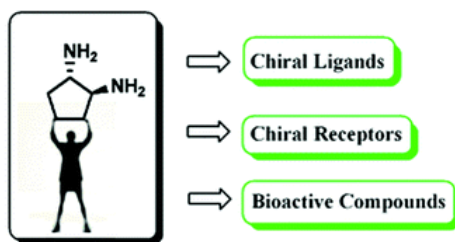


- *trans*-Cyclopentane-1,2-diamine: the second youth of the forgotten diamine
González-Sabín, J.; Rebolledo, F.; Gotor, V. *Chem. Soc. Rev.* **2009**, *38*, 1916 – 1925.

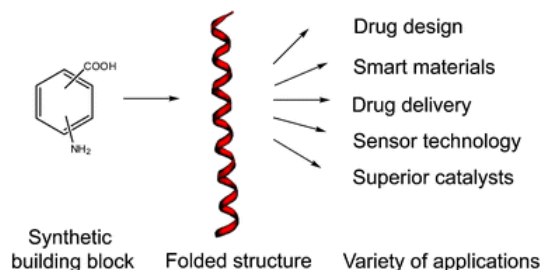
Abstract:



Despite its early description, *trans*-cyclopentane-1,2-diamine has been underestimated historically. Its non-commercial availability, extreme instability and complexity of the classical reported syntheses have produced far less interest amongst chemists than its higher homologue *trans*-cyclohexane-1,2-diamine, perhaps the most widely used diamine for the synthesis of ligands and receptors. However, the recent development of novel and efficient synthetic approaches has stimulated renewed interest in this chiral motif for a broad range of applications. In the first part of this *tutorial review* we shall discuss the existing methods for the preparation of *trans*-cyclopentane-1,2-diamine and some of its derivatives, in both racemic and enantioenriched forms. In subsequent sections, recent findings employing this diamine as a scaffold for chiral ligands, receptors and biologically active compounds will be highlighted.

- Recent advances in the development of aryl-based foldamers
Saraogi, I.; Hamilton, A. D. *Chem. Soc. Rev.* **2009**, *38*, 1726 – 1743.

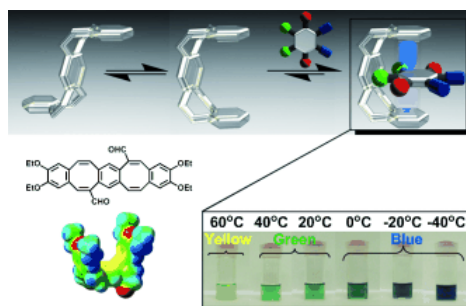
Abstract:



In recent years, significant effort has gone into making synthetic oligomers that can attain well-defined conformations analogous to the folding of biomolecules. The diversity of the structural building blocks ranges from peptidic and other aliphatic repeat units to aromatic ones, which do not have a natural counterpart. In this *critical review*, we will focus on the developments in aromatic foldamers in the last two years and their potential applications. This review will be of interest to people working on the structural and functional mimicry of biomolecules and will, we hope, stimulate further research into novel applications (149 references).

- Dynamic Molecular Tweezers Composed of Dibenzocyclooctatetraene Units: Synthesis, Properties, and Thermochromism in Host-Guest Complexes
Nishiuchi, T.; Kuwatani, Y.; Nishinaga, T.; Iyoda, M. *Chem. Eur. J.* **2009**, *15*, 6838-6847.

