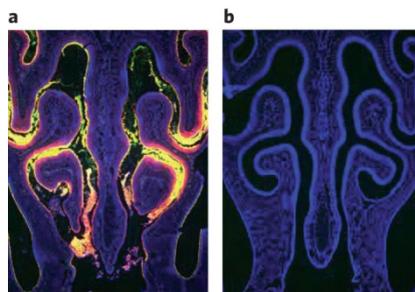


- POLYMER HYDROGELS Chaperoning vaccines
Staats, H. F.; Leong, K. W. *Nature Materials* **2010**, *9*, 537-538.

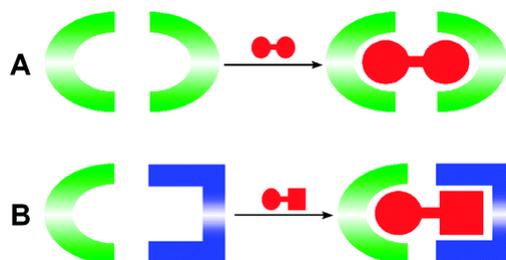
Abstract:



A cationic nanosized hydrogel (nanogel) shows controlled antigen delivery *in vivo* following intranasal administration and hence holds promise for a clinically effective adjuvant-free and needle-free vaccine system.

- Chemically Controlled Protein Assembly: Techniques and Applications
Fegan, A.; White, B.; Carlson, J. C. T.; Wagner, C. R. *Chem. Rev.* **2010**, *110*, 3315–3336.

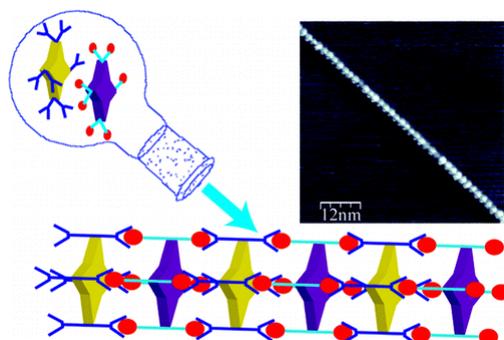
Abstract:



The study of biological processes has driven the efforts of modern molecular biology to unravel the microscopic capabilities of natural systems. Intrinsic to the experimental analysis of these life-governing principles is the process of testing, replicating, and visualizing the underlying biological mechanisms. As such, interacting with the nanoscale machinery of life becomes an increasingly apparent challenge. The range of this pursuit spans from DNA to RNA to proteins. Herein we review the assembly of proteins under the control of small molecule chemical signals, the dramatic strides made in the refinement of synthetic CID tools, and the divergent directions this work has taken as the concept of dimerization has expanded to a larger notion of chemically induced proximity (CIP) and how CIP has been used as both an investigative and a therapeutic tool. In addition, the potential for CID to be used to direct the assembly of supramolecular protein structures will also be reviewed.

- Straightforward Self-Assembly of Porphyrin Nanowires in Water: Harnessing Adamantane/ β -Cyclodextrin Interactions
Fathalla, M.; Neuberger, A.; Li, S. C.; Schmehl, R.; Diebold, U.; Jayawickramarajah, J. *J. Am. Chem. Soc.* **2010**, *132*, 9966–9967.

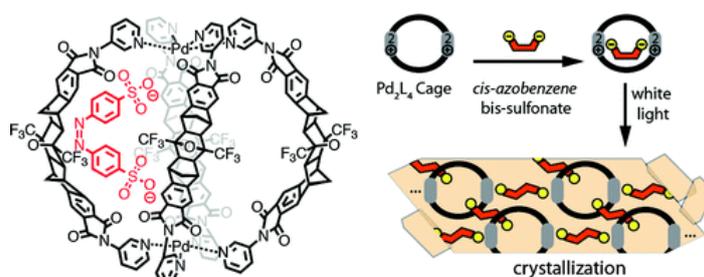
Abstract:



A convenient approach for the self-assembly of well-defined porphyrin nanowires in water, wherein the individual monomers do not aggregate via π - π interactions, is disclosed. These unidirectional and heteromeric assemblies are instead composed of robust β -CD/adamantane host/guest interactions. A combination of surface microscopies and fluorescence energy transfer experiments were conducted on the nanowires demonstrating their stability and resistance to disassembly.

