Supporting Information: Layer-Dependent Quasiparticle Electronic Structure of the P3HT:PCBM Interface from a First-Principles Substrate Screening GW Approach

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Table S1: Identification of P3HT and PCBM frontier orbitals in the $(P3HT)_2$:PCBM interface system, calculated at the Γ point. This is achieved via assignment of interface orbitals as either substrate or adsorbate orbitals when the expansion coefficient $|C_{i\mu}|^2$ is close to unity for a given interface orbital ϕ_μ.

	interface orbital	$\lvert C_{i\mu}\rvert^2$
$(P3HT)_2$ VBM	VBM	0.980
$(P3HT)_2$ CBM	CBM+3	0.978
PCBM HOMO	VBM-2	0.996
PCBM LUMO	CBM	0.979

Table S2: Identification of P3HT and PCBM frontier orbitals in the $(P3HT)_3$:PCBM interface system, calculated at the Γ point. This is achieved via assignment of interface orbitals as either substrate or adsorbate orbitals when the expansion coefficient $|C_{i\mu}|^2$ is close to unity for a given interface orbital ϕ_μ.

	interface orbital	$\lvert C_{i\mu}\rvert^2$
$(P3HT)_3$ VBM	VBM	0.957
$(P3HT)_3$ CBM	CBM+3	0.975
PCBM HOMO	VBM-3	0.997
PCBM LUMO	CBM	0.982

Table S3: Identification of P3HT and PCBM frontier orbitals in the $(P3HT)_4$:PCBM interface system, calculated at the Γ point. This is achieved via assignment of interface orbitals as either substrate or adsorbate orbitals when the expansion coefficient $|C_{i\mu}|^2$ is close to unity for a given interface orbital ϕ_μ.

	interface orbital	$\lvert C_{i\mu}\rvert^2$
$(P3HT)_4$ VBM	VBM	0.979
$(P3HT)_4$ CBM	CBM+3	0.900
PCBM HOMO	VBM-4	0.996
PCBM LUMO	CBM	0.977

Table S4: Identification of P3HT and PCBM frontier orbitals in the $(P3HT)_1$:PCBM:$(P3HT)_1$ interface system, calculated at the Γ point. This is achieved via assignment of interface orbitals as either substrate or adsorbate orbitals when the expansion coefficient $|C_{i\mu}|^2$ is close to unity for a given interface orbital ϕ_μ. The $(P3HT)_2$ is considered as the substrate for this interface.

	interface orbital	$\lvert C_{i\mu}\rvert^2$
$(P3HT)_2$ VBM	VBM	0.967
$(P3HT)_2$ CBM	CBM+3	0.971
PCBM HOMO	VBM-2	0.985
PCBM LUMO	CBM	0.956

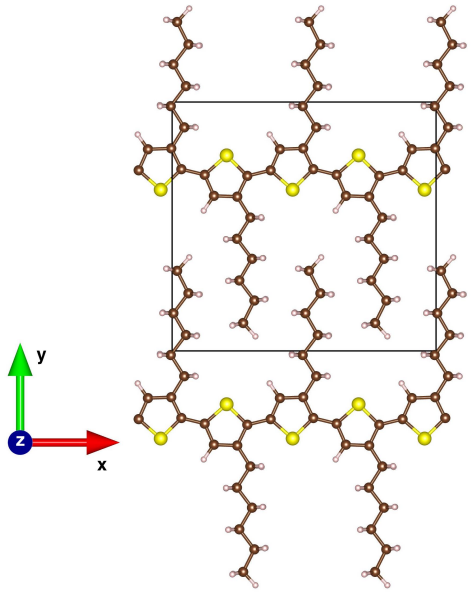

Figure S1: A top-view of the xy plane of the interface simulation cell, showing the 2D structure of the P3HT substrate. The PCBM molecule is not shown. We note that in the interface simulation cell, the x direction contains two unit cells of P3HT (four thiophene rings). More atoms than what are actually included in the simulation cell are shown, to better illustrate the nature of the periodicity of the P3HT substrate. Color code: C - brown, S - yellow, H - pink. This figure is rendered using VESTA.

