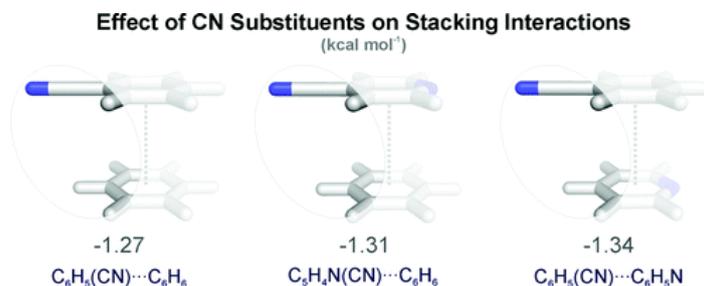
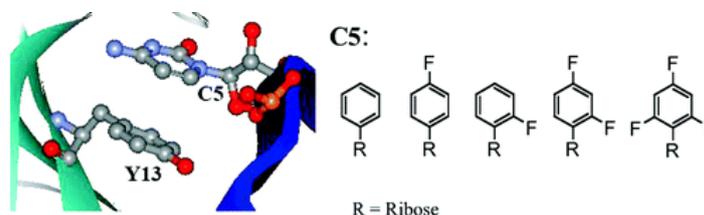


- Local Nature of Substituent Effects in Stacking Interactions
Wheeler, S. E. *J. Am. Chem. Soc.* **2011**, *133*, 10262–10274.

Abstract:

Popular explanations of substituent effects in π -stacking interactions hinge upon substituent-induced changes in the aryl π -system. This entrenched view has been used to explain substituent effects in countless stacking interactions over the past 2 decades. However, for a broad range of stacked dimers, it is shown that substituent effects are better described as arising from local, direct interactions of the substituent with the proximal vertex of the other ring. Consequently, substituent effects in stacking interactions are additive, regardless of whether the substituents are on the same or opposite rings. Substituent effects are also insensitive to the introduction of heteroatoms on distant parts of either stacked ring. This local, direct interaction viewpoint provides clear, unambiguous explanations of substituent effects for myriad stacking interactions that are in accord with robust computational data, including DFT-D and new benchmark CCSD(T) results. Many of these computational results cannot be readily explained using traditional π -polarization-based models. Analyses of stacking interactions based solely on the sign of the electrostatic potential above the face of an aromatic ring or the molecular quadrupole moment face a similar fate. The local, direct interaction model provides a simple means of analyzing substituent effects in complex aromatic systems and also offers simple explanations of the crystal packing of fluorinated benzenes and the recently published dependence of the stability of protein–RNA complexes on the regiochemistry of fluorinated base analogues [*J. Am. Chem. Soc.* 2011, *133*, 3687–3689].

- Control of the Stability of a Protein–RNA Complex by the Position of Fluorine in a Base Analogue
Benitex, Y.; Baranger, A.M. *J. Am. Chem. Soc.* **2011**, *133*, 3687–3689.

Abstract:

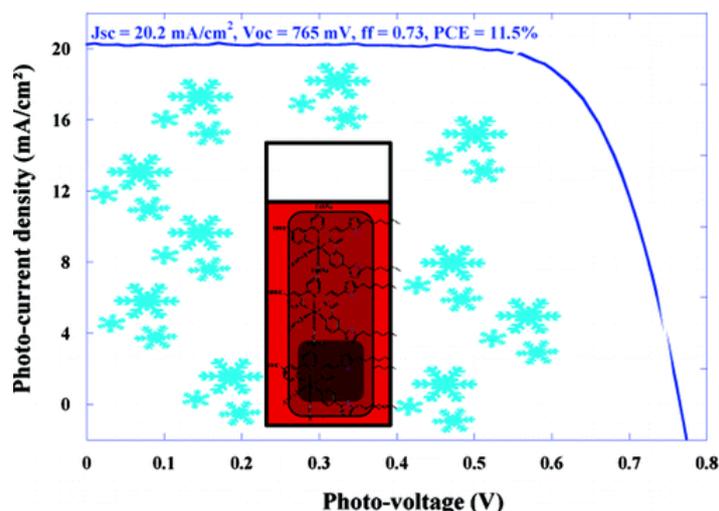
The effects of modifying the electronic characteristics of nonpolar base analogues substituted at positions involved in stacking interactions between SL2 RNA and the U1A protein are described. A surprisingly large difference in the stability between complexes formed with base analogues that differ only in the position of substitution of a single fluorine atom is observed. The results of high-level ab initio calculations of the interactions between the nonpolar base analogue and the amino acid side chain correlate with the experimentally observed trends in complex stability, which suggests that changes in stacking interactions that result from varying the position and degree of

fluorine substitution contribute to the effects of fluorine substitution on the stability of the U1A–SL2 RNA complex.

- Effect of Sensitizer Adsorption Temperature on the Performance of Dye-Sensitized Solar Cells Polymers from the Self-Assembly of a Small Monomer with Two Orthogonal Binding Interactions

Sauvage, F.; Decoppet, J.-D.; Zhang, M.; Zakeeruddin, S. M.; Comte, P.; Nazeeruddin, M.; Wang, P.; Grätzel, M. *J. Am. Chem. Soc.* **2011**, *133*, 9304-9310.

