



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:

L. Wang, L. Xia, G. Li, S. Ravaine, X. S. Zhao\*

Patterning the Surface of Colloidal Microspheres and Fabrication of Nonspherical Particles

N. Suzuki\*, D. Hashizume, H. Koshino, T. Chihara Transformation of 1-Zirconacyclopent-3-yne, a Five-Membered Cycloalkyne, into 1-Zirconacylopent-3-ene and Formal 1-Zirconacyclopenta-2,3-dienes

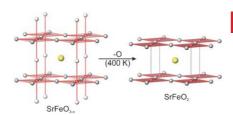
#### Books

Electrodeposition from Ionic Liquids

Frank Endres, Andrew P. Abbott, Douglas R. MacFarlane

reviewed by T. Welton \_ 4468

A soft reduction: The new layered oxoferrate(II) SrFeO<sub>2</sub> (see scheme: Fe red, Sr yellow, C gray) was synthesized by the reduction of the slightly oxygen-deficient perovskite SrFeO<sub>3-x</sub> at 400 K with CaH<sub>2</sub> in a form of topotactical reaction. The square-planar-coordinated iron(II) ions in SrFeO<sub>2</sub> exhibit a high-spin d<sup>6</sup> configuration with a doubly occupied d<sub>2</sub> orbital. SrFeO<sub>2</sub> orders antiferromagnetically at an unusual high Néel temperature of  $T_N = 473$  K.



# Highlights

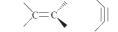
#### Layered Oxides

J. Köhler\* \_\_ \_ 4470 - 4472

Square-Planar Coordinated Iron in the Layered Oxoferrate(II) SrFeO<sub>2</sub>

Going to extremes: Deformed molecules with "planar" carbon atoms, orthogonal double bonds, nonlinear triple bonds, and aromatic rings distorted into a boat structure have interested chemists for decades. This essay traces the reasons for this fascination, and finds them in the psyche of the researcher: the wish to transgress the limits of normalcy, the insatiable curiosity to extend the limits of method and mind, and the eternal human joy to find something new while playing.







Essays

Theoretically Interesting Molecules

R. Hoffmann,\* H. Hopf\* \_\_\_ 4474 - 4481

Learning from Molecules in Distress

#### Reviews

#### Organic Ligands

C. Defieber, H. Grützmacher,

E. M. Carreira\* \_\_\_\_\_ 4482 - 4502

Chiral Olefins as Steering Ligands in Asymmetric Catalysis

The conceptually novel class of ligands,

the chiral dienes, complement traditional heteroatom-based ligands. In addition to a historical perspective on metal-olefin complexes, this Review summarizes various syntheses of chiral olefins (some are

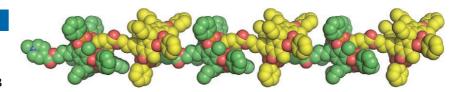
shown in the picture) that have found widespread application as ligands in asymmetric transition-metal-catalyzed processes, such as in the asymmetric conjugate addition of arylboronic acids to  $\alpha,\beta$ -unsaturated carbonyl compounds.

### **Communications**

#### Supramolecular Polymers

R. M. Yebeutchou, F. Tancini, N. Demitri, S. Geremia, R. Mendichi,

E. Dalcanale\* \_\_\_\_\_\_ 4504 – 4508



Host-Guest Driven Self-Assembly of Linear and Star Supramolecular Polymers

**Supramolecular plasticity**: The remarkable host–guest properties of phosphonate cavitands have been exploited in the self-assembly of supramolecular polymers (see picture) that feature guest-triggered reversibility and template-driven conver-

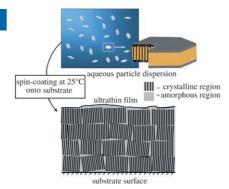
sion from linear into star-branched forms. The structurally similar but complexation-inefficient thiophosphonate cavitand acts as chain stopper to control the degree of polymerization.

#### **Polymer Films**

Q. Tong, M. Krumova,

S. Mecking\* \_\_\_\_\_ 4509 – 4511

Crystalline Polymer Ultrathin Films from Mesoscopic Precursors

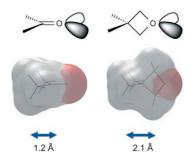


Caught on film: Ultrathin (50 nm) films of crystalline polyethylene were prepared at room temperature from prefabricated polymer nanocrystals functioning as building blocks. The very small particle size, in combination with the phenomenon that the amorphous regions are located at the surface exclusively in polymer single crystals, results in efficient interaction between particles in the films.

