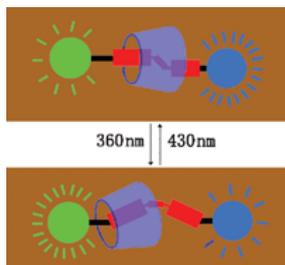


- Bright functional rotaxanes
Ma, X.; Tian, H. *Chem. Soc. Rev.* **2010**, *39*, 70 – 80.

Abstract:

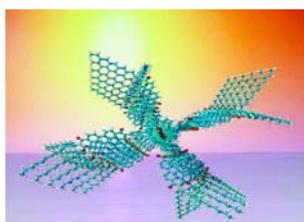


As a hot topic in research, various rotaxanes continue to be constructed. This *tutorial review* focuses mainly on bright rotaxanes with functional properties, which have been developed in recent years: fluorescent rotaxanes, rotaxanes as logic gates and information storage devices, gelation of rotaxanes, rotaxanes on solid surfaces, sensory rotaxanes, as well as rotaxanes related to biology and so on. Novel synthetic protocols towards several functional rotaxanes are also illustrated.

- Self-Assembly Strategies for Integrating Light Harvesting and Charge Separation in Artificial Photosynthetic Systems

Wasielwski, M. R. *Acc. Chem. Res.* **2009**, *42*, 1910–1921.

Abstract:



In natural photosynthesis, organisms optimize solar energy conversion through organized assemblies of photofunctional chromophores and catalysts within proteins that provide specifically tailored environments for chemical reactions. As with their natural counterparts, artificial photosynthetic systems for practical solar fuels production must collect light energy, separate charge, and transport charge to catalytic sites where multielectron redox processes will occur. While encouraging progress has been made on each aspect of this complex problem, researchers have not yet developed self-ordering and self-assembling components and the tailored environments necessary to realize a fully-functional artificial system.

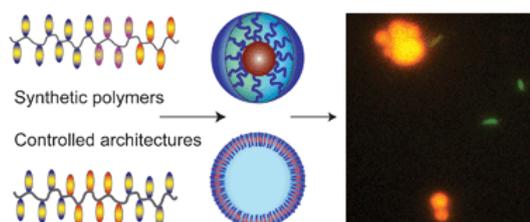
Previously researchers have used complex, covalent molecular systems comprised of chromophores, electron donors, and electron acceptors to mimic both the light-harvesting and the charge separation functions of photosynthetic proteins. These systems allow for study of the dependencies of electron transfer rate constants on donor–acceptor distance and orientation, electronic interaction, and the free energy of the reaction. The most useful and informative systems are those in which structural constraints control both the distance and the orientation between the electron donors and acceptors. Self-assembly provides a facile means for organizing large numbers of molecules into supramolecular structures that can bridge length scales from nanometers to macroscopic dimensions. The resulting structures must provide pathways for migration of light excitation energy among antenna chromophores, and from antennas to reaction centers. They also must incorporate charge conduits, that is, molecular “wires” that can efficiently move electrons and holes between reaction centers and catalytic sites. The central scientific challenge is to develop small, functional

building blocks with a minimum number of covalent linkages, which also have the appropriate molecular recognition properties to facilitate self-assembly of complete, functional artificial photosynthetic systems. In this Account, we explore how self-assembly strategies involving π -stacking can be used to integrate light harvesting with charge separation and transport.

Our current strategy uses covalent building blocks based on chemically robust arylene imide and diimide dyes, biomimetic porphyrins, and chlorophylls. We take advantage of the shapes, sizes, and intermolecular interactions—such as π - π and/or metal–ligand interactions—of these molecules to direct the formation of supramolecular structures having enhanced energy capture and charge-transport properties. We use small- and wide-angle X-ray scattering (SAXS/WAXS) from a synchrotron source to elucidate the solution phase structures of these monodisperse noncovalent aggregates. We expect that a greater understanding of self-assembly using π -stacking and molecular designs that combine those features with hydrogen bonding and metal-ligand bonding could simplify the structure of the building blocks for artificial photosynthetic complexes, while retaining their ability to assemble complex, photofunctional structures.

- Controlled polymer synthesis—from biomimicry towards synthetic biology
Pasparakis, G.; Krasnogor, N.; Cronin, L.; Davis, B. G.; Alexander, C. *Chem. Soc. Rev.* **2010**, *39*, 286 – 300.

