Digest Sep 2017
Highly Enantioselective Catalytic Vinylogous Propargylation of Coumarins Yields a Class of Autophagy Inhibitors

Dr. Hao Xu, Dr. Luca Laraia, Laura Schneider, Kathrin Louven, Prof. Dr. Carsten Strohmann, Dr. Andrey P. Antonchick and Prof. Dr. Herbert Waldmann

Angew. Chem. Int. Ed. 2017, 56(37), 11232

Abstract

A highly enantioselective copper-catalyzed vinylogous propargylic substitution has been developed. Aromatic and aliphatic propargylic esters react smoothly with substituted coumarins under mild reaction conditions to give the desired products with excellent yields and enantioselectivities. Subsequent single-step transformations enable the synthesis of a wide range of multifunctional and diverse compounds, and allow the efficient combination of different natural product fragments. Investigation of the obtained compound collection in cell-based assays monitoring changes in phenotype led to the discovery of a novel class of autophagy inhibitors.

Stereospecificity in Intramolecular Photoredox Reactions of Naphthoquinones: Enantioselective Total Synthesis of (−)-Spiroxin C

Dr. Yoshio Ando, Atsuko Hanaki, Ryota Sasaki, Prof. Dr. Ken Ohmori and Prof. Dr. Keisuke Suzuki

Angew. Chem. Int. Ed. 2017, 56(38), 11460

Abstract

Intramolecular photoredox reactions of naphthoquinone derivatives were found to proceed in a stereospecific manner. This method was used as a basis for the enantioselective total synthesis of (−)-spiroxin C.
Joseph Samec Research Group Digest

**Stereoselective Synthesis of Piperidines by Iridium-Catalyzed Cyclocondensation**
Tobias Sandmeier, Simon Krautwald and Prof. Dr. Erick M. Carreira

*Angew. Chem. Int. Ed.* **2017**, 56(38), 11515

**Abstract**

An iridium-catalyzed cyclocondensation of amino alcohols and aldehydes is reported. Intramolecular allylic substitution by an enamine intermediate and subsequent in situ reduction furnishes 3,4-disubstituted piperidines with high enantiospecificity and good diastereoselectivity. The modular approach and the broad functional group tolerance provide access to diverse piperidine derivatives, which were further functionalized to give a versatile set of products.

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**A Quadruple-Action Platinum(IV) Prodrug with Anticancer Activity Against KRAS Mutated Cancer Cell Lines**
Dr. Emanuele Petruzzella, Dr. Jeremy Phillip Braude, Prof. Janice R. Aldrich-Wright, Dr. Valentina Gandin and Prof. Dan Gibson

*Angew. Chem. Int. Ed.* **2017**, 56(38), 11539

**Abstract**

We developed a novel PtIV prodrug that simultaneously releases four different bioactive moieties inside the cancer cell. Its cytotoxicity against monolayer cultures (2D) and spheroid (3D) cancer cells is significantly better than cisplatin. It is 200–450-fold more potent than cisplatin against KRAS mutated pancreatic and colon cancers and is 40-fold more selective towards KRAS mutated cells compared to non-cancerous. This is important since RAS proteins play a role in regulating cell differentiation, proliferation, and survival and KRAS is mutated in 90% of pancreatic adenocarcinomas, 45% of colorectal cancers, and 35% of lung adenocarcinomas. The selectivity index, determined by dividing the IC50 value in non-cancerous cells by that of a cancerous cell line, is two-fold better than cisplatin, attesting to preferential cytotoxicity towards neoplastic cells.
Deaminative Strategy for the Visible-Light-Medi­ated Generation of Alkyl Radicals

Felix J. R. Klauck, Dr. Michael J. James and Prof. Dr. Frank Glorius


Abstract

A deaminative strategy for the visible-light-mediated generation of alkyl radicals from redox-activated primary amine precursors is described. Abundant and inexpensive primary amine feedstocks, including amino acids, were converted in a single step into redox-active pyridinium salts and subsequently into alkyl radicals by reaction with an excited-state photocatalyst. The broad synthetic potential of this protocol was demonstrated by the alkylation of a number of heteroarenes under mild conditions.

Nucleophilic Amination of Methoxy Arenes Promoted by a Sodium Hydride/Iodide Composite

Atsushi Kaga, Hirohito Hayashi, Hiroyuki Hakamata, Miku Oi, Prof. Masanobu Uchiyama, Prof. Ryo Takita and Prof. Shunsuke Chiba


Abstract

A method for the nucleophilic amination of methoxy arenes was established by using sodium hydride (NaH) in the presence of lithium iodide (LiI). This method offers an efficient route to benzannulated nitrogen heterocycles. Mechanistic studies showed that the reaction proceeds through an unusual concerted nucleophilic aromatic substitution.
A Continuous-Flow Process for Palladium-Catalyzed Olefin Cleavage by using Oxygen within the Explosive Regime

Dr. Christopher A. Hone, Anne O’Kearney-McMullan, Dr. Rachel Munday and Prof. Dr. C. Oliver Kappe

ChemCatChem 2017, 9(17), 3298

Abstract

A continuous-flow protocol for Pd-catalyzed olefin cleavage by using molecular oxygen as the sole oxidant to give carbonyl compounds was explored. The developed flow protocol allowed the use of a low catalyst loading (0.1 mol%), and decomposition of the active catalyst was prevented through stabilization by poly(ethylene glycol)-400 (PEG-400), which was present as a cosolvent. Radical scavengers inhibited the reaction, which indicated the involvement of a free-radical path in the reaction mechanism. The applicability of the continuous-flow protocol was demonstrated on several olefin substrates. The continuous-flow process enabled safe and scalable olefin cleavage.

Fabrication of Zinc Oxide Composite Microfibers for Near-Infrared-Light-Mediated Photocatalysis

Wan-Ni Wang, Fu Zhang, Chuan-Ling Zhang, Prof. Yan-Chuan Guo, Prof. Wei Dai and Prof. Hai-Sheng Qian

ChemCatChem 2017, 9(18), 3611

Abstract

The fabrication of photocatalysts driven by near-infrared (NIR) light is of great scientific and technological interest to make use of solar energy. NaYF₄ codoped with Yb³⁺ and Tm³⁺ upconversion nanoparticles are important nanotransducers that transfer NIR photons to high-energy photons (UV/Vis). In this work, we demonstrated an electrospinning technique to synthesize ZnO and porous ZnO composite microfibers embedded with a large amount of NaYF₄:Yb/Tm@NaYF₄ nanoparticles. The morphologies, chemical compositions, and phase of the as-prepared composites were investigated carefully by using field-emission scanning electron microscopy, TEM, X-ray photoelectron spectroscopy, fluorescence spectroscopy, and XRD. Steady-state and dynamic-state fluorescence spectra were used to demonstrate that the embedded NaYF₄:Yb/Tm@NaYF₄ core–shell nanoparticles can activate the ZnO nanoparticles under IR irradiation. The ZnO composite microfibers can efficiently transfer the NIR photons to the excited state of ZnO and activate the semiconductor to produce reactive oxygen species to result in the degradation of rhodamine B dyes.
Chiral Thioureas Promote Enantioselective Pictet–Spengler Cyclization by Stabilizing Every Intermediate and Transition State in the Carboxylic Acid-Catalyzed Reaction

Rebekka S. Klausen, C. Rose Kennedy, Alan M. Hyde, and Eric N. Jacobsen


An investigation of the mechanism of benzoic acid/thiourea co-catalysis in the asymmetric Pictet–Spengler reaction is reported. Kinetic, computational, and structure–activity relationship studies provide evidence that rearomatization via deprotonation of the pentahydro-β-carbolinium ion intermediate by a chiral thiourea-carboxylate complex is both rate- and enantioselectivity-determining. The thiourea catalyst induces rate acceleration over the background reaction mediated by benzoic acid alone by stabilizing every intermediate and transition state leading up to and including the final selectivity-determining step. Distortion–interaction analyses of the transition structures for deprotonation predicted using density functional theory indicate that differential π–π and C–H···π interactions within a scaffold organized by multiple hydrogen bonds dictate stereoselectivity. The principles underlying rate acceleration and enantiocontrol described herein are expected to have general implications for the design of selective transformations involving deprotonation of high-energy intermediates.

Total Synthesis of Unsymmetrically Oxidized Nuphar Thioalkaloids via Copper-Catalyzed Thiolane Assembly

Jacob J. Lacharity, Jeremy Fournier, Ping Lu, Artur K. Mailyan, Aaron T. Herrmann, and Armen Zakarian


An asymmetric total synthesis of (+)-6-hydroxythiobinupharidine (1b) and (−)-6-hydroxythionuphlutine (2b), a set of hemiaminal containing dimeric sesquiterpenes isolated from yellow water lilies of the Nuphar genus, is described. The central bis-spirocyclic tetrahydrothiophene ring was forged through the Stevens rearrangement of a sulfonium ylide, generated in situ from the coupling of a copper-carbene with a spirocyclic thietane. This strategy diverges both from the proposed biosynthesis 1 and previous syntheses of this family of alkaloids, 2,3 all of which employ dimerization of symmetric monomers to form the aforementioned thiaspirane. The coupling of unsymmetrical monomers allowed access to the unsymmetrically oxidized product 2b for the first time.
**B(C6F5)3-Catalyzed C–Si/Si–H Cross-Metathesis of Hydrosilanes**

Y. Ma, L. Zhang, Y. Luo, M. Nishiura, and Z. Hou


The substituent redistribution of hydrosilanes on silicon through C–Si and Si–H bond cleavage and reformation is of great interest and importance, but this transformation is usually difficult to achieve in a selective fashion. By using electron-rich aromatic hydrosilanes, we have achieved for the first time the selective C–Si/Si–H bond homo- and cross-metathesis of a series of hydrosilanes in the presence of a boron catalyst B(C6F5)3. This protocol features simple reaction conditions, high chemoselectivity, wide substrate scope, and high functionality tolerance, offering a new pathway for the synthesis of multisubstituted functional silanes.

