Chiral light detection via a chiral organic semiconductor transistor

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Chiral, circularly polarized (CP) light is central to many photonic technologies, including CP-ellipsometry based tomography[1,2], optical communication of spin information[3], and quantum-based optical computing and information processing[4,5]. To develop these technologies to their full potential would require the miniaturization and integration of suitable chiral photo-detecting devices. Organic field-effect transistors (OFETs), in which the active semiconducting layer is an organic material, allow the simple fabrication of ultra-thin, compact devices[6-8]. Here we demonstrate, for the first time, a CP light detecting OFET based on an asymmetrically-pure helically-shaped chiral semiconducting molecule known as a helicene[9]. We have shown that OFETs with a helicene semiconductor layer are solution-processible and have well-behaved device characteristics. Importantly, we find a highly specific photo-response to CP light, which is directly related to the handedness of the helicene molecule. We believe this opens up a unique possibility for CP detection in highly integrated photonic technologies.

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Organic semiconductors (OSCs) can be used in a range of different optoelectronic devices, including organic light-emitting transistors (OLETs)[10], photo-diodes (OPDs)[11] and photo-transistors[12-14]. One key advantage of such materials is the ability to tune factors such as the optical energy gap and the energy of the electron and hole transport levels, using chemical synthesis[6-8,15]. Additionally, the physical shape of the conjugated semiconducting electronic system can be varied, generating such forms as rectangular and disc-like small molecules, extended one-dimensional polymers, and spherical fullerenes. The impact of physical shape can be seen in the emission properties of aligned semiconducting polymers, where the alignment of the optical dipole moment with the physical backbone allows the creation of linearly polarized organic light emitting diodes[16].

With the growing interest in chiral photonics in such applications as quantum optics and optical spintronics, we reasoned that it should be possible to create a device from an organic semiconductor with a helically-shaped conjugated electronic system which could couple directly to helically-shaped light. If so, such a device would have an intrinsically chiral response, the right-handed helical molecule responding to right-handed CP photons, and the left-handed molecule to left-handed CP photons.

The helicenes are conjugated molecular semiconductors constructed from *ortho*-fused aromatic rings, where the inability for conjoined rings to occupy the same plane results in an intrinsically helical topology[9,17]. Consequently, helicenes come in both right-handed and left-handed chiral, so-called enantiomeric, forms (for example, see Fig 1a). Such helically chiral topology, coupled with their fully conjugated structure,

endows strong chiroptical properties to these molecules including high optical rotary power and strong circular dichroism. Furthermore, it has been reported that certain helicenes can self-assemble into homochiral supramolecular columns, which subsequently pack together to form large crystalline structures in both concentrated solution and thin films.[18-20] This supramolecular aggregation gives directionality and alignment to the helical electronic system, and can result in a dramatic increase in their chiroptical response[20] and strong enhancement of their nonlinear optical properties[21]. Additionality, such a propensity to crystallise makes them attractive materials for photo-transistors, where such molecular ordering should maximize both charge seperation and charge transport.

Helicenes, however, remain remarkably unexplored in solid-state optoelectronic devices. While there is one report of their use in OFETs[22], this did not exploit the chirality of the helicenes, instead using the material in a 50:50 mixture of both left- and right-handed enantiomeric forms (this 50:50 mixture is called a racemic mixture). Not only should the use of single-handed, enantiomerically-pure helicenes lead to efficient homochiral self-assembly and crystallization[21,23], but also render the resultant devices ideal candidates for CP light sensitive applications[24].

We elected to use the enantiomerically-pure 1-aza[6]helicene (Fig. 1a) in CP detecting OFETs, since it can be readily synthetically assembled and separated into its right- and left-handed enantiomeric forms[25]. We also note that it is chemically distinct from the tetrathia-[7]-helicene used in the single previous racemic helicene OFET study[22]. Unlike many small molecules used in OFETs, 1-aza[6]helicene has good

solubility in most organic solvents and hence is compatible with simple fabrication techniques such as spin coating, drop casting, and large-scale printing. Annealing at low temperature resulted in crystalline domains up to a few hundreds of nanometers in size, several hundred nanometers high, and uniformly distributed across the surface (Fig. 2a). Molecular coverage at the surface ensures efficient in-plane charge transport between domains. This is distinct to the racemic tetrathia-[7]-helicene which formed a nano-fibular morphology, giving poor charge transport properties and non-aligned helical directionality.

