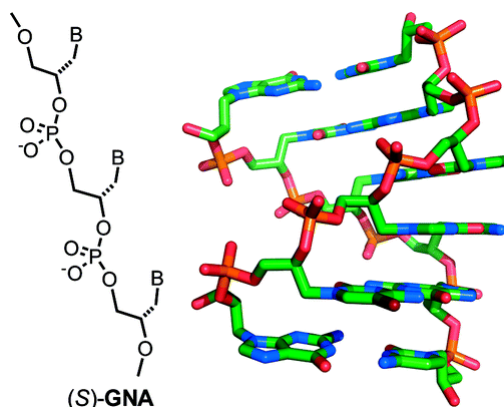


- Synthesis and Properties of the Simplified Nucleic Acid Glycol Nucleic Acid
Meggers, E.; Zhang, L. *Acc. Chem. Res.* **2010**, *43*, 1092–1102.

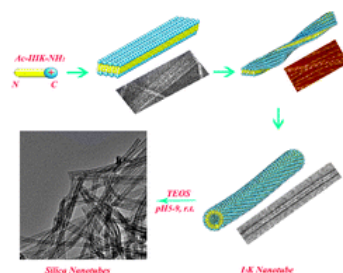
Abstract:



The nucleosides of glycol nucleic acid (GNA), with the backbone comprising just the three carbons and one stereocenter of propylene glycol (1,2-propanediol), probably constitute the simplest possible building blocks for a chemically stable nucleic acid that contains phosphodiester bonds. However, it was not until 2005 that the astonishing duplex formation properties of GNA homoduplexes were discovered in our laboratory. The *R*- and *S*-enantiomers of GNA, (*R*)-GNA and (*S*)-GNA, pair in like-symmetric combinations to form highly stable antiparallel duplexes in a Watson–Crick fashion, with thermal and thermodynamic stabilities exceeding those of analogous duplexes of DNA and RNA. Interestingly, (*R*)-GNA and (*S*)-GNA do not significantly cross-pair with each other, either in a parallel or antiparallel fashion. GNA discriminates strongly in favor of the Watson–Crick base-pairing scheme, with only slightly lower fidelity than DNA. Two (*S*)-GNA homoduplex structures recently determined by X-ray crystallography, one a brominated 6-mer duplex and the other an 8-mer duplex containing two copper(II) ions, reveal that the overall GNA double helix is distinct from canonical A- and B-form nucleic acids. The structure is perhaps best described as a helical ribbon loosely wrapped around the helix axis. Within the backbone, the propylene glycol nucleotides adopt two different conformations, *gauche* and *anti*, with respect to the torsional angles between the vicinal C3′–O and C2′–O bonds. A strikingly large backbone–base inclination results in extensive zipper-like interstrand and reduced intrastrand base–base interactions. This strong backbone–base inclination might explain the observation that neither the *R*- nor *S*-enantiomer of GNA cross-pairs with DNA, whereas (*S*)-GNA can interact with RNA strands that are devoid of G:C base pairs. Given the combination of structural simplicity, straightforward synthetic accessibility, and high duplex stability of GNA duplexes, GNA affords a promising nucleic acid scaffold for biotechnology and nanotechnology. Along these lines, we describe the functionalization of GNA duplexes through the incorporation of metal-ion-mediated base pairs. Finally, the properties of GNA discussed here reinforce its candidacy as one of the initial genetic molecules formed during the origins of life on Earth.

- Molecular self-assembly and applications of designer peptide amphiphiles
Zhao, X.; Pan, F.; Xu, H.; Yaseen, M.; Shan, H.; Hauser, C. A. E.; Zhang, S.; Lu, J. R. *Chem. Soc. Rev.* **2010**, *39*, 3480–3498.

