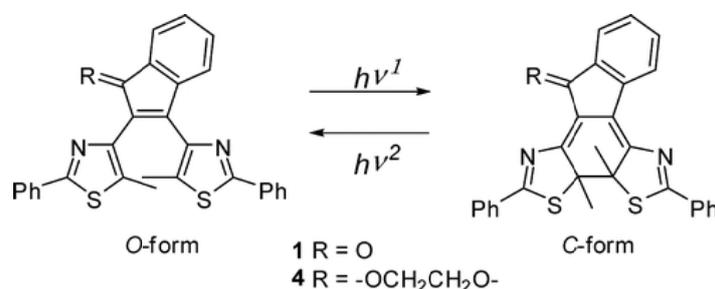


- Structurally Versatile Novel Photochromic Bisarylindenone and Its Acetal: Achievement of Large Cyclization Quantum Yield

Morinaka, K.; Ubukata, T.; Yokoyama, Y. *Org. Lett.* **2009**, *11*, 3890–3893.

Abstract:

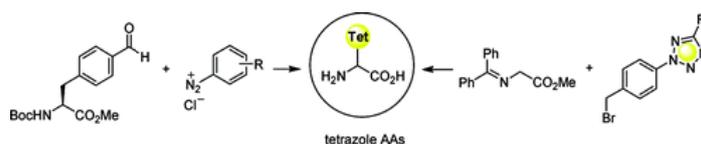


Bisarylindenones and an acetal derivative, a novel thermally irreversible photochromic family based on  $6\pi$ -electrocyclization with three easily modifiable functional groups, have been synthesized. 2,3-Bis(5-methyl-2-phenyl-4-thiazolyl)indenone showed photochromic back-and-forth reactions with two different visible lights. Its ethylene acetal recorded 0.81 as the photocyclization quantum yield in hexane, which is the largest value known to date for  $6\pi$ -electrocyclization in solution.

- Synthesis and Evaluation of Photoreactive Tetrazole Amino Acids

Wang, Y.; Lin, Q. *Org. Lett.* **2009**, *11*, 3570–3573.

Abstract:



Six photoreactive tetrazole amino acids were efficiently synthesized either by the de novo Kakehi tetrazole synthesis method or by alkylation of a glycine Schiff base with tetrazole-containing alkyl halides, and four of them showed excellent reactivity toward a simple alkene in the photoinduced 1,3-dipolar cycloaddition reaction in acetonitrile/PBS buffer (1:1) mixture.

- Conjugated dicarboxylate anodes for Li-ion batteries

Armand, M.; Grugeon, S.; Vezin, H.; Laruelle, S.; Ribi re, P.; Poizot, P.; Tarascon, J.-M. *Nature Materials* **2009**, *8*, 120-125.

Abstract:



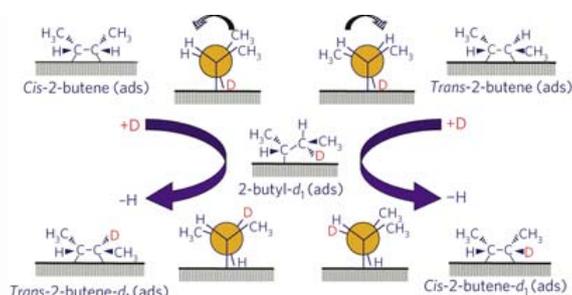
Present Li-ion batteries for portable electronics are based on inorganic electrodes. For upcoming large-scale applications the notion of materials sustainability produced by materials made through eco-efficient processes, such as renewable organic electrodes, is crucial. We here report on two organic salts,  $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$  (Li terephthalate) and  $\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$  (Li *trans-trans*-muconate), with carboxylate groups conjugated within the molecular core, which are respectively capable of reacting with two and one extra Li per formula unit at potentials of 0.8 and 1.4 V, giving reversible capacities of 300 and 150  $\text{mA h g}^{-1}$ . The activity is maintained at 80 °C with polyethyleneoxide-based electrolytes. A noteworthy advantage of the  $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$  and  $\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$  negative electrodes is their enhanced thermal stability over carbon electrodes in 1 M  $\text{LiPF}_6$  ethylene carbonate–dimethyl carbonate electrolytes, which should result in safer Li-ion cells. Moreover, as bio-inspired materials, both compounds are the

metabolites of aromatic hydrocarbon oxidation, and terephthalic acid is available in abundance from the recycling of polyethylene terephthalate.

2

- Tuning selectivity in catalysis by controlling particle shape  
Lee, I.; Delbecq, F.; Morales, R.; Albitzer, M. A.; Zaera, F. *Nature Materials* **2009**, *8*, 132-138.

