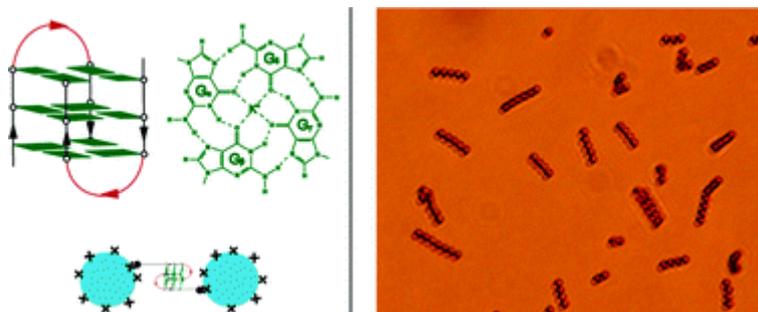
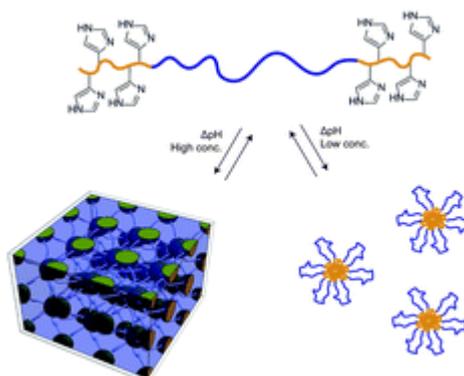


- Connecting magnetic micro-particles with DNA G-quadruplexes
Mukundan, V. T.; Tran, Q. M. N.; Miao, Y.; Phan, A. T. *Soft Matter* **2013**, *9*, 216-223.

Abstract:

Particle self-assembly using DNA has relied mainly on the interaction between complementary strands of double helix DNA. In contrast, G-quadruplex DNA has rarely been used in particle self-assembly. G-quadruplex DNA can adopt a wide range of structures with diverse topologies and stabilities controlled by cations. We report on the possibility of connecting micrometer-sized magnetic beads using DNA G-quadruplexes under a magnetic field. The average chain length of the resulting fragments was used to quantify the strength of the interaction, which was shown to depend on the nature and concentration of cations, the DNA sequences, the time duration and strength of the applied magnetic field. Through the use of different sequences, we propose that the length of bead chains could be quantitatively associated with the stability and structure of DNA G-quadruplexes formed between the beads. This work may allow us to control the interactions in colloidal assembly architectures using G-quadruplexes and also to study the structure, dynamics and other properties of the G-quadruplex “DNA glue”.

- pH-triggered self-assembly of biocompatible histamine-functionalized triblock copolymers
Lundberg, P.; Lynd, N. A.; Zhang, Y.; Zeng, X.; Krogstad, D. V.; Paffen, T.; Malkoch, M.; Nyström, A. M.; Hawker, C. J. *Soft Matter* **2013**, *9*, 82-89.

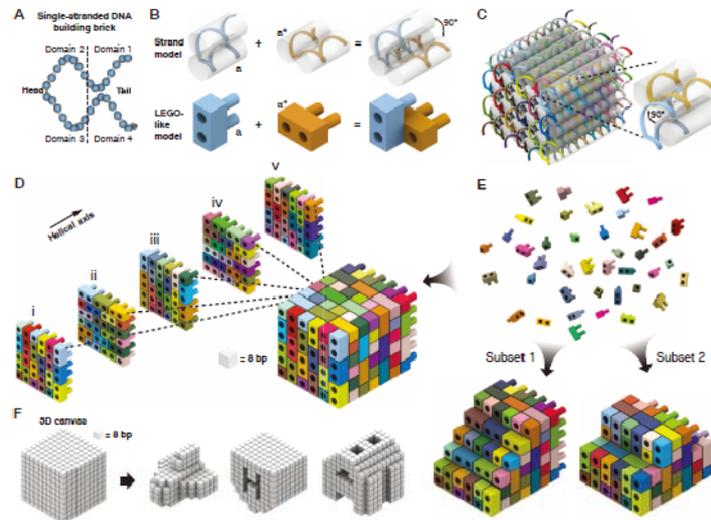
Abstract:

Histamine functionalized poly(allyl glycidyl ether)-*b*-poly(ethylene glycol)-*b*-poly(allyl glycidyl ether) (PAGE-PEO-PAGE) triblock copolymers represent a new class of physically cross-linked, pH-responsive hydrogels with significant potential for biomedical applications. These telechelic triblock copolymers exhibited abrupt and reversible hydrogelation above pH 7.0 due to a hydrophilic/hydrophobic transition of the histamine units to form a network of hydrophobic domains bridged by a hydrophilic PEO matrix. These hydrophobic domains displayed improved ordering upon increasing pH and self-assembled into a body centered cubic lattice at pH 8.0, while at lower concentrations formed well-

defined micelles. Significantly, all materials were found to be non-toxic when evaluated on three different cell lines and suggests a range of medical and biomedical applications.

- Three-Dimensional Structures Self-Assembled from DNA Bricks
Ke, Y.; Ong, L. L.; Shih, W. M.; Yin, P. *Science* **2012**, 338, 1177-1183.

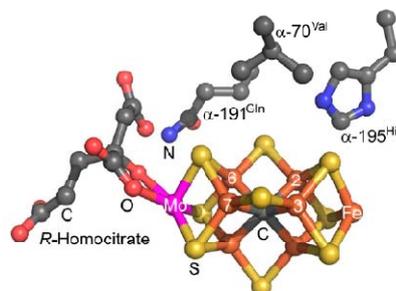
Abstract:



We describe a simple and robust method to construct complex three-dimensional (3D) structures by using short synthetic DNA strands that we call “DNA bricks.” In one-step annealing reactions, bricks with hundreds of distinct sequences self-assemble into prescribed 3D shapes. Each 32-nucleotide brick is a modular component; it binds to four local neighbors and can be removed or added independently. Each 8-base pair interaction between bricks defines a voxel with dimensions of 2.5 by 2.5 by 2.7 nanometers, and a master brick collection defines a “molecular canvas” with dimensions of 10 by 10 by 10 voxels. By selecting subsets of bricks from this canvas, we constructed a panel of 102 distinct shapes exhibiting sophisticated surface features, as well as intricate interior cavities and tunnels.

- Carbon dioxide reduction to methane and coupling with acetylene to form propylene catalyzed by remodeled nitrogenase
Yang, Z.-Y.; Moure, V. R.; Dean, D. R.; Seefeldt, L. C. *Proc. Nat. Acad. Sci. USA* **2012**, 109, 19644-19648.

Abstract:



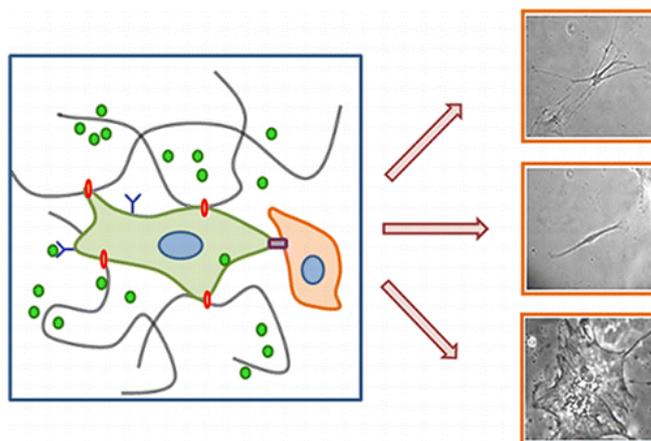
A doubly substituted form of the nitrogenase MoFe protein ($\alpha\text{-70}^{\text{Val}\rightarrow\text{Ala}}$, $\alpha\text{-195}^{\text{His}\rightarrow\text{Gln}}$) has the capacity to catalyze the reduction of carbon dioxide (CO_2) to yield methane (CH_4). Under optimized conditions, 1 nmol of the substituted MoFe protein catalyzes the formation of 21 nmol of CH_4 within 20 min. The catalytic rate depends on the partial pressure of CO_2 (or concentration of HCO_3^-) and the

electron flux through nitrogenase. The doubly substituted MoFe protein also has the capacity to catalyze the unprecedented formation of propylene ($\text{H}_2\text{C} = \text{CH}-\text{CH}_3$) through the reductive coupling of CO_2 and acetylene ($\text{HC}\equiv\text{CH}$). In light of these observations, we suggest that an emerging understanding of the mechanistic features of nitrogenase could be relevant to the design of synthetic catalysts for CO_2 sequestration and formation of olefins.

