Supporting Information
Well-Tempered Metadynamics as a Tool for Characterizing Multi-Component, Crystalline Molecular Machines

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A metadynamics run using both the in-plane orientation and the out-of-plane tilt of a single octafluoronaphthalene (OFN) molecule as CVs was used to reconstruct the free energy surface (FES) in Figure S1. The simulation was run using the parameters stated in the figure caption. The definition for the in-plane CV was identical to that described in detail in the main paper, while the out-of-plane tilt angle was defined as,

$$\sin\theta = \hat{y}_t \cdot \hat{z}_0$$

where, following the terminology used in the main text, $\hat{y}_t$ is the unit vector describing the instantaneous orientation of the OFN molecule at time t, and $\hat{z}_0$ is the unit vector in the z direction of the molecular frame, as defined in Figure 1 of the main text, at time $t = 0$.

It is satisfying to note that the features of the free FES are very similar to those reported previously from standard MD simulations,[1] with differences mainly due to the change in the reference frame for the calculation in the current work that makes the profile more symmetric about $\theta = 0°$. The FES presented here also represents a much higher degree of sampling.

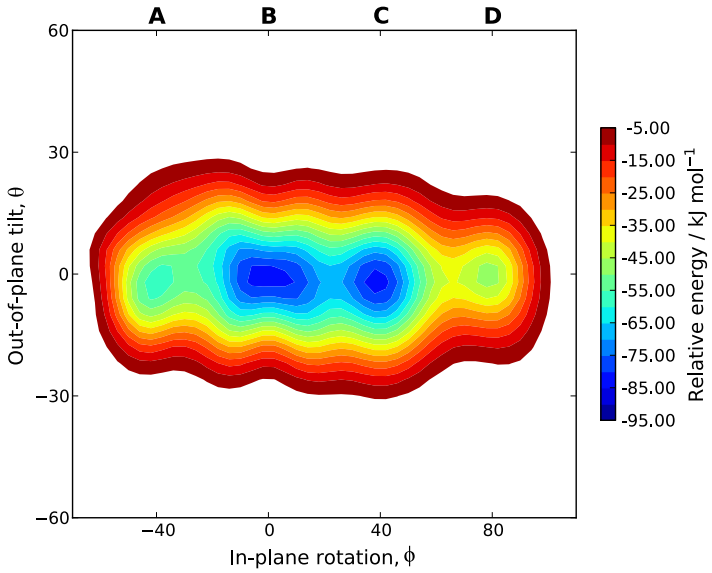


Figure S1: 2D FES obtained from a 1.5 ns metadynamics run using a single OFN molecule's tilt, θ, and in plane rotation, ϕ, as collective variables. The smoothly converging form of the metadynamics algorithm was used with Gaussian width, $\delta s = 8°$, deposition rate, $\omega = 1$ kJ mol^{-1} ps^{-1}, $\Delta T = 900$ K and $\tau_G = 250$ fs.

References

[1] Ilott, A. J.; Palucha, S.; Batsanov, A. S.; Wilson, M. R.; Hodgkinson, P. Elucidation of Structure and Dynamics in Solid Octafluoronaphthalene from Combined NMR, Diffraction, And Molecular Dynamics Studies. *J. Am. Chem. Soc.* **2010**, *132*, 5179–5185.