#### 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 POST-MASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US\$ 7225/6568 (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.



#### Wormholes through chemical space:

Spirocyclic oxetanes are described as analogues of morpholine and also as topological siblings of their carbonyl counterparts. They are particularly promising in terms of both their physicochemical properties and the ease with which they can be grafted onto molecular structures. The data collected highlight oxetanes as both the hydrophilic sister of a gem-dimethyl unit and the carbonyl group's lipophilic brother.

#### Oxetanes

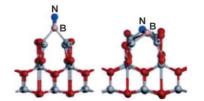
G. Wuitschik, M. Rogers-Evans,\* A. Buckl, M. Bernasconi, M. Märki, T. Godel, H. Fischer, B. Wagner, I. Parrilla, F. Schuler, J. Schneider, A. Alker, W. B. Schweizer, K. Müller,\*

E. M. Carreira\* \_\_\_\_\_ 4512 - 4515

Spirocyclic Oxetanes: Synthesis and **Properties** 



Add an N: The visible-light absorption of boron-doped mesoporous TiO<sub>2</sub> depends strongly on the state of the dopant (see picture), although the activity can be substantially enhanced by additional doping of nitrogen. The new O-Ti-B-N structure formed on the surface of the photocatalyst is highly active in collecting and separating the charge carriers, thereby greatly enhancing the visible light photocatalytic activity.

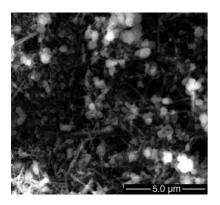


#### Titania-Based Photocatalysts

G. Liu, Y. Zhao, C. Sun, F. Li, G. Q. Lu,\* H.-M. Cheng\* \_\_\_\_\_ 4516 – 4520

Synergistic Effects of B/N Doping on the Visible-Light Photocatalytic Activity of Mesoporous TiO<sub>2</sub>





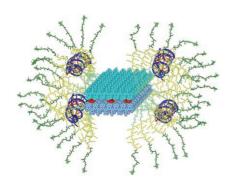
Higher-capacity lithium batteries can be fabricated by using  $\alpha$ -MnO<sub>2</sub> nanowires as the catalyst in a porous, composite oxygen cathode. In the depicted scanning electron micrograph of a composite positive electrode, deposits of Li<sub>2</sub>O<sub>2</sub>, which accumulates during discharge, can be seen within a porous matrix consisting of  $\alpha$ -MnO<sub>2</sub> and carbon.

#### Lithium-Oxygen Batteries

A. Débart, A. J. Paterson, J. Bao, P. G. Bruce\* \_\_\_\_\_ 4521 – 4524

α-MnO<sub>2</sub> Nanowires: A Catalyst for the O<sub>2</sub> Electrode in Rechargeable Lithium **Ratteries** 





Angew. Chem. Int. Ed. 2008, 47, 4453-4462

Therapeutic viruses: A filament-shaped artificial virus is formed by using a preorganized supramolecular nanoribbon as a template. The artificial virus (see picture), which is composed of the nanoribbon, small interfering RNAs (blue, double-helix shape), and hydrophobic guests (red), is highly efficient in delivering genes and drugs to the inside of cells.

#### Artificial Virus

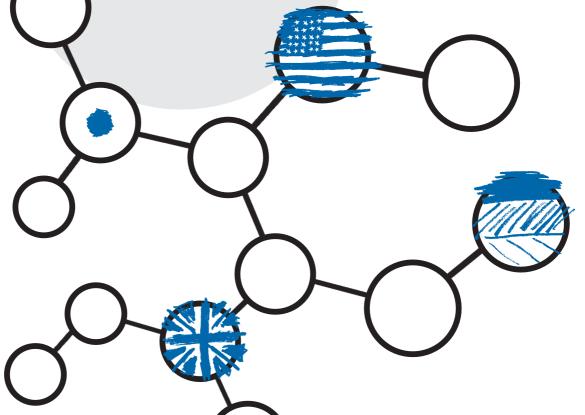
Y.-b. Lim, E. Lee, Y.-R. Yoon, M. S. Lee, M. Lee\* \_\_\_\_\_ 4525 – 4528

