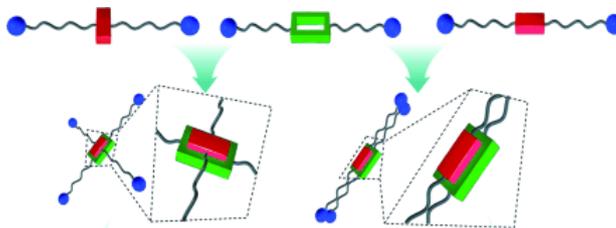


- Superamphiphiles Based on Directional Charge-Transfer Interactions: From Supramolecular Engineering to Well-Defined Nanostructures

Liu, K.; Wang, C.; Li, Z.; Zhang, X. *Angew. Chem. Int. Ed.* **2011**, *50*, 4952–4956.

Abstract:

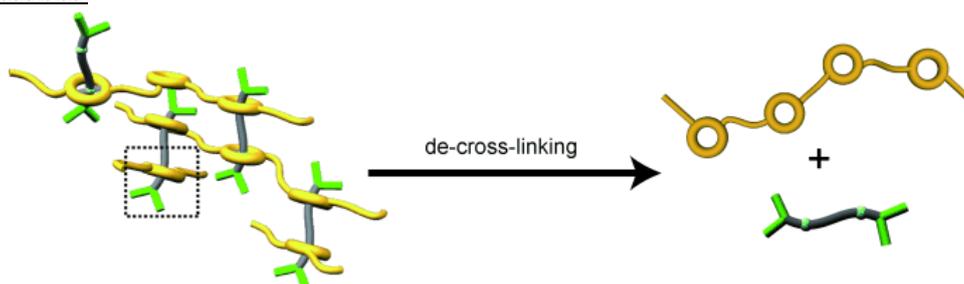


Give and take: X- or H-shape superamphiphiles form on the basis of directional charge-transfer complexes and lead to the formation of one-dimensional nanorods and two-dimensional nanosheets, respectively (see picture, blue: pyridinium ion, red: naphthalene derivatives, green: naphthalene diimide). The superstructures form after elaborate tuning of the building block structures.

- Size-Complementary Rotaxane Cross-Linking for the Stabilization and Degradation of a Supramolecular Network

Kohsaka, Y.; Nakazono, K.; Koyama, Y.; Asai, S.; Takata, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 4872–4875.

Abstract:

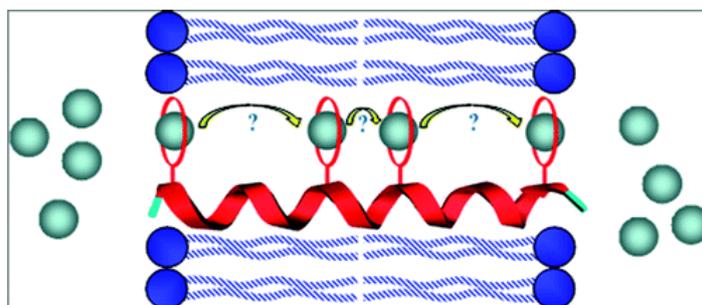


Break it down: Gels formed from rotaxane cross-linkers with end groups that are size-complementary to the macrocyclic cavity of wheel components (see picture) were prepared. The network structure was maintained in polar organic solvents or in the presence of a base to prevent hydrogen bonding. Anion exchange enabled the selective and efficient de-cross-linking of the gels.

- How Far Can a Sodium Ion Travel within a Lipid Bilayer?

Otis, F.; Racine-Berthiaume C.; Voyer, N. *J. Am. Chem. Soc.* **2011**, *133*, 6481-6483.

Abstract:



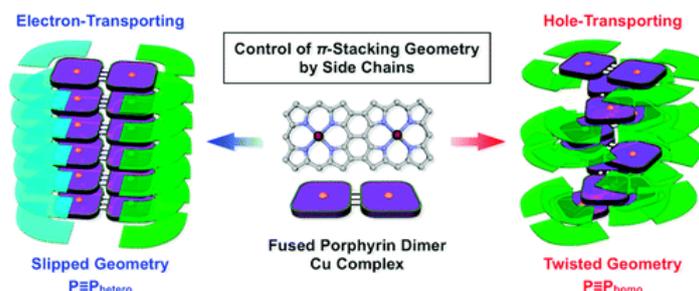
Analogues of a synthetic ion channel made from a helical peptide were used to study the mechanism of cation translocation within bilayer membranes. Derivatives bearing two, three, four, and six crown ethers used as ion relays were synthesized, and their transport abilities across lipid bilayers were

measured. The results showed that the maximum distance a sodium ion is permitted to travel between two binding sites within a lipid bilayer environment is 11 Å.

2

- Electron- or Hole-Transporting Nature Selected by Side-Chain-Directed π -Stacking Geometry: Liquid Crystalline Fused Metalloporphyrin Dimers
Sakurai, T.; Tashiro, K.; Honsho, Y.; Saeki, A.; Seki, S.; Osuka, A.; Muranaka, A.; Uchiyama, M.; Kim, J.; Ha, S.; Kato, K.; Takata, M.; Aida, T. *J. Am. Chem. Soc.* **2011**, *133*, 6537-6540.

