



# 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:

D. Kim, E. Kim, J. Kim, K. M. Park, K. Baek, M. Jung, Y. H. Ko, W. Sung, H. S. Kim, J. H. Suh, C. G. Park, O. S. Na, D.-k. Lee, K. E. Lee, S. S. Han, K. Kim\*

Direct Synthesis of Polymer Nanocapsules with a Noncovalently Tailorable Surface

T. Tsukahara, A. Hibara, Y. Ikeda, T. Kitamori\*

NMR Study on Water Confined in Extended Nanospaces

A. R. Fox, C. R. Clough, N. A. Piro, C. C. Cummins\*

A Terminal Nitride-to-Phosphide Conversion Sequence Followed by Tungsten Phosphide Functionalization Using a Diphenylphosphenium Synthon C. Filser, D. Kowalczyk, C. Jones, M. Wild, U. Ipe, D. Vestweber, H. Kunz\*

Synthetic Glycopeptides with Varied Sialyl Lewis<sup>x</sup> Structures as Cell-Adhesion Ligands for E-Selectin

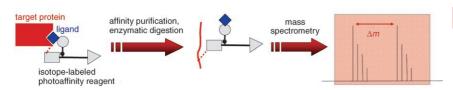
J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, H.-H. Strehblow, P. Keller, E. Rentschler, W. Kläui\*

Towards Nanostructured Water-Soluble and Catalytically Active Rhodium Clusters

R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher,\* M. Westerhausen\*

Synthesis and Properties of the THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide

Intimate Relationships between Metal Ions and Nucleic Acids		Meeting Reviews	
		R. K. O. Sigel 654	Ļ
		Books	
Ordered Porous Nanostructures and Applications	Ralf B. Wehrspohn	reviewed by M. J. Sailor 657	,
Inorganic Chemistry in Aqueous Solution	Jack Barrett	reviewed by R. Cannon 658	}



The target proteins of bioactive low-molecular-weight ligands can be discovered by the use of multifunctional photoaffinity labels in combination with mass spectrometry. The reagents contain a

biotin label for affinity purification of the protein–ligand complex and a stable isotope label to facilitate its mass spectrometric identification (see scheme).

## Highlights

#### Photoaffinity Reagents

A. Sinz\* \_\_\_\_\_ 660 – 662

Isotope-Labeled Photoaffinity Reagents and Mass Spectrometry To Identify Protein–Ligand Interactions



#### Photocycloaddition

J. Mattay\* \_\_\_\_\_ 663 – 665

Photochemistry of Arenes—Reloaded

$$X = C(CN)_2$$
,  $C(COOMe)_2$ ,  $O(COOMe)_2$ ,  $O(COOMe)_3$ ,  $O(COOMe)_4$ ,  $O(COOMe)_4$ ,  $O(COOMe)_5$ ,  $O(COOMe)_5$ ,  $O(COOMe)_6$ ,  $O(COOMe)_7$ ,  $O(COOMe)_8$ ,

A question of time: The intramolecular *meta* photocycloaddition of naphthalene was only recently discovered, even though the corresponding additions to a simple benzene derivative have been known for a long time. The most important factor in

the formation of the *meta* adduct is the irradiation time. The special features of the naphthalene structure finally give the opportunity for the stereoselective control of a *meta* photocycloaddition.

#### Reviews

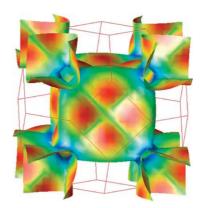
#### **Spintronics**

C. Felser,\* G. H. Fecher,

B. Balke \_\_\_\_\_\_ 668 – 699

Spintronics: A Challenge for Materials Science and Solid-State Chemistry

The right spin: Spintronics makes use of the electron spin, rather than just its charge. The subdiscipline of magneto-electronics deals with devices based on ferromagnetic materials. The illustration shows the Fermi surface (distribution of the highest occupied states in reciprocal space; the color indicates the Fermi velocity) of a typical material for magnetoelectronics and spintronics.

