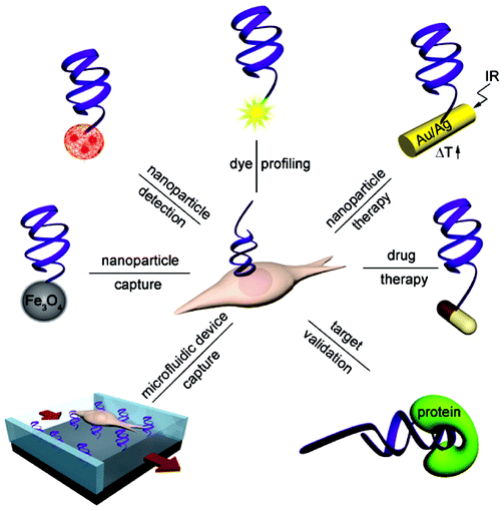
- Aptamers Generated from Cell-SELEX for Molecular Medicine: A Chemical Biology Approach
  Fang, X.; Tan, W. *Acc. Chem. Res.* **2010**, *43*, 48–57.
  Abstract:

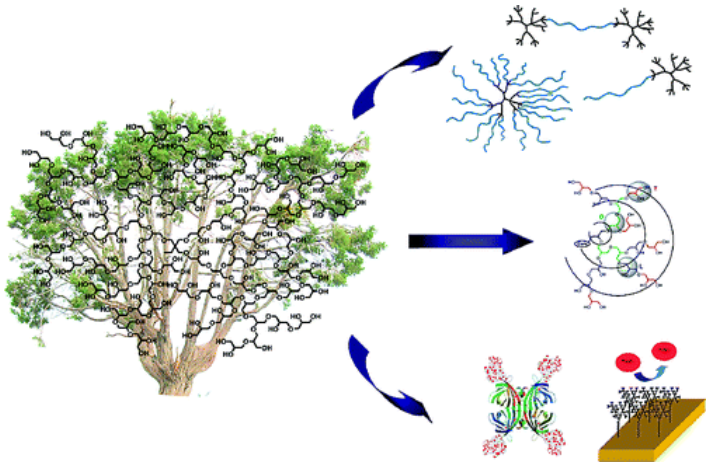


Molecular medicine is an emerging field focused on understanding the molecular basis of diseases and translating this information into strategies for diagnosis and therapy. This approach could lead to personalized medical treatments. Currently, our ability to understand human diseases at the molecular level is limited by the lack of molecular tools to identify and characterize the distinct molecular features of the disease state, especially for diseases such as cancer. Among the new tools being developed by researchers including chemists, engineers, and other scientists is a new class of nucleic acid probes called aptamers, which are ssDNA/RNA molecules selected to target a wide range of molecules and even cells. In this Account, we will focus on the use of aptamers, generated from cell-based selections, as a novel molecular tool for cancer research.

Cancers originate from mutations of human genes. These genetic alterations result in molecular changes to diseased cells, which, in turn, lead to changes in cell morphology and physiology. For decades, clinicians have diagnosed cancers primarily based on the morphology of tumor cells or tissues. However, this method does not always give an accurate diagnosis and does not allow clinicians to effectively assess the complex molecular alterations that are predictive of cancer progression. As genomics and proteomics do not yet allow a full access to this molecular knowledge, aptamer probes represent one effective and practical avenue toward this goal. One special feature of aptamers is that we can isolate them by selection against cancer cells without prior knowledge of the number and arrangement of proteins on the cellular surface. These probes can identify molecular differences between normal and tumor cells and can discriminate among tumor cells of different classifications, at different disease stages, or from different patients.

This Account summarizes our recent efforts to develop aptamers through cell-SELEX for the study of cancer and apply those aptamers in cancer diagnosis and therapy. We first discuss how we select aptamers against live cancer cells. We then describe uses of these aptamers. Aptamers can serve as agents for molecular profiling of specific cancer types. They can also be used to modify therapeutic reagents to develop targeted cancer therapies. Aptamers are also aiding the discovery of new cancer biomarkers through the recognition of membrane protein targets. Importantly, we demonstrate how molecular assemblies can integrate the properties of aptamers and, for example, nanoparticles or microfluidic devices, to improve cancer cell enrichment, detection and therapy.

- Hyperbranched Polyglycerols: From the Controlled Synthesis of Biocompatible Polyether Polyols to Multipurpose Applications
  Wilms, D.; Stiriba, S.-E.; Frey, H. *Acc. Chem. Res.* **2010**, *43*, 129–141.
  Abstract:

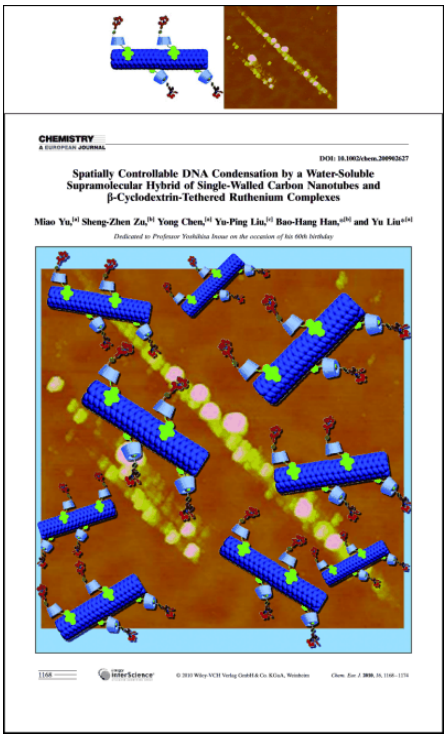


Dendritic macromolecules with random branch-on-branch topology, termed hyperbranched polymers in the late 1980s, have a decided advantage over symmetrical dendrimers by virtue of typically being accessible in a one-step synthesis. Saving this synthetic effort once had an unfortunate consequence, though: hyperbranching polymerization used to result in a broad distribution of molecular weights (that is, very high polydispersities, often $M_w/M_n > 5$). By contrast, a typical dendrimer synthesis yields a single molecule (in other words, $M_w/M_n = 1.0$), albeit by a labor-intensive, multistep process. But 10 years ago, Sunder and colleagues reported the controlled synthesis of well-defined hyperbranched polyglycerol (PG) via ring-opening multibranching polymerization (ROMBP) of glycidol. Since then, hyperbranched and polyfunctional polyethers with controlled molar mass and low polydispersities (M_w/M_n = 1.2−1.9) have been prepared, through various monomer addition protocols, by ROMBP. In this Account, we review the progress in the preparation and application of these uniquely versatile polyether polyols over the past decade.

