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Article

Understanding and Improving Triplet Exciton Transfer in Sensitized Silicon Solar Cells

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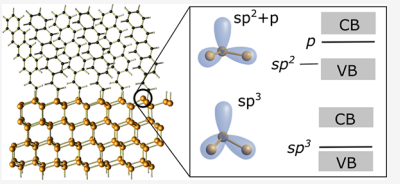
ABSTRACT: The triplet exciton transfer from tetracene to silicon has recently found interest in the context of efficiently harvesting high-energy photons with sensitized silicon solar cells. Density-functional calculations presented here show that at covalently bonded, atomically perfect interfaces, no exciton transfer can be expected. The situation changes, however, as soon as realistic interface models are taken into account. Unsaturated Si dangling bonds on *n*-type silicon assist the exciton transfer. The calculations show furthermore that incompletely bonded interfaces as well as horizontally attached seed molecules foster excitation transfer. Backfilling the interface, on the other hand, is detrimental to the interface's transport properties.



INTRODUCTION

With the development of sensitized solar cells, conventional solid-state photovoltaic technologies are now challenged by devices functioning at a molecular and nanolevel.[1−5] In particular, a sensitizing layer of singlet-fission material promises to break the Shockley−Queisser limit[6] for the silicon solar cell efficiency, which limits the theoretical maximum solar energy conversion to about 30%. Such a layer can in principle double the current generated by high-energy photons and significantly reduce energy losses from high-energy photons within the solar cell.[7,8] A high-energy photon is absorbed in the sensitizing layer by creating an excited singlet exciton state, which subsequently splits into two lower-energy triplet exciton states. The recombination of these triplets is spin-forbidden, which means that they have a long lifetime. Provided the triplet excitations can be transferred into the Si solar cell, they can be harvested for electric energy (see Figure 1).

Tetracene (Tc) is an archetypical material for singlet fission[9] and has been used successfully to sensitize Si solar cells.[10,11] However, the mechanism by which the triplet excitons are efficiently transferred from tetracene to silicon is not understood.[10−14] Einzinger et al.[10] suggested electric-field-effect passivation at the interface. A recent work by the Ehrler group[14] probes covalent bonding between the sensitizing layer and the Si surface for transfer optimization. Both the interface bonding configuration[15−18] and the functionalization of the molecules[19,20] can be expected to generate and/or modify electronic interface states and to affect the level alignment and carrier mobility[21,22] at the interface.

In a recent study,[23] some of the present authors discuss density-functional theory (DFT) calculations that suggest that interface defects play a major role in the exciton transfer from Tc to Si. The calculations, however, were made for a model system, Tc molecules van der Waals bonded to Si(111):H. In the present study, we go beyond these calculations and explore

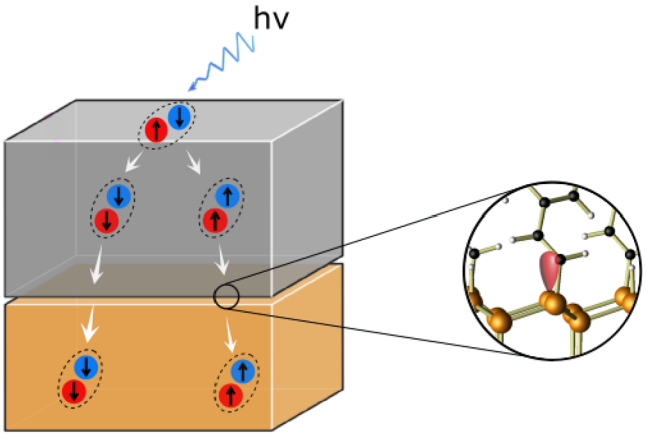


Figure 1. Sketch of a singlet fission-sensitized silicon solar cell. Absorption of a high-energy photon by the tetracene layer produces a singlet exciton. This singlet exciton undergoes singlet fission to generate two triplet excitons. These excitons are then transferred to the Si solar cell. An interface dangling bond defect is shown at rhs.

the triplet exciton transfer across covalently bonded Tc−Si(111):H interfaces. We focus on the structures prepared in ref 14: Ehrler and co-workers synthesized two tetracene derivatives, 5-((trimethylsilyl)-ethynyl)tetracene and 2-((trimethylsilyl)ethynyl)tetracene, where linker groups allow for the functionalization of Si(111):H surfaces with horizon-

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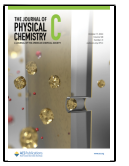

tally and vertically positioned tetracene molecules, respectively, forming a covalently bonded seed layer. Additionally, 1-pentyne was used for backfilling.

