Molecular Design, Self-Assembled and Folded Nanostructures, and their Molecular Dynamics

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Our philosophy:
To use innovative techniques to measure and novel methods to construct advanced materials and biomaterials, with an emphasis on molecular design and creative approaches to demonstrate new concepts, principles, and applications in the chemical, physical, and biological sciences.

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Molecular self-assembly effectively directs and enhances specific reaction pathways. Using perylene π-π stacking as molecular recognition codes, we succeeded in synthesizing a perylene bisimide macrocyclic dimer 2 and a concatenated dimer-dimer ring 4 from monomeric perylene bisimide.

In principle, many other cyclic structures such as 5-9, could have formed from reactants 1 or its assemblies 10-12, but dynamic self-assembly only amplifies two products, 2 and 4.

Concentrations of 1, 2, and 4 as a function of reaction time. Note that 2 quickly reaches a steady-state concentration.

1H-NMR spectra for 2, 3, & 4. Aromatic protons shift up-field due to increased perylene stacking.

Simulations using the NWChem molecular dynamics software module provide further insights into stacked configurations. (A) dimer ring 2; (B) concatenated dimer rings 4, cis configuration; (C) 4, trans configuration; (D) 4, tetramer stack configuration.

Molecular self-assembly inhibition leads to basket-shaped cyclophane formation with chiral dynamics

Variable temperature 1H-NMR spectra reveal that the jump-robe mechanism does not occur at low or room temperature and that the twisting mechanism becomes frozen out near -5C.

After the twisting motion of the perylene core is frozen (T<5C) the flexible handle can still flop left and right, exchanging geminal protons such as j and j’. Such motions, as shown in AM1 geometry minimized structures below, are significantly reduced below -15C.

Twisting rates were extracted by fitting simulated spectra (Gutowsky-Holm equations for two-site equally populated exchange) to the experimental perylene protons a. These rates were used to create an Eyring plot; the twisting barrier between P and M enantiomers was determined to be 13.4 ± 0.5 kcal/mol.

1,6,7,12-tetraphenoxy-substituted perylene is highly twisted and undergoes unimolecular cyclization rather than bimolecular or multimolecular cyclization. Frustration of intermolecular self-assembly discourages intermolecular reactions thus favoring intramolecular cyclization.

The resulting monocyclic monomer has a basket-shaped molecular structure with two possible exchange mechanisms: twisting of the perylene core between P and M enantiomers, and swinging of the TEG handle from one face to the other like a jump rope.

*Conditions: (1) NMM/N20, ap. to sat, at rt.

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