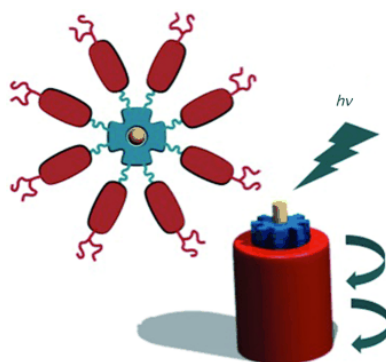
Abstract:



Short synthetic peptide amphiphiles have recently been explored as effective nanobiomaterials in applications ranging from controlled gene and drug release, skin care, nanofabrication, biomineralization, membrane protein stabilization to 3D cell culture and tissue engineering. This range of applications is heavily linked to their unique nanostructures, remarkable simplicity and biocompatibility. Some peptide amphiphiles also possess antimicrobial activities whilst remaining benign to mammalian cells. These attractive features are inherently related to their selective affinity to different membrane interfaces, high capacity for interfacial adsorption, nanostructuring and spontaneous formation of nano-assemblies. Apart from sizes, the primary sequences of short peptides are very diverse as they can be either biomimetic or *de novo* designed. Thus, their self-assembling mechanistic processes and the nanostructures also vary enormously. This *critical review* highlights recent advances in studying peptide amphiphiles, focusing on the formation of different nanostructures and their applications in diverse fields. Many interesting features learned from peptide self-organisation and hierarchical templating will serve as useful guidance for functional materials design and nanobiotechnology (123 references).

- Multichromophoric Phthalocyanine–(Perylenediimide)₈ Molecules: A Photophysical Study
Albert-Seifried, S.; Finlayson, C. E.; Laquai, F.; Friend, R. H.; Swager, T. M.; Kouwer, P. H. J.; Juríček, M.; Kitto, H. J.; Valster, S.; Nolte, R. J. M.; Rowan, A. E. *Chem. Eur. J.* **2010**, *16*, 10021-10029.

Abstract:



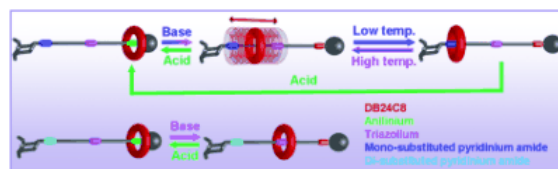
We describe the synthesis of a series of phthalocyanine (Pc)–perylene diimide (PDI)₈ “octad” molecules, in which eight PDI moieties are attached to a Pc core through alkyl-chain linkers. There is clear spectroscopic evidence that these octads can exist as non-aggregated “monomers” or form aggregates along the Pc cores, depending on the type of Pc and the solvent medium. In the low dielectric constant solvents, into which the octads are soluble, photoexcitation of the PDI units leads to rapid energy transfer to the Pc centre, rather than a charge separation between moieties. In octad monomers, the Pc singlet excited-state decays within tens of ps, whereas the excitons are stabilised in the aggregated form of the molecules, typically with lifetimes in the order of 1–10 ns. By contrast, in an octad design in which π – π interactions are suppressed by the steric hindrance of a corona of incompatible glycol tails around the molecule, a more straightforward photophysical interaction of

Förster energy transfer between the PDI moieties and Pc core may be inferred. We consider these molecules as prototypical multichromophoric aggregates, giving delocalised states with considerable flexibility of design.

- Bistable or Oscillating State Depending on Station and Temperature in Three-Station Glycorotaxane Molecular Machines

Busseron, E.; Romuald, C.; Coutrot, F. *Chem. Eur. J.* **2010**, *16*, 10021-10029.

