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:*

Books

Correspondence

Silver Acetylene Complexes (1)

In a recent publication, Krossing, Scherer, and co-workers reported interesting experimental results for homoleptic Ag^I acetylene complexes. In this Correspondence the interpretation of the X-ray analysis and the claim of "pseudo-gas-phase conditions" in the solid state are questioned.

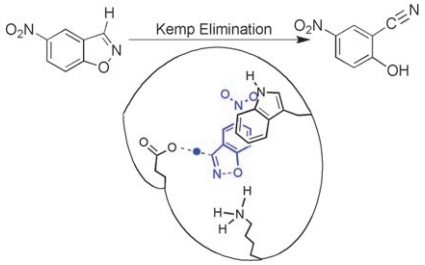
Silver Acetylene Complexes (2)

The comments of Krapp and Frenking are acknowledged, however, it is proposed that a detailed description of the nature of the metal–ligand bonding in the Ag^I acetylene complexes has to consider orbital interactions, in contrast to the electrostatic picture drawn by Krapp and Frenking.

Highlights

Directed Evolution

Intelligent design: The combination of computational design and directed evolution has allowed the creation and optimization of an artificial enzyme starting from a catalytically inactive protein scaffold. In this approach, glutamate, tryptophane, and lysine residues were introduced into a TIM barrel fold to yield an artificial enzyme for the Kemp elimination that was fine-tuned by directed evolution ($k_{cat}/K_m = 2590\ M^{-1}s^{-1}$, see picture).



Contents

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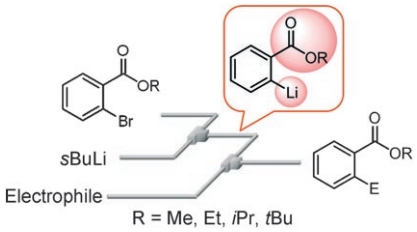
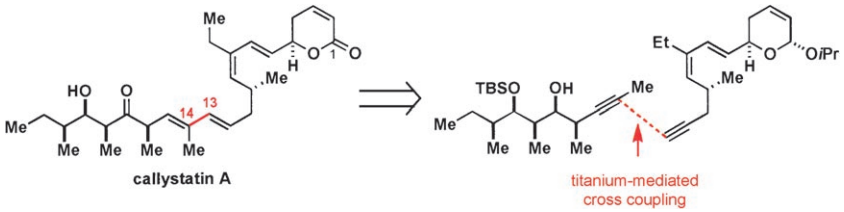
Go with the flow: An effective method for the generation and reaction of aryllithium compounds bearing an alkoxycarbonyl group is developed using microflow systems with very short residence times together with fast mixing and efficient temperature control. A wide range of alkoxycarbonyl groups including ethoxycarbonyl and methoxycarbonyl groups are tolerant of the microflow conditions.

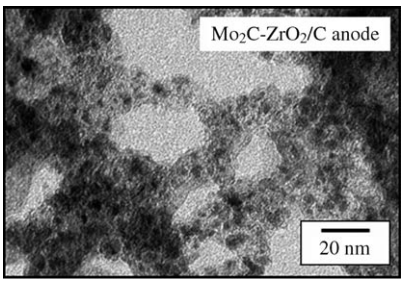


Microreactors



Using a modular approach: A concise synthesis of callystatin A has been developed. The modular pathway provides access to the highly unsaturated skeleton of the leptomycin natural products by using a complex titanium-mediated reductive alkyne–alkyne cross-coupling reaction as the key transformation (see scheme; TBS = *tert*-butyldimethylsilyl).

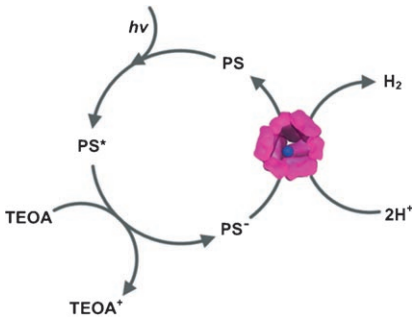
Natural Product Synthesis



Low temperature, high voltage! Direct oxidation of hydrocarbon fuels, including methane, ethane, propane, and butane, occurs over Pt-free anodes in a proton-conducting fuel cell in the temperature range 100–300 °C. A Mo_2C–ZrO_2/C anode (30 mg Mo_2C–ZrO_2 per cm^2) yields power densities equal to those obtained from Pt/C anodes (1–7 mg Pt per cm^2) and generates higher open-circuit voltages than the Pt/C anodes.