- Designing Biomaterials To Direct Stem Cell Fate

Cha, C.; Liechty, W. B.; Khademhosseini, A.; Peppas, N. A. *ACS Nano* **2012**, *6*, 9353-9358.

Abstract:

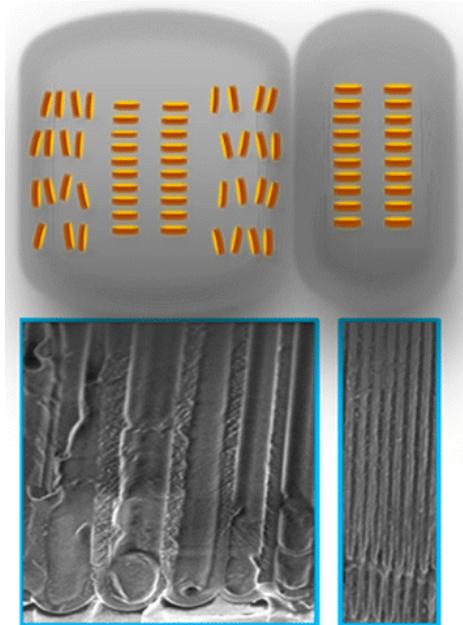


As stem cells are a cornerstone of regenerative medicine, research efforts have been extensively focused on controlling their self-renewal and differentiation. It is well-known that stem cells are tightly regulated by a combination of physical and chemical factors from their complex extracellular surroundings; thus, conventional cell culture approaches based purely on using soluble factors to direct stem cell fate have resulted in limited success. To account for the complexities of native stem-cell niches, biomaterials are actively investigated as artificial extracellular matrices in order to mimic the natural microenvironment. This Perspective highlights important areas related to the design of biomaterials to control stem cell behavior, such as cell-responsive ligands, mechanical signals, and delivery of soluble factors.

- Arrays of Aligned Supramolecular Wires by Macroscopic Orientation of Columnar Discotic Mesophases

Duran, H.; Hartmann-Azanza, B.; Steinhart, M.; Gehrig, D.; Laquai, F.; Feng, X.; Müllen, K.; Butt, H.-J.; Floudas, G. *ACS Nano* **2012**, *6*, 9359-9365.

Abstract:

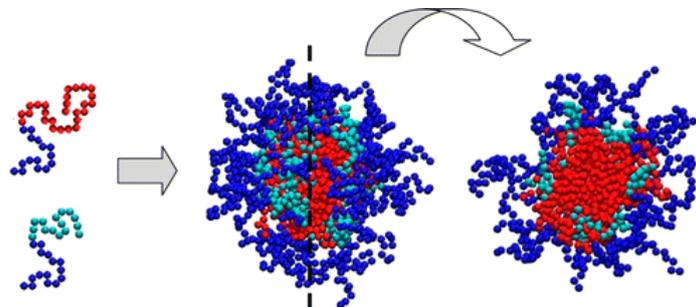


Structure formation, phase behavior, and dynamics of mono-bromo hexa-*peri*-hexabenzocoronene (HBC-Br) are strongly affected by the confinement of cylindrical nanopores with rigid walls. Using self-ordered nanoporous anodic aluminum oxide (AAO)-containing arrays of aligned nanopores with narrow size distribution as a confining matrix, pronounced alignment of the HBC-Br columns along the nanopore axes was found to be independent of the pore diameter. Hence, arrays of one-dimensional supramolecular HBC-Br wires with the columns uniformly oriented along the wire axes on a macroscopic scale were obtained, unlike with discotics bearing smaller cores. The formation of the crystalline herringbone structure is shifted to lower temperatures in nanopores with diameters of a few hundred nanometers, whereas the formation of this low-temperature phase is completely suppressed when the pore diameter is below 20 lattice parameters. Moreover, the cylindrical confinement affects the disk axial dynamics as well as the distribution of relaxation times.

- Brownian Dynamics Simulation of Comicellization of Amphiphilic Block Copolymers with Different Tail Lengths

Hafezi, M.-J.; Sharif, F. *Langmuir* **2012**, *28*, 16243–16253.

Abstract:

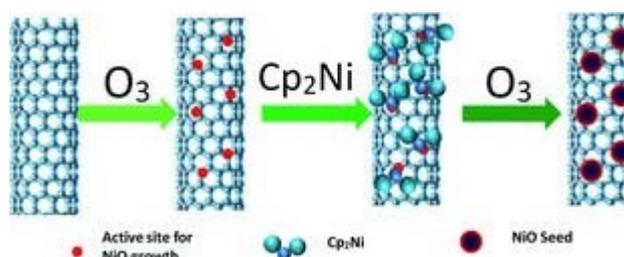


Brownian dynamics simulations were performed to study the self-assembly of mixed linear amphiphilic block copolymers. The molecules consist of similar hydrophilic heads and hydrophobic tails of different lengths. The model amphiphilic diblock copolymers have been selected to gain insight into the comicellization process in concentrated regimes, and the micelles were not kinetically frozen on the time scale of simulation. The critical micelle concentration (cmc), micelle size distribution, radius of gyration distribution, density profile of comicelles, shape anisotropy, and

dynamics of comicellization have been studied as a function of the varying molar fraction of components. The cmc's of systems rich in the molar fraction of each type were found to be close to the cmc of that component. It has also been found that at a certain concentration comicellization affects the cmc in mixed systems. The weight-average aggregate size distribution of mixed copolymers was found to be between the aggregate distributions of short and long copolymers and becomes broader because of mixing. Moreover, values of the most probable aggregate size and radius of gyration of comicelles follow the mixing rule. Results show that small aggregates are mainly made from shorter block copolymers, whereas longer block copolymers form the major portion of large clusters. Furthermore, the cores of the micelles are mainly composed of longer block copolymers, and in all cases, the concentrations of shorter block copolymers are more dominant in the outer part than in the interior regions. In addition, the dynamics of polymeric micelles was studied using tracer and extraction autocorrelation functions and their relaxation times. The tracer correlation time increases with increasing longer copolymer concentration and deviates positively from the mixing rule. We also find that the total extraction correlation time increases exponentially from short to long copolymers, but the presence of long block copolymers linearly increases the short copolymer extraction correlation times. Short block copolymers, however, linearly decrease the long copolymer correlation times.

- Preparation and Characterization of Conducting Mixed-Valence 9,9'-Dimethyl-3,3'-bicarbazyl Rectangular Nanowires
Tong, X.; Qin, Y.; Guo, X.; Moutanabbir, O.; Ao, X.; Pippel, E.; Zhang, L.; Knez, M. *Small* **2012**, *8*, 3590–3595.

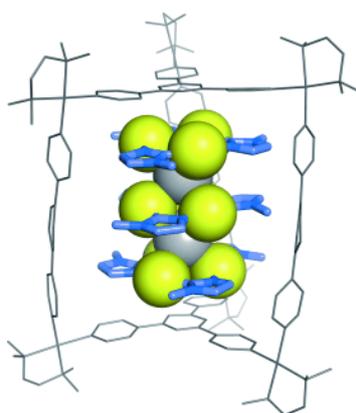
Abstract:



Highly crystalline NiO nanoparticles are uniformly grown on the walls of carbon nanotubes (CNTs) by atomic layer deposition (ALD) at moderate temperature. Their size and stoichiometry are controlled by the ALD process parameters. The obtained NiO/CNT hybrids exhibit excellent performance in the electro-oxidation of methanol.

- Triple-Decker $Au_3-Ag-Au_3-Ag-Au_3$ Ion Cluster Enclosed in a Self-Assembled Cage
Osuga, T.; Murase, T.; Fujita, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 12199-12201.

