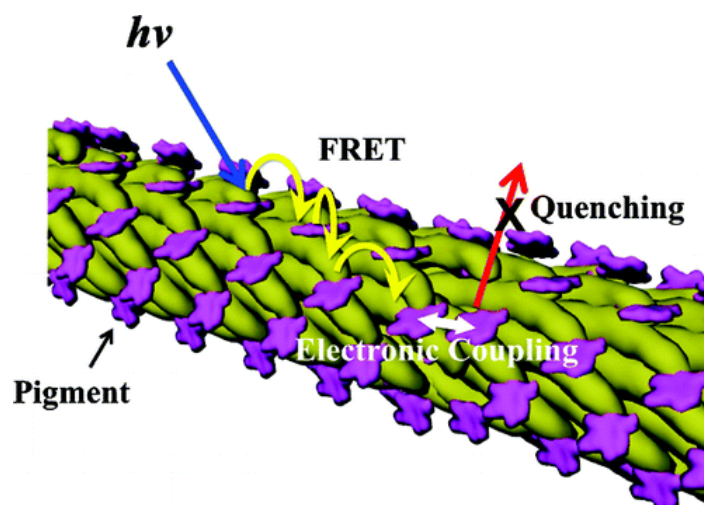


- Virus-Templated Assembly of Porphyrins into Light-Harvesting Nanoantennae
Nam, Y. S.; Shin, T.; Park, H.; Magyar, A. P.; Choi, K.; Fantner, G.; Nelson, K. A.; Belcher, A. M. *J. Am. Chem. Soc.*, **2010**, *132*, 1462–1463.

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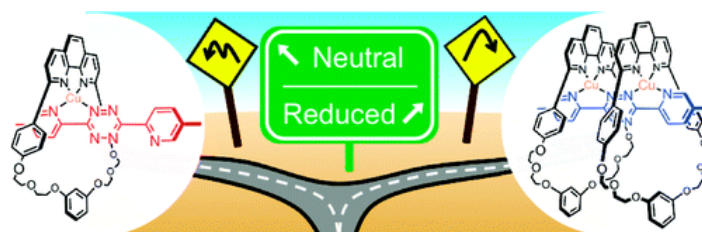
Abstract:



Biological molecules can be used as versatile templates for assembling nanoscale materials because of their unique structures and chemical diversities. Supramolecular organization of molecular pigments, as is found in the natural light-harvesting antenna, has drawn attention for its potential applications to sensors, photocatalytic systems, and photonic devices. Here we show the arrangement of molecular pigments into a one-dimensional light-harvesting antenna using M13 viruses as scaffolds. Chemical grafting of zinc porphyrins to M13 viruses induces distinctive spectroscopic changes, including fluorescence quenching, the extensive band broadening and small red shift of their absorption spectrum, and the shortened lifetime of the excited states. Based on these optical signatures we suggest a hypothetical model to explain the energy transfer occurring in the supramolecular porphyrin structures templated with the virus. We expect that further genetic engineering of M13 viruses can allow us to coassemble other functional materials (e.g., catalysts and electron transfer mediators) with pigments, implying potential applications to photochemical devices.

- Bilability is Defined when One Electron is Used to Switch between Concerted and Stepwise Pathways in Cu(I)-Based Bistable [2/3]Pseudorotaxanes
Share, A. I.; Parimal, K.; Flood, A. H. *J. Am. Chem. Soc.*, **2010**, *132*, 1665–1675.

Abstract:

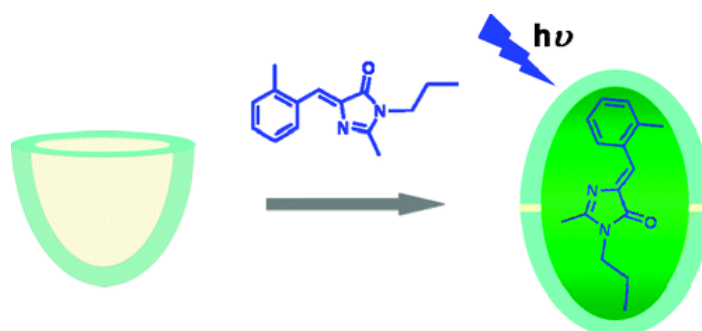


Supramolecular switches operate as simple machines by using a stimulus to turn stations off and on, generating thermodynamic differences that define bistability and enable motion. What has not been previously investigated, yet is required to gain further control over molecular movements for complex operations, is an understanding of how the same stimulus can also switch pathways off and on, thus, defining the kinetic property of bilability. To address this challenge, the mechanisms of the forward and return reactions of redox-switchable Cu(I)-based [2/3]pseudorotaxanes have been quantitatively

