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Organic Chemistry **281**

Asymmetric allylic alkylation catalyzed by Pd/Al_2O_3 modified with chiral phosphines

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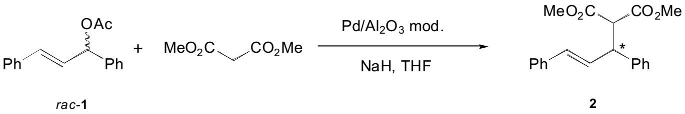
Soluble chiral Pd complexes afford excellent yields and enantioselectivities in asymmetric allylic alkylation reactions. Recently, the method has been extended to colloidal Pd modified by a chiral xylofuranoside diphosphite. This catalyst system affords up to 97% *ee* at medium conversions [1], and is one of the very few examples on highly enantioselective reactions on heterogeneous catalysts apart from the thoroughly investigated hydrogenation reactions. Here we report an extension of the method to other catalyst-modifier systems, using the same model reaction, the transformation of racemic **1** to **2**.



Allylic alkylation of **1** has been carried out on Pd/Al_2O_3 modified with various P-containing compounds such as (*S*,*S*)-chiraphos or (*R*)-BINAP. Several reaction parameters like the catalyst pretreatment, the reaction temperature and the concentrations of both the nucleophile and modifier have been studied. Under optimized reaction conditions high conversion and good chemo- and enantioselectivity were achieved at reasonably low catalyst/substrate and modifier/substrate ratios. Interestingly, the enantioselectivity of the homogeneous system with (*R*)-BINAP as ligand depends strongly on the reaction temperature, whereas the opposite holds for the heterogeneous system.

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Organic Chemistry **282**

Strand Invasion by α-tricyclo-DNA

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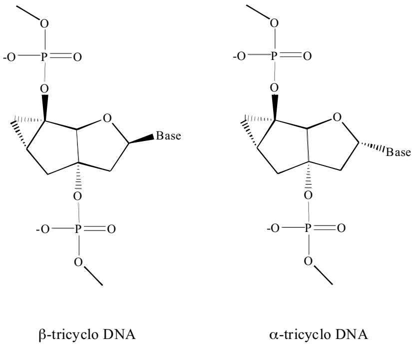
β-tricyclo (tc) DNA is a third generation antisense oligonucleotide that has been extensively studied in our lab [1]. We recently became interested in the pairing properties of the α-anomeric form and observed parallel orientation in the duplexes with natural DNA and RNA complements [2]. Interrestingly, within its own backbone series α-tc-DNA exhibits poor thermal stability which makes it a candidate for strand invasion applications. We present recent results on the triplex forming and strand invasion properties of α-tc DNA.



β-tricyclo DNA α-tricyclo DNA

[1] D. Ittig, S. Liu, D. Renneberg, D. Schümperli, and C. J. Leumann, *Nucleic Acids Research*, **2004**, *32*, 346–353

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Organic Chemistry **283**

Catalytic Electrophilic Amination of ß-Keto Ester

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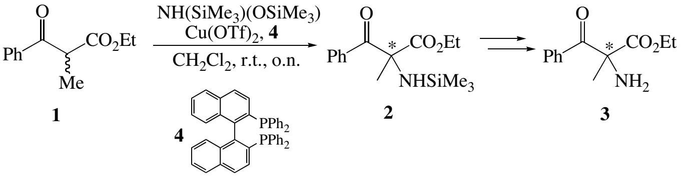
Very few catalytic asymmetric syntheses of α-amino acid involving carbon-nitrogen bond forming reactions have been described in literature.[1] Our group recently reported an efficient electrophilic amination of ß-keto esters catalyzed by chiral copper(II)-bisoxazoline.[2] However, this method gives α-hydrazino ß-keto esters, which are difficult to convert to the desired amino acids.



We present now a new direct α-amination of ß-keto ester **1** catalyzed by a copper(II)-binap (**4**) complex with bis(trimethylsilyl)-hydroxylamine as the nitrogen source. The reaction gives ß-keto-ester **2**, which is a convenient precursor of the corresponding α-amino acid **3**. Our efforts are currently directed toward the optimization of the reaction conditions and the full characterization of the products.

[1] Marigo, M.; Juhl, K.; Jørgensen, K.A.; *Angew. Chem. Int. Ed.*, **2003**, *42*, 1367.
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Organic Chemistry **284**

A target assembled tandem oligonucleotide probe assay based on excimer formation

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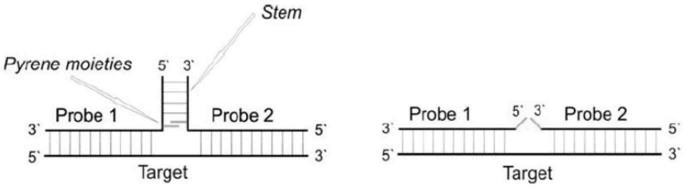
Freiestrasse 3, 3012 Bern, Switzerland

The tetracyclic hydrocarbon pyrene is well known for its ability to form an excimer emission band and has been studied extensively as a reporter fluorophore[1]. This dual probe assay based on excimer formation of incorporated pyrene moieties with an additional stem is able to discriminate a single-base insertion much better than does the assay with the pyrene moieties terminally attached.
We have studied the use of non-nucleosidic pyrene building block in the context of a dual probe assay. Of particular interest was the discrimination of single base mismatches. The results will be presented.



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Organic Chemistry **285**

Selective Interactions of Silver Ions with Peptides

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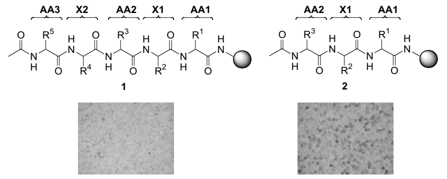
Numerous antibacterial silver compounds are used in medicine and hygiene. The combination of silver and organic materials is important because of supramolecular or surface aspects and the formation of nanostructures. There is a growing interest in exploiting their optoelectronic and chemical properties which have potential applications in nanoelectronics[1], bioanalytical processes[2] and catalysis.[3]

To gain insight into molecular interactions of silver ions with peptides we used a combinatorial approach. We synthesized two encoded split-and-mix peptide libraries containing the amino acids D/L-Asp, D/L-Ser, D/L-His, L-Tyr (**AAn**), linear spacers like Gly, ß-Ala, aminohexanoic acid and turn inducing motives like Pro-Gly, Pro-Aib and *trans*-2-aminocyclohexane carboxylic acid (**Xn**).



Herein we present selective Ag-peptide interactions identified in combinatorial screenings between the peptide libraries and $AgNO_3$.

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Organic Chemistry **286**

Synthesis Of A C-Nucleotide DNA Analogue

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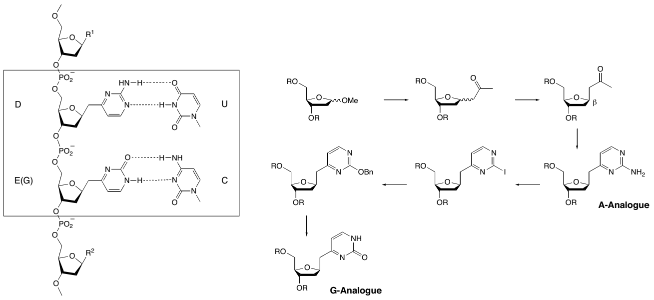
What came before A? This is a fundamental question in origin of life science.

Adapted from the fact that purine bases decompose under oxidative stress to the corresponding pyrimidines Siegel and Tor have proposed a possible precursor of present day DNA based only on pyrimidine bases [1, 2], in which the full set of bases is: D, E(G), C and U (see Scheme 1). In this work two new C-Nucleoside A and G Analogues were synthesized in order to test this hypothesis chemically and physicochemically.



Scheme 1: Pyrimidine based DNA and Synthesis of the Analogues.

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Organic Chemistry **287**

Selective, gold catalyzed alcohol oxidation in supercritical CO_2

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In the growing field of gold catalysis the oxidation of alcohols has attracted considerable attention [1,2]. However, the gold-catalyzed heterogeneous selective oxidation of alcohols to the corresponding aldehydes normally requires the use of environmentally harmful oxidants and solvents and the necessity of a base in aqueous solution. Generally, a very low activity is observed in solvent-free reactions. Therefore, the aim of the present study was to develop a reaction system based on the use of the simple oxidants O_2/air and supercritical CO_2 as environmentally benign solvent. Differently supported gold catalysts (TiO_2, Fe_2O_3, C) were used with the model substrate benzyl alcohol in a high pressure batch reactor (see scheme) [3].

$$\text{R-CH}_2\text{OH} \xrightarrow[\text{scCO}_2]{\text{Au/TiO}_2,\ \text{O}_2} \text{R-CHO}$$

Conversions, which were 2 to 10 times higher than in solvent-free reactions, and selectivities of more than 99% show the benefit of both gold as catalyst and $scCO_2$ as reaction medium. The phase behavior was studied in a view cell with IR-transmission and ATR-IR spectroscopy. Further improvement of the performance of the catalytic system may be achieved by fine tuning of the support properties, the size and the morphology of the gold particles, and finally the application of a continuous fixed-bed reactor.

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[2] Haruta, M., et al. *Res. Chem. Interm.*, **1998**, 24, 329.
[3] Kimmerle, B., Grunwaldt, J.-D., Baiker, A., *Top. Catal.*, **2007**, in press

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Organic Chemistry **288**

Fluorescent Chemosensors for Aqueous Hg(II).

