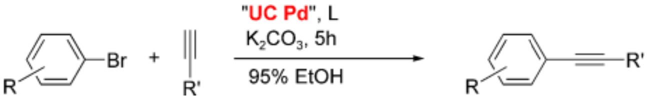
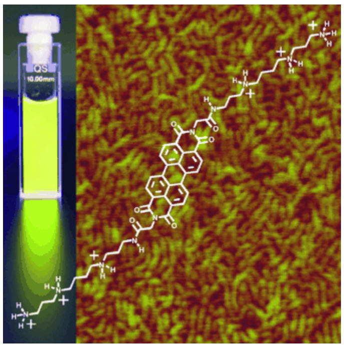
- UC Pd: A New Form of Pd/C for Sonogashira Couplings
  Duplais, C.; Forman, A. J.; Baker, B. A.; Lipshutz, B. H. *Chem. Eur. J.* **2010**, *16*, 3366-3371.
  Abstract:



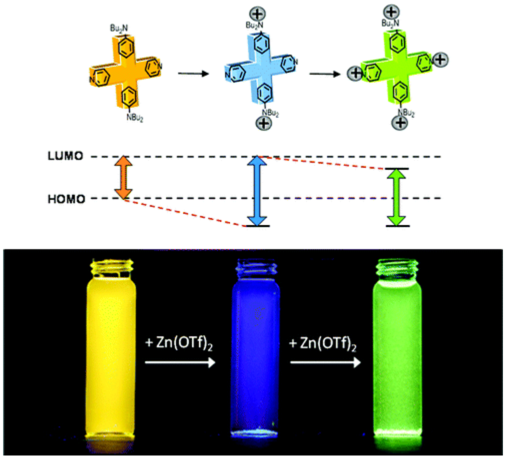
Screening of different sources of Pd/C shows reagents of highly variable nanoparticle sizes and oxidation states of the metal. Typically, catalysts with higher surface area are viewed as likely to be the more reactive. In this paper a new form of Pd/C, “UC Pd” is described that is shown to contain larger nanoparticles yet it is the most reactive catalyst of those sold commercially for Sonogashira coupling reactions. UC Pd functions efficiently in the absence of a copper co-catalyst, under very mild and “green” conditions using inexpensive 95 % EtOH at 50 °C. It is also the only form of Pd/C that can be recycled. In side-by-side reactions with several commercially available forms of Pd/C, none compete successfully with UC Pd under standardized conditions. Physical data obtained from extensive surface analysis using TEM, XRD, XPS, and CO-TPD measurements lead to an explanation behind the unique reactivity of this new recyclable form of Pd/C.

- Spermine-Functionalized Perylene Bisimide Dyes - Highly Fluorescent Bola-Amphiphiles in Water
  Rehm, S.; Stepanenko, V.; Zhang, X.; Rehm, T. H.; Würthner, F. *Chem. Eur. J.* **2010**, *16*, 3372-3382.
  Abstract:



A series of four spermine-functionalized perylene bisimide dyes without linkers (**1**) and with linkers (**2**-**4**) between the chromophore and the polyamine was synthesized. Protonation of the spermine moieties resulted in the formation of highly water-soluble dyes with up to six positively charged ammonium ions. The aggregation behavior of these strongly fluorescent bola-amphiphiles was studied in pure water as solvent by UV/Vis and fluorescence spectroscopy, and an astonishingly high fluorescence quantum yield of up to $\phi_{fl}=0.90$ was observed for PBI **1**. Atomic force microscopy and transmission electron microscopy were applied for the visualization of the aggregates on surfaces. Molecular modeling studies were performed by force-field calculations to explore the aggregate morphologies, which also provided valuable information on the influence of the additional alkylcarbonyl linkers. Our detailed spectroscopic and microscopic investigations revealed that the excellent optical properties of perylene bisimide chromophores can be used even in pure deionized water if their aggregation is efficiently suppressed.

- Cross-Conjugated Cruciform Fluorophores
  Zucchero, A. J.; McGrier, P. L.; Bunz, U. H. F. *Acc. Chem. Res.* **2010**, *43*, 397–408.
  Abstract:



In optoelectronic devices, chromophores can be designed at the molecular level to create materials with properties desired for advanced applications. Organic fluorophores in particular can be constructed with macroscopic properties that arise from two distinct contributions: (i) the collective impact of the molecular backbone and substituents and (ii) the connectivity within the molecule (that is, the spatial molecular architecture). Accordingly, the exploration of novel conjugated architectures is a productive area of current research.

Different two-dimensional, “X-shaped” conjugated materials have been synthesized for a variety of applications. They include spiro compounds, paracyclophanes, swivel-type dimers, bisoxazole-derived cruciforms, tetraethynylethenes, and tetrasubstituted tolanes. A subset of these compounds are constructed from two “perpendicular” π-conjugated linear arms connected through a central aromatic core; examples of these include tetrakis(arylethynyl)benzenes, tetrakis(styryl)benzenes, and tetrasubstituted thiophenes.

