and interface dipole effects on the alignment of the thiophene frontier orbital energies with the silicon band edges, showing it can be tuned on the order of eV. Our approach offers an integrated computational framework for the discovery of optimal semiconductor, linker, and catalyst systems for solar fuel and other photo- or electrochemical applications.

Geometry relaxation of an isolated thiophene molecule in the gas phase and chemisorbed on Si surfaces is performed using DFT within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).³⁴ We use the Quantum Espresso code³⁵ and norm-conserving pseudopotentials³⁶ with a 40 Ry planewave cutoff. An $8 \times 8 \times 8$ k -point grid is utilized for bulk convergence calculations, while only the Γ point is used for slab supercell calculations. These criteria result in total energy convergence to 1 meV/atom.

Our Si lattice constant of 5.46 Å in the diamond structure compares well with the experimental lattice constant of 5.43 Å and is consistent with previous work.³⁷ For studies of thiophene on passivated Si(111), a typical surface coverage is one molecule per 4×4 unit cell (as shown in the Supporting Information). We use eight layers of Si with 13 Å of vacuum,

minimizing interactions between slabs under periodic boundary conditions. The Si surface atoms are passivated by a mixed monolayer of thiophene and functional groups $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NHCH}_3$, $-\text{CH}_2\text{NH}_2$, or $-\text{Cl}$ on the top surface, and a homogeneous monolayer of the same functional groups terminates the bottom surface.

Upon chemisorption, the C–H bond at position 2 of the thiophene ring breaks, and a bond forms between the exposed C atom and a surface Si atom (Figure 1). After relaxation

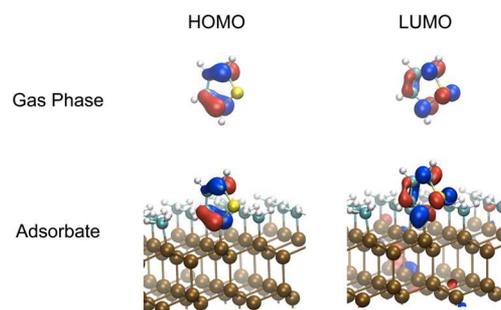


Figure 1. Thiophene HOMOs and LUMOs for gas phase and adsorbate, respectively. The atom color code is: Si (brown), C (cyan), S (yellow), and H (white).

within DFT-PBE, we find a C–Si bond length of 1.9 Å, oriented normal to the Si(111) surface (as shown in the Supporting Information). In addition to this fully optimized interface, we also consider, for comparison, two other constrained geometries: (i) a passivated Si(111) surface with the thiophene molecule replaced by a functional group whose coordinates are allowed to relax (all other degrees of freedom remaining frozen) and (ii) an isolated thiophene molecule with its geometry fixed to its chemisorbed geometry and an optimized hydrogen atom saturating position 2. All free atoms in these optimizations are relaxed such that Hellmann–Feynman forces are <25 meV/Å.

For optimized interface geometries, we calculate level alignment using many-body perturbation theory within the G_0W_0 approximation using the BerkeleyGW code.³⁸ Self-energy corrections to the DFT-PBE Kohn–Sham eigenvalues are computed in two steps. First, the dielectric function is constructed in the random phase approximation using a 12 Ry planewave cutoff, which is extended to finite frequency with a generalized plasmon-pole (GPP) model.³⁹ The inverse dielectric function is obtained with more than 3600 unoccupied states (extending 40 eV above the valence band edge). Second, self-energy corrections are evaluated within a G_0W_0 approximation using the same number of empty states and a static remainder approach⁴⁰ to approximately complete the unoccupied subspace.

For gas-phase thiophene (see details in the Supporting Information), our G_0W_0 approach results in -0.94 and 8.83 eV for the EA and IP, respectively, in excellent agreement with experimental data (-1.17 eV for EA⁴¹ and 8.86 ± 0.02 eV for IP⁴²) and prior work.⁴³ For comparison, Δ SCF with standard functionals has been reported to predict gas-phase IPs of small molecules with an average error of 0.3 eV with respect to the experiment.³³ In contrast, the DFT-PBE Kohn–Sham eigenvalues underestimate the IP-EA gap by over 5 eV.

