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Efficiency enhancement of small molecule organic solar cells using hexapropyltruxene as an interface layer[†]

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The quenching of excitons in organic solar cells can play a significant role in limiting their power conversion efficiency (PCE). In this article, we investigate the effect of a thin layer of hexapropyltruxene inserted at the interface between the electron donor boron subphthalocyanine chloride (SubPc) and its underlying hole contact in planar heterojunction solar cells. We find that a 3.8 nm hexapropyltruxene interlayer between the molybdenum oxide (MoO_x) hole contact and SubPc is sufficient to improve PCE in SubPc/C₆₀ fullerene solar cells from 2.6% to 3.0%, a ~20% performance improvement. While the absorption stays roughly the same, the comparison of external and internal quantum efficiencies reveals a significant increase in SubPc's contribution to the current for light with wavelengths between 520 and 600 nm. Microstructure and surface morphology assessed with *in situ* Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS) and Atomic Force Microscopy (AFM), are evaluated alongside *in situ* spectroscopic ellipsometry, and photoluminescence measurements. The microstructural investigations demonstrate changes to the surface and bulk of SubPc grown atop a hexapropyltruxene interlayer indicating that the latter acts as a template layer in a similar way as MoO_x . However, the improvement in PCE is found to be mainly via reduced exciton quenching at the MoO_x contact with the insertion of the hexapropyltruxene layer.

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1 Introduction

Recent performance development in organic solar cells (OSCs) shows remarkable progress, achieving power conversion efficiencies (PCE) of more than 13% in single-junction devices.^{1–5} Advantages such as their mechanical flexibility, portability, lightweight and potentially cost-efficient production on large area make OSCs promising alternative technology to silicon wafer-based solar cells,^{6,7} especially in the building-integrated PV market.^{7,8}

Interlayers between the photovoltaic active layer and the electrodes in OSC stacks have been studied meticulously as

OSCs have developed.^{13,14} They have been shown to improve the performance of the OSC devices^{15,16} as well as the stability.¹⁷ Molybdenum oxide (MoO_x) is a widely used interface modifier material in OSCs that facilitates an efficient hole contact between the anode and the photovoltaic active layer.^{4,5,18–21} However, it is reported that the ITO/ MoO_x anode quenches excitons generated in the active layer in OSCs if MoO_x and excitons can come into direct contact.^{22–24} This quenching effect can reduce the PCE of OSCs. By inserting an interlayer between the MoO_x layer and the photovoltaic active organic layer, the quenching effect can be effectively reduced by blocking excitons from reaching the MoO_x .²⁵ Several small organic molecules are shown to have this effect, e.g. rubrene, TAPC, and CBP.²² However, insertion of an additional interlayer has some side effects. A significant consequence of the insertion of interlayers is the change in morphology introduced by its template effect. Such a template layer thus can be used to influence the molecular ordering to increase the PCE of OSCs because the ordering of the molecules in the photovoltaic active layer of an OSC can have profound consequences on their performance,^{26–29} including improved absorption and more efficient exciton and charge carrier transport.^{26,30–32} Furthermore, the energy levels of the

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electrode materials can also be modified by the template layer,^{27,33,34} which is important for device performance.³³ Research on the template growth effect has been conducted with numerous organic small molecules, *e.g.* perylene-derivatives,^{35–37} acene,^{38,39} phenyl- and thiophene-based molecules,^{40–42} and graphene/graphene oxide.^{43–46} When being used, a template layer can take multiple functions in the solar cell stack, *e.g.* Duan *et al.*¹⁰ reported increased OSC efficiency using a template layer which also acted as the hole transporting layer (HTL). Thus, molecules that combine this exciton blocking effect together with templating properties for the photovoltaic active layer are of high interest for OSCs.

