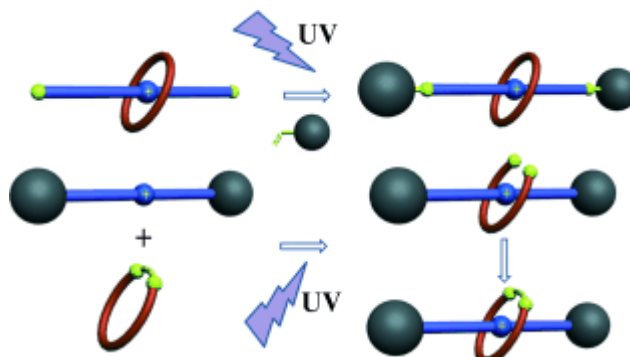


- Synthesis of a [2]Rotaxane Incorporating a “Magic Sulfur Ring” by the Thiol-Ene Click Reaction

1

Zheng, H.; Li, Y.; Zhou, C.; Li, Y.; Yang, W.; Zhou, W.; Zuo, Z.; Liu, H.; *Chem.-Eur. J.* **2011**, *17*, 2160-2167.

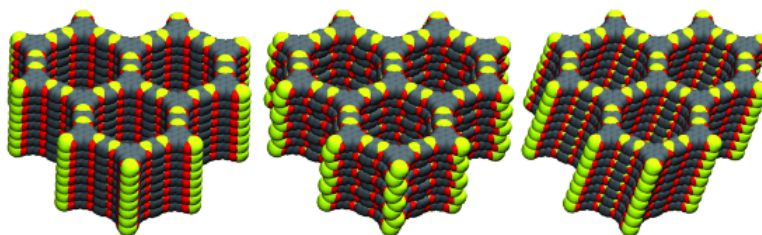
Abstract:



The mild and highly efficient thiol-ene click reaction has been used to construct a rotaxane incorporating dibenzo-24-crown-8 (DB24C8) and a dibenzylammonium-derived thread in high yield under the irradiation of UV light. A rotaxane containing a disulfide linkage in the macrocycle was also synthesized by the thiol-ene click reaction. It has been demonstrated that the formation of the [2]rotaxane with the disulfide bond in the macrocycle occurs by a mechanism that is different to the threading-followed-by-stoppering process. The successful construction of a rotaxane directly from its constituent components, the macrocycle containing a disulfide linkage and the dibenzylammonium hexafluorophosphate salt, suggests that the space within the macrocycle incorporating the disulfide linkage is smaller than the phenyl unit and a plausible reaction mechanism has been proposed as follows: A small amount of the initiator forms two radicals upon the absorption of UV irradiation; the radicals act as a “key” to “unlock” the disulfide bond in the macrocycle. The resulting crown ether like moiety in the macrocycle is clipped around the ammonium ion center in the dumb-bell-shaped compound. The [2]rotaxane is generated upon recombination of the disulfide linkage.

- The Structure of Layered Covalent-Organic Frameworks
Lukose, B.; Kuc, A.; Heine, T. *Chem.-Eur. J.* **2011**, *17*, 2388-2392.

Abstract:

