# Controlling anisotropic properties by manipulating the orientation of chiral small molecules

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# Abstract

Chiral π-conjugated molecules bring new functionality to technological applications and represent an exciting, rapidly expanding area of research. Their functional properties, such as the absorption and emission of circularly polarised light or the transport of spin-polarised electrons, are highly anisotropic. As a result, the orientation of chiral molecules critically determines the functionality and efficiency of chiral devices. Here we present a strategy to control the orientation of a small chiral molecule (2,2'-dicyano[6]helicene, **CN6H**): the use of organic and inorganic templating layers. Such templating layers can either force **CN6H** molecules to adopt a face-on orientation and self-assemble into upright supramolecular columns oriented with their helical axis perpendicular to the substrate, or an edge-on orientation with parallel-lying supramolecular columns. Through such control, we show that low- and high-energy chiroptical responses can be independently 'turned on' or 'turned off'. The templating methodologies described here provide a simple way to engineer orientational control, and by association, anisotropic functional properties of chiral molecular systems for a range of emerging technologies.

# Main text

Conjugated organic materials have enabled considerable advances in consumer electronics, in part due to their low cost, tunable optical and electronic properties, and compatibility with flexible, large-area device architectures. The performance of such devices is not only influenced by molecular structure, but how these molecules assemble in the solid state, and how the resultant molecular assemblies are oriented with respect to device-relevant interfaces. Molecular chirality is increasingly recognised as a strategy to expand the functionality of such devices, enabling the realisation of next-generation displays, polarisation selective photodetectors, enantioselective biosensors and room-temperature spintronic devices.[1–6] When considering appropriate chiral conjugated small molecule materials for such applications, the archetypal example is the family of fused aromatics called the helicenes. These molecules are comprised of $n \geq 5$ *ortho*-fused angularly arranged benzene rings, which give rise to a non-planar screw-shaped skeleton.[7] The intrinsically chiral and fully conjugated molecular structure of the helicenes affords them outstanding anisotropic chiroptical and charge transport properties, as well as the ability to filter electron spins at room temperature.[8–13]

Whilst structure-property relationships are still emerging, a critical parameter is the orientation of the helical molecular axis (and corresponding supramolecular chiral assembly) relative to other interfaces (see Figure 1a). This is due to the highly anisotropic nature of chiral-dependent properties. For example, in devices that make use of the Chiral Induced Spin Selectivity (CISS) effect, the orientation of chiral π-conjugated molecules with respect to the charge injection electrodes will dictate the spin polarisation of transmitted electrons.[14] Meanwhile, in photonic devices that make use of chiral cholesteric liquid crystalline materials, the pitch, thickness and orientation of the supramolecular helix determines the magnitude of the chiroptical response, through Bragg reflection and scattering.[15,16] As such, liquid crystal alignment layers – such as rubbed polyimide – are required to guide and control the growth of an ordered chiral structure.[17–19] Despite the clear influence of molecular (and supramolecular) orientation on the (chir)optoelectronic properties of chiral thin films, it remains challenging to effectively control the orientation of molecules relative to a substrate – especially when working with materials that do not demonstrate liquid crystal behaviour. Beyond the elegant examples of monolayer (2D) chiral molecule self-assembly on conductive (mainly metallic) surfaces[20–27], strategies to control chiral molecule orientation more widely – particularly in bulk thin films – are yet to be established.

Here we make use of organic (3,4,9,10-perylenetetracarboxylic dianhydride, PTCDA) and inorganic (Copper Iodide, CuI) templating layers to control the supramolecular assembly of **2,2'-dicyano[6]helicene** (**CN6H**, see Figure 1b – d) in thin films. These templating layers have been shown to strongly influence the packing of planar aromatic systems[28–31], and here we extend their use to control the assembly of chiral conjugated small molecules. For PTCDA, we find that π-π interactions force the supramolecular helical columns of **CN6H** to stand upright, with the helical axis perpendicular to the substrate. On the other hand, the same supramolecular columns adopt a flat-lying orientation on CuI, which we attribute to electrostatic interactions between the negatively charged CuI surface and the electron-poor aromatic rings of **CN6H**. The supramolecular orientation is shown to have a profound impact on the chiroptical response, with flat-lying columns demonstrating intense circular dichroism (CD) for electronic transitions polarised parallel to the **CN6H** columnar axis and upright supramolecular columns demonstrating strong CD for transitions polarised perpendicular. This study presents an elegant approach to control the supramolecular organisation of chiral small molecules that can be adapted to other chiral materials and incorporated into device fabrication protocols for a range of next-generation technologies.