Upon chemical adsorption, the thiophene molecule loses one H atom and covalently bonds to a surface Si atom, yet we observe much of the character of the isolated molecule remains.

The molecular HOMO and LUMO retain π and π^* symmetry, as shown in Figure 1, while HOMO-2 is still of σ character but now involves a C–Si bond. To evaluate the self-energy correction for the thiophene adsorbate frontier orbitals, we may no longer assume the combined adsorbate–substrate system Kohn–Sham eigenstates $\{\phi_{nk}^c\}$ are good approximate quasiparticle wavefunctions due to interface hybridization.^{26,44} However, provided that the adsorbate orbitals are sufficiently similar to their gas-phase counterparts $\{\phi_i^{\text{mol}}\}$, we may compute quasiparticle corrections via direct evaluation of $\langle \phi_i^{\text{mol}} | \hat{\Sigma}_c | \phi_i^{\text{mol}} \rangle$,²⁶ where $\hat{\Sigma}_c$ is the self-energy operator of the combined adsorbate–substrate system. This approach approximates the procedure of calculating the matrix elements $\langle \phi_{nk}^c | \hat{\Sigma}_c | \phi_{nk}^c \rangle$, then diagonalizing and projecting onto the isolated molecular orbitals. This scheme requires both the adsorbed system Hamiltonian, \hat{H}_c , and $\hat{\Sigma}_c$ to be nearly diagonal in the isolated molecular orbital basis $\{\phi_i^{\text{mol}}\}$ and the resonance to be sufficiently localized on the molecule. In prior work²⁶ on physisorbed systems, this approach led to qualitative agreement with photoemission. In this work, we show that it is applicable to a chemisorbed system.

Projected densities of states (PDOS) of the combined thiophene–Si(111) system on isolated thiophene molecular eigenstates, $\sum_{nk} |\langle \phi_{nk}^c | \phi_i^{\text{mol}} \rangle|^2 \delta(E - E_{nk})$, are shown in Figure 2a.

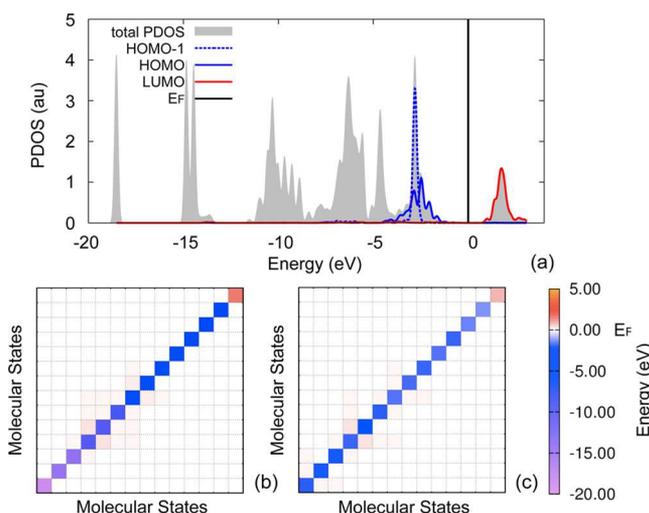


Figure 2. (a) Partial DOS associated with thiophene adsorbed on Si. Projections onto isolated molecular HOMO-1 (dashed blue), HOMO (blue), and LUMO (red) are also shown. We define E_F to be the average of the conduction band minimum and valence band maximum of the combined system (i.e., the middle of the gap). (b,c) Color map of the combined system Hamiltonian and self-energy operator projected onto isolated molecule eigenstates as diagonal terms. Off-diagonal terms give second-order perturbation theory corrections to the diagonal energies, which in this case are negligibly small compared with diagonal terms and molecular energy states.

The thiophene frontier orbitals maintain their gas-phase character upon adsorption, with minimal broadening due to the coupling with the surface, indicating that their energy resonances can be unambiguously determined.

