

Dual Nickel and Lewis Acid Catalysis for Cross-Electrophile Coupling: the Allylation of Aryl Halides with Allylic Alcohols

Jia, X.-G.; Guo, P.; Duan, J.; Shu, X.-Z.* [Chem. Sci., 2018, 9, 640-645.](#)

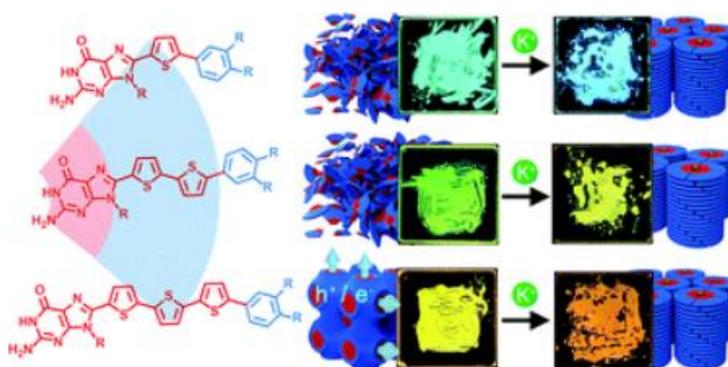


Controlling the selectivity in cross-electrophile coupling reactions is a significant challenge, particularly when one electrophile is much more reactive. We report a general and practical strategy to address this problem in the **reaction between reactive and unreactive electrophiles** by a **combination of nickel and Lewis acid catalysis**. This strategy is used for the coupling of aryl halides with allylic alcohols **to form linear allylarenes selectively**. The reaction tolerates a wide range of functional groups (*e.g.* silanes, boronates, anilines, esters, alcohols, and various heterocycles) and works with various allylic alcohols. Complementary to most current routes for the C3 allylation of an unprotected indole, this method provides access to C2 and C4–C7 allylated indoles. Preliminary mechanistic experiments reveal that the reaction might start with an aryl nickel intermediate, which then reacts with Lewis acid activated allylic alcohols in the presence of Mn.

Comment: In continuity with the article I proposed for week 16, you can find above an article describing a new methodology for the coupling of aryl halides with allylic alcohols. This approach is interesting because it seems to be scalable and takes place under mild conditions. Numerous examples are presented in the article in order to attest the efficiency of this method. The authors are still optimizing this approach in order to extend it to a higher number of molecules and systems.

Guanine–Oligothiophene Conjugates: Liquid-Crystalline Properties, Photoconductivities and Ion-Responsive Emission of Their Nanoscale Assemblies

Gan, K. P.; Yoshio, M.*; Sugihara, Y.; Kato, T.* [Chem. Sci., 2018, 9, 576-585.](#)



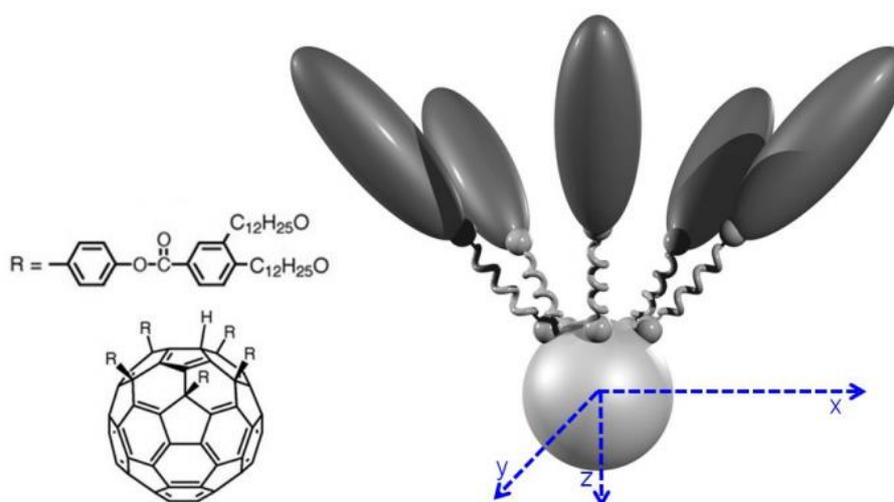
We here report the **supramolecular self-assembly** of hydrogen-bonded motifs for the development of nanostructured materials that exhibit dynamic functions such as stimuli-responsive properties and **molecular recognition behaviour**. We have designed and synthesised new

thermotropic bicontinuous and **columnar liquid-crystalline (LC) guanine–oligothiophene conjugates tethered** with **lipophilic chains**, which exhibit ionic, electronic and photoluminescence properties. Their potassium salt complexes self-assemble into thermotropic columnar LC phases. Time-of-flight photoconductivity measurements have revealed that the guanine–oligothiophene conjugates in the LC states possess charge transport abilities with either electron or ambipolar mobility values of 10^{-4} to 10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Furthermore, we have found that the complexation of potassium ions with the guanine motif could lead not only to structural change and thermal stabilization of the LC phases but also to a photoluminescence colour change in the solid states. The strategy presented in this work could lead to the design of new functional LC materials that could potentially be applicable as sensors and electronic devices.

Comment: I thought that this article may be useful for those who may work on liquid crystals. Indeed, stimuli-responsive liquid crystals have been synthesized and characterized (FTIR was used to control the response of the compounds to the presence of K^+). I don't know if it would be possible but, we (and by we, I mean Alexis) could use them with our motors to create some photoresponsive semiconductor materials. It is just pure speculation at the moment.

Molecular Organizations of Conical Mesogenic Fullerenes

Orlandi, S.*; Zannoni, C. [Soft Matter 2018, ASAP.](#)

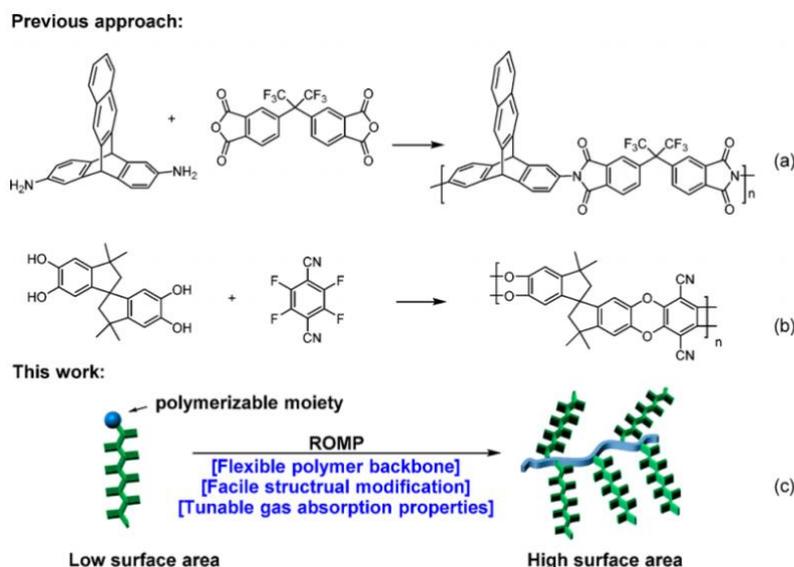


We have studied liquid crystal phases formed by **fullerenes functionalized with mesogenic groups** yielding a cone-shape molecular structure. We have modelled these shuttlecock-like molecules with a set of Gay-Berne particles grafted with flexible springs to a spherical core and we have studied, using Monte Carlo simulations, **their phase organization**, also with a view to examining their possible use as candidate organic photovoltaic materials. We have found that, on cooling from the isotropic phase, the system forms a columnar phase, like in the experimental work of Kato and coworkers [Kato et al., [Nature, 419, 702, 2002](#)]. However the phase is made of polar stacks extending not more than about ten molecules, which could limit their usefulness in enhancing and directing charge transport in possible photovoltaic applications.