# Results and discussion

As the bulk packing of helicenes can be complex, to achieve effective control of the molecular and supramolecular orientation it was first important to identify a representative helicene with a well-defined bulk packing.[32–34] **CN6H** was identified through a search of the Cambridge Structural Database and crystallises as a conglomerate in the hexagonal space group $P6_122$.[35] Crystal structure prediction (see Supplementary Information, SI, for details) reveals that the experimentally observed $P6_122$ polymorph is 3.3 kJ mol$^{-1}$ lower in energy than all remaining polymorphs, which means that polymorphism is highly unlikely. The most thermodynamically stable $P6_122$ polymorph stacks in homochiral supramolecular columns (Supplementary Figure 1), with the same handedness as the enantiopure molecule and where the helical axis is oriented along the crystallographic $c$-axis.[35] The unit cell of **CN6H** is particularly anisotropic due to the extended $c$-axis (*ca* 70 Å).[35] Charge-carrier mobility predictions (Supplementary Discussion 1) suggest that charge transport is strongly anisotropic, with maximum charge transport observed along the $c$-axis, *i.e.* along the homochiral columns. This emphasises the importance of controlling the molecular orientation for high performance devices. The synthesis and structure determination of **CN6H** is reported in the SI (Supplementary Notes, Supplementary Discussion 1).

With enantiopure **CN6H** in hand, we used Organic Molecular Beam Deposition (OMBD) to deposit thin films of thickness *ca* 78 nm on templated and non-templated substrates. We have optimised the procedure for the growth of the templating layers[30], and here we follow that same protocol. First, we studied the effect of the templating layers on the absorption and photoluminescence spectra of [*M*] and [*P*] **CN6H** (Figure 2). When analysing these spectra, it is important to consider the absorption of the neat templating layers (i.e., 20 nm of PTCDA and 100 nm of CuI, see the dashed lines in Figure 2). The electronic transitions of **CN6H** result in a vibronic sequence of absorption peaks below 400 nm (Extended Data 1). As the thickness of **CN6H** is the same in all three cases (78 nm), once the neat templating layers (Extended Data 2) have been subtracted, any apparent differences in absorption intensity we attribute to changes in (supra)molecular orientation.

Hypothesised differences in molecular orientation are also apparent in atomic force microscopy (AFM) and scanning electron microscopy (SEM) images. As can be seen in both the AFM and planar view SEM (Figure 2b, Extended Data 5 and 6), on non-interacting surfaces, **CN6H** forms small, regularly shaped domains with lateral grain sizes 58 ± 12 nm.

The root-mean-squared roughness ($R_q$), calculated from the total window of the AFM images, is $6.9 \pm 0.6$ nm. PTCDA-templated **CN6H** forms larger molecular clusters, with random shapes and surface profiles, which results in an increased $R_q$ ($10.8 \pm 0.6$ nm) and increased grain size ($105 \pm 59$ nm). Meanwhile, **CN6H** adopts a distinct platelet-like morphology on CuI, where grains elongate into regularly shaped rectangular domains with lateral grain sizes $153 \pm 42$ nm and heights of ~ 6 nm. The consistency of these domains results in significantly smoother films ($R_q = 1.5 \pm 0.3$ nm). Cross-sectional profiles of these platelets reveal a terrace-like topography, with step-spacing ~ 4 nm.