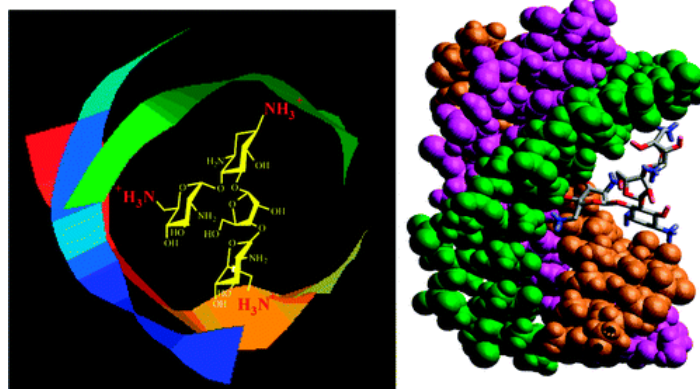


Covalent-Organic Frameworks (COFs) are a new family of 2D and 3D highly porous and crystalline materials built of light elements, such as boron, oxygen and carbon. For all 2D COFs, an AA stacking arrangement has been reported on the basis of experimental powder XRD patterns, with the exception of COF-1 (AB stacking). In this work, we show that the stacking of 2D COFs is different as originally suggested: COF-1, COF-5, COF-6 and COF-8 are considerably more stable if their stacking arrangement is either serrated or inclined, and layers are shifted with respect to each other by ~ 1.4 Å compared with perfect AA stacking. These structures are in agreement with to date experimental

data, including the XRD patterns, and lead to a larger surface area and stronger polarisation of the pore surface.

- New Approaches Toward Recognition of Nucleic Acid Triple Helices
Arya, D. P. *Acc. Chem. Res.* **2011**, *44*, 134–146.

Abstract:



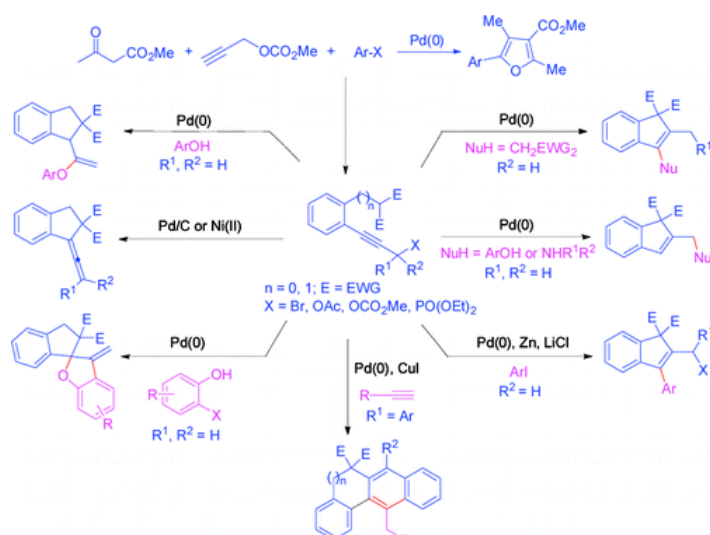
A DNA duplex can be recognized sequence-specifically in the major groove by an oligodeoxynucleotide (ODN). The resulting structure is a DNA triple helix, or triplex. The scientific community has invested significant research capital in the study of DNA triplexes because of their robust potential for providing new applications, including molecular biology tools and therapeutic agents. The triplex structures have inherent instabilities, however, and the recognition of DNA triplexes by small molecules has been attempted as a means of strengthening the three-stranded complex. Over the decades, the majority of work in the field has focused on heterocycles that intercalate between the triplex bases. In this Account, we present an alternate approach to recognition and stabilization of DNA triplexes.

We show that groove recognition of nucleic acid triple helices can be achieved with aminosugars. Among these aminosugars, neomycin is the most effective aminoglycoside (groove binder) for stabilizing a DNA triple helix. It stabilizes both the TAT triplex and mixed-base DNA triplexes better than known DNA minor groove binders (which usually destabilize the triplex) and polyamines. Neomycin selectively stabilizes the triplex (TAT and mixed base) without any effect on the DNA duplex. The selectivity of neomycin likely originates from its potential and shape complementarity to the triplex Watson–Hoogsteen groove, making it the first molecule that selectively recognizes a triplex groove over a duplex groove. The groove recognition of aminoglycosides is not limited to DNA triplexes, but also extends to RNA and hybrid triple helical structures.

Intercalator–neomycin conjugates are shown to simultaneously probe the base stacking and groove surface in the DNA triplex. Calorimetric and spectroscopic studies allow the quantification of the effect of surface area of the intercalating moiety on binding to the triplex. These studies outline a novel approach to the recognition of DNA triplexes that incorporates the use of noncompeting binding sites. These principles of dual recognition should be applicable to the design of ligands that can bind any given nucleic acid target with nanomolar affinities and with high selectivity.

