

## Supplementary Material

### Weak Intermolecular Forces, but High Melting Points

*Jiabin Gao,<sup>A</sup> Djamal Djaidi,<sup>A</sup> Christopher E. Marjo,<sup>B</sup> Mohan M. Bhadbhade,<sup>B</sup> Alison T. Ung,<sup>C</sup> and Roger Bishop<sup>A,D</sup>*

<sup>A</sup>School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia.

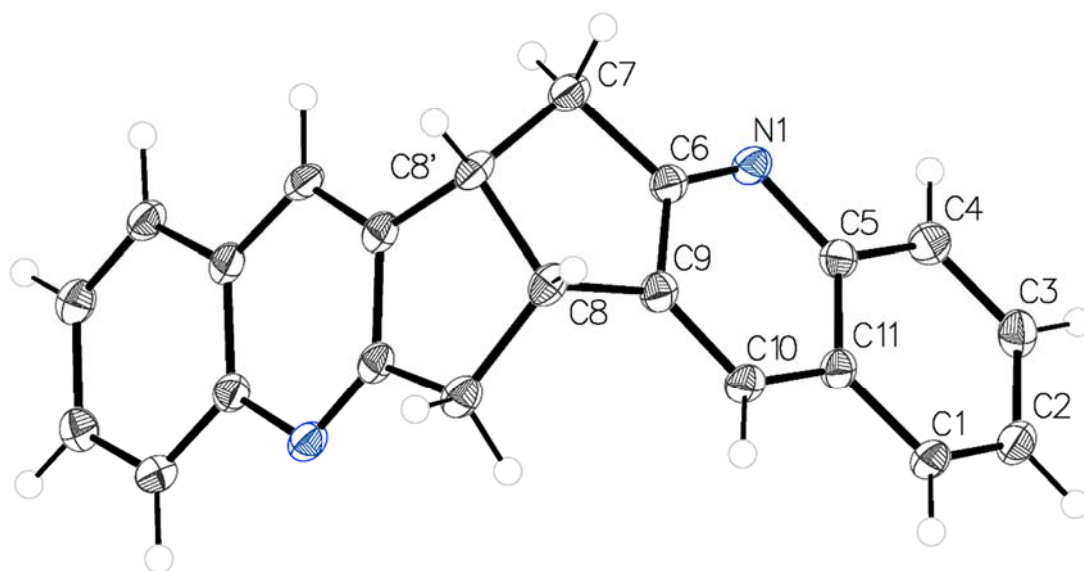
<sup>B</sup>Mark Wainwright Analytical Centre, The University of New South Wales, Sydney, NSW 2052, Australia.

<sup>C</sup>School of Mathematical and Physical Sciences, University of Technology Sydney, P. O. Box 123 Broadway, NSW 2007, Australia.

