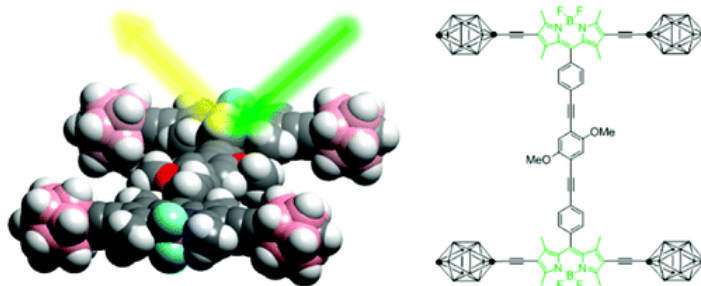
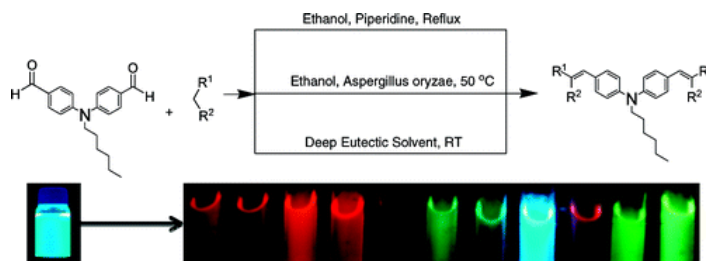


- Synthesis of Highly Fluorescent BODIPY-Based Nanocars
Godoy, J.; Vives, G.; Tour, J. M. *Org. Lett.* **2010**, *12*, 1464–1467.

Abstract:

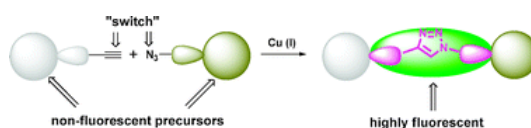
The convergent synthesis of inherently highly fluorescent nanocars incorporating 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY)-containing axles and *p*-carborane wheels is reported. These nanocars are expected to exhibit rolling motion with predetermined patterns over smooth surfaces, depending on their chassis. Their quantum yields of fluorescence ($\Phi_F > 0.7$) make them excellent candidates for imaging and tracking by single-molecule fluorescence microscopy. An analogue as a stationary control with *tert*-butyl groups instead of *p*-carborane wheels was also synthesized.

- Synthesis of Diphenylamine-Based Novel Fluorescent Styryl Colorants by Knoevenagel Condensation Using a Conventional Method, Biocatalyst, and Deep Eutectic Solvent
Sonawane, Y. A.; Phadtare, S. B.; Borse, B. N.; Jagtap, A. R.; Shankarling, G. S. *Org. Lett.* **2010**, *12*, 1456–1459.

Abstract:

Novel Y-shaped acceptor- π -donor- π -acceptor-type compounds, synthesized from 4,4'-hexyliminobisbenzaldehyde as electron donors and different active methylene compounds as electron acceptors, were produced by conventional Knoevenagel condensation alone, with a deep eutectic solvent, or with a lipase biocatalyst to compare the yield and recyclability among the three methods. Yield, reaction time, reaction temperature, and recyclability were compared among the three methods. The photophysical properties and thermal stability of the products were also investigated.

- Fluorogenic click reaction
Le Droumaguet, C.; Wang, C.; Wang, Q. *Chem. Soc. Rev.* **2010**, *39*, 1233 – 1239.

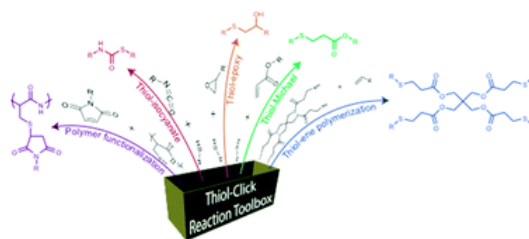
Abstract:

Fluorogenic Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reactions have emerged as a powerful tool for bioconjugation, materials science, organic synthesis and drug discovery. This

review highlights the design of the recent development of fluorogenic CuAAC reactions as well as their applications.

- Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis
Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355 – 1387.

Abstract:

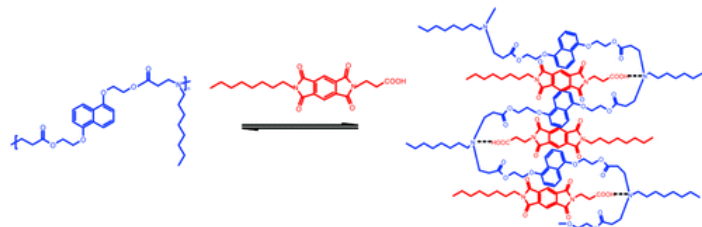


The merits of thiol-click chemistry and its potential for making new forays into chemical synthesis and materials applications are described. Since thiols react to high yields under benign conditions with a vast range of chemical species, their utility extends to a large number of applications in the chemical, biological, physical, materials and engineering fields. This *critical review* provides insight into emerging venues for application as well as new mechanistic understanding of this exceptional chemistry in its many forms (81 references).