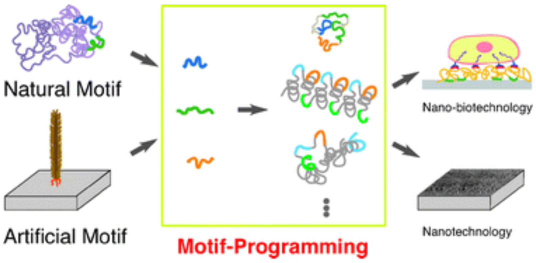
In this Account, we evaluate 1,4-distyryl-2,5-bis(arylethynyl)benzenes or cruciforms (XFs). Electronic substitution of this “X-shaped” cross-conjugated scaffold tunes both the energy levels of the frontier molecular orbitals (FMOs) and their spatial distribution in XFs. The resulting fluorophores exhibit FMO separation, imbuing XFs with unusual yet desirable properties for sensory applications.

Using model analytes, we examine how the underlying FMO arrangement and the nature of analyte interaction elicit observable responses. These studies provide a foundation for accessing functional responsive ratiometric cores, demonstrating the importance and unique potential of FMO-separated fluorophores.

We also highlight the essential contribution of serendipity in materials development. Moving beyond one-dimensional molecular wire-type fluorophores to two-dimensional “X-shaped” materials provides access to materials with unexpected and exciting properties. XFs represent such novel conjugated architectures, and their successful development has frequently has hinged on inspiration from structural components and principles developed in diverse research areas.

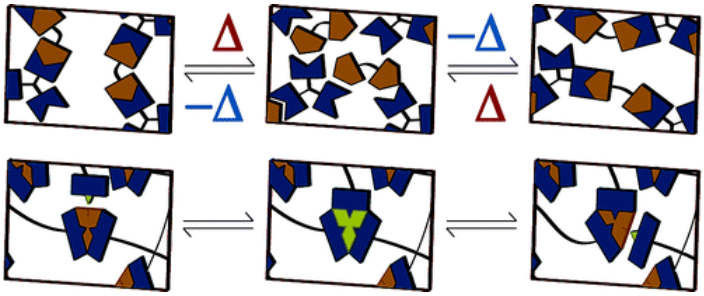
- Natural and artificial peptide motifs: their origins and the application of motif-programming

Shiba, K. *Chem. Soc. Rev.* **2010**, *39*, 117 – 126.
Abstract:



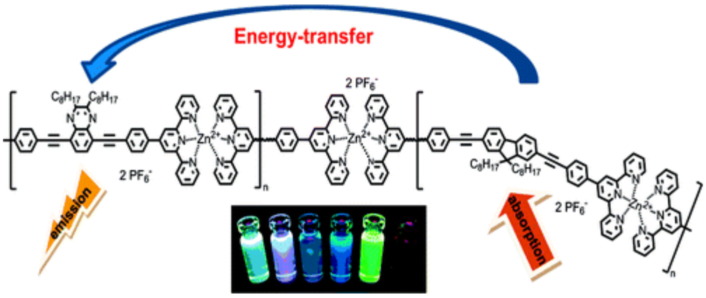
In this *tutorial review*, I discuss the nature and application of peptide motifs. Motifs are usually identified through analysis of the sequence of natural proteins and are linked to particular biological functions, though the association between a motif and its function is only speculative in some cases. In other cases, however, the transplantability and functional independence of motifs have been experimentally proven, providing us with the opportunity to use those motifs as programming units for biotechnological application. In addition to natural motifs, peptide aptamers created using *in vitro* evolution systems can also serve as motif units. The associated functions of these artificial motifs are related to their binding ability. Numerous binders against both natural biomolecules and inorganic materials have been created from peptide phage systems. By programming these natural and artificial motifs, artificial proteins with the potential to contribute to medical diagnosis and treatment, nanotechnology, and various areas of basic science have been created. In addition, the transplantability and functional independence of motifs provide insight into the nature of protein evolution.

- Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers
  Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. *Macromolecules* **2010**, *43*, 2643–2653.
  Abstract:



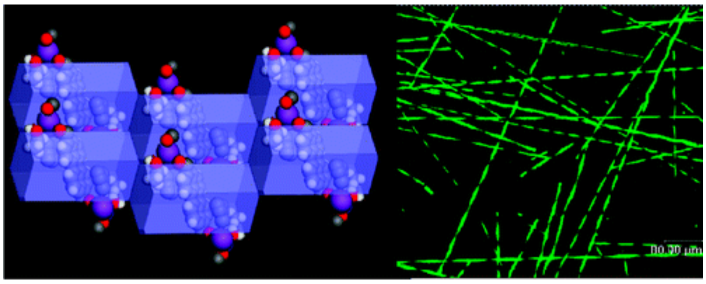
Polymer networks possessing reversible covalent cross-links constitute a novel material class with the capacity for adapting to an externally applied stimulus. These covalent adaptable networks (CANs) represent a trend in polymer network fabrication toward the rational design of structural materials possessing dynamic characteristics for specialty applications. Herein, we discuss the unique attributes of CANs that must be considered when designing, fabricating, and characterizing these smart materials that respond to either thermal or photochemical stimuli. While there are many reversible reactions which to consider as possible cross-link candidates in CANs, there are very few that are readily and repeatedly reversible. Furthermore, characterization of the mechanical properties of CANs requires special consideration owing to their unique attributes. Ultimately, these attributes are what lead to the advantageous properties displayed by CANs, such as recyclability, healability, tunability, shape changes, and low polymerization stress. Throughout this Perspective, we identify several trends and future directions in the emerging field of CANs that demonstrate the progress to date as well as the essential elements that are needed for further advancement.

