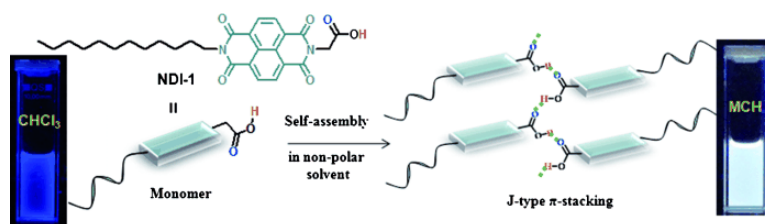


- Hydrogen-Bonding-Mediated J-Aggregation and White-Light Emission from a Remarkably Simple, Single-Component, Naphthalene diimide Chromophore.

Molla, M. R.; Ghosh, S. *Chem. Eur. J.* **2012**, *18*, 1290-1294.

Abstract:

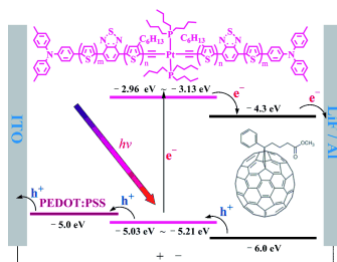


Almost pure white-light emission (fluorescence quantum yield=0.70) from a remarkably simple single-component, carboxylic acid appended naphthalenediimide (NDI) derivative has been reported. Aggregation-induced modulation of photophysical properties was attributed to hydrogen-bonding-mediated J-type π stacking among the NDI chromophores.

- DNA-Templated Assembly of Naphthalenediimide Arrays

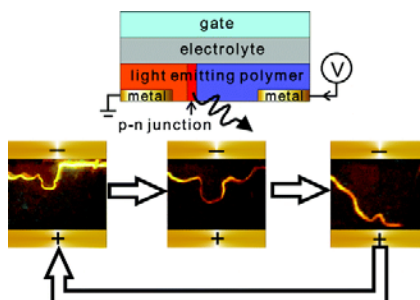
Dai, F.-R.; Zhan, H.-M.; Liu, Q.; Fu, Y.-Y.; Li, J.-H.; Wang, Q.-W.; Xie, Z.; Wang, L.; Yan, F.; Wong, W.-Y. *Chem. Eur. J.* **2012**, *18*, 196-201.

Abstract:



Four new solution-processible small-molecular platinum(II)-bis(aryleneethynylene) complexes consisting of benzothiadiazole as the electron acceptor and triphenylamine and/or thiophene as the electron donor were conveniently synthesized and characterized by physicochemical and computational methods, and utilized as the electron-donor materials in the fabrication of solution-processed bulk heterojunction (BHJ) solar cells. The effect of different electron-donor groups in these small molecules on the optoelectronic and photovoltaic properties was also examined. The optical and time-dependent density functional theory studies showed that the incorporation of stronger electron-donor groups significantly enhanced the solar-absorption abilities of the complexes. These molecular complexes can serve as good electron donors for fabricating BHJ devices by blending them with the [6,6]-phenyl-C71-butyric acid methyl ester (PC70BM) as the electron acceptor. The best power conversion efficiency of 2.37% was achieved with the open-circuit voltage of 0.83 V, short-circuit current density of 7.10 mA cm⁻² and fill factor of 0.40 under illumination of an AM 1.5 solar-cell simulator. The spin-coated thin films showed p-channel field-effect charge transport with hole mobilities of up to 2.4×10⁻⁴ cm² V⁻¹ s⁻¹ for these molecules. The present work illuminates the potential of well-defined organo metallic complexes in developing light-harvesting small molecules for efficient power generation in organic photovoltaics implementation.

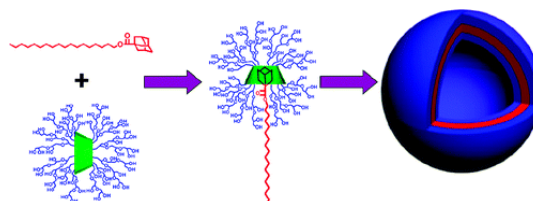
- Spatial Control of p-n Junction in an Organic Light-Emitting Electrochemical Transistor
- Liu, J.; Engquist, I.; Crispin, X.; Berggren, M. *J. Am. Chem. Soc.* **2012**, *134*, 901-904.

Abstract:

Low-voltage-operating organic electrochemical light-emitting cells (LECs) and transistors (OECTs) can be realized in robust device architectures, thus enabling easy manufacturing of light sources using printing tools. In an LEC, the p–n junction, located within the organic semiconductor channel, constitutes the active light-emitting element. It is established and fixated through electrochemical p- and n-doping, which are governed by charge injection from the anode and cathode, respectively. In an OECT, the electrochemical doping level along the organic semi conducting channel is controlled via the gate electrode. Here we report the merger of these two devices: the light-emitting electrochemical transistor, in which the location of the emitting p–n junction and the current level between the anode and cathode are modulated via a gate electrode. Light emission occurs at 4 V, and the emission zone can be repeatedly moved back and forth within an inter electrode gap of 500 μm by application of a 4 V gate bias. In transistor operation, the estimated on/off ratio ranges from 10 to 100 with a gate threshold voltage of -2.3 V and trans conductance value between 1.4 and 3 μS . This device structure opens for new experiments tunable light sources and LECs with added electronic functionality.