Comment: The work of modelisation is quite interesting and surprisingly understandable even if I am not into computer simulations. However, what is more interesting to me is the molecule by itself, that is, a shuttlecock-like mesogenic molecule composed of fullerene. The authors refer to [this work](#) for the experimental chemistry part, but more recent articles are presented in their references.

Porous Organic Polymers via Ring Opening Metathesis Polymerization

Zhao, Y.; He, Y.; Swager, T. M.* *ACS Macro Lett.* **2018**, *7*, 300–304.



Highly porous and **solution processable** organic polymers that can be structurally tailored for various applications are in great demand. Previously reported strategies to prepare porous polymers usually rely on a high level of crosslinking or structurally rigid polymer backbones. We now demonstrate that one-dimensional linear polymers with flexible backbones prepared through ring opening metathesis polymerization can be highly porous. This new strategy allows facile access to diversified porous organic polymers having **tunable mechanical/chemical properties** bearing different functionalities.

Comment: Due to their inherent rigidity, porous polymer are usually difficult to process, despite their interesting properties (e.g. gas absorption). The strategy explored by the authors relies on a **flexible backbone with the porous moieties as side chains**. Hence, the resulting polymer is more easily processable, and, more importantly, copolymers with tunable properties can be prepared.

Optical Sensing of Aromatic Amino Acids and Dipeptides by a Crown-Ether-Functionalized Perylene Bisimide Fluorophore

Weißenstein, A; Saha-Möller, C. R; Würthner, F* *Chem. Eur. J.* **2018**, *ASAP*.

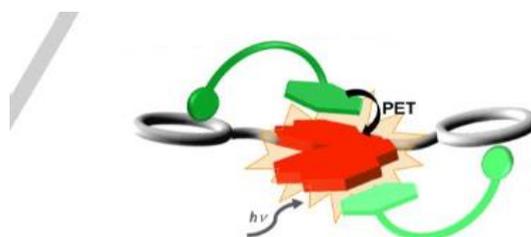


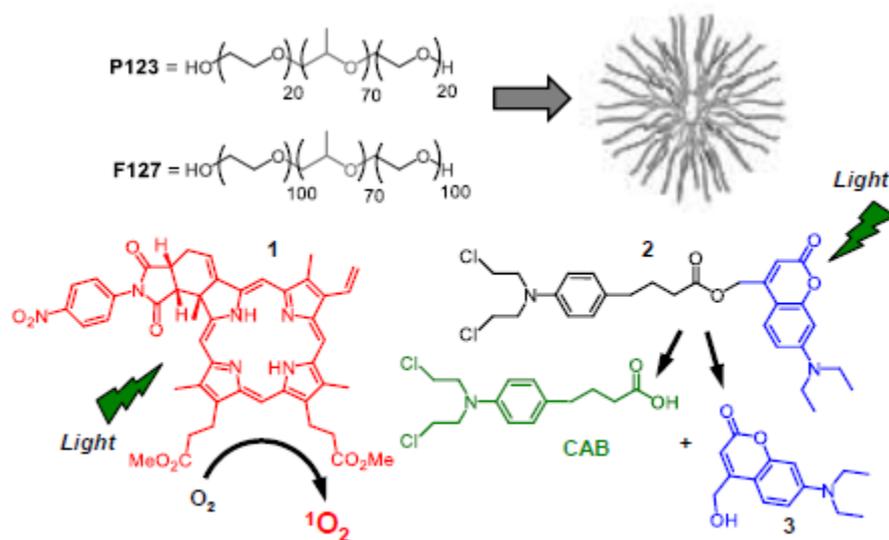
Figure 1. Schematic illustration of ditopic binding mode in a 1:2 host-guest complex of aromatic amino acid or dipeptide with crown ether bearing PBI receptor and fluorescence quenching by photoinduced electron transfer from electron-rich aromatic group of guest to the electron-poor PBI host (red: PBI core, grey: crown ether, green: aromatic amino acid or dipeptide).

We have studied in detail the host-guest binding properties of a crown ether equipped, fluorescent perylene bisimide (PBI) receptor with a series of aromatic amino acids and dipeptides by UV/Vis, fluorescence and NMR spectroscopy. Fluorescence titration experiments showed that electron-rich aromatic amino acids and dipeptides strongly quench the fluorescence of the electron-poor PBI host molecule. Benesi-Hildebrand plots of fluorescence titration data confirmed the formation of host-guest complexes with 1:2 stoichiometry. Binding constants determined by global analysis of UV/Vis and fluorescence titration experiments revealed values between 10^3 M^{-1} and 10^5 M^{-1} in acetonitrile/methanol (9:1) at 23 °C. These data showed that amino acid L-Trp having an indole group and dipeptides containing this amino acid bind to the PBI receptor more strongly than other amino acids and dipeptides investigated here. For dipeptides containing L-Trp or L-Tyr, the binding strength is dependent on the distance between the ammonium group and the aromatic unit of the amino acids and dipeptides leading to a strong sensitivity for Ala-Trp dipeptide. 1D and 2D NMR experiments also corroborated 1:2 host-guest complexation and indicated formation of two diastereomeric species of host-guest complexes. Our studies have shown that a properly functionalized PBI fluorophore functions as a molecular probe for the optical sensing of aromatic amino acids and dipeptides.

Comment: They describe a fluorescent probe to detect aromatic amino acids and dipeptides. The sensor modifies its optical properties through host-guest interactions with the target molecules

Light-Controlled Simultaneous “On Demand” Release of Cytotoxic Combinations for Bimodal Killing of Cancer Cells

Tessaro, A. L; Fraix, A; Failla, M; Cardile, V; Graziano, A. C. E; Estevão, B. M; Rescifina, A; Sortino, S.* [Chem. Eur. J 2018, ASAP.](#)



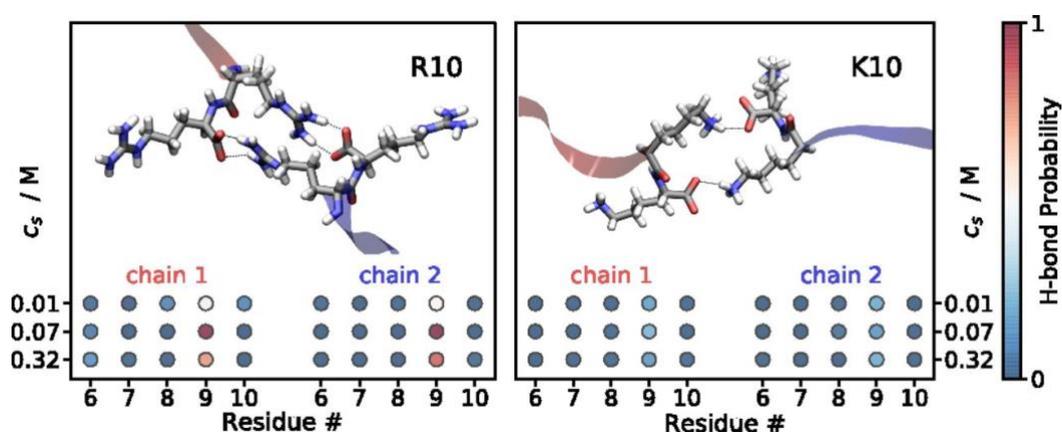
This contribution reports a novel entirely photocontrolled nanoplatform consisting in a binary mixture of Pluronic copolymers self-assembling in core-shell micelles and co-entrapping two photoactivatable components: a benzoporphyrin photosensitizer for photodynamic therapy (PDT) and a coumarin photocaged chemotherapeutic Chlorambucil (CAB). The resulting supramolecular micellar assembly is *ca.* 30 nm in diameter with polydispersity index below 0.1, stable for more than 72 h and exhibits excellent preservation of the photochemical properties of the two

photoresponsive components, despite they are confined within the same host nanocarrier. The appropriate regulation of the relative concentrations makes these components able to absorb the visible light in comparable amount, leading to the effective simultaneous photogeneration of singlet oxygen and photo-triggered decaging of CAB. This “on demand” release of cytotoxic combinations results in an amplified anticancer activity against MCF-7 human breast adenocarcinoma cells.