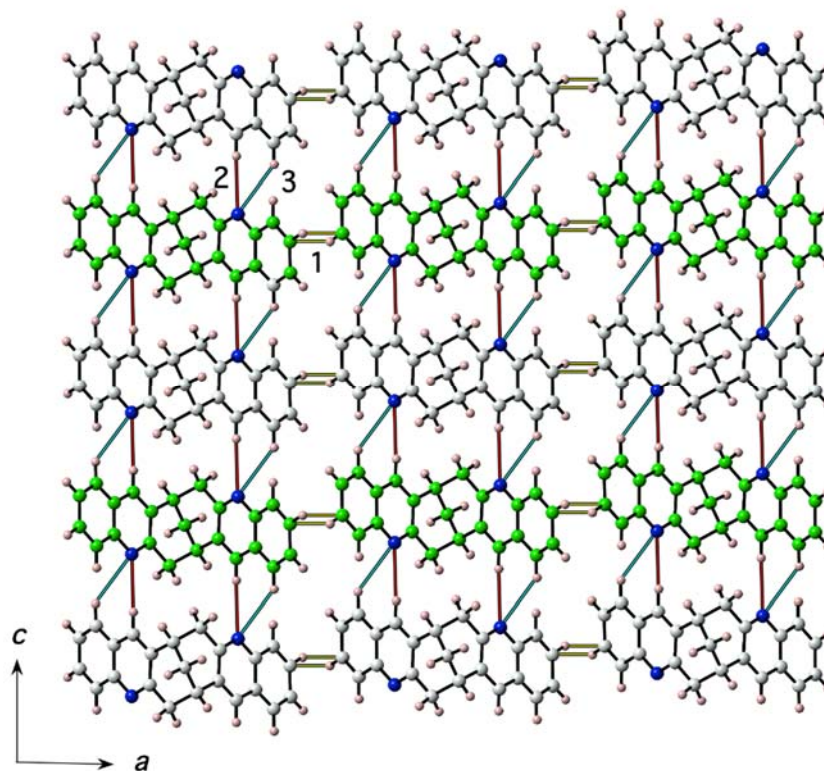
<sup>D</sup>Corresponding author. Email: [r.bishop@unsw.edu.au](mailto:r.bishop@unsw.edu.au)

Figure S1. ORTEP diagram showing the crystallographic numbering used for the crystal structure of **4**.

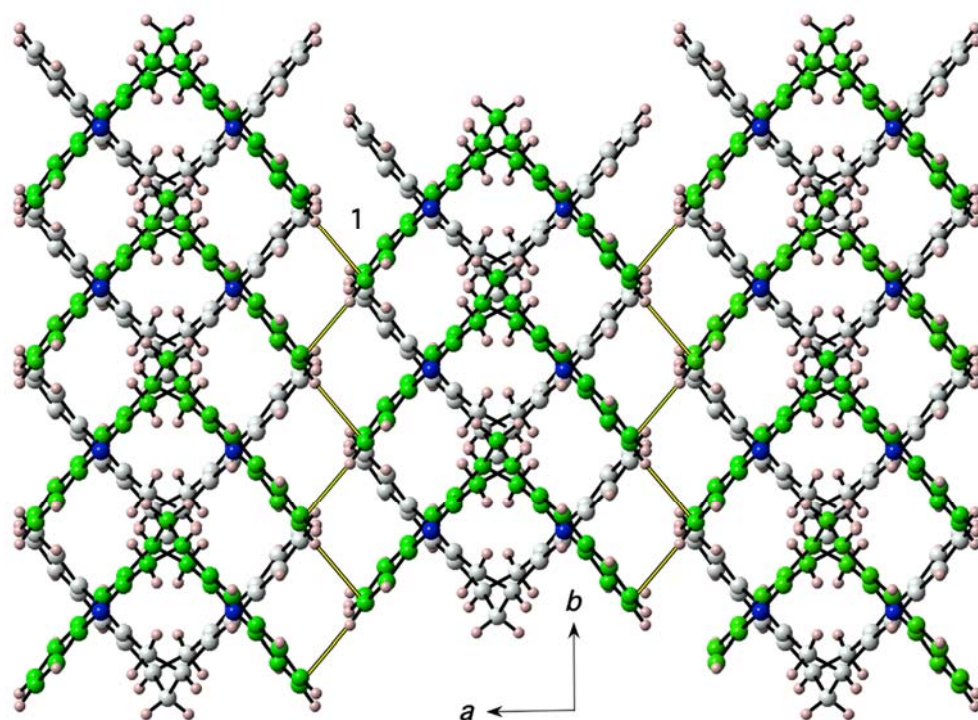
Figures S2, S3 and S4 depicting aspects of the crystal structure of **2**.