Hyperbranched PGs combine several remarkable features, including a highly flexible aliphatic polyether backbone, multiple hydrophilic groups, and excellent biocompatibility. Within the past decade, intense efforts have been directed at the optimization of synthetic procedures affording PG homo- and copolymers with different molecular weight characteristics and topology. Fundamental parameters of hyperbranched polymers include molar mass, polydispersity, degree of branching, and end-group functionality. Selected approaches for optimizing and tailoring these characteristics are presented and classified with respect to their application potential. Specific functionalization in the core and at the periphery of hyperbranched PG has been pursued to meet the growing demand for novel specialty materials in academia and industry.

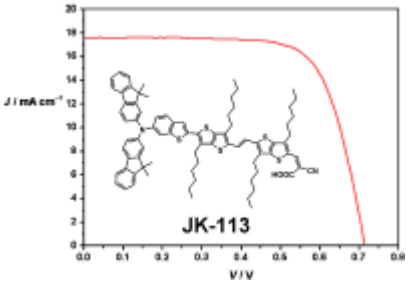
A variety of fascinating synthetic approaches now provide access to well-defined, complex macromolecular architectures based on polyether polyols with low polydispersity. For instance, a variety of linear−hyperbranched block copolymers has been reported. The inherent attributes of PG-based materials are useful for a number of individual implementation concepts, such as drug encapsulation or surface modification. The excellent biocompatibility of PG has also led to rapidly growing significance in biomedical applications, for example, bioconjugation with peptides, as well as surface attachment for the creation of protein-resistant surfaces.

- Spatially Controllable DNA Condensation by a Water-Soluble Supramolecular Hybrid of Single-Walled Carbon Nanotubes and β-Cyclodextrin-Tethered Ruthenium Complexes
  Yu, M.; Zu, S.-Z.; Chen, Y.; Liu, Y.-P.; Han, B.-H.; Liu, Y. *Chem. Eur. J*. **2010**, *16*, 1168-1174.
  Abstract:



A supramolecular hybrid is prepared by the supramolecular surface modification of single-walled carbon nanotube (SWCNT) with cationic β-cyclodextrin-tethered ruthenium complexes through a spacer molecule that contains both an adamantane and a pyrene moiety. By employing the supramolecular hybrid, spatially controllable DNA condensation along the SWCNT skeleton is achieved by anchoring cationic ruthenium complexes on the surface. Furthermore, because of the unique physiological properties of SWCNTs, the cationic supramolecular hybrid can be used as a nonviral gene delivery system with the ruthenium complexes as a fluorescent probe to monitor uptake of DNA by cells.

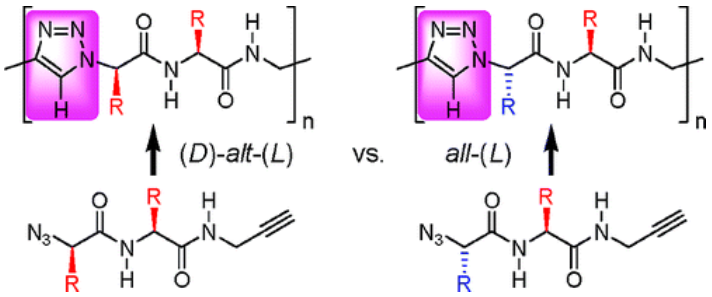
- High Molar Extinction Coefficient Organic Sensitizers for Efficient Dye-Sensitized Solar Cells
  Choi, H.; Raabe, I.; Kim, D.; Teocoli, F.; Kim, C.; Song, K.; Yum, J.-H.; Ko, J.; Nazeeruddin, M. K.; Grätzel, M. *Chem. Eur. J*. **2010**, *16*, 1193-1201.
  Abstract:



We have designed and synthesized highly efficient organic sensitizers with a planar thienothiophene-vinylene-thienothiophene linker. Under standard global AM 1.5 solar conditions, the JK-113-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 17.61 mA cm^{-2}, an open-circuit voltage

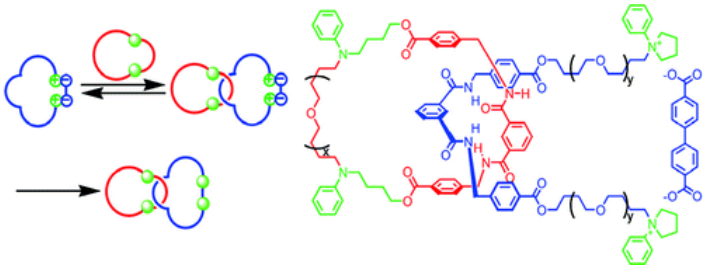
(V_{oc}) of 0.71 V, and a fill factor (*FF*) of 72 %, corresponding to an overall conversion efficiency (η) of 9.1 %. The incident monochromatic photo-to-current conversion efficiency (IPCE) of JK-113 exceeds 80 % over the spectral region from 400 to 640 nm, reaching its maximum of 93 % at 475 nm. The band tails off toward 770 nm, contributing to the broad spectral light harvesting. Solar-cell devices based on the sensitizer JK-113 in conjunction with a volatile electrolyte and a solvent-free ionic liquid electrolyte gave high conversion efficiencies of 9.1 % and 7.9 %, respectively. The JK-113-based solar cell fabricated using a solvent-free ionic liquid electrolyte showed excellent stability under light soaking at 60 ºC for 1000 h.

