Copper-Catalyzed Direct Alkynylation of Electron-Deficient Polyfluoroarenes with Terminal Alkynes Using O₂ as an Oxidant
 Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M. J. Am. Chem. Soc. 2010, 132, 2522–2223.
 <u>Abstract:</u>



A copper-catalyzed direct alkynylation of electron-deficient polyfluoroarenes with a wide range of terminal alkynes is realized for the first time. The reaction proceeds under mild conditions with O2 as an oxidant.

 Glycodynamers: Dynamic Polymers Bearing Oligosaccharides Residues – Generation, Structure, Physicochemical, Component Exchange, and Lectin Binding Properties Ruff, Y.; Buhler, E.; Candau, S. J.; Kesselman, E.; Talmon, Y.; Lehn, J. M. J. Am. Chem. Soc. 2010, 132, 2573–2584.

Abstract:



Dynamic glycopolymers have been generated by polycondensation through acylhydrazone formation between components bearing lateral bioactive oligosaccharide chains. They have been characterized as bottlebrush type by cryo-TEM and SANS studies. They present remarkable fluorescence properties whose emission wavelengths depend on the constitution of the polymer and are tunable by constitutional modification through exchange/incorporation of components, thus also demonstrating their dynamic character. Constitution-dependent binding of these glycodynamers to a lectin, peanut agglutinin, has been demonstrated.

Selective Pairwise Encapsulation Using Directional Interactions
 Gil-Ramirez, G.; Chas, M.; Ballester, P. J. Am. Chem. Soc. 2010, 132, 2520–2521.
 <u>Abstract:</u>



Trimethylamine *N*-oxide and trimethylphosphine oxide guests are pairwise encapsulated in a dimeric capsule self-assembled from a tetraurea aryl extended calix[4]pyrrole. The capsule possesses polar functional groups in its interior capable of controlling the orientation of the included guests. A modest selectivity is observed during the encapsulation process that is beyond the controls of size or shape exclusion.

• Dynamic Copper(I) Imaging in Mammalian Cells with a Genetically Encoded Fluorescent Copper(I) Sensor

Wegner, S. V.; Arslan, H.; Sunbul, M.; Yin, J.; He, C. *J. Am. Chem. Soc.* **2010**, *132*, 2567–2569. <u>Abstract:</u>



Copper, a key cofactor for many life processes, is toxic at elevated levels, and its availability is strictly controlled inside cells. Therefore, it is a challenge to visualize copper availability in the tight copperbinding environment of the cell. We report a genetically encoded fluorescent copper(I) sensor based on the copper(I)-binding-induced conformational change of a copper-responsive transcriptional regulator, Amt1. The resulting reporter, Amt1-FRET, is ratiometric, highly sensitive ($K_d = 2.5 \times 10^{-18}$ M), and selective toward copper(I). Its measured high affinity to copper(I) confirms the extremely low copper availability in yeast since Amt1 senses the upper limit of cellular copper levels in yeast and activates copper detoxification genes. Amt1-FRET operates in the dynamic range of the cellular copper buffer in mammalian cells and can report dynamic fluctuations of the cellular copper availability within minutes of perturbation. Thus, Amt1-FRET visualizes the tightly controlled copper availability in mammalian cells.

 A Contractile Electronic Switch Made of DNA Huang, Y. C.; Sen, D. J. Am. Chem. Soc. 2010, 132, 2663–2671. <u>Abstract:</u>



Double-helical DNA has been shown to conduct both electrons and electron holes, the latter over distances of >20 nm. DNA is thus a material of significant interest for the bottom-up construction of nanocircuitry. Here, we describe a contractile DNA nanoswitch, which can toggle between a structurally extended "off" state and a contracted "on" state, with a 40-fold conductivity difference between the two. To turn on, two short motifs of guanine–guanine mismatches in an otherwise standard double helix synapse to form a conductive G-quadruplex, bypassing an insulating element within the helix. This switch can be turned repeatedly on by treatment with millimolar concentrations of K⁺ and turned off by sequestration of the K⁺ by a crown ether. Circular dichroism and thymine–thymine photocross-linking experiments reveal that strand orientations within the on state G-quadruplex are wholly antiparallel and that the two conductive double-helices interface with the same face of the quadruplex. Although this DNA nanoswitch is chemically gated, it should be adaptable to other kinds of gating and thus serve as a prototype for increasingly sophisticated and complex electronic devices made of DNA.