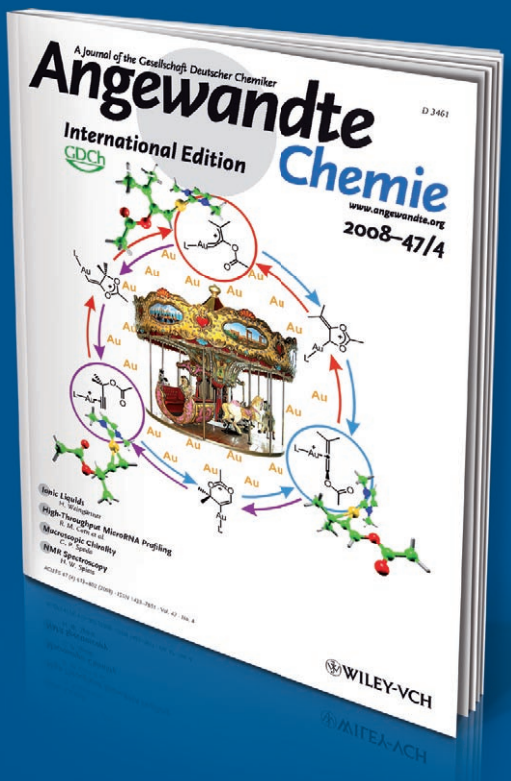
Fuel Cells

Matter of size: Platinum nanocluster formation inside protein cages (LiDps protein) was monitored by noncovalent mass spectrometry. The Pt clusters catalyze hydrogen formation in presence of an iridium photosensitizer (PS; see scheme, TEOA = triethanolamine), and their catalytic activity depends on the cluster size.



Biomimetic Synthesis

Incredibly swift



...!

Manuscripts submitted to *Angewandte Chemie* can be published in a matter of days, and that's including meticulous peer review, careful copy-editing, and author proofing. **The peer-review process requires an average of just 13 days, and 30% of all Communications are brought to readers within two months after submission of the original manuscript.** The articles are not only published rapidly, they are also swiftly assimilated within the scientific community, as reflected by the extremely high Immediacy Index of *Angewandte Chemie* (2007: 2.271).

GDCh
Gesellschaft Deutscher Chemiker

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

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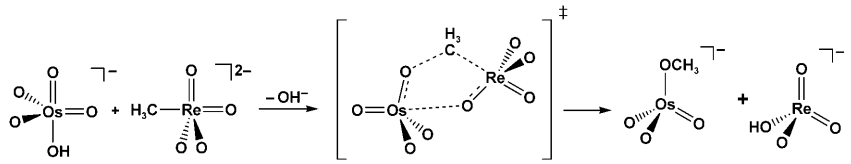
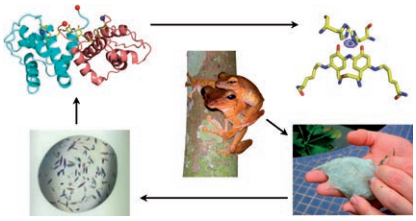


An easy transition: Facile generation of methanol is achieved by hydroxide-promoted transfer of a nucleophilic methyl group from methyltrioxorhenium to osmium tetroxide in basic aqueous medium via a cyclic transition state. ^{1}H NMR spectroscopy and density functional calculations are used to investigate reaction pathways.

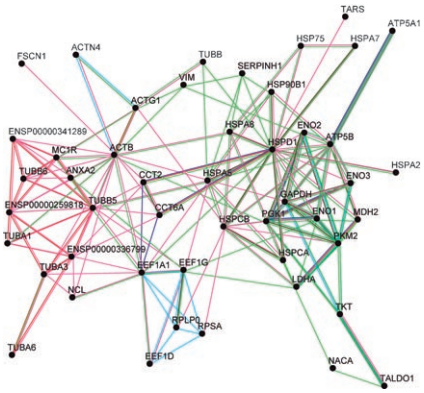
Hydroxylation

A smurfin' good structure: The 1.16 Å resolution crystal structure of ranasmurfin, a blue protein extracted from the foam nests of the Malaysian tree frog *Polypedates leucomystax*, reveals unusual post-translational chemical modifications. The chromophore involves an extended Zn-coordinated four-residue (Lys-Tyr-Tyr-Lys) inter-subunit cross-link of a kind not previously reported.