- Polypseudopeptides with Variable Stereochemistry: Synthesis via Click-Chemistry, Postfunctionalization, and Conformational Behavior in Solution
  Hartwig, S.; Hecht, S. *Macromolecules* **2010**, *43*, 242–248.
  Abstract:



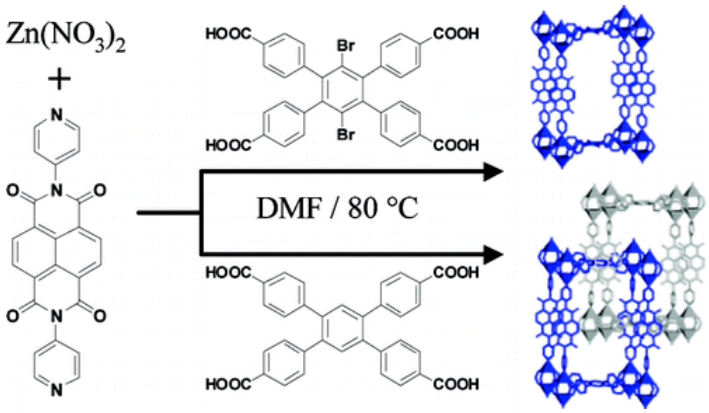
Polypseudopeptides with well-defined stereochemistries have been synthesized from readily available amino-acid-based building blocks by connecting (L,L)- or (L,D)-dipeptide AB-monomers carrying azide and alkyne termini via triazole amide-isosteres efficiently formed in the course of the "click" reaction. Deprotection of the thus-prepared lysine-based polypseudopeptides of both *all*-(L)- and (D)-*alt*-(L)-stereochemistries afforded water-soluble polymers with ionizable amino side chains, which could be fully labeled with pyrene chromophores via quantitative amide bond formation. The conformational behavior of the deprotected as well as the pyrene-labeled polymers was investigated using UV/vis, CD, and fluorescence spectroscopies. On one hand, the free polyamines display pH-dependent conformations in water. On the other hand, the pyrene-labeled polypseudopeptides change their conformation in response to varying organic solvent composition. Whereas the strictly alternating polypseudopeptides structurally resemble channel-forming peptides, such as the Gramicidin family, the incorporation of (D)-configured amino acids as well as triazole amide-isosteres should lead to interesting new materials for bioapplications.

- Effective Synthesis of Polymer Catenanes by Cooperative Electrostatic/ Hydrogen-Bonding Self-Assembly and Covalent Fixation
  Ishikawa, K.; Yamamoto, T.; Asakawa, M.; Tezuka, Y. *Macromolecules* **2010**, *43*, 168–176.
  Abstract:



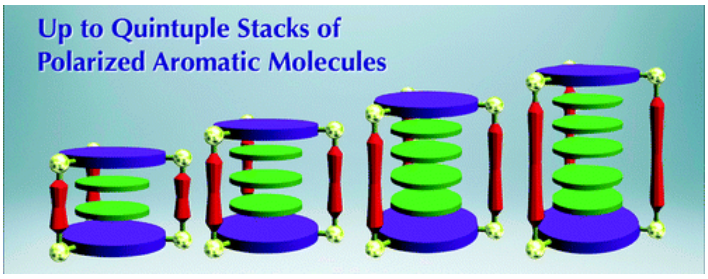
The cooperative electrostatic and hydrogen-bonding self-assembly of polymer precursors and the subsequent covalent conversion have been demonstrated as an effective means for the synthesis of polymer catenanes. Thus, a cyclic poly(tetrahydrofuran), poly(THF), having a hydrogen-bonding, isophthaloylbenzylic amide group (**I**) was prepared through an *electrostatic self-assembly* and *covalent fixation* with a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a dicarboxylate counteranion containing the hydrogen-bonding unit (**1**). Another telechelic poly(THF) having an isophthaloylbenzylic amide group at the center position and having *N*-phenylpyrrolidinium salt end groups carrying a biphenyldicarboxylate counteranion, **2**, was subsequently prepared and subjected to a covalent conversion reaction in the presence of the preformed cyclic poly(THF) having a hydrogen-bonding unit (**I**). A polymer [2]catenane comprised of the two different cyclic poly(THF) components, **I** and **II** (from **2**), has been isolated up to 7% yield as an acetone-insoluble fraction and unequivocally characterized by means of MALDI TOF mass spectroscopy together with ^{1}H NMR and SEC techniques.

- Control over Catenation in Metal−Organic Frameworks via Rational Design of the Organic Building Block
  Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp T. J. *J. Am. Chem. Soc.* **2010**, *132*, 950-952.
  Abstract:



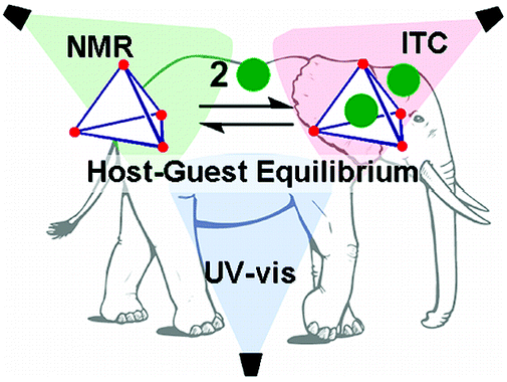
Metal−organic frameworks (MOFs), a hybrid class of materials comprising inorganic nodes and organic struts, have potential application in many areas due to their high surface areas and uniform pores and channels. One of the key challenges to be overcome in MOF synthesis is the strong propensity for catenation (growth of multiple independent networks within a given crystal), as catenation reduces cavity sizes and diminishes porosity. Here we demonstrate that rational design of organic building blocks, which act as strut-impervious scaffolds, can be exploited to generate highly desired noncatenated materials in a controlled fashion.

- Engineering Double to Quintuple Stacks of a Polarized Aromatic in Confined Cavities
  Yamauchi, Y.; Yoshizawa, M.; Akita, M.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132,* 960-966.
  Abstract:



Discrete, well-defined stacks of the polarized aromatic pyrene-4,5-dione (1) were assembled in the cavities of organic-pillared coordination cages (2). The number (n) of stacked guests depends on the pillar length, and up to quintuple stacks (n = 5) were observed when long (16.5 Å) organic pillar ligands were incorporated. As previously reported, pyrene-4,5-dione (1) assembles into infinite columnar stacks in the solid state, but the present work demonstrates that the polarized 1 has a strong propensity to stack in layers even in the absence of crystal packing effects. For n = 2 and 3 structures, crystallographic studies revealed that 1 stacks by π–π interactions in the cavity in such a way that a net dipole moment is canceled. These results emphasize the important role of dipole–dipole interactions as well as π-stacking interactions in the formation of columnar stacks of 1.

