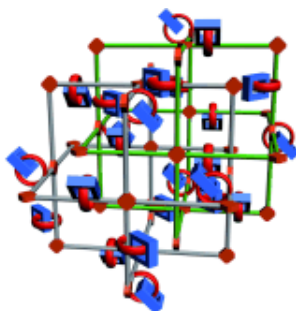


- A Catenated Strut in a Catenated Metal–Organic Framework

Li, Q.; Sue, C. H.; Basu, S.; Shveyd, A. K.; Zhang, W.; Barin, G.; Fang, L.; Sarjeant, A. A.; Stoddart, J. F.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2010**, *49*, 6751–6755.

Abstract:

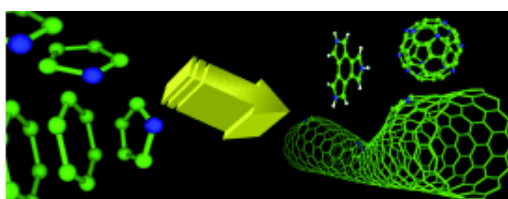


MIMs meet MOFs: Mechanically interlocked molecules (MIMs), in the form of donor–acceptor [2]catenane-containing struts of exceptional length, have been incorporated into a three-dimensional catenated metal–organic framework (MOF) at precise locations and with uniform relative orientations. Catenation is expressed simultaneously within the struts and the framework.

- A Nanoscale Jigsaw-Puzzle Approach to Large  $\pi$ -Conjugated Systems

Gao, X.; Zhang, S. B.; Zhao, Y.; Nagase, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 6764–6767.

Abstract:

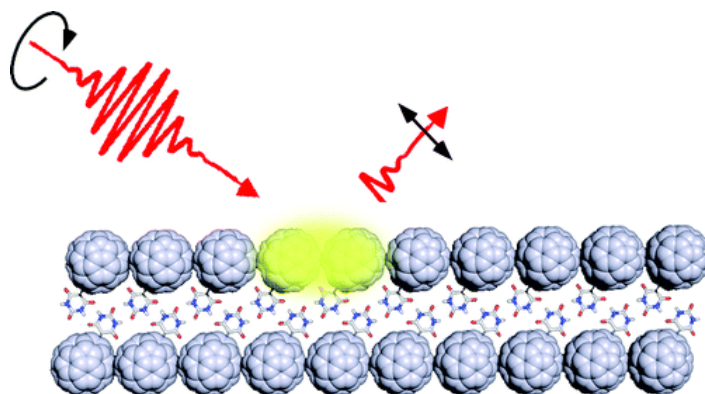


Piecing the puzzle together: A simple model of stability for hybrid carbon-conjugated materials is revealed and computationally verified. Based on this model, a simple “jigsaw-puzzle” strategy towards the design for a family of highly viable hybrid carbon-conjugated materials is proposed.

- Self-Assembly of Supramolecular Fullerene Ribbons via Hydrogen-Bonding Interactions and Their Impact on Fullerene Electronic Interactions and Charge Carrier Mobility

Chu, C. C.; Raffy, G.; Ray, D.; Guerso, A. D.; Kauffmann, B.; Wantz, G.; Hirsch, L.; Bassani, D. *M. J. Am. Chem. Soc.* **2010**, *132*, 12717–12723.

Abstract:



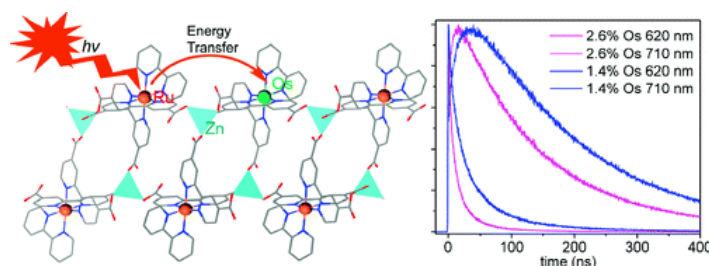
The anisotropy of the electronic interactions between fullerenes in crystalline solids was examined using a confocal fluorescence microscope by probing the polarization of the fluorescence emission

