



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](http://www.angewandte.org) soon:

C. Costentin, M. Robert, J. Savéant, C. Tard

**Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers**

A. Wilbuer, D. H. Vlecken, D. J. Schmitz, K. Kräling, K. Harms, C. P. Bagowski, E. Meggers\*

**Iridium Complex with Antiangiogenic Properties**

R. Rose, S. Erdmann, S. Bovens, A. Wolf, M. Rose, S. Hennig, H. Waldmann, C. Ottmann\*

**Identification and Structure of Small-Molecule Stabilizers of 14-3-3 Protein-Protein Interactions**

A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein\*

**A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica**

M. Walz, M. Schirmer, F. Vollnhals, T. Lukaszczuk, H.-P. Steinrück, H. Marbach\*

**Electrons as “Invisible Ink”! Fabrication of Nanostructures by Local Electron Beam Induced Activation of SiO<sub>x</sub>**

A. Takaoka, L. C. H. Gerber, J. C. Peters\*

**Access to Well-Defined Ruthenium(II) and Osmium(II) Metalloradicals**

J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao\*

**Single Fused Gene Approach to Photoswitchable and Fluorescent Biliproteins**

D. Šišak, L. B. McCusker,\* G. Zandomenighi, B. Meier,\* D. Bläser, R. Boese,\* W. B. Schweizer, R. Gilmour, J. D. Dunitz\*

**The Crystal Structure of Ribose – At Last!**



“When I was eighteen I wanted to be the first person to live on the moon.

If I could be anyone for a day, I would be a scientist 1000 years from now ...”

This and more about Tetsuro Majima can be found on page 3564.

## Author Profile

Tetsuro Majima \_\_\_\_\_ 3564

Eugene E. van Tamelen (1925–2009)

## Obituary

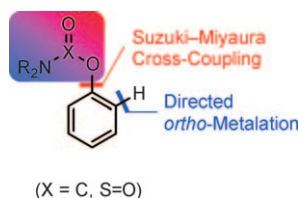
B. Åkermark \_\_\_\_\_ 3565–3566

No Small Matter

Felice C. Frankel, George M. Whitesides

## Books

reviewed by A. Lorke \_\_\_\_\_ 3567



**Twice as good:** This highlight illustrates the development of new protocols for the efficient synthesis of polysubstituted arenes. The dual role of carbamate and sulfamate substituents as directing and leaving groups has been exploited in efficient reaction sequences of directed *ortho*-metalation and chemoselective nickel-catalyzed Suzuki-Miyaura cross-coupling reactions (see structure).

## Highlights

### Arene Functionalization

C. E. I. Knapcke,  
A. Jacobi von Wangelin\* \_\_\_\_\_ 3568–3570

A Synthetic Double Punch: Suzuki-Miyaura Cross-Coupling Mates with C–H Functionalization

## Reviews

### Biofuels

K. Kohse-Höinghaus,\* P. Oßwald,  
T. A. Cool, T. Kasper, N. Hansen,  
F. Qi, C. K. Westbrook,  
P. R. Westmoreland \_\_\_\_\_ **3572–3597**

Biofuel Combustion Chemistry:  
From Ethanol to Biodiesel



**Not wanting to be a flaming nuisance:** Partial replacement of conventional hydrocarbon fuels with biofuels has become a reality. Insight into their combustion chemistry is obtained from laboratory flame experiments using molecular-

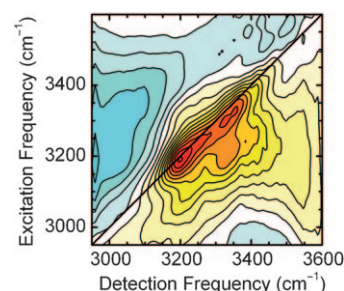
beam mass spectrometry and complementary combustion modeling. Such investigations are a basis to assess the hazardous emission potential of alternative fuels.

### Hydrated DNA

Ł. Szyc, M. Yang, E. T. J. Nibbering,  
T. Elsaesser\* \_\_\_\_\_ **3598–3610**

Ultrafast Vibrational Dynamics and Local Interactions of Hydrated DNA

**Short process:** The vibrational dynamics of DNA oligomers and their interaction with the surrounding water shell can be studied with a wide range of hydration levels by nonlinear infrared spectroscopy in the femtosecond time domain (see picture, yellow-red and blue regions correspond to different vibrational transitions). The results give detailed insight into the coupling of different functional groups and into basic processes of DNA–water interaction.