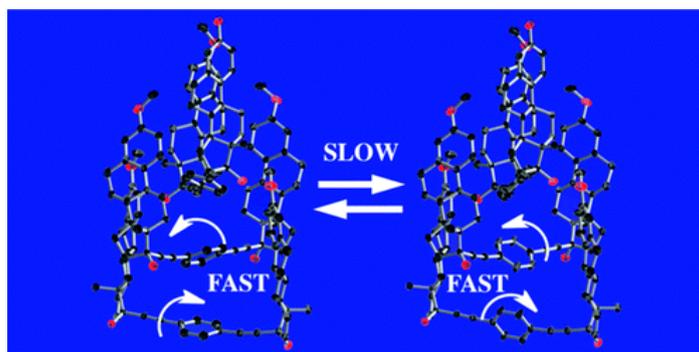
Abstract:



Novel liquid crystalline (LC) semiconductors were prepared from the copper complex of a fused porphyrin dimer as the electroactive core by attaching to its periphery dodecyl and semifluoroalkyl side chains site-specifically ($P\equiv P_{\text{hetero}}$) and semifluoroalkyl side chains alone ($P\equiv P_{\text{homo}}$). The former and latter formed rectangular columnar and orthorhombic LC mesophases, respectively, where the stacking geometries of the π -conjugated core are quite different from one another. Although the π -electronic properties of the core units in $P\equiv P_{\text{hetero}}$ and $P\equiv P_{\text{homo}}$ in solution are substantially identical to one another, transient photocurrent profiles of their LC states under time-of-flight conditions clearly showed that $P\equiv P_{\text{hetero}}$ behaves as an n-type semiconductor, whereas $P\equiv P_{\text{homo}}$, in contrast, behaves as a p-type semiconductor.

- Anisochronous Dynamics in a Crystalline Array of Steroidal Molecular Rotors: Evidence of Correlated Motion within 1D Helical Domains
Rodriguez-Molina, B.; Farfàn, N.; Romero, M.; Méndez-Stivalet, J. M.; Santillan, R.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2011**, *133*, 7280–7283.

Abstract:



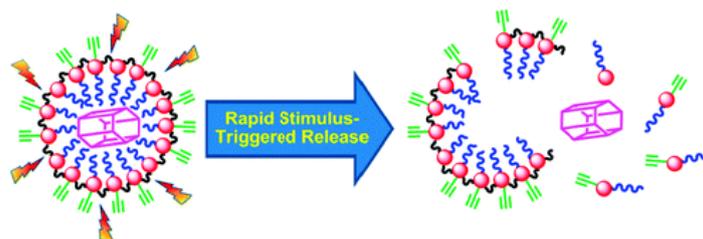
We describe the solid-state dynamics of a molecular rotator (2) consisting of a *p*-phenylene rotor flanked by two ethynyl steroidal moieties that act as a stator. Single-crystal X-ray diffraction analysis of polymorph I revealed a packing motif containing 1D columns of nested rotors arranged in helical arrays (space group $P3_2$) with the central phenylenes disordered over two sites related by an 85° rotation about their 1,4-axes. Unexpected line shapes in quadrupolar-echo ^2H NMR measurements between 155 and 296 K for the same polymorph with a deuterated phenylene isotopologue ($2-d_4$)

were simulated by trajectories involving fast ($>10^8 \text{ s}^{-1}$) 180° rotation (twofold flips) in each of the two rotationally disordered sites and slower exchange (2×10^4 to $1.5 \times 10^6 \text{ s}^{-1}$) between them. A negative activation entropy and a low enthalpic barrier for the slower 85° exchange are interpreted in terms of highly correlated processes within the 1D helical domains.

- Rapid Release of Entrapped Contents from Multi-Functionalizable, Surface Cross-Linked Micelles upon Different Stimulation

Zhang, S.; Zhao, Y. *J. Am. Chem. Soc.* **2010**, *132*, 10642–10644.

Abstract:

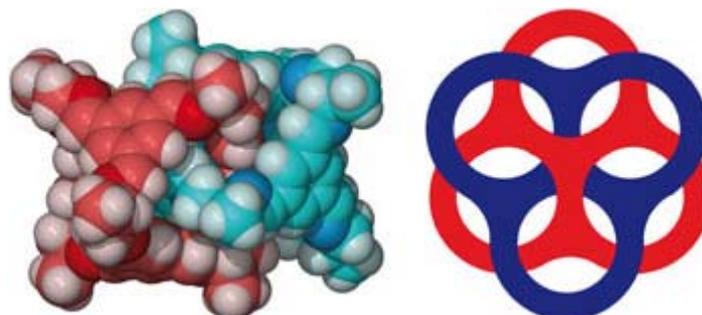


Hydrophobic guests such as pyrene could be readily trapped inside the micelles of an alkynylated surfactant in the presence of an azide-functionalized cross-linker using the click reaction. The cross-linker was designed to contain cleavable bonds such as geminal diol, disulfide, and acetal. The resulting pyrene-containing water-soluble nanoparticle was under electrostatic stress when diluted below the CMC of the surfactant. Extremely rapid ($<1 \text{ min}$) release of the hydrophobic content was observed when the cross-linker was cleaved. This method combines the ease of physical entrapment and the precision of chemical ligation, and potentially is highly useful in the delivery and controlled release of pharmaceutical agents.

- Triply interlocked covalent organic cages

Hasell, T.; Wu, X.; Jones, J. T. A.; Bacsá, J.; Steiner, A.; Mitra, T.; Trewin, A.; Adams, D. J.; Cooper, A. I. *Nature Chem.* **2010**, *2*, 750-755.