Filamentous Artificial Virus from a Self-Assembled Discrete Nanoribbon



4455

# Incredibly international!





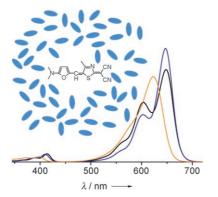
Although Angewandte Chemie is owned by the German Chemical Society (Gesellschaft Deutscher Chemiker, GDCh) and is published by Wiley-VCH in a charming small town in southwest Germany, it is international in every other respect. Authors and referees from around the globe contribute to its success. Most of the articles are submitted from China (20%), USA (16%), and Japan (13%) - only then comes Germany (12%). Most of the referee reports come from Germany and the USA, but Japan and Western Europe are also well represented.

service@wiley-vch.de www.angewandte.org





**Solvatochromism elucidated**: UV/Vis and electrooptical absorption spectroscopy were used to elucidate the effect of solvent on the electrical and optical properties of three merocyanine dyes. Changes in the shape of the Vis absorption band in solvents of different polarity [e.g., the depicted dye in Et<sub>2</sub>O (black), AcOEt (blue), and MeCN (orange)] are explained by different excited-state dipole moments of the respective vibronic transitions.



#### Push-Pull Chromophores

F. Würthner,\* G. Archetti, R. Schmidt, H.-G. Kuball\* \_\_\_\_\_\_ 4529 – 4532

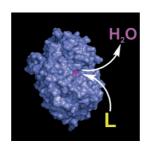
Solvent Effect on Color, Band Shape, and Charge-Density Distribution for Merocyanine Dyes Close to the Cyanine Limit



The relaxation rate of water proton nuclei can be used to screen ligands (L; see picture) directed to the metal binding site in paramagnetic metalloproteins by NMR spectroscopy. The very high concentration of water protons provides an enormous

sensitivity and permits the use of unpre-

cedentedly low amounts of protein.

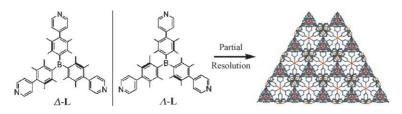


#### Protein Ligand Screening

I. Bertini,\* M. Fragai, C. Luchinat, E. Talluri \_\_\_\_\_\_ 4533 – 4537

Water-Based Ligand Screening for Paramagnetic Metalloproteins





Tunable NLO activity: The title compounds were efficiently assembled from the enantiopure and threefold-symmetric tris (4-pyridylduryl) borane ligand L through coordinative bonds. The Cdorganoboron framework (see picture)

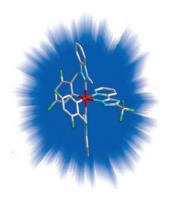
exhibits a significant second harmonic generation response and, more importantly, the NLO activity can be tuned by means of different encapsulated counteranions.

#### Metal-Organoboron Frameworks

Y. Liu, X. Xu, F. Zheng,
Y. Cui\* \_\_\_\_\_\_ 4538 – 4541

Chiral Octupolar Metal-Organoboron NLO Frameworks with (14,3) Topology





**Bright & blue**: A strategy for reducing metal-chelate internal strain enables the preparation of blue emitting iridium(III) carbene complexes (see picture; Ir red, N light blue, F green). The phosphorescent OLED fabricated from one of these complexes shows remarkable CIE coordinates of (0.16, 0.13) and peak efficiencies of 6.0% photons per electron, 6.3 cd A<sup>-1</sup>, and 4.0 lm W<sup>-1</sup>.

