Supplementary Information

Experimental and molecular dynamics studies of anthraquinone dyes in a nematic

liquid-crystal host: a rationale for observed alignment trends

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Nematic-isotropic transition temperatures

The nematic-isotropic transition temperatures for E7 and the guest-host mixtures are reported in Table S1 along with the corresponding reduced temperatures, T/T_{NI}, at 300 K, which was the temperature used for the experimental dichroic order parameter measurements and the MD simulations.

Table S1 Experimental nematic-isotropic transition temperatures, T_{NI}, and reduced temperatures, T / T_{NI}, at 300 K for E7 alone and the dye-E7 guest-host mixtures.

Mixture	T_{NI} / °C	T / T_{NI}
E7	59.4	0.902
15SB3-E7	59.6	0.902
15NB3-E7	60.6	0.899
15NB3OH-E7	59.4	0.902
26B3-E7	61.8	0.896
26B3OH-E7	61.7	0.896

In general, the order parameter of a nematic system increases with a decrease in temperature at temperatures $<T_{NI}$, which are often expressed as reduced temperatures. In the systems studied here, adding the dyes to E7 gave a very small decrease of 0.000-0.006 in the reduced temperature.

Polarized UV-visible absorption spectra and dichroic ratios over the full spectral range
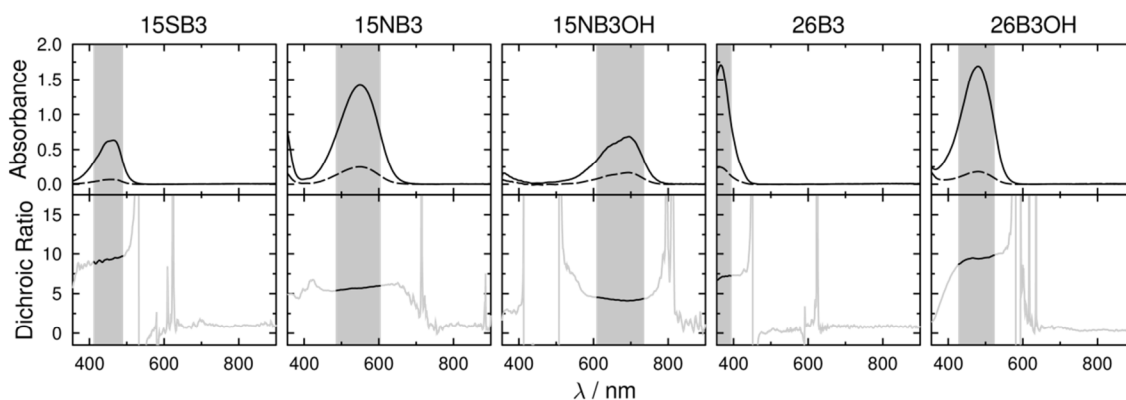

Fig. S1 Polarized UV-visible absorption spectra of aligned samples of the dyes in E7 (top) and respective dichroic ratios over the full spectral range (bottom). The visible bands are highlighted in grey.

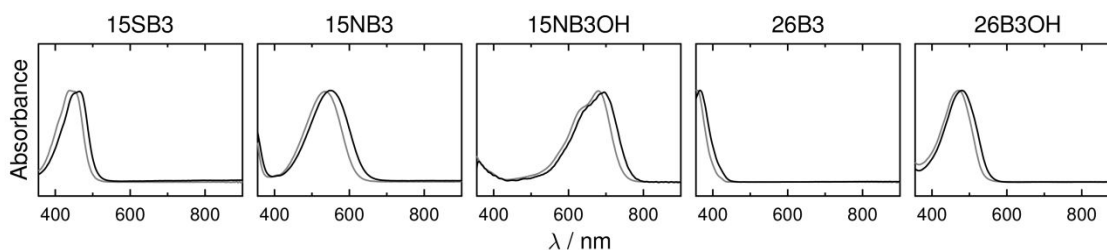**UV-visible absorption spectra of the dyes in E7 and in *p*-xylene**

