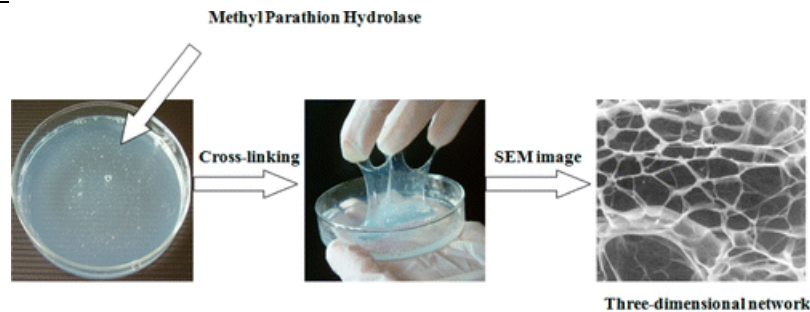


- Entrapment of Methyl Parathion Hydrolase in Cross-Linked Poly(γ -glutamic acid)/Gelatin Hydrogel

1

Xie, J.; Zhang, H.; Li, X.; Shi, Y. *Biomacromolecules* **2014**, *15*, 690–697.

Abstract:

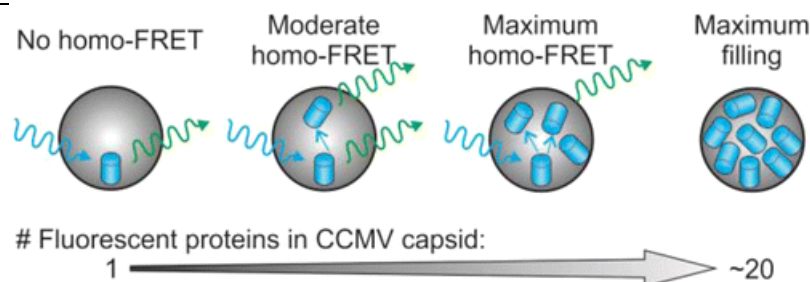


Entrapment of MethylParathion Hydrolase in Cross-linked Poly(γ -glutamic acid)/Gelatin Hydrogel

Methyl parathion hydrolase (MPH) is an important enzyme in hydrolyzing toxic organophosphorus (OP) compounds. However, MPH is easily deactivated when subjected to extreme environmental conditions and is difficult to recover from the reaction system for reuse, thereby limiting its practical application. To address these shortcomings, we examined the entrapment of MPH in an environment-friendly, biocompatible and biodegradable cross-linked poly(γ -glutamic acid)/gelatin hydrogel. The cross-linked poly(γ -glutamic acid)/gelatin hydrogels were prepared with different gelatin/poly(γ -glutamic acid) mass ratios using water-soluble carbodiimide as the cross-linking agent. The MPH-entrapped cross-linked poly(γ -glutamic acid)/gelatin hydrogel (CPE–MPH) not only possessed improved thermostability, pH stability, and reusability but also exhibited enhanced efficiency in hydrolyzing OP compounds. Furthermore, CPE–MPH possesses high water-absorbing and water-retaining capabilities. We believe that the cross-linked poly(γ -glutamic acid)/gelatin hydrogels are an attractive carrier for the entrapment of diverse enzymes, affording a new approach for enzyme entrapment.

- Predicting the Loading of Virus-Like Particles with Fluorescent Proteins
Rurup, W. F.; Verbij, F.; Koay, M. S. T.; Blum, C.; Subramaniam, V.; Cornelissen, J. J. L. M. *Biomacromolecules* **2014**, *15*, 558–563.

Abstract:



The virus-like particle (VLP) of the Cowpea Chlorotic Mottle Virus (CCMV) has often been used to encapsulate foreign cargo. Here we show two different rational design approaches, covalent and noncovalent, for loading teal fluorescent proteins (TFP) into the VLP. The covalent loading approach allows us to gain control over capsid loading on a molecular level. The achieved loading control is used to accurately predict the loading of cargo into CCMV VLP. The effects of molecular confinement were compared for the differently loaded VLPs created with the covalent method. We see that the loading of more than 10 fluorescent proteins in the 18 nm internal cavity of the CCMV capsid gives rise to a maximum efficiency of homo-FRET between the loaded proteins, as measured by

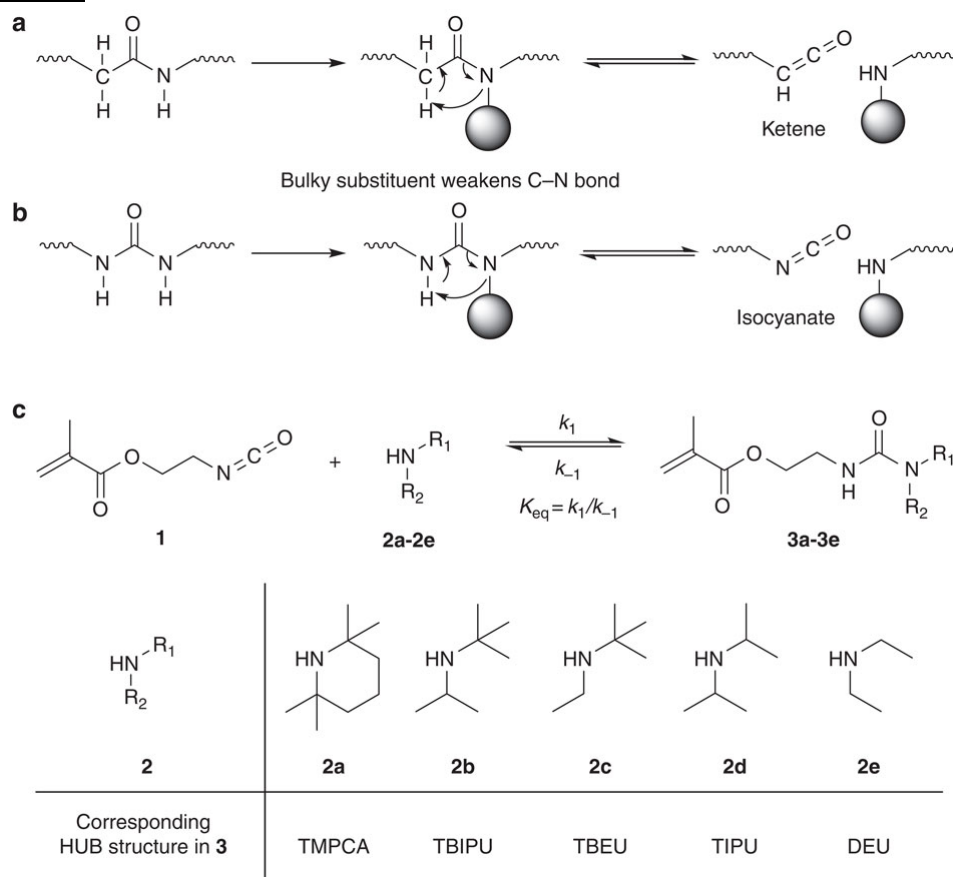
fluorescence anisotropy. This shows that already at low levels of VLP loading molecular crowding starts to play a role.

2

- Dynamic urea bond for the design of reversible and self-healing polymers

Ying, H.; Zhang, Y.; Cheng, J. *Nature Commun.* **2014**, *5*, 3218.