- Palladium-Catalyzed Cyclization of Propargylic Compounds
Guo, L.-N.; Duan, X.-H.; Liang, Y.-M. *Acc. Chem. Res.* **2011**, *44*, 111–122.

Abstract:



Many groups have explored the scope of the palladium-based cyclization of propargylic compounds since Tsuji's first report in 1985. Through the proper positioning of an internal nucleophilic center and the judicious selection of an appropriate external nucleophile, the synthetic chemist can effectively assert control over the course of the reaction and its products. However, initial investigations were very limited: only heterocyclic compounds were originally synthesized. We have found the palladium-catalyzed cyclization of propargylic compounds to be a very efficient method for producing both carbocyclic and heterocyclic compounds. In this Account, we discuss the cyclization reactions of functionalized propargylic compounds with a variety of nucleophiles that we have developed over the past few years. We also review similar reactions reported by other groups.

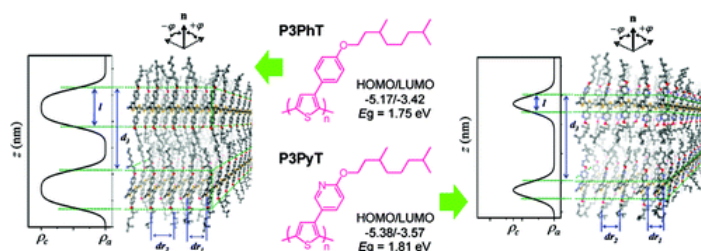
We focus here on the cyclization of functionalized propargylic compounds containing a carbon nucleophilic center that is in close proximity to the propargylic moiety. We conducted a detailed investigation of their cyclizations with carbon nucleophiles, with nitrogen nucleophiles, with oxygen nucleophiles, and without nucleophiles. We have developed several efficient and useful methods for the synthesis of indenenes, naphthalenes, polycycles, and spirocyclic compounds. All of these reactions proceed satisfactorily under very mild conditions; high regio- and stereoselectivity have been observed as well. In the course of our studies, we provided the first demonstration of a novel tandem C–H activation/bis-cyclization reaction of propargylic compounds with terminal alkynes.

In addition, we used external nucleophiles to investigate the cyclization of functionalized propargylic compounds that bear an unsaturated carbon–carbon or carbon–heteroatom bond. We presented the first report of the use of external nucleophiles to initiate a novel cyclization of functionalized propargylic compounds containing an electrophile. This revelation provided a fresh perspective through the discovery of a new type of domino cyclization of propargylic compounds.

Metal-catalyzed cyclization of propargylic compounds can provide indenenes, cyclopentanones, cyclic carbonates, benzofurans, and a range of other cyclic molecules. A thorough understanding of the mechanisms involved in this class of reaction affords exceptional synthetic control, as shown here by our development of efficient procedures and reagents for palladium-catalyzed propargylic cyclizations.

- Synthesis and Characterization of Polythiophenes Bearing Aromatic Groups at the 3-Position
Ohshimizu, K.; Takahashi, A.; Rho, Y.; Higashihara, T.; Ree, M.; Ueda, M. *Macromolecules* **2011**, *44*, 719–727.

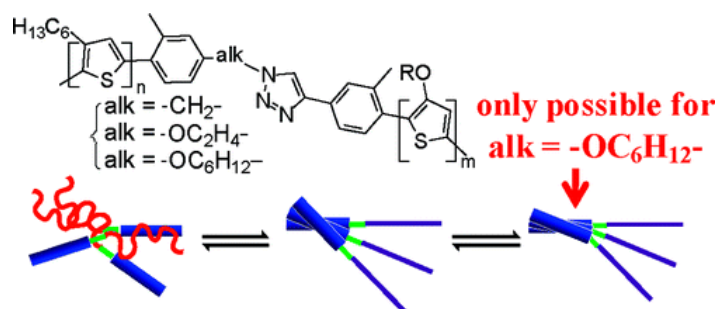
Abstract:



Regioregular poly(3-(4'-(3'',7''-dimethyloctoxy)phenyl)thiophene) (P3PhT) and poly(3-(4'-(3'',7''-dimethyloctoxy)-3'-pyridinyl)thiophene) (P3PyT) were successfully prepared with reasonably high molecular weights and low polydispersity indices by the Grignard metathesis (GRIM) polymerization. These polymers were found to be thermally stable up to 360–390 °C, depending on the phenyl or pyridinyl linker in the bristle. Both polymer films revealed a molecularly multilayer structure (i.e., lamellar structure) whose layers stacked normal to the film plane; each lamella consists of two sublayers, namely ordered and amorphous layers. The amorphous sublayer was composed of a bilayer formed from the bristles. The ordered sublayer in P3PhT consisted of laterally stacked 3-phenylthiophene backbone chains, whereas that of P3PyT consisted of thiophene backbone chains without the pyridinyl linker. These ordered sublayer formations led a longer π -conjugation length. The enhanced π -conjugation lengths were reflected in their optical and electronic properties, showing that both P3PhT and P3PyT exhibited a lower highest occupied molecular orbital (HOMO) level and lower energy band gap compared to those of poly(3-hexylthiophene) (P3HT). Overall, the structure and properties of P3PhT and P3PyT make them promising materials for advanced polymer solar cells having an excellent performance.

- Influence of the Presence and Length of an Alkyl Spacer on the Supramolecular Chirality of Block Copoly(thiophene)s
Van den Bergh, K.; Willot, P.; Cornelis, D.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2011**, *44*, 728–735.

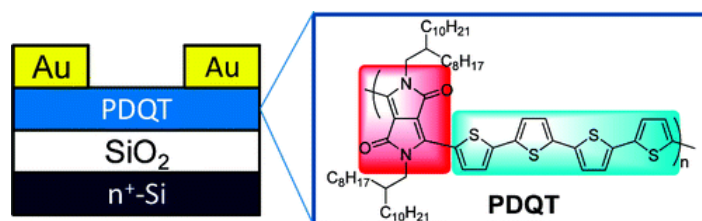
Abstract:



Three block copolymers, P3AT-1-*b*-P3AOT, P3AT-2-*b*-P3AOT, and P3AT-6-*b*-P3AOT, composed of an alkyl- and alkoxy-substituted poly(thiophene) block which are connected by a nonconjugated flexible alkyl spacer of variable length, were synthesized by coupling the azide- and acetylene-functionalized homopolymers using the click reaction. GPC and ^1H NMR analysis confirmed the formation of the block copolymers. Next, the influence of the presence and length of the alkyl spacer on the electronic properties was investigated with UV–vis and emission spectroscopy. Also, the influence of the length of the alkyl spacer on the aggregation behavior was studied with UV–vis and CD spectroscopy, which is possible due to the chirally substituted P3AOT block. All these experiments revealed that the supramolecular structure of the P3AT block is affected by the P3AOT block, but if a long alkyl spacer is present between the blocks, an additional reorganization of the P3AOT block is possible, which is not the case for shorter alkyl spacers or in the absence of a spacer.

- Annealing-Free High-Mobility Diketopyrrolopyrrole–Quaterthiophene Copolymer for Solution-Processed Organic Thin Film Transistors
Li, Y.; Sonar, P.; Singh, S. P.; Soh, M. S.; Meurs, M.; Tan, J. *J. Am. Chem. Soc.* **2011**, *133*, 2198–2204.