- Light-Triggered Crystallization of a Molecular Host–Guest Complex
Clever, G. H.; Tashiro, S.; Shionoya, M. *J. Am. Chem. Soc.* **2010**, *132*, 9973–9975.

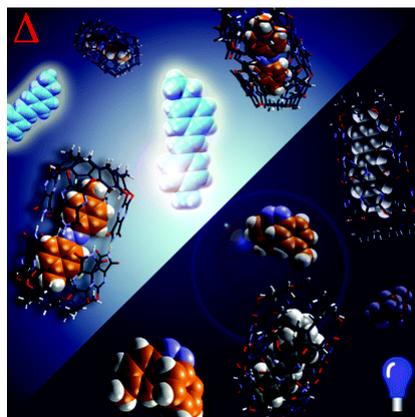
Abstract:



The control of structural changes in supramolecular assemblies is a key point in the development of molecular machines. The reversible photoisomerization of organic compounds such as azobenzene using light as an external input is especially suited because no waste products are generated. Based on our previous studies on the quantitative encapsulation of suitably sized bis-sulfonate guests by a self-assembled, metal–organic cage consisting of four rigid, bent bis-monodentate pyridyl ligands and two Pd(II) ions, we show here how the light-switchable guest *cis*-4,4′-azobenzene bis-sulfonate can be expelled from its 1:1 host–guest complex triggered by its photoisomerization to the *trans*-isomer. Using a highly soluble, PEGylated cage derivative, the full reversibility of this light-driven encapsulation/release process is demonstrated. In contrast, a sample of the less soluble, unsubstituted cages including 1 equiv of the *cis*-guest was shown to result in immediate crystallization upon photoisomerization of the guest. X-ray structure analysis confirmed the guest molecules having left the cavity of the host and on the contrary joining the cages into a polymeric material by binding to their Pd(II) centers from outside.

- Supramolecular Control of Fluorescence through Reversible Encapsulation
Dube, H.; Ams, M. R.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2010**, *132*, 9984–9985.

Abstract:

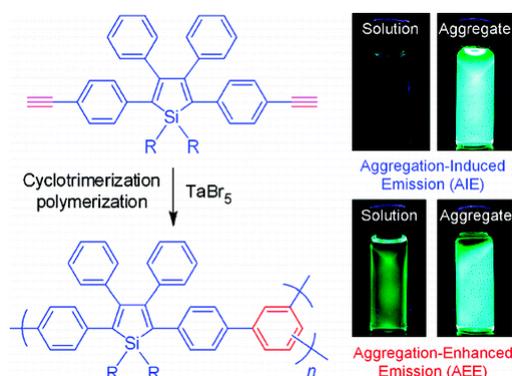


The *trans* to *cis* isomerization of 4,4'-dimethylazobenzene by the nonchemical stimuli light and heat alters its guest binding properties, allowing control over encapsulation of a second guest. We show here how this remote control for reversible encapsulation can be used as a supramolecular fluorescence on/off switch. If *trans*-4-ethyl-4'-methylstilbene is used as the second guest its fluorescence is altered depending on whether it is free in solution or encapsulated. We demonstrate that the change in fluorescence is indeed a consequence of the controlled encapsulation state of the stilbene by correlation of fluorescence and ^1H NMR data.

- Hyperbranched Conjugated Polysiloles: Synthesis, Structure, Aggregation-Enhanced Emission, Multicolor Fluorescent Photopatterning, and Superamplified Detection of Explosives

Liu, J.; Zhong, Y.; Lam, J. W. Y.; Lu, P.; Hong, Y.; Yu, Y.; Yue, Y.; Faisal, M.; Sung, H. H. Y.; Williams, I. D.; Wong, K. S.; Tang, B. Z. *Macromolecules* **2010**, *43*, 4921–4936.