- Synthesis and Characterization of New Self-Assembled Metallo-Polymers Containing Electron-Withdrawing and Electron-Donating Bis(terpyridine) Zinc(II) Moieties
  Schlütter, F.; Wild, A.; Winter, A.; Hager, M. D.; Baumgaertel, A.; Friebe, C.; Schubert, U. S. *Macromolecules* **2010**, *43*, 2759–2771.
  Abstract:



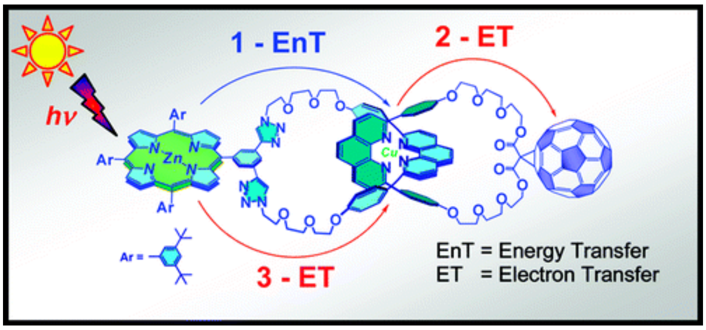
A series of rigid π-conjugated bis(terpyridines) (**M1**–**M7**) bearing electron-acceptor spacer units in 4′-position was synthesized in moderate to high yields by Pd^0-catalyzed Sonogashira cross-coupling reactions. The compounds were fully characterized by NMR spectroscopy, MALDI–TOF mass spectrometry, elemental analysis and their photophysical properties were discussed in detail. These new bis(terpyridines) were applied for the self-assembly reaction with Zn^{II} ions to form metallo-homo polymers (**P1**–**P7**). Broadened NMR signals and UV–vis titration experiments confirmed the successful polymerization. The electro-optical properties of the materials were investigated in detail. Band gaps up to 2.08 eV and bright blue to orange photoluminescence with quantum yields of 18 to 66% were observed strongly depending on the nature of the π-conjugated bis(terpyridine) system. In combination with electron-donor ditopic terpyridine ligands (**MD1** and **MD2**), two Zn^{II} random copolymers (**R1** and **R2**) were synthesized. These materials were investigated by UV–vis absorption and photoluminescence experiments in dilute solution and in the solid state, prepared by spin-coating from DMF solutions. Thereby, random copolymer **R2** featured an energy transfer from the donor to the acceptor part in dilute solution.

- Polymer-Induced Self-Assembly of Small Organic Molecules into Ultralong Microbelts with Electronic Conductivity
  Huang, M.; Schilde, U.; Kumke, M.; Antonietti, M.; Cölfen, H. *J. Am. Chem. Soc.* **2010**, *132*, 3700–3707.
  Abstract:



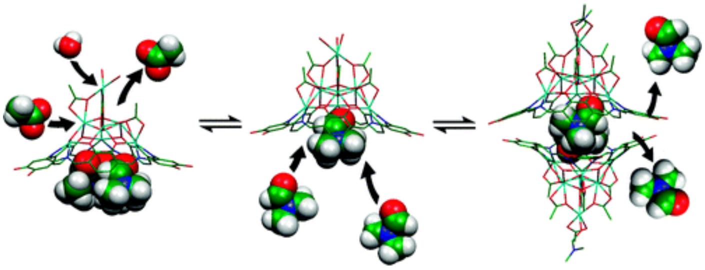
The principle of polymer-controlled crystallization of inorganic materials has been successfully transferred to functional aromatic organic dyes, in this instance 3,4,9,10-perylenetetracarboxylic acid potassium salt (PTCAPS), after its single-crystal structure was determined. The cationic double hydrophilic block copolymer poly(ethylene glycol)-block-branched-poly(ethyleneimine) (PEG-b-PEI) was used as the polymer additive to modify the crystallization of PTCAPS. Ultralong hierarchically structured PTCAPS microbelts with constant width and thickness of each individual belt have been fabricated. The belts are a mesocrystalline assembly of primary nanoparticles with high-energy anionic {001} faces stabilized by polymer complexation. Polarization microscopy, X-ray diffraction, optical absorption spectra, and fluorescence spectra indicate the favorable orientation of the 1D microbelts in the close-stacking direction and reveal a specific 1D superstructure fluorescence. Electrical conductivity measurements performed on a single nanobelt disclose in the doped state a remarkably high electronic conductivity and further demonstrate extended, wirelike π–π interactions along the [020] long axis of the belts. Together with the very large length of the belts and their organic–organic hybrid nanostructure, this makes these organic wires potentially interesting for the field of nano-/micro-optoelectronics.

