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Design and Characterization of Photo-responsive Supramolecular Aggregates

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Introduction
Supramolecular chemistry concerns the manner in which molecular building blocks associate via non-covalent interactions and form aggregates. The particular building block in this research is ADA, a molecule that isomerizes reversibly around an N-N double bond upon irradiation with different wavelengths of light. The large structural changes in the molecule that result from isomerization have the potential to modulate the properties of a supramolecular aggregate.

Abstract
The photo-responsive molecule 4,4'-azobenzene dicarboxylic acid (ADA) was studied under a variety of environmental conditions for the purpose of understanding aggregation behavior and geometries. The data show that self-aggregation of ADA at low pH is under hierarchical control giving rise to the formation of a variety of structures dependent on the procedure for their formation; typically, the aggregates have a preferential asymmetric geometry despite the symmetry of the constituent molecules. Moreover, the use of a chiral template macromolecule (poly-glutamate) during the formation of the aggregate can affect the structure of the supramolecular species and direct its chirality. Finally, the aggregates containing the cis isomer of ADA were shown to retain their ability to photo-isomerize to the aggregates of the trans form.

Materials and Methods
- Absorption (UV-Vis) and Circular Dichroism (CD) measurements were performed with a Jasco V-630 and J-815, respectively. UV irradiation was performed using a 100 Watt Hg Lamp (365 nm).
- Both UV and visible irradiation were performed at basic or acidic pH for 15 min intervals.
- The aggregates explored were cis- or trans-ADA alone and in the presence of poly-Glutamic acid; low pH conditions were obtained by decreasing the pH from 7 to 3 in one step (fast) or in steps of 0.5 pH units (slow).

Aggregation of ADA with Poly-Glutamatic acid
The presence of poly-L-Glu promotes the formation of a chiral aggregate of ADA with a very intense CD signal. The inversion of the signal related to the aggregate when poly-D-Glu is used shows that the chirality is induced by the template.

Conclusions
When the pH of a trans-ADA solution is quickly reduced from 7 to 3, a blue shift and hypochromicity of the absorption band indicate that a parallel assembly, known as an H-aggregate, is formed. In this geometry, both π−π stacking and hydrogen bonds are possible, making the aggregate very compact and strong and preventing trans-ADA from photoswitching. If the pH is brought back to 7, the trans-ADA returns to its monomeric form and is able to photosomerize again.

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Fast pH decrease of trans-ADA results in formation of an H-aggregate, that will prevent the isomerization to the cis form upon irradiation with UV light. Molecule regains photoswitching capabilities upon pH increase and disaggregation.