Controlling anisotropic properties by manipulating the orientation of chiral small molecules

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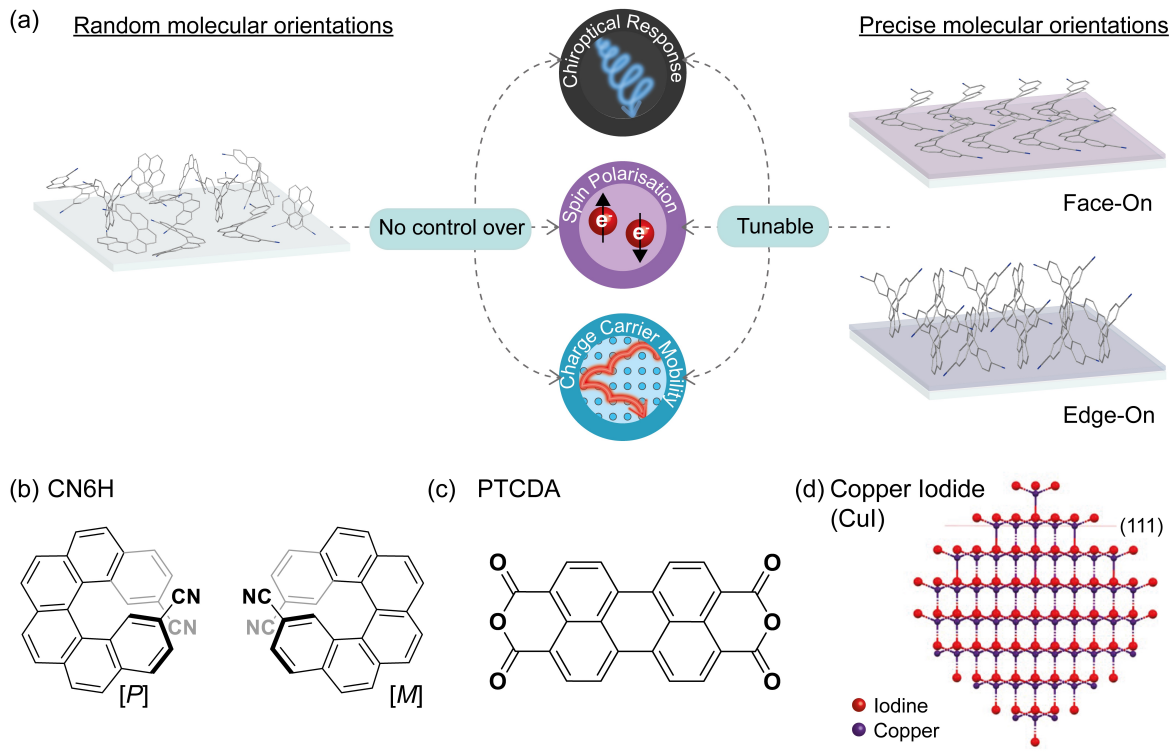

Figure 1: A schematic describing the motivation for this work and a description of the materials used. (a) A cartoon describing the impact of random molecular orientations and precise molecular orientations on the anisotropic properties of chiral functional materials, and an illustration of the face-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