- [2]Catenanes Decorated with Porphyrin and [60]Fullerene Groups: Design, Convergent Synthesis, and Photoinduced Processes
  Megiatto Jr., J. D.; Schuster, D. I.; Abwandner, S.; de Miguel, G.; Guldi, D. M. *J. Am. Chem. Soc.* **2010**, *132*, 3847–3861.
  Abstract:



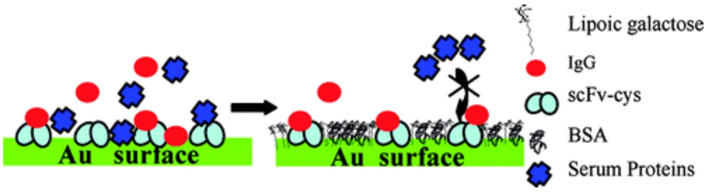
A new class of [2]catenanes containing zinc(II)–porphyrin (ZnP) and/or [60]fullerene (C_{60}) as appended groups has been prepared. A complete description of the convergent synthetic approach based on Cu(I) template methodology and "click" 1,3-dipolar cycloaddition chemistry is described. This new electron donor–acceptor catenane family has been subjected to extensive spectroscopic, computational, electrochemical and photophysical studies. ^{1}H NMR spectroscopy and computational analysis have revealed that the ZnP–C_{60}–[2]catenane adopts an extended conformation with the chromophores as far as possible from each other. A detailed photophysical investigation has revealed that upon irradiation the ZnP singlet excited state initially transfers energy to the (phenanthroline)$_2$–Cu(I) complex core, producing a metal-to-ligand charge transfer (MLCT) excited state, which in turn transfers an electron to the C_{60} group, generating the ZnP–$[Cu(phen)_2]^{2+}$–$C_{60}^{\bullet-}$ charge-separated state. A further charge shift from the $[Cu(phen)_2]^{2+}$ complex to the ZnP subunit, competitive with decay to the ground state, leads to the isoenergetic long distance $ZnP^{\bullet+}$–$[Cu(phen)_2]^{+}$–$C_{60}^{\bullet-}$ charge-separated radical pair state, which slowly decays back to the ground state on the microsecond time scale. The slow rate of back-electron transfer indicates that in this interlocked system, as in previously studied covalently linked ZnP−C_{60} hybrid materials, this process occurs in the Marcus-inverted region.

- Capsule Formation, Carboxylate Exchange, and DFT Exploration of Cadmium Cluster Metallocavitands: Highly Dynamic Supramolecules
  Frischmann, P. D.; Facey, G. A.; Ghi, P. Y.; Gallant, A. J.; Bryce, D. L.; Lelj, F.; MacLachlan, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 3893–3908.
  Abstract:



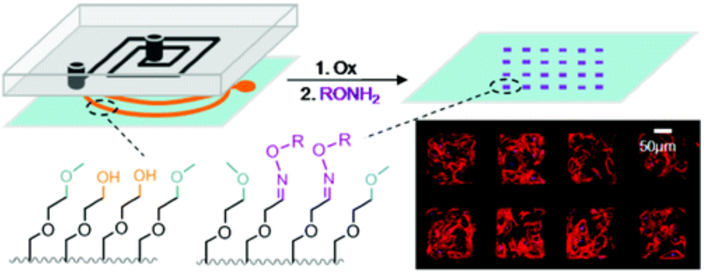
A family of molecular heptacadmium carboxylate clusters templated inside [3 + 3] Schiff base macrocycles has been isolated and studied by variable temperature solution and solid-state NMR spectroscopy, single-crystal X-ray diffraction (SCXRD), and density functional theory (DFT) calculations. These metallocavitand cluster complexes adopt bowl-shaped structures, induced by metal coordination, giving rise to interesting host−guest and supramolecular phenomena. Specifically, dimerization of these metallocavitands yields capsules with vacant coordination and hydrogen-bonding sites accessible to encapsulated guests. Strong host−guest interactions explain the exceptionally high packing coefficient (0.80) observed for encapsulated *N*,*N*-dimethylformamide (DMF). The guest-accessible hydrogen-bonding sites arise from an unusual μ_3-OH ligand bridging three cadmium ions. Thermodynamic and kinetic studies show that dimerization is an entropy-driven process with a highly associative mechanism. In DMF the exchange rate of peripheral cluster supporting carboxylate ligands is intrinsically linked to the rate of dimerization and these two seemingly different events have a common rate-determining step. Investigation of guest dynamics with solid-state ^{2}H NMR spectroscopy revealed 3-fold rotation of an encapsulated DMF molecule. These studies provide a solid understanding of the host−guest and dynamic properties of a new family of metallocavitands and may help in designing new supramolecular catalysts and materials.

