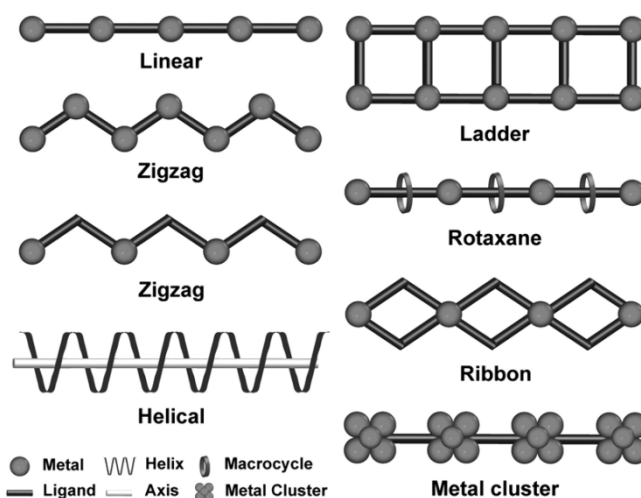


- One-Dimensional Coordination Polymers: Complexity and Diversity in Structures, Properties, and Applications

Leong, W. L.; Vittal, J. J. *Chem. Rev.* **2011**, *111*, 688–764.

Abstract:



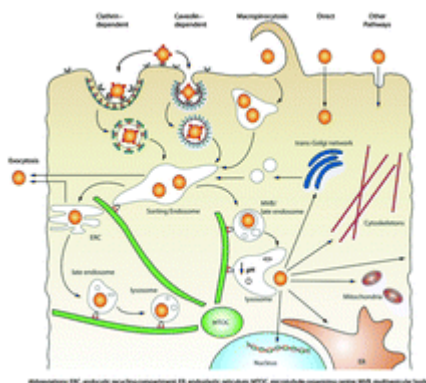
Crystal engineering of coordination polymers, which involves self-assembly of organic ligands with appropriate functional groups and metal ions with specific directionality and functionality, is one of the facile routes to produce materials of technological importance. The metal–ligand coordination bonds have been widely exploited in organizing molecular building blocks into diverse supramolecular architectures, making use of the strength of coordination bonds and directionality associated with metal ions. The nonmolecular compounds in which the basic building blocks containing metal ions and organic ligands assemble infinitely leading to one-, two-, and three-dimensional networks are commonly known as coordination polymers or metal–organic frameworks (MOFs).

Of these one-dimensional coordination polymer (1D CP), being the simplest topological type of coordination array, is found to be ubiquitous in nature and dominating the literature. The relative simplicity of the 1D chains and their ease of formation by self-assembly allow us to incorporate functional properties at the metal centers or in the backbone of the organic linkers very easily to develop strategies for engineering multifunctional polymeric materials.

The number of publications in the area of coordination polymers has grown from 515 hits until the end of 1993 to more than 5800 hits according to the recent SciFinder database search. Hence, it is not the intension of this review to provide a comprehensive collection of literature. Therefore, we attempt to cover literature from 1993 until the end of 2009. Of these, the major portion is occupied by the linear and zigzag 1D CPs. Inevitably, a number of structures will be excluded in this review. For this reason, this review rather focuses on the recent progress made on these two types of structures emphasizing on unusual packing and interesting properties with selected examples from the literature. At the outset we sincerely apologize to the authors for any omission of their contributions on 1D CPs.

- Strategies for the intracellular delivery of nanoparticles
Chou, L. Y. T.; Ming, K.; Chan, W. C. W. *Chem. Soc. Rev.* **2011**, *40*, 233-245.

Abstract:

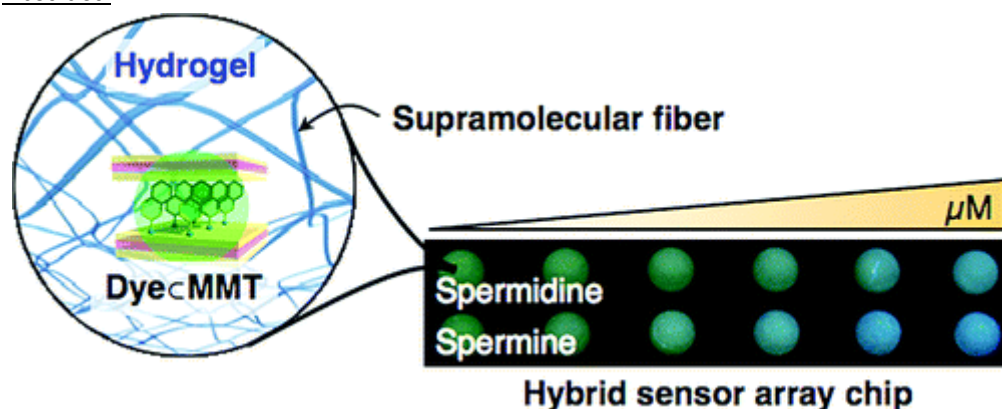


The ability to target contrast agents and therapeutics inside cells is becoming important as we strive to decipher the complex network of events that occur within living cells and design therapies that can modulate these processes. Nanotechnology researchers have generated a growing list of nanoparticles designed for such applications. These particles can be assembled from a variety of materials into desirable geometries and configurations and possess useful properties and functionalities. Undoubtedly, the effective delivery of these nanomaterials into cells will be critical to their applications. In this *tutorial review*, we discuss the fundamental challenges of delivering nanoparticles into cells and to the targeted organelles, and summarize strategies that have been developed to-date.

- Montmorillonite–Supramolecular Hydrogel Hybrid for Fluorocolorimetric Sensing of Polyamines

Ikeda, M.; Yoshii, T.; Matsui, T.; Tanida, T.; Komatsu, H.; Hamachi, I. *J. Am. Chem. Soc.* **2011**, *133*, 1670–1673.

Abstract:

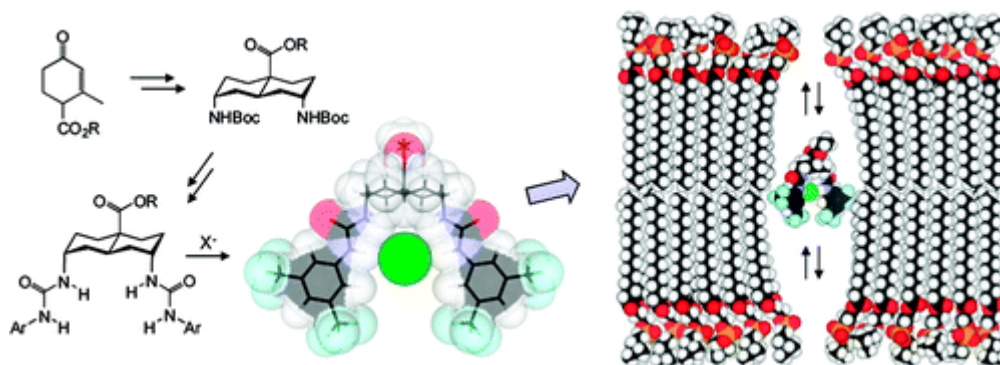


Fluorescent sensor materials for rapidly and conveniently detecting polyamines in biological fluids are highly desirable for cancer diagnosis. We herein describe the hybridization of a supramolecular hydrogel with a layered inorganic host adsorbing a fluorescent dye which produces a fluorocolorimetric sensor for spermine and spermidine, important biomarkers for cancers, in artificial urine.

- Diaxial Diureido Decalins as Compact, Efficient, and Tunable Anion Transporters

Hussain, S.; Brotherhood, P. R.; Judd, L. W.; Davis, A. P. *J. Am. Chem. Soc.* **2011**, *133*, 1614–1617.

Abstract:

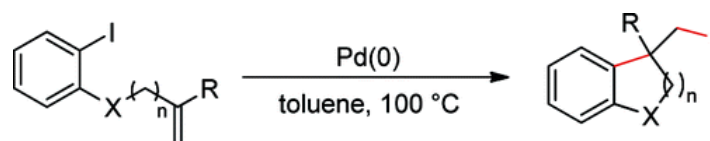


Decalins bearing two axial -NHCONHAr substituents and an ester-linked alkyl side chain have been synthesized and studied as anion receptors and transporters. The design relates to steroid-based “cholapods” but is more compact and less intrinsically lipophilic. Transport rates depend on both NHAr and the alkyl side chain. High activities can be achieved; with optimal substitution, chloride-nitrate exchange across vesicle membranes is measurable at transporter/lipid ratios as low as 1:250 000.

- Palladium-Catalyzed Carboiodination of Alkenes: Carbon–Carbon Bond Formation with Retention of Reactive Functionality

Newman, S. G.; Lautens, M. J. *Am. Chem. Soc.* **2011**, *133*, 1778–1780.