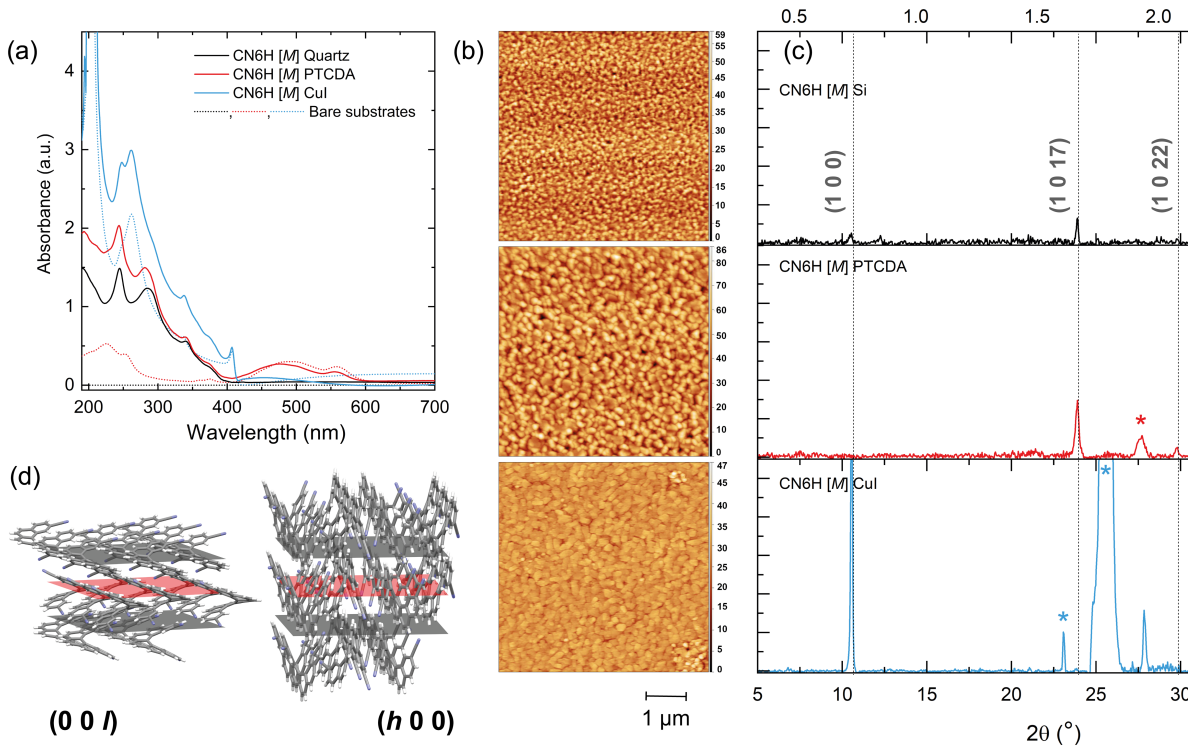

Figure 2: Spectroscopic and morphological characterisation of untemplated and templated CN6H thin films. (a) Absorbance of untemplated (quartz) and templated (PTCDA, CuI) **CN6H** [*M*] (solid lines) and the bare substrates (dashed lines), (b) Atomic force microscopy images (scale bar is 1 µm) of untemplated 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].