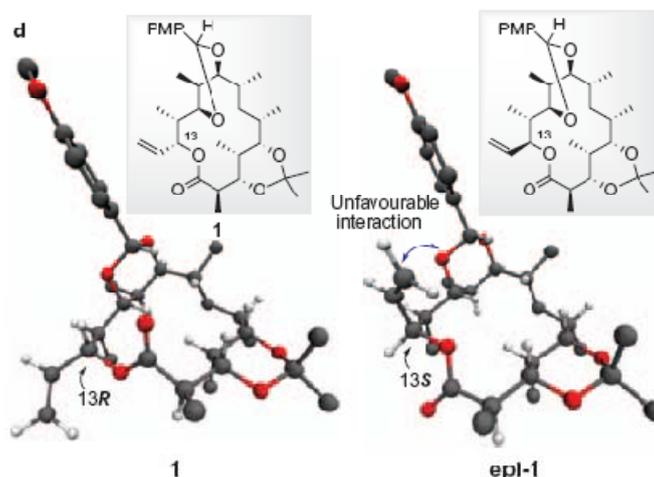
Abstract:



A catalytic process for the selective formation of *cis* olefins would help minimize the production of unhealthy *trans* fats during the partial hydrogenation of edible oils. Here we report on the design of such a process on the basis of studies with model systems. Temperature programmed desorption data on single crystals showed that the isomerization of *trans* olefins to their *cis* counterparts is promoted by (111) facets of platinum, and that such selectivity is reversed on more open surfaces. Quantum mechanics calculations suggested that the extra stability of *cis* olefins seen on hydrogen-saturated Pt(111) surfaces may be due to a lesser degree of surface reconstruction, a factor found to be significant in the adsorption on close-packed platinum surfaces. Kinetic data using catalysts made out of dispersed tetrahedral Pt nanoparticles corroborated the selective promotion of the *trans*-to-*cis* isomerization on the (111) facets of the metal. Our work provides an example for how catalytic selectivity may be controlled by controlling the shape of the catalytic particles.

- Total synthesis and study of 6-deoxyerythronolide B by late-stage C–H oxidation  
Stang, E. M.; White, M. C. *Nature Chem.* **2009**, *1*, 547-551.

Abstract:

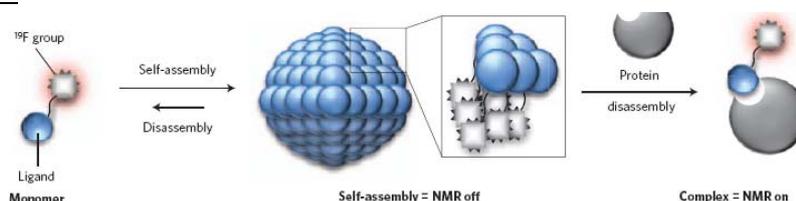


Among the frontier challenges in chemistry in the twenty-first century are the interconnected goals of increasing synthetic efficiency and diversity in the construction of complex molecules. Oxidation reactions of C–H bonds, particularly when applied at late stages of complex molecule syntheses, hold special promise for achieving both these goals. Here we report a late-stage C–H oxidation strategy in the total synthesis of 6-deoxyerythronolide B (6-dEB), the aglycone precursor to the erythromycin

antibiotics. An advanced intermediate is cyclized to give the 14-membered macrocyclic core of 6-dEB using a late-stage (step 19 of 22) C–H oxidative macrolactonization reaction that proceeds with high regio-, chemo- and diastereoselectivity (>40:1). A chelate-controlled model for macrolactonization predicted the stereochemical outcome of C–O bond formation and guided the discovery of conditions for synthesizing the first diastereomeric 13-epi-6-dEB precursor. Overall, this C–H oxidation strategy affords a highly efficient and stereochemically versatile synthesis of the erythromycin core.

- Self-assembling nanoprobe that display off/on  $^{19}\text{F}$  nuclear magnetic resonance signals for protein detection and imaging  
Takaoka, Y.; Sakamoto, T.; Tsukiji, S.; Narazaki, M.; Matsuda, T.; Tochio, H.; Shirakawa, M.; Hamachi, I. *Nature Chem.* **2009**, *1*, 557-561.

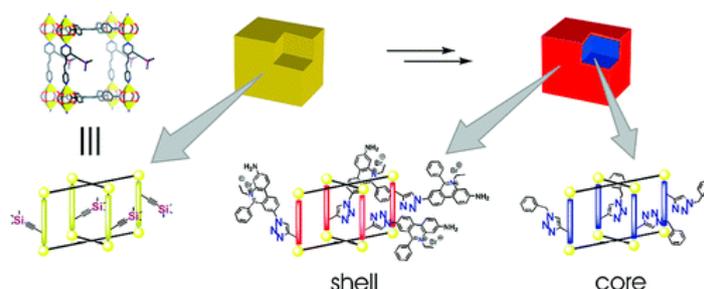
Abstract:



Magnetic resonance imaging (MRI) is one of the most promising techniques for the non-invasive visualization of biomarkers and biologically relevant species, both in vivo and ex vivo. Although  $^1\text{H}$  MRI with paramagnetic contrast agents, such as  $\text{Gd}^{3+}$  complexes and iron oxide, is widely used, it often suffers from low contrast because of the large background signals caused by the abundant distribution of protons in biological samples. Here we report the use of supramolecular organic nanoparticles to detect specific proteins by  $^{19}\text{F}$ -based MRI in an off/on mode. In NMR spectroscopy these designed probes are silent when aggregated, but in the presence of a target protein they disassemble to produce a sharp signal. This 'turn-on' response allowed us to visualize clearly the protein within live cells by  $^{19}\text{F}$  MRI and construct an in-cell inhibitor assay. This recognition-driven disassembly of nanoprobe for a turn-on  $^{19}\text{F}$  signal is unprecedented and may extend the use of  $^{19}\text{F}$  MRI for specific protein imaging.

