

A Cruciform 6,6'-Dipentacenyl: Synthesis, Solid-State Packing and Applications in Thin-Film Transistors

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Organic field-effect transistors (OFETs) have attracted great interest in recent years as a potential low-cost alternative to amorphous silicon-based transistors for many applications in electronics.^[1] Charge-carrier mobility in an OFET device is strongly related to the crystalline structure of the organic semiconductor, that is, the molecular packing mode is one of the critical factors governing the intermolecular electronic interaction and charge transport.^[2] It is known that charge-carrier transport depends on being able to hop between the molecules in the region, therefore, the molecular arrangement in a good semiconductor needs to provide sufficient overlap of the π orbitals of conjugated organic molecules to enable efficient charge migration between neighbouring molecules.^[2a]

Typical small-molecule-based organic semiconductors, such as oligoacenes and α -oligothiophenes, generally adopt a herringbone arrangement in the crystal structure, as shown in Figure 1a. In this packing motif, unfavourable π orbital repulsion and favourable CH- π electrostatic interactions between adjacent molecules drive the molecules to adopt an edge-to-face arrangement.^[1a,2d,3] However, this molecular packing mode also results in a reduction in the intermolecular electronic interaction.^[4,2d,5] Theoretical calculations suggested that face-to-face π stacking would increase the π orbital overlap and thus enhance the charge carrier mobility

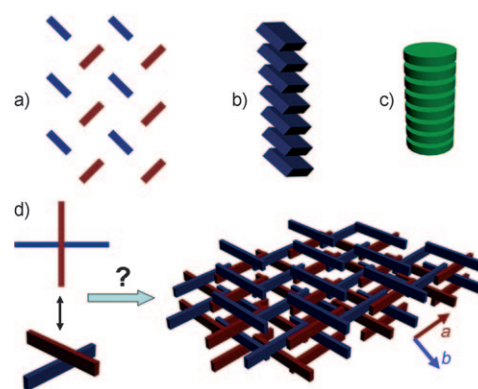


Figure 1. Illustration of different packing structures of organic semiconductors: a) a herringbone motif; b) tilted face-to-face motif; c) columnar π stacking; d) a possible two-dimensional π stacking from cruciform molecules.

by maximising electronic coupling between adjacent molecules.^[5] Therefore, in the last several years different groups have reported several strategies of molecular design to tune the packing mode from herringbone to a cofacial π -stacking motif, as illustrated in Figure 1b. In this motif, the molecules usually show a tilted (or offset) face-to-face arrangement in the crystalline form due to the molecular orbital repulsion. Anthony et al. reported that the introduction of bulky alkynyl groups into the *meso* positions of pentacene could disrupt aromatic edge-to-face interactions and tune the packing structure from a herringbone mode to a face-to-face π -stacking motif.^[6] Bao et al. found that tetracene with halogen atoms at the 5 and 11 positions adopted a face-to-face π -stacking motif with enhanced charge transport.^[7] Holmes et al. also reported that fused α -oligothiophenes with relatively high C/H ratios can adopt a face-to-face arrangement in crystals due to the diminished CH- π interactions.^[8] The chalcogen-chalcogen interaction was introduced by Kobayashi et al. to obtain face-to-face π -stacking of oligoacenes.^[9] Moreover, typical disc-like molecules, such as triphenylene and hexabenzocoronene derivatives, generally adopt a face-

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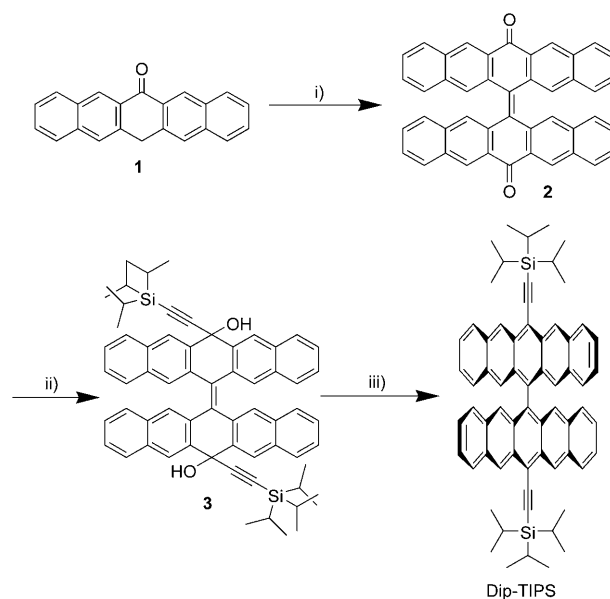
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to-face π -stacking mode to allow one-dimensional charge transport along the stacking axis (Figure 1c).^[10]