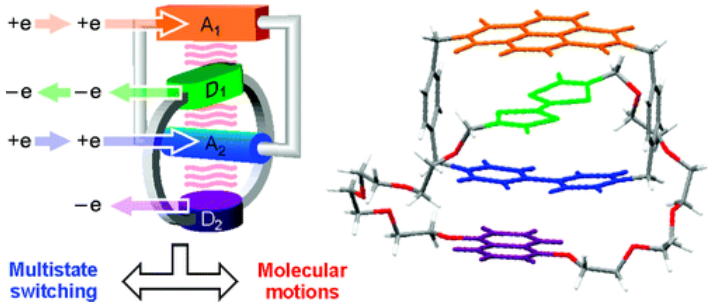
- External and Internal Guest Binding of a Highly Charged Supramolecular Host in Water: Deconvoluting the Very Different Thermodynamics
  Sgarlata, C.; Mugridge, J. S.; Pluth, M. D.; Tiedemann, B. E. F.; Zito, V.; Arena, G.; Raymond, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 1005–1009.
  Abstract:



NMR, UV–vis, and isothermal titration calorimetry (ITC) measurements probe different aspects of competing host–guest equilibria as simple alkylammonium guest molecules interact with both the exterior (ion-association) and interior (encapsulation) of the $[Ga_4L_6]^{12-}$ supramolecular assembly in water. Data obtained by each independent technique measure different components of the host–guest equilibria and only when analyzed together does a complete picture of the solution thermodynamics emerge. Striking differences between the internal and external guest binding are found. External binding is enthalpy driven and mainly due to attractive interactions between the guests and the exterior surface of the assembly while encapsulation is entropy driven as a result of desolvation and release of solvent molecules from the host cavity.

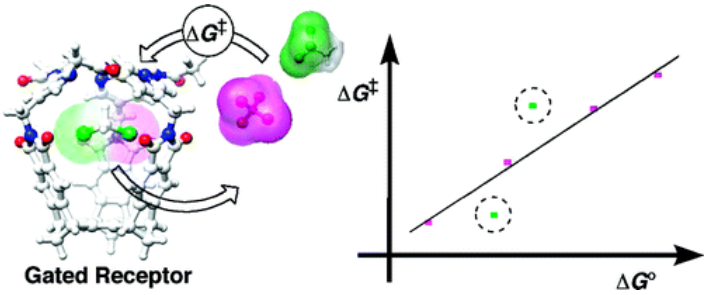
- Probing Donor–Acceptor Interactions and *Co*-Conformational Changes in Redox Active Desymmetrized [2]Catenanes
  Cao, D.; Amelia, M.; Klivansky, L. M.; Koshkakaryan, G.; Khan, S. I.; Semeraro, M.; Silvi, S.; Venturi, M.; Credi, A.; Liu, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1110–1122.

Abstract:



We describe the synthesis and characterization of a series of desymmetrized donor–acceptor [2]catenanes where different donor and acceptor units are assembled within a confined catenated geometry. Remarkable translational selectivity is maintained in all cases, including two fully desymmetrized [2]catenanes where both donors and acceptors are different, as revealed by X-ray crystallography in the solid state, and by ^{1}H NMR spectroscopy and electrochemistry in solution. In all desymmetrized [2]catenanes the *co*-conformation is dominated by the strongest donor and acceptor pairs, whose charge-transfer interactions also determine the visible absorption properties. Voltammetric and spectroelectrochemical experiments show that the catenanes can be reversibly switched among as many as seven states, characterized by distinct electronic and optical properties, by electrochemical stimulation in a relatively narrow and easily accessible potential window. Moreover in some of these compounds the oxidation of the electron donor units or the reduction of the electron acceptor ones causes the circumrotation of one molecular ring with respect to the other. These features make these compounds appealing for the development of molecular electronic devices and mechanical machines.

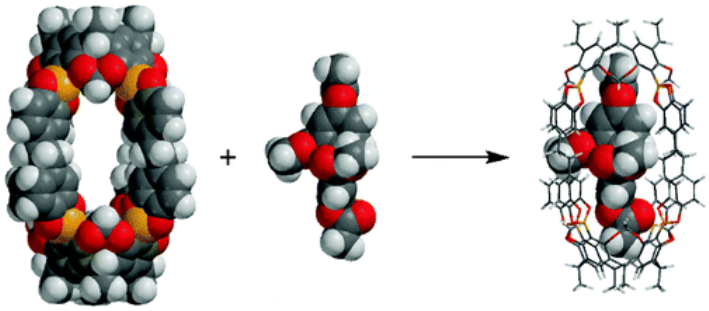
- Gated Molecular Recognition and Dynamic Discrimination of Guests
  Rieth, S.; Bao, X.; Wang, B.-Y.; Hadad, C. M.; Badjić, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 773–776.
  Abstract:



Some highly efficient enzymes, e.g., acetylcholinesterase, use gating as a tool for controlling the rate by which substrates access their active site to direct product formation. Mastering gated molecular encapsulation could therefore be important for manipulating reactivity in artificial environments, albeit quantitative relationships that describe these processes are unknown. In this work, we examined the interdependence between the thermodynamics ($\Delta G°$) and the kinetics ($\Delta G_{in}^{‡}$ and $\Delta G_{out}^{‡}$) of encapsulation as mediated by gated molecular basket **1**. For a series of isosteric guests (**2**–**6**, 106–107 Å^3) entering/exiting **1**, we found a linear correlation between the host–guest affinities ($\Delta G°$) and the free energies of the activation ($\Delta G_{in}^{‡}$ and $\Delta G_{out}^{‡}$), which was fit to the following equation: $\Delta G^{‡} = \rho\Delta G° + \delta$. Markedly, the kinetics for the entrapment of smaller guest **7** (93 Å^3) and bigger guest **8** (121 Å^3) did not follow the free energy trends observed for **2**–**6**. Thus, it appears that the kinetics of the gated encapsulation mediated by **1** is a function of the encapsulation's favorability

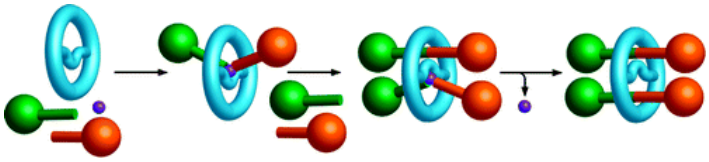
(Δ*G*°) and the guest's profile. When the size/shape of guests is kept constant, a linear dependence between the encapsulation potential (Δ*G*°) and the rate of guests' entering/departing basket ($\Delta G_{in/out}^{\ddagger}$) holds. However, when the potential (Δ*G*°) is fixed, the basket discriminates guests on the basis of their size/shape via dynamic modulation of the binding site's access.