Given these observations, we sought to characterise differences in the molecular orientation of the supramolecular columns of templated and non-templated **CN6H** thin films using X-ray diffraction (XRD, Figure 2c). To assign crystallographic planes and index peaks in the XRD we used the known crystal structure,[35] from which we simulated a powder XRD profile (Supplementary Figure 2, Supplementary Table 1). In this one-dimensional (1D) XRD experiment, only out-of-plane diffraction from lattice planes with some alignment parallel to the substrate are probed (the $Q_z$ direction in reciprocal space). We illustrate the alignment of the planes associated with the highest intensity simulated XRD reflections for face-on and edge-on oriented **CN6H** (see Supplementary Discussion 2). We expect to see XRD reflections from the (0 0 6), (1 0 17) and (1 0 22) lattice planes at $2\theta = 7.5°$, $24°$ and $30°$ ($Q = 0.53$ Å$^{-1}$, $1.68$ Å$^{-1}$ and $2.09$ Å$^{-1}$) respectively for face-on oriented **CN6H** and the (1 0 0) reflection at $10.5°$ ($Q = 0.75$ Å$^{-1}$) for edge-on oriented **CN6H**, as these planes would be aligned either parallel or almost parallel to the substrate for each orientation. PTCDA-templated **CN6H** shows weak reflections at $24°$ and $30°$, corresponding to the (1 0 17) and (1 0 22) planes expected for a face-on orientation. CuI-templated **CN6H** displays a high intensity, narrow peak from the (1 0 0) plane at $10.5°$, giving an initial indication of strong preferential orientation in this film (Figure 2c). Meanwhile the XRD profile of untemplated **CN6H** follows that of the powder reveals two low intensity peaks at $10.5°$ and $24°$ related to reflections from the (1 0 0) and (1 0 17) lattice planes suggesting multiple orientations of the **CN6H** supramolecular columns are present in the film (Figure 2c). The (0 0 6) and (1 0 5) reflections depicted in Supplementary Discussion 2 are expected at $7.5°$ and $12.2°$ respectively, but are not observed in any of the templated XRD profiles because they are either too weak or not aligned parallel to the substrate.

To further understand the XRD data, we evaluated the crystallographic orientation and degree of molecular order using two-dimensional (2D) grazing incidence wide angle X-ray scattering (GIWAXS) (Figure 3a-c, Extended Data 7). We combined the 2D scattering patterns with simulated 2D patterns for various orientations of **CN6H** using the *simDiffraction* Matlab toolbox and the established crystal packing.[35,36] Full details for the experimental and simulated GIWAXS are provided in the methods section. We first compared the orientation of **CN6H** thin films by indexing 1D in-plane and out-of-plane Q-dependent intensity profiles sampled from the 2D GIWAXS patterns (Supplementary Table 2). As expected, the out-of-plane profiles closely resemble the XRD patterns in Figure 2c. Diffraction patterns from the bare substrate and templating layers are provided in Supplementary Figure 10. The 2D GIWAXS pattern of **CN6H** on bare silicon (Figure 3a) consists of several Debye-Scherrer diffraction rings, with the highest intensities originating from the (1 0 0), (1 0 5) and (1 0 17) lattice planes at Q values of 0.75 $\text{Å}^{-1}$, 0.87 $\text{Å}^{-1}$ and 1.68 $\text{Å}^{-1}$ respectively. Consistent with the weak intensity XRD peaks (Figure 2c), the appearance of complete diffraction rings indicates a low degree of molecular order and randomly oriented **CN6H** crystallites (Extended Data 8). The experimental data can be well-matched with the simulated scattering pattern from a very broad distribution of molecular orientations (Figure 3d, g). For PTCDA-templated **CN6H**, the scattering appears as broad arcs rather than complete rings, confirming preferential orientation (Figure 3b). The (1 0 17) and (0 0 $l$) lattice planes scatter more strongly in the out-of-plane ($Q_z$) direction and the (1 0 0) reflection is more prominent in-plane, which indicates the supramolecular columns of **CN6H** adopt a face-on orientation. This interpretation is supported by our simulations, with scattering from the (0 0 6) plane centred out-of-plane and a reasonably broad distribution of crystallite orientations (Figures 3e, 3h and Extended Data 8). The 2D GIWAXS pattern of CuI-templated **CN6H** consists of the distinctive, high intensity diffraction features (so-called Bragg spots) typically observed for systems with a high degree of molecular order and preferential orientation. In Q-space these Bragg spots occupy positions along layer lines parallel to the substrate (indexed in Supplementary Discussion 3), which are comparable to those typically observed in fibre diffraction measurements.[36,37] The observed scattering patterns can be simulated by having the (1 0 0) plane oriented parallel to the substrate in an edge-on orientation with a very narrow distribution around the dominant orientation (i.e., a high degree of order). The degree of molecular order and orientation of supramolecular columns of **CN6H** were further evaluated by studying the angular distribution of the scattering intensity from specific lattice planes, discussed further in Supplementary Figure 4.