- Selective Bifunctional Modification of a Non-catenated Metal–Organic Framework Material via “Click” Chemistry  
Gadzikwa, T.; K. Farha, O.; D. Malliakas, C.; G. Kanatzidis, M.; T. Hupp, J.; T. Nguyen, S. *J. Am. Chem. Soc.* **2009**, *131*, 13613–13615.

Abstract:



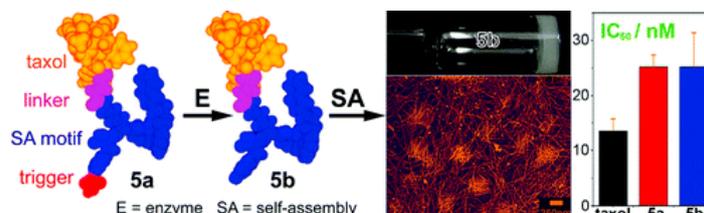
A noncatenated, Zn-based metal–organic framework (MOF) material bearing silyl-protected acetylenes was constructed and postsynthetically modified using “click” chemistry. Using a solvent-based, selective deprotection strategy, two different organic azides were “clicked” onto the MOF

crystals, resulting in a porous material whose internal and external surfaces are differently functionalized.

- Enzyme-Instructed Molecular Self-assembly Confers Nanofibers and a Supramolecular Hydrogel of Taxol Derivative

Gao, Y. Kuang, Y.; Guo, Z.; Guo, Z.; J. Krauss, I.; Xu, B. *J. Am. Chem. Soc.* **2009**, *131*, 13576–13577.

Abstract:

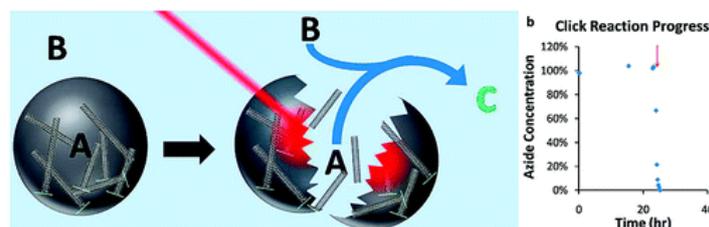


By covalently connecting taxol with a motif that is prone to self-assemble, we successfully generate the precursor (5a), the hydrogelator (5b), and hydrogel of a taxol derivative without compromising the cytotoxic activity of the taxol. This approach promises a general method to create nanofibers of therapeutic molecules that have a dual role, as both the delivery vehicle and the drug itself.

- Chemicals On Demand with Phototriggerable Microcapsules

Pastine, S. J.; Okawa, D.; Zettl, A.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2009**, *131*, 13586–13587.

Abstract:

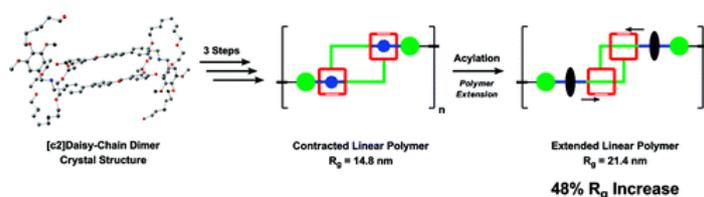


We report the development of phototriggerable microcapsules and demonstrate the concept of protection and remote release of chemical species. Light-rupturable, liquid-filled microcapsules were prepared by coencapsulation of carbon nanotubes using a simple and robust interfacial polymerization technique. The incorporation of carbon nanotubes endows the microcapsules with the ability to respond to an external optical event. The triggered release of the liquid contents for the microcapsules may be achieved either in air or within a liquid medium via irradiation with a near-IR laser. Rupture of the impermeable shell-wall under irradiation is presumed to be due to an increase in internal pressure due to optothermal heating of the CNTs. The storage and triggered release of reactive small molecules and catalysts was demonstrated in the context of remotely initiated “click” reaction and ring-opening metathesis polymerization.

- Switching and Extension of a [c2]Daisy-Chain Dimer Polymer

Clark, P. G.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 13631–13633.

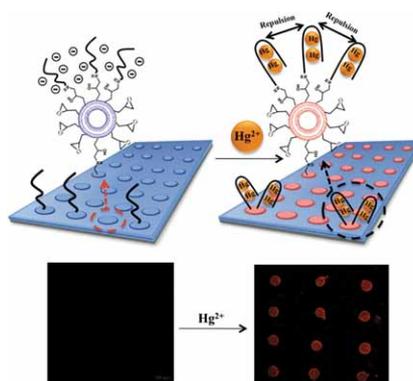
Abstract:



We report the synthesis of a [c2]daisy-chain dimer via ruthenium-catalyzed ring-closing olefin metathesis. Confirmation of the interlocked nature of the structure was achieved through single-crystal X-ray diffraction analysis. The dimer could be readily switched from the bound to the unbound conformation by treatment with 3.0 equiv of KOH and subsequently reprotonated by treatment with 3.0 equiv of HPF<sub>6</sub>. Azide functionalization of the dimer enabled incorporation in linear step-growth polymer chains using the alkyne-azide “click” reaction. Gel permeation chromatography coupled with multiangle laser light scattering analysis showed the polymers contained 22 dimers and had a radius of gyration of 14.8 nm. Acylation of the amines of the dimers sterically forced elongation of the interlocked units, and MALLS analysis of the polymer showed a 48% increase in the  $R_g$  (21.4 nm).