Abstract:

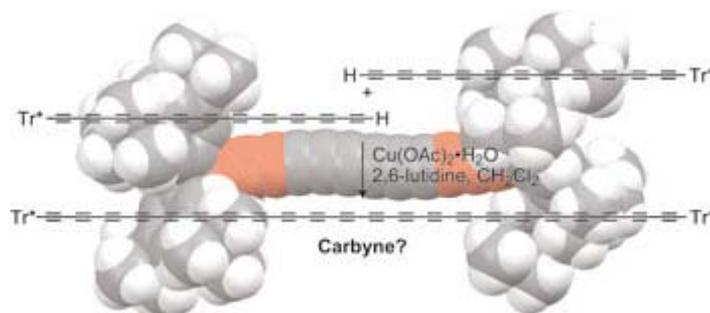


Interlocked molecules comprise two or more separate components that are joined by ‘mechanical’ rather than covalent bonds. In other words, these molecular assemblies cannot be dissociated without the cleavage of one or more chemical bonds. Although recent progress has enabled the preparation of such topologies through coordination or templating interactions, three-dimensional interlocked covalent architectures remain difficult to prepare. Here, we present a template-free one-pot synthesis of triply interlocked organic cages. These 20-component dimers consist of two tetrahedral monomeric cages each built from four nodes and six linkers. The monomers exhibit axial chirality, which is recognized by their partner cage during the template-free interlocking assembly process. The dimeric cages also include two well-defined cavities per assembly, which for one of the

systems studied led to the formation of a supramolecular host–guest chain. These interlocked organic molecules may prove useful as part of a toolkit for the modular construction of complex porous solids and other supramolecular assemblies.

- Synthesis of polyynes to model the *sp*-carbon allotrope carbyne
Chalifoux, W. A.; Tykwinski, R. R. *Nature Chem.* **2010**, *2*, 967-971.

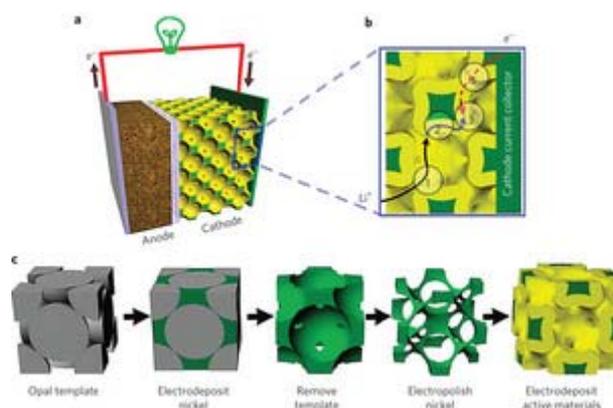
Abstract:



Carbyne is an allotrope of carbon composed of *sp*-hybridized carbon atoms. Although its formation in the laboratory is suggested, no well-defined sample is described. Interest in carbyne and its potential properties remains intense because of, at least in part, technological breakthroughs offered by other carbon allotropes, such as fullerenes, carbon nanotubes and graphene. Here, we describe the synthesis of a series of conjugated polyynes as models for carbyne. The longest of the series consists of 44 contiguous acetylenic carbons, and it maintains a framework clearly composed of alternating single and triple bonds. Spectroscopic analyses for these polyynes reveal a distinct trend towards a finite gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital for carbyne, which is estimated to be ≈ 485 nm (≈ 2.56 eV). Even the longest members of this series of polyynes are not particularly sensitive to light, moisture or oxygen, and they can be handled and characterized under normal laboratory conditions.

- Three-dimensional bicontinuous ultrafast-charge and -discharge bulk battery electrodes
Zhang, H.; Yu, X.; Braun, P. V. *Nature Nanotech.* **2011**, *6*, 277-281.

Abstract:

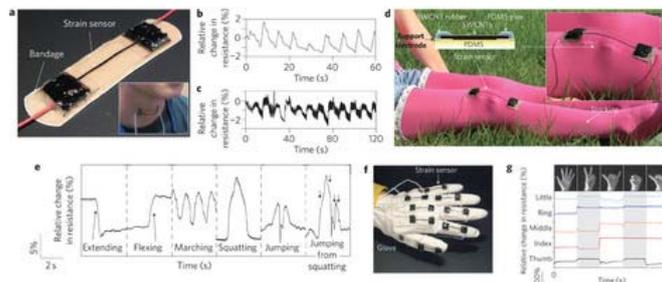


Rapid charge and discharge rates have become an important feature of electrical energy storage devices, but cause dramatic reductions in the energy that can be stored or delivered by most rechargeable batteries (their energy capacity). Supercapacitors do not suffer from this problem, but are restricted to much lower stored energy per mass (energy density) than batteries⁸. A storage technology that combines the rate performance of supercapacitors with the energy density of

batteries would significantly advance portable and distributed power technology. Here, we demonstrate very large battery charge and discharge rates with minimal capacity loss by using cathodes made from a self-assembled three-dimensional bicontinuous nanoarchitecture consisting of an electrolytically active material sandwiched between rapid ion and electron transport pathways. Rates of up to 400C and 1,000C for lithium-ion and nickel-metal hydride chemistries, respectively, are achieved (where a 1C rate represents a one-hour complete charge or discharge), enabling fabrication of a lithium-ion battery that can be 90% charged in 2 minutes.

- A stretchable carbon nanotube strain sensor for human-motion detection
Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Najafabadi, A.; Futaba, D. N.; Hata, K. *Nature Nanotech.* **2011**, *6*, 296–301.