Abstract:

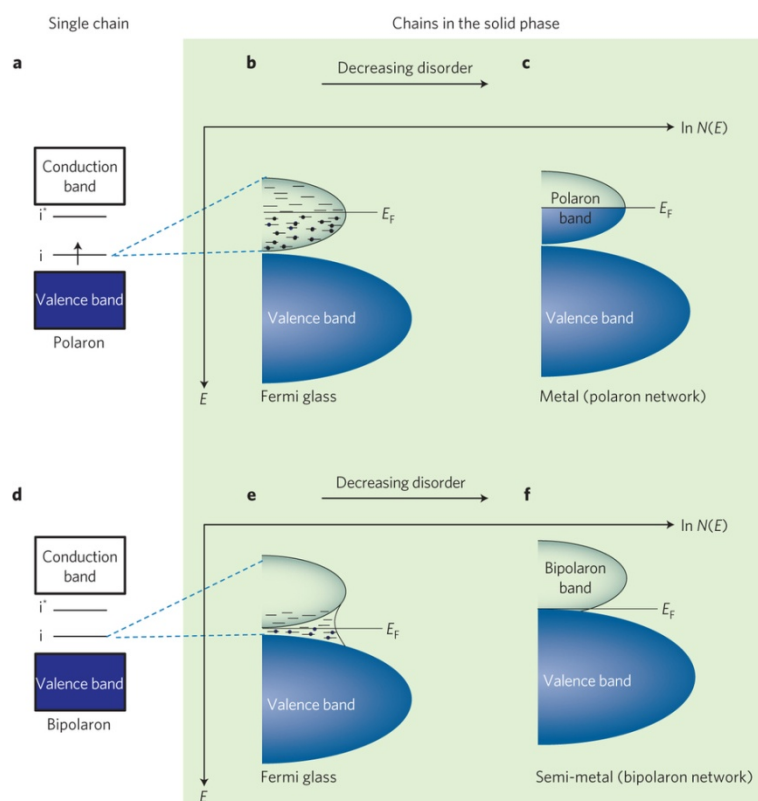


Polymers bearing dynamic covalent bonds may exhibit dynamic properties, such as self-healing, shape memory and environmental adaptation. However, most dynamic covalent chemistries developed so far require either catalyst or change of environmental conditions to facilitate bond reversion and dynamic property change in bulk materials. Here we report the rational design of hindered urea bonds (urea with bulky substituent attached to its nitrogen) and the use of them to make polyureas and poly(urethane-urea)s capable of catalyst-free dynamic property change and autonomous repairing at low temperature. Given the simplicity of the hindered urea bond chemistry (reaction of a bulky amine with an isocyanate), incorporation of the catalyst-free dynamic covalent urea bonds to conventional polyurea or urea-containing polymers that typically have stable bulk properties may further broaden the scope of applications of these widely used materials.

- Semi-metallic polymers

Bubnova, O.; Khan, Z. U.; Wang, H.; Braun, S.; Evans, D. R.; Fabretto, M.; Hojati-Talemi, P.; Dagnelund, D.; Arlin, J.-B.; Geerts, Y. H.; Desbief, S.; Breiby, D. W.; Andreasen, J. W.; Lazzaroni, R.; Chen, W. M.; Zozoulenko, I.; Fahlman, M.; Murphy, P. J.; Berggren, M.; Crispin, X. *Nature Mater.* **2014**, *13*, 190.

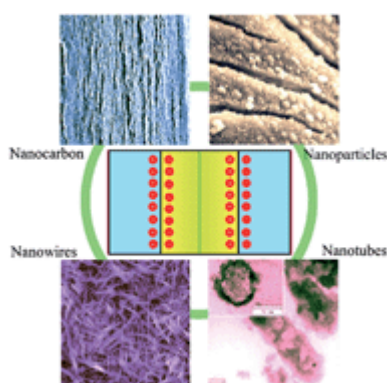
Abstract:



Polymers are lightweight, flexible, solution-processable materials that are promising for low-cost printed electronics as well as for mass-produced and large-area applications. Previous studies demonstrated that they can possess insulating, semiconducting or metallic properties; here we report that polymers can also be semi-metallic. Semi-metals, exemplified by bismuth, graphite and telluride alloys, have no energy bandgap and a very low density of states at the Fermi level. Furthermore, they typically have a higher Seebeck coefficient and lower thermal conductivities compared with metals, thus being suitable for thermoelectric applications. We measure the thermoelectric properties of various poly(3,4-ethylenedioxythiophene) samples, and observe a marked increase in the Seebeck coefficient when the electrical conductivity is enhanced through molecular organization. This initiates the transition from a Fermi glass to a semi-metal. The high Seebeck value, the metallic conductivity at room temperature and the absence of unpaired electron spins makes polymer semi-metals attractive for thermoelectrics and spintronics.

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

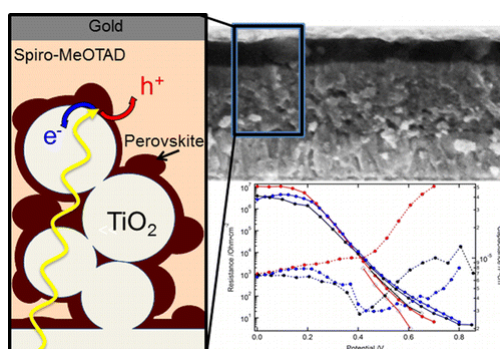
Abstract:



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.

- 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.

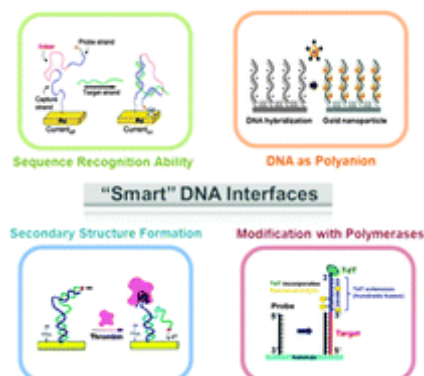
Abstract:



Mesoscopic solid-state solar cells based on the inorganic–organic hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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.

- “Smart” DNA interfaces
Tjong, V.; Tang, L.; Zauscher, S.; Chilkoti, A. *Chem. Soc. Rev.* **2014**, 43, 1612-1626.

Abstract:



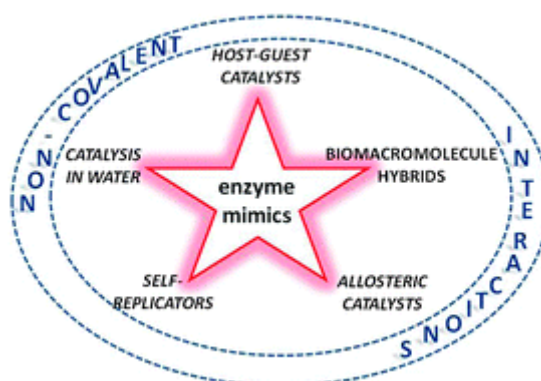
This review focuses on surface-grafted DNA, and its use as a molecular building block that exploits its

unique properties as a directional (poly)anion that exhibits molecular recognition. The selected examples highlight innovative applications of DNA at surfaces and interfaces ranging from molecular diagnostics and sequencing to biosensing.

5

- Supramolecular catalysis. Part 2: artificial enzyme mimics
Raynal, M.; Ballester, P.; Vidal-Ferranab, A.; van Leeuwen, P. W. N. M. *Chem. Soc. Rev.* **2014**, 43, 1734-1787.

