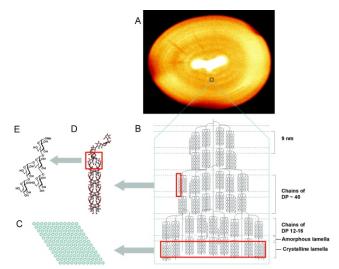
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 First Principles Insight into the r-Glucan Structures of Starch: Their Synthesis, Conformation, and Hydration

Damager, I.; Engelsen, S. B.; Blennow, A.; Møller, B. L.; Motawia, M. S. *Chem. Rev.* **2010**, *110*, 2049–2080.

Abstract:

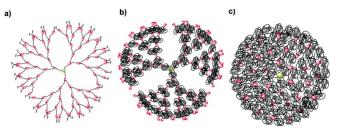


Carbohydrates constitute the most abundant group of organic compounds found in nature. Oxygenic photosynthesis, the process energizing carbon dioxide fixation in the biosphere, is estimated to 1011 tons of dry weight biomass per year, most of it being carbohydrate.1 For human consumption, the abundance of starch and the possibility to carry out large-scale purification, derivatization and processing provide unique and straightforward options to design starch crops harboring new valuable functionalities offering diversified uses in the food and nonfood sectors.2,3 These include raw materials for the design of advanced and healthy foods to combat obesity and other lifestyle-related diseases4 or to replace gelatin.

 Single-Electron Transfer and Single-Electron Transfer Degenerative Chain Transfer Living Radical Polymerization

Rosen, B. M.; Percec, V. Chem. Rev. 2009, 109, 5069-5119.

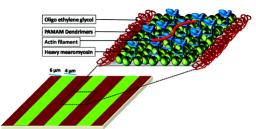
Abstract:



As we move forward through the 21st century, a major challenge for polymer chemistry will be to approach the complexity and fidelity of biological macromolecules via synthetic processes. The structural perfection of biological macromolecules is the result of enzymatically controlled and templated condensation polymerizations.1 Some progress has been made in harnessing biological polymerization for materials applications.2 However, it is free-radical polymerization, not condensation polymerization, that currently dominates in industrial applications and also in academic research, largely due to the broad array of compatible unsaturated monomers and relatively mild reaction conditions.

Application of Poly(amidoamine) Dendrimers for Use in Bionanomotor Systems
 Kolli, M. B.; Day, B. S.; Takatsuki, H.; Nalabotu, S. K.; Rice, K. M.; Kohama, K.; Gadde, M. K.,
 Kakarla, S. K.; Katta, A.; Blough, E. R. *Langmuir* 2010, 26, 6079–6082.

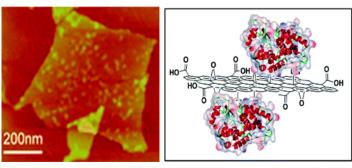
Abstract:



The study and utilization of bionanomotors represents a rapid and progressing field of nanobiotechnology. Here, we demonstrate that poly(amidoamine) (PAMAM) dendrimers are capable of supporting heavy meromyosin dependent actin motility of similar quality to that observed using nitrocellulose, and that microcontact printing of PAMAM dendrimers can be exploited to produce tracks of active myosin motors leading to the restricted motion of actin filaments across a patterned surface. These data suggest that the use of dendrimer surfaces will increase the applicability of using protein biomolecular motors for nanotechnological applications.

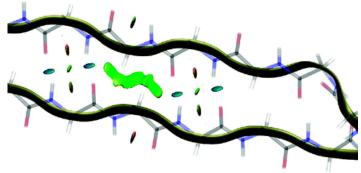
Graphene Oxide as a Matrix for Enzyme Immobilization
Zhang, J.; Zhang, F.; Yang, H.; Huang, X.; Liu, H.; Zhang, J.; Guo, S. Langmuir 2010, 26, 6083–6085.

