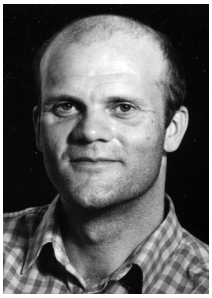
**VIP** *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*



## Author Profile



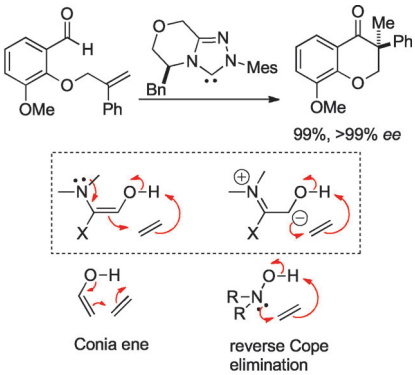
*"When I was eighteen I wanted to be an astronaut—the ultimate travel experience.*
*Young people should study chemistry because it is the science that strives to achieve complete understanding and control over matter, that is, the world we live in. …"*
This and more about Sjoerd Harder can be found on page 7978.



## Books



## Highlights




**N-Heterocyclic carbenes** interact with aldehydes to generate the Breslow intermediate, a rendering of the prototypical electrophile into a nucleophile (umpolung). Recent work has indicated that these intermediates may also add to simple, unpolarized alkenes. The use of a chiral precatalyst leads to the generation of the derived adducts with high yields and very high selectivities.

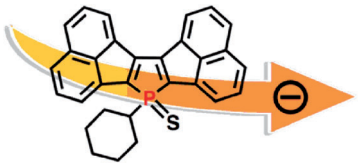
***Asymmetric Organocatalysis***

# Contents




**For the USA and Canada:**
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

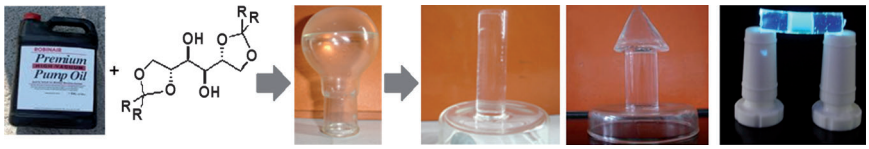
# Communications



**A profusion of phospholes**: Diacenaphtho[1,2-*b*:1′,2′-*d*]phospholes, a new class of arene-fused phosphole π-systems, were synthesized and their structural and electrochemical properties studied. The P-sulfide derivative (see picture) has a high electron-transporting ability ($\mu_E = 2.4 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$) in a vacuum-deposited film.

## Extended π-Systems

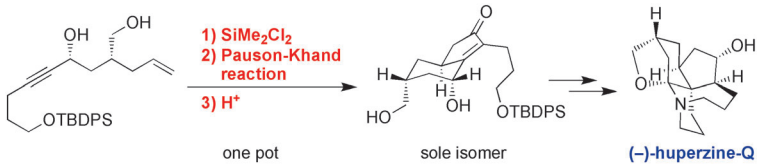




**Sweet and low**: Two sugar-based supergelators can congeal oils to produce highly transparent gels with glass-like refractive indices showing low UV transmittance and high visible transmittance and remarkable self-healing properties. This unique blend of properties can be exploited to make soft optical devices from these gels.

## Organogels



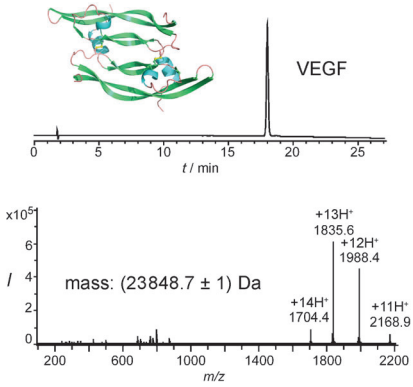



**Right on Q**: The first asymmetric total synthesis of (−)-huperzine-Q, which possesses six stereogenic centers and a spiroaminal moiety, has been achieved in 19 steps and 16.4% overall yield. This synthesis involved a novel stereoselective Pauson–Khand reaction, a vinyl Claisen rearrangement, and a biomimetic spiroaminal formation. TBDPS = *tert*-butyldiphenylsilyl.

