

Electronic Supplementary Information (ESI)

Charge Mobility Anisotropy of Functionalized Pentacenes in Organic Field Effect Transistors Fabricated by Solution Processing

Jessica Wade,^a Florian Steiner,^a Dorota Niedzialek,^a David T. James,^a Youngsuk Jung,^b
Dong-Jin Yun,^b Donal D. C. Bradley,^a Jenny Nelson^a and Ji-Seon Kim^{a,*}

^a*Department of Physics and Centre for Plastic Electronics, Imperial College London, London
SW7 2AZ, United Kingdom*

^b*Center for Computational & Analytical Science, Samsung Advanced Institute of Technology
(SAIT), Kiehung, Kyungki-do, South Korea*

**E-mail: ji-seon.kim@imperial.ac.uk*

SI0. Highly Aligned Needles of TIPS-Pentacene

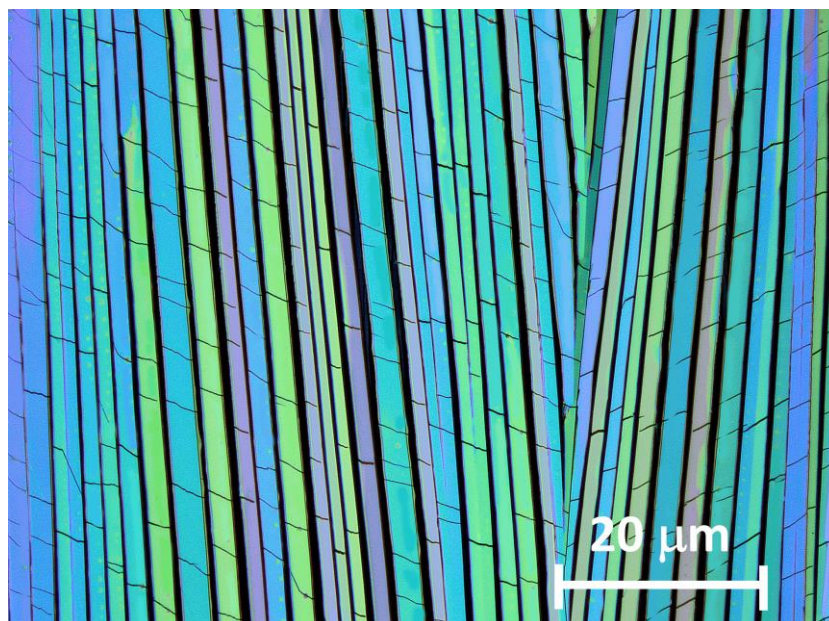


Figure SI0: Cross-polarised image of highly aligned needles of TIPS-pentacene zone-cast at substrate displacement-rates of $500\mu\text{ms}^{-1}$ on SiO_2 substrates, taken at a 20 x optical zoom.

SII. Charge Transport Simulations

Charge carrier mobilities of TIPS-pentacene and TES-pentacene are calculated by a multi-scale approach whereby charge transport parameters are derived from semi-empirical, quantum-chemical calculations and used to obtain angular dependent mobilities. While the crystal and molecular structure of TIPS-pentacene has been identified by Anthony et al.¹, the orientation of TES-pentacene molecules in the unit cell is to our knowledge unavailable in literature. A molecular mechanics based approach allowed us to determine the complete packing structure of TES-pentacene – the crystallographic information file (cif) is provided in the supporting information (SI2). We assume the configuration of TIPS- and TES-pentacene is similar to that demonstrated by Chen et al. using two-dimensional XRD, who found that TIPS-pentacene films orient parallel to its unit cell vectors (100) and (010) on amorphous carbon and silicon waver substrates (see Figure SI1).²

Hole transfer integrals J are quantified applying the projective method to a pair of neighbouring molecules.³ The electronic structure of the molecules is calculated with density functional theory using the B3LYP functional and a 6-31G* basis set. The calculated values of J are presented in Table SII. TIPS-pentacene has two high transfer integrals in the (100) and $(1\bar{1}0)$ direction, whereas TES-pentacene has only one, in the (100) direction. Troisi et al. found also high transfer integrals for TIPS-pentacene in those directions, only the absolute values are slightly different.⁴ The calculation of the orbital overlap is in agreement with experimental observations stating that TIPS-pentacene is organized in two-dimensional brick-wall structures, while TES-pentacene has a one-dimensional slipped-stack structure.⁵