Additionally, we perform an analysis of the combined system Hamiltonian projected onto isolated molecular eigenstates, $\langle \phi_i^{\text{mol}} | \hat{H}_c | \phi_i^{\text{mol}} \rangle$. In Figure 2b, we show a density plot where (i) the diagonal terms reflect $\langle \phi_i^{\text{mol}} | \hat{H}_c | \phi_i^{\text{mol}} \rangle$, with i running from the lowest occupied orbital to the LUMO, and (ii) the off-diagonal terms are colored according to their contribution to

second-order perturbation theory corrections to the diagonal energies, that is, $(|\langle \phi_i^{\text{mol}} | \hat{H}_c | \phi_j^{\text{mol}} \rangle|^2) / (E_i^{\text{mol}} - E_j^{\text{mol}})$, where the denominator is the difference in DFT eigenvalues of the isolated molecular orbitals. Figure 2c is a companion plot, with H_c replaced by $\Sigma_c - V_{xc}$. The small off-diagonal contributions in both color maps clearly indicate negligible coupling between molecular orbitals induced by chemisorption.

The small off-diagonal contributions to H_c and Σ_c in the isolated molecular orbital basis provide justification for the use of diagonal matrix elements of G_0W_0 in Figure 2c to predict organic–semiconductor level alignment. The results are shown in Figure 3. Following previous work,²³ one can partition the self-energy correction into three terms: the bare exchange (Σ_X), the screened exchange minus the bare exchange (Σ_{SX-X}), and the Coulomb hole contributions (Σ_{CH}). Examining the differences in these terms between the gas phase and adsorbed molecule, we observe that for most of the occupied states $\Delta\Sigma_X$ is close to 0, and that $\Delta\Sigma_{SX-X} \approx -2\Delta\Sigma_{CH}$, an indicator²³ that static polarization dominates the changes in orbital energies on going from gas phase to adsorbate. Summing these contributions for each orbital, we find a $\Delta\Sigma$ of ~ 1.66 eV independent of orbitals, also consistent with static polarization upon chemisorption on semiconductors being the dominate effect, similar to physisorption on metals in previous works.^{23,26}

It is straightforward to compute the static polarization response of the substrate to an excitation in the form of molecular frontier orbitals via a much more efficient, alternative approach to G_0W_0 , as we now show. We first construct the charge density $\rho_i^{\text{mol}}(r) = |\phi_i^{\text{mol}}(r)|^2$ associated with adding an extra electron/hole for each unoccupied/occupied molecular state i . This charge density implies an external potential $V_i^{\text{mol}}(r)$ on Si substrate. Then, we calculate the electronic potential change $\Delta V_{\text{slab}}(r)$ induced on the Si substrate self-consistently with DFT due to the fixed external potential $V_i^{\text{mol}}(r)$. Finally, the static polarization energy, P , is determined via the integral $P = (1/2) \int dr \rho_i^{\text{mol}}(r) \Delta V_{\text{slab}}(r)$. Using this approach, we obtain a polarization energy of 1.57 eV from $\rho_{\text{HOMO}}^{\text{mol}}$ and 1.60 eV from $\rho_{\text{LUMO}}^{\text{mol}}$, in excellent quantitative agreement with our G_0W_0 value of $\Delta\Sigma$ of ~ 1.66 eV. Our results imply that the majority of the effect found in computationally expensive higher level G_0W_0 calculation for the combined system versus the isolated system can be computed at this lower level of theory.

Given these results, we now have a general parameter-free and computationally efficient prescription for computing frontier orbital energies (redox levels) of a broad class of covalent organic–semiconductor interfaces. In Figure 3a, we summarize this approach for thiophene chemisorbed on Si-CH₃. From a DFT calculation of the adsorbate system, we obtain an initial alignment of the semiconductor band edge and adsorbate molecule states. A G_0W_0 calculation correcting the bulk semiconductor band edge is performed as a secondary initial step. This assumes that polarization effects associated with surface functionalization have a negligibly small impact on semiconductor band edges due the small dielectric susceptibility of the organic overlayer. Then, if $\langle \phi_i^{\text{mol}} | \hat{H}_c | \phi_j^{\text{mol}} \rangle$ off-diagonal contributions are small, as in the example here, one can proceed as follows: First, a gas-phase G_0W_0 calculation provides a correction, Σ_0 , to the adsorbate IP and EA. Second, a substrate-induced nonlocal polarization correction is computed to model the self-energy change upon adsorption. As shown in Figure 3a, a DFT-PBE calculation gives the Si band gap 0.6 eV and an adsorbate molecule HOMO–LUMO gap of 4.13 eV. A G_0W_0 calculation corrects the Si band gap to 1.25 eV and the

