## VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:



## Author Profile

*"The most important thing I learned from my parents is 'persistence is power'.*
*My favorite place on earth is Hawaii …"*
This and more about Keiji Maruoka can be found on page 580.



## News


S. Shaik


I. Marek


Y. Apeloig


K. Maruoka

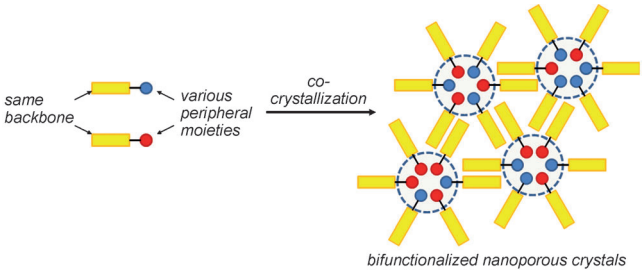


## Books

# Highlights

## Porous Organic Crystals



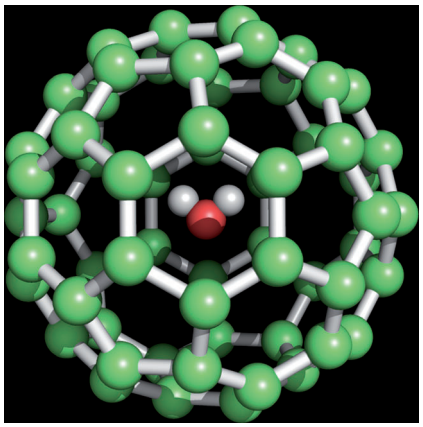



**Alloying allowed**: The self-assembling motifs of rigid steroid molecules (see scheme, left) into nanoporous crystals allows the combination of functional groups (shown in red and blue) inside the pores of binary, ternary, and quaternary co-crystals, resulting multifunctional porous materials.

## Endohedral Fullerene



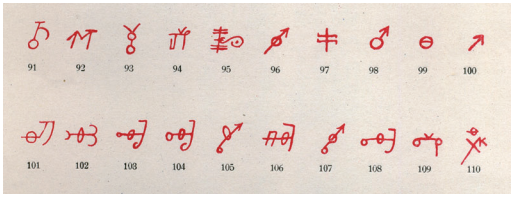
**Dry water in a wet dungeon?** An isolated $H_2O$ molecule has been trapped permanently inside hydrophobic $C_{60}$ (see picture; green C, white H, red O). The endohedral fullerene $H_2O@C_{60}$ was synthesized by opening, filling, and reclosing the carbon cage. The incarcerated water does not alter the structure of the cage, but it confers an appreciable dipole moment to the new entity with its intrinsically apolar carbon sphere.



# Essays

## Symbolism of Arrows





**Alchemists incorporated arrows** in their symbolism (see picture) hundreds of years before modern chemists adopted arrows in chemical equations. The next time you insert an arrow in a chemical text consider why precisely that arrow is needed. What does it really mean? How did we learn to use arrows in chemistry? What do our arrows have in common with those of abstract artists?

**For the USA and Canada:**
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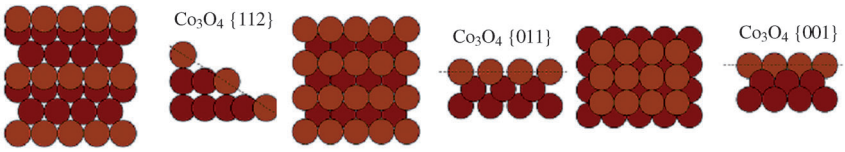
# Minireviews




**Shape-controlled nanocrystals** (NCs) are a new frontier in heterogeneous catalysis. Research into these NCs has shown that the catalytic properties of a material are sensitive not only to the size but also to the shape of the NCs owing to well-defined facets. Shape-controlled NCs may serve to bridge the gap between model surfaces and real catalysts.

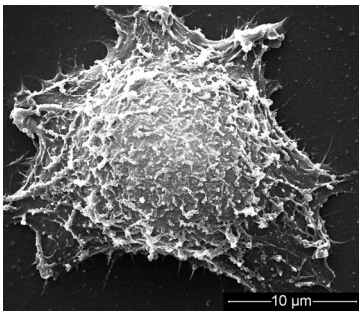


# Reviews


**Relatively related**: Relativistic effects in the valence shell of the chemical elements reach a maximum in the triad Pt–Au–Hg and influence their catalytic activity in organic reactions. The catalytic activity for some representative reactions is examined together with other relevant properties, such as toxicity, price, and availability. For the reactions considered, gold is generally preferred to mercury or platinum catalysts.