Fig. S2 Scaled UV-visible absorption spectra of the dyes in E7 (black) and at 2×10^{-4} mol dm^{-3} in *p*-xylene (grey).
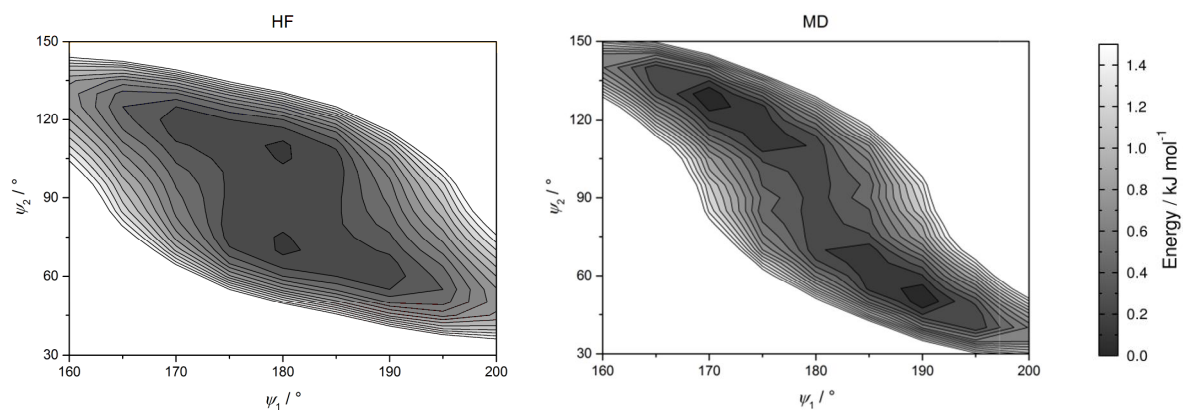
MD force field parameterisation

Fig. S3 Expanded plots of the potential energy surfaces for the two C-N-C-C dihedral angles of M3, showing HF energies (left) and MD energies calculated using the fitted parameters given in Table 2 (right). These plots are equivalent to Fig. 9 but show a smaller range of angles and the energy only at 0-1.5 kJ mol^{-1} to illustrate the local minima in the well. Contours are shown at intervals of 0.1 kJ mol^{-1}.

MD simulations

In accordance with the methods we reported previously for the MD simulation of 26B3OH in E7 from an isotropic starting geometry,[S1] a verification analysis was carried out to confirm that a run time of 500 ns was appropriate for the guest-host MD simulations of all five dyes from a pseudo-nematic starting geometry discussed in this report.

No aggregation of the dye molecules was apparent during the simulations. The analyses reported here were carried out over 30-500 ns because the simulations used a pseudo-nematic starting geometry; otherwise, they are equivalent to the analyses that we reported in the Supporting Information of an earlier paper,[S1] which were carried out over 120-500 ns for a simulation that used an isotropic starting geometry in which the nematic phase required time to develop.