The inner-sphere reorganization energy λ_m is calculated using the well-established approach presented in reference.⁶ The energies of the neutral and cation species constrained into the minimum-energy neutral or cation geometries are calculated using DFT, again with the hybrid functional B3LYP and the basis set 6-31G*. The internal reorganization energies λ_m for TIPS- and TES-pentacene are found

to be 138 meV and 142 meV. These are significantly higher than the internal reorganization energy of pentacene (95 meV).⁷ Since the outer-sphere reorganization energy is complicated to quantify, we assume a generic total reorganization energy λ of 0.5 eV for TIPS- and TES-pentacene which might be an overestimation. Smaller λ would result in higher mobilities which are expected to leave the angular distribution of mobilities unchanged. Since, despite the uncertainty in λ , the reorganisation energy will in all cases be larger than the charge transfer integrals J (see Table SII) we are in the non-adiabatic limit and can use non-adiabatic Marcus theory for the rate of charge transfer, k_{ij} :

$$k_{ij} = \frac{2\pi}{\hbar} \frac{|J_{ij}|^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right) \quad (1)$$

k_{ij} is the Marcus hopping rate which depends on the reorganization energy λ , the charge transfer integral J_{ij} and the difference in site energies ΔE_{ij} . k_B is the Boltzmann factor and T refers to the temperature. Several experimental studies indicate that charge transport in TIPS-pentacene is at the limit between polaron hopping and band-like transport. Sakanoue et al. reported on the band-like temperature dependence of the mobility in TIPS-pentacene field effect transistors.⁸ In contrast, Hall-Effect measurements indicate localized charge carriers and hopping transport.⁹ This ambiguous behaviour can be theoretically described in two ways. Troisi proposed a semi-classical model where charge carriers are localized by classic lattice vibrations although the temperature dependence of the mobility stays band like.¹⁰ Further, an approach based on Levich-Jortner formula¹¹ considers nuclear vibrations quantum mechanically.¹² This is necessary when the energy of the nuclear vibrations is significant which is often presumed for ultra-pure crystals.¹² Being crucial for the temperature dependence of the mobility, lattice vibrations do not play an important role for the angular dependency of the mobility at a fixed temperature.¹³ Moreover, Kwiatkowski et al. suggested that the spreading of the transfer integral and site energies is dominated by zero-point fluctuations even at room temperature.¹⁴ This implies that the fundamental transport mechanism stays unchanged considering the Levich-Jortner formula or the Marcus theory.¹⁰ Thus, Marcus theory is employed in the following calculation. The angular resolved mobilities are simulated using the master equation.

$$\mu = \frac{1}{F} \sum_{i \neq j} k_{ij} \vec{r}_{ji} \frac{\vec{F}}{F} \quad (2)$$

μ is the charge carrier mobility, F refers to the applied electric field and r_{ji} describes the vector between the lattice sites i and j . The mobility is calculated in the direction of the applied electric field F . Theoretically, all terms in equation (1) and (2) containing the electric field or the transfer integral are direction dependent. This includes ΔE_{ij} because it is dependent on the transferred charge and the electric field. This leads to the angular dependent hole mobilities presented in Figure 7.

The simulated hole mobilities of TIPS-pentacene are consistent with several previous studies.^{8,15,16} The only outliers are the recent record hole mobilities of TIPS-pentacene (4.6 cm²/Vs and 11 cm²/Vs) reported by Giri et al. and Diao et al.^{17,18} Here, the crystal structure had been changed by straining the TIPS-pentacene film and therefore does not refer to the same crystal structure as the calculations presented above. The discrepancy between modelled and experimental mobilities in TES-pentacene (see Figure 7) might be due to crystal defects being particularly disruptive for one-dimensional charge transport.

There are several reasons for the superior charge transport properties between TIPS-pentacene and TES-pentacene. TIPS-pentacene has two high transfer integrals while TES-pentacene is dominated by the charge transfer integral in the (100) direction. As a result TIPS-pentacene shows two-dimensional charge transport, whereas TES-pentacene is limited to one-dimensional transport. One-dimensional transport is obviously more affected by lattice defects as these irregularities represent a trap or barrier which cannot be surrounded by charge carriers. Therefore, the charge transport dimensionality can be considered of particular importance for the practical application in field effect transistors. Secondly, the absolute values of the charge transfer integrals are higher for TIPS- than for TES-pentacene.