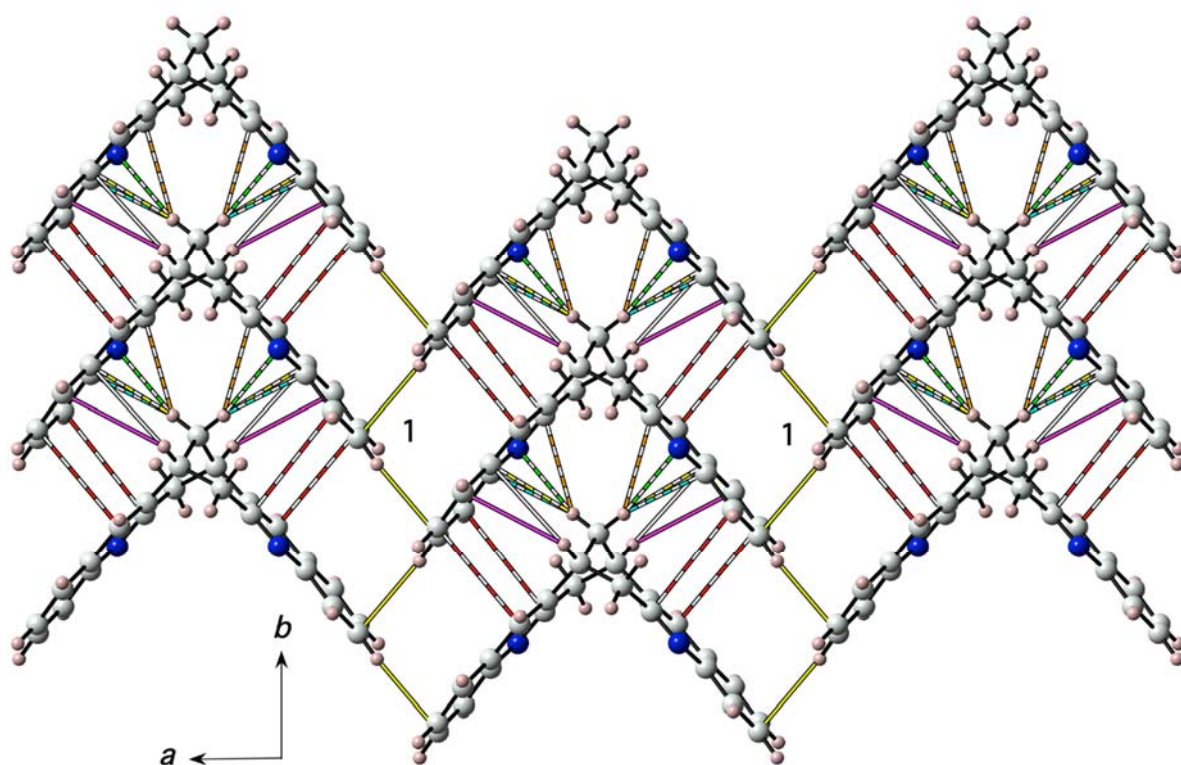
**Figure S1.** ORTEP diagram for the crystal structure of **4** showing the displacement ellipsoids at 50% probability for the non-hydrogen atoms. The crystallographic numbering system is also indicated.



**Figure S2.** The crystal structure of racemic **2** projected onto the *ac* plane. Atom colour code: N dark blue, and C of the opposite enantiomers green or off-white. Intermolecular attractions are represented as solid rods: 1 (yellow, 2.73 Å) is a C–H... $\pi$  contact, whereas 2 (red, 2.61 Å) and 3 (light blue, 2.99 Å) are C–H...N interactions.



**Figure S3.** The crystal structure of **2** projected onto the *ab* plane. Like enantiomers are linked by chains of C–H... $\pi$  interactions (1, yellow solid rods) along the *b* direction.



**Figure S4.** The crystal structure of **2** projected onto the *ab* plane and showing the C–H $\cdots$  $\pi$ ,  $\pi\cdots\pi$ , and C–H $\cdots$ N intermolecular attractions operating between molecules of the same chirality. Individual interactions are described in detail in the main text (Figure 7, upper).