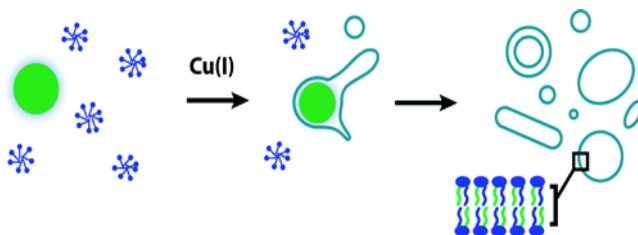
- A Linear-Hyper branched Supramolecular Amphiphile and Its Self-Assembly into Vesicles with Great Ductility

Tao, W.; Liu, Y.; Jiang, B.; Yu, S.; Huang W.; Zhou, Y.; Yan, D. *J. Am. Chem. Soc.* **2012**, *134*, 762–764.

Abstract:

A linear-hyper branched supramolecular amphiphile was synthesized through the non covalent coupling of adamantane-functionalized long alkyl chain (AD- C_n , $n = 12, 18, 30$) and hyper branched poly glycerol grafted from β -cyclo dextrin (CD- g -HPG) by the specific AD/CD host–guest interactions. The obtained supramolecular C_n - g -HPGs self-assembled into unilamellar vesicles with great ductility that could be disassembled readily under a competitive host of β -CD.

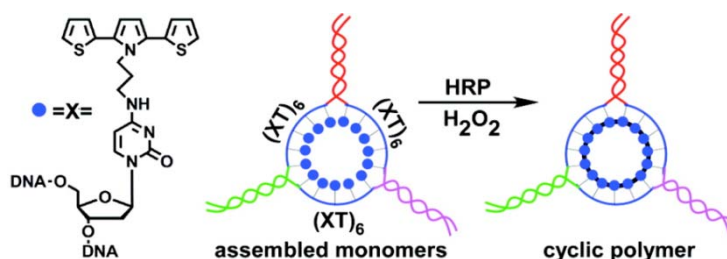
- Membrane Assembly Driven by a Biomimetic Coupling Reaction
Budin, I.; Devaraj, N. K. *J. Am. Chem. Soc.* **2012**, *134*, 751-753.

Abstract :

One of the major goals of synthetic biology is the development of non-natural cellular systems. In this work, we describe a catalytic biomimetic coupling reaction capable of driving the de novo self-assembly of phospholipid membranes. Our system features a coppercatalyzed azide–alkyne cycloaddition that results in the formation of a triazole-containing phospholipid analogue. Concomitant assembly of membranes occurs spontaneously, not requiring preexisting membranes to house catalysts or precursors. The substitution of efficient synthetic reactions for key biochemical processes may offer a general route toward synthetic biological systems.

- DNA-Programmed Modular Assembly of Cyclic and Linear Nanoarrays for the Synthesis of Two-Dimensional Conducting Polymers

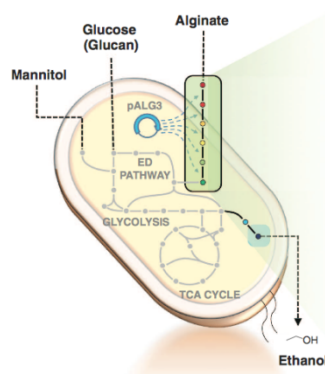
Chen W.; Schuster, G.-B. *J. Am Chem Soc*, **2012**, 134, 840-843.

Abstract:

Nanometer-scale arrays of conducting polymers were prepared on scaffolds of self-assembling DNA modules. A series of DNA oligomers was prepared, each containing six 2,5-bis(2-thienyl)pyrrole (SNS) monomer units linked covalently to N4 atoms of alternating cytosines placed between leading and trailing 12-nucleobase recognition sequences. These DNA modules were encoded so the recognition sequences would uniquely associate through Watson–Crick assembly to form closed-cycle or linear arrays of aligned SNS monomers. The melting behavior and electrophoretic migration of these assemblies showed cooperative formation of multicomponent arrays containing two to five DNA modules (i.e., 12–30 SNS monomers). The treatment of these arrays with horseradish peroxidase and H_2O_2 resulted in oxidative polymerization of the SNS monomers with concomitant ligation of the DNA modules. The resulting cyclic and linear arrays exhibited chemical and optical properties typical of conducting thiophene-like polymers, with a red-end absorption beyond 1250 nm. AFM images of the cyclic array containing 18 SNS units revealed highly regular 10 nm diameter objects.

- An Engineered Microbial Platform for Direct Biofuel Production from Brown Macroalgae
Wargacki, A. J.; Leonard, E.; Win, M. N.; Regitsky, D. D.; Santos, C. N. S.; Kim, P. B.; Cooper, S. R.; Raisner, R. M.; Herman, A.; Sivitz, A. B.; Lakshmanaswamy, A.; Kashiyaama, Y.; Baker, D.; Yoshikuni, Y. *Science* **2012**, 335, 308-313.

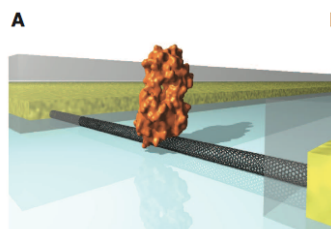
Abstract:



Prospecting macroalgae (seaweeds) as feedstocks for bioconversion into biofuels and commodity chemical compounds is limited primarily by the availability of tractable microorganisms that can metabolize alginate polysaccharides. Here, we present the discovery of a 36-kilo-base pair DNA fragment from *Vibrio splendidus* encoding enzymes for alginate transport and metabolism. The genomic integration of this ensemble, together with an engineered system for extracellular alginate depolymerization, generated a microbial platform that can simultaneously degrade, uptake, and metabolize alginate. When further engineered for ethanol synthesis, this platform enables bioethanol production directly from macroalgae via a consolidated process, achieving a titer of 4.7% volume/volume and a yield of 0.281 weight ethanol/weight dry macroalgae (equivalent to ~80% of the maximum theoretical yield from the sugar composition in macroalgae).