COMPUTATIONAL METHODS

Figure 2 shows the structures used in the present work to model the interfaces prepared in the experiment: V and VP

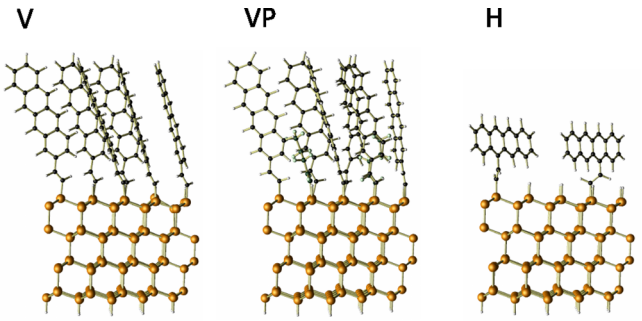

Figure 2. Side views of the V, VP, and H structures (see text) used here to model the Tc/Si(111) interface. Orange, black, and gray balls indicate Si, C, and H, respectively.

represent structures with vertically bonded tetracene molecules with and without 1-pentyne backfilling; H is used to label interfaces with horizontally bonded tetracenes.

Here, spin-polarized DFT calculations are performed using the Quantum ESPRESSO package[24,25] with norm-conserving pseudopotentials. The PBE functional[26] within the generalized-gradient approximation (GGA) is used to describe the electron exchange and correlation (XC) effects. Dispersion interactions are taken into account using Grimme's DFT-D3 approach.[27] Hybrid DFT calculations are performed using the HSE06[28] functional. Excited-state potential-energy surfaces obtained from constrained DFT[29−32] are used for ab initio molecular dynamics (AIMD) calculations that describe the time evolution of the excitation.[33,34] The Berendsen thermostat is used for temperature control.[35] Computationally, the present work is on the same footing as ref 23.

The covalently bonded Tc−Si(111):H interfaces[14] are modeled here with the V, VP, and H structures shown in Figure 2. They have a 5 × 2 lateral periodicity and are characterized by a minimum molecule−molecule distance of 3.33, 2.87 (Tc−Tc distance, 2.43 Tc−pentyne distance), and 3.18 Å, respectively. The supercells contain 8 atomic Si layers, an overlayer consisting of 6 (V, VP) and 2 (H) tetracene molecules, 2 1-pentyne molecules (VP), and a vacuum region of 10 Å. The Brillouin zone sampling is done using a 2 × 2 × 1 mesh.

RESULTS AND DISCUSSION

We calculate molecular (Tc) binding energies of 2.5 and 5.2 eV for the V−H interface models. The difference is due to the enhanced dispersion interaction between horizontally attached molecules and the substrate.

In ref 23, it was shown that HSE06 provides roughly correct excitation energies for both Tc and Si, while PBE underestimates the Si band gap but provides meaningful data for Tc and the exciton dynamics at the purely physisorbed interface.[23] Based on this, we use HSE06 for quantitative results but rely on PBE for the computationally demanding AIMD calculations.

In Figure 3, the band alignment calculated within HSE06 for the V, VP, and H interface structures can be seen. Type-II, i.e.,

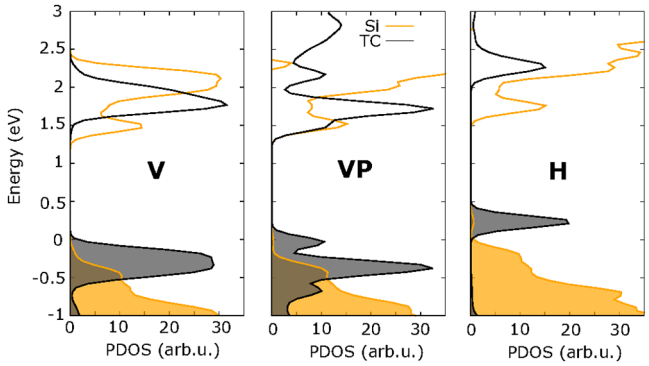

Figure 3. Density of states and band alignment for Tc overlayers covalently bonded to Si(111) calculated on the HSE06 level of theory. The ideal V, VP, and H structures shown in Figure 2 are considered. Energies refer to the Si valence band maximum (VBM). Black and orange denote Tc- and Si-related states, respectively.