Abstract:



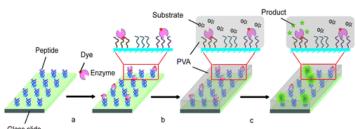
Graphene oxide (GO), having a large specific surface area and abundant functional groups, provides an ideal substrate for study enzyme immobilization. We demonstrated that the enzyme immobilization on the GO sheets could take place readily without using any cross-linking reagents and additional surface modification. The atomically flat surface enabled us to observe the immobilized enzyme in the native state directly using atomic force microscopy (AFM). Combining the AFM imaging results of the immobilized enzyme molecules and their catalytic activity, we illustrated that the conformation of the immobilized enzyme is mainly determined by interactions of enzyme molecules with the functional groups of GO.

Revealing Noncovalent Interactions
Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. J. Am. Chem. Soc. 2010, 132, 6498–6506.
Abstract:



Molecular structure does not easily identify the intricate noncovalent interactions that govern many areas of biology and chemistry, including design of new materials and drugs. We develop an approach to detect noncovalent interactions in real space, based on the electron density and its derivatives. Our approach reveals the underlying chemistry that compliments the covalent structure. It provides a rich representation of van der Waals interactions, hydrogen bonds, and steric repulsion in small molecules, molecular complexes, and solids. Most importantly, the method, requiring only knowledge of the atomic coordinates, is efficient and applicable to large systems, such as proteins or DNA. Across these applications, a view of nonbonded interactions emerges as continuous surfaces rather than close contacts between atom pairs, offering rich insight into the design of new and improved ligands.

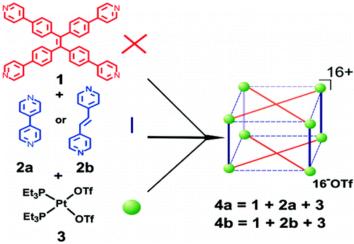
Exploring Peptide Space for Enzyme Modulators
Fu, J.; Cai, K.; Johnston, S. A.; Woodbury, N. W. J. Am. Chem. Soc. 2010, 132, 6419–6424.
Abstract:



A method is presented for screening high-density arrays to discover peptides that bind and modulate enzyme activity. A polyvinyl alcohol solution was applied to array surfaces to limit the diffusion of product molecules released from enzymatic reactions, allowing the simultaneous measurement of enzyme activity and binding at each peptide spot. For proof of concept, it was possible to identify peptides that bound to horseradish peroxidase, alkaline phosphatase, and β -galactosidase and substantially altered enzyme activity by comparing the binding level of peptide to enzyme and bound enzyme activity. This basic technique may be generally applicable to find peptides or other small molecules that modify enzyme activity.

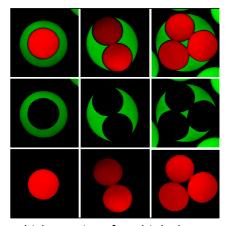
 Metallosupramolecular Tetragonal Prisms via Multicomponent Coordination-Driven Template-Free Self-Assembly
Wang, M.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. J. Am. Chem. Soc. 2010, 132, 6282–6283.

Abstract:



We present a general strategy for the synthesis of stable 3-D metallosupramolecular tetragonal prisms in which multicomponent coordination-driven self-assembly allows for single supramolecular species to be formed. The appropriate stoichiometric combination of a tetraphenylethylene-based tetratopic donor (1), a linear dipyridine donor (2), and a 90° platinum metal complex (3) affords tetragonal prisms (4) as single products. The compounds have been characterized by multinuclear NMR spectroscopy and electrospray ionization mass spectrometry. The size of the supramolecules was determined by pulsed-gradient spin–echo NMR and modeled with molecular force field simulation methods.