Comment: A nice self-assembled system made by a copolymer that can release cytotoxic singlet oxygen by photoactivation.

The C-Terminal Extension Landscape of Naturally Presented HLA-I Ligands

Tesei, G.; Vazdar, M.; Jensen, M. R.; Cragnell, C.; Mason, P. E.; Heyda, J.; Skepö, M.; Jungwirth, P.; Lund, M.* *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 11428.

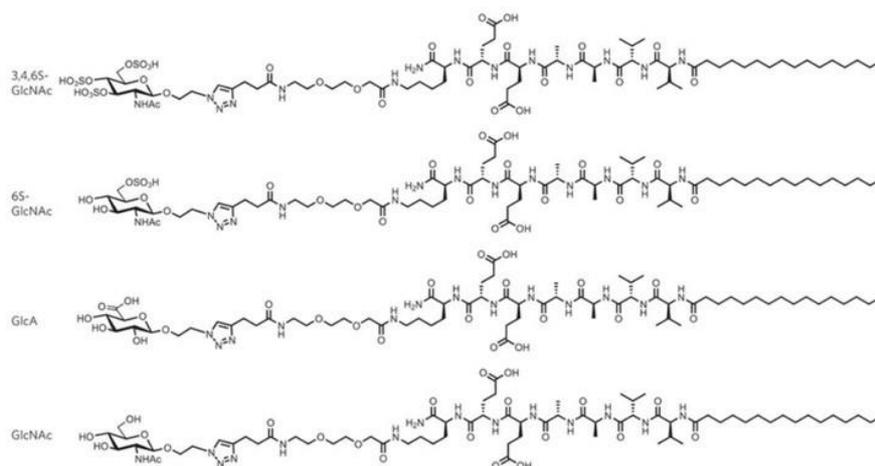


Small-angle X-ray scattering (SAXS) measurements reveal a striking difference in intermolecular interactions between two short highly charged peptides—deca-arginine (R10) and deca-lysine (K10). Comparison of SAXS curves at high and low salt concentration shows that R10 self-associates, while interactions between K10 chains are purely repulsive. The self-association of R10 is stronger at lower ionic strengths, indicating that the attraction between R10 molecules has an important electrostatic component. SAXS data are complemented by NMR measurements and potentials of mean force between the peptides, calculated by means of umbrella-sampling molecular dynamics (MD) simulations. All-atom MD simulations elucidate the origin of the R10–R10 attraction by providing structural information on the dimeric state. The last two C-terminal residues of R10 constitute an adhesive patch formed by stacking of the side chains of two arginine residues and by salt bridges formed between the like-charge ion pair and the C-terminal carboxyl groups. A statistical analysis of the Protein Data Bank reveals that this mode of interaction is a common feature in proteins.

Comment: Arginine-rich cell-penetrating peptides are promising candidates for intracellular drug delivery. These highly-charged cationic peptides have the **ability to spontaneously traverse biological membranes**. (The mechanism for this direct mode of entry is not yet fully understood.) In this report, **Arg₁₀** is shown to **self-associate** at low-to-intermediate ionic strengths, owing to an interaction mode which is present in the structure of a significant number of proteins. This interaction might also enhance the bio-availability of this oligopeptide.

Sulfated Glycopeptide Nanostructures for Multipotent Protein Activation

Lee, S. S.; Fyrner, T.; Chen, F.; Álvarez, Z.; Sleep, E.; Chun, D. S.; Weiner, J. A.; Cook, R. W.; Freshman, R. D.; Schallmo, M. S.; Katchko, K. M.; Schneider, A. D.; Smith, J. T.; Yun, C.; Singh, G.; Hashmi, S. Z.; McClendon, M. T.; Yu, Z.; Stock, S. R.; Hsu, W. K.; Hsu, E. L.; Stupp, S. I.* [Nat. Nanotechnol. 2017, 12, 821.](#)

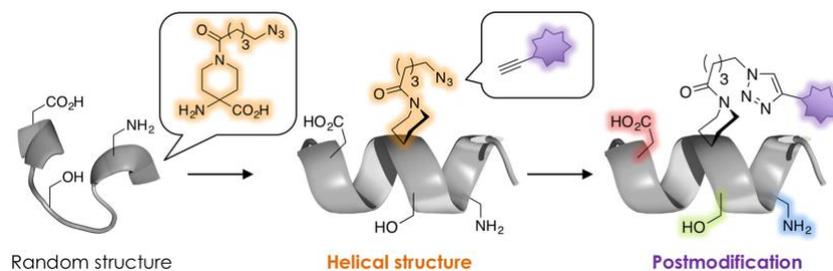


Biological systems have evolved to utilize numerous proteins with capacity to bind polysaccharides for the purpose of optimizing their function. A well-known subset of these proteins with binding domains for the highly diverse sulfated polysaccharides are important growth factors involved in biological development and tissue repair. We report here on supramolecular sulfated glycopeptide nanostructures, which display a trisulfated monosaccharide on their surfaces and bind five critical proteins with different polysaccharide-binding domains. Binding does not disrupt the filamentous shape of the nanostructures or their internal β -sheet backbone, but must involve accessible adaptive configurations to interact with such different proteins. The glycopeptide nanostructures amplified signalling of bone morphogenetic protein 2 significantly more than the natural sulfated polysaccharide heparin, and promoted regeneration of bone in the spine with a protein dose that is 100-fold lower than that required in the animal model. These highly bioactive nanostructures may enable many therapies in the future involving proteins.

Comment: Combining glycans with proteins is a well-established natural partnership common to many functions of biological systems e.g. neonatal Fc receptors recognize glycans on the surface of antibodies. Using this motif, Stupp *et al* have designed a bioactive nanomaterial that is exceptionally good at stimulating bone regeneration. They studied in vivo the effect of the supramolecular nanomaterial on the activity of the growth factor BMP-2. They report that **100 times less of the protein was needed for a successful spinal fusion in an animal model.**

Preorganized Cyclic α,α -Disubstituted α -Amino Acids Bearing Functionalized Side Chains That Act as Peptide-Helix Inducers

Kobayashi, H.; Misawa, T.; Matsuno, K.; Demizu, Y.* [J. Org. Chem. 2017, 82, 10722.](#)

