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Supporting Information

Restriction of rotational relaxation of the butadiyne-bridged porphyrin dimer in ultrathin films

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Scheme S1 The proposed structures of the **D**-DABCO ladder-like and branched-like packings in the LBF forming from the solution of D in the presence of 45 equiv DABCO.



Figure S1 Comparison of UV-Vis spectra in CHCl₃ of the following **D** dimer solutions ($c = 1.6 \times 10^{-6}$ M) in chloroform: (1) 1%vol of dioxane, (2) 1%vol of AMP, (3) 2 equiv of DABCO, (4) 45 equiv of DABCO, and (1'-4') their respective emission spectra upon excitation at $\lambda = 450$ nm (divided by absorbance at the same wavelength).



Figure S2. UV-Vis absorbance spectra of cast films of (1) **D**-2DABCO and (2) **D**-45DABCO, (3) **D**-AMP, and (1'-3') their respective emission spectra upon excitation at $\lambda = 450$ nm.



Figure S3. Compression isotherms of **D**-AMP monolayers formed from solutions containing (1) 1% vol, (2) 5% vol, and (3) 10% vol of AMP.