• Self-assembled monolayers of bifunctional periodic mesoporous organosilicas for cell adhesion and cellular patterning
Abstract:

Periodic mesoporous organosilicas (PMOs), an important class of inorganic–organic functional hybrid materials, find numerous potential applications in nano- and biotechnologies due to their porous nature, large surface area (internal and external surfaces) and the structural diversity of their organosilica frameworks. In this contribution we report on the selective functionalization of both the internal and the external surfaces of PMOs with a fluorescent dye and bioactive molecules, respectively. Subsequently we used these unique bifunctionalized PMO nanoparticles for the preparation of non-patterned and patterned self-assembled monolayers (SAMs) on glass. In cell experiments we showed that these new biomaterial surfaces enhance cell adhesion. We were able to determine the position of the inside dye substituted PMOs of the biomolecule functionalized surface in relation to the position of the stained cells by fluorescence microscopy as well. Patterned SAMs of bifunctionalized PMOs lead to selective cellular patterning along the stripes (texture of the surface).

• Helix versus coil polypeptide macromers: gel networks with decoupled stiffness and permeability
Abstract:

As a platform for investigating the individual effects of substrate stiffness, permeability, and ligand density on cellular behavior, we developed a set of hydrogels with stiffness tuned by polymer backbone rigidity, independent of cross-link density and concentration. Previous studies report that poly(propargyl-L-glutamate) (PPLG), synthesized by ring-opening polymerization of the N-carboxy anhydride of γ-propargyl-L-glutamate (γpLglu), adopts a rigid a-helix conformation: we hypothesized that a random copolymer (PPDLG) with equal amounts of γpLglu and γ-propargyl-D-glutamate (γpDglu) monomers would exhibit a more flexible random coil conformation. The resulting
macromers exhibited narrow molecular weight distributions (PDI = 1.15) and were grafted with ethylene glycol groups using a highly efficient “click” azide/alkyne cycloaddition reaction with average grafting efficiency of 97% for PPLG and 85% for PPDLG. The polypeptide secondary structure, characterized via circular dichroism spectroscopy, FTIR spectroscopy, and dynamic light scattering, is indeed dependent upon monomer chirality: PPLG exhibits an α-helix conformation while PPDLG adopts a random coil conformation. Hydrogel networks produced by cross-linking either helical or random coil polypeptides with poly(ethylene glycol) (PEG) were analyzed for amount of swelling, gelation efficiency, and permeability to a model protein. In addition, the elastic modulus of helical and coil polypeptide gels was determined by AFM indentation in fluid. Importantly, we found that helical and coil polypeptide gels exhibited similar swelling and permeability but different stiffnesses, which correspond to predictions from the theory of semi-flexible chains.

- Donor-Induced Helical Inversion of 1,1’-Binaphthyl Connecting with Two Molybdenum Complexes
  **Abstract:**
  An atropisomeric biaryl molecule with a given absolute configuration could present two opposite helical conformations through the rotation around C-C single bond. To the best of our knowledge, the biaryl system is the simplest helical inversion model apart from stereomutation between two enantiomers. Herein, we first report such true helical inversion phenomena of biaryl compounds. Two [MoVIO₂(L)]-type complexes, in which L is a tridentate dioxoanionic pyridine O,N,O-ligand, are coalesced on the 2,2’,3,3’-positions of an (R)-1,1’-binaphthyl unit and an intramolecular dioxo bridge is formed by two Mo=O⋯Mo interactions. Exterior strong donors can coordinate to molybdenum to interrupt this dioxo bridge and inversions from negative to positive chirality are explicitly observed by circular dichroism spectroscopy, consistent with single-crystal X-ray diffraction analyses.

- Enantioselective Organocatalytic One-Pot Amination/aza-Michael/Aldol Condensation Reaction Sequence: Synthesis of 3-Pyrrolines with a Quaternary Stereocenter
  **Abstract:**
Primary amine-catalyzed direct conversion of α,α-disubstituted aldehydes into 3-pyrrolines with a quaternary stereocenter is reported. The one-pot enantioselective sequence is based on a α-amination, an aza-Michael addition of hydrazine, an aldol condensation dehydration and proceeds with good yields and excellent levels of enantioselectivity. Synthetically attractive applications including the formation of aziridinopyrrolidine or oxypyrrolidine derivatives with good yields and selectivities are also described.