arising from fullerene excimer-like emitting states. Crystals of C60 obtained by vacuum-sublimation or from chloroform solution exhibited no or little polarization ( $p = 0$  or 0.11, respectively), as expected from the high symmetry of the C60 fcc lattice or the low degree of anisotropy induced by included solvent molecules. The use of hydrogen-bonding to supramolecularly control interfullerene electronic interactions was explored using a fullerene derivative (1) combining a solubilizing 3,4-di-tert-butylbenzene group and a barbituric acid hydrogen-bonding (H-B) moiety. The crystal structure of 1 establishes the existence of fullerene H-B tapes along which interfullerene electronic interactions are expected to be large. In agreement with this, we observe very strong polarization of the fullerene excimer-like emission ( $p = 0.78$ ), indicative of a high degree of anisotropy in the fullerene interactions. The charge-carrier mobility of 1 as determined from OFET devices was found to be lower than that of C60 ( $1.2 \times 10^{-4}$  vs  $1.2 \times 10^{-2}$  cm<sup>2</sup>/s V), which is rationalized on the basis of the reduced dimensionality of 1 as a wire-like semiconductor and variations in the morphology of the device active layer revealed by AFM measurements.

- Energy Transfer Dynamics in Metal–Organic Frameworks

Kent, C. A.; Mehl, B. P.; Ma, L.; Papanikolas, J. M.; Meyer, T. J.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 12767–12769.

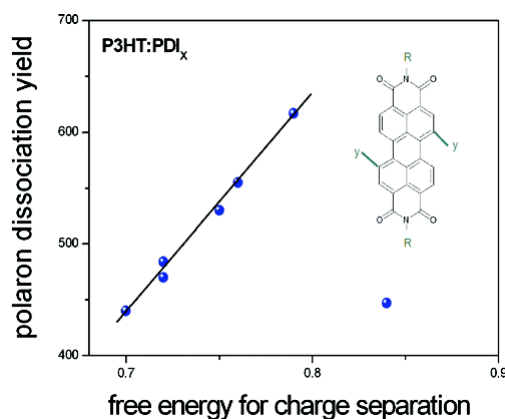
Abstract:



Isomorphous metal–organic frameworks (MOFs) based on  $\{M[4,4'-(HO_2C)_2\text{-bpy}]_2\text{bpy}\}^{2+}$  building blocks (where  $M = \text{Ru}$  or  $\text{Os}$ ) were designed and synthesized to study the classic Ru to Os energy transfer process that has potential applications in light-harvesting with supramolecular assemblies. The crystalline nature of the MOFs allows precise determination of the distances between metal centers by X-ray diffraction, thereby facilitating the study of the Ru→Os energy transfer process. The mixed-metal MOFs with 0.3, 0.6, 1.4, and 2.6 mol % Os doping were also synthesized in order to study the energy transfer dynamics with a two-photon excitation at 850 nm. The Ru lifetime at 620 nm decreases from 171 ns in the pure Ru MOF to 29 ns in the sample with 2.6 mol % Os doping. In the mixed-metal samples, energy transfer was observed with an initial growth in Os emission corresponding with the rate of decay of the Ru excited state. These results demonstrate rapid, efficient energy migration and long distance transfer in isomorphous MOFs.

- Acceptor Energy Level Control of Charge Photogeneration in Organic Donor/Acceptor Blends  
Shoae, S.; Clarke, T. M.; Huang, C.; Barlow, S.; Marder, S. R.; Heeney, M.; McCulloch, I.; Durrant, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 12919–12926.

