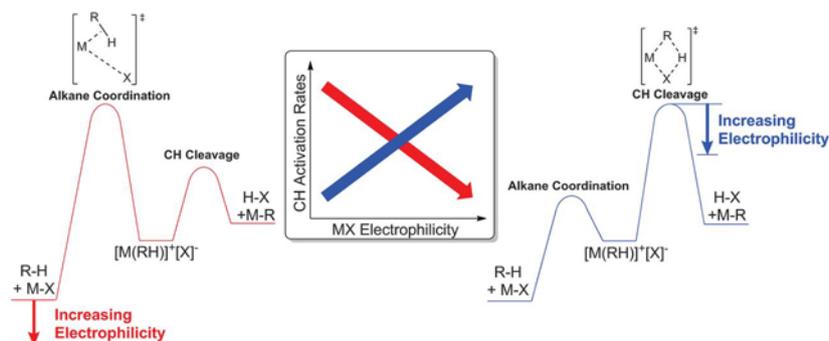


- Main-Group Compounds Selectively Oxidize Mixtures of Methane, Ethane, and Propane to Alcohol Esters

1

Hashiguchi, B. G.; Konnick, M. M.; Bischof, S. M.; Gustafson, S. J.; Devarajan, D.; Gunsalus, N.; Ess, D. H.; Periana, R. A. *Science* **2014**, *343*, 1232-1237.

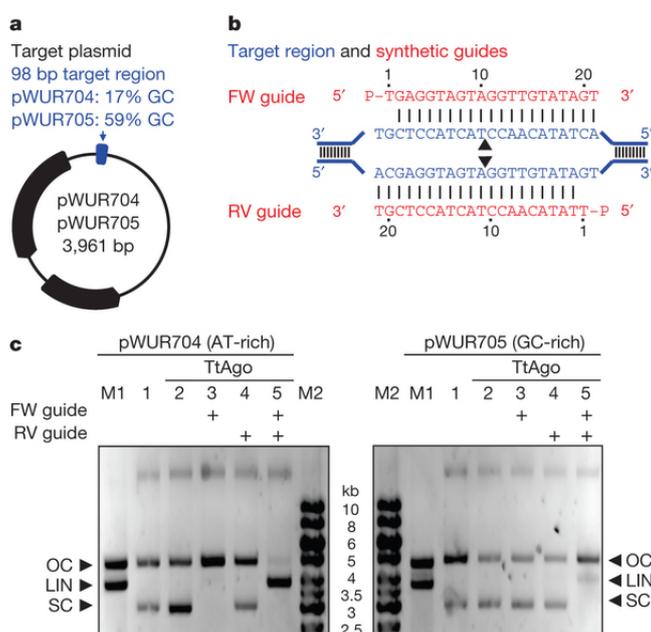
Abstract:



Much of the recent research on homogeneous alkane oxidation has focused on the use of transition metal catalysts. Here, we report that the electrophilic main-group cations thallium(III) and lead(IV) stoichiometrically oxidize methane, ethane, and propane, separately or as a one-pot mixture, to corresponding alcohol esters in trifluoroacetic acid solvent. Esters of methanol, ethanol, ethylene glycol, isopropanol, and propylene glycol are obtained with greater than 95% selectivity in concentrations up to 1.48 molar within 3 hours at 180°C. Experiment and theory support a mechanism involving electrophilic carbon-hydrogen bond activation to generate metal alkyl intermediates. We posit that the comparatively high reactivity of these d^{10} main-group cations relative to transition metals stems from facile alkane coordination at vacant sites, enabled by the overall lability of the ligand sphere and the absence of ligand field stabilization energies in systems with filled d-orbitals.

- DNA-guided DNA interference by a prokaryotic Argonaute
- Swarts, D. C.; Jore, M. M.; Westra, E. R.; Zhu, Y.; Janssen, J. H.; Snijders, A. P.; Wang, Y.; Patel, D. J.; Berenguer, J.; Brouns, S. J. J.; van der Oost, J. *Nature* **2014**, *507*, 258-261.

Abstract:

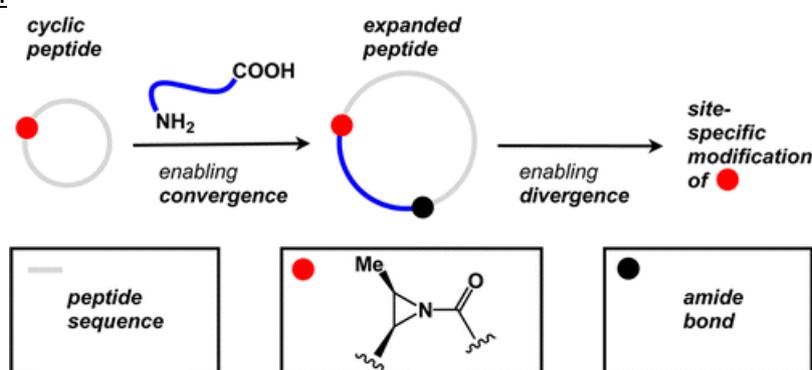


RNA interference is widely distributed in eukaryotes and has a variety of functions, including antiviral defence and gene regulation. All RNA interference pathways use small single-stranded RNA (ssRNA) molecules that guide proteins of the Argonaute (Ago) family to complementary ssRNA targets: RNA-guided RNA interference. The role of prokaryotic Ago variants has remained elusive, although bioinformatics analysis has suggested their involvement in host defence. Here we demonstrate that Ago of the bacterium *Thermus thermophilus* (TtAgo) acts as a barrier for the uptake and propagation of foreign DNA. *In vivo*, TtAgo is loaded with 5'-phosphorylated DNA guides, 13–25 nucleotides in length, that are mostly plasmid derived and have a strong bias for a 5'-end deoxycytidine. These small interfering DNAs guide TtAgo to cleave complementary DNA strands. Hence, despite structural homology to its eukaryotic counterparts, TtAgo functions in host defence by DNA-guided DNA interference.

- Site-Specific Integration of Amino Acid Fragments into Cyclic Peptides

White, C. J.; Hickey, J. L.; Scully, C. C. G.; Yudin, A. K. *J. Am. Chem. Soc.* **2014**, *136*, 3728–3731.

Abstract:

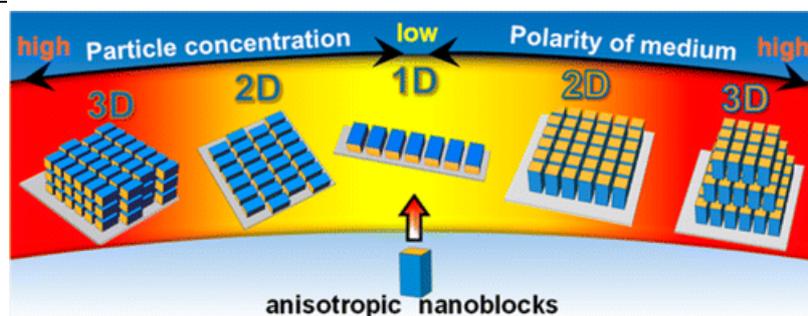


The concept of site-specific integration of fragments into macrocyclic entities has not yet found application in the realm of synthetic chemistry. Here we show that the reduced amidicity of aziridine amide bonds provides an entry point for the site-specific integration of amino acids and peptide fragments into the homodetic cyclic peptide architecture. This new synthetic operation improves both the convergence and divergence of cyclic peptide synthesis.

- Direction Control of Oriented Self-Assembly for 1D, 2D, and 3D Microarrays of Anisotropic Rectangular Nanoblocks

Nakagawa, Y.; Kageyama, H.; Oaki, Y.; Imai, H. *J. Am. Chem. Soc.* **2014**, *136*, 3716–3719.

