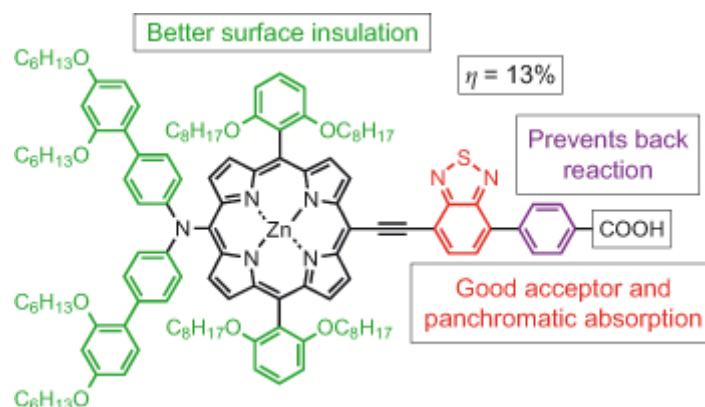


- Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers

1

Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. *Nature Chem.* **2014**, 6, 242–247.

Abstract:

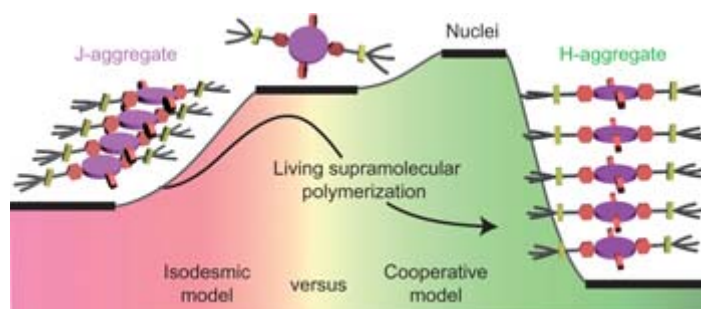


Dye-sensitized solar cells have gained widespread attention in recent years because of their low production costs, ease of fabrication and tunable optical properties, such as colour and transparency. Here, we report a molecularly engineered porphyrin dye, coded SM315, which features the prototypical structure of a donor– π -bridge–acceptor and both maximizes electrolyte compatibility and improves light-harvesting properties. Linear-response, time-dependent density functional theory was used to investigate the perturbations in the electronic structure that lead to improved light harvesting. Using SM315 with the cobalt(II/III) redox shuttle resulted in dye-sensitized solar cells that exhibit a high open-circuit voltage V_{oc} of 0.91 V, short-circuit current density J_{sc} of 18.1 mA cm^{-2} , fill factor of 0.78 and a power conversion efficiency of 13%.

- Living supramolecular polymerization realized through a biomimetic approach

Ogi, S.; Sugiyasu, K.; Manna, S.; Samitsu, S.; Takeuchi, M. *Nature Chem.* **2014**, 6, 188–195.

Abstract:

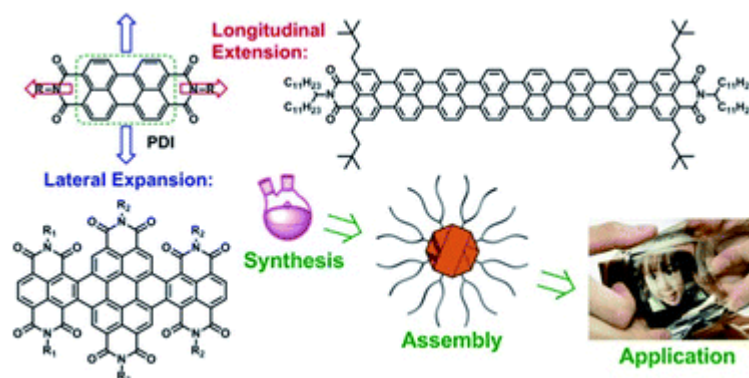


Various conventional reactions in polymer chemistry have been translated to the supramolecular domain, yet it has remained challenging to devise living supramolecular polymerization. To achieve this, self-organization occurring far from thermodynamic equilibrium—ubiquitously observed in nature—must take place. Prion infection is one example that can be observed in biological systems. Here, we present an ‘artificial infection’ process in which porphyrin-based monomers assemble into nanoparticles, and are then converted into nanofibres in the presence of an aliquot of the nanofibre, which acts as a ‘pathogen’. We have investigated the assembly phenomenon using isodesmic and cooperative models and found that it occurs through a delicate interplay of these two aggregation

pathways. Using this understanding of the mechanism taking place, we have designed a living supramolecular polymerization of the porphyrin-based monomers. Despite the fact that the polymerization is non-covalent, the reaction kinetics are analogous to that of conventional chain growth polymerization, and the supramolecular polymers were synthesized with controlled length and narrow polydispersity.

- Beyond perylene diimides: synthesis, assembly and function of higher rylene chromophores
Chen, L.; Lia, C.; Müllen, K. *J. Mater. Chem C*, **2014**, 2, 1938–1956.

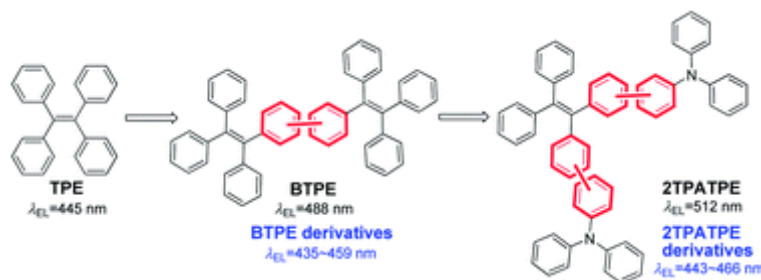
Abstract:



Perylene diimides are among the most important chromophores in dyestuff chemistry. They do not only have excellent thermal, chemical and photochemical stability, high absorption coefficients and fluorescence quantum yields but also permit various chemical functionalizations. Over the last decades, academic and industrial interest in this class of chromophores has steadily increased due to their favourable properties and potential application in various research fields like organic electronics, biochemistry, photophysics and supramolecular chemistry. Higher rylene diimide dyes (e.g. 2–6), however, are still in their infancy and must be further explored by combining more research efforts of chemists, physicists, biologists, and material scientists since these dyes possess unique optical, electrochemical, and electronic properties. One of the main obstacles in such rylene based dyes seems to be their synthetic challenges. Thus, in this feature article, we summarize the latest advances in the field of rylene diimide dyes focusing on synthetic strategies toward their preparation. The self-assembly behaviour and applications of larger rylene chromophores are discussed as well.

- Construction of efficient blue AIE emitters with triphenylamine and TPE moieties for non-doped OLEDs
Huang, J.; Jiang, Y.; Yang, J.; Tang, R.; Xie, N.; Li, Q.; Kwok, H. S.; Tang, B. Z.; Li, Z. *J. Mater. Chem C*, **2014**, 2, 2028–2036.

Abstract:

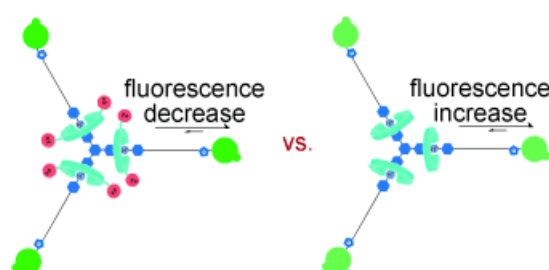


In this paper, by merging the hole-dominated triphenylamine (TPA) and tetraphenylethene (TPE) moieties together with different linkage positions, four derivatives of 1,2-bis[4'-(diphenylamino)biphenyl-4-yl]-1,2-diphenylethene (2TPATPE) were successfully synthesized with confirmed structures, and their thermal, optical and electronic properties were fully investigated. Thanks to the introduction of the meta-linkage mode on the TPE core, their π -conjugation length could be effectively restricted to ensure blue emission. The non-doped OLEDs based on these four emitters exhibit blue emissions from 443–466 nm, largely blue-shifted with respect to the green emission of 2TPATPE (514 nm). Meanwhile, good electroluminescence efficiencies with L_{\max} , $\eta_{C,\max}$, and $\eta_{P,\max}$ of up to 8160 cd m⁻², 3.79 cd A⁻¹, and 2.94 lm W⁻¹ respectively, have also been obtained, further validating our rational design of blue AIE fluorophores.