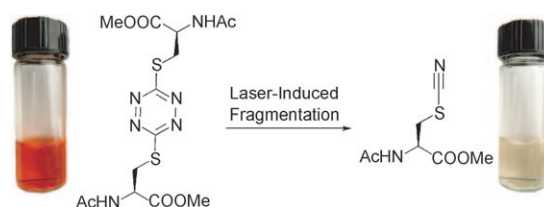
## Communications

### Phototriggering

M. J. Tucker, J. R. Courter, J. Chen,  
O. Atasoylu, A. B. Smith, III,\*  
R. M. Hochstrasser\* \_\_\_\_\_ **3612–3616**



Tetrazine Phototriggers: Probes for Peptide Dynamics



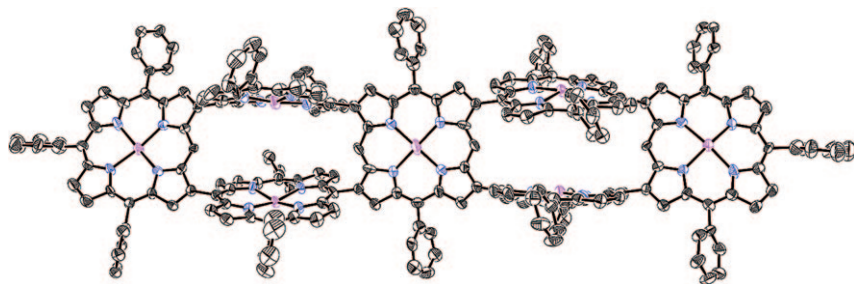
**Surrender your secrets, peptides!** Of several 3,6-disubstituted tetrazines examined as phototriggers for the investigation of peptide dynamics, the most useful candidates were disulfenyl tetrazines. The thiocyanate fragments resulting from photol-

ysis (see scheme) were detected by ultrafast infrared spectroscopy. Chromophore insertion into oxytocin and photofragmentation to trigger peptide relaxation were both demonstrated.

**For the USA and Canada:**  
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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.



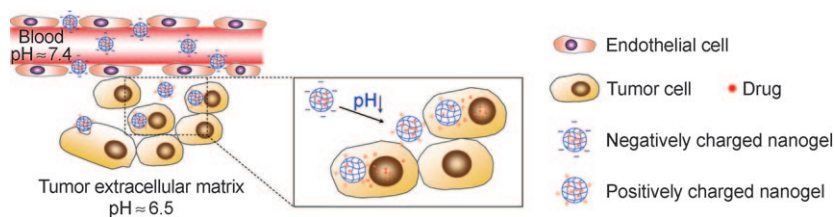
**Clicking together:** The Suzuki–Miyaura coupling of  $\beta,\beta'$ -diborylated porphyrin blocks and meso,meso'-dibrominated porphyrin blocks was used for the con-

struction of directly meso- $\beta$  doubly linked porphyrin rings including two tetraporphyrin rings, hexaporphyrin rings, and a bridged heptaporphyrin (see picture).

## Porphyrinoids

J. Song, N. Aratani,\* P. Kim, D. Kim,\*  
H. Shinokubo,\* A. Osuka\* – 3617–3620

Porphyrin “Lego Block” Strategy To Construct Directly meso- $\beta$  Doubly Linked Porphyrin Rings



**A positive (or negative) chameleon:** A nanogel that is negatively charged at physiological pH values and activated to be positively charged at tumor extracellular pH values was internalized efficiently by tumor cells both in vitro and in vivo

(see illustration). Intracellular drug release was also enhanced, probably as a result of a decrease in the interaction between the drug and the nanogel in its protonated state.