We applied hexapropyltruxene as an interlayer between MoO_x and the photovoltaic active layer in an OSC to examine its exciton blocking effect and molecular template growth effect. Hexapropyltruxene is an alkylated derivative of the parent truxene molecule, in which the six propyl groups are positioned at the three C sp³ sites of the compound.⁴⁷ The chemical structure of this molecule is shown in Fig. 1(a). Truxene derivatives have been applied as photosensitizers,⁴⁸ electron donor molecules,^{49–51} and hole transporting layers⁵² in OSCs due to their good thermal stability, optoelectronic properties and ease of being modified.^{52–54} Hexapropyltruxene has lower evaporation temperature in vacuum (around 100 °C at 5×10^{-7} mbar in our lab conditions) than rubrene, TAPC, and CBP (all above 150 °C), which will decrease the energy consumption in device fabrication if we replace the latter molecules with hexapropyltruxene as interlayer in OSCs. Besides, as hexapropyltruxene is nearly transparent in visible spectra (as seen in Fig. S1, ESI†), it will not absorb extra light to decrease the PCE of OSCs. Thus, hexapropyltruxene is a good replacement molecule to rubrene, TAPC, and CBP as interlayer

inside OSCs. *In situ* Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) and *in situ* spectroscopic ellipsometry were used hand-in-hand to investigate the change in the growth of a SubPc layer as an electron donor after inserting the hexapropyltruxene layer. AFM measurement was performed to investigate the surface topology change. Full planar heterojunction solar cell stacks using SubPc/C₆₀ as the photovoltaic active layer were fabricated to examine the performance change caused by insertion of the hexapropyltruxene layer. Steady-state and time-resolved photoluminescence spectroscopy (SSPL and TRPL) were carried out to evaluate the exciton quenching effect.

2 Experimental section

2.1 Sample fabrication

Si wafers (IDB Technologies Ltd, UK), Corning Eagle XG glass substrates and ITO-coated glass substrates (both from TFD Inc., USA), were purchased commercially. The hexapropyltruxene material was synthesised following Goubard *et al.*'s report.⁴⁷ The materials for single film ultraviolet-visible spectroscopy (UV-vis) measurement had a purity of more than 95%, determined by proton Nuclear Magnetic Resonance (¹H NMR). The material for cyclic voltammetry, multilayer thin film, and device fabrication was triple purified by thermal sublimation under vacuum. All organic materials (SubPc, C₆₀, BPhen, all by Luminescence Technology Corp., Taiwan) were purchased commercially in their sublimed versions (state purity >99%) and were used along with MoO_x (Luminescence Technology Corp., Taiwan) and Al (K. J. Lesker) as received.

We used three different vacuum chambers to fabricate our samples. They were: a multi-source bell-jar type "B30" vacuum

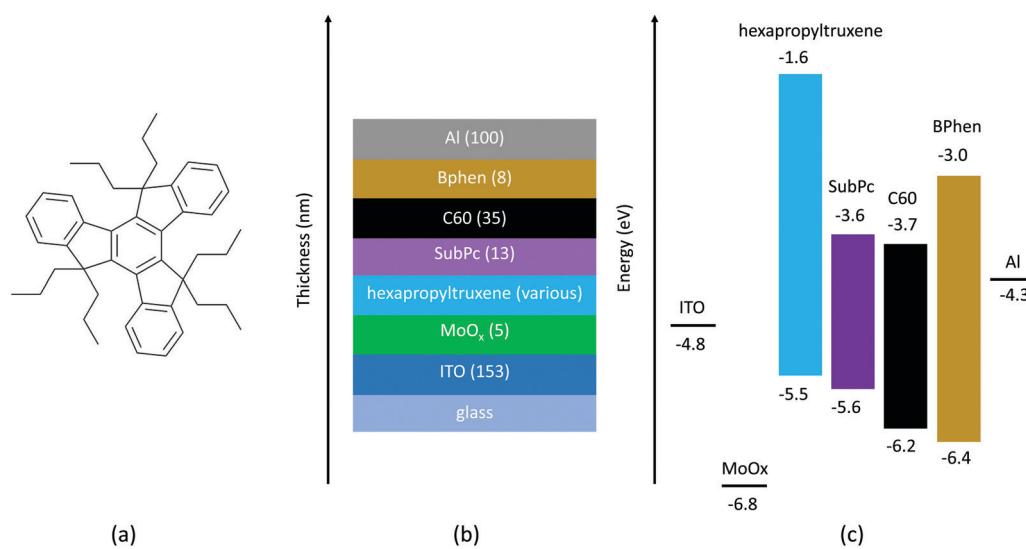


Fig. 1 Chemical structure of hexapropyltruxene, solar cell stack, and energy levels of the solar cells. (a) Chemical structure of hexapropyltruxene, (b) schematics of the investigated solar cell stacks with the individual layer thickness given in nanometres, (c) energy levels of materials used in this work. The indicated energy levels of SubPc (cyclic voltammetry, CV) and C₆₀ (ultraviolet photoelectron spectroscopy, UPS & inverse photoemission spectroscopy, IPES) are taken from literature.⁹ The energy levels of electrodes and MoO_x (UPS) are taken from literature.^{10,11} The energy levels of BPhen (UPS) are taken from literature.¹² The HOMO–LUMO levels of hexapropyltruxene are determined by cyclic voltammetry (see ESI, Fig. S2).