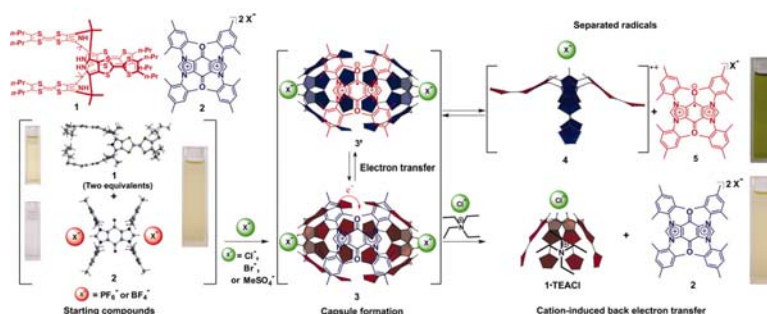
Abstract:



In this paper we focus upon the role of interfacial energetics in influencing the separation of charge transfer states into dissociated charge carriers in organic donor/acceptor blend films. In particular, we undertake transient optical studies of films comprising regioregular poly(3-hexylthiophene) (P3HT) blended with a series of perylene-3,4:9,10-tetracarboxydiimide (PDI) electron acceptors. For this film series, we observe a close correlation between the PDI electron affinity and the efficiency of charge separation. This correlation is discussed in the context of studies of charge photogeneration for other organic donor/acceptor blend films, including other polymers, blend compositions, and the widely used electron acceptor 3'-phenyl-3'H-cyclopropa[1,9](C60-Ih)[5,6]fullerene-3'-butanoic acid methyl ester (PCBM).

- Ion-Mediated Electron Transfer in a Supramolecular Donor-Acceptor Ensemble  
Park, J. S.; Karnas, E.; Ohkubo, K.; Chen, P.; Kadish, K. M.; Fukuzumi, S.; Bielawski, C. W.; Hudnall, T. W.; Lynch, V. M.; Sessler, J. L. *Science* **2010**, *329*, 1324-1327.

Abstract:



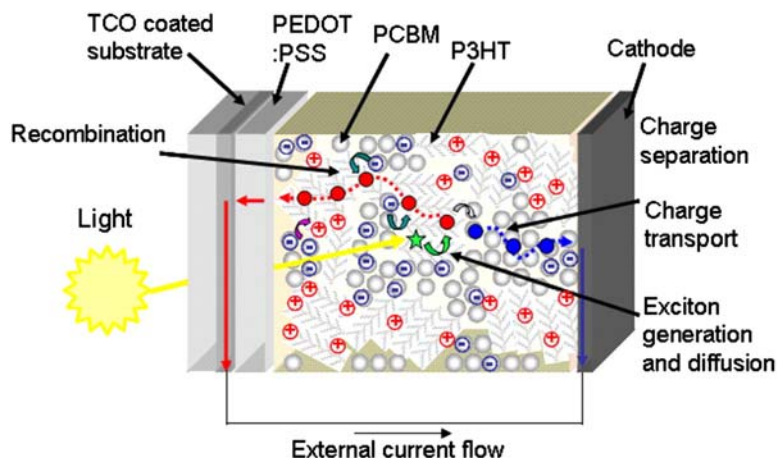
Ion binding often mediates electron transfer in biological systems as a cofactor strategy, either as a promoter or as an inhibitor. However, it has rarely, if ever, been exploited for that purpose in synthetic host-guest assemblies. We report here that strong binding of specific anions (chloride, bromide, and methylsulfate but not tetrafluoroborate or hexafluorophosphate) to a tetrathiafulvalene calix[4]pyrrole (TTF-C4P) donor enforces a host conformation that favors electron transfer to a bisimidazolium quinone (BIQ<sup>2+</sup>) guest acceptor. In contrast, the addition of a tetraethylammonium cation, which binds more effectively than the BIQ<sup>2+</sup> guest in the TTF-C4P cavity, leads to back electron transfer, restoring the initial oxidation states of the donor and acceptor pair. The products of these processes were characterized via spectroscopy and x-ray crystallography.

- Charge-density-based analysis of the current–voltage response of polythiophene/fullerene photovoltaic devices

Shuttle, C. G.; Hamilton, R.; O'Regan, B. C.; Nelson, J.; Durrant, J. R. *Proc. Nat. Acad. Sci. USA* **2010**, *107*, 16448-16452.

