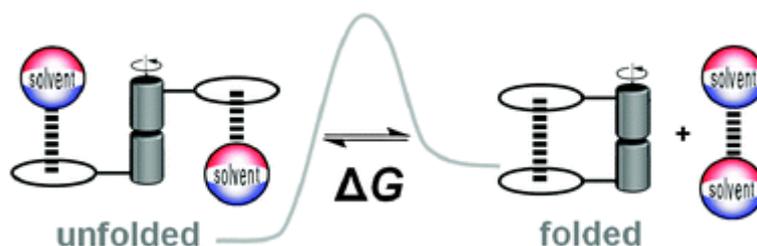


- Molecular balances for quantifying non-covalent interactions
Mati, I. K.; Cockroft, S. L. *Chem. Soc. Rev.* **2010**, *39*, 4195-4205.

Abstract:

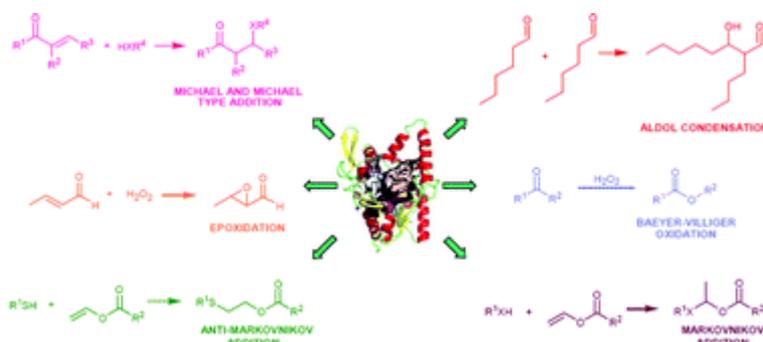


Molecular interactions underlie the whole of chemistry and biology. This *tutorial review* illustrates the use of rotameric folding molecules, topoisomers, atropoisomers, and tautomers as molecular balances for quantifying non-covalent interactions. This intramolecular approach enables a wide variety of interactions to be examined with a degree of geometric control that is difficult to achieve in supramolecular complexes. Synthetic variation of molecular balances allows the fundamental physicochemical origins of molecular recognition to be systematically examined by providing insights into the interplay of geometry and solvation on non-covalent interactions.

- Hydrolases: catalytically promiscuous enzymes for non-conventional reactions in organic synthesis

Busto, E.; Gotor-Fernández, V.; Gotor, V. *Chem. Soc. Rev.* **2010**, *39*, 4504-4523.

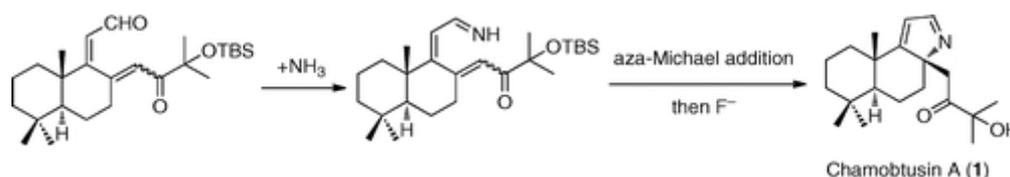
Abstract:



During the last three decades the use of hydrolases for the catalysis of environmentally friendly organic processes under mild reaction conditions has been well documented. Hydrolases have shown themselves to be ideal tools for the acceleration of synthetic transformations because of their high stability, catalytic efficiency, commercial availability and broad substrate specificity in a wide spectrum of biocatalyzed processes. In recent years, novel examples have appeared related to non-conventional reactions catalyzed by hydrolytic enzymes. Amongst these, lipases and acylases have gained much attention as promiscuous biocatalysts showing good levels of reactivity in C–C bond formation, C–heteroatom bond formation, oxidative processes, and novel hydrolytic reactions. This *critical review* covers recent investigation in the field of catalytic promiscuity, and highlights the most surprising and uncommon activities that this class of enzymes shows in organic synthetic transformations (111 references).

- Synthesis of (\pm)-Chamobtusin A by a Presumed Biomimetic Aza-Cyclization
Kuzuya, K.; Mori, N.; Watanabe, H. *Org. Lett.* **2010**, *12*, 4709-4711.

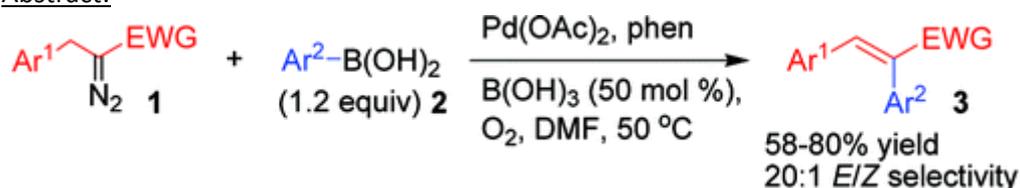
Abstract:



A total synthesis of (\pm)-chamobtusin A has been accomplished on the basis of our presumed biosynthetic pathway: the imine formation of keto aldehyde followed by intramolecular aza-Michael addition.