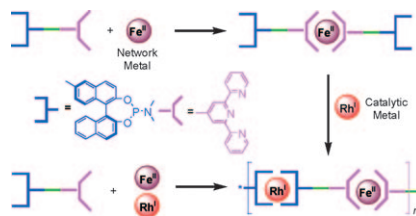
## Drug Delivery

J.-Z. Du, T.-M. Sun, W.-J. Song, J. Wu,  
J. Wang\* – 3621–3626

A Tumor-Acidity-Activated Charge-Conversional Nanogel as an Intelligent Vehicle for Promoted Tumoral-Cell Uptake and Drug Delivery



**Three in one:** Orthogonal coordination of  $\text{Fe}^{\text{II}}$  and  $\text{Rh}^{\text{I}}$  with a single heteroditopic ligand results in the formation of self-supported heterogeneous chiral catalysts (see scheme). The compounds are highly active, enantioselective, and reusable in the heterogeneous asymmetric hydrogenation of various functionalized olefin derivatives.



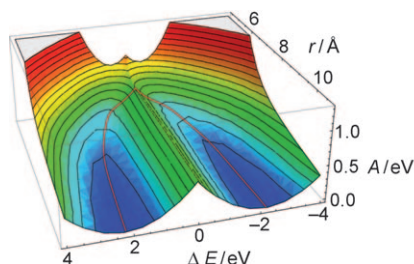
## Asymmetric Catalysis

L. Yu, Z. Wang, J. Wu, S. J. Tu,  
K. Ding\* – 3627–3630

Directed Orthogonal Self-Assembly of Homochiral Coordination Polymers for Heterogeneous Enantioselective Hydrogenation



**The distance dependences** of all electron-transfer parameters, including electronic coupling, were computed for the  $\text{Ru}^{2+}$ – $\text{Ru}^{3+}$  electron self-exchange reaction in aqueous solution. It was found that the probability for electron exchange is a maximum at a  $\text{Ru}^{2+}$ – $\text{Ru}^{3+}$  distance of 5.6 Å (see free-energy surface), which is significantly smaller than the envelopes of the  $[\text{Ru}(\text{H}_2\text{O})_6]^{n+}$  complexes



## Electron Transfer

H. Oberhofer,  
J. Blumberger\* – 3631–3634

Insight into the Mechanism of the  $\text{Ru}^{2+}$ – $\text{Ru}^{3+}$  Electron Self-Exchange Reaction from Quantitative Rate Calculations

# Frontiers of Chemistry: From Molecules to Systems

A One-Day Symposium

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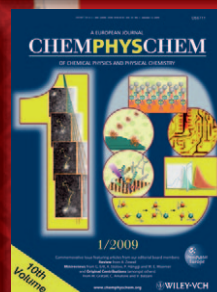


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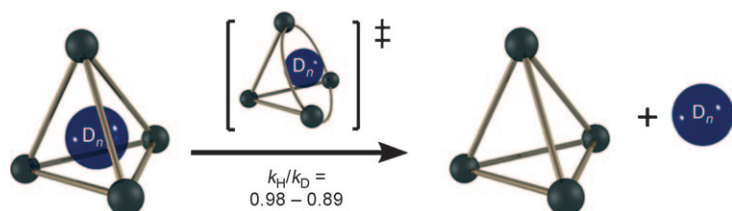
E. Amouyal, M. Che,  
F. C. De Schryver,  
A. R. Fersht, P. Göllitz,  
J. T. Hynes, J.-M. Lehn

## Topics

catalysis, biochemical imaging,  
chemical biology, bionanotechnology,  
proteomics, spectroscopy, solar cells



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**Does size really matter?** Inverse kinetic isotope effects of up to 11 % are observed in the guest-exchange process from a highly charged supramolecular host (see picture). While the observed isotope

effects can be understood in terms of the smaller steric requirements of deuterium, they are more fully explained in terms of coupling of the host aperture dilation with the guest C–H/D vibrational modes.