Fig. S4 shows histograms of the angle, θ, between the host director and the long molecular axis, defined here as the minimum moment of inertia axis, for each of the five dye molecules in each simulation, starting at 30 ns and ending at either 100, 300 or 500 ns. Both the histograms and the respective values of S_θ show that there are significant differences between the dyes in each run at early times, whereas the respective sets of values are more comparable over a range of 30-500 ns. Hence, we considered 500 ns to be an appropriate run time at an acceptable computational expense.
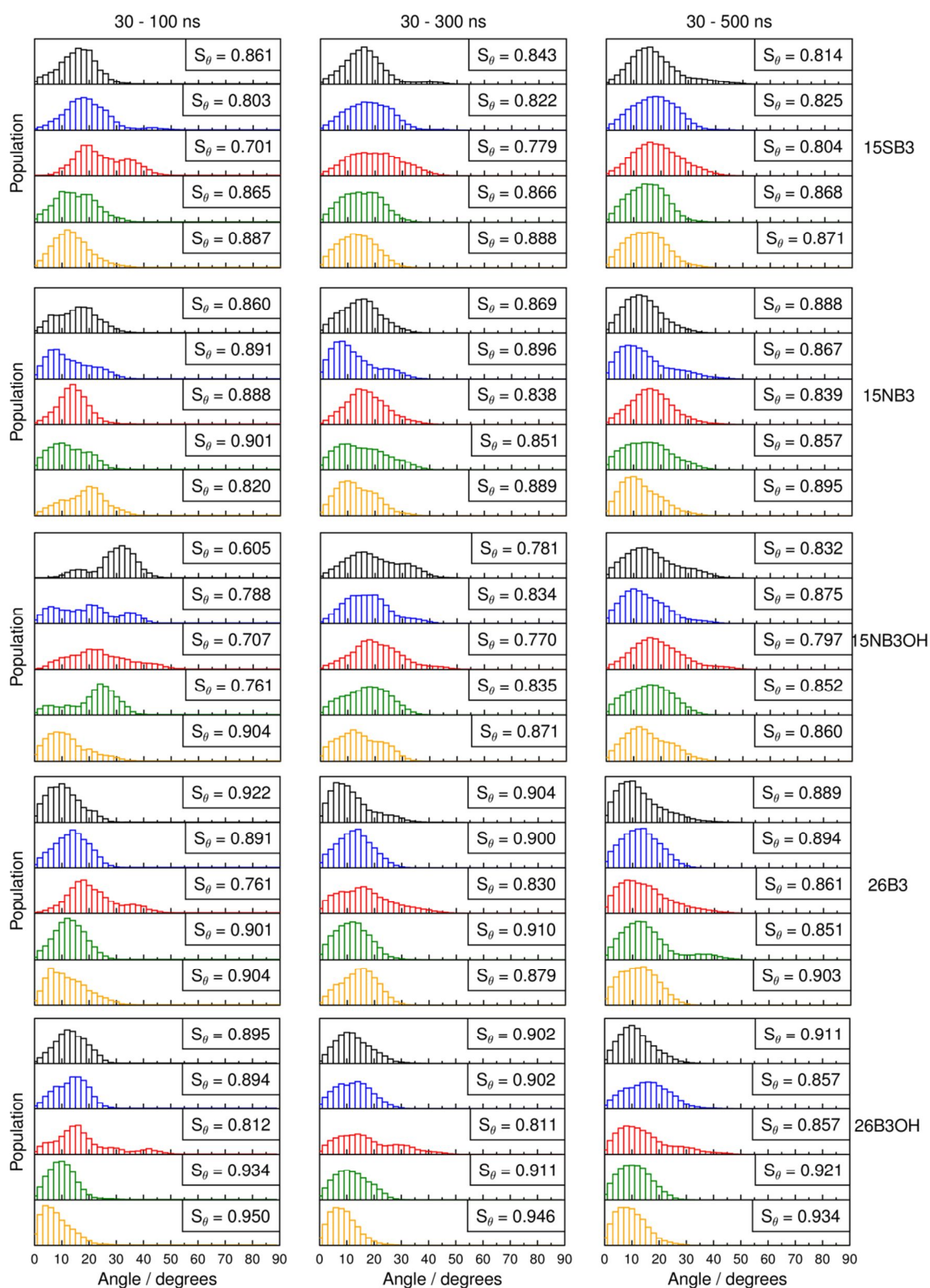
Fig. S4 Histograms of the angles, θ, between the long molecular axis of each of the five dye molecules (represented by different colours) and the host director within each simulation, measured over the indicated time periods for the five guest-host simulations starting from pseudo-nematic starting geometries, and normalised for each time range. Insets give S_θ values for each dye, obtained by averaging over each time range.

Figs S5-S9 show unit vectors that estimate the orientations explored around the host director for each of the dye molecules and for the same three time ranges used in Fig. S4. The approach used here is the same as that we reported previously, where we discussed its limitations and benefits.[S1]