- Polydiacetylene-Liposome Microarrays for Selective and Sensitive Mercury(II) Detection  
Lee, J.; Jun, H.; Kim, J. *Adv. Mater.* **2009**, 3674-3677.

Abstract:



Polydiacetylene (PDA) liposome microarrays are developed for selective and sensitive mercury ( $\text{Hg}^{2+}$ ) detection. The PDA mercury sensors are designed to produce red fluorescence emission upon binding with  $\text{Hg}^{2+}$ , when the ssDNA aptamers on the PDA surface recognize and wrap around mercury ions and the resulting bulky T-Hg-T complexes repulse each other.

- Ultrathin Silicon Circuits With Strain-Isolation Layers and Mesh Layouts for High-Performance Electronics on Fabric, Vinyl, Leather, and Paper  
Kim, D-H; Kim, Y-S; Wu, J.; Liu, Z.; Song, J.; Kim, H-S.; Huang, Y.Y.; Hwang, K-C.; Rogers J.A. *Adv. Mater.* **2009**, 3703-3707.

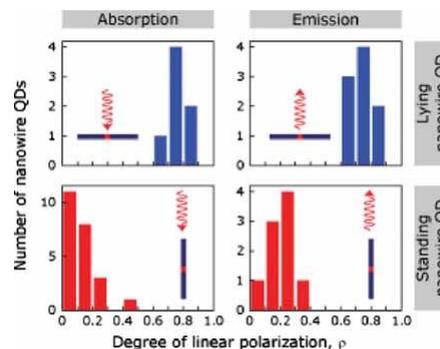
Abstract:



We present various stretchable high-performance CMOS circuit demonstrations on unconventional substrates, such as fabric, vinyl, leather, and paper. Electronics on such substrates, especially paper, open up new and important application possibilities for electronics. Theoretical analysis reveals the underlying mechanics of these systems; electrical tests under mechanical cycling demonstrate the robustness of the designs.

- Orientation-Dependent Optical-Polarization Properties of Single Quantum Dots in Nanowires van Weert, M. H. M.; Akopian, N.; Kelkensberg, F.; Perinetti, U.; van Kouwen, M. P.; Gómez Rivas, J.; Borgström, M. T.; Algra, R. E.; Verheijen, M. A.; Bakkers, E. P. A. M.; Kouwenhoven, L. P.; Zwiller, V. *Small* **2009**, *5*, 2134-2138.

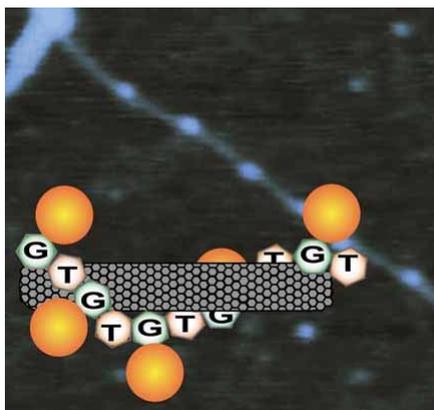
Abstract:



The absorption and emission polarization of single semiconductor nanowire quantum dots is studied. The polarization of light absorbed or emitted by such dots strongly depends on the orientation of the nanowire with respect to the directions along which light is incident or emitted (see image). This result is vital for photonic applications based on quantum dots, such as generation of entangled photons.

- Water-Soluble DNA-Wrapped Single-Walled Carbon-Nanotube/Quantum-Dot Complexes Zhou, Z.; Kang, H. G.; Clarke, M. L.; De Paoli Lacerda, S. H.; Zhao, M.; Fagan, J. A.; Shapiro, A.; Nguyen, T.; Hwang, J. *Small* **2009**, *5*, 2149-2155.

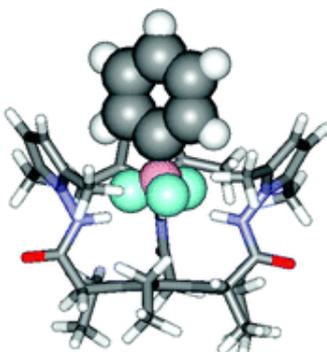
Abstract:



**A new nanomaterial** conjugation technique is presented to effectively bind semiconductor quantum dots (QDs) onto single-walled carbon nanotubes (SWCNTs) via covalent amidation, employing single-stranded DNA oligonucleotides as linkers (see schematic and AFM image). This technique provides a measurement platform for the study of their interactions involving photoinduced charge transfer between QDs and SWCNTs at the nanoscale.

- A synthetic receptor for hydrogen-bonding to fluorines of trifluoroborates.  
Restorp, P.; Berryman, P.; Sather, A. C.; Ajami, D.; Rebek Jr., J. *Chem. Commun.* **2009**, 5692 – 5694.