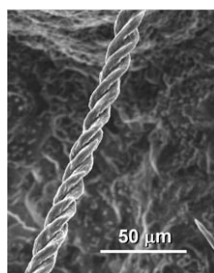
## Supramolecular Chemistry

J. S. Mugridge, R. G. Bergman,\*  
K. N. Raymond\* — 3635 – 3637

Does Size Really Matter? The Steric Isotope Effect in a Supramolecular Host–Guest Exchange Reaction



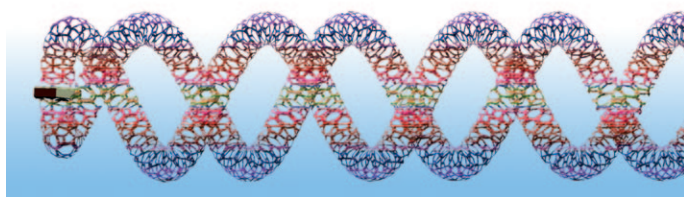
**A new twist on semiconductors:** The evaporation of Na from ionic intermetallic NaSi at 800 °C leads to the formation of double-helical silicon microtubes. The tubes have nanogranular or smooth surfaces and a twinned structure with voids in the tube wall. A mechanism is proposed for the formation of the double-helical microtubes.



## Silicon Microstructures

H. Morito,\* H. Yamane — 3638 – 3641

Double-Helical Silicon Microtubes



**Let's twist:** Levo- or dextrorotatory carbon-nanotube (CNT) arrays were twisted into a double helix (see picture) on a layered double hydroxide flake through a self-organization process

during growth by chemical vapor deposition. The as-grown CNT arrays in the double helix are able to carry a high current that can be modulated.

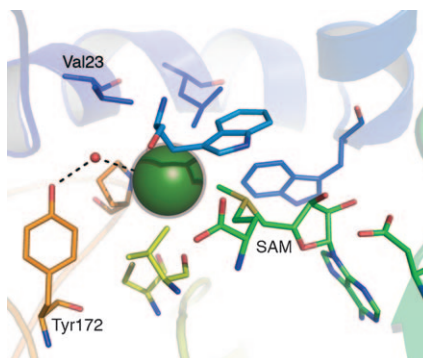
## Nanostructures

Q. Zhang, M. Q. Zhao, D. M. Tang, F. Li,  
J. Q. Huang, B. L. Liu, W. C. Zhu,  
Y. H. Zhang, F. Wei\* — 3642 – 3645

Carbon-Nanotube-Array Double Helices



**It's a gas!** The structure of the halo-methane-producing halo/thiocyanate methyltransferase enzyme from plants has been determined. The halide ion and the methyl group of S-adenosyl-L-methionine (SAM) were modeled into the active site (see picture; chloride: green sphere; SAM: C green, O red, S yellow, N blue), which indicated their predisposition for reaction.



## Structural Biology

J. W. Schmidberger, A. B. James,  
R. Edwards, J. H. Naismith,  
D. O'Hagan\* — 3646 – 3648

Halomethane Biosynthesis: Structure of a SAM-Dependent Halide Methyltransferase from *Arabidopsis thaliana*



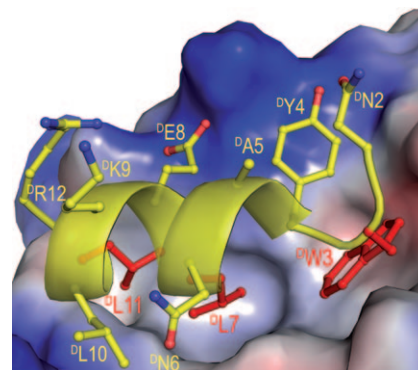
## Protein Structures

M. Liu, M. Pazgier, C. Li, W. Yuan, C. Li, W. Lu\* — 3649–3652



A Left-Handed Solution to Peptide Inhibition of the p53–MDM2 Interaction

**Throwing tumors a left-hook punch:** The oncoprotein MDM2 negatively regulates the activity and stability of the tumor suppressor protein p53, and is an important molecular target for anticancer therapy. Mirror-image phage display identified a high-affinity D-peptide ligand of MDM2 (see structure) that could be developed into a potent and protease-resistant p53 activator with potential antitumor activity.