- Single-Molecule Lysozyme Dynamics Monitored by an Electronic Circuit
Choi, Y.; Moody, I. S.; Sims, P. C.; Hunt, S. R.; Corso, B. L.; Perez, I.; Weiss, G. A.; Collins, P. G. *Science* **2012**, 335, 319-324.

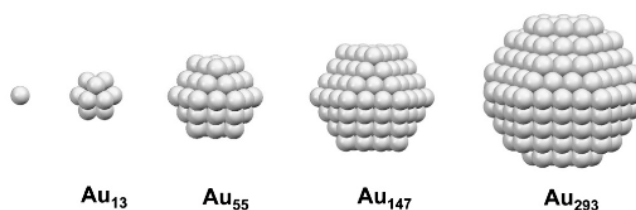
Abstract:



Tethering a single lysozyme molecule to a carbon nanotube field-effect transistor produced a stable, high-bandwidth transducer for protein motion. Electronic monitoring during 10-minute periods extended well beyond the limitations of fluorescence techniques to uncover dynamic disorder within a single molecule and establish lysozyme as a processive enzyme. On average, 100 chemical bonds are processively hydrolyzed, at 15-hertz rates, before lysozyme returns to its nonproductive, 330-hertz hinge motion. Statistical analysis differentiated single-step hinge closure from enzyme opening, which requires two steps. Seven independent time scales governing lysozyme's activity were observed. The pH dependence of lysozyme activity arises not from changes to its processive kinetics but rather from increasing time spent in either nonproductive rapid motions or an inactive, closed conformation.

- Atomically precise gold nanocrystal molecules with surface plasmon resonance
Qian, H.; Zhu, Y.; Jin, R. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, 109, 696-700.

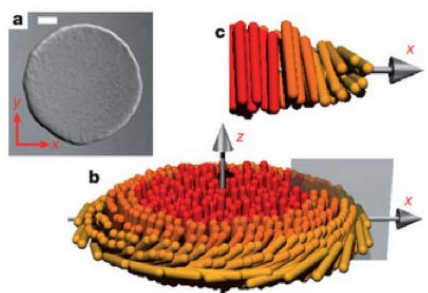
Abstract:



Since Faraday's pioneering work on gold colloids, tremendous scientific research on plasmonic gold nanoparticles has been carried out, but no atomically precise Au nanocrystals have been achieved. This work reports the first example of gold nanocrystal molecules. Mass spectrometry analysis has determined its formula to be $\text{Au}_{333}(\text{SR})_{79}$ ($\text{R} = \text{CH}_2\text{CH}_2\text{Ph}$). This magic sized nanocrystal molecule exhibits fcc-crystallinity and surface plasmon resonance at approximately 520 nm, hence, a metallic nanomolecule. Simulations have revealed that atomic shell closing largely contributes to the particular robustness of $\text{Au}_{333}(\text{SR})_{79}$, albeit the number of free electrons (i.e., $333 - 79 = 254$) is also consistent with electron shell closing based on calculations using a confined free electron model. Guided by the atomic shell closing growth mode, we have also found the next larger size of extraordinary stability to be $\text{Au}_{530}(\text{SR})_{100}$ after a size-focusing selection—which selects the robust size available in the starting polydisperse nanoparticles. This work clearly demonstrates that atomically precise nanocrystal molecules are achievable and that the factor of atomic shell closing contributes to their extraordinary stability compared to other sizes. Overall, this work opens up new opportunities for investigating many fundamental issues of nanocrystals, such as the formation of metallic state, and will have potential impact on condensed matter physics, nanochemistry, and catalysis as well.

- Reconfigurable self-assembly through chiral control of interfacial tension
Gibaud, T.; Barry, E.; Zakhary, M. J.; Henglin, M.; Ward, A.; Yang, Y.; Berciu, C.; Oldenbourg, R.; Hagan, M. F.; Nicastro, D.; Meyer, R. B.; Dogic, Z. *Nature* **2012**, 481, 348-351.

Abstract:



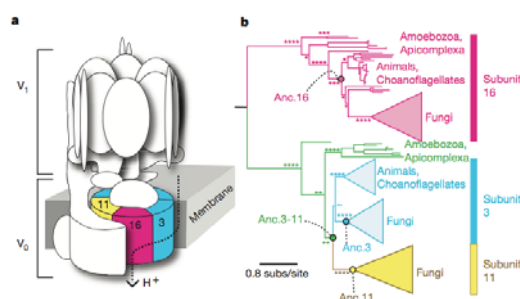
From determining the optical properties of simple molecular crystals to establishing the preferred handedness in highly complex vertebrates, molecular chirality profoundly influences the structural, mechanical and optical properties of both synthetic and biological matter on macroscopic length scales. In soft materials such as amphiphilic lipids and liquid crystals, the competition between local chiral interactions and global constraints imposed by the geometry of the self-assembled structures leads to frustration and the assembly of unique materials. An example of particular interest is smectic liquid crystals, where the two-dimensional layered geometry cannot support twist and chirality is consequently expelled to the edges in a manner analogous to the expulsion of a magnetic field from superconductors. Here we demonstrate a consequence of this geometric frustration that leads to a new design principle for the assembly of chiral molecules. Using a model system of colloidal membranes, we show that molecular chirality can control the interfacial tension, an

important property of multi-component mixtures. This suggests an analogy between chiral twist, which is expelled to the edges of two-dimensional membranes, and amphiphilic surfactants, which are expelled to oil–water interfaces. As with surfactants, chiral control of interfacial tension drives the formation of many polymorphic assemblages such as twisted ribbons with linear and circular topologies, starfish membranes, and double and triple helices. Tuning molecular chirality *in situ* allows dynamical control of line tension, which powers polymorphic transitions between various chiral structures. These findings outline a general strategy for the assembly of reconfigurable chiral materials that can easily be moved, stretched, attached to one another and transformed between multiple conformational states, thus allowing precise assembly and nanosculpting of highly dynamical and designable materials with complex topologies.