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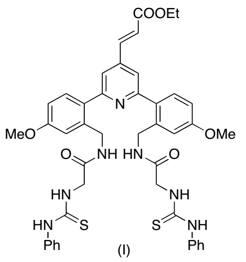
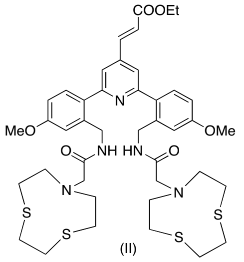
A solution phase analogue (I) of biarylpyridene fluorophore discovered on solid support [1] has been synthesized and its fluorescent properties upon addition of Hg(II) have been investigated. Titration with $HgCl_2$ (in pH 7 buffer) showed ca. 2-fold fluorescence enhancement as a function of added Hg(II), with a binding constant of K_a=5.5x10^{-5} M^{-1}. We have found that titration with an excess of Hg(II) leads to a decrease in fluorescence consistent with competitive formation of 2:1 Hg(II):ligand complex.

Another interesting compound serving as fluorophore with the same biarylpyridene signaling subunit (II) has also been found. As a binding domain, S-containing crown ether has been chosen. This compound displayed strongly-enhanced fluorescence upon addition of Hg(II), with lesser increases seen upon addition of AgOTs and $CdCl_2$.





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CHIMIA **2007**, *61*, No. 7/8

Organic Chemistry **289**

Aerobic Oxidation of Xanthene Catalyzed by Au^{3+}/CeO_2

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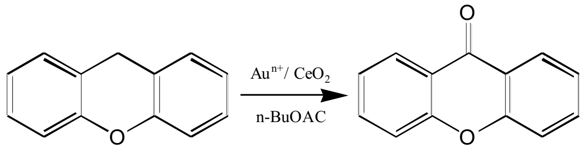
Since the pioneer work of Haruta [1], it is well known that supported gold nanoparticles catalyze some oxidation reactions with molecular oxygen as the sole oxidant. The real nature of active sites (Au^0 or Au^{n+}) is, however, still debated. [2] Our aim was to develop supported Au^{3+} catalysts and test them in benzylic oxidations, a reaction that has not been investigated before with gold catalysts.

An extensive catalyst screening revealed that the best composition was $AuCl_3$ supported on CeO_2. This catalyst, containing only 0.1 wt% Au, transformed xanthene quantitatively to xanthenone at 100°C (Scheme below).



During the synthesis of the catalyst special care was taken to avoid reduction of gold and the cationic form was maintained also during the oxidation reaction. In addition, prereduction of the catalyst by hydrogen at 125°C reduced the activity in xanthene oxidation to one-half. Kinetic analysis revealed that the reaction rate increased linearly with increasing substrate concentration, but it was independent of the oxygen partial pressure in the range 0.5-2 bar.

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[2] Qi Fu, Howard Saltsburg, Maria Flytzani-Stephanopoulos, *Science,* **2003**, *301*, 935.

Organic Chemistry **290**

Electrophilic Trifluoromethylation With Iodine(III) Compounds

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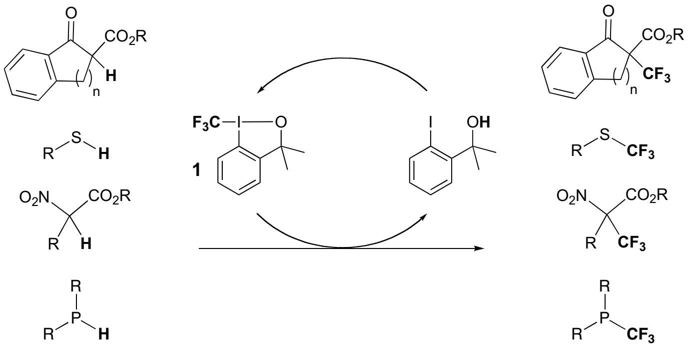
ETH Zürich, CH-8093 Zürich, Switzerland

Organofluorine compounds are important targets both in academia and industry. They show modified physico-chemical and physiological properties as compared to their non fluorinated counterparts. The develpoment of mild and selective methods for the introduction of CF_3 groups into complex molecules constitutes one of the most challenging tasks of modern organic chemistry.

Here we present a new, easily accessible, mild, and recyclable electrophilic trifluoromethylation reagent **1** based on hypervalent iodine. **1** can be used to transfer a CF_3 group to nucleophiles, such as acidic carbonyl compounds, thiols, and phosphines. [1]



[1] a) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579;
b) I. Kieltsch, P. Eisenberger, A. Togni, *Angew. Chem.* **2007**, *119*, 768.

Organic Chemistry **291**

Homo-DNA Molecular Beacons

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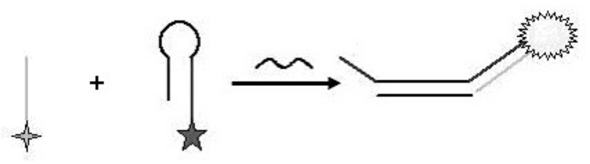
Molecular beacons (MBs) are stem-loop DNA probes used for identifying and reporting the presence and localization of nucleic acid targets *in vitro* and *in vivo*. Recently, we showed that MBs with a homo-DNA stem exhibit increased DNA-target binding selectivity due to the orthogonality of the homo-DNA pairing system [1]. We now extended this project by introducing a novel approach for reporting the presence of a target which does not rely on fluorescence dequenching but on the *de novo* generation of fluorescence *via* homo-DNA templated chemical synthesis of a fluorophore or homo-DNA templated non-covalent reconstitution of an enzyme that transforms a non-fluorescent substrate into a fluorophore.



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Organic Chemistry **292**

Towards the synthesis of pyrrolidino pseudouridine

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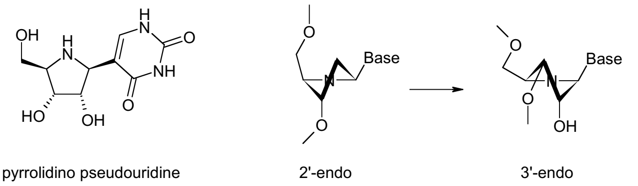
Pyrrolidino nucleotides as third strand constituents are expected to stabilize DNA triplexes because of salt-bridge formation between target DNA duplex phosphate residues and the pyrrolidino ring nitrogens of the third strand, in addition to the base-base contacts (dual recognition).

Stability measurements of the pyrrolidino 2'-deoxy-pseudoisocytidine[1] and the pyrrolidino 2'-deoxy-pseudouridine[2] showed that the former modification lead to a stabilization, whereas the latter destabilized the triplex. One possible explanation is that the conformation of the pyrrolidino 2'-deoxy-pseudouridine (2'-endo) is generally unfavorable for dual recognition.

We therefore decided to synthesize pyrrolidino pseudouridine for which the 3'-endo conformation can be expected to be energetically more favorable. We present the synthesis of pyrrolidino pseudouridine as well as its incorporation into triplex forming oligonucleotides.



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Organic Chemistry **293**

Investigating the transition between the two helical conformations of Polyproline

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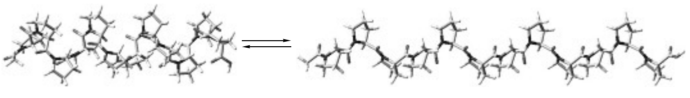
Poly-L-proline adopts two stable helical conformations depending upon the solvent. In the polyproline I (PPI) helix all peptide bonds are in *s-cis* conformations, whereas in the polyproline II (PPII) helix they are in *s-trans* conformations [1].



This poster presents investigations on the cooperative transformation from the left-handed PPII helix to the right-handed PPI helix. Our special interest concerns the starting point of the amide bond isomerisation in this system of two well defined secondary structures. We studied the thermodynamic equilibrium and the kinetics of this conversion by CD spectroscopy in aqueous phosphate buffer, 1-propanol and mixtures thereof. 4-Azidoprolines (Azp) were incorporated as probes into dodecamers, since (4*R*)Azp shifts the equilibrium to the PPII and (4*S*)Azp to the PPI conformation [2,3]. Furthermore a variation of the functionality at the termini of the peptides shows large effects on the studied equilibrium.

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Organic Chemistry **294**

1-1'-Bridged Derivatives of 4,4'-Bisaryl-2,2'-bibenzimidazoles as Building Blocks for Supramolecular Structures

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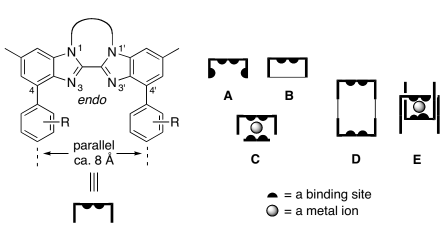
Derivatives of 4,4'-bisaryl-2,2'-bibenzimidazole[1] have the potential to participate in novel, complex supramolecular structures, due to their unique photophysical, coordination, and complexation properties. Although 2,2-bibenzimidazole (BBI) has been studied extensively, the supramolecular applications of BBI derivatives remain largely undiscovered. Bridging of the 1,1'-positions forces 4,4'-bisaryl-BBI to adopt a U-shaped conformation that can be manipulated to generate various, higher order structures.

A series of bridged BBI ligands have been synthesized and their complexation, photophysical, and crystal structure properties have been examined. Also, recently uncovered supramolecular applications will be presented.