- Elucidation of the Active Conformation of Vancomycin Dimers with Antibacterial Activity against Vancomycin-Resistant Bacteria
  Abstract:

Covalently linked vancomycin dimers have attracted a great deal of attention among researchers because of their enhanced antibacterial activity against vancomycin-resistant strains. However, the lack of a clear insight into the mechanisms of action of these dimers hampers rational optimization of their antibacterial potency. Here, we describe the synthesis and antibacterial activity of novel vancomycin dimers with a constrained molecular conformation achieved by two tethers between vancomycin units. Conformational restriction is a useful strategy for studying the relationship between the molecular topology and biological activity of compounds. In this study, two vancomycin units were linked at three distinct positions of the glycopeptide (vancosamine residue (V), C terminus (C), and N terminus (N)) to form two types of novel vancomycin cyclic dimers. Active NC-VV-linked dimers with a stable conformation as indicated by molecular mechanics calculations selectively suppressed the peptidoglycan polymerization reaction of vancomycin-resistant Staphylococcus aureus in vitro. In addition, double-disk diffusion tests indicated that the antibacterial activity of these dimers against vancomycin-resistant enterococci might arise from the inhibition of enzymes responsible for peptidoglycan polymerization. These findings provide a new insight into the biological targets of vancomycin dimers and the conformational requirements for efficient antibacterial activity against vancomycin-resistant strains.

- Synthesis of a Library of Fluorescent 2-Aryl-3-trifluoromethylnaphthofurans from Naphthols by Using a Sequential Pummerer-Annulation/Cross-Coupling Strategy and their Photophysical Properties
  Abstract:
A library of 2-aryl-3-trifluoromethylnaphthofurans was synthesized with high efficiency from simple naphthols. In this synthesis, the Pummerer-type annulation of naphthols with 3-(2,2,2-trifluoroethylidene)-2,4-dithiapentane 2-oxide was followed by a cross-coupling of the resulting 2-methylthio-3-trifluoromethylnaphthofurans with a variety of arylzinc reagents. A palladium complex, Pd-PEPPSI-IPr, was the most efficient catalyst for the arylation step, which represents the first cross-coupling of aryl sulfides by using an N-heterocyclic-carbene-ligated palladium complex. This library consists of new π-expanded molecules, all of which are fluorescent in the solid state as well as in solution. Their photophysical properties, such as absorption and emission, fluorescence quantum yields, and fluorescence lifetimes, were thoroughly investigated. This library was also useful to identify acidochromic molecules.

- The hexadehydro-Diels-Alder reaction


Abstract:

Arynes (aromatic systems containing, formally, a carbon-carbon triple bond) are among the most versatile of all reactive intermediates in organic chemistry. They can be ‘trapped’ to give products that are used as pharmaceuticals, agrochemicals, dyes, polymers and other fine chemicals. Here we explore a strategy that unites the de novo generation of benzyne-through a hexadehydro-Diels-Alder reaction-with their in situ elaboration into structurally complex benzenoid products. In the hexadehydro-Diels-Alder reaction, a 1,3-diyn is engaged in a [4+2] cycloisomerization with a ‘diynophile’ to produce the highly reactive benzyne intermediate. The reaction conditions for this simple, thermal transformation are notable for being free of metals and reagents. The subsequent and highly efficient trapping reactions increase the power of the overall process. Finally, we provide examples of how this de novo benzyne generation approach allows new modes of intrinsic reactivity to be revealed.

