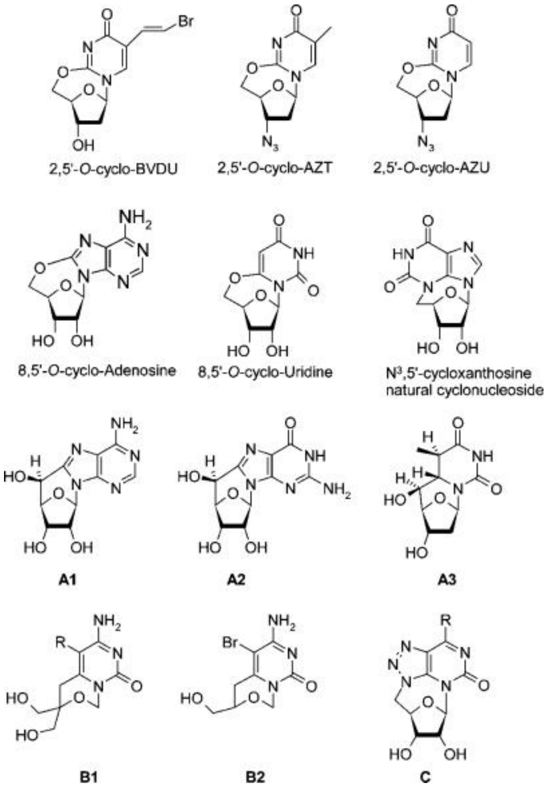
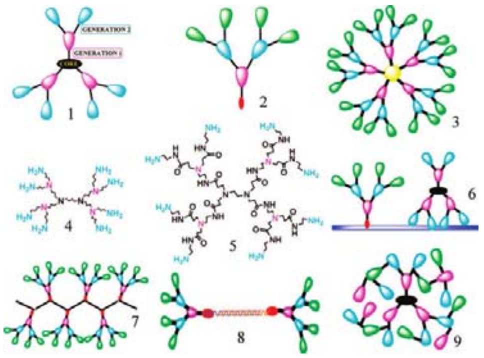
- Preparation of Cyclonucleosides
  Mieczkowski, A.; Roy, V.; Agrofoglio, L. A. *Chem. Rev.* **2010**, *110,* 1828–1856.
  Abstract:



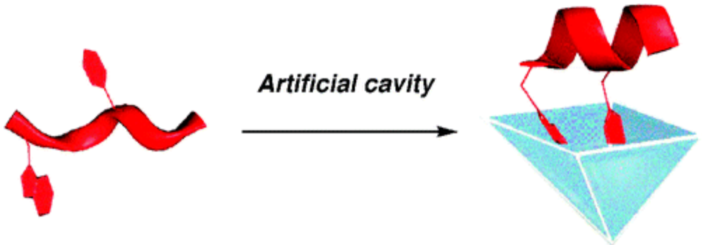
The study of the biological activity of nucleosides has been a fundamental and fruitful field of research since the 1940s and 1950s. It was then that the role of nucleic acids in cells was established, ultimately resulting in the identification of the double-helix structure of DNA and the explanation of the genetic role. As their metabolic processes became understood, so the investigation of close analogues of the components of nucleic acids grew. Some of the compounds resulting from this work, indeed, modified pyrimidine and purine nucleoside derivatives, have been shown to possess antiviral, antimetabolic, and antibacterial properties.

- Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, Photonics, and Nanomedicine
  Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010,** *110,* 1857–1959.
  Abstract:



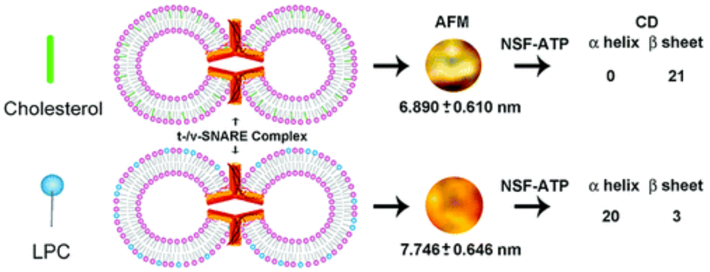
Dendrimer chemistry1,2 largely relies on supramolecular properties.3 Since the pioneering work on iterative reaction sequences4,5 and dendrimer syntheses,6–8 the supramolecular dendritic aspects8–10 have been extended to the macromolecular nanoscale.9 In this review, we focus on the functions and applications of dendrimers resulting from supramolecular and physical properties. We will not address the synthetic aspects that have been the subject of many reviews.