Abstract:

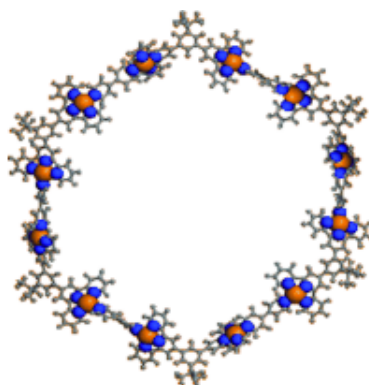


High-yield, straightforward synthesis of two- and three-station [2]rotaxane molecular machines based on an anilinium, a triazolium, and a mono- or disubstituted pyridinium amide station is reported. In the case of the pH-sensitive two-station molecular machines, large-amplitude movement of the macrocycle occurred. However, the presence of an intermediate third station led, after deprotonation of the anilinium station, and depending on the substitution of the pyridinium amide, either to exclusive localization of the macrocycle around the triazolium station or to oscillatory shuttling of the macrocycle between the triazolium and monosubstituted pyridinium amide station. Variable-temperature ^1H NMR investigation of the oscillating system was performed in CD_2Cl_2 . The exchange between the two stations proved to be fast on the NMR timescale for all considered temperatures (298–193 K). Interestingly, decreasing the temperature displaced the equilibrium between the two translational isomers until a unique location of the macrocycle around the monosubstituted pyridinium amide station was reached. Thermodynamic constants K were evaluated at each temperature: the thermodynamic parameters ΔH and ΔS were extracted from a Van't Hoff plot, and provided the Gibbs energy ΔG . Arrhenius and Eyring plots afforded kinetic parameters, namely, energies of activation E_a , enthalpies of activation ΔH^\ddagger , and entropies of activation ΔS^\ddagger . The ΔG values deduced from kinetic parameters match very well with the ΔG values determined from thermodynamic parameters. In addition, whereas signal coalescence of pyridinium hydrogen atoms located next to the amide bond was observed at 205 K in the oscillating rotaxane and at 203 K in the two-station rotaxane with a unique location of the macrocycle around the pyridinium amide, no separation of ^1H NMR signals of the considered hydrogen atoms was seen in the corresponding nonencapsulated thread. It is suggested that the macrocycle acts as a molecular brake for the rotation of the pyridinium–amide bond when it interacts by hydrogen bonding with both the amide NH and the pyridinium hydrogen atoms at the same time.

- Hexameric Palladium(II) Terpyridyl Metallomacrocycles: Assembly with 4,4'-Bipyridine and Characterization by TWIM Mass Spectrometry

Perera, S.; Li, X.; Soler, M.; Schultz, A.; Wesdemiotis, C.; Moorefield, C. N.; Newkome, G. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 6539–6544.

Abstract:

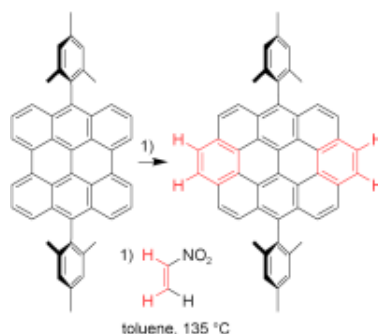


TWIM peaks: A macrocycle containing 12 Pd^{II} terpyridyl centers was assembled using 4,4'-bipyridyl ligands and characterized by NMR and traveling wave ion mobility mass spectrometry (TWIM-MS). The macrocyclic architecture was also examined by tandem mass spectrometry and collisionally activated dissociation (CAD) experiments (see picture; Cgray, Nblue, Pdorange), and the resulting fragments were monitored by time-of-flight mass analysis.

- One-Step Conversion of Aromatic Hydrocarbon Bay Regions into Unsubstituted Benzene Rings: A Reagent for the Low-Temperature, Metal-Free Growth of Single-Chirality Carbon Nanotubes

Fort, E. H.; Scott, L. T. *Angew. Chem. Int. Ed.* **2010**, *49*, 6626–6628.

Abstract:

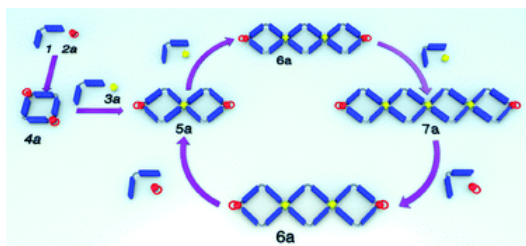


A tube ride: The controlled chemical synthesis of uniform, single-walled carbon nanotubes from short hydrocarbon templates, such as aromatic belts and geodesic nanotube end-caps, by a Diels–Alder cycloaddition/rearomatization strategy requires a potent “masked acetylene” capable of transforming hydrocarbon bay regions into new unsubstituted benzene rings in a single operation. Nitroethylene has been found to effect such benzannulations (see scheme).