- Lipoic Acid Glyco-Conjugates, a New Class of Agents for Controlling Nonspecific adsorption of Blood Serum at Biointerfaces for Biosensor and Biomedical Applications
  Wang, Y.; El-Boubbou, K.; Kouyoumdjian, H.; Sun, B.; Huang, X.; Zeng, X. *Langmuir* **2010**, *26,* 4119-4125.
  Abstract:



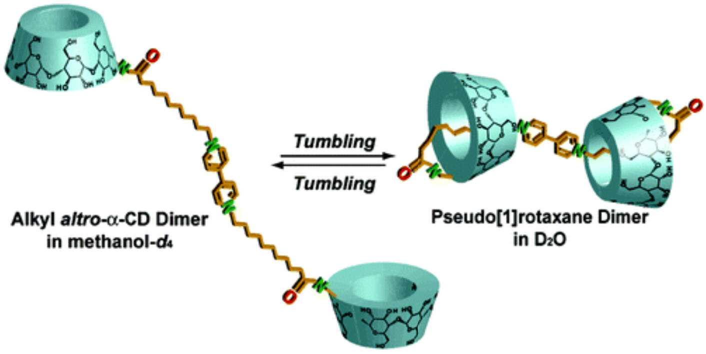
The carbohydrate-derived lipoic acid derivatives were studied as protein and cell resistant biomaterials. Six types of carbohydrates were examined for their abilities to reduce nonspecific adsorption of human serum and Hela cell using quartz crystal microbalance. Our data suggested that the structures of carbohydrates play an important role in resisting nonspecific binding. Specifically, the resistance was found to increase in the order lipoic fucose < lipoic mannose < lipoic *N*-acetyl glucosamine < lipoic glucose < lipoic sialic acid < lipoic galactose, where lipoic galactose derivative resisted most nonspecific adsorption. Furthermore, the combination of lipoic galactose and BSA was the most effective in reducing the adsorption of even undiluted human serum and the attachment of Hela cells while allowing specific binding. Several control experiments have demonstrated that the resistant-ability of mixed lipoic galactose and BSA was comparable to the best known system for decreasing nonspecific adsorption.

- Tandem Surface Microfluidic Lithography and Activation To Generate Patch Pattern Biospecific Ligand and Cell Arrays
  Pulsipher A.; Yousaf, M. N. *Langmuir* **2010**, *26*, 4130-4135.
  Abstract:



We report a rapid, inexpensive, and flexible methodology that combines microfluidic lithography and oxidative activation to pattern and chemically alter selective regions of SAMs on gold for subsequent chemoselective ligand immobilization. We demonstrate that PCC, a mild oxidant, can be used to convert hydroxyl-terminated SAMs to aldehydes and decorated with a variety of oxyamine-containing molecules. This strategy is compatible with cell culture and was employed to create a biospecific ligand platform for peptide-mediated, cell adhesion arrays. By using a number of different ligands and characterization tools, we showed that the generation of both cell patterning and ligand microarray patterning can be achieved. SAM formation, activation, ligand immobilization, and biospecific cell patterning are characterized by contact angle, cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and fluorescence microscopies.

- Switching from *altro*-α-Cyclodextrin Dimer to *pseudo*[1]Rotaxane Dimer through Tumbling
  Yamauchi, K.; Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Org. Lett.* **2010**, *12*, 1284–1286.
  Abstract:

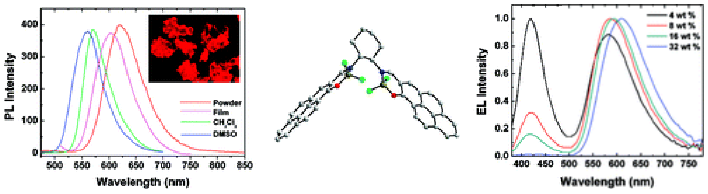


An alkyl *altro*-α-CD dimer was converted to the *pseudo*[1]rotaxane dimer through tumbling of the altropyranose unit of *altro*-α-CD in D_2O. The tumbling of the altropyranose unit was found to be a rotational vibration with 1.18×10^{-3} s^{-1} at 293 K. The activation free energy ($\Delta G^{\ddagger}_{288K}$) for the conformational change from an alkyl *altro*-α-CD dimer to *pseudo*[1]rotaxane dimer was 88.0 kJ mol^{-1}, which corresponds to the breakage of the hydrogen bond network for the tumbling of an altropyranose unit.

- Novel Bi-Nuclear Boron Complex with Pyrene Ligand: Red-Light Emitting as well as Electron Transporting Material in Organic Light-Emitting Diodes

  Zhou, Y.; Kim, J. W.; Kim, M. J.; Son, W.-J.; Han, S. J.; Kim, H. N.; Han, S.; Kim, Y.; Lee, C.; Kim, S.-J.; Kim, D. H.; Kim, J.-J.; Yoon, J. *Org. Lett.* **2010**, *12*, 1272–1275.

  Abstract:

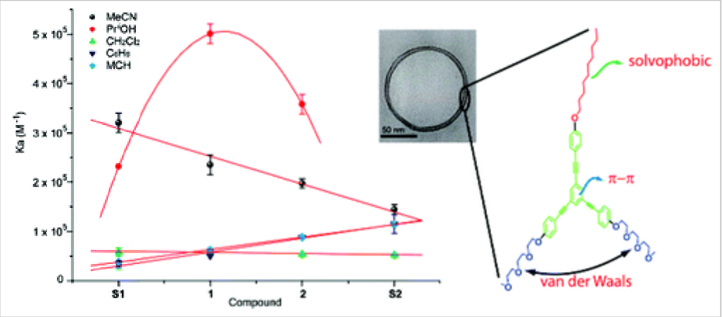


A novel boron complex bearing a pyrene ligand (CPB) was synthesized and introduced as the first example of a binuclear boron complex in organic light-emitting diodes. In the solid state, CPB2 exhibited strong red emission. In the devices, red emission with Commission International de L'Eclairage (CIE) coordinates of (0.57, 0.42) was obtained by tuning the weight concentration of CPB2. CPB2 behaved as both an emitting and electron transporting material.