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Organic Chemistry **295**

Subcomponent Exchanges in Self-Assembled Metallo-Organic Structures

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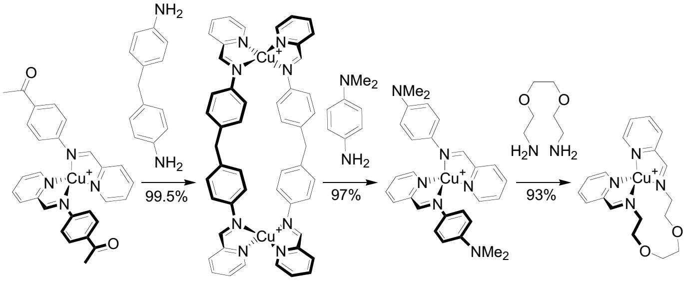
Using the principles of subcomponent self-assembly we can build structures that are held together by two kinds of reversible bonds, covalent (C=N) and coordinative (N□M) bonds, giving the possibility for dynamic sorting [1] and substitution [2, 3] to occur.

Substitution of ligand subcomponents in such metallo-organic complexes is governed by several factors, such as pH, electronic effects or the chelate effect, that can be used to quantitatively and selectively transform one structure into another. Combining these effects we have been able to design the three-step transformation of a series of copper containing structures shown below, where each step proceeds in predictably high yield [2].



[1] David Schultz and Jonathan R. Nitschke, *Angew. Chem. Int. Ed.* **2006**, *45*, 2453.
[2] David Schultz and Jonathan R. Nitschke, *J. Am. Chem. Soc.* **2006**, *128*, 9887.
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Organic Chemistry **296**

Towards sulfur terminated carbon nanotubes

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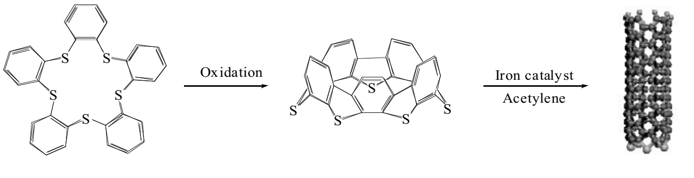
University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland

Carbon nanotube research is a very hot topic and there is still a vast research activity on this subject. Fabrication of different types of carbon nanotubes has meanwhile become a mature industrial task. However, all fabrication processes and nanotubes syntheses use physical methods for producing this material, no rational chemical synthesis exists so far.



1 **2**

There is evidence for an iron catalyst capable of polymerizing and dehydrogenating acetylene to graphitic structures. Provided that an appropriate template such as compound **2** could be obtained, one could expect carbon nanotubes growth on this template. Therefore, the problem consists in finding a route for the synthesis of the macrocycle **1** formed by five aromatic rings linked by five sulfur atoms, since the aromatic rings of compound **1** could be linked oxidatively by a known procedure. Such a template would allow for an uniformity of diameter, orientation and length of the nanotubes formed. Last step for the formation of macrocycle **1** is under investigation.

Organic Chemistry **297**

Protection of glycosides using orthogonal photolabile protecting groups

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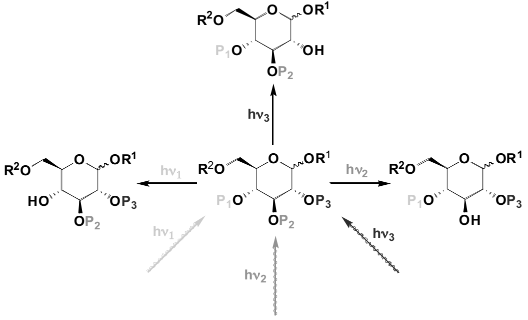
Recently, the Bochet group developed the concept of chromatic orthogonality consisting in the selective cleavage of two different photolabile protecting groups using two different wavelengths [1]. These sorts of cleavage only requiring light and no additional reagents could apply as an appropriate answer to the challenges of the automated oligosaccharide synthesis.



Our goal is to develop methods using known orthogonal photolabile protecting groups to protect hydroxyl groups of glucose as ethers to obtain a potential orthogonal two-dimensional wavelength system [2] [3] coupled with a third sequential photo-deprotection. We will in particular show the strategies involved for such type of protection using photolabile groups and our results in terms of selectivity.

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Organic Chemistry **298**

Reactivity of Benzofuran Aldehyde with Indoles in Presence of HBr

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S. Hell-Michel, K. Burri, D. Gillessen, K. Islam

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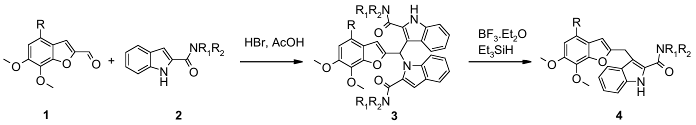
In order to explore the potential of 3-Benzofuran-2-ylmethyl-1H-indoles in the search of novel antibacterial agents, we studied different synthetic routes to introduce a methyl-2-benzofuran scaffold in position 3 of indoles. A first approach involved the reaction of 2-chloromethyl-benzofuran with the corresponding indole under basic conditions. However, using these reaction conditions, a non-reproducible mixture of two different C and N alkylated compounds was obtained. In order to increase the selectivity toward the C alkylated compound, we had explored alternative conditions such as the one described by Vlasova et al.[1]. We now wish to report the first reaction between a benzofuran-2-carbaldehyde **1** with indoles **2** under HBr conditions. Such a reaction leads in our case to an indolidene **3**, in which one of the indole nuclei is attached via its 2(C)-, the other via its 1(N)-position to the benzofuran moity, contrary to the doubly C alkylated dimer reported by Ovsyannikova et al.[2]. The so obtained bisindole **3** had the advantage that it could be reduced selectively with $BF_3.OEt_2$ and Et_3SiH[3] to the C alkylated, target compound **4**.



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Organic Chemistry **299**

Dyes for HD DVD Recordable Discs

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The 405 nm Optical Information Storage Technology is a new generation to store digital sound and video with high quality. The storage capacity of a single layer disc is 15 to 27 GB, compared to 0.7 GB for a CD-R disc and 4.7 GB for a DVD-R disc. The key to higher capacity is a smaller laser beam spot size, which is proportional to the wavelength λ of the light source and inversely proportional to the numerical aperture of the objective lens.

Two formats have been proposed for the 405 nm recordable discs based on organic dyes: BluRay and HD DVD. Our goal is to develop an organic dye satisfying all the demanding requirements of the product profile for both single layer and double layer HD DVD. Product development is made in close collaboration with Plasmon PLC, Melbourn (UK). Competing systems are based on inorganic phase change technology.

The poster will display the basic principles of such a recording system, the synthesis, the physical properties and the application of cationic dyes stabilized with metal complex anions.

Organic Chemistry **300**

Catalytic asymmetric formation of allylic amines with quaternary stereocenters via the aza-Claisen-rearrangement

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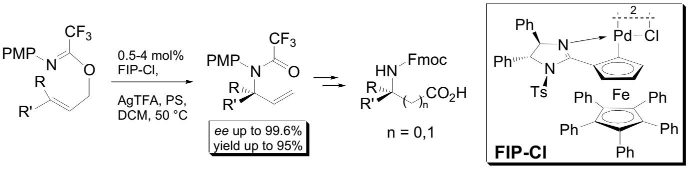
HCI D 102, CH-8093 Zürich

Enantiomerically pure allylic amines are valuable building blocks, since they possess two highly versatile functional groups. Two widely used methods for their preparation are the transition metal catalyzed allylic substitution[1] and the aza-Claisen rearrangement of trihaloacetimidates (Overman rearrangement).[2] However, none of these two methods previously permitted the enantioselective formation of quaternary stereocenters.



Our ferrocenyl imidazoline palladacycle catalyst FIP is ca. 100 times more reactive than the best previously known catalytic systems.[3] This allowed us to perform the title reaction with 3,3-disubstituted imidates (0.5 to 4 mol% catalyst) leading to the products with high yields and excellent *ee*'s.[4] The usefulness of these compounds was demonstrated by formation of α- and β-aminoacids with a quaternary stereocenter adjacent to the N atom.

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[4] D. F. Fischer, Z.-q. Xin, R. Peters, manuscript in preparation.

Organic Chemistry **301**

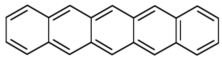
Synthesis, Crystal Structure and FET Mobility of Rubrene Derivatives

Ulrich Berens[†], Bertram Batlogg[‡], Wolfgang Kalb[‡], Hans-Jörg Kirner[†],
Beat Schmidhalter[†], Arno Stassen[‡].

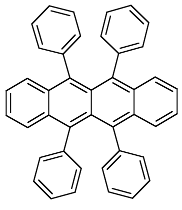
[†]Ciba Group Research, Klybeckstrasse, CH-4002 Basel, Switzerland
[‡] ETH Laboratory for Solid State Physics, CH 8093 Zürich, Switzerland

Recently, many new organic semiconductors (OSCs) have been synthesized to find a 'better' material than pentacene.[1] Flat aromatic molecules with good intermolecular overlap of π-orbitals and dense packing in the crystal structure are considered to be ideal for charge transport..[2]

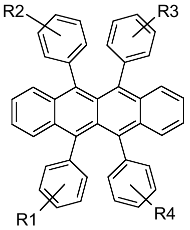
We have discovered that this 'ideal' structure is not necessary to obtain high field-effect mobilities. A series of substituted rubrenes was prepared and one derivative was found to have almost identical electrical transport properties as rubrene, whereas its crystal packing is far from the 'ideal'.



