

# Synthesis, properties, and device applications of functionalized acenes

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## ABSTRACT

Face-to-face interactions of aromatic molecules in the crystalline state may prove to be the most relevant for materials destined to be used in thin-film transistor or photovoltaic applications. We have designed functionalized pentacene derivatives that maximize these interactions in the solid state. We present here a description of a number of pi-stacked crystalline motifs that we can access, along with a discussion of the dependence of resistivity and band gap on the nature and amount of pi-overlap in the crystal.

**Keywords:** Pentacene, conductivity, organic crystals

## 1. Introduction

Pentacene and other organic semiconductors have recently been the subject of intense study for application in electronic devices. Recent reports of photovoltaic, transistor and lasing applications of these materials<sup>1</sup> have rekindled interest in this class of compounds the synthesis of which has been known since the 1940's.<sup>2</sup> Recurrent in all applications of these materials is the importance of solid-state order. While numerous fabrication techniques<sup>3</sup> have been applied to inducing  $\pi$ -stacked order in these flat aromatic molecules, little research into the effect of functionalization on either solid-state order or electronic properties of pentacenes has been reported. As part of our project involving crystal engineering the solid-state order of acenes, we have synthesized a series of functionalized materials that crystallize in three basic motifs.<sup>4</sup> We have already reported the remarkable increase in conductivity associated with one of these compounds (**1**), as a result of its increased  $\pi$ -overlap in the solid state.<sup>5</sup> We describe in this paper the resistivity measurements on crystals of pentacene derivatives whose solid-state order represent the remaining two motifs.

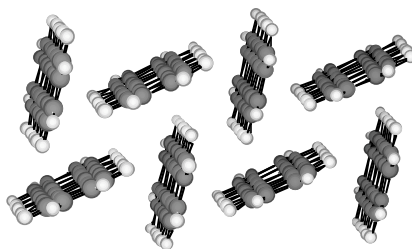


Figure 1. The native habit of pentacene, view down molecular long axis.

Unsubstituted pentacene crystallizes in a herringbone pattern, which is a result of maximization of both aromatic edge-to-face and face-to-face interactions. This arrangement of molecules leads to imperfect  $\pi$ -molecular orbital overlap.<sup>6</sup> Calculations suggest that this structural motif translates to a poor dispersion of the electronic bands in the molecule, implying that pentacene's transport properties are limited by its crystal packing.<sup>7</sup> Our approach to the solid-state engineering of pentacene involves disrupting the edge-to-face interactions by substitution at the perimeter (also known as the "peri" positions) of pentacene. By placing the main substituent remote from the pentacene backbone by use of a rigid (alkyne) spacer, face-to-face interactions are enhanced. The resulting pentacene derivatives are crystalline, with the solid-state arrangement of the individual molecules determined by both the size of the substituent and its location on the pentacene backbone.

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## 1.1. BACKGROUND

We have already reported the structure and properties of TIPS derivative **1**. This material packs in a two-dimensional array, and exhibits remarkably low resistivity ( $10^6$  ohm-cm along the pi-stacking axis) and band gap (0.6 eV along the pi-stacking axis) for a simple neutral organic solid (Figure 2).