In these three packing modes, the charge transport is three-dimensional anisotropic and it was presumed that the highest mobility would be observed along the major π -stacking direction whereas the lowest mobility would be found along the directions in which the molecules are insulated from one another.^[8a,11] In fact, such anisotropic charge transport was found in single crystals of organic semiconductors, such as rubrene.^[12] When molecular semiconductors are used in macroscopic thin-film devices, the charge-carrier mobilities in devices are usually much lower than the intrinsic mobility due to the disordered arrangement of these molecules between the source and drain electrodes. In an ideal device, all the molecules between the electrodes should form a mono-domain arrangement with the major π -stacking axis parallel to the source-to-drain electrode direction. However, in realistic cases, the molecules usually exist in a polycrystalline form with different orientations in thin films. Therefore, control of molecular order over macroscopic dimensions is one of the challenges in obtaining optimised performance and thus different physical processing methods and alignment techniques have been used to achieve high molecular order in films.^[13] Herein, we propose an alternative approach to solve these problems by a new molecular design concept, that is, if the molecules allow π stacking along two directions in the solid state, then two-dimensional isotropic charge transport can probably be achieved and this arrangement can partially eliminate the effect of random molecular orientation in thin films and result in improved macroscopic charge carrier mobility. Our design uses cruciform molecules that contain two long π -conjugated rods covalently linked at their central sites with a twist angle of about 90° (Figure 1d). Assuming that each of these two rods can form face-to-face π -stacking with other rods in the neighbouring molecules, such cruciform molecules can hopefully self-organize into a two-dimensional π -stacking network sheet with two nearly perpendicular stacking directions, thus allowing possible two-dimensional isotropic charge transport. Of course, the actual packing motif is also determined by the space-filling, and a packing motif in which the top rod in one molecule stacks with the bottom rod of another molecule forming a continuous head-to-tail π -stacking is thought to be one of the most likely packing structures (Figure 1d).

To test our concept, we chose a 6,6'-linked pentacene dimer, 13,13'-bis(triisopropylsilyl)ethynyl)-6,6'-dipentacenyl (Dip-TIPS), as the model compound (Scheme 1). Triisopropylsilyl ethynyl (TIPS) groups are introduced at the 13,13' positions to solubilise and stabilise the reactive pentacene units. Dip-TIPS is expected to have a large twisting angle between the two pentacene units, similar to the structure of 9,10-linked anthracene oligomers.^[14] The two long pentacene units are thought to overlap with other pentacenes in neighbouring molecules, as seen in 6,13-bis(triisopropylsilyl)ethynyl)pentacene (P-TIPS).^[6b] Herein, we report the successful synthesis, optical and electrochemical properties and single-



Scheme 1. Synthesis of Dip-TIPS. i) Pyridine, piperidine, pyridine *N*-oxide, FeSO₄, 83%; ii) TIPSA, *n*BuLi, THF, 40%; iii) NaH₂PO₂, NaI, CH₃COOH, 74%.

crystal structure of this cruciform molecule, and also a preliminary test of our concept through thin-film FET fabrication and characterisation. Our research disclosed that Dip-TIPS exhibited the expected structure and two-directional π stacking in the crystal structure and high FET mobilities (up to 0.11 cm² V⁻¹ s⁻¹) were achieved based on vapour-deposited thin films.

The synthesis of Dip-TIPS is shown in Scheme 1. To the best of our knowledge, the 6,6'-linked pentacene dimer can not be synthesized by normal Pd-catalysed cross-coupling reactions, such as Suzuki, Stille and Kumada reactions. Therefore, a key step is the successful synthesis of intermediate 6,6'-bispentacenequinone **2** from pentacenyl monoketone **1**^[16] by using a pyridine *N*-oxide and FeSO₄-mediated homo-coupling reaction,^[15] which has been applied to the preparation of the bisanthracenequinone. Treatment of **2** with triisopropylsilyl ethynyl lithium afforded diol **3** in 40% yield, and subsequent deoxygenation and aromatization of **3** with sodium iodide and sodium hypophosphite^[17] gave the desired Dip-TIPS as a deep blue solid in 74% yield.