- Solvophobic Effects in the Self-Assembly of Triangular-Shape Amphiphilic Oligo(phenylene ethynylenes)

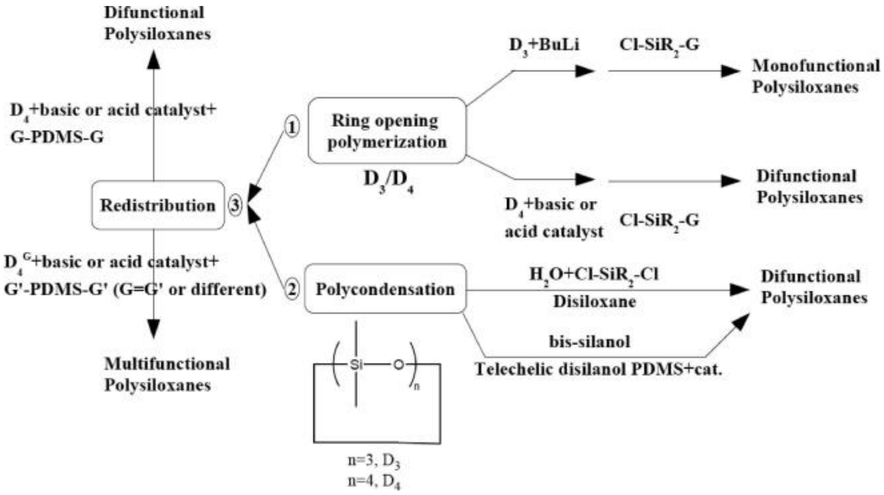
  García, F.; Aparicio, F.; Fernández, G.; Sánchez, L. *Org. Lett.* **2009**, *11*, 2748–2751.

  Abstract:



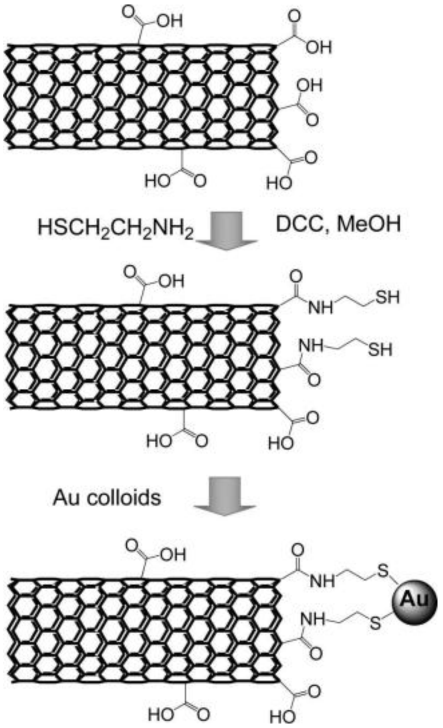
Triangular-shape OPEs, decorated in their periphery with a variable number of hydrophilic and hydrophobic substituents, have been synthesized to evaluate the influence of the solvent−solute and solute−solute interactions involved in their self-association. The similar size and electronic properties for these radial OPEs allow a direct evaluation of the solvophobic component of the π−π stacking since any preferential Coulombic or dispersion effect can be discarded. In addition, the formation of aggregates in solution is efficiently transferred to surfaces and the formation of hollow vesicles can be observed.

- Well-Architectured Poly(dimethylsiloxane)-Containing Copolymers Obtained by Radical Chemistry
  Pouget, E.; Tonnar, J.; Lucas, P.; Lacroix-Desmazes, P.; Ganachaud, F.; Boutevin, B. *Chem. Rev.* **2010**, *110,* 1233–1277.
  Abstract:



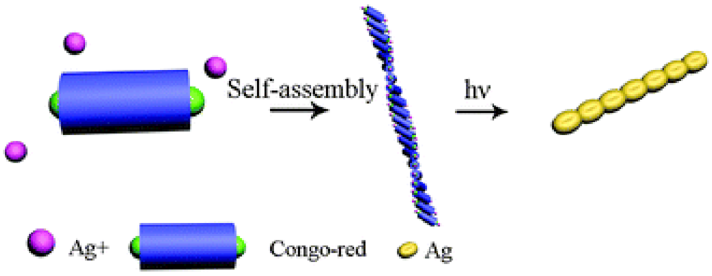
Thousands of industrial products have been commercialized ranging from linear chains (fluids) to slightly (rubbers) and highly (resins) cross-linked networks, leading to a wide range of applications. Silicone fluids are applied in areas like proceeding aids (26%), personal care (24%), paints and coatings (10%), paper coatings (15%), mechanical fluids (7%), and textile (5%). Due to their exceptional properties, silicone elastomers and resins have found applications in automotive (20%), electrical fitting (15%), medical/health (14%), appliances (9%), consumer goods (9%), textile coating (7%), business machines (5%), coatings (7%), and moldmarking (7%) areas.2 Polyorganosiloxanes exhibit exceptional properties as a result of the constitutive unit Si-O-Si of the polymer backbone. The value of the Si-O bond length is equal to 1.64 (0.03 Å,3 substantially smaller than that of the Si-O bond length calculated from the additivity of the atomic radii (1.83 Å). This is, on one hand, indebted to the partial doublebond character of the Si-O bond3 and, on the other hand, to the substantial ionic character (40-50%) of the Si-O bond (electronegativity of Si) 1.8 and O) 3.5). This is the reason why polyorganosiloxanes are considered to be “organic-inorganic” elastomers compared to pure organic elastomers (polybutadiene, polyisoprene).

