

Narrative progress report for:

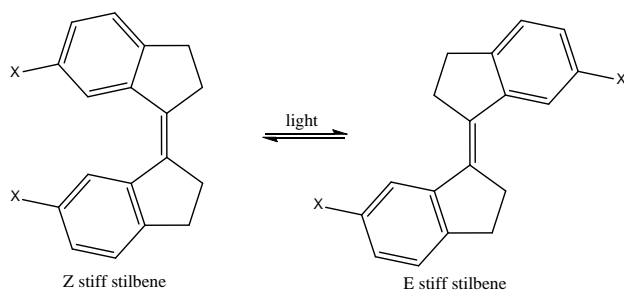
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New photoactuating polymers

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Over the past 10 months of the project our focus has been on:

1. Developing practical methods of synthesizing polymers of Z stiff stilbene (see structure below), including complex architectures and
2. Understanding the aggregation behavior of both isomers of stiff stilbene and the effect of molecular strain on such aggregation.



The two tasks are related because aggregation limits the achievable degrees of polymerization, the microstructure of resulting polymer melts and solids and photodynamic behavior. The current work relies on a combination of synthesis, physical measurements and quantum-chemical computations. In the course of this work we published a review on photochemistry of stiff stilbene, particularly in strained architectures, and are finishing a paper on aggregation behavior and self-assembly of short oligomers of stiff stilbene.

So far we have screened several polymerization methods to find that polyesterification appears to be most successful for polymerization of simple hydroxyl- and carboxy- stiff stilbenes, whereas topologically complex multi-stiff stilbene monomers can only be polymerized using 3<sup>rd</sup> generation Grubbs catalyst.

In studying aggregation behavior we have discovered a new phenomenon of photoallostery, which is observed in p-p stacked stiff stilbene dimers and trimers. Irradiation of these aggregates results in collective photoisomerization of all stacked chromophores, so that only all-Z and all-E isomers are experimentally observable. Quantum-chemical calculations indicate that the result is not due to decreased thermal stability of mixed E/Z isomers but suggest a specific combination of quantum yields, which results in undetectably low steady-state concentrations of mixed E/Z forms. Such photoallostery is potentially useful for bulk photoactuation, but its possibility has not been considered in the design of photoactuating polymers. We are now trying to develop a collaboration with a leading group in single-molecule force spectroscopy to study the relationship between force, photon flux and molecular geometry at the single-chain level.