**Valorization of Unconventional Lipids from Microalgae or Tall Oil via a Selective Dual Catalysis One-Pot Approach**

S. K. Hess, N. S. Schunck, V. Goldbach, D. Ewe, P. G. Kroth, and S. Mecking


A dual catalysis approach enables selective functionalization of unconventional feedstocks composed of complex fatty acid mixtures with highly unsaturated portions like eicosapentaenoate (20:5) along with monounsaturated compounds. The degree of unsaturation is unified by selective heterogeneous hydrogenation on Pd/γ-Al2O3, complemented by effective activation to a homogeneous carbonylation catalyst [(dtbpx)PdH(L)+] by addition of diprotonated diphosphine (dtbpxH2)(OTf)2. By this one-pot approach, neat 20:5 as a model substrate is hydrogenated to up to 80% to the monounsaturated analogue (20:1), this is functionalized to the desired C21 α,ω-diester building block with a linear selectivity of over 90%. This catalytic approach is demonstrated to be suitable for crude microalgae oil from Phaeodactylum tricornutum genetically engineered for this purpose, as well as tall oil, an abundant waste material. Both substrates were fully converted with an overall selectivity to the linear α,ω-diester of up to 75%.

**Utilizing Glycerol as an Ex Situ CO-Source in Pd-Catalyzed Alkoxy carbonylation of Styrenes**


*ACS Catal.*, 2017, 7 (9), pp 6089–6093

We report on an efficient Ir-catalyzed decarbonylation of glycerol, which could be coupled to an ensuing Pd-catalyzed alkoxy carbonylation of styrenes. The formation of hydrogen could be avoided by employing 1,4-benzoquinone (BQ) as an external oxidant. A wide variety of styrenes underwent the
esterification in good yields and high regioselectivity. Applying catalytic amounts of hexafluoroisopropanol provided access to alcohols other than methanol, which this transformation is often limited to. Finally, we demonstrate the suitability of this methodology for the preparation of three well-known nonsteroidal anti-inflammatory drugs (NSAIDs).

**Surface-Plasmon-Mediated Hydrogenation of Carbonyls Catalyzed by Silver Nanocubes under Visible Light**

M. J. Landry, A. Gellé, B. Y. Meng, C. J. Barrett, and A. Moores

*ACS Catal., 2017, 7 (9), pp 6128–6133*

Plasmonic nanoparticles are exciting and promising candidates for light-activated catalysis. We report herein the use of plasmonic nanocubes for the activation of molecular hydrogen and the hydrogenation of ketones and aldehydes via visible light irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes, at 80 °C. Only 1 atm of molecular hydrogen is required to access, using catalytic amounts of silver, primary, and secondary alcohols, with complete chemoselectivity for C═O over C═C reduction. The resulting catalytic system was studied over a scope of 12 compounds. Exposure to other wavelengths, or absence of light failed to provide activity, thus proving a direct positive impact of the plasmonic excitation to the catalytic activity. By varying the irradiation intensity, we studied the relationship between plasmon band excitation and catalytic activity and propose a potential reaction mechanism involving plasmon-activated hot electrons. This study expands the scope of reactions catalyzed by free-standing plasmonic particles and sheds light on H2 activation by silver surfaces.
Visible-light excitation of iminium ions enables the enantioselective catalytic $\beta$-alkylation of enals
Mattia Silvi, Charlie Verrier, Yannick P. Rey, Luca Buzzetti and Paolo Melchiorre*

*NATURE CHEMISTRY, 2017, 19, 868

Abstract
Chiral iminium ions—generated upon condensation of $\alpha,\beta$-unsaturated aldehydes and amine catalysts—are used extensively by chemists to make chiral molecules in enantioenriched form. In contrast, their potential to absorb light and promote stereocontrolled photochemical processes remains unexplored. This is despite the fact that visible-light absorption by iminium ions is a naturally occurring event that triggers the mechanism of vision in higher organisms. Herein we demonstrate that the direct excitation of chiral iminium ions can unlock unconventional reaction pathways, enabling enantioselective catalytic photochemical $\beta$-alkylations of enals that cannot be realized via thermal activation. The chemistry uses readily available alkyl silanes, which are recalcitrant to classical conjugate additions, and occurs under illumination by visible-light-emitting diodes. Crucial to success was the design of a chiral amine catalyst with well-tailored electronic properties that can generate a photo-active iminium ion while providing the source of stereochemical induction. This strategy is expected to offer new opportunities for reaction design in the field of enantioselective catalytic photochemistry.
Solvent-switchable continuous-breathing behavior in a diamondoid metal–organic framework and its influence on CO\textsubscript{2} versus CH\textsubscript{4} selectivity

Elliot J. Carrington, Craig A. McAnally, Ashleigh J. Fletcher, Stephen P. Thompson, Mark Warren and Lee Brammer*

*NATURE CHEMISTRY, 2017, 9, 882

Abstract

Understanding the behaviour of flexible metal–organic frameworks (MOFs)—porous crystalline materials that undergo a structural change upon exposure to an external stimulus—underpins their design as responsive materials for specific applications, such as gas separation, molecular sensing, catalysis and drug delivery. Reversible transformations of a MOF between open- and closed-pore forms—a behaviour known as ‘breathing’—typically occur through well-defined crystallographic transitions. By contrast, continuous breathing is rare, and detailed characterization has remained very limited. Here we report a continuous-breathing mechanism that was studied by single-crystal diffraction in a MOF with a diamondoid network, (Me2NH2)[In(ABDC)2] (ABDC, 2-aminobenzene-1,4-dicarboxylate). Desolvation of the MOF in two different solvents leads to two polymorphic activated forms with very different pore openings, markedly different gas adsorption capacities and different CO\textsubscript{2} versus CH\textsubscript{4} selectivities. Partial desolvation introduces a gating pressure associated with CO\textsubscript{2} adsorption, which shows that the framework can also undergo a combination of stepped and continuous breathing.
The structure and binding mode of citrate in the stabilization of gold nanoparticles


*NATURE CHEMISTRY, 2017, 9, 890

Fig. A Cs corrected HRTEM image captures the morphology of a representative AuNP, synthesized by NaBH4 reduction in the presence of sodium citrate and a 1:1 citrate:Au ratio.

Abstract

Elucidating the binding mode of carboxylate-containing ligands to gold nanoparticles (AuNPs) is crucial to understand their stabilizing role. A detailed picture of the three-dimensional structure and coordination modes of citrate, acetate, succinate and glutarate to AuNPs is obtained by 13C and 23Na solid-state NMR in combination with computational modelling and electron microscopy. The binding between the carboxylates and the AuNP surface is found to occur in three different modes. These three modes are simultaneously present at low citrate to gold ratios, while a monocarboxylate monodentate (1κO1) mode is favoured at high citrate:gold ratios. The surface AuNP atoms are found to be predominantly in the zero oxidation state after citrate coordination, although trace amounts of Auδ+ are observed. 23Na NMR experiments show that Na+ ions are present near the gold surface, indicating that carboxylate binding occurs as a 2e− L-type interaction for each oxygen atom involved. This approach has broad potential to probe the binding of a variety of ligands to metal nanoparticles.
Iterative assembly line synthesis of polypropionates with full stereocontrol

Teerawut Bootwicha, Julian M. Feilner, Eddie L. Myers and Varinder K. Aggarwal*

NATURE CHEMISTRY, 2017, 9, 896

Abstract

The polypropionate motif is ubiquitous, being characteristic of the most important family of natural products for human health, the polyketides. Numerous strategies have been devised to construct these molecules with high stereocontrol, but certain stereoisomers remain challenging to prepare. We now describe the development of an iterative assembly line strategy for the construction of polypropionates. An assembly line strategy for the synthesis of deoxypolypropionates has already been described. However, the introduction of carbinol units required the development of new building blocks and new reaction conditions. This has been achieved by the use of enantioenriched lithiated α-chlorosilanes [1-((2′thiochloromethyl(dimethyl)silyl)-methyl)-2-(methoxymethyl)-pyrrolidine], thus enabling the programmed synthesis of polypropionates in a fully stereocontrolled manner, including the stereochemically challenging anti–anti isomers. The versatility of the approach is exemplified in its extension to the synthesis of 1,3-related polyols. The methodology now allows access to a much wider family of polyketide natural products with stereochemistry being dialled in at will.
Chlorodifluoromethane-triggered formation of difluoromethylated arenes catalysed by palladium

Zhang Feng, Qiao-Qiao Min, Xia-Ping Fu, Lun An and Xingang Zhang*

*NATURE CHEMISTRY, 2017, 9, 918

Abstract

Difluoromethylated aromatic compounds are of increasing importance in pharmaceuticals, agrochemicals and materials. Chlorodifluoromethane (CICF2H), an inexpensive, abundant and widely used industrial raw material, represents the ideal and most straightforward difluoromethylating reagent, but introduction of the difluoromethyl group (CF2H) from CICF2H into aromatics has not been reported. Here, we describe a direct palladium-catalysed difluoromethylation method for coupling CICF2H with arylboronic acids and esters to generate difluoromethylated arenes with high efficiency. The reaction exhibits a remarkably broad substrate scope, including heteroarylboronic acids, and was used for difluoromethylation of a range of pharmaceuticals and biologically active compounds. Preliminary mechanistic studies revealed that a palladium difluorocarbene intermediate is involved in the reaction. Although numerous metal–difluorocarbene complexes have been prepared, the catalytic synthesis of difluoromethylated or difluoromethylenated compounds involving metal–difluorocarbene complexes has not received much attention. This new reaction therefore also opens the door to understand metal–difluorocarbene complex catalysed reactions.
Pd-catalyzed asymmetric allylic alkylations via C–H activation of N-allyl imines with glycinates

B. M. Trost, X. Li

Chemical Science 2017, 8, 6815.