- Folding a Polymer via Two-Point Interaction with an External Folding Agent: Use of H-Bonding and Charge-Transfer Interactions

De, S.; Koley, D.; Ramakrishnan, S. *Macromolecules* **2010**, *43*, 3183–3192.

Abstract:



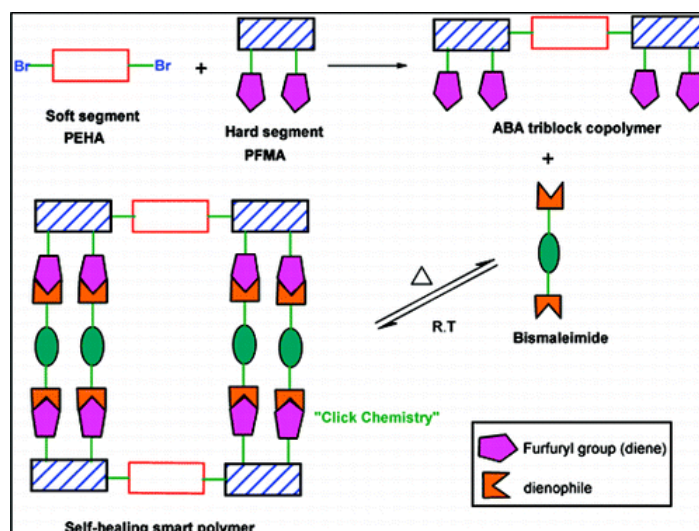
A polymer containing electron-rich aromatic donors (1,5-dialkoxynaphthalene (DAN)) was coerced into a folded state by an external folding agent that contained an electron-deficient aromatic acceptor (pyromellitic diimide (PDI)) unit. The donor-containing polymer was designed to carry a tertiary amine moiety in the linking segment, which served as an H-bonding site for reinforcing the interaction with the acceptor containing folding agent that also bore a carboxylic acid group. The H-bonding interaction of the carboxylic acid and the tertiary amine brings the PDI unit between two adjacent DAN units along the polymer backbone to induce charge-transfer (C-T) interactions, and this in turn causes the polymer chain to form a pleated structure. Evidence for the formation of such a pleated structure was obtained from NMR titration studies and also by monitoring the C-T band in their UV–visible spectra. By varying the length of the segment that links the PDI acceptor to the carboxylic acid group, we showed that the most effective folding agent was the one that had a single carbon spacer, as evident from the highest value of the association constant. Control experiments with propionic acid clearly demonstrated the importance of the additional C-T interactions for generating the folded structures. Further, solution viscosity measurements in the presence of varying amounts of the folding agent revealed a gradual stiffening of the chain in the case of the PDI carrying carboxylic acid, whereas no such affect was seen in the case of simple propionic acid. These

observations were supported by DFT calculations of the interactions of a dimeric model of the polymer with the various folding agents; here too the stability of the complex was seen to be highest in the case of the single carbon spacer.

- Smart “All Acrylate” ABA Triblock Copolymer Bearing Reactive Functionality via Atom Transfer Radical Polymerization (ATRP): Demonstration of a “Click Reaction” in Thermoreversible Property

Kavitha, A. A.; Singha, N. K. *Macromolecules* **2010**, *43*, 3193–3205.

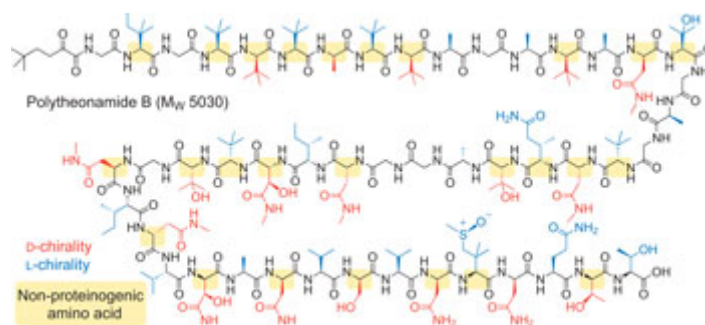
Abstract:



Tailor-made ABA triblock copolymers (poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF)) bearing a reactive pendant furfuryl group were successfully synthesized by atom transfer radical polymerization. The chemical compositions were calculated by ^1H NMR, and molecular weights and molecular weight distributions were determined by gel permeation chromatography analysis. The tensile properties of the triblock copolymers such as tensile strength, elongation at break, and tension set were studied. Differential scanning calorimetry (DSC) analysis and dynamic mechanical analysis (DMA) show the existence of two glass transition temperatures (T_g) and thereby the presence of well-defined soft and hard phase. Thermoreversible self-healing material was successfully prepared by using Diels–Alder reaction between this reactive furfuryl group (diene) of the ABA triblock copolymer and a bismaleimide (dienophile). Thermoreversible property of the polymer was confirmed by FTIR and DSC analysis. The self-healing nature of the polymers was characterized by scanning electronic microscopic analysis. Viscoelastic behavior of the Diels–Alder polymer was thoroughly studied by DMA studies.