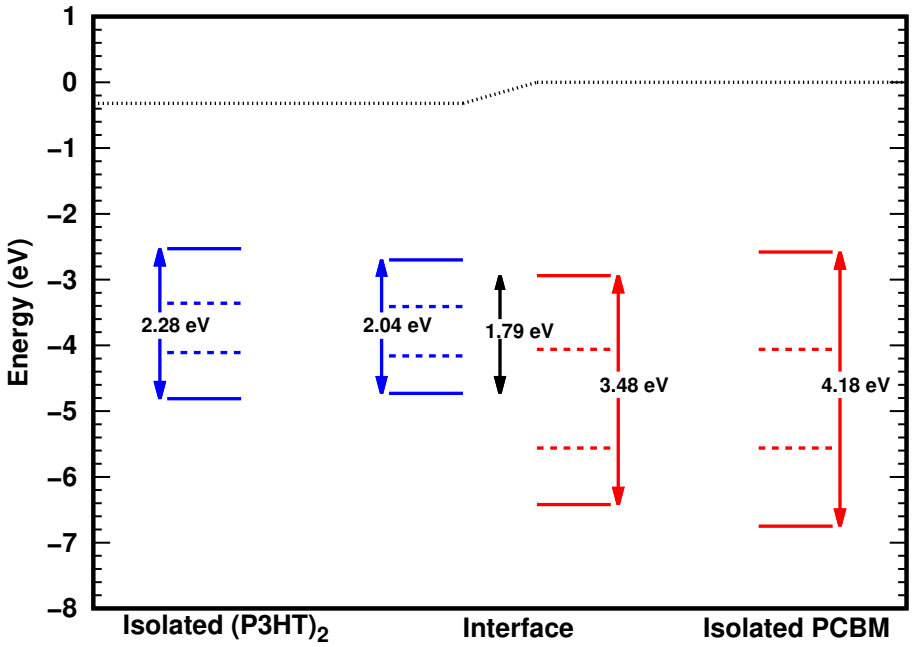

Figure S2: Energy level alignment at the Γ point for the $(P3HT)_2$:PCBM interface. Blue (red) lines indicate frontier energy levels of the isolated P3HT (PCBM) or the interface energy levels that are localized on P3HT (PCBM), with the latter discussed in Table S1. Blue arrows indicate the VBM-CBM band gaps of $(P3HT)_2$; red arrows indicate the HOMO-LUMO gaps of PCBM; and the black arrow indicates the fundamental gap of the interface system. Solid lines are from *GW* and dashed lines are from PBE. Vacuum levels on both sides of the interface are shown using dotted black lines. We align the isolated $(P3HT)_2$ or PCBM energy levels with their corresponding interface energy levels at the respective vacuum. The vacuum level difference across the interface is a reflection of the interface dipole. All energies are in eV.