Abstract

Herein is reported the first example of palladium-catalyzed asymmetric allylic alkylation (AAA) reactions involving 2-aza-π-allyl palladium intermediates. The 2-aza-π-allyl complex was generated via a novel mode of activation of N-allyl imines. Pd-catalyzed C(sp3)–H activation of N-allyl imines and subsequent nucleophilic attack by glycinates delivered vicinal diamino derivatives as the sole regioisomers with high levels of diastereo- and enantio-control in the presence of the chiral, bidentate (S,S)-Cy-DIOP ligand. This procedure is highly atom economical and could also be performed by a simple one-pot operation starting from aldehydes, allyl amines and glycinates under mild conditions. The products of this transformation could be converted into various useful derivatives, where the allyl substitution serves as a unique tool for differentiating the two amino moieties in the products.

Formal aromaticity transfer for palladium-catalyzed coupling between phenols and pyrrolidines/indolines

Z. Qui, J.-S. Li, C.-J. Li

Chemical Science 2017, 8, 6954.

Abstract

We herein describe a palladium-catalyzed formal aromaticity transfer coupling reaction between phenols and pyrrolidines or indolines to generate the corresponding N-cyclohexyl pyrroles or indoles. In this transformation, the aromaticity of phenols is formally passed on to the pyrrolidine or indoline units. Substituted phenols thus can serve as latent cyclohexyl equivalents for the fast construction of various N-cyclohexyl pyrroles and indoles.
Copper-catalyzed cyanothiolation to incorporate a sulfur-substituted quaternary carbon center

Y. Huang, X. Li, X. Wang, Y. Yu, J. Zheng, W. Wu, H. Jiang

Chemical Science 2017, 8, 7047.

Abstract

Sulfur-containing nitriles have important research value in the life sciences due to their diverse biological activities resulting from the sulfur and cyano functional groups. Herein, a copper-catalyzed cyanothiolation of N-tosylhydrazones with thiocyanates to generate α-arylthioalkanenitriles bearing sulfur-substituted quaternary carbon center atoms has been described. This novel protocol involves the procedure of copper carbene species promoting S-CN bond cleavage and C-CN/C–S bond reconstruction to introduce both sulfur and cyano groups onto a single carbon center. This cyanothiolation reaction will greatly enhance the synthetic utility of carbenoid species as new entries for the construction of diverse heteroatom-containing nitriles via cyanofunctionalization of metal–carbene species.

A complementary pair of enantioselective switchable organocatalysts

G. De Bo, D. A. Leigh, C. T. McTernan, S. Wang

Chemical Science 2017, 8, 7077.

Abstract

A pair of enantioselective switchable bifunctional catalysts are shown to promote a range of conjugate addition reactions in up to 95:5 e.r. and 95% conversion. Each catalyst can be switched OFF using conditions that switch the other catalyst ON. Catalyst ON:OFF ratios of up to 98:2 and 1:99 were achieved, with a ratio of reaction rates of up to 16:1 between the ON and OFF states, maintained over complete ON–OFF–ON and OFF–ON–OFF cycles. However, simultaneous operation of the catalyst pair in the same reaction vessel, which in principle could allow product handedness to be switched by simple E–Z isomerisation of the catalytic pair, was unsuccessful. In this first generation complementary pair of enantioselective switchable organocatalysts, the OFF state of one catalyst inhibits the ON state of the other.
It Is Not Just Up to the Substrate: Palladium(0) Cyclizes Nazarov Substrates through Intramolecular Allylic Alkylation

T. A. Ateşin, G. M. Martinez, D. Flores

Organometallics 2017, 36, 3589.

Abstract

Plausible mechanisms of Pd⁰-catalyzed cyclization of diketoesters were modeled using density functional theory calculations. Comparison of the reaction mechanisms of uncatalyzed and Pd⁰-catalyzed cyclizations revealed the vital role of the Pd⁰ catalyst. Both reactions favor a stepwise mechanism involving a proton transfer followed by carbon–carbon bond formation over either the reverse order or a concerted mechanism. The key step for the Pd⁰-catalyzed reaction is the formation of a relatively stable intermediate, an η³-allyl Pd²⁺ complex, in the lowest energy pathway. Our proposed mechanism is consistent with a Pd⁰-catalyzed intramolecular allylic alkylation reaction, previously referred to as “Nazarov-type” reactions. It is worth noting that, in contrast to many allylic alkylations, the Pd⁰-catalyzed cyclization does not require any additional reagents or an activated leaving group to form an η³-allyl Pd²⁺ complex; thus, the α-hydroxycyclopentenone is produced from diketoesters with no waste. Furthermore, the asymmetric version of this reaction is the first known example of the use of an allylic alkylation reaction for the synthesis of a chiral cyclopentenone unit.
Chemical Pulping Advantages of Zip-lignin Hybrid Poplar


ChemSusChem 2017, 10, 3565

Abstract

Hybrid poplar genetically engineered to possess chemically labile ester linkages in its lignin backbone (zip-lignin hybrid poplar) was examined to determine if the strategic lignin modifications would enhance chemical pulping efficiencies. Kraft pulping of zip-lignin and wild-type hybrid poplar was performed in lab-scale reactors under conditions of varying severity by altering time, temperature and chemical charge. The resulting pulps were analyzed for yield, residual lignin content, and cellulose DP (degree of polymerization), as well as changes in carbohydrates and lignin structure. Statistical models of pulping were created, and the pulp bleaching and physical properties evaluated. Under identical cooking conditions, compared to wild-type, the zip-lignin hybrid poplar showed extended delignification, confirming the zip-lignin effect. Additionally, yield and carbohydrate content of the ensuing pulps were slightly elevated, as was the cellulose DP for zip-lignin poplar pulp, although differences in residual lignin between zip-lignin and wild-type poplar were not detected. Statistical prediction models facilitated comparisons between pulping conditions that resulted in identical delignification, with the zip-lignin poplar needing milder cooking conditions and resulting in higher pulp yield (up to 1.41 % gain). Bleaching and physical properties were subsequently equivalent between the samples with slight chemical savings realized in the zip-lignin samples due to the enhanced delignification.
Abstract

Lignin and the quest for the origin of stable organic radicals in it have seen numerous developments. Although there have been various speculations over the years on the formation of these stable radicals, researchers have not been able to arrive at a solid, unequivocal hypothesis that applies to all treatments and types of lignin. The extreme complexity of lignin and its highly aromatic, cross-linked, branched, and rigid structure has made such efforts rather cumbersome. Since the early 1950s, researchers in this field have dedicated their efforts to the establishment of methods for the detection and determination of spin content, theoretical simulations, and reactions on model compounds and spin-trapping studies. Although a significant amount of published research is available on lignin or its model compounds and the reactive intermediates involved during various chemical treatments (pulping, bleaching, extractions, chemical modifications, etc.), the literature provides a limited view on the origin, nature, and stability of such radicals. Consequently, this review is focused on examining the origin of such species in lignin, factors affecting their presence, reactions involved in their formation, and methods for their detection.
Abstract

Optically transparent wood, combining optical and mechanical performance, is an emerging new material for light-transmitting structures in buildings with the aim of reducing energy consumption. One of the main obstacles for transparent wood fabrication is delignification, where around 30 wt % of wood tissue is removed to reduce light absorption and refractive index mismatch. This step is time consuming and not environmentally benign. Moreover, lignin removal weakens the wood structure, limiting the fabrication of large structures. A green and industrially feasible method has now been developed to prepare transparent wood. Up to 80 wt % of lignin is preserved, leading to a stronger wood template compared to the delignified alternative. After polymer infiltration, a high-lignin-content transparent wood with transmittance of 83 %, haze of 75 %, thermal conductivity of 0.23 W mK$^{-1}$, and work-to-fracture of 1.2 MJ m$^{-3}$ (a magnitude higher than glass) was obtained. This transparent wood preparation method is efficient and applicable to various wood species. The transparent wood obtained shows potential for application in energy-saving buildings.
Abstract

Organic electrolyte solutions (i.e. mixtures containing an ionic liquid and a polar, molecular co-solvent) are highly versatile solvents for cellulose. However, the underlying solvent–solvent and solvent–solute interactions are not yet fully understood. Herein, mixtures of the ionic liquid 1-ethyl-3-methylimidazolium acetate, the co-solvent 1,3-dimethyl-2-imidazolidinone, and cellulose are investigated using 1D and 2D NMR spectroscopy. The use of a triply-13C-labelled ionic liquid enhances the signal-to-noise ratio for 13C NMR spectroscopy, enabling changes in bonding interactions to be accurately pinpointed. Current observations reveal an additional degree of complexity regarding the distinct roles of cation, anion, and co-solvent toward maintaining cellulose solubility and phase stability. Unexpectedly, the interactions between the dialkylimidazolium ring C2−H substituent and cellulose become more pronounced at high temperatures, counteracted by a net weakening of acetate–cellulose interactions. Moreover, for mixtures that exhibit critical solution behavior, phase separation is accompanied by the apparent recombination of cation–anion pairs.
Abstract