- Inducing α-Helices in Short Oligopeptides through Binding by an Artificial Hydrophobic Cavity
  Dolain, C.; Hatakeyama, Y.; Sawada, T.; Tashiro, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 5564–5565.
  Abstract:



Short peptides were induced into α-helix conformations in water through enclathration to an artificial hydrophobic cavity. Peptides with two aromatic residues showed high affinity for the host, and these intermolecular aromatic–aromatic interactions specifically drove the helical folding of short peptides.

- Membrane Lipids Influence Protein Complex Assembly–Disassembly
  Shin, L.; Cho, W. J.; Cook, J. D.; Stemmler, T. L.; Jena, B. P. *J. Am. Chem. Soc.* **2010**, *132*, 5596–5597.
  Abstract:

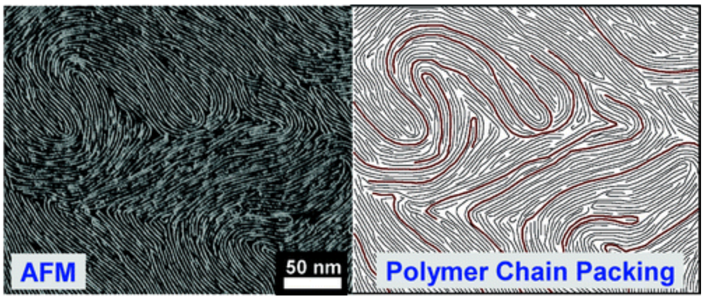


Approximately 11% smaller t-/v-SNARE ring complexes are generated using 50 nm cholesterol-associated vesicles as opposed to vesicles containing l-α-lysophosphatidylcholine (LPC), as observed using atomic force microscopy. Circular dichroism spectroscopy demonstrated that in the presence of LPC as opposed to cholesterol, *N*-ethylmaleimide-sensitive factor + adenosine triphosphate induces disassembly of β-sheet structures but not the α-helical contents within the t-/v-SNARE complex.

- Visualization of Polymer Chain Conformations in Amorphous Polyisocyanide Langmuir–Blodgett Films by Atomic Force Microscopy

Kumaki, J.; Kajitani, T.; Nagai, K.; Okoshi, K.; Yashima, E. *J. Am. Chem. Soc.* **2010**, *132*, 5604–5606.

Abstract:

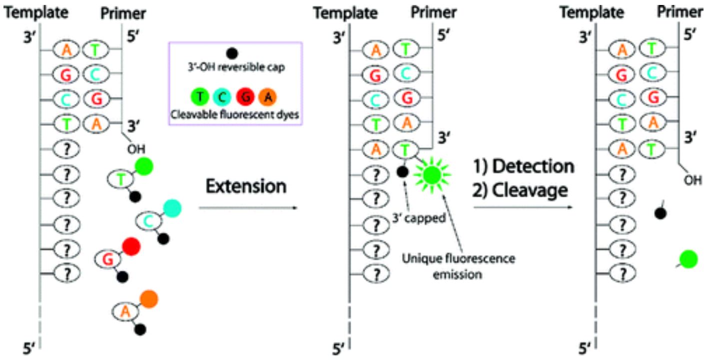


Polymer Langmuir monolayers are an ideal model for two-dimensional (2D) polymer chains, but our understanding of them is still limited. Using atomic force microscopy, we have for the first time successfully visualized the polymer chain packings in amorphous polyisocyanide monolayers deposited on mica. The long polymer chains, which were partially forced to form hairpin-like conformations, were sophisticatedly packed in the 2D film without any chain stacking. The trend of the persistent lengths of the polymers in the 2D films fairly corresponded to those of 3D chains in solution. The molecular-level information provided by direct observations such as these will improve our understanding of polymers in 2D space.

- An Integrated System for DNA Sequencing by Synthesis Using Novel Nucleotide Analogues

  Guo, J.; Yu, L.; Turro, N. J.; Ju, J. *Acc. Chem. Res.* **2010**, *43*, 551–563.

  Abstract:



The Human Genome Project has concluded, but its successful completion has increased, rather than decreased, the need for high-throughput DNA sequencing technologies. The possibility of clinically screening a full genome for an individual's mutations offers tremendous benefits, both for pursuing personalized medicine and for uncovering the genomic contributions to diseases. The Sanger sequencing method, although enormously productive for more than 30 years, requires an electrophoretic separation step that, unfortunately, remains a key technical obstacle for achieving economically acceptable full-genome results. Alternative sequencing approaches thus focus on innovations that can reduce costs.