- Palladium-Catalyzed Oxidative Cross-Coupling Reaction of Arylboronic Acids with Diazoesters for Stereoselective Synthesis of (*E*)- α,β -Diarylacrylates
Tsoi, Y.-T.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 4506-4509.

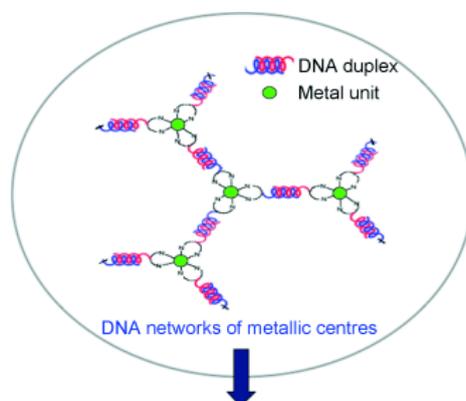
Abstract:



A Pd-catalyzed oxidative cross-coupling reaction of arylboronic acids with α -diazoesters was achieved using molecular oxygen as the sole reoxidant, and *E*- α,β -diarylacrylates were obtained in good yields and >20:1 *E*-to-*Z* selectivity.

- Metal-Complex/DNA Conjugates: A Versatile Building Block for DNA Nanoarrays
Ghosh, S.; Defrancq, E. *Chem.-Eur. J.* **2010**, *16*, 12780-12787.

Abstract:



Applications towards Materials Science and Biotechnology

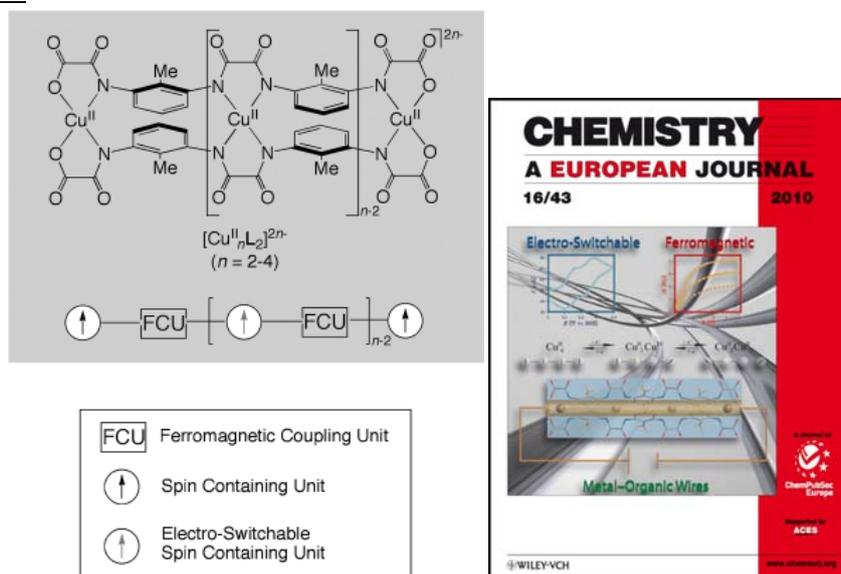
The use of DNA networks as templates for forming nanoarrays of metallic centres shows an exciting potential to generate addressable nanostructures. Inorganic units can be photoactive, electroactive and/or can possess magnetic and catalytic properties and can adopt different spatial arrangements due to their varied coordination nature. All these properties influence both the structure and function of passive DNA scaffolds and provide DNA nanostructures as a new platform for new materials in emerging technologies, such as nanotechnology, biosensing or biocomputing.

- Oligo-*m*-phenyleneoxalamide Copper(II) Mesocates as Electro-Switchable Ferromagnetic Metal–Organic Wires

Pardo, E.; Ferrando-Soria, J.; Dul, M.-C.; Lescouëzec, R.; Journaux, Y.; Ruiz-García, R.; Cano, J.; Julve, M.; Lloret, F.; Cañadillas-Delgado, L.; Pasán, J.; Ruiz-Pérez, C. *Chem.-Eur. J.* **2010**, *16*, 12838-12851.