Abstract:

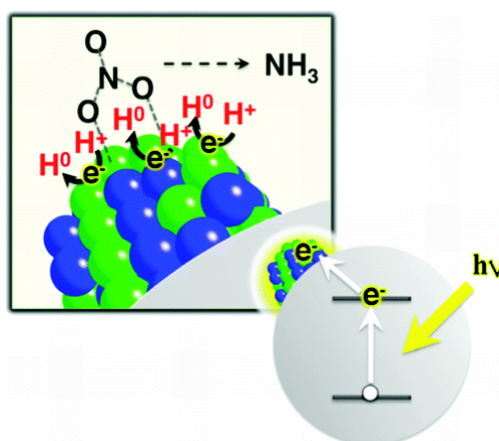


We report a palladium-catalyzed carbon–carbon bond-forming reaction between aryl iodides and alkenes. In contrast to traditional cross-coupling reactions, two new bonds are formed, and all of the atoms in the starting materials are incorporated into the product. The use of a palladium catalyst with bulky phosphine ligands is found to be crucial for reactivity.

- Highly Selective Ammonia Synthesis from Nitrate with Photocatalytically Generated Hydrogen on CuPd/TiO_2

Yamauchi, M.; Abe, R.; Tsukuda, T.; Kato, K.; Takata, M. *J. Am. Chem. Soc.* **2011**, *133*, 1150–1152.

Abstract:

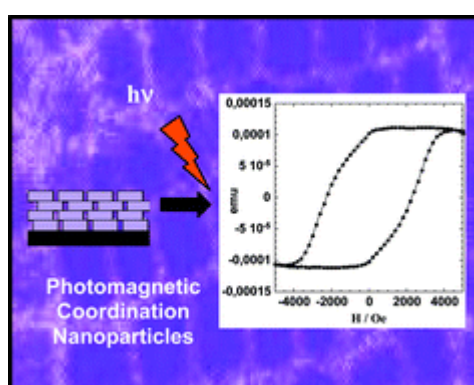


Body-centered-cubic type CuPd nanoalloys were synthesized by a chemical reduction method. Photocatalytic hydrogen evolution and nitrate reduction were simultaneously examined over CuPd nanoalloys deposited on TiO_2 (CuPd/TiO_2). The efficiency of hydrogen evolution over CuPd/TiO_2 was better than that over Pd/TiO_2 . As for nitrate reduction, ammonia was selectively (78%) produced with hydrogen generated photocatalytically over CuPd/TiO_2 . The continuous generation of nascent hydrogen atoms on the surface of the CuPd nanoalloy, where Cu and Pd are homogeneously mixed, led to the high selectivity for ammonia.

- Photo-induced magnetic bistability in a controlled assembly of anisotropic coordination nanoparticles

Volatron, F.; Heurtaux, D.; Catala, L.; Mathonière, C.; Gloter, A.; Stéphan, O.; Repetto, D.; Clemente-León, M.; Coronado, E.; Mallah, T. *Chem. Commun.* **2011**, 47, 1985-1987.

Abstract:

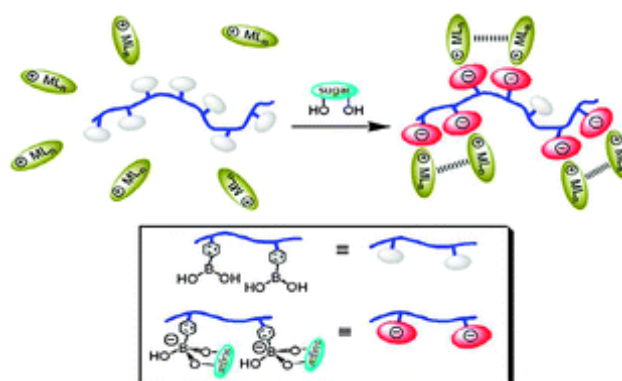


Anisotropic coordination nanoparticles of the photomagnetic network $\text{Cs}_2\text{Cu}_7[\text{Mo}(\text{CN})_8]_4$ are obtained through a surfactant-free high-yield synthetic procedure in water. These particles are organised as Langmuir–Blodgett films with a preferential orientation of the nano-objects within the film that exhibit a magnetic bistability below 20 K with a very large coercivity due to an efficient photo-transformation.

- “Proof-of-principle” concept for label-free detection of glucose and α -glucosidase activity through the electrostatic assembly of alkynylplatinum(II) terpyridyl complexes

Chung, C. Y.-S.; Chan, K. H.-Y.; Yam, V. W.-W. *Chem. Commun.* **2011**, 47, 2000-2002.

Abstract:



A two-component platinum(II) complex–polymer ensemble has been demonstrated for label-free spectroscopic detection of glucose and α -glucosidase activity, based on the electrostatic assembly of cationic platinum(II) complex molecules onto a glucose-bound anionic polymer.

- A self-assembled molecular team of boronic acids at the gold surface for specific capture of cis-diol biomolecules at neutral pH

Liang, L.; Liu, Z. *Chem. Commun.* **2011**, 47, 2255-2257.

