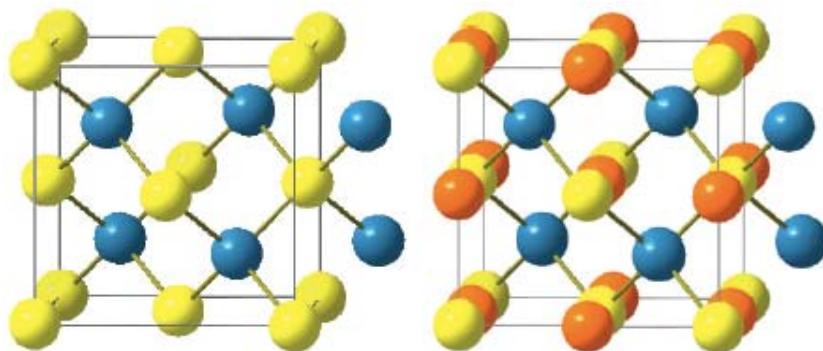


- Tunable multifunctional topological insulators in ternary Heusler compounds

Chadov, S.; Qi, X.; Kubler, J.; Fecher, G. H.; Felser, C.; Zhang, S. C. *Nature Materials* **2010**, *9*, 541-545.

1

Abstract:

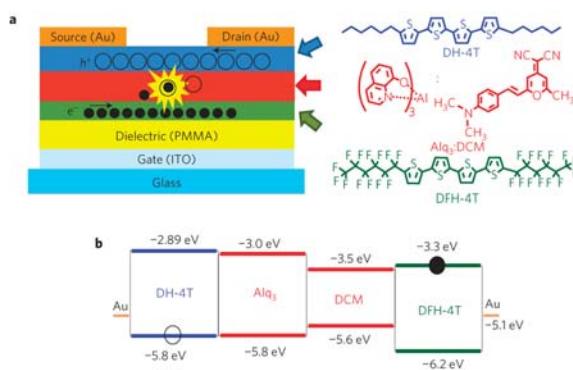


Recently the quantum spin Hall effect was theoretically predicted and experimentally realized in quantum wells based on the binary semiconductor HgTe. The quantum spin Hall state and topological insulators are new states of quantum matter interesting for both fundamental condensed-matter physics and material science. Many Heusler compounds with C1b structure are ternary semiconductors that are structurally and electronically related to the binary semiconductors. The diversity of Heusler materials opens wide possibilities for tuning the bandgap and setting the desired band inversion by choosing compounds with appropriate hybridization strength (by the lattice parameter) and magnitude of spin-orbit coupling (by the atomic charge). Based on first-principle calculations we demonstrate that around 50 Heusler compounds show band inversion similar to that of HgTe. The topological state in these zero-gap semiconductors can be created by applying strain or by designing an appropriate quantum-well structure, similar to the case of HgTe. Many of these ternary zero-gap semiconductors (LnAuPb, LnPdBi, LnPtSb and LnPtBi) contain the rare-earth element Ln, which can realize additional properties ranging from superconductivity (for example LaPtBi) to magnetism (for example GdPtBi) and heavy fermion behaviour (for example YbPtBi). These properties can open new research directions in realizing the quantized anomalous Hall effect and topological superconductors.

- Organic light-emitting transistors with an efficiency that outperforms the equivalent light-emitting diodes

Capelli, R.; Toffanin, S.; Generali, G.; Usta, H.; Facchetti, A.; Muccini, M. *Nature Materials* **2010**, *9*, 468-503.

Abstract:

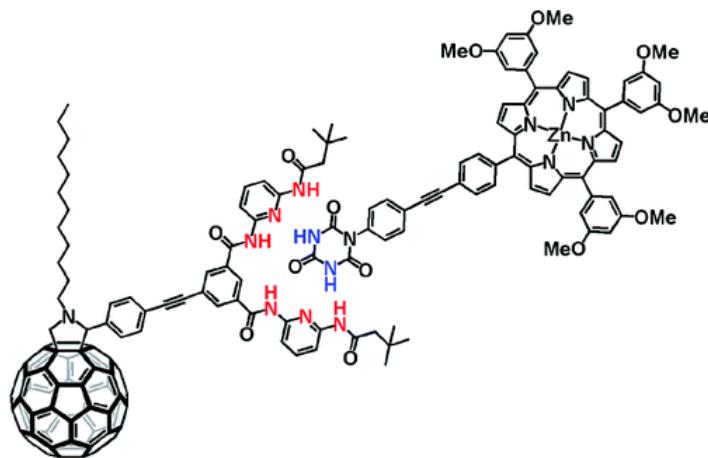


The potential of organic semiconductor-based devices for light generation is demonstrated by the commercialization of display technologies based on organic light-emitting diodes (OLEDs).
Nonetheless, exciton quenching and photon loss processes still limit OLED efficiency and brightness.
Organic light-emitting transistors (OLETs) are alternative light sources combining, in the same architecture, the switching mechanism of a thin-film transistor and an electroluminescent device.
Thus, OLETs could open a new era in organic optoelectronics and serve as testbeds to address general fundamental optoelectronic and photonic issues. Here, we introduce the concept of using a p channel/emitter/n-channel trilayer semiconducting heterostructure in OLETs, providing a new approach to markedly improve OLET performance and address these open questions. In this architecture, exciton–charge annihilation and electrode photon losses are prevented. Our devices are >100 times more efficient than the equivalent OLED,^{>2} more efficient than the optimized OLED with the same emitting layer and >10 times more efficient than any other reported OLETs.

2

- Pairing Fullerenes and Porphyrins: Supramolecular Wires That Exhibit Charge Transfer Activity
Wessendorf, F.; Grimm, B.; M. Guldin, D.; Hirsch, A. *J. Am. Chem. Soc.* **2010**, *132*, 10786–10795.

Abstract:



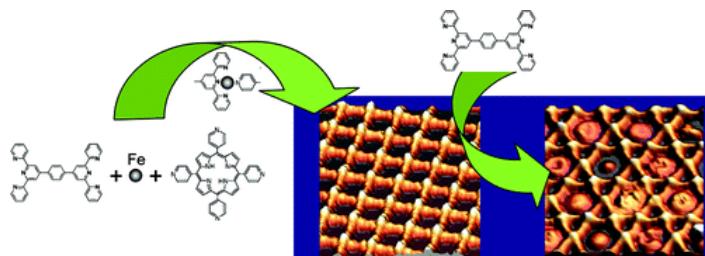
A concept is elaborated of pairing electron donors and electron acceptors that share a common trait, wire-like features, as a powerful means to realize a new and versatile class of electron donor–acceptor nanohybrids. Important variables are fine-tuning (i) the complexation strength, (ii) the electron/energy transfer behavior, and (iii) the solubilities of the resulting architectures. In particular, a series of supramolecular porphyrin/fullerene hybrids assembled by the hydrogen bonding of Hamilton receptor/cyanuric acid motif has been realized. Putting the aforementioned variables into action, the association constants (K_{ass}), as they were determined from ^1H NMR and steady-state fluorescence assays, were successfully tweaked with values in the range of 104–105 M⁻¹. In fact, our detailed studies corroborate that the latter reveal a dependence on the nature of the spacer, that is, p-phenylene-ethynylene, p-phenylene-vinylene, p-ethynylene, and fluorene, as well as on the length of the spacer. Complementary performed transient absorption studies confirm that electron transfer is indeed the modus operandi in our novel class of electron donor–acceptor nanohybrids, while energy transfer plays, if any, only a minor role. The accordingly formed electron transfer products, that is, one-electron oxidized porphyrins and one-electron reduced fullerenes, are long-lived with lifetimes that reach well into the time domain of tens of nanoseconds. Finally, we have used the distance dependence on electron transfer, charge separation and charge

recombination, to determine for the first time a β value (0.11 \AA^{-1}) for hydrogen-bonding-mediated electron transfer.

- Structural and Chemical Control in Assembly of Multicomponent Metal–Organic Coordination Networks on a Surface

Shi, Z.; Lin, N. *J. Am. Chem. Soc.* **2010**, *132*, 10756–10761.