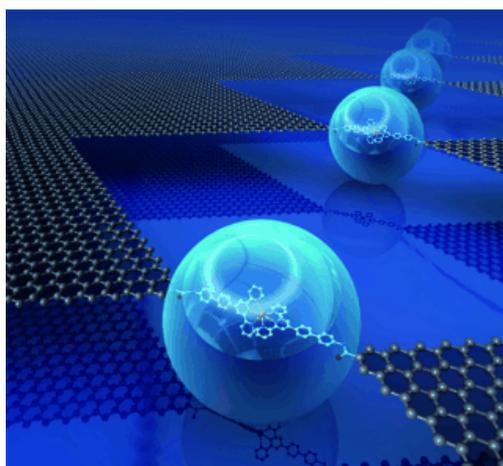
Abstract:



Silver in a gold mine: A triple-decker AuI–AgI ion cluster was synthesized by alternate alignment of cyclic trinuclear AuI complexes and AgI ions within a self-assembled cage. The box-shaped cavity of the cage is suitable not only for limiting the cluster number, but also for the stabilization of weakly associated metal ions, which cannot exist without the help of the cage.

- Building High-Throughput Molecular Junctions Using Indented Graphene Point Contacts
Cao, Y.; Dong, S.; Liu, S.; He, L.; Gan, L.; Yu, X.; Steigerwald, M. L.; Wu, X.; Liu, Z.; Guo, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 12228–12232.

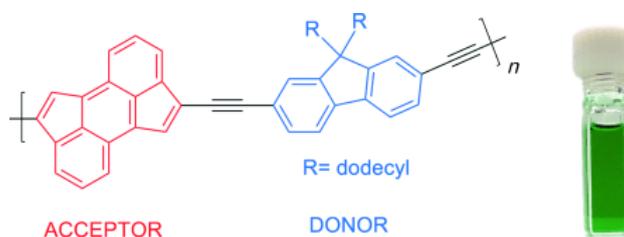
Abstract:



A molecular-scale gap array is introduced into a single-layer graphene sheet by a lithographic dash-line cutting process. Electrically active molecules are then covalently wired into these point contacts in high yield, thus forming stable molecular devices that for example are able to reversibly switch their conductance by chemical treatment.

- Electron Acceptors Based on an All-Carbon Donor–Acceptor Copolymer
Jellison, J. L.; Lee, C.-H.; Zhu, X.; Wood, J. D.; Plunkett, K. N. *Angew. Chem. Int. Ed.* **2012**, *51*, 12321–12324.

Abstract:

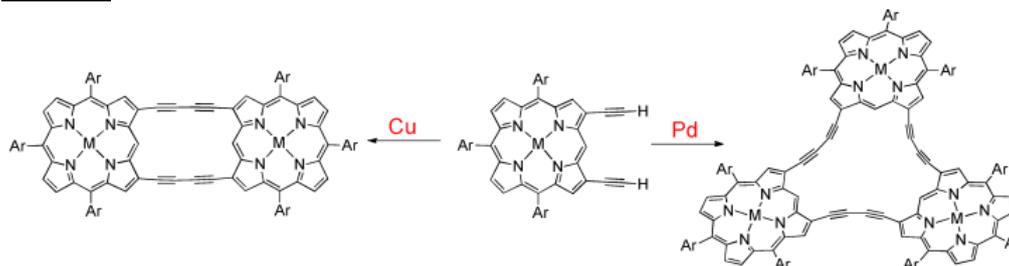


The Sonogashira cross-coupling polymerization of a dibrominated cyclopenta[*hi*]aceanthrylene and a diethynylfluorene derivative produced a donor–acceptor copolymer composed solely of cyclopenta-fused polycyclic aromatic hydrocarbons. The resulting polymer displays low band gaps (<1.5 eV), dual absorption bands, and electron-accepting behavior as demonstrated through fluorescence quenching of poly(3-hexylthiophene).

- Preferential Formation of Cyclic Trimers by Palladium-Catalyzed Oxidative Coupling Reactions of 2,18-Diethynylporphyrins

Tokuji, S.; Yorimitsu, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 12357–12361.

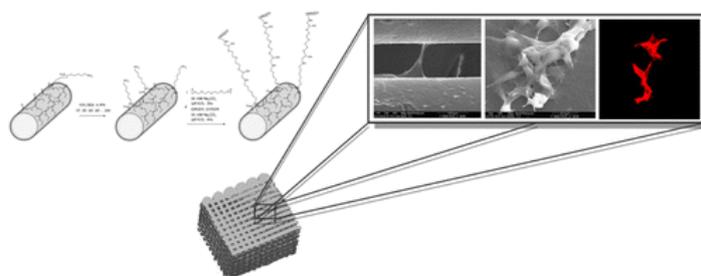
Abstract:



And palladium makes three: In contrast to the formation of cyclic dimers in the Cu-mediated reaction, Pd-catalyzed oxidative coupling of 2,18-diethynylporphyrins preferentially produced cyclic trimers (see scheme). A porphyrin hexamer with a doubly 1,3-butadiyne-bridged conjugated trimeric core and directly *meso*-appended peripheral porphyrin substituents was also synthesized.

- Three-Dimensional Poly(ϵ -caprolactone) Bioactive Scaffolds with Controlled Structural
Gloria, A.; Causa, F.; Russo, T.; Battista, E.; Della Moglie, R.; Zeppetelli, S.; De Santis, R.; Netti, P. A.; Ambrosio, L. *Biomacromolecules* **2012**, *13*, 3510–3521.

Abstract:



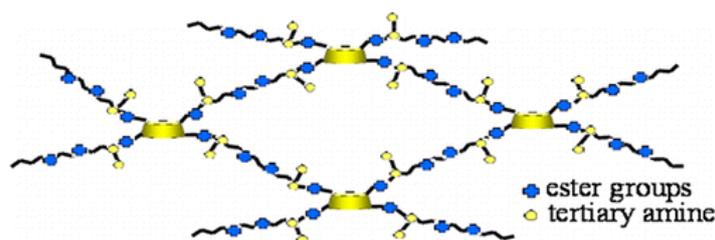
The requirement of a multifunctional scaffold for tissue engineering capable to offer at the same time tunable structural properties and bioactive interface is still unpaired. Here we present three-dimensional (3D) biodegradable polymeric (PCL) scaffolds with controlled morphology, macro-, micro-, and nano-mechanical performances endowed with bioactive moieties (RGD peptides) at the surface. Such result was obtained by a combination of rapid prototyping (e.g., 3D fiber deposition) and surface treatment approach (aminolysis followed by peptide coupling). By properly designing process conditions, a control over the mechanical and biological performances of the structure was achieved with a capability to tune the value of compressive modulus (in the range of 60–90 MPa, depending on the specific lay-down pattern). The macromechanical behavior of the proposed scaffolds was not affected by surface treatment preserving bulk properties, while a reduction of hardness from 0.50–0.27 GPa to 0.1–0.03 GPa was obtained. The penetration depth of the chemical treatment was determined by nanoindentation measurements and confocal microscopy. The efficacy of both functionalization and the following bioactivation was monitored by analytically quantifying

functional groups and/or peptides at the interface. NIH3T3 fibroblast adhesion studies evidenced that cell attachment was improved, suggesting a correct presentation of the peptide. Accordingly, the present work mainly focuses on the effect of the surface modification on the mechanical and functional performances of the scaffolds, also showing a morphological and analytical approach to study the functionalization/bioactivation treatment, the distribution of immobilized ligands, and the biological features.

- β -Cyclodextrin-poly(β -Amino Ester) Nanoparticles for Sustained Drug Delivery across the Blood–Brain Barrier

Gil, E. S.; Wu, L.; Xu, L.; Lowe, T. L. *Biomacromolecules* **2012**, *13*, 3533–3541.