- Carbon Nanotube-Inorganic Hybrids
  Eder, D. *Chem. Rev.* **2010**, *110,* 1348–1385.
  Abstract:



The world of nanomaterials provides exciting challenges and opportunities for chemists, physicists, biologists, and material scientists. The use of nanomaterials as building blocks for devices not only helps downscale conventional technologies by at least an order of magnitude but also offers a cheaper and more environmentally friendly production route, due to a drastic reduction in the necessary amount of raw materials, thus mimicking nature's efficient ways of managing with less when it comes to chemical and physical processing.1 Moreover, chemical and physical properties of substances can be considerably altered and fine-tuned when they exist on a nanoscopic scale, introducing the particle size as a powerful new parameter.2 The quantum dot (QD), a nanosized cluster displaying atom-like behavior,3 is a familiar example of this effect.

- Noble metal nanochains through helical self-assembly
  Fei, J.; Cui, Y.; Wang, A.; Zhu, P.; Li, J. *Chem. Commun.* **2010**, *46*, 2310 – 2312.
  Abstract:

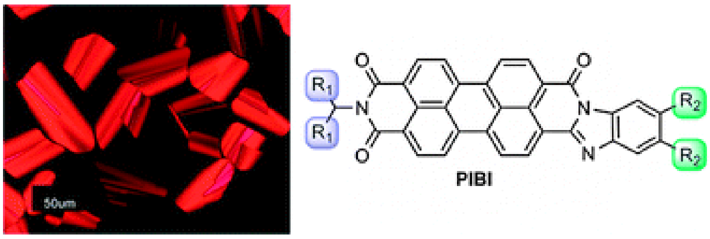


Silver nanochains composed of nanoparticles were prepared by photoreduction in situ under assistance of a helical self-assembly originating from coordination of Congo red and Ag^+. The special hierarchical nanostructures with different surface plasma resonance compared with silver nanoparticles have potential applications for electrical nanodevices.

- Synthesis and structure elucidation of discotic liquid crystalline perylene imide benzimidazole.

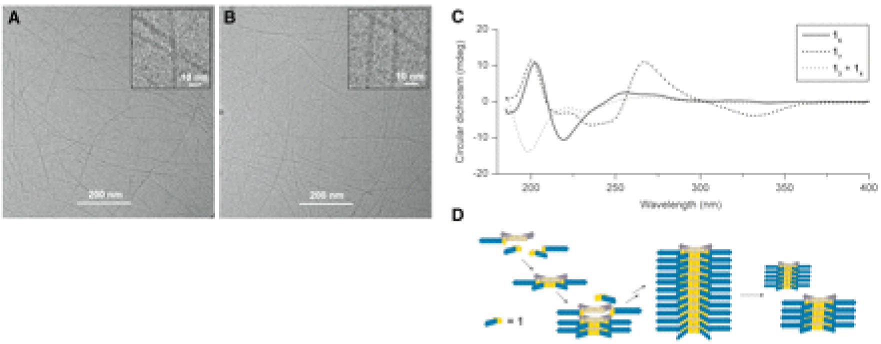
Wicklein, A.; Kohn, P.; Ghazaryan, L; Thurn-Albrecht, T; Thelakkat, M. *Chem. Commun.* **2010**, *46*, 2328 – 2330.

Abstract:



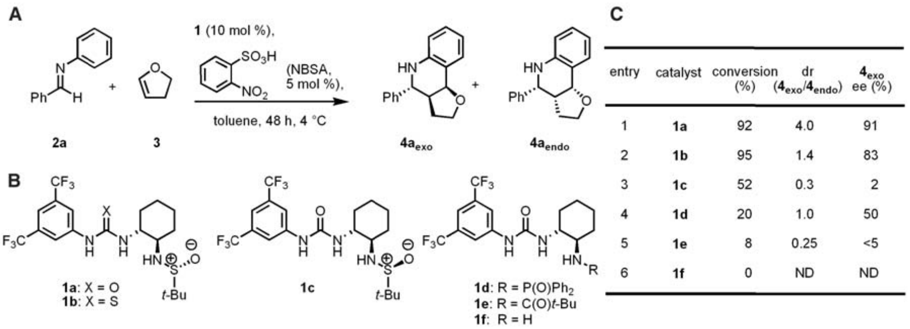
We report the synthesis of a soluble perylene imide benzimidazole (PIBI) and its structural, thermotropic, optical and electrochemical characterization with emphasis on discotic liquid crystalline properties.

