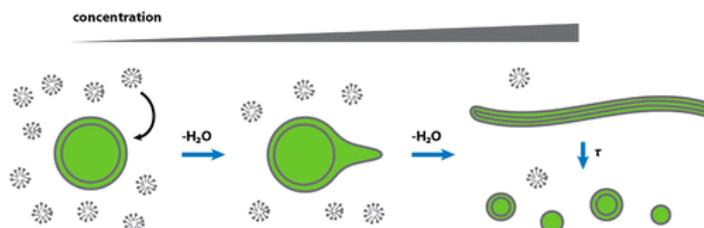


- Concentration-Driven Growth of Model protocell Membranes
Budin, I.; Debnath, A.; Szostak, J. W. *J. Am. Chem. Soc.* **2012**, *134*, 20812–20819.

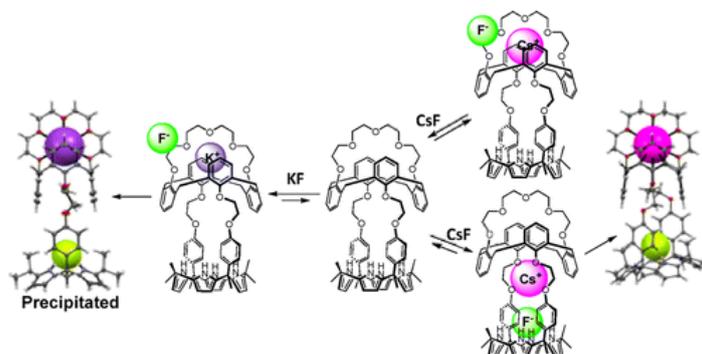
Abstract:



The first protocell membranes may have assembled from fatty acids and related single-chain lipids available in the prebiotic environment. Prior to the evolution of complex cellular machinery, spontaneous protocell membrane growth and division had to result from the intrinsic physicochemical properties of these molecules, in the context of specific environmental conditions. Depending on the nature of the chemical and physical environment, fatty acids can partition between several different phases, including soluble monomers, micelles, and lamellar vesicles. Here we address the concentration dependence of fatty acid aggregation, which is dominated by entropic considerations. We quantitatively distinguish between fatty acid phases using a combination of physical and spectroscopic techniques, including the use of the fluorescent fatty acid analogue Laurdan, whose emission spectrum is sensitive to structural differences between micellar and lamellar aggregates. We find that the monomer–aggregate transition largely follows a characteristic pseudophase model of molecular aggregation but that the composition of the aggregate phase is also concentration dependent. At low amphiphile concentrations above the critical aggregate concentration, vesicles coexist with a significant proportion of micelles, while more concentrated solutions favor the lamellar vesicle phase. We subsequently show that the micelle–vesicle equilibrium can be used to drive the growth of pre-existing vesicles upon an increase in amphiphile concentration either through solvent evaporation or following the addition of excess lipids. We propose a simple model for a primitive environmentally driven cell cycle, in which protocell membrane growth results from evaporative concentration, followed by shear force or photochemically induced division.

- KF and CsF Recognition and Extraction by a Calix[4]crown-5 Strapped Calix[4]pyrrole Multitopic Receptor
Kim, S. K.; Lynch, V. M.; Young, N. J.; Hay, B. P.; Lee, C.-H.; Kim, J. S.; Moyer, B. A.; Sessler, J. L. *J. Am. Chem. Soc.* **2012**, *134*, 20837–20843.

Abstract:



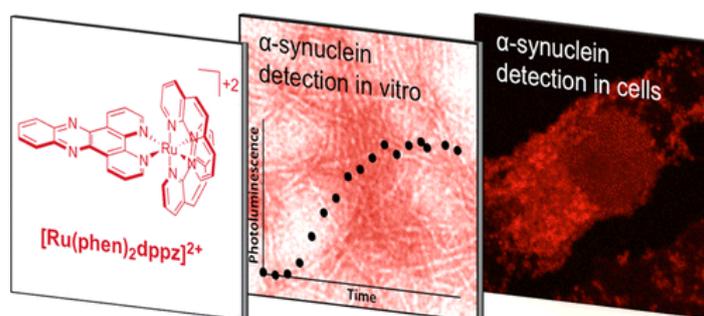
On the basis of ^1H NMR spectroscopic analyses and single crystal X-ray crystal structural data, the ion-pair receptor **1**, bearing a calix[4]pyrrole for anion binding and calix[4]arene crown-5 for cation

recognition, was found to act as a receptor for both CsF and KF ion-pairs. Both substrates are bound strongly but via different binding modes and with different complexation dynamics. Specifically, exposure to KF in 10% CD₃OD in CDCl₃ leads first to complexation of the K⁺ cation by the calix[4]arene crown-5 moiety. As the relative concentration of KF increases, then the calix[4]pyrrole subunit binds the F⁻ anion. Once bound, the K⁺ cation and the F⁻ anion give rise to a stable 1:1 ion-pair complex that generally precipitates from solution. In contrast to what is seen with KF, the CsF ion-pair interacts with receptor **1** in two different modes in 10% CD₃OD in CDCl₃. In the first of these, the Cs⁺ cation interacts with the calix[4]arene crown-5 ring weakly. In the second interaction mode, which is thermodynamically more stable, the Cs⁺ cation and the counteranion, F⁻, are simultaneously bound to the receptor framework. Further proof that system **1** acts as a viable ion-pair receptor came from the finding that receptor **1** could extract KF from an aqueous phase into nitrobenzene, overcoming the high hydration energies of the K⁺ and F⁻ ions. It was more effective in this regard than a 1:1 mixture of the constituent cation and anion receptors (**4** and **5**).

- Detection of α -Synuclein Amyloidogenic Aggregates in Vitro and in Cells using Light-Switching Dipyridophenazine Ruthenium(II) Complexes

Cook, N. P.; Kilpatrick, K.; Segatori, L.; Martí, A. A. *J. Am. Chem. Soc.* **2012**, *134*, 20776–20782.

Abstract:

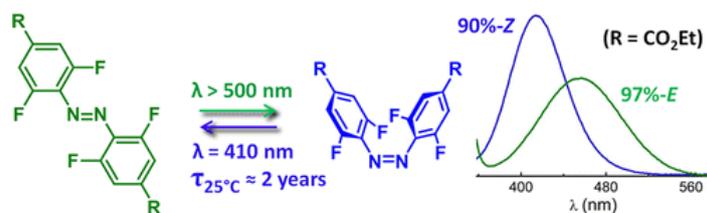


Protein aggregation is the hallmark of a number of neurodegenerative diseases including Parkinson's and Huntington's diseases. There is a significant interest in understanding the molecular mechanisms involved in the self-association and fibrillization of monomeric soluble proteins into insoluble deposits *in vivo* and *in vitro*. Probes with novel properties, such as red-shifted emission, large Stokes shifts, and high photostability, are desirable for a variety of protein aggregation studies. To respond to the increasing need for aggregation-responsive compounds suitable to cellular studies, we present a ruthenium(II) dipyridophenazine derivative, [Ru(phen)₂dppz]²⁺ (phen = 1,10-phenanthroline, dppz = dipyrido[3,2-a:2'-3'-c]phenazine), to study aggregation of α -synuclein (α S), which is associated with the development of Parkinson's disease. We demonstrated the use of [Ru(phen)₂dppz]²⁺ to monitor α S fibril formation in real-time and to detect and quantify α S aggregates in neuroglioma cells, thereby providing a novel molecular tool to study protein deposition diseases *in vitro* and *in vivo*.