characterized utilizing mechanistic cyclic voltammetry and employing a series of isosteric bis-bidentate ligands. First, the bistability of the switch is retained across the series of ligands: Reduction of the ligand drives the reaction forward where a [2]pseudorotaxane switches into a reduced [3]pseudorotaxane and reoxidation drives the switching cycle back to the beginning. Second, the switch is bilabile with the forward reaction following an association-activated interchange pathway (concerted), whereas the reverse reaction follows a different dissociation-based dethreading pathway (stepwise). The forward reaction is more sensitive to denticity (bidentate tetrazinyl ligand, $k_2 = 12\,000\text{ M}^{-1}\text{ s}^{-1}$, versus the monodentate pyrazinyl ligand, $k_2 = 1500\text{ M}^{-1}\text{ s}^{-1}$) than to electronics ($k_2 = 12\,000\text{ M}^{-1}\text{ s}^{-1}$ for methyl and trifluoromethyl substituents). The rate of return with the pyrazinyl ligand is $k_1 = 50\text{ s}^{-1}$. Consequently, both the mechanism and the thermodynamics of switching are stimuli dependent; they change with the oxidation state of the ligand. These findings have implications for the future design of molecular motors, which can be built from systems displaying allosterically coupled bistability and bilability.

- Activation of Fluorescent Protein Chromophores by Encapsulation
Baldrige, A.; Samanta, S. R.; Jayaraj, N.; Ramamurthy, V.; Tolbert, L. M. *J. Am. Chem. Soc.* **2010**, *132*, 1498–1499.

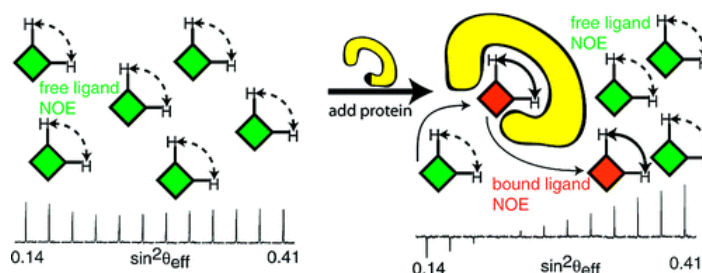
Abstract:



Chromophores related to fluorescent proteins, when sequestered into the “octaacid” capsule, recover their fluorescence. The fluorescence recovery is related to the inhibition of torsional motions within the cavity, implicating the single-bond torsion as an important contributor to internal conversion within this important class of chromophores.

- Pharmacophore Mapping via Cross-Relaxation during Adiabatic Fast Passage
Auer, R.; Kloiber, K.; Vavrinska, A.; Geist, L.; Coudevylle, N.; Konrat, R. *J. Am. Chem. Soc.* **2010**, *132*, 1480–1481.

Abstract:



A novel NMR method is demonstrated for the investigation of protein-ligand interactions. In this approach an adiabatic fast passage pulse, i.e. a long, weak pulse with a linear frequency sweep, is used to probe ^1H - ^1H NOEs. During the adiabatic fast passage the effective rotating-frame NOE is a

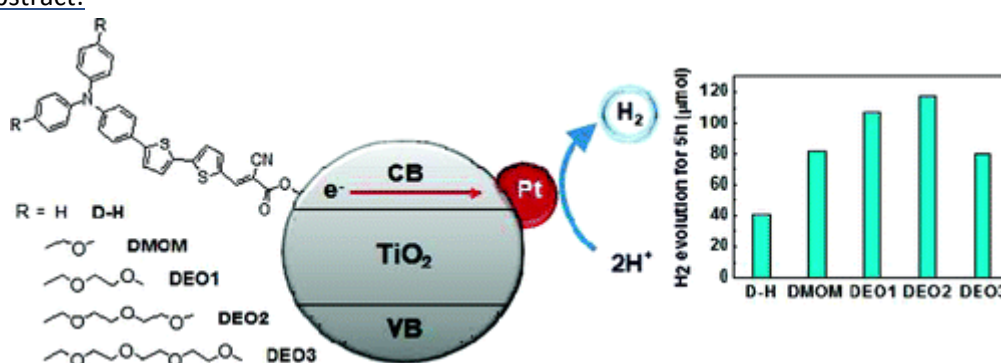
weighted average of transverse and longitudinal cross-relaxation contributions that can be tuned by pulse power and frequency sweep rate. It is demonstrated that the occurrence of spin diffusion processes leads to sizable deviations from the theoretical relationship between effective relaxation rate and effective tilt angle in the spin lock frame and can be used to probe protein–ligand binding. This methodology comprises high sensitivity and ease of implementation. The feasibility of this technique is demonstrated with two protein complexes, vanillic acid bound to the quail lipocalin Q83 and NAD^+ and AMP binding to alcohol dehydrogenase (ADH).