- Dynamic formation of self-organized corner-connected square metallocycles by stoichiometric control

Blanco, V.; García, M. D.; Platas-Iglesias, C.; Peinador, C.; Quintela, J. M. *Chem. Commun.* **2010**, *46*, 6672–6674.

Abstract:

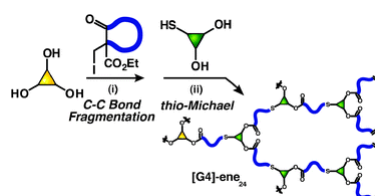


Corner-connected molecular squares were self-assembled from a three-component system formed by a bidentate ligand and two palladium or platinum complexes. The system is dynamic and the constitution of the species in solution can be modulated under stoichiometric control.

- A divergent synthesis of modular dendrimers via sequential C–C bond fragmentation thio-Michael addition

Hierold, J.; Gray-Weale, A.; Lupton, D. W. *Chem. Commun.* **2010**, 46, 6789-6791.

Abstract:

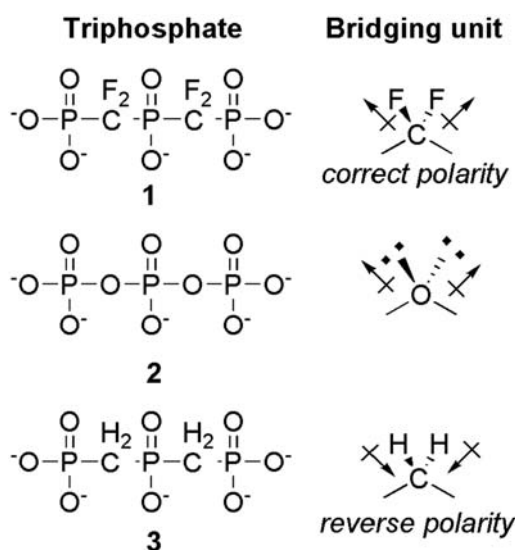


The C–C bond fragmentation of carbocycles has been developed as a new method for the divergent synthesis of dendrimers. The scope of this reaction was examined with the preparation of six first generation dendrimers from structurally diverse and readily available fragmentation precursors. By pairing the fragmentation with a thio-Michael reaction, the preparation of a [G4]-ene₂₄ dendrimer has been achieved.

- Synthesis and biological evaluation of fluorinated deoxynucleotide analogs based on bis-(difluoromethylene)triphosphoric acid

Surya Prakash, G. K.; Zibinsky, M.; Upton, T. G.; Kashemirov, B. A.; McKenna, C. E.; Oertell, K.; Goodman, M. F.; Batra, V. K.; Pedersen, L. C.; Beard, W. A.; Shock, D. D.; Wilson, S. H.; Olah, G. A. *Proc. Nat. Acad. Sci. USA* **2010**, 107, 15693-15698.

Abstract:

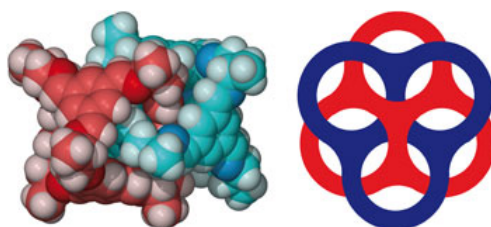


It is difficult to overestimate the importance of nucleoside triphosphates in cellular chemistry: They are the building blocks for DNA and RNA and important sources of energy. Modifications of biologically important organic molecules with fluorine are of great interest to chemists and biologists because the size and electronegativity of the fluorine atom can be used to make defined structural alterations to biologically important molecules. Although the concept of nonhydrolyzable nucleotides has been around for some time, the progress in the area of modified triphosphates was limited by the lack of synthetic methods allowing to access bisCF₂-substituted nucleotide analogs—one of the most interesting classes of nonhydrolyzable nucleotides. These compounds have “correct” polarity and the smallest possible steric perturbation compared to natural nucleotides. No other known nucleotides have these advantages, making bisCF₂-substituted analogs unique. Herein, we report a concise route for the preparation of hitherto unknown highly acidic and polybasic bis(difluoromethylene)triphosphoric acid **1** using a phosphorous(III)/phosphorous(V) interconversion approach. The analog **1** compared to triphosphoric acid is enzymatically nonhydrolyzable due to substitution of two bridging oxygen atoms with CF₂ groups, maintaining minimal perturbations in steric bulkiness and overall polarity of the triphosphate polyanion. The fluorinated triphosphoric acid **1** was used for the preparation of the corresponding fluorinated deoxynucleotides (dNTPs). One of these dNTP analogs (dT) was demonstrated to fit into DNA polymerase beta (DNA pol β) binding pocket by obtaining a 2.5 Å resolution crystal structure of a ternary complex with the enzyme. Unexpected dominating effect of triphosphate/Mg²⁺ interaction over Watson–Crick hydrogen bonding was found and discussed.

- Triply interlocked covalent organic cages

Hasell, T.; Wu, X.; Jones, J. T. A.; Bacsá, J.; Steiner, A.; Mitra, T.; Trewin, A.; Adams, D. J.; Cooper, A. I. *Nature Chemistry* **2010**, *2*, 750–755.

Abstract:



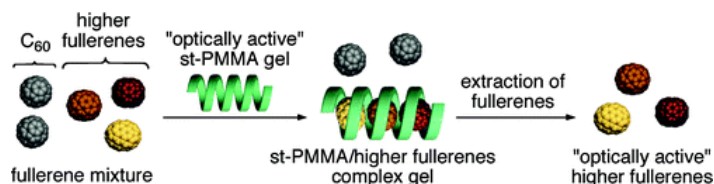
Interlocked molecules comprise two or more separate components that are joined by ‘mechanical’ rather than covalent bonds. In other words, these molecular assemblies cannot be dissociated without the cleavage of one or more chemical bonds. Although recent progress has enabled the preparation of such topologies through coordination or templating interactions, three-dimensional interlocked covalent architectures remain difficult to prepare. Here, we present a template-free one-pot synthesis of triply interlocked organic cages. These 20-component dimers consist of two tetrahedral monomeric cages each built from four nodes and six linkers. The monomers exhibit axial chirality, which is recognized by their partner cage during the template-free interlocking assembly process. The dimeric cages also include two well-defined cavities per assembly, which for one of the systems studied led to the formation of a supramolecular host–guest chain. These interlocked organic molecules may prove useful as part of a toolkit for the modular construction of complex porous solids and other supramolecular assemblies.

- Separation of C₇₀ over C₆₀ and Selective Extraction and Resolution of Higher Fullerenes by Syndiotactic Helical Poly(methyl methacrylate)

7

Kawauchi, T.; Kitaura, A.; Kawauchi, M.; Takeichi, T.; Kumaki, J.; Iida, H.; Yashima, E. *J. Am. Chem. Soc.* **2010**, *132*, 12191–12193.

Abstract:

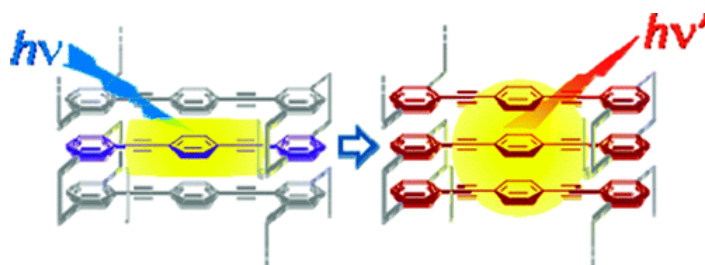


A one-handed helical polymer, syndiotactic poly(methyl methacrylate) (st-PMMA), recognizes the size and chirality of higher fullerenes through an induced-fit mechanism and can selectively extract enantiomers of the higher fullerenes, such as C₇₆, C₈₀, C₈₄, C₈₆, C₈₈, C₉₀, C₉₂, C₉₄, and C₉₆. This discovery will generate a practical and valuable method for selectively extracting the elusive higher fullerenes and their enantiomers and opens the way to developing novel carbon cage materials with optical activities.