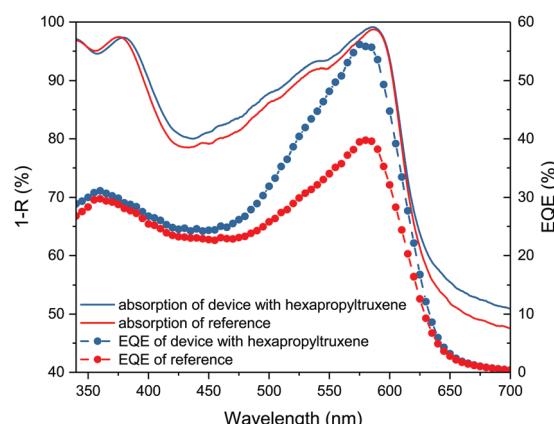


Fig. 4 External quantum efficiency (EQE) and UV-vis reflectance measurement results of reference devices without a hexapropyltruxene layer and the devices with 3.8 nm hexapropyltruxene between MoO_x and SubPc showing the best performance. R is the measured reflectance of the stack.

The improvement of photocurrent generation in the range from 520 nm to 600 nm is calculated to be *ca.* 40%. The estimated absorption ($1 - \text{reflectivity } R$) of the devices as measured in UV-vis reflectance measurement shows little change in the absorption behaviour of the active layer after the insertion of hexapropyltruxene. The small absorption difference is not sufficient to explain the high increase of EQE and photocurrent generation in the SubPc absorption region. Absorption simulations of solar cell stacks with 3.8 nm/without hexapropyltruxene were carried out and shown in ESI,[†] Fig. S9 and Table S1. This shows that after the insertion of hexapropyltruxene, the light absorption of the active layer slightly changes: SubPc absorbs less light while C₆₀ absorbs more. Calculations of the absorbed number of photons per unit area and time show that after the insertion of hexapropyltruxene, photon absorption of SubPc layer decreases from 36% of the total absorption of the stack to 32%, while C₆₀ absorption increases from 30% to 33%. It is due to changes in the cavity and the slight shift of the light interference before and after the insertion of hexapropyltruxene. However, the total absorption of the photovoltaic active layer stays similar after the insertion of the hexapropyltruxene layer according to the simulations. Thus, the change of the absorption behaviour in SubPc and C₆₀ layers can not account for the significant rise of EQE and photocurrent generation. We notice that this simulation result shows small difference comparing to the reflectivity measurement (estimated absorption ($1 - R$) calculated from reflectivity measurement shown in Fig. 4), which might be due to slightly different thicknesses in the measured films and simulation data. In any case, the small change in absorption behaviour of the active layer cannot explain the significant increase in EQE and photocurrent generation. Further simulations and UV-vis reflectance measurements confirm that the change in EQE is due to a corresponding change in IQE (see ESI,[†] Fig. S10).

In order to examine the effect that the hexapropyltruxene interlayer has on the growth of the subsequent SubPc, spectroscopic ellipsometry measurements of the device stack up to the