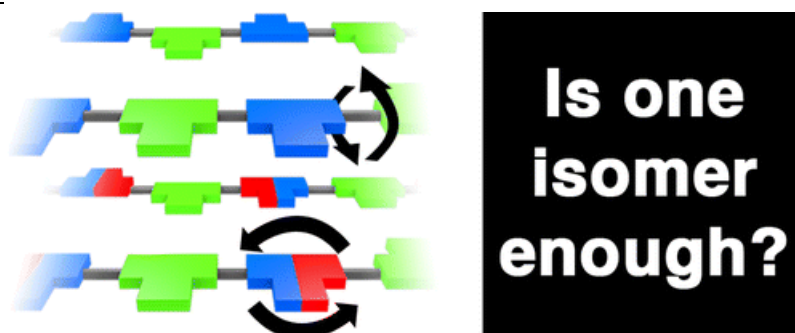
Abstract:



The design of artificial catalysts able to compete with the catalytic proficiency of enzymes is an intense subject of research. Non-covalent interactions are thought to be involved in several properties of enzymatic catalysis, notably (i) the confinement of the substrates and the active site within a catalytic pocket, (ii) the creation of a hydrophobic pocket in water, (iii) self-replication properties and (iv) allosteric properties. The origins of the enhanced rates and high catalytic selectivities associated with these properties are still a matter of debate. Stabilisation of the transition state and favourable conformations of the active site and the product(s) are probably part of the answer. We present here artificial catalysts and biomacromolecule hybrid catalysts which constitute good models towards the development of truly competitive artificial enzymes.

- Structural and Conformational Dispersion in the Rational Design of Conjugated Polymers
Jackson, N. E.; Savoie, B. M.; Kohlstedt, K. L.; Marks, T. J.; Chen, L. X.; Ratner, M. A. *Macromolecules* **2014**, 47, 987–992.

Abstract:



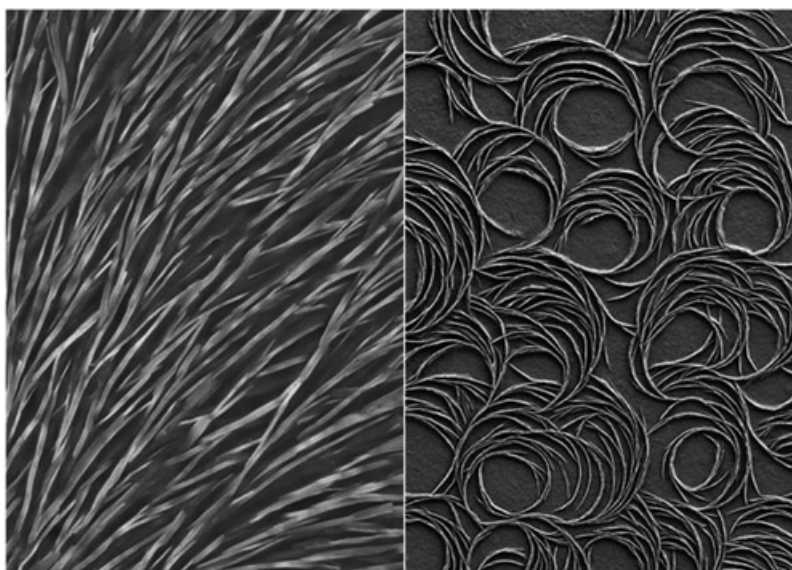
Quantum-chemical computation is a useful and widespread tool for understanding the electronic structure of conjugated polymers as well as predicting new synthetic targets. In this work, we assess the validity of considering a single conformational or structural isomer as representative of the entire conformational or structural distributions in ab-initio computations of figures-of-merit (dipole

moment, HOMO, LUMO, and optical gap). It is found from surveying numerous conjugated copolymers that considering only a single conformational or structural isomer can hide significant deviations in frontier molecular orbital energies and optical gaps as well as qualitative shifts in dipole moments. We discuss the limitations of not considering isomeric dispersion on the polymer's computed electronic properties and the implications these findings have on the rational design of conjugated polymers.

- Block Copolymer Self Assembly during Rapid Solvent Evaporation: Insights into Cylinder Growth and Stability

Paradiso, S. P.; Delaney, K. T.; García-Cervera, C. J.; Cenicerros, H. D.; Fredrickson, G. H. *ACS Macro Lett.* **2014**, 3, 35–39.

Abstract:

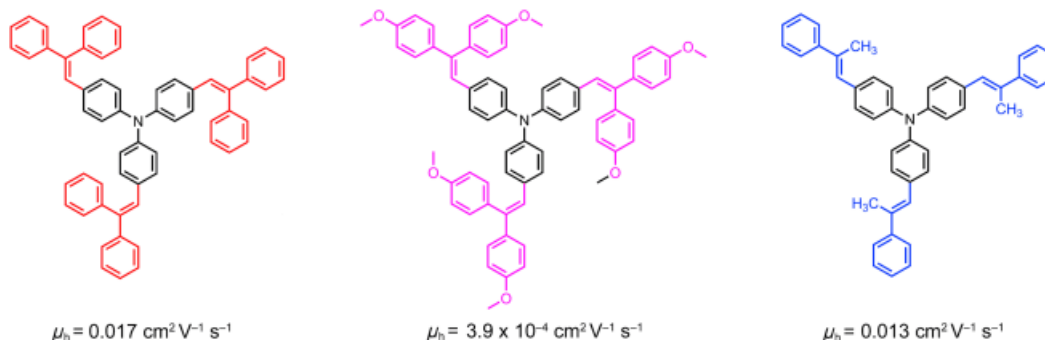


The formation of self-assembled microstructures of anionic polyelectrolyte, poly(acrylic acid) salts, on the surface of single-walled carbon nanotube thin films was studied by a fast phase separation process that filtrated a mixed dispersion composed of single-walled carbon nanotubes and poly(acrylic acid) derivatives on a membrane filter. The resulting microstructures of poly(acrylic acid) self-assembly were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, element mapping, and diffuse reflectance Fourier transform infrared spectroscopy. The influence factors including substrate, ion species, single-walled carbon nanotubes, and different kinds of carbon nanotubes were discussed comprehensively for the formation of microstructures of PAA self-assembly by a liquid–liquid phase separation.

- Phenylethenyl-Substituted Triphenylamines: Efficient, Easily Obtainable, and Inexpensive Hole-Transporting Materials

Malinauskas, T.; Daskeviciene, M.; Bubniene, G.; Petrikyte, I.; Raisys, S.; Kazlauskas, K.; Gaidelis, V.; Jankauskas, V.; Maldzius, R.; Jursenas, S.; Getautis, V. *Chem. Eur. J.* **2013**, 19, 15044–15056.

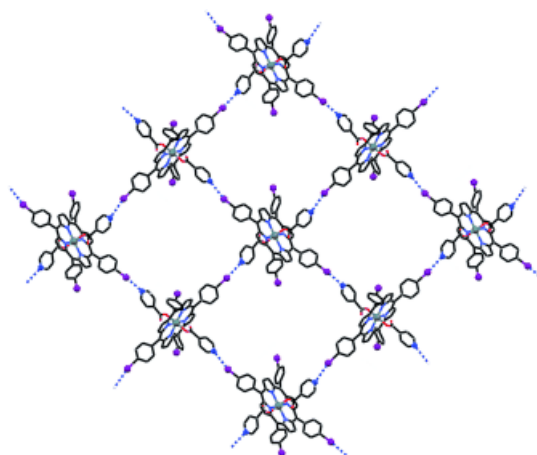
Abstract:



Star-shaped charge-transporting materials with a triphenylamine (TPA) core and various phenylethenyl side arm(s) were obtained in a one-step synthetic procedure from commercially available and relatively inexpensive starting materials. Crystallinity, glass-transition temperature, size of the π -conjugated system, energy levels, and the way molecules pack in the solid state can be significantly influenced by variation of the structure of these side arm(s). An increase in the number of phenylethenyl side arms was found to hinder intramolecular motions of the TPA core, and thereby provide significant enhancement of the fluorescence quantum yield of the TPA derivatives in solution. On the other hand, a larger number of side arms facilitated exciton migration through the dense side-arm network formed in the solid state and, thus, considerably reduces fluorescence efficiency by migration-assisted nonradiative relaxation. This dense network enables charges to move more rapidly through the hole-transport material layer, which results in very good charge drift mobility (μ up to $0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

- Exploring Supramolecular Self-Assembly of Tetraarylporphyrins by Halogen Bonding: Crystal Engineering with Diversely Functionalized Six-Coordinate Tin(L)₂–Porphyrin Tectons
Titi, H. M.; Patra, R.; Goldberg, I. *Chem. Eur. J.* **2013**, *19*, 14941–14949.

