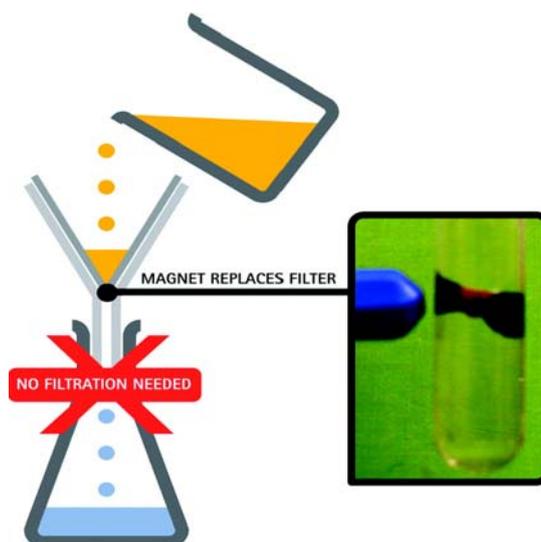


- Magnetically Recoverable Nanocatalysts

Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. *Chem. Rev.*, **2011**, *111*, 3036–3075.

1

Abstract:

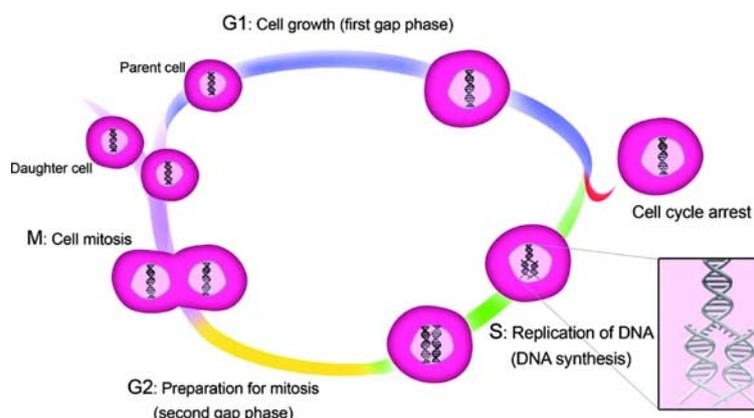


Catalysis is becoming a strategic field of science because it represents a new way to meet the challenges of energy and sustainability. These challenges are becoming the main concerns of the global vision of societal challenges and world economy. The societal pressure has been at the origin of the concept of green chemistry, which is becoming a leitmotiv in any important project dealing with this strategic domain of science. The concept of green chemistry, which makes catalysis science even more creative, has become an integral part of sustainability.

- Effect of Nanoparticles on the Cell Life Cycle

Mahmoudi, M.; Azadmanesh, K.; Shokrgozar, M. A.; Journeay, W. S.; Laurent, S. *Chem. Rev.*, **2011**, *111*, 3407–3432.

Abstract:



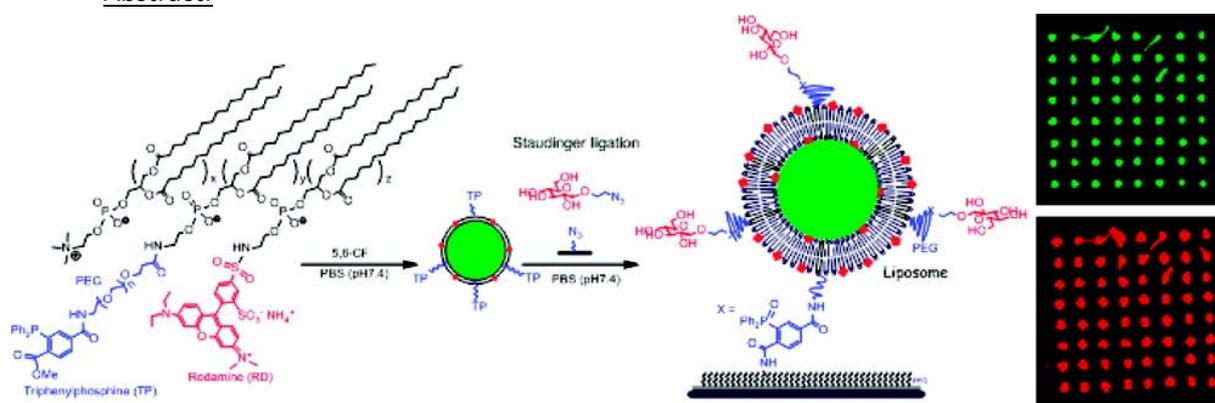
Nanoscience is often referred to as “key”, “horizontal”, or “enabling”, since it can virtually encompass all technological areas. Bringing together different areas of science, nanoscience benefits from a multidisciplinary approach in order to attain innovative solutions for many of the problems facing today’s society. A scientific and technological revolution has begun that is based on systematic organization, fabrication, or manipulation of matter in the nanometer length scale, where unique, distinctive material properties can be attained. To date, several nanotechnology-based products have been marketed including electronic components, scratch-free paint, sports equipments,

wrinkle- and stain-resistant fabrics, sun creams, and medical products. From a chronological point of view, nanoscience and nanotechnology were first employed in materials manufacturing applications such as composites and coatings, followed by incorporation of nanotech in electronics and information technology applications such as advanced memory chips and displays. Subsequently, nanoscience principles were applied in the fields of healthcare and life sciences to produce new products such as nanostructured medical devices and nanotherapeutics. Constantly increasing demand for nanoparticulate materials has resulted in the emergence and evolution of many companies in the fields of synthesis, functionalization, and application of nanoparticles both in vitro and in vivo. This is evidenced by the increasing number of nanoparticle-related publications in the past decade with most investigations reporting data on synthesis, characterization, and surface properties.

- Azide-Reactive Liposome for Chemoselective and Biocompatible Liposomal Surface Functionalization and Glyco-Liposomal Microarray Fabrication

Ma, Y.; Zhang, H.; Gruzdy, V.; Sun, X.-L. *Langmuir* **2011**, *27*, 13097-13103.