Pentacene



Rubrene



References

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Organic Chemistry **302**

Preparation of DNA Conjugates Employing [3+2]-Azide-Alkyne Cycloaddition Reactions

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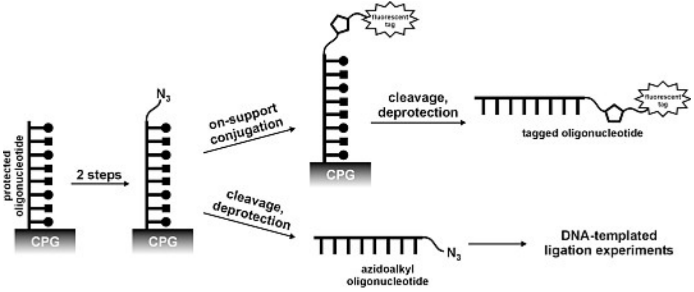
The design of oligonucleotide (ON) derivatives conjugated to non-nucleosidic molecules has attracted notable attention, as such chimeras can provide novel tools for bioorganic chemistry and molecular biology. Copper(I)-catalyzed azide-alkyne cycloadditions, which have been widely applied in different areas of organic and bioorganic chemistry,[1] have proven to be suitable for ON conjugation.[2]

With the aim to establish a simple method for the introduction of short azidoalkyl groups into ONs, we developed a convenient solid-support synthesis, with which the desired azide-bearing ON derivatives are readily accessible. Ligation experiments using such modified ONs both fully protected on solid support as well as unprotected in solution will be presented (see scheme).



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[2] Li, X.; Liu, D. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 4848-4870.

Organic Chemistry **303**

Gold nanoparticles functionalized with dendrimers as an organic matrix

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Georg Süss-Fink[1] and Robert Deschenaux[1]

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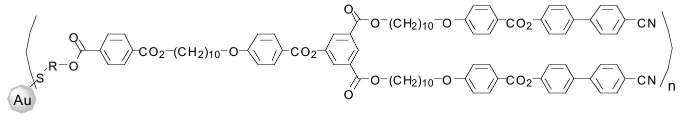
Dendrimers are regularly branched molecules characterized by a perfect structure. They arouse a great scientific interest because of their unique molecular architecture.[1] In addition, gold nanoparticles exhibit optical properties that depend on their size as well as on their organization.[2] The combination of gold nanoparticles with dendrimers leads to the incorporation of metal particles in a well organized organic matrix. Particles thus encapsulated are protected from agglomeration and see their polarity and solubility modified. In this project, gold nanoparticles end-functionalized with hydroxyl groups were esterified with dendrimers bearing a carboxylic acid function. This material was obtained in pure form after separation from unreacted particles and dendrimers *via* size exclusion chromatography. Transmission electron microscopy and polarized optical microscopy indicate that the dendrimers promote the organization of the gold particles in two and three dimensions.



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Organic Chemistry **304**

Synthesis and Properties of Ir(I) and Rh(I) Metal Complexes of Pentaalkyl Substituted Corannulene Derivatives

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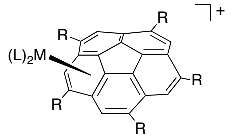
The synthesis of a metal complex having corannulene as ligand was first reported in 1997. [1] In 2006 Dorta and Siegel [2] reported metal complexes of Ir(I) and Rh(I) with monodentate and bidentate cyclic olefins. Such molecules bind η^6 in the solid state and the Rh(I) compounds show fluctional behavior at RT.



R = Me, *t*-Bu
M = Ir(I), Rh(I)
L = COE, COD, NBD

In the present work pentaalkyl substituted corannulene derivatives were used to prepare a series of analogous complexes with the goal of understanding substituent effects in the solid state and in solution. Preliminary results suggest accordingly with Dorta's work that all Ir(I) compounds do not show dynamic behavior at RT. In contrast, the new Rh(I) compounds having L = COD, NBD and R = Me, *t*-Bu do not show dynamic behavior at RT. An exception is the Rh(I) complex with L = COE and R = Me. These results demonstrate that changing the corannulene substituents and/or the metal ligand fragment correlates with changes in the complex's behavior.

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Organic Chemistry **305**

Peptides as Catalysts for Asymmetric 1,4-Addition Reactions of Aldehydes to Nitroalkenes

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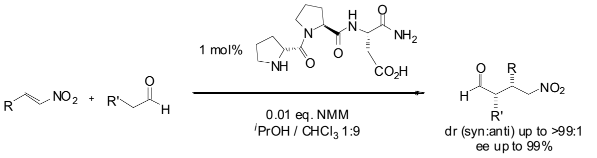
Recently our group introduced the peptides H-Pro-Pro-Asp-NH$_2$ and H-Pro-D-Ala-D-Asp-NH$_2$ as efficient catalysts for direct aldol reactions.[1] They were identified by combinatorial screening of a split and mix library, using the method of catalyst-substrate co-immobilization.[2] Computer modelling studies indicated that the distance between the secondary amine and the carboxylic acid is approximately 3Å longer, in comparison to that of proline. This finding suggested that the extra distance of 3Å could be spanned by two extra atoms. This led us to investigate asymmetric 1,4-addition reactions of aldehydes to nitroalkenes.



Preliminary experiments demonstrated that H-Pro-Pro-Asp-NH$_2$ and related peptides are efficient catalysts for these reactions. Using only 1 mol% of the catalyst affords up to 99% yield and selectivities up to 99% ee.

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Organic Chemistry **306**

Are Peptide Dendrimers Resistant to Proteases?

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Peptide dendrimers are useful models for proteins and can display catalytic activity as well as favourable properties for drug delivery [1]. In view of possible biomedical use of these dendrimers, an investigation of their proteolytic lability is important.[2] An early study showed that tryptic sites embedded in peptide dendrimers are indeed accessible to proteases [3]. We have now extended this study by high-throughput screening of combinatorial peptide dendrimer libraries against proteases, using a protease profiling protocol recently developed in our laboratory [4]. Both reactive and unreactive dendrimer sequences were identified and investigated in solution, compared with the corresponding linear peptides. The results of this investigation will be presented.

[1] a) E. Delort, T. Darbre, J.-L. Reymond, *J. Am. Chem. Soc.* **2004**, *126*, 15642-15643.
b) D. Lagnoux, T. Darbre, M. L. Schmitz, J.-L. Reymond, *Chem. Eur. J.* **2005**, *11*, 3941-3950.
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Organic Chemistry **307**

A new tetrathiafulvalene- tetracyanoanthraquinodimethane (TTF-TCNAQ) diad with a chemically tunable HOMO–LUMO gap

Jincai Wu,[a] Shi-Xia Liu,*[a] Antonia Neels,[b] Franck Le Derf,[c] Marc Sallé[c] and Silvio Decurtins[a]

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The molecules with low HOMO-LUMO gaps are of prime importance for the good performance of the organic electronic devices [1]. As a consequence, much effort has been devoted to the preparation of a variety of π-conjugated oligo- or polymers as well as to covalent linkage of a π-electron donor (D) to a π-electron acceptor(A) through a π or a σ-bonded bridge. The latter has received a great deal of attentions due to their potential application in fields such as molecular electronics, nonlinear optics, photovoltaics, artificial photosynthetic models and so on. Here, we report an imidazol-incorporated TTF-TCNAQ diad (Fig. 1) with tuning HOMO–LUMO gap in presence of DBU.

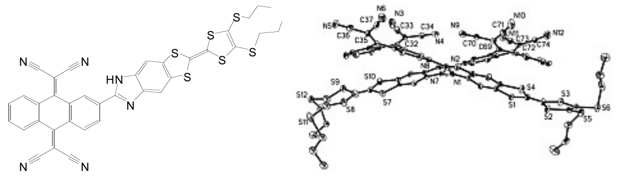

Fig. 1 Structure of TTF-TCNAQ Diad.

[1] Evgeny T., Jame Y. B., Vladimir K., Alex S. and Lev S. *Angew. Chem. Int. Ed.* **2005**, 44, 4015.

Organic Chemistry **308**

Synthesis and Photochemical Characterization of Conjugated Molecules Using Thiophene and Pyridine as Building Blocks

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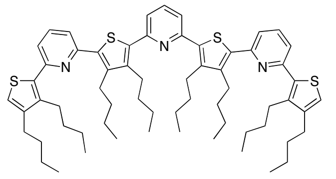
Conducting thiophene polymers are important in materials science applications such as organic light emitting devices and solar cells, but because of their polydispersive character the characterization is not direct. Consequently, due to their monodispersive character, conjugated oligothiophenes are frequently investigated as models for these materials [1]. Related to these are conjugated copolymers consisting of electron-donating and electron-accepting units, leading to lower energy band gaps than those of the corresponding homopolymers [2].



A series of oligomers containing alternating electron rich, tiophene, and electron poor, pyridine, as subunits was designed, successfully synthesized and had their photochemical properties characterized.

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[2] Shintaro Sasaki *et al.*, *J. Am. Chem. Soc.*, **1996**, 118, 10389.

Organic Chemistry **309**

Absolute configuration of chirally deuterated neopentane

J. Haesler, I. Schindelholz, E. Riguet, C. G. Bochet* & W. Hug*

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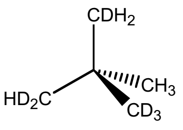
Fribourg, Switzerland

Determination of absolute configuration of asymmetrical molecules is a longstanding problem in chemistry. Recent advance in Raman Optical Activity (ROA)[1], combined with quantum chemical computations[2], is a promising spectroscopic technique for determination of the absolute configuration of a wide range of molecules.