Taken together, the AFM, SEM, GIWAXS, XRD and simulated crystallographic scattering patterns indicate three distinct morphologies and structures. In the absence of templating layers (i.e., on non-interacting substrates), there is no preferential order and a broad distribution of orientations. On PTCDA, the *c*-axis is nearly orthogonal to the substrate, with the supramolecular columns adopting a mainly upright, face-on orientation, although more tilted orientations are present (see Figure 3h, Extended Data 9). On CuI, the *c*-axis is oriented parallel to the substrate, with the supramolecular columns adopting a flat-lying, edge-on orientation (Extended Data 10). This molecular packing is not impacted by film thickness or post-deposition thermal annealing (Supplementary Figures 5 and 6).

Our interpretation of the mechanism that underpins the upright configuration of the supramolecular columns on PTCDA is as follows: PTCDA is understood to lie flat on non-interacting substrates, such that the $\pi$-electron rich conjugated core aligns parallel with the substrate surface. In this configuration, intermolecular interactions between the $\pi$-electron density of PTCDA and **CN6H** orient the **CN6H** molecules to align with the c-axis of the unit cell, nearly perpendicular to the substrate. CuI thin films grown at elevated substrate temperatures can contain grains with either $Cu^+$ and $I^-$ terminations on the surface, which persist when the films are cooled to room temperature.[30,38] The $I^-$ termination is energetically favoured along the (111) plane of CuI (Extended Data 10), which indicates that the surface of the CuI layer used here has a high electron density with a weak dipole normal to the substrate surface.[30,39] Considering a typical quadrupolar model for the helicene, the **CN6H** can arrange itself perpendicular to the substrate in a T-shape between the aromatic rings and the surface (Figure 1a). In this configuration, the repulsive Coulomb interactions between the negatively charged CuI surface and the aromatic rings in **CN6H** are minimised, which results in the alignment of **CN6H** molecules with their *c*-axis of the unit cell parallel to the substrate (i.e., flat-lying, edge-on oriented supramolecular columns). To better understand the role of the cyano groups on molecular packing on CuI surfaces, we have used Density Functional Theory to investigate the binding interactions in various configurations (Supplementary Discussion 4). These calculations show that the edge-on orientation seen with CN6H may not be unique and could occur in other helicene derivates. However, these calculations also highlight the importance of the helicene crystal structure (e.g., the formation of supramolecular columns) on the molecular packing at surfaces, introducing complexity with using computational calculations of isolated molecules. This suggests that PTCDA and CuI templating should be

suitable for orientation control in other chiral aromatic small molecules, which will provide opportunity to tune charge and spin transport for specific applications and device geometries.