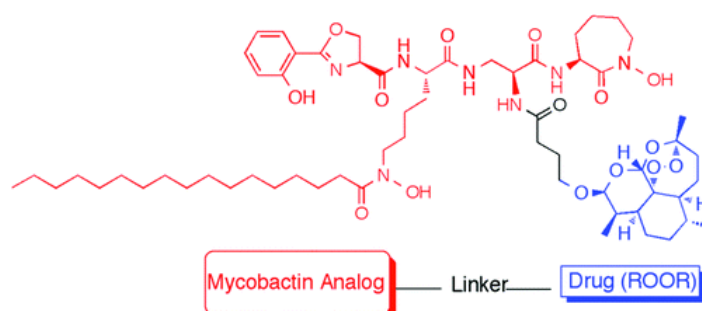
Abstract:



A donor–acceptor polymer semiconductor, PDQT, comprising diketopyrrolopyrrole (DPP) and β -unsubstituted quaterthiophene (QT) for organic thin film transistors (OTFTs) is reported. This polymer forms ordered layer-by-layer lamellar packing with an edge-on orientation in thin films even without thermal annealing. The strong intermolecular interactions arising from the fused aromatic DPP moiety and the DPP–QT donor–acceptor interaction facilitate the spontaneous self-assembly of the polymer chains into close proximity and form a large π – π overlap, which are favorable for intermolecular charge hopping. The well-interconnected crystalline grains form efficient intergranular charge transport pathways. The desirable chemical, electronic, and morphological structures of PDQT bring about high hole mobility of up to 0.97 cm²/(V·s) in OTFTs with polymer thin films annealed at a mild temperature of 100 °C and similarly high mobility of 0.89 cm²/(V·s) for polymer thin films even without thermal annealing.

- Design, Synthesis, and Study of a Mycobactin–Artemisinin Conjugate That Has Selective and Potent Activity against Tuberculosis and Malaria
Miller, M. J.; Walz, A. J.; Zhu, H.; Wu, C.; Moraski, G.; Mullmann, U.; Tristani, E. M.; Crumbliss, A. L.; Ferdig, M. T.; Checkley, L.; Edwards, R. L.; Boshoff, H. I. *J. Am. Chem. Soc.* **2011**, *133*, 2076–2079.

Abstract:

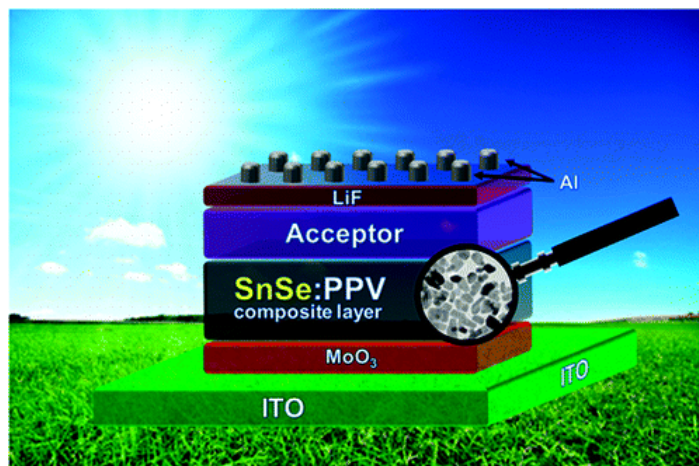


Although the antimalarial agent artemisinin itself is not active against tuberculosis, conjugation to a mycobacterial-specific siderophore (microbial iron chelator) analogue induces significant and selective antituberculosis activity, including activity against multi- and extensively drug-resistant strains of *Mycobacterium tuberculosis*. The conjugate also retains potent antimalarial activity. Physicochemical and whole-cell studies indicated that ferric-to-ferrous reduction of the iron complex of the conjugate initiates the expected bactericidal Fenton-type radical chemistry on the artemisinin component. Thus, this “Trojan horse” approach demonstrates that new pathogen-selective therapeutic agents in which the iron component of the delivery vehicle also participates in triggering

the antibiotic activity can be generated. The result is that one appropriate conjugate has potent and selective activity against two of the most deadly diseases in the world.