 Solution structure of a DNA double helix with consecutive metal-mediated base pairs Johannsen, S.; Megger, N.; Bohme, D.; Sigel, R. K. O.; Muller, J. *Nature Chemistry* 2010, 2, 229-234.
 Abstract:



The incorporation of non-natural base pairs into double-stranded DNA, especially those mediated by metal–ligand interactions, offers new opportunities for synthetic DNA materials. The structural implications of such modifications will help guide developments in this area, and a solution structure of a B-type DNA duplex containing consecutive metal-mediated base pairs has now been elucidated.

A palladium-catalysed enolate alkylation cascade for the formation of adjacent quaternary 4 and tertiary stereocentres
 Streuff, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M. *Nature Chemistry* 2010, *2*, 192-196.
 Abstract:



The selective construction of multiple adjacent stereocentres is an important challenge for synthetic organic methodology, and only a handful of catalytic methods exist that can forge adjacent quaternary and tertiary stereocentres. Here, a palladium-catalysed multiple-bond-forming cascade leads to the construction of such systems in high yield, diastereomeric ratio and enantiomeric excess.

• Formation and Superlattice of Long-Range-Ordered Self-Assembled Monolayers of Pentafluorobenzenethiols on Au(111)

Kang, H.; Lee, N.-S.; Ito, E.; Hara, M.; Noh, J. *Langmuir* **2010**, *26*, 2983–2985. <u>Abstract:</u>



The formation and surface structure of pentafluorobenzenethiol (PFBT) self-assembled monolayers (SAMs) on Au(111) formed under various experimental conditions were examined by means of scanning tunneling microscopy (STM). Although it is well known that PFBT molecules on metal surfaces do not form ordered SAMs, we clearly revealed for the first time that the adsorption of PFBT on Au(111) at 75 °C for 2 h yields long-range, well-ordered self-assembled monolayers having a (2 × 5V13)R30° superlattice. Our results will provide new insight into controlling the structural order of PFBT SAMs, which will be very useful in precisely tailoring the interface properties of metal surfaces in electronic devices.

• Fabrication of Porous Hierarchical Polymer/Ceramic Composites by Electron Irradiation of Organic/Inorganic Polymers: Route to a Highly Durable, Large-Area Superhydrophobic Coating

Lee, E. J.; Kim J. J.; Oh Cho, J. *Langmuir* **2010**, *26*, 3024–3030. <u>Abstract:</u>



Polymer/ceramic composite films with micro- and nanocombined hierarchical structures are fabricated by electron irradiation of poly(methyl methacrylate) (PMMA) microspheres/silicone grease. Electron irradiation induces volume contraction of PMMA microspheres and simultaneously

transforms silicone grease into a ceramic material of silicon oxycarbide with many nanobumps. As a result, highly porous structures that consist of micrometer-sized pores and microparticles decorated with nanobumps are created. The fabricated films with the porous hierarchical structure exhibit good superhydrophobicity with excellent self-cleaning and antiadhesion properties after surface treatment with fluorosilane. In addition, the porous hierarchical structures are covered with silicon oxycarbide, and thus the superhydrophobic coatings have high hardness and strong adhesion to the substrate. The presented technique provides a straightforward route to producing large-area, mechanically robust superhydrophobic films on various substrate materials.

 Sugar-Decorated Sugar Vesicles: Lectin-Carbohydrate Recognition at the Surface of Cyclodextrin Vesicles Voskuhl, J.; Stuart, M. C. A.; Ravoo, B. J. *Chem. Eur. J.* 2010, *16*, 2790-2796. <u>Abstract:</u>