- Guest-Encapsulation Properties of a Self-Assembled Capsule by Dynamic Boronic Ester Bonds
  Nishimura, N.; Yoza, K.; Kobayashi, K. *J. Am. Chem. Soc.* **2010**, *132*, 777–790.
  Abstract:



Two molecules of tetrakis(dihydroxyboryl)-cavitand **1a** as an aromatic cavity and four molecules of 1,2-bis(3,4-dihydroxyphenyl)ethane **2** as an equatorial linker self-assemble into capsule **3a** via the formation of eight dynamic boronic ester bonds in $CDCl_3$ or C_6D_6. Capsule **3a** encapsulates one guest molecule, such as 4,4′-disubstituted-biphenyl and 2,6-disubstituted-anthracene derivatives, in a highly selective recognition event, wherein the guest substituents are oriented to both aromatic cavity ends of **3a**, as confirmed by a ^{1}H NMR study and X-ray crystallographic analysis. Capsule **3a** showed a significant solvent effect on guest encapsulation. The association constant (K_a) of **3a** with guests in C_6D_6 was much greater than that in $CDCl_3$ (450−48 000-fold). The encapsulation of guests within **3a** in C_6D_6 was enthalpically driven, whereas that in $CDCl_3$ tended to be both enthalpically and entropically driven. Thermodynamic studies suggest that the small K_a value in $CDCl_3$ arises from the character of $CDCl_3$ as a competitor guest molecule for **3a**, and not from the difference in stability of the boronic ester bonds of **3a** in both solvents. We propose a linker partial dissociation mechanism for the guest uptake and release into and out of **3a** based on the kinetic studies of guest@**3a** using 2D EXSY analysis, as well as structural analysis of a guest@**3b**. The rotation behavior of 4,4′-diacetoxy-2,2′-disubstituted-biphenyls within **3a** was also investigated, where the elongation of 2,2′-disubstituents of guests put the brakes on guest rotation within **3a**.

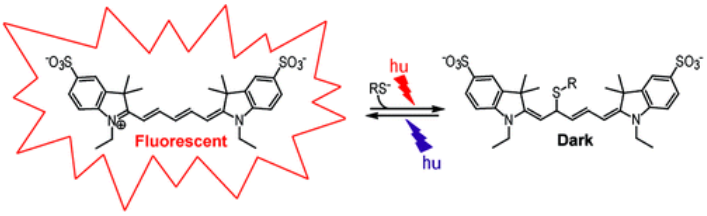
- Two Axles Threaded Using a Single Template Site: Active Metal Template Macrobicyclic [3]Rotaxanes
  Goldup, S. M.; Leigh, D. A.; McGonigal, P. R.; Ronaldson, V. E.; Slawin, A. M. Z. *J. Am. Chem. Soc.* **2010**, *132*, 315–320.
  Abstract:



Template approaches to rotaxanes normally require at least *n* − 1 template sites to interlock *n* components. Here we describe the one-pot synthesis of [3]rotaxanes in which a single metal template site induces formation of axles through each cavity of a bicyclic macrocycle. Central to the approach is that a portion of the bicyclic molecule acts as a ligand for a transition metal ion that

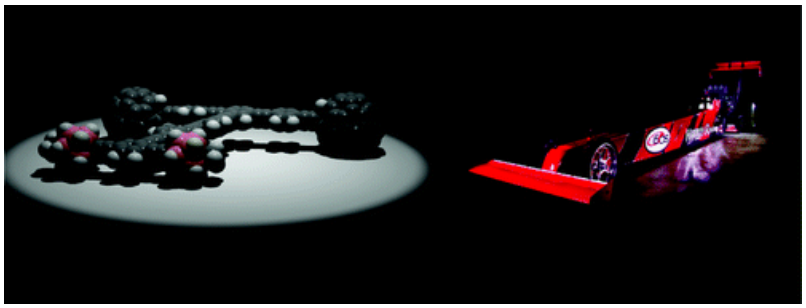
mediates covalent bond formation through one or other macrocyclic cavity, depending on the ligand's orientation, making a mechanical bond. The ligand can then rotate so that the transition metal can catalyze the formation of a second axle through the other macrocycle. Using this strategy with the Cu(I)-catalyzed azide–alkyne cycloaddition (the CuAAC reaction) generates a [3]rotaxane with two identical axles in up to 86% yield. [3]Rotaxanes with two different axles threaded through the macrobicyclic rings can also be created using a single template site, either by having copper(I) sequentially form both mechanical bonds (via the CuAAC reaction) using different sets of building blocks for each axle or by using two different reactions catalyzed by two different metal ions: a palladium(II)-mediated alkyne homocoupling to assemble the first thread through one cavity, followed by a copper(I)-mediated CuAAC reaction to form the second axle through the other ring.

- Photoswitching Mechanism of Cyanine Dyes
  Dempsey, G. T.; Bates, M.; Kowtoniuk, W. E.; Liu, D. R.; Tsien, R. Y.; Zhuang, X. *J. Am. Chem. Soc.* **2009**, *131*, 18192–18193.
  Abstract:



Cyanine dyes have been shown to undergo reversible photoswitching, where the fluorophore can be switched between a fluorescent state and a dark state upon illumination at different wavelengths. The photochemical mechanism by which switching occurs has yet to be elucidated. In this study, we have determined the mechanism of photoswitching by characterizing the kinetics of dark state formation and the spectral and structural properties of the dark state. The rate of switching to the dark state depends on the concentration of the primary thiol in the solution and the solution pH in a manner quantitatively consistent with the formation of an encounter complex between the cyanine dye and ionized thiol prior to their conjugation. Mass spectrometry suggests that the photoconversion product is a thiol–cyanine adduct in which covalent attachment of the thiol to the polymethine bridge disrupts the original conjugated π-electron system of the dye.