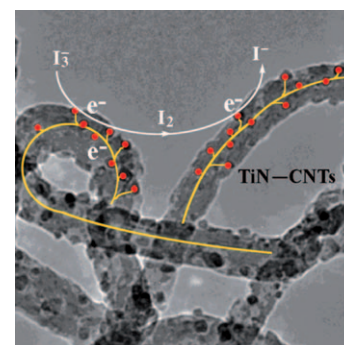
## Nanotechnology

G. R. Li, F. Wang, Q. W. Jiang, X. P. Gao,\* P. W. Shen — 3653–3656



Carbon Nanotubes with Titanium Nitride as a Low-Cost Counter-Electrode Material for Dye-Sensitized Solar Cells

**Mix and match:** The photovoltaic performance of carbon nanotubes with titanium nitride nanoparticles (TiN-CNTs; see picture), which is comparable to that of conventional platinum counter electrodes, is attributed to the ideal combination of the superior electrocatalytic activity of TiN nanoparticles and the high electrical conductivity of CNTs.



## Supramolecular Chemistry

S. Lena, P. Neviani, S. Masiero, S. Pieraccini, G. P. Spada\* — 3657–3660



Triggering of Guanosine Self-Assembly by Light



**Light switches:** The introduction of a photoactive moiety into a lipophilic guanosine derivative allows photocontrol

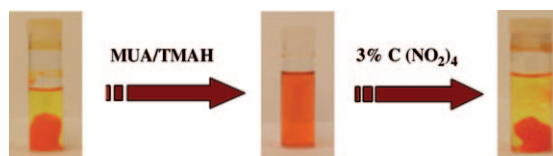
over the self-assembly of the molecule. The existence of G-quartets can be alternately switched on and off (see picture).

## Nanoassembly

I. R. Pala, I. U. Arachchige, D. G. Georgiev, S. L. Brock\* — 3661–3665



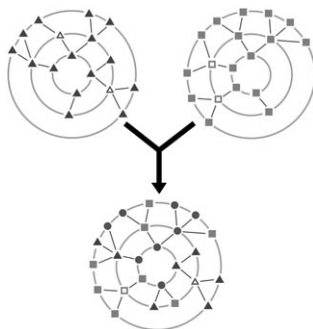
Reversible Gelation of II–VI Nanocrystals: The Nature of Interparticle Bonding and the Origin of Nanocrystal Photochemical Instability



**Programmable assembly and disassembly:** Chemical and spectroscopic studies show that Se–Se bond formation is responsible for the oxidation-induced aggregation of thiolate-capped CdSe nanocrystals to gels. Treatment with reducing agents leads to Se–Se bond

cleavage and dispersion of the gel. This process can be cycled, resulting in successively smaller particles (see picture; MUA = 11-mercaptoundecanoic acid, TMAH = tetramethylammonium hydroxide).

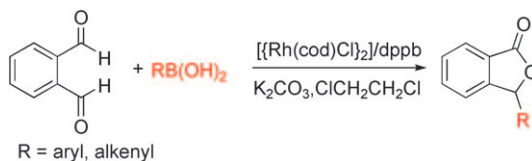
**Tactical target setting:** The merging of natural product and non-natural product based hierarchical scaffold trees annotated with bioactivity (see schematic illustration) together with brachiation along structural lines of biological relevance provides a novel strategy for the prospective identification of protein targets for compound collections inspired by natural product structures.



## Cheminformatics

S. Wetzel, W. Wilk, S. Chammaa, B. Sperl, A. G. Roth, A. Yektaoglu, S. Renner, T. Berg, C. Arenz, A. Giannis, T. I. Oprea, D. Rauh, M. Kaiser, H. Waldmann\* — 3666–3670

A Scaffold-Tree-Merging Strategy for Prospective Bioactivity Annotation of  $\gamma$ -Pyrones



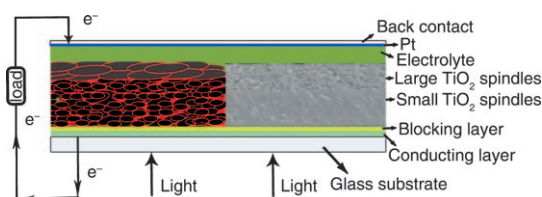
**First one and then the other:** A rhodium-catalyzed addition of aryl and alkenyl boronic acids to phthalaldehyde and subsequent intramolecular esterification is described (see scheme; cod = 1,5-cyclo-octadiene, dppb = 1,4-bis(diphenylphos-

phino)butane). The method is facile and practical for accessing 3-aryl and 3-alkenyl phthalides in moderate to good yields. Several functional groups are tolerated under the reaction conditions.