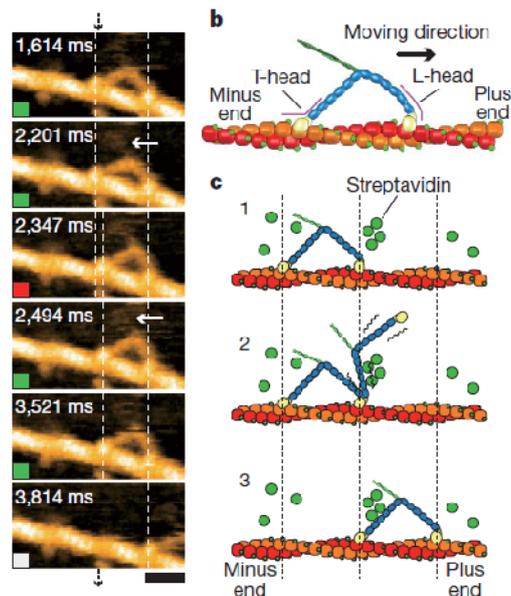
3

Abstract:



Double-stranded copper(II) string complexes of varying nuclearity, from di- to tetranuclear species, have been prepared by the Cu^{II} -mediated self-assembly of a novel family of linear homo- and heteropolytopic ligands that contain two outer oxamato and either zero (**1 b**), one (**2 b**), or two (**3 b**) inner oxamidato donor groups separated by rigid 2-methyl-1,3-phenylene spacers. The X-ray crystal structures of these Cu_n^{II} complexes ($n=2$ (**1 d**), 3 (**2 d**), and 4 (**3 d**)) show a linear array of metal atoms with an overall twisted coordination geometry for both the outer CuN_2O_2 and inner CuN_4 chromophores. Two such nonplanar *all-syn* bridging ligands **1 b–3 b** in an *anti* arrangement clamp around the metal centers with alternating *M* and *P* helical chiralities to afford an overall double *meso*-helicite-type architecture for **1 d–3 d**. Variable-temperature (2.0–300 K) magnetic susceptibility and variable-field (0–5.0 T) magnetization measurements for **1 d–3 d** show the occurrence of $S = nS_{Cu}$ ($n=2-4$) high-spin ground states that arise from the moderate ferromagnetic coupling between the unpaired electrons of the linearly disposed Cu^{II} ions ($S_{Cu}=1/2$) through the two *anti m*-phenylenediamidate-type bridges (J values in the range of $+15.0$ to 16.8 cm^{-1}). Density functional theory (DFT) calculations for **1 d–3 d** evidence a sign alternation of the spin density in the *meta*-substituted phenylene spacers in agreement with a spin polarization exchange mechanism along the linear metal array with overall intermetallic distances between terminal metal centers in the range of 0.7–2.2 nm. Cyclic voltammetry (CV) and rotating-disk electrode (RDE) electrochemical measurements for **1 d–3 d** show several reversible or quasireversible one- or two-electron steps that involve the consecutive metal-centered oxidation of the inner and outer Cu^{II} ions ($S_{Cu}=1/2$) to diamagnetic Cu^{III} ones ($S_{Cu}=0$) at relatively low formal potentials (E values in the range of +0.14 to 0.25 V and of +0.43 to 0.67 V vs. SCE, respectively). Further developments may be envisaged for this family of oligo-*m*-phenyleneoxalamide copper(II) double mesocates as electroswitchable ferromagnetic ‘metal–organic wires’ (MOWs) on the basis of their unique ferromagnetic and multicenter redox behaviors.

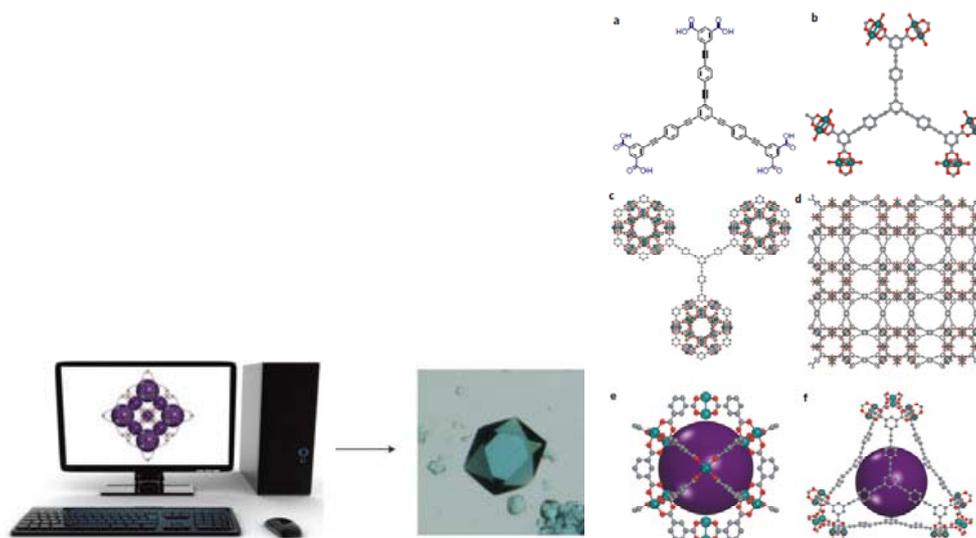
- Video imaging of walking myosin V by high-speed atomic force microscopy Kodera, N.; Yamamoto, D.; Ishikawa, R.; Ando, T. *Nature* **2010**, *468*, 72–76.