Abstract:

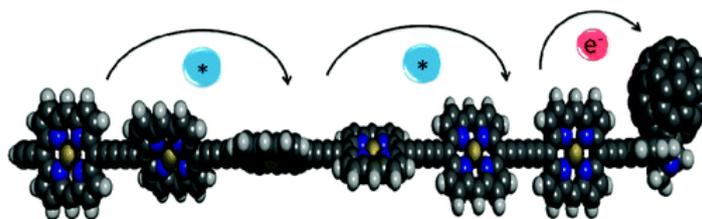


Employing a mesoscopic titania photoanode whose bilayer structure was judiciously selected to fit the optoelectronic characteristics of the Ru-based heteroleptic complex Na-cis-Ru(4,4'-(5-hexylthiophen-2-yl)-2,2'-bipyridine)(4-carboxylic-acid-4'-carboxylate-2,2'-bipyridine)(thiocyanate)₂, coded as C101, we investigated the effect of temperature for dye adsorption on the photovoltaic performance of dye-sensitized solar cells (DSCs). We found a significant efficiency enhancement upon lowering the temperature applied during the sensitizer uptake from solution. When the dye adsorption was performed at 4 °C, the photovoltaic performance parameters measured under standard reporting conditions (AM1.5 G sunlight at 1000 W/m² intensity and 25 °C), i.e., the open circuit voltage (V_{oc}), the short circuit photocurrent density (J_{sc}), the fill factor (FF), and consequently the power conversion efficiency (PCE), improved in comparison to cells stained at 20 and 60 °C. Results from electrochemical impedance spectroscopy (EIS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) show that the self-assembled layer of C101 formed at lower temperature impairs the back-electron transfer from the TiO₂ conduction band to the triiodide ions in the electrolyte more strongly than the film produced at 60 °C. Profiting from the favorable influence that the low-temperature dye uptake exerts on photovoltaic performance, we have realized DSCs showing a power conversion efficiency of 11.5%.

- Temperature Dependence of Charge Separation and Recombination in Porphyrin Oligomer–Fullerene Donor–Acceptor Systems

Kahnt, A.; Kärnbratt, J.; Esdaile, L. J.; Hutin, M.; Sawada, K.; Anderson, H. L.; Albinsson, B. *J. Am. Chem. Soc.* **2011**, *133*, 9863-9871.

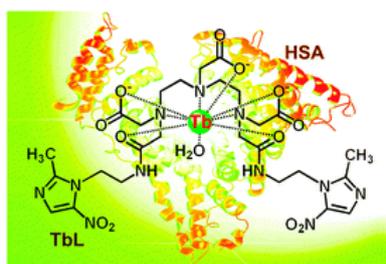
Abstract:



Electron-transfer reactions are fundamental to many practical devices, but because of their complexity, it is often very difficult to interpret measurements done on the complete device. Therefore, studies of model systems are crucial. Here the rates of charge separation and recombination in donor–acceptor systems consisting of a series of butadiyne-linked porphyrin oligomers ($n = 1–4, 6$) appended to C_{60} were investigated. At room temperature, excitation of the porphyrin oligomer led to fast (5–25 ps) electron transfer to C_{60} followed by slower (200–650 ps) recombination. The temperature dependence of the charge-separation reaction revealed a complex process for the longer oligomers, in which a combination of (i) direct charge separation and (ii) migration of excitation energy along the oligomer followed by charge separation explained the observed fluorescence decay kinetics. The energy migration is controlled by the temperature-dependent conformational dynamics of the longer oligomers and thereby limits the quantum yield for charge separation. Charge recombination was also studied as a function of temperature through measurements of femtosecond transient absorption. The temperature dependence of the electron-transfer reactions could be successfully modeled using the Marcus equation through optimization of the electronic coupling (V) and the reorganization energy (λ). For the charge-separation rate, all of the donor–acceptor systems could be successfully described by a common electronic coupling, supporting a model in which energy migration is followed by charge separation. In this respect, the C_{60} -appended porphyrin oligomers are suitable model systems for practical charge-separation devices such as bulk-heterojunction solar cells, where conformational disorder strongly influences the electron-transfer reactions and performance of the device.

- Terbium(III) complex as a luminescent sensor for human serum albumin in aqueous solution
Wang, X.; Wang, X.; Wang, Y.; Guo, Z. *Chem. Commun.* **2011**, 47, 8127-8129.

Abstract:



A terbium(III) complex exhibits a high selectivity for human serum albumin and emits strong luminescence upon recognition in aqueous solution.

- DNA-templated ensemble for label-free and real-time fluorescence turn-on detection of enzymatic/oxidative cleavage of single-stranded DNA
Yang, X.; Pu, F.; Ren, J.; Qu, X. *Chem. Commun.* **2011**, 47, 8133-8135.

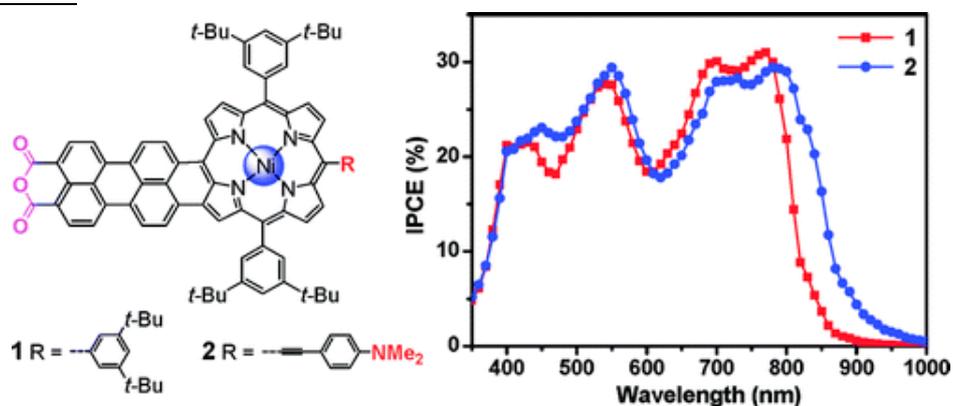
Abstract:

materials. Bioactive glasses and glass-ceramics, due to their tailorable properties in terms of chemical composition, reactivity, and easiness of manufacturing, represent good scaffolds for enzyme immobilization. These biomaterials are well known for their peculiar surface reactivity promoting, when contacted with real or simulated body fluids, the formation of an hydroxy-carbonate apatite layer. The aim of the present contribution has been to immobilize, *via* a covalent linkage, an enzyme on the glass surface through the formation of self-assembled monolayers (SAMs), in order to obtain a stable bio-conjugate useful as a material bio-implantable into the human body. The innovation of this study resides in the use of a new method of protein immobilization on the glass surface. Unlike other works, in which a preliminary silanization process has often been used, the introduction of gold nanoparticles (AuNPs) in the glass composition allowed us to exploit the easy SAMs formation process on the AuNPs dispersed in the bioactive glass matrix and, consequently, to immobilize an enzyme (soybean peroxidase, SBP, in the present case) on the SAMs. A thorough characterization of the materials, at different steps of the functionalization process, has been also reported, together with *in vitro* activity tests of immobilized SBP, compared with merely adsorbed SBP, and cytotoxicity tests using human osteoblast (MG-63) cells. Overall, a new bio-conjugate material, able to maintain its activity over time and to decrease the oxidative stress when in contact with MG-63 cells, has been obtained.

- Perylene Anhydride Fused Porphyrins as Near-Infrared Sensitizers for Dye-Sensitized Solar Cells

Jiao, C.; Zu, N.; Huang, K.-W.; Wang, P.; Wu, J. *Org. Lett.* **2011**, *13*, 3652-3655.

Abstract:

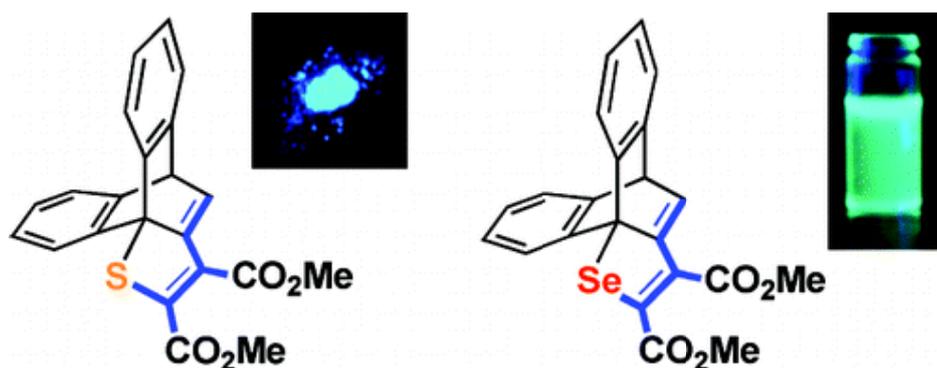


Two perylene anhydride fused porphyrins **1** and **2** have been synthesized and employed successfully in dye-sensitized solar cells (DSCs). Both compounds showed broad incident monochromatic photon-to-current conversion efficiency spectra covering the entire visible spectral region and even extending into the near-infrared (NIR) region up to 1000 nm, which is impressive for ruthenium-free dyes in DSCs.

- Fluorescent 3-Methylene-2,3-Dihydrochalcogenophenes Incorporated in a Rigid Dibenzobarrelene Skeleton

Ishii, A.; Yamaguchi, Y.; Nakata, N. *Org. Lett.* **2011**, *13*, 702-3705.

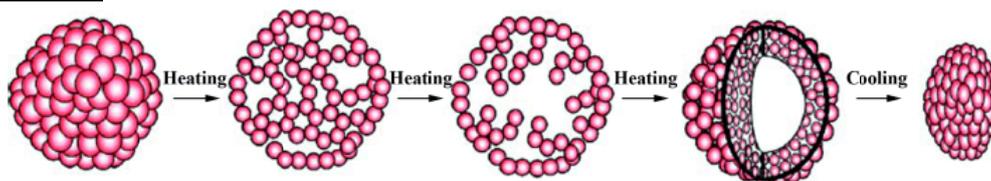
Abstract:



The fluorescent 3-methylene-2,3-dihydro-selenophene derivative ($\Phi_F = 0.86$ in CH_2Cl_2) incorporated in a dibenzobarrelenyl skeleton was synthesized by the reaction of a four-membered selenaplitanacycle with dimethyl acetylenedicarboxylate (DMAD) or reaction of bis(dibenzobarrelenyl) diselenide with DMAD in the presence of $\text{Pd}(\text{PPh}_3)_4$ and PPh_3 . A fluorescent sulfur homologue ($\Phi_F = 1.0$ in CH_2Cl_2) was also synthesized by the reaction of bis(dibenzobarrelenyl) disulfide with DMAD in the presence of $\text{Pd}(\text{PPh}_3)_4$. Selected chemical transformations of these diesters were also investigated.

- Thermally Induced Multimicellar-Aggregate-to-Vesicle Transition for a Dendritic Starch Ester
Tan, Y.; Xu, K.; Lu, C.; Liu, C.; Wang, P.; *Chem. Eur. J.* **2011**, *17*, 8277-8280.