To examine the chiroptical response of our enantiomerically-pure thin films, we carried out circular dichroism (CD) measurements (Fig. 2b). The annealed (+)-1-aza[6]helicene and (-)-1-aza[6]helicene films show a strong, equal and opposite response. This demonstrates the strong dependence of the optical absorption for each enantiomer on the handedness of chiral light. The film CD spectra are also red shifted compared to those in solution (Supplementary Information Fig. S1) due to packing effects in the solid state.

Right-handed (+)-1-aza[6]helicene and left-handed (-)-1-aza[6]helicene were then used as the semiconducting layer in bottom-gate, bottom-contact OFETs (Fig. 1b). The output curves of an (+)-1-aza[6]helicene OFET are shown in Fig. 3a. This particular helicene is a hole transporting material and gives well-behaved OFET characteristics, comprising of a linear region and a saturation region. The transfer characteristics shown in Fig. 3b indicate a turn-on voltage of -10 V, a low off-current in the region of 10^{-10} A, a high on/off ratio of 10^3, and a mobility of 10^{-4} cm^2/Vs. We note that the mobility is

three orders of magnitude higher than the value reported for the racemic tetrathia-[7]-helicene OFET[22]. Also shown in Fig. 3b is the transfer characteristics of an as spin-coated fresh device prior to annealing, clearly showing how the charge carrier mobility improves upon formation of the crystal domains in Fig. 2a. As expected, the fabricated OFET devices exhibit similar output and transfer characteristics regardless of which enantiomer of the 1-aza[6]helicene is used (see Supplementary Information, Fig. S4).

To explore the CP light responsivity of the enantiomerically-pure transistors, the response of annealed (+)-1-aza[6]helicene and (-)-1-aza[6]helicene OFETs to CP illumination were studied. To ensure sufficient absorption by the 1-aza[6]helicene films, emission from a UV lamp at 365 nm was chosen (to correspond to the CD maximum, see Fig. 2b), which led to the generation of 10 mW/cm^2 CP illumination using a linear polarizer and a quarter-wave plate. It can be estimated from the absolute absorption spectrum (Supplementary Information Fig. S3) that about 90% of incident photons are absorbed. The transfer characteristics before and during exposure to left- and right-handed CP illumination are shown in Fig. 4a and b for typical OFETs. Device reproducibility was very good, error bars indicating results for four different devices of each enantiomer. The off-current of our (+)-1-aza[6]helicene OFET was increased by an order of magnitude from 10^{-10} A to 10^{-9} A when it was exposed to 10 mW/cm^2 right-handed circularly polarized illumination (Fig. 4a). Illumination with CP light of the opposite handedness caused no obvious change in the off-current. An equal but opposite effect was observed in the case of the (-)-1-aza[6]helicene OFET: Left-handed

CP illumination gave an order of magnitude increase in off-current, whereas right-handed CP light had no discernable effect (Fig. 4b). The slightly better response of the OFET in Fig. 4b at higher gate voltages compared to that in Fig 4a is due to the lower dark current in the former; this is most likely due to the device-to-device variations in transistor performance which occur in polycrystalline OFETs. For both (+)- and (-)-1-aza[6]helicene OFETs, other device parameters, such as the on-current, threshold voltage and mobility, remained constant regardless of the chirality of the light used. The corresponding output curves of these two OFETs, under the handedness of CP illumination to which they were responsive, preserved good transistor behaviour under illumination conditions (see Supplementary Information, Fig. S5). Importantly, the off-current in both (+)-1-aza[6]helicene and (-)-1-aza[6]helicene devices was restored to 10^{-10} A when CP illumination was removed.

The fact that the handedness of the helicene employed controls the handedness of CP light to which the OFET responds, confirms chirality of the helicene to be central to the effect. To further certify this fact, a preliminary comparison study was performed on a 1-aza[6]helicene OFET fabricated from racemic material. The racemic helicene OFET showed an increase in the off-current to both left-handed and right-handed CP illumination and hence no selective CP response (see Supplementary Information, Fig. S6).

The change in the off-current upon CP illumination of the correct handedness can be attributed to excitons formed on helicene molecules close to the transistor channel[26] by the absorption of CP photons. Those excitons which dissociate into holes and

electrons give rise to a photogenerated leakage current between the biased source and drain electrodes. The fact that transistors constructed from the enantiomerically-pure helicene are CP selective can be related to their chiroptical response as indicated by the CD spectra of the bulk film on glass (Fig. 2b). The strong CP selectivity of the transistor photocurrent (Fig. 4a and b) indicates that the helicene molecules in the channel region have an enhanced chiroptical-selective photogeneration efficiency.

