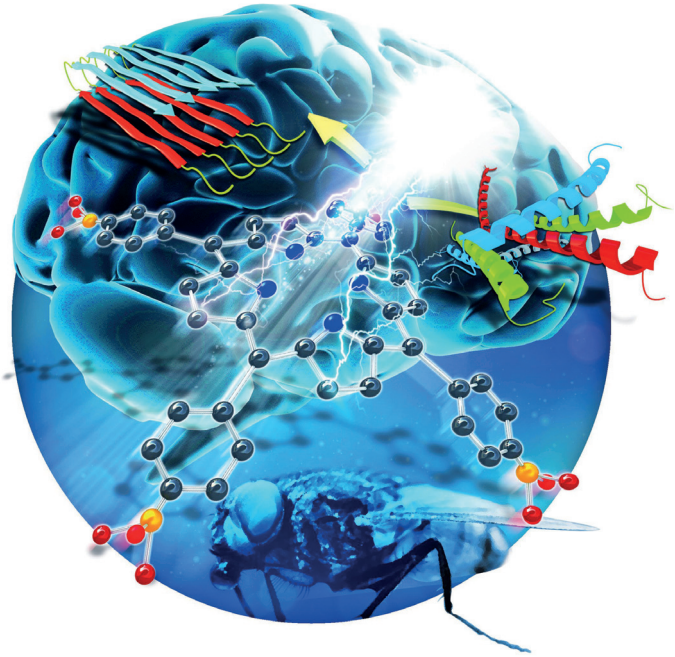
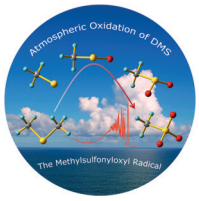
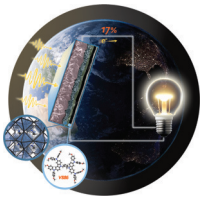


... inhibit β-amyloid aggregation and rescue postsynaptlc toxicity and behavior defects in the *Drosophila* Alzheimer's disease model under blue light. In their Communication on page 11472 ff., C. B. Park, K. Yu et al. present a chemical strategy for photodynamic suppression of β-amyloid aggregation using photosensitizing molecules.

Atmospheric Chemistry

In their Communication on page 11404 ff., H. Beckers et al. report the isolation of methylsulfonyloxyl radicals, key intermediates in the atmospheric oxidation of dimethyl sulfide.



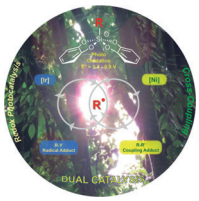


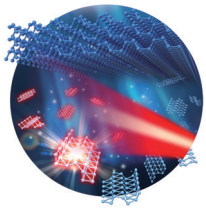
Solar Cells

M. K. Nazeeruddin et al. describe in their Communication on page 11409 ff. the synthesis of methoxydiphenylamine-substituted carbazol, a hole-transport material for perovskite solar cells.

Hypervalent Compounds

The photocatalytic oxidation of silicates to give alkyl radicals for homolytic transformations is described in the Communication by L. Fensterbank et al. on page 11414 ff.



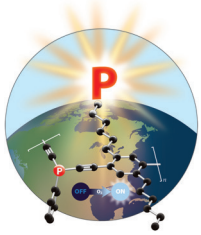


Photothermal Agents

The controllable synthesis of black phosphorus quantum dots as ultrasmall photothermal agents is described by X.-F. Yu, et al. in their Communication on page 11526 ff.

Hybrid Polymers

In their Communication on page 11438 ff., D. P. Gates and B. W. Rawe report a P-containing polymer that exhibits strong blue fluorescence turn-on upon exposure to molecular oxygen and UV light.



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Editorial

"... Why is chemistry overlooked when talking about light? Is the photon a physical particle per se? Are all important light-induced processes biological? Maybe the role of light for chemistry and the role of chemistry for light may be far less important than a few eccentric scientists would like to believe. From the perspective of a synthetically oriented photochemist, however, the facts are different ..."
Read more in the Editorial by Thorsten Bach.

Service

Author Profile

"My favorite author (fiction) is Roald Dahl and his short stories.
If I were not a scientist, I would be a historian. ..."
This and more about Christopher Barner-Kowollik can be found on page 11316.

News

M. El-Sayed

S. Sánchez Ordóñez

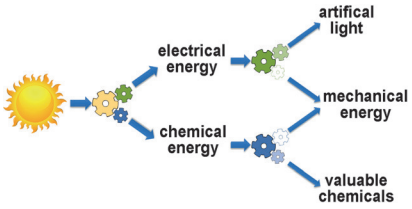
R. K. Thauer

E. N. Jacobsen

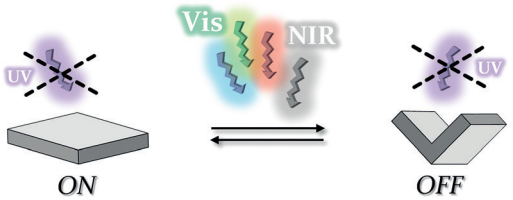
S. Grimme

Essays

See the light of day: Light is the fastest way of transferring energy and information through space, and in chemistry it can perform the dual role of reactant and product. Sunlight, a really unique reactant, represents our ultimate energy source. Chemists are engaged in designing systems for the conversion of light into electrical or chemical energy and vice versa to create a more sustainable way of life.