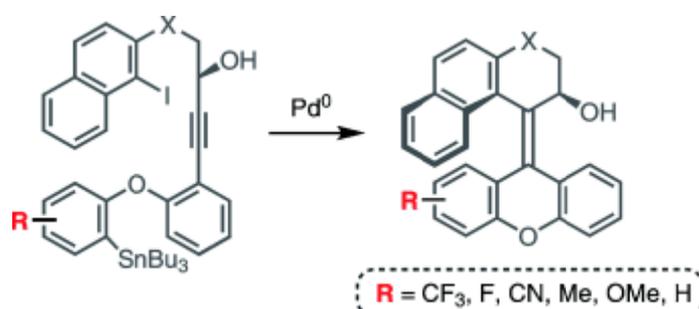
Abstract:



What a transition! A fast, temperature-induced transition from multimicellar aggregates to vesicles has been presented for a dendritic starch ester decorated with a temperature-sensitive group. The large micelles are multimicellar aggregates composed of unimolecular micelle units. The morphology transition is due to the reorganization of unimolecular micelles during a long-term heating process.

- Synthesis and Photochemical Investigations of Tetrasubstituted Alkenes as Molecular Switches—The Effect of Substituents
Tietze, L. F.; Düfert, M. A.; Hungerland, T.; Oum, K.; Lenzer, T. *Chem. Eur. J.* **2011**, *17*, 8452–8461.

Abstract:

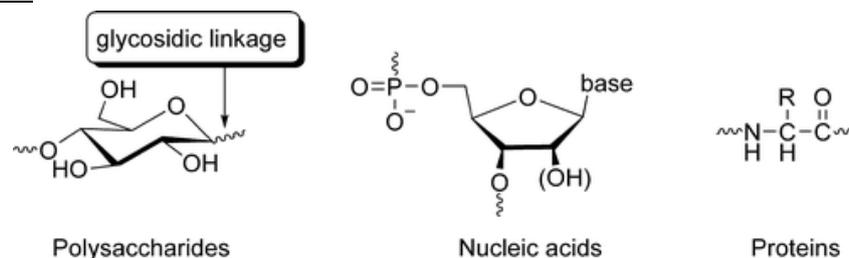


Molecular switches based on helical tetrasubstituted alkenes, substituted with either electron-withdrawing (CF₃, F, CN; 2□a–c, 3□a,c) or -donating substituents (Me, OMe; 2□d,e), have been synthesized from acyclic precursors 4 and 5 in a domino carbopalladation/Stille reaction. This palladium-catalyzed process allowed the rapid assembly of two C—C bonds, two six-membered

rings, and the tetrasubstituted double bond in a completely diastereoselective fashion. The electronic effects of the substituents on the overall switching process were investigated by alternating irradiation of two different wavelength regions. Although the substituents had only a small influence on the absorption maxima, drastic differences in the switching behavior were observed.

- Precision Polysaccharide Synthesis Catalyzed by Enzymes
Kadokawa, J.-I. *Chem. Rev.* **2011**, *111*, 4308–4345.

Abstract:



Polysaccharides are one of three major classes of natural polymers found in the plant, animal, and microbial kingdom, which are vital materials for important *in vivo* functions, e.g., providing an energy source, acting as a structural material, and conferring specific biological properties. They are structurally composed of monosaccharide residues linked through glycosidic linkages, which have very complicated structures owing to not only a variety of the monosaccharide structures but also the differences in stereo- and regio-types of the glycosidic linkages. In contrast, the other two major natural polymers, i.e., nucleic acids and proteins, have relatively simple structures because these natural polymers are constructed by a type of specific linkage between 20 kinds of amino acids and several kinds of nucleotides, respectively. A great variety of the polysaccharide structures contributes to serve a whole range of their functions in the host organism, and a subtle change in the structure of the monosaccharide unit or a type of glycosidic linkage has a profound effect on the properties and functions of the polysaccharides.

Chemical synthesis of the polysaccharide was first performed by an attempt of cellulose synthesis in 1941, and then attempts have been made to produce cellulose by traditional polymerization of glucose derivatives. For example, hydroxy groups of 2-, 3-, and 6-positions of glucose were protected and polycondensation of this glucose monomer with phosphorus pentoxide was performed to give the glucose polymer. This product was claimed to be composed of β -(1 \rightarrow 4)-glycosidic linkages; however, definite evidence of the structure was not sufficiently obtained. Then, although many efforts on polymerization had been devoted to chemical synthesis of polysaccharides with well-defined structures in stereo- and regioselectivities, only a few approaches successfully led to production of such polysaccharides. One approach is ring-opening polymerization of anhydrosugar monomers catalyzed by Lewis acid. After many attempts for this polymerization using various anhydrosugar monomers, cellulose with degree of polymerization (DP) of 19.3 was synthesized by the cationic ring-opening polymerization of 3,6-di-*O*-benzyl- α -d-glucose 1,2,4-orthopivalate and subsequent removal of the protective groups. On the other hand, acid-catalyzed ring-opening polyaddition of sugar oxazoline monomers derived from *N*-acetyl-d-glucosamine (GlcNAc) derivatives gave aminopolysaccharides with relatively controlled structures. For example, a 3,6-*O*-benzylated sugar oxazoline was polymerized with acid catalyst via ring-opening addition to give a dibenzyl chitin with molecular weights up to 4 900 (DP = ca. 13). Then, removal of benzyl groups was carried out to give chitin; however, complete deprotection did not take place. Because sugar monomers with protective groups have to be employed for the chemical synthesis of polysaccharides, subsequent