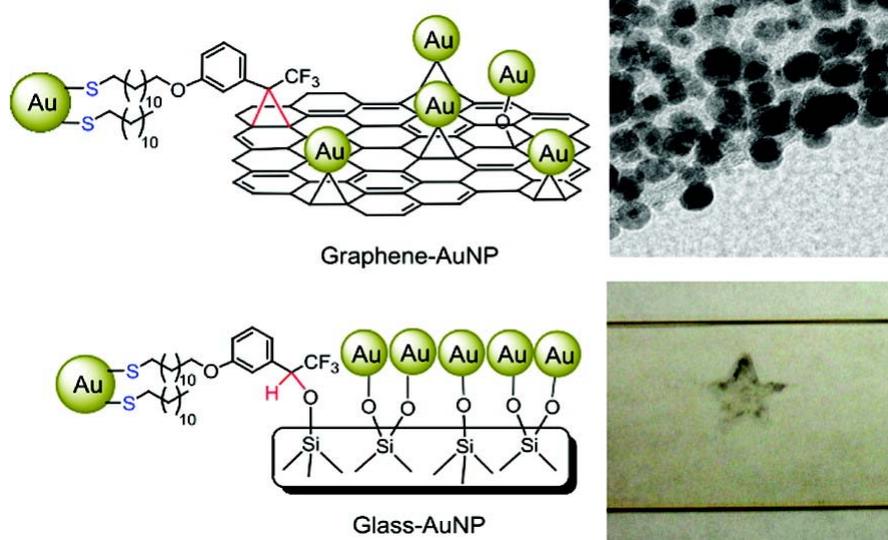
Abstract:



Chemically selective liposomal surface functionalization and liposomal microarray fabrication using azide-reactive liposomes are described. First, liposome carrying PEG-triphenylphosphine was prepared for Staudinger ligation with azide-containing biotin, which was conducted in PBS buffer (pH 7.4) at room temperature without a catalyst. Then, immobilization and microarray fabrication of the biotinylated liposome onto a streptavidin-modified glass slide via the specific streptavidin/biotin interaction were investigated by comparing with directly formed biotin-liposome, which was prepared by the conventional liposome formulation of lipid-biotin with all other lipid components. Next, the covalent microarray fabrication of liposome carrying triphenylphosphine onto an azide-modified glass slide and its further glyco-modification with azide-containing carbohydrate were demonstrated for glyco-liposomal microarray fabrication via Staudinger ligation. Fluorescence imaging confirmed the successful immobilization and protein binding of the intact immobilized liposomes and arrayed glyco-liposomes. The azide-reactive liposome provides a facile strategy for membrane-mimetic glyco-array fabrication, which may find important biological and biomedical applications such as studying carbohydrate-protein interactions and toxin and antibody screening.

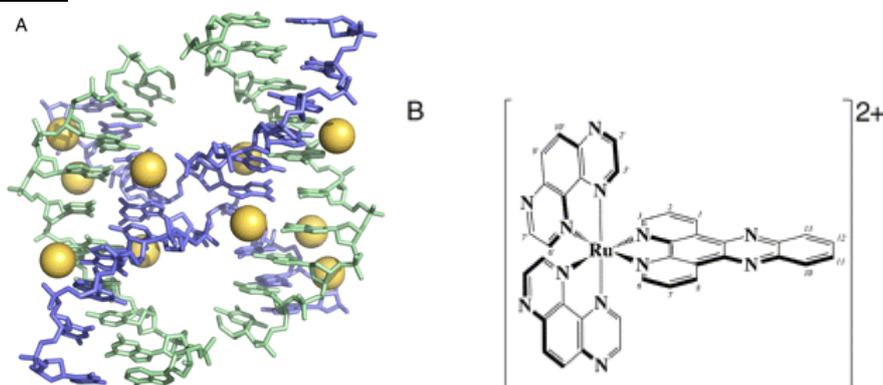
- Light-Activated Covalent Formation of Gold Nanoparticle-Graphene and Gold Nanoparticle-Glass Composites

Ismaili, H.; Geng, D.; Sun, A. X.; Kantzas, T. T.; Workentin, M. S. *Langmuir* **2011**, *27*, 13261-13268.

Abstract:

Monolayer protected gold nanoparticles (AuNPs) modified with a 3-aryl-3-(trifluoromethyl)diazirine functionality at its terminus (Diaz-AuNPs, 3.9 nm) were prepared and irradiated in the presence of two very different substrates, reduced graphene and glass. Upon irradiation, the terminal diazirine group loses nitrogen to generate a reactive carbene at the interface of the AuNPs that can then undergo addition or insertion reactions with functional groups on the graphene or glass surfaces, leading to the formation of graphene–AuNP and glass–AuNP hybrids, respectively. The AuNP hybrids were characterized using TEM, XRD, XPS, AFM, and UV–vis spectroscopy. Control experiments done in the absence of irradiation demonstrate that carbene activation is required for incorporation of significant AuNP onto the materials. The AuNP hybrids are robust and stable to excessive washing and centrifugation supporting the covalent nature of the interaction between the AuNP and the graphene or silicate glass substrates. Because the formation of the composite is light activated, it lends itself to photopatterning; this application is demonstrated for making the glass–AuNP composites.

- Structure determination of an intercalating ruthenium dipyridophenazine complex which kinks DNA by semiintercalation of a tetraazaphenanthrene ligand
Hall, J. P.; O’Sullivan, K.; Naseer, A.; Smith, J. A.; Kelly, J. M.; Cardin, C. J. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 17610-17614.

Abstract:

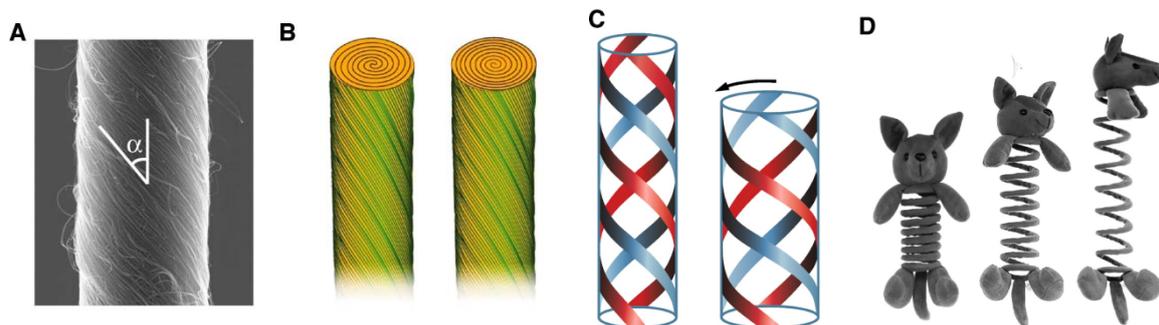
We describe a crystal structure, at atomic resolution (1.1 Å, 100 K), of a ruthenium polypyridyl complex bound to duplex DNA, in which one ligand acts as a wedge in the minor groove, resulting in

the 51° kinking of the double helix. The complex cation Λ -[Ru(1,4,5,8-tetraazaphenanthrene)₂(dipyridophenazine)]²⁺ crystallizes in a 1:1 ratio with the oligonucleotide d(TCGGCGCCGA) in the presence of barium ions. Each complex binds to one duplex by intercalation of the dipyridophenazine ligand and also by semiintercalation of one of the orthogonal tetraazaphenanthrene ligands into a second symmetrically equivalent duplex. The result is noncovalent cross-linking and marked kinking of DNA.