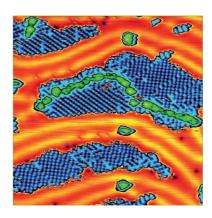


## **Communications**

#### Surface Chemistry

S. M. Driver, T. Zhang, D. A. King\* \_\_\_\_\_\_ **700-703** 

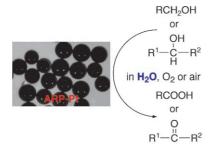
Massively Cooperative Adsorbate-Induced Surface Restructuring and Nanocluster Formation Atoms on the move:  $NO_2$  lifts the  $Au\{111\}$  herringbone surface reconstruction at 78 K through a massively cooperative restructuring step, which involves on the order of 600  $NO_2$  molecules (blue; see STM image) and 80–100 Au atoms. Mesoscopic island ordering is a precursor to the process, and Au nanoclusters (green/yellow) form as the restructuring proceeds.



#### For the USA and Canada:

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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.



Aerobic exercise: A dispersion of nanoparticles of platinum in an amphiphilic polystyrene—polyethylene glycol resin (ARP-Pt) contains particles with a mean diameter of 5.9 nm and a narrow size distribution throughout the resin. ARP-Pt is a readily recyclable catalyst for the aerobic oxidation of a wide variety of alcohols in water with an oxygen or air atmosphere under heterogeneous conditions (see picture).

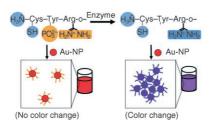
#### **Oxidation Catalysts**

Y. M. A. Yamada, T. Arakawa, H. Hocke, Y. Uozumi\* \_\_\_\_\_\_ **704 – 706** 

A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water



To change your colors: A colorimetric enzyme assay based on peptide-induced aggregation of gold nanoparticles (Au-NPs) has been developed to sense phosphatase activity. Once the phosphate group is eliminated by alkaline phosphatase, peptide-induced Au-NP aggregation is triggered, resulting in a significant change in absorbance at 650 nm.

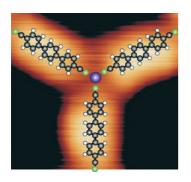


#### **Enzyme Activity**

Y. Choi, N.-H. Ho, C.-H. Tung\* 707 – 709

Sensing Phosphatase Activity by Using Gold Nanoparticles



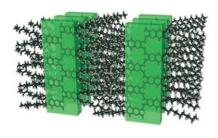


Independent symmetries characterize the evolving network and the metal surface on which the network forms in the surface-assisted assembly of ligands and metal centers to 2D honeycomb networks comprising threefold coordination motifs (see picture, Co purple, N green). This type of coordination, which is rarely encountered in 3D metal—organic frameworks, is promoted by the strict confinement of a 2D environment.

#### **Coordination Chemistry**

S. Stepanow, N. Lin,\* D. Payer,
U. Schlickum, F. Klappenberger,
G. Zoppellaro, M. Ruben, H. Brune,
J. V. Barth, K. Kern \_\_\_\_\_\_\_ 710-713

Surface-Assisted Assembly of 2D Metal— Organic Networks That Exhibit Unusual Threefold Coordination Symmetry



Colored ribbons: The soluble, electronrich conjugated title polymer (alkyl = dodecyl) with a regiosymmetric structure was synthesized by Grignard metathesis. The polymer displays strong thermochromism in solution. AFM images of spincoated films show the formation of nanoribbons, and 2D-WAXS analysis reveals 2D order in the bulk material (see picture). The polymer is thus a promising candidate for device applications.