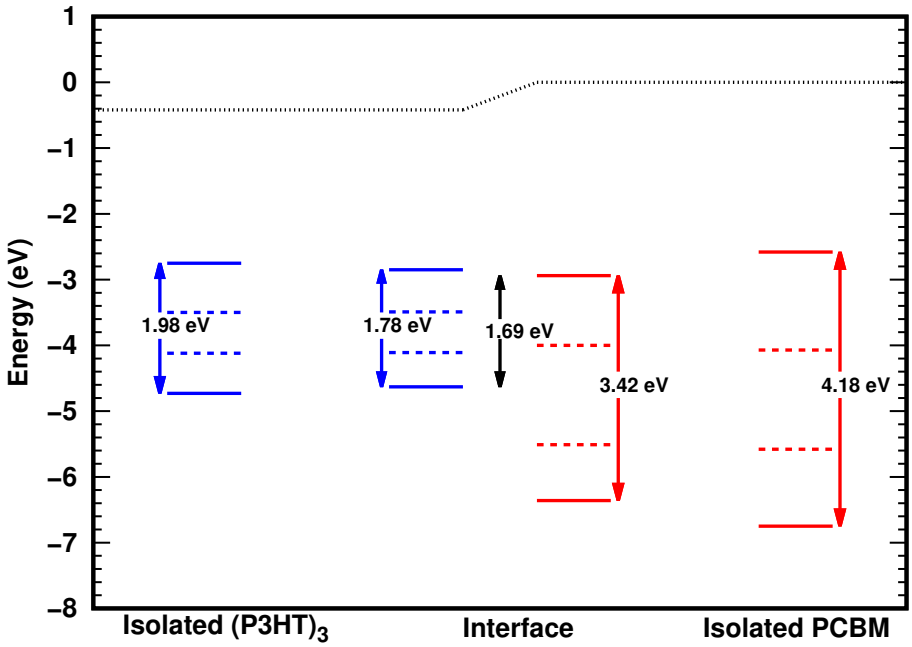

Figure S3: Energy level alignment at the Γ point for the $(P3HT)_3$:PCBM interface. Blue (red) lines indicate frontier energy levels of the isolated P3HT (PCBM) or the interface energy levels that are localized on P3HT (PCBM), with the latter discussed in Table S2. Blue arrows indicate the VBM-CBM band gaps of $(P3HT)_3$; red arrows indicate the HOMO-LUMO gaps of PCBM; and the black arrow indicates the fundamental gap of the interface system. Solid lines are from *GW* and dashed lines are from PBE. Vacuum levels on both sides of the interface are shown using dotted black lines. We align the isolated $(P3HT)_3$ or PCBM energy levels with their corresponding interface energy levels at the respective vacuum. The vacuum level difference across the interface is a reflection of the interface dipole. All energies are in eV.

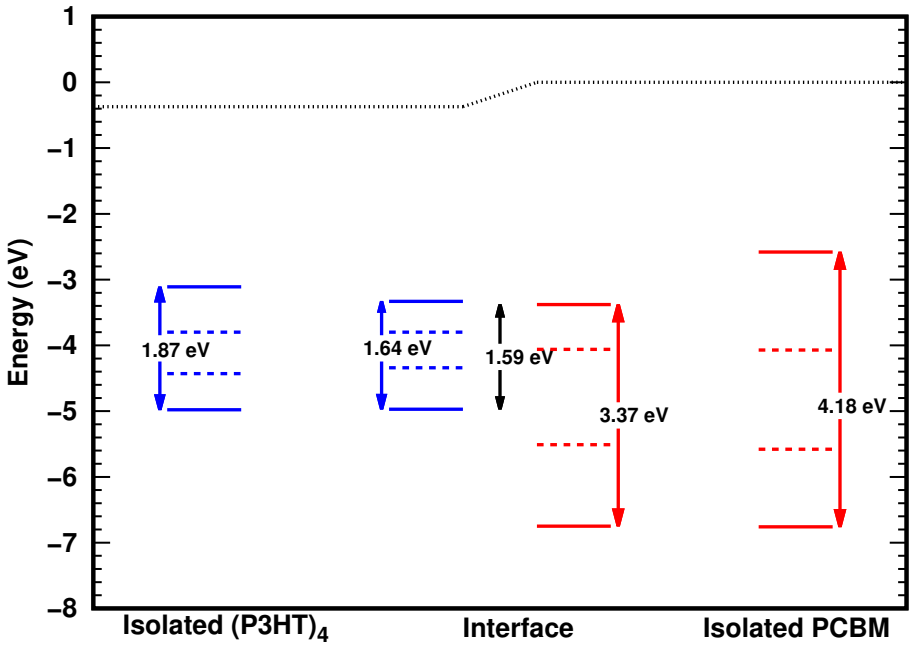

Figure S4: Energy level alignment at the Γ point for the $(P3HT)_4$:PCBM interface. Blue (red) lines indicate frontier energy levels of the isolated P3HT (PCBM) or the interface energy levels that are localized on P3HT (PCBM), with the latter discussed in Table S3. Blue arrows indicate the VBM-CBM band gaps of $(P3HT)_4$; red arrows indicate the HOMO-LUMO gaps of PCBM; and the black arrow indicates the fundamental gap of the interface system. Solid lines are from *GW* and dashed lines are from PBE. Vacuum levels on both sides of the interface are shown using dotted black lines. We align the isolated $(P3HT)_4$ or PCBM energy levels with their corresponding interface energy levels at the respective vacuum. The vacuum level difference across the interface is a reflection of the interface dipole. All energies are in eV.