Natural extractives are proposed as potential sustainable bioactive compounds for wood preservative formulations, and an enzyme-mediated reaction is employed to fix them onto the wood surface. This environmentally friendly process takes place thanks to the activity of the laccase enzyme and leads to the formation of covalent bonds between these compounds and the wood itself. This then diminishes the problem of its future leaching, giving rise to long-lasting wood protection treatments. Overall, our data show suitable biocidal properties for the raw extracts of Pinus spp. and Cryptomeria japonica. Phenolic compounds such as pinosylvin, pinosylvin monomethyl ether, pinocembrin, naringenin, and pinobanksin were found in the extracts of pine together with totarol and sugiol in the C. japonica extract and could explain the antifungal properties found. Fungal tests have revealed mass losses below 7% for wood treated with the toluene extracts of Pinus spp. and the ethanolic extract of C. japonica, pointing to this enzymatic green methodology as a promising alternative in the wood preservation field. Therefore, potential inclusion of these enzymatic strategies in the wood industry today is discussed and analyzed in a “green” scenario.
Ball Milling for Biomass Fractionation and Pretreatment with Aqueous Hydroxide Solutions

Tianjiao Qu, Ximing Zhang, Xingwei Gu, Lujia Han, Guanya Ji, Xueli Chen, and Weihua Xiao


Abstract

A promising approach in the selective separation and modification of cellulose from raw biomass under a mild alkali process was proposed. In our study, ball milling was applied to wheat straw prior to alkali treatment. With ball milling, ultrafine powder formed an amorphous microstructure and displayed a level of solubilization in aqueous NaOH higher than that of general ground samples. Alkali-treated ultrafine powder resulted in up to 93.76% removal of hemicellulose and 86.14% removal of lignin, whereas cellulose remains largely undissolved. A high glucose yield (98.48%) was obtained via a 72 h enzymatic hydrolysis. X-ray diffraction and solid state $^{13}$C cross-polarization magic angle spinning nuclear magnetic resonance analysis revealed evidence of the transformation of crystalline cellulose I to cellulose II in alkali-treated ultrafine wheat straw. Prolonging the alkaline treatment time can significantly decrease the level of cellulose hydrogen bonding and increase the hydrolysis yield. The combination of ultrafine ball milling and low-severity alkali treatment played a significant role in the cellulose supramolecular change, which can then be used for downstream biorefinery processes or as a feedstock for the biomaterial industry.
Effect of in Vivo Deuteration on Structure of Switchgrass Lignin

Xianzhi Meng, Barbara R. Evans, Chang Geun Yoo, Yunqiao Pu, Brian H. Davison, and Arthur J. Ragauskas


Abstract

Biomass deuteration is an effective engineering method that can be used to provide key insights into understanding of biomass recalcitrance and the complex biomass conversion process. In this study, production of deuterated switchgrass was accomplished by growing the plants in 50% D$_2$O under hydroponic conditions in a perfusion chamber. Cellulolytic enzyme lignin was isolated from deuterated switchgrass, characterized by Fourier transform infrared (FTIR), gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR) and compared with its protiated control sample to determine the effect of in vivo deuteration on the chemical structure of lignin. FTIR results showed that D$_2$O can be taken up by the roots and transported to the leaves, and deuterium was subsequently incorporated into hydroxyl and alkyl groups in the plant and its lignin through photosynthesis. According to GPC results, deuterated lignin had slightly higher molecular weight, presumably due to isotope effects. $^{31}$P and heteronuclear single quantum coherence (HSQC) NMR results revealed that lignin in the deuterated biomass preserved its native physicochemical characteristics. The conserved characteristics of the deuterated lignin show its great potential applications for structural and dynamic studies of lignocellulose by techniques such as neutron scattering.
Measuring the Purity of Chitin with a Clean, Quantitative Solid-State NMR Method

Catherine King, Robin S. Stein, Julia L. Shamshina, and Robin D. Rogers


Abstract

Chitin is a versatile biopolymer which can be extracted directly from biomass and used for the preparation of high value materials, but such materials often require high-purity chitin. However, complete removal of proteinaceous material from chitin, which is obtained from biomass sources, can be difficult to determine. Here we report a quick, nondestructive method to measure chitin content using solid-state multi CP $^{13}$C NMR, which requires only 105 min and allows for recovery of the sample. A calibration curve was constructed from spectra of mass-based mixtures of commercial chitin and bovine serum albumin protein. This allowed for the quantification of chitin content (and therefore purity) in both chitinous biomass and extracted chitin samples in a quick, clean, nondestructive manner that agreed with measurements made by the method of Black and Schwartz, within the error of each of the methods.
Reforming whole lignocellulosic biomass into value-added materials has yet to be achieved mainly due to the infusible nature of biomass and its recalcitrance to dissolve in common organic solvents. Recently, the solubility of biomass in ionic liquids (ILs) has been explored to develop all-lignocellulosic materials; however, efficient dissolution and therefore production of value-added materials with desired mechanical properties remain a challenge. This article presents an approach to producing high-performance lignocellulosic films from hybrid poplar wood. An autohydrolysis step that removes ≤50% of the hemicellulose fraction is performed to enhance biomass solvation in 1-ethyl-3-methyl imidazolium acetate ([C2mim][OAc]). The resulting biomass–IL solution is then cast into free-standing films using different coagulating solvents, yet preserving the polymeric nature of the biomass constituents. Methanol coagulated films exhibit a continuous 3D-network structure with dispersed domains of less than 100 nm. The consolidated films with controllable morphology and structural order demonstrate tensile properties better than those of quasi-isotropic wood. The methods for producing these biomass derivatives have potential for fabricating novel green materials with superior performance from woody and grassy biomass.
Lignin transformations for high value applications: towards targeted modifications using green chemistry


Green Chem., 2017, 19, 4200-4233

Abstract

Lignin represents a considerable source of renewable and bio-based carbon. Pulping processes enable lignin, together with all components of the lignocellulosic biomass, to enter valorizable streams. A current key objective is to further valorize this versatile aromatic biopolymer, and for that, to go beyond its mere energy use. Despite the emergence of numerous proposals for value-added products coming from lignin, most of them remain at the research stage. The main challenges arise from the complexity and heterogeneity of the lignin structure and resulting molecular properties, the variability of the biomass source, pre-treatment processes, and the growing environment. Keeping in mind that future integrated biorefineries must take into account environmental concerns, lignin processing in accordance with green chemistry principles should first be favoured. From this very perspective, this work proposes to review the most promising current routes towards fractionation and/or depolymerization of lignin. Those should represent sustainable treatment technologies potentially leading to a broad spectrum of marketable lignin-based molecules and products. First, lignin fractionation by selective precipitation using pH as well as green solvents, or by using membrane technologies, will be addressed. Then lignin depolymerization will be discussed at length, notably from a catalytic point of view and by hydrogenolysis; the knowledge about the fundamental chemistry stemming from the use of model compounds will be described. Substitution of organic solvents with environmentally harmless supercritical fluids or with negligible vapour pressure ionic liquids is of great interest to modify lignin, and is finally reviewed. Lastly, challenges for integrated biorefineries and for launching new lignin-based compounds and products will be discussed.
Highly efficient synchronized production of phenol and 2,5-dimethylfuran through a bimetallic Ni–Cu catalyzed dehydrogenation–hydrogenation coupling process without any external hydrogen and oxygen supply

Wei Li, Guoli Fan, Lan Yang and Feng Li

Green Chem., 2017, 19, 4353-4363

Abstract

2,5-Dimethylfuran (DMF) and phenol are considered as one of the new-fashioned liquid transportation biofuels and a key motif for industrial chemicals, respectively. Herein, a highly efficient vapor-phase dehydrogenation–hydrogenation coupling process over bimetallic Ni–Cu alloy nanocatalysts was established for the synchronized production of phenol and DMF with unprecedentedly high yields (>97%) from two cyclohexanol (CHL) and biomass-derived 5-hydroxymethylfurfural (HMF) substrates, without any external hydrogen and oxygen supply. Systematic characterization and catalytic experiments revealed that the production of phenol went through a consecutive triple-dehydrogenation process from CHL, while HMF was simultaneously hydrogenated into DMF using active hydrogen species generated from the dehydrogenation process. The bimetallic Ni–Cu alloy nanostructures derived from Ni–Cu–Al layered double hydroxide precursors and strong metal–support interactions play important roles in governing the present coupling process. An appropriate Ni–Cu alloy nanostructure could greatly facilitate the dehydrogenative aromatization of CHL, thus significantly improving the selectivities to both phenol and DMF. Such an unparalleled efficient, eco-friendly and versatile coupling process for the synchronized production of various substituted phenols and DMF makes it practically promising for large-scale industrial applications in terms of green chemistry and sustainable development.
A straightforward thiol–ene click reaction to modify lignocellulosic scaffolds in water

S. Kostić, J. K. Ber, K. Casdorff, V. Merk, I. Burgertab and E. Cabane*

Green Chem., 2017, 19, 4017-4022

Abstract

We report on a sustainable and straightforward approach to develop a hydrophobic layer on the surface of wood veneers via the Michael addition click reaction of alkanethiols. After treatment, the naturally hygroscopic wood scaffold shows superhydrophobic properties with contact angles above 150°.
Efficient and sustainable solvents for lignin dissolution: aqueous choline carboxylate solutions

Airong Xu, Xin Guo, Yibo Zhang, Zhiyong Li and Jianji Wang

Green Chem., 2017, 19, 4067-4073

Abstract

Lignin is a promising alternative to fossil resources for the production of fuels, biocomposites and value-added chemicals. To better utilize this kind of natural resource, it is still necessary to develop efficient lignin solvents. As such, 13 kinds of novel lignin solvents have been developed, in this work, by the addition of water into bio-derived choline carboxylate ionic liquids (ILs). The solubility of lignin has been determined at 25 °C as a function of IL contents. The effect of the anionic structure of the ILs on lignin solubility is systematically examined. It is found that among these solvents, six types of ILs exhibit highly efficient capacity for lignin dissolution at room temperature. The solubility of lignin increases with increasing alkyl chain length in the carboxylate anions, and a substitution of H in carboxylate anions by the OH or NH2 group as well as the use of choline di-/tri-carboxylates leads to the decrease of lignin solubility, or even makes the lignin insoluble in the solvents. From NMR measurements, these results have been explained by the strong hydration of the carboxyl group of the anions and the possible interaction of alkyl chains of the anions and cations with lignin. In addition, the dissolved lignin can be regenerated by addition of additional water, and no chemical reaction takes place during the dissolution and regeneration processes.
Abstract