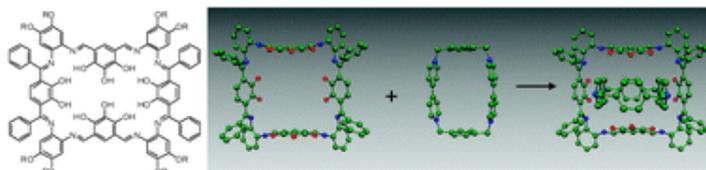
Abstract:



A tripodal receptor featuring three inwardly-directed hydrogen-bond donors binds covalently bound fluorine atoms of trifluoroborates through hydrogen-bonding.

- Cationic guest inclusion in widemouthed Schiff base macrocycles.  
Jiang, J.; MacLachlan, M. J. *Chem. Commun.* **2009**, 5695 – 5697.

Abstract:



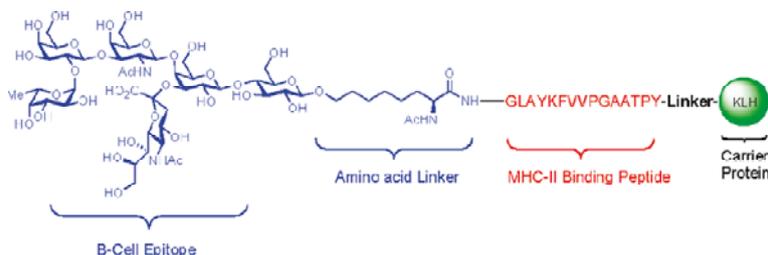
Conjugated Schiff base macrocycles with wide bores and conformational flexibility bind organic cations in their interiors, and can be used to assemble larger supramolecular structures.

- On the Emerging Role of Chemistry in the Fashioning of Biologics: Synthesis of a Bidomainal Fucosyl GM1-Based Vaccine for the Treatment of Small Cell Lung Cancer

Nagorny, P.; Kim, W. H.; Wan, Q.; Lee, D.; Danishefsky, S. J. *J. Org. Chem.* **2009**, *74*, 5157–5162.

8

Abstract:

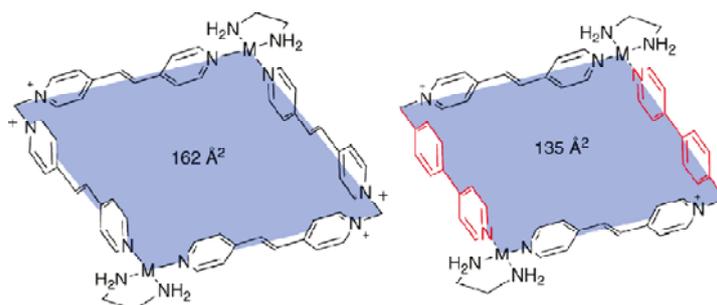


The synthesis of the novel small cell lung cancer (SCLC) fucosyl GM1-based vaccine construct, featuring insertion of the HLA-DR binding 15 amino acid sequence derived from *Plasmodium falciparum*, is described. The resultant glycopeptide has been synthesized in an efficient manner. Finally, successful conjugation of the glycopeptide to the keyhole limpet hemocyanin (KLH) carrier protein completed the preparation of the vaccine.

- Expanding the Cavity Size: Preparation of 2:1 Inclusion Complexes Based on Dinuclear Square Metalloacycles

Blanco, V.; Gutiérrez, A.; Platas-Iglesias, C.; Peinador, C.; Quintela, J. M. *J. Org. Chem.* **2009**, *74*, 6577–6583.

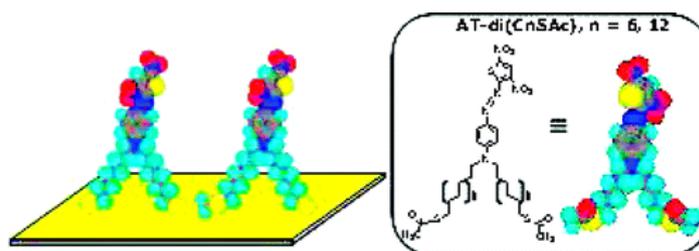
Abstract:



The self-assembly of two new ligands based on the *trans*-1,2-bis(4-pyridyl)ethylene motif with palladium or platinum complexes led to quadrangular metalocycles. 1,1'-Methylenebis(4-((*E*)-2-(pyridin-4-yl)vinyl)pyridinium gave the square metalocycles, while the second ligand, which is less symmetrical, gave a mixture of the regioisomeric metalocycles. The metalocycles display the ideal disposition of the  $\pi$ -acceptor units to maximize the  $\pi$ -stacking interactions with aromatic guests. Thus, molecular recognition of  $\pi$ -donor aromatic guests by square metalocycles produced the corresponding 2:1 inclusion complexes. On the other hand, starting from the mixture of regioisomers, the *incorrect* regioisomer rearranged to the *correct* metalocycle upon the addition of aromatic guests. On the basis of this behavior, a [3]catenane was obtained regioselectively from the mixture of the regioisomeric metalocycles and the appropriate cyclophane. The formation of this catenane was confirmed by NMR and X-ray crystallographic studies.

- Adsorption of Azothiophene Dye Having an N-Bridging Bidentate Tail Group on Gold
- Sook Bang, G.; Lee, J.; Baek, H. Y.; Lee, H.; Jun, K.; Rim Shin, S. *Langmuir* **2009**, *25*, 10788–10793.