staggered band alignment, is obtained for all models. This suggests the possibility of exciton dissociation at the interface with the transfer of electrons to Si. We probed that possibility by performing room-temperature AIMD, using a Tc-localized T_1 triplet exciton as the start configuration. However, at ideal interfaces, neither exciton nor charge transfer occurs. This holds for both vertically and horizontally attached tetracene molecules and is not affected by backfilling with 1-pentyne. This agrees with the experimental findings of Ehrler et al.,[14] who concluded that covalent bonding has a limited effect on the triplet energy transfer from tetracene to silicon.

Real interfaces are characterized by defects, which profoundly influence their electronic properties.[36] In the case of hydrogenated Si interfaces, the appearance of Si dangling bonds (db) due to missing hydrogen[37−40] is commonly observed[41] and considered in the following. In the case of *n*-type Si(111) as used experimentally,[12,42] the db state is doubly occupied in the ground state. The calculated densities of states for the V, VP, and H interface structures with a db^- defect are shown in Figure 4. The Si db^- state appears to be well separated above the Si valence band maximum (VBM) as well

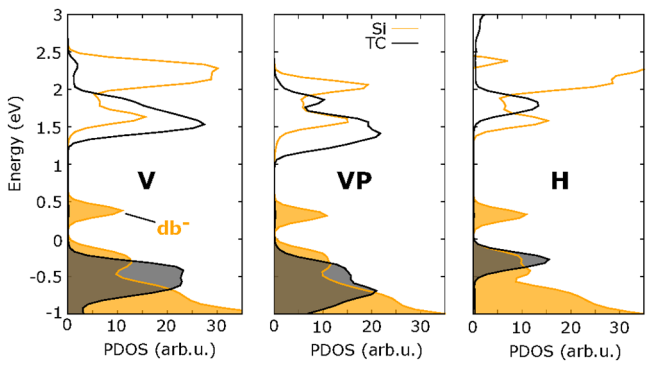

Figure 4. Density of states and band alignment for Tc overlayers covalently bonded to Si(111) calculated on the HSE06 level of theory. Here, V, VP, and H structures with an interface db^- defect are considered. Energies refer to the Si VBM. Black and orange denote Tc and Si-related states, respectively.

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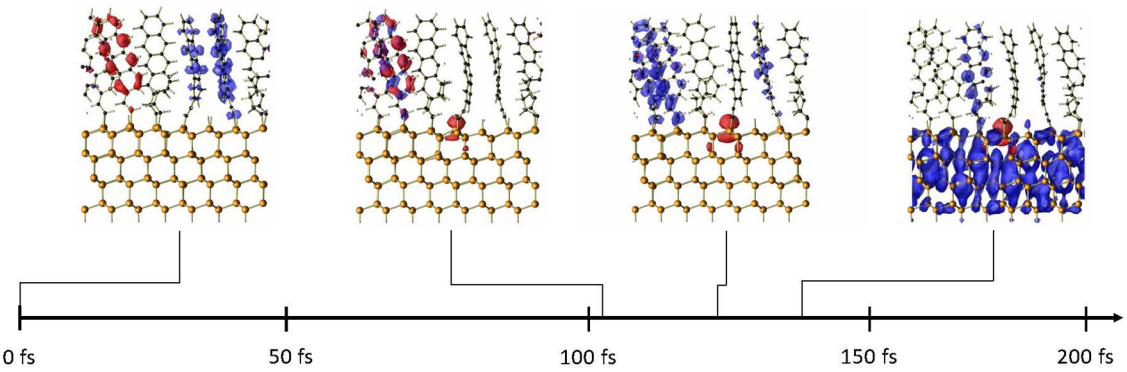

Figure 5. Calculated room-temperature dynamics of the exciton transfer at the Tc/Si(111) interface (VP model with a db defect, example trajectory with characteristic snapshots at 0, 105, 124, and 140 fs after the exciton has been trapped in the lowest molecular layer). Blue and red isosurfaces indicate electron and hole localization, respectively.

as above the occupied Tc states. The band alignment of the defective interface suggests hole transfer from Tc to Si.