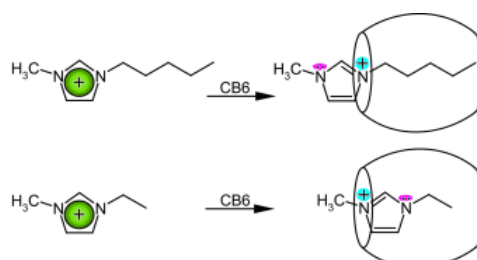
Abstract:



Novel dynamic molecular tweezers (DMTs) **3 a**, **3 b**, **4 a**, **4 b**, and **5 b**, composed of two tub-shaped dibenzocyclooctatetraene (DBCOT) units, were designed and synthesized. The cyclooctatetraene (COT) rings of these DMTs readily invert in solution, and the molecular structure shows rigid *syn* and *anti* forms in an equilibrium mixture in solution. The *syn* and *anti* conformers can be observed by NMR. The isomerization barriers of **3 a**, **3 b**, **4 a**, **4 b**, and **5 b** are in the range of 16.5-21.3 kcal mol⁻¹, depending on steric repulsion between substituents of the COT rings and protons of the central benzene ring. These DMTs form complexes with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 1,2,4,5-tetracyano-benzene (TCNB) in solution and in the solid state. The binding abilities of these DMTs increase with electron-donating substituents on COT, which increase the electron densities of the cavity of the *syn* form, as supported by theoretical calculations. In addition, elongation of the terminal alkoxy chains of the DMTs was found to cause the enhancement of van der Waals contact with guest molecules. Therefore, **5 b**, which has CH₂OMe groups on the COT rings and longer ethoxy groups on the terminal benzene rings, showed the highest electron density of the cavity and hence the highest binding ability with the electron-deficient guest molecules. Interestingly, solutions of **3 b**, **4 b**, and **5 b** show thermochromism in the presence of DDQ. A solution of **3 b** or **4 b** with DDQ in CHCl₃ is green due to charge-transfer interaction at room temperature and the color changes from green to yellow upon heating to 60 °C and from green to blue upon cooling to -40 °C, whereas the high complexation ability of **5 b** with DDQ only shows a change in the shade of blue.

- Electron Density Shift in Imidazolium Derivatives upon Complexation with Cucurbit[6]uril
Kolman, V.; Marek, R.; Strelcova, Z.; Kulhanek, P.; Necas, M.; Svec, J.; Sindelar, V. *Chem. Eur. J.* **2009**, *15*, 6926-6931.

Abstract:

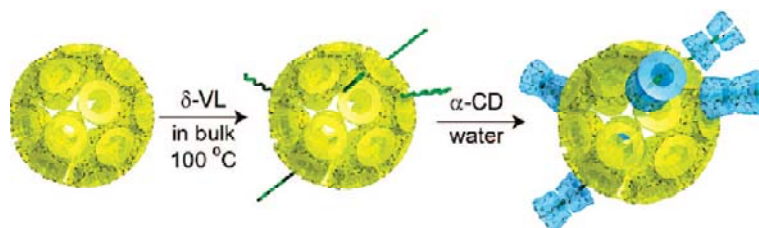


In this study, we have investigated the supramolecular interaction between series of 1-alkyl-3-methylimidazolium guests with variable alkyl substituent lengths and cucurbit[6]uril (CB6) in the solution and the solid state. Correct interpretation of ¹H NMR spectra was a key issue for determining the binding modes of the complexes in solution. Unusual chemical shifts of some protons in the ¹H NMR spectra were explained by the polarization of the imidazolium aromatic ring upon the complexation with the host. The formation of 1:1 complex between 1-ethyl-3-methylimidazolium

and CB6 is in disagreement with previously reported findings describing an inclusion of two guest molecules in the CB6 cavity.

- Nanospheres with Polymerization Ability Coated by Polyrotaxane
Osaki, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Org. Chem.* **2009**, *74*, 1858–1863.

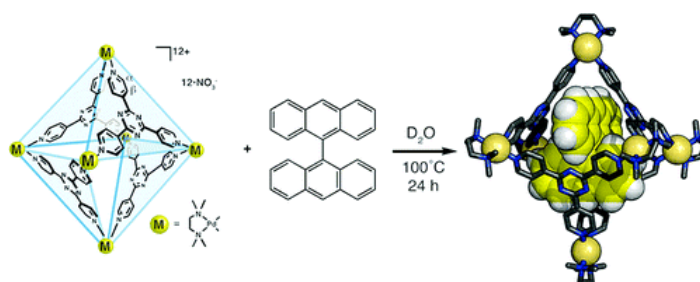
Abstract:



β -Cyclodextrin (β -CD)-based nanosphere **1** initiated the oligomerization of δ -valerolactone (δ -VL) on the surface of **1** to give oligo(δ -VL)-tethered β -CD nanosphere **2** in bulk. Atomic force microscopy indicated that the molecular size of **2** is twice that of **1**. The addition of α -CD to **2** leads to the formation of poly-pseudo-rotaxane on the surface of **2** to give a nanosphere with poly-pseudo-rotaxane (α -CD \supset **2**). 2D-NOESY NMR experiments showed correlation peaks between the inner protons of α -CD and the oligo(δ -VL) chains in an aqueous solution, indicating that the oligo(δ -VL) chains are included in the α -CD cavity. α -CD \supset **2** has a core of β -CDs with poly-pseudo-rotaxanes on the surface. It should be noted that **2** did not show polymerization ability for δ -VL, but after the formation of poly-pseudo-rotaxanes, oligo(δ -VL) of α -CD \supset **2** repropagated upon the addition of δ -VL. α -CD \supset **2** is significantly larger than nanospheres **1** and **2**. Additionally, postpolymerization increases the size of α -CD \supset **2**. These behaviors are reminiscent of the function of a spherical virus, which forms an ordered spherical structure and releases RNA chains from the capsid surface.

- Energy Transfer in a Mechanically Trapped Exciplex
Klosterman, J. K.; Iwamura, M.; Tahara, T.; Fujita, M. *J. Am. Chem. Soc.* **2009**, *131*, 9478–9479.

Abstract:

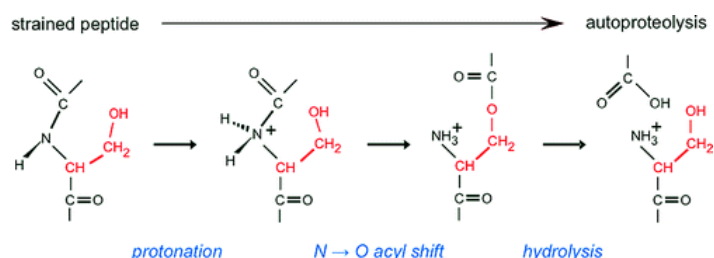


Host–guest complexes involving M_6L_4 coordination cages can display unusual photoreactivity, and enclathration of the very large fluorophore bisanthracene resulted in an emissive, mechanically trapped intramolecular exciplex. Mechanically linked intramolecular exciplexes are important for understanding the dependence of energy transfer on donor–acceptor distance, orientation, and electronic coupling but are relatively unexplored. Steady-state and picosecond time-resolved fluorescence measurements have revealed that selective excitation of the encapsulated guest fluorophore results in efficient energy transfer from the excited guest to an emissive host–guest exciplex state.

- Protein Autoproteolysis: Conformational Strain Linked to the Rate of Peptide Cleavage by the pH Dependence of the N → O Acyl Shift Reaction

Johansson, D. G. A.; Wallin, G.; Sandberg, A.; Macao, B.; Åqvist, J.; Hrd, T. *J. Am. Chem. Soc.* **2009**, *131*, 9475–9477.

Abstract:

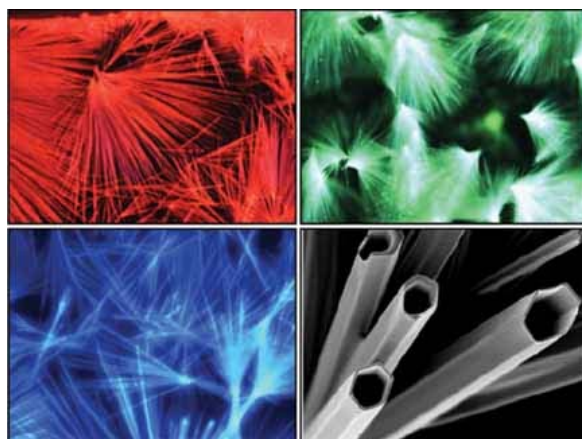


Nucleophilic attack by a side chain nucleophile on the adjacent peptide bond followed by N → O or N → S acyl shift is the primary step in protein autoproteolysis. Precursor structures of autoproteolytic proteins reveal strained (or twisted) amides at the site of cleavage, and we previously showed that SEA domain autoproteolysis involves substrate destabilization by 7 kcal/mol. However, the precise chemical mechanism by which conformational energy is converted into reaction rate acceleration has not been understood. Here we show that the pH dependence of autoproteolysis in a slow-cleaving mutant (1G) of the MUC1 SEA domain is consistent with a mechanism in which N → O acyl shift proceeds after initial protonation of the amide nitrogen. Unstrained amides have pK_a values of 0 with protonation on the oxygen, and autoproteolysis is therefore immeasurably slow at neutral pH. However, conformational strain forces the peptide nitrogen into a pyramidal conformation with a significantly increased pK_a for protonation. We find that pK_a values of 4 and 6, as in model compounds of twisted amides, reproduce the rate of autoproteolysis in the 1G and wild-type SEA domains, respectively. A mechanism involving strain, nitrogen protonation, and N → O shift is also supported by quantum-chemical calculations. Such a reaction therefore constitutes an alternative to peptide cleavage that is utilized in autoproteolysis, as opposed to a classical mechanism involving a structurally conserved active site with a catalytic triad and an oxyanion hole, which are not present at the SEA domain cleavage site.

- Photoluminescent peptide nanotubes

Ryu, J.; Lim, S.Y.; Park, C.B. *Adv. Mater.* **2009**, *21*, 1577-1581.

Abstract:

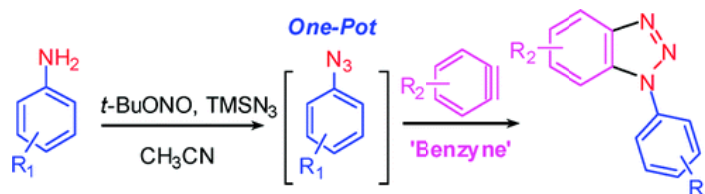


Photoluminescent peptide nanotubes are synthesized in an in situ incorporation of lanthanide complexes into peptide nanotubes through a self-assembly process. We found that peptide nanotubes and photosensitizer molecules exhibited a high synergistic effect on the enhancement of lanthanide photoluminescence through a cascaded energy-transfer mechanism.

5

- Benzyne Click Chemistry with in Situ Generated Aromatic Azides
Zhang, F.; Moses, J. E. *Org. Lett.* **2009**, *11*, 1587-1590.

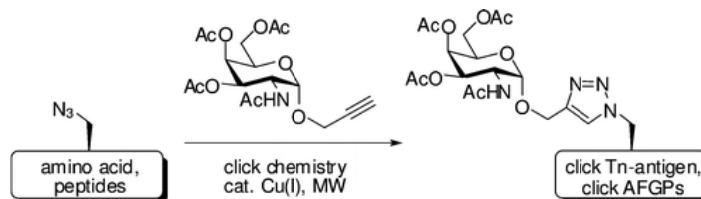
Abstract:



An efficient synthesis of substituted benzotriazoles using an azide-alkyne 1,3-dipolar cycloaddn. "click reaction" is described. Key to the procedure is the in situ generation of the reactive arom. azide and benzyne reaction partners.

- Synthesis of Fish Antifreeze Neoglycopeptides Using Microwave-Assisted "Click Chemistry"
Miller, N.; Williams, G. M.; Brimble, M. A. *Org. Lett.* **2009**, *11*, 2409-2412.