- Fluorescence Modulation in Tribranched Switchable [4]Rotaxanes

Zhang, J.-N.; Li, H.; Zhou, W.; Yu, S.-L.; Qu, D.-H.; Tian, H., *Chem. Eur. J.* **2013**, *19*, 17192–17200.

Abstract:

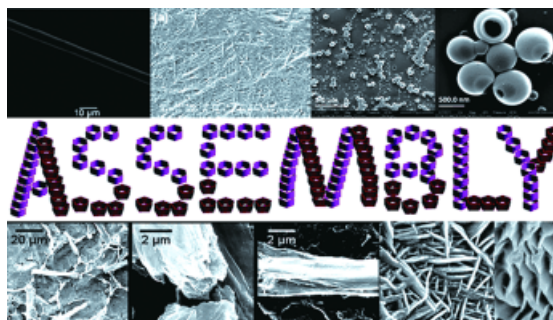


Two novel tribranched [4]rotaxanes with a 1,3,5-triphenylene core and three rotaxane arms have been designed, synthesized, and characterized by ¹H and ¹³C NMR spectroscopies and HR-ESI mass spectrometry. [4]Rotaxanes **1** and **2** each possess the same three-armed skeleton. Each arm incorporates two distinguishable binding sites for a dibenzo[24]crown-8 ring, namely a dibenzylammonium site and an *N*-methyltriazolium site, and is terminated by a 4-morpholinonaphthalimide fluorophore as a stopper. [4]Rotaxane **1** has three di-ferrocene-functionalized dibenzo[24]crown-8 rings whereas **2** has three simple dibenzo[24]crown-8 rings interlocked with the thread component. Uniform shuttling motions of the three macrocycles in both **1** and **2** can be driven by external acid–base stimuli, which were confirmed by ¹H NMR spectroscopy. However, [4]rotaxanes **1** and **2** show distinct modes of fluorescence modulation in response to external acid–base stimuli. [4]Rotaxane **1** exhibits a remarkable fluorescence decrease in response to the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, which can displace the ferrocene-functionalized macrocycle from the dibenzylammonium station to the *N*-methyltriazolium station. In contrast, the fluorescence intensity of [4]rotaxane **2** showed an enhancement with the addition of DBU. Time-resolved fluorescence measurements have been performed. The different photoinduced electron-transfer processes responsible for the fluorescence changes in the two molecular systems are discussed. Topological structures of this kind have significant potential for the design and construction of large and complex assemblies with controllable functions.

- Pillararene-Based Assemblies: Design Principle, Preparation and Applications

Zhang, H.; Zhao, Y. *Chem. Eur. J.* **2013**, *19*, 16862–16879.

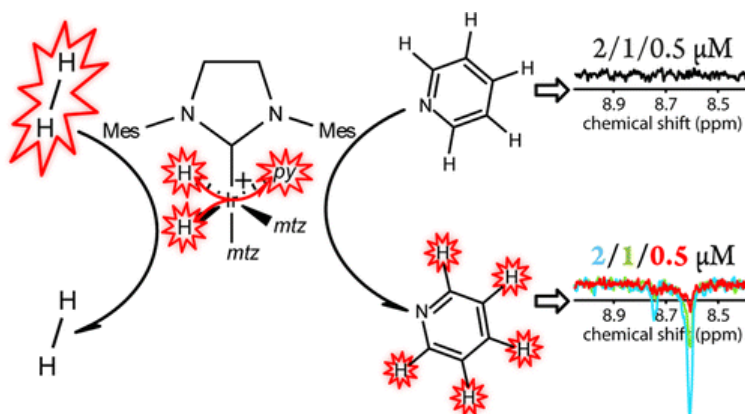
Abstract:



In this review, we highlight recent advancements on pillararene-based assemblies. The driving forces for the formation of the pillararene-based assemblies are discussed first. The host–guest interactions are deemed as not only general strategy for constructing assemblies but also essential components for preventing the assemblies from the dissociation. Solvent effect is also important in the assembling process, since it could influence the host–guest interactions and provide solvophobic effect on pillararenes for the assembly. Then, several pillararene-based assembly architectures are introduced, including pillararene-based interlocked structures, such as (poly)pseudorotaxanes, (poly)rotaxanes, and daisy chains, classified by their topological structures and synthetic strategy. The morphologies of the supramolecular assemblies are divided into several types, for example, nanospheres, nanotubes and supramolecular polymers. Furthermore, the functions and potential applications are summarized accompanied with related assembly structures. The review not only provides fundamental findings, but also foresights future research directions in the research area of pillararene-based assemblies.

- Toward Nanomolar Detection by NMR Through SABRE Hyperpolarization
Eshuis, N.; Hermkens, N.; van Weerdenburg, B. J. A.; Feiters, M. C.; Rutjes, F. P. J. T.; Wijmenga, S. S.; Tessari, M. J. *Am. Chem. Soc.* **2014**, *136*, 2695-2698.

Abstract:



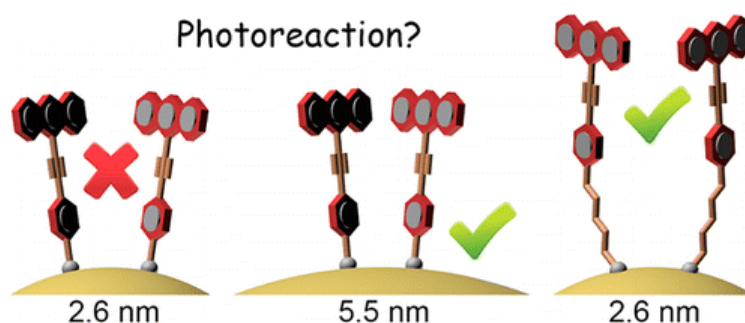
SABRE is a nuclear spin hyperpolarization technique based on the reversible association of a substrate molecule and para-hydrogen ($p\text{-H}_2$) to a metal complex. During the lifetime of such a complex, generally fractions of a second, the spin order of $p\text{-H}_2$ is transferred to the nuclear spins of the substrate molecule via a transient scalar coupling network, resulting in strongly enhanced NMR signals. This technique is generally applied at relatively high concentrations (mM), in large excess of substrate with respect to metal complex. Dilution of substrate ligands below stoichiometry results in progressive decrease of signal enhancement, which precludes the direct application of SABRE to the NMR analysis of low concentration (μM) solutions. Here, we show that the efficiency of SABRE at low

substrate concentrations can be restored by addition of a suitable coordinating ligand to the solution. The proposed method allowed NMR detection below 1 μM in a single scan.

- Support Curvature and Conformational Freedom Control Chemical Reactivity of Immobilized Species

Zdobinsky, T.; Maiti, P. S.; Klajn, R. *J. Am. Chem. Soc.* **2014**, *136*, 2711-2714.

Abstract:

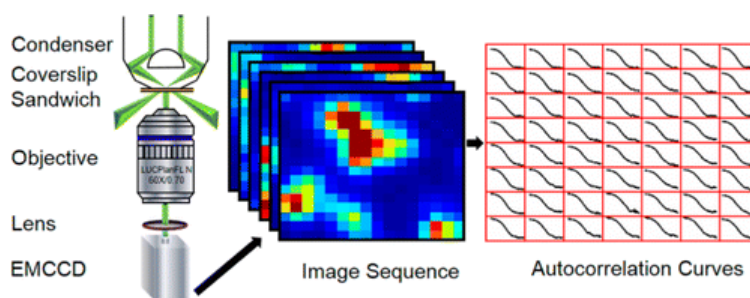


We show that bimolecular reactions between species confined to the surfaces of nanoparticles can be manipulated by the nature of the linker, as well as by the curvature of the underlying particles.

- Tempo-Spatially Resolved Scattering Correlation Spectroscopy under Dark-Field Illumination and Its Application to Investigate Dynamic Behaviors of Gold Nanoparticles in Live Cells

Liu, H.; Dong, C.; Ren, J. *J. Am. Chem. Soc.* **2014**, *136*, 2775–2785.