Abstract:



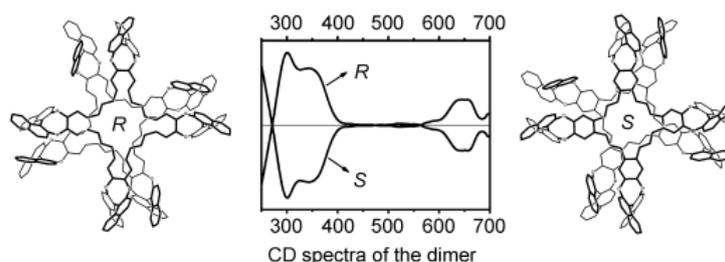
β -CD-poly(β -amino ester) nanoparticles

Novel biodegradable polymeric nanoparticles composed of β -cyclodextrin and poly(β -amino ester) segments have been developed for sustained drug delivery across the blood–brain barrier (BBB). The nanoparticles have been synthesized by cross-linking β -cyclodextrin with poly(β -amino ester) via the Michael addition method. The chemical, physical, and degradation properties of the nanoparticles have been characterized by matrix-assisted laser desorption/ionization time-of-flight, attenuated total reflectance Fourier transform infrared spectroscopy, nuclear magnetic resonance, dynamic light scattering, and atomic force microscopy techniques. Bovine and human brain microvascular endothelial cell monolayers have been constructed as in vitro BBB models. Preliminary results show that the nanoparticles do not affect the integrity of the in vitro BBB models, and the nanoparticles have much higher permeability than dextran control across the in vitro BBB models. Doxorubicin has been loaded into the nanoparticles with a loading efficiency of 86%, and can be released from the nanoparticles for at least one month. The developed β -cyclodextrin-poly(β -amino ester) nanoparticles might be useful as drug carriers for transporting drugs across the BBB to treat chronic diseases in the brain.

- A Chiral Phthalocyanine Dimer with Well-Defined Supramolecular Symmetry Based on π – π Interactions

Wang, K.; Qi, D.; Wang, H.; Cao, W.; Li, W.; Jiang, J. *Chem. Eur. J.* **2012**, *18*, 15948–15952.

Abstract:



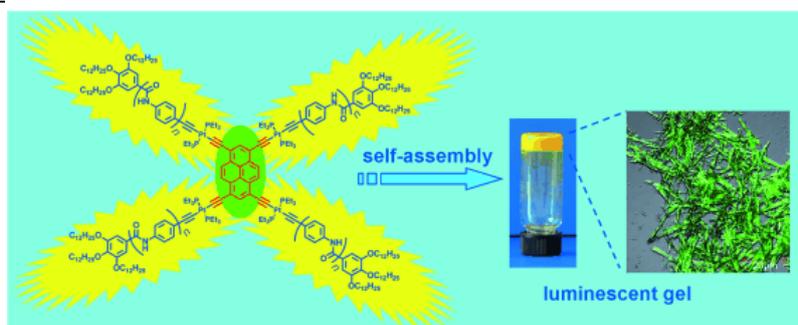
Cooperation is the name of the game: The first example of a chiral phthalocyanine dimer with well-defined supramolecular weight and symmetry formed through cooperative multiple π – π interactions

among nine pairs of aromatic moieties between two chiral phthalocyaninato zinc molecules has been clarified (see figure).

- Design and Preparation of Platinum–Acetylide Organogelators Containing Ethynyl–Pyrene Moieties as the Main Skeleton

Xu, X.-D.; Zhang, J.; Yu, X.; Chen, L.-J.; Wang, D.-X.; Yi, T.; Li, F.; Yang, H.-B. *Chem. Eur. J.* **2012**, *18*, 16000–16013.

Abstract:

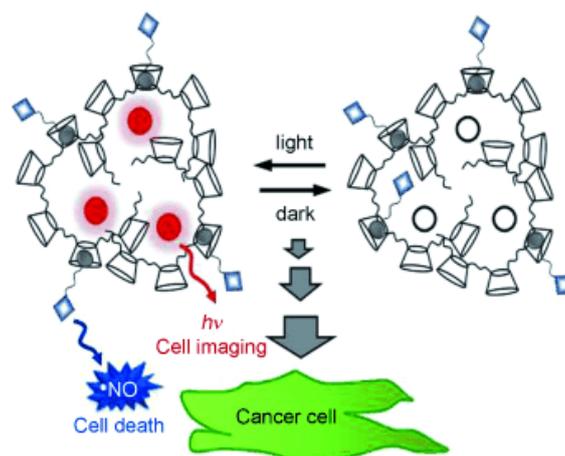


Platinum gel: A series of new platinum–acetylide complexes containing ethynyl–pyrene moieties as the main skeleton were synthesized and characterized (see figure). These complexes showed stable gel properties in many solvents. Moreover, it was found that the structural factors played an important role during the gel formation. Particularly, the complexes with four platinum–acetylide fragments presented potential applications as luminescent organometallic gels.

- Photoinduced Fluorescence Activation and Nitric Oxide Release with Biocompatible Polymer Nanoparticles

Deniz, E.; Kandoth, N.; Fraix, A.; Cardile, V.; Graziano, A. C. E.; Furno, D. L.; Gref, R.; Raymo, F. M.; Sortino, S. *Chem. Eur. J.* **2012**, *18*, 15782–15787.

Abstract:

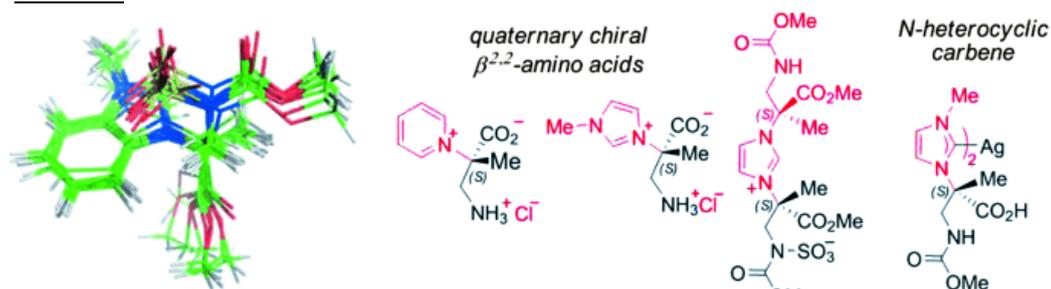


A viable strategy to encapsulate a fluorophore/photochrome dyad and a nitric oxide photodonor within supramolecular assemblies of a cyclodextrin-based polymer in water was developed. The two photoresponsive guests do not interact with each other within their supramolecular container and can be operated in parallel under optical control. Specifically, the dyad permits the reversible switching of fluorescence on a microsecond timescale for hundreds of cycles, and the photodonor enables the irreversible release of nitric oxide. Furthermore, these supramolecular assemblies cross the membrane of human melanoma cancer cells and transport their cargo in the cytosol. The

fluorescence of one component allows the visualization of the labeled cells, and its switchable character could, in principle, be used to acquire super-resolution images, while the release of nitric oxide from the other induces significant cell mortality. Thus, our design logic for the construction of biocompatible nanoparticles with dual functionality might evolve into the realization of valuable photoresponsive probes for imaging and therapeutic applications.

- Quaternary Chiral $\beta^{2,2}$ -Amino Acids with Pyridinium and Imidazolium Substituents
Mata, L.; Avenoza, A.; Busto, J. H.; Corzana, F.; Peregrina, J. M. *Chem. Eur. J.* **2012**, *18*, 15822–15830.