Abstract:

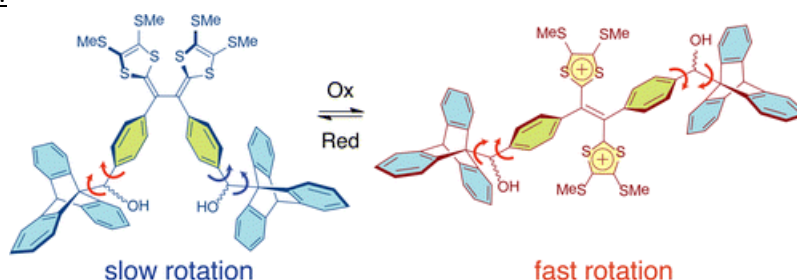


This study targets the construction of porphyrin assemblies directed by halogen bonds, by utilizing a series of purposely synthesized Sn(axial ligand)₂–(5,10,15,20-tetraarylporphyrin) [Sn(L)₂–TArP] complexes as building units. The porphyrin moiety and the axial ligands in these compounds contain different combinations of complimentary molecular recognition functions. The former bears *p*-iodophenyl, *p*-bromophenyl, 4'-pyridyl, or 3'-pyridyl substituents at the *meso* positions of the porphyrin ring. The latter comprises either a carboxylate or hydroxy anchor for attachment to the porphyrin-inserted tin ion and a pyridyl-, benzotriazole-, or halophenyl-type aromatic residue as the potential binding site. The various complexes were structurally analyzed by single-crystal X-ray diffraction, accompanied by computational modeling evaluations. Halogen-bonding interactions

between the lateral aryl substituents of one unit of the porphyrin complex and the axial ligands of neighboring moieties was successfully expressed in several of the resulting samples. Their occurrence is affected by structural (for example, specific geometry of the six-coordinate complexes) and electronic effects (for example, charge densities and electrostatic potentials). The shortest intermolecular I...N halogen-bonding distance of 2.991 Å was observed between iodophenyl (porphyrin) and benzotriazole (axial ligand) moieties. Manifestation of halogen bonds in these relatively bulky compounds without further activation of the halophenyl donor groups by electron-withdrawing substituents is particularly remarkable.

- Redox-Regulated Rotary Motion of a Bis(9-triptycyl)-TTFV System
Chen, G.; Zhao, Y. *Org. Lett.* **2014**, *16*, 668-671.

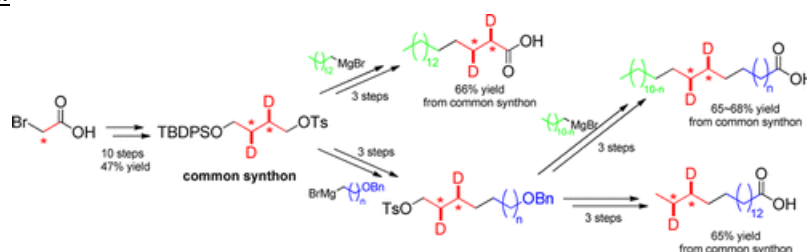
Abstract:



A tetrathiafulvalene vinyllogue (TTFV) unit was covalently linked to two benzyltriptycene molecular rotors to form a molecular gearset. Dynamic NMR studies showed that reversible redox reactions at the TTFV central unit exerted regulation over the rotational properties of the 9-triptycyl rotors.

- Highly Efficient Preparation of Selectively Isotope Cluster-Labeled Long Chain Fatty Acids via Two Consecutive Csp³–Csp³ Cross-Coupling Reactions
Lethu, S.; Matsuoka, S.; Murata, M. *Org. Lett.* **2014**, *16*, 844-847.

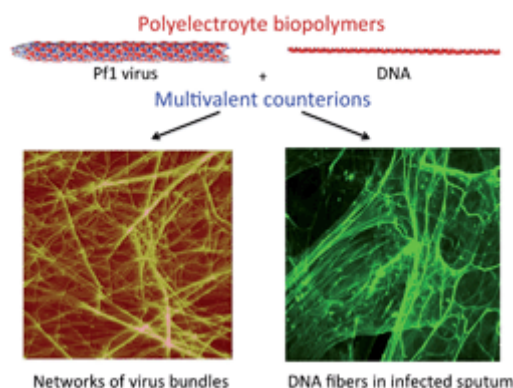
Abstract:



An efficient synthesis involving two copper-catalyzed alkyl–alkyl coupling reactions has been designed to easily access doubly isotope-labeled fatty acids. Such NMR- and IR-active compounds were obtained in excellent overall yields and will be further used for determining the conformation of an alkyl chain of lipidic biomolecules upon interaction with proteins.

- Polyelectrolyte properties of filamentous biopolymers and their consequences in biological fluids
Janmey, P. A.; Slochow, D. R.; Wang, Y.-H.; Wen, Q.; Cēbers, A. *Soft Matter* **2014**, *10*, 1439-1449.

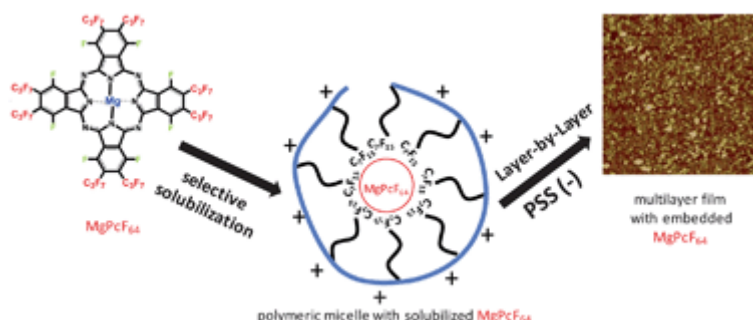
Abstract:



Anionic polyelectrolyte filaments are common in biological cells. DNA, RNA, the cytoskeletal filaments F-actin, microtubules, and intermediate filaments, and polysaccharides such as hyaluronan that form the pericellular matrix all have large net negative charge densities distributed over their surfaces. Several filamentous viruses with diameters and stiffnesses similar to those of cytoskeletal polymers also have similar negative charge densities. Extracellular protein filaments such collagen, fibrin and elastin, in contrast, have notably smaller charge densities and do not behave as highly charged polyelectrolytes in solution. This review summarizes data that demonstrate generic counterion-mediated effects on four structurally unrelated biopolymers of similar charge density: F-actin, vimentin, Pf1 virus, and DNA, and explores the possible biological and pathophysiological consequences of the polyelectrolyte properties of biological filaments.

- Polyelectrolyte multilayers with perfluorinated phthalocyanine selectively entrapped inside the perfluorinated nanocompartments
Kopeć, M.; Łapok, Ł.; Laschewsky, A.; Zapotoczny, S.; Nowakowska, M. M. *Soft Matter* **2014**, *10*, 1481-1488.