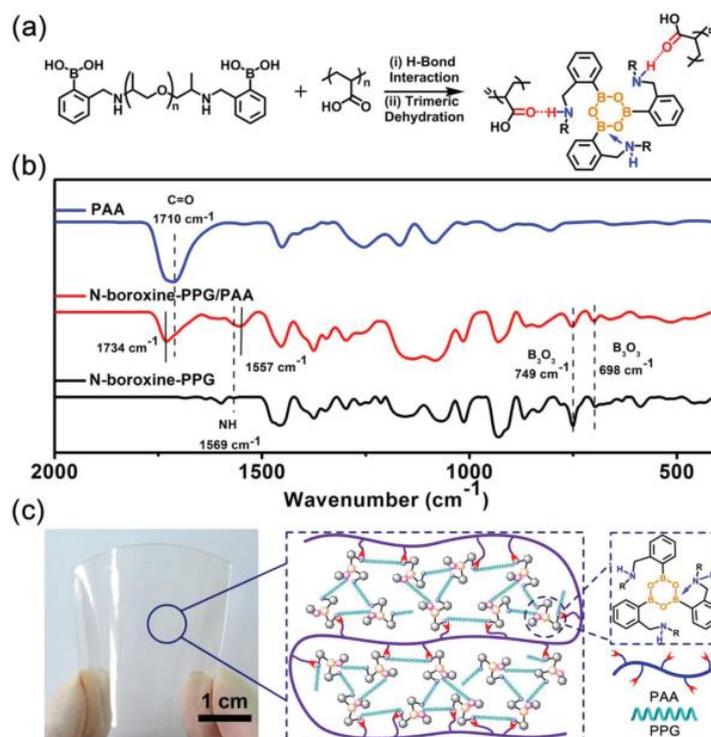


Preorganized cyclic α,α -disubstituted α -amino acids (dAA) bearing functionalized side chains that acted as peptide-helix inducers, which could be used for solid-phase peptide synthesis, were designed and synthesized. Furthermore, a helical octapeptide with the following amino acid sequence was prepared, and its preferred conformation was analyzed based on its CD spectra: $AC-X^1EYSAX^2KA-NH_2$ (**11**: $X^1 = \text{A}pi^{C4N3}$, $X^2 = \text{Ac}_6c$). The side-chain azido functional group of peptide **11** was efficiently converted to various 1,2,3-triazole groups via Huisgen 1,3-dipolar cycloaddition reactions involving different types of alkynes. The new cyclic dAA derivatives, which combine the advantages of conformational preorganization and side-chain functional groups, should prove to be a useful tool for the further development of biologically active peptides.

Comment: Helical structures in proteins are one of the most sought-after secondary structures for the development of biologically active peptides. Several promising peptide therapeutics currently in clinical trials (affibodies, alphabodies or high-mobility group protein 1 class) that target different protein-protein and protein-DNA interactions all share this common feature. **Mimics that can stabilize the helical structure** are very important whenever a mutation necessary for target binding leads to loss of the preferred secondary structure.

Room-Temperature Self-Healing and Recyclable Tough Polymer Composites Using Nitrogen-Coordinated Boroxines

Bao, C.; Jiang, Y.; Zhang, H.; Lu, X.; Sun, J.* *Adv. Funct. Mater.* **2018**, 1800560.

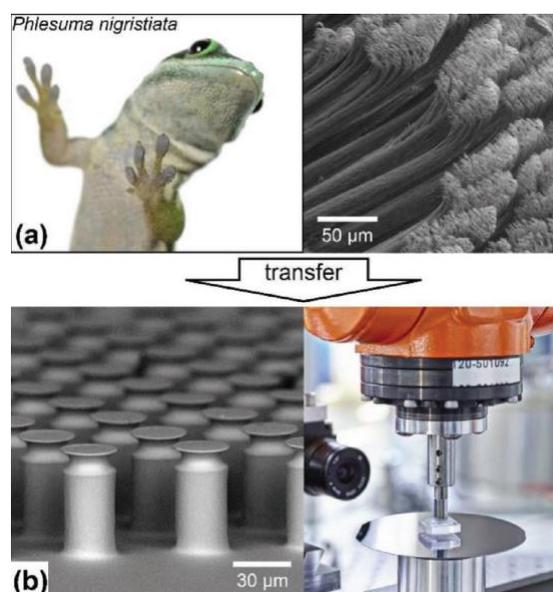


In this paper, **nitrogen-coordinated boroxines** are exploited for the fabrication of self-healing and recyclable polymer composites with enhanced mechanical properties. The 3D polymer networks cross-linked with nitrogen-coordinated boroxines are first synthesized through the trimerization of ortho-aminomethyl-phenylboronic acid groups at the terminals of poly(propylene glycol) (PPG) chains, and subsequently, the mechanically robust polymer composites are fabricated by utilizing the complexation of nitrogen-coordinated boroxine-containing PPG (N-boroxine-PPG) with poly(acrylic acid) (PAA) and hydrogen-bonding interactions between them. The N-boroxine-PPG is soft with a tensile strength of 0.19 MPa, whereas the tensile strengths of N-boroxine-PPG/PAA composites can be tailored to range from 1.7 to 12.7 MPa by increasing the PAA contents in the polymer composites. It is revealed that the **amine ligands can facilitate the formation and dissociation of nitrogen-coordinated boroxines at room temperature**. Moreover, the reversibility of nitrogen-coordinated boroxines and hydrogen-bonding interactions enable multiple cycles of healing and recycling of the damaged N-boroxine-PPG/PAA composites. The healed and recycled N-boroxine-PPG/PAA polymer composites regain most of their mechanical strength.

Comment: The incorporation of nitrogen-donor moieties into the boroxines-based system facilitates the dynamic exchange between boroxines and boronic acids at room temperature. And the formation of six-membered ring provides structural stability to increase the mechanical strength of the gel. The strategy can compensate the low chain mobility originating from the stiffness of the polymer, which limits the self-healing property, by the highly reversible nitrogen-coordinated boroxines dynamic covalent bonds.

Engineering Micropatterned Dry Adhesives: From Contact Theory to Handling Applications

Hensel, R.; * Moh, K.; Arzt, E. [Adv. Funct. Mater. 2018, 1800865.](#)



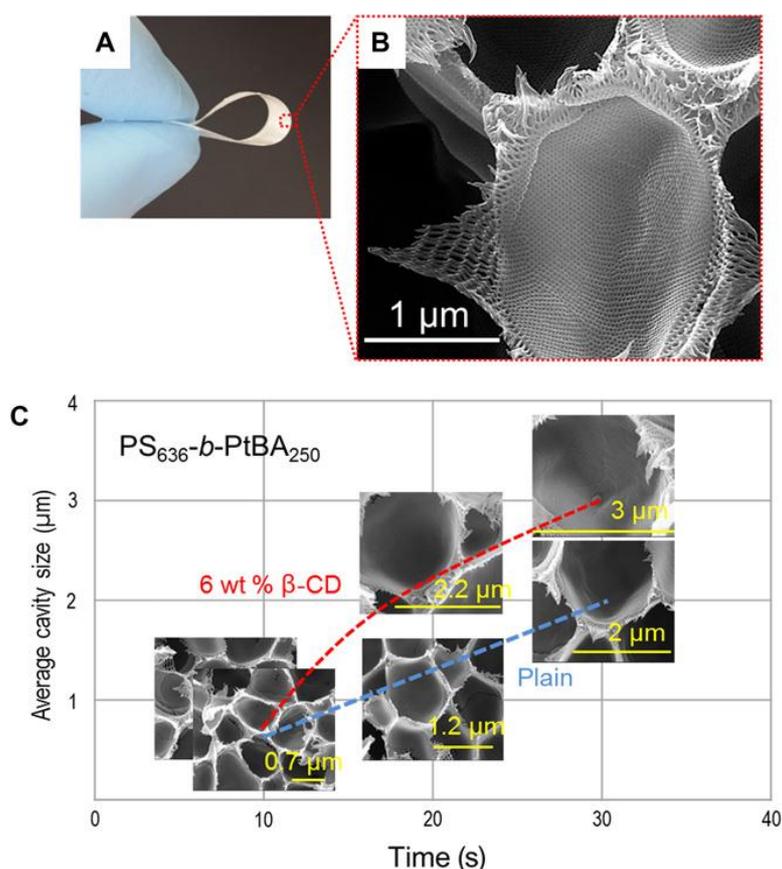
Reversible adhesion is the key functionality to grip, place, and release objects nondestructively. Inspired by nature, micropatterned dry adhesives are promising candidates for this purpose and have attracted the attention of research groups worldwide. Their enhanced adhesion compared to nonpatterned surfaces is frequently demonstrated. An important conclusion is that the **contact mechanics involved is at least as important as the surface energy and chemistry**. In this

paper, the roles of the contact geometry and mechanical properties are reviewed. With a focus on applications, the effects of substrate roughness and of temperature variations, and the long-term performance of micropatterned adhesives are discussed. The paper provides a link between the current, detailed understanding of micropatterned adhesives and emerging applications.