- Dicyanovinylnaphthalenes for neuroimaging of amyloids and relationships of electronic structures and geometries to binding affinities
The positron-emission tomography (PET) probe 2-[[2-fluoroethyl]methylamino]-2-naphthyl]ethylidene) (FDDNP) is used for the noninvasive brain imaging of amyloid-β (Aβ) and other amyloid aggregates present in Alzheimer’s disease and other neurodegenerative diseases. A series of FDDNP analogs has been synthesized and characterized using spectroscopic and computational methods. The binding affinities of these molecules have been measured experimentally and explained through the use of a computational model. The analogs were created by systematically modifying the donor and the acceptor sides of FDDNP to learn the structural requirements for optimal binding to Aβ aggregates. FDDNP and its analogs are neutral, environmentally sensitive, fluorescent molecules with high dipole moments, as evidenced by their spectroscopic properties and dipole moment calculations. The preferred solution-state conformation of these compounds is directly related to the binding affinities. The extreme cases were a nonplanar analog t-butyl-FDDNP, which shows low binding affinity for Aβ aggregates (520 nM $K_i$) in vitro and a nearly planar tricyclic analog cDDNP, which displayed the highest binding affinity (10 pM $K_i$). Using a previously published X-ray crystallographic model of 1,1-dicyano-2-[6-(dimethylamino) naphthalen-2-yl]propene (DDNP) bound to an amyloidogenic Aβ peptide model, we show that the binding affinity is inversely related to the distortion energy necessary to avoid steric clashes along the internal surface of the binding channel.

- Neuron-Targeted Copolymers with Sheddable Shielding Blocks Synthesized Using a Reducible, RAFT-ATRP Double-Head Agent

Abstract:
Adaptation of in vitro optimized polymeric gene delivery systems for in vivo use remains a significant challenge. Most in vivo applications require particles that are stericly stabilized, which significantly compromises transfection efficiency of materials shown to be effective in vitro. We present a multifunctional well-defined block copolymer that forms particles useful for cell targeting, reversible shielding, endosomal release, and DNA condensation. We show that targeted and stabilized particles retain transfection efficiencies comparable to the nonstabilized formulations. A novel, double-head agent that combines a reversible addition–fragmentation chain transfer agent and an atom transfer radical polymerization initiator through a disulfide linkage is used to synthesize a well-defined cationic block copolymer containing a hydrophilic oligoethylene glycol and a tetraethylene pentamine-grafted polycation. This material effectively condenses plasmid DNA into salt-stable particles that deshield under intracellular reducing conditions. In vitro transfection studies show that the reversibly shielded polyplexes afford up to 10-fold higher transfection efficiencies than the analogous stably shielded polymer in four different mammalian cell lines. To compensate for reduced cell uptake caused by the hydrophilic particle shell, a neuron-targeting peptide is further conjugated to the terminus of the block copolymer. Transfection of neuron-like, differentiated PC-12 cells demonstrates that combining both targeting and deshielding in stabilized particles yields formulations that are suitable for in vivo delivery without compromising in vitro transfection efficiency and are thus promising carriers for in vivo gene delivery applications.

- **Antibody-Linked Spherical Nucleic Acids for Cellular Targeting**

  **Abstract:**

  Spherical nucleic acid (SNA) constructs are promising new single entity gene regulation materials capable of both cellular transfection and gene knockdown, but thus far are promiscuous structures, exhibiting excellent genetic but little cellular selectivity. In this communication, we describe a strategy to impart targeting capabilities to these constructs through noncovalent functionalization with a complementary antibody-DNA conjugate. As a proof-of-concept, we designed HER2-targeting SNAs and demonstrated that such structures exhibit cell type selectivity in terms of their uptake, and significantly greater gene knockdown in cells overexpressing the target antigen as compared to the analogous antibody-free and off-target materials.
• Synthesis of Thieno-Bridged Porphyrins: Changing the Antiaromatic Contribution by the Direction of the Thiophene Ring

Abstract:
Two types of thieno-bridged porphyrins were synthesized by incorporating a thiophene group across their meso and β positions with different directions of the thiophene ring to investigate the aromaticity of these porphyrins with extended r-systems. The 2,3-thieno-bridged porphyrin showed a larger antiaromatic contribution than did the 3,4-thieno-bridged porphyrin. In the former, the antiaromatic contribution is based on a 20-π-electron conjugated circuit. The two thieno-bridged porphyrins were characterized by calculations of nucleus-independent chemical shift and anisotropy of the induced current density as well as by X-ray crystallography, NMR spectroscopy, UV–vis–NIR absorption spectroscopy, electrochemical studies, time-resolved excited-state analysis, and two-photon absorption cross section measurements. Chemical derivatization of the 2,3-thieno-bridged porphyrin was also demonstrated.