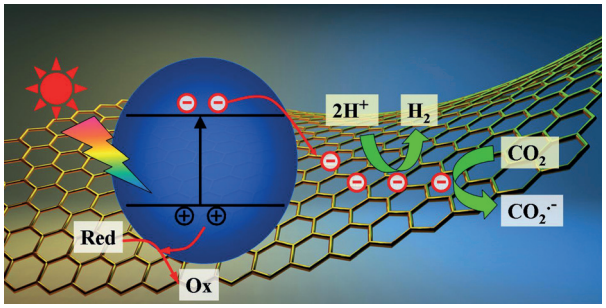


Minireviews



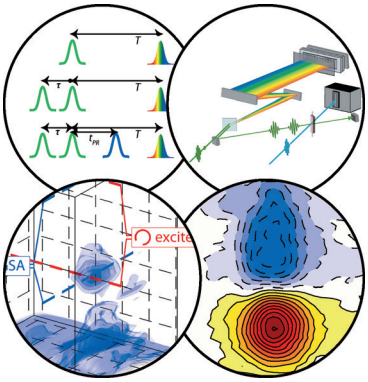
Let there be light: This Minireview outlines different conceptual strategies for the design of photochromic compounds that can be toggled between their two switching states by employing only low-energy visible (or near-infrared) light. All-visible-light photoswitches are promising candidates for future biomedical and material applications.

Reviews



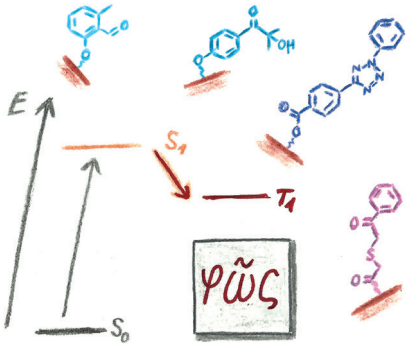
There's always the sun: Graphene-based photocatalysts for solar-fuel production are of significant interest in solving the global energy problem. The recent advances in the fabrication and application of graphene-based photocatalysts, including photocatalytic reduction of CO_2 to hydrocarbon fuels and photocatalytic splitting of water to H_2 are explored.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



Two dimensions provide more insight than one: Coherent electronic multidimensional spectroscopy in different variations allows the separation of photochemical reaction channels. This is demonstrated exemplarily for a molecular switch capable of light-induced ring-opening and ring-closure reactions, *cis–trans* isomerization, vibrational wavepacket dynamics, radical cation formation, and population relaxation.

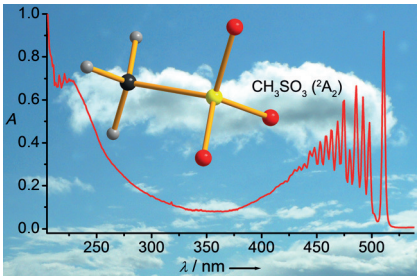
Multidimensional Spectroscopy



"There are only patterns": A range of efficient photochemical platforms for the spatially resolved functionalization of surfaces is described in this Review together with their specific advantages relative to alternative methods. There is already a powerful range of methods available, but orthogonal ligation processes driven by visible light remain largely elusive.

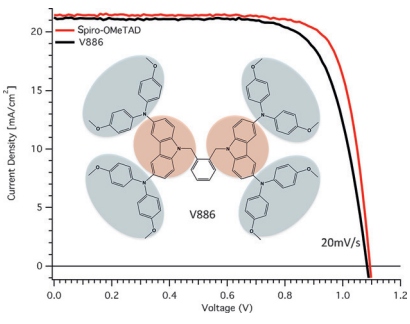
Surface Functionalization

Communications



Up in the air: Low-pressure flash pyrolysis of $CH_3SO_2OOSO_2CH_3$ has been used to generate the methylsulfonyloxyl radical (CH_3SO_3), one of the key intermediates in the atmospheric oxidation of dimethyl sulfide, which was subsequently isolated in solid noble-gas matrices. The radical has been characterized by UV/Vis and IR spectroscopy and its photoinduced ($\lambda \geq 360$ nm) tautomerization to CH_2SO_3H was observed.

Key Intermediates

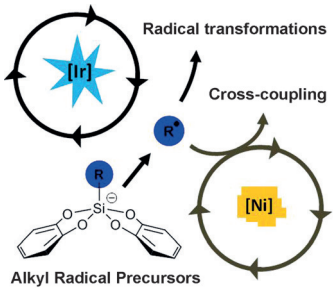


Quick and easy: The readily synthesized methoxydiphenylamine-substituted carbazole (V886), a hole-transporting material, has been used in perovskite solar cells with a power conversion efficiency of 17%. This is the second highest conversion efficiency after that of solar cells with the hole transporter Spiro-OMeTAD.