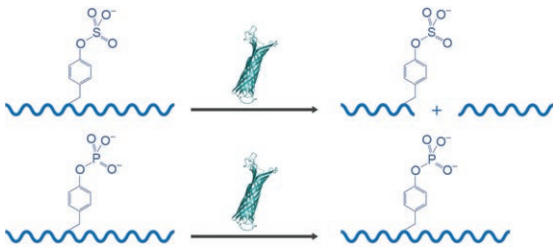


Blue Protein

Spying on SPIONs: Superparamagnetic iron oxide nanoparticles (SPIONs) bearing a mitochondrial targeting peptide (MTP), a cyclic RGD peptide for internalization (cRGD), and a fluorophore for tracking can be targeted to mitochondria. After magnetic isolation from the cells, 48 proteins are identified by mass spectrometry to be interacting with the MTP-cRGD-SPIONs in a network that consists of 308 interactions (see picture).



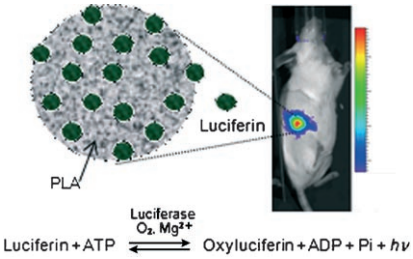
Protein Interactions



Picky eater: The bacterial protease OmpT has been engineered to cleave after sulfotyrosine residues in peptide substrates but not after phosphotyrosine (see scheme). A selection/counterselection screen was used to identify OmpT variants with the desired specificity and high levels of overall catalytic activity.

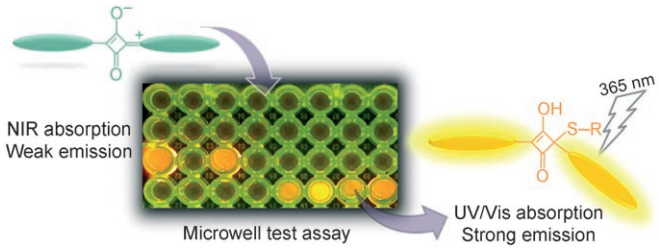
Protein Engineering

Contents



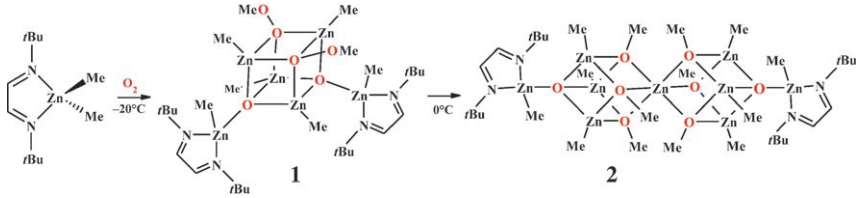
Please release me: Supercritical carbon dioxide was used as an antisolvent for the formation of nanoparticles that contain luciferin, a bioactive therapeutic, dispersed in poly(lactic acid) (PLA), a biodegradable polymer. These nanoparticles undergo slow and sustained drug release, which can be monitored by bioluminescence both in vitro and in vivo (see picture; ATP = adenosine triphosphate; ADP = adenosine diphosphate; Pi = inorganic phosphate).

Drug Delivery



Hunt for thiols: A nucleophilic thiol attack on a weakly fluorescent near-infrared (NIR) squaraine dye results in a conjugation break to form an adduct that absorbs in the UV/Vis region and is highly fluorescent. This fluorophore allows the selective detection of thiols either by colorimetry or fluorescence (see picture). The probe is suitable for the detection and estimation of the total aminothiol content in human blood plasma.

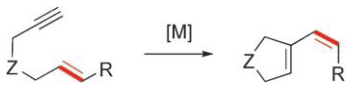
Molecular Probes



O what a reaction: The oxygenation of Me_2Zn-*t*Bu-DAB (*t*Bu-DAB = 1,4-di-*tert*-butyl-1,4-diazabutadiene) affords the unprecedented oxo(methylperoxide) cubane **1**, the corresponding double cubic oxo(methoxide) **2**, and the C–C coupled dinuclear methoxide [$(MeZn)_2$(*t*Bu-DAB-DAB(H)-*t*Bu)(μ-OMe)], the formation of which involves initial ZnO–OMe bond homolysis.

Radical Reactions

A skeleton in the closet: The unprecedented title rearrangement of 1,6-enynes has been observed with gold and platinum catalysts (see scheme, [M] = metal catalyst, Z = $C(CO_2Me)_2$, R = electron-donating group). This reaction is proposed to proceed through an open carbocationic species.