- Total synthesis of the large non-ribosomal peptide polytheonamide B
Inoue, M.; Shinohara, N.; Tanabe, S.; Takahashi, T.; Okura, K.; Itoh, H.; Mizoguchi, Y.; Iida, M.; Lee, N.; Matsuoka, S. *Nature Chemistry* **2010**, *2*, 280 – 285.

Abstract:

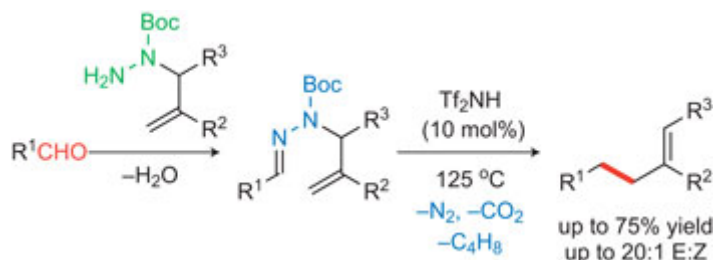


Polytheonamide B is by far the largest non-ribosomal peptide known at present, and displays extraordinary cytotoxicity (EC₅₀ = 68 pg ml⁻¹, mouse leukaemia P388 cells). Its 48 amino-acid residues include a variety of non-proteinogenic D- and L-amino acids, and the absolute stereochemistry of these amino acids alternate in sequence. These structural features induce the formation of a stable β-strand-type structure, giving rise to an overall tubular structure over 30 Å in length. In a biological setting, this fold is believed to transport cations across the lipid bilayer through a pore, thereby acting as an ion channel. Here, we report the first chemical construction of polytheonamide B. Our synthesis relies on the combination of four key stages: syntheses of non-proteinogenic amino acids, a solid-phase assembly of four fragments of polytheonamide B, silver-mediated connection of the fragments and, finally, global deprotection. The synthetic material now available will allow studies of the relationships between its conformational properties, channel functions and cytotoxicity

- Triflimide-catalysed sigmatropic rearrangement of *N*-allylhydrazones as an example of a traceless bond construction

Mundal, D. A.; Avetta, Jr, C. T.; Thomson, R. J. *Nature Chemistry* **2010**, 2, 294 – 297.

Abstract:



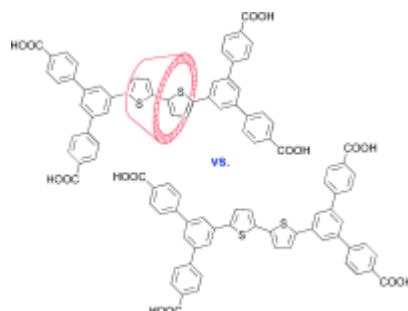
The recognition of structural elements (that is, retrons) that signal the application of specific chemical transformations is a key cognitive event in the design of synthetic routes to complex molecules. Reactions that produce compounds without an easily identifiable retron, by way of either substantial structural rearrangement or loss of the atoms required for the reaction to proceed, are significantly more difficult to apply during retrosynthetic planning, yet allow for non-traditional pathways that may facilitate efficient acquisition of the target molecule. We have developed a triflimide (Tf₂NH)-catalysed rearrangement of *N*-allylhydrazones that allows for the generation of a sigma bond between two unfunctionalized *sp*³ carbons in such a way that no clear retron for the reaction remains. This new 'traceless' bond construction displays a broad substrate profile and should open avenues for synthesizing complex molecules using non-traditional disconnections.

- A Conjugated Thiophene-Based Rotaxane: Synthesis, Spectroscopy, and Modeling

Zalewski, L.; Wykes, M.; Brovelli, S.; Bonini, M.; Breiner, T.; Kastler, M.; Dötz, F.; Beljonne, D.; Anderson, H. L.; Cacialli, F.; Samorì, P. *Chem. Eur. J.* **2010**, *16*, 3489-3496.