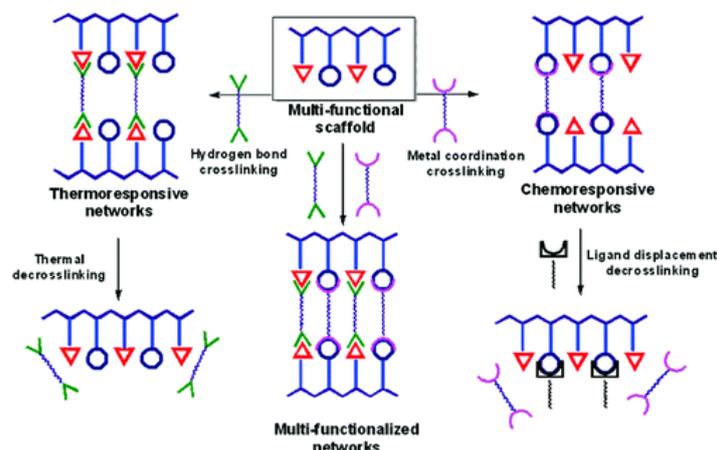
Abstract:



Devices made from stretchable electronic materials could be incorporated into clothing or attached directly to the body. Such materials have typically been prepared by engineering conventional rigid materials such as silicon, rather than by developing new materials. Here, we report a class of wearable and stretchable devices fabricated from thin films of aligned single-walled carbon nanotubes. When stretched, the nanotube films fracture into gaps and islands, and bundles bridging the gaps. This mechanism allows the films to act as strain sensors capable of measuring strains up to 280% (50 times more than conventional metal strain gauges), with high durability, fast response and low creep. We assembled the carbon-nanotube sensors on stockings, bandages and gloves to fabricate devices that can detect different types of human motion, including movement, typing, breathing and speech.

- Multiresponsive Reversible Polymer Networks Based on Hydrogen Bonding and Metal Coordination
Nair, K. P.; Breedveld, V.; Weck, M. *Macromolecules* **2011**, *44*, 3346–3357.

Abstract:

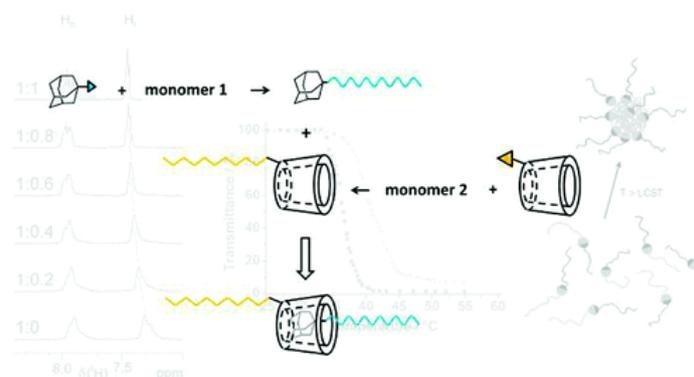


Side-chain-functionalized polymers containing hydrogen bonding and metal coordination sites have been synthesized using ring-opening metathesis polymerization. These polymers were cross-linked reversibly either selectively by using hydrogen bonding or metal coordination or simultaneously using both interactions through the addition of small molecule cross-linking agents. The hydrogen bonding motifs utilized for reversible cross-linking are based on cyanuric acid residues hydrogen bonded to 2,4-diaminotriazine-based cross-linking agents. The metal coordination motifs are based on palladated SCS pincer complexes coordinated to bispyridine cross-linking agents. By controlling the reversible cross-linking strategy, we were able to modulate (1) the rheology of the polymer networks from a free-flowing liquid to a highly elastic gel and vice versa and vary the dynamic moduli over 10 orders of magnitude and (2) the responsiveness of the networks to external stimuli such as temperature and ligand displacement agents. The hydrogen bonded cross-linking resulted in polymer networks that were thermally reversible whereas the metal coordinated cross-linked networks mainly showed chemoresponsive behavior. Since both interactions are fully orthogonal to each other, we successfully cross-linked the polymer using both interactions to obtain multiresponsive networks that exhibited both thermal and chemoresponsiveness. We were also able to selectively de-cross-link the hydrogen bonded cross-links of the multifunctionalized networks through competitive interactions at room temperature via the addition of a monotopic end-capping agent without affecting the metal coordinated cross-links. In contrast, the metal coordination could be de-cross-linked completely using a ligand displacement agent such as triphenylphosphine again without affecting the hydrogen bonded cross-links.

- Diblock Copolymer Formation via Self-Assembly of Cyclodextrin and Adamantyl End-Functionalized Polymers

Stadermann, J.; Komber, H.; Erber, M.; Däbritz, F.; Ritter, H.; Voit, B. *Macromolecules* **2011**, *44*, 3250–3259.

Abstract:



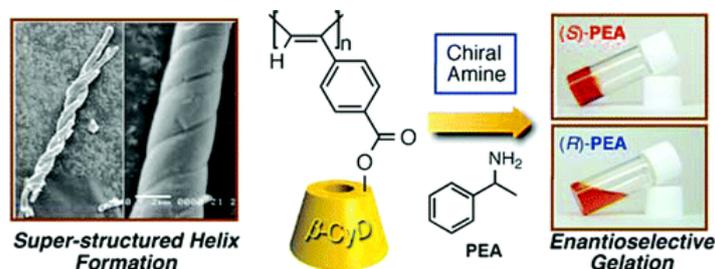
Two water-soluble polymers poly(2-methyl-2-oxazoline) and poly(*N*-isopropylacrylamide) with complexing moieties (β -CD and adamantane, respectively) located at the chain ends were prepared via controlled techniques. To verify the interaction of the β -CD- and adamantane-type polymer end groups in aqueous solution, detailed complexation studies were carried out by ^1H NMR spectroscopy. It could be proved, that the polymers undergo self-assembly to form the corresponding supramolecular diblock structure. Furthermore, the double-hydrophilic block assembly was observed to be switchable to a hydrophilic–hydrophobic configuration by adjusting temperature leading to reversible aggregate formation.

