

Large Photoresponsivity in High-Mobility Single-Crystal Organic Field-Effect Phototransistors

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A strong interest in organic devices has emerged recently due to their potential in large-area and low-cost electronics. However, the effects of light on the electrical performance of organic field-effect transistors (OFETs) has been hardly explored and mainly focused only on polymer-based devices.^[1–4] The preparation of OFETs exhibiting photoresponsivity, which could act as light sensors, photoswitches or optoelectronic memory elements, opens new avenues of research into promising device applications. Very recently, we reported on a new generation of materials for OFETs, which consists of low-molecular-weight molecules based on tetrathiafulvalene (TTF) derivatives. These materials were processed from solution and revealed very high mobility; these are two desirable conditions that have often been considered conflicting.^[5–6] The highest mobility was found for single crystals of dithiophene-tetrathiafulvalene (DT-TTF, $\mu_{\text{max}} = 1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[5] and dibenzo-tetrathiafulvalene (DB-TTF, $\mu_{\text{max}} = 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[6] (Figure 1a). Here, we demonstrate that these crystals combine high OFET performance with a large photoresponsivity and can thus operate as

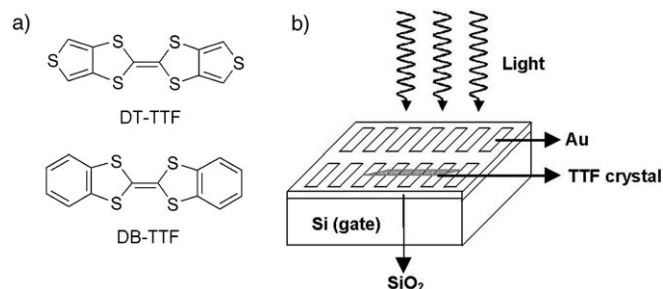


Figure 1. a) Molecular structure of dithiophene-tetrathiafulvalene (DT-TTF) and dibenzo-tetrathiafulvalene (DB-TTF). b) Device configuration.

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phototransistors, that is, light can be used as an additional parameter to control the number of mobile charges.

The synthesis of the molecules was carried out as previously described.^[7–8] Their UV/Vis spectra in the solid state showed a maximum wavelength absorption peak at 450 and 476 nm for DT-TTF and DB-TTF, respectively. The optical band gaps were then estimated from the absorption edges of the spectra and were found to be very similar, with values of 2.51 eV for DT-TTF and 2.36 eV for DB-TTF. These energy values indicate the facility to induce a transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO); that is, the lower the optical band gap is, the easier it will be to promote electrons from the HOMO to the LUMO by absorption of photons. Such electron transitions will then generate holes and electrons which will contribute to the resulting transport properties.

The phototransistor device configuration used is shown in Figure 1 b. To study the effect of light, a white-light lamp with energy of 2.5 W cm^{-2} was employed. Figure 2 displays the

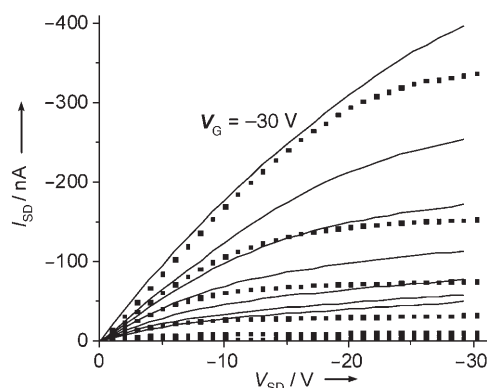


Figure 2. I_{SD} versus V_{SD} at V_{G} (from top to bottom) -30 , -25 , -20 , -15 , -10 , -5 and 0 V in the dark (.....) and under light (—) for a DT-TTF single-crystal OFET with channel length and width of 100 and 10 μm , respectively. No significant current was observed in the dark at $V_{\text{G}} < -5 \text{ V}$.

output characteristics (source-drain current I_{SD} versus the applied source-drain voltage V_{SD} at different gate voltages V_{G}) of a DT-TTF single-crystal OFET in the dark and under illumination. This material behaves as a *p*-type semiconductor since holes accumulate at the TTF- SiO_2 interface (conduction channel) and are responsible for the observed conductivity.^[5] For this reason, as a more negative gate voltage is applied, more holes are induced in the conduction channel, and the conductivity increases. This device exhibited a very high performance. The mobility of this crystal in the dark, determined in the linear regime ($-2 \text{ V} > V_{\text{SD}} > +2 \text{ V}$), was found to be $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the ON/OFF ratio, defined as $I_{\text{SD}}(\text{accumulation regime})/I_{\text{SD}}(\text{depletion regime})$, was 4×10^5 .^[9] A clear increase of the I_{SD} was observed under illumination, which can be explained by the photogeneration of additional mobile charge carriers. Photoconductivity in a TTF crystal was previously observed and was attributed to the presence of the TTF radical cation.^[10]

Figure 3, showing the transfer characteristics of this device in the dark and under illumination, clearly illustrates the effect of light. The shapes of the I_{SD} - V_G curves in the dark and with