- *o*-Fluoroazobenzenes as Readily Synthesized Photoswitches Offering Nearly Quantitative Two-Way Isomerization with Visible Light

Bléger, D.; Schwarz, J.; Brouwer, A. M.; Hecht, S. *J. Am. Chem. Soc.* **2012**, *134*, 20597–20600.

Abstract:



Azobenzene functionalized with *ortho*-fluorine atoms has a lower energy of the n-orbital of the Z-isomer, resulting in a separation of the *E* and *Z* isomers' $n \rightarrow \pi^*$ absorption bands. Introducing para-substituents allows for further tuning of the absorption spectra of *o*-fluoroazobenzenes. In particular, electron-withdrawing ester groups give rise to a 50 nm separation of the $n \rightarrow \pi^*$ transitions. Green and blue light can therefore be used to induce $E \rightarrow Z$ and $Z \rightarrow E$ isomerizations, respectively. The *o*-fluoroazobenzene scaffold is readily synthesized and can be inserted into larger structures via its aryl termini. These new azobenzene derivatives can be switched in both ways with high photoconversions, and their *Z*-isomers display a remarkably long thermal half-life.

- Molecular Alliance—From Orthosteric and Allosteric Ligands to Dualsteric/Bitopic Agonists at G Protein Coupled Receptors

Mohr, K.; Schmitz, J.; Schrage, R.; Tränkle, C.; Holzgrabe, U. *Angew. Chem. Int. Ed.* **2013**, *52*, 508–516.

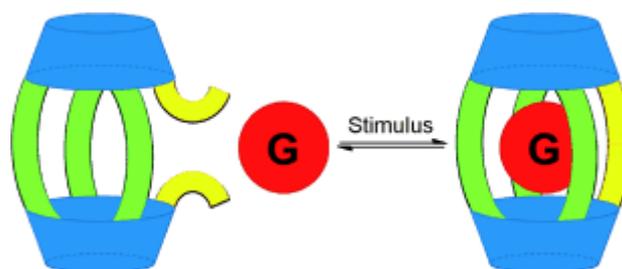
Abstract:



Cell-membrane-spanning G protein coupled receptors (GPCRs) belong to the most important therapeutic target structures. Endogenous transmitters bind from the outer side of the membrane to the “orthosteric” binding site either deep in the binding pocket or at the extracellular N-terminal end of the receptor protein. Exogenous modulators that utilize a different, “allosteric”, binding site unveil a pathway to receptor subtype-selectivity. However, receptor activation through the orthosteric area is often more powerful. Recently there has been evidence that orthosteric/allosteric, in other words “dualsteric”, hybrid compounds unite subtype selectivity and receptor activation. These “bitopic” modulators channel receptor activation and subsequent intracellular signaling into a subset of possible routes. This concept offers access to GPCR modulators with an unprecedented receptor-subtype and signaling selectivity profile and, as a consequence, to drugs with fewer side effects.

- Reversible Photochemically Gated Transformation of a Hemicarcerand to a Carcerand

Abstract:

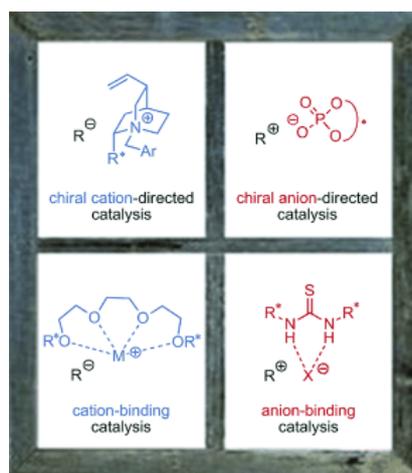


Guests in a gated community: Introduction of two anthracene groups into a linker in a hemicarcerand creates a new type of photochemically controlled gated hemicarcerand. The reversible opening and closing of the “gate” of the host is controlled photochemically. The encapsulation and release of the guest molecules such as 1,4-dimethoxybenzene is controlled by irradiation with light of different wavelengths.

- Asymmetric Ion-Pairing Catalysis

Brak, K.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2013**, *52*, 534-561.

Abstract:

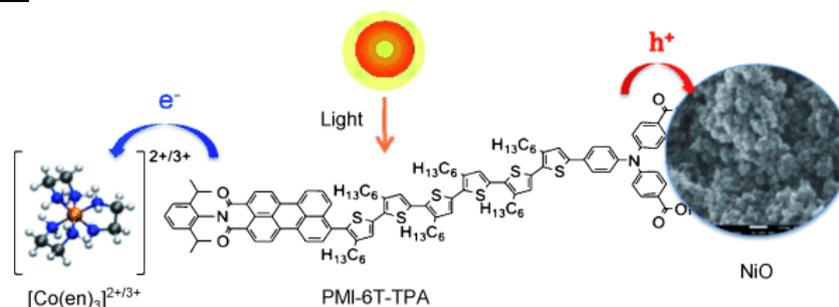


Charged intermediates and reagents are ubiquitous in organic transformations. The interaction of these ionic species with chiral neutral, anionic, or cationic small molecules has emerged as a powerful strategy for catalytic, enantioselective synthesis. This review describes developments in the burgeoning field of asymmetric ion-pairing catalysis with an emphasis on the insights that have been gleaned into the structural and mechanistic features that contribute to high asymmetric induction.

- Highly Efficient p-Type Dye-Sensitized Solar Cells based on Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes

Powar, S.; Daeneke, T.; Ma, M. T.; Fu, D.; Duffy, N. W.; Götz, G.; Weideler, M.; Mishra, A.; Bäuerle, P.; Spiccia, L.; Bach, U. *Angew. Chem. Int. Ed.* **2013**, *52*, 602–605.

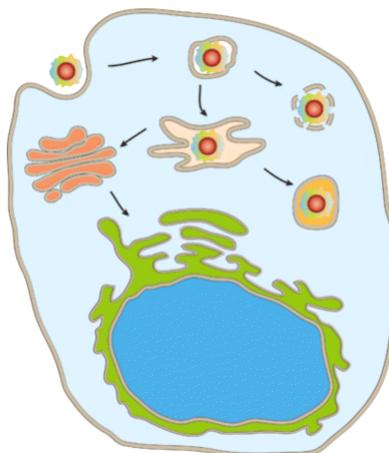
Abstract:



Co-produced: Using [Co(en)₃]^{2+/3+} based-electrolytes in p-type dye-sensitized solar cells (p-DSCs) gives record energy conversion efficiencies of 1.3% and open-circuit voltages up to 709 mV under simulated sun light. The increase in photovoltage is due to the more negative redox potential of [Co(en)₃]^{2+/3+} compared to established mediators.

- Emerging Techniques in Proteomics for Probing Nano–Bio Interactions
Lai, Z. W.; Yan, Y.; Caruso, F.; Nice, E. C. *ACS Nano* **2012**, *6*, 10438-10448.

