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Supporting Information for "Substitutional and orientational disorder in organic crystals: a symmetry-adapted ensemble model"

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S1. Obtaining the chemical potential, μ_τ, corresponding to disorder ratio τ.

Combining equations (1) and (3) we have:

$$\tau = \frac{1}{\Xi}\sum_m \frac{n_m}{N}\exp\left(\frac{-\tilde{E}_m + \mu n_m}{RT}\right). \quad \text{(S1)}$$

Incorporating the definition of the partition function (2) and rearranging, we have

$$\sum_m \left(\frac{n_m}{N} - \tau\right)\exp\left(\frac{-\tilde{E}_m + \mu n_m}{RT}\right) = 0. \quad \text{(S2)}$$

Summing over all the configurations that have a particular value of n, and defining

$$Q_n = \sum_m \exp\left(\frac{-\tilde{E}_m}{RT}\right), n_m = n, \quad \text{(S3)}$$

and

$$z = \exp\left(\frac{\mu}{RT}\right), \quad \text{(S4)}$$

we transform S2 to

$$\sum_{n=1}^{N}\left(\frac{n}{N} - \tau\right)Q_n z^n = 0. \quad \text{(S5)}$$

This is a rank N polynomial in z. Having calculated the Q_n, and selected a value of τ we can solve this polynomial to obtain a value of z and hence of μ. In principle, there should be N solutions to S5, leading to N values for the chemical potential. This is not physically realistic! However, Descartes' Law of Signs states that for any polynomial, the number of real, positive solutions will be equal to or less than the number of sign changes in the coefficients. Examining S5, it can be seen that the Q_n are always positive, and $n/N - \tau$ will change sign just once. Hence, there will be a maximum of one real, positive value of z. Any complex or real negative values of z will lead to physically meaningless complex values of μ which can be

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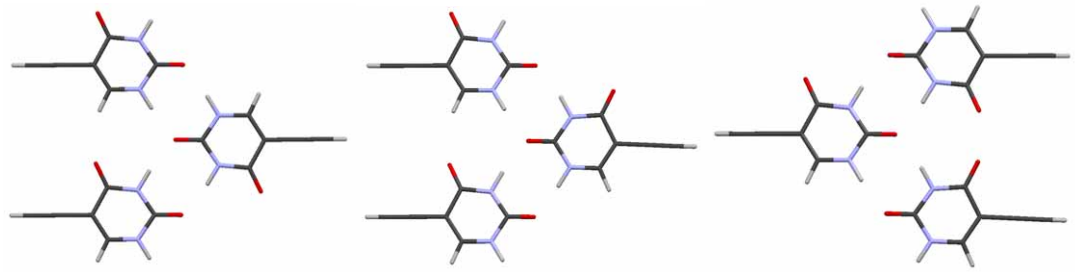
discarded. Hence, we can obtain μ_τ by finding the single real, positive solution of S5. After calculating Q_n, we can find this single solution using standard methods. A bisection search was used in this study.

S2 Trimer calculations based on the eniluracil ribbon

In the main paper (see Section 4.3), we have suggested that the exclusion of configurations containing O-O close contacts from ensemble calculations for eniluracil can be justified on the grounds that the growth of the hydrogen bonded ribbons (see Figure 5) will be impeded by the relative instability of these contacts. To substantiate this, we have calculated the binding energies of two trimers cut from eniluracil's hydrogen bonded ribbons, one with an O-O close contact and one without. These are shown in Figure S2.1. These trimers represent the most basic building blocks of their respective ribbons, and represent the smallest unit that has to form in, or from, a solution, in order for the relevant configurations to grow.



(a) (b) (c)

Figure S2.1. Trimers cut from eniluracil ribbons: (a) uniform non-polar, (b) polar, (c) with an O-O close contact.

The binding energy was calculated as $E_{bind} = E_{tri} - \sum E_{mono}$, the energy of the trimer minus the energy of each of the constituent molecules, with basis set superposition error compensated using the counterpoise method. *Ab initio* DFT calculations were carried out using GAUSSIAN03, at the B3LYP level of theory with a 6-31(d,p) basis set.

The result is that the uniform non-polar trimer has a binding energy of −108.3 kJ mol^{-1} and the polar trimer has a binding energy of −103.5 kJ mol^{-1}, while the trimer with the O-O close contact has a binding energy of −24.7 kJ mol^{-1}. It is therefore clear that the O-O close contact does indeed introduce a massive relative instability that can be expected to impair the formation of such units from solution.