#### **Conducting Polymers**

C. R. G. Grenier, W. Pisula, T. J. Joncheray, K. Müllen, J. R. Reynolds\* \_\_\_\_\_ 714-717

Regiosymmetric Poly(dialkylphenylenedioxythiophene)s: Electron-Rich, Stackable  $\pi$ -Conjugated Nanoribbons

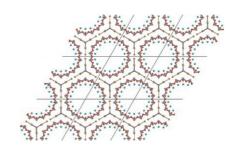


#### Semiconductor Materials

A. Shulman,

A. E. C. Palmqvist\* \_\_\_\_\_\_ 718 – 722

A Crystalline, Large-Pore, Microporous Semiconductor Tubes, dumbbells, and pyramids: A crystalline, large-pore, microporous semiconductor,  $|Rb_{18}|[Sb_{36}O_{54}][(SbTe_3)_2(Te_2)_6]$  (Rb-CTH-1), which consists of an 18-ring  $\{Sb_{18}O_{27}\}$  tubular unit surrounded by an intricate, ordered arrangement of trigonal-pyramidal  $\{SbTe_3\}^{3-}$  ions and  $Te_2^{2-}$  dumbbells and lined with Rb+ ions, has been prepared (see picture; turquoise R). This semiconductor has a band gap of approximately 850 meV.

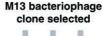


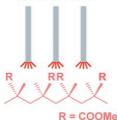
#### Polymer-Recognizing Peptides

- T. Serizawa,\* T. Sawada,
- T. Kitayama \_\_\_\_\_\_ 723 726



Peptide Motifs That Recognize Differences in Polymer-Film Surfaces





Potential of peptides: Peptide motifs that recognize variability in the surfaces of syndiotactic poly(methyl methacrylate) films are selected from phage libraries displaying 7-mer random peptides. The phage clones specifically bind to target films conditioned in the aqueous phases. Thus, peptides have the potential to recognize slight differences in surface structures and stereoregularities of single-component films.

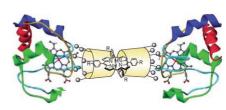
#### Supramolecular Chemistry

K. Kano,\* Y. Ishida \_\_\_\_\_\_ 727 – 730



Supramolecular Complex of Cytochrome c with a Polyanionic  $\beta$ -Cyclodextrin

A threesome: An anionic cyclodextrin binds electrostatically with cationic cytochrome c ( $K=2.3\times10^4\,\mathrm{M}^{-1}$ ,  $\Delta H=9.3\,\mathrm{kJ\,mol^{-1}}$ ,  $\Delta S=115\,\mathrm{J\,mol^{-1}}\,\mathrm{K}^{-1}$ ). The cyclodextrin covers the hemin pockets of about two-thirds of the cytc molecules. This association complex further complexes with a nonionic porphyrin to form a ternary complex in which static fluorescence quenching of the porphyrin by cytc takes place.



#### **Nonlinear Optics**

M. Samoc, J. P. Morrall, G. T. Dalton, M. P. Cifuentes,

M. G. Humphrey\* \_\_\_\_\_\_ 731 – 733

Two-Photon and Three-Photon Absorption in an Organometallic Dendrimer

Three at a time: The wavelength dependence of nonlinear absorption and nonlinear refraction of a peripherally nitrophenylethynyl-functionalized first-generation arylethynylruthenium dendrimer (see picture; dppe = 1,2-bis(diphenylphosphanyl)ethane) was examined in the range 625–1500 nm by employing fs pulses. The compound is a strong two-photon absorber in the range 600–800 nm and an exceptional three-photon absorber in the range 1100–1200 nm.

$$[Ru] = trans \cdot Ru(dppe)_{2}$$

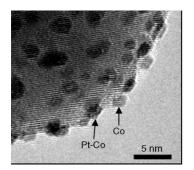
$$R = = \bigcirc = [Ru] = \bigcirc \cdot NO_{2}$$

$$[Ru]$$

$$[Ru]$$

$$[Ru]$$

$$[Ru]$$

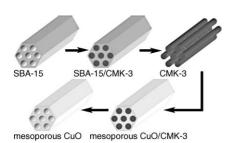


Highly active bimetallic catalysts, Pt–Co nanoparticles supported on yttria-stabilized zirconia (YSZ; see picture) can be prepared in a single step by co-impregnation. This system shows a high catalytic activity for the selective oxidation of CO in the presence of excess hydrogen, especially at temperatures below 423 K.