- Solution-Phase Synthesis of SnSe Nanocrystals for Use in Solar Cells
Franzman, M. A.; Schlenker, C. W.; Thompson, M. E.; Brutchey, R. L. *J. Am. Chem. Soc.* **2010**, *132*, 4060–4061.

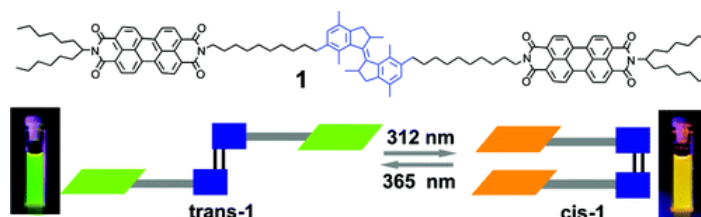
Abstract:



Nanocrystals of phase-pure tin(II) selenide (SnSe) were synthesized via a solution-phase route employing stoichiometric amounts of di-*tert*-butyl diselenide as a novel and facile selenium source. The direct band gap of the resulting nanocrystals ($E_g = 1.71$ eV) is significantly blue-shifted relative to the bulk value ($E_g = 1.30$ eV), a likely consequence of quantum confinement resulting from the relatively small average diameter of the nanocrystals ($\mu_D < 20$ nm). Preliminary solar cell devices incorporating SnSe nanocrystals into a poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] matrix demonstrate a significant enhancement in quantum efficiency and short-circuit current density, suggesting that this earth-abundant material could be a valuable component in future photovoltaic devices.

- Photoswitchable Intramolecular H-Stacking of Perylenebisimide
Wang, J.; Kulago, A.; Brownem, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2010**, *132*, 4191–4196.

Abstract:



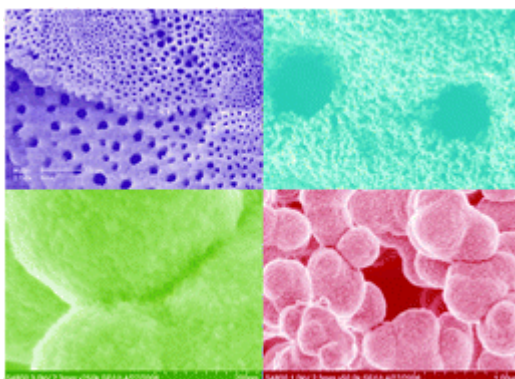
Dynamic control over the formation of H- or J-type aggregates of chromophores is of fundamental importance for developing responsive organic optoelectronic materials. In this study, the first example of photoswitching between a nonstacked and an intramolecularly H-stacked arrangement of perylenebisimides (PBI) is demonstrated. The system is composed of a central switching unit (overcrowded alkene) tethered to two PBI chromophores. *cis*–*trans* isomerization of the switching unit, induced by alternate irradiation at 312 and 365 nm, can drive two PBI chromophores reversibly between an intramolecularly “aggregated” and “nonaggregated” state. Distinct changes in UV–vis absorption and fluorescence spectra are observed following photoisomerization. This approach

allows for efficient control of intramolecular H-stack formation with no significant intermolecular interactions spanning over at least 4 orders of magnitude of concentration (from 10^{-8} to 10^{-4} M) and a range of solvents and temperatures.

- Self-formation phenomenon to hierarchically structured porous materials: design, synthesis, formation mechanism and applications

Yang, X.-Y.; Léonard, A.; Lemaire, A.; Tian, G.; Su, B.-L. *Chem. Commun.* **2011**, 47, 2763-2786.