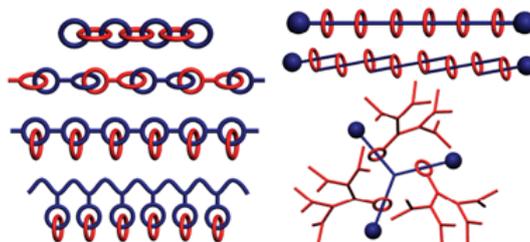
Abstract:



The controlled assembly of synthetic polymer structures is now possible with an unprecedented range of functional groups and molecular architectures. In this *critical review* we consider how the ability to create artificial materials over lengthscales ranging from a few nm to several microns is generating systems that not only begin to mimic those in nature but also may lead to exciting applications in synthetic biology (139 references).

- Mechanically bonded macromolecules
Fang, L.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Goddard III, W. A.; Stoddart, J. F. *Chem. Soc. Rev.* **2010**, *39*, 17 – 29.

Abstract:



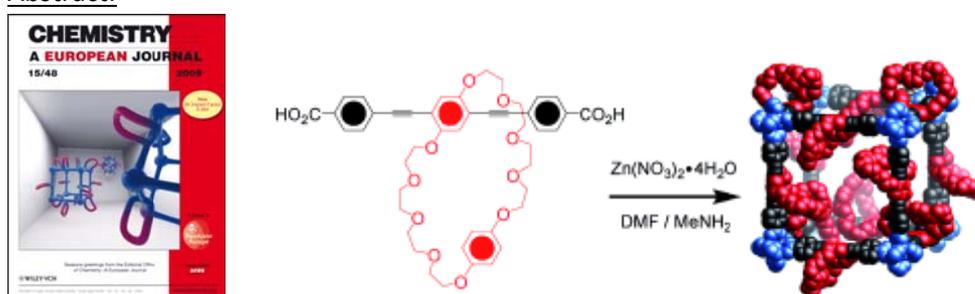
Mechanically bonded macromolecules constitute a class of challenging synthetic targets in polymer science. The controllable intramolecular motions of mechanical bonds, in combination with the processability and useful physical and mechanical properties of macromolecules, ultimately ensure their potential for applications in materials science, nanotechnology and medicine. This *tutorial*

review describes the syntheses and properties of a library of diverse mechanically bonded macromolecules, which covers (i) main-chain, side-chain, bridged, and pendant oligo/polycatenanes, (ii) main-chain oligo/polyrotaxanes, (iii) poly[*c*2]daisy chains, and finally (iv) mechanically interlocked dendrimers. A variety of highly efficient synthetic protocols—including template-directed assembly, step-growth polymerisation, quantitative conjugation, *etc.*—were employed in the construction of these mechanically interlocked architectures. Some of these structures, *i.e.*, side-chain polycatenanes and poly[*c*2]daisy chains, undergo controllable molecular switching in a manner similar to their small molecular counterparts. The challenges posed by the syntheses of polycatenanes and polyrotaxanes with high molecular weights are contemplated.

- Rigid-Strut-Containing Crown Ethers and [2]Catenanes for Incorporation into Metal-Organic Frameworks

Zhao, Y.-L.; Liu, L.; Zhang, W.; Sue, C.-H.; Li, Q.; Miljanić, O. Š.; Yaghi, O. M.; Stoddart, J. F. *Chem. Eur. J.* **2009**, *15*, 13356-12380.

Abstract:



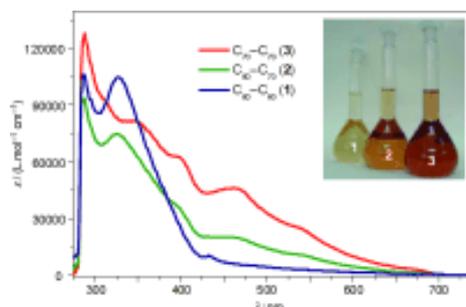
To introduce crown ethers into the struts of metal-organic frameworks (MOFs), general approaches have been developed for the syntheses of dicarboxylic acid dibenzo[30]crown-10 (DB30C10DA), dicarboxylic acid di-2,3-naphtho[30]crown-10 (DN30C10DA), dicarboxylic acid bisparaphenylene[34]crown-10 (BPP34C10DA), and dicarboxylic acid 1,5-naphthoparaphenylene[36]crown-10 (NPP36C10DA). These novel crown ethers not only retain the characteristics of their parent crown ethers since they can 1) bind cationic guests and 2) serve as templates for making mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes, but they also present coordination sites to connect with secondary building units (SBUs) in MOFs. The binding behavior of BPP34C10DA with 1,1'-dimethyl-4,4'-bipyridinium bis(hexafluorophosphate) (DMBP-2 PF₆) has been investigated by means of UV/Vis, fluorescence, and NMR spectroscopic techniques. The crystal superstructure of the complex DMBP-2 PF₆ ⋅ BPP34C10DA was determined by X-ray crystallography. The NPP36C10DA-based [2]catenane (H₂NPP36C10DC-CAT-4 PF₆) and the BPP34C10DA-based [2]catenane (H₂BPP34C10DC-CAT-4 PF₆) were prepared in DMF at room temperature by the template-directed clipping reactions of the planar chiral NPP36C10DA and BPP34C10DA with 1,1'-[1,4-phenylenebis(methylene)]di-4,4'-bipyridin-1-ium bis(hexafluorophosphate) and 1,4-bis(bromomethyl)benzene, respectively. The crystal structure of the dimethyl ester (BPP34C10DE-CAT-4 PF₆) of the [2]catenane H₂BPP34C10DC-CAT-4 PF₆ was investigated by X-ray crystallography, which revealed racemic *R* and *S* isomers with planar chirality present in the crystal in a 1:1 ratio. These crown ether based struts serve as excellent organic ligands to bind with transition metal ions in the construction of MOFs: the crown ethers BPP34C10DA and NPP36C10DA in the presence of Zn(NO₃)₂ · 4 H₂O afforded the MOF-1001 and MOF-1002 frameworks, respectively. The crystal structures of MOF-1001 and MOF-1002 are both cubic and display *Fm* $\bar{3}$ *m* symmetry. The unit cell parameter of the metal-organic frameworks is *a*=52.9345 Å. Since such

MOFs, containing electron-donating crown ethers are capable of docking incoming electron-accepting substrates in a stereoelectronically controlled fashion, the present work opens a new access to the preparation and application of MOFs.

- Fullerene Dimers (C_{60}/C_{70}) for Energy Harvesting

Delgado, J. L.; Espíldora, E.; Liedtke, M.; Sperlich, A.; Rauh, D.; Baumann, A.; Deibel, C.; Dyakonov, V.; Martín, N. *Chem. Eur. J.* **2009**, *15*, 12474-12482.

Abstract:

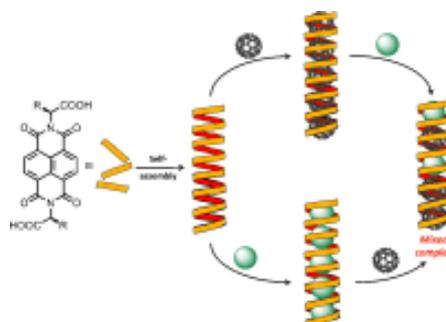


A new family of fullerene-based compounds, namely, soluble [60]- and [70]fullerene homodimers and the [60]/[70]heterodimer linked through 2-pyrazolino-pyrrolidino bridges, has been synthesised by simple procedures and in high yield. Electrochemical studies confirm their suitability to act as electron acceptors in combination with poly(3-hexylthiophene-2,5-diyl) (P3HT). Their optical properties in solution and in the solid state were studied. A significantly stronger absorption in [70]fullerene-containing dimers relative to [60]homodimer in solution in the visible range was observed. Furthermore, in all donor-acceptor blends studied an efficient charge transfer was observed by means of photoluminescence (PL), photoinduced absorption and light-induced electron spin resonance spectroscopy. The [70]homodimer was found to be a distinctive species, being the strongest PL quencher and most efficient acceptor with the longest lifetime of the charge-separated (polaron) states. As a consequence, bulk-heterojunction solar cells based on this novel [70]homodimer blended with P3HT demonstrated the highest quantum and power conversion efficiencies of 37 and 1 %, respectively, compared to those of [60]fullerene dimers.

- Ion Pairs and C_{60} : Simultaneous Guests in Supramolecular Nanotubes

Tamanini, E.; Pantoş, G. D.; Sanders, J. K. M. *Chem. Eur. J.* **2009**, *16*, 81-84.

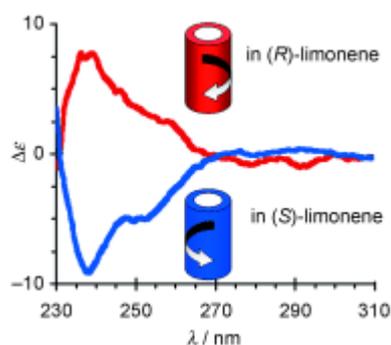
Abstract:



Naphthalenediimide-based supramolecular nanotubes act as size-selective receptors for ion pairs, as demonstrated by competition experiments with C_{60} (see picture). Fullerene forms mixed complexes inside the cavity of the nanotubes in the presence of the anion and ammonium ions of the appropriate size.