- Mechanosensitive Self-Replication Driven by Self-Organization
  Carnall, J. M. A.; Waudby, C. A.; Belenguer, A. M.; Stuart, M. C. A.; Peyralans, J. J.-P.; Otto, S. *Science* **2010**, *327*, 1502 – 1506.
  Abstract:



Self-replicating molecules are likely to have played an important role in the origin of life, and a small number of fully synthetic self-replicators have already been described. Yet it remains an open question which factors most effectively bias the replication toward the far-from-equilibrium distributions characterizing even simple organisms. We report here two self-replicating peptide-derived macrocycles that emerge from a small dynamic combinatorial library and compete for a common feedstock. Replication is driven by nanostructure formation, resulting from the assembly of the peptides into fibers held together by β sheets. Which of the two replicators becomes dominant is influenced by whether the sample is shaken or stirred. These results establish that mechanical forces can act as a selection pressure in the competition between replicators and can determine the outcome of a covalent synthesis.

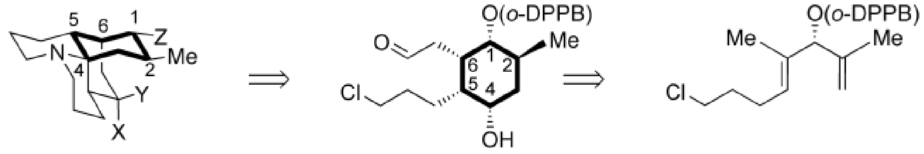
- Asymmetric Cooperative Catalysis of Strong Brønsted Acid–Promoted Reactions Using Chiral Ureas
  Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. *Science* **2010**, *327*, 986 – 990.
  Abstract:



entry	catalyst	conversion (%)	dr ($4_{exo}/4_{endo}$)	4_{exo} ee (%)
1	**1a**	92	4.0	91
2	**1b**	95	1.4	83
3	**1c**	52	0.3	2
4	**1d**	20	1.0	50
5	**1e**	8	0.25	<5
6	**1f**	0	ND	ND

Cationic organic intermediates participate in a wide variety of useful synthetic transformations, but their high reactivity can render selectivity in competing pathways difficult to control. Here, we describe a strategy for inducing enantioselectivity in reactions of protio-iminium ions, wherein a chiral catalyst interacts with the highly reactive intermediate through a network of noncovalent interactions. This interaction leads to an attenuation of the reactivity of the iminium ion and allows high enantioselectivity in cycloadditions with electron-rich alkenes (the Povarov reaction). A detailed experimental and computational analysis of this catalyst system has revealed the precise nature of the catalyst-substrate interactions and the likely basis for enantioinduction.

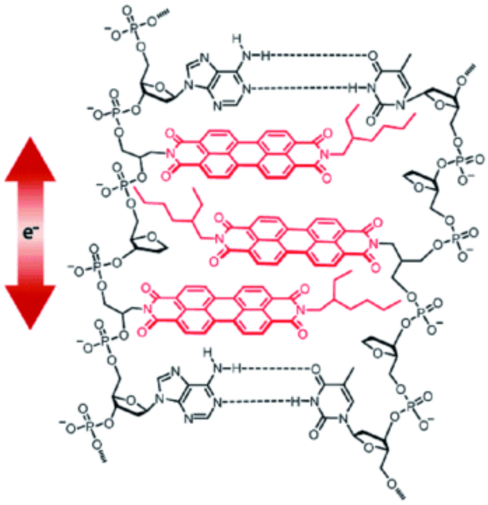
- Total Synthesis of (+)-Clavolonine, (_)-Deacetylfawcettiine, and (+)-Acetylfawcettiine
  Laemmerhold, K. M.; Breit, B. *Angew. Chem. Int. Ed.* **2010,** *49*, 2367 –2370.
  Abstract:



(+)-clavolonine (**1**): X,Y = O, Z = OH
(−)-deacetylfawcettiine (**2**): X = H, Y = OH, Z = OH
(+)-acetylfawcettiine (**3**): X = H, Y = OAc, Z = OAc

Three lycopodium alkaloids have been prepared by using a new strategy for constructing the central cyclohexane core (see scheme; *o*-DPPB=*ortho*-diphenylphosphanyl benzoyl). Thus stereoselective synthesis relying on substrate control was implemented; the key step involved a sequence of a (*o*-DPPB)-directed hydroformylation/carbonylene reaction and (*o*-DPPB)-directed hydroformylation.

- Electron Hopping among Cofacially Stacked Perylenediimides Assembled by Using DNA Hairpins
  Wilson, T. M.; Zeidan, T. A.; Hariharan, M.; Lewis, F. D.; Wasielewski, M. R. *Angew. Chem. Int. Ed*. **2010**, *49*, 2385 –2388.
  Abstract:



Charge on through: Perylenediimide chromophores incorporated into DNA hairpins serve as base-pair surrogates and form a zipperlike intercalated structure (see picture). Electron hopping was observed within the chromophore stacks upon one-electron reduction.