Abstract:



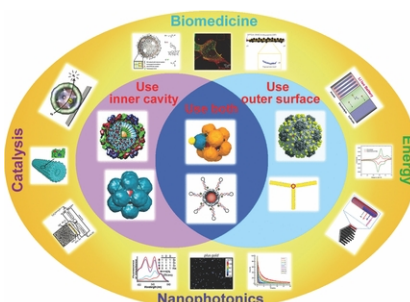
A novel perfluorinated magnesium phthalocyanine (MgPcF_{64}) was synthesized and employed to probe nanodomains in hydrophobically modified, amphiphilic cationic polyelectrolytes bearing alkyl and/or fluoroalkyl side chains. MgPcF_{64} was found to be solubilized exclusively in the aqueous solutions of the fluorocarbon modified polycations, occupying the perfluorinated nanocompartments provided, while analogous polyelectrolytes with alkyl side chains forming hydrocarbon nanocompartments could not host the MgPcF_{64} dye. Multilayer films were fabricated by means of the layer-by-layer (LbL) deposition method using sodium poly(styrene sulfonate) as a polyanion. Linear multilayer growth was confirmed by UV-Vis spectroscopy and spectroscopic ellipsometry. Atomic force microscopy studies indicated that the micellar conformation of the polycations is preserved in the multilayer films. Fluorescence spectroscopy measurements confirmed that MgPcF_{64} stays embedded inside the fluorocarbon domains after the deposition process. This facile way of

selectively incorporating water-insoluble, photoactive molecules into the structure of polyelectrolyte multilayers may be utilized for nanoengineering of ultrathin film-based optoelectronic devices.

- Fabrication of Nanoarchitectures Templated by Virus-Based Nanoparticles: Strategies and Applications

Li, F.; Wang, Q. *Small* **2014**, 2, 230-245.

Abstract:



Biomolecular nanostructures in nature are drawing increasing interests in the field of materials sciences. As a typical group of them, virus-based nanoparticles (VNPs), which are nanocages or nanorods assembled from capsid proteins of viruses, have been widely exploited as templates to guide the fabrication of complex nanoarchitectures (NAs), because of their appropriate sizes (ca. 20–200 nm), homogeneity, addressable functionalization, facile modification via chemical and genetic routes, and convenient preparation. Foreign materials can be positioned in the inner cavity or on the outer surface of VNPs, through either direct synthesis or assembling preformed nanomaterials. Simultaneous use of the inner and outer space of VNPs facilitates integration of multiple functionalities in a single NA. This review briefly summarizes the strategies for fabrication of NAs templated by VNPs and wide applications of these NAs in fields of catalysis, energy, biomedicine, and nanophotonics, etc.

- Peanut Leaf Inspired Multifunctional Surfaces

Yang, S.; Ju, J.; Qiu, Y.; He, Y.; Wang, X.; Dou, S.; Liu, K.; Jiang, L. *Small* **2014**, 2, 294-299.

Abstract:

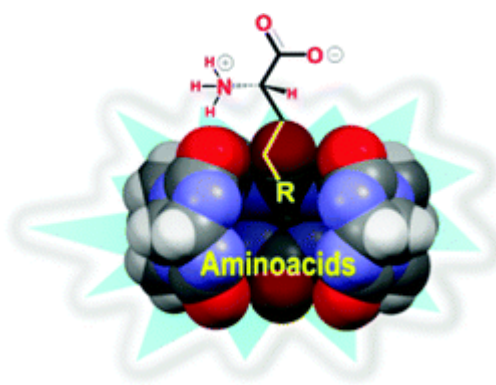


Nature has long served as a source of inspiration for scientists and engineers to design and construct multifunctional artificial materials. The lotus and the peanut are two typical plants living in the aquatic and the arid (or semiarid) habitats, respectively, which have evolved different optimized solutions to survive. For the lotus leaf, an air layer is formed between its surface and water, exhibiting a discontinuous three-phase contact line, which resulted in the low adhesive superhydrophobic self-cleaning effect to avoid the leaf decomposition. In contrast to the lotus leaf,

the peanut leaf shows high-adhesive superhydrophobicity, arising from the formation of the quasi-continuous and discontinuous three-phase contact line at the microscale and nanoscale, respectively, which provides a new avenue for the fabrication of high adhesive superhydrophobic materials. Further, this high adhesive and superhydrophobic peanut leaf is proved to be efficient in fog capture. Inspired by the peanut leaf, multifunctional surfaces with structural similarity to the natural peanut leaf are prepared, exhibiting simultaneous superhydrophobicity and high adhesion towards water.

- “Turn-on” fluorescent sensor array for basic amino acids in water
Minami, T.; Esipenko, N. A.; Zhang, B.; Isaacs, L.; Anzenbacher, Jr., P. *Chem. Commun.* **2014**, 50, 61-63.

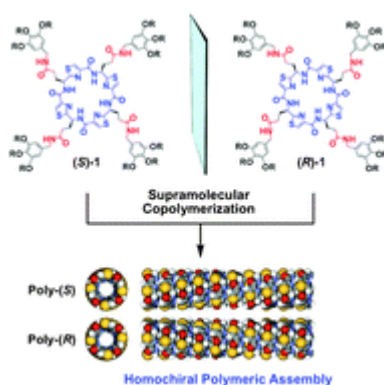
Abstract:



Amino acids and their derivatives are recognized and analyzed in water using a turn-on fluorescent cucurbituril based sensor array. Multivariate analysis (LDA and HCA) clearly shows that the sensor array can discriminate amino acids from the corresponding amines which are produced by the action of amino acid decarboxylases.

- Homochiral supramolecular polymerization of bowl-shaped chiral macrocycles in solution
Sato, K.; Itoh, Y.; Aida, T. *Chem. Sci.* **2014**, 5, 136-140.

Abstract:

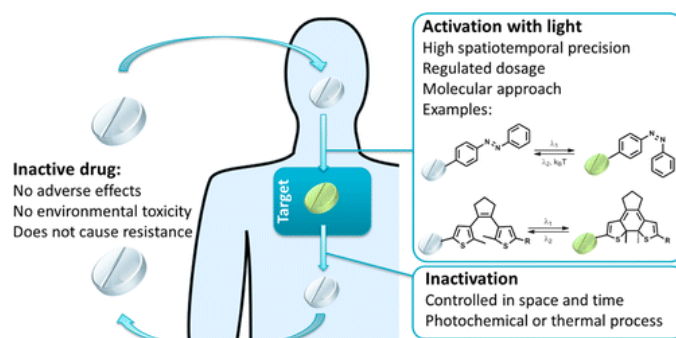


Chiral monomers 1 and 2, carrying C_4 - and C_3 - symmetric bowl-shape peptide macrocycle cores, respectively, undergo supramolecular polymerization in solution *via* van der Waals and hydrogen bonding interactions. Size-exclusion chromatographic studies, using UV and CD detectors, on the supramolecular copolymerization of their enantiomers demonstrated that these monomers are the first chiral macrocycles that polymerize enantioselectively with a strong preference for chiral self-sorting.

- Photopharmacology: Beyond Proof of Principle

Velema, W. A.; Szymanski, W.; Feringa, B. L. *J. Am. Chem. Soc.* **2014**, *136*, 2178-2191.

Abstract:

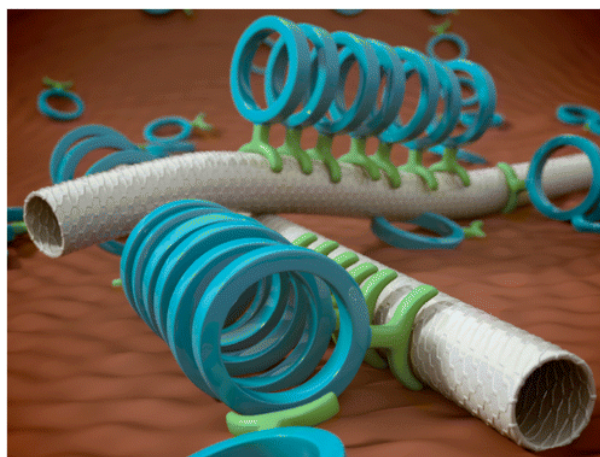


Pharmacotherapy is often severely hindered by issues related to poor drug selectivity, including side effects, environmental toxicity, and the emergence of resistance. Lack of selectivity is caused by the inability to control drug activity in time and space. Photopharmacology aims at solving this issue by incorporating photoswitchable groups into the molecular structure of bioactive compounds. These switching units allow for the use of light as an external control element for pharmacological activity, which can be delivered with very high spatiotemporal precision. This Perspective presents the reader with the current state and outlook on photopharmacology. In particular, the principles behind photoregulation of bioactivity, the challenges of molecular design, and the possible therapeutic scenarios are discussed.