- Chirality in Dynamic Supramolecular Nanotubes Induced by a Chiral Solvent
Isare, B.; Linares, M.; Zargarian, L.; Fermandjian, S.; Miura, M.; Motohashi, S.; Vanthuyne, N.; Lazzaroni, R.; Bouteiller, L. *Chem. Eur. J.* **2009**, *16*, 173-177.

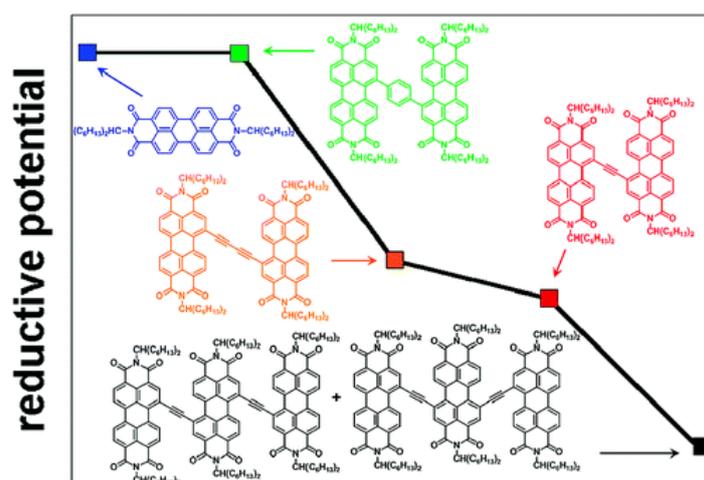
Abstract:



Amplification of chirality has been reported in polymeric systems. It has also been shown that related effects can occur in polymer-like dynamic supramolecular aggregates, if a subtle balance between noncovalent interactions allows the coupling between a chiral information and a cooperative aggregation process. In this context, we report a strong majority-rules effect in the formation of chiral dynamic nanotubes from chiral bisurea monomers. Furthermore, similar helical nanotubes (with the same circular dichroism signature) can be obtained from racemic monomers in a chiral solvent. Competition experiments reveal the relative strength of the helical bias induced by the chiral monomer or by the chiral solvent. The nanotube handedness is imposed by the monomer chirality, whatever the solvent chirality. However, the chirality of the solvent has a significant effect on the degree of chiral induction.

- Conjugated Dimeric and Trimeric Perylenediimide Oligomers
Yan, Q.; Zhao, D. *Org. Lett.* **2009**, *11*, 3426–3429.

Abstract:

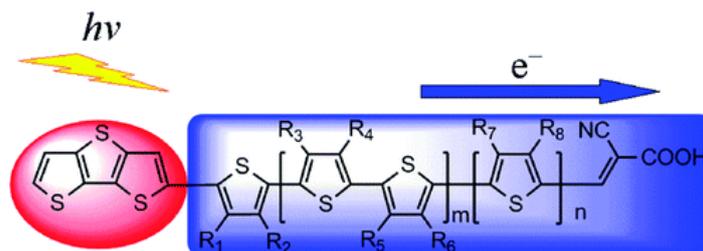


Dimeric and trimeric molecules comprising perylenediimide units conjugatively linked by phenylene, ethynylene, or a butadiynylene spacer via the bay positions were prepared. Electrochemical and photophysical characterizations showed that oligomers connected by C–C triple bond(s) exhibited effectively lowered LUMO compared to the monomer. Molecular modeling confirmed that the C–C triple bond realized efficient delocalization of frontier orbitals, while phenylene was less competent in extending the conjugation, partially due to steric interactions.

- Organic Dyes Incorporating the Dithieno[3,2-*b*:2',3'-*d*]thiophene Moiety for Efficient Dye-