Abstract:



Micrometric linear chains (1D arrays), monolayers (2D arrays), and superstructures (3D arrays) of anisotropic Mn₃O₄ nanocuboids were selectively produced by oriented self-assembly through evaporation of a dispersion. The 1D arrays were basically formed on a substrate via oriented self-

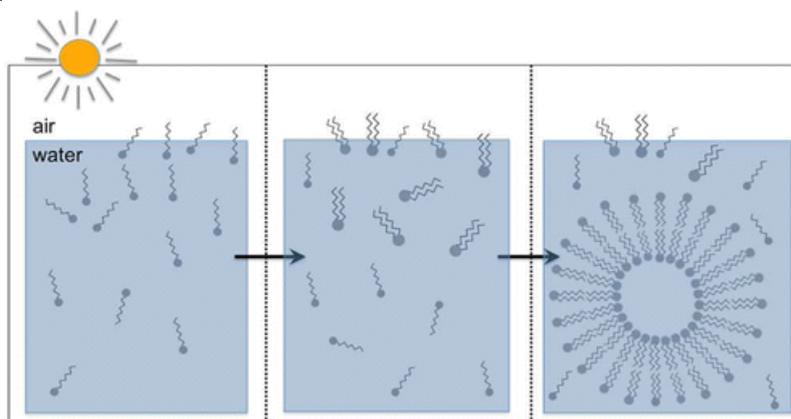
assembly of the rectangular crystals in the 100 direction. The 2D and 3D microarrays were obtained by adjusting the particle concentration of the dispersion. The [001] direction of tetragonal crystal was controlled to be parallel and perpendicular to the substrate by changing the polarity of the medium.

3

- Photoinitiated Synthesis of Self-Assembled Vesicles

Griffith, E. C.; Rapf, R. J.; Shoemaker, R. K.; Carpenter, B. K.; Vaida, V. *J. Am. Chem. Soc.* **2014**, *136*, 3784-3787.

Abstract:

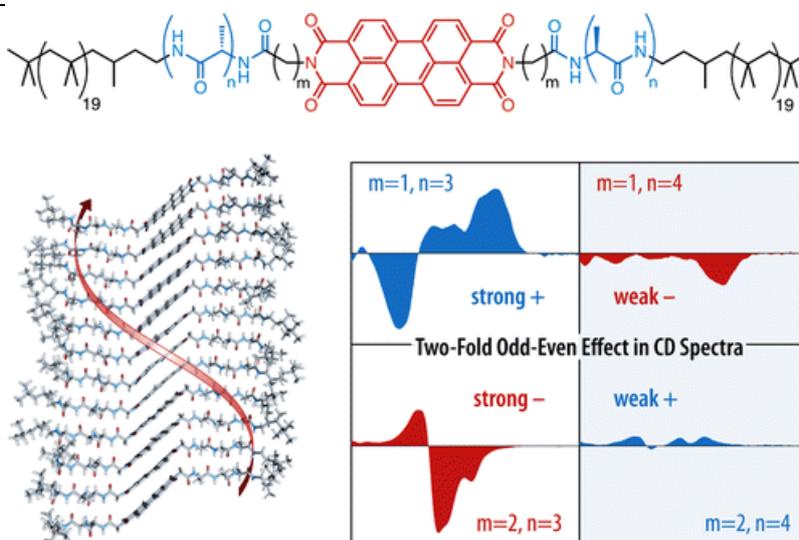


The aqueous photochemistry of 2-oxooctanoic acid (a single-tailed surfactant) results in the synthesis of a double-tailed surfactant product followed by spontaneous self-assembly into vesicles. The photochemical mechanism is detailed here, and the reaction products are identified using mass spectrometry. Then, the self-assembled vesicles are characterized using dynamic light scattering, fluorescence microscopy, and NMR. Further, their stability over time and in the presence of MgCl₂ salt is demonstrated. This work contributes to membrane evolution through the provision of a prebiotic route for the synthesis of plausible membrane components and subsequent self-assembly of a primitive enclosure.

- Two-Fold Odd-Even Effect in Self-Assembled Nanowires from Oligopeptide-Polymer-Substituted Perylene Bisimides

Marty, R.; Nigon, R.; Leite, D.; Frauenrath, H. *J. Am. Chem. Soc.* **2014**, *136*, 3919-3927.

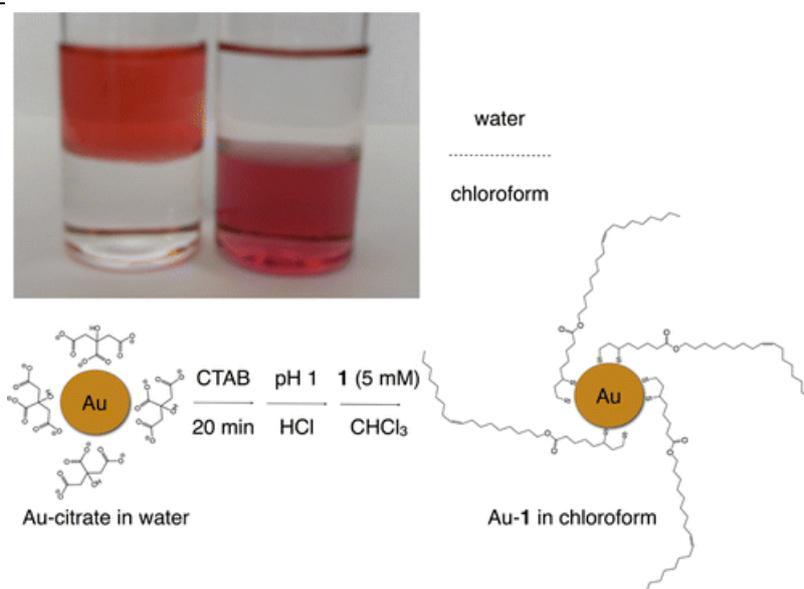
Abstract:



Organic nanowires are important building blocks for nanoscopic organic electronic devices. In order to ensure efficient charge transport through such nanowires, it is important to understand in detail the molecular parameters that guide self-assembly of π -conjugated molecules into one-dimensional stacks with optimal constructive π - π overlap. Here, we investigated the subtle relationship between molecular structure and supramolecular arrangement of the chromophores in self-assembled nanowires prepared from perylene bisimides with oligopeptide-polymer side chains. We observed a “two-fold” odd–even effect in circular dichroism spectra of these derivatives, depending on both the number of l-alanine units in the oligopeptide segments and length of the alkylene spacer between chromophore and oligopeptide substituents. Our results indicate that there is a complex interplay between the translation of molecular chirality into supramolecular helicity and the molecules’ inherent propensity for well-defined one-dimensional aggregation into β -sheet-like superstructures in the presence of a central chromophore. Strong excitonic coupling as expressed by the appearance of hypsochromically and bathochromically shifted UV–vis absorptions and strong CD signals was systematically observed for molecules with an odd number of l-alanines in the side chains. The latter derivatives gave rise to nanowires with a significantly higher electron mobility. Our results, hence, provide an important design rule for self-assembled organic nanowires.

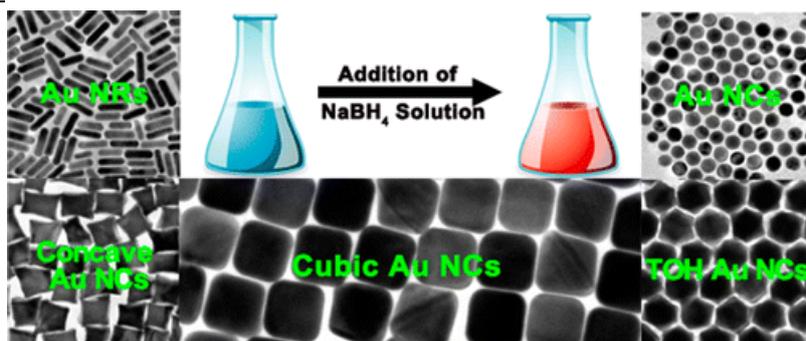
- Phase Transfer of Noble Metal Nanoparticles to Organic Solvents
Lista, M.; Liu, D. Z.; Mulvaney, P. *Langmuir* **2014**, *8*, 1932–1938.