- Torsional Carbon Nanotube Artificial Muscles

Foroughi, J.; Spinks, G. M.; Wallace, G. G.; Oh, J.; Kozlov, M. E.; Fang, S.; Mirfakhrai, T.; Madden, J. D. W.; Shin, M. K.; Kim, S. J.; Baughman, R. H. *Science* **2011**, 334, 494-497.

Abstract:

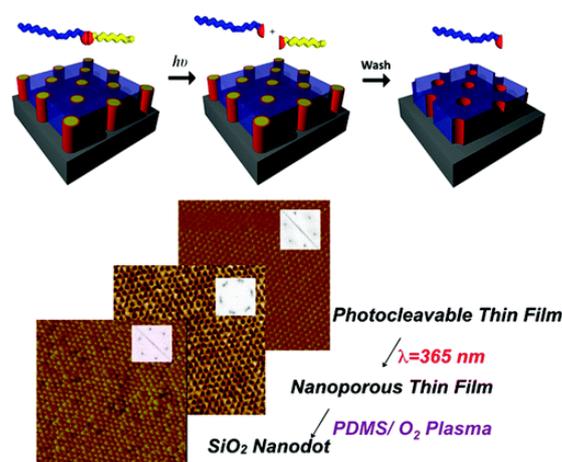


Rotary motors of conventional design can be rather complex and are therefore difficult to miniaturize; previous carbon nanotube artificial muscles provide contraction and bending, but not rotation. We show that an electrolyte-filled twist-spun carbon nanotube yarn, much thinner than a human hair, functions as a torsional artificial muscle in a simple three-electrode electrochemical system, providing a reversible 15,000° rotation and 590 revolutions per minute. A hydrostatic actuation mechanism, as seen in muscular hydrostats in nature, explains the simultaneous occurrence of lengthwise contraction and torsional rotation during the yarn volume increase caused by electrochemical double-layer charge injection. The use of a torsional yarn muscle as a mixer for a fluidic chip is demonstrated.

- Highly Ordered Nanoporous Thin Films from Photocleavable Block Copolymers

Zhao, H.; Gu, W.; Sterner, E.; Russell, T. P.; Coughlin, E. B.; Theato, P. *Macromolecules* **2011**, 44, 6433–6440.

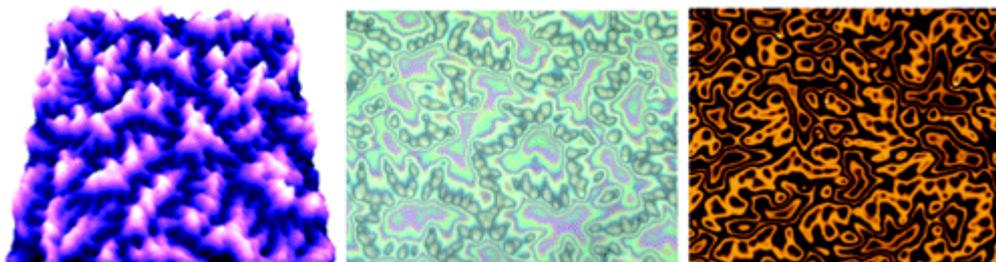
Abstract:



Poly(styrene-block-ethylene oxide) with an o-nitrobenzyl ester photocleavable junction (PS-hv-PEO) was synthesized by a combined RAFT polymerization and “click chemistry” approach and represents the first report utilizing this method for the synthesis of photocleavable block copolymers. After solvent annealing, highly ordered thin films were prepared from PS-hv-PEO. Following a very mild UV exposure and successive washing with water, PS-hv-PEO thin films were transformed into highly ordered nanoporous thin PS films with pore diameters of 15–20 nm and long range ordering (over $2\ \mu\text{m} \times 2\ \mu\text{m}$). Afterwards the pores were filled with PDMS by spin-coating in combination with capillary forces. After treatment with oxygen plasma to remove the PS templates, highly ordered arrays of silica nanodots were obtained. This represents the first template application example from highly ordered nanoporous thin films derived from block copolymers featuring a photocleavable junction.

- Synthesis and Assembly of Butyl Rubber–Poly(ethylene oxide) Graft Copolymers: From Surface Patterning to Resistance to Protein Adsorption
Bonduelle, C. V.; Karamdoust, S.; Gillies, E. R. *Macromolecules* **2011**, *44*, 6405–6415.

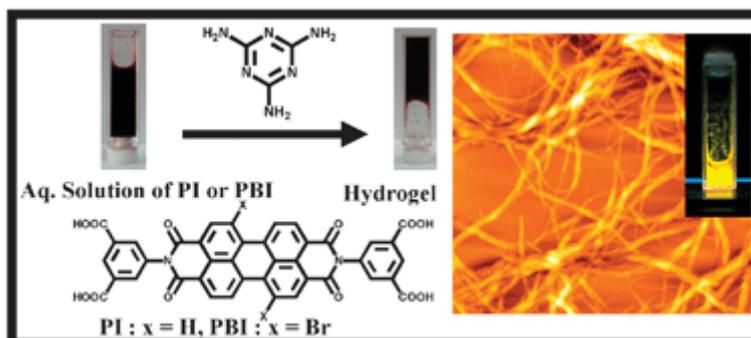
Abstract:



The patterning of copolymers on surfaces is of interest both for a fundamental understanding of polymer assembly processes and for applications ranging from microelectronics to biomaterials. Graft copolymers can provide new opportunities to control polymer composition and architecture, thus opening possibilities for new assembly processes and patterns. In this work, the reaction of a butyl rubber derivative functionalized with activated carbonates along the polymer backbone was reacted with amine terminated poly(ethylene oxide) (PEO–NH₂) to provide butyl rubber–PEO graft copolymers. The high efficiency of this reaction allowed for control of the PEO content by the number of equivalents of PEO–NH₂ used and its molecular weight, providing a small library of graft copolymers. This approach also provided butyl rubber–PEO graft copolymers with unprecedentedly high PEO content. Thin films of the polymers, prepared by spin-casting were studied by a number of techniques including atomic force microscopy, polarized optical microscopy, profilometry, and confocal fluorescence microscopy following the adsorption of a fluorescent protein. Interestingly, as the PEO content of the copolymers increased, an evolution from complex micrometer scale to nanometer scale patterns was observed. This was accompanied by resistance of the surfaces to protein adsorption at high PEO content, demonstrating that function can evolve from the complex interplay of thermodynamic and kinetic factors governing the assembly of these thin films.