(R)-[$^2H_1$, $^2H_2$, $^2H_3$]-neopentane

We describe the asymmetric synthesis of (R)-[$^2H_1$, $^2H_2$, $^2H_3$]-neopentane which possess structural chirality of the utmost delicacy and the assigment of its absolute configuration using ROA spectroscopy [3].

[1] W. Hug & G. Hangartner, *J. Raman Spectrosc.* **1999**, *30*, 841–852
[2] W. Hug & J. Haesler, *Int. J. Quantum Chem.* **2005**, *104*, 695-715
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Organic Chemistry **310**

Synthesis of a Combinatorial Natural Cyclic Peptides Library Using a New TagsFree Encoding Method

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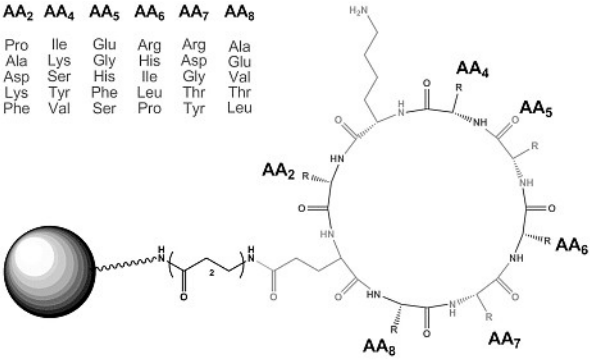
Here we report a self-encoding one-bead one-compound library of 15625 cyclic peptides**[1]** using a combinatorial split and mix approach. A new encoding method – TagsFree– based on amino acid analysis and computational methods, was applied to identify the sequences**[2]**. The library was used to study the sequence dependence of the on-bead cyclisation propensity. Sequences have been discovered showing prevailing patterns as turn inducers.



AA_2	AA_4	AA_5	AA_6	AA_7	AA_8
Pro	Ile	Glu	Arg	Arg	Ala
Ala	Lys	Gly	His	Asp	Glu
Asp	Ser	His	Ile	Gly	Val
Lys	Tyr	Phe	Leu	Thr	Thr
Phe	Val	Ser	Pro	Tyr	Leu

Fig 1: Representation of a combinatorial cyclic-octapeptides-library

[1] Dummy P., *Org. Biomol. Chem.*, **2006**, *4*, 2628.
[2] Kofoed J., J-L. Reymond, *Submitted*

Organic Chemistry **311**

Studies on Long Chain Substituted Extended Porphyrins – new Mesophases ?

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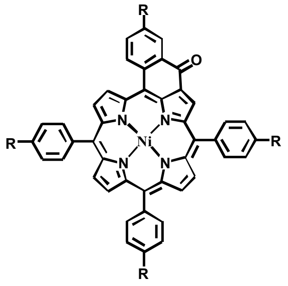
University of Neuchâtel, Rue Emile Argand 11, CH-2009 Neuchâtel,
Switzerland

We synthesized a series of different substituted oxonaphthoporphyrins.



R = (CH$_2$)$_n$CH$_3$; OCO-long chain

Starting from this type of molecules, we checked the ability of the synthetic methods to produce bi – and multicyclized extended porphyrins.[1]
All the final products will be tested for their optical and liquid crystalline properties.
Molecules of this shape should form columnar discotic mesophases and they could have interesting properties with regard to electron transfer processes.
We envisage these molecules could be good candidates for applications such as OLED’s or solar cells.

[1] J. Org. Chem. **2003**, 68, 9200-9208

Organic Chemistry **312**

A Novel Strategy for the Synthesis of Irregular Cyclic Polypyrrole Derivatives

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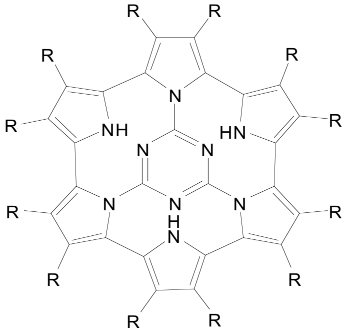
Institut de chimie, Université de Neuchâtel, Av. de Bellevaux 51,
2009 Neuchâtel, Switzerland

Polypyrroles have interesting optical, nonlinear optical and electrical conduction properties [1, 2]. A better understanding of the properties of the polymer itself and of the electropolymerization process can be expected from the study of short cyclic oligomers. These compounds represent a new type of materials due to the irregular cyclic structure. Ongoing project include efforts toward the irregular cyclic polypyrrole derivatives **1**.



R= H or alkyl **1**

The results of these investigations will be shown and discussed.

[1] S. Millefiori, A. Alparone, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 25
[2] C.P. Andrieux, P. Hapiot, P. Audebert, L. Guyard, M. Guyen Dinh An, L. Groenendaal, E.W. Meijer *Chem. Mater.* **1997**, *9*, 723.

Organic Chemistry **313**

Dearomatisation *via* [Cr(arene)(CO)$_3$] Complexes : Synthetic Studies toward Bicyclic Molecules

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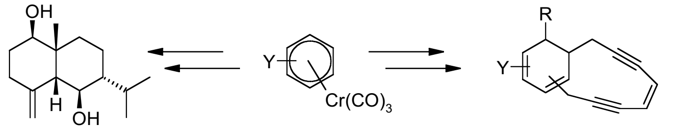
Ansermet, CH-1211 Geneva 4, Switzerland

Coordination of an arene with the [Cr(CO)$_3$] fragment enables the nucleophilic attack. Subsequent alkylation of the anionic cyclohexadienyl complex intermediate at the metal center and reductive elimination gives *trans* cyclohexadiene.[1] This Cr-mediated dearomatisation sequence can be combined with ring closing metathesis to access *cis*-fused ring systems bearing a methyl group at one ring junction.[2] This strategy could be used to reach bioactive natural compound as the 5-*epi*-eudesma-4(15)-ene-1*β*,6*β*-diol which a rare *cis*-eudesmane.[3] We have also applied the nucleophile/electrophile addition reaction to the elaboration of novel cyclic enediynes introducing a propargyl group either *via* nuclephilic or electrophilic reagents.



5-*epi*-eudesma-4(15)-ene-1*β*,6*β*-diol

Bicyclo[8.3.1] enediynes

[1] *Transition Metal Arene π-Complexes in Organic Synthesis and Catalsis*, ed. E. P. Kündig, *Topics in Organometallic Chemistry*, vol 7, Springer Verlag, Berlin, Heidelberg, New York, 2004.
[2] Kundig, E. P.; Bellido, A.; Kaliappan, K. P.; Pape, A. R.; Radix, S. *Org. Biomol. Chem.* **2006**, *4*, 342.
[3] Jiang, H. X.; Li, Y.; Pan, J.; Gao, K. *Helv. Chim. Acta* **2006**, *89*, 558.

Organic Chemistry **314**

Synthesis of New Triphenylene Dimers Linked with Rigid Spacer

Damien Thevenet, Reinhard Neier*

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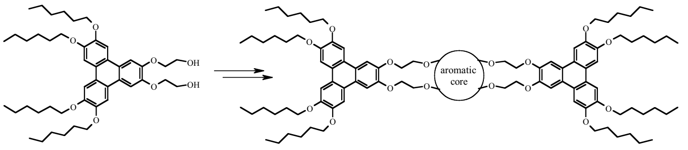
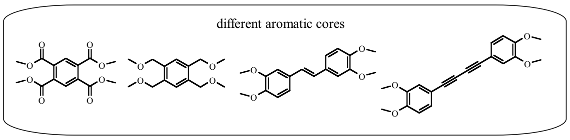
Discotic liquid crystals are unique nanostructures with remarkable electronic and optoelectronic properties [1]. Triphenylene derivatives play a major role in the research on discotic liquid crystals. A liquid crystal dimer is composed of molecules containing two mesogenic groups linked often, via a flexible spacer or more rarely, through a rigid spacer.





We are testing different strategies to connect two triphenylenes derivatives [2] **1** with a rigid linker, in order to obtain a material which forms a self-organization in hexagonal columnar mesophase.

[1] Kumar, S., *Liquid Crystals*. **2005**, *32*, 1089-1113 .
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Organic Chemistry **315**

New organic lighting materials for printable electronics

Roger Pretot*, Paul van der Schaaf, R. Kolly, F. Schwarzenbach

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For the past forty years inorganic semiconductors have been the backbone of the semiconductor industry. However, there has been a growing R&D effort in "organic electronics" to improve the semiconducting, conducting, and light-emitting properties of organics through novel synthesis and deposition techniques. Compared to traditional inorganic semiconductors, organic semiconductors exhibit excellent additional material properties.

Especially organic electronic materials in liquid solutions offer a disruptive technology enabling the direct printing of integrated (opto)-electronic systems onto almost any kind of substrate.

Ciba Group Research participates in an European Strategic Research Project (EU STREP) called **ROLLED** [1]. The project team consists of 7 partners, three research institutes (VTT, Finland; INM, Germany; CSEM, Switzerland) and four industrial partners (Ciba; UPM-Kymmene, Finland; Hansaprint, Finland; PolyIC, Germany). The project's goal is the development of a cost-effective, volume-scale, roll-to-roll manufacturing technology for the realization of flexible OLED devices with arbitrary size and shape pixels and displays on web. The task of Ciba in this project is the development of new materials for printable formulations. Novel materials and gravure printed OLED performance data will be discussed.

[1] Rolled is funded under the 6th EU-Framework programme (FP6-2003-IST-2-004315).