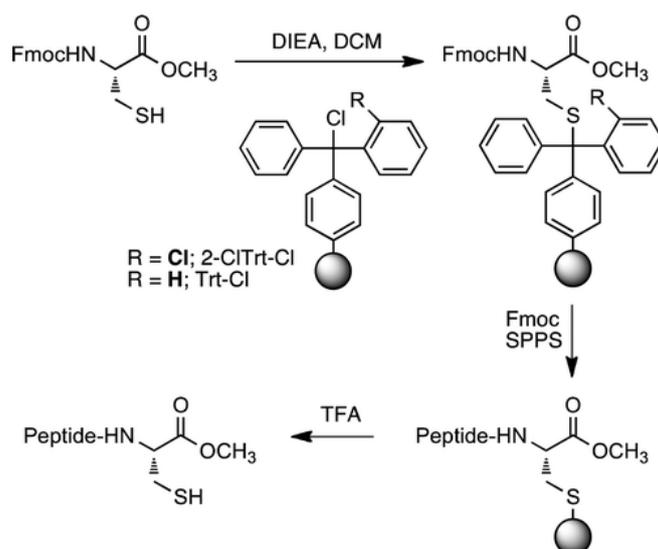
Abstract:



The reactions of cyclic sulfamidates as electrophiles with a variety of nitrogen-containing aromatic heterocycle nucleophiles, such as pyridines, *N*-alkylimidazoles and *N*-methylbenzimidazol, was explored. In all cases, although the nucleophilic substitution reactions occurred on quaternary centres, elimination products were not detected. The inversion of configuration at this quaternary centre was determined by X-ray diffraction analysis and the enantiomeric excess of the reactions was checked by chiral HPLC. This synthetic approach allowed us to obtain a new family of chiral charged $\beta^{2,2}$ -amino acids, including a new bisamino acid that incorporates an imidazolium salt as a cross-linker. In this context, the treatment of these chiral imidazolium salts with Ag_2O opens the way to new chiral *N*-heterocyclic carbenes, which are important substrates in the fields of organometallic and organocatalytic chemistry. Additionally, we have done a thorough conformational analysis of these β -amino acid derivatives, both in the solid state and in solution. The most important conformational feature of these acyclic systems is the rigidity of the $\text{N-CH}_2\text{-C-N}^+$ dihedral angle, which is essentially due to the *gauche* effect.

- Synthesis of Peptides Containing C-Terminal Methyl Esters Using Trityl Side-Chain Anchoring: Application to the Synthesis of α -Factor and α -Factor Analogs
Diaz-Rodriguez, V.; Mullen, D. G.; Ganusova, E.; Becker, J. M.; Distefano, M. D. *Org. Lett.* **2012**, *14*, 5648–5651.

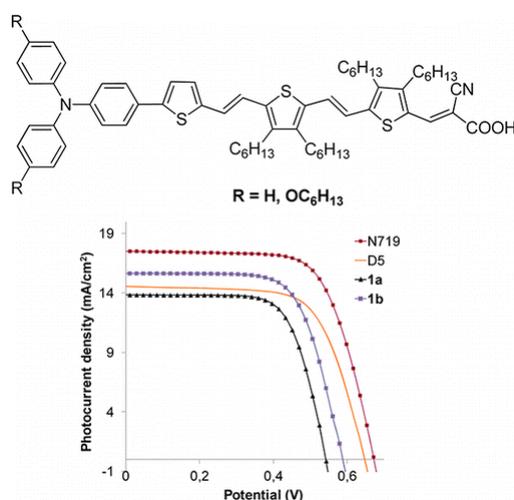
Abstract:



A new cysteine anchoring method was developed for the synthesis of peptides containing C-terminal cysteine methyl esters. This method consists of attachment of Fmoc-Cys-OCH₃ to either 2-ClTrt-Cl or Trt-Cl resins (via the side-chain thiol) followed by preparation of the desired peptide using Fmoc-based SPPS. We applied this method to the synthesis of the mating pheromone **a**-factor and a 5-FAM labeled **a**-factor analog. The peptides were obtained with high yield and purity and were shown to be bioactive in a growth arrest assay.

- Organic Dyes Incorporating Oligothiénylenevinylene for Efficient Dye-Sensitized Solar Cells
Aljarilla, A.; López-Arroyo, L.; de la Cruz, P.; Oswald, F.; Meyer, T. B.; Langa, F. *Org. Lett.* **2012**, *14*, 5732–5735.

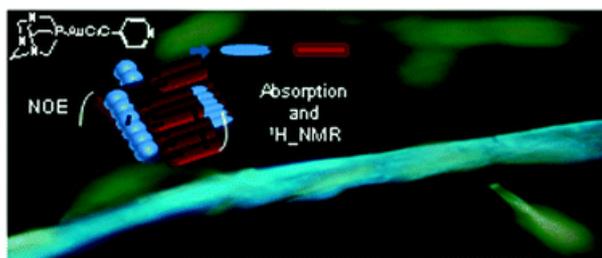
Abstract:



Two new organic dyes incorporating triphenylamine as a donor and oligothiénylenevinylene as a bridge have been synthesized. The new dyes cover the entire visible region and have a power conversion of up to 6.25%.

- A luminescent hydrogel based on a new Au(I) complex
Gavara R.; Llorca J.; Lima J.C.; Rodríguez L. *Chem. Commun.* **2013**, *49*, 72–74.

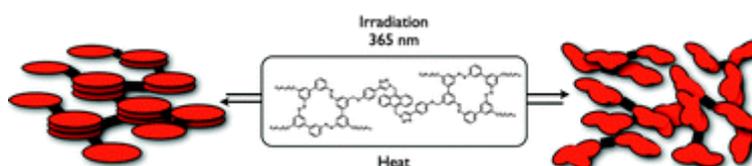
Abstract:



The reaction of the water soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) with $[\text{Au}(\text{C}\equiv\text{C}-\text{C}_5\text{H}_4\text{N})]_n$ yields the highly luminescent water soluble $[(\text{PTA})\text{Au}(4\text{-pyridylethynyl})]$ complex. A detailed analysis of the compound shows the formation of gel structure giving rise to very long fibers, being the first example reported with such a simple structure.

- Switchable 3D networks by light controlled π -stacking of azobenzene macrocycles
Reuter R.; Wegner H.A. *Chem. Commun.* **2012**, 48, 12142–12158.

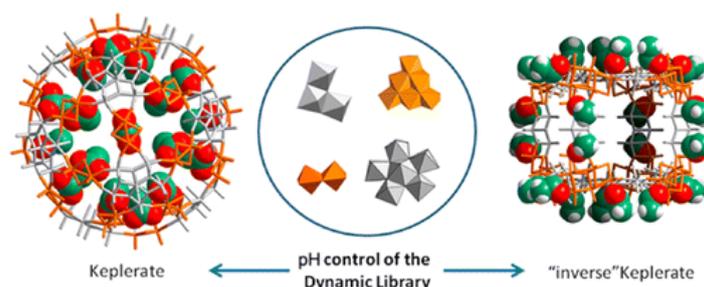
Abstract:



Azobenzene macrocycles were designed for switchable π -stacking interaction. After efficient preparation and characterization of azobenzene macrocycles containing electron rich as well as electron poor elements a dimeric analogue was synthesized, which formed reversibly 3D-networks. Gel formation was observed with aromatic solvents representing the first example of this type based on switchable azobenzene macrocycles.

- Cubic Box versus Spheroidal Capsule Built from Defect and Intact Pentagonal Units
Bannani, F.; Floquet, S.; Leclerc-Laronze, N.; Haouas, M.; Taulelle, F.; Marrot, J.; Kögerler, P.; Cadot, E. *J. Am. Chem. Soc.* **2012**, 134, 19342–19345.

Abstract:

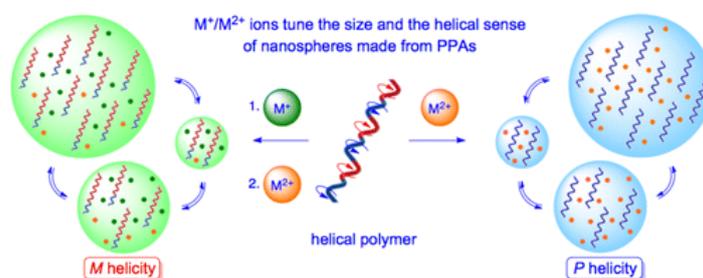


The high-nuclearity polyoxothiomolybdate $[\text{H}_8\text{Mo}_{84}\text{S}_{48}\text{O}_{188}(\text{H}_2\text{O})_{12}(\text{CH}_3\text{COO})_{24}]^{32-}$ has been prepared and characterized by single-crystal X-ray crystallography and ^1H NMR, IR, Raman, and UV–vis spectroscopy. The solid-state structure reveals an unprecedented and intriguing arrangement consisting of a nanoscaled anionic cube. The surprisingly open structure of this $\{\text{Mo}_{84}\}$ -type cubic box features a large inner void that is accessible via its six open square faces with diameters of ca. 9 Å. Importantly, this molecular system appears to be highly functionalizable because of the presence of 24 exposed exchangeable acetate ligands.