Abstract:



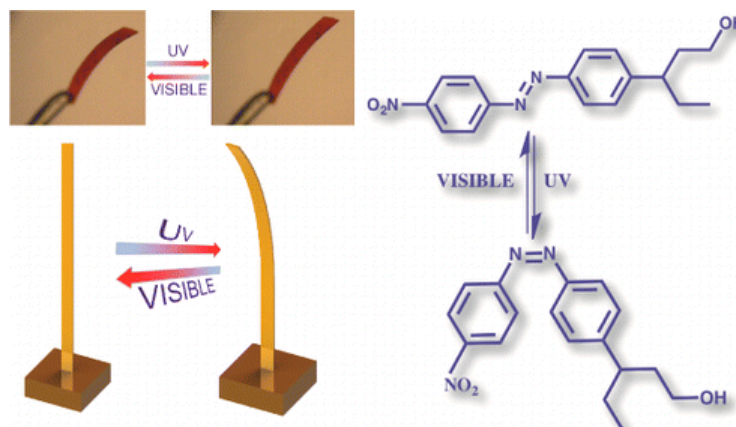
In this study, a new tempo-spatially resolved fluctuation spectroscopy under dark-field illumination is described, named dark-field illumination-based scattering correlation spectroscopy (DFSCS). DFSCS is a single-particle method, whose principle is similar to that of fluorescence correlation spectroscopy (FCS). DFSCS correlates the fluctuations of the scattered light from single nanoparticle under dark-field illumination. We developed a theoretical model for translational diffusion of nanoparticles in DFSCS system. The results of computer simulations documented that this model was able to well describe the diffusion behaviors of nanoparticles in uniformly illuminated field. The experimental setup of DFSCS was achieved by introducing a dark-field condenser to the frequently used bright-field microscope and an electron multiplying charge-coupled device (EMCCD) as the array detector. In the optimal condition, a stack of 500 000 frames were collected simultaneously on 64 detection channels for a single measurement with acquisition rate of 0.5 ms per frame. We systematically investigated the effect of certain factors such as particle concentration, viscosity of the solution, and heterogeneity of gold nanoparticles (GNPs) samples on DFSCS measurements. The experiment data confirmed theoretical model proposed. Furthermore, this new method was successfully used for investigating dynamic behaviors of GNPs in live cells. Our preliminary results demonstrate that DFSCS

is a practical and affordable tool for ordinary laboratories to investigate the dynamic information of nanoparticles in vitro as well as in vivo.

- Model for Photoinduced Bending of Slender Molecular Crystals

Nath, N. K.; Pejov, L.; Nichols, S. M.; Hu, S.; Saleh, N.; Kahr, B.; Naumov, P. *J. Am. Chem. Soc.* **2014**, *136*, 2757–2766.

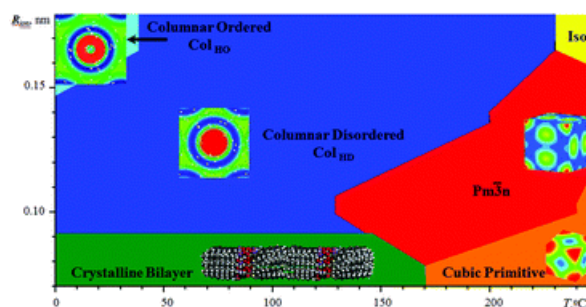
Abstract:



The growing realization that photoinduced bending of slender photoreactive single crystals is surprisingly common has inspired researchers to control crystal motility for actuation. However, new mechanically responsive crystals are reported at a greater rate than their quantitative photophysical characterization; a quantitative identification of measurable parameters and molecular-scale factors that determine the mechanical response has yet to be established. Herein, a simple mathematical description of the quasi-static and time-dependent photoinduced bending of macroscopic single crystals is provided. This kinetic model goes beyond the approximate treatment of a bending crystal as a simple composite bilayer. It includes alternative pathways for excited-state decay and provides a more accurate description of the bending by accounting for the spatial gradient in the product/reactant ratio. A new crystal form (space group $P2_1/n$) of the photoresponsive azo-dye Disperse Red 1 (DR1) is analyzed within the constraints of the aforementioned model. The crystal bending kinetics depends on intrinsic factors (crystal size) and external factors (excitation time, direction, and intensity).

- The effect of the shape of the mesogenic group on the structure and phase behavior of 2,3,4-tris(dodecyloxy)benzenesulfonates with alkaline cations
- Shcherbina, M. A.; Bakirov, A. V.; Yakunin, A. N.; Beginn, U.; Yan, L.; Möller, M.; Chvalun, S. N. *Soft Matter* **2014**, *10*, 1746-1757.

Abstract:

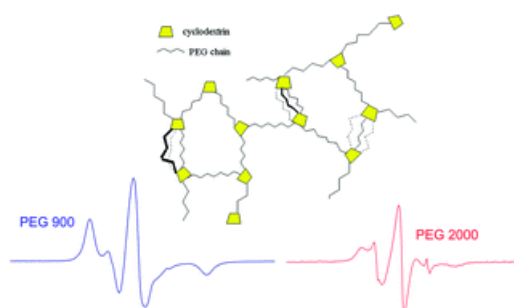


Synthesis and mesophase structure characterisation are reported for a group of alkali salts of 2,3,4-tris(dodecyloxy)benzenesulfonic acid. As revealed by a combination of polarizing optical microscopy, differential scanning calorimetry and X-ray scattering, variation of the effective mesogen shape due to changes of the cation size leads to systematic transformation of the materials' phase behaviour. Thermotropic mesophases of different types and dimensionalities were observed: 1D (smectic bilayers), 2D (ordered and disordered columnar phases), and 3D (high-temperature micellar mesomorphic phase, low-temperature crystalline one). Cubic packing prevails when the cation size is small and, thus, the effective mesogen shape is close to the conic one. With increasing ion size, the mesogen shape becomes more tapered, and columnar mesophases appear to be more stable.

- Properties of polyethylene glycol/cyclodextrin hydrogels revealed by spin probes and spin labelling methods

Ionita, G.; Ariciu, A. M.; Turcu, I. M.; Chechik, V. *Soft Matter* **2014**, *10*, 1778-1783.

Abstract:

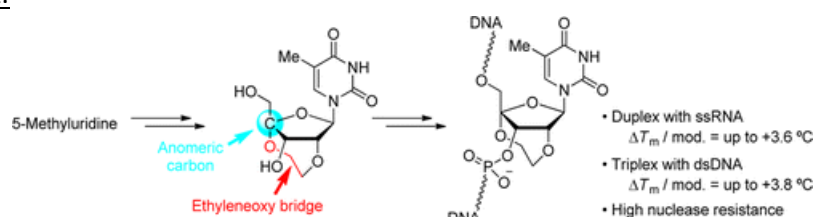


The properties of a gel consisting of a covalent network formed by the reaction of isocyanate end-capped polyethylene glycol (PEG) with β -cyclodextrin, were investigated by EPR spectroscopy. Spin-labelled cyclodextrin was incorporated into the cross-link points of the gel and at the chain ends. The dynamics of the gel fibres as reported by the spin label, was found to be sensitive to the H-bonding ability of the solvent, density of cross-links and temperature. Addition of spin probes (e.g., TEMPO and adamantane-TEMPO) to the unlabelled gel made it possible to characterise the solvent pools in the gel. While TEMPO was uniformly distributed throughout the solvent pools, the adamantane derivative was located at the gel fibre-solvent pool interface; these two probes thus reported on the different locations in the solvent pools. At low temperature, the gels were shown to prevent ice crystallisation in the solvent pools resulting in the formation of supercooled water. Both probes showed that the water froze at ca. 250 K, thus suggesting that the properties of the supercooled water are uniform across the solvent pools.

- Synthesis and Properties of 2'-O,4'-C-Ethyleneoxy Bridged 5-Methyluridine

Hari, Y.; Morikawa, T.; Osawa, T.; Obika, S. *Org. Lett.* **2013**, *15*, 3702-3705.