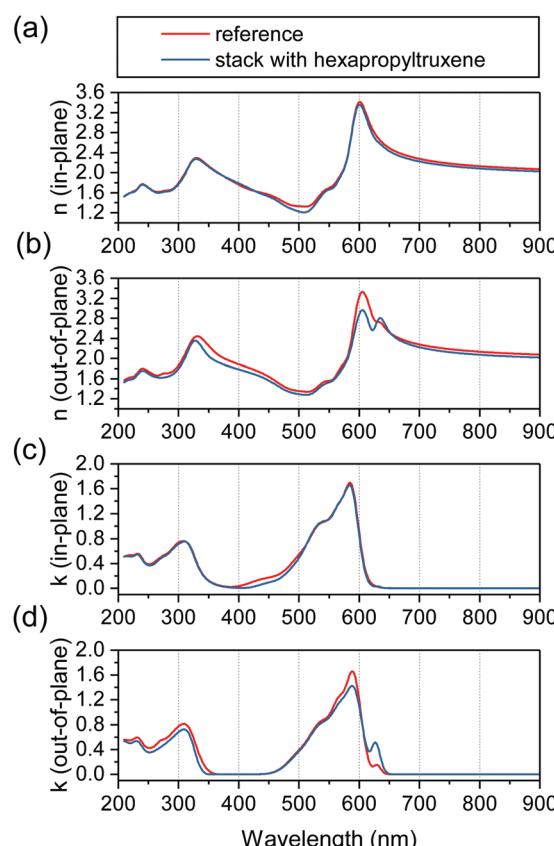


Fig. 5 In-plane and out-of-plane refractive overall indices n , k of the reference device stack (Si/MoO_x (5 nm)/SubPc (13 nm)/C₆₀ (35 nm)) and a device stack with hexapropyltruxene (Si/hexapropyltruxene (3.8 nm)/MoO_x (5 nm)/SubPc (13 nm)/C₆₀ (35 nm)). (a) In-plane refractive indices n , (b) out-of-plane refractive indices n , (c) in-plane refractive indices k , (d) out-of-plane refractive indices k .

C₆₀ layer with and without hexapropyltruxene were carried out *in situ* during the deposition of the SubPc layer. The SubPc layer was modelled as a uniaxial layer, *i.e.* with different in-plane and out-of-plane refractive indices. The derived refractive indices, shown in Fig. 5, reveal that the in-plane optical property of the stack stays similar after inserting the hexapropyltruxene interlayer, which is in line with the absorptance measurements.

The out-of-plane refractive indices, however, shows a notable difference between the stack with hexapropyltruxene and without. For the out-of-plane refractive index k , there is a peak at 630 nm rise after the insertion of the hexapropyltruxene layer. This increase seems to come at the cost of weakening the peak at 590 nm. Similarly, for the out-of-plane refractive index n , a trade-off in peak intensities between 605 and 633 nm is observed. These changes in absorption behaviour happen in the absorption wave range of SubPc. This indicates that the insertion of the hexapropyltruxene interlayer modifies the out-of-plane optical properties of SubPc in between MoO_x and SubPc layers, which might be a consequence of the change in the molecular ordering of SubPc.

In order to corroborate these results, *in situ* GIWAXS measurements were carried out using VC-C.⁵⁵ The results are shown