- Stimuli-Responsive Helical Poly(phenylacetylene)s Bearing Cyclodextrin Pendants that Exhibit Enantioselective Gelation in Response to Chirality of a Chiral Amine and Hierarchical Super-Structured Helix Formation

7

Maeda, K.; Mochizuki, H.; Osato, K.; Yashima, E. *Macromolecules* **2011**, *44*, 3217–3226.

Abstract:

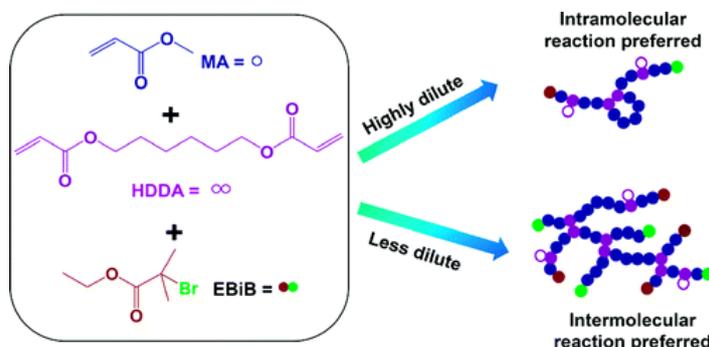


Novel poly(phenylacetylene)s bearing a β -cyclodextrin (CyD) residue connected to the phenyl ring through an ester (poly-**2 β**) and an ether linkage (poly-**3 β**) as well as an amide linkage (poly-**1 β**) were synthesized and their chiroptical properties were investigated with circular dichroism (CD) and absorption spectroscopies. The chiroptical studies demonstrated that the linkage groups play an important role in the conformational change induced by external chiral and achiral stimuli, such as temperature, solvent, and interactions with a chiral amine. Poly-**1 β** and poly-**2 β** showed a unique enantioselective gelation in response to the chirality of a chiral amine, and the polymers further formed hierarchical superstructured helical assemblies on a micrometer scale with a controlled helix sense, as evidenced by the scanning electron microscopy observations.

- Atom Transfer Radical Copolymerization of Monomer and Cross-Linker under Highly Dilute Conditions

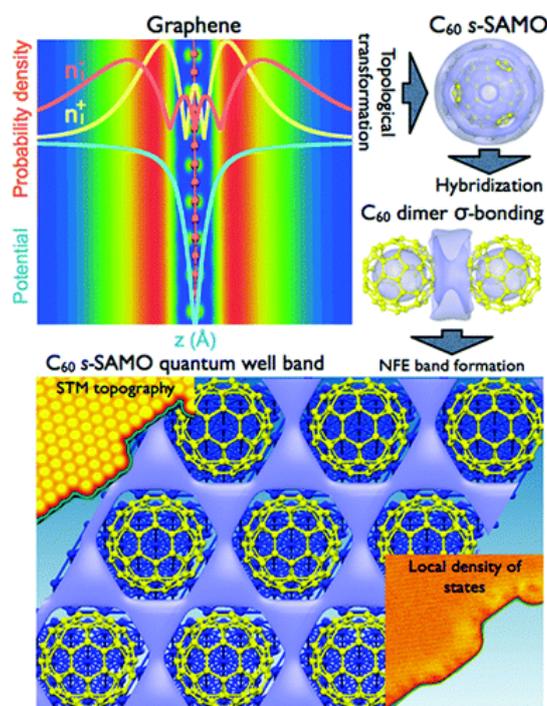
Li, W.; Yoon, J. A.; Zhong, M.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 3270–3275.

Abstract:



The influence of dilution on the degree of intra- or intermolecular cross-linking reactions during the copolymerization of a monomer and a divinyl cross-linker via atom transfer radical polymerization (ATRP) technique was studied. To maximize intramolecular cross-linking, highly dilute systems with 0.5–10 vol % of monomer plus cross-linker vs solvent were used. The fraction of branched polymers formed through intermolecular consumption of pendant vinyl groups was calculated for each system through multipeak splitting of the gel permeation chromatography (GPC) curves. Progressive dilution of the reaction media resulted in the formation of products containing less branched polymers. Absolute molecular weights and compactness of the formed polymers determined by GPC with a multiangle laser light scattering (MALLS) detector further confirmed the formation of majority nonbranched polymer structures in more dilute systems, indicating an enhanced level of intramolecular cross-linking reactions in this case.

- The Electronic Properties of Superatom States of Hollow Molecules
Feng, M.; Zhao, J.; Huang, T.; Zhu, X.; Petek, H. *Acc. Chem. Res.* **2011**, *44*, 360–368.
Abstract:



Electronic and optical properties of molecules and molecular solids are traditionally considered from the perspective of the frontier orbitals and their intermolecular interactions. How molecules condense into crystalline solids, however, is mainly attributed to the long-range polarization interaction. In this Account, we show that long-range polarization also introduces a distinctive set of diffuse molecular electronic states, which in quantum structures or solids can combine into nearly-free-electron (NFE) bands. These NFE properties, which are usually associated with good metals, are vividly evident in sp^2 hybridized carbon materials, specifically graphene and its derivatives.