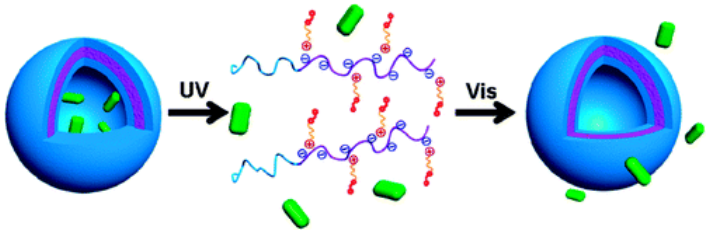
- Molecular Machinery: Synthesis of a "Nanodragster"
  Vives, G.; Kang, J. H.; Kelly, K. F.; Tour, J. M. *Org. Lett.* **2009**, *11*, 5602–5605.
  Abstract:



The synthesis and imaging by scanning tunneling microscopy of a mixed wheeled nanovehicle composed of a *p*-carborane small-wheeled short front axle and a C_{60} large-wheeled long rear axle that has been termed a nanodragster due to the structural relation to a dragster are reported. This

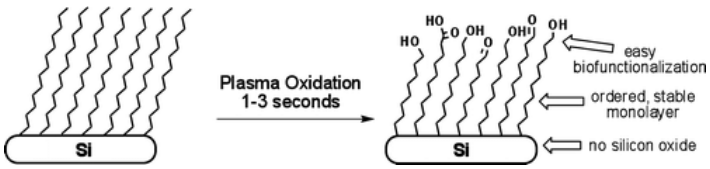
nanodragster is expected to exhibit motion at a lower temperature than pure C_{60}-wheeled nanocars and should allow the investigation of the role played by *p*-carborane wheels in directional motion.

- Photocontrolled Self-Assembly and Disassembly of Block Ionomer Complex Vesicles: A Facile Approach toward Supramolecular Polymer Nanocontainers
  Wang, Y.; Han, P.; Xu, H.; Wang, Z.; Zhang, X.; Kabanov V. A. *Langmuir* **2010**, *26*, 709–715.
  Abstract:



A new concept of designing a photocontrollable supramolecular polymer nanocontainer through the electrostatic association between an azobenzene-containing surfactant (AzoC10) and a double-hydrophilic block ionomer, poly(ethylene glycol)-*b*-poly(acrylic acid) (PEG_{43}–PAA_{153}), is described. Such a block ionomer complex can self-assemble in aqueous solution and form vesicle-like aggregates, which are composed of a poly(ethylene glycol) corona and a poly(acrylic acid) shell associated with azobenzene-containing surfactant. The photoisomerization of azobenzene moieties in the block ionomer complex can reversibly tune the amphiphilicity of the surfactants, inducing the disassembly of the vesicles. Such block ionomer complex vesicles are further evaluated as nanocontainers capable to encapsulate and release guest solutes on demand controlled by light irradiation. For example, the vesicles encapsulating the fluorescein sodium display clear spherical images observed by fluorescence microscopy. However, such fluorescence-marked images disappear after releasing the solute from the vesicles triggered by the UV light. Such novel materials are of both basic and practical significance, especially as prospective nanocontainers for cargo delivery.

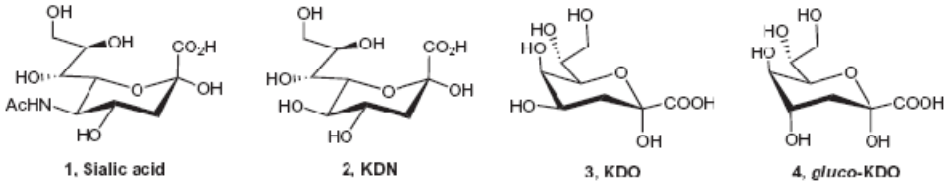
- Controlled Oxidation, Biofunctionalization, and Patterning of Alkyl Monolayers on Silicon and Silicon Nitride Surfaces using Plasma Treatment
  Rosso, M.; Giesbers, M.; Schro, K.; Zuilhof, H. *Langmuir* **2010**, *26*, 866–872.
  Abstract:



A new method is presented for the fast and reproducible functionalization of silicon and silicon nitride surfaces coated with covalently attached alkyl monolayers. After formation of a methyl-terminated 1-hexadecyl monolayer on H-terminated Si(100) and Si(111) surfaces, short plasma treatments (1−3 s) are sufficient to create oxidized functionalities without damaging the underlying oxide-free silicon. The new functional groups can, e.g., be derivatized using the reaction of surface aldehyde groups with primary amines to form imine bonds. In this way, plasma-treated monolayers on silicon or silicon nitride surfaces were successfully coated with nanoparticles, or proteins such as avidin. In addition, we demonstrate the possibility of micropatterning, using a soft contact mask during the plasma treatment. Using water contact angle measurements, ellipsometry, XPS, IRRAS,

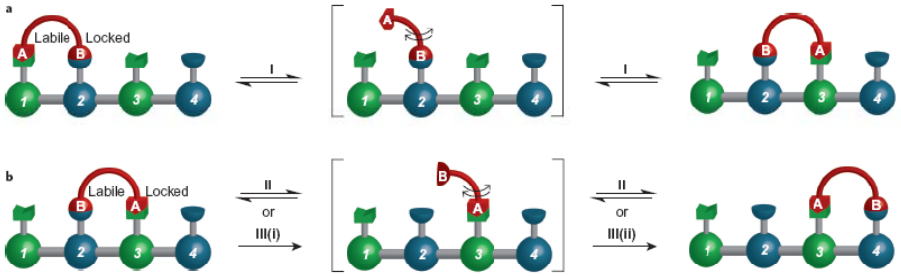
AFM, and reflectometry, proof of principle is demonstrated of a yet unexplored way to form patterned alkyl monolayers on oxide-free silicon surfaces.

- Chemoenzymatic synthesis of differentiallyprotected 3-deoxysugars
  Gillingham, D. G.; Stallforth, P.; Adibekian, A.; Seeberger, P. H.; Hilvert, D. *Nature Chemistry* **2010**, *2*, 102 – 105.
  Abstract:



3-Deoxysugars are important constituents of complex carbohydrates. For example, 2-keto-3-deoxy-D-manno-octulosonic acid (KDO) is an essential component of lipopolysaccharides in Gram-negative bacteria, 2-keto-3-deoxy-D-glycero-D-galactononulosonic acid (KDN) is widely found in carbohydrates of the bacterial cell wall and in lower vertebrates, and sialic acid is a common cap of mammalian glycoproteins. Although ready access to such sugars would benefit the creation of vaccine candidates, antibiotics and small-molecule drugs, their chemical synthesis is difficult. Here we present a simple chemoenzymatic method for preparing differentially protected 3-deoxysugar derivatives from readily available starting materials. It exploits the promiscuous aldolase activity of the enzyme macrophomate synthase (MPS) to add pyruvate enolate diastereoselectively to a wide range of structurally complex aldehydes. A short synthesis of KDN illustrates the utility of this approach. Enzyme promiscuity, which putatively fosters large functional leaps in natural evolution, has great promise as a source of synthetically useful catalytic transformations.

