

Charge Injection Rates in Hybrid Nanosilicon-Polythiophene Bulk Heterojunction Solar Cells: Supporting Information

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1 Influence of the exchange and correlation energy functional on the energy levels

A system consisting of a hydrogen-passivated nanocrystal of 17 Si atoms with a physisorbed thiophene (T) molecule [Fig. 1-a)] was used as a benchmark to evaluate the influence of the exchange and correlation energy functional on the alignment between the energy levels of the silicon nanocrystals and those of the mono/oligothiophenes. We performed both an LDA calculation using the method presented in the main article text and a calculation using the hybrid functional of Heyd, Scuseria and Ernzerhof (HSE) [1] (details of the HSE calculations are given below). The HSE functional accurately describes the silicon bandgap (1.31 eV, to compare with the experimental value of 1.12 eV [2]) and the thermodynamic properties of thiophene [1], and therefore can provide insight into the impact of the LDA gap underestimation in our calculations. The results of both calculations are shown in Fig. 1-b). The comparison shows that the exchange energy has a strong effect on the absolute positions of the electronic energy levels, in particular of the unfilled electron states, which are shifted up by about 1 eV. However, it has a weaker effect on the relative alignment between the NC and T levels (the T LUMO is 0.7 eV above the nanocrystal LUMO in LDA, and 0.5 eV in HSE).

Description of the HSE calculation The HSE calculations were carried out using the CPMD package [3]. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a cutoff energy of 100 Ry. Norm-conserving Troullier-Martins (TM) pseudopotentials were used. Those were optimised independently from the pseudopotentials used for the SIESTA calculations. Mulliken populations [5] $\{p_{i\alpha}\}$ for each level i and atom α were obtained by projection of the Kohn-Sham wavefunctions into atom-centered Slater orbitals. A localisation function was defined as

$$P_X(E) = \frac{\sum_{\{\alpha \in X\}} p_{i\alpha}}{\sum_{\alpha} p_{i\alpha}} \delta(E_i - E),$$

where X is either the NC or T, and δ is a Gaussian broadening function.

References

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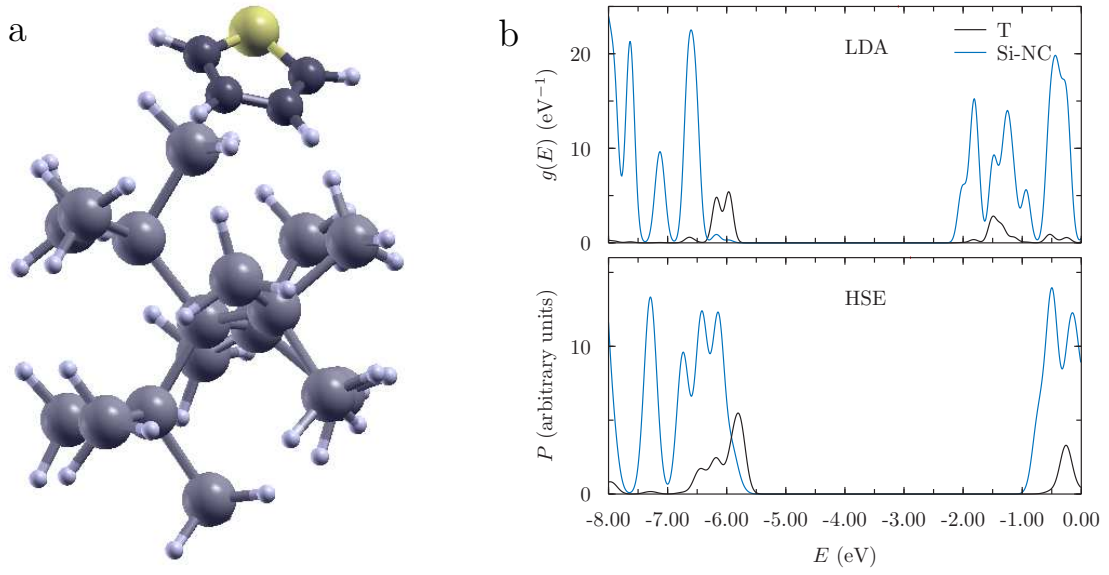


Figure 1: (a) Benchmark system, and (b) comparison of the energy levels and respective projected density of states (g) obtained with the LDA with the energy levels, and respective localisation, obtained with the HSE functional.