The DNA sequencing by synthesis (SBS) approach has shown great promise as a new sequencing platform, with particular progress reported recently. The general fluorescent SBS approach involves (i) incorporation of nucleotide analogs bearing fluorescent reporters, (ii) identification of the incorporated nucleotide by its fluorescent emissions, and (iii) cleavage of the fluorophore, along with the reinitiation of the polymerase reaction for continuing

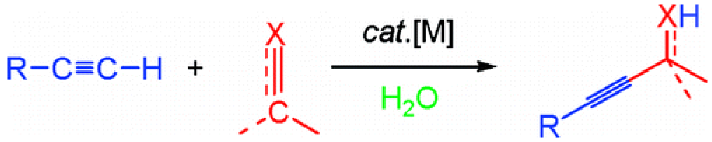
sequence determination. In this Account, we review the construction of a DNA-immobilized chip and the development of novel nucleotide reporters for the SBS sequencing platform.

Click chemistry, with its high selectivity and coupling efficiency, was explored for surface immobilization of DNA. The first generation (G-1) modified nucleotides for SBS feature a small chemical moiety capping the 3′-OH and a fluorophore tethered to the base through a chemically cleavable linker; the design ensures that the nucleotide reporters are good substrates for the polymerase. The 3′-capping moiety and the fluorophore on the DNA extension products, generated by the incorporation of the G-1 modified nucleotides, are cleaved simultaneously to reinitiate the polymerase reaction. The sequence of a DNA template immobilized on a surface via click chemistry is unambiguously identified with this chip–SBS system.

The second generation (G-2) SBS system was developed based on the concept that the closer the structures of the added nucleotide and the primer are to their natural counterparts, the more faithfully the polymerase would incorporate the nucleotide. In this approach, the polymerase reaction is performed with the combination of 3′-capped nucleotide reversible terminators (NRTs) and cleavable fluorescent dideoxynucleotides (ddNTPs). By sacrifice of a small amount of the primers permanently terminated by ddNTPs, the majority of the primers extended by the reversible terminators are reverted to the natural ones after each sequencing cycle. We have also developed the 3′-capped nucleotide reversible terminators to solve the problem of deciphering the homopolymeric regions of the template in conventional pyrosequencing. The 3′-capping moiety on the DNA extension product temporarily terminates the polymerase reaction, which allows only one nucleotide to be incorporated during each sequencing cycle. Thus, the number of nucleotides in the homopolymeric regions are unambiguously determined using the 3′-capped NRTs.

It has been established that millions of DNA templates can be immobilized on a chip surface through a variety of approaches. Therefore, the integration of these high-density DNA chips with the molecular-level SBS approaches described in this Account is expected to generate a high-throughput and accurate DNA sequencing system with wide applications in biological research and health care.

- The Development of Catalytic Nucleophilic Additions of Terminal Alkynes in Water
  Li, C.-J. *Acc. Chem. Res.* **2010**, *43*, 581–590.
  Abstract:



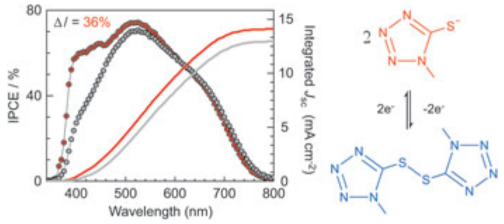
One of the major research endeavors in synthetic chemistry over the past two decades is the exploration of synthetic methods that work under ambient atmosphere with benign solvents, that maximize atom utilization, and that directly transform natural resources, such as renewable biomass, from their native states into useful chemical products, thus avoiding the need for protecting groups. The nucleophilic addition of terminal alkynes to various unsaturated electrophiles is a classical (textbook) reaction in organic chemistry, allowing the formation of a C–C bond while simultaneously introducing the alkyne functionality. A prerequisite of this classical reaction is the stoichiometric generation of highly reactive metal acetylides.

Over the past decade, our laboratory and others have been exploring an alternative, the catalytic and direct nucleophilic addition of terminal alkynes to unsaturated electrophiles in water. We found that various terminal alkynes can react efficiently with a wide range of such electrophiles in water (or organic solvent) in the presence of simple and readily available catalysts, such as copper, silver, gold, iron, palladium, and others. In this Account, we describe the development of these synthetic methods, focusing primarily on results from our laboratory.

