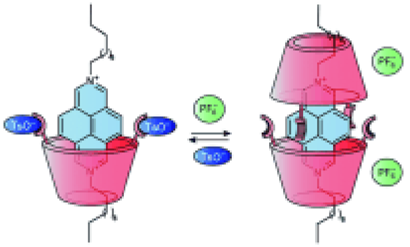
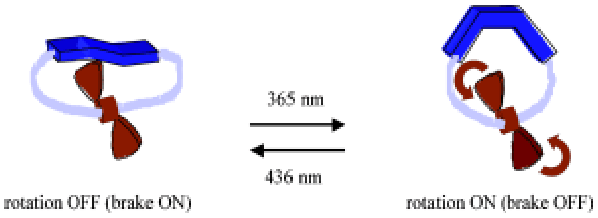
- Self-Assembly of Calix[6]arene-Diazapyrenium Pseudorotaxanes: Interplay of Molecular Recognition and Ion-Pairing Effects
  Semeraro, M.; Arduini, A.; Baroncini, M.; Battelli, R.; Credi, A.; Venturi, M.; Pochini, A.; Secchi, A.; Silvi, S. *Chem. Eur. J.* **2010**, *16*, 3467-3475.
  <u>Abstract:</u>



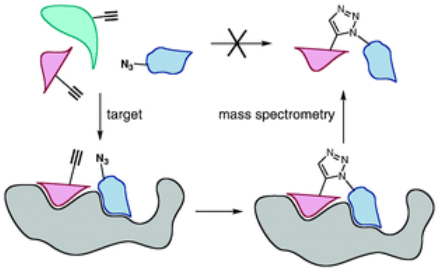
The calix[6]arene wheel **CX** forms pseudorotaxane species with the diazapyrenium-based axle **1**·$2PF_6$ in CH_2Cl_2 solution. The macrocyclic component is a heteroditopic receptor, which can complex the electron-acceptor moiety of the axle inside its cavity and the counterions with the ureidic groups on the upper rim. The self-assembled supramolecular species is a complex structure, which involves three components - the wheel, the axle and its counterions - that can mutually interact and affect. The stoichiometry of the resulting supramolecular complex depends on the nature and concentration of the counterions. Namely, it is observed that in dilute solution and with low-coordinating anions the axle takes two wheels, whereas with highly coordinating anions or in concentrated solutions the complex has a 1:1 stoichiometry.

- A Light-Controlled Molecular Brake with Complete ON-OFF Rotation
  Basheer, M. C.; Oka, Y.; Mathews, M.; Tamaoki, N. *Chem. Eur. J.* **2010**, *16*, 3489-3496.
  <u>Abstract:</u>



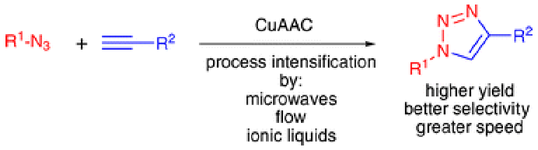
A light-controlled molecular machine based on cyclic azobenzenophanes consisting of a dioxynaphthalene rotating unit and a photoisomerizable dioxyazobenzene unit bridged by methylene spacers is reported. In compounds **1** and **2**, 1,5- and 2,6-dioxynaphthalene moieties, respectively, are linked to *p*-dioxyazobenzene by different methylene spacers (*n* = 2 in **1 a** and **2**; *n*=3 in **1 b**), whereas a 1,5-dioxynaphthalene moiety is bonded to *m*-dioxyazobenzene by bismethylene spacers in **3**. In **1 b** and **2**, the naphthalene ring can rotate freely in both the *trans* and *cis* states at room temperature. The rotation speed can be controlled either by photoinduced reversible *trans-cis* (*E-Z*) isomerization of the azobenzene or by keeping the system at low temperature, as is evident from its NMR spectra. Furthermore, for the first time, we demonstrate a light-controlled molecular brake, wherein the rotation of the naphthalene moiety through the cyclophane is completely OFF in the *trans* isomer of compound **3** due to its smaller cavity size. Such restricted rotation imparts planar chirality to the molecule, and the corresponding enantiomers could be resolved by chiral HPLC. However, the rotation of the naphthalene moiety is rendered ON in the *cis* isomer due to its increased cavity size, and it is manifested experimentally by the racemization of the separated enantiomers by photoinduced *E-Z* isomerization.