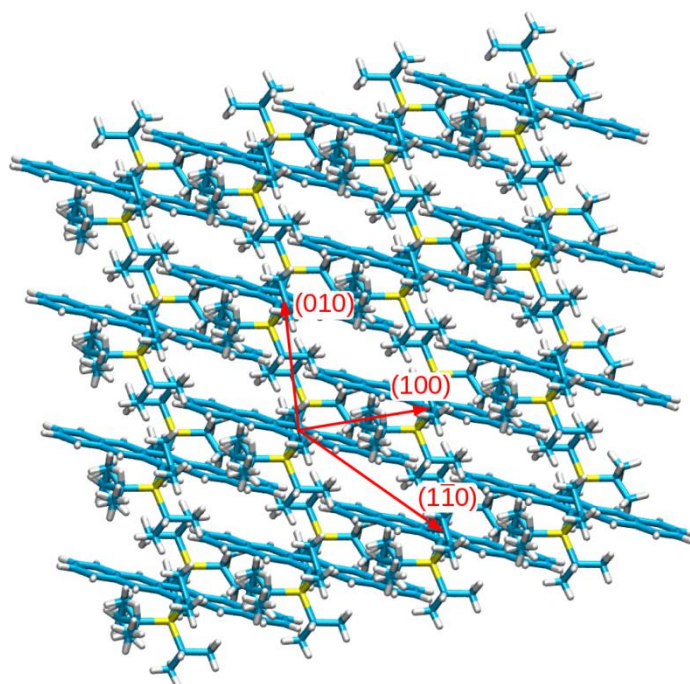


Figure S11. Molecular configuration of first layer of TIPS-pentacene on amorphous carbon and silicon wafer substrates.² This 2-dimensional structure is the basis of our theoretical study.

	TIPS-pentacene	TES-pentacene
Charge Transfer Integrals	(meV)	(meV)
(100)	53.7	93.58
(010)	0.21	1.08
(001)	1.17	4.26
(1 $\bar{1}$ 0)	64.8	6.94×10^{-4}
Inner-Sphere	(meV)	(meV)
Reorganisation Energy	138	142

Table S11. Calculated inner-sphere reorganisation energies and relevant charge transfer integrals between HOMO levels for TIPS- and TES-pentacene. TIPS-pentacene has two high transfer integrals indicating 2-dimensional transport while TES-pentacene has only one relatively high one which implies 1-dimensional transport. The inner-sphere reorganisation energies of TIPS- and TES-pentacene are found to be similar.

SI2 Extracting the Crystal Structure of TES Pentacene

Methods

Both TIPS and TES-pentacene structures have been published by Ostroverkhova et al. and can be obtained via Cambridge Crystallographic Data Centre (CCDC) deposited as under numbers 172476 and 1028702, respectively (Figure SI2.1).¹⁵

Structures Analysis

Although both TIPS- and TES-pentacenes have quite similar structures (Figure SI2.1), the subtle differences change the relative orientation of the molecules and the π -stacking distances between the pentacene cores, both parameters crucial for the charge transport abilities (Figure SI2.2). Only comparison of the unit cell parameters (table in Figure SI2.2) suggests differences in the 010 (b) and 001 (c) direction. The 001 direction is the lamellae direction, the least relevant for the charge transport due to a larger spacing between the pentacenes cores (~ 20 and ~ 15 Å for the TIPS and TES, respectively) and the presence of the bulky alkyl side chains. The smaller 001 distance in the TES-pentacene comes from the interdigitation of its (less bulky and more flexible than TIPS-chains; note that this flexibility is even increased by the Silicon bridging atom) side chains.

The “b” cell parameter of the TES structure is by ~ 2 Å higher suggesting that the molecules in that direction are further away from each other. Looking closer as the distances between the neighboring molecules (Table in the Figure SI2.2) revealed that the TIPS-pentacene structure has in both “a” and “b” directions smaller π -stacking distances (both plane-to-plane (3.1 – 3.5 Å) and ring-to-ring (7.7 – 7.8 Å), presented in Figure SI2.2A). Furthermore, the relative orientation of the pentacene cores in both a and b directions of the TIPS-pentacene molecules (Figure SI2.2A) is much more face-to-face than of the TES-pentacenes (Figure SI2.2B) what should enable a 2D (in a and b direction) charge transport in case of TIPS-pentacene structure. A confirmation of a favorable for a 2D charge transport molecules orientation in TIPS-pentacenes comes from X-ray analysis (provided by Dr Youngsuk Jung and Dr Dong-Jin Yun at Samsung Advanced Institute of Technology (SAIT)), where a peak

corresponding to the (120) plane suggest an order in the ab-direction, with the spacing between the {120} planes of ~ 3.8 Å, consistent with the π -stacking distances in the TIPS-pentacenes.

Experimental Details regarding the X-ray Data

X-ray diffraction (XRD) measurements were performed at the grazing incidence XRD setup at the PAL (Pohang Accelerator Laboratory, 10C1 beam line) synchrotron in South Korea.