#### Heterogeneous Catalytic Oxidation

Supported Pt-Co Catalysts for Selective CO Oxidation in a Hydrogen-Rich Stream





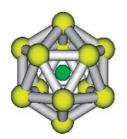
**Order, order:** Mesoporous copper oxide was synthesized for the first time by double replication from ordered mesoporous silica SBA-15 via the ordered mesoporous carbon intermediate CMK-3 (see picture). The new material has potentially exciting applications in catalysis or lithium-ion batteries.

#### Mesoporous Copper Oxide

X. Lai, X. Li,\* W. Geng, J. Tu, J. Li, S. Qiu \_\_\_\_\_\_\_ **738-741** 

Ordered Mesoporous Copper Oxide with Crystalline Walls





**Trapped in a cage**: Combined experimental and theoretical evidence shows that the stannaspherene  $\mathrm{Sn_{12}}^{2-}$  can trap a transition-metal or f-element atom (green) to form a stable endohedral cluster (see figure). The central metal atom induces very little distortion in the icosahedral cage. The clusters can be viewed as "superatoms" for use in materials with tunable magnetic, electronic, and chemical properties.

#### Endohedral Tin Cages

L.-F. Cui, X. Huang, L.-M. Wang, J. Li,\* L.-S. Wang\* \_\_\_\_\_\_\_ **742 – 745** 

Endohedral Stannaspherenes  $M@Sn_{12}^-$ : A Rich Class of Stable Molecular Cage Clusters

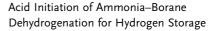


 $H_3NBH_3 \xrightarrow{acid} [H_2B(NH_3)]^+ \longrightarrow [H_2NBH_2]_n + [HNBH]_n + H_2$ 

Liberating hydrogen: Strong Lewis or Brønsted acids react with ammonia borane (H<sub>3</sub>NBH<sub>3</sub>) to form an in situ boronium cation, resulting in the formation of a mixture of cyclic and acyclic  $\mathsf{BNH}_x$  oligomers and the liberation of  $\mathsf{H}_2$  (see scheme). A proposed mechanism is supported by an examination of the reaction thermodynamics using density functional theory.

#### Hydrogen Storage

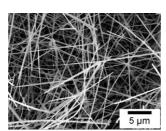
F. H. Stephens, R. T. Baker,\* M. H. Matus, D. J. Grant, D. A. Dixon\* \_\_\_\_\_\_ **746-749** 





VIP

**Long and thin:**  $SnO_2$  nanowires with tetragonal structure were successfully synthesized by a thermal evaporation method without any conventional metal catalysts. The enhanced electrochemical performance of  $SnO_2$  nanowires is believed to result from the combination of unique nanostructures with a high length/diameter ratio and the absence of traditional metal catalysts.



#### Nanostructures

M.-S. Park, G.-X. Wang, Y.-M. Kang, D. Wexler, S.-X. Dou, H.-K. Liu\* **750 – 753** 

Preparation and Electrochemical Properties of SnO<sub>2</sub> Nanowires for Application in Lithium-Ion Batteries



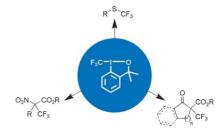
#### **Electrophilic Substitution**

I. Kieltsch, P. Eisenberger,
A. Togni\* \_\_\_\_\_\_ 754 – 757

Mild Electrophilic Trifluoromethylation of Carbon- and Sulfur-Centered Nucleophiles by a Hypervalent Iodine(III)–CF<sub>3</sub> Reagent

#### Inexpensive, recyclable, and activable:

these are the features of a new mild electrophilic trifluoromethylation reagent that can be used to transfer a  $CF_3$  group to C-centered nucleophiles, such as  $\beta$ -keto esters and  $\alpha$ -nitro esters, and to S-centered nucleophiles (see scheme).