- Significance of Hydrophilic Characters of Organic Dyes in Visible-Light Hydrogen Generation Based on TiO_2

Lee, S.-H.; Park, Y.; Wee, K.-R.; Son, H.-J.; Cho, D. W.; Pac, C.; Choi, W.; Kang, S. O. *Org. Lett.*

2010, *12*, 460–463.

Abstract:

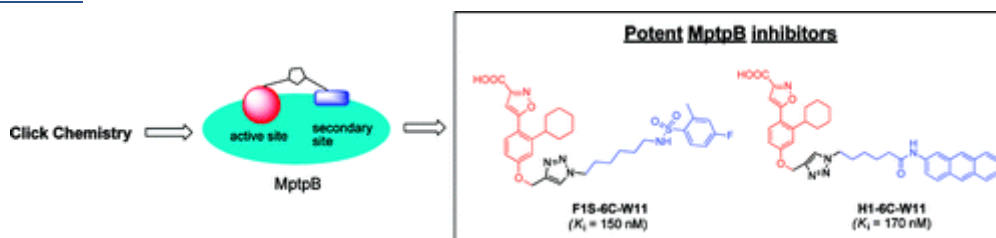


A series of dyes were synthesized to examine the roles of the hydrophilic characteristics of R in sensitized hydrogen generation by dye-grafted Pt/ TiO_2 under visible light irradiation. The hydrogen-generation efficiencies and optimum amounts of the dyes grafted to Pt/ TiO_2 were affected substantially by the hydrophilic and steric effects of R; moderately hydrophilic DEO1 and DEO2 showed higher sensitization activity at a lower loading than hydrophobic D-H.

- High-Throughput Discovery of *Mycobacterium tuberculosis* Protein Tyrosine Phosphatase B (MptpB) Inhibitors Using Click Chemistry

Tan, L. P.; Wu, H.; Yang, P.-Y.; Kalesh, K. A.; Zhang, X.; Hu, M.; Srinivasan, R.; Yao, S. Q. *Org. Lett.* **2009**, *11*, 5102–5105.

Abstract:

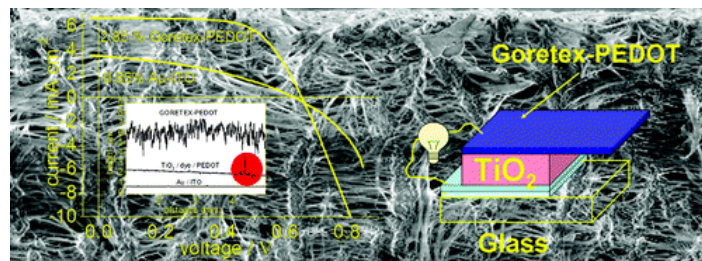


A 3500-member library of bidentate inhibitors against protein tyrosine phosphatases (PTPs) was rapidly assembled using click chemistry. Subsequent high-throughput screening had led to the discovery of highly potent (K_i as low as 150 nM) and selective MptpB inhibitors, some of which represent the most potent MptpB inhibitors developed to date.

- Flexible and Compressible Goretex–PEDOT Membrane Electrodes for Solid-State Dye-

Mozer, A. J.; Panda, D. K.; Gambhir, S.; Romeo, T. C.; Winther-Jensen, B.; Wallace, G. G. *Langmuir* **2010**, *26*, 1452–1455.

Abstract:

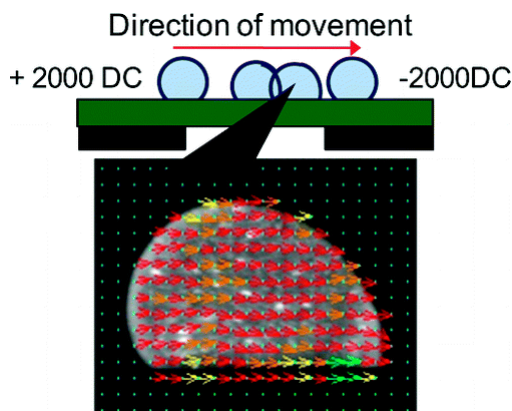


A porous, flexible electrode based on a PTFE (Teflon) membrane (Goretex) coated with a metallic current collector and a conducting polymer (poly(3,4-ethylenedioxythiophene), PEDOT) has been developed for applications in solid-state dye-sensitized solar cells. Its low sheet resistance and compressibility make it an ideal electrode on uneven TiO_2 surfaces with high efficiency and reproducibility. The porous nature of the electrode enables the feed-through of reactants and treatment agents, which opens up exciting opportunities to interface these photoelectrochemical devices with electrocatalytic, energy conversion, and storage systems. Postfabrication bonding of the photoanode and the Goretex–Au–PEDOT electrode is demonstrated.

- Water Droplets' Internal Fluidity during Horizontal Motion on a Superhydrophobic Surface with an External Electric Field

Sakai, M.; Kono, H.; Nakajima, A.; Sakai, H.; Abe M.; Fujishima A. *Langmuir* **2010**, *26*, 1493–1495.