Cycloisomerization Reactions

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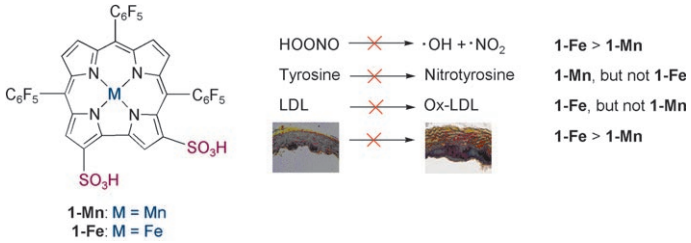
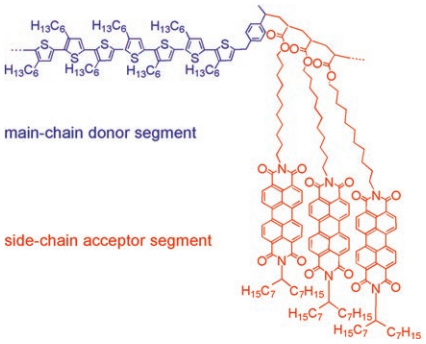
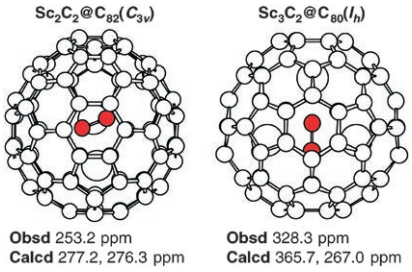


Antioxidants that work! The iron corrole **1-Fe** (see picture) is a potent catalyst for decomposition of reactive oxygen and nitrogen species that binds selectively to lipoproteins. The complex also affects cholesterol levels and its cellular efflux. **1-Fe** is more effective than natural antioxidants in reducing atherosclerosis development in mice. LDL = low-density lipoprotein.

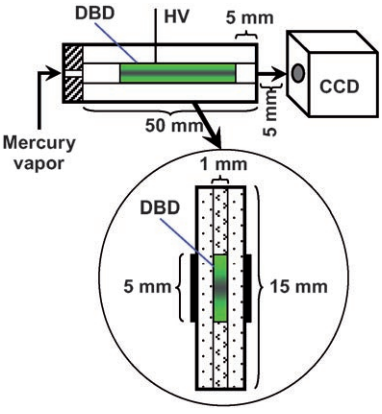
Efficient combination of two polymerization reactions allowed various complex issues in photovoltaic devices, such as light absorption, the presence of a donor–acceptor heterojunction, photoluminescence quenching, crystallinity, and microphase separation, to all be addressed in a single block copolymer (see picture).



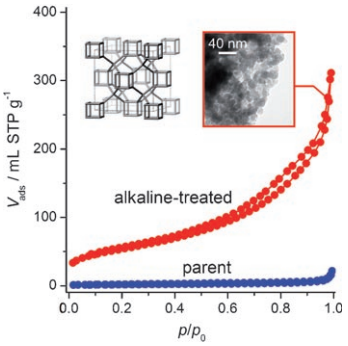


Seeing the filling in fullerenes: The ^{13}C NMR chemical shifts of the C_2 units in $Sc_2C_2@C_{82}(C_{3v})$, $Sc_2C_2@C_{84}(D_{2d})$, $[Sc_3C_2@C_{80}(I_h)]^-$ (see picture), adamantylidene adduct of $Sc_3C_2@C_{80}(I_h)$ were observed for the first time and agree well with the calculated values. The ^{13}C NMR chemical shifts of all cage carbon atoms in these fullerenes were assigned by 2D INADEQUATE NMR measurements.

Honey, I shrunk the spectrometer: The use of atmospheric-pressure dielectric-barrier discharge (DBD) as a radiation source for atomic optical emission spectrometry (OES) allowed the construction of a miniaturized DBD–OES system. A microsequential injection configuration (the picture shows the DBD unit and its cross-sectional configuration, HV = discharge power) provides favorable analytical performance for the system, as demonstrated for the determination of mercury.