- Nanospheres with Tunable Size and Chirality from Helical Polymer–Metal Complexes

Freire, F.; Seco, J. M.; Quiñoá, E.; Riguera, R. *J. Am. Chem. Soc.* **2012**, *134*, 19374–19383.

Abstract:

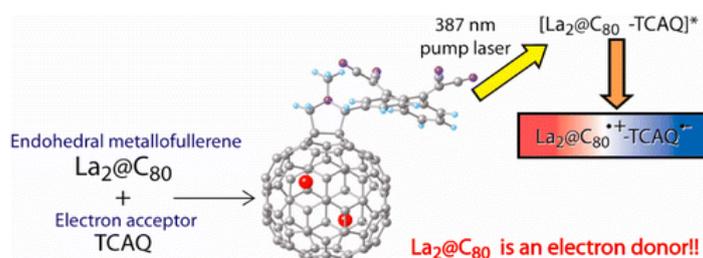


A new family of nanospheres is made by complexation of divalent metals (i.e., Ca^{2+} , Ba^{2+}) and poly(phenylacetylene) polymers bearing α -methoxyphenylacetic acid (MPA) pendants with high content of the cis isomer responsible for their helical structures. The resulting helical polymer–metal complex (HPMC) nanospheres present two interesting properties: (a) their diameter can be tuned to different sizes, to growth or to shrink, by changing the metal ion or the polymer/metal ion ratio, and (b) the helicity on the surface and the interior of the particle can be tuned to any of the two helical senses (*M* or *P*) by selection of the metal ion. The role of the solvent, the metal ion, and the helicity of the polymer in the aggregation are discussed. The ability of these nanospheres to encapsulate is demonstrated with examples.

- An Endohedral Metallofullerene as a Pure Electron Donor: Intramolecular Electron Transfer in Donor–Acceptor Conjugates of $\text{La}_2@C_{80}$ and 11,11,12,12-Tetracyano-9,10-anthra-*p*-quinodimethane (TCAQ)

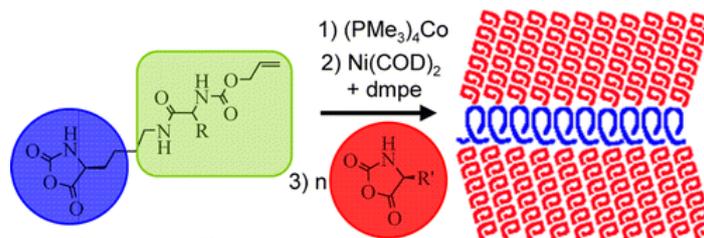
Takano, Y.; Obuchi, S.; Mizorogi, N.; García, R.; Herranz, R. A.; Rudolf, M.; Guldi, D. M.; Martín, N.; Nagase, S.; Akasaka, T. *J. Am. Chem. Soc.* **2012**, *134*, 19401–19408.

Abstract:



An endohedral metallofullerene, $\text{La}_2@C_{80}$, is covalently linked to the strong electron acceptor 11,11,12,12-tetracyano-9,10-anthra-*p*-quinodimethane (TCAQ) by means of the Prato reaction, affording two different [5,6]-metallofulleropyrrolidines, namely **1a** and **2a**. **1a** and **2a** were isolated and fully characterized by means of MALDI-TOF mass, UV–vis–NIR absorption, and NMR spectroscopies. In addition, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) corroborated the unique redox character of **2a**, that is, the presence of the electron-donating $\text{La}_2@C_{80}$ and the electron-accepting TCAQ. Although a weak electronic coupling dictates the interactions between $\text{La}_2@C_{80}$ and TCAQ in the ground state, time-resolved transient absorption experiments reveal that in the excited state (i.e., π – π^* centered at $\text{La}_2@C_{80}$) the unprecedented formation of the $(\text{La}_2@C_{80})^{+\bullet}-(\text{TCAQ})^{-\bullet}$ radical ion pair state evolves in nonpolar and polar media with a quantum efficiency of 33%.

- Tandem Catalysis for the Preparation of Cylindrical Polypeptide Brushes
Rhodes, A. J.; Deming, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 19463–19467.

Abstract:

Here, we report a method for synthesis of cylindrical copolypeptide brushes via N-carboxyanhydride (NCA) polymerization utilizing a new tandem catalysis approach that allows preparation of brushes with controlled segment lengths in a straightforward, one-pot procedure requiring no intermediate isolation or purification steps. To obtain high-density brush copolypeptides, we used a “grafting from” approach where alloc- α -aminoamide groups were installed onto the side chains of NCAs to serve as masked initiators. These groups were inert during cobalt-initiated NCA polymerization and gave allyloxycarbonyl- α -aminoamide-substituted polypeptide main chains. The alloc- α -aminoamide groups were then activated in situ using nickel to generate initiators for growth of side-chain brush segments. This use of stepwise tandem cobalt and nickel catalysis was found to be an efficient method for preparation of high-chain-density, cylindrical copolypeptide brushes, where both the main chains and side chains can be prepared with controlled segment lengths.

- Molecular daisy chains

Rotzler, J.; Mayor, M. *Chem. Soc. Rev.* **2013**, 42, 44-62.

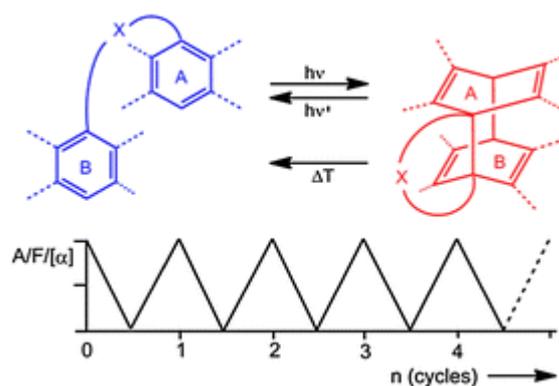
Abstract:

This tutorial review summarizes the progress made towards mechanically interlocked daisy chains. Such materials can be seen as a further development in polymer science, where the conventional covalent interlinking bonds are replaced by supramolecular binding concepts. Materials in which the mechanical bond is an integral part of the polymeric backbone are expected to possess unique macroscopic properties and are therefore the synthetic aim in an ever growing research community. After introducing general considerations about daisy chains, the most common analytic methods to get insight into the aggregation behaviour of such self-complementary monomers are presented. Cyclodextrins/aromatic rods, crown ethers/cationic rods and pillararenes/alkyl chains are systems used to achieve daisy chain-like molecular arrays. By comparison of the reported systems, conclusions about an improved structural design are drawn.

- Optical switches with biplanemers obtained by intramolecular photocycloaddition reactions of tethered arenes

Meier, H.; Cao, D. *Chem. Soc. Rev.* **2013**, 42, 143-155.

Abstract:

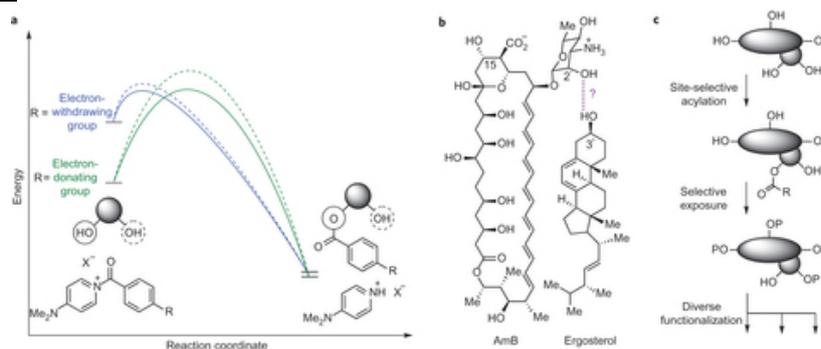


The dimerization of anthracene by a $[4\pi + 4\pi]$ cycloaddition is one of the oldest and best known reactions in photochemistry. In the series of tethered bichromophoric arenes, this reaction type could be extended to anthracene–naphthalene, naphthalene–naphthalene and recently even to anthracene–benzene and naphthalene–benzene systems. Cyclophanes, which can be regarded as twofold or multiple tethered systems, are not discussed here. The cycloisomerizations are performed by irradiation at the long-wavelength absorption ($\lambda > 270$ nm), whereas shorter wavelengths ($\lambda < 270$ nm) lead to cycloreversions, which can be also achieved by a thermal route. The systems represent therefore a P- and T-type photochromism, which can be used for optical or chiroptical switches. An acceleration of the switch is possible by a singlet energy transfer (light harvesting antenna effect) in dendritic compounds. In the past 5 to 10 years many applications of these switches were studied in the context of photonic devices, sensor techniques, lithographic processes, imaging techniques, data processing and data storage.