## Natural Products



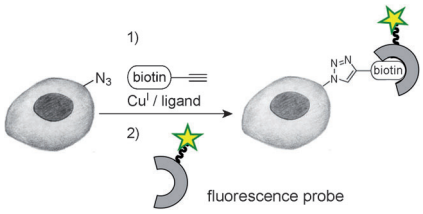
**Efficient access**: The 204-residue covalent-dimer vascular endothelial growth factor (VEGF, see picture) with full mitogenic activity was prepared from three unprotected peptide segments by one-pot native chemical ligations. The covalent structure of the synthetic VEGF was confirmed by precise mass measurement, and the three-dimensional structure of the synthetic protein was determined by high-resolution X-ray crystallography.




## Chemical Protein Synthesis

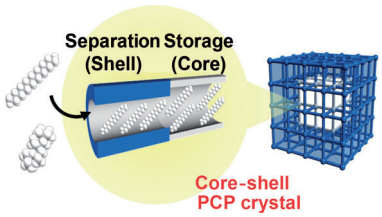
# Contents

**Raising the bar**: The efficacy of bioorthogonal reactions for bioconjugation has been thoroughly evaluated in four different biological settings. Powered by the development of new biocompatible ligands, the copper-catalyzed azide–alkyne cycloaddition (see picture) has brought about unsurpassed bioconjugation efficiency, and thus it holds great promise as a highly potent and adaptive tool for a broader spectrum of biological applications.




## Bioconjugation

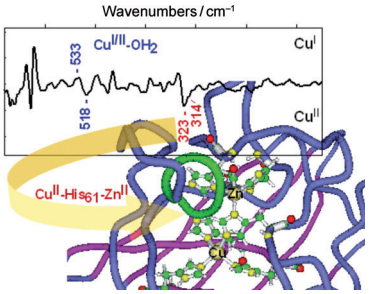





**Crystal extractor**: Heterostructured porous coordination polymer crystals fabricated using epitaxial growth have two contradictory porous functions, namely size selectivity and high storage. The crystals not only extract linear petroleum molecules from a mixture with its branched isomer, even at very low concentrations of linear isomer (1 wt%), but also shows improved accumulation of the molecules in its pores.

## Metal–Organic Frameworks

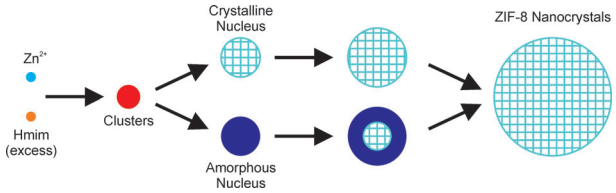





**Vibrations of the metal active site** of the Cu,Zn-superoxide dismutase enzyme were analyzed by far-infrared difference spectroscopy (see picture) and theoretical normal mode calculation. Both electrochemically triggered $Cu^I$ and $Cu^{II}$ redox states show well-defined infrared vibrational modes, notably modes of the histidine ligands, the $Cu^{II}$-$His_{61}$-$Zn^{II}$ bridge and of the water pseudo-ligand.

## Far-Infrared Spectroscopy

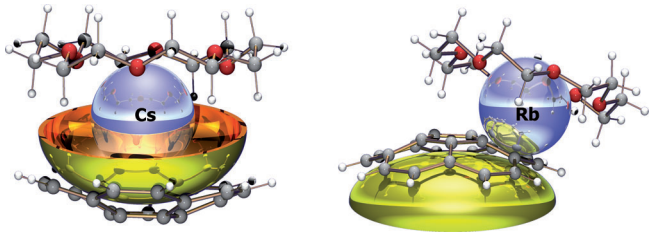





**Prenucleation clusters**: In situ synchrotron X-ray scattering with a one-second time resolution revealed the occurrence of nano-sized clusters during the nucleation and early growth of nanocrystals of a zeolitic imidazolate framework (ZIF). The complex crystallization process exhibits similarities with crystallization processes of zeolites from solution. Hmim = 2-methylimidazole.