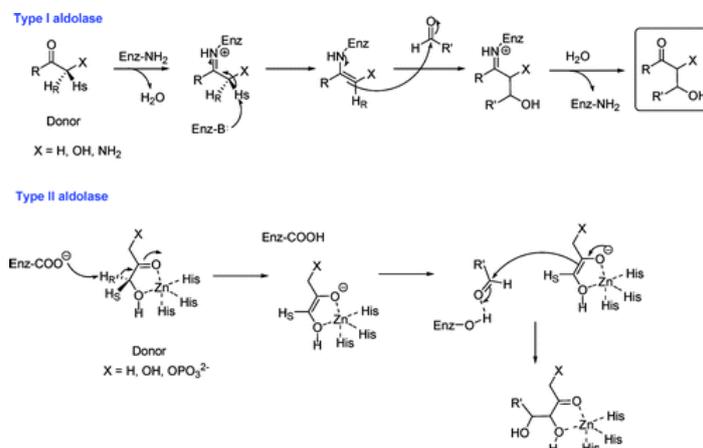
deprotection procedure is necessarily conducted to give free polysaccharides. Furthermore, perfect stereocontrol of glycosidic linkages has not often been achieved.

On the basis of the above backgrounds and viewpoints, almost in the past two decades, an enzymatic approach as a superior method to the traditional chemical one has been employed for the polysaccharide synthesis with highly stereo- and regioselectivities, which has attracted much attention and is still developing to provide a variety of new polysaccharides. This review focuses on precision polysaccharide synthesis catalyzed enzymes and describes *in vitro* synthetic approaches by isolated enzymes. Therefore, synthesis of polysaccharides from uridine diphosphate (UDP)-sugar substrates catalyzed by synthetic enzymes is not included.

- C–C Bond-Forming Lyases in Organic Synthesis

Brovetto, M.; Gamenara, D.; Saenz Méndez, P.; Seoane, G. A. *Chem. Rev.* **2011**, *111*, 4346–4403.

Abstract:



Lyases are enzymes that catalyze the bond construction and breaking by means other than hydrolysis or redox reactions. Such enzymes are particular in the sense that they only require one substrate for the reaction in one direction, but two substrates for the reverse reaction. Even though hydrolases have been the most employed biocatalysts in organic synthesis, an increasing number of recent articles deals with lyase-catalyzed synthesis of several interesting intermediates and final products.

Lyases are classified as EC 4, and there are seven subclasses of lyases, depending on the bond type involved. EC 4.1.x.x are carbon–carbon lyases, and this is the most important and abundant subclass. This subclass has four subcategories, namely, carboxy lyases (EC 4.1.1.x), aldehyde lyases (EC 4.1.2.x), oxoacid lyases (EC 4.1.3.x), and other carbon–carbon lyases (EC 4.1.99.x).

Stereoselective C–C bond construction is of utmost importance in organic synthesis. In this regard, enzymes are increasingly recognized as useful catalysts for asymmetric organic preparations. Enzymatic C–C bond formation is frequently highly chemo-, regio-, diastereo-, and enantioselective. Moreover, biocatalytic processes are performed under mild conditions and often in neutral aqueous solutions. As a result of the high selectivity and mild conditions employed, protective group chemistry can be avoided. Finally, the amount of waste generated because of avoidance of protective groups, chiral auxiliaries, and side products is minimized. Therefore, biocatalytic processes turn into an attractive, efficient, and environmentally friendly option for synthetic design.

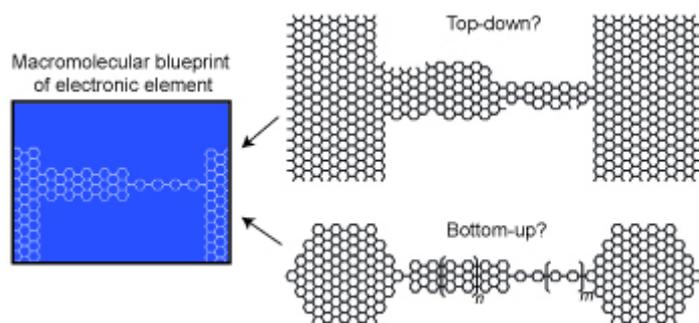
Despite of these advantages, the widespread use of biocatalysts in organic synthesis depends on several factors, including availability of enzymes, transferability of protocols, and reliability of obtained results.

Several types of enzymes that catalyze C–C bond formation are known. Many of those biocatalysts are lyases. Among them, aldolases and hydroxynitrile lyases (oxynitrilases) are highlighted because of their use in organic synthesis. This review will focus on lyase catalyzed C–C bond formation, presenting an overview of the latest developments in the field during the past decade, with emphasis in the synthetic applications of enzymatic aldol, acyloin condensation, and cyanohydrin reactions.

- Blueprinting macromolecular electronics

Palma, C.-A.; Samorì, P. *Nature Chemistry* **2011**, *3*, 431-436.

Abstract:

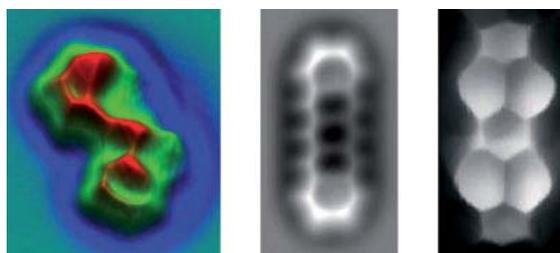


Recently, by mastering either top-down or bottom-up approaches, tailor-made macromolecular nano-objects with semiconducting properties have been fabricated. These engineered nanostructures for organic electronics are based on conjugated systems predominantly made up of sp^2 -hybridized carbon, such as graphene nanoribbons. Here, we describe developments in a selection of these nanofabrication techniques, which include graphene carving, stimulus-induced synthesis of conjugated polymers and surface-assisted synthesis. We also assess their potential to reproduce chemically and spatially precise molecular arrangements, that is, molecular blueprints. In a broad context, the engineering of a molecular blueprint represents the fabrication of an integrated all-organic macromolecular electronic circuit. In this Perspective, we suggest chemical routes, as well as convergent on-surface synthesis and microfabrication approaches, for the ultimate goal of bringing the field closer to technology.