- Assemblies of perylene diimide derivatives with melamine into luminescent hydrogels
Sukul, P. K.; Asthana, D.; Mukhopadhyay, P.; Summa, D.; Muccioli, L.; Zannoni, C.; Beljonne, D.; Rowan, A. E.; Malik, S. *Chem. Commun.* **2011**, *47*, 11858-11860.

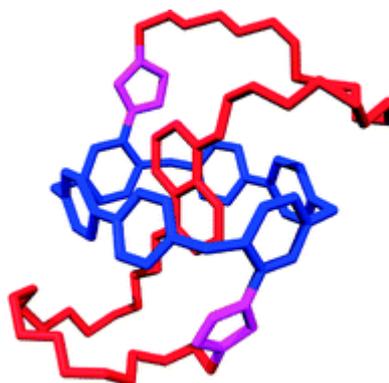
Abstract:



We report unique and spontaneous formation of hydrogels of perylene derivatives with melamine. The luminescent gel network is formed by H-type aggregation of the perylene core, supramolecularly cross-linked by melamine units. As a result of controlled aggregation in the extended nanofibers, strong exciton fluorescence emission is observed.

- Donor–acceptor molecular figures-of-eight
Boyle, M. M.; Forgan, R. S.; Friedman, D. C.; Gassensmith, J. J.; Smaldone, R. A.; Stoddart, J. F.; Sauvage, J.-P. *Chem. Commun.* **2011**, 47, 11870–11872.

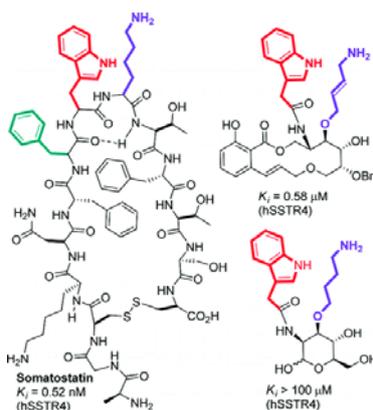
Abstract:



The intermolecular template-directed synthesis, separation and characterisation of two constitutional isomers that are self-complexing donor–acceptor [1]rotaxanes has been achieved by click chemistry, starting from a π -electron deficient tetracationic cyclophane containing two azide functions and a π -electron rich 1,5-dioxynaphthalene-containing polyether chain terminated by propargyl groups.

- Synthesis of a Benzomacrolactone-Based Somatostatin Mimetic
Zhou, J.; Matos, M.-C.; Murphy, P. V. *Org. Lett.* **2011**, 13, 5716–5719.

Abstract:

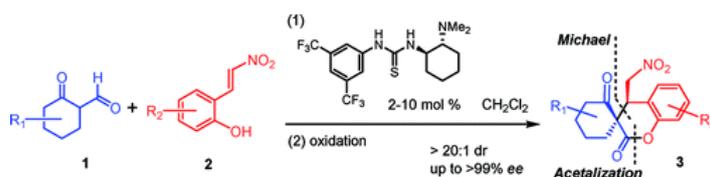


The benzomacrolactone is a framework found in numerous natural products. The synthesis of an orthogonally functionalized benzomacrolactone from D-glucosamine and a salicylic acid derivative is described. This macrolactone was used for the synthesis of a somatostatin mimetic that has submicromolar affinity for the human somatostatin receptor 4 (hSSTR4).

- Asymmetric Synthesis of 3,4-Dihydrocoumarin Motif with an All-Carbon Quaternary Stereocenter *via* a Michael–Acetalization Sequence with Bifunctional Amine-thiourea Organocatalysts

Hong, B.-C.; Kotame, P.; Lee, G.-H. *Org. Lett.* **2011**, *13*, 5758–5761.

Abstract:

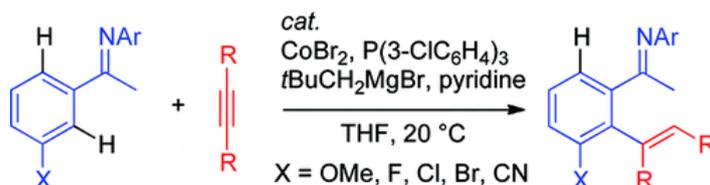


Asymmetric domino Michael–acetalization reactions of 2-hydroxynitrostyrene and 2-oxocyclohexanecarbaldehyde with a bifunctional thiourea-tertiary-amine organocatalyst, e.g., the Takemoto catalyst, followed by oxidation providing the 1',3-spiro-2'-oxocyclohexan-3,4-dihydrocoumarin having one all-carbon quaternary stereocenter with excellent diastereo- and enantioselectivities (up to >99% ee), are described. The structures and absolute configurations of the products were confirmed by X-ray analysis.

- Cobalt-Catalyzed, Room-Temperature Addition of Aromatic Imines to Alkynes via Directed C–H Bond Activation

Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283–17295.

Abstract:



A quaternary catalytic system consisting of a cobalt salt, a triarylphosphine ligand, a Grignard reagent, and pyridine has been developed for chelation-assisted C–H bond activation of an aromatic imine, followed by insertion of an unactivated internal alkyne that occurs at ambient temperature. The reaction not only tolerates potentially sensitive functional groups (e.g., Cl, Br, CN, and tertiary amide), but also displays a unique regioselectivity. Thus, the presence of substituents such as methoxy, halogen, and cyano groups at the *meta*-position of the imino group led to selective C–C

bond formation at the more sterically hindered ortho positions. Under acidic conditions, the hydroarylation products of dialkyl- and alkylarylacetylenes underwent cyclization to afford benzofulvene derivatives, while those of diarylacetylenes afforded the corresponding ketones in moderate to good yields. A mechanistic investigation into the reaction with the aid of deuterium-labeling experiments and kinetic analysis has indicated that oxidative addition of the ortho C–H bond is the rate-limiting step of the reaction. The kinetic analysis has also shed light on the complexity of the quaternary catalytic system.

- Light-Induced Enantiospecific 4π Ring Closure of Axially Chiral 2-Pyridones: Enthalpic and Entropic Effects Promoted by H-Bonding
Kumarasamy, E.; Jesuraj, J. L.; Omlid, J. N.; Ugrinov, A.; Sivaguru, J. *J. Am. Chem. Soc.* **2011**, *133*, 17106-17109.