• Populated Intermediates in the Thermal Unfolding of the Human Telomeric Quadruplex

Abstract:
Thermal denaturation profiles of several model oligonucleotides of the human telomere DNA sequence including d[A(GGGTTA)3GGG] (Tel22) were determined using circular dichroism (CD), fluorescence of adenine → 2-aminopurine analogs, and fluorescence resonance energy transfer (FRET) to monitor the unfolding process at specific locations within the quadruplex. The resulting optical spectra vs temperature data matrices were analyzed by singular value decomposition (SVD) to ascertain the minimum number of species required to reproduce the unfolding spectral profiles. Global nonlinear least-squares fitting of the SVD amplitude vectors was used to estimate thermodynamic parameters and optical spectra of all species for a series of unfolding mechanisms that included one-, two-, and three-step sequential pathways F → Iₙ → U, n = 0, 1, or 2) as well as two mechanisms with spectroscopically distinct starting structures (F₁ and F₂). The CD and FRET data for Tel22 unfolding between 4 and 94 °C in 25 mM KCl were best described by a sequential unfolding model with two intermediates, while the 2-aminopurine analogs required one intermediate. The higher melting intermediate I₂ had a transition midpoint temperature (Tₘ) of 61 °C and a CD spectrum with a maximum and minimum at 265 and 245 nm, respectively. The fluorescence emission
spectra of the 2-aminopurine and FRET derivatives suggest greater solvent exposure of the 5'-AGGGTTA- segment in the intermediate compared to the folded state. The spectroscopic properties of the 61 °C intermediate suggest that it may be a triple helical structure.

- Improvement of Interfacial Contacts for New Small-Molecule Bulk-Heterojunction Organic Photovoltaics
  Abstract:

  The influence of protonation reactions between poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) and a thiazolo[3,4-c]pyridine small-molecule donor are reported; these result in poor solar-cell performance due to a barrier for charge extraction. The use of a NiOx contact eliminates such deleterious chemical interactions and results in substantial improvements in open-circuit voltage, fill factor, and an increased power conversion efficiency from 2.3% to 5.1%.

- Flexible Three-Dimensional Organic Field-Effect Transistors Fabricated by an Imprinting Technique
  Abstract:
Flexible three-dimensional organic field-effect transistors with high performance are developed utilizing simple imprint technology. Owing to the multiplied vertical channels with short channel length of 0.9 μm, the devices show high output current density and fast dynamic response within 140 ns, which corresponds to as high as 7 MHz. The present fabrication process using imprint technique has advantages in low-cost, a high throughput, and easy processes.

- A Solid Advancement for Dye-Sensitized Solar Cells  
  Abstract:

Switching to solids: Solid-state dye-sensitized solar cells are achieving efficiencies similar to those of their counterparts with liquid electrolytes. The new p-type semiconductor CsSnI3 was found to be an excellent replacement for the traditional I−/I3− redox system. The picture shows a cross section of a dye-sensitized solar cell based on CsSnI3.

- Multivalency as a Chemical Organization and Action Principle  
  Abstract:

Multivalent interactions can be applied universally for a targeted strengthening of an interaction between different interfaces or molecules. The binding partners form cooperative, multiple receptor–ligand interactions that are based on individually weak, noncovalent bonds and are thus generally reversible. Hence, multi- and polyvalent interactions play a decisive role in biological systems for recognition, adhesion, and signal processes. The scientific and practical realization of this principle will be demonstrated by the development of simple artificial and theoretical models, from natural systems to functional, application-oriented systems. In a systematic review of scaffold architectures, the underlying effects and control options will be demonstrated, and suggestions will be given for designing effective multivalent binding systems, as well as for polyvalent therapeutics.
Flexible Vertical Light Emitting Diodes

Abstract:

Strategies are presented to achieve ultrathin light-emitting diodes using the technique of epitaxial liftoff in ways that protect the materials from the etchants used for release and tether the devices to the underlying wafer for subsequent transfer printing onto substrates of interest. The results lead to an advanced interconnection scheme and vertical device layout that facilitate electrical contacts and system integration on flexible substrates.