Smart Microgel Capsules from Macromolecular Precursors
Seiffert, S.; Thiele, J.; Abate, A. R.; Weitz, D. A. J. Am. Chem. Soc. 2010, 132, 6606–6609.
Abstract:

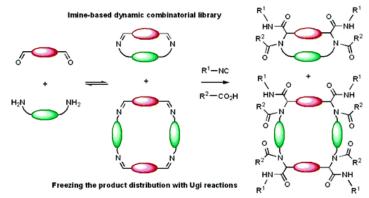


Microgel particles and capsules which consist of multiple layers can be fabricated using droplet microfluidics, but in existing methods, emulsion templating forms layers of dissimilar polarity. In this paper, we fabricate functional microgel capsules that consist of two *miscible* yet distinct layers. We use microfluidic devices to template micrometer-sized drops that are loaded with prepolymerized precursors and solidify them through a polymer-analogous reaction. This allows the particle morphology to be controlled and prevents pronounced interpenetration of the different layers despite their miscibility. We use polyacrylamide and poly(*N*-isopropylacrylamide) precursors to form thermoresponsive core–shell microparticles and demonstrate their utility for encapsulation and controlled release applications.

5

Freezing Imine Exchange in Dynamic Combinatorial Libraries with Ugi Reactions: Versatile
 Access to Templated Macrocycles

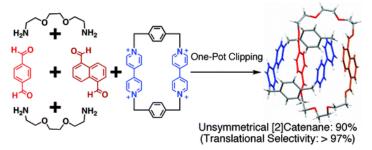
Wessjohann, L. A.; Rivera, D. G.; León, F. *Org. Lett.* **2007**, *9*, 4733–4736. <u>Abstract:</u>



A novel approach to freeze the imine exchange process in dynamic combinatorial libraries by Ugi reactions was developed. Macrocyclic oligoimine libraries previously formed and altered by addition of metal templates are efficiently quenched by multiple multicomponent reactions. The approach may be considered as an alternative to the typical reduction with borohydrides and delivers polyazamacrocycles with variable side arms. High dilution is not required to achieve high yields.

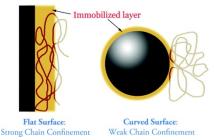
Dual Selectivity Expressed in [2 + 2 + 1] Dynamic Clipping of Unsymmetrical [2]Catenanes
Koshkakaryan, G.; Cao, D.; Klivansky, L. M.; Teat, S. J.; Tran, J. L.; Liu, Y. Org. Lett. 2010, 12, 1528–1531.

Abstract:



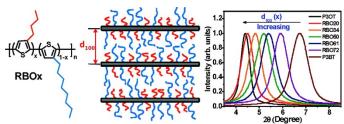
A π -templated dynamic [2 + 2 + 1] clipping protocol is established for the synthesis of [2]catenanes from two parts dialdehyde, two parts diamine, and one part tetracationic cyclophane. It is further diversified for the selective formation of an unsymmetrical [2]catenane showing great translational selectivity by employing two different dialdehydes in a one-pot reaction. The dual selectivity and the dynamic nature are verified by 1 H NMR spectroscopy, X-ray single-crystal structural studies, and exchange experiments.

Immobilized Polymer Layers on Spherical Nanoparticles
Harton, S. E.; Kumar, S. K.; Yang, H.; Koga, T.; Hicks, K.; Lee, H. K.; Mijovic, J.; Liu, M.; Vallery, R. S.; Gidley, D. W. *Macromolecules* 2010, 43, 3415–3421.
Abstract:



Polymer properties, such as their mechanical strength, barrier properties, and dielectric response, can be dramatically improved by the addition of nanoparticles. This improvement is thought to be because the surface area per unit mass of particles increases with decreasing particle size, R, as 1/R. This favorable effect has to be reconciled with the expectation that at small enough R the nanoparticles must behave akin to a solvent and cause a deterioration of properties. How does this transition in behavior from large solutes to the solvent limit occur? We conjecture that for small enough particles the layer of polymer affected by the particles ("bound" polymer layer) must be much smaller than that for large particles: the favorable effect of increasing particle surface area can thus be overcome and lead to the small solvent limit with unfavorable mechanical properties, for example. To substantiate this picture requires that we measure and compare the "bound polymer layer" formed on nanoparticles with those near large particles with equivalent chemistry. We have implemented a novel strategy to obtain uniform nanoparticle dispersion in polymers, a problem for many previous works. Then, by combining theory and a suite of experimental techniques, including differential scanning calorimetry and positron annihilation lifetime spectroscopy, we show that the immobilized poly(2-vinylpyridine) layer near 15 nm diameter silica particles (1 nm) is considerably thinner than that at flat silica surfaces (4 to 5 nm), which is the limit of an infinitely large particle. We have also determined that the changes in the polymer's glass-transition temperature due to the presence of this strongly interacting surface are very small in both well-dispersed nanocomposites and thin films (<100 nm). Similarly, the polymer's fragility, as determined by dielectric spectroscopy, is also found to be little affected in the nanocomposites relative to the pure polymer. While a systematic study of the dependence of the bound polymer layer thickness on particle size remains an outstanding challenge, this first study provides conclusive evidence for the hypothesis that the bound polymer layer can be significantly smaller around nanoparticles than at chemically similar flat surfaces.