We then evaluated how these distinct molecular and supramolecular orientations impact the chiroptical response of the thin films, given the anisotropic nature of such measurements. The solution-state CD of **CN6H** [*M*] and **CN6H** [*P*] are provided in Supplementary Figure 6. The electronic CD spectra of hexahelicenes are characterised by two intense bands of opposite sign at high and low energy (Figure 4).[40] The transitions associated to the low energy bands (vibronic structure in the range 340-400 nm ) are mainly B-symmetric, while the higher energy ones are mainly A-symmetric (range 270-340 nm, Supplementary Figure 8). These bands have been attributed to transitions mainly polarised along the *bc*-plane (B-band) or the *a*-axis (A-band) of **CN6H**.[40] To ensure our thin film CD spectra were free from linear artefacts, we measured the CD spectrum with the thin films oriented in various configurations with respect to the detector (Supplementary Figure 9), and found the lineshapes/intensities to be identical. In the case of untemplated **CN6H**, the lineshape and relative intensity of the A- and B-bands is comparable to CD spectra of molecules in solution. The same is not true for the CD spectra of templated **CN6H**: with considerable suppression of either the A- (CuI-templated **CN6H**) or B-bands (PTCDA-templated **CN6H**) observed as function of (supra)molecular orientation. The suppressed B-band apparent in the CD spectra of PTCDA-templated **CN6H** is consistent with the fact that transitions with components polarised along the *c*-axis of the unit cell cannot be excited when the helicenes are oriented face-on, as would be expected for upright supramolecular columns. Meanwhile the suppressed A-band observed in CuI-templated **CN6H** is consistent with the **CN6H** adopting an edge-on configuration, and flat-lying supramolecular columns. CD-imaging over a large area (4 × 4 mm) reveals the chiroptical response is incredibly uniform (Supplementary Figure 10), i.e. **CN6H** crystallises into enantiopure domains. To further support this interpretation, we also employed time-dependent approximate second-order coupled-cluster singles and doubles model calculation at the RI-CC2/def2-TZVPP level of theory. The simulated CD response of **CN6H** oriented at different angles to the substrate is qualitatively in agreement with the experimental trend (Supplementary Figure 11), which supported the predicted orientational effect.

In summary, this study presents a simple but highly effective means to engineer a desired chiroptical response without modification of molecular structure. Furthemore, it suggests a means to engineer precise molecular orientations in highly ordered thin films of

chiral chromophores. Given that equivalent anisotropy is observed in other chiral-dependent properties, such as electron spin control through the CISS effect, this versatile strategy to contol molecular orientation should find broad applicability in the rapidly expanding area of chiral technologies.

## Conclusion

While there is a rapidly growing interest in exploiting chiral molecules for technological applications, the highly anisotropic nature of chiral-dependent properties presents an ongoing challenge. Without device compatible methods to orient (non-liquid crystalline) chiral materials in a controlled manner, chiral technologies will not reach their full potential. Beyond this technological need, the self-assembly of chiral molecules on substrates has long intrigued scientists and engineers. Whilst elegant studies have been reported the 2D crystallisation of helicenes on metal surfaces, strategies to control molecular orientation in the bulk have so far remained elusive. We present the an effective strategy to control the orientation of a chiral molecule in the solid state, using organic and inorganic templating layers. Whilst untemplated **CN6H** thin films display very weak preferential molecular orientation, templating allows for the selective formation of (supra)molecular orientations of **CN6H** either parallel or perpendicular to the substrate. The significance of these molecular configurations is showcased by measuring the chiroptical response of the oriented thin films. The orientation and bulk order in the solid state has a profound impact on the chiroptical properties of helicenes as their electronic transitions are polarised along different axes of the unit cell. This versatile and simple approach for manipulating molecular orientation in thin films should be translatable to a range of other chiral materials. Furthermore, uniform molecular orientations are expected to have equally strong impact on other anisotropic chiral properties, such as CISS. As such, we believe this methodology will allow for the integration of chiral small molecules into a range of next-generation devices, such as the active layers of light emitting diodes or photodetectors, or as charge transport layers for spin-polarised carrier injection and extraction.

## Acknowledgements

## Author contribution statement

J.W., M. J. F and S. H developed the concepts behind this research. F. S. synthesised the chiral small molecule (**CN6H**). J.W. and D-K. K. fabricated the samples as well as performing the spectroscopic experiments, 1D X-Ray Diffraction and Atomic Force Microscopy. R. C. K and J. A. Smith performed the GIWAXS and X-Ray simulations. J. A. Schmidt, K. J., J. N., E. R. J., L. M. L., E. W and A. A. A. performed the quantum chemical calculations and CSP. F. S. and T. M. performed the TD-DFT and CD simulations. J. W., M. J. F., S. H., K. J., J. N. supervised the study and obtained funding. All authors contributed to the writing of the manuscript.

## Competing Interests Statement

The authors declare the following competing financial interest(s): M. Fuchter is an inventor on a patent concerning chiral blend materials (WO2014016611).