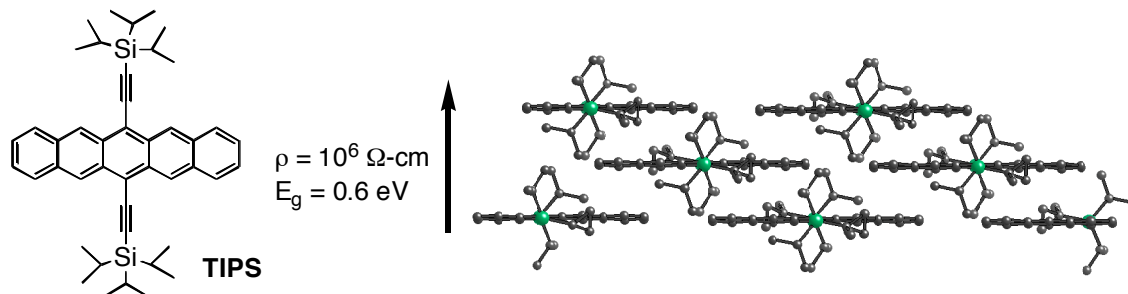
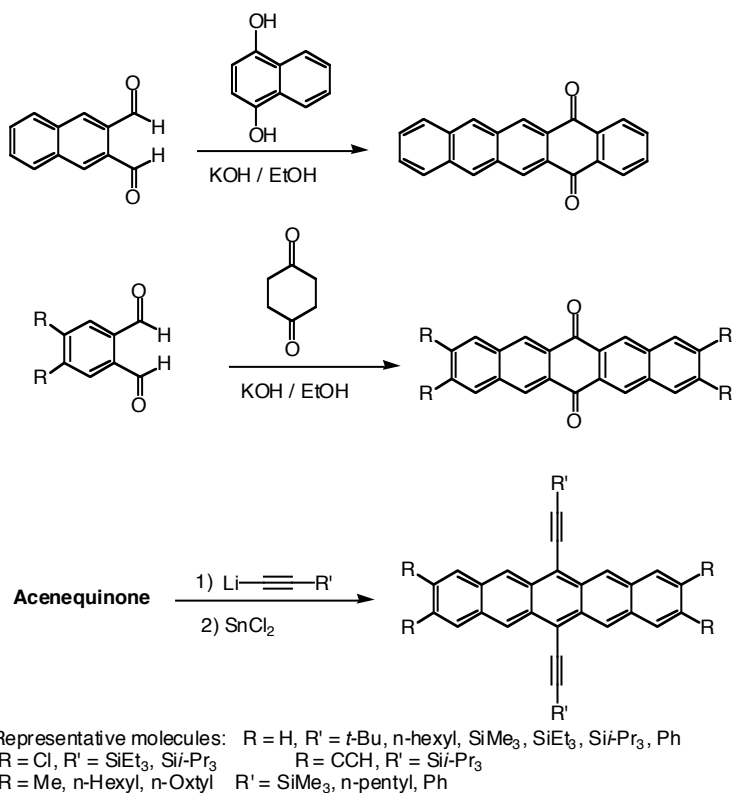


Figure 2. TIPS pentacene **1**. Structure, stacking and electronic properties.

The TIPS derivative is the only one prepared and analyzed so far that adopts this two-dimensional pi-stacking motif. Due to the large number of derivatives we have prepared that adopt different, one-dimensional molecular orderings in the solid-state, we performed a detailed investigation of the changes in electronic properties induced by changes in one-dimensional packing.

## 2. SYNTHESIS AND INTRINSIC MOLECULAR PROPERTIES



Scheme 1. Typical synthesis of pentacene derivatives.

The synthesis of alkyne-substituted pentacenes is extremely straightforward, involving only a single synthetic step from a pentacenequinone. While 6,13-pentacenequinone is commercially available, other pentacenequinones were synthesized by double or quadruple aldol condensations (Scheme 1). This method is extremely versatile, and allows for the installation of further functionalization on the pentacene backbone. A few of the derivatives we have prepared are also shown in Scheme 1.

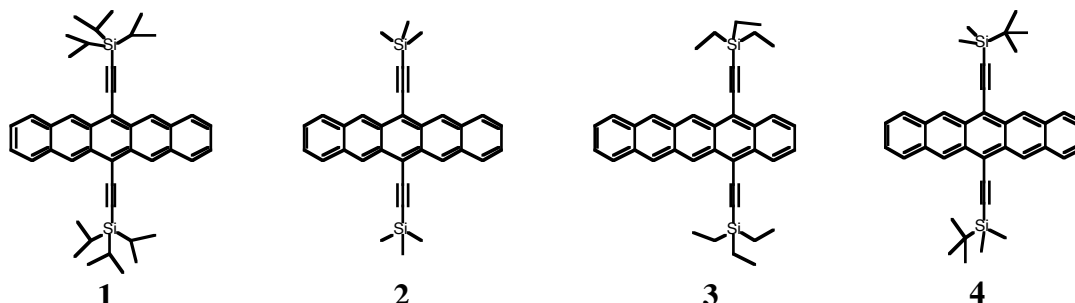


Figure 3. The acene derivatives considered in this report: Triisopropylsilylethynyl (TIPS) **1**, Trimethylsilylethynyl (TMS) **2**, Offset triethylsilylethynyl (TES) **3** and tert-butyl dimethylsilylethynyl (TBDMS) **4**.

