Electron Donor-Acceptor Interactions Directed Self Assembly of Organic Nanostructures

Yi Liu, Organic Facility
The Molecular Foundry, Lawrence Berkeley National Laboratory

Scientific Thrust Area

The growing needs for miniaturization and better efficiency of electronic devices have inspired enormous interests in obtaining novel semiconductor nanostructures. One particular challenge is to obtain nanostructures with continuous interface between electron rich *p*-type materials and electron deficient *n*-type materials in order to facilitate charge separation and charge transport. This demands the understanding of organization principles of electroactive groups with molecular precision in multi-component systems, which also motivates the design and synthesis of new electron donors and acceptors. Our research focuses on utilizing the donor-acceptor interactions to direct the assembly of functional high-order nanostructures for the application in organic electronics.

Research Achievement

We have demonstrated the directed self-assembly of functional molecular and supramolecular assemblies, including interlocked molecular machines, highly ordered donor-acceptor stacks, and 1D organic nanowires.

High-fidelity Assemblies of Interlocked Molecules for Molecular Machinery

High-yield, one-pot synthesis of various interlocked structures have been developed to provide a convenient approach towards the development of sophisticated switchable molecular systems that are responsive towards electrochemical or photochemical stimuli. Examples include the expeditious formation of [2]rotaxanes[1] (Figure 1a) and dynamic switchable [2]catenanes[2,3] (Figure 1b) from multi-component reactions.

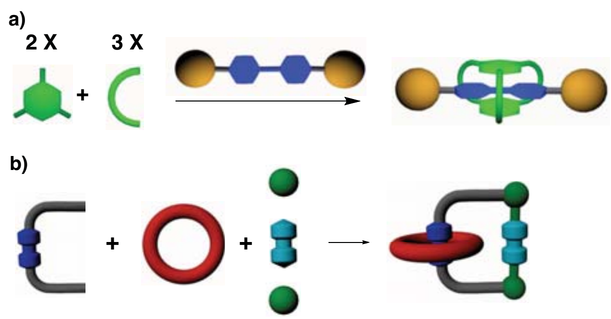

Figure 1. Cartoon representations of the one-pot assembly approach for the synthesis of a) [2]rotaxanes, and b) [2]catenanes.

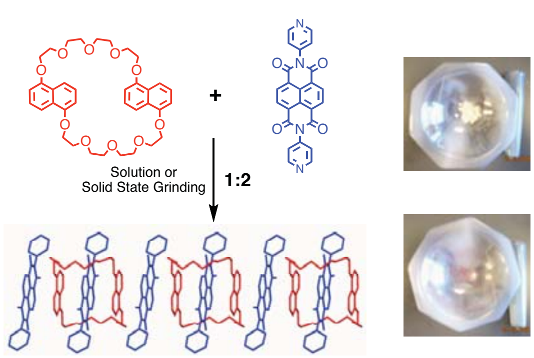

Figure 2. Assembly of alternative donor-acceptor stacks.

Supramolecular Aggregates as Novel Electronic Materials

We have shown a unique host-guest system that rapidly leads to extended 1D alternative donor-acceptor (ADA) stacks.[4] (Figure 2) The 1:2 complex can be obtained as a precipitate from solution within minutes or, more remarkably, from a solid-to-solid mechanical grinding process. The ADA stacking was confirmed by single crystal and powder XRD analysis and further characterized by solid state CPMAS ^{13}C and ^{15}N NMR spectroscopy. Current findings not only provide a convenient way to a novel class of ADA stacks involving macrocyclic host, but also represent an important step in transferring electro-active host-guest systems from solution to the solid state. Investigations on their electronic and photophysical properties are currently underway.

1D Organic Nanoribbons Based on Liquid Crystaline Materials

Organic supramolecular aggregates with defined topology, such as 1D nanowires and nanotubes, represent attractive building blocks for electronic devices. We have obtained twisted organic nanoribbons with the width around 200 nm from the drop cast solution of a series of triphenylene derivatives, as indicated by scanning electron microscopy. (Figure 3) The nanoribbon formation is highly dependent on the nature of the solvent. The characterization of photoconductivity and electron transporting properties are currently underway.