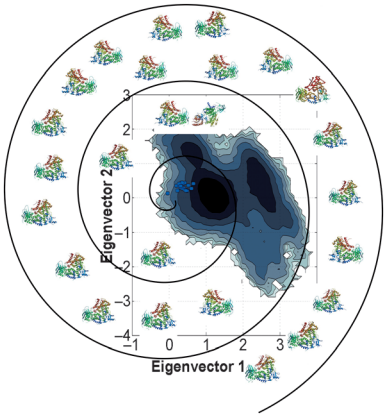
# Communications




**Stable and biocompatible**: The chemical composition of synthesized cationic thiolate-monolayer-protected gold nanorods was precisely determined. In vitro cell culture experiments showed no cytotoxicity of these nanorods, and the number of nanorods that were taken up by each cancer cell exceeded two million particles (see picture).

## Computational Chemistry





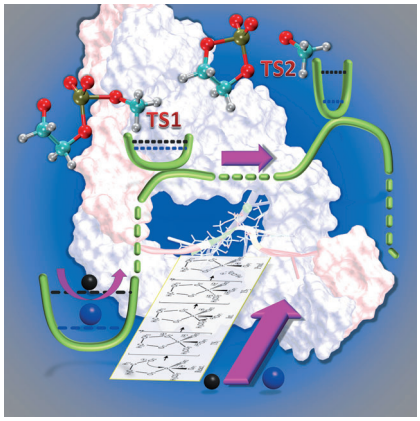

**Kinase binding**: The mechanism of molecular recognition in the pharmacologically relevant phosphoinositide 3-kinase PI3K-γ has been investigated. The analysis of molecular dynamics simulations, free energy calculations, and docking interactions suggests that a combination of two proposed limiting mechanisms, conformational selection and induced fit, may best explain binding events between the ligand and its target.

## Reaction Mechanisms



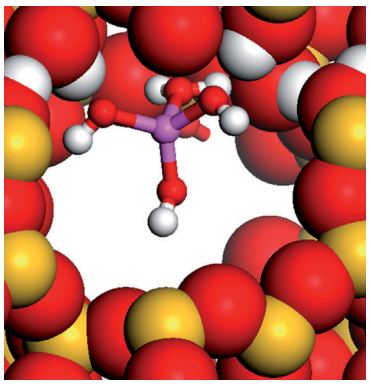


**Model behavior**: The primary and secondary kinetic isotope effects for a model compound which represents RNA cleavage transesterification were calculated and compared with experimental measurements. Based on the good agreement between theory and experiments, the energy profile, reaction pathway, and two distinct transition states for the reactions of the model compound and two thio-substituted analogues were characterized (see scheme).

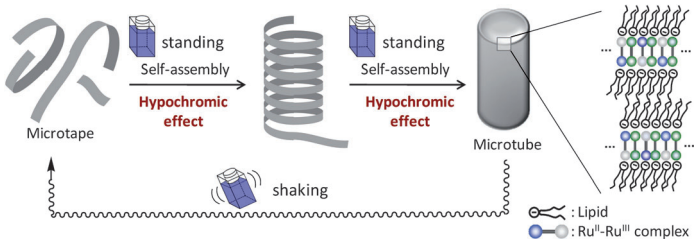



## Zeolites





**Birth of a silanol nest**: Reaction paths for the extraction of Al and Si from zeolites by reaction with steam were investigated by first-principles DFT calculations. The results show that dealumination is energetically favored over desilication (see picture: O red, Si yellow, Al purple, H white).

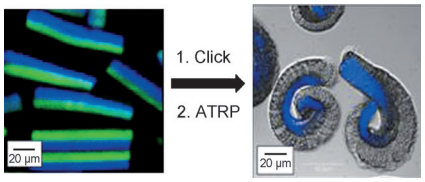



**Mix and shake**: Lipid packaged dinuclear ruthenium(II,III) complexes of class III mixed-valence state produce a reversible hypochromic effect upon external physical stimuli, such as shaking, due to the arrangement of transition dipole moments. The effect is accompanied by tubular-to-ribbon structural changes (see scheme).

## Supramolecular Chemistry

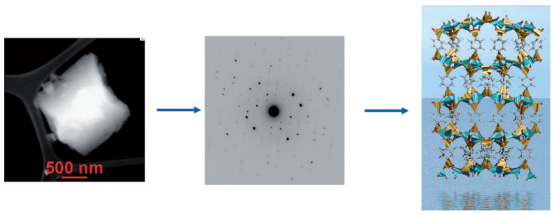


**The bends**: Surface modification of multicompartmental microcylinders by spatioselective click chemistry and subsequent surface-initiated atom-transfer radical polymerization (ATRP) yield novel amphiphilic microcylinders (see scheme). Depending on the aspect ratio of the microcylinders, they can be bent or coiled.