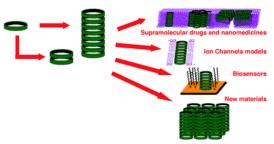
Crystalline Random Conjugated Copolymers with Multiple Side Chains: Tunable Intermolecular Interactions and Enhanced Charge Transport and Photovoltaic Properties Wu, P.-T.; Ren, G.; Jenekhe, S. A. *Macromolecules* 2010, 43, 3306–3313.
Abstract:



Random poly(3-butylthiophene-co-3-octylthiophene) of several compositions were synthesized and found to be highly crystalline in spite of the statistical arrangement of the different-sized side chains. The melting ($T_{\rm m}$) and recrystallization ($T_{\rm c}$) temperatures of the random copolythiophenes varied continuously with composition. The interlayer d_{100} stacking distance in the lamellar crystalline

structure of the random copolymers, determined from X-ray diffraction of films, varied linearly with copolymer composition over the entire range. Fullerene-based bulk heterojunction solar cells made from the random copolythiophenes had power conversion efficiencies of up to 3.0% under 100 mW/cm² AM1.5 illumination in air, which is significantly enhanced compared to the homopolymers and their physical blends. The space charge limited current mobility of holes in the random copolythiophenes was enhanced compared to poly(3-butylthiophene) and physical blends of the homopolymers. Transmission electron microscopy images of the bulk heterojunction thin films showed that the random copolythiophenes had a worm-like nanoscale phase-separated morphology beneficial to solar cells. These results demonstrate that random copolymerization and multiple-sized side chains provide a facile means of fine-tuning the structural and electronic/optoelectronic properties of conjugated polymers. The results also provided new insights on the lamellar crystalline packing of side-chain bearing conjugated polymers.

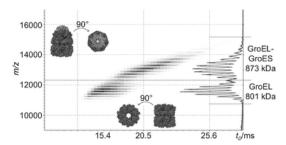
 Towards functional bionanomaterials based on self-assembling cyclic peptide nanotubes Brea, R. J.; Reiriz, C.; Granja, J. R. Chem. Soc. Rev. 2010, 39, 1448 – 1456.
Abstract:



In recent years, considerable effort has been devoted to the preparation of artificial nanotubular materials. One of the most successful approaches for the construction of noncovalently bonded nanotube entities is the self-assembly of cyclic polypeptides in stacks that are stabilized by hydrogen bonds. This *tutorial review* covers the history and current situation for synthetic organic nanostructures obtained from self-assembling cyclic peptides. In particular, we describe the evolution to cyclic peptides that not only allow the modification of the outer surface but also the inner cavity by paying special attention to peptide rings that contain cyclic γ -amino acids. In this respect, we describe the synthesis, properties and application of a new class of homo- and heterodimeric supramolecular assemblies that are precursors of cyclic α , γ -peptide nanotubes.

• Ion mobility mass spectrometry of proteins and protein assemblies Uetrecht, C.; Rose, R. J.; van Duijn, E.; Lorenzen, K.; Heck, A. J. R. *Chem. Soc. Rev.* **2010**, *39*, 1633 – 1655.