- *In situ* click chemistry: probing the binding landscapes of biological molecules
  Mamidyala, S. K.; Finn, M. G. *Chem. Soc. Rev.* **2010**, *39*, 1252 – 1261.
  Abstract:



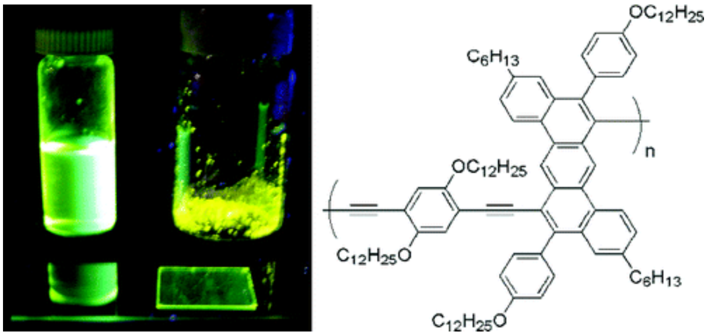
Combinatorial approaches to the discovery of new functional molecules are well established among chemists and biologists, inspired in large measure by the modular composition of many systems and molecules in Nature. Many approaches rely on the synthesis and testing of individual members of a candidate combinatorial library, but attention has also been paid to techniques that allow the target to self-assemble its own binding agents. These fragment-based methods, grouped under the general heading of target-guided synthesis (TGS), show great promise in lead discovery applications. In this *tutorial review*, we review the use of the 1,3-dipolar cycloaddition reaction of organic azides and alkynes in a kinetically-controlled TGS approach, termed *in situ* click chemistry. The azide–alkyne reaction has several distinct advantages, most notably high chemoselectivity, very low background ligation rates, facile synthetic accessibility, and the stability and properties of the 1,2,3-triazole products. Examples of the discovery of potent inhibitors of acetylcholinesterases, carbonic anhydrase, HIV-protease, and chitinase are described, as are methods for the templated assembly of agents that bind DNA and proteins.

- Click chemistry under non-classical reaction conditions
  Kappe, C. O.; Van der Eycken, E. *Chem. Soc. Rev.* **2010**, *39*, 1280 – 1290.
  Abstract:



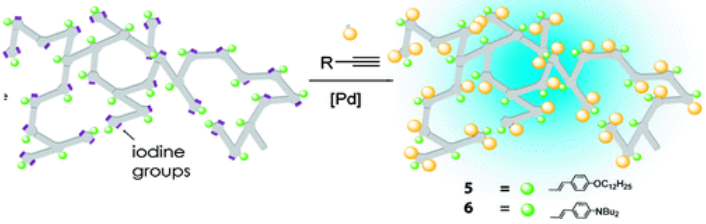
First described almost a decade ago, "click" reactions such as the Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) are widely used today in organic and medicinal chemistry, in the polymer and material science field, and in chemical biology. While most click reactions can be performed at room temperature there are instances where some form of process intensification is required. In this *tutorial review*, aimed at the synthetic chemistry community, examples of click chemistry carried out under non-classical reaction conditions, such as for example applying microwave heating or continuous flow processing will be highlighted.

- Synthesis of Stair-Stepped Polymers Containing Dibenz[*a*,*h*]anthracene Subunits
  Chan, J. M. W.; Kooi, S. E.; Swager, T. M. *Macromolecules* **2010**, *43*, 2789–2793.
  Abstract:



Polycyclic aromatic monomers based on substituted dibenz[*a*,*h*]anthracene frameworks have been prepared in high yields. From these, several fluorescent stair-stepped conjugated polymers containing fused aromatic subunits have been synthesized via Sonogashira polycondensations and Glaser-type oxidative couplings. The new polymers were characterized by NMR spectroscopy, gel-permeation chromatography (GPC), UV–vis, and fluorescence spectroscopy.

- Hyperbranched Conjugated Polymers: Postfunctionalization
  Kub, C.; Tolosa, J.; Zucchero, A. J.; McGrier, P. L.; Subramani, C.; Khorasani, A.; Rotello, V. M.; Bunz, U. H. F. *Macromolecules* **2010**, *43*, 2124–2129.
  Abstract:

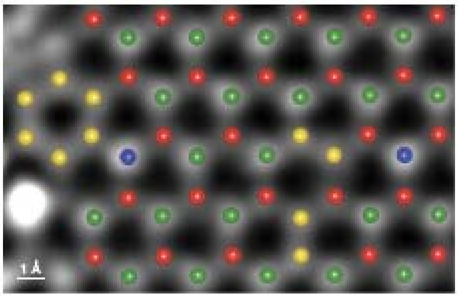


In this contribution, the synthesis of two different hyperbranched poly(phenylene vinylene-phenylene ethynylene) (HB-PPV-PPE, **3a**–**b**) scaffolds are reported. The necessary AB$_2$ monomer **2** is obtained by an asymmetric Horner reaction and contains two iodine substituents and one ethynyl group. This AB$_2$ monomer provides, after Sonogashira polymerization, a hyperbranched conjugated polymer decorated with iodine groups, suitable to be further functionalized with terminal alkynes **4a**–**t** by a Pd-catalyzed coupling. Elemental analysis of the postfunctionalized polymers **5a**–**t** and **6a**–**q** reveals nearly complete substitution of the iodine groups. As a consequence of the replacement, substantial increases in fluorescence quantum yields as well as variation in the optical response of the new polymers are observed. The spectroscopic properties of the postfunctionalized polymers were investigated in solution and in the solid state. The emission of the formed hyperbranched polymers shows a strong dependence on the functional groups attached to the conjugated structure and ranges from 510 nm for **5a** to 602 nm for **6h**. In all cases, solid-state emission is surprisingly strong and red-shifted compared with emission observed in solution.

- Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy

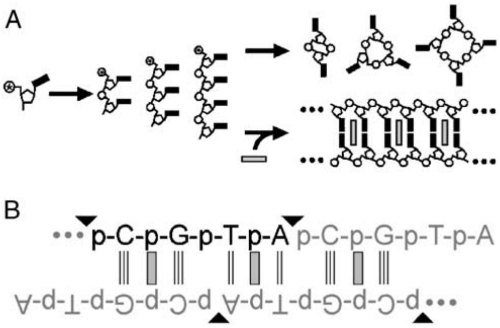
Krivanek, O. L.; Chisholm, M. F.; Nicolosi, V.; Pennycook, T. J.; Corbin, G. J.; Dellby, N.; Murfitt, M. F.; Own, C. S.; Szilagyi, Z. S.; Oxley, M. P.; Pantelides, S. T.; Pennycook, S. J. *Nature* **2010**, *464*, 571-574.

Abstract:



Direct imaging and chemical identification of all the atoms in a material with unknown three-dimensional structure would constitute a very powerful general analysis tool. Transmission electron microscopy should in principle be able to fulfil this role, as many scientists including Feynman realized early on. It images matter with electrons that scatter strongly from individual atoms and whose wavelengths are about 50 times smaller than an atom. Recently the technique has advanced greatly owing to the introduction of aberration-corrected optics. However, neither electron microscopy nor any other experimental technique has yet been able to resolve and identify all the atoms in a non-periodic material consisting of several atomic species. Here we show that annular dark-field imaging in an aberration-corrected scanning transmission electron microscope optimized for low voltage operation can resolve and identify the chemical type of every atom in monolayer hexagonal boron nitride that contains substitutional defects. Three types of atomic substitutions were found and identified: carbon substituting for boron, carbon substituting for nitrogen, and oxygen substituting for nitrogen. The substitutions caused in-plane distortions in the boron nitride monolayer of about 0.1 Å magnitude, which were directly resolved, and verified by density functional theory calculations. The results demonstrate that atom-by-atom structural and chemical analysis of all radiation-damage-resistant atoms present in, and on top of, ultra-thin sheets has now become possible.

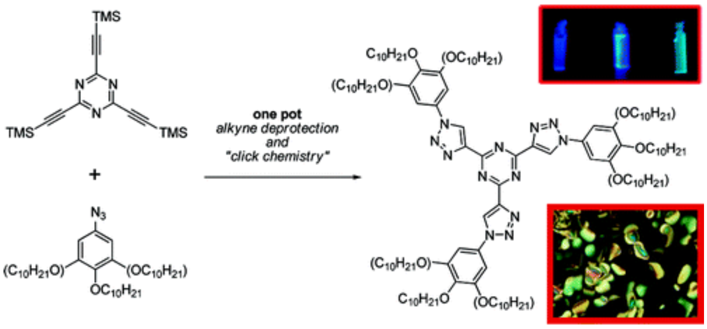
- Intercalation as a means to suppress cyclization and promote polymerization of base-pairing oligonucleotides in a prebiotic world
  Horowitz, E. D.; Engelhart, A. E.; Chen, M. C.; Quarles, K. A.; Smith, M. W.; Lynn, D. G.; Hud, N. V. *Proc. Natl. Acad. Sci. USA.* **2010**, *107*, 5288-5293.
  Abstract:



The RNA world hypothesis proposes that nucleic acids were once responsible for both information storage and chemical catalysis, before the advent of coded protein synthesis.