The three packing motifs found in the crystalline ethynylated pentacenes are represented by the four molecules shown in Figure 3. The structure and electronic properties for **1** have already been reported in detail, and summarized in Section 1.1. While the crystal structures for **2** – **4** have been reported, their electronic properties have not, and will be discussed below.<sup>8</sup> The most notable feature of these materials is their solubility, which is typically > 100 mg / mL in chloroform at room temperature. These pentacene derivatives dissolve in a wide range of solvents, from ethyl acetate to chlorobenzene. Also notable is the oxidative stability of these compounds. Whereas solutions of unsubstituted pentacene (in trichlorobenzene) bleach within an hour when left exposed to air and laboratory lighting, solutions of the silylethynylated pentacenes maintain their deep blue color for weeks to months under the same conditions. This increased stability appears to carry over into evaporated films, which also maintain their color over extended periods of time. The increased stability is likely due to an increase in oxidation potential of the silylethynylated pentacenes. Unsubstituted pentacene has a quasi-reversible oxidation at 530 mV (vs. SCE). On average, the silylethynylated pentacenes undergo a highly reversible oxidation at 840 mV, an increase of 300 mV. While this increase certainly explains the molecules' resistance to oxidative decomposition, the functionalization itself shuts down the alternative decomposition pathway: Typically, acenes polymerize by an electrocyclic dimerization of the internal acene rings. The functional groups on the *peri* positions of these rings in our derivatives prevent this dimerization from occurring.

### 3. CRYSTAL PACKING AND ELECTRONIC PROPERTIES OF THE CRYSTALS

For the study of solid-state order and resistivity, crystals of these derivatives were grown by slow precipitation from organic solvents (typically hexanes) at –20 °C. All of the  $\pi$ -stacked materials presented here have an inter-pentacene distance of  $3.41 \pm 0.03$  Å, i.e. within Van der Waals radius. Resistivities along all crystallographic axes were measured by attaching leads with silver or carbon paint in an arrangement following the Montgomery method. The measurements were performed by heating the samples to 100 °C in a nitrogen-filled glove box, which lowered the resistance by 1 - 2 orders of magnitude, and then allowing the sample to cool slowly, taking rapid measurements at or near electrical equilibrium (i.e. without the RC time constant delay). A further advantage of this method is that by making an Arrhenius plot of the temperature dependence of resistivity one may derive the bandgap of the materials using the relation

$$\rho = \rho_0 \exp(-E_a/k_b T)$$

where  $\rho$  is resistivity,  $E_a$  is activation energy,  $k_b$  is the Boltzmann constant and  $T$  is absolute temperature. The logarithm of  $\rho$  is plotted against  $T^{-1}$  to find  $E_a$ , which is equal to half the band gap.

### 3.1 SLIP-STACKED PACKING

Pentacene derivatives substituted at the 6, 13-positions with relatively small substituents on the alkyne can be represented as shown in Figure 4 (left).

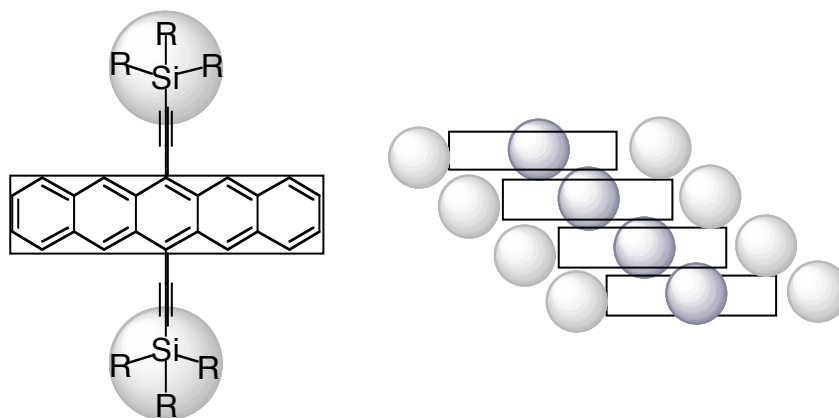


Figure 4. General scheme for slip-stack packing.