- Electronic tuning of site-selectivity

Wilcock, B. C.; Uno, B. E.; Bromann, G. L.; Clark, M. J.; Anderson, T. M.; Burke, M. D. *Nature Chemistry* **2012**, *4*, 996–1003.

Abstract:

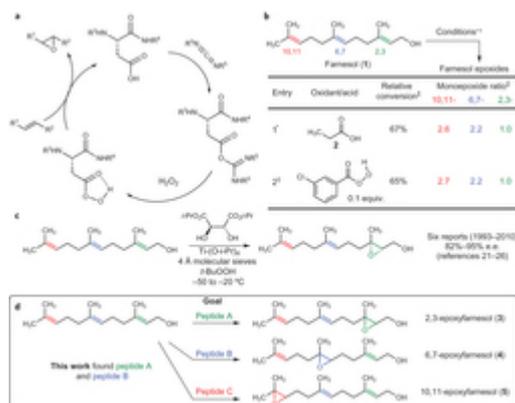


Site-selective functionalizations of complex small molecules can generate targeted derivatives with exceptional step efficiency, but general strategies for maximizing selectivity in this context are rare. Here, we report that site-selectivity can be tuned by simply modifying the electronic nature of the reagents. A Hammett analysis is consistent with linking this phenomenon to the Hammond postulate: electronic tuning to a more product-like transition state amplifies site-discriminating interactions between a reagent and its substrate. This strategy transformed a minimally site-selective acylation reaction into a highly selective and thus preparatively useful one. Electronic tuning of both an acylpyridinium donor and its carboxylate counterion further promoted site-divergent functionalizations. With these advances, we achieve a range of modifications to just one of the many hydroxyl groups appended to the ion channel-forming natural product amphotericin B. Thus,

electronic tuning of reagents represents an effective strategy for discovering and optimizing site-selective functionalization reactions.

- Combinatorial evolution of site- and enantioselective catalysts for polyene epoxidation
Lichtor, P. A.; Miller, S. J. *Nature Chemistry* **2012**, *4*, 990–995.

Abstract:

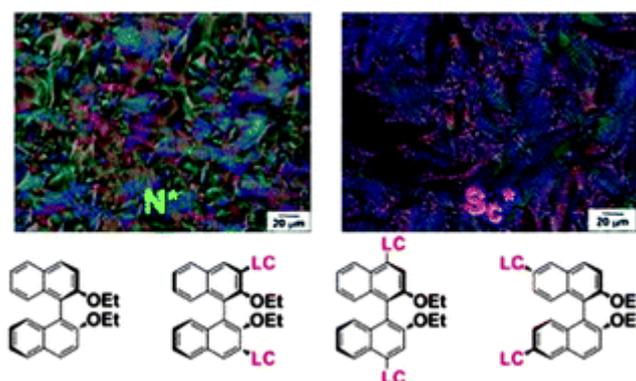


Selectivity in the catalytic functionalization of complex molecules is a major challenge in chemical synthesis. The problem is magnified when there are several possible stereochemical outcomes and when similar functional groups occur repeatedly within the same molecule. Selective polyene oxidation provides an archetypical example of this challenge. Historically, enzymatic catalysis has provided the only precedents. Although non-enzymatic catalysts that meet some of these challenges became known, a comprehensive solution has remained elusive. Here, we describe low molecular weight peptide-based catalysts, discovered through a combinatorial synthesis and screening protocol, that exhibit site- and enantioselective oxidation of certain positions of various isoprenols. This diversity-based approach, which exhibits features reminiscent of the directed evolution of enzymes, delivers catalysts that compare favourably to the state-of-the-art for the asymmetric oxidation of these compounds. Moreover, the approach culminated in catalysts that exhibit alternative-site selectivity in comparison to oxidation catalysts previously described.

- Chirality transfer from atropisomeric chiral inducers to nematic and smectic liquid crystals – synthesis and characterization of *di*- and *tetra*-substituted axially chiral binaphthyl derivatives

Goh, M.; Park, J.; Han, Y.; Ahn, S.; Akagi, K. *J. Mater. Chem.* **2012**, *22*, 25011–25018.

Abstract:



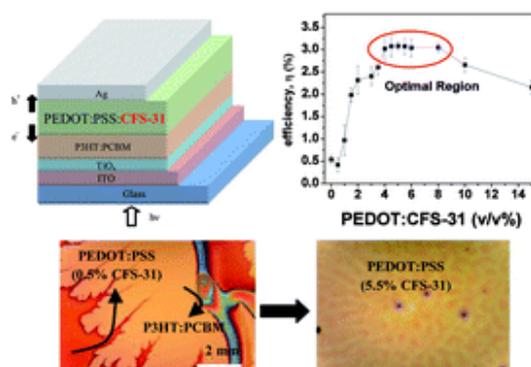
The chirality transfer of axially chiral binaphthyl derivatives bearing liquid crystal (LC) moieties at the *n, n'* positions (*n* = 3, 4, 6) of the binaphthyl rings to nematic (N) and smectic (S) LCs is investigated.

Chiral nematic LCs (N^* -LCs) are prepared by adding a small amount of the chiral binaphthyl derivative into host N-LCs composed of cyanobiphenyl mesogen cores. The binaphthyl derivative with phenylcyclohexyl (PCH) type LC moieties at the 4,4' positions of the binaphthyl ring [D-4,4'] exhibits a low helical twisting power (HTP) of $11 \mu\text{m}^{-1}$. In contrast, those with LC moieties at the 3,3' and 6,6' positions of the binaphthyl rings [D-3,3' and D-6,6'] exhibit high HTPs of $153 \mu\text{m}^{-1}$ and $154 \mu\text{m}^{-1}$, respectively. Next, the binaphthyl derivatives are added into two types of S-LCs with phenylbenzoate mesogen cores: 4-(4-methylpentylloxy)phenyl-4-(decyloxy)benzoate [PhB1] and 4-(3-methylpentylloxy)phenyl-4-(decyloxy)benzoate [PhB2]. The mixture of the host LC, PhB1 or PhB2 with the chiral dopant, D-3,3' or D-6,6' shows chiral smectic LCs C (S_C^* -LCs). The highly twisted S_C^* phases with helical pitches of 1.2–1.4 μm are prepared in PhB1 and PhB2 by using the chiral dopant of D-6,6'. It is concluded that D-6,6' has a large helical twisting power and is the most favourable atropisomeric chiral inducer for chirality transfer to both N-LCs and S-LCs.

- Influence of a novel fluorosurfactant modified PEDOT:PSS hole transport layer on the performance of inverted organic solar cells

Lim, F. J.; Ananthanarayanan, K.; Luther, J.; Ho, G. W. *J. Mater. Chem.* **2012**, *22*, 25057–25064.