Abstract:



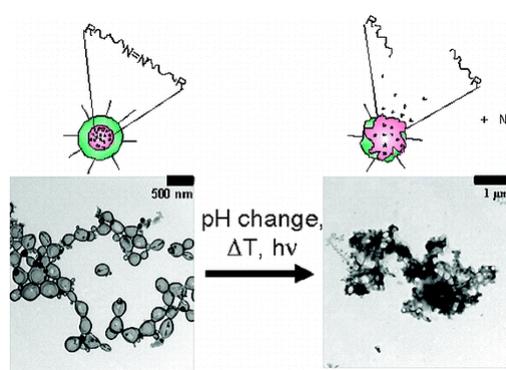
Hyperbranched poly(2,5-silole)s [*hb-P1*(*m*), *m* = 1, 6] are synthesized for the first time in this work. 1,1-Dialkyl-2,5-bis(4-ethynylphenyl)-3,4-diphenylsiloles [**1**(*m*)] were polymerized by TaBr₅, affording *hb-P1*(*m*) with high molecular weights (*M_w* up to 2.5×10^5) in high yields (up to 98%). The structures of *hb-P1*(*m*) were characterized by spectroscopic methods and the degree of branching of *hb-P1*(6) was determined to be 0.55. The hyperbranched polymers are soluble and stable, with no changes in solubility observed after they have been stored under ambient conditions for more than two years. Absorption and emission spectra of *hb-P1*(*m*) are red-shifted from those of **1**(*m*), indicating that the polymers are more conjugated than the monomers. Both **1**(*m*) and *hb-P1*(*m*) are nonemissive or weakly fluorescent when dissolved in their good solvents but become highly emissive when aggregated in their poor solvents or fabricated into thin solid films, showing unusual phenomena of aggregation-induced (AIE) and -enhanced emissions (AEE). Restriction of intramolecular rotations in the aggregate state is rationalized to be the main cause for the AIE and AEE effects.

Photoluminescence (PL) of **1(m)** and *hb-P1(m)* is tunable by varying their concentrations and morphologies. The polymers are readily cured when heated to high temperatures or upon photoirradiation, furnishing cross-linked networks with novel excitation wavelength-dependent emissions in the red spectral region. Photolithography of *hb-P1(m)* generates fluorescent photopatterns, with the exposed and unexposed areas emitting lights with different colors. The polymers function as sensitive fluorescent chemosensors for the detection of explosives, with a superamplification effect observed in the emission quenching of the polymer nanoaggregates by picric acid.

- Controlled Release from Polyurethane Nanocapsules via pH-, UV-Light- or Temperature-Induced Stimuli

Rosenbauer, E.-M.; Wagner, M.; Musyanovych, A.; Landfester, K. *Macromolecules* **2010**, *43*, 5083–5093.

Abstract:

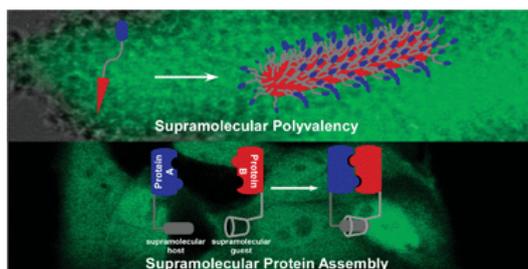


Polyurethane nanocapsules consisting of an aqueous core and a polymeric shell with included azo bonds as obtained via interfacial polyaddition of the monomers toluene-2,4-diisocyanate (TDI) and an azo-containing diol (VA-060) in inverse miniemulsion allow the selective release of encapsulated material by stimuli such as temperature, UV light, or pH change. The capsule degradation was detected by measuring time-dependently the fluorescence intensities of the dye sulforhodamine SR101, which is dissolved as the fluorescent marker in the core, by exposing the capsules to the different stimuli. Furthermore, the capsules were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The main components during the capsules' degradation were determined via nuclear magnetic resonance (NMR) spectrometry exemplary directly on the azo-monomer VA-060. The results present proof-of-principle studies of different controlled releases with a prototype of polyurethane capsules using the fluorescence dye sulforhodamine SR101 as a model system.