Abstract:

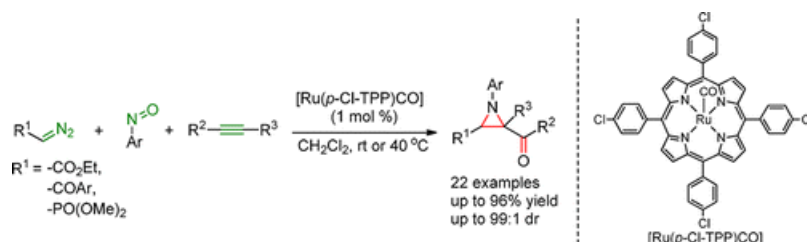


2'-O,4'-C-Ethyleneoxy bridged 5-methyluridine (EoNA-T), possessing a seven-membered linkage and an anomeric 4'-carbon, was synthesized and introduced into oligonucleotides by using an automated

DNA synthesizer. The EoNA-modified oligonucleotides significantly stabilized the duplexes with single-stranded RNA and triplexes with double-stranded DNA relative to the natural oligonucleotide and oligonucleotides modified by another seven-membered bridged 5-methyluridine, 2',4'-BNA^{COC}-T. In addition, EoNA-T showed excellent nuclease resistance.

- Ruthenium Porphyrin Catalyzed Three-Component Reaction of Diazo Compounds, Nitrosoarenes, and Alkynes: An Efficient Approach to Multifunctionalized Aziridines
Reddy, A. R.; Zhou, C.-Y.; Che, C.-M. *Org. Lett.* **2014**, *16*, 1048-1051.

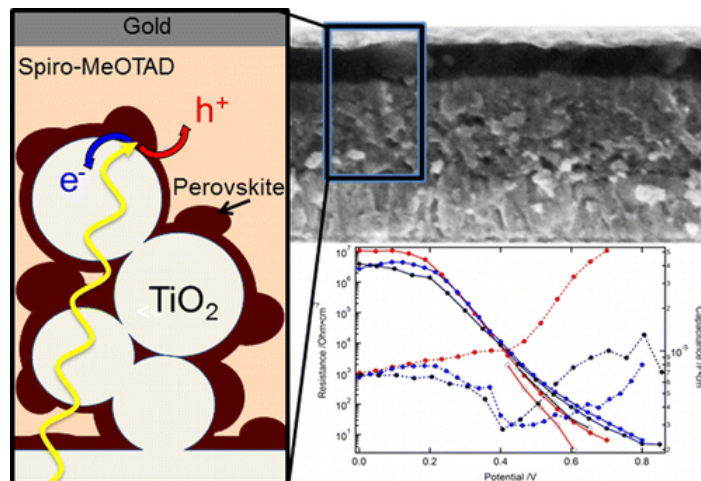
Abstract:



A ruthenium porphyrin catalyzed three-component reaction of diazo compounds, nitrosoarenes, and alkynes gives multifunctionalized aziridines in good to high yields and with moderate to high diastereoselectivity.

- Impedance Spectroscopic Analysis of Lead Iodide Perovskite-Sensitized Solid-State Solar Cells
Dualet, A.; Moehl, T.; T  treault, N.; Teuscher, J.; Gao, P.; Nazeeruddin, M. K.; Gr  tzel, M. *ACS Nano* **2014**, *8*, 362–373.

Abstract:



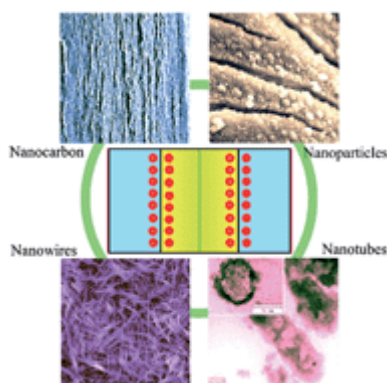
Mesoscopic solid-state solar cells based on the inorganic–organic hybrid perovskite $CH_3NH_3PbI_3$ in conjunction with the amorphous organic semiconductor spiro-MeOTAD as a hole transport material (HTM) are investigated using impedance spectroscopy (IS). A model to interpret the frequency response of these devices is established by expanding and elaborating on the existing models used for the liquid and solid-state dye-sensitized solar cells. Furthermore, the influence of changing the additive concentrations of tert-butylpyridine and LiTFSI in the HTM and varying the HTM overlayer thickness on top of the sub-micrometer thick TiO_2 on the extracted IS parameters is investigated. The internal electrical processes of such devices are studied and correlated with the overall device performance. In particular, the features in the IS responses that are attributed to the ionic and

electronic transport properties of the perovskite material and manifest as a slow response at low frequency and an additional RC element at intermediate frequency, respectively, are explored.

9

- Inorganic nanostructured materials for high performance electrochemical supercapacitors
Liu, S.; Sun, S.; You, X.-Z. *Nanoscale* **2014**, 6, 2037–2045.

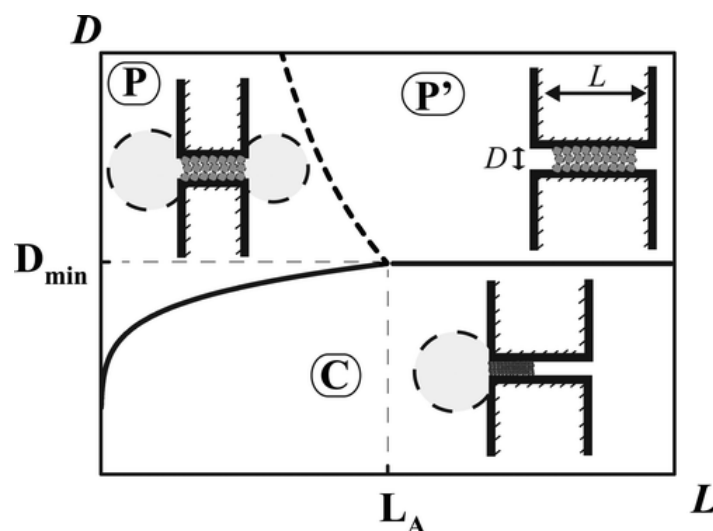
Abstract



Electrochemical supercapacitors (ES) are a well-known energy storage system that has high power density, long life-cycle and fast charge–discharge kinetics. Nanostructured materials are a new generation of electrode materials with large surface area and short transport/diffusion path for ions and electrons to achieve high specific capacitance in ES. This mini review highlights recent developments of inorganic nanostructure materials, including carbon nanomaterials, metal oxide nanoparticles, and metal oxide nanowires/nanotubes, for high performance ES applications.

- Nanopore-Based Characterization of Branched Polymers
Sakaue, T.; Brochard-Wyart, F. *ACS Macro Lett.* **2014**, 3, 194–197.

Abstract:

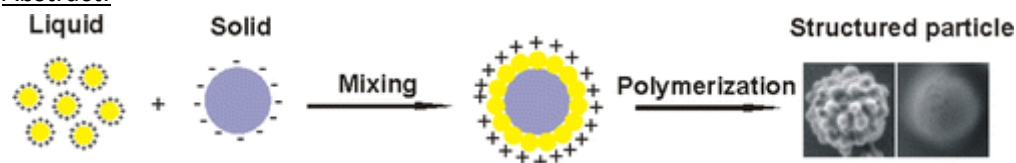


We propose a novel characterization method of randomly branched polymers based on the geometrical property of such objects in confined spaces. The central idea is that randomly branched polymers exhibit a passing/clogging transition across the nanochannel as a function of the channel size. This critical channel size depends on the degree of the branching, whereby allowing the extraction of the branching information of the molecule.

- A Facile Route toward Structured Hybrid Particles Based on Liquid–Solid Assembly

Zhang, Y.; Landfester, K.; Taden, A. *Macromolecules* **2014**, *47*, 1030–1038.