Figs S5-S9 show that the orientations explored over a time range 30-100 ns encompass a relatively narrow range for some dyes, and that the five dyes within each simulation do not explore comparable orientations. When a longer time range of 30-500 ns is used, the orientations encompass a fuller range and are more comparable for the five dyes within each simulation. Hence, as in our earlier report, the plots of the unit vectors presented here provide additional qualitative support for the use of 500 ns as a suitable simulation time to study the five dye molecules in these guest-host mixtures.
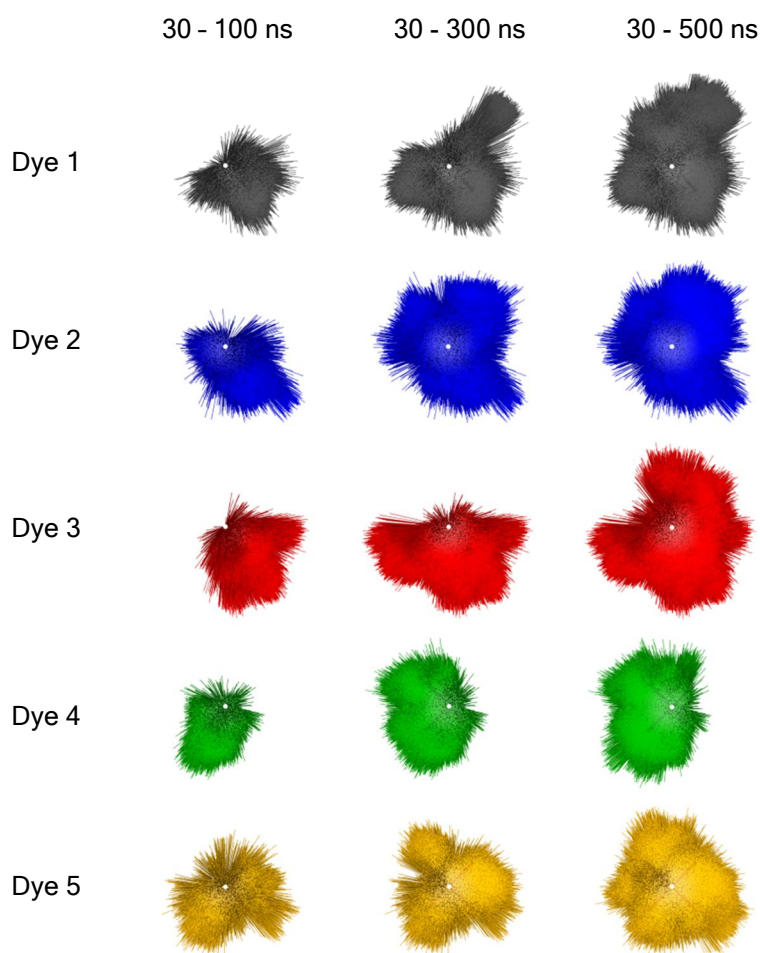

Fig. S5 Estimates of the orientations explored by the long molecular axis of each of the five 15SB3 molecules (represented by different colours that are consistent with the colours given Fig. S4) during the guest-host simulation. Orientations are drawn as unit vectors and viewed

down the host director axis (central points in white), with all vectors shown for each of the time ranges labelled above.
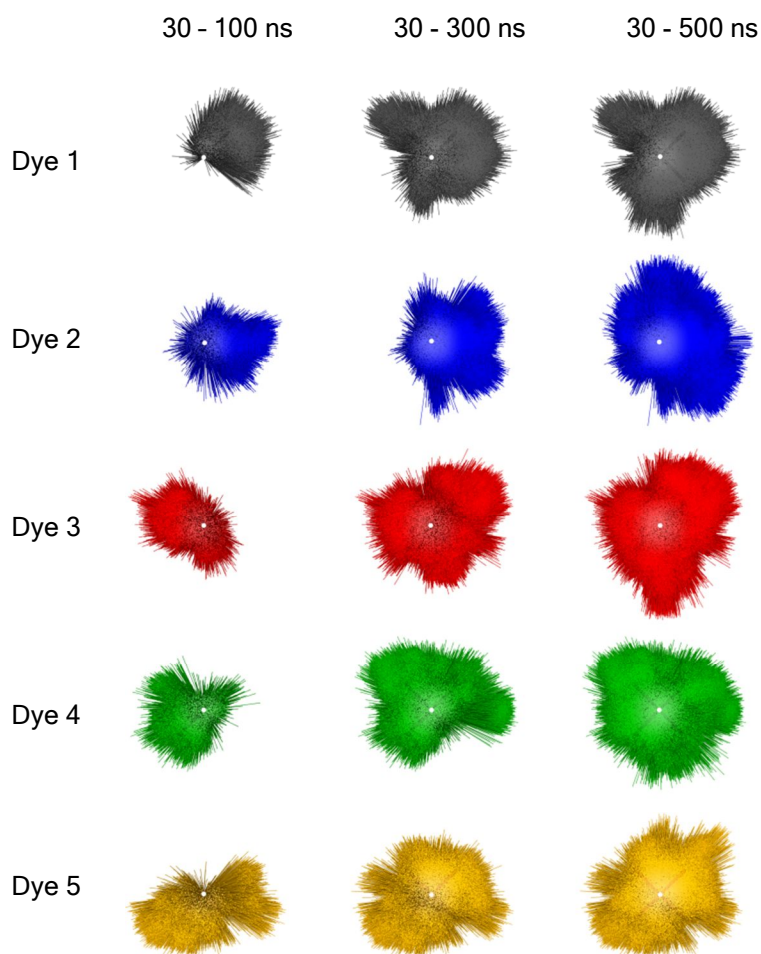