Electrophoretic Build-Up of Alternately Multilayered Films and Micropatterns Based on Graphene Sheets and Nanoparticles and their Applications in Flexible Supercapacitors

Abstract:

Graphene nanosheets and metal nanoparticles (NPs) have been used as nano-building-blocks for assembly into macroscale hybrid structures with promising performance in electrical devices. However, in most graphene and metal NP hybrid structures, the graphene sheets and metal NPs (e.g., AuNPs) do not enable control of the reaction process, orientation of building blocks, and organization at the nanoscale. Here, an electrophoretic layer-by-layer assembly for constructing multilayered reduced graphene oxide (RGO)/AuNP films and lateral micropatterns is presented. This
assembly method allows easy control of the nano-architecture of building blocks along the normal direction of the film, including the number and thickness of RGO and AuNP layers, in addition to control of the lateral orientation of the resultant multilayered structures. Conductivity of multilayered RGO/AuNP hybrid nano-architecture shows great improvement caused by a bridging effect of the AuNPs along the out-of-plane direction between the upper and lower RGO layers. The results clearly show the potential of electrophoretic build-up in the fabrication of graphene-based alternately multilayered films and patterns. Finally, flexible supercapacitors based on multilayered RGO/AuNP hybrid films are fabricated, and excellent performance, such as high energy and power densities, are achieved.

- Structural analysis of strained quantum dots using nuclear magnetic resonance

  Abstract:

  Strained semiconductor nanostructures can be used to make single-photon sources, detectors and photovoltaic devices, and could potentially be used to create quantum logic devices. The development of such applications requires techniques capable of nanoscale structural analysis, but the microscopy methods typically used to analyse these materials are destructive. NMR techniques can provide non-invasive structural analysis, but have been restricted to strain-free semiconductor nanostructures because of the significant strain-induced quadrupole broadening of the NMR spectra. Here, we show that optically detected NMR spectroscopy can be used to analyse individual strained quantum dots. Our approach uses continuous-wave broadband radiofrequency excitation with a specially designed spectral pattern and can probe individual strained nanostructures containing only $1 \times 105$ quadrupole nuclear spins. With this technique, we are able to measure the strain distribution and chemical composition of quantum dots in the volume occupied by the single confined electron. The approach could also be used to address problems in quantum information processing such as the precise control of nuclear spins in the presence of strong quadrupole effects.

- Photocurrent of a single photosynthetic protein

  Abstract:
Photosynthesis is used by plants, algae and bacteria to convert solar energy into stable chemical energy. The initial stages of this process—where light is absorbed and energy and electrons are transferred—are mediated by reaction centres composed of chlorophyll and carotenoid complexes. It has been previously shown that single small molecules can be used as functional components in electric and optoelectronic circuits, but it has proved difficult to control and probe individual molecules for photovoltaic and photoelectrochemical applications. Here, we show that the photocurrent generated by a single photosynthetic protein—photosystem I—can be measured using a scanning near-field optical microscope set-up. One side of the protein is anchored to a gold surface that acts as an electrode, and the other is contacted by a gold-covered glass tip. The tip functions as both counter electrode and light source. A photocurrent of ~10 pA is recorded from the covalently bound single-protein junctions, which is in agreement with the internal electron transfer times of photosystem I.

- **PEGylated PRINT Nanoparticles: The Impact of PEG Density on Protein Binding, Macrophage Association, Biodistribution, and Pharmacokinetics**

  **Abstract:**

  In this account, we varied PEGylation density on the surface of hydrogel PRINT nanoparticles and systematically observed the effects on protein adsorption, macrophage uptake, and circulation time. Interestingly, the density of PEGylation necessary to promote a long-circulating particle was dramatically less than what has been previously reported. Overall, our methodology provides a rapid screening technique to predict particle behavior in vivo and our results deliver further insight to what PEG density is necessary to facilitate long-circulation.
• Water-Driven Micromotors
  **Abstract:**

  We demonstrate the first example of a water-driven bubble-propelled micromotor that eliminates the requirement for the common hydrogen peroxide fuel. The new water-driven Janus micromotor is composed of a partially coated Al–Ga binary alloy microsphere prepared via microcontact mixing of aluminum microparticles and liquid gallium. The ejection of hydrogen bubbles from the exposed Al–Ga alloy hemisphere side, upon its contact with water, provides a powerful directional propulsion thrust. Such spontaneous generation of hydrogen bubbles reflects the rapid reaction between the aluminum alloy and water. The resulting water-driven spherical motors can move at remarkable speeds of 3 mm s⁻¹ (*i.e.*, 150 body length s⁻¹), while exerting large forces exceeding 500 pN. Factors influencing the efficiency of the aluminum–water reaction and the resulting propulsion behavior and motor lifetime, including the ionic strength and environmental pH, are investigated. The resulting water-propelled Al–Ga/Ti motors move efficiently in different biological media (*e.g.*, human serum) and hold considerable promise for diverse biomedical or industrial applications.

• Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication
  **Abstract:**

  This Viewpoint highlights the ability of molecular bottlebrushes to serve as highly tunable building blocks for creating nanostructured materials via molecular templating, solution aggregation, and melt self-assembly. Recent achievements in the synthesis of discrete nano-objects, micellar structures, and periodic nanomaterials from bottlebrush copolymers are emphasized, and future opportunities in this area of polymer science are briefly discussed.

• Soybean Oil Based Fibers Made Without Solvent or Heat
  **Abstract:**
Thiol–ene chemistry was harnessed to enable production of thermochemically stable thermoset fibers containing 50–87 wt % acrylated epoxidized soybean oil and 49–72% biobased carbon without using solvent or heat. In this demonstration, the fibers were made by simultaneous electrospinning and photocuring of a liquid monomer mixture, which could be translated to other fiber manufacturing processes such as melt blowing or Force spinning. Scanning electron micrographs illustrate the fiber quality and an average diameter of about 30 μm. Photochemical conversion kinetics of functional groups during light exposure were measured by real-time Fourier transform infrared spectroscopy, providing insight into the advantages of using high-functionality monomers and thiol–ene chemistry in this application.

- Construction of Fullerocyclobutene Derivatives through Copper(I)-Mediated Radical Annulation of C₆₀Cl₆ with Aryl Acetylenes
  Abstract:

  ![Image of Fullerocyclobutene Derivatives]

  Have a radical ball! Reaction of C₆₀Cl₆ with aryl acetylenes through a copper(I)-mediated annulation route to form fullerocyclobutene derivatives is reported. The fullerocyclobutenes are obtained in 36–53% yields and a possible radical mechanism is proposed for this novel reaction.

- Organocatalytic One-Pot Oxidative Cleavage of Terminal Diols to Dehomologated Carboxylic Acids
  Abstract:

  ![Image of Organocatalytic One-Pot Oxidative Cleavage]

  The organocatalytic one-pot oxidative cleavage of terminal 1,2-diols to one-carbon-unit-shorter carboxylic acids is described. The combination of 1-Me-AZADO (cat.), NaOCl (cat.), and NaClO₂ caused smooth one-pot oxidative cleavage under mild conditions. A broad range of substrates including
carbohydrates and N-protected amino diols were converted without epimerization. Terminal triols and tetraols respectively underwent cleavage of their C-2 and C-3 moieties to afford their corresponding two- and three-carbon-unit-shorter carboxylic acids.

- Selecting speed-dependent pathways for a programmable nanoscale texture by wet interfaces


  **Abstract:**

  The realization of well-defined and ordered structures on the nanoscale is a main issue in nanoscience and nanotechnology, biotechnology and other related fields like plastic or organic electronics. Among the bottom-up approaches, to date, self-assembly (equilibrium aggregates) received a major attention. In spite of this, far from equilibrium conditions allow for the generation of a wider landscape of organized systems depending on the set of control parameters employed. Under an adaptation vision of the structures, here we report some case studies showing how it is possible to programme and control the nanoscale features of ordered super- or supra-aggregates at wet interfaces by modulating the dynamic parameters. In particular, speed is foreseen as a threshold factor for changing the aggregation mechanism along with the shape and degree of order of the structures as well as, within a specific aggregation path, their size and defectivity.