Abstract:

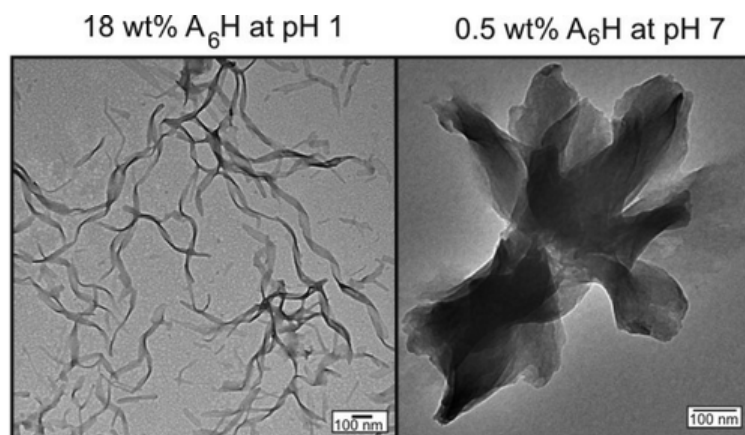


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Structured hybrid particles with strongly improved colloidal stability are synthesized through a facile fabrication method based on the assembly of miniemulsion droplets containing liquid monomeric precursors onto solid nanoparticles. Classical heterocoagulation experiments between solid particles with similar compositions are performed for comparison and result in coagulated samples. A two-step mechanism is proposed which involves polymerization to fixate the final hybrid particle morphology after electrostatically driven self-assembly. Negatively charged polyacrylonitrile (PAN) nanoparticles with a high degree of semicrystallinity are utilized as solid core and combined with positively charged monomer droplets of varying compositions. A simple adjustment of miniemulsion composition enables the tailored synthesis of raspberry or core-shell structured hybrid particles. While the ζ -potential strongly affects the colloidal stability, adjusting the T_g of the polymer and/or the cross-linking degree after polymerization is an efficient tool to determine the final latex morphology. As-prepared hybrid dispersions can form transparent films with embedded PAN domains with an undisturbed high degree of semicrystallinity and thus show potentials in a wide variety of applications, e.g., for coatings and adhesives with reinforced mechanical properties and improved barrier performance.

- Tuning Chelation by the Surfactant-Like Peptide A₆H Using Predetermined pH Values
Castelletto, V.; Hamley, I. W.; Segarra-Maset, M. D.; Berdugo Gumbau, C.; Miravet, J. F.; Escuder, B.; Seitsonen, J.; Ruokolainen, J. *Biomacromolecules* **2014**, *15*, 591–598.

Abstract:



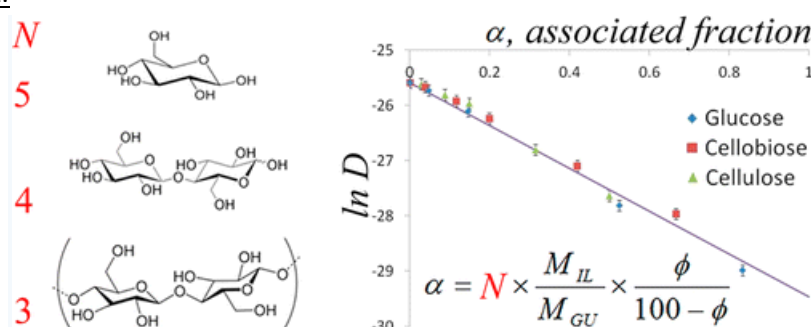
We examine the self-assembly of a peptide A₆H comprising a hexa-alanine sequence A₆ with a histidine (H) “head group”, which chelates Zn²⁺ cations. We study the self-assembly of A₆H and binding of Zn²⁺ ions in ZnCl₂ solutions, under acidic and neutral conditions. A₆H self-assembles into nanotapes held together by a β -sheet structure in acidic aqueous solutions. By dissolving A₆H in acidic ZnCl₂ solutions, the carbonyl oxygen atoms in A₆H chelate the Zn²⁺ ions and allow for β -sheet formation at lower concentrations, consequently reducing the onset concentration for nanotape formation. A₆H mixed with water or ZnCl₂ solutions under neutral conditions produces short sheets or pseudocrystalline tapes, respectively. The imidazole ring of A₆H chelates Zn²⁺ ions in neutral

solutions. The internal structure of nanosheets and pseudocrystalline sheets in neutral solutions is similar to the internal structure of A₆H nanotapes in acidic solutions. Our results show that it is possible to induce dramatic changes in the self-assembly and chelation sites of A₆H by changing the pH of the solution. However, it is likely that the amphiphilic nature of A₆H determines the internal structure of the self-assembled aggregates independent from changes in chelation.

- Diffusion of 1-Ethyl-3-methyl-imidazolium Acetate in Glucose, Cellobiose, and Cellulose Solutions

Ries, M. E.; Radhi, A.; Keating, A. S.; Parker, O.; Budtova, T. *Biomacromolecules* **2014**, *15*, 609–617.

Abstract:

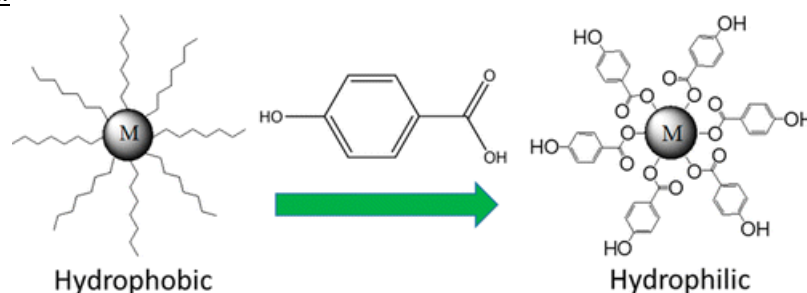


Solutions of glucose, cellobiose and microcrystalline cellulose in the ionic liquid 1-ethyl-3-methyl-imidazolium ([C2mim][OAc]) have been examined using pulsed-field gradient ¹H NMR. Diffusion coefficients of the cation and anion across the temperature range 20–70 °C have been determined for a range of concentrations (0–15% w/w) of each carbohydrate in [C2mim][OAc]. These systems behave as an “ideal mixture” of free ions and ions that are associated with the carbohydrate molecules. The molar ratio of carbohydrate OH groups to ionic liquid molecules, α , is the key parameter in determining the diffusion coefficients of the ions. Master curves for the diffusion coefficients of cation, anion and their activation energies are generated upon which all our data collapses when plotted against α . Diffusion coefficients are found to follow an Arrhenius type behavior and the difference in translational activation energy between free and associated ions is determined to be 9.3 ± 0.9 kJ/mol.

- Simple Ligand Exchange Reactions Enabling Excellent Dispersibility and Stability of Magnetic Nanoparticles in Polar Organic, Aromatic, and Protic Solvents

Wang, X.; Tilley, R. D.; Watkins, J. J. *Langmuir* **2014**, *6*, 1514-1521.

Abstract:



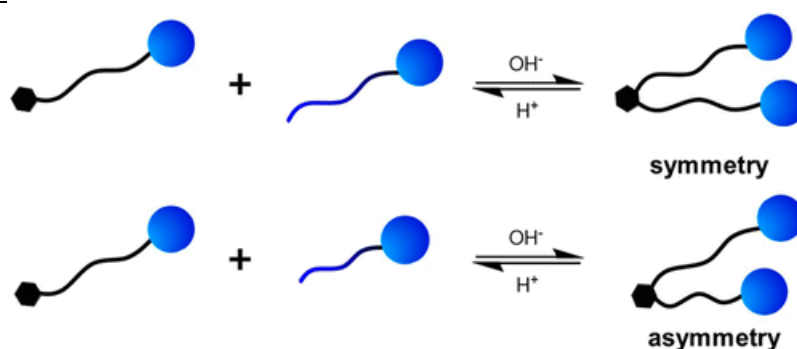
The use of magnetic nanoparticles (MNPs) in real-world applications is often limited by the lack of stable solutions of monodisperse NPs in appropriate solvents. We report a facile one-pot ligand exchange reaction that is fast, efficient, and thorough for the synthesis of hydrophilic MNPs that are

readily dispersed in polar organic and protic solvents (polarity index = 3.9–7.2) including alcohols, THF, DMF, and DMSO for years without precipitation. We emphasize the rational selection of small-molecule ligands such as 4-hydroxybenzoic acid (HBA), 3-(4-hydroxyphenyl)propionic acid (HPP), and gallic acid (GAL) that provide strong bonding with the MNP (FePt and FeO_x) surfaces, hydrophilic termini to match the polarity of target solvents, and offer the potential for hydrogen-bonding interactions to facilitate incorporation into polymers and other media. Areal ligand densities (Σ) calculated based on the NP core size from transmission electron microscopy (TEM) images, and the inorganic fractions of NPs derived from thermogravimetric analysis (TGA) indicated a significant (2–4 times) increase in the ligand coverage after the exchange reactions. Fourier transform infrared spectrometry (FTIR) and ¹H nuclear magnetic resonance (NMR) studies also confirmed anchoring of carboxyl groups on NP surfaces. In addition, we demonstrate a facile one-step in situ synthesis of FePt NPs with aromatic ligands for better dispersibility in solvents of intermediate polarity (polarity index = 1.0–3.5) such as toluene, chlorobenzene, and dichloromethane. The creation of stable dispersions of NPs in solvents across the polarity spectrum opens up new applications and new processing windows for creating NP composites in a variety of host materials.