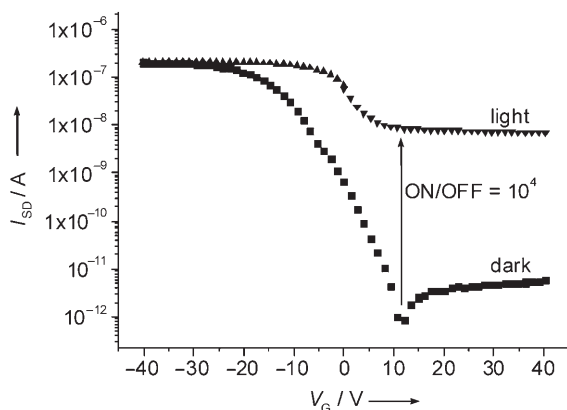


Figure 3. Transfer characteristics (I_{SD} vs. V_G) at $V_{SD} = 10$ V for the same device in Figure 2 in the dark (■) and under light (▲).

light do not differ substantially. However, the ratio of photocurrent to dark current $I_{SD}(\text{light})/I_{SD}(\text{dark})$ is much higher in the depletion mode (OFF state) than in the accumulation regime (ON state). This is due to the fact that at high negative gate

voltages, the conductivity is mainly dominated by the field-induced charges, whereas below the threshold voltage the device is charge-depleted and only the light-induced charges can contribute to the measured I_{SD} . Remarkably, a very high ratio $I_{SD}(\text{light})/I_{SD}(\text{dark})$ on the order of $\approx 10^4$ was observed at $V_G = 10$ V. At this gate voltage we estimate that the photoinduced charge-carrier density is $2.3 \times 10^{16} \text{ cm}^{-3}$. This behaviour implies that it is possible to switch the device ON by means of two possible control parameters or gates: either by applying a negative gate voltage or with illumination. When one of these gates is turned off (i.e. no incident light or $V_G > 10$ V), the effect of the other is then maximised. These devices could, therefore, be used for potential applications, such as light sensors.

The OFET devices based on single crystals of DB-TTF exhibit similar behaviour under illumination. However, much lower $I_{SD}(\text{light})/I_{SD}(\text{dark})$ ratios of the order of ≈ 3 were obtained. This is due to the fact that these devices were not completely depleted even when applying a high positive gate voltage; therefore, the contribution of the field-induced charges to the measured current is dominating for all applied gate voltages. The fact that DB-TTF is conducting in the OFF state is an indication of some unintentional doping and is in accordance with its lower oxidation potential.^[11]

We also studied the time response of the phototransistors. Figures 4a and 4c show how I_{SD} changes with time when