In fact, room-temperature AIMD results in exciton transfer from Tc to Si. Snapshots from an example trajectory are shown in Figure 5. The initial state corresponds to a Tc-localized triplet exciton. As time progresses, the exciton hole is transferred to the silicon substrate. At about 100 fs, it is partially hosted by the Si db state. Its transfer to Si is completed after about 130 fs. A few fs later, the exciton electron is also transferred to Si.

Additional microscopic insight is gained from Figure 6, where the time evolution of the Kohn−Sham states

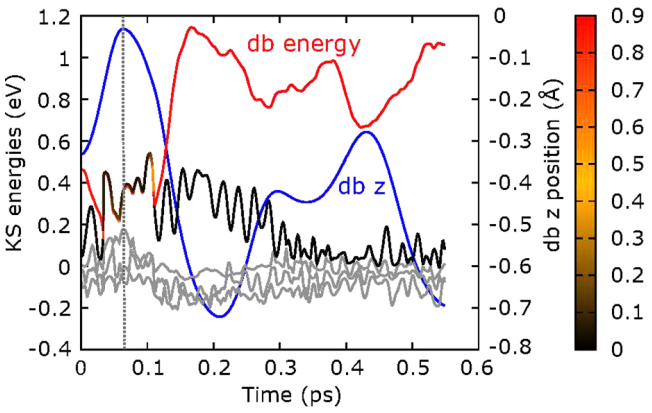

Figure 6. Evolution of Tc valence as well as Si db state energies along the AIMD trajectory shown in Figure 5. The color code shows state localization in Si (red) and Tc (black), respectively. Also shown is the z position of the Si db surface atom (blue, displacement along the surface normal).

corresponding to the trajectory in Figure 5 is shown. Initially, the excited electron occupies the lowest Tc conduction band state; the corresponding hole in the Tc valence band is energetically below the doubly occupied Si db state. The Si surface atom hosting the db state vibrates. As it moves up, the db state energy is lowered in energy because for up positions, it has predominantly sp^3 character. The db energy lowering leads to energetical degeneracy, and subsequent hybridization, with the uppermost Tc valence state hosting the exciton hole. This quenches the barrier for hole transfer from Tc to Si. In the example considered here, the transfer starts at around 40 fs and ends at around 110 fs. The middle of the hybridization period corresponds to the maximum z position of the Si db surface atom, marked with the dotted line in Figure 6. Its subsequent down movement is accompanied by a transition to sp^2 + p hybridization,[43] i.e., an energy increase of the Si db state. This lifts the degeneracy with the Tc top valence state and leads to complete localization of the exciton hole at Si.

The calculations discussed above show that interface defects in the form of Si db may greatly assist in exciton transfer across the covalently bonded Tc/Si interface. This is in line with earlier findings for van der Waals bonded interfaces.[23] However, further morphological details of the interface also affect the exciton transfer. The comparison of the calculated densities of states for the V and VP structures shown in Figures 3 and 4 shows that the backfilling with 1-pentyne lowers the Tc conduction band energies relative to the Si conduction band edge. This is due to the larger dispersion of the molecular states resulting from the higher interface density, which will hinder exciton electron transfer. In Figures 3 and 4, it can also be seen that horizontally bonded Tc units have conduction band states clearly above the corresponding Si states, thus fostering the electron transfer across the interface. The electron transfer should also be fostered by incompletely bonded interfaces. In Figure 7, the densities of states of VP structures, where all, half, and none of the Tc molecules are covalently bonded to Si, are shown. It is seen that the Tc conduction