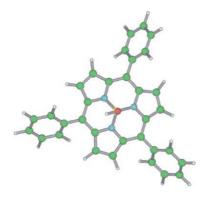


#### **Contracted Porphyrins**

N. Kobayashi,\* Y. Takeuchi,
A. Matsuda \_\_\_\_\_\_ 758 – 760



meso-Aryl Subporphyrins



Ring-contracted porphyrins: meso-Aryl subporphyrins were synthesized by using a method in which tripyrrolylborane acts as a template for the Adler method. This study demonstrates that, although the subporphyrins retain porphyrinic properties, ring contraction has a significant impact on the electronic structure. The picture shows the DFT-optimized structure of the meso-phenyl subporphyrin (B yellow, N blue, O red, C green, H white).

#### Amide Metathesis

C. M. Bell, D. A. Kissounko, S. H. Gellman,\* S. S. Stahl\* \_\_\_ **761 – 763** 



Catalytic Metathesis of Simple Secondary Amides



Trading places: The metathesis of secondary amides through a transacylation mechanism has been achieved by employing catalytic quantities of an organic imide and a Brønsted base (see scheme). Equilibrium-controlled exchange between various amide pairs is demonstrated for substrates bearing *N*-alkyl and *N*-aryl substituents.

#### Liquid Crystals

K. Kishikawa,\* K. Oda, S. Aikyo,
S. Kohmoto \_\_\_\_\_\_\_ **764–768** 



Columnar Superstructures of Non-Disc-Shaped Molecules Generated by Arene– Perfluoroarene Face-to-Face Interactions



From post to pillar: Non-disc-shaped molecules with pentafluorophenyl and trialkoxyphenyl groups linked by an ester junction self-organize into an ordered columnar superstructure in the mesophase by using arene–perfluoroarene faceto-face interactions.

#### **Natural Product Synthesis**

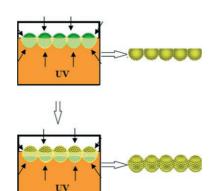
B. S. Lucas, V. Gopalsamuthiram,
S. D. Burke\* \_\_\_\_\_\_ 769-772



Total Synthesis of Phorboxazole B

Challenge met: In the synthesis of phorboxazole B, a highly efficient hetero-Diels—Alder reaction was used to construct the key C33—C39 linchpin, allowing for the completion of the C18—C46 fragment (see picture). Coupling with a suitable C3—C17 partner was followed by late-stage formation of the oxazole unit, macrocyclization, and deprotection to afford synthetic phorboxazole B.

Freestanding porous gold films with arrays of spherical pores or hollow spheres were fabricated photochemically. UV irradiation of a polystyrene-sphere (PS) colloidal crystal template floating on a solution containing HAuCl<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub> led to gold deposition, and then PS removal gave a spherical-pore array. Irradiating the shell/sphere structure upsidedown on fresh precursor solution gave a hollow-sphere array after PS removal (see picture).



#### **Porous Materials**

F. Sun,\* J. C. Yu\* \_\_\_\_\_\_ 773 – 777

Photochemical Preparation of Two-Dimensional Gold Spherical Pore and Hollow Sphere Arrays on a Solution Surface



54-78% yield, 4:1 to 19:1 d.r., 84-99% ee

Simple chiral amines catalyze a highly chemo- and enantioselective aziridination of  $\alpha,\beta$ -unsaturated aldehydes to provide 2-formylaziridines in good yields and with up to 99% *ee.* The synthetic utility of this

organocatalytic method was exemplified in a two-step asymmetric synthesis of  $\beta$ -amino acid esters with readily removable protecting groups (see scheme;  $R^1 = tert$ -butoxycarbonyl, benzyloxycarbonyl).