The polarization interaction is primarily manifested in the screening of an external charge at a solid/vacuum interface. It is responsible for the universal image potential and the associated unoccupied image potential (IP) states, which are observed even at the He liquid/vacuum interface. The molecular electronic properties that we describe are derived from the IP states of graphene, which float above and below the molecular plane and undergo free motion parallel to it. Rolling or wrapping a graphene sheet into a nanotube or a fullerene transforms the IP states into diffuse atom-like orbitals that are bound primarily to hollow molecular cores, rather than the component atoms. Therefore, we named them the superatom molecular orbitals (SAMOs). Like the excitonic states of semiconductor nanostructures or the plasmonic resonances of metallic nanoparticles, SAMOs of fullerene molecules, separated by their van der Waals distance, can combine to form diatomic molecule-like orbitals of C_{60} dimers. For larger aggregates, they form NFE bands of superatomic quantum structures and solids.

The overlap of the diffuse SAMO wavefunctions in van der Waals solids provides a different paradigm for band formation than the valence or conduction bands formed by interaction of the more tightly bound, directional highest occupied molecular orbitals (HOMOs) or the lowest unoccupied molecular orbitals (LUMOs). Therefore, SAMO wavefunctions provide insights into the design of molecular materials with potentially superior properties for electronics.

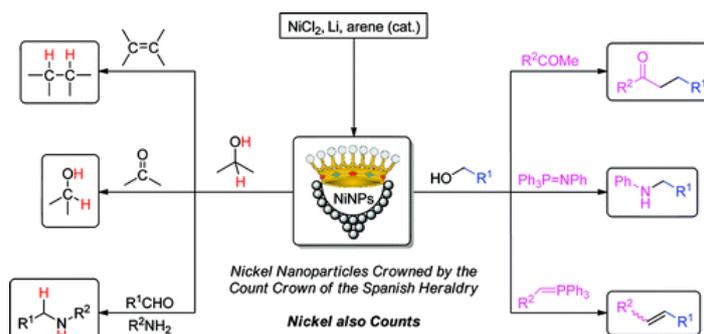
Physicists and chemists have thought of fullerenes as atom-like building blocks of electronic materials, and superatom properties have been attributed to other elemental gas-phase clusters based on their size-dependent electronic structure and reactivity. Only in the case of fullerenes, however, do the superatom properties survive as delocalized electronic bands even in the condensed phase. We emphasize, however, that the superatom states and their bands are usually unoccupied and therefore do not contribute to intermolecular bonding. Instead, their significance lies in the electronic properties they confer when electrons are introduced, such as when they are excited optically or probed by the atomically sharp tip of a scanning tunneling microscope.

We describe the IP states of graphene as the primary manifestation of the universal polarization response of a molecular sheet and how these states in turn define the NFE properties of materials derived from graphene, such as graphite, fullerenes, and nanotubes. Through low-temperature scanning tunneling microscopy (LT-STM), time-resolved two-photon photoemission spectroscopy (TR-2PP), and density functional theory (DFT), we describe the real and reciprocal space electronic properties of SAMOs for single C60 molecules and their self-assembled 1D and 2D quantum structures on single-crystal metal surfaces.

- Nickel Nanoparticles in Hydrogen Transfer Reactions

Alonso, F.; Riente, P.; Yus, M. *Acc. Chem. Res.* **2011**, *44*, 379–391.

Abstract:



The transfer hydrogenation of organic compounds is a much safer and more environmentally benign process than reduction reactions involving molecular hydrogen, metal hydrides, or dissolving metals. In transfer hydrogenation, 2-propanol is often preferred as the source of hydrogen because it is cheap, easy to remove, and environmentally friendly. This class of transformation has been mostly pursued through the use of expensive noble metals, such as Ru, Pd, and so forth; research involving cheaper catalytically active metals has been relatively neglected.

On the other hand, alcohols have recently emerged as desirable alkylating agents, a useful alternative to organic halides, in reactions of hydrogen autotransfer, also known as the “borrowing of hydrogen” methodology. For instance, the α-alkylation of ketones with alcohols is an atom-efficient process that produces water as the only byproduct in the presence of a noble metal catalyst. Hydrogen autotransfer is also successful in the synthesis of amines through a reductive aza-Wittig reaction, which involves an iminophosphorane and primary alcohol under iridium catalysis. The in situ oxidation–Wittig olefination of primary alcohols with stabilized phosphorus ylides is a commonly practiced method in organic synthesis that precludes the necessity of handling aldehydes. These reactions are normally performed in one pot but sequentially; thus the course of the alcohol oxidation needs monitoring before the ylide addition.

In this Account, we describe the development of our discovery that nickel(0), in the form of nanoparticles, can replace the more expensive noble metals in both transfer hydrogenation and

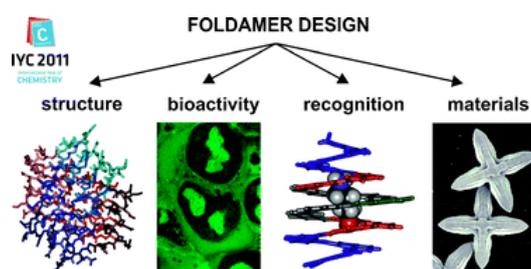
hydrogen autotransfer reactions. These nanoparticles were found to catalyze the transfer hydrogenation of olefins and carbonyl compounds, as well as the reductive amination of aldehydes, with 2-propanol as the hydrogen donor. All reactions proceeded in the absence of base, and the catalyst could be easily and successfully reutilized in the case of the carbonyl compounds. The catalyst was fully characterized, and the reaction mechanism, kinetics, and heterogeneous nature of the process were established through a variety of experiments. Moreover, the nickel nanoparticles enabled the activation of primary alcohols for the α -alkylation of ketones and reductive aza-Wittig reaction, with the latter leading to secondary amines. For the first time, these two reactions were achieved with a catalyst that was not one of the noble metals.