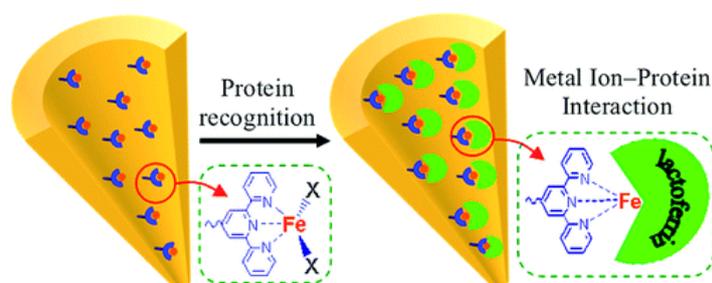
Abstract:



Nonbiaryl axially chiral 2-pyridones were synthesized and employed for light-induced electrocyclic 4π ring closure leading to bicyclo- β -lactam photoproducts in solution. The enantioselectivity in the photoproducts varied from 22 to 95% depending on the reaction temperature and the ability of the axially chiral chromophore to form intramolecular and/or intermolecular H-bonds with the solvent. On the basis of the differential activation parameters, entropic control of the enantiospecificity was observed for 2-pyridones lacking the ability to form H-bonds. Conversely, enthalpy played a significant role for 2-pyridones having the ability to form H-bonds.

- Metal Ion Affinity-based Biomolecular Recognition and Conjugation inside Synthetic Polymer Nanopores Modified with Iron–Terpyridine Complexes
Ali, M.; Nasir, S.; Nguyen, Q. H.; Sahoo, J. K.; Tahir, M. N.; Tremel, W.; Ensinger, W. *J. Am. Chem. Soc.* **2011**, *133*, 17307-17314.

Abstract:



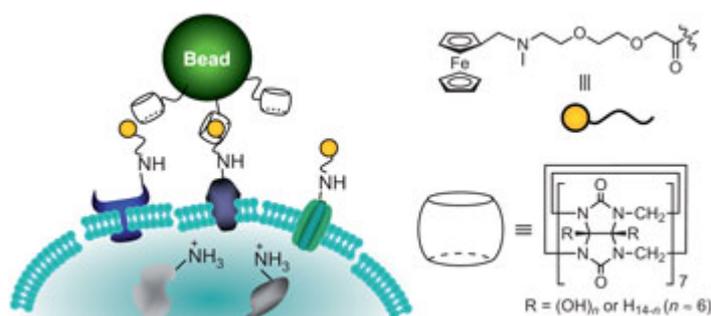
Here we demonstrate a novel biosensing platform for the detection of lactoferrin (LFN) via metal–organic frameworks, in which the metal ions have accessible free coordination sites for binding, inside the single conical nanopores fabricated in polymeric membrane. First, monolayer of amine-terminated terpyridine (metal–chelating ligand) is covalently immobilized on the inner walls of the nanopore via carbodiimide coupling chemistry. Second, iron–terpyridine (iron–terPy) complexes are

obtained by treating the terpyridine modified-nanopores with ferrous sulfate solution. The immobilized iron–terPy complexes can be used as recognition elements to fabricate biosensing nanodevice. The working principle of the proposed biosensor is based on specific noncovalent interactions between LFN and chelated metal ions in the immobilized terpyridine monolayer, leading to the selective detection of analyte protein. In addition, control experiments proved that the designed biosensor exhibits excellent biospecificity and nonfouling properties. Furthermore, complementary experiments are conducted with multipore membranes containing an array of cylindrical nanopores. We demonstrate that in the presence of LFN in the feed solution, permeation of methyl viologen (MV^{2+}) and 1,5-naphthalenedisulphate (NDS^{2-}) is drastically suppressed across the iron–terPy modified membranes. On the basis of these findings, we envision that apart from conventional ligand–receptor interactions, the designing and immobilization of alternative functional ligands inside the synthetic nanopores would extend this method for the construction of new metal ion affinity-based biomimetic systems for the specific binding and recognition of other biomolecules.

- Supramolecular fishing for plasma membrane proteins using an ultrastable synthetic host–guest binding pair

Lee, D.-W.; Park, K. M.; Banerjee, M.; Ha, S. H.; Lee, T.; Suh, K.; Paul, S.; Jung, H.; Kim, J.; Selvapalam, N.; Ryu, S. H.; Kim, K. *Nature Chem.* **2011**, *3*, 154-159.

Abstract:



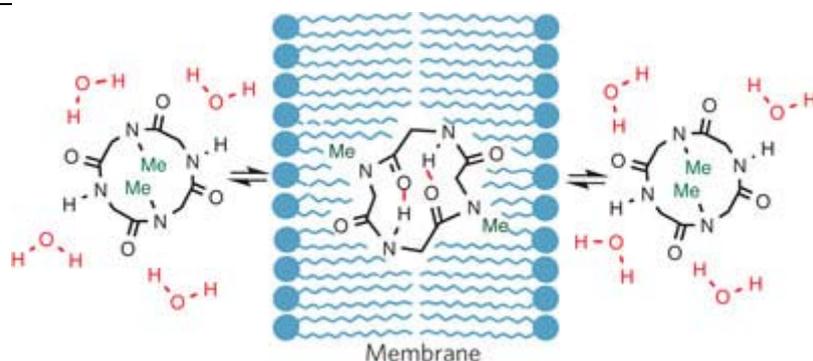
Membrane proteomics, the large-scale global analysis of membrane proteins, is often constrained by the efficiency of separating and extracting membrane proteins. Recent approaches involve conjugating membrane proteins with the small molecule biotin and using the receptor streptavidin to extract the labelled proteins. Despite the many advantages of this method, several shortcomings remain, including potential contamination by endogenously biotinylated molecules and interference by streptavidin during analytical stages. Here, we report a supramolecular fishing method for membrane proteins using the synthetic receptor–ligand pair cucurbit[7]uril–1-trimethylammoniomethylferrocene (CB[7]–AFC). CB[7]-conjugated beads selectively capture AFC-labelled proteins from heterogeneous protein mixtures, and AFC-labelling of cells results in the efficient capture of membrane proteins by these beads. The captured proteins can be recovered easily at room temperature by treatment with a strong competitor such as 1,1'-bis(trimethylammoniomethyl)ferrocene. This synthetic but biocompatible host–guest system may be a useful alternative to streptavidin–biotin for membrane proteomics as well as other biological and biotechnological applications.