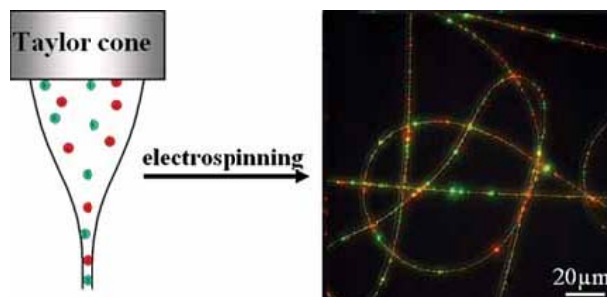
Abstract:



Microwave-enhanced click glycoconjugation of a propargylated α -GalNAc sugar moiety with an azido-functionalized amino acid or multi-azido-functionalized peptides using a catalytic quantity of Cu(I) enabled a high-yielding and rapid synthesis of a "Tn-antigen mimic" and click analogs of antifreeze glycopeptides. This methodol. demonstrates a valuable synthetic platform for the synthesis of biol. relevant neoglycopeptides.

- Encapsulation of Multiple Biological Compounds Within a Single Electrospun Fiber
Dong, B.; Smith, M. E.; Wnek, G. E. *Small* **2009**, *5*, 1508-1512.

Abstract:

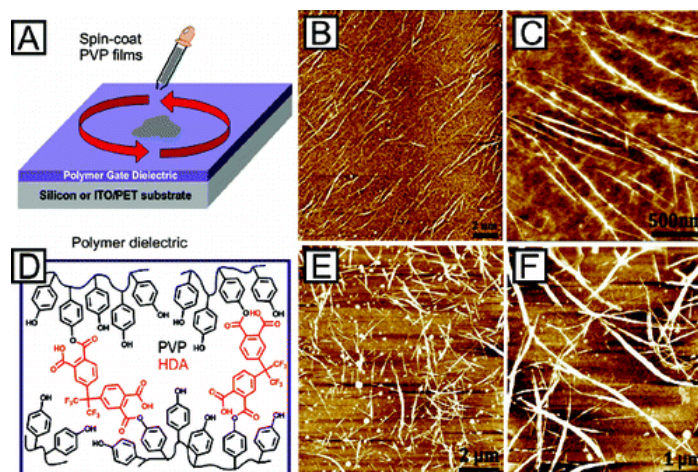


Encapsulation of multiple biological compounds within a single electrospun fiber is achieved by a combination of electrospinning and the encapsulation of bioactive compounds using nanoparticles (see image). Compared to the encapsulation of a single component inside electrospun fiber, the

encapsulation of two components offers the opportunity to control the release of two materials at the same time, which should have great potential in the field of tissue engineering.

- Self-Sorted Nanotube Networks on Polymer Dielectrics for Low-Voltage Thin-Film Transistors
Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao, Z. *Nano Lett.* **2009**, *9*, 2526–2531.

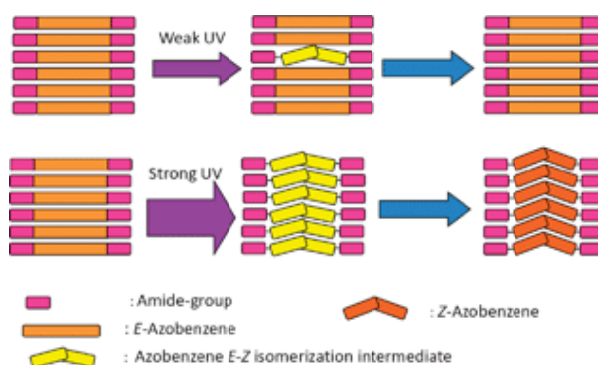
Abstract:



Recent exploitations of the superior mechanical and electronic properties of carbon nanotubes (CNTs) have led to exciting opportunities in low-cost, high performance, carbon-based electronics. In this report, low-voltage thin-film transistors with aligned, semiconducting CNT networks are fabricated on a chemically modified polymer gate dielectric using both rigid and flexible substrates. The multifunctional polymer serves as a thin, flexible gate dielectric film, affords low operating voltages, and provides a platform for chemical functionalization. The introduction of amine functionality to the dielectric surface leads to the adsorption of a network enriched with semiconducting CNTs with tunable density from spin coating a bulk solution of unsorted CNTs. The composition of the deposited CNT networks is verified with Raman spectroscopy and electrical characterization. For transistors at operating biases below 1 V, we observe an effective device mobility as high as 13.4 cm²/Vs, a subthreshold swing as low as 130 mV/dec, and typical on-off ratios of greater than 1,000. This demonstration of high performance CNT thin-film transistors operating at voltages below 1 V and deposited using solution methods on polymeric and flexible substrates is an important step toward the realization of low-cost flexible electronics.