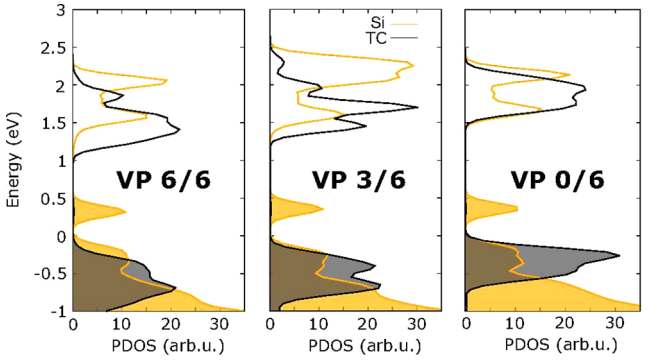

Figure 7. Density of states and band alignment for Tc overlayers covalently bonded to Si(111) calculated on the HSE06 level of theory. Here, VP structures are compared where all (6/6), half (3/6), and none (0/6) of the Tc molecules are covalently bonded to Si. Energies refer to the Si VBM. Black and orange denote Tc and Si-related states, respectively.

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states move up in energy upon reduction of interface bonds. The rareness of transfer events in conjunction with the numerical expense of the excited-state AIMD make it difficult to quantify the defect-induced increase of exciton transfer rates. However, the comparison of the trajectories calculated for completely and incompletely bonded interfaces suggests that nonbonded molecules speed up the exciton transfer by about 10−30 fs. This underlines the importance of the band level alignment at the interface for the optimization of the exciton transport.

CONCLUSIONS

In summary, the present calculations show that the covalent attachment of a seed layer of tetracene derivatives to the silicon surface does not per se enhance the exciton transfer properties of the interface. In fact, exciton transfer does not occur at perfectly bonded ideal interfaces. However, common db defects—which are by no means restricted to the Si(111) surface (see, e.g., ref 39)—dramatically improve the exciton transfer properties. On *n*-type Si, they give rise to interface states above the Tc valence band edge that vary in energy and shuttle the exciton holes into Si bulk. The exciton electron follows with a few fs delay. The latter process is supported by bonding the Tc molecules horizontally rather than vertically to the substrate as well as by incomplete interface bonding. The backfilling of the interface with 1-pentyne, on the other hand, actually hinders the electron transfer. Generally, our work underlines the importance of interface defects for the triplet exciton transfer from the sensitizing layer to the Si substrate. They may actually help to break the Shockley−Queisser limit. This is expected to be a common feature for covalently bonded sensitizing layers on Si substrates, which can be exploited to enhance the solar cell efficiency. Additionally, the present calculations show that the energy alignment at the interface—sensitive to the interface bonding as well as the functionalization of the molecular species—can be engineered to enhance the charge transfer.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) O'Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* **1991**, *353*, 737.

(2) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595−6663.

(3) Mula, G.; Manca, L.; Setzu, S.; Pezella, A. Photovoltaic properties of PSi impregnated with eumelanin. *Nanoscale Res. Lett.* **2012**, *7*, 377.

(4) Pinna, E.; Melis, C.; Antidormi, A.; Cardia, R.; Sechi, E.; Cappellini, G.; D'Ischia, M.; Colombo, L.; Mula, G. Deciphering Molecular Mechanisms of Interface Buildup and Stability in Porous Si/Eumelanin Hybrids. *International Journal of Molecular Sciences* **2017**, *18*, 1567.

(5) Antidormi, A.; Aprile, G.; Cappellini, G.; Cara, E.; Cardia, R.; Colombo, L.; Farris, R.; d'Ischia, M.; Mehrabanian, M.; Melis, C.; et al. Physical and Chemical Control of Interface Stability in Porous Si−Eumelanin Hybrids. *J. Phys. Chem. C* **2018**, *122*, 28405−28415.

(6) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510−519.

(7) Dexter, D. Two ideas on energy transfer phenomena: Ion-pair effects involving the OH stretching mode, and sensitization of photovoltaic cells. *J. Lumin.* **1979**, *18−19*, 779−784.

(8) Rao, A.; Friend, R. Harnessing singlet exciton fission to break the Shockley−Queisser limit. *Nat. Rev. Mater.* **2017**, *2*, 17063.

(9) Luther, J. M.; Johnson, J. C. An exciting boost for solar cells. *Nature* **2019**, *571*, 38.

(10) Einzinger, M.; Wu, T.; Kompalla, J.; Smith, H.; Perkinson, C.; Nienhaus, L.; Wieghold, S.; Congreve, D.; Kahn, A.; Bawendi, M.; et al. Sensitization of silicon by singlet exciton fission in tetracene. *Nature* **2019**, *571*, 90−94.