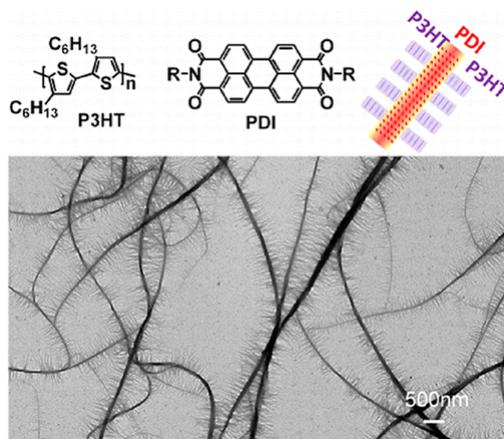
Abstract:



The convergence of nanoscience and biomedicine is expected to bring momentous advances in the fight against a wide range of diseases. The first generation of nanomedicines, exemplified by Doxil, Abraxane, and Pegasys, has already shown favorable clinical outcomes in the treatment of cancer and infectious diseases. A major goal for second generation nanomedicines is to facilitate formulation and improve drug pharmacokinetics of therapeutics, subsequently reducing side effects and enhancing therapeutic efficacy. In order to achieve this, nanomedicines have to circumvent an array of biological barriers, such as the endothelium of blood vessels, the epithelium of the gastrointestinal track, and/or the blood–brain barrier. Understanding the complex and dynamic interactions between particles and biological systems is emerging as a rapidly developing scientific frontier that will provide fundamental and conceptual frameworks to improve drug carrier design for safe and effective therapy. For these reasons, there is increasing activity in probing nano–bio interactions. Studies have shown that exposure of nanoparticles to biological fluids (*e.g.*, plasma, interstitial fluid, and cytoplasm) leads to adsorption of proteins on the nanoparticle surfaces, forming a protein corona that significantly influences the particle properties and their biological behavior, such as cellular uptake. Once nanoparticles have been internalized by cells, they are subject to various cellular regulatory machineries allowing them to be processed and transported to specific intracellular locations, such as lysosomes and nuclei. The ability to characterize and control such intracellular processing is the essence of improving temporal and spatial profiling of therapeutics and facilitating optimal access and delivery to their specific pharmacological targets.

- Growth of Polythiophene/Perylene Tetracarboxydiimide Donor/Acceptor Shish-Kebab Nanostructures by Coupled Crystal Modification
Bu, L.; Pentzer, E.; Bokel, F. A.; Emrick, T.; Hayward, R. C. *ACS Nano* **2012**, *6*, 10924-10929.

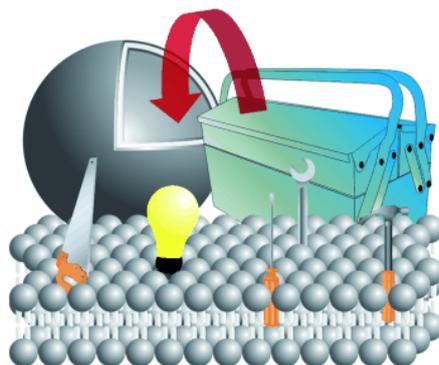
Abstract:



Self-assembled crystalline organic nanostructures containing electron donor and acceptor materials hold promise as building blocks for photovoltaic devices. We show that coupled crystallization of poly(3-hexyl thiophene) (P3HT) and perylene tetracarboxydiimide (PDI) induced by solvent evaporation, wherein both components modify crystallization of the other, gives rise to donor/acceptor “shish-kebabs” with tunable nanostructures. P3HT kinetically stabilizes supersaturated solutions of PDI and modifies the growth of PDI crystals, leading to formation of extended PDI shish nanowires that in turn serve as heterogeneous nucleation sites for fibrillar P3HT kebabs during solvent casting. The dimensions of these nanostructures can be tailored through variations in donor/acceptor ratio or solvent quality, and the method is shown to be general to several other poly(3-alkyl thiophenes) and perylene derivatives, thus providing a simple and robust route to form highly crystalline nanophase separated organic donor/acceptor assemblies.

- Self-Assembled Vesicles with Functionalized Membranes
Gruber, B.; König, B. *Chem. Eur. J.* **2013**, *19*, 438-448.

Abstract:



Biological membranes play a key role for the function of living organisms. Thus, many artificial systems have been designed to mimic natural cell membranes and their functions. A useful concept for the preparation of functional membranes is the embedding of synthetic amphiphiles into vesicular bilayers. The dynamic nature of such noncovalent assemblies allows the rapid and simple development of bio-inspired responsive nanomaterials, which find applications in molecular recognition, sensing or catalysis. However, the complexity that can be achieved in artificial functionalized membranes is still rather limited and the control of their dynamic properties and the analysis of membrane structures down to the molecular level remain challenging.

- Anion Influence in Directing and Altering the Stereochemistry of the Double [2+2] Reaction of Bis-Pyridyl Dienes in their Silver Complexes: A Green Synthetic Route
Santra, R.; Garai, M.; Mondal, D.; Biradha, K. *Chem. Eur. J.* **2013**, *19*, 489–493.

7

Abstract:



Getting selectively organized: Molecules of bis-pyridyl dienes have been stereoselectively photodimerized to form their strained double [2+2] reaction products by using argentophilic forces (see scheme). A pronounced influence of anions and the efficiency of a mechanochemical synthesis have also been described.

- Cooperative Supramolecular Polymerization: Comparison of Different Models Applied on the Self-Assembly of Bis(merocyanine) Dyes
Fernández, G.; Stolte, M.; Stepanenko, V.; Würthner, F. J. *Chem. Eur. J.* **2013**, *19*, 206–217.

Abstract:



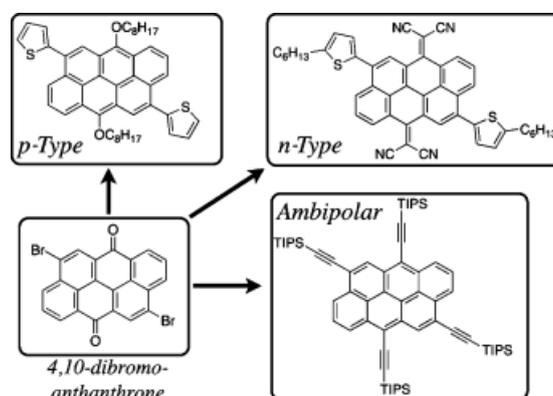
Three new molecular building blocks **1 a–c** for supramolecular polymerization are described that feature two dipolar merocyanine dyes tethered by *p*-xylylene spacers. Concentration- and temperature-dependent UV/Vis spectroscopy in chloroform combined with dynamic light scattering, capillary viscosimetry and atomic force microscopy investigations were applied to elucidate the mechanistic features of the self-assembly of these strongly dipolar dyes. Our detailed studies reveal that the self-assembly is very pronounced for bis(merocyanines) **1 a,b** bearing linear alkyl chains, but completely absent for bis(merocyanine) **1 c** bearing sterically more bulky ethylhexyl substituents. Both temperature- and concentration-dependent UV/Vis data provide unambiguous evidence for a cooperative self-assembly process for bis(merocyanines) **1 a,b**, which was analyzed in detail by the Meijer–Schening–Van-der-Schoot model (applicable to temperature-dependent data) and by the Goldstein–Stryer model (applicable to concentration-dependent data). By combining both methods all parameters of interest to understand the self-assembly process could be derived, including in particular the nucleus size (8–10 monomeric units), the cooperativity factor (ca. 0.006), and the nucleation and elongation constants of about 10³ and 10⁶ M⁻¹ in chloroform at room temperature,

respectively.

- 4,10-Dibromoanthanthrone as a New Building Block for p-Type, n-Type, and Ambipolar π -Conjugated Materials

Giguère, J.-B.; Verolet, Q.; Morin, J.-F. *J. Chem. Eur. J.* **2013**, *19*, 372–381.