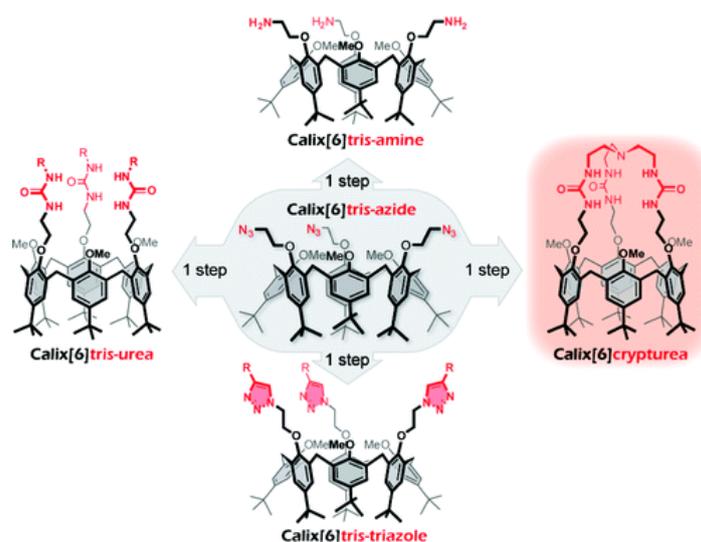
Sensitized Solar Cells

Yang, H.-Y.; Yen, Y.-S.; Hsu, Y.-C.; Chou, H.-H.; Lin, J. T. *Org. Lett.* **2010**, *12*, 16–19.

Abstract:

New dipolar compounds incorporating a dithieno[3,2-b:2',3'-d]thiophene unit as the electron donor, an oligothiophene moiety as the conjugated spacer, and 2-cyanoacrylic acid as the electron acceptor have been synthesized. These nonarylamine type metal-free organic compounds have been successfully used as the sensitizers of dye-sensitized solar cells (DSSCs). The conversion efficiencies of the DSSCs range from 3.54 to 5.15% under AM 1.5 G irradiation. The best efficiency reached 70% of the ruthenium dye N719-based standard cell fabricated and measured under similar conditions.

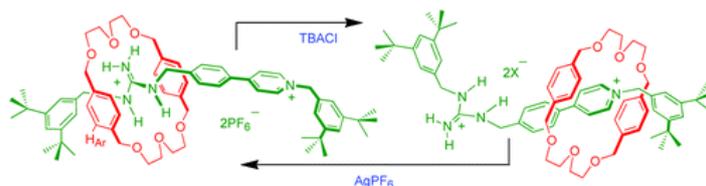
- Synthesis of the First Calix[6]crypturea via a Versatile Tris-azide Precursor
Mnand, M.; Jabin, I. *Org. Lett.* **2009**, *11*, 673–676.

Abstract:

Various nitrogenous calix[6]arene based receptors have been synthesized in one step from a new C_{3v} symmetrical calix[6]arene intermediate decorated with azido groups. Hence, the first calix[6]crypturea has been obtained in high yield through a unique one-pot process consisting of a domino Staudinger/aza-Wittig reaction followed by a [1 + 1] macrocyclization reaction with a tripodal amine. The conformational properties and some of the host-guest properties of the new calix[6]arene derivatives have been studied by NMR spectroscopy.

- A Guanidinium Ion-Based Anion- and Solvent Polarity-Controllable Molecular Switch
Lin, T.-C.; Lai, C.-C.; Chiu, S.-H. *Org. Lett.* **2009**, *11*, 613–616.

Abstract:

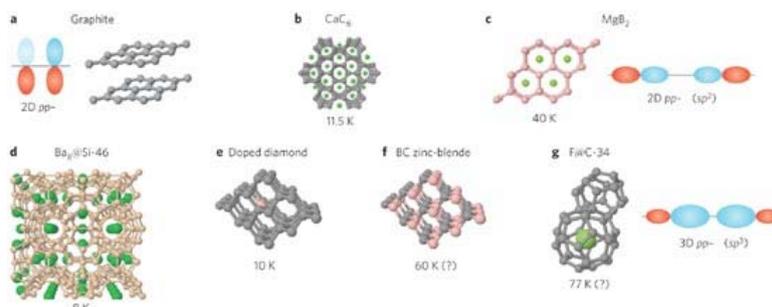


The macrocycle bis-*p*-xylyl[26]crown-6 (BPX26C6) is capable of complexing guanidinium ions in a [2]pseudorotaxane-like manner in solution. A corresponding molecular switch can be operated through changes in solvent polarity or the addition and removal of halogen and acetate anions.

- Superconducting group-IV semiconductors

Blase, X.; Bustarret, E.; Chapelier, C.; Klein, T.; Marcenat, C. *Nature Materials* **2009**, *8*, 375-382.