Dip-TIPS has good solubility in normal organic solvents, such as chloroform and THF. The UV/Vis absorption spectra recorded in chloroform and in thin film are shown in Figure 2. Dip-TIPS shows similar absorption bands to P-TIPS, with the absorption maximum (λ_{max} = 637 nm) slightly blueshifted with respect to the latter (λ_{max} = 642 nm),^[6] which indicates that there is only weak electronic coupling between the two pentacene units in Dip-TIPS. The absorption spectrum of Dip-TIPS in thin film displays an obvious bathochromic shift (11 nm), which suggests that the molecules adopt a π -aggregated form in the solid state. An air-saturated solution of Dip-TIPS in toluene is stable for weeks under ambient conditions. The photo-stability was also

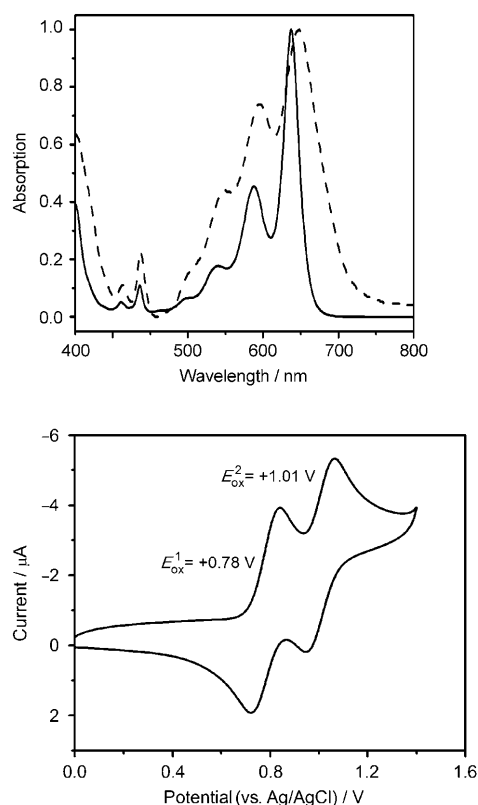


Figure 2. Top: Normalised UV/Vis absorption spectra of Dip-TIPS in CHCl_3 (—) and in thin films on quartz substrate (----). Bottom: Cyclic voltammogram of Dip-TIPS ($10^{-3} \text{ mol L}^{-1}$) in CH_2Cl_2 ; scan rate 50 mV s^{-1} , vs. Ag/AgCl.

tested and Dip-TIPS displayed a half-life ($t_{1/2}$) of around 350 min upon irradiation of white light (100 W), as monitored by UV/Vis spectroscopy, whereas P-TIPS had a $t_{1/2}$ of about 140 min under the same conditions (see the Supporting Information), which indicates that Dip-TIPS has better photo-stability than P-TIPS. The electrochemical properties of Dip-TIPS were investigated in CH_2Cl_2 by using cyclic voltammetry. As shown in Figure 2, two reversible oxidation waves were observed, with half-wave potentials at 0.78 V (E_{ox}^1) and 1.01 V (E_{ox}^2) versus AgCl/Ag. The HOMO energy level of Dip-TIPS is -5.13 eV , as calculated from the oxidation potential onset, which is close to that of P-TIPS (-5.11 eV),^[18] which implies that Dip-TIPS has a similar oxidation stability to P-TIPS. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of Dip-TIPS, which started to decompose at 405°C under nitrogen. Differential scanning calorimetry (DSC) measurement of Dip-TIPS did not show any transitions below 350°C . Compared with P-TIPS, which melts at 261°C ,^[19] its “dimer” form Dip-TIPS melted above the decomposition temperature, probably because of its strong intermolecular interactions. The good thermal stability of Dip-TIPS allowed us to prepare thin films by vacuum sublimation (350°C at 10^{-4} to 10^{-5} Pa) and to fabricate FET devices.

The solid-state packing structure of Dip-TIPS was studied by crystallographic analysis. A single crystal of Dip-TIPS

suitable for X-ray diffraction analysis was successfully grown by slow diffusion of methanol into a solution of Dip-TIPS in chloroform, and the single-crystal structure is shown in Figure 3.^[20] The two pentacene units display a large twist-