- Recent advances in submolecular resolution with scanning probe microscopy

Gross, L. *Nature Chemistry* **2011**, *3*, 273-278.

Abstract:

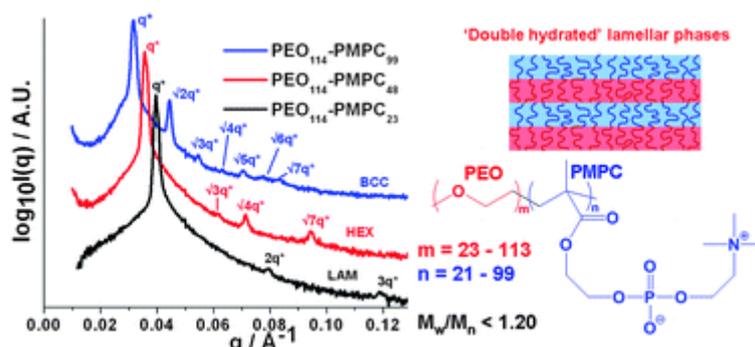


Recently scanning probe microscopy has made tremendous progress in imaging organic molecules with high lateral resolution. Atoms and bonds within individual molecules have been clearly resolved, indicating the exciting potential of this technique for studying molecular structures, bonding within and between molecules, molecular conformational changes and chemical reactions at the single-molecule level. It turns out that the key step enabling such studies is an atomically controlled functionalization of the microscope tip. In this Perspective, the different techniques used for high-

resolution molecular imaging, their implementations, advantages and limitations are described, and possible scientific areas of applications are discussed.

- Self-assembly of double hydrophilic block copolymers in concentrated aqueous solution
Blanazs, A.; Warren, N.; Lewis, A.; Armes, S.; Ryan, A. *Soft Matter* **2011**, *7*, 6399-6403.

Abstract:



We report the unusual aqueous (micro)phase separation of binary mixtures of two biocompatible, hydrophilic homopolymers and the corresponding double-hydrophilic diblock copolymers of poly(ethylene oxide) (PEO) and poly[2-(methacryloyloxy)ethyl phosphorylcholine] (PMPC). SAXS analysis of these double hydrophilic block copolymers in concentrated aqueous solution shows highly hydrated nano-structures and a hydration mechanism is proposed based on these data.

- Biocompatible and biodegradable polymersomes for pH-triggered drug release
Liu, G.; Lv, L.; Chen, C.; Liu, X.; Hu, X.; Ji, J. *Soft Matter* **2011**, *7*, 6629-6636.

Abstract:



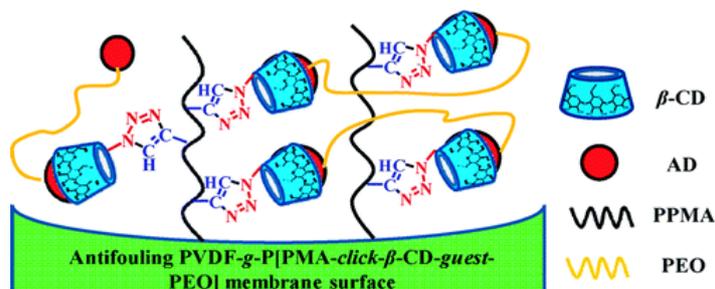
Nano-sized biocompatible and biodegradable polymersomes were prepared based on poly(D,L-lactide)-block-poly(2-methacryloyloxyethyl phosphorylcholine) (PLA-b-PMPC) diblock copolymers and applied for the release anti-cancer drugs. Hydrophobic doxorubicin (DOX) and hydrophilic doxorubicin hydrochloride (DOX·HCl) were successfully loaded into the polymersome membrane and polymersome interior, respectively. The in vitro release studies demonstrated that the release of DOX and DOX·HCl from polymersomes was highly pH-dependent, i.e. significantly faster drug release at mildly acidic pH of 5.0 compared to physiological pH 7.4. Furthermore, DOX·HCl-loaded polymersomes exhibited faster drug release than DOX-loaded polymersomes under the same pH conditions. The highly pH-dependent release behavior was attributed to the hydrolysis of PLA-b-PMPC, which would result in morphological transformation from polymersome to micelle with a triggered release of the encapsulated drugs. The drug-loaded polymersomes were shown to rapidly enter HepG2 cells, localize in their endosome/lysosomes with acidic pH environment and display

enhanced intracellular release of the drugs into the cytosol. These biocompatible and acid pH-sensitive polymersomes might have great potential for cancer therapy.

- Poly(vinylidene fluoride) Graft Copolymer Membranes with “Clickable” Surfaces and Their Functionalization

Cai, T.; Neoh, K. G.; Kang, E. T. *Macromolecules* **2011**, *44*, 4258–4268.