Abstract:

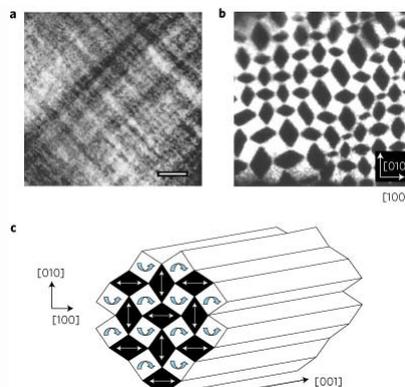


Despite the amount of experimental and theoretical work on doping-induced superconductivity in covalent semiconductors based on group IV elements over the past four years, many open questions and puzzling results remain to be clarified. The nature of the coupling (whether mediated by electronic correlation, phonons or both), the relationship between the doping concentration and the critical temperature (T_c), which affects the prospects for higher transition temperatures, and the influence of disorder and dopant homogeneity are debated issues that will determine the future of the field. Here, we present recent achievements and predictions, with a focus on boron-doped diamond and silicon. We also suggest that innovative superconducting devices, combining specific properties of diamond or silicon with the maturity of semiconductor-based technologies, will soon be developed.

- From chessboard tweed to chessboard nanowire structure during pseudospinodal decomposition

Ni, Y.; Khachatryan, A. G. *Nature Materials* **2009**, *8*, 410-414.

Abstract:

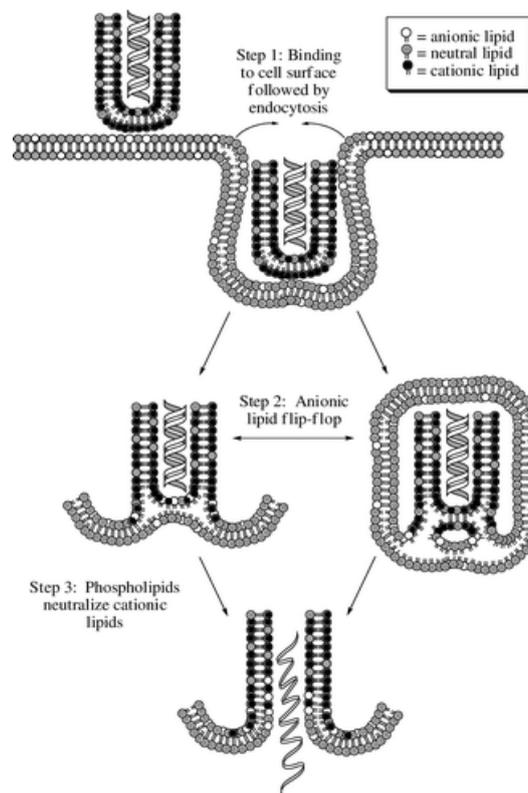


Microstructure evolution in complex nonlinear systems is of great interest from both scientific and engineering viewpoints. Here, we consider an important case of such an evolution, a coherent decomposition of a homogeneous parent phase involving the symmetry-lifting crystal lattice rearrangement of the product phase. It is shown that under certain conditions the transformation develops as a pseudospinodal decomposition, which is defined as a transformation with continuous changes of the compositions of both decomposed phases towards their equilibrium values. The pseudospinodal decomposition starts by the formation of a nanodomain precursor state with a so-called tweed structure. The three-dimensional modelling demonstrates that this tweed structure has an underlying chessboard feature, and this arrangement is a template for the further microstructure development that eventually produces a coherent two-phase chessboard nanowire pattern. The proposed theory and modelling describe the mechanism of the pseudospinodal decomposition and predict all observed three-dimensional features of the chessboard structure.

- Nonviral Vectors for Gene Delivery

Mintzer, M. A.; Simanek, E. E. *Chem. Rev.* **2009**, *109*, 259-302.

Abstract:



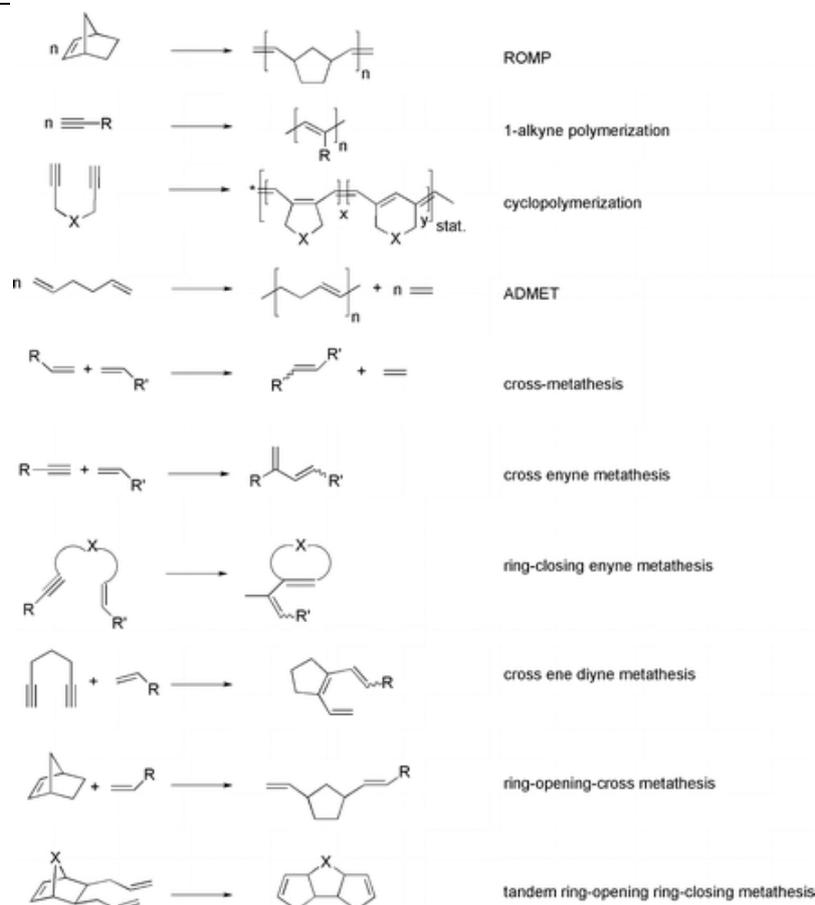
Gene therapy has gained significant attention over the past two decades as a potential method for treating genetic disorders such as severe combined immunodeficiency, cystic fibrosis, and Parkinson's disease, as well as an alternative method to traditional chemotherapy used in treating cancer. Research efforts are currently focused on designing effective carrier vectors that compact and protect oligonucleotides for gene therapy: free oligonucleotides and DNA are rapidly degraded by serum nucleases in the blood when injected intravenously. Initial research concentrated on using viral carriers, including both retroviruses and adenoviruses, as these vectors exhibited high efficiency at delivering both DNA and RNA to numerous cell lines. However, fundamental problems associated with viral vector systems, including toxicity, immunogenicity, and limitations with respect to scale-up

procedures, encouraged the investigation of other potential scaffolds exogenous DNA into targeted tissue.

Nonviral vector systems, including cationic lipids, polymers, dendrimers, and peptides, all offer potential routes for compacting DNA for systemic delivery. However, unlike viral analogues that have evolved means to overcome cellular barriers and immune defense mechanisms, nonviral gene carriers consistently exhibit significantly reduced transfection efficiency as they are hindered by numerous extra- and intracellular obstacles. However, biocompatibility and potential for large-scale production make these compounds increasingly attractive for gene therapy. As a result, a significant amount of research in the past decade has focused on designing cationic compounds that can form complexes with DNA and can avoid both in vitro and in vivo barriers for gene delivery. In the following sections, the main barriers for nonviral gene delivery will be discussed, and the current strategies for overcoming these obstacles will be illustrated by compound class.

- Polymer-Supported Well-Defined Metathesis Catalysts
Buchmeiser, M. R. *Chem. Rev.* **2009**, *109*, 303-321.

Abstract:



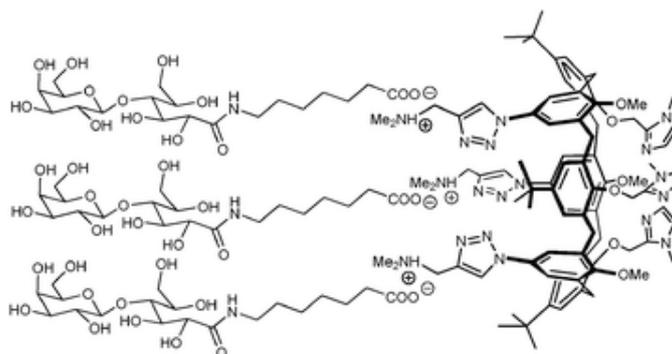
Since its discovery, olefin metathesis has experienced dramatic developments and is nowadays considered to be one of the most important C-C bond-forming reactions, allowing for the synthesis of both well-defined, functional (block co-) polymers and complex organic molecules including medium-sized and large ring structures. The fact that these reactions can be carried out in an enantioselective way widened the range of applications from commodity chemicals to the synthesis of optically active compounds relevant to pharmaceutical chemistry.