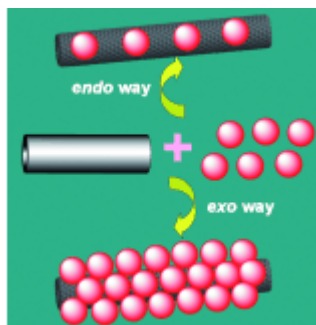
Abstract:



On a superhydrophobic surface, the internal fluidity of water droplets with different volumes (15, 30 μL) and their horizontal motion in an external electric field were evaluated using particle image velocimetry (PIV). For driving of water droplets on a superhydrophobic coating between parallel electrodes, it was important to place them at appropriate positions. Droplets moved with slipping. Small droplets showed deformation that is more remarkable. Results show that the dielectrophoretic force induced the initial droplet motion and that the surface potential gradient drove the droplets after reaching the middle point between electrodes.

- Carbon Nanotube and Gold-Based Materials: A Symbiosis
Singh, R.; Premkumar, T.; Shin, J.-Y.; Geckeler, K.-E. *Chem. Eur. J.* **2010**, *16*, 1728-1743.

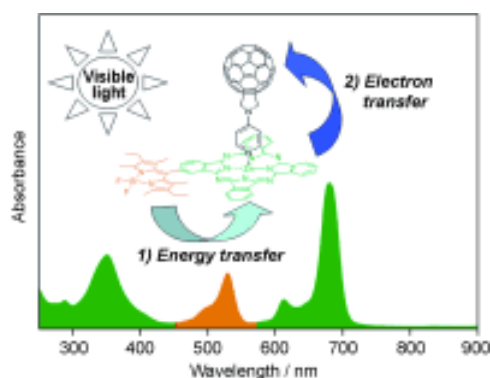
Abstract:



Carbon nanotubes constitute a novel class of nanomaterials with potential applications in many areas. The attachment of metal nanoparticles to carbon nanotubes is new way to obtain novel hybrid materials with interesting properties for various applications such as catalysts and gas sensors as well as electronic and magnetic devices. Their unique properties such as excellent electronic properties, a good chemical stability, and a large surface area make carbon nanotubes very useful as a support for gold nanoparticles in many potential applications, ranging from advanced catalytic systems through very sensitive electrochemical sensors and biosensors to highly efficient fuel cells. Here we give an overview on the recent progress in this area by exploring the various synthesis approaches and types of assemblies, in which nanotubes can be decorated with gold nanoparticles and explore the diverse applications of the resulting composites.

- A Panchromatic Supramolecular Fullerene-Based Donor-Acceptor Assembly Derived from a Peripherally Substituted Bodipy-Zinc Phthalocyanine Dyad
Rio, Y.; Seitz, W.; Gouloumis, A.; Vázquez, P.; Sessler, J. L.; Guldi, D. M.; Torres, T. *Chem. Eur. J.* **2010**, *16*, 1296-1305.

Abstract:

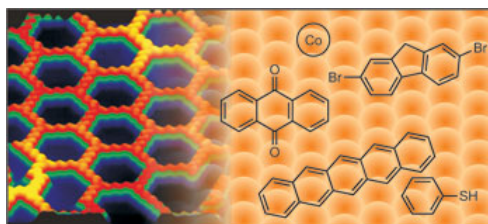


A panchromatic 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene-zinc phthalocyanine conjugate (Bodipy-ZnPh) **1** was synthesized starting from phthalocyanine aldehyde **4**, via dipyrromethane **3** and dipyrromethene **2**. Conjugate **1** represents the first example in which a Bodipy unit is tethered to the peripheral position of a phthalocyanine core. Electrochemical and optical measurements provided evidence for strong electronic interactions between the Bodipy and ZnPh constituents in the ground state of **1**. When conjugate **1** is subjected to photoexcitation in the spectral region corresponding to the Bodipy absorption, the strong fluorescence characteristic of the latter subunit is effectively quenched (i.e., $\geq 97\%$). Excitation spectral analysis confirmed that the photoexcited Bodipy and the tethered ZnPh subunits interact and that intraconjugate singlet energy transfer occurs with an

efficiency of ca. 25 %. Treatment of conjugate **1** with *N*-pyridylfulleropyrrolidine (**8**), an electron-acceptor system containing a nitrogen ligand, gives rise to the novel electron donor-acceptor hybrid **1**↔**8** through ligation to the ZnPc center. Irradiation of the resulting supramolecular ensemble within the visible range leads to a charge-separated Bodipy-ZnPc⁺-C₆₀⁻ radical-ion-pair state, through a sequence of excited-state and charge transfers, characterized by a remarkably long lifetime of 39.9 ns in toluene.