We also observed that nickel nanoparticles can activate alcohols in the presence of phosphorus ylides. In this case, although the autotransfer of hydrogen failed, the reaction could be used as a key tool to construct carbon-carbon double bonds. In this respect, we describe the one-pot synthesis of stilbenes from alcohols through a Wittig-type olefination reaction promoted by nickel nanoparticles. We report a wide range of polymethoxylated and polyhydroxylated stilbenes, including the naturally occurring polyphenol resveratrol. The utility of the nickel nanoparticles was exceptional in all of the aforementioned reactions when compared with other forms of nickel, including Raney nickel.

- Synthetic foldamers

Guichard, G.; Huc, I. *Chem. Commun.* **2011**, *47*, 5933-5941.

Abstract:

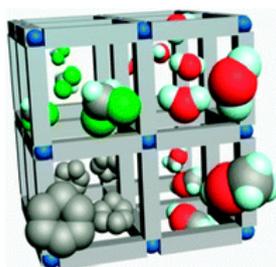


From oligomers to protein-sized architectures, foldamers introduce new tools and concepts to develop bioactive substances, synthetic receptors and materials.

- Role of solvents in coordination supramolecular systems

Li, C.-P.; Du, M. *Chem. Commun.* **2011**, *47*, 5958-5972.

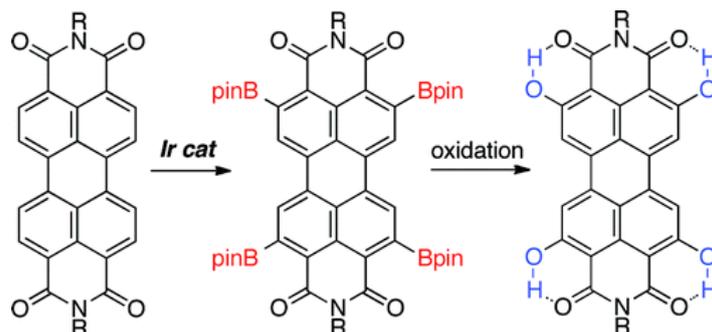
Abstract:



This feature article comments how the solvent element can significantly influence the assemblies, structures, and functions of coordination supramolecular systems in a kinetic or thermodynamic manner.

- Iridium-Catalyzed Direct Tetraborylation of Perylene Bisimides

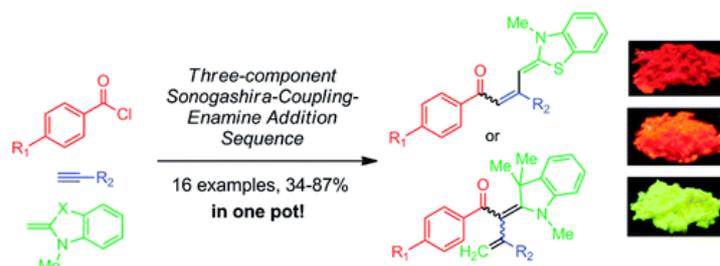
Teraoka, T.; Hiroto, S.; Shinokubo, H. *Org. Lett.* **2011**, *13*, 2532-2535.

Abstract:

Treatment of perylene bisimides (PBIs) with bis(pinacolato)diboron in the presence of an iridium catalyst provides tetraborylated PBIs at 2,5,8,11-positions in good yields with perfect regioselectivity. The planar structure of the perylene core has been confirmed by X-ray diffraction analysis. Oxidation of tetraborylated PBI with hydroxylamine hydrochloride affords tetrahydroxy PBI in excellent yield, which exhibits a substantially blue-shifted absorption spectrum due to an intramolecular hydrogenbonding interaction between carbonyl and hydroxy groups.

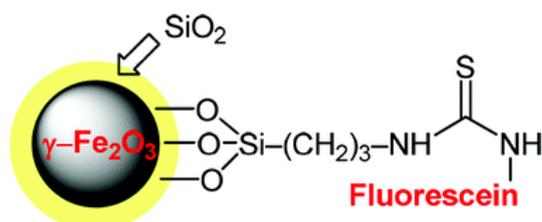
- Rapid Access to Unusual Solid-State Luminescent Merocyanines by a Novel One-Pot Three-Component Synthesis

Muschelknautz, M.; Frank, W.; Müller, T. T. J. *Org. Lett.* **2011**, *13*, 2556–2559.

Abstract:

A novel consecutive three-component coupling–enamine addition synthesis gives access to three types of diene merocyanines in a selective fashion and in good yields. Moreover, all these push–pull systems are intensely red or yellow emissive in the solid state and display large Stokes shifts.

- Fluorescent magnetic nanoparticles for biomedical applications
Chekina, N.; Horák, D.; Jendelová, P.; Trchová, M.; Beneš, M. J.; Hrubý, M.; Herynek, V.; Turnovcová, K.; Syková, E. *J. Mater. Chem.* **2011**, *21*, 7630-7639.