The solid-state order depicted in Figure 4 shows the view along the direction of the short-axis of the pentacenes, demonstrating the slip-stacking of the acenes, and the essential insulation of these stacks by the functional groups on adjacent acenes. While this packing motif represents the solid-state order with the least amount of  $\pi$ -overlap between pentacene units of the three we have discovered, it is by far the most common. A typical example of a material showing this sort of order is the trimethylsilyl derivative **2** (Figure 5).

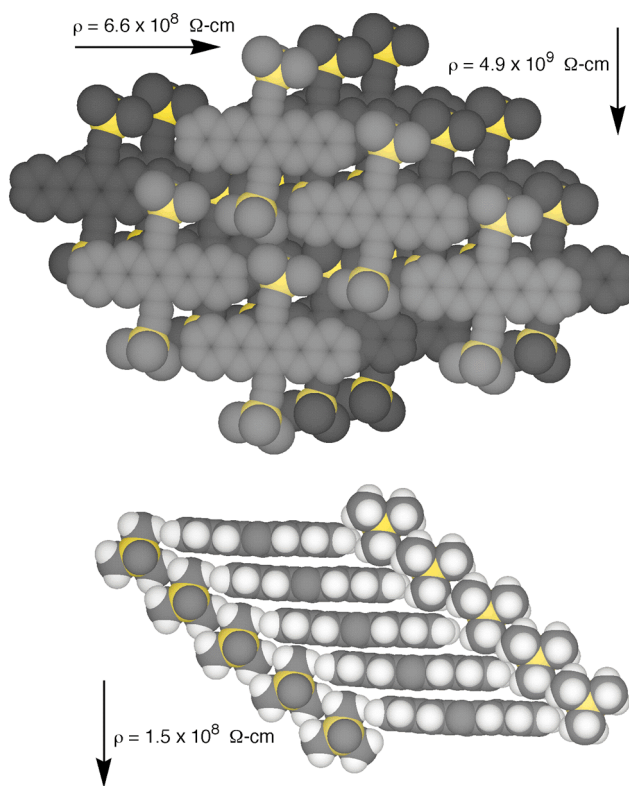


Figure 5. Solid-state order of trimethylsilyl derivative **2**. Top: View normal to  $\pi$ -face of pentacene. Bottom: View normal to the short axis of the pentacenes.

As expected, the resistivity in these crystalline materials is anisotropic, with resistivity varying by an order of magnitude along different crystalline axes. Charge carrier transport is expected to be most facile through the  $\pi$ -faces of the acenes, thus the resistivity down the slip-stack axis for pentacene derivative **2** is the lowest, at roughly  $2 \times 10^8$  ohm-cm. The resistivity across the  $\pi$ -surfaces (horizontally across Figure 5, center) is  $6 \times 10^8$  ohm-cm. Across the short axis of the pentacenes (and, consequently, in the direction of the highest density of saturated solubilizing groups) the resistivity is the highest, at  $5 \times 10^9$  ohm-cm. The importance of  $\pi$ -overlap is more clearly reflected in the band gaps derived from the temperature-dependent resistivity data. The band gap along the  $\pi$ -stacking axis is a remarkably small 0.86 eV, whereas the gaps across the long and short axes of the pentacene units are a surprisingly large 3.26 eV and 3.70 eV, respectively. Calculations of the band gap for this material at two different levels of theory are both in agreement with these values.<sup>9</sup>