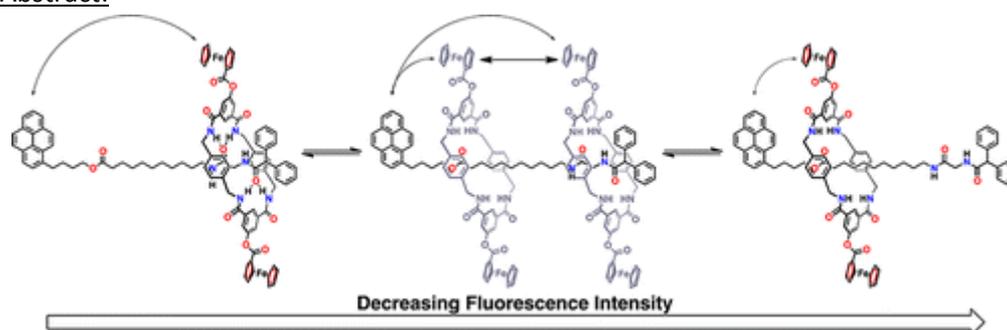
Abstract:



New p-type, n-type, and ambipolar molecules were synthesized from commercially available 4,10-dibromoanthanthrone dye. Substitution at the 4,10- and 6,12-positions with different electron-rich and electron-poor units allowed the modulation of the optoelectronic properties of the molecules. A bis(dicyanovinylene)-functionalized compound was also prepared with a reduction potential as low as -50 mV versus Ag^+ with a crystalline two-dimensional lamellar packing arrangement. These characteristics are important prerequisites for air-stable n-type organic field-effect transistor applications

- A Three-Level Luminescent Response in a Pyrene/Ferrocene Rotaxane
- Mateo-Alonso, A.; Ehli, C.; Guldi, D. M.; Prato, M. *Org. Lett.* **2013**, *15*, 84–87.

Abstract:

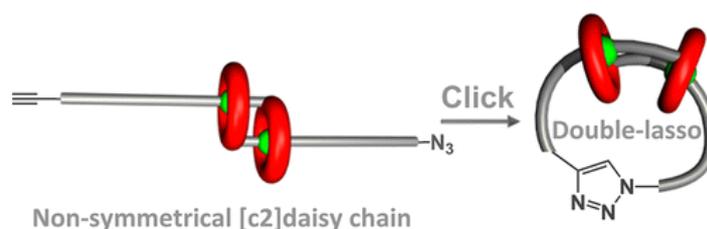


A solvent switchable rotaxane equipped with a pyrene stopper and with two ferrocenyl units on the macrocycle is reported, in which three different states, two nondegenerate and one degenerate, can be obtained in different solvents at room temperature. This is accompanied by high contrast changes in fluorescence intensity of the pyrene stopper by the presence of the ferrocenyl moieties on the macrocycle, which quench the emission of pyrene more efficiently with proximity.

- Straightforward Synthesis of a Double-Lasso Macrocycle from a Nonsymmetrical [c2]Daisy Chain

Romuald, C.; Cazals, G.; Enjalbal, C.; Coutrot, F. *Org. Lett.* **2013**, *15*, 184–187.

Abstract:

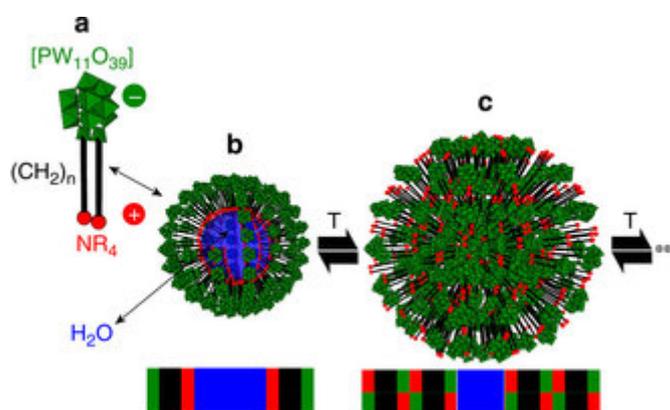


The straightforward synthesis of a double-lasso macrocycle from a nonsymmetrical [c2]daisy chain, using the copper(I)-catalyzed Huisgen alkyne–azide 1,3-dipolar cycloaddition, is described. The preparation of the nonsymmetrical alkyne azide [c2]daisy chain precursor was realized in situ via the exchange of the monomers contained in both symmetrical alkyne and azide [c2]daisy chains and was followed by mass spectrometry.

- Bolaform surfactants with polyoxometalate head groups and their assembly into ultra-small monolayer membrane vesicles

Landsmann, S.; Luka, M.; Polarz, S. *Nature Communications* **2012**, *3*, 1299.

Abstract:

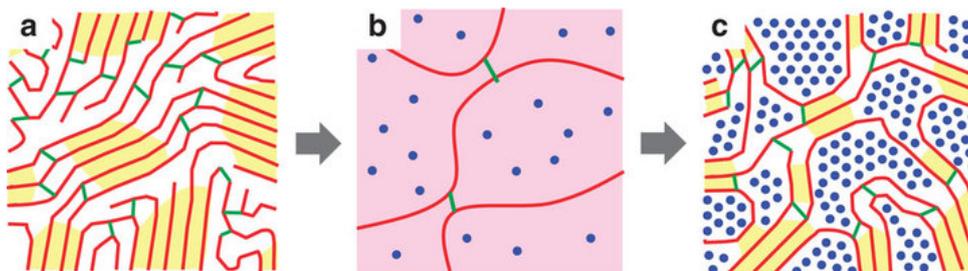


Surfactants are indispensable in established technologies as detergents or emulsification agents, and also in recent studies for controlling the growth of nanoparticles or for creating nanocarriers. Although the properties of conventional, organic surfactants are thoroughly explored, strong interest persists in surfactants that possess unique features inaccessible for ordinary systems. Here we present dipolar, bolaform surfactants with a head group comprising of 11 tungsten atoms. These novel compounds are characterized by an exceptionally low critical self-organization concentration, which leads to monolayer vesicles with a diameter of only 15 nm, that is, substantially smaller than for any other system. The membrane of the vesicles is impermeable for water-soluble and oil-soluble guests. Control over release kinetics, which can be followed via the quantitative fluorescence quenching of confined fluorophores, is gained by means of pH adjustments.

- High internal quantum efficiency in fullerene solar cells based on crosslinked polymer donor networks

Liu, B.; Png, R-Q.; Zhao, L-H.; Chua, L-L.; Friend, R. H.; Ho, P. K. H. *Nature Communications* **2012**, *3*, 1321.

Abstract:

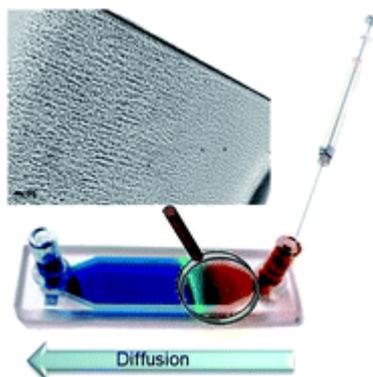


The power conversion efficiency of organic photovoltaic cells depends crucially on the morphology of their donor–acceptor heterostructure. Although tremendous progress has been made to develop new materials that better cover the solar spectrum, this heterostructure is still formed by a primitive spontaneous demixing that is rather sensitive to processing and hence difficult to realize consistently over large areas. Here we report that the desired interpenetrating heterostructure with built-in phase contiguity can be fabricated by acceptor doping into a lightly crosslinked polymer donor network. The resultant nanotemplated network is highly reproducible and resilient to phase coarsening. For the regioregular poly(3-hexylthiophene):phenyl-C61-butyrate methyl ester donor–acceptor model system, we obtained 20% improvement in power conversion efficiency over conventional demixed blend devices. We reached very high internal quantum efficiencies of up to 0.9 electron per photon at zero bias, over an unprecedentedly wide composition space. Detailed analysis of the power conversion, power absorbed and internal quantum efficiency landscapes reveals the separate contributions of optical interference and donor–acceptor morphology effects.

- Chemical-gradient directed self-assembly of hydrogel fibers

Ziemecka, I.; Koper, G. J. M.; Olive, A. G. L.; van Esch, J. H. *Soft Matter* **2013**, *9*, 1556-1561.