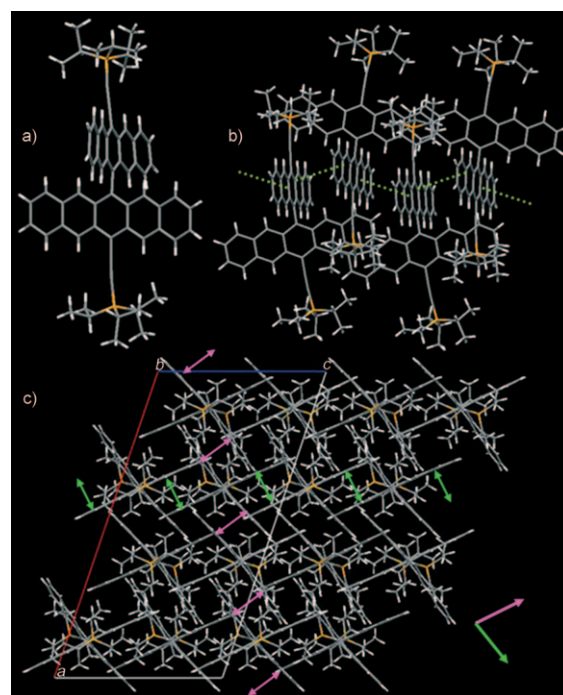


Figure 3. Single-crystal structure of Dip-TIPS: a) side view; b) illustration of the π -stacking motif along one axis; c) 3D packing structure viewed along the b axis.

ing angle of about 78° with one of the pentacene units being nearly planar and the other showing a small deviation from planarity, due to the strong steric congestion induced by the two pentacene fragments (Figure 3a). The dihedral angle and bond length of the central C–C bond ($1.51 \text{ \AA}$) in Dip-TIPS are similar to those observed for 9,9'-bianthracenyl.^[21] As expected, the two pentacene units can form slipped face-to-face π stacking with those of neighbouring molecules, with a typical π – π distance of around $3.4 \text{ \AA}$. Interestingly, the π stacking is in a head-to-tail and zig-zag motif, that is, along one π -stacking axis the upper pentacene fragment in one molecule stacks with the lower pentacene unit in the neighbouring molecule to form a continuous head-to-tail stacked chain (Figure 3b). This zig-zag-type π stacking is probably due to the space filling requirement especially when the bulky TIPS groups are presented. The π -stacking obviously runs in two directions in the single crystal, as can clearly be seen from the three-dimensional packing structure (Figure 3c). Two π -stacking axes with an intersection angle that is nearly same as the twisting angle between the pentacene units are observed. To the best of our knowledge, this is the first example of a semiconductor that can adopt a two-dimensional isotropic π -stacking. This unique packing structure and the strong intermolecular interactions indicate

that Dip-TIPS will probably show two-dimensional isotropic charge transport and has potential applications for thin-film FETs with less dependence on the molecular orientation.

The field-effect transistor devices were fabricated by vapour deposition of Dip-TIPS onto an octadecyltrichlorosilane (OTS)-modified SiO₂/Si substrate and standard characterisations were done under ambient conditions. As shown in Figure 4, all devices showed typical p-channel FET re-

value dropped. In addition, under fixed T_s , the mobilities increased as the film thickness was increased from 20 to 70 nm and a maximum FET mobility of 0.11 cm²V⁻¹s⁻¹ was obtained. The average mobility for our devices under optimised conditions is 0.08 cm²V⁻¹s⁻¹. This value is at least one order of magnitude larger than those reported for other cross-shaped or spiro-like semiconductors reported in the literature.^[22] To understand the dependence of FET mobility

on T_s , the morphology of the deposited thin films was examined by atomic force microscopy (AFM). It is clear that films at higher substrate temperature (e.g., 200 °C) showed large, highly interconnected, rod-like crystalline grains, probably due to the decreased nucleation density (Figure 4).^[23] At lower temperatures (e.g., 150 °C), Dip-TIPS forms polycrystalline films with granular crystallites with averaged sizes of about 100 nm; a lot of gaps exist between these crystallites. The increased crystal size and improved molecular order may contribute to the higher mobility observed at 200 °C compared with those deposited at 150 °C. In addition, the diminished gaps between crystallites may account for the decreased threshold voltage at higher T_s . It is also known that the mobility can be affected by traps from

either environmental or dielectric layers, so the film thickness is another important factor in determining the FET mobility.^[24] At smaller thicknesses, traps and hopping barriers can severely diminish the FET mobility, as observed here.