The illumination intensity and time dependent CP photo-response of the OFETs was additionally investigated. The steady-state photocurrent was found to saturate at intensity levels of about 5 mW/cm^2 (see Supplementary Information, Fig. S7). This type of saturation is typical of other photo-transistors.[12] The time dependent photo-response (Fig. 5) was very good, with a fast rise-time of 2.6 ms. The rise-time is close to the theoretical fastest response time of these OFETs of about 1 ms (calculated from the carrier transit time across the channel $L^2/\mu V_D$). It is slightly longer due to additional factors such as the contact-gate capacitance charging time. The longer photo-response decay-time of 6.2 ms is indicative of the emptying of charge traps; such traps, common at the grain boundaries in polycrystalline OFETs, can be seen in the shape of the transfer characteristics (Fig. 3b), and would additionally explain the observed steady-state photocurrent saturation.

The quantum efficiency of these very first, proof-of-concept, CP detecting OFETs was 0.1%, similar to that previously reported for (non-CP responsive) organic photo-transistors[13] with a similar mobility. The efficiency could be increased in the future by increasing the charge carrier mobility, hence charge extraction efficiency, via

chemical synthesis[6-8,15]. Additionally, variation of the helicene chemical structure should allow the absorption band to be tuned to longer wavelengths, as demonstrated for benzothiophene-helicenes (absorption edge about 600 nm)[27] and squarilium small molecules (absorption edge about 1.2 μm)[13], for CP detection across the visible into the infra-red. Furthermore, helicenes which form larger crystalline domains (better coverage, less trapping) and are ambient stable are additional future targets for this area.

In summary, using enantiomerically-pure 1-aza[6]helicene, the first CP responsive photo-FETs based on a chiral organic semiconductor were successfully demonstrated. The off-current was found to undergo a rapid, fully reversible change by an order of magnitude when the enantiomeric helicene photo-FETs were exposed to chiral light of the correct handedness. The intrinsic self-crystallization of helicene thin films allows for device optimization via crystalline domain formation. This proof-of-concept chiral photo-transistor opens up a wide range of potential applications of single enantiomer helicenes in CP-light detecting organic semiconductor devices. Patterning techniques available for solution-processable organic semiconductors, such as high-resolution ink-jet printing, should allow the creation of arrays of micron-scale CP-light sensitive devices, as well as integration with CMOS electronics[28]. The down-scaling of device dimensions via nano-level imprinting and other methods should also allow the creation of nanometre sized transistors, and ultimately single molecule devices[29]. The advantage of the transistor architecture also allows the CP photo-FET to be used as part of a circuit, such as the p-type component of a complementary inverter or ring oscillator, increasing

sensitivity by modulating a much larger DC or AC signal. Such devices should have significant impact across chiral photonics.

Methods Summary:

1-Aza[6]helicene[25] was prepared as previously reported and separated using preparative chiral HPLC. Helicene racemic and enantiomeric OFETs were fabricated by spin coating a 150 nm layer onto a pre-patterned SiO_2/Si wafer substrates (insulating layer thickness 230 nm) from 15 mg/ml solution in toluene to form a bottom-gate, bottom-contact device. The surface of the wafer was treated by a self-assembled monolayer (SAM) octadecyltrichlorosilane (OTS, Sigma Aldrich) through vapour deposition and the Au source and drain electrodes were treated by a pentafluorobenzene thiol SAM (PFBT, Sigma Aldrich) to reduce the contact resistance. Annealing conditions were 110°C for 30 minutes under nitrogen. OFET channel lengths L and widths W were 10 μm and 1 cm respectively. The output and transfer characteristics were recorded by Agilent 4156C semiconductor parameter analyzer. Mobility μ_{SAT} and threshold voltage V_T were extracted from the saturation regime transfer characteristics at V_D = -60 V using $I_D = \mu_{SAT}[C_iW/2L](V_G - V_T)^2$, where V_D, V_G, I_D and C_i are the drain voltage, gate voltage, drain current and insulator capacitance per unit area, respectively (see Supplementary Information).[7,12] AFM was performed on silica substrates by the tapping mode of Veeco Multimode. 10 mW/cm^2 CP illumination was generated from the UV lamp (Honle UV technology; UV head 250) through a UV linear polarizer and quarter-wave plate (Comar Optics). Transfer characteristics under illumination were

recorded using the experimental sequence of dark, matched CP light, mismatched CP light, and then dark. Time dependent modulation was with a Stanford Research Systems SR540 optical chopper. The OFETs were unstable under ambient operation, measurements being conducted in a nitrogen-filled glovebox.