- Tailoring molecular layers at metal surfaces
Bartels, L. *Nature Chemistry* **2010**, *2*, 87-95.

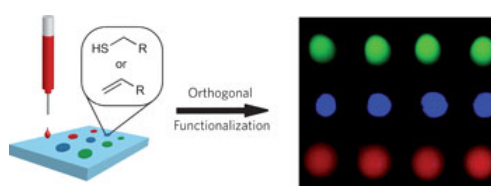
Abstract:



The design of networks of organic molecules at metal surfaces, highly attractive for a variety of applications ranging from molecular electronics to gas sensors to protective coatings, has matured to a degree that patterns with multianometre unit cells and almost any arbitrary geometry can be fabricated. This Review provides an overview of vacuum-deposited organic networks at metal surfaces, using intermolecular hydrogen bonding, metal–atom coordination and *in situ* polymerization. Recent progress in these areas highlights how the design of surface patterns can benefit from the wealth of information available from solution- and bulk-phase chemistry, while at the same time providing novel insights into the nature of such bonds through the applicability of direct scanning probe imaging at metal surfaces.

- A versatile approach to high-throughput microarrays using thiol-ene chemistry
Gupta, N.; Lin, B. F.; Campos, L. M.; Dimitriou, M. D.; Hikita, S. T.; Treat, N. D.; Tirrell, M. V.; Clegg, D. O.; Kramer, E. J.; Hawker, C. J. *Nature Chemistry* **2010**, *2*, 138-145.

Abstract:

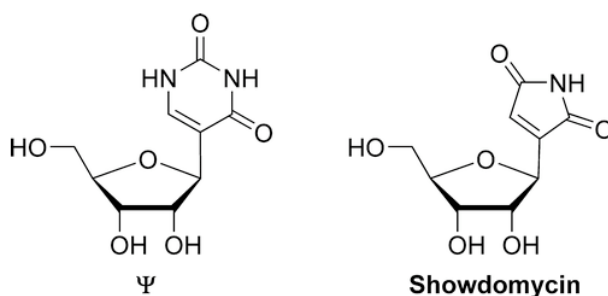


Microarray technology has become extremely useful in expediting the investigation of large libraries of materials in a variety of biomedical applications, such as in DNA chips, protein and cellular microarrays. In the development of cellular microarrays, traditional high-throughput printing strategies on stiff, glass substrates and non-covalent attachment methods are limiting. We have developed a facile strategy to fabricate multifunctional high-throughput microarrays embedded at the surface of a hydrogel substrate using thiol-ene chemistry. This user-friendly method provides a platform for the immobilization of a combination of bioactive and diagnostic molecules, such as peptides and dyes, at the surface of poly(ethylene glycol)-based hydrogels. The robust and orthogonal nature of thiol-ene chemistry allows for a range of covalent attachment strategies in a fast and reliable manner, and two complementary strategies for the attachment of active molecules are demonstrated.

- C-Nucleosides: Synthetic Strategies and Biological Applications

Tambask, J.; Hocek, M.; Koovsk, P. *Chem. Rev.* **2009**, *109*, 6729–6764.

Abstract:



While natural and synthetic N-nucleosides are vulnerable to enzymatic and acid-catalyzed hydrolysis of the nucleosidic bond, their C-analogues are much more stable. Several C-nucleosides are naturally occurring compounds, e.g., pseudouridine (isolated from the yeast t-RNA) and showdomycin (an antibiotic). Development of novel synthetic methodologies allowed the preparation of a large variety of synthetic analogues, which found numerous applications in medicinal chemistry and chemical biology. Most important biologically active C-nucleosides are the inhibitors of purine nucleosides phosphorylase or IMP dehydrogenase. A number of artificial aryl-C-nucleosides capable of π -stacking are being vigorously investigated as building blocks in chemical biology. In the past few years, several Artificial Expanded Genetic Information Systems (AEGIS)(1) have been successfully developed as prime examples of synthetic biology, a newly emerging interdisciplinary area, with the ultimate goal to design systems where high-level behaviors of the living matter are mimicked by artificial chemical systems.(2, 3)