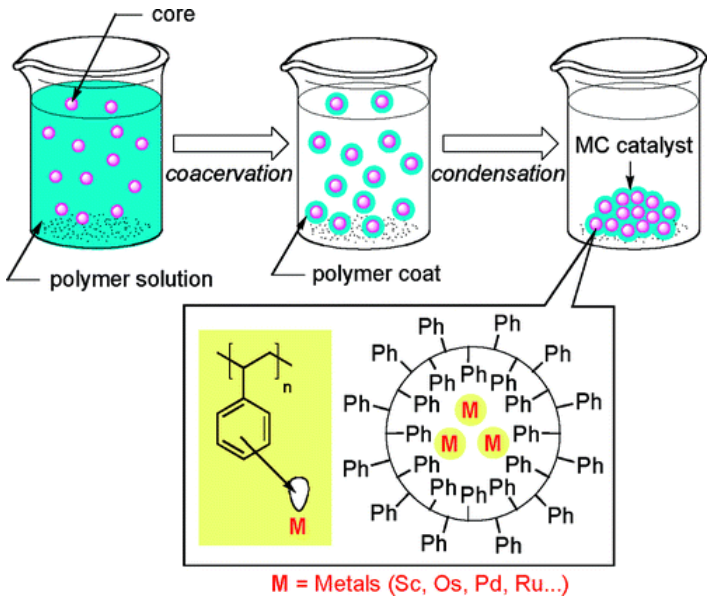
- A synthetic small molecule that can walk down a track
  von Delius, M.; Geertsema, E. M.; Leigh, D. A. *Nature Chemistry* **2010**, *2*, 96 – 101.
  Abstract:



Although chemists have made small-molecule rotary motors, to date there have been no reports of small-molecule linear motors. Here we describe the synthesis and operation of a 21-atom two-legged molecular unit that is able to walk up and down a four-foothold molecular track. High processivity is conferred by designing the track-binding interactions of the two feet to be labile under different sets of conditions such that each foot can act as a temporarily fixed pivot for the other. The walker randomly and processively takes zero or one step along the track using a ‘passing-leg’ gait each time the environment is switched between acid and base. Replacing the basic step with a redox-mediated, disulfide-exchange reaction directionally transports the bipedal molecules away from the minimum-energy distribution by a Brownian ratchet mechanism. The ultimate goal of such studies is to produce

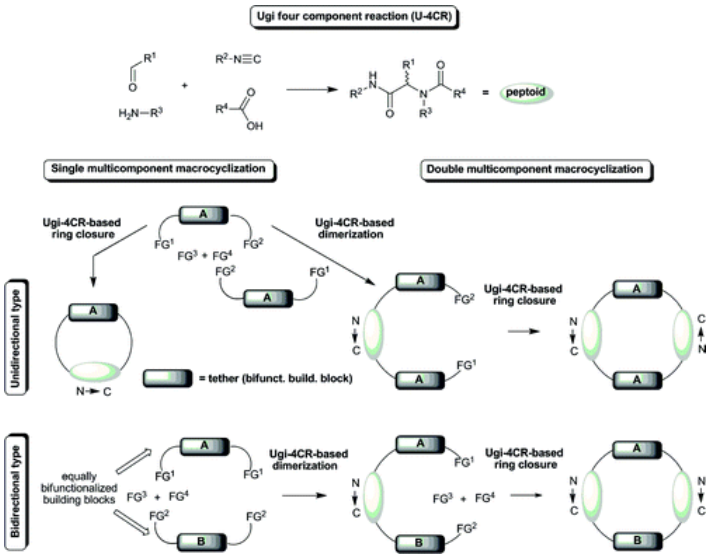
artificial, linear molecular motors that move directionally along polymeric tracks to transport cargoes and perform tasks in a manner reminiscent of biological motor proteins.

- "Microencapsulated" and Related Catalysts for Organic Chemistry and Organic Synthesis
  Akiyama, R.; Kobayashi, S. *Chem. Rev.* **2009**, *109,* 594-642.
  Abstract:



As a new method for immobilizing metal catalysts onto polymers, the microencapsulation method was first introduced in 1998. Before that, microcapsules had been used for coating and isolating substances until their activity is needed. Their application to medicine and pharmacy was extensively studied. The idea of the new method is to apply the microencapsulation technique for immobilization of catalysts onto polymers. That is, catalysts would be physically enveloped by thin films of polymers (polystyrene derivatives in many cases) and at the same time immobilized by interaction between π electrons of the benzene rings of the polystyrenes, which are used as a polymer backbone, and vacant orbitals of the catalysts (metal compounds). The catalysts were new types of heterogeneous catalysts and were named as "microencapsulated (MC) catalysts". Microcapsules in these catalysts are backbones of immobilized catalysts such as cross-linked polymers and inorganic materials such as silica gel and alumina, and thus are completely different from conventional microcapsules that are used for protection. After that, polymer incarcerated (PI) catalysts, which are more robust against many solvents, were developed based on the MC technique. In this review, we describe such unprecedented polymer-supported catalysts as MC catalysts and PI catalysts, which can create recoverable, reusable, and highly active heterogeneous metal catalysts for several organic reactions. While MC and PI catalysts are heterogeneous catalysts, they are very different from conventional heterogeneous catalysts in many aspects. Therefore, we describe more details of these catalysts in this review, which may be a little bit different from other review articles. On the other hand, we will not discuss other immobilized catalysts in this review, which are treated in detail in other contributions to this issue.