Our studies include the following: (i) catalytic reaction of terminal alkynes with acid chloride, (ii) catalytic addition of terminal alkynes to aldehydes and ketones, (iii) catalytic addition of alkynes to C═N bonds, and (iv) catalytic conjugate additions. Most importantly, these reactions can tolerate various functional groups and, in many cases, perform better in water than in organic solvents, clearly defying classical reactivities predicated on the relative acidities of water, alcohols, and terminal alkynes. We further discuss multicomponent and enantioselective reactions that were developed.

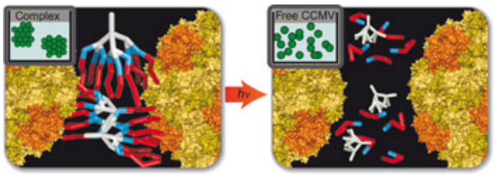
These methods provide an alternative to the traditional requirement of separate steps in classical alkyne reactions, including the pregeneration of metal acetylides with stoichiometric, highly basic reagents and the preprotection of sensitive functional groups. Accordingly, these techniques have greatly enhanced overall synthetic efficiencies and furthered our long-term objective of developing Grignard-type reactions in wáter.

- An organic redox electrolyte to rival triiodide/iodide in dye-sensitized solar cells
  Wang, M.; Chamberland, N.; Breau, L.; Moser, J.-E.; Humphry-Baker, R.; Marsan, B.; Zakeeruddin, S. M.; Grätzel, M. *Nature Chemistry* **2010**, *2*, 385 – 389.
  Abstract:



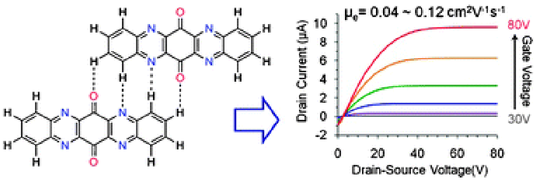
Dye-sensitized solar cells (DSCs) have achieved impressive conversion efficiencies for solar energy of over 11% with an electrolyte that contains triiodide/iodide as a redox couple. Although triiodide/iodide redox couples work efficiently in DSCs, they suffer from two major disadvantages: electrolytes that contain triiodide/iodide corrode electrical contacts made of silver (which reduces the options for the scale up of DSCs to module size) and triiodide partially absorbs visible light. Here, we present a new disulfide/thiolate redox couple that has negligible absorption in the visible spectral range, a very attractive feature for flexible DSCs that use transparent conductors as current collectors. Using this novel, iodide-free redox electrolyte in conjunction with a sensitized heterojunction, we achieved an unprecedented efficiency of 6.4% under standard illumination test conditions. This novel redox couple offers a viable pathway to develop efficient DSCs with attractive properties for scale up and practical applications.

- Self-assembly and optically triggered disassembly of hierarchical dendron–virus complexes
  Kostiainen, M. A.; Kasyutich, O.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *Nature Chemistry* **2010**, *2*, 394 – 399.
  Abstract:



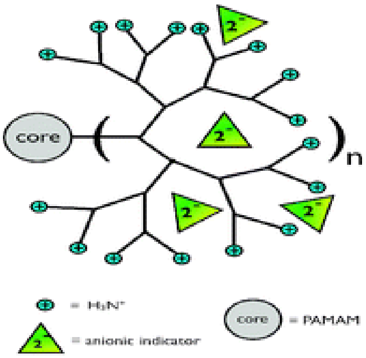
Nature offers a vast array of biological building blocks that can be combined with synthetic materials to generate a variety of hierarchical architectures. Viruses are particularly interesting in this respect because of their structure and the possibility of them functioning as scaffolds for the preparation of new biohybrid materials. We report here that cowpea chlorotic mottle virus particles can be assembled into well-defined micrometre-sized objects and then reconverted into individual viruses by application of a short optical stimulus. Assembly is achieved using photosensitive dendrons that bind on the virus surface through multivalent interactions and then act as a molecular glue between the virus particles. Optical triggering induces the controlled decomposition and charge switching of dendrons, which results in the loss of multivalent interactions and the release of virus particles. We demonstrate that the method is not limited to the virus particles alone, but can also be applied to other functional protein cages such as magnetoferritin.