- Evolution of increased complexity in a molecular machine.

Finnigan, G. C.; Hanson-Smith, V.; Stevens, T. H.; Thornton, J. W. *Nature* **2012**, *481*, 360-364.

Abstract:

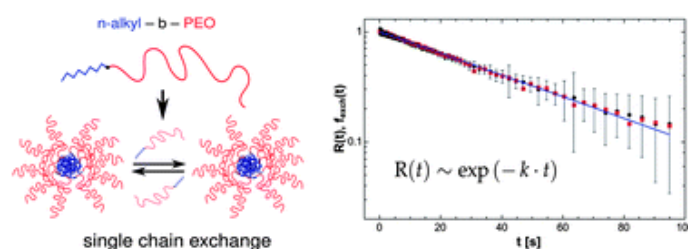


Many cellular processes are carried out by molecular ‘machines’—assemblies of multiple differentiated proteins that physically interact to execute biological functions. Despite much speculation, strong evidence of the mechanisms by which these assemblies evolved is lacking. Here we use ancestral gene resurrection and manipulative genetic experiments to determine how the complexity of an essential molecular machine—the hexameric transmembrane ring of the eukaryotic V-ATPase proton pump—increased hundreds of millions of years ago. We show that the ring of Fungi, which is composed of three paralogous proteins, evolved from a more ancient two-paralogue complex because of a gene duplication that was followed by loss in each daughter copy of specific interfaces by which it interacts with other ring proteins. These losses were complementary, so both copies became obligate components with restricted spatial roles in the complex. Reintroducing a single historical mutation from each paralogue lineage into the resurrected ancestral proteins is sufficient to recapitulate their asymmetric degeneration and trigger the requirement for the more elaborate three-component ring. Our experiments show that increased complexity in an essential molecular machine evolved because of simple, high-probability evolutionary processes, without the apparent evolution of novel functions. They point to a plausible mechanism for the evolution of complexity in other multi-paralogue protein complexes.

- Equilibrium exchange kinetics in n-alkyl–PEO polymeric micelles: single exponential relaxation and chain length dependence

Zinn, T.; Willner, L.; Lund, R.; Pipich V.; Richter, D. *Soft Matter* **2012**, *8*, 623-626.

Abstract:

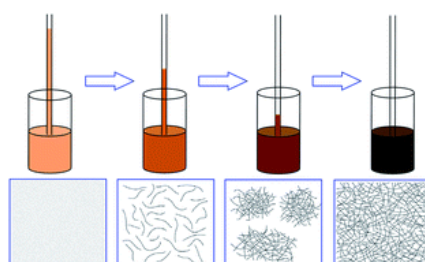


In this communication we present first results on the chain exchange kinetics of n-alkyl-PEO polymeric micelles by time-resolved small angle neutron scattering. We found that the rate strongly depends on the alkyl-chain length and that the relaxation function almost perfectly follows the single exponential decay predicted by theory. The key achievement of this study is the experimental verification that core block polydispersity accounts for the almost logarithmic time decay in block copolymer micelles as recently suggested by Choi *et al.* The results thus directly show that unimer exchange is the main mechanism for molecular exchange in block copolymer micelles.

- Sol-gel transition of poly(3-hexylthiophene) revealed by capillary measurements: phase behaviors, gelation kinetics and the formation mechanism

Xu, W.; Tang, W.; Lv, H.; Li, J.; Zhao, X.; Li, H.; Wang N.; Yang, X. *Soft Matter* **2012**, 8, 726-733.

Abstract:

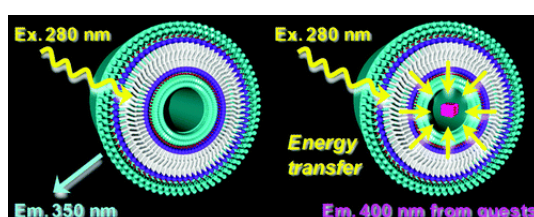


π -Conjugated organogels of poly(3-hexylthiophene) (P3HT) are prepared *via* the addition of a marginal solvent, anisole, into solutions of P3HT. We initiate a novel and facile route to determine the gelation threshold of P3HT nanowire dispersions by capillary measurements. The effects of the P3HT concentration (c), anisole volume fraction (ϕ) and temperature (T) on the phase behaviors are discussed. A thermodynamic c - ϕ phase diagram is constructed, in which the P3HT dispersion is divided into four regions: solution, sol, sol-gel blend and gel. The concentration and solvent dependent sol-gel transition kinetics shows that the gelation process could be accelerated *via* increasing c and ϕ . The gelation temperature gives an exponential relationship with the concentration of P3HT and the anisole volume fraction. Morphological studies reveal the formation process and the topological structure of the P3HT microgel clusters. Based on the above results, a three-stage physical scenario for the sol-gel transition of P3HT dispersions is proposed.

- Soft Nanotubes Acting as a Light-Harvesting Antenna System.

Kameta, N.; Ishikawa, K.; Masuda, M.; Asakawa, M.; Shimizu, T. *Chem. Mater.* **2012**, 24, 209-214.