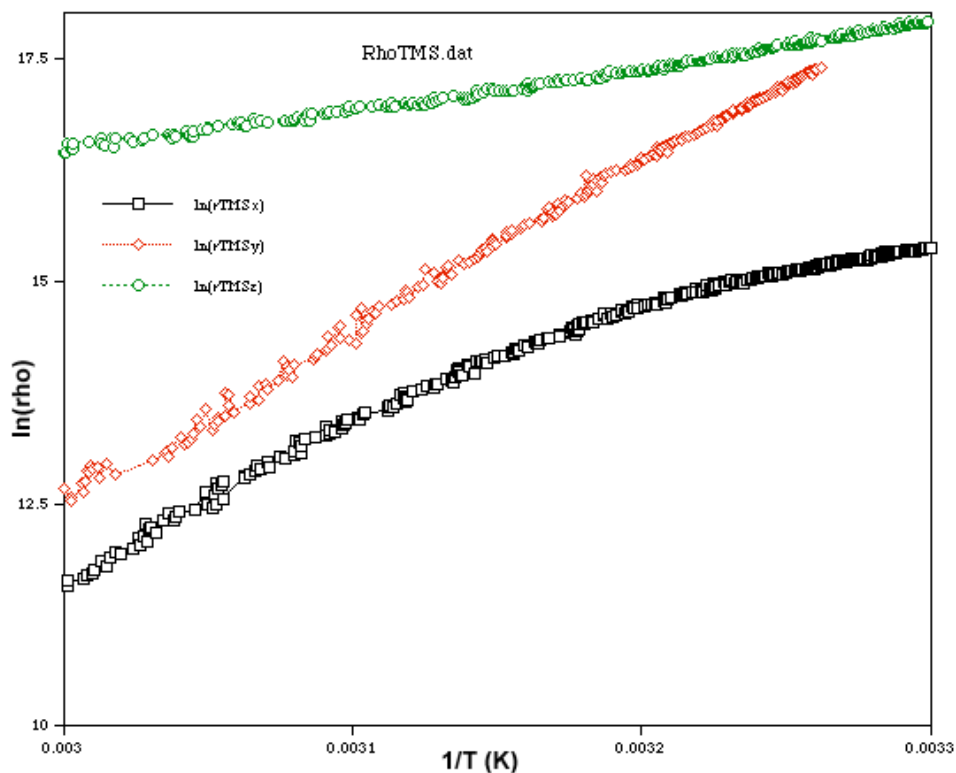


Figure 6.  $\ln(\rho)$  vs  $1/T$  plots for TMS compound **2** along all crystallographic axes. The a-axis (circles) = across the short axis of the  $\pi$ -faces of the acenes, b-axis (diamonds) =  $\pi$ -stacking axis and c-axis (squares) across the short axis of the  $\pi$ -faces of the acenes.

A number of different derivatives also pack in the same arrangement as compound **2**, with the only significant difference being the amount of “slip” in the slip stacks (e.g. the triethylsilyl derivative shown for comparison in Figure 7). Small changes in the size of the alkyne functional group only serve to slightly decrease the amount of  $\pi$ -surfaces that are overlapping. Not surprisingly, none of these other derivatives exhibited properties superior to the trimethylsilyl derivative **2**.

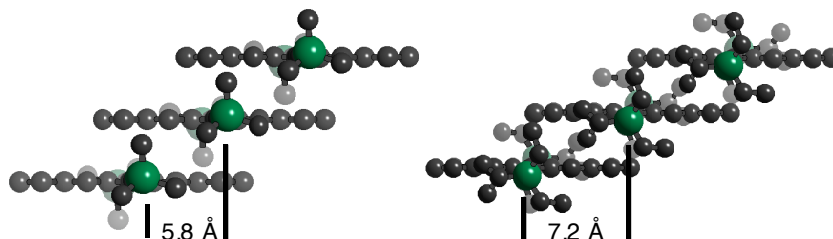


Figure 7. Triethylsilyl (right) versus trimethylsilyl (left) derivatives showing increase in “slip”, decrease in  $\pi$ -overlap.

### 3.2 COLUMNAR PACKING

One of the more obvious crystal motifs to explore involves moving from a “slip-stack” to a simple column. In essence, like straightening a deck of cards, the pentacene molecules stack vertically with very high overlap of the pi-faces. We have only observed this order in two derivatives: One crystallized in this motif fortuitously, the other was engineered. These two different molecules had quite different electronic properties.