## Tables

N/A

# Figure Legends/Captions

**Figure 1: A schematic describing the motivation for this work and a description of the materials used**. (a) A cartoon describing the impact of random molecular orientations and precise molecular orientations on the anisotropic properties of chiral functional materials, and an illustration of the face- and edge-on molecular orientations, (b, c, d) Chemical structures of materials used in this work, including PTCDA, CuI and CN6H [*P*] and [*M*].

**Figure 2: Spectroscopic and morphological characterisation of untemplated and templated CN6H thin films.** (a) Absorbance of untemplated (quartz) and templated (PTCDA, CuI) **CN6H** [*M*] (solid lines) and the bare substrates (dashed lines), (b) Atomic force microscopy images (scale bar is 1 µm) of untemplated and templated **CN6H [*M*]** and (c) corresponding XRD pattern of untemplated (Si) and templated (PTCDA, CuI) **CN6H [*M*]**. In the AFM, features of randomly oriented (untemplated), upright (PTCDA templated) and flat-lying (CuI templated) CN6H columns are evident in the surface topography. In the XRD, the Substrate peaks are indicated with asterisks and the planes involved with reflections for PTCDA-templated **CN6H** (1 0 17) and (1 0 22) and for CuI-templated **CN6H** (1 0 0) are labelled. Comparable data for **CN6H** [*P*] is provided in the Extended Data (3 and 4). (d) Illustration of (0 0 *l*) and (*h* 0 0) lattice planes for **CN6H** and face-on and edge-on orientations visualised using Mercury[41].

**Figure 3: Experimental and simulated 2D GIWAXS diffraction patterns of untemplated and templated CN6H thin films.** Experimental and simulated 2D GIWAXS patterns, and proposed molecular packing of untemplated (**a-c**), PTCDA templated (**d-f**) and CuI templated (**g-i**) **CN6H** [*M*]. The 2D GIWAXS pattern of untemplated **CN6H** (**a**) is composed of several Deby-Scherrer rings which are replicated by simulating a very broad distribution of molecular orientations (**b**), characteristic of randomly oriented crystallites (**c**). For PTCDA-templated **CN6H**, the 2D scattering pattern consists of broad arcs (**d**) which are reproduced by simulating a reasonably broad distribution of crystallite orientations with the (0 0 6) plane aligned parallel to the substrate (**e**). This is indicative of a mainly upright, face-on **CN6H** molecular orientation with the *c*-axis aligned perpendicular to the substrate (**f**). The 2D GIWAXS pattern of CuI templated **CN6H** is composed of distinct Bragg spots (**g**) which are replicated by simulating a very narrow distribution of crystallite distributions with the (1 0 0) plane aligned parallel to the substrate (**h**). This is consistent with a highly ordered edge-on configuration with the *c*-axis aligned parallel to the substrate (**i**). Comparable data for **CN6H** [*P*] is provided in the Extended Data (7). The supramolecular columns of CN6H were visualised using Mercury[41].

**Figure 4: The molecular origins of optical transitions in CN6H and chiroptical spectra acquired for untemplated and templated thin films.** (a) Symmetries of the A- and B-symmetric transitions of the **CN6H** molecule. The a, b and c-axes of the unit cell are indicated in the inset. (b) Experimental CD spectra for untemplated (quartz) and templated (PTCDA, CuI) **CN6H** [*M*]. Comparable data for **CN6H** [*P*] is provided in Supplementary Figure 7. The spectral ranges of the A- and B-symmetric transitions are indicated with blue and grey shaded boxes. In the case of upright supramolecular columns (PTCDA templated), A-symmetric transitions are strengthened, whilst B-symmetric transitions are strengthened for flat-lying supramolecular columns (CuI templated).