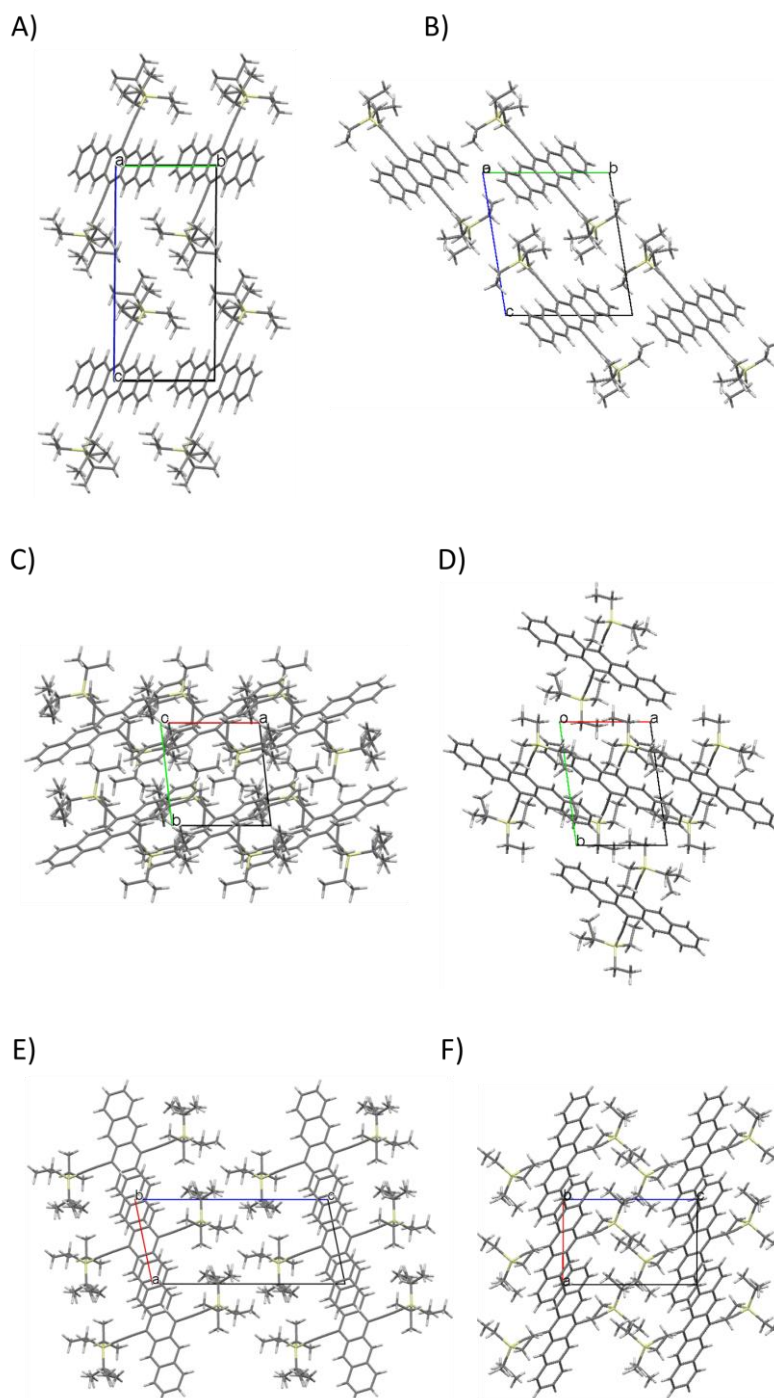
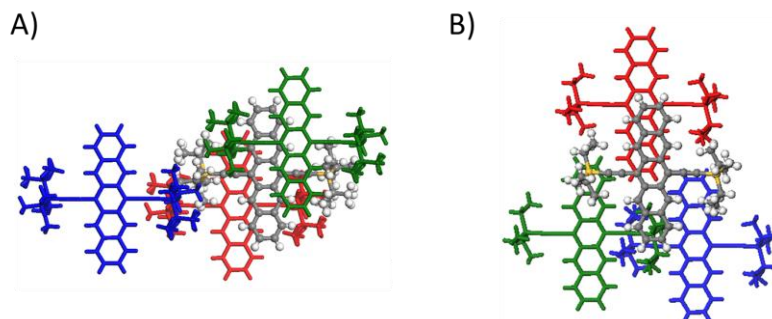


Figure SI2.1 Orthographic projections of the triclinic unit cells of the TIPS- (A, C & E) and TES-pentacenes (B, D & F) structures. The red, green and blue colours correspond to x, y and z directions, respectively.



Distance:	Plane-to-Plane			middleRing-to-middleRing		
Direction:	100 (Å)	010 (Å)	001 (Å)	100 (Å)	010 (Å)	001 (Å)
A) TIPS	3.5	3.1	7.4	7.7	7.8	17
B) TES	3.5	5.7	5.7	7.2	10	11

Figure SI2.1. The in-plane orientation of the TIPS- (A) and TES-pentacenes' closest neighbours in the x (red), y (green) and z (blue) directions. The table presents the distances between the middle rings in the corresponding directions ("middleRing-to-middleRing"), and the π -stacking distances of the neighbouring molecules ("Plane-to-Plane").

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