- Multitiered 2D π -Stacked Conjugated Polymers Based on Pseudo-Geminal Disubstituted [2.2]Paracyclophane

Jagtap, S. P.; Collard, D. M. *J. Am. Chem. Soc.* **2010**, *132*, 12208–12209.

Abstract:



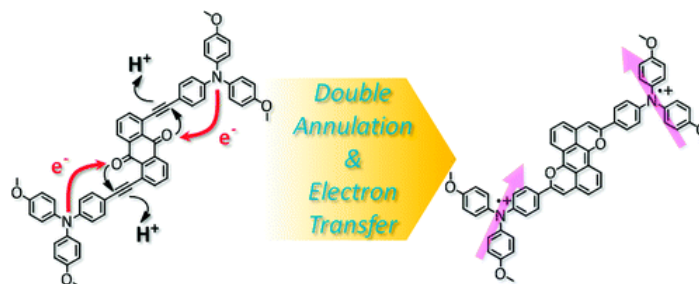
Interchain interactions between π -systems have a strong effect on the electronic structure of conjugated organic materials. This influence has previously been explored by the spectroscopic and electrochemical characterization of molecules in which pairs of conjugated oligomers are held in a stacked fashion by attachment to a rigid scaffold. We have prepared a new polymer which uses a pseudo-geminal disubstituted [2.2]paracyclophane scaffold to hold 1,4-bis(phenylethynyl)-2,5-dialkoxybenzene (PE₃) chromophores in a π -stacked fashion over their entire length and in an extended multitier arrangement. Solutions of this new polymer display a Stokes shift of 171 nm, compared to just ca. 30 nm for previous models in which only the terminal phenyl rings of the PE₃ chromophore are held in a stacked arrangement. This suggests that interchain interactions of π -systems over their entire length in a multitier assembly provides for relaxation of the excited state to a stable "plane" electronic state which is responsible for emission. This stabilization is not available in the stacked dimer or other regioisomers of the polymer which possess lesser degrees of overlap. Thus, the architecture of the soluble polymer mimics that of segments of conjugated polymers in semiconducting thin films and will provide a platform for the exploration of the nature of charge carriers and excitons in these important materials.

- Double Protonation of 1,5-Bis(triaryl amino ethynyl)anthraquinone To Form a Paramagnetic Pentacyclic Dipyrylium Salt

Prabhakara Rao, K.; Kusamoto, T.; Toshimitsu, F.; Inayoshi, K.; Kume, S.; Sakamoto, R.; Nishihara, H. *J. Am. Chem. Soc.* **2010**, *132*, 12472–12479.

8

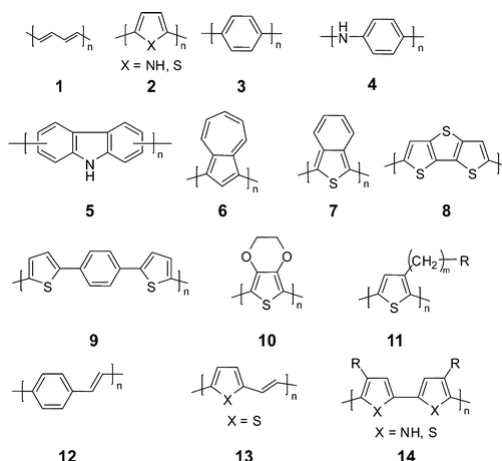
Abstract:



Protonation-induced intramolecular cyclization reactions of new donor (D)–acceptor (A) and D–A–D conjugated molecules 1-triarylminoethynylantraquinone (**1-AmAq**) and 1,5-bis(triarylminoethynyl)anthraquinone (**1,5-Am₂Aq**), respectively, were achieved. The former undergoes monoprotonation with bis(trifluoromethanesulfonyl)imide acid (TFSIH) to give pyrylium salt [**1-AmPyl**]**TFSI**, whereas the latter undergoes a novel double proton cyclization reaction to yield 1,5-bis(triarylmino)dipyrylium salt [**1,5-Am₂Pyl₂**]**(TFSI)₂** with a new pentacyclic backbone. This divalent cationic salt can be reduced to give the neutral species 2,8-bis(triarylmino)benzo[*de*]isochromeno[1,8-*gh*]chromene (**[1,5-Am₂Pyl₂]⁰**), which maintains the planar pentacyclic backbone. The obtained condensed-ring compounds show unique optical, electrochemical, and magnetic properties due to the extremely narrow HOMO–LUMO gap. In particular, the dication [**1,5-Am₂Pyl₂]²⁺** shows paramagnetic behavior with *two spins* centered on two triarylmino moieties through valence tautomerization with the pentacyclic backbone.

- Electrochemistry of Conducting Polymers—Persistent Models and New Concepts
Heinze, J.; Frontana-Uribe, B.-A.; Ludwigs, S. *Chem. Rev.* **2010**, *110*, 4724–4771.

Abstract:



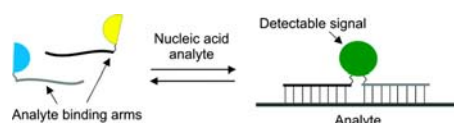
The interest of electrochemists in conducting polymers is based on several topics. The method of choice for preparing conducting polymers, with the exception of PA, is the anodic oxidation of suitable monomeric species, such as pyrrole, thiophene, or aniline. From the viewpoint of molecular electrochemistry, the most relevant aspect concerns the mechanism of electropolymerization involving initially the formation of oligomers followed by nucleation and growth steps, leading to polymeric materials. Mechanistic details are important for optimizing the conditions of electropolymerization. They play a decisive role in determining the quality of the fabricated materials.

Against this background of accelerated progress between 2000 and 2009, the scope of this review will be mainly limited to novel electrochemical findings in the field of CPs, involving the formation with mechanistic and electrosynthetic aspects, the charge storage mechanism, and related details. On the one hand, basic properties and processes of CPs will be discussed in light of recent results. On the other hand, an overview of recent electropolymerization methods, including the preparation of nanostructures and new architectures as well as new strategies for tuning their properties, will be given. For those readers who are interested in detailed descriptions of properties and applications of CPs, several just published textbooks are available.

- Binary Probes for Nucleic Acid Analysis

Kolpashchikov, D. M. *Chem. Rev.* **2010**, *110*, 4709–4723.

Abstract:



Over the last four decades nucleic acid hybridization techniques have been widely used for the detection of specific nucleic acid sequences. In this approach a 15-nucleotide or longer DNA or RNA strand (the probe) forms complementary duplexes with the analyzed nucleic acid (analyte). Since the development of the first hybridization-based procedures by Hall and Spiegeleman and by Bolton and McCarty, oligo- and polynucleotide probes have become routinely used as laboratory tools for nucleic acid analysis. The examples of such techniques include Southern and Northern blots, fluorescent in situ hybridization, and DNA microarrays. Furthermore, the introduction of real-time detection approaches, such as molecular beacon (MB) probes, has enabled fast assays, in which the fluorescence change is detected immediately after probe hybridization, thus avoiding the need to separate the probe–analyte hybrid from the excess of the unbound probe. However, low selectivity of the probe–analyte hybridization creates complications in the analysis of single-base differences between two polynucleotides. Indeed, a 15-nucleotide-long probe has a similar affinity to a fully complementary analyte and to an analyte containing a single noncomplementary base.