Two constitutional structural schemes are proposed attempting to unify and rationalize a series of focused NMR and chromatographic determinations aimed at providing an integrated picture for the structure of softwood kraft lignin. The complexity of native softwood lignin when coupled with the complexity of the kraft pulping process is known to lead to a rather heterogeneous material that has eluded us to date. The present work embarks at applying state-of-the-art quantitative 1D and 2D NMR methods on carefully isolated softwood kraft lignin samples and fractions. The accumulated data, when coupled with size exclusion chromatography, mass spectrometric analyses and literature accounts that pertain to the chemistry of kraft pulping, provide the following picture for softwood kraft lignin. Softwood kraft lignin is composed of two distinct fractions that can be separated by using anhydrous acetone. The acetone insoluble fraction is a somewhat branched polymeric material that still contains a variety of native wood lignin bonding patterns, albeit in significantly reduced abundance, as well as new structures induced during the process. The acetone soluble fraction is a significantly more branched and less polymeric material with an abundance of chemical structures that may be created when oligomeric phenols react under kraft pulping conditions. To account for the presence of the various moieties in these two fractions, kraft pulping fragmentation and repolymerization chemistries are extensively invoked, including radical processes initiated by sulfur.
Insight into forced hydrogen re-arrangement and altered reaction pathways in a protocol for CO2 catalytic processing of oleic acid into C8–C15 alkanes

Shiyou Xing, Pengmei Lv,* Haoran Yuan,abd Lingmei Yang,abd Zhongming Wang,abde Zhenhong Yuan* and Yong Chenabd

*Green Chem., 2017,19, 4157-4168

Abstract

A new vision of using carbon dioxide (CO2) catalytic processing of oleic acid into C8–C15 alkanes over a nano-nickel/zeolite catalyst is reported in this paper. The inherent and essential reasons which make this achievable are clearly resolved by using totally new catalytic reaction pathways of oleic acid transformation in a CO2 atmosphere. The yield of C8–C15 ingredients reaches 73.10 mol% in a CO2 atmosphere, which is much higher than the 49.67 mol% yield obtained in a hydrogen (H2) atmosphere. In the absence of an external H2 source, products which are similar to aviation fuel are generated where aromatization of propene (C3H6) oxidative dehydrogenation (ODH) involving CO2 and propane (C3H8) and hydrogen transfer reactions are found to account for hydrogen liberation in oleic acid and achieve its re-arrangement in the final alkane products. The reaction pathway in the CO2 atmosphere is significantly different from that in the H2 atmosphere, as shown by the presence of 8-heptadecene, γ-stearolactone, and 3-heptadecene as reaction intermediates, as well as a CO formation pathway. Because of the highly dispersed Ni metal center on the zeolite support, H2 spillover is observed in the H2 atmosphere, which inhibits the production of short-chain alkanes and reveals the inherent disadvantage of using H2. The CO2 processing of oleic acid described in this paper will significantly contribute to future CO2 utilization chemistry and provide an economical and promising approach for the production of sustainable alkane products which are similar to aviation fuel.
Renewable high-density spiro-fuels are synthesized from lignocellulose-derived cyclic ketones for the first time, which show higher density, higher neat heat of combustion and lower freezing point compared with other biofuels synthesized from the same feedstock, and thus represent a new type of renewable high-density fuel attractive for practical applications.

A novel Pd-catalyzed intermolecular cascade oxidative amination of homoallylic alcohols to yield β-amino ketones has been developed by using TBHP as the terminal oxidant. The synthetic utility of the reaction can be performed by installing the carbonyl and amino groups along an alkyl chain in one step, offering several advantages such as simple starting materials and easy operation. The resultant β-amino ketones should have potential applications in the fields of biopharmaceutical and functional materials.

We report a new hydrothermal and basic-additive free process for synthesizing a core(singel-crystalline HBEA zeolite)–echinus(nickel phyllosilicate) catalyst, which exhibits excellent reactivity and stability for hydrogenation reactions. Desilication and dealumination processes generate substantial $\text{SiO}_3^{2-}$ ions and exposed Si–OH groups to form nickel phyllosilicate on the external and internal surfaces of zeolite.


$\beta$-C(sp$^3$)–H functionalization on the ‘privileged’ piperazine nucleus has been disclosed using ruthenium catalysis. The ruthenium catalyzed synthesis of a variety of piperazine fused indoles from ortho-piperazinyl (hetero)aryl aldehydes is presented. This transformation takes place via the dehydrogenation of piperazine followed by an intramolecular nucleophilic addition of the transient enamine moiety onto the carbonyl group and aromatization cascade.
Péter Pongrácz, Anas Abu Seni, László T. Mika, László Kollár. **Palladium-catalysed enantioselective hydroaryloxycarbonylation of styrenes by 4-substituted phenols.** *Molecular Catalysis*, 2017, **438**, 15–18
DOI: [10.1016/j.mcat.2017.05.010](https://doi.org/10.1016/j.mcat.2017.05.010)

**Highlights**
- A variety of aryl 2-aryl- and 3-arylpropionates were synthesised in palladium-catalysed carbonylation.
- The enantioselective hydroaryloxycarbonylation of 4-substituted styrenes was carried out.
- The reaction shows high functional group tolerance regarding both the substrate and the O-nucleophile.

![Chemical Reaction](attachment:image1)

Yantao Wang, Frederic Delbecq, Witold Kwapiszki, Christophe Len. **Application of sulfonated carbon-based catalyst for the furfural production from D-xylose and xylan in a microwave-assisted biphasic reaction.** *Molecular Catalysis*, 2017, **438**, 167–172
DOI: [10.1016/j.mcat.2017.05.031](https://doi.org/10.1016/j.mcat.2017.05.031)

**Highlights**
- Microwave activation for the dehydration of d-xylose to furfural.
- Water-CPME as biphasic system to limit the production of humin.
- Sulfonated carbon-based catalyst from Miscanthus *x giganteus* is an efficient acid catalyst system for the synthesis of furfural.
- The reusability of the catalyst was efficient during ten cycles.
- Application to xylan and rice husk gave the furfural in good yields.
DOI: [10.1016/j.mcat.2017.06.004](https://doi.org/10.1016/j.mcat.2017.06.004)

**Highlights**
- Performance of [Emim]Br, [Bmim]Br and FDCA in biomass conversion was studied.
- Fructose converted into 5-HMF in [Bmim]Br but nearly no 5-HMF produced in [Emim]Br.
- 5-HMF synthesis mechanism in fructose/FDCA/[Emim]Br system were well investigated.
- [Emim]Br promote the ionization of −COOH to catalyze hydroxyl lose to give 5-HMF.
- Two tautomers of ionic liquid have different catalytic activity in biomass conversion.

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Hyeon-Gook Kim, Chung-Sun Lim, Dong-Woo Kim, Deug-Hee Cho, Dong-Koo Lee, Jin Suk Chung. **Multifunctional alkanolamine as a catalyst for CO₂ and propylene oxide cycloaddition.** *Molecular Catalysis*, 2017, **438**, 121–129
DOI: [10.1016/j.mcat.2017.05.026](https://doi.org/10.1016/j.mcat.2017.05.026)

**Highlights**
- Eco-friendly organic catalysts were developed for the reaction of CO₂ and PO.
- A conformational structure of organic catalysts was described by DFT.
- The mechanism relies on the synergistic effects between OH and amine groups.
- The optimum values of the CO₂ reaction conditions were obtained by BBD.
Cobalt-Catalyzed Silylcarbonylation of Unactivated Secondary Alkyl Tosylates at Low Pressure
Joan E. Roque Peña and Erik J. Alexanian

A catalytic preparation of silyl enol ethers from unactivated secondary alkyl tosylates is reported. An inexpensive cobalt catalyst is used under mild conditions with low pressures of carbon monoxide. Nucleophilic, anionic cobalt carbonyls facilitate the catalytic activation of a range of alkyl tosylates. The silylcarbonylation offers a practical approach to synthetically valuable silyl enol ethers from simple starting materials.

Synthesis of Silicon and Germanium-Containing Heterosumanenes via Rhodium-Catalyzed Cyclodehydrogenation of Silicon/Germanium–Hydrogen and Carbon–Hydrogen Bonds
Dandan Zhou, Ya Gao, Bingxin Liu, Qitao Tan, and Bin Xu

A three-step synthesis of C3-symmetric trisilasumanene and trigermasumanene, heteroanalogues of the π-bowl sumanene, was achieved using a threefold rhodium-catalyzed cyclodehydrogenation of Si/Ge–H and C–H bonds as the key step. Trigermasumanene was proven to adopt a planar geometry by single crystal X-ray diffraction for the first time. The optical properties were also investigated by UV–vis and fluorescence spectroscopy.

Utilization of MeOH as a C1 Building Block in Tandem Three-Component Coupling Reaction
Kaushik Chakrabarti, Milan Maji, Dibyajyoti Panja, Bhaskar Paul, Sujan Shee, Gourab Kanti Das, and Sabuj Kundu
Org. Lett., 2017, 19 (18), 4750

Ru(II) catalyzed tandem synthesis of α-branched methylated ketones via multicomponent reactions following the hydrogen borrowing process is described. This nonphosphine-based air and moisture stable catalyst efficiently produced various methylated ketones using methanol as a methylating agent. This system was found to be highly effective in three-component coupling between methanol, primary alcohols, and methyl ketones. A proposed catalytic cycle for the α-methylation is supported by DFT calculations as well as kinetic experiments.
Yuyu Cheng, Yuzhe Han, and Pengfei Li
Org. Lett., 2017, 19 (18), 4774

A reaction has been developed for the chiral phosphine-catalyzed enantioselective [1 + 4] annulation of Morita–Baylis–Hillman carbonates with electron-deficient olefins via a Michael alkylation process. Morita–Baylis–Hillman carbonates reacted smoothly with β,γ-unsaturated α-keto ester and α,β-unsaturated ketone substrates under 1,2-bis((2R,5R)-2,5-dimethylphospholano)benzene monoxide catalysis to furnish a wide range of optically active 2,3-dihydrofurans in high yields (up to 95%) with excellent asymmetric induction (up to >99% ee, >20:1 dr). This protocol represents an efficient strategy for the synthesis of optically active multifunctional 2,3-dihydrofurans via an asymmetric Michael alkylation domino reaction.