Abstract:



Nanoparticles are finding increasing application because of their unusual optical properties. Processing these materials would be drastically simplified if they could be routinely dispersed into a wide variety of polar and nonpolar solvents. We report the synthesis of a new bidentate thiol ligand, (Z)-octadec-9-en-1-yl-5-(1,2-dithiolan-3-yl)pentanoate, and demonstrate its ability to phase transfer gold nanospheres (5–70 nm), nanorods, and silver nanoparticles efficiently from water into various organic solvents. The protocol obviates the need for solid-phase steps or polymeric ligands. Electronic spectra and electron micrographs demonstrate that the particles are fully dispersed in a variety of organic solvents after transfer.

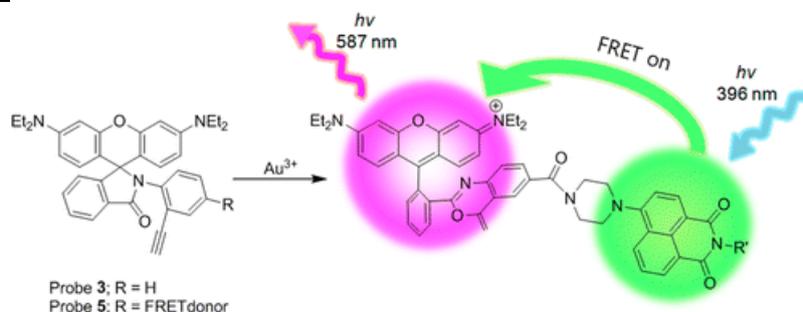
- High Yield Seedless Synthesis of High-Quality Gold Nanocrystals with Various Shapes
Zhang, J.; Xi, C.; Feng, C.; Xia, H.; Wang, D.; Tao, X. *Langmuir* **2014**, *9*, 2480–2489.

Abstract:

In this Article, high-quality gold nanocrystals (Au NCs) with various shapes including concave cubic, trisoctahedral, cubic, rod-like, and quasi-spherical have been successfully produced in high yield via adding a trace amount of NaBH_4 solution into growth solutions mainly composed of HAuCl_4 , ascorbic acid, and surfactants. The sizes and shapes of as-prepared Au NCs can be tuned by the compositions of the growth solutions and the amount of NaBH_4 added. The electrocatalytic performance of differently shaped Au NCs for methanol oxidation was studied; as-prepared trisoctahedral or concave cubic Au NCs are more highly active electrocatalysts for methanol oxidation due to the presence of high-index facets on their surface.

- Ground-State Elevation Approach To Suppress Side Reactions in Gold-Sensing Systems Based on Alkyne Activation

Seo, H.; Jun, M. E.; Ranganathan, K.; Lee, K.-H.; Kim, K.-T.; Lim, W.; Rhee, Y. M.; Ahn, K. H. *Org. Lett.* **2014**, *16*, 1374-1377.

Abstract:

A novel approach to suppress the side reactions observed in the reaction-based gold-sensing systems based on the alkyne activation is disclosed. By elevating steric strain around the reaction site, the gold ion promoted ring-opening process in rhodamine-lactam probes is significantly accelerated, which also leads to suppression of those possible side reactions. As a result, the probes show very high sensitivity in addition to excellent selectivity toward gold species. Furthermore, bioimaging of gold species in live cells was demonstrated with a FRET version.

- Dendron Synthesis and Carbohydrate Immobilization on a Biomaterial Surface by a Double-Click Reaction

Bini, D.; Russo, L.; Battocchio, C.; Natalello, A.; Polzonetti, G.; Doglia, S. M.; Nicotra, F.; Cipolla, L. *Org. Lett.* **2014**, *16*, 1298-1301.

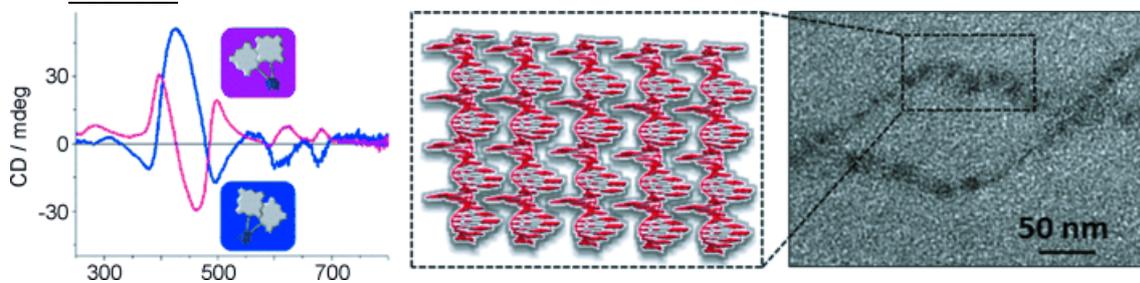
Abstract:



The synthesis of new dendrons and their immobilization on collagen patches via thiol–ene photoclick reaction, followed by chemoselective alkoxyamino–carbonyl conjugation to carbohydrates is presented. XPS, FTIR, and ELLA assays confirmed the effectiveness of the collagen multivalent neoglycosylation.

- Supramolecular ssDNA Templated Porphyrin and Metalloporphyrin Nanoassemblies with Tunable Helicity
Sargsyan, G.; Leonard, B. M.; Kubelka, J.; Balaz, M. *Chem. Eur. J.* **2014**, *20*, 1878–1892.

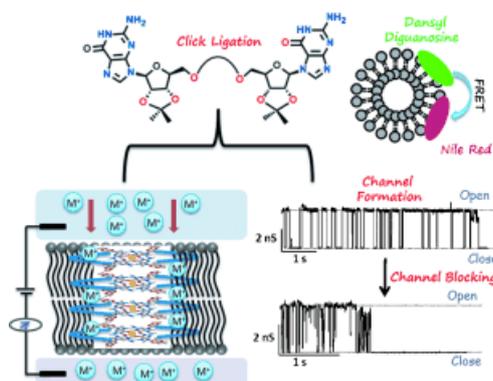
Abstract:



Free-base and nickel porphyrin–diaminopurine conjugates were formed by hydrogen-bond directed assembly on single-stranded oligothymidine templates of different lengths into helical multiporphyrin nanoassemblies with highly modular structural and chiroptical properties. Large red-shifts of the Soret band in the UV/Vis spectroscopy confirmed strong electronic coupling among assembled porphyrin–diaminopurine units. Slow annealing rates yielded preferentially right-handed nanostructures, whereas fast annealing yielded left-handed nanostructures. Time-dependent DFT simulations of UV/Vis and CD spectra for model porphyrin clusters templated on the canonical B-DNA and its enantiomeric form, were employed to confirm the origin of observed chiroptical properties and to assign the helicity of porphyrin nanoassemblies. Molar CD and CD anisotropy g factors of dialyzed templated porphyrin nanoassemblies showed very high chiroptical anisotropy. The DNA-templated porphyrin nanoassemblies displayed high thermal and pH stability. The structure and handedness of all assemblies was preserved at temperatures up to +85 °C and pH between 3 and 12. High-resolution transition electron microscopy confirmed formation of DNA-templated nickel(II) porphyrin nanoassemblies and their self-assembly into helical fibrils with micrometer lengths.

- Triazole-Tailored Guanosine Dinucleosides as Biomimetic Ion Channels to Modulate Transmembrane Potential
Kumar, Y. P.; Das, R. N.; Kumar, S.; Schütte, O. M.; Steinem, C.; Dash, J. *Chem. Eur. J.* **2014**, *20*, 3023–3028.