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## Methods

### Thin film preparation

CN6H was synthesised as described in the Supporting Information and used with no further purification. All thin films (templating layers, CN6H layers) were grown by organic molecular beam deposition in a Kurt J. Lesker Spectros 100 system at a base pressure of $3 \times 10^{-7}$ mbar. The materials were evaporated from powders held in separate Knudsen cells at a rate of either 0.1 or 0.5 Å s$^{-1}$ on clean silicon and quartz substrates. The substrates were cleaned in an ultrasonic bath with acetone and isopropyl alcohol (Sigma-Aldrich), followed by 10 minutes in a UV ozone cleaner (Ossila). These rates were chosen based on the quantity of material and our previous investigations into organic and inorganic templating layers.[1] The film thickness and deposition rates were monitored using quartz crystal microbalances sensors (INFICON) placed near the sources and substrates. The thicknesses of the PTCDA ($t$ = 20 nm) and CuI ($t$ = 100 nm) layers have been optimised in our previous work.[1] Unless otherwise stated, the substrates were all kept at room temperature during deposition with the temperature monitored by a thermocouple placed near the substrate. In the case of CuI, to promote the growth of large grains and pinhole-free films, the substrates were held at 100 °C.

### Photophysical characterisation

Absorption spectra of films deposited on clean quartz substrates were measured by a Cary 300 UV–vis spectrometer (Agilent Technologies). The CD data were collected using a Chirascan (Applied Photophysics) instrument.

### Atomic Force Microscopy and Scanning Electron Microscopy

Surface characterisation of the films was carried out using tapping mode atomic force microscopy with an Asylum Research MFP-3D microscope. Images were processed using the open-source software Gwyddion.[2] Roughness values were calculated using the root mean square roughness of the total AFM image, with the standard deviation of three separate images being quoted as the error. Lateral grain sizes were calculated from the processed AFM images using a watershed to define the grain boundaries.

### XRD and GIWAXS

X-ray diffraction (XRD) scans in the fixed $\theta$–$2\theta$ geometry were conducted on a Philips X'Pert Pro Panalytical using a Cu Kα source ($\lambda$ = 1.5406 Å) at a current of 40 A and voltage of 40 V.

Powder XRD and crystal packing images were simulated in VESTA using a previously reported crystallographic information file (CIF)[3].

GIWAXS measurements were performed using a Xeuss 2.0 (Xenocs) system equipped with a liquid gallium MetalJet (Excillum) source producing 9.24keV X-rays. In this experiment, high intensity X-rays are directed at sample surfaces in a grazing incidence configuration (incident angle = 0.15°) and the scattered X-rays are detected by a vertically offset Pilatus3R 1M (Dectris) 2D X-ray detector positioned ~300mm from the sample. The sample to detector distance was calibrated using a silver behenate standard. During measurement, the sample chamber and flight tubes were held under vacuum to minimise background air scatter.

Data was corrected and reduced using the GIXSGUI Matlab toolbox[4]. All 2D scattering patterns were processed using the PyFAI python library. 2D GIWAXS simulations were performed with the same CIF using the WAXS package in the *SimDiffraction* Matlab toolbox[5]. All simulations used a uniaxial model with a Pseudo-Voigt distribution in the out-of-plane direction. Key simulation parameters corresponding to the molecular ordering and orientation of **CN6H** on each substrate are provided in Supplementary Table 2.

**Computational calculations**

Crystal structure prediction was performed using the CrystalPredictorII[6,7]/DMACRYS[8] workflow. The tentative crystal structures were subsequently relaxed at the B86bPBE/DZP level with the XDM dispersion correction using the SIESTA program. This was followed by B86bPBE-XDM single-point energy calculations using the projector augmented-wave (PAW) method with the Quantum ESPRESSO program.[9]

Charge-carrier mobility calculations were performed in GAUSSIAN16[10] at a B3LYP/6-31G(d) level of theory[11][12] using non-adiabatic semiclassical Marcus theory[13] (assuming hopping transport) and an outer reorganisation energy of 0.3 eV. For further details please refer to the Supporting Information.

Excited-state calculations were performed by the time-dependent, second-order approximate coupled-cluster singles and doubles model, in conjunction with the resolution-of-identity method (RI-CC2 method) with the def2-TZVPP basis-set using Turbomole. The UV–Vis and CD spectra were calculated by the same level of theory and the rotational strengths obtained in length gauge were expanded by Gaussian functions, where the bandwidth at $1/e$ height is fixed at 0.5 eV, unless otherwise stated.