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Abstract:

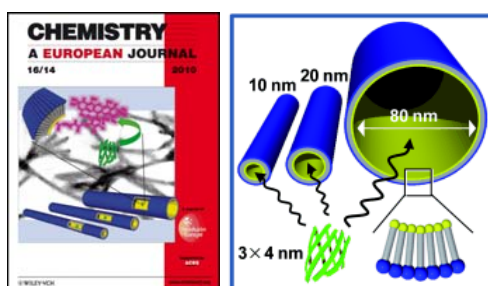


A dithiophene rotaxane **1**- β -CD and its shape-persistent corresponding dumbbell **1** were synthesized and fully characterized. 2D NOESY experiments, supported by molecular dynamics calculations, revealed a very mobile macrocycle (β -CD). Steady-state and time-resolved photoluminescence experiments in solution were employed to elucidate the excited-state dynamics for both systems and to explore the effect of cyclodextrin encapsulation. The photoluminescence (PL) spectrum of **1**- β -CD was found to be blueshifted with respect to the dumbbell **1** (2.81 and 2.78 eV, respectively). Additionally, in contrast to previous observations, neither PL spectra nor the decay kinetics of both threaded and unthreaded systems showed changes upon increasing the concentration or changing the polarity of the solutions, thereby providing evidence for a lack of tendency toward aggregation of the unthreaded backbone.

- Self-Assembly Confinement Effect of Organic Nanotubes Toward Green Fluorescent Protein (GFP) Depending on the Inner Diameter Size

Kameta, N.; Minamikawa, H.; Someya, Y.; Yui, H.; Masuda, M.; Shimizu, T. *Chem. Eur. J.* **2010**, *16*, 4217-4223.

Abstract:

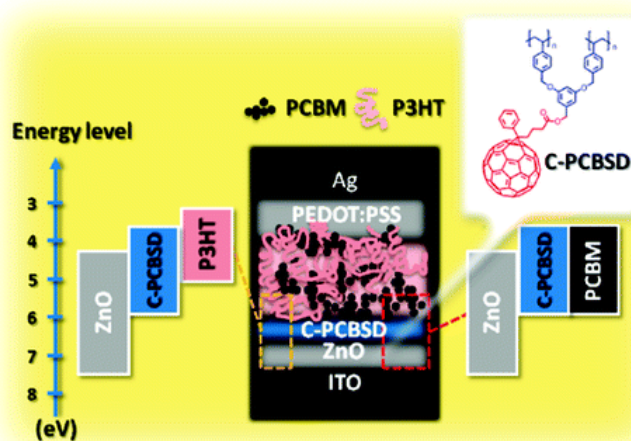


Transportation, release behavior, and stability of a green fluorescent protein (GFP, 3×4 nm) in self-assembled organic nanotubes with three different inner diameters (10, 20, and 80 nm) have been studied in terms of novel nanocontainers. Selective immobilization of a fluorescent acceptor dye on the inner surface enabled us to not only visualize the transportation of GFP in the nanochannels but to also detect release of the encapsulated GFP to the bulk solution in real time, based on fluorescence resonance energy transfer (FRET). Obtained diffusion constants and release rates of GFP markedly decreased as the inner diameter of the nanotubes was decreased. An *endo*-sensing procedure also clarified the dependence of the thermal and chemical stabilities of the GFP on the inner diameters. The GFP encapsulated in the 10 nm nanochannel showed strong resistance to heat and to a denaturant. On the other hand, the 20 nm nanochannel accelerated the denaturation of the encapsulated GFP compared with the

rate of denaturation of the free GFP in bulk and the encapsulated GFP in the 80 nm nanochannels. The confinement effect based on rational fitting of the inner diameter to the size of GFP allowed us to store it stably and without denaturation under high temperatures and high denaturant concentrations.

- Highly Efficient and Stable Inverted Polymer Solar Cells Integrated with a Cross-Linked Fullerene Material as an Interlayer
Hsieh, C. H.; Cheng, Y. J.; Li, P. J.; Chen, C. H.; Duboscq, M.; Liang, R. M.; Hsu, C. S. *J. Am. Chem. Soc.* **2010**, *131*, 4887–4893.

Abstract:



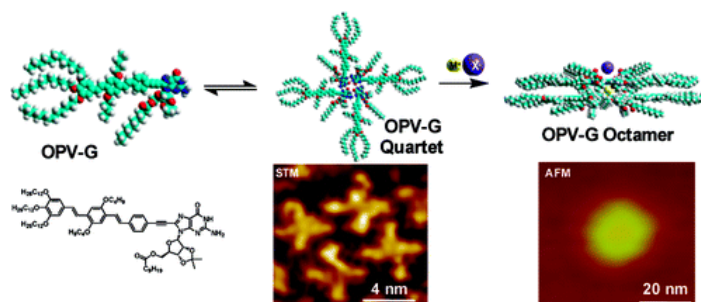
A novel PCBM-based n-type material, [6,6]-phenyl-C61-butyric styryl dendron ester (PCBSD), functionalized with a dendron containing two styryl groups as thermal cross-linkers, has been rationally designed and easily synthesized. In situ cross-linking of PCBSD was carried out by heating at a low temperature of 160 °C for 30 min to generate a robust, adhesive, and solvent-resistant thin film. This cross-linked network enables a sequential active layer to be successfully deposited on top of this interlayer to overcome the problem of interfacial erosion and realize a multilayer inverted device by all-solution processing. An inverted solar cell device based on an ITO/ZnO/C-PCBSD/P3HT:PCBM/PEDOT:PSS/Ag configuration not only achieves enhanced device characteristics, with an impressive PCE of 4.4%, but also exhibits an exceptional device lifetime without encapsulation; it greatly outperforms a reference device (PCE = 3.5%) based on an ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag configuration without the interlayer. This C-PCBSD interlayer exerts multiple positive effects on both P3HT/C-PCBSD and PCBM/C-PCBSD localized heterojunctions at the interface of the active layer, including improved exciton dissociation efficiency, reduced charge recombination, decreased interface contact resistance, and induction of vertical phase separation to reduce the bulk resistance of the active layer as well as passivation of the local shunts at the ZnO interface. Moreover, this promising approach can be applied to another inverted solar cell, ITO/ZnO/C-PCBSD/PCPDTBT:PC71BM/PEDOT:PSS/Ag, using PCPDTBT as the p-type low-band-gap conjugated polymer to achieve an improved PCE of 3.4%. Incorporation of this cross-linked C60 interlayer could become a standard procedure in the fabrication of highly efficient and stable multilayer inverted solar cells.

- Persistent, Well-Defined, Monodisperse, π -Conjugated Organic Nanoparticles via G-Quadruplex Self-Assembly

Rodríguez, D. G.; Janssen, P. G.A.; Rapún, R. M.; Cat, I. D.; Feyter, D. S.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2010**, *131*, 4710–4719.

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Abstract:

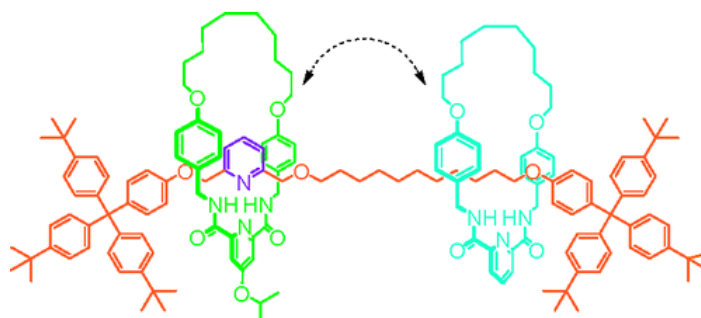


Several oligo(p-phenylene-vinylene) oligomers capped with a guanosine or a guanine moiety have been prepared via a palladium-catalyzed cross-coupling reaction. Their self-assembly, in both the absence and presence of alkaline salts, has been studied by means of different techniques in solution (NMR, MS, UV-vis, CD, fluorescence), solid state (X-ray diffraction), and on surfaces (STM, AFM). When no salt is added, these π -conjugated molecules self-associate in a mixture of hydrogen-bonded oligomers, among which the G-quartet structure may be predominant if the steric hindrance around the guanine base becomes important. In contrast, in the presence of sodium or potassium salts, well-defined assemblies of eight functional molecules (8mers) can be formed selectively and quantitatively. In these assemblies, the π -conjugated oligomers are maintained in a chirally tilted (J-type) stacking arrangement, which is manifested by negative Cotton effects, small bathochromic absorption and emission shifts, and fluorescence enhancements. Furthermore, these self-assembled organic nanostructures, \sim 1.5–2.0 nm high and 8.5 nm wide, exhibit an extraordinary stability to temperature or concentration changes in apolar media, and they can be transferred and imaged over solid substrates as individual nanoparticles, showing no significant dissociation or further aggregation.

- Sequence Isomerism in [3]Rotaxanes

Fuller, A.-M. L.; Leigh, D. A.; Lusby, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 4954–4959.