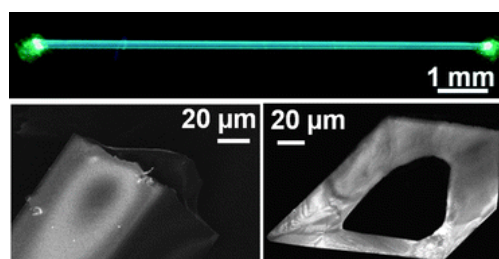
Abstract:



Amphiphilic monomers, which were quantitatively synthesized from a dehydration reaction between a glycolipid and naphthalene-boronic acids, self-assembled in organic solvents to selectively form tape-like structures (nanotape) and tubular structures (nanotube) depending on the bond position of the boron atom in the naphthalene ring. The nanotube has a strong narrow fluorescence band attributable to the monomer species of the naphthalene group, whereas the nanotape has a weak broad fluorescence band at a relative longer wavelength region based on the excimer species of the naphthalene group. Light energy adsorbed by the naphthalene groups densely and regularly organized in the bilayer membrane wall of the nanotube was transferred, with high quantum efficiency, into anthracene as an acceptor encapsulated in the nanochannel. The supramolecular nanotube proved to be able to act as a light-harvesting antenna.

- Supramolecular interaction-induced self-assembly of organic molecules into ultra-long tubular crystals with wave guiding and amplified spontaneous emission.
Xu, Y.; Zhang, H.; Li, F.; Shen, F.; Wang, H.; Li, X.; Yu, Y.; Ma, Y. *J. Mater. Chem.* **2012**, *22*, 1592-1597.

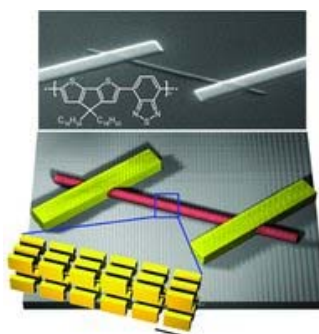
Abstract:



Ultra-long tubular crystals (length up to 10 mm and diameter of 70 μm) of a small organic functional molecule, 1,4-bis(2-cyano-2-phenylethenyl)benzene (BCPEB), are successfully prepared through a physical vapor transport (PVT) method. On the basis of crystal structural analysis and density functional theory calculations, we show that the formation of such tubular crystals is drawn by the branched hydrogen bonds between the BCPEB molecules. High crystalline quality, highly ordered molecular orientation, and hollow-like topological structure enable the crystal to exhibit optical wave guided emission behaviors with low optical loss (3 dB mm^{-1}) and highly polarized emission (the polarized ratio is about 20). Amplified spontaneous emission (ASE) characteristics of the tubular crystals were also studied; the net gain coefficients at the peak wavelength and the threshold are 91.7 cm^{-1} and 36 kW cm^{-2} , respectively.

- Organic Field-Effect Transistors based on Highly Ordered Single Polymer Fibers
Wang, S.; Kappl, M.; Liebewirth, I.; Müller, M.; Kirchhoff, K.; Pisula, W.; Müllen, K. *Adv. Mater.* **2012**, *24*, 417-420.

Abstract:

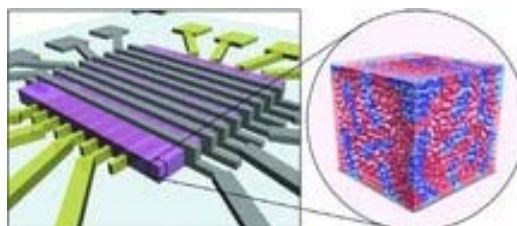


Ultrahigh-mobility organic field-effect transistors (OFETs) based on a CDT-BTZ donor-acceptor copolymer are realized by reaching high molecular order and pronounced alignment in single fibers within a short OFET channel via solution processing. The macromolecules directionally self-assemble in a quasi crystal-like order in the fibers providing in this way an unhindered charge carrier pathway with mobilities as high as $5.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

- Structural and Electrical Characterization of a Block Copolymer-Based Unipolar Nonvolatile Memory Device

Kang, N-G.; Cho, B.; Kang, B-G.; Song, S.; Lee, T.; Lee, J-S. *Adv. Mater.* **2012**, 24, 385-390.

Abstract:

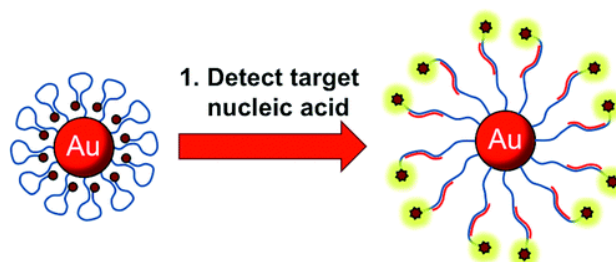


Electronic devices based on a series of synthesized block copolymers are demonstrated. In particular, a block copolymer system with a lamellar structure exhibits unipolar switching behavior. This study provides a simple strategy based on the adjustment of the block ratio in block copolymers to control the polymer morphology and thus the electrical and switching properties of polymer-based memory devices.

- Design, Synthesis, and Characterization of Nucleic-Acid-Functionalized Gold Surfaces for Biomarker Detection

Adams, N. M.; Jackson, S. R.; Haselton, F. R.; Wright, D. W. *Langmuir* **2012**, 28, 1068-1082.