Abstract:

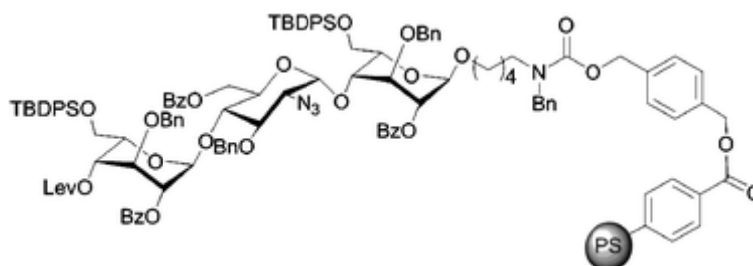


We report a single-step strategy called self-assembled molecular team to generate boronate affinity ligands that can specifically capture cis-diol biomolecules at neutral pH, which provides three significant advantages: a simple procedure, high affinity and high specificity.

- A new linker for solid-phase synthesis of heparan sulfate precursors by sequential assembly of monosaccharide building blocks

Czechura, P.; Guedes, N.; Kopitzki, S.; Vazquez, N.; Martin-Lomas, M.; Reichardt, N.-C. *Chem. Commun.* **2011**, 47, 2390-2392.

Abstract:

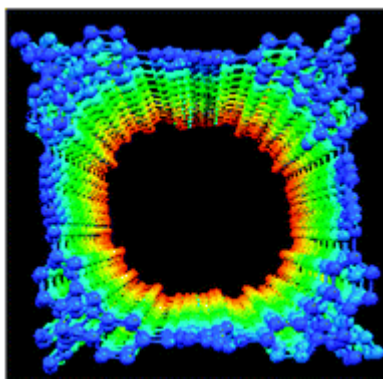


A novel ester type linker which upon cleavage releases the glycans as carbamate protected aminoglycosides was successfully employed in the sequential assembly of L-idose and azido glucose monosaccharide building blocks to heparan sulfate precursors.

- Aromatic single-walled organic nanotubes self-assembled from NH-bridged azacalix[2]triptycene[2]pyridine

Xue, M.; Chen, C.-F. *Chem. Commun.* **2011**, 47, 2318-2320.

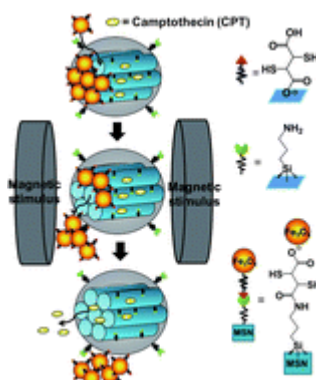
Abstract:



A novel triptycene-derived NH-bridged azacalixarene can self-assemble into an aromatic single-walled organic nanotube with large dimensions by four one-dimensional hydrogen bond chains.

- Multifunctional magnetically removable nanogated lids of Fe_3O_4 -capped mesoporous silica nanoparticles for intracellular controlled release and MR imaging
Chen, P.-J.; Hu, S.-H.; Hsiao, C.-S.; Chen, Y.-Y.; Liu, D.-M.; Chen, S.-Y. *J. Mater. Chem.* **2011**, *21*, 2535-2543.

Abstract:



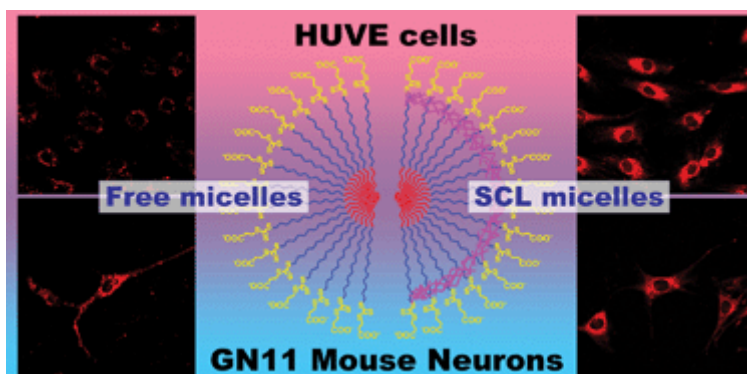
In this study, a novel nanocarrier ($\text{MSN}@Fe_3O_4$) is constructed using a facile technology by capping mesoporous silica nanoparticles (MSN) with monodispersed Fe_3O_4 nanoparticles through chemical bonding. The chemical links provide adhesion, which permits the magnetic nanoparticles, as nano-caps, to efficiently cover the mesoporous pores on the mesoporous silica matrix and be tightly bonded with the matrix surface. Without magnetic stimulus, none or only a negligible amount of the drug can be released from the $\text{MSN}@Fe_3O_4$. However, when subjected to an external controllable magnetic field, a quantity of nano-caps can be remotely and precisely removed, giving tunable release profiles for an anticancer drug, (*S*)-(+)-camptothecin (CPT), with various dosages depending upon the strength and time period of magnetic induction. The transverse relaxivity (r_2) of the $\text{MSN}@Fe_3O_4$ nanocarriers was measured to be about $121.57 \text{ s}^{-1}\text{mM}^{-1} \text{ Fe}$, which is larger than that for the reported mesoporous silica nanoparticles decorated with magnetite nanocrystals. Therefore, $\text{MSN}@Fe_3O_4$ nanocarriers could perform well as T_2 -type MR contrast enhancement agents for cell or molecular imaging. In addition, the $\text{MSN}@Fe_3O_4$ nanocarriers also demonstrate fairly high cell uptake efficiency. Together with its versatile magnetic manipulation, this new type of $\text{MSN}@Fe_3O_4$ nanosystem can be considered as a new class of multifunctional nanodevice, with combined tunable drug release and nanoimaging modalities for a variety of biomedical uses.