Comment: A brief feature article about a bio-inspired research field – reversible adhesion. It shows the connections between the studies of structures, principle of interactions and further applications. The study on the weak van der Waals interactions were performed at the microscopic scale, but more weak interactions are still waiting to be explored at a scale that is much smaller than this.

Artificial 3D Hierarchical and Isotropic Porous Polymeric Materials

Chisca, S.; Musteata, V. E.; Sougrat, R.; Behzad, A. R.; Nunes, S. P.* [*Science Advances*, 2018, 4, eaat0713.](#)



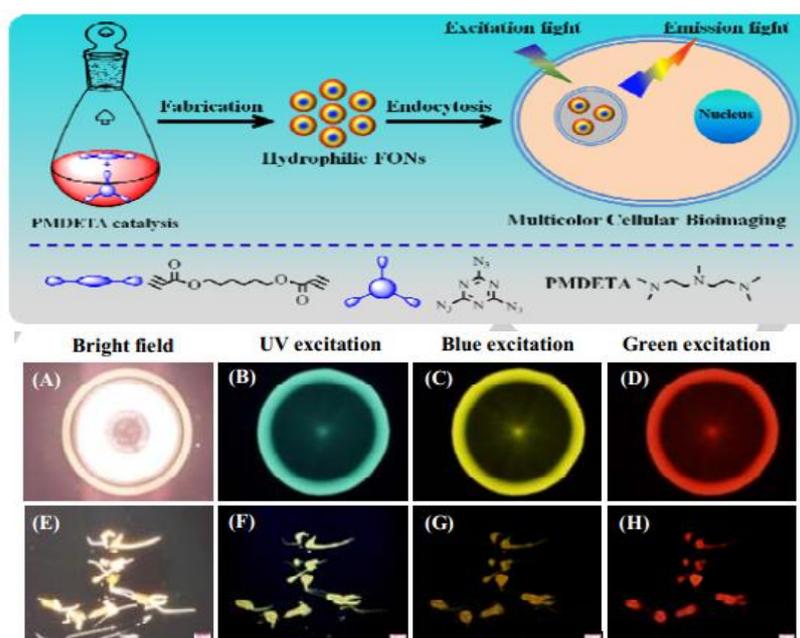
Hierarchical porous materials that replicate complex living structures are attractive for a wide variety of applications, ranging from storage and catalysis to biological and artificial systems. However, the preparation of structures with a high level of complexity and long-range order at the mesoscale and microscale is challenging. We report a simple, nonextractive, and nonreactive method used to prepare three-dimensional porous materials that mimic biological systems such as marine skeletons and honeycombs. This method exploits the concurrent occurrence of the self-assembly of block copolymers in solution and macrophase separation by nucleation and growth. We obtained a long-range order of micrometer-sized compartments. These compartments are interconnected by ordered cylindrical nanochannels. The new approach is demonstrated using polystyrene-*b*-poly(*t*-butyl acrylate), which can be further explored for a broad range of

applications, such as air purification filters for viruses and pollution particle removal or growth of bioinspired materials for bone regeneration.

Comment: They show a simple method to obtain flexible films with complex hierarchical and isotropic porous structures within 5 min. These films are constituted by micrometer-sized compartments which are interconnected by long-range hexagonally ordered nanochannels.

An Unconventional Polymerization Route to Hydrophilic Fluorescent Organic Nanoparticles for Multicolor Cellular Bioimaging

Ban, Q.; Kong, J.; Hou, Y.; Chen, J.*; Sun, W.; Zhang, X.; Wu, S.* [Chem. Asian J. 2018, ASAP.](#)

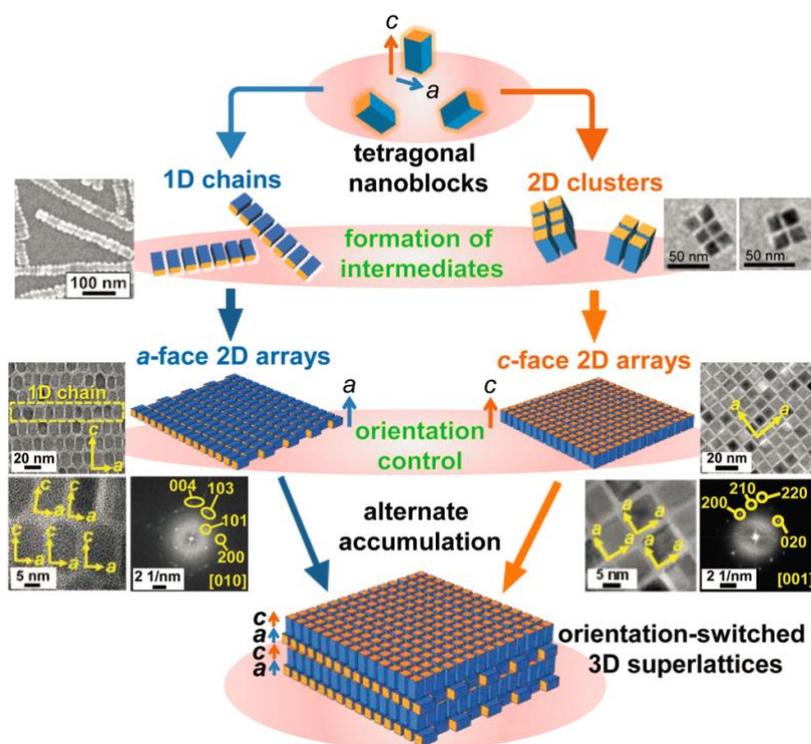


We demonstrated an unconventional polymerization route to synthesize hydrophilic fluorescent organic nanoparticles (FONs) for multicolor cellular bioimaging in this contribution. Actually, it benefits from our unexpected discovery of a rapid polymerization reaction between 1, 6-hexanediol dipropiolate and 2, 4, 6-triazide-1, 3, 5-triazine under the catalysis of N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA). Interestingly, the 2, 4, 6-triazide-1, 3, 5-triazine and PMDETA system can also induce rapid free radical polymerization **at room temperature**. The as-prepared FONs exhibited promising water solubility and stability with an average diameter of 20 nm. The excitation wavelength-dependent fluorescent properties enable the FONs with **blue, yellow, and red fluorescent emission under UV**, blue, and green excitation, respectively. The cytotoxicity of FONs was investigated by Cell Counting Kit (CCK-8) assay, indicating a good biocompatibility. More importantly, the cell uptake experiment verified the FONs were excellent fluorescent nanoprobes for multicolor cellular bioimaging. Therefore, this unconventional route provides a novel fabrication strategy of the highly hydrophilic FONs for biomedical applications.

Comment: The facile fabrication of hydrophilic fluorescent organic nanoparticles was quick, occurs catalytically at room temperature, and is efficient, scalable, and convenient. The novel fabrication route of hydrophilic fluorescent organic nanoparticle may have great potential for future biomedical applications.

Layer-by-layer Manipulation of Anisotropic Nanoblocks: Orientation-switched Superlattices Through Orthogonal Stacking of A and C Directions

Nakagawa, Y.; Matsumoto, R.; Kageyama, H.; Oaki, Y.; Imai, H.* [Nanoscale 2018, ASAP](#).

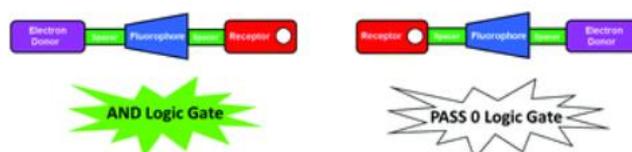


Nanometer-scale switching of the crystallographic orientation enables production of novel superlattices for exploration of new functions. Elaborate multilayered architectures of Mn_3O_4 nanocuboids were constructed by a convective self-assembly process. The nanometric cuboids were accumulated into orientation-switched superlattices on micrometric scales by controlling the a and c directions of the tetragonal crystal periodically. The orthogonal stacking of the tetragonal nanoblocks was achieved through the layer-by-layer manipulation process of two types of 2D arrays with different orientations.