Abstract:

The dynamic behaviour of myosin V molecules translocating along actin filaments has been mainly studied by optical microscopy. The processive hand-over-hand movement coupled with hydrolysis of adenosine triphosphate was thereby demonstrated. However, the protein molecules themselves are invisible in the observations and have therefore been visualized by electron microscopy in the stationary states. The concomitant assessment of structure and dynamics has been unfeasible, a situation prevailing throughout biological research. Here we directly visualize myosin V molecules walking along actin tracks, using high-speed atomic force microscopy. The high-resolution movies not only provide corroborative ‘visual evidence’ for previously speculated or demonstrated molecular behaviours, including lever-arm swing, but also reveal more detailed behaviours of the molecules, leading to a comprehensive understanding of the motor mechanism. Our direct and dynamic high-resolution visualization is a powerful new approach to studying the structure and dynamics of biomolecules in action.

- *De novo* synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities
Farha, O. K.; Yazaydin, A. O.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nature Chemistry* **2010**, 2, 944–948.

Abstract:

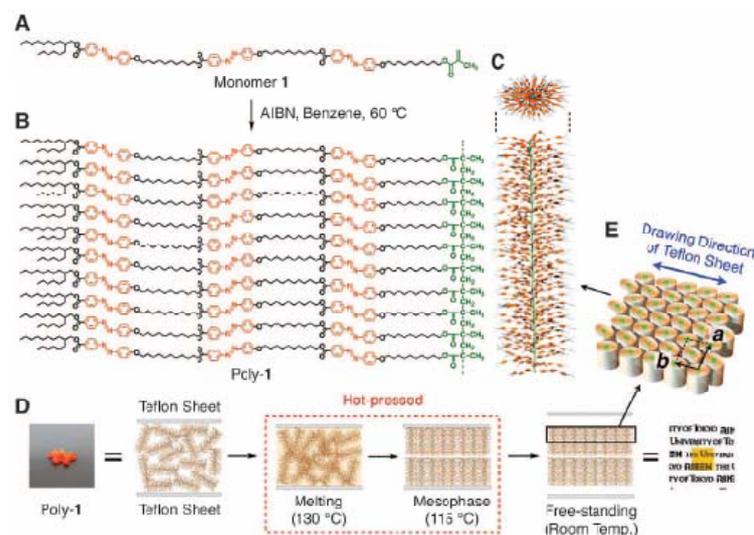


Metal–organic frameworks—a class of porous hybrid materials built from metal ions and organic bridges—have recently shown great promise for a wide variety of applications. The large choice of building blocks means that the structures and pore characteristics of the metal–organic frameworks can be tuned relatively easily. However, despite much research, it remains challenging to prepare frameworks specifically tailored for particular applications. Here, we have used computational modelling to design and predictively characterize a metal–organic framework (**NU-100**) with a particularly high surface area. Subsequent experimental synthesis yielded a material, matching the calculated structure, with a high BET surface area ($6,143 \text{ m}^2 \text{ g}^{-1}$). Furthermore, sorption measurements revealed that the material had high storage capacities for hydrogen (164 mg g^{-1}) and carbon dioxide ($2,315 \text{ mg g}^{-1}$)—gases of high importance in the contexts of clean energy and climate alteration, respectively—in excellent agreement with predictions from modelling.

- Large-Area Three-Dimensional Molecular Ordering of a Polymer Brush by One-Step Processing

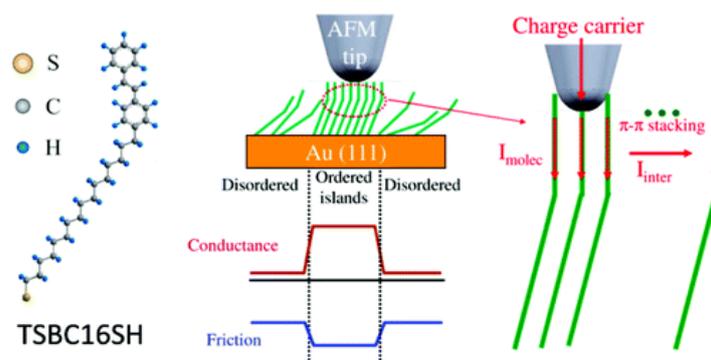
Hosono, N.; Kajitani, T.; Fukushima, T.; Ito, K.; Sasaki, S.; Takata, M.; Aida, T. *Science* **2010**, *330*, 808 – 811.