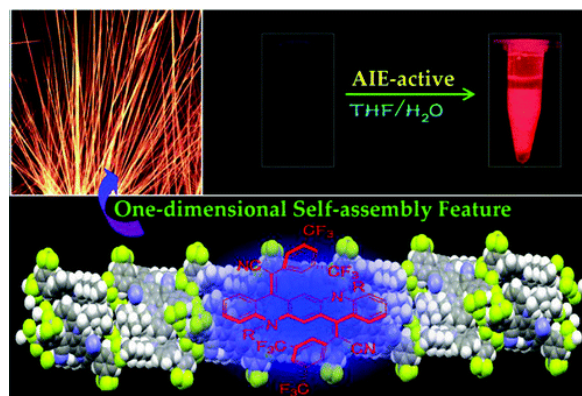
Abstract:



Nucleic-acid-functionalized gold surfaces have been used extensively for the development of biological sensors. The development of an effective biomarker detection assay requires careful design, synthesis, and characterization of probe components. In this Feature Article, we describe fundamental probe development constraints and provide a critical appraisal of the current methodologies and applications in the field. We discuss critical issues and obstacles that impede the sensitivity and reliability of the sensors to underscore the challenges that must be met to advance the field of biomarker detection.

- Quinoacridine Derivatives with One-Dimensional Aggregation-Induced Red Emission Property
Javed, I.; Zhou, T.; Muhammad, F.; Guo, J.; Zhang, H.; Wang, Y. *Langmuir* **2012**, 28, 1439-1446.

Abstract:

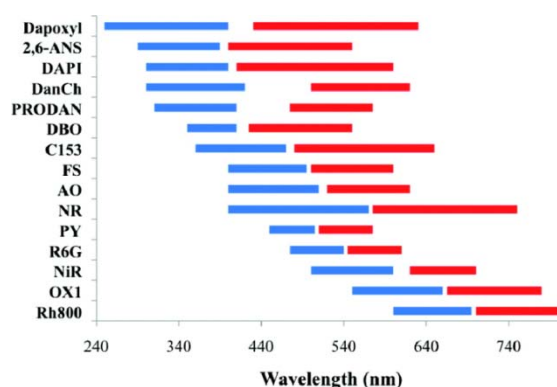


A new series of acceptor–donor–acceptor (A–D–A) type quinoacridine derivatives (**1–3**) with aggregation-induced red emission properties were designed and synthesized. In these compounds, the electron-withdrawing 2-(3,5-bis(trifluoromethyl)phenyl)acetonitrile groups act as electron-accepting units, while the alkyl-substituted conjugated core acts as electron-donating units. The restriction of intramolecular rotation was responsible for the AIE behavior of compounds **1–3**. All compounds were employed as building blocks to fabricate one-dimensional (1-D) organic luminescent nano- or microwires based on reprecipitation or slow evaporation approaches. Morphological transition from zero-dimensional (0-D) hollow nanospheres to 1-D nanotubes has been observed by recording SEM and TEM images of aggregated states of compound **2** in THF/H₂O mixtures at different aging time. It was demonstrated that the synthesized compounds with different lengths of alkyl chains displayed different wire formation properties. The single-crystal X-ray analysis of compound **2** provided reasonable explanation for the formation of 1-D nano- or microstructures.

- Fluorescent Dyes and Their Supramolecular Host/Guest Complexes with Macrocycles in Aqueous Solution

Dsouza, R. N.; Pischel, U.; Nau, W. M. *Chem. Rev.* **2011**, *111*, 7941–7980.

Abstract :

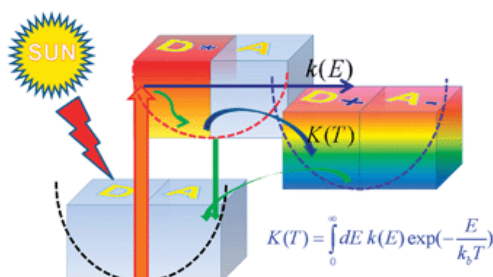


The fluorescence of organic molecules depends sensitively on their environment. Fluorescent dyes have accordingly become popular molecular probes not only to determine microenvironmental parameters, such as the polarity of media, but also to follow their relocation and distribution dynamics in microheterogeneous systems such as membranes, micelles, and cellular media as well as interfaces, polymers, and discrete supramolecular systems. They have been found particularly useful to monitor the formation of discrete host/guest complexes with macrocyclic structures, which can serve as molecular containers (nanocavities) of fluorescent dyes. The inclusion of the dye into their (generally hydrophobic) cavity is accompanied by a large change in the microenvironmental parameters, which has been abundantly used in supramolecular chemistry to determine, on one

hand, the association thermodynamics and kinetics and, on the other hand, the binding of competitors by indicator displacement methodologies. In fact, the binding of fluorescent dyes provides a *par excellence* educational example for the formation of supramolecular assemblies, which dates back to the first observation of room temperature luminescence in cyclodextrins^(1, 2) and has later found additional use for other, mostly polarity-sensitive, dyes.⁽³⁻⁵⁾

- Charge transfer in organic molecules for solar cells: theoretical perspective
Zhao, Y.; Liang, W. Z. *Chem. Soc. Rev.* **2012**, 41, 1075-1087.

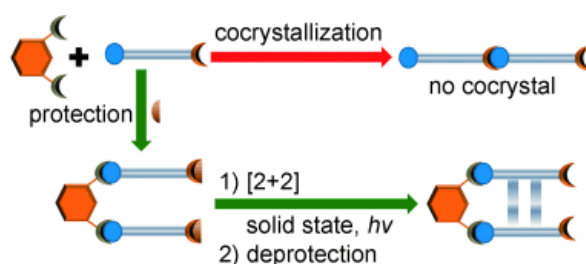
Abstract:



This *tutorial review* primarily illustrates rate theories for charge transfer and separation in organic molecules for solar cells. Starting from the Fermi's golden rule for weak electronic coupling, we display the microcanonical and canonical rates, as well as the relationship with the Marcus formula. The fluctuation effect of bridges on the rate is further emphasized. Then, several rate approaches beyond the perturbation limit are revealed. Finally, we discuss the electronic structure theory for calculations of the electronic coupling and reorganization energy that are two key parameters in charge transfer, and show several applications.