## Metal–Organic Frameworks

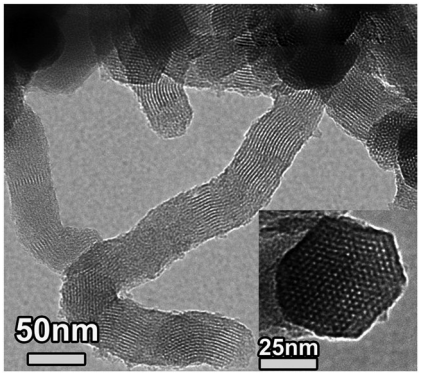
# Contents



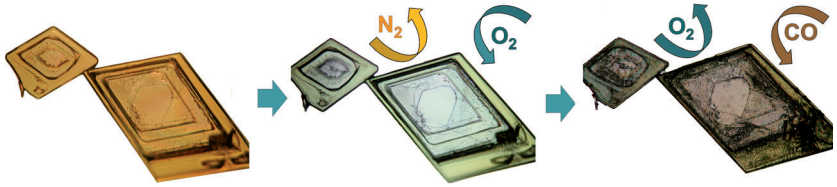

**The ion size matters**: The structures of corannulene monoanions crystallized with $Cs^+$ and $Rb^+$ ions in the presence of [18]crown-6 reveal the intrinsic binding preferences of alkali metals and allow evaluation of the bowl deformation caused by negative charge distribution and metal binding. The large cesium cation coordinates exclusively to the concave face of $C_{20}H_{10}^-$, whereas the smaller rubidium cation exhibits convex binding.



**Helical organosilica** materials were synthesized for the first time using a novel binaphthyl-based chiral co-monomer in less than 1 hour. The incorporation of a chiral co-monomer in the wall was shown to influence the curvature of the helical materials. As the amount of the chiral co-monomer was increased, the degree of curvature increased, illustrating the importance of this monomer to the overall morphology.

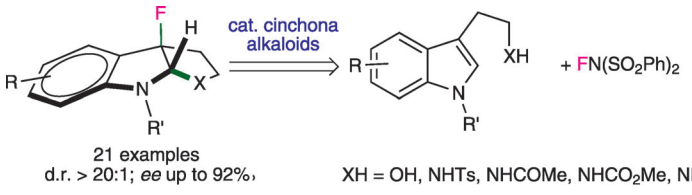




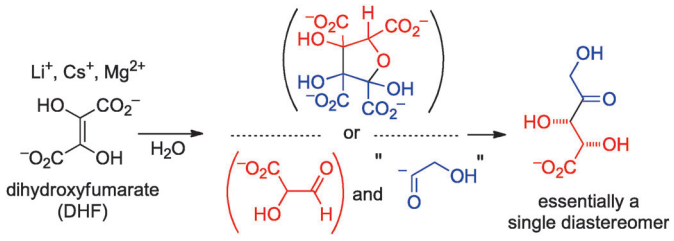

**Three gases, one crystal**: Rhodium NHC complexes undergo back-to-back single-crystal-to-single-crystal transformations by selective nonreversible ligand exchange reactions (see picture). Slow diffusion of $O_2$ converts a dinitrogen complex into a dioxygen complex, and CO subsequently replaces $O_2$.






**Enantioenriched fluorinated heterocycles** can be prepared through fluorocyclizations of prochiral indoles (see scheme; Ts = tosyl, Bn = benzyl, Boc = *tert*-butoxycarbonyl). More than twenty examples for this cascade fluorination–cyclization, which is catalyzed by cinchona alkaloids and employs *N*-fluorobenzenesulfonimide as the electrophilic fluorine source have been explored, and an unprecedented catalytic asymmetric difluorocyclization has also been identified.

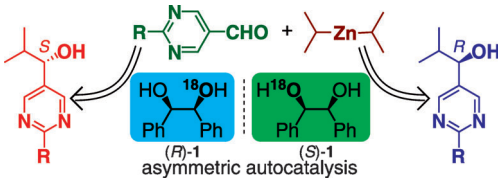
# Contents




**Jack of all trades**: Water-soluble salts of DHF underwent self-condensation to afford the *threo* diastereomer of pentulosonic acid, through differing reaction pathways contingent on the metal salt used (see scheme). This transformation exemplifies the diverging roles of DHF as a nucleophile (a synthon for α-hydroxyacetyl anion) and an electrophile (an α-carboxyglycolaldehyde equivalent).