Abstract:



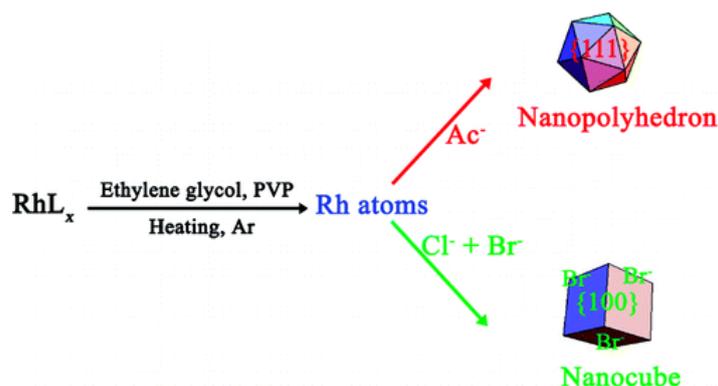
Rational molecular design and processing, enabling large-area molecular ordering, are important for creating high-performance organic materials and devices. We show that, upon one-step hot-pressing with uniaxially stretched Teflon sheets, a polymer brush carrying azobenzene-containing mesogenic side chains self-assembles into a freestanding film, where the polymer backbone aligns homeotropically to the film plane and the side chains align horizontally. Such an ordered structure forms through translation of a one-dimensional molecular order of the Teflon sheet and propagates from the interface macroscopically on both sides of the film. The resultant wide-area bimorph configuration allows the polymer film to bend rapidly and reversibly when the azobenzene units are photoisomerized. The combination of polymer brushes with hot-pressing and Teflon sheets provides many possibilities in designing functional soft materials.

- Influence of Molecular Ordering on Electrical and Friction Properties of ω -(*trans*-4-Stilbene)Alkylthiol Self-Assembled Monolayers on Au (111)
Qi, Y.; Liu, X.; Hendriksen, B. L. M.; Navarro, V.; Park, J. Y.; Ratera, I.; Klöpp, J. M.; Edder, C.; Himpsel, F. J.; Fréchet, J. M. J.; Haller, E., E; Salmeron, M. *Langmuir* **2010**, *26*, 16522–16528
Abstract:



The electrical and friction properties of ω -(*trans*-4-stilbene)alkylthiol self-assembled monolayers (SAMs) on Au(111) were investigated using atomic force microscopy (AFM) and near edge X-ray absorption fine structure spectroscopy (NEXAFS). The sample surface was uniformly covered with a molecular film consisting of very small grains. Well-ordered and flat monolayer islands were formed after the sample was heated in nitrogen at 120 °C for 1 h. While lattice resolved AFM images revealed a crystalline phase in the islands, the area between islands showed no order. The islands exhibit substantial reduction (50%) in friction, supporting the existence of good ordering. NEXAFS measurements revealed an average upright molecular orientation in the film, both before and after heating, with a narrower tilt-angle distribution for the heated film. Conductance-AFM measurements revealed a 2 orders of magnitude higher conductivity on the ordered islands than on the disordered phase. We propose that the conductance enhancement is a result of a better π - π stacking between the *trans*-stilbene molecular units as a result of improved ordering in islands.

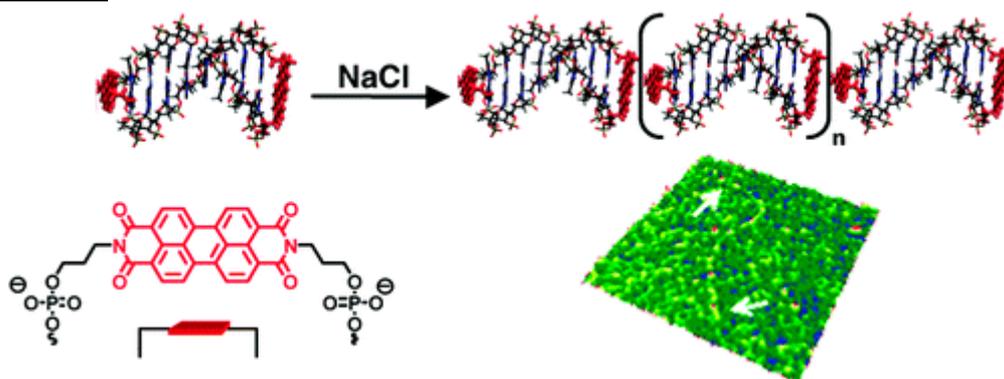
- Seedless Polyol Synthesis and CO Oxidation Activity of Monodisperse (111)- and (100)-Oriented Rhodium Nanocrystals in Sub-10 nm Sizes
Zhang, Y.; Grass, M. E.; Huang, W.; Somorjai, G. A. *Langmuir* **2010**, *26*, 16463-16468.
Abstract:



Monodisperse sub-10 nm (6.5 nm) sized Rh nanocrystals with (111) and (100) surface structures were synthesized by a seedless polyol reduction in ethylene glycol, with poly(vinylpyrrolidone) as a capping ligand. When using $[\text{Rh}(\text{Ac})_2]_2$ as the metal precursor, (111)-oriented Rh nanopolyhedra containing 76% (111)-twinned hexagons (in 2D projection) were obtained; whereas, when employing RhCl_3 as the metal precursor in the presence of alkylammonium bromide, such as tetramethylammonium bromide and trimethyl(tetradecyl)ammonium bromide, (100)-oriented Rh nanocubes were obtained with 85% selectivity. The {100} faces of the Rh nanocrystals are stabilized by chemically adsorbed Br^- ions from alkylammonium bromides, which led to (100)-oriented nanocubes. Monolayer films of the (111)-oriented Rh nanopolyhedra and (100)-oriented Rh nanocubes were deposited on silicon wafers in a Langmuir–Blodgett trough to make model 2D nanoarray catalysts. These nanocatalysts were active for CO oxidation by O_2 , and the turnover frequency was independent of nanoparticle shape, consistent with that previously observed for Rh(111) and Rh(100) single crystals.

- Hydrophobic Self-Assembly of a Perylenediimide-Linked DNA Dumbbell into Supramolecular Polymers
Neelakandan, P. P.; Pan, Z.; Hariharan, M.; Zheng, Y.; Weissman, H.; Rybtchinski, B.; Lewis, F. *D. J. Am. Chem. Soc.* **2010**, *132*, 15808–15813.

Abstract:



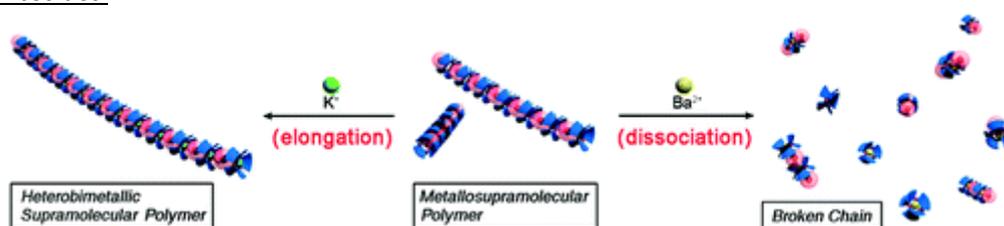
The self-assembly of DNA dumbbell conjugates possessing hydrophobic perylenediimide (PDI) linkers separated by an eight-base pair A-tract has been investigated. Cryo-TEM images obtained from dilute solutions of the dumbbell in aqueous buffer containing 100 mM NaCl show the presence of structures corresponding to linear end-to-end assemblies of 10–30 dumbbell monomers. The formation of assemblies of this size is consistent with analysis of the UV–vis and fluorescence spectra of these solutions for the content of PDI monomer and dimer chromophores. Assembly size is dependent upon the concentration of dumbbell and salt as well as the temperature. Kinetic analysis

of the assembly process by means of salt-jump stopped-flow measurements shows that it occurs by a salt-triggered isodesmic mechanism in which the rate constants for association and dissociation in 100 mM NaCl are $3.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and 1.0 s^{-1} , respectively, faster than the typical rate constants for DNA hybridization. TEM and AFM images of samples deposited from solutions having higher concentrations of dumbbell and NaCl display branched assemblies with linear regions $>1 \mu\text{m}$ in length and diameters indicative of the formation of small bundles of dumbbell end-to-end assemblies. These observations provide the first example of the use of hydrophobic association for the assembly of small DNA duplex conjugates into supramolecular polymers and larger branched aggregates.

- Assembly Modulation by Adjusting Countercharges of Heterobimetallic Supramolecular Polymers Composed of Tris(spiroborate) Twin Bowls

Danjo, H.; Hirata, K.; Noda, M.; Uchiyama, S.; Fukui, K.; Kawahata, M.; Azumaya, I.; Yamaguchi, K.; Miyazawa, T. *J. Am. Chem. Soc.* **2010**, *132*, 15556–15558.

Abstract:



Heterobimetallic supramolecular polymers were prepared by treatment of the supramolecular polymers composed of tris(spiroborate) type molecular connecting modules with a potassium cation. On the other hand, the addition of a barium cation led to dissociation of the supramolecular polymer chain. Modulation of polymer formation was realized by the use of small metal cations as a control factor.

- Size-Dependent LCST Transitions of Polymer-Coated Gold Nanoparticles: Cooperative Aggregation and Surface Assembly

Gibson, M. I.; Paripovic, D.; Klok, H.-A. *Adv. Mat.* **2010**, *42*, 4721-4725.

Abstract:



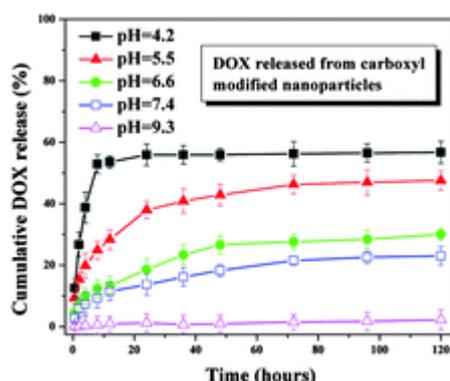
Nanoparticles working together. Thermoresponsive polymer-coated nanoparticles are shown to display size dependent, cooperative, lower critical solution temperature behavior. This was exploited to direct the assembly of appropriate nanoparticles onto complementary polymer brush coated surfaces.