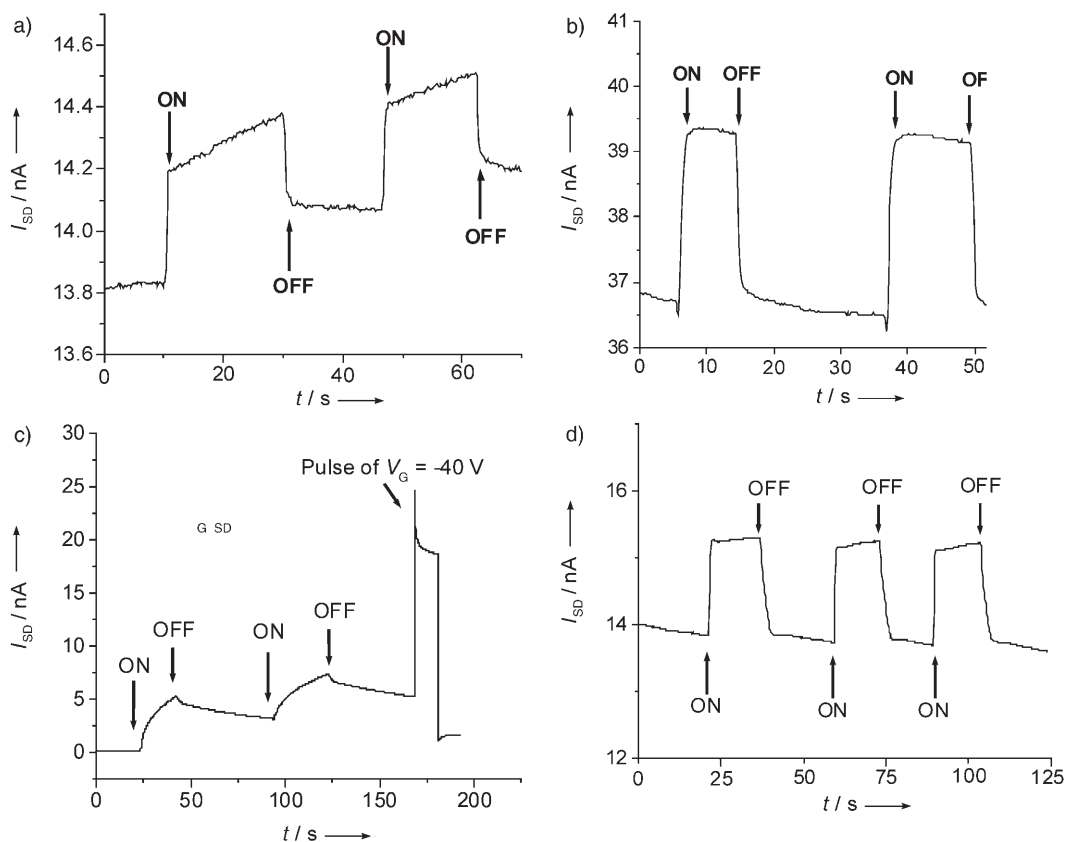


Figure 4. I_{SD} versus time when switching the light on and off for a DB-TTF OFET at a) $V_{SD} = 1$ V and $V_G = 0$ V and b) $V_{SD} = 1$ V and $V_G = -40$ V and for a DT-TTF OFET at c) $V_{SD} = 1$ V and $V_G = 0$ V and d) $V_{SD} = 1$ V and $V_G = -40$ V.

switching on and off the light at $V_{SD}=1$ V and $V_G=0$ V for a DB-TTF single-crystal OFET, exhibiting a mobility of $0.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the dark, and the above-characterised DT-TTF single-crystal OFET, respectively. A very fast response of the measured current when switching on the light was observed. Nevertheless, some persistent photoconductivity remained after turning the light off. This persistent photoconductivity was previously observed in other organic polymeric thin films and was attributed to the slow recombination of holes and electrons.^[4] After exposure to light, the photogenerated charge carriers (holes and electrons) in the organic material are spatially separated, with the more mobile positive charges (holes) drifting towards the channel, whilst the almost immobile negative charges (electrons) are trapped. Upon turning off the light source, the holes recombine with the electrons following two relaxation processes i) a fast component corresponding to the recombination of the closely spaced charge carriers and ii) a slow process resulting from the recombination of well-separated carriers. Interestingly, such persistent conductivity is not observed in the DB-TTF and DT-TTF OFETs when a high negative gate voltage is simultaneously applied to the SiO_2 substrate (Figures 4b and 4d). The persistent current, observed in the phototransistors when no gate voltage is applied, remains for hours. However, by applying a high negative gate voltage pulse the initial current is recovered (Figure 4c). This interesting phenomena was recently observed by Dutta and Narayan^[4a] in an OFET of a thin film of poly(3-hexylthiophene). They speculated that after the termination of illumination, I_{SD} rapidly decays due to the recombination of proximal carriers and, subsequently, the trapped electrons screen the gate voltage, which leads to a higher I_{SD} in a metastable state (i.e. the charges trapped at the interface contribute to the electric field created by the gate voltage). By applying a negative gate voltage, I_{SD} increases due to the accumulation of holes but also results in an increased rate of recombination of the electrons trapped in centres near the interface.

The conduction mechanism of the studied phototransistors is still under investigation and further studies are required. However, we can envisage that these devices could be interesting to operate as organic optoelectronic memory elements. The devices show some persistent photocurrent after turning off the light for hours (write), but this persistent photocurrent can be removed by applying a high negative gate voltage (erase). In addition, the devices were stable (in air) for weeks when several cycles of switching on and off the light were applied.

In conclusion, we demonstrated for the first time that single crystals of DT-TTF and DB-TTF behave as organic field-effect phototransistors. The organic semiconductor DT-TTF is, in particular, a very promising material not only because of its high OFET performance but also for its potential use in optoelectronic applications as it exhibits a very large photoresponsivity. This material could thus be employed as light detector or in memory devices.

Experimental Section

Silicon substrates with a 200 nm thermally grown oxide layer were purchased from Wacker Siltronic AG. Electrode fabrication was carried out in an electron beam pattern generator (EBPG5 HR 100 kV FEG) using a double poly(methyl methacrylate) (PMMA) resist. 4 nm of Ti and 26 nm of Au were evaporated at liquid-nitrogen temperature to ensure a smooth surface, and lift-off was done in acetone.

DT-TTF and DB-TTF were synthesised as previously described.^[7–8] The DT-TTF and DB-TTF single-crystal phototransistors were prepared by heating a saturated solution of the donor in chlorobenzene at about 60°C and pouring it over the substrates containing the microfabricated electrodes at room temperature. The solvent was allowed to evaporate very slowly for about 2 h in a sealed container giving rise to good-quality, long plate crystals, some of which bridged the electrodes.

The transport measurements were carried out in a Probe Station microscope coupled to an ADwin Gold external data acquisition system. Solid UV/Vis spectra were performed in a Varian Cary 5 spectrometer.

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- [11] DB-TTF shows two separate reversible one-electron oxidations with $E_{1/2}^1$ and $E_{1/2}^2$ of 0.62 and 0.97 V, respectively (in $\text{CH}_3\text{CN}/0.1\text{ M TBAPF}_6$ vs SCE). The values found for DT-TTF in the same conditions are $E_{1/2}^1=0.67$ V and $E_{1/2}^2=0.97$ V.

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