Biocompatible and Biodegradable Materials for Organic Field Effect Transistors

(SUPPLEMENTARY INFORMATION)

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In the supplementary information, we give more details on the materials selected for the fabrication of organic field effect transistors. The SI starts with a brief insight into the rationale of selecting natural or nature-inspired materials grouped in the chapter Natural or Nature-inspired Materials for OFETs. In the following chapter Materials Synthesis and Analysis the fabrication route of the perylene diimide investigated in this work is reported. In the Materials Characterization section dielectric spectroscopy investigations of adenine, guanine, glucose and caffeine as well as their evaluation through FTIR and X-ray diffraction techniques are presented, providing more thorough evidence that such materials are very good insulating dielectrics. Further examples of transistors, not included in the main text are presented in the section Examples of Fabricated Devices, including organic field effect transistors with natural dielectrics from the sugar family (i.e. sucrose and lactose), or other natural semiconductors (i.e. beta carotene and indigo).
1. Natural or Nature-inspired Materials for OFETs

Notes on natural dielectrics

Glucose, lactose and sucrose are examples of many other simple small molecules in the sugar family. They are industrially produced on a very large scale, are non-toxic and have excellent film forming properties, when solution processed from water and/or dimethyl sulfoxide (DMSO). Adenine and guanine are small molecules in the nucleobase family of compounds comprising also cytosine, thymine, and uracil. Being small molecules, they are amenable for scrupulous purification, they can be solution processed in traditional roll to roll approaches, but also vacuum processed in thin films of thicknesses scaled down to 2.5 nm. Their natural abundance, low cost and low toxicity make these materials interesting candidates for organic electronics.

Notes on natural semiconductors

Beta-carotene, the red pigment of carrots is a naturally occurring compound having its optical, non-linear optical, fluorescence and even semiconducting properties recently investigated by various groups. [1-4]

Indigo is a naturally occurring compound, which has historically been extracted from plants in the *Indigofera* genus. Nowadays the synthetic production of indigo has made possible the high scale production of blue cotton yarn cloths with the main application of the compound remaining the blue jeans industry. Nevertheless, the low toxicity of indigo made possible the acceptance of its salt form as a food colouring, under
the name Indigotine, labelled as E 132 food colour number in the European Union and FD&C Blue No. 2 in the United States of America.\[^5\] Although the electronic and energetic levels of indigo were recently investigated, no report of using indigo as organic semiconductor in field effect devices appeared so far.\[^6,7\]

![Indigo](image)

*Notes on semiconductors known as dyes in various application fields*

Perylene diimide is the widely-accepted, very-low-toxicity, scarlet-red colour pigment employed in cosmetics with applications in lipsticks, nail enamels and hair colours. Nowadays many perylene dyes are produced on an industrial scale and commercially available under trade names such as Red Dye 190 or Lumogen\(^\text{®}\) F.\[^8\] The remarkable chemical inertness of perylene diimides is a prerequisite for their very low acute toxicity that opens up numerous applications in cosmetic industry as red pigments for hair colorants, nail enamels and lipsticks. We intentionally performed toxicity evaluation of the EH-PDI material used as n-type semiconductor in this study. In-vivo tests with oral administration of EH-PDI in mice showed that the maximal tolerance dose for this compound exceeds 8000 mg kg\(^{-1}\). This value is comparable with the toxicity of commonly edible substances such as sugar, but definitely less toxic than table salt, for which a LD\(_{50}\) of \(~3500\) mg kg\(^{-1}\) in mice was recorded. Perylene diimides are also known as good n-type organic semiconductors widely used in organic solar cells.\[^9\]
Indanthrene yellow G and indanthrene brilliant orange RF (derivatives of natural occurring anthraquinone) are both used widely in textile industry as vat dyes for fabrics colouring as well as in electronics industry as a colour filter for image forming applications. However, their low toxicity, biodegradability and ability to metabolize proposed these compounds to color sausage skin in food industry.

2. Materials Synthesis and Analysis

Perylene diimide (EH-PDI) was synthesized as shown in Scheme 1. Perylene-3,4,9,10-tetracarboxylic acid dianhydride (5 g, 12.8 mmol) was mixed with 60 ml of freshly distilled quinoline, 15 g (116 mmol) of 2-ethylhexylamine and ca. 100 mg of Zn(OAc)$_2$H$_2$O.

Scheme 1: Fabrication route of the perylene diimide semiconductor.
The resulting mixture was heated at reflux for 2 hrs, then cooled down to room temperature and poured into 600 ml of 10% aqueous HCl. The precipitate formed was filtered off, extracted with methanol and dried in air. The obtained crude sample of PDI was further purified by column chromatography. Elution with a CH₂Cl₂-methanol mixture (95.5:0.5 v/v) resulted in a pure compound EH-PDI. Final purification was achieved by sublimation at 450-500 °C under a reduced pressure of ca. 10⁻² mbar. The yield of EH-PDI after all purification steps was in the range of 45-55%.

¹H NMR (400 MHz, CDCl₃,) δ= 8.83 (d, 4H, H-Ar), 8.75 (d, 4H, H-Ar), 4.31 (m, 4H, NCH₂), 2.14 (m, 2H, CH), 1.58 (m, 8H, CH₂), 1.50 (m, 8H, CH₂), 1.13 (t, 6H, CH₃), 1.06 (t, 6H, CH₃), ppm. Chemical analysis: C₄₀H₄₂N₂O₄.

Calculated: C, 78.15; H, 6.89; N, 4.56. Found: C, 77.95; H, 6.97; N, 4.61.

IR spectrum (KBr pellet): ν= 745, 809, 1178, 1247, 1308, 1346, 1380, 1403, 1441, 1577, 1594, 1615, 1650, 1695, 2859, 2873, 2930, 2930, 2958 cm⁻¹.