An artificial glycocalix self-assembles when unilamellar bilayer vesicles of amphiphilic β -cyclodextrins are decorated with maltose and lactose by host-guest interactions. To this end, maltose and lactose were conjugated with adamantane through a tetra(ethyleneglycol) spacer. Both carbohydrateadamantane conjugates strongly bind to β -cyclodextrin ($K_a \approx 4 \times 10^4 \text{ M}^{-1}$). The maltose-decorated vesicles readily agglutinate (aggregate) in the presence of the lectin concanavalin A, whereas the lactose-decorated vesicles agglutinate in the presence of peanut agglutinin. The orthogonal multivalent interaction in the ternary system of host vesicles, guest carbohydrates, and lectins was investigated by using isothermal titration calorimetry, dynamic light scattering, UV/Vis spectroscopy, and cryogenic transmission electron microscopy. It was shown that agglutination is reversible, and the noncovalent interaction can be suppressed and eliminated by the addition of competitive inhibitors, such as D-glucose or β -cyclodextrin. Also, it was shown that agglutination depends on the surface coverage of carbohydrates on the vesicles.

Vectorial Electron Transfer in Donor-Photosensitizer-Acceptor Triads Based on Novel Bistridentate Ruthenium Polypyridyl Complexes
 Kumar, R. J.; Karlsson, S.; Streich, D.; Rolandini Jensen, A.; Jäger, M.; Becker, H.-C.; Bergquist, J.; Johansson, O.; Hammarström, L. Chem. Eur. J. 2010, 16, 2830-2842.
 <u>Abstract:</u>



The first examples of rodlike donor-photosensitizer-acceptor arrays based on bis-2,6-di(quinolin-8-yl)pyridine Ru^{II} complexes 1a and 3a for photoinduced electron transfer have been synthesized and

investigated. The complexes are synthesized in a convergent manner and are isolated as linear, single isomers. Time-resolved absorption spectroscopy reveals long-lived, photoinduced charge-separated states (τ_{CSS} (1a)=140 ns, τ_{CSS} (3a)=200 ns) formed by stepwise electron transfer. The overall yields of charge separation (\geq 50 % for complex 1a and \geq 95 % for complex 3a) are unprecedented for bistridentate Ru^{II} polypyridyl complexes. This is attributed to the long-lived excited state of the [Ru(dqp)₂]²⁺ complex combined with fast electron transfer from the donor moiety following the initial charge separation. The rodlike arrangement of donor and acceptor gives controlled, vectorial electron transfer, free from the complications of stereoisomeric diversity. Thus, such arrays provide an excellent system for the study of photoinduced electron transfer and, ultimately, the harvesting of solar energy.

 Total Synthesis of Chloptosin, a Potent Apoptosis-Inducing Cyclopeptide Yu, S.-M.; Hong, W.-X.; Wu, Y.; Zhong, C.-L.; Yao, Z.-J. Org. Lett. 2010, 12, 1124–1127. <u>Abstract:</u>



A bidirectional total synthesis of chloptosin has been achieved in 16 operations (32 individual reactions) and 3% overall yield from the readily available materials. Palladium-catalyzed tryptophan synthesis, diastereoselective selenocyclization and oxidative deselenation successfully served as key steps in construction of the dimeric core amino acid. 2-Bromo-1-ethyl pyridinium tetrafluoroborate was efficiently employed in the peptide couplings with spatial encumbrance in this synthesis.

 Unsymmetrical Triangular Schiff Base Macrocycles with Cone Conformations Jiang, J.; MacLachlan, M. J. Org. Lett. 2010, 12, 1020–1023.
 <u>Abstract:</u>



Two new unsymmetrical Schiff base macrocycles with isosceles triangle shapes have been prepared. The macrocycles adopt cone-shaped conformations that rapidly interconvert at high temperature. Dynamic NMR studies show that the macrocycle that is tautomerized to the keto-enamine isomer is slower to flip than is the one in the enol-imine state. These macrocycles are good hosts for binding organic cations in their interiors.