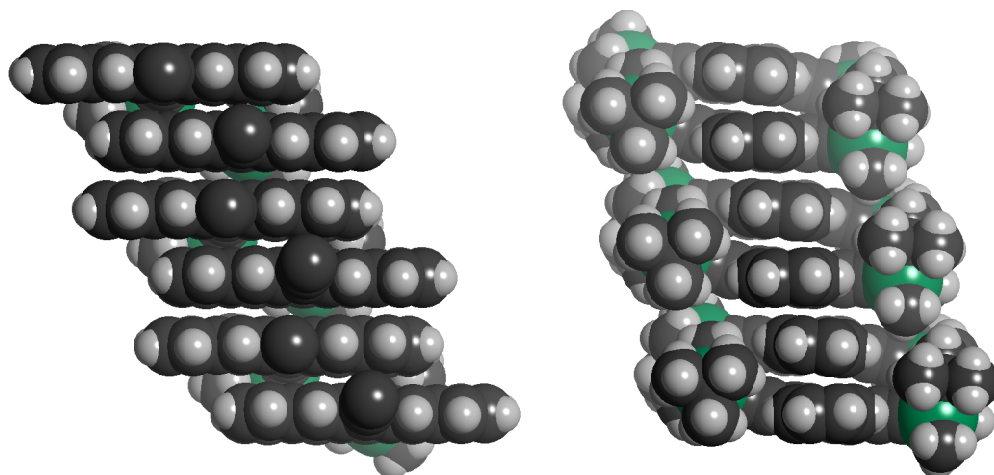


Figure 8. TBDMS ethynyl pentacene **4**. Left: View down acene short axis, showing columnar packing (functional groups removed for clarity). Right: View down acene long-axis.

The TBDMS derivative **4** is the only compound we have studied with non-symmetrical functional groups, and is the only one that crystallized in two different morphologies. The major polymorph is a slip-stacked array similar to that adopted by **2**. The minor polymorph adopts a novel, columnar stacking. In order to adopt this columnar arrangement, there is significant distortion of the alkynes, and the molecules in the column appear to be “paired” – that is, along the stacking axis there are different average distances between adjacent acenes (this can most easily be seen in the diagram on the right in Figure 8). The short stacking distance (e.g. the first two acenes in the stack on the right, Figure 8) is 3.38 Å, while the long stacking distance (e.g. the second and third acenes in the stack on the right, Figure 8) is 3.45 Å. The resistivity of this derivative could only be measured along the pi-stacking axis, due to the size of the crystals that could be grown of this derivative. The resistivity for this derivative is the lowest for any pentacene derivative measured except for **1**, at  $1.6 \times 10^7$  ohm-cm. However, the band gap proved to be a less impressive 1.9 eV.

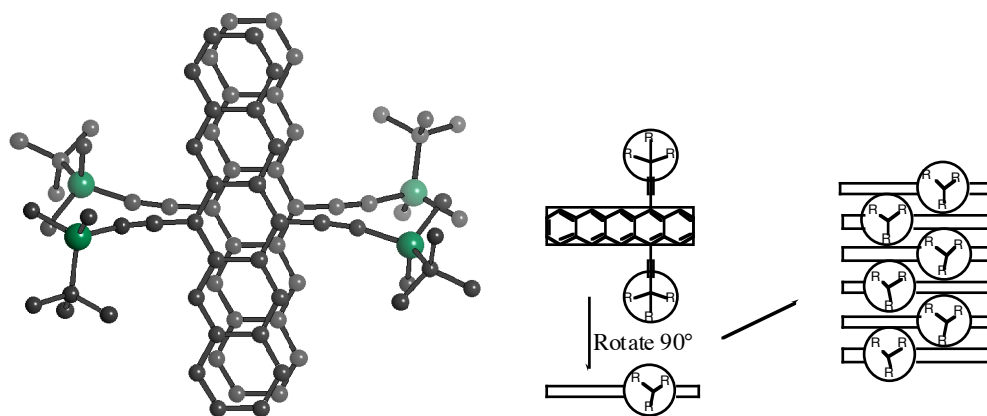


Figure 9. Derivative **4** inspired the preparation of the “offset” derivative **3** (represented middle) with expected columnar order (right).