(11) Daiber, B.; Maiti, S.; Ferro, S. M.; Bodin, J.; van den Boom, A. F. J.; Luxembourg, S. L.; Kinge, S.; Pujari, S. P.; Zuilhof, H.; Siebbeles, L. D. A.; et al. Change in Tetracene Polymorphism Facilitates Triplet Transfer in Singlet Fission-Sensitized Silicon Solar Cells. *J. Phys. Chem. Lett.* **2020**, *11*, 8703−8709.

(12) MacQueen, R. W.; Liebhaber, M.; Niederhausen, J.; Mews, M.; Gersmann, C.; Jäckle, S.; Jäger, K.; Tayebjee, M. J. Y.; Schmidt, T. W.; Rech, B.; et al. Crystalline silicon solar cells with tetracene interlayers: the path to silicon-singlet fission heterojunction devices. *Mater. Horiz.* **2018**, *5*, 1065−1075.

(13) Piland, G. B.; Burdett, J. J.; Hung, T.-Y.; Chen, P.-H.; Lin, C.-F.; Chiu, T.-L.; Lee, J.-H.; Bardeen, C. J. Dynamics of molecular excitons near a semiconductor surface studied by fluorescence quenching of polycrystalline tetracene on silicon. *Chem. Phys. Lett.* **2014**, *601*, 33−38.

(14) van den Boom, A. F. J.; Ferro, S.; Gelvez-Rueda, M.; Zuilhof, H.; Ehrler, B. Toward Improving Triplet Energy Transfer from Tetracene to Silicon Using a Covalently Bound Tetracene Seed Layer. *J. Phys. Chem. Lett.* **2023**, *14*, 4454−4461.

(15) Molteni, E.; Cappellini, G.; Cardia, R.; Onida, G.; Mula, G. Eumelanin Adsorption on Silicon: Optical Properties of Si(001)-Adsorbed Eumelanin Tetrameric Protomolecules. *J. Phys. Chem. C* **2020**, *124*, 9376−9384.

(16) Seino, K.; Schmidt, W. G.; Bechstedt, F. Organic modification of surface electronic properties: A first-principles study of uracil on Si(001). *Phys. Rev. B* **2004**, *69*, No. 245309.

(17) Molteni, E.; Cappellini, G.; Onida, G.; Fratesi, G. Optical properties of organically functionalized silicon surfaces: Uracil-like nucleobases on Si(001). *Phys. Rev. B* **2017**, *95*, No. 075437.