- Asymmetric and Symmetric Bolaform Supra-Amphiphiles: Formation of Imine Bond Influenced by Aggregation

Wang, G.; Wu, G.; Wang, Z.; Zhang, X. *Langmuir* **2014**, 6, 1531-1535.

Abstract:

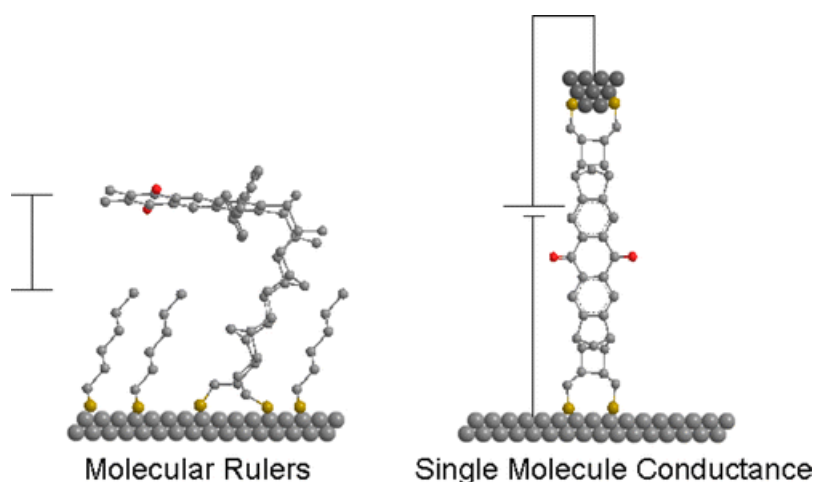


A series of bolaform supra-amphiphiles with different symmetries were fabricated through dynamic benzoic imine bond formation. The pH dependence of imine formations of these supra-amphiphiles were characterized. We found that the extent of the imine formation of these supra-amphiphiles were different. The supra-amphiphiles with a poorer symmetry always exhibited a lower imine formation at a given pH. Therefore, the varied extent of imine bond formation indicate the different aggregations of these supra-amphiphiles, which are controlled by the molecular symmetry of the supra-amphiphiles.

- Surface-Bound Norbornylogous Bridges as Molecular Rulers for Investigating Interfacial Electrochemistry and as Single Molecule Switches

Darwish, N.; Paddon-Row, M. N.; Gooding, J. J. *Acc. Chem. Res.* **2014**, 47, 385–395.

Abstract:



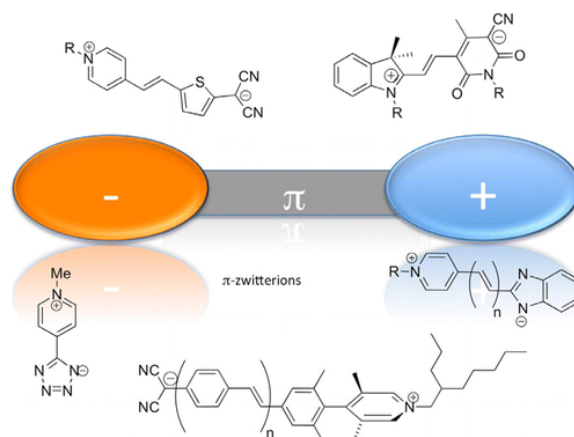
Electron transfer (ET) reactions through molecules attached to surfaces, whether they are through single molecules or ensembles, are the subject of much research in molecular electronics, bioelectronics, and electrochemistry. Therefore, understanding the factors that govern ET is of high importance. The availability of rigid hydrocarbon molecular scaffolds possessing well-defined configurations and lengths that can be systematically varied is crucial to the development of such devices.

In this Account, we demonstrate how suitably functionalized norbornylogous (NB) systems can provide important insights into interfacial ET processes and electrical conduction through single molecules. To this end, we created NB bridges with *vic-trans*-bismethylenethiol groups at one end so they can assemble on gold electrodes and redox species at the distal ends. With these in hand, we then formed mixed self-assembled monolayers (SAMs) containing a small proportion of the NB bridges diluted with alkanethiols. As such, the NB bridges served as molecular rulers for probing the environment above the surface defined by the diluent species. Using this construct, we were able to measure the interfacial potential distribution above the diluent surface, and track how variation in the ionic distribution in the electrical double layer impacts ET kinetics.

Using the same construct, but with a redox molecule that remains neutral in both oxidized and reduced states, we could explore the impact of the chemical environment near a surface on ET processes. These results are important, because with conventional surface constructs, ET occurs across this interfacial region. Such knowledge is therefore relevant to the design of molecular systems at surfaces involving ET.

With a second family of molecules, we investigated aspects of single-molecule electrical conduction using NB bridges bearing *vic-trans*-bismethylenethiol groups at both ends of the bridge. This gave us insights into distance-dependent electron transport through single molecules and introduced a method of boosting the conductance of saturated molecules by incorporating aromatic moieties in their backbone. These partially conjugated NB molecules represent a new class of molecular wires with far greater stability than conventional completely conjugated molecular wires. Of particular note was our demonstration of a single molecule switch, using a NB bridge containing an embedded anthraquinone redox group, the switching mechanism being via electrochemically controlled quantum interference.

- π -Conjugated Zwitterions as Paradigm of Donor–Acceptor Building Blocks in Organic-Based Materials
Beverina, L. Pagani, G. A. *Acc. Chem. Res.* **2014**, *47*, 319–329.

Abstract:

The very peculiar characteristics of zwitterions, as well as a clear and unambiguous definition, have been overlooked in past literature. However, these compounds are particularly important in view of the impact they have had in the recent past and will likely continue to have in the future as components of performing functional organic and hybrid materials. In this Account, we primarily aim to define critically important organic concepts of zwitterions regarding both their design and nomenclature. We will particularly focus on a specific kind of zwitterions we define as π -conjugated zwitterions.

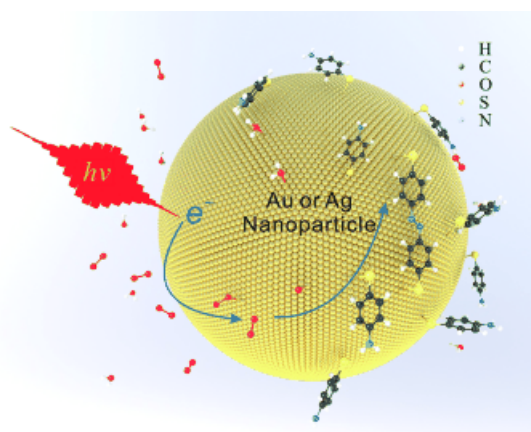
These types of zwitterions are systems pertaining to the class of donor–acceptor (push–pull) molecules. In the ground state, they are preferentially represented in terms of an electron donor moiety bearing a negative net charge, and electron acceptor one bearing a positive net charge connected by a conjugated bridge. As such, they are possibly the most effective example of push–pull structure, possessing relevant features for applications like nonlinear optics, photovoltaics, imaging, and high capacitance dielectrics. In addition, the interaction between these dipolar compounds and the environment is highly specific and can be exploited in the construction of well-organized nanostructures, both in solution and in the solid state. According to the Gold Book of IUPAC for nomenclature, the distinction between zwitterions and the charged molecule called a betaine is subtle. The betaine is a particular class of zwitterion possessing an onium atom not bearing a hydrogen. The two terms are often considered equivalent, thus generating confusion while retrieving literature. In this Account, we define and describe π -conjugated zwitterions systems that are dipolar in the ground state, admitting resonance limiting structures that are neutral and chargeless. For the purpose of this Account and to the benefit of researchers striving to retrieve materials-related zwitterion literature data, we suggest to use the term π -zwitterions instead of the commonly used plain term “zwitterions”. We show that this definition enables the clear identification of a class of compounds having unique properties distinct from “dipolar conjugated compounds.” We describe the most common donor and acceptor groups in π -zwitterions. In particular, we focus our attention on the special case of the nitrile functionality, which tends to be contiguous to a negative charge. We also address special emphasis to benzenoid components that are substituted by heteroaromatic units in π -zwitterions, because the HOMO–LUMO energetic consequences are specifically involved in these cases. We make reference to the paradigmatic case of π -zwitterions second order nonlinear optical properties. Here, the value of the first hyperpolarizability β versus the alternation in bond length turns out to be a measure of the balance of the chargeless and the dipolar contribution to the description of the zwitterion ground state. We also report literature data, collected both from our group and others, concerning π -zwitterions

containing heteroaromatic and/or nitrile groups, those based on the most performing acceptors so far described, and merocyanines. With particular reference to merocyanines, we show how π -zwitterions can play a fundamental role in the fast growing field of organic photovoltaics. Finally, we present π -zwitterions made up of heteroaromatic groups that open new scenarios in heteroaromatic chemistry.

- Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances

Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 2353–2357.

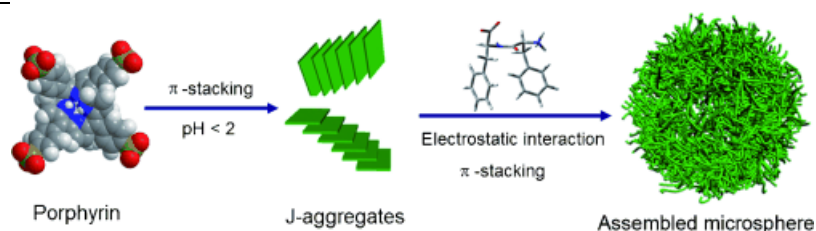
Abstract:



Surface plasmon resonances (SPRs) have been found to promote chemical reactions. In most oxidative chemical reactions oxygen molecules participate and understanding of the activation mechanism of oxygen molecules is highly important. For this purpose, we applied surface-enhanced Raman spectroscopy (SERS) to find out the mechanism of SPR-assisted activation of oxygen, by using *p*-aminothiophenol (PATP), which undergoes a SPR-assisted selective oxidation, as a probe molecule. In this way, SPR has the dual function of activating the chemical reaction and enhancing the Raman signal of surface species. Both experiments and DFT calculations reveal that oxygen molecules were activated by accepting an electron from a metal nanoparticle under the excitation of SPR to form a strongly adsorbed oxygen molecule anion. The anion was then transformed to Au or Ag oxides or hydroxides on the surface to oxidize the surface species, which was also supported by the heating effect of the SPR. This work points to a promising new era of SPR-assisted catalytic reactions.

- Multifunctional Porous Microspheres Based on Peptide–Porphyrin Hierarchical Co-Assembly
Zou, Q.; Zhang, L.; Yan, X.; Wang, A.; Ma, G.; Li, J.; Möhwald, H.; Mann, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 2366–2370.

Abstract:



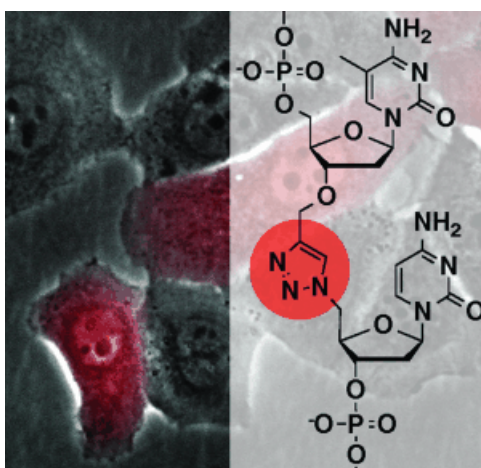
Photocatalytically active, multi-chambered, biomolecule-based microspheres were prepared by hierarchical co-assembly of simple dipeptides and porphyrins. The colloidal microspheres are highly

hydrated and consist of a network of J-aggregate nanoscale substructures that serve as light-harvesting antennae with a relatively broad spectral cross-section and considerable photostability. These optical properties can be exploited in photocatalytic reactions involving inorganic or organic species. Taken together, these structural and functional features suggest that soft porous biomolecule-based colloids are a plausible photosynthetic model that could be developed towards demonstrating aspects of primitive abiotic cellularity.

- Transcription of Click-Linked DNA in Human Cells

Birts, C. N.; Sanzone, A. P.; El-Sagheer, A. H.; Blaydes, J. P.; Brown, T.; Tavassoli, A. *Angew. Chem. Int. Ed.* **2014**, 53, 2362–2365.

Abstract:

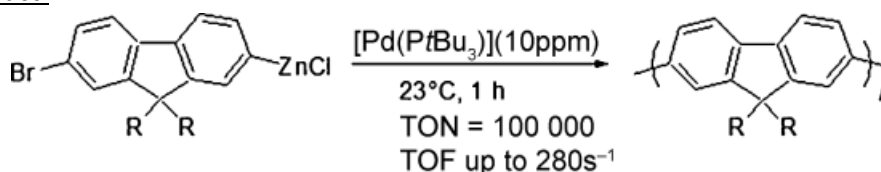


Click DNA ligation promises an alternative to the current enzymatic approaches for DNA assembly, with the ultimate goal of using efficient chemical reactions for the total chemical synthesis and assembly of genes and genomes. Such an approach would enable the incorporation of various chemically modified bases throughout long stretches of DNA, a feat not possible with current polymerase-based methods. An unequivocal requirement for this approach is the biocompatibility of the resulting triazole-linked DNA. The correct function of this unnatural DNA linker in human cells is demonstrated here by using a click-linked gene encoding the fluorescent protein mCherry. Reverse transcription of mRNA isolated from these cells and subsequent sequencing of the mCherry cDNA shows error-free transcription. Nucleotide excision repair (NER) is shown to not play a role in the observed biocompatibility by using a NER-deficient human cell line. This is the first example of a non-natural DNA linker being functional in a eukaryotic cell.

- Palladium-Catalyzed Chain-Growth Polycondensation of AB-type Monomers: High Catalyst Turnover and Polymerization Rates

Tkachov, R.; Senkovskyy, V.; Beryozkina, T.; Boyko, K.; Bakulev, V.; Lederer, A.; Sahre, K.; Voit, B.; Kiri, A. *Angew. Chem. Int. Ed.* **2014**, 53, 2402–2407.

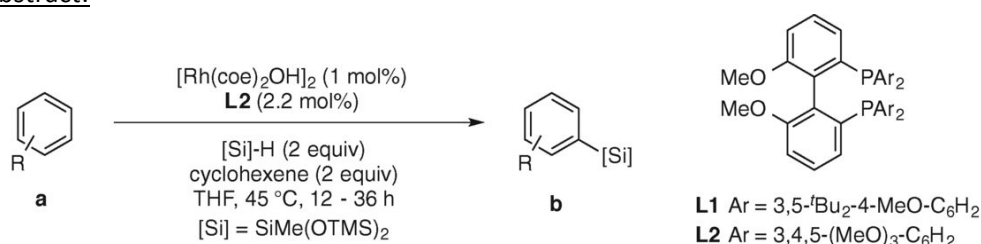
Abstract:



Chain-growth catalyst-transfer polycondensations of AB-type monomers is a new and rapidly developing tool for the preparation of well-defined π -conjugated (semiconducting) polymers for various optoelectronic applications. Herein, we report the Pd/PtBu₃-catalyzed Negishi chain-growth polycondensation of AB-type monomers, which proceeds with unprecedented TONs of above 100 000 and TOFs of up to 280 s⁻¹. In contrast, related AA/BB-type step-growth polycondensation proceeds with two orders of magnitude lower TONs and TOFs. A similar trend was observed in Suzuki-type polycondensation. The key impact of the intramolecular (vs. intermolecular) catalyst-transfer process on both polymerization kinetics and catalyst lifetime has been revealed.

- Rhodium-Catalyzed Intermolecular C–H Silylation of Arenes with High Steric Regiocontrol
Cheng, C.; Hartwig, J. F. *Science* **2014**, 343, 853-857.