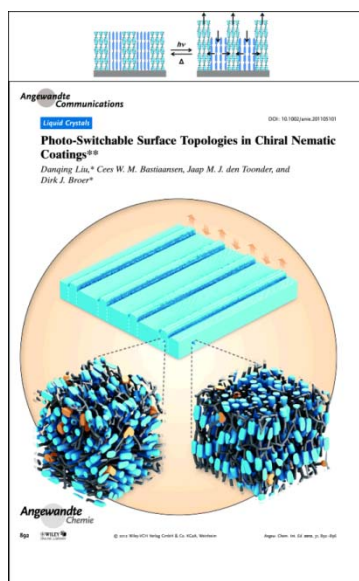
- A Supramolecular Protecting Group Strategy Introduced to the Organic Solid State: Enhanced Reactivity through Molecular Pedal Motion
Elacqua, E.; Kaushik, P.; Groeneman, R. H.; Sumrak, J. C.; Bučar, D. K.; MacGillivray, L. R. *Angew. Chem. Int. Ed.* **2012**, 51, 1037-1041.

Abstract:



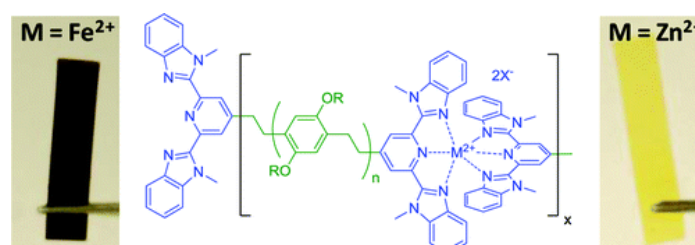
A supramolecular protecting group strategy has been applied to achieve solid-state photodimerizations of olefins lined with a combination of hydrogen-bond-donor and -acceptor groups. Esters were used as protecting groups to generate head-to-head photodimers that were readily converted into diacids. A protected olefin equipped with a stilbene unit exhibits enhanced reactivity that is ascribed to pedal motions in the solid state (orange hexagons: template; blue circles: recognition sites).

- Photo-Switchable Surface Topologies in Chiral Nematic Coatings
Liu, D.; Bastiaansen, C. W. M.; Toonder, J. M. J.; Broer, D. J. *Angew. Chem. Int. Ed.* **2012**, 51, 892-896.

Abstract:

An enlightening answer: Dynamic surface photo-responsive topologies of a polymer coating were realized by introducing azobenzene crosslinkers into liquid-crystal polymer networks (see picture). The principle of these coatings is based on breaking the molecular order in the liquid-crystal polymer networks. Under irradiation of UV light the azobenzene compound isomerizes from the *trans* to the *cis* conformation.

- Structure–Property Relationships in Metallosupramolecular Poly(p-xylylene)s
Burnworth, M.; Rowan, S. J.; Weder, C. *Macromolecules* **2012**, *45*, 126–132.

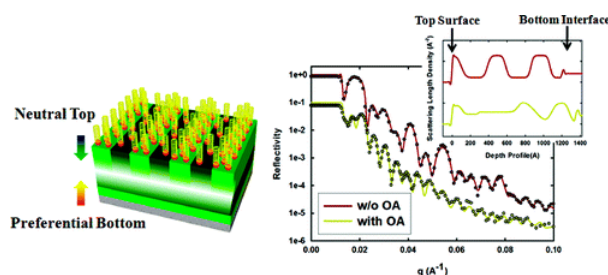
Abstract:

The self-assembly polymerization of ditopic monomers via metal–ligand binding is a facile route for the preparation of metallosupramolecular polymers. Here this approach was used for the synthesis of supramolecularpoly(p-xylylene)s based on 2,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip) end-capped telechelic oligomers with a p-xylylene core and different metal salts. These polymers can be readily processed from solution and merge the ease of processing of supramolecular materials with the good thermal stability of the p-xylylene core. The nature of the metal cation (Fe²⁺, Zn²⁺, La³⁺) and counteranion (ClO₄[−], OTf[−], NTf₂[−]) was systematically varied, and a tetrafunctional supramolecular cross-linker was used to probe how these modifications influence the materials' properties. Interestingly, and in contrast to other metallosupramolecular polymers, where the nature of the metal salt plays a critical role, only minor property differences were observed for the materials studied. Instead, the properties of the supramolecularpoly(p-xylylene)s investigated appear to be primarily governed by the crystalline nature of the telechelic oligomer. We note that minor impurities in the latter can exert a significant influence on the metallosupramolecular polymer's properties and report a new protocol for the synthesis and purification of Mebip-end-capped p-xylylenetelechelic oligomers.

- Orientation Change of Diblock Copolymer Thin Films by the Addition of Amphiphilic Surfactants: Effect of Film Thickness and Surfactant Concentration

Son, J. G.; Kang, H.; Kim, K.; Lee, J.; Nealey, P. F.; Char, K. *Macromolecules* **2012**, *45*, 150–158.