Abstract:



PVDF-*g*-PPMA copolymers bearing pendant propargyl functionalities were prepared by thermally induced graft copolymerization of propargyl methacrylate (PMA) from the ozone-preactivated poly(vinylidene fluoride) (PVDF) backbones. Microporous membranes were fabricated from the PVDF-*g*-PPMA comb copolymers by phase inversion in aqueous media. The PVDF-*g*-PPMA membrane and pore surfaces with pendant propargyl moieties from the PPMA side chains could be further functionalized via the one-step surface-initiated thiol-*yne* click reaction or alkyne-azide click reaction. The electrolyte-responsive PVDF-*g*-P[PMA-*click*-MPS] membranes were prepared via thiol-*yne* click reaction with 3-mercapto-1-propanesulfonic acid sodium salt (MPS) on the microporous PVDF-*g*-PPMA membranes. The permeability of aqueous solutions through the PVDF-*g*-P[PMA-*click*-MPS] membranes exhibited a dependence on the electrolyte concentration. The PVDF-*g*-P[PMA-*click*-β-CD] membranes were synthesized via the alkyne-azide click reaction of mono(6-azido-6-desoxy)-β-cyclodextrin (azido-β-CD) on the PVDF-*g*-PPMA membranes. The PVDF-*g*-P[PMA-*click*-β-CD-guest-PEO] membranes, from surface inclusion complexation of *diadamantyl*-poly(ethylene oxide) (AD-PEO) guest polymer with the β-cyclodextrin (β-CD) host molecules, exhibited good resistance to protein adsorption and fouling under continuous-flow conditions.

- Supramolecular Glycopolymers in Water: A Reversible Route Toward Multivalent Carbohydrate-Lectin Conjugates Using Cucurbit[8]uril

Geng, J.; Biedermann, F.; Zayed, J. M.; Tian, F.; Scherman, O. A. *Macromolecules* **2011**, *44*, 4276–4281.

Abstract:



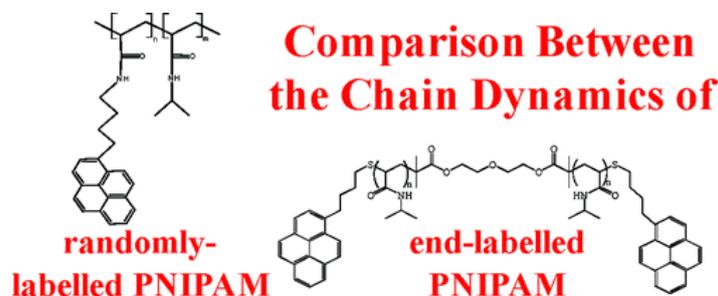
Supramolecular self-assembly and *reversible* switching has been demonstrated for the first time between monovalent and multivalent carbohydrate ligands and the multivalency effect on lectin binding has been investigated. The self-assembly process is mediated through noncovalent interactions between pendant moieties on a polymer scaffold and a monosaccharide-functionalized viologen with cucurbit[8]uril (CB[8]) acting as a “supramolecular handcuff”. The rate of binding of the

tetrameric lectin Concanavalin A (Con A) to a mannose-containing supramolecular glycopolymer was investigated through a standard turbidimetric assay.

- Long-Range Polymer Chain Dynamics of Pyrene-Labeled Poly(*N*-isopropylacrylamide)s Studied by Fluorescence

Yip, J.; Duhamel, J.; Qiu, X. P.; Winnik, F. M. *Macromolecules* **2011**, *44*, 5363–5372.

Abstract:

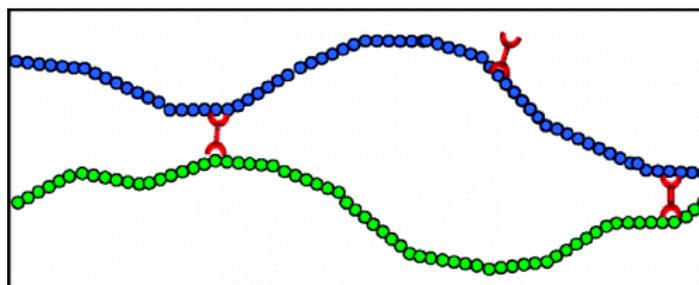


The long-range polymer chain dynamics (LRPCD) of poly(*N*-isopropylacrylamide) (PNIPAM) were studied by steady-state and time-resolved fluorescence. Two types of fluorescently labeled PNIPAM constructs were considered. One polymer set, named $\text{Py}_2\text{-PNIPAM-Y}$, where $5.6 \text{ kDa} < Y < 44 \text{ kDa}$ is the molecular weight of the polymer, consisted of five monodisperse PNIPAMs that carried 1-pyrenyl-butyl groups at each chain end (functionalization level >75%). The second polymer set consisted of five polydisperse PNIPAMs $75 \text{ kDa} < M_n < 104 \text{ kDa}$ randomly labeled with pyrene (0.1 mol % < pyrene content < 6.0 mol %). Pyrene was selected as its ability to form an excimer from the encounter of two pyrenyl pendants covalently attached onto the polymer yields quantitative information about the LRPCD of a given backbone. The fluorescence data were analyzed according to the Birks scheme for the pyrene end-labeled PNIPAMs and the fluorescence blob model (FBM) for the randomly labeled PNIPAMs. The parameters describing the process of pyrene excimer formation were found to yield equivalent trends regardless of the PNIPAM construct as would be expected since both PNIPAM constructs are essentially pyrene-labeled PNIPAM in nature. Comparison of the parameters describing the LRPCD of PNIPAM and polystyrene obtained with either end- or randomly labeled polymers led to the conclusion that PNIPAM and polystyrene have similar LRPCD in solution as expected from the similarity in bulkiness of their side-chain. This study confirms the claim made first with polystyrene that randomly labeled polymers can be used to obtain quantitative information on the LRPCD of a given polymeric backbone and that they constitute an appealing alternative to end-labeled polymers.

- Scaling Laws in Supramolecular Polymer Networks

Xu, D.; Craig, S. L. *Macromolecules* **2011**, *44*, 5465–5472.