- On-resin N-methylation of cyclic peptides for discovery of orally bioavailable scaffolds

White, T. R.; Renzelman, C. M.; Rand, A. C.; Rezai, T.; McEwen, C. M.; Gelev, V. M.; Turner, R. A.; Linington, R. G.; Leung, S. S. F.; Kalgutkar, A. S.; Bauman, J. N.; Zhang, Y.; Liras, S.; Price, D. A.; Mathiowetz, A. M.; Jacobson, M. P.; Lokey, R. S. *Nat. Chem. Biol.* **2011**, 7, 810–817.

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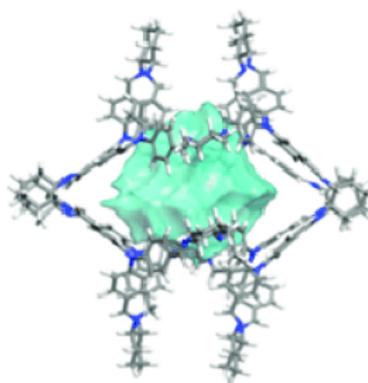
Abstract:



Backbone N-methylation is common among peptide natural products and has a substantial impact on both the physical properties and the conformational states of cyclic peptides. However, the specific impact of N-methylation on passive membrane diffusion in cyclic peptides has not been investigated systematically. Here we report a method for the selective, on-resin N-methylation of cyclic peptides to generate compounds with drug-like membrane permeability and oral bioavailability. The selectivity and degree of N-methylation of the cyclic peptide was dependent on backbone stereochemistry, suggesting that conformation dictates the regiochemistry of the N-methylation reaction. The permeabilities of the N-methyl variants were corroborated by computational studies on a 1,024-member virtual library of N-methyl cyclic peptides. One of the most permeable compounds, a cyclic hexapeptide (molecular mass = 755 Da) with three N-methyl groups, showed an oral bioavailability of 28% in rat.

- Large Self-Assembled Chiral Organic Cages: Synthesis, Structure, and Shape Persistence
Jelfs, K. E.; Wu, X.; Schmidtman, M.; Jones, J. T. A.; Warren, J. E.; Adams, D. J.; Cooper, A. I. *Angew. Chem. Int. Ed.* **2011**, 50, 10653–10656.

Abstract:



2.9 nm

Keep the cage filled: Two large organic cages (see example) with void diameters of 1.2 nm were synthesized through [8+12] imine condensation reactions. The materials become amorphous upon solvent removal and show little permanent porosity. Molecular dynamics simulations give an insight into the mechanism of these processes, suggesting strategies for synthesizing larger shape-persistent organic cages in the future.

- Identification of $\alpha 2$ Macroglobulin as a Major Serum Ghrelin Esterase
Eubanks, L. M.; Stowe, G. N.; Marin, S. D. L.; Mayorov, A. V.; Hixon, M. S.; Janda, K. D. *Angew. Chem. Int. Ed.* **2011**, *50*, 10699–10702.

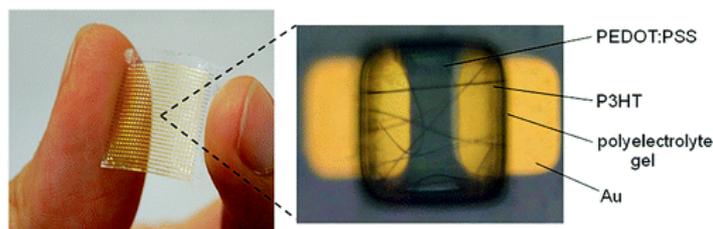
Abstract:



Fishing for a protein: An analogue of the appetite-stimulating hormone ghrelin containing a phosphonofluoridate moiety and a terminal alkyne functions as a probe to capture the protein $\alpha 2$ macroglobulin (red; see picture). The extraction of the protein is highly selective and a previously undocumented catalytic activity of $\alpha 2$ macroglobulin as a hydrolase for ghrelin has been identified.

- Periodic Array of Polyelectrolyte-Gated Organic Transistors from Electrospun Poly(3-hexylthiophene) Nanofibers
Lee, S. W.; Lee, H. J.; Choi, J. H.; Koh, W. G.; Myoung, J. M.; Hur, J. H.; Park, J. J.; Cho, J. H.; Jeong, U. *Nano Lett.* **2010**, *10*, 347–351.

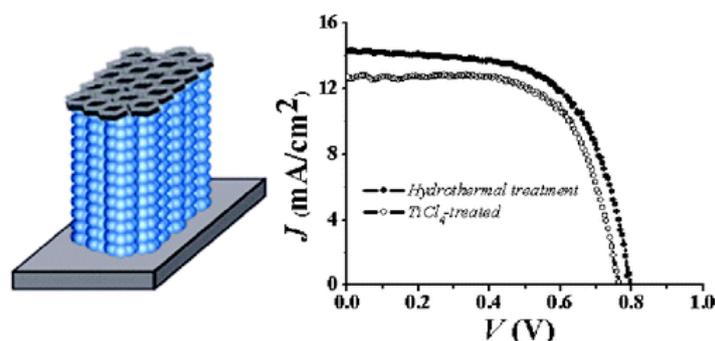
Abstract:



High-performance organic field-effect transistors (OFETs) based on polyelectrolyte gate dielectric and electrospun poly(3-hexylthiophene) (P3HT) nanofibers were fabricated on a flexible polymer substrate. The use of UV-crosslinked hydrogel including ionic liquids for the insulating layer enabled fast and large-area fabrication of transistor arrays. The P3HT nanofibers were directly deposited on the methacrylated polymer substrate. During UV irradiation through a patterned mask, the methacrylate groups formed covalent bonds with the patterned polyelectrolyte dielectric layer, which provides mechanical stability to the devices. The OFETs operate at voltages of less than 2 V. The average field-effect mobility and on/off ratio were $\sim 2 \text{ cm}^2/(\text{Vs})$ and 10^5 , respectively.

- High Efficiency Dye-Sensitized Solar Cells Based on Hierarchically Structured Nanotubes
Ye, M.; Xin, X.; Lin, C.; Lin, Z. *Nano Lett.* **2011**, *11*, 3214–3220.