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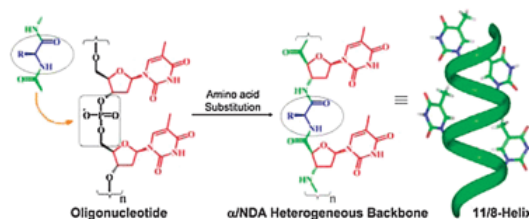
Abstract:



A key challenge for organic electronics research is to develop device models that correctly account for the structural and energetic disorder typically present in such materials. In this paper we report an approach to analyze the electrical performance of an organic electronic device based upon charge extraction measurements of charge densities and transient optoelectronic measurements of charge carrier dynamics. This approach is applied to a poly(3-hexyl thiophene) (P3HT)/6,6 phenyl C61 butyric acid methyl ester (PCBM) blend photovoltaic device. These measurements are employed to determine the empirical rate law for bimolecular recombination losses, with the energetic disorder present in the materials being accounted for by a charge-density-dependent recombination coefficient. This rate law is then employed to simulate the current/voltage curve. This simulation assumes the only mechanism for the loss of photogenerated charges is bimolecular recombination and employs no fitting parameters. Remarkably the simulation is in good agreement with the experimental current/voltage data over a wide range of operating conditions of the solar cell. We thus demonstrate that the primary determinant of both the open-circuit voltage and fill factor of P3HT:PCBM devices is bimolecular recombination. We go on to discuss the applicability of this analysis approach to other materials systems, and particularly to emphasize the effectiveness of this approach where the presence of disorder complicates the implementation of more conventional, voltage-based analyses such as the Shockley diode equation.

- Novel helical foldamers: organized heterogeneous backbone folding in 1:1  $\alpha$ /nucleoside-derived- $\beta$ -amino acid sequences  
Chandrasekhar, S.; Kiranmai, N.; Udaya Kiran, M.; Sharada Devi, A.; Kumar Reddy, G. P.; Idris, M.; Jagadeesh, B. *Chem. Commun.* **2010**, *46*, 6962-6964.

Abstract:



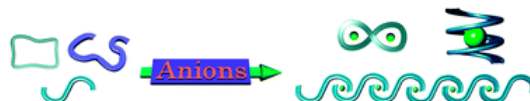
Secondary structural conformation of hybrid oligo-peptides comprised of 1 : 1 alternating Nucleoside Derived  $\beta$ -Amino acid (NDA) and L-amino acid residues has been reported. The studies reveal that

the NDA residues organize the heterogeneous backbone featuring the surface properties of both nucleic acids and peptides, to adopt a novel 11/8-helical fold.

- Anion-controlled foldamers

Juwarker, H.; Jeong, K.-S. *Chem. Soc. Rev.* **2010**, *39*, 3664-3674.

Abstract:

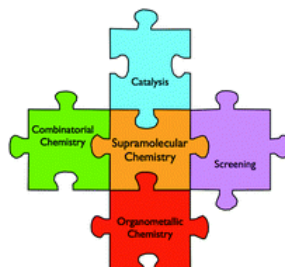


This *tutorial review* provides a summary of anion-mediated folding of linear and cyclic oligomers as well as anion-responsive behaviours of related polymeric architectures. Anions have emerged as a significant focus of the supramolecular community and here we review their impact on directing the secondary structures of synthetic oligomers and polymers while modulating physical properties *e.g.* molecular recognition. Oligomers and polymers responsive to anionic guests are typically constructed with hydrogen bond donors complementary to the target anions. Anion binding within the cavities leads to folding and helical wrapping of linear and cyclic oligomers as well as control over macromolecular properties of polymers. This review covers the impact of anion binding on guiding the secondary structures of single-stranded folded oligomers (foldamers) and cyclic oligomers (macrocycles), and on modulating the physical properties of select polymer architectures.

- The uses of supramolecular chemistry in synthetic methodology development: examples of anion and neutral molecular recognition

Joyce, L. A.; Shabbir, S. H.; Anslyn, E. V. *Chem. Soc. Rev.* **2010**, *39*, 3621-3632.