## Anisotropic Materials

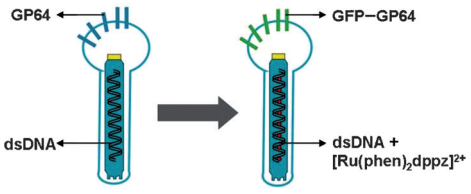





**Automated diffraction tomography** was used to collect electron-diffraction data for solving the crystal structure of ECS-3, which is the first example of a crystalline hybrid organic–inorganic aluminosilicate with open porosity, generated by a regular arrangement of phenylene rings interconnecting aluminosilicate layers (see picture; Al turquoise, C gray, O red, Si gold).

## Hybrid Materials





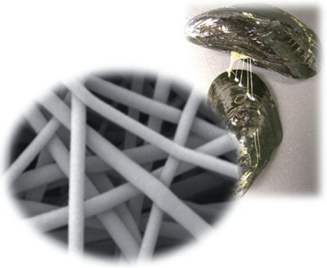

**Dual-color virus particles** were obtained by labeling a glycoprotein (GP64) on the surface of a baculovirus with a green fluorescent protein (GFP) and labeling the nucleic acid (dsDNA) at the same time with the red fluorescent [Ru(phen)$_2$(dppz)]$^{2+}$ complex during the viral replication in host cells, by using an in vivo virus self-assembly system. This labeling strategy does not affect the viral infectivity.

## Virus Labeling

## Nanostructures



**Sticky stuff**: The novel composite nanofibrous scaffolds based on mussel adhesive proteins (MAPs) provide a mechanically durable structural backbone with the function of bioactive peptides. It can also be easily coated with a variety of biomolecules. This biofunctionalized nanofiber platform could be a promising tool for successful tissue-engineering applications.

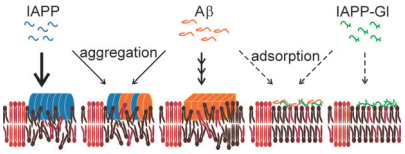


MAP-based composite nanofibrous scaffolds

## Amyloid–Peptide Interactions

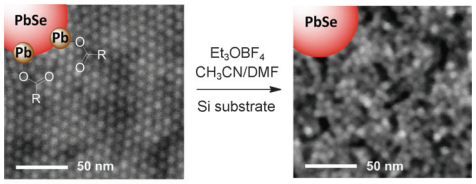


**Membrane controlled protein assembly**: A study of the amyloid interaction of the islet amyloid polypeptide (IAPP), β-amyloid (Aβ), and a mixture of both with an anionic model raft membrane showed the dominant effect of IAPP on the aggregation process and on the hydrogen-bonding pattern of the assemblies present in the mixture (see picture). The analysis of the interaction of Aβ with IAPP-GI—a non-amyloidogenic IAPP mimic—confirmed these findings.




## Nanocrystals






PbSe-Oleate *insulating*

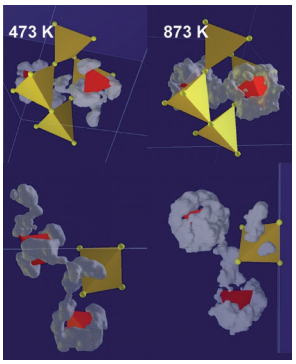
Bare PbSe *no particle etching increase in conductivity*

**Ole-ain't**: Trialkyl oxonium salts are universal reagents for native-ligand stripping of carboxylate- (e.g., oleate-), phosphonate-, and amine-passivated nanocrystal thin films and dispersions to give bare or $BF_4^-$/DMF-passivated surfaces. Meerwein-activated PbSe nanocrystal thin films (see picture) show hole mobilities of about 2–4 $cm^2V^{-1}s^{-1}$, which suggest applications of this process in fabricating high-performance devices.