Abstract:

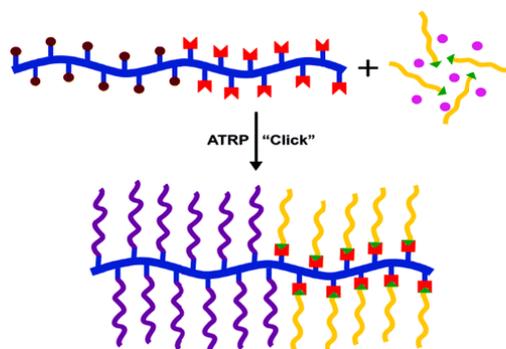


The linear rheological properties of networks formed by adding bis-Pd(II) cross-linkers to poly(4-vinylpyridine) (PVP) solution are examined, and the scaling law relationships between the zero shear viscosity (η_0) of the networks versus the concentration of PVP solution (C_{PVP}), the concentration of cross-linkers (C_X), and the number density of elastically active chains (v_{phantom}) are experimentally determined. The scaling law relationships are compared to the theoretical expectations of the sticky Rouse and sticky reptation models [*Macromolecules* 2001, 34, 1058–1068], and both qualitative and quantitative differences are observed.

- One-Pot Synthesis of Brush Diblock Copolymers through Simultaneous ATRP and Click Coupling

Han, D.; Tong, X.; Zhao, Y. *Macromolecules* **2011**, 44, 5531–5536.

Abstract:

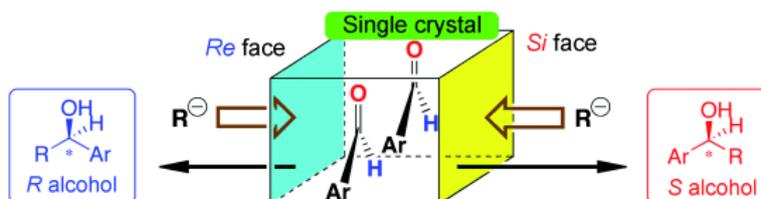


To our knowledge, there are few reports on combined use of “grafting from” and “grafting onto” to synthesize brush diblock copolymers. Deffieux and co-workers used a precursor diblock copolymer of poly(chloroethyl vinyl ether) (PCEVE) and poly(hydroxy ethyl vinyl ether) (POHEVE) to attach separately arms of polystyrene (PS) and poly(ethylene oxide) (PEO), obtaining the (PCEVE-g-PS)-b-(POHEVE-g-PEO) brush diblock copolymer. They first grafted polystyryllithium onto the reactive chloro functions of the PCEVE block (“grafting onto”) and then polymerized ethylene oxide by means of anionic polymerization from the hydroxyl functions of the POHEVE block (“grafting from”). In another study, starting with a different precursor diblock copolymer of PCEVE and poly(2-(1,3-dioxane) ethyl vinyl ether) (PAC EVE), they first used living cationic polymerization initiated by 1,3-dioxane pendant groups to grow arms of poly(methyl vinyl ether) (PMVE) (“grafting from”) and then attached PS onto the PCEVE block (“grafting onto”) through the anionic coupling reaction. Although the strategy allows for the preparation of high molar mass and narrow PDI samples, very strict experimental conditions are necessary for living ionic polymerization and coupling reaction, and removal of uncoupled polymer chains or purification following the formation of the first brush was needed before making the second brush. In this paper, we present a robust, one-pot synthetic method for preparing brush diblock copolymers via the combined use of “grafting from” and “grafting onto”.

- Enantioselective C — C Bond Formation as a Result of the Oriented Prochirality of an Achiral Aldehyde at the Single-Crystal Face upon Treatment with a Dialkyl Zinc Vapor

Kawasaki, T.; Kamimura, S.; Amihara, A.; Suzuki, K.; Soai, K. *Angew. Chem. Int. Ed.* **2011**, 50, 6796–6798.

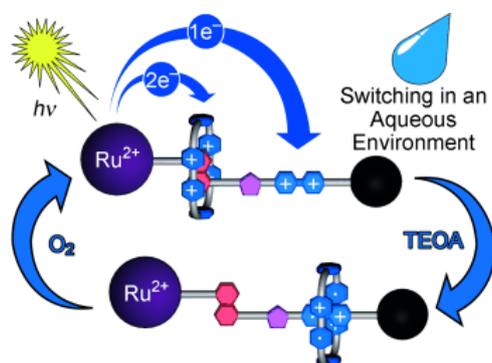
Abstract:



Show your best face: An achiral pyrimidine-5-carbaldehyde that forms an achiral crystal (**P1**) with enantiotopic (001) and ($\bar{0}\bar{0}\bar{1}$) faces underwent enantioselective addition of $i\text{Pr}_2\text{Zn}$ to the single exposed enantiotopic surface to give highly enantiomerically enriched *S* and *R* secondary alcohols (see scheme). The absolute configuration of the alcohol product correlated with the orientation of the prochiral aldehyde in the achiral crystal lattice.

- A Light-Stimulated Molecular Switch Driven by Radical–Radical Interactions in Water
Li, H.; Fahrenbach, A. C.; Coskun, A.; Zhu, Z.; Barin, G.; Zhao, Y.-L.; Botros, Y. Y.; Sauvage, J.-P.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 6782–6788.

Abstract:



A redox-controllable bistable [2]rotaxane has been synthesized using templation and click chemistry. With assistance from a sacrificial electron donor, light-triggered switching through numerous cycles can be initiated by radical-pairing interactions between the reduced forms of the cyclophane and the bipyridinium unit in aqueous solution in the absence of air. In the presence of air (O_2), the interactions are reset by donor–acceptor charge transfer.