**Crystal Structure Prediction**

The 2,2'-dicyano-[6]helicene molecule was geometry optimised using GAUSSIAN16[10] at B3LYP[14]/6-31G(d,p) level of theory, tight convergence criteria and assuming no symmetry. Based on the optimised geometry, the charges from electrostatic potentials using a grid-based method (ChelpG)[15] were computed. Based on the optimised helicene geometry and point charges, the CRYSTALPREDICTOR II[6,7] software package was used to generate tentative polymorphs within a polymorphic range of 20 kJ mol$^{-1}$. The CSP search was performed with only one molecule in the asymmetric unit ($Z'$=1) and assuming rigid molecules. 500,000 crystal minimisations were performed across the following space groups: P1, P$\overline{1}$, P2$_1$, P2$_1$/c, P2$_1$2$_1$2, P2$_1$2$_1$2$_1$, Pna21, Pca2$_1$, Pbca, Pbcn, C$_2$/c, Cc, C2, Pc, Cm, P2$_1$/m, C2/m, P2/c, C222$_1$, Pmn2$_1$, Cmc2$_1$, Aba2, Fdd2, Iba2, Pnna, Pccn, Pbcm, Pnnm, Pmmn, Pnma, Cmcm, Cmca, Fddd, Ibam, P4$_1$, P4$_3$, I$\overline{4}$, P4/n, P4$_2$/n, I4/m, I4$_1$/a, P4$_1$2$_1$2, P4$_3$2$_1$2, P$\overline{4}$2$_1$c, I$\overline{4}$2d, P3$_1$, P3$_2$, R3, P$\overline{3}$, R$\overline{3}$, P3$_1$21, P3$_2$21, R$\overline{3}$c, R3c, P6$_1$, P6$_3$, P6$_3$/m, P2$_1$3, Pa$\overline{3}$, P222$_1$, Pba2, P6$_1$22. All stable crystal structures were subsequently clustered to remove duplicates using the CCDC COMPACK[16] executable.

All tentative polymorphs obtained from the CSP search were relaxed in DMACRYS[8] using distributed multipoles and the repulsion-dispersion potential to the Williams 1999 (W99) parameters.[17] Upon energy re-ranking using DMACRYS, the experimentally observed P6$_1$22 polymorph resulted in the 38$^{th}$ lowest-lying polymorph. All 38 lowest-lying structures were periodically relaxed with the SIESTA program[18,19] using the B86bPBE functional[20,21], the double-zeta plus polarisation (DZP) basis set, and the exchange-hole dipole-moment (XDM) dispersion correction [22–24]. Subsequent single-point energy calculations were peformed with the Quantum ESPRESSO program[25] and the projector augmented-wave method[26], also using B86bBPE-XDM. All parameter settings were consistent with our previous work.[9]

**Charge-carrier Mobility Calculations**

The single molecule in the asymmetric unit was geometry relaxed at the B3LYP[11,12]/6-31G(d) level of theory. The relaxed molecule was then projected onto equivalent positions using the crystal symmetry operations to construct a 3 x 3 x 3 supercell. The transfer integrals between all pairs of molecules within a 15 Å centre-of-mass to centre-of-mass cut-off. The transfer integral was calculated by projecting the orbitals of a pair of molecules onto a basis set defined by the unperturbed orbitals of the individual molecules.[27] The electron and hole Marcus charge-transfer rates in all directions were computed with non-adiabatic Marcus theory[13] assuming no energetic disorder and by solving the Master equation. An outer-sphere

reorganisation energy of 0.30 eV. The inner-sphere reorganisation energy was computed based on the single molecule and using the four-point method.[28] The absolute value for the outer-sphere reorganisation energy is not known, the calculated values of the charge mobility cannot be considered as absolute. However, the calculated mobilities do allow direct comparison between different crystal structures and transport directions where the same outer-sphere reorganisation energy has been used.

## Data availability

Data for the main and extended figures are available at: 10.14469/hpc/10763

## Code availability

N/A

## Methods-only references

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