- Combining supramolecular chemistry with biology

Uhlenheuer, D. A.; Petkau, K.; Brunsveld, L. *Chem. Soc. Rev.* **2010**, *39*, 2817 – 2826.

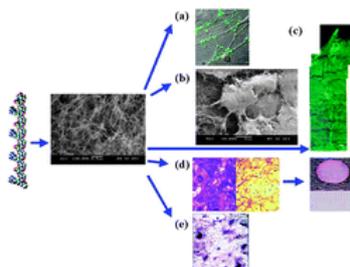
Abstract:



Supramolecular chemistry has primarily found its inspiration in biological molecules, such as proteins and lipids, and their interactions. Currently the supramolecular assembly of designed compounds can be controlled to great extent. This provides the opportunity to combine these synthetic supramolecular elements with biomolecules for the study of biological phenomena. This tutorial review focuses on the possibilities of the marriage of synthetic supramolecular architectures and biological systems. It highlights that synthetic supramolecular elements are for example ideal platforms for the recognition and modulation of proteins and cells. The unique features of synthetic supramolecular systems with control over size, shape, valency, and interaction strength allow the generation of structures fitting the demands to approach the biological problems at hand. Supramolecular chemistry has come full circle, studying the biology and its molecules which initially inspired its conception.

- Designer self-assembling peptide nanofiber biological materials
Hauser, C. A. E.; Zhang, S. *Chem. Soc. Rev.* **2010**, 39, 2780 – 2790.

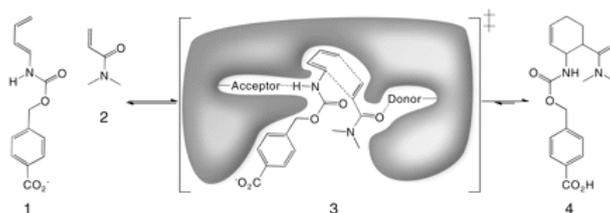
Abstract:



Scientists and bioengineers have dreamed of designing materials from the bottom up with the finest detail and ultimate control at the single molecular level. The discovery of a class of self-assembling peptides that spontaneously undergo self-organization into well-ordered structures opened a new avenue for molecular fabrication of biological materials. Since this discovery, diverse classes of short peptides have been invented with broad applications, including 3D tissue cell culture, reparative and regenerative medicine, tissue engineering, slow drug release and medical device development. Molecular design of new materials using short peptides is poised to become increasingly important in biomedical research, biomedical technology and medicine, and is covered in this *tutorial review*.

- Computational Design of an Enzyme Catalyst for a Stereoselective Bimolecular Diels-Alder Reaction
Siegel, J. B.; Zanghellini, A.; Lovick, H. M.; Kiss, G.; Lambert, A. R.; St.Clair, J. L.; Gallaher, J. L.; Hilvert, D.; Gelb, M. H.; Stoddard, B. L.; Houk, K. N.; Michael, F. E.; Baker, D. *Science* **2010**, 329, 309 – 313.

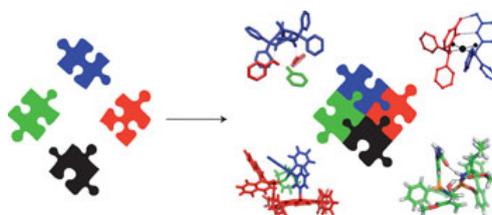
Abstract:



The Diels-Alder reaction is a cornerstone in organic synthesis, forming two carbon-carbon bonds and up to four new stereogenic centers in one step. No naturally occurring enzymes have been shown to catalyze bimolecular Diels-Alder reactions. We describe the de novo computational design and experimental characterization of enzymes catalyzing a bimolecular Diels-Alder reaction with high stereoselectivity and substrate specificity. X-ray crystallography confirms that the structure matches the design for the most active of the enzymes, and binding site substitutions reprogram the substrate specificity. Designed stereoselective catalysts for carbon-carbon bond-forming reactions should be broadly useful in synthetic chemistry.