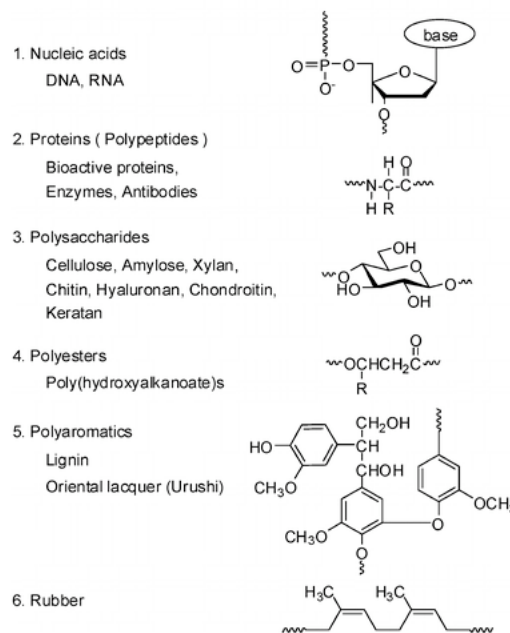
To date, no comprehensive review dealing with all synthetic approaches and assessment of their pros and cons has been published. In this comprehensive review article, a critical overview of all individual synthetic approaches and their merit is presented in context of the current needs of medicinal chemistry and chemical biology. Beside the synthetic approaches, applications of C-nucleosides in medicinal chemistry (e.g., antiviral or antitumor agents), chemical biology (e.g., studying of certain enzyme reactions and extension of the genetic alphabet), and other areas (e.g., fluorescent labeling and artificial DNA constructs, etc.) are summarized and critically evaluated, and some prospective future developments both in the synthesis and in potential applications are outlined.

- Enzymatic Polymer Synthesis: An Opportunity for Green Polymer Chemistry

Kobayashi, S.; Makino, A. *Chem. Rev.* **2009**, *109*, 5288–5353.

Abstract:

Typical Examples of Natural Biomacromolecules



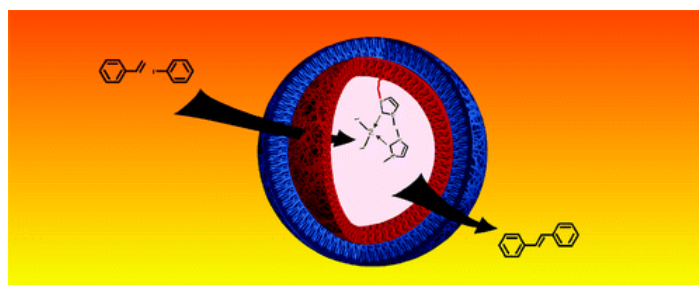
Polymeric materials, natural and unnatural, are indispensable to the modern society. They are widely used from everyday life usages as commodity materials to industry and technology usages in the fields such as electronics, machinery, communications, transportations, pharmacy, and medicine as highly advanced materials. Today, it is hard to think of the present society without polymeric materials.

Developments of various polymeric materials have been owed to epoch-making innovative works as exemplified typically by the discovery of Ziegler–Natta catalyst, the concept of living polymerization, the discovery of conducting polymers, and the discovery of metathesis catalyst. These observations demonstrate that new polymeric materials are often brought about by new production methods including polymerization catalysts. Historically, polymerization catalysts utilized classical catalysts of acids (Brønsted acids, Lewis acids, and various cations), bases (Lewis bases and various anions), and radical generating compounds since the 1920s, the early stage of polymer chemistry. In the following stage, the catalysts started to use the transition metals in Ziegler–Natta catalyst in the 1950s and later in the metathesis catalyst, as well as using the rare-earth metals in these catalysts. These catalysts still have major roles in the polymer synthesis.

- Nanoreactors for Polymerizations and Organic Reactions

Monteiro, M. J. *Macromolecules* **2010**, *43*, 1159–1168.

Abstract:



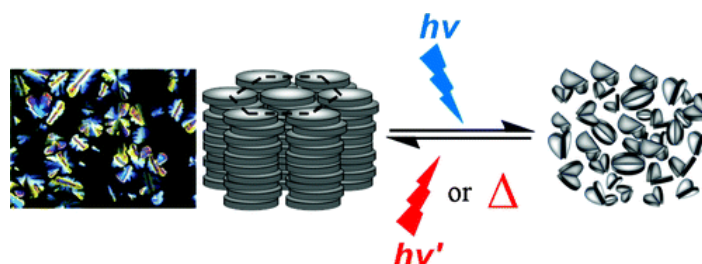
The aim of this Perspective is to use the knowledge of the underpinning kinetic and thermodynamic precepts that govern free-radical and “living” radical water-based heterogeneous polymerizations and apply this to small molecule organic reactions in nanoreactors. The difficulty in applying “living” radical polymerization to water-based heterogeneous systems has led to such an understanding,

including partitioning of agents between the phases, nucleation of particles, and other phenomena including superswelling. This knowledge has allowed us to prepare polymers in heterogeneous systems with well-defined molecular weight distributions and particle size distributions. However, to overcome the physical chemistry constraints, researchers had to develop complex nanoreactor systems. For the field of small molecule organic reactions in heterogeneous systems to be industrially relevant and to grow rapidly, such physical chemistry precepts should be more greatly developed.

- Synthesis and Optical/Thermal Behavior of New Azo Photoisomerizable Discotic Liquid Crystals

Westphal, E.; Bechtold, I. H.; Gallardo, H. *Macromolecules* **2010**, *43*, 1319–1328.