- Multiple Multicomponent Macrocyclizations (MiBs): A Strategic Development Toward Macrocycle Diversity
  Wessjohann, L. A.; Rivera, D. G.; Vercillo, O. E. *Chem. Rev.* **2009**, *109,* 796-814.
  Abstract:



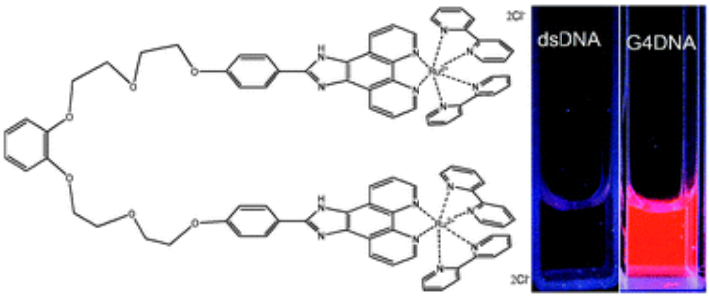
Macrocycles are of high significance in areas as diverse as drug development and supramolecular chemistry. They can be considered as privileged molecules because they can combine flexibility and conformational bias. They allow a certain conformational adaptation for binding and at the same time can have an improved overall energy term while binding, compared to linear molecules. Recently, a diversity-oriented macrocyclization strategy termed multiple multicomponent macrocyclization including bifunctional building blocks (MiB) was developed which allows producing constitutionally diverse and complex macrocycles from simple building blocks in one pot.

This review will concentrate on those approaches which produce macrocycles wherein the MCR is (also) responsible for the macrocyclization itself. MCR-based macrocyclization strategies are very suitable to generate highly diverse macrocyclic scaffolds displaying sufficient molecular complexity to resemble natural product-like ones. Recently, this issue has been addressed by the development of a diversity-oriented strategy for macrocycle synthesis termed multiple multicomponent macrocyclization including bifunctional building blocks (MiB). The MiB approach embodies an original concept of how organic chemists can design and create complex macrocycles, natural or other, from simple building blocks in a very straightforward and versatile process suitable for library construction. The Ugi four-component reaction (U-4CR) in its original form is currently the most studied MCR in macrocyclizations. Accordingly, the first sections of this review will concentrate on the Ugi-variant of MiBs to demonstrate the underlying principles of macrocycle formation and diversity generation followed by other multiple MCR macrocyclizations in later sections.

- High fluorescence selectivity and visual detection of G-quadruplex structures by a novel dinuclear ruthenium complex

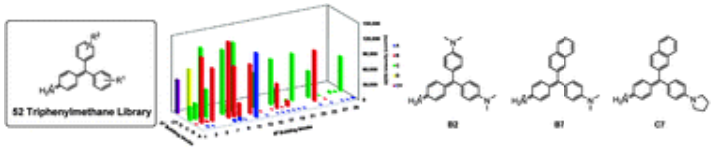
  Xu, L.; Zhang, D.; Huang, J.; Deng, M.; Zhang, M.; Zhou, X. *Chem. Commun.* **2010**, *46*, 743 – 745.

  Abstract:



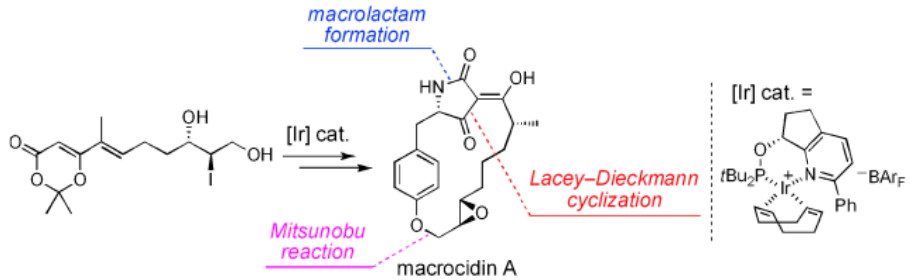
A novel dinuclear ruthenium(II) complex with high fluorescent selectivity between DNA quadruplex structures and duplex structures was generated, and using an iodide-quenching strategy, G-quadruplex structures can be easily distinguished from duplex structures by the naked eye.

- Combinatorial synthesis of a triphenylmethine library and their application in the development of Surface Enhanced Raman Scattering (SERS) probes.
  Cho, S. J.; Ahn, Y. H.; Maiti, K. K.; Dinish, U. S.; Fu, C. Y.; Thoniyot, P.; Olivo, M.; Chang Y. T. *Chem. Commun.* **2010**, *46*, 722 – 724.
  Abstract:



The first synthesis of a triphenylmethine (TM) library of compounds and screening of their Surface Enhanced Raman Scattering (SERS) capability was carried out to identify novel Raman reporters with high sensitivity. We identified three novel SERS reporters (B2, B7, and C7) with higher signal intensity than that of commonly used crystal violet (CV). These reporters may find potential applications in developing sensitive SERS based biosensors.

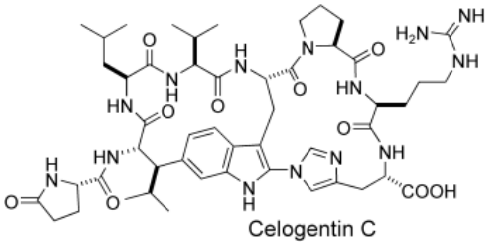
- Total Synthesis and Absolute Configuration of Macrocidin A, a Cyclophane Tetramic Acid Natural Product
  Yoshinari, T.; Ohmori, K.; Schrems, M. G.; Pfaltz, A.; Suzuki, K. *Angew. Chem. Int. Ed*. **2010**, *49*, 881 –885.
  Abstract:



Stereocontrolled access to the cyclophane framework of macrocidin A has been achieved for the first time. The key steps include the iridium-catalyzed asymmetric hydrogenation without fission of the C—I bond, the macrolactam formation by intramolecular ketene trapping, and the Lacey-Dieckmann cyclization for the construction of the tetramic acid ring.

- Total Synthesis of Celogentin C by Stereoselective C—H Activation
  Feng, Y.; Chen, G. *Angew. Chem. Int. Ed*. **2010**, *49*, 958–961.

Abstract:



Celogentin C

A total gent: Inspired by the biosynthesis of celogentin C, a highly stereoselective and efficient palladium-catalyzed C—H functionalization strategy is employed to construct the key Leu-Trp linkage of this bicyclic compound. A streamlined synthesis is completed in 23 steps from simple amino acid building blocks.