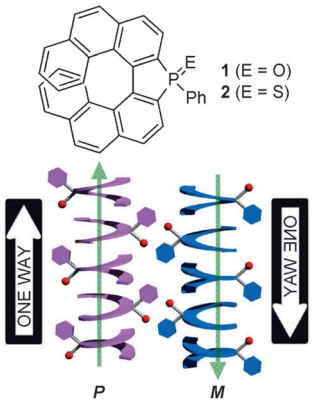
## Oxide Ion Conductors



**Mobile oxide ions**: A remarkably high oxide ion conductivity at low temperatures has been found in an ordered δ-$Bi_2O_3$ superstructure with the composition $Bi_{1-x}V_xO_{1.5+x}$ ($x = 0.087$ and 0.095), and attributed to a combination of highly polarizable sublattice with vacancies, central atoms able to support variable coordination numbers and geometries, as well as rotational flexibility of these coordination polyhedra, co-existing in a pseudo-cubic structure (see picture).



**One-way street**: A new family of $\lambda^5$-phospha[7]helicenes which form one-dimensional columnar stacks in the solid state were synthesized (see scheme). Neighboring stacks have opposite dipole directions and, in the case of the racemic phosphole sulfide based helicene, columns with a given dipole direction consist of one enantiomer, whereas columns with the opposite dipole direction consist of the other enantiomer.




## Heterocyclic Chemistry

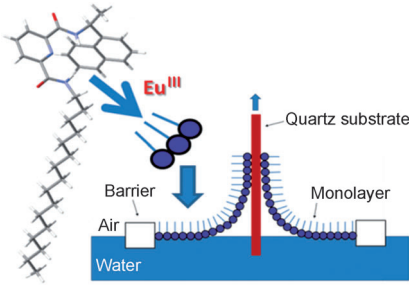


**Historic chemistry**: The discovery of a set of greenish pellets from ancient plaster at the La Blanca archaeological site (Guatemala) provides evidence that the Maya people used a material akin to Maya Blue also outside of pottery, murals, sculptures or religious context. Obviously, the Maya people developed different preparative strategies to obtain inorganic–organic hybrid materials.

## Historical Pigments

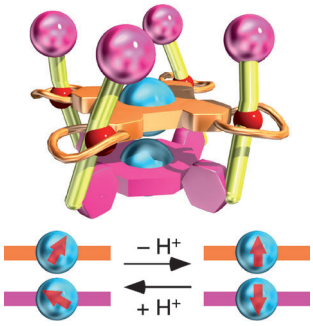


**Europium union**: The development of chiral amphiphilic self-assembled complexes by europium(III)-directed synthesis is described. These systems form stable Langmuir–Blodgett (LB) films on quartz slides to give stable monolayers that exhibit the first example of time-delayed $Eu^{III}$-centered emission and circularly polarized luminescence (CPL) from an LB film.




## Lanthanides



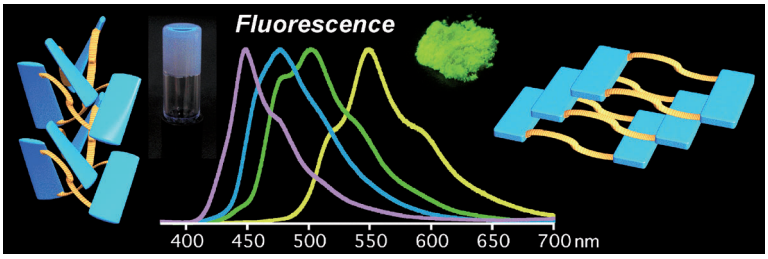



**Firmly tied**: A four-fold rotaxane was prepared from a porphyrin unit with four alkylammonium chains and a phthalocyanine unit with four peripheral crown ethers. In a dinuclear $Cu^{2+}$ complex of the four-fold rotaxane, the $Cu^{2+}$–porphyrin and the $Cu^{2+}$–phthalocyanine moieties were stacked efficiently on one another to afford spin–spin communication. The spin states were switched reversibly (see picture).

## Rotaxanes

## π-Aggregation Control

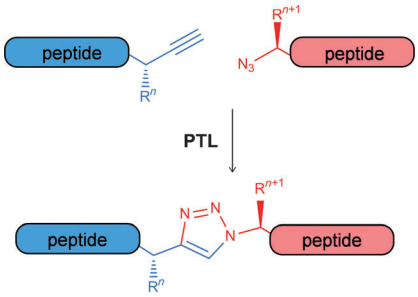





**Cyclic and flexible**: A simple molecular design for controlling the packing structure and solid-state properties of π-conjugated skeletons is proposed. A subtle difference of the flexible alkylene linker chain lengths of cyclic terthiophene dimers leads to distinct packing structures, and accordingly the solid-state properties, such as the gelation ability and photophysical properties.