3. Materials Characterization

Dielectric characterization of the gate dielectrics was performed with metal-insulator-metal capacitors using a Novocontrol Alpha Analyzer. FTIR characterization was performed on aluminium coated glass slides using a VERTEX 70 FTIR Spectrophotometer. X-ray diffraction was performed using a Bruker AXS X-ray Diffractometer (Cu-Kα) X-ray Diffractometer. AFM investigation was performed using a Digital Instruments Dimension 3100 microscope working in tapping mode.

Impedance spectroscopy measurements of spin coated glucose as well as evaporated adenine, guanine and caffeine films are shown in Fig. S1a-b and S2a-b. The
essentially flat permittivity versus bias voltage, as well as the low losses over a wide
frequency range recommends glucose, adenine, guanine and caffeine as dielectric
materials in OFETs.

Fig. S1  a) Dielectric spectroscopy of adenine. Measured parameters: dielectric constant
~3.85 at 1000 Hz and breakdown voltage ~1.5 MV cm$^{-1}$; b) Dielectric spectroscopy of
guanine. Measured parameters: dielectric constant ~4.35 at 1000 Hz and breakdown
voltage ~3.5 MV cm$^{-1}$.

Fig. S2  a) Dielectric spectroscopy for a spin cast film of glucose. Measured parameters:
dielectric constant ~6.35 at 1000 Hz and dielectric breakdown voltage ~1.5 MV cm$^{-1}$; b)
Dielectric permittivity as a function of applied bias voltage for an evaporated film of
caffeine. Measured parameters: dielectric constant ~4.1 and dielectric breakdown
voltage ~2 MV cm$^{-1}$.

Despite its excellent dielectric behaviour (as shown in Fig. S2b), producing
OFETs with caffeine as a stand alone dielectric represented a difficult task, mainly due to
its high tendency for crystallization. Consequently, thin films of caffeine typically contained pin holes whereas thicker evaporated films had very high roughness (sometimes greater than rms ~100 nm). A dielectric constant of ~ 4.1 at 1000 Hz was recorded for caffeine.

The FTIR and XRD spectra of adenine in Fig. S3 and S4, as well as the FTIR spectra of evaporated glucose in Fig. S5, confirm that the evaporation processed materials are identical to the precursor powder.

**Fig. S3 FTIR of Adenine. Comparison between the FTIR spectra of vacuum processed adenine and the as-received material-solution processed in a mixture of ethyl alcohol and water.**
**Fig. S4** Comparison of the X-ray diffraction of evaporated adenine thin film (1 μm thick, bottom graph) and the as-received material (top graph).

**Fig. S5** FTIR of Glucose. Comparison between the spectra of vacuum processed glucose and the as-received material-solution processed in deionised water.
In a similar fashion to adenine and glucose, the evaporated phase was also confirmed to be similar to the precursor powder for guanine thin films.

4. Examples of Fabricated Devices

Examples of transistors with D-(+ ) glucose (0.9 g ml\(^{-1}\) in deionized water), lactose (0.25 g ml\(^{-1}\) in DMSO), and sucrose (1.9 g ml\(^{-1}\) in deionised water) dielectrics are displayed in Fig. S6a-c.

![Graphs showing transfer characteristics](image)

*Fig S6* a) Transfer characteristics of an OFET with a glucose gate dielectric and beta-carotene organic semiconductor; b) Transfer characteristics of an OFET with lactose in DMSO as dielectric and beta-carotene as organic semiconductor; c) Transfer characteristics of an OFET with sucrose as dielectric and beta-carotene as organic semiconductor. The large hysteresis occurring in the case of sucrose-based OFET is presumably due to the presence of mobile ionic impurities in sucrose.
Although the dielectric property of the spin coated films of glucose containing also caffeine were not improved by the addition of caffeine, the performances of the organic field effect transistors improved in terms of lower leakage and higher on-currents achieved (Figure S7a-b)) which may be due, we presume, to a better film forming of glucose with caffeine on aluminium gate electrodes.

**Fig. S7** a-b) Transfer and output characteristics of field effect transistors on glass substrates with natural p-type (solution processed beta-carotene) as organic semiconductor; c-d) Transfer and output characteristics of field effect transistors with n-type (vacuum processed indigo) as organic semiconductor. Gate dielectrics are based on glucose and caffeine in (a-b) and glucose in (c-d).
Figure S7c-d) displays the transfer and output characteristics of an organic field effect transistor having vacuum processed indigo as natural organic semiconductor deposited on the top of solution cast dielectric film of glucose.

One of the problems with most degradable polymers is the large surface roughness. The surface of Ecoflex films displays a root-mean-square (rms) roughness of ~80 nm. Evaporation of aluminium gate electrodes does not reduce the surface roughness to values lower than ~50 nm, so thicker dielectric films should be evaporated to avoid the leakage through the dielectric. The operation voltage of the transistor built directly on Ecoflex foil is in the range of 30-40 V (Fig. S8), primarily due to the inherent roughness of the Ecoflex foil.

**Fig. S8** Transfer and output characteristics of OFETs with a 2 µm adenine gate dielectric and 150 nm perylene diimide semiconductor on plain Ecoflex.

Transfer and output characteristics of a high performance OFET having a combined inorganic (aluminium oxide)-organic (adenine and guanine) for the dielectric and perylene diimide for the organic semiconductor is presented in Fig. S9a-b.
Fig. S9 a-b) Transfer and output characteristics of an OFET having a combined inorganic (aluminum oxide)-organic (adenine and guanine) dielectric. Field effect mobility $\mu = 0.016 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $C_{ox} = 81.6 \text{ nF cm}^{-2}$.