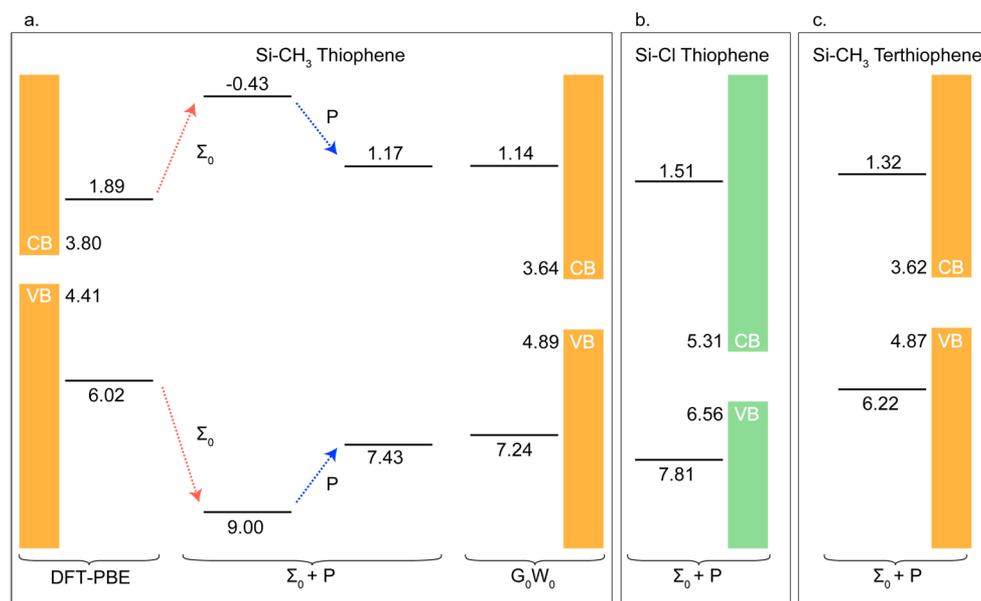


Figure 3. (a) HOMO and LUMO energy levels (in eV) of adsorbate thiophene relative to the CH_3 -terminated Si(111) valence band maximum (VBM) and conduction band minimum (CBM) from DFT-PBE, $\Sigma_0 + P$, and G_0W_0 . (b) $\Sigma_0 + P$ orbital energies for adsorbate thiophene relative to Cl-terminated Si. (c) $\Sigma_0 + P$ orbital energies for adsorbate terthiophene relative to CH_3 -terminated Si. Electron-donating $-\text{CH}_3$ groups tune Si band edge and reduce the energy barrier between the Si CBM and adsorbate LUMO compared with $-\text{Cl}$ passivated surfaces.

gas-phase HOMO–LUMO gap by 5.3 eV. Surface polarization effects, $P_{\text{LUMO}}^{\text{mol}} = 1.60$ eV and $P_{\text{HOMO}}^{\text{mol}} = 1.57$ eV, provide an additional correction to molecular orbital energies upon adsorption, resulting in level alignment in good agreement with a more rigorous and computationally expensive interface G_0W_0 calculation.

In the remainder of this work, we use this more efficient approach to explore tuning thiophene–Si energy level alignment through different surface functionalizations, R. We study the fully passivated surfaces with completely optimized geometries unless otherwise indicated. The total dipole moment per chemisorbed molecule includes two contributions: the intrinsic dipole of molecule and the induced dipole on the molecule–Si interface due to interface charge rearrangement upon chemisorption. The band edge shift is found to be linear with the change of interface dipole moment, as in prior work.^{45,46} The change of interface dipole moment, $\Delta\mu_{\perp}$, is computed as a difference between functional group R-terminated and H-terminated Si surfaces. As shown in Table 1, we find that electron-donating groups, $-\text{NHCH}_3$, $-\text{OCH}_3$, and $-\text{CH}_3$, can increase the energy difference of Si VBM and adsorbate HOMO and reduce the energy barrier between the Si CBM and adsorbate LUMO. Electron-withdrawing groups, for