Organic Chemistry **316**

New pyrene derivatives for use as DNA labels

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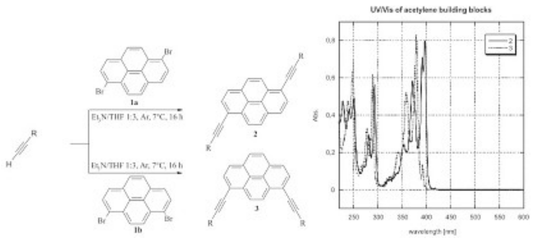
New artificial building blocks suitable for incorporation into oligonucleotides are described. Based on our previous work with non-nucleosidic polyaromatic derivatives we synthesised novel pyrene building blocks with extended π-systems. Symmetrical compounds containing alkinyl-substituents were obtained via the Sonogashira coupling reaction with the corresponding di-bromopyrene (see scheme) [1].

The novel modified oligonucleotides showed advanced spectroscopic properties, compared to the previously studied systems [2,3]. UV/Vis-, fluorescence- and CD-spectra as well as thermal denaturation experiments will be presented.



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Organic Chemistry **317**

Synthesis of Supramolecular Building Blocks

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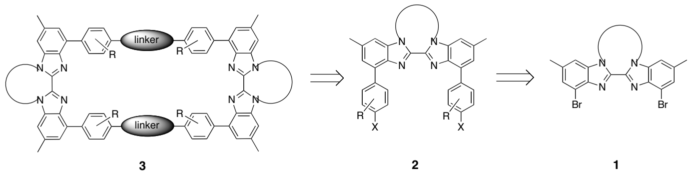
Supramolecular architectures can be constructed via self-assembly of molecular building blocks. Topologically interesting structures such as molecular rectangles, catenanes, and knots are synthetically accessible by this strategy.[1,2]

Our project deals with the synthesis and study of *N,N'*-bridged 4,4'-dibromo-bibenzimidazoles (**1**) and *N,N'*-bridged 4,4'-bisaryl-bibenzimidazoles (**2**) as molecular building blocks.[3] *N,N*-bridging of the bibenzimidazole unit locks the U-shape conformation, which is useful for constructing molecular rectangles (**3**). Furthermore, the cavity created by the bibenzimidazole unit is potentially capable of binding transition metal ions.



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Organic Chemistry **318**

Modified *B*-Alkylcatecholboranes as Radical Precursors

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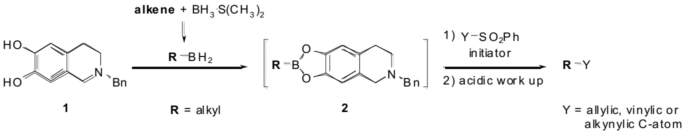
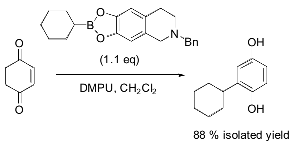
C-C bond forming radical reactions involving *B*-alkylcatecholboranes as radical precursors are well documented [1, 2]. However, in some cases product isolation is difficult due to the presence of catechol as by-product. For example, radical addition to 1,4-benzoquinone delivers a 2-alkyl-1,4-hydroquinone which is not easily separated from catechol.
Here we present a new approach involving modified *B*-alkylcatecholboranes **2** which are generated from the tetrahydroisoquinoline derivative **1** and alkylboranes. The modified catechol **1** is easily removed by an acidic aqueous work up.



This new approach allows to isolate the 2-substituted hydroquinone products from the conjugate addition to 1,4-benzoquinone in high yields.



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Organic Chemistry **319**

Formation of Stable Nitronates in the Radical Reaction of *B*-Alkylcatecholboranes with Tetranitromethane

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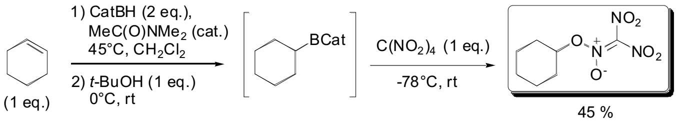
We have shown that *B*-alkylcatecholboranes are good alkyl radical precursors which react intermolecularly with a variety of unsaturated systems to form new C-C bonds [1]. Recently, we found that these radical precursors add to nitro groups creating a C-O bond. For example, a stable cyclohexyl dinitro nitronate is formed in the radical reaction of *B*-cyclohexylcatecholborane with tetranitromethane as the radical trap.



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Organic Chemistry **320**

New chiral ligands for Cu-catalyzed asymmetric conjugate addition

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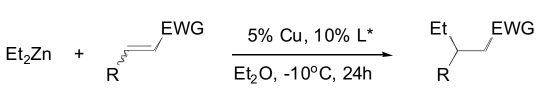
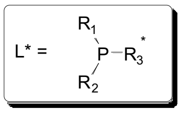
The conjugate addition reaction has received an impressive interest in the past decades. Many efforts have been made in designing efficient systems and identifying new ligands to improve enantioselectivities with specific families of substrates [1].
We have demonstrated that phosphoramidite ligands based on atropoisomerically flexible biphenol unit are also excellent ligands (ee's up to 99.5%) [2].
Consequently, we have synthesized a new class of phosphorous ligands and applied them in the copper-catalyzed 1,4 addition of diethylzinc to various Michael acceptors (ee's up to 96%).





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Organic Chemistry **321**

A Novel Class of Phosphorous Ligands: Synthesis and Applications

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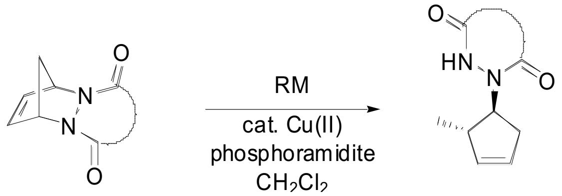
In our ongoing work on desymmetrization of bicyclic hydrazines, we were particularly interested in the report concerning asymmetric opening of these derivatives with alkyl metals and copper-phosphoramidite catalysts (Scheme 1) [1].



Scheme 1

Although this transformation proved to be very efficient, several points outlined by the authors were intriguing. To understand this observation, we investigated this reaction more in details. We could demonstrate that phosphoramidites reacted with trialkylaluminium and new ligands are formed. We will report here this new class of ligands, their synthesis and their application in copper catalyzed nucleophilic ring opening of bicyclic hydrazines [2].

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Organic Chemistry **323**

Alcohols and Water as Hydrogen Atom Source in Radical Reactions: A Kinetic Investigation

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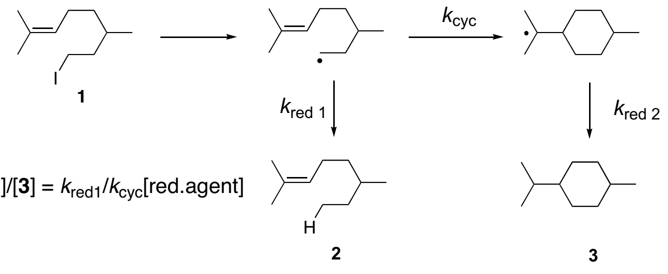
We have recently reported that alkyl radicals, generated by decomposition of *B*-alkylcatecholboranes under dioxygen or peroxide initiation, can be reduced by alcohol-catecholborane complexes [1]. We have applied this reaction for the reduction of halides, deoxygenation of alcohols and cyclization reactions.

The kinetic of the hydrogen transfer step has been investigated with 8-iodo-2,6-dimethyloct-2-ene **1** as a radical clock.



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Organic Chemistry **322**

Highly Efficient Pd-Catalyzed Desymmetrization Reactions

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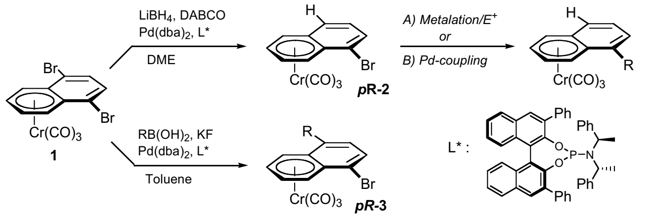
Highly enantioenriched (η^6-arene)tricarbonylchromium(0) complexes whose chirality originates from the 1,2-disubstitution pattern of the arene and the coordination of the metal to one enantiotopic face of the arene are powerful chirons in asymmetric synthesis. Robust, planar chiral arene complexes also increasingly find application as chiral ligands in asymmetric catalysis [1]. A potentially very attractive catalytic route is the desymmetrization of *meso*-complexes by a chiral catalyst.
We here detail a complete study of the catalytic asymmetric hydrogenolysis of **1** leading to the formation of highly enantioenriched planar chiral π-complex **2**, and its further transformations [2][3].



This chemistry has now been extended to asymmetric coupling reactions.

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Organic Chemistry **324**

Synthesis of copper(I) imine complexes through dynamic self-assembly and their selective transformation

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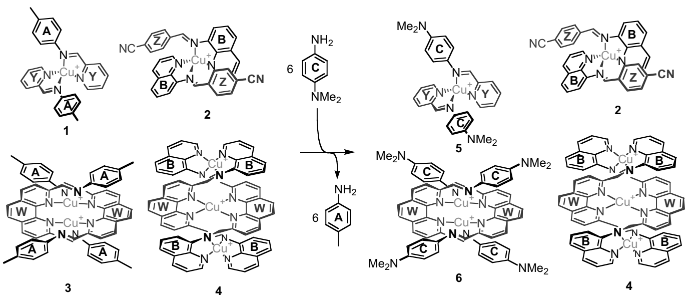
Subcomponent self-assembly involving reversible imine (C=N) bonds and Cu(I)–imine coordination gives access to a wide range of molecular architectures [1]. The dynamic nature of these molecules often leads to unusual structure-based reactivity patterns [2, 3].
We are investigating the reorganization pathways of the amine and aldehyde subcomponents around the copper (I) template through suitable tuning of steric and electronic properties. We may thus be able to select a subset of molecules within an assembly of constitutionally similar molecules for performing reactions such as imine substitution.