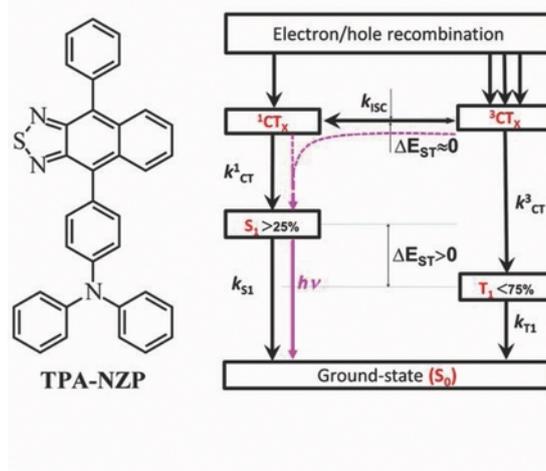
Abstract:



A “click” ion channel platform has been established by employing a clickable guanosine azide or alkyne with covalent spacers. The resulting guanosine derivatives modulated the traffic of ions across the phospholipid bilayer, exhibiting a variation in conductance spanning three orders of magnitude (pS to nS). Förster resonance energy transfer studies of the dansyl fluorophore with the membrane binding fluorophore Nile red revealed that the dansyl fluorophore is deeply embedded in the phospholipid bilayer. Complementary cytosine can inhibit the conductance of the supramolecular guanosine channels in the phospholipid bilayers.

- Employing ~100% Excitons in OLEDs by Utilizing a Fluorescent Molecule with Hybridized Local and Charge-Transfer Excited State
Li, W.; Pan, Y.; Xiao, R.; Peng, Q.; Zhang, S.; Ma, D.; Li, F.; Shen, F.; Wang, Y.; Yang, B.; Ma, Y. *Adv. Funct. Mater.* **2014**, *24*, 1609–1614.

Abstract:

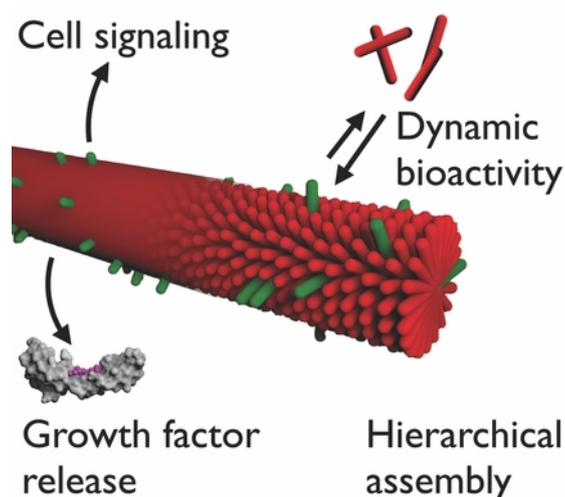


In principle, the ratio (Φ) of the maximum quantum efficiencies for electroluminescence (EL) to photoluminescence (PL) can be expected to approach unity, if the exciton (bound electron–hole pair) generated from the recombination of injected electrons and holes in OLEDs has a sufficiently weak binding energy. However, seldom are examples of $\Phi > 25\%$ reported in OLEDs because of the strongly bound excitons for most organic semiconductors in nature. Here, a twisting donor–acceptor triphenylamine-thiadiazol molecule (TPA-NZP) exhibits fluorescent emission through a hybridized local and charge-transfer excited state (HLCT), which is demonstrated from both fluorescent solvatochromic experiment and quantum chemical calculations. The HLCT state possesses two combined and compatible characteristics: a large transition moment from a local excited (LE) state and a weakly bound exciton from a charge transfer (CT) state. The former contributes to a high-

efficiency radiation of fluorescence, while the latter is responsible for the generation of a high fraction of singlet excitons. Using TPA-NZP as the light-emitting layer in an OLED, high Φ values of 93% (at low brightness) and 50% (at high brightness) are achieved, reflecting sufficient employment of the excitons in the OLED. Characterization of the EL device shows a saturated deep-red emission with CIE coordinates of (0.67, 0.32), accompanied by a rather excellent performance with a maximum luminance of 4574 cd m^{-2} and a maximum external quantum efficiency (η_{ext}) of $\sim 2.8\%$. The HLCT state is a new way to realize high-efficiency of EL devices.

- 25th Anniversary Article: Supramolecular Materials for Regenerative Medicine
Boekhoven, J.; Stupp, S. I. *Adv. Mater.* **2014**, *26*, 1642–1659.

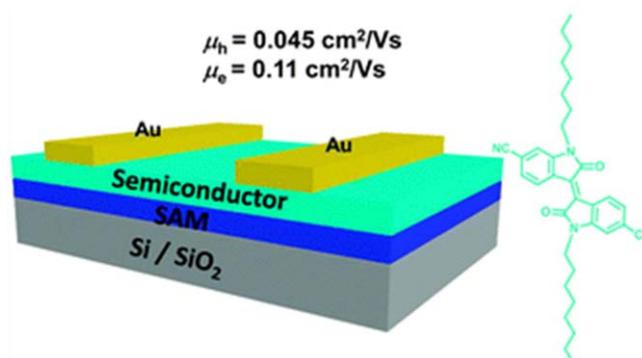
Abstract:



In supramolecular materials, molecular building blocks are designed to interact with one another via non-covalent interactions in order to create function. This offers the opportunity to create structures similar to those found in living systems that combine order and dynamics through the reversibility of intermolecular bonds. For regenerative medicine there is a great need to develop materials that signal cells effectively, deliver or bind bioactive agents in vivo at controlled rates, have highly tunable mechanical properties, but at the same time, can biodegrade safely and rapidly after fulfilling their function. These requirements make supramolecular materials a great platform to develop regenerative therapies. This review illustrates the emerging science of these materials and their use in a number of applications for regenerative medicine.

- Cyanated isoindigos for n-type and ambipolar organic thin film transistors
Yue, W.; He, T.; Stolte, M.; Gasanger, M.; Wurthner, F. *Chem. Commun.* **2014**, *50*, 545-547.

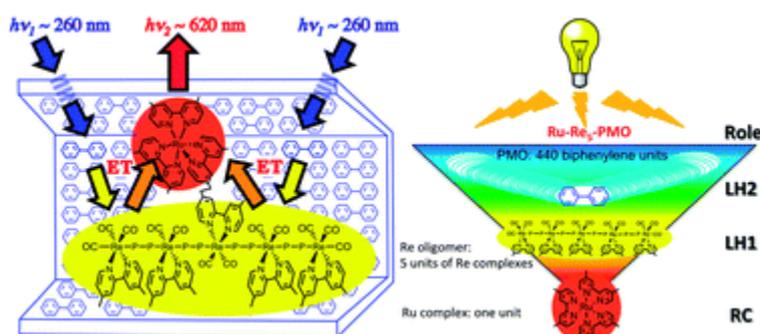
Abstract:



A set of three core-cyanated isoindigos was synthesized by palladium-catalyzed cyanation of core-brominated isoindigos. With decreased LUMO level to -3.88 eV, the dicyanated isoindigo 5 showed ambient-stable electron mobility up to 0.044 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in OTFTs with SAMs of TPA, while it exhibited ambipolar charge transport behaviour (0.11 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for electrons and 0.045 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes) on FOPA-modified substrates.

- Efficient light harvesting *via* sequential two-step energy accumulation using a Ru-Re₅ multinuclear complex incorporated into periodic mesoporous organosilica
Yamamoto, Y.; Takeda, H.; Yui, T.; Ueda, Y.; Koike, K.; Inagaki, S.; Ishitani, O. *Chem. Sci.* **2014**, *5*, 639-648.