Perovskite Solar Cells

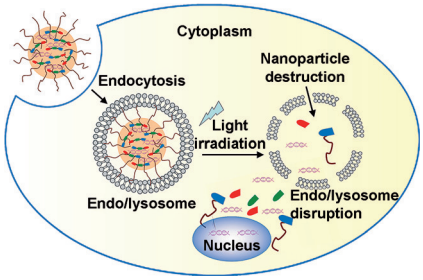
Hypervalent Compounds

Silicates can be used as latent alkyl radical precursors. Upon visible-light photocatalytic oxidation of easily accessed and bench-stable bis-catecholato silicates, a series of functionalized alkyl radicals, including highly reactive primary ones have been engaged in homolytic transformations. This oxidative photocatalyzed process can be efficiently merged with nickel catalysis for C–C coupling.



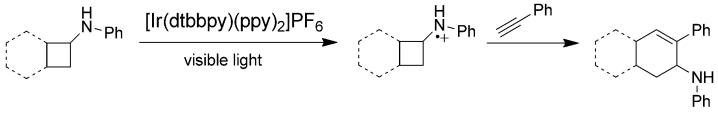
Frontispiece

Gene Vectors



Special delivery! A photoactive polymeric gene delivery vector can concurrently escape from the endo/lysosome and unpack nucleic acids in cytosol in a single light irradiation process. The polymer, which comprises a fluorogen with aggregation-enhanced-emission characteristics and a linker that can be cleaved by reactive oxygen species, forms nanoparticles that bind DNA and are endocytosed by cells.

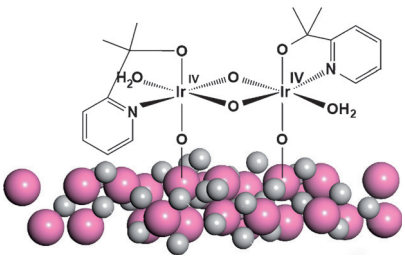
Photocatalysis



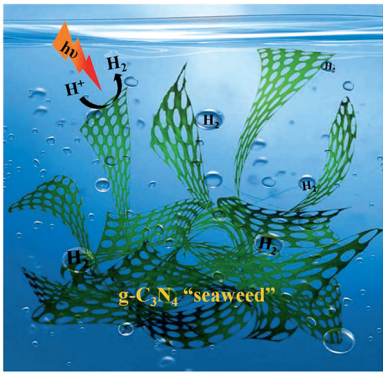
Cyclohexene derivatives are obtained by a mild procedure using visible-light photocatalysis. Monocyclic and bicyclic cyclobutylanilines successfully undergo intermolecular [4+2] annulation with terminal and internal alkynes to generate a variety of amine-substituted cyclohexenes including new hydrindan and decalin derivatives with good to excellent diastereoselectivity. dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, ppy = 2-phenylpyridine.

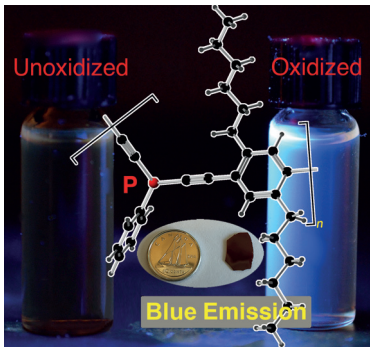
Photoelectrochemistry

Stable solar water splitting in acidic solutions is made possible by decorating hematite with iridium-based water oxidation catalysts. A cathodic shift of up to 250 mV is observed by the heterogenized catalysts, which are as thin as a monolayer (see picture). More stable operation is achieved with the IrO_x catalysts upon photoelectrodeposition.



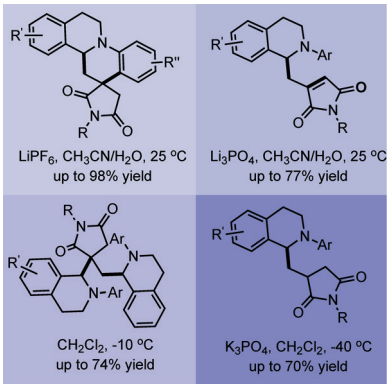
Weeding out hydrogen: A straightforward template-free freeze-drying method affords a graphitic-C_3N_4 "seaweed" architecture of one-dimensional mesoporous fibers. This seaweed architecture has a highly efficient photocatalytic activity for hydrogen evolution from water under visible-light irradiation that is better than most reported nanostructured g-C_3N_4 catalysts.



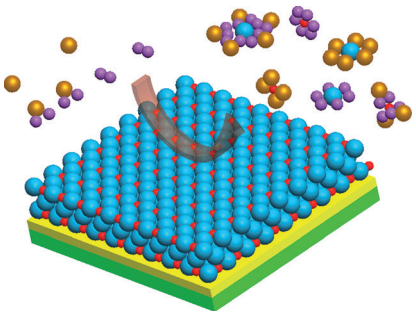


P-polymer brings light: A new phosphorus-containing macromolecule, PPYP, has been synthesized that features phosphorus atoms incorporated between phenylene alkynyl groups. PPYP selectively exhibits blue fluorescence (see picture) when the phosphorus center is oxidized and, therefore, is of potential interest for sensor applications.