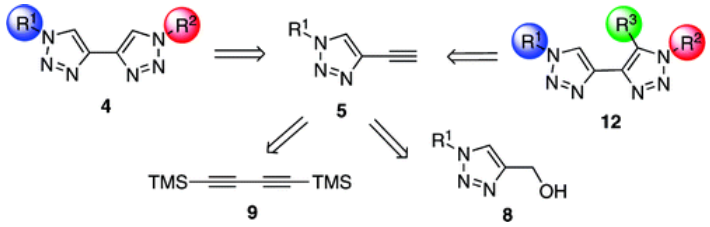
However, it is difficult to imagine how nucleic acid polymers first appeared, as the abiotic chemical formation of long nucleic acid polymers from mononucleotides or short oligonucleotides remains elusive, and barriers to achieving this goal are substantial. One specific obstacle to abiotic nucleic acid polymerization is strand cyclization. Chemically activated short oligonucleotides cyclize efficiently, which severely impairs polymer growth. We show that intercalation, which stabilizes and rigidifies nucleic acid duplexes, almost totally eliminates strand cyclization, allowing for chemical ligation of tetranucleotides into duplex polymers of up to 100 base pairs in length. In contrast, when these reactions are performed in the absence of intercalators, almost exclusively cyclic tetra- and octanucleotides are produced. Intercalator-free polymerization is not observed, even at tetranucleotide concentrations > 10,000-fold greater than those at which intercalators enable polymerization. We also demonstrate that intercalation-mediated polymerization is most favored if the size of the intercalator matches that of the base pair; intercalators that bind to Watson–Crick base pairs promote the polymerization of oligonucleotides that form these base pairs. Additionally, we demonstrate that intercalation-mediated polymerization is possible with an alternative, non-Watson–Crick-paired duplex that selectively binds a complementary intercalator. These results support the hypothesis that intercalators (acting as 'molecular midwives') could have facilitated the polymerization of the first nucleic acids and possibly helped select the first base pairs, even if only trace amounts of suitable oligomers were available.

- Tris(triazolyl)triazine via Click-Chemistry: A C_3 Electron-Deficient Core with Liquid Crystalline and Luminescent Properties
  Beltrán, E.; Serrano, J. L.; Sierra, T.; Giménez, R. *Org. Lett.* **2010**, *12*, 1404–1407.
  Abstract:



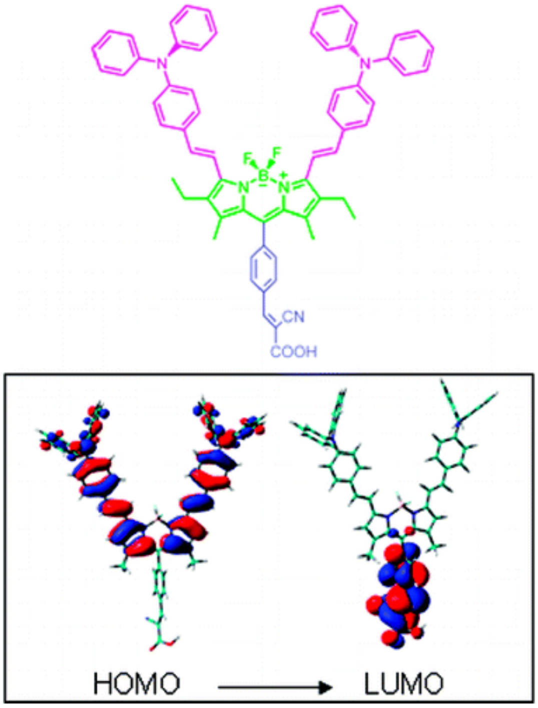
The synthesis of a novel core based on tris(triazolyl)triazine has been accomplished by a one-pot procedure that combines a 3-fold deprotection of alkyne groups and "click chemistry" of the aromatic alkyne and azide precursors. The procedure is straightforward for the preparation of functional materials for organic electronics. Indeed, compounds with low reduction potential are obtained. These compounds also show liquid crystalline behavior, displaying columnar mesophases at room temperature, and are luminescent in the visible region both in solution and in thin films

- "Click" Synthesis of Nonsymmetrical Bis(1,2,3-triazoles)
  Aizpurua, J. M.; Azcune, I.; Fratila, R. M.; Balentova, E.; Sagartzazu-Aizpurua, M.; Miranda, J. I. *Org. Lett.* **2010**, *12*, 1584–1587.
  Abstract:



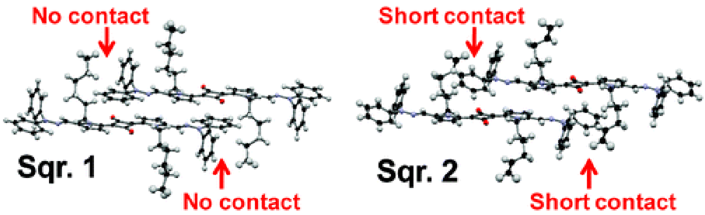
Unsymmetrically 1,1′-disubstituted 4,4′-bis-1*H*-1,2,3-triazoles **4** have been prepared from 4-ethynyl-1,2,3-triazoles **5** and azides. Following a “double-click” strategy, two complementary approaches were implemented for the preparation of the key 4-ethynyltriazole intermediates **5**: (a) the stepwise Swern oxidation/Ohira−Bestman alkynylation of readily available 4-hydroxymethyl-1,2,3-triazoles **8** and (b) the stepwise cycloaddition of TMS-1,4-butadiyne **9**. The method is highlighted by its compatibility with orthogonally protected and functionalized saccharide−peptide hybrids and its ability to be extended to the trisubstituted counterparts **12**.