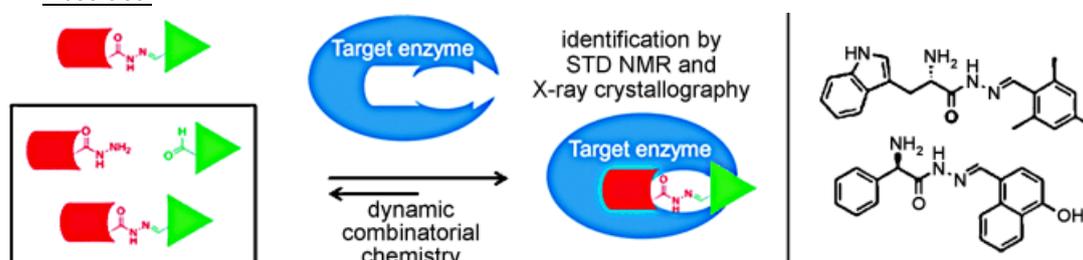
Abstract:



An efficient artificial light harvesting (LH) system was developed *via* sequential two-step energy accumulation. A periodic mesoporous organosilica with bridging biphenyl groups in the framework (**Bp-PMO**) was used as an LH antenna. The center of a linear-shaped Re(I) pentanuclear complex was connected to a Ru(II) trisdiimine complex through a covalent bond, these served as the first and second energy acceptors, respectively, (**Ru-Re₅**). Hybridization was achieved with the non-ionic surfactant $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$ in an acetonitrile solution, and in the hybrid (**Ru-Re₅-Bp-PMO**), the **Ru-Re₅** molecules were adsorbed in an orderly fashion in the mesopores of the **Bp-PMO**. Photons absorbed by 437 \pm 43 of the Bp units were first accumulated in the five Re units in **Ru-Re₅** and then transferred to only one Ru unit, which emitted the light strongly.

- Structure-Based Design of Inhibitors of the Aspartic Protease Endothiapepsin by Exploiting Dynamic Combinatorial Chemistry
Mondal, M.; Radeva, N.; Köster, H.; Park, A.; Potamitis, C.; Zervou, M.; Klebe, G.; Hirsch A. K. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 3259–3263.

Abstract:



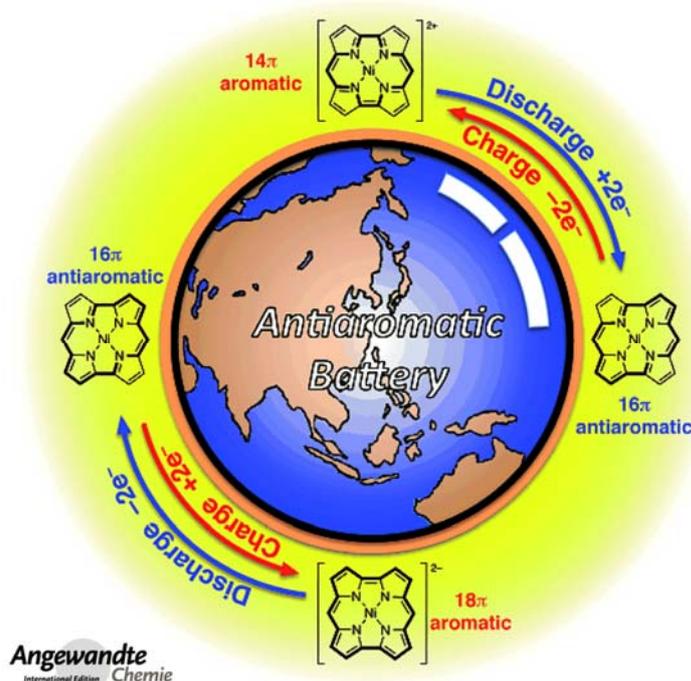
Structure-based design (SBD) can be used for the design and/or optimization of new inhibitors for a biological target. Whereas de novo SBD is rarely used, most reports on SBD are dealing with the optimization of an initial hit. Dynamic combinatorial chemistry (DCC) has emerged as a powerful strategy to identify bioactive ligands given that it enables the target to direct the synthesis of its

strongest binder. We have designed a library of potential inhibitors (acylhydrazones) generated from five aldehydes and five hydrazides and used DCC to identify the best binder(s). After addition of the aspartic protease endothiapsin, we characterized the protein-bound library member(s) by saturation-transfer difference NMR spectroscopy. Cocrystallization experiments validated the predicted binding mode of the two most potent inhibitors, thus demonstrating that the combination of de novo SBD and DCC constitutes an efficient starting point for hit identification and optimization.

- An Antiaromatic Electrode-Active Material Enabling High Capacity and Stable Performance of Rechargeable Batteries

Shin, J.-Y.; Yamada, T.; Yoshikawa, H.; Awaga, K.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2014**, 53, 3096–3101.

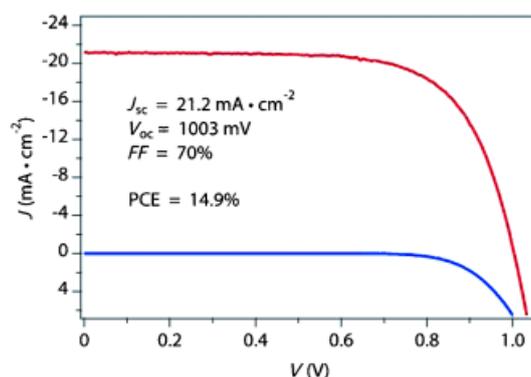
Abstract:



Although aromatic compounds occupy a central position in organic chemistry, antiaromatic compounds have demonstrated little practical utility. Herein we report the application of an antiaromatic compound as an electrode-active material in rechargeable batteries. The performance of dimesityl-substituted norcorrole nickel(II) complex (NiNC) as a cathode-active material was examined with a Li metal anode. A maximum discharge capacity of about 207 mAhg⁻¹ was maintained after 100 charge/discharge cycles. Moreover, the bipolar redox property of NiNC enables the construction of a Li metal free rechargeable battery. The high performance of NiNC batteries demonstrates a prospective feature of stable antiaromatic compounds as electrode-active materials.

- Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting
Pellet, N., Gao, P., Gregori, G., Yang, T.-Y., Nazeeruddin, M. K., Maier, J. and Grätzel, M. *Angew. Chem. Int. Ed.* **2014**, 53, 3151–3157.

Abstract:

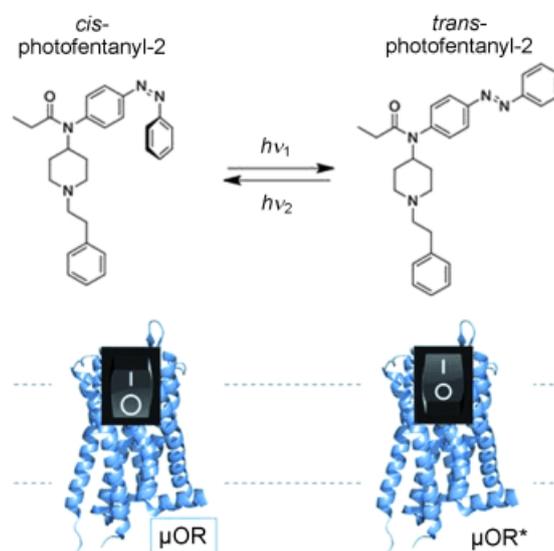


Hybrid organic–inorganic lead halide perovskite APbX_3 pigments, such as methylammonium lead iodide, have recently emerged as excellent light harvesters in solid-state mesoscopic solar cells. An important target for the further improvement of the performance of perovskite-based photovoltaics is to extend their optical-absorption onset further into the red to enhance solar-light harvesting. Herein, we show that this goal can be reached by using a mixture of formamidinium ($\text{HN}=\text{CHNH}_3^+$, FA) and methylammonium (CH_3NH_3^+ , MA) cations in the A position of the APbI_3 perovskite structure. This combination leads to an enhanced short-circuit current and thus superior devices to those based on only CH_3NH_3^+ . This concept has not been applied previously in perovskite-based solar cells. It shows great potential as a versatile tool to tune the structural, electrical, and optoelectronic properties of the light-harvesting materials.

- A Photochromic Agonist for μ -Opioid Receptors

Schönberger, M.; Trauner D. *Angew. Chem. Int. Ed.* **2014**, *53*, 3264–3267.