Comment: Elaborated 3D superlattices were constructed using an alternating process of accumulating a-face and c-face 2D arrays through a convective self-assembly process. It is a nice work using the layer-by-layer assembly.

Molecular Engineering of Logic Gate Types by Module Rearrangement in 'Pourbaix Sensors': The Effect of Excited-state Electric Fields

Spiteri, J. C.; Denisov, S. A.; Jonusauskas, G.; Klejna, S.; Szacilowski, K.; McClenaghan, N. D.; Magri, D. C.* [Org. Biomol. Chem. 2018, ASAP](#).

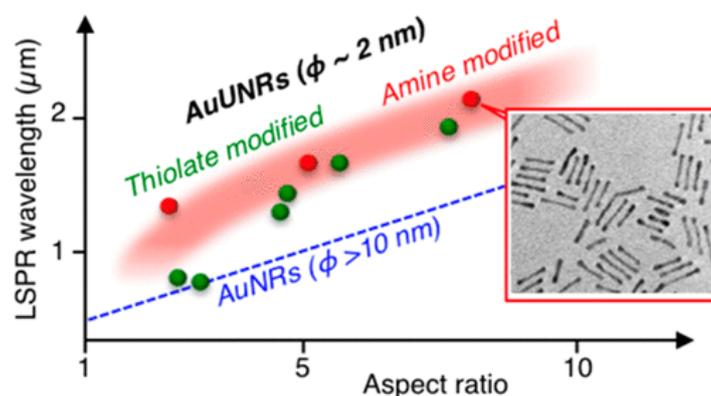


Two types of fluorescent logic gates are accessed from two different arrangements of the same modular components, one as an AND logic gate (1) and the other as a PASS 0 logic gate (2). The logic gates were designed with an 'electron-donor-spacer1-fluorophore-spacer2-receptor' format and demonstrated in 1 : 1 (v/v) methanol/water. The molecules consist of ferrocene as the electron donor, 4-aminonaphthalimide as the fluorophore and a tertiary alkylamine as the receptor. In the presence of high H^+ and Fe^{3+} levels, regioisomers 1a and 1b switch 'on' as AND logic gates with fluorescence enhancement ratios of 16-fold and 10-fold, respectively, while regioisomers 2a and 2b are functionally dormant, exhibiting no fluorescence switching. The PASS 0 logic of 2a and 2b results from the transfer of an electron from the excited state fluorophore to the ferrocenium unit under oxidising conditions as predicted by DFT calculations. Time-resolved fluorescence spectroscopy provided lifetimes of 8.3 ns and 8.1 ns for 1a and 1b, respectively. The transient signal recovery rate of 1b is ~ 10 ps while that of 2b is considerably longer on the nanosecond timescale. The divergent logic attributes of 1 and 2 highlight the importance of field effects and opens up a new approach for regulating logic-based molecules.

Comment: The rearrangement of the donor and acceptor module has a huge effect on the two-input logic gates for H^+ and Fe^{3+} . It helps to consider the regulatory directional electron transfer phenomenon when designing molecules.

Gold Ultrathin Nanorods with Controlled Aspect Ratios and Surface Modifications: Formation Mechanism and Localized Surface Plasmon Resonance

Takahata, R. ; Yamazoe, S. ; Koyasu, K. ; Imura, K. ; Tsukuda, T.* *J. Am. Chem. Soc.* **2018**, *ASAP*.



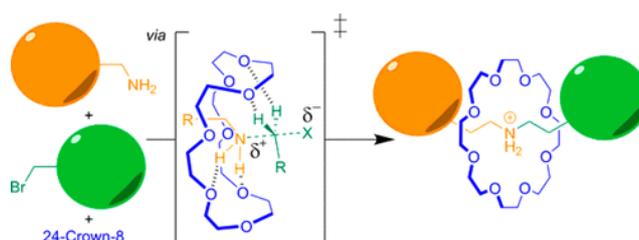
We synthesized gold ultrathin nanorods (AuUNRs) by slow reductions of gold(I) in the presence of oleylamine (OA) as a surfactant. Transmission electron microscopy revealed that the lengths of AuUNRs were tuned in the range of 5–20 nm while keeping the diameter constant (~ 2 nm) by changing the relative concentration of OA and Au(I). It is proposed on the basis of time-resolved optical spectroscopy that AuUNRs are formed via the formation of small (< 2 nm) Au spherical clusters followed by their one-dimensional attachment in OA micelles. The surfactant OA on AuUNRs was successfully replaced with glutathionate or dodecanethiolate by the ligand exchange approach. Optical extinction spectroscopy on a series of AuUNRs with different aspect ratios (ARs) revealed a single intense extinction band in the near-IR (NIR) region due to the longitudinal localized surface plasmon resonance (LSPR), the peak position of which is red-shifted with the AR. The NIR bands of AuUNRs with $AR < 5$ were blue-shifted upon the ligand exchange from

OA to thiolates, in sharp contrast to the red shift observed in the conventional Au nanorods and nanospheres (diameter >10 nm). This behavior suggests that the NIR bands of thiolate-protected AuUNRs with AR < 5 are not plasmonic in nature, but are associated with a single-electron excitation between quantized states. The LSPR band was attenuated by thiolate passivation that can be explained by the direct decay of plasmons into an interfacial charge transfer state (chemical interface damping). The LSPR wavelengths of AuUNRs are remarkably longer than those of the conventional AuNRs with the same AR, demonstrating that the miniaturization of the diameter to below ~2 nm significantly affects the optical response. The red shift of the LSPR band can be ascribed to the increase in the effective mass of electrons in AuUNRs.

Comment: Interesting paper about the synthesis of gold nanorods of precise size and shape, and the influence of these parameters on the plasmonic resonance effect. The work done is quiet far away of our skills but Jacky (sorry Chuan) should enjoy it because they present a lot of techniques to characterize these particles.

Spontaneous Assembly of Rotaxanes From a Primary Amine, Crown Ether and Electrophile

Fielden, D. P. S.; Leigh, A. D.*; McTernan, T. C.; Perez-Saavedra, B.; Vitorica-Yrzebal, I.
J. Am. Chem. Soc. **2018**, *ASAP*

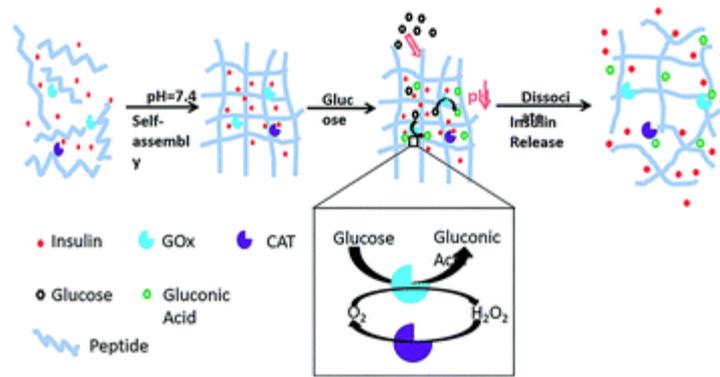


We report the synthesis of crown ether-ammonium, amide and amine [2]rotaxanes via transition state stabilization of axle-forming reactions. In contrast to the two-step “clipping” and “capping” strategies generally used for rotaxane synthesis, here the components assemble into the interlocked molecule in a single, reagent-less, step under kinetic control. The crown ether accelerates the reaction of the axle-forming components through the cavity to give the threaded product in a form of metal-free active template synthesis. Rotaxane formation can proceed through the stabilization of different transition states featuring 5-coordinate (e.g., S_N2) or 4-coordinate (e.g., acylation, Michael addition) carbon. Examples prepared using the approach include crown-ether-peptide rotaxanes and switchable molecular shuttles.