- Coupling of Carbon and Peptide Nanotubes

Montenegro, J.; Vázquez-Vázquez, C.; Kalinin, A.; Geckeler, K. E.; Granja, J. R. *J. Am. Chem. Soc.* **2014**, *136*, 2484-2491.

Abstract:

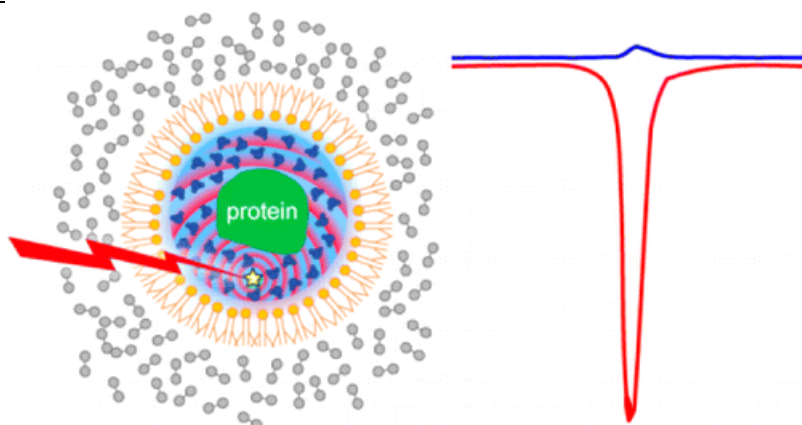


Two of the main types of nanotubular architectures are the single-walled carbon nanotubes (SWCNTs) and the self-assembling cyclic peptide nanotubes (SCPNTs). We here report the preparation of the dual composite resulting from the ordered combination of both tubular motifs. In the resulting architecture, the SWCNTs can act as templates for the assembly of SCPNTs that engage the carbon nanotubes noncovalently via pyrene “paddles”, each member of the resulting hybrid stabilizing the other in aqueous solution. The particular hybrids obtained in the present study formed highly ordered oriented arrays and display complementary properties such as electrical conductivity. Furthermore, a self-sorting of the cyclic peptides toward semiconducting rather than metallic

SWCNTs is also observed in the aqueous dispersions. It is envisaged that a broad range of exploitable properties may be achieved and/or controlled by varying the cyclic peptide components of similar SWCNT/SCPN hybrids.

- Reverse Micelles As a Platform for Dynamic Nuclear Polarization in Solution NMR of Proteins
Valentine, K. G.; Mathies, G.; Bédard, S.; Nucci, N. V.; Dodevski, I.; Stetz, M. A.; Can, T. V.; Griffin, R. G.; Wand, A. J. *Am. Chem. Soc.* **2014**, *136*, 2800–2807.

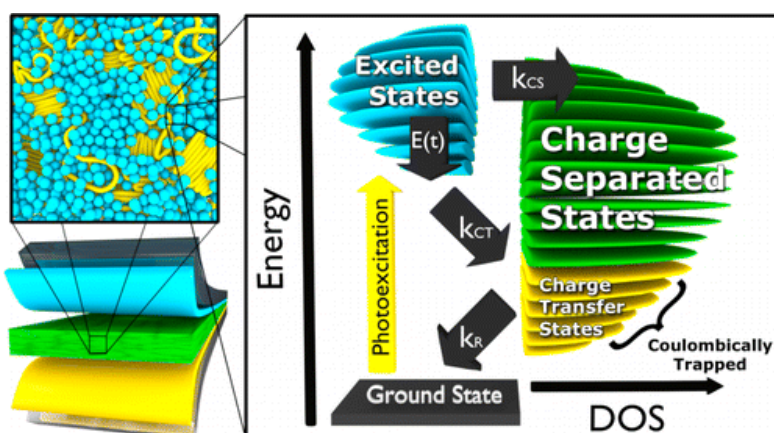
Abstract:



Despite tremendous advances in recent years, solution NMR remains fundamentally restricted due to its inherent insensitivity. Dynamic nuclear polarization (DNP) potentially offers significant improvements in this respect. The basic DNP strategy is to irradiate the EPR transitions of a stable radical and transfer this nonequilibrium polarization to the hydrogen spins of water, which will in turn transfer polarization to the hydrogens of the macromolecule. Unfortunately, these EPR transitions lie in the microwave range of the electromagnetic spectrum where bulk water absorbs strongly, often resulting in catastrophic heating. Furthermore, the residence times of water on the surface of the protein in bulk solution are generally too short for efficient transfer of polarization. Here we take advantage of the properties of solutions of encapsulated proteins dissolved in low viscosity solvents to implement DNP in liquids. Such samples are largely transparent to the microwave frequencies required and thereby avoid significant heating. Nitroxide radicals are introduced into the reverse micelle system in three ways: attached to the protein, embedded in the reverse micelle shell, and free in the aqueous core. Significant enhancements of the water resonance ranging up to -93 at 0.35 T were observed. We also find that the hydration properties of encapsulated proteins allow for efficient polarization transfer from water to the protein. These and other observations suggest that merging reverse micelle encapsulation technology with DNP offers a route to a significant increase in the sensitivity of solution NMR spectroscopy of proteins and other biomolecules.

- Unequal Partnership: Asymmetric Roles of Polymeric Donor and Fullerene Acceptor in Generating Free Charge
Savoie, B. M.; Rao, A.; Bakulin, A. A.; Gelinas, S.; Movaghar, B.; Friend, R. H.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **2014**, *136*, 2876–2884.

Abstract:

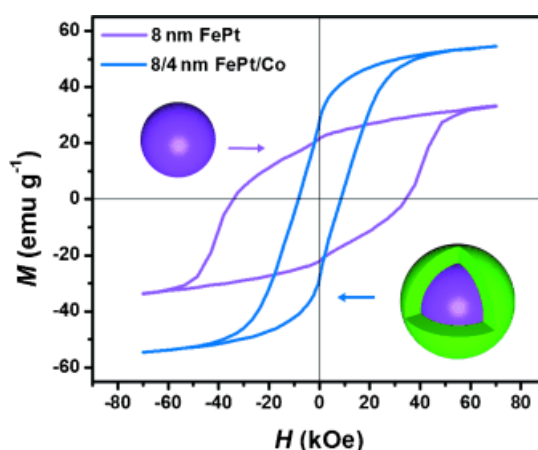


Natural photosynthetic complexes accomplish the rapid conversion of photoexcitations into spatially separated electrons and holes through precise hierarchical ordering of chromophores and redox centers. In contrast, organic photovoltaic (OPV) cells are poorly ordered, utilize only two different chemical potentials, and the same materials that absorb light must also transport charge; yet, some OPV blends achieve near-perfect quantum efficiency. Here we perform electronic structure calculations on large clusters of functionalized fullerenes of different size and ordering, predicting several features of the charge generation process, outside the framework of conventional theories but clearly observed in ultrafast electro-optical experiments described herein. We show that it is the resonant coupling of photogenerated singlet excitons to a high-energy manifold of fullerene electronic states that enables efficient charge generation, bypassing localized charge-transfer states. In contrast to conventional views, our findings suggest that fullerene cluster size, concentration, and dimensionality control charge generation efficiency, independent of exciton delocalization.