Abstract:



In this study, discotic azo compounds were prepared by a reductive coupling of 5-nitroisophthalic acid followed by a convergent synthesis, resulting in five new examples of azo photoisomerizable discotic molecules, which differ from each other by the linking groups (ester, amide or 1,3,4-oxadiazole) and number of aliphatic chain (4 or 8). The thermal and liquid crystalline properties of the compounds were completely characterized by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction analysis. Two products presented a stable columnar hexagonal mesophase with 95 and 134 °C of range. The results obtained show that the choice of the linking group and number of aliphatic chains has a significant influence in the materials properties. The photoisomerization capacity was evaluated in solution by spectroscopic methods and also by ^1H NMR, indicating that these molecules are promising candidates for controlling the conductivity in electro-optical devices.

- Transition-metal phosphors with cyclometalating ligands: fundamentals and applications
Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 638 – 655.

Abstract:



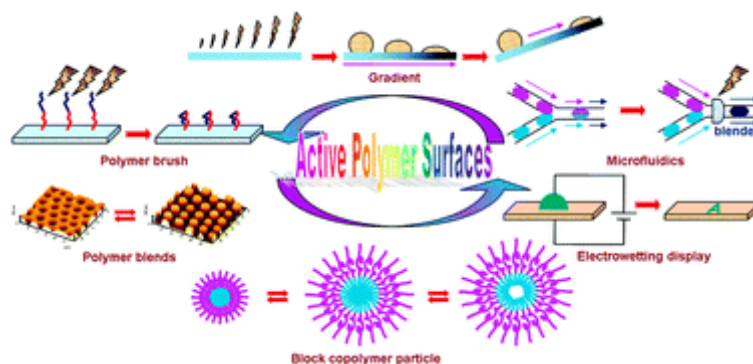
One goal of this *critical review* is to provide advanced methodologies for systematic preparation of transition-metal based phosphors that show latent applications in the field of organic light emitting diodes (OLEDs). We are therefore reviewing various types of cyclometalating chelates for which the

favorable metal–chelate bonding interaction, on the one hand, makes the resulting phosphorescent complexes highly emissive in both fluid and solid states at room temperature. On the other hand, fine adjustment of ligand-centered $\pi-\pi^*$ electronic transitions allows tuning of emission wavelength across the whole visible spectrum. The cyclometalating chelates are then classified according to types of cyclometalating groups, *i.e.* either aromatic C–H or azolic N–H fragment, and the adjacent donor fragment involved in the formation of metallacycles; the latter is an N-containing heterocycle, N-heterocyclic (NHC) carbene fragment or even diphenylphosphino group. These cyclometalating ligands are capable to react with heavy transition-metal elements, namely: Ru(II), Os(II), Ir(III) and Pt(II), to afford a variety of highly emissive phosphors, for which the photophysical properties as a function of chelate or metal characteristics are systematically discussed. Using Ir(III) complexes as examples, the C^N chelates possessing both C–H site and N-heterocyclic donor group are essential for obtaining phosphors with emission ranging from sky-blue to saturated red, while the N^N chelates such as 2-pyridyl-C-linked azolates are found useful for serving as true-blue chromophores due to their increased ligand-centered $\pi-\pi^*$ energy gap. Lastly, the remaining NHC carbene and benzyl phosphine chelates are highly desirable to serve as ancillary chelates in localizing the electronic transition between the metal and remaining lower energy chromophoric chelates. As for the potential opto-electronic applications, many of them exhibit remarkable performance data, which are convincing to pave a broad avenue for further development of all types of phosphorescent displays and illumination devices (94 references).

- Active and responsive polymer surfaces

Zhang, J.; Han, Y. *Chem. Soc. Rev.* **2010**, 39, 676 – 693.

Abstract:

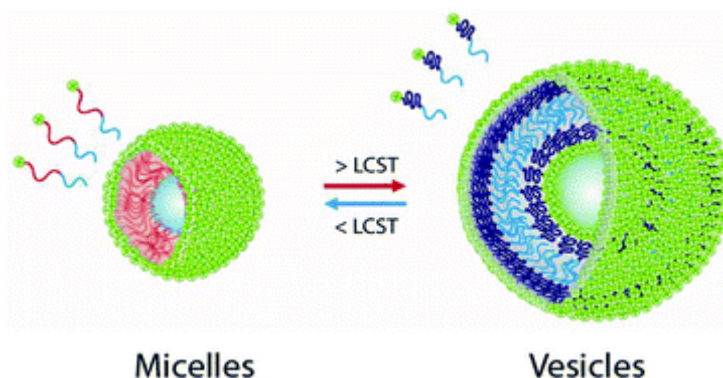


A central challenge in polymer science today is creating materials that dynamically alter their structures and properties on demand, or in response to changes in their environment. Surfaces represent an attractive area of focus, since they exert disproportionately large effects on properties such as wettability, adhesiveness, optical appearance, and bioactivity, enabling pronounced changes in properties to be accomplished through subtle changes in interfacial structure or chemistry. In this *critical review*, we review the recent research progress into active and responsive polymer surfaces. The chief purpose of this article is to summarize the advanced preparation techniques and applications in this field from the past decade. This review should be of interest both to new scientists in this field and the interdisciplinary researchers who are working on “intelligent” polymer surfaces (117 references).