## Protein Chemical Synthesis

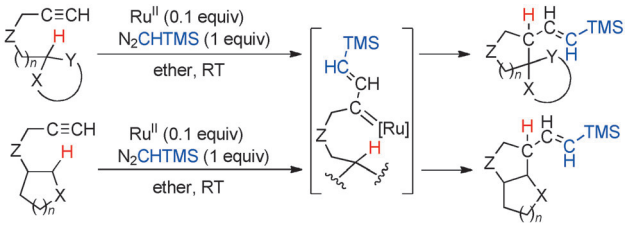





**"Click" protein**: $Cu^{I}$-catalyzed cycloaddition of azides and terminal alkynes has been applied to the successive ligations of three unprotected peptide fragments. Peptidomimetic triazole ligation (PTL, see scheme) as a new method for the chemical production of bioactive proteins is applied for the synthesis of a triazole-containing analogue of the 97 amino acid protein cystatin A.

## Homogeneous Catalysis

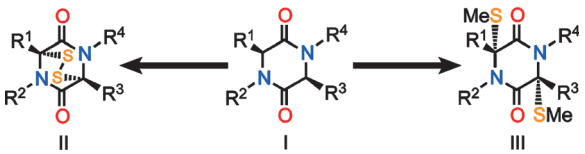





**A novel tandem** Ru-catalyzed carbene addition to terminal alkynes/insertion into $C_{sp^3}$–H bonds in alkynyl acetals, ethers, and amines has been accomplished under mild reaction conditions (see scheme; TMS = trimethylsilyl). This cascade provides an efficient approach to form complex spiro and fused bicyclic structures by 1,5- and 1,6-hydride shift/cyclization sequences from vinylcarbene Ru intermediates.

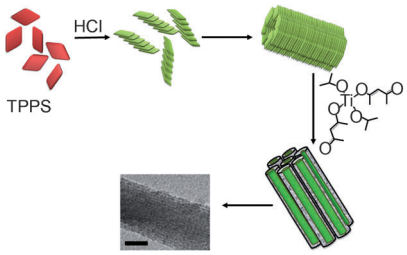
## Natural Product Synthesis





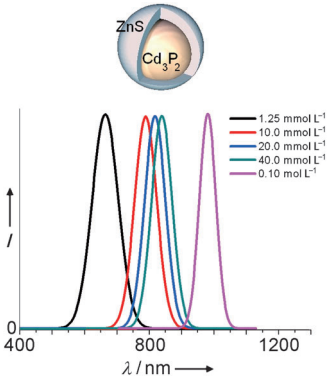

**Sulfurs in action**: A practical and simple method has been developed for the introduction of sulfur atoms into 2,5-diketopiperazines (**I**) under mild conditions. The reaction provides more or less complex epidithiodiketopiperazines (**II**) and bis-methylthiodiketopiperazines (**III**).

**Enveloping porphyrin arrays**: Supramolecular arrays of self-assembled tetrakis(4-sulfonatophenyl)porphyrin (TPPS) molecules have been enveloped with an ultrathin layer of titanium dioxide (see picture; scale bar: 25 nm). Integration of the hybrid components at close-to-molecular dimensions preserves optical and chiral properties of J-aggregate superstructures but also enhances photocatalytic activity of $TiO_2$.




## Hybrid Materials



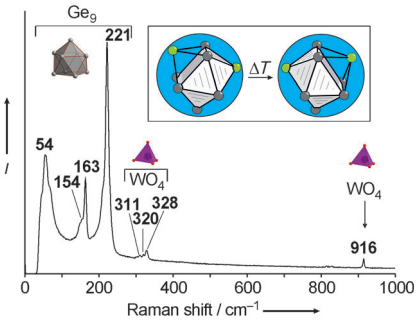



**By designing highly soluble precursors**, $Cd_3P_2$/ZnS quantum dots (QDs) can be prepared at room temperature. They are shown to be air-stable, size-tunable, and of high optical quality (quantum yields over 50%). A large photoluminescence range can be covered by simple modulation of the concentration of reactants (see picture) and of the temperature (30 °C, 90 °C).

## Quantum-Dot Synthesis



**Crystal engineering**: The syntheses, crystal structures, Raman spectra, and thermal properties of $Cs_{10}[Ge_9]_2[WO_4]$ and $Cs_{11}[Ge_9]_2[VO_4]$ containing $[Ge_9]^{4-}$ clusters and oxometallate anions $[MO_4]^{x-}$ ($M$ = W und V) are reported. The picture shows a Raman spectrum obtained from single crystals of the double salt $Cs_{10}[Ge_9]_2[WO_4]$ as well as the temperature-dependent $Ge_9$ cluster relocation in $Cs_{11}[Ge_9]_2[VO_4]$.