Abstract:



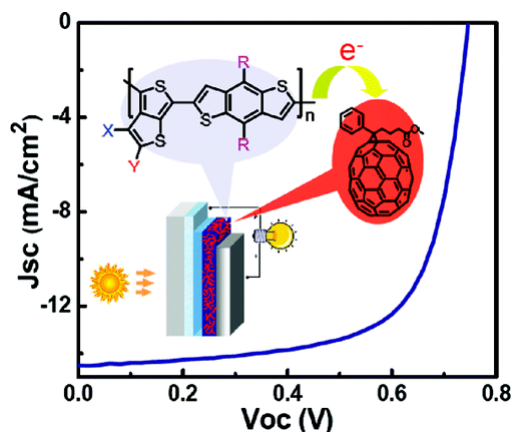
The principles of supramolecular chemistry have successfully permeated through a broad range of organic chemistry subdisciplines. One subdiscipline that is not routinely associated with supramolecular chemistry is that of organic synthetic methodology. Though sometimes indiscernible, non-bonded and bonding supramolecular interactions play a large role in chemical reactions and catalysis. Many synthetic methods hinge on the creation of anionic charge, albeit just partial, at some step during this process, and hence are prime targets for molecular recognition interactions. Examples are artificial enzymes, biomimetic catalysis, organocatalysis, and many of the catalysts that are derived from a combinatorial screen. Further, supramolecular chemistry is playing an increasingly large role in high-throughput analytical techniques. This *tutorial review* ties together supramolecular approaches to methodology creation, combinatorial screening, and analytical protocols. The goal is to show, and further predict, that supramolecular chemistry will continually increase its impact in organic synthetic methodology development.

- A New Class of Semiconducting Polymers for Bulk Heterojunction Solar Cells with Exceptionally High Performance

Liang, Y.; Yu, L. *Acc. Chem. Res.* **2010**, *43*, 1227–1236.

Abstract:

6



Solar cells based on the polymer–fullerene bulk heterojunction (BHJ) concept are an attractive class of low-cost solar energy harvesting devices. Because the power conversion efficiency (PCE) of these solar cells is still significantly lower than that of their inorganic counterparts, however, materials design and device engineering efforts are directed toward improving their output. A variety of factors limit the performance of BHJ solar cells, but the properties of the materials in the active layer are the primary determinant of their overall efficiency.

The ideal polymer in a BHJ structure should exhibit the following set of physical properties: a broad absorption with high coefficient in the solar spectrum to efficiently harvest solar energy, a bicontinuous network with domain width within twice that of the exciton diffusion length, and high donor–acceptor interfacial area to favor exciton dissociation and efficient transport of separated charges to the respective electrodes. To facilitate exciton dissociation, the lowest unoccupied molecular orbital (LUMO) energy level of the donor must have a proper match with that of the acceptor to provide enough driving force for charge separation. The polymer should have a low-lying highest occupied molecular orbital (HOMO) energy level to provide a large open circuit voltage ( $V_{oc}$ ). All of these desired properties must be synergistically integrated to maximize solar cell performance. However, it is difficult to design a polymer to fulfill all these requirements.

In this Account, we summarize our recent progress in developing a new class of semiconducting polymers, which represents the first polymeric system to generate solar PCE greater than 7%. The polymer system is composed of thieno[3,4-*b*]thiophene and benzodithiophene alternating units. These polymers have low bandgaps and exhibit efficient absorption throughout the region of greatest photon flux in the solar spectrum (around 700 nm). The stabilization of the quinoidal structure from thieno[3,4-*b*]thiophene is believed to be primarily responsible for these properties. Additionally, the rigid backbone enables the polymer to form an assembly with high hole mobility. Proper side chains on the polymer backbone ensure good solubility and miscibility with fullerene acceptors. The flexibility in structural tuning on the polymer backbone provides the polymers with relatively low-lying HOMO energy levels and enhanced  $V_{oc}$ , short-circuit current density ( $J_{sc}$ ), and fill factor (FF) and, thus, enhanced PCE.

All of these features indicate that the polymer system exhibits a host of properties that are indeed synergistically combined, leading to the enhancement in solar cell output. Our preliminary results demonstrate why these polymers are excellent materials for solar energy conversion and represent prime candidates for further improvements through research and development.