Abstract:



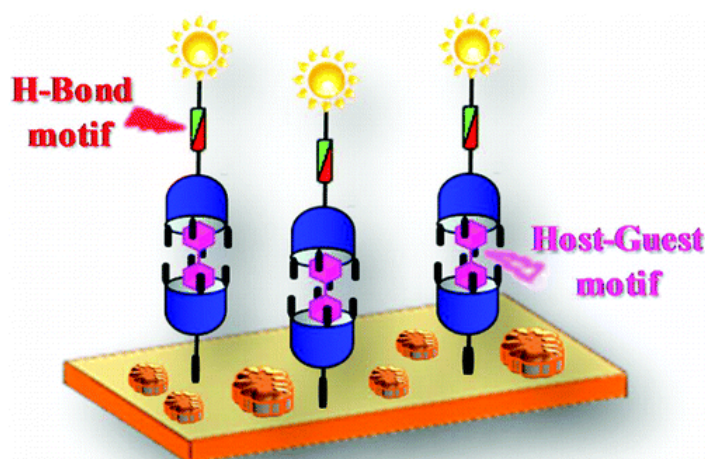
We describe a strategy for assembling different macrocycles onto a nonsymmetrical rotaxane thread in a precise sequence. If the macrocycles are small and rigid enough so that they cannot pass each other then the sequence is maintained mechanically, affording stereoisomerism in a manner reminiscent of atropisomerism. The method is exemplified through the synthesis of a pair of [3]rotaxane diastereomers that are constitutionally identical other than for the sequence of the different macrocycles on the thread. The synthesis features the iterative binding of different palladium(II) pyridine-2,6-dicarboxamide complexes to a pyridine ligand on

the thread followed by their macrocyclization by ring-closing olefin metathesis. Removal of the palladium(II) from the first rotaxane formed frees the pyridine site to coordinate to a second, different, palladium(II) pyridine-2,6-dicarboxamide unit which, following macrocyclization, provides a multiring rotaxane of predetermined macrocycle sequence.

- Hierarchical Self-Assembly on Silicon

Tancini, F.; Genovese, D.; Montalti, M.; Cristofolini, L.; Nasi, L.; Prodi, L.; Dalcanale, E. *J. Am. Chem. Soc.* **2010**, *132*, 4781–4789.

Abstract:

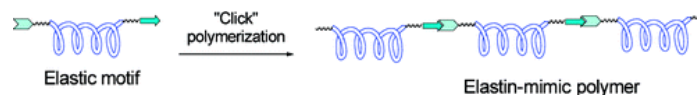


A set of modular components was designed, synthesized, and combined to yield an innovative, robust, and reliable methodology for the self-assembly of large supramolecular structures on silicon wafers. Specific host–guest and H-bonding motifs were embedded in a single molecule by exploiting the remarkable complexing properties of tetrakisphosphonate cavitands toward methylammonium and methylpyridinium salts and the outstanding homo- and heterodimerization capability of the ureidopyrimidone moiety. An assembly/disassembly sequence in solution was devised to assess the orthogonality and reversibility of H-bonding and host–guest interactions. The entire process was fully tested and characterized in solution and then successfully transferred to the solid state. The selected binding motifs resulted to be fully compatible in the assembly mode and individually addressable in the disassembly mode. The complete orthogonality of the two interactions allows the molecular level control of each step of the solid-state assembly and the predictable response to precise external stimuli. Complementary surface analysis techniques, such as atomic force microscopy (AFM), ellipsometry, and fluorescence, provided the univocal characterization of the realized structures in the solid state.

- Bioinspired Modular Synthesis of Elastin-Mimic Polymers To Probe the Mechanism of Elastin Elasticity

Chen, Y.; Guan, Z. *J. Am. Chem. Soc.* **2010**, *132*, 4577–4579.

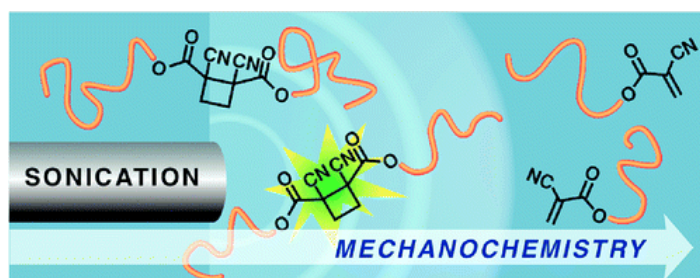
Abstract:



Bioinspired modular synthesis of elastin-mimic polymers (EMPs) is achieved via Cu-catalyzed alkyne-azide cyclization (CuAAC). By changing the module, EMPs with different secondary structures determined by circular dichroism (CD) spectra in trifluoroethanol (TFE) solution are obtained. The EMPs are characterized by measuring the lower critical solution temperatures (LSCTs) and the bulk mechanic properties under the conditions of both dry and hydrated forms. The unique molecular design enables us to probe mechanistic questions and assess the structure–property relationship of the EMPs. Our results indicate that, instead of a highly organized secondary structure, hydrophobic hydration is critical for the elasticity of EMPs.

