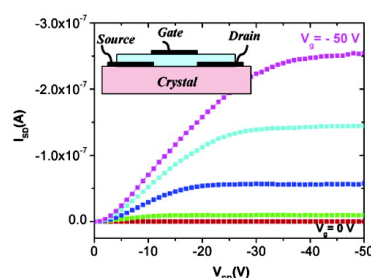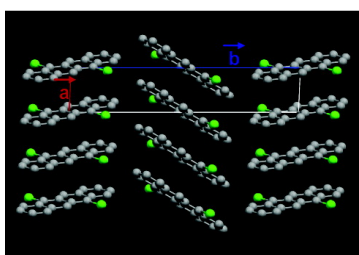Communication

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Synthesis, Crystal Structure, and Transistor Performance of Tetracene Derivatives

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The performance of organic thin-film transistors (OTFTs) is affected by various factors, including molecular properties such as effective conjugation length and redox potentials, solid-state packing, thin-film morphology, and material stability.[1] Despite great progress in understanding many of these factors, fundamental aspects of carrier transport, especially the role of solid-state packing, still remain unclear. Quantum mechanical calculations have predicted that high mobility in OTFTs can be obtained when conjugated molecules have strong interactions with neighboring molecules to maximize the overlap of π molecular orbitals.[2] In addition, Curtis and co-workers have recently made a structural analysis on some common organic semiconductors, discussing the correlation between solid-state packing and transport.[3a] Theoretically speaking, a cofacial π stacking structure is expected to provide more efficient orbital overlap and thereby facilitate carrier transport. So far, however, most of the organic semiconductors that have shown high mobility and high on/off ratio in polycrystalline thin-film devices have a herringbone structure which reduces the overlap.[4] In fact, there has been little experimental evidence that π stacked materials have higher mobility. This may be because of the scarcity of π stacked materials[3,5,6] and the difficulty in examining transport properties at molecular levels. The mobility in polycrystalline films was not intrinsic but was dependent more on the purity of the conjugated molecules and the film morphology. Single-crystal devices, which are in principle free of grain boundaries, are ideal for the investigation of intrinsic carrier transport properties of molecular semiconductors.[7] To study the effect of molecular packing on charge transport, it would be optimal to have two materials that differ only in the molecular packing while the other parameters, such as injection barrier, are as similar as possible. In this work, we designed and synthesized halogenated tetracene derivatives, in which the molecular packing is sensitive to the substituents while their HOMO levels are similar. They provide an ideal system for investigating structure−property relationships among organic semiconductors. The solid-state packing pattern of conjugated molecules depends on the nature of both the conjugated core and functional groups.[3]

Semiempirical calculations showed that substitution of bromo or chloro groups in tetracene lowers both HOMO and LUMO levels. The substitution of functional groups was expected to alter not only the size and shape of the molecule but also the electronic properties, which may result in a change of the packing mode of tetracene derivatives. Previously, Sarma and Desiraju pointed out that halogen groups promote π stacking.[8] Also, Anthony and co-workers reported
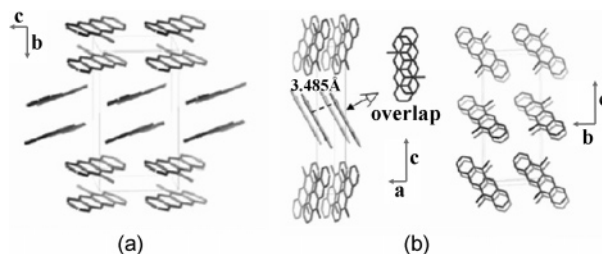

Figure 1. Crystal structures of 5-chlorotetracene (**CT**) (a) and 5,11-dichlorotetracene (**DCT**) (b). Note that **CT** has a herringbone-type structure but **DCT** π stacks along an *a* molecular axis.

that one or more substitutions of relatively bulky groups into peripositions of polyacenes disrupt the herringbone structure of the compounds.[6]

Halogenated tetracene derivatives were synthesized from tetracene using copper chloride, copper bromide, or *n*-bromosuccinimide (NBS) in chlorobenzene or bromobenzene. The products were soluble in common organic solvents and purified by recrystallization or column chromatography. The cyclic voltammogram, given in Figure S1, showed that 5-chlorotetracene (**CT**) and 5,11-dichlorotetracene (**DCT**) have an onset oxidation potential of 0.31 and 0.32 V, respectively, implying that they have almost the same HOMO levels as predicted in the semiempirical calculations. Single crystals were grown from either solution or vapor phase[9] for structural analysis and transistor fabrication. Interestingly, monosubstituted tetracene derivatives were platelets, and disubstituted derivatives were needle-shaped crystals. As shown in Figure 1, the crystal structures, analyzed by single-crystal X-ray diffraction, revealed that **DCT** has a face-to-face slipped π stacking motif and the intermolecular distance between neighboring molecules is about 3.485 Å. Pitch and roll angles were measured to be 20.48° and 14.53°, respectively. These relatively small angles leave good spatial overlap between two adjacent molecules.[3a] On the other hand, **CT**, which is isostructural to 5-bromotetracene (**BT**), is packed in a herringbone-type pattern. Two molecules are tilted in the same direction, and pairs of molecules are arranged in the herringbone pattern (see Supporting Information).