• Poly(*N*-isopropylacrylamide) Gel Prepared Using a Hydrophilic Polyrotaxane-Based Movable Cross-Linker

Imran, A. B.; Seki, T.; Ito, K.; Takeoka, Y. *Macromolecules* **2010**, *43*, 1975–1980. <u>Abstract:</u>



A novel type of thermosensitive polymer gel was fabricated using a hydrophilic polyrotaxane as a movable cross-linker and *N*-isopropylacrylamide (NIPA) as a monomer. An optical transparence, mechanical softness, abnormal swelling capacity, and unprecedentedly fast thermosensitivity are among the salient features of this new polyNIPA gel in comparison with typical polyNIPA gels prepared by bifunctional cross-linker such as *N*,*N'*-methylenebisacrylamide (TN gels) and a previously reported polyNIPA gel using a hydrophobic polyrotaxane as a cross-linker. Whereas TN gels can take more than a day to undergo full deswelling in response to sudden temperature change, our new gel collapses in ~10 min. The hydrophilicity and movability of the cross-linker contribute to these unprecedented properties of this thermosensitive polyNIPA gel. Moreover, this new type of cross-linker can be applied to any of the conventional gels made by radical polymerization and will likely improve the stimuli responses and mechanical properties of the gels.

Hydrogen-Bond Engineering in Supramolecular Polymers: Polarity Influence on the Self-Assembly of Benzene-1,3,5-tricarboxamides
 Mes, T.; Smulders, M. M. J.; Palmans, A. R. A.; Meijer, E. W. *Macromolecules* 2010, 43, 1981–
 1991.
 <u>Abstract:</u>
 Solution
 Solution
 Solution



Benzene-1,3,5-tricarboxamides (BTAs) comprising alkyl side chains form supramolecular polymers in dilute solution and in the solid state as a result of the 3-fold helical arrangement of the intermolecular hydrogen bonds. We investigated systematically the role of polarity on the self-assembling behavior of BTAs in dilute solution and, when incorporated in polymeric materials, on their ability to phase segregate. In dilute solutions, the polarity was gradually increased by mixing in methyl *tert*-butyl ether (in which BTAs are molecularly dissolved) into methylcyclohexane (in which BTAs form stable helical aggregates). We observed a significant decrease in the stability of BTA aggregates after the addition of small amounts of ether. This strong dependence on the polarity with the BTA motif, a wide range of backbone polarities was covered. Commercially available polymers as well as polymers that were synthesized via ring-opening metathesis polymerization were evaluated. BTA motifs connected to apolar telechelics formed stable phase segregated nanorods. Increasing the polarity resulted in a decrease of the stability, and this eventually resulted in the loss of nanorod formation. This systematic study on the influence of polarity on self-assembly gives us a detailed understanding of the potential to use BTAs as functional nanorods in various applications.

• Microfluidic lab-on-a-chip platforms: requirements, characteristics and applications

Mark, D.; Haeberle, S.; Roth, G.; von Stetten, F.; Zengerle, R. *Chem. Soc. Rev.* **2010**, *39*, 1153 - 1182.

Abstract:



This critical review summarizes developments in microfluidic platforms that enable the miniaturization, integration, automation and parallelization of (bio-)chemical assays (see S. Haeberle and R. Zengerle, Lab Chip, 2007, 7, 1094-1110, for an earlier review). In contrast to isolated application-specific solutions, a microfluidic platform provides a set of fluidic unit operations, which are designed for easy combination within a well-defined fabrication technology. This allows the easy, fast, and cost-efficient implementation of different application-specific (bio-)chemical processes. In our review we focus on recent developments from the last decade (2000s). We start with a brief introduction into technical advances, major market segments and promising applications. We continue with a detailed characterization of different microfluidic platforms, comprising a short definition, the functional principle, microfluidic unit operations, application examples as well as strengths and limitations of every platform. The microfluidic platforms in focus are lateral flow tests, linear actuated devices, pressure driven laminar flow, microfluidic large scale integration, segmented flow microfluidics, centrifugal microfluidics, electrokinetics, electrowetting, surface acoustic waves, and dedicated systems for massively parallel analysis. This review concludes with the attempt to provide a selection scheme for microfluidic platforms which is based on their characteristics according to key requirements of different applications and market segments. Applied selection criteria comprise portability, costs of instrument and disposability, sample throughput, number of parameters per sample, reagent consumption, precision, diversity of microfluidic unit operations and the flexibility in programming different liquid handling protocols (295 references).