- Supramolecular catalysis beyond enzyme mimics
Meeuwissen, J.; Reek, J. N. H. *Nature Chemistry* **2010**, *2*, 615–621.

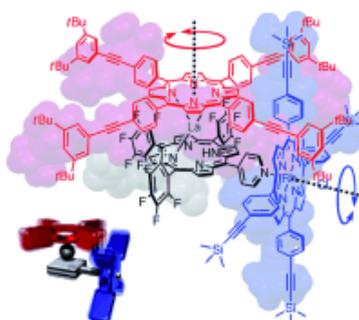
Abstract:



Supramolecular catalysis — the assembly of catalyst species by harnessing multiple weak intramolecular interactions — has, until recently, been dominated by enzyme-inspired approaches. Such approaches often attempt to create an enzyme-like 'active site' and have concentrated on reactions similar to those catalysed by enzymes themselves. Here, we discuss the application of supramolecular assembly to the more traditional transition metal catalysis and to small-molecule organocatalysis. The modularity of self-assembled multicomponent catalysts means that a relatively small pool of catalyst components can provide rapid access to a large number of catalysts that can be evaluated for industrially relevant reactions. In addition, we discuss how catalyst–substrate interactions can be tailored to direct substrates along particular reaction paths and selectivities.

- A Bevel-Gear-Shaped Rotor Bearing a Double-Decker Porphyrin Complex
Ogi, S.; Ikeda, T.; Wakabayashi, R.; Shinkai, S.; Takeuchi, M. *Chem. Eur. J.* **2010**, *16*, 8285–8290.

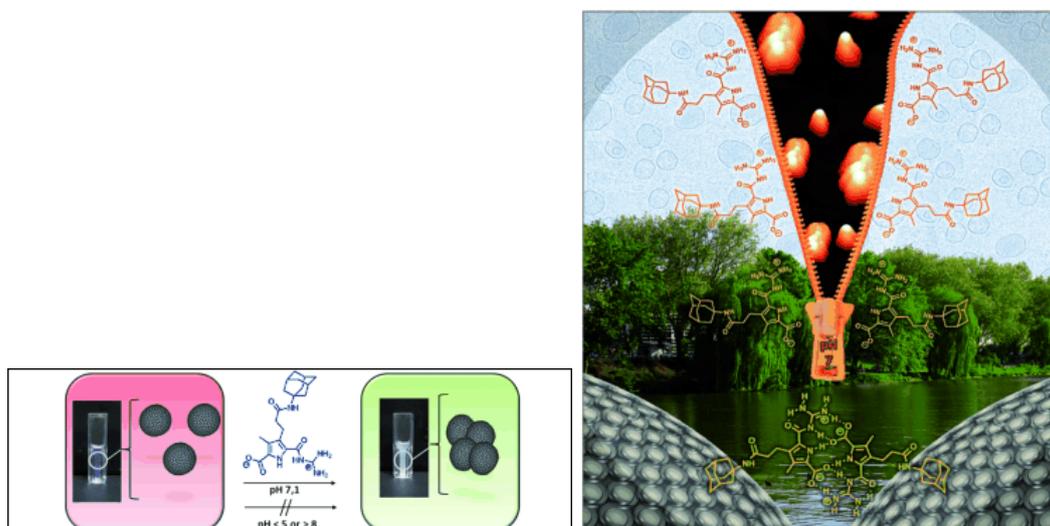
Abstract:



Supramolecular rotor: The interlocking of two porphyrin-based molecular rotors into a bevel-gear-shaped structure is demonstrated (see figure). The mechanical interactions between the teeth of the two porphyrin rotors enabled them to mesh and rotate with almost identical activation energies. Switching the rotational activities of one rotor by using chemical stimulation induced a change in the cooperative rotational motions of both rotors.