(18) Molteni, E.; Fratesi, G.; Cappellini, G.; Onida, G. Optical Properties of Free and Si(001)-Adsorbed Pyrimidinic Nucleobases. *Phys. Status Solidi b* **2018**, *255*, No. 1700497.
(19) Dardenne, N.; Cardia, R.; Li, J.; Malloci, G.; Cappellini, G.; Blase, X.; Charlier, J.-C.; Rignanese, G.-M. Tuning Optical Properties of Dibenzochrysenes by Functionalization: A Many-Body Perturbation Theory Study. *J. Phys. Chem. C* **2017**, *121*, 24480−24488.
(20) Cardia, R.; Malloci, G.; Mattoni, A.; Cappellini, G. Effects of TIPS-Functionalization and Perhalogenation on the Electronic, Optical, and Transport Properties of Angular and Compact Dibenzochrysene. *J. Phys. Chem. A* **2014**, *118*, 5170−5177. PMID: 24946056.
(21) Sio, W. H.; Verdi, C.; Poncé, S.; Giustino, F. Ab initio theory of polarons: Formalism and applications. *Phys. Rev. B* **2019**, *99*, No. 235139.
(22) Sancho-García, J.; Pérez-Jiménez, A. A theoretical study of π-stacking tetracene derivatives as promising organic molecular semiconductors. *Chem. Phys. Lett.* **2010**, *499*, 146−151.
(23) Krenz, M.; Gerstmann, U.; Schmidt, W. G. Defect-Assisted Exciton Transfer across the Tetracene-Si(111):H Interface. *Phys. Rev. Lett.* **2024**, *132*, No. 076201.
(24) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **2009**, *21*, No. 395502.
(25) Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Nardelli, M. B.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys.: Condens. Matter* **2017**, *29*, 465901.
(26) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(27) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(28) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207−8215.
(29) Kaduk, B.; Kowalczyk, T.; Van Voorhis, T. Constrained density functional theory. *Chem. Rev.* **2012**, *112*, 321−370.
(30) Pankratov, O.; Scheffler, M. Localized excitons and breaking of chemical bonds at iii-v (110) surfaces. *Phys. Rev. Lett.* **1995**, *75*, 701.
(31) Artacho, E.; Rohlfing, M.; Côté, M.; Haynes, P. D.; Needs, R. J.; Molteni, C. Structural Relaxations in Electronically Excited Poly (p a r a-phenylene). *Phys. Rev. Lett.* **2004**, *93*, No. 116401.
(32) Tiago, M. L.; Ismail-Beigi, S.; Louie, S. G. Photoisomerization of azobenzene from first-principles constrained density-functional calculations. *J. Chem. Phys.* **2005**, *122*, No. 094311.
(33) Frigge, T.; Hafke, B.; Witte, T.; Krenzer, B.; Streubuhr, C.; Syed, A. S.; Trontl, V. M.; Avigo, I.; Zhou, P.; Ligges, M.; et al. Optically excited structural transition in atomic wires on surfaces at the quantum limit. *Nature* **2017**, *544*, 207.
(34) Nicholson, C. W.; Lücke, A.; Schmidt, W. G.; Puppin, M.; Rettig, L.; Ernstorfer, R.; Wolf, M. Beyond the molecular movie: Dynamics of bands and bonds during a photoinduced phase transition. *Science* **2018**, *362*, 821−825.
(35) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.* **1984**, *81*, 3684−3690.
(36) Moritz, D. C.; Ruiz Alvarado, I. A.; Zare Pour, M. A.; Paszuk, A.; Frieß, T.; Runge, E.; Hofmann, J. P.; Hannappel, T.; Schmidt, W. G.; Jaegermann, W. P-Terminated InP(001) Surfaces: Surface Band Bending and Reactivity to Water. *ACS Appl. Mater. Interfaces* **2022**, *14*, 47255−47261.
(37) Stutzmann, M.; Biegelsen, D. K. Microscopic nature of coordination defects in amorphous silicon. *Phys. Rev. B* **1989**, *40*, 9834−9840.
(38) Astakhov, O.; Carius, R.; Petrusenko, Y.; Borysenko, V.; Barankov, D.; Finger, F. The relationship between hydrogen and paramagnetic defects in thin film silicon irradiated with 2 MeV electrons. *J. Phys.: Condens. Matter* **2012**, *24*, No. 305801.
(39) Rohrmüller, M.; Schmidt, W. G.; Gerstmann, U. Electron paramagnetic resonance calculations for hydrogenated Si surfaces. *Phys. Rev. B* **2017**, *95*, No. 125310.
(40) George, B. M.; Behrends, J.; Schnegg, A.; Schulze, T. F.; Fehr, M.; Korte, L.; Rech, B.; Lips, K.; Rohrmüller, M.; Rauls, E.; et al. Atomic Structure of Interface States in Silicon Heterojunction Solar Cells. *Phys. Rev. Lett.* **2013**, *110*, No. 136803.
(41) Owman, F.; Mårtensson, P. STM study of structural defects on in situ prepared Si(111)1 × 1-H surfaces. *Surf. Sci.* **1995**, *324*, 211−225.
(42) Niederhausen, J.; MacQueen, R. W.; Lips, K.; Aldahhak, H.; Schmidt, W. G.; Gerstmann, U. Tetracene Ultrathin Film Growth on Hydrogen-Passivated Silicon. *Langmuir* **2020**, *36*, 9099−9113.
(43) Braun, C.; Neufeld, S.; Gerstmann, U.; Sanna, S.; Plaickner, J.; Speiser, E.; Esser, N.; Schmidt, W. G. Vibration-Driven Self-Doping of Dangling-Bond Wires on Si(553)-Au Surfaces. *Phys. Rev. Lett.* **2020**, *124*, No. 146802.

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