- A Panchromatic Boradiazaindacene (BODIPY) Sensitizer for Dye-Sensitized Solar Cells
  Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299–3302.
  Abstract:



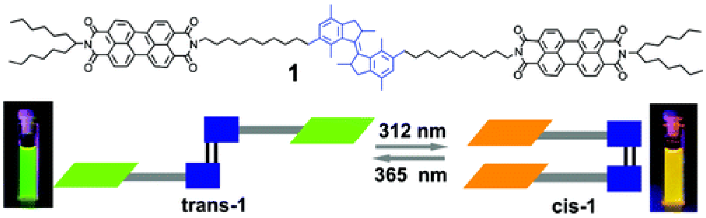
A novel distyryl-substituted boradiazaindacene (BODIPY) dye displays interesting properties as a sensitizer in DSSC systems, opening the way to further exploration of structure−efficiency correlation within this class of dyes.We now propose that, when judiciously designed, BODIPY dyes have certain unique features that could make them highly advantageous compared to most other organic dyes, and thus, they are highly promising in this regard. BODIPY dyes have high extinction coefficients (70 000–80 000 M^{-1} cm^{-1}) and can easily be modified with any desired functionalities. Absorption peak can be moved to longer wavelengths through simple modifications, keeping strong absorption cross sections. BODIPY dyes have inherent asymmetry in charge redistribution when they undergo $S_0 \rightarrow S_1$ transition upon excitation, increasing the charge density on the *meso*-carbon (C-8), while decreasing it in most other positions in the boradiazaindacene system . This inherent directionality of charge redistribution pinpoints C-8 as the optimal position of charge injection. The directionality observed in excitation can be further enhanced with strategically placed electron-withdrawing and electron-donating groups, and on the basis of earlier work, cyanoacrylic acid and 4-*N*,*N*′-diphenylaminophenyl groups are to be of tremendous utility in this regard.

- Marked Alkyl- vs Alkenyl-Substitutent Effects on Squaraine Dye Solid-State Structure, Carrier Mobility, and Bulk-Heterojunction Solar Cell Efficiency
  Bagnis, D.; Beverina, L.; Huang, H.; Silvestri, F.; Yao, Y.; Yan, H.; Pagani, G. A.; Marks, T. J.; Facchetti, A. *J. Am. Chem. Soc.* **2010**, *132*, 4074-4075.
  Abstract:



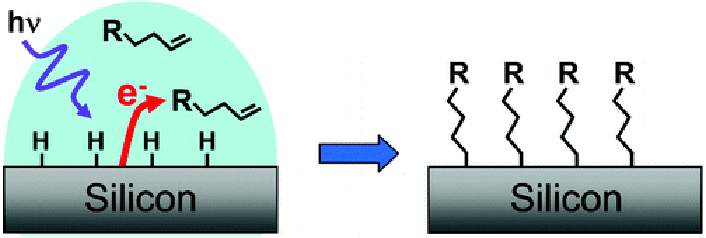
We report two new squaraine dyes substituted at the pyrrolic rings with n-hexyl (squaraine 1) or n-hexenyl (squaraine 2) chains. Although internal molecular structure variations are minimal, the presence of the terminal double bond results in a much more compact solid-state structure, dramatically affecting charge transport in the thin films; the hole mobility of 2 is ~5× that of 1, and the BHJ OPV power conversion efficiency (PCE) of 2 is ~2× that of 1. PCEs surpassing 2% for ambient solution-processed devices are demonstrated, the largest so far achieved for squaraine-based organic solar cells.

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



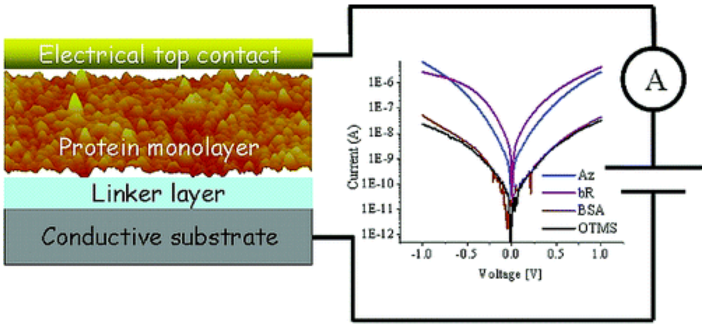
Dynamic control over the formation of H- or J-type aggregates of chromophores is of fundamental importance for developing responsive organic optoelectronic materials. In this study, the first example of photoswitching between a nonstacked and an intramolecularly H-stacked arrangement of perylenebisimides (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.