In summary, we report a novel molecular design concept for high-performance organic semiconductors by using cruciform molecules as potential 2D isotropic charge transporting materials. The designed cruciform, Dip-TIPS, exhibits the desired two-directional isotropic face-to-face π stacking, and FET mobilities of up to 0.11 cm²V⁻¹s⁻¹ were obtained based on vapour-deposited thin films. Although this value is not at the highest level of all types of organic semiconductors, it is the highest among all cross-shaped and spiro-like organic semiconductors. Dip-TIPS represents the first example of three-dimensional semiconductors with two isotropic π -stacking axes. Studies of the 3D anisotropic charge transport in the single crystals are ongoing in our groups. Further chemical modifications of bispentacene quinone **2** can also be performed to tune the molecular packing and material processibility of 6,6'-dipentaceny-based materials in the future.

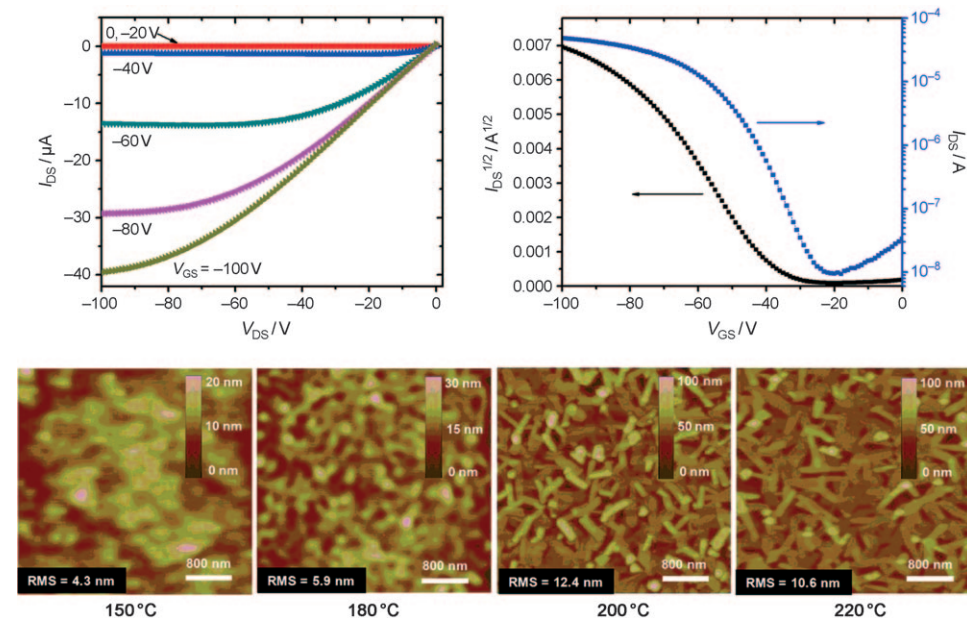


Figure 4. Top: Output and transfer characteristics of Dip-TIPS-based field-effect transistors, $T_s = 200$ °C. Bottom: AFM images of vapour-deposited thin films of Dip-TIPS at different substrate temperatures, T_s , during deposition. Scale bars are 800 nm.

sponses. The FET mobilities for Dip-TIPS vary significantly with the substrate temperature, T_s , and film thickness, as summarized in Table 1. The mobilities increased from $T_s = 150$ to 200 °C but at higher temperatures, such as 220 °C, the

Table 1. Summary of FET characteristics of vapour-deposited thin films of Dip-TIPS on OTS-treated Si/SiO₂ at different substrate temperatures (T_s) and film thickness.

T_s [°C]	Thickness ^[a] [nm]	Mobility ^[b] [cm ² V ⁻¹ s ⁻¹]	V_T ^[c] [V]	I_{on}/I_{off} ^[d]
150	70	9.7×10^{-3}	-51	$> 10^3$
180	70	0.067	-36	$> 10^3$
200	20	8.0×10^{-3}	-45	$> 10^3$
200	45	0.042	-46	$> 10^3$
200	70	0.11	-37	$> 10^3$
220	45	0.023	-52	$> 10^5$
220	70	0.05	-30	$> 10^3$

[a] The average active layer film thickness was measured in situ by using a quartz-crystal thickness monitor. [b] Mobility values were determined at the saturation regime ($V_{DS} = -90$ V). [c] Values of V_T were obtained from a plot of $I_{DS}^{1/2}$ vs. V_{GS} after extrapolation of the linear region to the V_{GS} axis. [d] Values of I_{on}/I_{off} were extracted from the transfer characteristics: I_{on} and I_{off} were defined as $V_{GS} = -100$ V, $V_{DS} = -90$ V and $V_{GS} = -20$ V, $V_{DS} = -90$ V, respectively.

Experimental Section

Full details of the syntheses and characterisations of the compounds studied herein are given in the Supporting Information.

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