- Masked Cyanoacrylates Unveiled by Mechanical Force
Kryger, M. J.; Ong, M. T.; Odom, S. A.; Sottos, N. R.; White, S. R.; Martinez, T. J.; Moore, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 4558–4559.

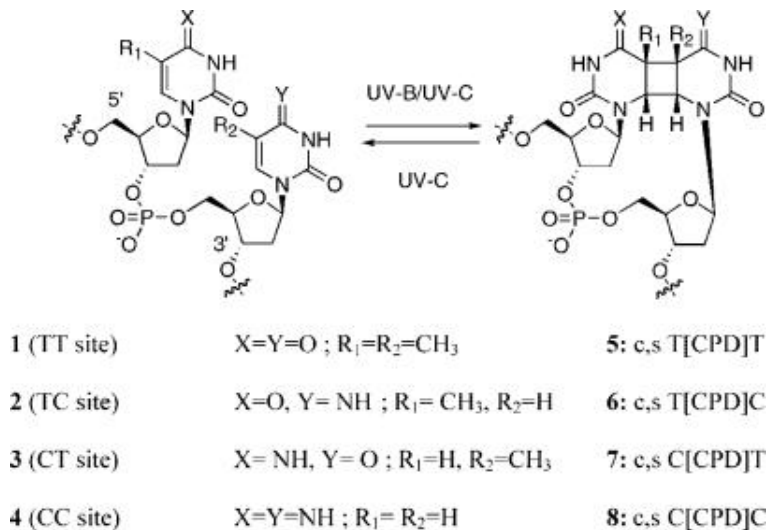
Abstract:



Mechanical damage of polymers is often a destructive and irreversible process. However, desirable outcomes may be achieved by controlling the location of chain cleavage events through careful design and incorporation of mechanically active chemical moieties known as mechanophores. It is possible that mechanophores can be used to generate reactive intermediates that can autopolymerize or cross-link, thus healing mechanically induced damage. Herein we report the generation of reactive cyanoacrylate units from a dicyanocyclobutane mechanophore located near the center of a polymer chain. Because cyanoacrylates (which are used as monomers in the preparation of superglue) autopolymerize, the generated cyanoacrylate-terminated polymers may be useful in self-healing polymers. Sonication studies of polymers with the mechanophore incorporated into the chain center have shown that selective cleavage of the mechanophore occurs. Trapping experiments with an amine-based chromophore support cyanoacrylate formation. Additionally, computational studies of small-molecule models predict that force-induced bond cleavage should occur with greater selectivity for the dicyanocyclobutane mechanophore than for a control molecule.

- Spore Photoproduct: A Key to Bacterial Eternal Life
Desnous, C.; Guillaume, D.; Clivio, P. *Chem. Rev.* **2010**, *110*, 1213–1232.

Abstract:

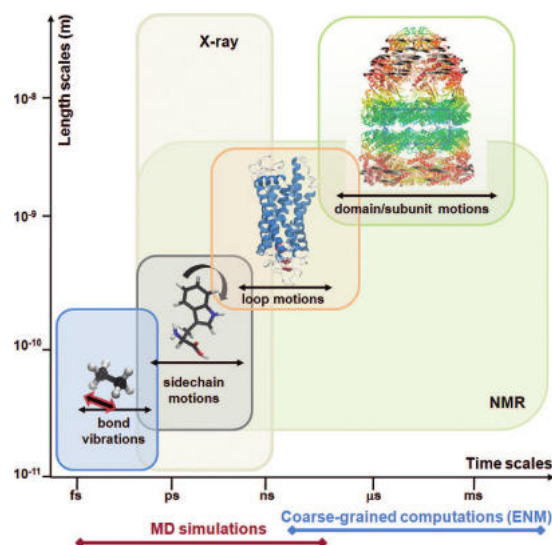


The cells of all living organisms are continuously exposed to a large variety of harmful agents that can induce either temporary or permanent deleterious effects. In response to these genotoxic stresses, only those cells endowed with efficient defense mechanisms have been able to overcome life's challenges and evolutionary demands and survive. By directly targeting DNA nucleobases, solar UV radiation is a ubiquitous and particularly potent physical agent capable of altering the genome integrity. The most deleterious UV wavelengths are those in the 200-280 nm range (UV-C). Fortunately for humanity, although UV-C permeates space, it does not in fact reach the surface of the earth thanks to the presence of ozone and other protective layers high in the atmosphere. Nevertheless, there are important industrial uses for artificially produced UV-C, mostly exploiting its germicidal properties. Though UV radiation-induced DNA damage (UV damage or photodamage) has had an indisputable evolutionary function, from a conservative standpoint the only cells able to transmit their genetic material unaltered are those capable of minimizing the frequency of the photodamage and/or those possessing accurate DNA repair pathways.

