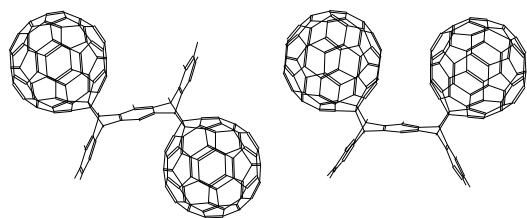


## Progress Towards the Rational, Bench-Top Synthesis of Organic Nanotubular Molecules

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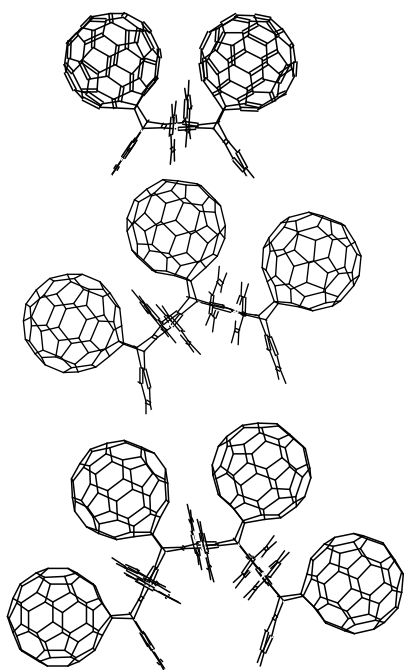
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In our studies of new fullerene chemistries, we investigated the Diels-Alder reactivity between  $C_{60}$  and linear acenes [1,2,3,4]. Anthracene is the smallest linear acene that is reactive with  $C_{60}$ . All larger acenes (e.g., tetracene, pentacene, hexacene, heptacene, etc.) are also reactive. Our intent was to prepare Diels-Alder adducts of large linear acenes in the hopes of adding two or more fullerenes across a single acene backbone. For example, two equivalents of  $C_{60}$  can in principle add across a pentacene molecule to give either a *cis* or a *trans*-bis[60]fullerene adduct.

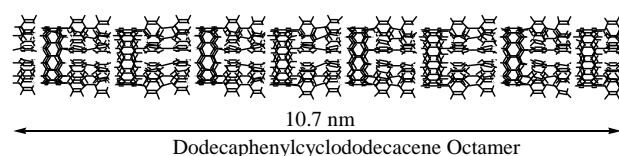
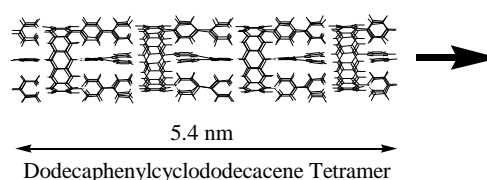
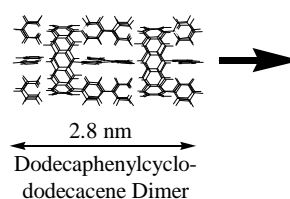
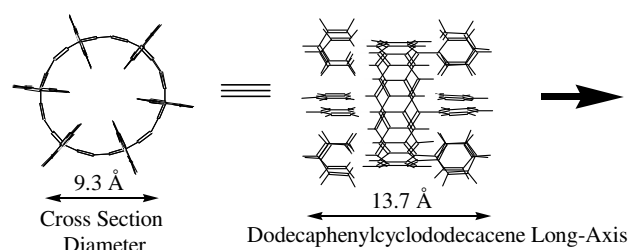


Before preparing structures of this type, several chemical and physical obstacles had to be overcome including the lack of regioselectivity in fullerene cycloadditions across the acenes as well as the inherent instability and insolubility of the acenes themselves. Successful strategies to overcome all three obstacles will be discussed.

Most remarkable is that fullerenes are found to add across linear acenes with exceptionally high diastereoselectivity. In each case, the all *cis* adduct is preferred and only traces (at best) of *trans* adduct are observed. A variety of experimental and computational data suggests that favorable fullerene-fullerene  $\pi$ -stacking interactions are responsible for the high *cis* diastereoselectivity.



The results imply an elegant synthesis of phenyl substituted cyclacene compounds and, following phenyl coupling, nanotubular molecules. Both will be discussed.



[1] G.P. Miller and J. Mack, "Completely Regioselective, Highly Stereoselective Syntheses of *cis*-Bisfullerene[60] Adducts of 6,13-Disubstituted Pentacenes," *Organic Letters* **2000**, 2, 3979.

[2] G.P. Miller, J. Mack, and J. Briggs, " $\pi$ -Stacking Interactions in *cis*-Bisfullerene[60] Adducts of 6,13-Disubstituted Pentacenes," *Organic Letters* **2000**, 2, 3983.

[3] G.P. Miller, J. Mack, and J. Briggs, "Completely Regioselective, Highly Stereoselective Formation of Bisfullerene[60] Adducts of 6,13-Dialkynyl Substituted Pentacenes," *Fullerenes- Volume 11, Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters*, P.V. Kamat, D.M. Guldi, and K.M. Kadish, Eds., The Electrochemical Soc.: Pennington, NJ, **2001**, 202.

[4] G.P. Miller\* and J. Briggs, "Progress Towards the Synthesis of Tris- and Tetrakis[60]Fullerene Adducts of Linear Acenes: Synthesis and Diels-Alder Reactivity of 5,7,12,14-Tetraphenylpentacene," *Fullerenes- Volume 12, Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters*, P.V. Kamat, D.M. Guldi, and K.M. Kadish, Eds., The Electrochemical Soc.: Pennington, NJ, **2002**, 279.