## Prebiotic Chemistry

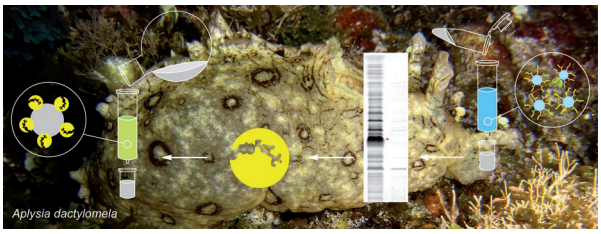





**Trigger happy**: Chiral oxygen isotopomers of hydrobenzoin ([$^{18}$O](*R*)-**1** and [$^{18}$O](*S*)-**1**) acted as chiral triggers to induce the enantioselective addition of *i*Pr$_2$Zn to pyrimidine-5-carbaldehyde. An extremely small chiral influence arising from the presence of the oxygen isotope ($^{18}$O) is amplified through asymmetric autocatalysis to enantioenrich the 5-pyrimidyl alkanol product.

## Asymmetric Induction

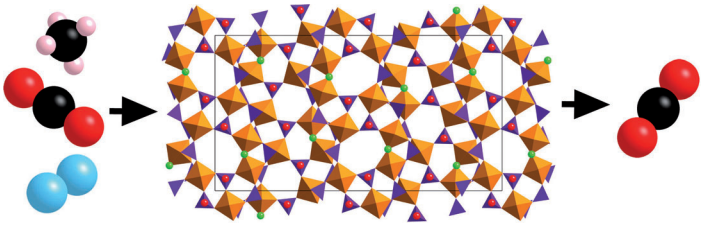





**A bidirectional affinity** system has been developed for the identification of cancer-related natural products and their biological targets. Aplysqualenol A is thus selectively identified as a ligand of the dynein light chain. The use of forward and reverse affinity methods suggests that both small-molecule isolation and target identification can be conducted using conventional molecular biological methods.

## Natural Product Binding

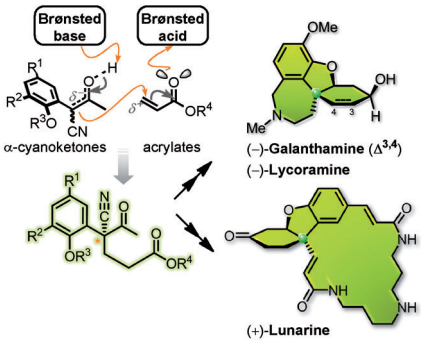




**Less is more**: An open-framework zirconium phosphate with unusual 7-ring channels was synthesized ionothermally from a deep-eutectic solvent. This small-pore material displays a $CO_2/CH_4$ adsorption ratio (17.3 at 1 bar) that is significantly higher than that of typical 8-ring materials, making it highly attractive for $CO_2/CH_4$ separations.

## Ionothermal Synthesis

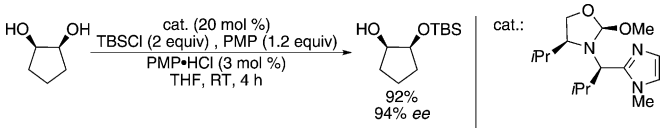
# Contents




**Divergent route**: A direct C–C bond-forming approach to the key aryl-substituted all-carbon quaternary stereogenic center present in bioactive hydrodibenzofuran alkaloids has been discovered. This approach involves an unprecedented organocatalytic enantioselective Michael addition of α-cyanoketones with acrylates (see scheme) and was used in a novel and divergent synthetic strategy for the title compounds in asymmetric fashion.