Abstract:

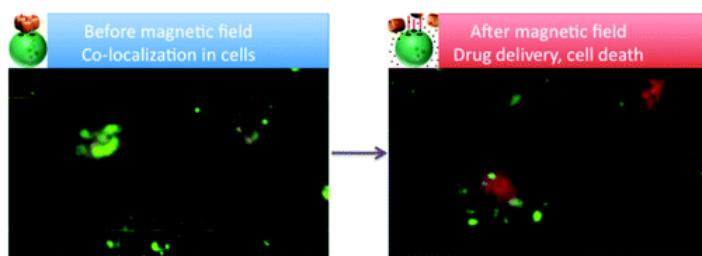


Surface-supported supramolecular self-assembly has been used to generate multicomponent two-dimensional metal–organic coordination networks on a Au(111) surface. The networks consist of linker ligands of $4',4'''$ -(1,4-phenylene)bis(2,2':6',2''-terpyridine) and nodal ligands of 5,10,15,20-tetra(4-pyridyl)porphyrin that are connected by pyridine–Fe–terpyridine motifs. Scanning tunneling microscopy revealed the coexistence of two polymorphic types of network structures (rhombus and Kagome). Through control of the dosage of the constituent ligands, homogeneous structural phases were obtained selectively. In particular, the rhombus structure could be converted into the more complex and more open Kagome structure by inclusion of guest molecules. Finally, coordination networks providing structural and chemical homogeneity were realized by judiciously choosing the dosages of the constituent ligands and the chemical substitution of the porphyrin ligands.

- Noninvasive Remote-Controlled Release of Drug Molecules in Vitro Using Magnetic Actuation of Mechanized Nanoparticles

Thomas, C. R.; Ferris, D. P.; Lee, J.-H.; Choi, E.; Cho, M. H.; Kim, E. S.; Stoddart, J. F.; Shin, J.-S.; Cheon, J.; Zink, J. I. *J. Am. Chem. Soc.* **2010**, *132*, 10623–10625.

Abstract:



Mesoporous silica nanoparticles are useful nanomaterials that have demonstrated the ability to contain and release cargos with mediation by gatekeepers. Magnetic nanocrystals have the ability to exhibit hyperthermic effects when placed in an oscillating magnetic field. In a system combining these two materials and a thermally sensitive gatekeeper, a unique drug delivery system can be produced. A novel material that incorporates zinc-doped iron oxide nanocrystals within a mesoporous silica framework that has been surface-modified with pseudorotaxanes is described. Upon application of an AC magnetic field, the nanocrystals generate local internal heating, causing the molecular machines to disassemble and allowing the cargos (drugs) to be released. When breast cancer cells (MDA-MB-231) were treated with doxorubicin-loaded particles and exposed to an AC

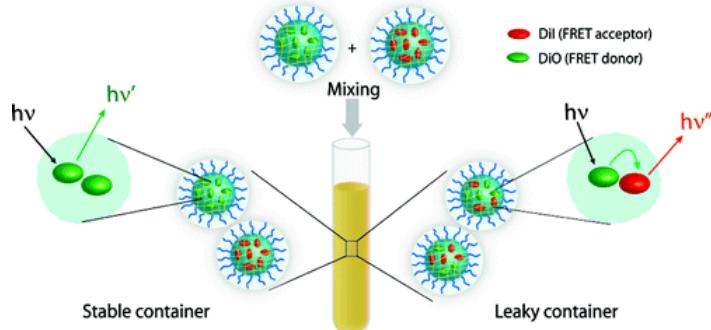
field, cell death occurred. This material promises to be a noninvasive, externally controlled drug delivery system with cancer-killing properties.

4

- Noncovalent Encapsulation Stabilities in Supramolecular Nanoassemblies

Jiwpanich, S.; Ryu, J.-H.; Bickerton, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **2010**, *132*, 10683–10685.

Abstract:

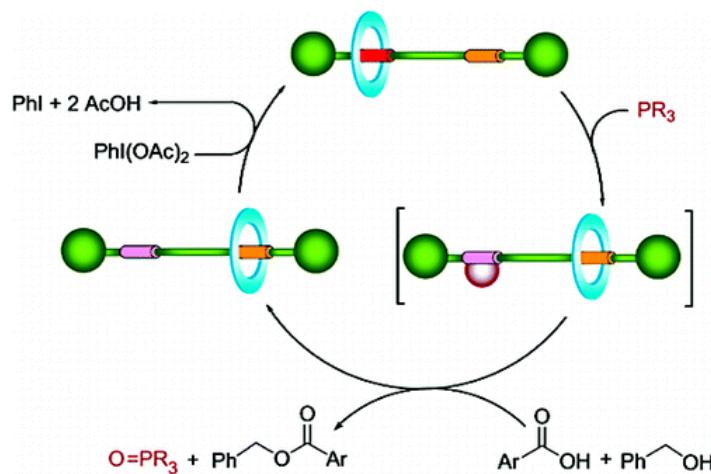


Exchange dynamics of lipophilic guest molecules, encapsulated in supramolecular nanoassemblies in aqueous solutions, have implications in evaluating the stability of drug delivery vehicles. This is because exchange dynamics is related to the propensity of a nanocarrier to be leaky. We describe a fluorescence resonance energy transfer (FRET) based method to evaluate guest exchange dynamics in the aqueous phase. We have utilized this method to analyze the stability of encapsulation in polymeric nanogels and other related amphiphilic nanoassemblies.

- Azodicarboxamides as Template Binding Motifs for the Building of Hydrogen-Bonded Molecular Shuttles

Berná, J.; Alajarín, M.; Orenes, R.-A. *J. Am. Chem. Soc.* **2010**, *132*, 10741–10747.

Abstract:



Azodicarboxamides ($R_2NCON=NCONR_2$) are shown to act as new templates for the assembly of unprecedented azo-functionalized hydrogen-bond-assembled [2]rotaxanes. Moreover, these binding sites can be reversibly and efficiently interconverted with their hydrazo forms through a hydrogenation-dehydrogenation strategy of the nitrogen–nitrogen bond. This novel chemically switchable control element has been implemented in stimuli-responsive molecular shuttles that work through a reversible azo/hydrazo interconversion, producing large amplitude net positional changes with a good discrimination between the binding sites of the macrocycle in both states of the shuttle.

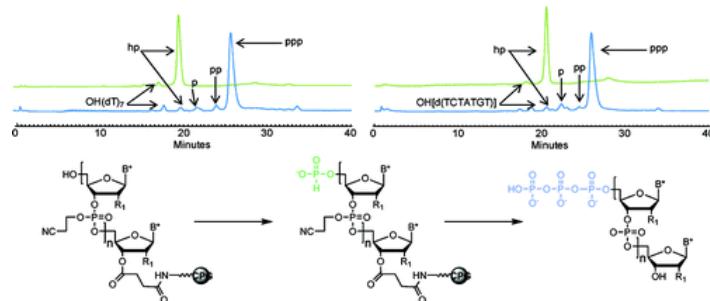
These molecular shuttles are able to operate by two different mechanisms: in a discrete mode through two reversible and independent chemical events and, importantly, in a continuous regime through a catalyzed ester bond formation reaction in which the shuttle acts as an organocatalyst. In this latter, the incorporation of both states of the shuttle into this simple chemical reaction network promotes a dynamic translocation of the macrocycle between two nitrogen and carbon-based stations of the thread allowing an energetically uphill esterification process to take place.

5

- Efficient Solid-Phase Chemical Synthesis of 5'-Triphosphates of DNA, RNA, and their Analogues

Zlatev, I.; Lavergne, T.; Debart, F.; Vasseur, J.-J.; Manoharan, M.; Morvan, F. *Org. Lett.* **2010**, 12, 2190–2193.

Abstract:

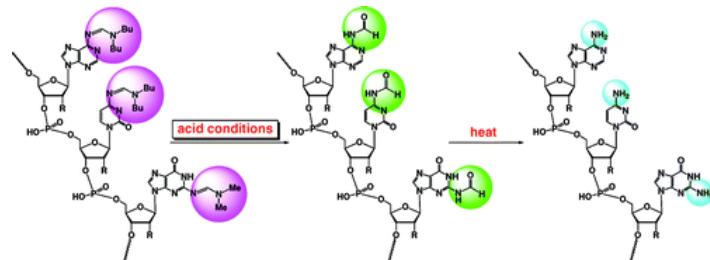


A robust, reproducible, and scalable method for the solid-phase synthesis of 5'-triphosphates of DNA, RNA, and their chemically modified analogues using 5'-H-phosphonate intermediates is described. 5'-Triphosphates of oligonucleotides with varying lengths and sequences containing different 5'-terminal nucleotides, with and without internal sugar-backbone modifications, were efficiently prepared as crude products or further purified by HPLC.