- Thermally induced micelle to vesicle morphology transition for a charged chain end diblock copolymer

Moughton, A. O.; O'Reilly, R. K. *Chem. Commun.* **2010**, 46, 1091 - 1093.

Abstract:

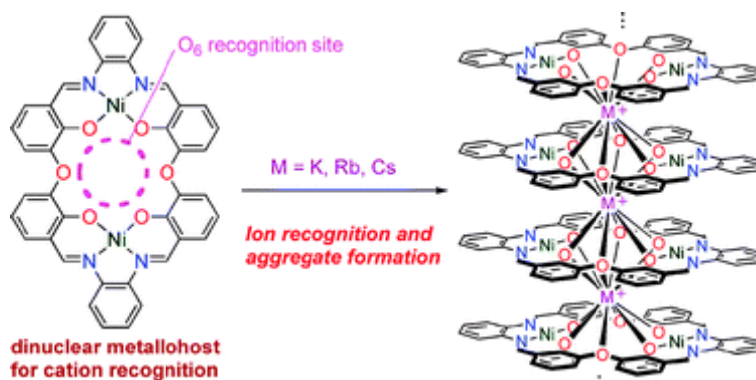


A quaternary amine end functionalised diblock copolymer (PtBuA-b-PNIPAM) has been synthesised using RAFT polymerisation and shown to undergo a thermally induced morphology transition from micelles to vesicles, as evidenced by TEM, AFM, SLS and DLS analyses.

- Highly efficient regulation of cation recognition and promotion of self-assembly by metalation of a macrocyclic bis(N_2O_2) ligand with nickel(II).

Akine, S.; Utsuno, F.; Nabeshima, T. *Chem. Commun.* **2010**, 46, 1029 - 1031.

Abstract:

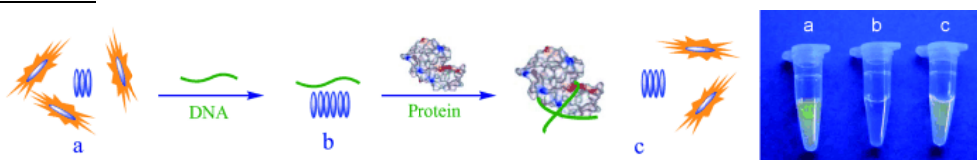


Metalation of a bis(N_2O_2) macrocyclic ligand 1 with nickel(II) acetate afforded a dinuclear metallohost 2, resulting in a significant enhancement of recognition ability of alkali metal ions and the promotion of self-aggregation.

- Fluorescence Turn-On Detection of a Protein through the Reduced Aggregation of a Perylene Probe

Wang, B.; Yu, C. *Angew. Chem. Int. Ed.* **2010**, 49, 1485 -1488.

Abstract:



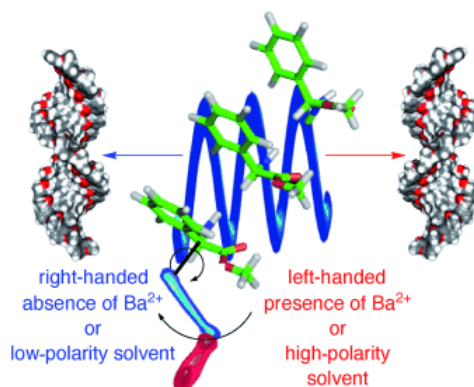
Sensitivity that won't break the bank: The addition of an anti-lysozyme DNA aptamer (a polyanion) to a cationic perylene probe that exists in aqueous solution as a mixture of the fluorescent free monomer and aggregate forms shifted the equilibrium and resulted in fluorescence quenching (see

schematic representation). The subsequent introduction of lysozyme weakened DNA binding to the perylene aggregates and led to fluorescence recovery.

- Control of the Helicity of Poly(phenylacetylene)s: From the Conformation of the Pendant to the Chirality of the Backbone

Louzao, I.; Seco, J. M.; Quiñoá, E.; Riguera, R. *Angew. Chem. Int. Ed.* **2010**, *49*, 1430–1433.

Abstract:



Helix sense selection: Tuning the conformational equilibrium of the pendants of poly(phenylacetylene)s allows selection of the helicity of the polymer in a reversible way. Complexation with appropriate metal cations (e.g. Ba^{2+}) or changing the polarity of the solvent permits the reversible selection of the desired helix sense. A full picture of the mechanism explaining this phenomenon is presented.