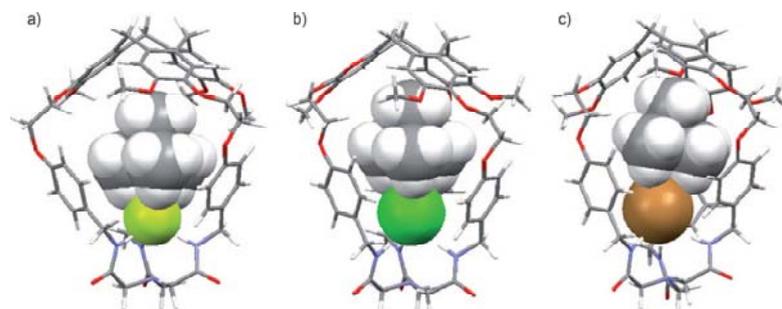
Abstract:



Dye-sensitized solar cells (DSSCs) based on hierarchically structured TiO₂ nanotubes prepared by a facile combination of two-step electrochemical anodization with a hydrothermal process exhibited remarkable performance. Vertically oriented, smooth TiO₂ nanotube arrays fabricated by a two-step anodic oxidation were subjected to hydrothermal treatment, thereby creating advantageous roughness on the TiO₂ nanotube surface (i.e., forming hierarchically structured nanotube arrays—nanoscopic tubes composed of a large number of nanoparticles on the surface) that led to an increased dye loading. Subsequently, these nanotubes were exploited to produce DSSCs in a backside illumination mode, yielding a significantly high power conversion efficiency, of 7.12%, which was further increased to 7.75% upon exposure to O₂ plasma.

- The Cooperative Effect in Ion-Pair Recognition by a Ditopic Hemicyptophane Host
Perraud, O.; Robert, V.; Martinez, A.; Dutasta, J.-P. *Chem. Eur. J.* **2011**, *17*, 4177-4182.

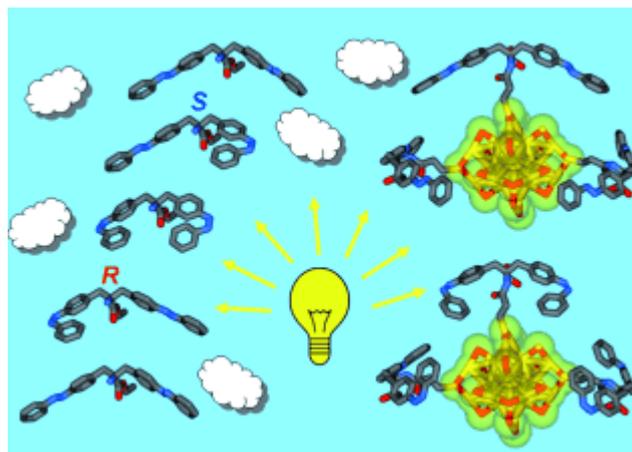
Abstract:



The heteroditopic hemicyptophane **1**, which bears a tripodal anion binding site and a cation recognition site in the molecular cavity, proved to be an efficient ion-pair receptor. The hemicyptophane host binds anions selectively depending on shape and hydrogen-bond-accepting ability. It forms an inclusion complex with the Me₄N⁺ ion, which can simultaneously bind anionic species to provide anion@[1·Me₄N⁺] complexes. The increased affinity of [1·Me₄N⁺] for anionic species is attributed to a strong cooperative effect that arises from the properly positioned binding sites in the hemicyptophane cavity, thus allowing the formation of the contact ion pair. Density functional theory calculations were performed to analyze the Coulomb interactions of the ion pairs, which compete with the ion-dipole ones, that originate in the ion–hemicyptophane contacts.

- Bis(azobenzene)-Based Photoswitchable, Prochiral, C_α-Tetrasubstituted α-Amino Acids for Nanomaterials Applications
Fatás, P.; Longo, E.; Rastrelli, F.; Crisma, M.; Toniolo, C.; Jiménez, A. I.; Cativiela, C.; Moretto, A. *Chem. Eur. J.* **2011**, *17*, 12606-12611.

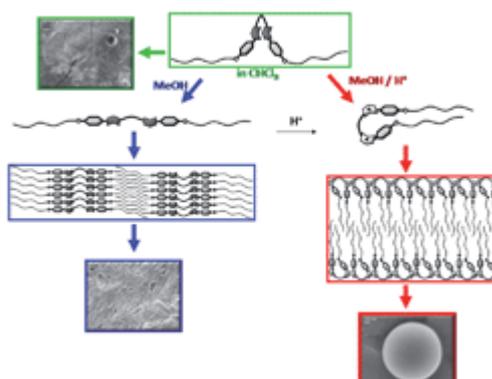
Abstract:



Light-driven chirality: Sequential light-driven isomerization of prochiral, bis(azobenzene)-containing amino acids results in the formation of chiral entities that have been characterized by different techniques. Metal nanoparticles conjugated with these amino acids retain the photoswitching properties and show conformation-dependent magnetic susceptibility that can be reversibly controlled by irradiation (see figure).

- Stimulus responsive self-assembly of Gemini Amphiphilic Pseudopeptides
Rubio, J.; Alfonso, I.; Burguete, M. I.; Luis, S. V. *Soft Matter* **2011**, 7, 10737-10748.

Abstract:



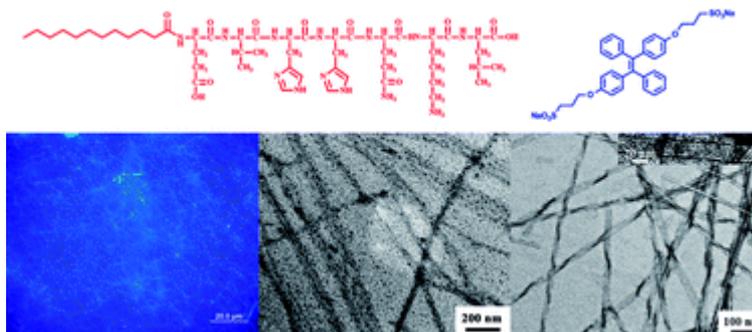
Amphiphilic amino acid derived compounds are very interesting for the design of building blocks able to self-assemble into highly ordered nanostructures, in a hierarchical and controlled fashion. With this aim, the modular synthesis and the full characterization of simple Gemini Amphiphilic Pseudopeptides (GAPs) have been carried out. These compounds were designed to establish intermolecular interactions in a hierarchical way to finally render supramolecular assemblies into well-ordered nanostructures, such as fibers, tubes, tapes or spherical vesicles. Different structural variables have been implemented, such as the amino acid side chain, the length of the central spacer and the nature of the hydrophobic tails. Besides, the effect of the environment was systematically checked, by performing the studies in solvents of different polarities (chloroform, methanol or aqueous methanol) and at different pHs (neutral, basic and acidic). The non-covalent self-assembling abilities and the structural features of the GAPs have been studied in the solid (SEM, TEM and FT-IR) and in the solution states (NMR, UV, CD, FT-IR and fluorescence spectroscopy). Moreover, the connection between the solution and the solid states has been established by monitoring the slow evaporation of the solvent by ATR FT-IR. This study has allowed the establishment of a relationship between the chemical structures of the GAPs and their abilities to form nanostructures. In some optimal cases (especially for the valine derivatives with medium-length spacers and two

decyloxybenzyl hydrophobic tails), they behaved as stimulus responsive self-assembling nanostructures, which form amorphous materials from non-polar solvents, nano-fibers from polar environments at neutral or basic pH and vesicles when become protonated at acidic pH values. A reasonable structural model to explain the experimental observations can be proposed through the combination of the results from the different techniques.