- 5-Hydroxymethylcytosine – the elusive epigenetic mark in mammalian DNA


  **Abstract:**

  Over the past decade, epigenetic phenomena claimed a central role in cell regulatory processes and proved to be important factors for understanding complex human diseases. One of the best understood epigenetic mechanisms is DNA methylation. In the mammalian genome, cytosines (C) were long known to exist in two functional states: unmethylated or methylated at the 5-position of
the pyrimidine ring (5mC). Recent studies of genomic DNA from the human and mouse brain, neurons and from mouse embryonic stem cells found that a substantial fraction of 5mC in CpG dinucleotides is converted to 5-hydroxymethyl-cytosine (hmC) by the action of 2-oxoglutarate- and Fe(II)-dependent oxygenases of the TET family. These findings provided important clues in a long elusive mechanism of active DNA demethylation and bolstered a fresh wave of studies in the area of epigenetic regulation in mammals. This review is dedicated to critical assessment of the most popular techniques with respect to their suitability for analysis of hmC in mammalian genomes. It also discusses the most recent data on biochemical and chemical aspects of the formation and further conversion of this nucleobase in DNA and its possible biological roles in cell differentiation, embryogenesis and brain function.

- Deep-Blue-Emitting Heteroleptic Iridium(III) Complexes Suited for Highly Efficient Phosphorescent OLEDs
  Abstract:

  We report on the design, synthesis, and characterization of four new heteroleptic iridium(III) complexes bearing 2′,6′-difluoro-2,3′-bipyridine and pyridyl-azole ligands. The photophysical properties and cyclic voltammetry of the complexes were also investigated. All compounds display highly efficient genuine blue phosphorescence ($\lambda_{max}$ ca. 440 nm), at room temperature in solution and in thin film, with quantum yield in the range 0.77–0.87 and 0.62–0.93, respectively. We found that introduction of the bulky tert-butyl substituents on the cyclometalated or azolated chelates can effectively reduce detrimental aggregation, which results in a loss of color purity. Comprehensive density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches have been performed on the ground and excited states of the here reported complexes, in order to gain deeper insights into their structural and electronic features as well as to ascertain the nature of the excited states involved into the electronic absorption processes. Moreover, electron spin density analysis and total electron density difference at the lowest-lying triplet state (T$_1$) were performed for shedding light onto the nature of the emitting excited state. Finally, the fabrication of the organic light-emitting diodes (OLEDs), employing the bulkiest derivative among the here reported phosphorescent dopants, was successfully made. The devices exhibit remarkable maximum external quantum efficiency (EQE) as high as 7.0%, in nonoptimized devices, and power efficiency (PE) of 4.14 lm W$^{-1}$, together with a true-blue chromaticity $CIE_{xy} = 0.159, 0.185$ recorded at 300 cd m$^{-2}$.

- Multistimuli Responsive Dendritic Organogels Based on Azobenzene-Containing Poly(aryl ether) Dendron
A new poly(benzyl ether) dendritic organogelator Azo-G3 containing azobenzene in its inner layer was designed and synthesized, and fully characterized. The dendron Azo-G3 was found to be a highly efficient and versatile organogelator toward various apolar and polar organic solvents with the critical gelation concentrations (CGCs) approaching 0.05 wt %, indicating that the dendron belongs to the category of supergelators. Further studies revealed that the intermolecular multiple π–π stacking interactions might be responsible for guiding the self-assembly processes and the gel formation. Most interestingly, these dendritic organogels exhibited multiple stimuli-responsive behaviors upon exposure to environmental stimuli including temperature, sonication, light, and shear stress.

- Designed synthesis of a metal cluster-pillared coordination cage
  Abstract:

An unprecedented polynuclear metal cluster-pillared triangular prism was built by a macrocycle-directing strategy. Discrete architectures of three silver cluster-involved metallosupramolecules were characterized by single crystal X-ray crystallography and spectroscopy studies.

- Bis(benzimidazolium) axles and crown ether wheels: a versatile templating pair for the formation of [2]rotaxane molecular shuttles
  Abstract:
Condensation of an aldehyde appended benzimidazolium cation with a 1,2-benzenediamine in the presence of a crown ether allows formation of a second benzimidazole group and the facile synthesis of a [2]rotaxane molecular shuttle. The ease of this reaction and the versatility of the initial templating interaction between the benzimidazolium cation and crown ether allows for the preparation of [2]rotaxane molecular shuttles with crown ether macrocycles of various shapes and sizes. The synthesis and dynamic properties of a set of five [2]rotaxane molecular shuttles are described including the first examples of rotaxanes containing the larger macrocycles dibenzo[30]crown-10 (DB30C10) and bis-meta-phenylene-[26]crown-8 (BMP26C8).