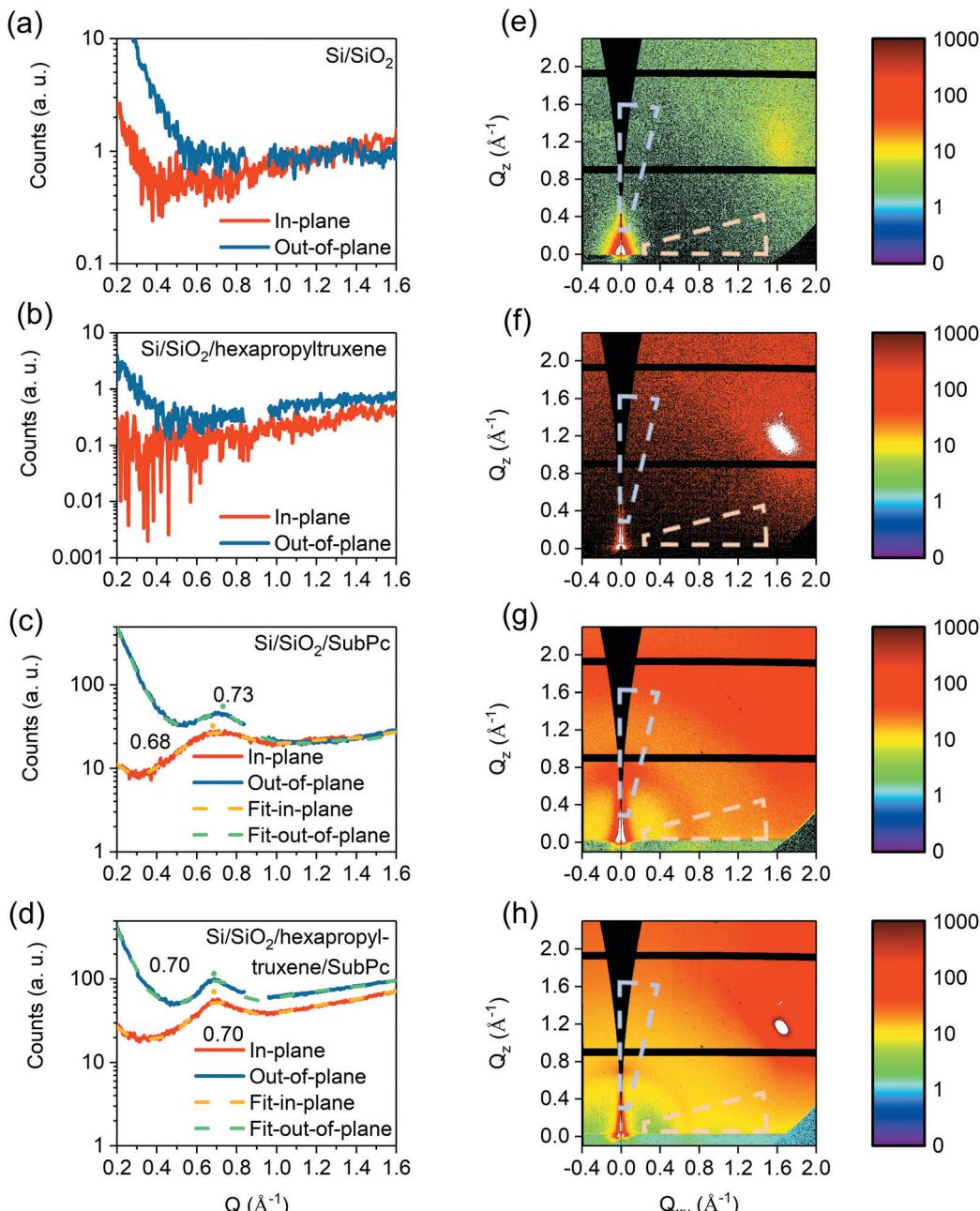


Fig. 6 Plots of the GIWAXS results obtained through measurements at Diamond Light Source's I07 beamline. In-plane and out-of-plane line cuts for (a) Si/SiO₂, (b) Si/SiO₂/hexapropyltruxene (3.8 nm), (c) Si/SiO₂/SubPc (13 nm), and (d) Si/SiO₂/hexapropyltruxene (3.8 nm)/SubPc (13 nm) multilayer films. GIWAXS images of (e) Si/SiO₂, (f) Si/SiO₂/hexapropyltruxene (3.8 nm), (g) Si/SiO₂/SubPc (13 nm), and (h) Si/SiO₂/hexapropyltruxene (3.8 nm)/SubPc (13 nm) multilayer films. Line-cut sections are indicated with dashed wedges in the figure.

In Fig. 6. The high intensity spot around $Q_{xy} = 1.6 \text{\AA}^{-1}$ originates from the Si/SiO₂ substrate. We find a SubPc peak at around 0.7\AA^{-1} . It could be either SubPc(110) peak (0.67\AA^{-1}) or SubPc(011) peak (0.74\AA^{-1}). In SubPc single crystal structure, (110) peak is systematically absent.⁶⁸ Thus, this broad peak could be SubPc(011) peak. Line-cut profiles (15°) in horizontal (in-plane) and perpendicular (out-of-plane) directions were analyzed. The fitting result is shown in Fig. 6 and Table 1. From the fitted full width at half maximum (FWHM) and peak

maximum heights, we can find that the SubPc peak becomes sharper in both in-plane and out-of-plane directions after the insertion of hexapropyltruxene. This indicates a larger crystalline size of SubPc after the insertion of the hexapropyltruxene interlayer. The peak center locations of the SubPc(011) plane shift to 0.70\AA^{-1} from 0.68\AA^{-1} (in-plane) and 0.73\AA^{-1} (out-of-plane) after the insertion of the hexapropyltruxene interlayer. This peak shift might be an indication of a change of crystal structure of SubPc after the insertion of hexapropyltruxene,