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Supplementary Information

Accompanies this Letter.

Author Contributions

Y.Y. carried out thin film and device fabrication and transistor, photo-transistor, AFM and spectroscopic studies. R.C.d.C. carried out the helicene synthetic preparation. A.J.C. and M.J.F. devised and oversaw the study. M.J.F. obtained the funding. Y.Y, A.J.C. and M.J.F. wrote the paper.

Additional Information

The authors declare no competing financial interests.

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Figure Legends

Figure 1: (**a**) Molecular structure of the two helically-chiral forms of the organic semiconductor 1-aza[6]helicene, where (+)-1-aza[6]helicene is the right-handed form and (-)-1-aza[6]helicene is the left-handed form; (**b**) Bottom-gate, bottom-contact circularly polarized light-detecting organic field-effect transistor (OFET) in which the active organic semiconductor material is either (+)-1-aza[6]helicene or (-)-1-aza[6]helicene.
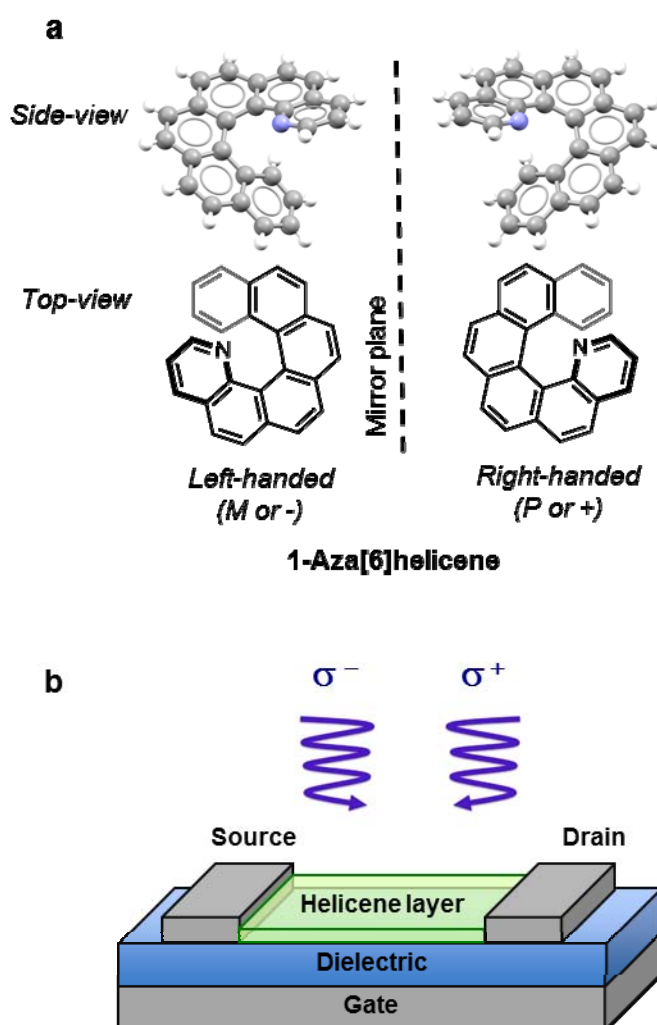
Figure 2: **(a)** AFM of annealed (+)-1-aza[6]helicene thin films on silica substrates. **(b)** Circular dichroism (CD) of annealed (+)-1-aza[6]helicene and (-)-1-aza[6]helicene thin films on silica substrates