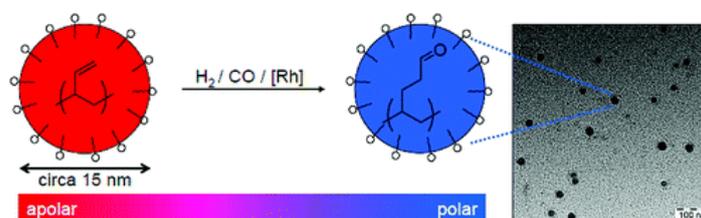
Abstract:



The novel azothiophene derivatives [AT-di(CnSAC) ( $n = 6$  and  $12$ )], an azo linkage (NdN) that bridges one phenyl ring with an N-bridging dialkylthioacetate tail and one thiophene ring, are synthesized and characterized. The azothiophene derivatives substituted with electron-withdrawing groups are blue in color, exhibit a bathochromic shift of a longer wavelength, and are electrochemically active. The formation and characterization of AT-di(CnSAC) SAMs with a bidentate tail group of the N-bridging dialkylthioacetate have been studied by surface sensitive techniques such as grazing angle Fourier transform infrared (FT-IR), a quartz crystal microbalance (QCM), spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). It has been shown that the adsorption reaction of the thioacetate group is almost spontaneous and the N-bridging dialkylthioacetate SAMs with longer methylene length have a packing density higher than that with a shorter methylene length. However, the sulfur tethers of the N-bridging dialkylthioacetate show incomplete binding of sulfur atoms in AT-di(CnSAC) SAMs.

- Conveniently Accessible Polymer Nanoparticles of Adjustable Polarity  
Korthals, B.; Morant-Miñana, M. C.; Hohberger, C.; Mecking, S. *Langmuir* **2009**, *25*, 10554–10557.

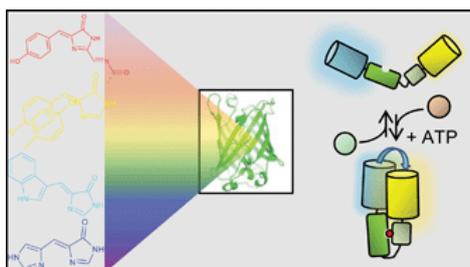
Abstract:



The postpolymerization modification by hydroformylation of 1,2-polybutadiene nanoparticles provides access to colloiddally stable aqueous dispersions of <20 nm particles. Their polarity can be adjusted via the degree of conversion of double bonds over a broad range. Fluorescence studies illustrate the polarity of the environment experienced by pyrene as a probe molecule.

- The structure and function of fluorescent proteins  
Sample, V.; Newman, R. H.; Zhang, J. *Chem. Soc. Rev.* **2009**, *38*, 2852 – 2864.

Abstract:

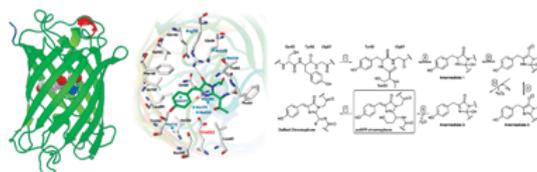


The current complement of fluorescent proteins (FPs) contains color variants whose emission spectra span most of the visible spectrum, providing researchers with a versatile toolset of fluorescent

probes for live cell imaging applications. FP family members generate their chromophores autocatalytically through a series of posttranslational modifications. The fluorescence characteristics of GFP-family members are influenced in important ways by the local microenvironment surrounding the chromophore. In this *tutorial review*, we first examine the molecular factors that influence the photophysical properties of FP family members and then briefly discuss some of the ways in which these fascinating proteins have been applied to the field of live cell imaging.

- Green fluorescent protein: structure, folding and chromophore maturation  
Craggs, T. D. *Chem. Soc. Rev.* **2009**, *38*, 2865 – 2875.

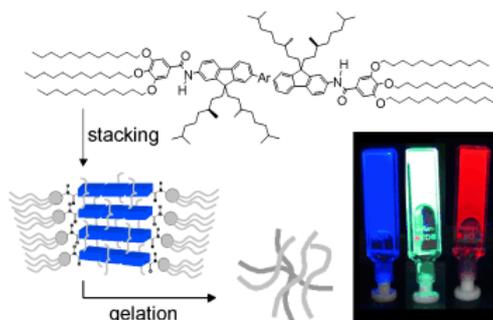
Abstract:



The prolific use of green fluorescent protein and its variants throughout cellular biology relies on the post-translational formation of the chromophore, which proceeds without the need for any additional enzymes or cofactors, except molecular oxygen. In order to form the mature chromophore, the polypeptide backbone must undergo four distinct processes: folding, cyclisation, oxidation and dehydration. This *tutorial review* looks in detail at the proposed mechanisms for chromophore formation arising out of experimental and computational studies. The folding process is discussed, and the role that the native state plays in catalysing the initial cyclisation and subsequent chemistry is analysed. The specific functions of four conserved residues (Y66, G67, R96 and E222) in the maturation process are also presented. A greater understanding of the maturation process of fluorescent proteins from both jellyfish and coral species will profit the ongoing quest for brighter, faster maturing, genetically-encodable fluorescent probes of all colours, thus increasing their utility throughout the biomedical sciences.