## Solid-Sate Chemistry

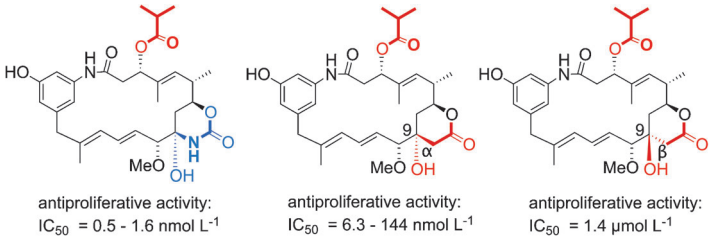


**Touchscreen testing**: A biomolecular detection platform is presented that utilizes a capacitive touchscreen to measure DNA concentration. The technology is ready for integration into touchscreen-equipped smart phones or smart pads, and should truly accelerate the realization of personalized portable biosensors.

## Biosensors

## Natural Products

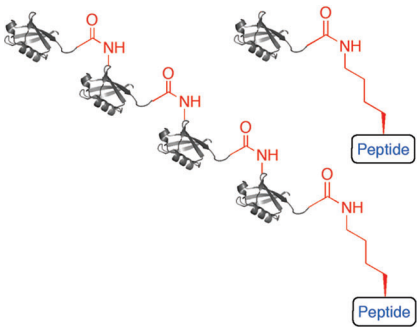





**Working hand in hand!** The synthetic power of three mutant strains that produce ansamitocin and geldanamycin is combined with chemical synthesis, thus leading to 27 new ansamitocin derivatives. Structure–activity studies show that the N of the carbinolamide moiety is not important for cytotoxic activity but the α orientation of the OH group at C9 is key [see structures; chemical synthesis (red), mutasynthesis (blue), biosynthesis (black)].

## Ubiquitin Chains

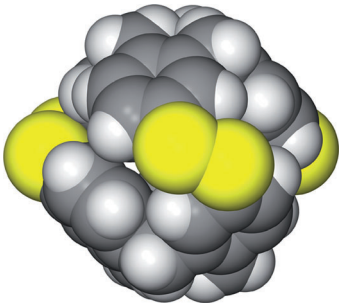





**Adding one at a time**: A general and effective synthesis yields a peptide attached to mono-, di-, tri-, and tetraubiquitin (Ub) chains (see picture for peptides with Ub and $Ub_4$), linked through lysine residues K48 or K63. These sets of ubiquitinated peptides were prepared in good quantities, and the activity of the enzymes UCH-L3 and IsoT with these different substrates was studied.

## Host–Guest Chemistry

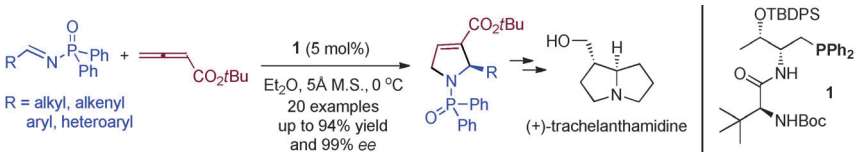




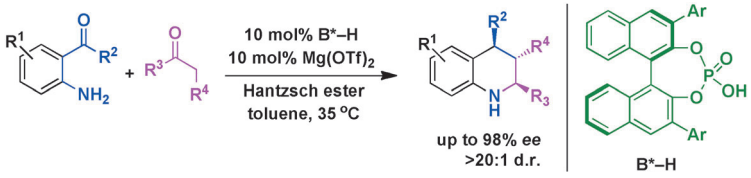
**Into the crypt**: Direct coupling of cyclotrithiophenolene gives a new class of cryptophane with labile disulfide linkages, which is the smallest cryptophane yet reported. The new cryptophane (see structure, S yellow, C gray, H light gray) is shown to bind methane or nitrogen in solution.

## Organocatalysis





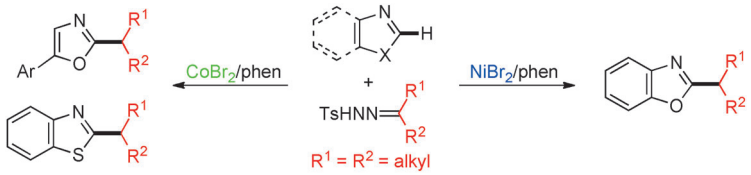

**A fast one**: The title reaction proceeds in the presence of 5 mol% of the catalyst **1**, and is complete within an hour. The 2-alkyl- and 2-aryl-substituted 3-pyrroline products are obtained in good yield and with high enantioselectivity. The application of the method to the concise formal synthesis of (+)-trachelanthamidine is also demonstrated. Boc = *tert*-butoxycarbonyl, M.S. = molecular sieves, TBDPS = *tert*-butyldiphenylsilyl.