Direct Access to 2,3,4,6-Tetrasubstituted Tetrahydro-2H-pyrans via Tandem SN2′–Prins Cyclization
Jimena Scoccia, Sixto J. Pérez, Victoria Sinka, Daniel A. Cruz, Juan M. López-Soria, Israel Fernández, Víctor S. Martín, Pedro O. Miranda, and Juan I. Padrón
Org. Lett., 2017, 19 (18), 4834

A new, direct, and diastereoselective synthesis of activated 2,3,4,6-tetrasubstituted tetrahydro-2H-pyrans is described. In this reaction, iron(III) catalyzed an SN2′–Prins cyclization tandem process leading to the creation of three new stereocenters in one single step. These activated tetrahydro-2H-pyrane units are easily derivatizable through CuAAC conjugations in order to generate multifunctionalized complex molecules. DFT calculations support the in situ SN2′ reaction as a preliminary step in the Prins cyclization.

Direct Irradiation of Aryl Sulfides: Homolytic Fragmentation and Sensitized S-Oxidation
Sergio M. Bonesi, Stefano Crespi, Daniele Merli, Ilse Manet, and Angelo Albini
The direct irradiation of diphenyl sulfide and p-substituted thioanisoles in the presence of oxygen was investigated by means of both steady state and laser flash photolysis experiments. Two competitive pathways took place from the triplet excited state of thioanisoles, C–S bond cleavage, finally leading to aryl sulfinic acid and sensitized oxidation leading to S-oxidation. Co-oxidation of dodecyl methyl sulfide occurred efficiently implying that an S-persulfoxide intermediate is involved during the sensitized oxidation. On the other hand, triplet state of diphenyl sulfide also showed competitive C–S bond cleavage giving phenyl sulfinic acid and ionization to diphenyl sulfide radical cation that in turn led to diphenyl sulfide. The rate constants of the above reactions were determined by time-resolved experiments.

Modular Construction of Protected 1,2/1,3-Diols, -Amino Alcohols, and -Diamines via Catalytic Asymmetric Dehydrative Allylation: An Application to Synthesis of Sphingosine
Shinji Tanaka, Ramachandran Gunasekar, Tatsuya Tanaka, Yoko Iyoda, Yusuke Suzuki, and Masato Kitamura

A new enantioselective catalysis has been developed for the one-step construction of methylene-bridged chiral modules of 1,2- and 1,3-OH and/or NH function(s) from δ- or λ-OH/NHBoc-substituted allylic alcohols and “H2C═O”/“H2C═NBoc”. A protonic nucleophile, either in situ-generated CH2OH or CH2NHBoc, is intramolecularly allylated to furnish eight possible 1,2-O,O, -O,N, -N,O, and -N,N chiral modules equipped with an ethenyl group in high yields and enantioselectivities. The utility of this method has been demonstrated in the five-step synthesis of sphingosine.

Trifluoromethanesulfonate Anion as Nucleophile in Organic Chemistry
Bibek Dhakal, Luis Bohé, and David Crich

Although the triflate ion is not generally perceived as a nucleophile, many examples of its behavior as such exist in the literature. This Synopsis presents an overview of such reactions, in which triflate may be either a stoichiometric or catalytic nucleophile, leading to the suggestion that nucleophilic catalysis
by triflate may be more common than generally accepted, albeit hidden by the typical reactivity of organic triflates which complicates their observation as intermediates.

**Aliphatic C(sp3)–H Bond Activation Using Nickel Catalysis: Mechanistic Insights on Regioselective Arylation**

Sukriti Singh, Surya K, and Raghavan B. Sunoj

*J. Org. Chem., 2017, 82 (18), 9619*

Transition-metal-catalyzed C(sp3)–H bond activation in aliphatic compounds are of current interest. Lack of mechanistic insights on Ni-catalyzed C(sp3)–H activation using 8-aminoquinoline as a directing group motivated us to examine an interesting direct arylation of an aliphatic tertiary amide by using density functional theory. The catalysis employed Ni(II) precatalyst, 4-iodoanisole as an arylating agent, sodium carbonate, and mesitylenic acid as additives in DMF solvent. Examination of a comprehensive set of mechanistic pathways helped us learn that the most preferred route begins with a bidentate chelate binding of deprotonated substrate to the Ni. The C–H activation in the catalyst–substrate complex via a cyclometalation deprotonation provides a five-membered nickelacycle intermediate, which upon the rate-limiting oxidative insertion to aryl iodide forms a Ni(IV)–aryl intermediate. The ensuing reductive elimination furnishes the desired arylated product. We note that the explicit inclusion of sodium carbonate, mesitylenic acid, and solvent molecules on sodium ion all are critical in identifying the most favorable pathway. Of the two types of C(sp3)–H bonds in the substrate [2-methyl-2-phenyl-N-(quinolin-8-yl)heptanamide], the energies for the regiocontrolling reductive elimination is predicted to be more in favor of the methyl group than the methylene of the pentyl chain, in excellent agreement with the previous experimental observation.

**Total Synthesis of β-d-ido-Heptopyranosides Related to Capsular Polysaccharides of Campylobacter jejuni HS:4**

Pengfei Zhang, Rachel Hevey, and Chang-Chun Ling

*J. Org. Chem., 2017, 82 (18), 9662*

The 6-deoxy-β-d-ido-heptopyranoside related to the capsular polysaccharides of C. jejuni HS:4 is very remarkable, owing to the unique, multifaceted structural features that have been combined into one molecule, which include (1) the rare ido-configuration, (2) the unusual 7-carbon backbone, and (3) the challenging β-(1→2)-cis-anomeric configuration. Two distinct strategies toward the total synthesis of this interesting target are reported. The first involved establishment of the β-d-idopyranosyl
configuration from β-d-galactopyranosides, prior to a C-6-homologation extending the d-hexose to the desired 6-deoxy-d-heptose. However, this approach encountered difficulties due to the significantly reduced reactivity of the 6-position of the β-d-idopyranosides, so instead a second strategy was employed, which involved first carrying out a 6-homologation on the less flexible d-galactopyranose, followed by a very successful conversion to the desired β-d-ido-configuration found in the target heptopyranoside (2). This report is the first successful synthesis of the 6-deoxy-β-d-ido-heptopyranoside, which could possess interesting immunological properties.

**Bisphosphine-Ligated Nickel Pre-catalysts in C(sp2)–N Cross-Couplings of Aryl Chlorides: A Comparison of Nickel(I) and Nickel(II)**

Christopher M. Lavoie, Robert McDonald, Erin R. Johnson and Mark Stradiotto


The influence of ancillary ligand and nickel oxidation state in the nickel-catalyzed C(sp2)–N cross-coupling of aryl chlorides is examined by use of experimental and DFT methods for the first time, focusing on (L)NiCl and (L)Ni(o-tolyl)Cl pre-catalysts (PAd-DalPhos, L1; dppf, L2). Whereas Ni(II) pre-catalysts generally out-performed Ni(I) species in our study, the viability and in some cases superiority of Ni(I) pre-catalysts in challenging aminations is established. Computational analyses support the viability of Ni(0)/Ni(II) cycles featuring rate-limiting C–N reductive elimination, as well as parallel Ni(I)/Ni(III) mechanisms involving rate-limiting C–Cl oxidative addition.

**Iron-Mediated Oxidative C–H Alkylation of S,S-Functionalized Internal Olefins via C(sp2)–H/C(sp3)–H Cross-Coupling**

Quannan Wang, Jiang Lou, Ping Wu, Kaikai Wu and Zhengkun Yu


Mediated by a catalytic amount of FeCl3, the C–H alkylation of S,S-functionalized internal olefins, i.e., α-oxo ketene dithioacetals and their analogues, was efficiently achieved using simple ethers and toluene derivatives as the coupling partners, di-tert-butyl peroxide (DTBP) as the oxidant, and DABCO·6 H2O as the additive. The alkylthio functionality is essential for the internal olefinic C–H bond to undergo such an alkylation with the O-adjacent C(sp3)–H bonds of the ethers and the benzylic C–H bonds of the toluene derivatives, respectively. Tetrasubstituted olefins were thus synthesized and further transformed to highly substituted pyrazoles and isoxazoles. The strategy to activate an internal olefinic C–H bond by polarizing its parent olefinic C=C bond with both the dialkylthio group and an electron-withdrawing functionality was investigated. The mechanistic studies suggest a radical pathway for the C(sp2)–H/C(sp3)–H cross-coupling reactions. The present protocol provides a convenient route to tetrasubstituted olefins.
2-Iodoxybenzoic Acid Tosylates: the Alternative to Dess–Martin Periodinane Oxidizing Reagents
Mekhman S. Yusubov, Pavel S. Postnikov, Roza Ya. Yusubova, Akira Yoshimura, Gerrit Jüriens, Andreas Kirschning and Viktor V. Zhdankin

Two powerful hypervalent iodine(V) oxidants, DMP-OTs (1-tosyloxy-1,1-diaceatoxy-1H-1λ5-benzo[d][1,2]iodoxol-3-one) and IBX-OTs (1-tosyloxy-1-oxo-1H-1λ5-benzo[d][1,2]iodoxol-3-one) show high reactivity in the oxidation of structurally complex primary and secondary alcohols, which are highly functionalized polyketide or terpene fragments or steroids. The yields of the corresponding carbonyl compounds are even higher for the protocol that uses pyridine as additive. The oxidations proceed very rapidly at room temperature leaving the protective groups and π-systems intact and affording the corresponding carbonyl compounds in good to excellent yields. Moreover, IBX-OTs is an efficient reagent for the oxidative dehydrogenation of steroidal alcohols to the corresponding enones.