- Molecular Recognition of Vesicles: Host-Guest Interactions Combined with Specific Dimerization of Zwitterions
Voskuhl, J.; Fenske, T.; Stuart, M. C. A.; Wibbeling, B.; Schmuck, C.; Jan Ravoo, B. *Chem. Eur. J.* **2010**, *16*, 8300-8306.

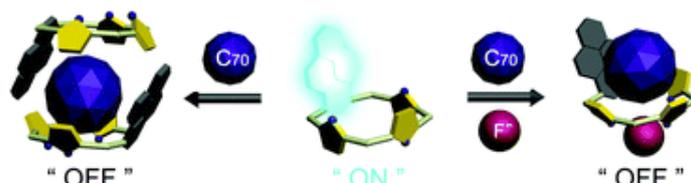
Abstract:



The aggregation of β -cyclodextrin vesicles can be induced by an adamantyl-substituted zwitterionic guanidiniocarbonylpyrrole carboxylate guest molecule (**1**). Upon addition of **1** to the cyclodextrin vesicles at neutral pH, the vesicles aggregate (but do not fuse), as shown by using UV/Vis and fluorescence spectroscopy, dynamic light scattering, ζ -potential measurements, cryogenic transmission electron microscopy, and atomic force microscopy. Aggregation of the vesicles is induced by a twofold supramolecular interaction. First, the adamantyl group of **1** forms an inclusion complex with β -cyclodextrin. Second, at neutral pH the guanidiniocarbonylpyrrole carboxylate zwitterion dimerizes through the formation of hydrogen-bonded ion pairs. Because the dimerization of **1** depends on the zwitterionic protonation state of **1**, the aggregation of the cyclodextrin vesicles is also pH dependent; the cyclodextrin vesicles do not interact at pH 5 or 9, at which **1** is either cationic or anionic and, therefore, not self-complementary. These observations are consistent with molecular recognition of the vesicles through a combination of two different supramolecular interactions, that is, host-guest inclusion and dimerization of zwitterions, at the bilayer membrane surface.

- Anion-modulated, highly sensitive supramolecular fluorescence chemosensor for C_{70}
Yoo, J.; Kim, Y.; Kim, S. J.; Lee, C. H. *Chem. Commun.* **2010**, *46*, 5449 – 5451.

Abstract:

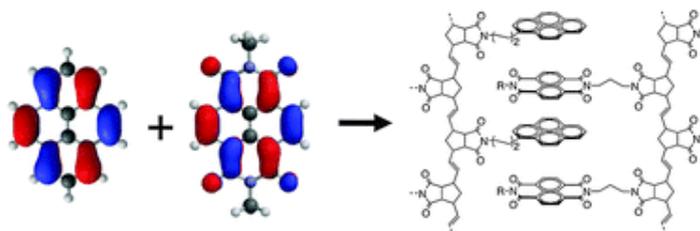


A new readily synthesized fluorescent chemosensor, calix[1]pyreno[3]pyrrole, displays excellent affinity with C_{70} . Anion-induced facile conformational changes and the dynamic nature of the receptor could be an excellent scaffold for sensing electron-deficient guests.

- Evidence of preferential π -stacking: a study of intermolecular and intramolecular charge transfer complexes

Kumar, N. S. S.; Gujrati, M. D.; Wilson, J. N. *Chem. Commun.* **2010**, 46, 5464 – 5466.

Abstract:

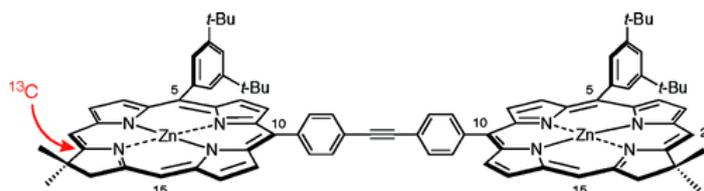


Nine combinations of π -electron donors and acceptors were examined by UV-vis, fluorescence and 1H -NMR spectroscopy to identify π -stacked charge transfer complexes in macromolecular and supramolecular constructs. The high association constant of pyrene and naphthalene diimide suggests a preferentially π -stacking pair rationalized by frontier orbital congruence.