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Organic Chemistry **325**

Triple Helical DNA modified by polyaromatic building blocks

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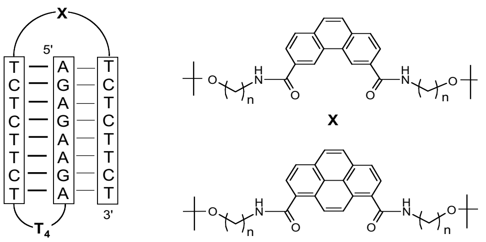
Pyrene and phenanthrene building blocks were used for the study of intramolecular triplex formation. It was found that the polyaromatic building blocks lead to a significant stabilization of intramolecular triple helices. Description of the relative orientation of the pyrene building blocks is rendered possible by the observation of exciton coupling in the circular dichroism spectra.

Furthermore, clamp-type oligonucleotides containing a non-nucleosidic pyrene linker were shown to form stable triplexes with a polypurine target strand containing a terminal pyrene or phenanthrene moiety. Stacking interactions between the unnatural building blocks enhance triplex stability and lead to strong excimer or exciplex formation, which is monitored by fluorescence spectroscopy.

The high mismatch sensitivity of the triplex formation allowed the construction of a *Triplex Forming Molecular Beacon* that leads to the efficient discrimination of single nucleotide mismatches. The binding of a clamp-type oligonucleotide containing two terminally attached pyrene molecules to the target sequence is easily monitored through excimer formation.



Organic Chemistry **326**

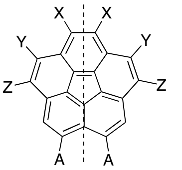
Synthesis of 1,3,5,7,9-penta-Substitueted Corannulene

Roman Maag, Tomoharu Hayama, Jay S. Siegel*

Institute of Organic Chemistry, University of Zurich, Winterthurerstr. 190, 8057 Zurich, Switzerland.

The most widely used method to access corannulene derivatives with mirror symmetry (**1**) follows the route from the corresponding naphthalene derivative to the substituted fluoranthene.[1] The general synthesis of *sym*-pentasubstituted corannulenes with 5-fold symmetry (**2**) was achieved using the pentachloride, i.e., **2**, with X = Cl, which in turn comes from a five-fold symmetric chlorination of the parent hydrocarbon.[2]

Despite these efficient methods, the synthesis of corannulene derivatives with five *different* groups at the 1,3,5,7,9-positions (**3**) remains unsolved. An additional challenge is to design unique functional groups for 1, 2, 3, 4 and 5, such that every site in **3** is selectively addressable. This platform is envisioned to be the basis for a library of corannulene derivatives.



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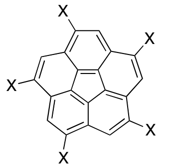

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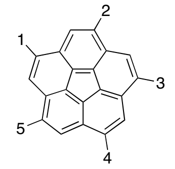

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[1] Seiders, T. J.; Elliot, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999,** *121*, 7804.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323.

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Organic Chemistry **327**

Tandem 1,5-Hydrogen Transfer - Cyclisation Mediated by Diethyl Thiophosphite

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Recently, we developed a tandem 1,5-hydrogen transfer - cyclisation process using diethylphosphite and DLP.[1] This reaction has been used to elaborate a wide variety of simple bicyclic and spirocyclic systems with low to good stereoselectivity. We now wish to report an improved procedure involving thiophosphites. The use of thiophosphites allows to carry out this cascade reaction under milder conditions and leads to enhanced diastereomeric ratios. Furthermore the cyclic thiophosphonates produced by this reaction are particularly attractive as they have been proven to be more efficiently transformed.[2]

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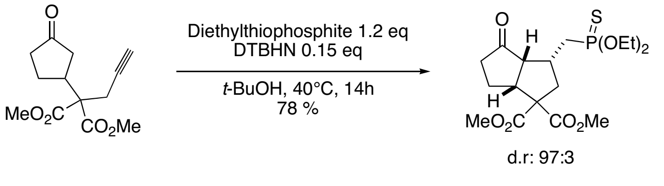

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Organic Chemistry **328**

New $PhSO_2N_3$ –mediated cyclization of dienes and enynes

Nathalie Mantrand, Philippe Renaud*

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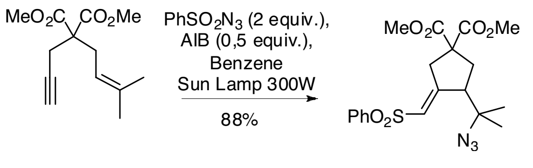
Radical reactions represent a valuable tool for organic synthesis [1]. For instance, the use of carbon-centred radicals has become widespread, particularly for ring formation. The reaction of 1,6-dienes or enynes with a range of sulfonyl compounds $ArSO_2Y$ (Y = Cl, Br, CN, SePh) has been reported by several groups. Nevertheless sulfonyl azide reagents were never used.

We reported recently an efficient method for intermolecular carboazidation of alkenes [2] using pyridine- or phenylsulfonyl azide. We demonstrate here that the benzenesulfonyl azide is also a suitable reagent for the radical cyclization of 1,6-dienes or enynes.



The free radical azidosulfonylation-cyclization process is useful for the preparation of a wide range of azidosulfones in good to excellent yields.

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Organic Chemistry **329**

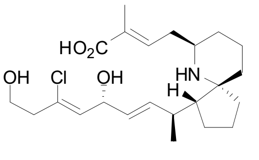
Toward a New Synthesis of Azaspirocyclic Core of Pinnaic Acid

Nathalie Mantrand, Philippe Renaud*

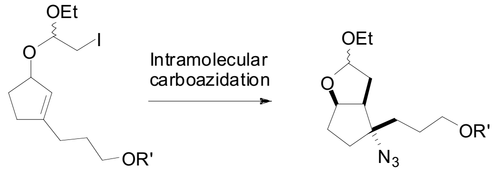
University of Berne, Freiestrasse 3, CH-3012 Bern, Switzerland

The marine alkaloid pinnaic acid was isolated in 1996 from the marine sponge *Pinna Muricata*[1] by Uemura and co-workers. This alkaloid bears a unique highly functionalized spiranic core representing the main synthetic challenge towards this natural product.

We envisioned that the azaspirocyclic core could be prepared via the intramolecular radical cyclization-azidation[2] reaction of a iodoacetal.



Pinnaic Acid



[1] Chou, T. ;Kuramoto, M.; Otani, Y.; Shikano, M.; Yasawa, K.; Uemura, D.; *Tetrahedron Lett.* **1996**, *37*, 3871.

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Organic Chemistry **330**

New Synthetic Pathway for Rhazinilam Analogues

Ana-Maria Buciumas, Olivier Vallat, Reinhard Neier*

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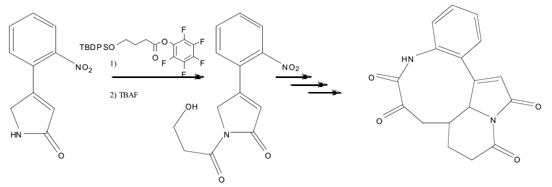
Rhazinilam is a natural product with antitumoral properties[1].

The starting material for our planned synthesis of rhazinilam and derivatives of rhazinilam is 2-nitroacetophenone. Bromination, replacing the halogen by the azido group, followed by Mukaiyama reaction and cyclisation to the five membered ring by Staudinger reaction gave compound **1** in good yield.



1 **2** **rhazinilam analogue**

The main reaction in this new synthetic pathway is acylation of nitrogen[2], reaction which allow us obtaining the six membered ring after oxidation to aldehyde, Wittig and Michael reaction. Methods to achieve the cyclisation to the nine membered ring are the next challenge of our project.

[1] Olivier Baudoin*, Daniel Guénard and Françoise Guéritte, Mini-Reviews in Organic Chemistry, 2004, 1, 333-341;

[2] Hermann Köhler and Hans Gerlach, and André S. Dreiding, Helvetica Chimica Acta, 1984, 67, 1783-1793.

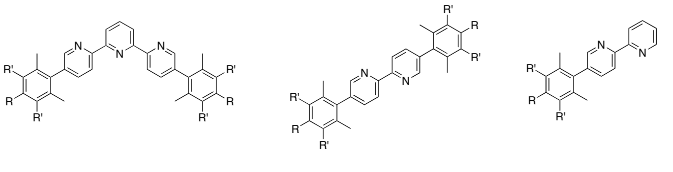
Organic Chemistry **331**

Photophysical Properties of ß-Substituted Terpyridines and Bipyridines

K. Arias, E. Zysman-Coleman, J. Siegel*

Organic Chemistry Institute, University of Zürich, Winterthurerstrasse 190, 8057, Zürich, Switzerland

En route to the synthesis of supramolecular structures,[1] it was discovered that aryl-substituted terpyridines and bipyridines, in particular the ß-substituted derivatives, are efficient chromophores. This project focuses on tuning the photophysical properties, such as quantum yields,[2] emission maxima, and emission lifetimes, of these compounds by altering the electron-donating capability of the aryl substituent.