#### Blue Light-Emitting Diodes

C.-F. Chang, Y.-M. Cheng, Y. Chi,\* Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou,\* C.-C. Chen, C.-H. Chang, C.-C. Wu\* \_\_\_\_\_\_\_\_ 4542 – 4545

Highly Efficient Blue-Emitting Iridium(III) Carbene Complexes and Phosphorescent OLEDs



# **Contents**

#### Metallamacrocycles

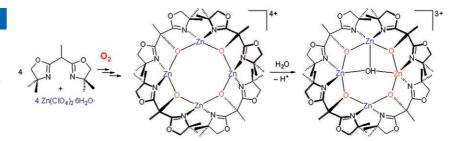
B. Jacques, C. Dro,

S. Bellemin-Laponnaz,\* H. Wadepohl,

L. H. Gade\* \_\_\_\_\_ 4546 – 4550



Self-Assembly of a Cyclic Zn<sub>4</sub>O<sub>4</sub> Tetramer by Aerobic Oxidation of a Bisoxazoline: A Molecular "Nest" for Nucleophilic OH<sup>-</sup>



Nesting hydroxide: Coordination and aerobic oxidation of a bisoxazoline  $Me_2box$  is coupled with self-assembly to form a highly ordered  $[(Me_2box)O_4Zn_4]^{4+}$ 

complex. The metallamacrocycle acts as a nest-like hydroxide receptor (see scheme, right) and shows catalytic phosphatase activity.



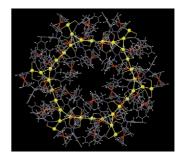
#### Supramolecular Chemistry

S.-Y. Yu,\* Q.-F. Sun, T. K.-M. Lee, E. C.-C. Cheng, Y.-Z. Li,\*

V. W.-W. Yam\* \_\_\_\_\_ 4551 – 4554



Au<sub>36</sub> Crown: A Macrocyclization Directed by Metal-Metal Bonding Interactions **Lord of the golden rings**: A giant, crown-like  $Au_{36}$  ring aggregate with continuous metal-metal contacts (see picture; gold(I) centers are in ball and stick representation) is formed by an  $Au^I$ — $Au^I$  bonding interaction directed self-assembly.

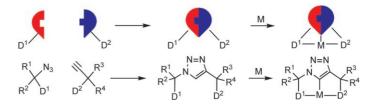


#### Homogeneous Catalysis

E. M. Schuster, M. Botoshansky,
M. Gandelman\* \_\_\_\_\_ 4555 – 4558



Pincer Click Ligands



It all clicks into place: The use of "click chemistry" has been found to be highly advantageous for the selective and rapid combinatorial synthesis of a family of pincer-type ligands from relatively simple

building blocks (see scheme). This synthetic strategy provides access to a range of well-defined transition-metal catalysts which exhibit extremely high catalytic efficiency in the Heck reaction.

#### Heterogeneous Catalysis

M. V. Luzgin, V. A. Rogov,

S. S. Arzumanov, A. V. Toktarev,

A. G. Stepanov,\*

V. N. Parmon \_\_\_\_\_\_ 4559 – 4562

Understanding Methane Aromatization on a Zn-Modified High-Silica Zeolite

It takes two: A high level of conversion of <sup>13</sup>C atoms of methane into the products of methane/propane coaromatization on zeolite Zn/H-BEA has been demonstrated by <sup>13</sup>C solid-state NMR spectroscopic analysis and GC-MS. The isotope-labeling experiments show the mechanism consists of the methylation of aromatic compounds formed from the propane followed by ring-expansion/contraction (see scheme).



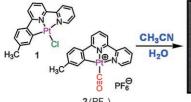
A state of (con)fusion: The introduction of a confused pyrrole ring into a *meso*-aryl sapphyrin framework destabilizes the macrocycle and forces a fusion reaction to occur. Subsequent metalation with rhenium results in further mutation to form a domino-fused sapphyrin with a fused penta-ring system (see scheme).

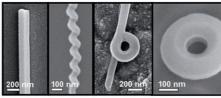
#### Porphyrinoids

I. Gupta, A. Srinivasan, T. Morimoto, M. Toganoh, H. Furuta\* \_\_\_\_ 4563 – 4567

N-Confused and N-Fused *meso-*Aryl Sapphyrins







Wheely springy wires: Freestanding and crystalline submicrometer wires, springs, and wheels are grown in aqueous acetonitrile dispersions starting from the orga-

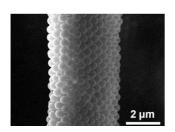
noplatinum(II) complexes **1** and **2**(PF<sub>6</sub>). The growth mechanism is proposed to involve ligand-substitution reactions and electrostatic and Pt<sup>II</sup>····Pt<sup>II</sup> interactions.