Abstract:



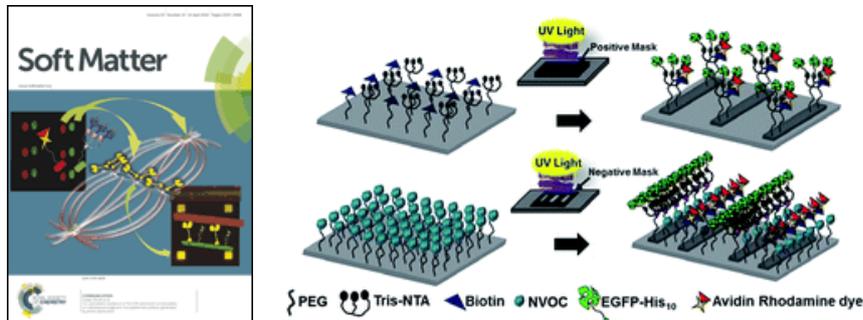
Opioid receptors (ORs) are widely distributed in the brain, the spinal cord, and the digestive tract and play an important role in nociception. All known ORs are G-protein-coupled receptors (GPCRs) of family A. Another well-known member of this family, rhodopsin, is activated by light through the cis/trans isomerization of a covalently bound chromophore, retinal. We now show how an OR can be combined with a synthetic azobenzene photoswitch to gain light sensitivity. Our work extends the reach of photopharmacology and outlines a general strategy for converting Family A GPCRs, which account for the majority of drug targets, into photoreceptors.

- Co- and distinct existence of Tris-NTA and biotin functionalities on individual and adjacent micropatterned surfaces generated by photo-destruction

12

Biswa, A.; Saha, A.; Ghosh, D.; Jana, B.; Ghosh, S. *Soft Matter* **2014**, *10*, 2341-2345.

Abstract:

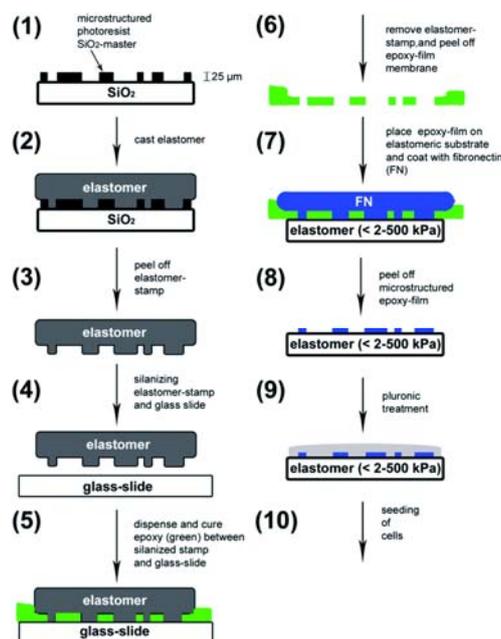


Micropatterned surfaces with Tris-NTA and biotin functionalities both in the same micropattern as well as individually in adjacent micropatterns are generated by UV light illumination through photo-masks. These surfaces are extremely useful for the immobilization of oligohistidine and biotin tagged multiple biomolecules/proteins.

- Defined 2-D microtissues on soft elastomeric silicone rubber using lift-off epoxy-membranes for biomechanical analyses

Hampe, N.; Jonas, T.; Wolters, B.; Hersch, N.; Hoffmann, B.; Merkel, R. *Soft Matter* **2014**, *10*, 2431-2443.

Abstract:



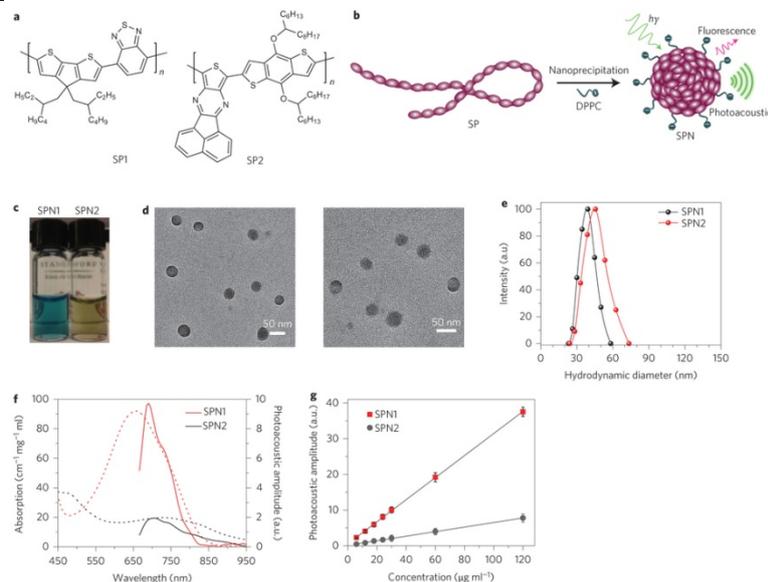
Surface patterning with complex molecules has become a valuable tool in cell biology and biotechnology, as it enables one to control cell shape and function in culture. However, this technique for micro-contact printing is normally performed on rigid substrates, e.g. Petri dishes or glass. Despite the fact that these substrates can easily be patterned they are artificially stiff environments for cells affecting their morphology and function. Those artifacts can be avoided on tissue elasticity resembling substrates, leading to a nature like cell morphology and behavior. However, reproducible patterning of very soft elastomeric substrates is challenging. Here, we

describe a simple and highly accurate method through cavities of lift-off membranes for protein patterning of silicone rubber substrates in an elasticity range down to 1.5 kPa without altering their mechanical properties. Membranes are made of epoxy resin with feature sizes that can be chosen almost arbitrarily including widths down to 5 μm and aspect ratios of 100 and more. Different feature shapes were used to actively manipulate cell adhesion, cell morphology and the actin cytoskeleton on soft substrates. Manipulation of cytoskeletal organization furthermore allowed the comparison of myofibril alignment and cellular forces of cardiac myocytes. These data could show that cell forces are largely unaffected upon active disordering of overall myofibril alignment on a single cell level while aligned multicellular systems generate cell forces in an additive manner.

- Semiconducting polymer nanoparticles as photoacoustic molecular imaging probes in living mice

Pu, K.; Shuhendler, A. J.; Jokerst, J. V.; Mei, J.; Gambhir, S. S.; Bao, Z.; Rao, J. *Nature Nanotechnol.* **2014**, *9*, 233-239.

Abstract:

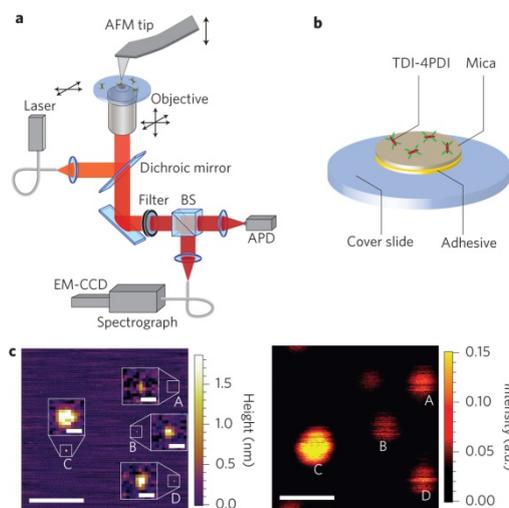


Photoacoustic imaging holds great promise for the visualization of physiology and pathology at the molecular level with deep tissue penetration and fine spatial resolution. To fully utilize this potential, photoacoustic molecular imaging probes have to be developed. Here, we introduce near-infrared light absorbing semiconducting polymer nanoparticles as a new class of contrast agents for photoacoustic molecular imaging. These nanoparticles can produce a stronger signal than the commonly used single-walled carbon nanotubes and gold nanorods on a per mass basis, permitting whole-body lymph-node photoacoustic mapping in living mice at a low systemic injection mass. Furthermore, the semiconducting polymer nanoparticles possess high structural flexibility, narrow photoacoustic spectral profiles and strong resistance to photodegradation and oxidation, enabling the development of the first near-infrared ratiometric photoacoustic probe for in vivo real-time imaging of reactive oxygen species-vital chemical mediators of many diseases. These results demonstrate semiconducting polymer nanoparticles to be an ideal nanoplatform for developing photoacoustic molecular probes.