- Normal Mode Analysis of Biomolecular Structures: Functional Mechanisms of Membrane Proteins

Bahar, I.; Lezon, T. R.; Bakan, A.; Shrivastava, I. H. *Chem. Rev.* **2010**, *110*, 1463–1497.

Abstract:

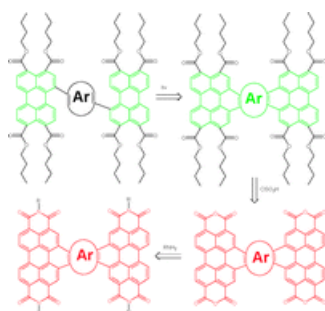


The ability of macromolecules to sample *an ensemble of conformations* has been evident for decades, starting from the statistical mechanical theory and simulations of polymers.¹⁻³ A polymer chain of N atoms enjoys $3N - 6$ internal degrees of freedom, which gives rise to infinitely many conformations. Even a simple model of $N > 100$ atoms where bond lengths and bond angles are fixed, and dihedral angles are restricted to discrete isomeric states say three states per bond has access to $3^{N-3} \approx 1.9 \times 10^{46}$ conformations. Proteins, too, are polymers, and have access to ensembles of conformations. The main structural difference between proteins and other chain molecules is that, under physiological conditions, proteins sample a significantly narrower distribution of conformations compared to disordered polymers. Their conformational variations are confined to the neighborhood of a global energy minimum that defines their “native state”.

- A design concept of planar conjugated ladder oligomers of perylene bisimides and efficient synthetic strategy via regioselective photocyclization.

Yuan, Z.; Xiao, Y.; Qian, X. *Chem. Commun.* **2010**, 46, 2772 – 2774.

Abstract:

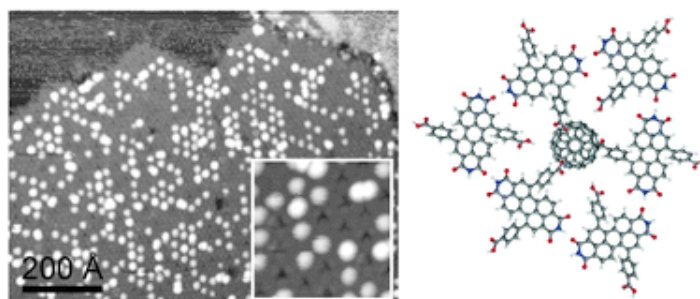


By photocyclization, benzene, thieno[3,2-b]thiophene, and fluorene units were embedded between the two perylene units. Symmetric oligomeric perylene bisimide **6** displays broad absorption and strong electron-accepting ability.

- Tailoring pores for guest entrapment in a unimolecular surface self-assembled hydrogen bonded network

Phillips, A. G.; Perdigão, L. M. A.; Beton, P. H.; Champness, N. R. *Chem. Commun.* **2010**, 46, 2775 – 2777.

Abstract:

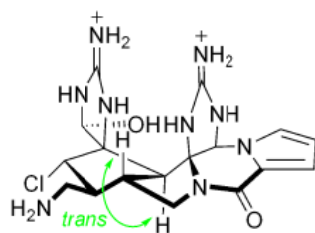


A unimolecular hydrogen-bonded network is formed by a perylene-diimide derivative following surface self-assembly leading to the formation of pores of appropriate dimensions to accommodate regularly spaced guest C_{60} molecules.

- Total Synthesis of the Marine Alkaloid Palau'amine

Jessen, H. J.; Gademann, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 2972 – 2974.

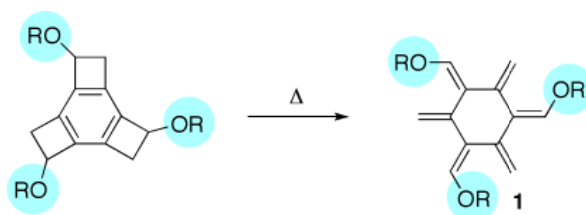
Abstract:



The marine alkaloid palau'amine has been prepared for the first time in totally synthetic form by a series of cascade and one-pot transformations. These reactions exploit the inherent reactivity of functional groups and deliver interesting solutions to daunting synthetic challenges.

- Hexaradialenes by Successive Ring Openings of Tris(alkoxytricyclobutabenzene)s: Synthesis and Characterization
Shinozaki, S.; Hamura, T.; Ibusuki, Y.; Fujii, K.; Uekusa, H.; Suzuki, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 3026 – 3029.

Abstract:



You rang m'lord? Thermally induced successive ring openings of tris(alkoxytricyclobutabenzene) to hexaradialene are described. The isomerization reaction was highly stereoselective to afford a stereodefined hexaradialene **1**, given that the hydroxy groups on the four-membered rings were protected by bulky substituents.