Abstract:

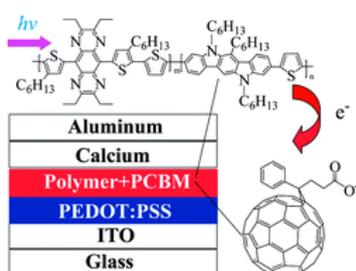
The simultaneous combination of optical and magnetic resonance imaging (MRI) would greatly benefit *in vivo* disease diagnosis as well as *in situ* monitoring of living cells. In order to design dual detection of cells involving simultaneous imaging by fluorescent microscopy and MRI, nanoparticles with two reporters, a fluorescent dye and a superparamagnetic core, included in one particle were synthesized and characterized. The γ -Fe₂O₃ nanoparticles obtained by coprecipitation and oxidation

were coated with silica (SiO_2) or carboxymethyl chitosan (CMCS) and labeled with fluorescein isothiocyanate (FITC). The fluorescent label was covalently bound to the nanoparticles and was not quenched by the iron oxide core. The nanoparticles successfully labeled rat mesenchymal stem cells (rMSCs) *in vitro*. Relaxation time measurements found large amounts of iron inside the cells with FITC-labeled $\gamma\text{-Fe}_2\text{O}_3\text{-SiO}_2\text{-AP}$ nanoparticles. Both MR and fluorescent imaging of a rat brain with implanted rMSCs labeled with FITC-labeled CMCS-modified silica-coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were performed.

- Pyrazino[2,3-g]quinoxaline-based conjugated copolymers with indolocarbazole coplanar moieties designed for efficient photovoltaic applications

Peng, Q.; Liu, K.; Qin, Y.; Xu, Y.; Li, M.; Dai, L. *J. Mater. Chem.* **2011**, *21*, 7714-7722.

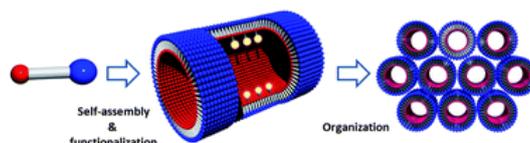
Abstract:



A series of low band gap copolymers consisting of electron-accepting pyrazino[2,3-g]quinoxaline (PQx) and an electron-donating indolo[3,2-b]carbazole and thiophene units have been designed and synthesized by Stille coupling polymerization. Their optical and electrical properties could also be finely modulated for photovoltaic application by adjusting the donor/acceptor ratios. UV-vis measurements showed that increasing the content of PQx units led to enhanced absorption. The band gaps obtained from UV-vis spectra, CV scanning, and DFT modeling all indicated a narrowing band gap with increasing the PQx content in the copolymer structure. The photovoltaic solar cells (PSCs) based on these copolymers were fabricated and tested with a structure of ITO/PEDOT:PSS/copolymer:PCBM/Ca/Al under the illumination of AM 1.5G, 100 mW cm^{-2} . The best performance was achieved using P3/[70]PCBM blend (1 : 3) with $J_{sc} = 9.55 \text{ mA cm}^{-2}$, $V_{oc} = 0.81 \text{ V}$, FF = 0.42, and PCE = 3.24%, which is the highest efficiency for the PQx and indolo[3,2-b]carbazole based devices. The present results also indicate that the efficient photovoltaic materials with suitable electronic and optical properties can be achieved by just fine-tuning the ratios of the strong electron-deficient acceptors and large- π planar donors.

- Supramolecular organic nanotubes: how to utilize the inner nanospace and the outer space
Kameta, N.; Minamikawa, H.; Perevyazko, M. *Soft Matter*, **2011**, *7*, 4539-4561.

Abstract:



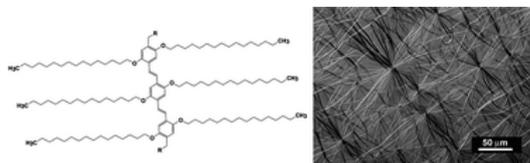
Organic nanotubes (ONTs) are tubular nanostructures prepared from small organic molecules or macromolecules. These structures have attracted growing attention because their inner and outer spaces exhibit unique properties that may be exploited for potential applications. In the first part of this review, we describe methodologies to construct well-defined ONTs: how to control the dimensions, discriminate the inner and outer surfaces, and functionalize the nanostructures. The

well-defined ONTs contain cylindrical nanospaces that can capture, store, and release various nanomaterials, from small molecules to macromolecules. The ONTs' outer spaces and surfaces play critical roles in dispersibility, organization, and manipulation of the ONTs. In the second part, we describe the ONTs' physicochemical properties and utilization of the inner and outer spaces, emphasizing the advantages of ONTs over other types of nanomaterials. Smaller nanomaterials can be efficiently captured in the nanospaces of the ONTs via selective surface interactions. For example, encapsulation of proteins in the ONT nanospaces prevents them from chemical or thermal denaturation. Furthermore, the encapsulated materials can be released in response to external stimuli, such as pH or temperature, which can alter the surface charge and/or fluidity. These unique properties of ONTs allow them to be utilized for biomaterials and drug delivery applications.

- Insight into the gelation habit of oligo(*para*-phenylene vinylene) derivatives: effect of end-groups

Dasgupta, D.; Srinivasan, S.; Rochas, C.; Thierry, A.; Schröder, A.; Ajayaghosh, A.; Guenet, J. M. *Soft Matter*, **2011**, 7, 2797-2804.

Abstract:



This paper reports a study on the gelation habits of organogels prepared in benzyl alcohol from derivatives of oligo(*p*-phenylene vinylene) (OPV) bearing C₁₆H₃₃ aliphatic wings and a series of end groups on the backbone. Significant differences are observed based on whether or not these end groups can establish hydrogen bonds with adjacent OPV molecules or with the solvent. It is particularly shown that the fibril structure, the morphology and the molecular organization not only depend upon the aliphatic wings and/or the π - π interactions of the backbones but equally on the nature of these end groups. Evidence highlighting a homogeneous nucleation process for gel formation are also presented and discussed. Discrepancies with thermoreversible gels of covalent polymers are also stressed. Not so unexpectedly, the sequence of surfactant addition was found to be decisive, as quite different results are obtained when C₁₂E₅ is added before SDS.