Fig. S6 Estimates of the orientations explored by the long molecular axis of each of the five 15NB3 molecules (represented by different colours, consistent with Fig. S4) during the guest-host simulation. Orientations are drawn as unit vectors and viewed down the host director axis (central points in white), with all vectors shown for each of the time ranges labelled above.
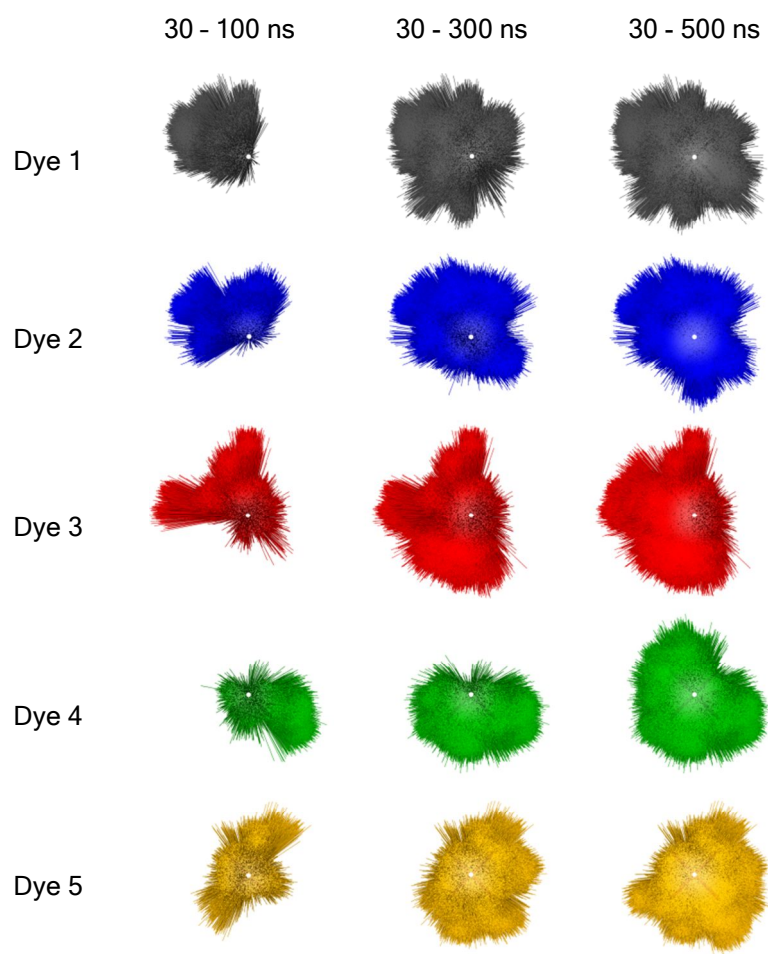
Fig. S7 Estimates of the orientations explored by the long molecular axis of each of the five 15NB3OH molecules (represented by different colours, consistent with Fig. S4) during the guest-host simulation. Orientations are drawn as unit vectors and viewed down the host director axis (central points in white), with all vectors shown for each of the time ranges labelled above.
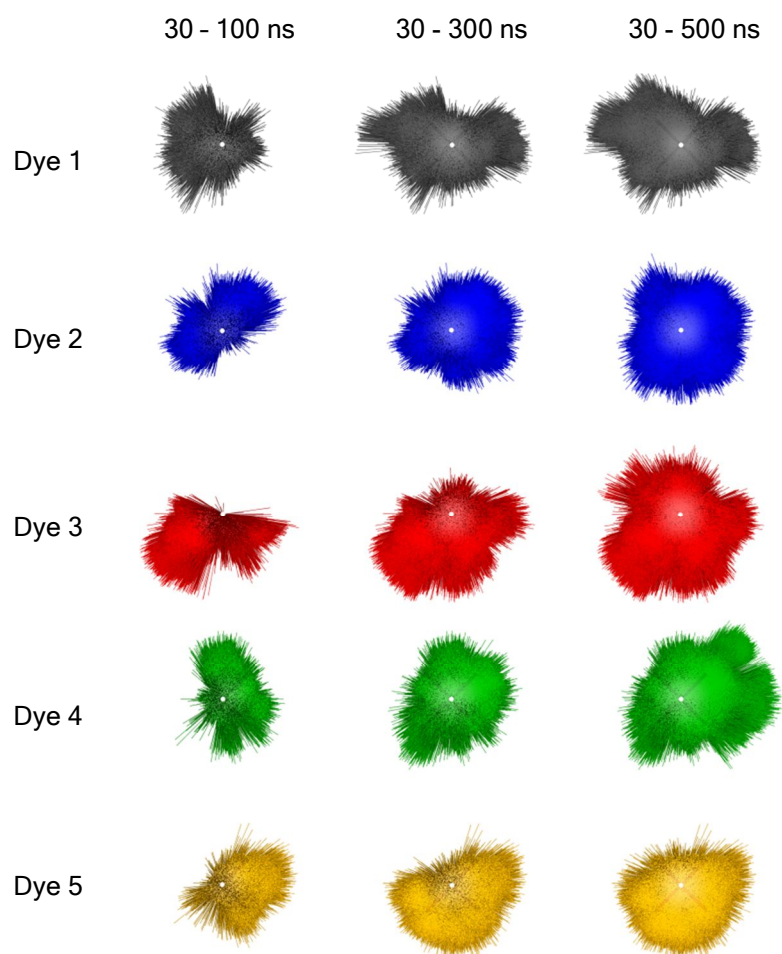