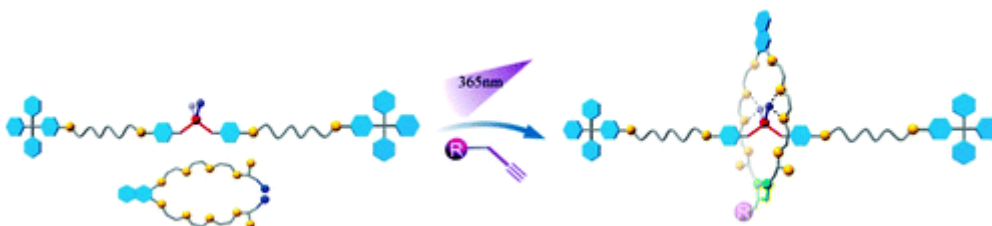


- Synthesis of Sulfuric Macrocycles and a Rotaxane through Thiol-yne Click and Dithiol Coupling Reactions

7

Zhou, W.; Zheng, H.; Li, Y.; Liu, H.; Li, Y. *Org. Lett.* **2010**, *12*, 4078–4081.

Abstract:

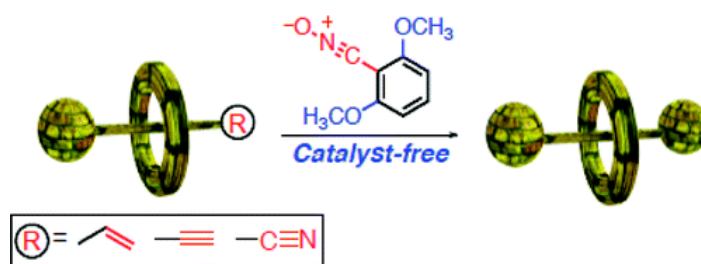


A macrocycle and a rotaxane were constructed by virtue of the thiol-yne click reaction under the irradiation of light in high yield, which can proceed at ambient temperature and humidity under an air atmosphere. Two disulfide macrocycles were synthesized through a simple dithiol coupling reaction, which exhibited high stability and a weak assembly interaction with a dialkylammonium ion.

- C–C Bond-Forming Click Synthesis of Rotaxanes Exploiting Nitrile N-Oxide

Matsumura, T.; Ishiwari, F.; Koyama, Y.; Takata, T. *Org. Lett.* **2010**, *12*, 3828–3831.

Abstract:



**Click End-Capping Reaction with Nitrile N-Oxide**

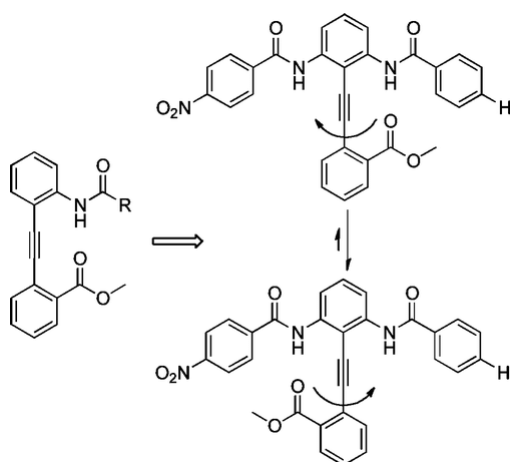
**•High Yield •Practical Reaction •C–C Bond Formation**

A click end-capping reaction exploiting nitrile *N*-oxide to rotaxane was described with emphasis of productivity of the protocol via stable C–C bond formation. Establishment of a pH-driven molecular shuttling system was also demonstrated by practical neutralization of the *sec*-ammonium group of the rotaxane axle with potassium hydroxide.

- Designed Molecular Switches: Controlling the Conformation of Benzamido-diphenylacetylenes

Jones, I. M.; Hamilton, A. D. *Org. Lett.* **2010**, *12*, 3651–3653.

Abstract:



With the goal of creating a molecular switch, the hydrogen-bonded diphenylacetylene structure has been modified such that an equilibrium now exists between two intramolecular H-bonded states. Through X-ray crystallography and <sup>1</sup>H NMR analysis it is shown that this equilibrium can be biased in a predictable manner by modulating the relative acidity of the amide NH's.