- Surface functionalization of magnetic mesoporous silica nanoparticles for controlled drug release

Chang, B.; Guo, J.; Liu, C.; Qian, J.; Yang, W. *J. Mater. Chem.* **2010**, *20*, 9941-9947.

Abstract:

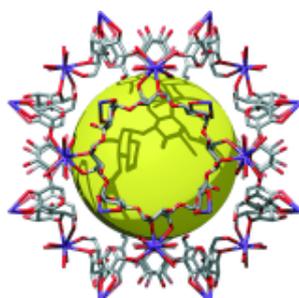
9



The modified sol-gel approach to the synthesis of well-structured magnetic mesoporous silica nanoparticles (M-MSNs) was described, which comprised magnetic nanoparticles resided within the mesoporous nanoparticles. A diversity of surface modification was subjected to systematic investigation using organic silanes, eventually resulting in the decoration with the carboxyl ($-\text{COOH}$), methyl phosphonate ($-\text{PO}_3^-$), amino ($-\text{NH}_2$) and phenyl ($-\text{Ph}$) groups on the surface of M-MSNs. The careful characterizations demonstrated that the modified M-MSNs displayed the specifically charged surfaces and differently porous characters, yet without showing any influence on the shape and size. To exploit their potential in cancer treatment, we extensively studied the drug loading capacity and sustained release behaviour of the modified M-MSNs for representative drugs. The hydrophilically modified M-MSNs with $-\text{COOH}$ and $-\text{PO}_3^-$ were beneficial for loading the water-soluble doxorubicin hydrochloride (DOX) through electrostatic attraction. The results demonstrated that M-MSNs- PO_3^- achieved a higher loading content and M-MSNs- COOH presented a distinct pH-responsible release behavior. On the other hand, M-MSNs- Ph displayed a controlled release rate in a short term *via* the weakened hydrogen bonding interaction. The cytotoxicity of modified M-MSNs to normal cells and macrophage uptake indicated that the modified M-MSNs were suitable as drug carriers. These mesoporous nanoparticles were non-toxicity to HeLa cells, while the drug-loaded nanoparticles apparently led to the unambiguous cytotoxicity as a result of the sustained release of drugs. These results have an important implication that the modified M-MSNs are promising as platforms for storing the hydrophilic or hydrophobic anticancer drugs for tumour therapy.

- Metal-Organic Frameworks from Edible Natural Products
Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2010**, *46*, 8630-8634.

Abstract:



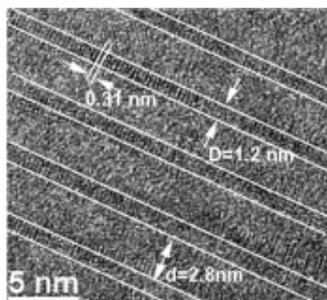
Let them eat MOFs: Take a spoonful of sugar (γ -cyclodextrin to be precise), a pinch of salt (most alkali metal salts will suffice), and a swig of alcohol (Everclear fits the bill), and you have a robust,

renewable, nanoporous (Langmuir surface area $1320 \text{ m}^2 \text{ g}^{-1}$) metal–organic framework for breakfast (CD-MOF-1; see picture, C gray, O red, K purple; yellow sphere: pore).

- Controlled Colloidal Growth of Ultrathin Single-Crystal ZnS Nanowires with a Magic-Size Diameter

Deng, Z.; Yan, H.; Liu, Y. *Angew. Chem. Int. Ed.* **2010**, *46*, 8695-8698.

Abstract:

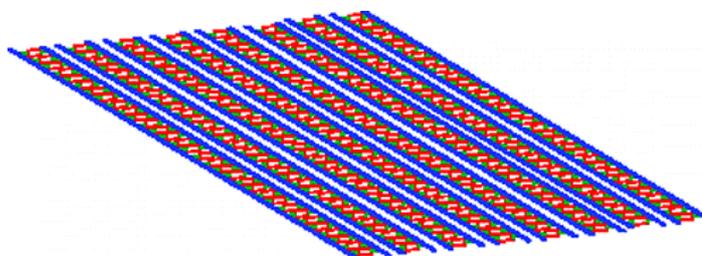


Down to the thin wire: A facile colloidal chemistry method is demonstrated for the controlled growth of highly uniform ultrathin single-crystal ZnS nanowires with a magic-size diameter as low as 1.2 nm (see HRTEM image). These ultrathin nanowires could find broad use in sensors, photodetectors, and host materials for diluted magnetic semiconductors.