**Two steps in one reaction**: The title relay reaction relies on a combination of an achiral Lewis acid and a chiral Brønsted acid (B*-H in the scheme). This one-pot method provides access to tetrahydroquinoline derivatives with multiple continuous stereogenic centers in high stereoselectivity (>20:1 d.r., 98% *ee*).

## Asymmetric Relay Catalysis

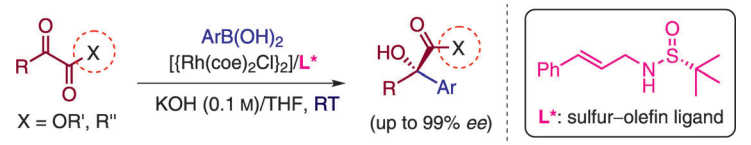





**A matter of catalyst**: Azole compounds can be directly alkylated with *N*-tosylhydrazones that bear unactivated alkyl groups (see scheme; phen = 1,10-phenanthroline, Ts = *p*-toluenesulfonyl). Nickel catalysis enables the introduction of simple secondary alkyl chains into benzoxazole compounds, whereas the alkylation of 5-aryloxazoles and benzothiazole is possible by using a cobalt catalyst.

## C–H Functionalization

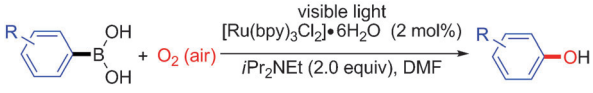





**Simply the best**: The title reaction has been achieved by asymmetric rhodium catalysis employing an extremely simple, chiral *N*-(sulfinyl)cinnamylamine ligand. A variety of highly enantioenriched, tertiary α-hydroxy carbonyl derivatives were easily accessed at room temperature under mild conditions with enantioselectivities of up to 99%.

## Asymmetric Catalysis



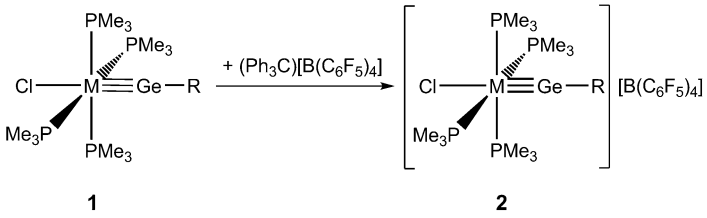



**To shed light on**: The title reaction allows the generation of a variety of functionalized phenols and analogues using $[Ru(bpy)_3Cl_2]\cdot 6H_2O$ as the photocatalyst under very mild reaction conditions. This reaction not only incorporates an oxygen atom from molecular oxygen directly into the product, but also expands the application of visible-light photocatalysis. bpy = bipyridine.

## Photochemistry

## Germylidyne Complexes



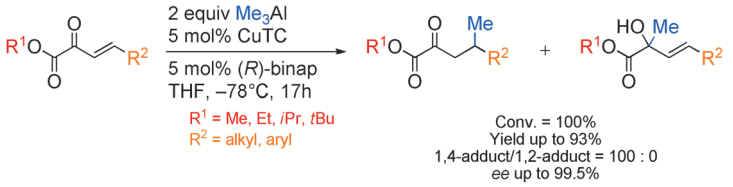



1 2

**Ge force**: One-electron oxidation of the 18 valence electron (VE) germylidyne complexes **1** provides access to the first open-shell germylidyne complexes **2** (see scheme; M = Mo, W; R = $C_6H_3$-2,6-$Mes_2$) that are analogous to metal alkylidyne complexes. The geometric and electronic structures of the 17 VE complexes **2** were determined by a combination of experimental and theoretical methods.

## Asymmetric Catalysis

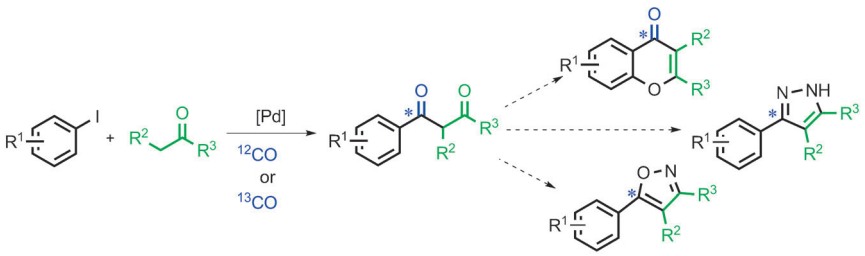





**Not a cop out**: The copper-catalyzed asymmetric conjugate addition of organometallic reagents to Michael acceptors is an important methodology for forming a C–C bond in an enantioselective manner. Such an addition of $Me_3Al$ to β,γ-unsaturated α-ketoesters is described to proceed in high yield and selectivity. CuTC = copper(I) thiophene-2-carboxylate.