Table 1. VBM–VBM_H Is the Band Edge Shift, Si Surface Valence Band Maximum to Vacuum, from H-Terminated to Functional Group R-Terminated Surfaces^a

Si-R	VBM–VBM _H (eV)	$\Delta\mu_{\perp}/A$ (D/nm ²)
$-\text{NHCH}_3$	–1.44	–3.81
$-\text{OCH}_3$	–1.1	–2.91
$-\text{CH}_3$	–0.89	–2.36
$-\text{CH}_2\text{NH}_2$	0.29	0.76
$-\text{Cl}$	1.1	2.92

^a $\Delta\mu_{\perp}$ is defined as the interface dipole moment difference between functional group R-terminated and H-terminated Si surfaces.

example, $-\text{Cl}$, tune the Si band-edges and relative level alignments in the opposite fashion. We observe a remarkable range of shifts, of 2.5 eV, with these functional groups. The large change in the Si CBM–adsorbed thiophene LUMO energy barrier between a Si surface passivated by an electron-donating group $-\text{CH}_3$ and an electron-withdrawing group $-\text{Cl}$ is illustrated in Figure 3a,b. In Table 2, we show that the thiophene molecule is a stronger electron-donating group than $-\text{CH}_3$, so a higher ratio of thiophene in a mixed $-\text{CH}_3$ / $-\text{C}_4\text{H}_3\text{S}$ monolayer on the surface leads to a decrease in the energy barrier between the Si CBM and adsorbate LUMO. By increasing thiophene coverage up to 50%, we observe a VBM shift of 0.3 eV.

We further explore tuning the Si CBM–adsorbate LUMO alignment through changing guest molecules. Terthiophene exhibits a smaller HOMO–LUMO gap of 6.2 eV with low gas-phase EA of 0.66 eV below vacuum level (from a G_0W_0 calculation). It would be expected, if all other factors were similar to thiophene (chemisorbing perpendicularly via an analogous C–Si bond on methyl-terminated Si surface), that terthiophene would have frontier orbitals more closely aligned with the VBM and CBM of silicon. However, by our calculations, its gap renormalization associated with surface polarization upon absorption is relatively small, only 0.66 eV compared with 1.57 eV for thiophene, due to elongation of the HOMO charge distribution away from the surface along the surface normal direction. Overall, the CBM–LUMO and VBM–HOMO barriers are 0.2 and 1.0 eV less, respectively, than the thiophene–Si interface (Figure 3c). This comparison illustrates that static polarization effects are sensitive to the localization of the molecular frontier orbitals relative to the substrate. Hence, to significantly reduce the CBM–LUMO barrier, simply extending a thiophene wire is insufficient; instead good molecular candidates would be those with the LUMO already localized close to Si substrate.

In summary, we have demonstrated a general and efficient method for determination of molecular orbital resonance

Table 2. Impact of Thiophene Coverage on Band-Edge Shifts of Mixed Methyl and Thiophene Terminated, Referenced to the H-Terminated Si Surface, and Interface Dipole Moment Difference

$-\text{CH}_3$ coverage	$-\text{C}_4\text{H}_3\text{S}$ coverage	VBM $-\text{VBM}_\text{H}$ (eV)	$\Delta\mu_\perp/A$ (D/nm ²)
100%	0%	-0.89	-2.36
93.75%	6.25%	-0.99	-2.49
75%	25%	-1.14	-2.90
50%	50%	-1.21	-3.09

energies on semiconductor surfaces applicable when the relevant molecular orbitals are approximately unperturbed relative to the gas phase. Thiophene chemisorbed on functionalized Si(111) surfaces is in this limit, and our calculations show that our approximate method results in excellent agreement with more rigorous and computationally expensive G_0W_0 calculations. We also find that interface dipoles associated with a range of tested functional groups can shift the band edges of semiconductors by large amounts (on the order of eV) and have a substantial effect on the level alignments at these interfaces. Our method offers an integrated computational framework for the discovery of hybrid interface systems for solar fuel and other photo- or electrochemical applications.

■ ASSOCIATED CONTENT

📄 Supporting Information

Supercell geometry and gas-phase frontier orbital energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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