- UV-Induced Grafting of Alkenes to Silicon Surfaces: Photoemission versus Excitons
  Wang, X.; Ruther, R. E.; Streifer, J. A.; Hamers, R. J. *J. Am. Chem. Soc.* **2010**, *132*, 4048–4049.
  Abstract:



The mechanism of photochemical grafting of alkenes to H-terminated silicon has remained poorly understood. Here we demonstrate the importance of a previously unrecognized initiation process, photoelectron ejection (photoemission), as a facile way of initiating photochemical grafting of liquid alkenes to silicon surfaces when using ultraviolet light. A comparison of Si samples with vastly different photocarrier lifetimes showed no difference in the efficiency of alkene grafting. However, differences in the reactivities of different alkenes with different terminal groups that correlate with the electron affinities of these groups were observed. Our results indicate that photoemission is an effective way of initiating grafting because the irreversible nature of photoemission leaves the sample with a net excess of holes that have no corresponding electrons with which to recombine, while in a competing exciton mechanism, the net concentration of holes is limited by recombination processes.

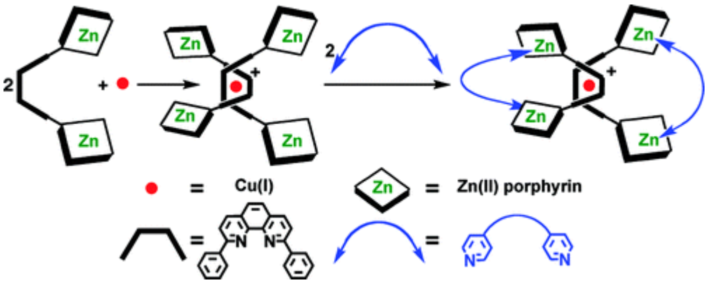
- Proteins as Electronic Materials: Electron Transport through Solid-State Protein Monolayer Junctions
  Ron, I.; Sepunaru, L.; Itzhakov, S.; Belenkova, T.; Friedman, N.; Pecht, I.; Sheves, M.; Cahen, D. *J. Am. Chem. Soc.* **2010**, *132*, 4131–4140.
  Abstract:



Electron transfer (ET) through proteins, a fundamental element of many biochemical reactions, is studied intensively in aqueous solutions. Over the past decade, attempts were made to integrate proteins into solid-state junctions in order to study their electronic conductance properties. Most such studies to date were conducted with one or very few molecules in the junction, using scanning probe techniques. Here we present the high-yield, reproducible preparation of large-area monolayer junctions, assembled on a Si platform, of proteins of three different families: azurin (Az), a blue-copper ET protein, bacteriorhodopsin (bR), a membrane protein-chromophore complex with a proton pumping function, and bovine serum albumin (BSA). We achieve highly reproducible electrical current measurements with these

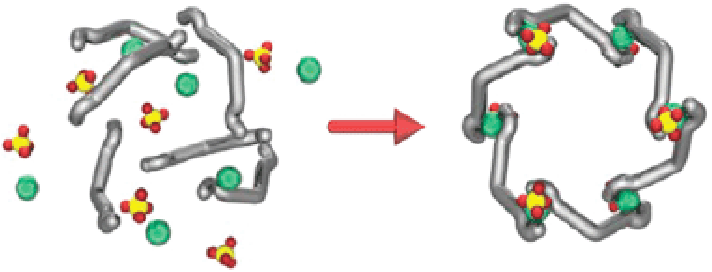
three types of monolayers using appropriate top electrodes. Notably, the current−voltage (*I*−*V*) measurements on such junctions show relatively minor differences between Az and bR, even though the latter lacks any known ET function. Electron Transport (ETp) across both Az and bR is much more efficient than across BSA, but even for the latter the measured currents are higher than those through a monolayer of organic, C18 alkyl chains that is about half as wide, therefore suggesting transport mechanism(s) different from the often considered coherent mechanism. Our results show that the employed proteins maintain their conformation under these conditions. The relatively efficient ETp through these proteins opens up possibilities for using such biomolecules as current-carrying elements in solid-state electronic devices.