Abstract:

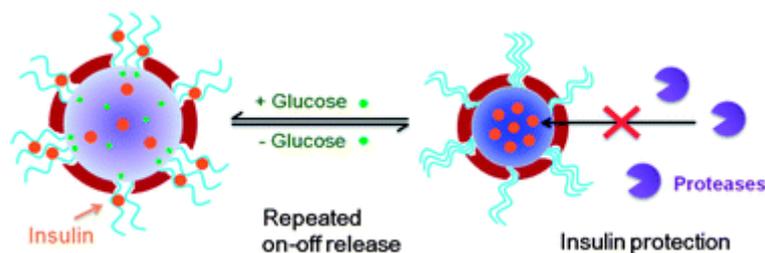


We demonstrate and investigate how a propagating acidic wave in a solution of dibenzoyl-L-cystine (DBC) can lead to the orientation and alignment of self-assembled fibers constituting a hydrogel. Taking advantage of its pH-induced self-assembly, a hydrogel composed of parallel fibers can be formed by propagating a pH gradient front from one part of a cell to the other. The diffusing species (typically the ion pair $H^+ - Cl^-$) control the velocity of the pH-gradient front and, therefore, their diffusion rate should match the gelation rate so as to attain complete orientation.

- A glucose-responsive complex polymeric micelle enabling repeated on–off release and insulin protection

Liu, G.; Ma, R.; Ren, J.; Li, Z.; Zhang, H.; Zhang, Z.; An, Y.; Shi, L. *Soft Matter* **2013**, *9*, 1636-1644.

Abstract:

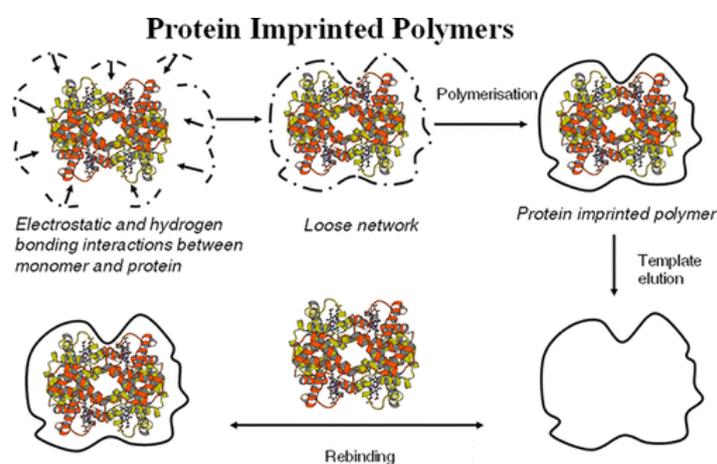


We developed a glucose-responsive complex polymeric micelle (CPM) through the self-assembly of two types of diblock copolymers, poly(ethylene glycol)-*b*-poly(aspartic acid-*co*-aspartamidophenylboronic acid) (PEG-*b*-P(Asp-*co*-AspPBA)) and poly(*N*-isopropylacrylamide)-*b*-poly(aspartic acid-*co*-aspartamidophenylboronic acid) (PNIPAM-*b*-P(Asp-*co*-AspPBA)). By controlling the weight ratio between PNIPAM and PEG ($W_{\text{PNIPAM}}/W_{\text{PEG}} = 6/4$), the block copolymers form complex micelles with a novel core-shell-corona structure. By following this structure, the continuous PNIPAM shell collapsed on the glucose-responsive P(Asp-*co*-AspPBA) core. As a result, the CPM exhibits a reversible swelling in response to changes in the glucose concentration, enabling the repeated on-off release of insulin regulated by glucose level. Furthermore, the CPM could effectively protect the encapsulated insulin against protease degradation. Therefore, this glucose-responsive CPM provides a simple and powerful strategy to construct a self-regulated insulin delivery system for diabetes treatment.

- Protein Crystallization and Biosensor Applications of Hydrogel-Based Molecularly Imprinted Polymers

Reddy, S. M.; Phan, Q. T.; El-Sharif, H.; Govada, L.; Stevenson, D.; Chayen, N. E. *Biomacromolecules* **2012**, *13*, 3959–3965.

Abstract:

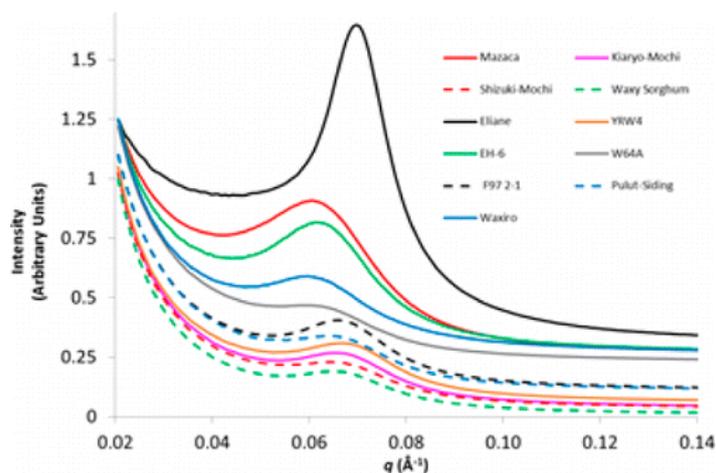


We have characterized the imprinting capability of a family of acrylamide polymer-based molecularly imprinted polymers (MIPs) for bovine hemoglobin (BHb) and trypsin (Tryp) using spectrophotometric and quartz crystal microbalance (QCM) sensor techniques. Bulk gel characterization on acrylamide (AA), N-hydroxymethylacrylamide (NHMA), and N-isopropylacrylamide (NiPAM) gave varied selectivities when compared with nonimprinted polymers. We have also harnessed the ability of the MIPs to facilitate protein crystallization as a means of evaluating their selectivity for cognate and noncognate proteins. Crystallization trials indicated improved crystal formation in the order NiPAM < AA < NHMA. QCM studies of thin film MIPs confirm this trend with N-hydroxymethyl acrylamide MIPs exhibiting best discrimination between MIP and NIP and also cognate/noncognate protein loading. Equivalent results for acrylamide MIPs suggested that the cavities were equally selective for both

proteins, while N-isopropylacrylamide MIPs were not selective for either cognate BHB or noncognate BSA. All BHB MIP-QCM sensors based on AA, NHMA, or NiPAM were essentially nonresponsive to smaller, noncognate proteins. Protein crystallization studies validated the hydrophilic efficacy of MIPS indicated in the QCM studies.

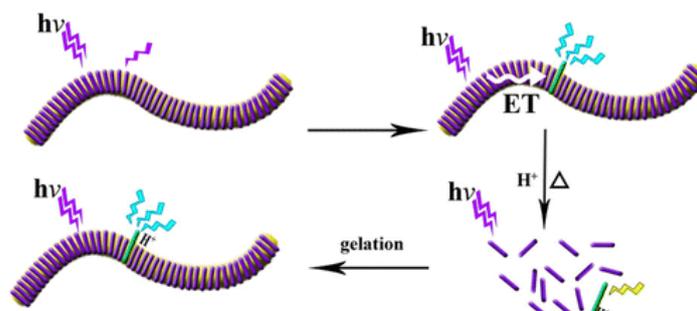
12

- Relations between Molecular, Crystalline, and Lamellar Structures of Amylopectin
Witt, T.; Douth, J.; Gilbert, E. P.; Gilbert, R. G. *Biomacromolecules* **2012**, *13*, 4273–4282.
Abstract:



Chain (branch) length distributions (CLD) from size-exclusion chromatography of a series of waxy starches were parametrized using both an empirical and a biosynthesis-based method and correlated with their crystalline–amorphous lamellar properties obtained from X-ray scattering. Correlations were best seen with the biosynthesis-based parametrization. This showed for the first time that the following links between the CLD and lamellar parameters, the average interlamellar repeat distance and the distribution of these distances, were decreased by an increase in the proportion of very short branches and were increased by an increase in the proportion of intermediate and longer chains; further, the shoulder and linear sections of the CLD were found to affect the lamellar repeat distance and distribution. These effects are rationalized in terms of branch-length effects on the production of crystallites and the presence of portions of longer branches in the amorphous regions.