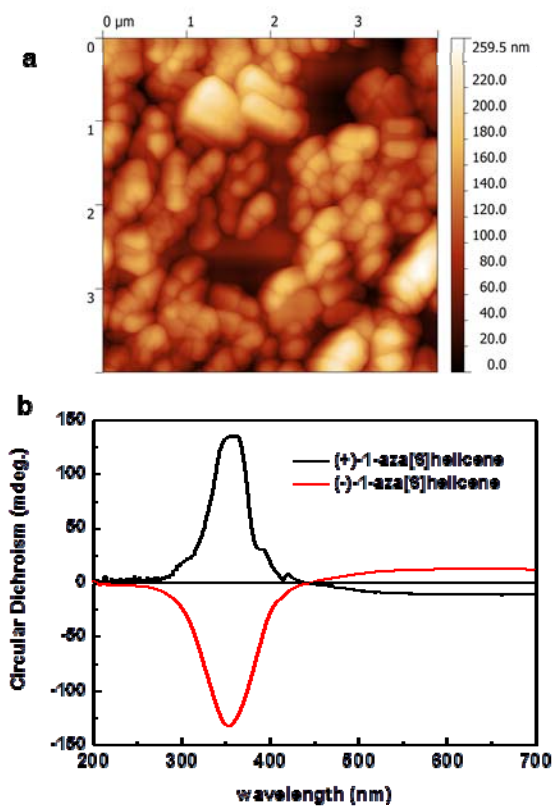
Figure 3: (**a**) Output characteristics and (**b**) transfer characteristics (at $V_D = -60$ V) of fresh (red squares) and annealed (black squares) (+)-1-aza[6]helicene OFETs.
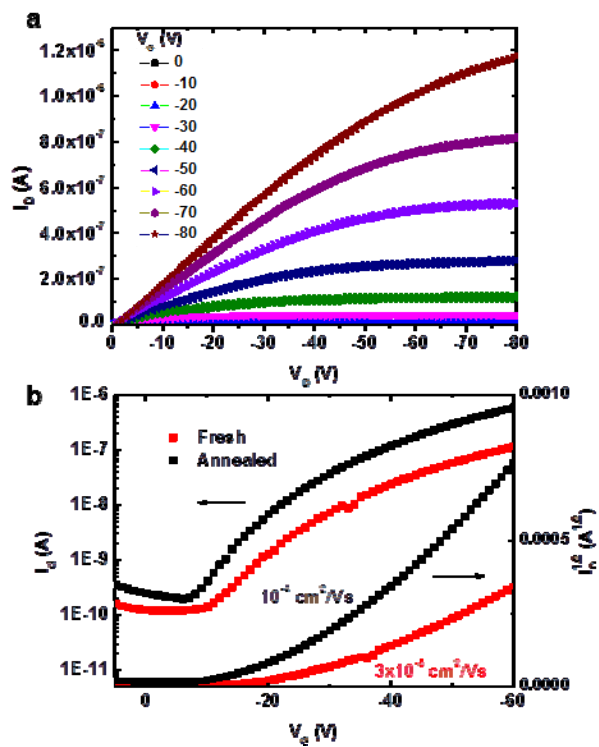
Figure 4: Response of annealed (**a**) (+)-1-aza-[6]helicene and (**b**) (-)-1-aza-[6]helicene OFETs to exposure to left-handed (black squares) and right-handed (blue circles) CP light; The intensity of the CP illumination was 10 mW/cm^2 at 365 nm; The transfer characteristics were measured at V_D = -60 V. Transfer characteristics in the absence of CP illumination (red triangles) are also shown as a reference. Error bars indicate ± one standard deviation of the average response of 4 different OFETs of each enantiomer.
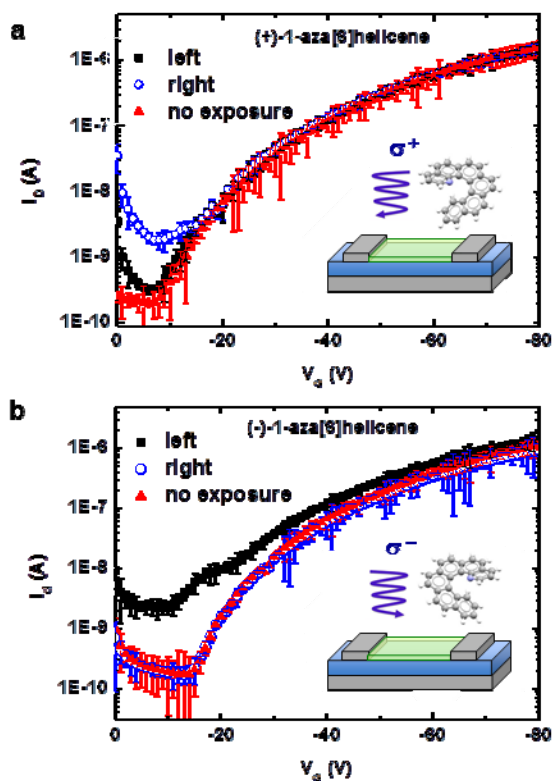
Figure 5: Time dependent response of the drain current I_D of an annealed (+)-1-aza-[6]helicene OFET to right-handed CP illumination at a frequency of 98 Hz; The current was measured at a constant drain and gate bias of $V_D = -60$ V and $V_G = -10$ V respectively.