#### Asymmetric Catalysis

J. Vesely, I. Ibrahem, G.-L. Zhao, R. Rios, A. Córdova\* \_\_\_\_\_\_\_ 778-78

Organocatalytic Enantioselective Aziridination of  $\alpha,\beta$ -Unsaturated Aldehydes



$$R^{1}$$
 $+$ 
 $Et_{3}SiOTf$ 

Give and take: Both a strong electron

donor (1) and a strong electron acceptor  $(P(OPh)_3)$  are necessary for a highly

selective, nickel-catalyzed coupling reac-

tion between alkenes, aldehydes, and silyl

triflates (see scheme; cod = cycloocta-1,5-

diene, Tf = trifluoromethanesulfonyl). This synergistic effect may also be useful in other transformations catalyzed by NHC-metal complexes (NHC = N-heterocyclic carbene).

#### Catalytic Coupling Reactions

C.-Y. Ho, T. F. Jamison\* \_\_\_\_\_ 782 - 785

Highly Selective Coupling of Alkenes and Aldehydes Catalyzed by  $[Ni(NHC)\{P(OPh)_3\}]: \mbox{ Synergy between a Strong } \sigma \mbox{ Donor and a Strong } \pi \mbox{ Acceptor}$ 



On the fluor: Highly regioselective nucleophilic difluoromethylation of 1,2-cyclic sulfates and sulfamidates leads after selective desulfonylation to  $\beta$ -

difluoromethylated and  $\beta$ -difluoromethylenated alcohols and amines (see scheme), which are highly useful building blocks in the life sciences.

#### Fluorine Chemistry

C. Ni, J. Liu, L. Zhang, J. Hu\* 786-789

A Remarkably Efficient Fluoroalkylation of Cyclic Sulfates and Sulfamidates with PhSO $_2$ CF $_2$ H: Facile Entry into  $\beta$ -Difluoromethylated or  $\beta$ -Difluoromethylenated Alcohols and Amines



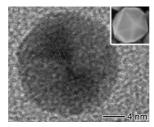


#### Nanostructures

Y. Xiong, J. M. McLellan, Y. Yin, Y. Xia\* \_\_\_\_\_\_ **790 – 794** 



Synthesis of Palladium Icosahedra with Twinned Structure by Blocking Oxidative Etching with Citric Acid or Citrate Ions

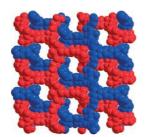


A remedy for etching: Citric acid and citrate ion were used to prevent oxidative etching from the reaction system by taking advantage of their strong binding to Pd surfaces. This method allowed Pd icosahedra (see picture) to be formed in yields as high as 80%.

#### Microporous Materials

J. M. Taylor, A. H. Mahmoudkhani, G. K. H. Shimizu\* \_\_\_\_\_\_ **795 – 798** 

A Tetrahedral Organophosphonate as a Linker for a Microporous Copper Framework



Role reversal: A copper phosphonate network is synthesized using a ligand-directed, rather than a cluster-directed, approach. The doubly interpenetrated diamondoid framework (see space-filling representation) contains accessible micropores, as demonstrated by CO<sub>2</sub> sorption experiments.



Supporting information is available on the WWW (see article for access details).



A video clip is available as Supporting Information on the WWW (see article for access details).

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## Corrigenda

In this Communication, the x axis of the main spectrum shown in Figure 4 should read hv/meV. The axis of the inset is correct as published.

A Crystalline Microporous Narrow-Bandgap Semiconductor

A. E. C. Palmqvist,\* B. B. Iversen, E. Zanghellini, M. Behm,

G. D. Stucky \_\_\_\_\_ 699-704

Angew. Chem. Int. Ed. 2004, 43

DOI 10.1002/anie.200351284

Reference [9a] of this Communication should read as follows:

[9] a) D. Olea, S. S. Alexandre, P. Amo-Ochoa, A. Guijarro, F. de Jesús, J. M. Soler, P. J. de Pablo, F. Zamora, J. Gómez-Herrero, Adv. Mater. 2005, 17, 1761.

Diameter-Tunable CdTe Nanotubes Templated by 1D Nanowires of Cadmium Thiolate Polymer

H. Niu, M. Y. Gao\* \_\_\_\_\_ 6462–6466

Angew. Chem. Int. Ed. 2006, 45

DOI 10.1002/anie.200601779

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