Abstract:



Traditionally, mass spectrometry has been a powerful analytical method enabling the structural analysis of small molecules, and later on peptides and proteins. With the advent of native mass

spectrometry, using a combination of electrospray ionisation and time of flight analysis, mass spectrometry could also be applied to the mass determination of large protein complexes such as ribosomes and whole viruses. More recently, ion mobility has been coupled to mass spectrometry providing a new dimension in the analysis of biomolecules, with ion mobility separating ions according to differences in size and shape. In the context of native mass spectrometry, ion mobility mass spectrometry opens up avenues for the detailed structural analysis of large and heterogeneous protein complexes, providing information on the stoichiometry, topology and cross section of these assemblies and their composite subunits. With these characteristics, ion mobility mass spectrometry offers a complementary tool in the context of structural biology. Here, we *critically review* the development, instrumentation, approaches and applications of ion mobility in combination with mass spectrometry, focusing on the analysis of larger proteins and protein assemblies (185 references).

 Golgi-modifying properties of macfarlandin E and the synthesis and evaluation of its 2,7dioxabicyclo[3.2.1]octan-3-one core

Schnermann, M. J.; Beaudry, C. M.; Egorova, A. V.; Polishchuk, R. S.; Sütterlin, C.; Overman, L. E. *Proc. Nat. Acad. Sci.* **2010**, *107*, 6158-6163.

Abstract:

Golgi-modifying properties of the spongian diterpene macfarlandin E (MacE) and a synthetic analog, *t*-Bu-MacE, containing its 2,7-dioxabicyclo[3.2.1]octan-3-one moiety are reported. Natural product screening efforts identified MacE as inducing a novel morphological change in Golgi structure defined by ribbon fragmentation with maintenance of the resulting Golgi fragments in the pericentriolar region. *t*-Bu-MacE, which possesses the substituted 2,7-dioxabicyclo[3.2.1]octan-3-one but contains a *tert*-butyl group in place of the hydroazulene subunit of MacE, was prepared by chemical synthesis. Examination of the Golgi-modifying properties of MacE, *t*-Bu-MacE, and several related structures revealed that the entire oxygen-rich bridged-bicyclic fragment is required for induction of this unique Golgi organization phenotype. Further characterization of MacE-induced Golgi modification showed that protein secretion is inhibited, with no effect on the actin or microtubule cytoskeleton being observed. The conversion of *t*-Bu-MacE and a structurally related des-acetoxy congener to substituted pyrroles in the presence of primary amines in protic solvent at ambient temperatures suggests that covalent modification might be involved in the Golgi-altering activity of MacE.

 L-amino acids catalyze the formation of an excess of D-glyceraldehyde, and thus of other D sugars, under credible prebiotic conditions

Breslow, R.; Cheng, Z.-L.; *Proc. Nat. Acad. Sci.* **2010**, *107*, 5723-5725. <u>Abstract:</u>

Previous work by us, and others, has shown that the formation of amino acids on prebiotic earth with the geometric arrangement called the L configuration can be understood. Some meteorites of the carbonaceous chondritic type deliver unusual amino acids, with alpha-methyl groups, which have an excess of the L isomers. We previously showed that in decarboxylative transamination reactions under credible prebiotic conditions they produce normal amino acids that also have a preference for the L isomer, as is found in our proteins. We, and others, showed that as little as a 1% excess of the L isomers could be amplified up to a 95/5 ratio of L over D on simple evaporation of a solution, so life could start with such a solution in which the dominant L isomers would be selectively chosen. We now find that the geometry of sugars referred to D, as in D-ribose or D-glucose, is not an independent mystery. D-glyceraldehyde, the simplest sugar with a D center, is the basic unit on which other sugars are built. We find that the synthesis of glyceraldehyde by reaction of formaldehyde with glycolaldehyde is catalyzed under prebiotic conditions to D/L ratios greater than 1, to as much as 60/40, by a representative group of L-amino acids (with the exception of L-proline). The D/L glyceraldehyde ratio in water solution is amplified to 92/8 using simple selective solubilities of the D and the DL forms. This D center would then be carried into the prebiotic syntheses of larger sugars.