## Synthetic Methods

Z. Ye, G. Lv, W. Wang, M. Zhang, J. Cheng\* — 3671–3674

Rhodium-Catalyzed Cascade Reaction: Aryl Addition/Intramolecular Esterification to Access 3-Aryl and 3-Alkenyl Phthalides



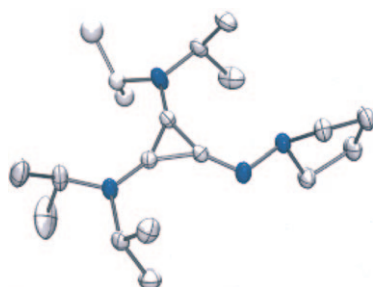
**Little and large:** A double-layered photoanode constructed from small and large single-crystal anatase TiO<sub>2</sub> nanospindles achieves 8.3% energy-conversion efficiency in a dye-sensitized solar cell (see

picture). One layer of the double-layer structure serves mainly to harbor numerous dye molecules, and the other primarily enhances light harvesting by multiple scattering.

## Solar Cells

Y. Qiu, W. Chen, S. Yang\* — 3675–3679

Double-Layered Photoanodes from Variable-Size Anatase TiO<sub>2</sub> Nanospindles: A Candidate for High-Efficiency Dye-Sensitized Solar Cells



**Give me four:** In contrast to typical imines, the central nitrogen atom in cyclopropenyl-derived carbeneimines (see example; C gray, N blue) can donate up to four electrons to form coordination complexes.

## Ligand Development

H. Bruns, M. Patil, J. Carreras, A. Vázquez, W. Thiel, R. Goddard, M. Alcarazo\* — 3680–3683

Synthesis and Coordination Properties of Nitrogen(I)-Based Ligands

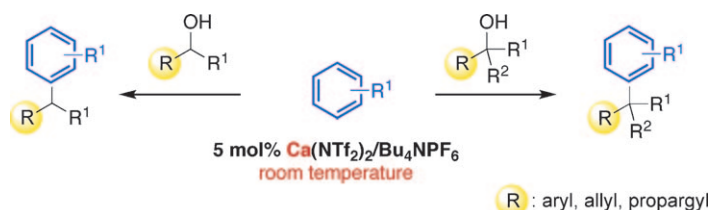


## Arene Functionalization

M. Niggemann,\* M. J. Meel 3684–3687



Calcium-Catalyzed Friedel–Crafts Alkylation at Room Temperature



A novel calcium catalyst was found to efficiently functionalize electron-rich arenes with secondary and tertiary benzylic, propargylic, and allylic alcohols under very mild reaction conditions. The

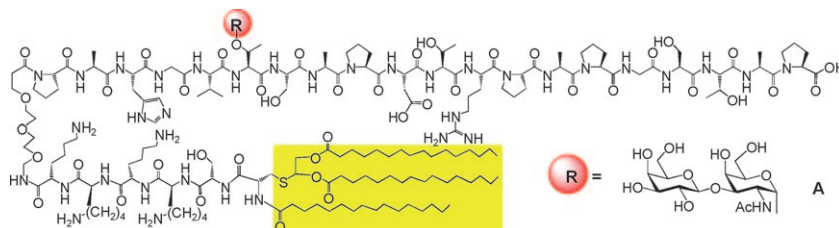
new catalyst system significantly enlarges the scope of the reaction, which was previously limited except for the few examples with secondary benzylic alcohols.

## Vaccine Synthesis

A. Kaiser, N. Gaidzik, T. Becker, C. Menge, K. Groh, H. Cai, Y.-M. Li, B. Gerlitzki, E. Schmitt, H. Kunz\* 3688–3692



Fully Synthetic Vaccines Consisting of Tumor-Associated MUC1 Glycopeptides and a Lipopeptide Ligand of the Toll-like Receptor 2



Fragment condensation of a protected Pam<sub>3</sub>Cys lipopeptide with unprotected tumor-associated MUC1 glycopeptides opens the way to vaccine candidates such as A. These vaccines elicit selective

immune responses in mice although they lack an immunodominant carrier protein. In principle, such vaccines are applicable to humans.



Supporting information is available on [www.angewandte.org](http://www.angewandte.org) (see article for access details).



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

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