- Impact of local compressive stress on the optical transitions of single organic dye molecules

Stöttinger, S.; Hinze, G.; Diezemann, G.; Oesterling, I.; Müllen, K.; Basché, T. *Nature Nanotechnol.* **2014**, *9*, 182-186.

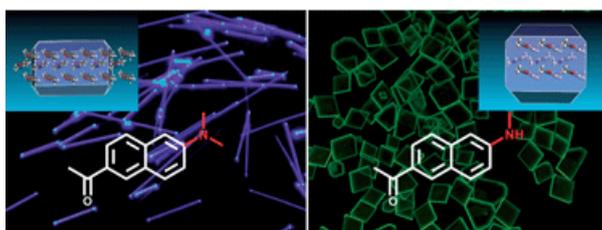
Abstract:



The ability to mechanically control the optical properties of individual molecules is a grand challenge in nanoscience and could enable the manipulation of chemical reactivity at the single-molecule level. In the past, light has been used to alter the emission wavelength of individual molecules or modulate the energy transfer quantum yield between them. Furthermore, tensile stress has been applied to study the force dependence of protein folding/unfolding and of the chemistry and photochemistry of single molecules, although in these mechanical experiments the strength of the weakest bond limits the amount of applicable force. Here, we show that compressive stress modifies the photophysical properties of individual dye molecules. We use an atomic force microscope tip to prod individual molecules adsorbed on a surface and follow the effect of the applied force on the electronic states of the molecule by fluorescence spectroscopy. Applying a localized compressive force on an isolated molecule induces a stress that is redistributed throughout the structure. Accordingly, we observe reversible spectral shifts and even shifts that persist after retracting the microscope tip, which we attribute to transitions to metastable states. Using quantum-mechanical calculations, we show that these photophysical changes can be associated with transitions among the different possible conformers of the adsorbed molecule.

- Tailoring the self-assembled structures and photonic properties of organic nanomaterials
Yao, W.; Zhao, Y. S. *Nanoscale* **2014**, *6*, 3467–3473.

Abstract



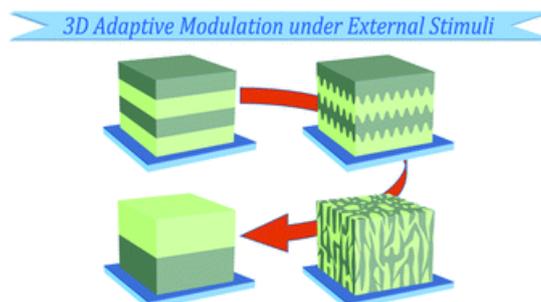
Organic nanomaterials have attracted more and more attention for their applications in nanophotonics due to their high photoluminescence quantum efficiencies, color tunabilities, and size-dependent optical properties. With the distinctive features of photoluminescence, waveguiding and dimensional confinement, different organic nanostructures, such as 0D nanoparticles, 1D nanowires

and 2D nanosheets, have a significant influence on their photonic properties. Therefore, it is of great importance and scientific interest to develop the strategy for tailoring the self-assembled structures with specific photonic behaviors in desired manners. In this mini review, we give a brief review of the recent work on the control of self-assembled organic nanostructures, and the tunable photonic properties of the predetermined structures.

- Self-organization and nanostructural control in thin film heterojunctions

Cataldo, S.; Sartorio, C.; Giannazzo, F.; Scandurra, A.; Pignataro, B. *Nanoscale* **2014**, *6*, 3566–3575.

Abstract:

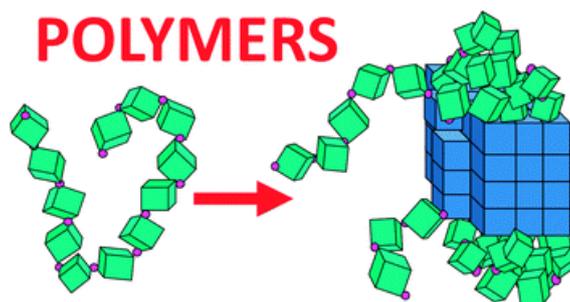


In spite of more than two-decades of studies of molecular self-assembly, the achievement of low cost, easy-to-implement and multi-parameter bottom-up approaches to address the supramolecular morphology in three-dimensional (3D) systems is still missing. In the particular case of molecular thin films, the 3D nanoscale morphology and function are crucial for both fundamental and applied research. Here we show how it is possible to tune the 3D film structure (domain size, branching, etc.) of thin film heterojunctions with nanoscale accuracy together with the modulation of their optoelectronic properties by employing an easy two-step approach. At first we prepared multi-planar heterojunctions with a programmed sequence of nanoscopic layers. In a second step, thermal stimuli have been employed to induce the formation of bulk heterojunctions with bicontinuous and interdigitated phases having a size below the exciton diffusion length. Importantly, the study of luminescence quenching of these systems can be considered as a useful means for the accurate estimation of the exciton diffusion length of semiconductors in nanoscale blends. Finally, nearly a thousand times lower material consumption than spin coating allows a drastic reduction of material wasting and a low-cost implementation, besides the considerable possibility of preparing thin film blends also by employing materials soluble in different solvents.

- Some unique features of polymer crystallization

Reiter, G. *Chem. Soc. Rev.* **2014**, *43*, 2055-2065.

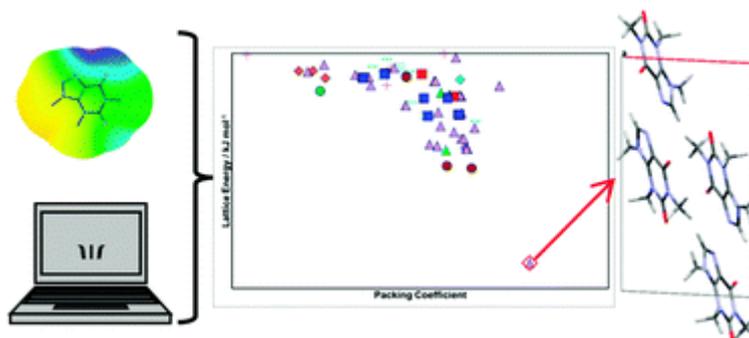
Abstract:



Mono-lamellar single crystals in thin films provide suitable model systems for studying crystallisation of long chain polymers, making distinct differences with respect to small molecules visible. Due to the high viscosity of polymeric melts, transport toward the growth front is slow and the corresponding crystal growth can suitably be followed in time. Besides being able to investigate generic processes in controlling crystal morphology like epitaxial growth or growth front instabilities, thin film studies reveal unique features of polymer crystallisation. In particular, it is possible to observe a logarithmic spatio-temporal evolution of the lamellar crystal thickness, caused by continuous rearrangements leading to regions of differing degrees of meta-stability within polymer single crystals. As a consequence of the kinetically determined lamellar thickness and the corresponding variations in melting temperature, polymer crystals allow for self-seeding, *i.e.*, crystals can be re-grown from a melt which contains a few thermodynamically stable remnants of pre-existing crystals acting as seeds. Hence, when a single crystal is molten, all remnants have a unique orientation and thus also the crystals re-grown from these seeds. The logarithmic time-dependence of the variation in crystal thickness is reflected in a number of seeds decreasing exponentially with increasing seeding temperature. Despite their molecular complexity and some unique features, polymers proved to be valuable systems for detailed studies of crystal growth, allowing testing of theoretical concepts of morphology development.

- Predicting crystal structures of organic compounds
Price, S. L. *Chem. Soc. Rev.* **2014**, *43*, 2098-2111.