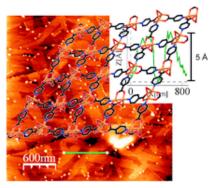
Charge stabilization in a closely spaced ferrocene-boron dipyrrin-fullerene triad
Wijesinghe, C. A.; El-Khouly, M. E.; Blakemore, J. D.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F.
Chem. Commun. 2010, 46, 3301 – 3303.

Abstract:



New molecular triads composed of closely spaced ferrocene—boron dipyrrin—fullerene, 1 and triphenylamine—boron dipyrrin—fullerene, 2 are synthesized, and photoinduced electron transfer leading to charge stabilization is demonstrated using a femtosecond transient spectroscopic technique.

Single layers of a multifunctional laminar Cu(I,II) coordination polymer
Amo-Ochoa, P.; Welte, L.; González-Prieto, R.; Sanz Miguel, P. J.; Gómez-García, C. J.; Mateo-Martí, E.; Delgado, S.; Gómez-Herrero, J.; Zamora, F. Chem. Commun. 2010, 46, 3262 – 3264.
Abstract:

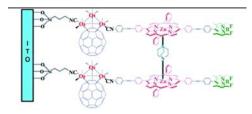


A multifunctional bidimensional mixed-valence copper coordination polymer $[Cu_2Br(IN)_2]n$ (IN = isonicotinato) has been characterized in crystal phase and isolated on graphite surface as single sheets.

Peptoid Macrocycles: Making the Rounds with Peptidomimetic Oligomers
Yoo, B.; Shin, S. B. Y.; Huang, M. L.; Kirshenbaum, K. Chem. Eur. J. 2010, 16, 5528-5537.
Abstract:

Macrocyclic constraints are often employed to rigidify the conformation of flexible oligomeric systems. This approach has recently been used to organize the structure of peptoid oligomers, which are peptidomimetics composed of chemically diverse N-substituted glycine monomer units. In this review, we describe advances in the synthesis and characterization of cyclic peptoids. We evaluate how the installation of covalent constraints between the oligomer termini or side chains has been effective in defining peptoid conformations. We also discuss the potential applications for this promising family of macrocyclic peptidomimetics.

Remarkably Efficient Photocurrent Generation Based on a [60]Fullerene-Triosmium Cluster/Zn-Porphyrin/Boron-Dipyrrin Triad SAM
Lee, C. Y.; Jang, J. K.; Kim, C; H.; Jung, J.; Park, B. K.; Park, J.; Choi, W.; Han, Y.-K.; Joo, T.; Park, J. T. Chem. Eur. J. 2010, 16, 5586-5599.
Abstract:



A new artificial photosynthetic triad array, a [60]fullerene-triosmium cluster/zinc-porphyrin/boron-dipyrrin complex ($\bf 1$, Os₃C₆₀/ZnP/Bodipy), has been prepared by decarbonylation of Os₃(CO)₈(CN(CH₂)₃Si(OEt)₃)(μ_3 - η^2 : η^2 -C₆₀) ($\bf 6$) with Me₃NO/MeCN and subsequent reaction with the isocyanide ligand CNZnP/Bodipy ($\bf 5$) containing zinc porphyrin (ZnP) and boron dipyrrin (Bodipy) moieties. Triad $\bf 1$ has been characterized by various spectroscopic methods (MS, NMR, IR, UV/Vis, photoluminescence, and transient absorption spectroscopy). The electrochemical properties of $\bf 1$ in

