# Supporting Information

# Charge transport in a two-dimensional molecular organic semiconductor

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# Field effect mobility measurements.

The output characteristics of **Ge-crucifrom** samples show the effect of contact resistances. Though the Au electrodes were treated with PFBT, the effects of contact resistance are more pronounced in straight-annealed samples. This can be understood by comparing AFM topographic images. The presence of bulky domains in straight annealed samples might have caused this rough interface between the electrode and the material.



**Figure SI 1.** Output characteristics with  $\Delta VGS = -20V$  of **Ge-cruciform** (top) step-annealed to  $120^{\circ}C$  and (bottom) annealed straight to  $120^{\circ}C$ .



Figure SI 2: Output characteristics (top) and transfer characteristics at  $\Delta V_{DS} = -50V$  (bottom) of unannealed Ge-crucifrom.

#### **Charge Generation Layer TOF measurements.**

Figure SI 3 shows the hole photocurrent transients on linear and log–log scales, at room temperature and for an applied electric field  $E = 3.3 \times 10^4$  V/cm, and after annealing the sample at 50, 75 and 100°C for 20 minutes. The transit time was estimated from the change of slope of the photocurrent transient in the log–log plot,  $t_{tr} = 17$ , 9.2, 2 µs for 50, 75 and 100°C, respectively. The transit time corresponds to a mobility of  $\mu = 2.5 \times 10^{-5}$ ,  $4 \times 10^{-5}$  and  $\times$  <sup>-4</sup> cm<sup>2</sup>/Vs for 50, 75 and 100°C, respectively.





**Figure SI 3.** Hole photocurrent transients on linear and log–log scale for a film of **Ge-cruciform**, at RT and for an applied electric field  $E = 3.3 \times 10^4$  V/cm: a) after being annealed for 20 minutes at 50°C; b) after being annealed for 20 minutes at 75°C; c) after being annealed for 20 minutes at 100°C.

For the as-cast (RT), 50 and 75°C samples we have studied the hole mobility field dependence, as shown in Figure SI 4. Unfortunately we were not able to do so for the sample annealed at 100°C, because at electric field higher than  $3.3 \times 10^4$  V/cm, the time scale was below the resolution of our system. For the same reason we could not perform any TOF measurements on the samples annealed at 120°C.



Figure SI 4. CGL-TOF hole field dependence mobility at RT and after subsequent stepannealing.



0.00 nm



**Figure SI 5.** AFM height images of **Ge-cruciform** a) unannealed, b)  $50^{\circ}$ C, c)  $75^{\circ}$ C, and d)  $100^{\circ}$ C



Energy levels of the planar heterojunction

Figure SI 6. Energy levels of the planar heterojunction.

## Microscopy.



**Figure SI 7.** SEM images of **Ge-cruciform**. (a) and (b) are of a single film spun from carbon disulphide at different magnification. Film (c) was prepared with chlorobenzene. Film (d) was deposited from a carbon disulphide solution and is the only film to undergo heat treatment (120°C for 20 minutes).

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## **Photophysics.**



**Figure SI 8.** Absorption spectra for **Ge-cruciform** films prepared from carbon disulphide or chlorobenzene. Two films for each solvent were prepared, one of which was annealed straight to  $120^{\circ}$ C for 20 minutes. An additional film was prepared from carbon disulphide. The film was annealed for 20 minutes at each of the following temperatures 50, 75, 100 and  $120^{\circ}$ C in successive order.

## Profilometry



**Figure SI 9.** Measurement of thickness from a Dektak profiler for **Ge-cruciform** spun from carbon disulphide and annealed at 50, 75, 100 and 120°C in 20 minutes steps. To obtain an indication of film thickness after spin-coating, the film was scratched 5 times. The film thickness was found to be approximately 250 nm.



**Figure SI 10.** Measurement of thickness from a Dektak profiler for **Ge-cruciform** spun from carbon disulphide annealed straight to 120 °C for 20 minutes. Here the film has 6 scratches and the film has an approximate thickness of 250 nm.

Absorption spectra were obtained with a Varian Cary 300 UV-Visible Spectrophotometer. Figure SI 11 shows the normalised absorption spectra of the **Ge-cruciform** (solid line) and Lumogen (dotted line).



**Figure SI 11.** Normalised absorption spectra of a thin film of **Ge-cruciform** (solid line) and Lumogen Red (dotted line).