 Cationic Conjugated Polymers for Optical Detection of DNA Methylation, Lesions, and Single Nucleotide Polymorphisms
 Duan X : Liu L : Feng E : Wang S Acc. Chem Res 2010 43, 260–270

Duan, X.; Liu, L.; Feng, F.; Wang, S. Acc. Chem. Res. **2010**, 43, 260–270. Abstract:



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Simple, rapid, and sensitive technologies to detect nucleic acid modifications have important applications in genetic analysis, clinical diagnosis, and molecular biology. Because genetic modifications such as single nucleotide polymorphisms (SNP), DNA methylation, and other lesions can serve as hallmarks of human disease, interest in such methods has increased in recent years. This Account describes a new strategy for the optical detection of these DNA targets using cationic conjugated polymers (CCPs).

Because of their unique signal amplification properties, researchers have extensively investigated conjugated polymers as optical transducers in highly sensitive biosensors. Recently, we have shown that cationic polyfluorene can detect SNPs within the DNA of clinical samples. When we incorporated deoxyguanosine triphosphate (dGTP-FI) into the DNA chain at an SNP site where the target/probe pair is complementary, we observed higher fluorescence resonance energy transfer (FRET) efficiency between cationic polyfluorene and fluorescein label on the dGTP. By monitoring the change in emission intensity of cationic polyfluorene or fluorescein, we identified the homozygous or heterozygous SNP. The high sensitivity of this assay results from the 10-fold enhancement of fluorescein emission intensity by the FRET from polyfluorene. This method can detect allele frequencies (the proportion of all copies of a gene that is made up of a particular gene variant) as low as 2%. Using this novel method, we clearly discriminated among the SNP genotypes of 76 individuals of Chinese ancestry.

Improving on this initial system, we designed a method for multicolor and one-tube SNP genotyping assays based on cationic polyfluorene using fluorescein-labeled deoxyuridine triphosphate (dUTP-FI) and Cy3-labeled deoxycytidine triphosphate (dCTP-Cy3) in extension reactions. We also developed a one-step method for direct detection of SNP genotypes from genomic DNA by combining allele-specific PCR with CCPs. In 2008, we developed a new method for DNA methylation detection based on single base extension reaction and CCPs. Treatment of DNA with bisulfite followed by PCR amplification converts unmethylated DNA into a C/T polymorphism, which allows us to characterize the methylation status of the target DNA. Furthermore, we used CCPs to detect DNA lesions caused by ultraviolet light irradiation for the first time. By monitoring the color change of cationic polythiophene before and after DNA cleavage, we also detected oxidative damage to DNA by hydroxyl radical.

These CCP-based new assays avoid primer labeling, cumbersome workups, and sophisticated instruments, leading to simpler procedures and improved sensitivity. We expect that these features could lead to major advances in human disease diagnostics and genomic study in the near future.

• Hydrogen bonded aryl amide and hydrazide oligomers: a new generation of preorganized soft frameworks

Zhao, X.; Li, Z. T. *Chem. Commun.* **2010**, *46*, 1601 – 1616. <u>Abstract:</u>



Hydrogen bonded aryl amide and hydrazide foldamers may adopt folded, zigzag or other extended conformations, depending on the positions of the amides and hydrogen bonding sites on the aromatic rings. In recent years, several series of such preorganized frameworks have been developed as efficient acyclic receptors for binding both neutral and ionic guests. The backbones can also be readily modified and appended with discrete functional units. Therefore, they have also been widely utilized in designing new molecular tweezers, for assembling ordered supramolecular architectures, and for directing the formation of complicated macrocyclic systems. This feature article highlights the recent advances, with a primary focus on our own work.

 Self-organized nanofibers and nanorods of porphyrins bearing hydrogen bonding motifs Radivojevic, A.; Likhtina, I.; Shi, X.; Singh, S.; Drain, C. M. Chem. Commun. 2010, 46, 1643 -1645.

Abstract:



Porphyrins bearing uracyl motifs at the four meso positions self-organize via homo-complementary hydrogen bonds and -stacking into nanofibers, nanorods and thin films on mica and glass surfaces depending on deposition conditions.

 Total Synthesis of (_)-Haliclonacyclamine C Smith, B. J.; Sulikowski, G. A. Angew. Chem. Int. Ed. 2010, 49, 1599–1602. <u>Abstract:</u>



(+)-Haliclonacyclamine C

First in its class: The synthesis of the tetracyclic alkylpiperidine marine alkaloid (±)-haliclonacyclamine C has been completed, with a longest linear sequence of 24 steps. The key transformations are the stereoselective hydrogenation of an unsaturated macrocyclic bis(piperidine) and a ring-closing alkyne metathesis reaction.