- Amplifying Emission Enhancement and Proton Response in a Two-Component Gel
Xue, P.; Lu, R.; Zhang, P.; Jia, J.; Xu, Q.; Zhang, T.; Takafuji, M.; Ihara, H. *Langmuir* **2012**, *29*, 417–425.
Abstract:



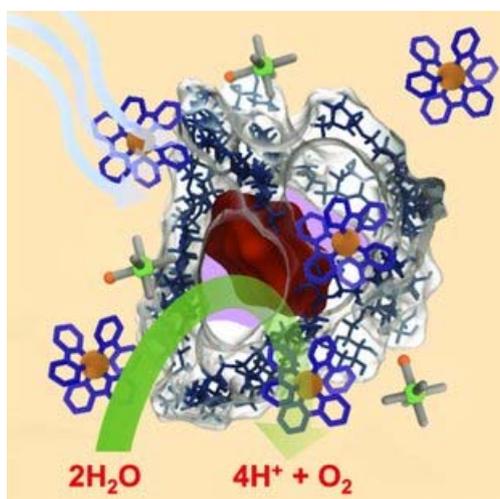
A glutamide gelator, **1**, was synthesized, and a weak emission enhancement was observed during its gelation. In addition, **1** could be an excellent scaffold for successfully embedding an energy acceptor, **2**, into its aggregate to obtain highly efficient energy transfer. An amplification of the emission

enhancement was observed in the two-component gels compared to that of the neat gel of **1** during gel formation. For example, **1** induced only a 2.5-fold increase in emission intensity, whereas a 23-fold enhanced emission could be observed in the two-component gel with only 1.6 mol % **2**. Furthermore, two-component gels had an excited proton response. In systems with low acceptor concentrations, the hot solution red-shifted the fluorescence from blue to yellow upon the addition of a proton, which continuously blue-shifted with decreasing temperature to form the gel given that the binding of the gelator to the proton is weakened during coassembly. Moreover, the casting film formed by the two-component wet gel had an excellent response to volatile acids such as hydrochloric acid, trifluoroacetic acid, and so on and could be reversibly recovered by exposure to NH_3 .

- Simple Photosystem II Water Oxidation Centre Analogues in Visible Light Oxygen and H^+ Generation

Kim, Y.-Y.; Williams, D.; Meldrum, F. C.; Walsh, D. *Small* **2013**, *9*, 61–66.

Abstract:

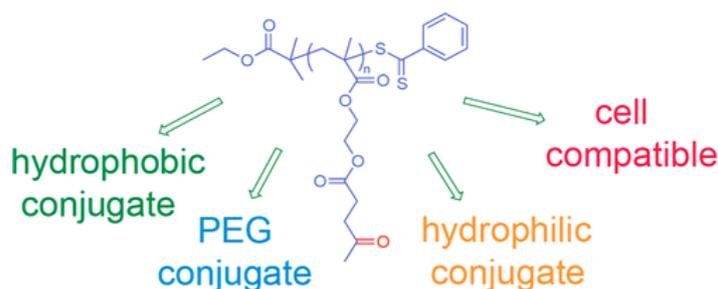


Calcium manganese oxide nanoparticles for application in water oxidation are synthesized by combination with a carboxylated biopolymer stabilizing agent to form very simple but effective analogues of the photosynthetic PSII oxygen evolving complex. The relative efficiency of these materials for production of O_2 and protons under visible light-promoted reactions is evaluated and prolonged reaction lifetimes are observed.

- Keto-Functionalized Polymer Scaffolds as Versatile Precursors to Polymer Side-Chain Conjugates

Liu, J.; Li, R. C.; Sand, G. J.; Bulmus, V.; Davis, T. P.; Maynard, H. D. *Macromolecules* **2013**, *46*, 8–14.

Abstract:

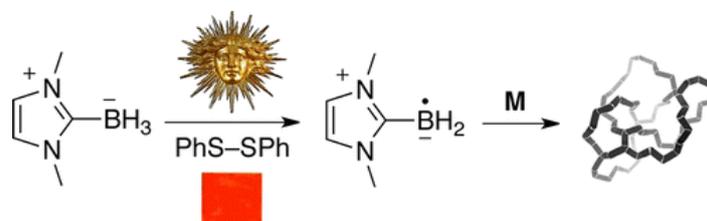


A new methacrylate monomer with a reactive ketone side chain, 2-(4-oxopentanoate)ethyl methacrylate (PAEMA), was synthesized and subsequently polymerized by reversible addition–fragmentation chain transfer (RAFT) polymerization to give a polymer with a narrow molecular weight distribution (PDI = 1.25). The polymer was chain extended with poly(ethylene glycol methyl ether methacrylate) (PEGMA) to yield a block copolymer. Aminoxy-containing small molecules and oligoethylene glycol were conjugated to the ketone functionality of the side chains in high yields. Cytotoxicity of the oxime-linked tetra(ethylene glycol) polymer to mouse fibroblast cells was investigated; the polymer was found to be noncytotoxic up to 1 mg/mL. The ease with which this polymer is functionalized suggests that it may be useful in forming tailored polymeric medicines.

- Soft Photopolymerizations Initiated by Dye-Sensitized Formation of NHC-Boryl Radicals under Visible Light

Telilel, S.; Schweizer, S.; Morlet-Savary, F.; Graff, B.; Tschamber, T.; Blanchard, N.; Fouassier, J.-P.; Lelli, M.; Lacôte, E.; Lalevé, J. *Macromolecules* **2013**, *46*, 43–48.

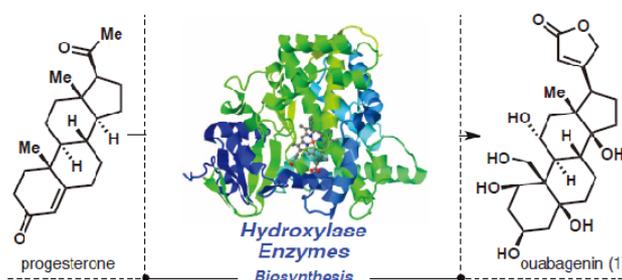
Abstract:



A procedure for the production of N-heterocyclic carbene–boryl radicals (NHC-BH₂[•]) upon visible light irradiation under soft conditions is presented. New acridine orange (dye)/diphenyl disulfide/NHC–BH₃ and dye/sulfonium salt/NHC–BH₃ three-component initiating systems are introduced for the efficient visible light photopolymerization of trimethylolpropane triacrylate. The new systems could be extended to polymerization reactions in water (hydroxyethyl acrylate and hydroxyethyl methyl acrylate), which proceeded with strongly improved polydispersity. The chemical mechanisms are investigated through EPR and photolysis experiments.

- Strategic Redox Relay Enables A Scalable Synthesis of Ouabagenin, A Bioactive Cardenolide
Renata, H.; Zhou, Q.; Baran, P. S. *Science* **2013**, *339*, 59-63.