Because the columnar morphology is the minor polymorph of crystals of compound **4**, detailed study of the electronic properties were severely limited by the available quantities of the crystals. We thus sought to engineer a new derivative that would yield more of the columnar motif. Careful consideration of derivative **4** led us to a scheme to engineer a columnar order in pentacenes. As shown on the left in Figure 9, the bend in the acetylene units is quite severe, but would be eliminated were the alkyne functional groups shifted to adjacent rings. As shown in the middle of this Figure, the molecules would be able to adopt a columnar arrangement without necessitating distortion of the alkynes, and thus this motif might constitute the major morphology of the material. In fact we discovered that careful control of size of the alkyne substituents is crucial to attaining this crystalline order. If the substituent is too large, the molecules will still “dimerize”, but these molecule pairs then arrange in a herringbone motif similar to unsubstituted pentacene. If the alkyne substituent group is too small, the materials are not oxidatively stable and only endoperoxide materials can be isolated. The triethylsilyl group is the only one that allows the formation of a stable material with the desired columnar order (Figure 10).

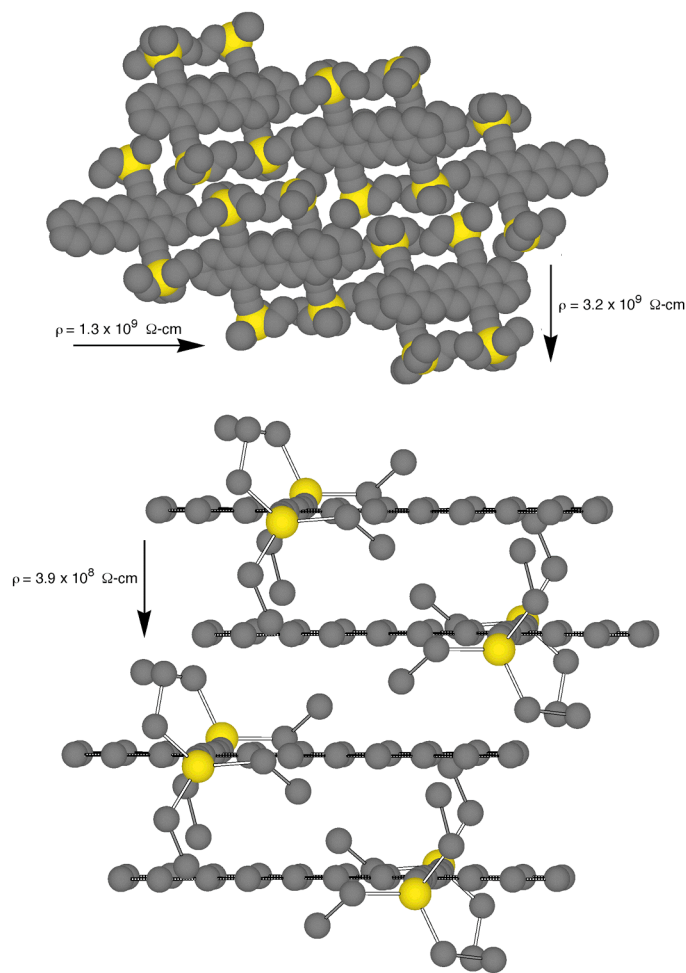


Figure 10. Solid-state order of derivative **3**. Top: View normal to the  $\pi$ -faces. Bottom: View normal to the short axis of the pentacene, showing columnar order.

As expected, resistivity is significantly lower down the  $\pi$ -stacking axis than along the other two axes in the crystal. Even though there is significantly more  $\pi$ -overlap in this system, the resistivity down the columns ( $4 \times 10^8$  ohm-cm) is not significantly better than for the slip-stacked derivatives, and is a full order of magnitude higher than similar columnar-stacked **4**. The resistivity across the remaining axes ( $1 \times 10^9$  ohm-cm and  $3 \times 10^9$  ohm-cm, respectively) are actually marginally *worse* than in the slip-stacked case. The band gaps emphasize this trend: Down

the  $\pi$ -stacking axis, the band gap is a significant 1.4 eV. Across the less conducting  $\pi$ -surfaces (Figure 10, top, horizontal and vertical), the band gaps are 1.75 and 2.89 eV.