- Building Nanocomposite Magnets by Coating a Hard Magnetic Core with a Soft Magnetic Shell

Liu, F.; Zhu, J.; Yang, W.; Dong, Y.; Hou, Y.; Zhang, C.; Yin, H.; Sun, S. *Angew. Chem. Int. Ed.* **2014**, 53, 2176–2180.

Abstract:



Controlling exchange coupling between hard magnetic and soft magnetic phases is the key to the fabrication of advanced magnets with tunable magnetism and high energy density. Using FePt as an example, control over the magnetism in exchange-coupled nanocomposites of hard magnetic face-centered tetragonal (fct) FePt and soft magnetic Co (or Ni, Fe₂C) is shown. The dispersible hard magnetic fct-FePt nanoparticles are first prepared with their coercivity (H_c) reaching 33 kOe. Then core/shell fct-FePt/Co (or Ni, Fe₂C) nanoparticles are synthesized by reductive thermal

decomposition of the proper metal precursors in the presence of fct-FePt nanoparticles. These core/shell nanoparticles are strongly coupled by exchange interactions and their magnetic properties can be rationally tuned by the shell thickness of the soft phase. This work provides an ideal model system for the study of exchange coupling at the nanoscale, which will be essential for building superstrong magnets for various permanent magnet applications in the future.

- Electron Transfer in a Supramolecular Associate of a Fullerene Fragment
Gallego, M.; Calbo, J.; Aragó, J.; Calderon, R. M. K.; Liquido, F. H.; Iwamoto, T.; Greene, A. K.; Jackson, E. A.; Pérez, E. M.; Ortí, D. E.; Guldi, D. M.; Scott, L. T.; Martín, N. *Angew. Chem. Int. Ed.* **2014**, 53, 2166–2169.

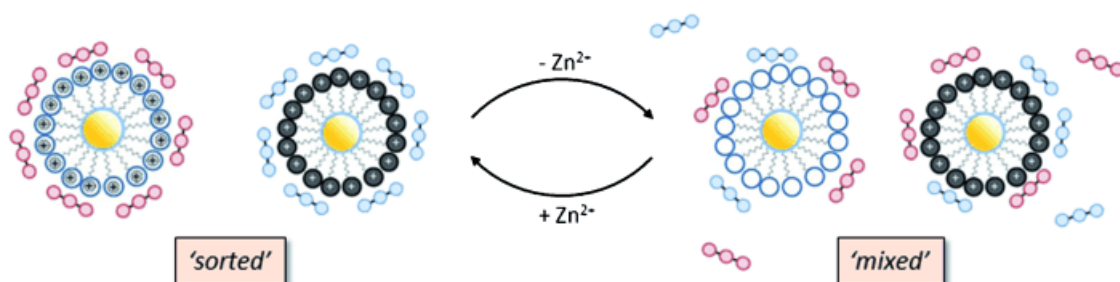
Abstract:



Herein, we investigate the association of a fullerene fragment, hemifullerene C₃₀H₁₂, with an electron-donating bowl-shaped tetrathiafulvalene derivative (truxTTF). UV/Vis titrations and DFT calculations support formation of the supramolecular complex, for which an association constant of log K_a=3.6±0.3 in CHCl₃ at room temperature is calculated. Remarkably, electron transfer from truxTTF to C₃₀H₁₂ to form the fully charge-separated species takes place upon irradiation of the associate with light, constituting the first example in which a fullerene fragment mimics the electron-accepting behavior of fullerenes within a supramolecular complex.

- Zn²⁺-Regulated Self-Sorting and Mixing of Phosphates and Carboxylates on the Surface of Functionalized Gold Nanoparticles
Pezzato, C.; Scrimin, P.; Prins, L. J. *Angew. Chem. Int. Ed.* **2014**, 53, 2104–2109.

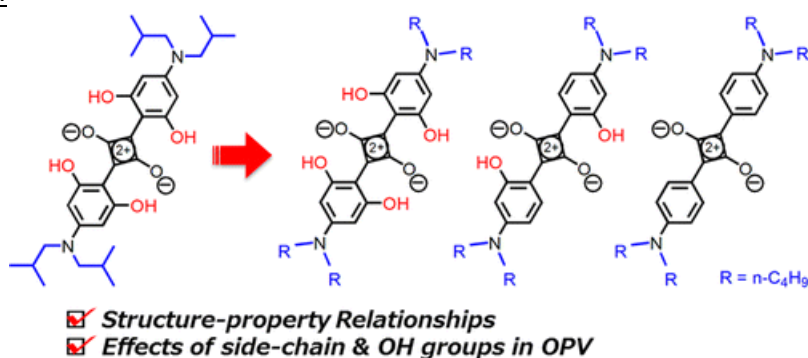
Abstract:



Herein, we describe the self-sorting of phosphate- and carboxylate-containing molecules on the surface of monolayer-protected gold nanoparticles. Self-sorting is driven by selective interactions between the phosphate probe and Zn^{2+} complexes in one monolayer; these interactions force the carboxylate probe to move to a second type of nanoparticle. This process effectively separates the probes and causes their localization in well-defined spaces surrounding the nanoparticles. The removal/addition of Zn^{2+} metal ions from the system is used to convert the system from an ordered to a disordered state and vice versa. The possibility to control the location and transport of populations of molecules in a complex mixture creates new perspectives for the development of innovative complex catalytic systems that mimic nature.

- A Series of Squaraine Dyes: Effects of Side Chain and the Number of Hydroxyl Groups on Material Properties and Photovoltaic Performance
Chen, G.; Sasabe, H.; Sasaki, Y.; Katagiri, H.; Wang, X.-F.; Sano, T.; Hong, Z.; Yang, Y.; Kido, J. *Chem. Mater.* **2014**, 26, 1356–1364.

Abstract:



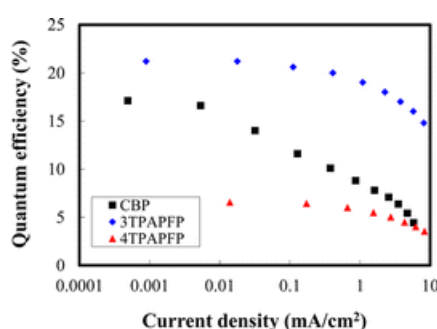
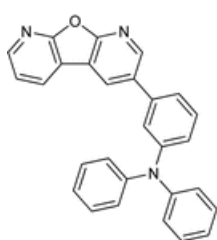
Squaraine dyes are considered an important group of photoactive materials in the field of organic photovoltaic devices. In this work, we purposely tuned the side chains and number of hydroxyl (OH) groups in a series of squaraine (SQ) dyes, i.e., SQ1–4, to investigate the effect of structural variations on the material properties as well as the performance of these dyes as donor materials in bulk heterojunction (BHJ) photovoltaic cells. The material structure and properties of these SQs were systematically characterized using various tools. Solution-processed BHJ photovoltaic cells based on these SQ compounds combined with [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) as an acceptor gave efficient power conversion efficiencies greater than 4.0% under AM 1.5G solar illumination at 100 mW/cm². Our observations show that the OH groups deepened the highest occupied molecular orbital (HOMO) of the donor and thus enhanced the open-circuit voltage, whereas the linear chain improved the charge transport properties in the BHJ films. Both the side chain and the number of OH groups play important roles in determining the aggregation behavior of these SQs in solid-state films: SQ1, which contains four OH groups and branched side chains, exhibits J-aggregation because of the steric hindrance of its side chains; SQ2, which contains four OH groups

and linear side chains, exhibits both H-aggregation and J-aggregation; SQ3, which contains two OH groups and linear side chains, exhibits preferential H-aggregation; SQ4, which contains linear side chains without OH groups, exhibits J-aggregation, this is most likely because of its strong intermolecular coupling and intermolecular hydrogen-bonding interactions to form a head-to-tail packing mode, i.e., J-aggregation. Interestingly, the absorption of J-aggregates in BHJ cells contributes to the cells' photoresponse at long wavelengths, and thus results in higher photocurrent. Our results demonstrate a clear relationship between the molecular structures of SQ dyes and their physical properties that govern their photovoltaic performance.