- Oligonucleotide Synthesis Involving Deprotection of Amidine-Type Protecting Groups for Nucleobases under Acidic Conditions

Ohkubo, A.; Kuwayama, Y.; Nishino, Y.; Tsunoda, H.; Seio, K.; Sekine, M. *Org. Lett.* **2010**, 12, 2496–2499.

Abstract:



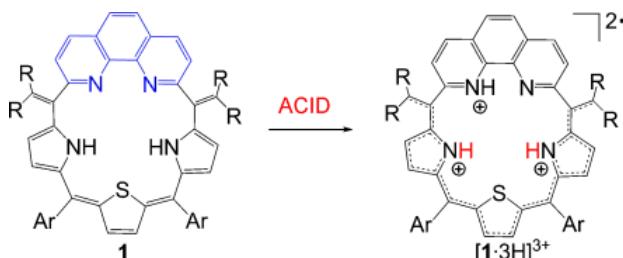
Amidine-type protecting groups, i.e., *N,N*-dimethylformamidine (dmf) and *N,N*-dibutylformamidine (dbf) groups, introduced into nucleobases were rapidly removed under mild acidic conditions using imidazolium triflate (IMT) or 1-hydroxybenztriazole (HOBT). This new deprotection strategy allowed a 2'-*O*-methyl-RNA derivative bearing a base-labile group to be efficiently synthesized using a silyl-type linker. It was also found that our new method could be applied to the synthesis of an unmodified RNA oligomer.

- Protonation-Induced Formation of a Stable Singlet Biradicaloid Derived from a Modified

Sapphyrin Analogue

Ishida, M.; Karasawa, S.; Uno, H.; Tani, F; Naruta, Y. *Angew. Chem. In. Ed.* **2010**, *49*, 5906–5909.

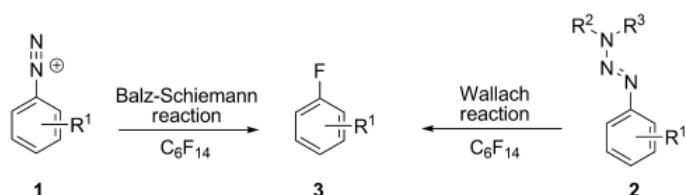
6

Abstract:

Acid does the trick: A novel 1,10-phenanthroline-embedded sapphyrin analogue **1** (see scheme; R=COOEt, Ar=p-tolyl) bearing meso alkylidene double bonds has been synthesized. Interestingly, the protonated form of **1** ($[1\cdot3\text{H}]^{3+}$) exhibits singlet biradicaloid character.

- Synthesis of Aryl Fluorides on a Solid Support and in Solution by Utilizing a Fluorinated Solvent

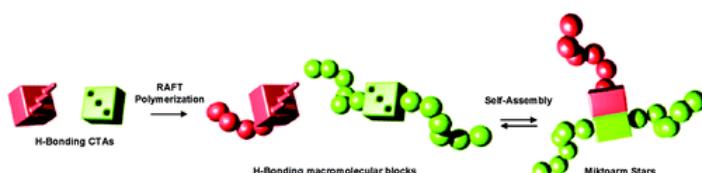
Döbele, M.; Vanderheiden, S.; Jung, N.; Bräse, S. *Angew. Chem. In. Ed.* **2010**, *49*, 5986–5988.

Abstract:

F for fast: The perfluorinated solvent C_6F_{14} is the key to a new variant of the Balz–Schiemann reaction for the synthesis of fluorinated arenes. Triazenes are converted into fluoroarenes under mild conditions on a support and in solution (see scheme). The method is straightforward and inexpensive, and yields previously difficult-to-prepare fluoroarenes in high purity.

- Heterocomplementary H-Bonding RAFT Agents as Tools for the Preparation of Supramolecular Miktoarm Star Copolymers

Chen, S.; Bertrand, A.; Chang, X.; Alcouffe, A.; Ladavire, C.; Gérard, J.-F.; Lortie, F.; Bernard, J. *Macromolecules* **2010**, *43*, 5981–5988.