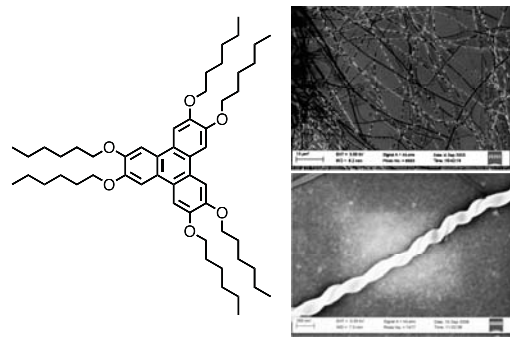

Figure 3. SEM images of organic nanoribbons based on a triphenylene derivative.

Future Work

Design and synthesis of molecular switches containing complementary donor-acceptor pairs is currently underway. Meanwhile, the knowledge obtained from the donor-acceptor systems will be applied on the exploration of small molecule-based *p*-type and *n*-type electronic materials for photovoltaic applications.

Publications

1.Klivansky, L. M.; Koshkakaryan, G.; Cao, D.; **Liu, Y.***, "Linear π-Acceptor Templated Dynamic Clipping to Macrobicycles and [2]Rotaxanes", *Angew. Chem. Int. Ed.* **2009**, *in press*. DOI: 10.1002/anie.200900716.

2. Koshkakaryan, G.; Parimal, K.; He, J.; Zhang, X.; Abliz, Z.; Flood, A. H.; **Liu, Y.***, "π-Stacking Enhanced Dynamic Self-Assembly of Donor-Acceptor Metallo-[2]Catenanes from Diimide Derivatives and Crown Ethers", *Chem. Eur. J.* **2008**, *14*, 10211-10218.

3. **Liu, Y.***; Bruneau, A.; He, J.; Abliz, Z., "Palldaium(II) Directed Self Assembly of Dynamic Donor-Acceptor [2]Catenanes", *Org. Lett.* **2008**, *10*, 765-768.

4. Koshkakaryan, G.; Klivansky, L. M.; Cao, D.; Snauko, M.; Teat, S. J.; Struppe, J. O.; **Liu, Y.***, "Alternative Donor-Acceptor Stacks from Crown Ethers and Naphthalene Diimide Derivatives: Rapid, Selective Formation from Solution and Solid State Grinding", *J. Am. Chem. Soc.* **2009**, *131,* 2078-2079.

5. Juluri, B. K.; Kumar, A. S.; **Liu, Y.**; Ye, T.; Yang, Y-W.; Flood, A. H.; Stoddart, J. F.; Weiss, P. S.; Huang, T. J., "A Nanomechanical Actuator Driven Electrochemically by Artificial Molecular Muscles", *ACS Nano* **2009**, *3,*291-300.

6. **Liu, Y.***; Zhang, X.; Klivansky, L. M.; Koshkakaryan, G., "Enhancing the Reactivity of 1,2,3-Triazoles in 'Click' Macrocycles by Face-to-Face Dibenzylammonium Ion Binding", *Chem. Commun.* **2007**, *45*, 4773-4775.

7. **Liu, Y.***; Klivansky, L. M.; Khan, S. I.; Zhang, X., "Templated Synthesis of Desymmetrized [2]Catenanes with Excellent Translational Selectivity", *Org. Lett.* **2007**, *9*, 2577-2580.

8. **Liu, Y.***, "Self-Assembled Ring-in-Ring Complexes from Metal-Ligand Coordination Macrocycles and β-Cyclodextrin", *Tetrahedron Lett.* **2007**, *48*, 3871-3874.

9. Nygaad, S.; **Liu, Y.**; Stein, P.; Flood, A. H.; Jeppesen, J. O., "Using Molecular Force to Overcome Steric Barriers in a Spring-Like Molecular Ouroborous", *Adv. Funct. Mater.* **2007**, *17*, 751-762.