- Coordination Chemistry-Assembled Porphyrinic Catenanes
  Beyler, M.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2010**, *132*, 4409–4417.
  Abstract:



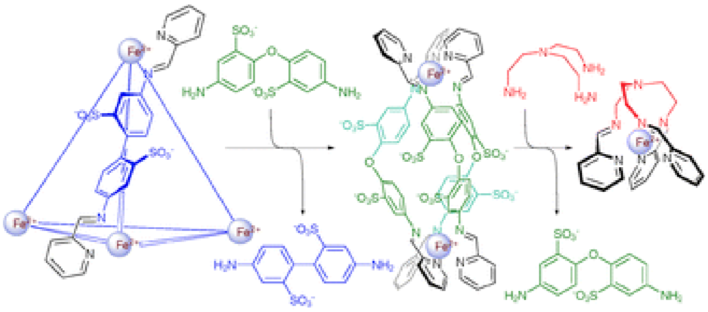
Non covalent [2]catenanes were synthesized in high yield as kinetic products or as thermodynamic products after completion of an equilibrium. These sophisticated architectures were assembled in two steps, from an oblique bis-zinc(II) porphyrin and two different dipyridyl chelates, by using Cu(I)−N interactions to assemble acyclic complexes and Zn(II)−N interactions to generate rings. ^{1}H NMR including 2D COSY and ROESY experiments were used to characterize each compound. Spectrophotometric titrations highlight the influence of geometry in terms of distances and angles in non covalent coordinated assemblies. In fact, it was proved that a perfect fit leads to highly stable coordination chemistry-assembled species.

- Self-assembly of neutral hexanuclear circular copper(II) meso-helicates: topological control by sulfate ions
  Tanh Jeazet, H. B.; Gloe, K.; Doert, T.; Kataeva, O. N.; Jäger, A.; Bernhard, G.; Büchner, B.; Gloe, K. *Chem. Commun.* **2010**, *46*, 2373 – 2375.
  Abstract:



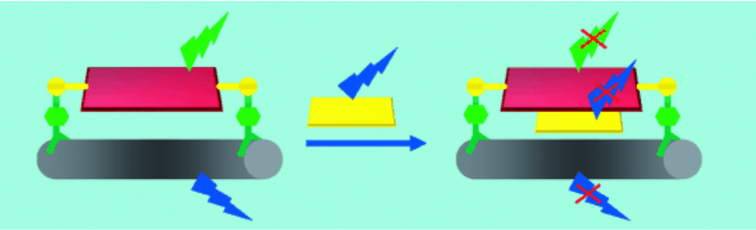
Bis-pyridylimine ligands with different linking elements are capable of forming unique hexanuclear circular Cu(II) meso-helicates; the self-assembly is controlled by coordination of sulfate ions to the metal centres.

- Sequential self-assembly of iron structures in water
  Mal, P.; Nitschke, J. R. *Chem. Commun.* **2010**, *46*, 2417 – 2419.
  Abstract:



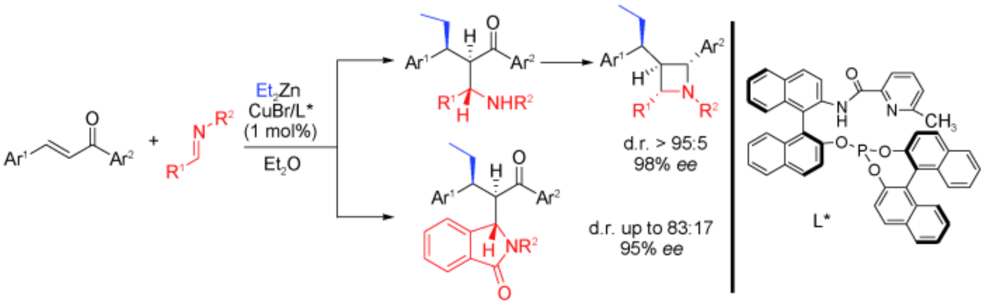
The deterministic behaviour of a sequential self-assembling system may be expressed in the form of an algorithm that predicts the products of self-assembly at any ratio of input subcomponents.

- Supramolecular Interactions at the Inorganic–Organic Interface in Hybrid Nanomaterials
  Liu, H.; Zuo, Z.; Guo, Y.; Li, Y.; Li, Y. *Angew. Chem. Int. Ed*. **2010**, *49*, 2705 –2707.
  Abstract:



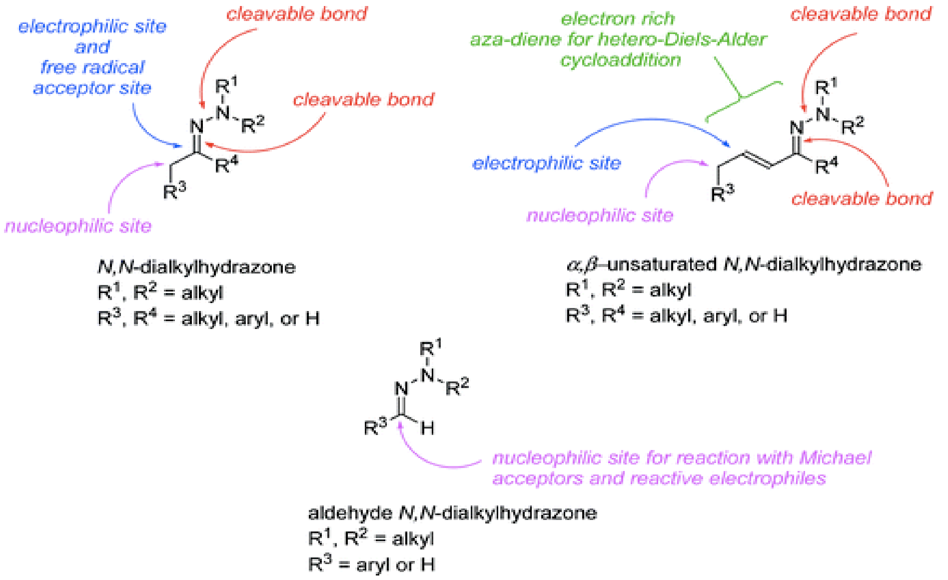
Pickpocket: Perylene can be detected by inorganic-organic nanomaterials comprising ZnO nanorods (gray cylinder) and perylene diimide derivatives (red rectangle). Intercalation of perylene (yellow rectangle) in a molecular pocket at the inorganic-organic interface results in fluorescence quenching of the three components with a detection limit as low as 10^{-12} M.

- Diastereo- and Enantioselective Catalytic Tandem Michael Addition/Mannich Reaction: Access to Chiral Isoindolinones and Azetidines with Multiple Stereocenters
  Guo, S.; Xie, Y.; Hu, X.; Xia, C.; Huang, H. *Angew. Chem. Int. Ed*. **2010**, *49*, 2728 –2731.
  Abstract:



Michael and Mannich cooperate: A rapid and reliable approach to highly functionalized chiral isoindolindone and azetidine derivatives, possessing multiple contiguous stereogenic centers, has been achieved (see scheme).

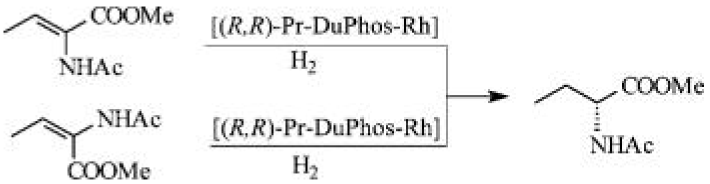
- N,N-Dialkylhydrazones in Organic Synthesis. From Simple N,N-Dimethylhydrazones to Supported Chiral Auxiliaries
  Lazny, R.; Nodzewska, A. *Chem. Rev.* **2010**, *110*, 1386–1434.
  Abstract:



The well-known properties of the carbonyl group render aldehydes and ketones prominent substrates in both C−C and C−heteroatom bond forming methodologies of organic synthesis. In practical syntheses, nitrogen analogues of aldehydes and ketones such as enamines, imines, or hydrazones, acting as synthetic equivalents of the carbonyl compounds, are often preferred. From a synthesis point of view, N,N-dialkylhydrazones offer many advantages: high nucleophilicity of their metalated species, regioselectivity, controlled α-monoalkylation, and the possibility of using the hydrazone moiety as a chiral auxiliary or a multifunctional linker in solid-phase synthesis.

Even though N,N-dialkylhydrazones show very diverse reactivity and can participate in polar, free radical, pericyclic, and organometallic catalytic reactions, it is their reactivity as aldehyde and ketone synthetic equivalents, where they participate in nucleophile−electrophile interactions, that has found major uses in synthesis. The goal of this review is to bring the reader up to date regarding the synthetic utility of these important and versatile reagents.

- Unexpected Inversions in Asymmetric Reactions: Reactions with Chiral Metal Complexes, Chiral Organocatalysts, and Heterogeneous Chiral Catalysts
  Bartk, M. *Chem. Rev.* **2010**, *110*, 1663–1705.
  Abstract:



The recognition of the optical activity of organic compounds, followed by the detailed analysis of optical isomerism, laid the foundation for the development of asymmetric syntheses, a group of reactions of fundamental significance. Asymmetric syntheses, available in great varieties, are the indispensable source of a large number of chiral compounds that have become essential for human society. Some of the most important procedures that belong to this group are asymmetric organocatalytic, asymmetric homogeneous and heterogeneous metal catalytic reactions, and enzyme-catalyzed procedures. One of the main tasks of pertinent research is the development of chiral catalysts that enable the preparation of the required product in the highest possible enantiomeric excess (ee). The value of ee depends on a number of known and yet unknown factors not only for a given reaction but also for each individual compound within a reaction type.