Radical control: A radical mechanism for *N*-tetrahydroisoquinolines (THIQ) in the presence of oxygen was successfully accomplished by employing a dicyanopyrazine-derived chromophore (DPZ) as a photoredox catalyst. The substrates can undergo either addition-cyclization, addition-elimination, addition-coupling, or addition-protonation by judiciously regulating the reaction conditions. Four types of N-heterocycles are generated in moderate to excellent yields.

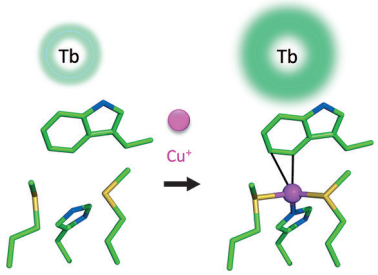


Less dissolution: Pt$M_{0.05}$ (M = Ni, Co, Fe, Pd, Mo, Cu, Cr, and Au) alloys were synthesized by simple electrodeposition and employed as counter-electrode (CE) electrocatalysts for liquid-junction dye-sensitized solar cells (DSSCs). Alloying of platinum with transition metals for forming competitive reactions is believed to be a promising strategy for increasing the dissolution resistance of CE electrocatalysts.



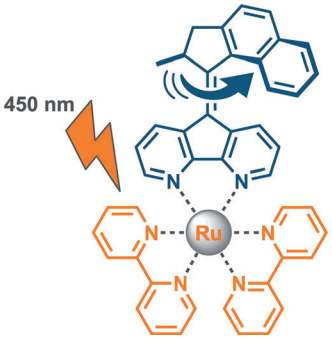
Cation–π Interactions

New strategy: A selective probe for Cu^{I} among physiological cations is described, which harnesses a 3D arrangement of four amino acids as the binding site, inspired by the metallo-chaperone CusF. Luminescence signal transduction results from modulation of the antenna effect through a cation–π interaction that increases intersystem crossing and subsequent lanthanide sensitization.



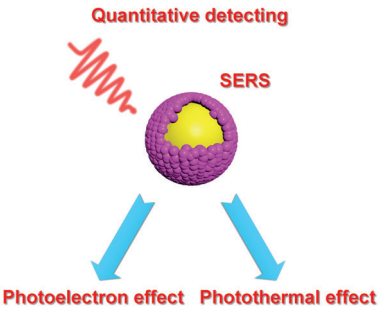
Molecular Motors

A positive spin: A molecular motor containing a 4,5-diazafluorenyl ligation motif can be coordinated to ruthenium(II) ions (see figure). After complexation, the photoisomerization process can be driven by visible instead of UV light. Unexpectedly, a large enhancement of the speed of rotation was observed, which can be ascribed to contraction of the diazafluorenyl unit upon metal coordination.

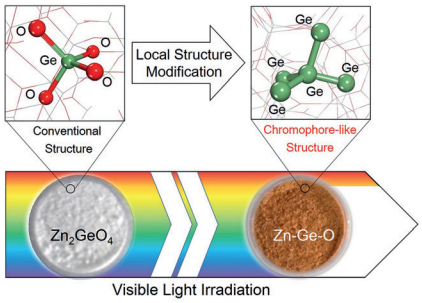


Photochemistry

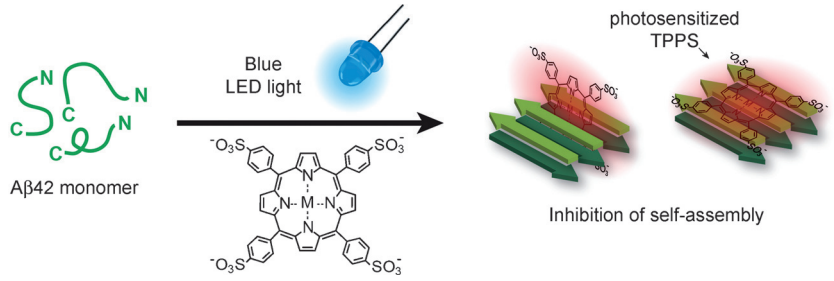
The contribution ratio of the SPR-induced photothermal and photoelectrocatalytic effects during catalytic reactions can be detected. The photothermal effect can be measured by surface-enhanced Raman scattering (SERS), and the photoelectrocatalytic process can be proved by SERS using *p*-aminothiophenol as the probe molecule.



Semiconductor Chromophores



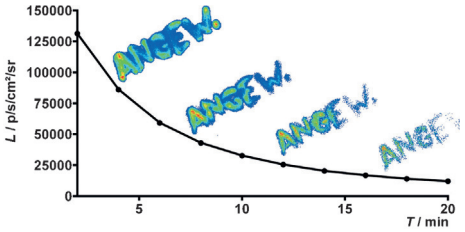
Ge up: Unexpectedly a Zn-Ge-O semiconductor responds to visible light. It is shown that it contains a built-in chromophore-like structure. By a combination of systematic characterizations and theoretical calculations, the origin of the visible-light response can be attributed to the unusual presence of metallic Ge—Ge bonds which act in a similar way to organic chromophores.