- Multicolour Self-Assembled Fluorene Co-Oligomers: From Molecules to the Solid State via White-Light-Emitting Organogels  
Abbel, R.; van der Weegen, R.; Pisula, W.; Surin, M.; Leclère, P.; Lazzaroni, R.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Eur. J.* **2009**, *15*, 9737 – 9746.

Abstract:



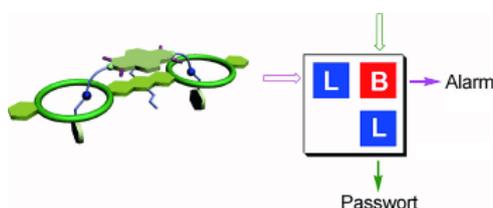
**Hierarchical aggregation:** The self-assembly process of a set of fluorene co-oligomers with emission colours covering the entire visible spectrum has been studied in dilute and concentrated solution and in the solid state to reveal a hierarchical aggregation mechanism involving one-dimensional fibres and lyotropic gels (see figure).

Five fluorene-based co-oligomers have been prepared to study their self-assembly in a wide range of concentrations, from dilute solutions to the solid state. Subtle changes to the chemical structures, introduced to tune the emission colours over the entire visible range, induce strong differences in aggregation behaviour. Only two of the fluorescent co-oligomer derivatives self-assemble to form soluble fibrils from which fluorescent organogels emerge at higher concentrations. In contrast, the other compounds form precipitates. Mixed fluorescent co-oligomer systems exhibit partial energy transfer, which allows the creation of white-light-emitting gels. Finally, a mechanism for the hierarchical self-assembly of this class of materials is proposed based on experimental results and molecular modelling calculations.

- A Double Plug-Socket System Capable of Molecular Keypad Locks through Controllable Photooxidation

Jiang W.; Han, M.; Zhang, H.-Y.; Zhang, Z.-J.; Liu, Y. *Chem. Eur. J.* **2009**, *15*, 9938 – 9945.

Abstract:



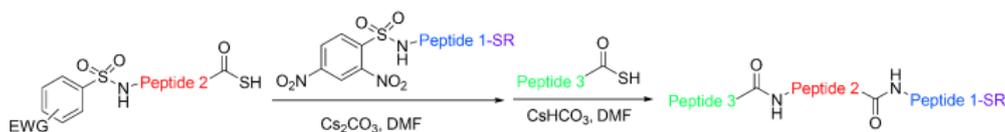
**Plugged in security:** Several molecular double plug-socket species can be formed through modulating the disassembly and reassembly of a bis(crown ether) host and a secondary dialkylammonium guest. These species cannot only be regarded as switchable « molecular shields » for the protection of the anthracene group from photooxidation, but they can also perform the functions of molecular keypad locks (see figure; B=base, L=light).

Two robust divalent complexes have been successfully constructed by using complementary rigid spacers (anthracene vs. 1,4,5,8-naphthalenediimide (NDI)) and two pairs of [24]crown-8 ethers and secondary dialkylammonium functionalities as binding motifs. It was demonstrated that properly selected, rigid spacers are more efficient than flexible ones for achieving strong multivalent association. This is presumably due to the preorganization of the rigid spacers, the cooperation between charge-transfer interactions of rigid spacers, and the complexation of the binding motifs. Furthermore, the intermolecular photoinduced electron transfer (PET) between rigid spacers in these robust complexes could be switched on and off by modulating their complexation through acid-base reactions, which is reminiscent of a plug-socket system capable of electron transfer. In addition, the self-sensitized photooxidation of the divalent host with anthracene as a spacer can be completely inhibited after complexation with the divalent guests that contain NDI as spacers. This process could also be understood by invoking intermolecular PET and could be turned on and off through acid-base reactions. The photophysical and photochemical properties of these robust complexes have been interpreted as molecular keypad locks with alarm systems. Thus, a double plug-socket system and molecular keypad locks were successfully integrated inside robust multivalent systems and then the normal molecular devices were endowed with logic functions.

- Triblock Peptide and Peptide Thioester Synthesis With Reactivity-Differentiated Sulfonamides and Peptidyl Thioacids

Crich, D.; Sharma, I. *Angew. Chem. Int. Ed.* **2009**, *15*, 7591 - 7594.

Abstract:

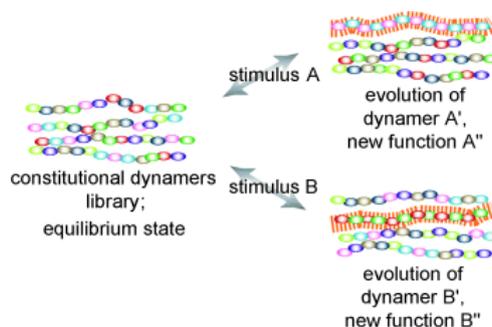


**One after the other:** Triblock peptide synthesis was achieved at ambient temperature by sequential reaction of sulfonamide-protected peptidyl thioacids first with highly reactive 2,4-dinitrobenzenesulfonamides and second with more moderately reactive sulfonamides to produce the oligopeptides in good yields. The method is compatible with C-terminal thioesters and thus presents a new approach for native chemical ligation strategies.