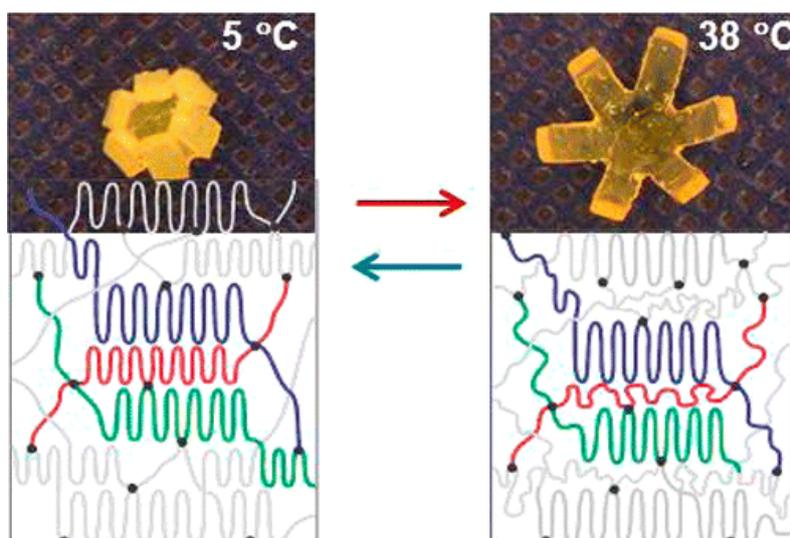
Abstract:



Currently, organic crystal structure prediction (CSP) methods are based on searching for the most thermodynamically stable crystal structure, making various approximations in evaluating the crystal energy. The most stable (global minimum) structure provides a prediction of an experimental crystal structure. However, depending on the specific molecule, there may be other structures which are very close in energy. In this case, the other structures on the crystal energy landscape may be polymorphs, components of static or dynamic disorder in observed structures, or there may be no route to nucleating and growing these structures. A major reason for performing CSP studies is as a complement to solid form screening to see which alternative packings to the known polymorphs are thermodynamically feasible.

- Shapeshifting: Reversible Shape Memory in Semicrystalline Elastomers
Zhou, J.; Turner, S. A.; Brosnan, S. M.; Li, Q.; Carrillo, J.-M. Y.; Nykypanchuk, D.; Gang, O.; Ashby, V. S.; Dobrynin, A. V.; Sheiko, S. *Macromolecules* **2014**, *47*, 1768–1776.

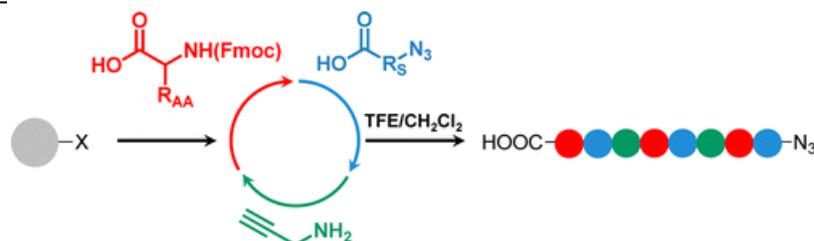
Abstract:



We present a general strategy for enabling reversible shape transformation in semicrystalline shape memory (SM) materials, which integrates three different SM behaviors: conventional one-way SM, two-way reversible SM, and one-way reversible SM. While two-way reversible shape memory (RSM) is observed upon heating and cooling cycles, the one-way RSM occurs upon heating only. Shape reversibility is achieved through partial melting of a crystalline scaffold which secures memory of a temporary shape by leaving a latent template for recrystallization. This behavior is neither mechanically nor structurally constrained, thereby allowing for multiple switching between encoded shapes without applying any external force, which was demonstrated for different shapes including hairpin, coil, origami, and a robotic gripper. Fraction of reversible strain increases with cross-linking density, reaching a maximum of ca. 70%, and then decreases at higher cross-linking densities. This behavior has been shown to correlate with efficiency of securing the temporary shape.

- Primary Structure Control of Oligomers Based on Natural and Synthetic Building Blocks
Chan-Seng, D.; Lutz, J.-F. *ACS Macro Lett.* **2014**, *3*, 291–294.

Abstract:

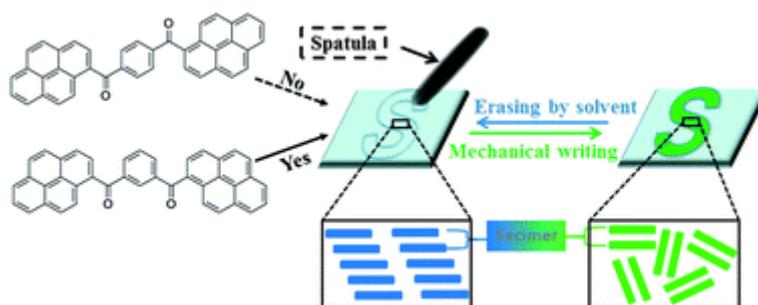


Solid-phase synthesis was exploited for the preparation of oligomers constructed from natural and synthetic building blocks by combining the formation of amide bonds and copper-assisted alkyne–azide cycloaddition reactions extending the variety of oligomers with well-defined primary structures accessible through this technique and providing control over the spacing between amino acids.

- Bis-pyrene-based supramolecular aggregates with reversibly mechanochromic and vapochromic responsiveness

Li, W.; Wang, L.; Zhang, J.-P.; Wang, H. *J. Mater. Chem. C.* **2014**, *2*, 1887–1892.

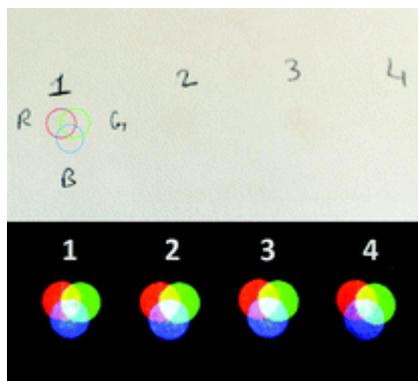
Abstract:



We have designed and synthesized bis-pyrene derivatives, where the two pyrene units are connected by para-phthaloyl (p-BP) and meta-phthaloyl (m-BP) linkers. The compound p-BP in the condensed state does not respond to mechanical shearing. The fluorescence emission of supramolecular aggregates of compound m-BP in the condensed state shows reversibly mechanochromic and vapochromic behavior. The dual-responsive phenomena were characterized by UV-vis and fluorescence spectroscopy. Furthermore, the changes of the supramolecular structures of p-BP and m-BP were analyzed by powder X-ray diffraction (XRD) and time-resolved fluorescence spectroscopy, which indicated that the dual-responsive mechanism is related to their intermolecular interactions and packing modes. Scanning electron microscopy (SEM) was utilized to study the morphology of m-BP in the different emission states. Finally, the multi-cycled information recording and erasing on m-BP-based film was demonstrated.

- Red-green-blue printing using luminescence-upconversion inks
Manikyarao Meruga, J.; Baride, A.; Cross, W.; Kellara, J. J.; May, P. S. *J. Mater. Chem C* **2014**, *2*, 2221–2227.

Abstract:



Recent advances in producing pre-defined 2D patterns of upconversion nanophosphors via photolithography and printing techniques present new opportunities for the use of these materials in security applications. Here, we demonstrate an RGB additive-color printing system that produces highly-resolved pre-defined patterns that are invisible under ambient lighting, but which are viewable as luminescent multi-color images under NIR excitation. Patterns are generated by independent deposition of three primary-color (red, green and blue) upconverting inks using an aerosol jet printer. The primary-color inks are printed as isolated and overlapping features to produce images that simultaneously emit red, green, blue, cyan, magenta, yellow and white upconversion luminescence. The dependence of the chromaticity of certain secondary colors (cyan and magenta) and white on NIR excitation power density can be exploited as an additional authentication feature. The development of an RGB upconversion printing system paves the way for an entirely new arena in security printing.