#### Organometallic Superstructures

W. Lu, S. S.-Y. Chui, K.-M. Ng, C.-M. Che\* \_\_\_\_\_\_ 4568 – 4572

A Submicrometer Wire-to-Wheel Metamorphism of Hybrid Tridentate Cyclometalated Platinum(II) Complexes





Staying in line: Aqueous colloids (particle diameter 10–500 nm) are directionally frozen and freeze-dried to produce aligned microwires, which can be fused together by heat treatment with complete retention of the morphology. The method is generic: by controlling surface charge, the approach can be applied to metals, metal oxides, and organic polymers. A single microwire formed by the assembly of polystyrene colloids is shown.

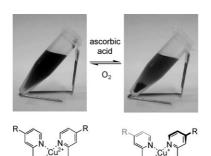
#### Microwires

H. Zhang,\* J.-Y. Lee, A. Ahmed,
I. Hussain, A. I. Cooper \_\_\_\_\_ **4573 – 4576** 

Freeze-Align and Heat-Fuse: Microwires and Networks from Nanoparticle Suspensions



Complex control of solubility: Singlewalled nanotubes (SWNTs) can be dissolved in organic solvents by formation of a complex with a 2,2'-bipyridine derivative and Cu through mechanochemical highspeed vibration milling. The conformational change of the Cu<sup>1</sup>/Cu<sup>11</sup> complexes resulting from chemical oxidation–reduction reactions induces different solubilities of the SWNTs because of differences in the  $\pi$ - $\pi$  stacking interactions.



SWNTs

#### Carbon Nanotubes

K. Nobusawa, A. Ikeda,\* J. Kikuchi,

S. Kawano, N. Fujita,

S. Shinkai \_\_\_\_\_\_ 4577 - 4580

Reversible Solubilization and Precipitation of Carbon Nanotubes through Oxidation-Reduction Reactions of a Solubilizing Agent



**SWNTs** 

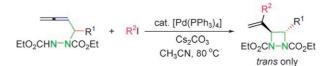
# **Contents**

#### Cyclizations

X. Cheng, S. Ma\* \_\_\_\_\_ 4581 - 4583



[Pd(PPh<sub>3</sub>)<sub>4</sub>]-Catalyzed Diastereoselective Synthesis of *trans*-1,2-Diazetidines from 2,3-Allenyl Hydrazines and Aryl Halides



**Strain, what strain?** Pd<sup>o</sup>-catalyzed cyclization of easily accessed and diversely substituted 2,3-allenyl hydrazines with aryl halides afforded 1,2-diazetidines with two chiral centers in high regio- and diaste-

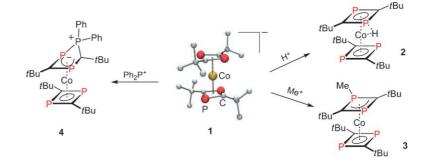
reoselectively (*trans* only; see scheme). Optically active 1,2-diazetidines were synthesized by using enantiomerically enriched 2,3-allenyl hydrazines.

#### Sandwich Complexes

R. Wolf, A. W. Ehlers, J. C. Slootweg, M. Lutz, D. Gudat, M. Hunger, A. L. Spek, K. Lammertsma\* 4584 – 4587



The Homoleptic Sandwich Anion  $[Co(P_2C_2tBu_2)_2]^{-}$ : A Versatile Building Block for Phosphaorganometallic Chemistry



A sandwich recipe: Treatment of the anthracene complex  $[Co(\eta^4-C_{14}H_{10})_2]^-$  with  $tBuC\equiv P$  leads to the new diphosphacy-clobutadiene sandwich anion 1, which can

be converted into the unprecedented phosphaorganometallic complexes **2–4** upon treatment with different electrophiles (see scheme).

#### Synthetic Methods

D. A. Alonso, S. Kitagaki, N. Utsumi, C. F. Barbas III\* \_\_\_\_\_\_ 4588 – 4591



Towards Organocatalytic Polyketide Synthases with Diverse Electrophile Scope: Trifluoroethyl Thioesters as Nucleophiles in Organocatalytic Michael Reactions and Beyond

Hot ester nucleophiles! Trifluoroethyl thioesters are effective nucleophiles in direct organocatalytic asymmetric Michael reactions with  $\alpha,\beta$ -unsaturated

aldehydes (above). Electronic tuning of thioesters allows for the generation of enolates that also participate in aldol and amination reactions (below).