- Probing the Rate of Hole Transfer in Oxidized Synthetic Chlorin Dyads via Site-Specific ^{13}C -Labeling

Nieves-Bernier, E. J.; Diers, J. R.; Taniguchi, M.; Holten, D.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2010**, 75, 3193–3202.

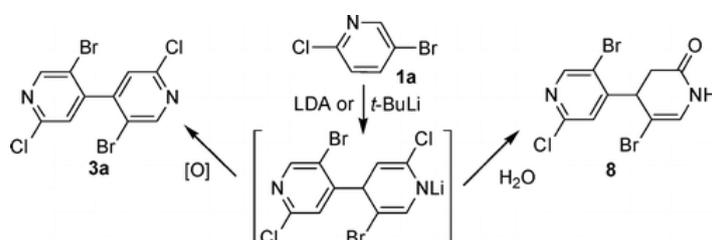
Abstract:



Understanding electronic communication among interacting constituents of multicomponent molecular architectures is important for rational design in diverse fields including artificial photosynthesis and molecular electronics. One strategy for examining ground-state hole/electron transfer in an oxidized tetrapyrrolic array relies on analysis of the hyperfine interactions observed in the EPR spectrum of the π -cation radical. This strategy has been previously employed to probe the hole/electron-transfer process in oxidized multiporphyrin arrays of normal isotopic composition, wherein 1H and ^{14}N serve as the hyperfine “clocks”, and in arrays containing site-specific ^{13}C -labels, which serve as additional hyperfine clocks. Herein, the hyperfine-clock strategy is applied to dyads of dihydroporphyrins (chlorins). Chlorins are more closely related structurally to chlorophylls than are porphyrins. A de novo synthetic strategy has been employed to introduce a ^{13}C label at the 19-position of the chlorin macrocycle, which is a site of large electron/hole density and is accessible synthetically beginning with ^{13}C -nitromethane. The resulting singly ^{13}C -labeled chlorin was coupled

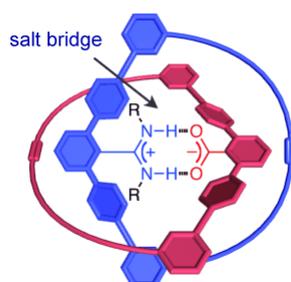
with an unlabeled chlorin to give a dyad wherein a diphenylethyne linker spans the 10-positions of the two zinc chlorins. EPR studies of the monocations of both the natural abundance and ^{13}C -labeled zinc chlorin dyads and benchmark zinc chlorin monomers reveal that the time scale for hole/electron transfer is in the 4–7 ns range, which is 5–10-fold longer than that in analogous porphyrin arrays. The slower hole/electron transfer rate observed for the chlorin versus porphyrin dyads is attributed to the fact that the HOMO is a_{1u} -like for the chlorins versus a_{2u} -like for the porphyrins; the a_{1u} -like orbital exhibits little (or no) electron/hole density at the site of linker attachment whereas the a_{2u} -like orbital exhibits significant electron/hole density at this site. Collectively, the studies of the chlorin and porphyrin dyads provide insights into the structural features that influence the hole/electron-transfer process.

- Synthesis of Polyhalogenated 4,4'-Bipyridines via a Simple Dimerization Procedure
Abboud, M.; Mamane, V.; Aubert, E.; Lecomte, C.; Fort, Y. *J. Org. Chem.* **2010**, *75*, 3224–3231.
Abstract:



Polyhalogenated 4,4'-bipyridines were conveniently synthesized in a single step starting from dihalopyridines. A mechanism was proposed on the basis of experiments performed with 2-chloro-5-bromopyridine **1a**. 2-Chloro-4-lithio-5-bromopyridine **A1** was produced via ortholithiation of **1a** by using either LDA or *t*-BuLi bases. When LDA was used, dimer **3a** containing two chlorines and two bromine atoms was formed predominantly accompanied by several byproducts whose structure and mechanism of formation are discussed. In the case of *t*-BuLi, although the major product was 2-chloropyridine **7**, a new pyridone product **8** was formed that is probably the result of the dihydropyridine intermediate hydrolysis. The dimerization procedure involving LDA was employed to prepare a large number of halogenated 4,4'-bipyridines in moderate to good yields. In some specific cases, halogenated 3,4' and 2,4'-bipyridines were obtained in lower yields and their structures were unambiguously assigned by X-ray diffraction analysis.

