Cooperative Self-Assembly of Oligo(*m*-phenyleneethynylenes) into Supramolecular Polymers

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A highly cooperative supramolecular polymerization mechanism was sought from bisfunctionalized m-phenyleneethynylene (mPE) oligomers. Three mPE oligomers were synthesized with lengths of four (1), six (2), and eight (3) monomer units containing terminal pyridine monomer units. Upon the addition of trans-dichlorobis(acetonitrile)palladium to a solution of oligomer, polymerization was observed by MALDI MS, UV spectroscopy, NMR, and isothermal titration calorimetry. Preliminary evidence is consistent with a cooperative polymerization mechanism of pyridine-palladium coordination and π - π stacking causing nucleation-elongation polymerization for the tetramer and octamer (\mathbf{A}), and macrocyclization followed by columnar aggregation for the hexamer (\mathbf{B}).

$$TgO \longrightarrow \bigcap_{N} OTg \qquad PdCl_{2}(CH_{3}CN)_{2}$$

$$Tg = -(CH_{2}CH_{2}O)_{3}CH_{3}$$

$$1: n=2$$

$$2: n=4$$

$$3: n=6$$

$$A \qquad B$$

Towards a Gated Synthetic Ion Channel for Controlled Ion Transport

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Synthetic ion channels are integral tools for understanding the ion transport mechanism across biomembranes. In addition, they also provide easy access to biosensors and some therapeutic agents. Ion transport in living systems is a controlled phenomenon and it is essential to have the same control in a synthetic ion channel. Here, we report our preliminary work in the design and synthesis of a "Gated" pore that may find use in a synthetic ion channel. The basic design of the gated pore involves attachment of an azobenzene unit to the secondary face of β -Cyclodextrin (β -CD) with an appropriate tether. Cis-trans isomerism of the azobenzene unit will be used to modulate the ion flow through the pore. Computational results of the tether design and the synthesis of the modified β -CD will be discussed.