β-Amyloids

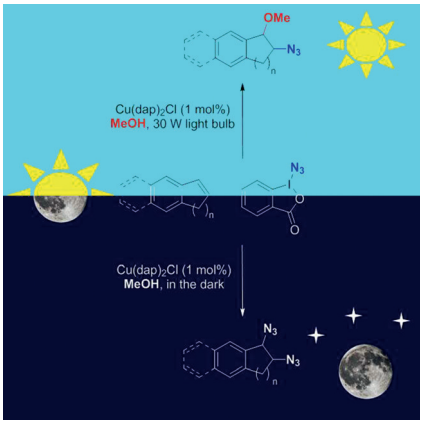
Front Cover

Photoinduced inhibition of β-amyloid (Aβ) aggregation was achieved with *meso*-tetra(4-sulfonatophenyl) porphyrin (TPPS, with M = $2H^+$, Zn^{2+}, Cu^{2+}, Mn^{2+}) under blue LED illumination. The light-driven efficacy of TPPS is attributed to the strong binding affinity of TPPS to Aβ and photooxidation of Aβ. Aβ toxicity was relieved in a photoexcited-TPPS-treated *Drosophila* Alzheimer's disease model.



Persistent Luminescence

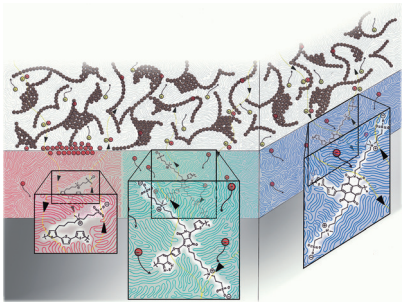
Long lifetime and nontoxic: Nanoparticles made of the conjugated polymer MEH-PPV and a near-infrared (NIR) dye can generate NIR-persistent luminescence emission with a lifetime of nearly one hour at room temperature. This new optical property was evaluated for optical imaging applications in living mice.



Photochemistry

Out of the light, into the dark: Copper photoredox catalysis combined with a hypervalent iodine azide reagent enables methoxy azidation of alkenes. In contrast, in the absence of light, the same copper catalyst affords double azidation to give vicinal 1,2-diazides. The double functionalization proceeds under mild reaction conditions, with a switch between light and dark controlling the degree of azidation. dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline.

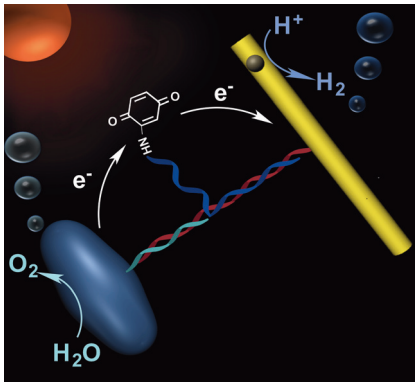
Organic electronics: Three conjugated polymer zwitterions of variable bandgap were synthesized and incorporated as cathode modification layers in bulk heterojunction solar cells, boosting the power conversion efficiency (PCE) to over 10%. Structure–property relationships identified key optical and electronic characteristics that lead to the observed high efficiencies.



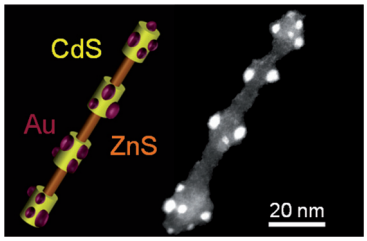
Solar Cells

Photocatalysis

TiO_2 and CdS nanocrystals were organized into a Z-scheme photosynthesis system by using DNA as a structure-directing agent. Increased H_2 production from water splitting was observed compared to either the photocatalyst alone or dispersed mixtures of the two. The inclusion of the electron mediator benzoquinone equidistant between the TiO_2 and CdS through DNA assembly further increased H_2 production.

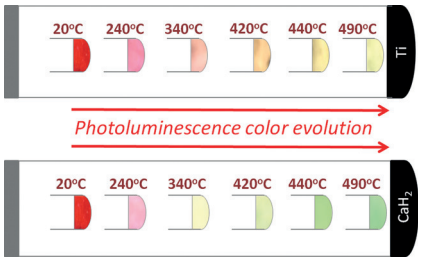


Nanorods



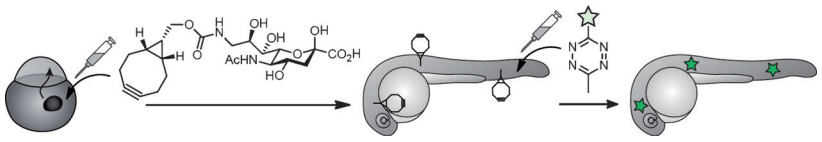
Three in one: A unique 1D ternary heteronanorod (ZnS) with segmented node sheaths (CdS) decorated by metal nanoparticles (Au) is constructed by a sequential chemical-transformation strategy. The arrangement enables steered charge flow for electron–hole separation and hence efficient photocatalysis.