Abstract:

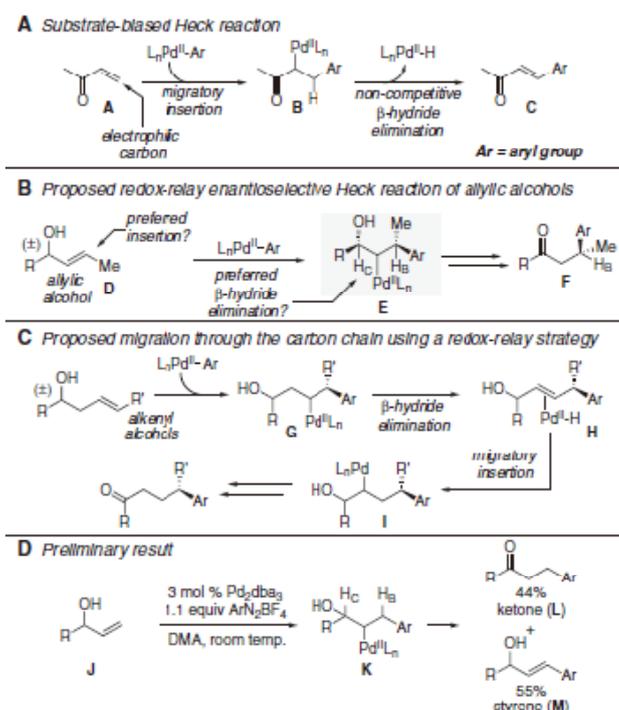


Here, we report on a scalable route to the polyhydroxylated steroid ouabagenin with an unusual take on the age-old practice of steroid semisynthesis. The incorporation of both redox and stereochemical relays during the design of this synthesis resulted in efficient access to more than 500 milligrams of a key precursor toward ouabagenin-and ultimately ouabagenin itself-and the discovery of innovative methods for carbon-hydrogen (C-H) and carbon-carbon activation and carbon-oxygen bond homolysis. Given the medicinal relevance of the cardenolides in the treatment of congestive heart failure, a variety of ouabagenin analogs could potentially be generated from the key intermediate as

a means of addressing the narrow therapeutic index of these molecules. This synthesis also showcases an approach to bypass the historically challenging problem of selective C-H oxidation of saturated carbon centers in a controlled fashion.

- Enantioselective Heck Arylations of Acyclic Alkenyl Alcohols Using a Redox-Relay Strategy
Werner, E. W.; Mei, T.-S.; Burckle, A. J.; Sigman, M. S. *Science* **2012**, *338*, 1455-1458.

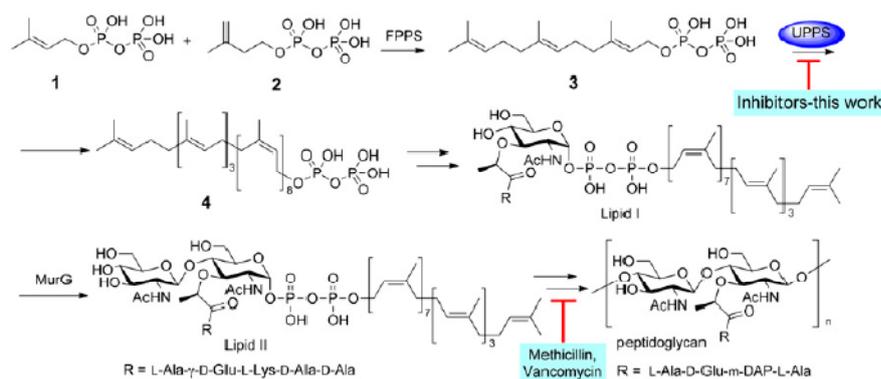
Abstract:



Progress in the development of asymmetric Heck couplings of arenes and acyclic olefins has been limited by a tenuous understanding of the factors that dictate selectivity in migratory insertion and β -hydride elimination. On the basis of key mechanistic insight recently garnered in the exploration of selective Heck reactions, we report here an enantioselective variant that delivers β -, γ -, or δ -aryl carbonyl products from acyclic alkenol substrates. The catalyst system imparts notable regioselectivity during migratory insertion and promotes the migration of the alkene's unsaturation toward the alcohol to ultimately form the ketone product. The reaction uses aryldiazonium salts as the arene source, yields enantiomeric products from opposite starting alkene configurations, and uses a readily accessible ligand. The racemic nature of the alkenol substrate does not bias the enantioselection.

- Antibacterial drug leads targeting isoprenoid biosynthesis
Zhu, W.; Zhang, Y.; Sinko, W.; Hensler, M. E.; Olson, J.; Molohon, K. J.; Lindert, S.; Cao, R.; Li, K.; Wang, K.; Wang, Y.; Liu, Y.-L.; Sankovsky, A.; de Oliveira, C. A. F.; Mitchell, D. A.; Nizet, V.; McCammon, J. A.; Oldfield, E. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 123-128.

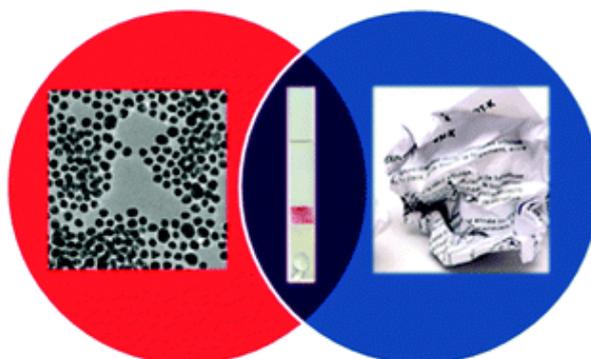
Abstract:



With the rise in resistance to antibiotics such as methicillin, there is a need for new drugs. We report here the discovery and X-ray crystallographic structures of 10 chemically diverse compounds (benzoic, diketo, and phosphonic acids, as well as a bisamidine and a bisamine) that inhibit bacterial undecaprenyl diphosphate synthase, an essential enzyme involved in cell wall biosynthesis. The inhibitors bind to one or more of the four undecaprenyl diphosphate synthase inhibitor binding sites identified previously, with the most active leads binding to site 4, outside the catalytic center. The most potent leads are active against *Staphylococcus aureus* [minimal inhibitory concentration (MIC)₉₀ ~ 0.25 μg/mL], and one potently synergizes with methicillin (fractional inhibitory concentration index = 0.25) and is protective in a mouse infection model. These results provide numerous leads for antibacterial development and open up the possibility of restoring sensitivity to drugs such as methicillin, using combination therapies.

- Paper-based nanobiosensors for diagnostics
Parolo, C.; Merkoçi, A. *Chem. Soc. Rev.* **2013**, *42*, 450-457.

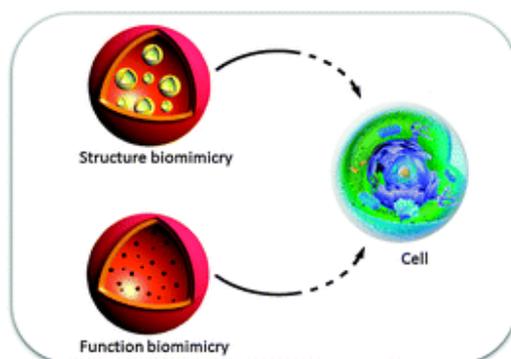
Abstract:



In this review we discuss how nanomaterials can be integrated in diagnostic paper-based biosensors for the detection of proteins, nucleic acids and cells. In particular first the different types and properties of paper-based nanobiosensors and nanomaterials are briefly explained. Then several examples of their application in diagnostics of several biomarkers are reported. Finally our opinions regarding future trends in this field are discussed.

- Multicompartmentalized polymeric systems: towards biomimetic cellular structure and function
Marguet, M.; Bonduelle, C.; Lecommandoux, S. *Chem. Soc. Rev.* **2013**, *42*, 512-529.