- Hexa-peri-hexabenzocoronene (HBC)-Incorporated Single- and Double-Stranded Polynorbornenes

Chen, C.-W.; Chang, H.-Y.; Lee, S.-L.; Hsu, I.-J.; Lee, J.-J.; Chen, C.-H.; Luh, T.-Y. *Macromolecules* **2010**, *43*, 8741–8746.

Abstract:

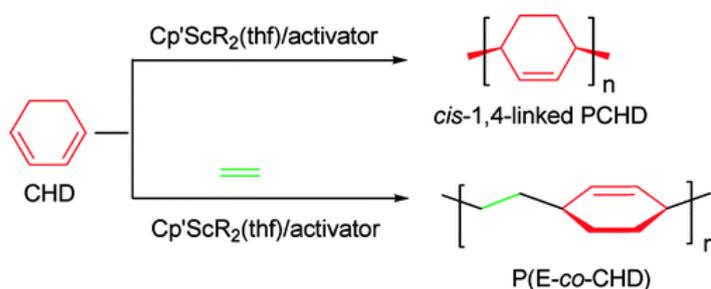


Double-stranded polymeric ladderphane **1** using HBC as linkers and the single-stranded comblike polynorbornene **2** with HBC pendants are synthesized by the ring-opening metathesis polymerization using the first-generation Grubbs catalyst. The photophysical properties of these HBC-incorporated polymers indicate significant interactions between adjacent polynuclear aromatic chromophores which are comparable with those of aggregated forms of the HBC cores. No liquid crystal properties, however, are observed in these polymers. The STM images of **1** and **2** demonstrate the unique properties of polynorbornene derivatives having *N*-aryl-5,6-endopyrrolidene pendants or linkers where the polymers are self-assembled to form ordered two-dimensional arrays on the HOPG surface.

- Scandium-Catalyzed Regio- and Stereospecific *cis*-1,4-Polymerization of 1,3-Cyclohexadiene and Copolymerization with Ethylene

Li, X.; Hou, Z. *Macromolecules* **2010**, *43*, 8904–8909.

Abstract:

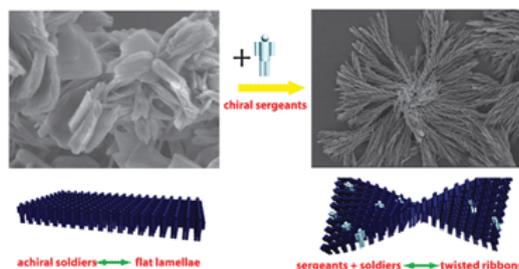


In the presence of an activator such as $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$, the half-sandwich scandium dialkyl complexes $\text{Cp}'\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$ (**1**), C_5Me_5 (**2**), $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ (**3**)) showed excellent regio- and stereoselectivity for the polymerization of 1,3-cyclohexadiene (CHD) and its copolymerization with ethylene. The homopolymerization of CHD afforded soluble crystalline *cis*-1,4-linked poly(CHD)s with very high stereoselectivity (tacticity up to 99 mol %). The copolymerization of CHD with ethylene gave the corresponding copolymers with a wide range of CHD contents (10–67 mol %) in a regio- and stereospecific 1,4-*cis* fashion.

- Amplification of chirality in *N,N'*-1,2-ethanediylbisbenzamides: from planar sheets to twisted ribbons

Aparicio, F.; Vicente, F.; Sánchez, L. *Chem. Commun.* **2010**, 46, 8356-8358.

Abstract:

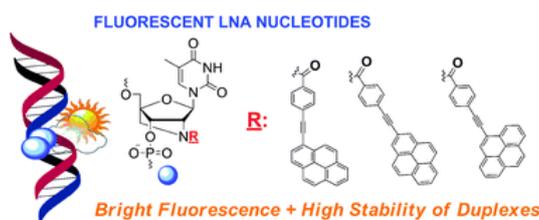


A remarkable sergeants-and-soldiers effect is observed in the coassembly of *N,N'*-1,2-ethanediylbisbenzamides onto surfaces that experience an amplification of chirality able to transform flat lamellae into twisted ribbons.

- Novel interstrand communication systems within DNA duplexes based on 1-, 2- and 4-(phenylethynyl)pyrenes attached to 2'-amino-LNA: high-affinity hybridization and fluorescence sensing

Astakhova, I. V.; Lindegaard, D.; Korshun, V. A.; Wengel, J. *Chem. Commun.* **2010**, 46, 8362-8364.

Abstract:



Functionalisation of 2'-amino-LNA oligonucleotides with 1-, 2- and 4-(phenylethynyl)pyrene fluorophores *via* a carbonyl linker (PEPyc) resulted in efficient interstrand communication systems in nucleic acid duplexes, providing effective tools for stabilization of nanostructures and fluorescence monitoring of DNA self-assembly.