Comment: So, finally, this paper is accepted in JACS. The work done seems more a “reheating” project than a real breakthrough but it teaches us a bit about the mechanism of the synthesis of this type of rotaxane and especially how to sell a paper to a high impact journal.

Injectable Self-assembled Peptide Hydrogels for Glucose-mediated Insulin Delivery

Fu, M.‡; Zhang, C.‡; Dai, Y.‡; Li, X.; Pan, M.; Huang, W.; Qian, H.*; Ge, L.* *Biomater. Sci.* **2018**, *Advance Article*

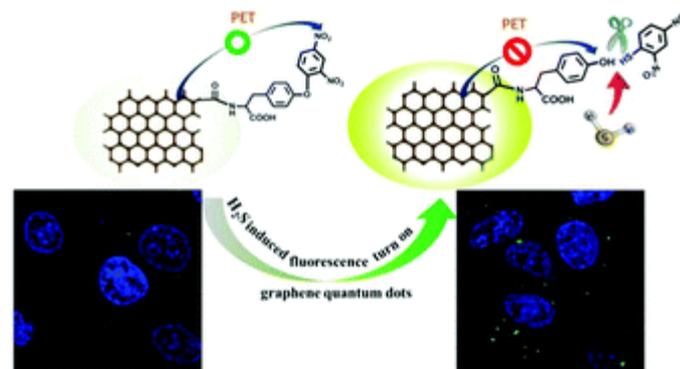


Closed-loop glucose-responsive insulin delivery with excellent biocompatibility has the potential to improve the health and quality of life of diabetic patients. Herein, we developed an excellent glucose responsive insulin delivery system using a pH-sensitive peptide hydrogel loaded with insulin and a glucose-specific enzyme. The designed peptide can be used as a carrier that is loaded with insulin and enzyme via a self-assembly process under physiological conditions. When hyperglycemia is encountered, the enzymatic conversion of glucose into gluconic acid leads to a decrease in the local pH, and the hydrogel is disassembled because of the strong inter- and intramolecular electrostatic repulsions between ornithine (Orn) residues; this is followed by the release of insulin. The glucose-responsive hydrogel system was characterized by studying its structure, conformation, rheology, morphology, acid sensitivity and the amounts of consistent release of insulin in vitro and in vivo. In vivo experiments indicated that the closed-loop insulin glucose-responsive system could efficiently regulate blood glucose in streptozocin-induced (STZ-induced) type 1 diabetic rats for 8 days.

Comment: Although the topic (glucose-mediated insulin delivery) is not directly related to the work in our group, it is a great example of a closed loop, smart drug design and delivery. It does use the same techniques (CD, TEM, rheology) we do for hydrogel characterization.

Graphene Quantum Dots Based Fluorescence Turn-On Nanoprobe for Highly Sensitive and Selective Imaging of Hydrogen Sulfide in Living Cells

Li, N.; Than, A.; Chen, L.; Xi, F.; Liu, J.; Chen, P.* *Biomater. Sci.* **2018**, *6*, 779-784



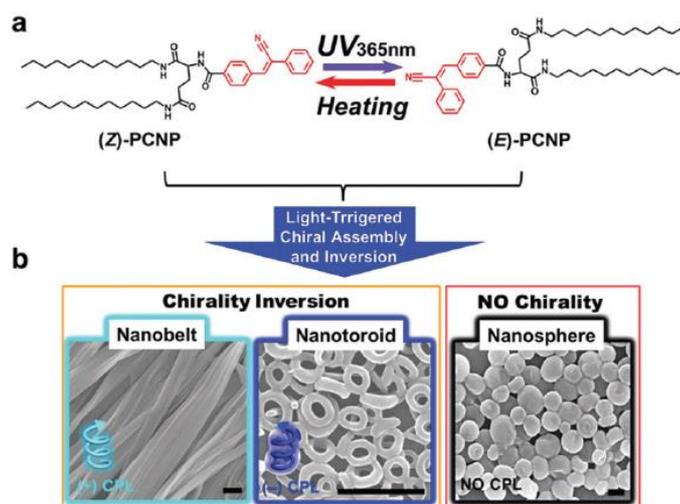
Hydrogen sulfide (H₂S), being an important gaseous signaling molecule, has been gaining increasing attention for its involvement in a wide range of physiological processes. Herein, we developed a novel fluorescence turn-on nanoprobe for selective and sensitive detection of H₂S based on graphene quantum dots (GQDs) conjugated with (2,4-dinitrophenoxy)tyrosine (DNPTYR). Taking advantage of its high fluorescence quantum yield, biocompatibility, photo-

stability, and ease to be uptaken by cells, the GQD-based fluorescence probe was further employed for real-time monitoring of the triggered dynamic change of the intracellular H₂S level in live cells.

Comment: Very interesting article. I am convinced by their strategy and actually do not have so many remarks.

Light-triggered Self-assembly of a Cyanostilbene-conjugated Glutamide from Nanobelts to Nanotoroids and Inversion of Circularly Polarized Luminescence

Jin, X.; Yang, D.; Jiang, Y.; Duan, P.*; Liu, M.* [Chem. Commun. 2018, 54, 4513.](#)



Light irradiation was found to trigger the self-assembly of a cyanostilbene-conjugated dialkyl glutamide from nanobelts to nanotoroids, which emitted inverse circularly polarized luminescence.

Comment: Nanobelt, nanotoroid and nanosphere could be formed by controlling the ration of Z/E cyanostilbene.

PEG-nanotube Liquid Crystals as Templates for Construction of Surfactant-free Gold Nanorods

Kameta, N.; Shiroishi, H.* [Chem. Commun. 2018, 54, 4665.](#)

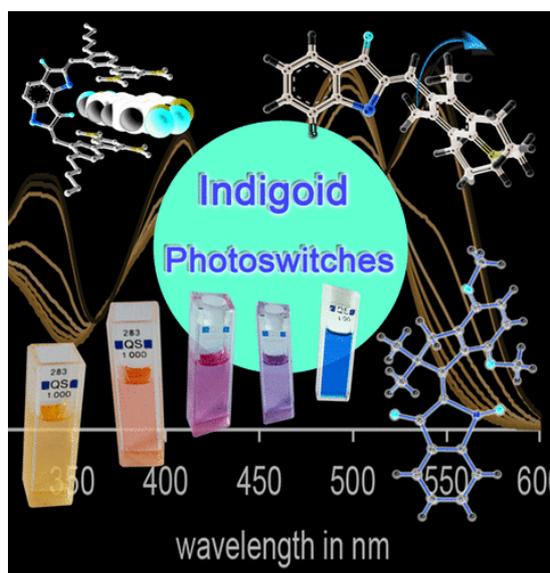


Lytotropic liquid crystals, in which nanotubes coated with polyethylene glycol were aligned side-by-side in aqueous dispersions, acted as templates for the construction of surfactant-free gold nanorods with controllable diameters, functionalizable surfaces, and tunable optical properties.

Comment: A very interesting research which provides a template method to construct surfactant-free gold nanorods of controllable diameters.

Indigoid Photoswitches: Visible Light Responsive Molecular Tools

Petermayer, C.; Dube, H.* [*Acc. Chem. Res.* 2018, ASAP.](#)



Indigoid photoswitches comprise a class of chromophores that are derived from the parent and well-known indigo dye. Different from most photoswitches their core structures absorb in the visible region of the spectrum in both isomeric states even without substitutions, which makes them especially interesting for applications not tolerant of high-energy UV light. Also different from most current photoswitching systems, they provide highly rigid structures that undergo large yet precisely controllable geometry changes upon photoisomerization. The favorable combination of pronounced photochromism, fast and efficient photoreactions, and high thermal bistability have led to a strongly increased interest in indigoid photoswitches over the last years. As a result, intriguing applications of these chromophores as reversible triggering units in supramolecular and biological chemistry, the field of molecular machines, or smart molecules have been put forward. In this Account current developments in the synthesis, mechanistic understanding of light responsiveness, advantageous properties as phototools, and new applications of indigoid photoswitches are summarized with the focus on hemithioindigo, hemiindigo, and indigo as key examples.