- Polymeric micelles using pseudo-amphiphilic block copolymers and their cellular uptake

Benaglia, M.; Alberti, A.; Spisni, E.; Papi, A.; Treossi, E.; Palermo, V. *J. Mater. Chem.* **2011**, *21*, 2555-2562.

7

Abstract:

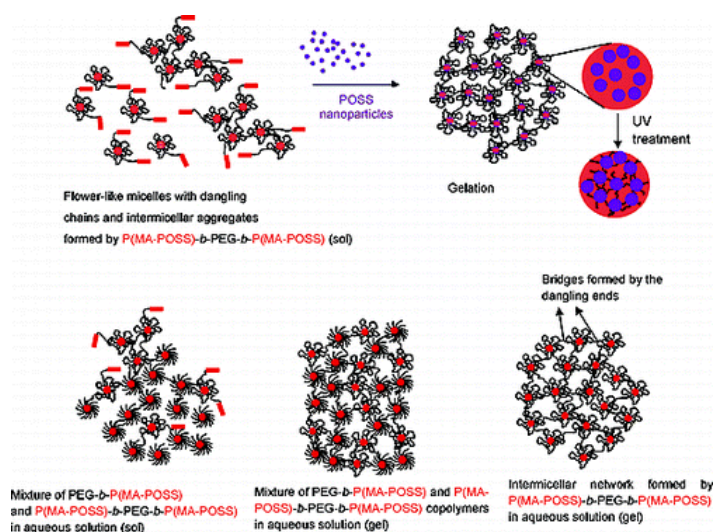


A PS-*b*-PMA block copolymer bearing a terminal carboxylic group has been synthesized using 3-(benzylsulfanyl thiocarbonylsulfanyl) propionic acid as RAFT agent. When dispersed in methanol, this block copolymer displays pseudo-amphiphilic behaviour providing micelles which can be suspended in water by osmosis. The carboxylic terminations are fundamental during the self-assembling process contributing to the formation of nanosized monodispersed particles. Furthermore, the anionic corona confers the to micelles stability in aqueous media. The core of the micelles was loaded with Nile Red to achieve the intracellular delivery of a lipophilic substance; this was demonstrated by Confocal Laser Scanning Microscopy. The particles, when loaded with doxorubicin, are able to overcome the intrinsic resistance of LoVo-MDR cancer cells. Further stabilization is given to the micelles by covalent shell crosslinking using triethylene glycol diacrylate. Because of the increased intracellular stability of the crosslinked micelles, they stain, when loaded with Nile Red, the aqueous cytosol instead of the lipophilic compartments. The unimers constituting the micelles were covalently labeled with fluorescein to follow their fate once incorporated into the cells.

- Tailoring Micelle Formation and Gelation (PEG-P(MA-POSS)) Amphiphilic Hybrid Block Copolymers

Tan, B. H.; Hussain, H.; He, C. B. *Macromolecules*, **2011**, *44*, 622–631.