- Fluorescent nanofibrils constructed by self-assembly of a peptide amphiphile with an anionic dye

Yu, D.; Deng, M.; He, C.; Fan, Y.; Wang, Y. *Soft Matter* **2011**, *7*, 10773-10779.

Abstract:

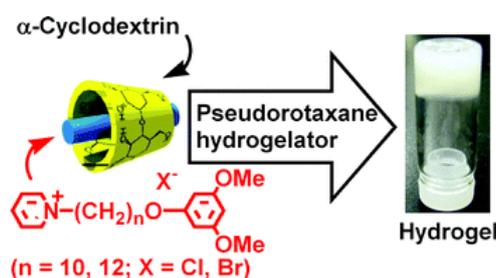


The interaction between a peptide amphiphile C_{12} -A β (11-17) and an anionic dye TPE with aggregation-induced emission (AIE) feature at different pH has been studied. C_{12} -A β (11-17) was constructed by attaching a key fragment of amyloid β -peptide (A β (11-17)) to a dodecanoic acid through an amide bond. It was found that highly fluorescent nanofibrils can be constructed through the self-assembly of C_{12} -A β (11-17) with TPE. Moreover, formation, structure and fluorescence intensity of the nanofibrils can be modulated by changing pH and the concentration of C_{12} -A β (11-17). In the solution of 0.05 mM C_{12} -A β (11-17) and 0.05 mM TPE, as the pH decreases, the fluorescence intensity of the mixed solution is invariable at pH > 7.0, then fast increases to the maximum while $4.0 < \text{pH} < 7.0$, and finally fast decreases at pH < 4.0. Only at pH 4.0-7.0, fluorescent nanofibrils of less than 5 μm length with the β -sheet secondary structure are formed upon the addition of TPE molecules. In 1.0 mM C_{12} -A β (11-17) solution with 0.05 mM TPE, the fluorescence intensity of the mixed solution keeps increasing as the pH decreases in the pH range of 3.4-11.0, and the mixture forms strongly fluorescent nanotapes of more than 50 μm length with an ordered β -sheet structure at pH 3.0 or relatively weaker fluorescent nanoribbons with a random coil structure at pH 10.0.

- Physical gels based on supramolecular gelators, including host-guest complexes and pseudorotaxanes

Suzaki, Y.; Taira, T.; Osakada, K. *J. Mater. Chem.* **2011**, *21*, 930-938.

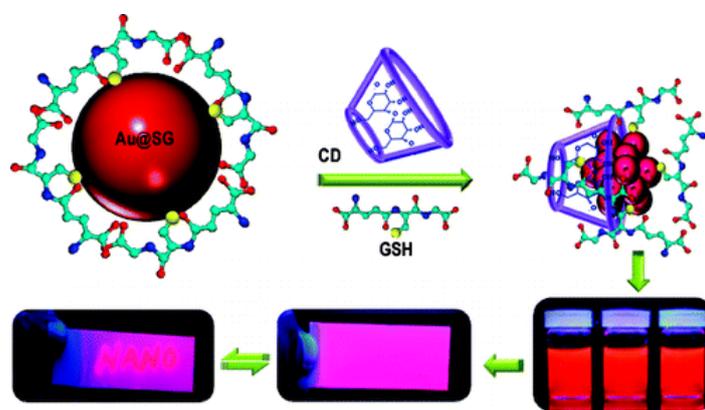
Abstract:



This article reviews recent studies on the gels formed by host–guest complexes, rotaxane and pseudorotaxanes. Pseudorotaxanes of crown ethers and rotaxanes of cyclic viologens with organic axle molecules form organogels through bonding of the functional end groups of the axle component. Cyclodextrins and cucurbiturils form gels in organic media and in aqueous mineral acids, respectively. The host–guest complexes and the pseudorotaxane of these macrocyclic compounds form hydrogels. These physical gels can be changed to sols by heating or addition of competing guests. Precise control of the gelation was enabled by using these supramolecules as the hydrogelator. Amphiphilic N-alkylpyridiniums and α -cyclodextrin form the hydrogel composed of their pseudorotaxanes. The mechanism of the gelation is described.

- Quantum Clusters in Cavities: Trapped Au₁₅ in Cyclodextrins
Sidharth Shibu, E.; Pradeep, T. *Chem. Mater.* **2011**, *23*, 989–999.

Abstract:



We have prepared Au₁₅ quantum clusters anchored to α -, β -, and γ -cyclodextrin (CD) cavities. The synthesis process involves the core etching of larger clusters and the simultaneous trapping of the clusters formed inside the CD cavities. The clusters were characterized by various tools, such as optical absorption and luminescence spectroscopies, electrospray ionization–mass spectrometry (ESI-MS), X-ray photoelectron spectroscopy (XPS), circular dichroism spectroscopy, and two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy. Trapping of the cluster in the CD cavity was proven by circular dichroism and also by rotational Overhauser effect spectroscopy (ROESY), in terms of the distinct cross peak between proton “e” of the glutathione (–SG) ligand and the “H3” proton of CD. Dynamic light scattering (DLS) studies showed a hydrodynamic diameter of \sim 3–4 nm, indicating one CD molecule per cluster with an extension of one water of hydration. The clusters are intensely luminescent, with major lifetime components of 28, 71, and 24 ps for Au₁₅@ α CD, Au₁₅@ β CD, and Au₁₅@ γ CD, respectively. The clusters also are strongly luminescent in the solid state. Both in the solution and in the solid state, the luminescence is sensitive to solvents/vapors. The clusters adhere to glass plates, and the solvent dependency of luminescence was used to create patterns that are erased upon gradual evaporation of the solvent. This self-erasing property was further demonstrated with clusters supported on a thin layer chromatography (TLC) plate. Selective detection of metal ions using the luminescence of the clusters is reported. Evaporation of the cluster solutions leads to luminescent gel-like materials.