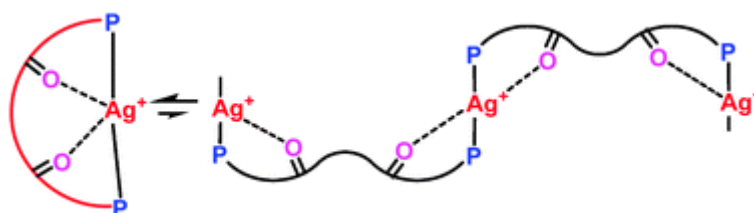
Abstract:



In this paper, we will thoroughly review a novel and versatile self-formation phenomenon that can be exploited to target porous hierarchies of materials without need of any external templates only on the basis of the chemistry of metal alkoxides and alkylmetals. These hierarchically porous materials have unique structures, which are made of either parallel funnel-like/straight macrochannels or 3D continuous interconnected macroporous foams with micro/mesoporous walls. The self-generated porogen mechanism has been proposed, leading to a series of techniques to tailor porous hierarchy, i.e. the use of different chemical precursors (single metal alkoxides, mixed metal alkoxides, single molecular precursors with two different alkoxide functionalities, alkylmetals, etc., ...), the control of their hydrolysis and condensation rates (pH, chelating agents,...) and the addition of alkoxysilanes as co-reactant. Various chemical compositions from single or binary metal oxides, to aluminosilicates, aluminophosphates, silicoaluminophosphates, metallophosphates,... can be prepared, offering a panel of potential applications. Some perspectives have been proposed to transform the synthesized materials with a hierarchy of pore sizes to micro–meso–macroporous crystalline materials with zeolite architectures. The advantages of this self-formation preparation method have been discussed compared to traditional templating methods. The possibility to combine with other strategies, for example soft or hard templating, to target even more sophisticated hierarchically meso–macroporous materials with specific structure and function for various applications has been presented. The “hierarchical catalysis” concept has been re-visited.

- Self-assembled polymers of silver(I) with a chiral diphosphine ligand
Nasser, N.; Puddephatt, R. J. *Chem. Commun.* **2011**, 47, 2808-2810.

Abstract:

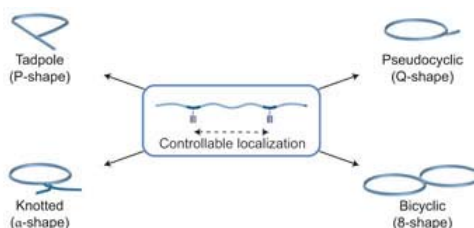


Silver(I) salts, AgX , form self-assembled polymers with the chiral diphosphine ligand *R,R-trans*- $\text{C}_6\text{H}_{10}(\text{NHCO-2-C}_6\text{H}_4\text{PPh}_2)_2$, **1**, of formula $\{\text{Ag}_2\text{X}_2(\mu\text{-1})\}_n$ and ring-opening polymerization of the *trans* chelate complex $[\text{Ag}(\text{1})]\text{X}$ has given the helical polymer $[\{\text{Ag}(\mu\text{-1})\}_n]\text{X}_n$, when $\text{X} = \text{CF}_3\text{SO}_3$.

- Controlled folding of synthetic polymer chains through the formation of positionable covalent bridges

Schmidt, B. V. K. J.; Fechler, N.; Falkenhagen, J.; Lutz, J.-F. *Nature Chemistry* **2011**, *3*, 236–240.

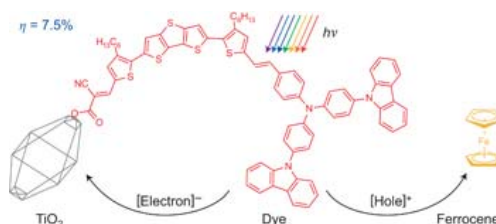
Abstract:



Covalent bridges play a crucial role in the folding process of sequence-defined biopolymers. This feature, however, has not been recreated in synthetic polymers because, apart from some simple regular arrangements (such as block co-polymers), these macromolecules generally do not exhibit a controlled primary structure—that is, it is difficult to predetermine precisely the sequence of their monomers. Herein, we introduce a versatile strategy for preparing foldable linear polymer chains. Well-defined polymers were synthesized by the atom transfer radical polymerization of styrene. The controlled addition of discrete amounts of protected maleimide at precise times during the synthesis enabled the formation of polystyrene chains that contained positionable reactive alkyne functions. Intramolecular reactions between these functions subsequently led to the formation of different types of covalently folded polymer chains. For example, tadpole (P-shaped), pseudocyclic (Q-shaped), bicyclic (β-shaped) and knotted (α-shaped) macromolecular origamis were prepared in a relatively straightforward manner.