## Organocatalysis



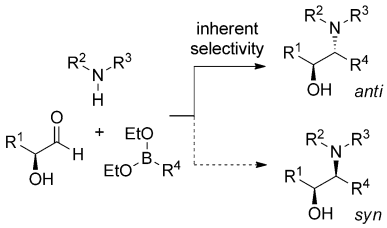



## Organocatalysis



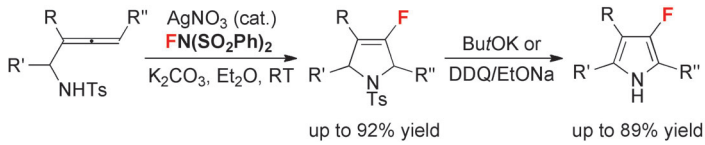
**Ex-changing places**: A highly enantioselective desymmetrization of 1,2-diols has been developed in which the catalyst utilizes reversible covalent bonding to the substrate to achieve both high selectivity and rate acceleration (see scheme, PMP = pentalmethylpiperidine, TBS = *tert*-butyldimethylsilyl). Induced intramolecularity is responsible for the enhanced rate, thus allowing the reaction to be performed at room temperature.

**Multicomponent Petasis reactions**: The first diastereoselective Petasis reaction catalyzed by chiral biphenols that enables the synthesis of *syn* and *anti* β-amino alcohols in pure form has been developed. The reaction exploits a multicomponent approach that involves boronates, α-hydroxy aldehydes, and amines (see scheme).




## Multicomponent Reactions



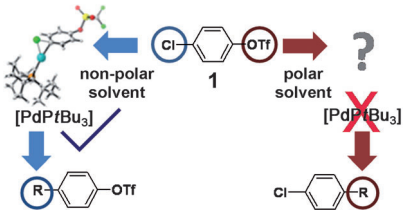



## Organofluorine Chemistry



**A nice combination**: The intramolecular oxidative aminofluorination of allenes using silver catalysis and $FN(SO_2Ph)_2$ as the fluorinating reagent has been developed. This reaction represents an efficient method for the synthesis of various 4-fluoro-2,5-dihydropyrrole compounds. Further transformation provided the corresponding fluorinated pyrrole derivatives in good yields (see scheme).

# Contents




**Suzuki coupling** of the bifunctional substrate **1** using $[Pd_2(dba)_3]/PtBu_3$ gives selectivity for C—Cl in nonpolar solvents but for C—OTf in polar solvents. The results of computational and experimental studies suggest that the catalytically active species in polar solvents under conditions employing coordinating additives is inconsistent with monoligated $[Pd(PtBu_3)]$. Instead, the data are consistent with an anionic palladium complex as the active species.

***Cross-Coupling***



Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

This article is available online free of charge (Open Access)



## *Service*

# Corrigenda

Synthesis of Gold Nano-hexapods with Controllable Arm Lengths and Their Tunable Optical Properties

D. Y. Kim, T. Yu, E. C. Cho, Y. Ma, O O. Park, Y. Xia* ——— **6328–6331**

*Angew. Chem. Int. Ed.* **2011**, *50*

DOI 10.1002/anie.201100983

The authors of this Communication have noticed a typographical error in the experimental section of the Supporting Information. The volume of aqueous $NaBH_4$ solution, which was used for preparing spherical Au seeds, should be 0.6 ml rather than 6 ml. This error does not influence any other parts of the paper. The authors sincerely apologize for this mistake and any inconvenience it may have caused.

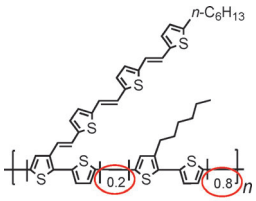
All-Polymer Solar Cells from Perylene Diimide Based Copolymers: Material Design and Phase Separation Control

E. J. Zhou, J. Z. Cong, Q. S. Wei, K. Tajima,* C. H. Yang, Prof.K. Hashimoto* ——— **2799–2803**

*Angew. Chem. Int. Ed.* **2011**, *50*

DOI 10.1002/anie.201005408

In this Communication, the structure of **PT1** is not correct in Scheme 1 on page 2799. The correct structure is shown below. Also, the ratio between the units with and without the conjugated side chain should be 0.2:0.8, not 0.8:0.2.




**PT1**

In the Supporting Information, the structure of **PT1** in Figure S2 on page S4 is also incorrect. The correct structure is shown above. Also, on page S14 "Monomer **4** (130 mg, 0.8 mmol)" should be corrected to "Monomer **4** (130 mg, 0.2 mmol)".