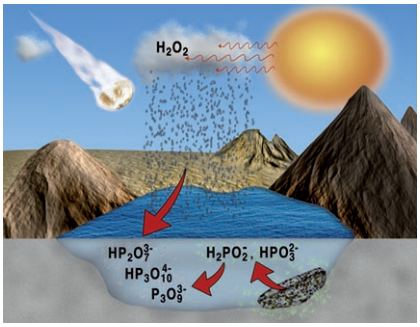


Clathrasils go functional: Nanosized octadecasil crystals with tunable size and variable Si/Al ratio have been synthesized by controlled desilication of the parent clathrasil in alkaline medium. Extremely small (10–25 nm) nanocrystals with high external surface area (200 $m^2 g^{-1}$) and preserved crystallinity were attained (see picture). This result widens the scope of this class of materials, opening room for catalytic applications.

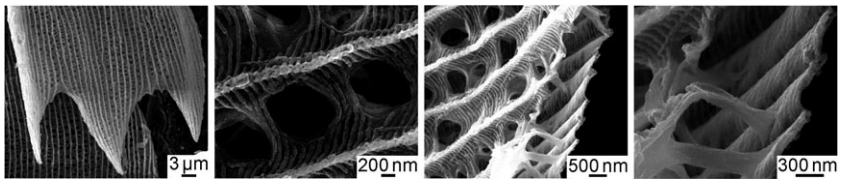


Clathrates

Bringing phosphorus to life: The prebiotic origin of key biomolecules such as RNA and ATP is contingent on a source of condensed phosphates, such as pyrophosphate and triphosphate. Condensed phosphates can be produced at high yields from the oxidation of H-phosphonate or H-phosphinate. Reactive phosphates were likely abundant on the early earth's surface, setting the stage for prebiotic chemistry that led to the evolution of life.

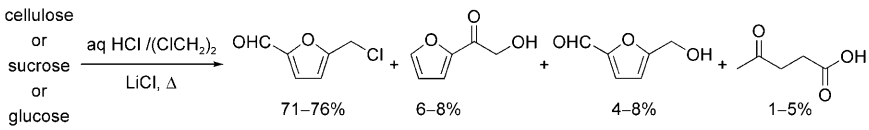


Prebiotic Chemistry



Rutile replicas of butterfly scales: Rutile titania-based structures, retaining the morphology of wing scales of a *Morpho* butterfly (see pictures), are synthesized using an automated, surface sol–gel process. By doping a titanium alkoxide precursor solution with a tin alkoxide, rutile structures were formed at 450 °C. This method may be used to apply rutile coatings on other organic templates for biomedical, filtration, or optical applications.

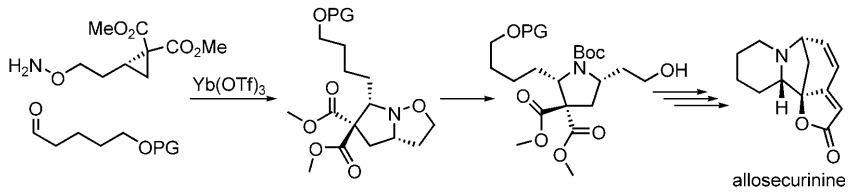
3D Nanostructures



Fueling up with furans: Cellulose can be converted into furanic biofuels in unprecedented yields using an inexpensive, simple process involving concurrent hydrolysis, dehydration, and chlorine substitution reactions coupled with continuous extraction into an organic phase (see scheme). Furanic ethers, such as those that can be derived from the products above, are known diesel additives.

Biofuels

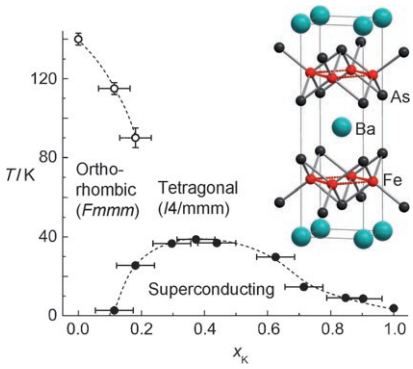
Contents



Safe and secure: An efficient methodology which provides access to homochiral 2,5-*cis* pyrrolidines in excellent yields starting from chiral alkoxyamine cyclopropanes was used in the total synthesis of (−)-allosecurinine (see scheme). The synthesis proceeds with enantiomeric purity in 15 steps with an overall yield of 5%. OTf: trifluoromethanesulfonate, Boc: *tert*-butoxycarbonyl, PG: protecting group.