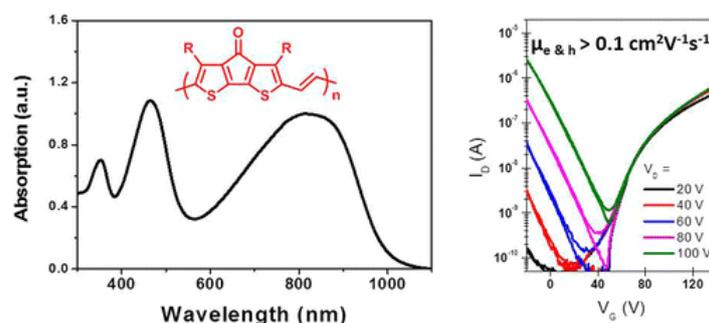
Abstract:



The cell is certainly one of the most complex and exciting systems in Nature that scientists are still trying to fully understand. Such a challenge pushes material scientists to seek to reproduce its perfection by building biomimetic materials with high-added value and previously unmatched properties. Thanks to their versatility, their robustness and the current state of polymer chemistry science, we believe polymer-based materials to constitute or represent ideal candidates when addressing the challenge of biomimicry, which defines the focus of this review. The first step consists in mimicking the structure of the cell: its inner compartments, the organelles, with a multicompartmentalized structure, and the rest, i.e. the cytoplasm minus the organelles (mainly cytoskeleton/cytosol) with gels or particular solutions (highly concentrated for example) in one compartment, and finally the combination of both. Achieving this first structural step enables us to considerably widen the gap of possibilities in drug delivery systems. Another powerful property of the cell lies in its metabolic function. The second step is therefore to achieve enzymatic reactions in a compartment, as occurs in the organelles, in a highly controlled, selective and efficient manner. We classify the most exciting polymersome nanoreactors reported in our opinion into two different subsections, depending on their very final concept or purpose of design. We also highlight in a thorough table the experimental sections crucial to such work. Finally, after achieving control over these prerequisites, scientists are able to combine them and push the frontiers of biomimicry further: from cell structure mimics towards a controlled biofunctionality. Such a biomimetic approach in material design and the future research it will stimulate, are believed to bring considerable enrichments to the fields of drug delivery, (bio)sensors, (bio)catalysis and (bio)technology.

- Near Infrared Absorbing Soluble Poly(cyclopenta[2,1-b:3,4-b']dithiophen-4-one)vinylene Polymers Exhibiting High Hole and Electron Mobilities in Ambient Air
Fei, Z.; Gao, X.; Smith, J.; Pattanasattayavong, P.; Domingo, E. B.; Stingelin, N.; Watkins, S. W.; Anthopoulos, T. D.; Kline, R. J.; Heeney, M. *Chem. Mater.* **2013**, *25*, 59–68.

Abstract:

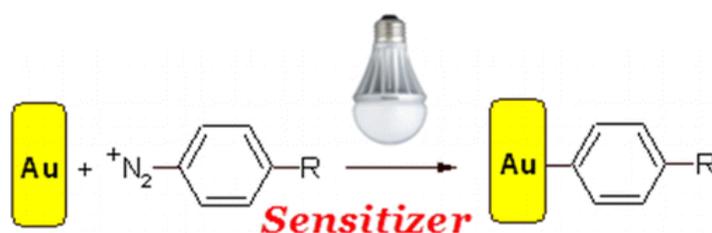


We report the synthesis of two novel cyclopenta[2,1-b:3,4-b']dithiophen-4-one monomers containing solubilizing alkyl groups in the peripheral 3,5 positions. Polymerization with (E)-1,2-bis(tributylstannyl)-ethylene under Stille coupling conditions afforded the first reported examples of soluble poly(cyclopentadithiophen-4-one)vinylenes. The resulting polymers absorb in the near-infrared, with a maximum thin film absorbance around 815 nm and have optical band gaps of 1.25 eV. The polymers exhibit promising ambipolar field effect transistor performance, with average saturated mobilities of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons. The ambipolar transistors operate in both the hole and electron transport regimes in ambient air. Prolonged exposure to ambient atmosphere leads to a gradual loss of the electron transport behavior, with little change observed in the p-type mobility.

- Sensitized Photografting of Diazonium Salts by Visible Light

Bouriga, M.; Chehimi, M. M.; Combellas, C.; Decorse, P.; Kanoufi, F.; Deronzier, A.; Pinson, J. *Chem. Mater.* **2013**, *25*, 90–97.

Abstract:

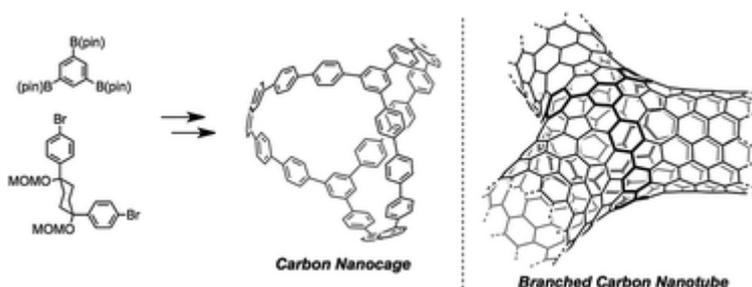


Visible irradiation of a gold surface dipped into a solution of diversely substituted aryldiazonium salts in the presence of a photosensitizer ($\text{Ru}(\text{bipy})_3^{2+}$ or eosinY) leads to a modification of the surface by attached aryl groups. A grafted nanometer thick polyphenylene film is obtained. The reaction is extended to a polyvinylchloride (PVC) surface. The mechanism proposed for the formation of this film involves the formation of an aryl radical that reacts with the surface and then with the first grafted aryl group. The film is characterized by infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), water contact angles, and ellipsometry.

- Synthesis and properties of all-benzene carbon nanocages: a junction unit of branched carbon nanotubes

Matsui, K.; Segawa, Y.; Namikawa, T.; Kamada, K.; Itami, K. *Chem. Sci.* **2013**, *4*, 84–88.

Abstract:

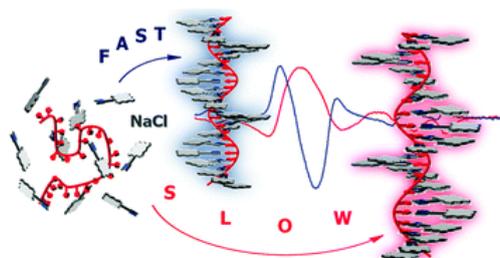


The first synthesis of an all-benzene carbon nanocage **1**, which represents a junction unit of branched carbon nanotubes, has been achieved. A stepwise assembly of six L-shaped units [*cis*-di(*p*-bromophenyl)cyclohexane derivative] and two three-way units (1,3,5-triborylbenzene) by cross-coupling and homocoupling provided the unstrained cyclic precursor. Acid-mediated aromatization of cyclohexane moieties in the precursor resulted in the formation of carbon nanocage **1**.

Photophysical measurements and DFT studies revealed the unique properties of **1**, such as D_3 symmetry with degenerate HOMO/HOMO - 1 and LUMO/LUMO + 1, high fluorescence quantum yield ($\Phi_F = 0.87$), and a relatively large two-photon absorption cross section (500 GM at 590 nm), which are attractive for various applications.

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- Formation and helicity control of ssDNA templated porphyrin nanoassemblies
Sargsyan, G.; Schatz, A.A.; Kubelka, J.; Balaz, M. *Chem. Commun.* **2013**, 49, 1020–1022.
Abstract:



We report the formation of left- (M-helix) and right-handed (P-helix) nanoassemblies of a porphyrin–diaminopurine conjugate (Por–DAP) templated by a single stranded oligodeoxythymidine (dT40) via directional hydrogen bonding. The supramolecular helicity can be controlled by the ionic strength, Por–DAP:dT40 ratio, and annealing rate.