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Tetrabenzoporphyrin Organic Semiconductors for Flexible Organic Thin Film Transistors and Circuits

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Organic semiconductors present several technological advantages as the active materials in the development of new, flexible electronics. Here we provide an overview of current developments in organic thin-film field-effect transistor (OFET)[1] and circuit technologies. Discussion and analysis are presented in the context of tetrabenzoporphyrin (TBP), a solution-processable organic semiconductor that forms polycrystalline thin-films[2], can be modified via well-known synthetic chemistry methods[3, 4], and has demonstrated high electronic performance[5-7].

OFETs are fabricated typically in either coplanar (or bottom-contact) and staggered (or top-contact) device structures, with highly doped crystalline silicon as the substrate and gate electrode, and SiO_2 as the gate dielectric. For TBP, thin-films were fabricated by dissolving a precursor molecule, tetrabicycloporphyrin (CP), in common organic solvents. Spun-cast films of the precursor exhibit amorphous, insulating behavior; following a thermal anneal in either vacuum or N_2, the amorphous film converts to polycrystalline TBP, with crystal sizes exceeding 1 μm.

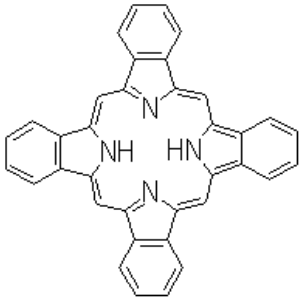

Fig. 1: The TBP single-molecule.

TBP OFETs typically display field-effect mobilities, μ_{FE}, on the order of 10^{-2} cm^2/V-s, in the saturation regime, ON-/OFF-current ratios exceeding 10^5, OFF-state currents around 100 pA, and subthreshold slopes (S) around 1 V/decade. Many organic semiconductors, including TBP, demonstrate considerable hysteresis in their transfer characterstics; TBP OFETs exhibit threshold voltages, V_T, of -20 – -15 V transferring from the ON-state to the OFF-state, and 0 – +5 V transferring from the OFF-state to the ON-state. TPB thin-films exhibit a HOMO and LUMO level of 5.1 and 2.9 eV, respectively; Au forms ohmic source-drain electrodes[6]. TBP OFET transfer characteristics also display a high degree of linearity as compared to other small molecule and polymer OFETs, which combined with the low subthreshold slope, indicates that trap states are likely confined to the grain boundaries and do not dominate device performance[7].

Many organic semiconductors, TBP included, exhibit environmental drawbacks, including sensitivity to light and ambient gases. For example, exposure to ambient laboratory conditions increases the overall thin-film conductivity in TBP OFETs, increasing μ_{FE} and S, lowering the ON-/OFF-current ratio, and positivelt shifting V_T. Preliminary experimental results indicate that air exposure produces shallow band tail trap states and increases the overall density of states. Encapsulation of has been performed with different materials and found not only to improve OFET air stability, but to alter the electrical performance of the TBP OFETs.

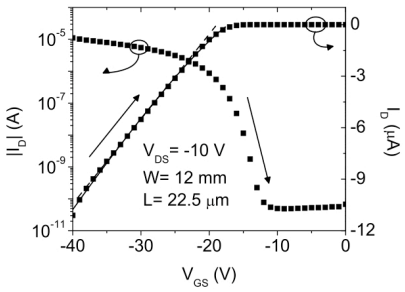

Fig. 2: Linear regime transfer characteristics of a TBP OFET on SiO_2.

Successful commercialization of organic electronics for flexible electronics will rely upon the development of flexible organic insulators. Several groups have successfully fabricated

OFETs, circuit, and displays on flexible substrates, such as plastics and textiles[8, 9]. We have fabricated TBP OFETs utilizing the solution-processable organic insulators benzocyclobutene (BCB) from Dow Chemical (USA), and TCI-01, an oligomeric resin from Merck Chemicals (UK), on both flexible and rigid substrates. Electrical performance is found to be very dependent upon the insulator film quality. Rigid devices using TCI-01 in a staggered electrode configuration demonstrated V_T=+2.6 V, μ_{FE}=4x10^{-4} cm^2/V-s at V_{GS}=-40 V, and a high subthreshold slope. However, subthreshold conduction increased, lowering the ON-/OFF-current ratio. Hysteresis is effectively eliminated, which combined with the increased subthreshold conduction, indicates the charge density in the channel has changed, possibly due to reduced surface trap states. Staggered electrode TBP OFETs fabricated on plastic substrates utilized BCB as the gate insulator, and were processed up to 250 °C to cure the BCB. These devices demonstrated μ_{FE}=10^{-2} cm^2/V-s and V_T= -5.7 V. However, cracking in the insulator due to bending of the substrate lead to high gate leakage current.

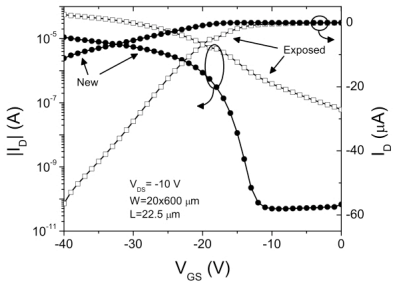

Fig. 3: Linear regime transfer characteristics for a TBP OFET on SiO_2 before and after exposure to air.

Newer developments in organic transistors and circuits have focused on solving lingering issues concerning ambipolar charge transport and high performance polycrystalline materials. Chua *et al.* recently demonstrated ambipolar polymer OFET behavior by using BCB as the gate insulator, proposing that traps generated by the SiO_2 surface preferentially trap electrons[10]. Ambipolar and light emitting OFETs have also been demonstrated using asymmetric source and drain electrodes, as well as bilayer films to improve ambipolar charge injection[11, 12]. Polymer OFET have also recently demonstrated μ_{FE}≈0.1 cm^2/V-s, combined with polycrystallinity and air stability[13]. TBP is also possible to modify; our ongoing collaboration has produced metal-substituted TBP OFETs with μ_{FE}>0.1 cm^2/V-s. Further modifications seek to enhance crystallinity and precursor solubility, lower the thermal conversion temperature, and increase air stability.

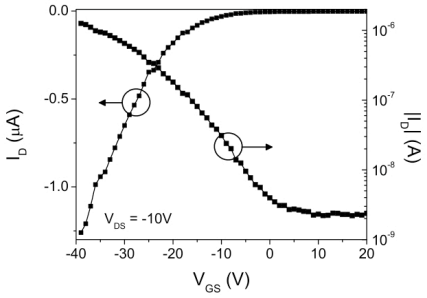

Fig. 3: Linear regime transfer characteristics of a TBP OFET on flexible plastic with BCB as the gate insulator.

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