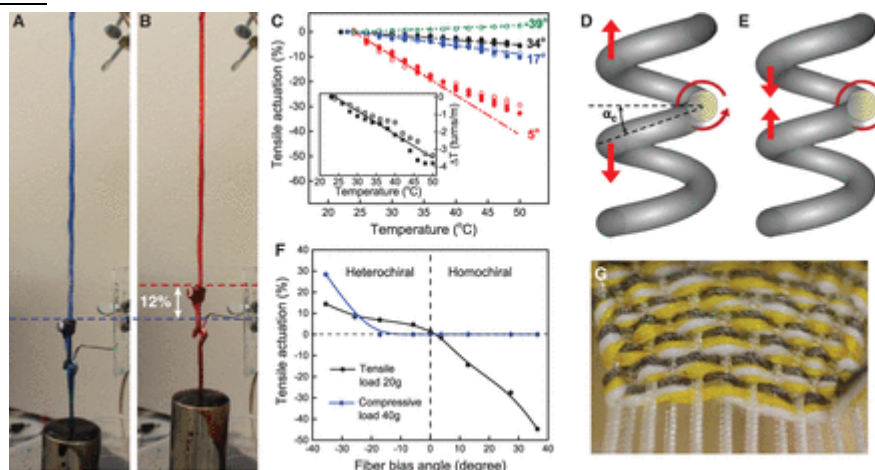
Abstract:



Regioselective C–H functionalization of arenes has widespread applications in synthetic chemistry. The regioselectivity of these reactions is often controlled by directing groups or steric hindrance ortho to a potential reaction site. Here, we report a catalytic intermolecular C–H silylation of unactivated arenes that manifests very high regioselectivity through steric effects of substituents meta to a potential site of reactivity. The silyl moiety can be further functionalized under mild conditions but is also inert toward many common organic transformations, rendering the silylarene products useful building blocks. The remote steric effect that we observe results from the steric properties of both the rhodium catalyst and the silane.

- Artificial Muscles from Fishing Line and Sewing Thread
Haines, C. S.; Lima, M. D.; Li, N.; Spinks, G. M.; Foroughi, J.; Madden, J. D. W.; Kim, S. H.; Fang, S.; Jung de Andrade, M.; Göktepe, F.; Göktepe, Ö.; Mirvakili, S. M.; Naficy, S.; Lepró, X.; Oh, J.; Kozlov, M. E.; Kim, S. J.; Xu, X.; Swedlove, B. J.; Wallace, G. G.; Baughman, R. H. *Science* **2014**, 343, 868-872.

Abstract:

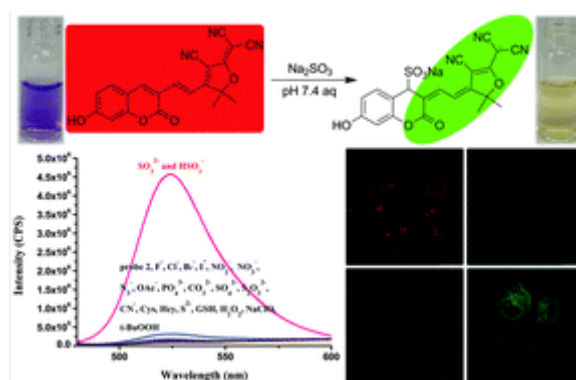


The high cost of powerful, large-stroke, high-stress artificial muscles has combined with performance limitations such as low cycle life, hysteresis, and low efficiency to restrict applications. We demonstrated that inexpensive high-strength polymer fibers used for fishing line and sewing thread can be easily transformed by twist insertion to provide fast, scalable, nonhysteretic, long-life tensile and torsional muscles. Extreme twisting produces coiled muscles that can contract by 49%, lift loads over 100 times heavier than can human muscle of the same length and weight, and generate 5.3 kilowatts of mechanical work per kilogram of muscle weight, similar to that produced by a jet engine. Woven textiles that change porosity in response to temperature and actuating window shutters that could help conserve energy were also demonstrated. Large-stroke tensile actuation was theoretically and experimentally shown to result from torsional actuation.

- A water-soluble near-infrared probe for colorimetric and ratiometric sensing of SO_2 derivatives in living cells

Wu, M.-Y.; Li, K.; Li, C.-Y.; Hou, J.-T.; Yu, X.-Q. *Chem. Commun.* **2014**, 50, 183-185.

Abstract:

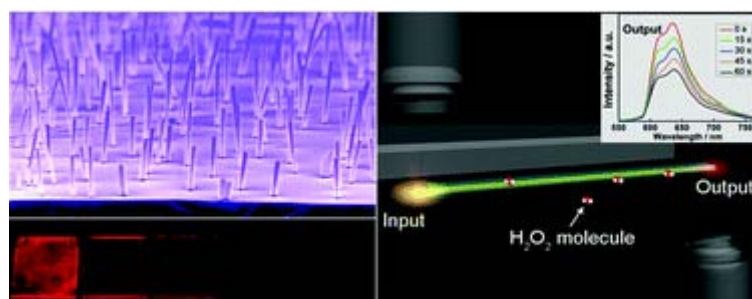


A coumarin TCF-based water soluble near-infrared fluorescent probe was presented, which could be used for the rapid, colorimetric and ratiometric detection of SO_2 derivatives with a detection limit of 0.27 nM. Moreover, this probe could successfully image the analyte in living cells.

- Tailoring the structures and compositions of one-dimensional organic nanomaterials towards chemical sensing applications

Cui, Q. H.; Zhao, Y. S.; Yao, J. *Chem. Sci.* **2014**, 5, 52-57.

Abstract:

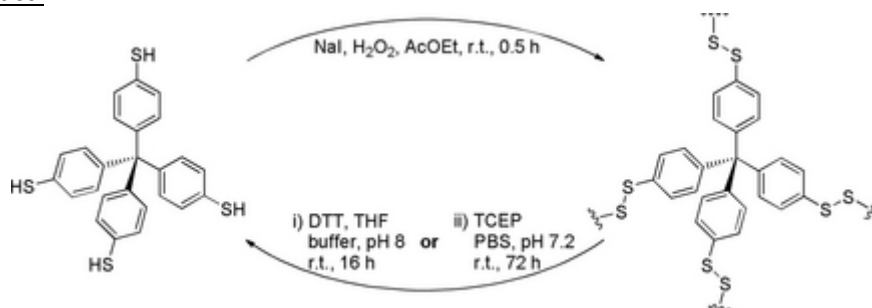


One-dimensional (1D) organic nanostructures and their hierarchical assemblies have sparked great interest in sensing applications recently owing to convenient detection, high sensitivity and selectivity, and real-time monitoring with fast response time afforded by systems that utilize them. In this mini-review, we focus on the construction and modulation of 1D nanostructures from single- or multicomponent organic compounds, and the relevant approaches that have employed them into

sensing applications. Furthermore, major obstacles and future steps towards ultimate organic nanosensors based on 1D structures are discussed.

- Tetrakis-(4-thiophenyl)methane: Origin of a Reversible 3D-Homopolymer
Monnereau, L.; Nieger, M.; Muller, T.; Bräse, S. *Adv. Funct. Mater.* **2014**, 24, 1054–1058.

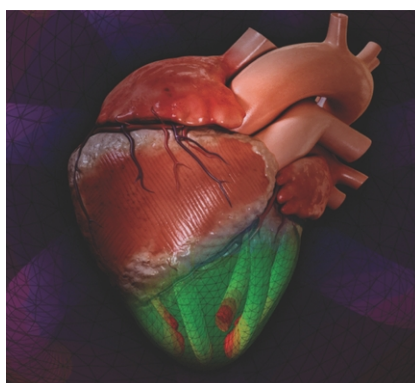
Abstract:



The efficient syntheses of tetrakis(thiophenol)methane and of a new poly(disulfide) hyper-crosslinked polymer based on the former monomer are described. Controlled de-polymerization as well as surface post-functionalization are successfully conducted on this novel material. Direct prove of post-functionalization is obtained through solid-state fluorescence emission spectroscopy, and the number of unreacted thiol-functions on the surface of the polymeric material is indirectly quantified by de-polymerization of the post-functionalized material.

- A Bioinspired Soft Actuated Material
Roche, E. T.; Wohlfarth, R.; Overvelde, J. T. B.; Vasilyev, N. V.; Pigula, F. A.; Mooney, D. J.; Bertoldi, K.; Walsh, C. J. *Adv. Mater.* **2014**, 26, 1200–1206.

Abstract:



A class of soft actuated materials that can achieve lifelike motion is presented. By embedding pneumatic actuators in a soft material inspired by a biological muscle fibril architecture, and developing a simple finite element simulation of the same, tunable biomimetic motion can be achieved with fully soft structures, exemplified here by an active left ventricle simulator.