Abstract:

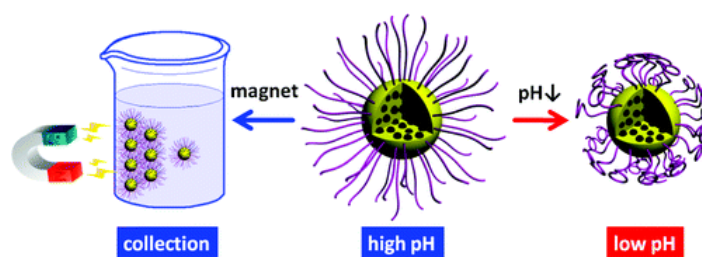


We demonstrate that hydrophobic POSS (polyhedral oligomeric-silsesquioxane) nanoparticles, added to block copolymer solutions of poly(ethylene glycol) (PEG) and poly(methacrylisobutyl polyhedral

oligomeric silsesquioxane) P(MA-POSS) as the hydrophilic and hydrophobic blocks respectively, could be employed to tailor their micelle formation, gelation, and rheological performance. For example, the hydrodynamic size of the micelles, formed by PEG_{5k}-*b*-P(MA-POSS)_{3.6}, increased from 13.6 ± 1.0 to 56.9 ± 3.7 , an increase of more than four times, with 0.1 wt % (with respect to block copolymer) POSS nanoparticles in solution. However, the micelles retain their spherical morphology with core-shell structure as evidenced by calculating the values of dimensionless ratios, R_g/R_h for micelles as a function of added POSS nanoparticles content. For P(MA-POSS)-*b*-PEG_{10k}-*b*-P(MA-POSS) triblock copolymers, which is associative in nature, addition of POSS nanoparticles resulted in formation of more robust and stronger hydrogels with a significantly higher storage modulus, G' , yield strengths, σ_y , and lower critical gelation concentration, c_g , as compared with those for the pristine triblock copolymer. The presence of eight vinyl groups, attached to the POSS nanoparticles under investigations, is also exploited for further enhancement of rheological properties of the hydrogels with UV treatment. Finally, gel formation is induced in aqueous solutions of PEG_{5k}-*b*-P(MA-POSS)_{3.6} diblock copolymer by introducing P(MA-POSS)-*b*-PEG_{10k}-*b*-P(MA-POSS) triblock copolymer chains, and the rheological performance of the produced hydrogels, with certain compositions, is even superior to that of pure triblock copolymer gel.

- Synthesis of Magnetic Spherical Polyelectrolyte Brushes
Chen, K; Zhu, Y.; Zhang, Y.; Li, L.; Lu, Y.; Guo, Z. *Macromolecules* **2011**, *44*, 632–639.

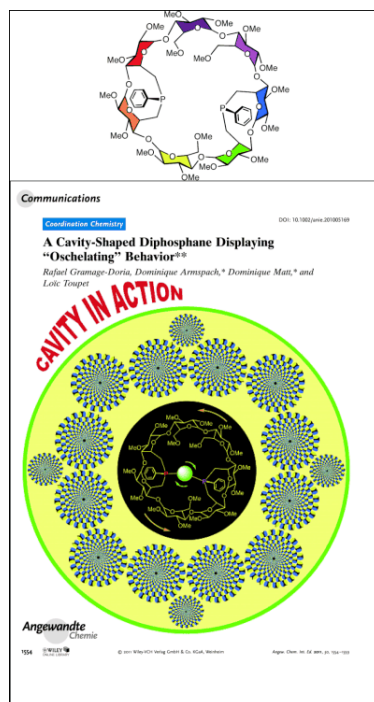
Abstract:



Magnetic spherical polyelectrolyte brushes (MSPB) with embedded magnetite nanoparticles in core were successfully synthesized and characterized by dynamic light scattering (DLS), a scanning electron microscope (SEM), a high resolution transmission electron microscope (HRTEM), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and a vibrating sample magnetometer (VSM). At first, oleic acid modified magnetite nanoparticles (MNP) were synthesized by the coprecipitation method and then embedded into the polystyrene core by miniemulsion polymerization to obtain magnetic polystyrene latices (MPL). Finally, magnetic spherical poly(acrylic acid) (PAA) brushes were synthesized by photoemulsion polymerization. Effects of MNP and acrylic acid (AA) content on the brush structure were studied in detail. The obtained MSPB are narrowly dispersed, pH sensitive, superparamagnetic, and redispersible after aggregating by external magnetic field. Magnetic control is thus introduced into nanosized spherical polyelectrolyte brushes to achieve the recovery and controllable delivery. This approach opens a new way for the recoverable and cost-effective applications of spherical polyelectrolyte brushes.

- A Cavity-Shaped Diphosphane Displaying “Oschelating” Behavior
Gramage-Doria, R.; Armspach, D.; Matt, D.; Toupet, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 1554–1559.

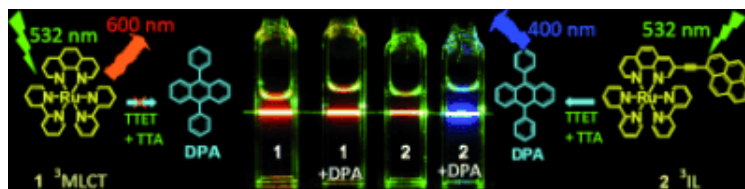
Abstract:



A molecular balance wheel: Transition metals form β -cyclodextrin-derived diphosphane chelate complexes (picture: ligand structure) in which a fast oscillatory motion about the metal ion takes place ("oschelating behavior"). The observed movement occurs without dissociation of the metal–phosphorus bond.