- Amidinium Carboxylate Salt Bridges as a Recognition Motif for Mechanically Interlocked Molecules: Synthesis of an Optically Active [2]Catenane and Control of Its Structure
Nakatani, Y.; Furusho, Y.; Yashima, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 5463–5467.
Abstract:



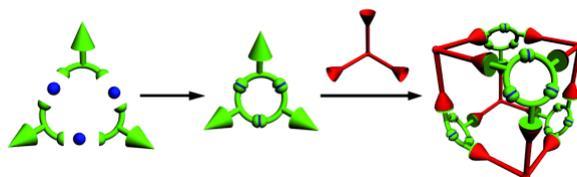
Salty catenane: An optically active [2]catenane was synthesized by utilizing an amidinium carboxylate salt bridge (see picture). The relative motion of the two macrocyclic components was completely controlled by an acid/base or Zn^{2+} /cryptand couple.

10

- Combining Metallasupramolecular Chemistry with Dynamic Covalent Chemistry: Synthesis of Large Molecular Cages

Granzhan, A.; Riis-Johannessen, T.; Scopelliti, R.; Severin, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 5515–5518.

Abstract:

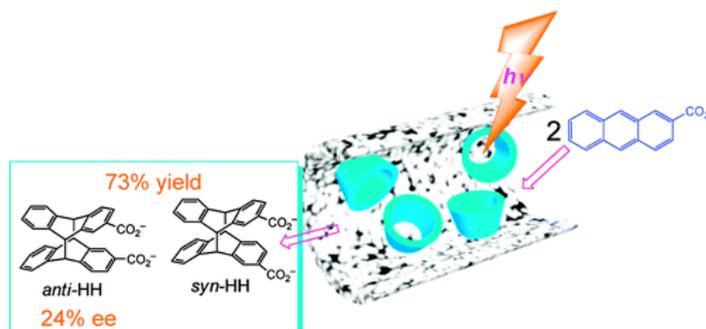


Ru-built cube: By combining metallasupramolecular chemistry with dynamic covalent chemistry, complex nanostructures can be formed. Large cages are synthesized by reaction of trinuclear metallamacrocycles containing pendant aldehyde groups (see picture; Ru blue, aldehyde linkers green) with triamines (red).

- Supramolecular Photochirogenesis with Cyclodextrin–Silica Composite. Enantiodifferentiating Photocyclodimerization of 2-Anthracenecarboxylate with Mesoporous Silica Wall-Capped γ -Cyclodextrin

Qiu, H.; Yang, C.; Inoue, Y.; Che, S. *Org. Lett.* **2009**, *11*, 1793–1796.

Abstract:



γ -Cyclodextrin (CD) immobilized on a mesoporous silica wall to cap one of the CD portals switched the product distribution of photocyclodimerization of 2-anthracenecarboxylate from head-to-tail to head-to-head with a significant enhancement of the enantiopurity of the chiral head-to-head product. CDs have been frequently employed as chiral hosts in supramolecular photochirogenesis because of their versatile ability to bind various organic guests, ready availability, and inherently chiral nature. Recently, we have reported the enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate (AC) catalyzed by native γ -CD, which yields head-to-tail (HT) dimers 1 and 2 (Scheme 2) as major products. Mesoporous silica, possessing size-tunable pores (2–50 nm) of high surface area and large pore volume, is a promising candidate for scaffolding catalyst. CD modified with active alkyloxysilane groups can be tethered to the mesoporous silica wall. We believe that the silica wall will effectively block one of the CD portals, allowing penetration of AC molecules only from the opposite side of the wall.