Abstract:

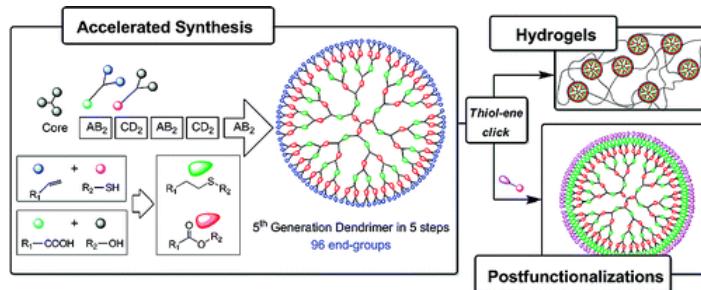
Supramolecular miktoarm stars (AB₂ type) composed of poly (methyl methacrylate)-polystyrene₂ (PMMA-PS₂), poly(isoprene)-polystyrene₂ (PI-PS₂), and poly(vinyl acetate)-polystyrene₂ (PVAc-PS₂) were successfully synthesized by assembling reversible addition–fragmentation chain transfer (RAFT)-polymerized chains bearing hydrogen-bonding heterocomplementary associating units. To this end, thymine and diaminopyridine-functionalized chain transfer agents were designed to efficiently mediate the polymerization of vinyl acetate, methyl methacrylate, isoprene, and styrene. The selective associations of the resulting hydrogen-bonding macromolecular building blocks

PVAc/PS, PI/PS, and PMMA/PS were demonstrated by ^1H NMR in CDCl_3 solutions. Miktoarm stars formation in the bulk was also confirmed by transmission electronic microscopy.

- Accelerated Growth of Dendrimers via Thiol-Ene and Esterification Reactions

Montaez, M. I.; Campos, L. M.; Antoni, P.; Hed, Y.; Walter, M. V.; Krull, B. T.; Khan, A.; Hult, A.; Hawker, C. J.; Malkoch, M. *Macromolecules* **2010**, *43*, 6004–6013.

Abstract:

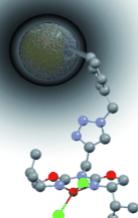


By taking advantage of the orthogonal nature of thiol-ene coupling and anhydride based esterification reactions, a facile and chemoselective strategy to dendritic macromolecules has been developed. The ability to interchange growth steps based on thiol-ene and anhydride chemistry allows the synthesis of fifth-generation dendrimers in only five steps and under benign reaction conditions. In addition, the presented coupling chemistries eliminate the traditional need for protection/deprotection steps and afford dendrimers in high yield and purity. The modularity of this strategy coupled with the latent reactivity of the alkene/hydroxyl chain ends was demonstrated by using different cores (alkene and hydroxyl functional), various AB_2 and CD_2 monomers and a range of chain end groups. As a result, three dendritic libraries were prepared which exhibited tunability of both the chemical functionality and physical properties including the fabrication of PEG hydrogels.

- Nanoparticles as Semi-Heterogeneous Catalyst Supports.

Schätz, A.; Reiser, O.; Stark, W. *Chem. Eur. J.* **2010**, *16*, 8950–8967.

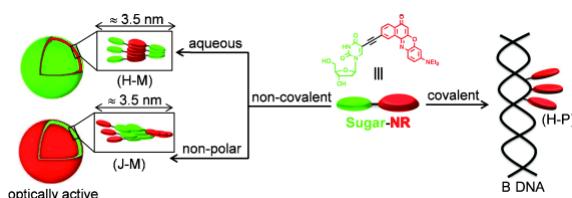
Abstract:



Nanoparticles can serve as semi-heterogeneous supports since they readily disperse in common solvents and combine high surface area with excellent accessibility. Reversible agglomeration through solvent changes and magnetic separation provide technically attractive alternatives to classical catalyst filtration. This account places emphasis on recent developments in this emerging area.

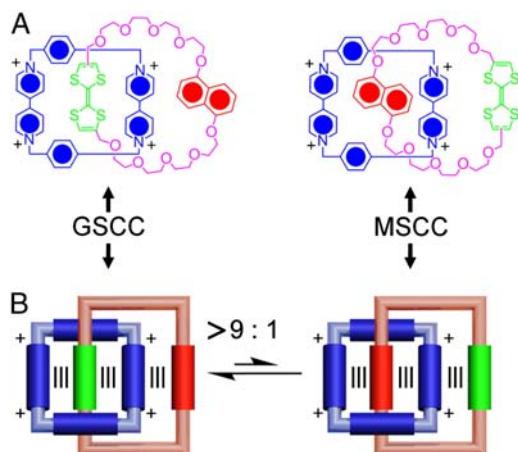
- Non-covalent Versus Covalent Control of Self-Assembly and Chirality of Nile Red-modified Nucleoside and DNA

Varghese, R.; Wagenknecht, H.-A. *Chem. Eur. J.* **2010**, *16*, 9040–9046.