Photoluminescence



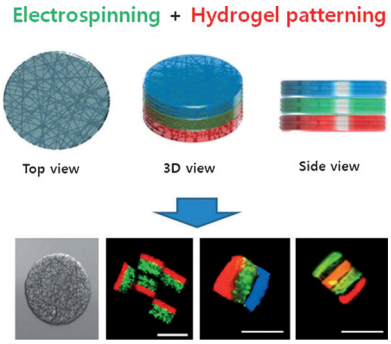
Color palette: The controlled reduction of dopants at different temperatures was carried out to study the photoluminescent properties of single-phase oxide materials. The change of the oxidation state of dopants leads to fine tuning of the emission color of the materials. This approach was illustrated with the progressive reduction of the red phosphor $SrAl_2O_4:Eu^{3+}$ to green phosphor $SrAl_2O_4:Eu^{2+}$ to target yellow luminescence. (Ti, CaH_2 = oxygen getters.)

Fluorescence Imaging



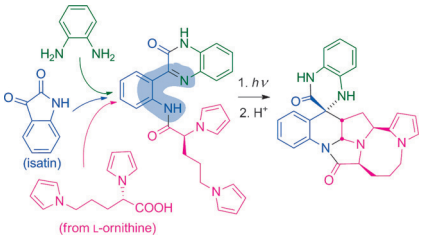
How exSiating! Systemic fluorescence imaging of cell-surface glycans inside a live animal is described for the first time. Metabolic incorporation of a cyclooctyne-functionalized sialic acid into glycans during zebrafish embryogenesis followed by ligation with a fluorogenic tetrazine enables the visualization of sialoglycoconjugates.

Multi-compartmental hydrogel microparticles were fabricated by combining electrospinning and photopatterning processes. Each compartment was made of a fiber matrix with a different composition. The resultant microparticles have a potential for various biomedical applications such as bioassay, drug delivery, and tissue engineering.

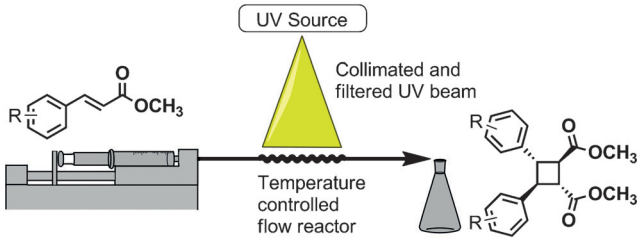


Soft Matter

Rings in three dimensions: Cyclic imines containing an *o*-amido group undergo excited-state intramolecular proton transfer to generate amino azaxylylenes. The amino azaxylylenes undergo intramolecular cycloadditions to tethered unsaturated pendants to yield complex heterocyclic three-dimensional molecular architectures.

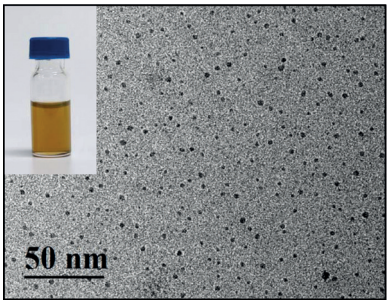


Cycloaddition



Go with the flow: A flow photochemical platform with a novel cone reactor has been used to facilitate significant improvement in the [2+2] photocycloaddition of cinnamate derivatives. A bis-(thiourea) has been identified that significantly increases the conversion and diastereoselectivity with a number of substrates.

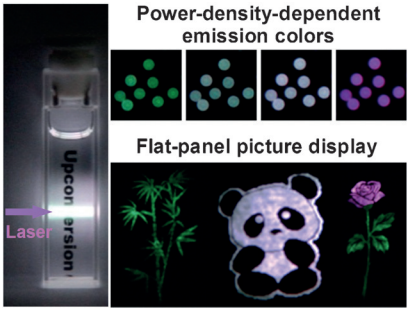
Flow Chemistry



A liquid exfoliation method based on a combination of probe sonication and bath sonication was adopted to synthesize black phosphorus quantum dots (BPQDs). These displayed a high extinction coefficient of 14.8 $Lg^{-1}cm^{-1}$, a photothermal conversion efficiency of 28.4%, and good biocompatibility, and can thus be used as highly effective photothermal agents for cancer therapy.

Photothermal Agents

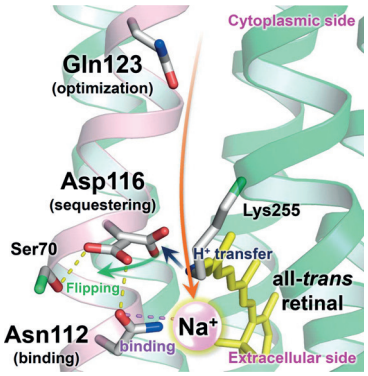
Photochemistry



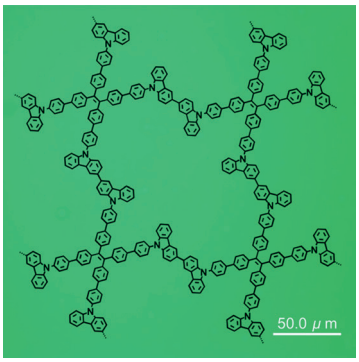
Seeing the light: An upconversion nanostructure comprises several lanthanide ions integrated in a single system. The balance of numerous narrow emission bands covering the full visible spectrum results in white-light emission. The emission colors can be determined by changing the excitation power density (see picture), which manipulates the photon transfer pathways to bring potential applications such as multicolor displays or imaging.