TBAI/K2S2O8 Initiated Radical Cyclization to Synthesize β-Arylsulfonyl Naphthalenes from Homopropargylic Alcohols and Sulfonyl Hydrazides
Xiaodong Yang, Lianbiao Zhao, Bingxiang Yuan, Zhenjie Qi and Rulong Yan

A metal-free radical addition method for the synthesis of β-arylsulfonyl naphthalenes with homopropargylic alcohols and sulfonyl hydrazides has been developed. In this reaction, sulfonyl hydrazide is employed as the source of sulfonyl radical to produce the desired sulfone directly. There is the first example for homopropargyl alcohol through direct intramolecular addition of vinyl radical to arenes with sulfonyl radical, which is initiated by the TBAI/K2S2O8 reaction system and generates the desired products in moderate yields.
Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: a review and perspective


Catalysis Science & Technology 2017, 7, 3659-3675

The present critical review reports the recent progress of the last 15 years in the selective epoxidation of vegetable oils and their derivatives, in particular unsaturated fatty acids (UFAs) and fatty acid methyl esters (FAMEs). Epoxidized vegetable oils (EVOs) have drawn much attention in recent years in the chemical industry since they are environmentally friendly, biodegradable, renewable, highly available and non-toxic. Four major types of catalysts are used to produce epoxidized fatty acid compounds: homogeneous, heterogeneous, polyoxometalates and lipases. EVOs are currently produced in industry by a homogeneous catalytic conventional epoxidation process, in which the unsaturated oils are converted with percarboxylic acids, such as peracetic or performic acid. However, this method suffers from several drawbacks such as (1) relatively low selectivity for epoxides due to oxirane ring opening, (2) corrosion problems caused by the strong acids in an oxidizing environment, etc. Thus, in view of the principles of green chemistry, the development of new catalytic systems for the selective epoxidation of vegetable oils and their derivatives is an actual task. Furthermore, in our opinion, epoxidized fatty acids and epoxidized fatty acid methyl esters can be a promising substitute for EVOs because the starting materials for their production have a lower viscosity and higher reactivity, which will significantly increase the productivity of the epoxidation process. In this work, we tried to determine the prospects of using the main catalytic methods in industry to obtain epoxidized fatty acid compounds.
Different catalytic behaviors of Pd and Pt metals in decalin dehydrogenation to naphthalene

Kyeounghak Kim, Jinho Oh, Tae Wan Kim, Ji Hoon Park, Jeong Woo Han and Young-Woong Suh

Catalysis Science & Technology, 2017, 7, 3728-3735

The catalytic dehydrogenation from decalin to tetralin to naphthalene is usually performed over supported Pd or Pt catalysts at a high temperature due to the endothermic nature of the reaction. However, the mechanistic studies of the catalytic activity and selectivity are not still sufficient to understand the dehydrogenation reaction on these metal surfaces. In this study, we mechanistically investigated the dehydrogenation reaction of decalin to tetralin to naphthalene on Pd and Pt catalysts using density functional theory (DFT) calculations combined with experimental validation. We firstly explored the relative energy profile of the entire elementary steps of the dehydrogenation reaction. Our theoretical results demonstrate that the conversion of decalin to tetralin on the Pt catalyst is energetically more preferred to that on Pd. On the other hand, Pd exhibits an energetically more favored reaction pathway in the conversion of tetralin to naphthalene than Pt. It is found that the difference in the catalytic activity and selectivity between Pd and Pt originates from the different structural and chemical characteristics of the metals. Our experimental results also support that decalin is more easily dehydrogenated over Pt/C while the dehydrogenation of tetralin is more facile over Pd/C.
Water as a catalytic switch in the oxidation of aryl alcohols by polymer incarcerated rhodium nanoparticles

Jack O. Weston, Hiroyuki Miyamura, Tomohiro Yasukawa, Dedi Sutarma, Chloe A. Baker, Preabjot K. Singh, Mariela Bravo-Sanchez, Naoko Sano, Peter J. Cumpson, Yulia Ryabenkova, Shū Kobayashi and Marco Conte

Catalysis Science & Technology, 2017, 7, 3985-3998

One of the major goals in the oxidation of organic substrates, and especially for alcohol oxidation, is the use of molecular oxygen as the oxidant under mild conditions. Here we report the synthesis and testing of Rh polymer incarcerated catalysts, using a metal so far not used for alcohol oxidation reactions, in which the catalytic activity towards aryl alcohol oxidation, for substrates like 1-phenylethanol and benzyl alcohol, is switched on by the addition of water as co-solvent in toluene. This is done by using air as oxidant at atmospheric pressure, in one of the mildest reaction conditions reported for this class of reaction. The promoting effect of water to higher conversions was observed also for rhodium over alumina supported catalysts, which were used as a benchmark allowing in all cases high conversion and selectivity to the ketone or the aldehyde within a short reaction time. The effect of water was explained as a medium capable to promote the oxidation of the alcohol to the ketone in a biphasic system assisted by phase transfer catalysis. This is particularly relevant for alcohols like 1-phenylethanol or benzyl alcohol that are not soluble in water at room temperature, and for which alternative oxidation routes are needed, as well as to switch on the catalytic activity of metal nanoparticles in a facile and green manner for the activation of molecular oxygen. Aliphatic alcohols like 1-octanol and 3-octanol were also tested, still showing Rh based catalysts as promising materials for this reaction if toluene only was used as solvent instead.

Connection between macroscopic kinetic measurables and the degree of rate control

Mikkel Jørgensen and Henrik Grönbeck

Catalysis Science & Technology, 2017, 7, 4034-4040

Catalytic reactions are commonly characterized by measuring reaction orders and apparent activation energies. In the present work, these macroscopic measurables are related to the degree of rate control ($\chi_i$), which describes how the overall kinetics is influenced by the elementary reactions. The reaction orders are found to be $\chi_i$-weighted sums over the microscopic rates, derived with respect to pressure. Similarly, the apparent activation energy is shown to be a sum over the individual reaction-energy-barriers, weighted by $\chi_i$. The results couple macroscopic kinetics to the microscopic scale, which can facilitate analysis of catalytic reaction kinetics.
Switchable synthesis of furfurylamine and tetrahydrofurfurylamine from furfuryl alcohol over RANEY® nickel

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Catalysis Science & Technology, 2017, 7, 4129-4135

RANEY® Ni proved to be an effective heterogeneous catalyst for switchable reductive amination of furfuryl alcohol to tetrahydrofurfurylamine and furfurylamine with NH₃ by simply adding or not adding 1.0 MPa H₂ into the reaction bulk. After further optimization of the reaction conditions, we finally obtained 94.0% yield of tetrahydrofurfurylamine and 78.8% yield of furfurylamine with high selectivity. By extensively studying the catalytic pathways and mechanism of catalyst deactivation with XRD and XPS characterization, we have confirmed that an excess amount of H₂ in the reaction bulk leads to the deep hydrogenation of the furan ring while an insufficient amount of H₂ leads to the formation of Ni₃N and the deactivation of the catalyst.

The effect of surface chemistry on the performances of Pd-based catalysts supported on activated carbons


Catalysis Science & Technology, 2017, 7, 4162-4172

In this work we investigated in detail the effects of nitric acid on the surface chemistry of two carbons, activated by steam and by phosphoric acid, meant to identify the nature and the concentration of the oxidized surface species. To this aim, the oxidized carbons were characterized by means of a large number of complementary techniques, including micro-Raman spectroscopy, N₂ physisorption, Boehm titration method, ¹³C solid state nuclear magnetic resonance, X-ray photoelectron spectroscopy, diffuse reflectance infrared and inelastic neutron scattering spectroscopy. Carboxylic and carboxylate groups are mainly formed, the latter stabilized by the extended conjugation of the π electrons and being more abundant on small and irregular graphitic platelets. We demonstrated that the presence of oxygen-containing groups acts against the palladium dispersion and causes the appearance of an appreciable induction time in hydrogenation reactions. The carbon with more oxygenated surface species (and in particular more carboxylate groups) must be chosen in the hydrogenation of polar substrates, while it is detrimental to the hydrogenation of nonpolar substrates.
Platinum clusters with precise numbers of atoms for preparative-scale catalysis
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Nature Communications 8, 2017, 688

Subnanometer noble metal clusters have enormous potential, mainly for catalytic applications. Because a difference of only one atom may cause significant changes in their reactivity, a preparation method with atomic-level precision is essential. Although such a precision with enough scalability has been achieved by gas-phase synthesis, large-scale preparation is still at the frontier, hampering practical applications. We now show the atom-precise and fully scalable synthesis of platinum clusters on a milligram scale from tiara-like platinum complexes with various ring numbers (n = 5–13). Low-temperature calcination of the complexes on a carbon support under hydrogen stream affords monodispersed platinum clusters, whose atomicity is equivalent to that of the precursor complex. One of the clusters (Pt10) exhibits high catalytic activity in the hydrogenation of styrene compared to that of the other clusters. This method opens an avenue for the application of these clusters to preparative-scale catalysis.