- N-heteroquinones: quadruple weak hydrogen bonds and n-channel transistors
  Tang, Q. ; Liang, Z. ; Liu, J. ; Xu, J. ; Miao, Q. *Chem. Commun.* **2010**, 46, 2977 – 2979.
  Abstract:



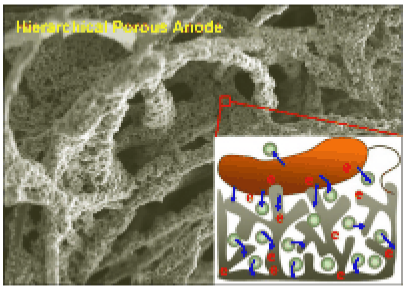
This study demonstrates that the easily synthesized N-heteroquinones, having unusual quadruple weak hydrogen bonds of a DDAA–AADD pattern, can function as n-type organic semiconductors in OTFTs with high electron mobility.

- Amino-terminated PAMAM dendrimers electrostatically uptake numerous anionic indicators
  Rainwater, J. C.; Anslyn, E. V. *Chem. Commun.* **2010**, 46, 2904 – 2906.
  Abstract:



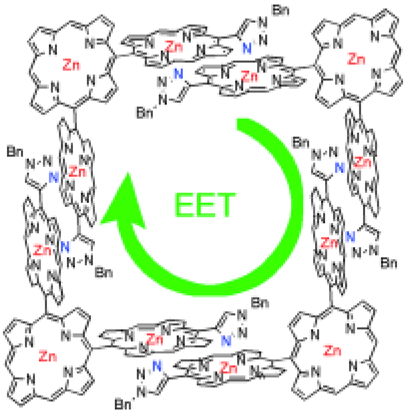
Generational trends in the uptake of multiple anionic indicators by unmodified commercially-available PAMAM dendrimers are described, and evidence of an electrostatic driving force in these high stoichiometry indicator–dendrimer interactions is offered.

- Three-Dimensional Conductive Nanowire Networks for Maximizing Anode Performance in Microbial Fuel Cells
  Zhao, Y.; Watanabe, K.; Nakamura, R.; Mori, S.; Liu, H.; Ishii, K.; Hashimoto, K. *Chem. Eur. J.* **2010**, *16*, 4982-4985.
  Abstract:



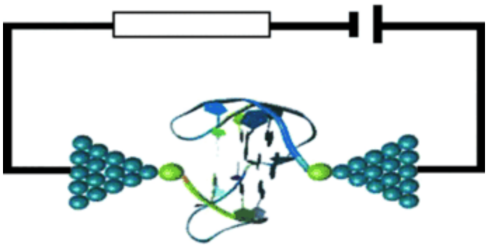
Pore genius: A nanoporous composite of graphite felt and polyaniline was developed and used as the anode of a microbial fuel cell, resulting in an order of magnitude increase in power output. The hierarchical conductive anode is a promising strategy for constructing highly efficient microbial fuel cells (see figure).

- Large Porphyrin Squares from the Self-Assembly of *meso*-Triazole-Appended L-Shaped *meso-meso*-Linked Zn^{II}-Triporphyrins: Synthesis and Efficient Energy Transfer
  Maeda, C.; Kim, P.; Cho, S.; Park, J. K.; Lim, J. M.; Kim, D.; Vura-Weis, J.; Wasielewski, M. R.; Shinokubo, H.; Osuka, A. *Chem. Eur. J.* **2010**, *16*, 5552-5561.
  Abstract:



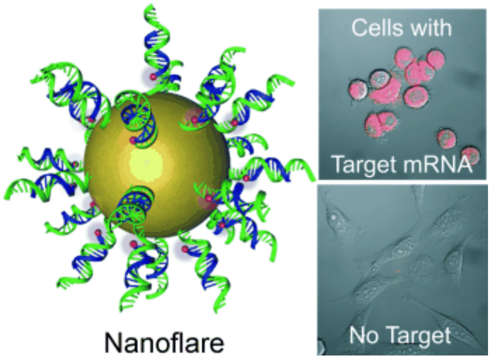
meso-Triazolyl-appended Zn^{II}-porphyrins were readily prepared by Cu^{I}-catalyzed 1,3-dipolar cycloaddition of benzyl azide to *meso*-ethynylated Zn^{II}-porphyrin (click chemistry). In noncoordinating $CHCl_3$ solvent, spontaneous assembly occurred to form tetrameric array $(3)_2$ from *meso-meso*-linked diporphyrins 3, and dodecameric porphyrin squares $(4)_4$ and $(5)_4$ from the L-shaped *meso-meso*-linked triporphyrins 4 and 5. The structures of these assemblies were examined by ^1H NMR spectra, absorption spectra, and their gel permeation chromatography (GPC) retention time. Furthermore, the structures of the dodecameric porphyrin squares $(4)_4$ and $(5)_4$ were probed by small- and wide-angle X-ray scattering (SAXS/WAXS) measurements in solution using a synchrotron source. Excitation-energy migration processes in these assemblies were also investigated in detail by using both steady-state and time-resolved spectroscopic methods, which revealed efficient excited-energy transfer (EET) between the *meso-meso*-linked Zn^{II}.