- Ruthenium(II) Polyimine Complexes with a Long-Lived ^3IL Excited State or a $^3\text{MLCT}/^3\text{IL}$ Equilibrium: Efficient Triplet Sensitizers for Low-Power Upconversion
Ji, S.; Wu, W.; Guo, H.; Zhao, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 1626–1629.

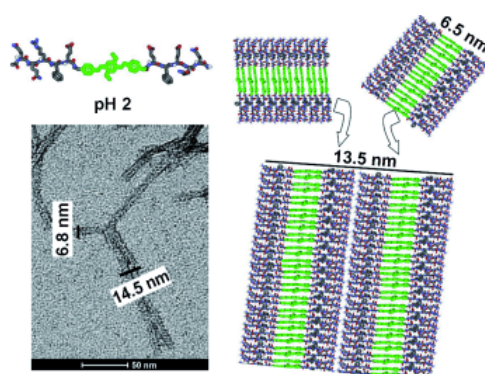
Abstract:



Up, up, and away! The long-lived ^3IL excited states of Ru^{II} polyimine complexes were found to be more efficient in sensitizing upconversion based on triplet–triplet annihilation (TTA) and energy transfer (TTET) than the shorter-lived $^3\text{MLCT}$ excited states (see picture). Upconversion occurs with an anti-Stokes shift of up to 0.77 eV.

- Synthesis and Self-Assembly of Oligo(*p*-phenylenevinylene) Peptide Conjugates in Water
Mba, M.; Moretto, A.; Armelao, L.; Crisma, M.; Toniolo, C.; Maggini, M. *Chem.-Eur. J.* **2011**, *17*, 2044-2047.

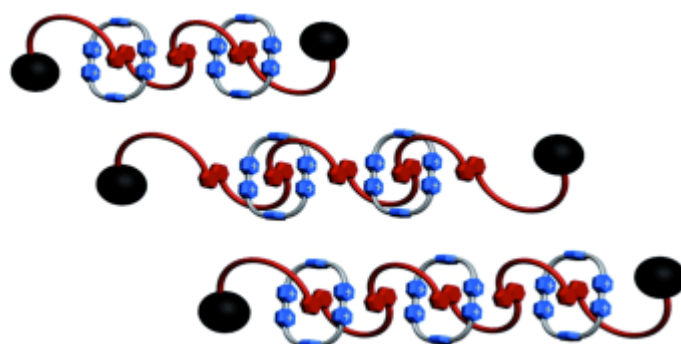
Abstract:



Fluorescent hydrogels: Peptide hybrids composed of an oligo(*p*-phenylenevinylene)-based ω -amino acid and a β -sheet-forming sequence reversibly self-assemble into fluorescent hydrogels upon a change in pH (see graphic). This study highlights how the combination of peptides and π -conjugated oligomers could be a fruitful approach towards the control of self-assembled structures.

- Donor–Acceptor Oligorotaxanes Made to Order
Basu, S.; Coskun, A.; Friedman, D. C.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Barin, G.; Yang, J.; Fahrenbach, A. C.; Goddard III, W. A.; Stoddart, J. F. *Chem.-Eur. J.* **2011**, *17*, 2107-2119.

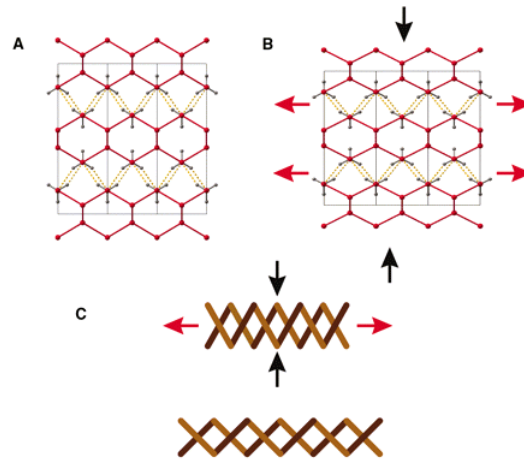
Abstract:



Five donor–acceptor oligorotaxanes made up of dumbbells composed of tetraethylene glycol chains, interspersed with three and five 1,5-dioxynaphthalene units, and terminated by 2,6-diisopropylphenoxy stoppers, have been prepared by the threading of discrete numbers of cyclobis(paraquat-*p*-phenylene) rings, followed by a kinetically controlled stoppering protocol that relies on click chemistry. The well-known copper(I)-catalyzed alkyne–azide cycloaddition between azide functions placed at the ends of the polyether chains and alkyne-bearing stopper precursors was employed during the final kinetically controlled template-directed synthesis of the five oligorotaxanes, which were characterized subsequently by ^1H NMR spectroscopy at low temperature (233 K) in deuterated acetonitrile. The secondary structures, as well as the conformations, of the five oligorotaxanes were unraveled by spectroscopic comparison with the dumbbell and ring components. By focusing attention on the changes in chemical shifts of some key probe protons, obtained from a wide range of low-temperature spectra, a picture emerges of a high degree of folding within the thread protons of the dumbbells of four of the five oligorotaxanes—the fifth oligorotaxane represents a control compound in effect—brought about by a combination of $\text{CH}\cdots\text{O}$ and π – π stacking interactions between the π -electron-deficient bipyridinium units in the rings and the π -electron-rich 1,5-dioxynaphthalene units and polyether chains in the dumbbells. The secondary structures of a foldamer-like nature have received further support from a solid-state superstructure of a related [3]pseudorotaxane and density functional calculations performed thereon.

- Unusual Thermoelastic Properties of Methanol Monohydrate
Grima, J. N.; Attard, D.; Gatt, R. *Science* **2011**, *331*, 687-688.

Abstract:

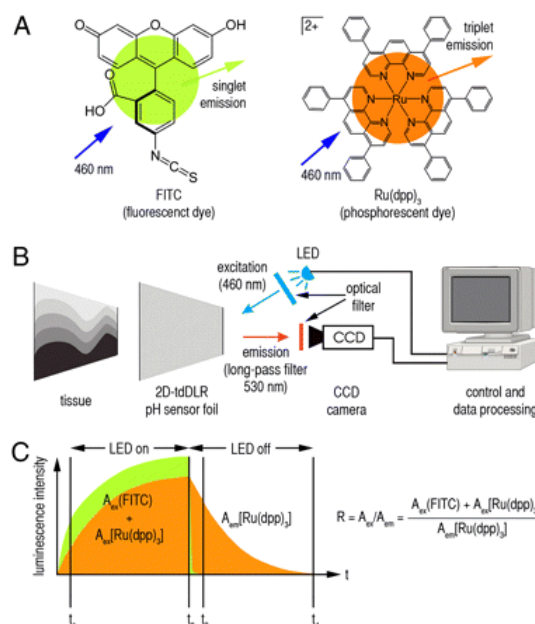


When a material is heated, we expect it to expand, and when squeezed on all sides by hydrostatic pressure, we expect it to shrink, but materials or structures can respond in unexpected ways. Some may exhibit negative thermal expansion (NTE)—shrinking when heated (1–8)—or negative compressibility (NC) (8–13)—expanding when subjected to a positive hydrostatic pressure—and some may exhibit both properties. For crystalline materials, the response can be anisotropic—observed along only some directions in a crystal (see the figure), and may only be observed in particular ranges of temperatures or pressures. On page 742 in this issue, Fortes *et al.* (8) report such anomalous properties from an experimental investigation on methanol monohydrate, a simple molecular crystal of a deuterated 1:1 compound of methanol and water. Such materials, used singly or in combination with conventional materials, can have useful mechanical and optical properties.

- 2D luminescence imaging of pH in vivo

Schreml, S.; Meier, R. J.; Wolfbeis, O. S.; Landthaler, M.; Szeimies, R.-M.; Babilas, P. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 2432-2437.

Abstract:



Luminescence imaging of biological parameters is an emerging field in biomedical sciences. Tools to study 2D pH distribution are needed to gain new insights into complex disease processes, such as wound healing and tumor metabolism. In recent years, luminescence-based methods for pH measurement have been developed. However, for in vivo applications, especially for studies on humans, biocompatibility and reliability under varying conditions have to be ensured. Here, we present a referenced luminescent sensor for 2D high-resolution imaging of pH in vivo. The ratiometric sensing scheme is based on time-domain luminescence imaging of FITC and ruthenium(II)tris-(4,7-diphenyl-1,10-phenanthroline). To create a biocompatible 2D sensor, these dyes were bound to or incorporated into microparticles (aminocellulose and polyacrylonitrile), and particles were immobilized in polyurethane hydrogel on transparent foils. We show sensor precision and validity by conducting in vitro and in vivo experiments, and we show the versatility in imaging pH during physiological and chronic cutaneous wound healing in humans. Implementation of this technique may open vistas in wound healing, tumor biology, and other biomedical fields.