Membrane Proteins

Ion transport: The conserved NDQ (Asn, Asp, Gln) motif in *Krokinobacter* rhodopsin 2 (KR2), a novel light-driven outward Na^+ pump, is found to play a specific role. The D116 residue receives and sequesters protons for Na^+ uptake and the uptake process is kinetically optimized by Q123. The N112 residue participates in Na^+ binding in the O photointermediate. Thus, the NDQ motif works cooperatively for vectorial Na^+ transport.



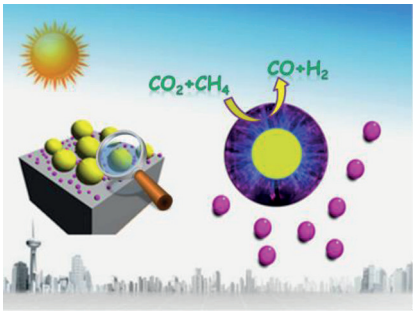
Luminescent Materials

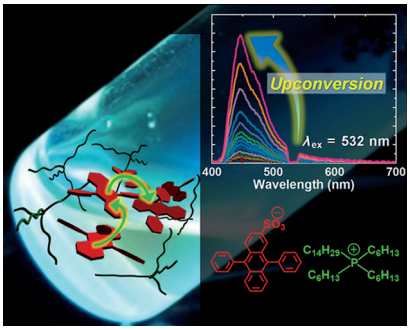


Thin but brilliant: Porous π-networks (see structure) were synthesized from monomers designed by a general strategy to contain a core enabling aggregation-induced emission, twisted linkers, and electropolymerizable peripheral units. The thickness of the resulting highly emissive porous polymer films could be controlled precisely, and films with a thickness below 10 nm were used for the sensitive detection of explosives by electron transfer.

Photocatalysis

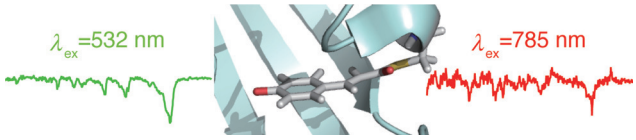
Storing solar energy: Gold enhances the catalytic performance of a Rh/SBA-15 catalyst in the dry reforming process of methane under visible-light irradiation (see picture). The highly energetic electrons excited by local surface plasmon resonances of gold facilitated the polarization and activation of carbon dioxide and methane under thermal conditions.





On a collision course: Fluorescent ionic liquids (ILs) that show triplet–triplet-annihilation-based photon upconversion (TTA-UC) are reported. The presence of nanostructured ionic chromophore networks explains the fast triplet energy migration and consequent efficient TTA-UC emission detected at a low excitation power comparable to solar irradiance.

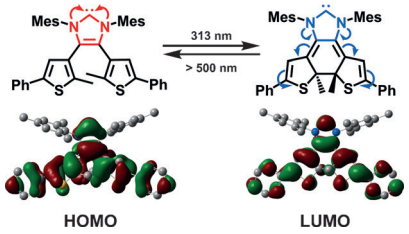
Ionic Liquids



Pick and choose: Photoactive yellow protein was used to measure the effect of changing the excitation wavelength (λ_{ex}) on the Raman optical activity (ROA) spectra of a protein. The data demonstrate that selecting an appropriate excitation wavelength is a key factor for extracting structural information on the protein active site using ROA spectroscopy.

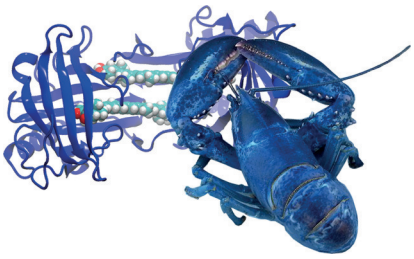
Raman Spectroscopy

With the flip of a switch: Light was used to reversibly switch the electronic structure of an isolable N-heterocyclic carbene (NHC). UV-induced electrocyclic ring closure produced a relatively electrophilic NHC, whereas subsequent exposure to visible light reversed these changes. The distinct electronic states were utilized to achieve at-will capture and release of ammonia.



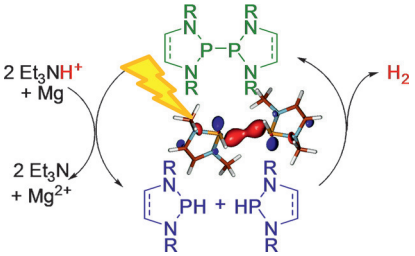
Photoswitches

True blue: The pigment protein β-crustacyanin, which is responsible for the blue color of lobsters, tunes the color of its two bound astaxanthin chromophores through electrostatic polarization and steric planarization.