chlorobenzene (CB) have been examined by cyclic voltammetry; the general feature of the cyclic voltammogram of ${f 1}$ is nine reversible one-electron redox couples, that is, the sum of those of ${f 5}$ and 116. DFT has been applied to study the molecular and electronic structures of 1. On the basis of fluorescence-lifetime measurements and transient absorption spectroscopic data, 1 undergoes an efficient energy transfer from Bodipy to ZnP and a fast electron transfer from ZnP to C₆₀; the detailed kinetics involved in both events have been elucidated. The SAM of triad 1 (1/ITO; ITO=indium-tin oxide) has been prepared by immersion of an ITO electrode in a CB solution of 1 and diazabicyclooctane (2:1 equiv), and characterized by UV/Vis absorption spectroscopy, water contact angle, X-ray photoelectron spectroscopy, and cyclic voltammetry. The photoelectrochemical properties of 1/ITO have been investigated by a standard three-electrode system in the presence of an ascorbic acid sacrificial electron donor. The quantum yield of the photoelectrochemical cell has been estimated to be 29 % based on the number of photons absorbed by the chromophores. Our triad 1 is unique when compared to previously reported photoinduced electron-transfer arrays, in that C_{60} is linked by π bonding with little perturbation of the C_{60} electron delocalization.

Advantageous Use of ^tBu₂P-N=P(ⁱBuNCH₂CH₂)₃N in the Hiyama Coupling of Aryl Bromides and Chlorides

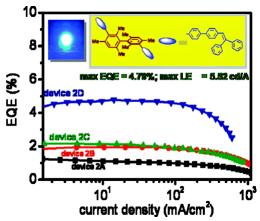
Raders, S. M.; Kingston, J. V.; Verkade, J. G. J. Org. Chem. 2010, 75, 1744–1747. Abstract:

An efficient catalytic route to biaryls by employing (generally) only 0.25 mol % of Pd(OAc)₂ and 0.5 mol % of 1 in the Hiyama coupling reaction is reported. High yields for electron-rich, -neutral, and deficient aryl chlorides are obtained. A variety of phenylsiloxanes undergo coupling with aryl bromides and chlorides with low Pd(OAc)₂/1 loadings.

Nondoped Pure-Blue OLEDs Based on Amorphous Phenylenevinylene-Functionalized Twisted Bimesitylenes

Moorthy, J. N.; Venkatakrishnan, P.; Natarajan, P.; Lin, Z.; Chow, T. J. J. Org. Chem. 2010, 75, 2599-2609.

Abstract:



The twisted bimesitylene scaffold hinders crystallization and imparts amorphous nature to the oligophenylenevinylenes (OPVs) generated by 2- and/or 4-fold functionalization. The resultant phenylenevinylenes 1-5 with unique molecular topology exhibit excellent thermal and solid-state luminescence properties. The amorphous nature permits their application as pure-blue emissive 12materials in OLEDs. Under nondoped conditions, the device performances observed surpass those for analogous and simple oligophenylenevinylenes known so far; for example, the device based on OPV 2 as an emitting material and structurally analogous Bim-DPAB as a hole-transporting material yields pure-blue electroluminescence with an external quantum efficiency of ca. 4.70% at 20 mA/cm², which is higher than those reported for nondoped pure-blue OPV emitters.

Triggering of Guanosine Self-Assembly by Light Lena, S.; Neviani, P.; Masiero, S.; Pieraccini, S.; Spada, G. P. Angew. Chem. Int. Ed. 2010, 49, 3657-3660.

Abstract:



Light switches: The introduction of a photoactive moiety into a lipophilic guanosine derivative allows photocontrol over the self-assembly of the molecule. The existence of G-quartets can be alternately switched on and off (see picture).

Fully Synthetic Vaccines Consisting of Tumor-Associated MUC1 Glycopeptides and a Lipopeptide Ligand of the Toll-like Receptor 2 Kaiser, A.; Gaidzik, N.; Becker, T.; Menge, C.; Groh, K.; Cai, H.; Li, Y.-M.; Gerlitzki, B.; Schmitt, E.; Kunz, H. Angew. Chem. Int. Ed. 2010, 49, 3688-3692. Abstract:

Fragment condensation of a protected Pam₃Cys lipopeptide with unprotected tumor-associated MUC1 glycopeptides opens the way to vaccine candidates such as A. These vaccines elicit selective immune responses in mice although they lack an immunodominant carrier protein. In principle, such vaccines are applicable to humans.