Abstract:

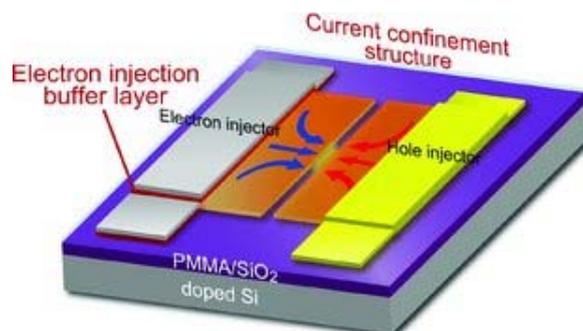


Under ambient conditions the long term stability of non-encapsulated organic solar cells with conventional device architecture is lower than the technical lifetime of devices with an inverted configuration. The removal of the interface between the ITO (indium tin oxide) layer and the acidic PEDOT:PSS layer along with the substitution of a low work function metal electrode with a high work function metal electrode in the inverted device configuration renders relatively higher stability in these devices. However, one of the main inherent difficulties involving the fabrication of devices with such inverted architecture is the wettability of the hydrophilic PEDOT:PSS onto the photoactive layer such as the P3HT:PCBM blend which is hydrophobic in nature. To overcome this, we have used a novel fluorosurfactant, Capstone® Dupont™ FS-31 (CFS-31), as a substitute to the conventional Zonyl FS-300 as an additive to PEDOT:PSS. A smooth and uniform PEDOT:PSS layer was coated onto the P3HT:PCBM blend layer by addition of CFS-31 alone without any further treatments. Using this surfactant, an efficiency of 3.1% and a stable device performance (up to 400 hours) under ambient conditions without encapsulation have been achieved.

- Current-Confinement Structure and Extremely High Current Density in Organic Light-Emitting Transistors

Sawabe, K.; Imakawa, M.; Nakano, M.; Yamao, T.; Hotta, S.; Iwasa, Y.; Takenobu, T. *Adv. Mater.* **2012**, *24*, 6141–6146.

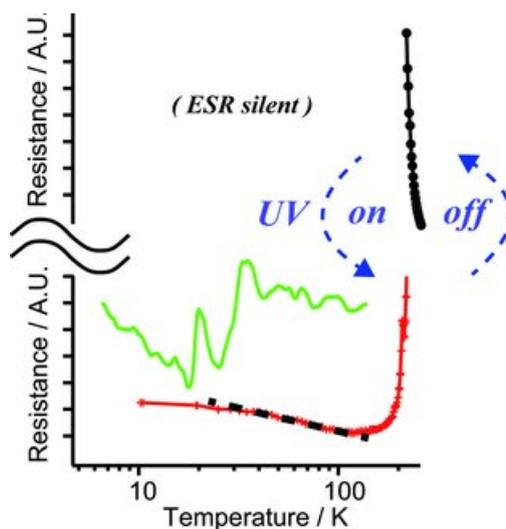
Abstract:



Extremely high current densities are realized in single-crystal ambipolar light-emitting transistors using an electron-injection buffer layer and a current-confinement structure via laser etching. Moreover, a linear increase in the luminance was observed at current densities of up to 1 kA cm^{-2} , which is an efficiency-preservation improvement of three orders of magnitude over conventional organic light-emitting diodes (OLEDs) at high current densities.

- Simultaneous Control of Carriers and Localized Spins with Light in Organic Materials
Naito, T.; Karasudani, T.; Ohara, K.; Takano, T.; Takahashi, Y.; Inabe, T.; Furukawa, K.; Nakamura, T. *Adv. Mater.* **2012**, *24*, 6153–6157.

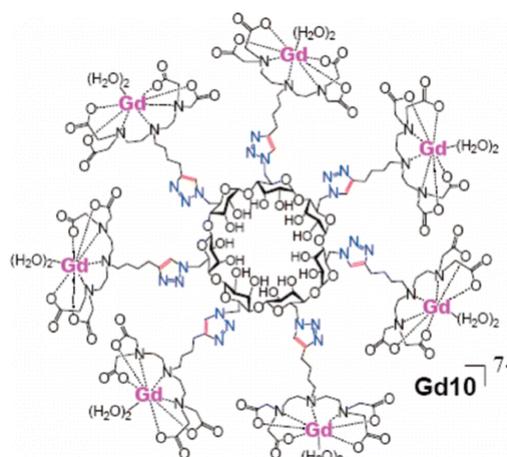
Abstract:



An organic insulating crystal reversibly becomes a magnetic conductor under UV irradiation. The rapid and qualitative change in the physical properties is wavelength selective and explained by charge transfer between donor and photochemically active acceptor molecules. The photochemical redox reaction in the crystal produces a partially filled band and localized spins simultaneously.

- Macromolecular Imaging Agents Containing Lanthanides: Can Conceptual Promise Lead to Clinical Potential?
Bryson, J. M.; Reineke, J. W.; Reineke, T. M. *Macromolecules* **2012**, *45*, 8939–8952.

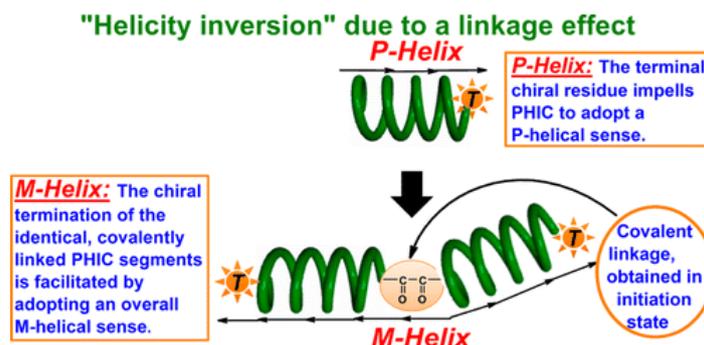
Abstract:



Macromolecular magnetic resonance imaging (MRI) contrast agents are increasingly being used to improve the resolution of this noninvasive diagnostic technique. All clinically approved T_1 contrast agents are small molecule chelates of gadolinium [Gd(III)] that affect bound water proton relaxivity. Both the small size and monomeric nature of these agents ultimately limit the image resolution enhancement that can be achieved for both contrast enhancement and pharmacokinetic/biodistribution. The multimeric nature of macromolecules, such as polymers, dendrimers, and noncovalent complexes of small molecule agents with proteins, has been shown to significantly increase the image contrast and resolution due to their large size and ability to incorporate multiple Gd(III) chelation sites. Also, macromolecular agents are advantageous as they have the ability to be designed to be nontoxic, hydrophilic, easily purified, and aggregation-resistant and have a controllable three-dimensional macromolecular structure housing the multiple lanthanide chelation sites. For these reasons, large molecule diagnostics have the ability to significantly increase the relaxivity of water protons within the targeted tissues and thus the image resolution for many diagnostic applications. The FDA approval of a contrast agent that consists of a reversible, noncovalent coupling of a small Gd(III) chelate with serum albumin for blood pool imaging (marketed under the trade names of Vasovist and Ablivar) proved to be one of the first diagnostic agent to capitalize on these benefits from macromolecular association in humans. However, much research and development is necessary to optimize the safety of these unique agents for *in vivo* use and potential clinical development. To this end, recent works in the field of polymer, dendrimer, and noncovalent complex-based imaging agents are reviewed herein, and the future outlook of this field is discussed.

- “Helicity Inversion”: Linkage Effects of Chiral Poly(*n*-hexyl isocyanate)s
Shah, P. N.; Min, J.; Chae, C.-G.; Nishikawa, N.; Suemasa, D.; Kakuchi, T.; Satoh, T.; Lee, J.-S. *Macromolecules* **2012**, *45*, 8961–8969.

Abstract:



Poly(*n*-hexyl isocyanate)s (PHICs) with chiral moieties at both ends of their polymeric chains were synthesized by living anionic polymerizations. Such PHICs were synthesized using a bidirectional initiator (sodium naphthalenide (Na-Naph)) and terminated with a chiral acid chloride, (*S*)-2-acetoxypropionyl chloride ((*S*)-Ct). Na-Naph created a covalent linkage in the middle of the chains by radical–radical coupling. PHICs containing a chiral moiety at both ends adopted conformations with an opposite helical sense in comparison with those PHICs that had the same chiral moiety at only one end of their chain. By observing these structural differences, it was hypothesized that such a “helicity inversion” occurred in the PHICs due to the covalent linkage in the middle of the chain. Therefore, to prove this assumption about helicity inversion, a comparison study of the helical behaviors between the PHIC with the chiral moiety at both ends and the PHIC with the chiral moiety at only one end was performed. The synthesized PHICs were characterized using size exclusion chromatography–multiangle laser light scattering (SEC-MALLS), MALDI-TOF mass spectrometry, NMR spectrometry, and circular dichroism (CD).