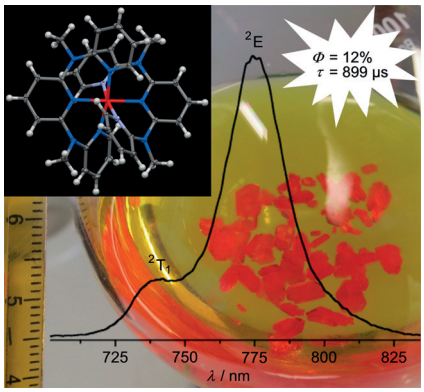
Photobiology

Photocatalysis



Hydrogen cycle: Highly selective photochemical dehydrocoupling converts N-heterocyclic phosphanes to diphosphanes and H_2, and is a key step in a reaction cycle enabling photocatalytic reductive generation of H_2 from Et_3NH^+. Computational studies suggest that the reaction is initiated by the formation of dimeric molecular associates whose electronic excitation yields H_2 and two phosphanyl radicals.

Luminescent Complexes



Strong, long-lived, and sharp NIR phosphorescence (775 nm, $\Phi = 12\%$, $\tau = 899\ \mu s$) is achieved in the soluble chromium(III) complex $[Cr(ddpd)_2]^{3+}$ (ddpd = *N*,*N*′-dimethyl-*N*,*N*′-dipyridin-2-ylpyridine-2,6-diamine) by ligand-field tuning through optimization of the ligand's bite angle and σ-donor strength. $^3O_2$ quenches the emission, allowing for optical oxygen sensing. The highly stable complex is easy to prepare in high yields from inexpensive starting materials.

DOI: 10.1002/anie.201583914

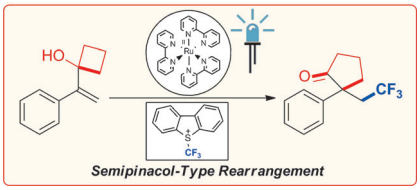
Flashback: 50 Years Ago . . .

A range of reviews showed just how important various spectroscopic techniques had become. H. T. Witt et al. discussed the use of flashlight techniques in the analysis of photosynthetic processes by studying the time variation of the absorption spectra of chloroplasts after excitation. A. Almenningen et al. outlined the theory of electron diffraction for the study of gas-phase molecules, L. Vellutz and M. Legrand discussed progress in optical circular dichroism, and F. Schneider et al. summarized the use of electron paramagnetic resonance in organic chemistry.

The Communications section also contained contributions that featured spectroscopic techniques. T. Kruck and W. Lang reported on the synthesis of $HIr(PF_3)_4$ and on the NMR spectra of $HM(PF_3)_4$, where M = Co, Rh, Ir. Coupling with the ^{31}P and ^{19}F nuclei means that the proton signal should theoretically split into a multiplet containing 65 lines, although there was a degree of overlap of the signals. In another Communication, W. Lüttke and K. Wilhelm described how they used infrared spectroscopy to study methylenetriphenylphosphoranes. They concluded that the bond between the phosphorus and the methylene carbon atom has only a slight double-bond character, which is useful to know for understanding Wittig reaction.

Angewandte Chemie has always published stimulating chemistry, not least the report by F. Korte et al. on the separation of hashish extract and the subsequent isolation and identification of tetrahydrocannabinolcarboxylic acid. At the time, this acid was regarded as the "missing link" in the biosynthetic pathway of the active principles of hashish.

Read more in Issue 10/1965.



Circle of light: A visible-light-mediated photoredox semipinacol-type rearrangement proceeding by 1,2 alkyl migration was developed. The transformation involves a radical–polar mechanism, in which photoinduced trifluoromethylation of a C=C bond is followed by ring expansion of a cationic intermediate. This process constitutes the first report of ionic alkyl migration in photoredox catalysis and proceeds under mild conditions with visible light.

Photocatalysis

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

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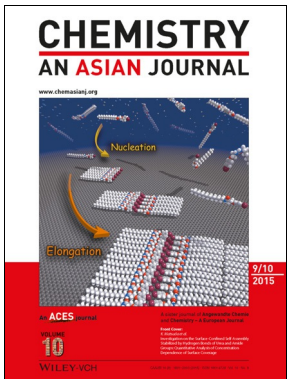

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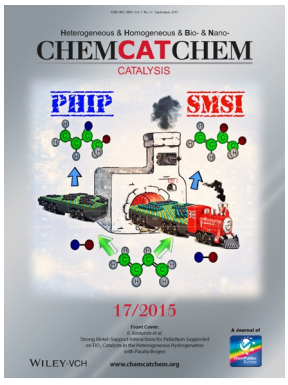

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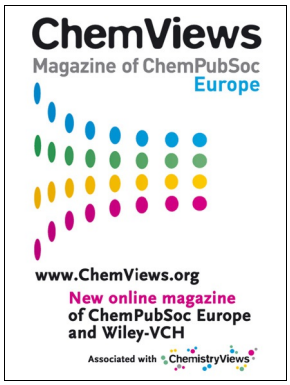

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