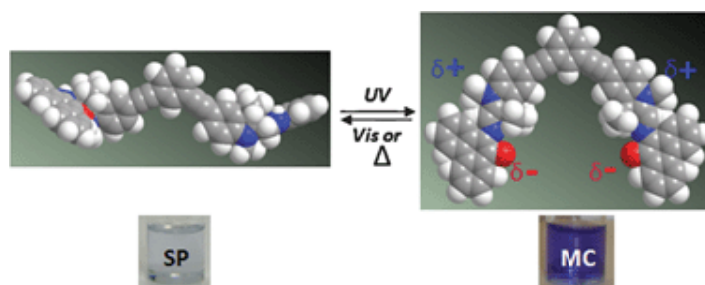
- Photoisomerization of an azobenzene gel by pulsed laser irradiation.
Uchida, K.; Yamaguchi, S.; Yamada, H.; Akazawa, M.; Katayama, T.; Ishibashi, Y.; Miyasaka, H. *Chem. Commun.* **2009**, 4420 – 4422.

Abstract:



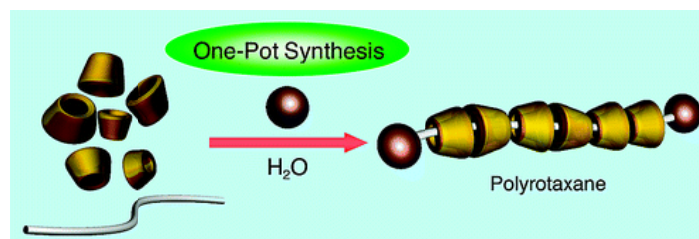
A decalin gel consisting of a 3,3-bis[[(octylamino)carbonyl]propoxy]azobenzene derivative with H-aggregation showed a photon-density dependent E-Z isomerization, indicating the cooperating isomerization of each module.

- A tailored spirooxazine dimer as a photoswitchable binding tool.
Kumar, S.; Watkins, D. L.; Fujiwara, T. *Chem. Commun.* **2009**, 4369 – 4371.
Abstract:



A uniquely angled spirooxazine dimer was synthesized as a smart photoswitch for sensing and delivery applications; the dimer showed reversible binding and release ability towards a palladium catalyst.

- One-Pot Synthesis of Native and Permethylated R-Cyclodextrin-Containing Polyrotaxanes in Water.
Arai, T.; Hayashi, M.; Takagi, N.; Takata, T. *Macromolecules* **2009**, 42, 1881-1887.
Abstract:



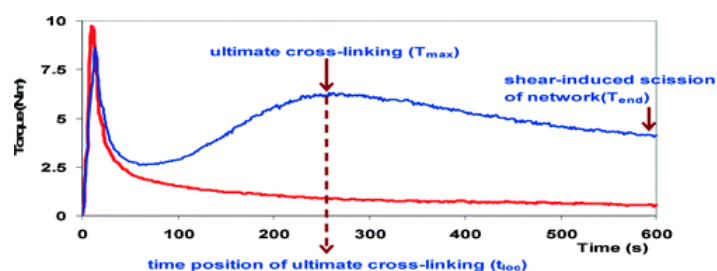
Efficient one-pot synthesis in water of polyrotaxanes, with native and permethylated R-cyclodextrins (R-CD and PMe R-CD) as the wheel components, is described. The procedure involves initial mixing of R-CDs and an amine-terminated linear polymer, which acts as the axle, by sonication and subsequent addition of an end-capping agent for the axle terminal amino groups. The polyrotaxanes were prepared by mixing the axle and wheel components by sonication for 30 min at room temperature and standing overnight if necessary, followed by treatment with a bulky isocyanate in water at 0 °C for an hour. Both amine-terminated polytetrahydrofuran (ATPT) and poly(ethylene glycol) (ATPEG) afforded the corresponding polyrotaxanes (PRXs) in good yields (27-49%) in the case of a native R-CD