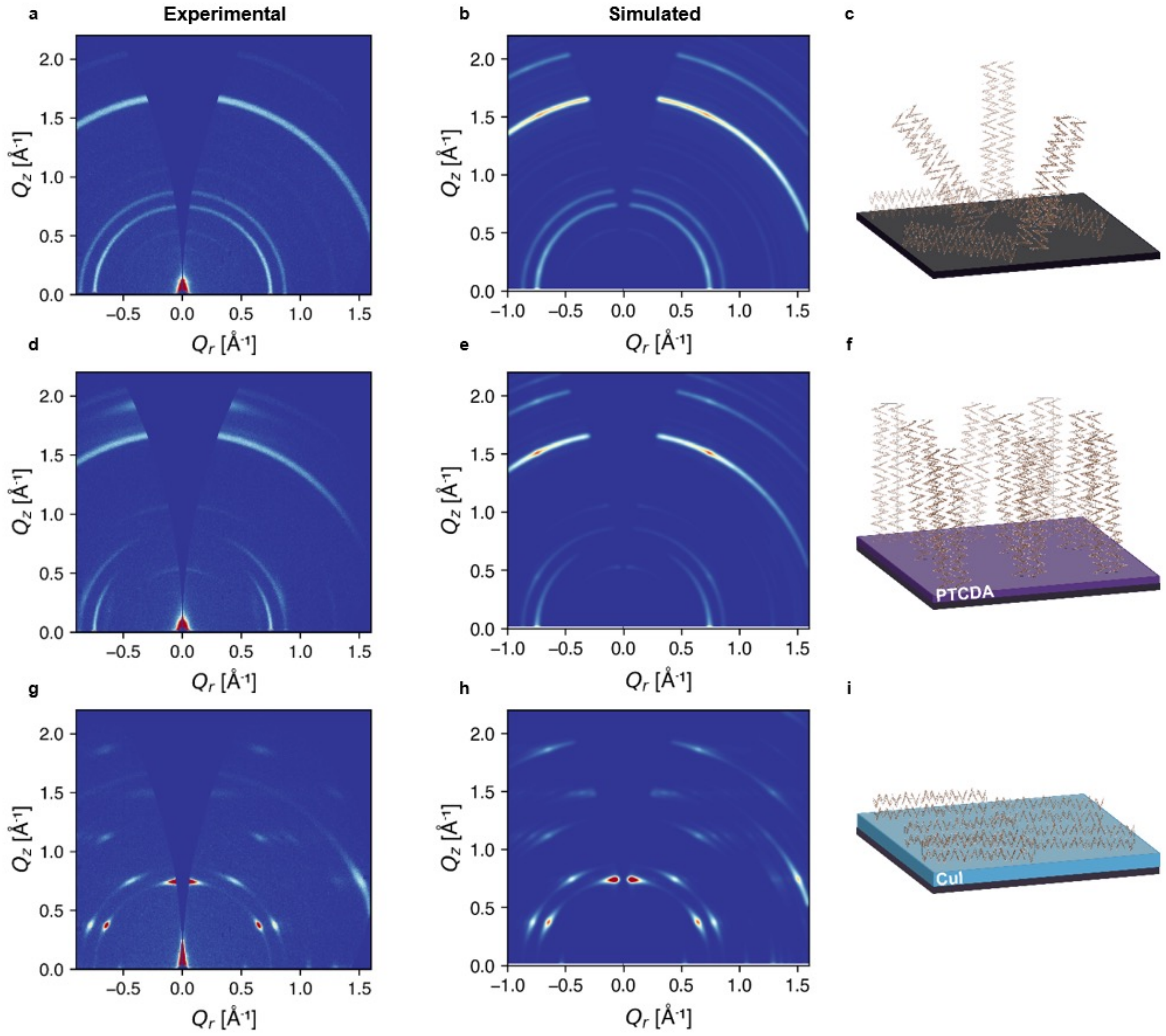

Figure 3: Experimental and simulated 2D GIWAXS diffraction patterns of untemplated and templated CN6H thin films. Experimental and simulated 2D GIWAXS patterns, and proposed molecular packing of untemplated (**a-c**), PTCDA templated (**d-f**) and CuI templated (**g-i**) **CN6H** [*M*]. The 2D GIWAXS 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].

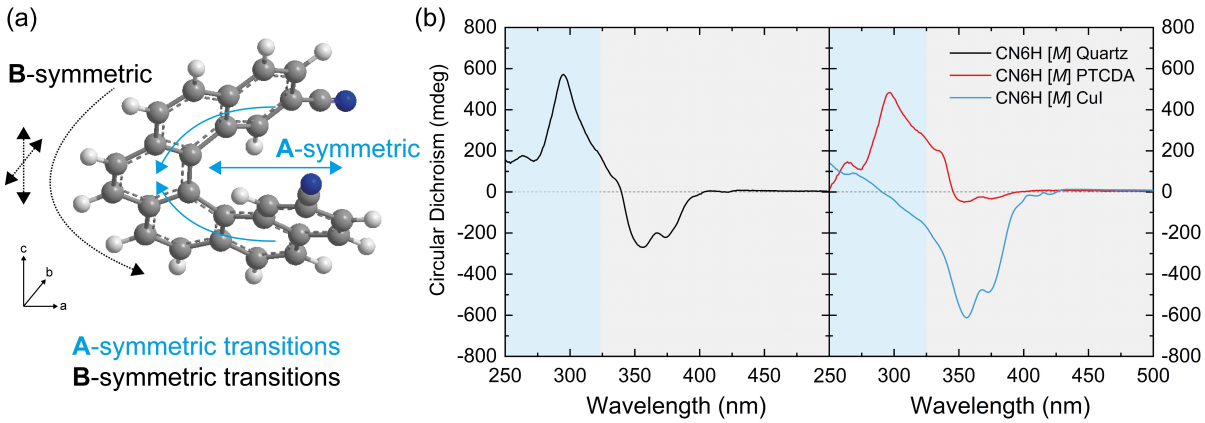

Figure 4: The molecular origins of optical transitions in CN6H and chiroptical spectra acquired for untemplated and templated thin films. (a) Symmetries of the A- and B-symmetric transitions of the **CN6H** molecule. The a, b and c-axes of the unit cell are indicated in the inset. (b) Experimental CD 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).