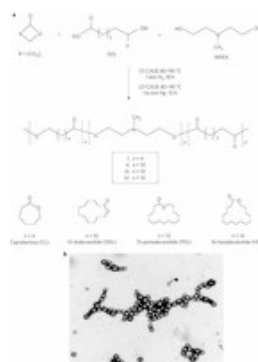
Abstract:



We systematically investigated the effect of surfactant addition on the orientational change in polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer films as a function of film thickness and surfactant (oleic acids (OAs)) concentration using microscopic analysis, neutron reflectivity, and theoretical calculations. The orientation of PS-*b*-PMMA films containing OAs as surfactants was found to be determined by the competitions among the surfactant-assisted neutral field and preferential fields at both top surface and bottom interface. In the case of a BCP film containing a small amount of OAs, the integer film thickness of domain spacing L_0 (long spacing of lamellae-forming BCP) prefers to form the perpendicular orientation of microdomains while the parallel orientation is observed when the film thickness is close to the half-integers of L_0 . We also found that the periodic orientation of block domains gradually dies out to the perpendicular orientation as the film thickness as well as the surfactant concentration is increased. Neutron reflectivity analysis of deuterated polystyrene-block-poly(methyl methacrylate) (dPS-*b*-PMMA) block copolymer thin films containing OA surfactants was also performed to gain insights into the orientation of BCP films across film thickness due to the addition of OAs. With the free energy calculations on BCPs mixed with OA surfactants at different film thicknesses, the periodic orientation of block domains is qualitatively confirmed.

- Biodegradable poly(amine-co-ester) terpolymers for targeted gene delivery
Zhou, J.; Liu, J.; Cheng, C. J.; Patel, T. R.; Weller, C. E.; Piepmeier, J. M.; Jiang, Z.; Saltzman, W. M. *Nature Mater.* **2012**, *11*, 82-90.

Abstract:

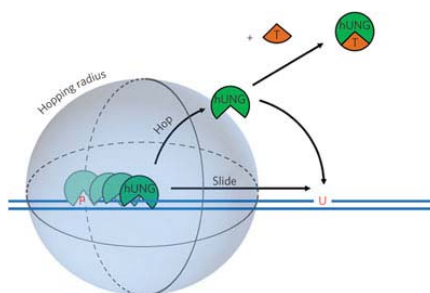


Many synthetic polycationic vectors for non-viral gene delivery show high efficiency *in vitro*, but their usually excessive charge density makes them toxic for *in vivo* applications. Here we describe the synthesis of a series of high molecular weight terpolymers with low charge density, and show that

they exhibit efficient gene delivery, some surpassing the efficiency of the commercial transfection reagents Polyethylenimine and Lipofectamine 2000. The terpolymers were synthesized via enzyme-catalyzed copolymerization of lactone with dialkyldiester and amino diol, and their hydrophobicity adjusted by varying the lactone content and by selecting a lactone comonomer of specific ring size. Targeted delivery of the pro-apoptotic TRAIL gene to tumour xenografts by one of the terpolymers results in significant inhibition of tumour growth, with minimal toxicity both *in vitro* and *in vivo*. Our findings suggest that the gene delivery ability of the terpolymers stems from their high molecular weight and increased hydrophobicity, which compensates for their low charge density.

- Timing facilitated site transfer of an enzyme on DNA
Schonhofs, J. D.; Stivers, J. T. *Nature Chem. Biol.* **2012**, 8, 205-210.

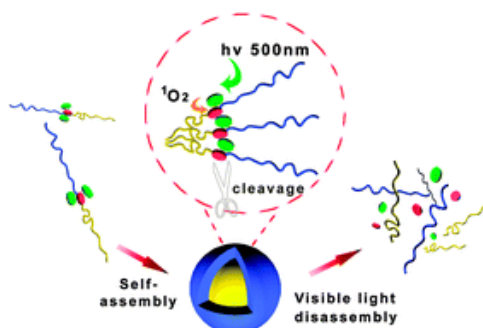
Abstract:



Many enzymes that react with specific sites in DNA have the property of facilitated diffusion, in which the DNA chain is used as a conduit to accelerate site location. Despite the importance of such mechanisms in gene regulation and DNA repair, there have been few viable approaches to elucidate the microscopic process of facilitated diffusion. Here we describe a new method in which a small-molecule trap (uracil) is used to clock a DNA repair enzyme as it hops and slides between damaged sites in DNA. The 'molecular clock' provides unprecedented information: the mean length for DNA sliding, the one-dimensional diffusion constant, the maximum hopping radius and the time frame for DNA hopping events. In addition, the data establish that the DNA phosphate backbone is a sufficient requirement for DNA sliding.

- Visible light-responsive micelles formed from dialkoxyanthracene-containing block copolymers
Yan, Q.; Hu, J.; Zhou, R.; Ju, Y.; Yin, Y.; Yuan, J. *Chem. Commun.* **2012**, 48, 1913-1915.

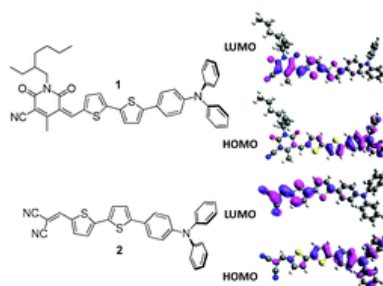
Abstract:



A class of dialkoxyanthracene-containing diblock copolymers is synthesized which possesses visible light-responsivity. These copolymers can self-assemble into a micellar structure in water. Green visible light (540 nm) is able to scissor these anthracene species and cleave the diblock copolymer into two fragments, inducing disassembly of the self-assembled micelles.

- Absorption enhancement of oligothiophene dyes through the use of a cyanopyridone acceptor group in solution-processed organic solar cells
Gupta, A.; Ali, A.; Bilic, A.; Gao, M.; Hegedus, K.; Singh, B.; Watkins, S. E.; Wilson, G. J.; Bach, U.; Evans, R. A. *Chem. Commun.* **2012**, 48, 1889-1891.

Abstract:



Improvements in the performance of small molecule-based organic solar cells have been reported through the use of a cyanopyridone acceptor group. This acceptor fragment enhances the absorbance of an oligothiophene-based dye and enables the addition of a solubilising alkyl chain that facilitates simple device fabrication from solution.