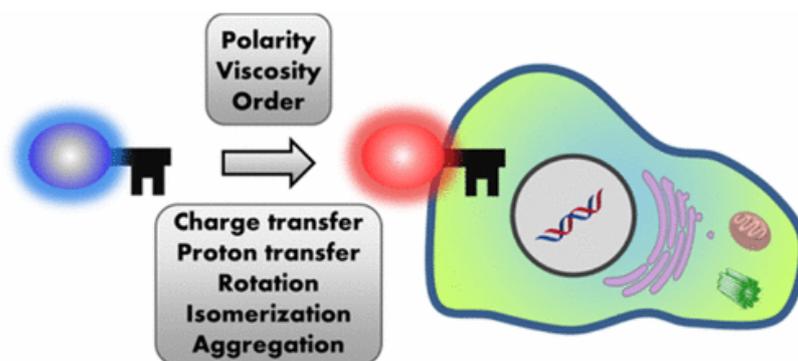
Many methods for the synthesis of hemithioindigos are known, but derivatives with a fourth substituent at the double bond could not easily be prepared because of the resulting increased steric hindrance in the products. Recent efforts in our laboratory have provided two different methods to prepare these highly promising photoswitches in very efficient ways. One method is especially designed for the introduction of sterically hindered ketones while the second one allows rapid structural diversification in only three high-yielding synthetic steps.

Given the lesser prominence of indigoid photoswitches, mechanistic understanding of their excited state behavior and therefore rational design opportunities for photophysical properties are also much less developed compared to, for example, azobenzenes or stilbenes. By testing different substitution patterns, we were able to produce strongly beneficial property combinations in hemithioindigo, hemiindigo, or indigo photoswitches, for example, red-light responsiveness together with very high thermal bistability of the switching states. This is of particular importance for photopharmacological and biological applications of these switches to reduce the damage from high-energy light and to enable deep penetration of the light into tissues. An additional ground state twisting in hemithioindigo allowed us to control the type of light-induced bond rotation simply by the polarity of the solvent. With the aid of time-resolved spectroscopy and quantum yield measurements, we could show that in apolar cyclohexane exclusive double bond rotation takes place while in polar DMSO sole single bond rotation is observed. Such precise control over geometrical changes is of great interest for the construction of future sophisticated molecular machinery. In this field, we have introduced hemithioindigo photoswitches as novel core structure for molecular motors providing very fast directional motions upon irradiation with visible light. The mechanism of the directional rotation adheres to a four-step process, which could directly be observed in situ with a slower second-generation motor. Further applications of indigoid photoswitches were made in our laboratory in the realms of photocontrolled folding and host-guest chemistry as well as in molecular digital information processing showcasing the great versatility and enormous future promise of indigoid photoswitches.

Comment: Dube's research are focused on these unusual photoswitches which have already proven their versatility. I enjoy how they cover the whole spectrum of research on these objects going from the design to the applications.

Solvatochromic and Fluorogenic Dyes as Environment-Sensitive Probes: Design and Biological Applications

Klymchenko, A.* [Acc. Chem. Res. 2017, 50, 366-375.](#)



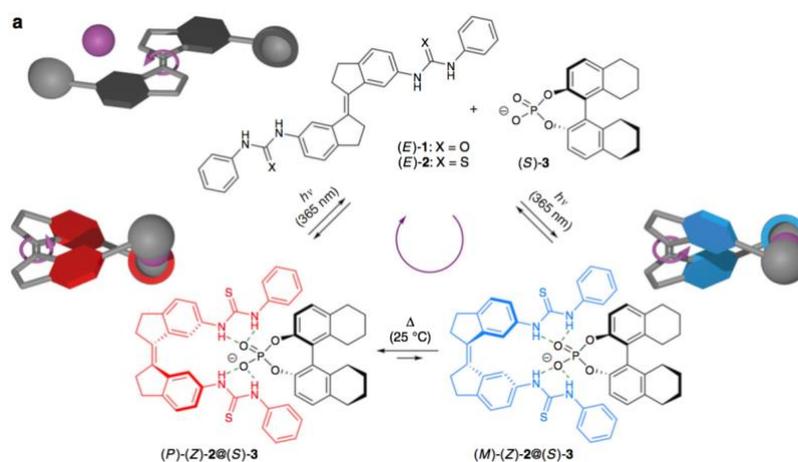
Fluorescent environment-sensitive probes are specially designed dyes that change their fluorescence intensity (fluorogenic dyes) or color (e.g., solvatochromic dyes) in response to change in their microenvironment polarity, viscosity, and molecular order. The studies of the past decade, including those of our group, have shown that these molecules become universal tools in fluorescence sensing and imaging. In fact, any biomolecular interaction or change in biomolecular organization results in modification of the local microenvironment, which can be directly monitored by these types of probes. In this Account, the main examples of environment-sensitive probes are summarized according to their design concepts. Solvatochromic dyes constitute a large class of environment-sensitive probes which change their color in response to polarity. Generally, they are *push-pull dyes undergoing intramolecular charge transfer*. Emission of their highly polarized excited

The design and synthesis of new stimuli-responsive hydrogen-bonding monomers that display a **diversity of self-assembly pathways is of central importance in supramolecular chemistry**. Here we describe the aggregation properties of a simple, intrinsically C_2 -symmetric enantiopure bicyclic cavity compound bearing a terminally unsubstituted ureidopyrimidinone fragment fused with a pyrrole moiety in different solvents and in the absence and presence of C_{60} and C_{70} guests. The tetrameric cyclic aggregate is selectively obtained in chlorinated solvents, where only part of the available hydrogen bonding sites are utilized, whereas in toluene or upon addition of C_{70} guests, further aggregation into tubular supramolecular polymers is achieved. The open-end cyclic assemblies rearrange into a closed-shell capsule upon introduction of C_{60} with an accompanied symmetry breaking of the monomer. **Our study demonstrates that a C_{60} switch can be used to simultaneously control the topology and occupancy of tubular assemblies** resulting from the aggregation of small monomers.

Comment: A couple of things about this paper: a) Although there are quite some examples on ditopic UPys, even rigid bis-UPys, this family of molecules represent an outlier due to the position of the “sticky” ends (see above). Moreover, they highlight the multi-dimensionality of the self-assembly process.

Supramolecularly Directed Rotary Motion in a Photoresponsive Receptor

Wezenberg, S. J.; Feringa, B. L.* [*Nat. Commun.* **2018**, *9*, 1984.](#)



Stimuli-controlled motion at the molecular level has fascinated chemists already for several decades. Taking inspiration from the myriad of dynamic and machine-like functions in nature, a number of strategies have been developed to control motion in purely synthetic systems. Unidirectional rotary motion, such as is observed in ATP synthase and other motor proteins, remains highly challenging to achieve. **Current artificial molecular motor systems rely on intrinsic asymmetry or a specific sequence of chemical transformations**. Here, we present an alternative design in which **the rotation is directed by a chiral guest molecule**, which is able to bind non-covalently to a light-responsive receptor. It is demonstrated that the rotary direction is governed by the guest chirality and hence, can be selected and changed at will. This feature offers unique control of directional rotation and will prove highly important in the further development of molecular machinery.

Comment: Short, simple, difficult to dispute. If you introduce the axial chirality to a motor in a non-covalent manner, you thereafter control the direction of motion. I encourage you to go and read the reviewers comments.