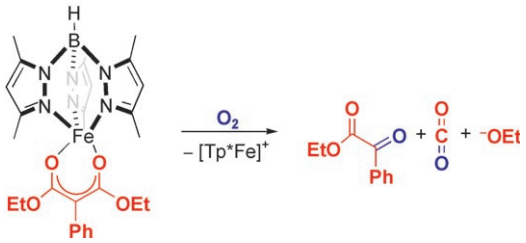
Natural Products

Doping improves performance: Iron arsenides $(Ba_{1-x}K_x)Fe_2As_2$ with the $ThCr_2Si_2$-type structure exhibit superconductivity at 3–38 K depending on the potassium doping level. Superconductivity occurs before the structural distortion of the parent compound $BaFe_2As_2$ ($x = 0$) is completely suppressed by doping (see phase diagram; ● critical temperature, ○ phase-transition temperature). Doping decreases the bond angles in the iron arsenide layers, suggesting a strong coupling of structural and electronic degrees of freedom.



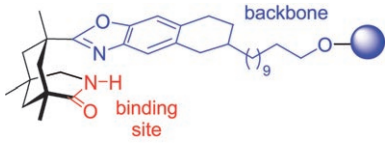
Superconductivity

Position available: A pentacoordinate iron(II) complex that binds and activates dioxygen shows dioxygenase activity and cleaves diethyl phenylmalonate, in analogy to acetylacetone dioxygenase (see scheme). The mechanism for the model compound allows interesting hypotheses to be made about the enzyme function.



Biomimetic O_2 Activation

A happy couple: A chiral complexing agent was modified with an ω-hydroxyalkyl linker and immobilized on a Wang resin and on a methoxypolyethylene glycol (MPEG 2000). The immobilized templates **1** served in an enantioselective photochemical reaction with impressive selectivity (e.r. 92:8 to 96:4) and stability over several cycles.



1

Photochemical Synthesis

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).

Service

Corrigendum

N-Terminal Protein Modification through a Biomimetic Transamination Reaction

J. M. Gilmore, R. A. Scheck, A. P. Esser-Kahn, N. S. Joshi, M. B. Francis* — **5307–5311**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200600368

In Figure 1 b of this Communication, the signal corresponding to unmodified myoglobin is incorrectly labeled with *m*/*z* 16692. The Figure with the correct value of *m*/*z* 16962 is given here.

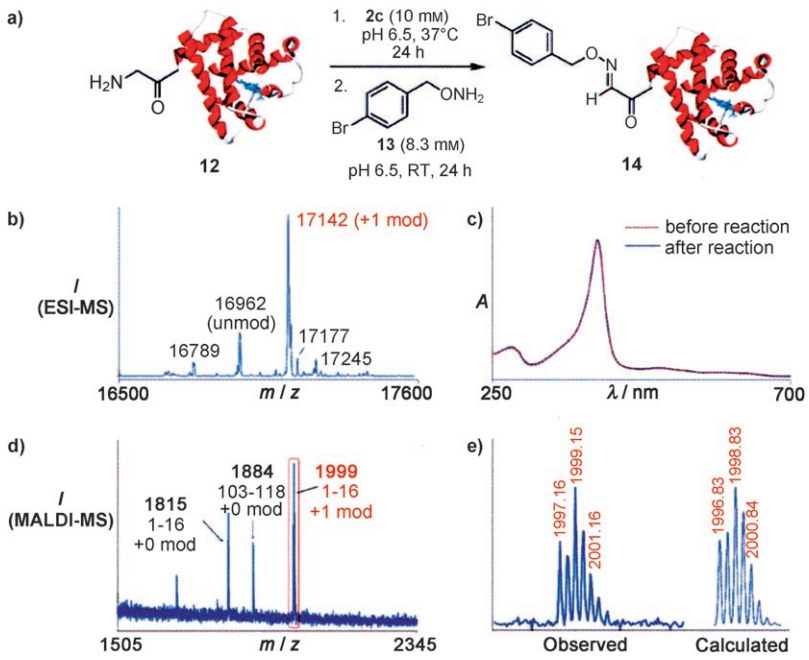


Figure 1. Site-selective protein modification with PLP. a) Myoglobin was treated with **2c** at 37 °C for 24 h. After removal of small molecules by gel filtration, oxime **14** was formed after reaction with **13**. b) ESI-LCMS studies indicated that only one modification had occurred. c) UV/Vis spectra of **12** subjected to the reaction conditions in the absence (dotted red) and presence (dashed blue) of **2c**. d) Product **14** was digested with trypsin, and the resulting fragments were analyzed by MALDI-TOF MS. The only modified fragment observed contained the N-terminal residue. e) Predicted (left) and observed (right) isotope patterns for the modified myoglobin peptide fragment shown in (d). All MS values agree with those predicted within 0.01 %.