- High-efficiency dye-sensitized solar cells with ferrocene-based electrolytes
Daeneke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. *Nature Chemistry* **2011**, *3*, 213–217.

Abstract:



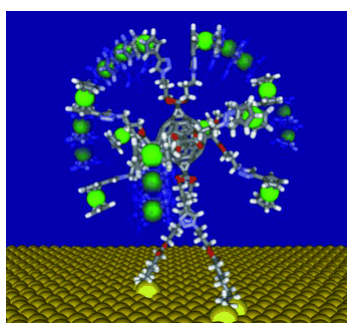
Dye-sensitized solar cells based on iodide/triiodide (I^-/I_3^-) electrolytes are viable low-cost alternatives to conventional silicon solar cells. However, as well as providing record efficiencies of up to 12.0%, the use of I^-/I_3^- in such solar cells also brings about certain limitations that stem from its corrosive nature and complex two-electron redox chemistry. Alternative redox mediators have been investigated, but these generally fall well short of matching the performance of conventional I^-/I_3^- electrolytes. Here, we report energy conversion efficiencies of 7.5% (simulated sunlight, AM1.5, $1,000 \text{ W m}^{-2}$) for dye-sensitized solar cells combining the archetypal ferrocene/ferrocenium (Fc/Fc^+) single-electron redox couple with a novel metal-free organic donor–acceptor sensitizer (Carbz-

PAHTDTT). These Fc/Fc⁺-based devices exceed the efficiency achieved for devices prepared using I⁻/I₃⁻ electrolytes under comparable conditions, revealing the great potential of ferrocene-based electrolytes in future dye-sensitized solar cells applications. This improvement results from a more favourable matching of the redox potential of the ferrocene couple with that of the new donor–acceptor sensitizer.

- Molecular Motion Inside an Adsorbed [5:1] Fullerene Hexaadduct Observed by Ultrafast Cyclic Voltammetry

Fortgang, P.; Maisonhaute, E.; Amatore, C.; Delavaux-Nicot, B.; Iehl, J.; Nierengarten, J. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 2364–2367.

Abstract:

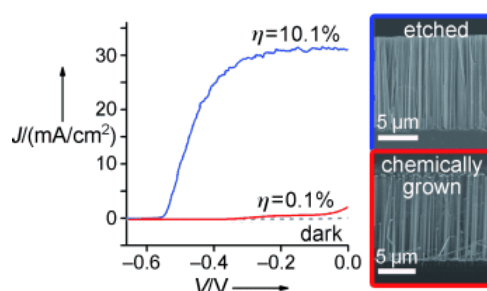


A rigid 3D scaffold in a 2D world! A mixed [5:1] fullerene hexaadduct that bears ten peripheral ferrocene redox subunits has been anchored onto a gold surface (see picture, green: iron, black: carbon, white: hydrogen, red: oxygen, blue: nitrogen). Ultrafast cyclic voltammetry investigations revealed that both intramolecular electron hopping and molecular motions influence the electron transfer from the ferrocene moieties to the electrode.

- Understanding the Origin of the Low Performance of Chemically Grown Silicon Nanowires for Solar Energy Conversion

Yuan, G.; Aruda, K.; Zhou, S.; Levine, A.; Xie, J.; Wang, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 2334–2338.

Abstract:



Wired: Electrochemical impedance spectroscopy (ESI) reveals that high energy-conversion efficiencies are attainable on vertically aligned Si nanowires obtained by electroless etching (see picture). The key reason for the low performance of chemically grown Si nanowires lies in the mid-gap traps as a result of growth chemistry.