- Direct Measurement of Electrical Transport Through G-Quadruplex DNA with Mechanically Controllable Break Junction Electrodes
  Liu, S.-P.; Weisbrod, S. H.; Tang, Z.; Marx, A.; Scheer, E.; Erbe, A. *Angew. Chem. Int. Ed.* **2010**, *49*, 3313-3316.
  Abstract:



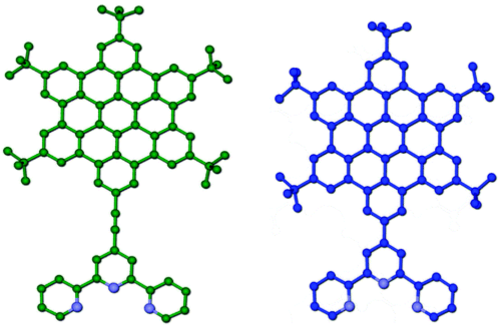
Totally wired: The folding of G-quadruplexes leads to a stacking of the G-bases, which provide a relatively large conductance. Stretching these complexes results in changes to the resistance that are only slightly over a broad range of molecular lengths. G-quadruplexes can thus be seen as molecular wires with adjustable length.

- Gold Nanoparticles for Biology and Medicine
  Giljohann, D. A.; Seferos, D. S.; Daniel, W. L.; Massich, M. D.; Patel, P. C.; Mirkin, C. A. *Angew. Chem. Int. Ed.* **2010**, *49*, 3280-3294.
  Abstract:



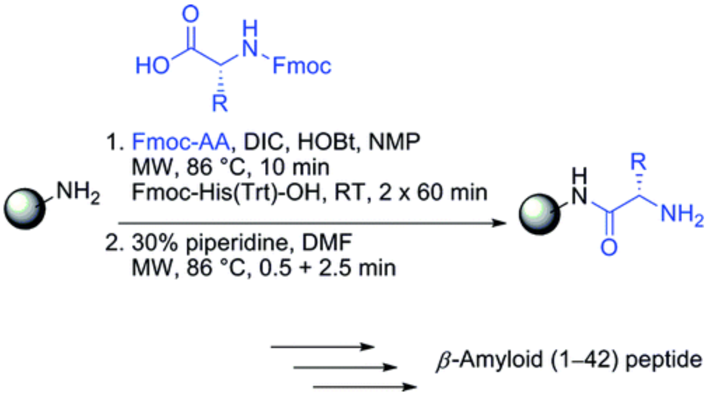
Sitting on a gold mine: Gold nanoparticles have been developed and studied as gene-regulating agents, drug carriers, photoresponsive therapeutics, and as imaging platforms (see the nanoflare, which allows detection of mRNA by fluorescence microscopy). These structures have new properties that are advantageous for biological applications. This Review highlights the synthesis of gold nanoparticles and their application from cell-based assays to therapeutic materials.

- Superaromatic Terpyridines: Hexa-*peri*-hexabenzocoronenes with Tridentate Functionality
  Murphy, F. A.; Draper, S. M. *J. Org. Chem.* **2010**, *75*, 1862–1870.
  Abstract:



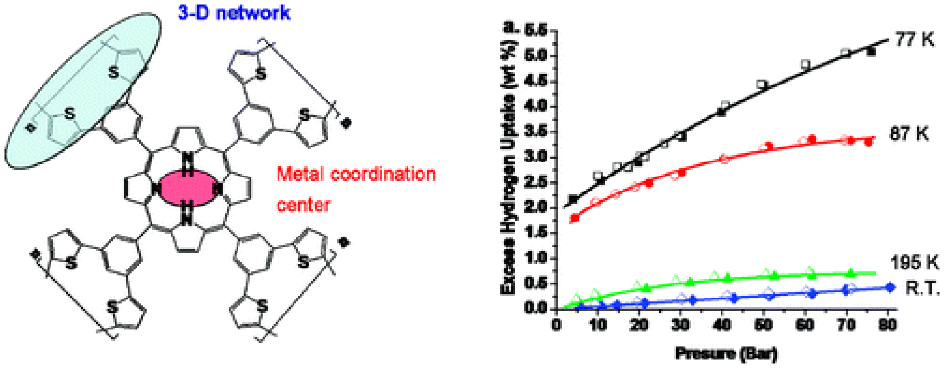
Two superaromatic terpyridine ligands (**1** and **2**) incorporating a hexa-*peri*-hexabenzocoronene (HBC) unit at the 4′-position have been prepared. In **1**, the terpyridine and the HBC domains are directly fused, while in **2**, they are separated by an acetylene linker. Also presented is the synthesis and characterization of several novel HBC derivatives, including 2-iodo-5,8,11,14,17-penta-*tert*-butylhexa-*peri*-hexabenzocoronene (**7**), a valuable synthetic intermediate. Different synthetic routes to **1** and **2** are employed, and two alternative methods resulted in excellent yields of **2**. The optical properties of both novel terpyridines are examined using UV–visible absorption and emission spectroscopy. The single-crystal X-ray structures of **7** and a precursor, 4-iodo-4′-*tert*-butylphenylacetylene (**5**), are discussed.

- Direct Solid-Phase Synthesis of the β-Amyloid (1–42) Peptide Using Controlled Microwave Heating
  Bacsa, B.; Bósze, S.; Kappe, C. O. *J. Org. Chem.* **2010**, *75*, 2103–2106.
  Abstract:



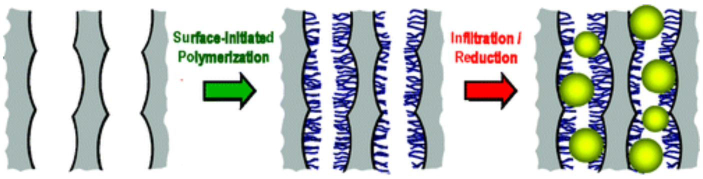
Standard linear Fmoc/*t*-Bu solid-phase synthesis of the 42-mer β-amyloid (1–42) peptide was achieved under controlled microwave conditions at 86 °C using inexpensive DIC/HOBt as coupling reagent on ChemMatrix resin. In order to avoid racemization of the sensitive amino acids, the coupling of the three His residues in the difficult peptide sequence was performed at room temperature. The desired peptide was obtained within 15 h overall processing time in high yield and purity (78% crude yield).

- Nanoporous Polyporphyrin as Adsorbent for Hydrogen Storage
  Xia, J.; Yuan, S.; Wang, Z.; Kirklin, S.; Dorney, B.; Liu, D.-J.; Yu, L. *Macromolecules* **2010**, *43*, 3325–3330.
  Abstract:



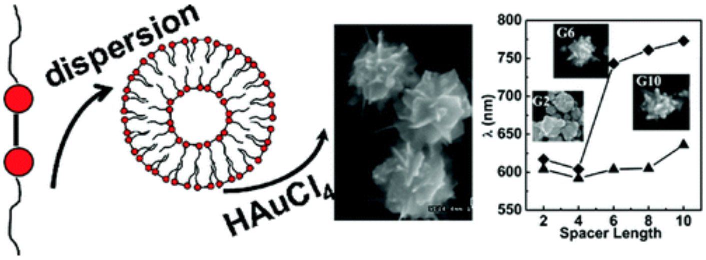
Novel polyporphyrins with high surface area over 1500 m^2/g have been synthesized, and their hydrogen absorption capacities were measured. Porphyrin functionalized with thiophenyl groups was designed as starting monomer; the porphyrin cores offer coordination sites for metal ions which could potentially enhance the interaction with hydrogen for favorable hydrogen storage while the thiophenyl groups are used for cross-linking the monomers under oxidative coupling conditions to yield highly porous networks. These polyporphyrins adsorb up to 5.0 mass % H_2 at 77 K and 65 bar. Compared with metal free polymer, iron(II)-containing polymer shows finite increase in heat of adsorption for hydrogen, suggesting a promising approach for designing high heat of adsorption porous materials.