- Structural and Functional Evolution of a Library of Constitutional Dynamic Polymers Driven by Alkali Metal Ion Recognition

Fujii, S.; Lehn, J.-M. *Angew. Chem. Int. Ed.* **2009**, *15*, 7635 - 7638.

Abstract:

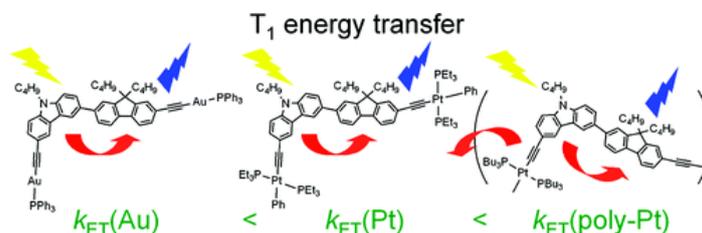


**Aptly folded:** Dynamic polymer libraries were generated by polycondensation through reversible imine bonds and can undergo driven evolution under the double stimuli of donor-acceptor stacking and metal-ion binding (see picture). The specific binding modes of alkali metal ions are associated with specific constitutional changes and with different optical natures that reflect the presence and the positions of donor and acceptor units within the folded dynamer.

- Intrachain Electron and Energy Transfers in Metal Diynes and Polyynes of Group 10-11 Transition Elements Containing Various Carbazole and Fluorene Hybrids.

Aly, S. M.; Ho, C.-L.; Wong, W.-Y.; Fortin, D.; Harvey, P. D. *Macromolecules* **2009**, *42*, 6902–6916.

Abstract:



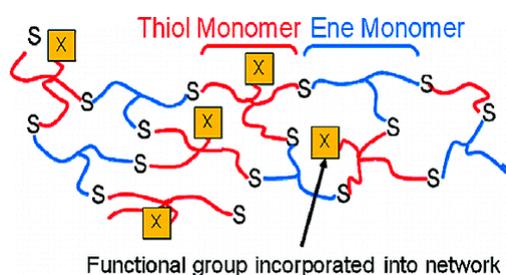
A series of soluble and thermally stable group 10 platinum(II) polyyne polymers of the type  $[-C\equiv C-Pt(PBu_3)_2-C\equiv C-X-]_n$  along with their corresponding dinuclear model compounds  $[Ph-Pt(PEt_3)_2-C\equiv C]_2-X-$  and  $[Ph_3P-Au-C\equiv C]_2-X-$  where  $X = F, Cz', Cz, Cz-F, (Cz)_2, (Cz)_3$  and  $Cz-F-Cz$ ;  $F = 2,7$ -fluorene,  $Cz' = 2,7$ -carbazole,  $Cz = 3,6$ -carbazole, were prepared and characterized. The electronic spectra (absorption, excitation, emission and ns transient absorption spectra) and the photophysical properties of these metalated compounds in 2MeTHF at 298 and 77 K are reported. These findings are correlated to the computational data obtained by density functional theory (DFT).

Evidence for intramolecular singlet electron and triplet energy transfers from the **Cz** chromophore to the **F** moiety is provided and discussed in detail for those with organic spacers consisting of the carbazole–fluorene hybrids. The rate for electron transfer is very rapid ( $k_{\text{et}} > 4 \times 10^{11} \text{ s}^{-1}$  at 298 K) whereas that for triplet–triplet energy transfer is much slower ( $k_{\text{ET}} \sim \text{ca. } 10^3 \text{ s}^{-1}$  time scale). The  $k_{\text{ET}}$  values for the digold dyads are lower than that found for the diplatinum analogues, which are slower than the corresponding platinum-containing polymers. The observed increase in  $k_{\text{ET}}$  for the dinuclear systems is explained by the triplet excited state population of the diplatinum species as compared to the digold congener, and for the polymers, the larger rates (twice as fast) are due to the presence of two fluorene chromophores flanking the carbazole-containing unit, hence providing two pathways to relaxation.

- Oxygen Transport Properties of Thiol-Ene Networks.

Kwisnek, L.; Nazarenko, S.; Hoyle, C. E. *Macromolecules* **2009**, *42*, 7031–7041.

Abstract:



Oxygen transport characteristics, i.e., permeability, diffusivity, and solubility, have been determined for a variety of photopolymerized thiol-ene networks. Despite the abundance of thiol-ene research and the importance of such information, it is until now absent from the literature. One model network, which showed high oxygen barrier properties, was selected for further modification. Covalent bonding of functional groups to the network was enabled by an interesting approach: thio-Michael addition of various functionalized acrylates to a tetrathiol monomer. Cyano, hydroxyl, amide, and alkyl functional groups were explored. These new modified thiols were subsequently copolymerized with an isocyanuratebased multifunctional ene. This modification technique enabled a study on how different functional groups embedded in a uniform network affect  $T_g$  and oxygen barrier properties. All studied networks exhibited oxygen diffusivity and permeability which both spanned nearly 3 orders of magnitude. Correlation of both oxygen permeability and oxygen diffusivity with  $T_g$  was observed. This correlation allows the prediction of oxygen barrier properties of thiol-ene networks using  $T_g$ .