Ti(O-i-Pr)4-promoted photoenolization Diels–Alder reaction to construct polycyclic rings and its synthetic applications
Baochao Yang, Kuaikuai Lin, Yingbo Shi & Shuanhu Gao
Nature Communications 8, 2017, 622

Stereoselective construction of polycyclic rings with all-carbon quaternary centers, and vicinal all-carbon quaternary stereocenters, remains a significant challenge in organic synthesis. These structures can be found in a wide range of polycyclic natural products and drug molecules. Here we report a Ti(O-i-Pr)4-promoted photoenolization/Diels–Alder (PEDA) reaction to construct hydroanthracenol and related polycyclic rings bearing all-carbon quaternary centers. This photolysis proceeds under mild conditions and generates a variety of photo-cycloaddition products in good reaction efficiency and stereoselectivity (48 examples), and has been successfully used in the construction of core skeleton of oncocalyxones, tetracycline and pleurotin. It also provides a reliable method for the late-stage modification of natural products bearing enone groups, such as steroids. The total synthesis of oncocalyxone B was successfully achieved using this PEDA approach.

Hydrodeoxygenation of water-insoluble bio-oil to alkanes using a highly dispersed Pd–Mo catalyst
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Nature Communications 8, 2017, 591

Bio-oil, produced by the destructive distillation of cheap and renewable lignocellulosic biomass, contains high energy density oligomers in the water-insoluble fraction that can be utilized for diesel and valuable fine chemicals productions. Here, we show an efficient hydrodeoxygenation catalyst that combines highly dispersed palladium and ultrafine molybdenum phosphate nanoparticles on silica. Using phenol as a model substrate this catalyst is 100% effective and 97.5% selective for hydrodeoxygenation to cyclohexane under mild conditions in a batch reaction; this catalyst also demonstrates regeneration ability in long-term continuous flow tests. Detailed investigations into the nature of the catalyst show that it combines hydrogenation activity of Pd and high density of both Brønsted and Lewis acid sites; we believe these are key features for efficient catalytic hydrodeoxygenation behavior. Using a wood and bark-derived feedstock, this catalyst performs hydrodeoxygenation of lignin, cellulose, and hemicellulose-derived oligomers into liquid alkanes with high efficiency and yield.
Rational development of catalytic Au(I)/Au(III) arylation involving mild oxidative addition of aryl halides

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Nature Communications 8, 2017, 565

The reluctance of gold to achieve oxidative addition reaction is considered as an intrinsic limitation for the development of gold-catalyzed cross-coupling reactions with simple and ubiquitous aryl halide electrophiles. Here, we report the rational construction of a Au(I)/Au(III) catalytic cycle involving a sequence of Csp²–X oxidative addition, Csp²–H auration and reductive elimination, allowing a gold-catalyzed direct arylation of arenes with aryl halides. Key to this discovery is the use of Me-Dalphos, a simple ancillary (P,N) ligand, that allows the bottleneck oxidative addition of aryl iodides and bromides to readily proceed under mild conditions. The hemilabile character of the amino group plays a crucial role in this transformation, as substantiated by density functional theory calculations.

Hydrogen bonds to Au atoms in coordinated gold clusters

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Nature Communications 8, 2017, 576

It is well known that various transition elements can form M···H hydrogen bonds. However, for gold, there has been limited decisive experimental evidence of such attractive interactions. Herein we demonstrate an example of spectroscopically identified hydrogen bonding interaction of C–H units to Au atoms in divalent hexagold clusters ([Au₆]²⁺) decorated by diphosphine ligands. X-ray crystallography reveals substantially short Au–H/Au–C distances to indicate the presence of attractive interactions involving unfunctionalized C–H moieties. Solution ¹H and ¹³C NMR signals of the C–H units appear at considerably downfield regions, indicating the hydrogen-bond character of the interactions. The Au···H interactions are critically involved in the ligand-cluster interactions to affect the stability of the cluster framework. This work demonstrates the uniqueness and potential of partially oxidised Au cluster moieties to participate in non-covalent interaction with various organic functionalities, which would expand the scope of gold clusters.
Stereodivergent synthesis with a programmable molecular machine
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Abstract
It has been convincingly argued that molecular machines that manipulate individual atoms, or highly reactive clusters of atoms, with Ångström precision are unlikely to be realized. However, biological molecular machines routinely position rather less reactive substrates in order to direct chemical reaction sequences, from sequence-specific synthesis by the ribosome4 to polyketide synthases where tethered molecules are passed from active site to active site in multi-enzyme complexes. Artificial molecular machines have been developed for tasks that include sequence-specific oligomer synthesis and the switching of product chirality a photo-responsive host molecule has been described that is able to mechanically twist a bound molecular guest20, and molecular fragments have been selectively transported in either direction between sites on a molecular platform through a ratchet mechanism. Here we detail an artificial molecular machine that moves a substrate between different activating sites to achieve different product outcomes from chemical synthesis. This molecular robot can be programmed to stereoselectively produce, in a sequential one-pot operation, an excess of any one of four possible diastereoisomers from the addition of a thiol and an alkene to an $\alpha,\beta$-unsaturated aldehyde in a tandem reaction process. The stereodivergent synthesis includes diastereoisomers that cannot be selectively synthesized through conventional iminium–enamine organocatalysis. We anticipate that future generations of programmable molecular machines may have significant roles in chemical synthesis and molecular manufacturing.
Biological fabrication of cellulose fibers with tailored properties
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Abstract
Cotton is a promising basis for wearable smart textiles. Current approaches that rely on fiber coatings suffer from function loss during wear. We present an approach that allows biological incorporation of exogenous molecules into cotton fibers to tailor the material's functionality. In vitro model cultures of upland cotton (Gossypium hirsutum) are incubated with 6-carboxyfluorescein–glucose and dysprosium–1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid–glucose, where the glucose moiety acts as a carrier capable of traveling from the vascular connection to the outermost cell layer of the ovule epidermis, becoming incorporated into the cellulose fibers. This yields fibers with unnatural properties such as fluorescence or magnetism. Combining biological systems with the appropriate molecular design offers numerous possibilities to grow functional composite materials and implements a material-farming concept.
Molecular Control of the Band Edge Movement and the Recombination Process in Donor–Acceptor Hemicyanine-Sensitized Solar Cells

Neeta Karjule, Munavar Fairoos Mele Kavungathodi, and Jayaraj Nithyanandhan


(10C)

**Abstract**

The presence of downward shift in the band edge and the recombination reactions in the hemicyanine-sensitized solar cell reduces the open-circuit potential (VOC) and the short-circuit current density (JSC), which in turn decreases the dye cell performance. Choosing either an electrolyte possessing minimum overpotentials or a systematic dye design which can efficiently suppress the diffusion of charged species toward the TiO$_2$ can improve the overall power conversion efficiency (PCE). Here, a series of donor–acceptor (D–A) hemicyanine dyes were synthesized utilizing a planar heterotriangulene (HT) or triphenylamine (TPA) donor and alkyl-functionalized indolium carboxylic acid acceptor unit. By introducing strong HT donor instead of TPA, the photophysical, and electrochemical properties of D–A dyes are significantly modulated. The strong donor nature of HT and effective passivation of surface by hydrophobic alkyl chains close to the anchoring group for NC3 dye exhibits an average PCE of 4.34% with a VOC of 0.416 V, JSC of 20.04 mA cm$^{-2}$, and fill factor (ff) of 52.03% under simulated AM 1.5G illumination (100 mW cm$^{-2}$) without 3α,7α-dihydroxy-5β-cholic acid coadsorbent (CDCA). The intrinsic dipole of the hemicyanine dye and the presence of Li$^+$ ions in iodide/triiodide redox couple without tert-butylpyridine (TBP) additive induces a downward shift in conduction band edge (ECB) of TiO$_2$. By rational molecular design, the extend of shift in ECB is controlled and enhanced the VOC. Electrochemical impedance spectroscopy (EIS) studies revealed the high charge transfer resistance (Rct) and long lifetime (τ) of injected electrons in HT-based dyes than that of TPA derivatives, which provide insight into the passivation of Li$^+$ and I$^-$ ions by current D–A dye design possessing alkyl functionalities to increase both the JSC and VOC.
Abstract

Hybrid nanomaterials comprising metal–graphitic interfaces are uniquely suitable to probe molecular interactions and the associated phenomena such as charge transfer and adsorbate spillover effects. Herein, we study the modulation of the electronic and chemical properties of gold nanoparticle-decorated single-walled carbon nanotubes (SWCNT) using Raman spectroscopy and measurements of field-effect transistor (FET) characteristics. SWCNT are extremely sensitive to changes in the local electronic environment and therefore gold-analyte interactions may be probed both through changes in FET characteristics (as an electrical transducer) and in surface-enhanced Raman scattering (as a chromophore). We study these changes both experimentally and theoretically in order to elucidate the electronic structure of complex nanocomposites, and the information gathered from these experiments is applied to the study of biomolecular interactions with gold nanoparticle-decorated SWCNT. This study, in addition to providing deeper understanding of metal–graphitic interfaces, will offer a combined approach to SWCNT biosensing methodology based on the dual monitoring of the FET–Raman characteristics, which we demonstrate through detection of glutathione.
Abstract

The structure of a protonated diketopiperazine dipeptide, cyclo-diphenylalanine, is studied by means of infrared multiple photon dissociation spectroscopy combined with quantum chemical calculations. Protonation exclusively occurs on the oxygen site and, in the most stable conformer, results in an intramolecular OH···π interaction, accompanied by a CH···π interaction. Higher-energy conformers with free OH and NH···π interactions are observed as well, due to kinetic trapping. Optimization of the intramolecular interactions involving the aromatic ring dictates the geometry of the benzyl substituents. Changing the chirality of one of the residues has consequences on the CH···π interaction, which is of CαH···π nature for LD, while LL shows a CβH···π interaction. Higher-energy conformers also display some differences in the nature of the intramolecular interactions.

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