- Nanochemistry in Confined Environments: Polyelectrolyte Brush-Assisted Synthesis of Gold Nanoparticles inside Ordered Mesoporous Thin Films
  Calvo, A.; Fuertes, M. C.; Yameen, B.; Williams, F. J.; Azzaroni, O.; Soler-Illia, G. J. A. A. *Langmuir* **2010**, *26,* 5559-5567.
  Abstract:



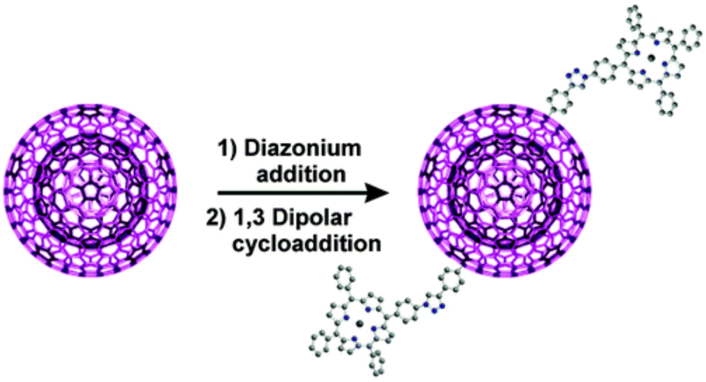
A robust and straightforward strategy allowing the controlled confinement of metal nanoparticles within the 3D framework of mesoporous films is presented. The chemical methodology is based on the inner surface modification of mesoporous silica films with polyelectrolyte brushes. We demonstrate that the macromolecular building blocks significantly enhance the site-selective preconcentration of nanoparticle precursors in the inner environment of the mesoporous film. Then, chemical reduction of the preconcentrated precursors led to the formation of metal nanoparticles locally addressed in the mesoporous structure. We show that the synergy taking place between two versatile functional nanobuilding blocks (ordered mesocavities and polymer brushes) can produce stable embedded nanoparticles with tuned optical properties in a very simple manner. As a general framework, the strategy can be easily adapted to different sets of polymer brushes and mesoporous films in order to regulate the monomer–precursor interactions and, consequently, manipulate the site-selective character of the different chemistries taking place in the film. We consider that the "integrative chemistry" approach described in this work provides new pathways to manipulate the physicochemical characteristics of hybrid organic–inorganic advanced functional assemblies based on the rational design of chemistry and topology in confined environments.

- Vesicle-Directed Generation of Gold Nanoflowers by Gemini Amphiphiles and the Spacer-Controlled Morphology and Optical Property
  Zhong, L.; Zhai, X.; Zhu, X.; Yao, P.; Liu, M. *Langmuir* **2010**, *26*, 5876-5881.
  Abstract:



In this article, we developed an effective approach to generate gold nanoflowers (AuNFs) by vesicles made from a series of gemini amphiphiles (G2-G10) with different spacer lengths. The gemini amphiphiles were found to form vesicles in aqueous solution. Upon mixing with vesicles in the presence of $AgNO_3$, $HAuCl_4$ could be reduced into gold nanoflowers by ascorbic acid. The vesicles directed the growth of the AuNFs, and the spacer length of the gemini amphiphiles showed obvious control of the morphology and optical properties of the formed AuNFs. At a lower $HAuCl_4$ concentration, the minimum-sized AuNFs were formed when vesicles from the amphiphile with a spacer length of 4 were applied. Upon increasing the spacer length, branched nanoflowers are predominantly produced. A seed-growth mechanism together with the conformational change of the spacer of the gemini amphiphiles was proposed according to the studies on reaction processes. In addition, the formed gold nanoflowers showed obvious surface-enhanced Raman scattering activity for R6G. The present method provided an efficient, controllable way to synthesize branched gold nanostructures.

- Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) using Diazonium Compounds and "Click" Chemistry
  Flavin, K.; Chaur, M. N.; Echegoyen, L.; Giordani, S. *Org. Lett.* **2010**, *12*, 840–843.
  Abstract:



A novel versatile approach for the functionalization of multilayer fullerenes (carbon nano-onions) has been developed, which involves the facile introduction of a variety of simple functionalities onto their surface by treatment with in situ generated diazonium compounds. This approach is complemented by use of “click” chemistry which was used for the covalent introduction of more complex porphyrin molecules.