Abstract:

A DNA-based covalent versus a non-covalent approach is demonstrated to control the optical, chirooptical and higher order structures of Nile red (**Nr**) aggregation. Dynamic light scattering and TEM studies revealed that in aqueous media **Nr**-modified 2'-deoxyuridine aggregates through the cooperative effect of various non-covalent interactions including the hydrogen bonding ability of the nucleoside and sugar moieties and the π -stacking tendency of the highly hydrophobic dye. This results in the formation of optically active nanovesicles. A left-handed helically twisted H-type packing of the dye is observed in the bilayer of the vesicle as evidenced from the optical and chirooptical studies. On the other hand, a left-handed helically twisted J-type packing in vesicles was obtained from a non-polar solvent (toluene). Even though the primary stacking interaction of the dye aggregates transformed from H \rightarrow J while going from aqueous to non-polar media, the induced supramolecular chirality of the aggregates remained the same (left-handed). Circular dichroism studies of DNA that contained several synthetically incorporated and covalently attached **Nr**-modified nucleosides revealed the formation of helically stacked H-aggregates of **Nr** but—in comparison to the noncovalent aggregates—an inversed chirality (right-handed). This self-assembly propensity difference can, in principle, be applied to other hydrophobic dyes and chromophores and thus open a DNA-based approach to modulate the primary stacking interactions and supramolecular chirality of dye aggregates.

- Isolation by crystallization of translational isomers of a bistable donor-acceptor [2]catenane
Wanga, C.; Olsona, M. A.; Fang, L.; Benítez, D.; Tkatchouk, E.; Basu, S.; Basuray, A. N.; Zhang, D.; Zhu, D.; Goddard, W. A.; Stoddart, J. F. *Proc. Nat. Acad. Sci.* **2010**, *107*, 13991-13996.

Abstract:

The template-directed synthesis of a bistable donor-acceptor [2]catenane wherein both translational isomers—one in which a tetrathiafulvalene unit in a mechanically interlocked crown ether occupies the cavity of a cyclobis(paraquat-*p*-phenylene) ring and the other in which a 1,5-dioxynaphthalene unit in the crown ether resides inside the cavity of the tetracationic cyclophane—exist in equilibrium in solution, has led to the isolation and separation by hand picking of single crystals colored red and green, respectively. These two crystalline co-conformations have been characterized separately at

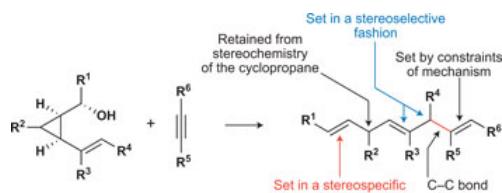
both the molecular and supramolecular levels, and also by dynamic NMR spectroscopy in solution where there is compelling evidence that the mechanically interlocked molecules are present as a complex mixture of translational, configurational, and conformational isomers wherein the isomerization is best described as being a highly dynamic and adaptable phenomenon.

9

- Convergent and stereospecific synthesis of complex skipped polyenes and polyunsaturated fatty acids

Macklin, T. K.; Micalizio, G. C. *Nature Chemistry* **2010**, 2, 638–643.

Abstract:

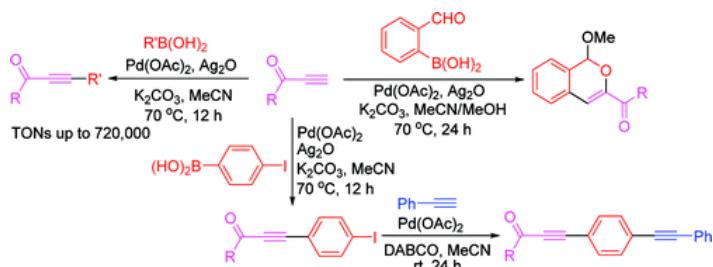


Skipped polyenes (that is, 1,4-dienes and higher homologues) are stereodefined components of a vast array of biologically important natural products, including polyunsaturated fatty acids. Although widespread in nature, these architectures are generally considered to represent significant barriers to efficient chemical synthesis. Partial reduction of skipped polyynes provides a pathway to a subset of such structures, but general chemical methods for the preparation of skipped polyenes that contain varied stereochemistries and substitution patterns are lacking. Here, we describe a metal-promoted reductive cross-coupling reaction between vinylcyclopropanes and alkynes (or vinylsilanes) that provides stereoselective access to a diverse array of skipped polyenes through a process that establishes one C–C bond, generates up to three stereodefined alkenes, and can be used to introduce stereogenic centres at the central positions of the skipped polyene motif. We also demonstrate the significance of the present bond construction by preparing substituted and stereodefined polyunsaturated synthetic fatty acids.

- Palladium-Catalyzed Cross-Coupling of Electron-Poor Terminal Alkynes with Arylboronic Acids under Ligand-Free and Aerobic Conditions

Zhou, M.-B.; Wei, W.-T.; Xie, Y.-X.; Lei, Y.; Li, J.-H. *J. Org. Chem.* **2010**, 75, 5635–5642.

Abstract:

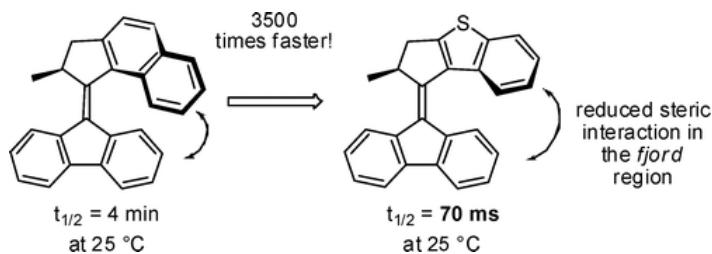


Palladium-catalyzed cross-coupling reaction of terminal alkynes with arylboronic acids has been described. In the presence of $\text{Pd}(\text{OAc})_2$ and Ag_2O , a variety of terminal alkynes, including electron-poor terminal alkynes, smoothly underwent the reaction with numerous boronic acids to afford the corresponding internal alkynes in moderate to good yields. Moreover, this methodology was applied to the synthesis of 1H -isochromenes and diarynes. It is noteworthy that the reaction proceeds under ligand-free and relative lower loading Pd conditions, and the maximal TONs (turnover numbers) of the reaction are up to 720,000.

- Rotary Molecular Motors: A Large Increase in Speed through a Small Change in Design

Landaluce, T. F.; London, G.; Pollard, M. M.; Rudolf, P.; Feringa, B. L. *J. Org. Chem.* **2010**, *75*, 5323–5325. 10

Abstract:

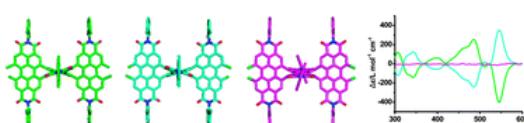


Reducing the steric interaction between the upper-half and the lower-half of a light-driven rotary molecular motor by decreasing the size of the aromatic moiety in the upper-half from a naphthalene to a benzothiophene results in an almost 3500 times faster rotation.

- Chiral nanoribbons based on doubly-linked oligo-perylene bisimides

Zhen, Y.; Yue, W.; Li, Y.; Jiang, W.; Di Motta, S.; Di Donato, E.; Negri, F.; Ye, S.; Wang, Z. *Chem. Commun.* **2010**, *46*, 6078-6080.

Abstract:

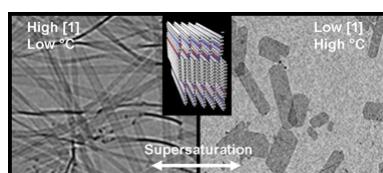


A facile strategy towards conformationally stable chiral ladder-type oligo-perylene bisimides is established *via* copper-mediated *Ullmann* coupling. Absolute configurations are determined with the help of quantum-chemical calculations.

- Kinetic switching between two modes of bisurea surfactant self-assembly

Vos, M. R. J.; Leclère, P. E. L. G.; Meekes, H.; Vlieg, E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Commun.* **2010**, *46*, 6063-6065.

Abstract:



The size and shape of a surfactant aggregate could be altered by using supersaturation like in crystal growth, rather than applying common laws that drive surfactant aggregate formation.