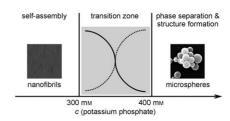
#### **Biomaterials**

U. K. Slotta,\* S. Rammensee, S. Gorb, T. Scheibel\* \_\_\_\_\_\_\_ 4592 – 4594

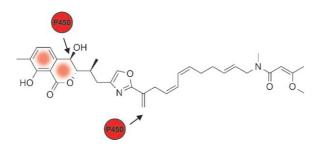


An Engineered Spider Silk Protein Forms Microspheres

Fibrils or spheres? Spider silk proteins belong to the class of natively unfolded proteins. Depending on the experimental conditions, these proteins form nanofibrils or microspheres following two distinct aggregation pathways. A detailed model describes the assembly mechanism of spider silk proteins into microspheres.



4595 - 4599



Unusual biochemistry: The pathway to the antifungal ajudazols (ajudazol A is shown) has been deduced by cloning and sequencing of the gene cluster in the myxobacterium Chondromyces crocatus,

coupled with insertional mutagenesis. Ajudazol biosynthesis incorporates several unusual features, including the first P450-catalyzed dehydrogenation identified in bacterial metabolism.

#### Biosynthetic Mechanisms

K. Buntin, S. Rachid, M. Scharfe,

H. Blöcker, K. J. Weissman,

R. Müller\* \_\_\_\_\_

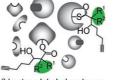
Production of the Antifungal

Isochromanone Ajudazols A and B in Chondromyces crocatus Cm c5: Biosynthetic Machinery and Cytochrome P450 Modifications









A chemical proteomic strategy has been applied directly to bacterial proteomes, and  $\beta$ -lactones have been identified as important natural product derivatives with a high affinity to various enzyme classes (see picture). This approach may serve as a potent tool for the identification of novel antibacterial targets, the study of their function, and the definition of novel lead structures for the design of enzyme inhibitors.

#### Medicinal Chemistry

T. Böttcher, S. A. Sieber\* \_\_\_ 4600 - 4603

 $\beta$ -Lactones as Privileged Structures for the Active-Site Labeling of Versatile Bacterial **Enzyme Classes** 



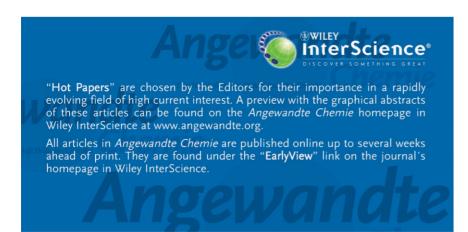


Supporting information is available on www.angewandte.org (see article for access details).



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

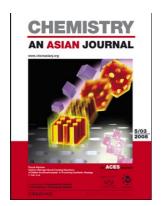
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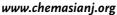


# Spotlights Angewandte's Sister Journals \_\_\_\_\_ Keywords \_\_\_\_\_

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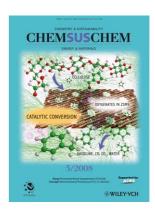
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# Corrigendum

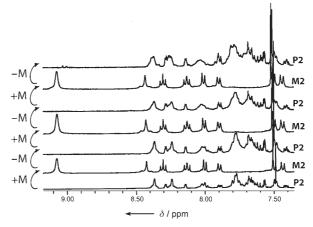
Reversible Switching between Macrocyclic and Polymeric States by Morphological Control in a Constitutional Dynamic System

S. Ulrich, J.-M. Lehn\* \_\_\_\_\_ 2240-2243

Angew. Chem. Int. Ed. 2008, 47

DOI 10.1002/anie.200704946

In Figure 5 of this Communication, the arrows were incorrectly labeled. The correct version is shown below.



**Figure 5.** <sup>1</sup>H NMR spectra (400 MHz) showing the reversible switching process between the metallomacrocycle **M2** and polymer **P2** in  $CDCl_3/CD_3CN$  (6:4) at 50 mm. +M refers to the addition of 1 equiv of  $Pb(OTf)_2$  and -M refers to the addition of 1 equiv of [2.2.2]cryptand to remove the metal cation from the macrocyclic complex.