wheel. The coverage ratio of the axle component with the wheel component of the PRXs ranged from 85% to 96% when the molecular weight of the axle was M_n 1000-1800, while it was 54% when the axle was long (M_n 7700). The polyrotaxanes (PMePRXs) with PME R-CD and ATPT were similarly obtained in high yields. In this case, the yield of the PMePRXs was unusually high (66 and 69%) when a higher molecular weight axle (M_n 4100 and 7100, respectively) was used. The formation of a PMePRX from ATPEG axle proceeded with low efficiency. The present work provides the first synthesis of polyrotaxanes with PME R-CD in solution.

- A Study on Melt Grafting of *N*-Halamine Moieties onto Polyethylene and Their Antibacterial Activities.

Badrossamay, M. R.; Sun, G. *Macromolecules* **2009**, *42*, 1948-1954.

Abstract:

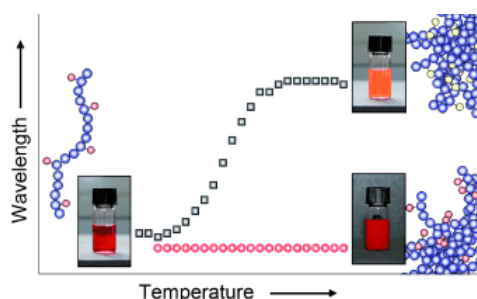


Radical melt graft polymerizations of low-density polyethylene (PE) during reactive extrusion were investigated. In the absence of any reactive monomer, effects of peroxide initiator concentration and type, reaction temperature, and rotor speed of reactive extrusion on the polymer reactions were studied by monitoring mixing torque, and proper reaction conditions for the grafting reaction were proposed. Afterward, radical melt graft polymerizations of PE with several amide monomers including methacrylamide (MAM), *N*-*tert*butylacrylamide (NTAAM), and *N*-*tert*-butylmethacrylamide (NTMAM) were continued. Fourier transform spectroscopy (FTIR) analysis and nitrogen analysis confirmed that MAM and NTAAM were successfully grafted onto PE. Monomer structures affected grafting efficiency and polymer chain combination. After exposure to chlorine bleach, the graft modified products exhibited powerful antibacterial properties against *Escherichia coli* and *Staphylococcus aureus*.

- Soluble Polymeric Dual Sensor for Temperature and pH Value

Pietsch, C.; Hoogenboom, R.; Schubert, U. S. *Angew. Chem. Int. Ed.* **2009**, *48*, 5653–5656.

Abstract:

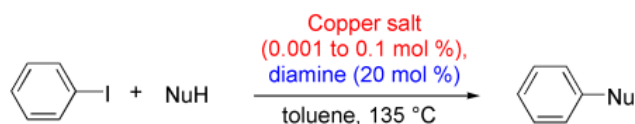


Two birds with one stone: A thermoresponsive copolymer (see picture, blue beads) bearing a pH-responsive solvatochromic dye (red beads) acts as the first dual sensor for temperature and pH value (black curve). When the hydrophilicity of the copolymer is increased by using a monomer with more

hydrophilic side chains, the dual sensing capabilities are lost (red curve), thus providing new insights into the hydration of thermoresponsive polymers.

- Copper-Catalyzed Cross-Couplings with Part-per-Million Catalyst Loadings
Larsson, P.-F.; Correa, A.; Carril, M.; Norrby, P.-O.; Bolm, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 5691–5693.