Fig. S8 Estimates of the orientations explored by the long molecular axis of each of the five 26B3 molecules (represented by different colours, consistent with Fig. S4) during the guest-host simulation. Orientations are drawn as unit vectors and viewed down the host director axis (central points in white), with all vectors shown for each of the time ranges labelled above.
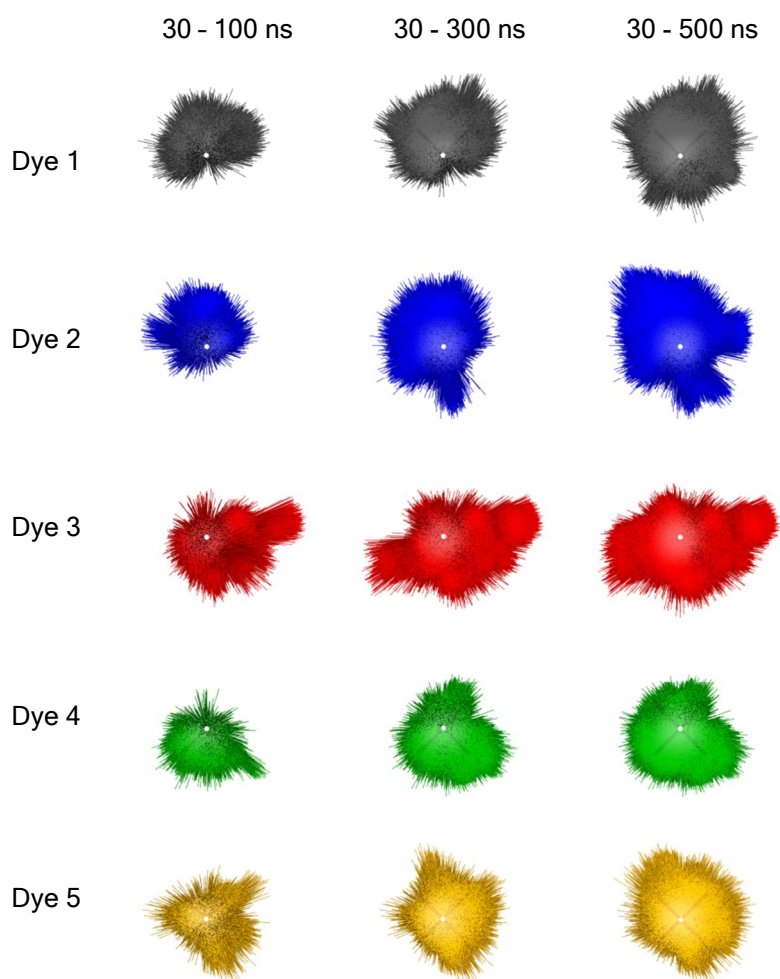
Fig. S9 Estimates of the orientations explored by the long molecular axis of each of the five 26B3OH molecules (represented by different colours, consistent with Fig. S4) during the guest-host simulation. Orientations are drawn as unit vectors and viewed down the host director axis (central points in white), with all vectors shown for each of the time ranges labelled above.

References

S1.   Sims, M. T.; Abbott, L. C.; Cowling, S. J.; Goodby, J. W.; Moore, J. N., *Chem. - Eur. J.,* 2015, **21**, 10123-10130.