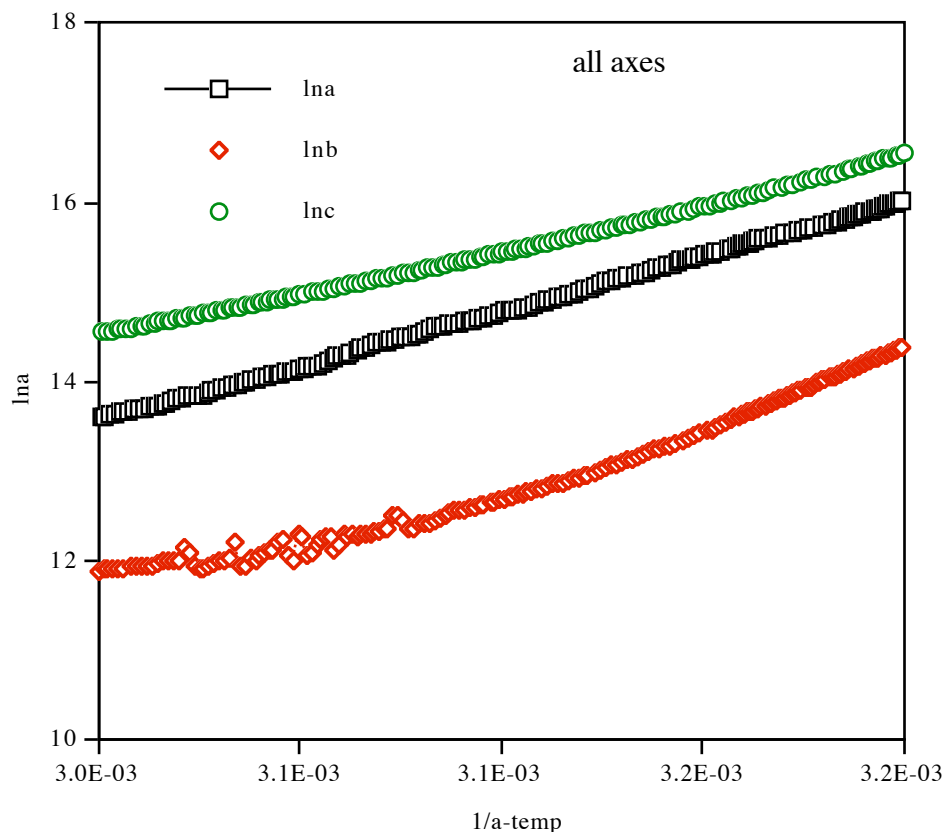


Figure 11.  $\ln(\rho)$  vs.  $1/T$  plots for offset TES compound **3** along all crystallographic axes. The a-axis (squares) = across pi-stacks, b-axis (diamonds) = pi-stacking axis and c-axis (circles) = along the short axis of the acenes.

It is interesting to note that while the resistivity along the pi-stacking axis for **4** is lower than along the same axis for **3**, the conductivity band gap along this axis is significantly lower for **3** than for **4**. This phenomenon is likely due to the lower symmetry in the crystal, caused by the alternate spacings between pi-faces noted for derivative **4**.

#### 4. COMPARISON OF RESISTIVITIES RELATED TO SOLID-STATE ORDER: CONCLUSIONS

The two new derivatives described in this report all have resistivities several orders of magnitude lower than that reported for unsubstituted pentacene. By eliminating edge-to-face interactions in the crystal, the solid-state order is dominated by  $\pi$ -stacking, leading to better orbital overlap and thus stronger  $\pi$ -interaction throughout the solid. Neither of the two pi-face arrangements described here possesses the remarkably low resistivities of the previously reported triisopropylsilyl derivative **1**.<sup>5</sup> While both of these packing motifs exhibit significant  $\pi$ -stacking in the solid state, we were surprised to discover that the amount of  $\pi$ -stacking does not directly correlate to resistivity. Even though the  $\pi$ -overlap in columnar derivative **3**, for example, is significantly better than in slip-stacked **2**, the resistivities are only marginally better, and the band-gap measured along the  $\pi$ -stacking axis is *significantly larger* for this derivative. Band structure calculations for derivatives **1** – **3** support these results. In accordance with prior theoretical treatment,<sup>10</sup> it appears that the precise relationship between the acenes, rather than simply the amount of pi-overlap, is the determining factor for electrical properties.

## ACKNOWLEDGMENTS

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