- Above 20% External Quantum Efficiency in Thermally Activated Delayed Fluorescence Device Using Furodipyridine-Type Host Materials

Im, Y.; Lee, J. Y. *Chem. Mater.* **2014**, 26, 1413–1419.

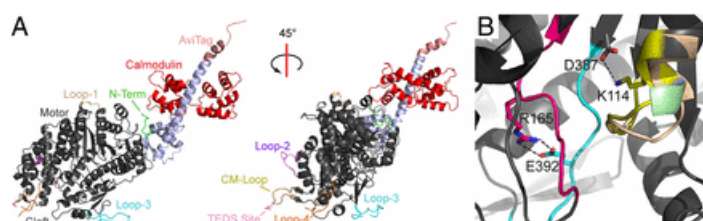
Abstract:



High efficiency green thermally activated delayed fluorescence device with a quantum efficiency above 20% was developed using a bipolar host material, 3-(furo[2,3-b:5,4-b']dipyridin-3-yl)-N,N-diphenylaniline (3TPAPFP), derived from furodipyridine core structure. The furodipyridine based 3TPAPFP showed a singlet and triplet energy for efficient energy transfer to thermally activated delayed fluorescent dopant, (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN), and bipolar charge transport properties for balanced hole and electron density. A high quantum efficiency of 21.2% was achieved in the fluorescent device using the 3TPAPFP host doped with 4CzIPN dopant at a very low doping concentration of 1%.

- A vertebrate myosin-I structure reveals unique insights into myosin mechanochemical tuning
Shuman, H.; Greenberg, M. J.; Zwolak, A.; Lin, T.; Sindelar, C. V.; Dominguez, R.; Ostap, E. M., *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 111, 2116–2121.

Abstract:



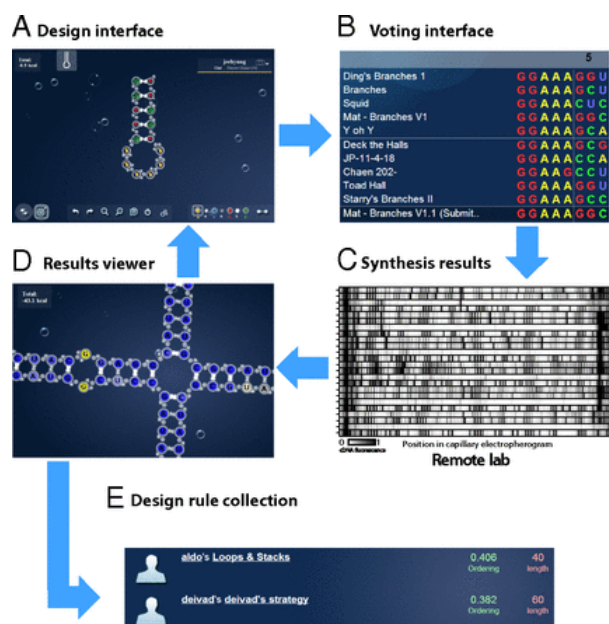
Myosins are molecular motors that power diverse cellular processes, such as rapid organelle transport, muscle contraction, and tension-sensitive anchoring. The structural adaptations in the motor that allow for this functional diversity are not known, due, in part, to the lack of high-resolution structures of highly tension-sensitive myosins. We determined a 2.3-Å resolution structure of apo-myosin-Ib (Myo1b), which is the most tension-sensitive myosin characterized. We identified a striking unique orientation of structural elements that position the motor's lever arm. This

orientation results in a cavity between the motor and lever arm that holds a 10-residue stretch of N-terminal amino acids, a region that is divergent among myosins. Single-molecule and biochemical analyses show that the N terminus plays an important role in stabilizing the post power-stroke conformation of Myo1b and in tuning the rate of the force-sensitive transition. We propose that this region plays a general role in tuning the mechanochemical properties of myosins.

- RNA design rules from a massive open laboratory

Lee, J.; Kladwang, W.; Lee, M.; Cantu, D.; Azizyan, M.; Kim, H.; Limpaecher, A.; Yoon, S.; Treuille, A.; Das, R.; Ete, R. N. A. P. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 2122-2127.

Abstract:

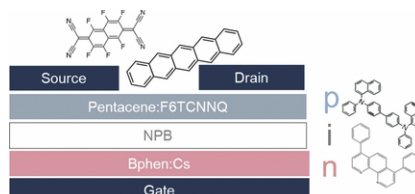


Self-assembling RNA molecules play critical roles throughout biology and bioengineering. To accelerate progress in RNA design, we present EteRNA, the first internet-scale citizen science “game” scored by high-throughput experiments. A community of 37,000 nonexperts leveraged continuous remote laboratory feedback to learn new design rules that substantially improve the experimental accuracy of RNA structure designs. These rules, distilled by machine learning into a new automated algorithm EteRNABot, also significantly outperform prior algorithms in a gauntlet of independent tests. These results show that an online community can carry out large-scale experiments, hypothesis generation, and algorithm design to create practical advances in empirical science.

- Organic Junction Field-Effect Transistor

Lüsse, B.; Kleemann, H.; Kasemann, D.; Ventsch, F.; Leo, K. *Adv. Funct. Mater.* **2014**, *24*, 1011–1016.

Abstract:



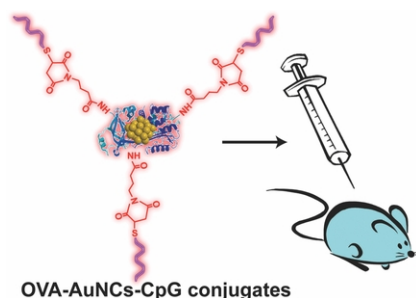
The realization and performance of a novel organic field-effect transistor—the organic junction field-effect transistor (JFET)—is discussed. The transistors are based on the modulation of the thickness of

a depletion layer in an organic pin junction with varying gate potential. Based on numerical modeling, suitable layer thicknesses and doping concentrations are identified. Experimentally, organic JFETs are realized and it is shown that the devices clearly exhibit amplification. Changes in the electrical characteristics due to a variation of the intrinsic and the p-doped layer thickness are rationalized by the numerical model, giving further proof to the proposed operational mechanism.

- Engineered CpG-Antigen Conjugates Protected Gold Nanoclusters as Smart Self-Vaccines for Enhanced Immune Response and Cell Imaging

Tao, Y.; Ju, E.; Li, Z.; Ren, J.; Qu, X. *Adv. Funct. Mater.* **2014**, 24, 1004–1010.

Abstract:



OVA-AuNCs-CpG conjugates

A facile one-pot synthesis of fluorescent AuNCs by using ovalbumin-CpG oligodeoxynucleotides (ODNs) conjugates as the templates, which can elicit specific immunological responses, is demonstrated. Through dual-delivery of protein antigen and CpG ODNs, the as-prepared AuNCs can act as smart self-vaccines to assist in generation of high immunostimulatory activity while simultaneously act as an imaging agent. The AuNCs-based vaccines are not thought to have not been reported so far, making this platform the first example of the usage of AuNCs as effective vaccines. Furthermore, compared with the antigen, the immunostimulatory activity of the as-prepared AuNCs can not only be retained, but also can be effectively enhanced. These findings suggest the AuNCs-based vaccines may be utilized as safe and efficient immunostimulatory agents that are able to prevent and/or treat a variety of ailments.