R = H, Me, OMe, NMe_2
R' = H, Me

The three types of aryl-substituted polypyridines under study: 5',5"-bisaryl-2,2':6',2"-terpyridines, 5,5'-bisaryl-2,2'-bipyridines, and 5-aryl-2,2'bipyridines.

[1] Loren, J.C., Siegel, J.S., *Angew. Chem. Int. Ed.*, **2001**, *4*, 754.

[2] Demas, J.N., Crosby, G.A., *J. Phys. Chem.*, **1971**, *8*, 991.

Organic Chemistry **332**

Synthetic Approaches to Heterocorannulene

Jay Siegel, Nelli Rahanyan

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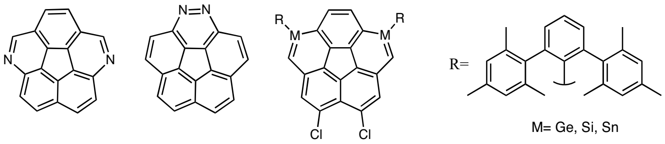
8057 – Zürich, Switzerland

Corannulene ($C_{20}H_{10}$) is a bowl-shaped aromatic hydrocarbon, the skeleton of which constitutes 1/3 of the fullerene C60. Although synthesis of corannulene predates C60 by more than 20 years, no heteroatom replacements ($C_{19}XH_9$) are known. One can reasonably expect heteroatom replacement to alter the dynamic, electronic and photochemical properties with respect to the parent hydrocarbon. Our primarly targets are aza and/or group IV metalloderivatives of corannulene. The synthetic approach takes advantage of methods we developed for the synthesis of 1,6,7,10-tetrasubstitutedfluoranthenes and related azafluoranthenes.

We are exploring amine-arene couplings and nitrene[1] insertion chemistry to understand the scope of these reaction for introducing nitrogen into the corannulene frame. For the group IV metalloids, we are pursuing a route based on a modification of Tokitoh's[2] method to metallophenanthrenes, but using a steric blocking group developed in our labs. Recent results will be presented.



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[2] Sasamoro T.; Inamura K.; Hoshino, W.; Nakata, N.; Mizuhata, Y.; Watanabe, Y.; Furukawa Y.; Tokitoh N. Organometallics **2006**, 25, 3533-3536

doi:10.2533/chimia.2007.500 CHIMIA **2007**, *61*, No. 7/8

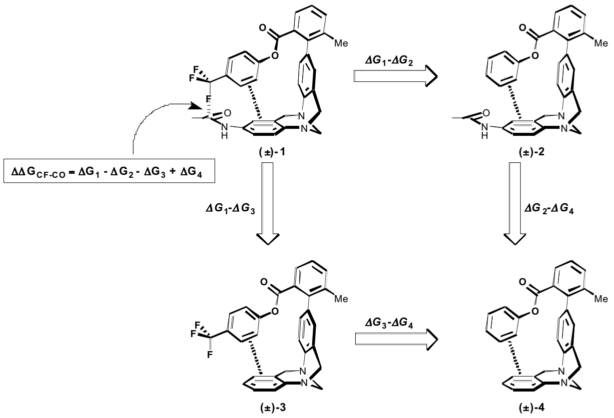
Organic Chemistry **333**

Measurement of Orthogonal Dipolar C–F•••C=O Interactions

Felix R. Fischer, Fraser Hof, François Diederich*

ETH Zürich, Hönggerberg, HCI, CH-8093 Zürich, Switzerland

In order to assess the free energy ΔG of an orthogonal C–F•••C=O dipolar interaction, we modified the *Wilcox* torsional balance. The molecule exists in two well-defined conformations. The equilibrium constant between a closed conformation where the CF_3 group of (±)**1** comes to rest within *Van der Waals* distance of the appended acetamide group on the face component and an open conformation is determined by NMR-spectroscopy. The perturbation of the major edge-to-face interaction is attributed to the dipolar interaction. Applying the double-mutant cycle provides accurate free energies for an orthogonal C–F•••C=O interaction [1].



[1] F. Hof, D. M. Scofield, W. B. Schweizer, F. Diederich, *Angew. Chem.* **2004**, *116*, 5166-5169; *Angew. Chem. Int. Ed.* **2004**, *43*, 5056-5059.

Physical Chemistry **334**

Excited state H-atom translocation along a four-membered ammonia wire

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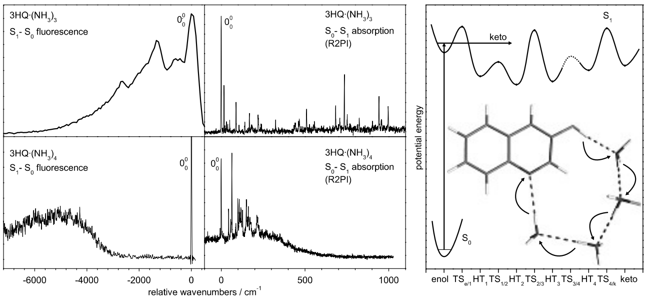
We explore the entrance channel and reaction threshold of unidirectional excited state H-atom transfer reactions along hydrogen-bonded $(NH_3)_n$ wires and their dependence upon the number of constituents therein. $S_0 \rightarrow S_1$ excitation of supersonically cooled enol-3-hydroxyquinoline·$(NH_3)_4$ leads to H-atom transfer along the wire and emission from the keto- and/or intermediate species. On the other hand, the $n = 3$ cluster emits from the enol form without undergoing enol → keto reaction. *Ab initio* calculations predict translocation pathways from the S_1 enol-3HQ to its keto form, by passing several transition states and local minima. The number of constituents is crucial for the height of the first barrier and the profile of the S_1 potential energy hypersurface.



Physical Chemistry **335**

Conformation-specific ultraviolet and infrared spectroscopy of cold, protonated Ac-Phe-(Ala)$_5$-Lys and Phe-(Ala)$_{10}$-Lys: Spectroscopic signatures of gas phase helix formation

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The alpha-helix is an important structural motif in biological molecules, and the factors governing its formation are being studied using a variety of techniques. One approach is to study helix-forming molecules in the gas phase to determine the characteristics intrinsic to the peptide which stabilize helical structures. Previous studies using ion mobility have suggested that polyalanines capped at the C-terminus with a lysine residue are helical in the gas phase, but are not helical in the absence of the lysine or with it at the N-terminus.[1] We have studied similar molecules with a phenylalanine chromophore using conformation-specific ultraviolet and infrared spectroscopy in a cold ion trap. We observe at least four conformers of Ac-Phe-(Ala)$_5$-Lys+H$^+$ but just a single major conformer of Phe-(Ala)$_{10}$-Lys+H$^+$. The amide N-H stretch frequencies provide signatures of the different types of hydrogen bonding present in each conformer. The bonding environments range from the free NH groups at the N-terminus of the peptides to amide groups in the center and C-terminus which are in strong helical N-H···O=C hydrogen bonds. The nonhelical molecules Ac-Lys-Phe-(Ala)$_{10}$+H$^+$ and Phe-(Ala)$_{10}$+H$^+$ provide a comparison by which we can determine the spectral signatures of helical molecules.

[1] M. Kohtani and M.F. Jarrold *J. Am. Chem. Soc.* **2004,** *126,* 8454.

Physical Chemistry **336**

Vibrational predissociation in hydrogen bonded dimer: The case of HF and its isotopomers

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We use $(HF)_2$ as a model system to understand the dynamics in hydrogen bonded systems. This particularly simple system has been widely used both in experimental and theoretical studies. Here we focus on the remarkable mode selectivity in vibrational predissociation process (VP) [1]. For instance, in experiments using highly resolved pulsed jet CW-CRDS, we have shown that the state involving two quanta of the bonded HF stretching mode has a VP lifetime τ_{PD} of only ~50 ps while that involving two quanta of the free HF stretching mode is more than 1 ns [2]. Measurements with the HF·DF isotopomer are currently in progress.

From a theoretical point of view, we have used the accurate fully 6-dimensional electronic potential hypersurface SO-3 established previously in our group [3] to study the VP with classical trajectory calculations. This combined study provides a more detailed understanding of the dynamics in this dimer. We present here our results of lifetimes and absorption spectra for several excitations involving the two stretching modes which we compare to the experimental results [4]. The theoretical work can also provide a benchmark in investigation for classical dynamics simulations.

[1] Note that the following references are non exhaustive but only exemplary: T. R. Dyke, B. J. Howard, W. J. Klemperer, *J. Chem. Phys.* **1972**, *56*, 2442; A. S. Pine, W. J. Lafferty, *J. Chem., Phys.* **1983**, *78*, 2154; K. von Puttkamer, M. Quack, *Mol. Phys.* **1987**, *62,* 1047; K. von Puttkamer, M. Quack, *Chem. Phys.* **1989**, *139*, 31; M. Quack, M. Suhm, *J. Chem. Phys.* **1991**, *95*, 28; M. von Dirke, Z. Bàcíc, D. H. Zhang, J. Z. H. Zhang, *J. Chem., Phys.* **1995**, *102*, 1382.
[2] M. Hippler, L. Oeltjen, M. Quack, *to be published.*
[3] W. Klopper, M. Quack, M. Suhm, *J. Chem. Phys.* **1998**, *108*, 10096.

[4] C. Manca, M. Quack, M. Willeke, *in preparation.*