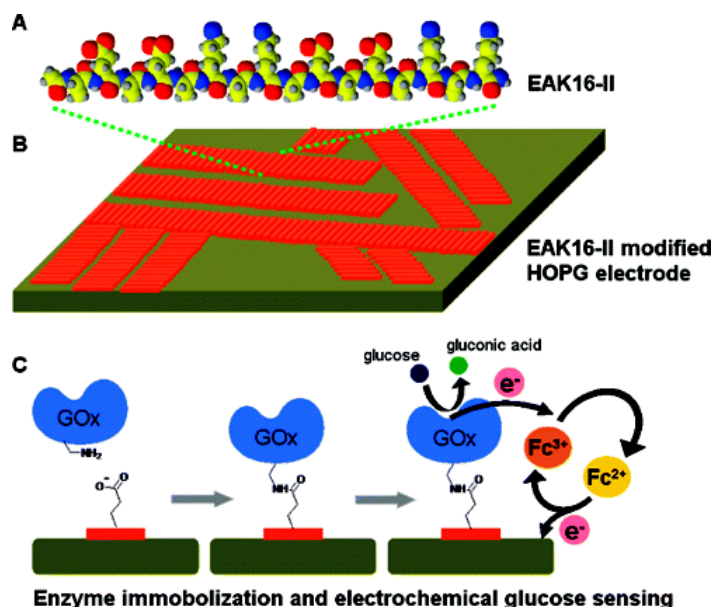
Abstract:



Homeopathic doses: The presence of 0.001 mol % of a copper salt can be sufficient to catalyze arylation reactions of various nucleophiles with phenyl iodide. The two most important factors governing the reaction outcome are the ligand quantity and the temperature.

- Ionic-Complementary Peptide Matrix for Enzyme Immobilization and Biomolecular Sensing
Yang, H.; Fung, S.-Y.; Pritzker, M.; Chen, P. *Langmuir* **2009**, *25*, 7773–7777.

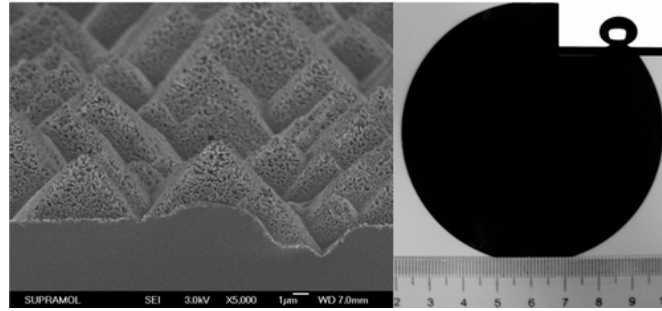
Abstract:



A novel electrochemical biosensing platform is described using biocompatible, self-assembled ionic-complementary peptide nanofibers. The compatibility of a graphite electrode modified by these peptide nanofibers with enzymes is demonstrated using a model enzyme glucose oxidase (GOx). A glucose biosensor has been successfully fabricated by incorporating this enzyme into the modified electrode. From measurement of its electrode response and sensitivity, this nanofiber-modified electrode shows promise as an enzyme-based biosensor. The findings presented here demonstrate excellent potential of the use of ionic-complementary peptides to modify electrode surfaces for biomolecular sensing and diagnostics.

- Simple Approach to Wafer-Scale Self-Cleaning Antireflective Silicon Surfaces
Qi, D.; Lu, N.; Xu, H.; Yang, B.; Huang, C.; Xu, M.; Gao, L.; Wang, Z.; Chi, L. *Langmuir*, **2009**, *25*, 7769–7772.

Abstract:



A simple approach to wafer-scale self-cleaning antireflective hierarchical silicon structures is demonstrated. By employing the KOH etching and silver catalytic etching, pyramidal hierarchical structures were generated on the crystalline silicon wafer, which exhibit strong antireflection and superhydrophobic properties after fluorination. Furthermore, a flexible superhydrophobic substrate was fabricated by transferring the hierarchical Si structure to the NOA 63 film with UV-assisted imprint lithography. This method is of potential application in optical, optoelectronic, and wettability control devices.