From a synthetic chemist's point of view, the applicability of metathesis to both polymer and organic chemistry must be regarded as a direct consequence of the achievements in organometallic chemistry, i.e., of catalyst and initiator development. The development of well-defined, single-component metathesis catalysts paved the way for all types of metathesis-based reactions such as ring-opening metathesis polymerization (ROMP), 1-alkyne polymerization, cyclopolymerization, acyclic diene metathesis (ADMET) polymerization, cross-metathesis (CM), tandem metathesis, enyne metathesis, and ring-opening cross metathesis. In 2005, the main of this protagonists chemistry were awarded the Nobel Price in Chemistry.

- Spontaneous formation of vesicles in a catanionic association involving a head and tail functionalized amino-calix[6]arene

Bize, C.; Garrigues, J. C.; Blanzat, M.; Rico-Lattes, I.; Bistri, O.; Colasson, B.; Reinaud, O. *Chem. Commun.* **2010**, 46, 586 – 588.

Abstract:

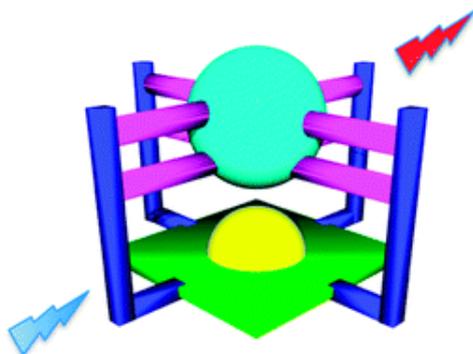


An amino-calix[6]arene was combined with sugar-based surfactants, using an acid–base reaction, to obtain an original catanionic association. Physicochemical studies showed the spontaneous formation of stable vesicles in aqueous solution.

- Sensitization of the NIR emission of Nd(III) by the 4 atropisomer of a *meso*-tetraphenyl porphyrin bearing four 8-hydroxyquinolinylamide chelates

Eckes, F.; Bulach, V.; Guenet, A.; Strassert, C. A.; De Cola, L.; Hosseini, M. W. *Chem. Commun.* **2010**, 46, 619 – 621.

Abstract:



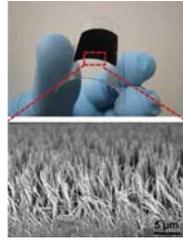
The 4 atropisomer of the *meso* tetrakis 8-hydroxyquinolinylamide porphyrin and its Pd complex binds Nd(III) and sensitizes efficiently its near infrared (NIR) emission when excited in the visible domain.

- Flexible Carbon-Nanofiber Connectors with Anisotropic Adhesion Properties

Ko, H.; Zhang, Z.; Ho, J. C.; Takei, K.; Kapadia, R.; Chueh, Y.-L.; Cao, W.; Cruden, B. A.; Javey, A. *Small* **2010**, *6*, 22-26.

11

Abstract:

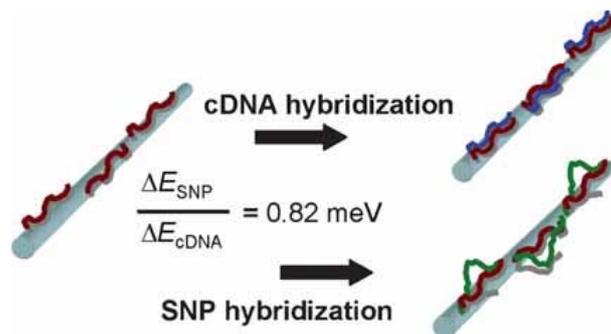


Flexible carbon nanofiber (CNF) connectors are enabled by the direct transfer of vertical CNF arrays grown on silicon substrates to plastic substrates (see image). The vertical geometry of the CNF arrays provides strong shear adhesion strength with minimal disengagement forces. By controlling the tilt angle of the CNF arrays, directional shear adhesion properties are enabled.

- Detection of a Single Nucleotide Polymorphism Using Single-Walled Carbon-Nanotube Near-Infrared Fluorescence

Jeng, E. S.; Nelson, J. D.; Prather, K. L. J.; Strano, M. S. *Small* **2010**, *6*, 40-43.

Abstract:



The detection of a single nucleotide polymorphism (SNP) using single-walled carbon nanotube (SWNT) fluorescence is demonstrated for SWNTs coated in a probe DNA sequence (see image) via a fluorescence-energy increase of only 0.8 meV upon addition of the complement containing a SNP. This mechanism is simple, label- and enzyme-free, and the properties of the probe DNA that enable this detection are examined.