Field-effect transistors were fabricated on single crystals with graphite ink as electrodes and parylene as gate dielectric; its capacitance was about 2 nF/cm. The transistor channel is varied mainly with overall size and dimensions of crystals. The mobility of **DCT** grown from the vapor phase, which was extracted from saturation regions in Figure 2b, was as high as 1.6 cm^2/V·s, and the on/off ratio was 10^5. These transistor performances are very reproducible, but a mobility of 1.6 cm^2/V·s may not be the upper limit since we have not optimized crystal growth and device fabrication. Note that the highest reported mobility of a tetracene single crystal with the herringbone structure is 1.3 cm^2/V·s.[10]

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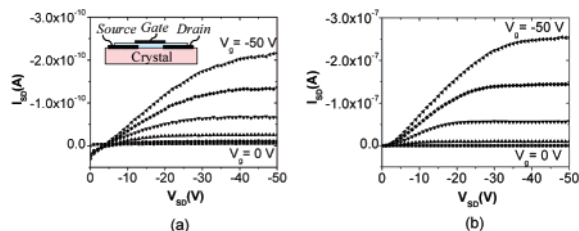[‡] Lund University.
[§] Stanford University.

Figure 2. Current−voltage characteristics of single-crystal transistors based on 5-chlorotetracene (**CT**) with channel dimension $W/L = 0.83$ (a) and 5,11-dichlorotetracene (**DCT**) with $W/L = 0.13$ (b). Inset shows device configuration of the transistors. The drain bias was swept from 0 to −50 V at a gate bias between 0 and −50 V in −10 V steps.
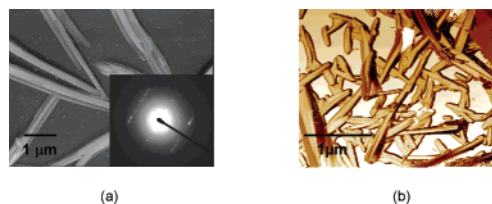

Figure 3. (a) TEM image and corresponding electron diffraction pattern of a **DCT** thin film deposited on a TEM grid at a substrate temperature of 50 °C. (b) AFM image of a **DCT** thin film deposited on an octadecyltrimethoxysilane (OTS)-treated SiO_2 substrate at a substrate temperature of 0 °C.

Table 1. Summary of Crystal Packings and Field-Effect Mobilities of Single-Crystal Transistors Based on Tetracene Derivatives

	crystal growth	structure	mobility (cm²/V·s)	on/off
CT	solution	herringbone	1.4×10^{-4}	10^3
BT	solution	herringbone	2.4×10^{-3}	10^2
	vapor	herringbone	0.3	10^2
DCT	vapor	π stack	1.6	10^5
tetracene[10]	vapor	herringbone	1.3	

Since the substitution of electron-withdrawing groups lowers the HOMO level of tetracene, carrier injection into **DCT** would be less efficient. Nevertheless, **DCT** had higher mobility, which may be due to the π stacking structure facilitating carrier transport.[11] To establish a direct correlation between solid-state packing and transport properties, single-crystal growth and device fabrication should be optimized to make it possible to measure intrinsic mobility. However, the high mobility in **DCT**, compared to other organic semiconductors purified and grown by the same method,[9] suggests to us that the slipped π stacking motif distinguishes **DCT** from other organic semiconductors with the herringbone packing.

We also built field-effect transistors on single crystals grown from solution. The transistor performance of the crystals depends on the quality of the crystals. As given in Table 1, crystals grown from solution showed much poorer transistor behavior than those from vapor. This may be attributed to rough surfaces, crystal imperfection, and high impurity concentration in crystals grown from solution due to solvent incorporation into the intramolecular position in the weakly bound van der Waals network of molecules. This is important because the conduction channel is located within the first few monolayers of the single crystals at the semiconductor−dielectric interface. In addition to the above factors, flowing inert gases used in vapor-phase growth may prevent impurities from being incorporated in crystals.[9]

For comparison, thin-film transistors were also fabricated on highly n-doped silicon wafers in both top and bottom contact configuration. **CT** was thermally evaporated at 10^{-6} Torr to yield cloudy films, showing no field effect in any kind of device. Mobility of thin-film transistors based on **DCT** varied with substrate temperature and surface properties of SiO_2. The best mobility in thin-film devices, 10^{-3} cm²/V·s, is achieved when **DCT** was evaporated onto octadecyltrimethoxysilane (OTS)-treated SiO_2 (300 nm)/Si substrate held at 0 °C. This relatively low mobility can be explained as a result of poor film morphology. TEM and AFM images (Figure 3) showed that evaporated molecules of tetracene derivatives did not cover the whole area of the transistor channel and that the crystallites are not well interconnected. Even though the crystals are large and possess very high crystallographic regularity (evidenced in the electron diffraction pattern inset in Figure 3a), the deposition process does not appear to favor a sufficiently high nucleation rate to cover the surface efficiently,

providing a poor conducting pathway. However, considering the high mobility measured on single-crystal transistors, we believe that the thin-film mobility could be significantly increased.

In summary, halogenated tetracene derivatives were synthesized and grown into single crystals. Monosubstituted 5- bromo- and 5-chlorotetracenes have the herringbone-type structure, while 5,11-dichlorotetracene has the π stacking structure. The mobility of 5,11-dichlorotetracene was as high as 1.6 cm²/V·s in single-crystal transistors. The π stacking structure, which enhances π orbital overlap and facilitates carrier transport, may thus be responsible for this high mobility. Currently, further studies on crystal growth and device fabrication are being carried out in order to measure the intrinsic mobility of 5-chlorotetracene and 5,11-dichlorotetracene, which have almost the same oxidation level but different solid-state packings.

Supporting Information Available: Experimental procedures, results of semiempirical calculations, cyclic voltammogram, and summary of thin-film transistor performance (PDF); X-ray crystallography files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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