## Palladium Catalysis

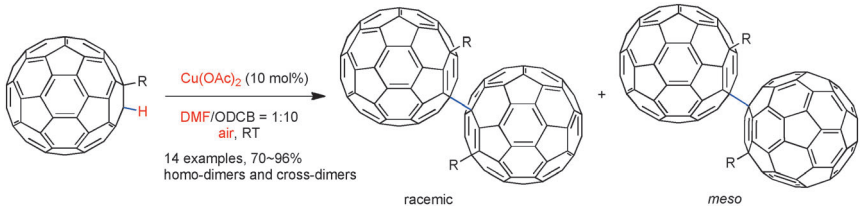




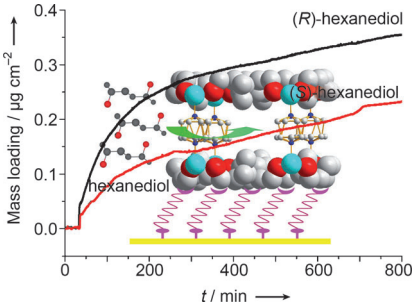

**With a hint of CO**: The first Pd-catalyzed carbonylative α-arylations of simple ketones with carbon monoxide is presented for the direct synthesis of 1,3-diketones (see scheme). The method uses only stoichiometric amounts of CO, and hence allows for the simple installment of carbon isotopes into the core structures of heterocyclic compounds.

## Fullerenes






**Dimers are a girl's best friend**: The title reaction allows the formation of single-bonded fullerene dimers with extremely high chemical yield and high compatibility with various functional groups, which are highly soluble in organic solvents. The use of $Cu(OAc)_2$ catalyst with dimethylformamide or acetonitrile as additives under air is the critical factor in achieving the highly efficient catalytic dimerization.

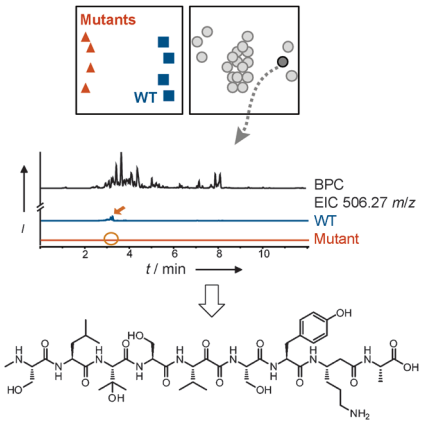



**Stuck on you**: Preferred (110) and (001) orientation of enantiopure $[\{Zn_2((+)cam)_2(dabco)\}_n]$ ((+)cam = (1*R*,3*S*)-(+)-camphoric acid, dabco = 1,4-diazabicyclo(2.2.2)octane) thin films can be controlled by carboxylate and pyridyl groups on self-assembled monolayers (SAMs). With a quartz crystal microbalance, the enantioselective adsorption of enantiomeric hexanediol pairs by enantiopure surface-attached metal–organic frameworks (SURMOF) $[Zn_2((\pm)cam)_2(dabco)]$ pairs can be demonstrated (see picture).

### *Metal–Organic Frameworks*

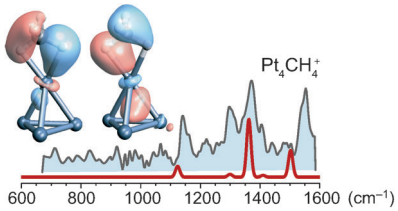


**Come to the fore**: The novel myxobacterial metabolite myxoprincomide is easy to overlook in the complex LC-MS data recorded for the metabolome of *Myxococcus xanthus* DK1622, such that advanced analytical techniques were needed for its discovery. By enhancing genomics-based natural products research with powerful analytical tools for in-depth metabolome mining, two additional such "hidden" metabolites have been uncovered.




### *Natural Products*






**Stretch Me–H**: Methane activated by adsorption on small platinum clusters is characterized by the vibrational fingerprint of the cluster complex. The C–H bond activation is distributed over two bonds, which corresponds with a decreased activation of each of the bonds but should lead to improved control over the reactivity of methane.

### *Methane Activation*



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