 Induced-Fit Binding of the Macrocyclic Noncovalent Inhibitor TMC435 to its HCV NS3/NS4A Protease Target
 Cummings, M. D.; Lindberg, J.; Lin, T.-I.; de Kock, H.; Lenz, O.; Lilja, E.; Fellander, S.; Baraznenok, V.; Nyström, S.; Nilsson, M.; Vrang, L.; Edlund, M.; Rosenquist, A.; Samuelsson, B.; Raboisson, P.; Simmen, K. Angew. Chem. Int. Ed. 2010, 49, 1652 –1655.

Abstract:



If the shoe fits: TMC435, a noncovalent small-molecule inhibitor of the hepatitis C virus (HCV) NS3/NS4A protease, is currently undergoing clinical evaluation as an HCV therapeutic. In the crystal structure of the noncovalent NS3/NS4A protease-TMC435 complex the bound inhibitor exploits induced-fit binding. The new structure is consistent with the emerging view of viral resistance to NS3/NS4A protease inhibitors.

• Gel-expanded to gel-condensed transition in neurofilament networks revealed by direct force measurements

Beck, R.; Deek, J.; Jones, J. B.; Safinya, C. R. *Nature Materials* **2010**, *9*, 40-46. <u>Abstract:</u>



Neurofilaments (NF)—the principal cytoskeletal constituent of myelinated axons in vertebrates consist of three molecular- weight subunit proteins NF-L (low), NF-M (medium) and NF-H (high), assembled to form mature filaments with protruding unstructured C-terminus side arms1–5. Liquidcrystal gel networks of side-arm-mediated neurofilament assemblies have a key role in the mechanical stability of neuronal processes. Disruptions of the neurofilament network, owing to neurofilament over-accumulation or incorrect side- arm interactions, are a hallmark of motor-neuron diseases including amyotrophic lateral sclerosis3–9. Using synchrotron X-ray scattering, we report on a direct measurement of forces in reconstituted neurofilament gels under osmotic pressure (P). With increasing pressure near physiological salt and average phosphorylation conditions, NF-LMH, comprising the three subunits near in vivo composition, or NF-LH gels, undergo for P > Pc \approx 10 kPa, an abrupt non-reversible gel-expanded to gel-condensed transition. The transition indicates side-

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arm- mediated attractions between neurofilaments consistent with an electrostatic model of interpenetrating chains.

Highly efficient photocathodes for dye-sensitized tandem solar cells
 Nattestad, A.; Mozer, A. J.; Fischer, M. K. R.; Cheng, Y.-B.; Mishra, A.; Bäuerle, P.; Bach, U.
 Nature Materials 2010, 9, 31-35.



Thin-film dye-sensitized solar cells (DSCs) based on mesoporous semiconductor electrodes are lowcost alter- natives to conventional silicon devices1,2 . High-efficiency DSCs typically operate as photoanodes (n-DSCs), where photocurrents result from dye-sensitized electron injection into n-type semiconductors. Dye-sensitized photocathodes (p-DSCs) operate in an inverse mode, where dyeexcitation is followed by rapid electron transfer from a p-type semi- conductor to the dye(dyesensitized hole injection). Such p-DSCs and n-DSCs can be combined to construct tandem solar cells3 (pn-DSCs) with a theoretical efficiency limitation well beyond that of single-junction DSCs (ref. 4). Nevertheless, the efficiencies of such tandem pn-DSCs have so far been hampered by the poor performance of the available p-DSCs (refs 3, 5–15). Here we show for the first time that p-DSCs can convert absorbed photons to electrons with yields of up to 96%, resulting in a sevenfold increase in energy conversion efficiency compared with previously reported photocathodes. The donoracceptor dyes, studied as photocathodic sensitizers, comprise a variable-length oligothiophene bridge, which provides control over the spatial separation of the photo- generated charge carriers. As a result, charge recombination is decelerated by several orders of magnitude and tandem pn-DSCs can be constructed that exceed the efficiency of their individual components.